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DSC studies on organic melting point temperature standards

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Abstract

A series of organic melting point temperature standards are available for which the liquefaction temperature has been determined by stepwise heating under near equilibrium conditions. The present work explores their use in the accurate calibration of DSC equipment. Two methods have been used, each of which has been shown to have advantages. In the first, a stepwise heating procedure has been adopted which is analogous to that used in calibrating the standards. The final step corresponds to the certified liquefaction temperature. In the alternative procedure the extrapolated onset temperature has been determined for zero heating rate. This work provides experimental confirmation that the extrapolated onset temperature at zero heating rate corresponds to the certified thermodynamic liquefaction temperature.

Keywords: DSC; Temperature calibration; Organic melting point temperature standards

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1. Introduction

LGC Limited (previously known as the Laboratory of the Government Chemist) offers a range of organic reference materials intended for the calibration of equipment used for the determination of melting points of samples contained in glass capillary tubes. Certified temperatures for the onset of melting, the meniscus point and liquefaction point were provided by the Laboratoire National D'Essais in Paris, France and the National Research Centre for Certified Reference Materials, Beijing, China. Temperatures were measured by platinum resistance thermometry with values traceable to the International Temperature Scale of 1990 (ITS-90) [1]. Both laboratories provided values measured under dynamic conditions at a heating rate of 0.2 °C min^{-1}. The Laboratoire National D'Essais also provided values measured under near equilibrium conditions by stepwise heating where the temperature of the sample was raised in increments of 0.005–0.01 °C with 15 min periods between the steps. These measurements under near equilibrium conditions provide an ideal starting point from which to examine the procedures used in the accurate temperature calibration of DSC equipment.

The selection of materials for the temperature calibration of DSC equipment has been discussed in considerable detail by Cammenga et al. [2]. Indium and tin are obvious choices since their freezing temperatures are defined fixed points on the ITS-90 temperature scale. However, organic reference materials may find a place when subsequent measurements are to be made on pharmaceuticals or other organic substances where the thermal characteristics differ from those of metals.

Two approaches have been adopted for the accurate calibration of DSC equipment under near equilibrium conditions. In one the melting temperature of the calibrant at zero heating rate is obtained from measurements made under dynamic conditions. The extrapolated onset temperature of the melting peak is measured at a series of heating rates and the values extrapolated to zero heating rate. The calibration correction is then obtained by comparing the temperature at zero heating rate with the value for the reference material. The approach was investigated by Gesellschaft für Thermische Analyse e. V. (GEFTA) as part of a programme of work established to bring forward recommendations for calibrating DSC equipment. In their report [3] the authors describe the use of indium and tin as reference materials together with a number of other metals and non-metals where the melting temperatures were reasonably well established.

In the other approach, often referred to as isothermal calibration, the temperature of the sample is raised stepwise with isothermal intervals between the steps until melting is complete. Richardson [4] advocated the use of stepwise heating as a method of calibration. Its advantage in the determination of purity by DTA and DSC has been recognised for some time [5,6]. The procedure is analogous to that used by the Laboratoire

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National D'Essais and thus the temperature of the final step in a DSC experiment should correspond to the certified liquefaction temperature measured under near equilibrium conditions. This may be compared with the dynamic method where the use of the extrapolated onset temperature to define the melting temperature is both convenient and reproducible but the construction lacks precise experimental justification.

This paper describes the evaluation of the LGC reference materials as temperature standards in DSC. The melting behaviour has been investigated by DSC using both dynamic and stepwise heating. The results have allowed the relative merits of the two approaches to the temperature calibration of DSC equipment to be assessed. In particular the physical significance of the extrapolated onset temperature has been investigated.

2. Experimental

The LGC organic reference materials used in the present work were naphthalene (LGC2402), benzil (LGC2403), benzoic acid (LGC2405) and anisic acid (LGC2407). These materials were calibrated by the Laboratoire National D'Essais and have certified liquefaction temperatures measured under near equilibrium conditions.

The DSC experiments were made using a Mettler DSC 822^e. It was operated with the 'tau lag' correction disabled. Regular performance checks were carried out over the 6-month period of the work to ensure consistency in the results.

Samples of the organic reference materials (2.5 mg) were sealed into 40 μL aluminium crucibles and heated in an atmosphere of argon (80 cm^3 min^{-1}). Significant mass losses recorded for samples when heated in open crucibles from 25 °C to their respective melting temperatures emphasised the need for sealed crucibles in the DSC experiments. To confirm that material had not been lost during the DSC experiments the crucibles were weighed on completion of the measurements. Dynamic experiments were carried out at heating rates of 0.5, 1, 2, 3, 5, 7.5 and 10 °C min^{-1}. Stepwise experiments used increments of 0.05 °C with 30 min intervals between the steps. A new sample was used for each measurement in both techniques.

3. Results and discussion

In expressing the results we have used the following symbols:

T_{cert}: the certified temperature of liquefaction under near equilibrium conditions;
T_e: extrapolated onset temperature of the melting curve recorded under dynamic conditions;
$T_{\beta=0}$: the extrapolated onset temperature at zero heating rate;
T_{step}: temperature corresponding to complete melting (final step) in a stepwise heating experiment;
$\partial T_e/\partial\beta$: the gradient of the linear plot of extrapolated onset temperature against heating rate.

The certified liquefaction temperatures of the organic reference materials under near equilibrium conditions are shown in Table 1.

Table 1
Certified liquefaction temperatures for the organic reference materials under near equilibrium conditions

Material	Temperature, T_{cert} (°C)
Naphthalene	80.27
Benzil	94.86
Benzoic acid	122.41
Anisic acid	183.34

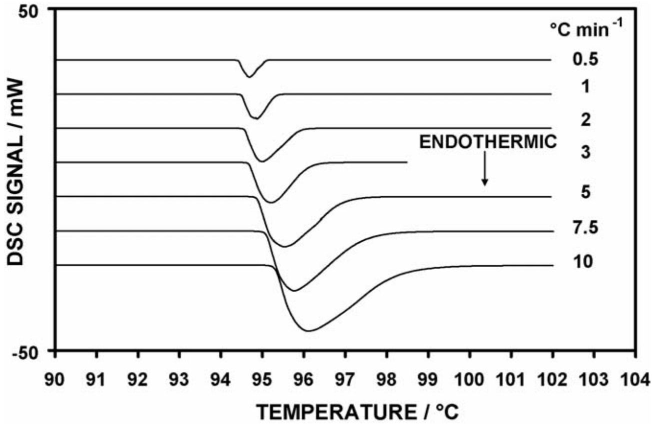

Fig. 1. DSC curves for benzil at heating rates from 0.5 to 10 °C min^{-1} (sample mass, 2.5 mg; atmosphere, argon).

All the reference materials gave well defined melting curves under linear heating conditions. This is exemplified by the results for benzil. Fig. 1 shows the melting curves recorded at heating rates from 0.5 to 10 °C min^{-1}. The corresponding extrapolated onset melting temperatures are plotted against heating rate in Fig. 2. There is a clear linear relationship (correlation coefficient 0.998) between T_e and heating rate with an intercept corresponding to zero heating rate of $T_{\beta=0} = 94.39 \pm 0.01$ °C. The value of $T_{\beta=0}$ was calculated by linear regression assuming the error to be restricted to the temperature measurements. The associated uncertainty is the standard deviation.

The results for the four reference materials are summarised in Table 2. For naphthalene the data were better represented

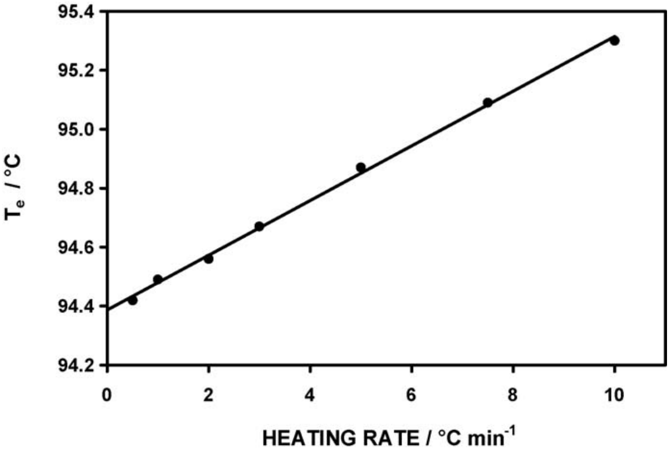

Fig. 2. Plot of extrapolated onset temperature (T_e) against heating rate from DSC measurements on benzil (sample mass, 2.5 mg; atmosphere, argon).

Table 2
Comparison between the melting temperatures obtained for organic reference materials from dynamic measurements extrapolated to zero heating rate and by stepwise heating

Material	Naphthalene	Benzil	Benzoic acid	Anisic acid
$T_{\beta=0}$ (°C)	79.82 ± 0.03	94.39 ± 0.01	121.91 ± 0.04	182.97 ± 0.03
$(\partial T_e/\partial \beta)$ (min)	0.082 ± 0.005	0.091 ± 0.002	0.083 ± 0.007	0.108 ± 0.006
T_{step} (°C)	79.86 ± 0.03	94.40 ± 0.03	121.91 ± 0.03	182.93 ± 0.09
$(T_{step} - T_{\beta=0})$ (°C)	0.04 ± 0.04	0.01 ± 0.03	0.00 ± 0.05	−0.04 ± 0.09

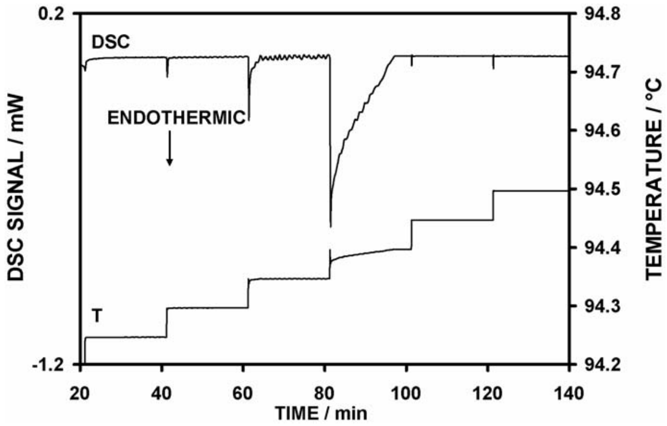

Fig. 3. DSC and temperature curves for the stepwise melting of benzil (sample mass, 2.5 mg; step increment, 0.05 °C; atmosphere, argon).

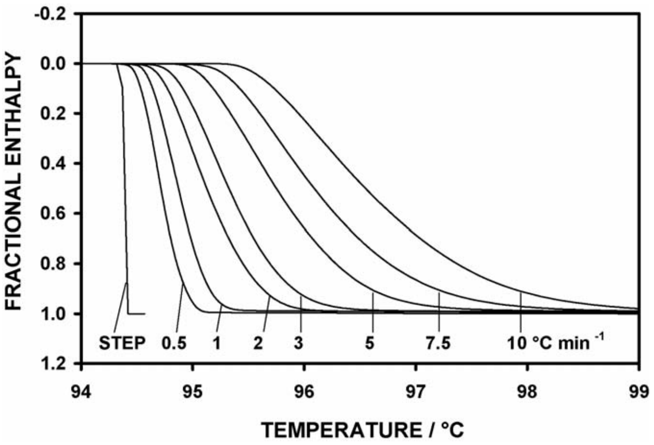

Fig. 4. Plot of fractional enthalpy against temperature for DSC studies on the fusion of benzil under stepwise heating and at a range of heating rates from 0.5 to 10 °C min^{-1} (sample mass, 2.5 mg; atmosphere, argon).

by a quadratic relationship leading to $T_{\beta=0} = 79.88 \pm 0.02$ °C. The difference between this value and that obtained by the linear extrapolation is on the limits of the combined uncertainties. Rather than varying the procedure from one set of measurements to another we have retained a linear extrapolation throughout the work.

The stepwise heating procedure is illustrated in Fig. 3 which shows the melting curve for benzil accompanying a series of 0.05 °C temperature steps. The onset of melting is shown by a slight increase in the noise level of the DSC signal. This proved to be a very sensitive indication of the onset of melting in stepwise experiments. The final step at which melting is entirely complete is readily identified. Four series of measurements were carried out and each gave the same value $T_{step} = 94.40$ °C. Thus the uncertainty is within the resolution of the technique and we have assigned a value of half the temperature step height, i.e. ±0.03 °C.

The results obtained for all four reference materials are shown in Table 2. The results establish the high precision that can be achieved in the measurement of temperature using the stepwise DSC technique. Only for anisic acid was there any variation between the results from the different measurements. The uncertainty associated with the mean result is the standard deviation and incorporates both the error in the measurements and half the temperature step height.

A direct comparison between the temperature range over which melting occurs in the two techniques may be made by plotting the fractional enthalpy against temperature. Fig. 4 shows the results for benzil and demonstrates the very narrow temperature range of melting in stepwise heating compared with linear heating. In the stepwise method very nearly all the melting occurs in just two steps, i.e. 0.1 °C.

The close agreement between the values of T_{step} and $T_{\beta=0}$ shown in Table 2 is of particular significance. The values of T_{step} are identified with the thermodynamic liquefaction temperatures which in turn are linked to ITS-90 through the certified values. Thus this agreement provides experimental confirmation that the extrapolated onset temperature at zero heating rate corresponds to the thermodynamic liquefaction temperature.

Table 3 show the values of $(T_{cert} - T_{step})$ and $(T_{cert} - T_{\beta=0})$. These constitute the temperature calibration corrections for our DSC instrument. There appears to be a monotonic increase in the calibration correction from the melting temperature of naphthalene to that of benzoic acid, although the change is scarcely greater than the combined uncertainties. It is of interest that both

Table 3
Calibration correction determined by stepwise heating and from dynamic measurements extrapolated to zero heating rate

Material	Naphthalene	Benzil	Benzoic acid	Anisic acid
$(T_{cert} - T_{step})$ (°C)	0.41 ± 0.03	0.46 ± 0.03	0.50 ± 0.03	0.41 ± 0.09
$(T_{cert} - T_{\beta=0)})$ (°C)	0.45 ± 0.03	0.47 ± 0.01	0.50 ± 0.04	0.37 ± 0.03

the dynamic and stepwise calibration methods lead to a melting temperature for anisic acid which points to a small decrease in the calibration correction from the value for benzoic acid.

From the standpoint of calibrating DSC equipment there is little to choose between the two techniques. The uncertainties in the results are similar. In principle the calibration by stepwise heating may be refined by decreasing the magnitude of the temperature steps. Thus for benzil we obtained the value $T_{\mathrm{step}} = 94.39 \pm 0.01\,^{\circ}\mathrm{C}$ from experiments in which the temperature steps were reduced to $0.02\,^{\circ}\mathrm{C}$. However, this was at the expense of a considerable increase in the time taken for the measurements, even when using the results of the $0.05\,^{\circ}\mathrm{C}$ step experiments as a guide to a suitable starting temperature. In the stepwise method the sample is at a temperature near the melting temperature for a considerable time and hence it is restricted to very stable materials.

The dynamic method has advantages for high temperature calibration where the design of the equipment may make it difficult to implement small step increases in temperature. The calibration correction may be transferred to non-zero heating rates using the gradients $(\partial T_{\mathrm{e}}/\partial\beta)$ shown in Table 2. Höhne et al. [3] have shown that the 'true' temperature corresponding to a measured extrapolated onset temperature T_{e} at a heating rate β is $T_{\mathrm{e}} + (T_{\mathrm{cert}} - T_{\beta=0}) - \beta(\partial T_{\mathrm{e}}/\partial\beta)$ (using the present nomenclature). There is some variation in the values of $(\partial T_{\mathrm{e}}/\partial\beta)$ although for naphthalene, benzil and benzoic acid the variation is about equal to the combined uncertainties. However, we have observed a significant change in the gradient $(\partial T_{\mathrm{e}}/\partial\beta)$ when the measurements are made on metals [7].

It has already been pointed out that the dynamic results for naphthalene are more precisely represented by a quadratic expression. The difference between the linear and quadratic extrapolations of the calibration correction from zero heating rate to $10\,^{\circ}\mathrm{C\,min^{-1}}$ is $0.06\,^{\circ}\mathrm{C}$ which is about the experimental uncertainty. At higher heating rates the predicted differences become much more significant. However, this assumes that the expressions for the gradient remain unchanged. It is evident that the gradient needs to be thoroughly investigated before any attempt is made to transfer the calibration correction from one heating rate to another or from one substance to another – a conclusion in keeping with the observations of the previous authors [3].

4. Conclusions

The organic temperature standards are suitable organic materials for the calibration of DSC equipment. They are particularly useful in providing a means of calibrating equipment in the temperature gap which occurs in the use of the metals gallium and indium. The measured temperatures show the high precision that can be obtained in the measurement of melting temperatures with samples as small as 3 mg. The calibration correction obtained by stepwise heating is secure since the method is analogous to that used in calibrating the melting standards by the Laboratoire National D'Essais. The results show that in the alternative dynamic approach the extrapolated onset temperature at zero heating rate corresponds to the thermodynamic liquefaction temperature. In principle the calibration correction obtained by the dynamic method may be transferred to other heating rates but the gradient $(\partial T_{\mathrm{e}}/\partial\beta)$ needs to be determined for the sample under investigation over the heating range of interest.

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