How Tzero™ Technology Improves DSC Performance
Part III: The Measurement of Specific Heat Capacity

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Abstract. Specific heat capacity (Cp) is a fundamental thermodynamic property. Its measurement by DSC is a key indicator of changes in structure. Traditional DSC has been used to measure Cp using ASTM standard E1269, which requires three scans: a baseline scan, a scan using a sapphire standard, and the sample scan (1). Advanced Tzero™ technology, available with the Q1000 DSC, offers a significant advance in the ease and reliability of measuring Cp.

Background. In order to raise the temperature of a material, heat must be supplied. The amount of energy necessary to heat one gram of the material one degree Celsius is the specific heat capacity. Cp is a characteristic thermodynamic property of a material. It is a measure of how the material stores additional energy at the molecular level as it is heated. For example, if the molecules in the material can only vibrate, as in a crystal, then Cp is low; if they can also rotate and translate, then the Cp is higher. When a material is heated through the glass transition region, the molecules gain mobility, the material softens, and Cp increases. So Cp indicates changes in structure.

Why is Cp Important to Measure? As measured by DSC, Cp is an absolute quantity. It quantifies how much heat must be delivered to a substance to heat it over a temperature range, for example, to the molding temperature. Figure 1 shows Cp data for polyethylene terephthalate (PET) showing that the amount of energy required to heat this material increases with temperature and goes through a peak during the crystalline melt. The total energy required to heat a quantity of PET from one temperature (T) to another is just the integral of this data over that temperature range. And how much heat must be removed to cool it to a temperature where the dimensions are stable (for example, where the end-product can be removed from the mold) can be obtained from similar Cp data taken in cooling. Hence, this Cp information, as a function of temperature, is necessary engineering input for simulation software to predict processing conditions.
The Cp of a material should always be positive. Apart from time-dependent processes, its value is independent of heating rate, and also sample size. So it is the natural way to compare data run under different conditions. For example, in Figure 2 the heat flow data is shown for polymethylmethacrylate (PMMA) taken at four different scanning rates and than normalized for Cp. The observed differences can be attributed to the time dependence of the Tg transition.

**DSC Measurement of Cp.** In an ideal DSC there would be no heat flow signal unless a sample with heat capacity were being heated, or some other thermal process was taking place. In this ideal DSC, the empty pan baseline would be a straight line at zero milliwatts. If a sample were heated in this ideal DSC then the displacement from the zero line would be given by:

\[
d\mathcal{Q}/dt = \mathrm{Cp} \times \beta \times W \quad (\text{eq. 1})
\]

where \(d\mathcal{Q}/dt\) is heat flow, \(\beta\) is heating rate and \(W\) is the sample specimen mass.

The problem is that most DSC’s exhibit a substantial heat flow offset even when there is no sample present, and this heat flow signal is strongly dependent on heating rate, temperature and other factors (2). So in order to obtain Cp from a traditional DSC it has been necessary to subtract an empty pan baseline run under identical conditions, before determining Cp from equation 1. A further limitation is that the calibration of the instrument, both temperature scale and heat flow, is critical. Standard methods recommend a comparative technique whereby a specific heat capacity reference material is measured under identical conditions and the sample Cp is obtained by comparing their respective heat flow data as their ratio (1). This lengthy procedure requires three analytical runs, each bracketed by equilibration steps as illustrated in Figure 3.

Because so much extra effort must be used to obtain Cp, most DSC methods call for the less quantitative, heat flow signal, which carries the arbitrary component of the offset, slope and curvature imposed by the instrument baseline. Were it not for the extra difficulty, all DSC data would be reported in Cp units.

The solution is Advanced Tzero™ technology, available on the Q1000. In a recent advance from TA Instruments, a new DSC has been developed that provides an additional Tzero™ thermocouple sensor on the measurement cell (3, 4). This allows the use of a more complete heat flow equation that takes into account the asymmetries in
the cell. As a result, the DSC heat flow signal in the absence of a sample is very close to the theoretical zero heat flow line (2), as illustrated in Figure 4. Using Advanced Tzero™ technology, the DSC and the pan response is incorporated into the initial calibration of the instrument. This means that whenever a sample is run, practically all of the thermal effects of the cell and sample pan are analytically removed from the heat flow output.

So the only difference between the heat flow and Cp is a constant normalization factor. The Q1000 with Advanced Tzero™ technology, therefore, provides a direct measure of Cp with a single scan. An example of the direct Cp data available with the Q1000 is shown in Figure 5. This has several important ramifications. First, there is no extra time required with the Q1000 to obtain Cp data, which as discussed previously, is a more accurate form of DSC data. Second, every DSC scan on the Q1000 is a potential Cp analysis. Third, even when the data is left in heat flow units it has the same absolute character as Cp; namely, the instrumental character has been removed, which makes analysis more accurate.

**Cp from MDSC©.** Modulated DSC® is an alternative approach to obtaining specific heat capacity information (5). MDSC is capable of generating Cp data with an accuracy of up to +/- 2%. While faster than the three experiment ASTM approach, traditional MDSC was somewhat time consuming as it uses underlying heating rates of <5°C/min. This limitation is reduced by the 5°C/min MDSC experiments provided by Tzero™ technology, available on the Q100, and the 10°C/min MDSC experiments of Advanced Tzero™ technology, available on the Q1000. Hence, while a slower underlying rate and longer period still ensure optimum accuracy, accurate Cp data is available in a much shorter time by MDSC using either the Q100 or Q1000. In addition, the Q100 or Q1000 provide Cp units on all three modulated signals: total, reversing, and non-reversing. This provides additional analytical benefits.

Figure 6 shows the heat capacity of polystyrene obtained at 10°C/min heating and cooling using the Q1000 and MDSC©. One of the advantages provided by the presentation of
heat flow data in the form of heat capacity information is that all of the results may be easily compared on the same axis.

**Conclusion.** Cp is a fundamental, thermodynamic property of material and is the best way to compare samples. With past DSC technology, the only way to generate Cp was with the time consuming ASTM method. Advanced Tzero™ technology available on the Q1000 provides maximum analytical flexibility. The Q1000 is the only instrument on the market today that provides three ways to measure heat capacity: 1) directly, 2) 3-run ASTM E1269 method, and 3) using MDSC.

![Figure 6. Polystyrene heating and cooling showing all MDSC signals in Cp units](image)

**References**


2. “How Tzero™ Technology Improves DSC Performance, Part I: Flat Baseline and Glass Transition Measurements”, TA Instruments Applications Note ____.


5. “Modulated DSC Theory”, TA Instruments Applications Brief TA211