# Modulated DSC® Paper #4
# Advanced Tzero MDSC; Calculation of MDSC Signals, Including Phase Lag Correction

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**ABSTRACT**
This paper describes some advanced calculated signals available from MDSC® when applied to the latest Tzero™ Technolgy available in the latest Q Series DSC modules.

**INTRODUCTION**

An earlier paper, entitled "Modulated DSC; Calculation and Calibration of MDSC Signals" (1), presented a discussion on the basic approach that has been used to calculate MDSC signals since commercialization of the technique in 1992. With introduction of Tzero DSC technology in 2001, an improved approach to calculating MDSC signals was developed. This approach takes advantage of the unique characteristics of Tzero technology, that provides for the separate measurement of heat flow for both the sample and reference sides of the calorimeter (2,3). This ability to make two simultaneous differential measurements is the result of having a third thermocouple as part of the heat flow measuring system. This third thermocouple, called the Tzero thermocouple, is common to the measurement of the independent heat flow for both the sample and reference sides and can be seen in Figure 1, which shows a cross-section of a Tzero DSC cell.

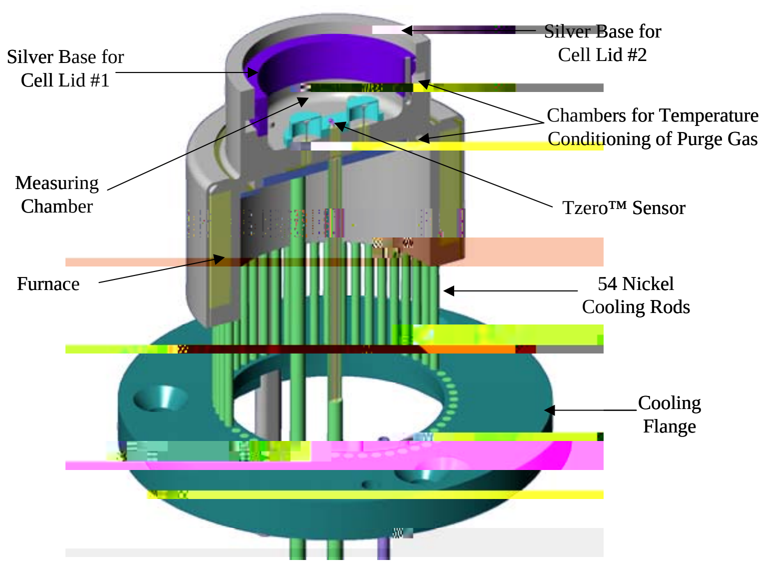


Figure 1

The ability to make two simultaneous differential measurements with Tzero technology permits separate MDSC signals to be calculated for both the sample and reference sides of the calorimeter (3). After the signals are calculated in real-time during the experiment, they are then subtracted to remove the effect of the sample pan and calorimeter on the sample results. This approach provides the following advantages over the traditional MDSC approach that uses a single differential measurement:

- The Reversing Heat Capacity calibration constant is much more stable as the modulation period is changed (4).
- The Total and Nonreversing signals have significantly improved baselines (reduced slope and curvature)
- Any difference in mass between the sample and reference pans is automatically corrected (requires user to enter pan masses into control software)
- The Phase Lag (between temperature and heat flow) correction is improved due to elimination of the effect of changes in phase between the sample and reference calorimeters

This paper will provide a brief introduction to some of the basic mathematics used by Tzero technology, but will primarily focus on the process of calculating MDSC signals including Phase Lag correction. A more complete mathematical description of Tzero DSC and MDSC signals is provided in previous published papers (2,3).

## Tzero™ DSC TECHNOLOGY

$$dH/dt \qquad \frac{T}{R_r} \qquad T_0 \frac{1}{R_s} \quad \frac{1}{R_r} \qquad C_r \quad C_s \frac{dT_s}{d} \quad C_r \frac{d\ \ T}{d}$$

where:

dH/dt = differential heat flow rate (mW, mJ/s, W/g etc.)

T = temperature difference between the sample and reference sensors

To = temperature difference between sample sensor and Tzero thermocouple

Rr = thermal resistance ( C/W) of reference sensor

Rs = thermal resistance of sample sensor

Cr = heat capacitance (J/g C) of reference sensor

Cs = heat capacitance of sample sensor

dTs/dt = heating rate of sample sensor

d T/dt = difference in sample and reference sensor heating rates

**Tzero MDSC SIGNALS**

The above equation is used to calculate the DSC heat flow from Tzero technology. This equation is not used in the calculation of MDSC Tzero signals. Instead, the modulated heat flow and modulated temperature for the sample and reference sides of

Figure 5

Figure 6

Secondly, once the plot of the desired signals is obtained, phase correction is performed using options (Graph - Instrument Parameters - Temperature Limits) in the Thermal Advantage software as shown in Figures 7 and 8. The analyst should select two temperatures, one below and one above the temperature range of interest, where there is no transition occurring. The software will then shift the Heat Flow Phase signal to values of zero at those two temperatures and perform phase lag adjustment using the corrected value of the Heat Flow Phase signal as shown in Figure 9. All of the phase-corrected signals are now available, including the plotted In-Phase Heat Flow signal.

Figure 7

Figure 8

Figure 9

Note that phase-lag correction does not influence the Total signal and only affects the Reversing signal in the middle of the melting range. This minor deviation on the area of the melting peak in the Reversing signal has no effect on the measurement of Initial Crystallinity for reasons that will be further discussed in a subsequent paper entitled "Measurement of Initial Crystallinity in Semi-crystalline Polymers (4).

**SUMMARY**

Tzero DSC technology permits a more accurate measurement of phase lag between the heating rate and heat flow rate signals. During transitions in a material, heat absorbed or released by the sample causes a change in the phase lag that can have a slight affect on the calculated signals, especially in the melting region. Phase correction of the signals can be performed but the affect on most transitions is not significant and phase correction is seldom done. Although not discussed here, some researchers have shown that the Heat Flow Phase signal, which changes during transitions in materials, provides additional information or sensitivity in analyzing some transitions.

## REFERENCES


1. Modulated DSC; Calculation and Calibration of MDSC Signals; TA Instruments Technical Paper TP 007.
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## KEY WORDS

modulated dsc, mdsc, tzero, phase lag,





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