Agenda

- **Morning: Techniques and Applications**
  - Case Study – Automotive Industry
  - Differential Scanning Calorimetry
  - Thermogravimetric Analysis
  - Simultaneous Differential Thermal Analysis
  - Microcalorimetry and Thermal Physical Properties
  - Dynamic Mechanical Analysis (Q800 and RSA)
- **Afternoon: Techniques and Applications:**
  - Rheology (DHR and ARES) – Techniques and Applications
  - Case Studies – Rheology/DSC/TGA/SDT
  - Rubber Rheology
  - Case Studies – Rubber Rheology and DSC

Wrap up about 4:00 pm

Materials Characterization by Thermal Analysis (DSC & TGA), Rheology, and Dynamic Mechanical Analysis

Charles Potter, Sarah Cotts & Don DiPietro
Applications Scientists & Sales Representative

What Does TA Instruments Make?

- Differential Scanning Calorimeters
- Thermogravimetric Analyzers
- Simultaneous Differential Thermal Analyzers
- Microcalorimeters of many types
- Thermal Mechanical Analyzers and Dilatometers

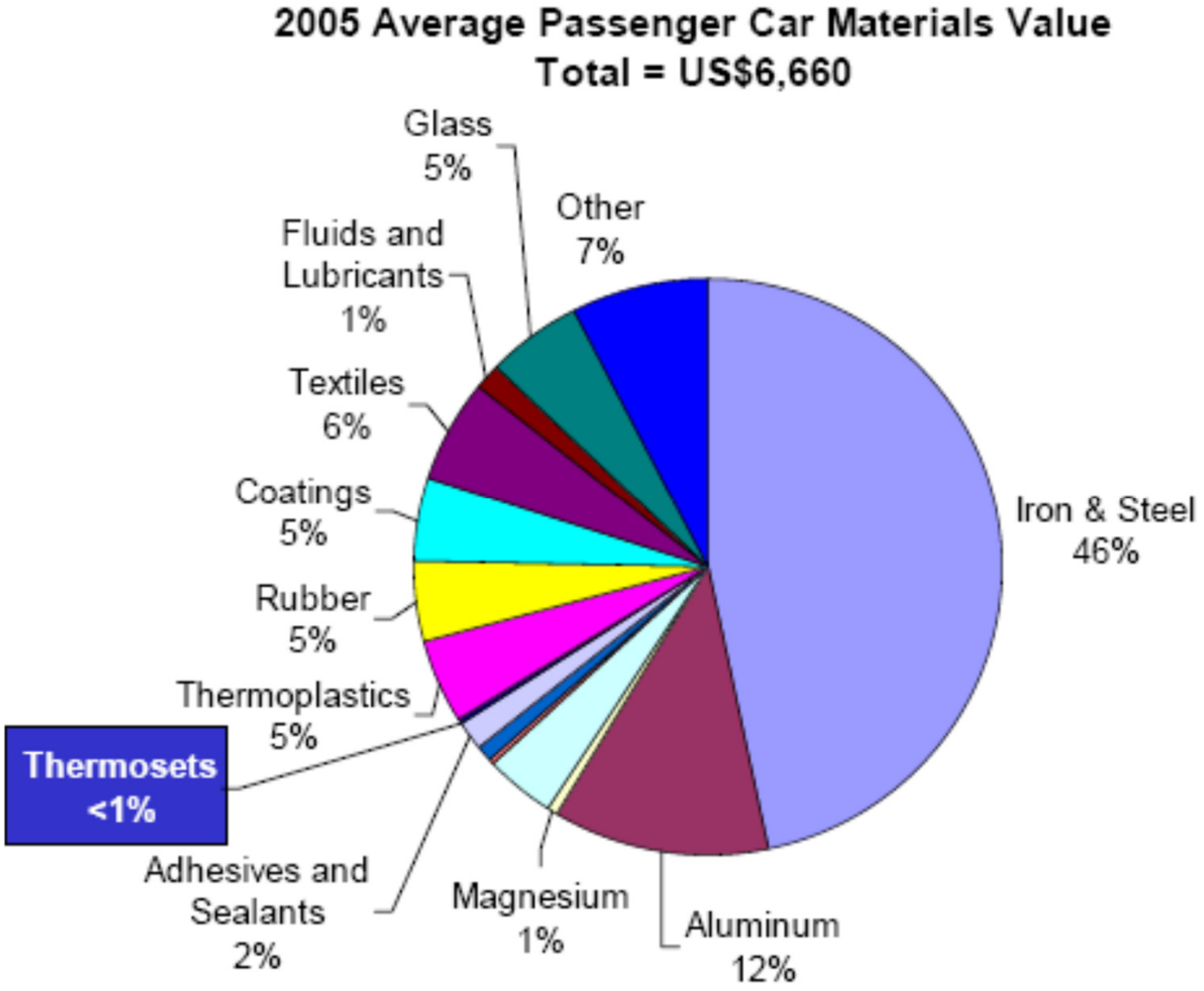
What Does TA Instruments Make?

- Thermal Diffusivity
- Thermal Conductivity
- Mechanical Testers
- Dynamic Mechanical Analyzers
- Rotational Rheometers
- Rubber Rheometers

- Case Study -

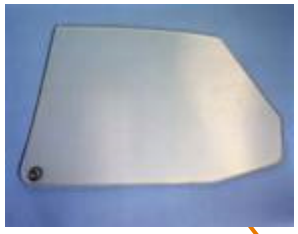
Thermal Analysis in the Automotive Industry

Composition of an Automobile



Building a Lighter Automobile

Lightweight Glazing

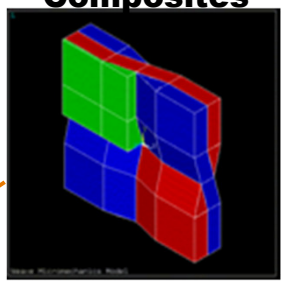


30% weight reduction

Magnesium Alloy

50% weight reduction

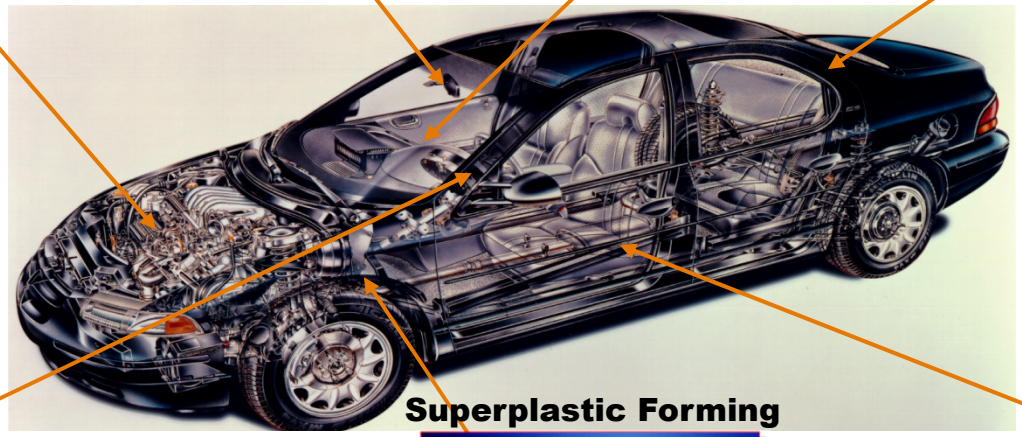
Thermoplastic Composites



Reduces mass by 60%

Metal Matrix Composites

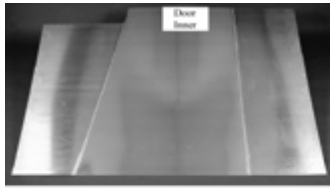
Powertrain components - 40% weight reduction

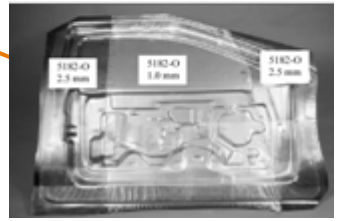


Hydroforming

40% weight reduction / 50% reduction in part count

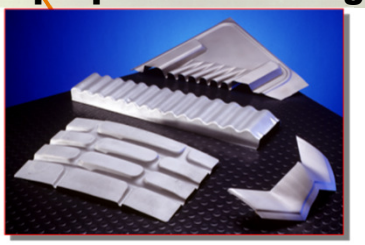
Aluminum Tailor Welded Blanks





35% weight reduction / reduction in part count

Superplastic Forming



40% weight reduction / 10 X reduction in part count

Photo: Courtesy of GKN Aerospace

What is Thermal Analysis?

- Thermal analysis is a series of techniques that provide physical property measurements as a function of temperature, time, and other variables.

Common Techniques Include…

- Differential Scanning Calorimetry (DSC) - heat
  - Modulated DSC® (MDSC®)
- Thermogravimetric Analysis (TGA) – weight
  - Simultaneous DSC/TGA (SDT)
  - Vapor sorption analysis
- Thermomechanical Analysis (TMA) - dimension
- Dynamic Mechanical Analysis (DMA) - modulus
  - Can also be considered a “solids rheometer”

Analysis of Automotive Materials

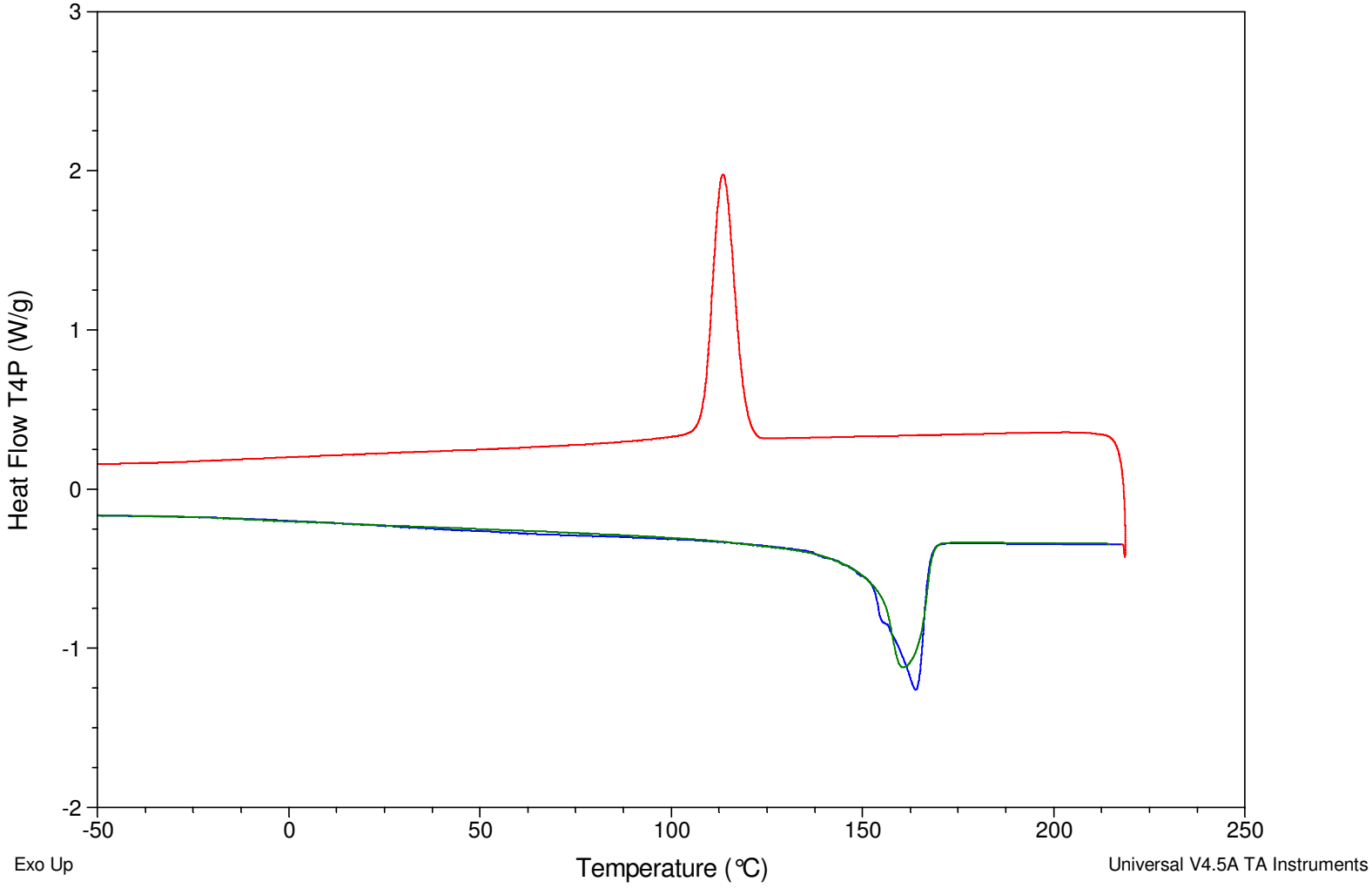
- What is it?
- Thermoplastics
- Thermosets
- Amorphous Material
- Rubber and Elastomers

“What is it?”

- “What is it?” or “What is it not?”

- DSC and TGA, along with infrared spectroscopy, are an excellent starting point for characterization of new or unknown materials.

In Canada You will need a bunch of this to buy anything … including a CAR



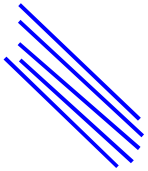
Thermoplastic Polymers

Agenda – Thermoplastics

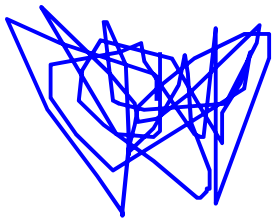
- What are thermoplastics?
- Melting
- Crystallization
- Crystalline Content
- Thermal Stability
- Oxidative Stability

Thermoplastics

Semi-Crystalline (or Amorphous)



Crystalline Phase
melting temperature Tm
(endothermic peak)

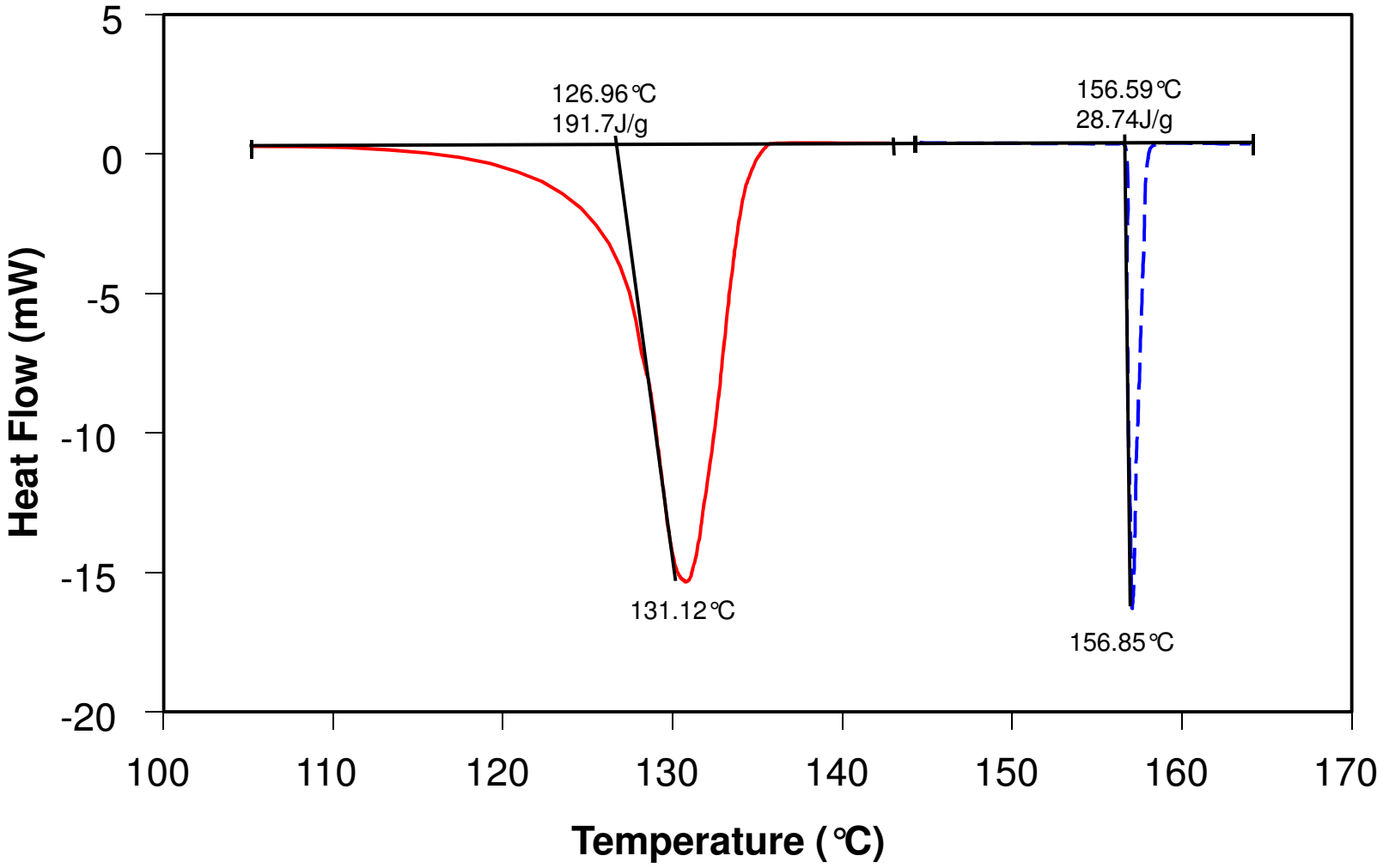


Amorphous Phase
glass transition
temperature (Tg)
(causing ΔCp)

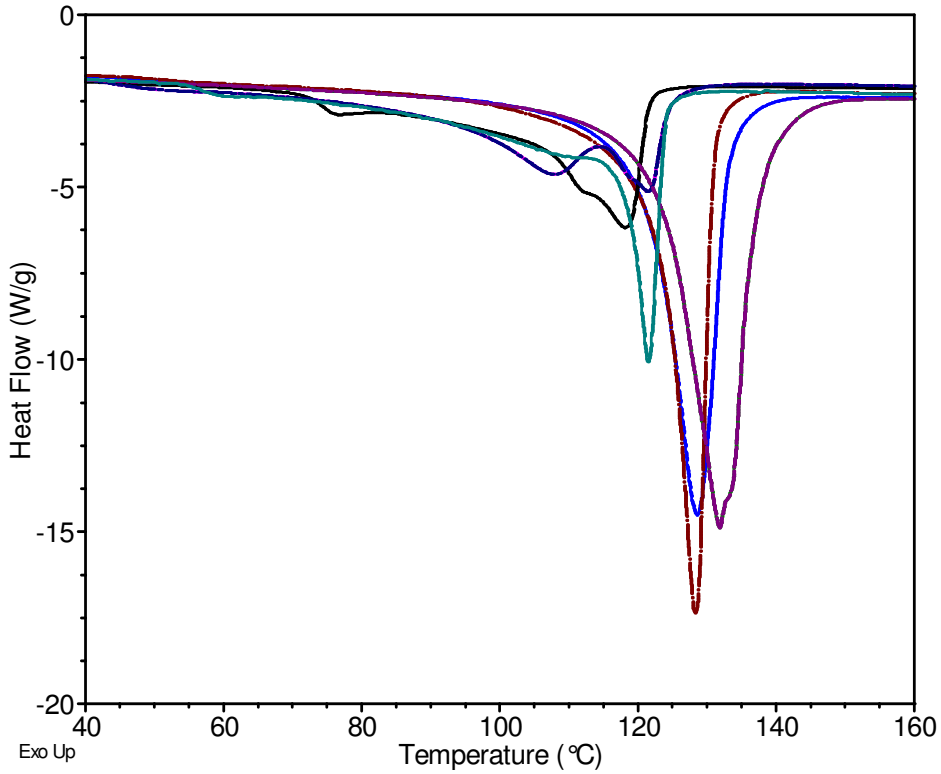
$Tg < Tm$

Crystallizable polymer can crystallize
on cooling from the melt at Tc
($Tg < Tc < Tm$)

DSC Melting of Polyethylene vs Indium



Different Types of Polyethylene



Peak shape depends on:

- Molecular weight distribution and branching
- Crystallinity
- Crystallite morphology as determined by thermal history
- Differences affect end-use performance

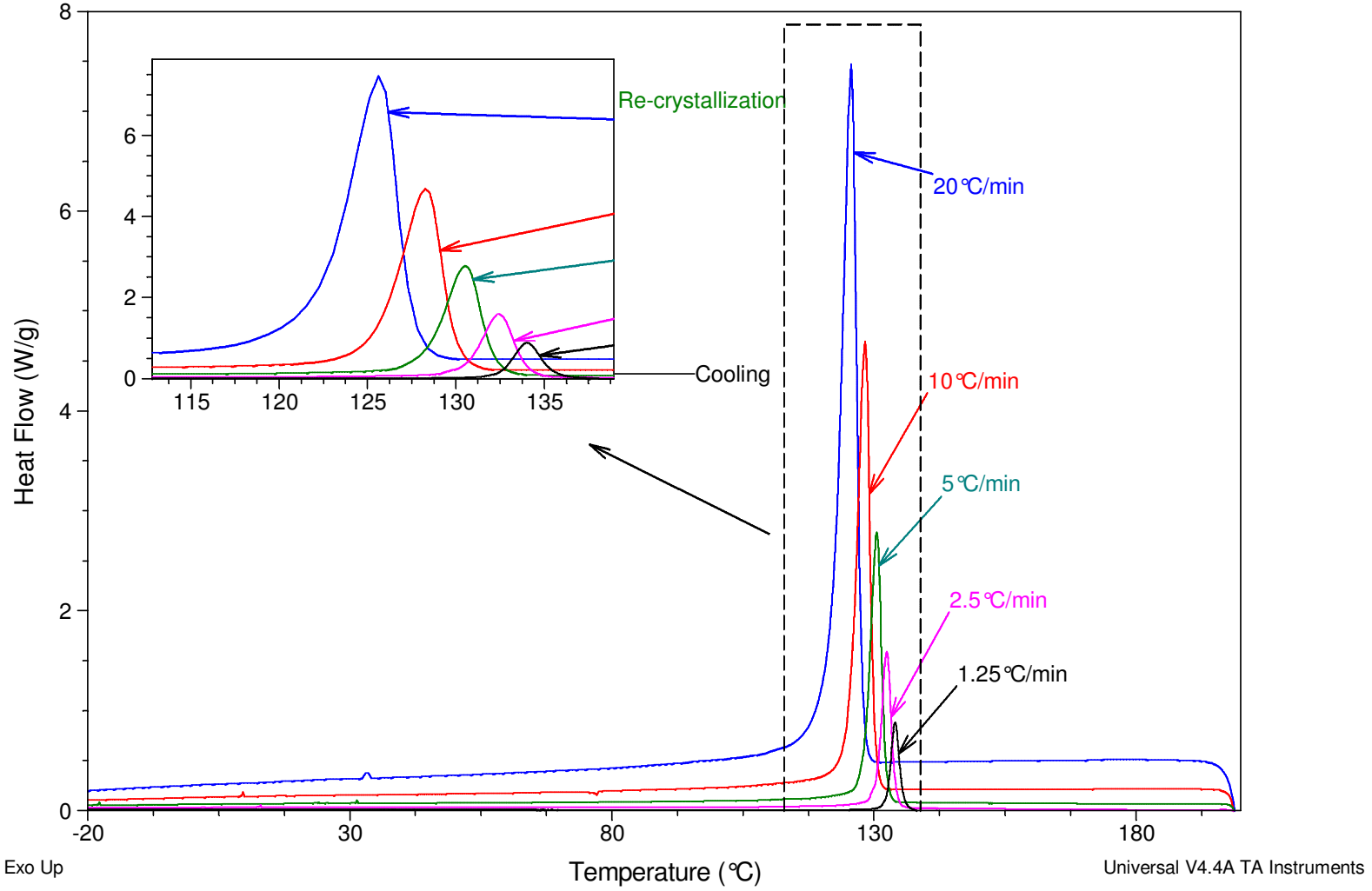
Crystallization

- Crystallization is 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
- Crystallization is a kinetic, two-step process
  - Nucleation
  - Crystal growth

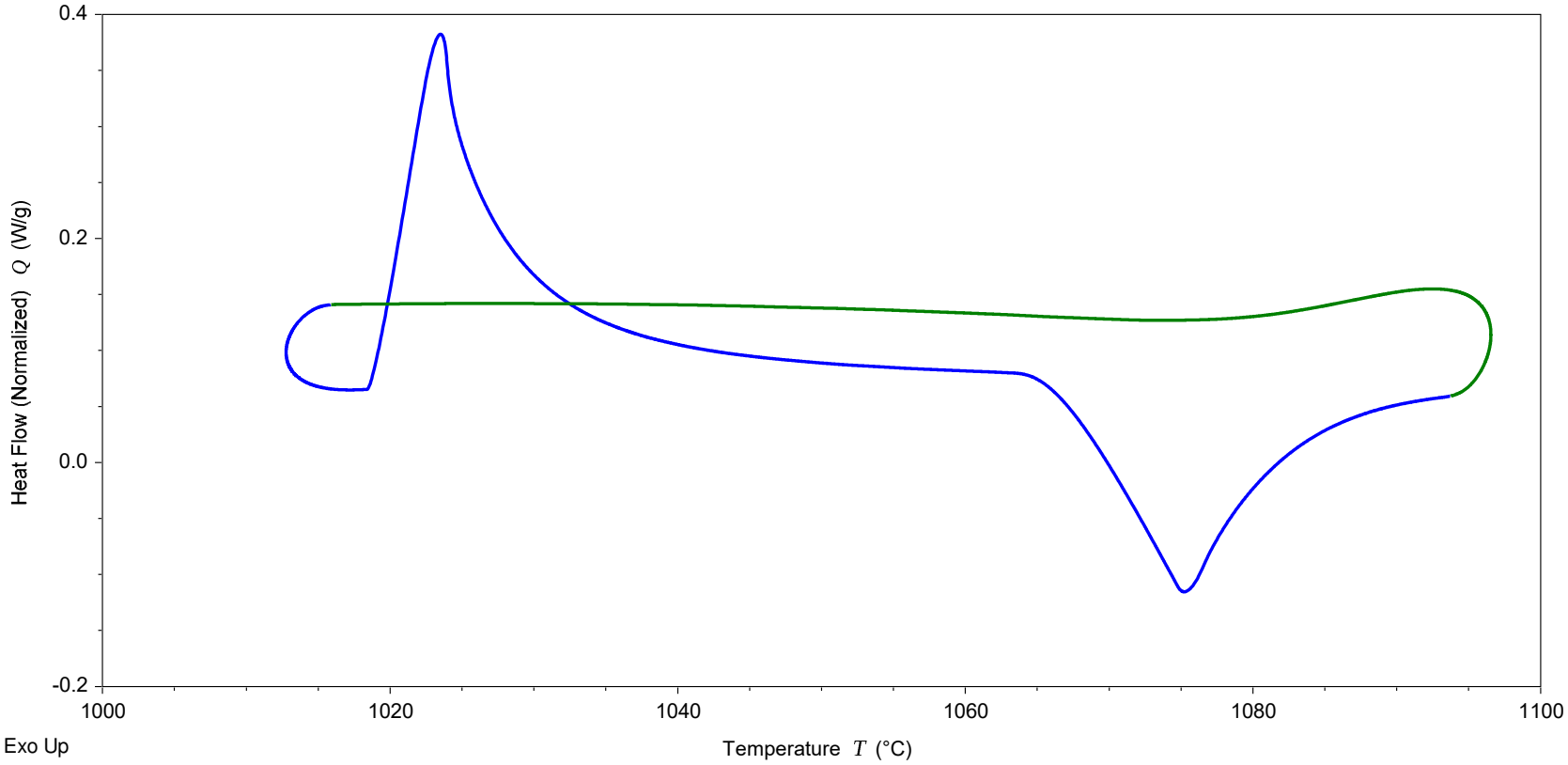
Crystallization

- Crystallization is a kinetic process which is typically studied either while cooling or isothermal, 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

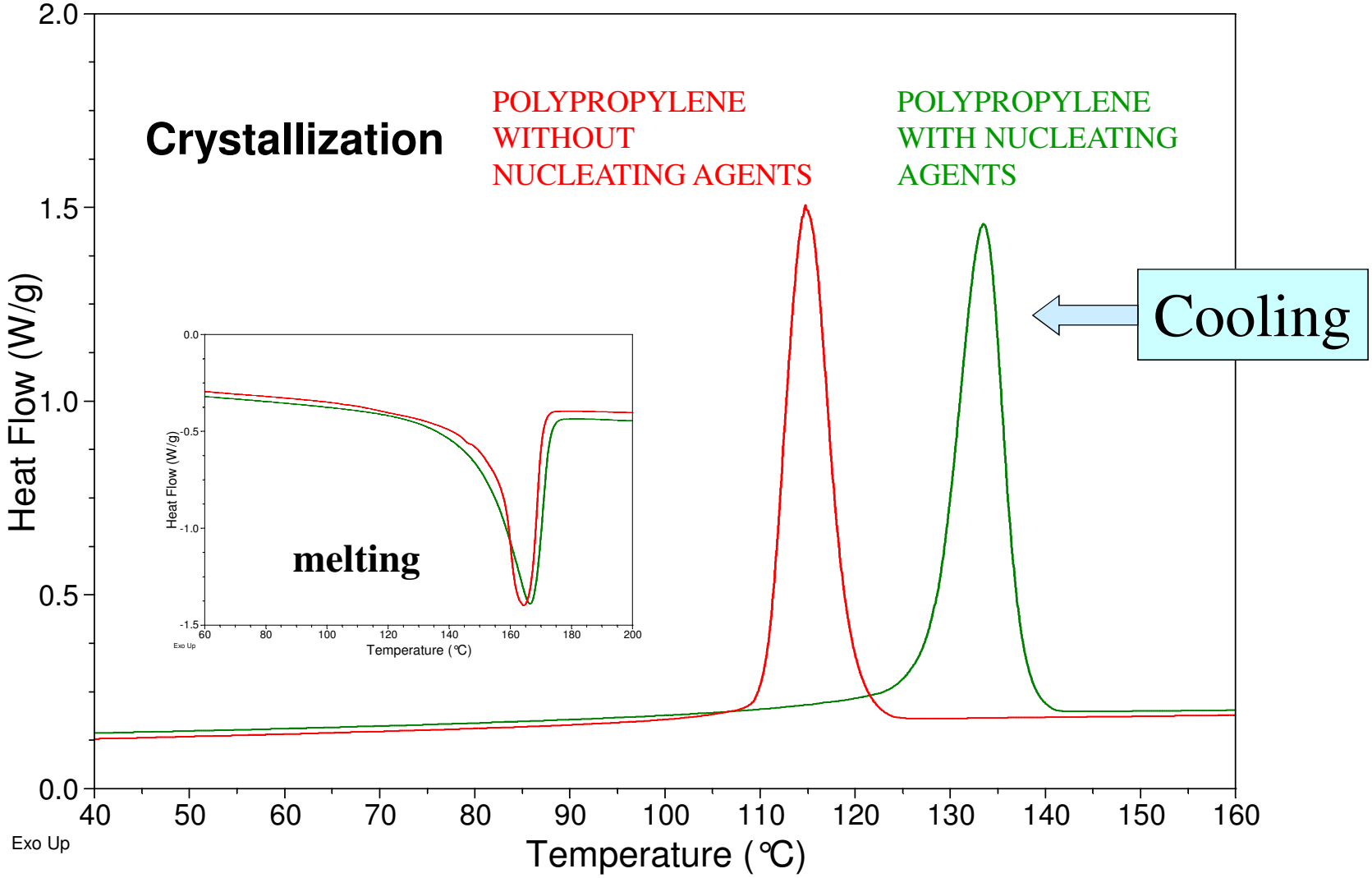
Effect of Cooling Rate



What is and what is happening?

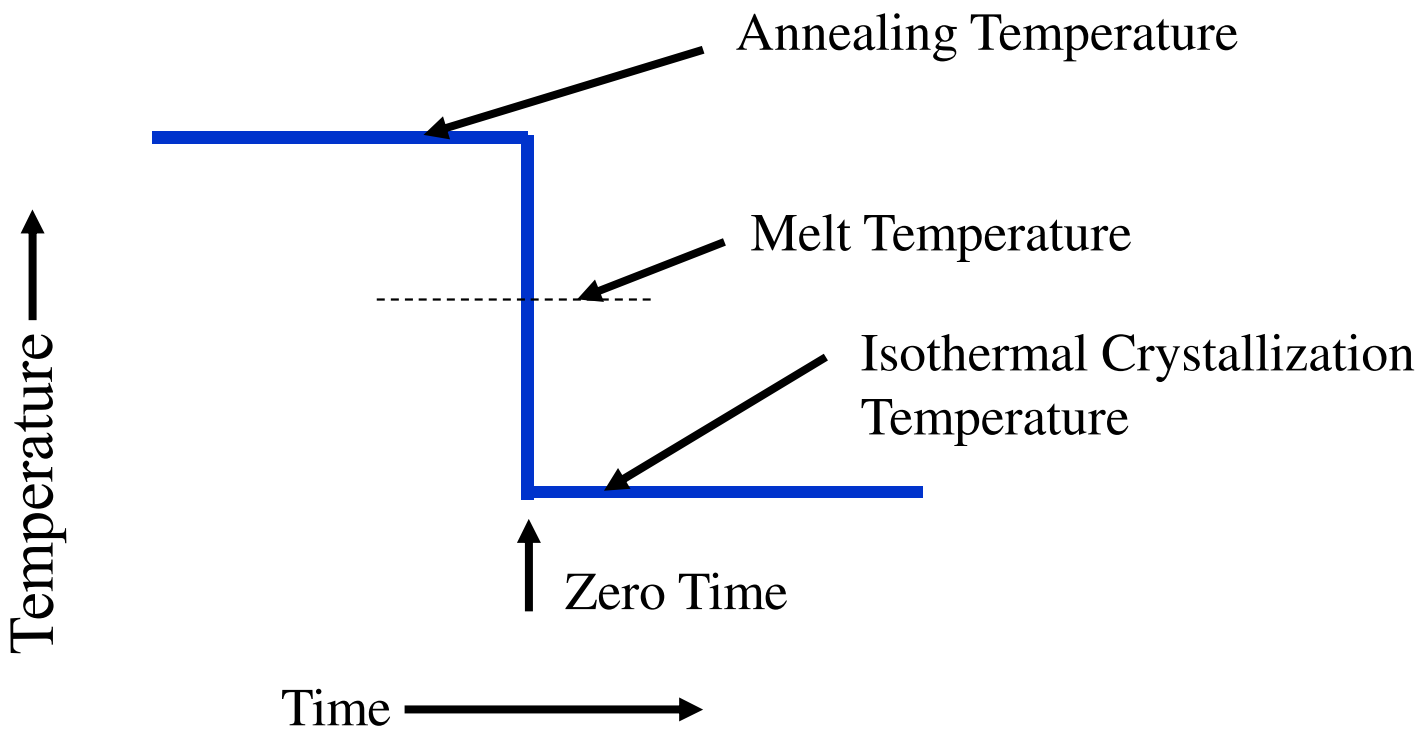


Effect of Nucleating Agents

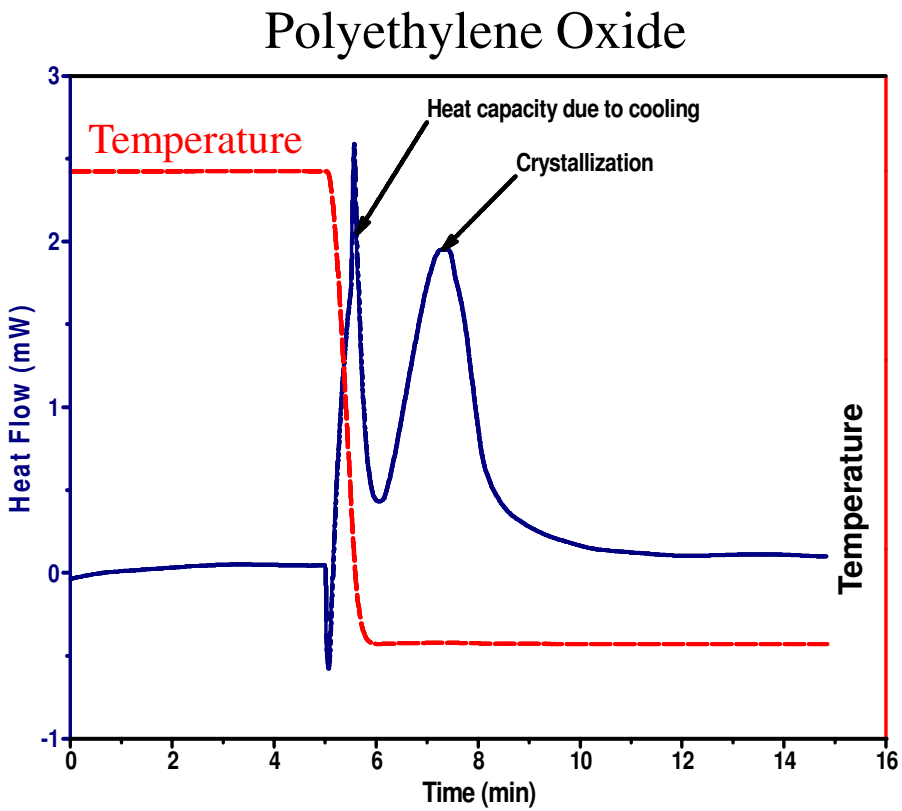


What is Isothermal Crystallization?

- A Time-To-Event Experiment

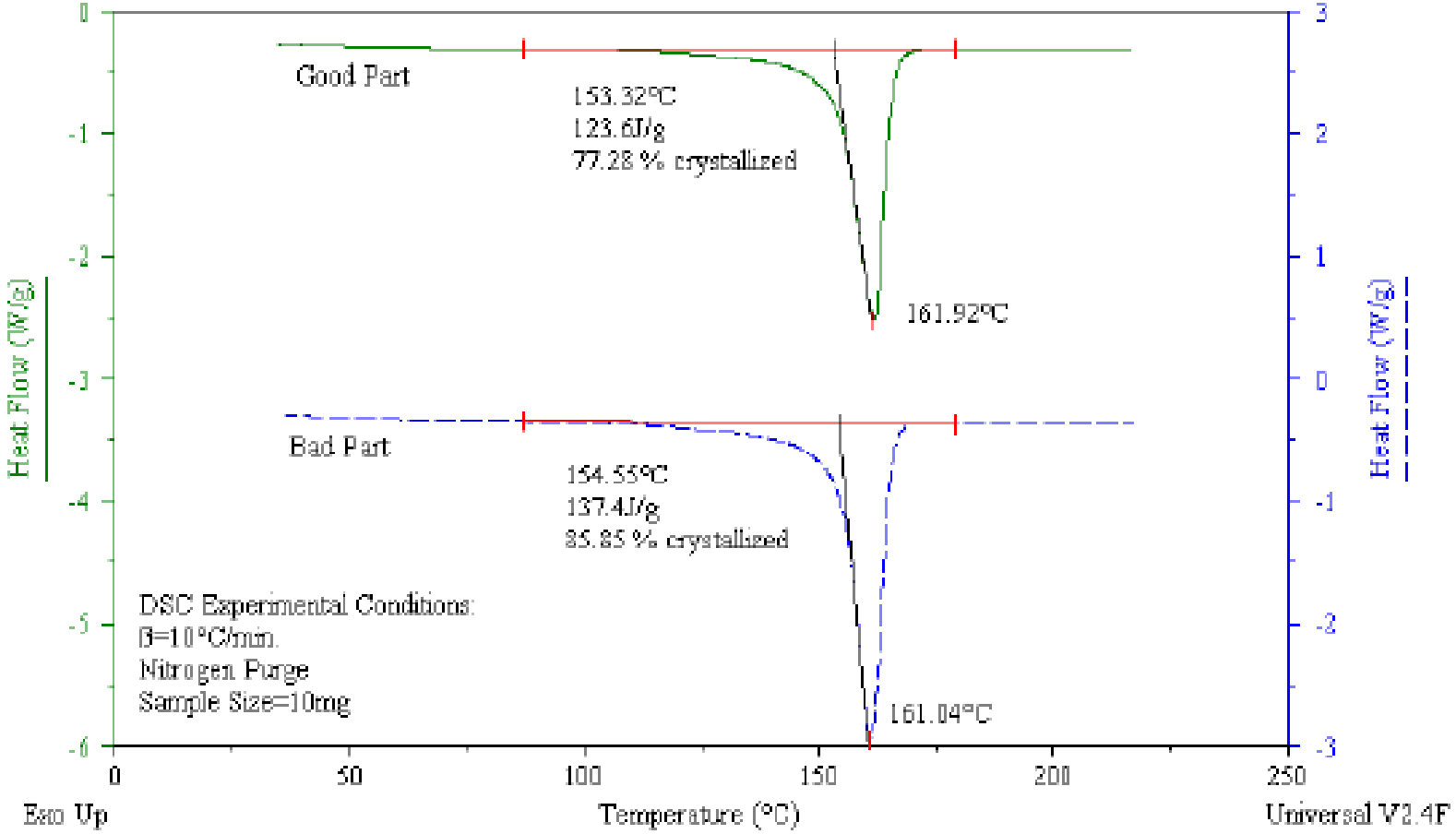


Isothermal Crystallization

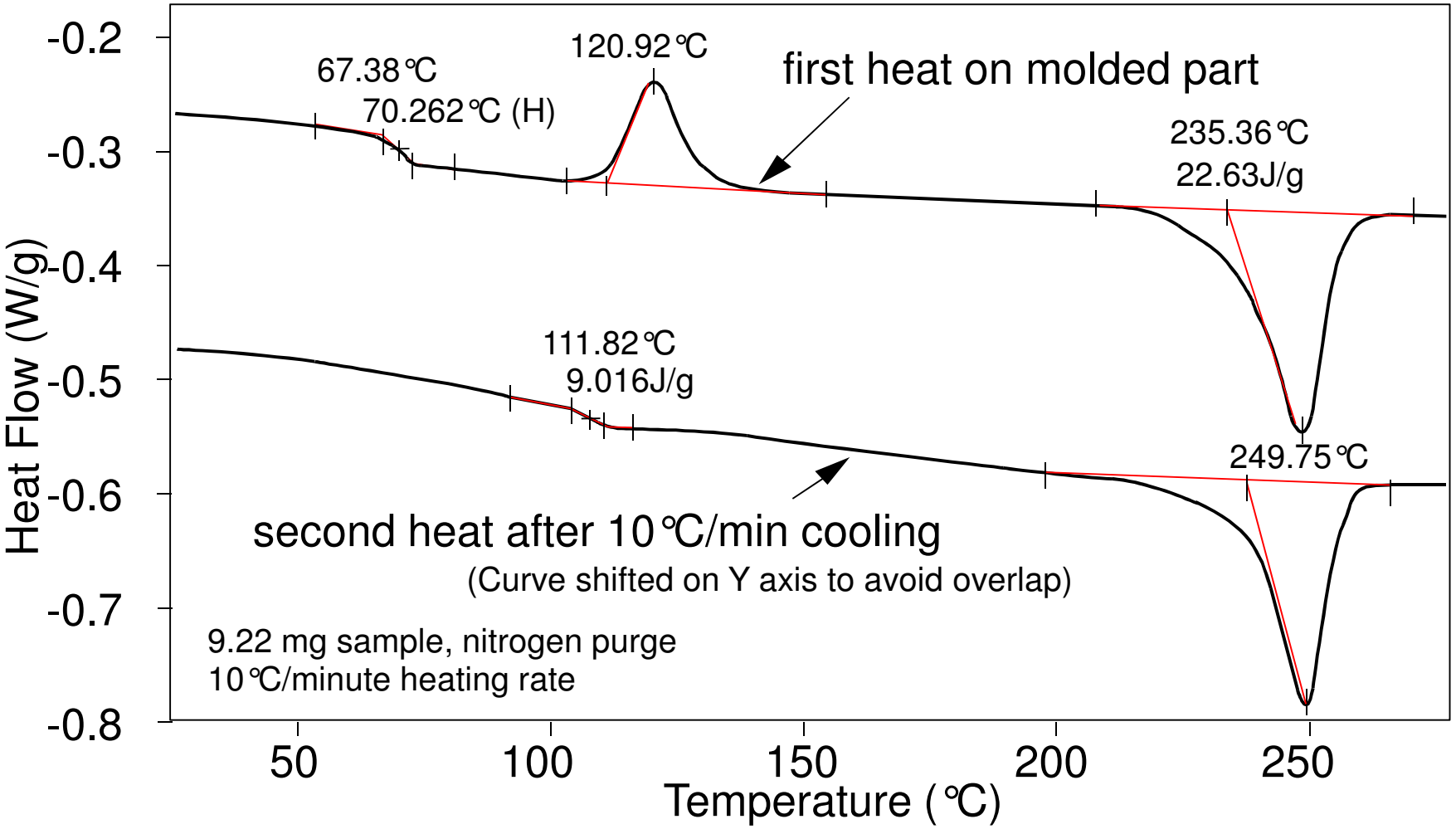


- Time-to-Tmax characterizes differences
- A time-to-event analysis
- Requires rapid cooling and equilibration

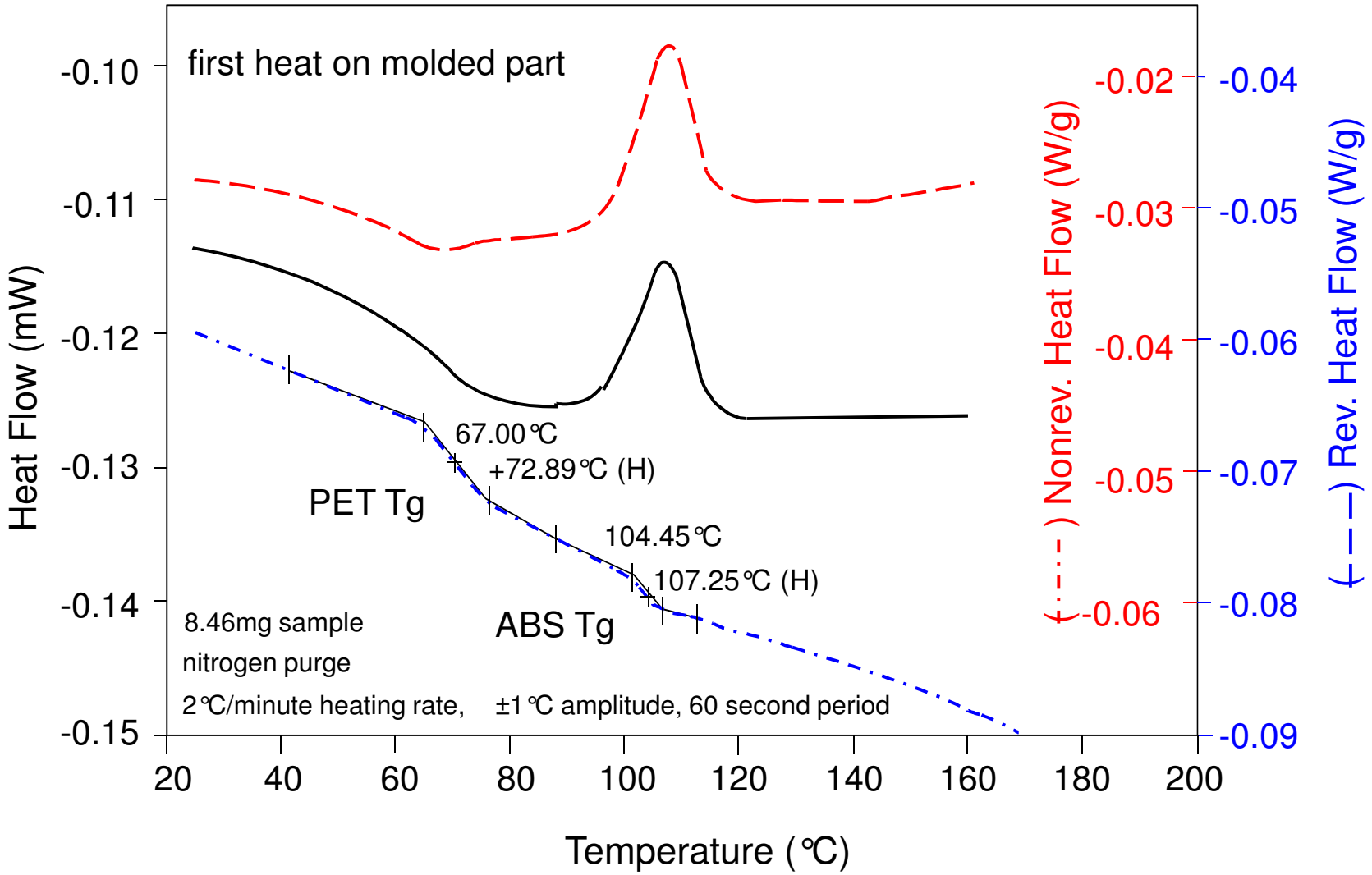
Determination of Crystallinity of a common Automotive Thermoplastic:



PET/ABS Blend - Conventional DSC



PET/ABS Blend - MDSC



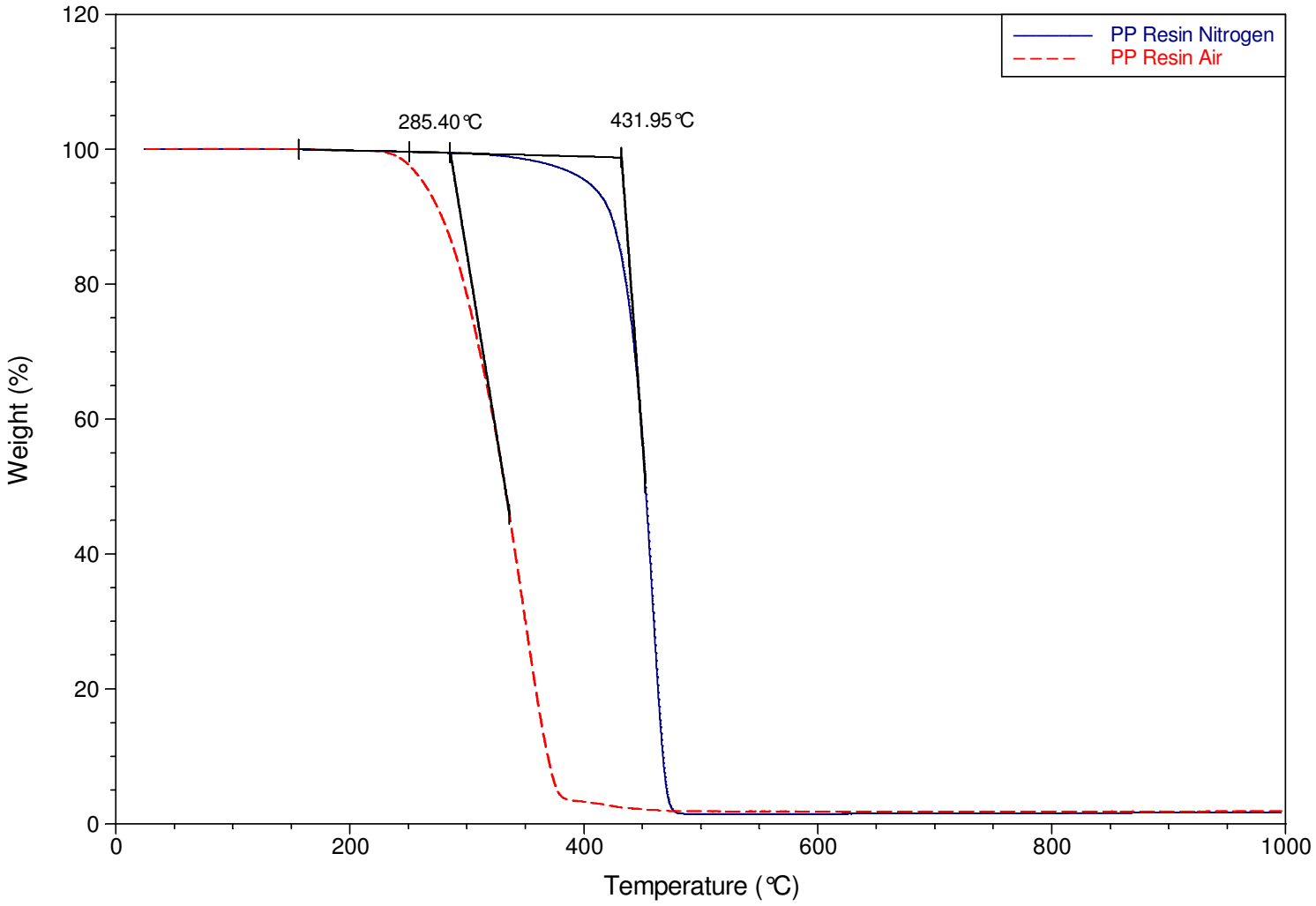
Thermal and Oxidative Stability

- Thermal and Oxidative Stability
  - Can be studied by multiple techniques
  - Studied in inert or oxidizing atmospheres
  - TGA – Best starting point
    - Weight loss or gain
  - DSC
    - Change in heat flow (typically exothermic)
  - Can also see the effect in other techniques like DMA & TMA

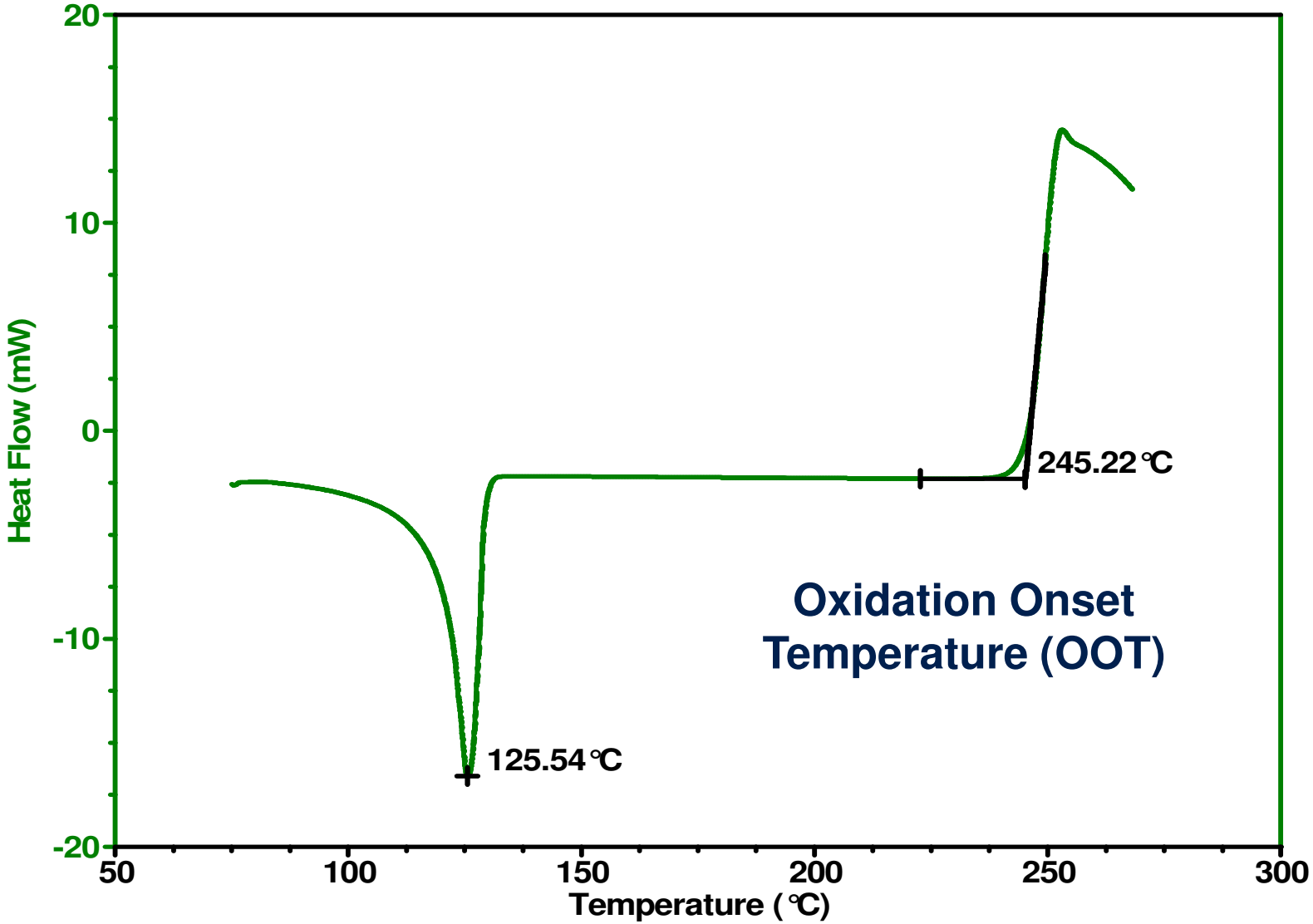
Starting Point for Material Characterization

- First Step – Thermogravimetric Analysis
- Look for:
  - Thermal and Oxidative Stability
  - Volatiles
  - Decomposition Temperature
  - Weight Loss Profile
    - Number of Steps
  - Residue
    - Char/Ash/Filler Presence

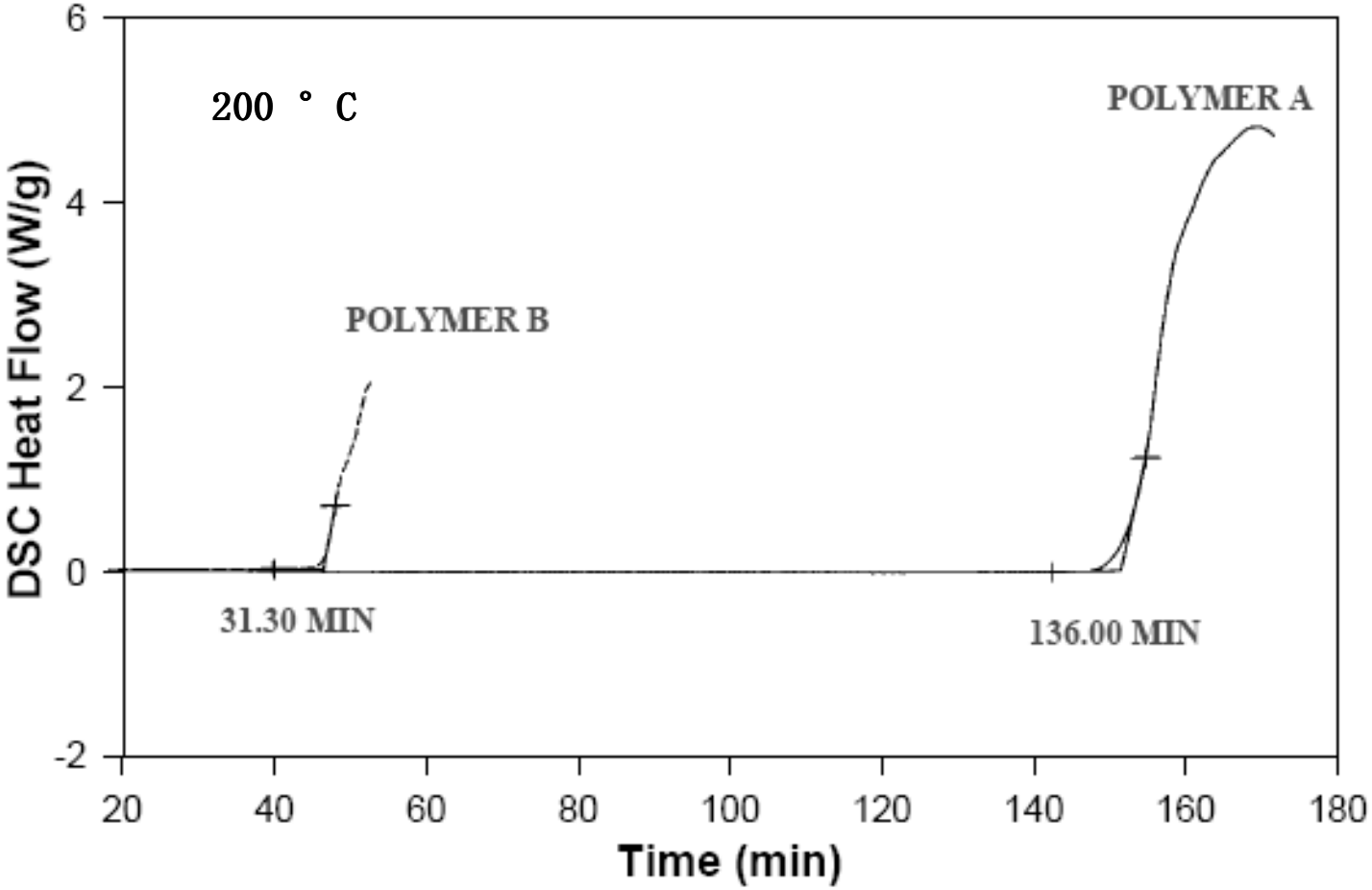
Oxidative Stability - Polypropylene



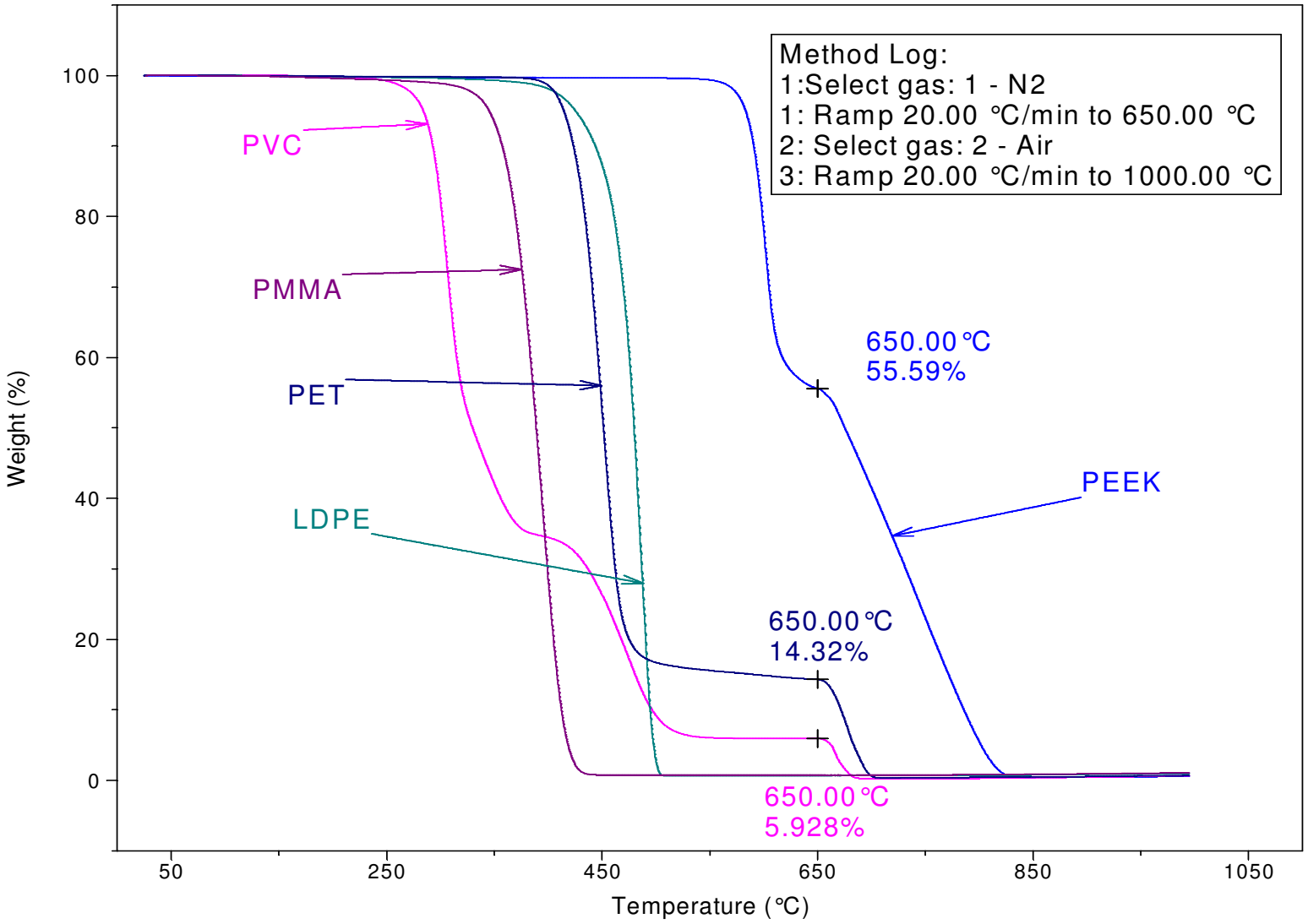
Polyethylene Oxidation Onset Temperature



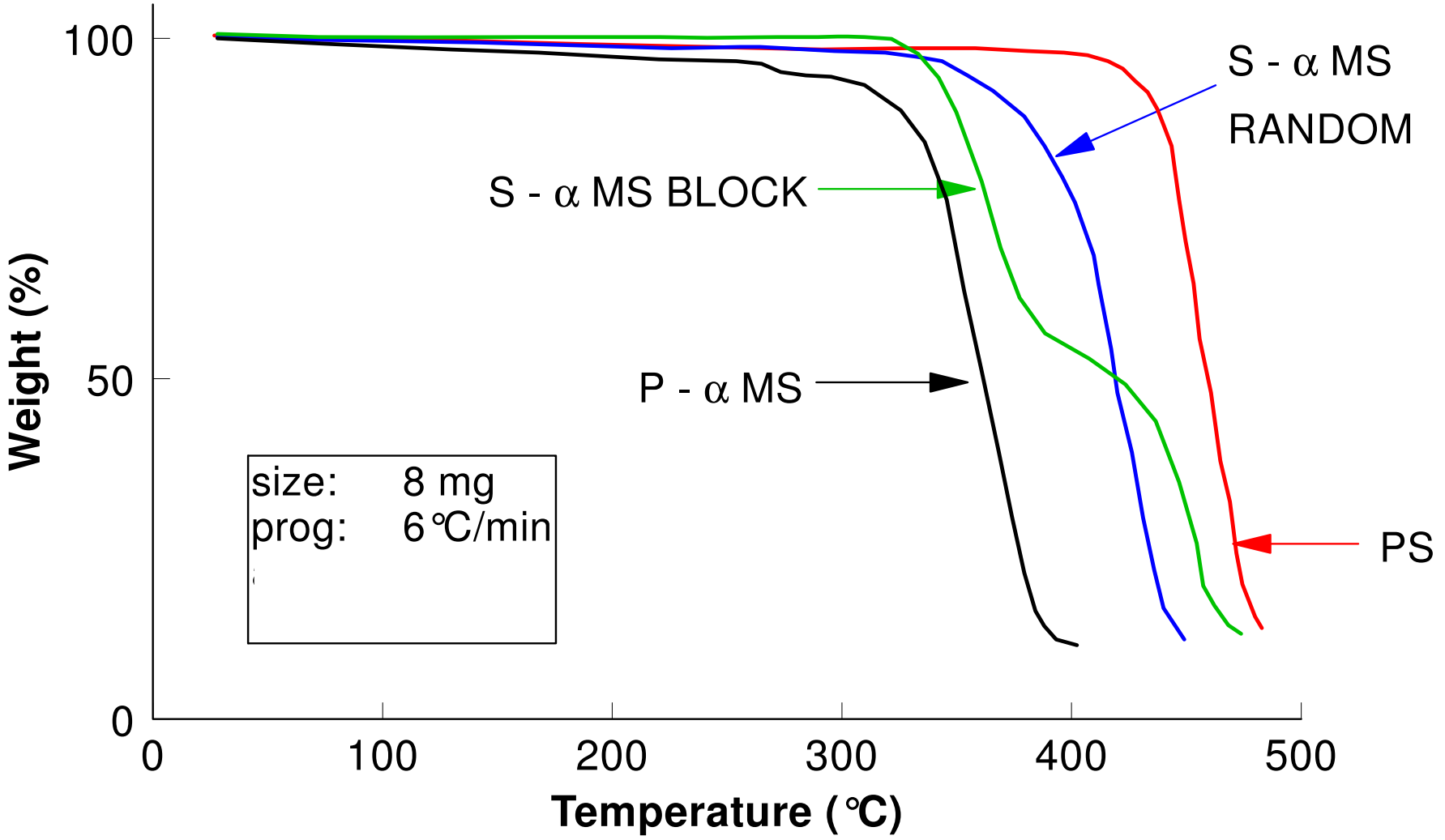
OIT of LDPE of Cable Coatings



Thermal Stability of Polymers



Block versus Random Copolymers

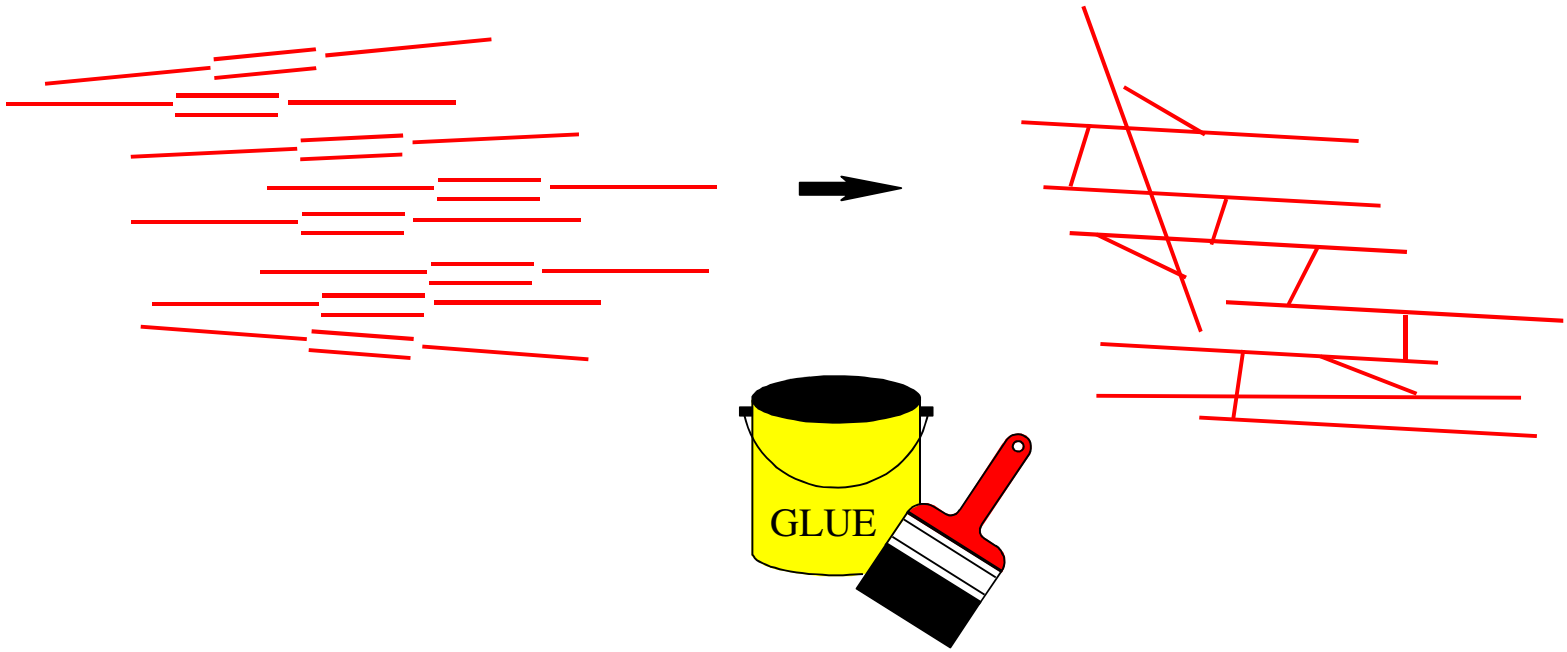


Thermosets

Thermosets

$$A + B \rightarrow C$$

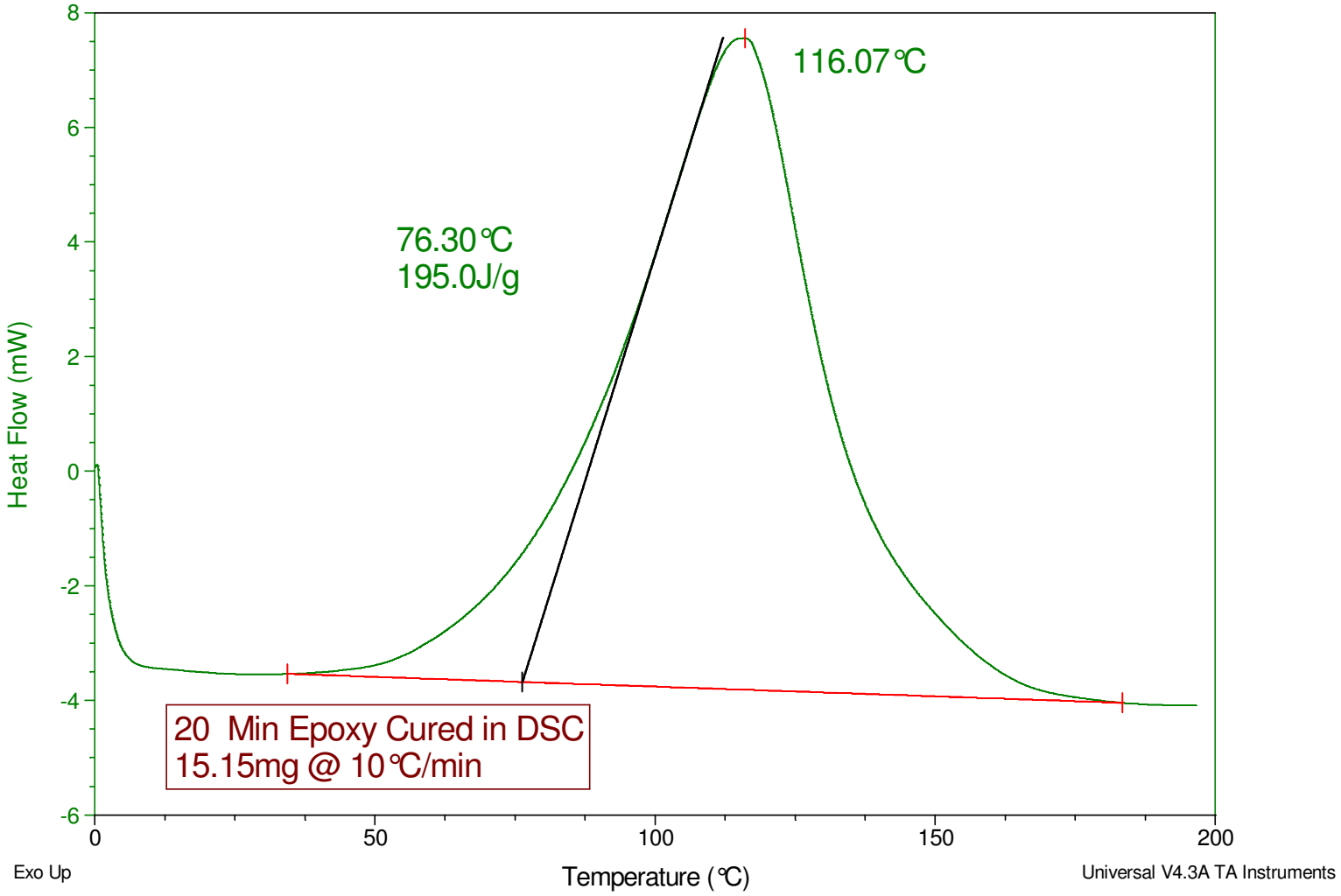
Thermosetting polymers react (cross-link) irreversibly. A+B will give out heat (exothermic) when they cross-link (cure). After cooling and reheating C will have only a glass transition Tg.



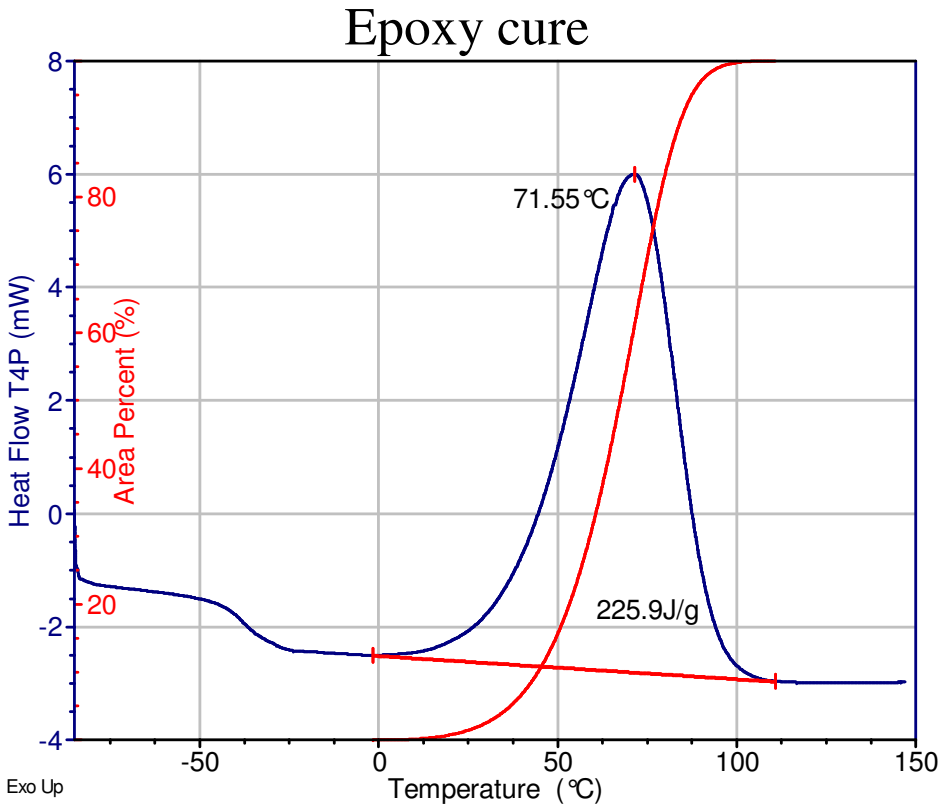
Thermosetting Polymers

- Thermogravimetric Analysis
  - Thermal and Oxidative Stability
  - Composition and Filler
  - Flame Retardants
- Differential Scanning Calorimetry
  - Glass Transition Temperature
  - Heat of Reaction
  - Heat Capacity
  - Extent of cure
- Other Techniques
  - Viscosity
  - Modulus
  - Dimensional Change and CTE
  - Thermal Conductivity
  - Dielectric
  - Others

Curing of a Thermosetting Material



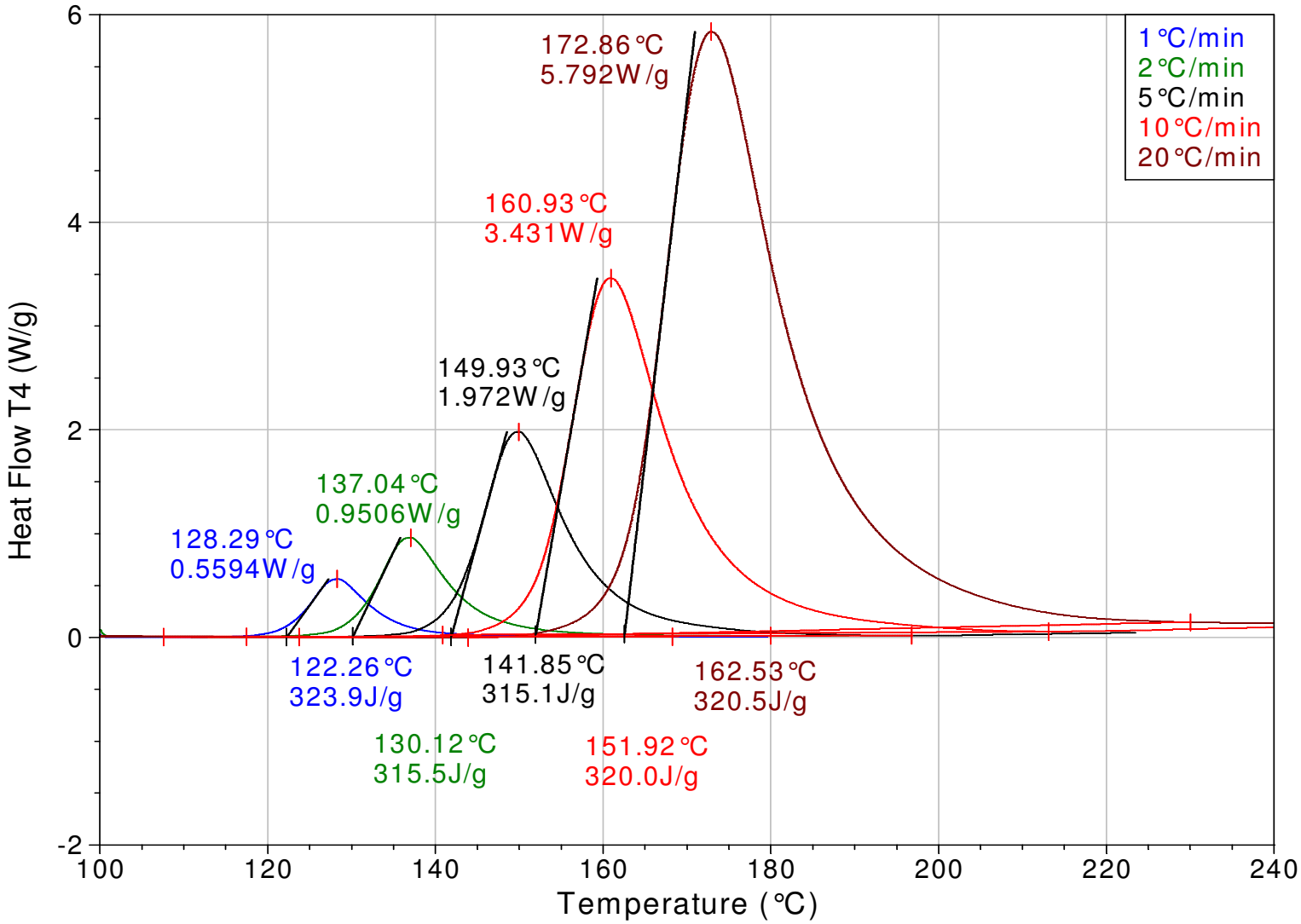
Kinetically Controlled Processes



- Interpretation of peak shape
- Heat flow displacement proportional to reaction rate, dx/dt
- Fraction of peak area is fraction reacted, x
- Kinetic equation:

  $dx/dt = fn(x) * Ke^{Ea/RT}$
- Predict reaction rates

Effect of Heating Rate

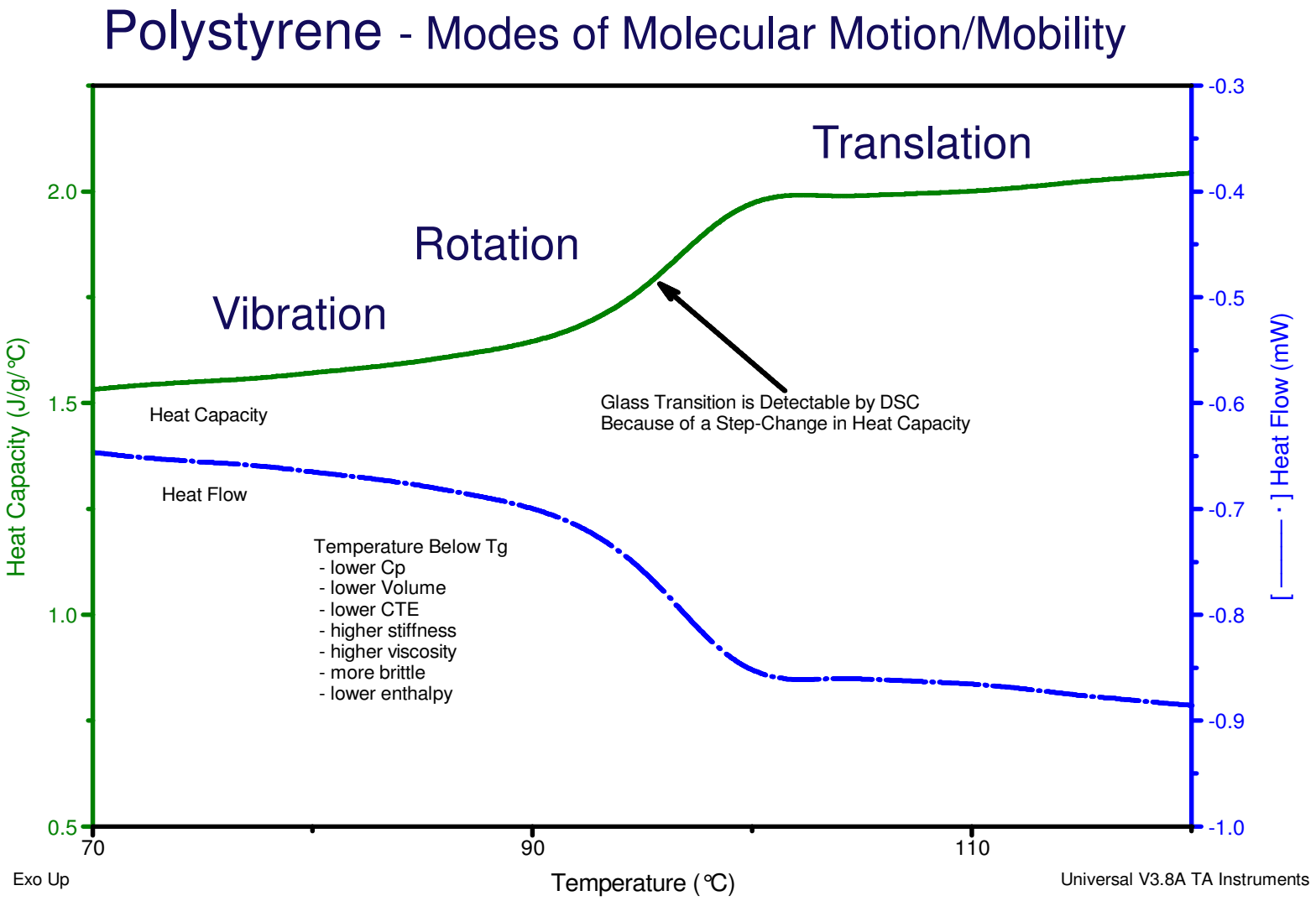


Amorphous Structure

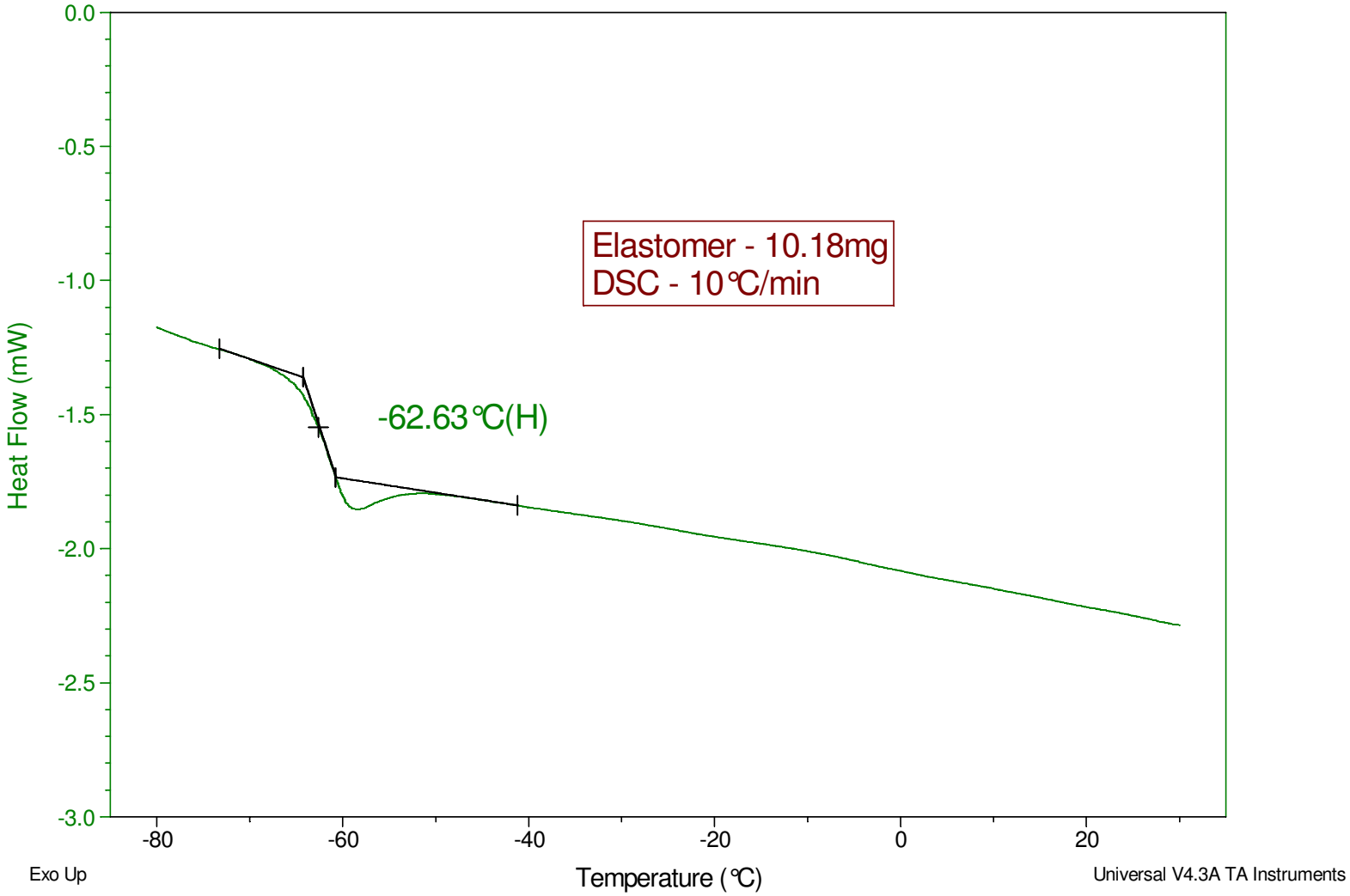
Characterization of Amorphous Structure

- 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 properties and reactivity

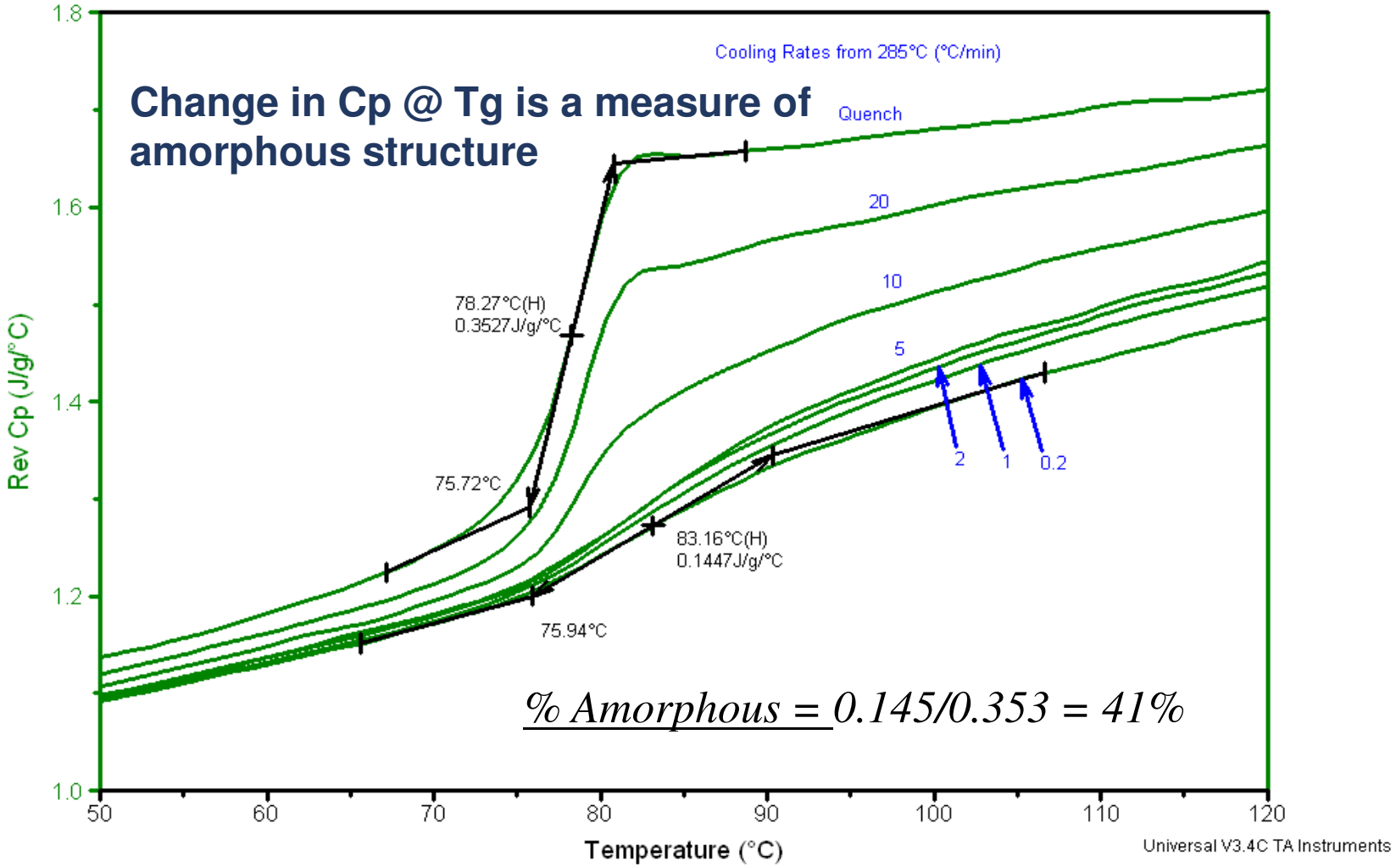
Changes at the Tg



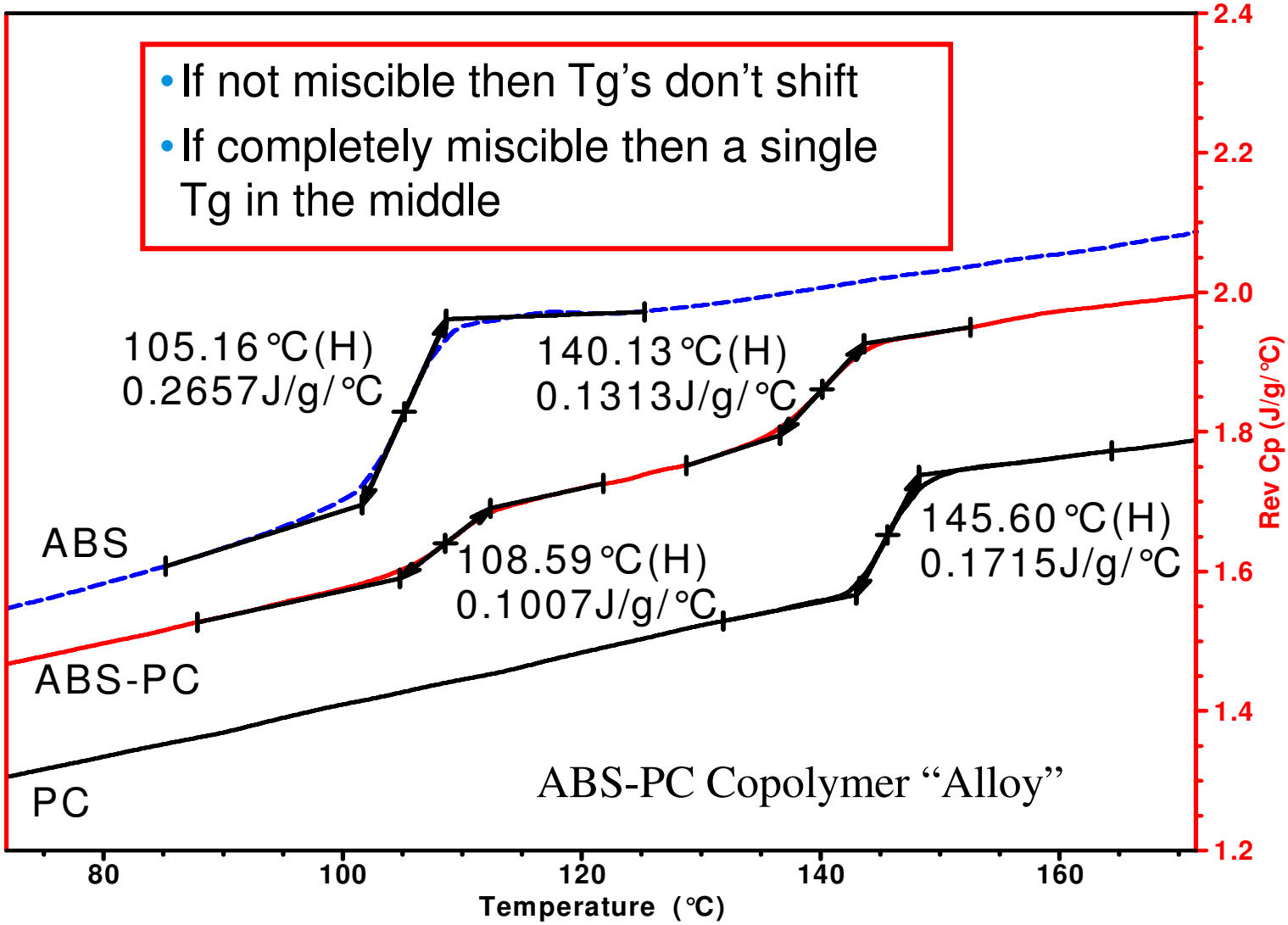
Elastomer Tg by DSC



Quantification of Amorphous Structure



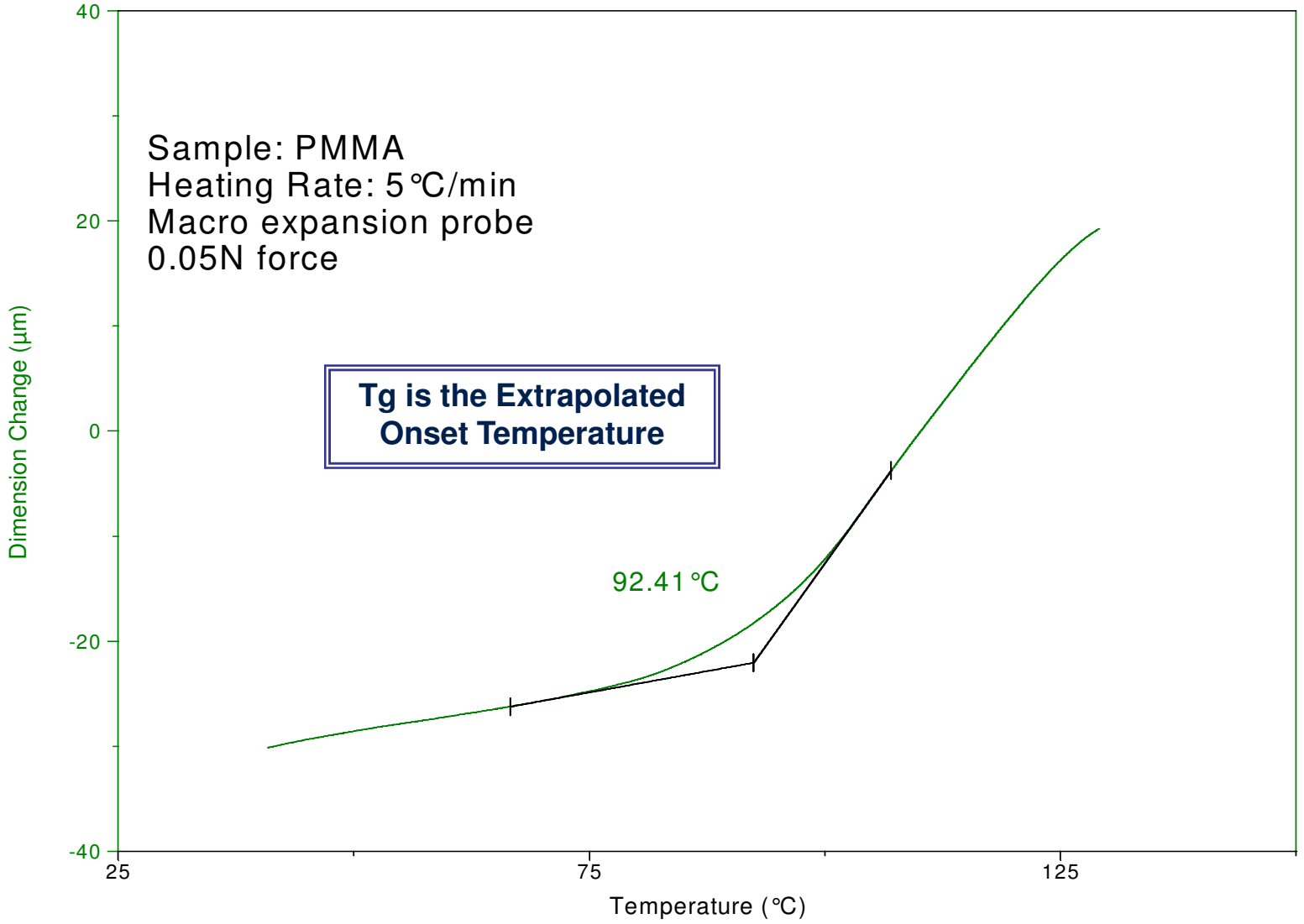
Partially Miscible Amorphous Phases



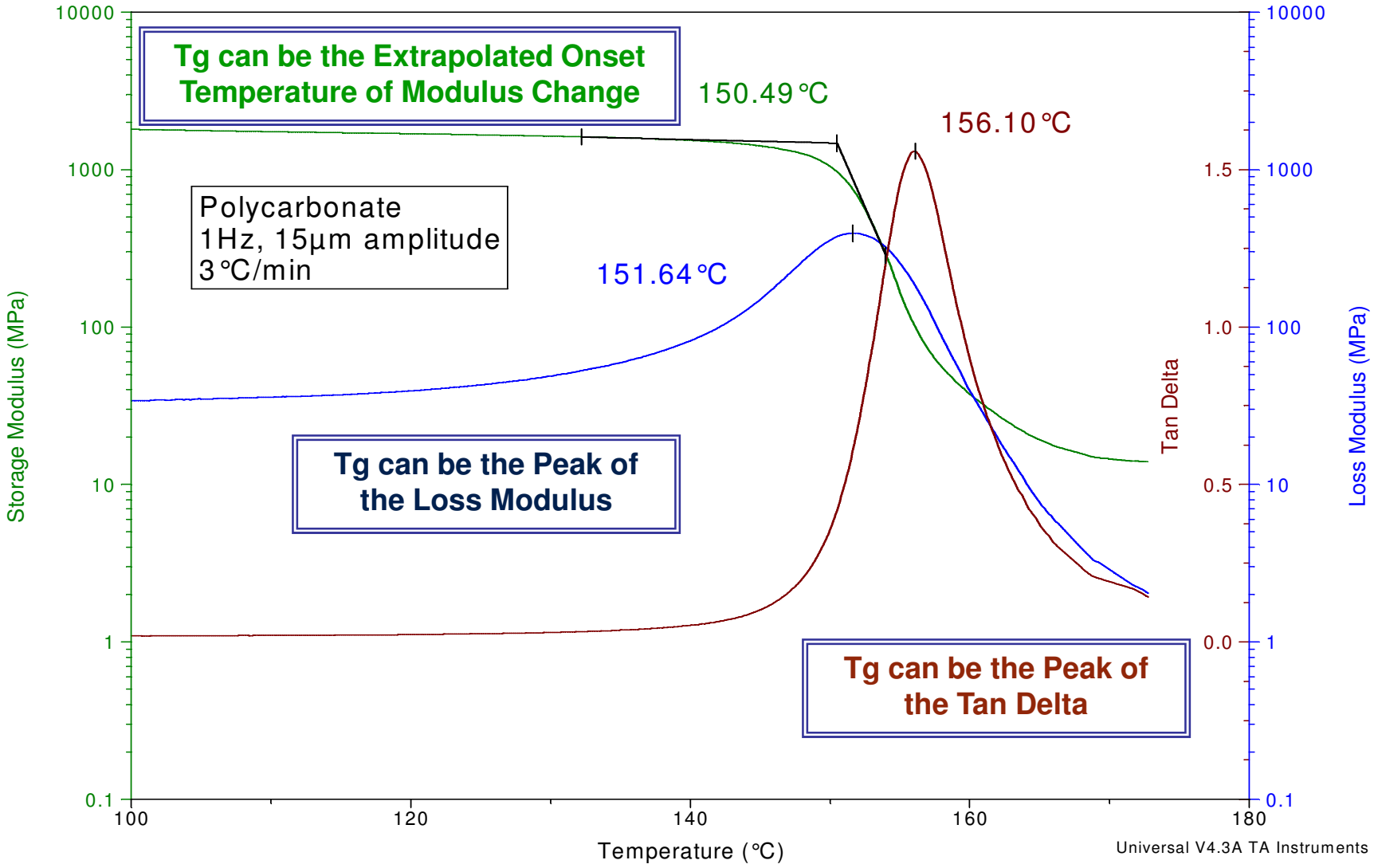
Glass Transition by TMA and DMA

- Thermomechanical Analysis
  - More sensitive than DSC by over 10x
  - Get CTE measurement as well
  - Use MTMA™ to separate kinetic events that may mask Tg
- Dynamic Mechanical Analysis (DMA)
  - Much more sensitive than DSC by over 1000x
  - Get storage and loss modulus
  - Study the effect of frequency

Glass Transition Temperature by TMA



Glass Transition Temperature by DMA

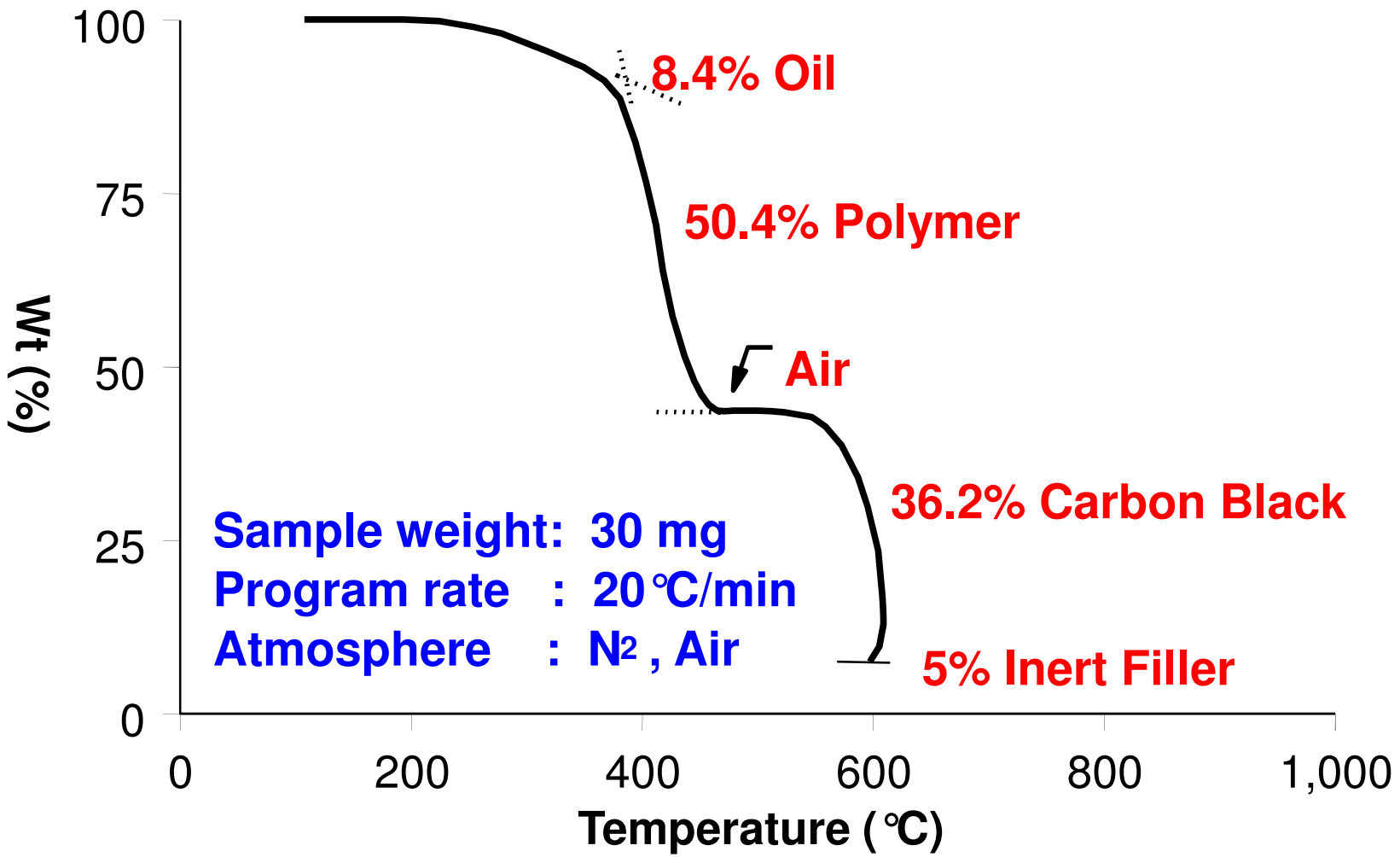


Overview of DSC and TGA for Rubber and Elastomers

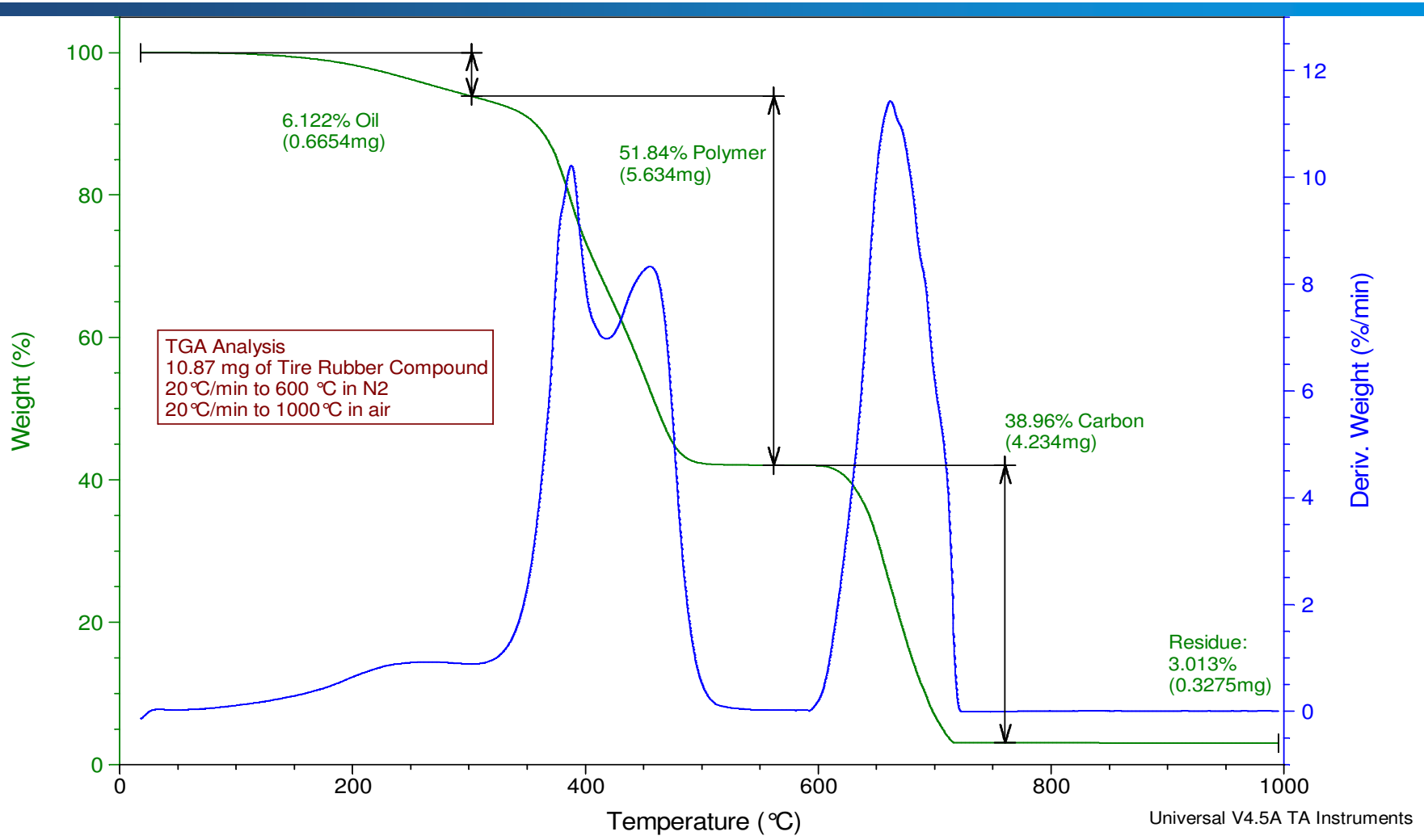
Thermogravimetric Analysis (TGA)

- TGA measures amount and rate of weight change vs. temperature or time in a controlled atmosphere
- Used to determine composition and thermal stability up to 1000°C (55 & 550); 1200°C (Discovery 5500) & 1500°C (650 SDT)
- Characterizes materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration

Styrene-Butadiene Rubber Analysis

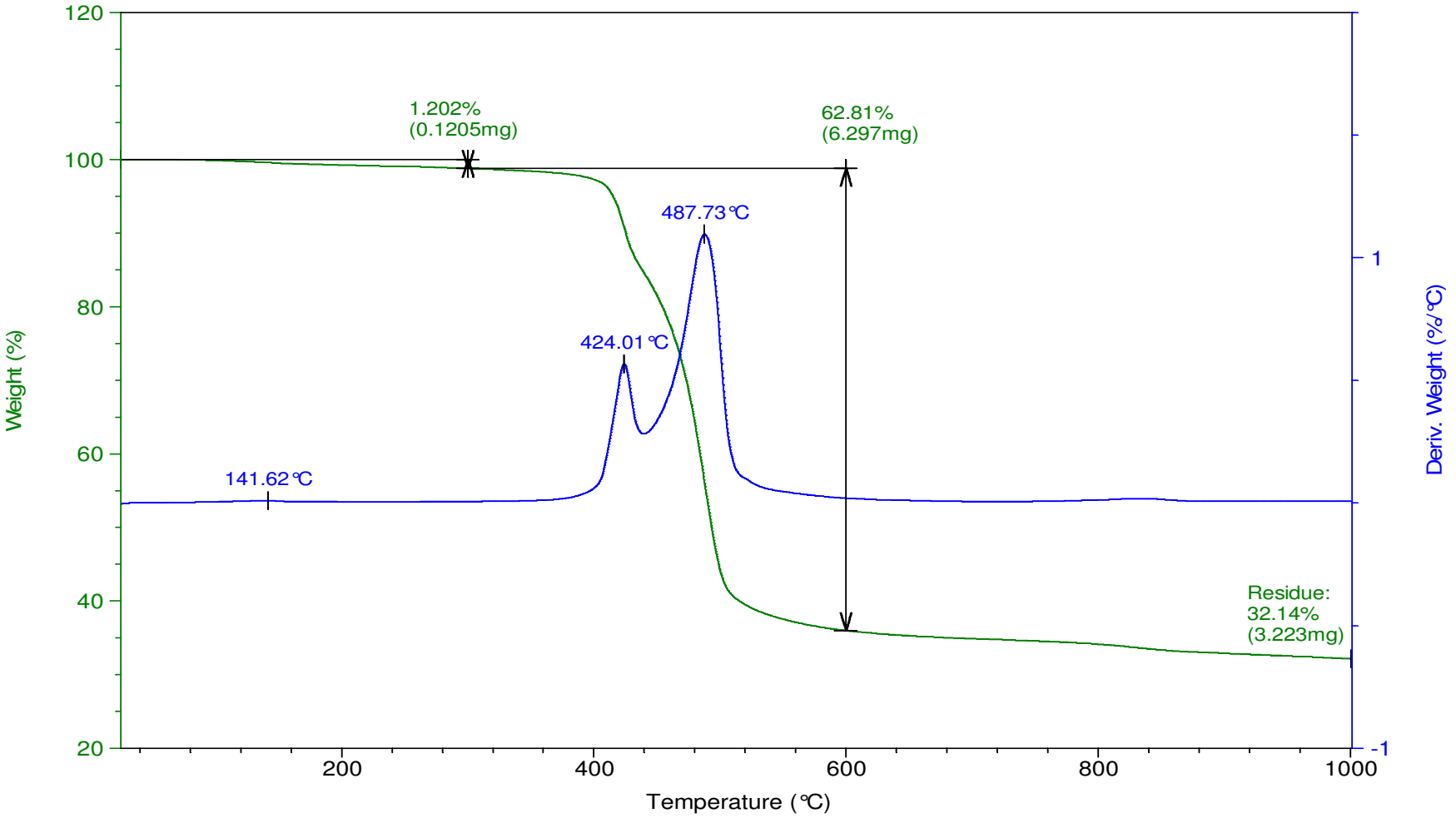


TGA of Tire Rubber



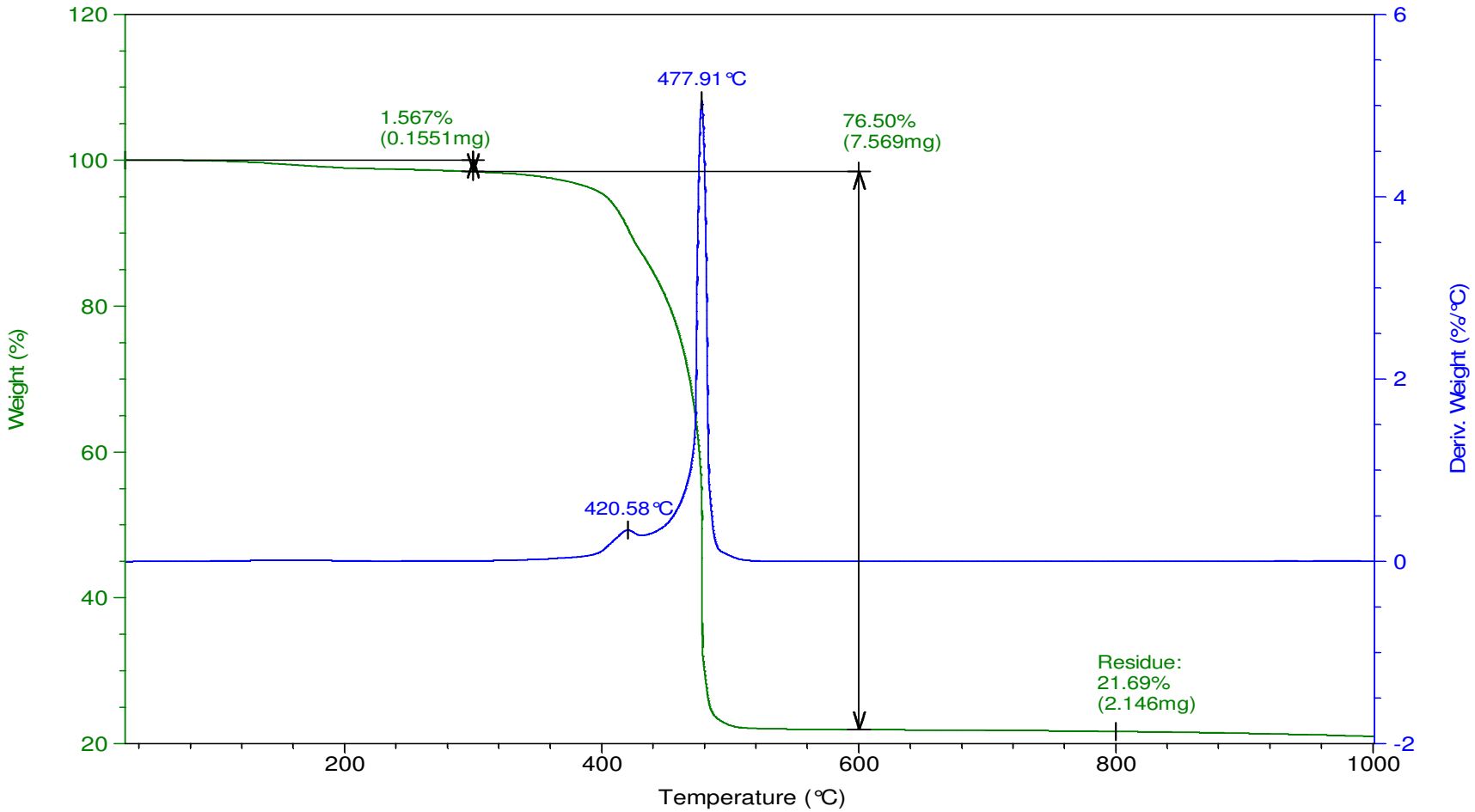
TGA of Rubber in Nitrogen

Sample: Rubber 10C/min N2 - Green Colorant
Size: 10.0264 mg

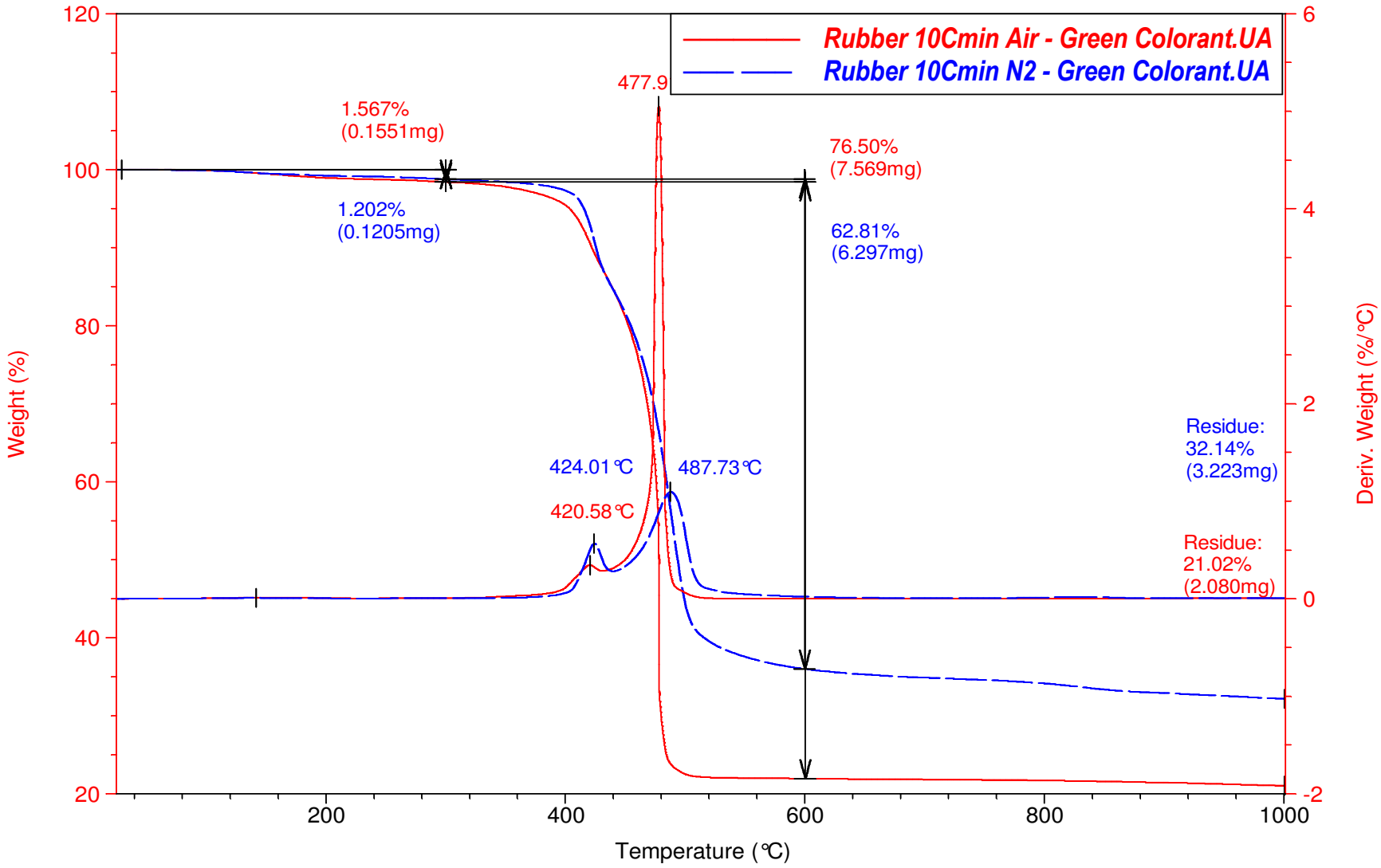


TGA Rubber in Air

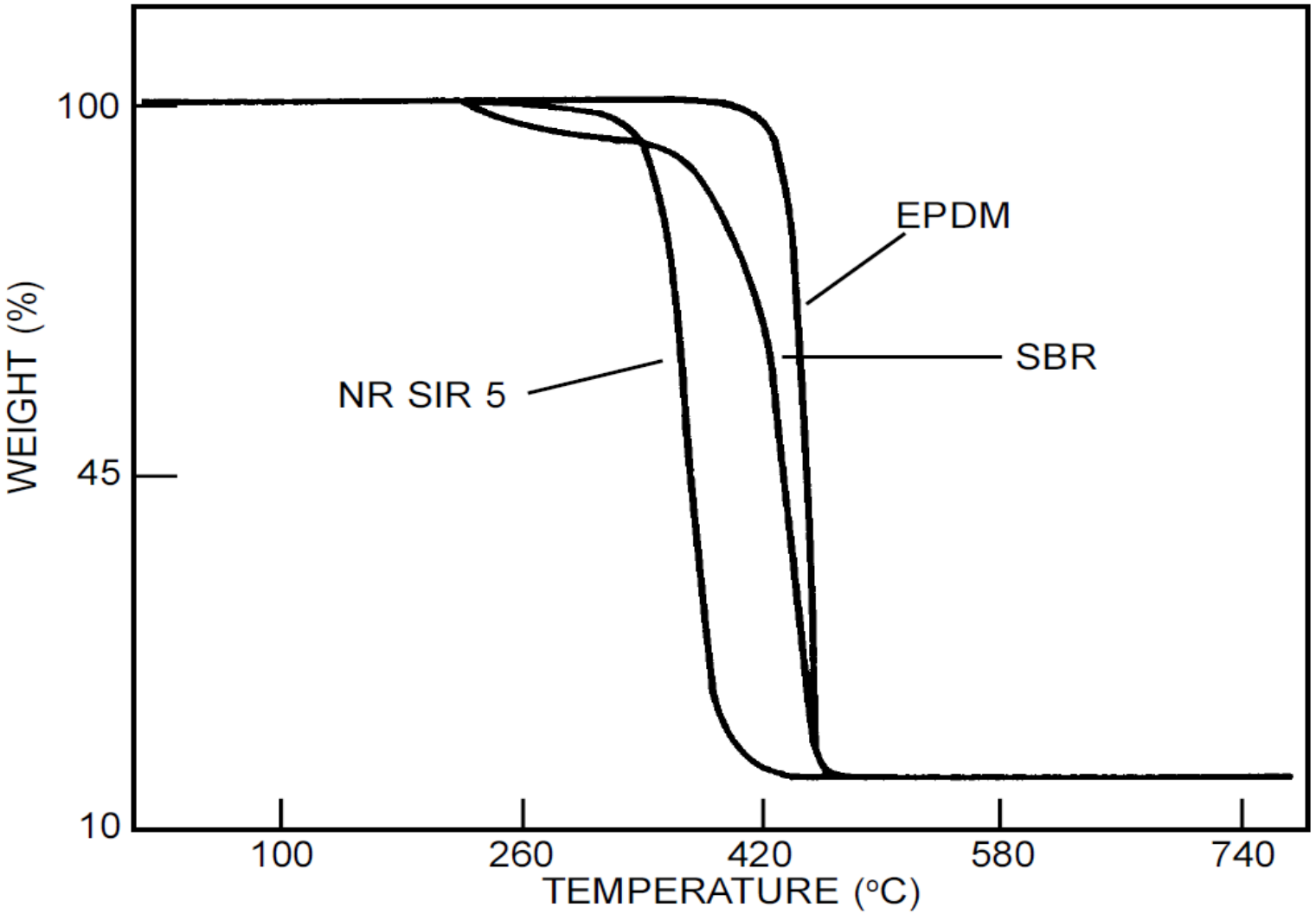
Sample: Rubber 10C/min Air - Green Colorant
Size: 9.8941 mg



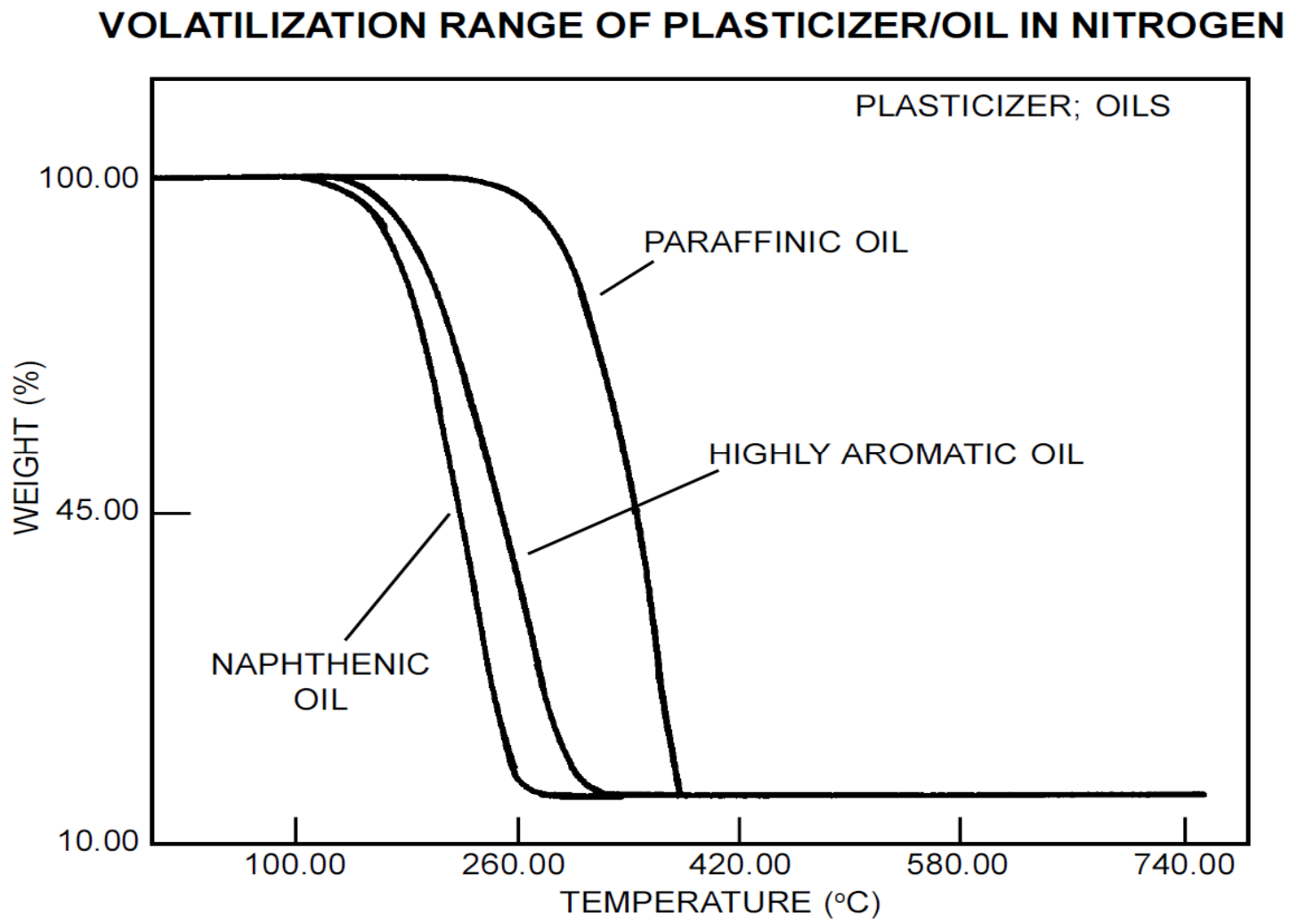
TGA Rubber in Air vs Nitrogen



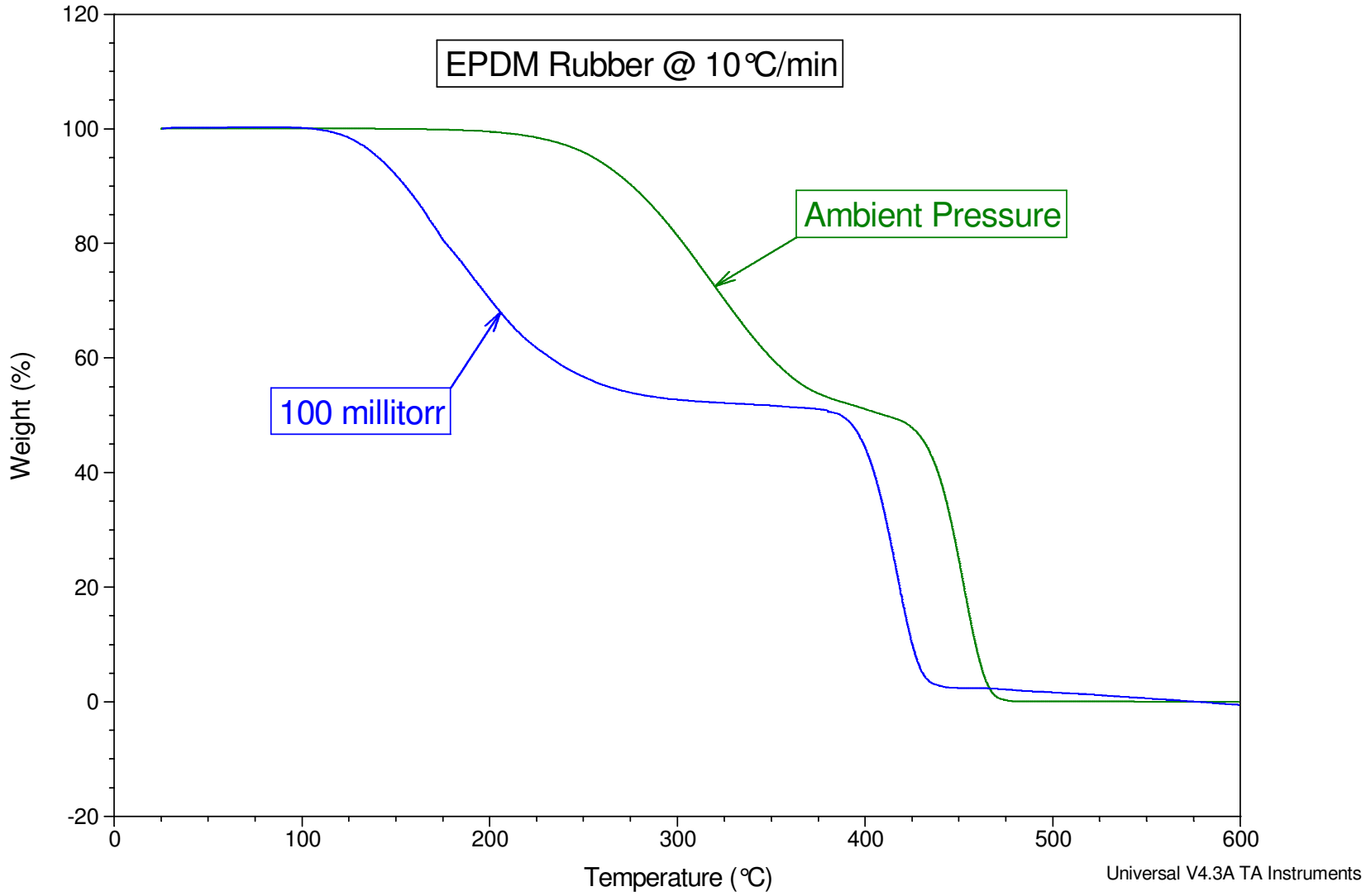
Decomposition of Elastomers in Nitrogen



Volatilization of Plasticizers/Oils



Vacuum Can Improve Separation



Summary

- Thermal analysis is widely used in the automotive industry
- The techniques used to characterize the automotive materials are universally applicable to other industries since they use same materials
- So let's look at each of the common thermal-analytical materials in greater detail

DISCOVER the WORLD'S FINEST line of
DIFFERENTIAL SCANNING CALORIMETERS

TA Instruments DSC Models

DSC 25
DSC 250
DSC 2500

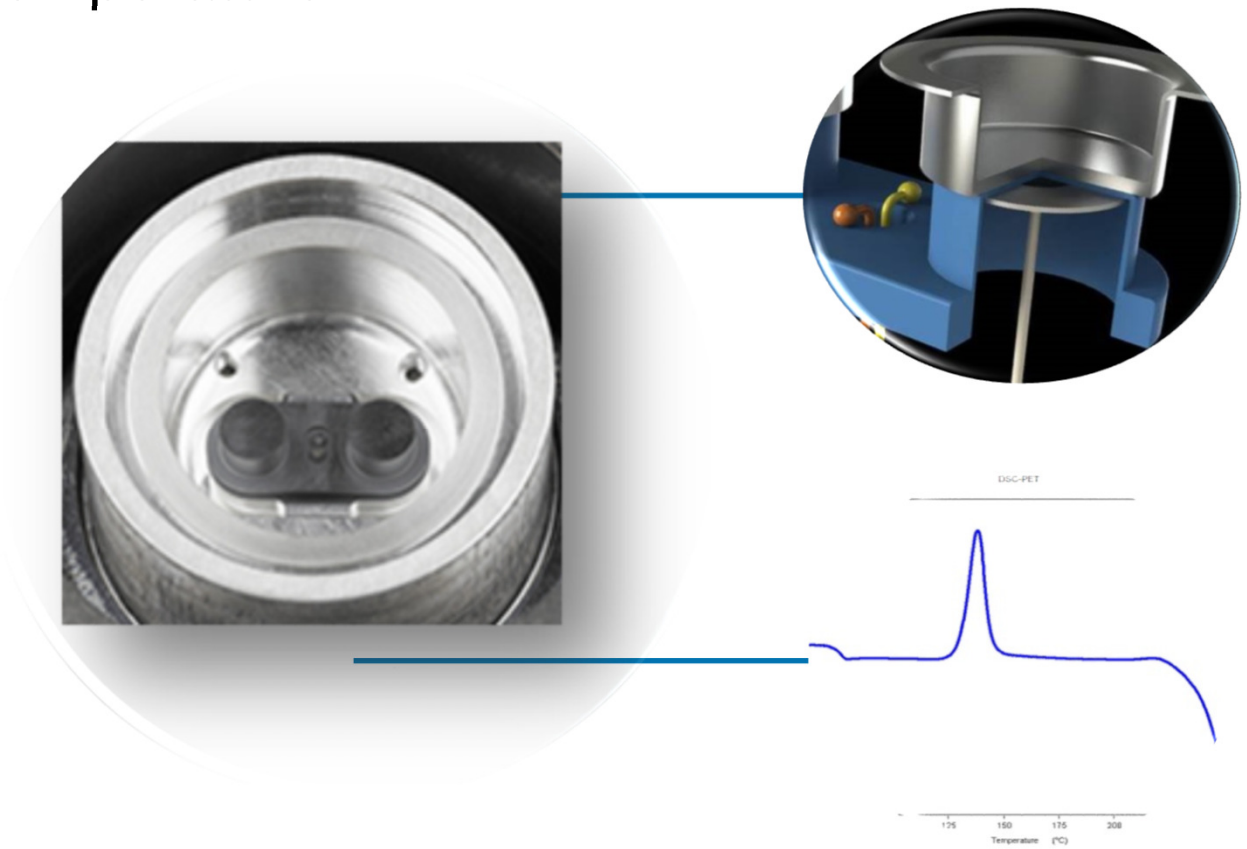
AutoQ20

Q2000

Discovery 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



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.

Instrument setup factors affecting calibration

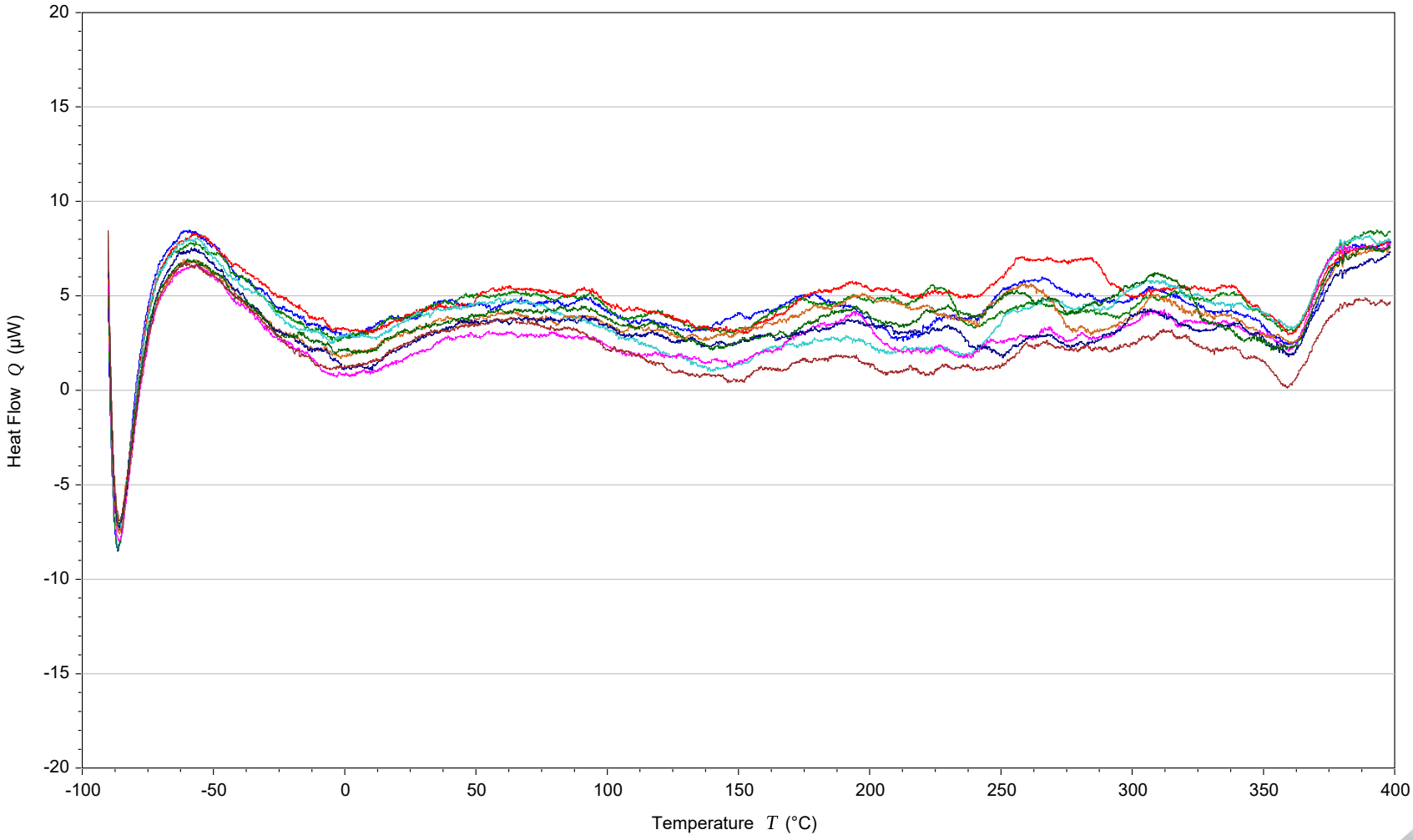
- Purge Gas
  - Re-calibrate baseline/Tzero, temperature and cell constant
  - Thermal conductivity of helium ≠ Thermal conductivity of nitrogen/air/oxygen ≠ Thermal conductivity of argon
- Cooling Accessories
  - Re-calibrate baseline/Tzero, temperature and cell constant
  - The position of the cooling 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

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)

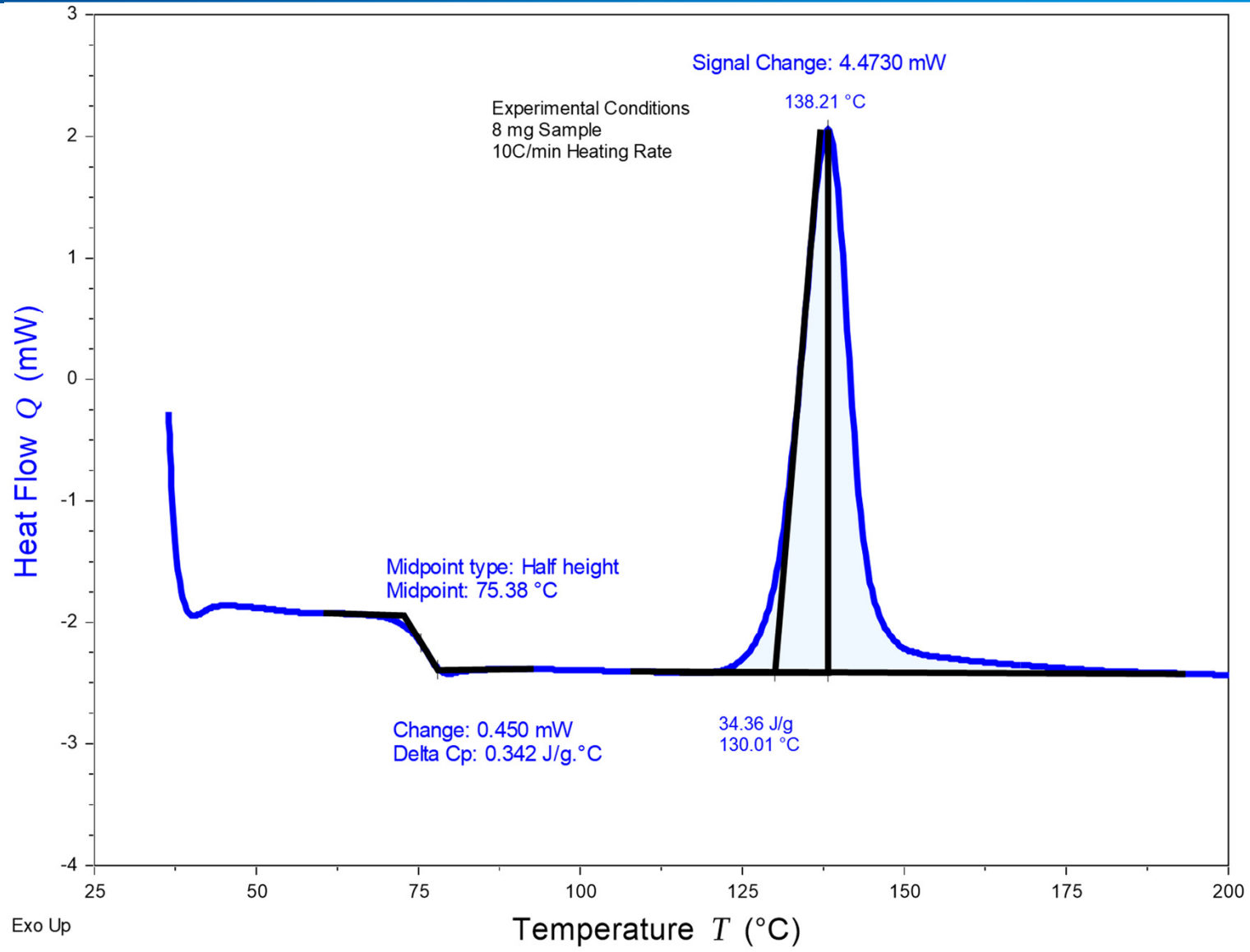
- Verification
  - Determine how often to verify data
  - Run a reference material as a sample (in standard mode)
  - Compare results vs literature values
  - If results are within your tolerance – system checks out and does not need re-calibration
  - If results are out of tolerance, then re-calibrate

Empty Cell Baseline – DSC2500

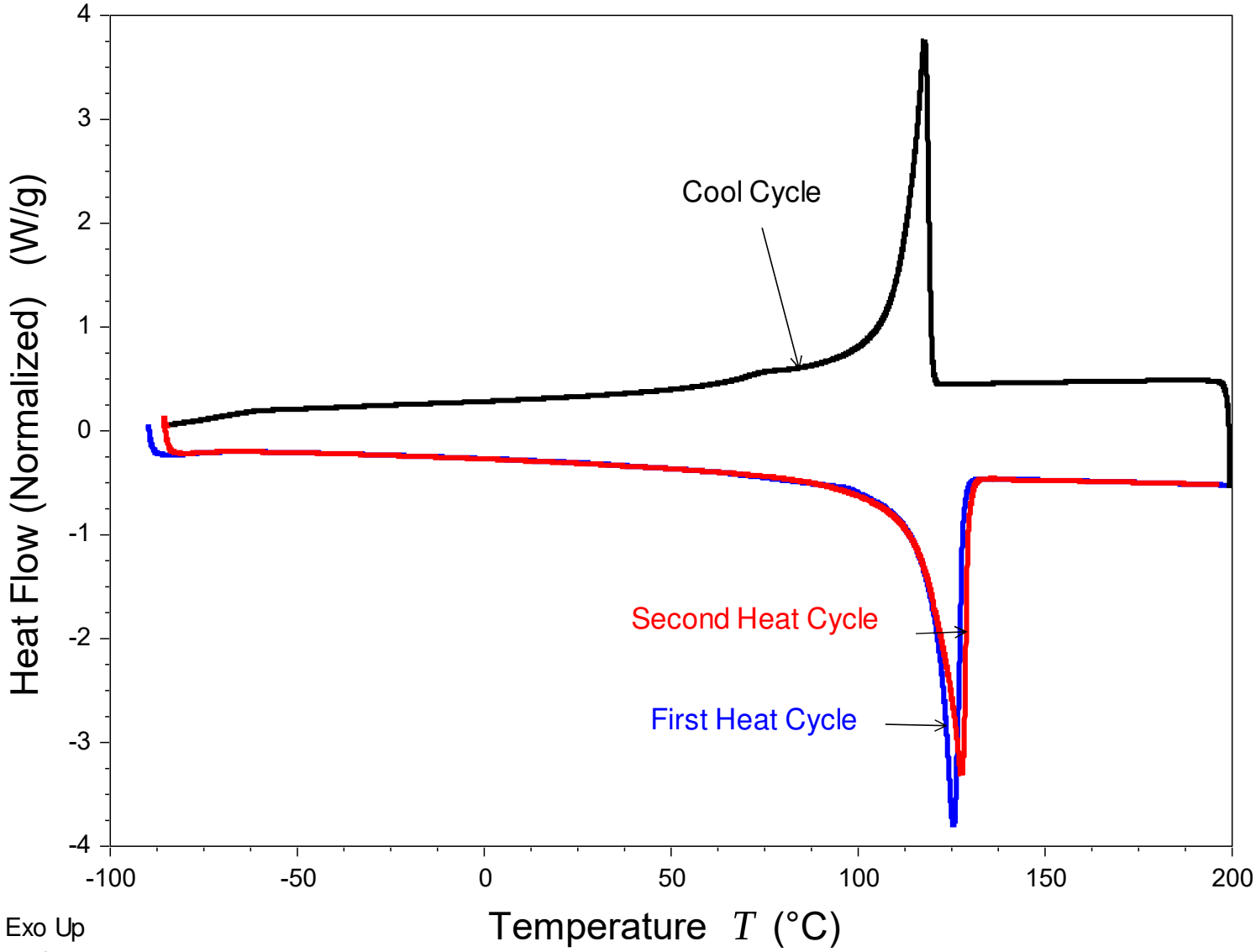


“This … is really amazing!”

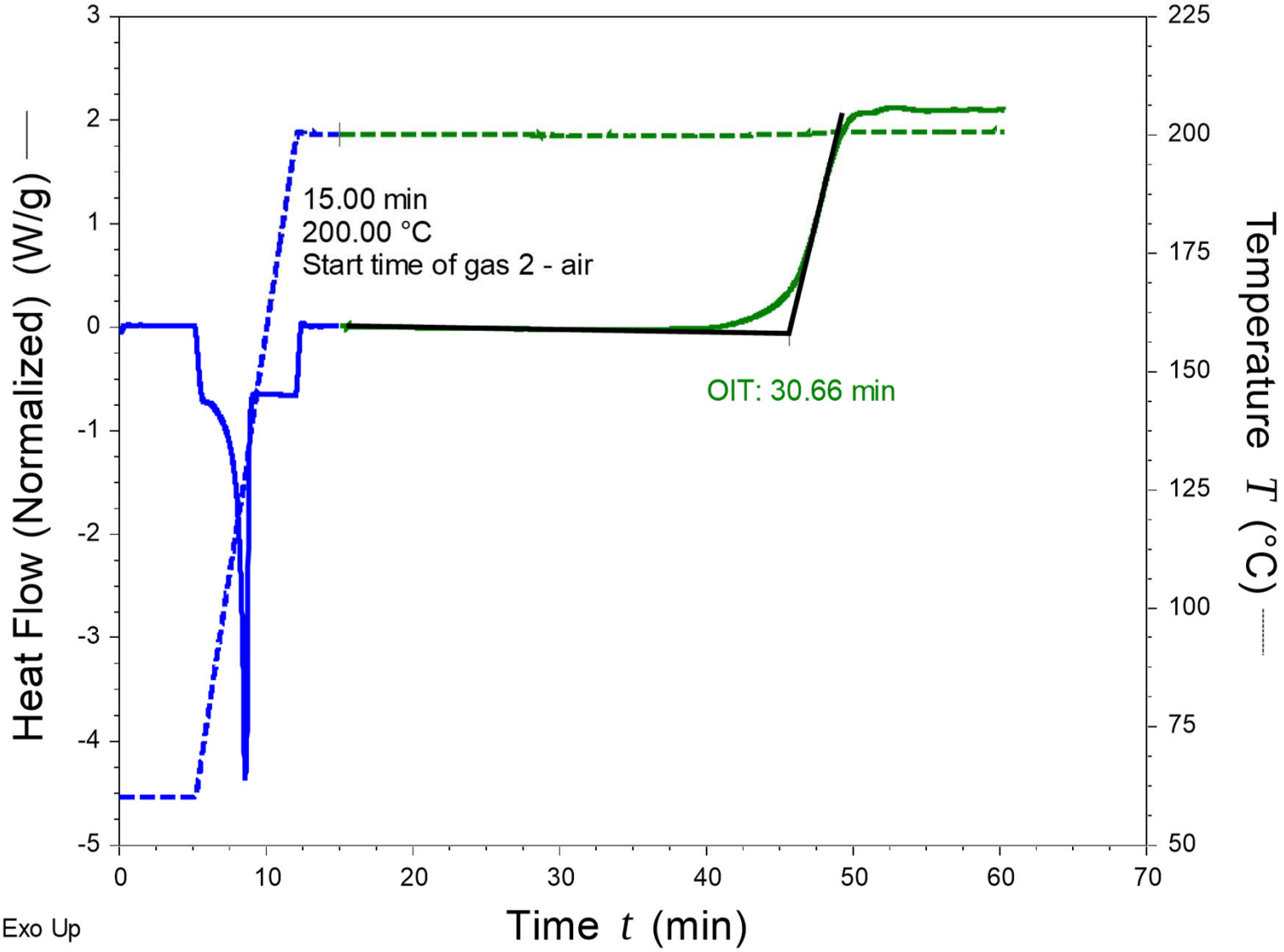
Heat Flow Change During a Transition



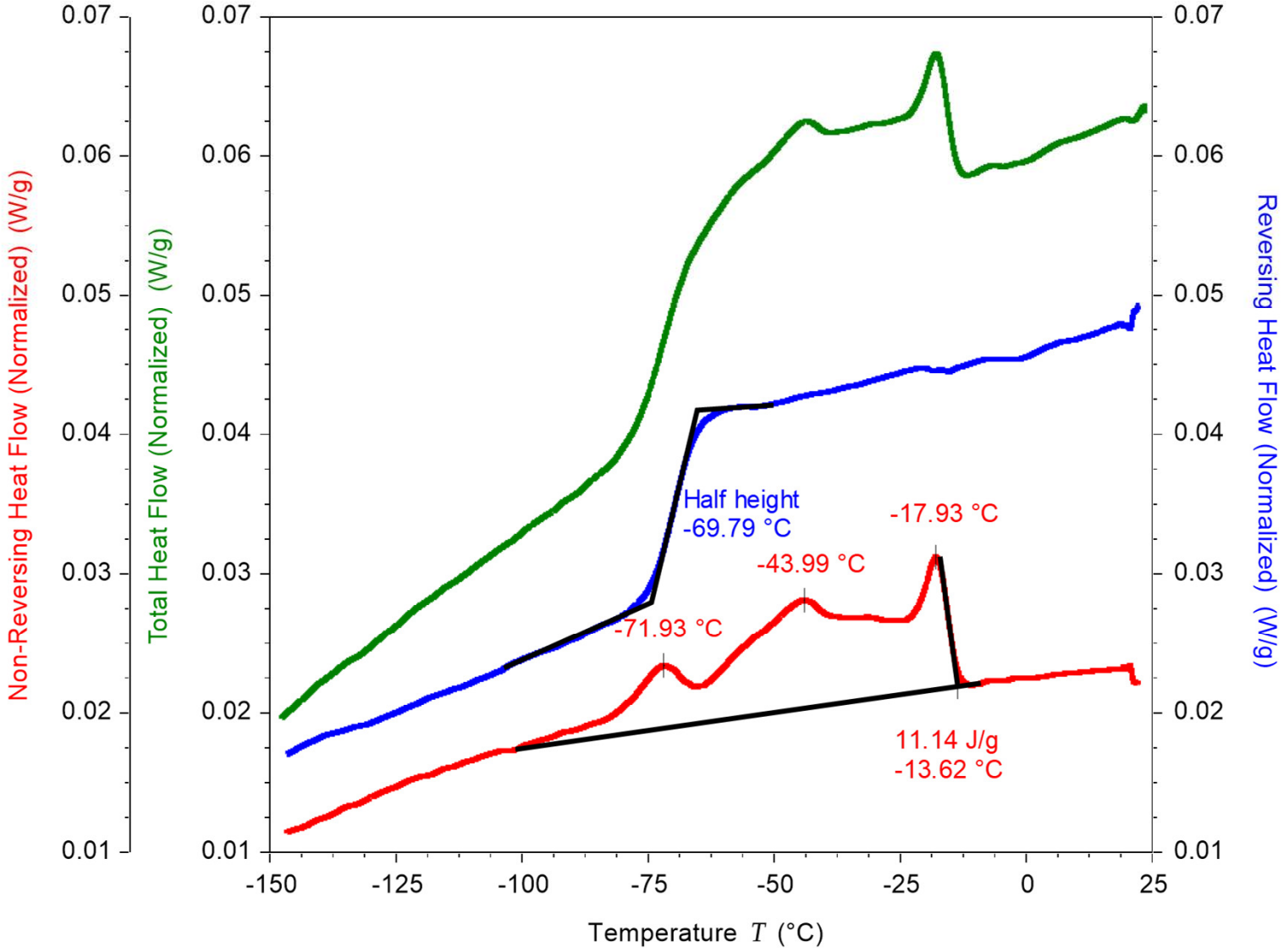
Heat Cool Heat of High Density Polyethylene



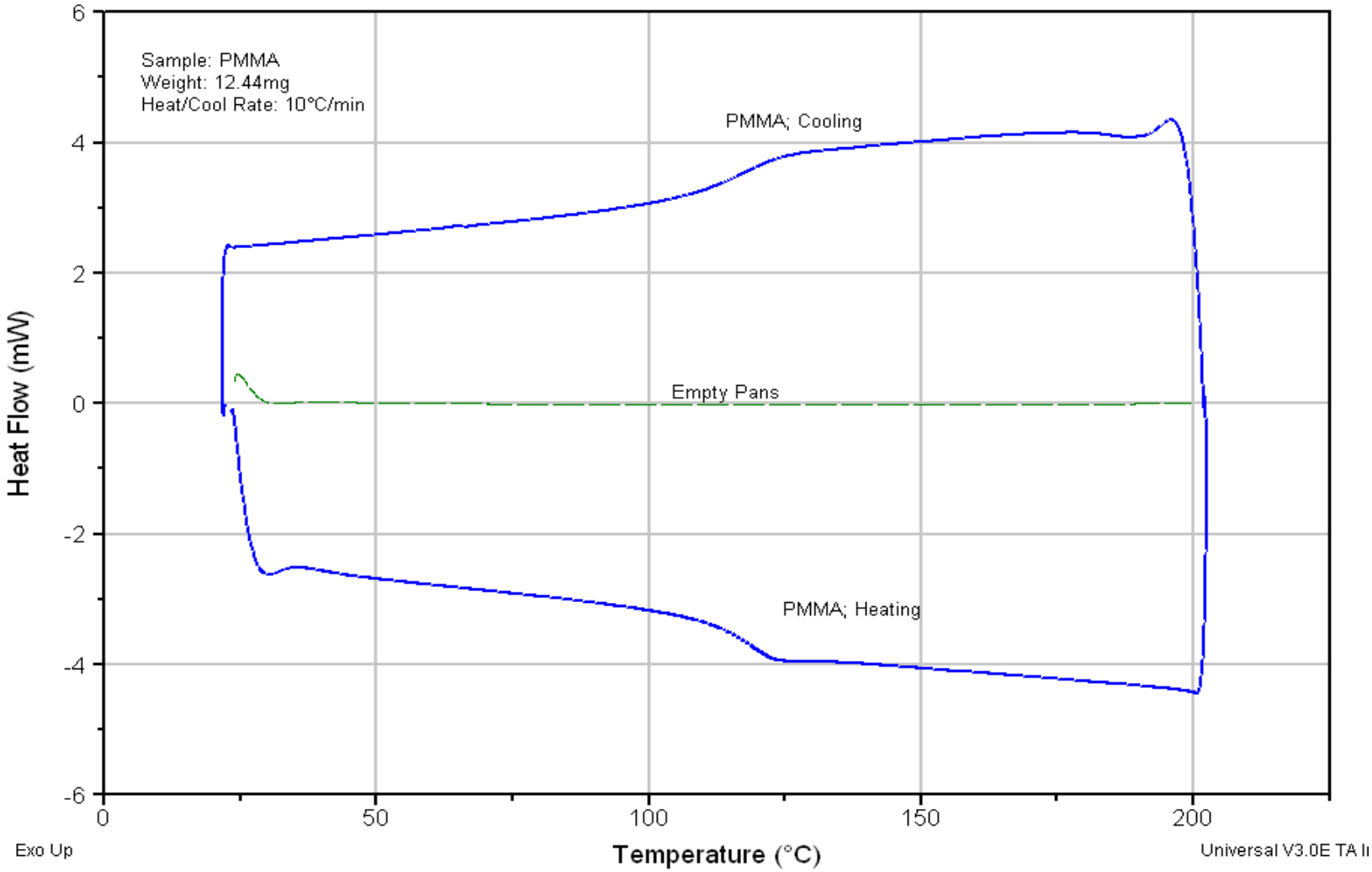
Oxidative Induction Time of Polyolefin Film



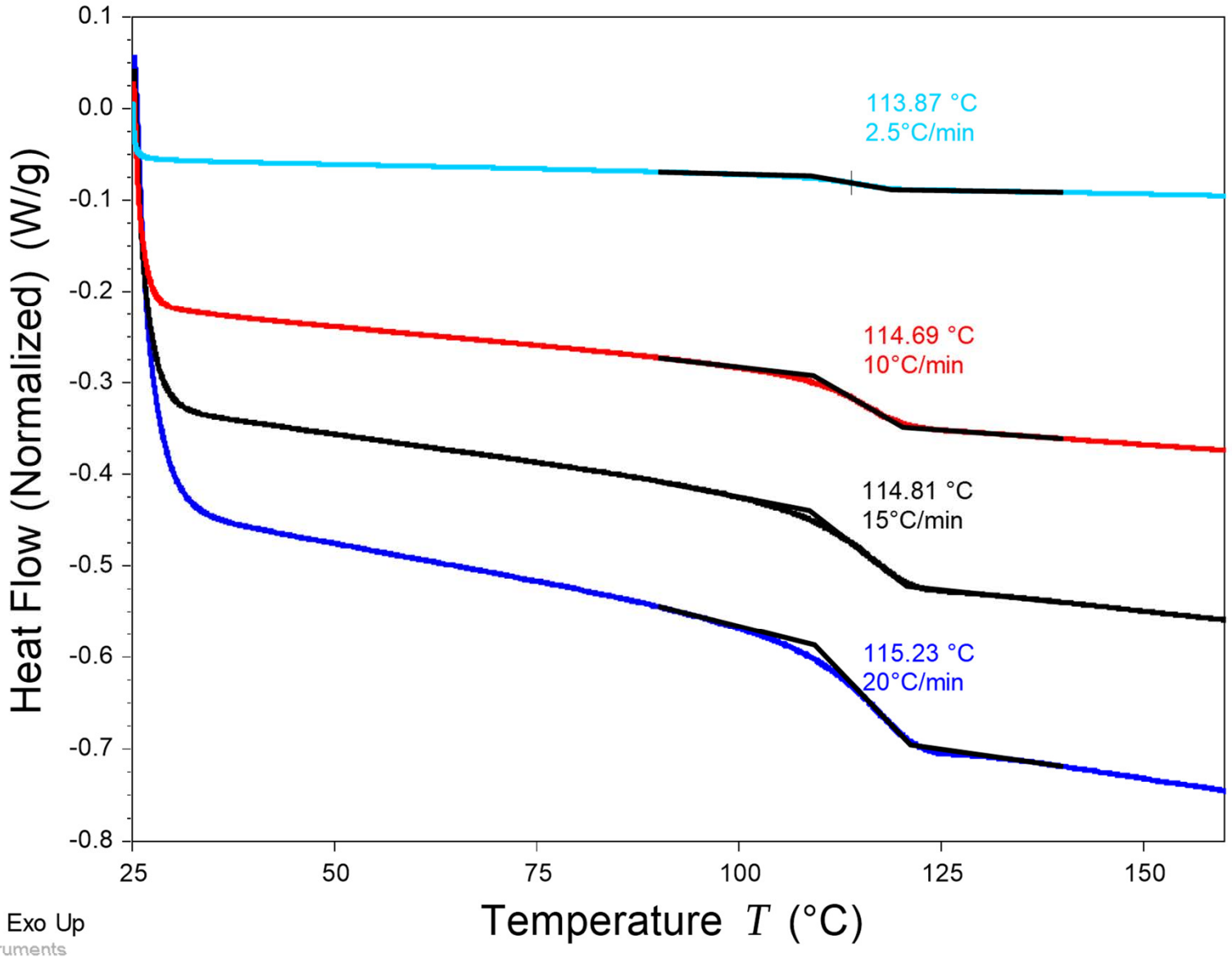
MDSC of a Process Oil
Separation of a Tg from Crystallization



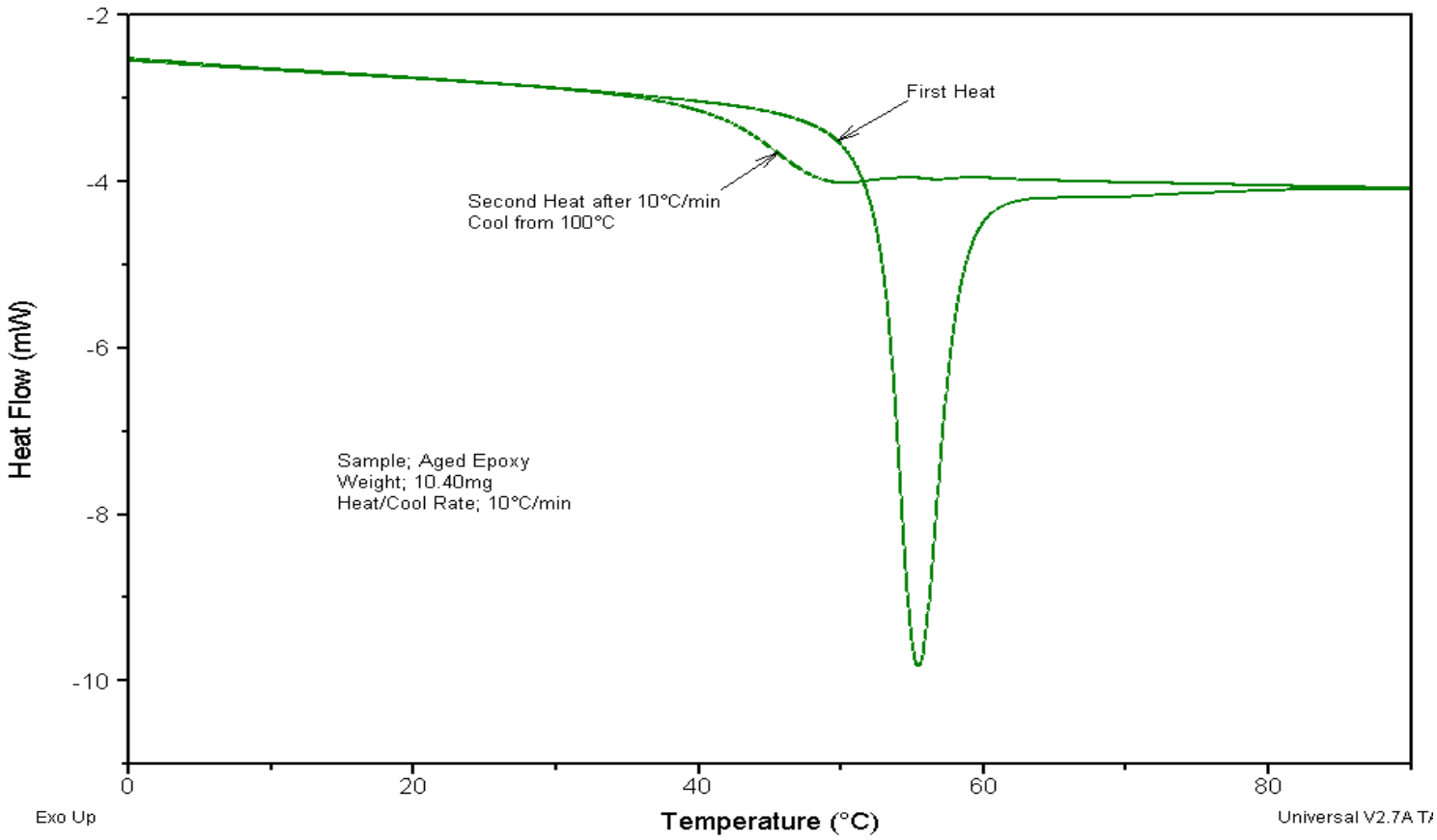
A Glass Transition is Reversible



10mg PMMA Sample at Different Heating Rates

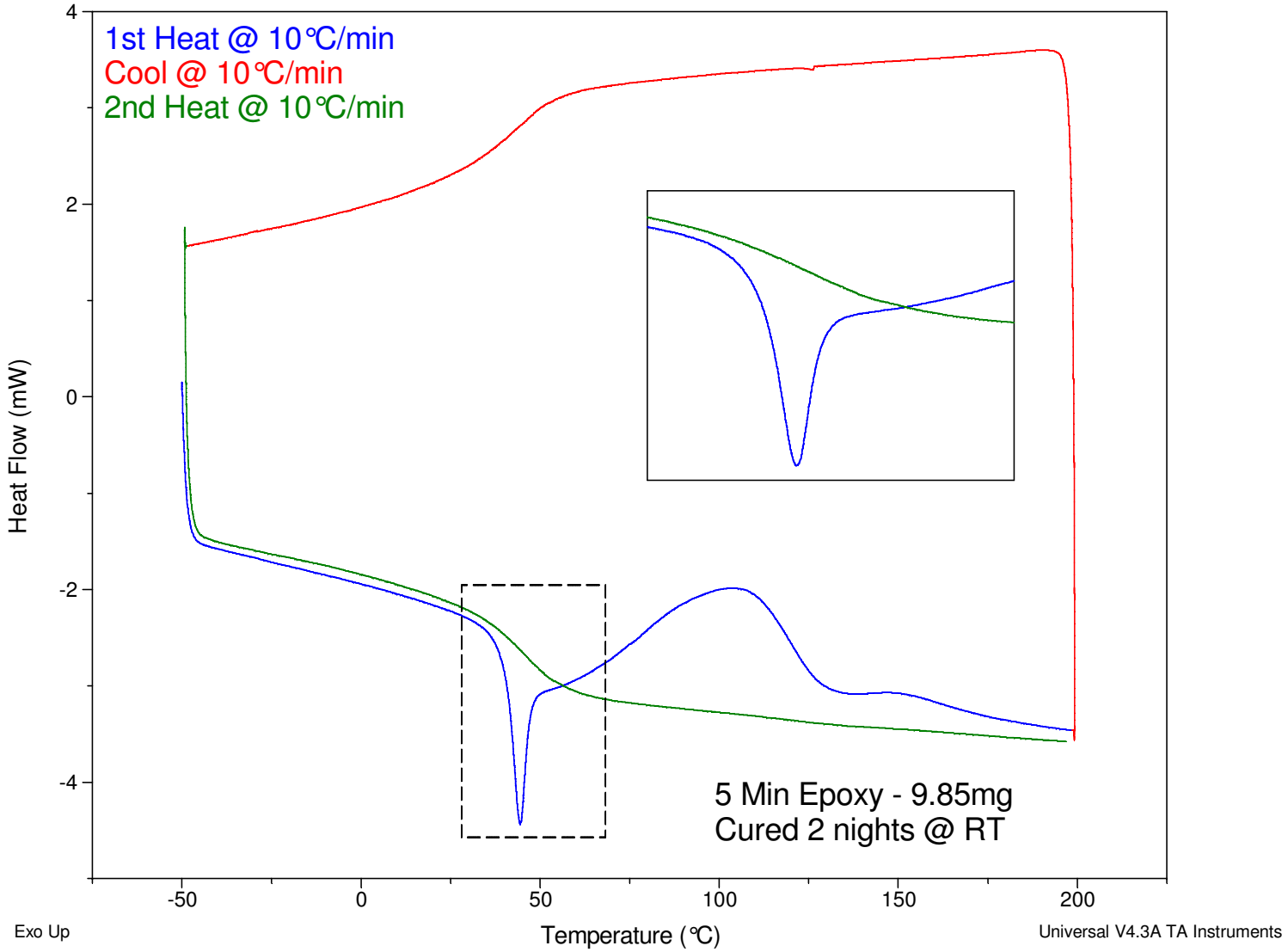


Aged Epoxy: The Tg On The First Heat Cycle

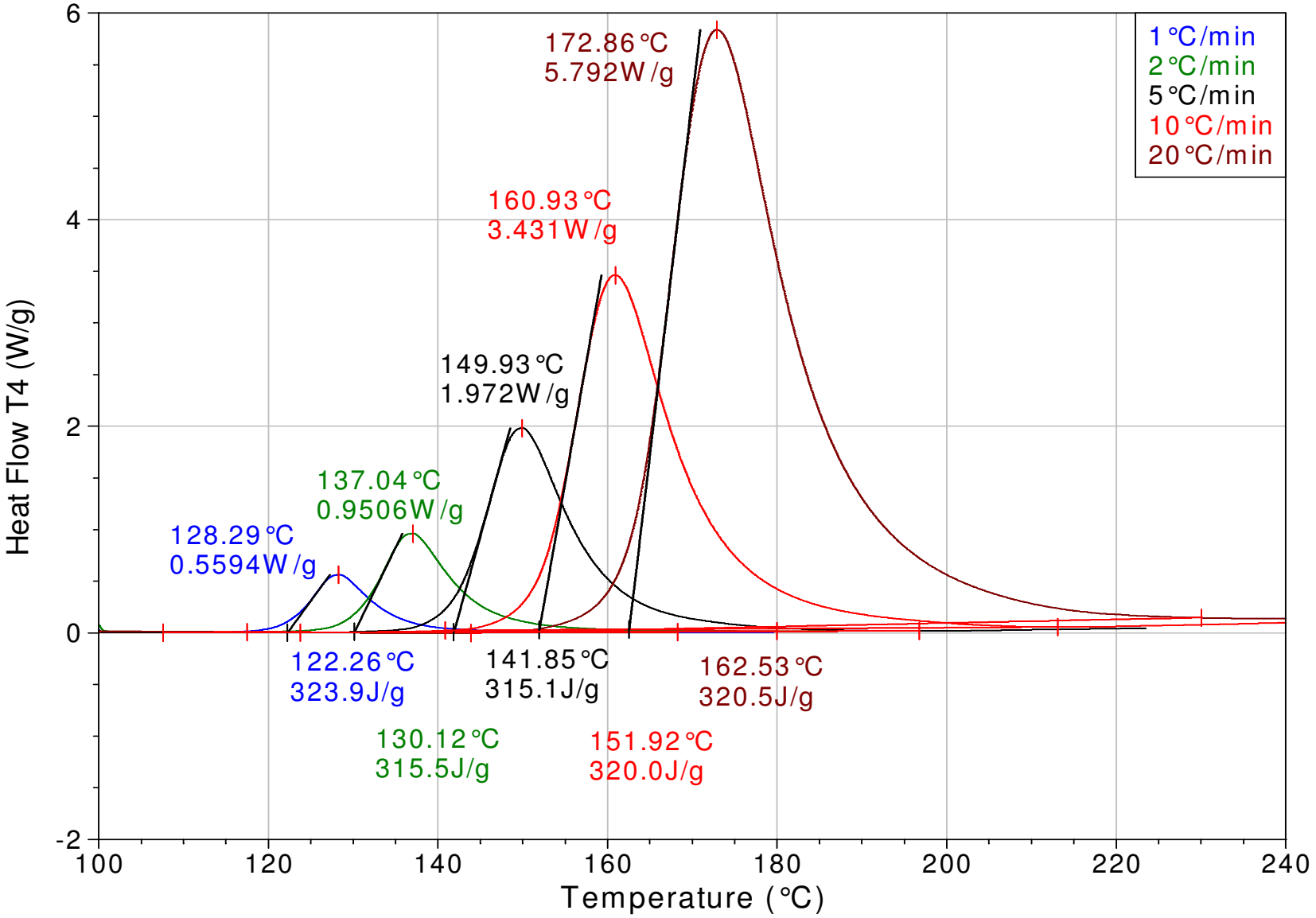


Depending on the thermal history of amorphous (glassy) polymers, the glass transition can appear as a simple step in the baseline or one that has a substantial endothermic peak that can be misinterpreted as a melting peak.

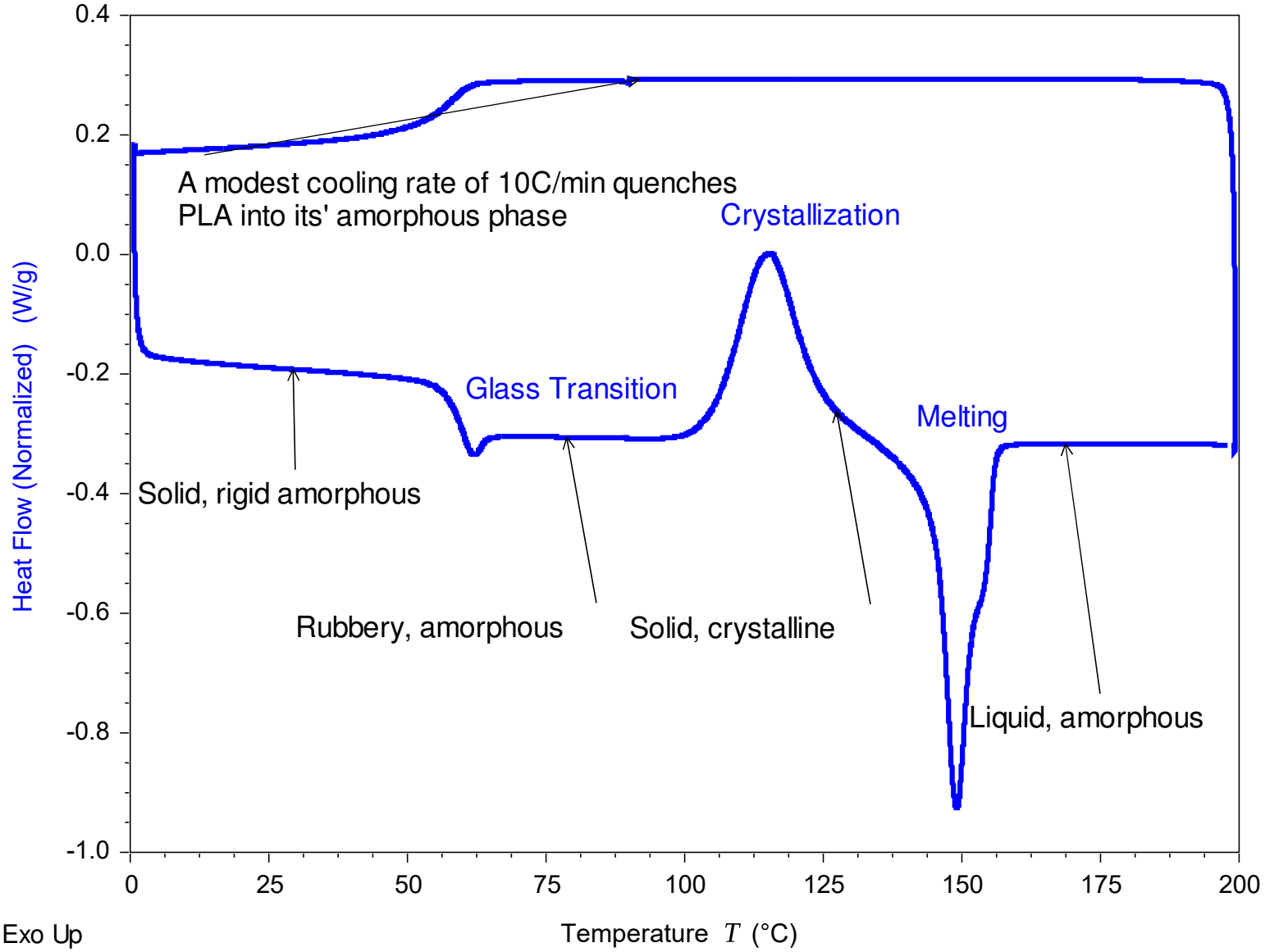
Epoxy Cured 48 Hours : Heat Cool Heat



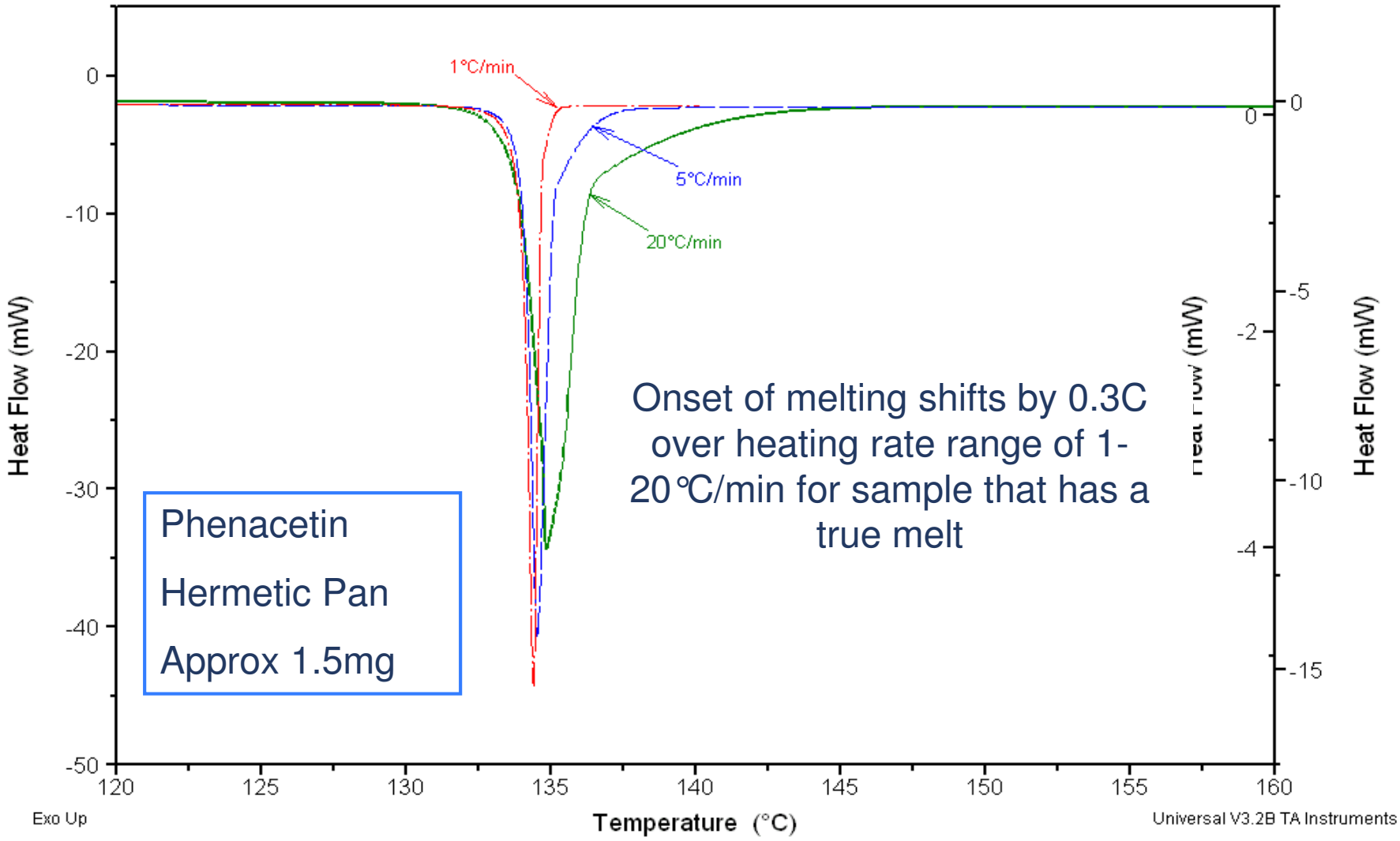
Curing reactions are kinetic in nature



DSC Analysis of Polylactic Acid (PLA)

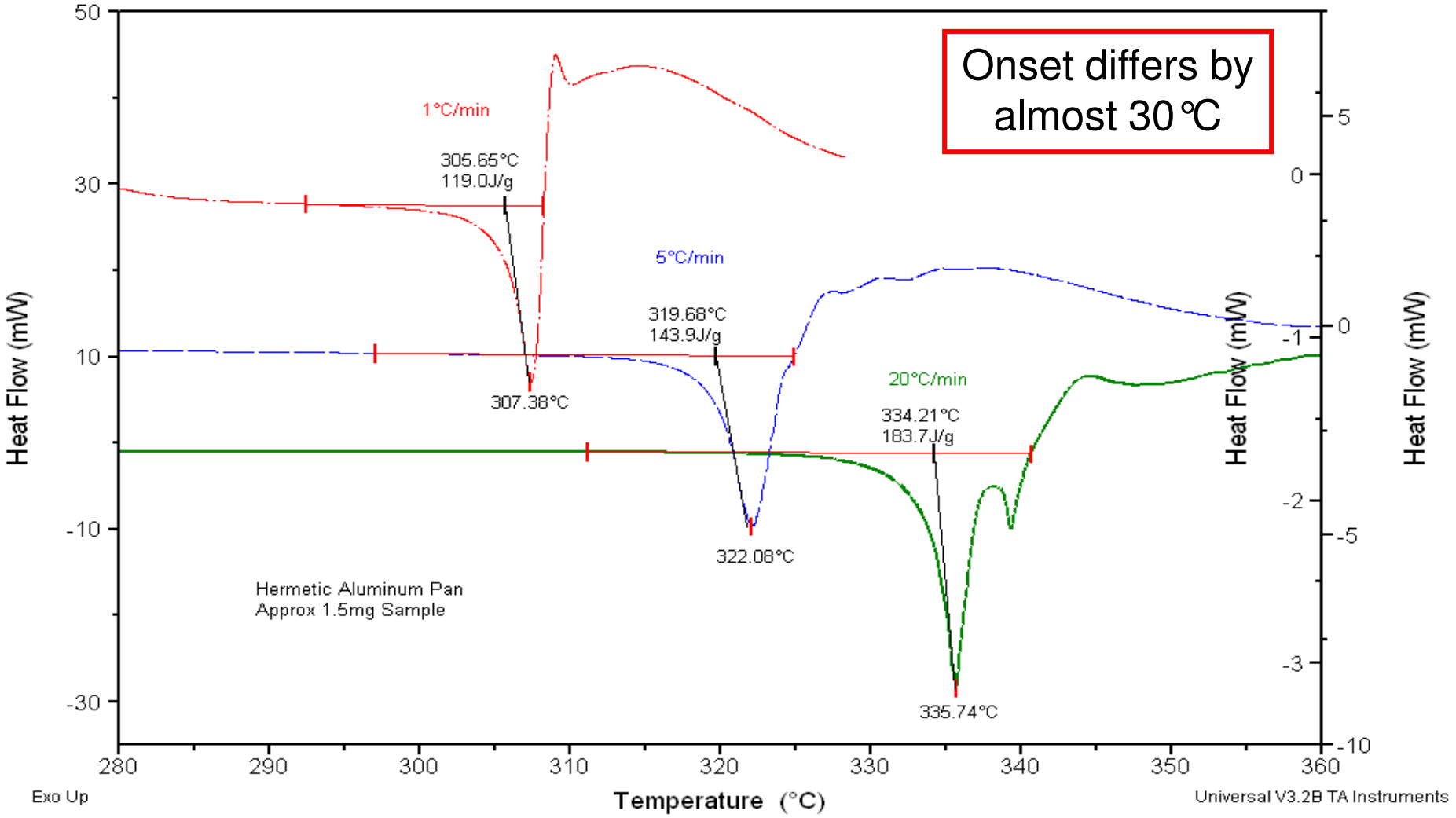


Melting is Not Heating Rate Dependent

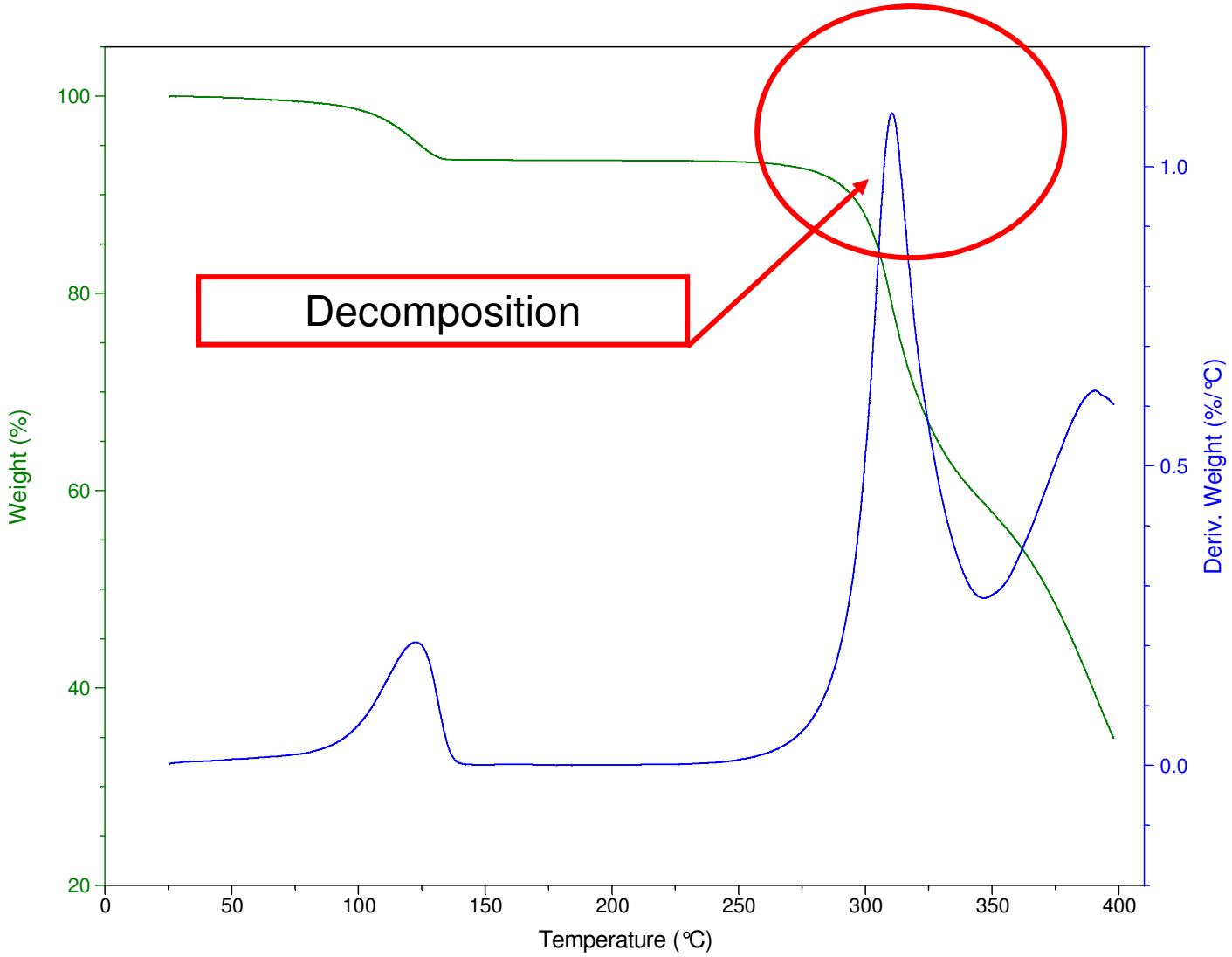


Ciprofloxacin Hydrochloride Decomposes

Decomposition is kinetic (heating rate dependent)

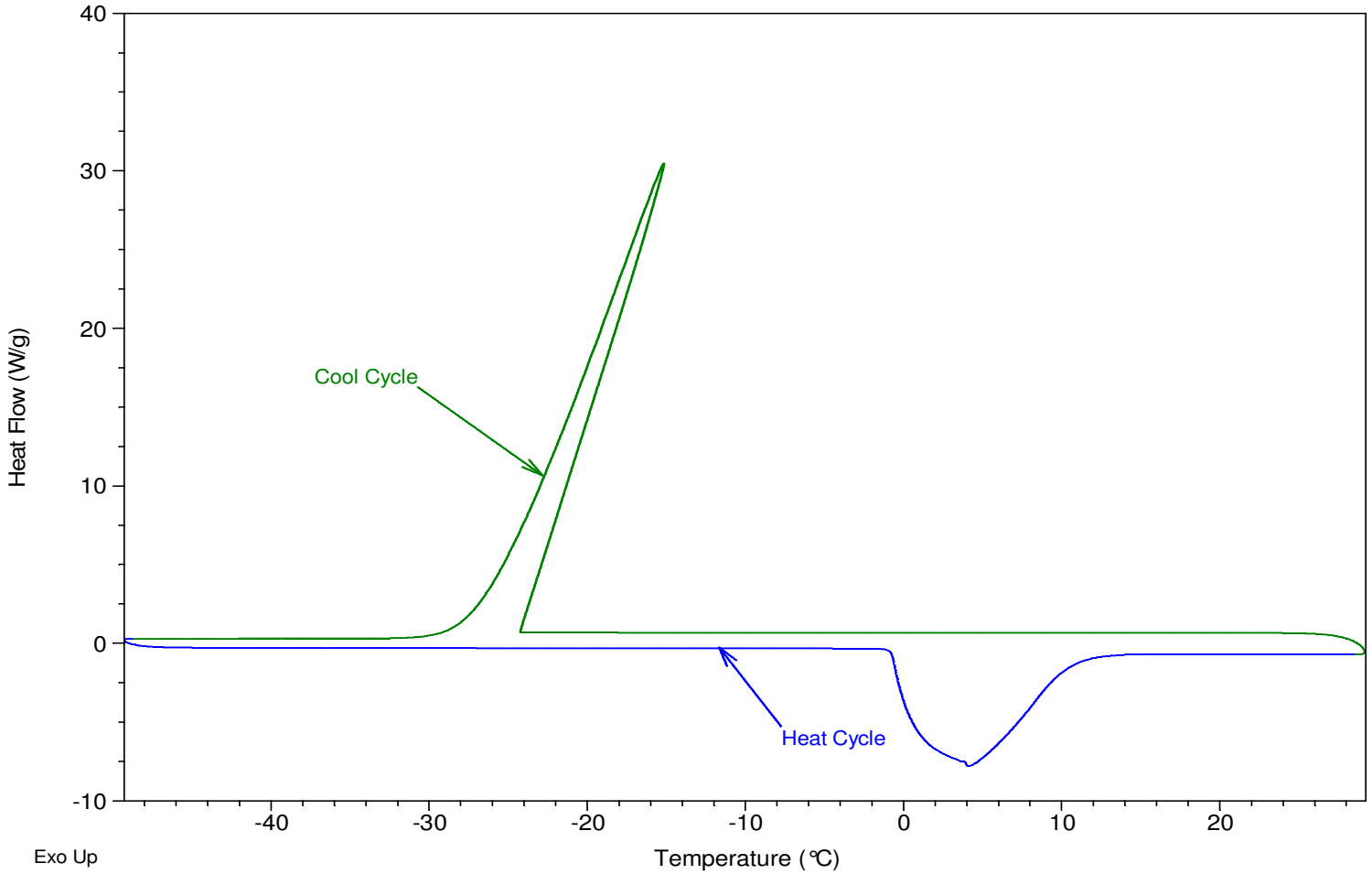


TGA of Ciprofloxacin Hydrochloride



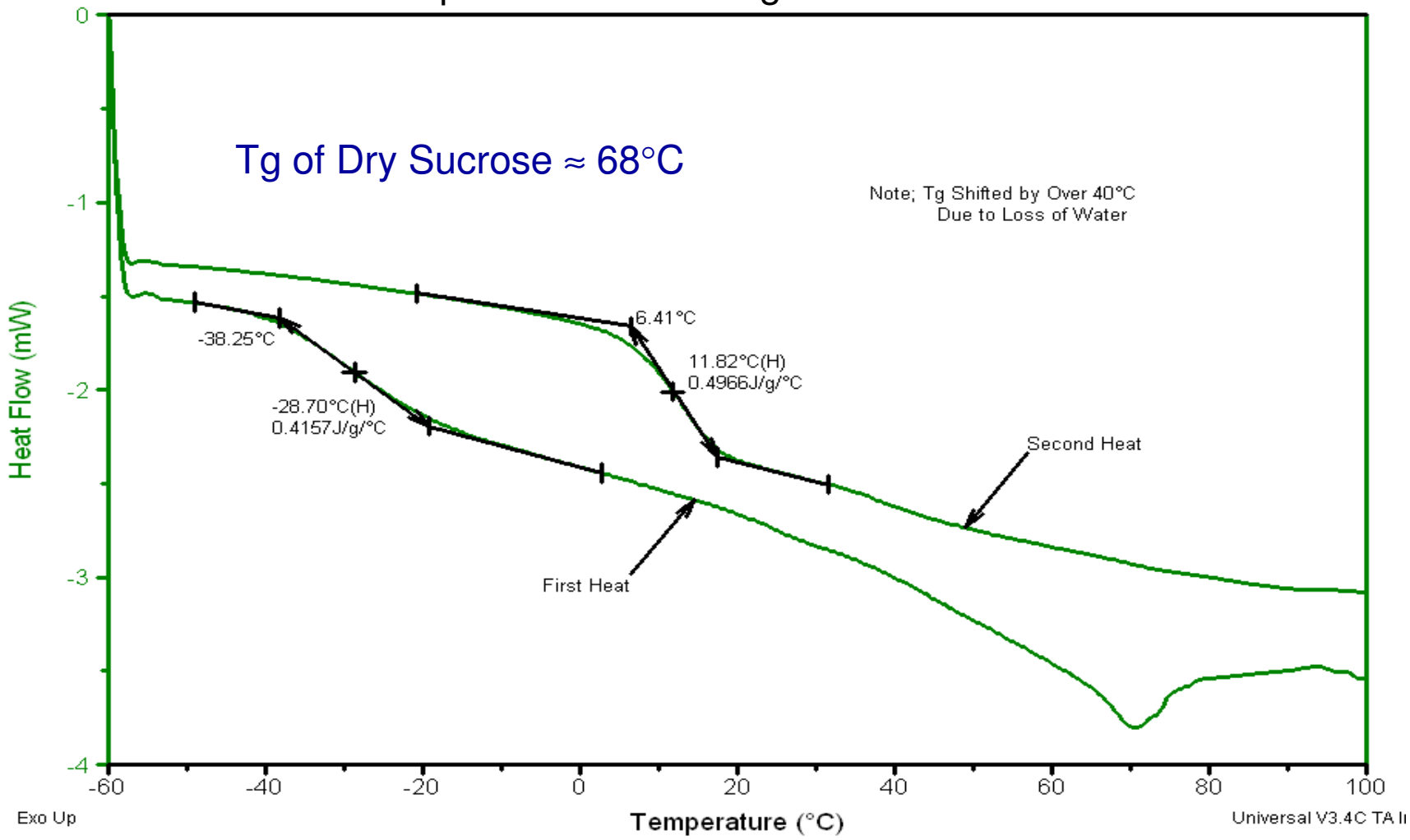
DSC of Water

Sample: Distilled, deionized water
Size: 5.0000 mg



Absorbed Moisture Acts as a Plasticizer to Lower the Glass Transition of Sucrose

Implications for storage conditions



Summary - DSC

- Differential Scanning Calorimetry determines transition temperatures, heat capacity, monitor reactions, and determine kinetics of processes
- DSC, along with TGA, is widely used because of its ease of operation and small sample requirements
- Most all technology based industries rely on DSC.


TA Instruments
The WORLD'S FINEST line of
THERMOGRAVIMETRIC ANALYZERS

Discovery TGA Instruments

Discovery 5500

Discovery TGA

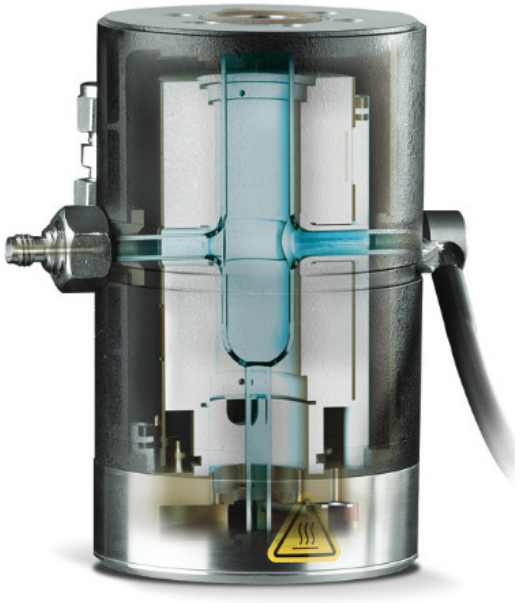
Discovery TGA and Q500/50 Specifications

	TGA 5500	Discovery TGA	TGA 55/550 Q500/Q50
Temperature Range	Ambient to 1200°C	Ambient to 1200°C	Ambient to 1000°C
Isothermal Temperature Accuracy	±1°C	±1°C	±1°C
Heating Rate Range	0.1 to 500°C/min (Linear) >1600°C/min (Ballistic)	0.1 to 500°C/min (Linear) >1600°C/min (Ballistic)	0.1 to 100°C/min (Linear)
Sample Weight Capacity	1000mg	750 mg	1000 mg
Dynamic Weighing Range	1000mg	100 mg	1000 mg
Baseline Dynamic Drift (50-1000°C)	< 10 µg	10 µg	<50 µg

TGA Furnace Options

IR Furnace

Wire Wound (Pt/Rh) Furnace



EGA Furnace

Yahhh, Look what I have created. I have made fire (2)

What is Thermogravimetric Analysis (TGA)?

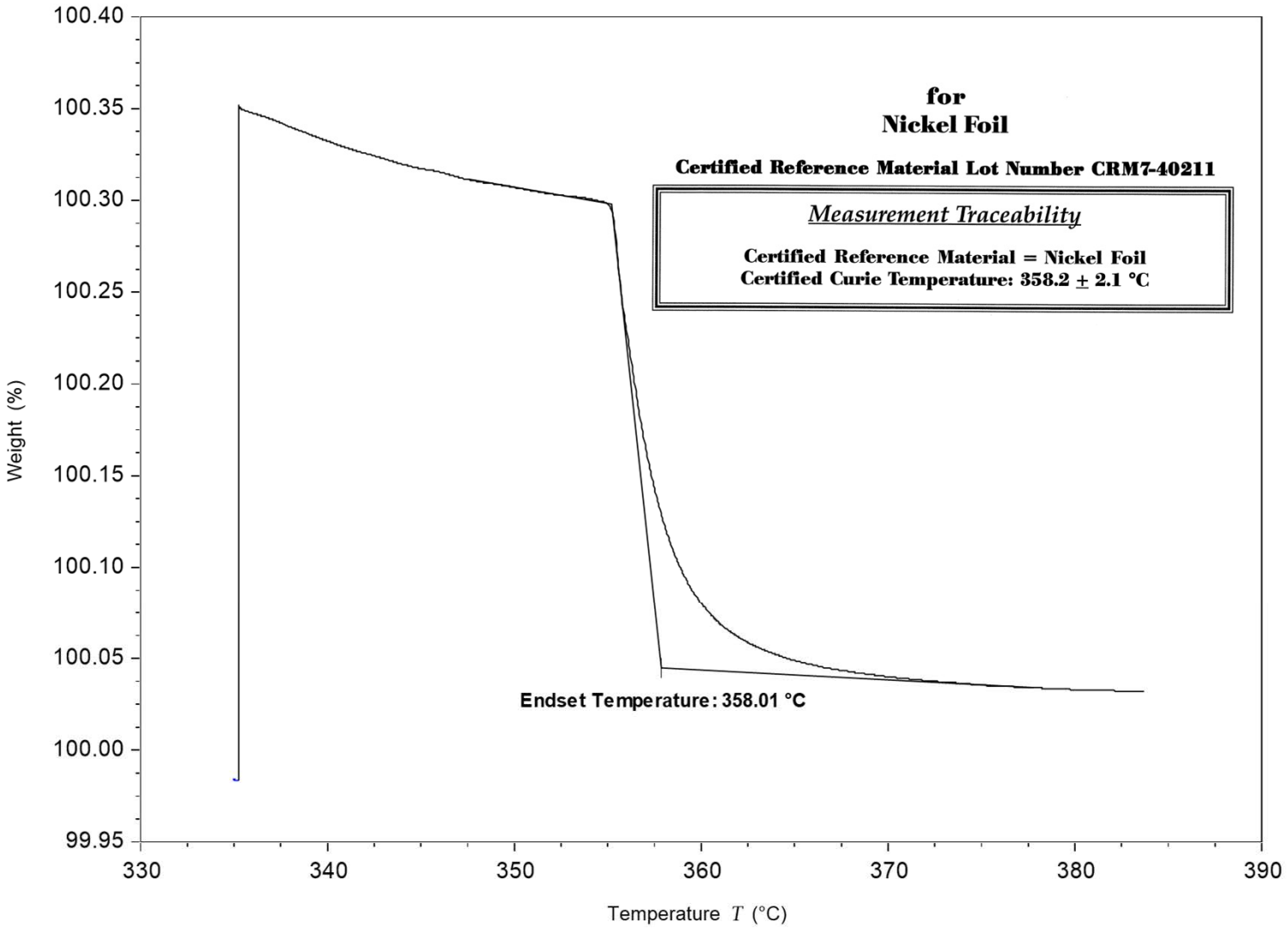
- Thermogravimetric Analysis (TGA) measures weight/mass change (loss or gain) and the rate of weight change as a function of temperature, time and atmosphere.

- Measurements are used primarily to determine the composition of materials and to predict their thermal stability. The technique can characterize materials that exhibit weight loss or gain due to sorption/desorption of volatiles, decomposition, oxidation and reduction.

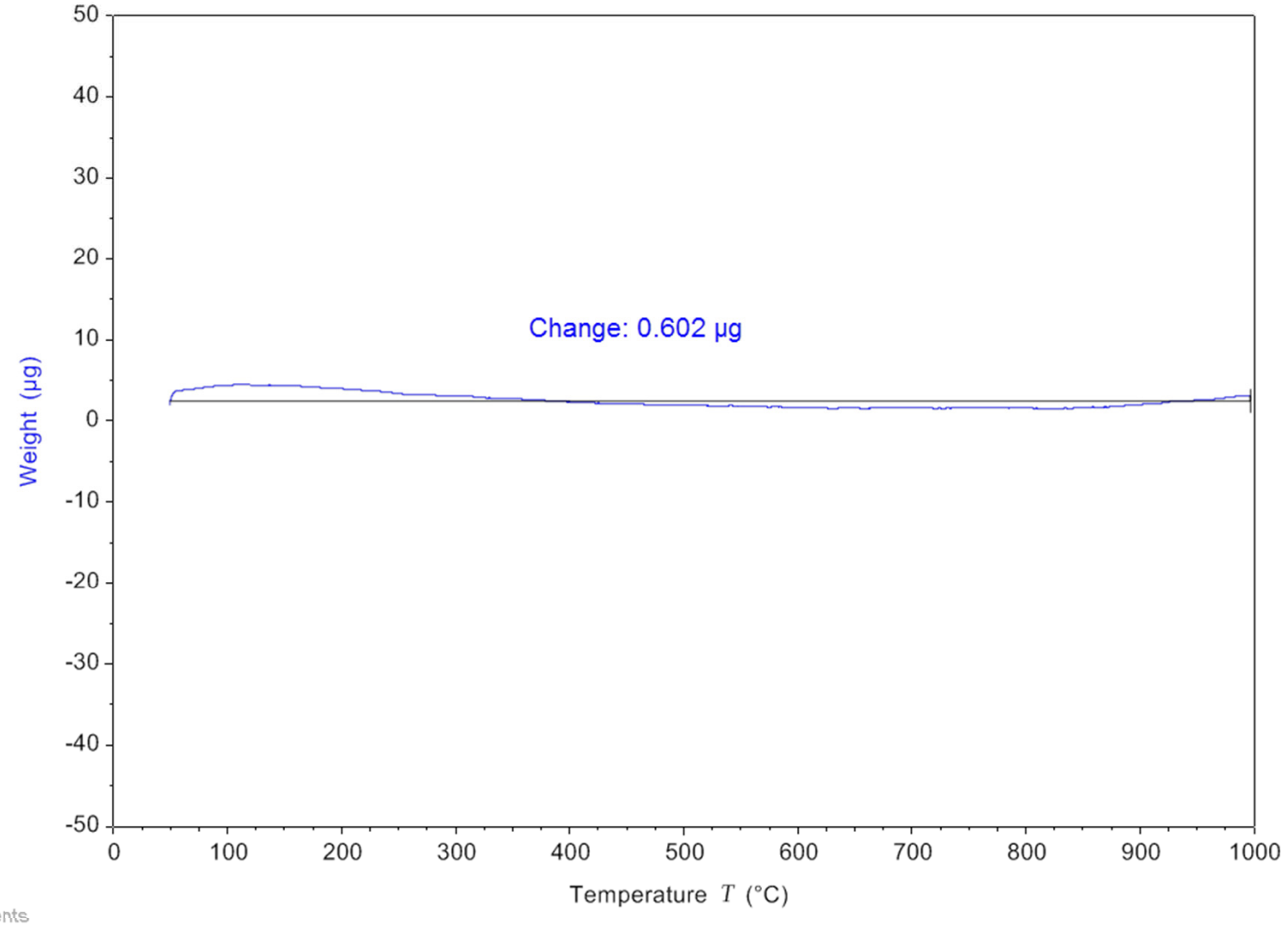
What TGA Can Tell You?

- 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

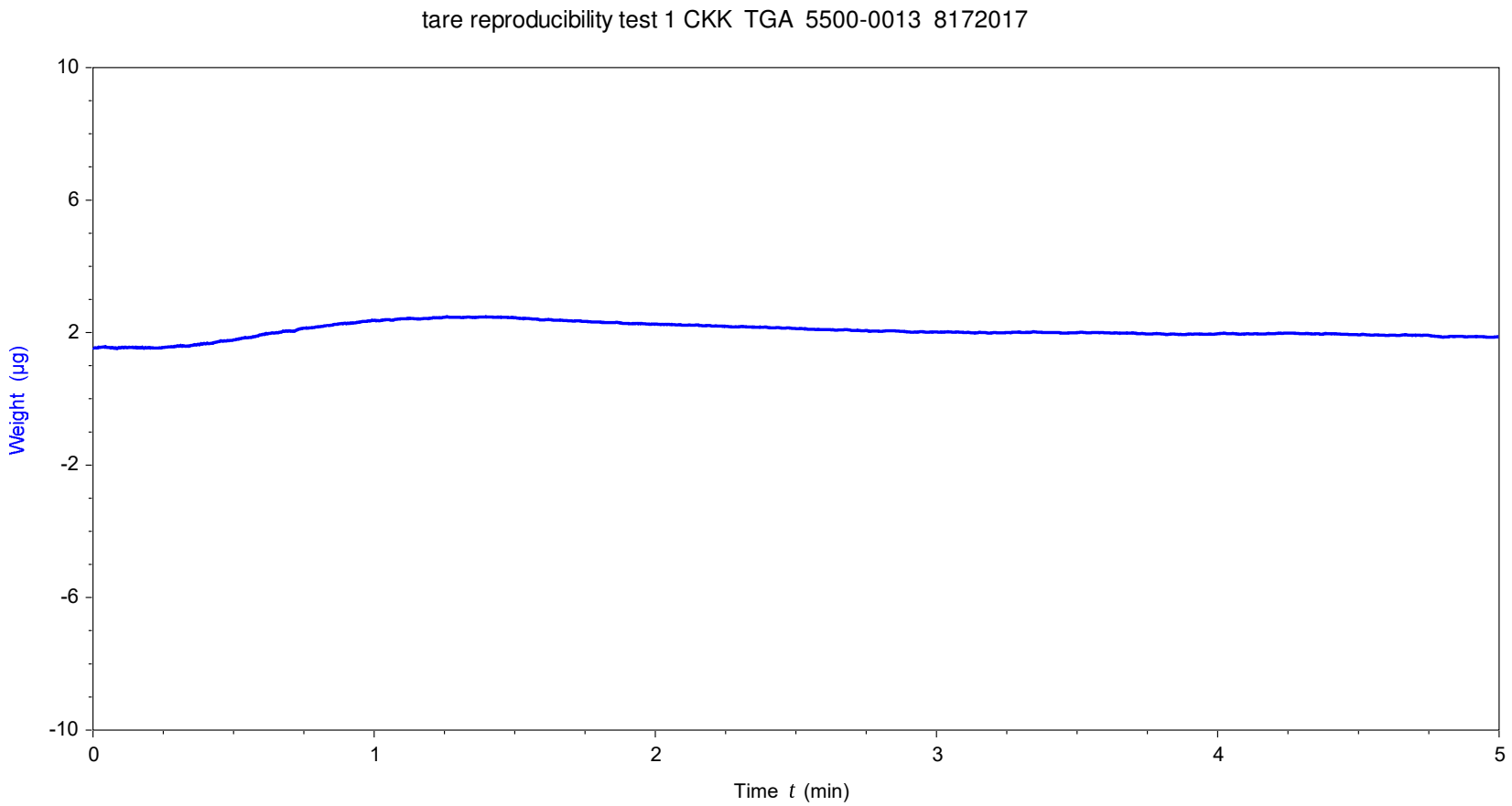
TGA – Temperature Verification



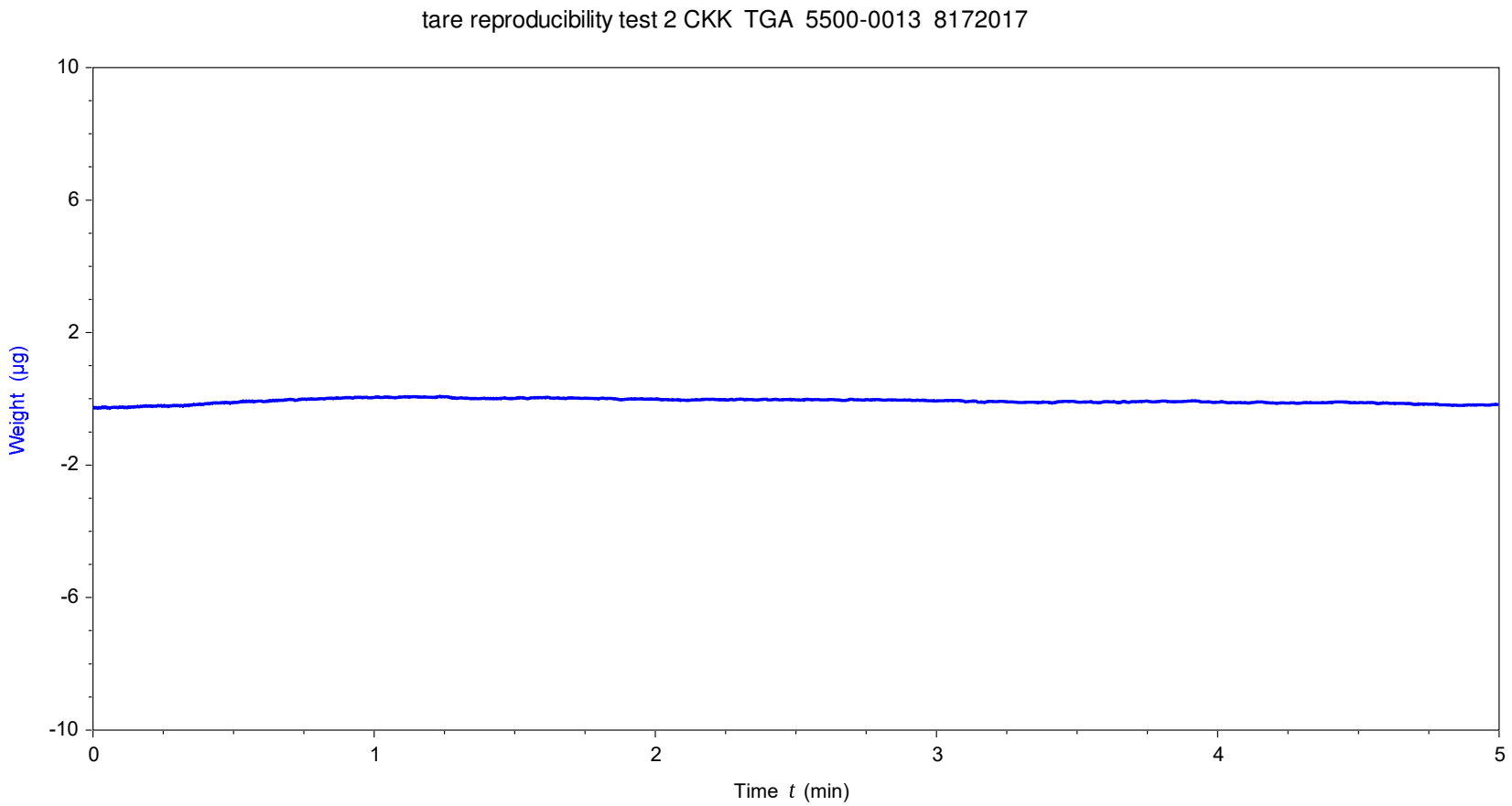
Discovery TGA 5500 Baseline Performance



Tare reproducibility study Discovery 5500



Tare reproducibility study Discovery 5500



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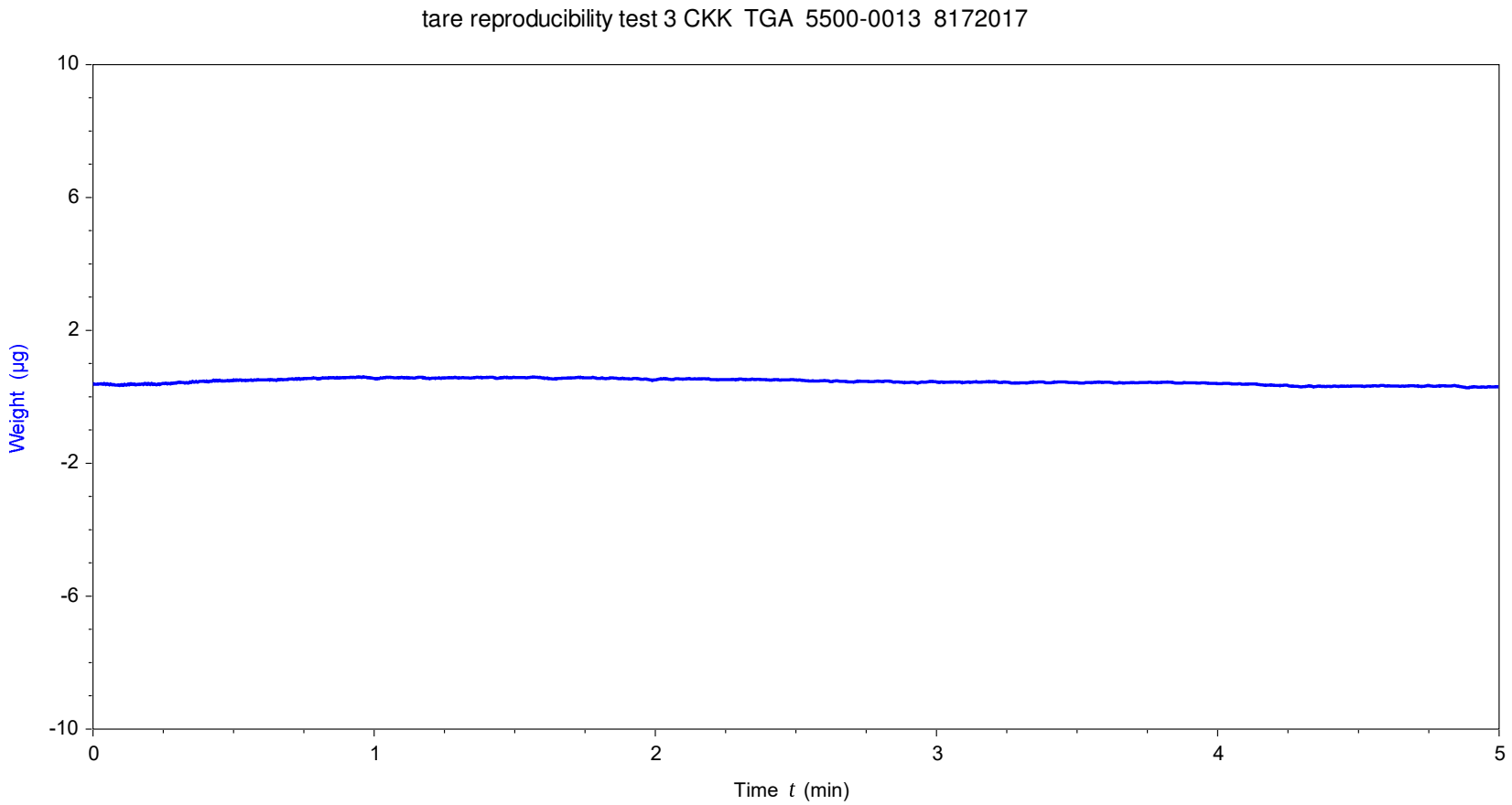

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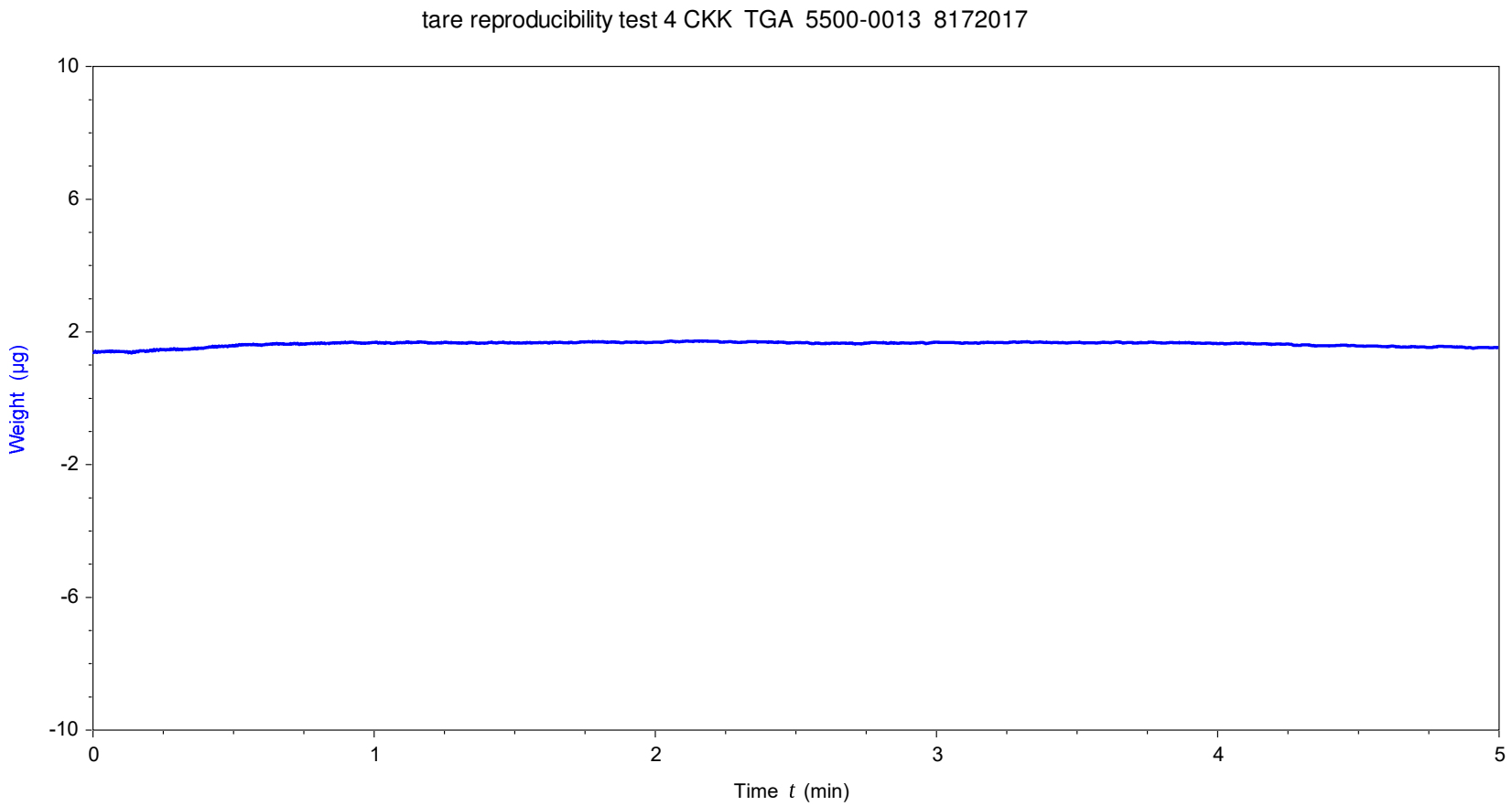

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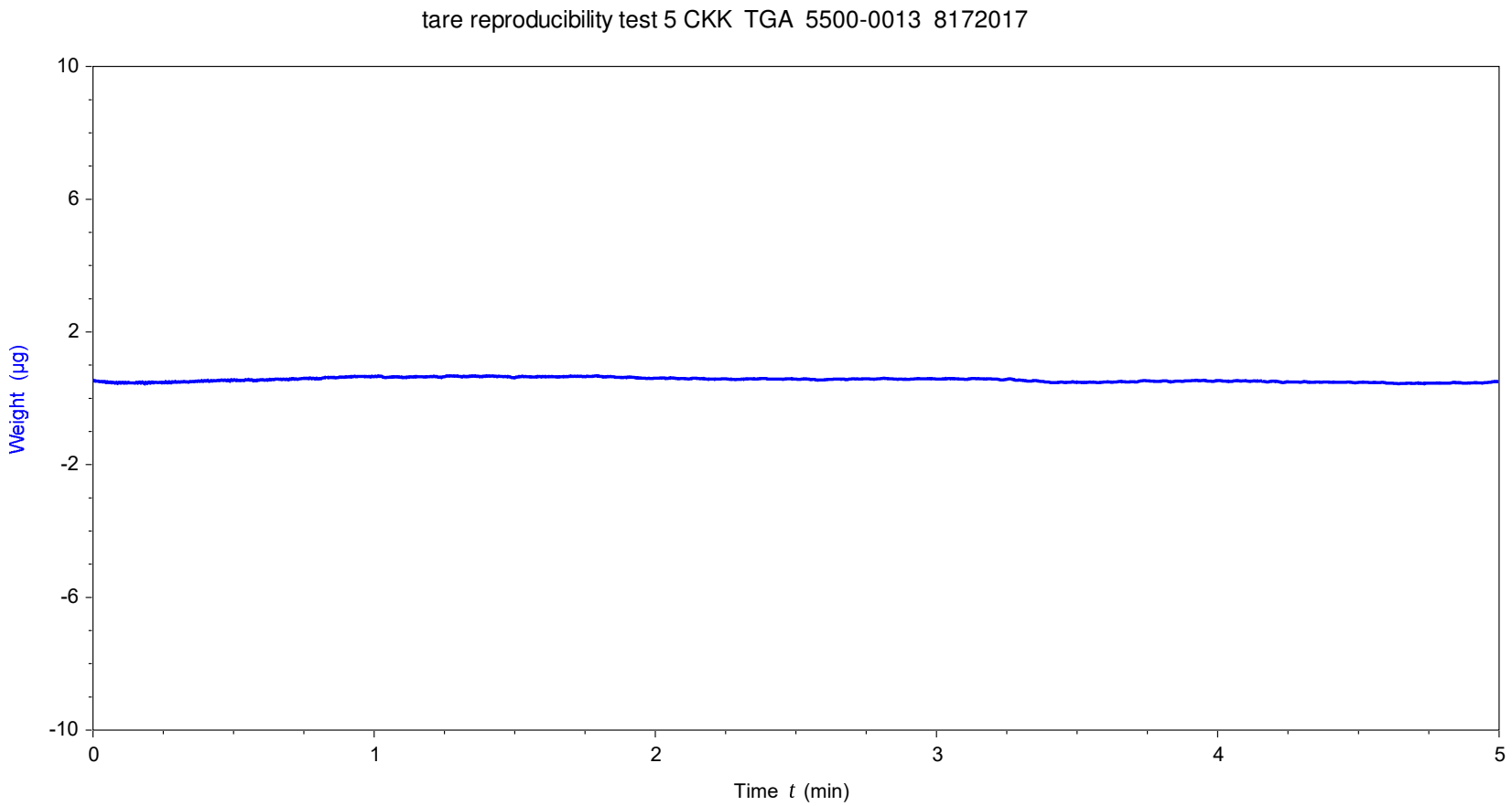
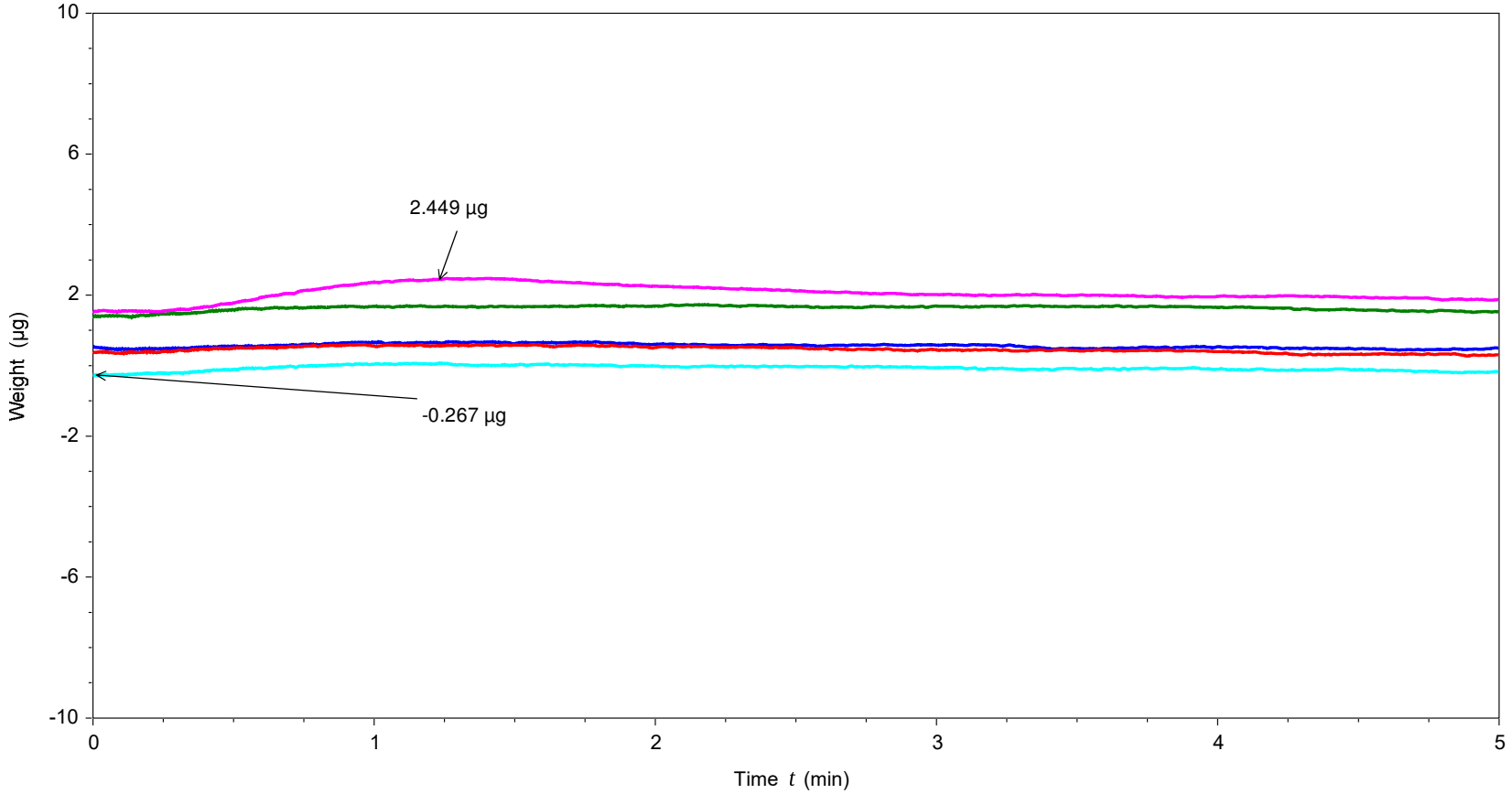
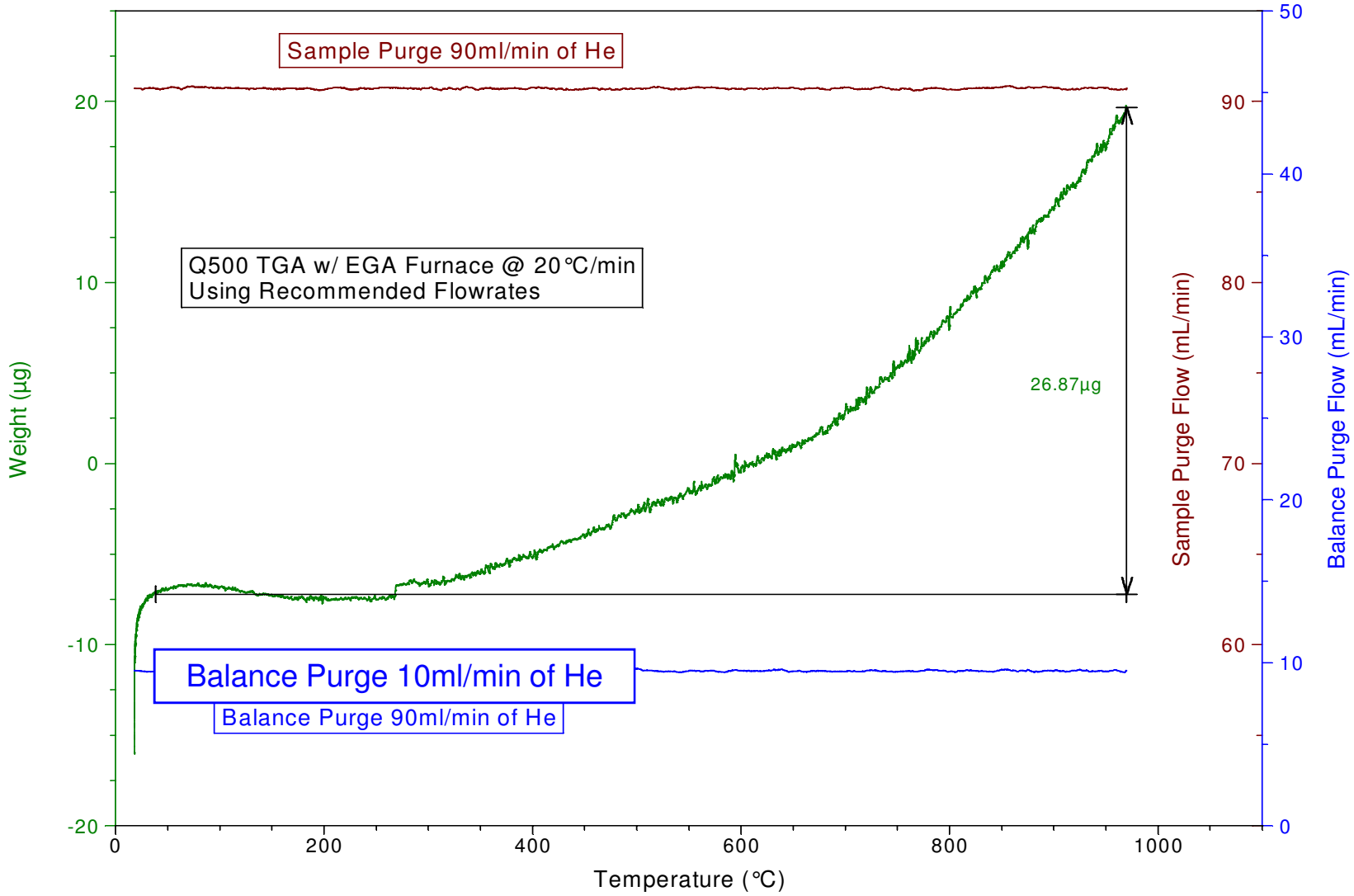


Tare reproducibility study Discovery 5500 Overlay

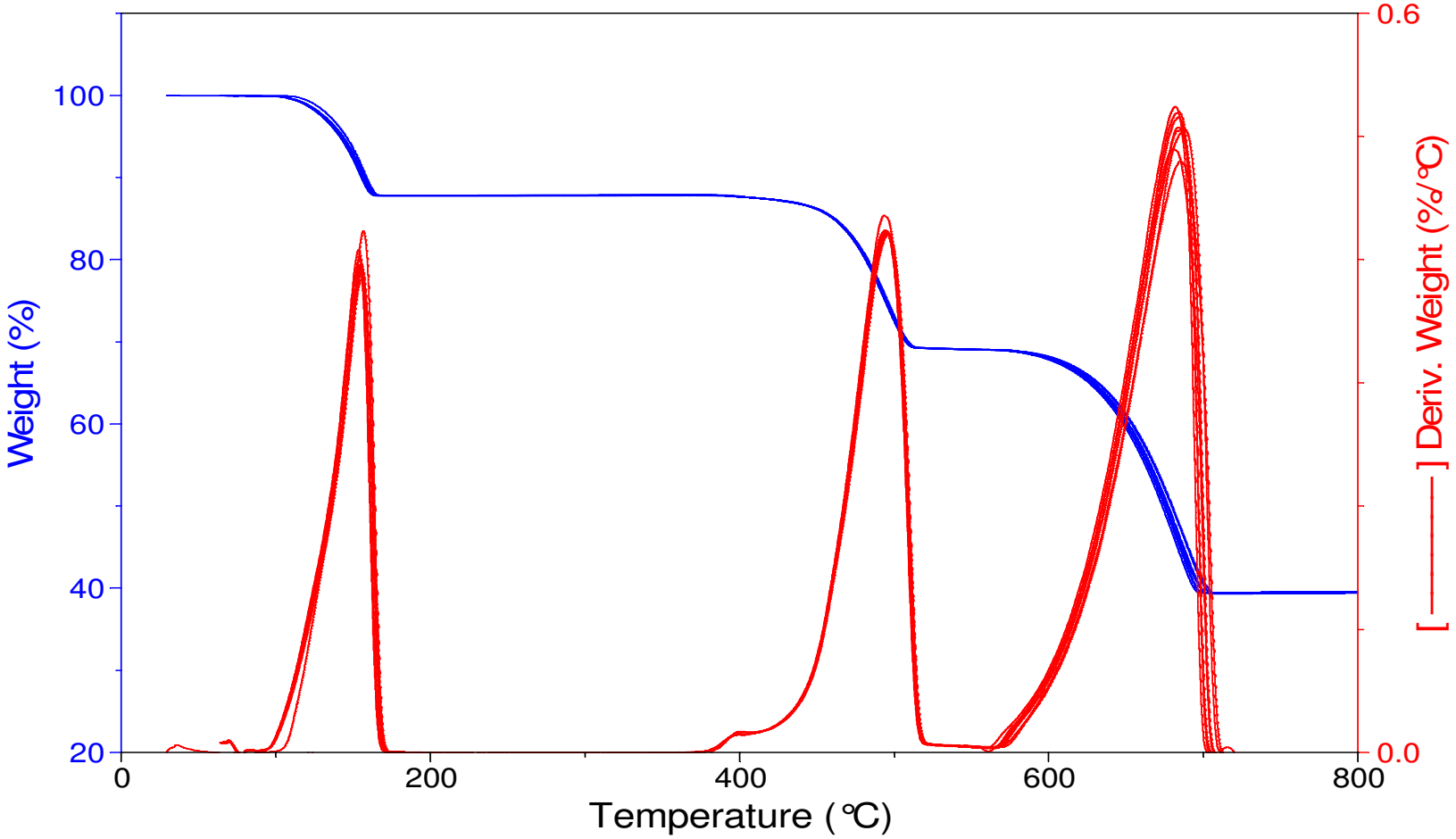


Q 500/50 Baseline Performance

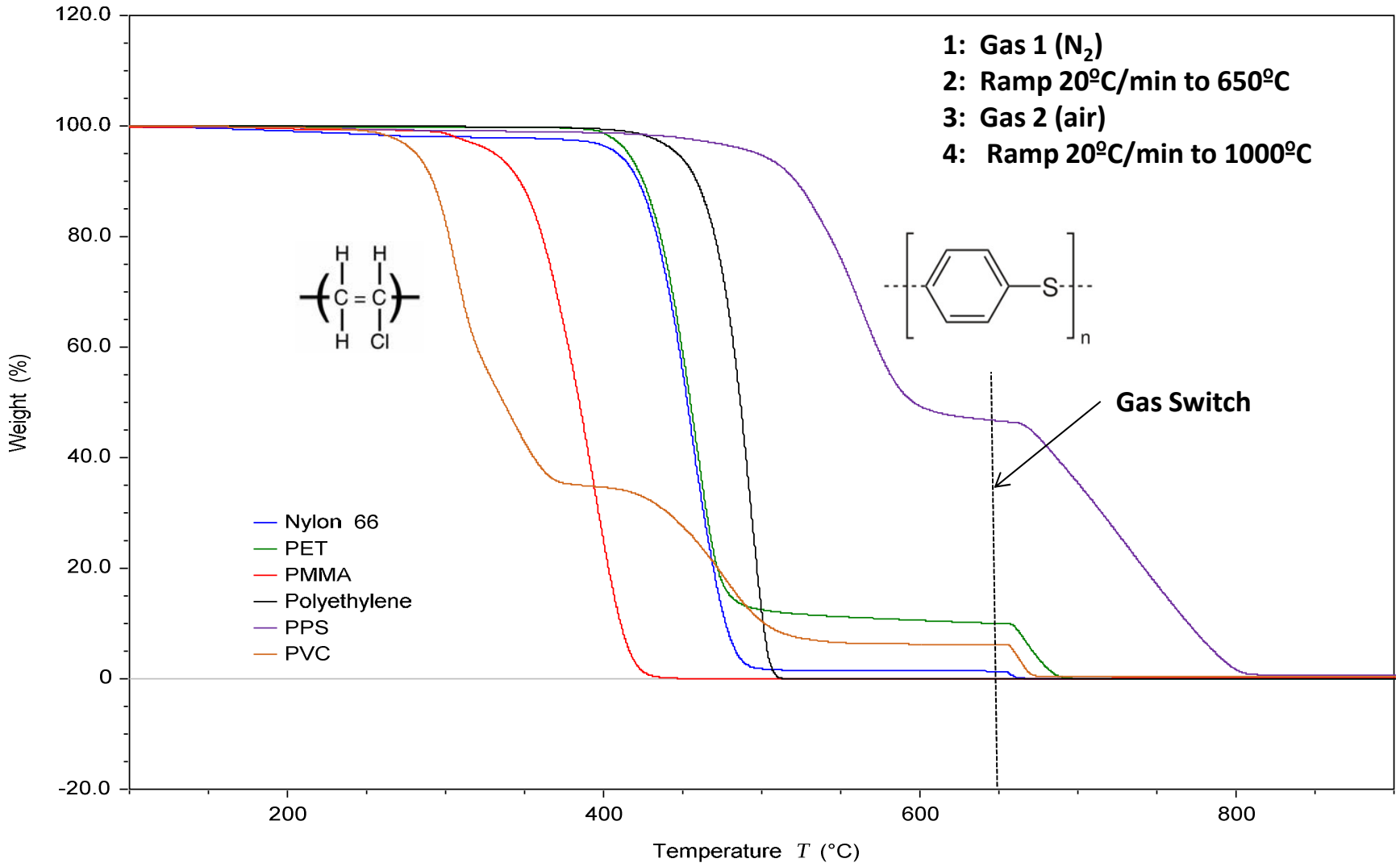


Calcium Oxalate Repeatability

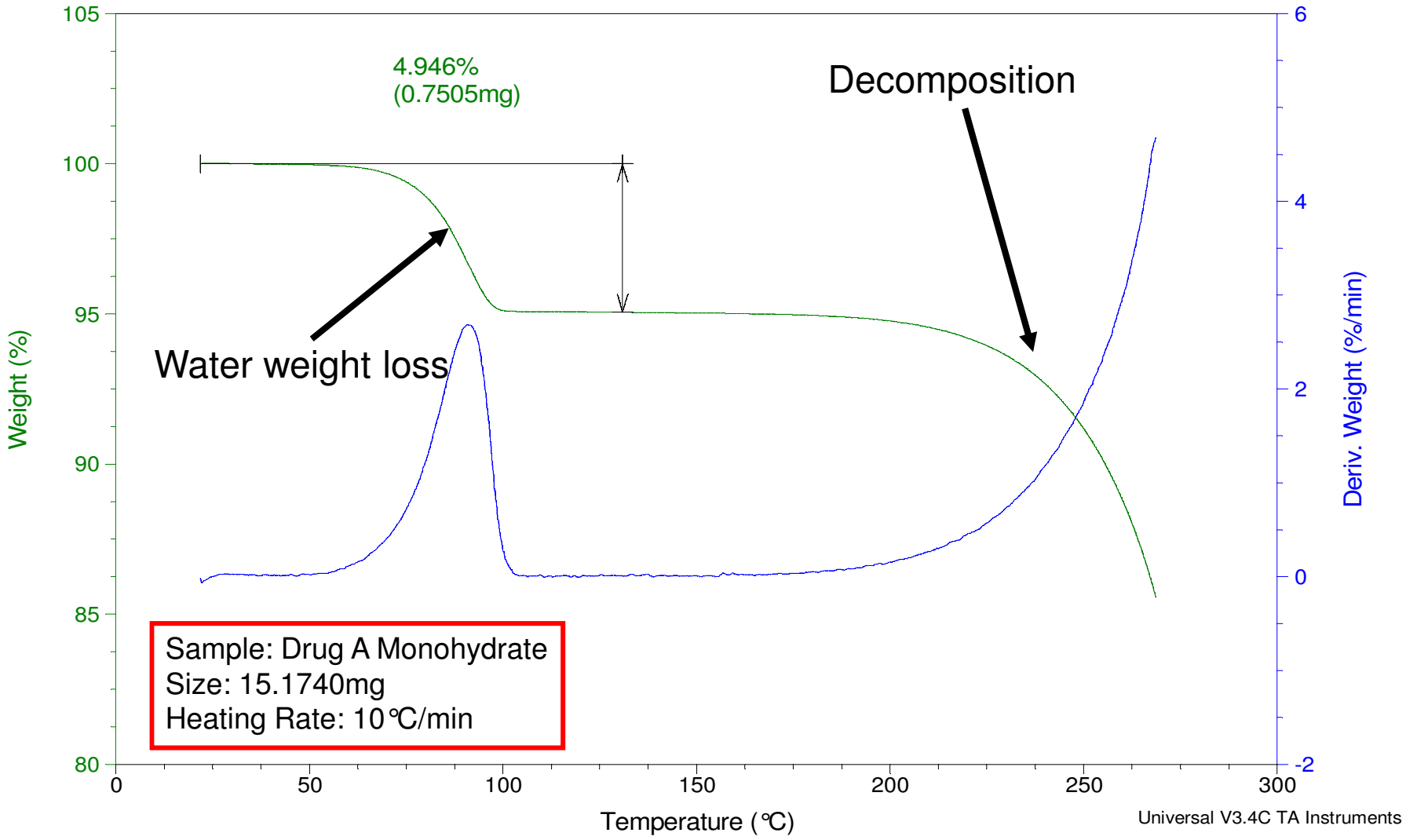
Overlay of 8 runs, same conditions



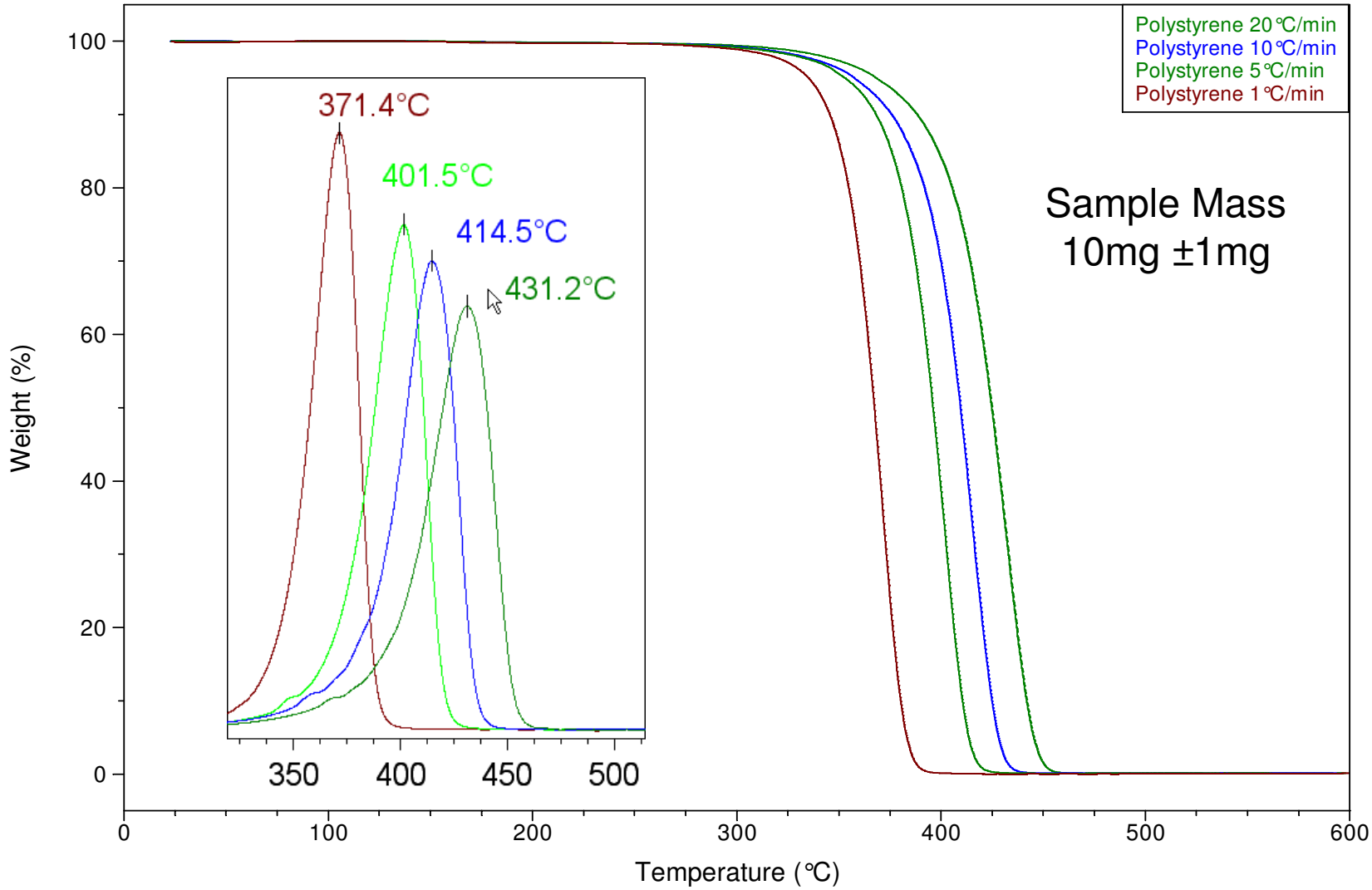
Thermal Stability of Polymers



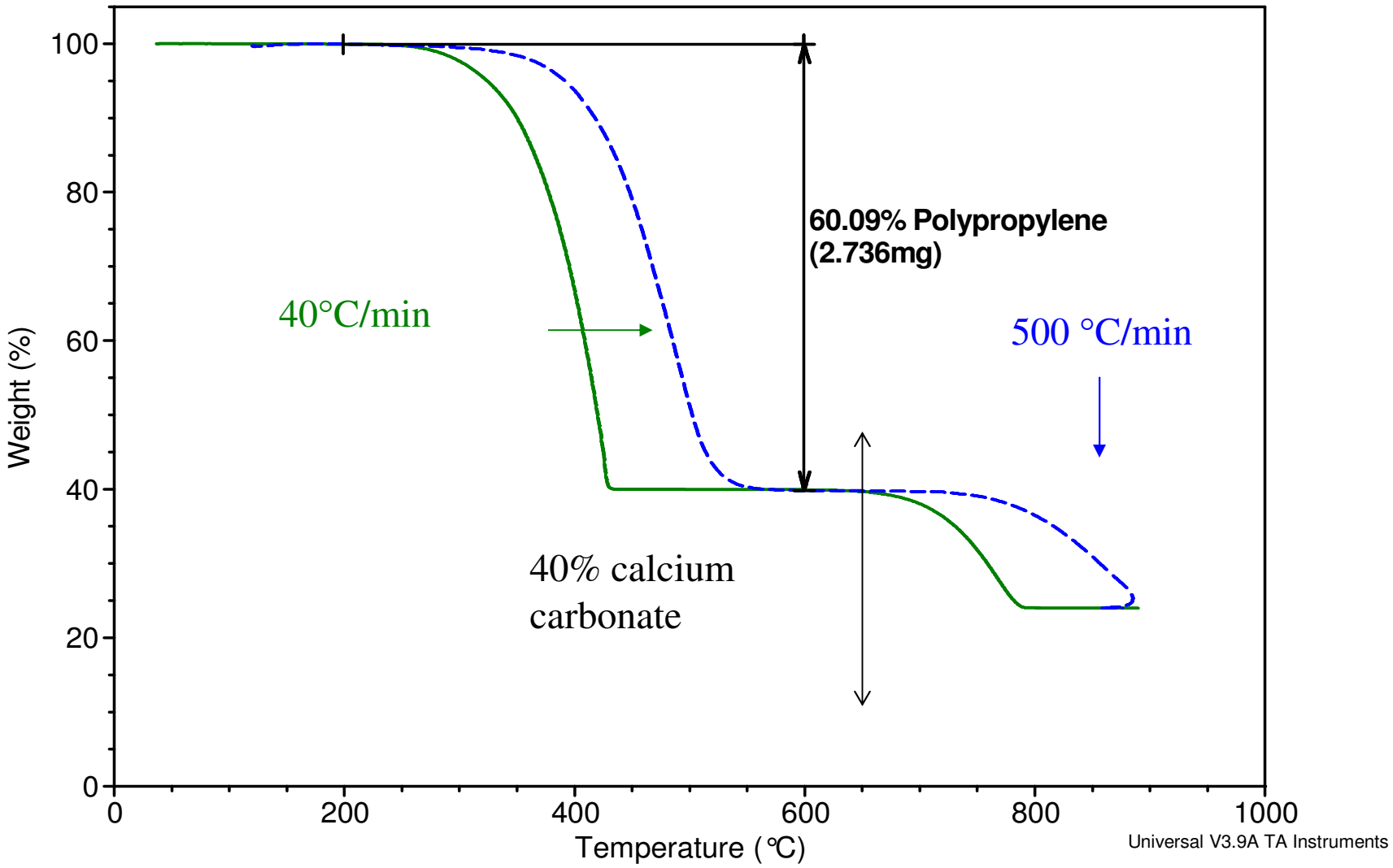
TGA of Drug A Monohydrate



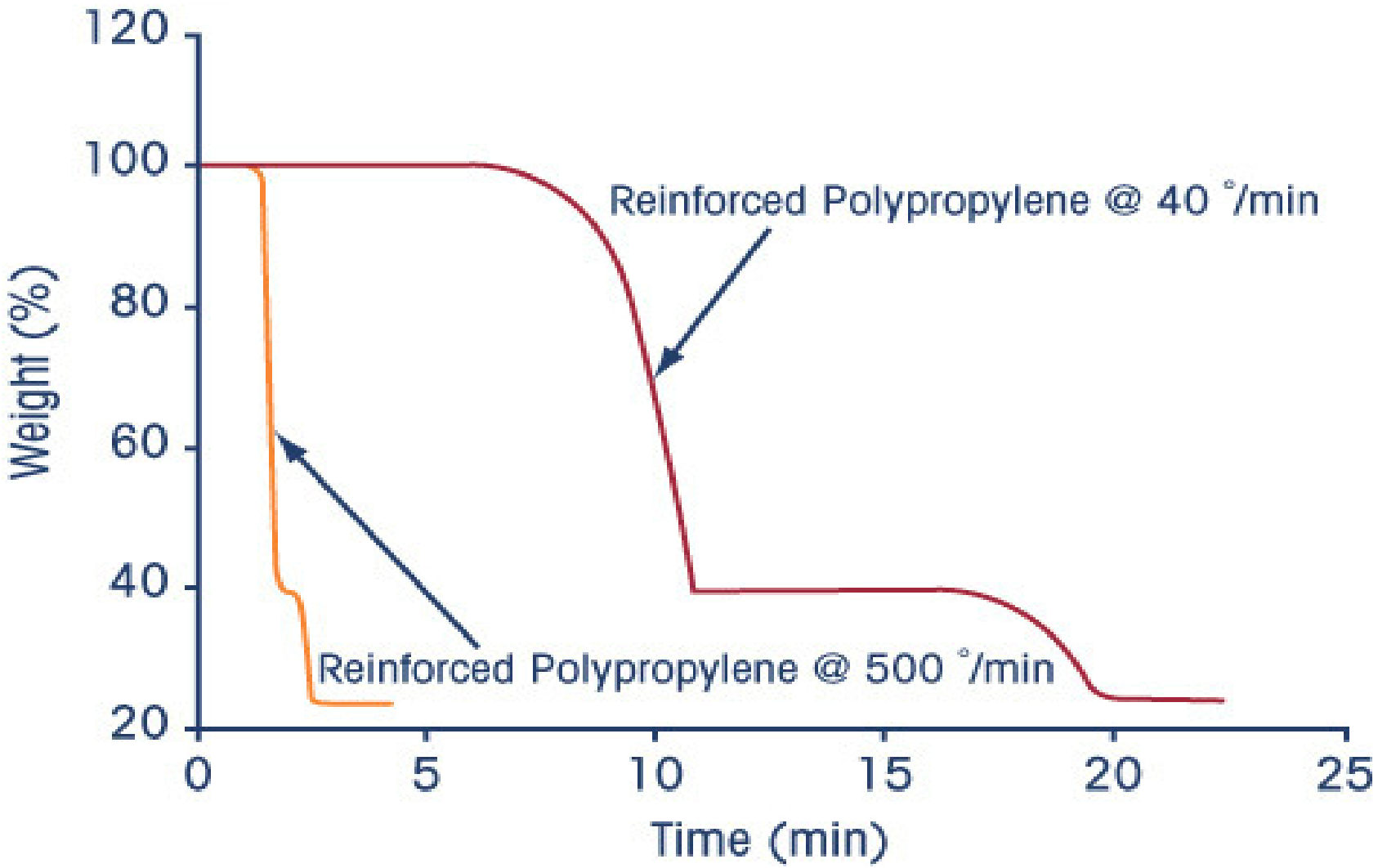
Higher heating rates increase the observed decomposition temperature



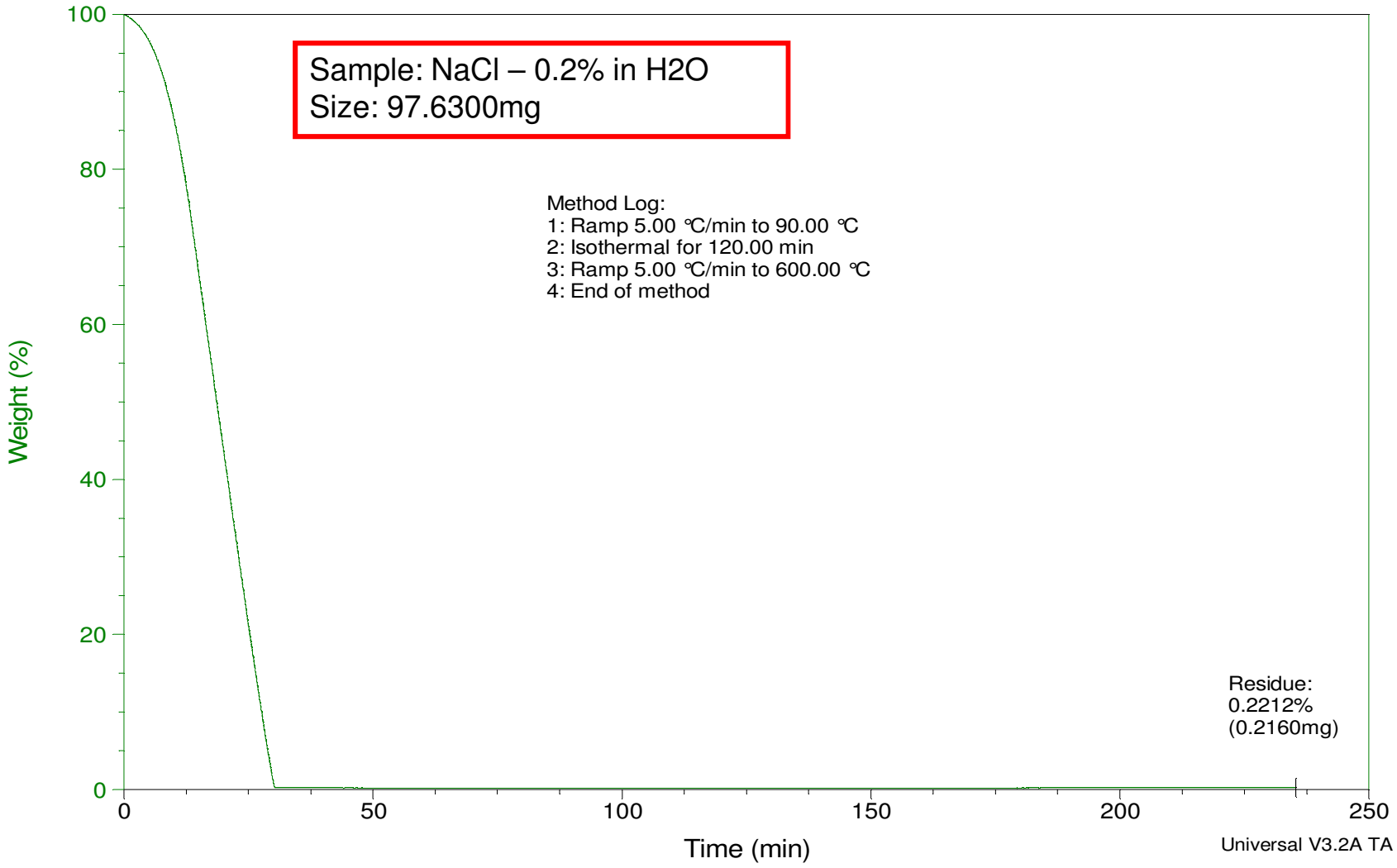
High-Heating Rate TGA Analysis



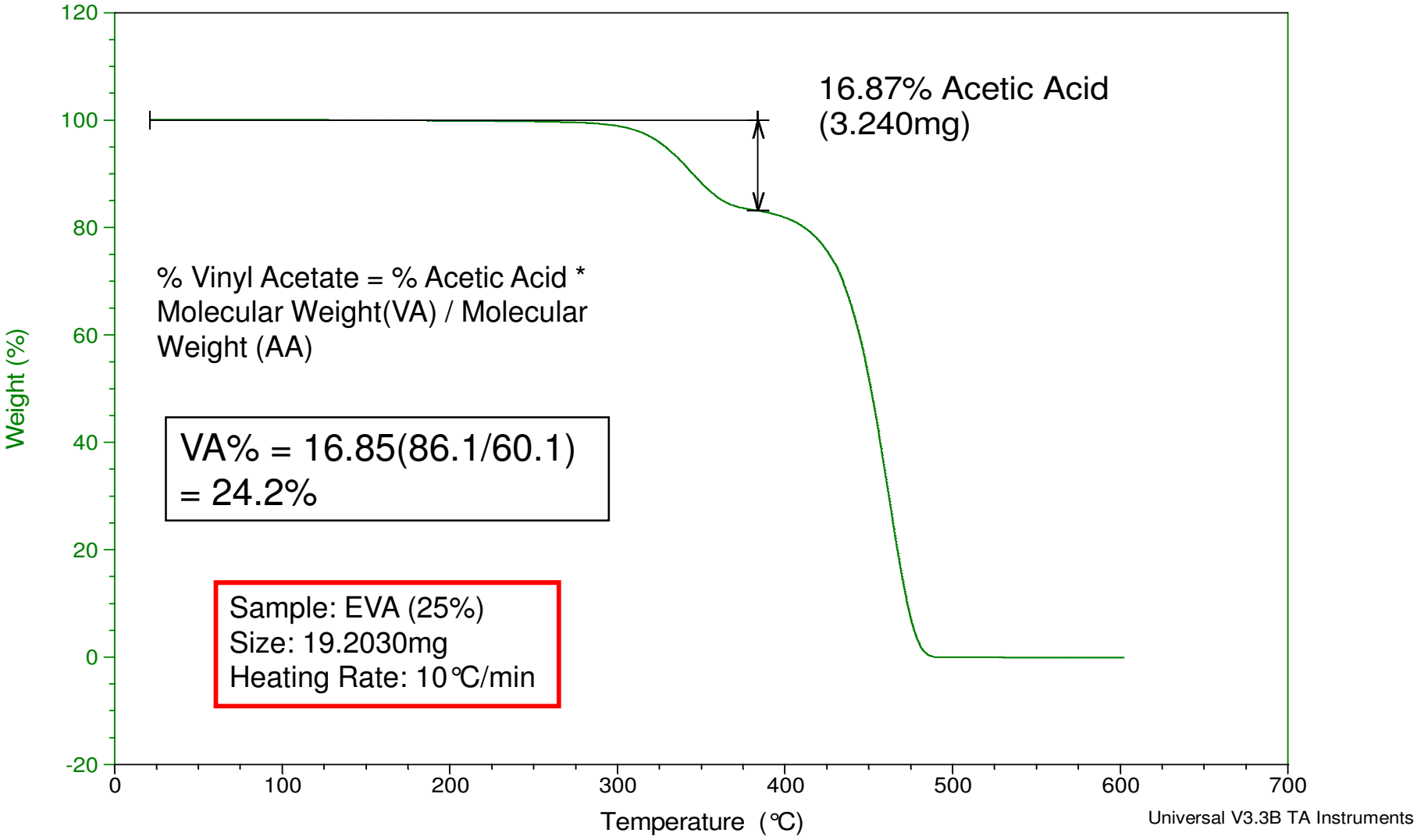
High-Heating Rate TGA Analysis



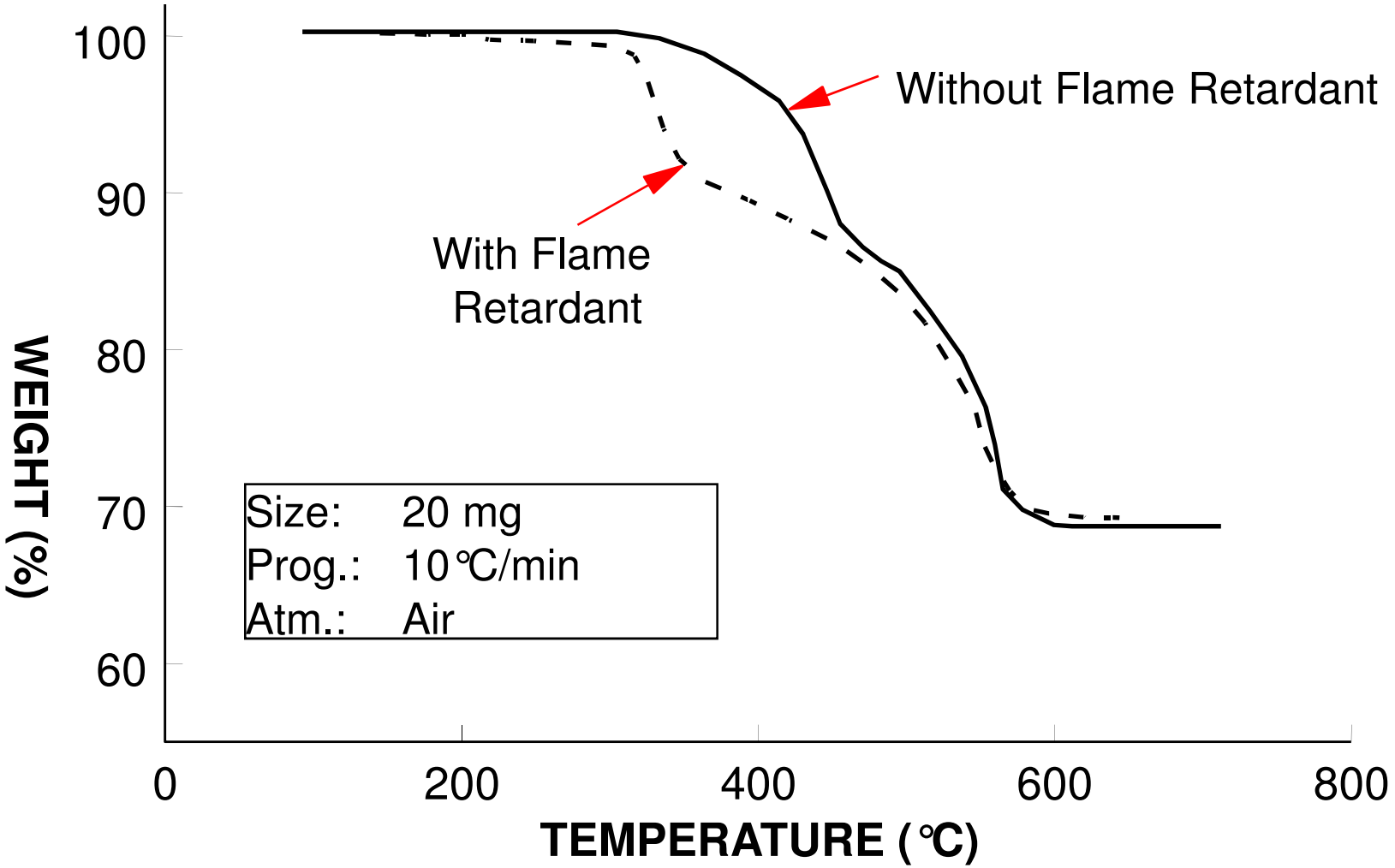
Residue Determination - 0.2% Salt Solution



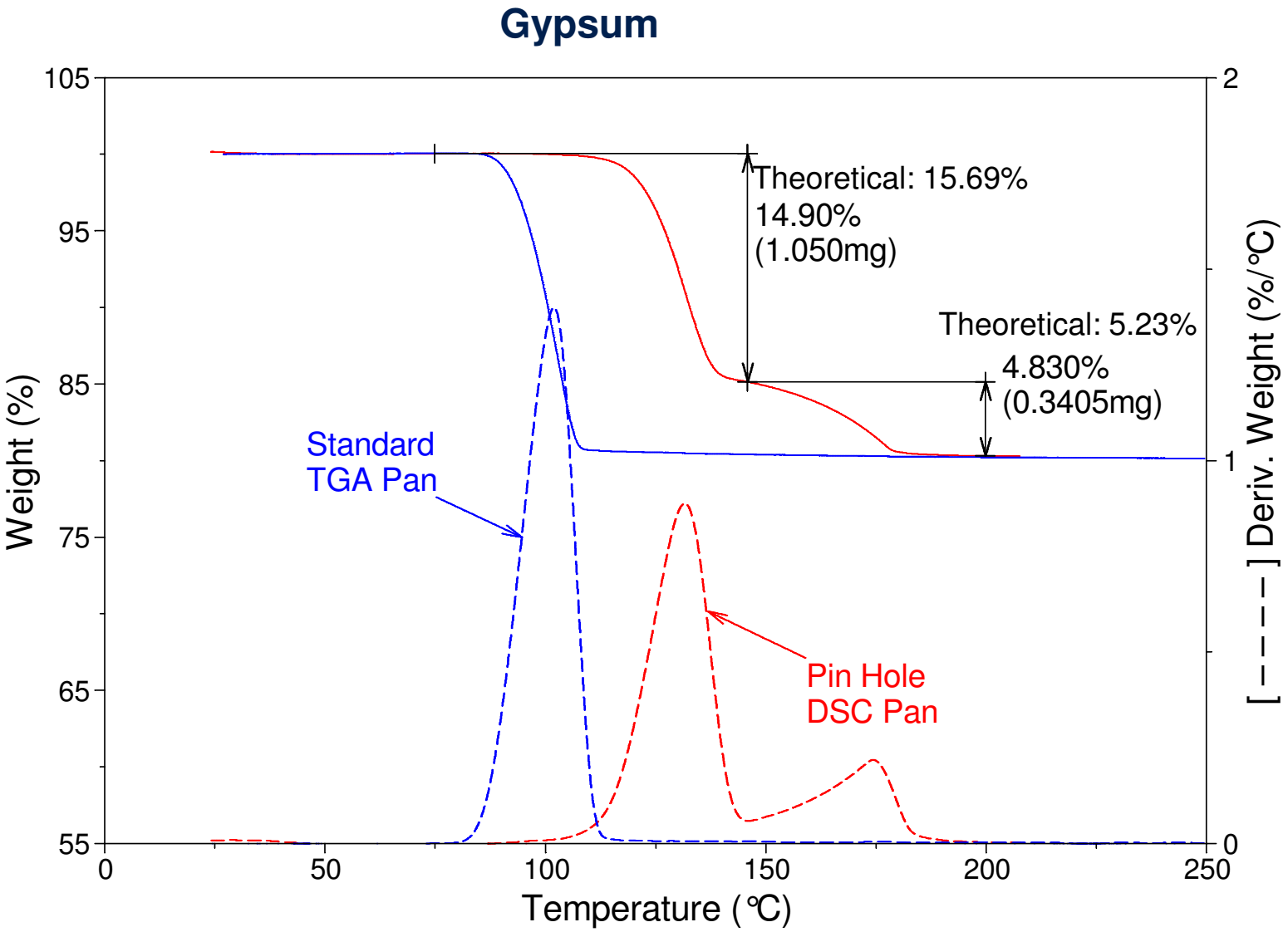
EVA Copolymer



Effect of Flame Retardant



Effect of DSC Pinhole pans on TGA resolution



The Discovery Mass Spectrometer (DMS)

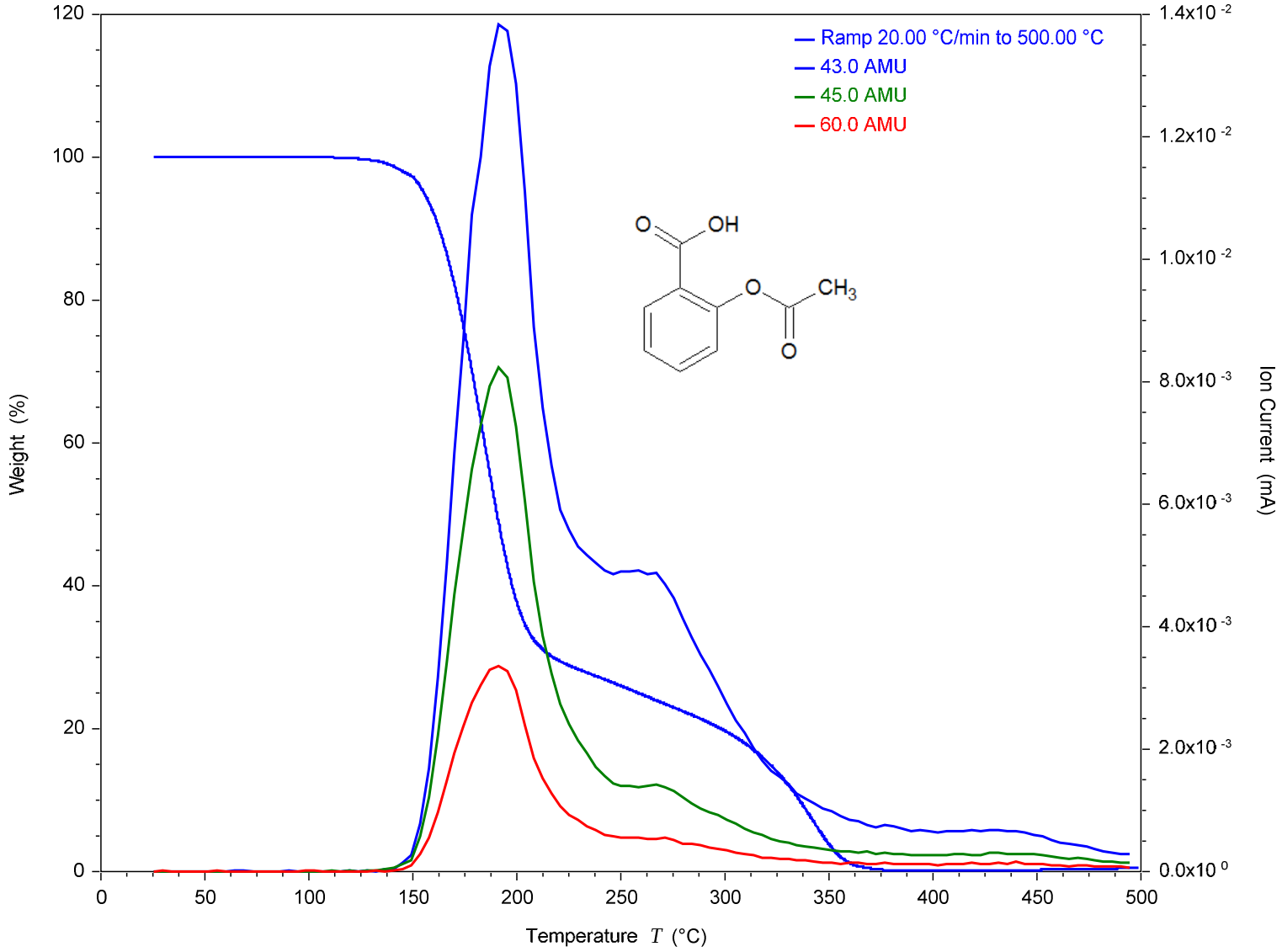
- Benchtop, unit resolution quadrupole mass spec designed and optimized for evolved gas analysis (EGA)

- Quadrupole detection system includes…
  - a closed ion source
  - a quadrupole mass filter assembly
  - dual detector system (Faraday and Secondary Electron Multiplier)

  …ensuring excellent sensitivity from ppb to percent concentrations

"Back off man I'm a scientist"

TGA-MS Example: Aspirin



Summary - TGA

- Thermogravimetric Analysis determines decomposition temperatures, rates of decomposition and volatilization, kinetics of weight loss, boiling points, vapor pressure, composition of multicomponent products and much more.

- TGA, along with DSC, is widely used because of its ease of operation and small sample requirements

- Most all technology based industries rely on TGA.

What Does TA Instruments Make?

- Differential Scanning Calorimeters
- Thermogravimetric Analyzers
- **Simultaneous Differential Thermal Analyzers**
- Microcalorimeters of many types
- Dilatometers and Thermomechanical Analyzers
- Thermal Diffusivity
- Thermal Conductivity
- Mechanical Testers
- Dynamic Mechanical Analyzers
- Rotational Rheometers
- Rubber Rheometers

Simultaneous Differential Thermal Analysis (SDT)

Introducing the Discovery SDT 650

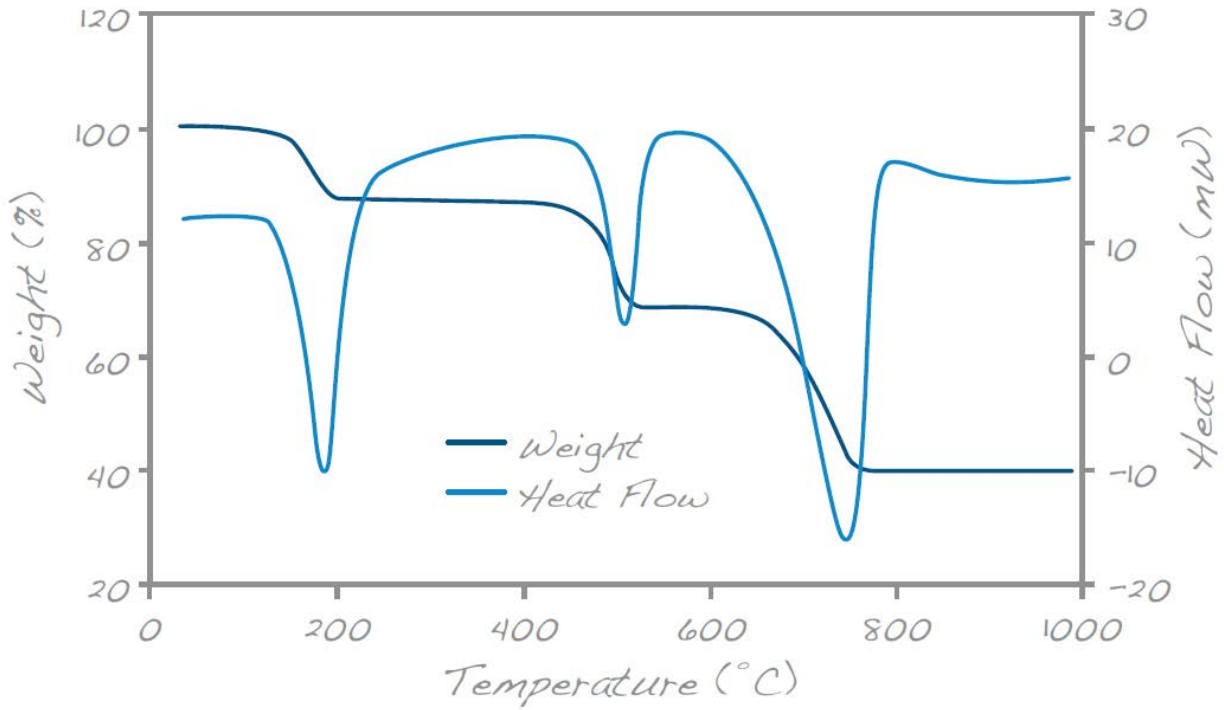
Discovery SDT 650

- Features and Technology
- Performance
- Applications

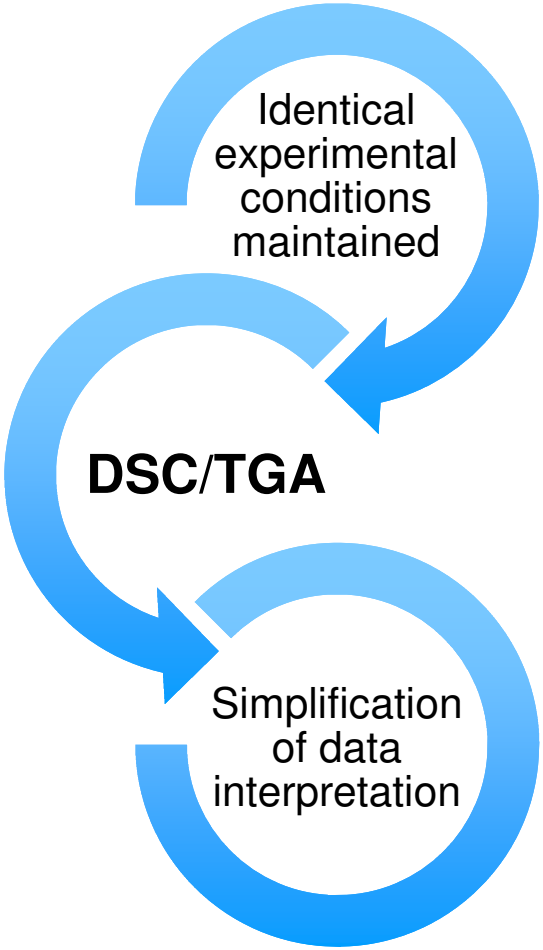
"This is the coolest thing I've ever seen"

Simultaneous DSC-TGA (SDT)

Simultaneous application of *Differential Scanning Calorimetry (DSC)* and *Thermogravimetry (TGA)* of a material will measure both *heat flow* and *weight change* as a function of time, temperature and atmosphere in a single experiment.



Simultaneous DSC-TGA (SDT)



- Identical experimental DSC and TGA conditions:
  - Sample Mass
  - Heating Rate
  - Atmosphere (purge gas and flow rate)
  - Sample Crucible
- Simplification of data interpretation
  - Is the sample weight stable during an endothermic or exothermic thermal event?
  - The complimentary information allows differentiation between endothermic and exothermic events which have no associated weight loss (melting and crystallization) and those which involve a weight change (volatilization, oxidation, degradation).

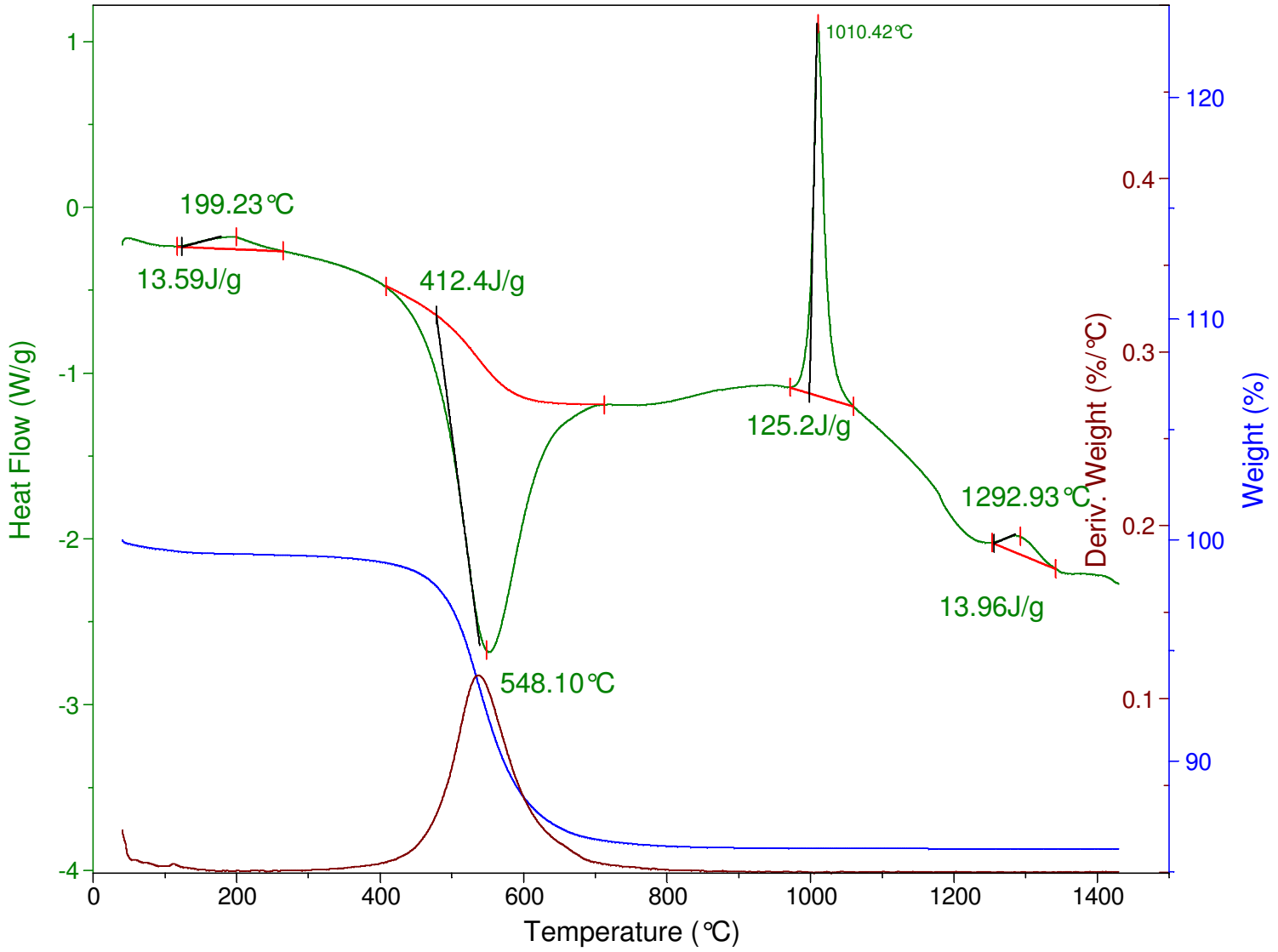
Discovery SDT 650

An excellent addition to the Discovery Thermal Suite

Discovery Series instrument features

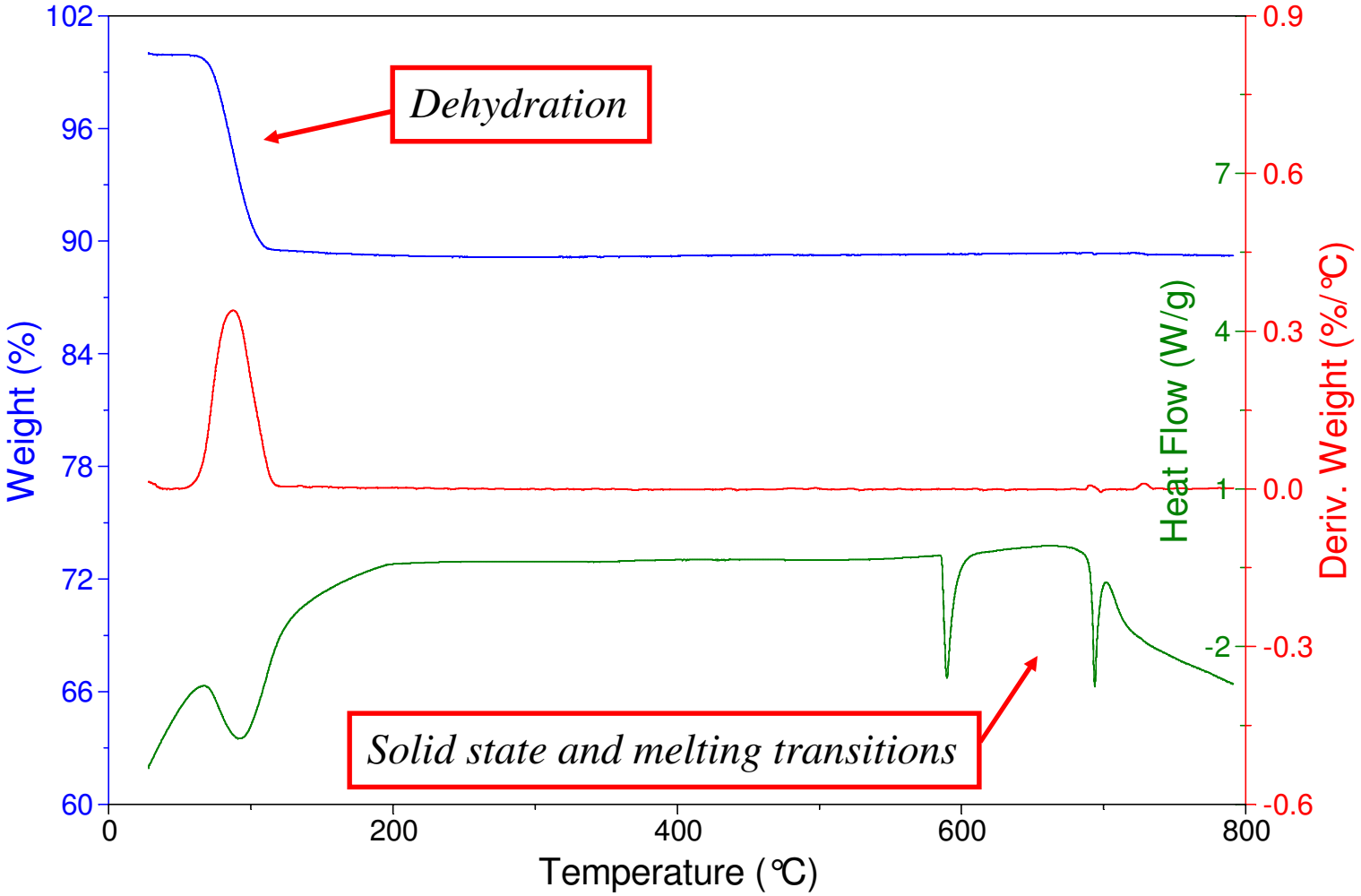
- *Enhancements to technology*
- *Best-in-class performance without pre- and post- test data manipulation*

TGA-DSC Kaolin Clay

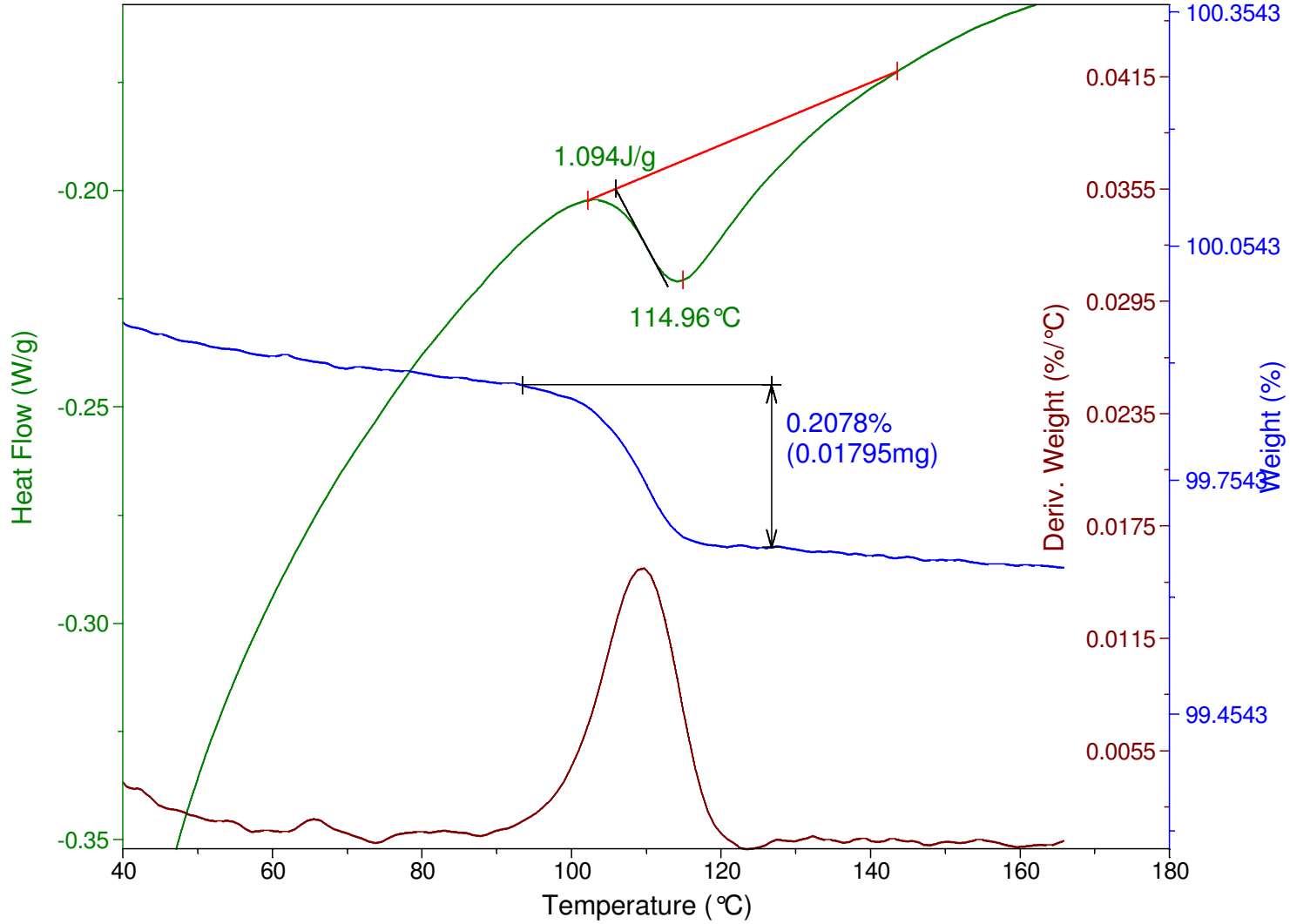


DSC-TGA Sodium Tungstate

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

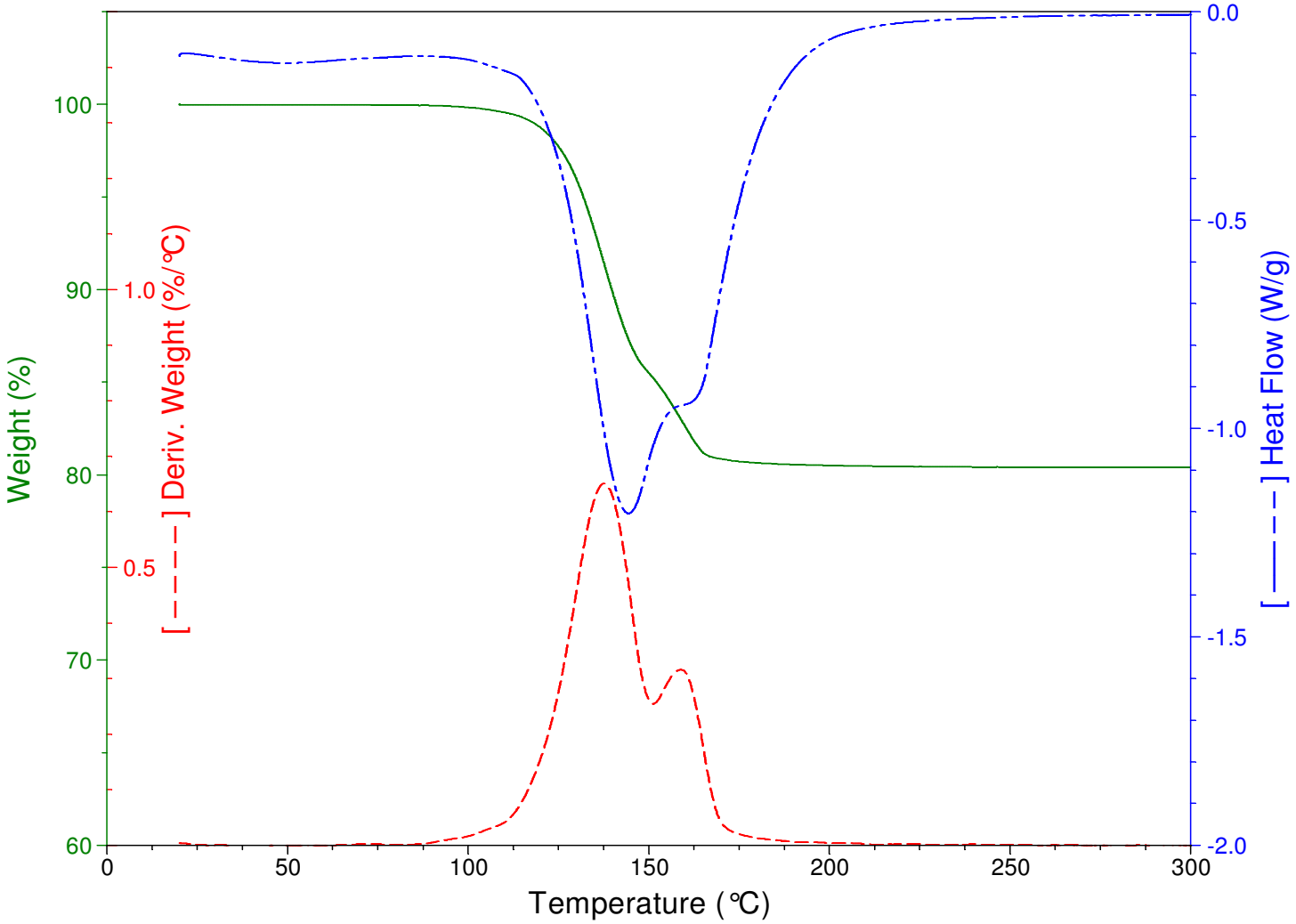


Dehydration Sensitivity



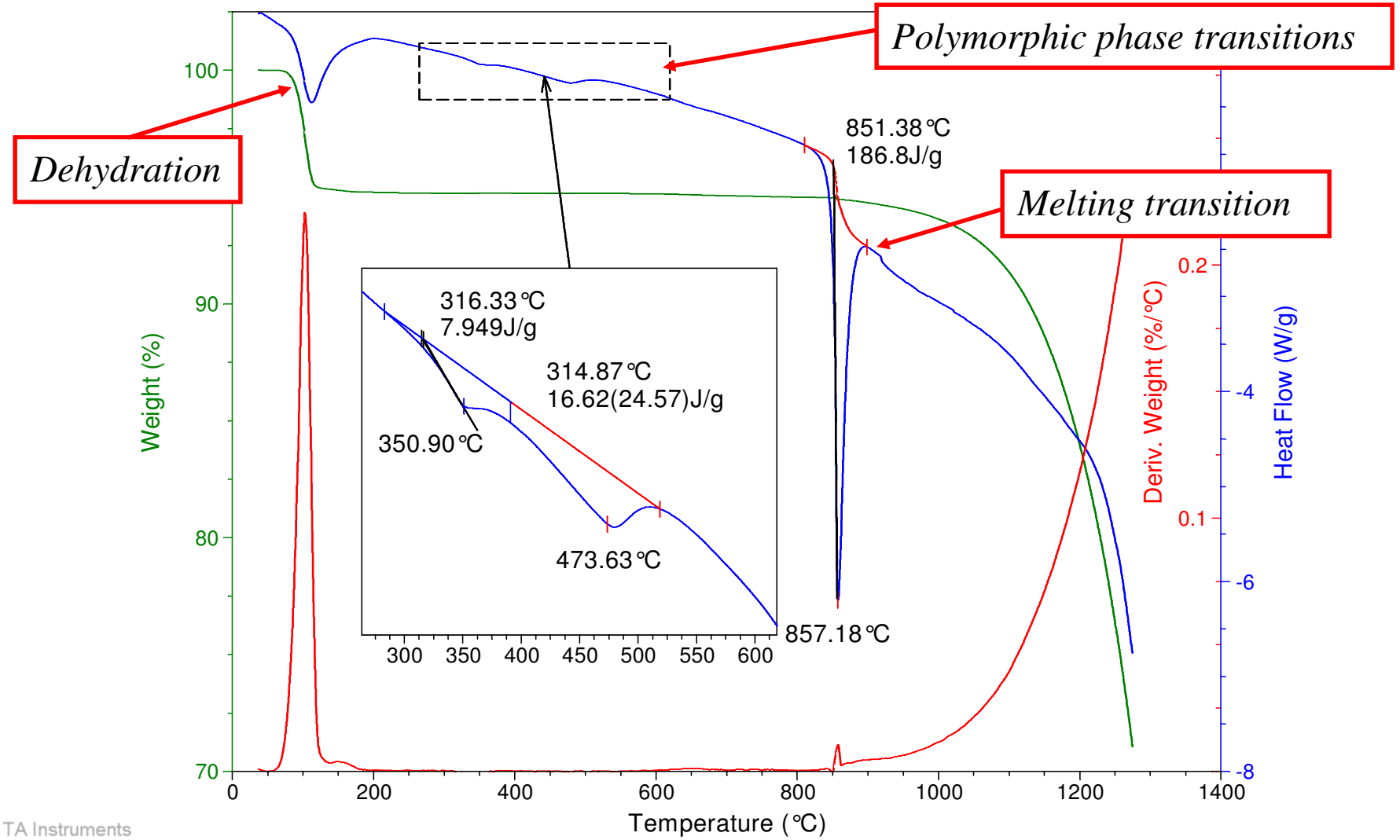
DSC-TGA Gypsum

Alumina sample pans with lids and heated at 10°C/min

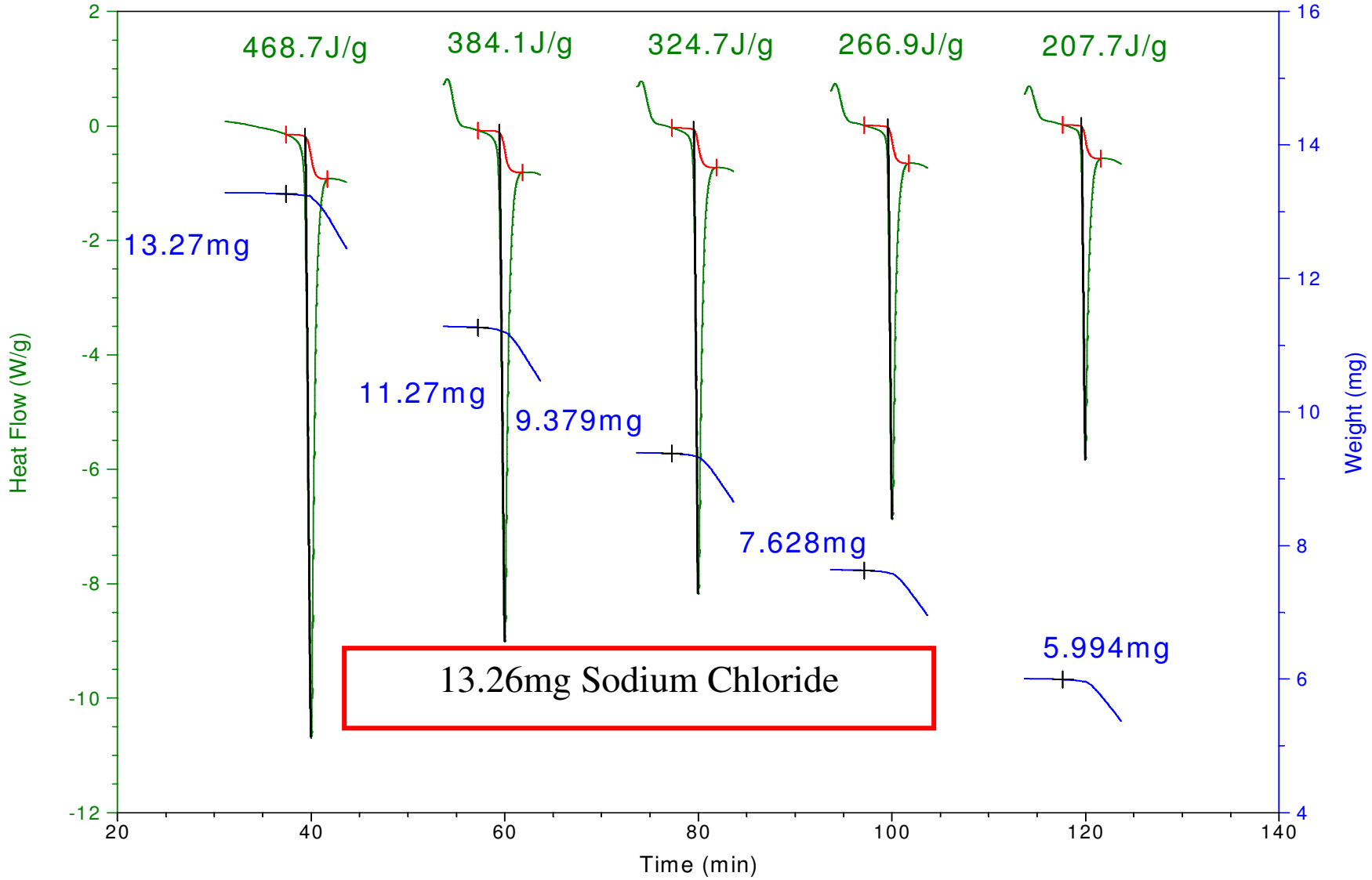


TGA-DSC Soda Ash

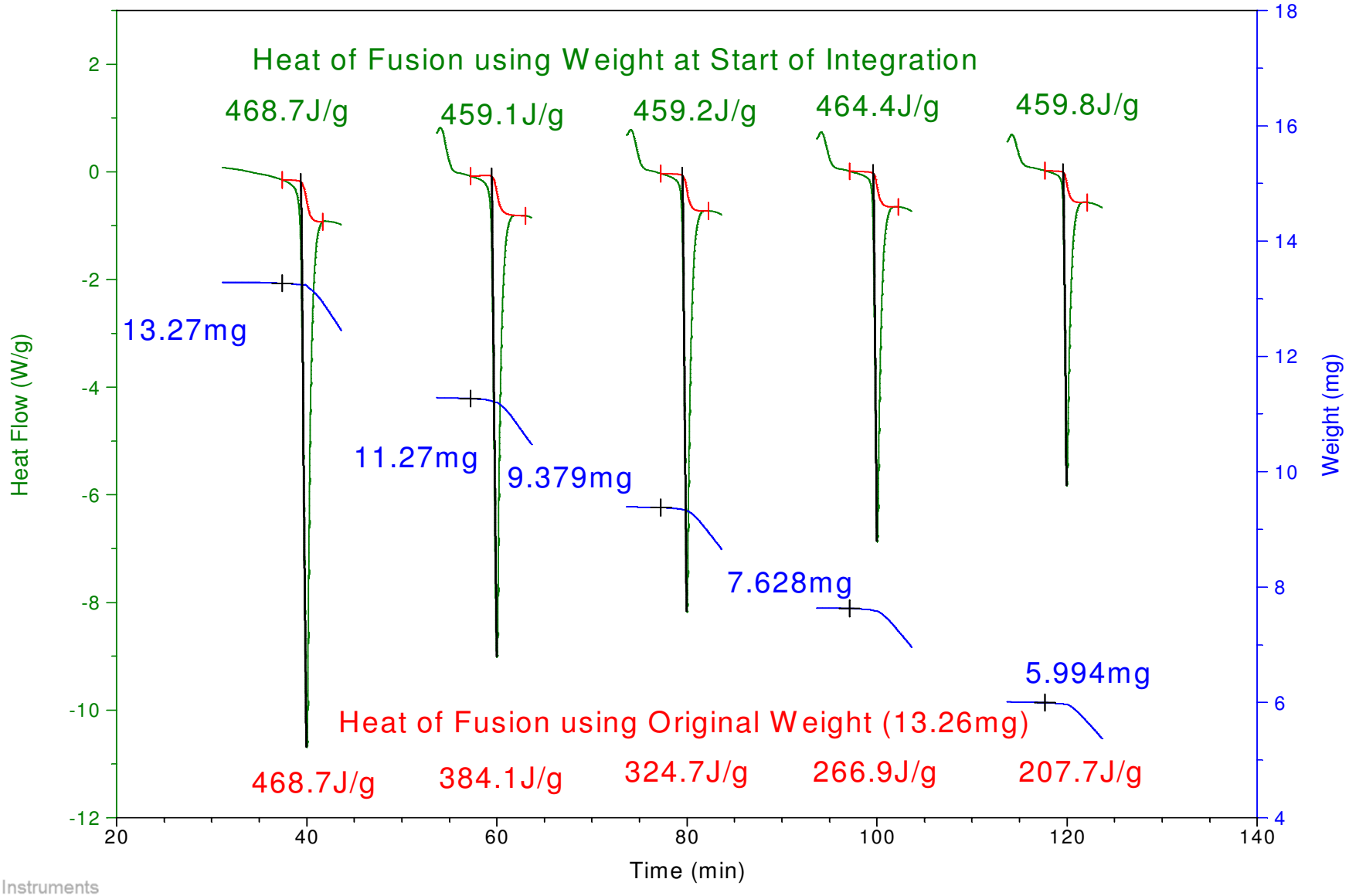
Heat flow Integrations automatically normalized using weight at start of transition



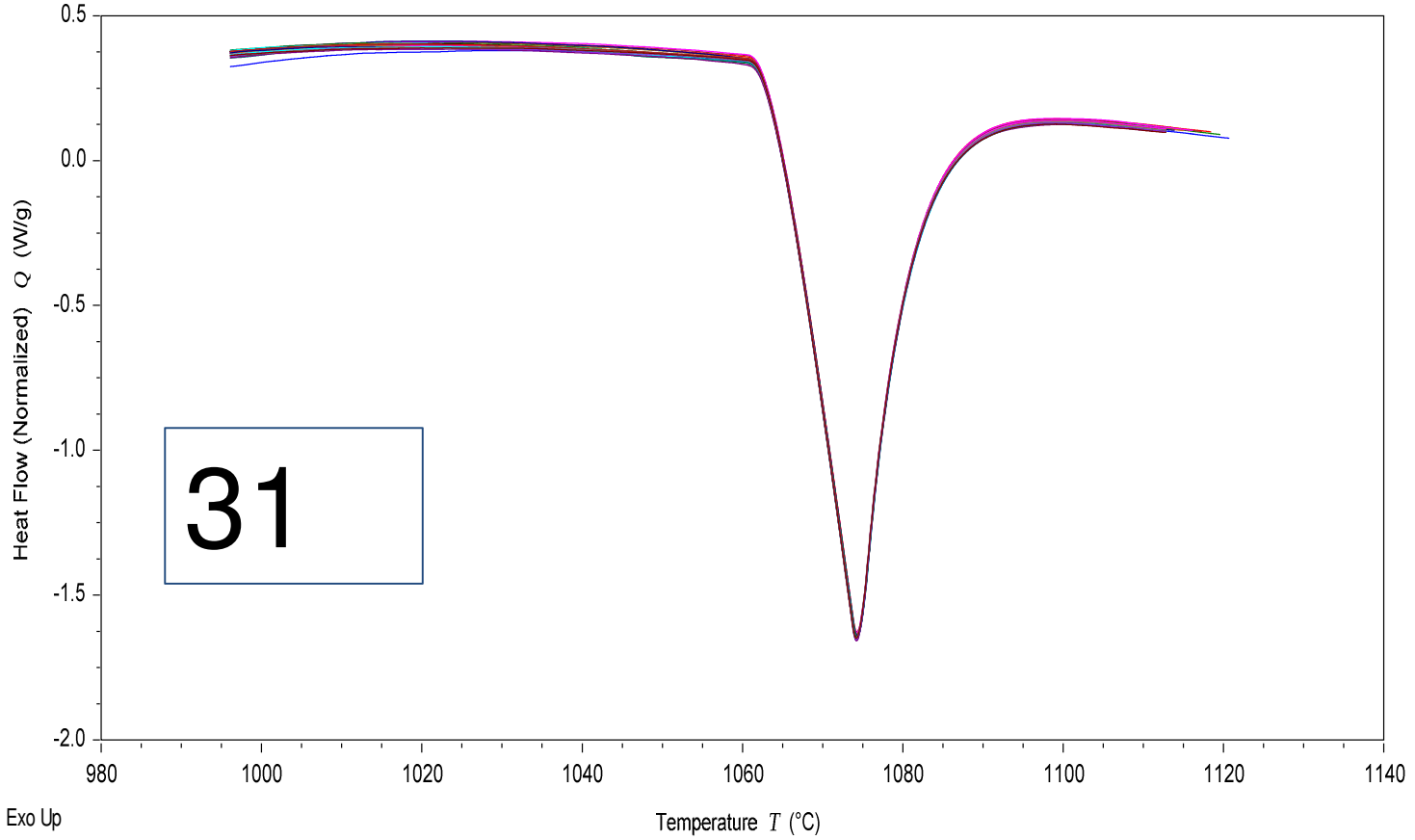
Heat of Fusion Using Original Weight



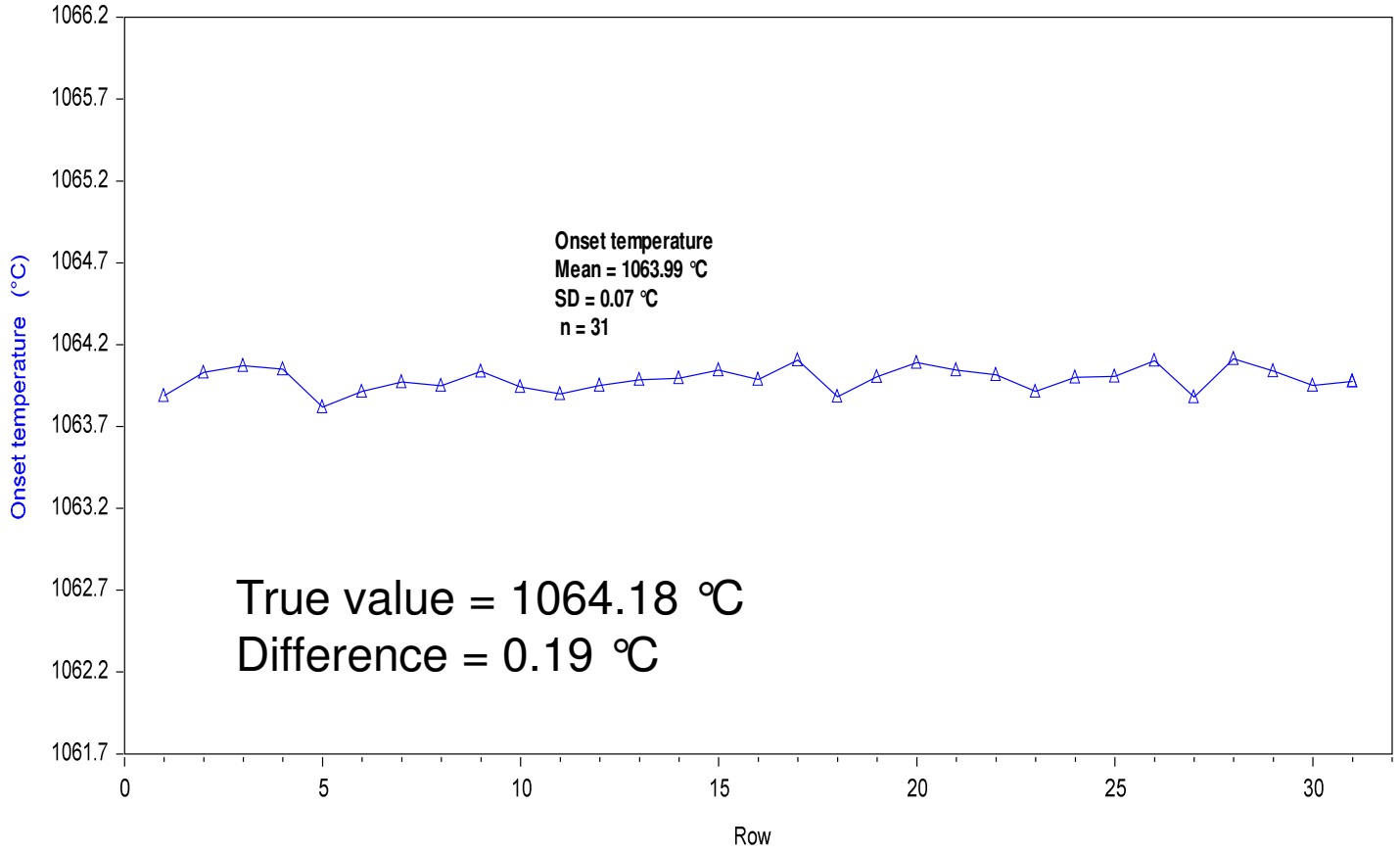
Significance of Normalized Weight



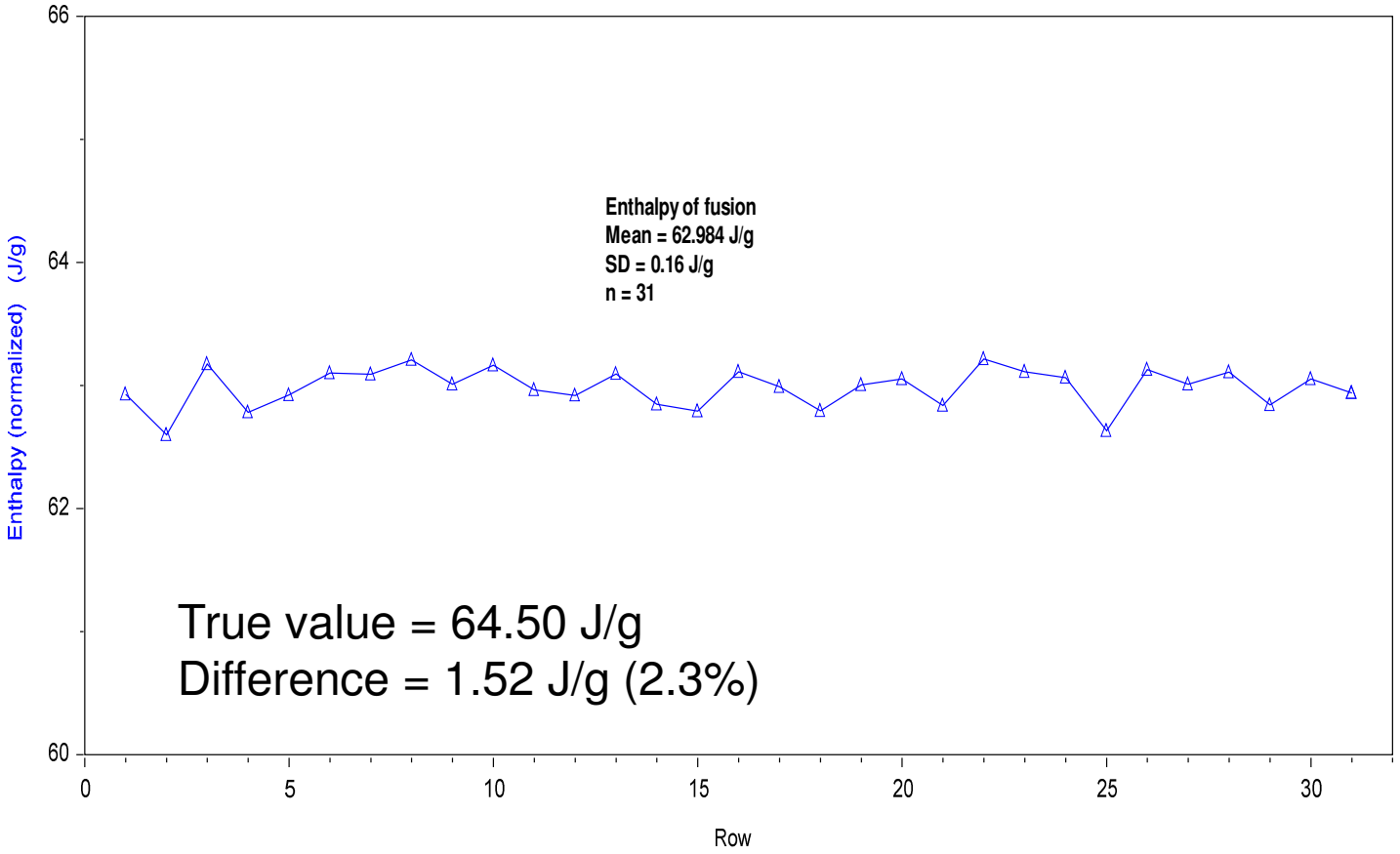
Gold melting – How many runs are shown here? Closest guess wins a movie ticket or Starbucks gift card:



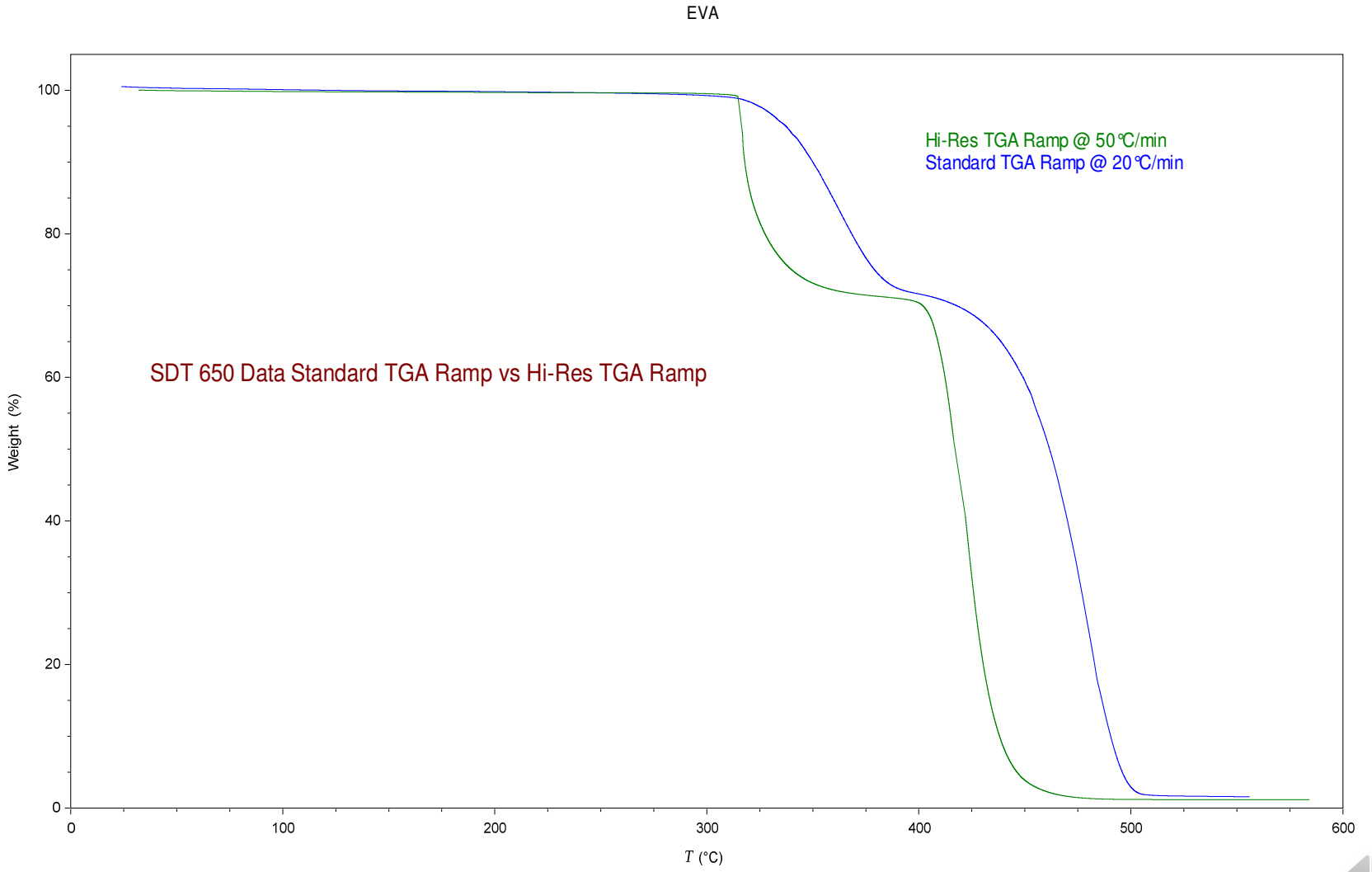
Melting point measurements



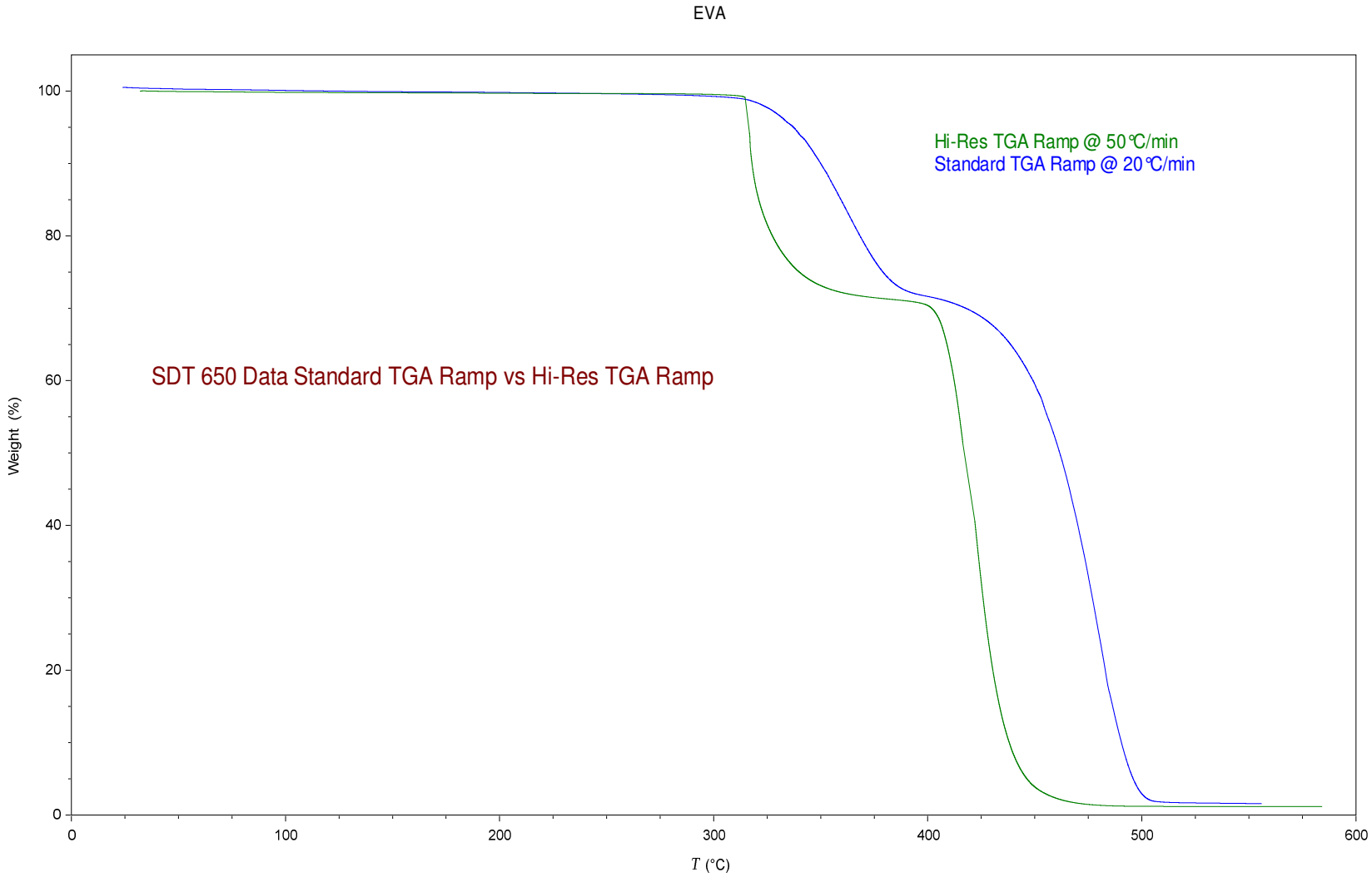
Enthalpy of fusion measurements



Hi-Res™ TGA for Improved Resolution



Hi-Res™ TGA for Improved Resolution



Why Upgrade from the Q600 SDT?

Features and Function

- Advance Features
  - MDSC® for Cp
  - Hi-Res™ TGA for better separation
  - MTGA™ for kinetics
- Better Performance
  - Lower weight drift
  - Improved gas handling
    - Better vacuum
    - Gas blending module
- Reliable Automation
  - 30-position autosampler
  - Automated calibrations & verifications

Features and Function

- Innovative “App-Style” Touch Screen
  - Graphical design for enhanced usability
  - Information, status and great data just One-Touch-Away™
  - Touch screen on all models
- Easy quick change beams
- Powerful TRIOS Software
- 5 year warranty on furnaces

The World's Finest Simultaneous DSC/TGA

- The new Discovery SDT series will out perform any SDT on the market, including the Q600
  - Better weight baseline
  - Cp determination
  - Dual-sample TGA mode
- An excellent companion to the Discovery Series DSC's, TGA's and Rheometers
- Remember:
  - Performance
  - Reliability & productivity
  - Usability
  - World Wide service & support
  - 5 year warranty on furnaces

What Does TA Instruments Make?

- Differential Scanning Calorimeters
- Thermogravimetric Analyzers
- Simultaneous Differential Thermal Analyzers
- **Microcalorimeters of many types**
- Dilatometers and Thermomechanical Analyzers
- Thermal Diffusivity
- Thermal Conductivity
- Mechanical Testers
- Dynamic Mechanical Analyzers
- Rotational Rheometers
- Rubber Rheometers

Microcalorimeters of Many Types

Definition

Calorimetry – (n) Measurement of the amount of heat evolved or absorbed in a chemical reaction, [biological process,] change of state or formation of a solution.
American Heritage Dictionary

Modern Calorimeters

- **Differential Scanning Calorimeter (DSC)**
- **Isothermal Titration Calorimeter (ITC)**
- **Isothermal Microcalorimeter (IMC)**
- Combustion Calorimeter (Bomb Calorimeter)
- Adiabatic Calorimeter
- Hazards Calorimeter
- **Solution Calorimeter**
- **Sorption Calorimeter**
- Respiratory Calorimeter
- Animal Calorimeter **....**

Modern Microcalorimeters

Isothermal Microcalorimeter

Differential Scanning Calorimeter

Isothermal Titration Calorimeter

Differential Scanning Calorimeter

Differential Scanning Calorimeter

Isothermal Microcalorimetry (IMC)

Sensitive

mW µW nW

More Sensitive

TAM Air

TAM IV & TAM 48

MC DSC

Nano ITC

8 – samples
8 – reference
20 mL sample Vol.
Temp Range: 5 to 90 ℃

3 – samples
1 – reference
Sample Flexibility
≤ 1 mL sample Vol.
Temp Range: -40 to 150 ℃

1-48 – samples
Sample Flexibility
1-20 mL sample Vol.
Temp Range: 15 – 150 ℃

1 – sample
Max Sensitivity
1 mL or 190 µL cells
Temp Range: 2 – 80 ℃

Isothermal Microcalorimeters

- General Purpose:
  - **T**hermal **A**ctivity **M**onitors (e.g. TAM IV, TAM 48, TAM AIR) are general purpose IMC which can be accessorized to study many different processes such as materials stability and compatibility, cement curing, heats of solution, pharmaceutical stability, and microbiological growth.

- Specialized:
  - An isothermal titration calorimeter (ITC) is an IMC specifically designed to measure the heats of interaction when one liquid is titrated into another. ITC is used to study intermolecular binding, surfactant properties (e.g. micelles), and enzyme kinetics.

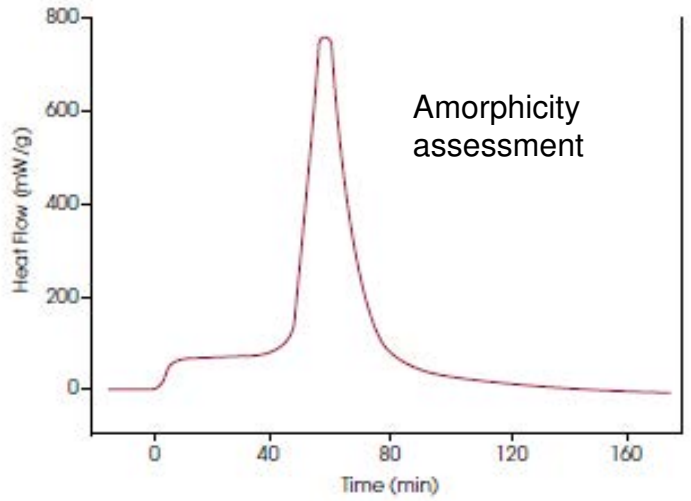
TAM Isothermal Microcalorimeter

TAM IV and 48 Configurations

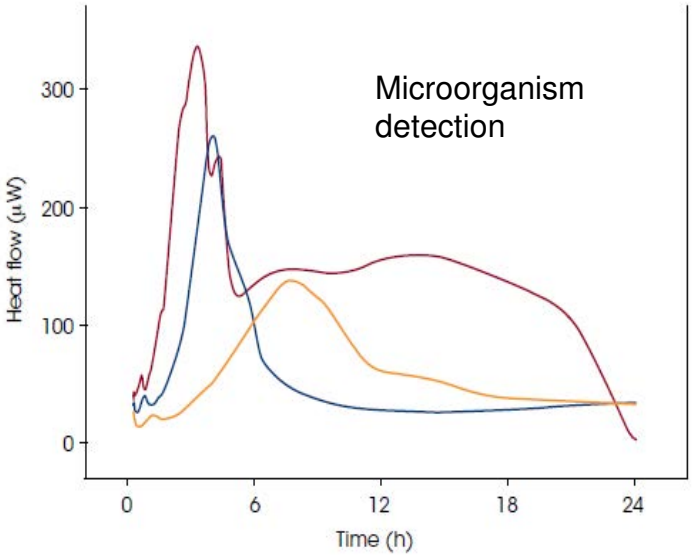
Microcalorimetry – A Universal Technique

- Isothermal microcalorimetry is a technique for a direct measurement of heat production or consumption of a sample
- Virtually all chemical, physical, and biological processes result in either heat production or heat consumption.
- Calorimetry quantifies the amount and rate of heat release in terms of heat flow, heat and heat capacity.
- Calorimetry is a non-specific technique making it ideal for studying almost all kind of biological, physical and chemical processes in life sciences, material sciences and within the pharmaceutical field.

TAM IV – The Universal IMC

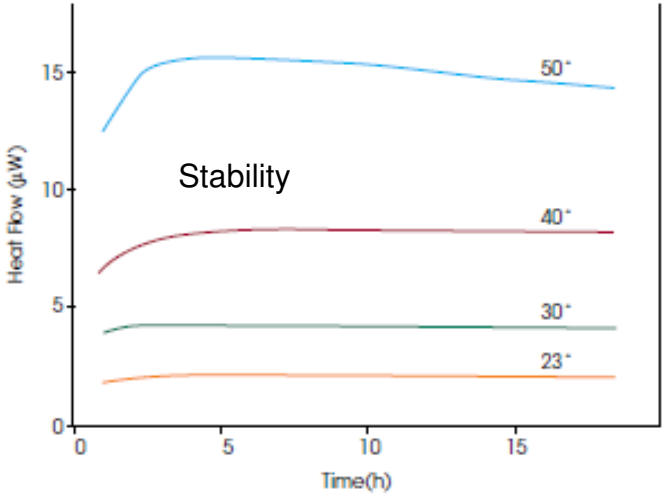


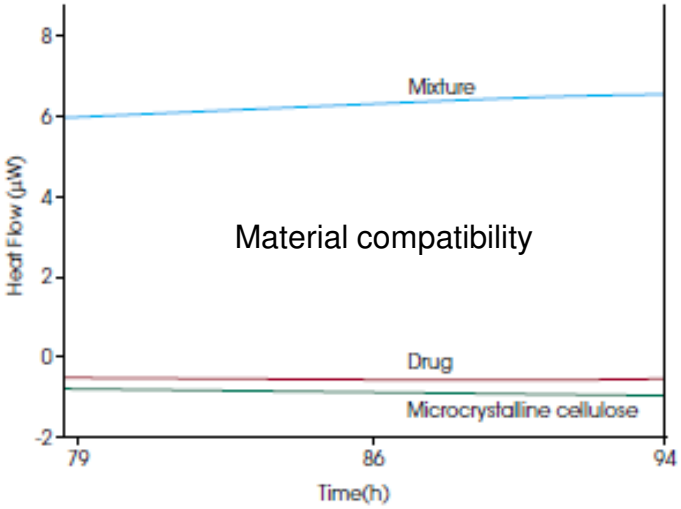
Amorphicity assessment



Microorganism detection

TAM IV – The Universal IMC





TAM IV – Flexibility in Size and Sensitivity

Sample size

Absolute Sensitivity

TAM IV – Sample Handling Systems

The TAM IV offers a complete array of ampoules in two basic types; closed and open.

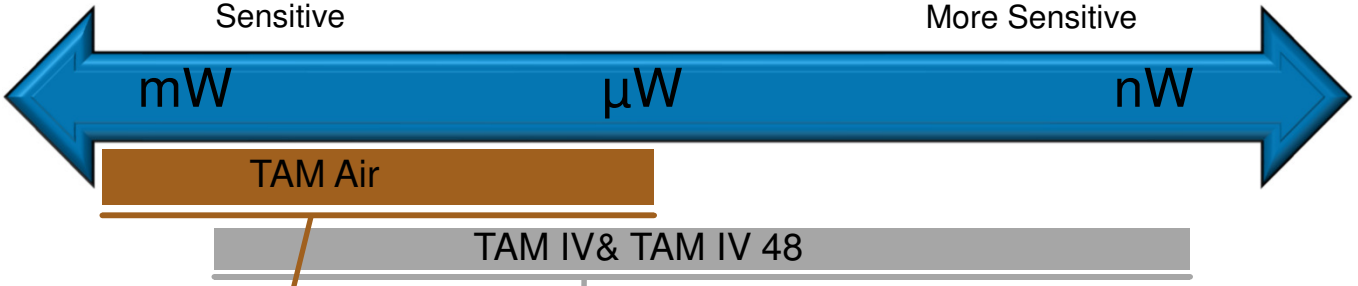
- Closed, also referred to as static, ampoules contain the specimen in a static fashion: no manipulation of the sample is performed during the measurement.
- Open ampoules are part of the micro reaction system for the direct manipulation or modification of the sample or its surroundings during the experiment.

Summary - Isothermal Microcalorimetry

- Calorimetry is nondestructive and noninvasive
- Monitor all kinds of processes:
  Chemical, Physical and Biological
- Not dependent on the physical shape of the sample
- Solids, liquids and gases can be studied
- No chemical derivatization or immobilization
- No need for sample preparation
- Non-specific
- Microcalorimetry continuously and directly measures the process under study - Real-time data

TAM – Air
Isothermal Microcalorimetry

TAM – Thermal Activity Monitors



5 – 90 °C

Flexible

interchangeable calorimeter blocks depending on sample

Sample sizes

from 20 mL up to 125 mL

3 channel version

Large samples up to 125 mL

8 channel version

- Samples up to 20 mL
- Possibility to add and mix *in situ*

4 – 150 °C

Flexible

one system multiple possibilities

Modular

add functionality by choice of calorimeters, sample handling systems and accessories

Sample sizes

from less than 1 mL up to 125 mL

4 channel version

highest flexibility and sensitivity

48 channel version

highest throughput

TAM Air IMC

- TAM Air consists of a thermostat and a calorimeter
- The air based thermostat precisely controls the calorimeter temperature and minimize outside temperature disturbances.
- The calorimeters are held together in a single removable block, with either 8 or 3 individual calorimeters
- Each calorimeter is a twin heat flow calorimeter, consisting of a sample and a reference side

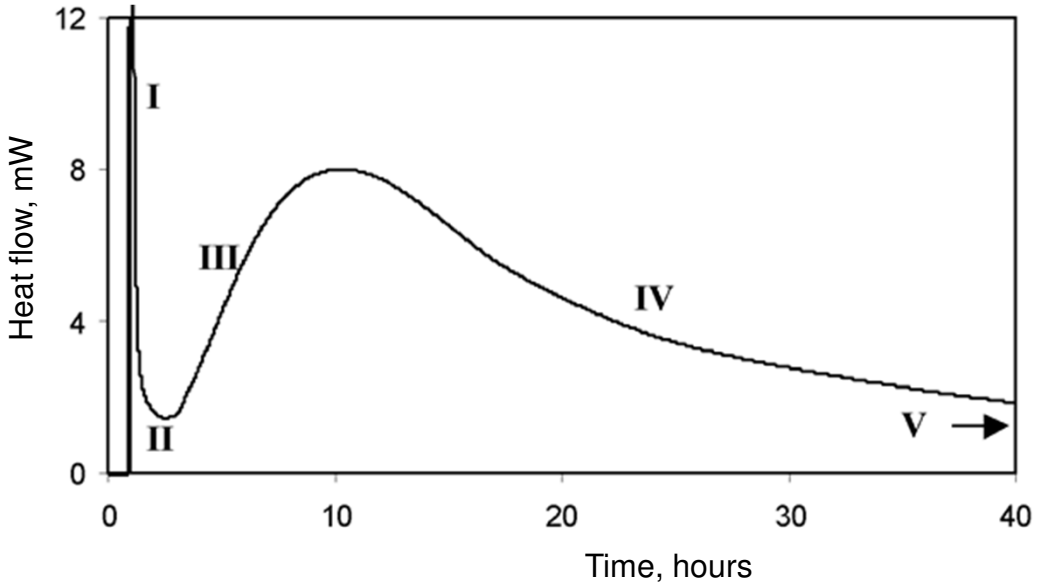
Sample Handling

- Static ampoules available in glass, HDPE plastic and stainless steel
- Admix ampoule is available in 20 mL size with and without motor for stirring


Admix Ampoule with manual stirring


Admix Ampoule with stirring motor

Cement Hydration Process

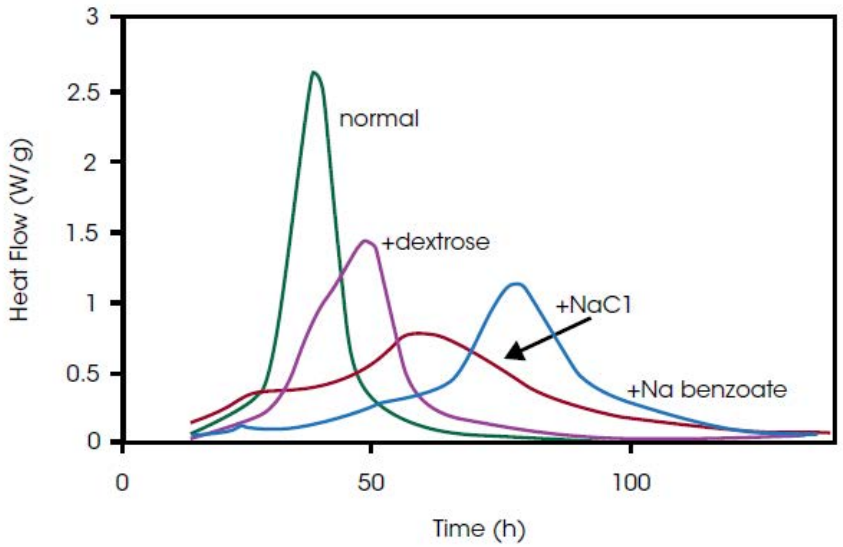


I. Rapid initial process – Dissolution of ions and initial hydration
II. Dormant period – Associated with a low heat evolution and slow dissolution of silicates
III. Acceleration period – Silicate hydration
IV. Retardation period – Sulfate depletion and slowing down of the silicate hydration process
V. Long term reactions

Food Fermentation

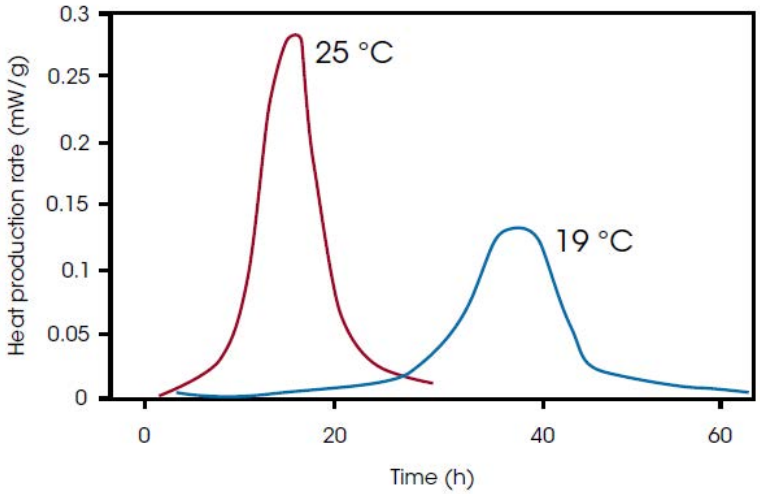
Fermentation of

- milk
- beer &wine
- cheese
- pro-biotic foods



Calorimetry can be used to study the properties of microbial cultures such as

- assess differences between different cultures
- measure their doubling time
- the influence of additives
- the influence of temperature



Lars Wadsö: Milk Fermentation studied by Isothermal Calorimetry
TA Instruments AN 314-04

Power of TAM Air

- Multi-sample capacity for simultaneous analysis
  - Eight- or three-channel true twin calorimeters each with low noise, high sensitivity and excellent long term stability
- Easy and robust operation
  - TAM Air 8 and 3 channel calorimeter can easily be exchanged depending on sample needs
- Sample flexibility with a choice of ampoule configurations
- Increased measurement specificity with external probes

Isothermal Titration Calorimetry

Isothermal Microcalorimetry

Sensitive

mW µW nW

More Sensitive

TAM Air

TAM IV & TAM 48

MC DSC

Nano ITC

8 – samples
8 – reference
20 mL sample Vol.
Temp Range: 5 to 90 ℃

3 – samples
1 – reference
Sample Flexibility
≤ 1 mL sample Vol.
Temp Range: -40 to 150 ℃

1-48 – samples
Sample Flexibility
1-20 mL sample Vol.
Temp Range: 15 – 150 ℃

1 – sample
Max Sensitivity
1 mL or 190 µL cells
Temp Range: 2 – 80 ℃

Excellent!!

Nano ITC

Isothermal Titration Calorimetry (ITC)

- ITC is recognized as “Gold Std” technique for measuring molecular binding reactions

- Only technique that gives full thermodynamic profile of a molecular binding reaction in one experiment
  - Enthalpy - ΔH
  - Entropy - ΔS
  - Stoichiometry – n

- Nano ITC offers maximum flexibility
  - Nano ITC Standard Volume - 1.0 ml sample cell volume
  - Nano ITC Low Volume - 190 µL sample cell volume

- Affinity ITC technology is the most advanced on the market
  - True power compensation ITC
  - Both Affinity ITC SV and LV instruments are newest technology

Isothermal Titration Calorimetry - Basics

Experiment:

- Mix two solutions
- Measure the Heat (ΔH)
- Analyze heat changes using an assumed model

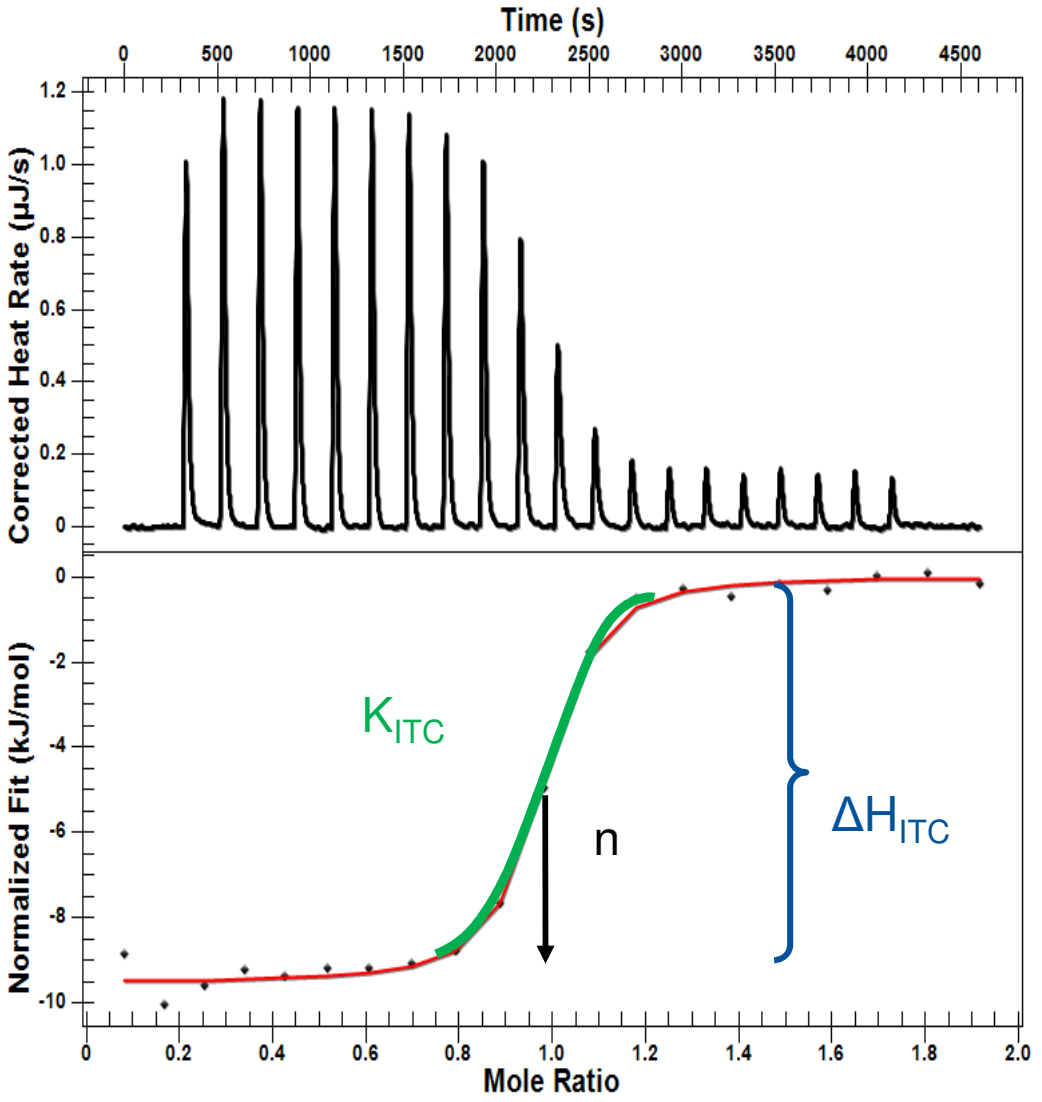
$\Delta G = -RT\ln K_a = \Delta H - T\Delta S$

Calculate:

- K_d, ΔG, ΔS, stoichiometry
- ΔC_p, $\Delta[H^+]$, K_m, k_{cat}, K_i

Rationalize:

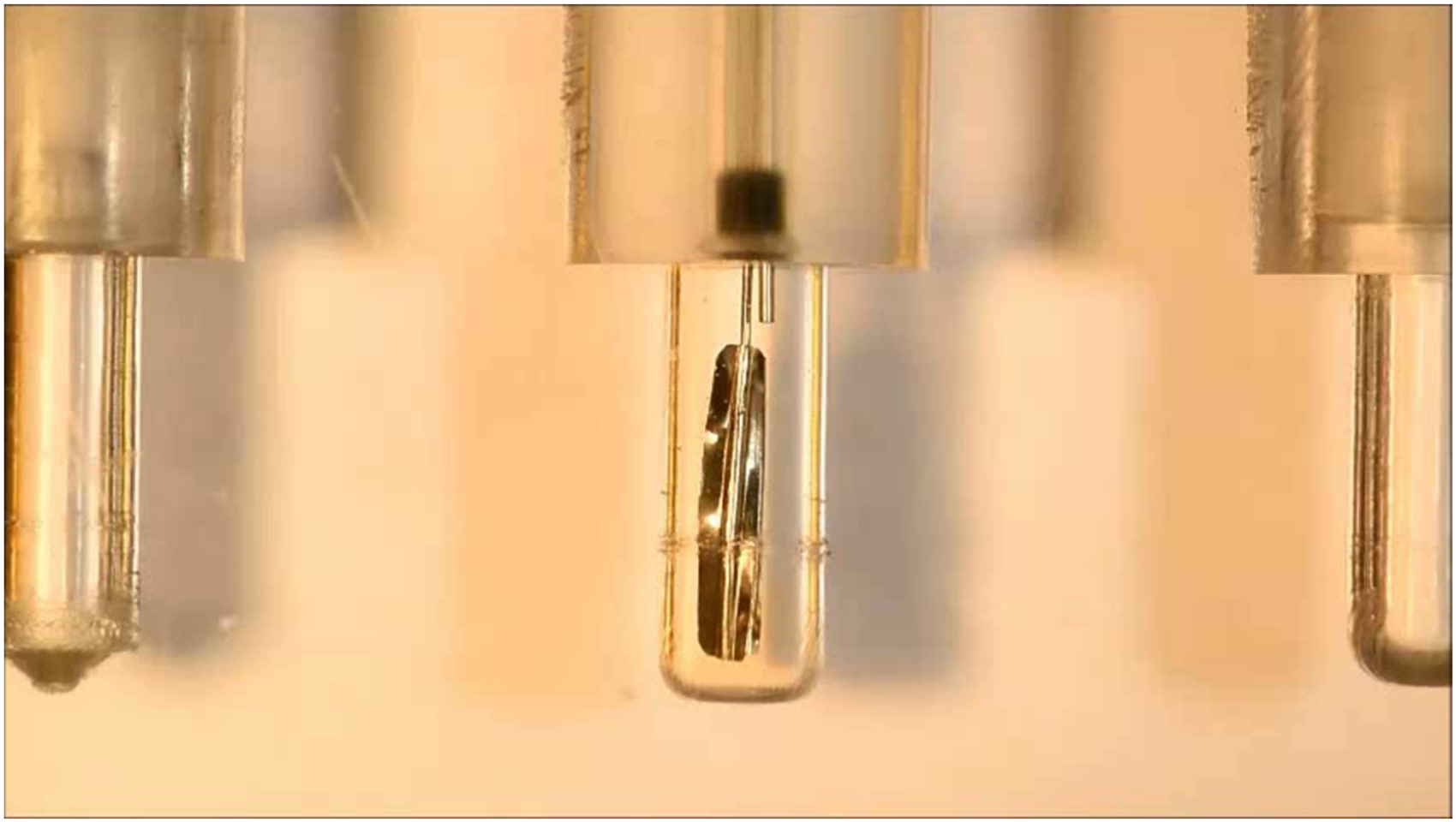
- Change in biomolecular structure
- Lead optimization
- Change due to Mutant Activities



Affinity ITC and Affinity ITC Auto

- Innovative advancement of ITC hardware
- Field upgradeable to fully automated configuration
- Reliable & robust autosampler for unattended ITC operation
- Performance is unmatched by any other ITC
- Easy user selectable manual sample loading without disconnecting autosampler or reconfiguring instrument
- Easy sample reclamation from cell and injection syringe
- Highest quality ITC data obtained with every titration
- Easy-to-use, powerful software features
- Maximum productivity for any molecular interaction analysis

New Mixing technology!



Temperature Scanning Microcalorimetry

Scanning Microcalorimetry

Sensitive

mW µW nW

More Sensitive

Discovery DSC

MC DSC

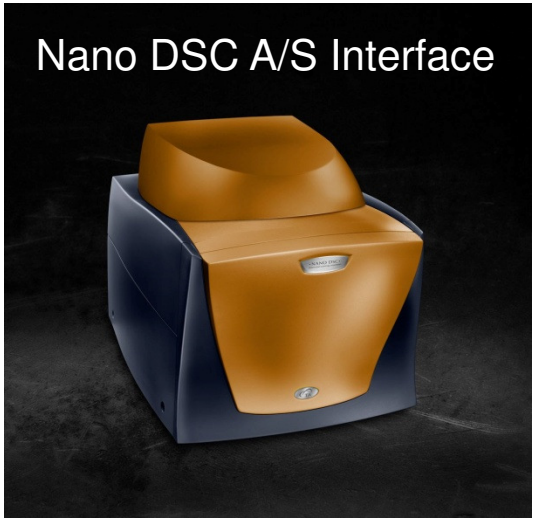
Nano DSC

Diffusion-bonded Sensor
Autosampler
Sample Size: up to 20 mg
Scan Rate: 0.1 – 100 °C/min

3 – samples
1 – reference
Sample Flexibility
≤ 1 mL sample Vol.
Scan Rate: 0 - 2 °C/min

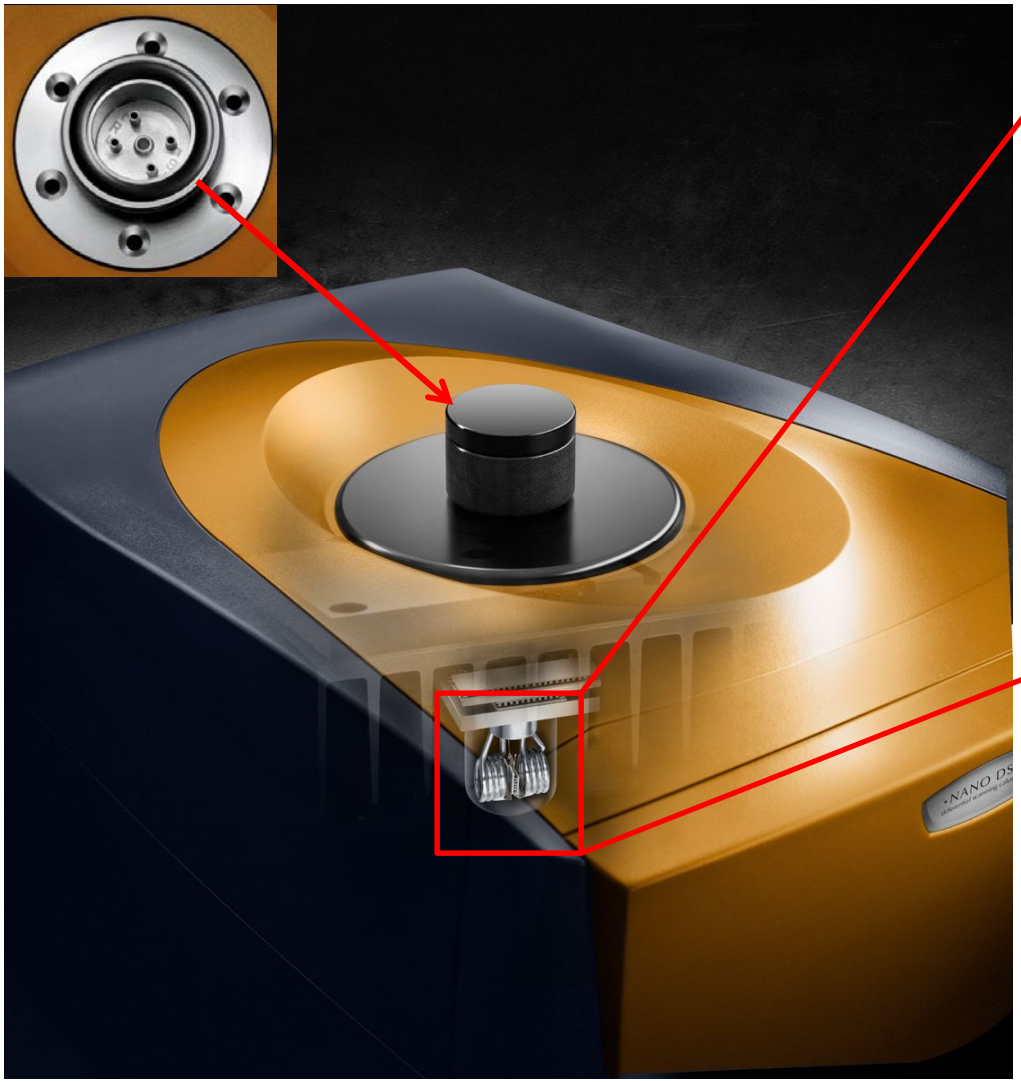
1 – sample
1 – reference
In-solution sample
300 µL active cell Vol.
Scan Rate: 0.001 - 2 °C/min
Automated sample handling

Nano DSC Instruments



- Unmatched performance of any DSC instrument
- Newest DSC technology
- Reduced manufacturing/delivery time
- Improved field serviceability

Nano DSC Design

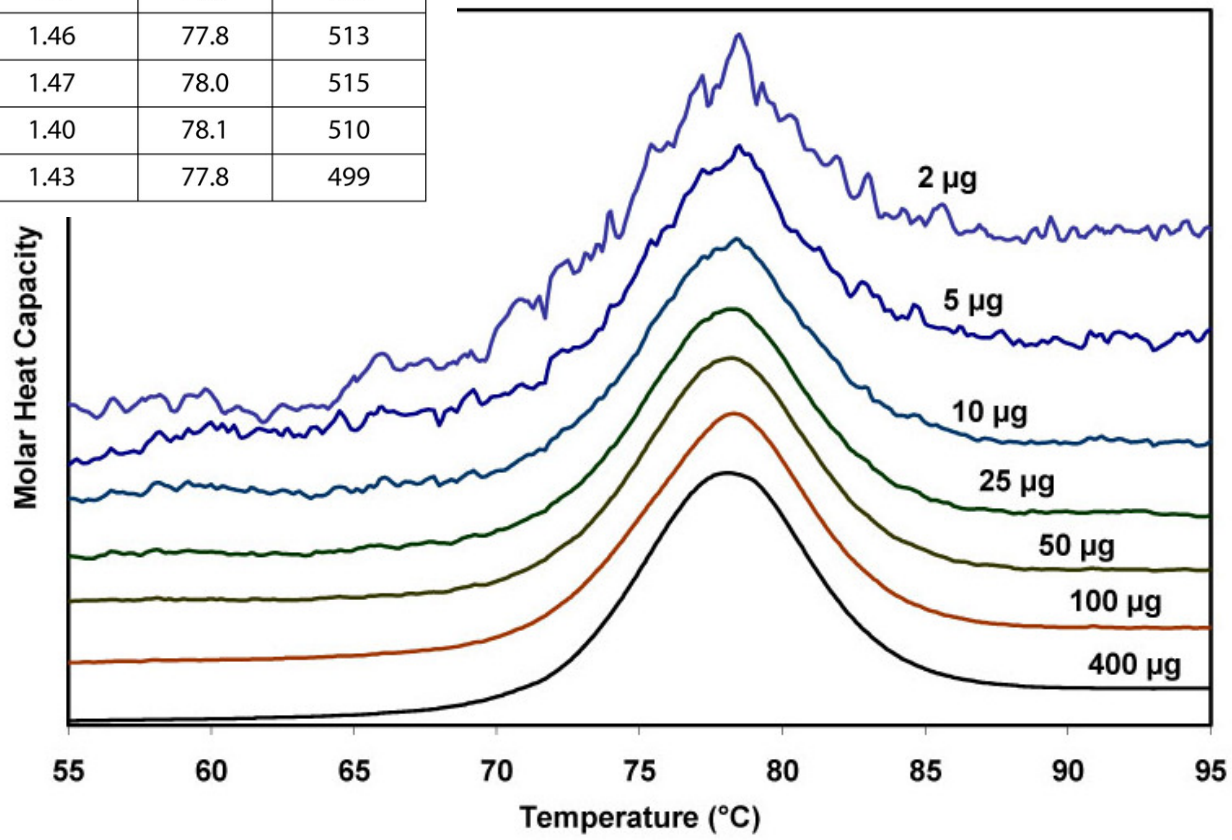


Nano DSC

- **Platinum capillary cells**
- **USB connection to computer**
- **Innovative sensor design**
- **Superior sensitivity**

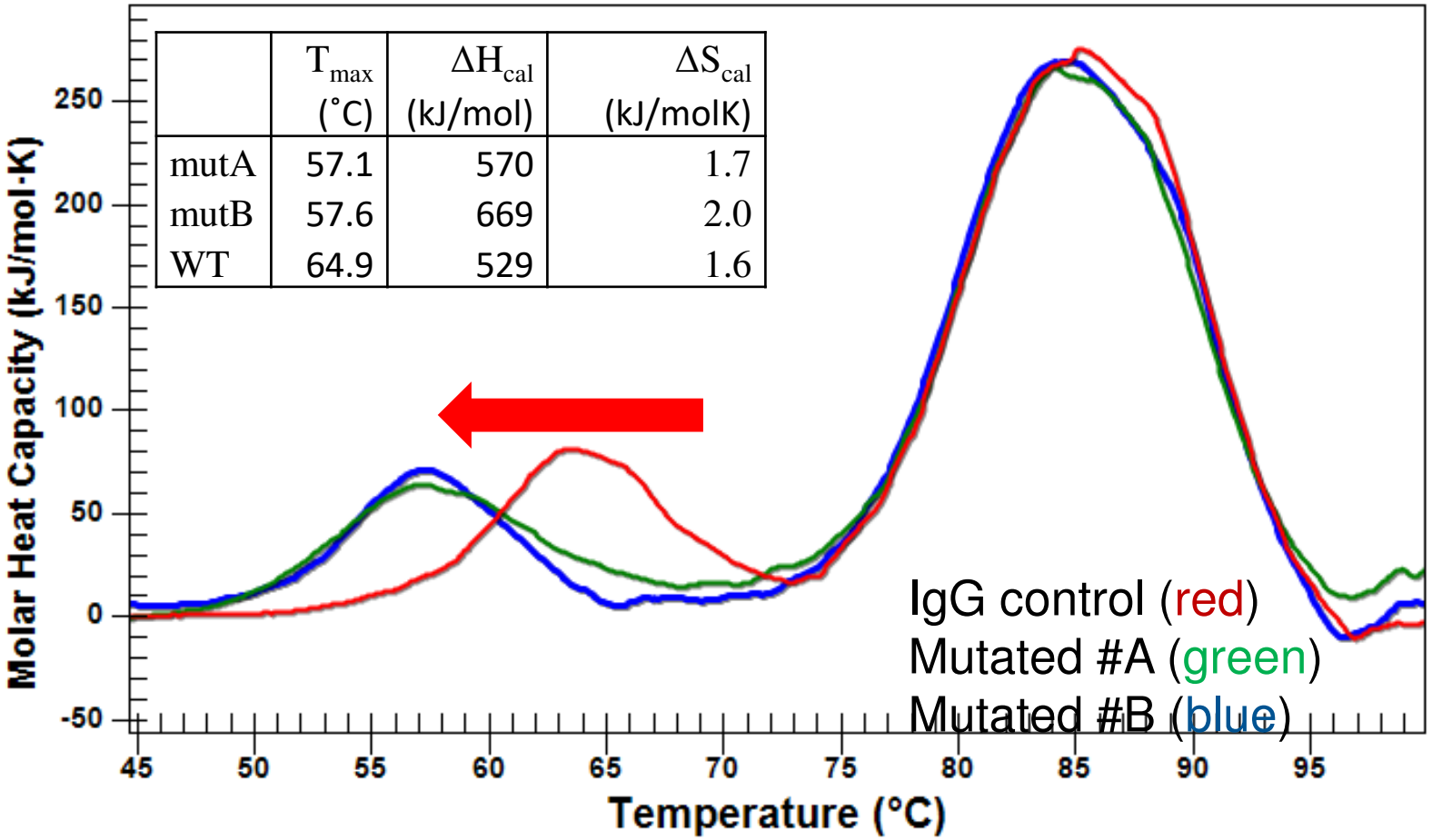
Nano DSC Sensitivity

Lysozyme in cell (µg)	Calorimetric		van't Hoff	
	ΔH (kJ mol^{-1})	ΔS (kJ K^{-1} mol^{-1})	T_m (°C)	ΔH (kJ mol^{-1})
400	512	1.46	78.0	515
100	512	1.46	78.0	509
50	517	1.47	77.9	513
25	513	1.46	77.8	513
10	515	1.47	78.0	515
5	490	1.40	78.1	510
2	503	1.43	77.8	499



Nano DSC of IgG and CH_2 Variants

	T_{max} (˚C)	ΔH_{cal} (kJ/mol)	ΔS_{cal} (kJ/molK)
mutA	57.1	570	1.7
mutB	57.6	669	2.0
WT	64.9	529	1.6



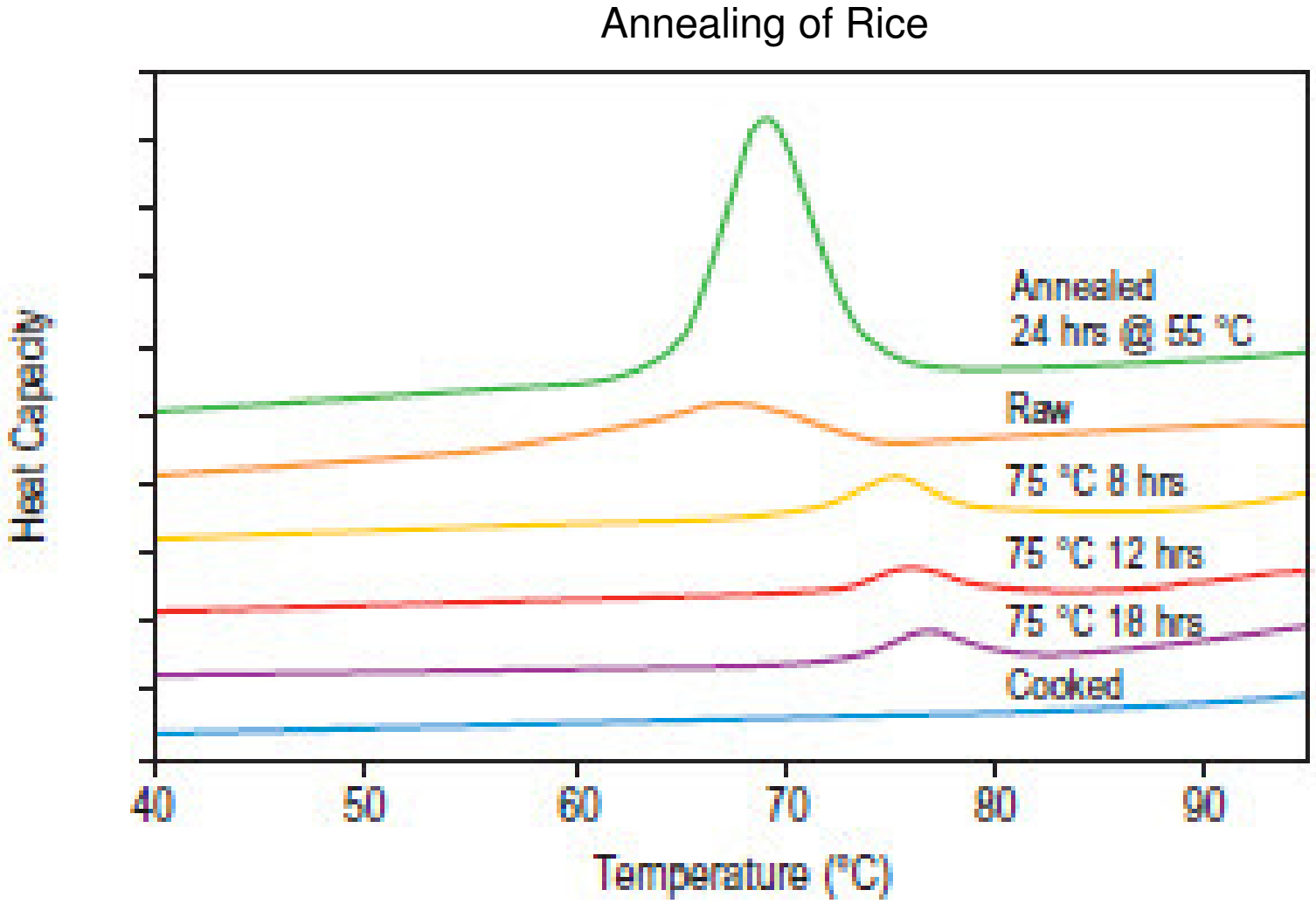
Nano DSC Autosampler System Advantages

- Maximum flexibility
- Fixed capillary cell with unmatched sensitivity
- Smallest active sample cell volume for any fixed cell DSC
- Nano DSC sensitivity is the best on the market
- Ease-of-use is unmatched: Sample loading, cell cleaning, Autosampler
- Complete suite of data acquisition and analysis tools
- Nano DSC is used in a wide variety of application

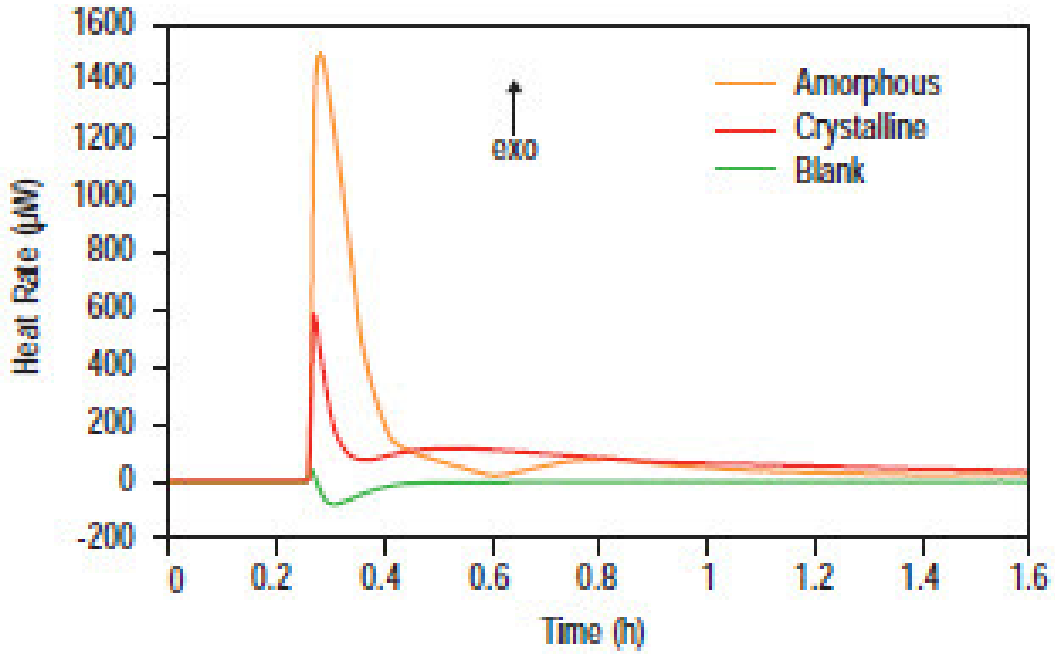
Multi-Cell Differential Scanning Calorimetry (MC-DSC)

Multi-Cell Differential Scanning Calorimetry

Phase Transitions in Foods



Amorphous vs. Crystallinity



Relevance of Crystallinity

- The presence of imperfections (amorphicity) in a crystal affect relevant *properties*.
- Properties affected are: *chemical stability*, *solubility*, *bioavailability*, *surface energy*.
- To have a material well characterized it is very important to have a good control over these key properties.

Calorimetry Summary

- A universal technique used in many industries
- Many types of calorimeters for different applications
- TA Instruments has the widest line of calorimeters
- Types of calorimeters:
  - TAM and TAM-AIR IMC
  - Isothermal Titration Calorimeters (ITC)
  - Differential Scanning Calorimeter (DSC)
  - Multi-Cell Differential Scanning Calorimeter
  - Solution Calorimeter
  - Sorption Calorimeter

What Does TA Instruments Make?

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- Simultaneous Differential Thermal Analyzers
- Microcalorimeters of many types
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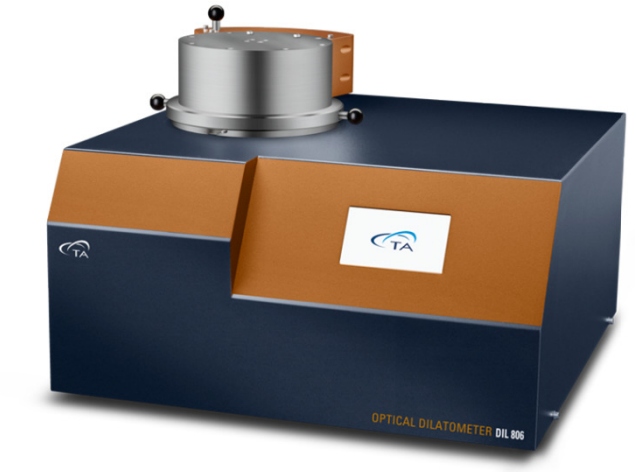
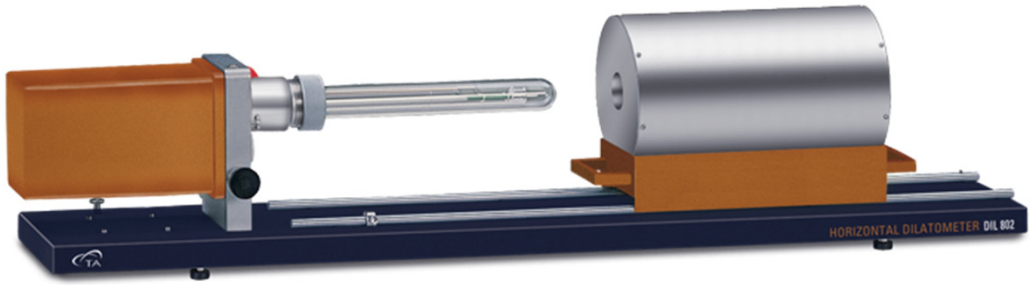
- Thermal Diffusivity
- Thermal Conductivity
- Mechanical Testers
- Dynamic Mechanical Analyzers
- Rotational Rheometers
- Rubber Rheometers

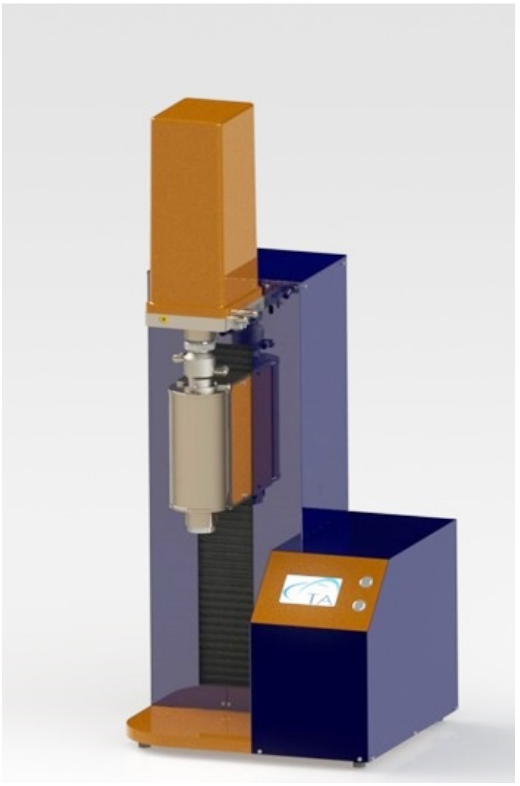
Dilatometers and Thermomechanical Analyzers

The youngest person to receive an Oscar was 5 year old Shirley Temple.

Dilatometer Products from TA Instruments

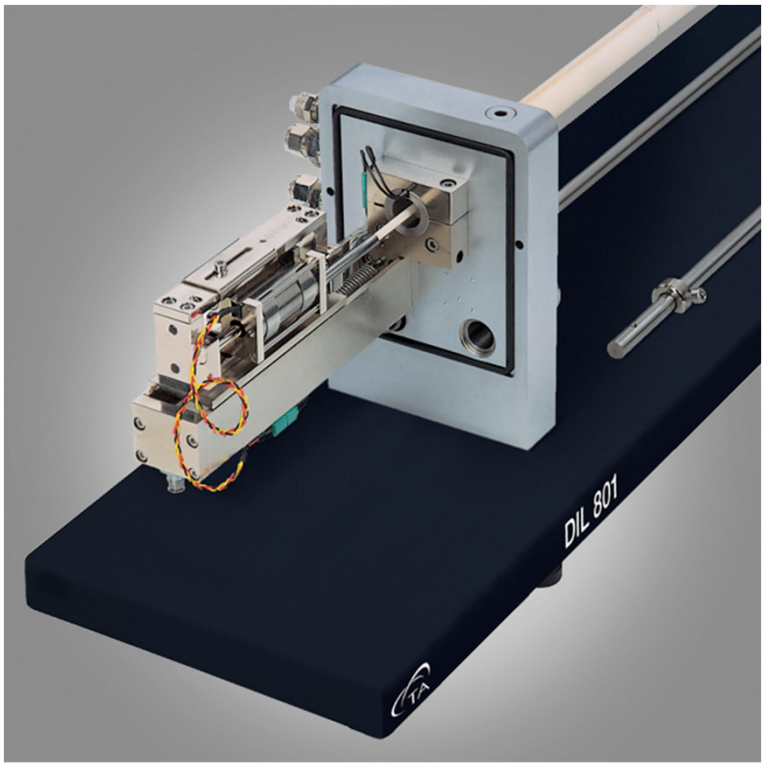


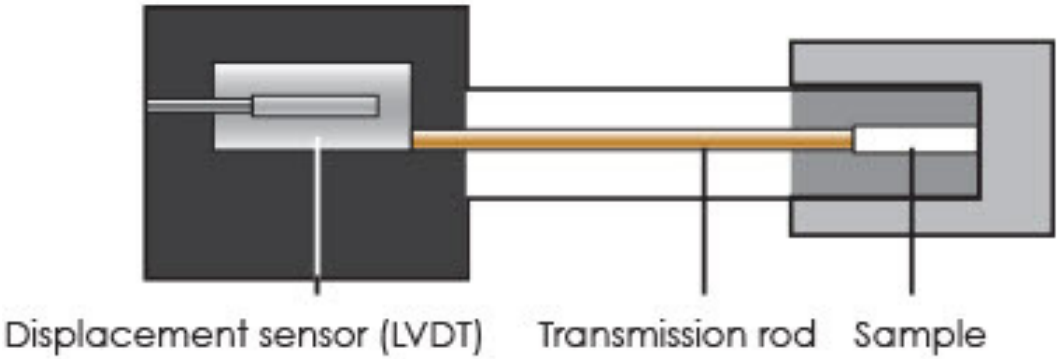




Dilatometry is a technique that measures change in length, sample temperature and furnace temperature to facilitate the measurement of the coefficient of thermal expansion (CTE), softening point, determination of phase and glass transitions.

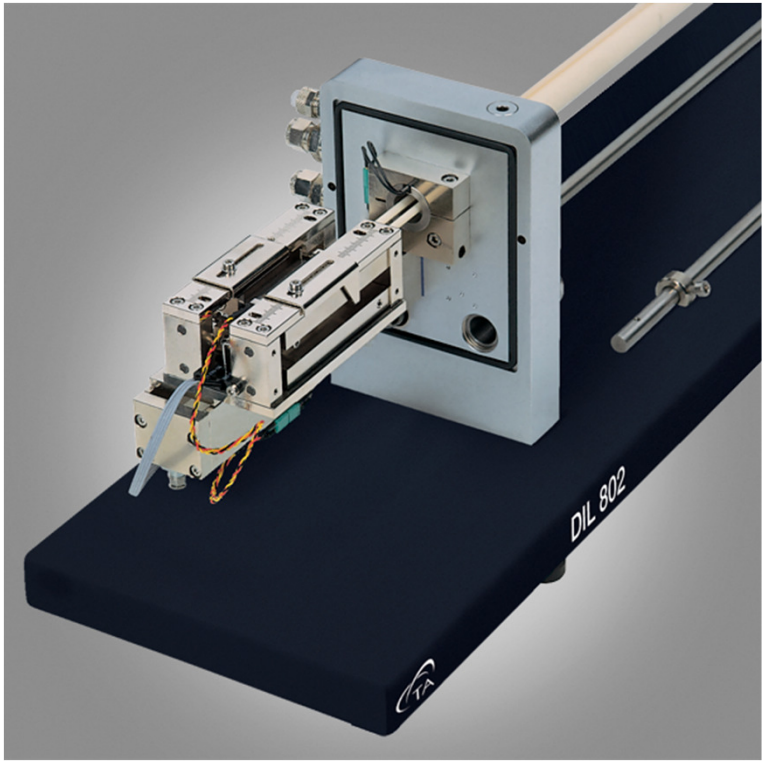
Horizontal Dilatometers
DIL 801/801L

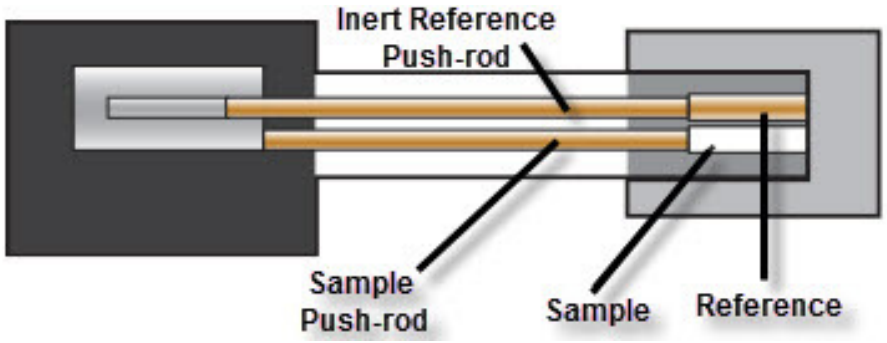




- Air/Inert Gas/Vacuum

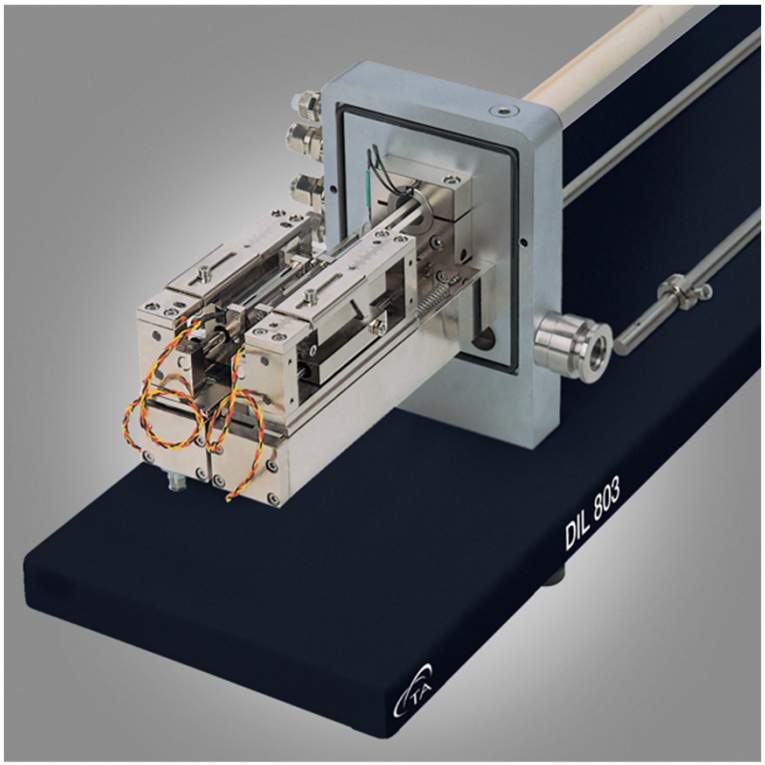
Horizontal Dilatometers
DIL 802/802L

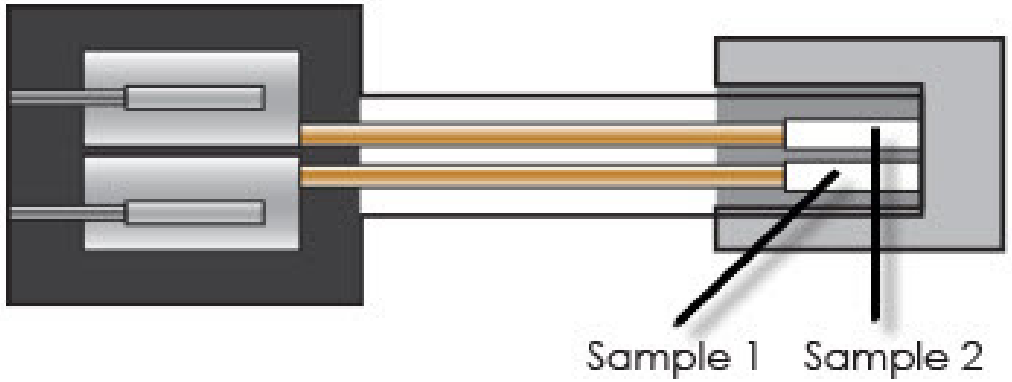




- Air/Inert Gas/Vacuum

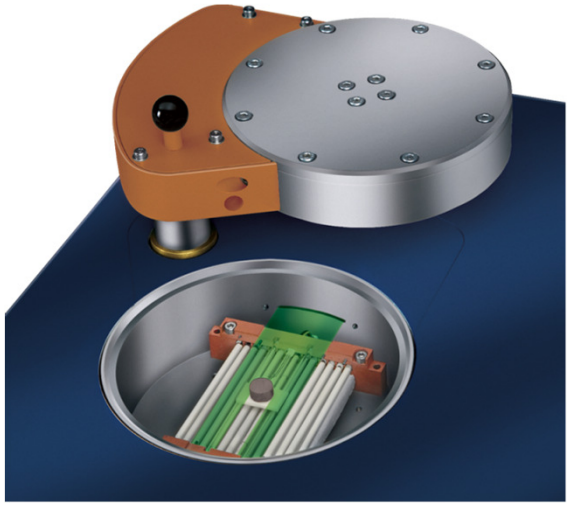
Horizontal Dilatometers
DIL 803/803L





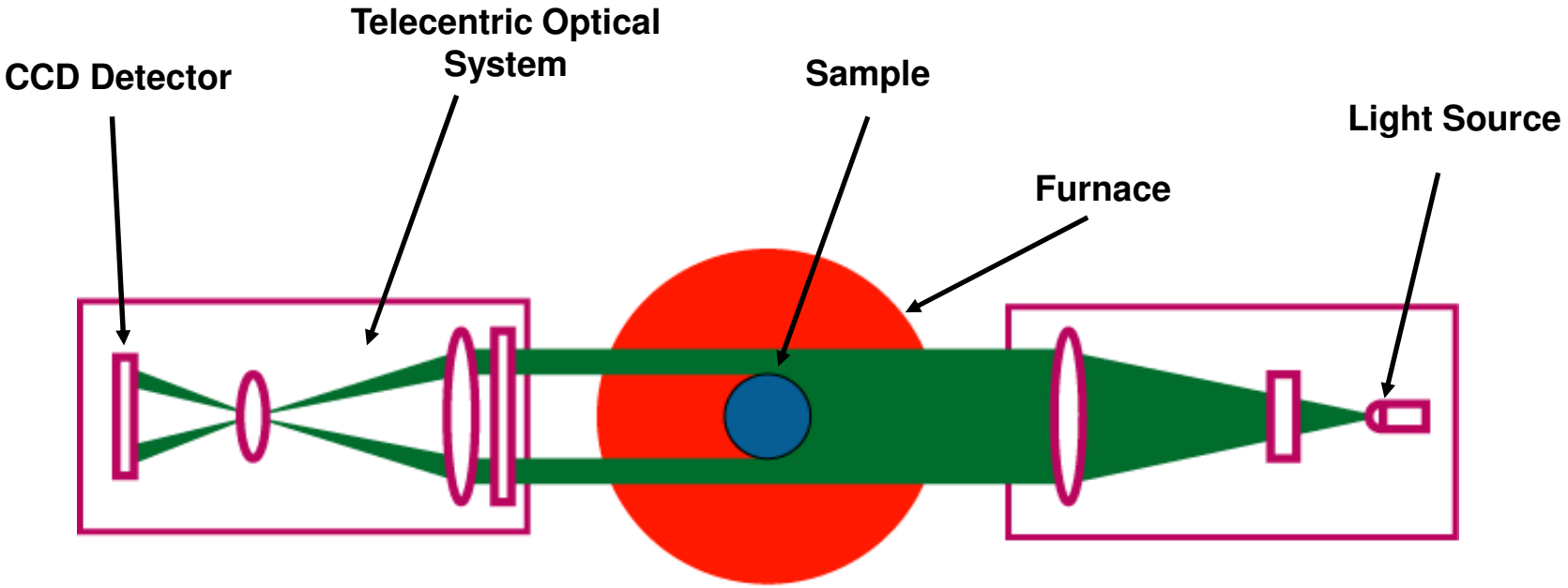
- Air/Inert Gas/Vacuum

Optical Dilatometer DIL 806



- Temperature range;
  - -160°C up to 700°C
  - RT°C up to 1000°C or 1400°C
- Resolution: 50nm, 0.1°C
- Accuracy: 0.05 x10^{-6} K^{-1}
- Atmosphere: inert gas, vacuum, air
- Sample Height: max 10 mm
- Sample Length: max 29 mm

Principal of DIL 806



$$\Delta L = \frac{CN}{M}$$

ΔL: length change
C: interval of the CCD pixel
N: the number of CCD pixels of two sample-edges
M: magnification of the optical system

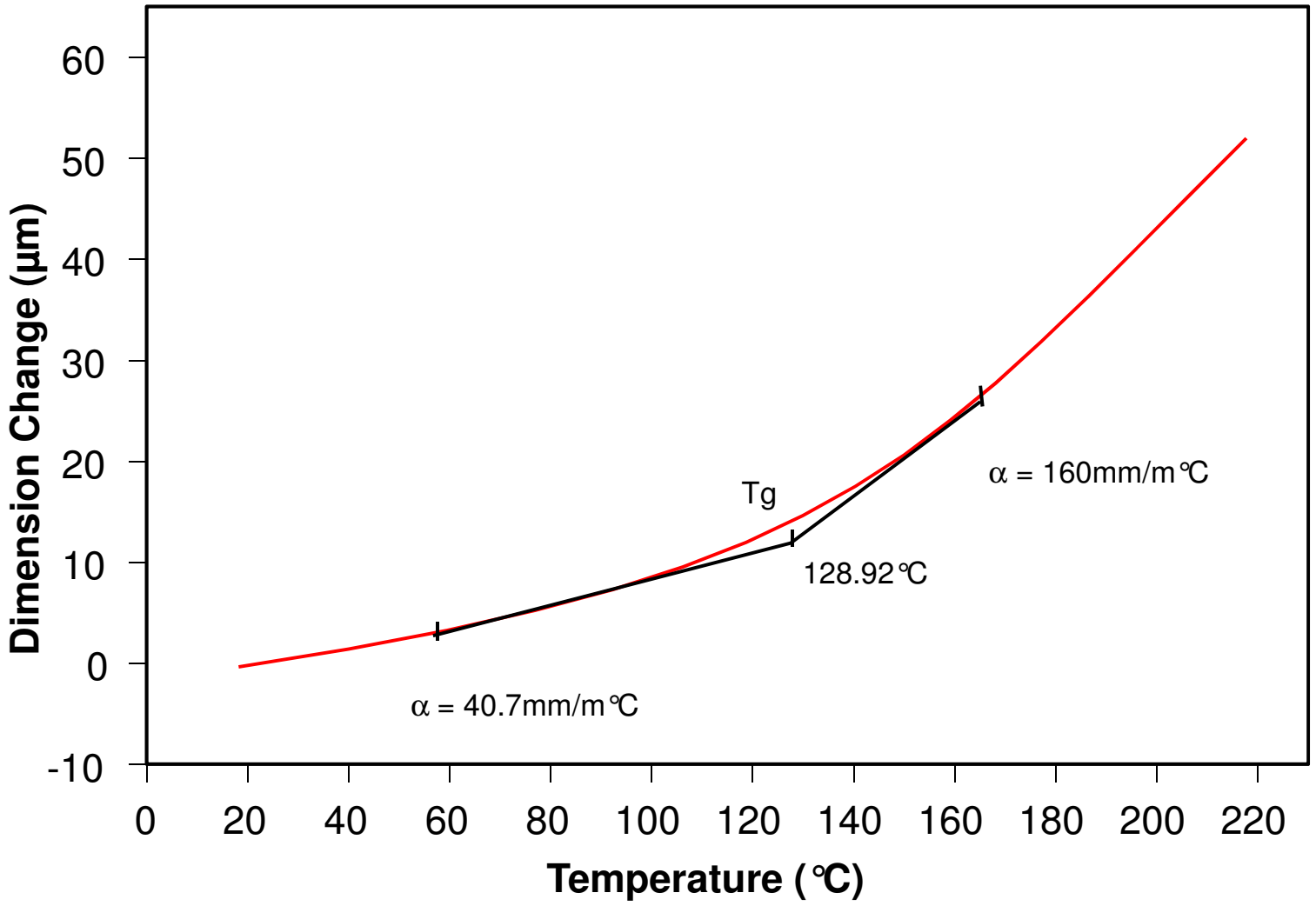
Thermomechanical Analysis

- Thermo-mechanical Analysis measures changes in the dimensions of a sample as a function of time, temperature and force in a controlled atmosphere.

- TMA can measure Coefficient of Thermal Expansion (CTE), along with transitions such as the glass transition (Tg).

- Advance TMA allows for viscoelastic measurements.

Expansion of a Printed Circuit Board



What Does TA Instruments Make?

- Differential Scanning Calorimeters
- Thermogravimetric Analyzers
- Simultaneous Differential Thermal Analyzers
- Microcalorimeters of many types
- Dilatometers and Thermomechanical Analyzers
- **Thermal Diffusivity**
- **Thermal Conductivity**
- Mechanical Testers
- Dynamic Mechanical Analyzers
- Rotational Rheometers
- Rubber Rheometers

Thermal Diffusivity and Thermal Conductivity

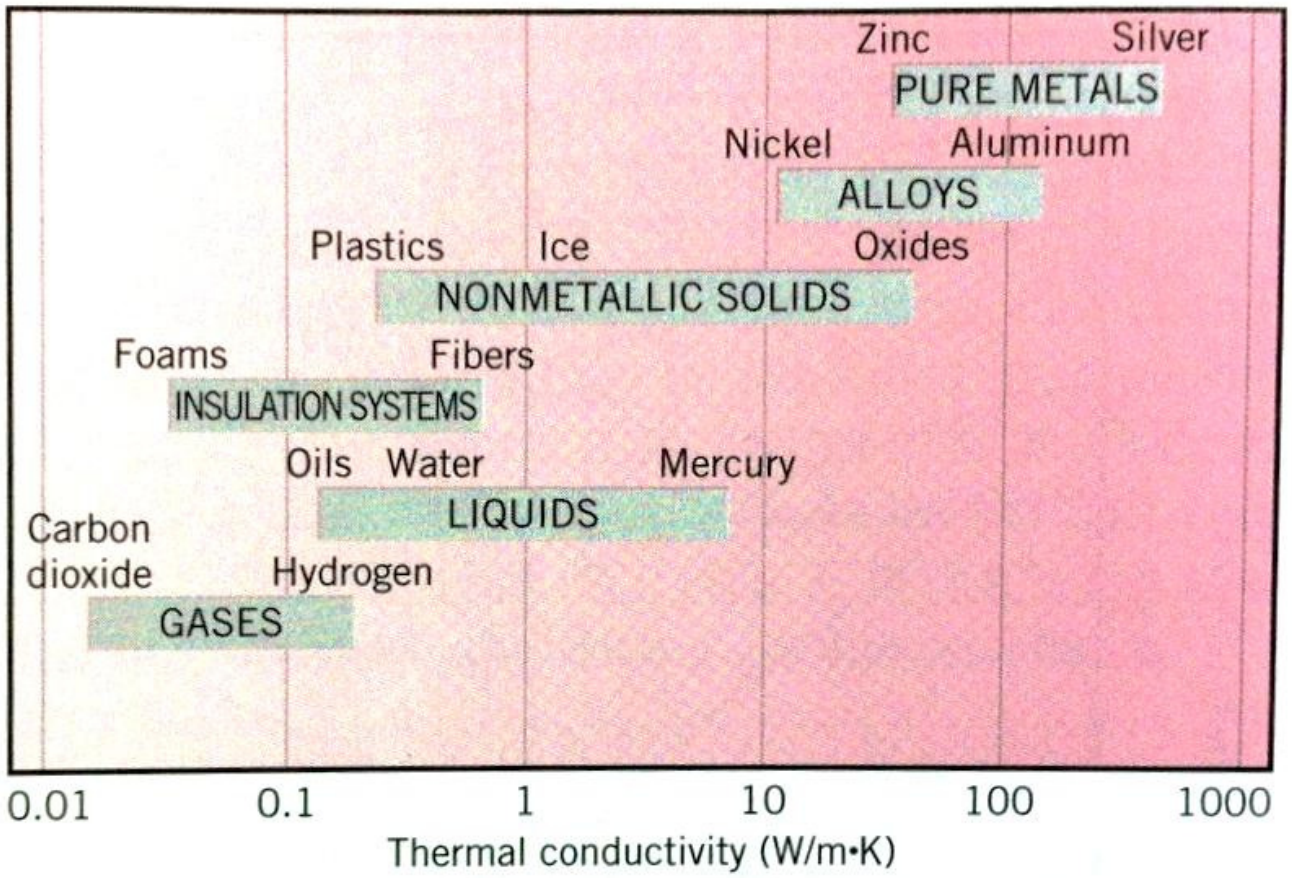
What is Thermal Conductivity?

- The ability of a material to transport heat along a linear dimension in response to a temperature difference along the same direction (measured in W/mK or Btu in/h ft^{2}F).

- Characterized by Fourier's Heat Equation

$$K = \frac{Q / A}{\Delta T / \Delta L}$$

Thermal Conductivity Ranges



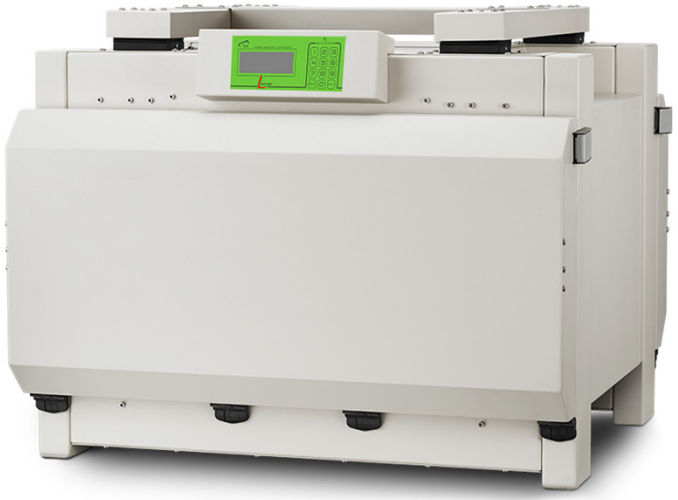
F.P. Incropera and D.P. DeWitt: *Fundamentals of Heat and Mass Transfer*, 5th Ed., Willey, NY 2002

Fox Heat Flow Meters

Fox 200

Fox 314

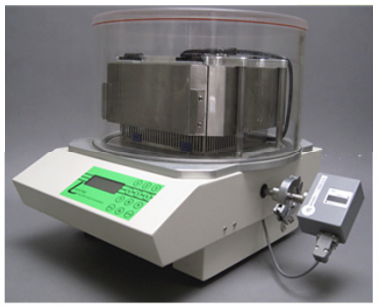
Fox 600



Fox 800

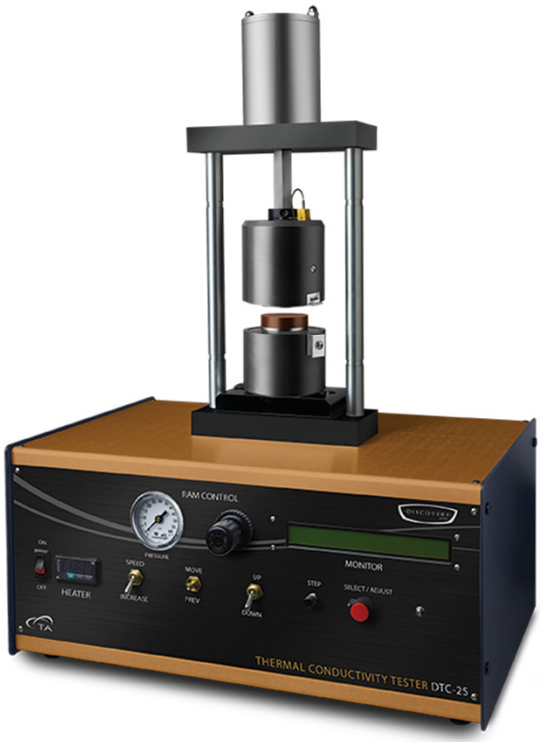
Available Features

- Vacuum down to 10^{-9} Torr
- Autosampler for higher throughput
- Subambient capabilities
- Specific heat measurement capabilities
- Rotational Systems
- Tuber100



Thermoconductivity Meters

DTC25



DTC300

Fox50

What is Thermal Diffusivity?

- Thermal diffusivity is the thermophysical property that defines the speed of heat propagation by conduction during changes of temperature. The higher the thermal diffusivity, the faster the heat propagation. The thermal diffusivity is related to the thermal conductivity, specific heat capacity and density.

Thermal Diffusivity $\alpha = \frac{\lambda}{\rho c_p}$ Thermal Conductivity

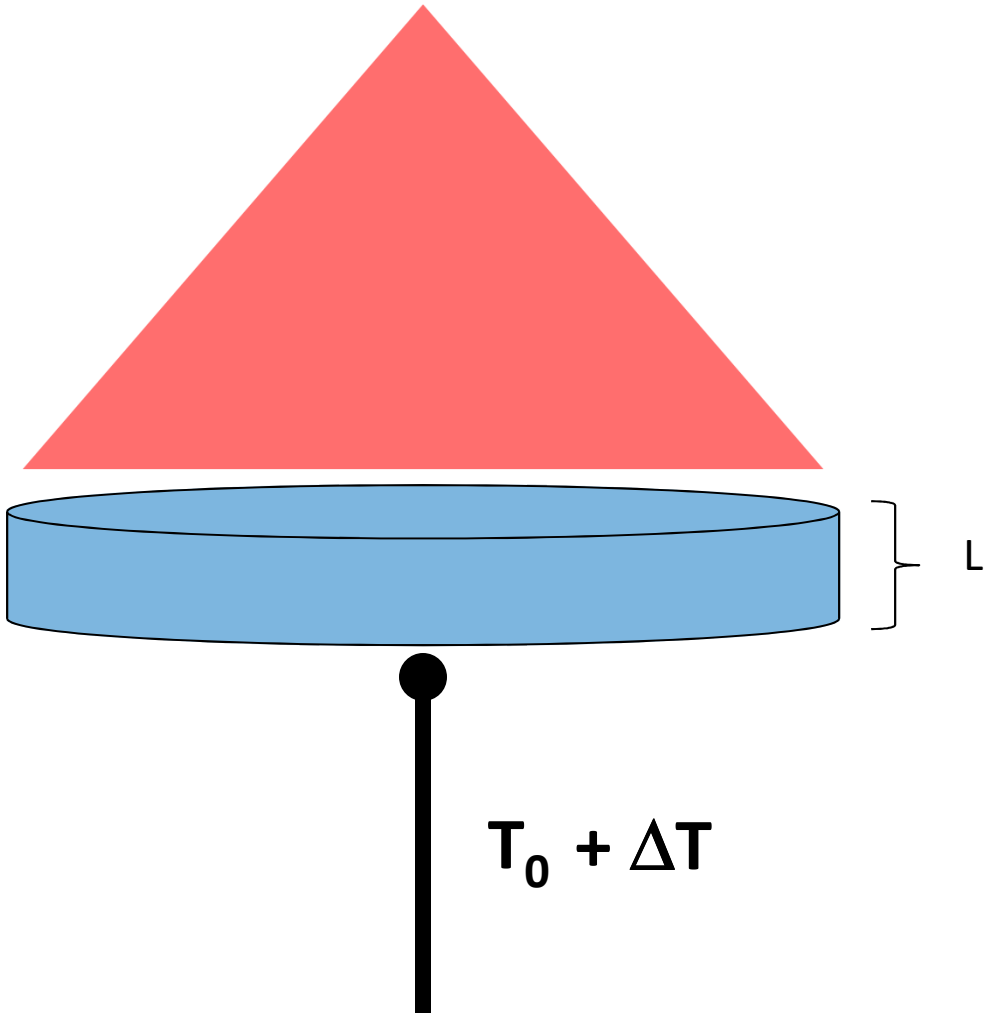
Density Specific heat capacity

Flash Diffusivity Instrumentation

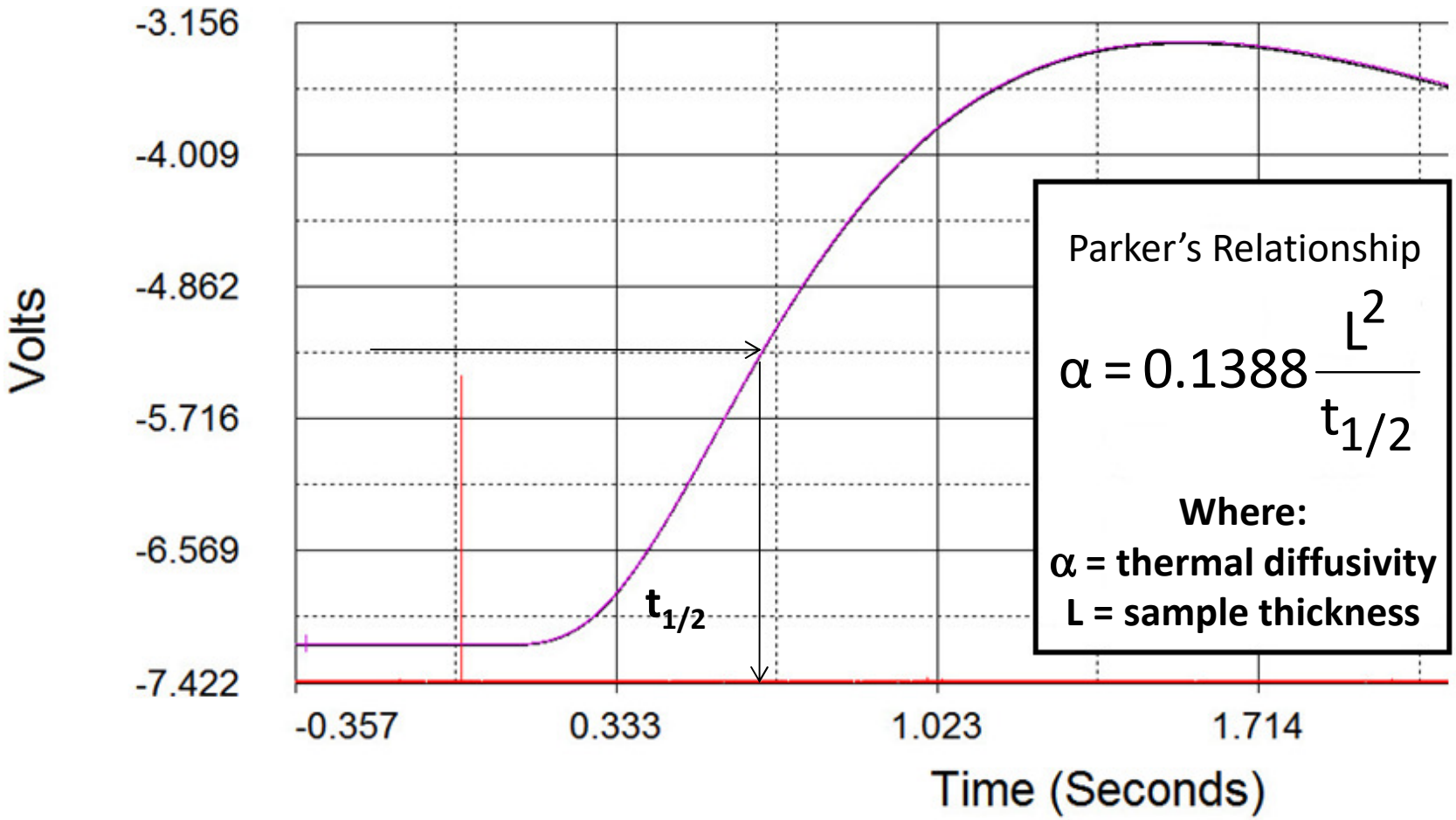
Discovery Xenon/Laser Flash

Discovery Laser Flash

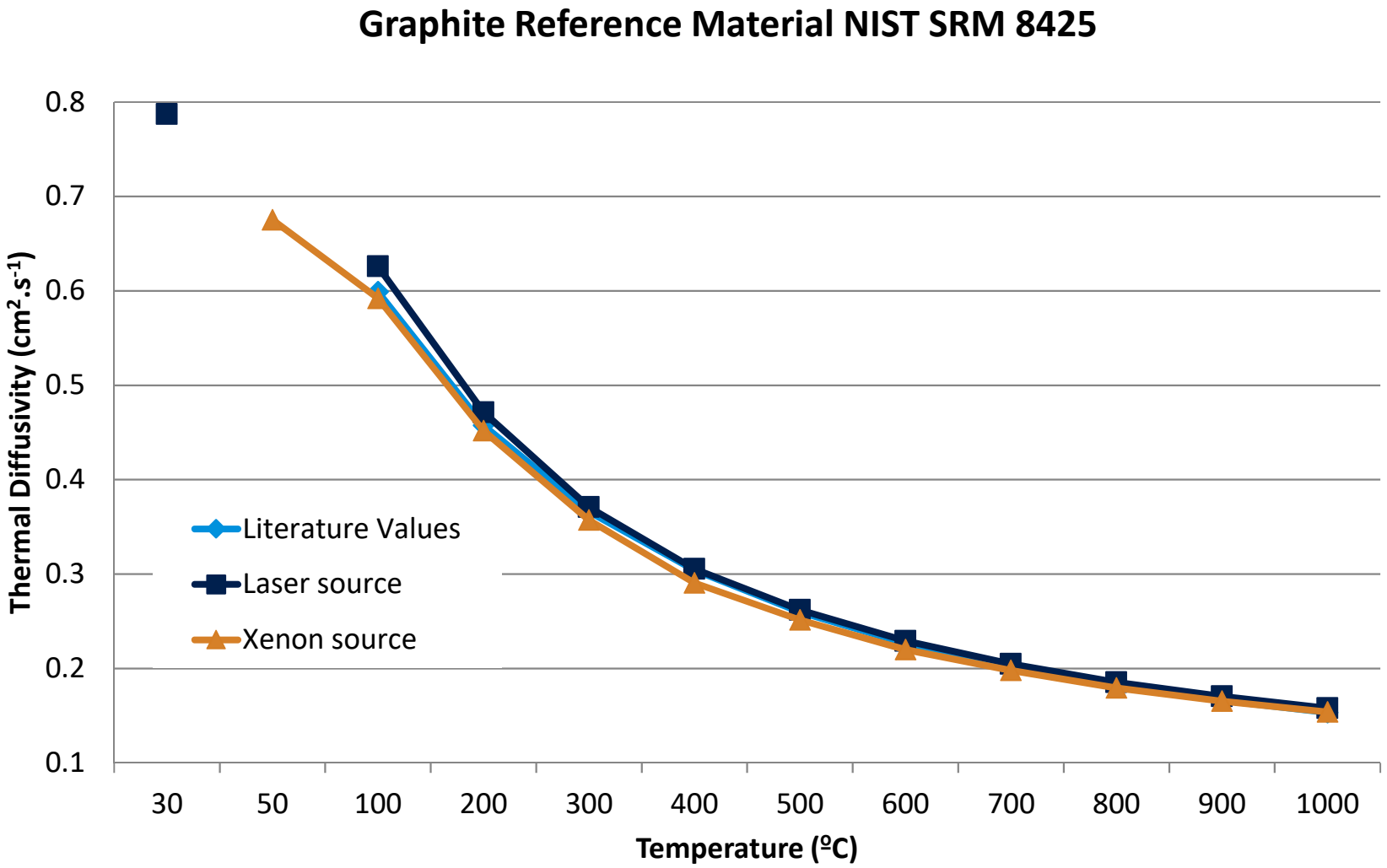
Flash Diffusivity Method



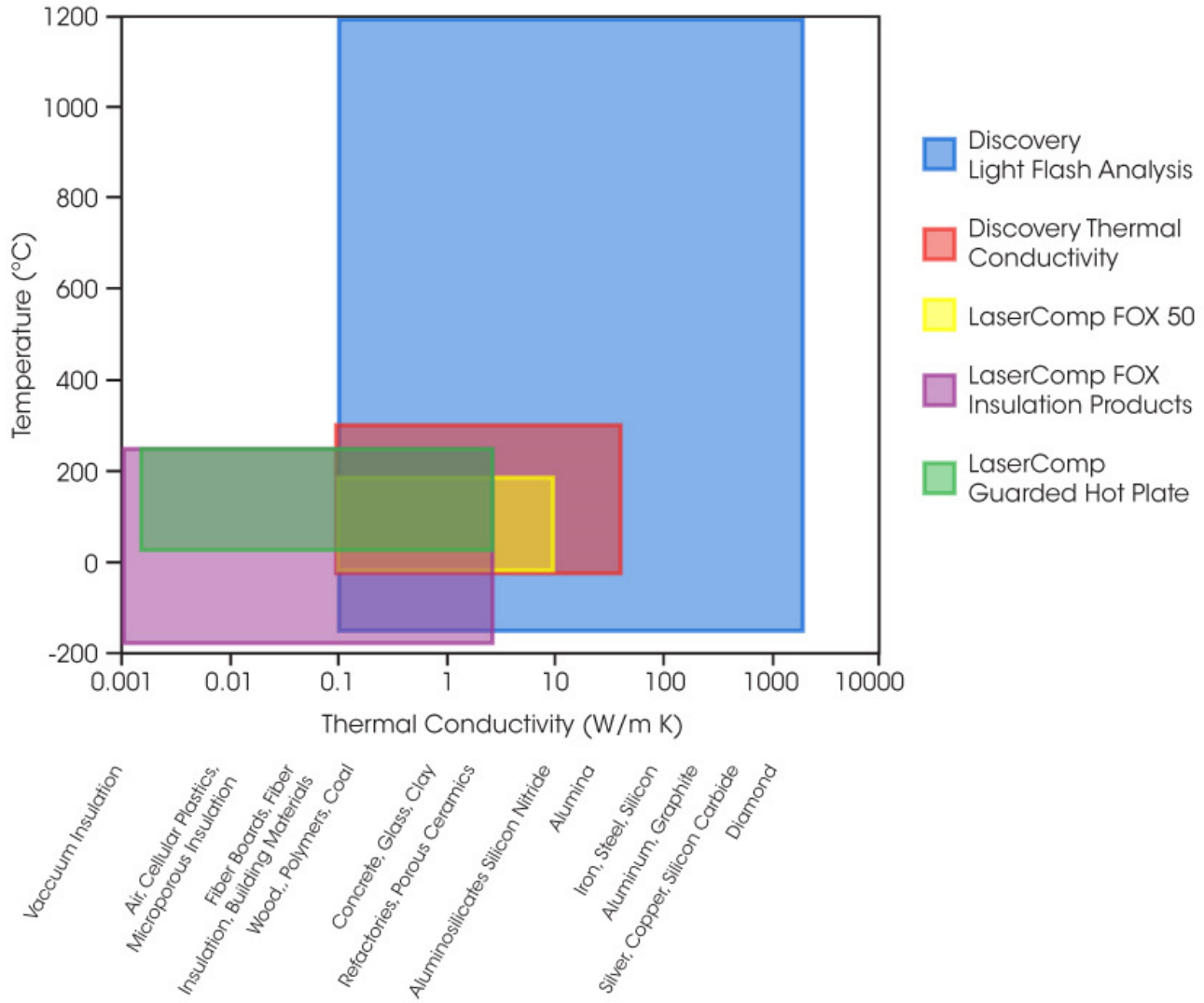
Thermogram in Flash Diffusivity



Flash Diffusivity Measurements



Dynamic Range of Thermal Conductivity



Thank You

The World Leader in Thermal Analysis,
Rheology, and Microcalorimetry