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Calibration of differential scanning calorimeters: A comparison between indium and diphenylacetic acid

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ABSTRACT

The close proximity in melting temperature of the LGC Limited DSC standards indium and diphenylacetic acid, has enabled a direct assessment to be made of any differences resulting from the use of a metal or an organic compound in the calibration of DSC equipment. Following calibration with indium, the equilibrium fusion temperatures for diphenylacetic acid, were determined by both the stepwise heating and extrapolation to zero heating rate methods. The results were in excellent agreement with the certificate values and established that indium may be used as a calibrant when making accurate DSC measurements on organic materials in the same temperature range and that it has the advantage that it is non-volatile and can be used a number of times without significant change. Similar agreement was obtained in the measurement of the enthalpy of fusion, although the larger heat capacity change on fusion of diphenylacetic acid resulted in a greater uncertainty than with indium.

1. Introduction

Calibration is at the heart of quantitative measurements by differential scanning calorimetry. Its purpose is to link the temperature and enthalpy (or heat flow) measurements to their ‘true’ values. In view of its crucial importance it is hardly surprising that there have been many publications dealing with the methodology of calibration and the choice of calibrants. Comprehensive discussions include those by Höhne et al. [1], Richardson and Charsley [2] and Della Gatta et al. [3].

There are two approaches to the accurate measurement of equilibrium temperatures of fusion by DSC. The method proposed by Höhne et al. [4] utilises the differential scanning calorimeter in its conventional dynamic mode and derives the equilibrium temperature by measuring the extrapolated onset temperature of the fusion peak over a range of heating rates and extrapolating the results to zero heating rate. An alternative method advocated by Richardson [5] uses stepwise heating through the fusion peak with isothermal periods between the steps. In this method the melting takes place under near-equilibrium conditions and the equilibrium fusion temperature is identified with the temperature of the final step. In a previous study of organic melting point temperature standards we established that the melting temperatures obtained by the extrapolation to zero heating rate method corresponded to the near-equilibrium values [6].

In principle, the measurement of enthalpy of fusion is more straightforward than that of temperature. The enthalpy is obtained from the peak area with results which should be independent of the heating rate. In practice, complications may arise: Richardson and Charsley [2] have pointed out that the area of the fusion peak extends over a temperature range and will contain contributions from both the enthalpy of fusion and the change in heat capacity. For metals the change in heat capacity is negligible but for the fusion of organic compounds it may become significant when making measurements of the highest accuracy. The elimination of the heat capacity component has been discussed in connection with the enthalpies of transition of rubidium nitrate [7].

The most frequently used DSC calibrants are metals with melting temperatures and enthalpies measured by adiabatic calorimetry under near-equilibrium conditions: indium is often the chosen calibrant. However, reference has been made to the desirability of calibrating equipment using substances that have the similar thermal properties to the compound to be investigated [8]. Price [9] has reported a different trend between temperature calibrations carried out with metals and organic compounds.

LGC Limited offers a range of organic and metal DSC standards whose temperatures and enthalpies of fusion have been determined by adiabatic calorimetry [10]. The close proximity in temperature of the standards indium (156.61 °C) and diphenylacetic acid (147.19 °C) provides the opportunity of making a direct assessment of any differences resulting from the use of a metal or an organic in the calibration of a DSC for temperature and enthalpy.

We have therefore carried out an accurate comparison of the equilibrium temperatures and the enthalpies of fusion of the two

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materials. The temperatures have been measured using both the extrapolation to zero heating rate and stepwise heating methods. The enthalpy of fusion at the equilibrium temperature has been determined by making allowance for the change in heat capacity using a procedure similar to that recommended by Richardson [11].

In addition, the influence of the form of the indium on both the temperature and enthalpy measurements has been investigated by comparing the results obtained from the LGC sample, which was supplied as small pellets, with those from high purity indium powder. The advisability of pre-melting indium samples before carrying out calibration measurements has also been assessed. The purpose of pre-melting is to improve the reliability of subsequent measurements by bringing about better thermal contact between the sample and the crucible. Metal calibrants are frequently pre-melted before use, but with many samples pre-melting is not an option.

2. Experimental

Indium was supplied by LGC Limited (LCC2601) and was in the form of 'tear-drop' shaped pellets 2–3 mm in diameter. It had a certified equilibrium fusion temperature of 156.61 ± 0.02 °C and an enthalpy of fusion of 3.296 ± 0.009 kJ mol^{-1} (28.71 ± 0.08 J g^{-1}). Indium powder was obtained from Alfa Aesar (Puratronic, 99.999% purity). In the present paper we will refer to the two samples of indium as 'LGC' and 'powder' respectively. Diphenylacetic acid (LCC2607) had a certified equilibrium fusion temperature of 147.19 ± 0.03 °C and an enthalpy of fusion of 31.16 ± 0.13 kJ mol^{-1} (146.8 ± 0.6 J g^{-1}).[1]

The volatility of the diphenylacetic acid was assessed by thermogravimetry using a Mettler TG 851 apparatus. The sample (2.5 mg) was contained in an open 20 μl aluminium crucible and heated at 10 °C min^{-1}. The measured mass loss at the onset of melting was about 3%. In view of this mass loss all subsequent DSC experiments were carried out with samples in encapsulated crucibles. Since the purpose of the present work was a comparison between indium and diphenylacetic acid the same procedure was adopted for indium. No mass loss was detected in the DSC experiments.

Temperature measurements were carried out using the Mettler DSC 822^{e} with the 'tau lag' disabled. The measurements were made using 2.5 mg of the diphenylacetic acid and 10 mg of the LGC and powdered indium in Mettler 40 μl aluminium crucibles. An atmosphere of nitrogen was maintained in the apparatus (80 cm^{3} min^{-1}). Considerable care was taken to ensure good thermal contact between the sample and the crucible. For LGC indium a thin section of the pellet was pressed flat between glass plates and then pressed into the crucible. The indium powder and diphenylacetic acid were evenly distributed in the crucible. Diphenylacetic acid was lightly crushed before use.

The extrapolated onset temperature measurements were performed at five different heating rates within the range 1–10 °C min^{-1} and a new sample was used at each heating rate. The stepwise heating experiments were made with 0.05 °C temperature steps and 10–20 min isothermal periods between the steps. The fusion temperature was identified with the temperature of the final step of the fusion process. The measurements were made in triplicate with a new sample for each experiment unless indicated otherwise.

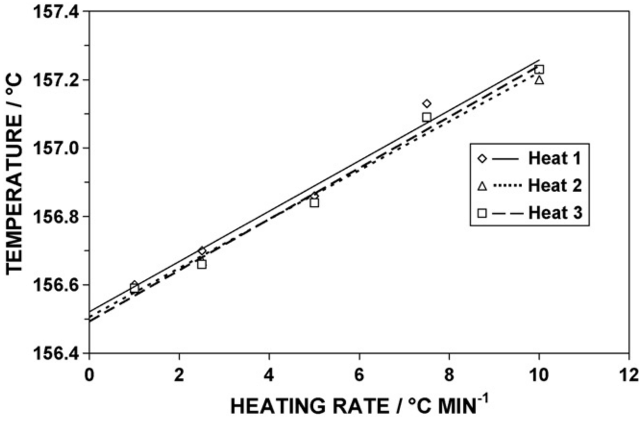

Fig. 1. Plot of extrapolated onset temperature against heating rate for LGC indium (sample mass, 10 mg; atmosphere, nitrogen).

The enthalpy measurements were performed using a PerkinElmer Diamond DSC. The samples were contained in TA Instruments low mass Tzero aluminium crucibles. The heating rate was 3 °C min^{-1} and an atmosphere of nitrogen was maintained in the apparatus (20 cm^{3} min^{-1}). The sample masses were the same as those used in the temperature measurements and the same care was taken to ensure good thermal contact between the sample and crucible. A new sample was used for each experiment unless indicated otherwise. The greater mass of indium used in these experiments compared to that of diphenylacetic acid was in recognition of its considerably smaller enthalpy of fusion. The uncertainties associated with the present measurements are single standard deviations unless otherwise stated.

3. Symbols

T_e represents the experimental extrapolated onset temperature. Unless otherwise stated all other temperatures are equilibrium values. $T_{\beta=0}$ and T_{step} are the experimental values obtained from the extrapolated onset and stepwise heating methods respectively. $\Delta_{\text{fus}}H$ is the experimental enthalpy of fusion at the melting temperature. β is the heating rate (°C min^{-1}).

4. Results and discussion

4.1. Equilibrium temperature measurements

The results of the extrapolation to zero heating rate experiments on LGC indium are plotted in Fig. 1. Each of the 5 samples studied was heated 3 times through the fusion peak in order to enable an accurate assessment to be made of the effect of pre-heating. An excellent linear correlation was found between T_e and the heating rate. The values for $T_{\beta=0}$ and the slopes of the lines are given in Table 1.

The agreement between the initial and subsequent fusion experiments within the limits of experimental error show that it is possible to make temperature measurements using indium to a

Table 1
Equilibrium temperature of fusion of LGC indium measured by the extrapolation to zero heating rate method.

Experiment	$T_{\beta=0}$/°C	$(dT_e/d\beta)$/min
First heating	156.52 ± 0.03	0.074 ± 0.006
Second heating	156.51 ± 0.03	0.072 ± 0.005
Third heating	156.49 ± 0.03	0.075 ± 0.004
Mean value	156.51 ± 0.02	0.074 ± 0.003
Certified value	156.61 ± 0.01[a]	–
Calibration correction	0.10 ± 0.02	–

[a] Single standard deviation.

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[1] The uncertainties associated with the certified values for indium and quoted on the certificate provide a level of confidence of approximately 95%. For diphenylacetic acid the uncertainties are an estimate of the total uncertainty and take into account both random and systematic error.

Table 2
Equilibrium temperature of fusion of indium powder measured by the extrapolation to zero heating rate method.

Experiment	$T_{\beta=0}/^\circ$C	$(\mathrm{d}T_e/\mathrm{d}\beta)$/min
First heating	156.50 ± 0.02	0.054 ± 0.003
Second heating	156.48 ± 0.02	0.053 ± 0.003
Third heating	156.47 ± 0.01	0.053 ± 0.002
Mean value	156.48 ± 0.01	0.053 ± 0.002

Table 3
Equilibrium temperature of fusion of LGC indium and indium powder measured by the stepwise heating method.

Experiment	LGC, $T_{\text{step}}/^\circ$C	Powder, $T_{\text{step}}/^\circ$C
First heating	156.52 ± 0.05	156.50 ± 0.03
Second heating	156.51 ± 0.05	156.52 ± 0.05
Mean value	156.52 ± 0.04	156.51 ± 0.03
Certified value	156.61 ± 0.01[a]	–
Calibration correction	0.09 ± 0.04	–

[a] Single standard deviation.

high degree of precision without recourse to pre-melting. However, it was found that if the indium sample was neither sufficiently thin nor firmly pressed flat into the crucible there was a significant decrease in the melting temperature from the first to second heating in the dynamic experiments. Therefore, where possible, pre-melting the sample would seem to be a sensible precaution.

Corresponding extrapolation to zero heating rate experiments were carried out on indium powder and the results are summarised in Table 2. It can be seen that the equilibrium fusion temperature is unchanged by melting and that the value agrees well with that obtained for the LGC sample. The magnitude of the gradients $\mathrm{d}T_e/\mathrm{d}\beta$ from the extrapolation to zero heating rate experiments for the powder is significantly smaller than those obtained for the LGC sample. Thermomicroscopy showed that the indium powder did not coalesce after fusion and retained its powdery nature. This accounts for the value of $\mathrm{d}T_e/\mathrm{d}\beta$ remaining unchanged on re-melting the sample rather than becoming similar to that of the LGC sample which was in the form of a single piece.

The results of the stepwise measurements on the LGC indium and indium powder are summarised in Table 3. An uncertainty corresponding to half the step height (0.025 °C) has been included in the results. The sharpness of the melting in stepwise heating is clear from the plot for LGC indium in Fig. 2 which shows the melting curve for the concluding temperature steps. Melting is seen to occur almost entirely over a single temperature step. The equilibrium temperatures for the two forms of indium are in excellent agreement and the values are unchanged by re-melting.

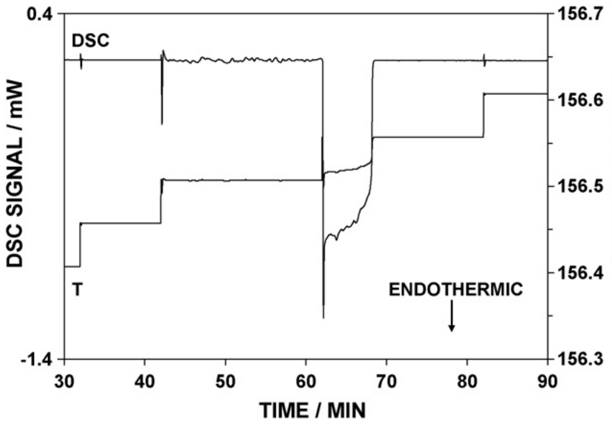

Fig. 2. DSC curve for LGC indium obtained under stepwise heating conditions (sample mass, 10 mg; step size, 0.05 °C; atmosphere, nitrogen).

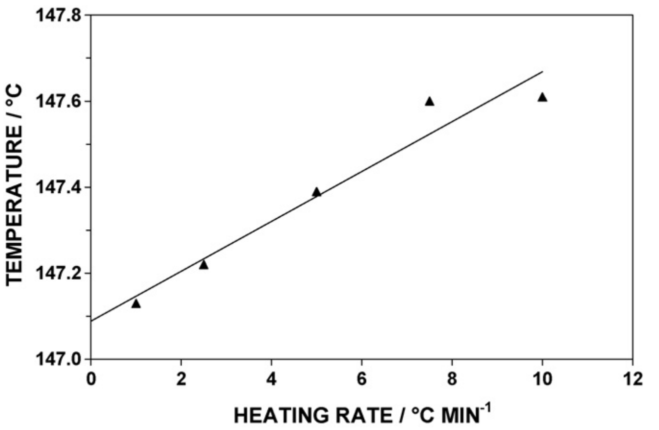

Fig. 3. Plot of extrapolated onset temperature against heating rate for LGC diphenylacetic acid (sample mass, 2.5 mg; atmosphere, nitrogen).

The agreement between the results for LGC indium and indium powder obtained by extrapolation to zero heating rate and stepwise heating clearly establishes the equality of the two methods for the determination of accurate equilibrium temperatures. This extends to a metal the agreement which was reported previously for organic melting point standards [6] and solid-solid phase transitions in rubidium and caesium nitrates [7,12]. The uncertainty in the results from the two methods is similar, although in the case of the stepwise heating it is dominated by the allowance made for the step height. This uncertainty can be reduced by decreasing the step height at the expense of more time consuming experiments.

The equilibrium fusion temperature of diphenylacetic acid was determined using the extrapolation to zero heating rate method. A new sample was used at each heating rate and was not re-heated in accordance with the recommendation in the certificate. The plot of T_e against heating rate is shown in Fig. 3 and the value for $T_{\beta=0}$ and the slope of the line are given in Table 4. The measured value was adjusted by applying the calibration correction obtained from the extrapolation to zero heating rate experiments on LGC indium (Table 1). A mean value of 147.19 ± 0.05 °C was given which is in excellent agreement with the certified value.

The value of the gradient $\mathrm{d}T_e/\mathrm{d}\beta$ of 0.058 ± 0.008 min obtained for diphenylacetic acid was smaller than that for LGC indium (0.074 ± 0.005 min) by an amount which exceeded the combined uncertainty. However, values of $\mathrm{d}T_e/\mathrm{d}\beta$ for both organic and inorganic compounds show considerable variation [4,8] and in some instances are greater than those for the metals. Our results for rubidium nitrate [7] show that even for the same compound the transitions between different crystal forms can lead to very different values of $\mathrm{d}T_e/\mathrm{d}\beta$.

The lack of consistency in the values of the gradient $\mathrm{d}T_e/\mathrm{d}\beta$ rules out experiments under dynamic conditions for the accurate measurement of temperatures unless it is known that the gradient has

Table 4
Determination of the equilibrium temperature of fusion of diphenylacetic acid by the extrapolation to zero heating rate and stepwise heating methods.

	$T_{\beta=0}/^\circ$C	$T_{\text{step}}/^\circ$C
Mean measured value	147.09 ± 0.05	147.08 ± 0.04
$(\mathrm{d}T_e/\mathrm{d}\beta)$/min	0.058 ± 0.008	–
Correction	0.10 ± 0.02	0.09 ± 0.03
Corrected value	147.19 ± 0.05	147.17 ± 0.04
Certified value	147.19 ± 0.03	147.19 ± 0.03

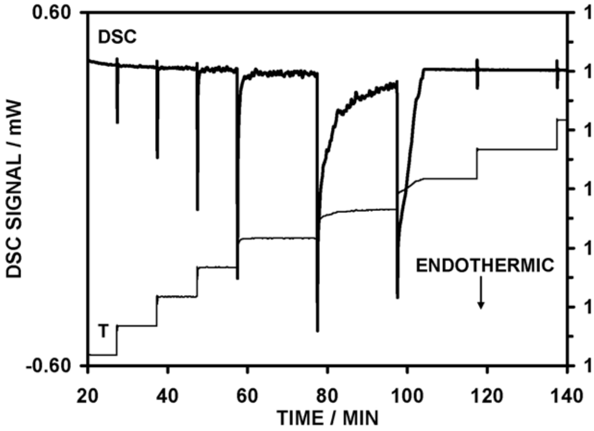

Fig. 4. DSC curve for LGC diphenylacetic acid obtained under stepwise heating conditions (sample mass, 2.5 mg; step size, 0.05 °C; atmosphere, nitrogen).

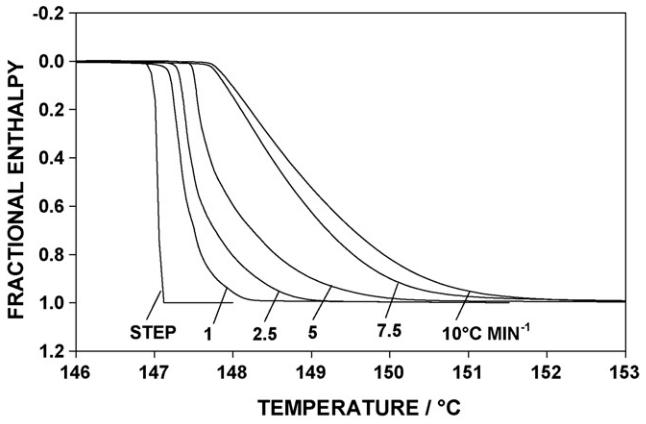

Fig. 5. Plot of fractional enthalpy against temperature for diphenylacetic acid obtained under stepwise and linear heating conditions (sample mass, 2.5 mg; atmosphere, nitrogen).

the same value for both the calibrant and the compound under investigation. The error, albeit generally small for modest heating rates, is proportional to the difference between the gradients for the calibrant and compound. Thus in the present case if the indium calibration had been made at 10 °C min^{-1} and the measurements on diphenylacetic acid made at the same heating rate, an error of ~0.2 °C would have resulted.

A typical DSC plot for the stepwise melting of diphenylacetic acid is shown in Fig. 4. The reduced temperature range of melting under stepwise heating is clearly evident in the incremental enthalpy plot in Fig. 5, where the stepwise and the linear heating rate DSC curves are compared. The equilibrium temperatures from the stepwise heating experiments on diphenylacetic acid are summarised in Table 4. The mean corrected value agrees with the certified value to within 0.02 °C, well within the uncertainties. This confirms the result obtained by the extrapolation to zero heating rate experiments and establishes the equivalence between a metal and an organic substance for DSC temperature calibration in a similar temperature range.

4.2. Enthalpy measurements

Typical DSC curves from the enthalpy measurements on LGC indium and indium powder are given in Fig. 6 and show the broader nature of the peaks for the powder sample. The determination of the enthalpy of fusion was simplified by the negligible heat capacity change on melting. The results in Table 5 were obtained using the PerkinElmer software and show excellent reproducibility. There was no change in the enthalpy on heating the samples for a second and third time. In a further series of experiments the LGC sample was cycled 20 times through its melting temperature at 10 °C min^{-1}. No change in enthalpy was observed.

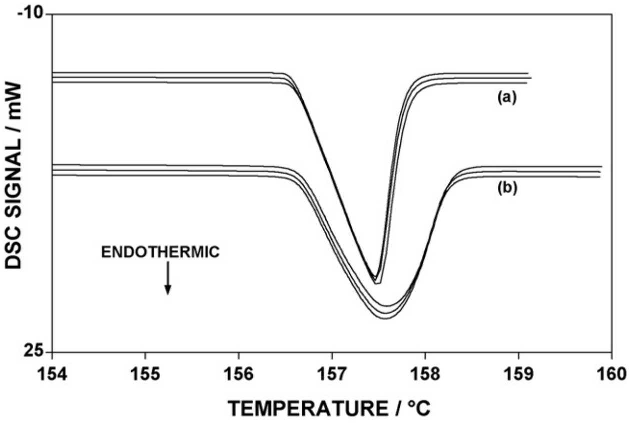

Fig. 6. DSC curves for (a) LGC indium and (b) indium powder showing effect of re-heating samples on the enthalpy of fusion (sample mass, 10 mg; heating rate, 10 °C min^{-1}; atmosphere, nitrogen).

Table 5
Measurements of the enthalpy of fusion of LGC indium and indium powder.

	LGC, $\Delta_{\text{fus}}H$/J g^{-1}	Powder, $\Delta_{\text{fus}}H$/J g^{-1}
First heating	28.71 ± 0.01	28.50 ± 0.06
Second heating	28.71 ± 0.03	28.49 ± 0.05
Third heating	28.72 ± 0.03	28.48 ± 0.05
Mean value	28.71 ± 0.02	28.49 ± 0.03
Certified value	28.71 ± 0.01[a]	–
Calibration factor	1.000 ± 0.002	–

[a] Single standard deviation.

There is a clear difference between the enthalpy results for the LGC and powder samples. The enthalpy of the indium powder is about 0.8% less than that of the LGC sample which is greater than the combined uncertainties in the results. The presence of an oxide coating on the powder seems a likely explanation for the discrepancy even though the sample used in the present work was from a previously unopened bottle. Such a coating might vary from one sample to another and with the length and conditions of storage. Therefore the use of indium powder, even of high purity, as a calibrant together with the assumption that the enthalpy of fusion is that of a solid sample may lead to a small systematic error in subsequent measurements.

The enthalpy of fusion of diphenylacetic acid was measured using LGC indium as the calibrant. The results from six determinations are summarised in Table 6. Melting occurred with a small but clearly discernable change in heat capacity and the enthalpy change was calculated by representing the temperature dependence of the initial and final capacities as linear (Fig. 7). The results were slightly dependent on the temperature range used

Table 6
Determination of the enthalpy of fusion of diphenylacetic acid.

	$\Delta_{\text{fus}}H$/J g^{-1}
Mean measured value	146.9 ± 0.3
Calibration factor	1.000 ± 0.002
Corrected value	146.9 ± 0.4
Certified value	146.8 ± 0.6

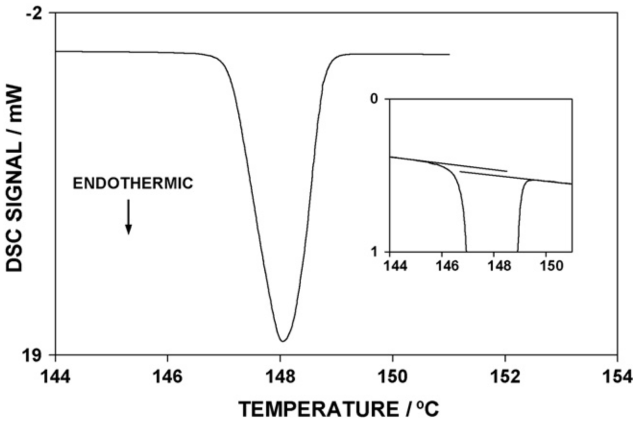

Fig. 7. DSC curves for LGC diphenylacetic acid showing heat capacity change on fusion (sample mass, 2.5 mg; heating rate, 10 °C min^{-1}; atmosphere, nitrogen).

in the calculations. Increasing the temperature range of by 0.5 and 1.0 °C changed the enthalpy value from $146.81 \pm 0.03\,\text{J}\,\text{g}^{-1}$ to 146.94 ± 0.13 and $147.01 \pm 0.10\,\text{J}\,\text{g}^{-1}$ respectively. The value in Table 6 ($146.9 \pm 0.3\,\text{J}\,\text{g}^{-1}$) is the mean value from the individual results together with an error that encompasses the range of the results. We have also used the PerkinElmer software for a sigmoidal baseline construction and obtained a value 0.2% greater than the present value.

The corrected enthalpy of fusion of diphenylacetic acid at the equilibrium temperature was found to be $146.9 \pm 0.4\,\text{J}\,\text{g}^{-1}$. This is in excellent agreement with the certified value of $146.8 \pm 0.6\,\text{J}\,\text{g}^{-1}$ and demonstrates that there is no significant difference in using a metal or an organic material for the enthalpic calibration of DSC equipment at similar temperatures.

5. Conclusions

The close proximity in temperature of the LGC Limited DSC standards indium and diphenylacetic acid, has enabled a direct assessment to be made of any differences resulting from the use of a metal or an organic substance in the calibration of DSC equipment. Following calibration with indium, the equilibrium fusion temperatures for diphenylacetic acid, measured by both the stepwise heating and extrapolation to zero heating rate methods, were found to be in excellent agreement with the certificate value. Although the enthalpy measurements with diphenylacetic acid showed a greater uncertainty than with indium, which arose from the larger heat capacity change on fusion, the results were also in agreement with the certified value.

These measurements clearly establish that indium may be used as a calibrant when making accurate DSC measurements on organic materials in the same temperature range. Indium has advantages in that it is non-volatile and as we have shown, can be re-melted at least 20 times without any significant change. However, measurements are often performed on samples at significantly lower temperatures than the melting point of indium and in these cases it may be advantageous to use one of the organic standards which melt in a similar temperature range. Work is at present in progress using these standards to assess the magnitude of the temperature dependence of the errors in temperature and enthalpy if only a single point calibration is performed using indium [13].

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