Differential Scanning Calorimetry (DSC) Practical Training Course

2020

Part 1

Calibration & Optimization & Trios

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TA Instruments

Training Course Agenda (Part 1)

- Introduction
  - Technique
  - Tzero™ Technology vs. Heat flux DSC
- Experimental Method
- Calibration & Verification
  - Tzero or Baseline (Heat Flux DSC)
  - Heat Flow
  - Temperature
- Optimisation of Experimental Conditions
  - Sample Preparation & Sample Cups
  - Heating/Cooling Rate
- Trios Software: Tips & Tricks

Introduction

Technique & Instrumentation

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DSC: The Technique

- Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere.

- These measurements provide quantitative and qualitative information about physical and chemical changes that involve ***endothermic*** or ***exothermic processes***, or ***changes in heat capacity***.

Definitions

- **Heat Capacity**: amount of heat required to heat up a sample by 1ºC

- ***Endothermic***: heat flow into the sample as a result of either heat capacity (while heating) and/or some endothermic process (melting, evaporation, etc.)

- ***Exothermic***: heat flow out of the sample as a result of either heat capacity (during cooling) or some exothermic process (crystallization, thermoset cure, oxidation, etc.)

Heat Flow in DSC

$$\mathbf{dQ/dt = Cp \,.\, dT/dt + f\,(t,T)}$$

where:

dQ/dt = heat flow (W/g or mW)

W = J/sec

Cp = specific heat capacity (J/g.ºC)

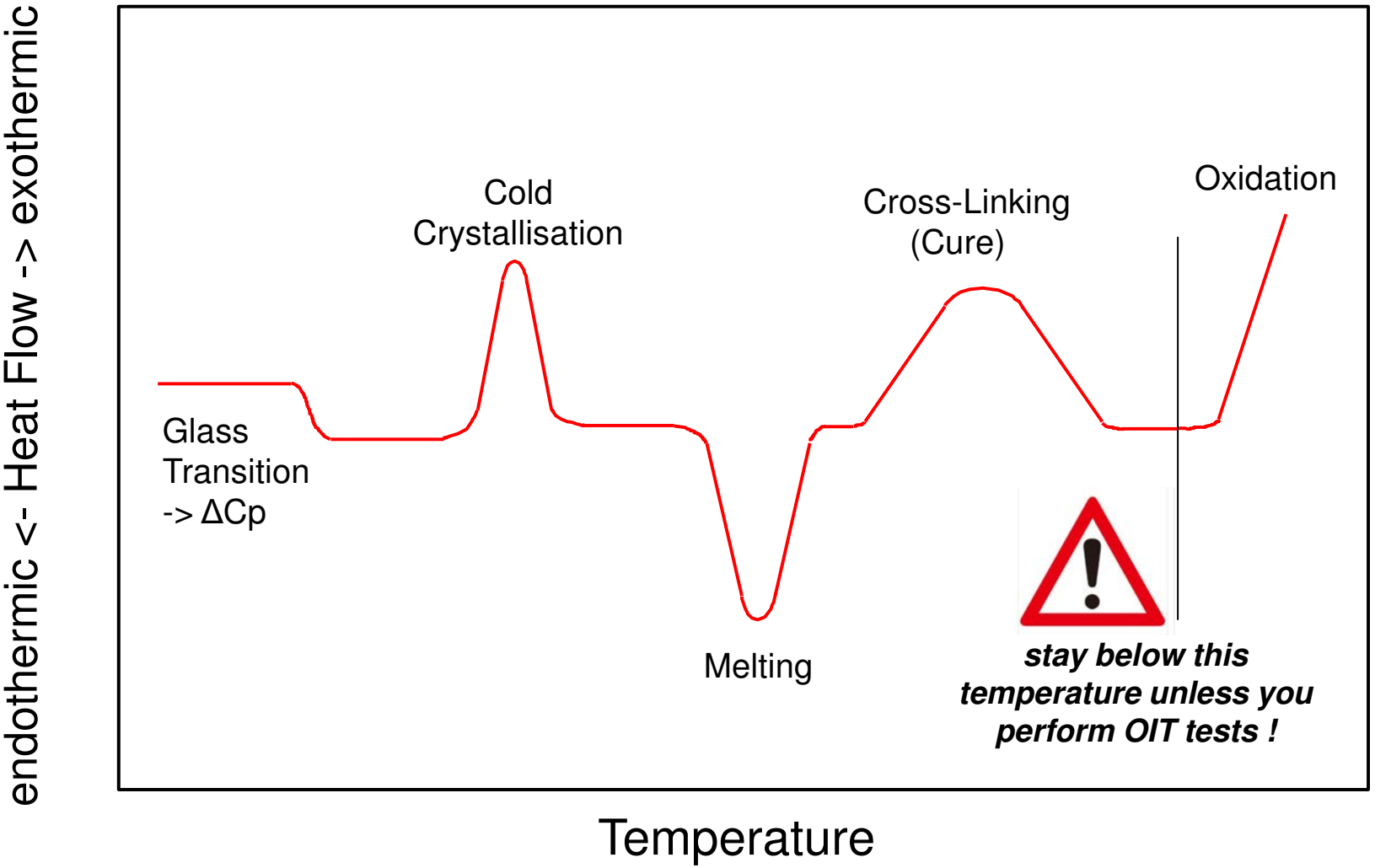
$$Cp(T) = a + b.T + c.T^2$$

dT/dt = heating rate (ºC/min)

f (t,T) = time dependent (kinetic) components

e.g. melting, crystallisation, curing,...

DSC Thermogram



How is Heat Flow Measured ?

DSC25xx with or without AS

Heat Flux DSC
DSC 25

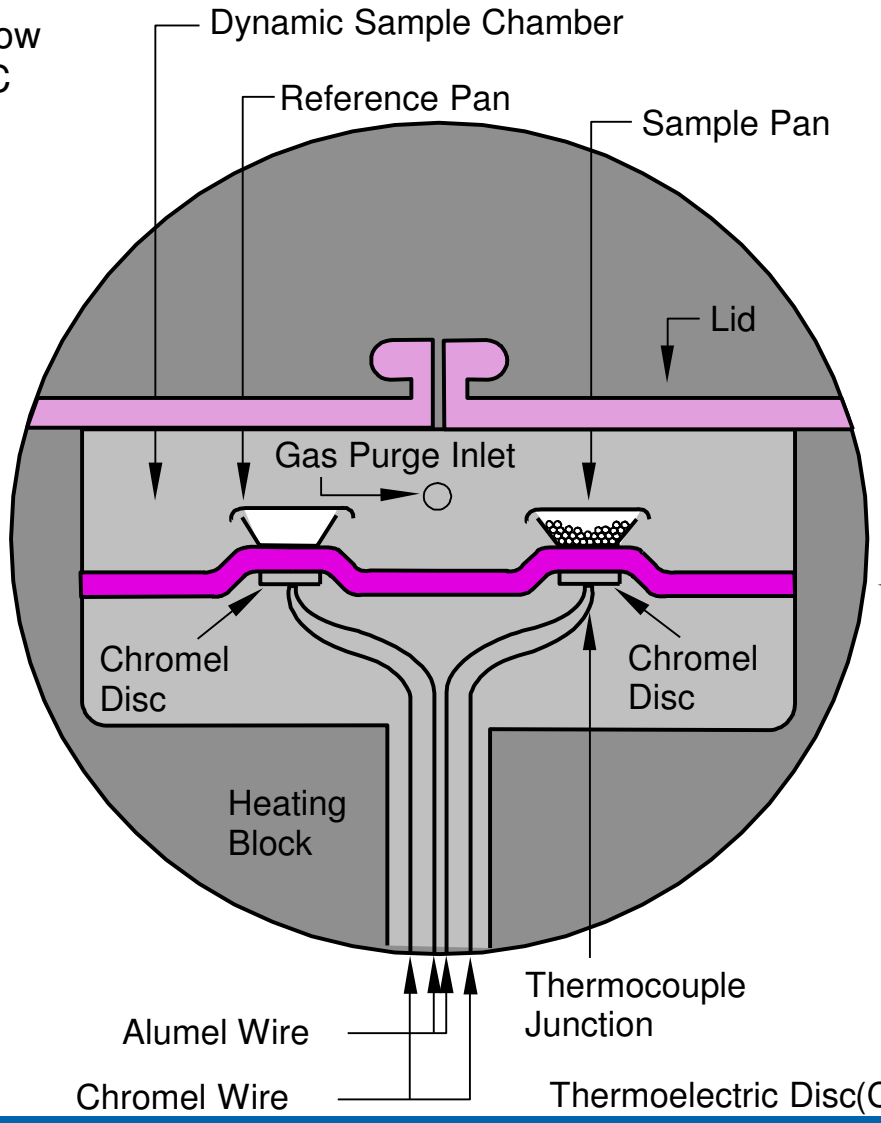
Basic Tzero™ DSC
DSC 250

Advanced Tzero™
DSC 2500

First generation
Discovery DSC
Advanced Tzero™

Heat Flux DSC Instrument DSC 25

Note: schematics show a 2920 heat flux DSC



$$dQ/dt = Q_s - Q_r$$

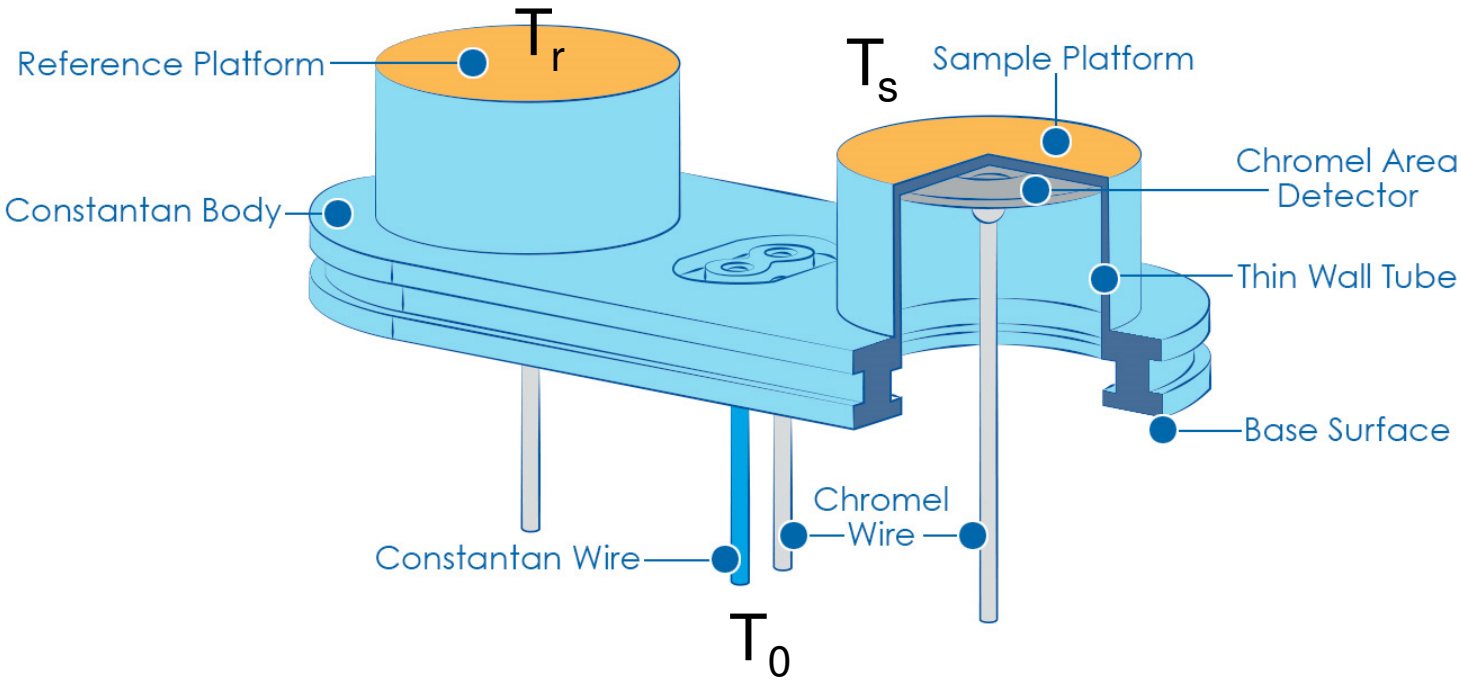
$$dQ/dt = \Delta T/R$$

$$\Delta T = T_s - T_r$$

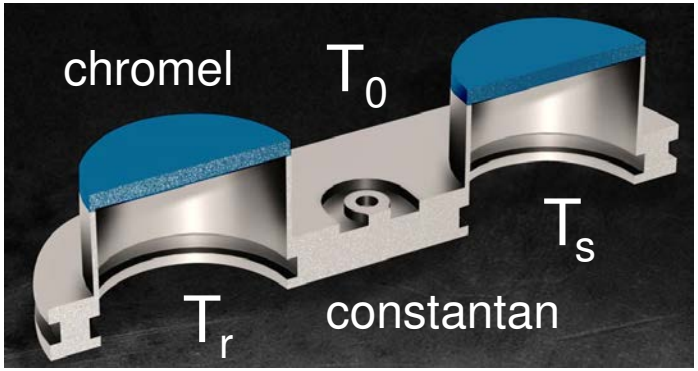
Assumes symmetry between sample and reference calorimeter

T1

Tzero™ Sensor



DSC 2500 – DSC 250 – (DSC 25)



First generation Discovery:
diffusion bonded sensors

Tzero™ Heat Flow Equation T4

$$q = q_s - q_r \qquad \Delta T = T_s - T_r \qquad \Delta T_0 = T_0 - T_s$$

$$q = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{dt} - C_r\frac{d\Delta T}{dt}$$

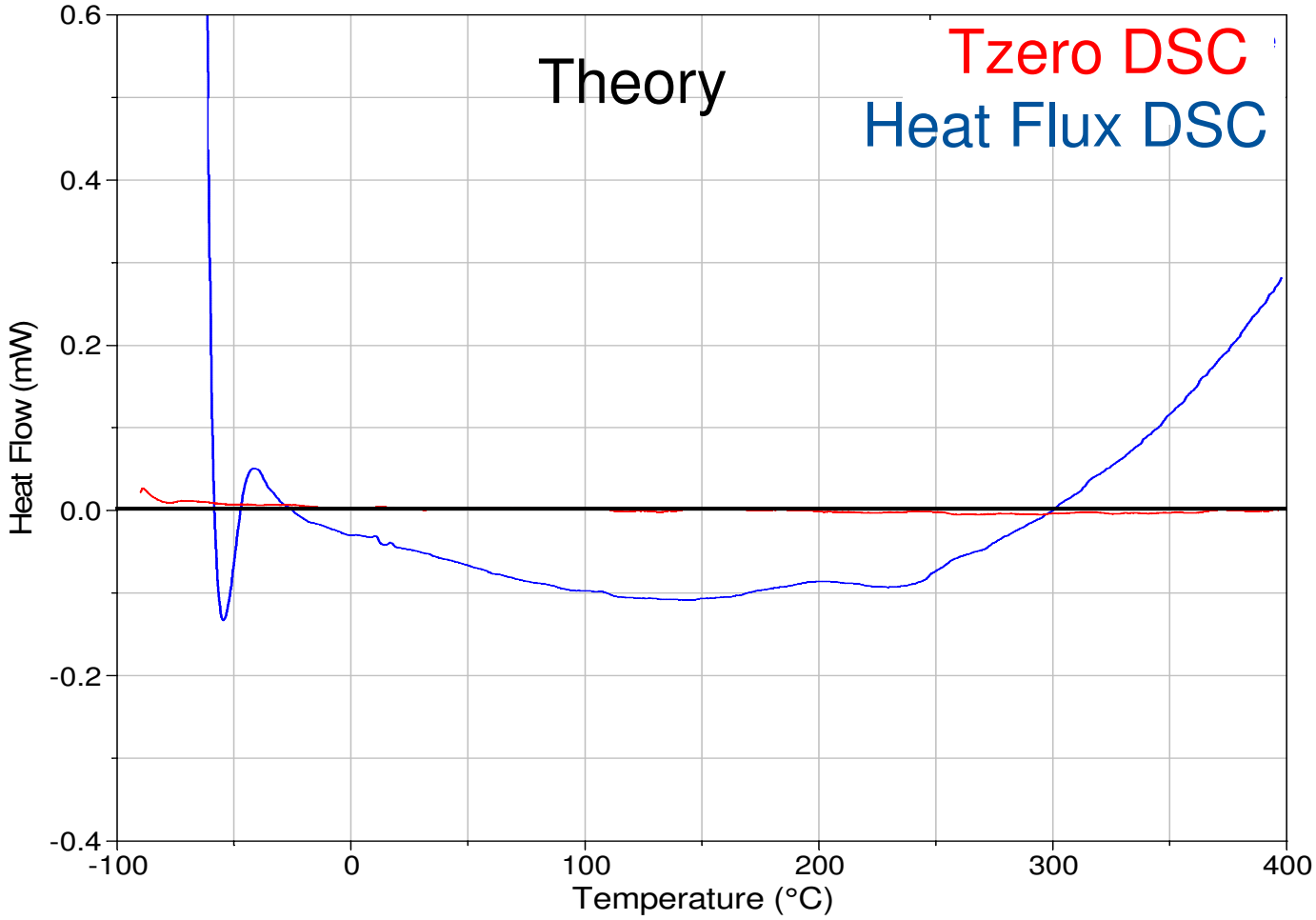
Principal DSC Heat Flow

Thermal Resistance Imbalance

Heat Capacity Imbalance

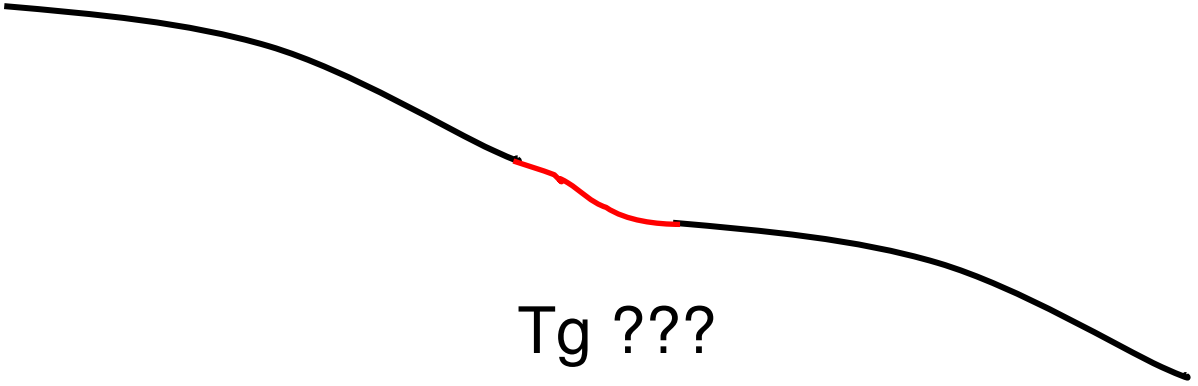
Heating Rate Difference

Baseline (= Empty Cell Run)



Baseline Curvature Hinders Detection of Weak Transitions

Weak, broad Tg



Tg ???

Tzero™ Heat Flow Terms T4

$$-\frac{\Delta T}{R_r}$$

Principal DSC Heat Flow
provides main heat flow signal
this is the only term used in heat flux DSC

$$\Delta T_0\left(\frac{1}{R_s}-\frac{1}{R_r}\right)$$

Thermal Resistance Imbalance

improve baseline

$$(C_r - C_s)\frac{dT_s}{dt}$$

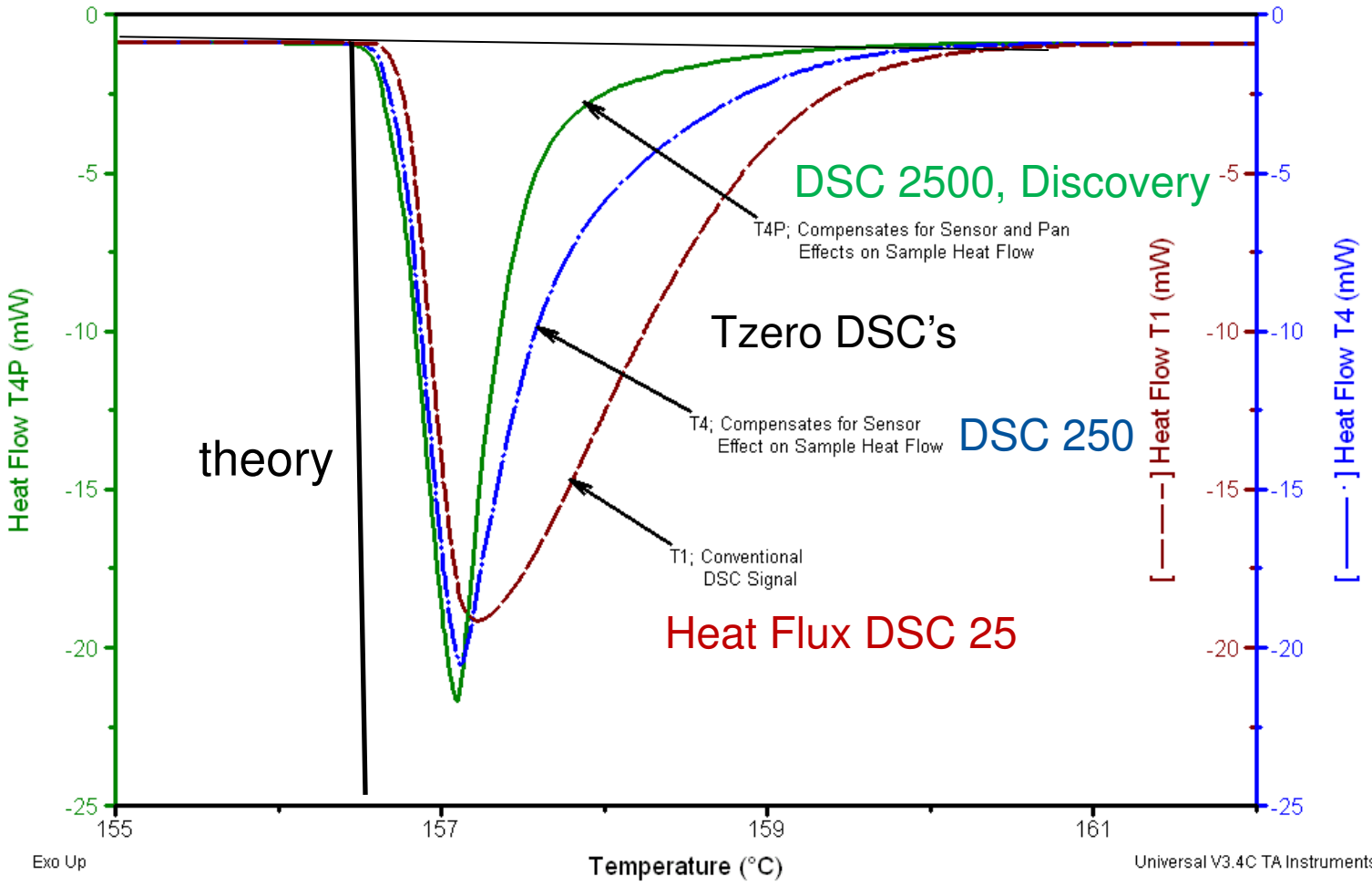
Heat Capacity Imbalance

$$-C_r\frac{d\Delta T}{dt}$$

Heating Rate Difference

improves resolution

Resolution : Indium Melting Run

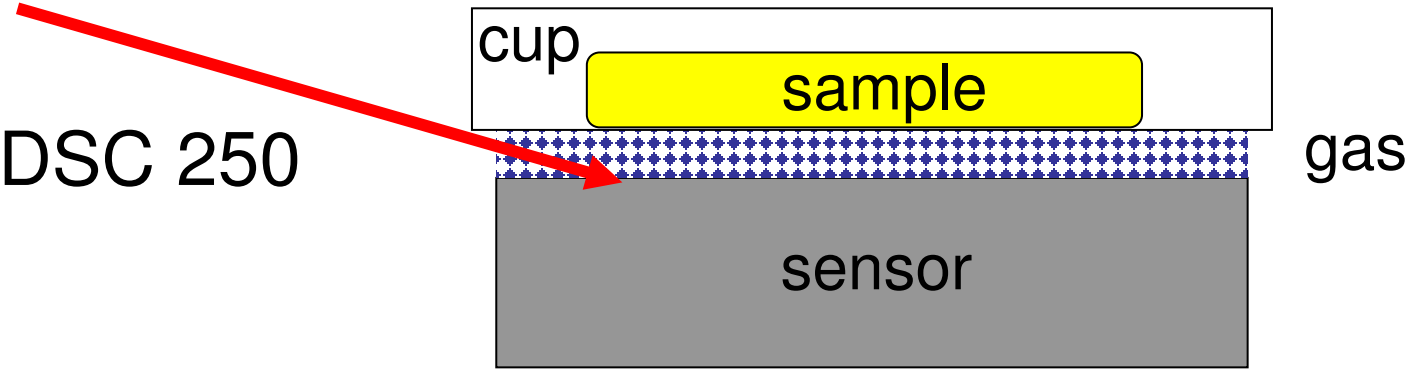


Temperature / Heating Rate

What temperature is being measured and displayed by the DSC ?

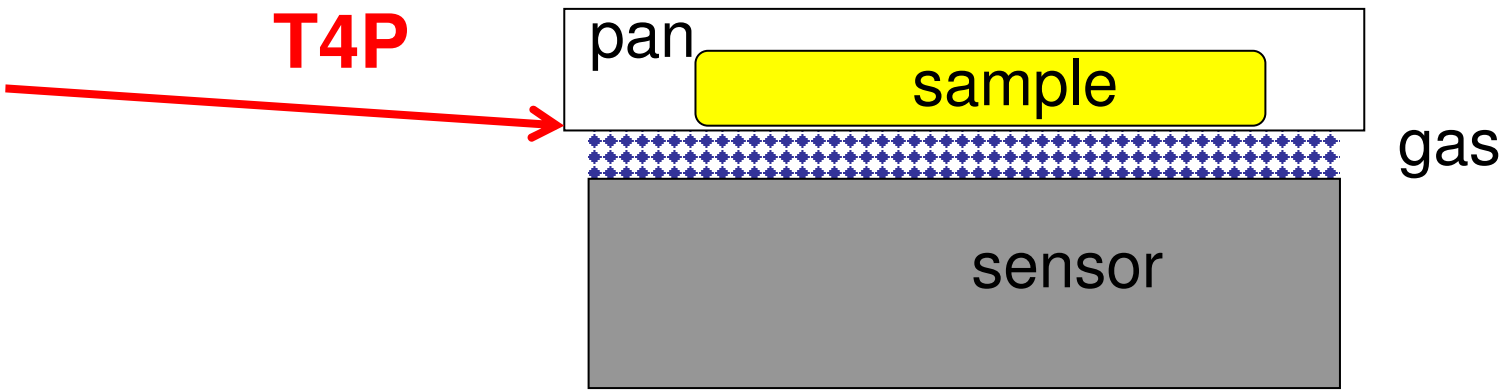
- The actual temperature of the sample is never measured by DSC
- Sensor Temp: used by most DSC's. It is measured at the sample platform with an area thermocouple

DSC 25 / DSC 250



Temperature / Heating Rate

- Pan Temp: calculated by DSC 2500 and Discovery based on pan material and shape
- Uses weight of pan, resistance of pan (type of pan), and thermoconductivity of purge gas
- Resolution even more improved



Experimental Method

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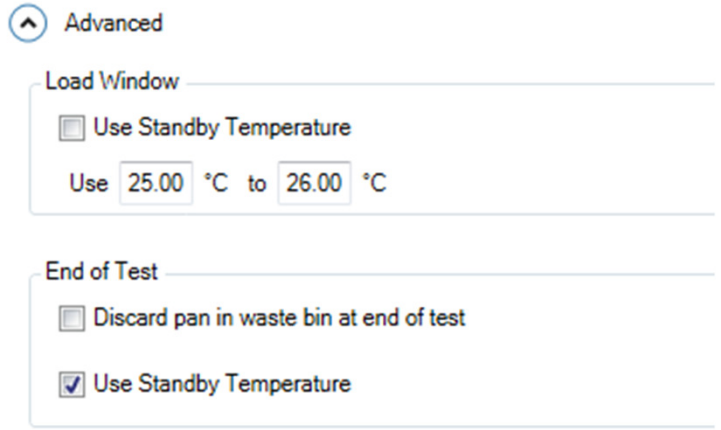
Heating/Cooling Method

- Heating Method

  (NOTE: No equilibrate segment necessary if starting at or near ambient temperature)

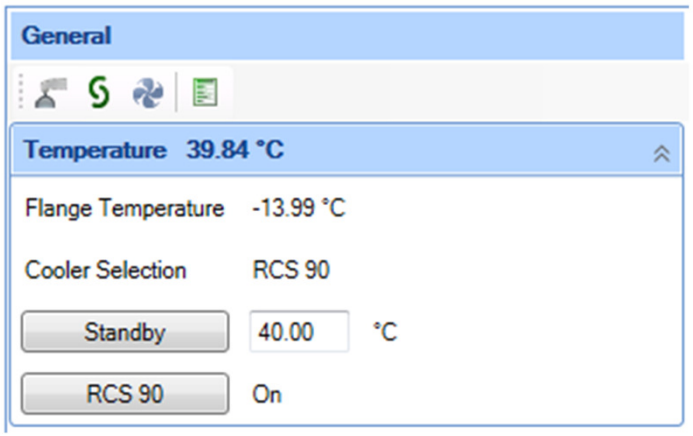
  1) Ramp 10ºC/min to 300ºC

  (NOTE: No equilibrate at RT necessary for cooling down, defined in post test options)



- Cooling Method

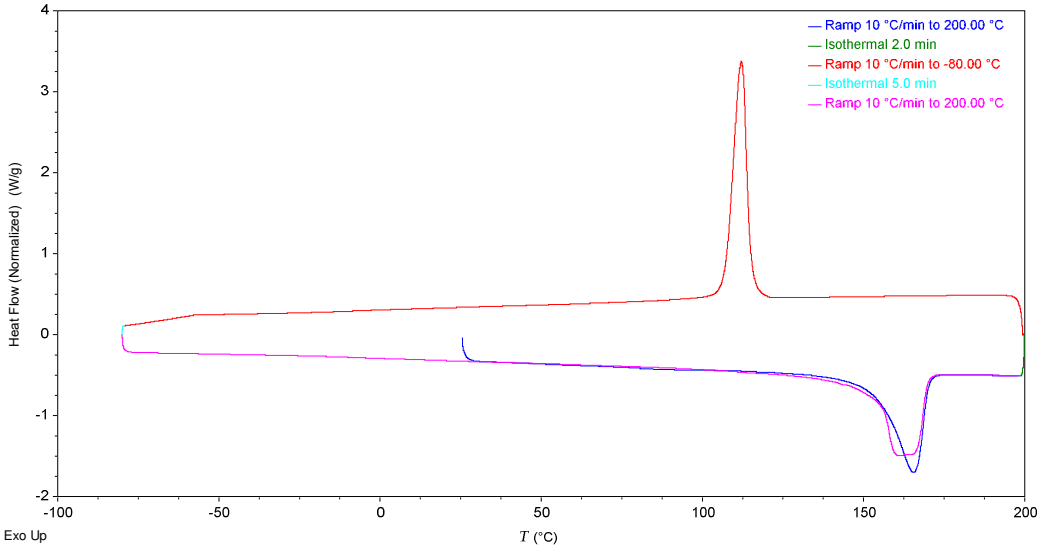
  1) Equilibrate at 300ºC
  2) Ramp 10ºC/min to 25ºC

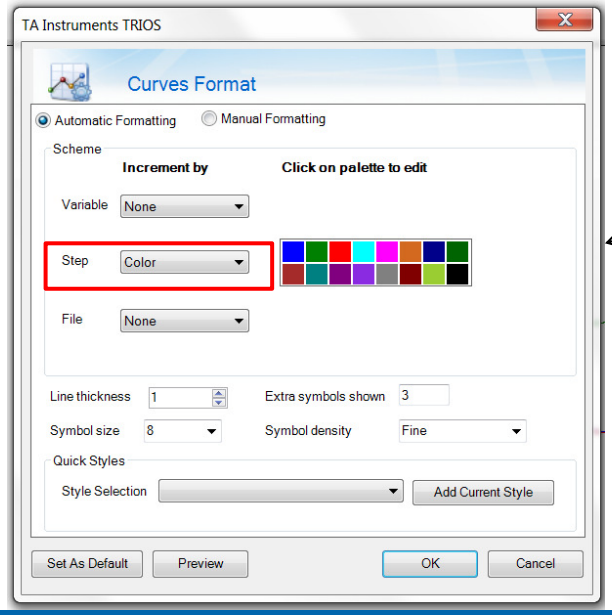


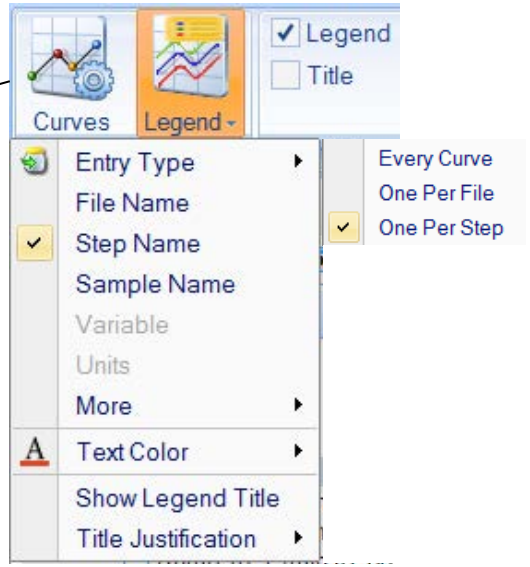
Ramp & Iso segment automatically trigger data collection

Heat-Cool-Reheat Method

1) Ramp 10ºC/min to 200ºC
2) Isothermal for 2.00 min
3) Ramp 10ºC/min to -80ºC
4) Isothermal for 5.00 min
5) Ramp 10ºC/min to 200ºC







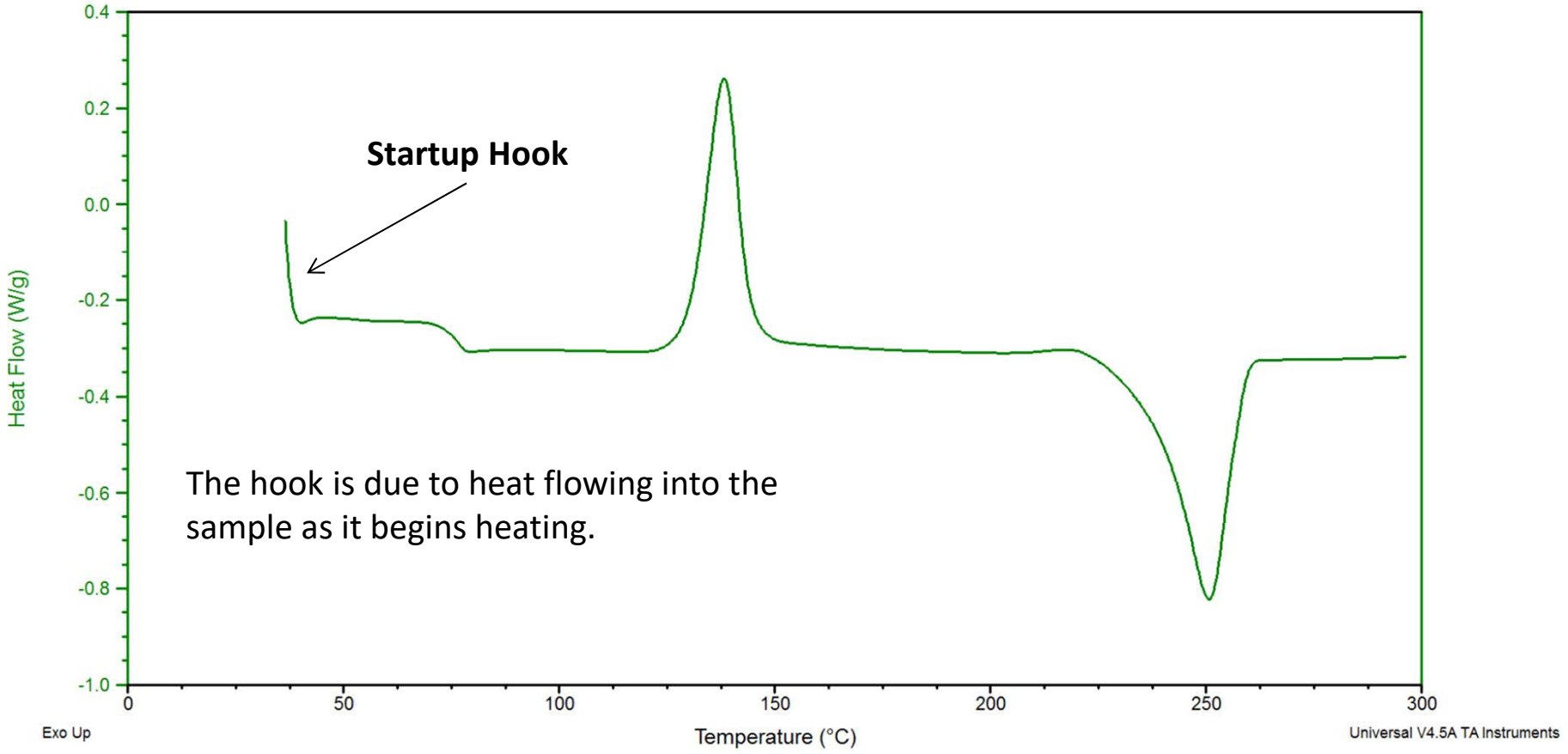
Method Design Rules

- **Start Temperature**
  Generally, the baseline should have 2 minutes to completely stabilise prior to the transition of interest. Therefore, at 10ºC/min, start at least 20ºC below the transition onset temperature.

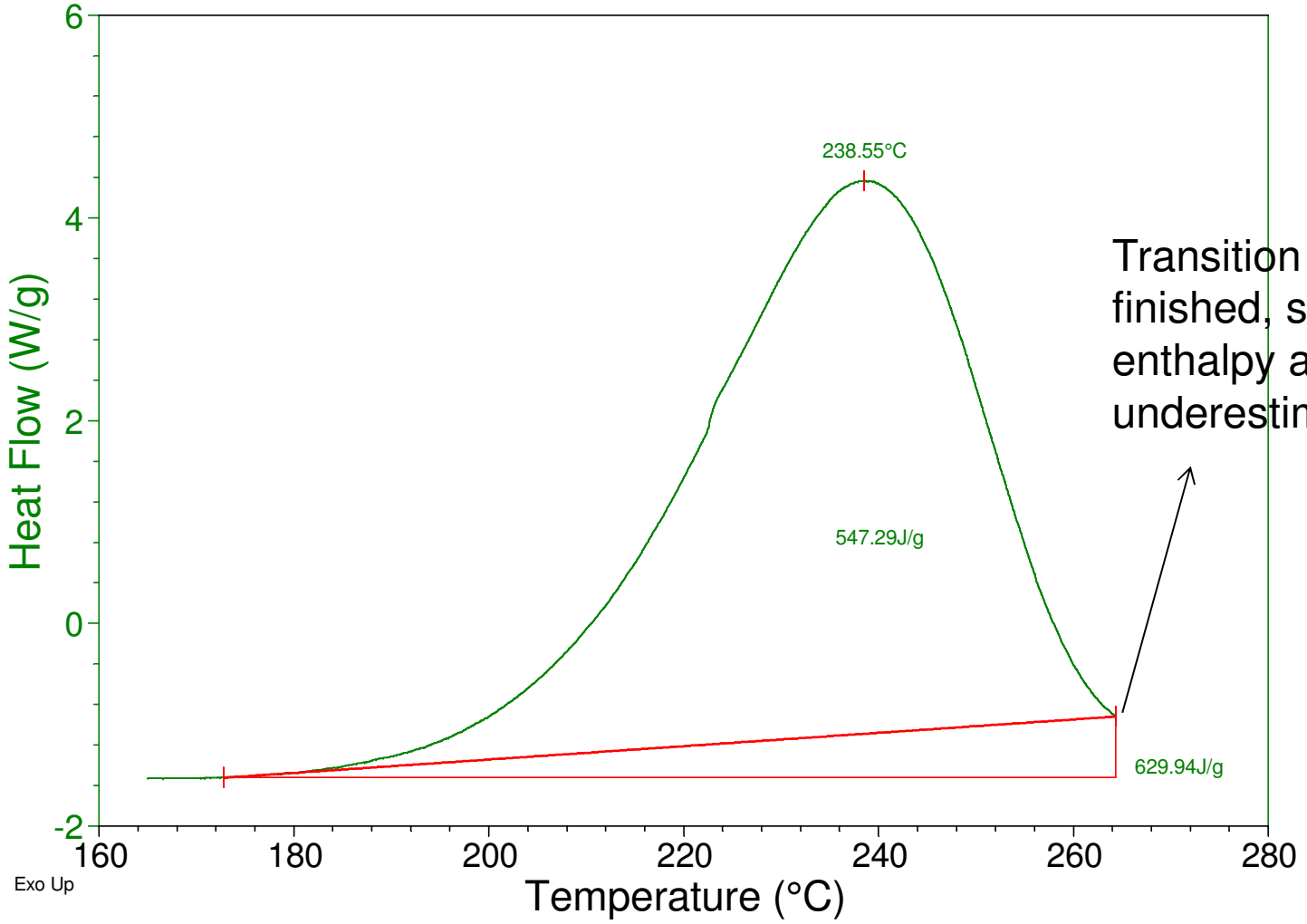
- **End Temperature**
  Allow a 2 minute baseline after the transition of interest in order to correctly select integration or analysis limits.
  But do not decompose the sample in the DSC cell !

Startup Hook in DSC

All DSC data will have an endothermic shift (on heating) at the beginning of the experiment. This is commonly referred to as the “Startup Hook”, or more specifically, the “Approach to Steady State”



Why have 2 min of baseline after ?



Transition not yet finished, so reaction enthalpy always underestimated

Calibration & Verification

Tzero or Baseline

Heat Flow

Temperature

TA Instruments

Calibration Overview

- Tzero calibration (Tzero DSC) 1
  - Discovery DSC, DSC 2500, DSC 250 in T4P or T4 mode

OR

- Baseline calibration (Heat Flux DSC)
  - DSC 25
  - (Tzero DSC if run in T1 mode)

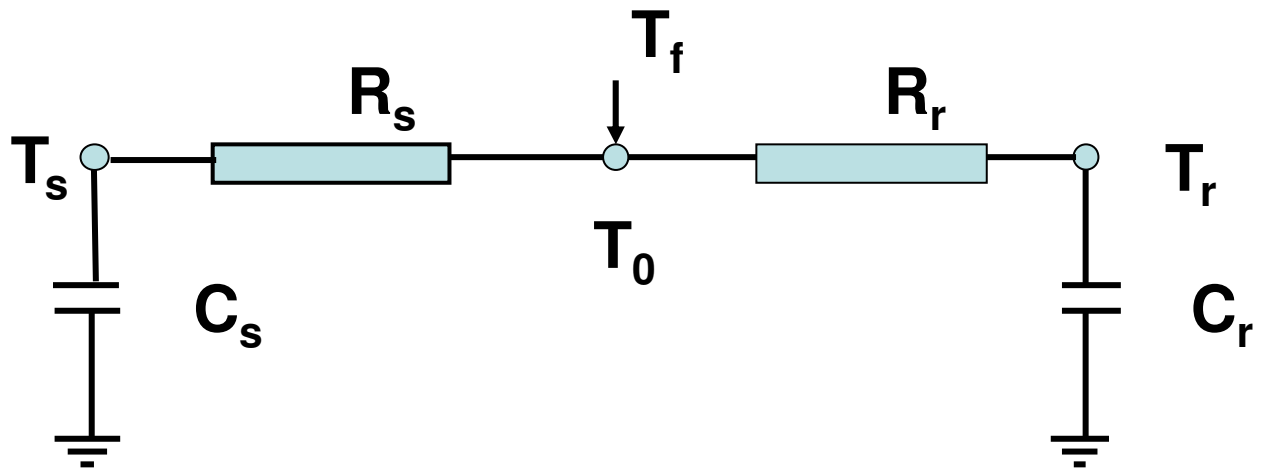
AND
- Heat flow: cell constant 2

AND
- Temperature

Always verify first before you decide to recalibrate !

Tzero™ Calibration for DSC 250(0) & Discovery

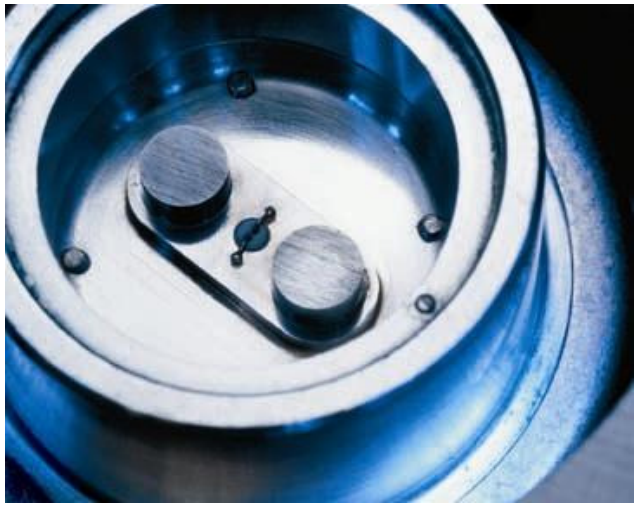
- Tzero calibration measures the C's & R's



$$q = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{dt} - C_r\frac{d\Delta T}{dt}$$

Measuring the C's & R's

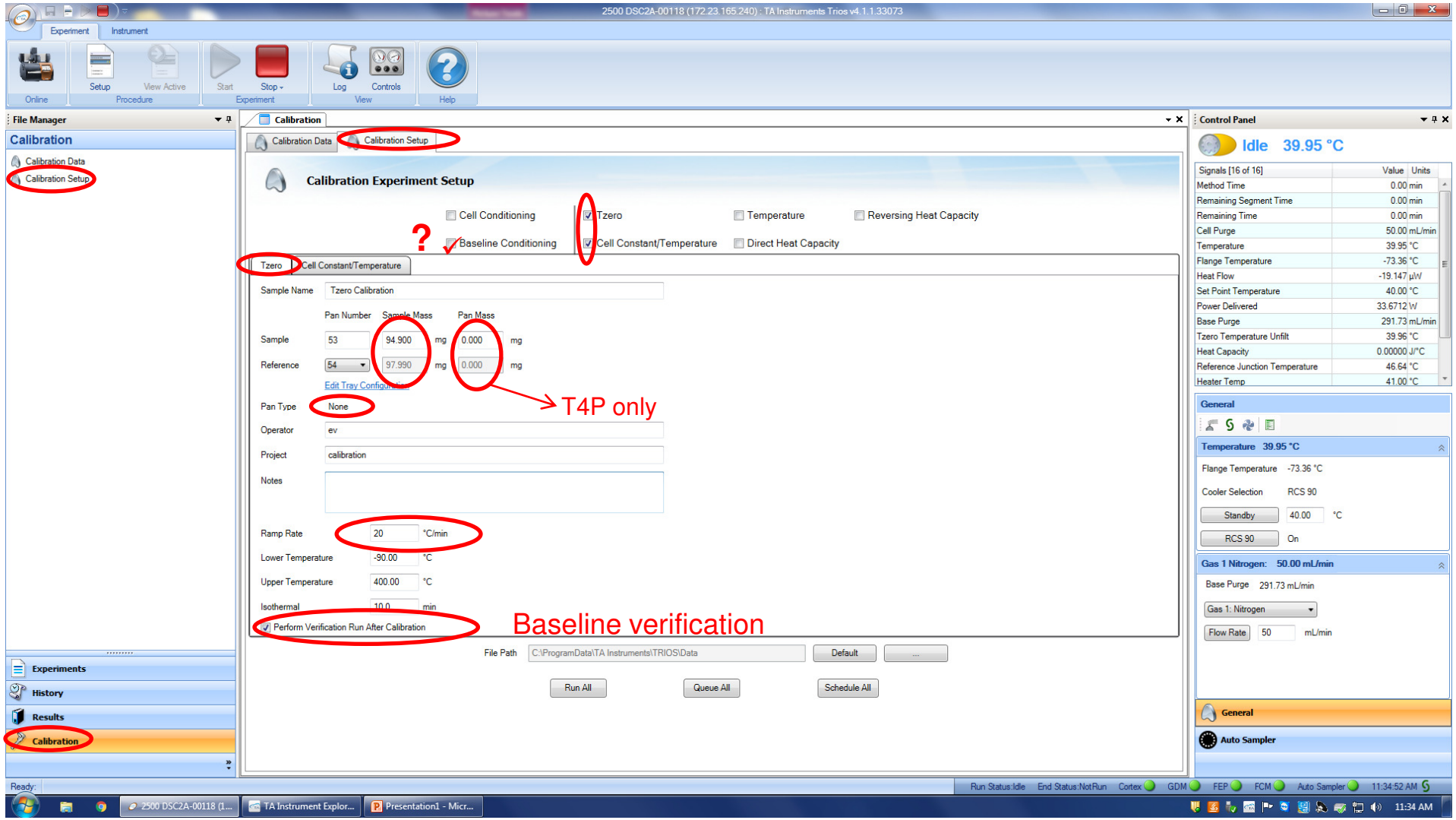
- Performed using calibration setup
  1. Run Empty Cell
  2. Run Sapphire on both Sample & Reference side



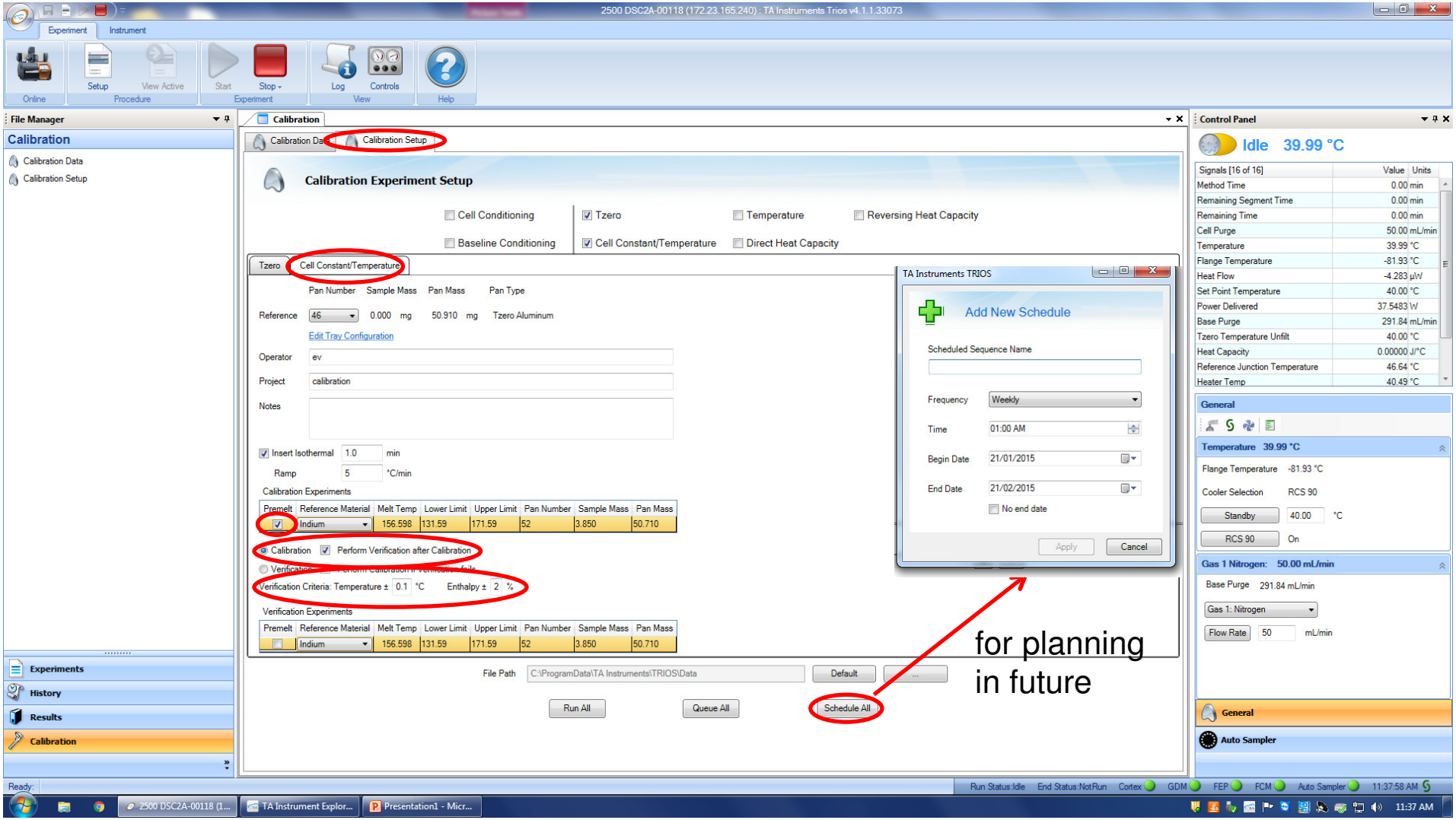
Tzero Calibration – DSC 2500 & DSC 250

- Might be good to cycle the cell several times between min/max temp to be used for calibration (baseline conditioning) prior to Tzero calibration
- Choice of temperature range for Tzero calibration: at least as broad as desired experimental range
- Do NOT run it at a heating rate lower than 10ºC/min, by preference 20ºC/min
- After Tzero calibration the temperature and enthalpy calibration is mandatory performed, e.g. with indium

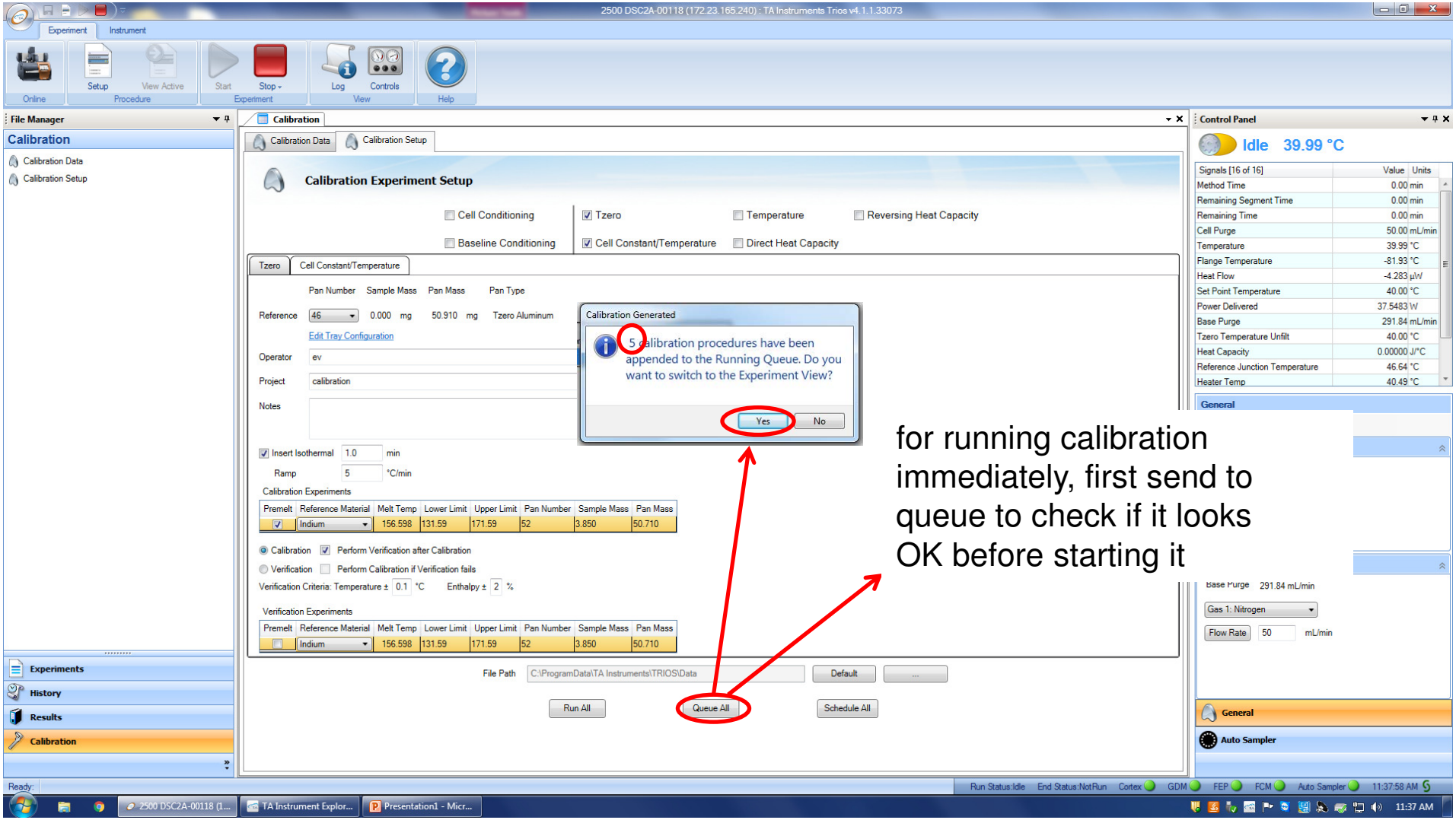
Discovery DSC Tzero Calibration



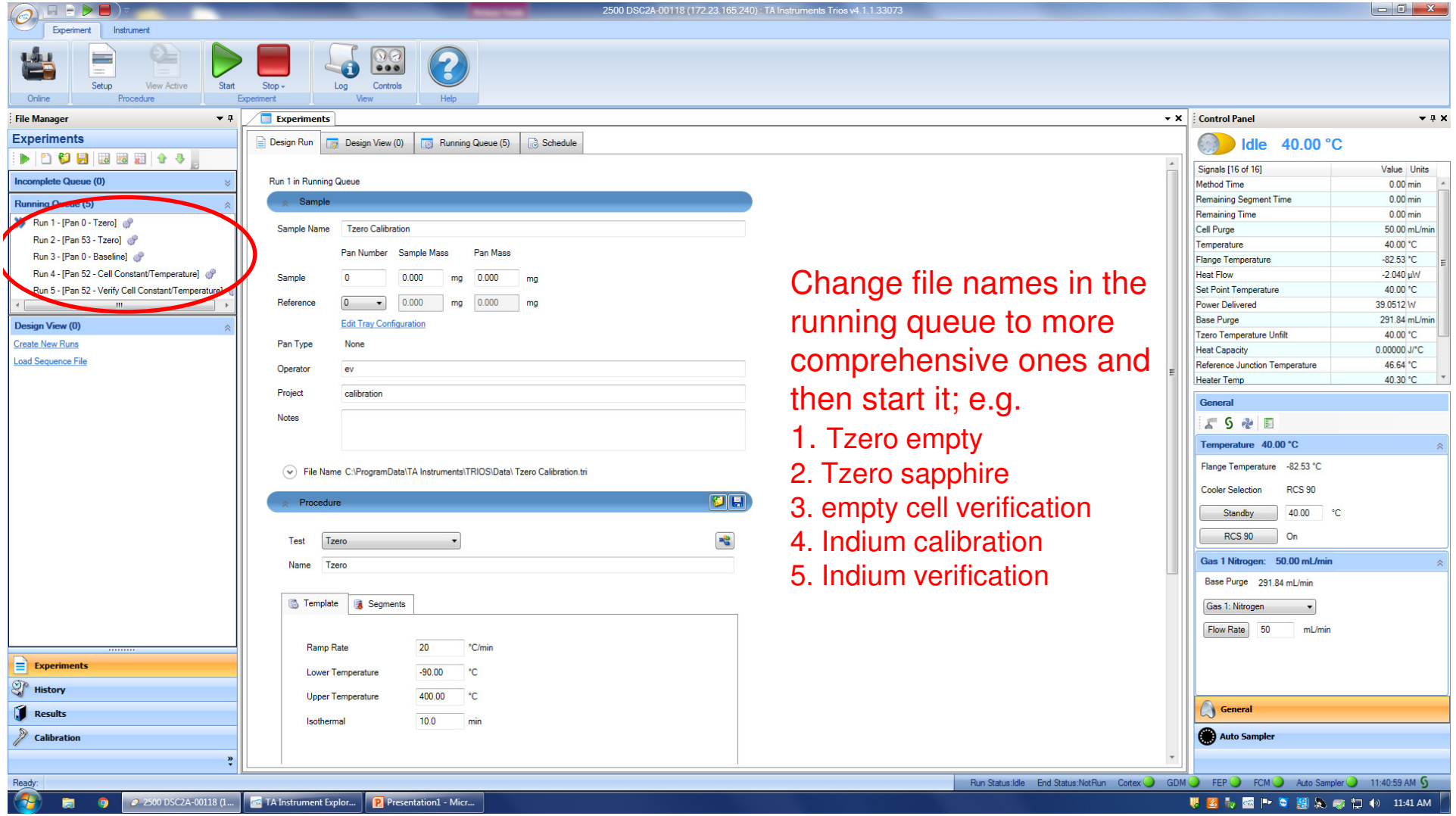
Discovery DSC Calibration



Discovery DSC Calibration



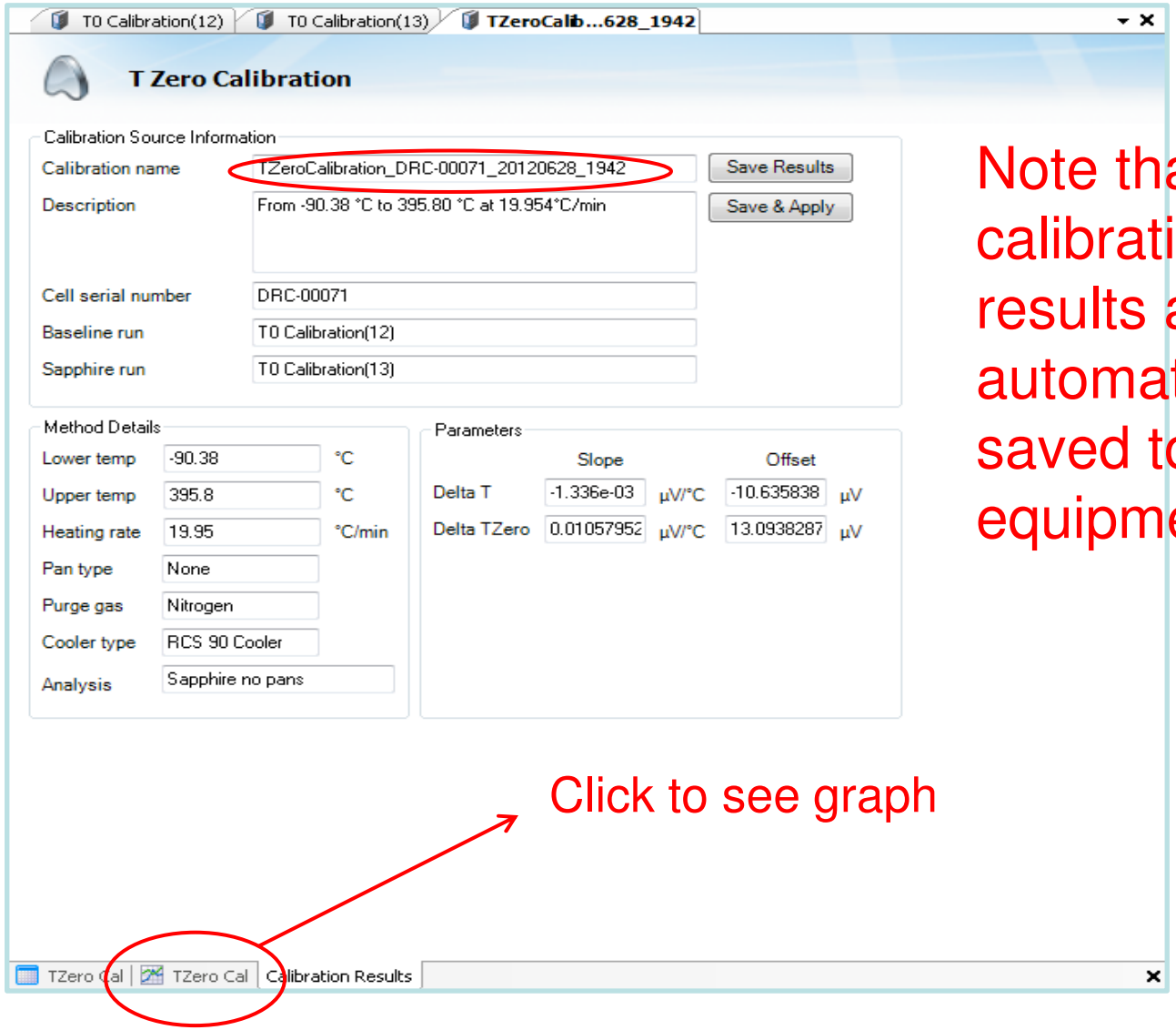
Discovery DSC Calibration



Change file names in the running queue to more comprehensive ones and then start it; e.g.

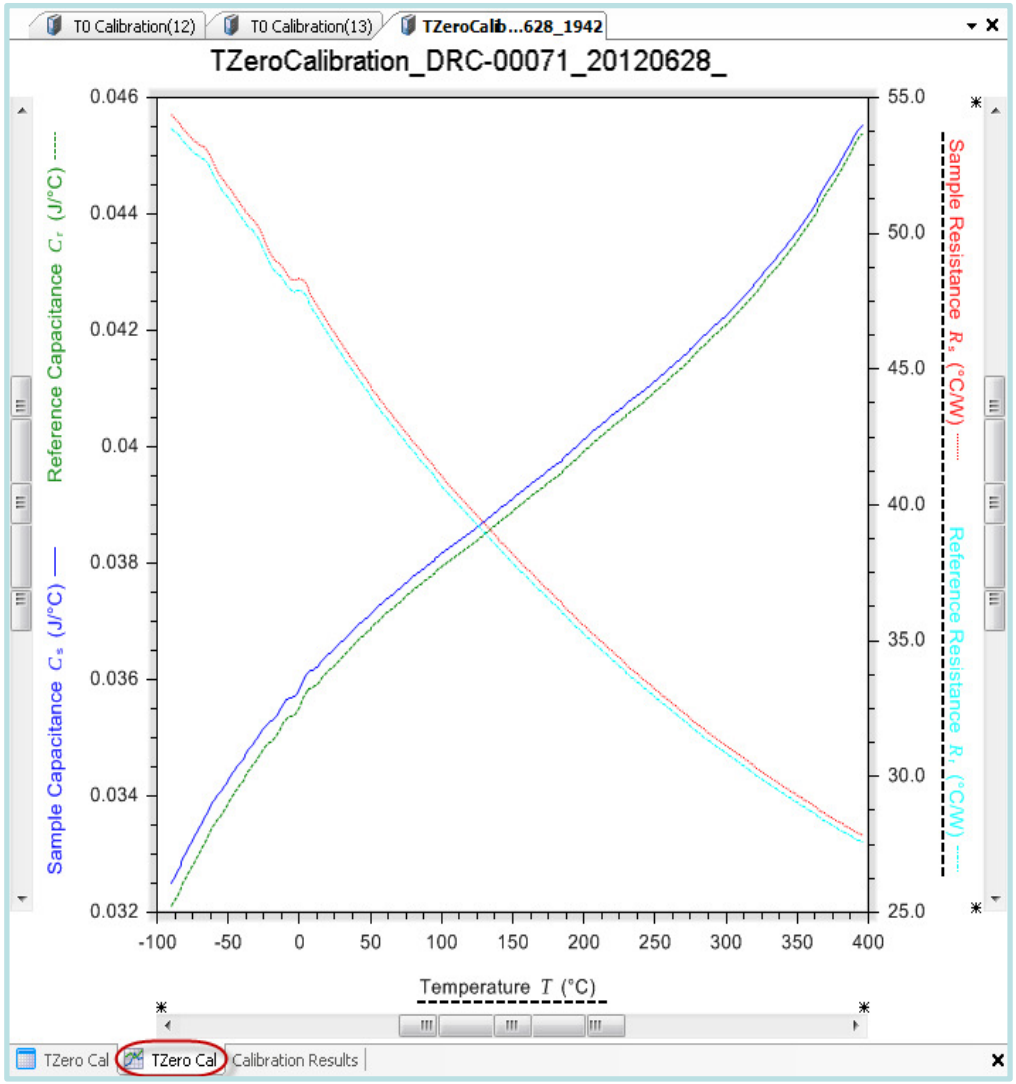
1. Tzero empty
2. Tzero sapphire
3. empty cell verification
4. Indium calibration
5. Indium verification

Viewing Tzero Calibration Results



Note that calibration results are automatically saved to the equipment

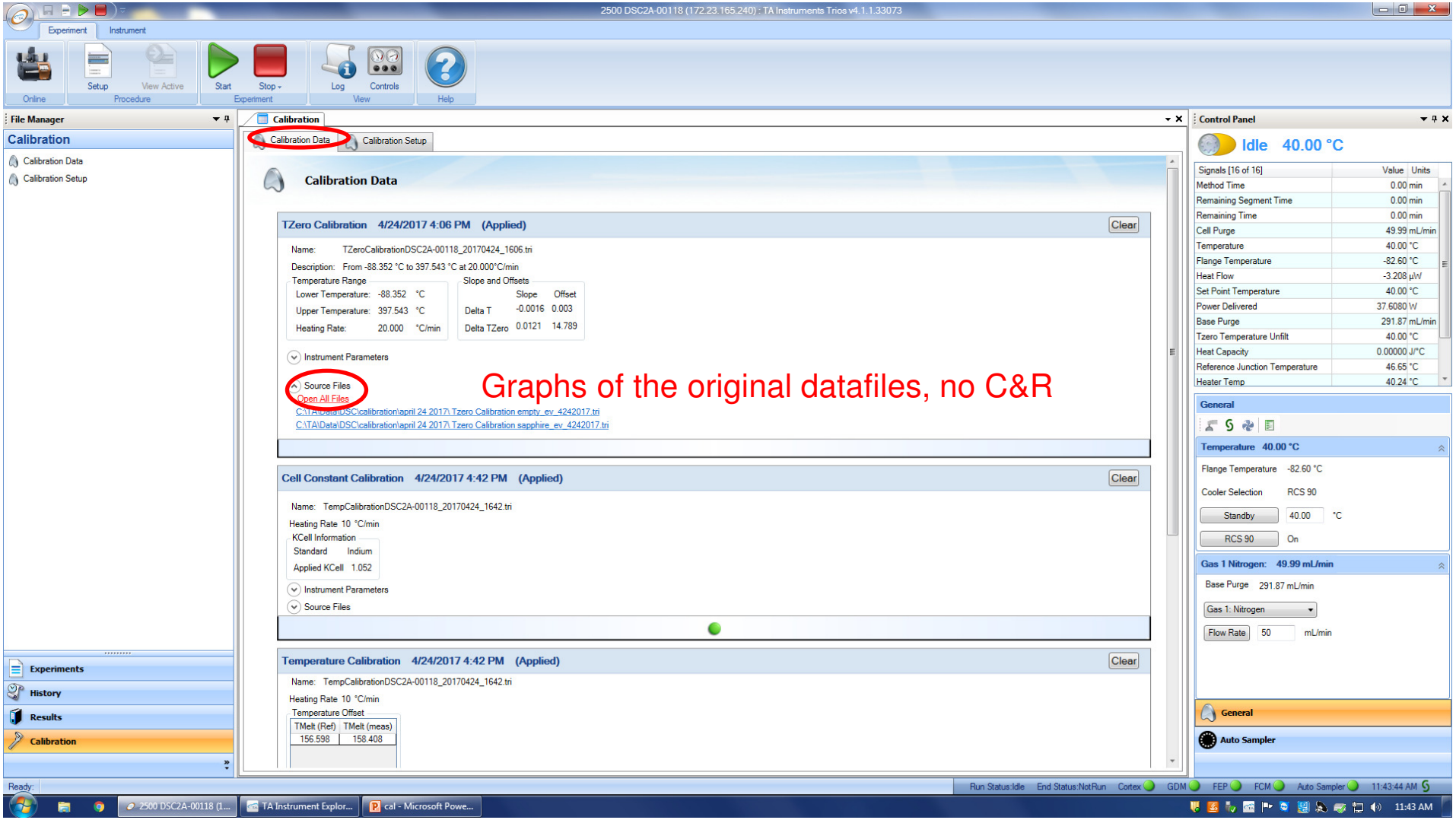
Viewing Tzero Calibration Results



Characteristics of the thermal resistances and heat capacities:
- Both curves should be smooth, with no steps, spikes or inflection points.
- Thermal resistances should always have negative slope that gradually decreases.
- Heat capacities should always have positive slope.

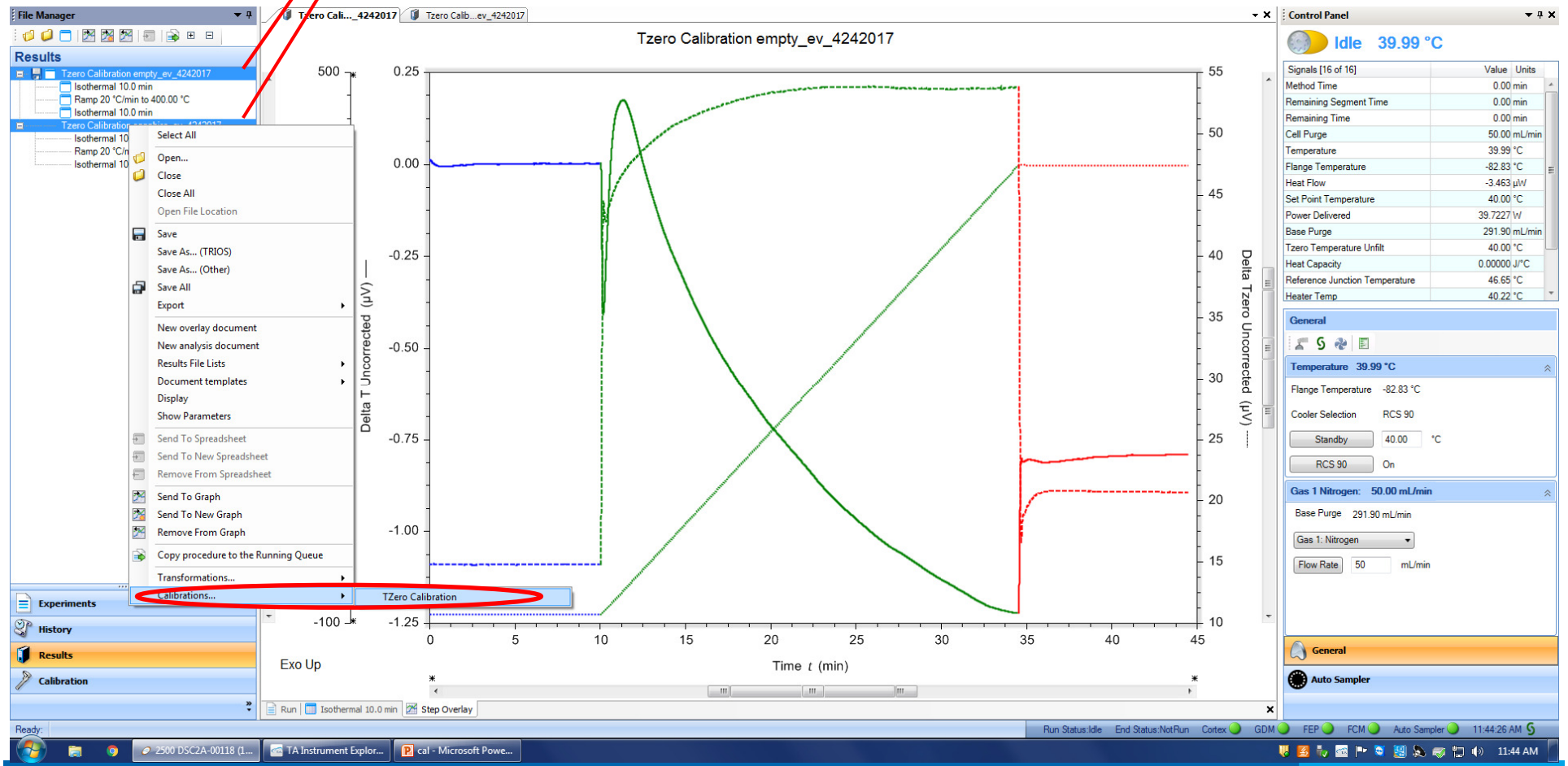
This cell is very well balanced. It is acceptable and usual to have larger differences between sample and reference.

Viewing Existing Tzero Calibration

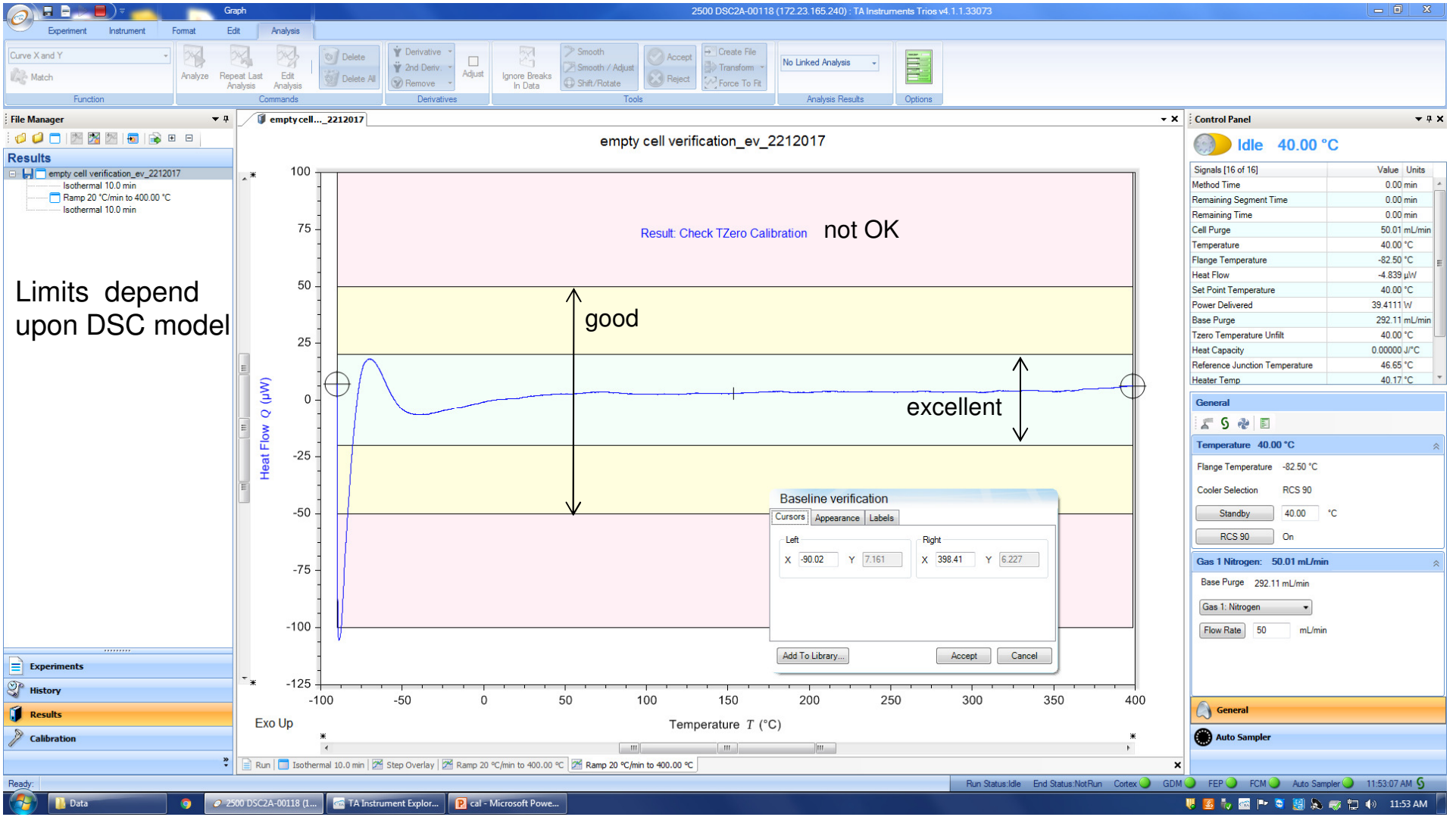


Viewing Existing Tzero Calibration

Highlight both files simultaneously, right click, calibrations, Tzero calibration, C&R are calculated, do not apply



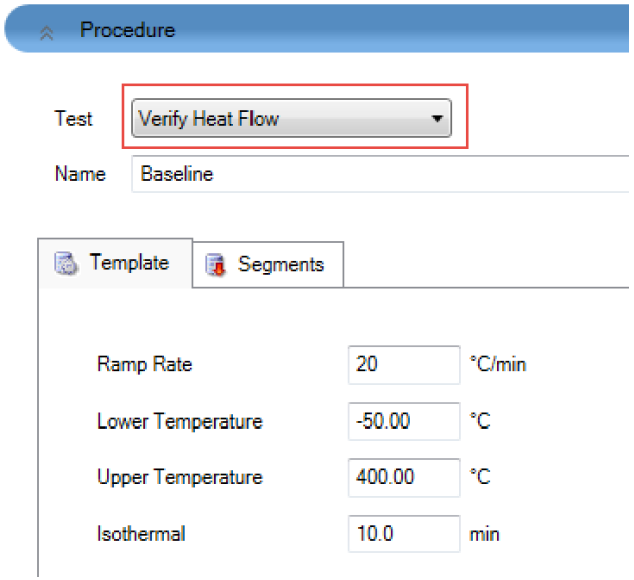
Baseline Verification



Baseline Verification

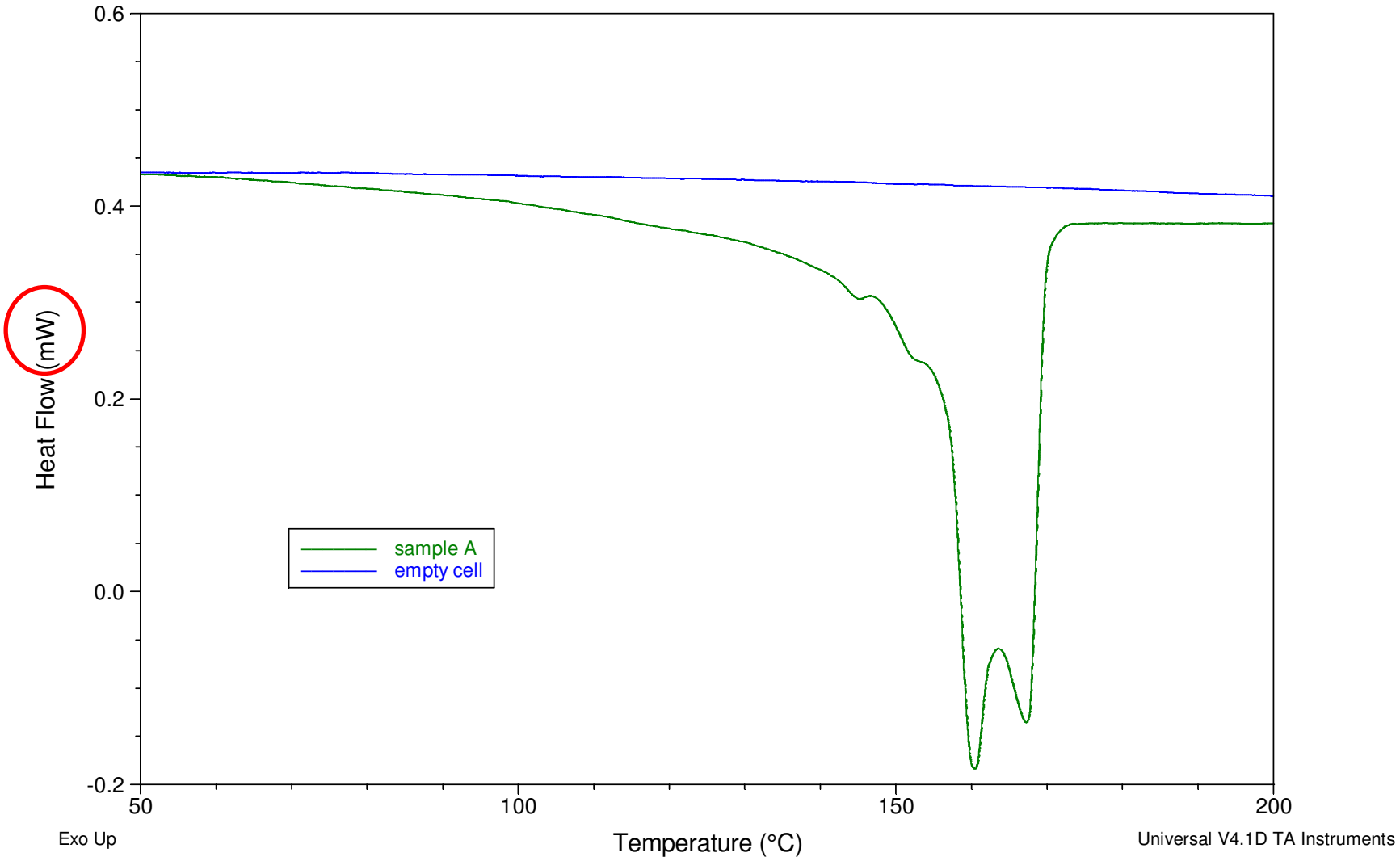
Tzero Calibration & Baseline Verification

- Always verify first the baseline before deciding to recalibrate Tzero !

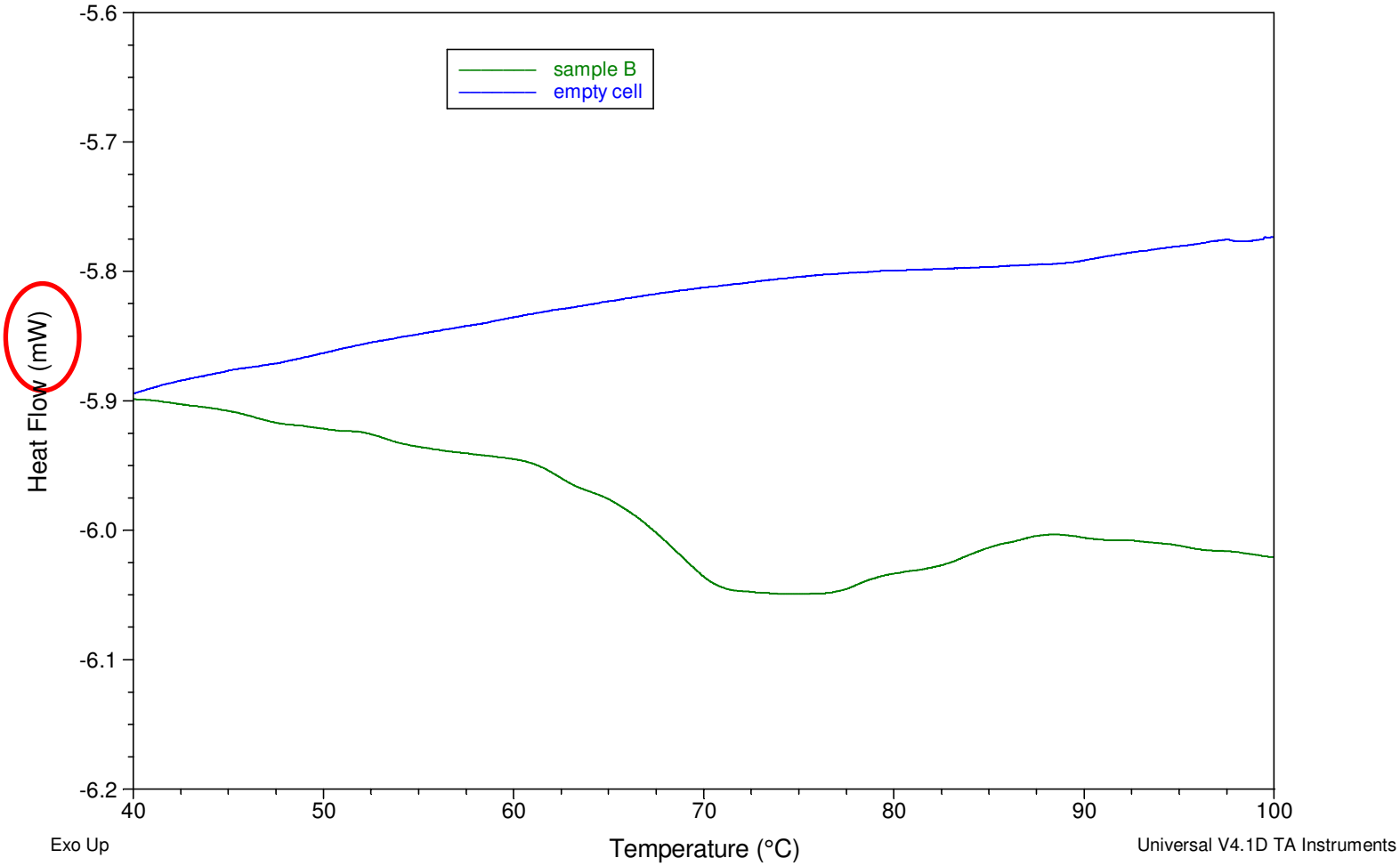


- Even if the verification is not OK, compare with sample transitions to check if flattest baseline is really required (plot overlay in mW)

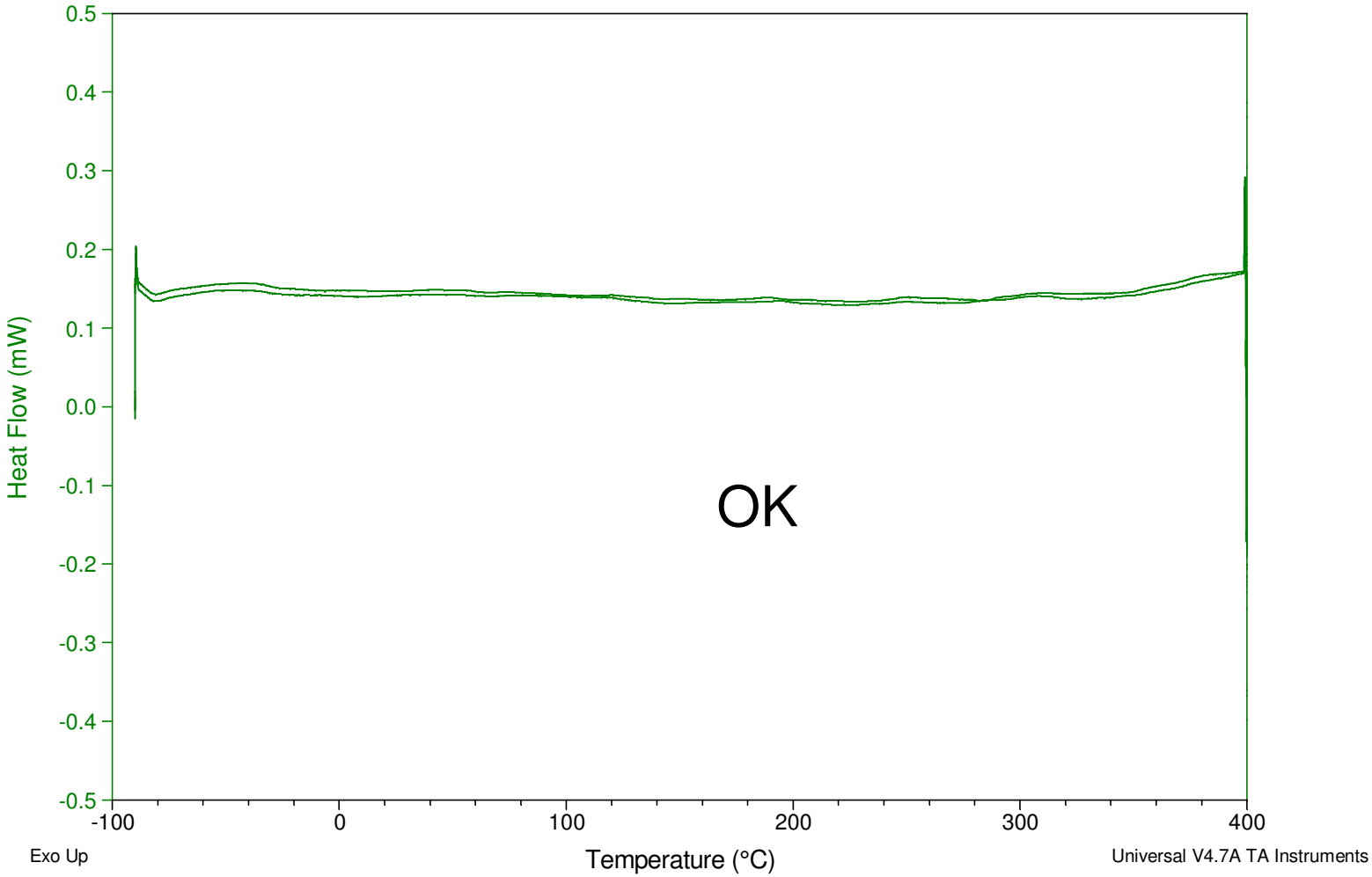
When to recalibrate ? NO



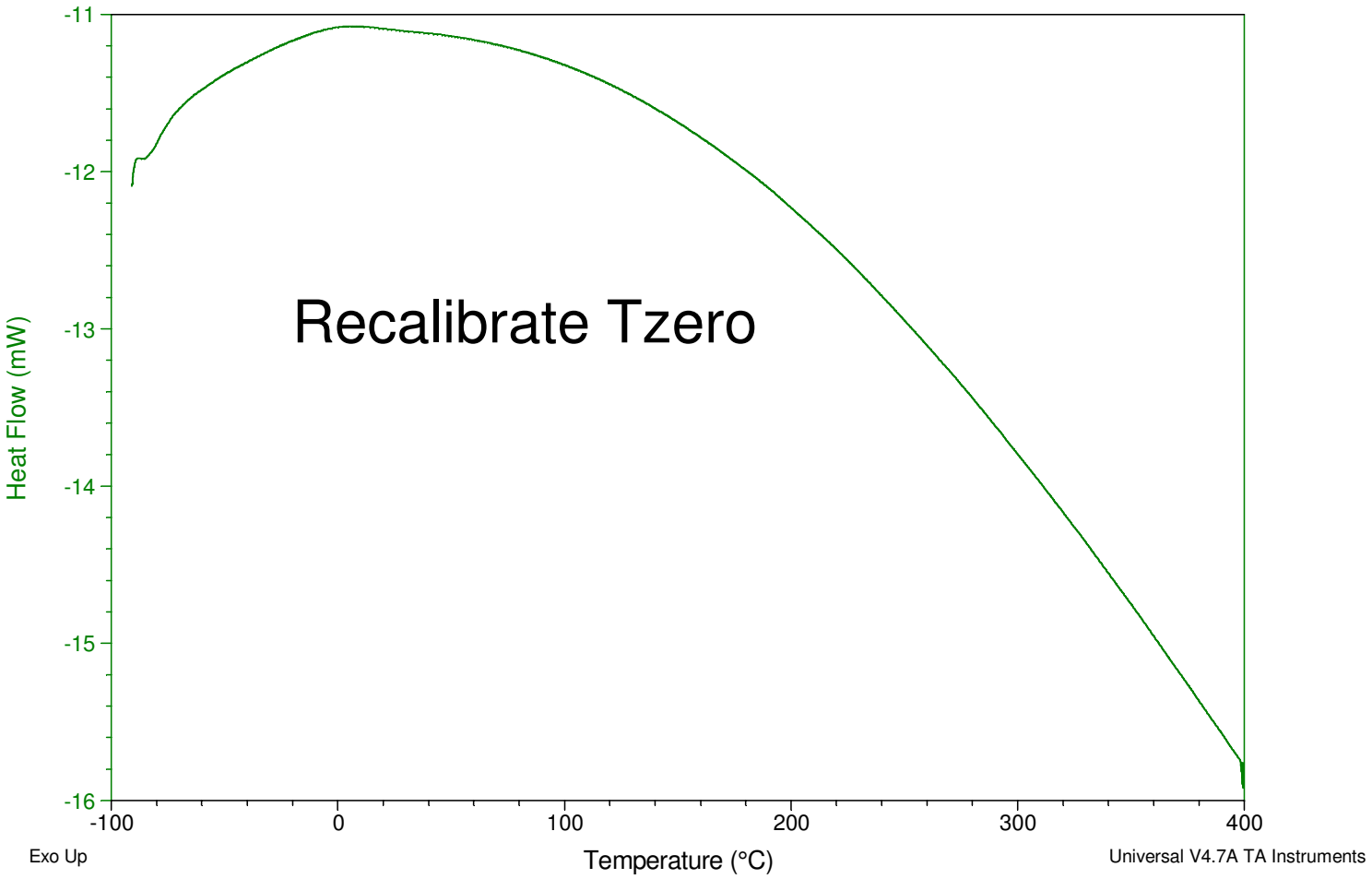
When to recalibrate ? YES



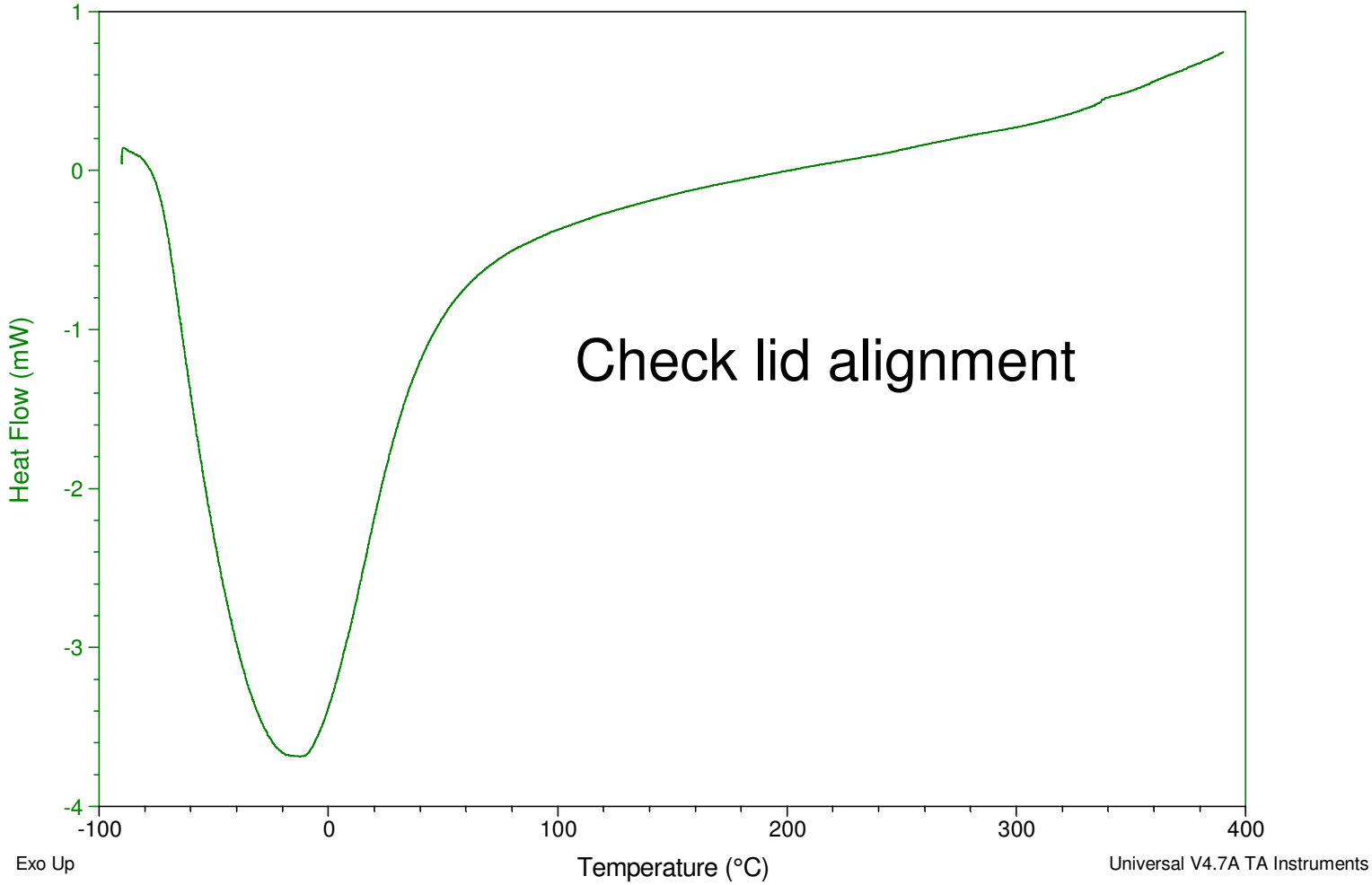
Baseline OK ? If not which action ?



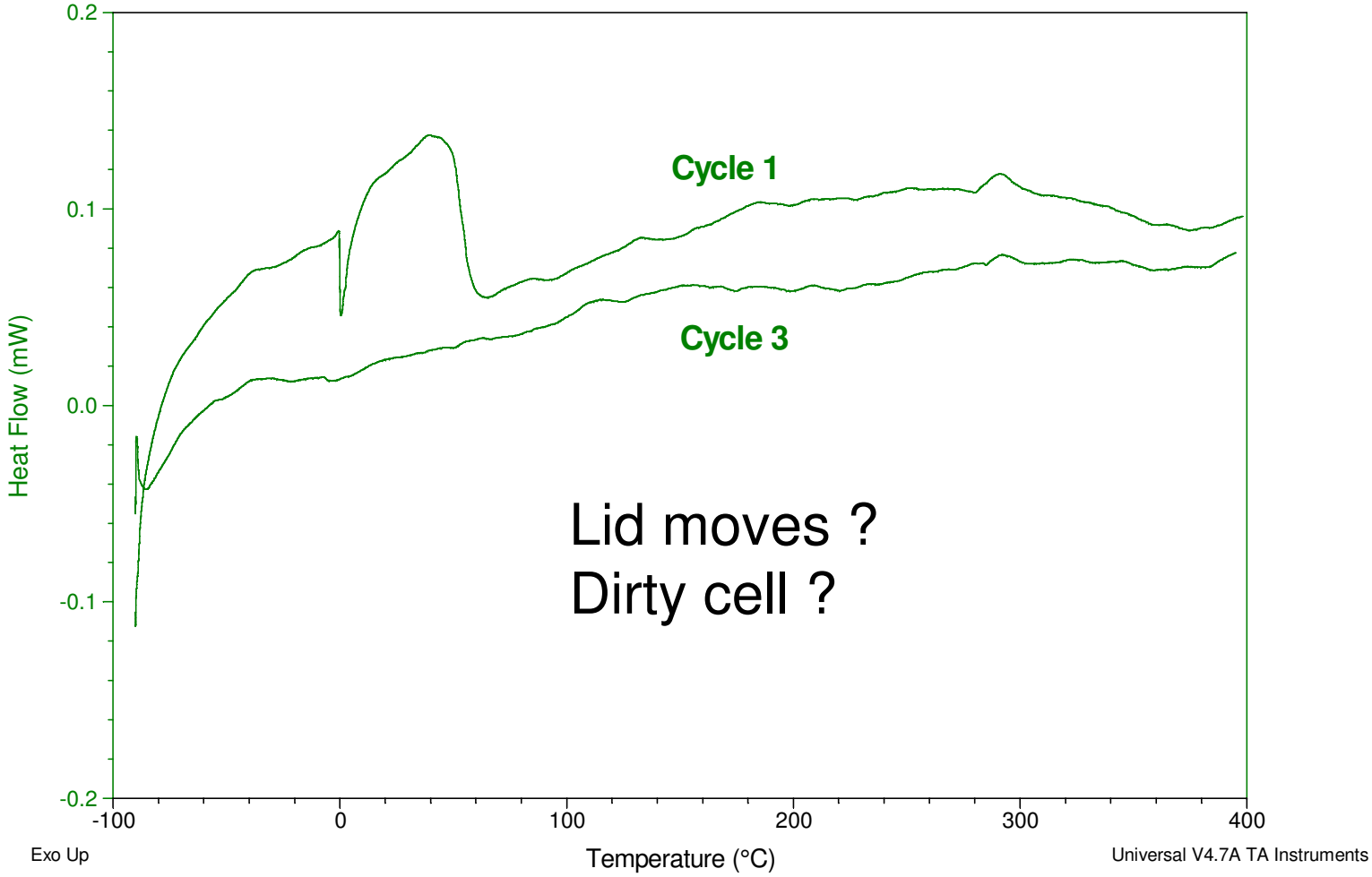
Baseline OK ? If not which action ?



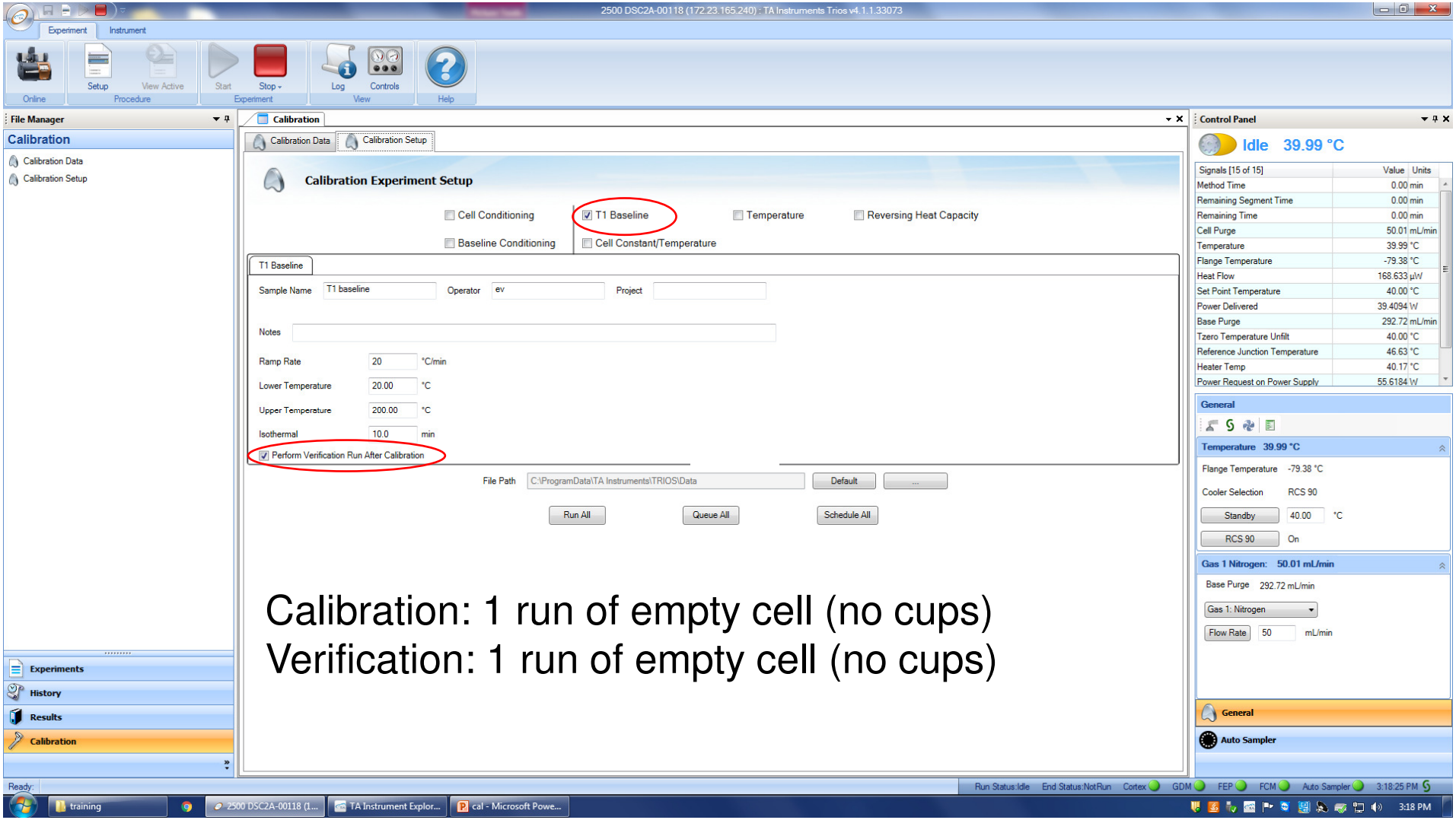
Baseline OK ? If not which action ?



Baseline OK ? If not which action ?

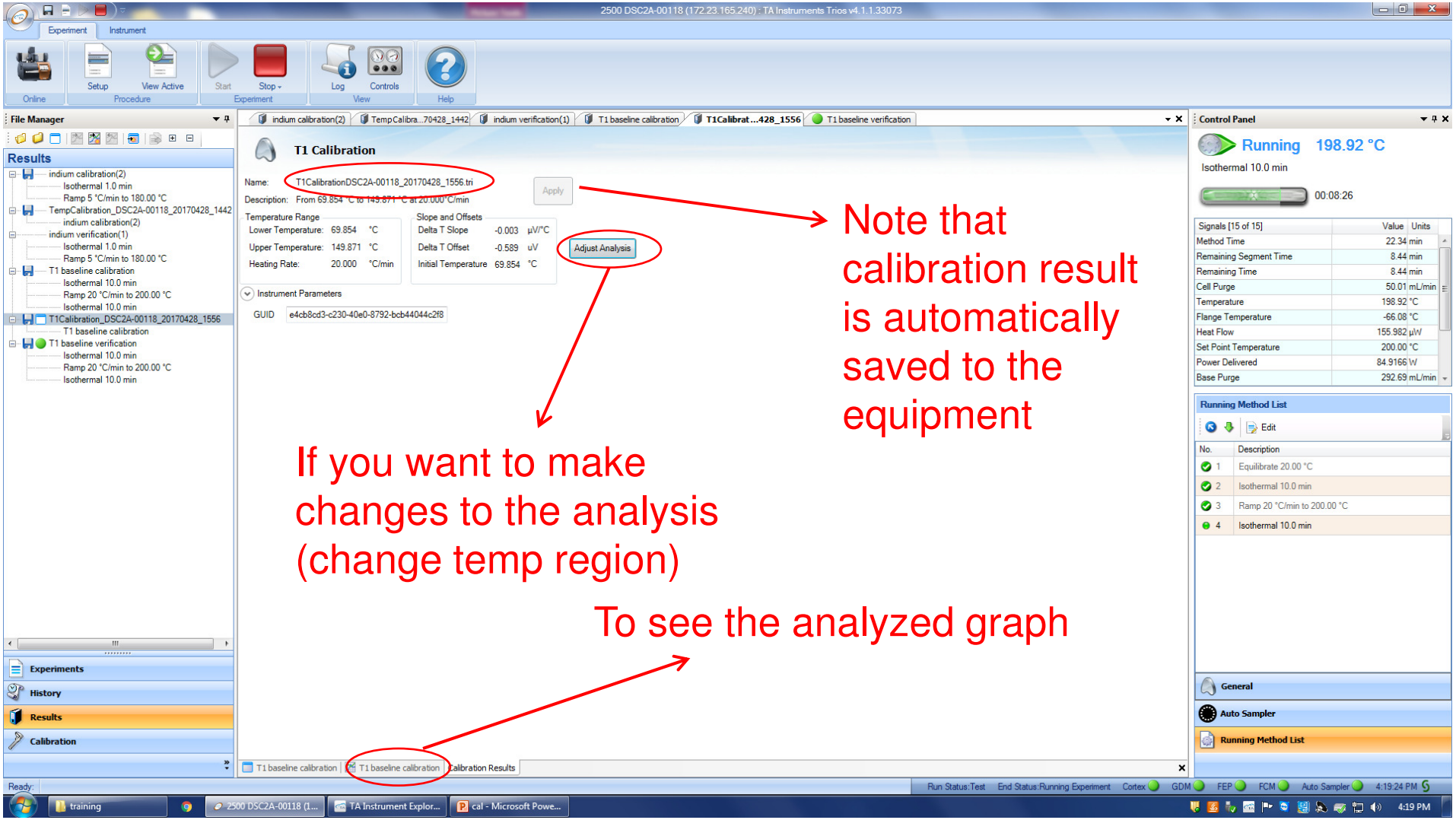


Baseline Calibration – DSC 25

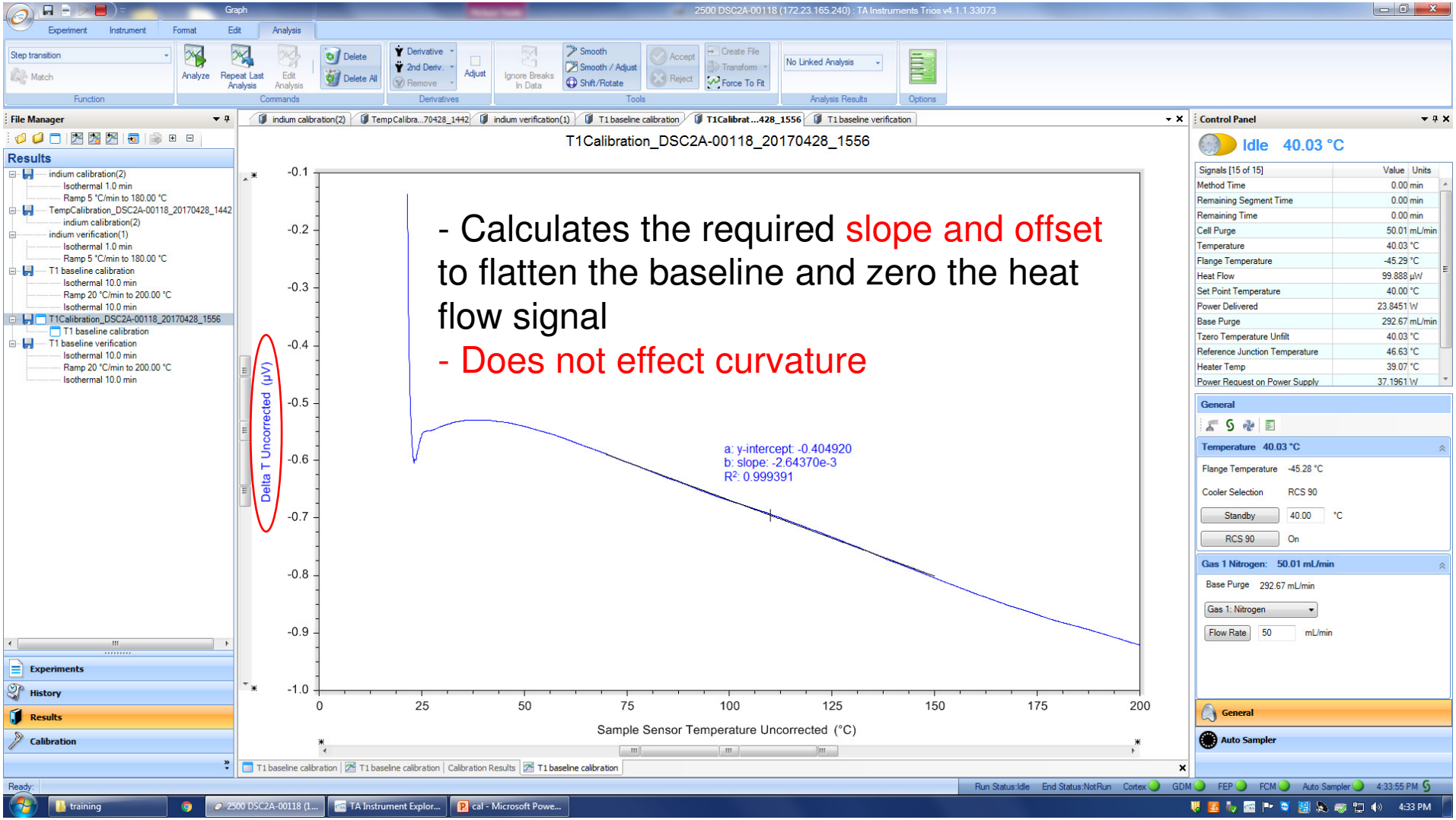


Calibration: 1 run of empty cell (no cups)
Verification: 1 run of empty cell (no cups)

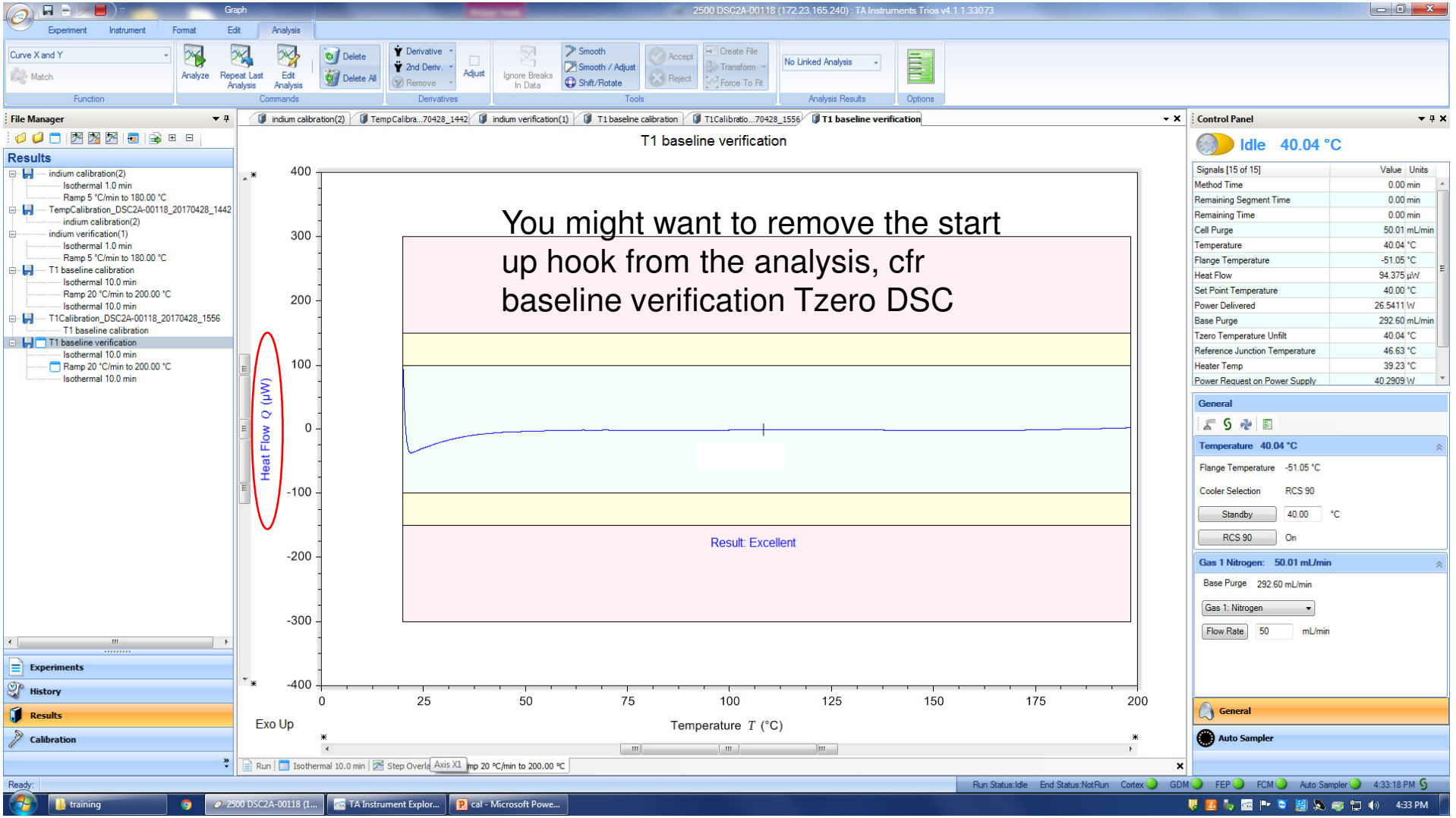
Baseline Calibration – DSC 25



Baseline Calibration – DSC 25



Baseline Verification – DSC 25



DSC Calibrations: Cell Constant & Temperature

- Cell constant is the calorimetric calibration which corrects for non-adiabatic heat transfer (heat lost to the surroundings)
- It is performed using a well-known melting standard such as indium

$$Cell\ Constant = \frac{\Delta H_f\ (literature)}{\Delta H_f\ (measured)}$$

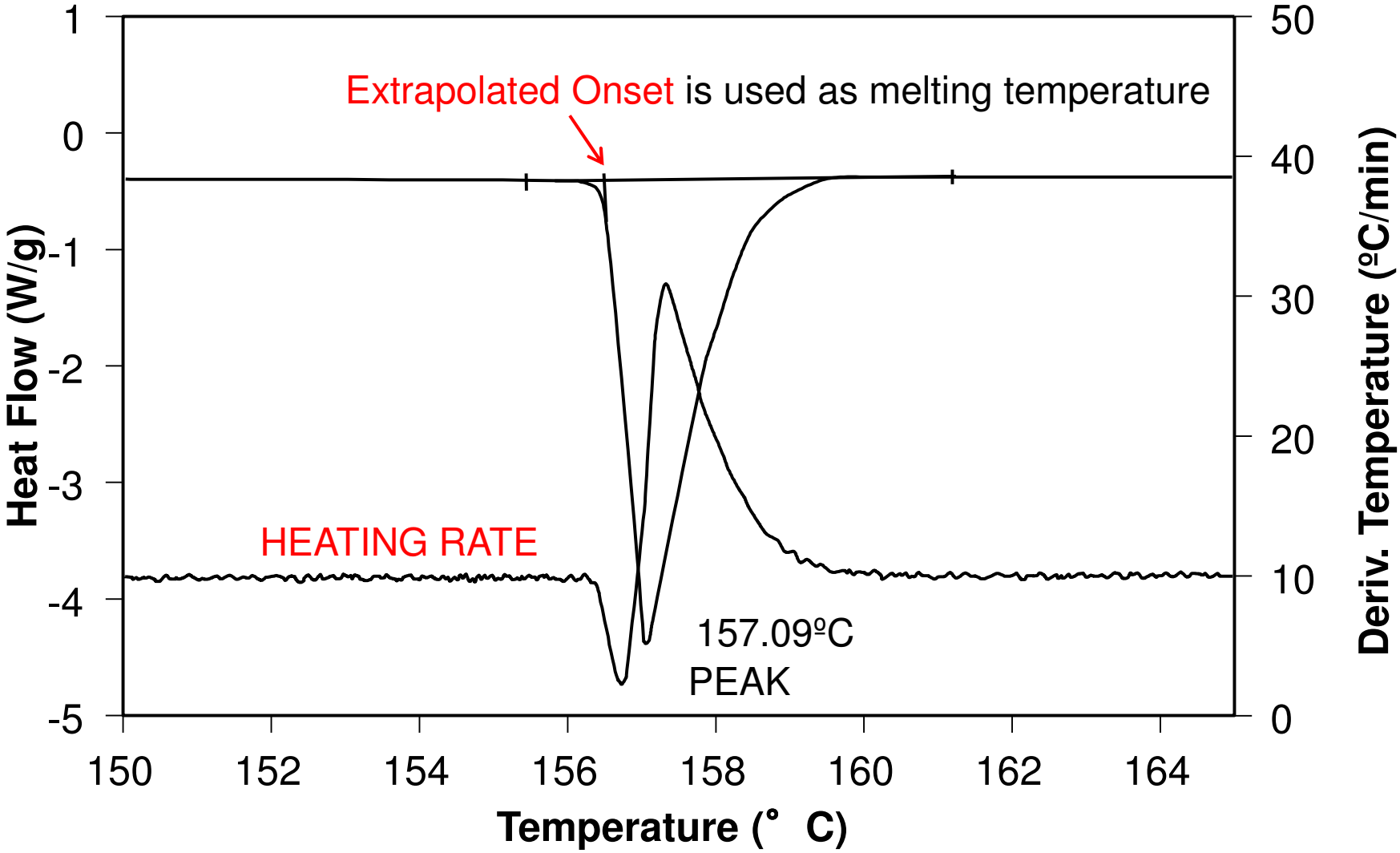
Cell constant is used as multiplication factor for heat flow; typically cell constant is close to 1.

- Temperature Calibration points are determined by comparing the measured melting onset temperature to the literature value
- TA Instruments software allows for up to 5 temperature calibration points
  - Generally, these should bracket the temperature range of interest for subsequent samples

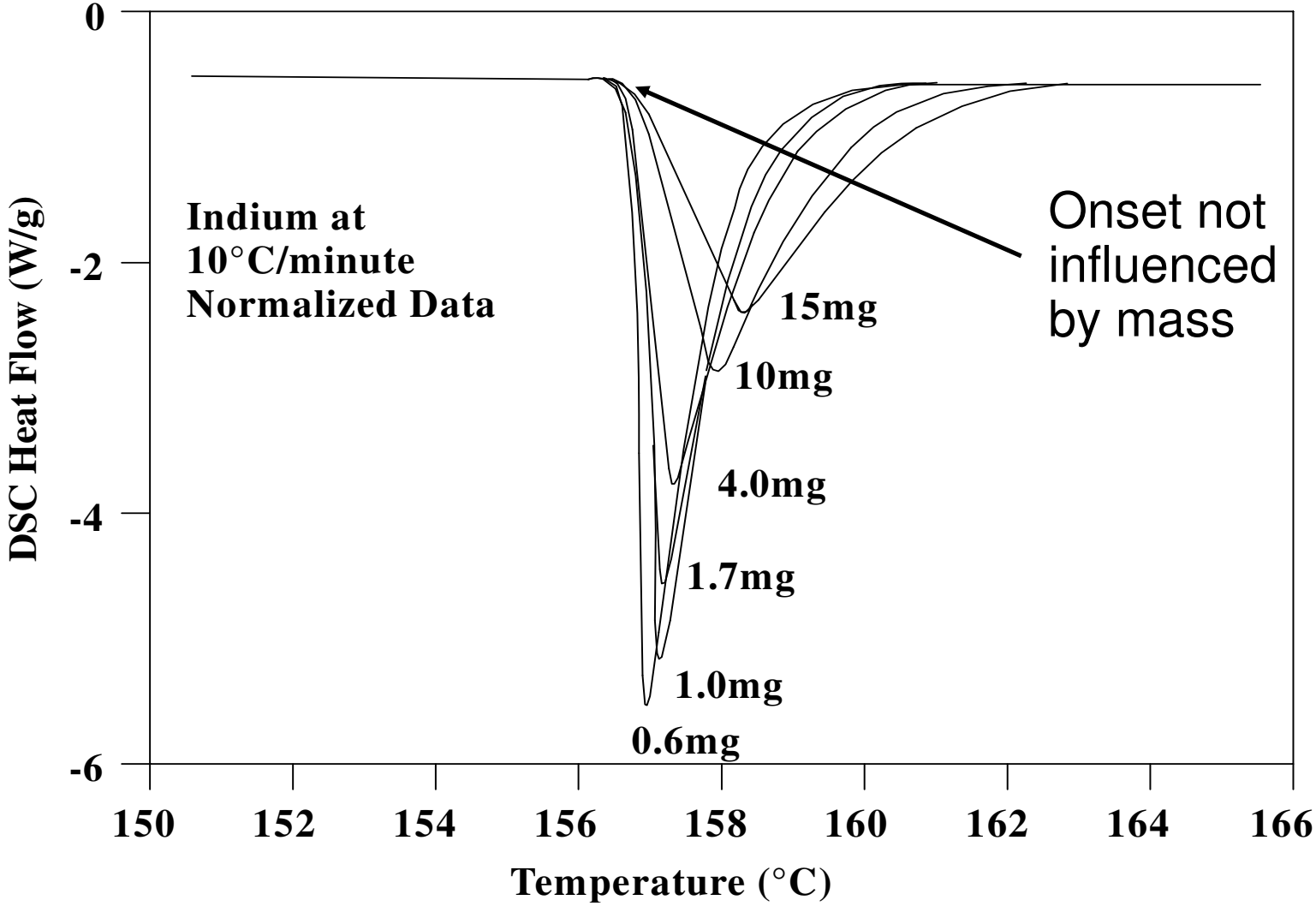
Heat Flow Calibration (Cell Constant)

- Heat Flow Calibration of Differential Scanning Calorimeters – ASTM E-968
- Enthalpy Calibration
- One Run -> Indium metal
  - Sample Weight 1-5 mg
  - Flatten and pre-melt sample the first time you run it
  - Re-use sample max 10 times
  - Heating rate of 10ºC/min recommended (heat flow calibration does not depend upon heating rate, but slow rates give more noise)
  - Dependent upon purge gas/flow rate and pan type

Temperature Calibration



Influence of Sample Mass



Temperature Calibration

- ASTM E967 method
  - Pure metals typically used
  - Calibration depends upon purge gas/flow rate and pan type
  - Calibration changes a little with heating rate
  - Temperature calibration (1 point) is automatically included when calibrating cell constant
  - Instead of 1 single temperature multiple calibration points (up to a maximum of five) can be used (specify temperature calib then)
  - Choose the calibration standards so that their transition temperatures span the interesting measuring region
  - Use tin, lead, gallium and zinc one time only

Temperature Calibration

- If you want to calibrate temperature with more than 1 standard choose temperature calibration and include all standards (also indium, despite the fact that indium has already been run for enthalpy calibration)
- If you want to run calibration with indium at a lower rate than 10ºC/min, by preference first perform cell constant calib at 10ºC/min, and subsequently temp calib only at the lower heating rate

Temperature and Enthalpy Standards

Enthalpy (cell constant)

- **Benzoic acid (147.3 J/g) Tm = 123° C**
- **Urea (241.8 J/g) Tm = 133° C**
- **Indium (28.71 J/g) Tm = 156.6° C**
- **Anthracene (161.9 J/g) Tm = 216° C**

Adamantane -65.54ºC 20.57 J/g

Temperature

- **Cyclopentane* -150.77° C**
- **Cyclopentane* -135.09° C**
- **Cyclopentane* -93.43° C**
- **Cyclohexane# -83° C**
- **Water# 0° C**
- **Gallium# 29.76° C**
- **Phenyl Ether# 30° C**
- **p-NitrotolueneE 51.45° C**
- **NaphthaleneE 80.25° C**
- **Indium# 156.60° C**
- **Tin# 231.95° C**
- **Lead* 327.46° C**
- **Zinc# 419.53° C**

* GEFTA recommended
Thermochim. Acta, 219 (**1993**) 333.

\# ITS 90 Fixed Point

E Zone refined organic compound (sublimes)

see TN-11

Traceable Calibration Materials

- Certified materials used to establish traceability of instrument calibration

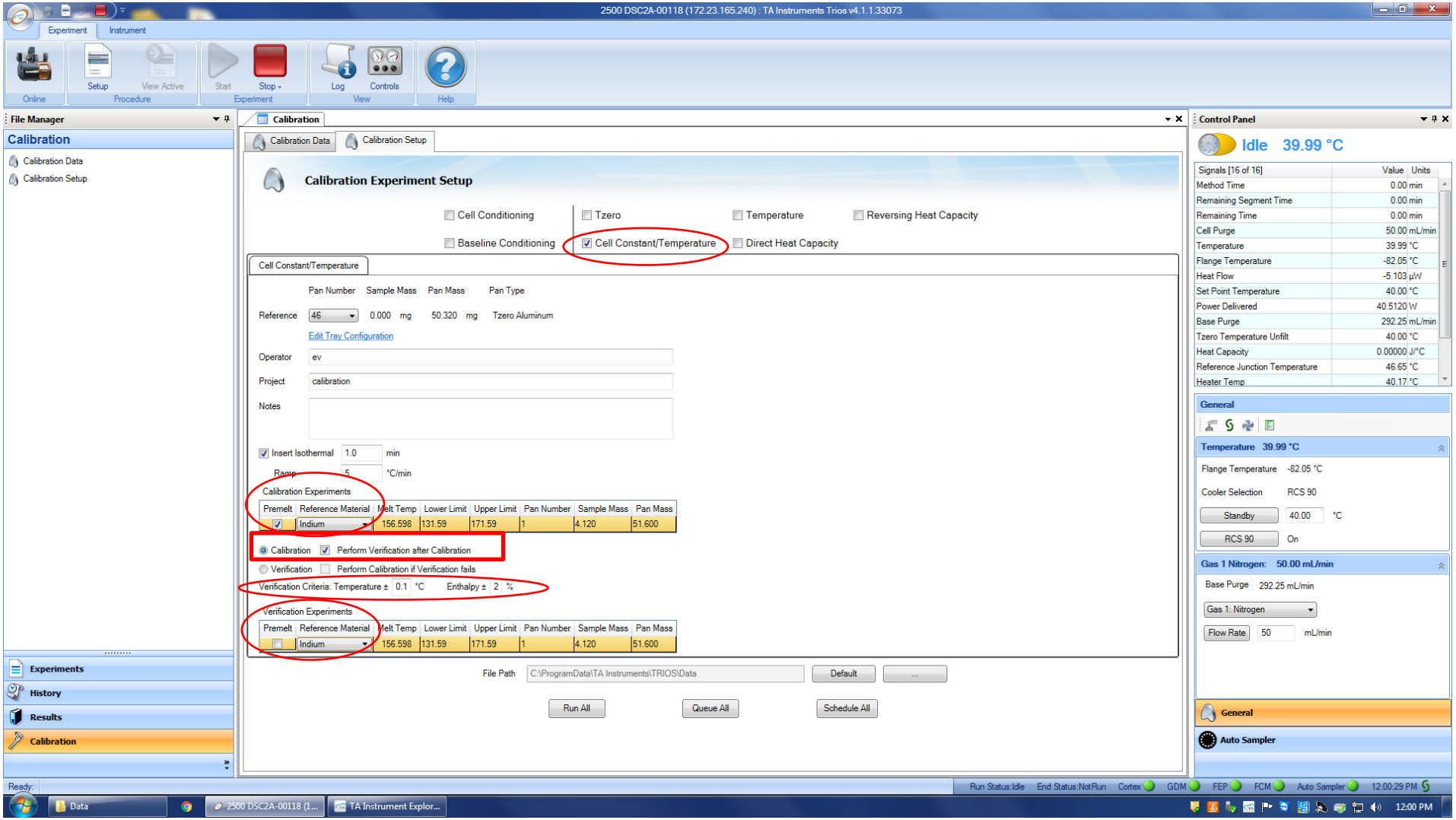
- NIST: US, Gaithersburg, MD 20899
  - http://www.ts.nist.gov/srm
- Laboratory of the Government Chemist, UK
  - http://www.lgc.co.uk/

- ISO certification often requires third party calibration of instruments:
  - Service provided by TA Instruments service representative using certified materials
  - Certificate of Calibration issued showing traceability of calibration to a national laboratory

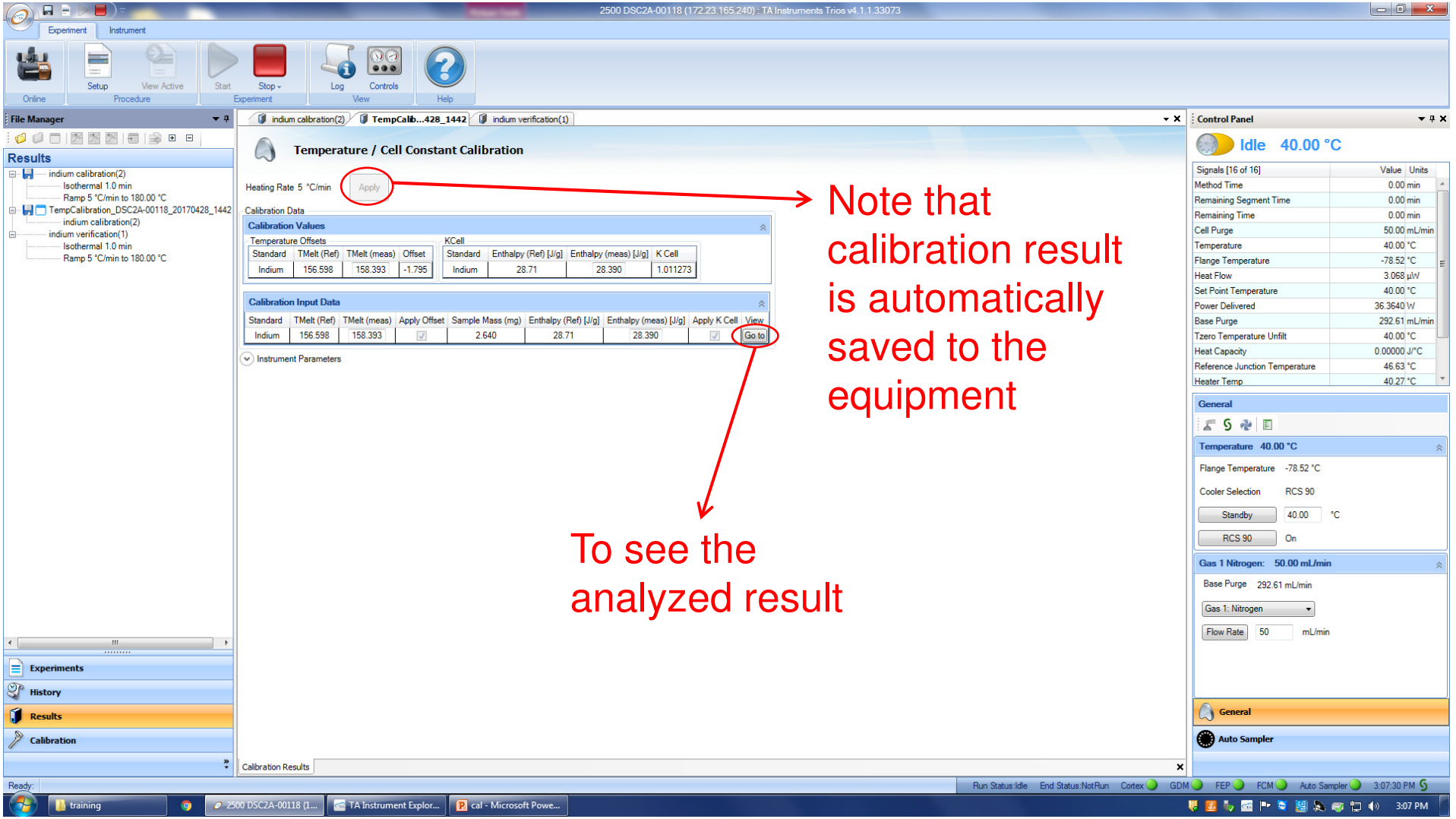
Verifying Heat Flow & Temperature

- Run Indium as a sample
- Analyze melt and record melt onset and heat of fusion
- Compare to known values
  - Melting of In 156.598ºC
  - Heat of Fusion 28.71J/g
- Always verify first before you decide to recalibrate

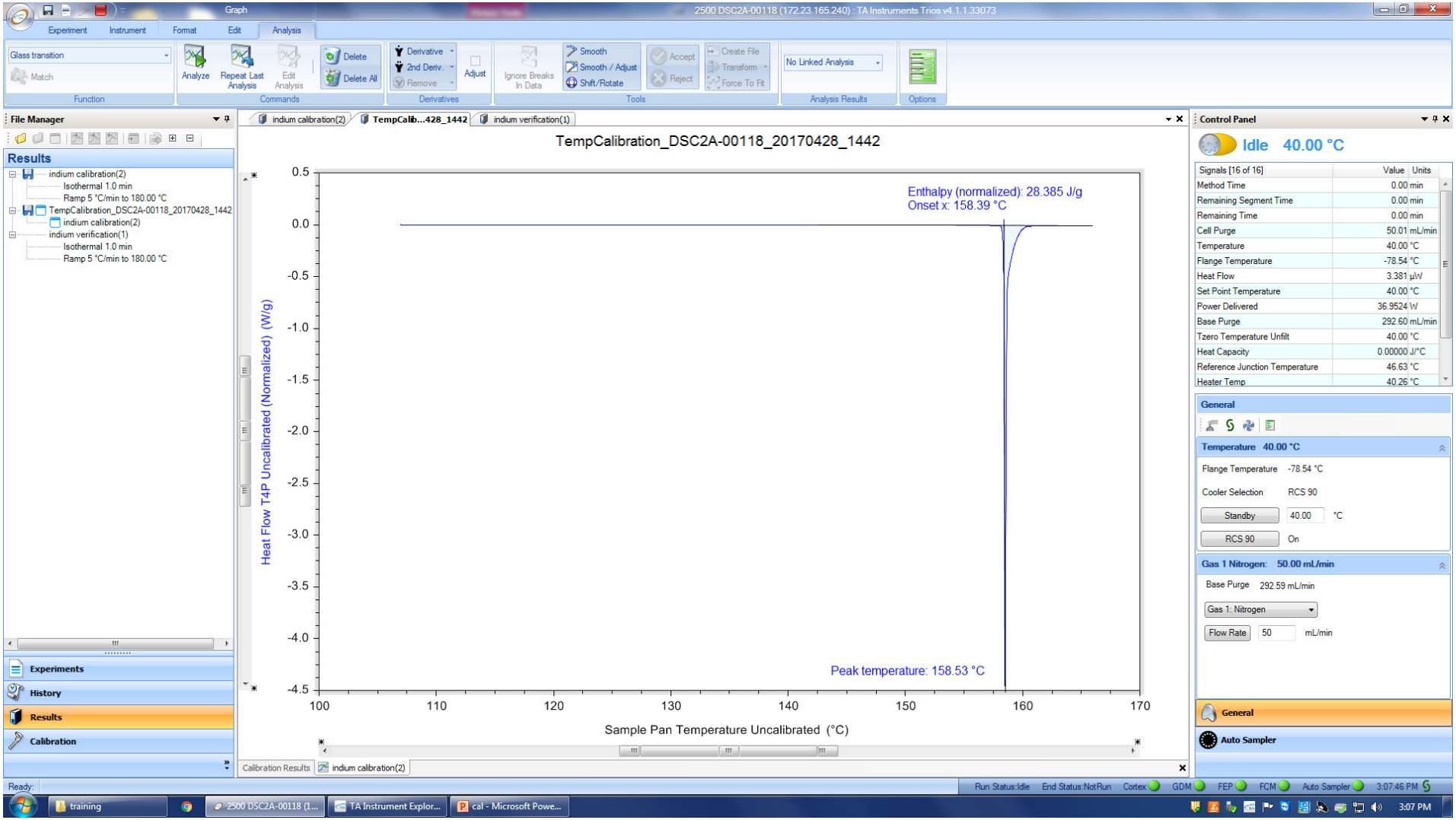
Calibration & Verification of Heat Flow & Temperature, All DSC's



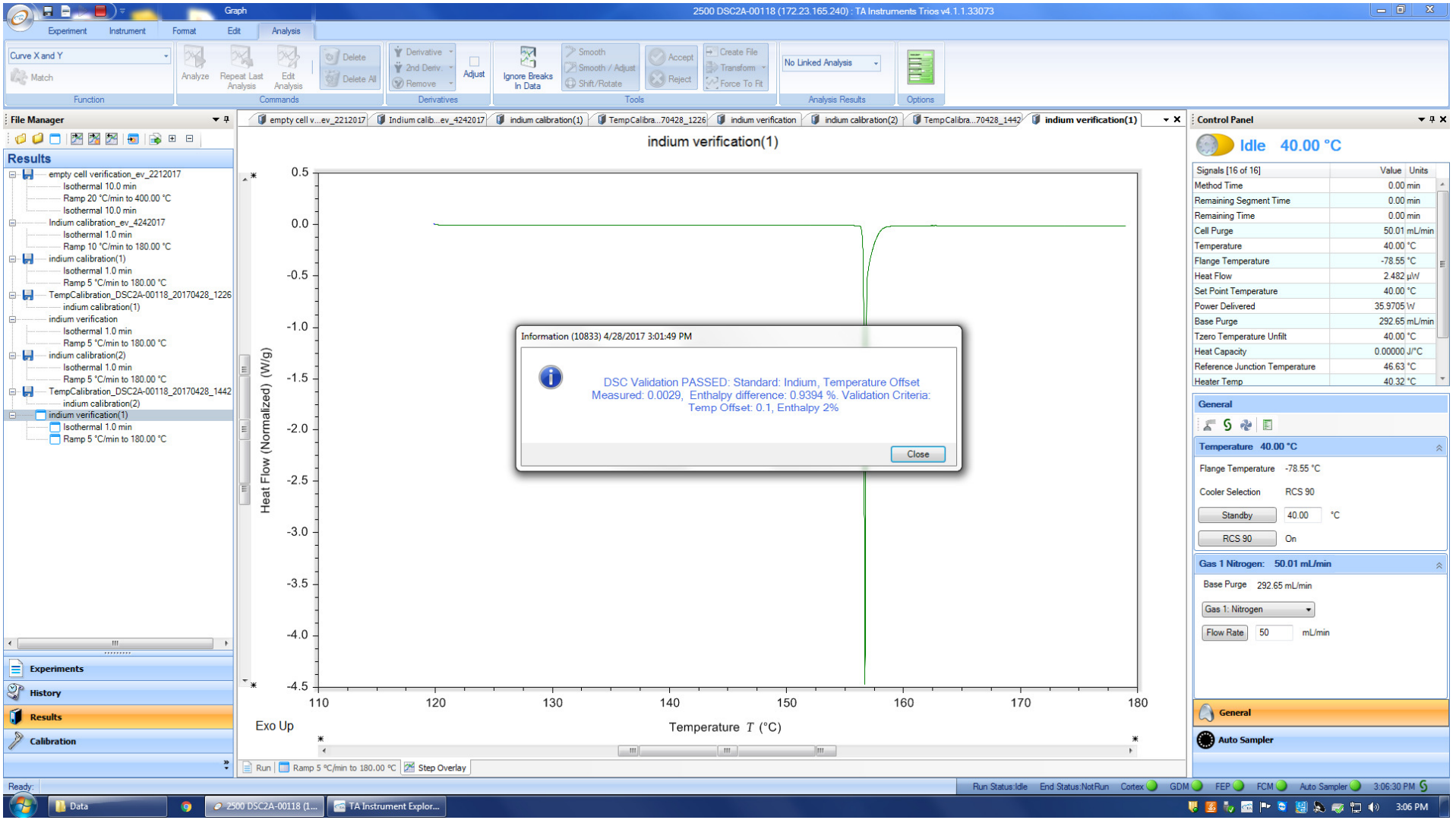
Calibration of Heat Flow & Temperature, All DSC's



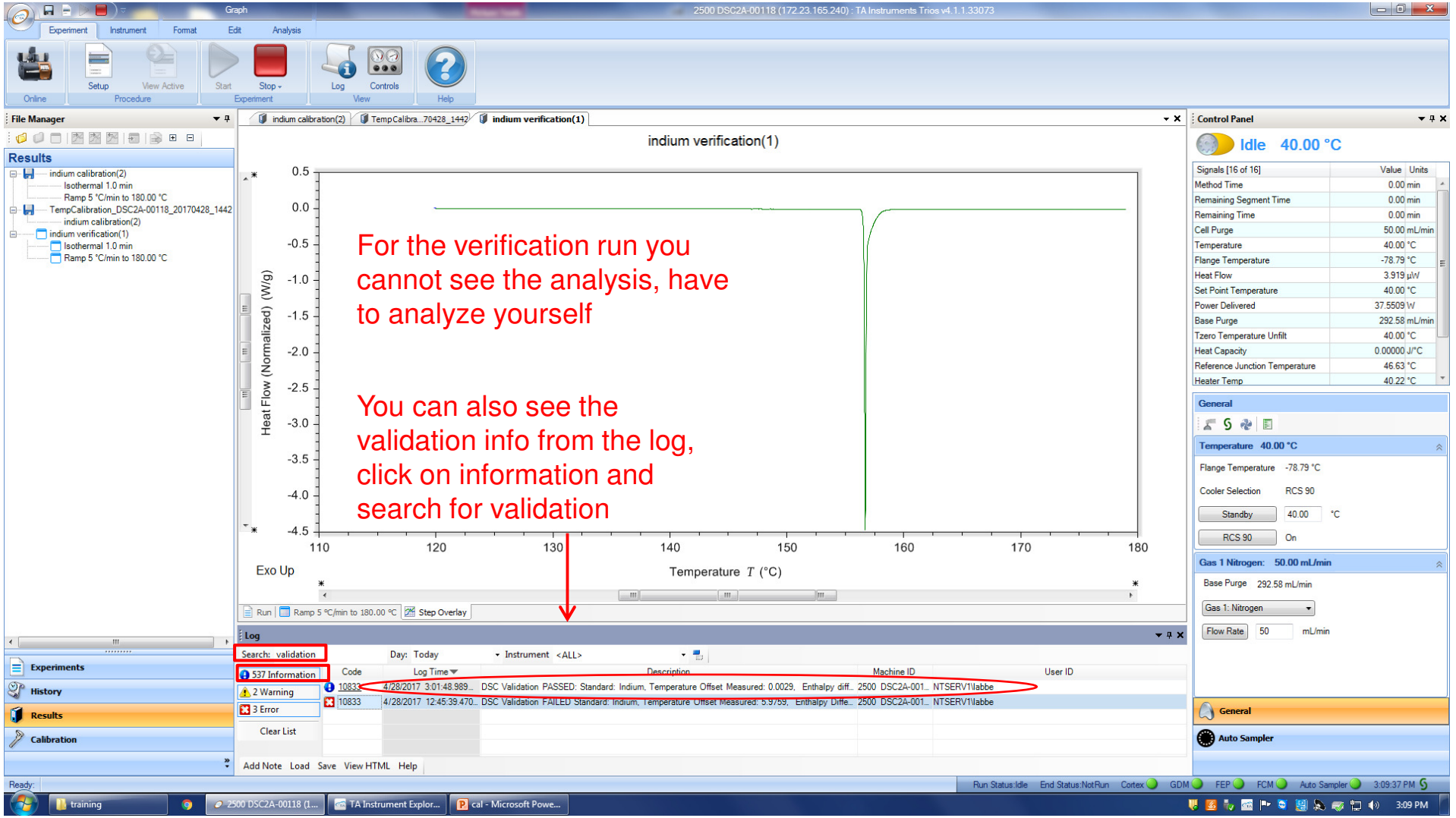
Calibration of Heat Flow & Temperature, All DSC's



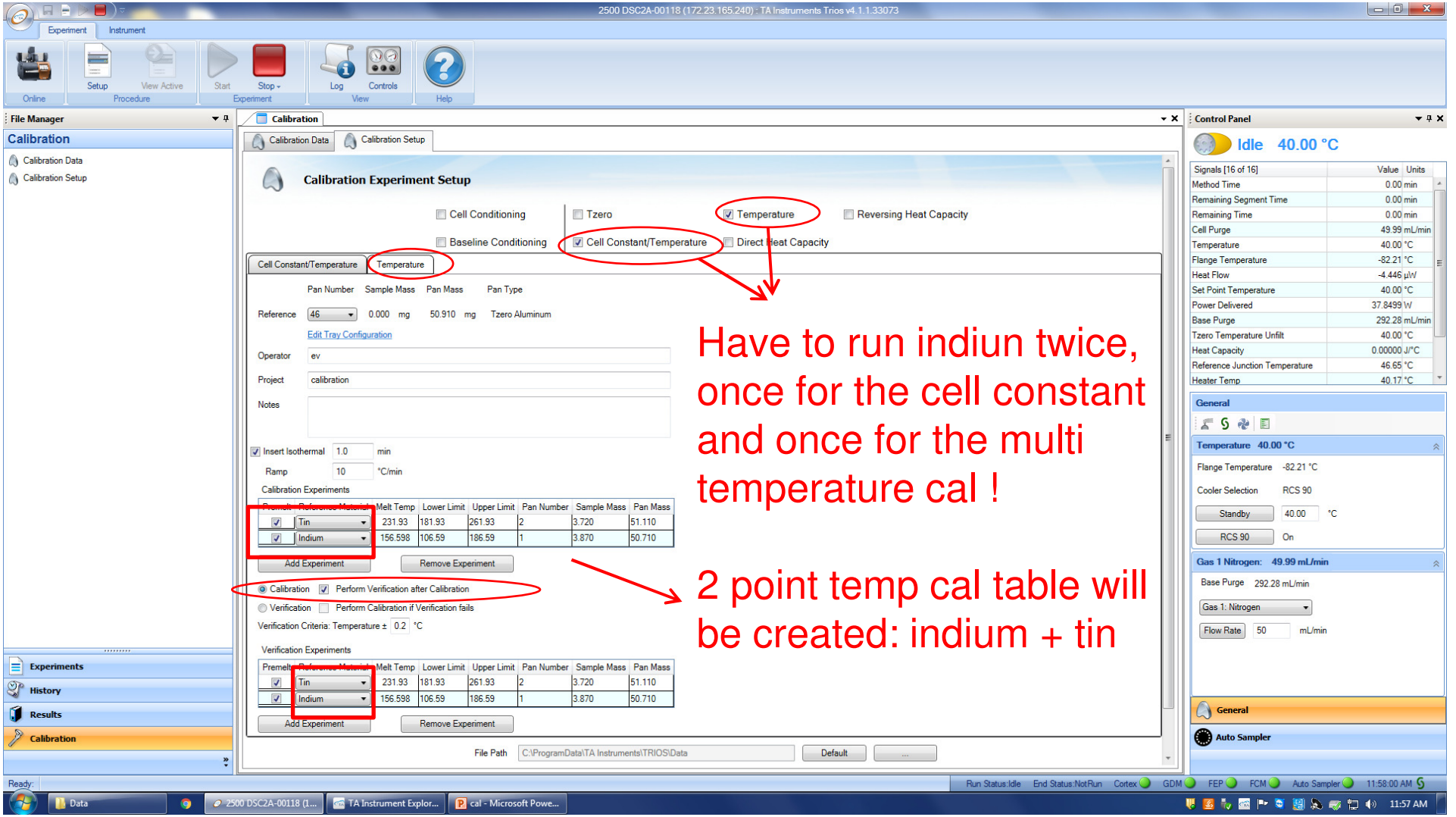
Verification of Heat Flow & Temperature, All DSC's



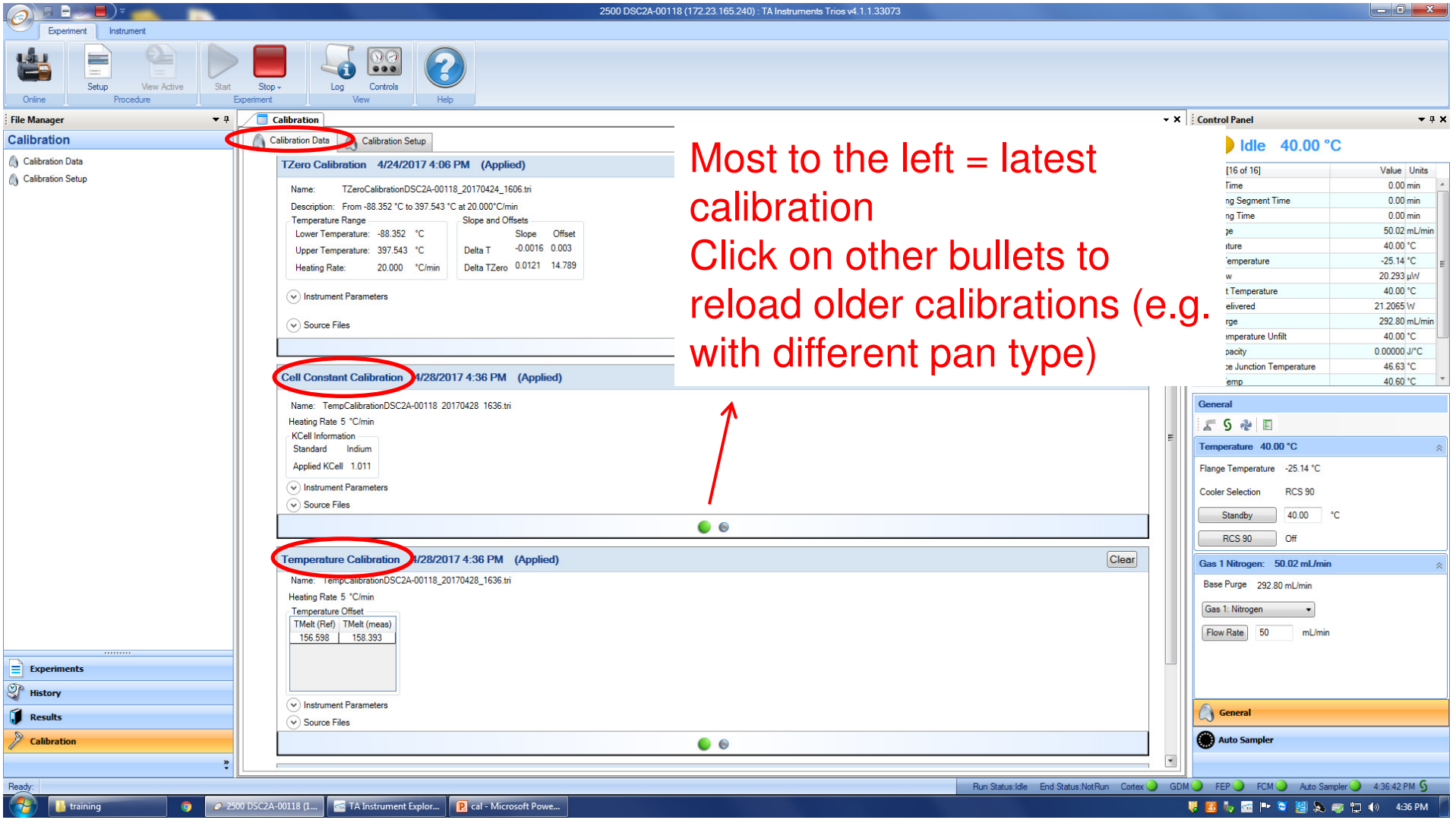
Verification of Heat Flow & Temperature, All DSC's



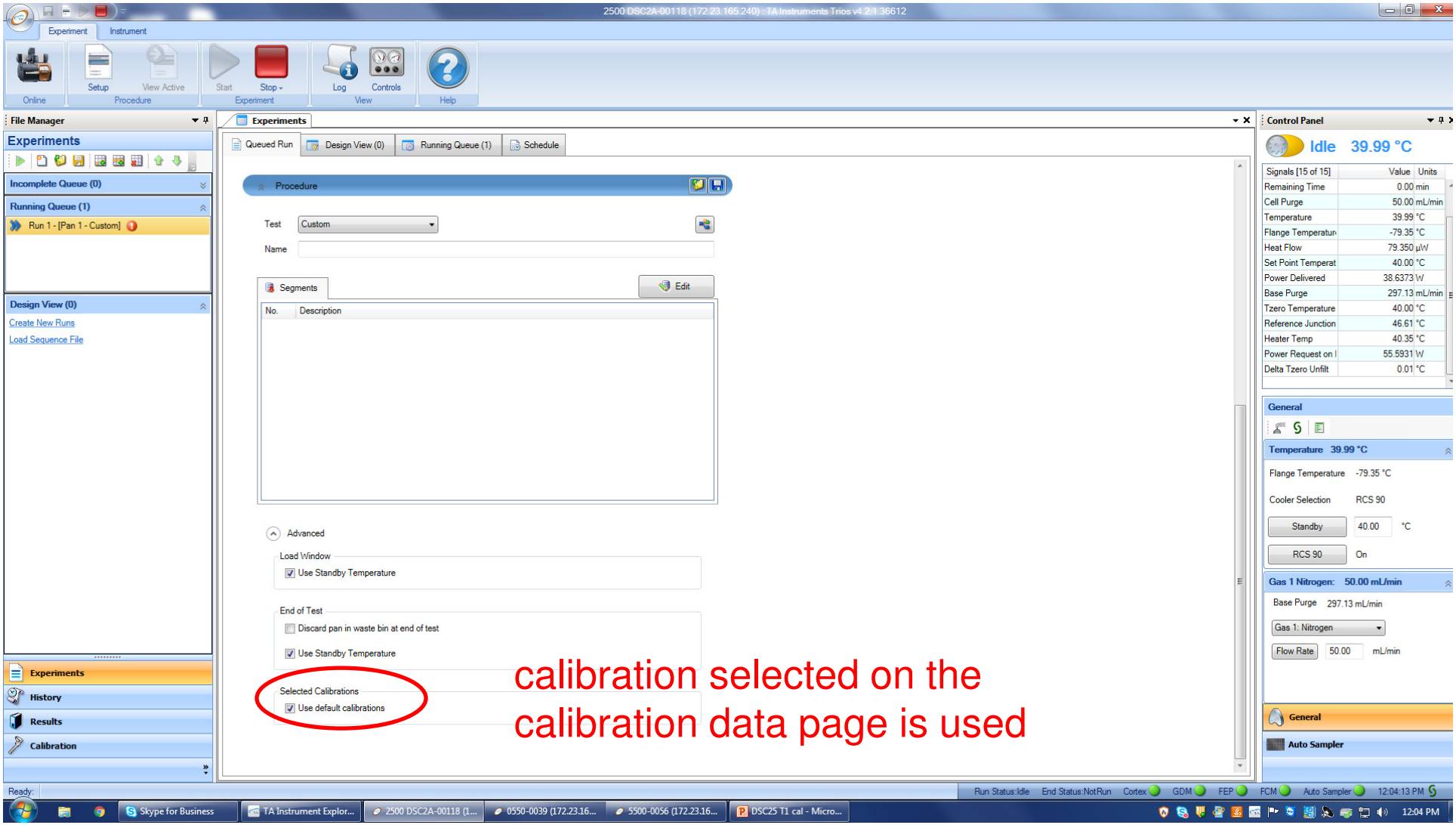
Heat Flow & Temperature Calibration: Temperature Calibration with Multiple Points



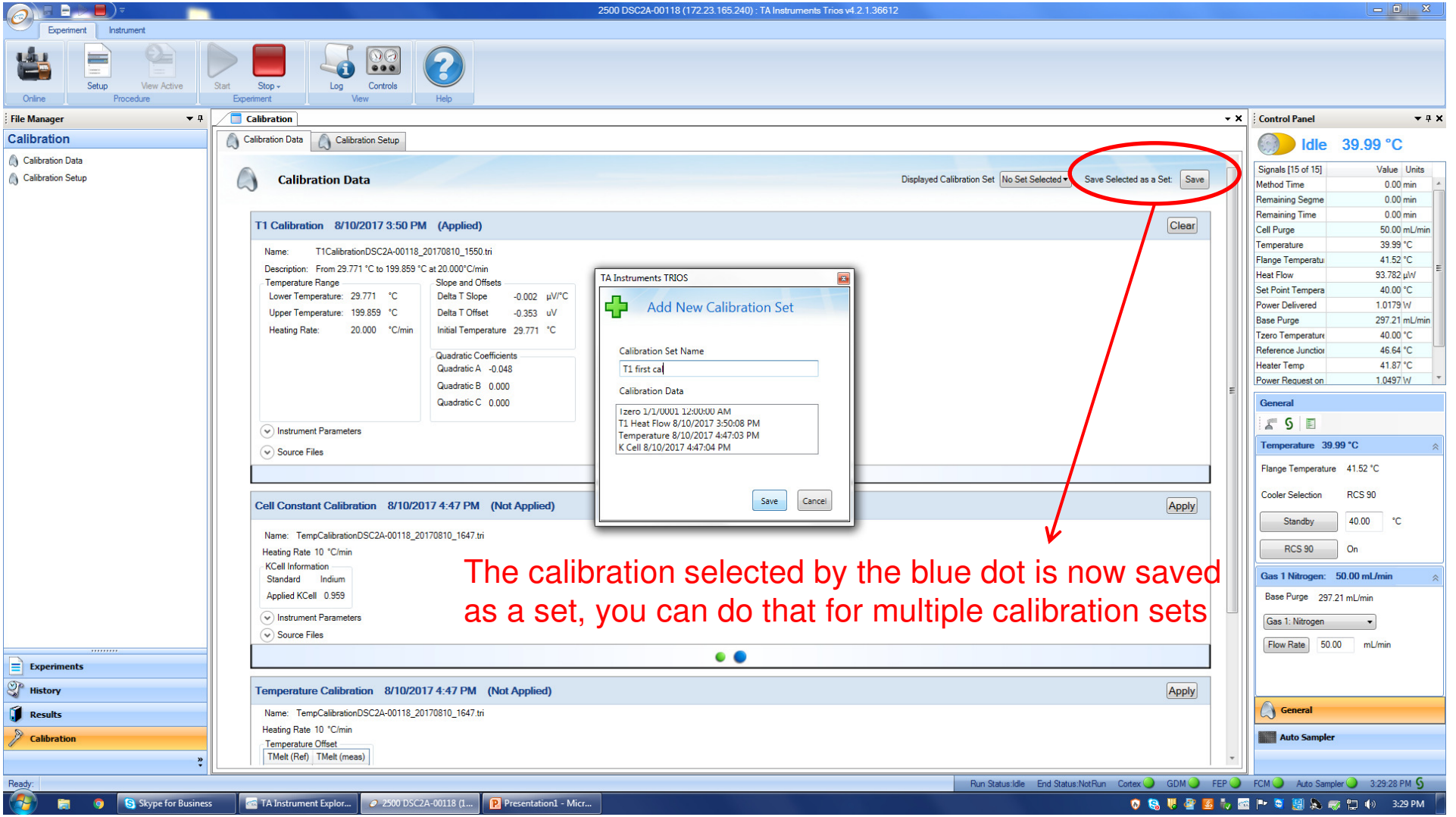
Reloading Older Cell Constant/Temperature Calibration



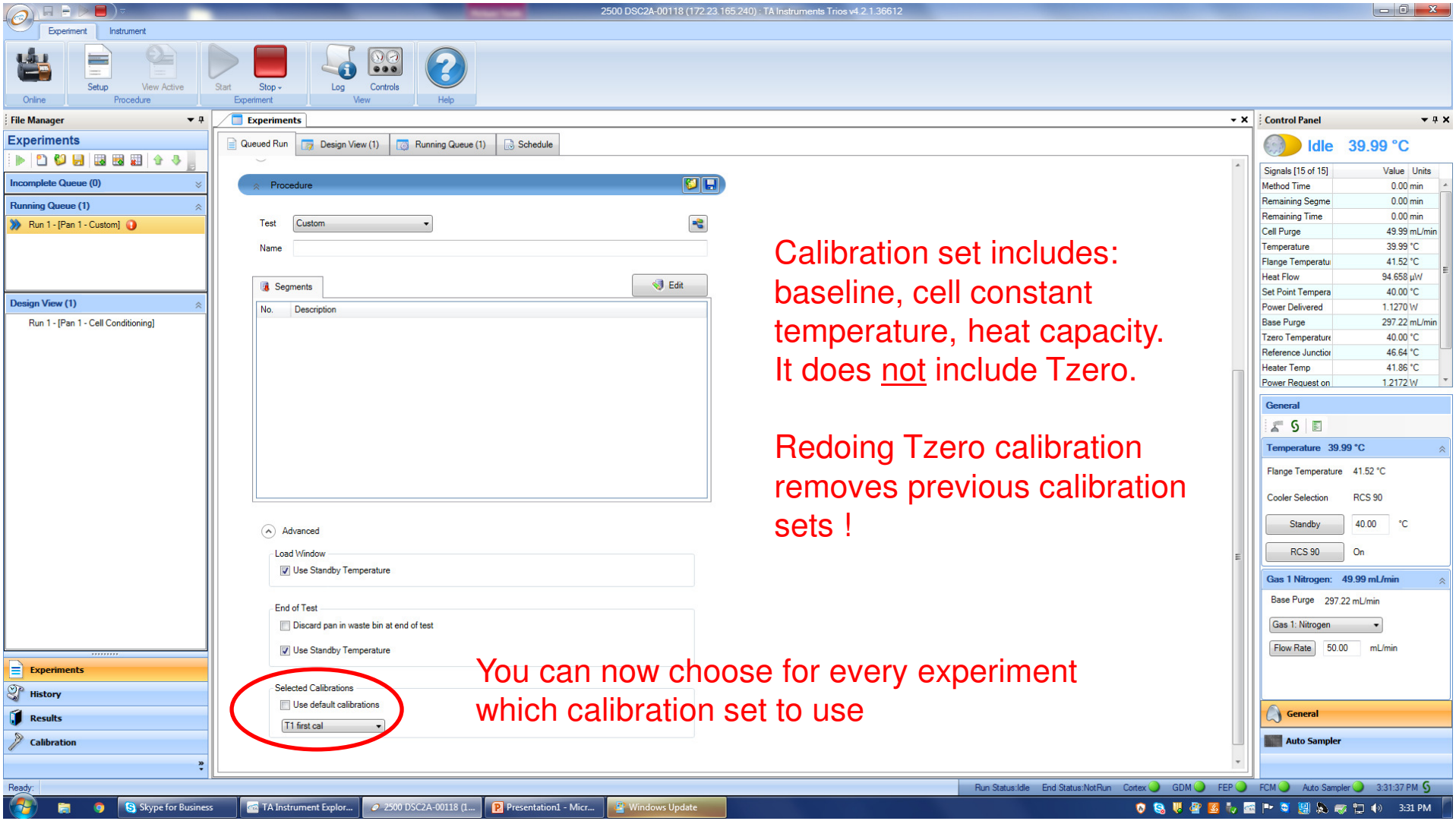
Discovery DSC 2nd Generation: Multiple Calibration Sets



Discovery DSC: Multiple Calibration Sets



Discovery DSC: Multiple Calibration Sets



Optimization of Experimental Conditions

Instrument Preparation

- **Cooling Accessories**
  - They should be operating and equilibrated prior to runs (so do not turn off between runs !)
- **Warm-up Time/Environment**
  - Electronics should be given at least one hour to stabilize for important samples if the instrument has been turned off (typically leave instrument always on)
  - Electronics are effected by ambient temperature. Avoid areas such as hoods or near an air conditioner
- **Purge Gas**
  - Make sure cylinder is not empty or moisture condensation will occur if cooler is on or still cold

Understanding Your Sample

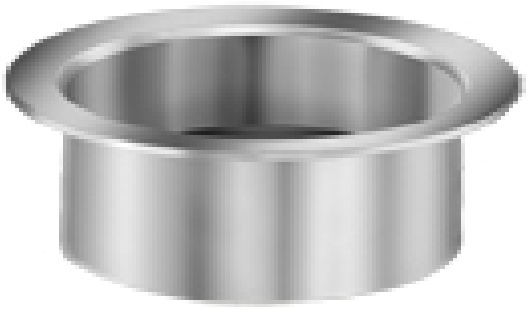
- Find out all you can about the sample
  - Form
  - Are there any volatiles (TGA) ?
  - Decomposition temp (TGA)
  - What transitions to expect ? In what temperature range ?
- This will help you choose
  - Max Temperature Range
  - Heating Rate
  - Sample Pans
  - Sample Size

Effective Sample Preparation

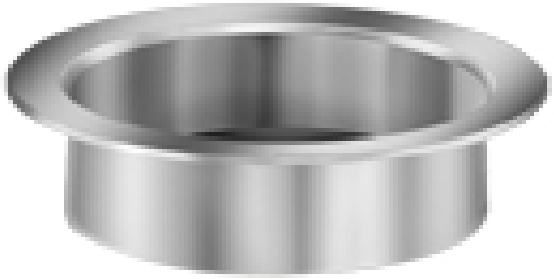
- Good sample preparation relies on two aspects:
  - Choose the proper pan
  - Load your sample effectively
- DSC Pan types:
  - Standard Pans: Appropriate for most solid samples (films, powders, polymer granule, etc)
  - Hermetic Pans: Designed primarily for samples which may evolve a volatile during heating
    - Can be used for small quantities of liquids as well
  - Specialty Pans
    - High Volume Pans: Used for larger quantities of liquids and solutions and for temperatures above boiling point

TA Instruments Tzero Pans

Tzero Pan



Tzero Low-Mass Pan



- The Tzero pan has been engineered to have a perfectly flat bottom and not to deform during crimping. This ensures the optimal contact between pan and sensor, minimizing the contact resistance and improving resolution.
- The Tzero Pan can be configured for crimped or hermetic use.
- The Tzero Low-Mass Pan is designed for the highest sensitivity when sample mass is limited (crimped use only).

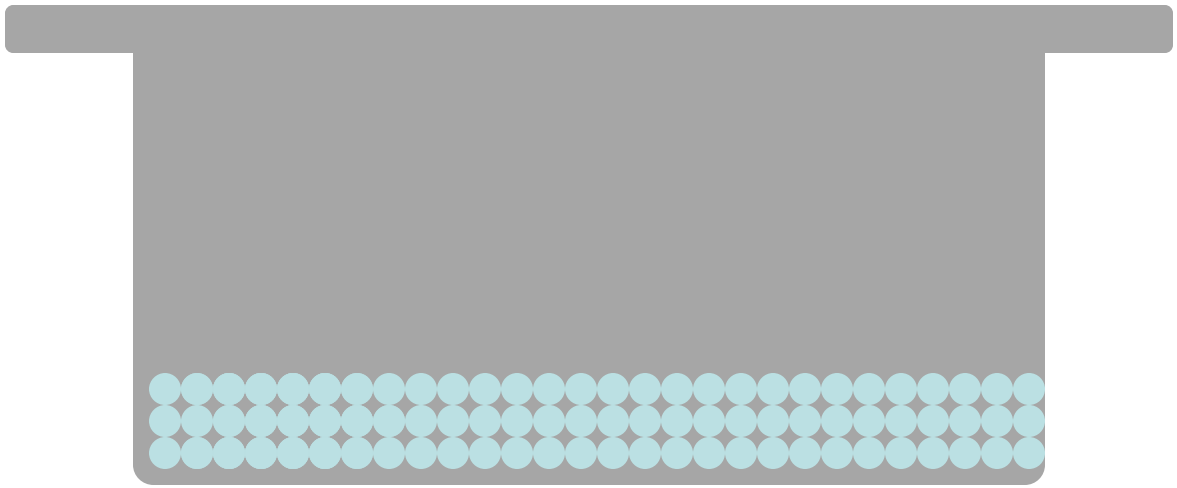
TA Instruments High Volume Pans

Pressure capability	3.8 MPa gauge (550 psig)
Temperature limit for aqueous solutions	250°C
Pan Volume Material	 100 µL (max) 302 SST
O-ring material	Viton

- The high volume pan is designed for measuring diluted solutions (larger volume improves sensitivity)
- The high volume pan allows measuring liquids above their boiling point (aluminum hermetic pan is limited to a pressure of 2-3 bar)

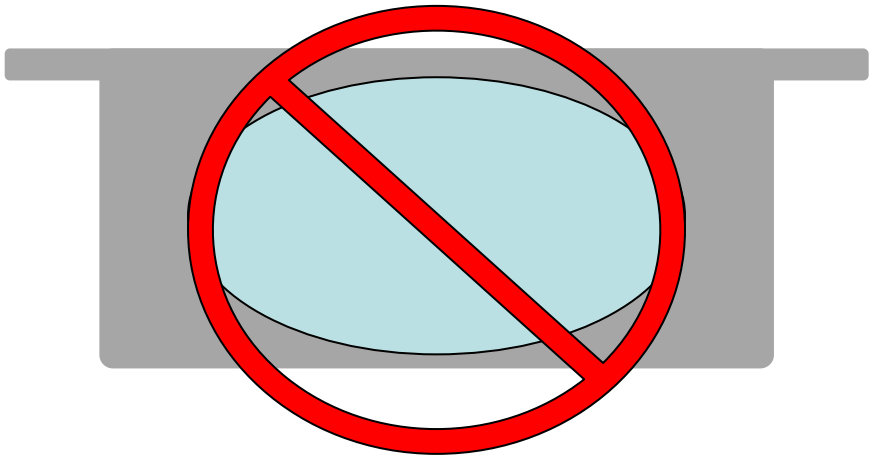
Sample Shape: Solids

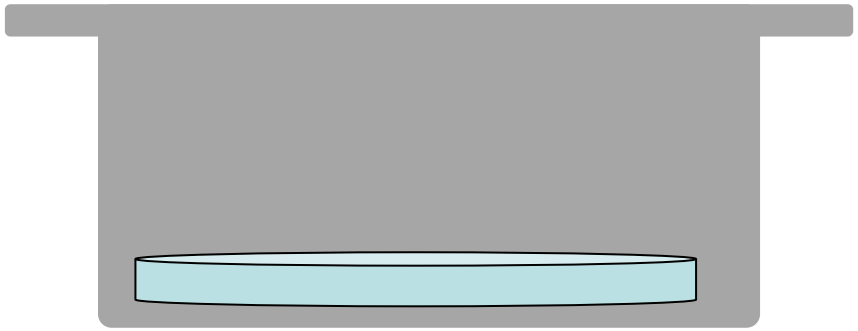
- Keep sample thin
- Cover as much as the bottom of pan as possible



Sample Shape: Solids

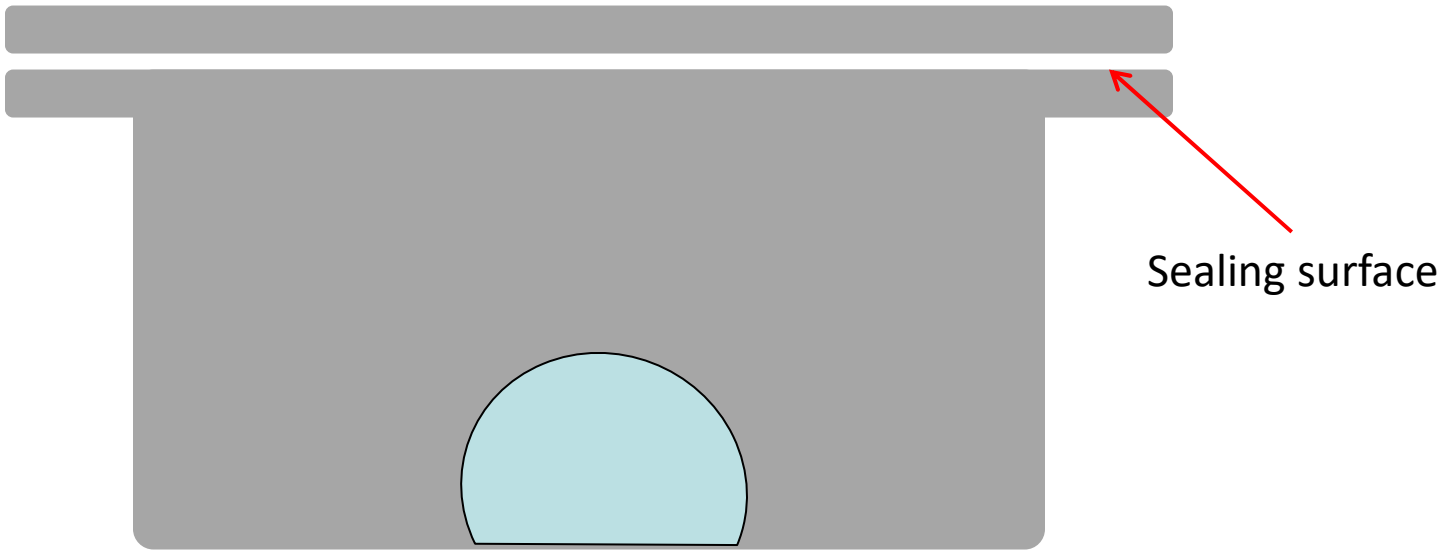
- Cut sample to make thin, don't crush (can introduce thermal history)
- If sample is a pellet, cut a cross section





Sample Shape: Liquids

- Use a pipette to place a single drop of liquid carefully in the middle of the pan
- Do not allow the liquid to wet the sealing surface of the pan !
- Use a hermetic lid



DSC: Sample Size

- In a DSC experiment, sample size is a trade-off between sensitivity and resolution
  - Larger samples = more sensitivity
  - Smaller samples = more resolution

- In general, it is best to use the smallest sample which does not compromise the required sensitivity
    - melting of metal or chemical < 5mg
    - melting or Tg of polymer : about 10 mg
    - composites or blends >10 mg

  - For accurate enthalpy measurements the sample weight must be determined with an accuracy of 0.01 mg

Heating/Cooling Rate

- High rates increase sensitivity

$$dQ/dt = Cp \cdot dT/dt + f(t,T)$$

- Low rates increase resolution by providing more time at any temperature

- **Good starting point is 10 or 20ºC/min**

Keeping the DSC Cell Clean

One of the first steps to ensuring good data is to keep the DSC cell clean

How do DSC cells get dirty ?

- Decomposing samples during DSC runs
  - Run TGA to determine the decomposition temperature, stay below that temperature !

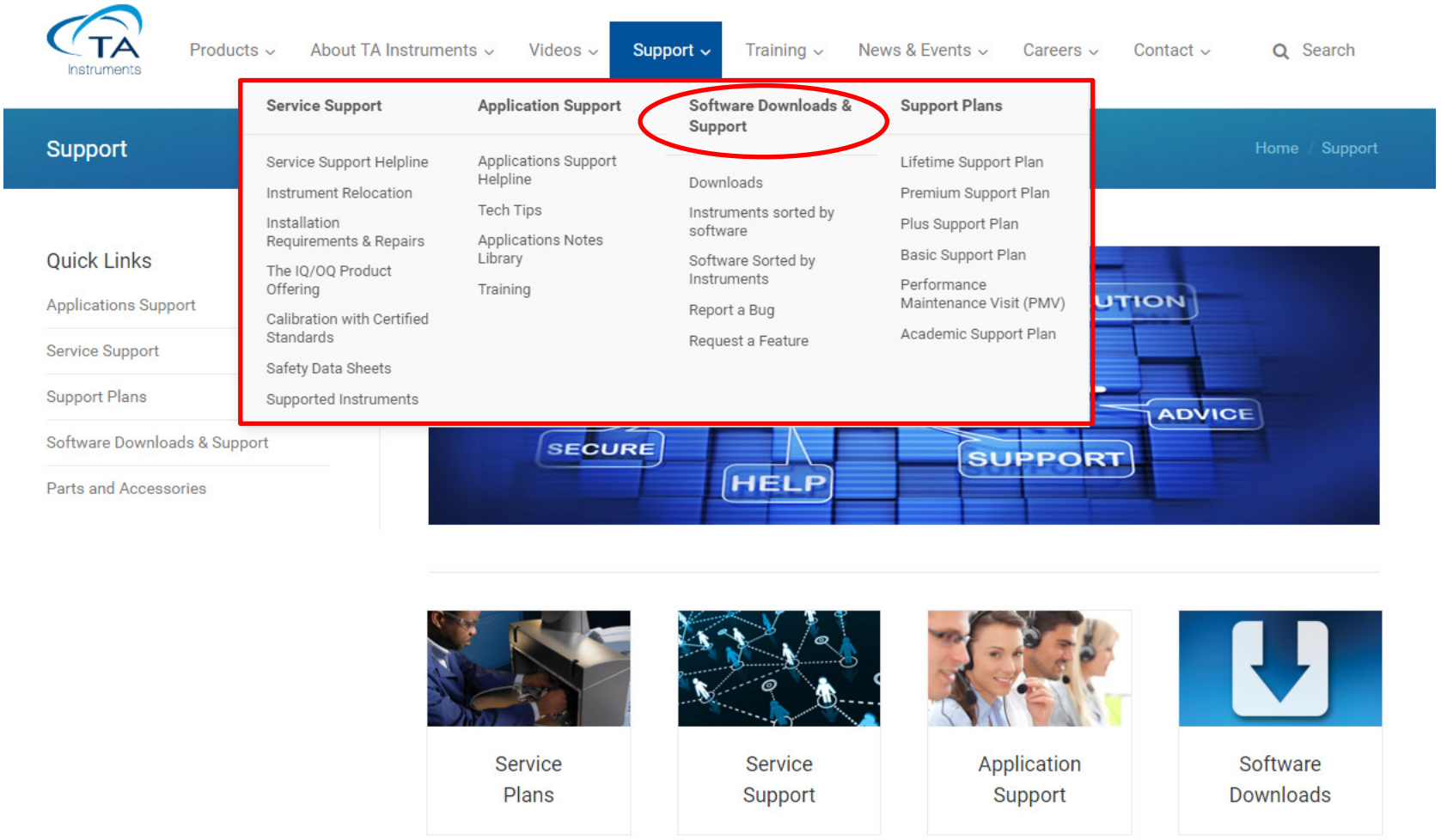
    Just because the instrument has a max temperature range of 550ºC (w/ RCS) doesn't mean you need to heat every sample to 550ºC !
- Samples spilling out of the pan
  - Use lids
  - Use hermetic pans if necessary
- Transfer from bottom of pan to sensor
  - Make sure bottom of pans stay clean

Help !?

- Software :
  - Case sensitive help, help topics, manual
- E-training (basic)
  - www.tainstruments.com
- TATechTips & Webinars
  - www.tainstruments.com
- Application library
  - www.tainstruments.com

Help and data analysis from your laptop ? Simply install the S/W from CD or download it !

www.tainstruments.com



Help on Desktop

TA Instruments

Thermal Discovery Series Manuals

To view the desired manual using Acrobat Reader, click the name in the list below:

TA Manual Supplement
(Contains important information applicable to all manuals.)

Instrument Documentation

Discovery DSC Getting Started Guide
Discovery DSC Getting Started Guide for DSC 25, DSC 250, DSC 2500
Discovery TGA Getting Started Guide
Discovery TGA Getting Started Guide for TGA 55, TGA 550, TGA 5500 - NEW!

Accessory Documentation

DSC High Pressure Capsule Kit Getting Started Guide
DSC High Volume Pan Kit Getting Started Guide
Liquid Nitrogen Pump System (LN2P) Getting Started Guide
Mass Spectrometer (MS) Getting Started Guide
Photocalorimeter Accessory (PCA) Getting Started Guide
Refrigerated Cooling System (RCS) Getting Started Guide
TGA HiRes™ Option Operator's Guide

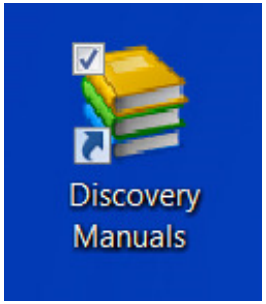
Software Documentation

What's New in TRIOS Software
Installing TRIOS Software

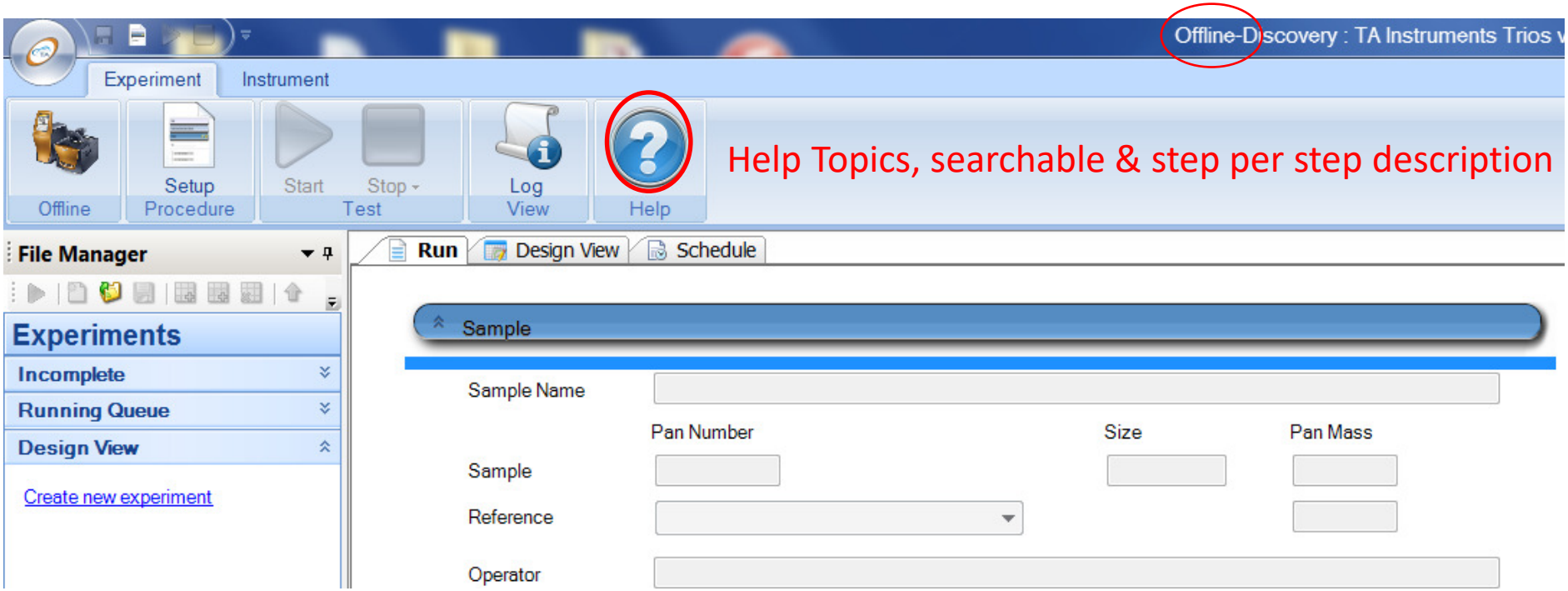
Miscellaneous Documentation

Thermal Discovery Series Installation Requirements

Issued September 2016

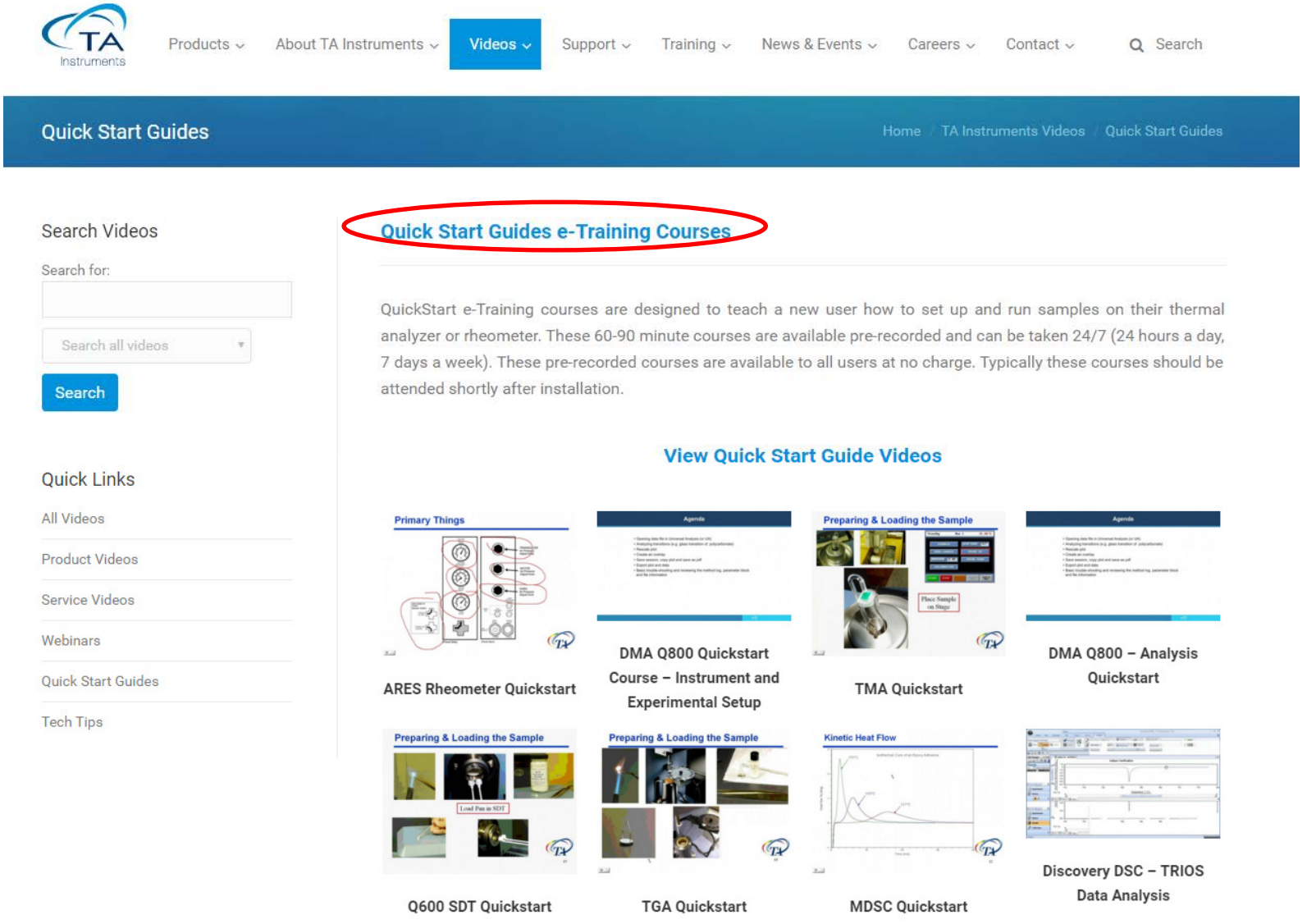


Trios



You can install an offline version of Trios on your laptop

www.tainstruments.com



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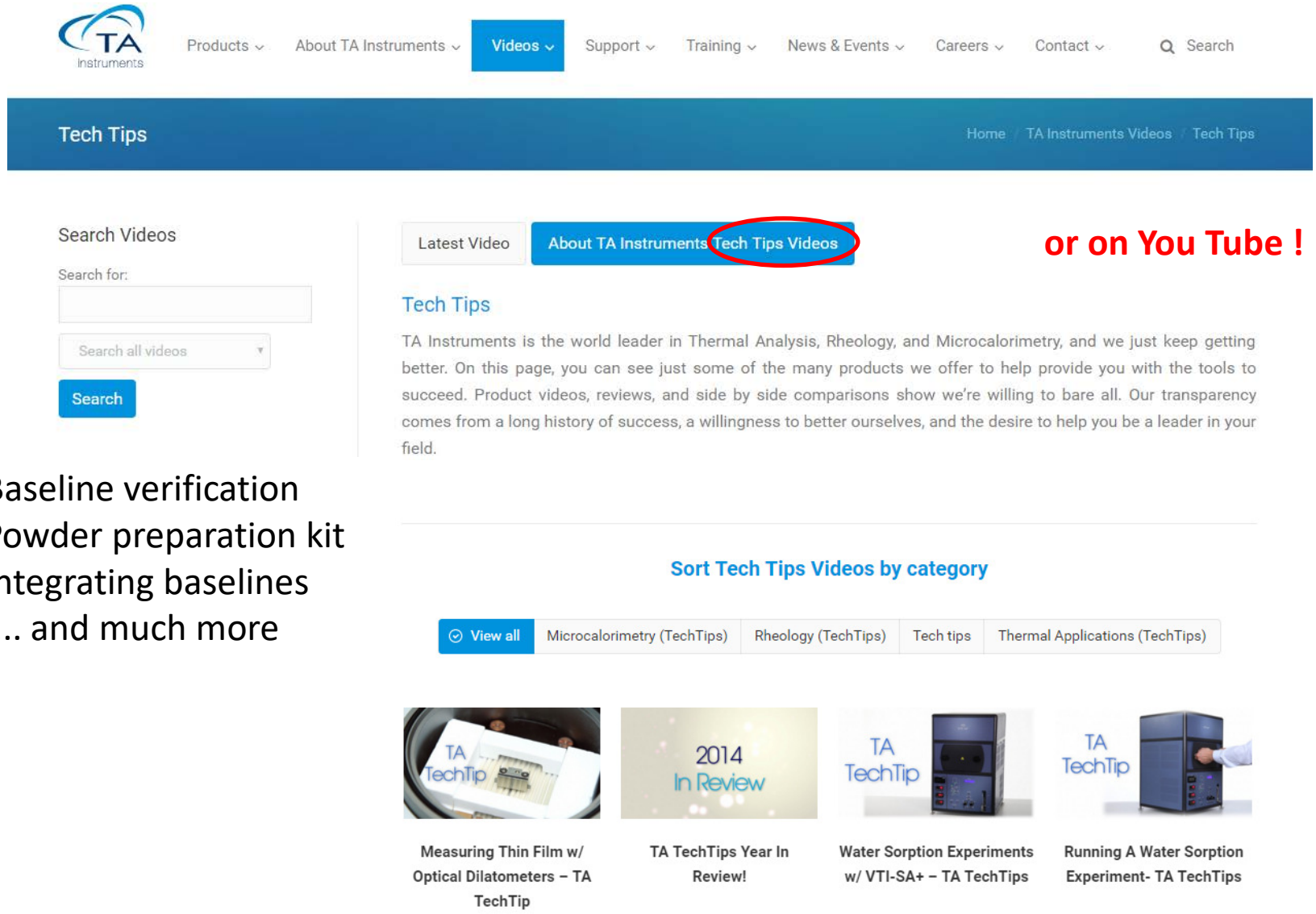

- Baseline verification
- Powder preparation kit
- Integrating baselines
- .... and much more

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Webinars

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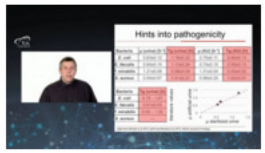
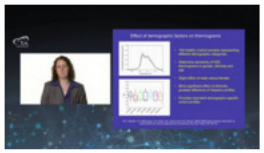
In Search of Calorimetric Answers to Events In Self Assemblies

Extensional Rheology in Polymer Processing



Uses of Isothermal Microcalorimetry in Urology



Plasma Protein Calorimetry For Clinical Diagnostics

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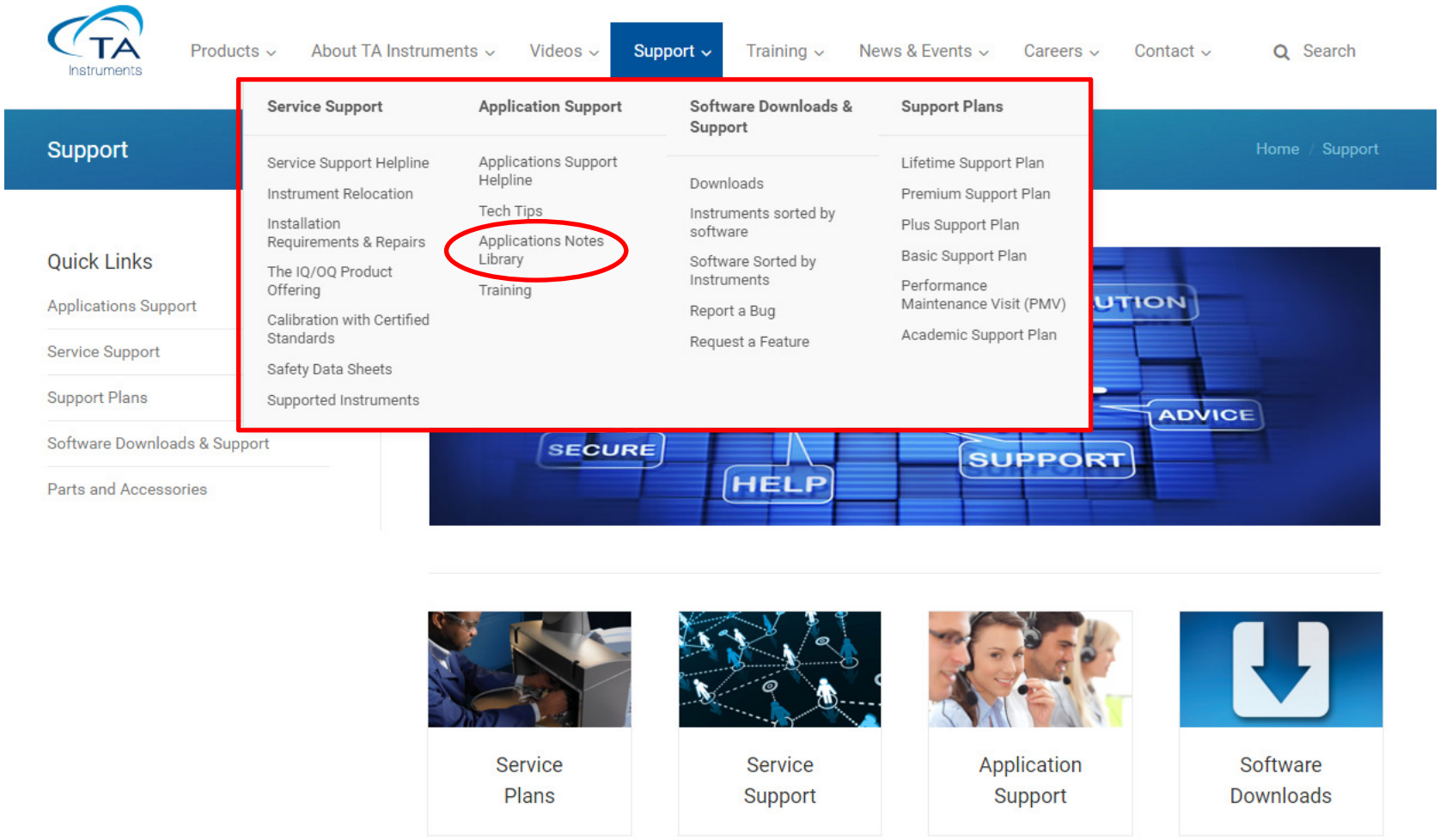
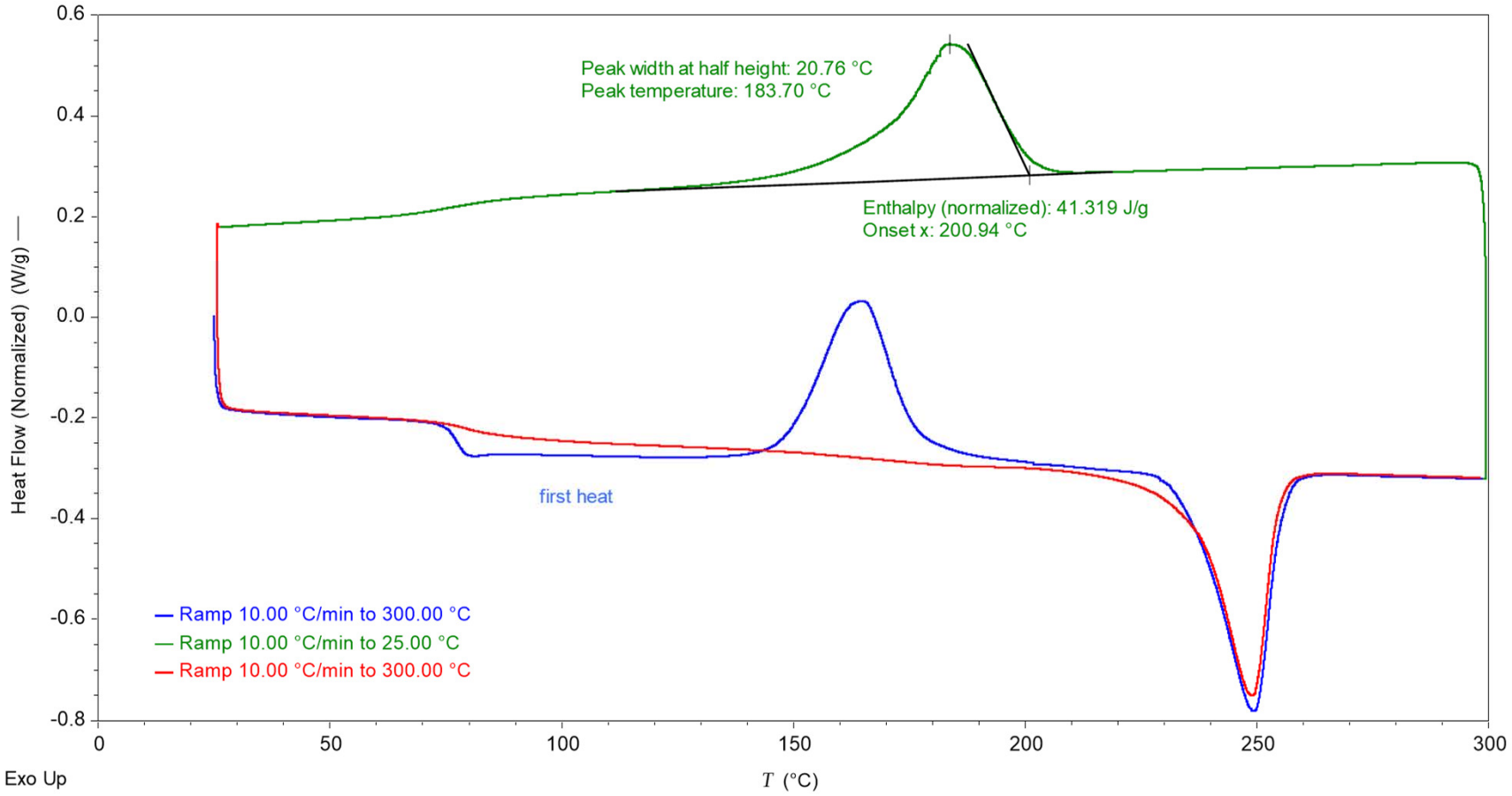


Trios Software

TA Instruments

PET (Heat-Cool-Heat)

C:/ProgramData/TAInstruments/Trios/Data/ExampleFiles/Thermal



PET (Heat-Cool-Heat) 1st Heat

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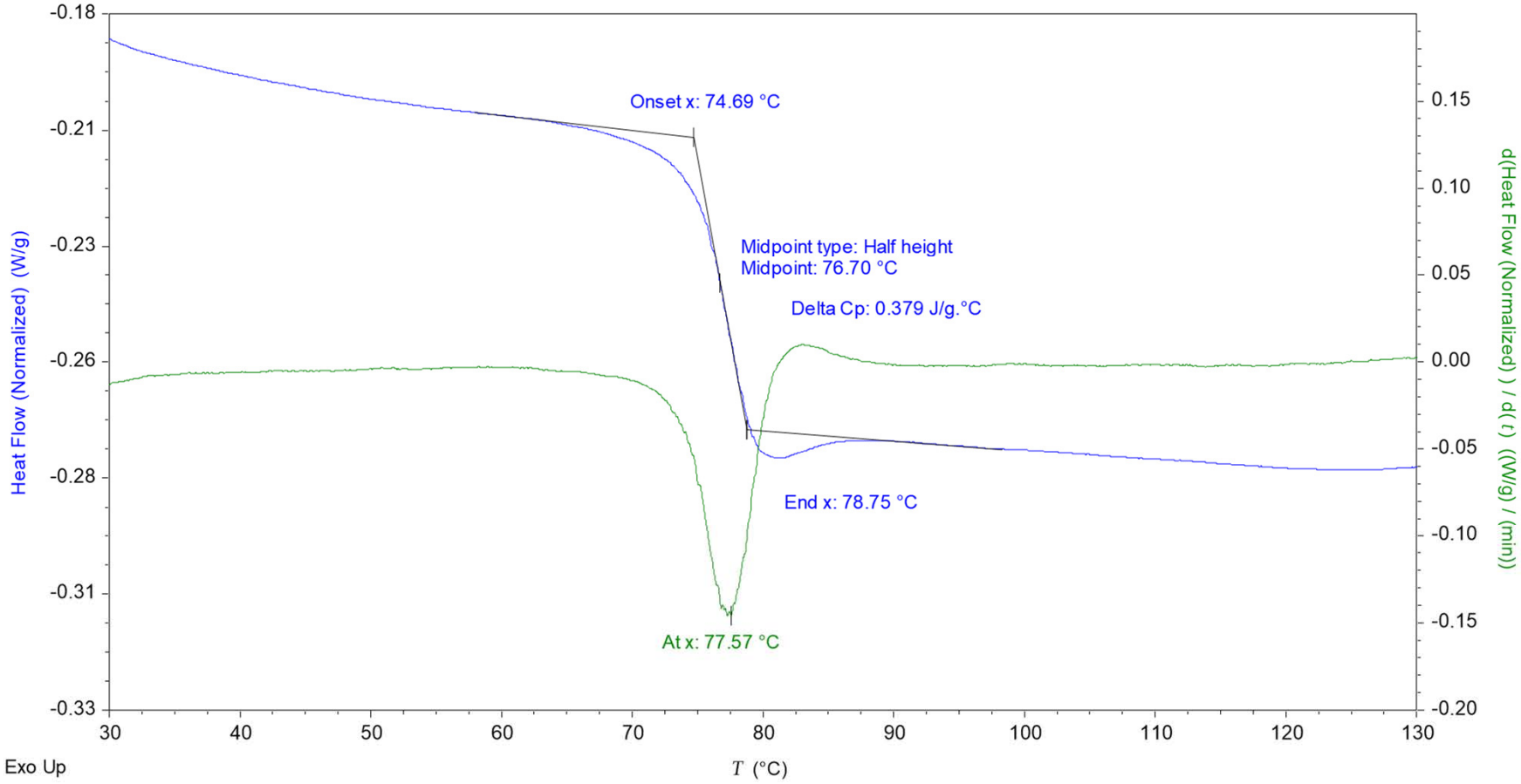
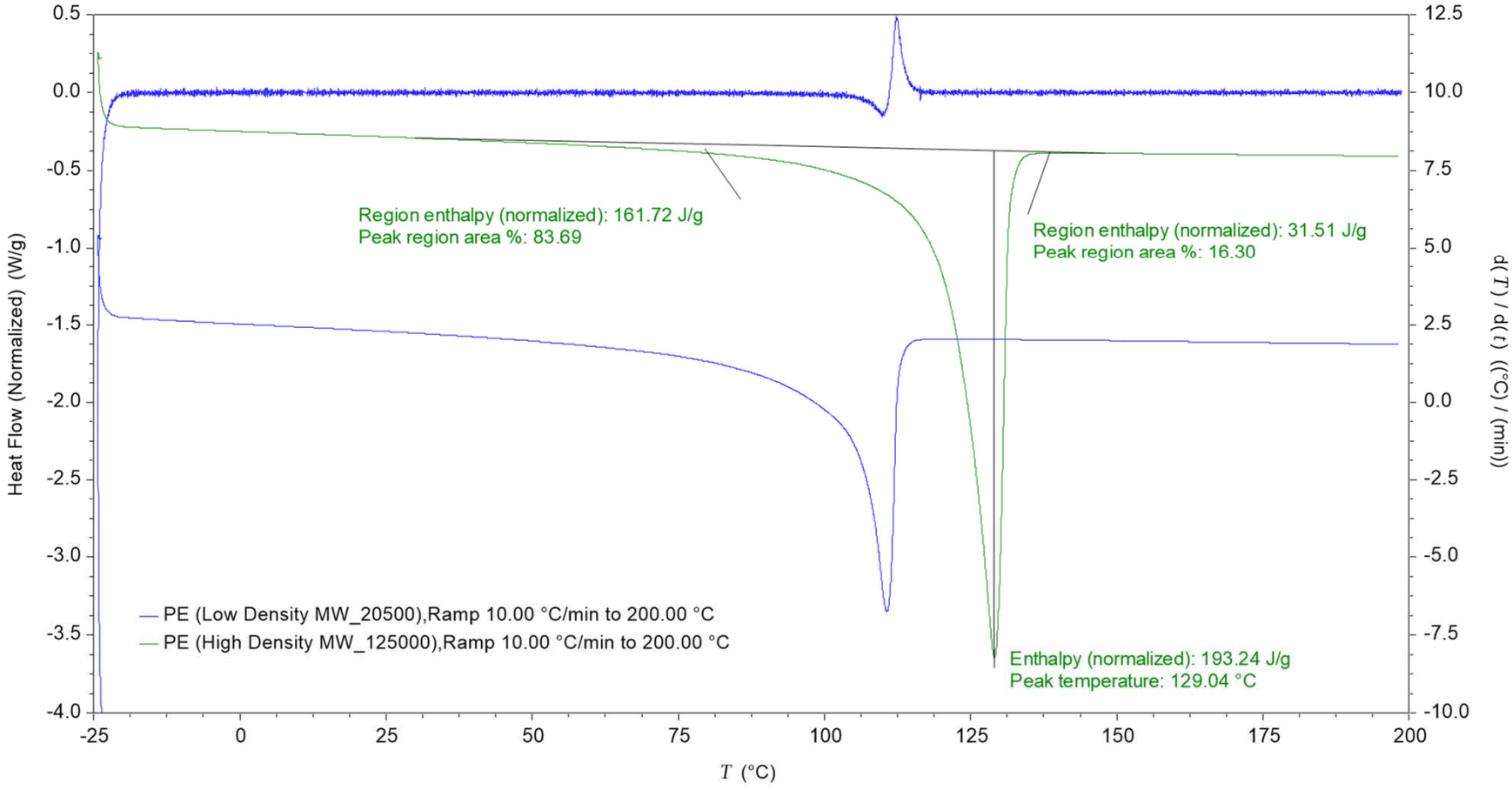


PE (Low & High Density) 2nd Heat

C:/ProgramData/TAInstruments/Trios/Data/ExampleFiles/Thermal



PBT 2nd Heat

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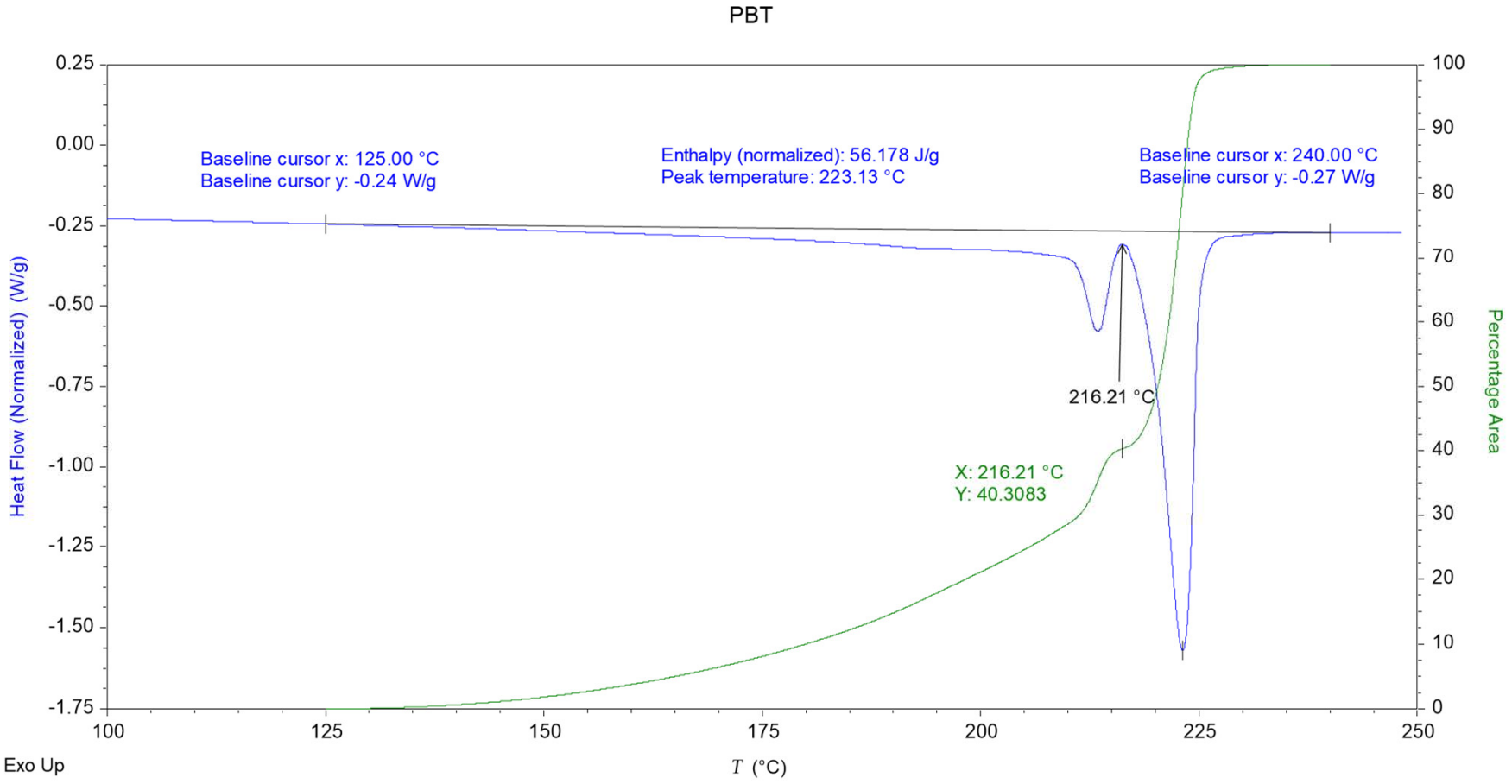
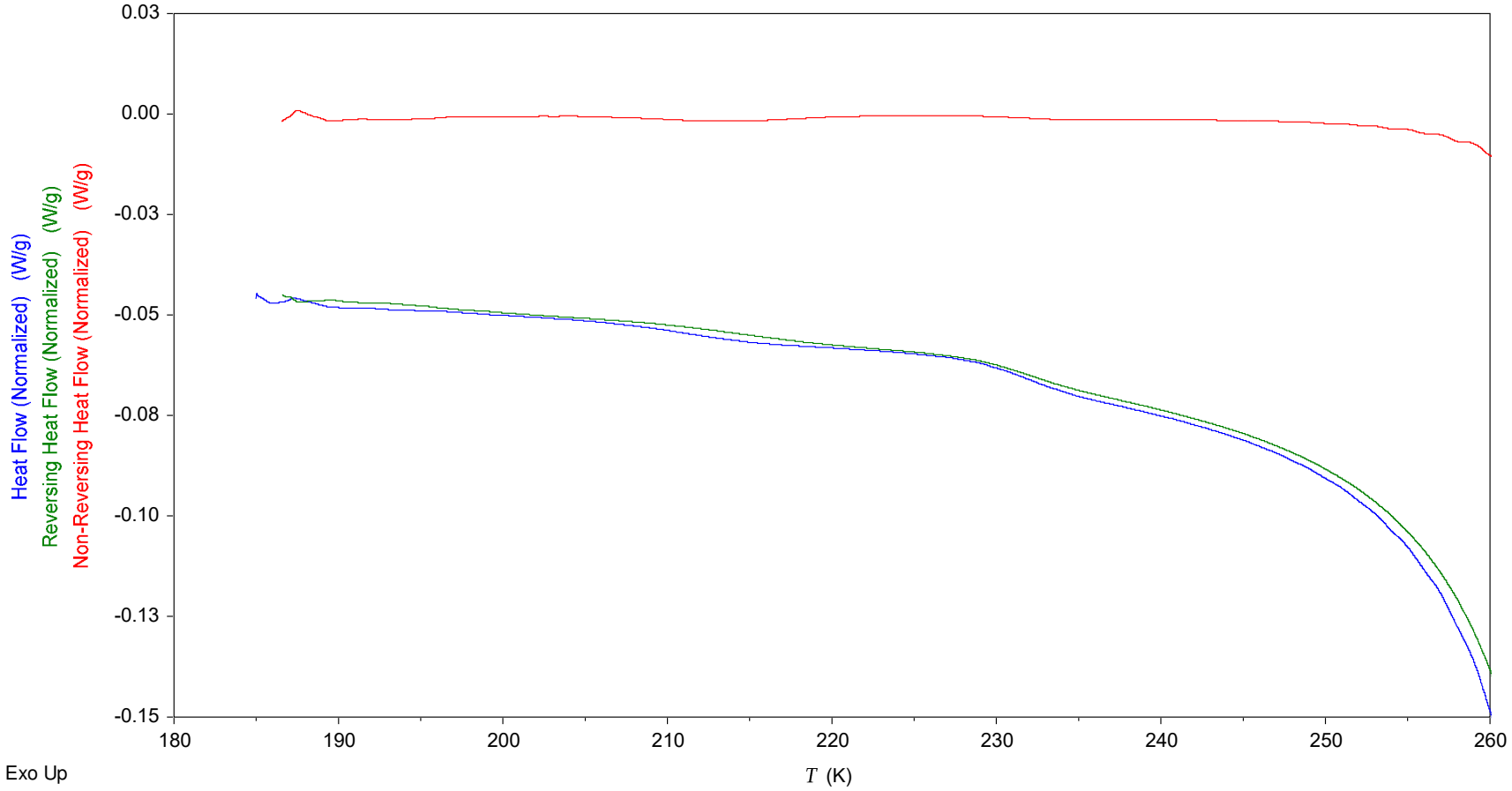
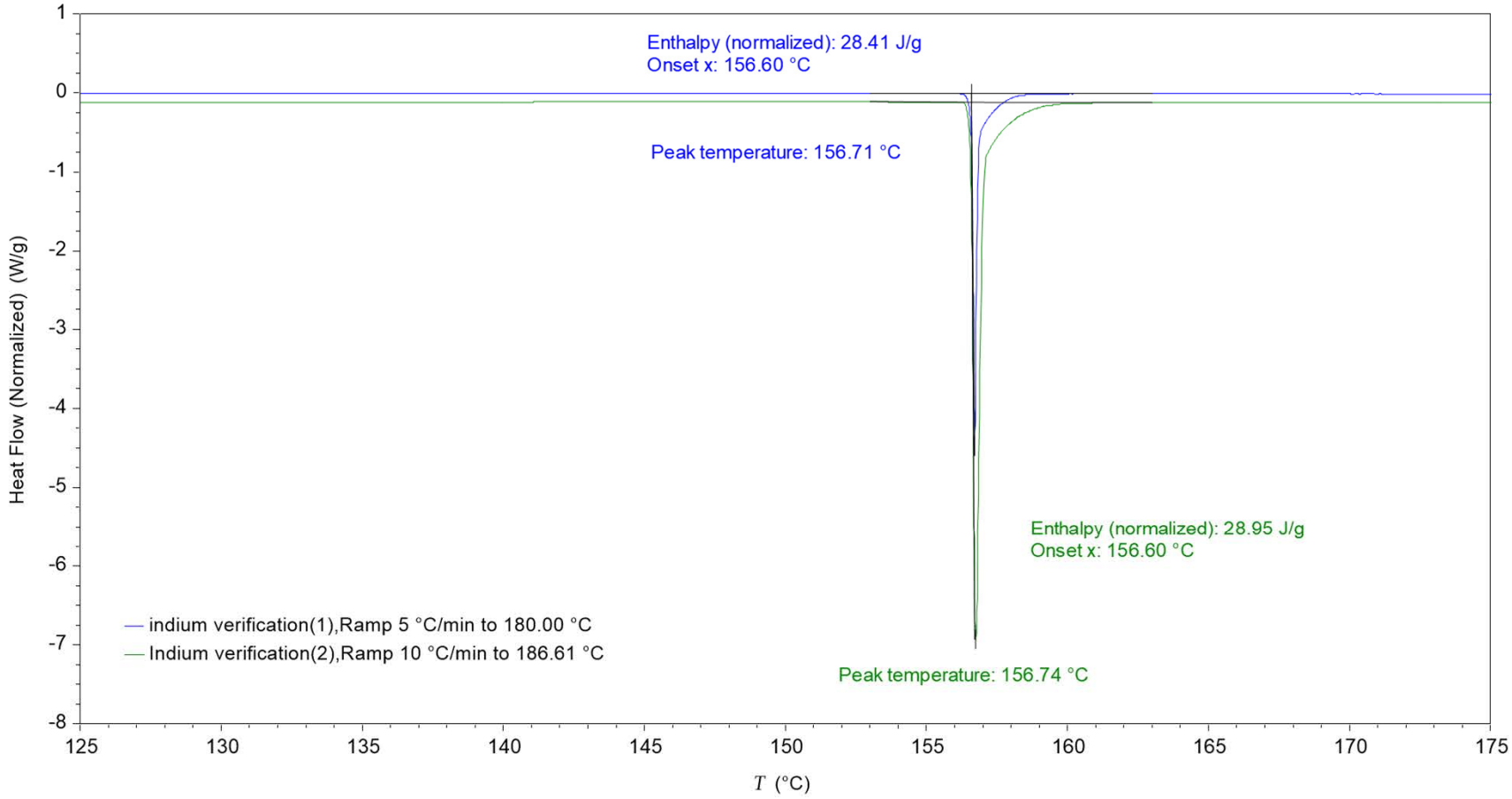


Liquid Sample MDSC 1st Heat



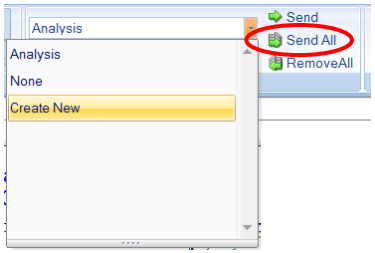
Note: temperature in K

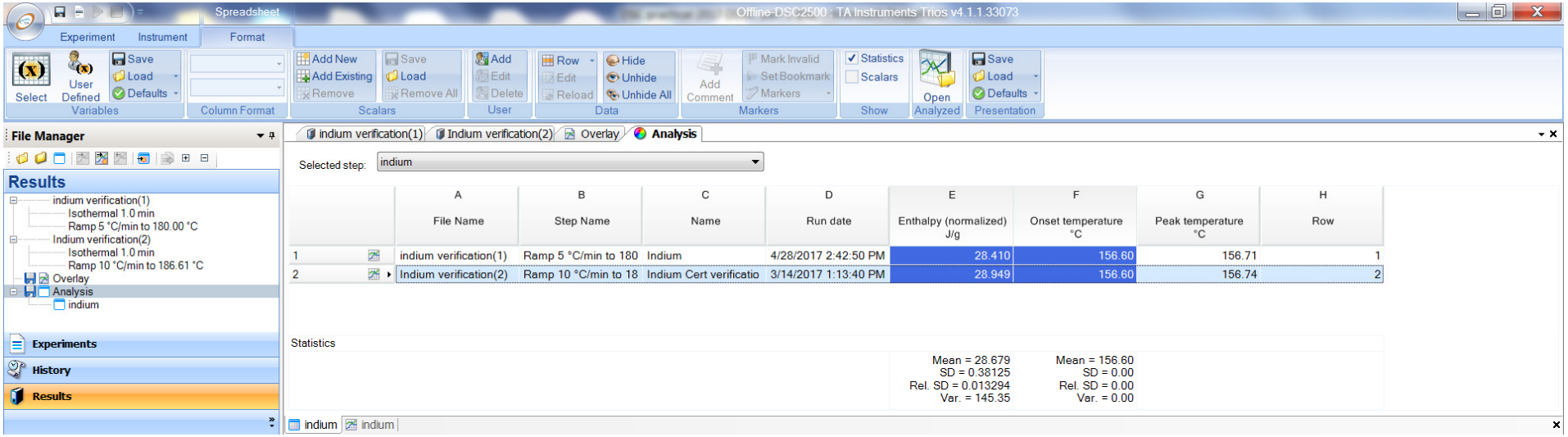
Indium Verification: Influence of Heating Rate



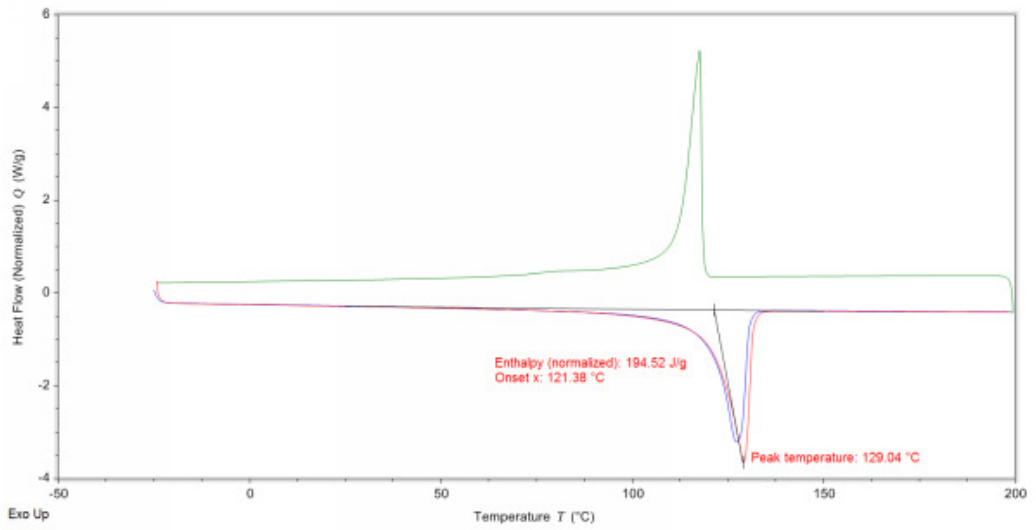
Use the analysis library to integrate both between 153 to 163ºC

Two Indium Verification Test: Statistics





Reporting



PE (High Density MW_125000)
3.8 mg

Segment 1	Equilibrate -25.00 °C
Segment 2	Ramp 10.00 °C/min to 200.00 °C
Segment 3	Mark End of Cycle
Segment 4	Ramp 10.00 °C/min to -25.00 °C
Segment 5	Mark End of Cycle
Segment 6	Ramp 10.00 °C/min to 200.00 °C
Segment 7	Mark End of Cycle

Peak Integration (enthalpy)

Enthalpy (normalized)	Peak temperature	Onset x
194.52 J/g	129.04 °C	121.376 °C

https://triosvideos.s3.amazonaws.com/Report%20View.mp4

Thank You !

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