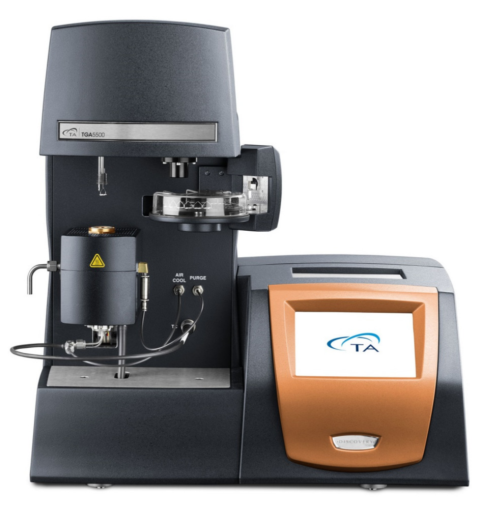
TA Instruments – Waters LLC

Thermogravimetric Analysis (TGA)



What is Thermogravimetric Analysis (TGA)?

- TGA measures weight/mass change (loss or gain) and the rate of weight change as a function of temperature, time and atmosphere
- Ideal first technique to characterize unknown or new materials

What TGA Can Tell You

- Moisture and Volatile Content
- Thermal Stability

} Extremely important when running DSC

- Oxidative Stability
- Composition of Multi-component system
- Decomposition Kinetics
  - Estimated Lifetime
- Effect of Reactive atmospheres
- Residue

Mechanisms of Weight Change in TGA

- Weight Loss:
  - Decomposition: The breaking apart of chemical bonds.
  - Evaporation: The loss of volatiles with elevated temperature.
  - Reduction: Interaction of sample to a reducing atmosphere (hydrogen, ammonia, etc.).
  - Desorption.

- Weight Gain:
  - Oxidation: Interaction of the sample with an oxidizing atmosphere.
  - Absorption.

All of these are kinetic processes (i.e. there is a rate at which they occur).

DSC-TGA (SDT): The Technique

Simultaneous DSC-TGA measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere from room temperature to 1500 °C.

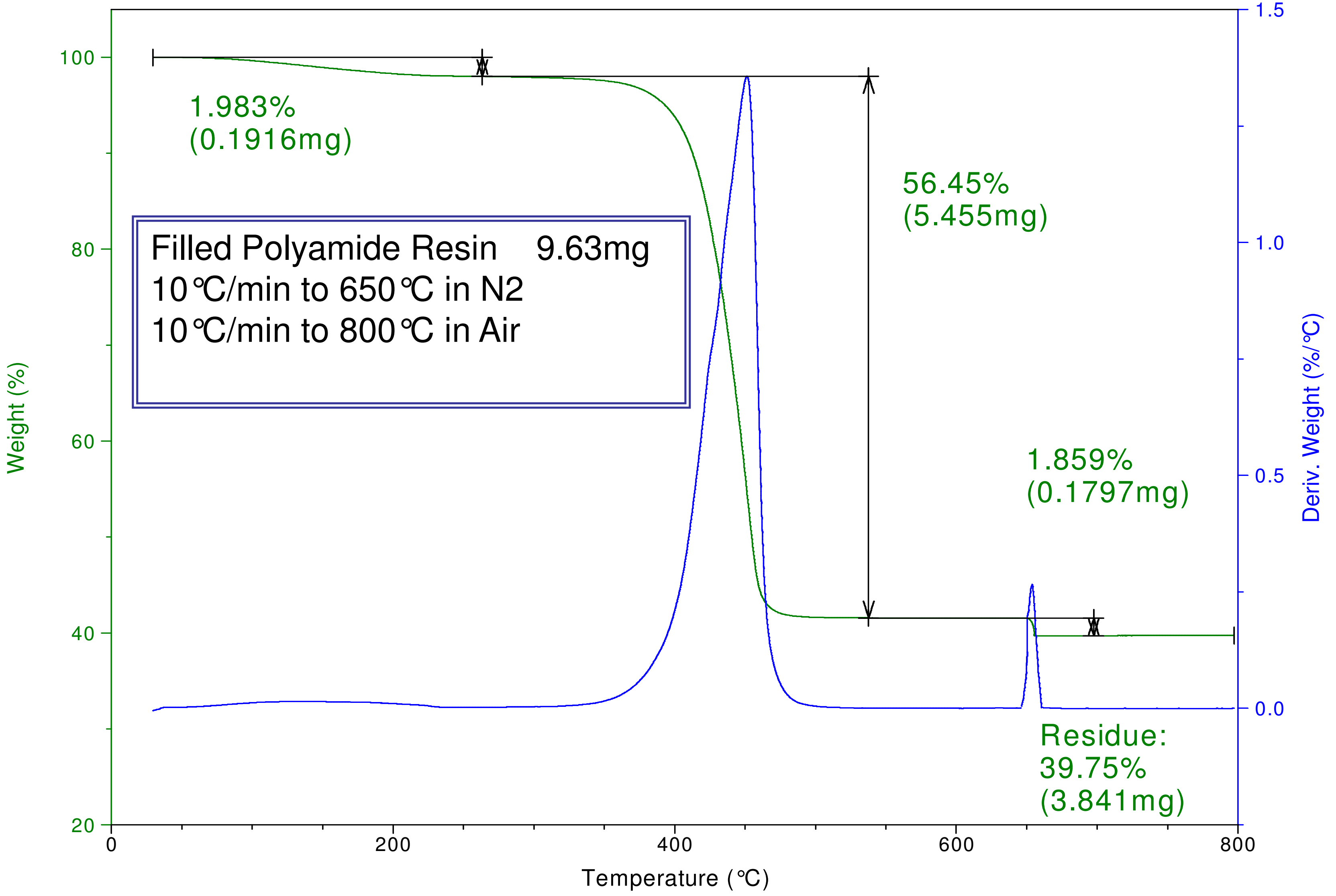
Information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization), and those which involve a weight loss (e.g., degradation).

What Simultaneous DSC-TGA Can Tell You

- Thermal Stability of Materials
- Oxidative Stability of Materials
- Composition of Multi-component Systems
- Estimated Lifetime of a Product
- Decomposition Kinetics of Materials
- The Effect of Reactive or Corrosive Atmospheres on Materials
- Moisture and Volatiles Content of Materials
- Residue

- Transition Temperatures
- Heats of Fusion and Reactions
- Melting and Boiling Points
- Heat capacity

A Typical TGA Result



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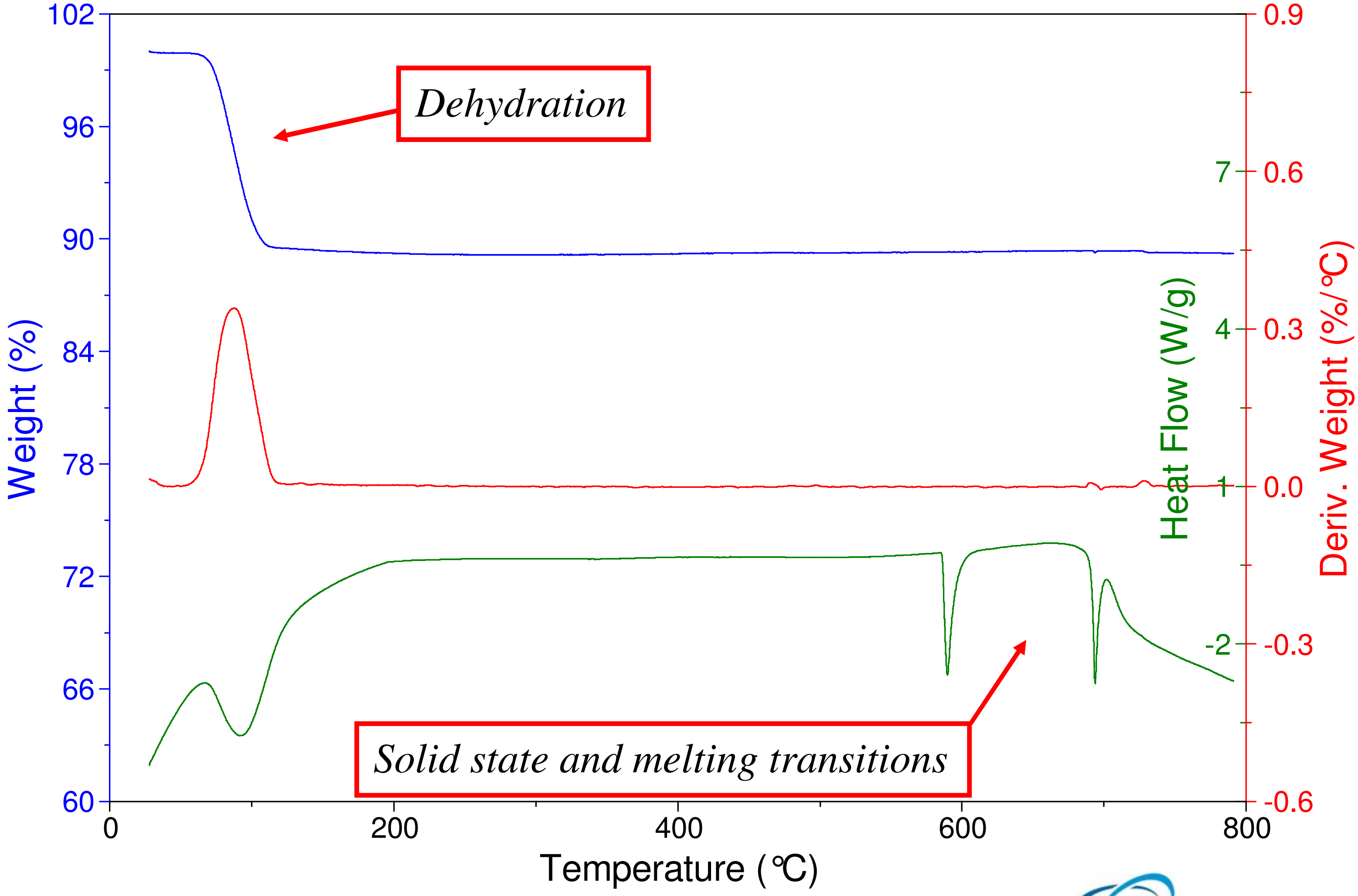
DSC-TGA Sodium Tungstate

Small Sample Size (3mg) and 10 ℃/min Heating Rate



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TA Instruments TGA/SDT Models

TGA 55
TGA 550
TGA 5500

Discovery TGA

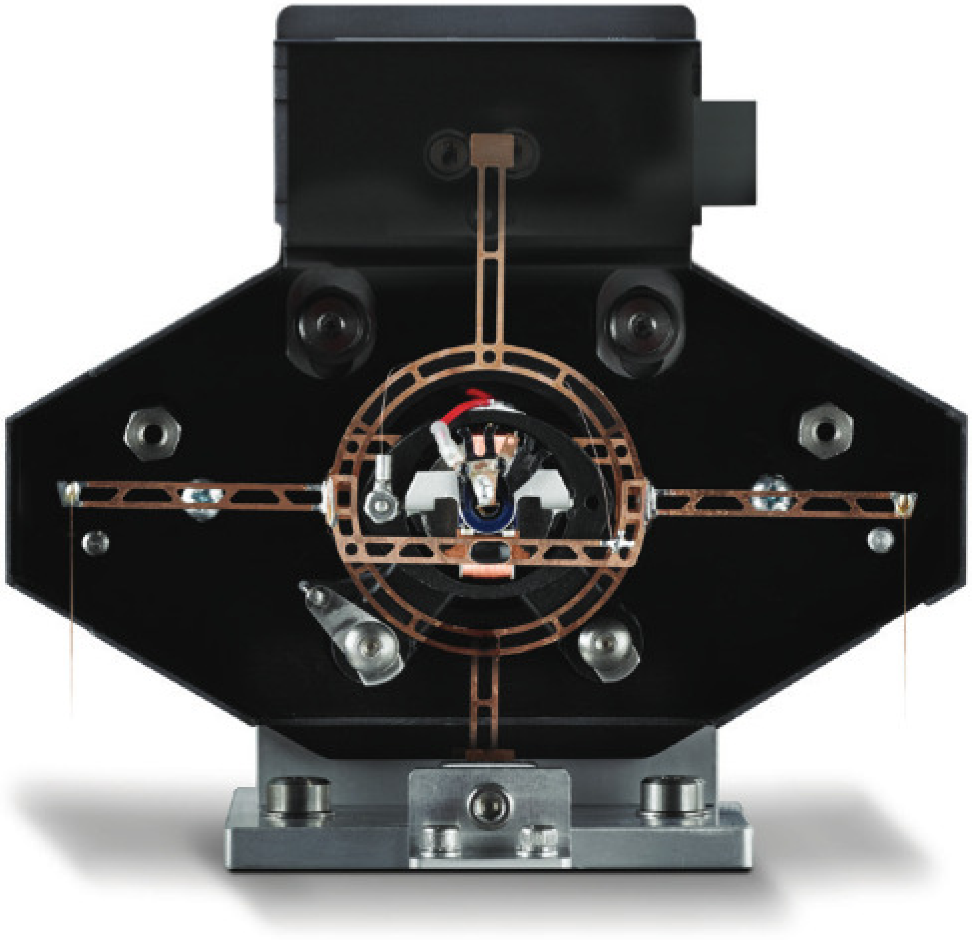
Q5000 IR

SDT 650

Q600

TGA: Schematic Diagram

TGA Balance and Operation



- Null-balance principle operation.
- Current is applied to the meter movement.
- Amount of current applied is proportional to the weight change.

TGA Furnace: Wire Wound Furnace

Wire Wound (Pt/Rh) Furnace

- Standard furnace for TGA 55 and 550
  - Similar to Q50/500
- Ambient to 1000 ℃
- Linear controlled heating rates of 0.01 to 100 ℃/min
- Ballistic heating rates >600 ℃/min
- Exchangeable with EGA furnace

Flow rate Balance/Sample :

40/60 ml/min

TGA Furnace Options: EGA Furnace

EGA Furnace

Flow rate Balance/Sample :

10/90 ml/min

- Optional for TGA55 and 550
  - Similar to Q50/500
- Ambient to 1000 ℃
- Linear controlled heating rates of 0.01 to 50 ℃/min
- Quartz liner makes furnace easy to clean
- Exchangeable with wire wound furnace

TGA Furnace: TGA 5500 Infra Red (IR) Furnace

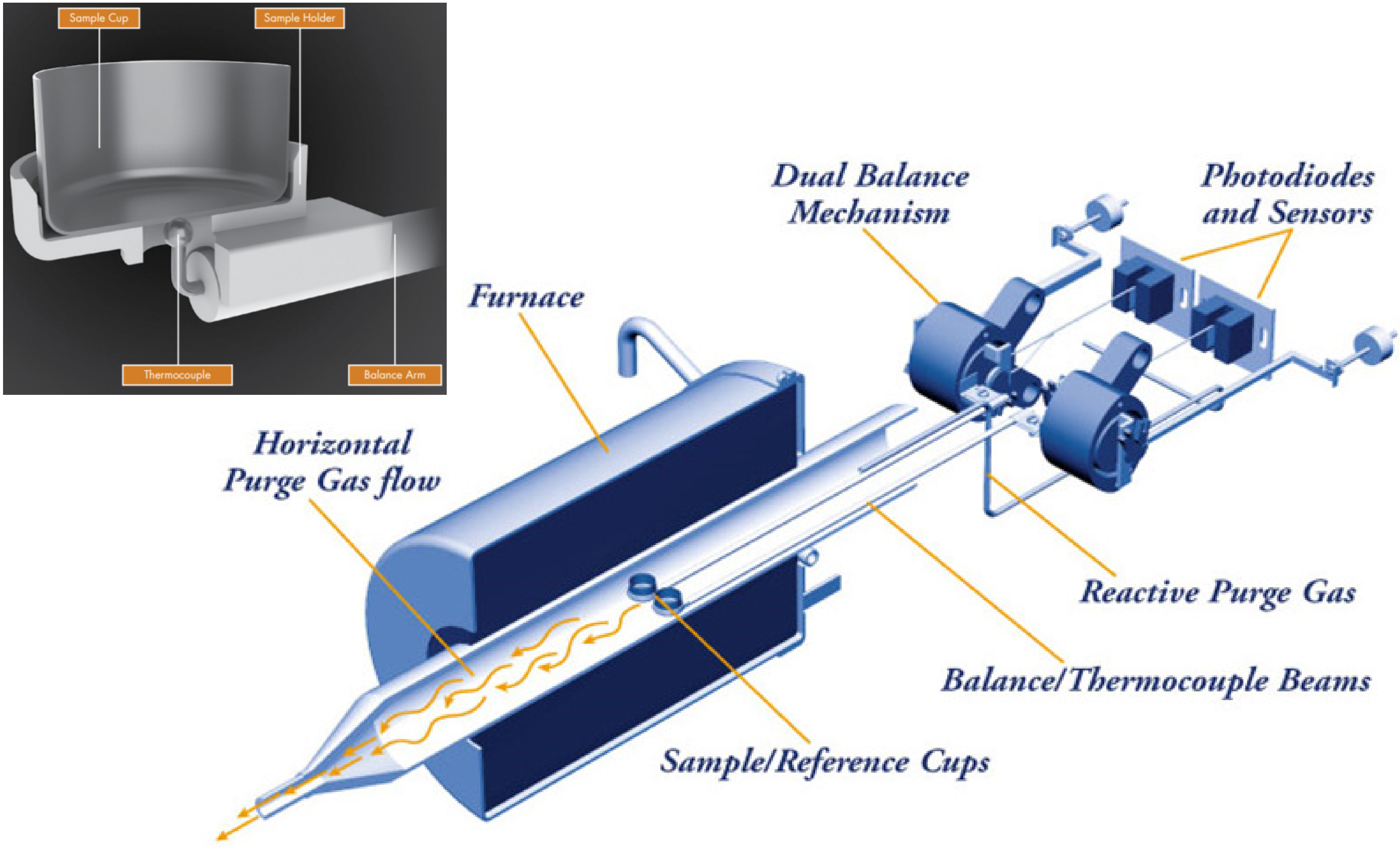
IR Furnace

Flow rate Balance/Sample :

25/25 ml/min

- Quartz halogen lamps as heating source
- Ambient to 1200℃
- Linear controlled heating rates of 0.01 to 500 ℃/min
- Ballistic heating rates >1500 ℃/min
- Integrated electromagnet for Temperature calibration with Curie point standards
- Evolved Gas Analysis (EGA)

SDT: Schematic Diagram



Instrument Hardware and Gas Selection Considerations

Gas Delivery Module and Mass Flow Controllers

- The gas 1 port purges both sample and balance areas. Gas 1 should be an inert gas (N_2, He, Ar)

- The gas 2 port is used when a different purge gas is required or gas switching is used. Typically this is air or O_2.

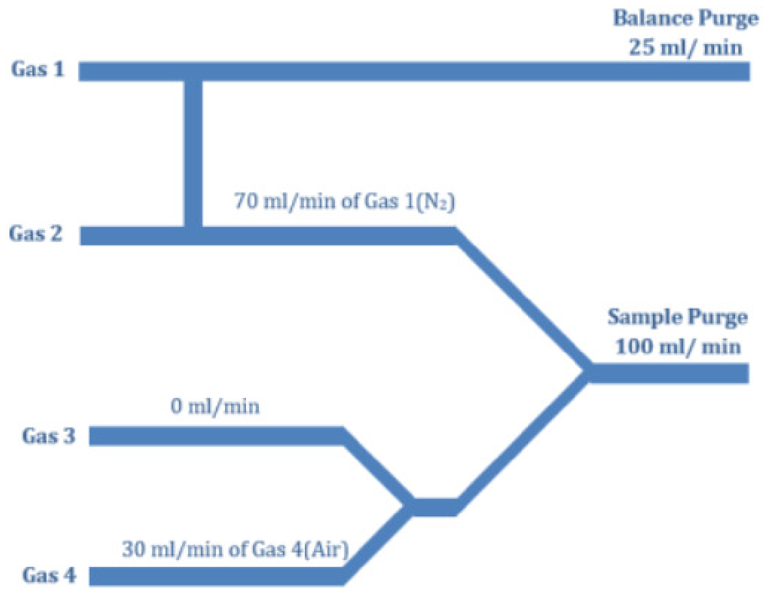
- Gas type is assigned to Mass Flow Controller in the Instrument section of the control software and chosen before on the setup page.

Gases used on TGA/SDT

- Nitrogen - inert, inexpensive and readily available
- Helium - inert, commonly used on TGA-MS
- Air/Oxygen - used when studying oxidative stability of materials, can sometimes improve resolution of weight loss events
- Gas mixing for specific atmospheres – hydrogen, carbon dioxide and other gases.

Blending Gas Delivery Module

- For use with TGA 550,TGA 5500 and SDT 650
- Allows blending two gases as main sample purge for a test. Nitrogen, helium, argon, oxygen, air, carbon dioxide, carbon monoxide, and forming gas (a blend of 4% hydrogen with 96% nitrogen) may be blended.



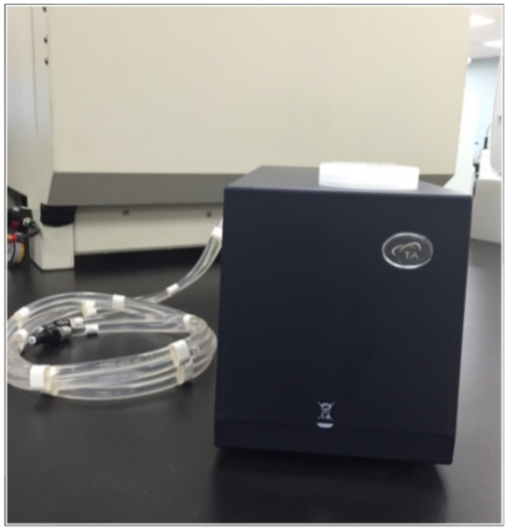
Four gases can be used in a test

Heat Exchanger - TGA

The heat exchanger contains a liquid reservoir that supplies the instrument with coolant to dissipate heat from the furnace.

The coolant exits the heat exchanger through the supply line, circulates to the furnace, and returns to the reservoir via the return line.

- Check the level and condition of the heat exchanger coolant periodically (about 3 months)
- To clean: empty old water, fill with distilled water and add TA Instruments TGA Conditioner (P/N 952377.901) (algae growth suppressor)
- For Q series, after filling, in software choose "Control \ Prime Exchanger"



Calibration

TGA Calibration and Verification

Two types of calibration are needed:

- Weight
- Temperature

Temperature calibration can be affected by:

- Purge gas and flow rate

  Thermal conductivity of helium ≠ Thermal conductivity of nitrogen/air/oxygen ≠ Thermal conductivity of argon
- Pan type
- Heating rates

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)

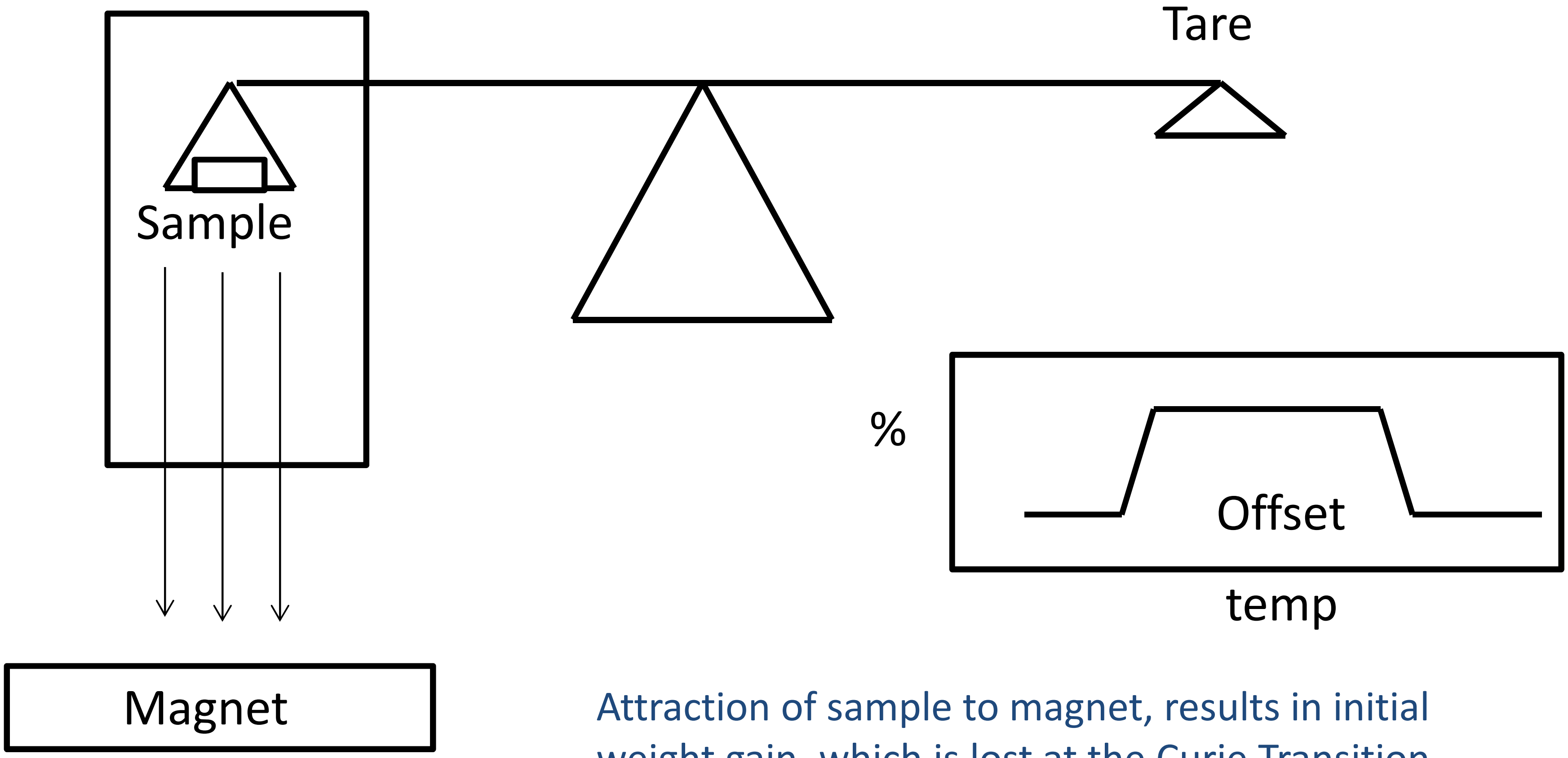
- Verification
  - Determine how often to verify data
  - Run a reference material as a sample (<u>in standard mode</u>)
  - Compare results vs literature values
  - Re-calibrate if results are out of tolerance

ASTM E 1582 - Calibration of Temperature Scale for Thermogravimetry

- The standard describes two methods by which the TGA can be calibrated for temperature; by melting point or magnetic transition. The most common approach for a TGA would be the magnetic transition approach.
- Curie Point Temperature - that temperature where the material loses its magnetic susceptibility - defined as offset point.
- Paramagnetic - a material that is susceptible to attraction by a magnet
- 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

TGA: Temperature Calibration

Vertical Balance Configuration

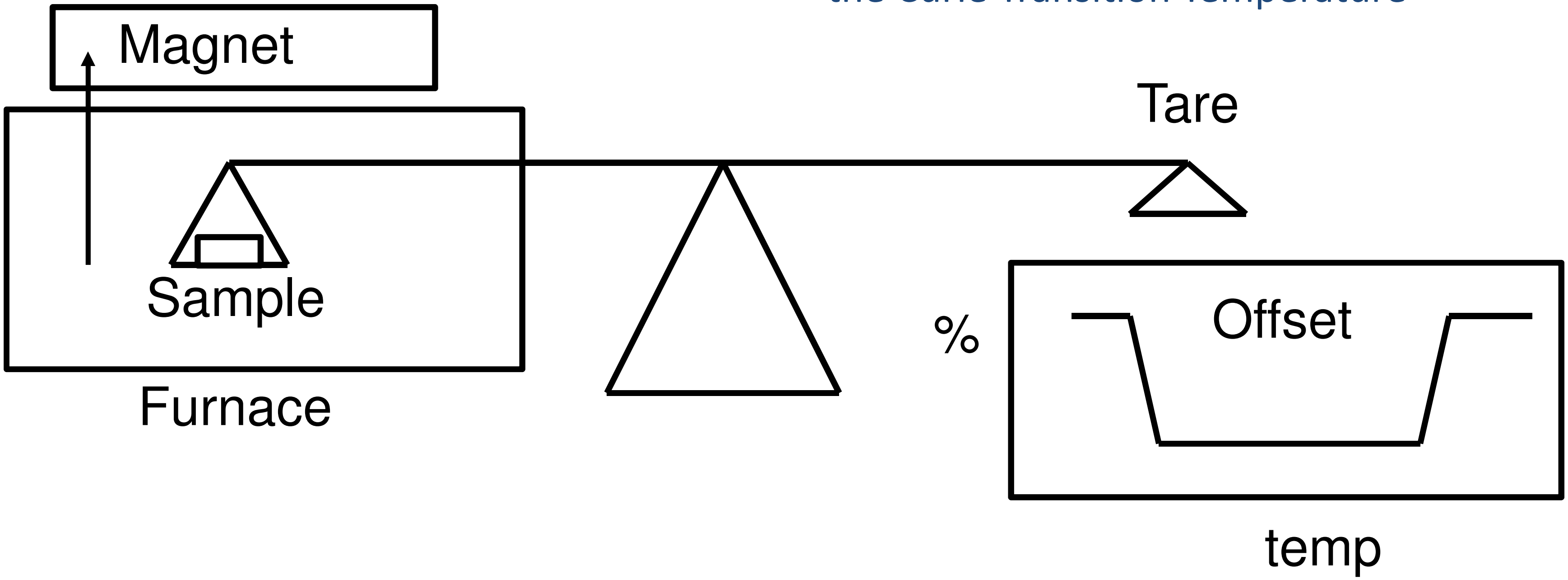


Attraction of sample to magnet, results in initial weight gain, which is lost at the Curie Transition Temperature

SDT: Temperature Calibration

Horizontal Balance Configuration

Attraction of sample to magnet,
results in initial weight loss, which is lost at
the Curie Transition Temperature



Curie Temperature Reference Materials

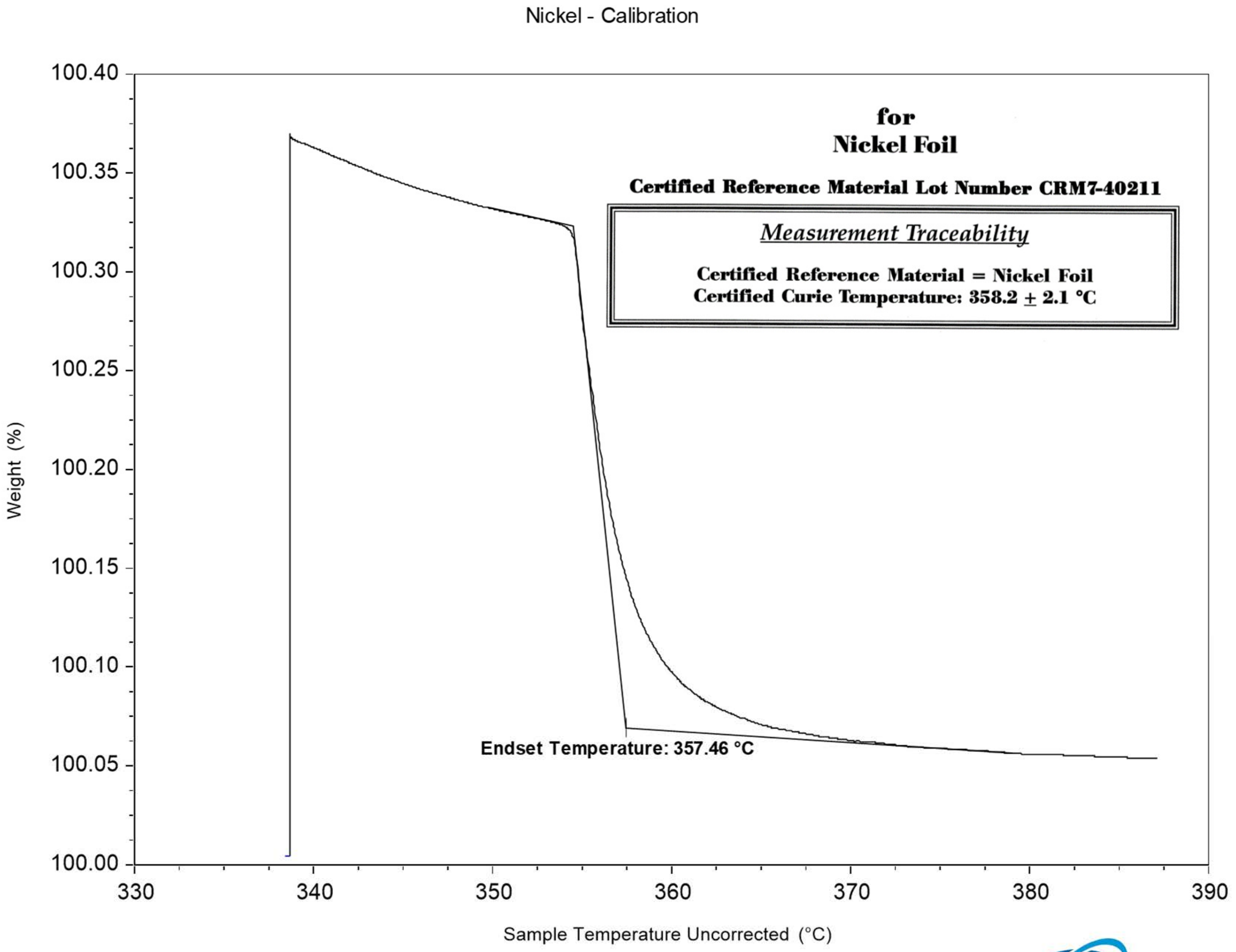
- International Confederation for Thermal Analysis and Calorimetry (ICTAC) developed a set of six certified and traceable Curie temperature reference materials for the calibration of TGA

Alumel	153℃
Nickel	358C
$Ni_{83}Co_{17}$	555℃
$Ni_{63}Co_{37}$	747℃
$Ni_{37}Co_{63}$	931℃
Cobalt	1116.0℃

- The materials permit temperature calibration in about 200 ℃ intervals over the range of 150 to 1120 ℃.

- TA Instruments is the exclusive worldwide distributor for these Curie point materials.

TGA – Temperature Calibration



Calcium Oxalate “Standard” Analysis

- Although Calcium Oxalate is not generally accepted as a “Standard Material,” it does have practical utility for INTRA-laboratory use.
- Carefully control the experimental conditions; i.e. pan type, purge gases/flow rates, heating rate.
- Particularly control the amount (~5mg) and the particle size of the sample and how you position it in the pan
- Perform multiple runs, enough to do a statistical analysis
- Analyze the weight changes and peak temperatures and establish the performance of YOU and YOUR instrument
- When performance issues come up, repeat the Calcium Oxalate analysis

Calcium Oxalate Decomposition

1. step $CaC_2O_4{\cdot}H_2O\ (s) \longrightarrow CaC_2O_4\ (s) + H_2O\ (g)$

Calcium Oxalate Monohydrate *Calcium Oxalate*

2. step $CaC_2O_4\ (s) \longrightarrow CaCO_3\ (s) + CO\ (g)$

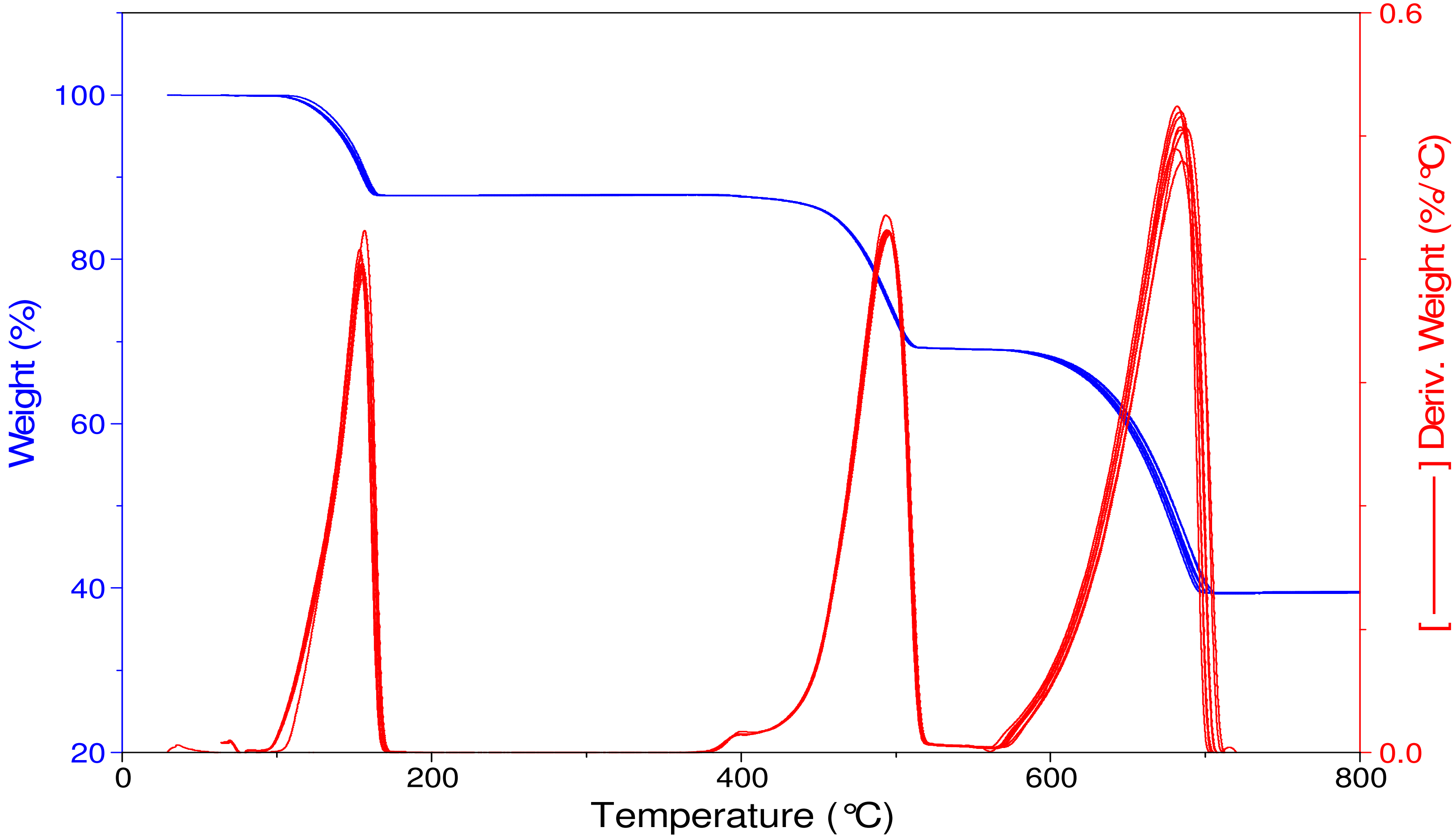
Calcium Oxalate *Calcium Carbonate*

3. step $CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)$

Calcium Carbonate *Calcium Oxide*

Calcium Oxalate Repeatability

Overlay of 8 runs, same conditions



Calcium Oxalate Repeatability

		Transition 1			Transition 2			Transition 3	
		Wt Change	Peak Temp		Wt Change	Peak Temp		Wt Change	Peak Temp
Run #		%	℃		%	℃		%	℃
1		12.13	156.68		18.78	493.37		29.62	684.33
2		12.22	153.60		18.75	494.17		29.56	680.43
3		12.20	155.40		18.76	495.6		29.63	684.11
4		12.21	155.58		18.77	495.98		29.69	688.11
5		12.21	154.05		18.75	494.72		29.54	684.28
6		12.20	154.91		18.73	495.62		29.58	684.83
7		12.21	155.09		18.77	494.71		29.61	683.92
8		12.20	153.52		18.77	493.84		29.57	681.85
Ave		12.20	154.85		18.76	494.75		29.60	683.98
Std Dev		0.028	1.08		0.016	0.93		0.048	2.24
Theoretical		12.3			19.2			30.1	
Accuracy		0.8%			2.3%			1.7%	
Precision		0.2%			0.1%			0.2%	

SDT Calibration and Verification

Types of calibration available:

- Weight Calibration: (TGA weight signal)
- DTA Signal Setup: Analyzing the Delta T signal data
- Temperature (Melting point or curie point standards as in TGA. Commonly use melting point standards)
- DSC Heat Flow
- MDSC Reversing Heat Capacity (SDT 650)

SDT Calibration and Verification

- DTA signal:

- Not required when using the SDT as a DSC-TGA (*i.e.*, only required when saving the Delta T signal.

- This run usually utilizes the same baseline run obtained for TGA Weight Calibration.

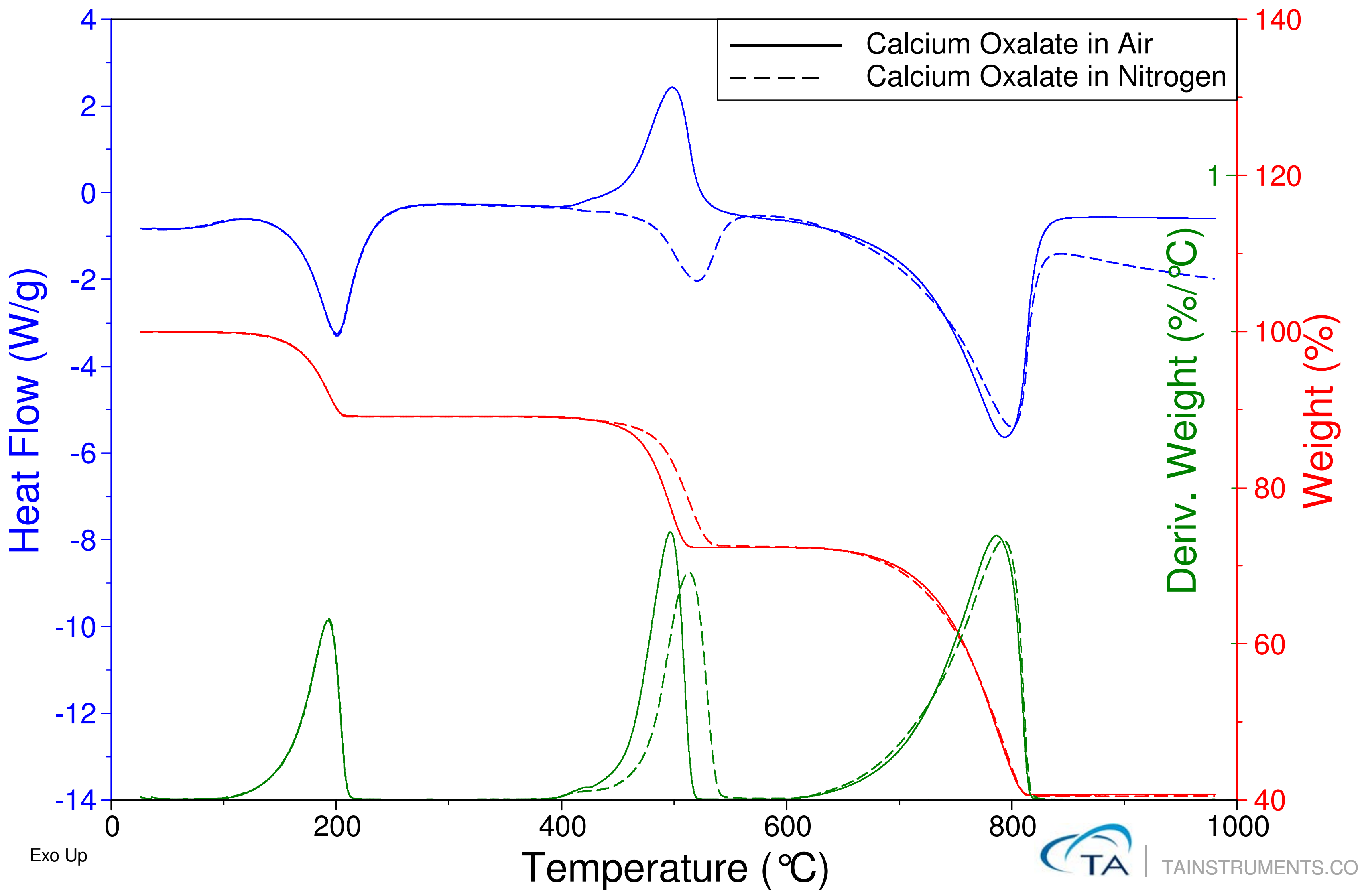
- Heat flow and cell constant:

-Based on analyzing the heat capacity curve for sapphire over the range 200 to 1500℃. Three experimental runs are required: two runs to generate the heat flow curve and another run to refine that calibration through cell constant calibration using a known metal standard (zinc, for example).

- MDSC Reversing heat capacity:

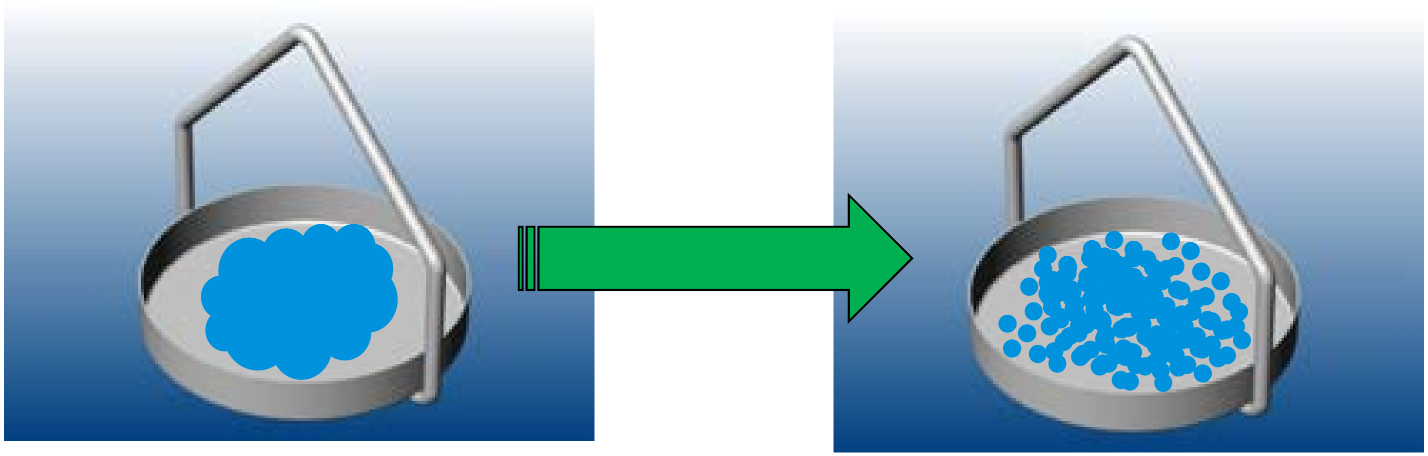
A heat capacity calibration curve is generated by running a sapphire sample over a desired temperature range using appropriate modulated conditions. The collected Reversing Heat Capacity curve is calibrated against the true value of the heat capacity of sapphire over the experimental temperature range

Calcium Oxalate in SDT



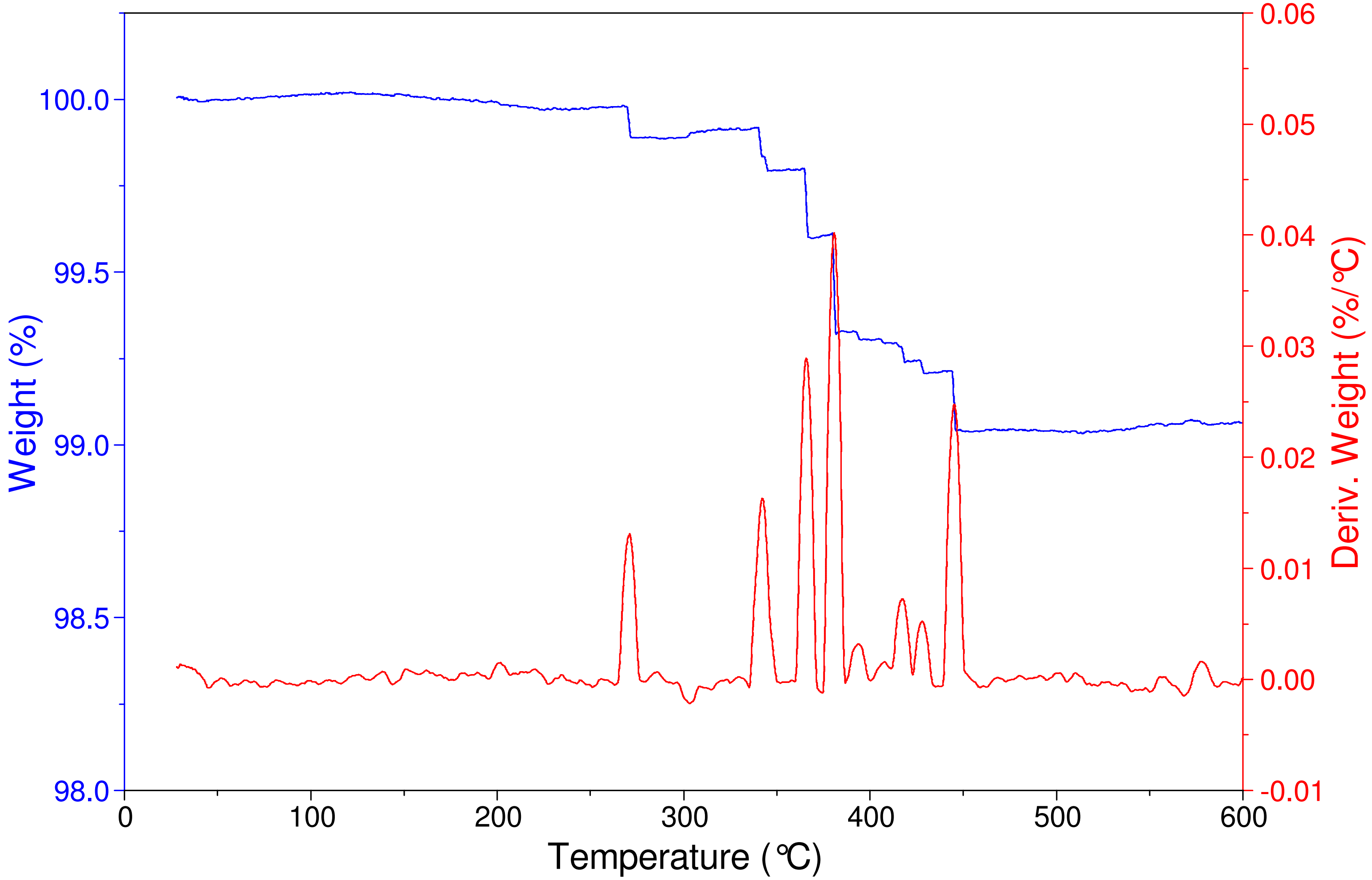
Sample prep & method Development

TGA: Sample Preparation

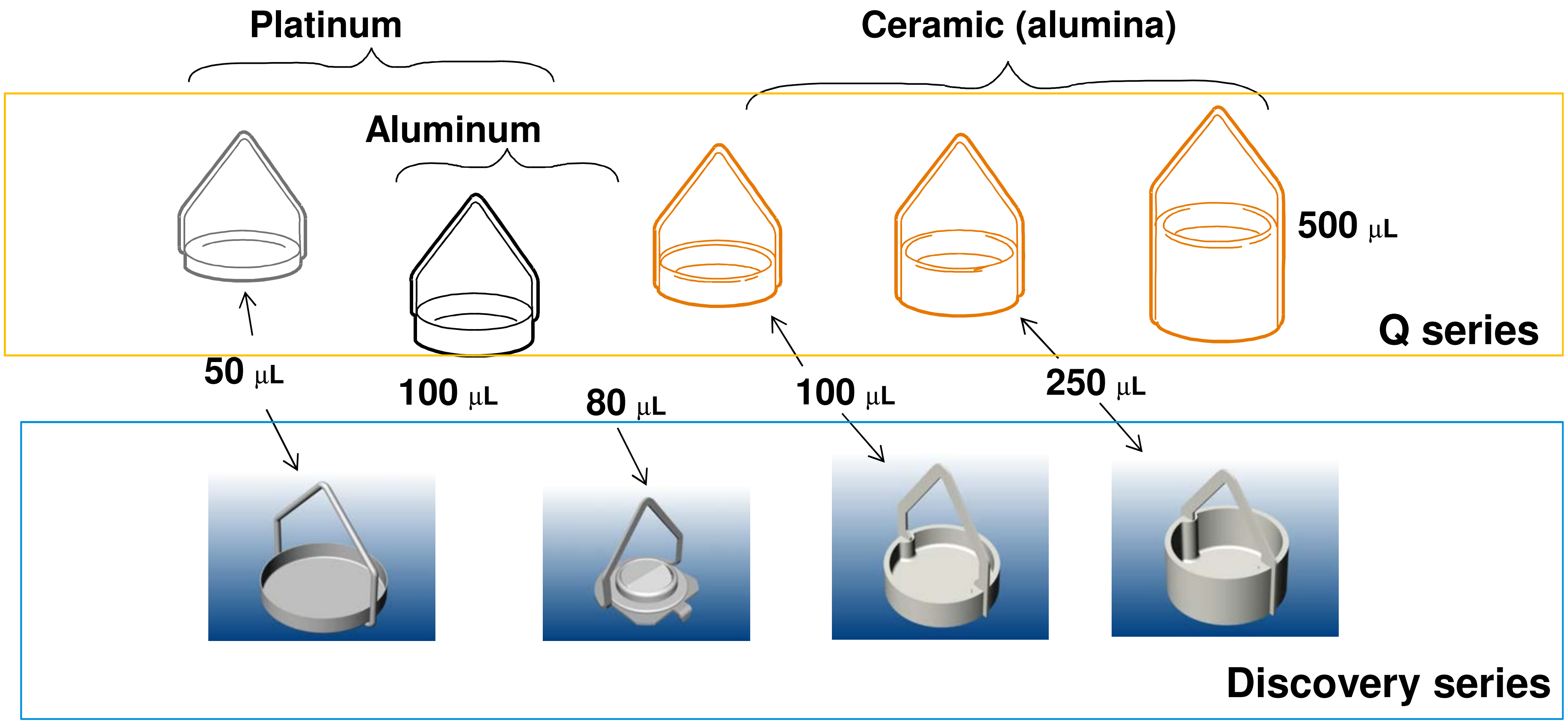


- Sample mass
  - 10-20mg for most applications
  - 50-100mg for measuring volatiles or residues
- If a TGA has a baseline drift of +/-25µg then this is 0.25% of a 10mg sample
- Use brass tweezers to eliminate static effects
- Tare a clean sample pan before every run
- Distribute sample evenly over bottom of pan
- Liquid samples - use hermetic pan with a pin-hole lid

TGA particle size matters, NaCl decrepitation



TGA: Sample Pans - Types/Sizes



Platinum

Aluminum

Ceramic (alumina)

50 µL

100 µL

80 µL

100 µL

250 µL

500 µL

Q series

Discovery series

Deep-walled pans are good for larger mass and low-density materials

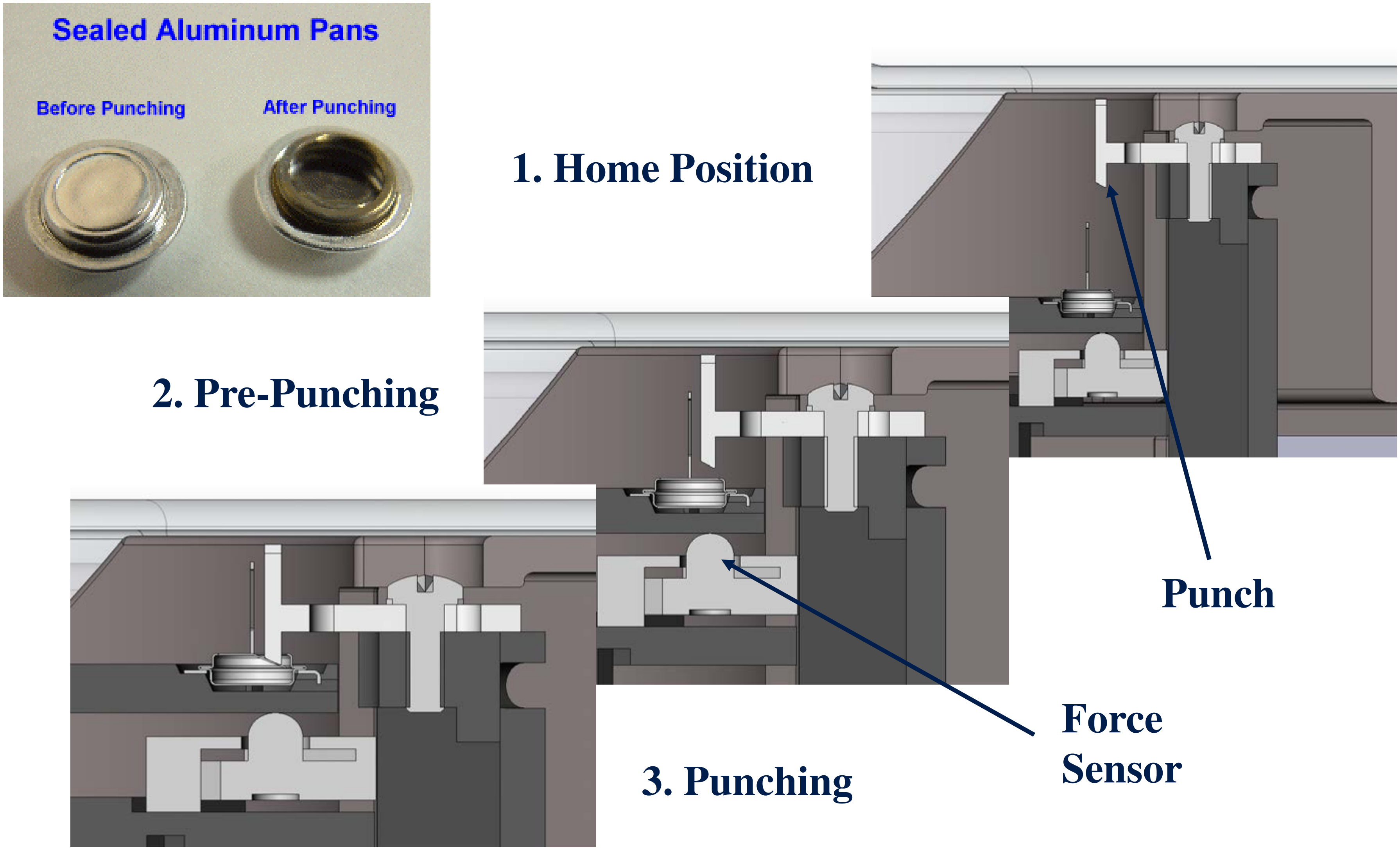
TGA: Sample Pan Selection

- Platinum (useful for most materials)
  - Easy to clean
  - Nonporous
  - Can alloy with most metals
  - Up to 1000°C

- Alumina (Ceramic)
  - Corrosives/Inorganics
  - Large samples
  - Porous, can be easily contaminated

- Aluminum (TGA) (designed for one-time use)
  - Lower cost, disposable
  - Lower temperature limit (<=600℃)

Sealed Aluminum Pans and Punching



1. Home Position

2. Pre-Punching

3. Punching

Punch

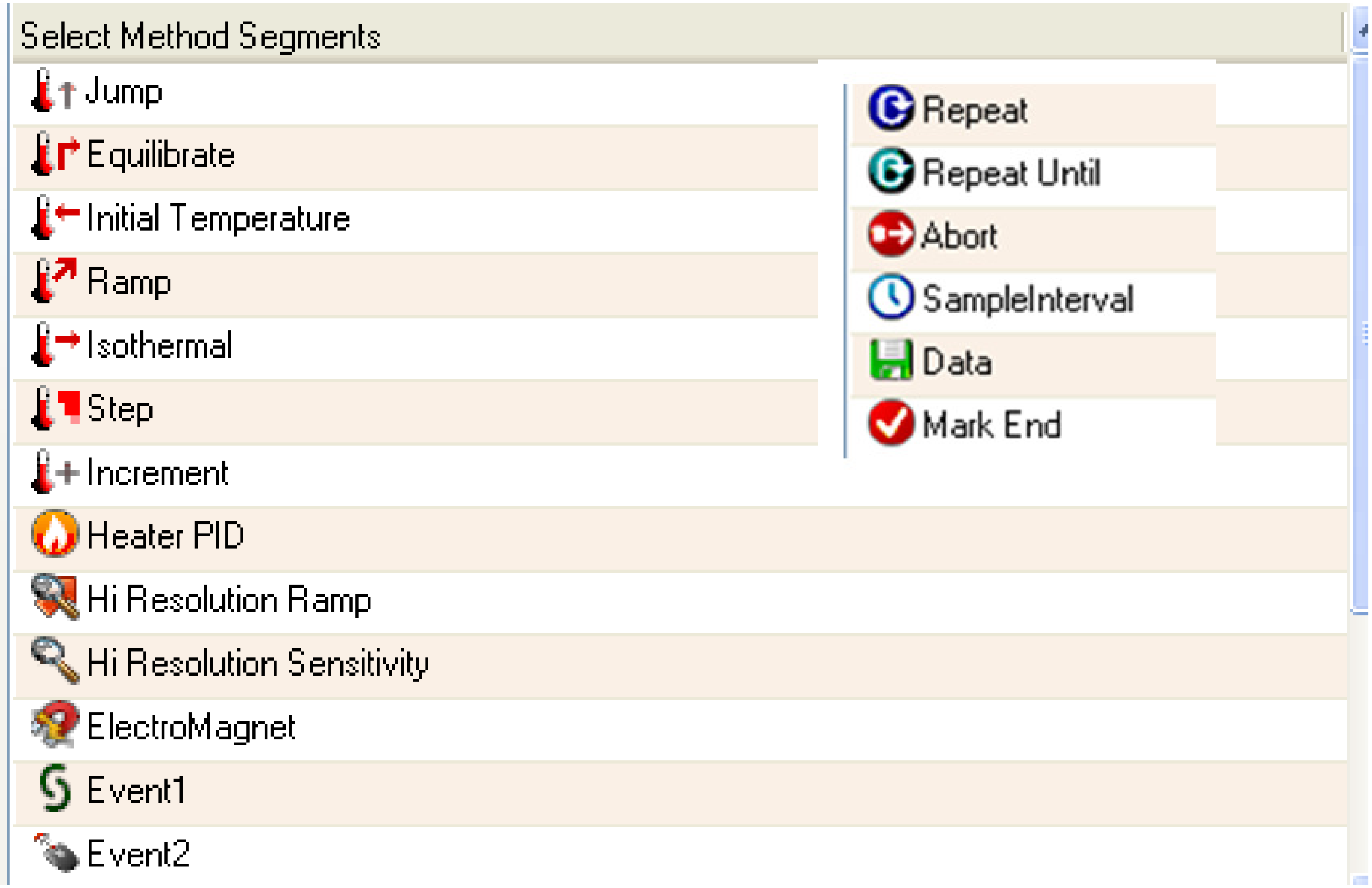
Force Sensor

TGA: Sample Pan Cleaning

- All sample pans are reusable (except Aluminum)
- If using platinum or alumina pans, a flame torch can be used to burn off organic residue. (do not flame Aluminum pans)

- Scrape off remaining ash (DSC fiberglass brush)
- Swab out with an organic solvent such as acetone or alcohol. Let it dry out before using it

Method Segments



Select Method Segments

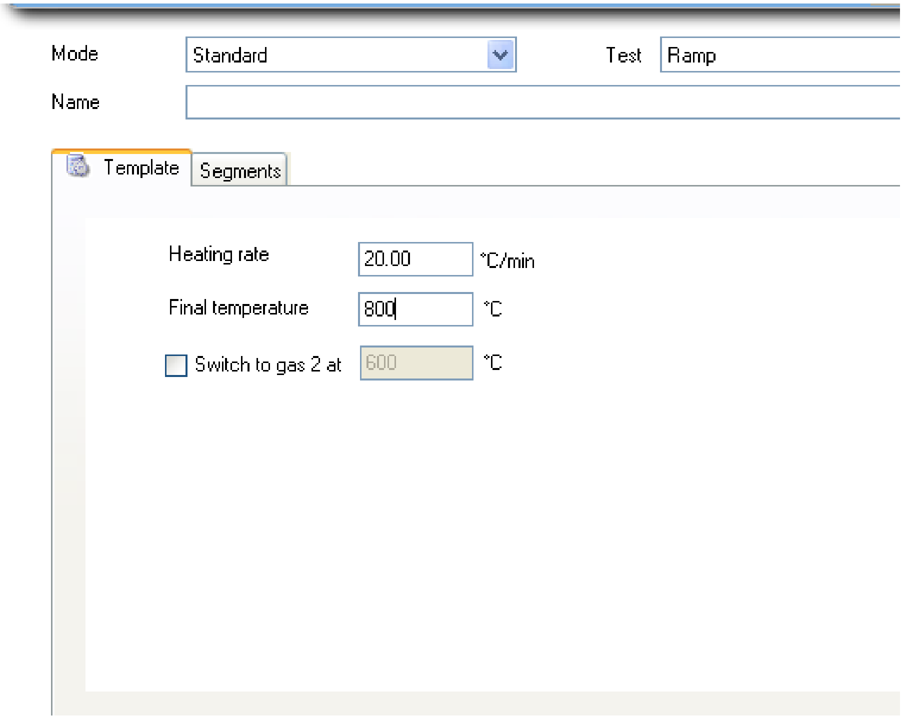
- Jump
- Equilibrate
- Initial Temperature
- Ramp
- Isothermal
- Step
- Increment
- Heater PID
- Hi Resolution Ramp
- Hi Resolution Sensitivity
- ElectroMagnet
- Event1
- Event2

- Repeat
- Repeat Until
- Abort
- SampleInterval
- Data
- Mark End

Typical Methods

- Ramp (heating) experiment:
    - Ramp 20℃/min. to 800℃

- Ramp and switch gas (carbon black content, residue)
    - Ramp 20℃/min. to 650℃
    - Select gas: 2
    - Ramp 20℃/min. to 1000℃



Mode Standard

Test Ramp

Name

Heating rate 20.00 °C/min

Final temperature 800 °C

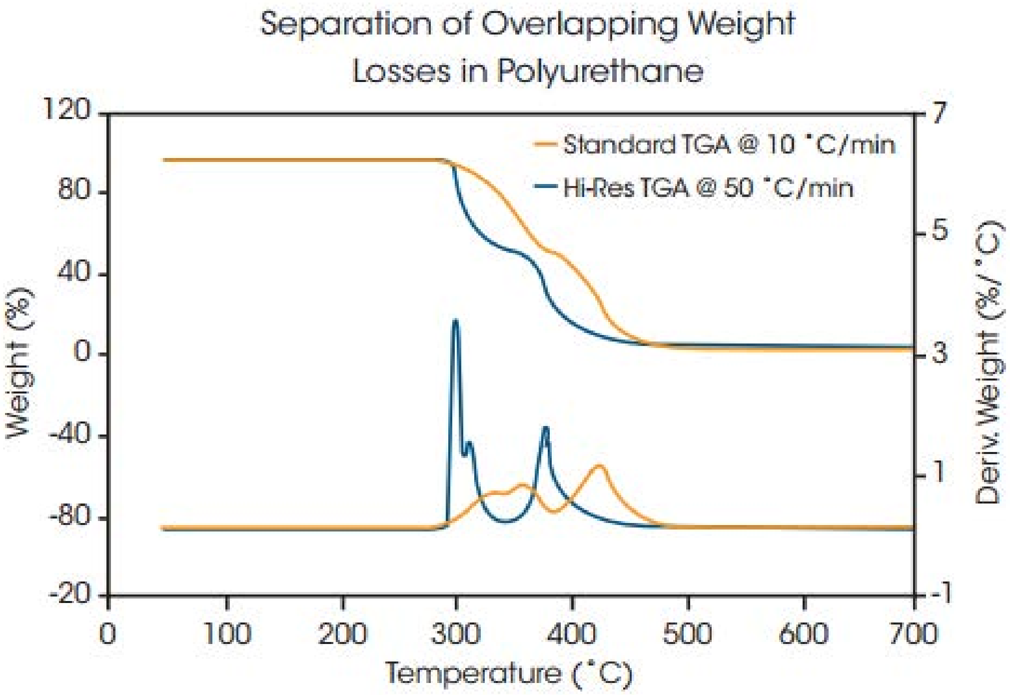
☐ Switch to gas 2 at 600 °C

Hi-Res^{TM} TGA

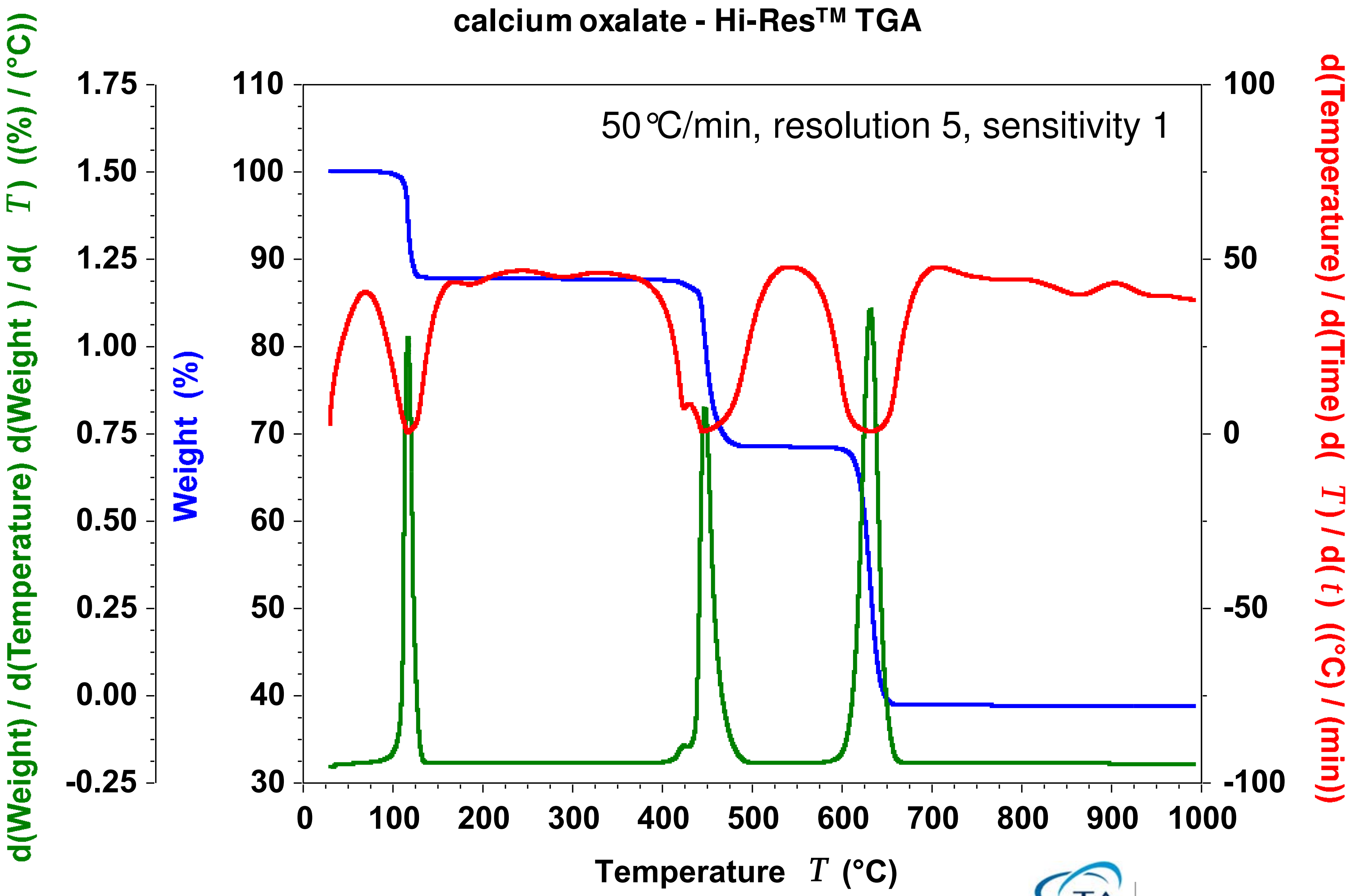
- In a Hi-Res^{TM} TGA experiment the heating rate is controlled by the rate of decomposition.

- Faster heating rates during periods of no weight loss, and slowing down the heating rate during a weight loss – therefore not sacrificing as much time

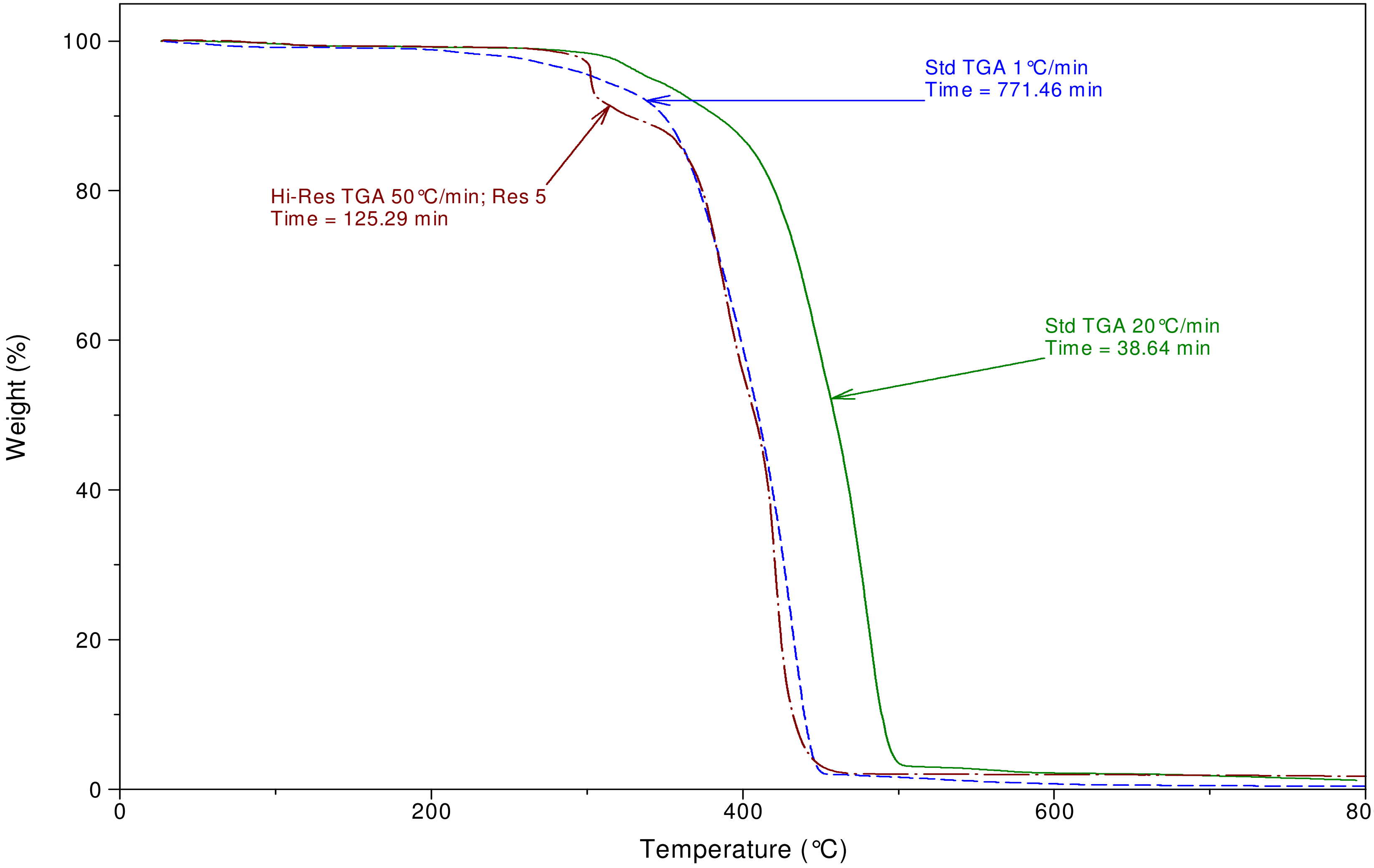
- Hi-Res^{TM} TGA can give better resolution or faster run times, and sometimes both



Hi-Res™ TGA of Calcium oxalate



Hi-Res^{TM} TGA vs. Std TGA of Nylon/PE Blend



Programming a Hi-Res^{TM} TGA experiment – Sensitivity Number

1. Sensitivity 1.0
2. Ramp 50℃/min, Res. 4.0 to 1000℃

Sensitivity: typically varies from 0 to 8.0

- Controls the response of the Hi-Res system to changes in decomposition rates (Δ wt%/min)
- Determines the ***increase*** in decomposition rate that warrants a reduction in the heating rate (or vice-versa)
- Higher sensitivity values make the Hi-Res system more responsive to small changes in the rate of reaction

Programming a Hi-Res™ TGA experiment – Resolution Number

1. Sensitivity 1.0
2. Ramp 50℃/min, Res. 4.0 to 1000℃

Resolution : typically varies from -8.0 to 8.0

- ➢ Adjusts the heating rate based on the sample decomposition rate (wt%/min)
- ➢ As the decomposition rate ***increases***, the heating rate is further decreased (and vice-versa).
- ➢ Higher resolution number (absolute value) results in a greater reduction in heating rate at smaller values of wt%/min

Programming a Hi-Res^{TM} TGA experiment – Heating Rate

1. Sensitivity 1.0
2. Ramp 50℃/min, Res. 4.0 to 1000℃

- TGA – Start @ 50℃/min unless volatiles then start @ 10-20℃/min
- SDT – Start @ 20℃/min unless volatiles then start @ 5-10℃/min

Advantages of MTGA™

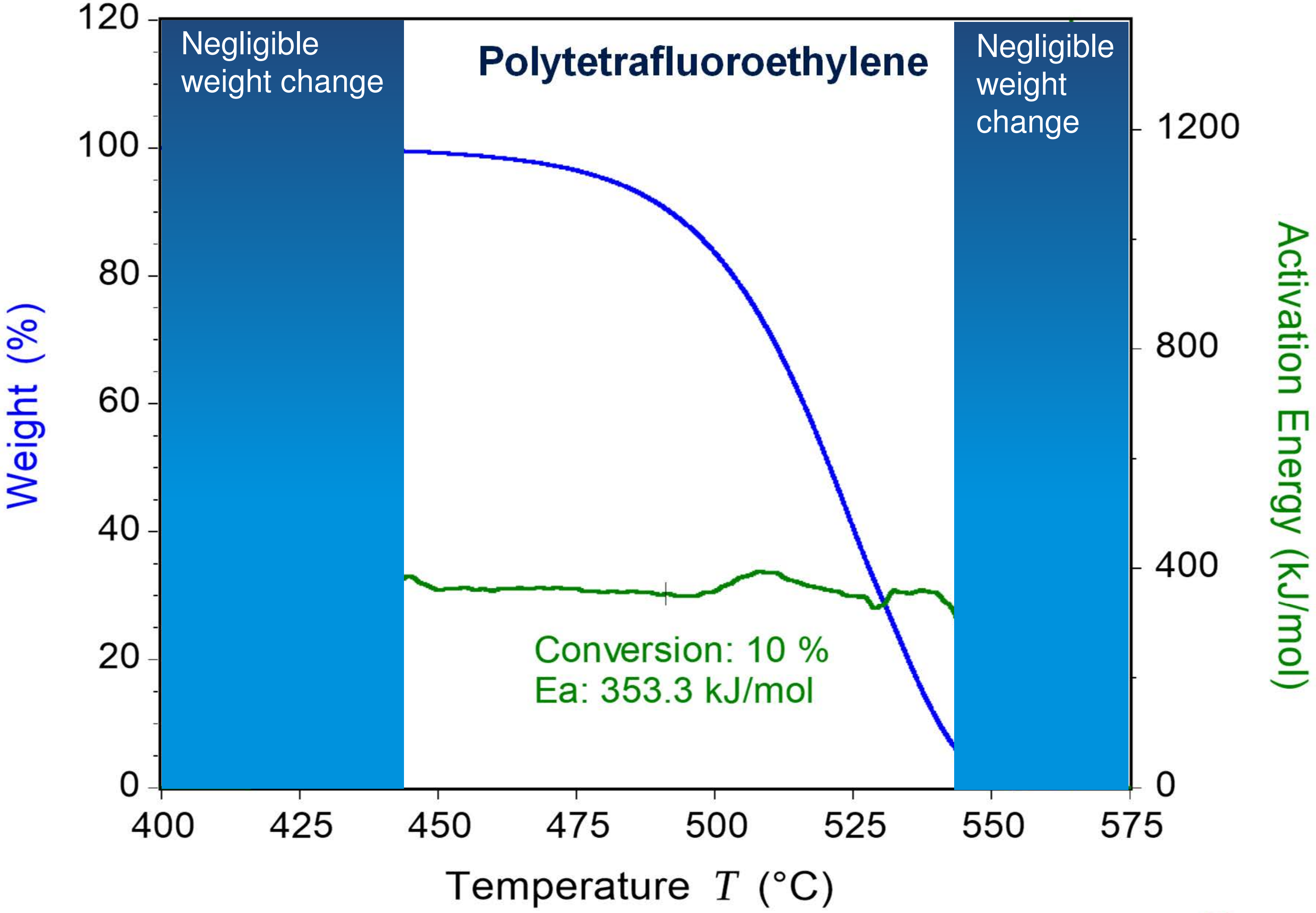
- One run needed to obtain activation energy. (ASTM E2958)
- Activation energy is a signal in the data file.
- Comparable with Flynn-Wall method for calculated *Ea* with the benefit of the reduced time.
- Method works under quasi-isothermal or ramping conditions.
- Activation energy is obtained as a continuous curve and so can be manipulated numerous ways. For example, it can be plotted as a function of conversion.
- Can be combined with Hi-Res™ to speed up experiments and more accurately handle multiple weight loss events.

Setting Up MTGA^{TM} Experiment - General Guidelines

- A scouting run at 10 ℃/min is useful to determine width of transitions.

- Range of consistent results:
  - Period = 300 s (practical range: 100 – 500s)
  - Amplitude = 3℃ (practical range: 1 – 10℃)
  - Ramp Rate = 1℃/min (practical range: 0.5 – 2 ℃/min)

PTFE: Modulated Ramping Experiment



Hi-Res™ TGA & MTGA™ Instruments

- Standard on:
  - Discovery TGA 5500 & Discovery SDT 650
  - Discovery TGA (Gen 1), Q5000IR TGA
- Optional on:
  - Discovery TGA 550
  - Q500 TGA
- Not available on:
  - Discovery TGA 55
  - Q50 TGA
  - Q600 SDT

Summary for TGA

- Typical starting sample mass = 10mg ± 1mg
- Typical starting ramp rate = 10℃/min
- Change above as needed
- Use Hi-Res™ and MTGA™ as needed

Applications:
Thermal Stability

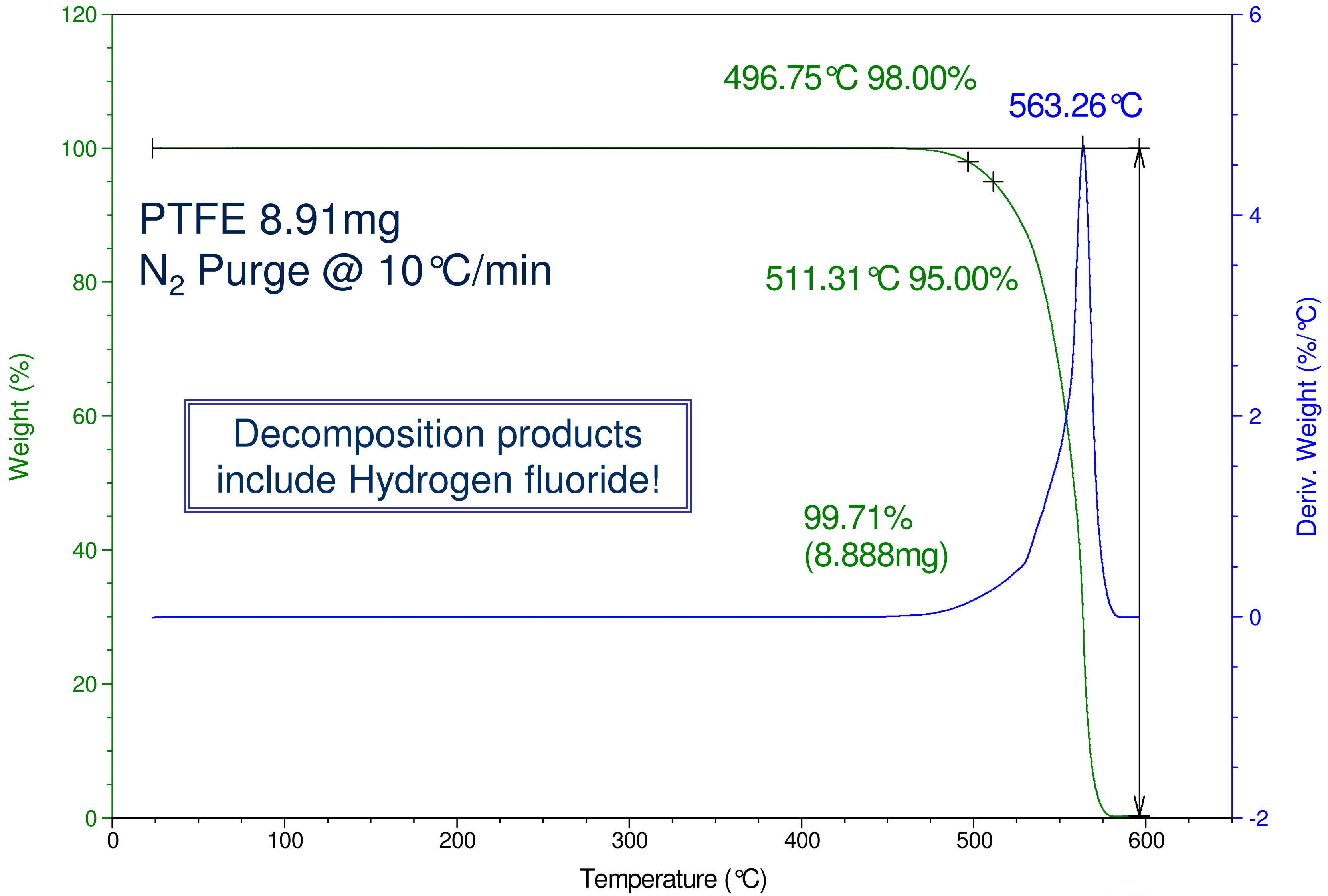
Thermal Stability

- Can be studied by multiple techniques
- May be studied w/ inert or oxidizing atmospheres
- TGA – Typically Best choice
    - Weight loss
- DSC
    - Change in heat flow (typically exothermic)

TGA Profile In Nitrogen and Air

- First Step in Materials Characterization
- Look for:
  - Thermal Stability
    - Volatilization/Decomposition Temperature
  - Weight Loss Profile
    - Number of Steps
  - Residue
    - Char/Ash/Filler Presence

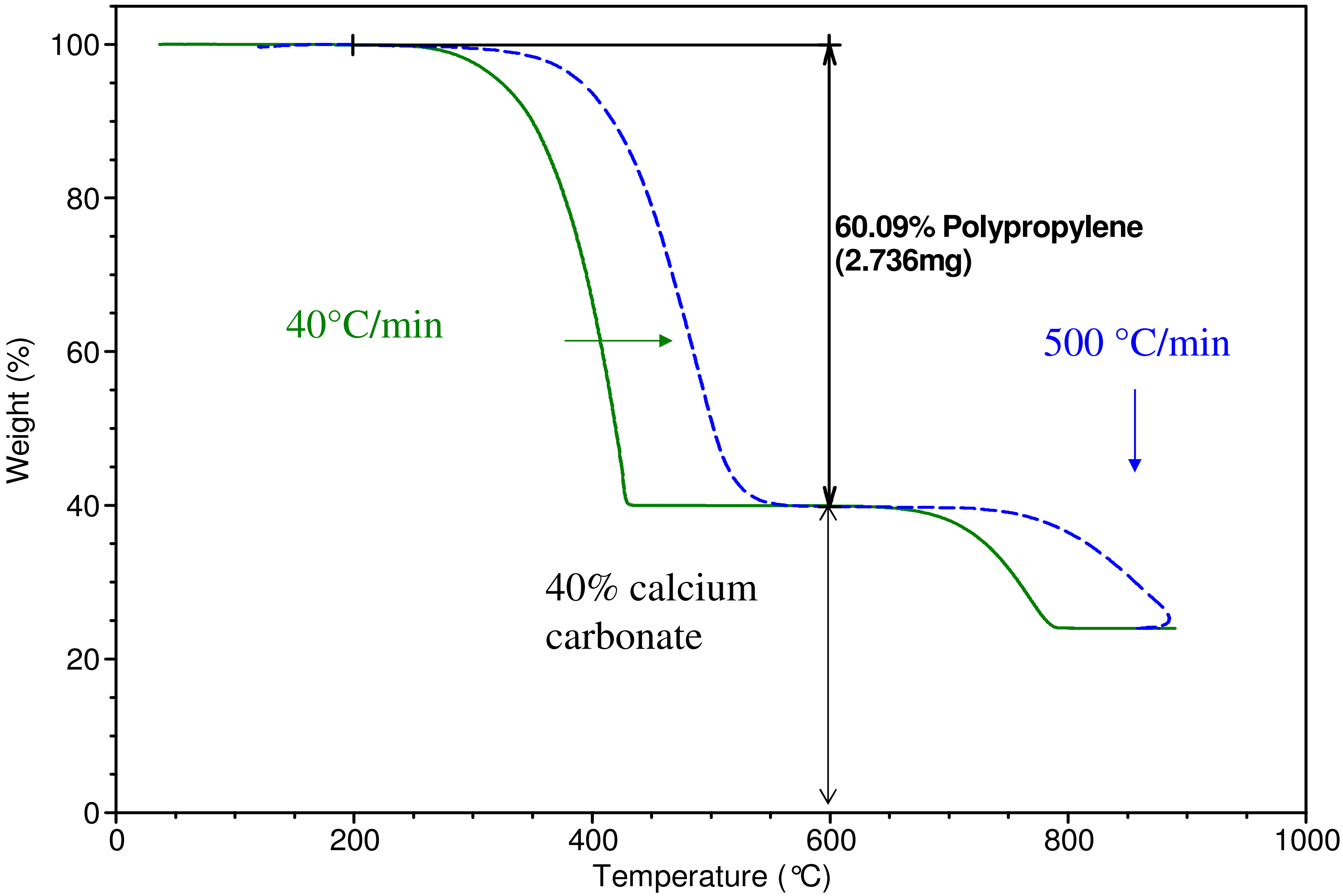
TGA Gives Upper Limit for DSC



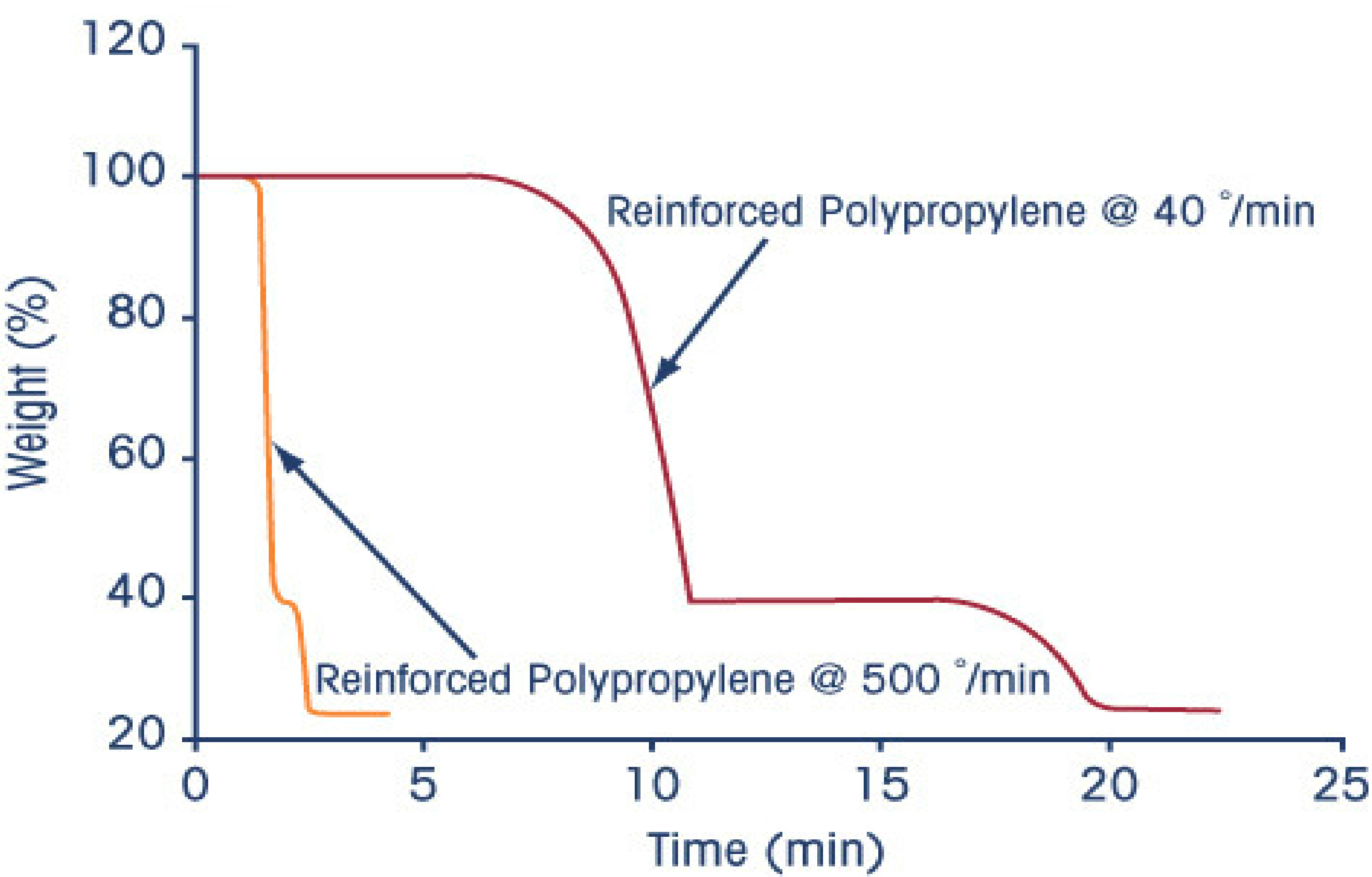
PTFE 8.91mg
N_2 Purge @ 10℃/min

Decomposition products include Hydrogen fluoride!

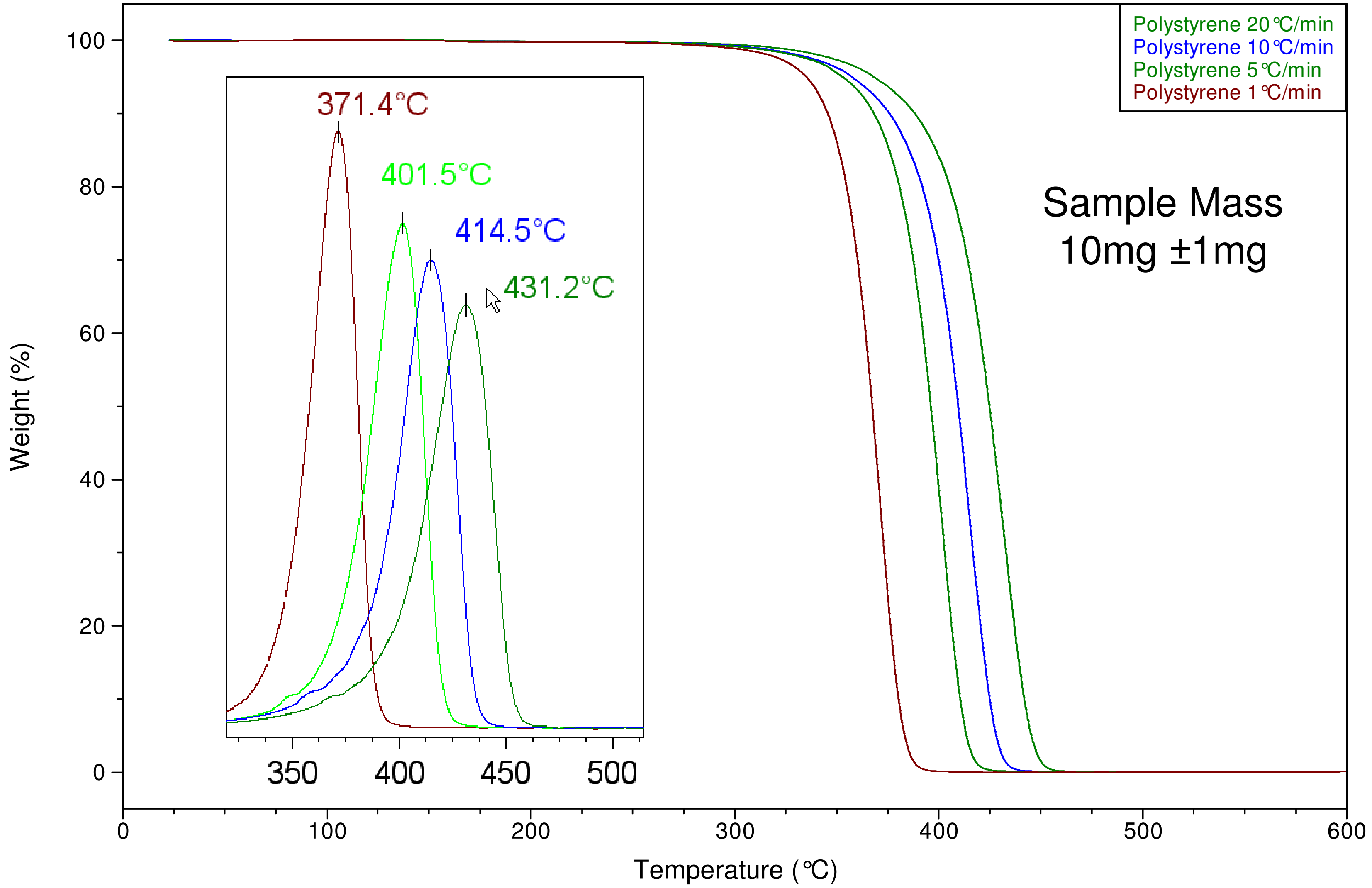
High-Heating Rate TGA Analysis



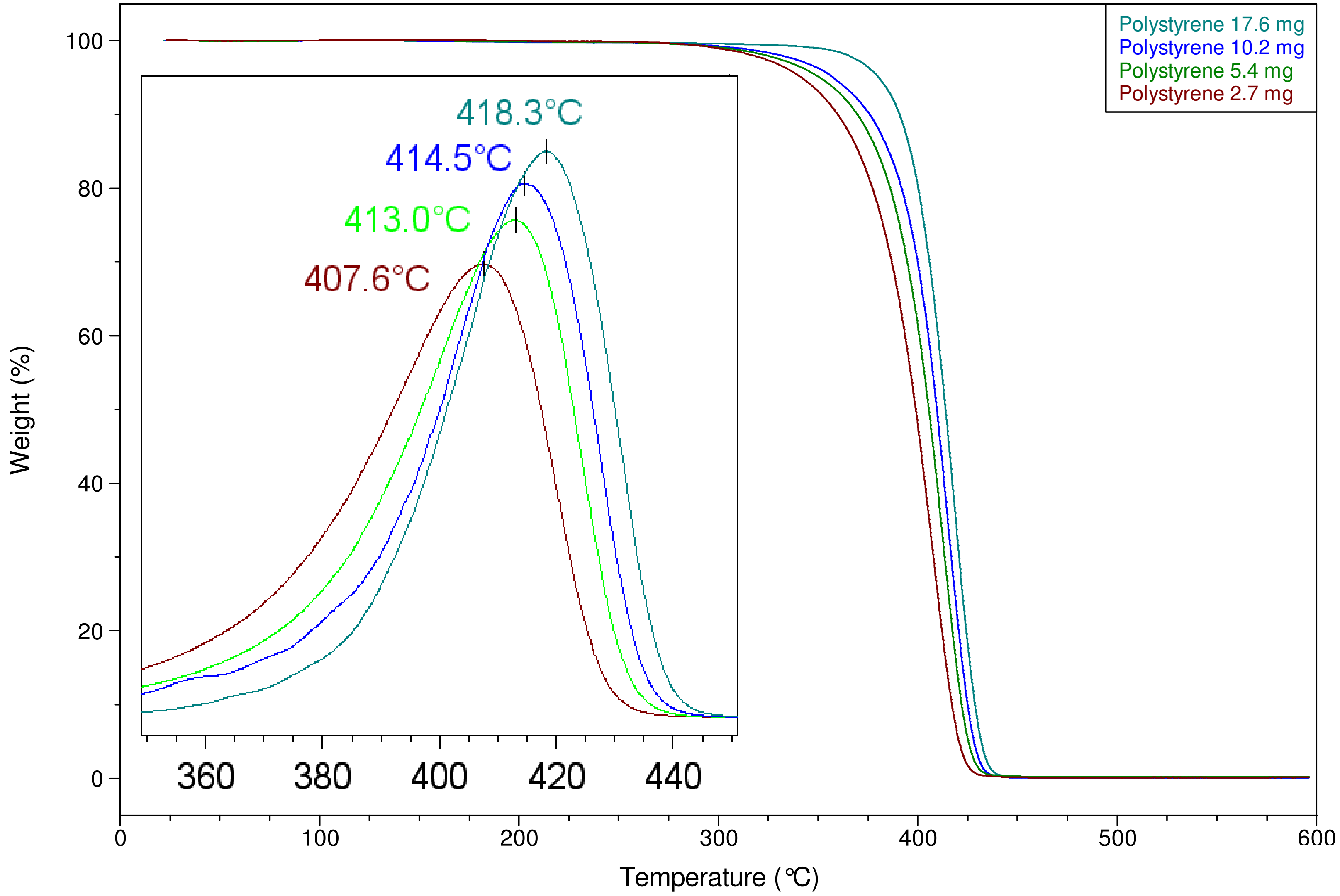
High-Heating Rate TGA Analysis



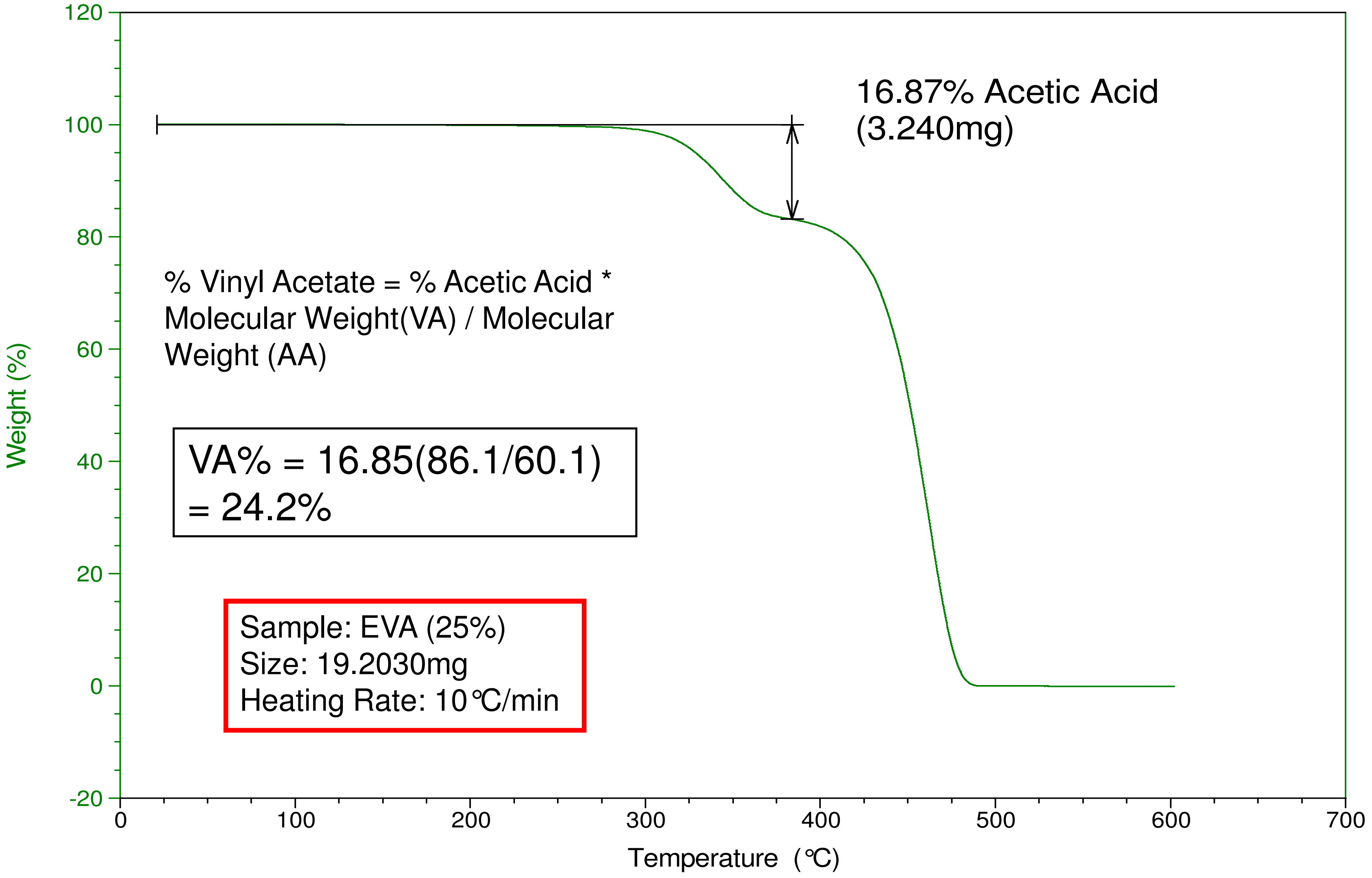
Higher heating rates increase the observed decomposition temperature



Larger sample mass increases the observed decomposition temperature



EVA Copolymer



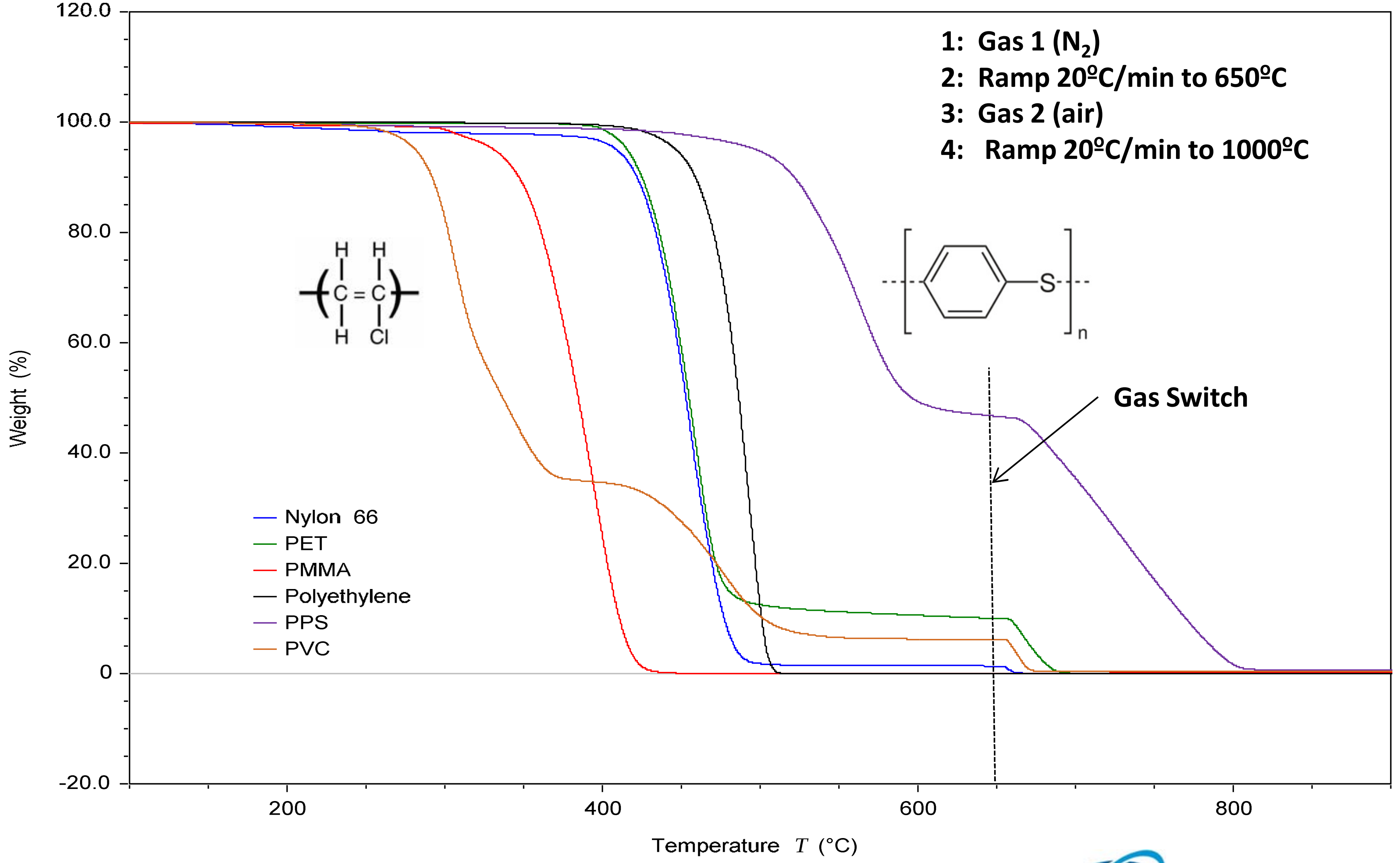
16.87% Acetic Acid
(3.240mg)

% Vinyl Acetate = % Acetic Acid * Molecular Weight(VA) / Molecular Weight (AA)

VA% = 16.85(86.1/60.1)
= 24.2%

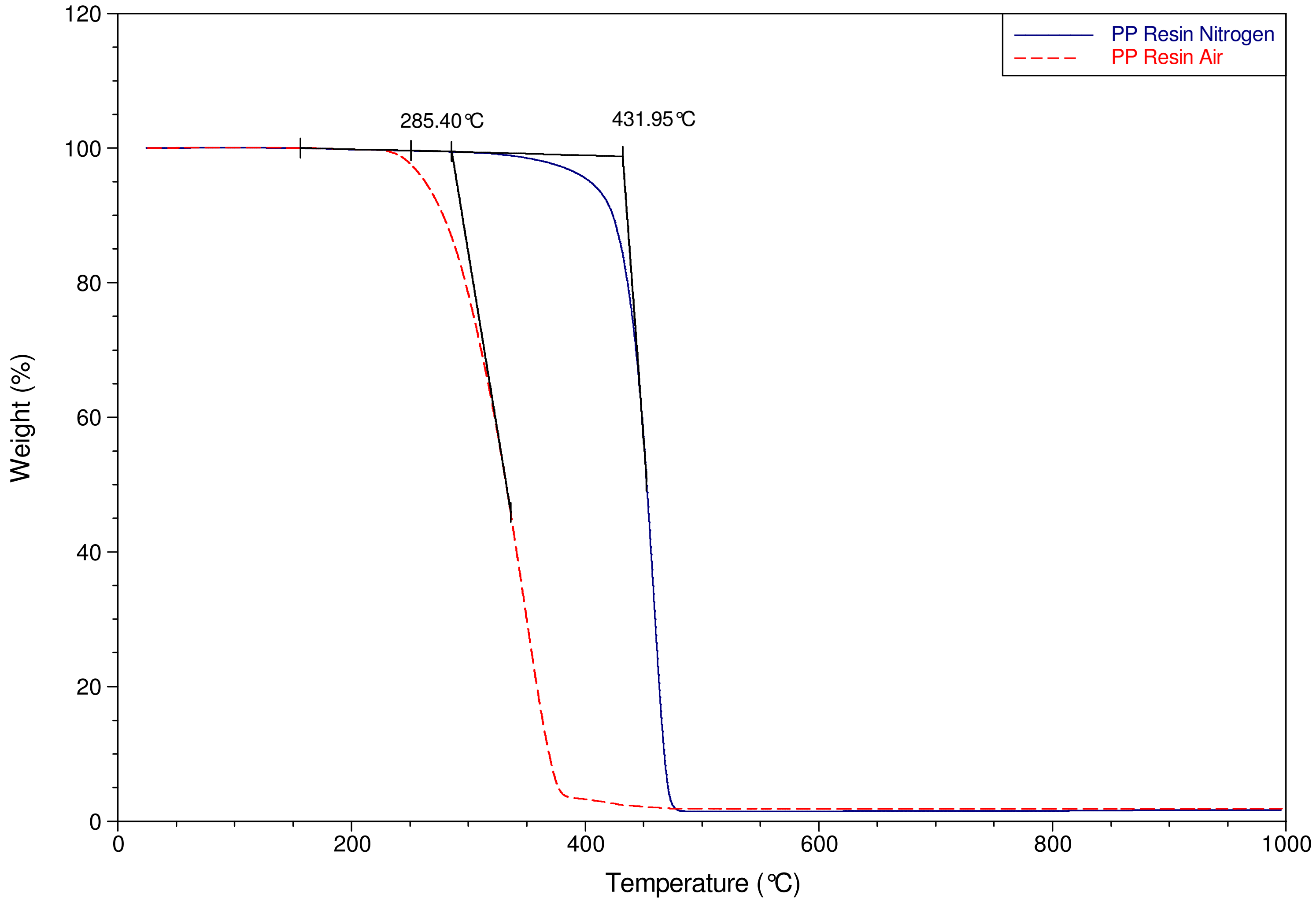
Sample: EVA (25%)
Size: 19.2030mg
Heating Rate: 10°C/min

Thermal Stability of Polymers

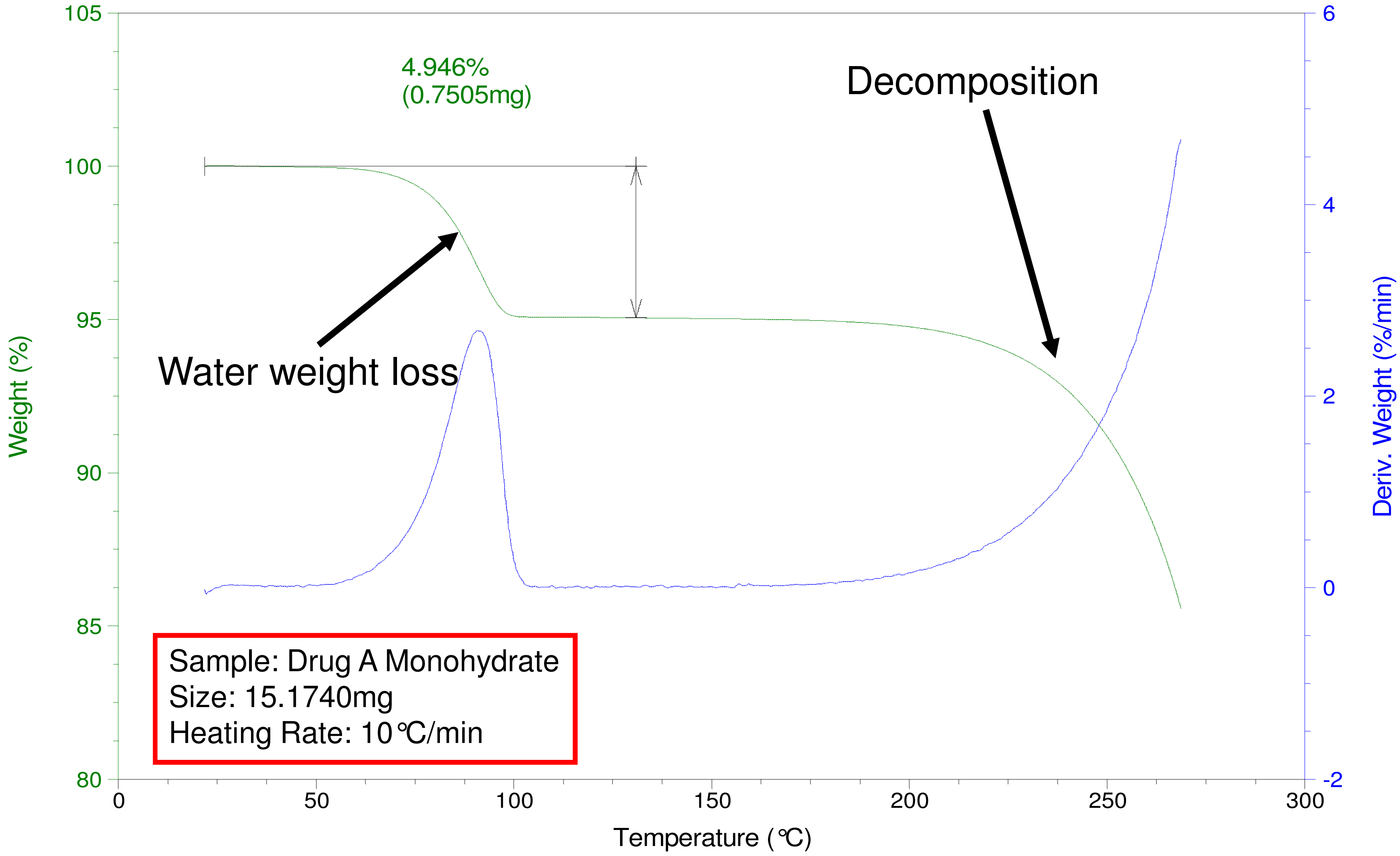

1: Gas 1 (N_2)
2: Ramp 20ºC/min to 650ºC
3: Gas 2 (air)
4: Ramp 20ºC/min to 1000ºC

Gas Switch

Oxidative Stability (Polypropylene)



TGA of Drug A Monohydrate



Decomposition

Water weight loss

Sample: Drug A Monohydrate
Size: 15.1740mg
Heating Rate: 10℃/min

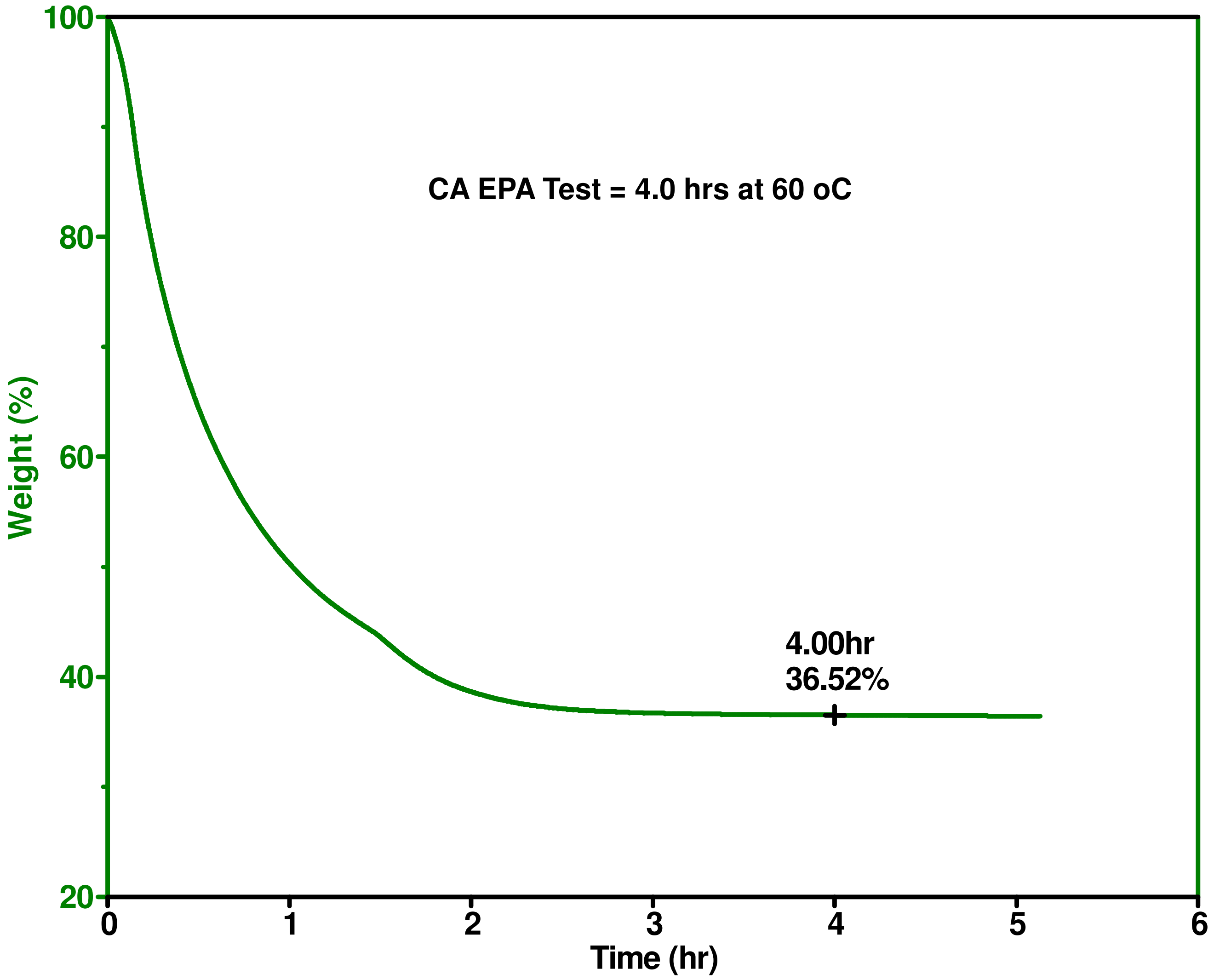
Loss-on-drying

- Pharmaceuticals
  - Lower Moisture Increases Shelf Life

- Chemicals
  - Don’t Want to Pay for Water

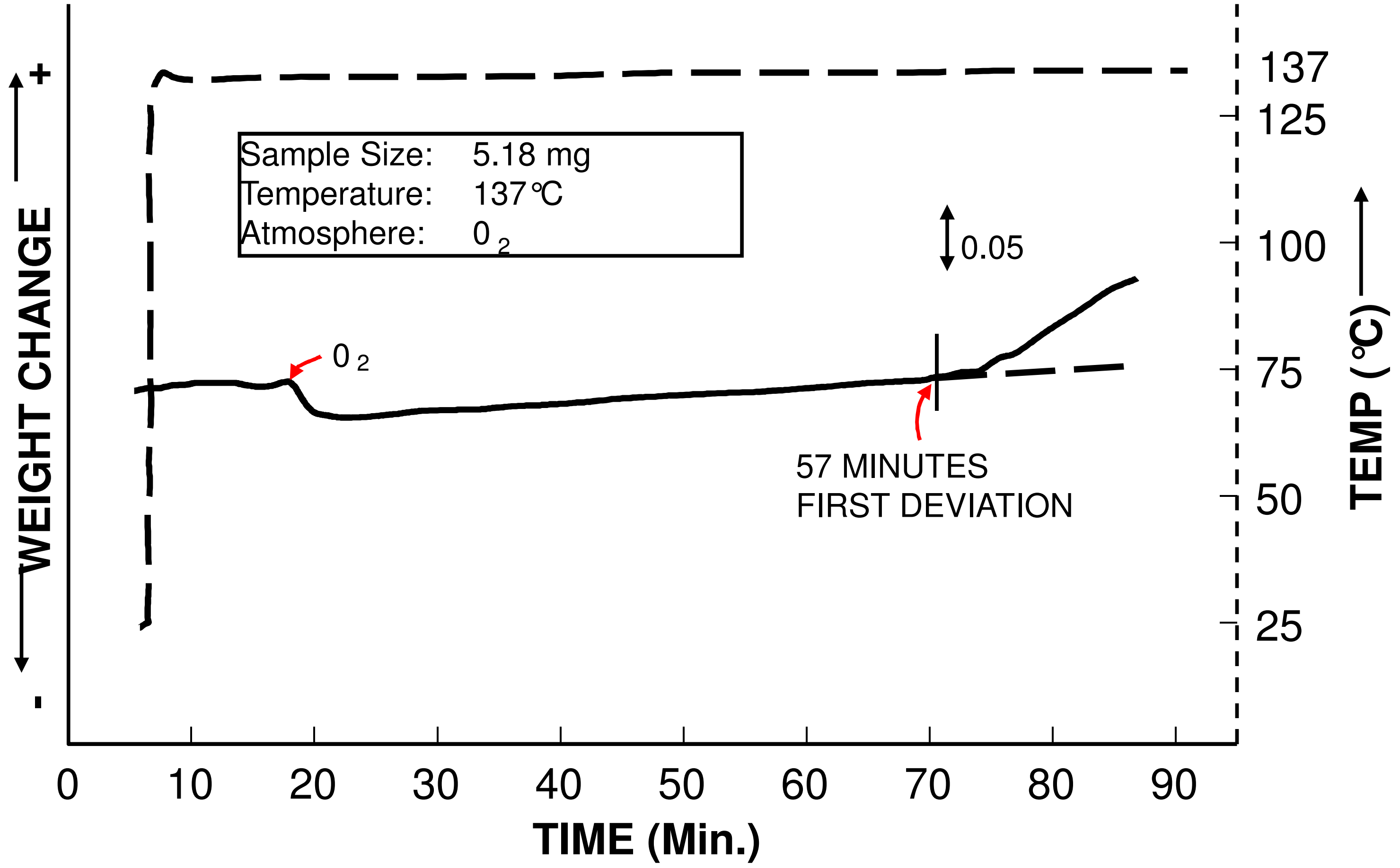
- Environmental Organic Burden
  - California EPA Test for Volatiles

Agricultural Chemical Loss-on-drying



Vegetable Oil Oxidative Stability

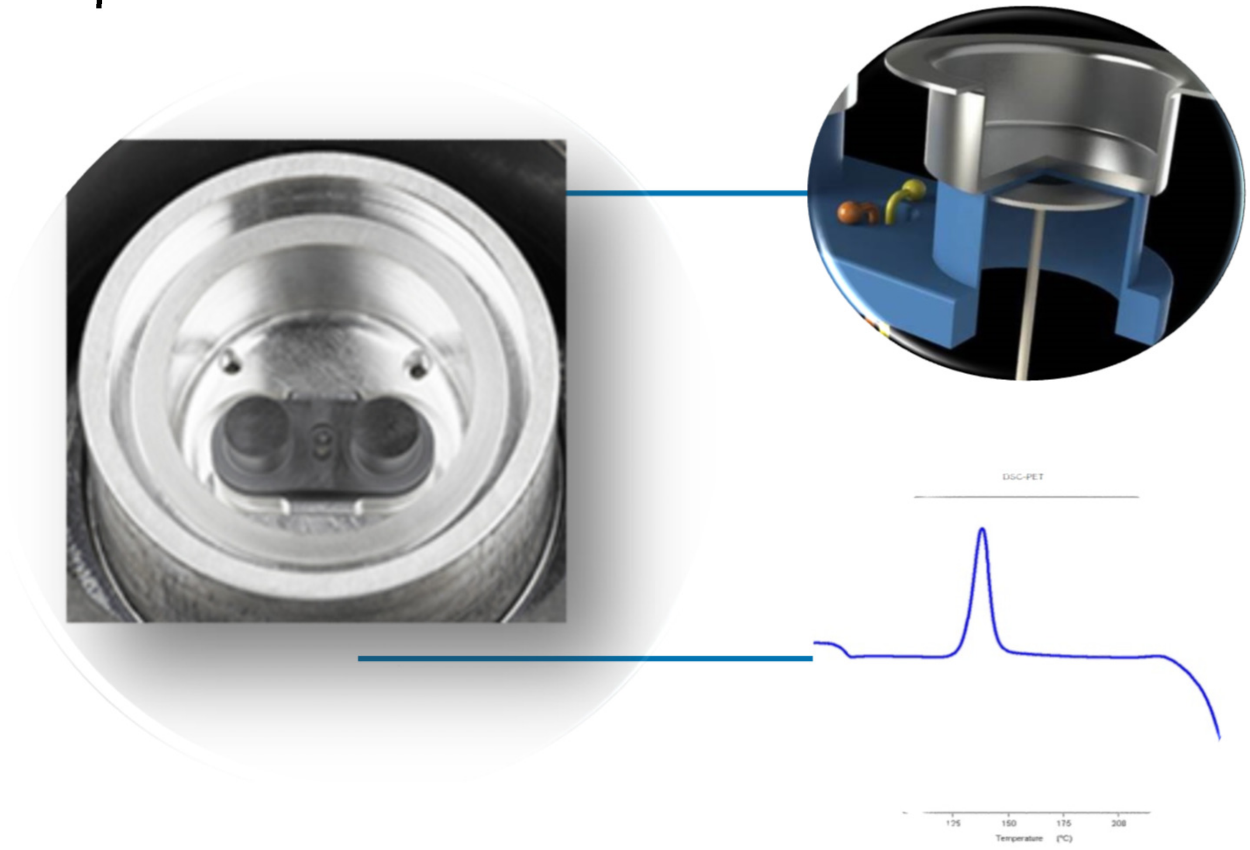
Similar principle to OIT experiment done by DSC



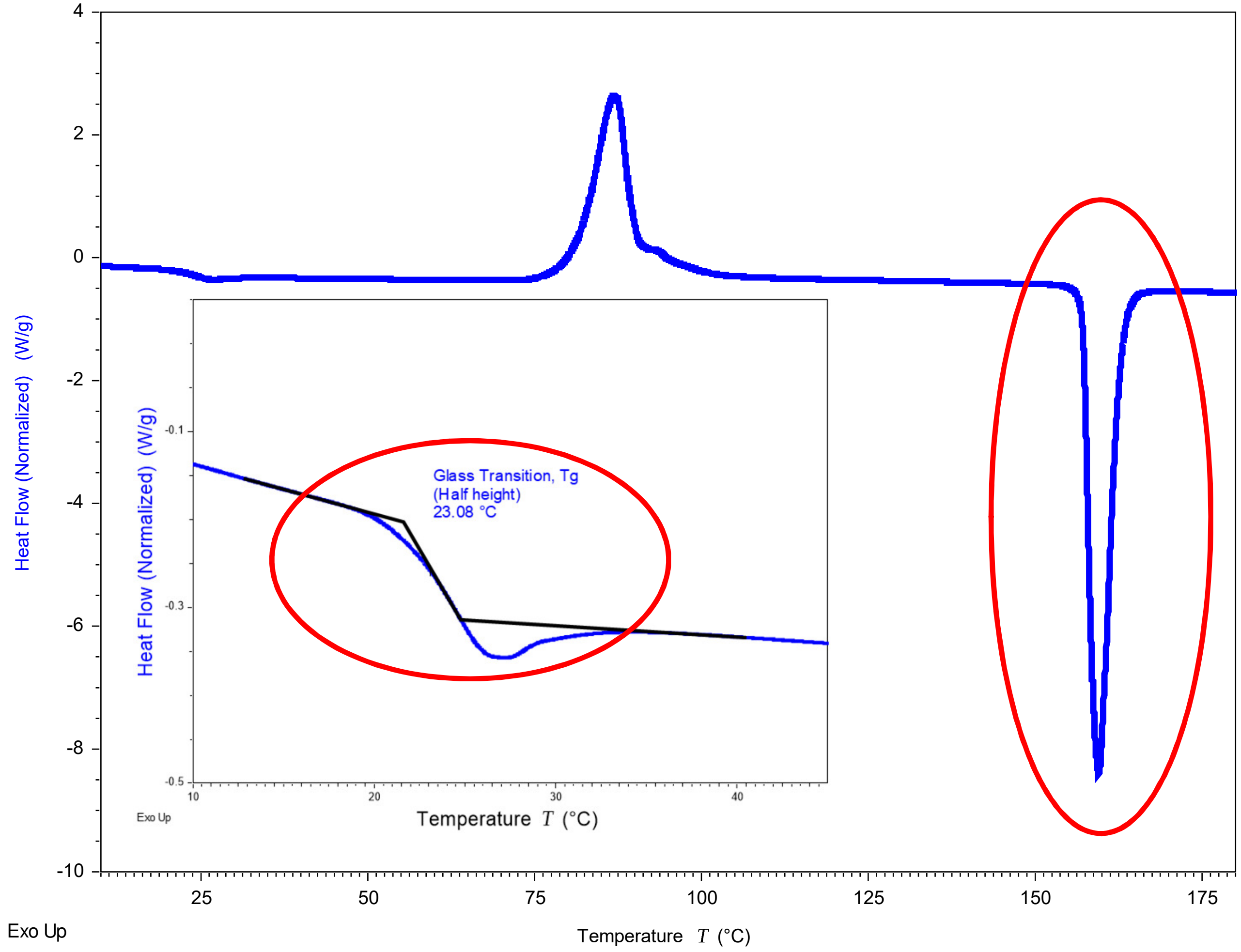
Differential Scanning Calorimetry (DSC)

What is a Differential Scanning Calorimetry

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



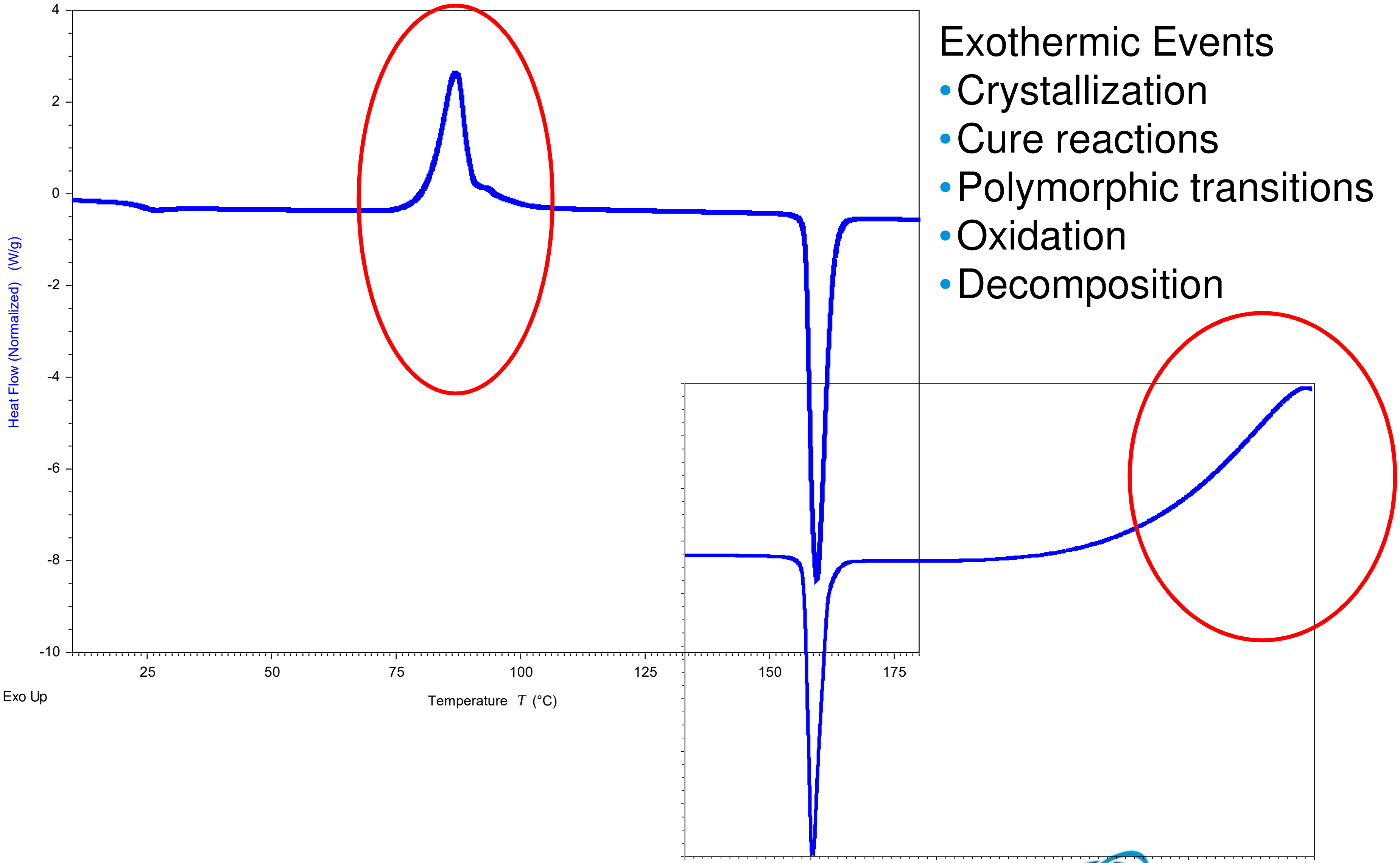
Endothermic Heat Flow – Heat Absorbed by Sample



Endothermic Events

- Glass transition
- Melting
- Evaporation/ volatilization
- Enthalpic recovery
- Polymorphic transitions
- Some decompositions

Exothermic Heat Flow – Heat Released by Sample



Exothermic Events

- Crystallization
- Cure reactions
- Polymorphic transitions
- Oxidation
- Decomposition

DSC Heat Flow Equation

$$\frac{dH}{dt} = \text{DSC heat flow signal}$$

$$(\text{mW or } \frac{\text{mJ}}{\text{s}})$$

$$\begin{aligned} Cp &= \text{Sample Heat Capacity} \\ &= \text{Sample Specific Heat x Sample Weight} \end{aligned}$$

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

$$\frac{dT}{dt} = \text{Heating Rate (°C/min)}$$

$$f(T, t) = \text{Heat flow that is function of time at an absolute temperature (kinetic)}$$

DSC Heat Flow

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

Heat Capacity

- Glass Transition
- Some Melting

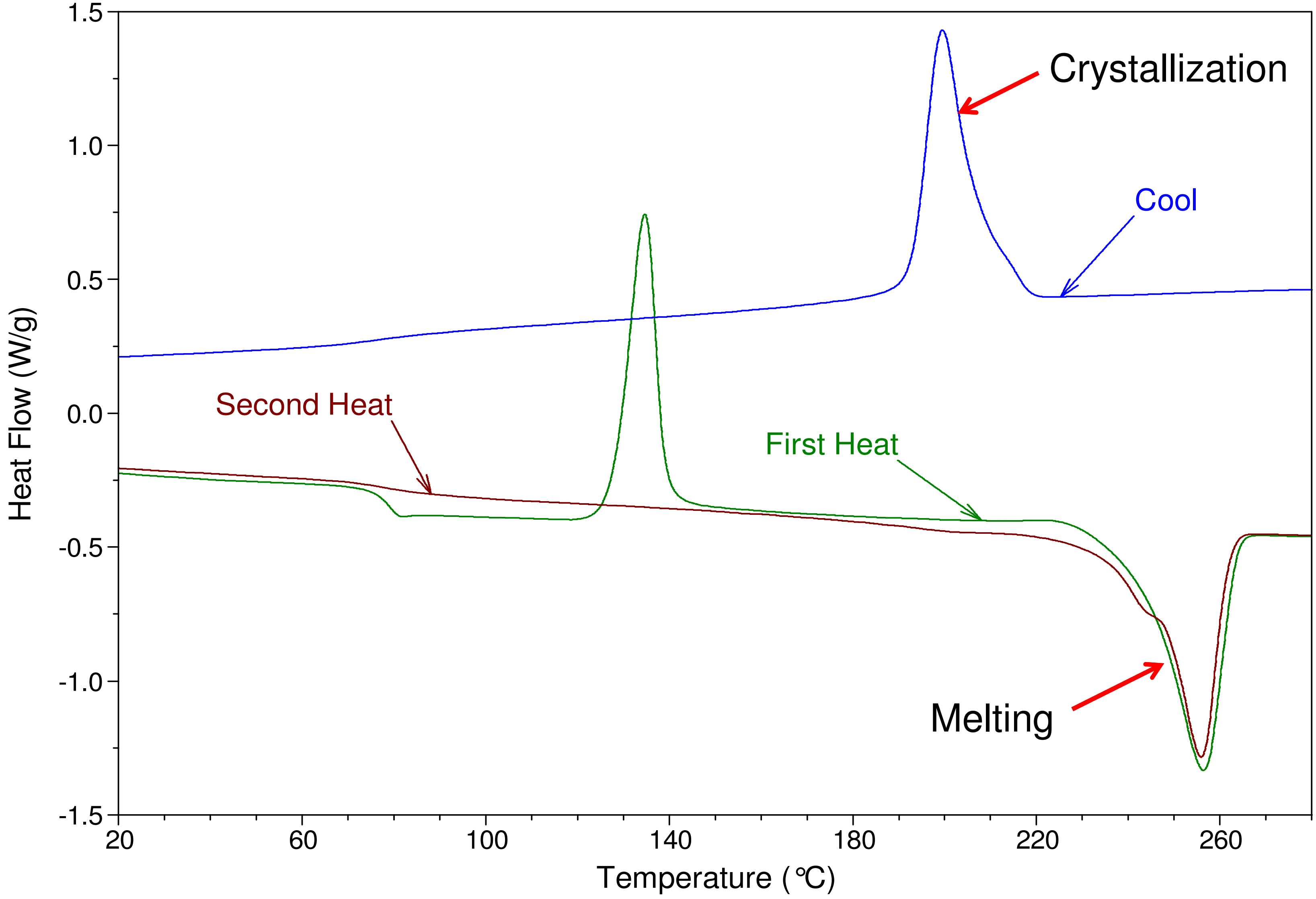
Kinetic

- Crystallization
- Some melting
- Cure reactions
- Volatilization
- Decomposition
- Denaturation

What DSC Can Tell You

- Identification of amorphous & crystalline material
- Identification of phase transitions and changes of state
- Specific Heat Capacity – measure of molecular mobility
- Heats of fusion & reactions
- Oxidative/Thermal Stability
- Reaction Kinetics

A typical Heat/Cool/Heat thermogram



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TA Instruments DSC Models

DSC 25
DSC 250
DSC 2500

Q200 &Q2000

AutoQ20

Discovery DSC

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

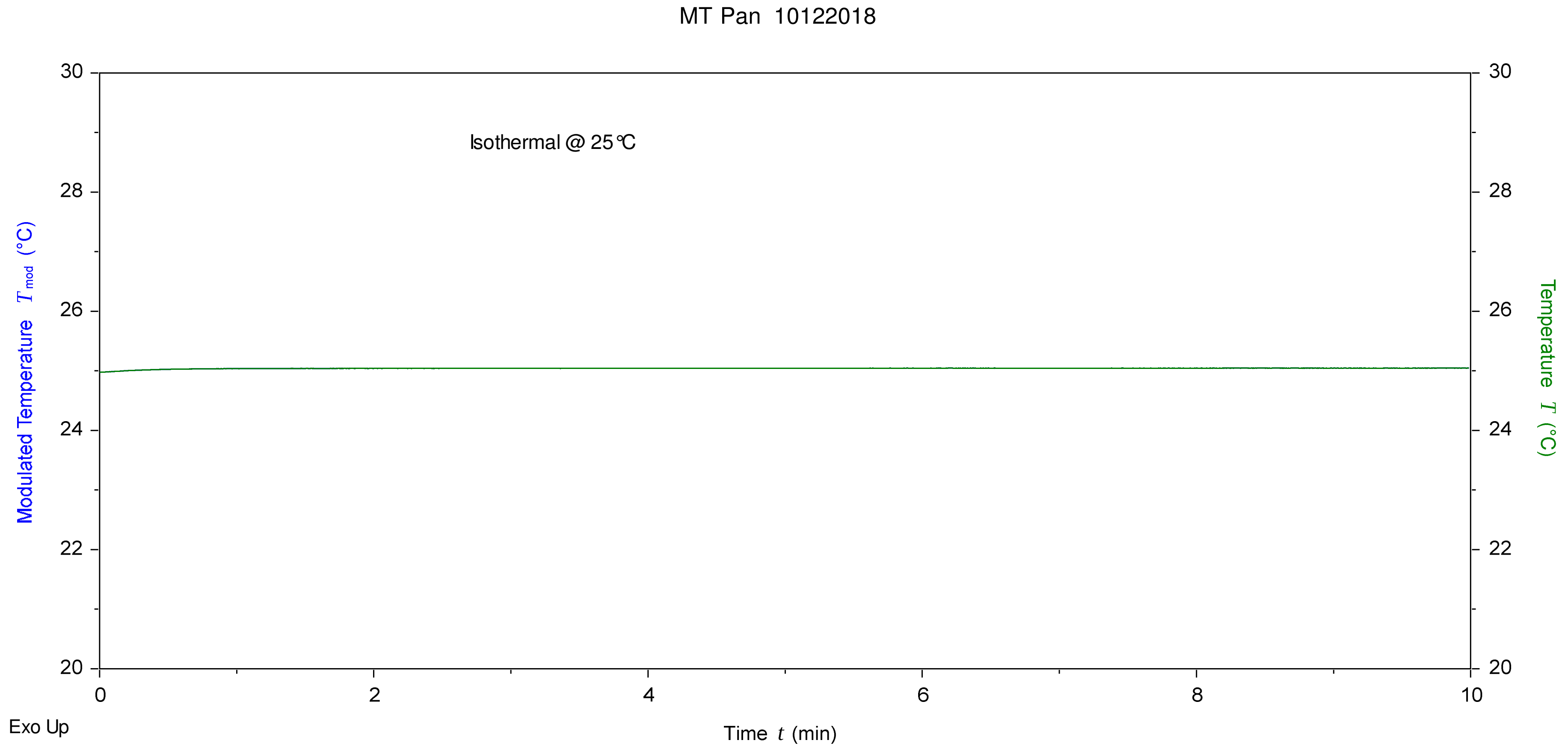
Modulated DSC®

- MDSC®
  - Uses sinusoidal temperature ramp overlaid upon linear ramp
  - Separates Heat Capacity and Kinetic transitions
  - Increases sensitivity to Heat Capacity changes (e.g. Tg)
  - Best available measurement of Heat Capacity

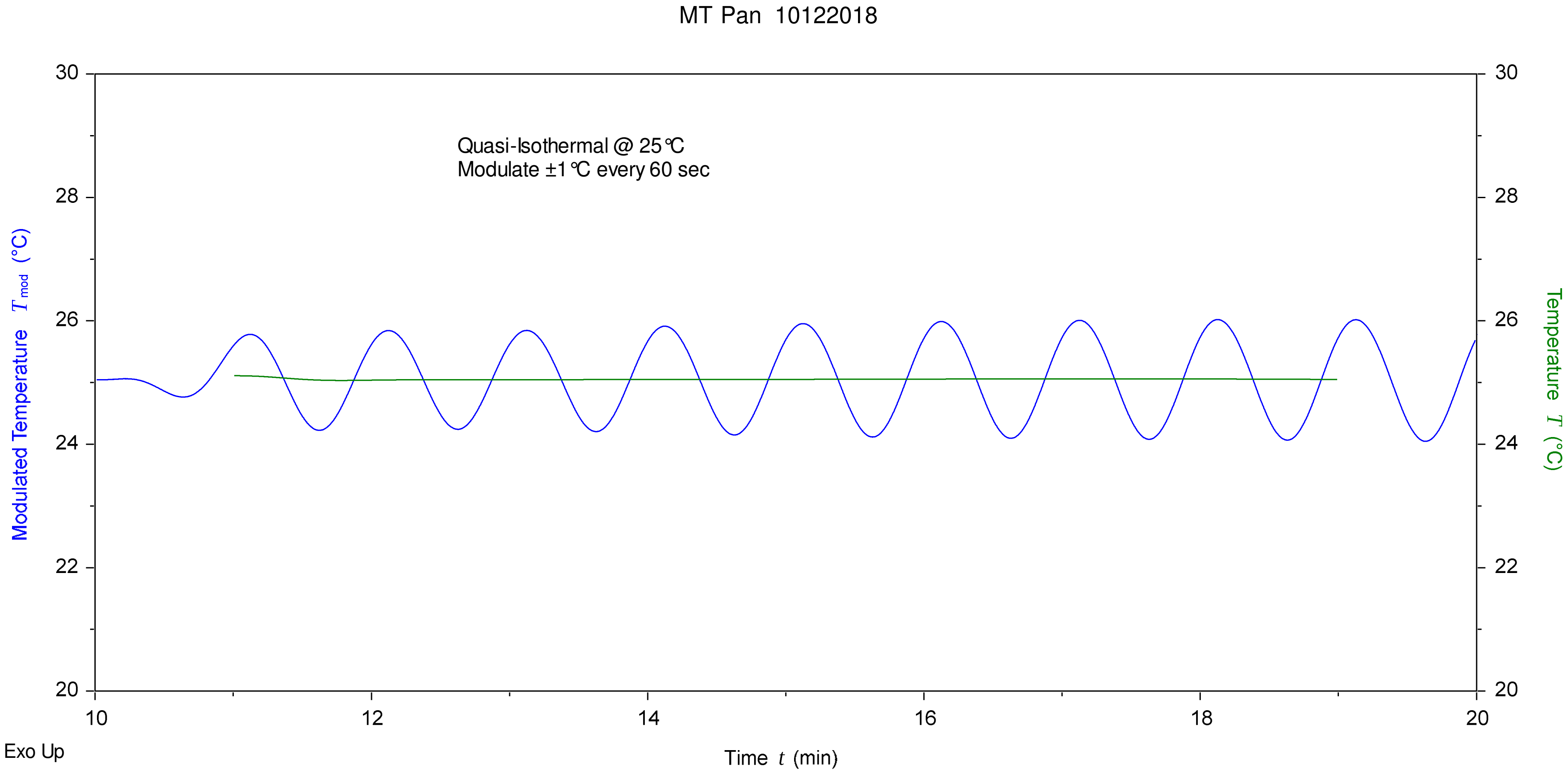
What is MDSC?

- MDSC separates the Total heat flow of DSC into two parts based on the response of the system to a changing heating rate. The changing heating rate is effected by ‘superimposing’ a sinusoidal heating rate on a linear heating rate.
- In general, only heat capacity and melting respond to the changing heating rate resulting in an increase in signal. Kinetic events tend to occur at different temperatures as a function of heating rate. For example, increasing the heating rate can shift decomposition to a higher temperature.
- The Reversing and Nonreversing signals of MDSC are not necessarily a measure of reversible and nonreversible properties.

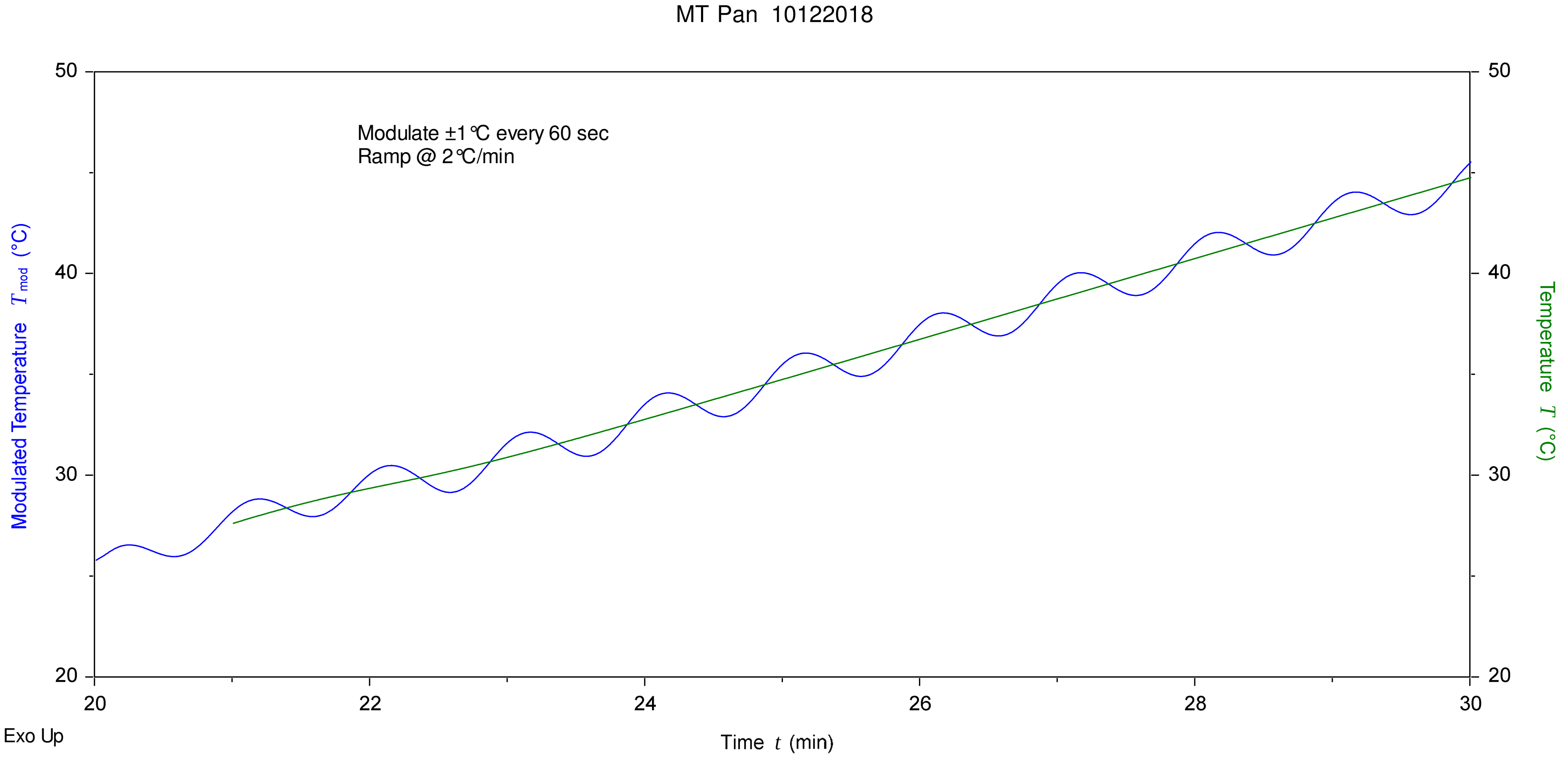
Isothermal @ 25°C



MDSC - Quasi-Isothermal @ 25°C



MDSC – 1°C amplitude, every 60 sec, @ 2°C/min



DSC Heat Flow – What the DSC Measures

$$\frac{dQ}{dt} = \text{DSC heat flow signal}$$

$$\begin{aligned} Cp &= \text{Sample Heat Capacity} \\ &= \text{Sample Specific Heat x Sample Weight} \end{aligned}$$

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

$$\frac{dT}{dt} = \text{Heating Rate}$$

$$f(T,t) = \text{Heat flow that is function of time and temperature (kinetic)}$$

MDSC® Theory: Heat Flow Signals

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

Total Heat Flow

- All Transitions

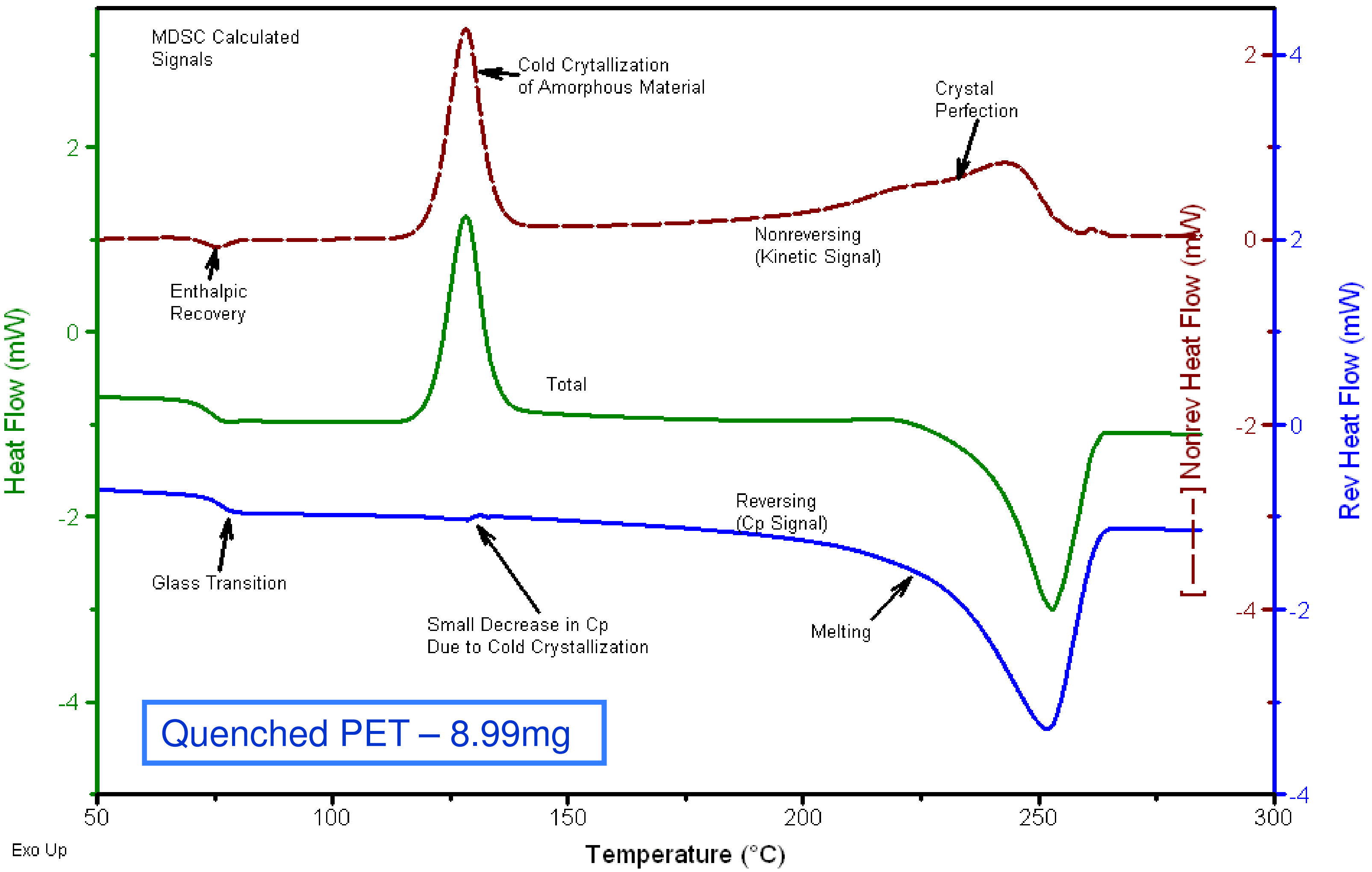
Reversing Heat Flow

- Heat Capacity
- Glass Transition
- Melting

Non-Reversing Heat Flow

- Enthalpic Recovery
- Evaporation
- Crystallization
- Thermoset Cure
- Denaturation
- Decomposition
- Some Melting
- Chemical Reactions

Calculated MDSC Heat Flow Signals



MDSC® Instruments

- Standard on:
  - All Discovery DSC's (2500, 250, 25 & Gen 1)
  - Discovery SDT 650 (for Cp only)
  - Q2000 DSC*
- Optional on:
  - Q200 & Q20 DSC, & some Q2000*
- Not available on:
  - Q600 SDT

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

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 (<u>in standard mode</u>)
  - 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

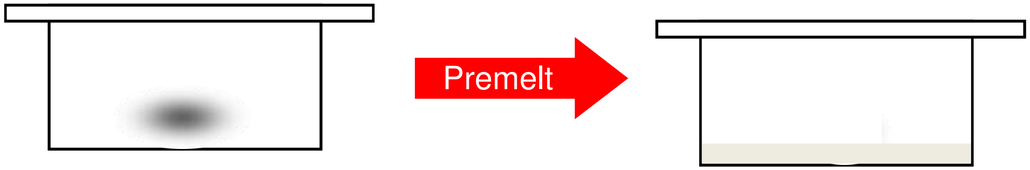
- An inert purge gas, such as nitrogen, where the flow rate is controlled to 10-50 ml/min +/- 5 ml/min

- 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

Temperature and Cell Constant Calibration

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



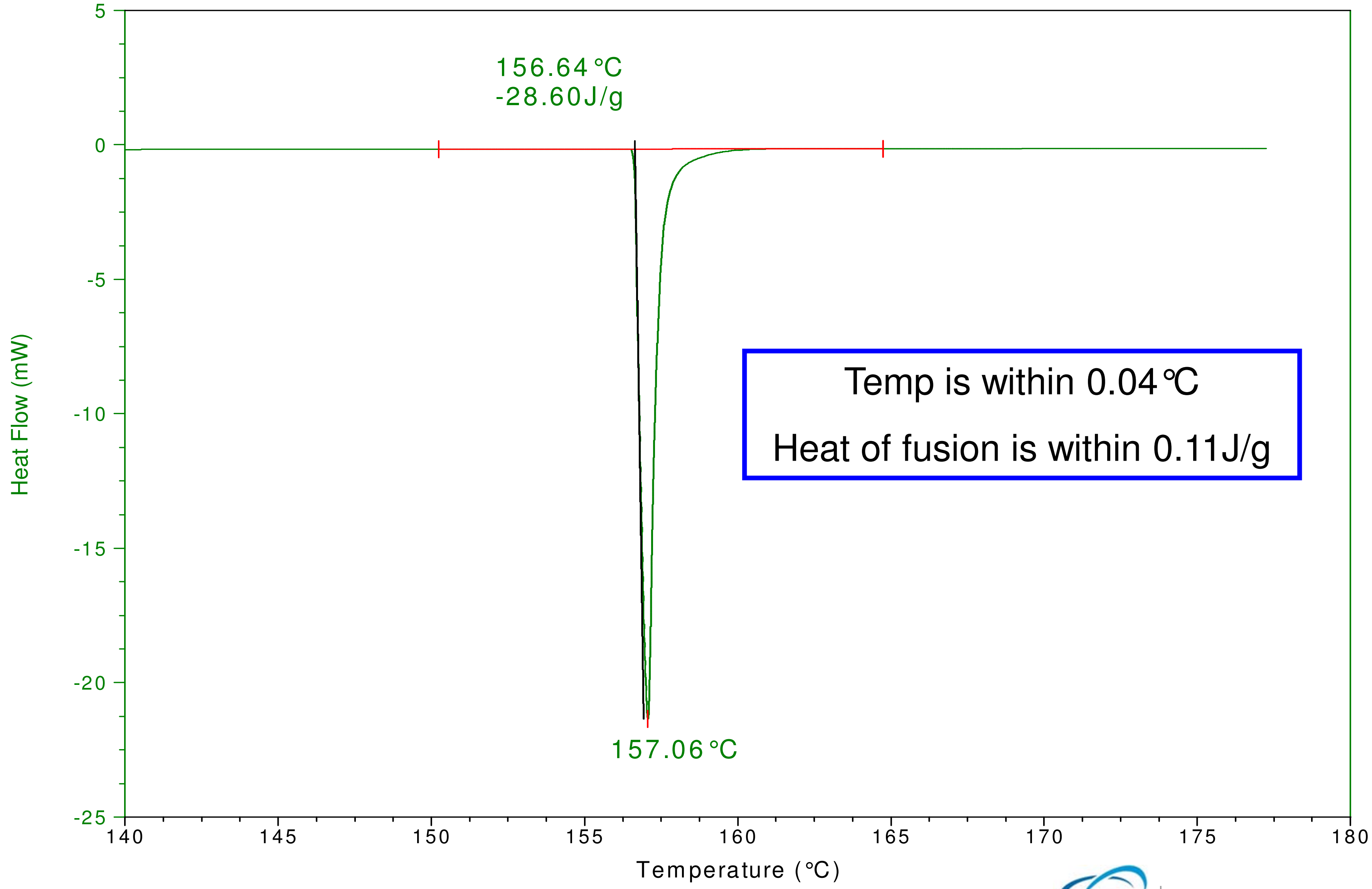
- Verify at least once a month

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

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℃
  - Heat of Fusion 28.71J/g

Verifying Cell Constant & Temperature



Temp is within 0.04℃

Heat of fusion is within 0.11J/g

Verifying Baseline

- Run Empty cell (no pans), -90℃ to 400℃ (w/ RCS) at 20℃/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

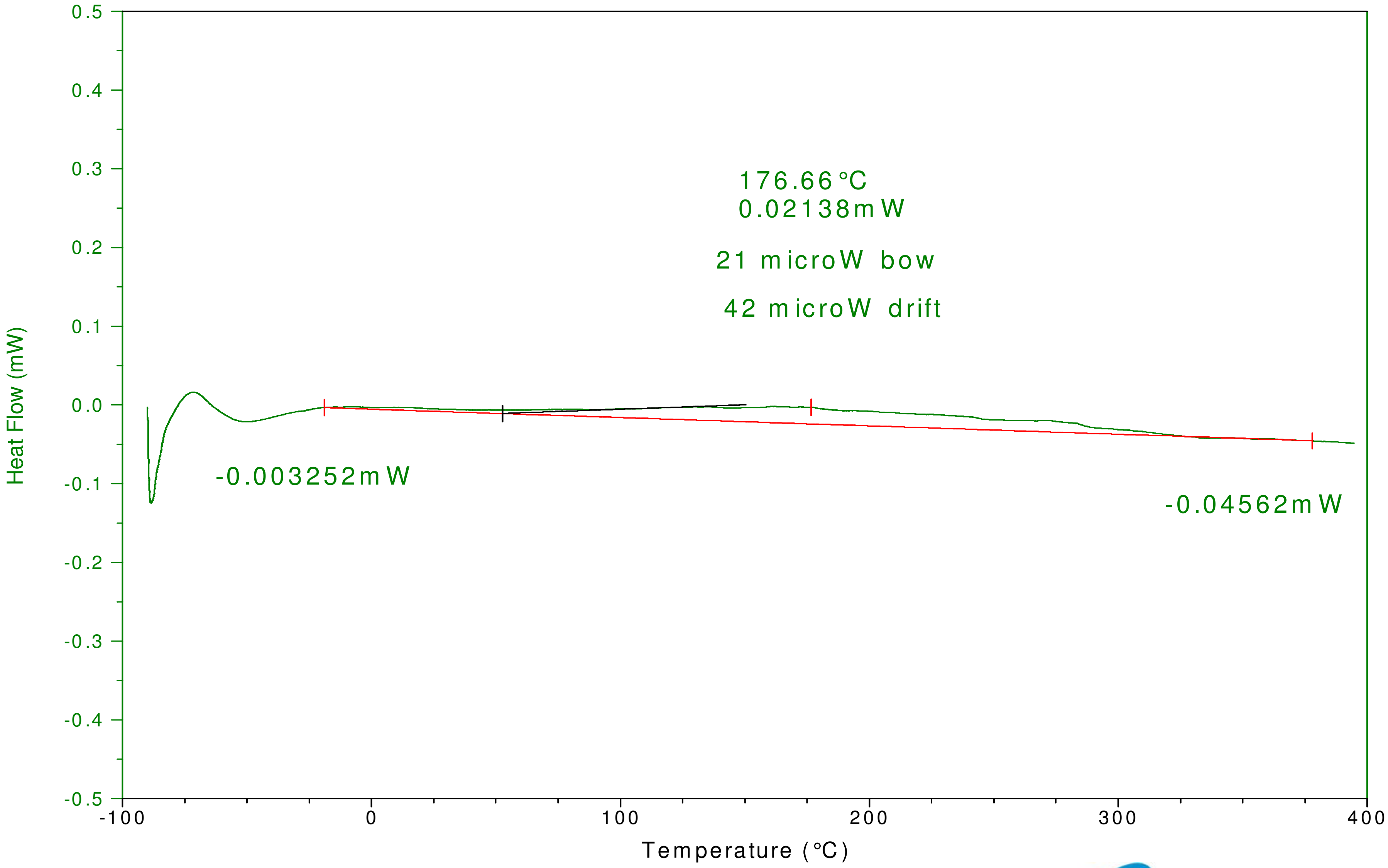
  - Measure drift and compare to instrument specifications.

  - 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

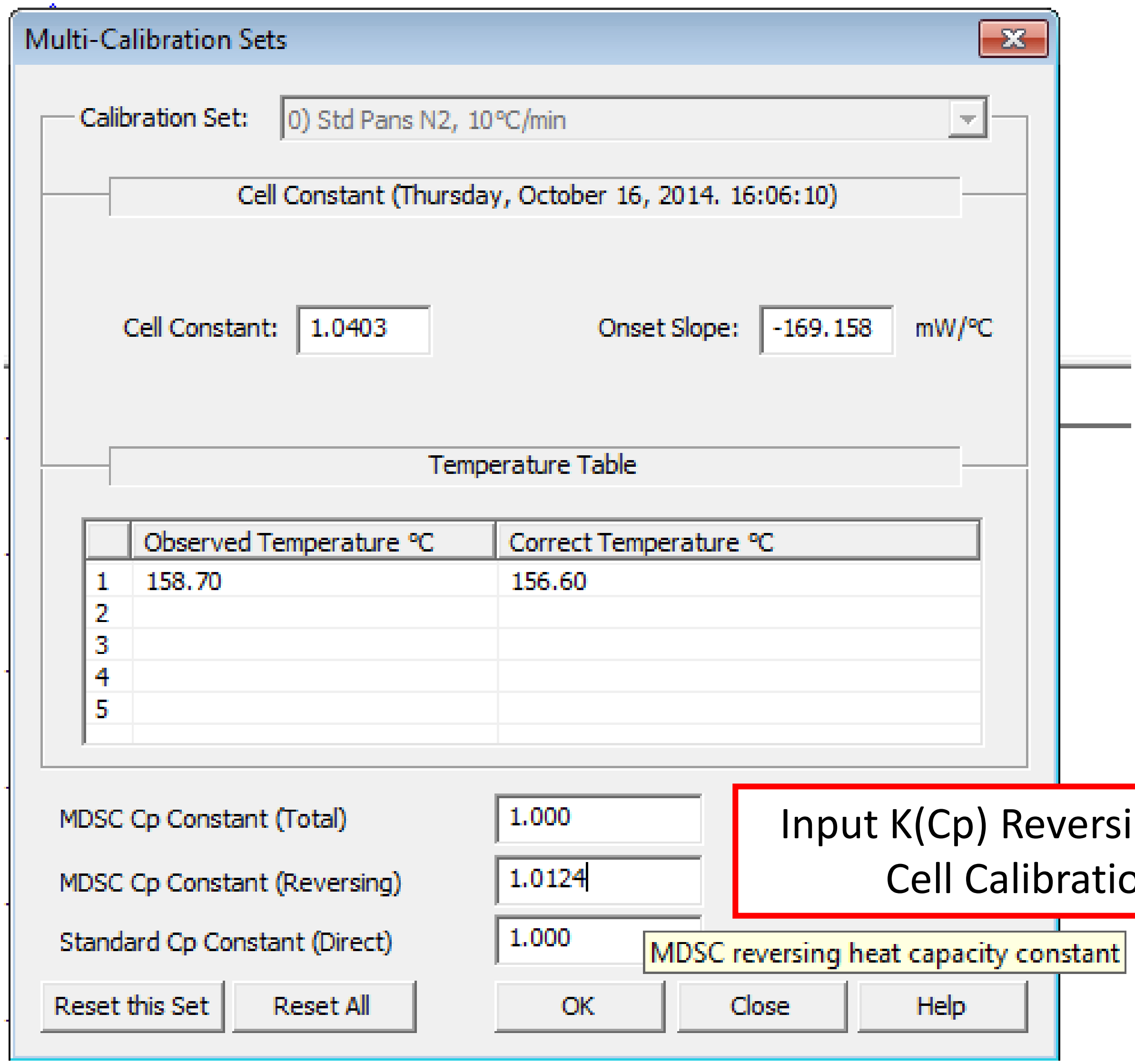
Verifying Baseline



MDSC Calibration – Q Series

- Calibrate your DSC as normal
  - Tzero™
  - Cell Constant
  - Temperature
- Cp Calibration is Optional
  - If you are **not** measuring absolute quantitative Cp
    - Use kCp value of 1.0 if using
- If measuring absolute quantitative Cp then…
- Need to calculate MDSC Cp Constant (Reversing)
- Leave the MDSC Cp Constant (Total) @ 1.0
- Set existing constant to 1.0
  - Run Sapphire sample

Update KCp (reversing) in cell/temperature table



Multi-Calibration Sets

Calibration Set: 0) Std Pans N2, 10°C/min

Cell Constant (Thursday, October 16, 2014. 16:06:10)

Cell Constant: 1.0403

Onset Slope: -169.158 mW/°C

Temperature Table

	Observed Temperature °C	Correct Temperature °C
1	158.70	156.60
2		
3		
4		
5		

MDSC Cp Constant (Total) 1.000

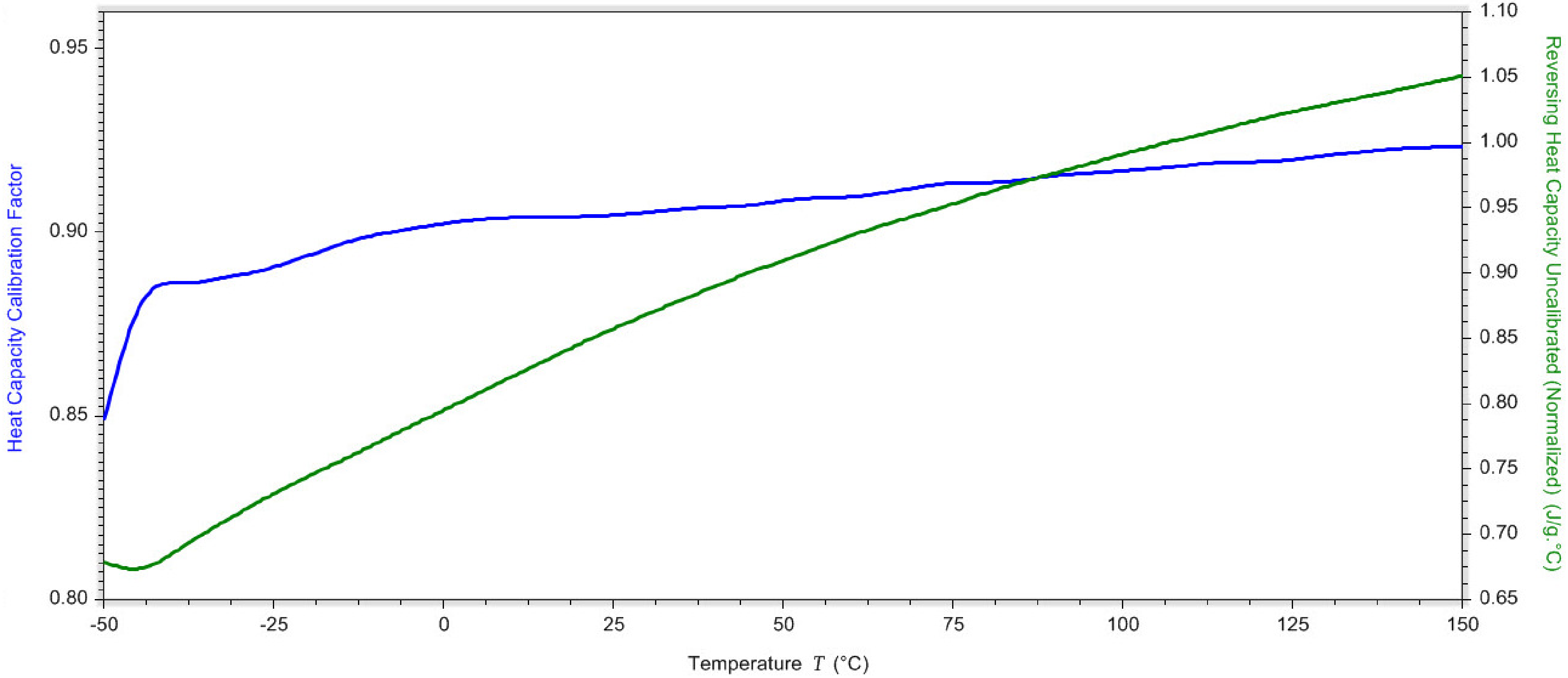
MDSC Cp Constant (Reversing) 1.0124

Standard Cp Constant (Direct) 1.000

MDSC reversing heat capacity constant

Input K(Cp) Reversing Value into Cell Calibration table

MDSC Cp calibration using TRIOS



KCp is determined as a continuous function of temperature in the Discovery DSC.

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

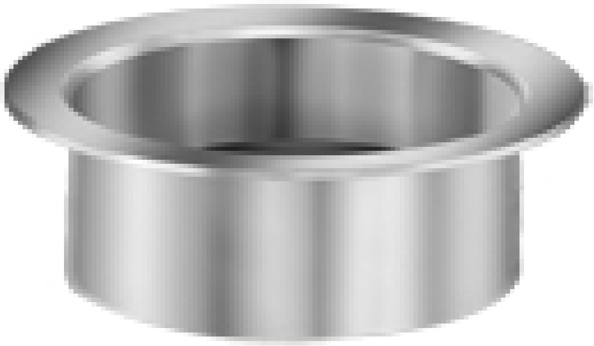
- Type of pan depends on:
    - Sample form
    - Volatilization
    - Temperature range

- Use lightest, flattest pan possible

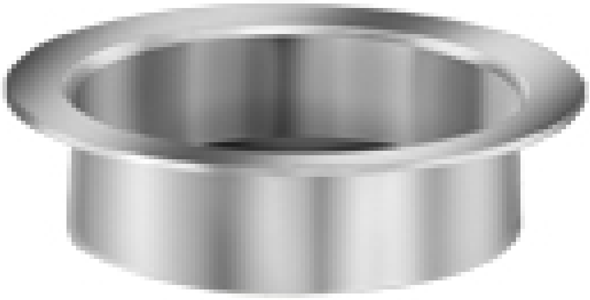
- Always use reference pan of the same type as sample pan

TA Instruments Tzero Pans (Aluminum)

Tzero Pan



Tzero Low-Mass Pan

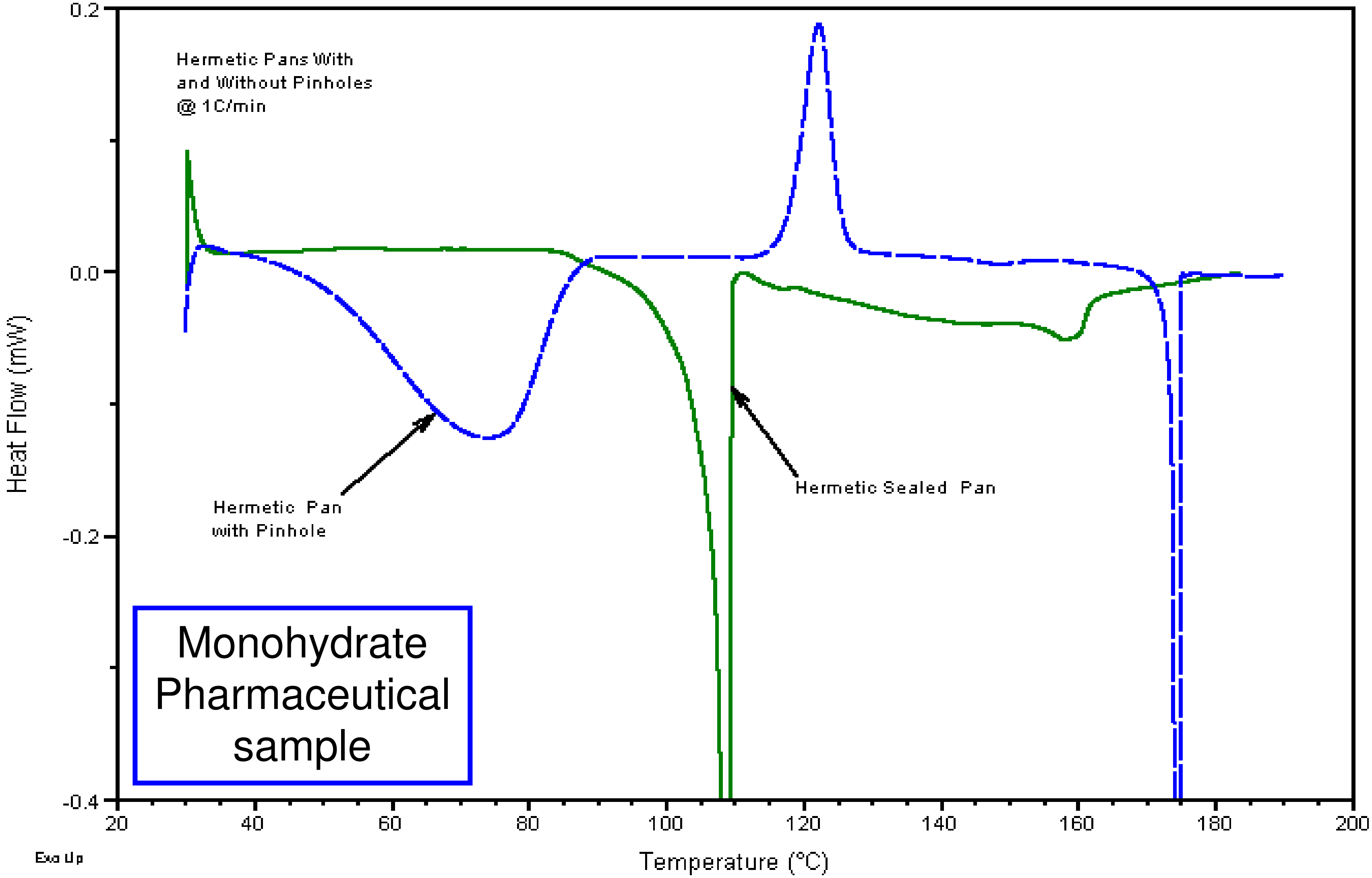


- The Tzero pan has been engineered to have a perfectly flat bottom and not to deform during crimping. This ensures the optimal contact between pan and sensor, minimizing the contact resistance and improving resolution.

- 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.

It Can Matter What Pan You Use



Monohydrate Pharmaceutical sample

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℃/min to appropriate temp (max of 550℃ on Q series, max. 400℃ 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

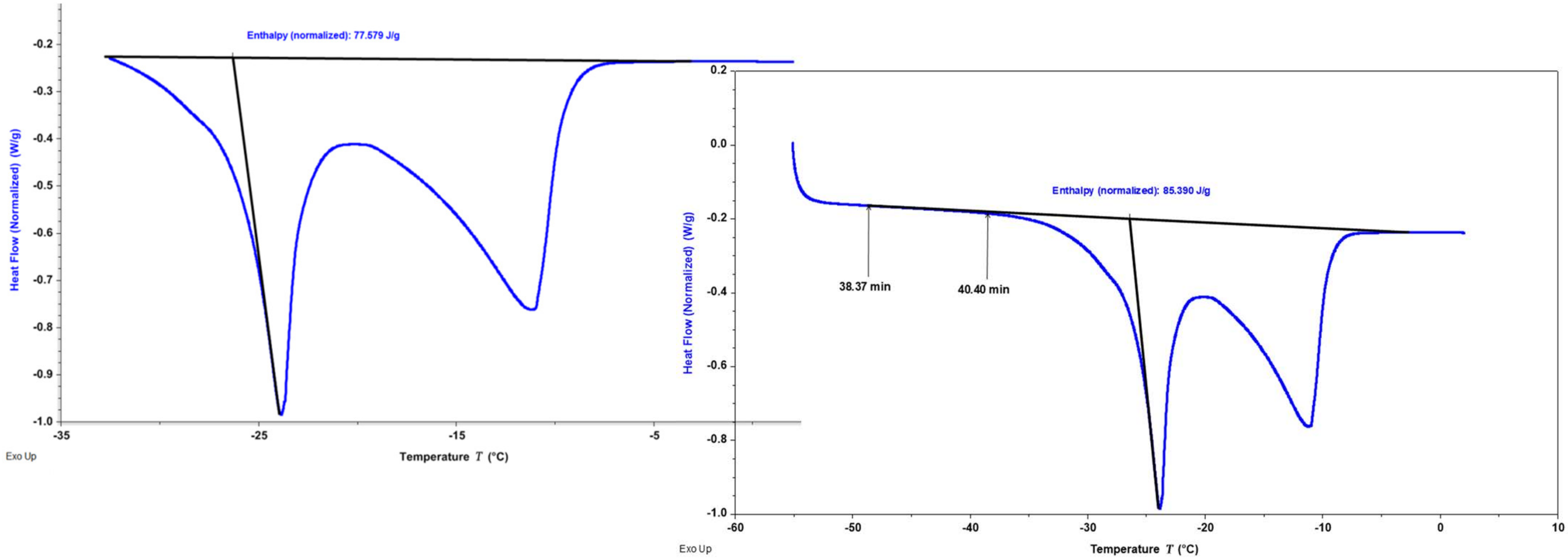
- Check out the TA Tech tip video on cleaning the DSC cell:

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

DSC General Method Recommendations

- Run a Heat-Cool-Heat at 10-20 ℃/min
- Use specific segments as needed, i.e. gas switch, abort, etc.
- Ensure that the starting temperature of the experiment is chosen to encompass the entire transition (see next slide)
- Modify heating rate based on what you’re looking for

Have 2 Minutes of Baseline



- Start Temperature
  - Generally, the baseline should have two (2) minutes to completely stabilize prior to the transition of interest. Therefore, at 10°C/min., start at least 20°C below the transition onset temperature
- End Temperature
  - Allow a two (2) minute baseline after the transition of interest in order to correctly select integration or analysis limits

Method Development

A Heat Cool Ramp Method

1) Ramp 10℃/min to -90℃ or Equilibrate to -90℃
2) Ramp 10℃/min to 200℃
3) Ramp 10℃/min to -90℃
4) Ramp 10℃/min to 200℃

How to Program MDSC?

- Period
  - Typically 60 seconds for transitions
  - Typically 120 seconds for Cp
- Heating rate
  - Typically 2-3°C/min
- Amplitude
  - Typically ±1°C for amorphous transitions and Cp
  - Use Heat-Iso amplitude for crystalline transitions

Starting Guidelines for Determining the Tg in Amorphous Materials – Conventional MDSC®

- Conventional MDSC conditions
  - Period: 60 second
    - Minimum period depends on pan type and pan mass
      - Can use 40 sec for low-mass Tzero pans
      - Use 200 sec for Hi-volume pans
  - Amplitude: ±1 °C
    - Increase for added sensitivity
  - Heating Rate 3 °C/min
    - Slow down heating rate for sharper transitions or large enthalpic recovery peaks

Starting Guidelines for crystallinity/melting studies: MDSC® Heat Only Conditions

- MDSC Heat-Only Conditions
  - Period: 60 second
    - Minimum period depends on pan type and pan mass
      - Can use 40 sec for low-mass Tzero pans
    - Heating Rate 2-3℃/min
      - Ensure 4-5 cycles through peak @ half-height of melt
    - Amplitude Heat-only (Heat-Only/Heat-Iso)

Parameters for Heat Capacity (Cp)

- Conventional MDSC conditions
  - Period 120 seconds
    - Can use 100 seconds with low-mass Tzero pans
  - Amplitude ±1 °C
  - Heating Rate 3 °C/min
    - Can also do Quasi-isothermal for specific temperatures

MDSC Conditions for Discovery SDT 650

- Used to measure Heat Capacity
- Amplitude = ±3℃
- Period = 200 seconds
- Heating Rate = 5℃/min

- Best above 300 or 400℃

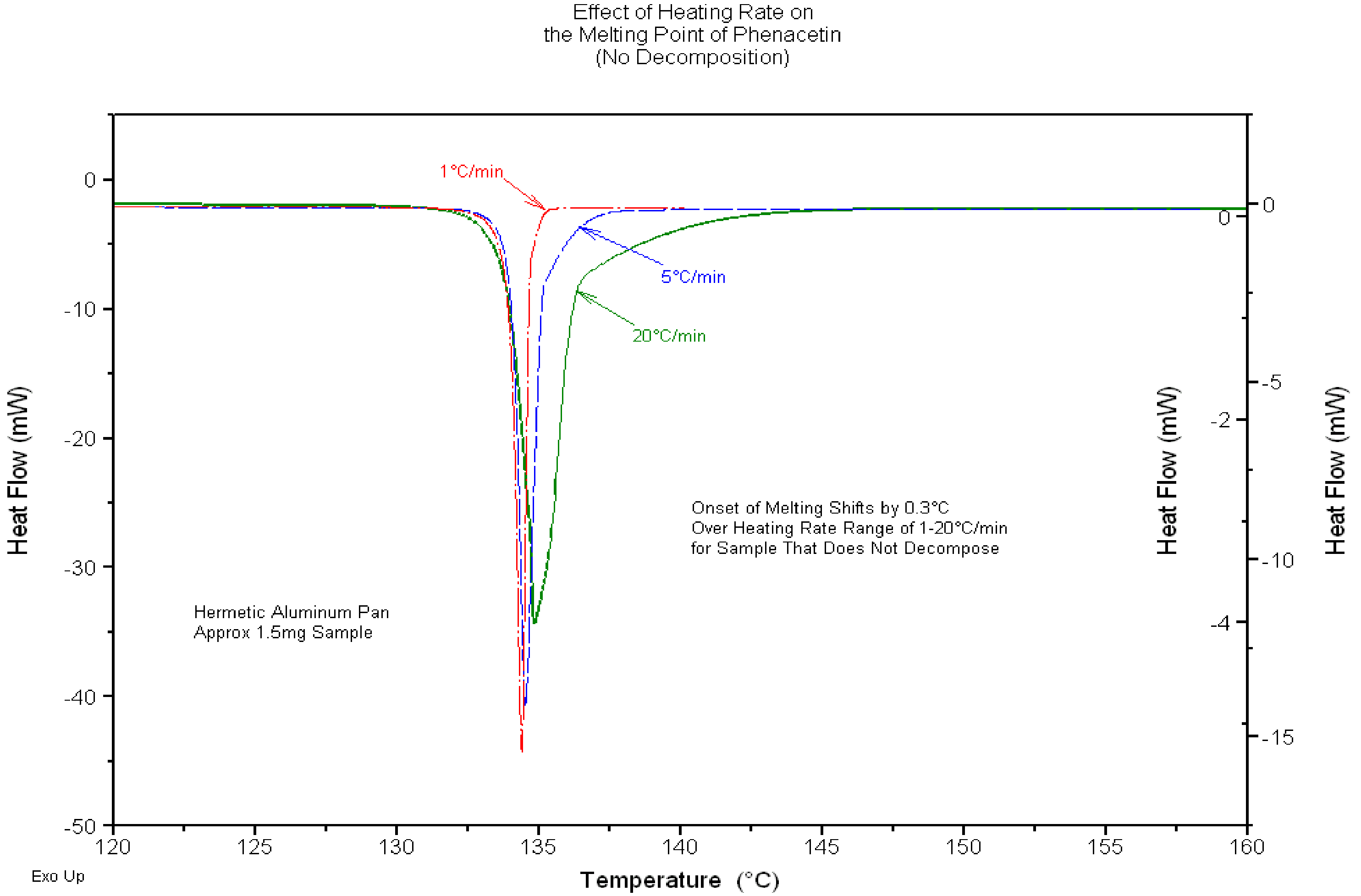
Summary for DSC

- Typical starting sample mass – depends on the size of the transition
  - 5-10mg for most polymers
  - 3-5 for chemical melting
  - <1 for explosives
- Typical starting ramp rate = 10°C/min (Heat-Cool-Heat)
  - Faster for better sensitivity
  - Slower for better resolution
- Change above as needed
- MDSC® as needed

Applications:

No Shift in Melt Temp with Heating Rate

Melt



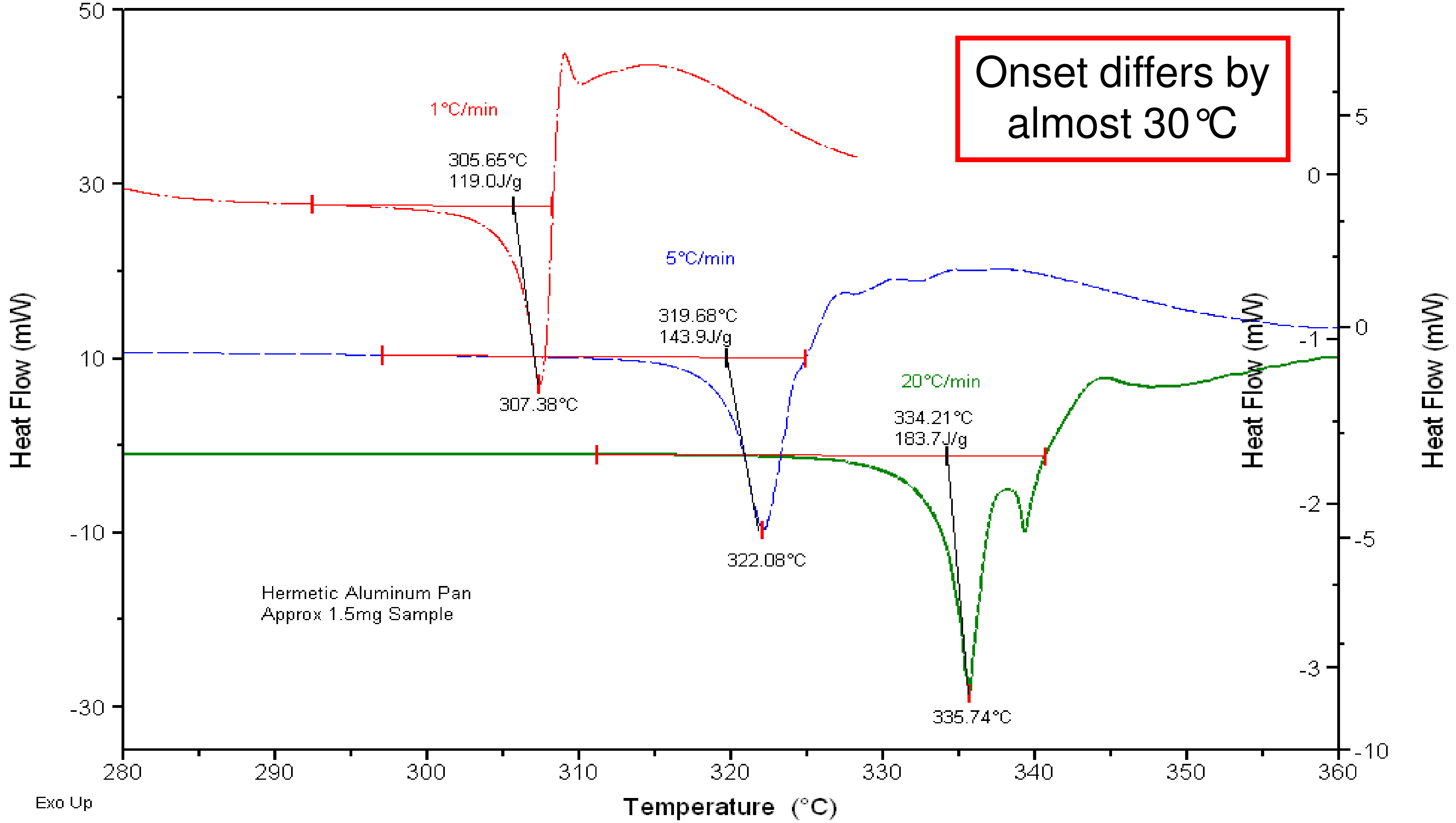
Effect of Heating Rate on
the Melting Point of Phenacetin
(No Decomposition)

Onset of Melting Shifts by 0.3°C
Over Heating Rate Range of 1-20°C/min
for Sample That Does Not Decompose

Hermetic Aluminum Pan
Approx 1.5mg Sample

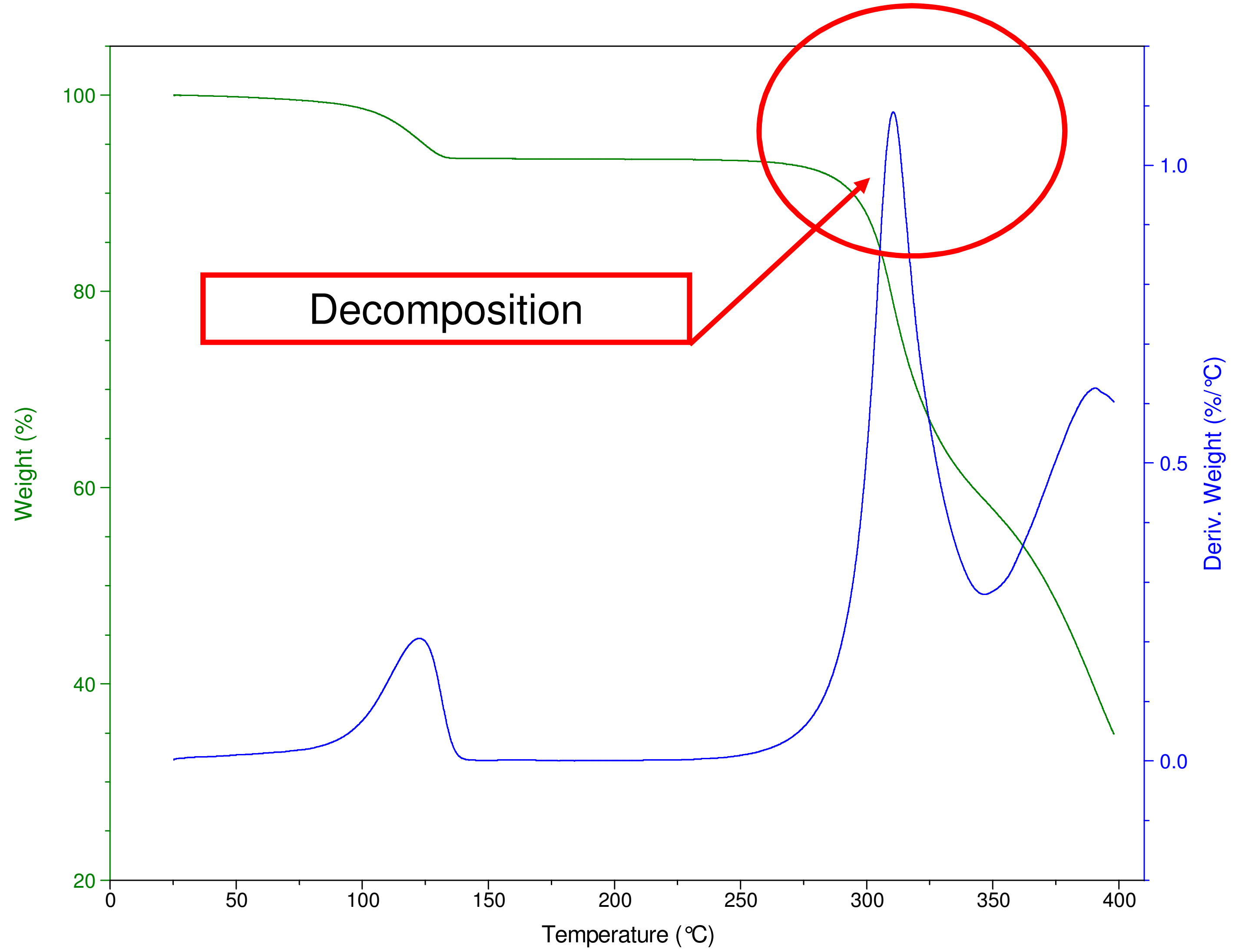
Ciprofloxacin Hydrochloride Decomposes

Decomposition is kinetic (heating rate dependent)



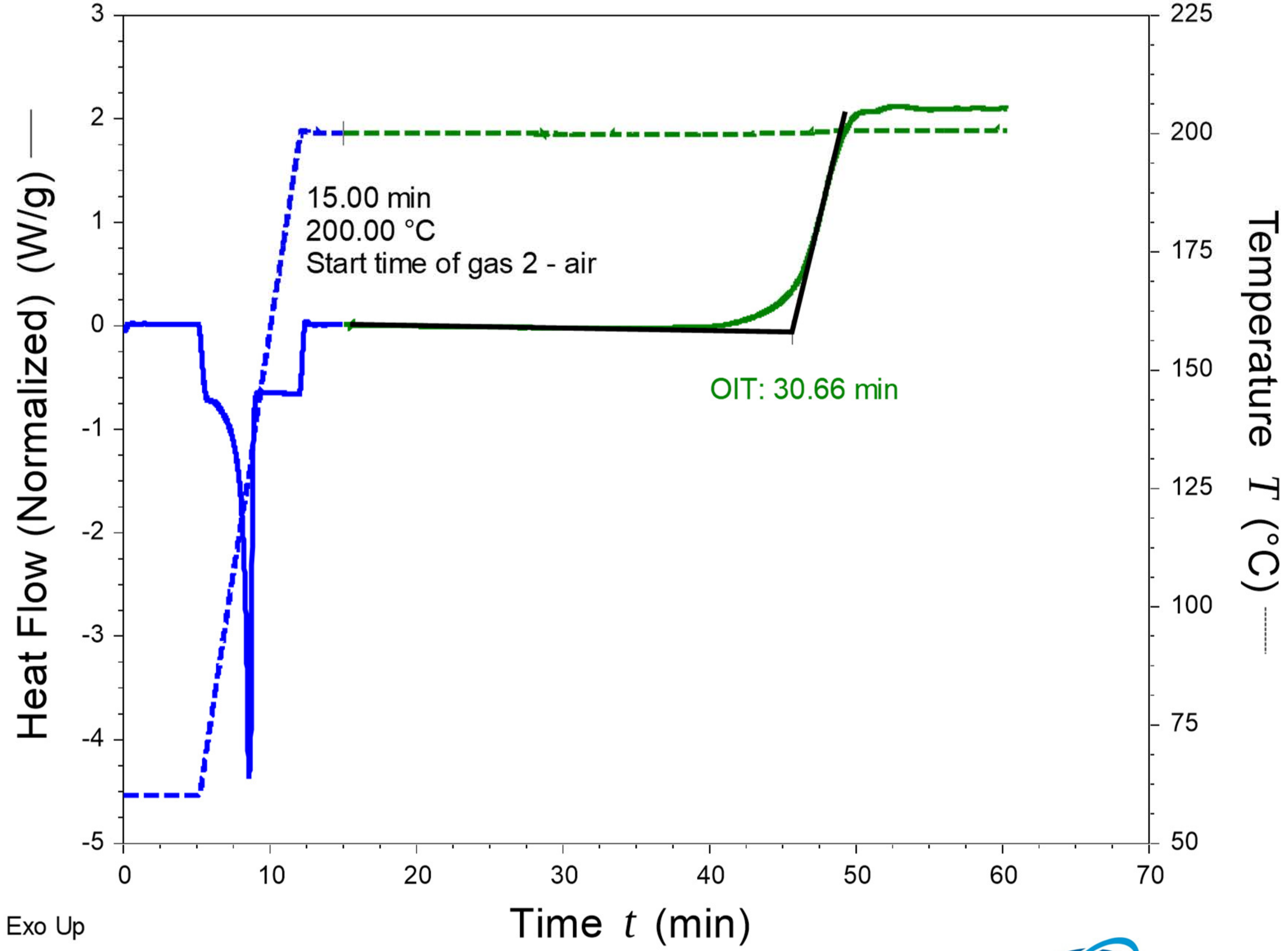
Onset differs by almost 30℃

TGA of Ciprofloxacin Hydrochloride

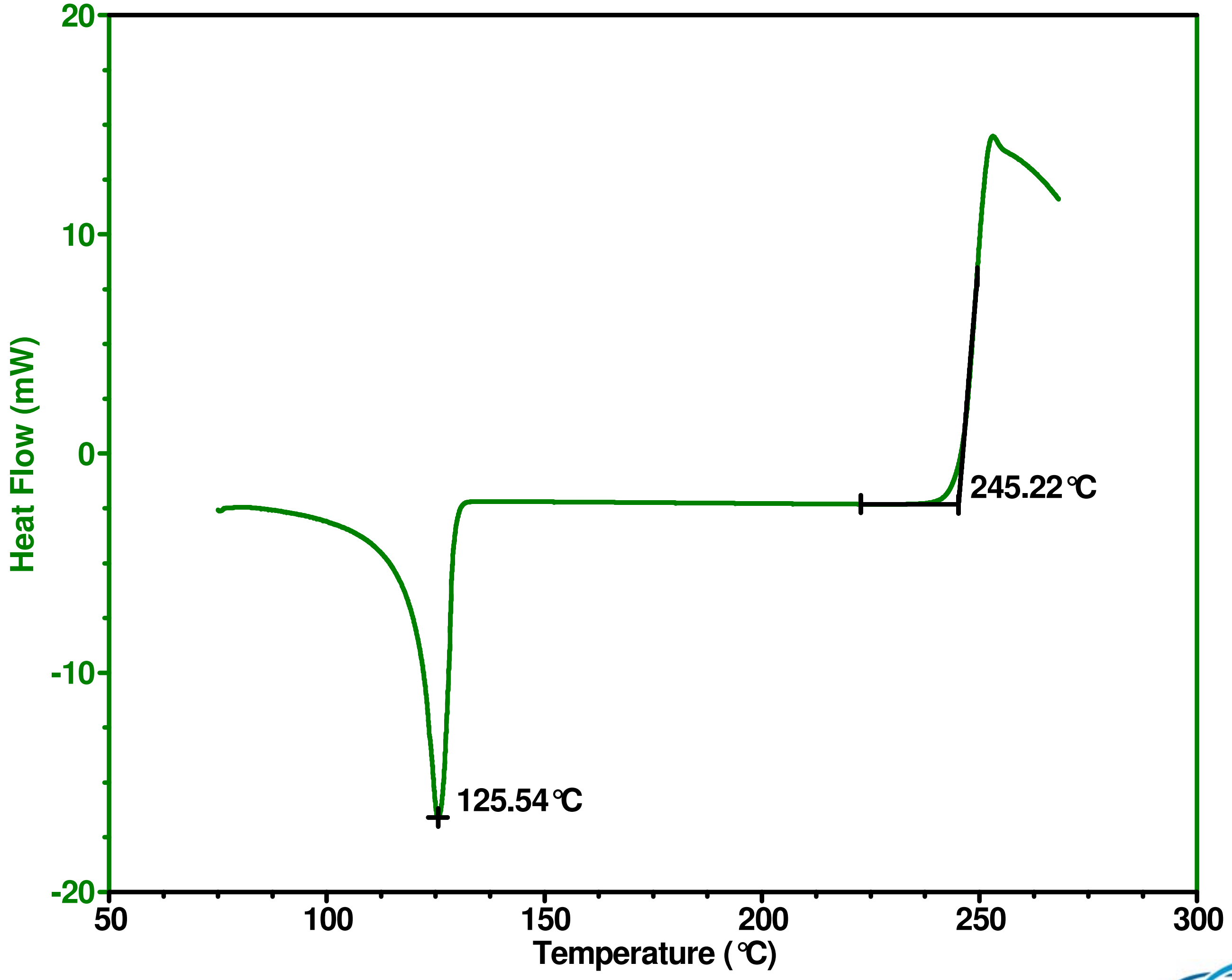


Decomposition

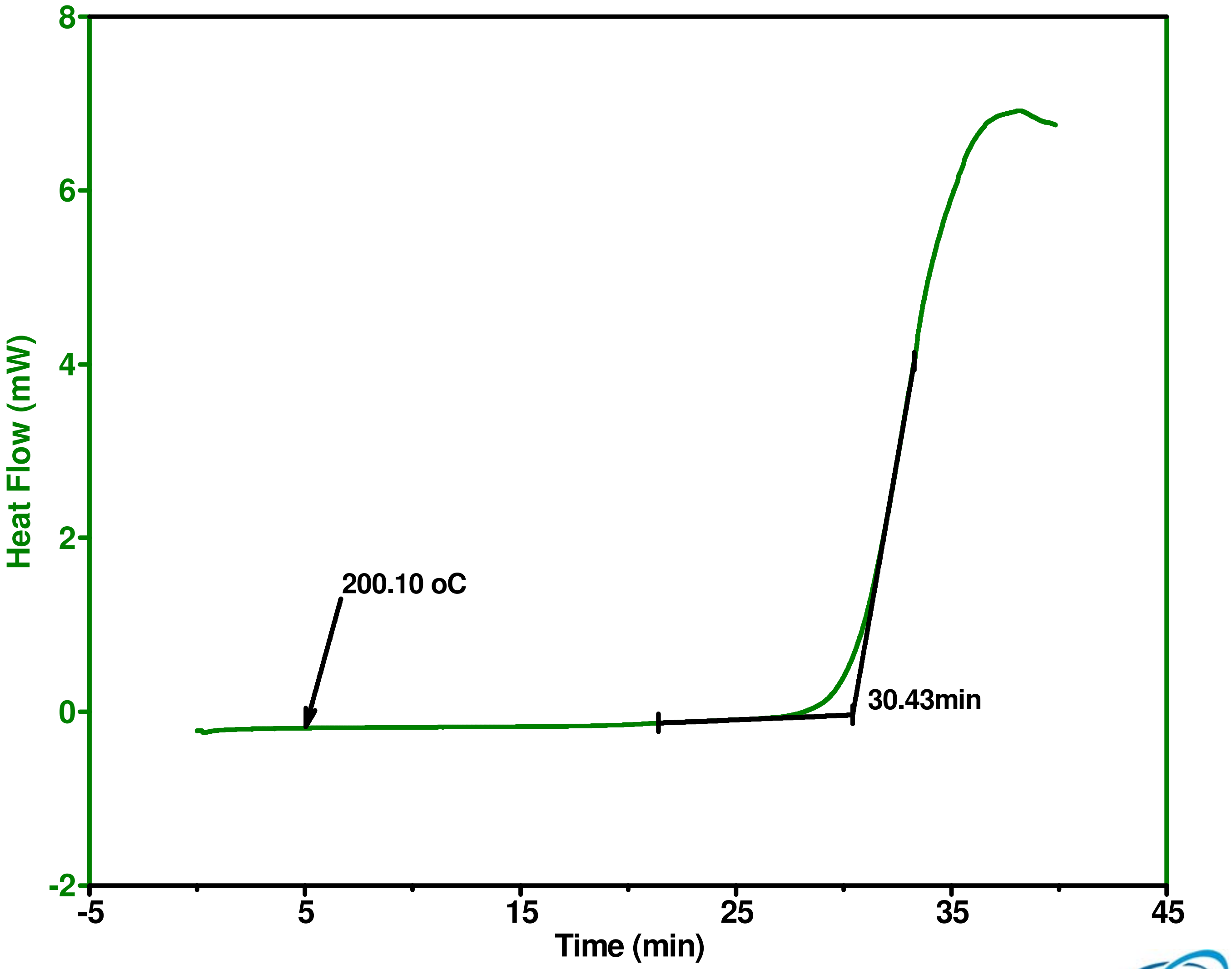
Oxidative Induction Time of Polyolefin Film



Polyethylene Oxidation Onset Temperature



Polyethylene Oxidation Induction Time



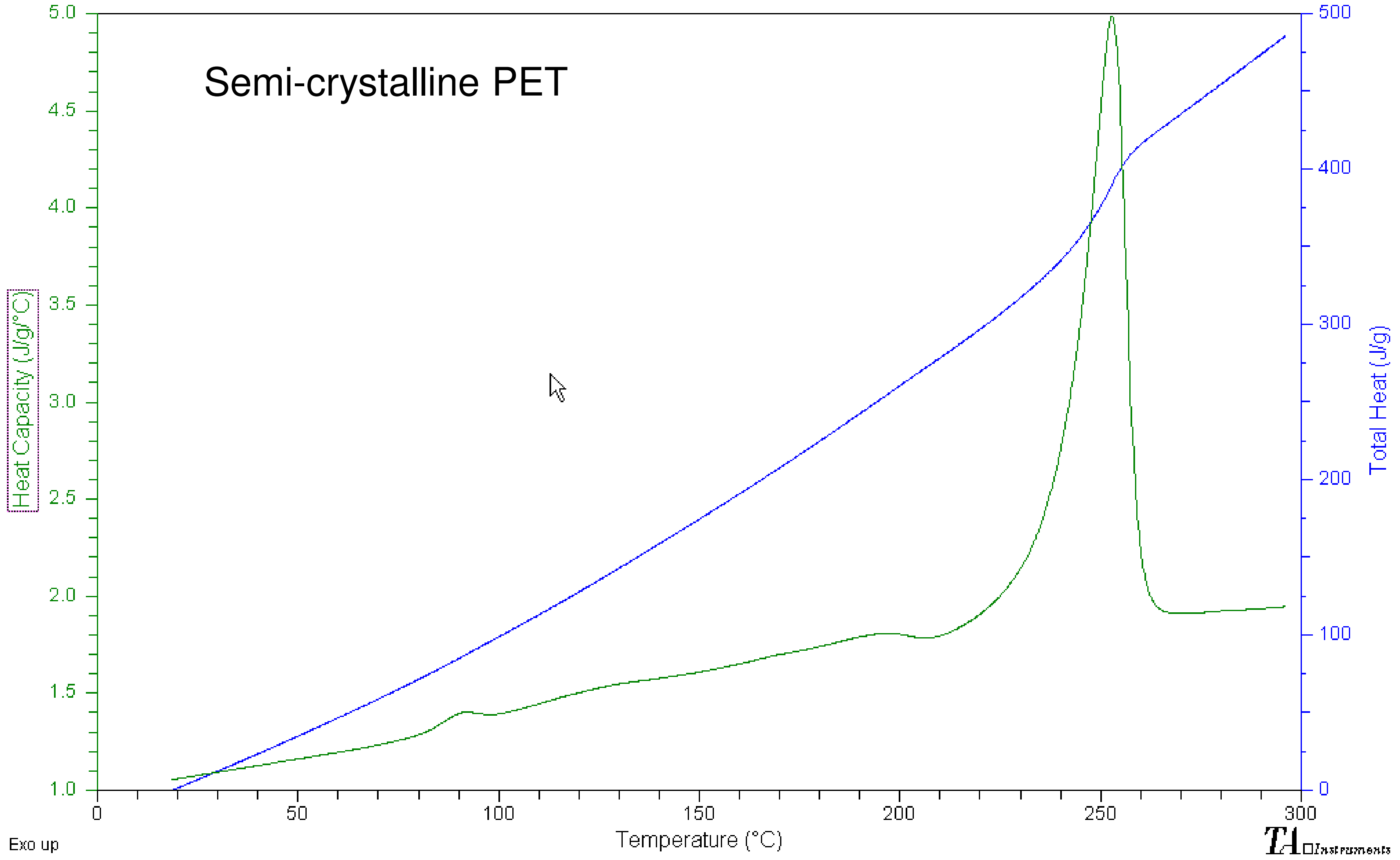
Applications:
Heat Capacity (Cp)

What is Heat Capacity?

- Heat capacity(Cp) is the amount of heat required to change the temperature of a material from T1 to T2
- Absolute thermodynamic property used by engineers in the design of processing equipment
- True Heat Capacity (no transition) is completely reversible; the material releases the same amount of heat as temperature is lowered from T2 to T1
- Specific Heat Capacity refers to a specific mass and temperature change for a material (J/g°C)

- Chemist's/Chemical Engineer's Definition

Heat Capacity and Total Heat of PET



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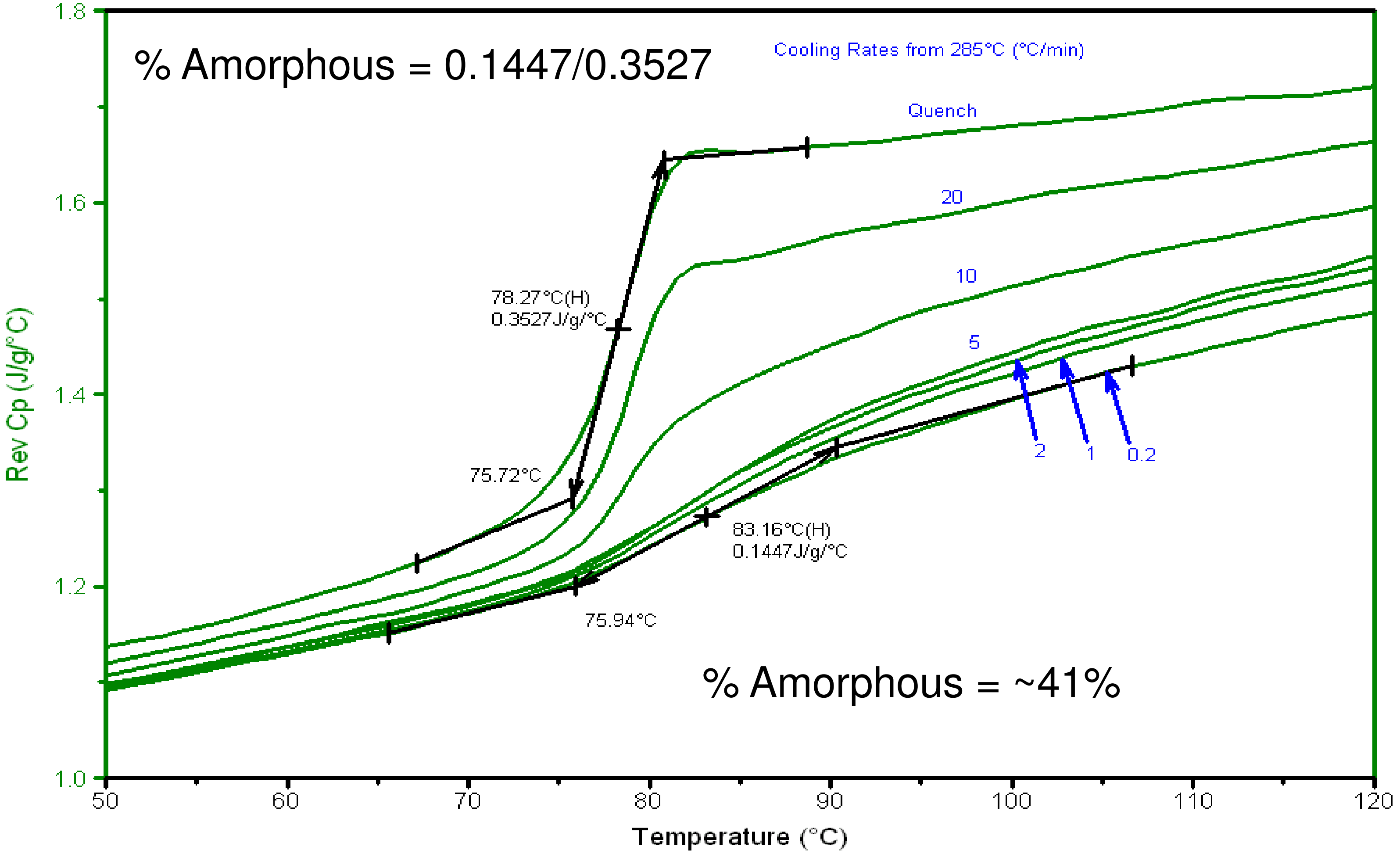
Material Scientist's Definition of Heat Capacity

- Heat capacity is directly related to molecular mobility
- Cp increases as molecular mobility increases
  - Higher Cp = More Mobility
  - Lower Cp = Less Mobility
  - Example: Amorphous structure is more mobile than crystalline structure
- Provides useful information about the physical properties of a material as a function of temperature
- Quantitative indicator of structure and stability

Change in Cp at Tg is a Measure of Amorphous Structure



Things to be Aware of

- DSC's do not measure heat capacity, but rather calculate it
    - From absolute value of the measured heat flow
- Most DSC's do not measure absolute heat flow
    - Has to be compensated for
    - For best accuracy requires stable and repeatable baseline
- DSC 2500 does measure absolute heat flow
    - Also, Discovery DSC & Q2000/1000 DSC

Things to be Aware of

- Heat Capacity calculated by a DSC is more appropriately called apparent heat capacity
    - Calculated signal contains the latent heat of phase change transitions
    - DSC calculated Cp signals also include all transitions because the heat flow signal is simply divided by heating rate to convert it to heat capacity units
    - A true value of Cp can only be obtained in temperature regions where there are no transitions (Heat Capacity Baseline)
    - Modulated DSC® (MDSC) Reversing Cp does not show kinetic events

Calculating Heat Capacity

- Depending on the DSC that you have there are three different ways to calculate Cp (Listed from least to most accurate)
    - ASTM E1269 (Three Run Method)
        - Applicable to all DSC’s
    - Direct Cp – Single Run Method
        - Applicable to DSC 2500, Discovery DSC, Q2000/1000 only
        - Fastest determination
    - MDSC® - Single Run Method
        - Any DSC w/ MDSC option
        - Most accurate determination

Calculating Heat Capacity

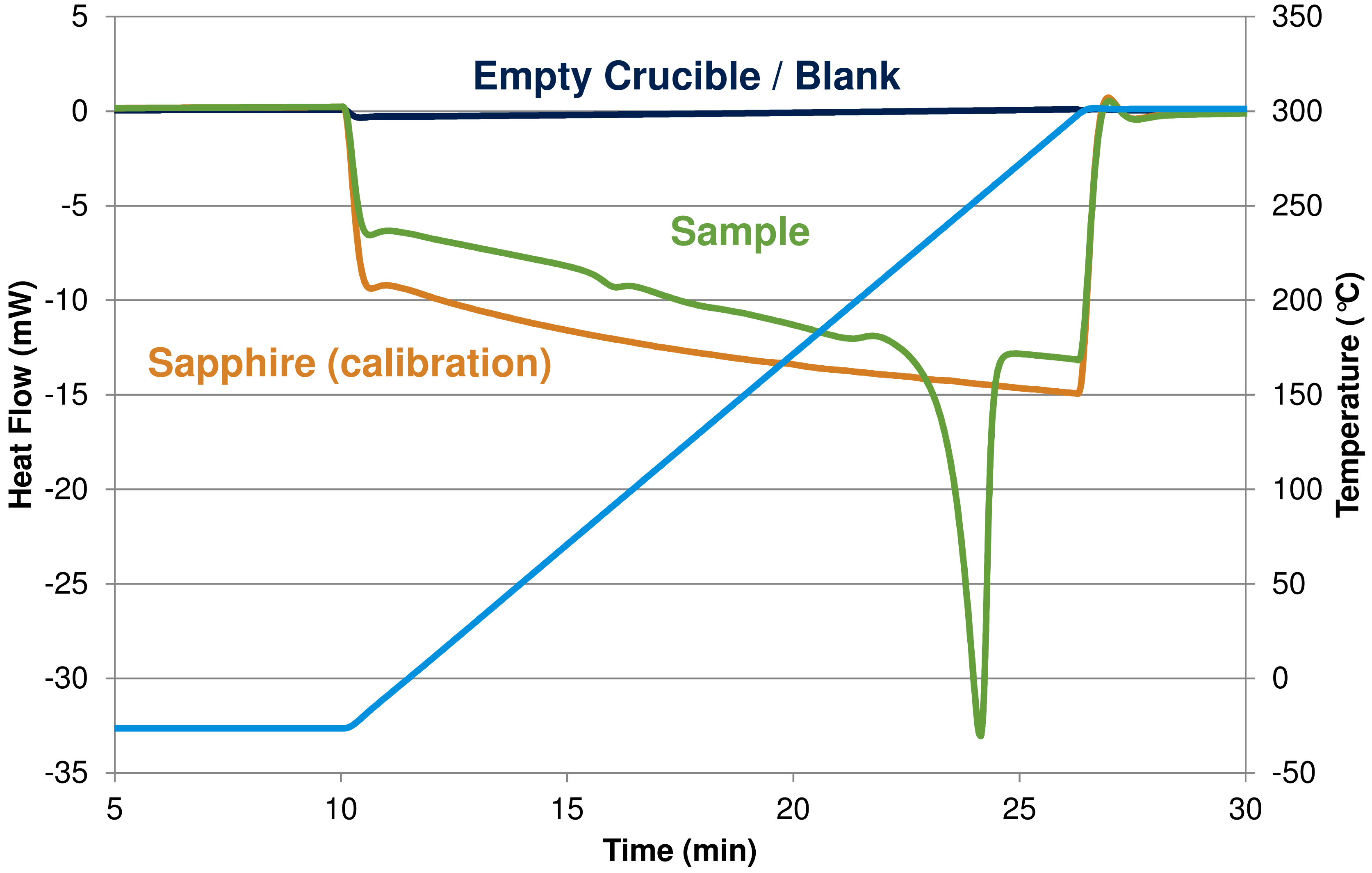
- ASTM Method E1269
  - Requires 3 runs
    - Run empty pans for baseline
      - Compensate for non-absolute measurement of heat flow)
    - Run standard (typically sapphire)
    - Run sample
- Typical Method
  - Starting temperature
  - Isothermal at starting temperature
  - Heat to final temperature
  - Isothermal at final temperature
- Generally considered to be repeatable to within 5%

ASTM Method E1269 (Three-Run Method)

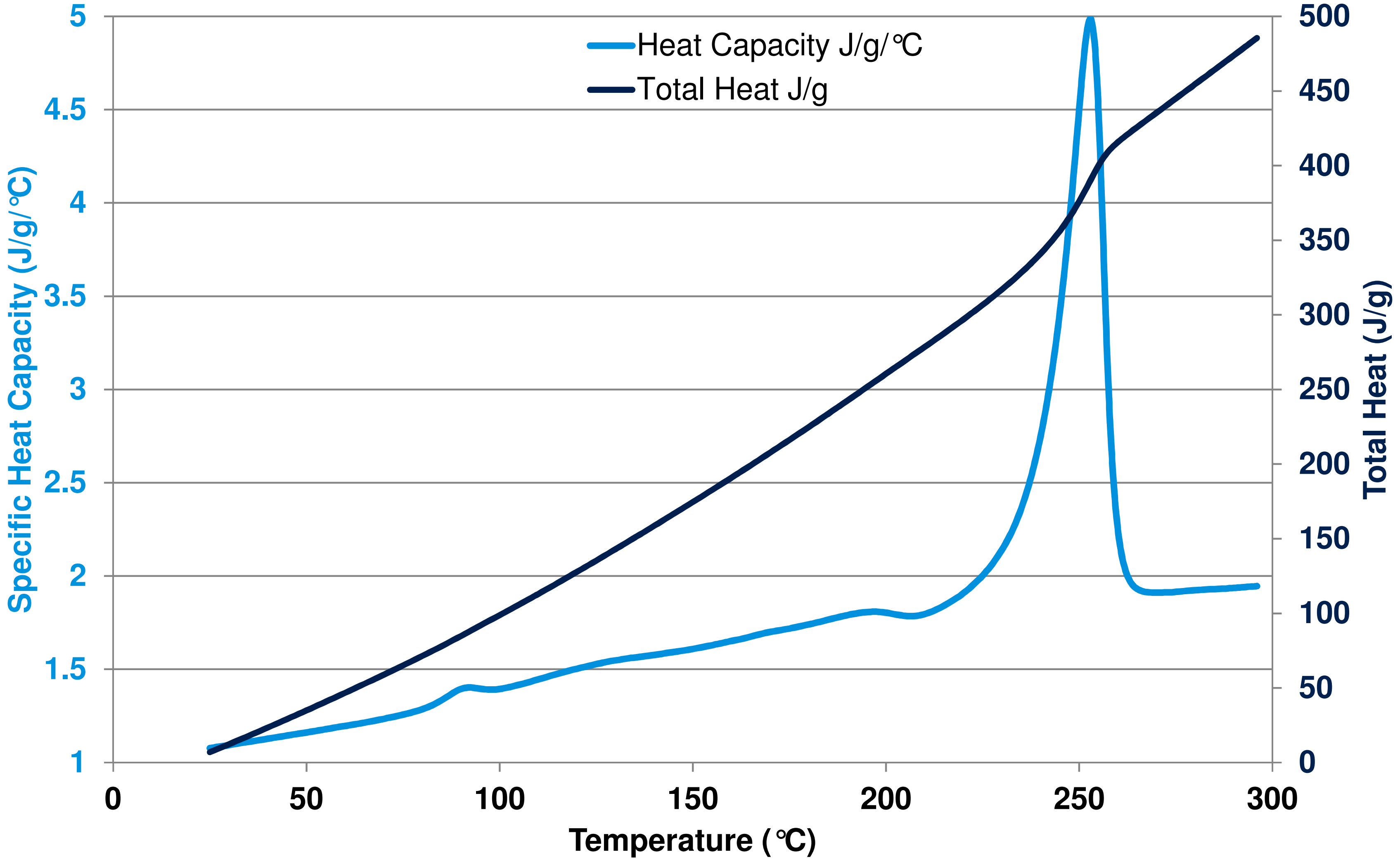
- Three experiments are run over a specific temperature range
  - Allow 10 minute isothermal at start and end
  - Use 10-20°C/min heating rate

1. Empty pan run
   - Match pan/lid weights to ± 0.05 mg
   - Used to establish a reference baseline (absolute heat flow)
2. Sapphire run
   - Used to determine calibration constant
   - Use same weight of pan/lid as above ± 0.05 mg
   - Typical weight is 20 – 25 mg
3. Sample run
   - Typical weight is 10 – 15 mg
   - Use same weight of pan/lid as above ± 0.05 mg

ASTM E1269 "3-Run" Method for Determining Cp



Specific Heat Capacity (ASTM Method)



ASTM E1269 1990 Round-Robin Testing

- Heat capacity was measured over a 40°C span
- Remember earlier I said that this was generally accepted to be repeatable to within 5%
- Repeatability by this Round-Robin Testing = ±6.2%

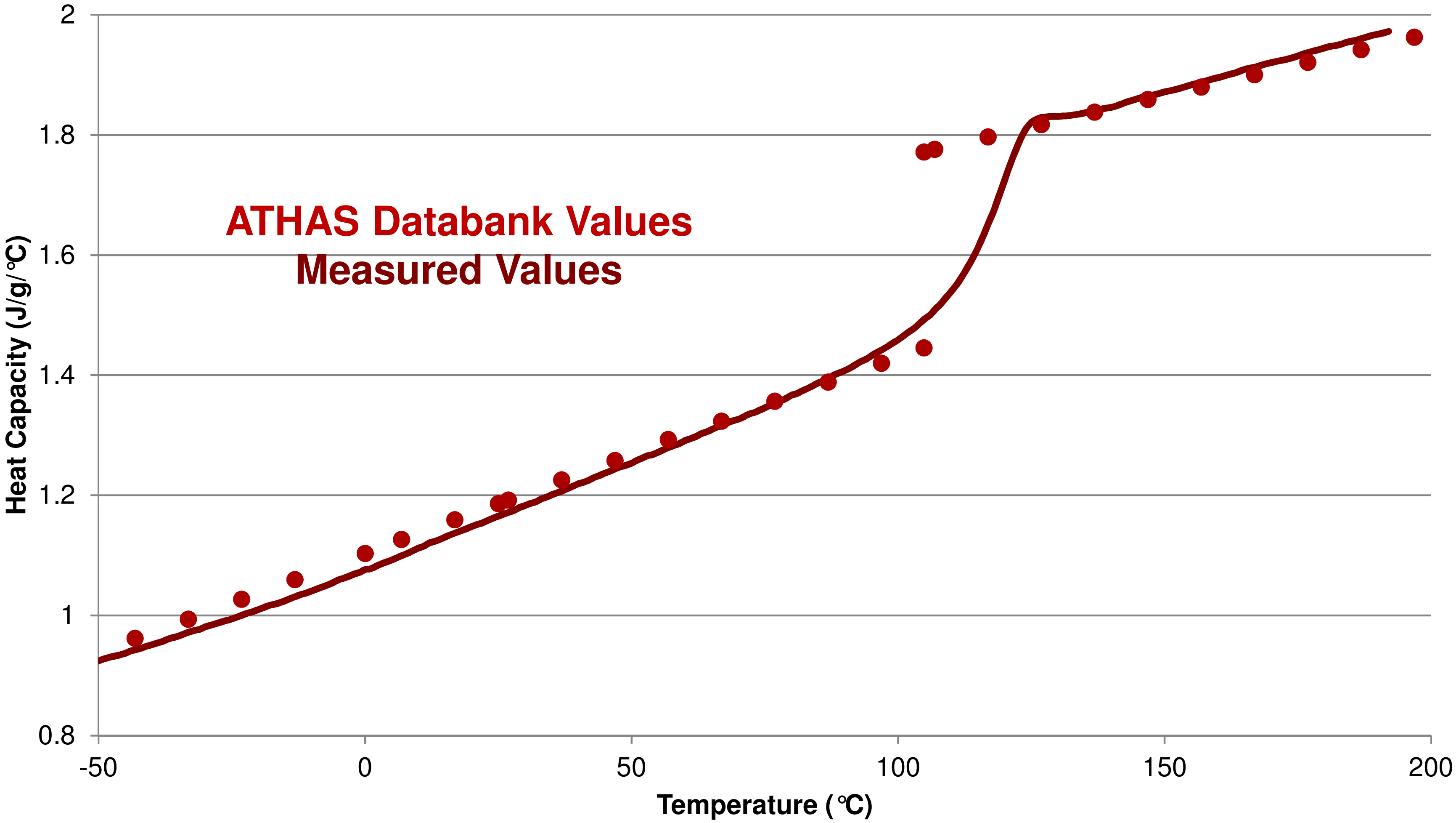
Direct Cp Measurement

- Unlike other DSC's, DSC's with advanced Tzero™ technology measure absolute heat flow:
  - Baseline is flat
  - Baseline is at 0 mW
- Example - DSC 2500
  - Also Discovery DSC, Q2000/1000
- By knowing absolute values of the heat flow and heating rate, heat capacity is calculated in real time and stored in data file
- Cp = [(dH/dt)/(dT/dt)] x K (K= calibration constant)
- Accuracy and precision is generally ± 2% with just single run measurements

Direct Cp Measurement

- Sapphire used as a calibration standard
- Typical Method
    - Heat @10-20℃/min
- Sample Size ~10mg
- For best results – use lowest mass pans possible

Direct Cp of PMMA – DSC 2500



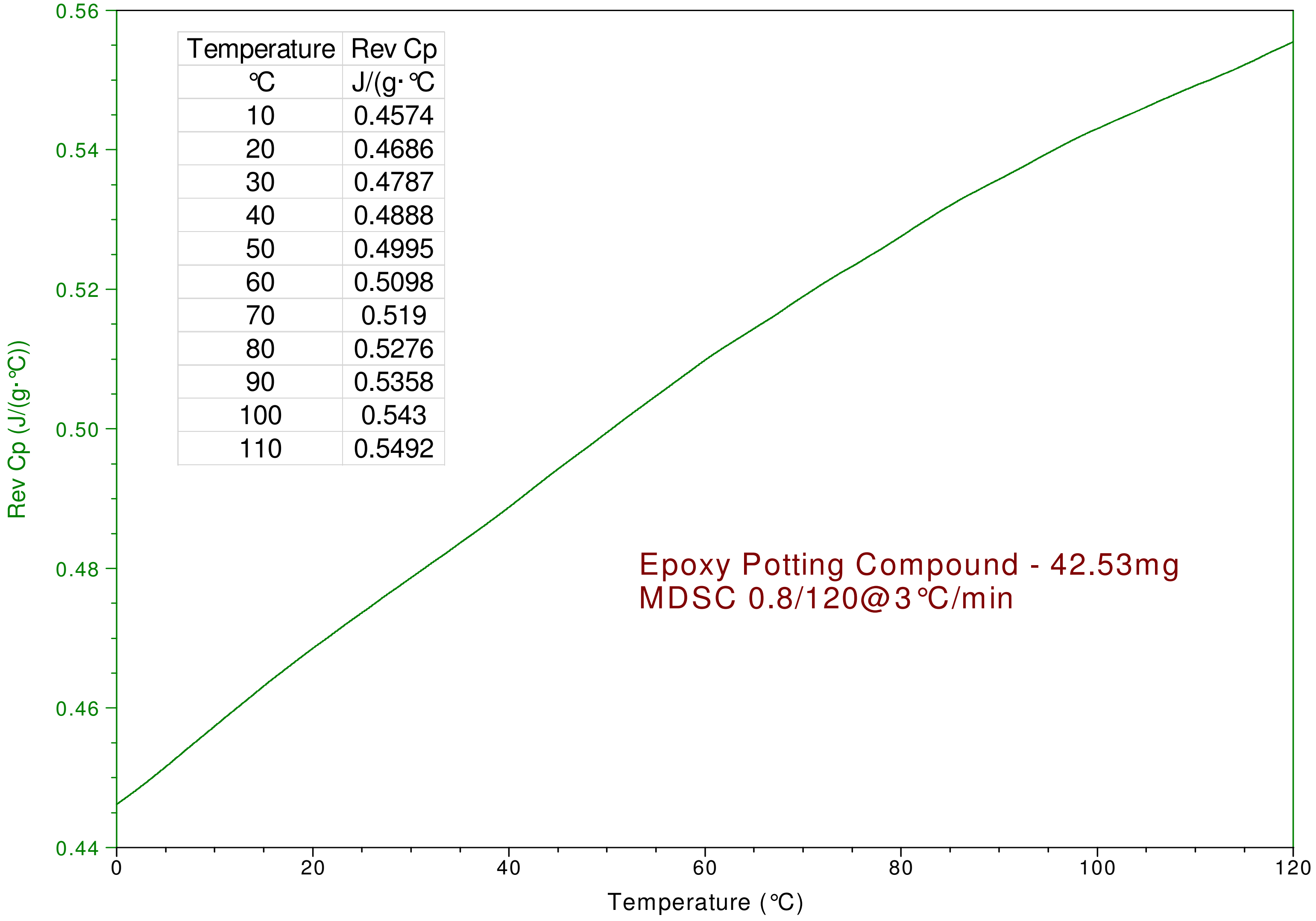
Modulated DSC®

- MDSC®
  - Uses sinusoidal temperature ramp overlaid upon linear ramp
  - Separates Heat Capacity and Kinetic transitions
  - Increases sensitivity to Heat Capacity changes (e.g. Tg)
  - Can determine Cp directly in a single run
  - Best available measurement of Heat Capacity
  - Accurate & repeatable to within 1-2% or better

Cp by MDSC

- Cp can be determined directly in a single run
- Multiple Cp signals
  - Reversing Heat Capacity (Rev Cp) is the quantitative Cp
- Rev Cp does not contain kinetic events
  - Will include non-Cp events like melting
- Rev Cp calibration constant should be calculated at the same period as experiments (uses Sapphire)
- Suggested Conditions:
  - Amplitude ±1 °C
  - Period 120 sec
  - Heating Rate 3 °C/min
  - Sample weight 10-15 mg

Heat Capacity by MDSC



Temperature	Rev Cp
℃	J/(g·℃
10	0.4574
20	0.4686
30	0.4787
40	0.4888
50	0.4995
60	0.5098
70	0.519
80	0.5276
90	0.5358
100	0.543
110	0.5492

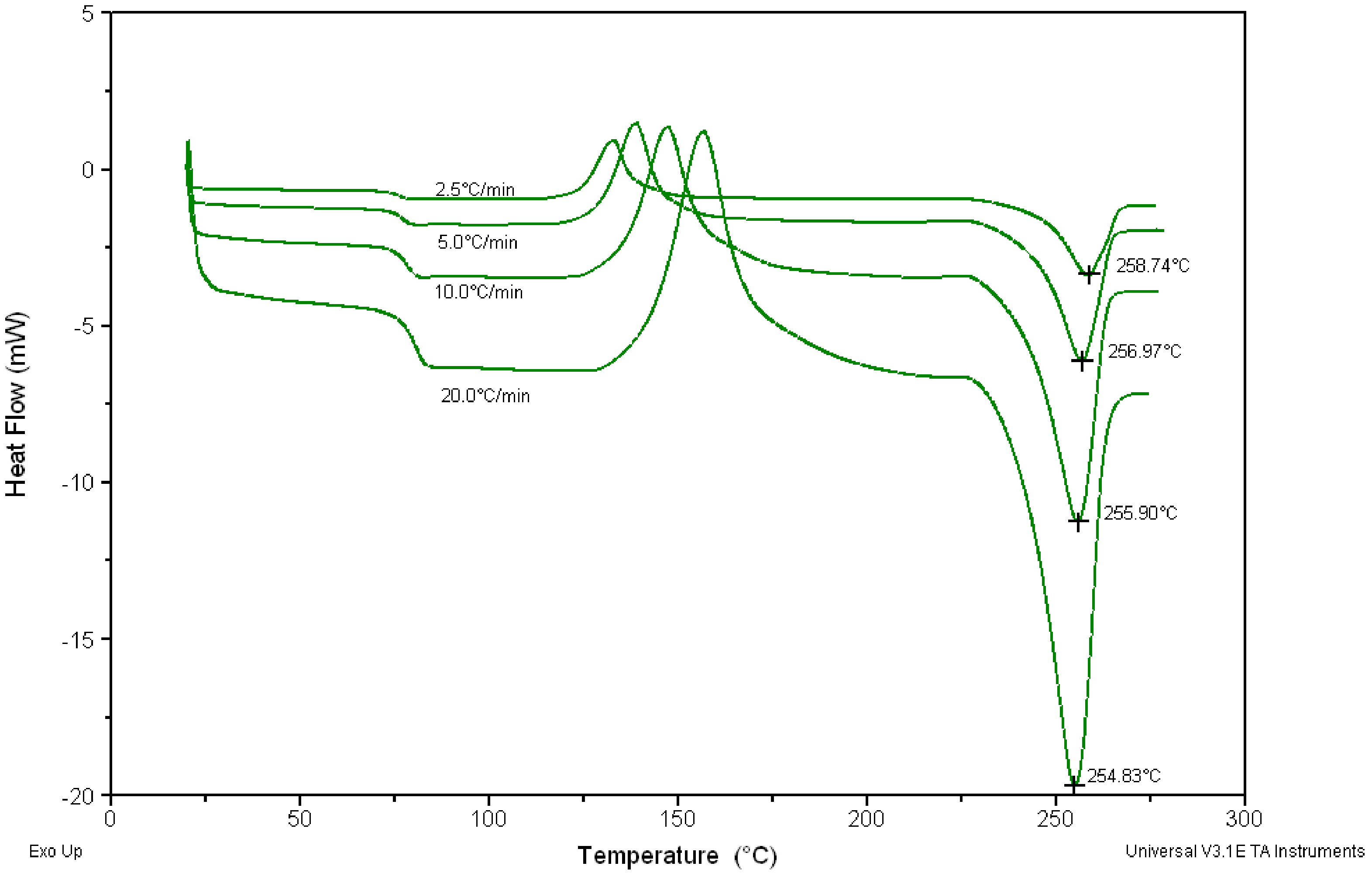
Epoxy Potting Compound - 42.53mg
MDSC 0.8/120@3℃/min

Run Time for Calculating Heat Capacity

- Assume 300℃ temperature range
- ASTM E1269 (Three Run Method) **(Slowest & least accurate)**
  - Typically ran @ 10℃/min so 30 min/run + 20 min isothermal
  - 150 min run time plus sample prep time
- Direct Cp – Single Run Method **(Fastest)**
  - Typically ran @ 20℃/min so 15 min/run, plus sample prep
  - If ran @ 10℃/min then 30 min/run, plus sample prep
- MDSC® - Single Run Method **(Most Accurate)**
  - Typically ran @ 3℃/min so 100 min/run, plus sample prep

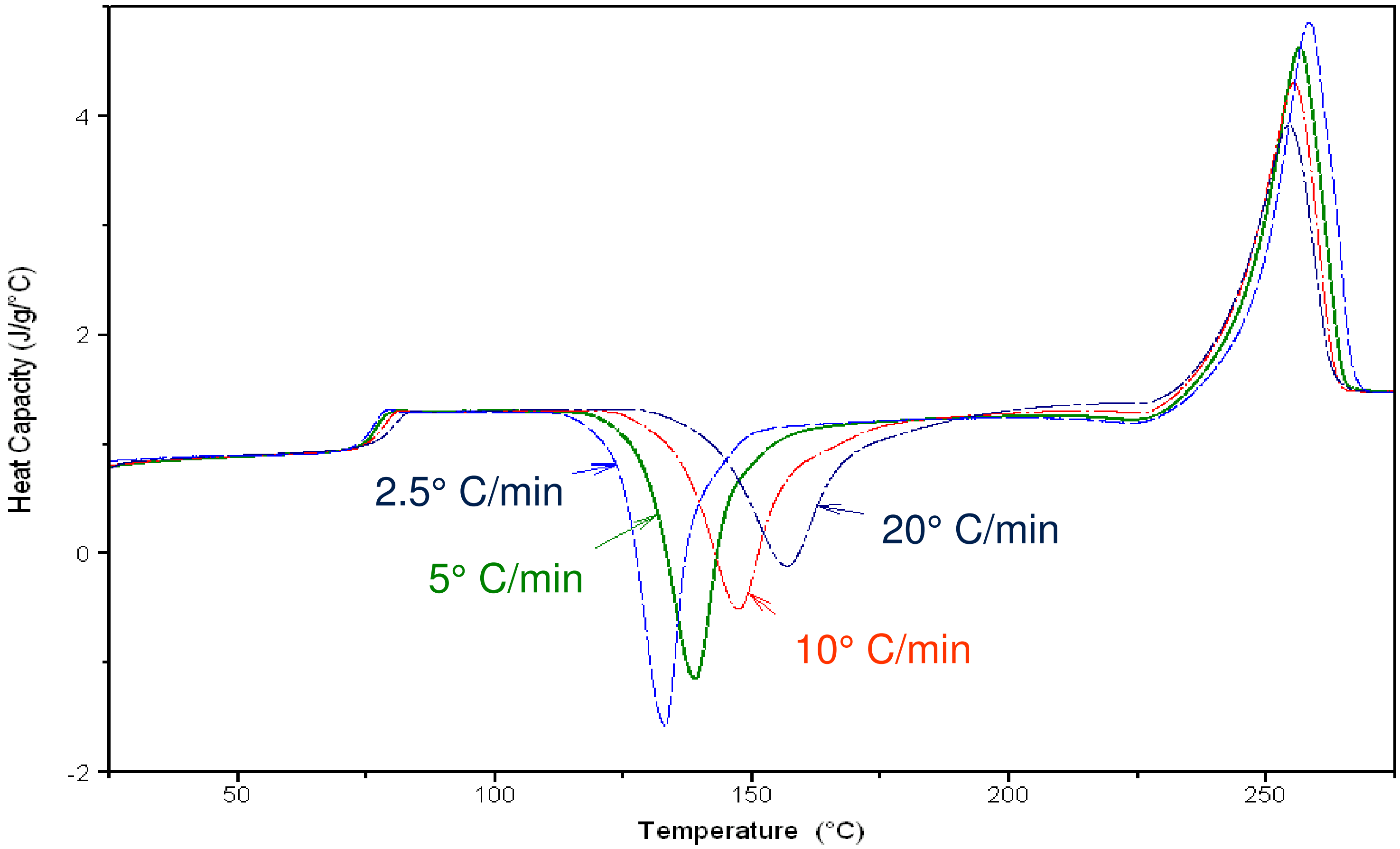
Traditional DSC

Heat Flow Signals Plotted at the Same Sensitivity for Four PET Experiments Performed at Different Heating Rates

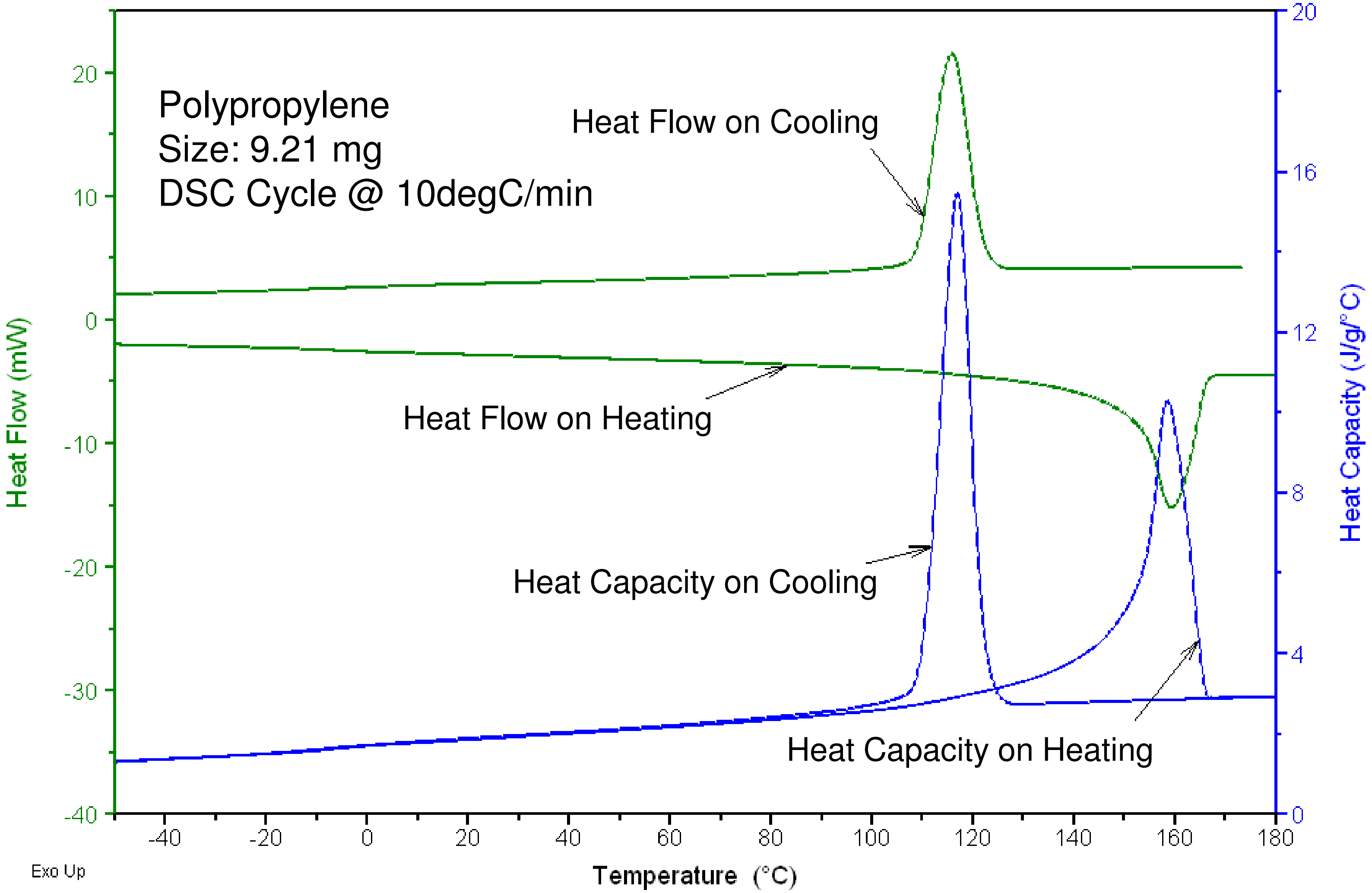


Benefit of Heat Capacity Signal

Utility of the Heat Capacity Signal for Illustrating the Effect Of Heating Rate on Kinetic Processes in Quench Cooled PET



Comparison of Heat Flow & Cp Signals



Polypropylene
Size: 9.21 mg
DSC Cycle @ 10degC/min

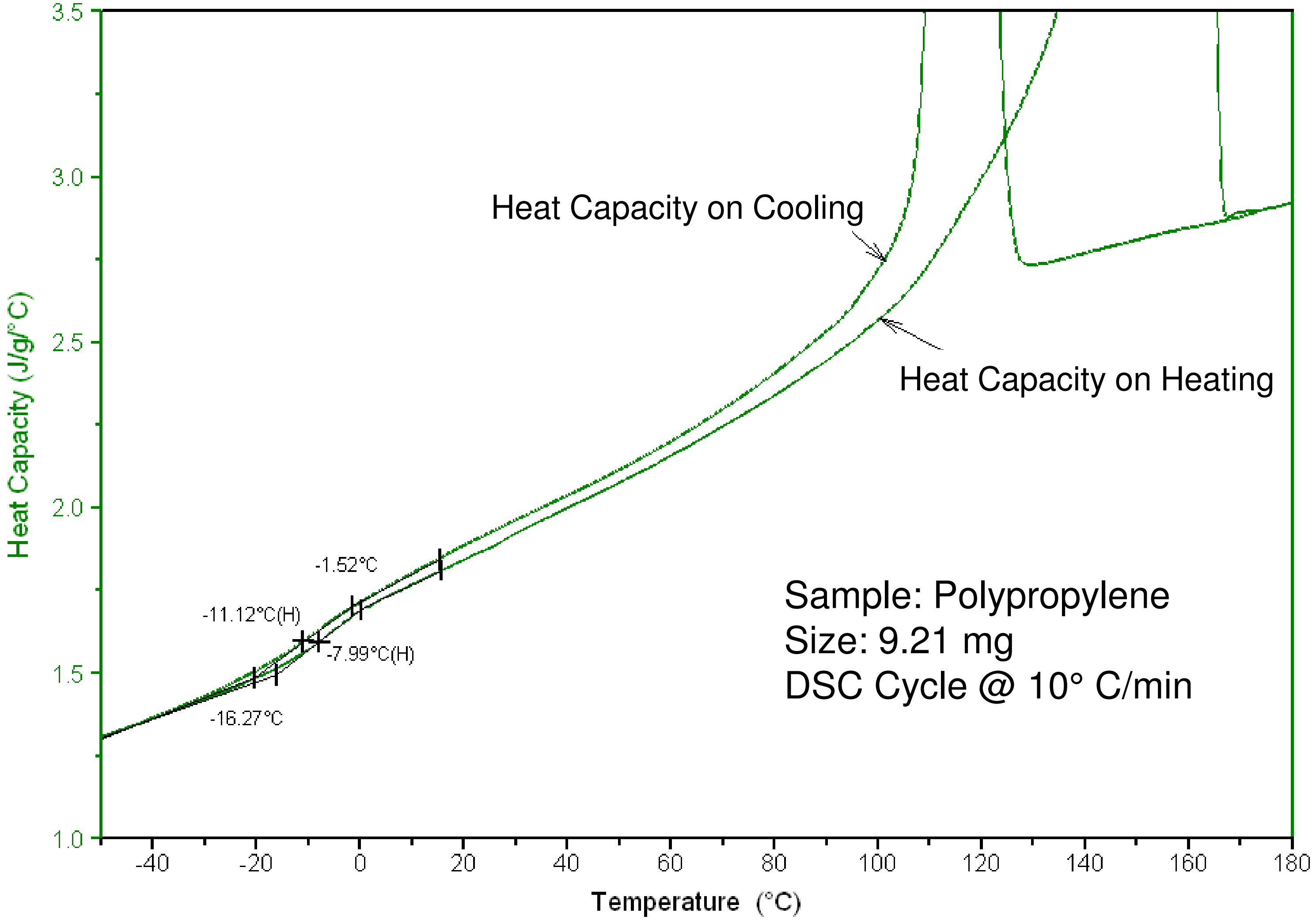
Heat Flow on Cooling

Heat Flow on Heating

Heat Capacity on Cooling

Heat Capacity on Heating

Weak Tg Visible in Tzero™ DSC Cp Signal



Sample: Polypropylene
Size: 9.21 mg
DSC Cycle @ 10° C/min

Applications: Amorphous Structure

(Glass Transition)

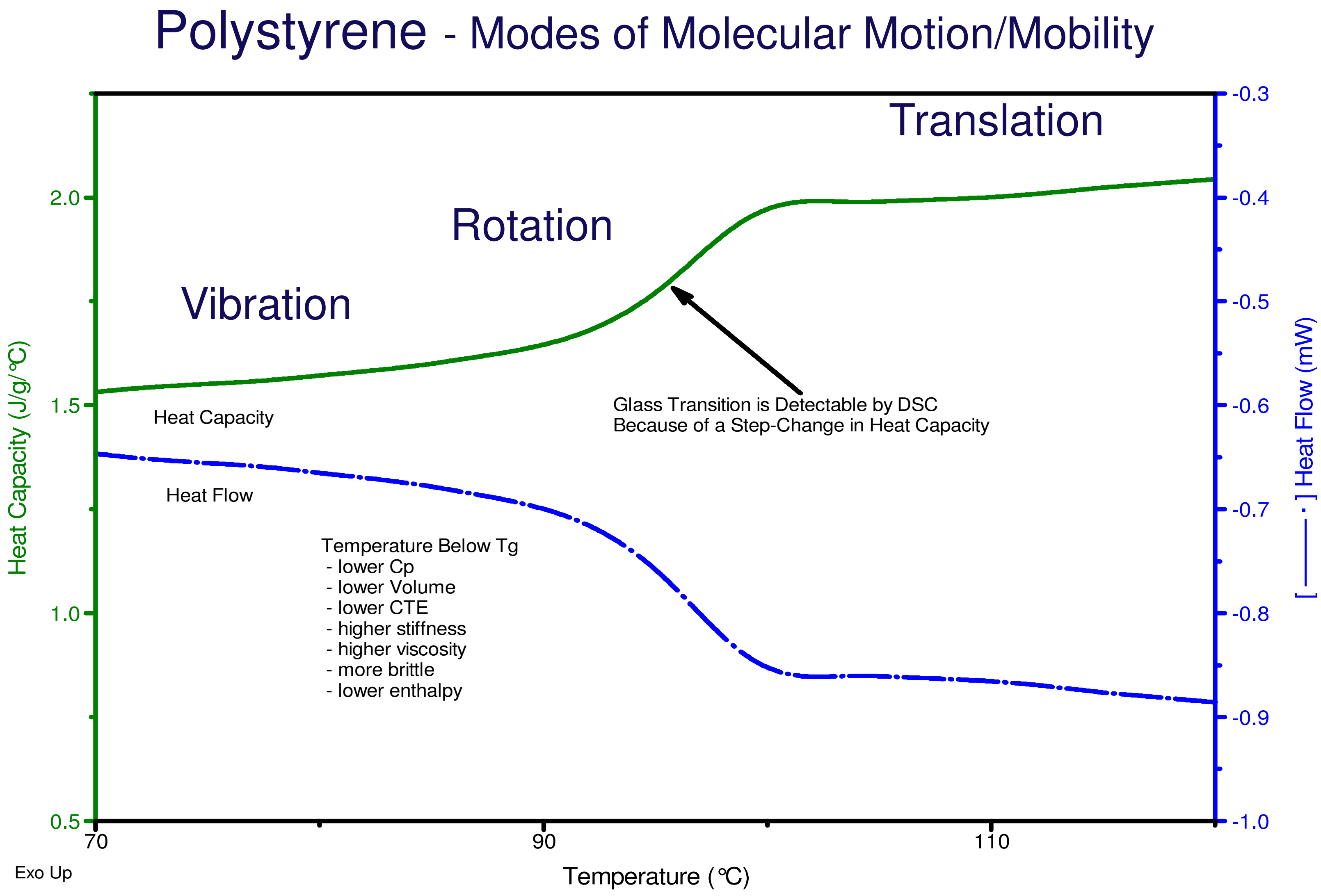
Amorphous Materials

- Amorphous Structure –
    - Randomly oriented molecules
    - No long-range order
    - Liquids, glassy or rubbery solids
    - Most polymers are either amorphous or semi-crystalline

Characterization of Amorphous Structure

- Glass Transition (Tg)
  - Due to amorphous (non-crystalline) structure
  - Due to macro-molecular motion (translational); i.e., the entire molecule is free to move relative to adjacent molecules.
  - Extremely important transition because the significant change in molecular mobility at Tg causes significant changes in physical and reactive properties.

Changes at the Tg



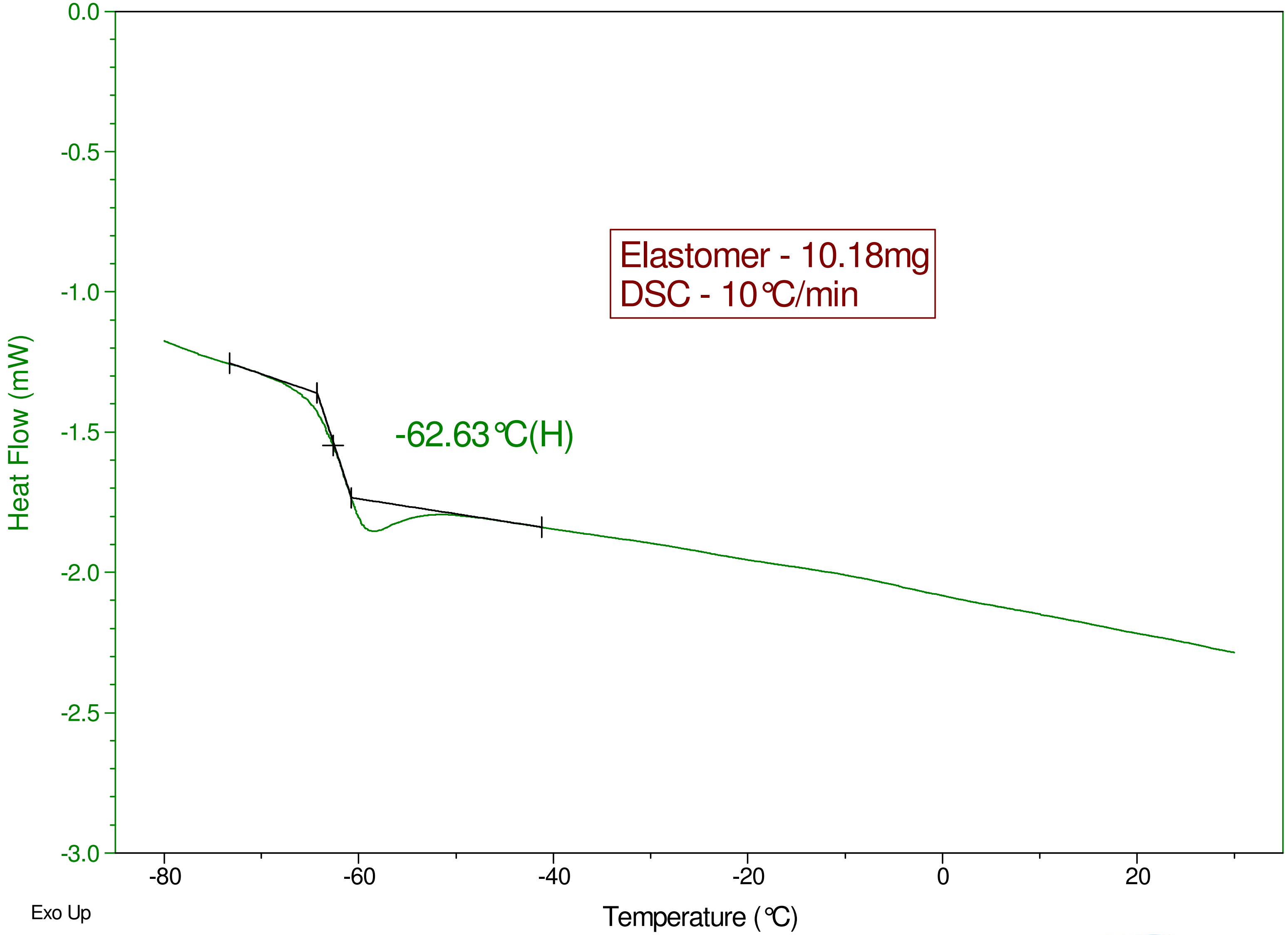
Glass Transition is Detectable by DSC
Because of a Step-Change in Heat Capacity

Temperature Below Tg
- lower Cp
- lower Volume
- lower CTE
- higher stiffness
- higher viscosity
- more brittle
- lower enthalpy

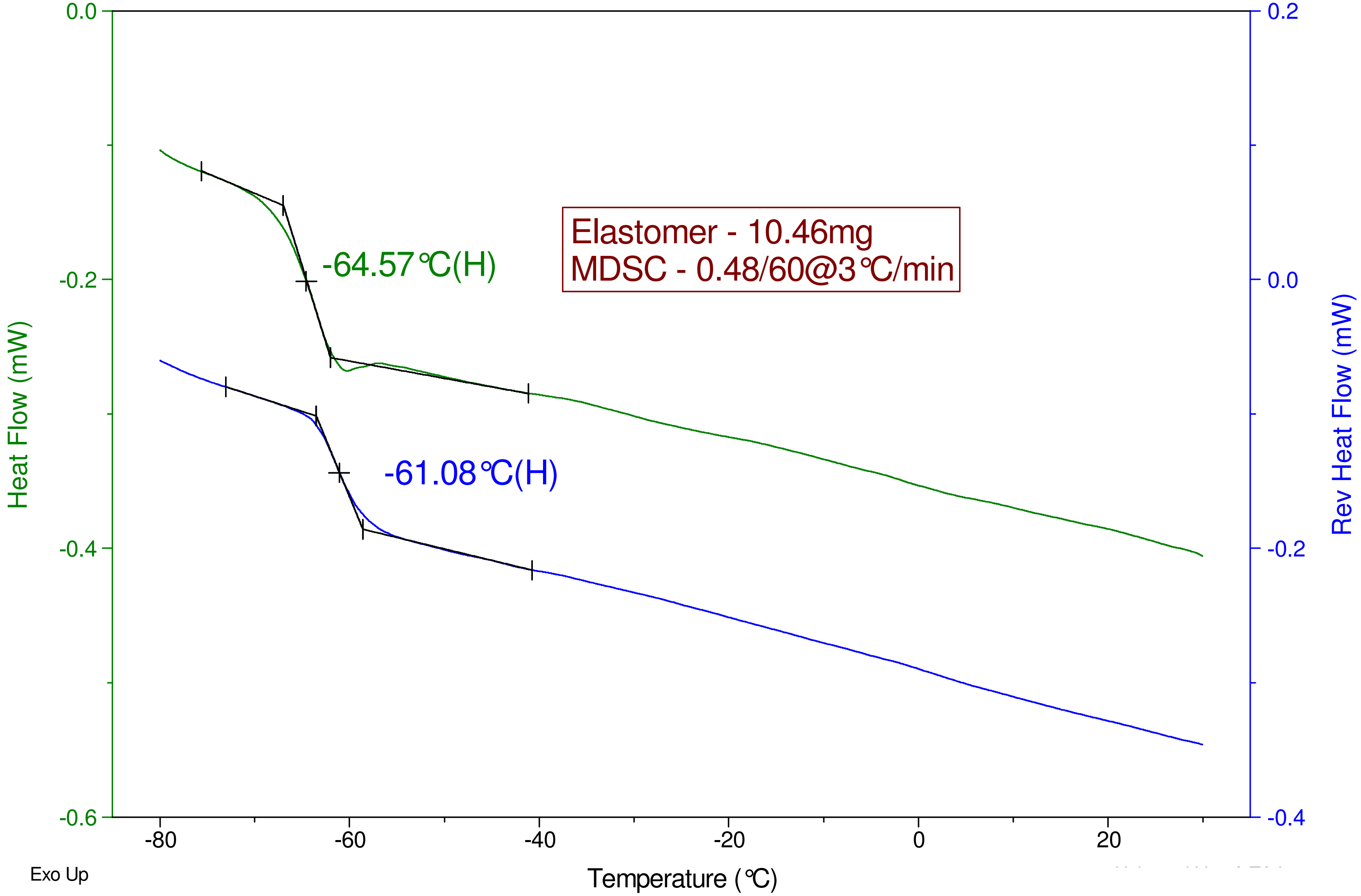
Glass Transition Analysis

- Reporting the Glass Transition (Tg) Temperature
  - Tg is always a temperature range and never a single temperature
  - When reporting a single temperature, it is necessary to state;
    - What point in the step change (onset, midpoint, end, etc.) is being measured
    - The experimental conditions used to measure Tg; such as technique (DSC, DMA, TMA, etc.), heating rate, sample size or weight, modulation conditions, etc.

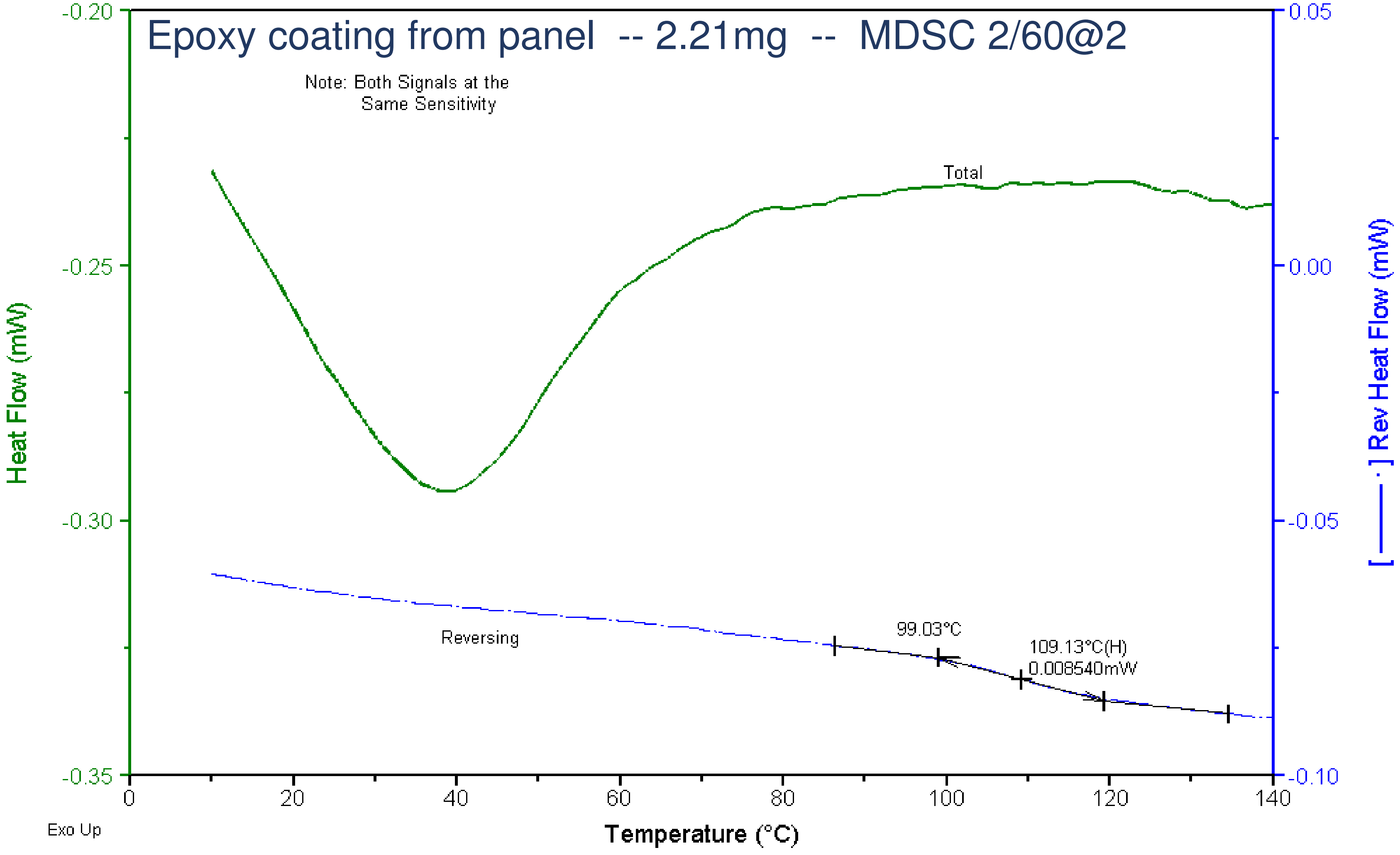
Elastomer Tg by DSC



Elastomer Tg by MDSC



MDSC® of Weak Tg



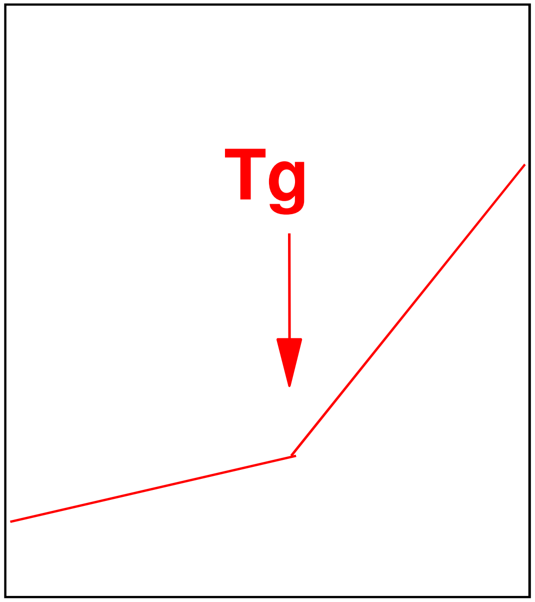
The Glass Transition (Tg)

- The glass transition is a step change in molecular mobility (in the amorphous phase of a sample) that results in the change of many physical properties
- The material is rigid below the glass transition temperature and rubbery above it. *Amorphous materials flow*, <u>they do not melt</u>
- The change in heat capacity at Tg is a measure of the amount of amorphous phase in the sample
- Enthalpic recovery at Tg is a measure of order in the amorphous phase. Annealing or storage at temperatures just below Tg permit development of order as the sample moves towards equilibrium

Effect of Tg on Physical Properties

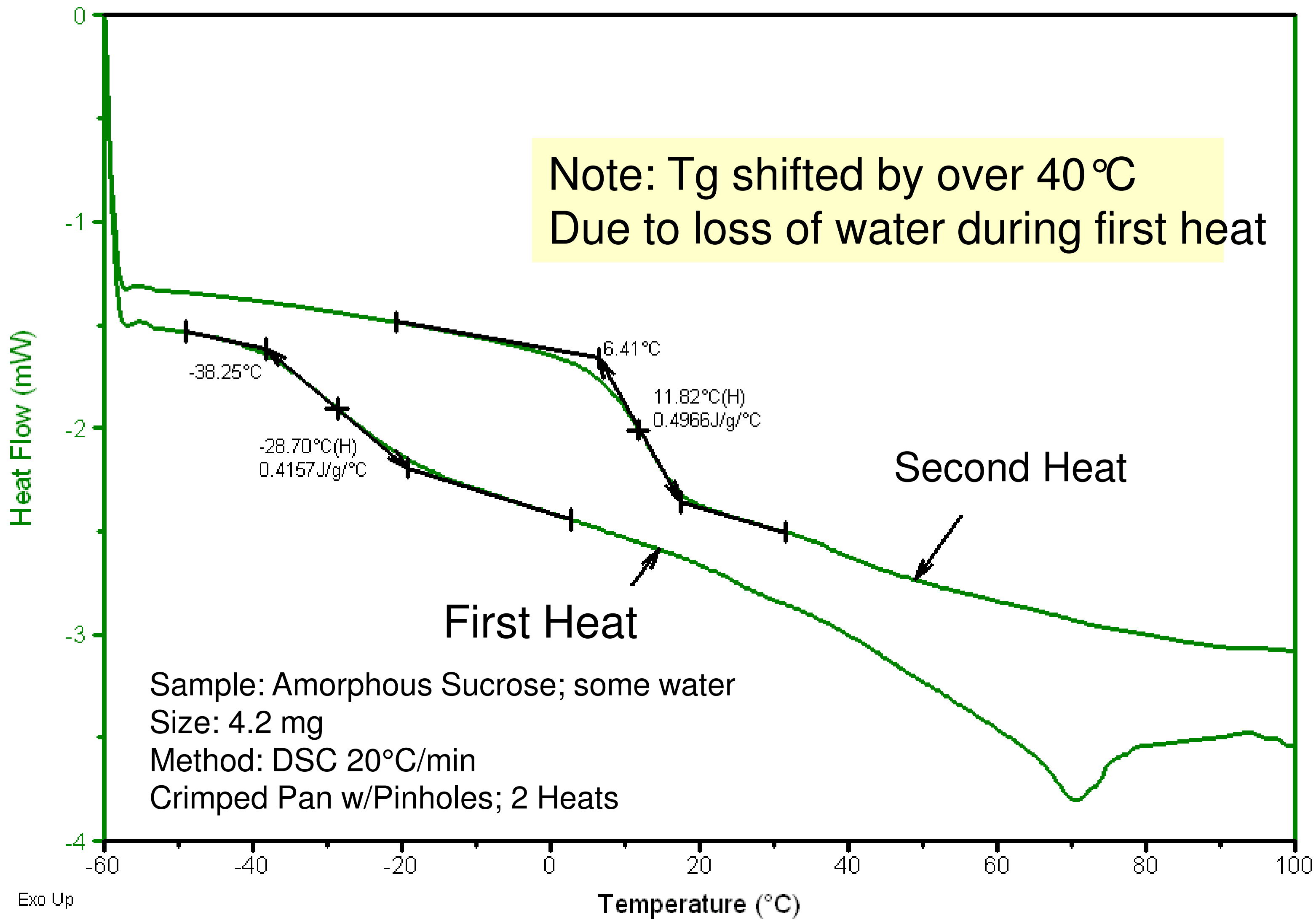
Physical property	Response on heating through Tg
Specific Volume	Increases
Modulus	Decreases
Coefficient of thermal expansion	Increases
Specific Heat	Increases
Enthalpy	Increases
Entropy	Increases

V,
1/E,
CTE,
Cp,
H, &
S



Temperature

Effect of Moisture on Tg by DSC

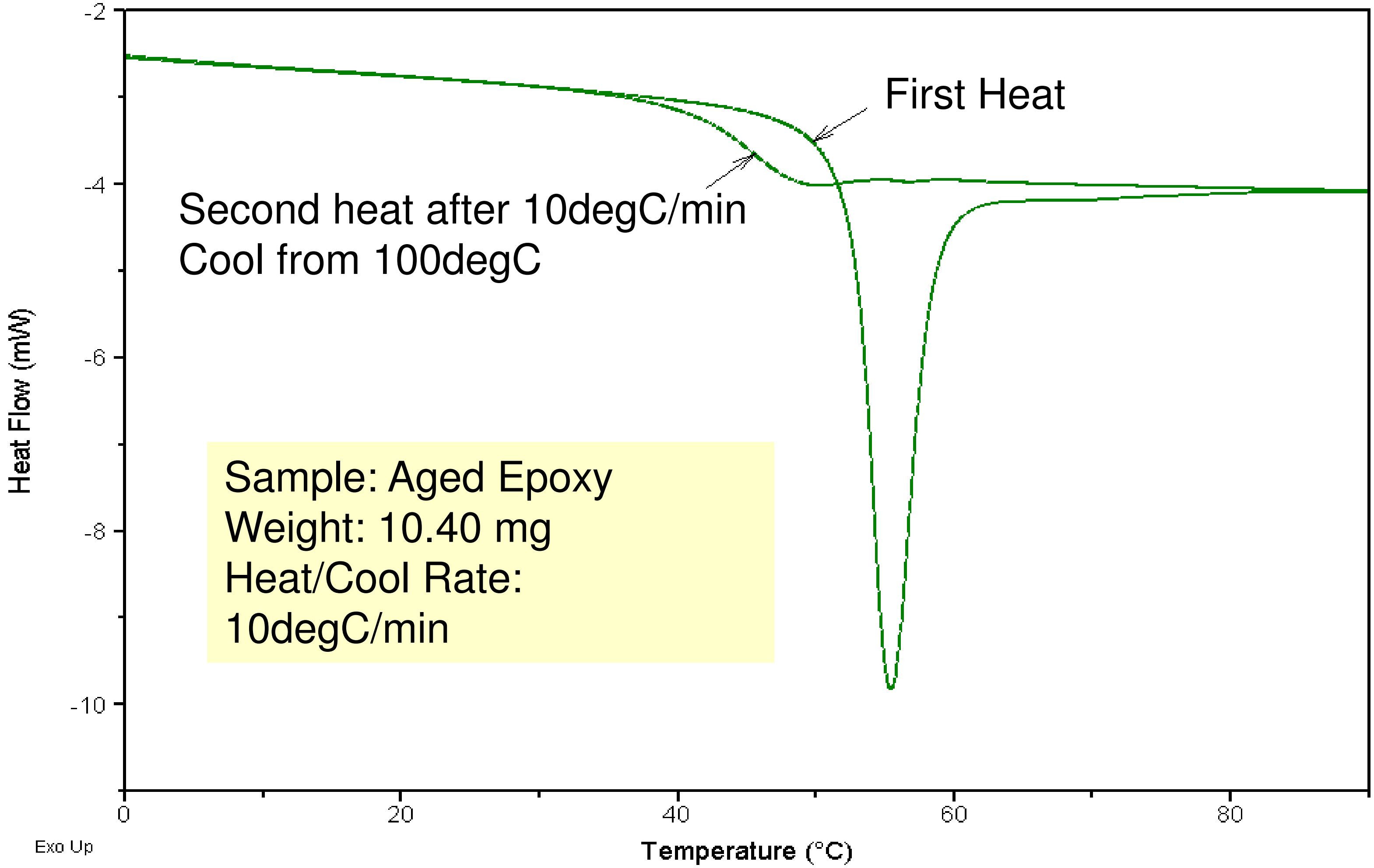


Note: Tg shifted by over 40℃
Due to loss of water during first heat

Sample: Amorphous Sucrose; some water
Size: 4.2 mg
Method: DSC 20°C/min
Crimped Pan w/Pinholes; 2 Heats

Tg of Aged Epoxy Sample by DSC

Aged Epoxy shows enthalpic recovery at glass transition during first heat



First Heat

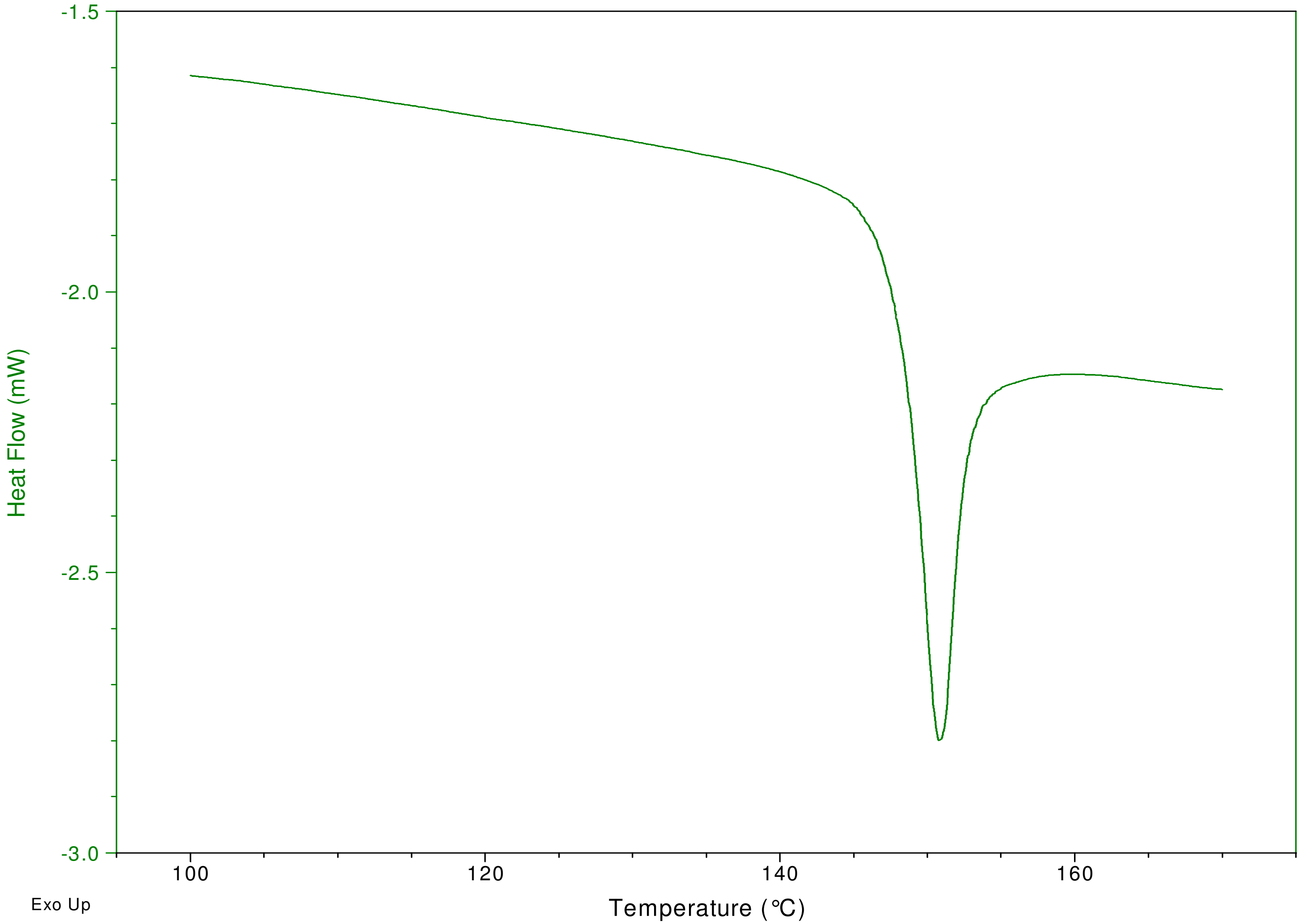
Second heat after 10degC/min
Cool from 100degC

Sample: Aged Epoxy
Weight: 10.40 mg
Heat/Cool Rate:
10degC/min

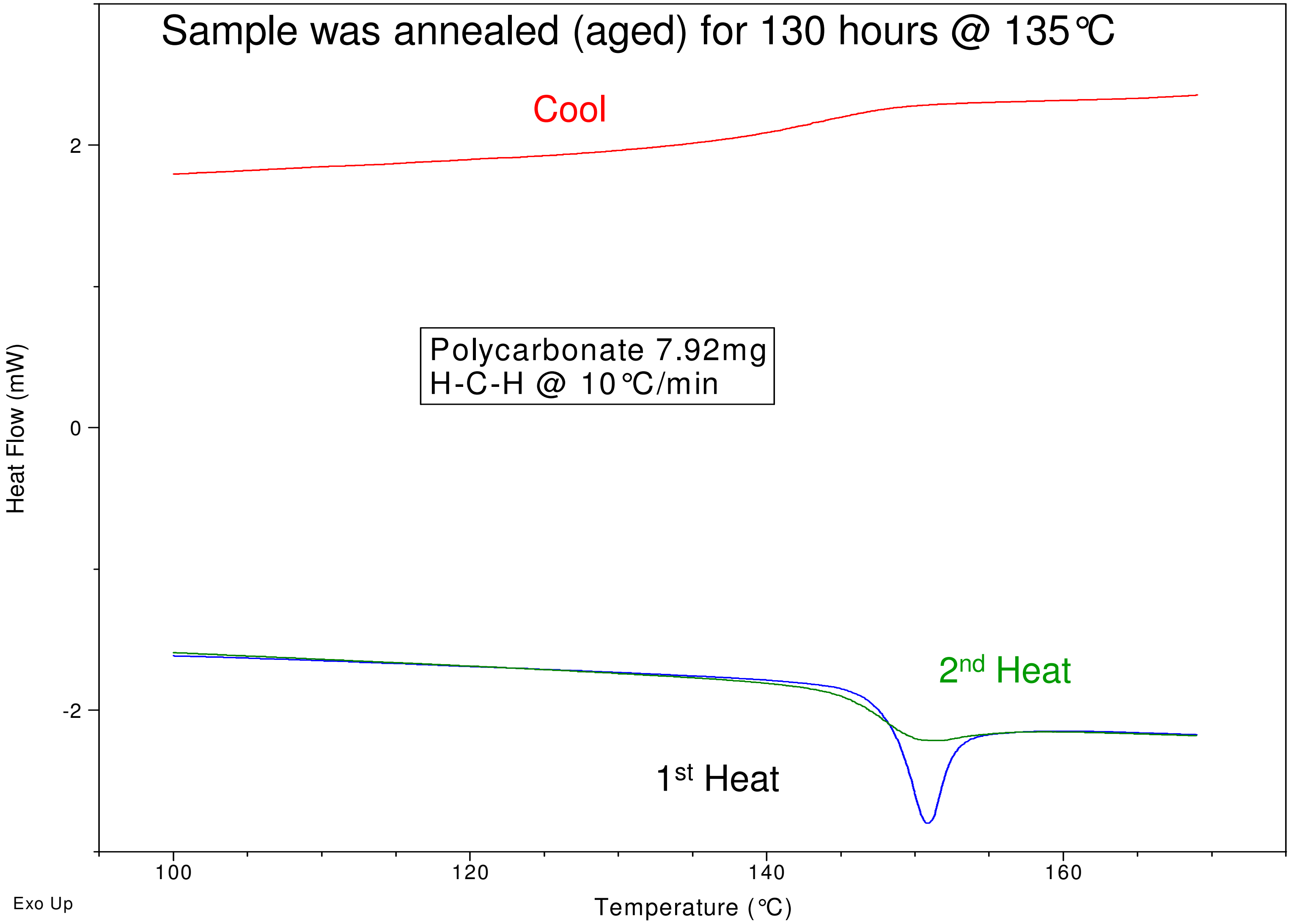
Is it a Tg?

- If not sure if a transition is a Tg
  - Run Heat-Cool-Heat (H-C-H)
    - If transition is a Tg then it should be present on cooling curve and 2nd heat
  - Run MDSC
    - A Tg will always show up in the Reversing Curve of a MDSC experiment
  - Run TMA or DMA

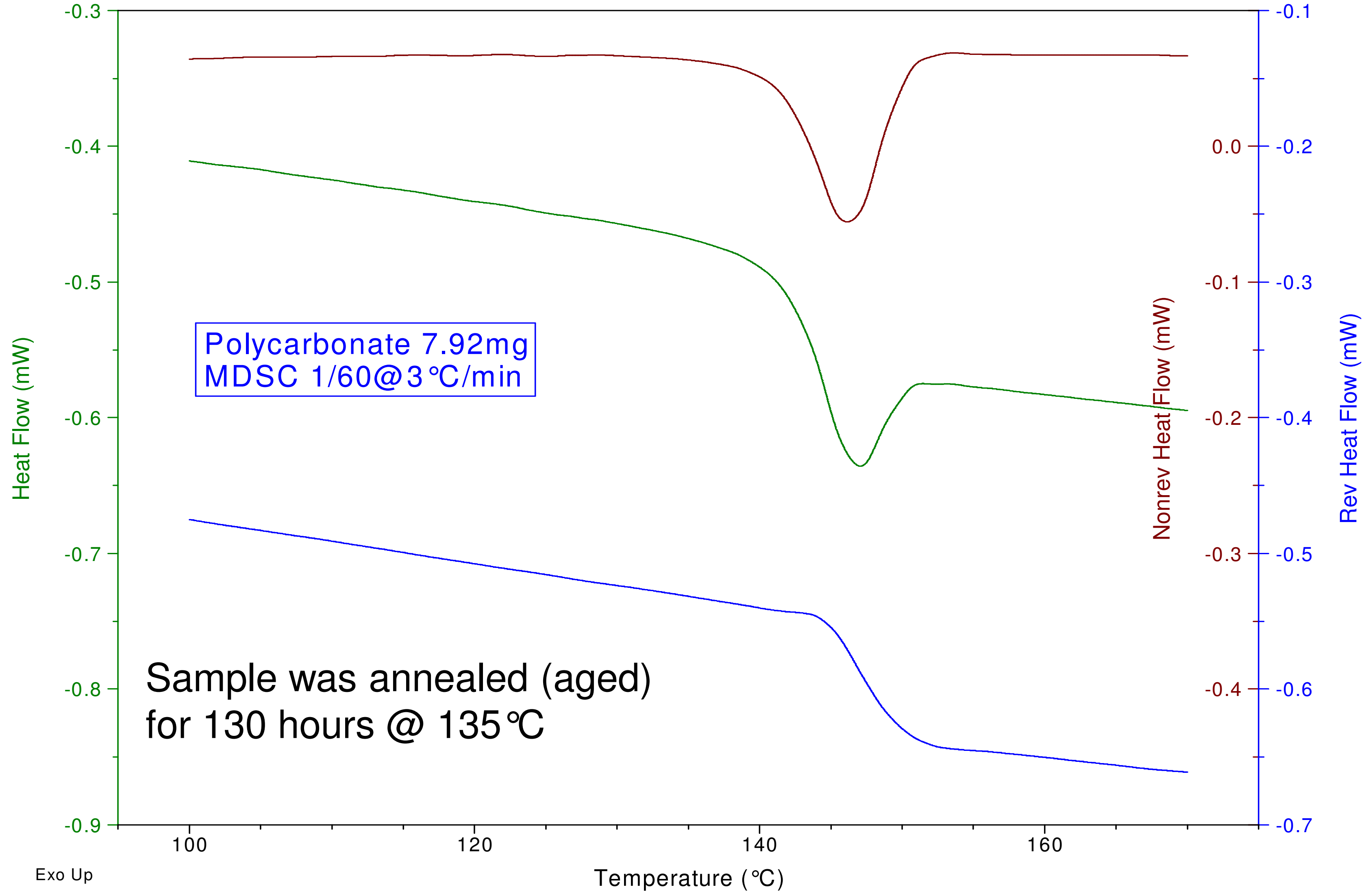
Is this a Tg or a Melt?



Now – Is this a Tg or a Melt?



MDSC of Aged Polycarbonate



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Applications:
Crystalline Structure
(Melting and Crystallization)

Semi-Crystalline Polymers

- Crystalline Structure –
  - Molecules arranged in well defined structures
  - Consists of repeating units
  - Polymers can have crystalline phases
    - Length of molecules prevents complete crystallization
- Semi-crystalline Polymers –
  - Both amorphous & crystalline solid phases
  - Examples are most common thermoplastics
    - Polyethylene, Polypropylene, etc

Melting

- Melting – The process of converting solid crystalline structure to liquid amorphous structure
  - Melting shows up as an endothermic peak in a DSC scan
  - The energy required to melt the crystalline phase is proportional to the amount of crystalline phase
- In most cases sensitivity isn't an issue with melting transitions
- Heating rate doesn't effect the onset of melting (much), but will effect resolution

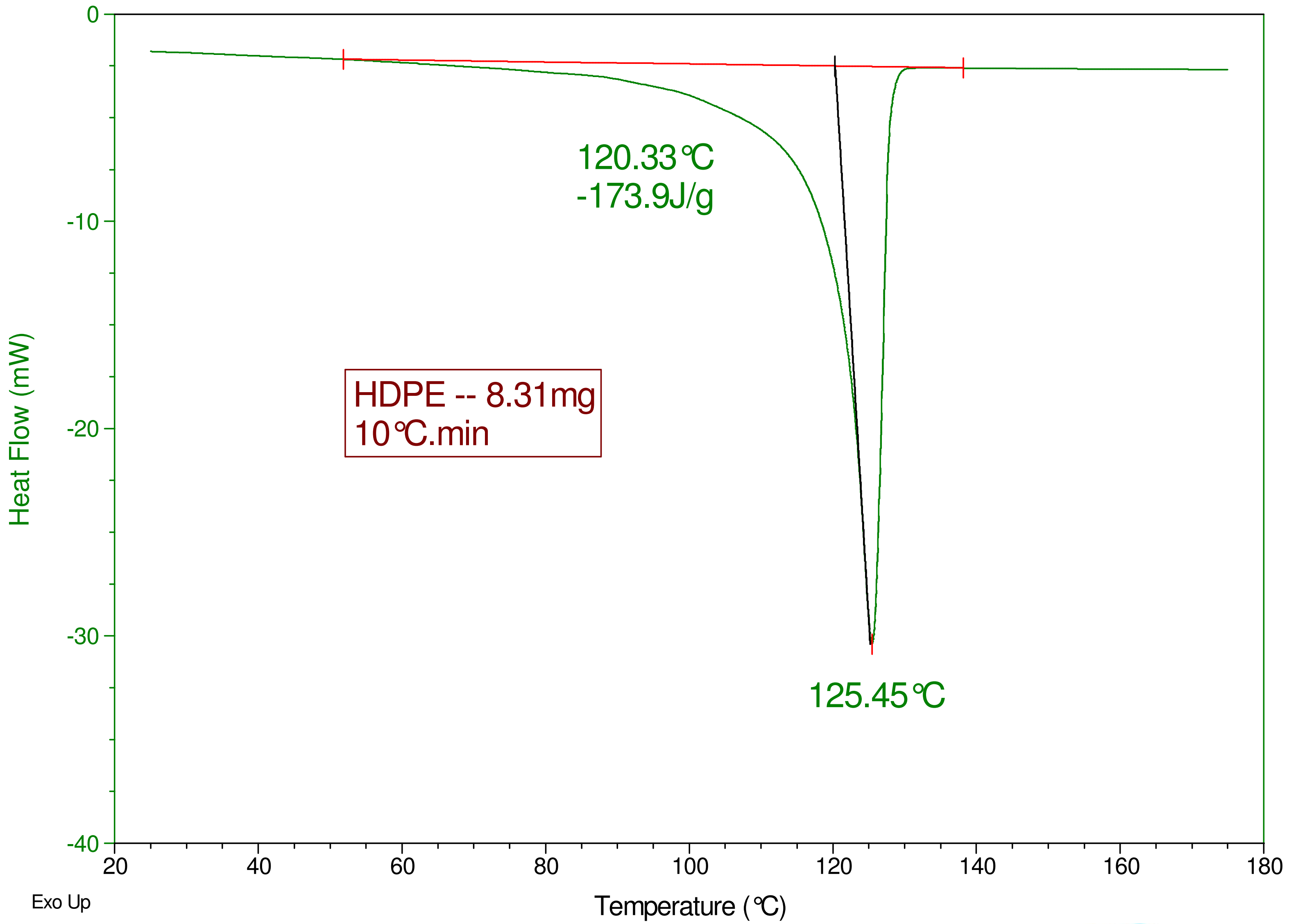
Definitions

- Thermodynamic Melting Temperature – The temperature where a perfect crystal would melt

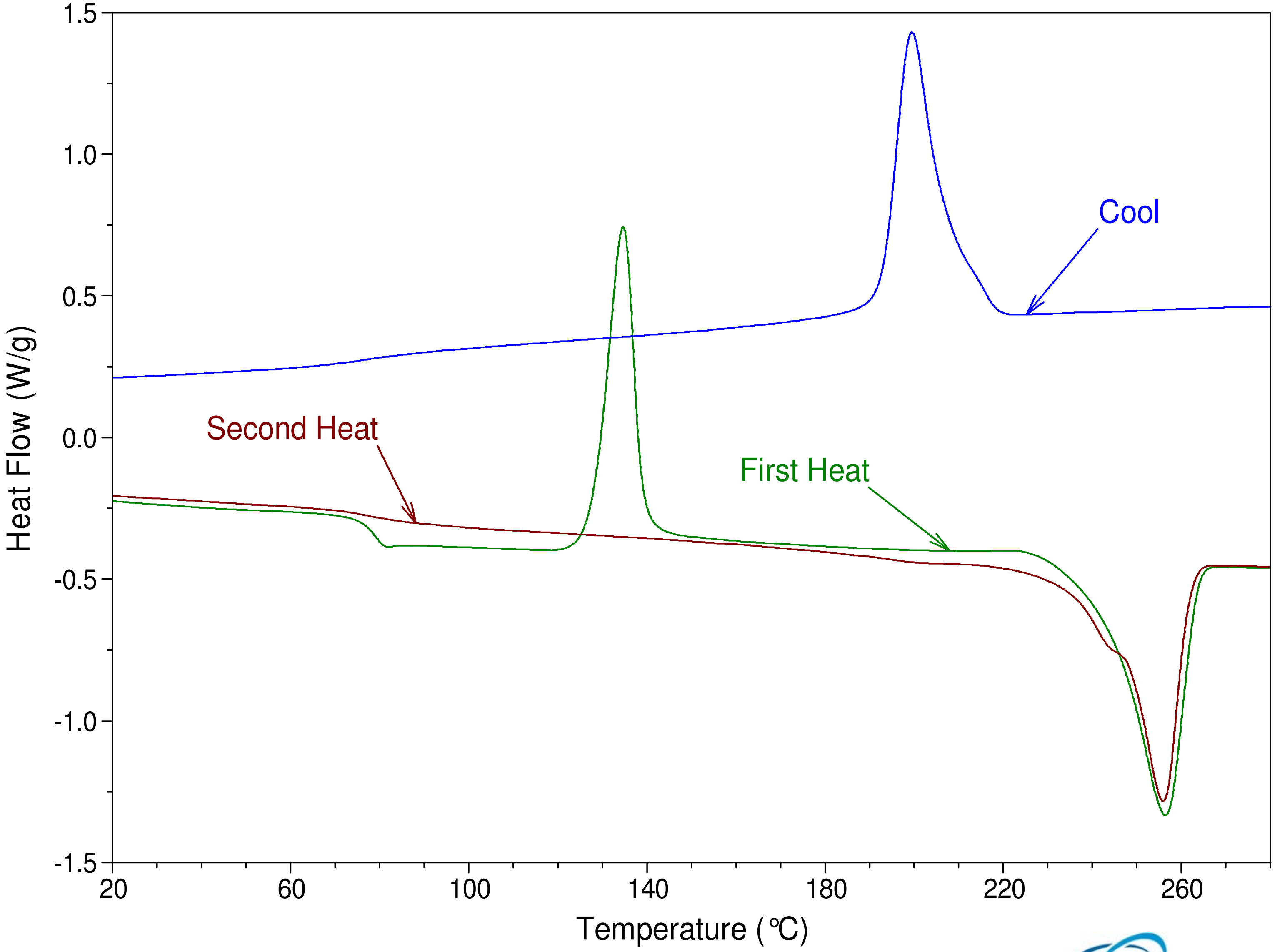
- Metastable Crystals – Crystals that melt at lower temperature due to imperfections

- Crystal Perfection – The process of metastable crystals melting at a temperature below their thermodynamic melting point and then (re) crystallizing into larger, more perfect crystals that will melt again at a higher temperature

Measurement of a Melt by DSC



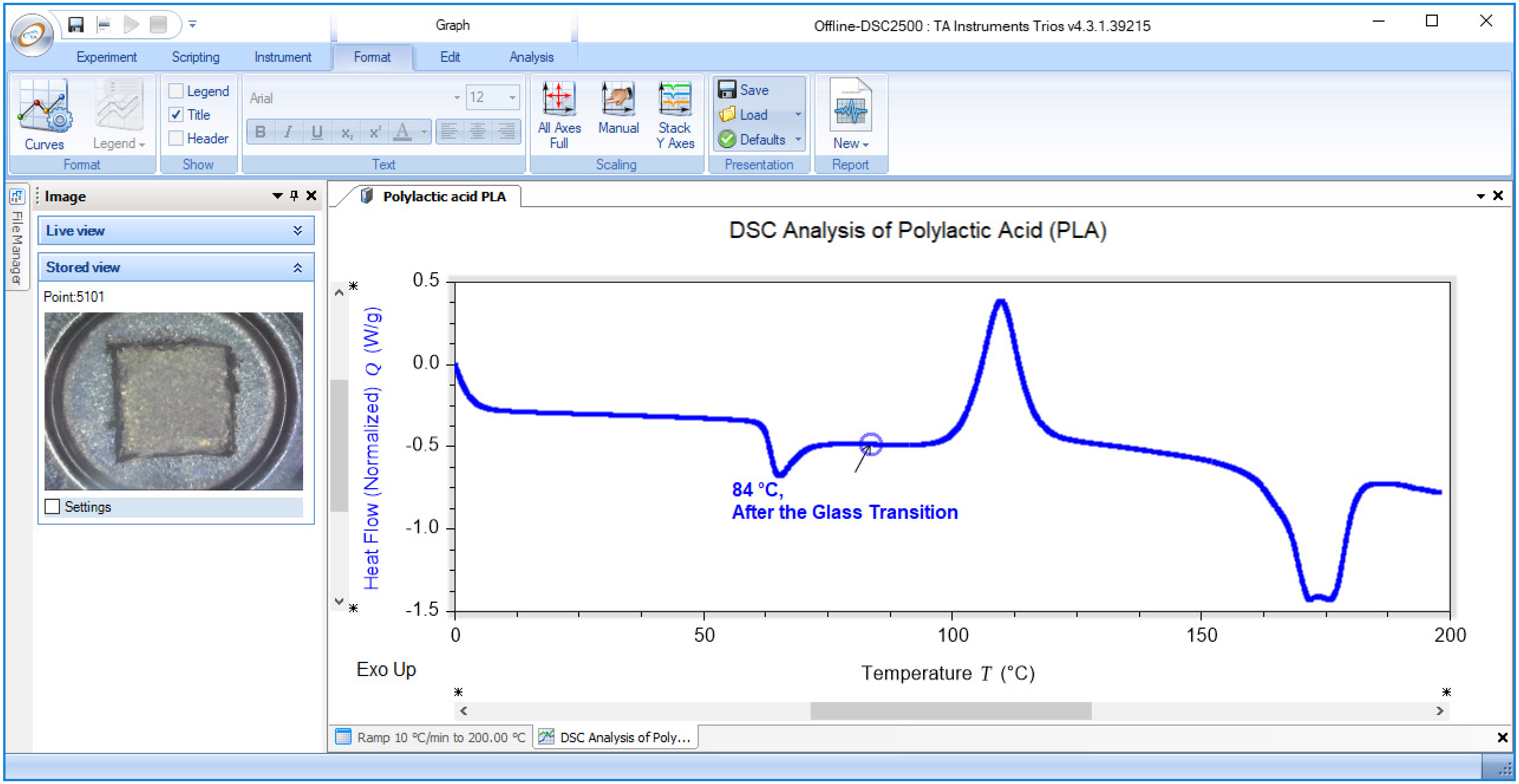
Heat-Cool-Heat of PET



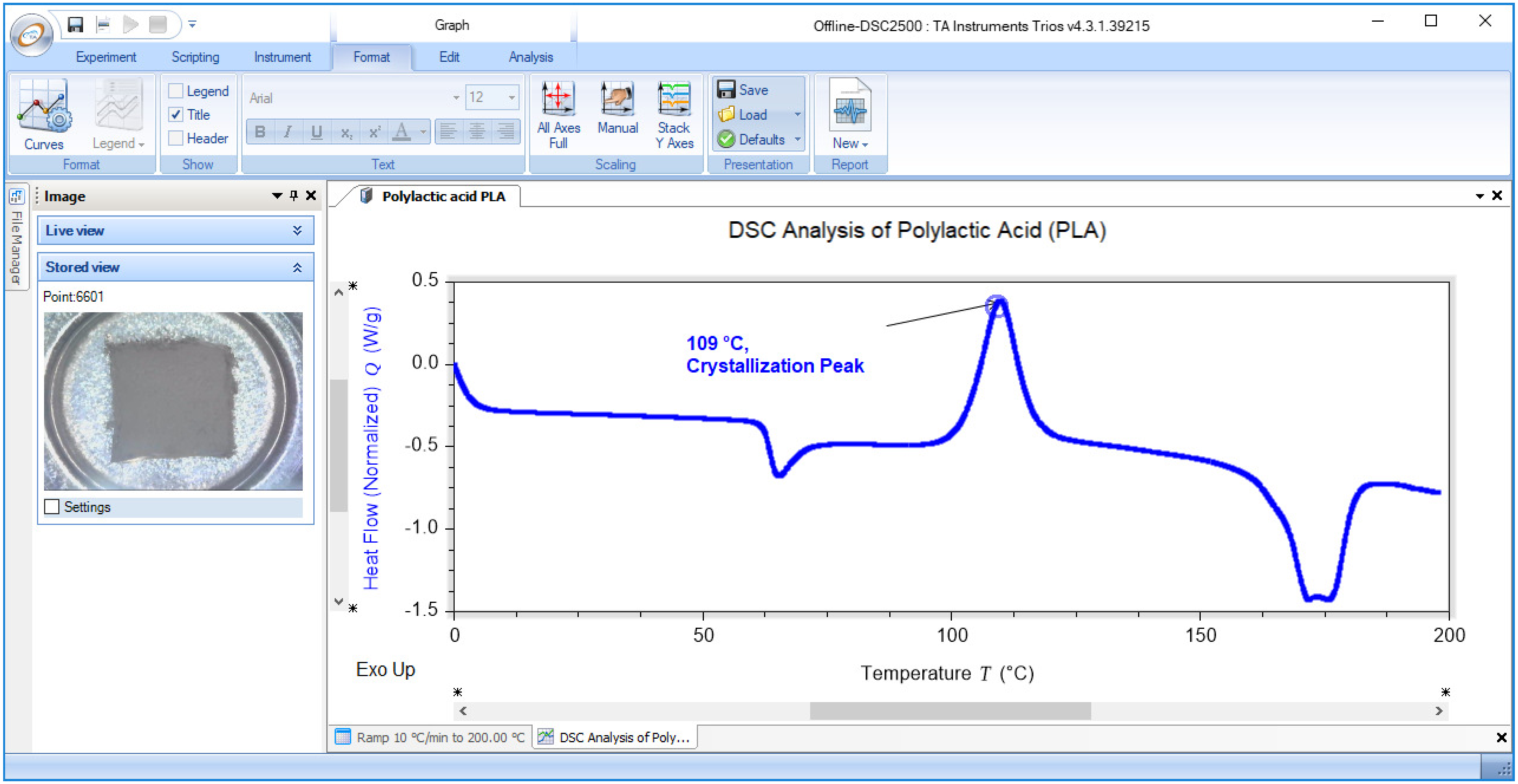
Discovery DSC Microscope Accessory

- Provides imaging and video capabilities during a DSC measurement on the Discovery DSC 2500, 250 and 25
- Includes a high resolution (1.3 MP vivid color) digital microscope camera with a long range working distance and magnification range of 10x-90x; with a typical magnification of 50-60x when focused on a sample pan in the DSC cell
- Collects individual images of up to 1 fps (frames per second) and video at 15 fps
- Illumination provided by several white light LEDs and an adjustable polarizer is included for viewing highly reflective materials and minimizing the amount of glare

DSC Analysis of Polylactic Acid (PLA): Post-Tg



DSC Analysis of Polylactic Acid (PLA): Crystallization Peak



Crystallinity

- Because crystalline structure can form as the sample is heated, the actual crystallinity of the sample is usually less than measured

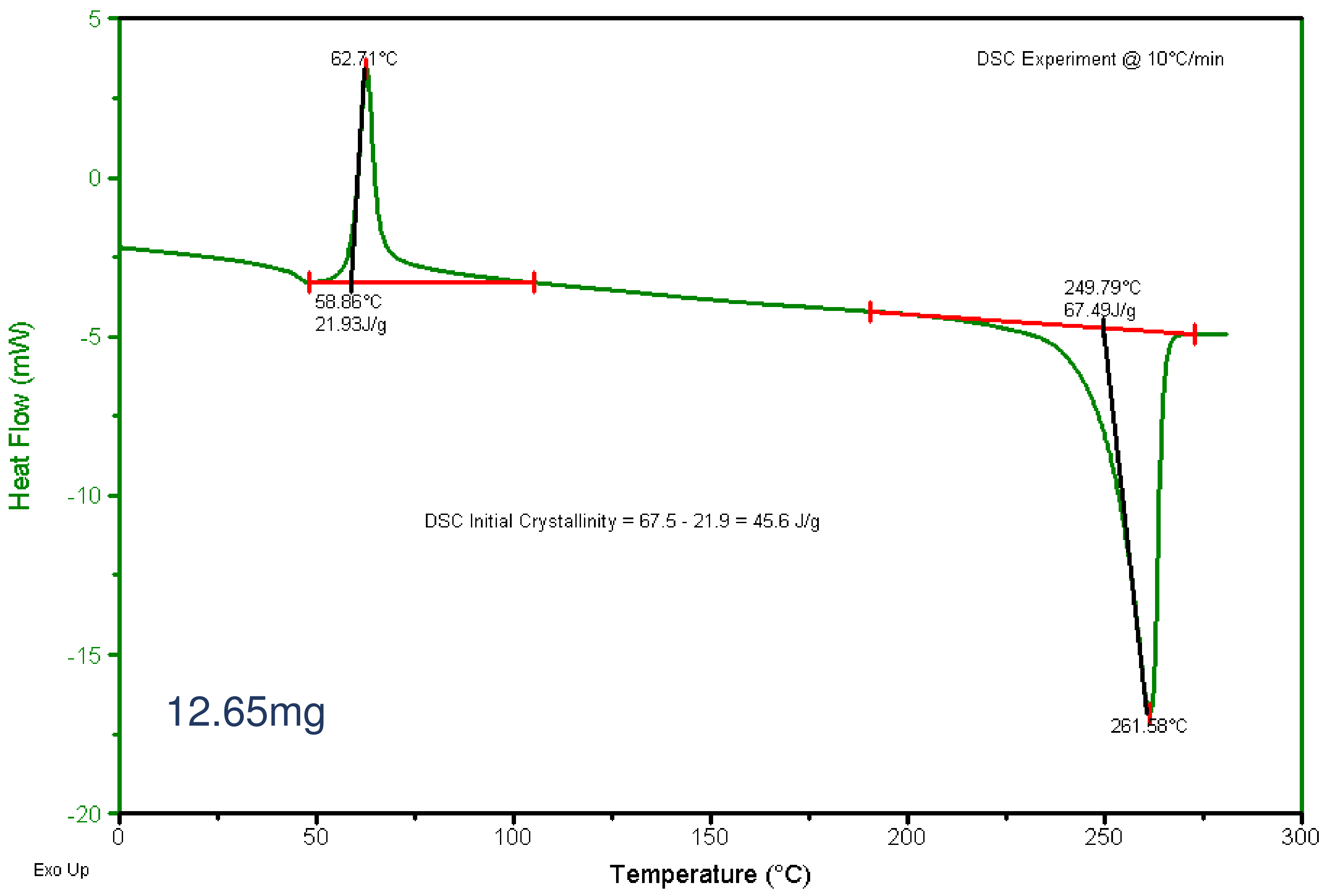
- Determining actual crystallinity is difficult with many semi-crystalline polymers.

- MDSC® measurements provide quantitative information about how crystallinity is changing during the heating experiment.

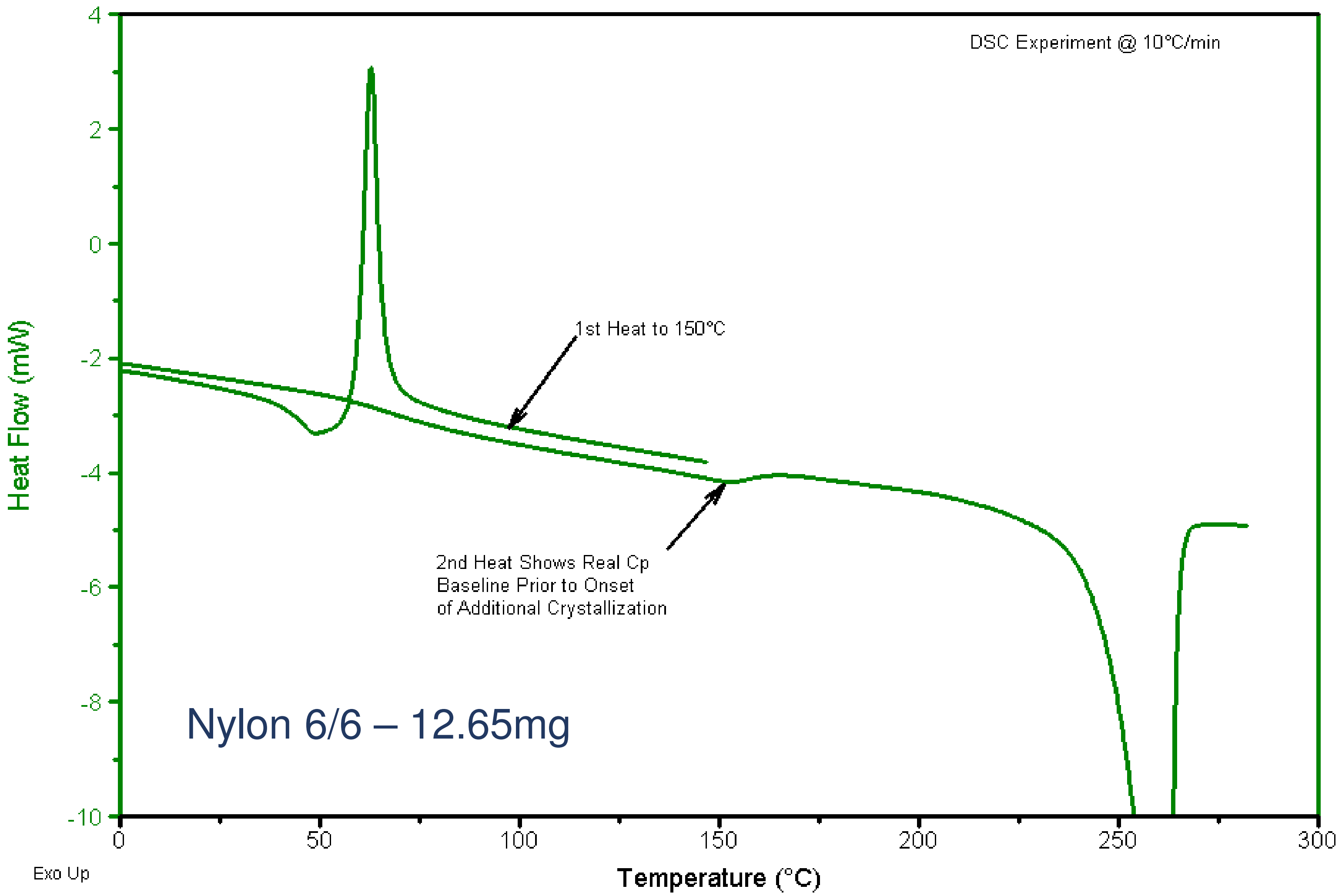
MDSC Approach for Melting

- MDSC “Initial Crystallinity” is always calculated from the sum of all crystallization exotherms and melting endotherms
  - Integrate the Nonreversing signal from the start of crystallization to the end of melting
  - Integrate the Reversing signal from the start of melting to the end of melting
- To illustrate this let’s look at Nylon 6/6

Nylon 6/6 with DSC @ 10°C/min



Partial Annealing in the DSC



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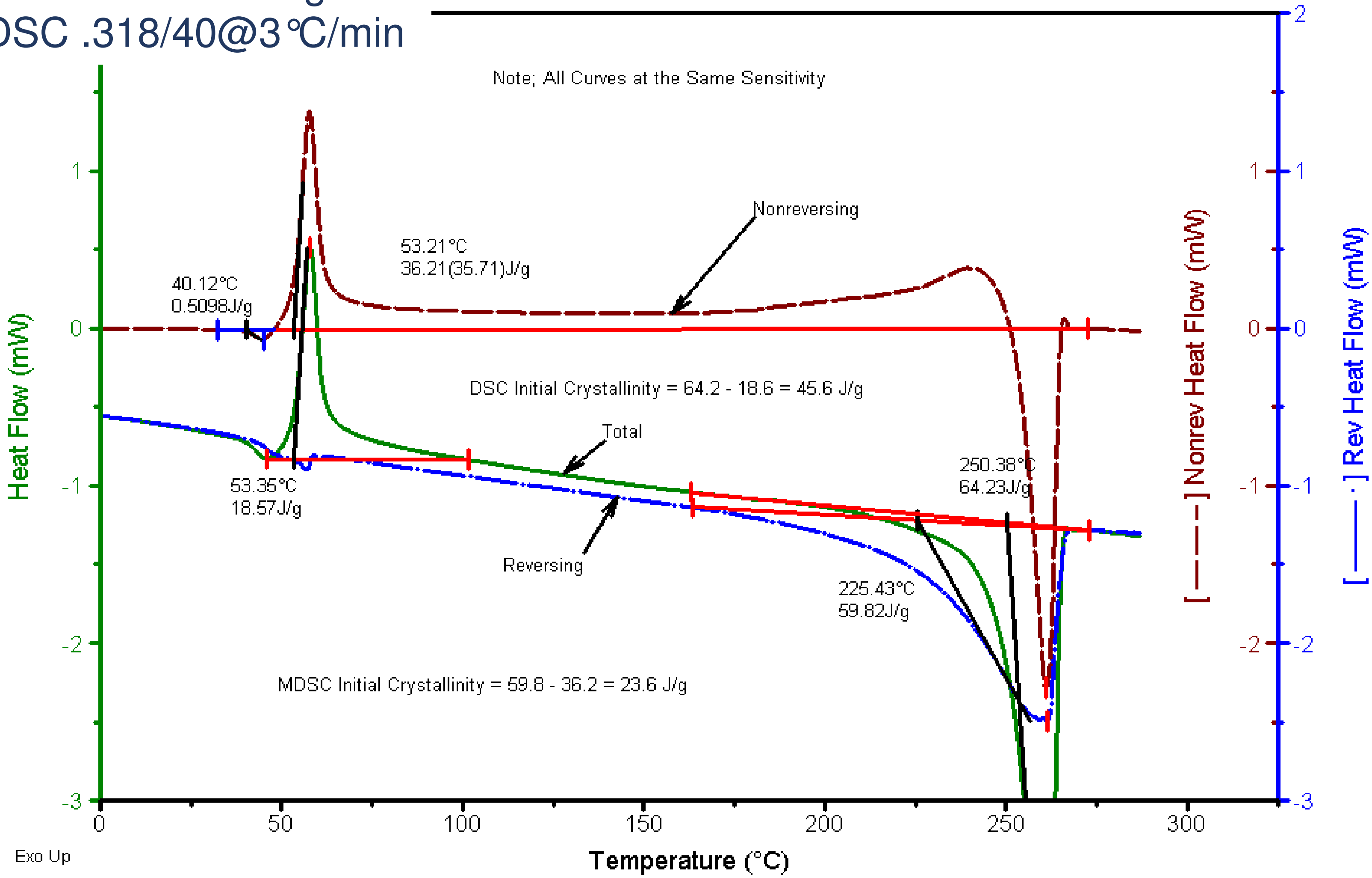
MDSC® of Nylon 6/6

Nylon 6/6 – 12.65mg
MDSC .318/40@3℃/min



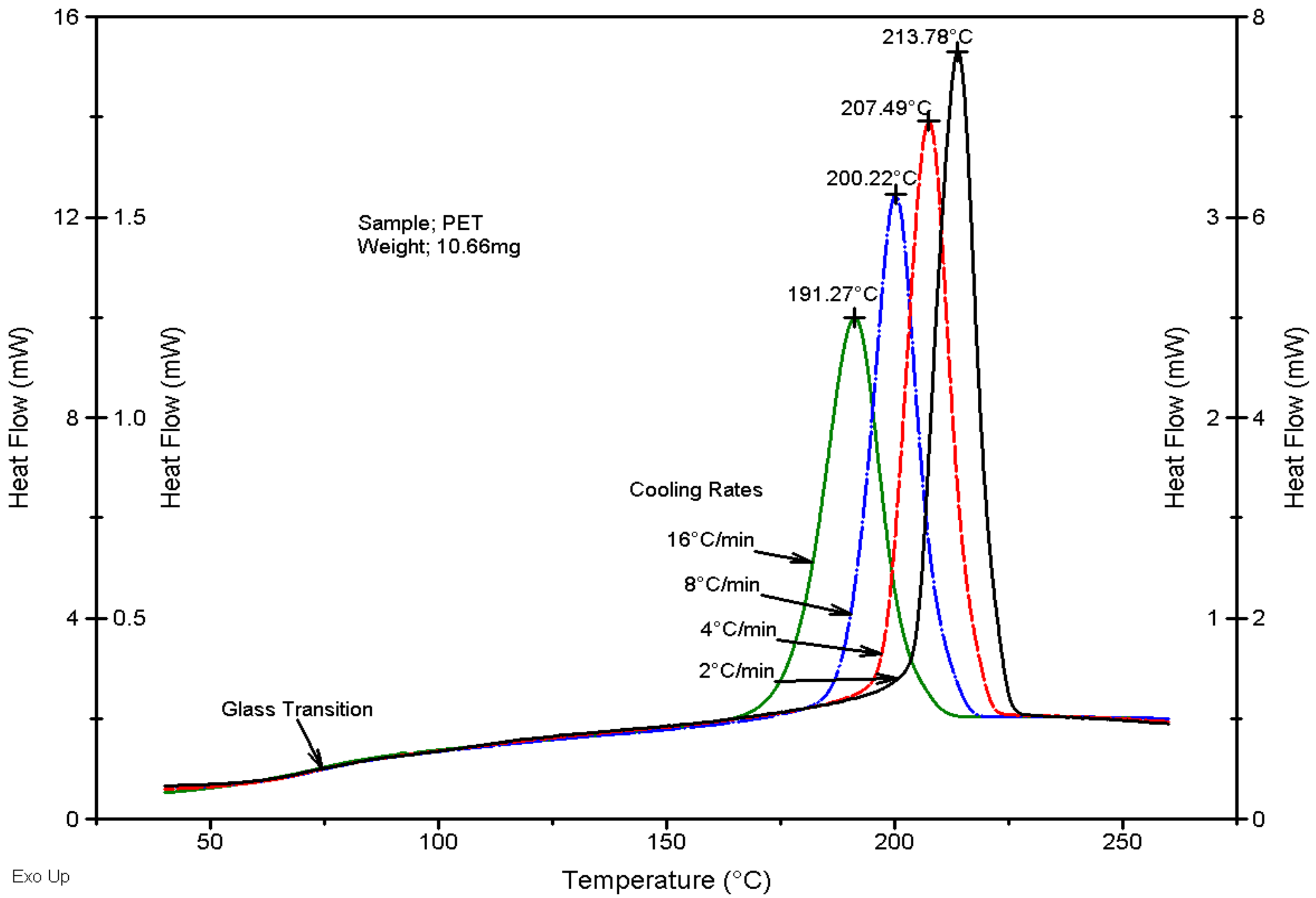
Crystallization

- Crystallization shows up as an exothermic peak in a DSC scan
- Crystallization is molten amorphous material changing to crystalline material upon cooling
- Cold-Crystallization is solid amorphous material changing to crystalline material upon heating
- Since crystallization is a kinetic transition, heating/cooling rate does effect the onset of crystallization, and will also effect resolution

Crystallization

- Crystallization is a kinetic process which is typically studied either while cooling or isothermally, but can also be studied during heating (Cold-Crystallization)
- Differences in crystallization temperature or time (at a specific temperature) between samples can affect end-use properties as well as processing conditions
- Isothermal crystallization is the most sensitive way to identify differences in crystallization rates

Effect of Cooling Rate on Crystallization

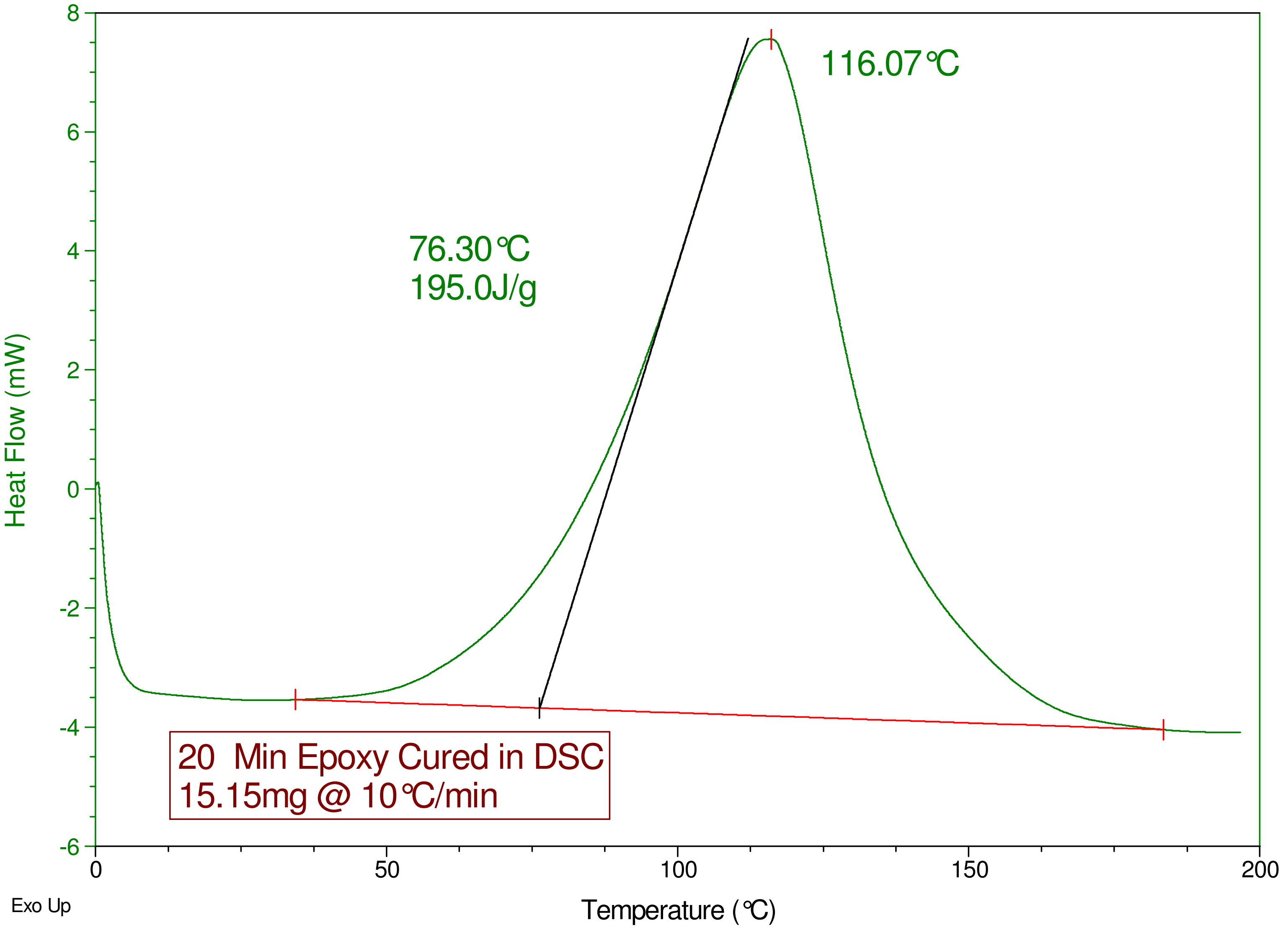


Applications:
Thermosets

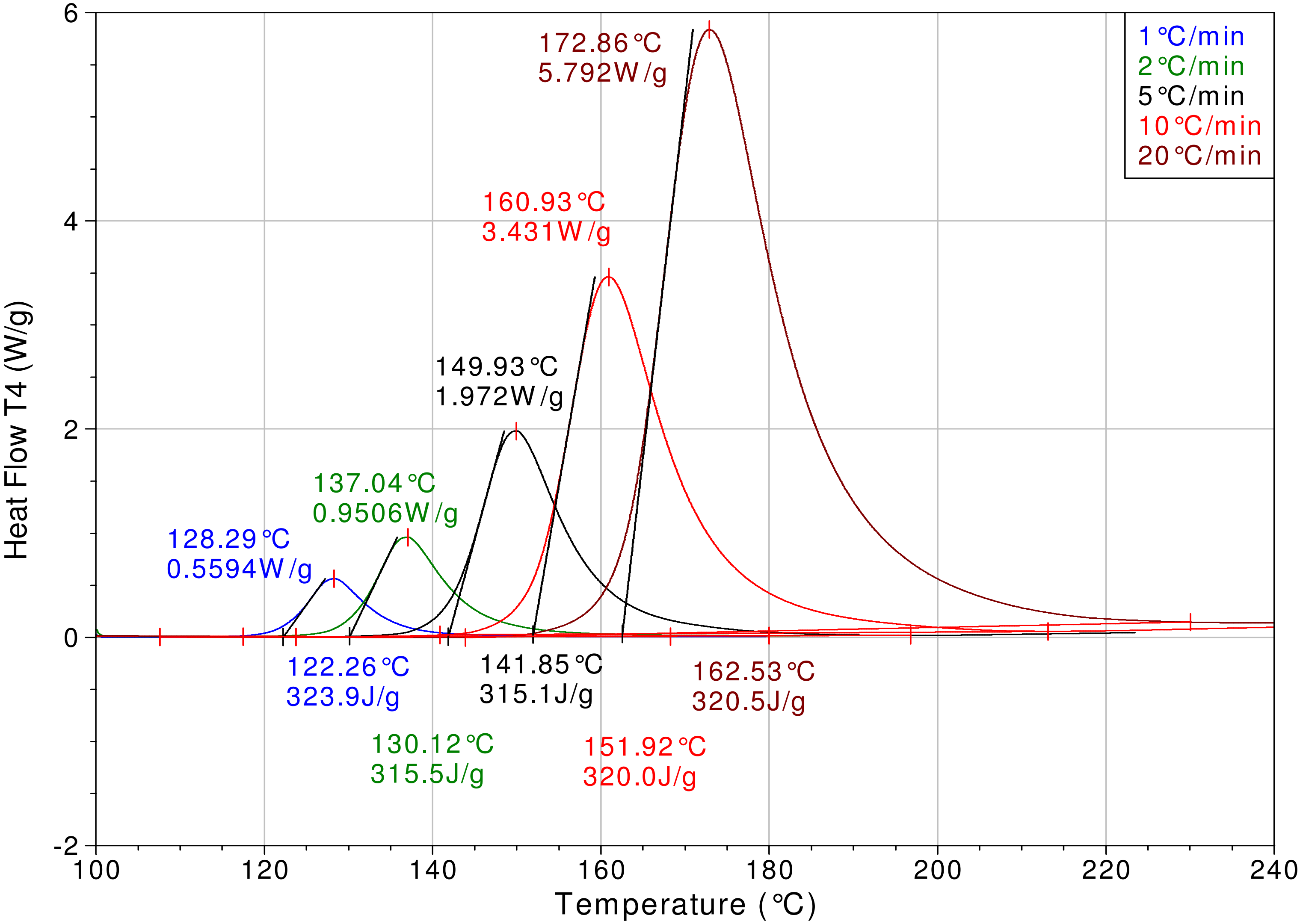
Thermoset Materials

- A “thermoset” is a cross-linked polymer formed by an irreversible exothermic chemical reaction
    - A common example is a 2 part epoxy adhesive
- With a DSC we can look at the curing of these materials, and the Tg of full or partially cured samples

Curing of a Thermosetting Material



Effect of Heating Rate



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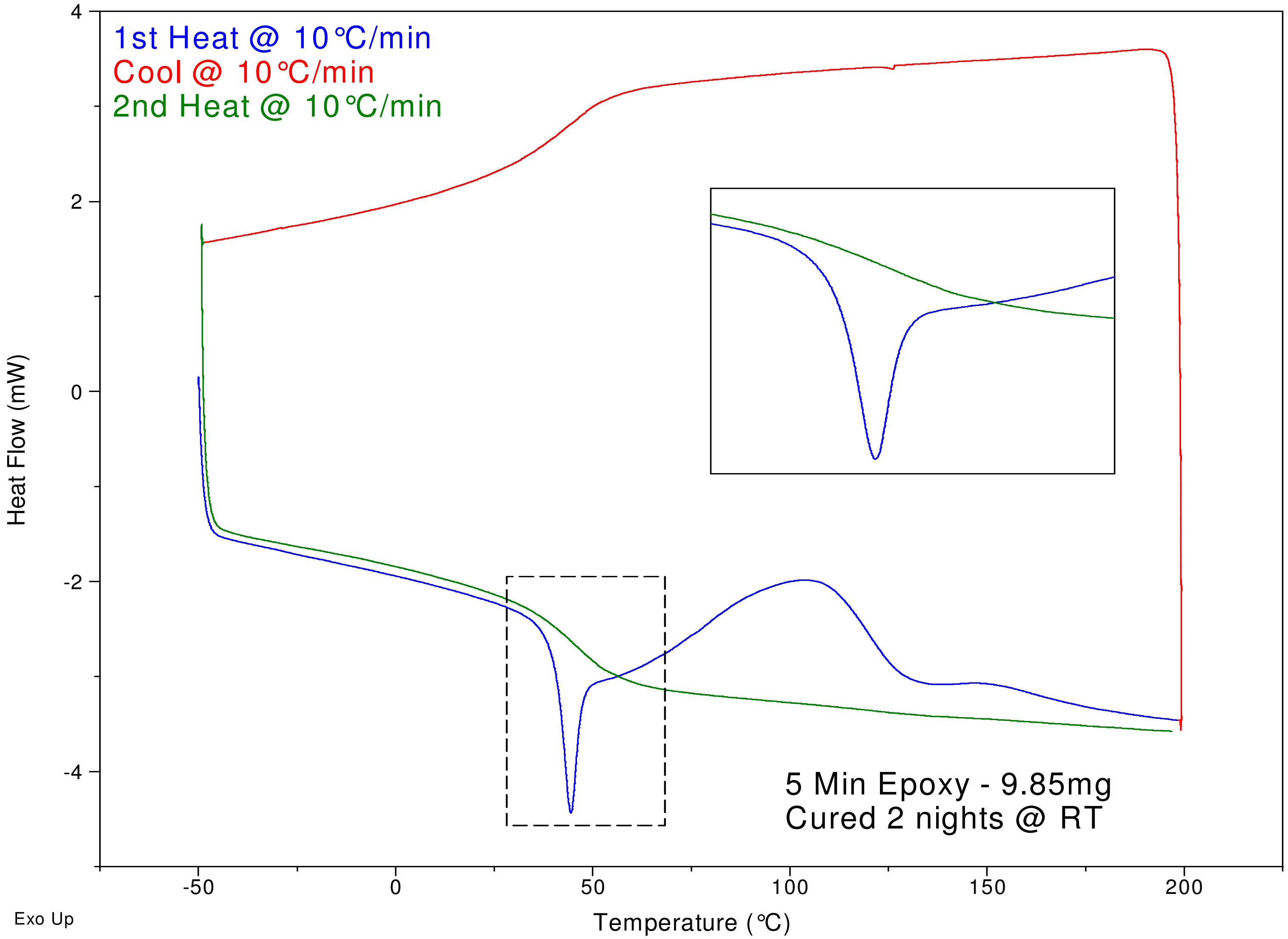
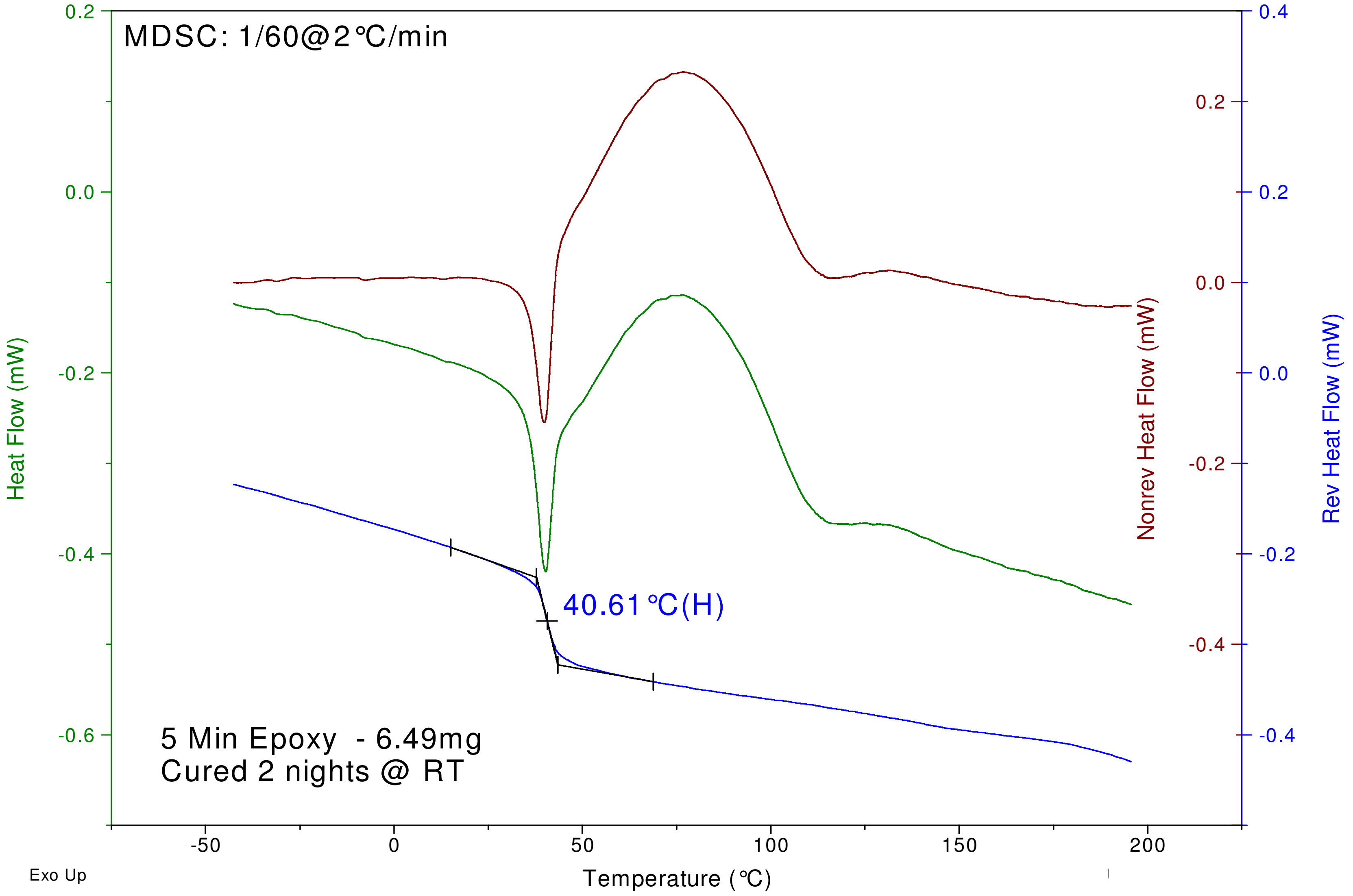
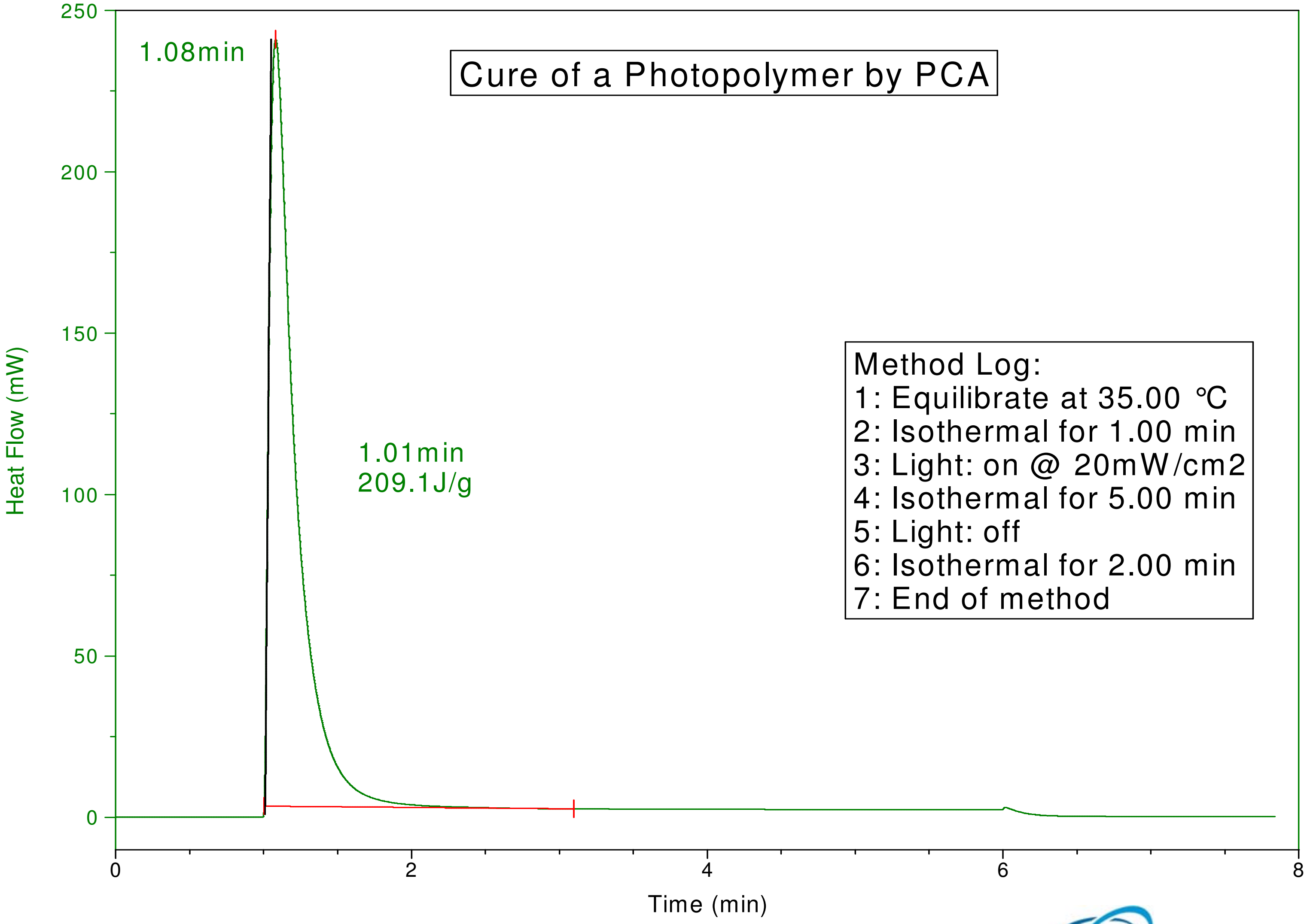
Epoxy Cured 48 Hours – Standard DSC



Epoxy Cured 48 Hours – MDSC®



Photopolymer Cure by PCA



Cure of a Photopolymer by PCA

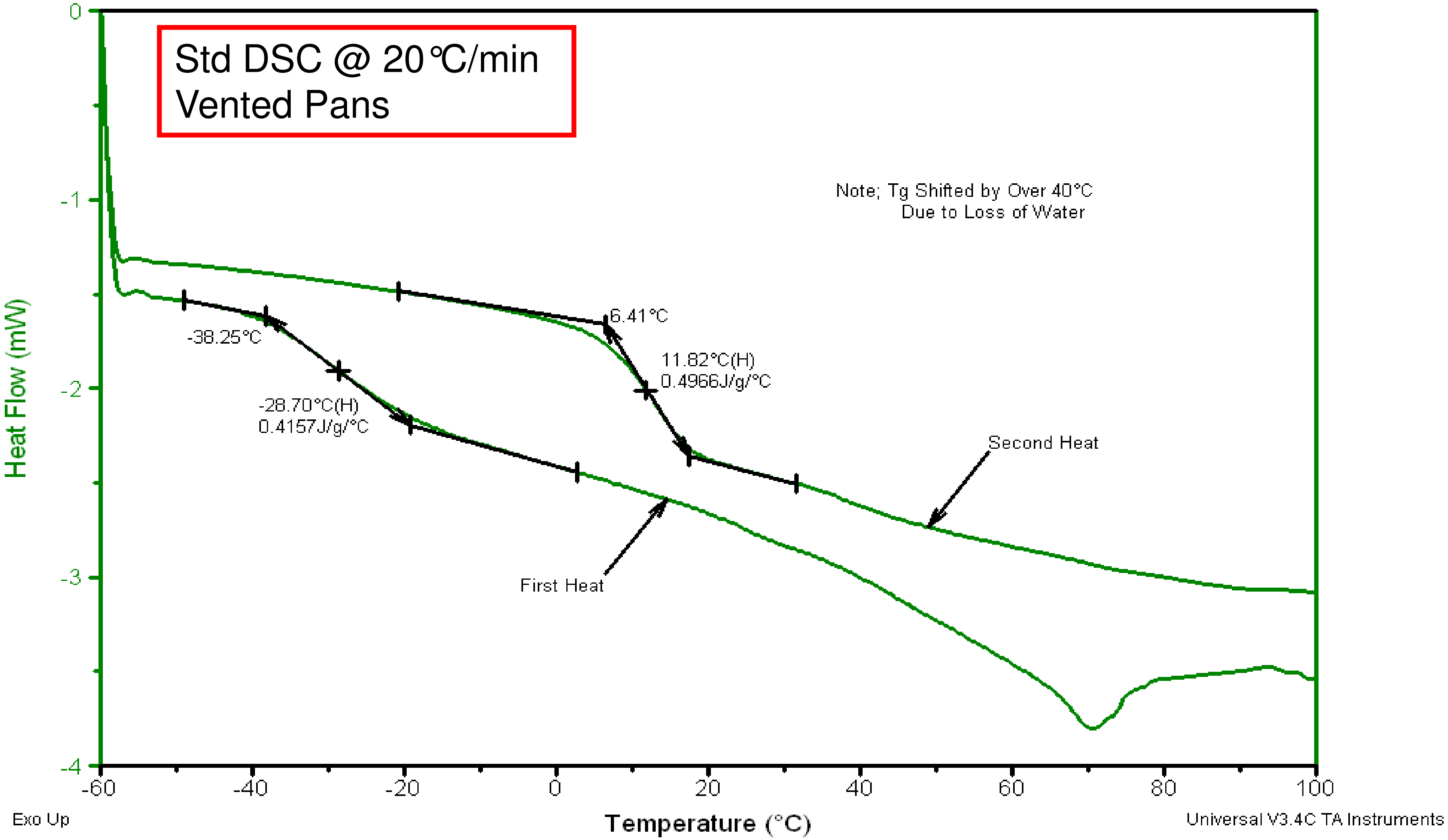
Method Log:
1: Equilibrate at 35.00 °C
2: Isothermal for 1.00 min
3: Light: on @ 20mW/cm2
4: Isothermal for 5.00 min
5: Light: off
6: Isothermal for 2.00 min
7: End of method

Pharmaceuticals

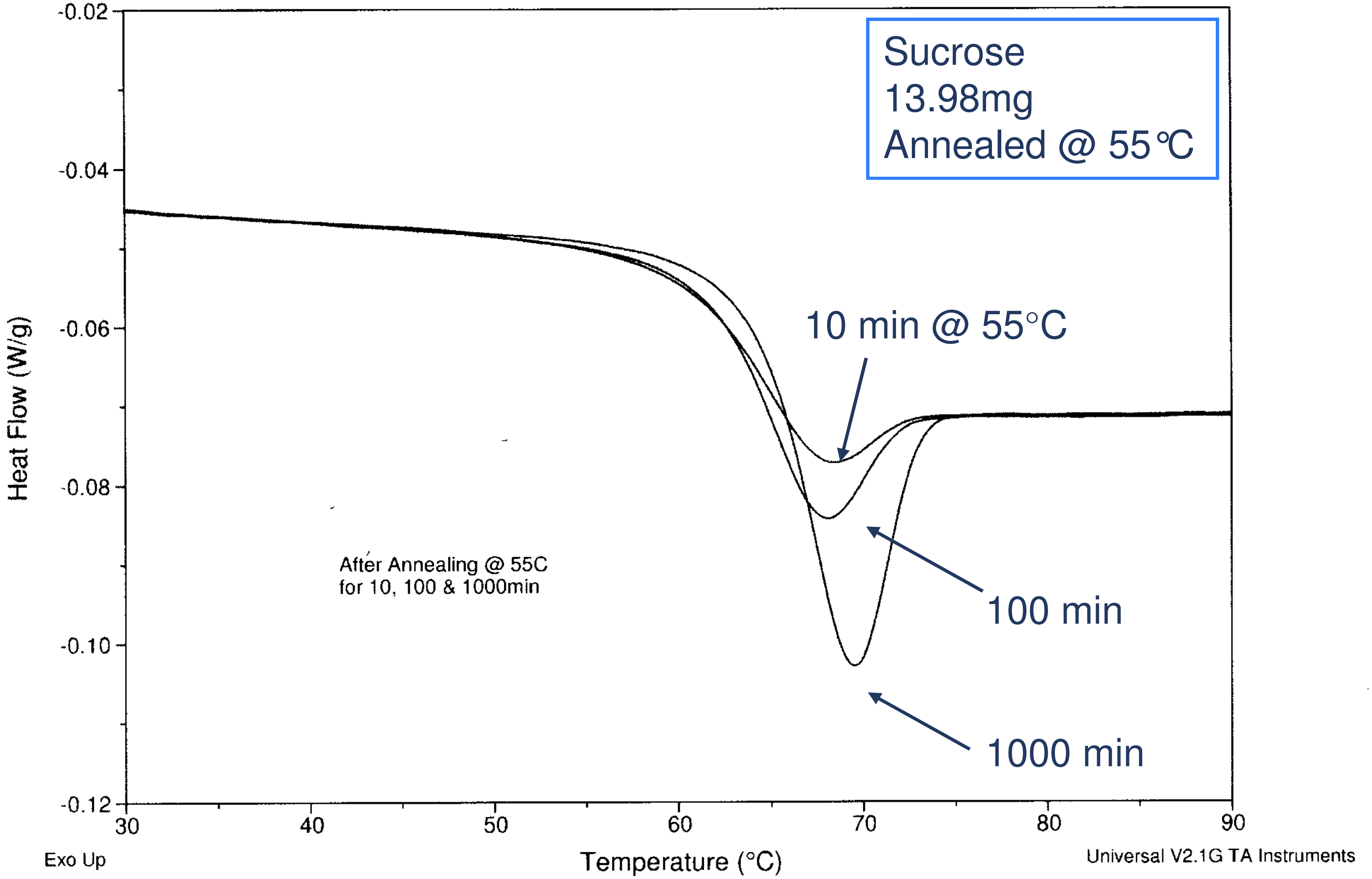
Pharmaceuticals

- Tg
- Melting
  - Purity
- Polymorphs
- General Recommendations
  - Use TGA to determine pan type
  - Use 1-5 mg samples (use 1mg for purity)
  - Initial H-C-H @ 10°C/min (1°C/min for purity)
  - If polymorphs present, heat faster to inhibit polymorphic transformations

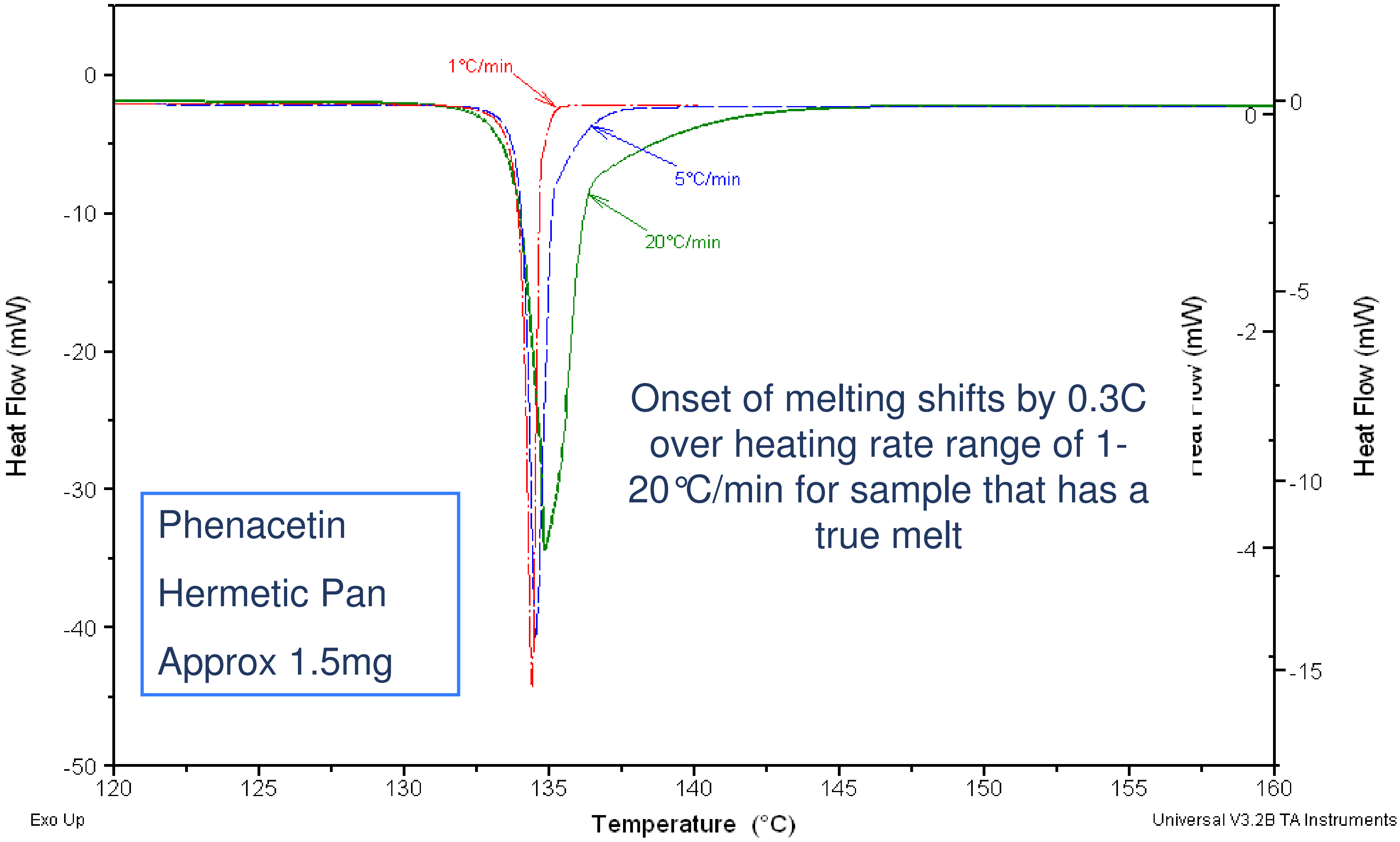
Tg of Sucrose Varies with Moisture Content



Structure Changes With Time



Melting is Not Heating Rate Dependent



Phenacetin

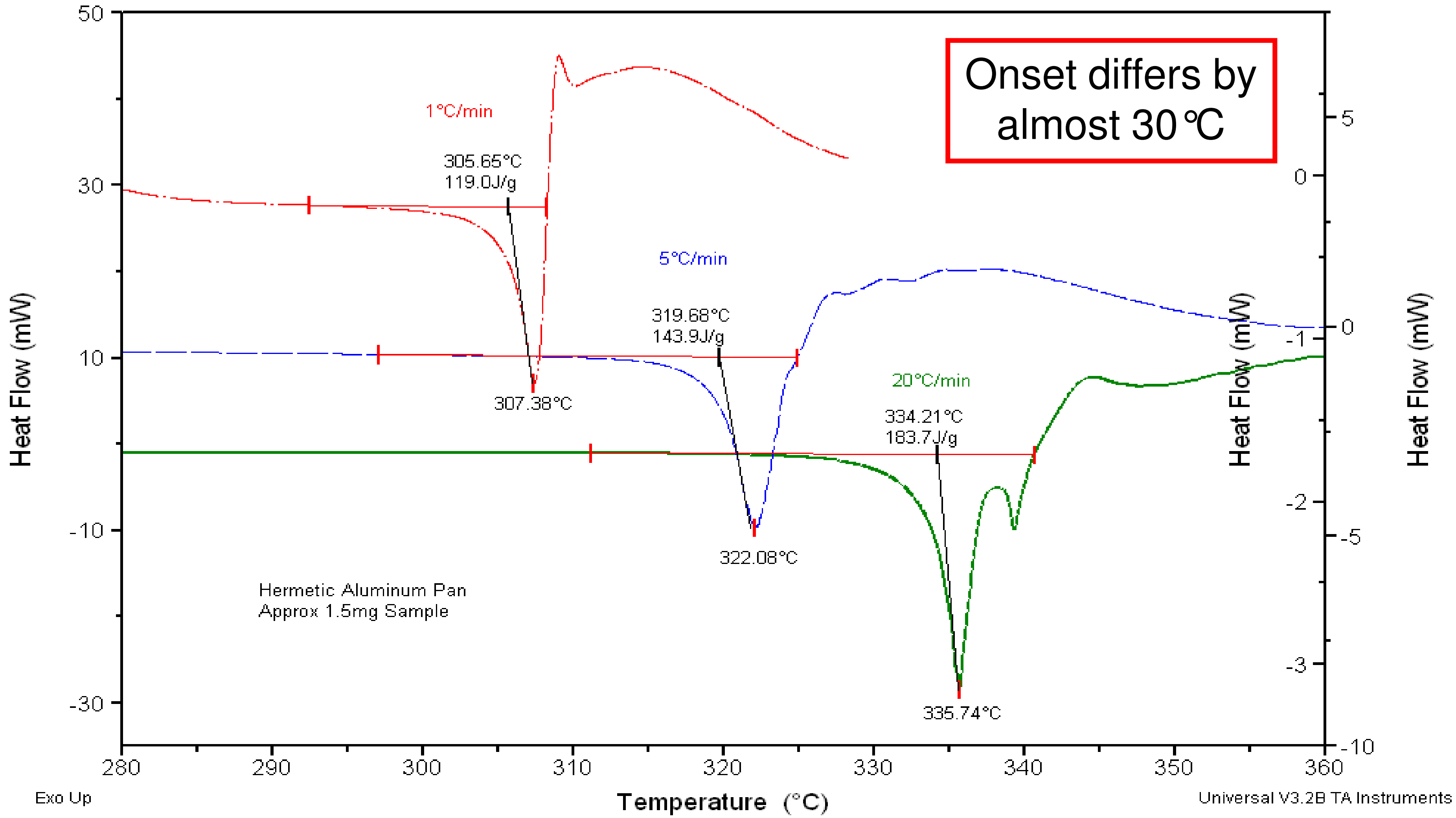
Hermetic Pan

Approx 1.5mg

Onset of melting shifts by 0.3C over heating rate range of 1-20℃/min for sample that has a true melt

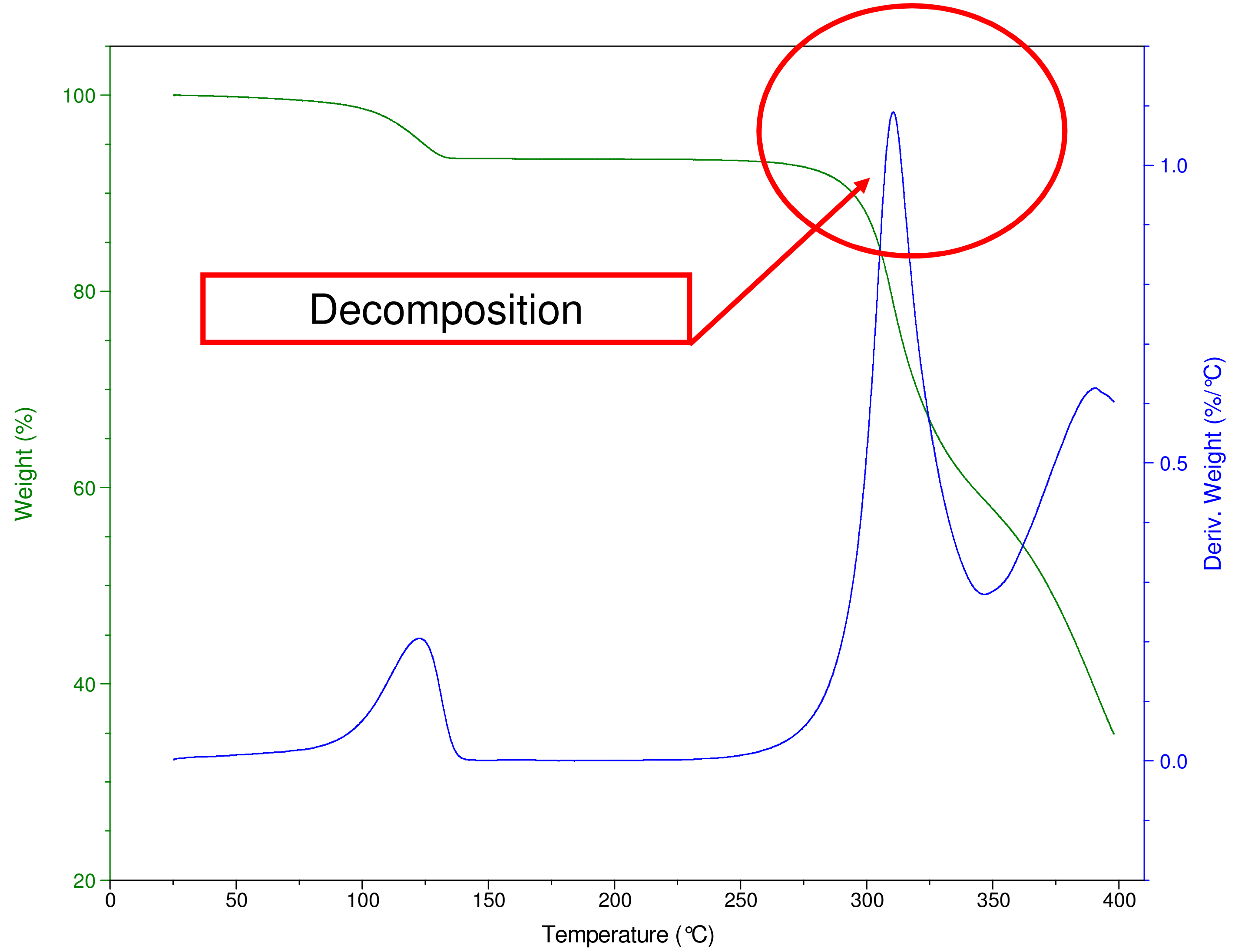
Ciprofloxacin Hydrochloride Decomposes

Decomposition is kinetic (heating rate dependent)

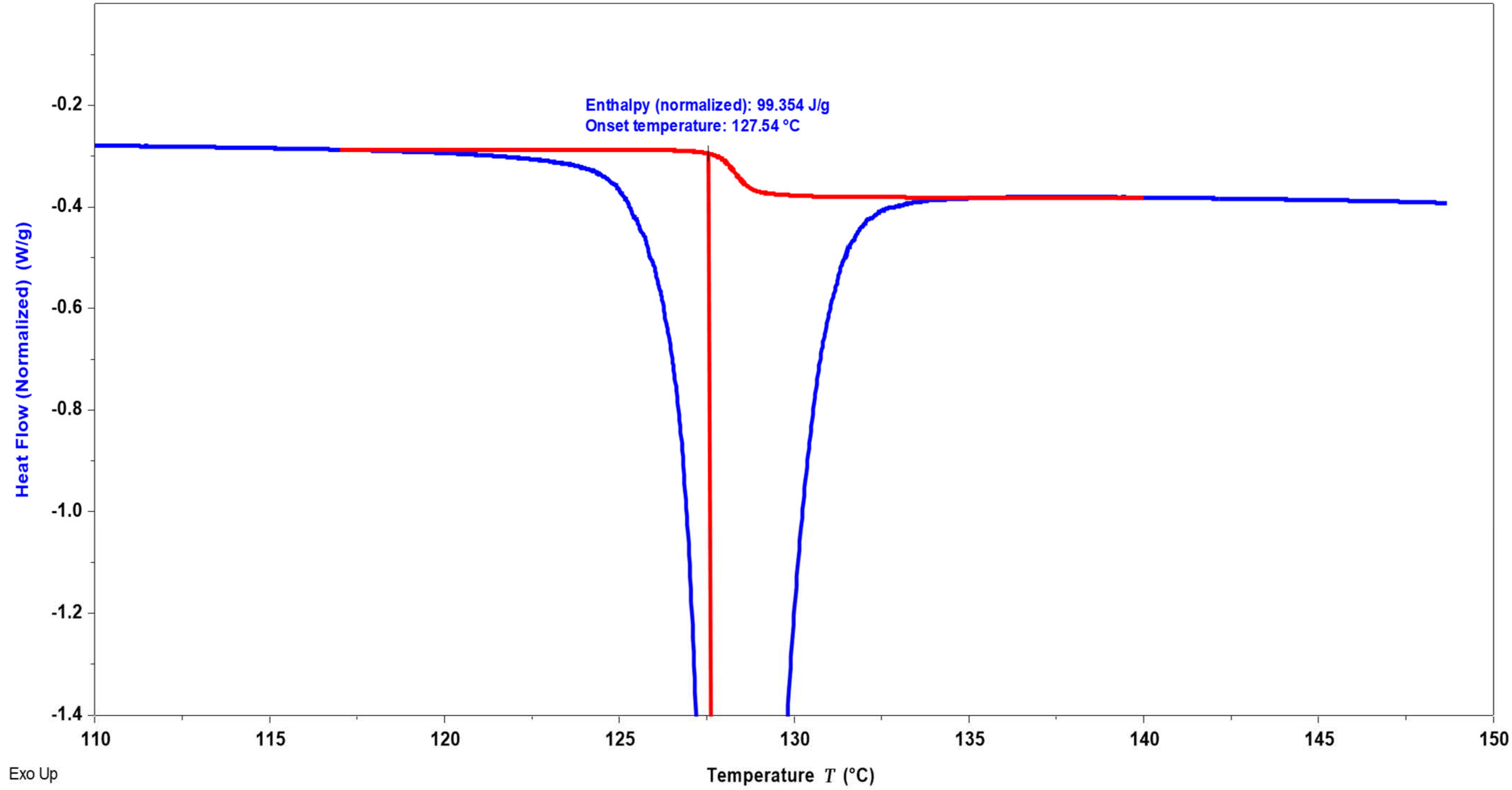


Onset differs by almost 30℃

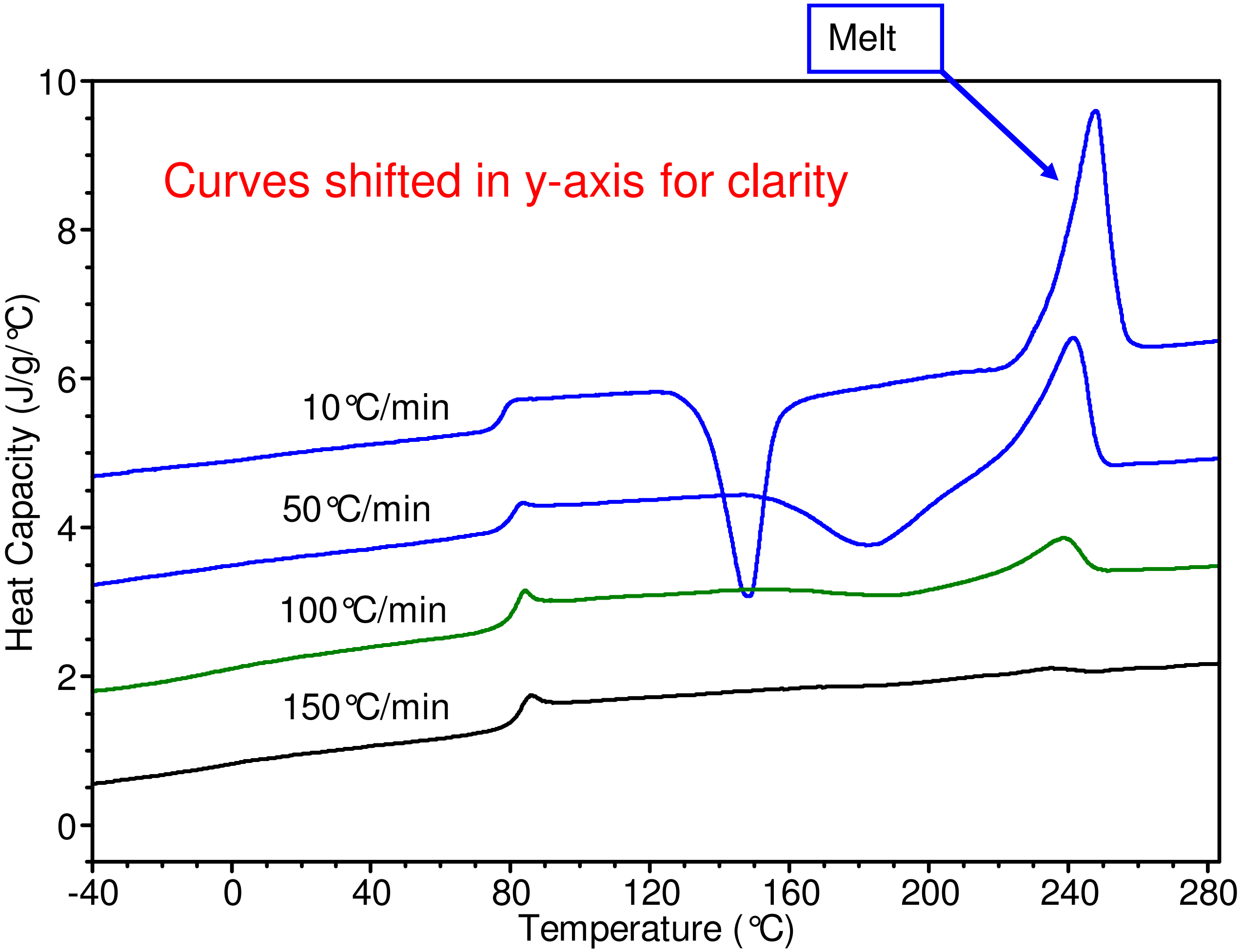
TGA of Ciprofloxacin Hydrochloride



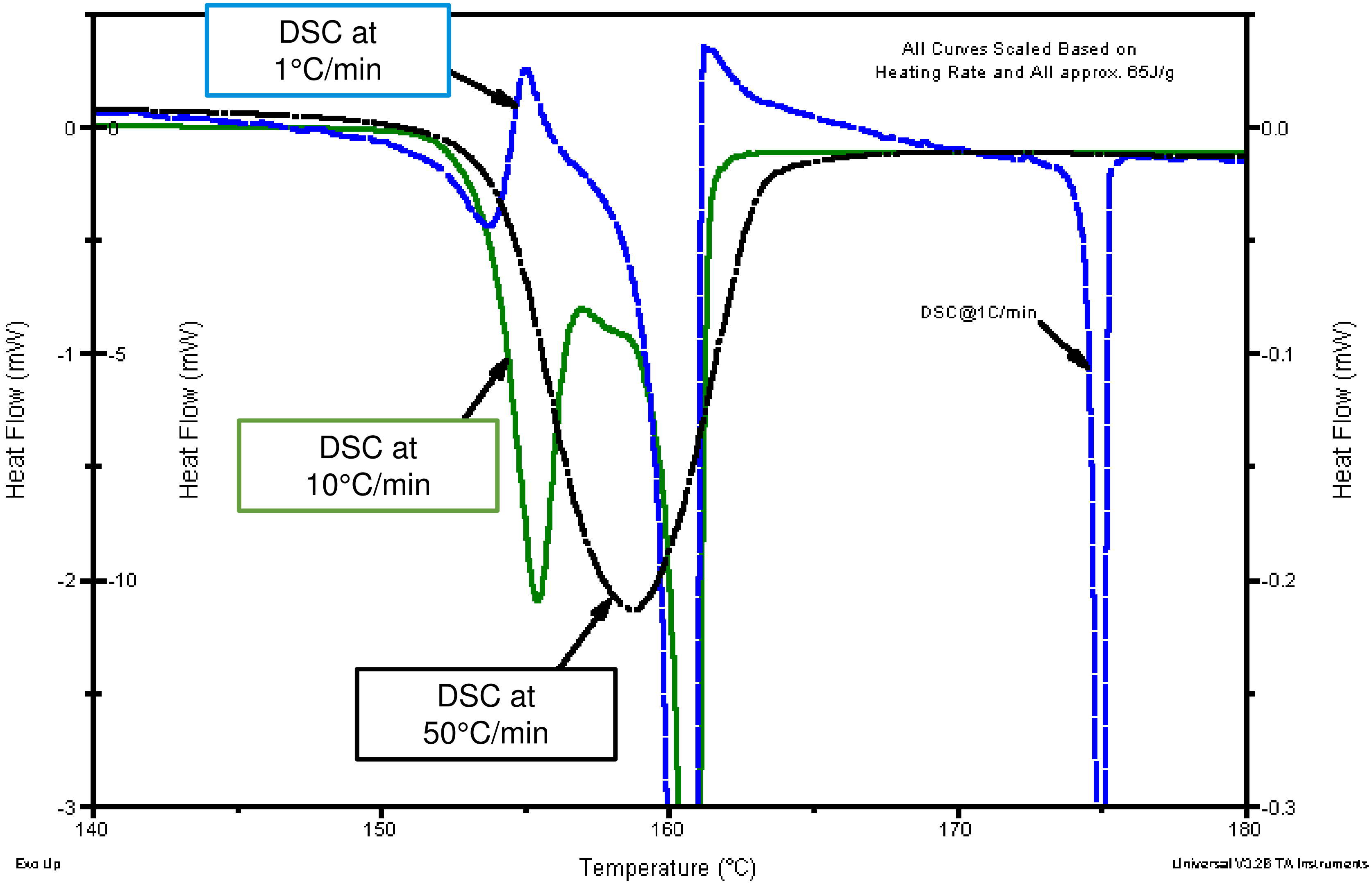
Integrating a melt peak using a sigmoidal baseline



Effect of Heating Rate on Melting



Effect of Heating Rate on Polymorph

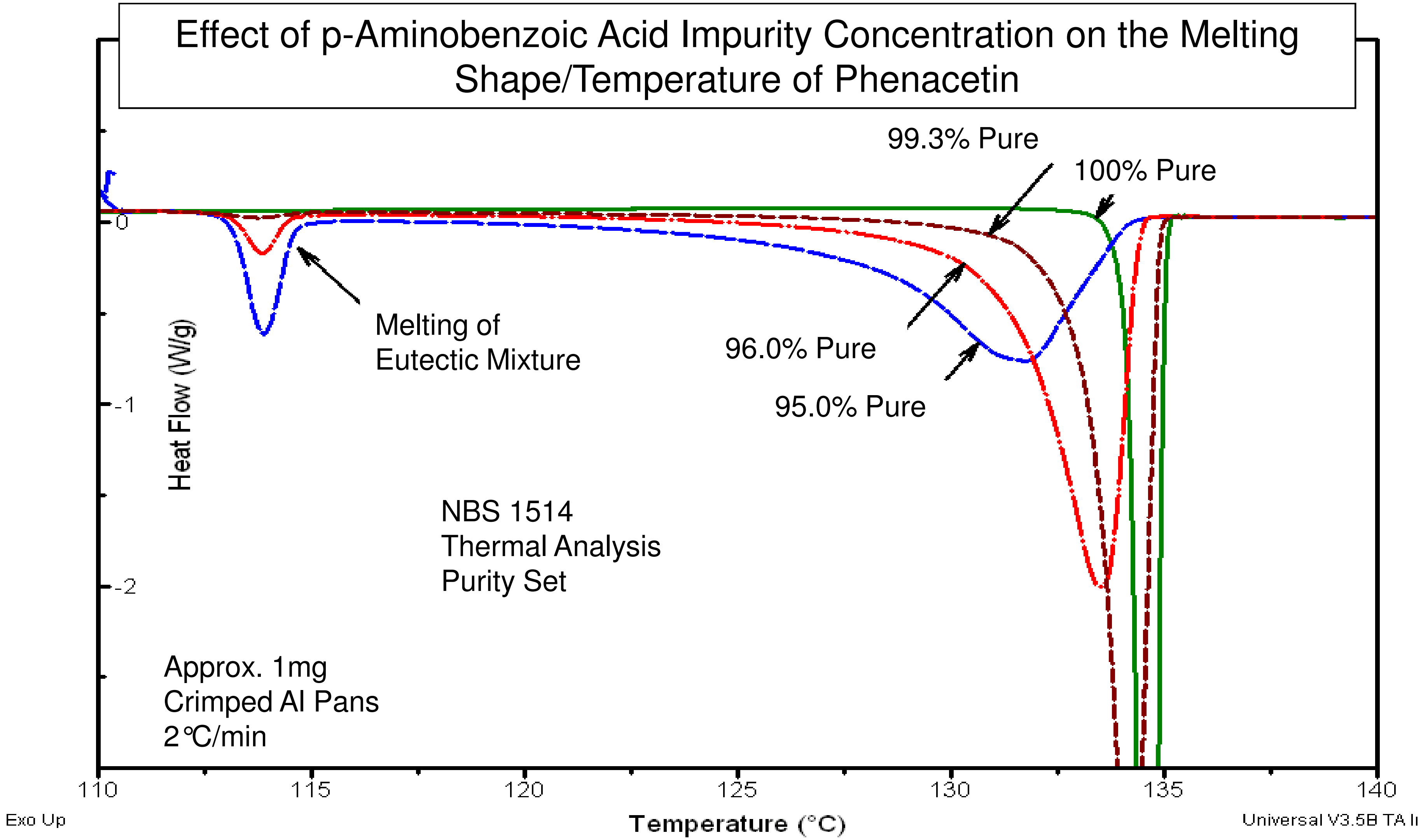


DSC at 1°C/min

DSC at 10°C/min

DSC at 50°C/min

Effect of Impurities on Melting



This Just Touched the Surface

- There is a lot more than can be done
- Crystallization studies
  - Isothermal & non-isothermal
- Kinetics
  - Crystallization
  - Crosslinking and curing
  - Decomposition
- Oxidative times
- ---- and more

Thank you for attending!

If you have questions or need help
Contact the TA Instruments Technical Helpline:
http://www.tainstruments.com/support/applications/applications-hotline/

Don’t forget http://www.tainstruments.com/