



High Precision Heat Capacity Measurements of Metals by Modulated DSC[®]

Carlton G. Slough, Ph.D. and Nathan D. Hesse, Ph.D.
TA Instruments, 109 Lukens Drive, New Castle DE 19720, USA

ABSTRACT

Accurate measurement of specific heat capacity (C_p) by Differential Scanning Calorimetry (DSC) requires more care over critical experimental details than is required for traditional measurements, such as enthalpy or transition temperatures. For example, matching sample and reference pan weights to within 0.05 mg is often recommended. The use of Modulated DSC[®] (MDSC[®]) increases the accuracy over the traditional three run method employed by standard DSC and makes C_p a signal that is captured during an experiment, rather than a post-test calculated result. In typical experiments, 2-3% accuracy is easily obtained by MDSC. Most metals have low C_p as compared to polymeric or low thermal conductivity materials. Experimental technique plays an even more critical role here in making accurate measurements. In addition to matching sample and reference pan weights, careful adjustment of sample mass and the superior baseline of the Q2000 / 1000 DSC are required to measure the C_p of metals to accuracies of 1%.

INTRODUCTION

The introduction of Modulated DSC[®] (MDSC) by TA Instruments in 1993 provided a new and easier way to measure specific heat capacity (C_p). The traditional measurement of C_p , as outlined in ASTM E1269, requires three separate experiments for baseline, calibration and sample analysis (1). Special software is normally used to calculate the C_p . In a MDSC experiment, modulation of the sample temperature permits the heat flow to be split into two components, one of which is dependent upon sample C_p and changes in C_p . With a properly calibrated system, the measurement of C_p by MDSC is more accurate than the three run method, with values of 2-3 % being easily obtained.

Sapphire is the traditional material used to calibrate a DSC for C_p measurements, with values ranging from about 0.4 J/g^{°C} at -100 °C to around 1.04 J/g^{°C} at 200 °C. The heat capacities of many solid polymers and organics are typically of this order of magnitude, making sapphire an excellent reference material choice. Conversely, metals typically have much lower values and they increase more slowly over the same temperature range. Thus experimental detail is more critical to making an accurate C_p measurement. It has been suggested that the C_p of metals should only be measured using quasi-isothermal MDSC not standard MDSC (2). In this experiment, the temperature is modulated about an average isothermal temperature. This paper shows that very accurate measurements of the C_p 's of metals can be made using Modulated DSC with sapphire as the calibrant.

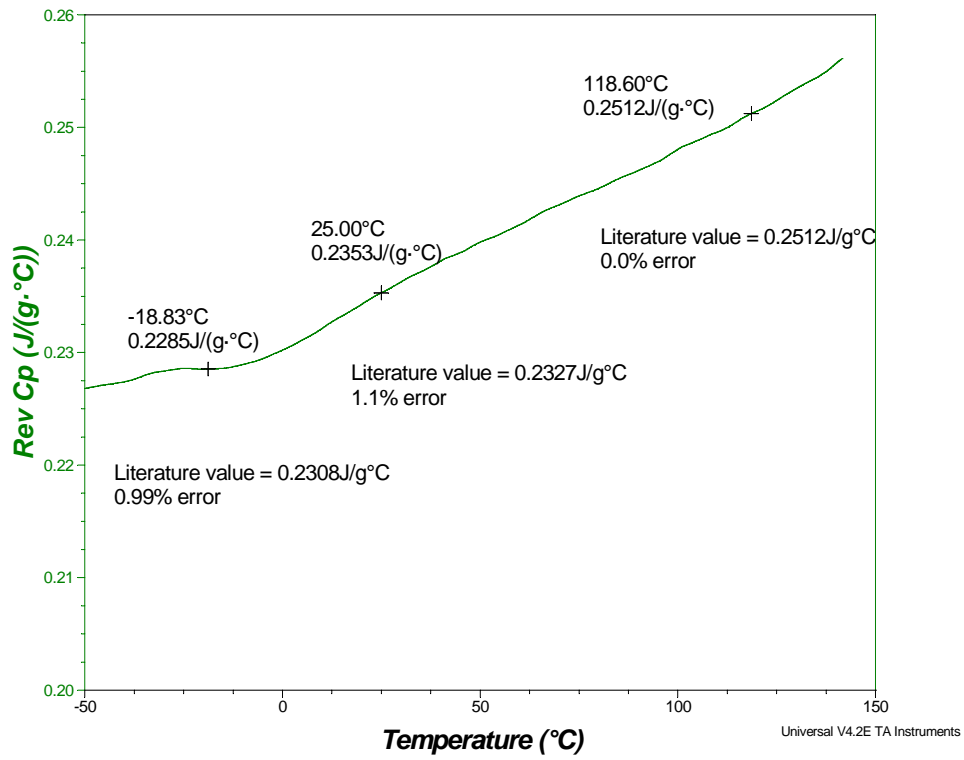
EXPERIMENTAL

A TA Instruments model Q1000 equipped with a refrigerated cooling system (RCS) was used. A 25.9 mg sapphire sample was used to calibrate the MDSC Reversing Cp signal. For calibration, the sapphire was heated -70 to 200 °C. The data was analyzed in 20 °C increments from -33.15 °C to 166.85 °C, and the ratio of the literature value of sapphire to the measured value was calculated at each of the eleven temperatures. The eleven values were then averaged to give a single calibration constant of 0.998, which was then applied to the DSC.

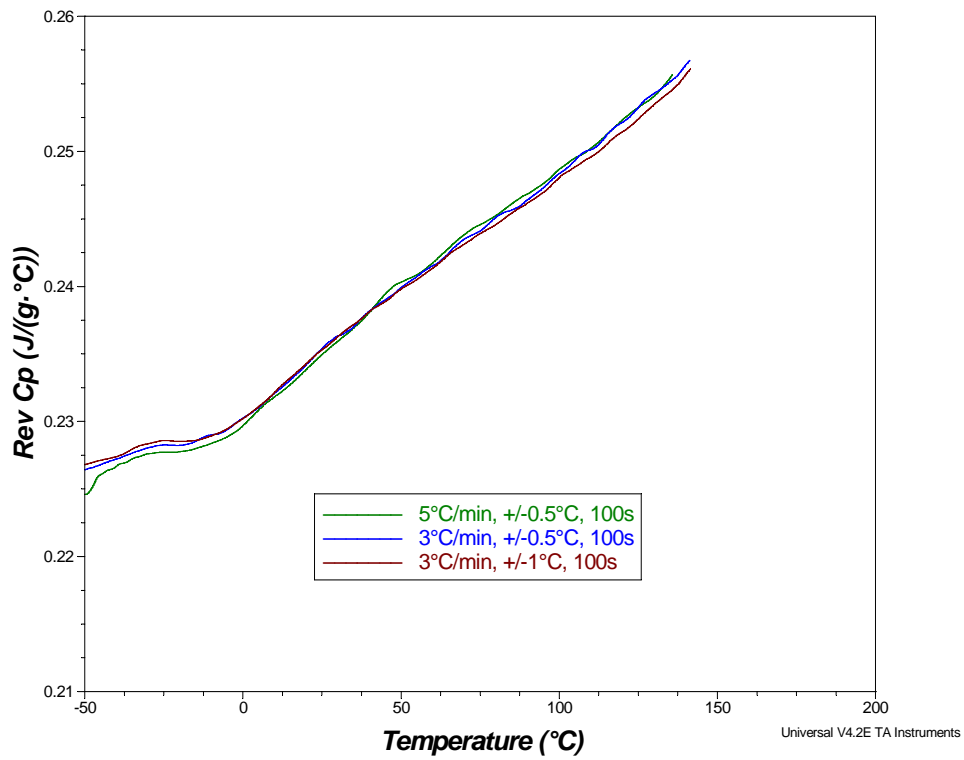
Prior to each measurement, the DSC baseline was cycled three times to ensure instrument stability. Standard aluminum pans were used to encapsulate the samples and the weight of each pan and lid combination was kept within ± 0.05 mg. Care was taken during the crimping process to ensure that the pan bottoms remained flat. The materials measured were indium, tin and gold, with masses in the range of 30-60 mg. The masses are larger than those typically used with low thermal conductivity materials in order to maintain signal strength. The indium was obtained from the Laboratory of Government Chemists and is certified reference material LGC2601 with purity of 99.99998 %. The gold was a 1mm diameter wire obtained from Alfa Aesar with a 99.999 % purity. The Tin was from Fisher Scientific and specified at 99.5 % purity.

RESULTS AND DISCUSSION

A typical indium plot is shown in Figure 1. A metal flake was cut from a larger sample and encapsulated in a standard aluminum pan. Modulation conditions were: ramp rate 3 °C/min, modulation amplitude ± 1 °C and modulation period 100 s. Both measured results and literature values (3,4) are indicated along with the accuracy at three points. Accuracy of about 1 % or less is obtained. When setting MDSC conditions, a modulation period of no less than 100 s is necessary to obtain accurate heat capacity values with standard aluminum pans (5). A heating rate between 1 and 5 °C/min is recommended and lastly an amplitude is selected. The selected amplitude should be sufficiently large to provide for both heating and cooling to occur during the experiment, since experience has shown that this gives the most accurate values (5). In this work, a 3 °C/min heating rate and ± 1 °C amplitude is used. The impact of changing ramp rate and modulation amplitude to what would usually be considered less optimal conditions is shown in Figure 2, which displays data from Figure 1 overlaid with two additional runs on the same indium sample. In the first case, the amplitude was lowered to ± 0.5 °C and in the second, the heating rate was increased to 5 °C/min. As can be seen from the data, the results obtained are relatively insensitive to changes in these parameters due to the high thermal conductivity of metals.



**Figure 1. Reversing heat capacity for indium with MDSC conditions:
3 °C/min., ±1 °C and 100 s.**



**Figure 2. Overlay of reversing heat capacity curves of indium
with different modulation conditions.**

The impact of sample form was also studied, since experience has shown that the best heat capacity data is obtained with thin, flat samples. This geometry, when the sample is encapsulated, serves to minimize the possibility of building up a temperature gradient across the sample and also the presence of air pockets. However, due to the high thermal conductivity of metals, sample geometry may not be as critical as with low thermal conductivity samples, especially in sample thickness. Figure 3 shows C_p results on a 1 mm diameter gold wire. For comparison, the thickness of the indium sample run was approximately 0.1 mm. The modulation conditions were 5 °C/min ramp rate, ± 0.5 °C amplitude and a 100 s period respectively. The accuracy is excellent with results well within 0.5 % of the literature values.

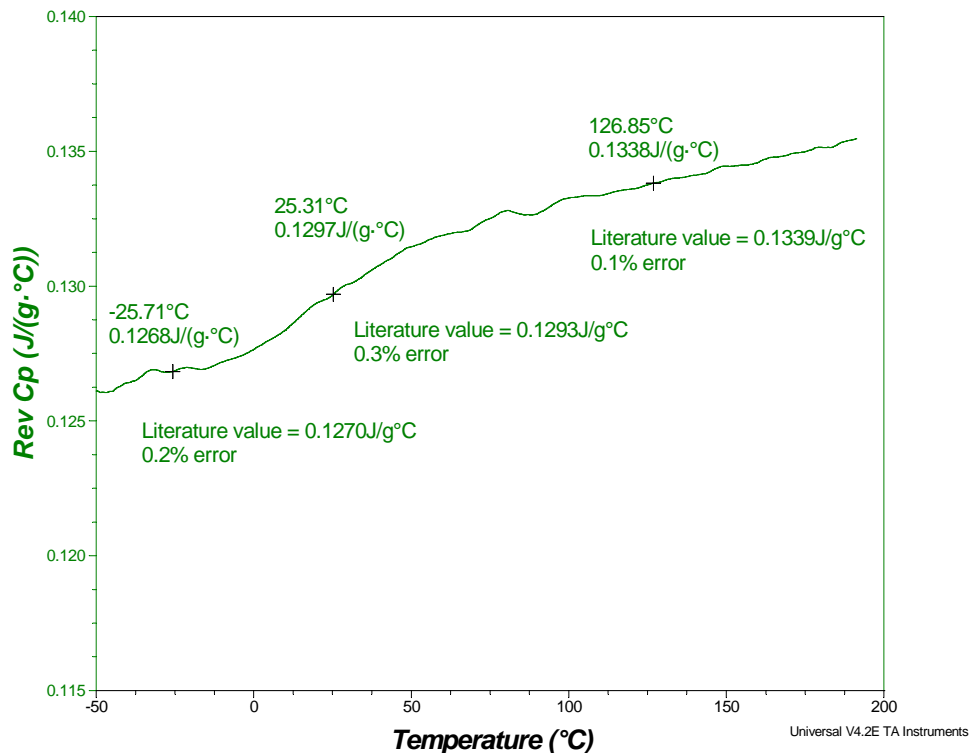


Figure 3. Reversing heat capacity results for a 1mm diameter gold wire sample.

Since experience with other materials encourages efforts to minimize the amount of air trapped in the sample, granulated samples are typically avoided. Figure 4 shows C_p results on 1 mm diameter tin granules, in which the modulation conditions were the same as for the gold sample in Figure 3. The accuracy of the results indicates that a granulated form is not an issue with metals.

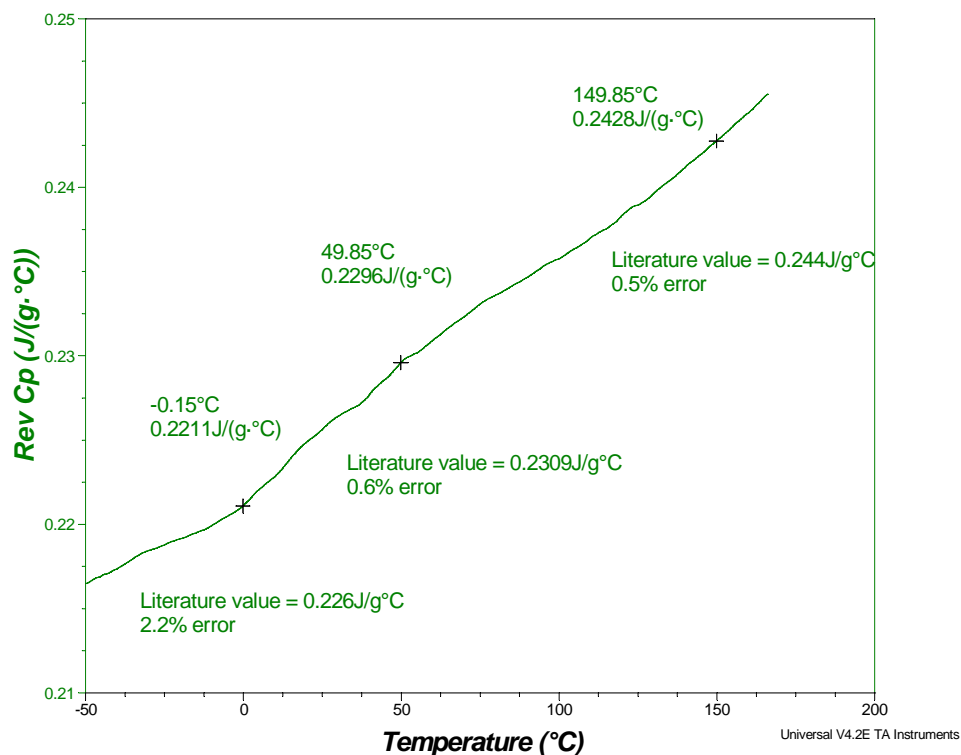


Figure 4. Reversing heat capacity results for ~1mm diameter tin granules

SUMMARY

The heat capacity results obtained on the metallic systems and reported here exceed the accuracy typically claimed for the MDSC technique. This is likely a result of the metals high thermal conductivities. The single most important requirement to obtaining good MDSC results is that the sample follows the temperature modulation effectively. This is the reason long modulation periods are critical to accurate Cp data. The high thermal conductivity of metals only adds to the ability of these types of samples to precisely follow the temperature modulation.

REFERENCES

1. E 1269, "Determining Specific Heat Capacity by Differential Scanning Calorimetry", ASTM International, West Conshohocken, PA.
2. L. Thomas and S. Aubuchon, *Heat Capacity Measurements Using Quasi-Isothermal Modulated DSC*, TA Instruments Application (TA 230).
3. Y.S. Touloukian and E.H. Buyco, *Thermophysical Properties of Matter, Vol. 4, Specific Heat, Metallic Elements and Alloys*, 1970.
4. CRC Handbook of Chemistry and Physics, 51st Edition, 1970-1971, D131.
5. L. Thomas, *Modulated DSC Paper #9, Measurement of Accurate Heat Capacity Values*, TA Instruments Application (TP 014).

KEY WORDS

DSC, MDSC, Heat Capacity, Cp Metals

TA INSTRUMENTS

United States

109 Lukens Drive, New Castle, DE 19720 • Phone: 1-302-427-4000 • E-mail: info@tainstruments.com

Canada

Phone: 1-905-309-5387 • E-mail: shunt@tainstruments.com.

Mexico

Phone: 52-55-5200-1860 • E-mail: mdominguez@tainstruments.com

Spain

Phone: 34-93-600-9300 • E-mail: spain@tainstruments.com

United Kingdom

Phone: 44-1-293-658-900 • E-mail: uk@tainstruments.com

Belgium/Luxembourg

Phone: 32-2-706-0080 • E-mail: belgium@tainstruments.com

Netherlands

Phone: 31-76-508-7270 • E-mail: netherlands@tainstruments.com

Germany

Phone: 49-6196-400-7060 • E-mail: germany@tainstruments.com

France

Phone: 33-1-304-89460 • E-mail: france@tainstruments.com

Italy

Phone: 39-02-2742-11 • E-mail: italia@tainstruments.com

Sweden/Norway

Phone: 46-8-555-11-521 • E-mail: sweden@tainstruments.com

Japan

Phone: 813-5479-8418 • E-mail: j-marketing@tainstruments.com

Australia

Phone: 613-9553-0813 • E-mail: sshamis@tainstruments.com

India

Phone: 91-80-2839-8963 • E-mail: india@tainstrument.com

China

Phone: 8610-8586-8899 • E-mail: info@tainstruments.com

Taiwan

Phone: 886-2-2563-8880 • E-mail: skuo@tainstruments.com

To contact your local TA Instruments representative visit our website at www.tainstruments.com

© Copyright 2007 TA Instruments