Impact of Tzero™ Technology on DSC Resolution

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ABSTRACT

Tzero™ Technology is a new DSC approach that utilizes an innovative DSC cell design and a more comprehensive heat flow measurement to dramatically reduce the traditional sources of instrument effects in a DSC measurement. It is known that the traditional DSC heat flow measurement during a transition includes the effects of the measuring system and the sample pans. Two major sources of error are the effect of differences in the sample sensor and reference sensor heating rates and the sample pan and reference pan heating rates during a transition. The Tzero™ DSC accounts for and includes these effects in the heat flow measurement. The result is sharper onsets, higher peaks and faster baseline returns during transitions. These benefits will be illustrated by specific examples that demonstrate the ability of the Tzero™ DSC to separate closely spaced transitions.

INTRODUCTION

The TA Instruments Q1000 DSC and Tzero™ Technology is a significant new development that further advances the ability of the thermal analyst to make high-resolution heat flow measurements. Without any preconceived design restrictions, a fundamentally new DSC was developed (1). It is understood that there are many instrument effects that degrade the resolution of sharp transitions such as first order melt transitions. The innovative design of the Q1000 DSC and Tzero™ Technology takes into account many aspects of the heat flow measurement that adversely impact resolution (2).

DSC is a differential measurement technique, based on twin sensors that are assumed to be identical. The differential heat flow signal is influenced by the heat storage within the two sample and reference sensors and pans, resulting in baseline effects and a broadening of the heat flow signal. In addition, during sharp transitions the heat flows to the sample and reference sensors and pans are very different.

Conventional heat flow measurements do not include these effects and as a result broadens the heat flow signal during transitions. The Q1000 DSC and Tzero™ Technology utilize two independent sensors and the thermal resistance and capacitance of these sensors are independently determined by calibration. During sharp, energetic transitions, the sample pan and sensor heating rates do not match the reference pan and sensor heating rates. By including the effect of heat rate differences between these two sensors, and the pans, the resolution of the Tzero™ heat flow measurement is dramatically improved.

Resolution is an important consideration during DSC methods development. Experimental conditions often need to be adjusted in order to obtain a sufficient level of resolution. Decreasing the amount of sample and the heating rate typically improve resolution but also decrease sensitivity and increase the experiment time. By improving the resolution of the instrument, one can obtain the level of resolution required without degrading sensitivity or increasing the time of an experiment.

This paper describes the impact of Tzero™ Technology on the resolution of sharp transitions. Several examples illustrating the resolution of the Q1000 DSC are shown. The results obtained represent typical results and are not intended to represent performance specifications. Rather, these results are intended to illustrate the resolution is improvements of Tzero™ Technology.

EXPERIMENTAL

A TA Instruments (New Castle, Delaware) Q1000 Differential Scanning Calorimeter was used in these experiments. A Refrigerated Cooling System (RCS) was used as cooling device. In all cases, the instrument was purged with dry nitrogen. After installing and conditioning the cooling device, instrument calibration was performed using the *Advantage for Q Series Calibration Wizard* over the temperature range of –90 to 400°C at a heating rate of 20°C/min. Temperature calibration of the Tzero heat flow signal was performed using certified high purity indium, also at a heating rate of 20°C/min.

The indium analysis utilized a nominal 1mg sample of certified high purity indium obtained from TA Instruments and encapsulated in a standard crimped aluminum pan. The sample was analyzed by equilibrating the sample at 180°C, then 50°C and then heating at 10°C/min through the melt transition. In this and all subsequent experiments, data was collected at a data sampling rate of 10pts/sec.

The dotriacontane was obtained from Fluka Chemie AG, >99.5% purity standard for GC. A nominal 1mg sample was encapsulated in a standard crimped aluminum pan, heated to 80°C, then quenched cooled to 0°C and heated at 10°C/min to 100°C.

For the TAWN resolution test a 5.0±0.1mg sample of 4, 4’-azoxyanisole, 98% purity, obtained from Aldrich Chemical was used.. The sample was weighed into a standard crimped aluminum pan (nominal mass 23mg,) heated to 145°C, held isothermal for 5 minutes and then cooled at 20°C/min to 30°C. The sample was then heated at 20°C/min to 165°C.

INDIUM MELT ANALYSIS

A sharp melt transition such as the indium melt illustrates the improvement in resolution achieved by Tzero™ Technology. When the sample is absorbing heat rapidly, the reference sensor and pan heating rates do not match the sample sensor and pan heating rates. Conventional heat flow measurements subtract the incorrect reference heat flow during this type of transition and the result is a broadening of the transition. Tzero™ Technology includes this effect and thereby improves the resolution; peaks are sharper, narrower and return to the baseline faster.

A comparison of the Tzero™ heat flow and conventional heat flow during the melt transition of a 1mg sample of indium heated at a typical rate of 10°C/min is shown in Figure 1. The Tzero™ peak height was 9.48mW compared to the conventional peak height of 5.97mW, an improvement of 59%. The Tzero™ peak width at half height was 0.25°C compared to 0.80°C for the conventional heat flow, an improvement of 69%.

A rapid return to baseline after a melt is very desirable and can be defined by the time constant, the time for the heat flow signal to return from the peak value to 63% (1/e) of the baseline value. The time constant was found to be 1.02 seconds compared to the conventional time constant of 3.13 seconds, an improvement of 67%.

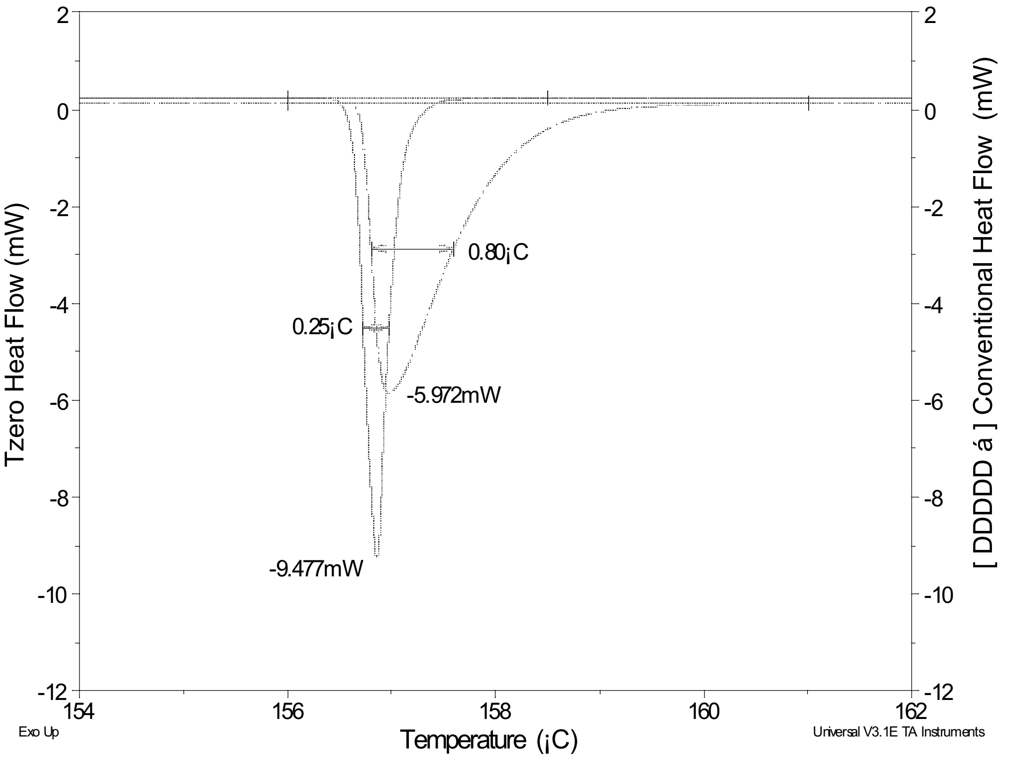

Figure 1.
Tzero vs. Conventional Indium Melt

The significant improvement in Q1000 Tzero™ heat flow resolution shown in figure 1 is a result of the removal of the broadening effect caused by the differences in the heating rates of the sample and reference sensors and pans. During the baseline region and during broad transitions, the heating rates of the two sensors and pans are the same and hence the heat flows are the same.

However, during sharp, energetic transitions such as an indium melt, there can be a significant difference between the heating rates of the reference and the sample sensors and pans. Figure 2 illustrates the magnitude of the difference between the sample and reference pan heating rates. Conventional heat flow measurements do not include this effect, and results in distortion of the peak shape of the transition. By including this effect, a dramatic improvement in the resolution of the Tzero™ heat flow shown in figure 1 is achieved.

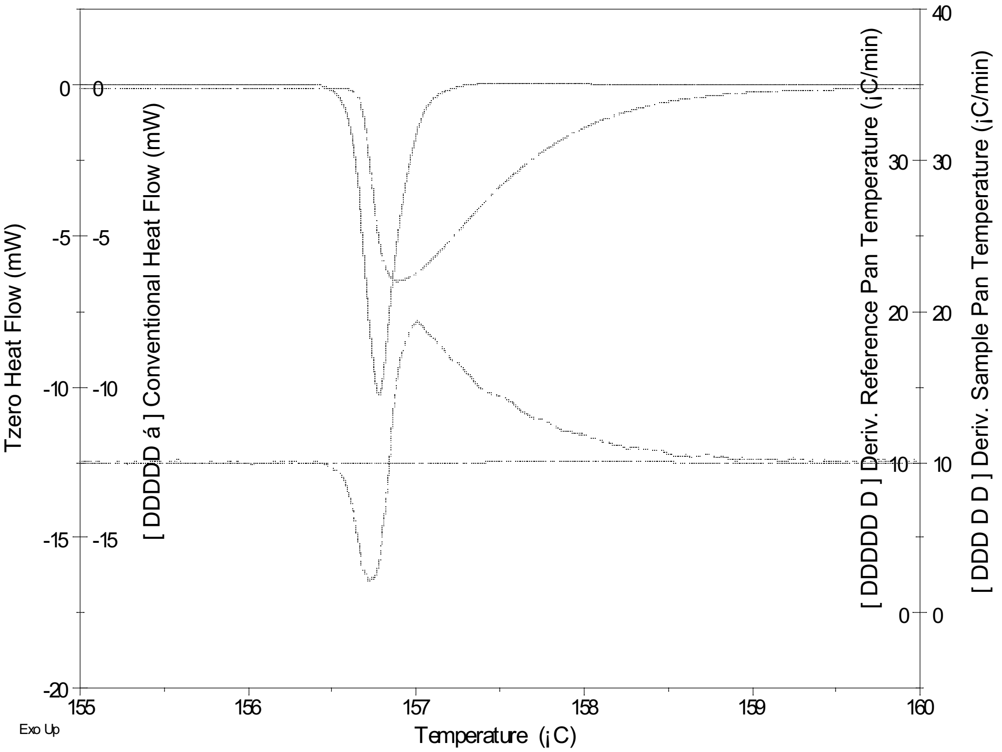

Figure 2.
Influence of Sample and Reference Heating Rates

DOTRIACONTANE

Dotriacontane, a long chain aliphatic hydrocarbon, molecular formula $C_{32}H_{66}$, may also be used to evaluate the capability of a DSC to resolve closely spaced peaks. When a nominal 1mg sample of the as-received material is heated at 1°C/min, two clearly resolved endothermic transitions are observed; a single solid-solid transition around 64°C and a larger solid-liquid transition around 68°C. When the sample is quenched from the melt, multiple polymorphic forms are induced and during subsequent heating two distinct solid-solid phase transitions are observed before the final solid-liquid transition.

An example of the melt of a 1mg sample of Dotriacontane at 10°C/min after it was quenched from the melt is shown in Figure 3. Typically, in order to adequately resolve these closely spaced peaks using conventional DSC, a slow heating rate of 1°C/min is used. In this example, using the improved resolution of the Q1000 DSC, resolution of the closely spaced transitions can be achieved at a heating rate of 10°C/min. The ability to effectively analyze closely spaced transitions at higher heating rates, thereby improving efficiency, is very useful in a modern laboratory.

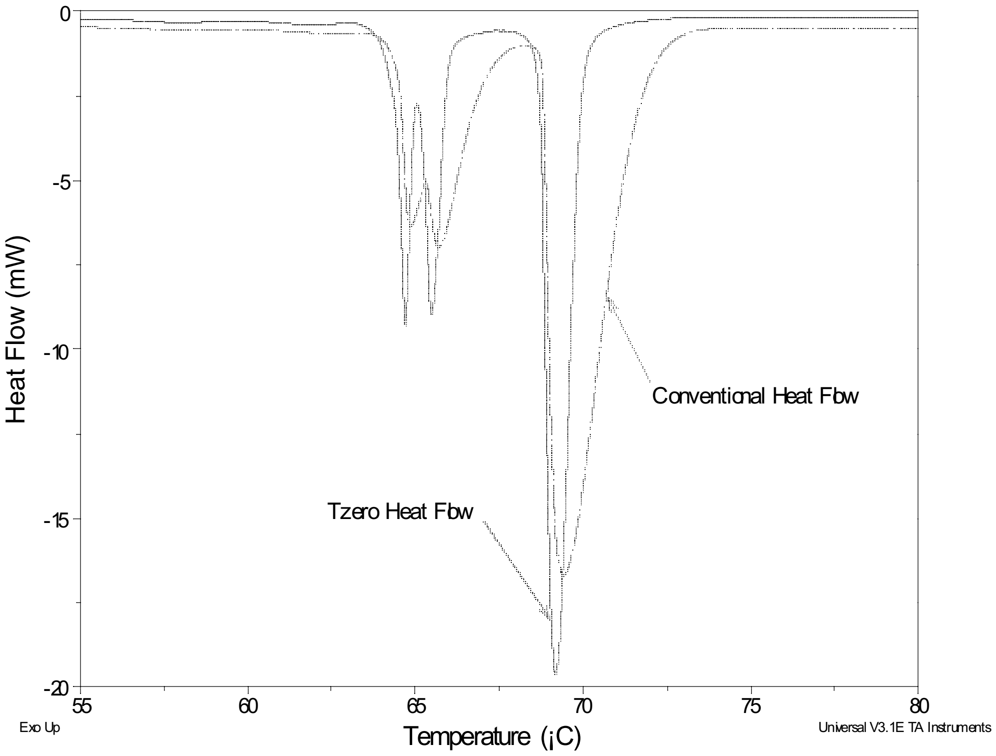

Figure 3
Dotriacontane Quenched from the Melt and Heated at 10°C/min

TAWN RESOLUTION

The Dutch Society for Thermal Analysis (TAWN) developed a comparative test of the resolution and sensitivity for DSC instruments (3). The test uses a sample of 4, 4'-azoxyanisole, that has a pair of endothermic transitions spaced ~17°C apart. The first is a large solid-liquid crystal transition at about 117°C and the second is a small liquid crystal-isotropic liquid transition at about 134°C. The resolution test heats a relatively large sample to 145°C, cools the sample at 20°C/min to 30°C, then heats the sample at 20°C/min through both transitions. The resolution test determines how well the two peaks are resolved based on the minimum in the heat flow signal between the two peaks divided by the peak height of the second transition. The lower the number, the better the resolution.

The experiment was performed as described earlier and a standard crimped aluminum sample pan with a nominal 23mg sample pan mass was used. The results comparing conventional heat flow and Tzero heat flow are shown in Figure 4. TAWN also specifies precisely how the data is to be presented and analyzed. The data was plotted and a linear baseline was drawn between 60°C and 160°C. A linear baseline was drawn between 100°C and 150°C. The difference between the minimum values of the heat flow signal between the two transitions and the baseline, designated A, was determined. The peak heights of the second transition, designated B, were then determined and the resolution was quantified by dividing A by B.

Using the TAWN definition, the resolution of the conventional heat flow was found to be 0.25 and the Tzero™ heat flow was 0.09, indicative of the excellent resolution of the Q1000 DSC and Tzero™ Technology.

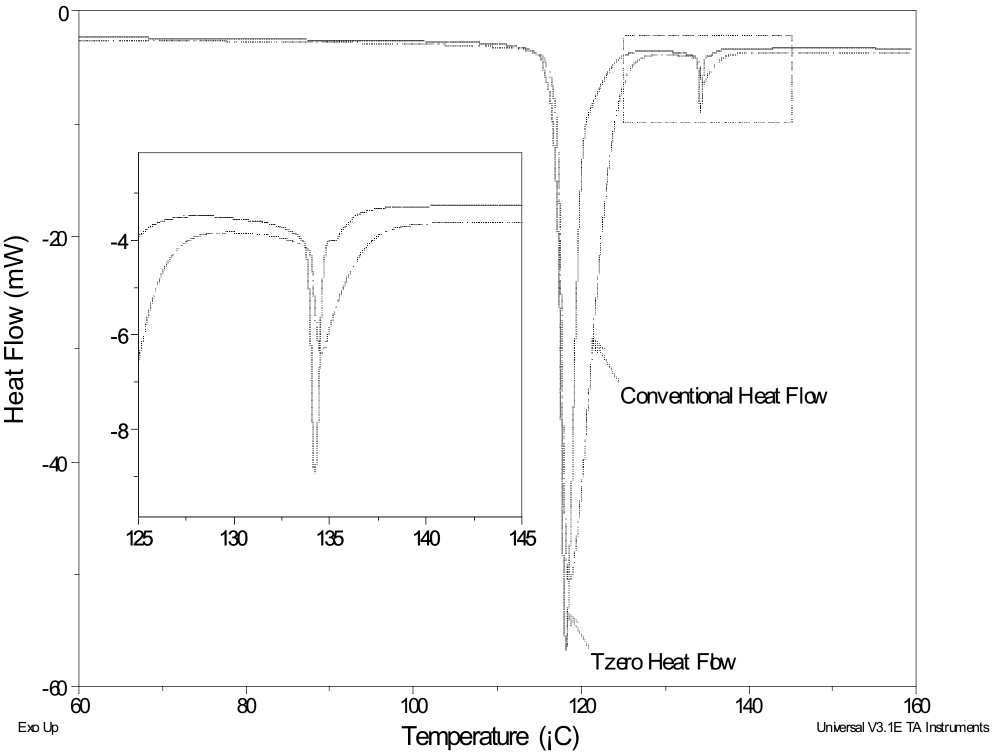

Figure 4
TAWN Resolution Test Result

CONCLUSION

The Q1000 DSC and Tzero™ Technology includes effects known to broaden transitions and is a dramatic improvement in the resolution of sharp transitions such as metal melts. By including sample and reference sensor and pan heating rate effects in the heat flow measurement, a more accurate representation of the thermal event is measured. Peaks measured using the Q1000 and Tzero™ technology are sharper, narrower and the return to baseline is faster. The Q1000 can be utilized to analyze materials more accurately and at faster rates, further improving efficiency in the modern laboratory.

REFERENCES

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3. P. J. van Ekeren, C. M. Holl, A. J. Witteveen, A Comparative Test of Differential Scanning Calorimeters, *Journal of Thermal Analysis*, Vol. 49, 1997, 1105-1114.