Making Accurate DSC and MDSC® Specific Heat Capacity Measurements with the Q1000 Tzero™ DSC

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ABSTRACT

Differential scanning calorimetry (DSC) has been used for more than thirty years to measure a wide variety of material properties including heat capacity. Although most DSC measurements are simple, fast, accurate and require only a single experiment, the measurement of heat capacity usually requires a minimum of three experiments and provided accuracies typically good to only ± 10 % (*1*).

An improved approach to making DSC measurements, providing a better baseline and more accurate heat flow values, has been developed and implemented in the TA Instruments Q1000 Tzero™ DSC. With the improvement in heat flow accuracy, it is now possible to measure Heat Capacity in a single run with an accuracy typically better than ± 5 %. The technique for making such measurements is described.

INTRODUCTION

The Q1000 DSC signals include heat flow and heat capacity as measured in the standard mode plus reversing heat capacity as measured by Modulated DSC® (MDSC®). In the standard mode, heat flow is continuously converted to heat capacity as described in equation 1.

$$Cp = \frac{HeatFlow}{HeatingRate} xK \qquad \text{(eq.1)}$$

Where:
- Cp = Specific Heat Capacity (J/g °C)
- $HeatFlow$ = W/g
- $HeatingRate$ = °C/min
- K = Calibration Constant (dimensionless)

Accurate measurements of both heat flow and heating rate are required to make accurate *Cp* measurements. Because of its unique use of the full four-term heat flow equation, that accounts for any imbalances within the measuring system and sample pans, the Q1000 measures the absolute value of heat flow versus the relative value measured by other DSCs (*2*). The four-term heat flow equation has the form:

$$\Delta q = -\frac{\Delta T}{R_r} + \Delta T_o\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{dt} - C_r\frac{d\Delta T}{dt} \qquad \text{(eq. 2)}$$

Where:

Δq	= Sample Heat Flow
$-\frac{\Delta T}{R_r}$	= Principle Heat Flow
$\Delta T_o\left(\frac{1}{R_s} - \frac{1}{R_r}\right)$	= Thermal Resistance Imbalance
$(C_r - C_s)\frac{dT_s}{dt}$	= Thermal Capacitance Imbalance
$-C_r\frac{d\Delta T}{dt}$	= Heating Rate Imbalance

Reversing heat capacity (MDSC mode) is measured in the same experiment used to measure DSC heat capacity and, therefore, has several significant advantages over just the DSC heat capacity measurement. It is usually more accurate and reproducible because of the way it is measured and provides a check of the heat capacity as measured in the faster DSC single-run approach.

$$\textit{Reversing Cp} = \frac{\textit{Amplitude of Modulated HeatFlow x } K_{Cp}}{\textit{Amplitude of Modulated HeatingRate}}$$

where K_{Cp} is the dimensionless heat capacity calibration constant.

By using amplitudes (total change) rather than absolute values for the heat flow and heating rate signals, the effects of baseline curvature or drift are eliminated. This means that runs are made over long periods (days) without any concern for baseline drift.

EXPERIMENTAL

DSC Instrument:	TA Instruments Q1000 Tzero™ DSC
Cooling System:	RCS
Purge Gas:	Nitrogen at 50 mL/min
Calibration Standards:	Indium for heat flow and sapphire for heat capacity
Pan Type:	Crimped Aluminum, approximately 23 mg
Sapphire Test Method:	DSC @ 20 °C/min from 0 to 300 °C MDSC isothermal at 56.8 and 256.8 °C; 100 s Period and ± 1 °C Amplitude Sample weight of 26.09 mg (disk)
Polyethylene Terephthalate Test Method:	DSC @ 20 °C/min from 0 to 150 °C MDSC isothermal at 50 and 125 °C; 100 s Period and ± 1 °C Amplitude Sample weight of 13.67 mg (film}

Polyethylene Test Method:	DSC @ 20 °C/min from 25 to 175 °C MDSC isothermal at 150 °C; 100 s Period and ± 1 °C Amplitude Sample weight of 15.53 mg cut pellet

One of the largest causes for inaccurate measurements is poor sample preparation. Whenever possible, use the following recommended conditions for polymers:

1. Use films rather than irregular pieces or chunks of material.
   Note: If it is necessary to use irregularly shaped pieces for the sample, it is best to use hermetic aluminum pans in order to not distort the bottom of the pan. With this type of pan, which is heavier (approximately 56 mg) and has less contact area with the sensor, results typically are not as good but still better than ± 10 % with multiple runs measurment. Be sure to calibrate with the type of pan to be used for the sample.
2. 14 ± 2 mg of sample (cut flat to fill pan bottom).
3. Crimped aluminum pans.
   Note: It is very important to keep the bottom of the pan flat. When crimping, use just enough pressure to crimp the lid but not distort the pan bottom.
4. Use same reference pan for all calibration and sample runs. All pans should be crimped to same height.

RESULTS AND DISCUSSION

Accuracy and reproducibility of heat capacity measurements on the Q1000 Tzero™ DSC are checked with three different kinds of samples.

- Sapphire disk
- Polyethylene Terephthalate (PET) film
- Polyethylene (PE) pellet (cut flat with razor blade)
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Prior to running samples, the DSC Heat Capacity and MDSC Reversing Heat Capacity signals are calibrated with a sapphire standard run under the same conditions used for all samples. In that experiment, the "Zero Heat Flow" segment is used to zero the heat flow at 100 °C. This segment eliminates any offset in the heat flow signal so that absolute values are obtained. It is the only time that the segment needs to be used unless runs are made over several days.

Each sample is run three times and is reloaded into the cell prior to each run to simulate real experiments on unknowns. Each experiment consists of a heating at 20 °C/min over a temperature range followed by isothermal MDSC measurements at one or more temperatures in that range but outside any transition region.

Figures 1-3 show the data plotted versus time for the first run in each series. Figures 4 and 5 show the same data plotted versus temperature for the polyethylene terephthalate (PET) and polyethylene (PE) samples, respectively. The glass transition can be seen in PET and melting in PE.

Tables 1-3 list heat capacity values obtained for each of the three runs on the three samples. DSC and MDSC results are shown along with the average value and standard

deviation for each of the test temperatures. Standard deviations are less than 3 % while average values are within 2 % of literature values.

SUMMARY

With proper sample preparation and experimental conditions, the Q1000 DSC is capable of providing accurate and reproducible heat capacity values from a single experiment. By doing both a DSC ramp and MDSC® isothermal test during the one experiment, it is possible to get an internal check on the quality of the results. Results are not only faster but typically better than those obtained from three experiments performed on non-Tzero™ types of DSC.

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KEYWORDS

differential scanning calorimetry, heat capacity, modulated differential scanning calorimetry, inorganics, minerals, polyesters, polyolefins, thermoplastic polymers,

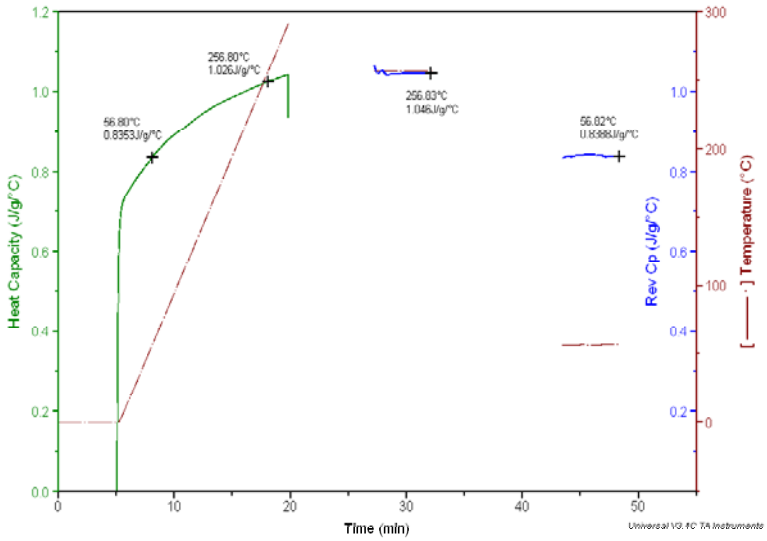

Figure 1 - DSC and MDSC® Heat Capacity on Sapphire Disk

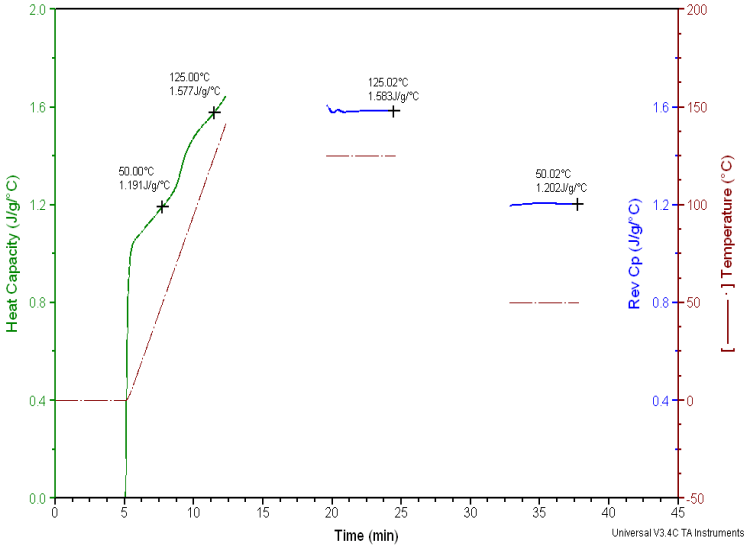

Figure 2 - DSC and MDSC® Heat Capacity on Polyethylene Terephthalate

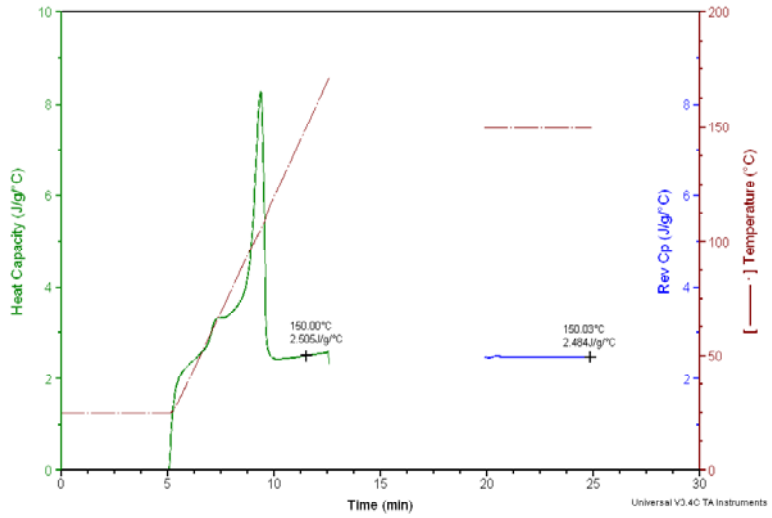

Figure 3 - DSC and MDSC® Heat Capacity on Polyethylene

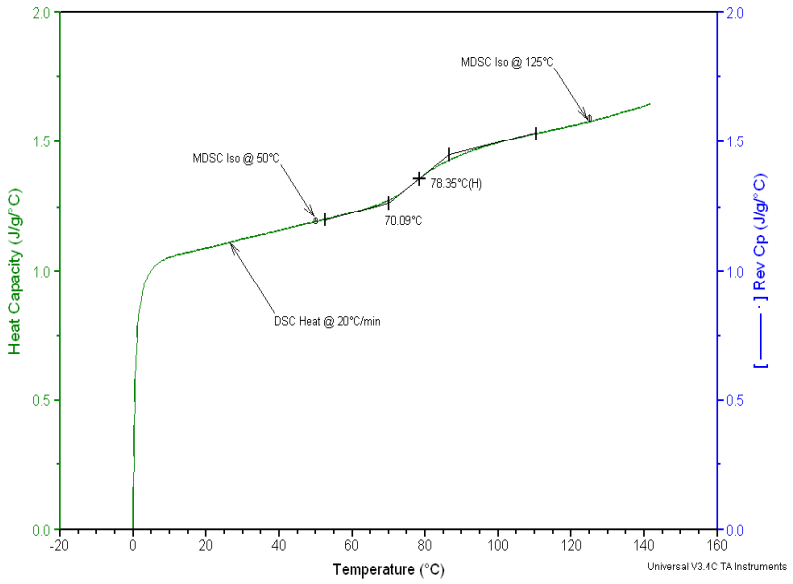

Figure 4 - DSC and MDSC® Heat Capacity Versus Temperature for Polyethylene Terephthalate

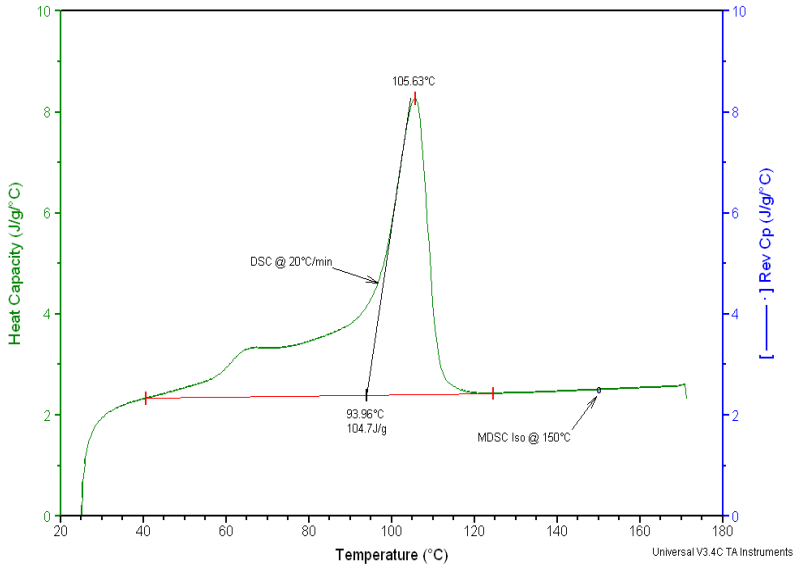

Figure 5 -DSC and MDSC® Heat Capacity Versus Temperature for Polyethylene

		Temperature (°C)		
Run		**56.8**	**156.8**	**256.8**
1	DSC @ 20 °C/min	0.84	0.96	1.03
	MDSC (iso)	0.87		1.08
2	DSC @ 20 °C/min	0.84	0.97	1.05
	MDSC (iso)	0.86		1.08
3	DSC @ 20 °C/min	0.86	1.00	1.10
	MDSC (iso)	0.87		1.08

	Mean	0.86	0.98	1.07
	Standard Deviation	0.01 (1 %)	--	0.02 (2 %)
	Literature Value NIST (*3*)	0.84	0.98	1.06

Table 1 - Sapphire DSC and MDSC® Heat Capacity (in J g^{-1} $°C^{-1}$) for Three Experiments

		Temperature (°C)	
Run		**50 °C**	**125 °C**
1	DSC @ 20 °C/min	1.19	1.58
	MDSC (iso)	1.20	1.58
2	DSC @ 20 °C/min	1.25	1.65
	MDSC (iso)	1.26	1.65
3	DSC @ 20 °C/min	1.26	1.66
	MDSC (iso)	1.27	1.66

	Mean	1.24	1.63
	Standard Deviation	0.03 (2 %)	0.04 (2 %)
	Literature Value ATHAS Data Bank (*4*)	1.26	NA[1]

[1]Varies with crystallinity.

Table 2 - PET DSC and MDSC® Heat Capacity (in J g^{-1} °C^{-1}) for Three Experiments

Run		**150 °C (Melt)**
1	DSC @ 20 °C/min	2.50
	MDSC (iso)	2.48
2	DSC @ 20 °C/min	2.54
	MDSC (iso)	2.52
3	DSC @ 20 °C/min	2.56
	MDSC (iso)	2.52

	Mean	2.52
	Standard Deviation	0.03 (1 %)
	Literature Value ATHAS Data Bank (*5*)	2.55

Table 3 - PE DSC and MDSC® Heat Capacity (in J g^{-1} °C^{-1}) for Three Experiments

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