



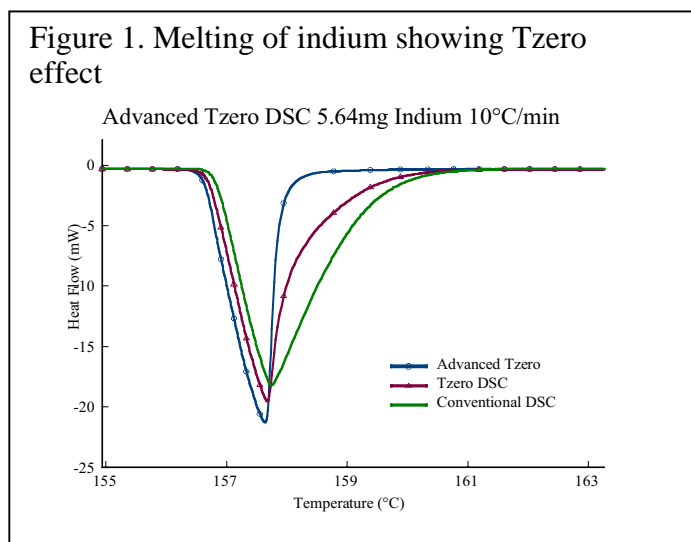
## How Tzero™ Technology Improves DSC Performance Part II. Peak Shape and Resolution

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**Abstract.** All DSC instrumentation, to a greater or lesser extent, distorts the theoretical shape of sharp peaks. TA Instrument's Q100 DSC and Q1000 DSC take a major step to rectify this situation by using Tzero™ technology. The result is a peak shape that better reflects the actual thermal event. This can be most easily observed in the shape of the melting of indium and in the resolution of closely spaced peaks. However, it is also a factor in the shape of every peak, and especially those peaks whose partial areas are analyzed, such as for purity and kinetics analysis.

**Background.** If you've used a spectrometer, a chromatograph or even a digital camera you know that a key aspect of recording data is resolution. For a DSC, resolution is the ability to separately analyze two phenomena that are closely spaced along the x-axis. In the detection and amplification of thermal events, as in other types of instrumentation, there is a tendency for the signal broaden or to become "smeared". For example, if a small sample of indium calibration material is heated at a fast scan rate, a symmetrical, gaussian-shaped peak is obtained. By contrast, if a large sample of indium is heated at a slow rate, an asymmetric peak with a straight leading edge followed by an exponential tail is obtained. But indium actually melts over a few hundredths of a degree Celsius, so both of these peak shapes are distortions of the "true" shape, which should be a sharp spike.

The DSC causes this distortion by the thermal resistance and thermal capacitance of the DSC cell and sample pan, and by non-linearity of the heating rate of the sensor caused by the heat released or absorbed by the sample. These thermal affects have long been known, and various corrections to the data have been offered (1, 2). In a recent breakthrough, TA Instruments has devised a DSC cell with a Tzero reference temperature sensor that allows these adverse thermal effects to be detected and compensated for as part of the measuring circuit (3, 4). The result is a heat flow signal that is a much truer representation of the actual



heat flow to/from the sample. This results in improved resolution for closely spaced thermal events.

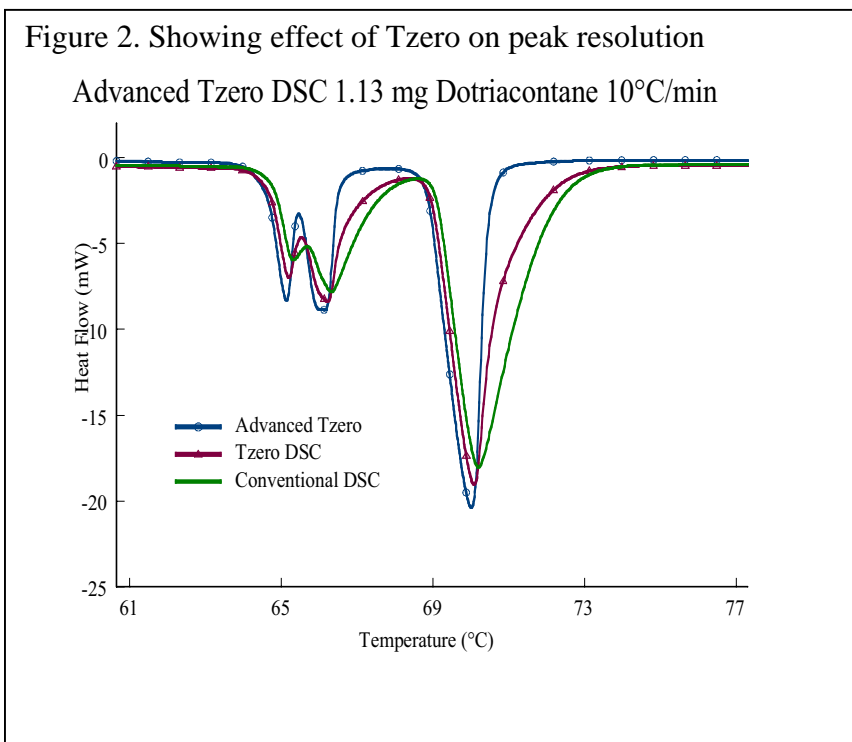
## EXPERIMENTAL RESULTS

**Indium.** Figure 1 shows the heat flow data from melting a standard sample of indium. The three curves are actually taken from the same indium run, but they also represent typical outputs of three different technologies. The broadest peak is that of the uncompensated heat flow data, achieved by TA Instruments Q10 DSC. Similar results would be obtained for other high quality heat flux DSC's. The middle curve is that of a DSC employing Tzero™ technology, this is included as standard on the Q100 DSC. With DSC the Tzero sensor is used to compensate for the smearing of the heat flow signal due to effects within the DSC cell, including those caused by thermal resistances, capacitances and rate asymmetries. The result is a heat flow signal with a resolution capability better than that of the best previous technology for resolution, namely, power compensation DSC.

The highest and sharpest curve in Figure 1 is that generated by Advanced Tzero™ technology. In this case the Tzero sensor is used to calibrate and remove not only the smearing effect of the DSC cell on the heat flow signal, but also that of the sample pan. The result is a DSC with an improvement in resolution better than any other commercial DSC. Perhaps the best indication that the heat flow data obtained is the truer response of the sample is that once the indium fusion is complete (at the top of the peak) the signal drops directly to the baseline. The effect of this compensation circuit is to shift the melting energy, which until now has been smeared to the tail of the indium melt, to where it belongs, namely, to the melting side of the peak.

**Polymorphism.** A good indication of resolution improvement comes when a sample is run which requires superior resolving

power, because there are closely spaced thermal events. Figure 2 shows the analysis of dotriacontane, a purified wax containing a 32 carbon linear chain. This material illustrates polymorphism, such that the material undergoes two crystal-crystal transitions prior to melting. All three endothermic transitions take place within a span of five degrees Celsius. At a 10°C/min scan rate, this is an excellent system to test DSC resolution capability. Using Advanced Tzero technology there is a complete return to the baseline between the second and third peak, whereas the conventional DSC approach fails to return to the baseline. Using Advanced Tzero technology the first and second peak are not completely resolved; however, the improvement over conventional DSC is evident.



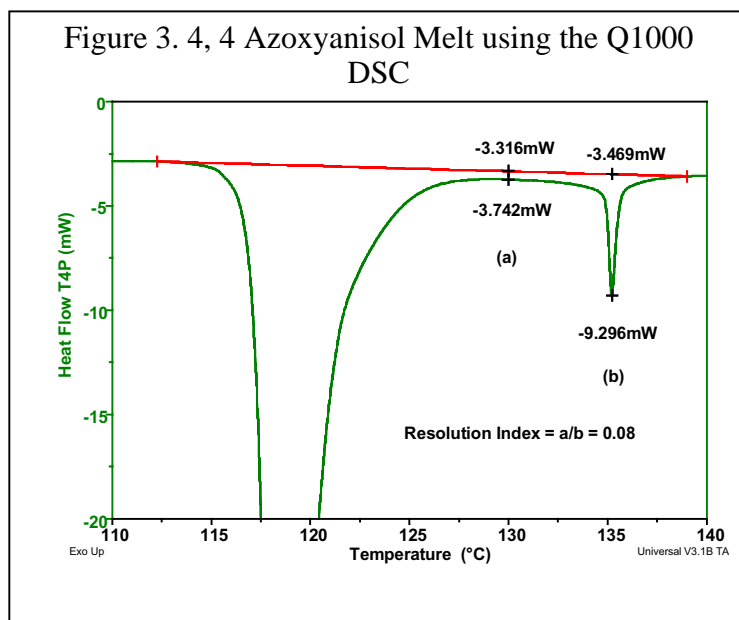
While dotriacontane may seem to be only of academic interest, it is typical of systems having a long aliphatic hydrocarbon chain and which often show polymorphism with a separation of only a few degrees Celsius. Even phospholipid membranes show this type of thermal behavior. Moreover, the study of polymorphism in the pharmaceutical and food industry benefits from high-resolution analysis.

**Purity and Kinetics.** Other applications that benefit from superior resolution include purity determination and kinetics. In these techniques the results are calculated by fitting the peak partial areas to a parametric equation. In the calculation of purity or kinetics parameters, the peak is divided up into twenty or more temperature intervals, and the corresponding areas are fitted to an equation. When a DSC is capable of high resolution each area represents the actual fraction of the total area over a specific, narrow, temperature range. When a DSC smears the data (as all DSC's do to a greater or lesser extent) then each area is contaminated by a contribution from its neighboring areas. As the peak is rising, this biases the data one way, and when it is falling it biases the data in the other. As a result of the improved resolution that is now possible utilizing Tzero™ Technology it should be possible to obtain more accurate kinetics and purity analyses.

**Quantifying Resolution.** Because of the importance of resolution, the Dutch Thermal Analysis Society devised a test (5) to compare the major DSC instruments under identical conditions running 4, 4 azoxyanisol (See Figure 3.). The sample is a liquid crystalline material, which melts into an ordered liquid state. (The absolute return to the peak baseline is not expected, as there is a Cp shift between the solid and the ordered liquid state.) Continued heating melts the ordered structure of the liquid. The resolution index was defined as the peak height of the second peak divided by the valley height between the peaks. While the published results of this interlaboratory test preceded the development of Tzero™ technology it has been possible to obtain identical samples and run them under identical conditions. The index results (0.13 for the Q100 DSC, and 0.08 for Q1000) indicate that Tzero technology matches power compensation, and Advanced Tzero technology improves on this by almost a factor of two.

**Tips for improved resolution.**

In the absence of a Q Series™ DSC, here are a few tips to help achieve better resolution. Use a thermally conductive, low mass sample pan; use a small sample, in good contact with the bottom of the pan, (pre-melt it, if possible); make sure the bottom of the sample pan is flat after crimping or sealing; use a slow heating rate and purge with helium gas (Note: purging with helium is not required with the Q Series DSC to improve resolution. All above data are taken using a nitrogen purge.)



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