Modulated DSC® Paper #9
Measurement of Accurate Heat Capacity Values

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ABSTRACT

Modulated DSC permits the accurate measurement of heat capacity of a material. Best results are obtained when experimental conditions are optimized to permit the quantitative flow of heat to the sample

INTRODUCTION

The eight previous papers in this series have focused on use of MDSC to measure transitions in materials. When measuring transitions, specific modulation conditions (modulation amplitude, period and average heating rate) were recommended to:

- Obtain a minimum number (4-5) of modulation cycles over the critical range of a transition so that a good separation of the Total heat flow signal into the heat capacity (Reversing) and kinetic (Nonreversing) components is achieved.
- Provide, or not provide, cooling of the sample during the temperature modulation cycle.
  - Cooling during modulation provides improved sensitivity for the measurement of transitions involving heat capacity (glass transition) or changes in heat capacity.
  - No cooling during modulation is recommended for the measurement of melting and crystallinity to avoid the possibility of crystallization and to permit the use of the raw modulated heat flow signal for verification of crystallization and crystal perfection processes.

This paper addresses the use of MDSC for the measurement of absolute heat capacity outside the region of a transition. Traditional DSC has been long used but its accuracy (± 10 %) is often less than desired. In addition, the measurement requires three experiments under the same experimental conditions and can take up to four hours to perform the required steps, consisting of a) a baseline run with empty pans; b) a calibration run, typically with sapphire as a standard; and c) the final sample run.

Modulated DSC enjoys a significant advantage over standard DSC because it does not require a stable baseline to achieve high accuracy. The measurement of **Reversing** heat capacity is only based on the amplitude of the modulated heat flow signal and not its average value. Standard DSC uses the average heat flow rate, which is only as stable as the baseline of the instrument. That is why three runs are usually required with standard DSC and also why they must be done in immediate succession in order to obtain the best results. The **Total** heat capacity signal of MDSC is also based on the absolute value of the heat flow signal, but is less accurate than in standard DSC because of the slower average heating rate used. For this reason, the Total signal is perfectly fine when expressed in heat flow (mW or W/g) units but should not be used to obtain absolute heat capacity values. Although the instrument control software allows input of a heat capacity calibration constant for the MDSC Total heat capacity signal, it is recommended that the user leave it at the default value of 1.00.

EXPERIMENTAL CONDITIONS

As stated above, the measurement of Reversing heat capacity is based on the amplitude of the modulated flow. Calculation of MDSC signals was discussed in a previous MDSC paper (1) and a portion is provided below.

Calculation of MDSC Signals

- The *Total Heat Flow* signal is calculated from the average value of the measured *Modulated Heat Flow* signal. The process of determining the average involves use of Fourier Transform (FT) analysis on the sine wave so that the average can be continuously (every 0.1 seconds) calculated, rather than use of the simple average, which would significantly limit resolution.

- The *Reversing Heat Flow* signal is calculated from the *Reversing Heat Capacity* signal. The calculations are as provided below and the data, with calculated signals, are shown in Figure 1. As with *Total Heat Flow*, the amplitudes of the heat flow and heating rate signals are calculated using Fourier Transform analysis.

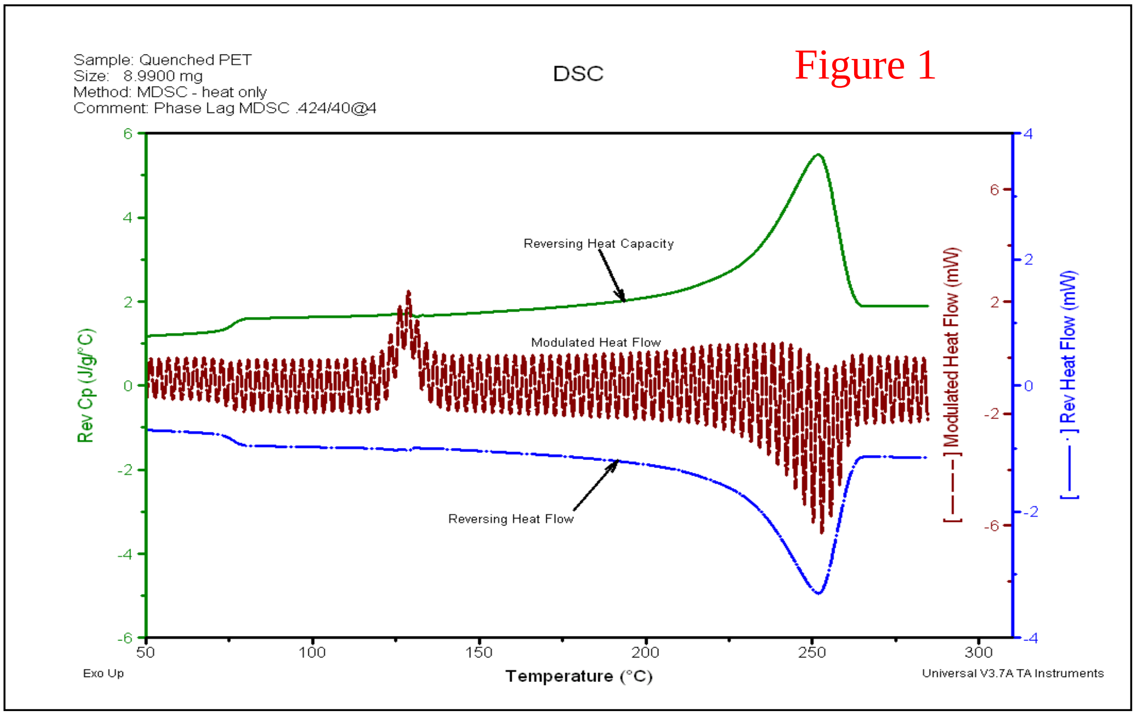
$$\text{Rev Cp} = \frac{\text{Heat Flow Amplitude}}{\text{Heating Rate Amplitude}} \text{ x KCp Rev}$$

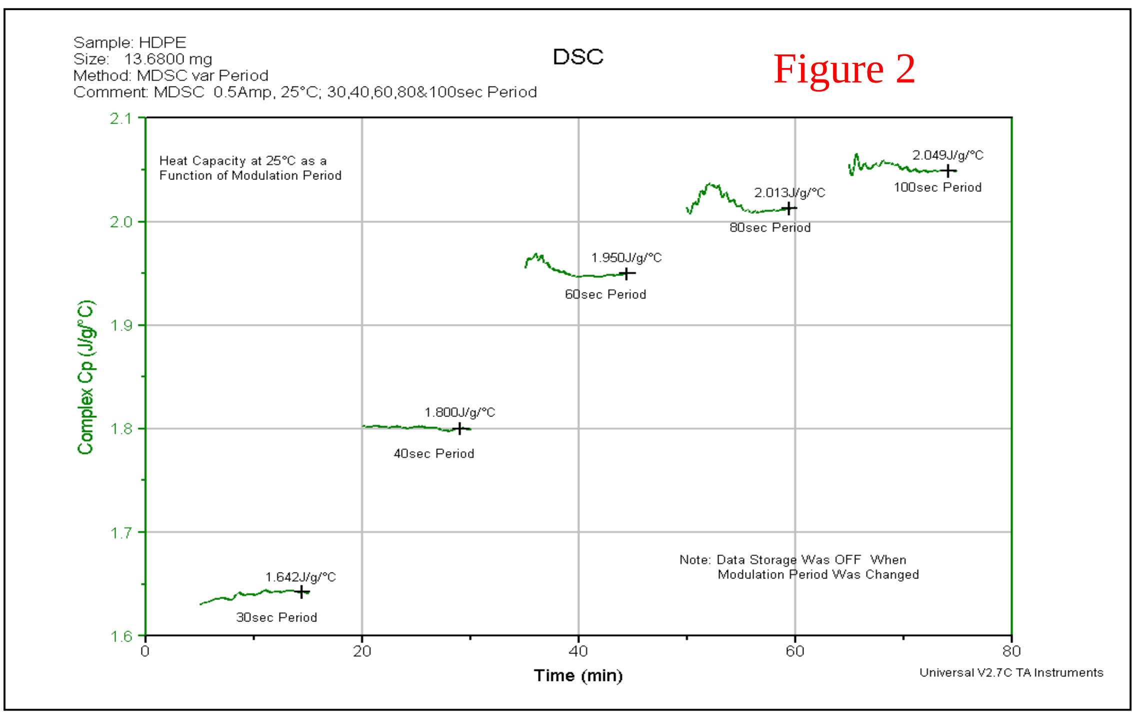
where: KCp Rev = Calibration Constant for Reversing Cp

Rev Heat Flow = Rev Cp x Average Heating Rate

- The *Nonreversing Heat Flow* signal is calculated by subtracting the *Reversing Heat Flow* signal from the *Total Heat Flow* signal.

Since the Reversing heat capacity signal is calculated from the change in modulated heat flow (heat flow amplitude) divided by the change in modulated heating rate, it is extremely important that there be sufficient time for complete heat flow otherwise the calculated heat capacity will be too low. The modulation experimental parameter that controls time for the flow of heat is the modulation period. As discussed in a previous MDSC paper in this series (2), it is necessary to **use a modulation period, which is slow enough to allow sufficient time for complete heat transfer.** This statement is even more important for the measurement of absolute heat capacity than it is for the measurement of typical transitions. The significant effect of the modulation period on the calculation of heat capacity is seen in Figure 2, an experiment performed on an older generation instrument (MDSC 2920) that was more affected by the modulation period than current TA Instruments Q Series instruments, as will be discussed and shown in Figure 3.

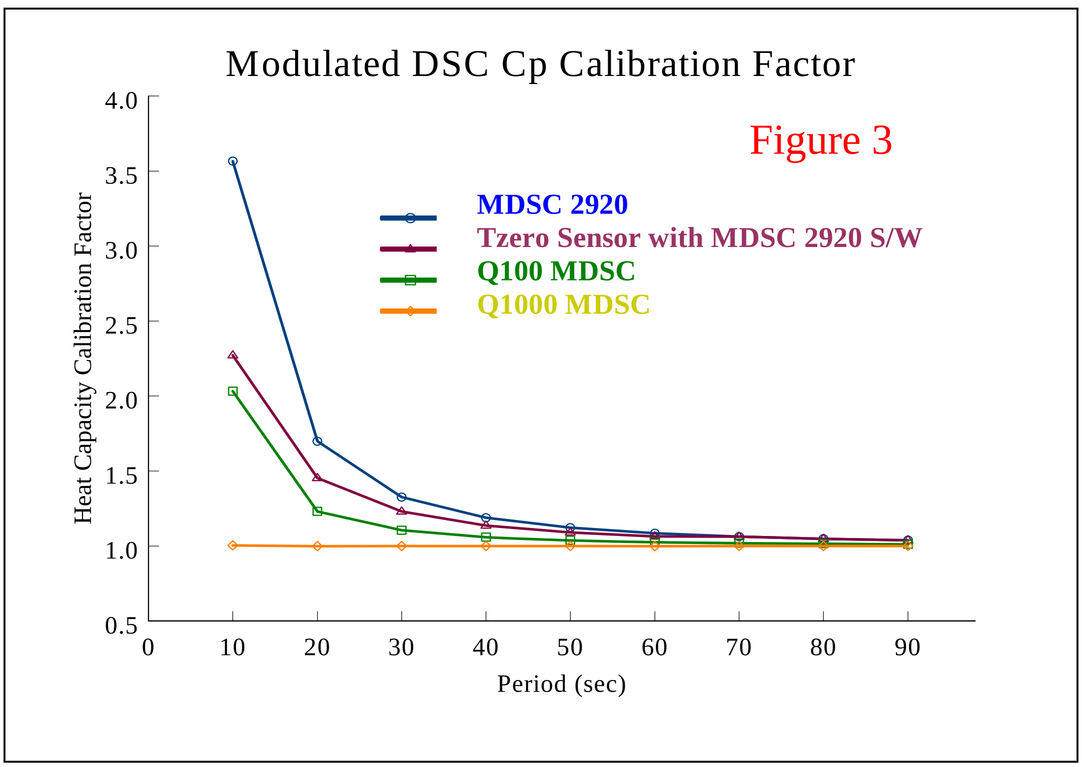




The results in Figure 2 illustrate the importance of the modulation period for obtaining accurate values of heat capacity. If the modulation period is too fast (shorter time), there will not be enough time for heat to flow between the sensor and sample. This will reduce the heat flow amplitude, which will result in a low value for the Reversing heat capacity and Reversing heat flow signals. Therefore, the operator can use the measured value of the Reversing Heat Capacity signal to determine how much time (modulation period) is required for quantitative heat flow.

Figure 2 was created using 13.7 mg of high-density polyethylene (HDPE) contained in a crimped pan with lid. The entire experiment was performed at 25 °C with a fixed temperature modulation amplitude of ± 0.5 °C. During the experiment, the temperature modulation period was successively increased from 30 to 40, 60, 80 and 100 seconds in ten-minute steps. As can be seen, the measured Complex Cp (Reversing Cp in Q-Series instruments) increases by approximately 20 % as the period is increased from 30 to 60 seconds. However, it only increases by about 5 % as the period is increased from 60 to 100 seconds. This indicates that 60 seconds is a reasonable period for this combination of sample and pan. Anything longer than 60 seconds has very little affect on the accuracy of the Cp measurement during the transition but can affect the absolute accuracy of the heat capacity signal as seen in Figure 3

Figure 3 shows that the heat capacity calibration factor for the **Reversing** heat capacity signal approaches a value of 1.00 at modulation periods greater than about 100 seconds for all instruments. This indicates quantitative heat flow and the need for very little correction. Shorter modulation periods may prevent complete heat flow during the time of the modulation and this requires the use of a calibration constant greater than 1.00 in order to obtain quantitative results.



RECOMMENDED CALIBRATION CONDITIONS FOR THE REVERSING HEAT CAPACITY SIGNAL

1. Set the calibration constant in the software to 1.00 prior to running the sample that will be used for calibration
2. Place the DSC in the MDSC mode
3. Prepare a 20-30 mg sapphire disk to calibrate for solids or a 10-15 mg sample of water to calibrate for aqueous solutions
4. Run solids in crimped aluminum pans with lids and run liquids in aluminum hermetic pans with lids.
5. Prepare a reference pan that is the same type used for the sample and has a weight that is within 50 micrograms of the sample pan
6. Select a temperature that is midway in the temperature range to be used for actual samples. Calibration is done at a single temperature because a single value is used for the calibration constant
7. Run the standard using the following conditions
    a. Data Storage <u>OFF</u>
    b. Equilibrate at <u>(desired temperature)</u>
    c. Modulate ± <u>1.0ºC</u> every <u>100 seconds</u> (use 120 seconds for hermetic pans)
    d. Isothermal for <u>5</u> minutes
    e. Data Storage <u>ON</u>
    f. Isothermal for <u>5</u> minutes
8. Plot the Reversing heat capacity signal versus time and determine the heat capacity value at the end of the 5 minute isothermal
9. Calculate the Reversing heat capacity calibration constant by dividing the theoretical value of the heat capacity of the sample at that temperature by the measured value

    Reversing Cp Calibration Constant (KCp) = Theoretical/Measured
10. Insert the new value of KCp for the value of 1.00 used during the calibration experiment. Typical values of KCp are in the range from about 1.00 to 1.10 for Q-Series instruments and 1.05 to 1.20 for the MDSC 2920.

RECOMMENDED CONDITIONS FOR MEASURING THE REVERSING HEAT CAPACITY OF SAMPLES

- The calibration constant determined above should be used to run all samples.
- Prepare samples that weigh between 10 and 15 mg in appropriate type pans.
- The Reversing heat capacity can be measured at a specific temperature(s) or over a range of temperatures by heating at an average heating rate of 3 ºC/min using a modulation period of 100 seconds (120 for hermetic pans) and a modulation amplitude of ± 1.0 ºC.

An advantage of the TA Instruments Q1000 DSC is that it can provide an accurate measurement of the **<u>Reversing</u>** heat capacity in the MDSC mode and an accurate measurement of the **<u>Total</u>** heat capacity in the standard DSC mode. This is an excellent way of comparing results from the two approaches and is discussed in a TA Instruments applications brief (3). Provided below is a summary from that paper of the two approaches on samples of sapphire, high density polyethylene (HDPE) and polyethylene terephthalate (PET).

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)

Prior to running samples, the DSC Heat Capacity and MDSC® Reversing Heat Capacity signals should be calibrated with a sapphire standard run under the same conditions used for all samples. In that experiment, the segment called "Zero Heat Flow" was used to "zero" the heat flow at 100 °C. This segment eliminates any offset in the heat flow signal with the result that absolute values are obtained. It is the only time that the segment needs to be used unless the experiments are made over several days.

Each sample is run three times and is reloaded into the cell prior to each run in order to simulate real experiments on unknowns. Each experiment consists of 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 4-6 display the data plotted versus time for the first run in each series. Figures 7 and 8 show the same data plotted versus temperature for the PET and PE samples. The glass transition (Tg) can be observed in the PET and melting in PE plot.

Tables 1-3 list heat capacity values obtained for each of the three experiments on the three samples. DCS 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.

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

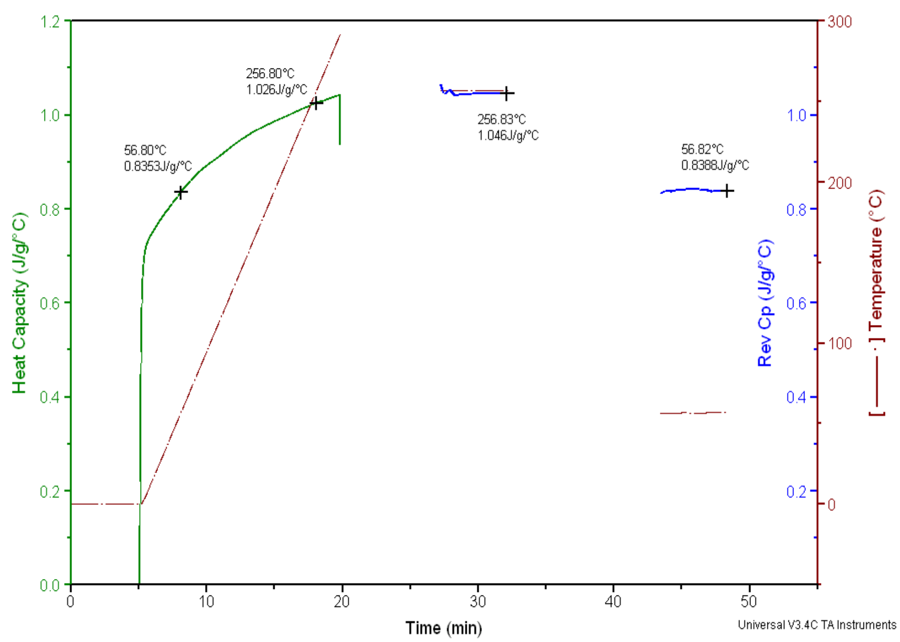


Figure 4. DSC and MDSC Heat Capacity on Sapphire Disc

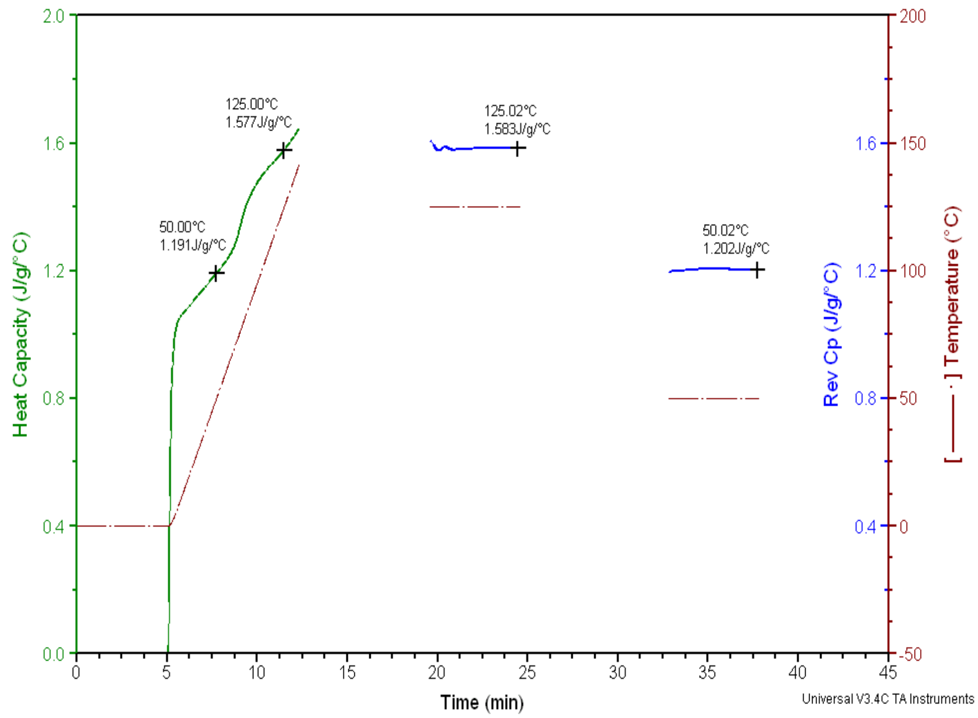


Figure 5. DSC and MDSC Heat Capacity on PET

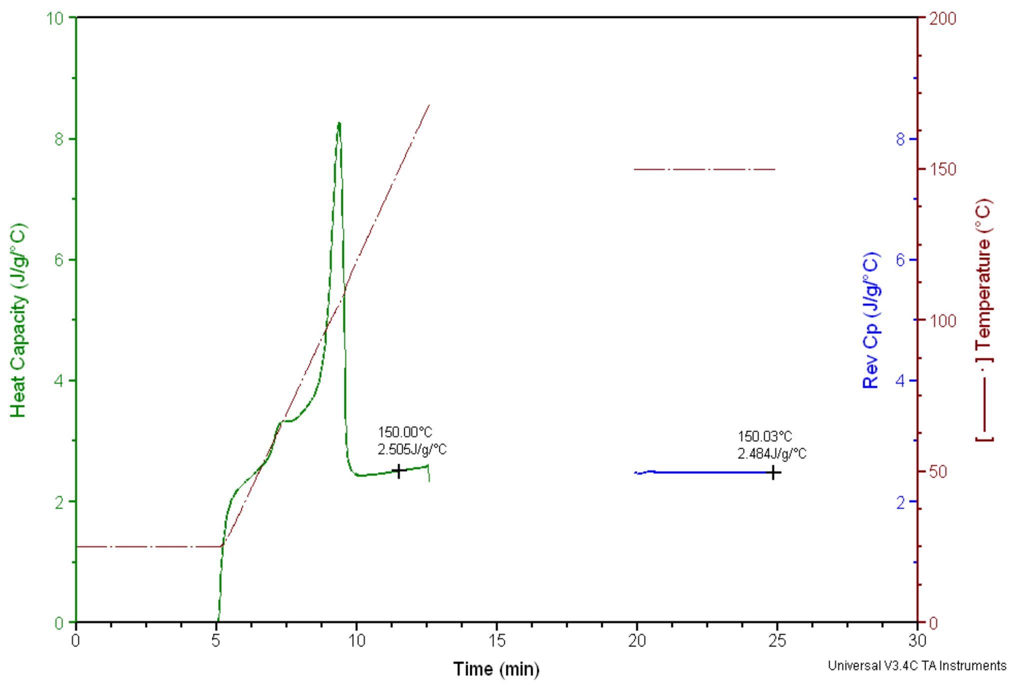


Figure 6. DSC and MDSC® Heat Capacity on PE

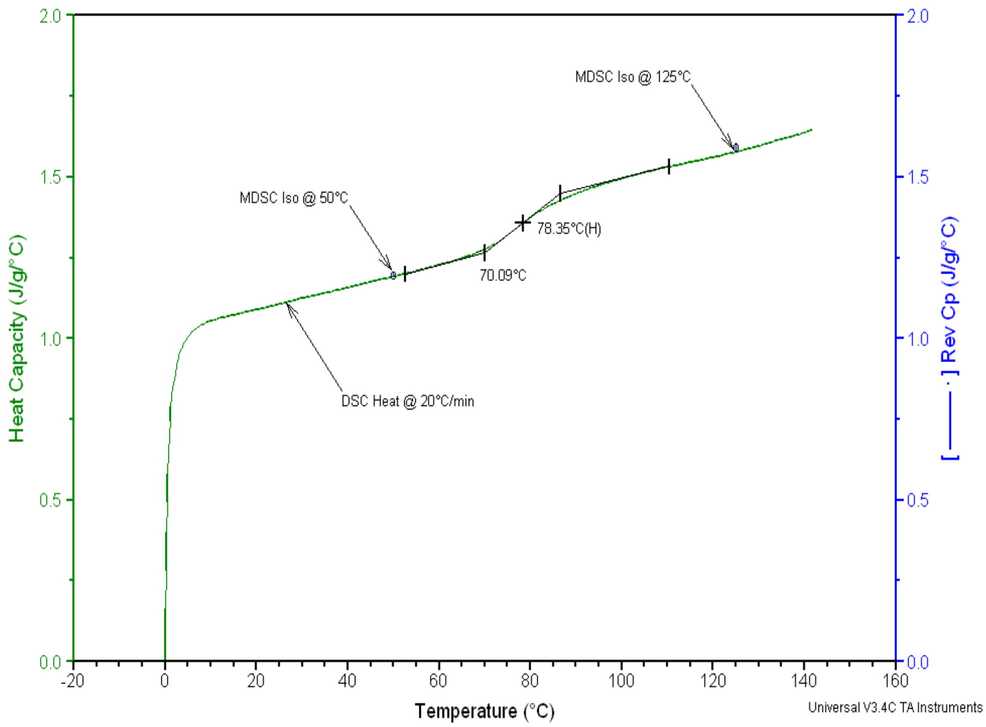


Figure 7. DSC and MDSC Heat Capacity Versus Temperature for PET

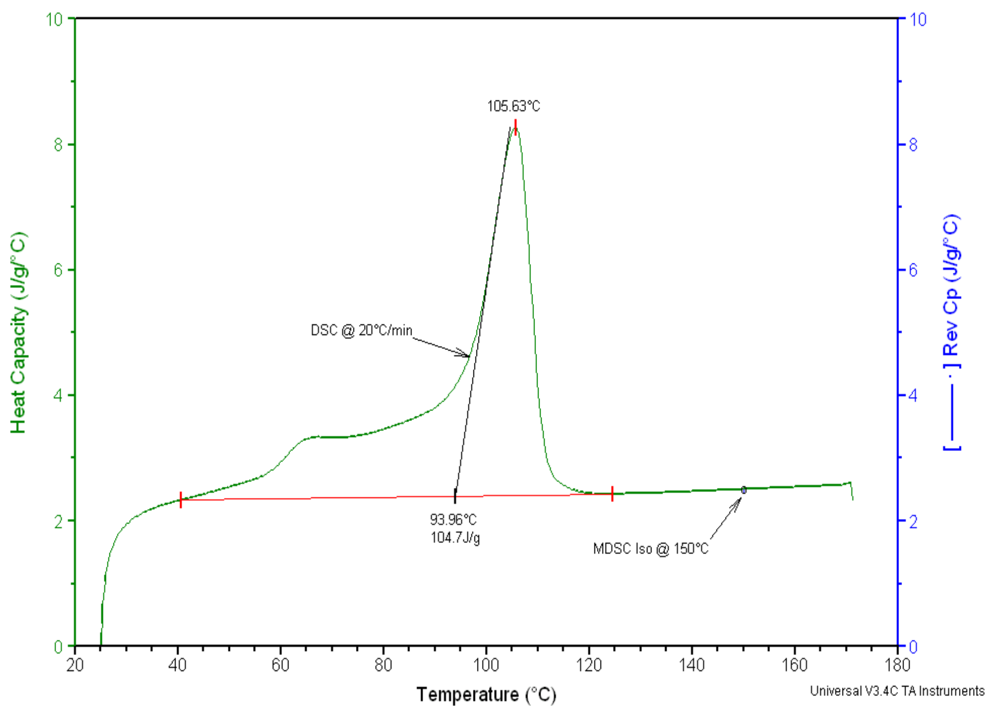


Figure 8. DSC and MDSC® Heat Capacity Versus Temperature for LDPE

		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	0.84		1.06

Table 1 - Sapphire DSC and MDSC® Heat Capacity 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	1.22	NA[1]

[1]Varies with crystallinity.

Table 2 - PET DSC and MDSC® Heat Capacity 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	2.55

Table 3 - PE DSC and MDSC® Heat Capacity for Three Experiments

SUMMARY

Modulated DSC permits the accurate measurement of **Reversing** heat capacity. Best results are obtained when experimental conditions are optimized to permit the quantitative flow of heat to the sample. This is primarily accomplished by using longer modulation periods of 100-120 seconds. When MDSC is used with a model Q1000 DSC, it is also possible to measure accurate **Total** heat capacity values. A combination of the two approaches in a single experiment permits an internal check of the accuracy by comparing results from the two approaches.

REFERENCES

1. Modulated Paper #2; Modulated DSC Basics; Calculation and Calibration of MDSC Signals; TA Instruments Technical Paper (TP 007).
2. Modulated DSC Paper #3; Optimization of MDSC Experimental Conditions; TA Instruments Technical Paper (TP 008).
3. "Making Accurate DSC and MDSC® Specific Heat Capacity Measurements with the Q1000 Tzero™ DSC"; TA Instruments Applications (Brief TA 310).

KEY WORDS
modulated differential scanning calorimetry, mdsc, dsc, heat capacity

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