Netzsch 404C DSC User Guide

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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:

(ΔC_P) Specific Heat as a function of temperature;
(ΔH) 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.

Administrative

TEMPO Access & Safety Training

Users seeking to obtain access to the TEMPO facility are required to complete a suite of safety requirements which 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.

Once the TEMPO and MRL safety requirements have been completed users may request daytime access through the website "**https://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 - 5 PM. 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 **https://ucsb.fbs.io/**. After reserving a time slot, you may log in at the beginning of your scheduled slot. Starting the timer 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.

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

Self-training on the instrument is available, after speaking with TEMPO staff. Users choosing to self-train are given a sample and some parameters to perform a measurement on. For users 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 of 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 cooled down to at least 100 °C.**

All samples must be 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 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)"**

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

Process and Theory

Each measurement uses two lidded crucibles made from the same material and of approximately identical masses. One crucible serves as an empty and inert reference and the other holds the sample. The crucibles sit on separate sensors, connected by a thermocouple. When heated in a shared environment any difference in heating rates produces an electrical signal via the thermocouple which is captured by the instrument.

In theory the use of a pair of virtually identical crucibles shouldn't produce a signal as there would be no difference in heating between them but the presence of 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.

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 (Cp) 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 (μV). 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.

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

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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 800 °C could in fact be occurring at a temperature of 725 °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 a measurement 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-rhodium 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.

TEMPO sells Al_2O_3 crucibles for $11 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. It also prevents the exposure of the instrument's internals to any unintended volatility or decomposition. Optimal sample dimensions are 6 mm 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 x 1.0 mm thick.

Each crucible will have advantages and disadvantages. Users must research the appropriate crucible type for their samples. 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. 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.

Atmosphere for Tests

The DSC can work in several gases with argon as its default. The systems setup uses 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.

Sample Preparation

Samples must be tested for decomposition or volatility in the TGA prior to use and the data and results confirmed by a TEMPO staff member. 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 safeguards 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.

Sample Shape

Ideally samples are shaped as flat disks, powders or pellets; as long as the sample maintains good thermal contact with the crucible floor. Powders may undergo sintering during the heating process and then deform, losing crucible contact. Thin films may also display curling or curvature upon heating, causing a similar loss. A sample of minimal thickness and maximum flat surface area is desired.

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:

Thermal Phase Transitions:

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

Specific Heat Capacity (C_p):

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

Transition Enthalpy:

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

Quantitative Data of Phase Transitions:

- 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 high accuracy data should consider performing multiple exploratory runs and attempt to narrow the temperature range over which they measure.

A general form for phase transition measurements is to first ramp to a value at least 60 °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, to at least 60 °C beyond their expected melting point.

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 (or in steps) to allow for equilibrium in between. 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

Computer   404 C DSC Furnace   TASC 414/4 Controller   Power Unit
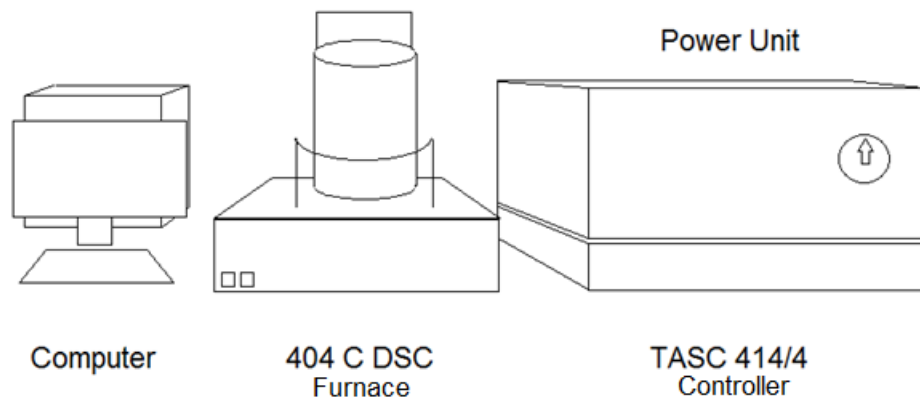
Instrument Components

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.

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

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 holds the reference crucible and the front holds the sample crucible. Each is placed in the center of its well and should sit flatly on the floor. The diameter of the sensor well is slightly larger than that of the crucibles so users should pay attention to positioning.

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 green wire guard in front of the sample chamber is there for users to steady their hands during placement.

For users performing quantitative measurements positioning of the crucible should be consistent throughout the series.
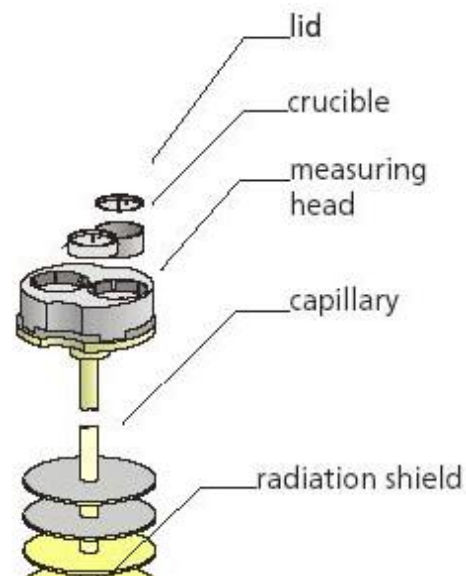
Evacuating and Backfilling Procedure

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 (**UHP**) argon as the Purge 1 gas and a dried air on Purge 2.

The vacuum pump has a line connecting to the right-back side of the DSC furnace unit and is fitted with a manometer, black handwheel and a small valve with a red lever. 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. Rotate the red lever until it is parallel to the tubing, as shown in the adjacent 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 will show the pressure decreasing. Note that the manometer is initially resting at a 0 reading.

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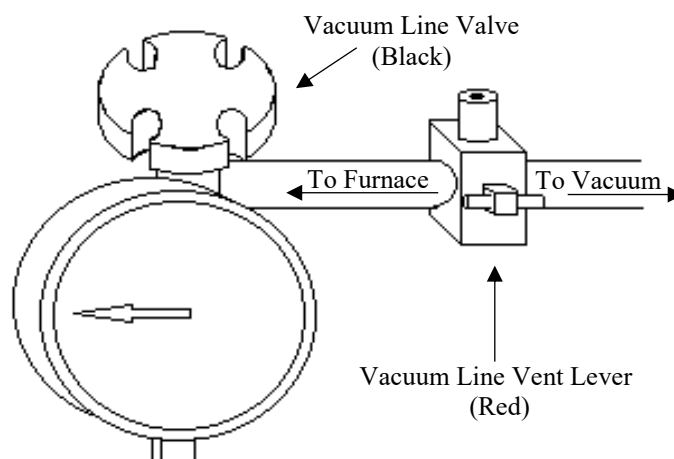
5. Allow the furnace to purge for approximately fifteen minutes. A red light should display on the front of the furnace at the vacuum panel which indicates when a vacuum has been established.

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.

Warning: 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 for instrument communication and measurements. Sample data and method programming are entered through this software. 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.

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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 differ by no more than 0.3 µV at the point of widest variation. If the difference exceeds 0.3 µV 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 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 cc/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 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 temperature calibration file should be chosen.

Temperature Calibration File

Multiple calibration files may be present, each attenuated to specific temperature ranges and testing conditions. For users measuring thermal events the default temperature calibration file (labeled Newest) will be appropriate. Users 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 unable to find an appropriate temperature calibration for the 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. Samples that are incompatible with alumina may be run in the Pt-Rh crucibles however these pans often alloy with the metal standards used to make the calibration files. Users will need to purchase alternative standards for use with the Pt-Rh pans.

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 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. Users planning on doing quantitative measurements should verify that an appropriate sensitivity file is already present. If a new sensitivity file is needed please speak with the MRL staff at least a week in advance of the 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		30.0					✓	☐	☐
2		500.0	10.00	0:47:00	10.00	1.00	✓	☐	☐
3		500.0		0:10:00	10.00		✓	☐	☐
4		700.0	2.50	1:20:00	60.00	24.00	✓	☐	☐
5		700.0		0:10:00	10.00		✓	☐	☐
6		710.0					✓	☐	☐
7		20.0	40.00	0:17:15			✓	☐	☐
8		20.0		2:00:00			✓	☐	☐

Conditions on Standby
✓ STC
☐ Purge1
☐ Purge2

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

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 **initial** step sets the temperature value that data begins recording at. Once the measurement program is started the instrument will attempt to reach this initial value but will not record any data until it stabilizes at that point. The lowest recommended starting temperature is 40 °C due to low heat limitations of the furnace heating element.

Initial Standby is an alternative to the initial step. This step allows users to instruct the furnace to heat to a given temperature and then hold that for a set of time prior to recording data. This performs similar to an unrecorded isothermal step but may be used to heat treat the sample prior to data recording. Either initial or initial standby may be used. Most measurements will use the initial step.

The **isothermal step** holds the sample chamber at its current temperature for a designated period of time. These are often used to allow the sample temperature to equilibrate before or

after a dynamic step. Preceding or following a dynamic step with isothermals of 10 to 15 minutes will increase measurement accuracy and reduce artifacts in the data.

Dynamic steps act as ramp rates or heating rates. A target temperature is selected, as well as a heating rate. Note 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 recommend. A faster rate may be set, such as 40 K/minute, for regions without interest. The instrument is capable of heating beyond 40 K/minute however this stresses the heating elements and may cause the sample chamber to overshoot the desired temperature. 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

In measurements that do not use corrections (baselines) there are often artifacts in the data at points where the furnace heating rate changes so users should set temperature programs with steady heating rates that go at least 40 °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 ± 5 K of the 40 °C standby temperature. This standby temperature is specified in your temperature program by the initial standby step.
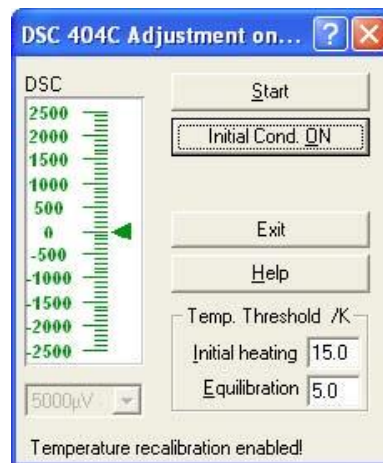
When ready users may select the start button to begin the measurement. After reaching the initial temperature and equilibrating the programmed measurement will begin and data points will be plotted on the screen as they are collected.

Measurement Conclusion

Once your measurement has finished, the data is automatically saved 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. Users can analyze their data in the Proteus software by double clicking the icon at the center of the desktop. Once open, data files can be selected using the *File* option, from the menu at the top of the screen or the folder icon in the toolbar.

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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 µV/mg. Notice the phase transition around 420°C.
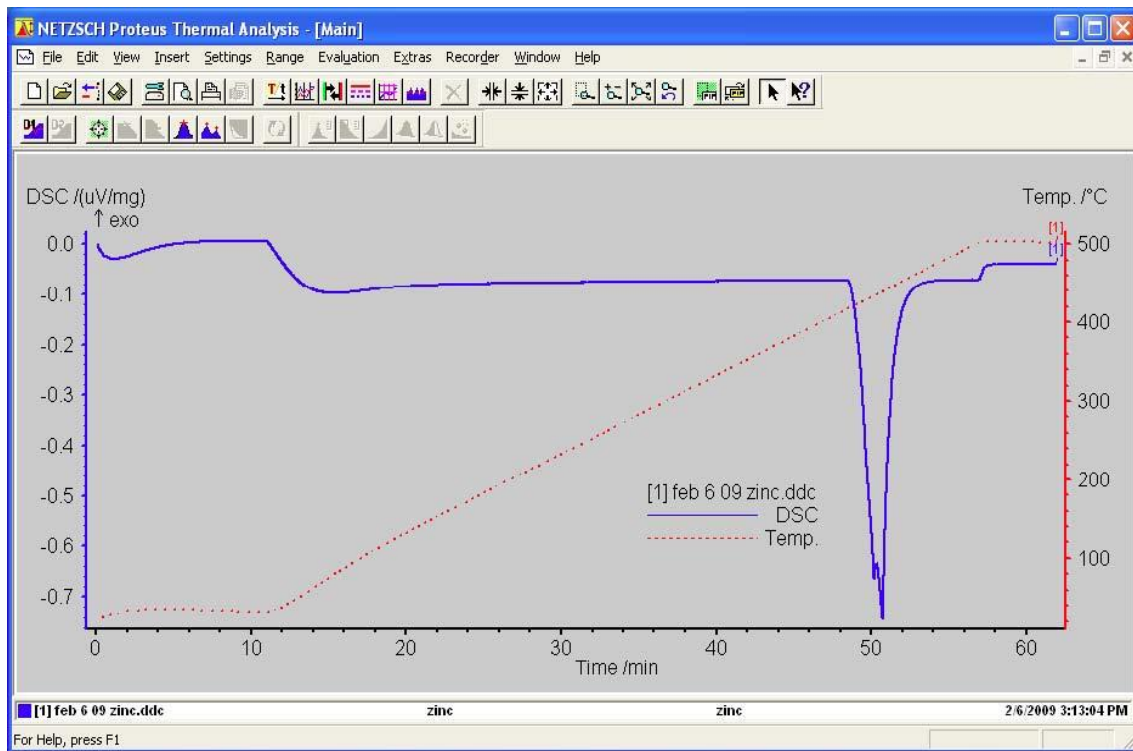
Curve Properties & Measurement Configuration

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.

Temperature X-Axis

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 [T↑] 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.

Hiding Line Segments

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. Alternatively they may right click a segment and select *Hide this segment*.

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.

Ending Notes

Further Reading

For more information the TEMPO Gauchospace page on differential scanning calorimetry contains several useful documents as well as the appendix to this guide. 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@ucsb.edu.

Interpreting DSC Data

TEMPO LABS, MATERIALS RESEARCH LABORATORY UCSB
Written by Burton Sickler

Interpreting DSC Data

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Interpreting DSC Data

Anatomy of a Peak
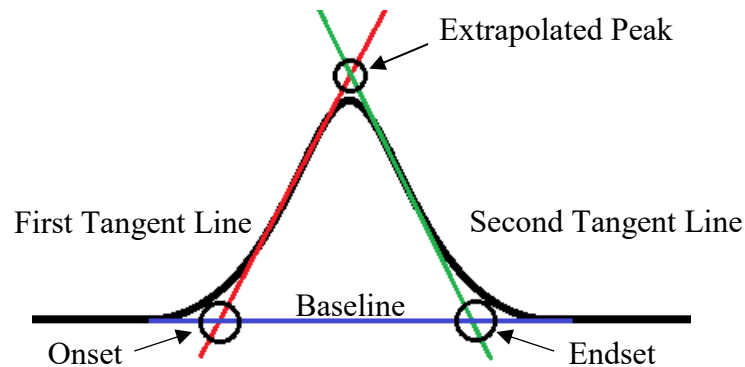
A DSC event peak typically contains the following components:

- **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_{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.

- **Peak Apex**: The location of the max peak value is subject to multiple variables. Its value is influenced by the thermal kinetics of the sample and the DSC system. The sample mass, shape, density, and crucible contact as well as the heating rate and gas environment will all impact at what temperature or time the phase transition will reach its maximum. As a result it is generally a poor indicator of a sample's properties.

Using Proteus

Identifying Transition Events

When a file is first opened in Proteus the default display use an x-axis of time and both temperature and signal along either y-axis. For the purposes of analyzing transition events users will find it useful to change the x-axis to temperature. This requires users will to first split the segments, hide isothermal portions and, if needed, spline segments together.

Interpreting DSC Data

Splitting a Curve into Segments

To cut a measurement curve into segments 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.
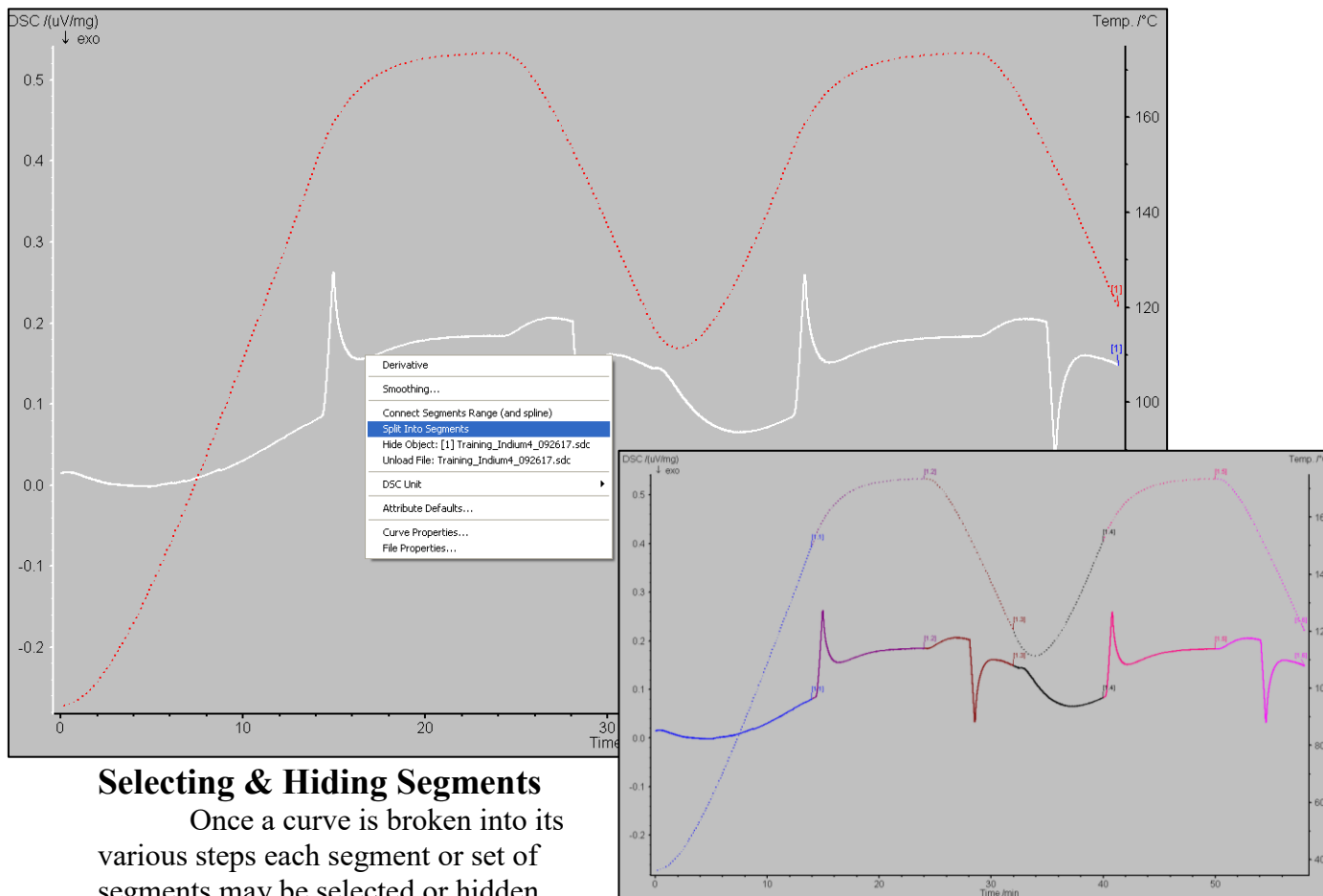
Selecting & Hiding Segments

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.

Interpreting DSC Data

Splining Segments

In the Proteus analysis software, splining a set of segments will create a new line who's 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.
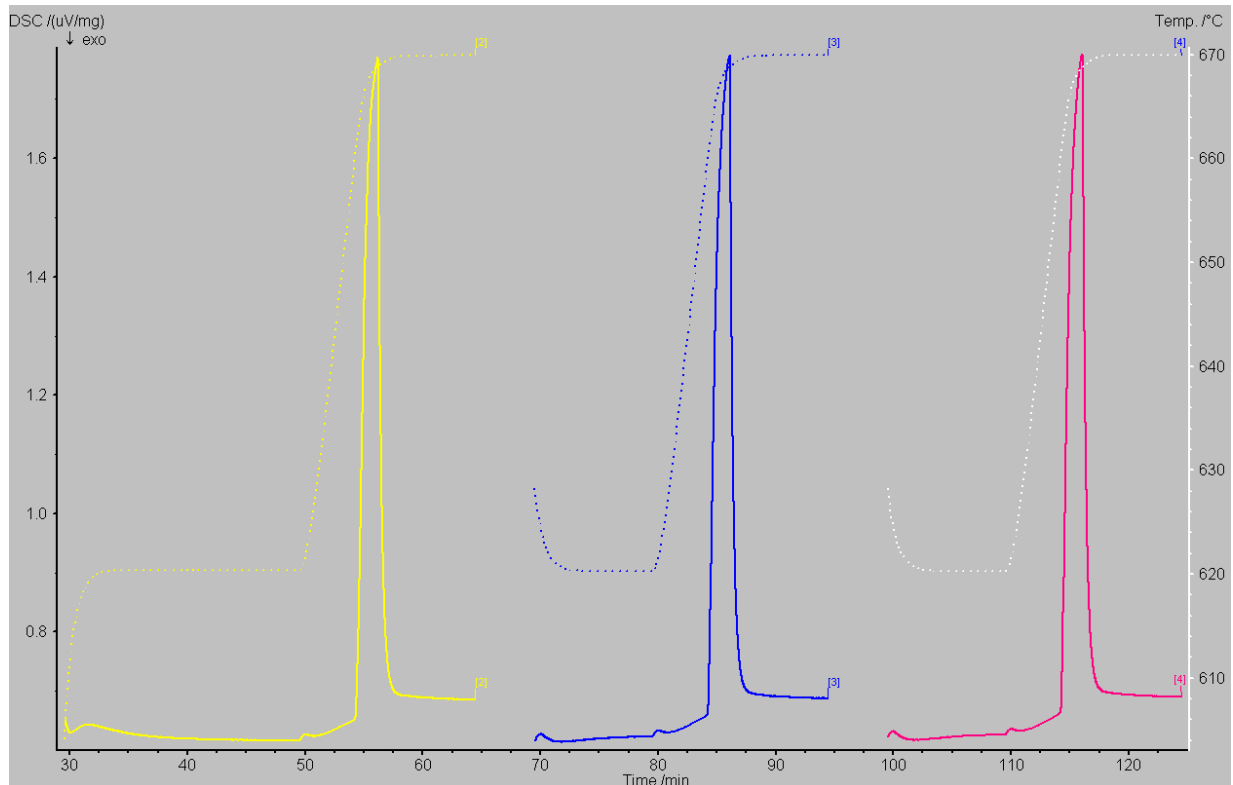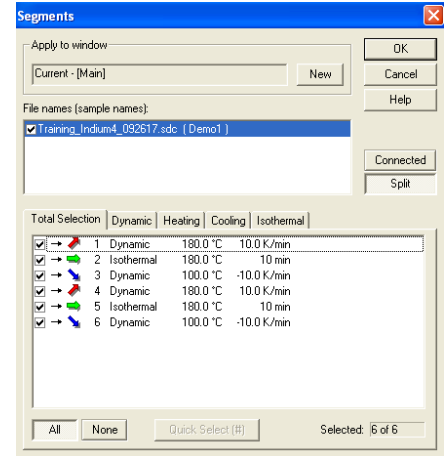
Interpreting DSC Data

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.

After selecting this button, if isothermal segments are still present, then users will be given a warning. Continuing through this warning will automatically hide any isothermal segments.
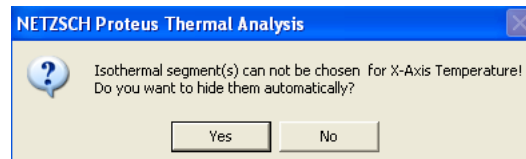
Identifying the Event Onset Temperature

First select the segment you are interested in analyzing by left clicking on the curve. Once selected thee 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

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.

Interpreting DSC Data

Using Manual Select

The automated onset and endset tools are both susceptible to the inclusion of errors. 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. 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.
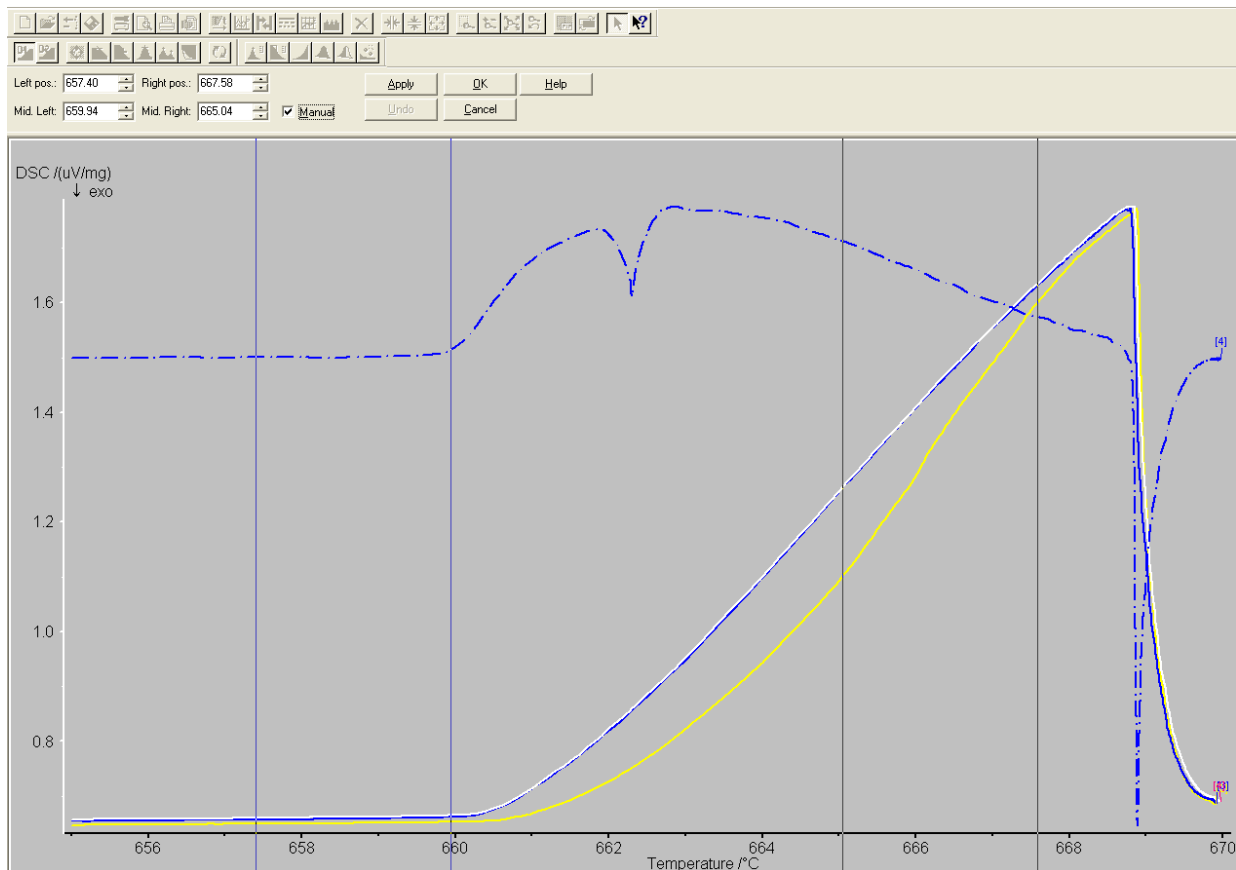
Interpreting DSC Data

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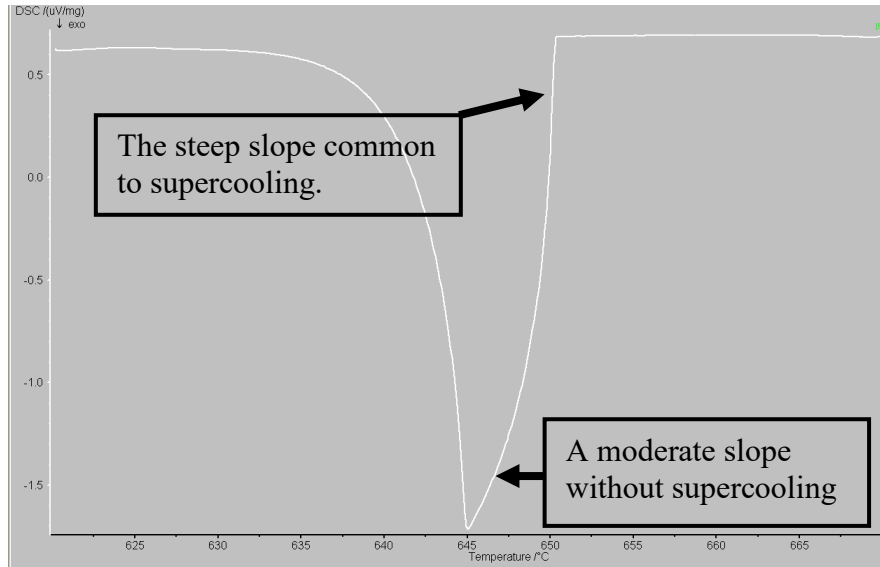
In this scenario the moderate slope region of the recrystallization peak should be used to generate a tangent line for the event. This will cause the software to project the line further back and provide a more accurate event temperature value. An example of this is given in the next image using a sample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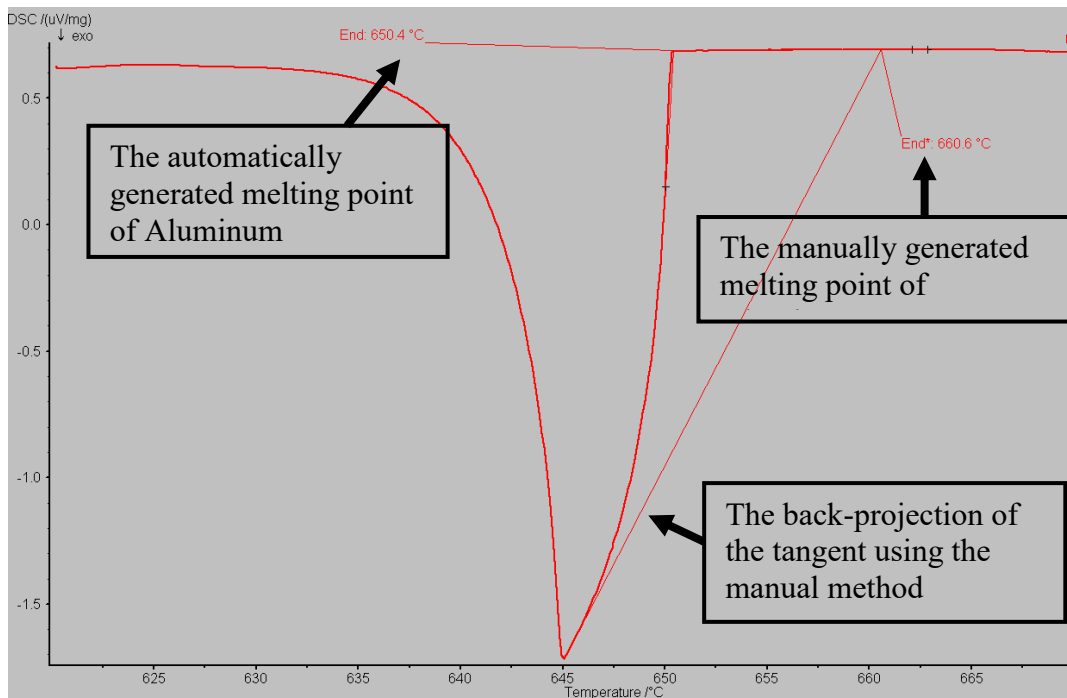
Interpreting DSC Data

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.

Melting Point Peak Examples
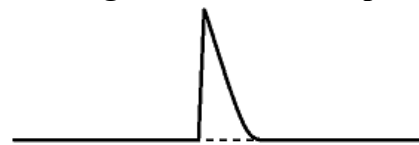
Pure Non-Organic Crystalline Material
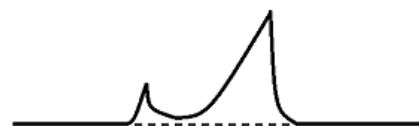
Signs of a Eutectic Impurity
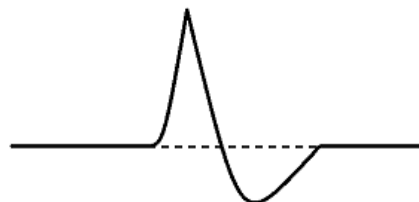
Signs of Possible Decomposition
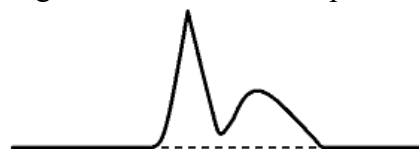
Signs of Possible Decomposition

Semi-Crystalline Polymer Material

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.

Interpreting DSC Data

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

Interpreting DSC Data

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 a region with more moderate slope.

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 and 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 even distribution across the crucible floor.

Recrystallization Point Peak Examples

a Pure Non-Organic Crystalline Material
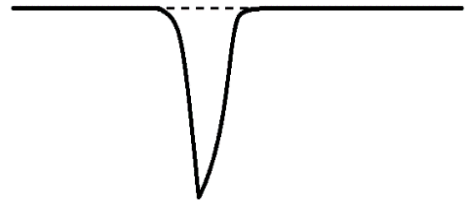
a Material Showing Multiple Supercooling Effects
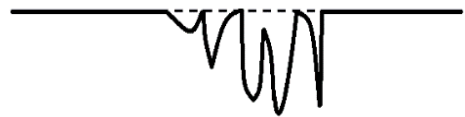
a Material with a Eutectic Impurity
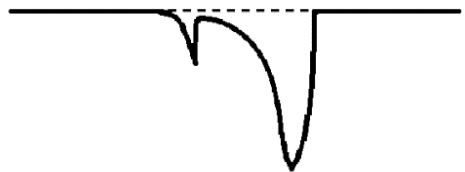
a Semi-Crystalline Polymer Material

10
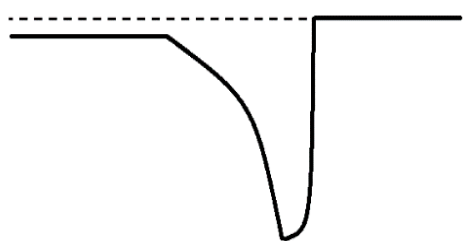
Interpreting DSC Data

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.

a Glass Transition Event

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.
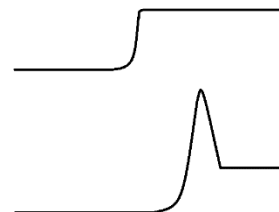
a Glass Transition Event with Enthalpy Relaxation

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.

Reporting the temperature of the glass transition is, to some degree, based on preference. No standard is currently established about which point along the curve is considered the official "temperature". Papers typically report either the onset, midpoint or endpoint temperature of the transition.

It is also important to note that the glass transition temperature will vary by instrumentation and technique. Measurement by means of a physical instrument, such as dynamic mechanical analysis (DMA) will often report a higher temperature than a DSC. This is due to the sensitivity of the detection method (mechanical versus electrical) and both measurements can be considered accurate and precise. Users reporting a glass transition temperature should also include the instrumentation and means of determining the temperature.

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.

404 C DSC "Pegasus" Quick Reference Guide

Power Unit

Computer   404 C DSC
            Furnace

TASC 414/4
Controller
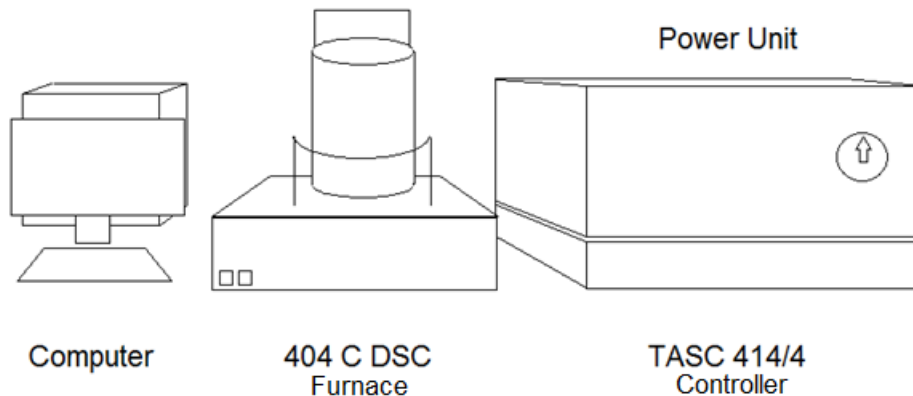
Powering on the instrument:

1. Each instrument component is powered on by a physical switch on their cases.
   a. The 404 C DSC switch is located on the left side at the back of the case.
   b. The TASC 414/4 switch is located on the right side at the back of the case.
   c. The power unit is controlled by a red dial on the front of the case. It must be rotated to on.
2. Allow the components a minimum of 15 minutes to warm up.
3. If you are planning to perform a measurement in a specialized environment then verify that the correct gas cylinder is connected to the instrument and that the cylinder valve is open.
4. Log into FBS and activate your reservation for the instrument to unlock computer use.

Note: The instrument will usually be powered on already.

Prepping your sample:

1. Each measurement requires two lidded crucibles of matching types. One will hold the sample and one will be empty and function as a reference. Both Al_2O_3 and Pt-Rh crucibles may be used. When choosing a crucible **make sure that your sample will not react with the crucible** type and that the crucible is appropriate for your measurement and temperature range.

2. It is generally wise to pre-heat a crucible to your desired maximum heat before using it in the DSC.

3. Take the mass of your sample crucible and reference crucible with their respective lids.

4. Take the mass of your sample. **All samples must be tested in the TGA for volatility or decomposition before they are used in the DSC**. Samples showing decomposition in their measurement temperature range cannot be run.

Note: Failure to use the correct crucible or adequately test for volatility could destroy the sensor head. The advisors of negligent users may be responsible for paying for the $8,000 replacement.
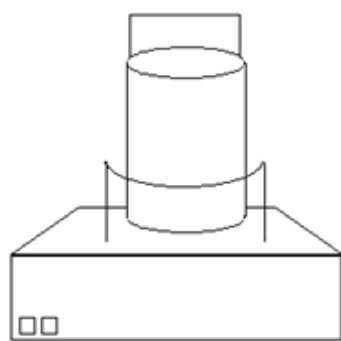
404 C DSC
Furnace

Loading your sample:

1. Open the DSC 404C software on the computer and verify that the DSC is at room temperature by looking at the status in the bottom right corner of the screen.
2. Verify that the "Vacuum" panel on the front of the furnace does not have a red led light on.
3. To open the furnace hold the safety button located on the right side panel of the furnace base and press the button with the upward arrow on the front of the furnace base. Both buttons must be pressed for the furnace to move.

Note: Do not open the furnace unless it is below 100 °C.

4. Once the furnace has raised an appropriate height use tweezers to gently place your crucibles on the sample holder.
   a. The reference crucible is placed in the back.
   b. The sample crucible is placed in the front.
5. You must be very gentle when placing the crucible on the sensor head as minor disturbances will affect the baseline. Use the green fencing around the furnace to stabilize your hands.
6. Ensure both crucibles sit flatly on the sensor and are generally in the center.
7. Lower the furnace by holding the safety and downward arrow buttons. **Visually inspect to make sure that the sample holder will not hit the furnace.** Once you have checked that it is clear, completely lower the furnace. Once fully lowered a green led will appear on the downward arrow on the front of the DSC.
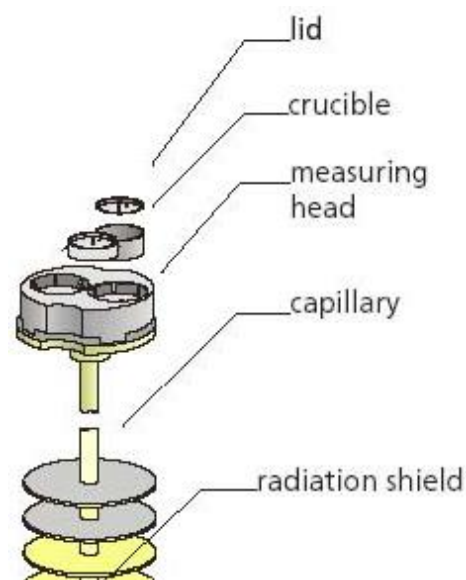
Purging the Furnace Chamber:

1. Check for a green LED on the downward arrow on the front of the DSC furnace base to make sure the furnace is fully lowered.
2. Check the front of the furnace base for the absence of green LED indicator lights on the purge 1 and 2 buttons. No gas should be flowing.
3. On top of the furnace, **above the sample chamber**, turn the arrow shaped black lever to the right to close the sample chamber vent.
4. Turn on the red vacuum pump located on the shelf above the DSC.

Vacuum Line Valve (Black)

To Furnace   To Vacuum

Vacuum Line Vent Lever (Red)

5. 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 diagram to the right. This closes the vacuum line.

6. Slowly open the vacuum line valve by rotating the hand wheel. Opening the valve rapidly may displace the crucibles in the furnace. The manometer should show the pressure decreasing.

7. Allow the furnace to purge for approximately fifteen minutes. A red light should display on the front of the furnace indicating when a vacuum is established.

8. 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.

9. On the front of the module press the button for the purge gas you intend to use.

10. Allow the furnace some time to backfill, but watch the pressure using the manometer at the back of the DSC. Once atmospheric pressure has been reached open the exhaust valve on the top of the furnace sample chamber. The black arrow should be pointing away from you. This process should generally be repeated three times to ensure an oxygen-poor environment.
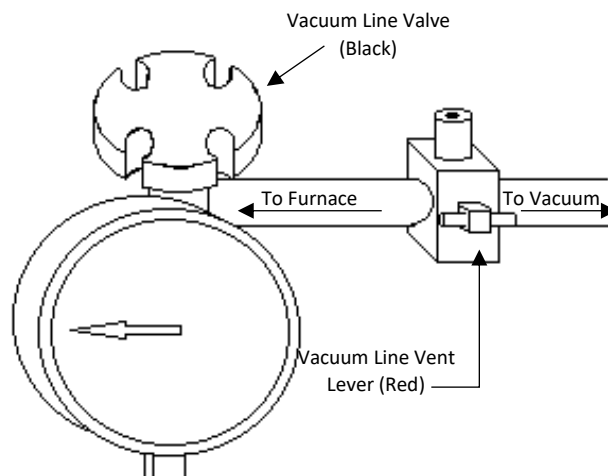
Note: The exhaust valve on the top of the furnace must be open when performing a measurement.

Running a Measurement:

1. Open the DSC 404C software on the DSC computer. The icon is located on the desktop.
2. At the top of the software select the *File* tab and from the drop-down menu select *New*.

3. In the Measurement Header window that appears enter the relevant information for your measurement. This will include
   a. Your sample identity
   b. Your sample crucible and lid mass
   c. Your sample mass if you are running a sample or standard
   d. The reference crucible mass
4. Confirm that the Crucible Type is correct for your crucible and then select *Continue*
5. Select the most recent calibration file and then select *Continue*.
6. Select a sensitivity file. The sensitivity calibration file must match your experimental parameters including heating rate, gas atmosphere and crucible type. If you are performing a measurement for phase transition data select *senzero* and then *Continue*.
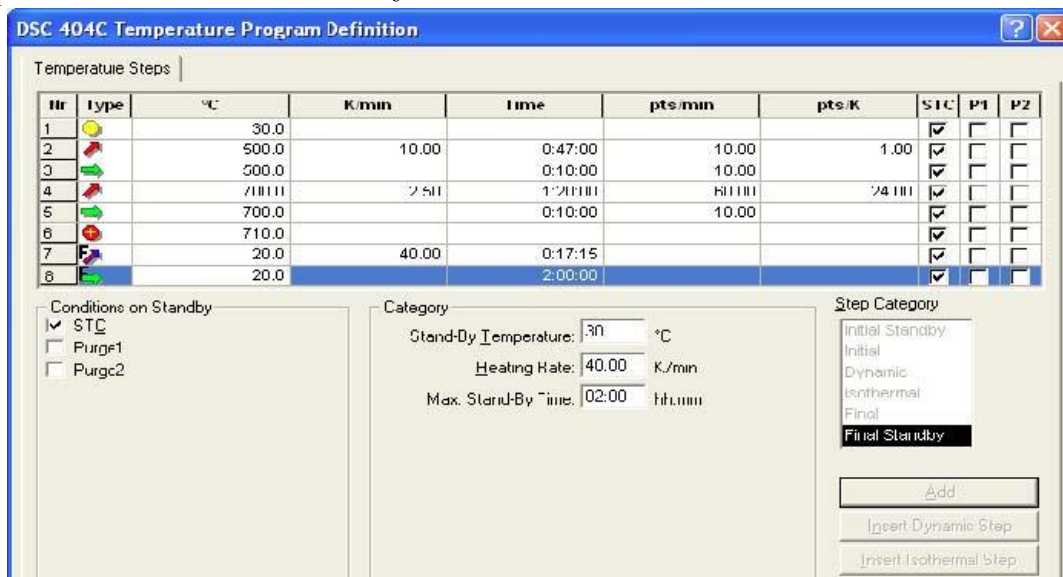
7. Design your temperature program. During this time you will set
   a. Your heating rate
   b. Your data acquisition rate
   c. The gas type for your experiment
8. When complete select *Continue*.
9. Name the data file and select where your data will be saved.
10. In the following window you may select *Initial Cond. ON* to instruct the furnace to begin heating to your start temperature. Once it reaches the starting temperature the system will attempt to equilibrate.
11. Before starting, **visually confirm that the vent on top of the furnace sample chamber is open and the arrow is pointing toward the back of the instrument**.
12. Press *Start* to begin the measurement.
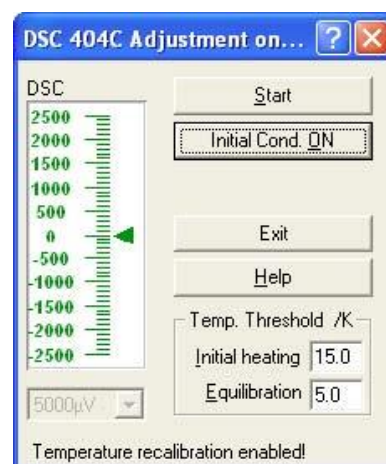
Chemical Behavior of Platinum, Aluminum Oxide and Graphite Crucibles

The following are critical for **PLATINUM**:
- halogens (Cl_2, F_2, Br_2), aqua regia
- Li_2CO_3, prior to emission of CO_2
- SiC from approx. 1000°C
- PbO, $FeCl_3$
- Be alloys (begin to evaporate just above the melting point)
- HCl with oxidation agents (e.g. chromic acid, manganates, iron(III) salts, molten salts)
- reducing atmospheres
- Pb, Zn, metalls such as Pb, Zn, Sn, Ag, Au, Hg, Li, Na, K, Sb, Bi, Ni, Fe, steel, As, Si
- Se above 320°C (immediate cooling and removal of the sample at the end of the measurement recommended to prevent evaporation of selenium)
- metal oxides with reducing substances such as C, organic compounds or H_2
- oxide in an inert gas atmosphere at higher temperatures (reduction)
- sulfur → roughening the surface
- alkali hydroxides, alkali carbonates, alkali sulfates, alkali cyanides and alkali rhodanides at higher temperatures
- $KHSO_4$ at higher temperatures
- carbon black or free carbon above 1000°C
- SiO_2 under reducing conditions
- SiC and Si_3N_4 at temperatures above 100°C (release of elementary Si)
- HBr, KCN solution at higher temperatures
- high-temperature resistant oxides above 1000°C

no resistance to:
- mixtures of KNO_3 and NaOH at 700°C under exclusion of air
- mixtures of KOH and K_2S at 700°C under exclusion of air
- LiCl at 600°C
- Na_2O_2 at 500°C under exclusion of air
- $MgCl_2$, $Ba(NO_3)_2$ at 700°C
- HBr, HJ, H_2O_2 (30%) and HNO_3 at 100°C
- KCl (the decomposition products which form during melting are damaging, melting point: 768°C)

limited resistance to:
- KHF_2, LiF, NaCl at 900°C
- mixtures of NaOH and $NaNO_3$ at 700°C under exclusion of air

The following are critical for **ALUMINUM OXIDE**:
- N_2 in the presence of carbon: formation of AlN, therefore it is dangerous to measure carbon black at higher temperatures in a nitrogen atmosphere
- F_2: formation of AlF_3 and O_2
- Cl_2: formation of $AlCl_3$ above 700°C
- sulfur: no reaction with liquid sulfur, in the presence of carbon in the gas phase, formation of sulfides at higher temperatures
- H_2S: formation of up to 3% Al_2S_3 when heated
- C: formation of carbides and Al from approx. 1400°C
- HF: quantitative reaction to AlF_3 and H_2O at higher temperatures
- $CuSO_4$: diffusion through the bottom of the crucible from approx. 1000°C
- compounds containing silicium, e.g. $MoSi_2$: contamination of Al_2O_3 from approx. 1200°C in inert gas; reactions at the contact points in air atmosphere
- metal fluorides: attack by the melt, formation of $[AlF_6]^3$ anions and salts similar to cryolites
- SiO_2 glass: glass melts dissolve Al_2O_3
- hydrogen sulfates of alkaline metals and alkaline-earth metals
- HCl: no reaction to 600°C, increased reaction in the presence of carbon at higher temperatures
- B_2O_3 or Borax: melt dissolves Al_2O_3, formation of aluminum borates and aluminum borides
- alkaline and alkaline-earth oxides and their salts with volatile anions: melts form aluminates or double oxides, important, for example, for hydroxides, nitrides, nitrates, carbonates, peroxides, etc.
- CaC_2: formation of Al_4C_3 when heated
- PbO: reaction from 700°C, also important for higher lead oxides and lead salts with anions of volatile acids
- UO_3: reaction begins at 450°C, analogous to PbO
- $Me^{II}O$: Me = Fe^{2+}, Cu^{2+}, Ni^{2+}, etc., formation of spinels; CaO above approx. 1200°C
- alkaline and alkaline-earth ferrites: melt dissolves Al_2O_3
  -zirconium alloys with melting range between 800°C and 1200°C: slow, weak reaction
- titanium alloys (very high oxygen affinity)
- reaction with iron-nickel and magnesium alloys possible at higher temperatures

The following are critical for **GRAPHITE**:
- O_2, reaction above 400°C
- molten metals, such as Fe, Co, Ni, Na
- N_2, reaction from 1700°C (formation of small amounts of cyanides)
- oxides (probable reduction upon direct contact)
- water vapor
- F_2, Br_2 at room temperature
- sulfur
- Si at approx. 1400°C (formation of SiC)
- chromic acid (aqueous)
- chlorosulfonic acid $ClSO_3H$

- SiO_2 →formation of SiC via intermediate product SiO (technical production of SiC above 1800°C; i.e. the reaction between SiO_2 and C definitely begins at lower temperatures)
- nitrous gases (NO, NO_2)
- sulfuric acid, H_2SO_4, concentrated at approx. 150°C, fuming H_2SO_4 at room temperature
- nitric acid, HNO_3, diluted at approx. 90°C, fuming HNO_3 at room temperature
- SO_3, from approx. 100°C
- danger of explosion with perchloric acid, $HClO_4$
- NaOCl, from approx. 50°C

No claim is made that this overview is exhaustive.
The temperatures given are primarily literature values. Therefore, the temperatures can shift to lower values under experimental conditions. In any case, it is advisable to run tests in separate furnaces.

Compatibility of Calibration Substances with Various Crucible Materials

The table below corresponds to our most current information. No claim is made that it is exhaustive. The user should regard it only as a guide.

Because this is a compilation of data from the literature (H. K. Cammenga et al., Thermochimica Acta, 219, 1993) and from our own experience, it is not possible to cover all possible combina-tions and measurement conditions. In case of doubt, it is advisable to run preliminary tests in a separate furnace. For platinum crucibles with Al_2O_3 inliners, basically the same data like for corundum crucibles applies. The only exception is nickel as a calibration substance. The melting point of nickel with 1455°C is above the recommended maximum working temperature for Pt crucibles on a type S sample carrier.

Crucible Material	Calibration Substance																				
	Cyclopentane	Water	Gallium	Indium	Tin	Lead	Zinc	Lithium Sulfate[2]	Aluminum	Silver[3]	Gold[3]	Barium Carbonate[2]	Potassium Perchlorate[2]	Potassium Chromate[2]	Silver Sulfate[2]	Rubidium Nitrate[2]	Nickel	Bismuth	Cyclohexane	Cesium Chloride[2]	Mercury
Corundum (Al_2O_3)	–	–	+	+	+	+	+	+	+	+	+	+	+	+	+	+	!	+	–	+	+
Graphite	–	–	+	+	+	+	+	+	+	+	–	?	?	?	?	?	–	?	–	?	?
Fused Silica	+	+	+	+	+	+	+	+	–	+	+	–	?	?	?	?	–	?	?	?	+
Aluminum[1]	+	+	–	+	+	+	+	+	–	–	–	–	+	–	+	+	–	+	+	+	+
Silver	+	+	–	–	–	–	–	?	–	–	–	–	+	+	?	+	–	–	?	+	–
Gold	+	+	!	!	–	–	–	+	–	–	–	?	+	?	?	+	–	–	?	+	–
Stainless Steel	+	+	!	+	!	+	–	?	–	–	–	–	?	–	–	?	–	+	?	+	+
Platinum	+	+	!	!	–	–	–	+	–	–	–	+	+	+	+	+	–	–	?	+	–
Tungsten	–	–	!	?	?	!	+	?	!	+	+	?	?	?	?	?	?	+	?	?	+

+	No solubility or effect on the melting temperature to be expected.
!	Corrosion processes possible with negligible changes in the melting temperature.
–	• Crucible melts. • Melt or transformation product reacts with the crucible material, resulting in greater changes n the melting temperature. • Combination not practicable.
?	Compatibility unknown.

[1] In air, aluminum forms a thin oxide layer on the surface, which improves the corrosion resistance of the metal. Similar is true for tungsten.
[2] Solid-solid transformation.
[3] Gold and Silvery stick in Al_2O_3 crucibles, but can normally be removed mechanically.

DSC Applications

Property	Method
Specific Heat Capacity as a function of time, $C_p(t)$	Specific heat capacity (C_p)
Enthalpy-temperature function	Enthalpy (ΔH)
Enthalpy changes, enthalpy of conversion	Integration
Enthalpy of fusion, crystallinity, (ΔH_{fus})	Integration, crystallinity
Melting Behavior (liquid content, liquid fraction)	Integration (partial areas), Conversion
Melting point, solidus and liquidus point, (T_M)	Onset, Purity and Integration
Melting point of semi-crystalline plastics, (T_M)	Peak, Integration
Purity of non-crystalline plastics	Purity
Melting point of the pure substance, (T_M)	Purity
Crystallization behavior, degree of crystallinity and supercooling	Onset, Integration and Conversion
Solid-Solid transition, polymorphism	Integration, Onset and Conversion
Vaporization, Sublimation and Desorption	Integration and Conversion
Boiling Point, (T_B)	Peak, Onset and Integration
Glass transition, amorphous softening, (T_G)	Glass Transition (T_G)
Curie temperature, temperature of a lambda transition, (T_C)	Peak and Integration
Thermal decomposition, pyrolysis, depolymerization	Integration, Onset and Kinetics
Temperature Stability	Onset, Integration and Kinetics
Chemical Reactions	Integration and Kinetics
Reaction Enthalpy, (ΔH_{rxn})	Integration
Oxidative degradation, oxidation stability, oxidation induction time	Onset
Content Determination	Content

NETZSCH

Software Manual

DSC Instruments

Temperature and Sensitivity Calibration

www.netzsch-thermal-analysis.com

To be explained:

- *Measurement of the calibration substances*

- *Evaluation of the measurements*

- *Creation of a temperature/sensitivity calibration file*

Please note the following additional information for the calibration procedure:

- The measurement conditions (e.g. heating rate, gases, type of crucible) for the calibration measurement and the subsequent sample measurement must be the same.
- Use an empty crucible for the reference position.
- Note all information for using the calibration substances in the provided documentation.

Melting point standards

Can be used for Al2O3 crucibles and Pt crucibles with Al2O3 liners; C10H16, In, Sn, Bi, Zn also for aluminum crucibles.

Adamantane (C10H16) → for the low temperature range

Indium (In) → most accurate value

Tin (Sn)

Bismut (Bi)

Zinc (Zn)

Aluminum (Al)

Silver (Ag) → melting point depends on oxygen partial pressure

Gold (Au) → very accurate value

For the low temperature range use C10H16, In, Sn, Bi, Zn.

Al, Ag and Au are not applicable to low temperature furnaces.
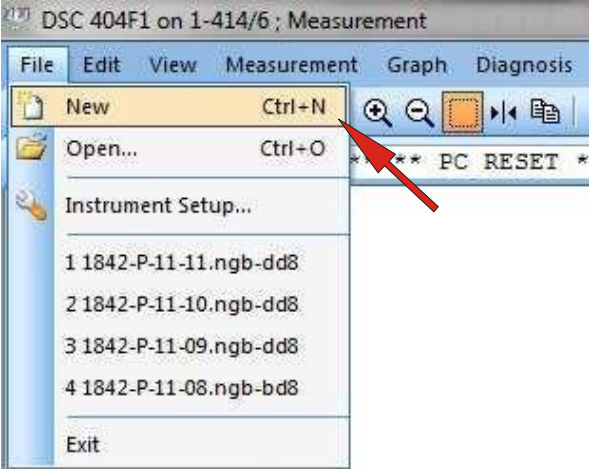
Standards showing polymorphic transitions

Can be used for Pt crucibles; RbNO3, KNO3, KClO4, Ag2SO4 and CsCl also for aluminum crucibles.

Rubidium nitrate (RbNO3) → only for temperature calibration and one heating step
(not useable for 2nd and 3rd heating)

Potassium nitrate (KNO3) → only for one heating step
(not useable for 2nd and 3rd heating)

Potassium perchlorate (KClO4) → only for one heating step
(not useable for 2nd and 3rd heating)

Silver sulphate (Ag2SO4) → only for one heating step
(not useable for 2nd and 3rd heating)

Cesium chloride (CsCl)

Potassium chromate (K2CrO4) → not applicable to low temperature furnaces

Barium carbonate (BaCO3) → not applicable to low temperature furnaces

Strontium carbonate (SrCO3) → not applicable to low temperature furnaces

1. Measurement of the Calibration Substances

	1. Open the NETZSCH-Proteus group.
	2. Select the instrument (e.g. DSC 404 F1).
	3. Select **New** in the **File** menu.

4. **Measurement Definition**

   Setup

   - Check the instrument setup.

     The values of the different properties must be checked and changed (if necessary).

   - Click **Forward**.

5. **Measurement Definition Header**

   - Select Measurement Type **Sample**.

     Optionally:
     Define **Laboratory**, **Project**, **Operator**, **Date** and **Material**.

     Define **Identity**, **Name** and enter the **sample mass**.

   - Set the checkmark **will not be used** for temperature calibration and also for sensitivity calibration.

   - Define the gas for **Purge 1**, **Purge 2** and **Protective**.

   - Click **Forward**.
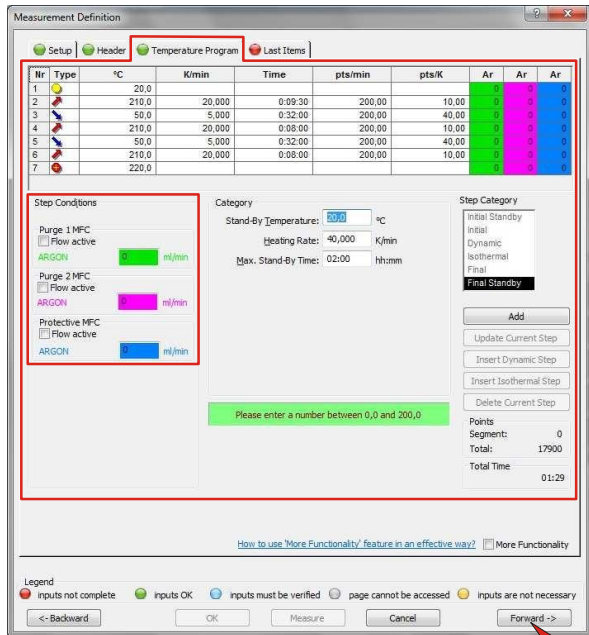
6. **Measurement Definition Temperature Program**

- Enter the temperature program for the first calibration substance.

  e.g. Indium (melting point 156.6°C)

  Carry out a measurement with 3 sequential heating segments up to 260°C and 2 cooling segments down to 50°C (see figure below). For the evaluation afterwards use only the peak from the 2nd and 3rd heating. See also all additional information on page 6 for a detailed description of the temperature program for each standard!
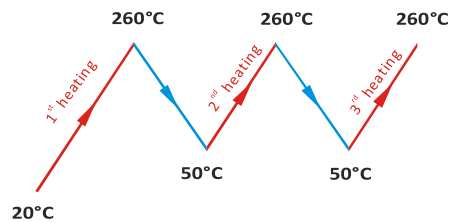
- Define the gas flow for purge and protective (e.g. purge 50 ml/min, protective 20 ml/min).

- Click **Forward**.

Heating rate: depending on the application
(e.g. 20 K/min)
Acquisition rate: 100 Points/min
Cooling rate: select a practicable cooling rate
(depending on the instrument)
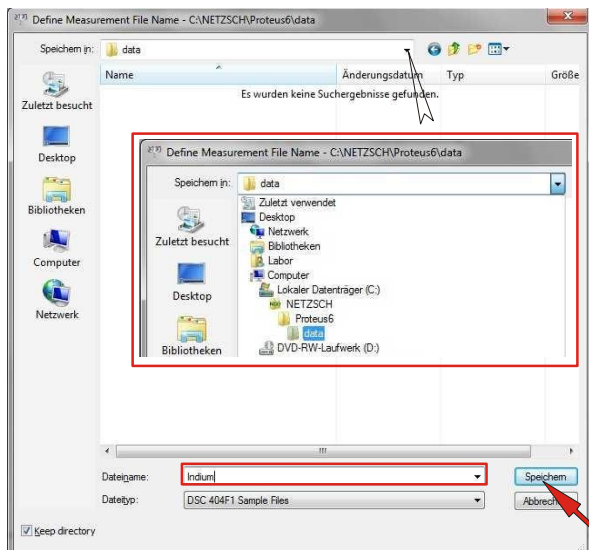
7. Define folder and file name and save the measurement.
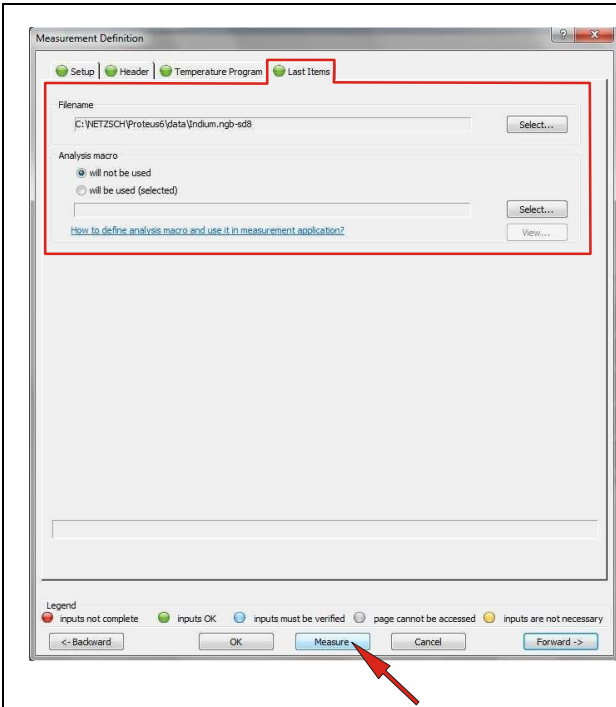
8. **Measurement Definition**

   Last Items

   - The previously selected folder and filename is shown in the window (to change folder and filename once again click the **Select** button).

   - Click **Measure**.
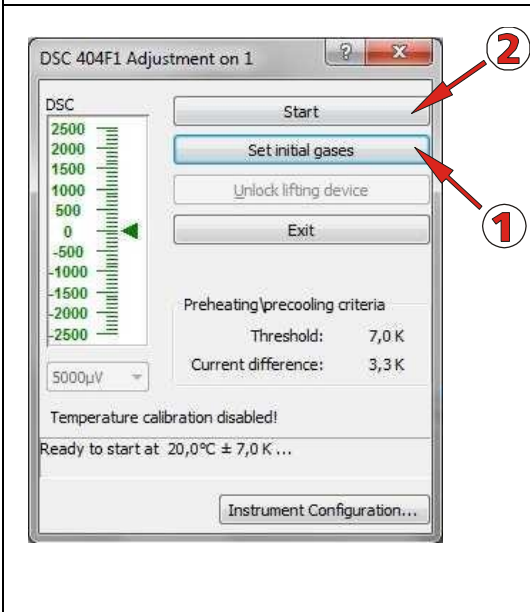
9. **Start** the **Measurement**

   - Push **Set initial gases**
     (the gas switches are set to the INITIAL start conditions (carried out automatically during preheating/ precooling)).

   - Click **Start**.

     If necessary, check the **Instrument Configuration**.

Additional Information for the Temperature Program

- *Carry out measurements for all standard materials with 3 heating and 2 cooling segments so that the melting peak is measured three times.*

- *Depending on the instrument configuration (e.g. furnace type, sample carrier) modify the end temperature of the heating segment (shown as an example in the table below) in such a way that the complete melting peak can be evaluated. Cool down to about 100°C below the melting point.*

- *For the evaluation use only the values from the 2nd and 3rd heating (both for temperature and sensitivity calibration).*
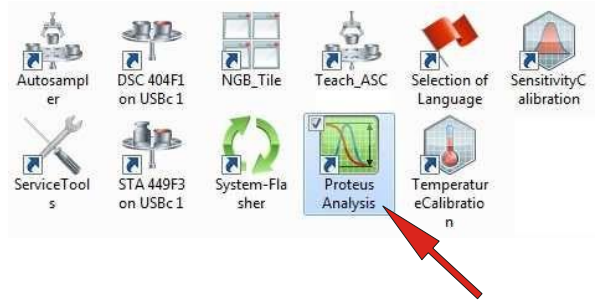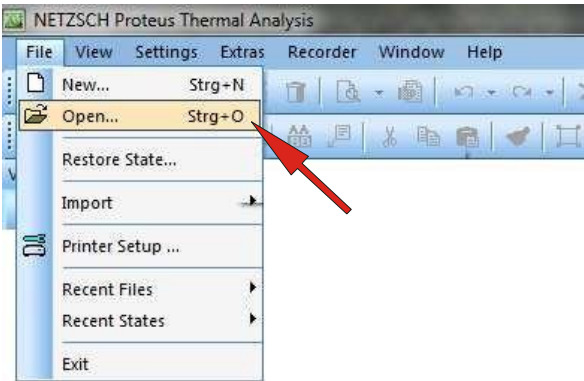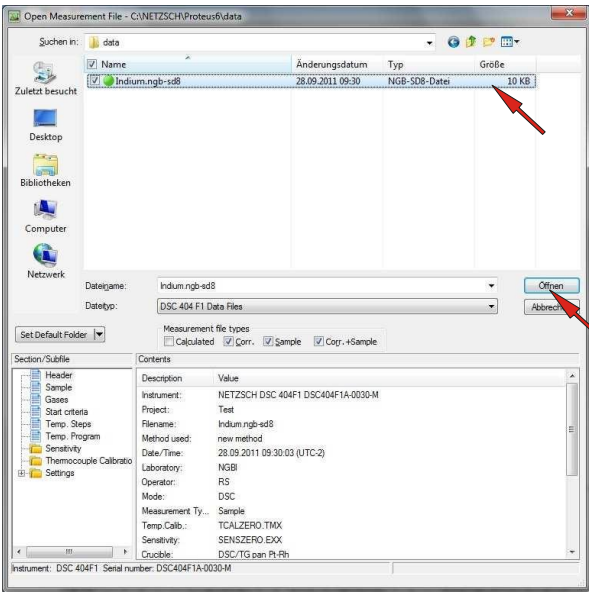
calibration substance	melting point in °C	temperature program (example)
Adamantane (C10H16) (for low temperature range)	-64.5	-120°C to -20°C (heating segment) *-20°C to -120°C (cooling segment)* -120°C to -20°C (heating segment) *-20°C to -120°C (cooling segment)* -120°C to 25°C (heating segment) (so that you can open the furnace)
Indium (In)	156.6	20°C to 260°C (heating segment) *260°C to 50°C (cooling segment)* 50°C to 260°C (heating segment) *260°C to 50°C (cooling segment)* 50°C to 260°C (heating segment)
Tin (Sn)	231.9	20°C to 340°C (heating segment) *340°C to 130°C (cooling segment)* 130°C to 340°C (heating segment) *340°C to 130°C (cooling segment)* 130°C to 340°C (heating segment)
Bismuth (Bi)	271.4	20°C to 380°C (heating segment) *380°C to 170°C (cooling segment)* 170°C to 380°C (heating segment) *380°C to 170°C (cooling segment)* 170°C to 380°C (heating segment)
Zinc (Zn)	419.6	20°C to 480°C (heating segment) *480°C to 320°C (cooling segment)* 320°C to 480°C (heating segment) *480°C to 320°C (cooling segment)* 320°C to 480°C (heating segment)
Aluminium (Al)	660.6	20°C to 760°C (heating segment) *760°C to 560°C (cooling segment)* 560°C to 760°C (heating segment) *760°C to 560°C (cooling segment)* 560°C to 760°C (heating segment)
Gold (Au)	1064.4	20°C to 1150°C (heating segment) *1150°C to 950°C (cooling segment)* 950°C to 1150°C (heating segment) *1150°C to 950°C (cooling segment)* 1150°C to 950°C (heating segment)

Heating rate: depending on the application (e.g. 20 K/min)

Acquisition rate: 100 Points/min

Cooling rate: select a practicable cooling rate (depending on the instrument)

2. Evaluation of the Measurements

	10. Open the **Proteus Analysis**.
	11. Select **Open** in the **File** menu.
	12. Open your respective measurement (the measurement file which you have saved under item 7). Continue with **Open**.

| | 13. Select **X-Temperature** in the **Settings** menu. The temperature is shown on the X axis. |

Temperature Calibration
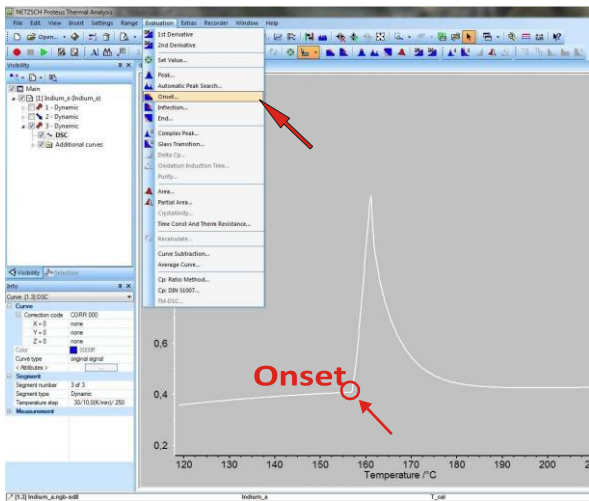
| | 14. Click on the DSC curve for selection. Select **Onset** in the **Evaluation** menu to determine the extrapolated onset. |
| | 15. To evaluate the extrapolated onset, define the right and left evaluation limit as shown in the figure and click **Apply**. |
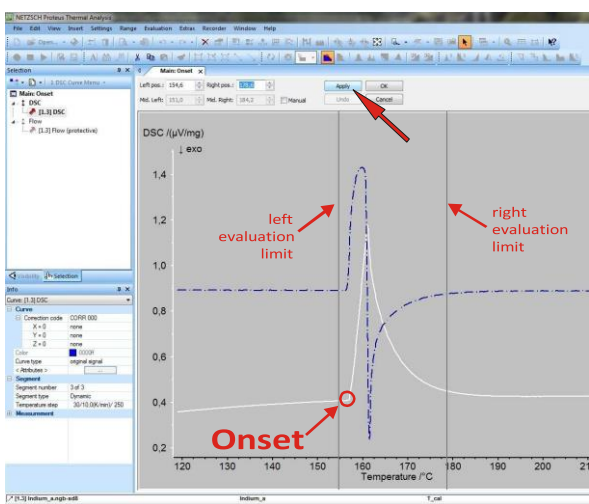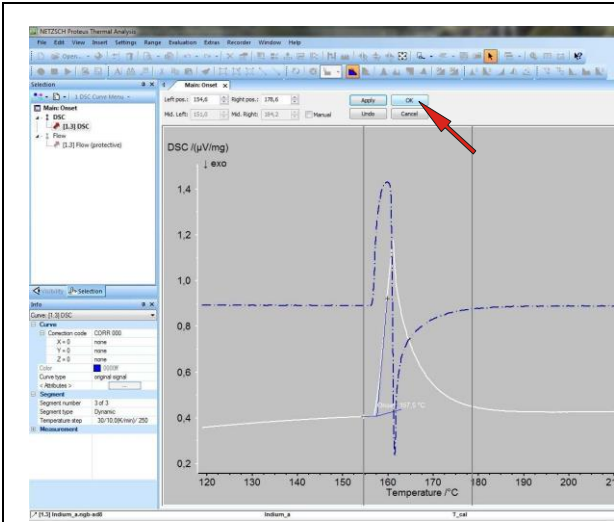
16. If the extrapolated onset was determined correctly, click **OK**. If not, it is still possible to change the right and left evaluation limit. To evaluate click **Apply**. If the extrapolated onset was determined correctly, click **OK**.

    Write down the determined onset value of the 2nd and 3rd measurement.

Sensitivity Calibration
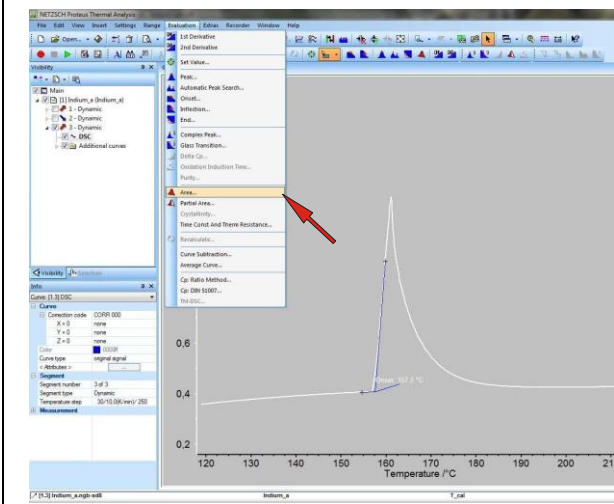
17. Select **Area** in the **Evaluation** menu.
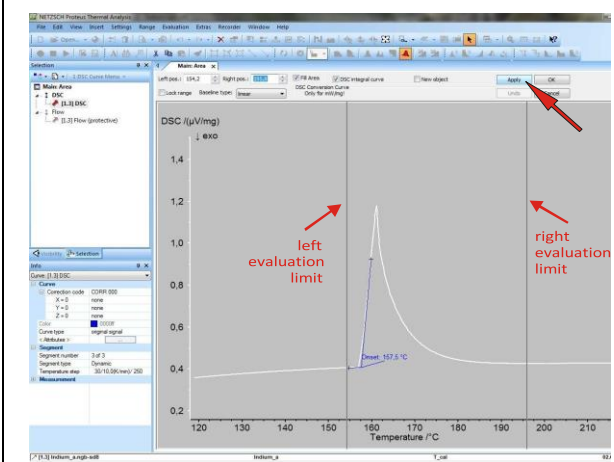
18. To evaluate the peak area, define the right and left evaluation limit as shown in the figure and click **Apply**.
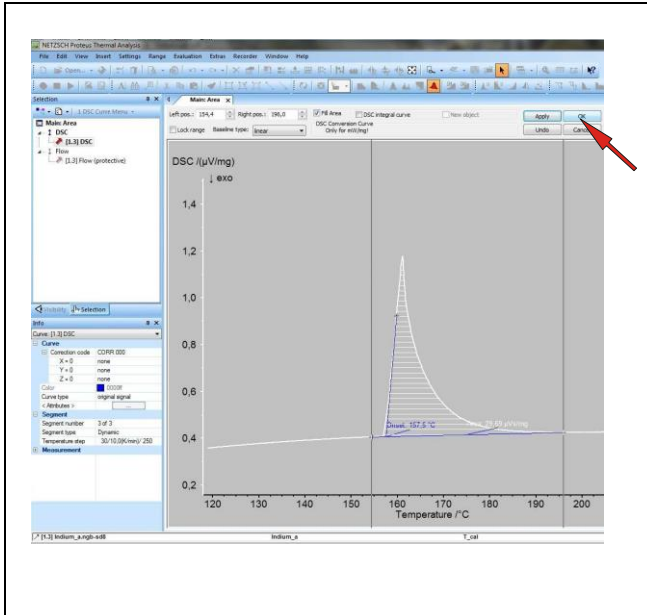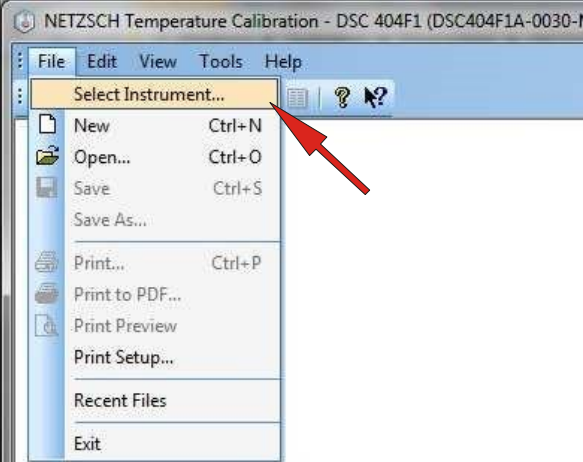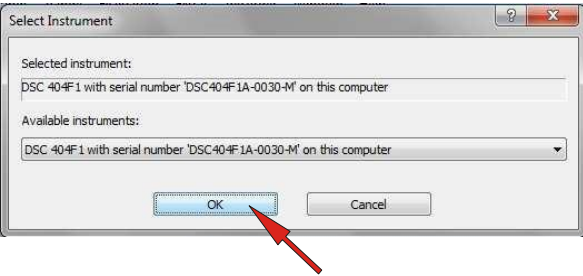
19. If the peak area was determined
correctly, click OK. If not, it is still possible to change the right and left evaluation limit. To evaluate click **Apply**. If the peak area was determined correctly, click **OK**.

Write down the determined peak area of the 2nd and 3rd measurement.

3. Creation of a Temperature/Sensitivity Calibration File

Temperature Calibration

20. Open **Temperature Calibration** in the NETZSCH-Proteus group.

21. Open **Select Instrument** in the **File** menu.

22. Select your instrument and click **OK**.
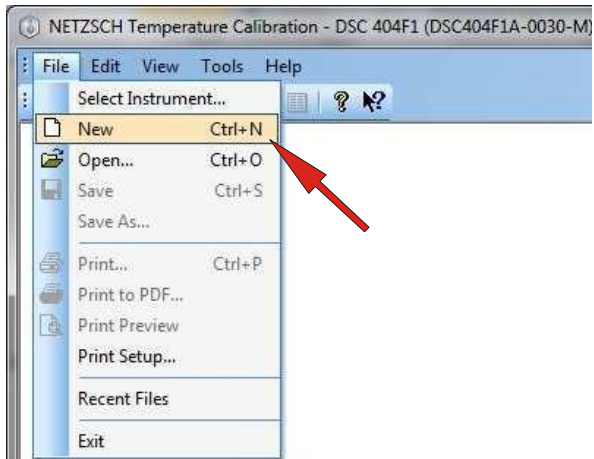
23. Select **New** in the **File** menu.
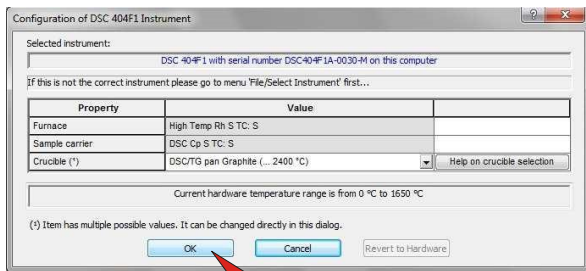
24. Check the instrument configuration (change if necessary).
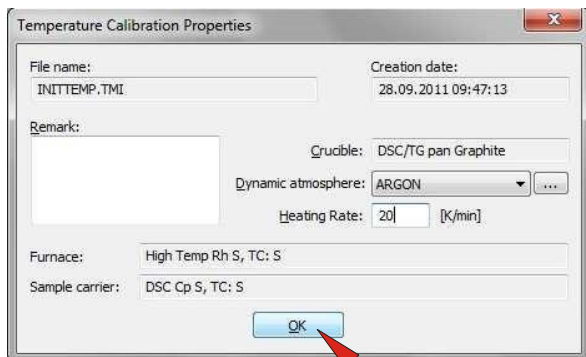
Continue with **OK**.

25. Define both the **atmosphere** and the **heating rate** used for the calibration measurements.

Continue with **OK**.
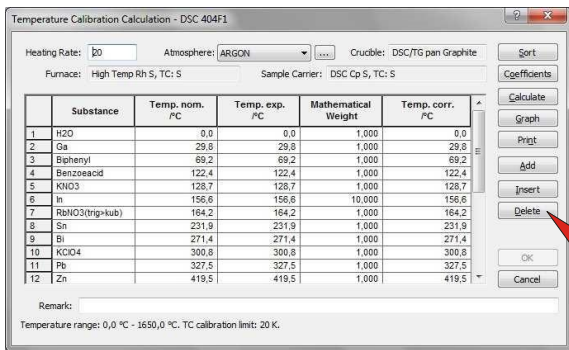
26. Click **Delete** to remove all materials you have not measured.
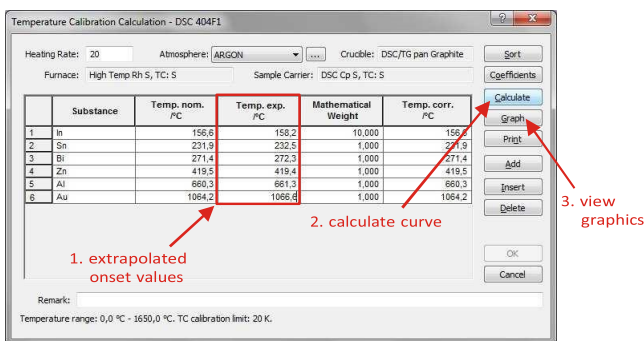
27. Enter the determined onset values for all calibration materials.

    Click **Calculate** to evaluate the curve.

    Click **Graph** to see the calibration curve.
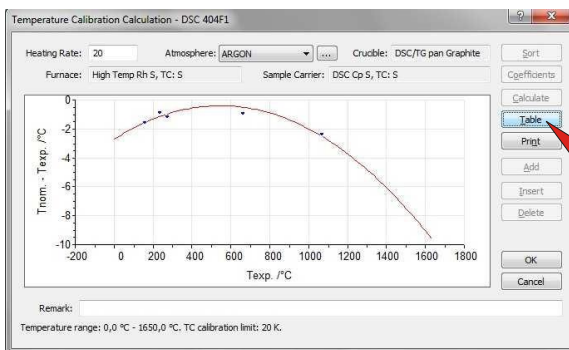
28. Check the correct form of the curve. The curve is acceptable if:

- The fitted curve goes through all points.
- **Temp. nom.** and **Temp. corr.** are nearly the same (depending on your requirements, e.g. **Temp. nom. - Temp. corr. ± 1-3 K).**

The column **Mathematical Weight** contains the mathematical weighing for the fit. It can be edited for each standard to change the shape of the calibration curve. From all calibration standards Indium can be measured with highest accuracy ⇒ Mathem. Weighing 10.

Click **Table** to change the input or accept the settings.
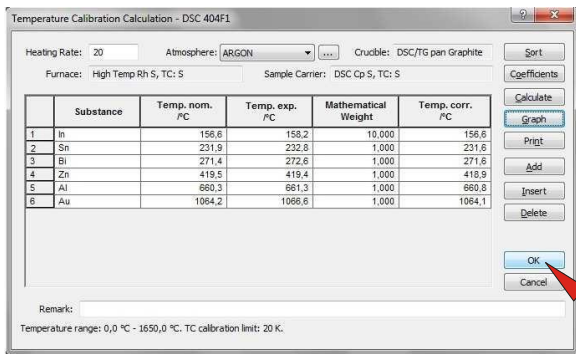
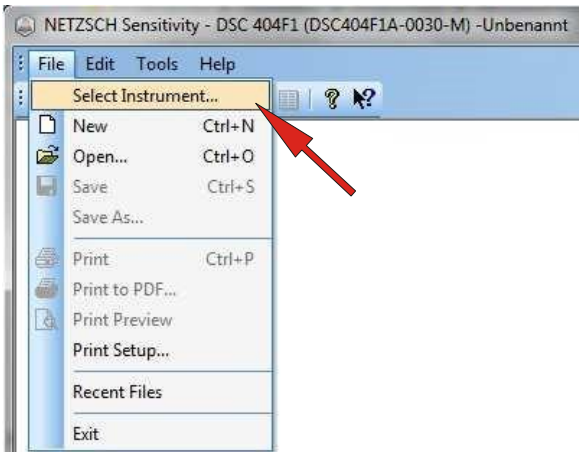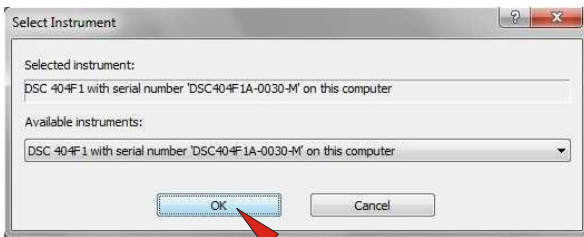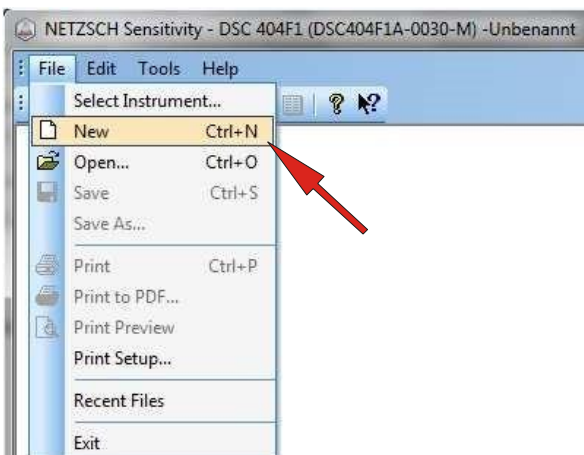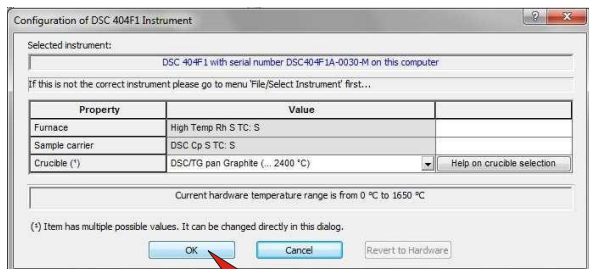|	
	29. Click **OK** to save the calculation.
	30. Select **Save as** in the **File** menu to save the data.
	31. Define the file name of the **temperature calibration file** and click **Save**.
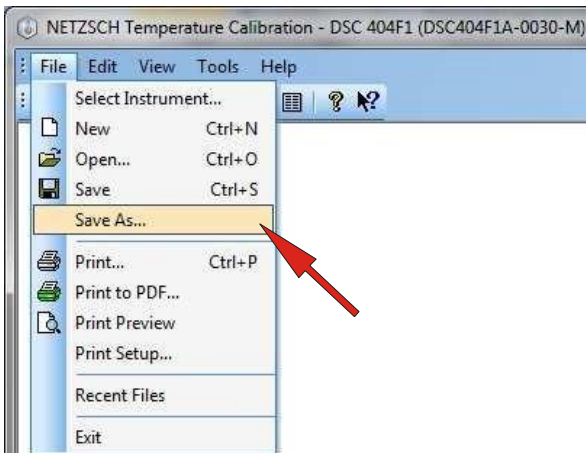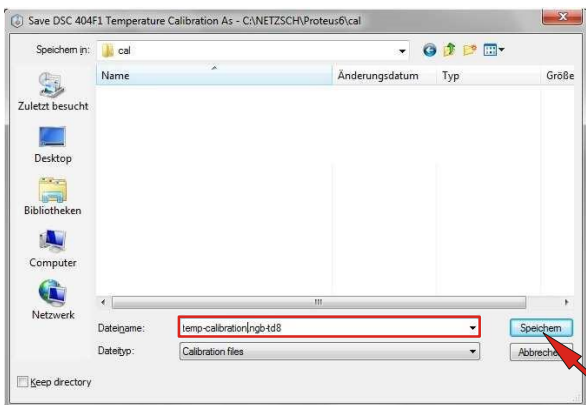
Sensitivity Calibration
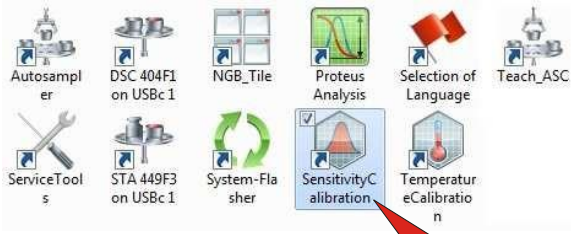
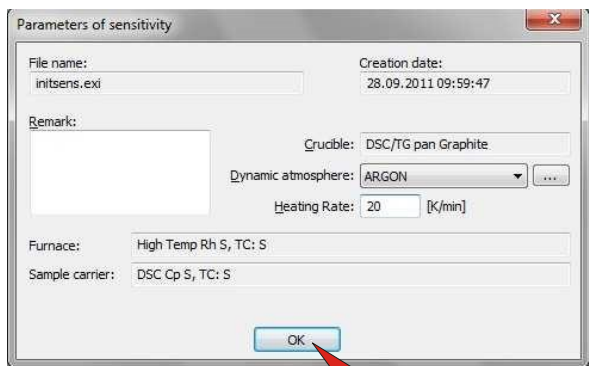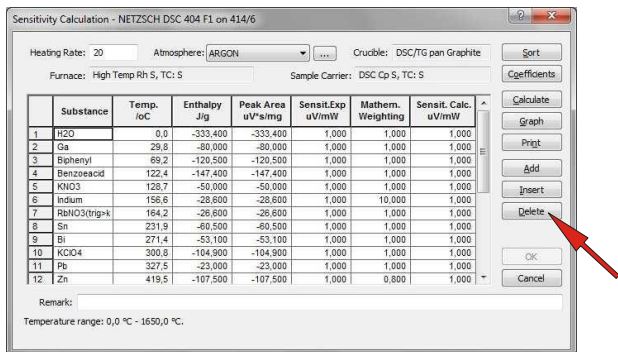|	
	32. Open **Sensitivity Calibration** in the NETZSCH-Proteus group.
	33. Open **Select Instrument** in the **File** menu.
	34. Select your instrument and click **OK**.
	35. Select **New** in the **File** menu.

36. Check the instrument configuration (change if necessary).

   Continue with **OK**.

37. Define both the **atmosphere** and the **heating rate** used for the calibration measurements.
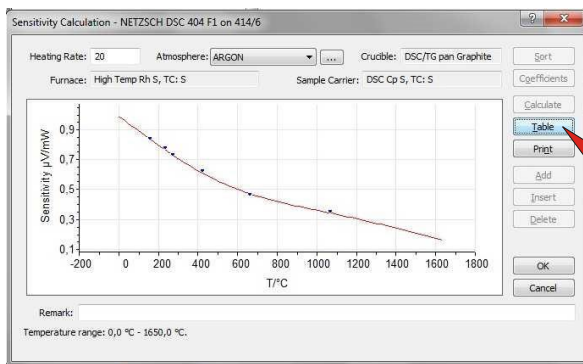
   Continue with **OK**.

38. Click **Delete** to remove all materials you have not measured.
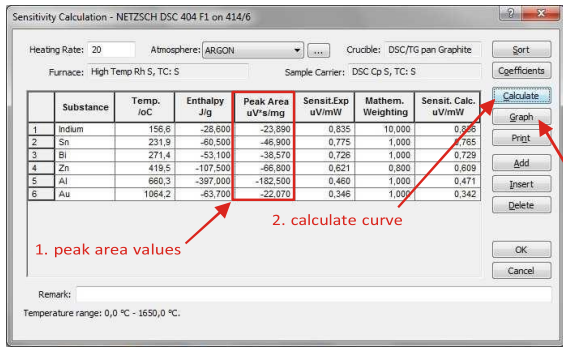
39. Enter the determined values for the peak area for all calibration materials.

   Click **Calculate** to evaluate the curve.

   Click **Graph** to see the calibration curve.

40. Check the correct form of the curve.
   The curve is acceptable if the deviation between **Sensit. Calc.** and **Sensit. Exp.** is less than ± 3%.

| Peak Area uV*s/mg	Sensit.Exp uV/mW	Mathem. Weighting	Sensit. Calc. uV/mW
-23,890	0,835	10,000	0,836
-46,900	0,775	1,000	0,765
-38,570	0,726	1,000	0,729
-66,800	0,621	0,800	0,609
-182,500	0,460	1,000	0,471
-22,070	0,346	1,000	0,342
	Sensit. Exp		Sensit. Calc.

The column **Mathem. Weighing** contains the mathematical weighing for the fit. It can be edited for each standard to change the shape of the calibration curve. From all calibration standards Indium can be measured with highest accuracy ⇒ Mathem. Weighing 10.
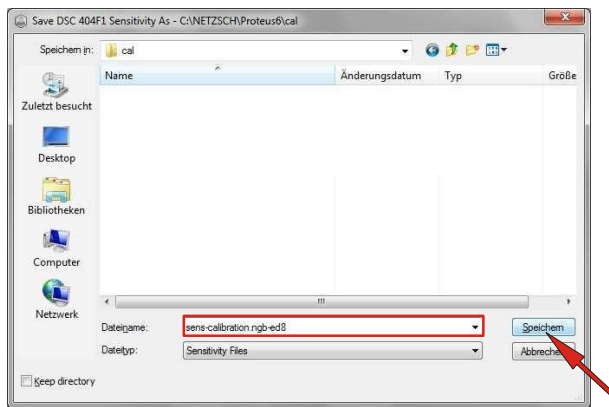
Click **Table** to change the input or accept the settings.
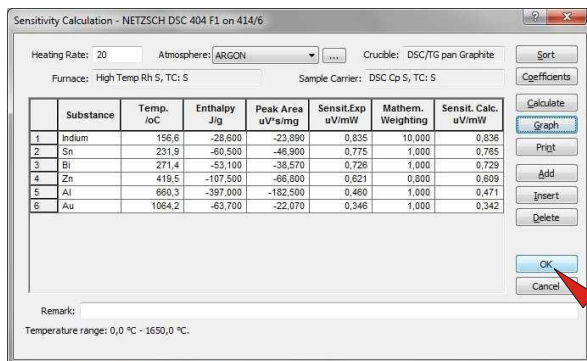
41. Click **OK** to save the calculation.
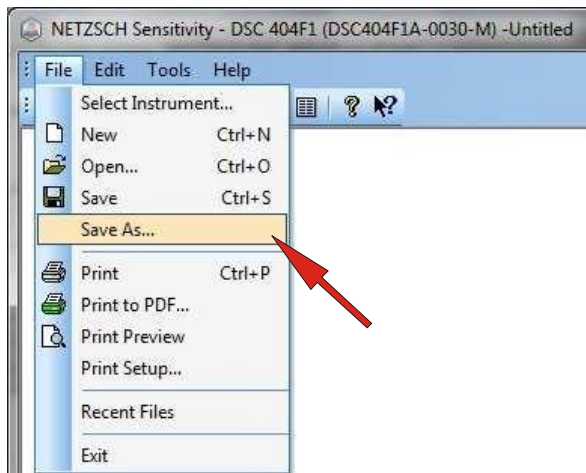
42. Select **Save as** in the **File** menu to save the data.

43. Define the file name of the **sensitivity calibration file** and click **Save**.

Accessing GauchoSpace

What is it: GauchoSpace is the learning management system for UCSB courses and projects, allowing instructors to create online sites for course materials and student activities. GauchoSpace is built using Moodle, an open source learning platform.

How the MRL uses GauchoSpace: The MRL uses GauchoSpace pages for several things including:

- Instrument Training Sign-Ups
- Lab Safety Documentation
- Lab Access Documentation
- References and Resources for all of our Instrument

Navigating to GauchoSpace: Users can access the site at
https://gauchospace.ucsb.edu.

Logging into GauchoSpace: To log into the site, users will need to use their UCSB Net ID. If you do not have a Net ID or are unsure if you have one please contact a TEMPO employee and we will help you figure it out.

Locating the TEMPO GauchoSpace Pages:

1. After logging into GauchoSpace with your UCSB Net ID, mouse over the Courses button in the top navigation bar.
2. From the drop-down menu select Project Sites.
3. Once the next page loads, scroll down until you locate the Materials Research Laboratory. Click this option.
4. Select *TEMPO Internal Users: Access and Safety Training* or *TEMPO Instrument Training and Resources* to load the GauchoSpace Pages.
5. Users will need the enrollment code **TEMPO** to enroll in the site.