Improved DSC Performance Using Tzero Technology

By R. Danley, T. Kelly, and J. Groh

A major new development in Differential Scanning Calorimetry technology has been recently announced, promising to combine the advantages of heat flux and power compensation devices. This article looks at the new system, Tzero, claimed to provide baseline stability and cell durability, combined with high resolution, and fast heating and cooling rates.

Thermal analysis is a series of techniques that measure physical properties vs. temperature. The most popular thermal analysis technique is Differential Scanning Calorimetry, commonly referred to as DSC. DSC measures endothermic and exothermic processes in materials as a function of temperature. DSC is used widely to characterise a broad range of materials including polymers, pharmaceuticals, food and biologicals, organic chemicals and inorganic materials, and is used in all types of labs including R&D, QC and analytical. Typical transitions measured include the Tg (Glass Transition), melting, crystallisation processes, curing and cure kinetics, onset of oxidation, and heat capacity.

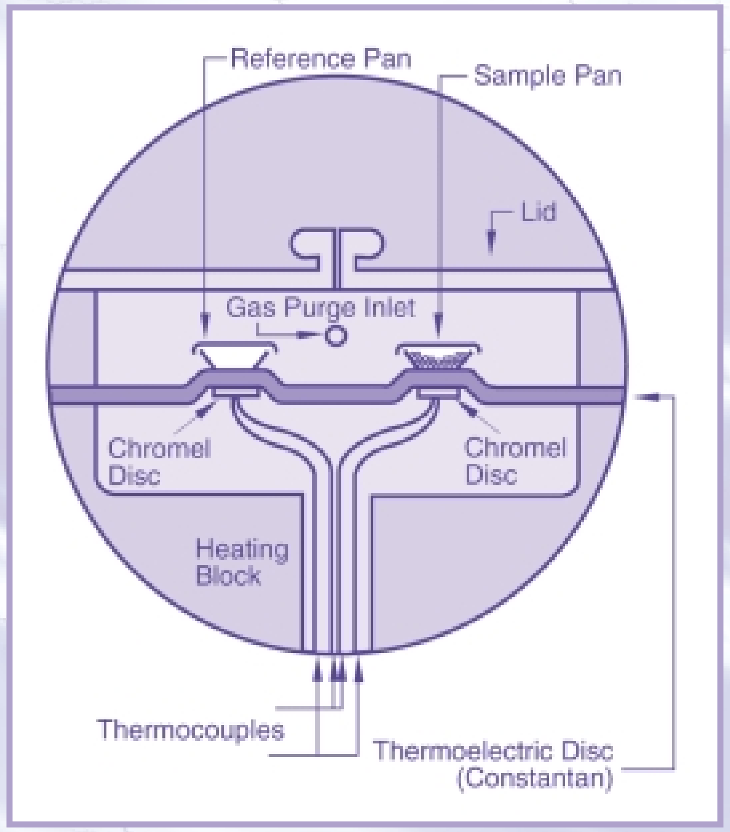

Figure 1: DSC heat flux device

The two major types of DSCs on the market today include the heat flux device and the power compensation device. The most popular of these techniques is the heat flux device. The advantage of heat flux has always been baseline stability and cell durability. Power compensation is known for resolution, and fast heating and cooling rates. Recently, a completely new line of DSCs has been introduced, based on the innovative Tzero technology, that is designed to incorporate the best features of both technologies.

Shown in Figure 1 is the most common design for a DSC heat flux device. The sample is encapsulated in an aluminum pan and along with an empty reference, sits on a thermoelectric disk surrounded by a furnace. As the furnace temperature is changed, normally in a linear fashion, heat is transferred to the sample and reference through the thermoelectric disk. The differential heat flow to the sample and reference is measured by area thermocouples using the thermal equivalent of Ohm's Law. The equation for heat flow, therefore, is as follows: q (sample heat flow) = DT (temperature difference between the sample and reference) ÷ R (resistance of the thermoelectric disk).

This simplified one-term equation, however, does not account for the heat flows into and out of the sensor and sample pan. The results achieved, though good, are not optimised with regards to baseline flatness, sensitivity, and resolution. Also important to note is that all manufacturers of DSCs use this same one-term equation, with all the inherent limitations. In order to use this relationship, many assumptions are made with regards to the symmetry between the sample and reference side of the cell that require impossibly precise manufacturing techniques.

The new DSC technology is specifically designed to account for these extraneous heat flows and offers, therefore, a much more accurate representation of the heat flow into and out of the sample. Figure 2 illustrates this new cell design. The sensor consists of a machined constantan body with separate raised platforms for the sample and reference. Raised platforms provide superior isolation of the sample and reference, and aid in reproducible pan placement for excellent data precision. The platforms are connected to the heating block base by thin-walled tubes that create thermal resistances between the platforms and the base. Fast signal response is ensured with the use of constantan. The temperatures of the sample and reference are measured with area thermocouples on the underside of each platform. The temperature of the base is measured using a third thermocouple.

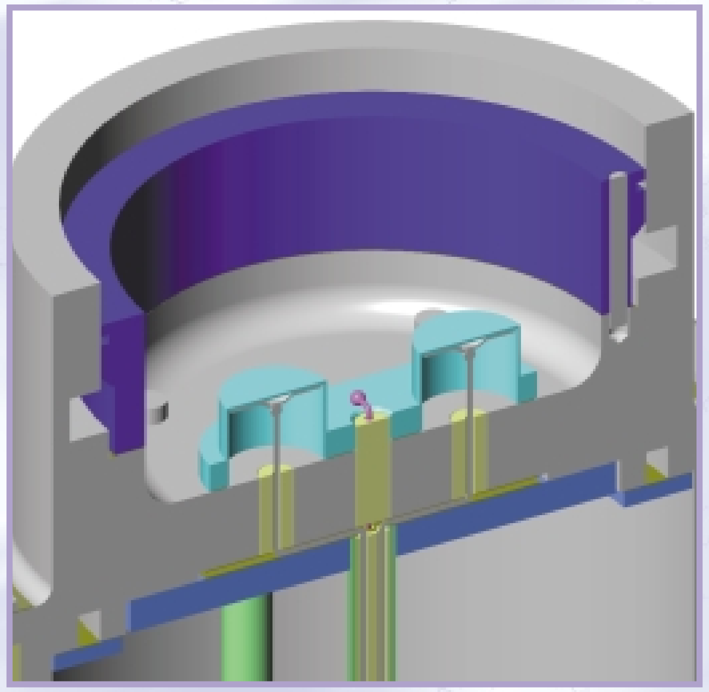

Figure 2: New DSC cell design showing separate raised platforms for sample and reference

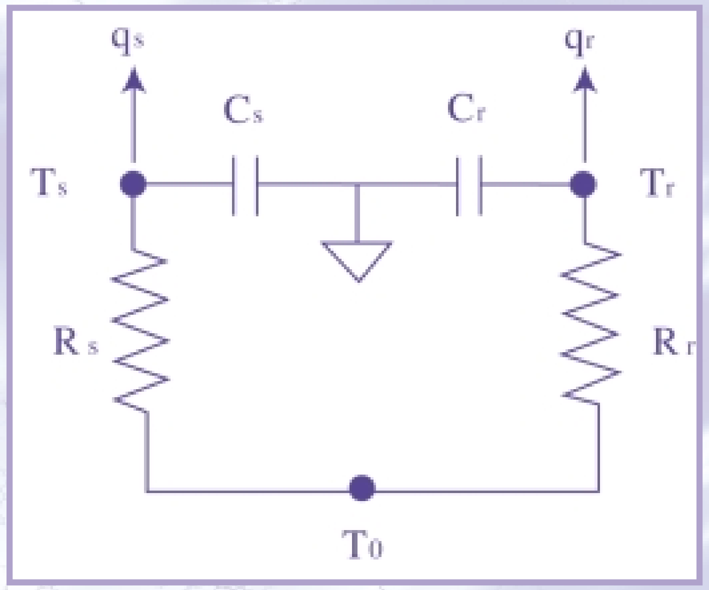

Figure 3: Thermal network model of new cell design

Figure 3 provides the thermal network model that represents this new cell design. The resultant heat flow expression that describes this cell design (designated the Tzero cell) is:

$$q = -\Delta T/R_R + \Delta T_o (R_R - R_S / R_R R_S) + (C_R - C_S)\, dT_S/d\tau - C_R (d\Delta T/d\tau)$$

Researchers have described similar equations in the past, but it has never been incorporated into a DSC sensor before. The first term in this fundamentally more accurate heat flow expression is the equivalent of the conventional single term DSC heat flow expression. The second and third terms account for differences between the sample and reference thermal resistances and capacitances respectively. These terms reflect imbalances in the instrument that are the primary source of instrument baseline deviations and have the biggest impact where the sample heat capacity is the predominant contributor to the heat flow. The fourth term accounts for the difference in heating rate between the sample and reference, and has its largest impact during enthalpic events such as melting. This equation can be modified further to account for pan heat flow effects. An important concluding point is that rather than assume cell symmetry, which is required when using the conventional one-term heat flow equation, the Tzero technology incorporates the fundamentally more accurate four-term heat flow equation and provides a way to model each individual DSC cell without assumptions.

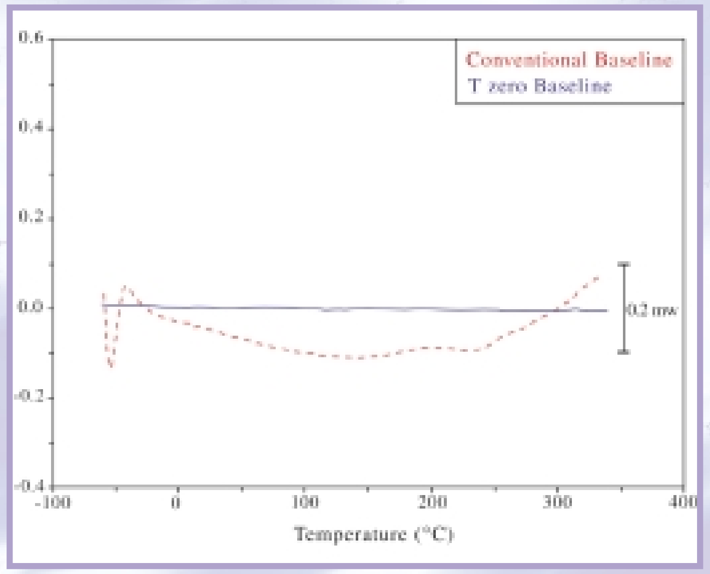

Figure 4: Comparison between the baselines of conventional DSC systems and the Tzero system

Tzero technology dramatically improves performance. Figure 4 illustrates the improvement in baseline obtained using the new cell. In a perfectly balanced DSC system, heating an empty cell at a constant rate should result in a perfectly flat baseline, or in other words, a constant heat flow of 0 mW. In addition, there should be no upset at the onset of heating or at the end of the experiment. Conventional DSCs typically have baselines that deviate 100 mW or more with initial and final upsets. The Tzero design yields baselines that deviate less than 10 mW with virtually no initial and final upsets.

In reality, baseline flatness is probably the most important factor when considering DSC 'sensitivity'. Raw signal noise is extremely important, but most transitions measured with DSC happen over an extended temperature range. A flat baseline provides the ability to detect very subtle transitions such as weak Tgs in highly crystalline or highly reinforced polymers and in lyophilised (freeze-dried) materials. For example, the new Tzero design is able to detect the Tg of polypropylene, normally not detectable by any current DSC.

Resolution is vastly improved as well with the new Tzero design. High-purity indium metal is a common standard used to calibrate the DSC as its melting point and enthalpy are well characterised. Figure 5 illustrates the improved resolution obtained on the peak of the indium melt. Higher peaks, sharper onsets, and a faster return to baseline are seen in the Tzero DSC data as compared to the standard DSC data.

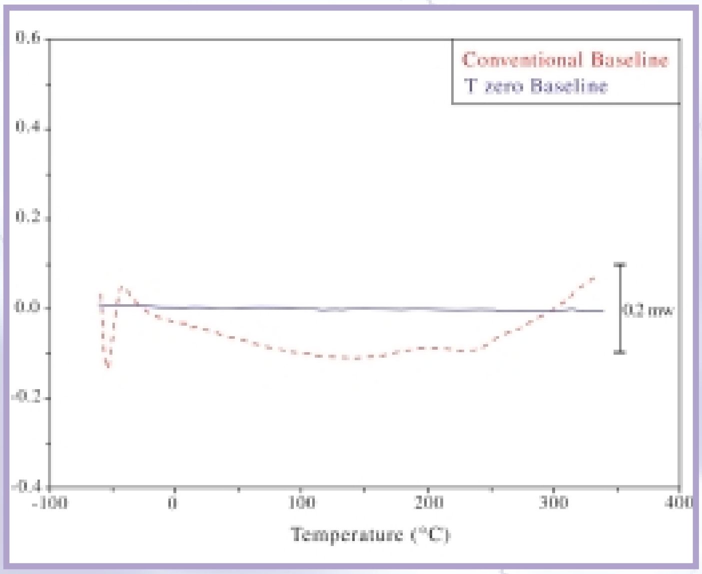

Figure 5: Improved resolution of Tzero obtained with the indium melt

Other benefits of the new cell include the direct, continuous measurement of sample heat capacity. Traditional DSC requires three experiments in order to obtain heat capacity, so the new Tzero technology can dramatically improve not only the accuracy of the heat capacity measurement, but also improves productivity. Heat capacity is a fundamental property of material and is crucial in structure determination, and important from a processing standpoint.

Modulated DSC experiments are also improved in that faster heating rates can be used and there is less dependence on period. In Modulated DSC, a sinusoidal heating profile is overlaid on the traditional linear heating ramp. With a Modulated DSC experiment, the Total Heat Flow can be separated into its two components: a heat capacity term called the Reversing Heat Flow and a kinetic term called the Non-Reversing Heat Flow. Modulated DSC is a powerful technique, but with existing DSC technology it is limited to heating rates of no more than 5˚C/min. With the Tzero DSC, faster heating rates are possible, improving productivity.

A major feature of the new Tzero-based DSCs involves the cooling systems. Heat flux designs provide better baselines due to large mass furnaces, and as a result, heating and cooling rates are adversely affected. With the new DSCs, cooling performance is greatly enhanced because of a series of nickel cooling rods that attach the DSC furnace and sensor housing to a nickel cooling flange. The cooling flange is direct coupled to a new family of cooling systems that provide high cooling rates, lower subambient temperatures, rapid temperature equilibration, with zero frosting problems. A final enhancement in the design is a new 50-position intelligent autosampler with patented optical sensors that assures maximum lab productivity. The autosampler incorporates an auto-calibration routine that greatly simplifies calibration.

In conclusion, the new DSCs with Tzero technology provide a fundamentally better DSC, incorporating a four-term heat flow equation that eliminates the assumptions necessary with the traditional one-term equation used by all other DSC manufacturers. Improvements include an unequalled baseline, superior resolution, direct heat capacity measurements, and faster Modulated DSC experiments. Other enhancements in the design provide for an intelligent autosampler and new cooling systems with higher cooling rates. No longer must the researcher choose between a heat flux device for superior baseline, or a power compensation device for improved resolution and fast cooling rates. Tzero technology provides the benefits of both.

R. Danley is an Engineering Research Associate, T. Kelly is VP, Worldwide Sales & Marketing, and J. Groh is Worldwide Marketing Manager, at TA Instruments, New Castle, DE (USA)

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