Adamantane – A New Certified and Traceable Reference Material for Subambient DSC Temperature and Enthalpy Calibration on Heating and Cooling

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ABSTRACT

An interlaboratory test is described to characterize adamantane as a new subambient temperature and enthalpy reference material. Certified and traceable values are obtained for transition temperature (–65.54 ± 0.20 °C) and transition enthalpy (20.57 ± 0.90 J/g) using NIST SRM 2225 Mercury as an internal standard. The low temperature adamanatane polymorphic transition is then used to characterize the temperature reporting performance of the TA Instruments Tzero Differential Scanning Calorimeter.

INTRODUCTION

Thermal analysts wishing to perform subambient DSC operations often request a low temperature certified reference material traceable to a National Metrology Institute (NMI). The only certified and traceable reference material currently available for this use is SRM 2225 Mercury, available from the United States National Institute of Standards and Technology (NIST). Because of the health hazards of mercury compounds and the difficulty in its safe disposal, many laboratories are reluctant to use mercury metal for calibration purposes.

Adamantane, a saturated three ring hydrocarbon with the unique structure shown in Figure 1, has been suggested as a subambient reference material (1, 2, 3, 4). It is a solid at room temperature with a low temperature solid-solid (polymeric) transition from face-centered cube to body centered tetragonal lattice near –65 °C (5). (Solid-solid transi-tions are preferred for calibration, as they do not super cool upon cooling.) Adamantane is available in high purity, is considered to be a low health hazard, low flammability, and low reactivity and is non-hazardous for transportation purposes. It sublimes before melting and so has no melting point.

A larger quantity of high purity adamantine was purchased from Sigma-Aldrich Fine Chemicals (Milwaukee, WI) to serve as a candidate reference material. Sigma-Aldrich reports that the material is >99 % pure. It was found to be 99.83 mol % pure by ASTM International standard E 928(6).

EXPERIMENTAL

The temperature and enthalpy of the adamantane polymorphic transition were measured using a series of TA instruments Differential Scanning Calorimeter models Q1000 and Q2000 equipped with Refrigerated (RCS) or Liquid Nitrogen Cooling Systems (LNCS). The aluminum sample pans used throughout were passivated for mercury service by heating for 30 minutes to 500 °C in an air atmosphere (3). A

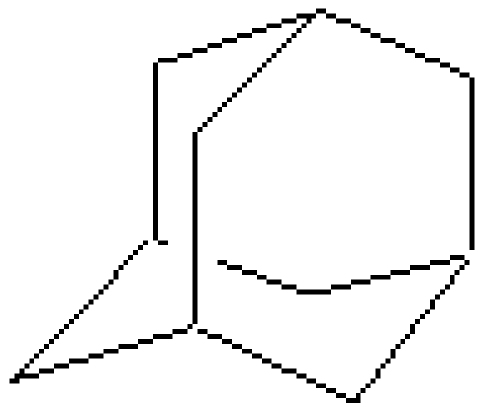

Figure 1 Adamantane structure (courtesy of Sigma-Aldrich Fine Chemicals).

weighed internal standard NIST SRM 2225 was run in the same pan as the adamantine at 2 °C/min from –75 to –25 °C. All samples and reference materials were weighed using a traceably calibrated Cahn C33 Microbalance readable to 1 µg. A typical thermal curve of the adamantane with its mercury internal reference material is presented in Figure 2.

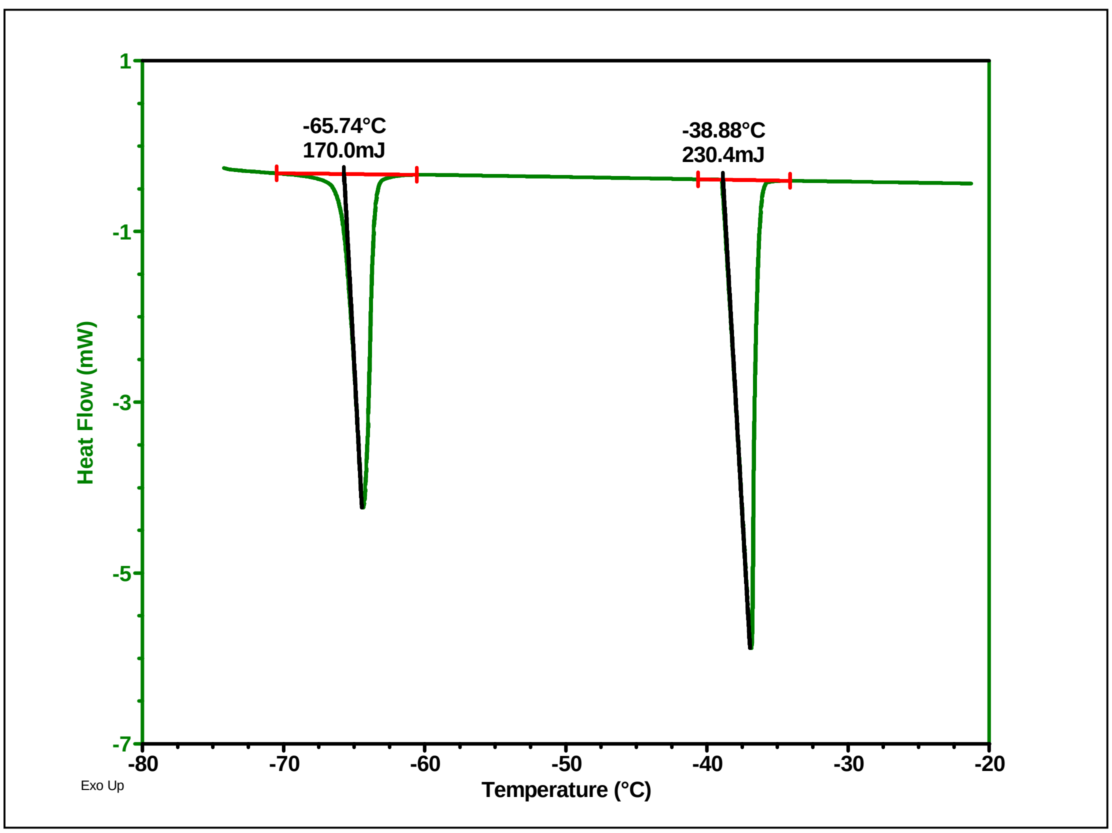

Figure 2 Adamantane and mercury thermal curve.

As a test for homogeneity, ten replicate determinations were performed using aliquots from three different parts of the lot of adamantane on three different instruments. All measurements were run on the materials as received.

CALCULATIONS

The temperature and enthalpy of the adamantane transition were determined by direct comparison to the mercury internal standard. The mean values for the 10 replicate determinations on each of the instruments are presented in Table 1. The results from the three aliquots are statistically similar demonstrating homogeneity. The overall mean value for the three laboratories is –65.542 °C with a pooled within laboratory repeatability standard deviation of 0.167 °C and a between laboratory reproducibility standard deviation of 0.110 °C.

Apparatus	Temperature (°C)	Std. Dev. (°C)	Enthalpy (J/g)	Std. Dev. (J/g)
Q1000	-65.415	0.046	20.970	0.686
Q2000	-65.615	0.168	20.446	0.964
Q1000	-65.595	0.231	20.279	0.811
Mean	-65.542		20.565	
Std. Dev.	0.110		0.361	
Pooled		0.167		0.828

Table 1 Adamanatane interlaboratory test results.

For enthalpy, the mean value for the three laboratories is 20.565 J/g with a pooled within laboratory repeatability standard deviation of 0.828 J/g and a between laboratory reproducibility standard deviation of 3.61 J/g.

These within laboratory repeatability and between laboratory reproducibility values are combined with the uncertainty of the NIST SRM mercury value as the square root of the sum of their squares to yield an overall measurement standard deviation of ±0.20 °C and ±0.90 J/g, respectively. These values statistically differ from the –64.53 °C transition temperature and 24.8 J/g enthalpy reported by Westrum (5, 7).

Because of the direct comparison of the temperature and enthalpy values of the adamanatane to the SRM mercury, the transition temperature and enthalpy values obtained are certified and traceable to an NMI. This thoroughly tested and validated reference material is now commercially available from TA Instruments in 0.4 g quantities as part number 970489.901.

Calibration on Cooling

One of the requirements for the quantitative heat flow measurement by DSC is that the temperature sensor needs to be external to the test specimen (8). The farther the temperature sensor is removed from the test specimen, the greater will be the difference between the indicated temperature and the actual specimen temperature, with the actual temperature ordinarily lagging behind the indicated temperature. That is, the indicated temperature is normally higher than the actual temperature under heating condition. Of course, this effect is corrected by temperature calibration in the normal way using indium (9,10).

Most DSC calibration is performed on heating. This leads to an error in the temperature indication on cooling due to hysteresis. Menczel and coworkers demonstrated that this hysterisis is a function of heating/cooling rates and is as much as 1.7 °C when even modest heating rates of 20 °C/min are used (11,12). These same authors suggested the use of liquid crystal materials that have little or no supercooling as a tool for the calibration of this effect. This approach is now manifested in ASTM International standard E 2069 (13).

This same approach may be used to characterize the hysteresis (tau lag) on cooling. A plot of the temperature offset for a rapid transition as a function of temperature rate of change was suggested by a number of authors as a tool for characterization of the performance of individual DSC instruments (1, 2, 4, 14).

Obtaining materials with little or no supercooling, ready availability and low of toxicity has proven to be a surprisingly difficult task. Many materials have been examined with modest success. One suitable candidate is adamantine suggested by Hakvoort and coworkers (3, 4).

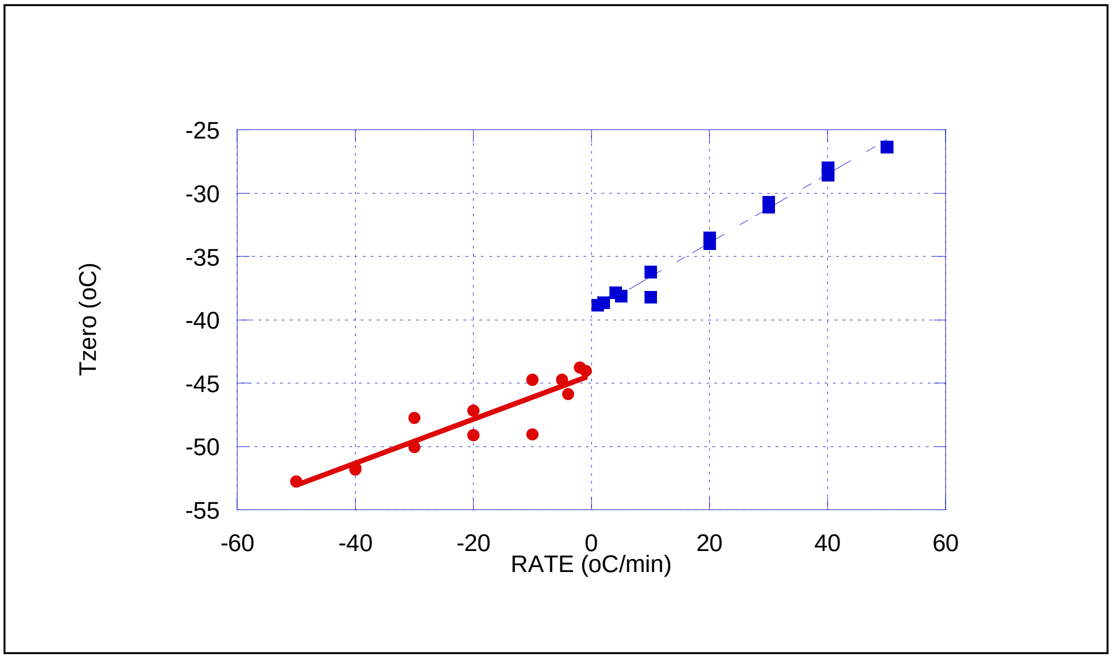

Figure 3 Effect of temperature rate of change on mercury indicated temperature.

EXPERIMENTAL

A single sample of adamantine and mercury was repeatedly heated and cooled under temperature program conditions ranging from –40 to +50 °C/min in a TA Instruments Q1000 DSC equipped with a Refrigerated Cooling System (RCS). The Q1000 with its Tzero Technology™ (15, 16) has the ability to determine and report temperatures from several positions along the heat flow path to the test specimen ranging from the temperature at the block surrounding the sample (T1), to the heat flow sensor (T4), and finally at the sample pan (T4P). The apparatus was first temperature calibrated using certified and traceable indium metal and ASTM International standard E967 (9,10).

DSC performance may be characterized using a plot of temperature offset as a function of temperature rate of change. An example using the mercury reference material is shown in Figure 3. Four characteristics of the curve may be observed including 1) the slope of the line upon heating (shown on the right), 2) the slope of the line upon cooling (shown on the left), 3) the value at zero heating rate, and 4) and offset in going from heating to cooling.

For mercury shown in Figure 3, the heating rate portion of the curve extrapolates to zero at the calibration temperature of –38 °C. The offset observed in going from heating to cooling is indicative of supercooling. And finally the lower line slope on cooling, compared to that for heating shows, that the instrument is optimized for cooling experiments.

Figure 4 shows a plot of the indicated temperature at the Pan Temperature (T4P) as a function of heating/cooling rate for adamantane. The slope of this line is called tau (τ) and is expressed in seconds. The value 1.7 s, confirmed by the work of Schick and coworkers (14), indicates a very low, almost negligible dependence of the indicated temperature on heating rate over the temperature rate of change from – 40 to +50 °C/min.

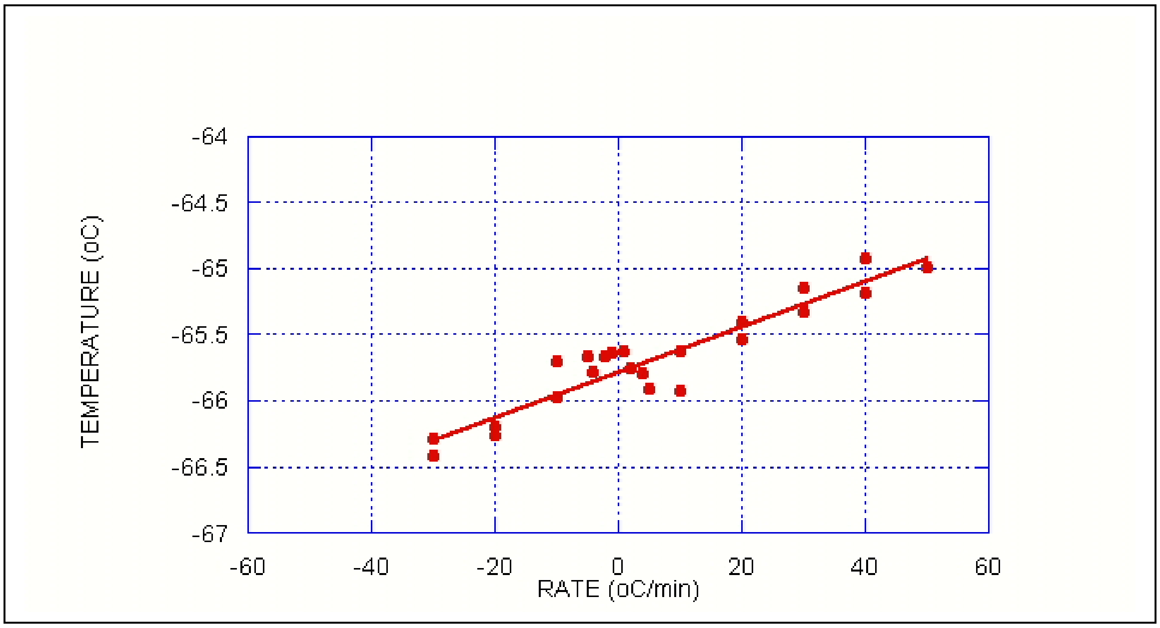

Figure 4 Effect of temperature rate of change on sample pan temperature using adamantane

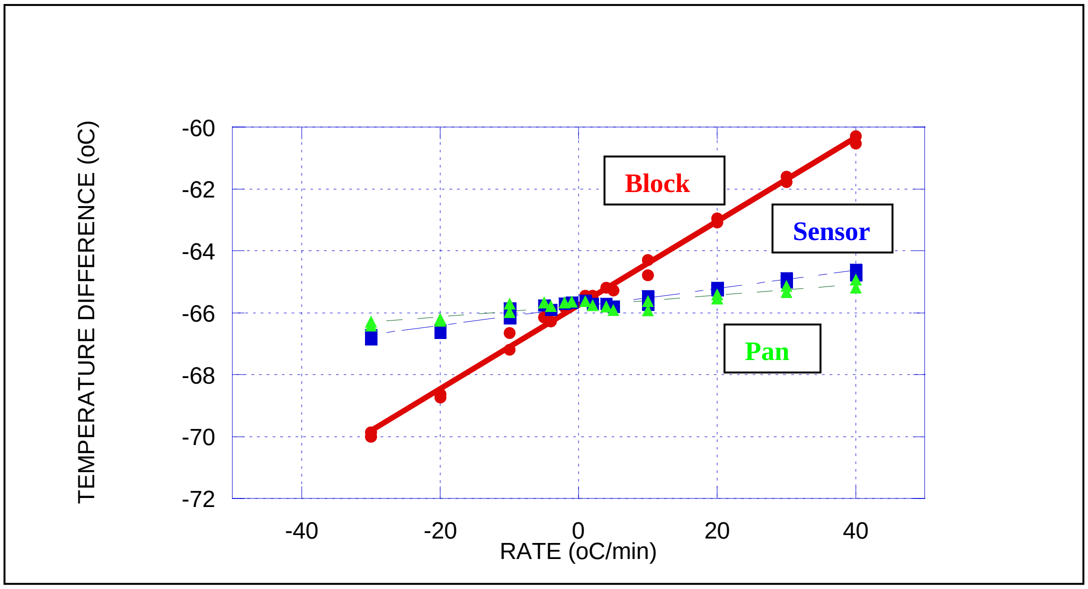

Figure 5 Effect of temperature rate of change on indicated temperature at measured at differing location

A comparative plot of the temperatures observed in various locations in the Tzero DSC is illustrated in Figure 5. This figure demonstrates the Boersma principle that the closer the measured temperature is to the test specimen, the more accurate (less tau lag) the temperature will be where the tau values are 7.8 s for the block temperature, 1.8 s for the heat flow sensor and 1.7 s for the pan temperature.

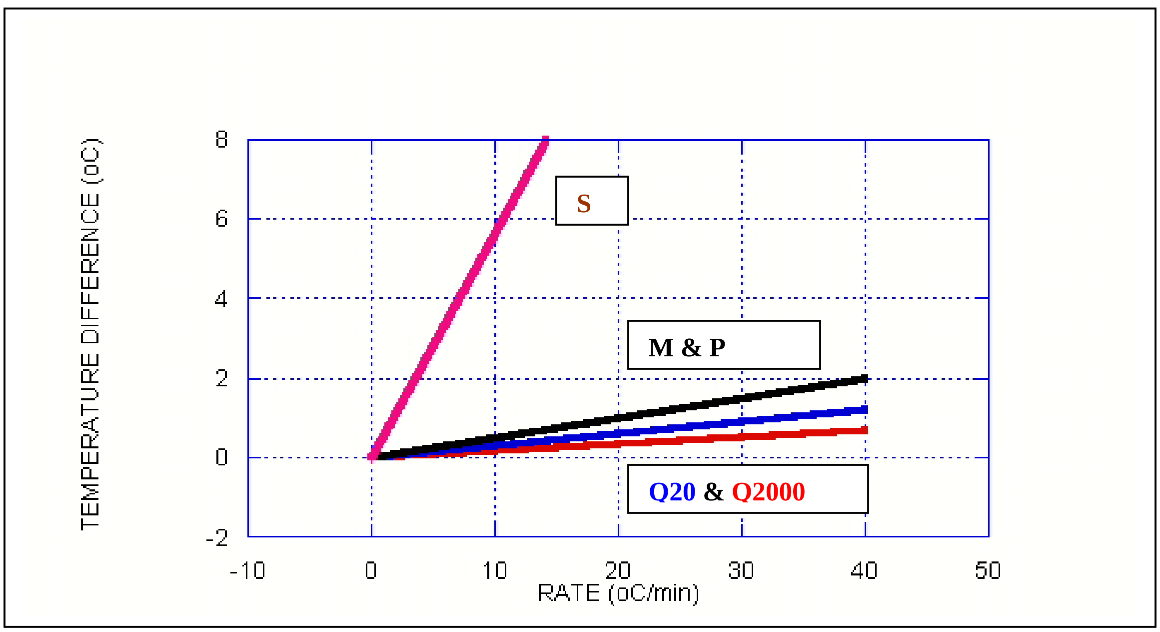

Figure 6 Effect of temperature rate of change on various DSC models (data taken from reference 14).

Finally Figure 6 shows the same kind of data obtained by Neuenfeld and Schick (14) presented in a similar format illustrating the very large range in DSC performance from one instrument model to another.

SUMMARY

In summary, a lot of adamantine was characterized in an interlaboratory test for its transition temperature and enthalpy to produce a certified reference material that is traceable to an NMI. This reference material is now commercially available for calibration in the subambient temperature region. This same material may be used to characterize the temperature rate of change dependence of any DSC, and may be used to calibrate instruments with a strong rate dependence upon heating and cooling. Finally, a Tzero technology based DSC is shown to have a very low, nearly negligible, temperature rate of change dependence over a 90 °C/min heating/cooling rate temperature range.

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