Improved DSC Performance Using Tzero™ Technology

G. Dallas, J. Groh, and T. Kelly

Tzero™ is a new Differential Scanning Calorimetry (DSC) technology that provides materials scientists with a fundamentally more accurate and comprehensive way of measuring heat flow. The heart of the technology is the revolutionary Tzero™ cell that makes more measurements than ever before, and delivers superior performance in **both** heating and cooling modes. The new technology is implemented in TA Instruments Q Series™ DSC Modules (Q1000, Q100, Q10).

DSC is a materials characterization technique, whose measurements include heat capacity, glass transitions (Tg), melting, crystallization, phase changes, curing processes, and onset of oxidation. The traditional approaches in DSC cell design are heat flux and power compensation. The former, pioneered by TA Instruments, is used by most suppliers, and offers superiority in baseline stability and sensitivity, while the latter design is recognized for resolution and fast heating / cooling capability. Tzero technology incorporates the best attributes of both designs, and elevates performance to unprecedented levels.

In the traditional heat flux design, a pan containing the sample and an equivalent empty one for reference, are set on identical platforms on a thermoelectric disk surrounded by a controlled temperature furnace. As the furnace temperature is programmed, heat is transferred to the sample and reference through the disk. Differential heat flows to and from the sample and reference are measured by identical chromel area thermocouples welded beneath each platform. A thermal equivalent of Ohm's Law provides a simple quantitative, single-term equation relating heat flow to differential temperature.

$$Q = \Delta T / R$$

Where: Q = sample heat flow
ΔT = temperature difference between the sample and reference
R = resistance of the thermoelectric disk

While this expression has universal acceptance, it is also recognized as an inexact, representation of the actual sample heat flow, for it assumes equivalence of known resistance and capacitance imbalances in the sample and reference sides of the cell (1,2). These imbalances, which are inherent in **all** DSC cell manufacturing processes, are uncompensated for in traditional DSC measuring circuitry, and produce thermal curves that are not optimized for baseline flatness, sensitivity, peak shape and resolution.

Tzero™ technology accounts for these imbalances and produces a more accurate representation of the actual heat flow to and from the sample. The benefits of Tzero over current DSC technology are:

- Essentially flat baselines with minimum start-up / endset "hooks". Typically an order of magnitude or more better than competitive designs, especially in subambient operation.
- Superior sensitivity due to flatter baselines and better signal:noise ratio
- The best available resolution (even compared with power compensation devices)
- Direct measurement of heat capacity.
- Faster MDSC® experiments (similar to standard DSC), plus improved data accuracy.

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Figure 1 illustrates the Tzero™ cell design. The sensor is a machined constantan body with separate raised sample and reference platforms, which provide signal isolation, and also aid in reproducible pan placement. Sample and reference temperatures are measured by area thermocouples on the underside of each platform. The temperature of the base is measured using a third thermocouple (To thermocouple), which also functions as the temperature control mechanism for the furnace. Its presence effectively separates the heat flow contributions from the sample and reference sides of the cell.

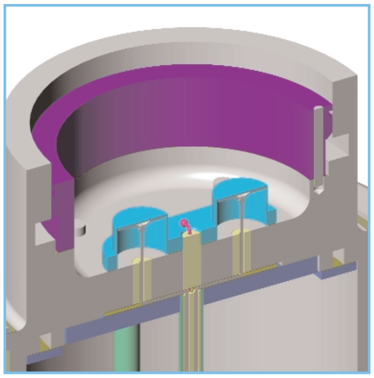


Figure 1

Figure 2

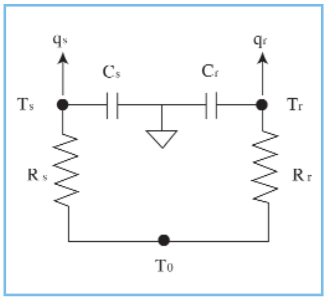


Figure 2 provides the thermal network model of the new design, from which a new four-term heat flow expression has been derived (1).

$$q = -\Delta T/R_R + \Delta T_0 (R_R - R_S/R_R R_S) + (C_R - C_S)\, dT_S/d\tau - C_R (d\Delta T/d\tau)$$

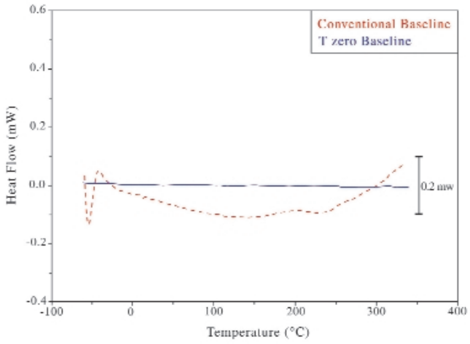
The first term is the equivalent of the conventional single term DSC heat flow expression. The next two terms account for thermal resistance and capacitance imbalances between the sample and reference sides of the cell, which are the primary source of instrument baseline deviations. Term four accounts for heating rate differences between the sample and reference, and is maximized during enthalpic events such as melting. The resulting heat flow signal provides a more accurate representation of the actual heat flowing to and from the sample. This level of implementation is termed Basic Tzero, and is available in the Q1000 and Q100 Calorimeters.

A higher level of implementation - **Advanced Tzero** - is available in the Q1000. It accounts for sensor and pan imbalance effects, and provides an even more accurate representation of the actual heat flows to and from the sample.

The Q10 DSC module offers the performance advantages of the Tzero cell, but employs only the traditional single term heat flow expression.

The new technology dramatically improves DSC baseline performance as seen in **Figure 3**. Traditional DSC baselines often deviate 100µW or more during a scan, and some may not be reproducible over the day, thus limiting the utility of baseline subtraction routines after a sample has been analyzed. The Tzero design yields baselines that are stable and can deviate less than 10µW with minimal initial / final upsets.

Figure 3



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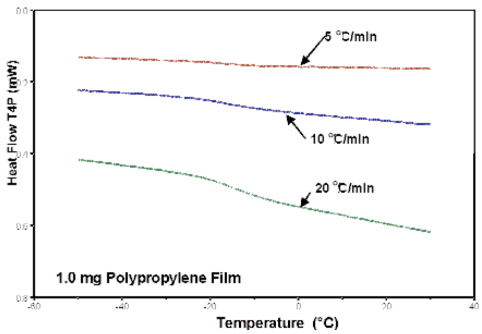
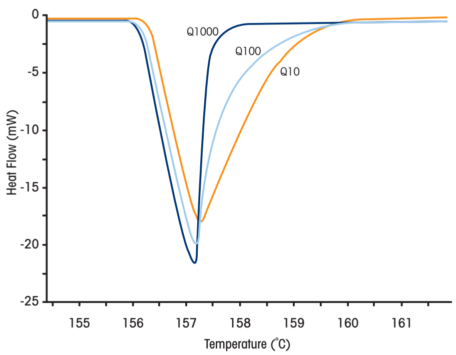
Baseline flatness is also the most important factor when considering DSC "sensitivity". A flat baseline is crucial to detection of subtle transitions, such as weak Tg's in highly crystalline, reinforced, or cross-linked polymers, and in lyophilized materials. The Tzero™ cell is able to detect the Tg of polypropylene, a measurement normally very difficult with traditional designs **(Figure 4)**.

Figure 4



Resolution is also vastly improved. **Figure 5** illustrates a comparison of Tzero and conventional DSC signals on the melt of high-purity indium, a common DSC calibrant. Similar results have been observed from comparisons of data from samples that exhibit polymorphism. Higher peaks, sharper onsets, and faster returns to baseline confirm the superiority of the Tzero approach over traditional heat flux and power compensation designs.

Figure 5

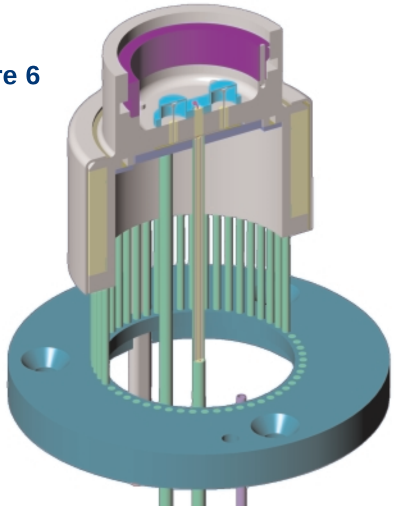


Another benefit, especially for engineers, is a direct, continuous measurement of sample heat capacity, which normally requires three separate experiments in a traditional design. Accuracy and productivity are also improved in this measurement of a fundamental material property that is crucial in structure determination and in material processing.

Tzero technology also makes Modulated DSC® (MDSC®) experiments more productive, since reduced dependence on the period of measurement permits the use of faster heating rates, akin to that used in standard DSC. Quantitative accuracy is also improved.

A major feature of the new Q Series™ DSC Modules involves performance on cooling. The Tzero cell is unique in that it is designed both for heating and cooling performance. A symmetrical array of nickel cooling rods attach the furnace and sensor housing to a nickel cooling flange, which is directly coupled to either the new mechanical or liquid nitrogen cooling systems. **Figure 6** shows the optimized design, which produces faster cooling rates, lower subambient temperatures, rapid temperature equilibration, and zero frosting problems. A new 50-position intelligent auto sampler further optimizes performance in unattended temperature cycling experiments.

Figure 6



References:

1. R. L. Danley and P.A Caulfield, *NATAS Proceedings*, 2001 (and references therein).
2. G. Dallas, J. Groh, T. Kelly and R. Danley, *American Laboratory*, August, 2001