Differential Scanning Calorimetry (DSC)

Q-series
Discovery
DSC2500
DSC250
DSC25

TA

Calibration & Verification

The DSC Heat Flow Rate Equation

- A DSC measures the difference in Heat Flow Rate between a sample and inert reference as a function of time and temperature.

$$\frac{dH}{dt} = Cp \frac{dT}{dt} + f(T, t)$$

- A DSC is calibrated for the heat flow enthalpy and temperature. Baseline calibrations are performed per manufacturers recommendations.

Calibration of Specific Instrument Models

Tzero

Measurement of Rs and Cs

- DSC2500
- DSC250
- 1st Generation Discovery
- Q2000
- Q200

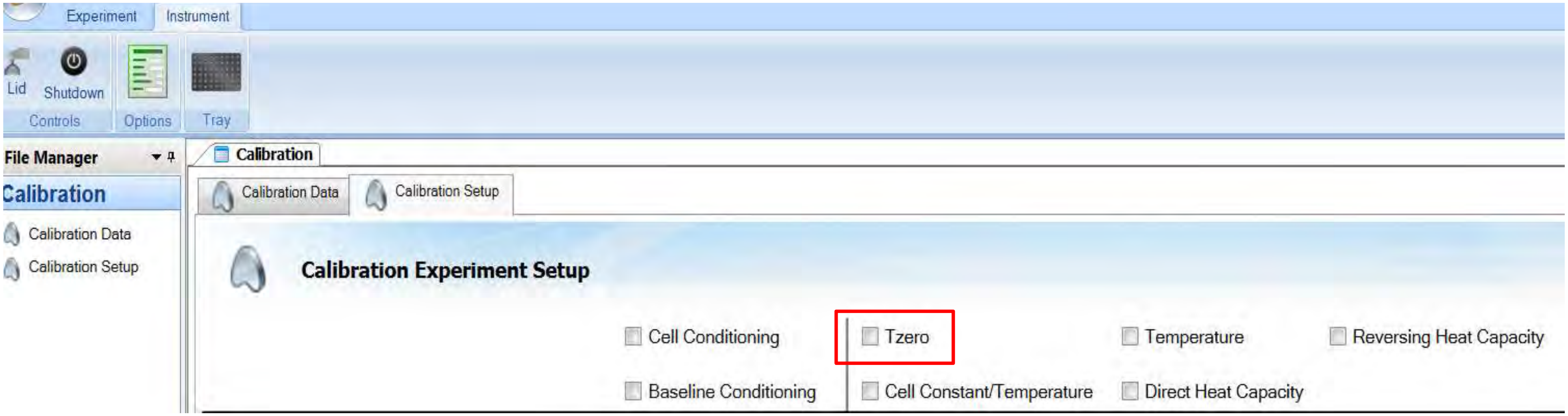
Baseline calibration

Measurement of slope and offset

- DSC 25
- Q20

Cell constant and temperature

- All DSCs


Experiment
Instrument
Lid
Shutdown
Controls
Options
Tray
File Manager
Calibration
Calibration Data
Calibration Setup
Calibration
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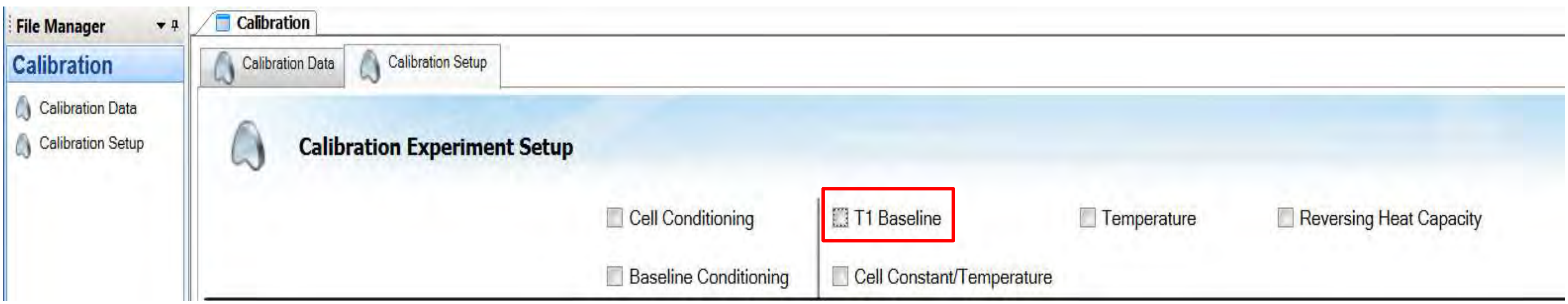
Calibration Setup
Calibration Experiment Setup
Cell Conditioning
Tzero
Temperature
Reversing Heat Capacity
Baseline Conditioning
Cell Constant/Temperature
Direct Heat Capacity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Calibration Experiment Setup
Cell Conditioning
T1 Baseline
Temperature
Reversing Heat Capacity
Baseline Conditioning
Cell Constant/Temperature

General Calibration and Verification Guidelines

- Calibration
  - Use Calibration Mode
  - Calibrate upon installation
  - Re-calibrate if does not pass verification or if instrument setup is modified (see previous slide)

- Verification
  - Determine how often to verify data
  - Run a reference material as a sample (in standard mode)
  - Compare results vs literature values
  - If results are within your tolerance – system checks out and does not need re-calibration
  - If results are out of tolerance, then re-calibrate

Requirements Prior to Calibration

- DSC cell must be free of contaminants
- An inert purge gas, such as nitrogen, where the flow rate is controlled to 10-50 ml/min +/- 5 ml/min
- A balance to weigh specimens and containers to at least +/- 0.1 mg. The balance should have a capacity greater than 20 mg.
- High purity reference materials (>99.99%) for calibration

Instrument Setup Factors Affecting Calibration

- Purge Gas Type
  - Re-calibrate baseline/Tzero, temperature and cell constant
  - Thermal conductivity of helium ≠ Thermal conductivity of nitrogen/air/oxygen ≠ Thermal conductivity of argon
- Cooling Accessories
  - Re-calibrate baseline/Tzero, temperature and cell constant
  - The position of the cooling head around the cell will affect the calibration of the instrument. Uninstallation and reinstallation of a cooling accessory or changing the cooling accessory warrants a complete re-calibration
- Pan Selection
  - Re-calibrate temperature and cell constant
  - It will not impact the baseline/Tzero calibration

ASTM E 967 - Standard Test Method for Temperature Calibration of DSC's

- For transition temperature, calibration is required with known reference standards.
  - Pure metals (indium, lead, etc.) typically used
  - Extrapolated onset is used as melting temperature
  - Sample is fully melted at the peak

- This test method consists of heating the calibration materials at a controlled rate in a controlled atmosphere through a region of known thermal transition.

- The heat flow into the calibration material or the difference of temperature between the calibration material and a reference is monitored and continuously recorded.

- A transition is marked by the absorption of energy by the specimen resulting in a corresponding endothermic peak in the heating curve.

ASTM E 967 - Temperature Calibration of DSC's

Indium (156.6°C)

Can be re-used, can pre-melt

Tin (231.9°C)

Has multiple crystalline forms, use once – no pre-melt

Zinc (419.5°C)

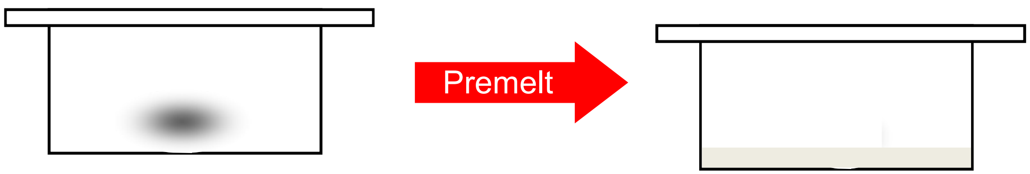
Can easily oxidize and alloy with container, use once – no pre-melt

ASTM E 968 - Standard Practice for Heat Flow (Enthalpy) Calibration of DSC's

- For enthalpy of a transition, calibration is required with known reference standards.
- This standard consists of calibrating the heat flow response of a DSC by recording the melting endotherm of a high-purity standard material as a function of time.
- The peak is then integrated (over time) to yield an area measurement proportional to the enthalpy of melting of the standard material.
- Indium is a commonly used reference standard.

Temperature and Cell Constant Calibration

- Prepare a 3-5 mg sample of indium and “pre-melt” prior to first use

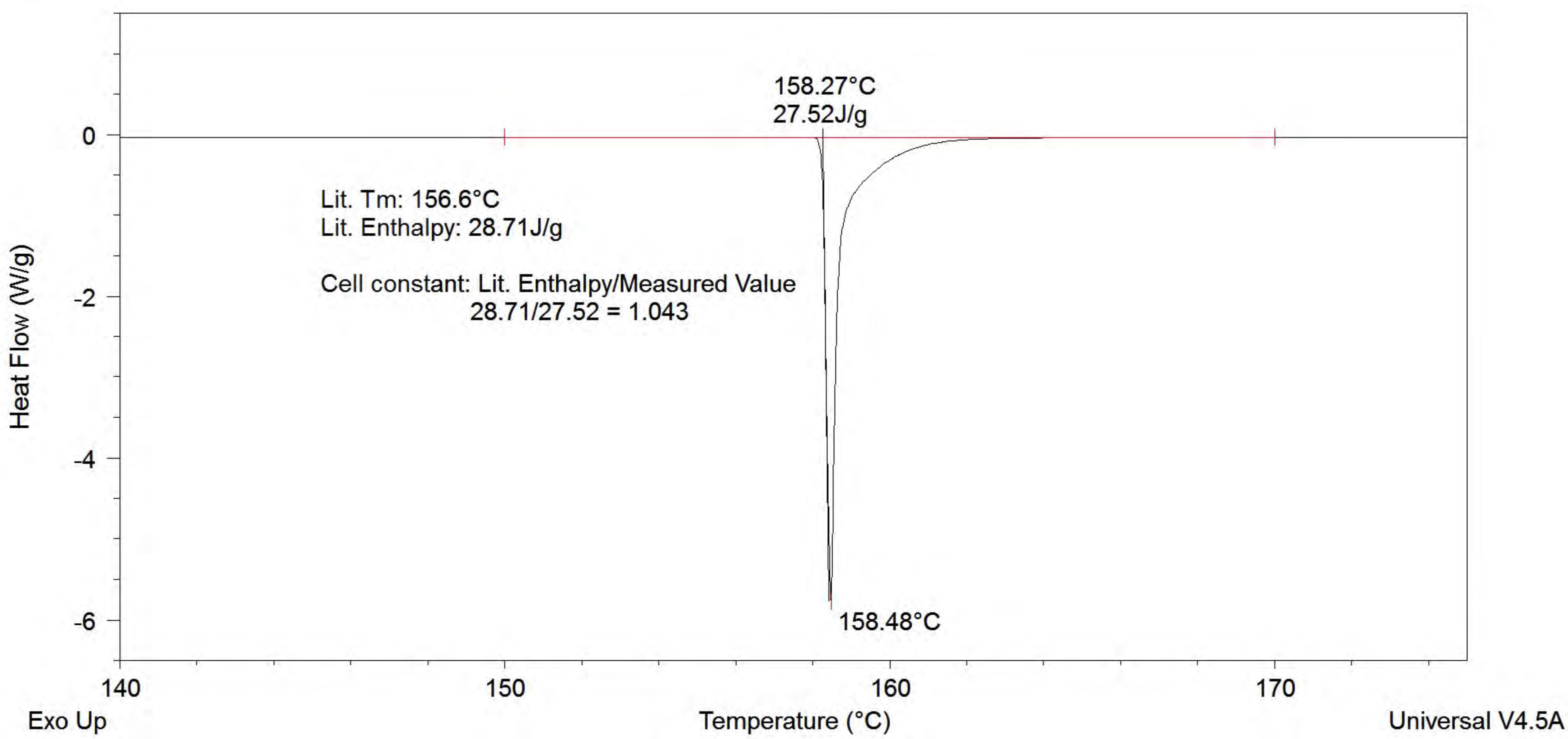


- Verify at least once a month

- Typical values for cell constant:
  - 0.9 to 1.2 (in N_2)
  - Helium will typically give higher values for the cell constant

Calorimetric and Temperature Calibration (Un-calibrated Data – No Correction Factors Applied)

Sample: Indium

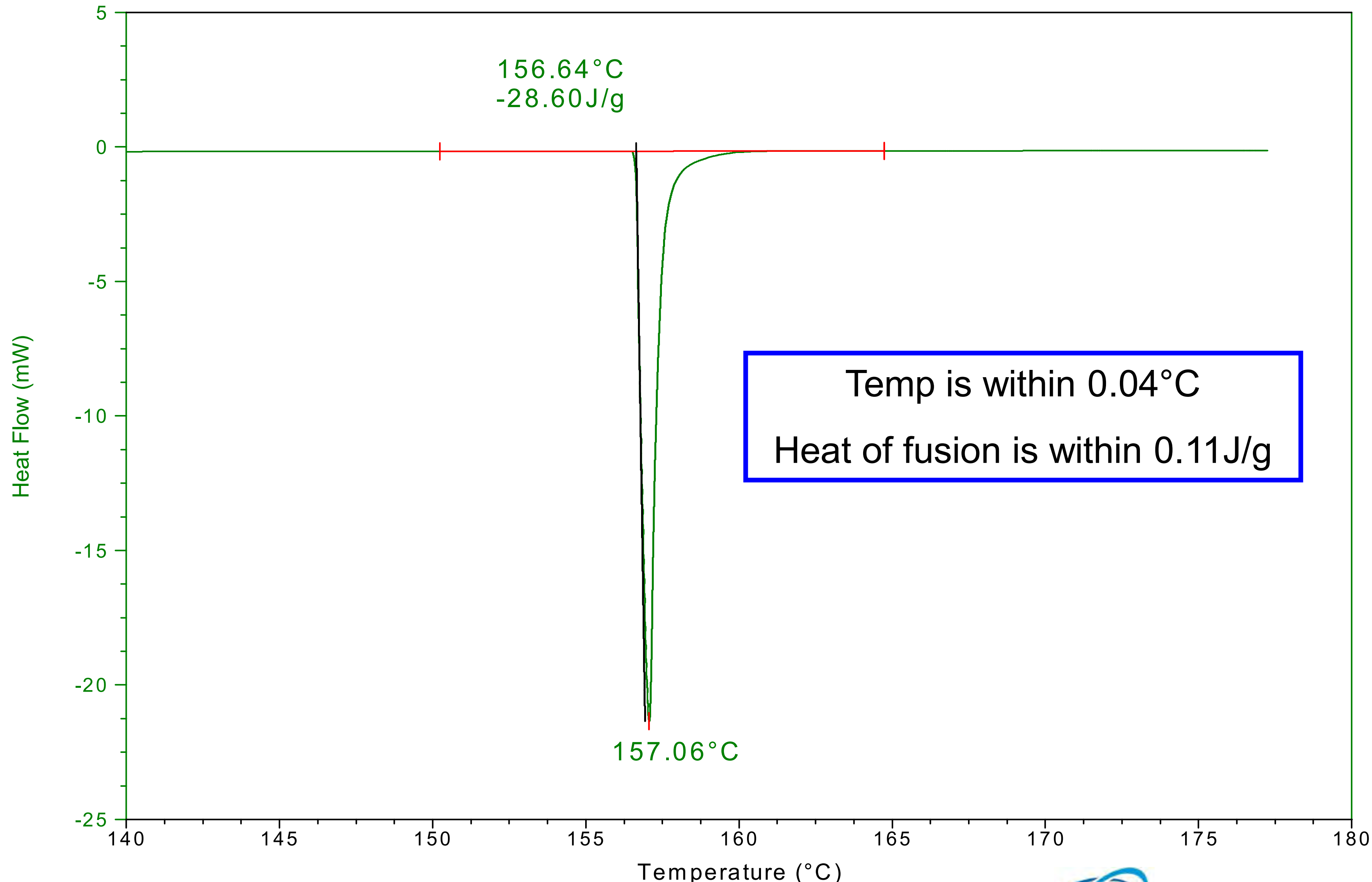


Indium melt from 155˚C to 157˚C

Verifying Cell Constant & Temperature

- Run Indium as a sample (i.e. in standard mode not calibration mode)
- Analyze melt and record melt onset & heat of fusion
- Compare to known values
  - Melting of In 156.6°C
  - Heat of Fusion 28.71J/g

Verifying Cell Constant & Temperature



Temp is within 0.04°C

Heat of fusion is within 0.11J/g

Reference Standards for Calibration

- 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

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

ITS 90 Fixed Point

E Zone refined organic compound (sublimes)

- 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-Nitrotoluene E 51.45°C
  - Naphthalene E 80.25°C
  - Indium # 156.60°C
  - Tin # 231.95°C
  - Lead* 327.46°C
  - Zinc # 419.53°C

Traceable Calibration Materials

- NIST DSC calibration materials:
  - SRM 2232 Indium, Tm = 156.5985°C
  - SRM 2220 Tin, Tm = 231.95°C
  - SRM 2222 Biphenyl, Tm = 69.41°C
  - SRM 2225 Mercury, Tm = -38.70°C

- NIST: Gaithersburg, MD 20899-0001
  - Phone: 301-975-6776
  - Fax: 301-948-3730
  - Email: SRMINFO@nist.gov
  - Website: http://ts.nist.gov/srm

Traceable Calibration Materials

- LGC DSC Calibration Materials:
  - LGC2601: Indium (TA p/n: 915060-901)
  - LGC2608: Lead
  - LGC2609: Tin
  - LGC2611: Zinc

- Laboratory of the Government Chemist, UK
  - Phone: 44 (0) 181 943 7565
  - Fax: 44 (0) 181 943 7554
  - Email: orm@lgc.co.uk

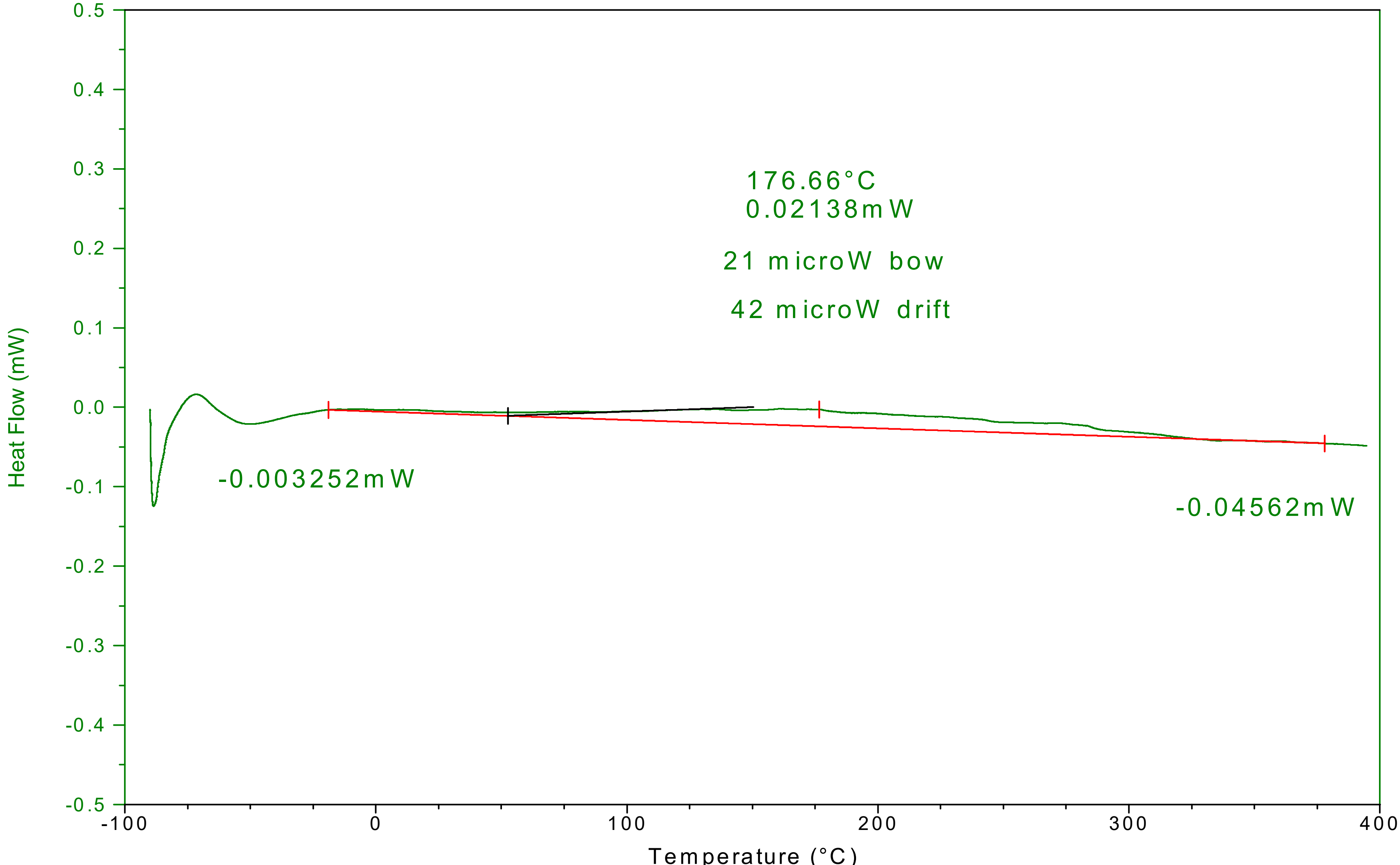
Verifying Baseline

- Run Empty cell (no pans), -90°C to 400°C (w/ RCS) at 20°C/min
  - Experiment is run in the standard mode
  - Plot mW vs. temperature on a 1mW scale
    - Should look fairly flat on this scale
    - Should be around zero heat flow
  - Measure drift and compare to instrument specifications.
  - Verify performance periodically

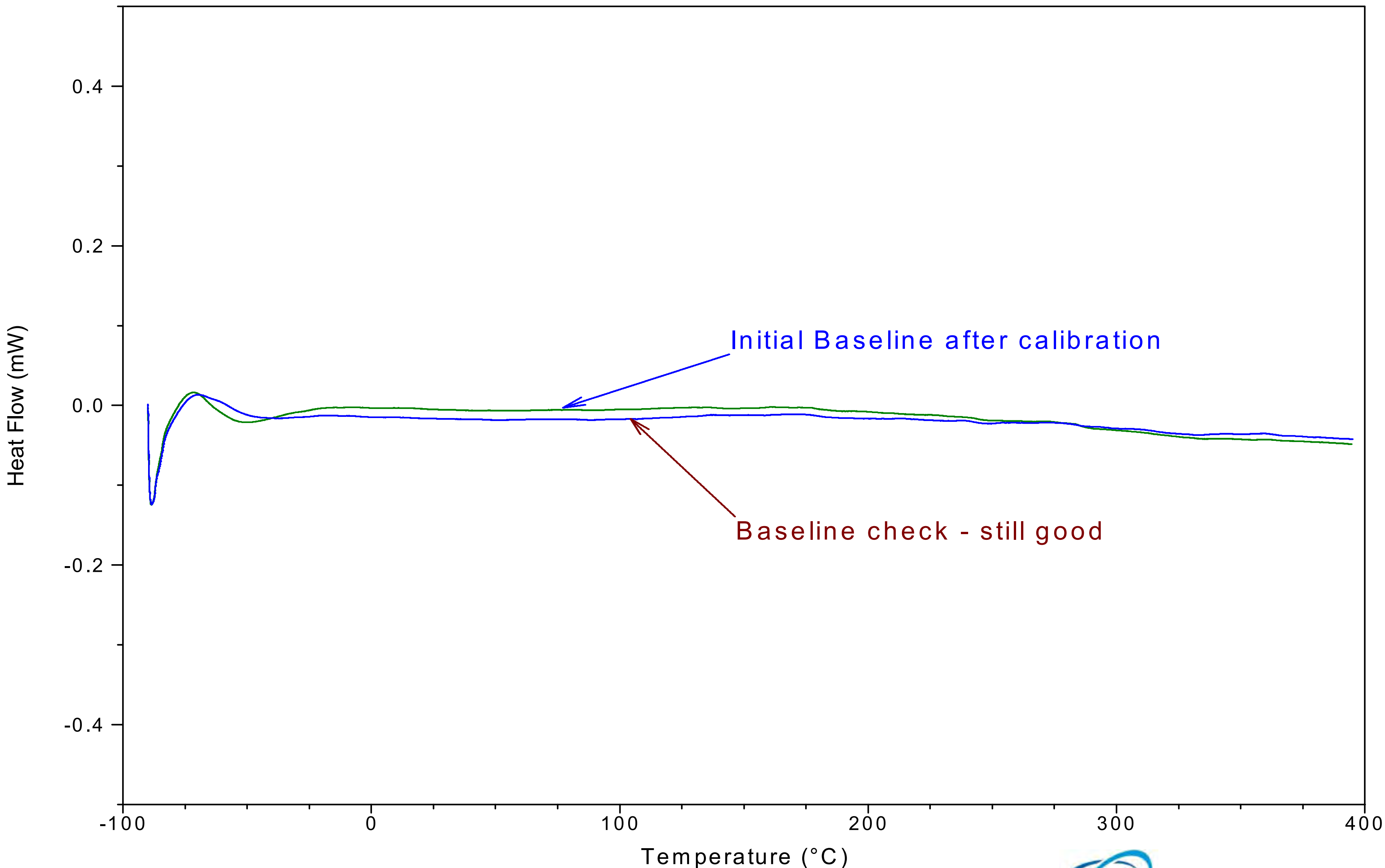
Verifying Baseline

- Importance of a flat baseline:
  - Detecting very weak transitions
  - Accurate integration of enthalpy
    - Kinetics, partial area analysis, extent of reactions
    - Initial crystallinity

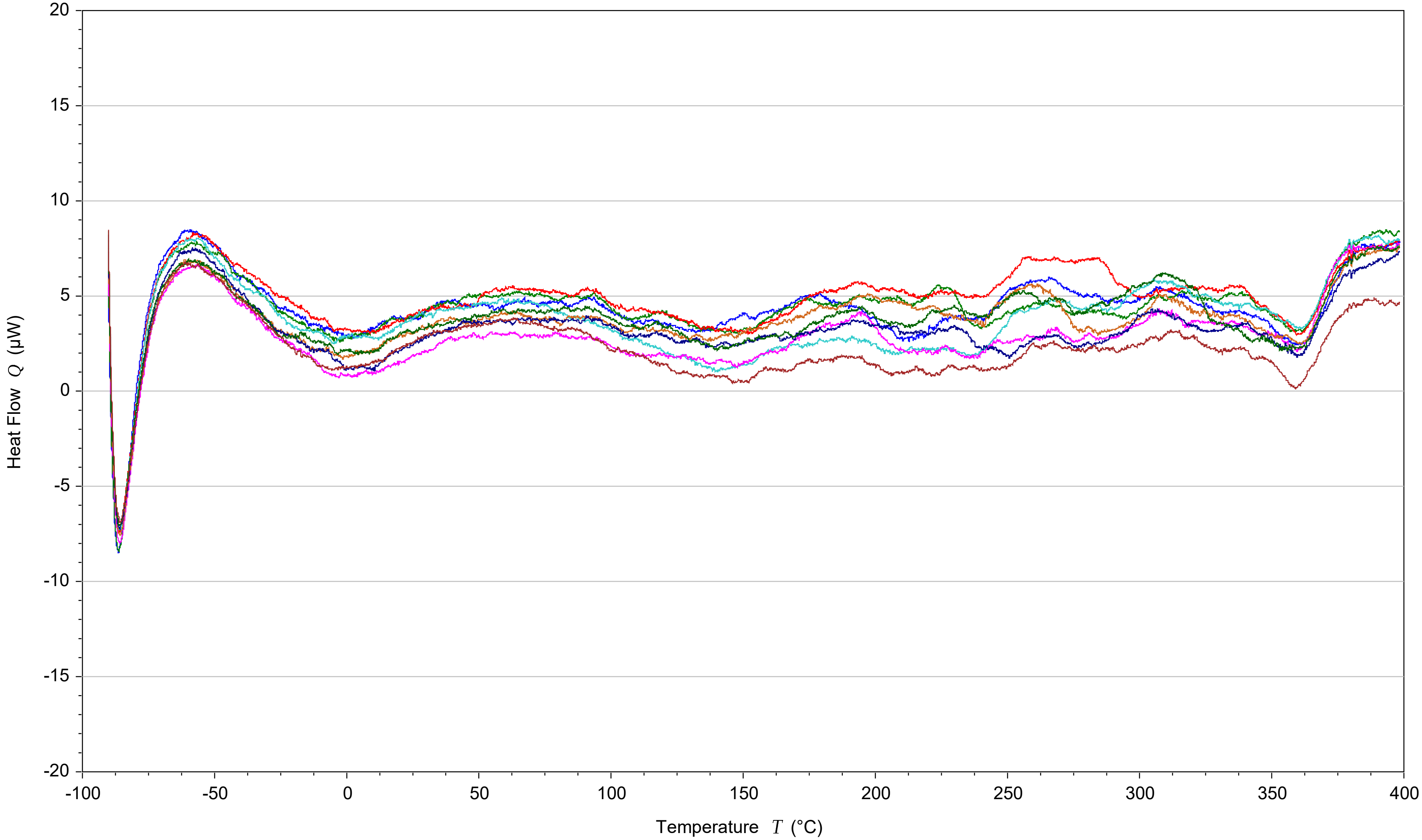
Verifying Baseline



Verifying Baseline



Empty Cell Baseline at 20 °C/min – DSC2500



Experimental Design: Instrument Set Up

Instrument Hardware and Gas Selection Considerations

Temperature Range Dependent On The Cooling System

- Finned Air Cooling System (FACS): Ambient to 725°C
- Quench Cooling Accessory (QCA): -180°C to 400°C
- Liquid Nitrogen Cooling System (LN2P): -180°C to 550°C
- RCS120: -120°C to 400°C
- RCS90: -90°C to 550°C
- RCS40: -40°C to 400°C

Purge Gas Selection

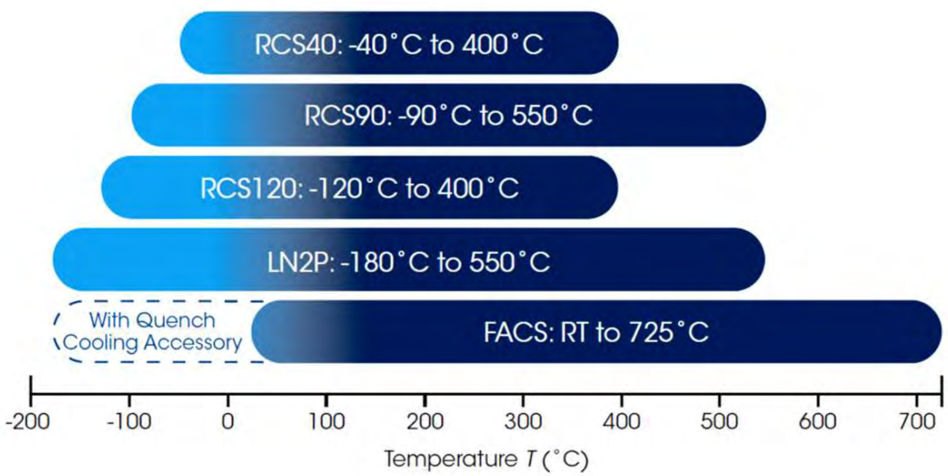
- **Nitrogen**
  - inert, inexpensive and readily available
  - flow rate of 50ml/min
- **Helium**
  - a high thermal conductivity gas which improves response time and cooling capabilities
  - the recommended purge gas when using the LN2 accessory at temperatures below -100°C
  - flow rates of 10-25ml/min are typically used; cell constant affected by flow rate
- **Air/Oxygen**
  - used when studying oxidative stability of materials

Sample Press and Pan Selection

- Aluminum: max. temperature of 600°C
- Gold
- Copper
- Graphite, Alumina
- Platinum
- Stainless Steel

Cooling Accessories

- Finned Air Cooling System (FACS): Ambient to 725°C
- Quench Cooling Accessory (QCA): -180°C to 550°C *
- Liquid Nitrogen Cooling System (LNCS): -180°C to 550°C
- RCS120: -120 °C to 400 °C
- RCS90: -90°C to 550°C
- RCS40: -40°C to 400°C



* Isothermal or slow heating ramp experiments above 400°C are not recommended.

Performance of the Cooling Accessories

RCS90 Controlled Cooling Rates, from 550°C (upper limit)*

Controlled Rate	To Lower Temperature
100°C/min	300°C
50°C/min	120°C
20°C/min	-20°C
10°C/min	-50°C
5°C/min	-75°C
2°C/min	-90°C

RCS40 Controlled Cooling Rates, from 400°C (upper limit)*

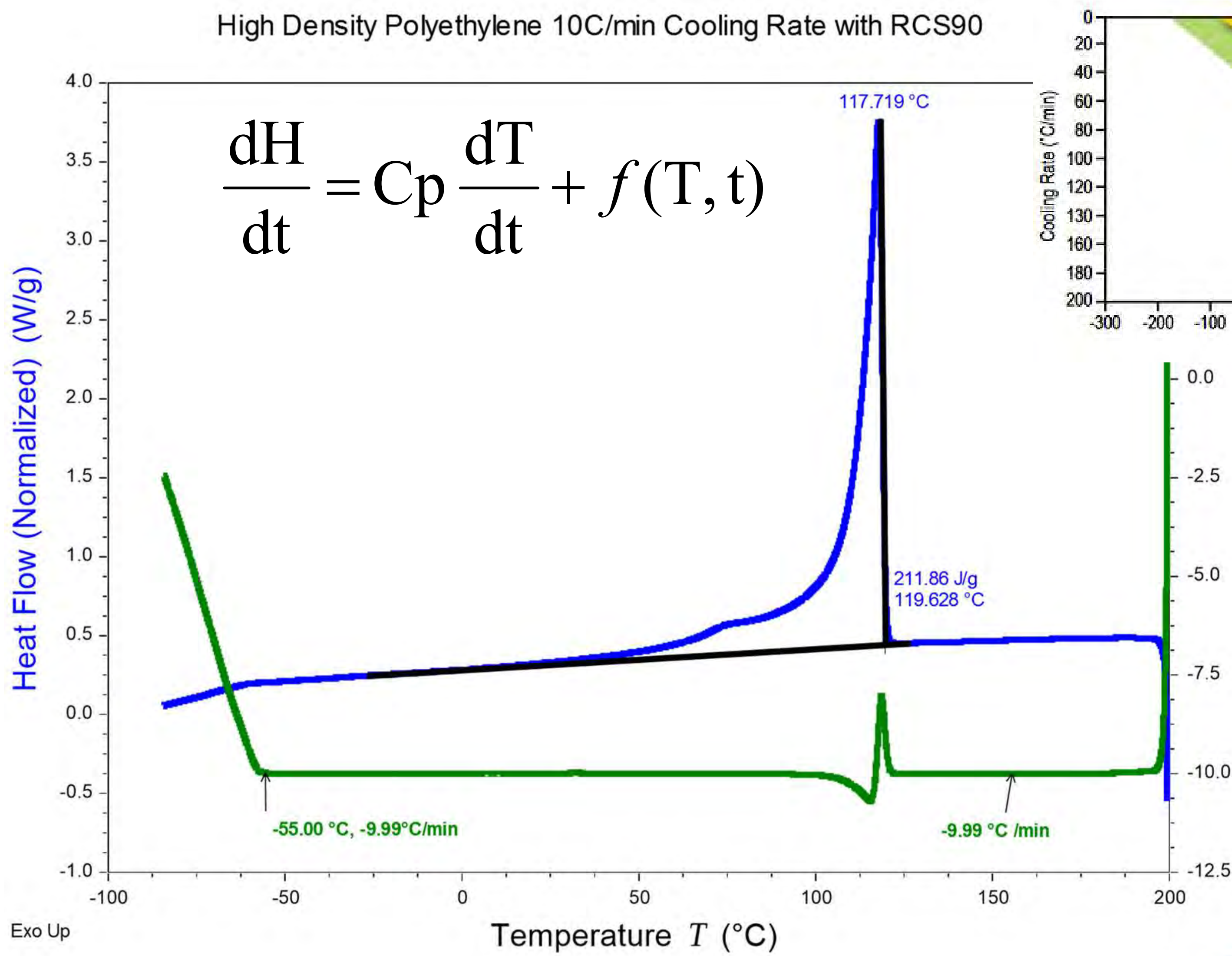
Controlled Rate	To Lower Temperature
65°C/min	250°C
50°C/min	175°C
20°C/min	40°C
10°C/min	0°C
5°C/min	-15°C
2°C/min	-40°C

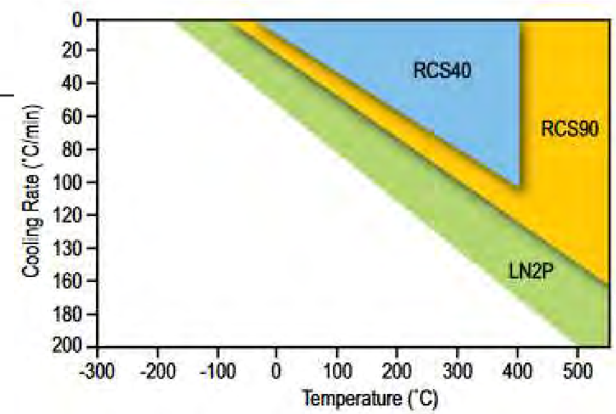
LNCS Controlled Cooling Rates, from 550°C (upper limit)*

Controlled Rate	To Lower Temperature
100°C/min	200°C
50°C/min	0°C
20°C/min	-100°C
10°C/min	-150°C
5°C/min	-165°C
2°C/min	-180°C

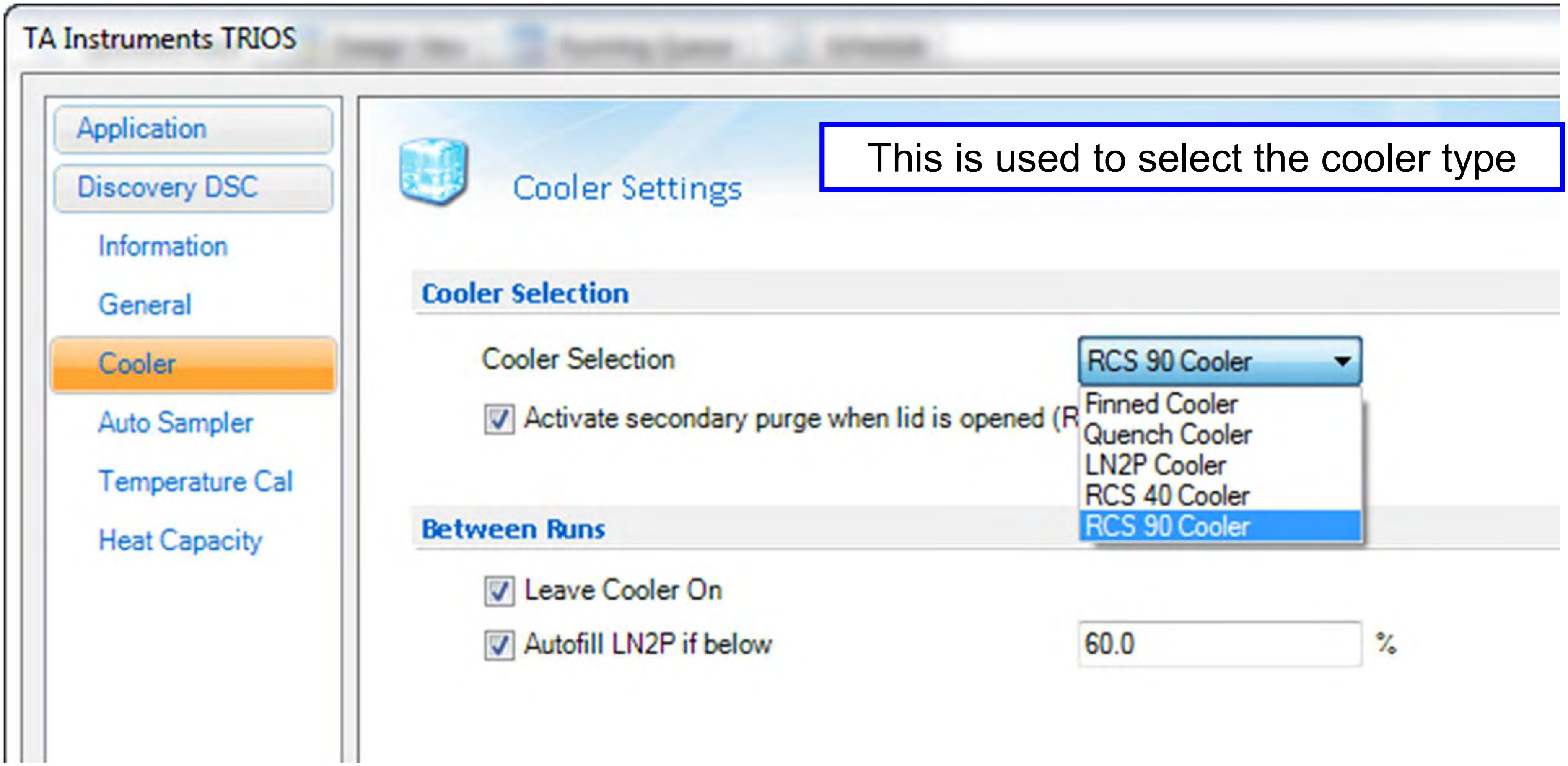
* Performance may vary slightly, depending on laboratory conditions.

Effect of Cooling Rate on Heat Flow

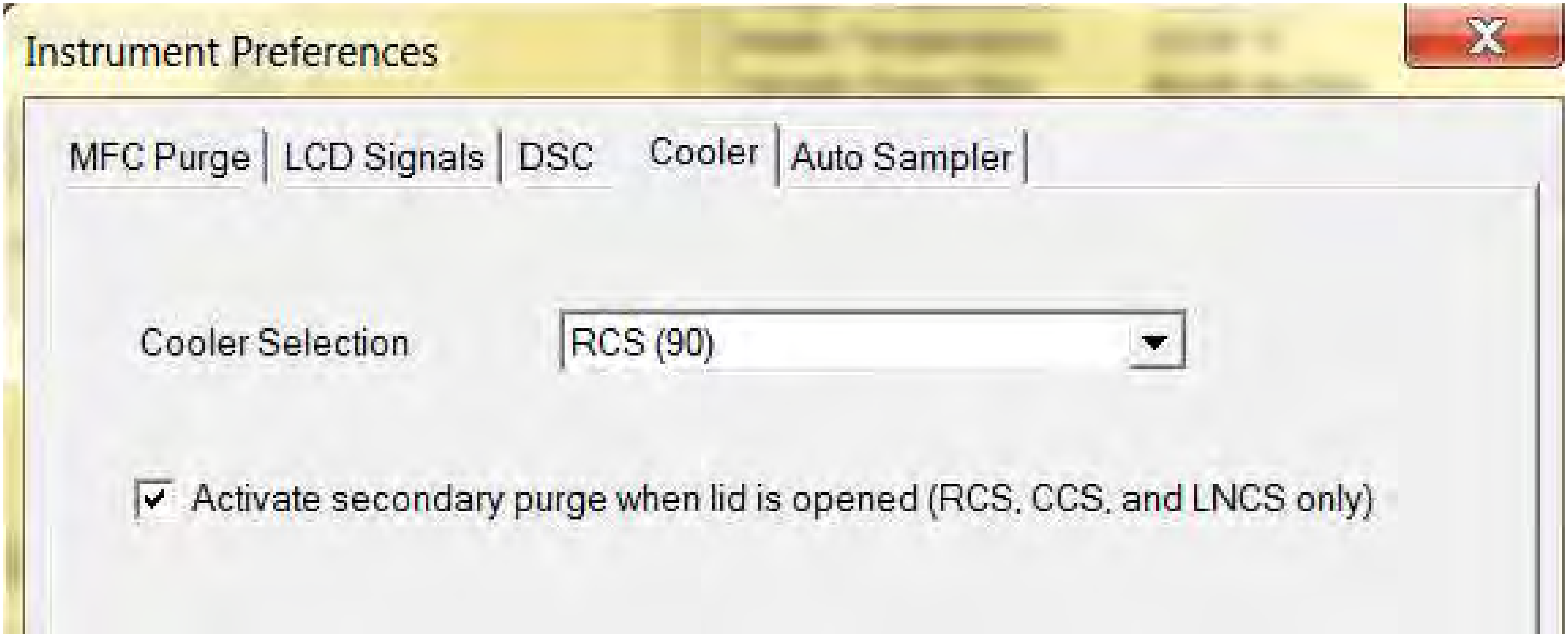




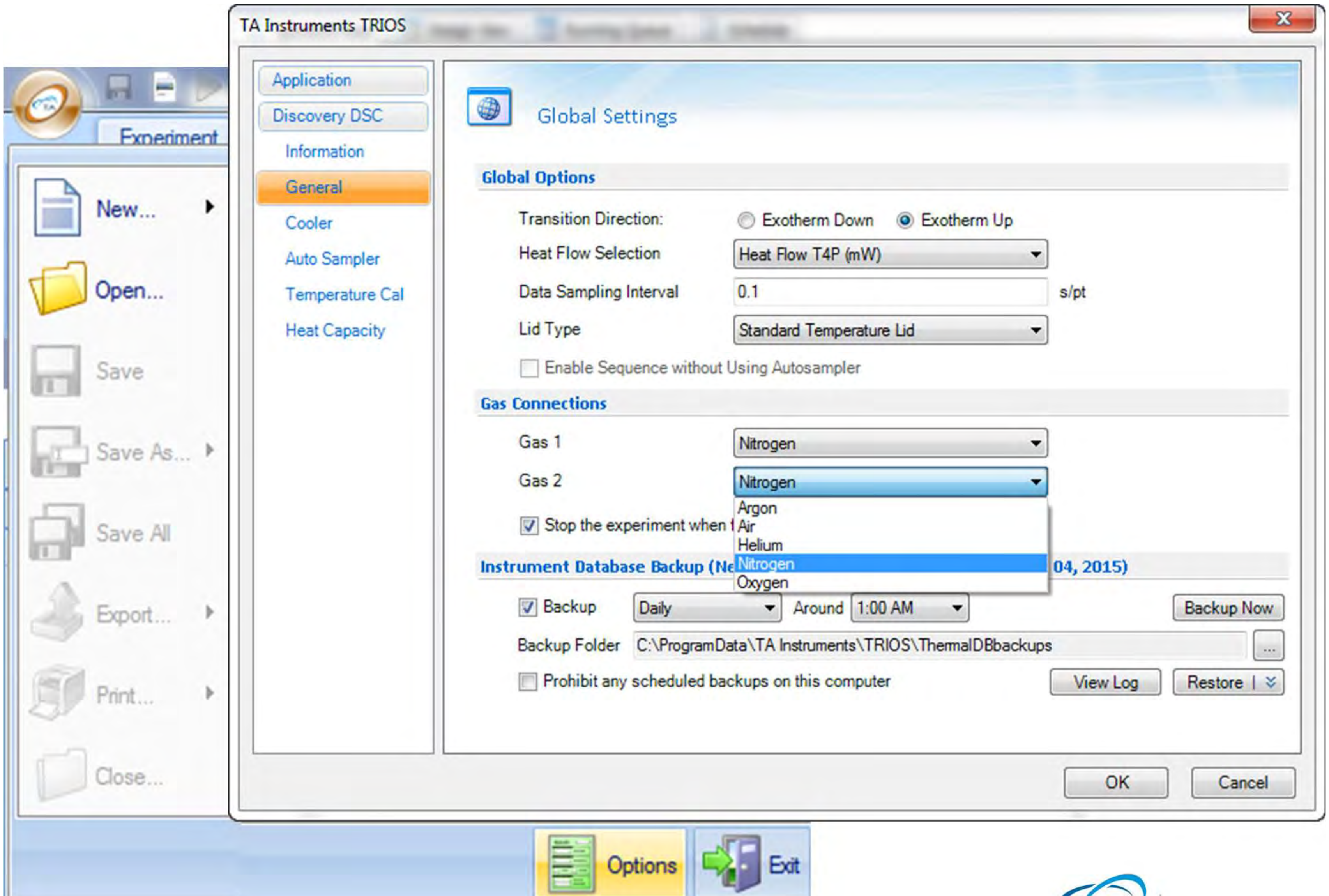
Selecting the Cooler – Discovery DSC



Selecting the Cooler – Q-series

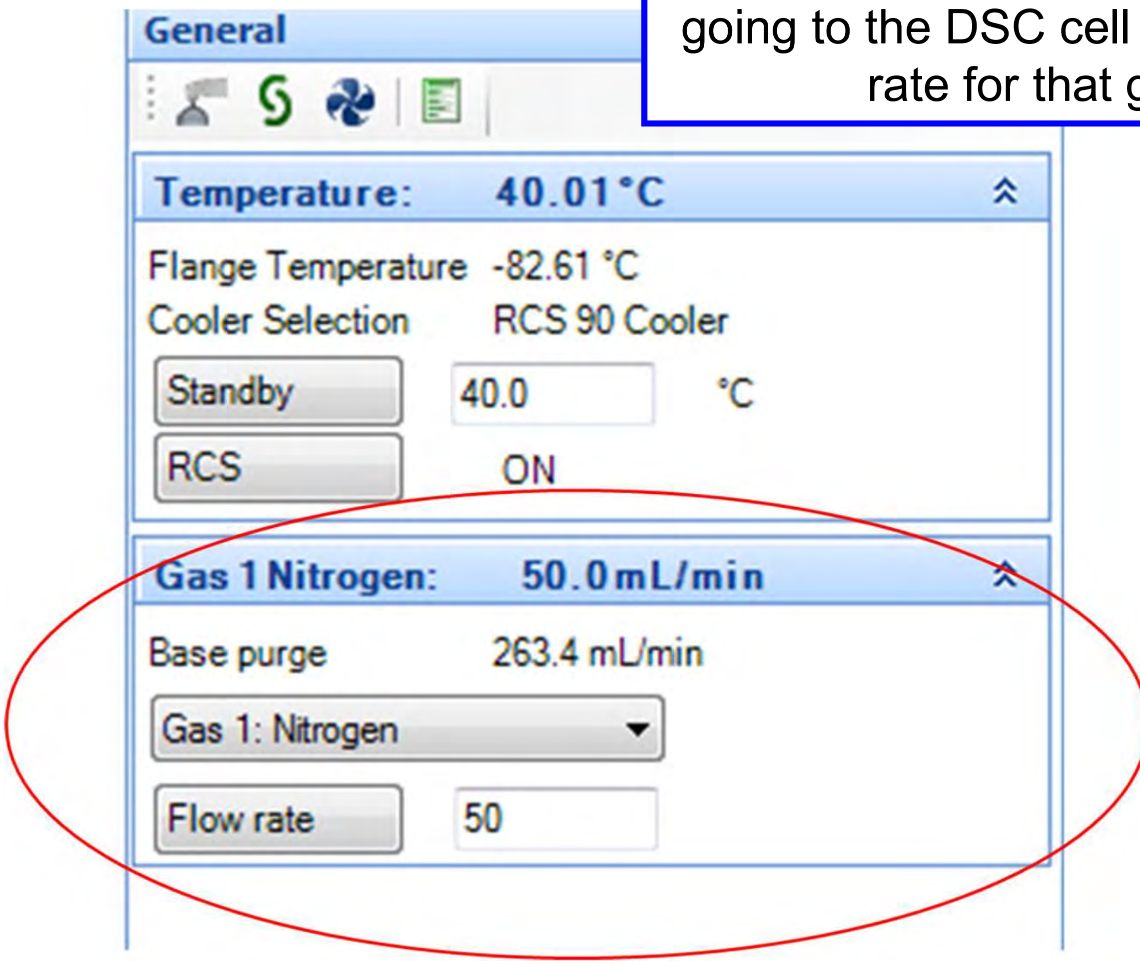


Selecting the Purge Gas – Discovery DSC

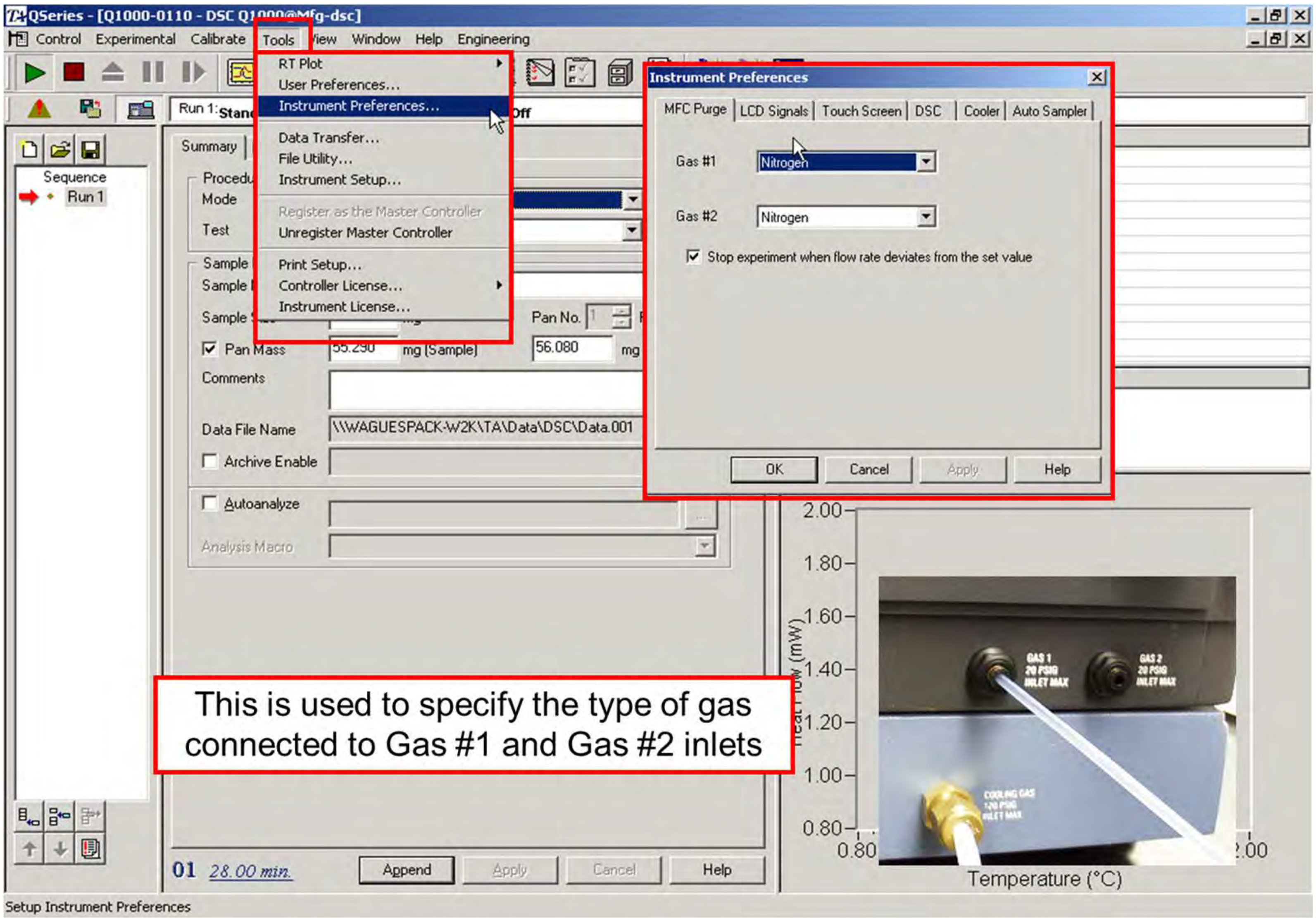


Setting the Purge Gas Flow Rate – Discovery DSC

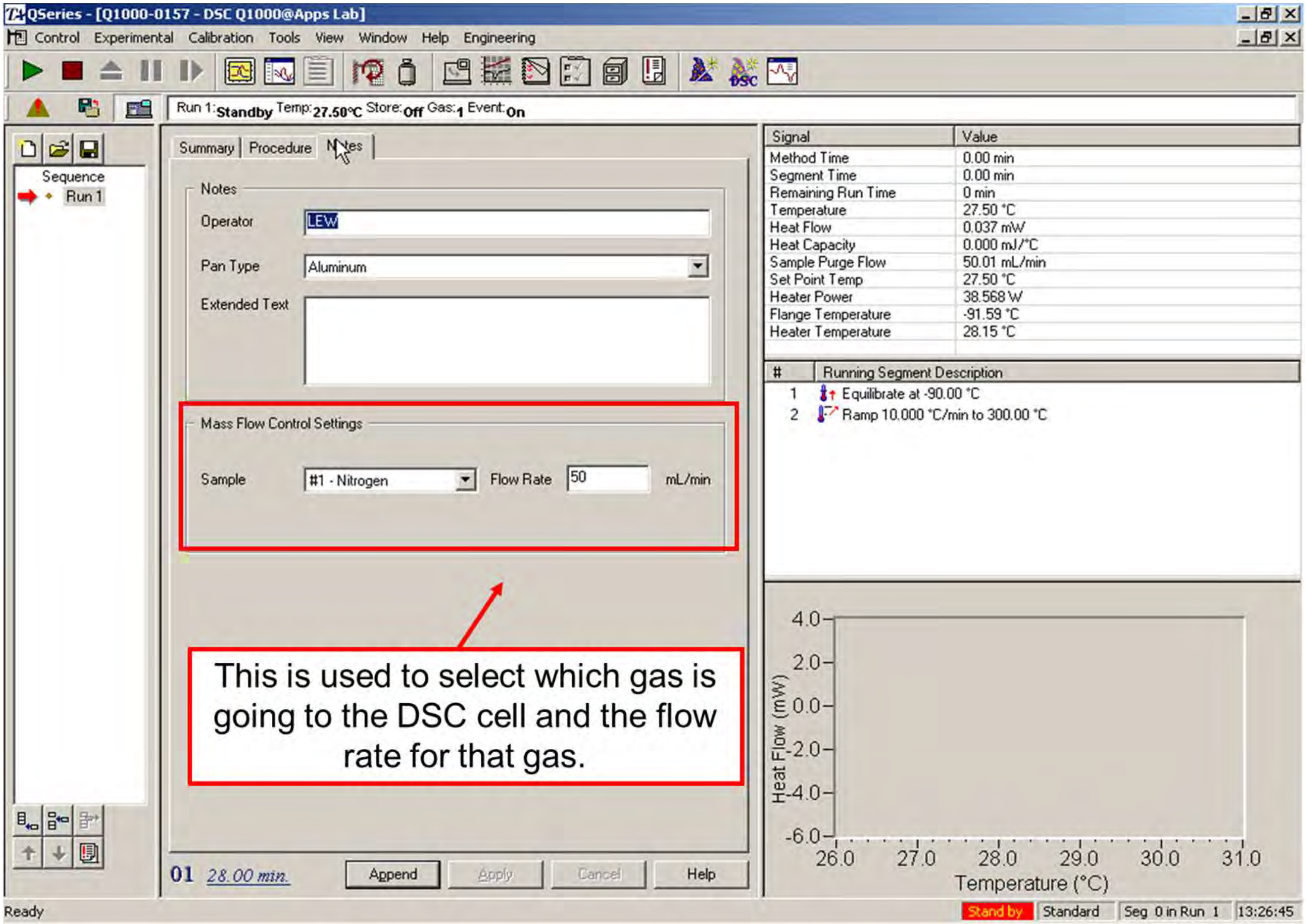
This is used to select which gas is going to the DSC cell and the flow rate for that gas.



Selecting the Purge Gas – Q-series DSC



Setting the Purge Gas Flow Rate – Q-series DSC



Recommended Purge Gas Flow Rates

Module	**Purge Port**
All TA DSC's	50 ml/min (N_2) or 25 ml/min (He)

- If purge gas is too slow - possible moisture accumulation & early aging of the cell
- If purge gas is too fast – excessive noise

Experimental design:
Sample Preparation and Considerations

TGA for DSC Experimental Design

- Thermogravimetric Analysis (TGA) measures weight loss or gain as a function of temperature, time and atmosphere.

- General applications of TGA include:
  - thermal stability
  - residual solvent, out gassing, moisture sorption/desorption
  - filler/fiber content
  - weight loss on cure

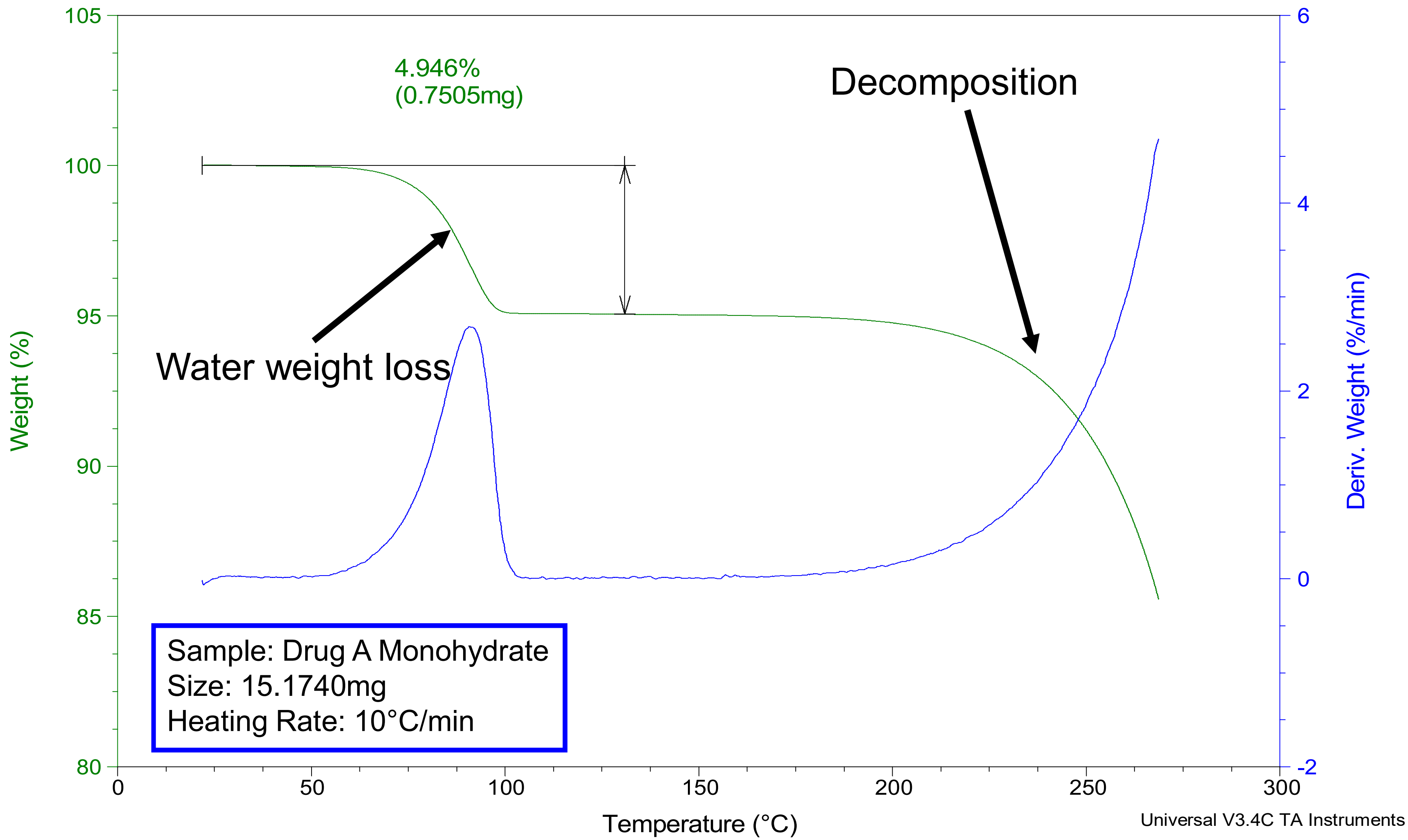
- TGA measurements are extremely useful in selecting experimental conditions for DSC experiments and for interpreting results.

Selecting Optimum Experimental Conditions

- If possible, run a TGA experiment before beginning DSC tests on new materials

- Heat approximately 10mg sample in the TGA at 10°C/min to determine:
  - Volatile content
    - Unbound water or solvent is usually lost over a broader temperature range at a lower temperature than a hydrate/solvate
  - Decomposition temperature
    - DSC results are of little value once the sample has lost 5% weight due to decomposition (not desolvation)
    - Decomposition is a kinetic process (time & temperature dependent). The measured decomposition temperature will shift to lower temperatures at slower heat rates

Typical TGA data: TGA of Drug A Monohydrate



Selecting Optimum Experimental Conditions

- Use TGA data to help select DSC experimental conditions
  - Standard (non-hermetic) vs. Hermetic (sealed) pans
    - Use hermetic pan if sample loses approximately 0.5% weight or more.
    - Use hermetic pan with pin hole lids if sample loses volatiles such as water
  - Maximum Temperature
    - Excessive decomposition will contaminate the DSC cell between runs
  - When comparing samples, always use the same experimental conditions

DSC Pan Selection

- High thermal conductivity – aluminum, gold, copper, platinum
- Inert - alodined aluminum, ceramic, graphite
- Flatness of the pan for optimal thermal contact
- Standard, non-hermetic vs. hermetic sealing
- Capacity/sample volume
- Temperature range

Sample Pans

- Type of pan depends on:
  - Sample form
  - Volatilization
  - Temperature range
- Use lightest, flattest pan possible
- Always use reference pan of the same type as sample pan

Tzero Press (P/N 901600.901)

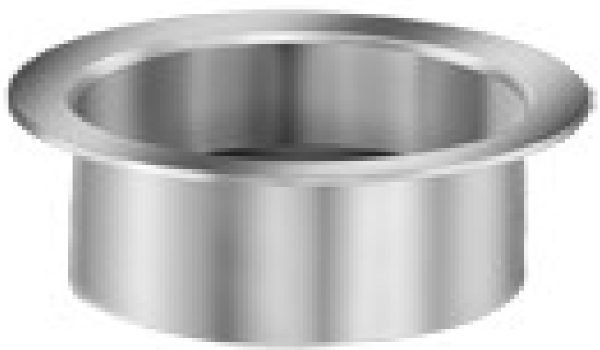
Tzero Press kit includes die sets for:

1. Tzero Pans / Tzero Lids and Tzero Low-Mass Pans / Tzero Lids (Black)
2. Tzero Pans / Tzero Hermetic Lids (Blue)
3. Standard Aluminum Pans / Lids (Green)
4. Standard Hermetic Pans / Lids (White)

The kit also includes one box each of Tzero Pans (100) and Tzero Lids (100).

TA Instruments Tzero Pans (Aluminum)

Tzero Pan

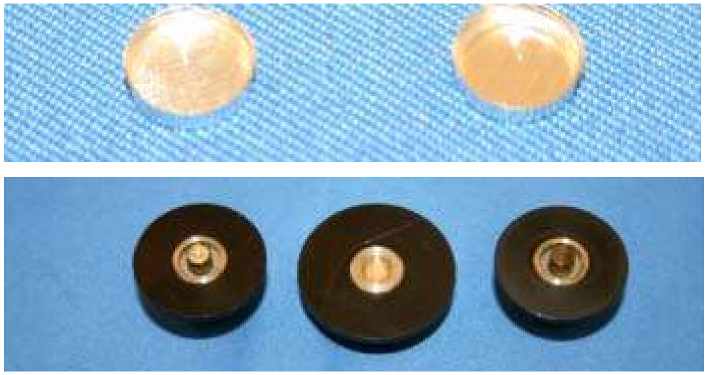


Tzero Low-Mass Pan

- 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 non-hermetic or hermetic use. P/N 901683.901 Tzero Pans (pkg. of 100)
- The Tzero Low-Mass Pan is designed for the highest sensitivity when sample mass is limited. P/N 901670.901 Tzero Low-Mass Pans (pkg. of 100). Can only be used with the non-hermetic Tzero lid.

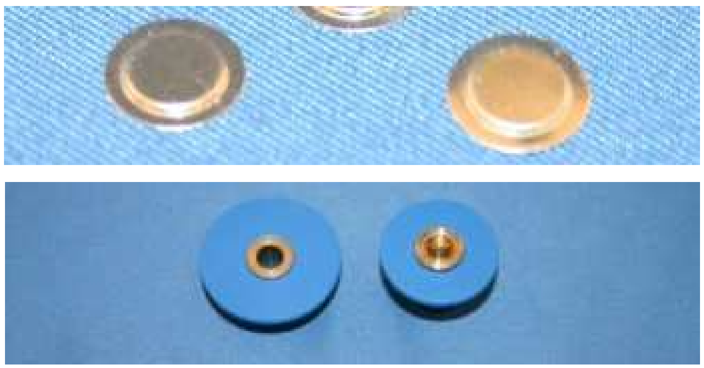
TA Instruments Tzero Pans

Tzero Lid



- Tzero Lid (P/N: 901671.901) - Lightweight aluminum lids for use in sample encapsulation with the Tzero Pans and the Tzero Low-Mass Pans. The seal is not hermetic.

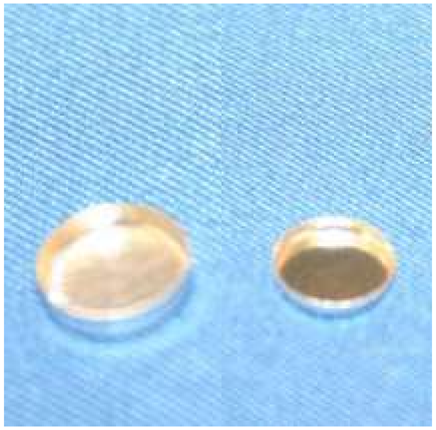
Tzero Hermetic Lid



- Tzero Hermetic Lid (P/N: 901684.901) (pkg. of 100) and P/N: 901685.901 Tzero Hermetic Pinhole Lid (75 micron diameter pinhole) (pkg. of 50). Used only with the Tzero pan, not the low mass Tzero pan

Standard Series DSC Aluminum Pans

- Part numbers for the pans and lid
  - 900760.901 Classic Aluminum Pans (pkg. of 200) (higher sidewall compared to the standard aluminum sample pans to accommodate larger samples)
  - 900786.901 Aluminum Sample Pans (pkg. of 200)
  - 900779.901 Aluminum Lids (pkg. of 200)
- Pan & lid weighs ~23mg, bottom of pan is flat
- use up to 600°C maximum
- Used for solid non-volatile samples
- Always use lid (see exceptions)
  - Lid improves thermal contact
  - Keeps sample from moving
- Exceptions to using a lid
  - Running oxidative experiment
  - Running PCA experiment



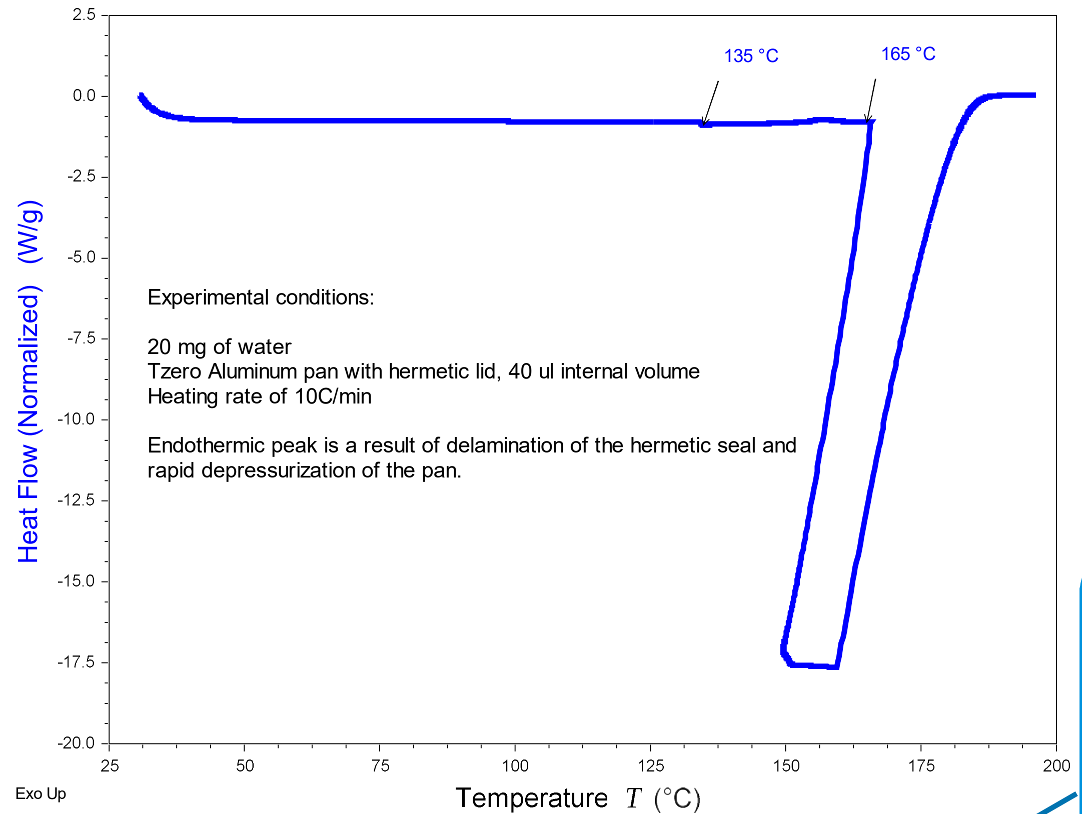
Standard Series DSC Other Pans (Non Hermetic)

- Standard pans are available in:
  - Gold (p/n 900866.901 pan, p/n 900868.901 lid):up to 725°C
  - Graphite (p/n 900874.901 pan, p/n 900873.901 lid): up to 725°C (in N_2)
- Standard Pans with no lids available
  - Platinum (p/n 900578.901): up to 725°C
  - Copper (p/n 900867.901) : up to 725°C

Sample Shape

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

Hermetic DSC Pans



Aluminum Hermetic

3 atm

Sample:

1. Liquid
2. Solid with volatile content

High Volume Stainless Steel

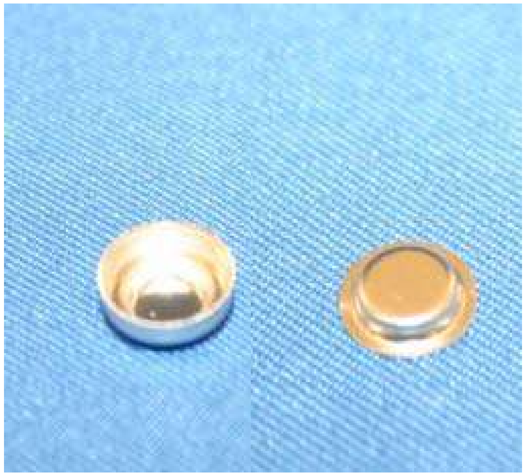
40 atm

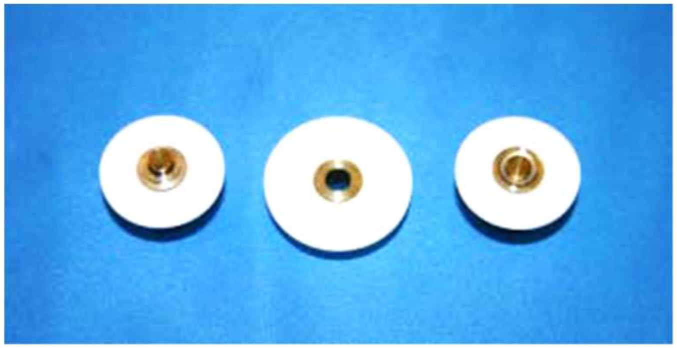
Gold Hermetic

6 atm

Standard Series Aluminum Hermetic Pans

- Part numbers for the pans and lid
  - 900793.901 Aluminum Sample Pans, Hermetic (pkg. of 200)
  - 900794.901 Aluminum Lids, Hermetic (pkg. of 200)
  - 900860.901 Hermetic Lids with Pinhole (pkg. of 50)
- Pan & Lid weigh ~55mg, bottom of pan is not as flat as standard pans
- Used for liquid samples and samples with volatiles
- Always use lid (same exceptions as before)
- After sealing pans, the lid should form a dome

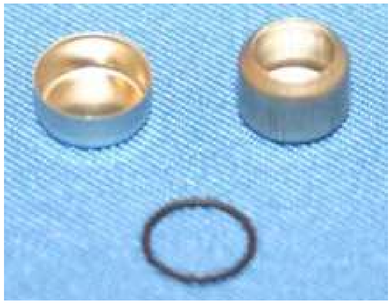




Hermetic Pans Summary

- Hermetic Pans are available in:
  - Aluminum: <600°C; <3 atm (300 kPa gauge)
  - Alodined Aluminum: <200°C; <3 atm (300 kPa gauge)
  - Gold: <725°C; <6 atm (600 kPa gauge)

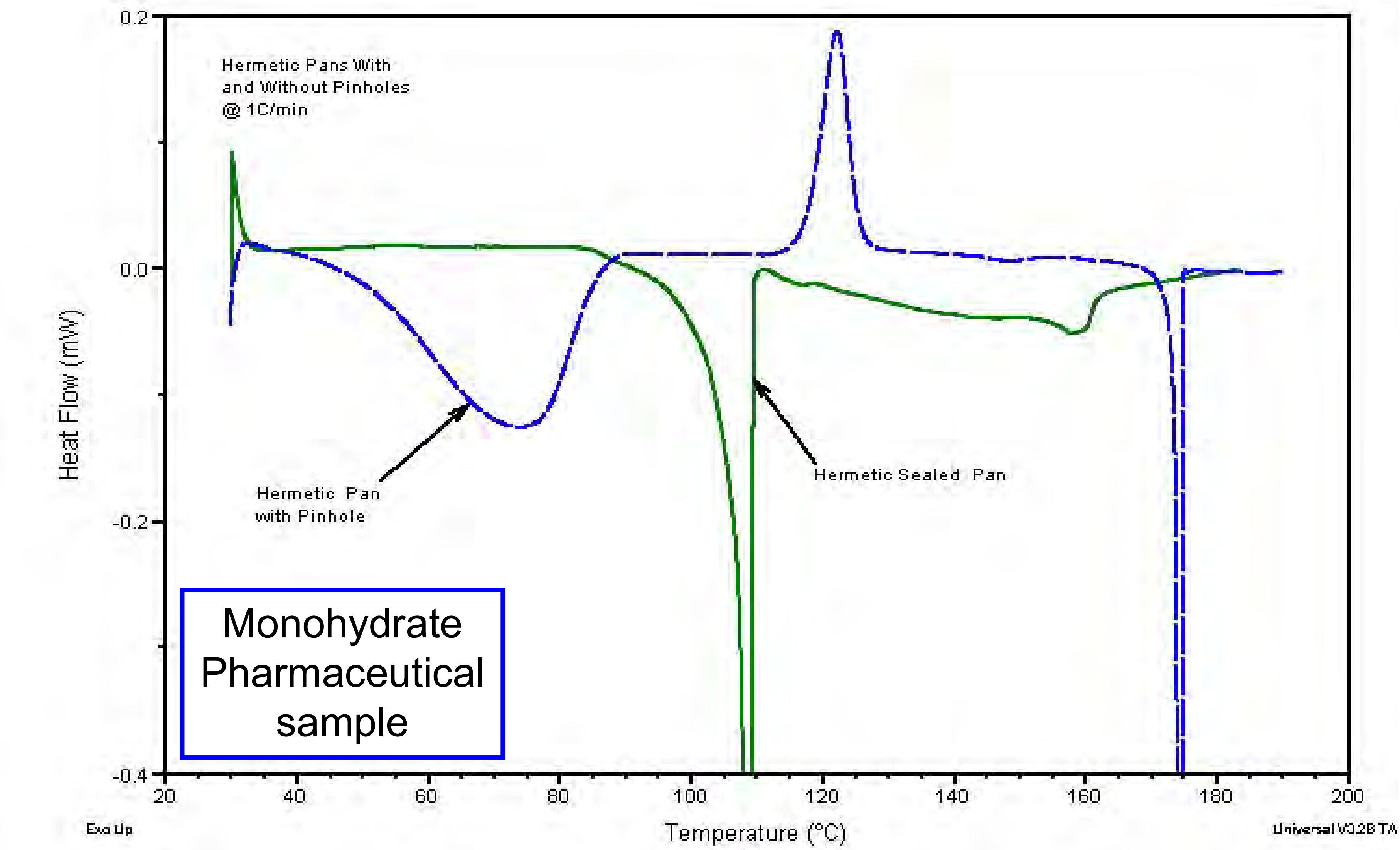
- Specialized Sealed Pans
  - High Volume: 100μL; <250°C; 37 atm (575 psi)
  - P/N 900825.901



  - High Pressure: 35μL; <300°C; 100 atm (1450 psi)
  - P/N 900808.901

Note: 3 atm is approximately 44 psi

It Can Matter What Pan You Use



What if Sample Spills out of the Pan? 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
  - Samples spilling out of the pan
  - Transfer from bottom of pan to sensor

Cleaning the Cell

- Use solvent – slightly damp swab with an appropriate solvent
  - Heat cell to 200°C for 10 min to drive off any remaining solvent

- If the cell is still dirty
  - Clean w/ brush
  - Be careful with the Tzero™ thermocouple
  - Fibers in cell from cleaning brush need to be removed

Cleaning Cell: Bake Out Procedure

- Bake out
  - Should be used as a last resort if none of the previous steps are effective
  - Involves Air purge and/or an open lid
  - Heat at 20°C/min to appropriate temp (max of 550°C on Q series, max. 400°C in Discovery)
  - Do NOT hold Isothermal at the upper temperature
  - Cool back to room temp & brush cell again

- Irrespective of the cleaning method used, always verify the baseline at the end of the cleaning procedure, and recalibrate the DSC if required

- Check out the TA Tech tip video on cleaning the DSC cell:

  https://www.youtube.com/watch?v=cclJXrbUICA

Sample Preparation: Optimization of Sample Mass

- Sample Preparation
  - Weight of 5-10 mg for polymers; 10-15 mg for cross-linked thermosets; 3-5 mg for metal or chemical melting
  - Goal is to achieve a change of 0.1-10mW heat flow in going through the transition

$$\frac{dH}{dt} = \boxed{Cp}\frac{dT}{dt} + f(T,t)$$

Heat Flow Change During a Transition