Tzero™ Technology and Linearity

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ABSTRACT

The Tzero™ Technology inherent in the TA Instruments Q100 and Q1000 Differential Scanning Calorimeters (DSCs) permits accurate melting parameters (temperature and enthalpy) to be obtained at temperatures up to four or five hundred Celsius degrees using a single point indium calibration.

INTRODUCTION

While Tzero™ Technology has dramatically reduced DSC baseline curvature; a less appreciated fact is that it has also substantially reduced calibration non-linearity. That is, after the usual indium calibration procedure, a DSC will normally be adequately calibrated up to about 250 ºC. But to be well calibrated over a wider temperature range, most DSC's should be calibrated using additional melting point standards to obtain accurate temperature and enthalpy calibration. The problem that requires using other, often less reliable, melting materials is instrument output non-linearity.

This linearity problem stems in part from the fact that DSCs employ non-linear sensors (e.g., thermocouples or resistance thermometers) as the devices to determine temperature and heat flow. Since the measurement system is non-linear with respect to temperature, this sensor output has traditionally been linearized using a calibration "look-up table", the purpose of which is to linearize temperature, and heat flow output with respect to temperature. These tables are factory determined and are based on the NIST standard values. This essentially assumes that the thermal characteristics of all analyzers are the same, that they do not change with time, and that they do not change when used with different purge gases and cooling systems. This assumption of calibration constancy is at odds with practical experience. For this reason standard methodology recommends calibration under the exact conditions of use (*1*). Frequent recalibration to optimize for each change in thermal method is time consuming and tedious. With the Tzero measuring principle the case is different.

Figure 1 - Q Series™ DSC

Q SERIES DSC

There are many design aspects that affect an instrument's performance. The design of the Q Series DSC (Figure 1) ensures that the thermal characteristics of the DSC cell are reproducible and stable over time, and are a predictable function of temperature. To that end all of the key components

in the DSC cell that link the sample sensor to the furnace and cooling system are welded or braised. Despite the large operational temperature range of the Q Series DSCs (-180 to 725 ºC), there is no slippage of bolted or clamped parts (*2*). Thus the cell thermal resistances that determine the baselines, thermal lags and the calibration constants are relatively invariant with respect to routine operations, and depend reproducibly on temperature (See Figure 2). Moreover, the sensor is designed such that a precision-machined vertical cylinder creates the thermal resistance that provides the measured difference in temperatures. A more common DSC alternative is a measured thermal resistance in a *horizontal* plane where the position and type of sample pan can materially affect the measurement.

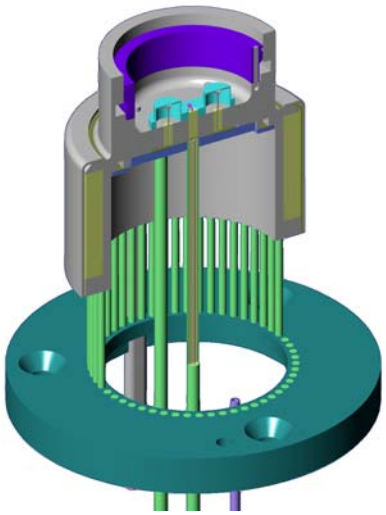


Figure 2. Q Cell cross-section

Tzero TECHNOLOGY

The conventional DSC heat flow equation employs a differential temperature measurement between the sample and reference sensors (ΔT), as shown in the first term of the equation below. The new Tzero Technology provides in addition, a second measurement of the differential temperature across the sample calorimeter thermal resistance (ΔT_0), plus an absolute temperature measurement at the base of the sensors. The latter comes from the "T_0" thermocouple that is centrally located in the cell and controls the temperature of the furnace. The ΔT_0 signal provides the means for an independent measurement of the physical characteristics of the sensor, namely its thermal resistance and thermal capacitance parameters. The calibration of these parameters (the "Tzero calibration") allows all these component values to be specifically taken into account in calculating the measured heat flow of the sample specimen. The equation derived for this DSC cell that incorporates this information is shown below (*3*).

$$q = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{d\tau} - C_r\frac{d\Delta T}{d\tau}$$

Primary calibration constant

Where:
Rs and Rr are the thermal resistances of the sample and reference calorimeters
Cs and Cr are the thermal capacitances of the sample and references calorimeters
ΔT is the differential signal from the sample and reference thermocouples
ΔT_0 is the temperature difference between the sample and the Tzero thermocouples
ΔTs/dt is the heating rate at the sample thermocouple
dΔT/dt is the difference in heating rates between the sample and reference thermocouples

This is the equation used to determine the heat flow data that is reported with a Q100 or Q1000 DSC. The C and R parameters are determined from the Tzero calibration performed occasionally by the DSC user. As previously described, the evaluation of terms two and three in the above equation correct for baseline curvature caused by

asymmetry; and term four compensates for the peak smearing which occurs because of thermal lags in the measurement-sample system (*3*).

This work demonstrates that the effect of evaluating the parameters of the four-term heat flow equation also results in a better temperature and enthalpy calibration of the instrument since the thermal resistance parameter, Rr, in the *first* term of the equation has been determined as a function of temperature for *that specific instrument, cooling system and purge gas*. This effectively updates the non-linearity corrections so that the cell calibration is now correct over a wider temperature range.

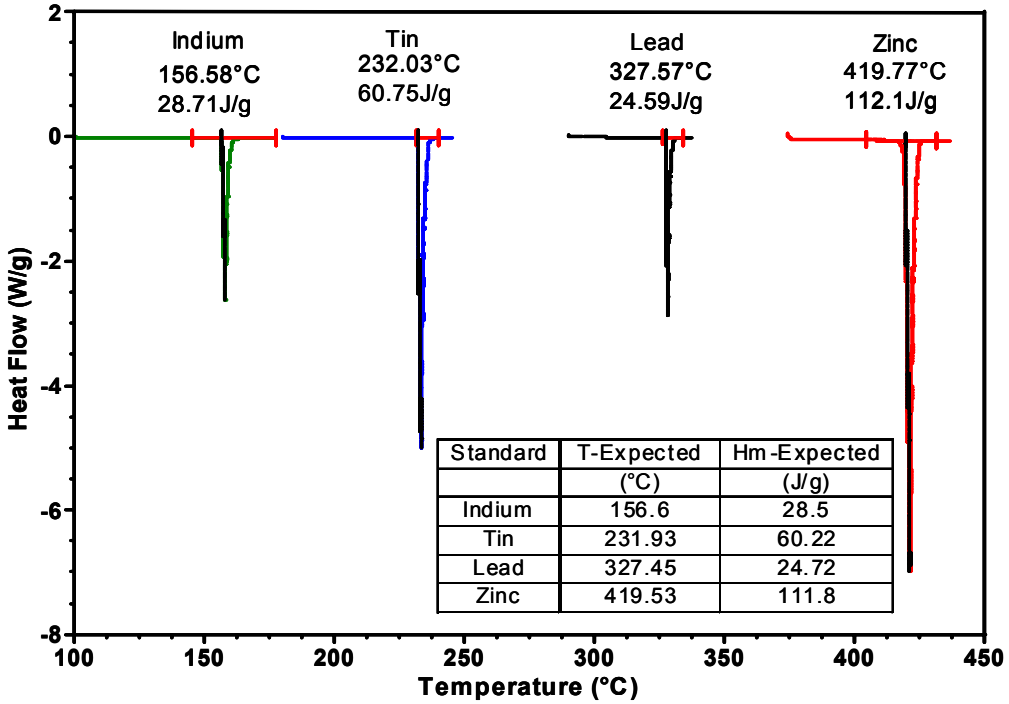
EXPERIMENTAL

A Q100 DSC was calibrated using the calibration wizard over the temperature range –20 to 440 ºC using standard conditions (20 ºC / min heating rate for baseline and sapphire calibration runs, and a 10 mg indium sample crimped in aluminum pans and heated at 10 ºC/min).

After the Tzero and Cell constant calibration, the indium sample was reloaded, and run. Six to ten milligram sample specimens of 99.999% tin, lead and zinc were also carefully prepared and weighed into standard aluminum pans. After crimping the pans containing the reference materials, the pans were further flattened to improve thermal contact - especially for the higher temperature melting standards (for which good thermal contact is particularly important). The heats and temperatures of melting were calculated for the four melting standards taking care to expand the heat flow scale sufficiently to be able to pick the optimum peak start and end.

RESULTS AND DISCUSSION

Figure 3 shows the thermal curves with results of the four melting experiments and the expected melting parameter values taken from the National Institute for Standards



Standard	T-Expected (°C)	Hm-Expected (J/g)
Indium	156.6	28.5
Tin	231.93	60.22
Lead	327.45	24.72
Zinc	419.53	111.8

Figure 3.
Melting points and enthalpies of melting
of four reference materials

and Technology (NIST) or the National Physics Laboratory (*2*). These experimental temperature values are within 0.25 ºC of NIST recognized reference values and the experimental enthalpies are within 1 % after only a one-point calibration using indium.

Figures 4 and 5 show the temperature and heat flow calibration data as a function of temperature after taking the results of the calculations and NIST data into an Excel® spreadsheet that is linked to the Universal Analysis software provided with the instrument

CONCLUSION

It is still true that for the most accurate and reliable determination of melting parameters it is preferable to calibrate using the exact conditions under which the melts are to be made, including the pan type. However, when the Q100 or Q1000 DSC is used up to a temperature of four or five hundred Celsius degrees, it is sufficient to calibrate with indium alone - rather than use multiple or alternate calibrants - for all but the most critical experiments. This convenience is made possible by Tzero technology. A final caveat to obtaining high accuracy data is an instrument in excellent working order and an experienced operator.

REFERENCES

1. E967 Standard Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers, ASTM International, West Conshohocken, PA
2. *Explanatory note:* The cooling system is bolted on but this junction does not undergo large swings in temperature that would cause slippage.
3. R. L. Danley, "A New Technology to Improve DSC Performance", *Thermochim. Acta,* **2003**, 395 pp. 201-208.
4. As posted on the following website: http://www.chemistry.ohio-state.edu/~gallaghe/ta/calib_stand.htm(2).

KEY WORDS

DSC, Linearity, Melting standards, Tzero, Enthalpy

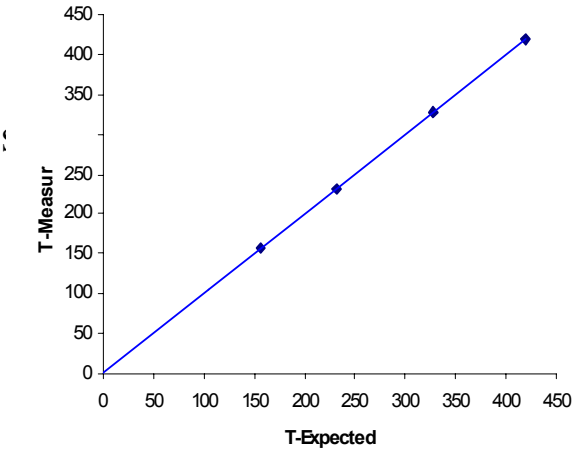
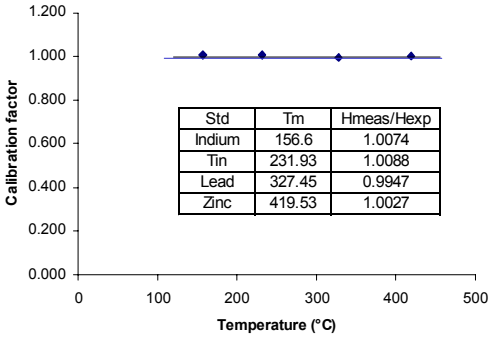


Figure 4
Validation of Temperature Linearity
After Calibration with Indium



Std	Tm	Hmeas/Hexp
Indium	156.6	1.0074
Tin	231.93	1.0088
Lead	327.45	0.9947
Zinc	419.53	1.0027

Figure 5
Validation of Heat Flow Linearity
After Calibration with Indium

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