

# The DSC “Pegasus” 404C User's Guide

## Introduction

The high temperature Netzsch Differential Scanning Calorimeter (DSC) is designed to quantitatively measure the energy absorbed or released by samples as they are heated; anywhere from room temperature up to 1400 °C. The DSC can measure many thermodynamic properties of samples including the:

- ( $\Delta C_p$ ) Specific Heat as a function of temperature;
- ( $\Delta H$ ) Transition & Reaction Enthalpies;
- ( $T_M$ ) Temperatures of Melting & Phase Transformations;
- ( $T_G$ ) Temperature and energy change of Glass Transition & Crystallization;

Tests are performed with an inert reference held in a shared chamber with the sample. Both reference and sample are exposed to the same heating rates and environment. Thermodynamic properties can then be calculated by comparison.

The DSC can heat from room temperature to 1400° C with tests usually performed in argon, although other gases may be used. It is recommended to avoid reducing atmospheres.

The instrument is not designed to handle sample decomposition or volatility and should not be used with reactive samples. Materials expected to undergo decomposition may be run on the TGA.



## Administrative

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### TEMPO Access & Safety Training

Users seeking to obtain access to the TEMPO facility are required to complete a suite of safety requirements. These can be found on the “Access and Safety Training” Gauchospace website. Instructions for reaching this website can be found in the appendix. All requirements must be satisfied before entering the TEMPO facility or speaking with the TEMPO manager, Amanda Strom.

Once the TEMPO and MRL safety requirements have been completed users may request daytime access through the website “<http://www.mrl.ucsb.edu/access>”.

All users are required to wear safety glasses, long pants and close-toed shoes whenever working in any MRL lab. This applies for **all** instrument use including logging onto a computer to retrieve data. If users are working with liquids then a lab coat is also required.

### Accessing the DSC

The lab is open Monday through Friday from 8 AM to 5 PM. Users should plan their DSC work to begin during these hours. Users do not need to be present while the DSC is running but it is good practice to verify the DSC is operating correctly before leaving.

Time may be reserved using the FBS system at UCSB.FBS.io. Once you have reserved a time slot you may log in at the beginning of your scheduled slot and start the timer. This will power on the monitor and allow you to perform your measurement. Access to the DSC, through

the FBS website, is granted to users after they complete instrument training. If the instrument is not currently reserved then users may also select the walk-up option on FBS.

Before using the DSC users should write down their name, 13 digit recharge number, advisor's name, and the start time on the paper log. On completion of the run the end time should also be noted. The paper log serves as a backup and allows for comments in the event of an error.

## Training

Users may self-train on the instrument after speaking with TEMPO staff. Users choosing to self train are given a sample and some parameters to perform a measurement on. For others interested in a guided training session, the training schedule is sent out quarterly via e-mail.

To enroll in a training session, users can sign up through the TEMPO Instrument Training and Resources page on Gauchospace.

## Safety & Housekeeping

The furnace is capable achieving very high temperatures. Users must take proper precautions to prevent damage to themselves, other users and the lab. Do not open or attempt to open the furnace without verifying that the interior has cool down to at least 100 °C.

All samples must be well labeled with the owner's name and their essential composition. Samples should not be left in the lab unless they are actively running in the DSC. Users should avoid leaving their samples in the instrument if they are not preparing for or performing a measurement.

## Acknowledgements

In any publications based on research done with MRL Facility instruments (ie in the TEMPO lab) or with help from MRL staff please acknowledge support from the National Science Foundation. Acknowledgements should be stated as:

**“The MRL Shared Experimental Facilities are supported by the MRSEC Program of the NSF under Award No. DMR 1720256; a member of the NSF-funded Materials Research Facilities Network ([www.mrfn.org](http://www.mrfn.org))”**

Acknowledgements such as these allow the MRL to obtain funding from the NSF and aid the NSF when they justify their requests for funding from congress.

# Basic Differential Calorimetry

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## Process and Theory

Each measurement uses two lidded crucibles made from the same material and of approximately identical masses. One crucible functions as an empty and inert reference and the other contains a sample for measurement. Each crucible sits on a separate sensor and is heated in a shared environment. When heated (or cooled) the presence of a sample produces a difference in the rate of temperature change for the sample crucible compared to the empty reference. This difference produces an electric signal through a thermocouple sensor. In events of phase transitions the relative difference in temperatures becomes more dramatic and produces visible peaks in the signal. The transition is often accompanied by a shift in specific heat capacity ( $C_p$ ) and, when plotted as a function of time, is seen by a shift in the slope of the line.

The temperature of each crucible is measured by a sensor connected to a thermocouple which translates temperature differences into a voltage potential. The temperature difference is measured in microvolts ( $\mu V$ ). This means the data accuracy and precision is influenced by the thermal contact of the crucibles to the sensors and of the sample to its crucible. Variations between crucibles may also affect data points.

In theory the use of virtually identical crucibles which are evenly and equally heated shouldn't produce a signal as there would be no difference between them but even minor defects may produce a signal. Fluctuations in the placement of the crucible on the sensor as well as thermal conductivity properties of the sensor head itself result in the appearance of a voltage difference. Although there isn't a practical means to achieve zero resting voltage, measurements may be improved by first collecting a baseline of the two empty crucibles. This baseline can then be used to correct the data collected during measurement of a material. The baseline correction must match the parameters of the sample measurement exactly, including heating program, gas type and crucibles.

Quantitative energy measurements require a calibration to convert the difference in temperature to energy. This may be accomplished with the use of a single standard run under the same conditions as the intended sample. Sapphire standards are often employed. Typically standards should be used with similar dimensions to the sample and with well documented heating capacities at the target temperature range.

## Thermal Lag

Optimizing a measurement in the DSC requires that users understand the role of thermal lag in the instrument. **Thermal lag**, in this context, is the difference in heating rate between two materials in a shared environment. Two identical materials, e.g. crucibles, would be expected to heat at the same rate when placed in a shared environment. The introduction of a sample material to only one of the crucibles will alter its properties. The sample containing crucible now is part of an equilibrium relationship with the material which causes it to heat at a different rate.

The difference in heating rate is what produces the electrical signal interpreted by the instrument and although it is ultimately responsible for the data obtained by the user, too much of a good thing can ruin the data. Measurements which take place over long temperature ranges lead to an accumulation of thermal lag to a degree that may lead to any resultant data being meaningless. If a sample is heated over a continuous 800 °C period then once the furnace has

reached its final value the sample containing crucible may have only just reached 725 °C. This would then mean that a melting point observed at 775 °C could in fact be occurring at a temperature of 700 °C.

## Hardware, Crucibles, & Gas

### Furnace and Temperature Sensors

The DSC 404C furnace is capable of reaching 1400° C and employs a passive cooling system using air flow. After heating cycles the sample chamber can take up to three hours to cool to room temperature. Since the slowest part of the cool down is from 200° C to room temperature, users with many samples may save time by starting a little warmer than room temperature. (This is not recommended for  $C_p$  measurements.) **The furnace should NOT be raised unless the sample temperature is below 100° C!**

Prior to DSC measurements all samples must be tested for decomposition temperatures or volatility. These events lead to the degradation of the sensor head and may result in the complete failure of the instrument. The cost of replacement for the sensor head is \$8,000 and may be assigned to users demonstrating negligence in the use of the device.

The sensor head is very sensitive to contact and may shift with forceful loading of the crucibles. It is recommended that the green fencing around the furnace be used to stabilize your hands when loading crucibles.

### Sample Crucibles

Crucibles are available as platinum-rubidium or alumina ( $Al_2O_3$ ). Other DSC crucibles such as quartz, graphite or  $ZrO_2$  may be purchased from other providers. Either alumina or Pt-Rh will work for most measurements. **Each crucible should have a lid and be preheated to the maximum planned measurement temperature before use.** Pre-heating may be done with a torch or inside a clean furnace. The pre-heating will help to remove dust or other particles that may have settled on your crucible as well as remove any adsorbed moisture prior to the measurement.



The MRL TEMPO Facility sells  $Al_2O_3$  crucibles for \$10 each. They are similar in appearance to the TGA crucibles but are **not** the same size and are **not** compatible. The DSC crucibles are a 6.8 mm outer diameter. The crucible lid should sit squarely on top of the crucible without sample contact. The lid serves to keep the heat of the reaction inside longer and improves measurement sensitivity. Additionally it prevents the exposure of the instrument's internals to any unintended volatility or decomposition. Any sample that fits may be used but optimal sample dimensions are 6 mm  $\varnothing$  x 1.0 mm thick for platinum and graphite crucibles. For  $Al_2O_3$  crucibles or platinum crucibles with  $Al_2O_3$  liners, the sample dimensions should be 5.2 mm  $\varnothing$  x 1.0 mm thick.

Each crucible will have advantages and disadvantages. Platinum crucibles will typically display much better heat transfer however they will alloy with most metal samples, ruining the pan, sample and data. They also tend to soften and stick to the sample carrier if they are hot for too long, although they will not melt. Platinum crucibles should be avoided at temperatures above 1000 °C. If a platinum crucible must be used at high temperatures a sapphire disk can be placed between the crucible and sensor head and may be purchased from Netzsch. In the event a

platinum crucible is needed and the sample contains metals, alumina liners may be used.

Alumina crucibles are cheaper than their platinum counterparts and may typically be used with most samples. While cheaper and more robust they do undergo a phase transition at about 800 °C, causing the crucible to turn translucent. Measurements looking for quantitative data around that temperature should opt for another crucible choice. Specific heat capacity measurements that require heating through that region may find increasing error as they move above the transition temperature.

**Extreme care must be taken to ensure that no crucible/sample reaction will occur before running the sample in the DSC.** One of the major causes of measuring head (sensor) death is crucible/sample reaction. The sensor replacement cost is approximately \$8,000. If in doubt, heat the sample in a crucible in a lab furnace before trying it in the DSC. The Faculty advisor of a negligent user who damages the DSC may be required to pay the cost of repair. A guide on crucible selection can be found on the TEMPO Instrument Training and Resources page on Gauchospace as well as in the appendix of this manual.

## Standards for Heat Capacity

There is a black and clear plastic box (about 2" x 1.5" x 0.75") in the DSC drawer which should have three sapphire standards of varying thickness and two Al<sub>2</sub>O<sub>3</sub> standards. Use the sapphire standard with a thickness that measures closest to the sample. If in doubt, use the 0.50 mm sapphire standard.

## Atmosphere for Tests

The DSC can work in most gases but argon is suitable for almost all tests. Some users like to use air as a process gas to prevent sample reduction. The systems default setup uses either Argon on Purge 1 or clean dry air on Purge 2. Other suitable gasses are nitrogen and oxygen. Nitrogen is available in the lab but may form nitrosyl compounds at temperatures beyond 700°C. Users interested in using oxygen would need to supply their own gas.

For tests requiring extremely high sensitivity helium serves as a completely inert gas with excellent thermal conductivity. Users interested in helium would need to supply their own gas. Please contact the MRL staff if you have questions about other gasses.

## Sample Preparation

Samples must be tested for decomposition or volatility in the TGA prior to use. Decomposition can lead to deposit buildup within the device and degrade instrument sensitivity. Some compounds may react with the sensor head damaging or destroying it. The use of a crucible lid helps to safeguard the device.

Users should consider four basic principles during sample preparation:

1. Selecting the right crucible.
2. Making and maintaining good thermal conduct between the sample and crucible.
3. Preventing contamination of the outer surfaces of the crucibles.
4. The influence of the atmosphere surrounding the sample.

## Thermal Contact

Ideally samples are flat disks, powders or pellets with disks typically demonstrating

better heat transfer. The sample should be flat to insure good thermal contact with the crucible floor. Powders may undergo sintering during the heating process and then deform, losing thermal contact with the crucible. Thin films may also display curling or curvature upon heating, causing a loss of thermal contact. A sample of minimal thickness and maximum flat surface area is desired.

Irregularly shaped samples may be optimized by sawing and grinding surfaces intended to contact the crucible floor. More brittle substances may be ground to a fine powder and then compacted into the crucible.

## Method Development

### Basic Measurement Requirements

Although the DSC is functionally quite simple, a good measurement requires some variation in methodology. Some basic guidelines for measurement criteria are:

For the Transition Enthalpy (aka Latent Heat).

- Sample & Crucible mass
- Temperature Calibration file
- Sensitivity file
- A Baseline Correction measurement.
- Sample measured as Sample+Correction

For the Specific Heat (aka Heat Capacity or  $C_p$ ):

- Sample & Crucible mass
- Temperature Calibration file
- Baseline Correction
- Heat Capacity Standard measured as Sample + Correction
- Sample measured as Sample + Correction

For the temperatures (Onset, Peak, Endset) of Melting & Phase Transformations and of Glass Transition & Crystallization:

- Sample & Crucible mass
- Temperature Calibration file
- Sample measured as Sample

For the temperature and quantitative energy change of Melting & Phase Transformations and of Glass Transition & Crystallization:

- Sample & Crucible mass
- Temperature Calibration file
- Sensitivity File.
- A Baseline Correction measurement.
- Sample measured as Sample+Correction

## Phase Transition Measurements

Measurements looking to determine the onset temperature of phase transitions are typically robust and least likely to be affected by experimental errors. Users looking to obtain as exact a value as possible should consider performing multiple runs in which they attempt to narrow the temperature range over which they measure.

An example of this type of measurement might begin with an exploratory test in which the material is heated over a range of  $\pm 50$  °C of their expected transition temperature. Once a crude temperature value has been reached then users may choose to rerun in a range of  $\pm 30$  °C. By narrowing the range over which the measurement is made the user reduces the error produced by thermal lag in the final value. Conversely if a phase transition were expected to occur at a temperature of 900 °C and the user's measurement range was from 100 – 1000 °C then the accumulation of thermal lag in the material might lead to an erroneous melting point of 950 °C.

A general form for phase transition measurements is to first ramp to a value at least 20 °C below the expected transition temperature and then hold at that temperature to equilibrate. Once the contents of the furnace are equilibrated users may ramp the temperature over their anticipated range.

## Heat Capacity Measurements

Similar to phase transition measurements, heat capacity measurements may also be subject to thermal lag induced error. Users desiring to measure heat capacity over large ranges of temperature may want to consider measuring heat capacity using a series of ramping periods with intermittent isothermal intervals to allow for equilibrium in between. That is, if the temperature range of interest is 500 – 1000 °C users may choose to heat the sample from 500 °C to 600 °C and then hold the sample at 600 °C for ten minutes before heating the sample again, up to 700 °C. This method helps to reduce the accumulation of thermal lag over long measurements.

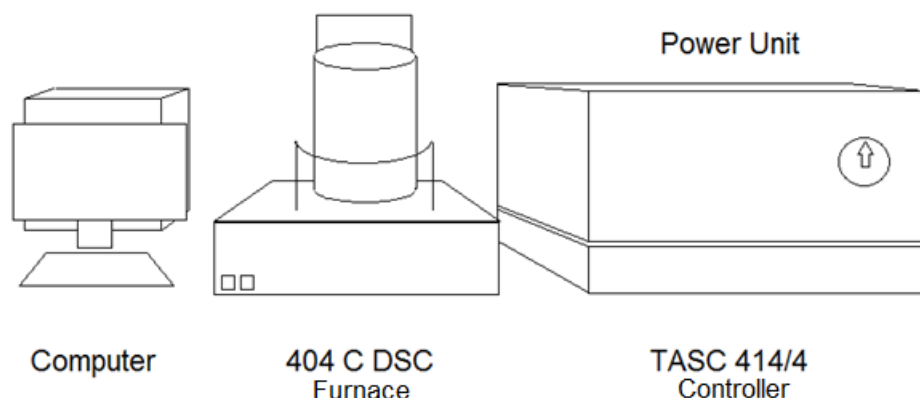
## Possible Issues

Theoretically a first order phase transition, such as melting or recrystallization, can be measured as many times as desired however this depends on two principles which may not always hold true.

1. Upon cooling the sample returns to its original state.
2. The sample does not demonstrate any evaporation, sublimation, reaction or other decomposition during the measurement.

# Hardware

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## Instrument Components

### Using the Instrument

#### Powering the Instrument On

The instrument should be given about 15 minutes to warm up after powering on. Each instrument component is powered on by physical switches located on their respective cases.

- The 404 C DSC switch is located on the left side at the back of the case.
- The TASC 414/4 switch is located on the right side at the back of the case.
- The power unit is controlled by a red dial on the front of the case. It must be rotated to on.

#### Operating the Furnace

The DSC furnace is raised and lowered using the two arrow buttons located on the front of the device in combination with the safety button on the ride side panel of the furnace base. The safety button and arrow button must both be pressed to move the furnace. Users should confirm that the vacuum indicator (to the right of the arrow buttons) does not have a red light on. If the furnace is under vacuum it should not be opened.

Once the furnace has been raised, and the crucibles loaded the furnace may be lowered again. **Prior to fully lowering the furnace users should visually confirm that it will not contact the measuring head.** Once the furnace has been fully lowered a green light should appear in the arrow button of the furnace base. If the light does not turn on check to make sure that the furnace is fully lowered. **Users should not raise the furnace unless it is below 100 °C.**

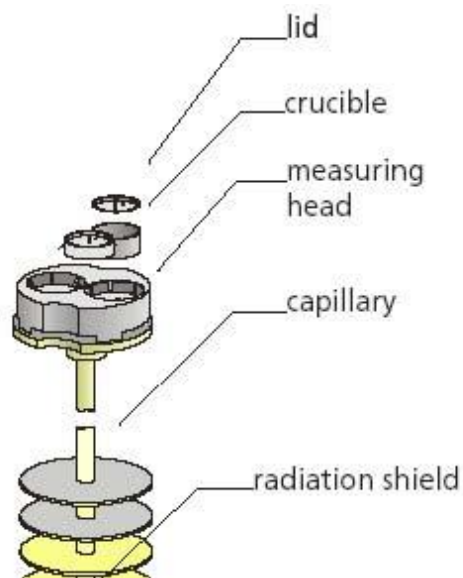


## Loading and Unloading Crucibles

The measurement head contains two wells for the placement of each crucible. The rear well is for the reference crucible and the front is for the sample crucible. Ideally each crucible is placed in the center of its well and sits flatly on the floor. The green wire guard in front of the sample chamber is there for users to steady their hands as they place the crucibles.

The sensor head is sensitive to misalignments which may throw off the instrument calibration. Users loading crucibles should try to minimize straining or bumping the measurement head as much as possible to avoid this.

The diameter of the sensor well is slightly larger than that of the crucibles which allows for some variability in position. For users performing quantitative measurements, i.e. calling for a baseline and standard, the positioning of the crucible should be consistent throughout the measurement series. When evacuating the furnace chamber, rapidly opening the vacuum line valve may also jostle the crucibles out of position.



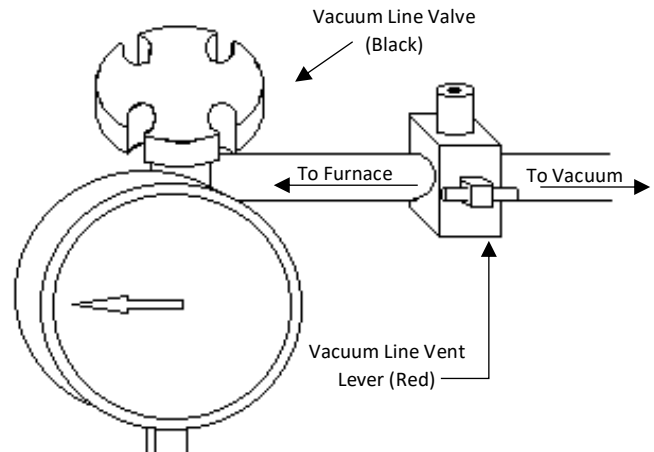
## Evacuating and Backfilling Procedure

Heat transfer from the furnace to the sample is directly affected by its gas environment. Most measurements benefit from a pure and uncontaminated environment which can be achieved by evacuating and backfilling the furnace using a high purity gas. The default configuration uses ultra high purity argon as the Purge 1 gas and a dried air on Purge 2.

Before purging the sample chamber users should first inspect the front of the furnace and look for a green LED light on the downward arrow, indicating that the furnace is fully lowered.

1. On top of the DSC furnace, **above the sample chamber**, turn the arrow shaped black lever to the right to close the sample chamber vent. The pipe attached to the exhaust vent should not show noticeable flow.
2. Turn on the red vacuum pump located on the shelf **above** the DSC controller.
3. The vacuum pump has a line connecting to the right-back side of the DSC furnace unit. The line is fitted with a manometer, black handwheel and a small valve with a red lever. Rotate the red lever until it is parallel to the tubing, as shown in the following diagram.

4. Slowly open the vacuum line valve by rotating the black hand wheel. Opening the valve rapidly may displace the crucibles in the furnace. The manometer should show the pressure decreasing. Note that the manometer is initially resting at a 0 reading, indicating atmospheric. As the vacuum builds it will drop to a maximum of -100 kPa.



5. Allow the furnace to purge for approximately fifteen minutes. A red light should display on the front of the furnace at the vacuum panel which indicates when a vacuum has been established. Aside from the red light indicator the furnace's vacuum button should not be used.
6. Close the line by using the handwheel to close the vacuum line valve. Turn off the pump and turn the red level until it is perpendicular, to vent the line.
7. On the front of the module press the button for the purge gas you intend to use.
8. Allow the furnace some time to backfill until the pressure gauge indicates a return to atmospheric pressure levels.
9. Once the sample has returned to approximately atmospheric levels, reopen the vent on top of the sample chamber using the arrow shaped black lever. Gas flow should remain on during this point and for the remainder of the measurement.

Users should perform about three iterations of evacuation and backfilling to insure a pure gas environment. **Once finished users must make sure the gas continues to flow and that the black arrow valve on top of the furnace is turned to open again. This is the same valve referenced in step 1 of the evacuating procedure.** This can be verified by placing a hand in front of the exhaust port to feel for air flow. **Failure to open the sample chamber valve before running a measurement may destroy the instrument and pose a danger to lab users.**

# Software

The DSC uses two applications, one for measurements and the other for analysis. The icons of both programs, DSC 404C and Proteus Analysis, are located on the desktop of the computer. Data may be accessed by transferring it to the TEMPO network hard drive, also located on the desktop.

The DSC 404C program is used to communicate with the DSC and perform the measurements. Sample data and thermal programming are entered through this software which then collects the data. All data is saved in a temporary file until the completion of the measurement making the computer sensitive to memory use during collection. Users should avoid use of the computer during measurement to prevent data loss.

To start a new measurement, open the DSC 404C software and from the top menu select new measurement. This will open the DSC 404C Measurement Header to begin designing a measurement program.

## DSC 404C Measurement Header

Users may enter the relevant information for their sample in this window. This information will be stored with the data collected during measurement and users may reference it during post-run analysis. The Proteus analysis software will also use information entered here to perform various calculations. At a minimum the measurement header will require the Measurement Type, Sample Identity, Sample Name, Reference and Sample Crucible Mass as well as a Sample Mass.

### Measurement Type

When designing a measurement, the “**Correction**” option functions as a baseline. Selecting a run type of “Correction” will allow users to run a measurement of the empty sample and reference crucibles. Users may then run their sample, using the same crucibles, as the “**Sample+Correction**” option and the correction (baseline) will be automatically removed from the data. The correction measurement data is retained and may be viewed in the analysis program Proteus. Without a recent correction file the Sample+Correction option will be grayed out and not selectable.

Correction runs must follow the same temperature program and use the same calibration files that the sample measurement will be run under. As the hardware in the furnace can change with use it is better that the baseline be created as close to the time of sample measurement as is feasible.

The screenshot shows the 'DSC 404C Measurement Header' window. It contains several input fields and sections:

- Measurement Type:** Radio buttons for 'Correction' (selected), 'Sample+Correction', and 'Sample'.
- Laboratory:** MRL
- Project:** Black Pearl
- Operator:** Jack Sparrow
- Date:** 02/26/09, 11:37:46
- Material:** baseline (dropdown menu)
- Instrument Setup Information:**
  - Crucible Type: DSC/TG pan Pt-Rh
  - Sample Carrier: DSC/(TG) HIGH RG 2
  - Sample Carrier TC: S
  - Furnace: STD Pt-Rh
  - Furnace TC: S
  - Measurement Mode: DSC
  - Temp. limit: No special temp. limitations
- Sample:**
  - Ident: SP245
  - Name: black pearl
  - Sample Mass: 0 mg
  - Crucible Mass: 252.400 mg
- Reference:**
  - Name: empty pan
  - Reference Mass: mg
  - Crucible Mass: 261.400 mg
- Purge Gas 1:** argon, Flow Rate: 50 ml/min
- Purge Gas 2:** ml/min
- Remark:** (empty text box)
- Buttons:** Help, CANCEL, OK, Continue ->
- Status Bar:** Current hardware temperature range is from 0 °C to 1500 °C

When doing  $C_p$  measurements, Netzsch suggests not using a Baseline Correction for more than three consecutive measurements without rechecking. It is also suggested, at least for critical measurements, the Baseline be done twice. Comparison of the two baselines should not differ by more than 0.3 microvolts at the point of widest variation. If they do then a third baseline should be run and the comparison between the baselines performed again.

Measurements looking for onset temperatures of thermal events generally do not require corrections and may run using the measurement type “**Sample**”.

## Sample Information

Many of the fields, such as laboratory and project are for user reference and do not need to be filled in. The material field is included in this and whatever entry is used does not affect future measurements or calculations. The **gas flow rate** field also does not affect any system settings but does allow users to note what parameters they chose to run at for future reference. The default setting for gas flow rate is approximately 75 mL/min.

Users should confirm that their crucible type is correct for their intended measurement and that the sample carrier field has “DSC(/TG) HIGH RG 2” written in. If something else is displayed then please inform the MRL staff before using the instrument.

Once the appropriate fields have been filled users may press Continue to move to the next step and select a temperature calibration. Selecting OK will abruptly end the measurement configuration.

## Temperature Calibration & Sensitivity Files

When designing a measurement, users will be required to specify a **Temperature and Sensitivity Calibration** file. The **Temperature Calibration** selection window will automatically open to the correct folder and the most recent calibration file should be chosen.

### Temperature Calibration File

Multiple calibration files may be present, each attenuated to specific temperature ranges and testing conditions. The user should select the temperature calibration file that covers their desired temperature range and was performed in similar conditions including:

- Crucible type
- Gas environment
- Heating rate

If users do not see an appropriate file for their intended measurement please speak with the MRL staff about having one made. Currently the DSC has calibration files designed for use with  $Al_2O_3$  crucibles which are appropriate for most phase transition measurements. For quantitative measurements that cannot use  $Al_2O_3$  please speak with the MRL staff.

### Sensitivity File

A **sensitivity calibration** file is required if the user wants quantitative energy information from their measurement. For phase transition measurements, which only look at temperature-

event relationships, the Senzero file may be selected. Quantitative measurements require a sensitivity file that matches the measurements parameters as closely as possible. When a sensitivity file is selected users may be able to measure energy changes in mW/mg and integrate peak areas in joules/gram.

The creation of a sensitivity calibration file is an involved process that requires measurements of five to six standards. If you plan on doing quantitative measurements please verify that an appropriate sensitivity file is already present. Users who need a new sensitivity file should speak with the MRL staff at least a week in advance of their intended measurement.

## Temperature Programming

**DSC 404C Temperature Program Definition**

Temperature Steps

nr	Type	°C	K/min	Time	pts/min	pts/K	STC	P1	P2
1	Initial Standby	30.0					<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
2	Dynamic	500.0	10.00	0:47:00	10.00	1.00	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
3	Dynamic	500.0		0:10:00	10.00		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
4	Dynamic	700.0	20.00	1:20:00	10.00	24.00	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
5	Dynamic	700.0		0:10:00	10.00		<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
6	Dynamic	710.0					<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
7	Final Standby	20.0	40.00	0:17:15			<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
8	Final Standby	20.0		2:00:00			<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Conditions on Standby

☒ STC  
☐ Purge1  
☐ Purge2

Category

Stand-By Temperature: 30 °C  
Heating Rate: 40.00 K/min  
Max. Stand-By Time: 02:00 Min

Step Category

Initial Standby  
Initial  
Dynamic  
Isothermal  
Final  
**Final Standby**

Add  
Insert Dynamic Step  
Insert Isothermal Step

Temperature programs are composed of, at minimum:

- The Initial Standby/Initial
- An Isothermal Step
- A Dynamic Step
- The Final Emergency Setting
- The Final Standby

The **initial standby** or **initial** steps set the temperature that the data begins recording at. Once the measurement starts the first temperature step begins but data will only be recorded once it has reached the “initial” value. That is, if you initially heat to 400 °C and specify an initial value of 360 °C then data will not be recorded until 360 °C is reached. Alternatively, the initial standby method lets users set a temperature value that the furnace will attempt to reach and stabilize at before beginning the measurement. In the same example the instrument will heat to 360 °C and hold at that value until a stability criterion has been reached. The first programmed temperature step will then begin and all data from that point will be recorded. It is recommended that users go no lower than 40 °C for their initial standby temperatures due to low heat limitations of the furnace heating element.

The **isothermal step** programs the DSC to hold the sample chamber at its current temperature for a designated period of time. These are often used to allow the sample chamber to stabilize following or preceding a dynamic step. Preceding and following a dynamic step with isothermals can decrease percent error in measurements.

**Dynamic steps** are where ramp rates or heating rates are designated. A target temperature is selected, as well as a heating rate. Notice that the target temperature is in °C and the heating rate is in K/min. Ramping speed can be changed based on interest in a specific temperature range. For ranges containing data of interest a ramping rate of 10-20 K/minute is recommended. A faster rate may be set, such as 30 K/minute, for regions without interest. The instrument is capable of 40 K/minute however this stresses the heating element and may cause the sample chamber to overshoot the desired temperature. During dynamic steps with a decreasing temperature (ie from 700 °C to 600 °C) the DSC employs passive cooling. Setting a heating rate of 10 K/min will instruct the DSC to attempt to keep the cooling to approximately that value. It is recommended that each dynamic step be preceded by an isothermal to allow the temperature of the sample and sample chamber to equilibrate.

Isothermal and dynamic steps also require a pts/min parameter which tells the instrument how often to record a data point during the step. **Data acquisition rates** can be changed based on interest in a specific temperature range. It may be entered as either points per degree or per minute. 60 points per minute is generally appropriate for sections of interest. The system has a limit of 24000 data points per measurement that it will notify you of, should your program go beyond that.

The **Final** step sets a safeguard temperature for the measurement. This will auto-populate with a value 10 °C higher than your highest temperature. If the instrument reaches this temperature it will automatically terminate the sequence as an effort to prevent damage to the instrument and sample. **Final Standby** programs the DSC with instructions on what to do once the sample has finished. The instrument will drop to the stand-by temperature at the heating rate designated, and attempt to hold it there for the given time. As this should always be a cooling step, the heating rate can be set to 40.0 K/min to allow the system to cool quickly and shorten the time needed per measurement.

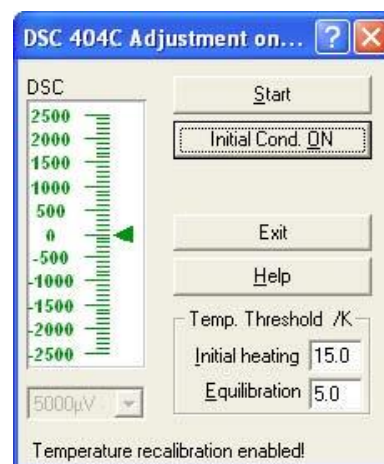
## Possible Issues

There are often anomalies in the data at points where the furnace heating range changes so users should set temperature programs with steady heating rates that go at least 20 °C beyond your desired end point. Shorter dynamic steps allow for an increase in measurement accuracy but run the risk of cutting off phase transition events prematurely or missing them altogether.

## DSC 404C Adjustment Window

After designing a temperature program and selecting continue, the DSC 404C adjustment window will appear. If a temperature recalibration file was selected the program will apply it at this point and the temperature indicated at the bottom right corner of the software screen will alter to reflect it. Selecting initial conditions on applies the options selected for the first step of the temperature program, i.e. the chosen gas flow and STC option if selected.

The Temp. Threshold /K fields specify an initial heating rate and equilibration range. In the adjacent example the furnace will heat at 15 K/min to within  $\pm 5$  K of the 40 °C standby temperature. This standby temperature is specified in your temperature program by the initial standby step.



When ready users may select the start button to begin the measurement. After reaching the initial temperature and equilibrating the programmed measurement will begin and data points will be plotted on the screen as they are collected. A total estimated measurement time is also displayed.


## Measurement Conclusion

Once your measurement has finished the program will automatically save the data in the user designated location. Users should wait until the furnace has cooled to a safe temperature of 40 °C before attempting to remove their sample.

Users **should not** turn off any component of the DSC once completing a measurement. **Shutting off the furnace power transformer before the furnace reaches a value below 500 °C will permanently damage the device.**

## The Proteus Analysis Program

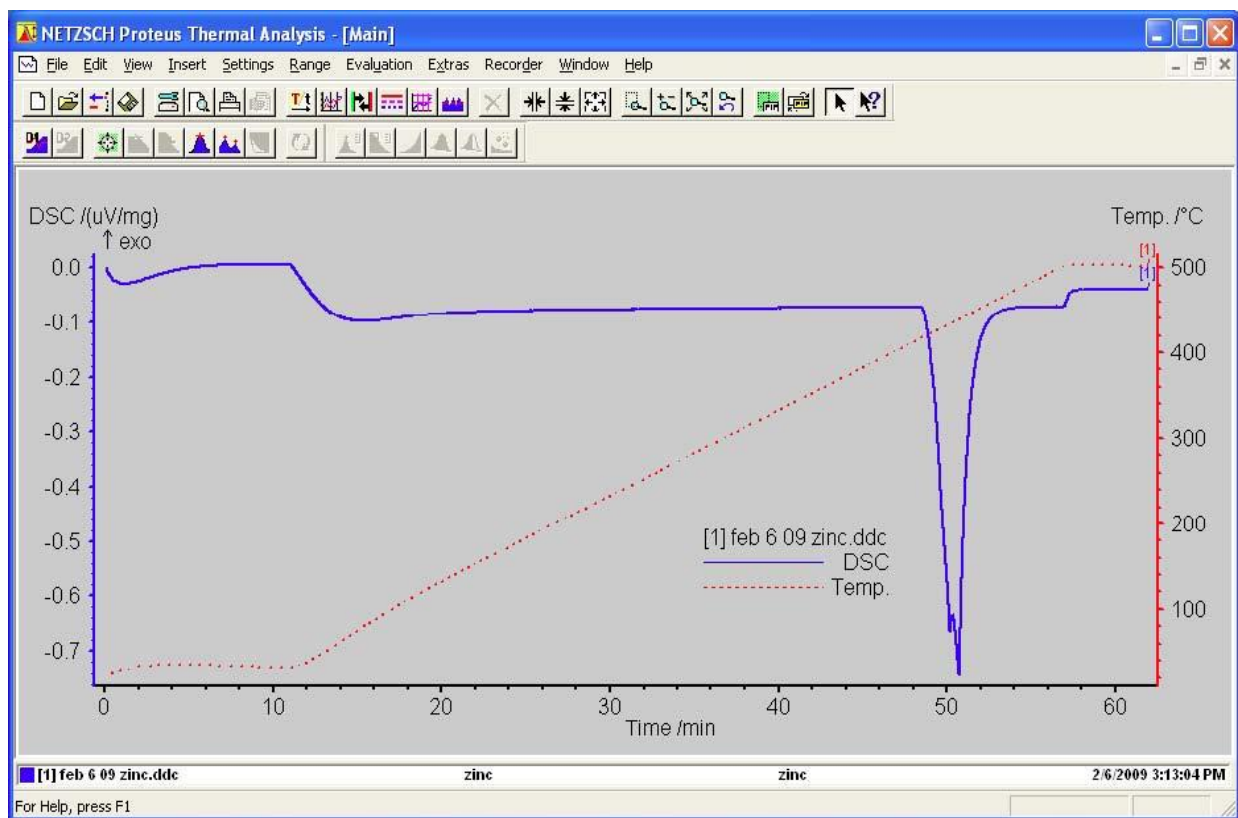
Data analysis can be performed on the Netzsch Proteus Software, located on the desktop. Once a run has completed the data is automatically saved. The save location is chosen prior to starting the measurement.

To analyze their data users should open the Proteus software by double clicking the icon at the center of the desktop. Once open users may open their data by selecting either File, from the menu at the top of the screen, or the folder icon  in the toolbar.


### The Proteus Interface

An example of a DSC measurement is shown below. The shown sample is heated to a peak of 500°C after a 10-minute equilibration period. The dotted red line shows the temperature over time and the blue shows the signal difference between the reference and tested material in units of  $\mu\text{V}/\text{mg}$ . Notice the phase transition around 440°C.





Curves may be right clicked to bring up some menu options for manipulation. Selecting the curve properties option will allow the user to customize the color and appearance of the line while the file properties option will bring up a window containing all of the measurement data stored in the file. This includes the user created temperature program and all the parameters that the measurement was performed under.

The software automatically displays time along the x-axis when opening new data however users looking for onset temperatures of transitions can display temperature as the x-axis by selecting the  button in the toolbar. This will cut your measurement into segments with each segment corresponding to one step in the temperature program. Isothermal segments will automatically be hidden as these will consist of a flat line.

Users wishing to high (or unhide) a line segment may right click on the curve and select view segments. This will produce a window listing each segment which users may check or uncheck to display.

## Exporting Data

Experimental results may be exported as either an ASCII or ANSI Unicode file. Typically users will want to select ASCII and then choose the **.csv** format. This will export their data as a comma separated values file which may then be opened in excel.

To export the data select the **Extras** option from the toolbar at the top of the Proteus window. In the drop down menu choose **Export Data**. Fill out the dialog box that should pop up and choose where you would like to export your data to.

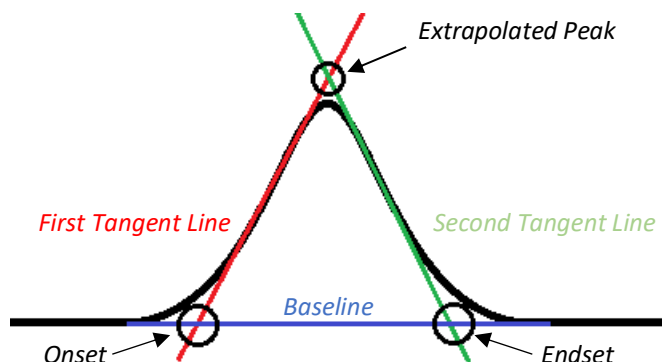


## **Retrieving Data**

To maintain the integrity of our instrument computers, USB access is disabled. Instead each instrument has access to a shared TEMPO hard drive, with a shortcut present on the desktop. Users may access that hard drive, from the instrument, and make a folder for themselves. They can then copy all data from the instrument computer to the shared hard drive. This hard drive may then be access by the shared computer in TEMPO labs, and data can be retrieved there using a USB device.

# Analyzing DSC Data

## Anatomy of a Peak



A DSC event peak typically contains the following components:

- **Baseline:** This is the expected signal (or change in signal) if no transition event occurs (e.g. if the enthalpy change of melting or  $H_{\text{fusion}}$  were zero). This is not always a flat line, as the specific heat capacity of a material is not guaranteed to be constant as temperature changes, or after a phase transition.
- **First Tangent Line:** This line is generated by an analytical program, (Proteus) and attempts to project a tangent along the most reasonable length of the phase transition's first peak. The criteria for "reasonable" in this scenario would be the longest length of approximately consistent slope.
- **Second Tangent Line:** Similar to the first tangent line, this is a projection along the second length of the peak using similar methods. This is also generated by an analytical program.
- **Onset:** The onset of a transition event is where the tangent line intersects the baseline. Users may want to use the first tangent line to look at the onset of a melting transition or use the second tangent line to look at the onset of a recrystallization event.
- **Endset:** The endset of an event occurs at the intersection of the tangent line with the baseline on the second half of a peak. Like the onset, users may choose the second tangent line to find the endset of a melting transition or the first tangent line to find the end point of a recrystallization event.

## Using Proteus

### Identifying Transition Events

Once a file is initially opened in Proteus the default display uses intervals of time on the x-axis and both temperature and signal along either y-axis. For the purposes of analyzing transition events users will find it much more useful to view the data using temperature as the x-axis. Before the axis can be altered users will need to split the segments, hide isothermal portions and, if needed, spline segments together.

To cut a measurement curve into segments, using Proteus, users will need to left-click on their curve of interest, causing it to turn white. Then, users will right click on the same curve to display a menu. From this menu select the “*Split Into Segments*” option. The curve should now be cut into multiple segments, of different colors, corresponding to each step in the programmed measurement. That is each segment corresponds to a dynamic or isothermal step according to the program used to gather the data.



Once a curve is broken into its various steps each segment or set of segments may be selected or hidden.

Right clicking on the background of the graph (the gray area) will open another menu allowing users to open the Segments window. This window will show a list of the various segments that the curve has been cut into. Selecting or deselecting the check boxes next to each segment will allow users to hide or portion.

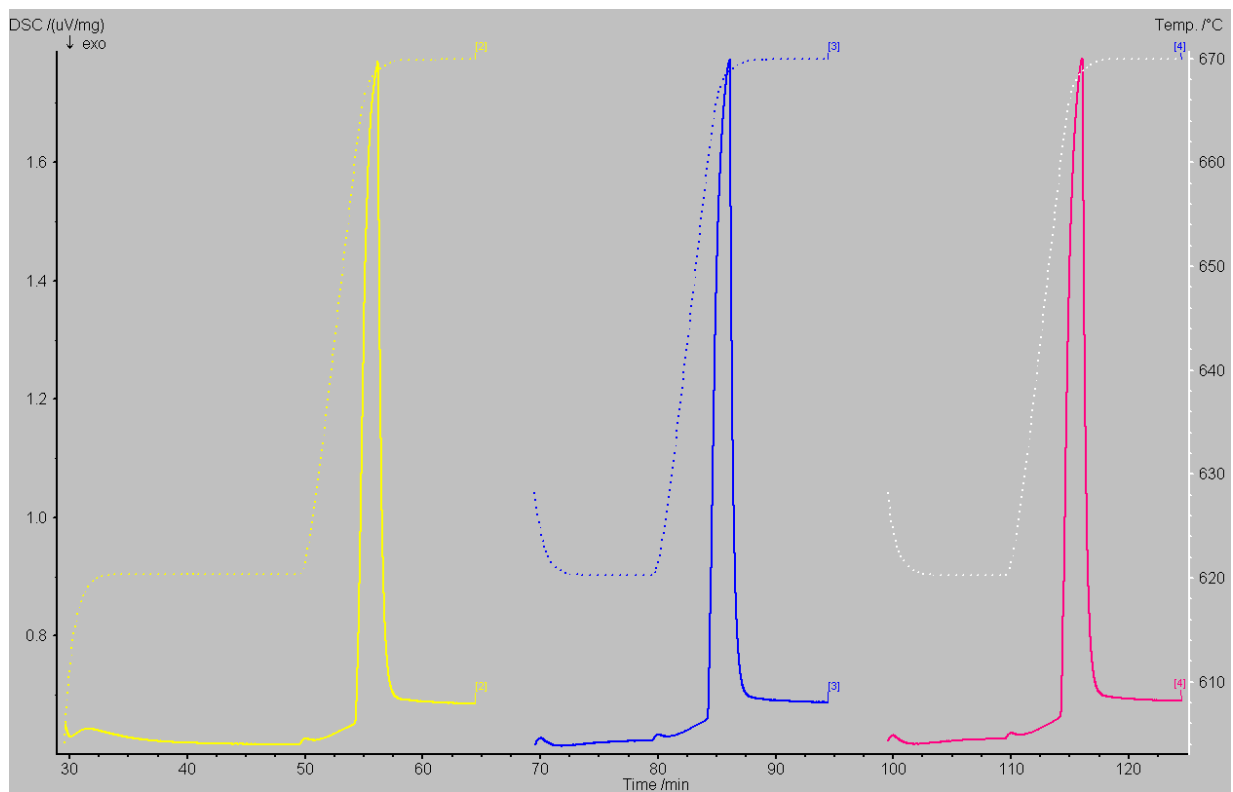
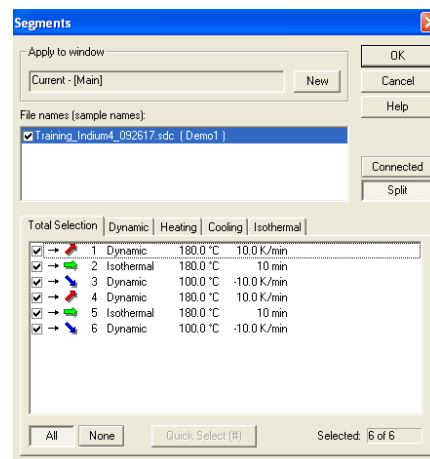
Generally if users are interested in looking at transition events they can uncheck the initial heating periods and any isothermal segments that do not contain portions of the relevant peaks. For transition events with peaks that spill over into two segments, the segment will needed to be splined.

## Splining Segments

In the Proteus analysis software, splining a set of segments will create a new line whose points include the data from the original segments. This new line can then be treated as a dynamic step and manipulated accordingly.

To spline your segments:

- Deselect any segments that you are not interested in so that they are hidden in the data display.
- Right click on any of the displayed segments to display a menu.
- Select “*Connect Segments Range (and spline)*” from the menu.
- A tool should appear at the top of the main display window, listing the segments you are about to connect. Continue connecting segments as needed.
- After deciding on each segment the connected lines should now be present with the original components hidden. The original line segments can always be restored by right clicking on the main background again and returning to the segments window.

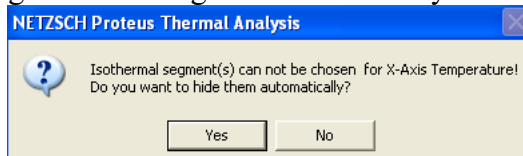


## Changing to a Temperature X-Axis

In the Proteus toolbar, at the top of the window, select the Temperature / time x-axis button. It should resemble a T / t with an arrow beneath it. The display will change the axis for you.



If isothermal segments are still present when selecting this button then users will be given a warning. Continuing through this warning will automatically hide any isothermal segments.



## Identifying the Event Onset Temperature

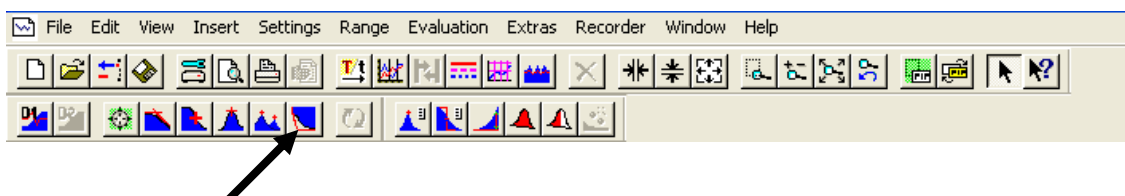
First select the segment you are interested in analyzing by left clicking on the curve. Once selected the curve should turn white. From the Proteus toolbar select the Onset icon. This will bring up two bounds on the main display as well as show the first derivative of your selected segment and add a second toolbar. The boundaries serve to identify which peak you want the software to analyze.



Drag the first bound to the left of the peak, making sure to include a sizeable portion of your baseline signal. Place the second boundary at the apex or maximum value of the peak and then select "Apply". The interpreted onset temperature should be automatically added to the main display screen.

## Identifying the Event Endset Temperature

Typically the event endset is more relevant to transition events that occur moving from a high temperature state to a lower temperature, such as recrystallization. Similar to the onset, a curve is selected and then the "Endset" button is selected from the toolbar. This time the left-side boundary is placed at the peak's maximum value and the right bound should include a portion of the apparent baseline. Selecting "Apply" will place the calculated temperature.

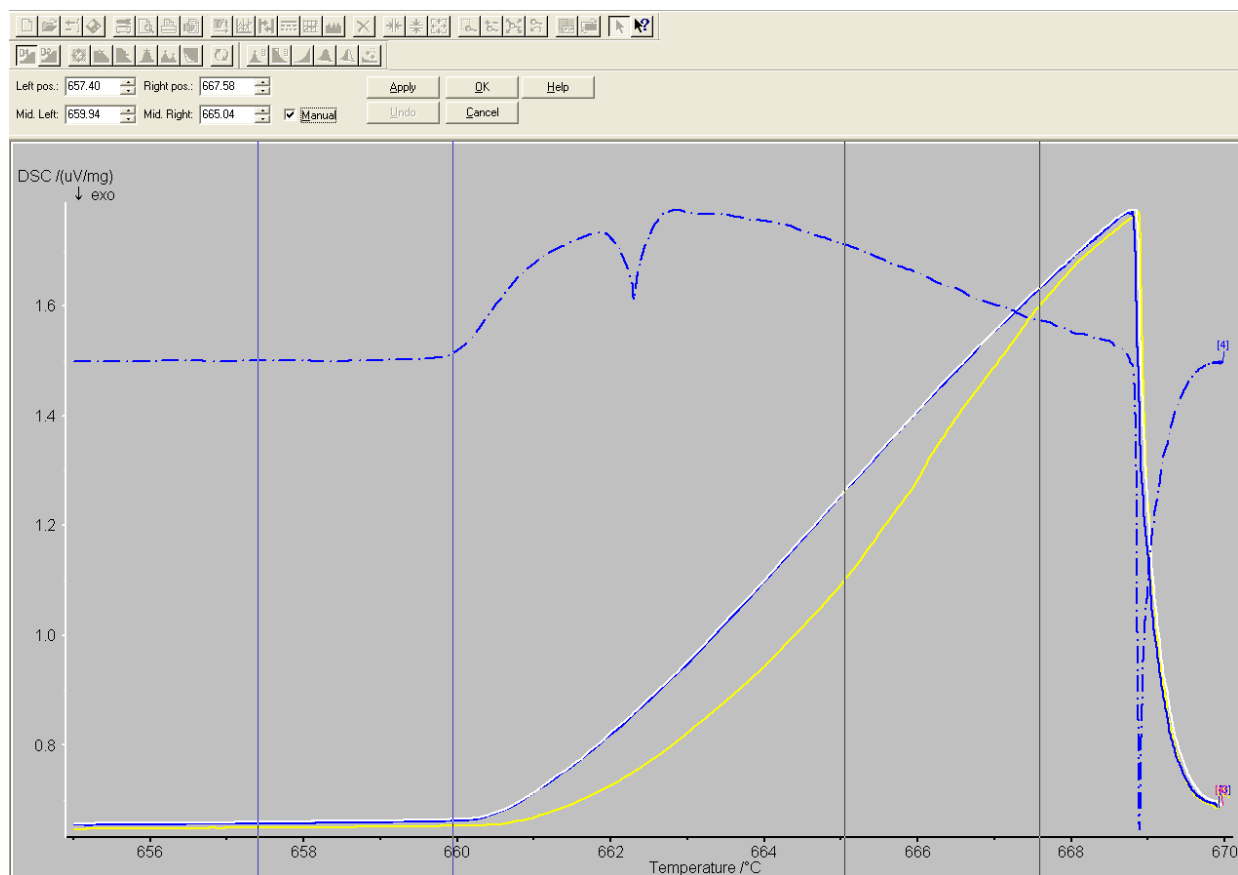


## Using Manual Select

The automated onset and endset tools are both susceptible to the inclusion of errors due to their algorithms. Users may find that they are able to obtain more accurate results using the manual option with both of these tools. To use the manual select, click the curve of interest and select the onset or endset tool of interest. In the toolbar that drops down check the box next to “Manual”.

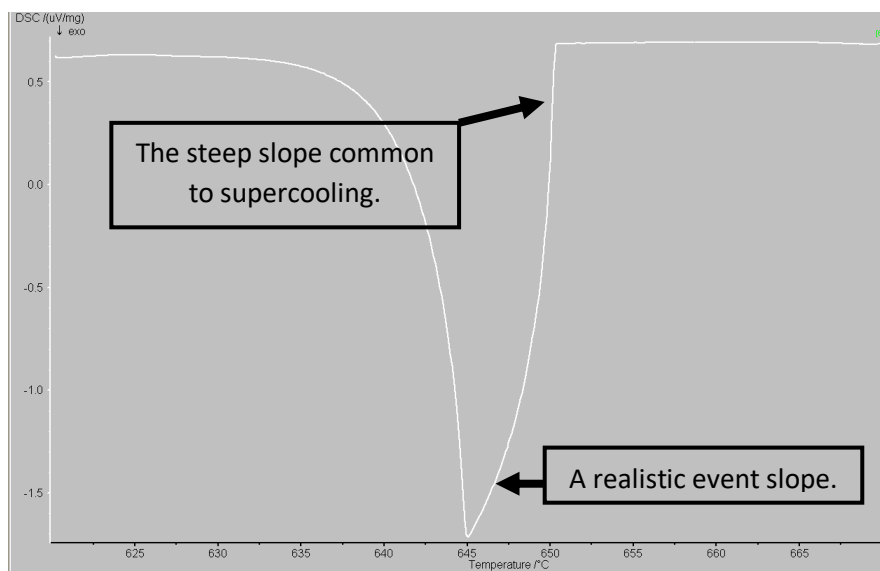


There should now be two set of bounds present on the display; a blue pair and a black pair. The blue bounds identify the portion of the curve that the software will use as the peak baseline. Ideally the user should highlight a region with a mostly consistent slope that is not too far from the peak. The black bounds are used to highlight the portion of the peak that would produce a tangent line most resembling the slope of the peak. Selecting apply will draw the new tangent line and give the event's temperature value.

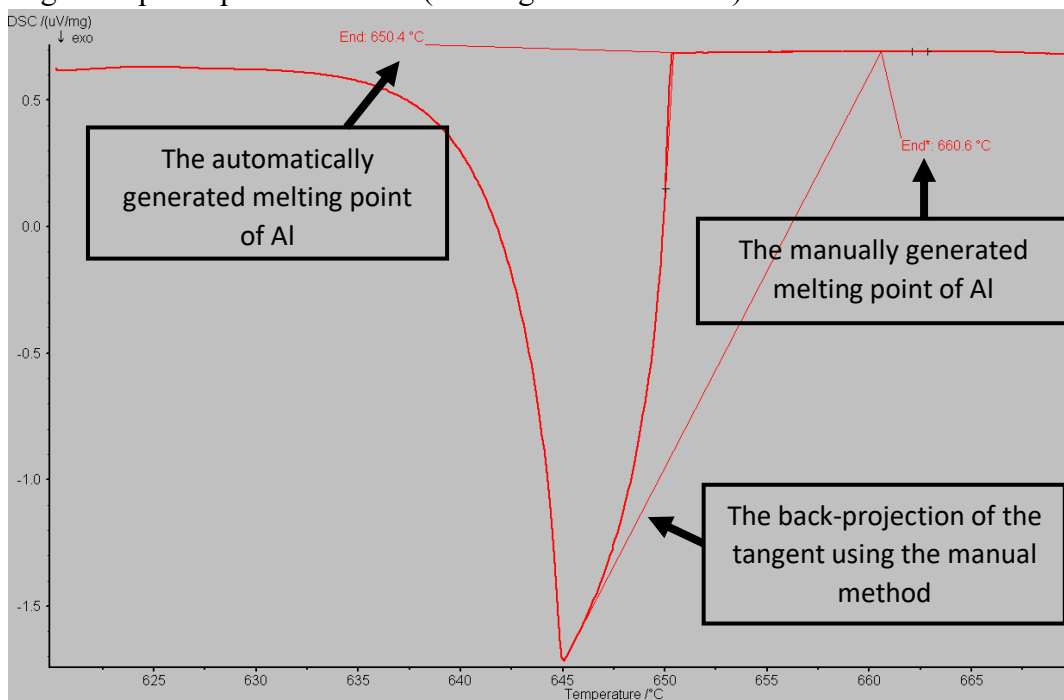


## Recrystallization Events

During recrystallization transitions it is common to see the sample demonstrate some level of supercooling. Because of the likelihood of such a phenomenon the determination of an endset temperature necessitates the use of the manual selection option. Supercooling may be identified by a sudden and sharply vertical slope on a recrystallization peak before shifting to a more reasonable value.



In this scenario the shallower region of the recrystallization peak should be used to generate a tangent line for the event. This will cause the software to project the line further back and provide a more accurate event temperature value. An example of this is given in the next image using a sample of pure aluminum (Melting Point 660.3 °C).



## Melting Point Peaks

Melting peak characteristics will vary in response to many variables. The melting points of pure materials are often characterized by an almost straight or linear line on the low temperature side of the peak. Impure or polymeric samples will display more concave sides and longer tails, while amorphous materials will display broader peaks due to size distribution of their internal structural components (i.e. crystal grains or polymer chains).

Peak width is also useful for data characterization. A pure crystalline material would be expected to have a sharp peak with a peak half-width range of 1-10 K. Polymers may demonstrate melting point peaks with half-widths of 10 K or broader.

### Multiple Melting Point Peaks

Samples may appear to indicate multiple melting points if other phase transition events occur within the measured temperature range. These may include phenomena such as glass transition points, Curie points or changes in crystallographic structure. A possible source of error may be sample dispersion. Samples which are not compacted or which contain air bubbles will appear to show multiple melting points. This is more likely to appear in powder samples and is often resolved after the first melting point measurement.

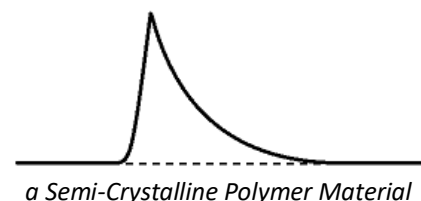
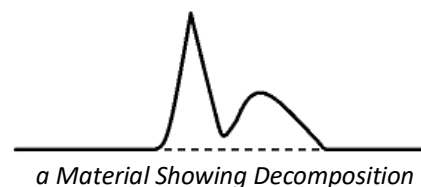
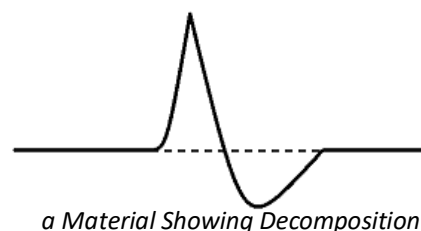
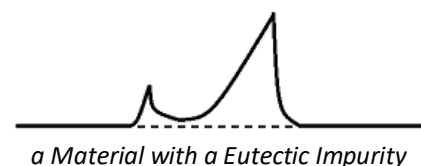
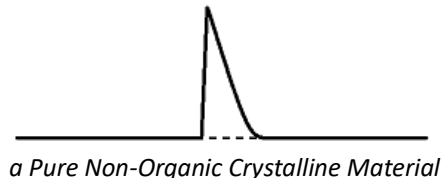
It is also possible that a sample may show two apparent melting point peaks during one run and not another. If two melting points are apparent in the first trial and not in succeeding measurements it may be indicative of the removal of an oxidative layer from the material. It is typical for most metals to hold an oxide layer on their surfaces but usually these would not be expected to be destroyed or greatly altered during melting.

Samples which did not originally demonstrate two melting peaks on their first trial but do so on their second and third measurements may be the result of two possibilities.

- 1. Oxidation:** Users should verify that the correct gas is connected, (Ultra High Purity Argon) and that the gas is flowing at the correct rate. After verifying this and checking that they have purged their sample chamber users considering a possible leak should contact a TEMPO employee for help.
- 2. Eutectic Formation:** Samples may be reacting with the crucible material to form a eutectic. This is highly likely to damage the instrument (and destroy the sample). Users should verify their samples will not react with their crucibles by consulting either the crucible selection guide located on Gauchospace or the appendix included in this manual.

After performing a measurement visual inspection of the sample may confirm if a

### Melting Point Peak Examples





eutectic is being formed. Samples may demonstrate discoloring or altered crystalline appearance. For eutectics, the appearance of multiple peaks should decrease as cycles continue and homogeneity is established however the final peak will be representative of the newly formed sample's properties and not the original materials.

## Polymorphism

Solid samples capable of existing in more than one form or crystal structure may produce two noticeable peaks (and onset points) during phase transitions. In this scenario the baseline used to interpret the first peak is also used on the second.

## Overlapping Peaks

If two events or peaks overlap a better resolution may be achieved by alternating heating rates during the measurement. Either higher or lower heating rates may be used. The measurement could also be rerun with a smaller quantity of sample.

## Recrystallization Point Peaks

Integration of recrystallization peaks should produce an area similar in size to the corresponding melting point peaks. Some differences may appear as a result of supercooling but the peak area should not deviate by more than 20%.

It is common for samples to show some level of **supercooling** effects during recrystallization. This is typically manifested by a difference between measured melting point and recrystallization. A reasonable range of disagreement would be 1-50 K. Substances that crystallize rapidly after nucleation would be expected to have a sharp and vertical peak before establishing a more gradual slope. Because of this supercooling effect users looking to establish a recrystallization point will need to project backwards from this shallower region.

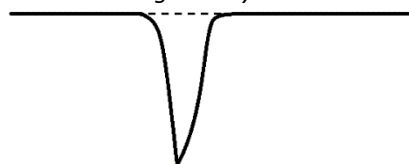
Materials that demonstrate **amorphous solidification** (i.e. form glasses on cooling) will not demonstrate easily noticeable peaks but instead will show a sudden change in specific heat capacity or shift in the baseline. Samples with eutectic impurities which solidify this way don't show their characteristic two peaks.

## Multiple Recrystallization Point Peaks

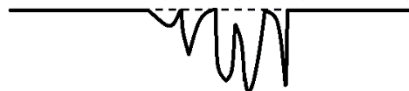
Samples that don't completely cover the crucible floor or which use small quantities of noble metals can form individual drops in their liquid phase. Each of these drops can exhibit different levels of supercooling, which form a series of smaller recrystallization peaks. The total area under these peaks should still approximately match the of the melting point. Measurements may benefit from rerunning the sample using more material or ensuring an evenly distributed layer

### Recrystallization Point Peak Examples

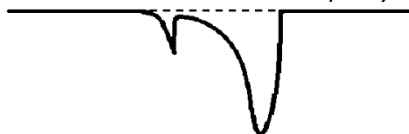
*a Pure Non-Organic Crystalline Material*



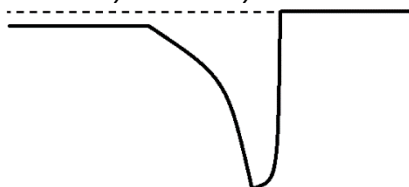
*a Material Showing Multiple Supercooling Effects*



*a Material with a Eutectic Impurity*



*a Semi-Crystalline Polymer Material*



across the crucible floor.

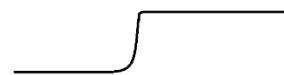
## Other Possible Peak Events

### Glass Transition Points ( $T_g$ )

The **glass transition point** is the temperature at which an amorphous material undergoes a transition from a brittle or hard state to a rubber-like viscous state. The transition is reversible and is known as **vitrification**. Measurements for glass transition points will typically follow two possible patterns.

1. **Glass Transition:** Peaks will show an abrupt and linear rise in signal before quickly leveling out.
2. **Glass Transition with Enthalpy Relaxation:** After the initial climb, the signal will drop again before leveling out. This is more commonly seen in samples that have been stored for a long period of time below the glass transition temperature. Samples undergoing repeated cycles should only show this event in the initial heating.

*a Glass Transition Event*



*a Glass Transition Event with Enthalpy Relaxation*



Transition events will typically occur over ranges of 10-30 K. Users suspecting that an event might be a glass transition point can verify this by using a furnace or other heating source to heat their samples to the event temperature and observing if the material has assumed a noticeable elastic, softened or liquid like quality. Users should not use the DSC to do this, as the furnace cannot be raised during a measurement or when the temperature exceeds 100 °C.

### Curie Transition Points ( $T_C$ )

Lambda transitions, or second order solid-solid transitions, can be difficult to detect on a DSC. Users looking to establish the temperature of a **ferromagnetic Curie transition** might find the TGA is capable of providing more exact data however the DSC may be of use for measurements looking to quickly find a temperature range at lower cost.

*a Curie Transition Event*



The Curie transition temperature ( $T_C$ ) is the temperature at which a permanent magnetic material loses its magnetic properties. The ordered magnetic moments found in ferromagnetic materials become disordered above the Curie temperature effectively terminating the net dipole.  $T_C$  peaks are usually slight and easily missed in data. Users should be careful to give a large buffer range when designing measurements to obtain the Curie temperature as artifacts may hide or alter the data.

# Ending Notes

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## Further Reading

For more information the TEMPO Gauchospace page on differential scanning calorimetry contains several useful documents, a quick reference guide and a guide to selecting the appropriate crucible type for your measurement. Users interested in using different operating parameters or using a different method are encouraged to speak with TEMPO staff.

Mettler-Toledo's website also contains a wealth of freely accessible documents and papers on thermal analysis principles and methods.

## Author Information

This manual was written by Burton Sickler, for the Materials Research Laboratory's TEMPO facilities; a MRSEC funded facility at the University of California, Santa Barbara. For questions, comments or to notify the author of errors please e-mail [bsickler@umail.ucsb.edu](mailto:bsickler@umail.ucsb.edu).