Modulated Differential Scanning Calorimetry (MDSC*) Q2000. MANUAL

In MDSC a more complex heating profile (temperature regime) is applied to the sample than is used in conventional DSC (see WebPage introduction).

When to run MDSC?

- Always run a standard DSC at 10 ^{o}C/min first.
- If a Tg is detectable and can be routinely analyzed, then you don't need to use MDSC.
- If the Tg is hard to detect, or has an enthalpic recovery, then run MDSC.
- If melting process looks normal (single endothermic peak) and there is no apparent crystallization as it is heated, then you don't need to run MDSC.
- However, if melt is not straightforward, or it is difficult to determine if crystallization is occurring as the sample is heated, use MDSC.
- If you want heat capacity (Cp) – run MDSC.

The actual complex temperature/time profile in MDSC depends on three variables: (1) underlying heating/cooling rate, (2) modulation period, (3) modulation temperature amplitude.

Underlying Heating/Cooling Rate: 1-5 ^{o}C/min. Slower heating rate than conventional DSC are preferred to allow sufficient modulations during a thermal event. At least 4-5 modulations are required.
Modulation Period: 40-100 seconds. As the period of modulation increases, the material has no longer to respond and the range of acceptable amplitudes increases. Period of Modulation = 60 is suggested.
Modulation Temperature Amplitude: ±0.5 to 2 ^{o}C. The larger the amplitude, the larger the heat flow response since the instantaneous heating rate is directly related to amplitude.
Sample size: 10-20 mg. Contact between sample material and DSC should be optimized by crimping. Flat thin samples are best**.**
Signal Selections: Time, Temperature, Heat Flow (HF), Reversible HF, Non-Rev. HF, Heat Capacity.

1. **CONVENTIONAL MDSC (Tg)**: In conventional MDSC experiments, all three variables are operator – selected and the experiment can be performed over the same temperature range while either heating or cooling. As in conventional DSC experiments, MDSC experiments provide valid information only if the material being evaluated is able to follow the temperature profile generated by instrument.

   When you perform a Conventional MDSC experiment, the following test parameters need to be specified:
   a.) **Start Temperature- Final Temperature:** The starting and final temperatures should be set to cover a wide enough temperature range to observe all the event of interest. Check by standard DSC.

b.) **Ramp Rate**: Select heating/cooling rate of 1-5 ºC/min (3 ºC/min suggested). Make sure that the rate chosen provides at least 4-5 complete temperature modulation (oscillations) over the temperature range of each transition studied.

c.) **Modulation Period**: Select a modulation period of 20 to 200 seconds. For most materials in crimped pans, 40 to 60 sec is recommended.

d.) **Modulation Temperature Amplitude:** Select the temperature amplitude of modulation between ±0.2 and 2 ºC/min (± 1.0 ºC or ± 0.75 ºC suggested). Larger amplitudes (±1.5 to 2.0 ºC) should be used when measuring the weak transitions. Smaller amplitudes should be used for analysis of sharper transitions which are only a few ºC wide. NOTE: Amplitudes below ±0.1 ºC are not recommended.

e.) **Additional conditions-** for most experiments, the system default values shown are recommended.

- **Advanced Parameters:** Data Sampling Interval- the default value is 0.2 second/point for DSC and MDSC. Load Temperature Range – do not check. The temperature range specified in the Post Test window will be used.
- **Post Test Parameters:** Unload Temperature- range 25 to 35 ºC.
  Delay time (in min)- the instrument will delay after reaching the load temperature range, before loading the sample. A delay time of 2 min should be used when an experiment ends with the cell at lower temperatures. Discard pan in waste bin- if you want.

f.) **Typical Parameters for Cp** (use conventional MDSC): Modulation temperature amplitude ± 0.75 ºC; Modulation period = 90s; Heating rate = 2 ºC/min.

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2. **HEAT – ONLY MDSC (Tm and Tc)**: Only modulation period and heating rate are operator-selectable in Heat Only MDSC experiments. The instrument automatically determines the modulation temperature amplitude required to ensure that the instantaneous heating rates go to zero (isothermal) at an extreme of the temperature modulation cycle.

   When studying melting events it is beneficial to adjust these variables so that the instantaneous minimum heating rate achieved is 0 ºC/min (isothermal). By not cooling the material at any time during the modulation, the possibility for "artificially" affecting any observed crystallization phenomena is eliminated. More importantly, when the instantaneous heating rate is zero, there is no heat flow associated with heat capacity and, therefore, any heat flow observed at the top of the raw modulated heat flow signal must be the result of kinetic phenomena:

   a.) **Start and Final Temperature**: The starting and final temperature should be set a wide enough temperature range to observe all the events of interest.

   b.) **Heating Rate:** Select an underlying heating rate of 3 ºC/min or less, if required to get 4-5 modulation cycles over the width of the melting point (measure at half-height).

c.) **Modulation Period:** Use a modulation period of 40 sec. Longer period 60 sec are recommended for polymer samples > than 15 mg..

d.) **Modulation Temperature Amplitude:** Once the values above entered, the temperature amplitude of modulation will automatically be determined (±0.477 ºC every 60 sec) after clicking Apply.

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3. **QUASI – ISOTHERMAL MDSC**: In quasi – isothermal MDSC experiments the underlying heating rate is zero. However, by selecting a modulation temperature amplitude and period, the material is still exposed to an instantaneous heating rate, which permits the isothermal measurement of heat capacity.

   Generally, comparable results are obtained for underlying heating rates between 1 and 5 ºC/min. However, for evolution of time – dependent events such as glass transition, the results obtained vary slightly with heating or cooling rate. Therefore, to obtain the most thermodynamically correct value for the glass transition temperature as well as the heat capacity change during transition, the underlying heating rate should be set to zero (isothermal). A measurement of heat capacity can still be made under isothermal conditions based on the instantaneous heating rate generated by the modulation.

   a.) **Start Temperature**: 10 ºC below the transition of interest.

   b.) **Isothermal Time**: A stabilization time (10 min) is allotted at each temperature to ensure the equilibrium heat capacity value is obtained.