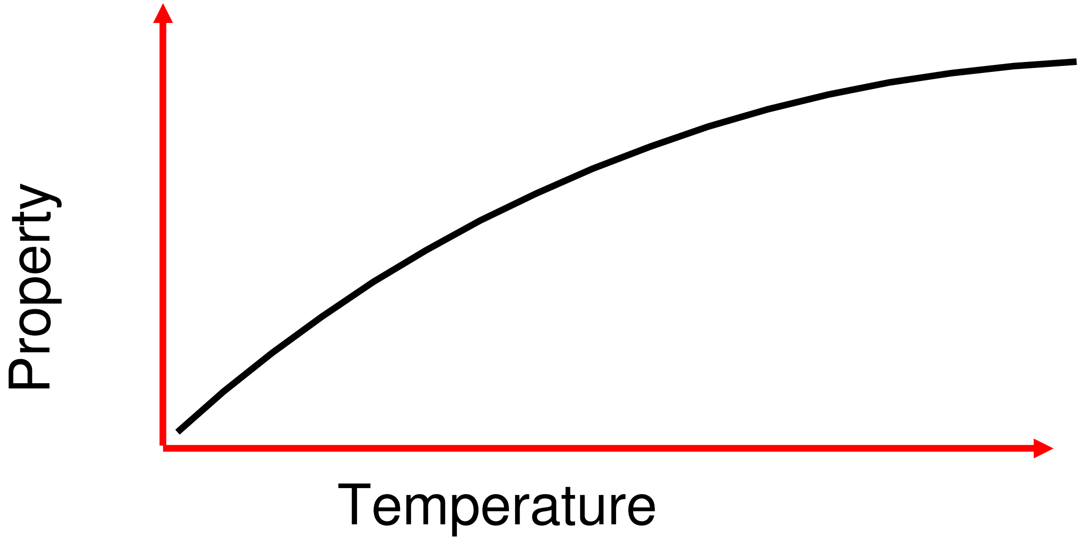
Thermal Analysis

An Introduction

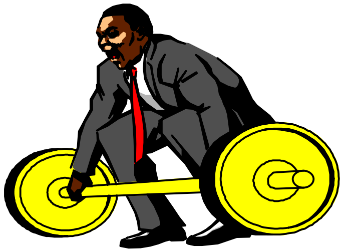
Thermal Analysis

"A collection of techniques that measure the property of a material as a function of temperature"

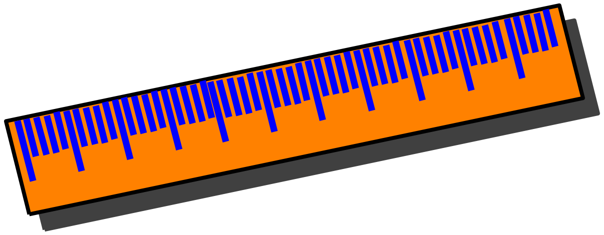


Typical Properties Measured

- Weight

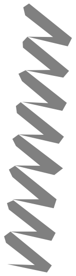


- Length



- Heat Flow

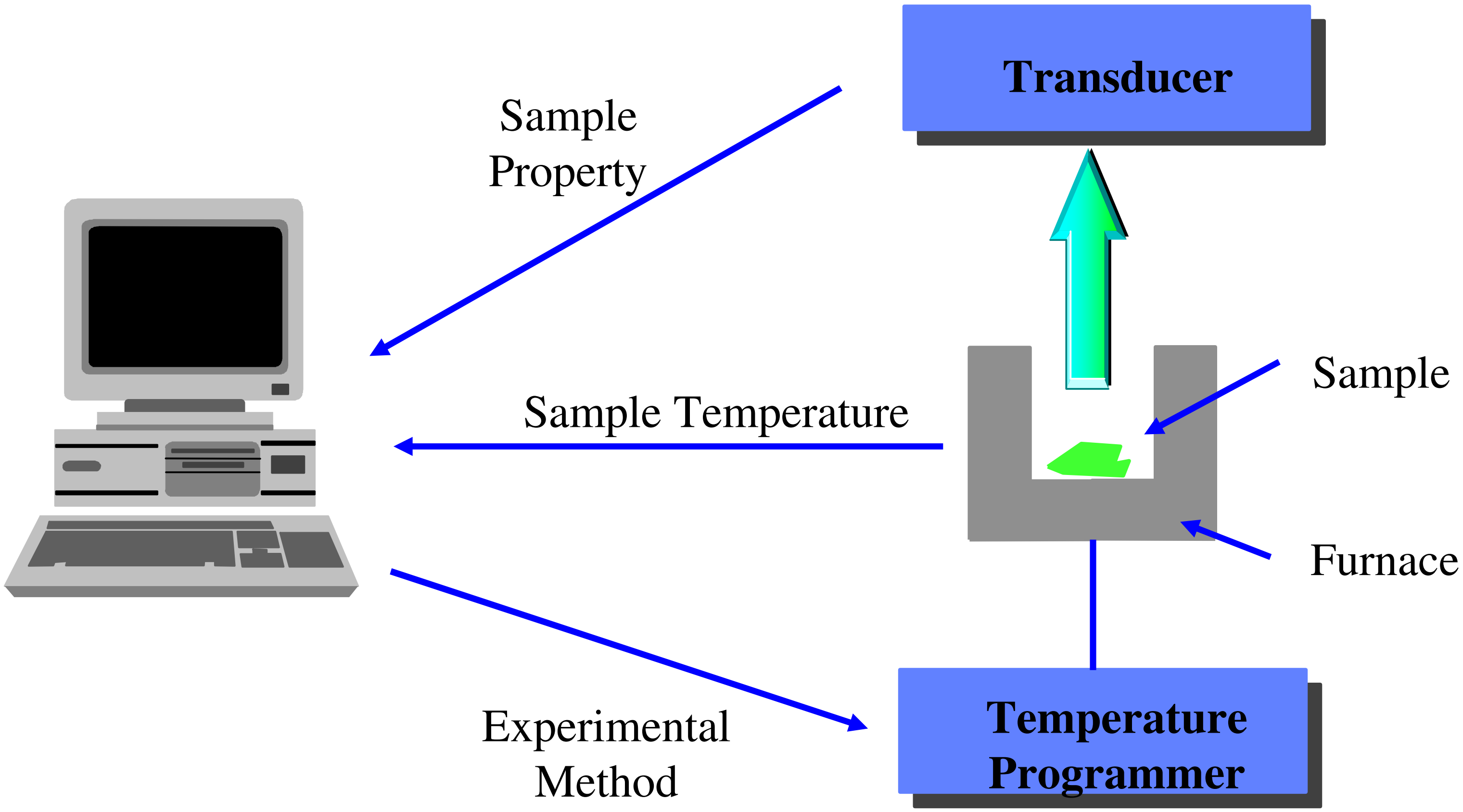
- Modulus



Thermal Analysis Techniques

- Differential Scanning Calorimetry (DSC)
- Differential Thermal Analysis (DTA)
- Thermogravimetric Analysis (TGA)
- Thermomechanical Analysis (TMA)
- Dynamic Mechanical Analysis (DMA)
- Dielectric Analysis (DEA)

What is a Thermal Analyser?

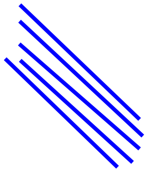


Type of Polymers

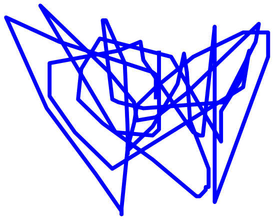
- **Thermoplastic**
  - ➔These polymers melt on heating and recrystallise on cooling. They can be processed and moulded.
- **Thermosets**
  - ➔These polymers cross-link (cure) on heating and form a 3-dimensional rigid matrix.
- **Elastomers**
  - ➔These are usually long chain polymers that are flexible at room temperature but brittle (i.e. below their Tg) at sub-ambient temperatures.
- **Blends**
  - ➔Physical or Chemical mixtures of any of the above types

Thermoplastic Polymers

Semi-Crystalline Polymer



Crystalline Phase
-this will melt and give and endothermic peak in the DSC



Amorphous Phase
- this will soften and give a glass transition (Tg)

Thermal History - Cooling Rates

- **Slow cooling from the melt**
  - This will give more time for the polymer chains to orientate and crystallise giving a higher crystallinity. On re-heating a larger fusion peak will be observed.
- **Fast cooling from the melt**
  - This will give less time for the polymer chains to orientate and crystallise giving a lower crystallinity. On re-heating a smaller fusion peak will be observed.

Factors Affecting Polymer Transitions

- Heating Rate
- Sample Size
- Sample Form
- Sample Pan
- Thermal History
- Degree of Crystallinity
- Filler

Differential Scanning Calorimetry (DSC) & Modulated DSC

Differential Scanning Calorimetry

- A ***calorimeter*** measures the heat into or out of a sample
- A ***differential calorimeter*** measures the heat of a sample relative to a reference
- A ***differential scanning calorimeter*** does all of the above and heats/cools the sample with a linear/modulating temperature ramp

Differential Scanning Calorimetry

- Differential Scanning Calorimetry (DSC) is most popular thermal analysis technique
- DSC measures endothermic and exothermic transitions as a function of temperature
  - ***Endothermic*** heat flows into a sample
  - ***Exothermic*** heat flows out of the sample
- Used to characterize polymers, pharmaceuticals, foods/biologicals, organic chemicals and inorganics
- Transitions measured include Tg, melting, crystallization, curing and cure kinetics, onset of oxidation and heat capacity

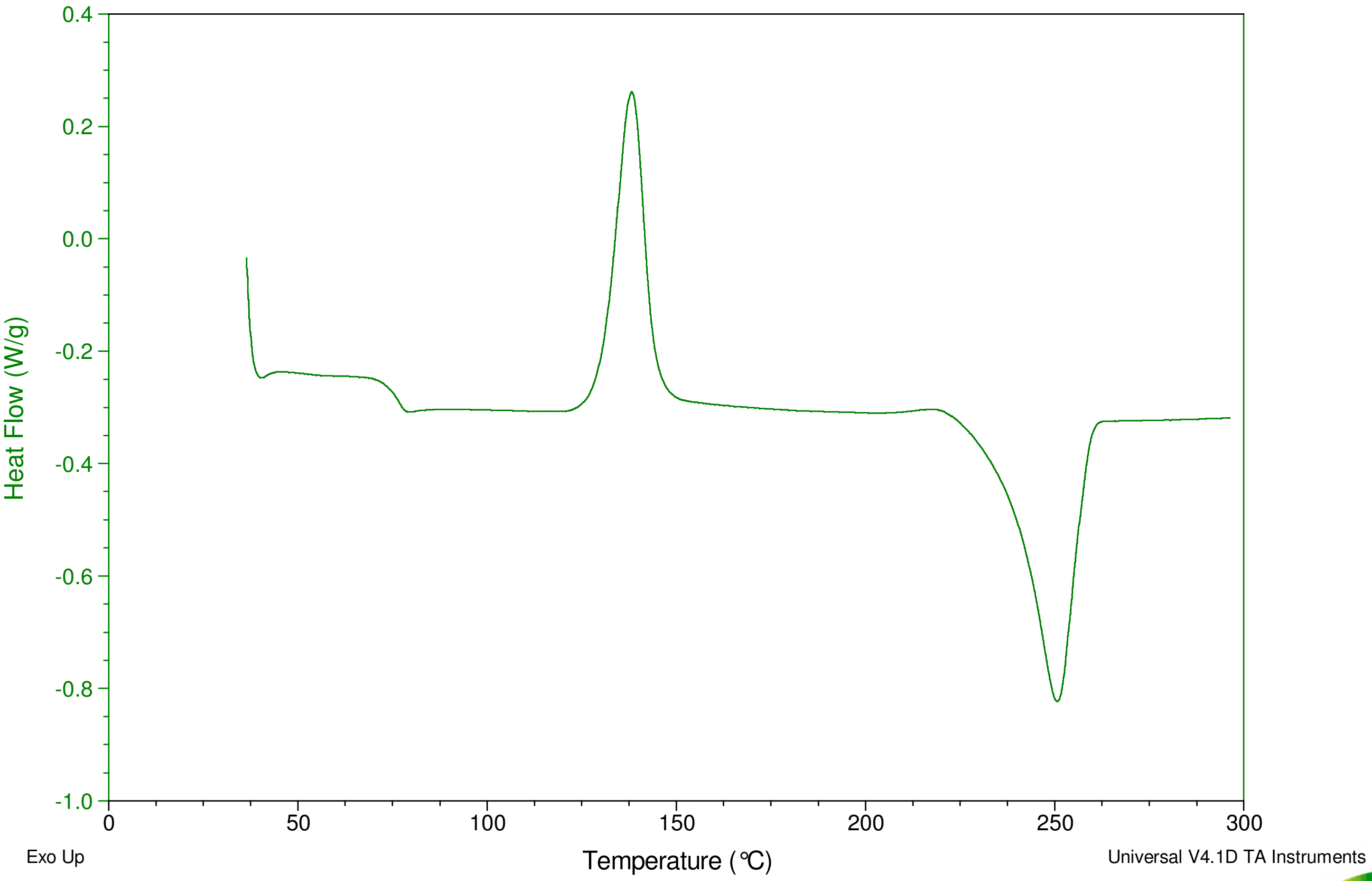
DSC: Terminology

- **Amorphous Phase** - The portion of material whose molecules are randomly oriented in space. Liquids and glassy or rubbery solids. Thermosets and some thermoplastics.
- **Crystalline Phase** - The portion of material whose molecules are regularly arranged into well defined structures consisting of repeat units. Very few polymers are 100% crystalline.
- **Semi-crystalline Polymers** - Polymers whose solid phases are partially amorphous and partially crystalline. Most common thermoplastics are semi-crystalline.
- **Melting** - The endothermic transition upon heating from a crystalline solid to the liquid state. This process is also called fusion. The melt is another term for the polymer liquid phase.
- **Crystallization** - The exothermic transition upon cooling from liquid to crystalline solid. Crystallization is a function of time and temperature.
- **Cold Crystallization** - The exothermic transition upon heating from the amorphous rubbery state to the crystalline state. This only occurs in semi-crystalline polymers that have been quenched (very rapidly cooled from the melt) into a highly amorphous state.
- **Enthalpy of Melting/Crystallization** - The heat energy required for melting or released upon crystallization. This is calculated by integrating the area of the DSC peak on a time basis.

Sample: PET (Quenched from the Melt)
Size: 7.8680 mg
Method: RT-->300℃ @ 10℃/min
Comment: He Purge=25mL/min

DSC

File: C:\TA\Data\DSC\Dsc-pet.001
Operator: Applications Laboratory
Run Date: 10-May-1995 14:44



TYPES OF DSC INSTRUMENTS

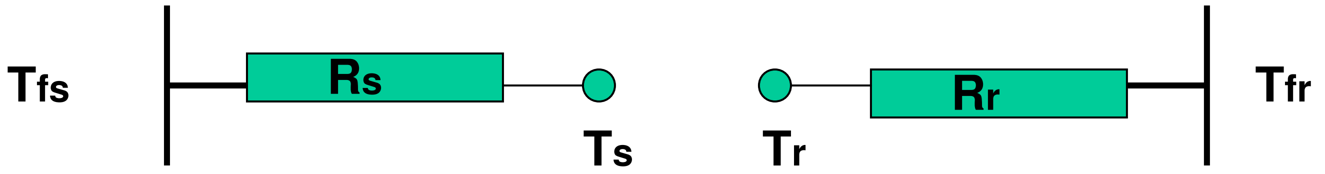
Two Major Types of DSC’s on Market Today:

Heat Flux DSC

and

Power Compensation DSC

HEAT FLUX DSC-PRINCIPLE OF OPERATION

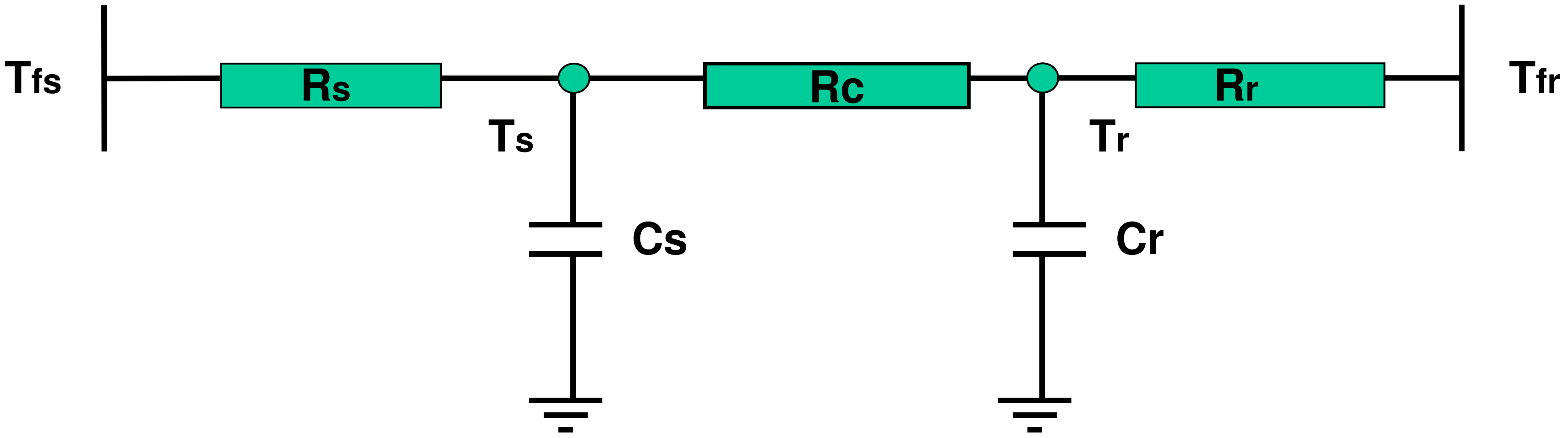


$$Q_s = \frac{T_s - T_{fs}}{R_s}$$

$$Q_r = \frac{T_r - T_{fr}}{R_r}$$

$$\Delta Q = Q_s - Q_r$$

HEAT FLUX DSC - EXPANDED PRINCIPLE OF OPERATION



$$Q = \frac{T_s - T_r}{R} + \underset{\substack{\uparrow \\ \text{Thermal} \\ \text{Resistance} \\ \text{Imbalance}}}{A} + \underset{\substack{\uparrow \\ \text{Thermal} \\ \text{Capacitance} \\ \text{Imbalance}}}{B} + \underset{\substack{\uparrow \\ \text{Heating} \\ \text{Rate} \\ \text{Imbalance}}}{C}$$

Tzero™ HEAT FLOW TERMS

Q Series DSC's

$-\dfrac{\Delta T}{R_r}$	**Principal DSC Heat Flow**
$\Delta T_0\left(\dfrac{1}{R_s}-\dfrac{1}{R_r}\right)$	**Thermal Resistance Imbalance**
$(C_r - C_s)\dfrac{dT_s}{d\tau}$	**Heat Capacity Imbalance**
$-C_r\dfrac{d\Delta T}{d\tau}$	**Heating Rate Difference**

Tzero™ HEAT FLOW TERM CONTRIBUTIONS

- Principal heat flow provides main heat flow signal
- Thermal resistance and heat capacity imbalance terms improve baseline
- Heating rate difference term improves resolution and MDSC® performance

Tzero™ DSC Cell

DSC: Heat Flow/Specific Heat Capacity

$$\Delta H = Cp\ \Delta T$$

or in differential form

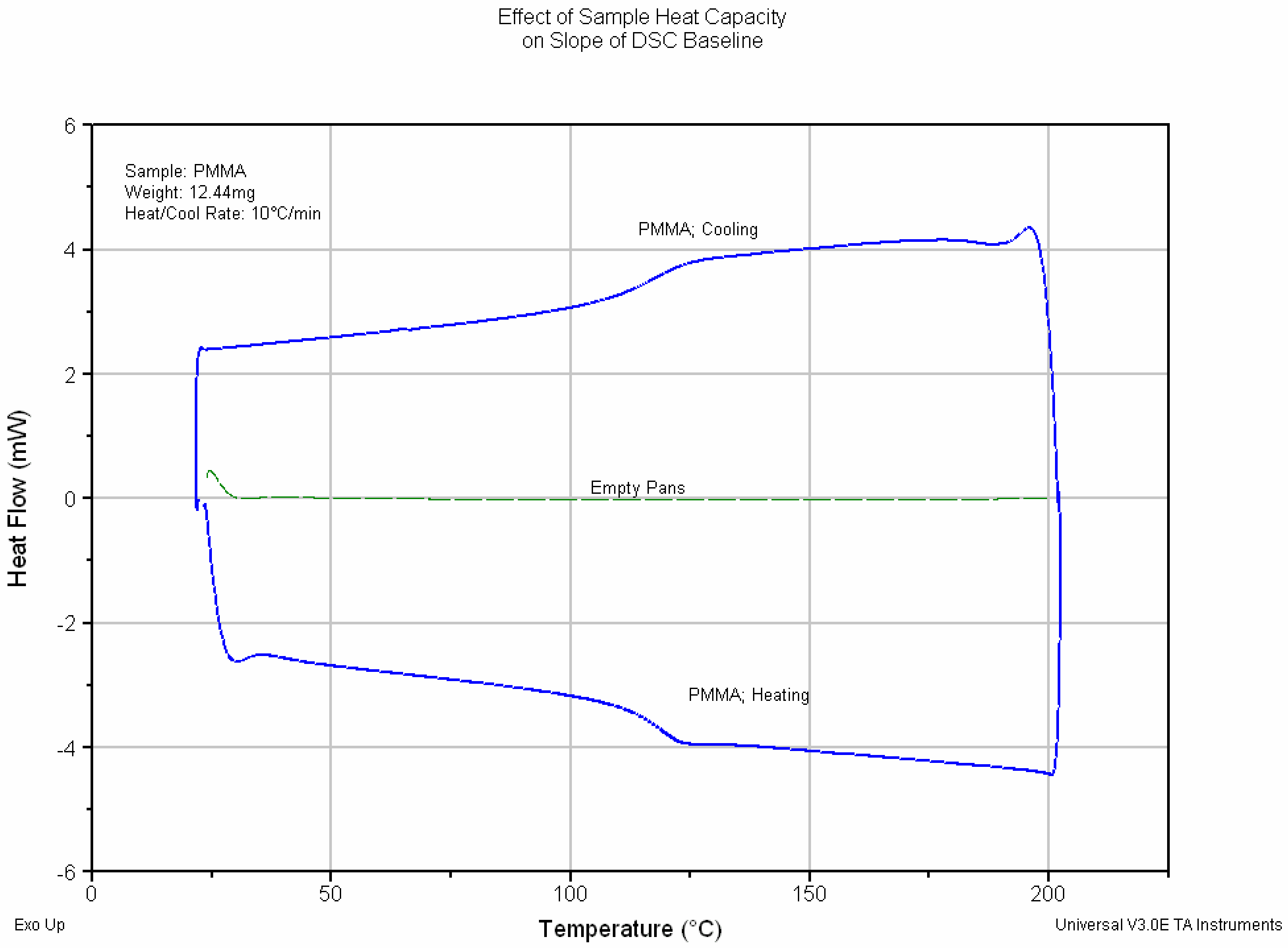
$dH/dt = Cp\ dT/dt$ + thermal events

where:

Cp = specific heat (J/g°C)
T = temperature (°C)
H = heat (J)
dH/dt = heat flow (J/min.)
mW = mJ/sec
dT/dt = heating rate (°C/min.)

assuming work & mass loss are zero

Baseline Slope due to Heat Capacity



DSC: Heat Flow Measurements

Calorimeter Signals

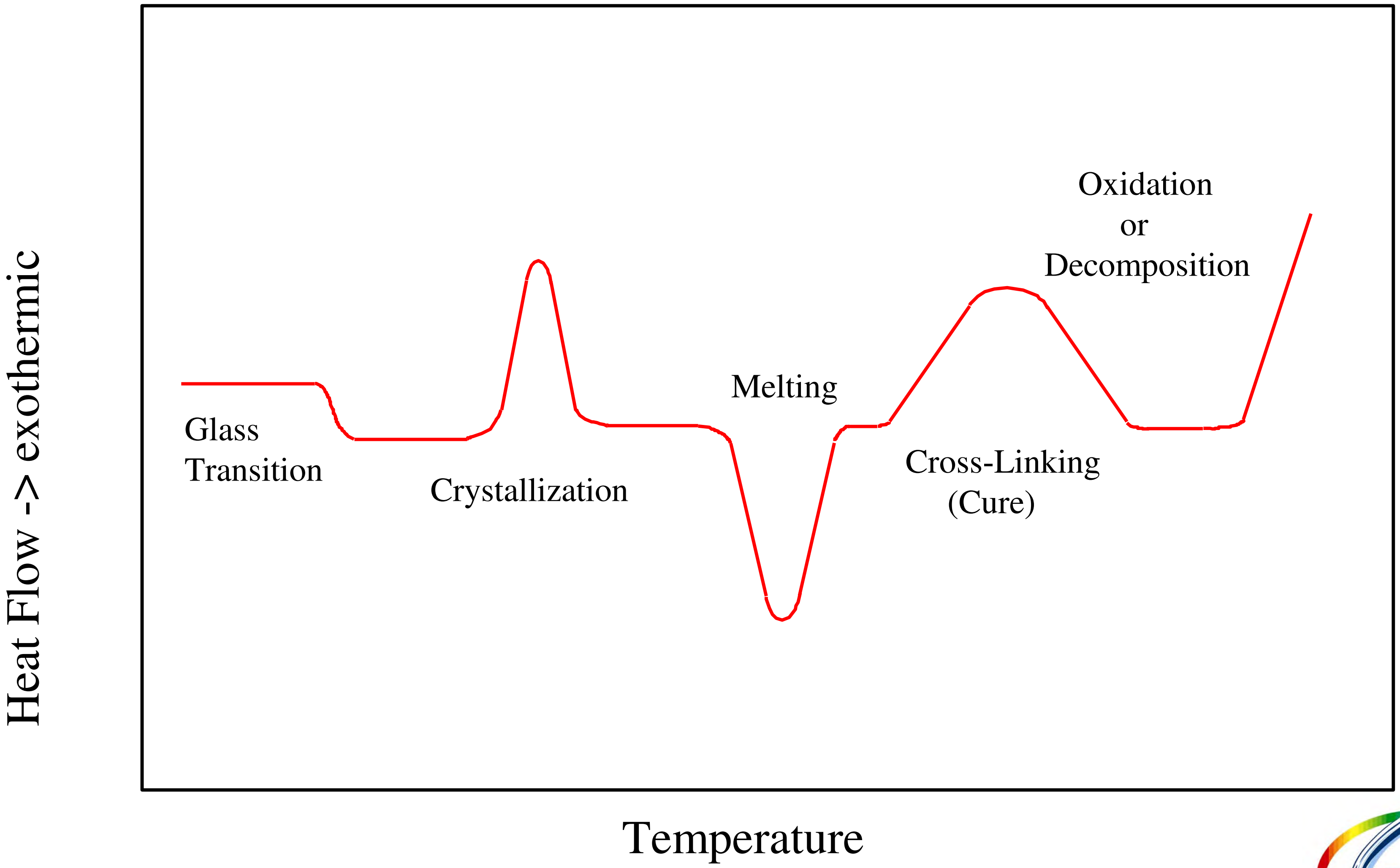
Time

Temperature

Heat Flow

Signal Change	**Properties Measured**
Heat Flow, absolute	Specific Heat
Heat Flow, shift	Glass Transition
Exothermic Peak	Crystallization or Cure
Endothermic Peak	Melting
Isothermal Onset	Oxidative Stability

DSC: Typical DSC Transitions



Modulated DSC®

Agenda

1. Understanding Heat Flow from DSC Experiments
2. Natural Limitations of DSC and How They Are Solved by MDSC
3. General Theory of MDSC
   - What Is Really Measured In MDSC Experiments
4. Calculation of MDSC Signals
5. Calibration
6. Optimization of MDSC Experimental ConditionsPractical Application of MDSC
   - Glass Transitions
   - Melting
   - Initial Crystallinity
   - Heat Capacity
   - Quasi-Isothermal Heat Capacity

Understanding Heat Flow from DSC Experiments

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

Where:

$$\frac{dH}{dt} = \text{DSC heat flow signal; Watts} = \text{J/s}$$

$$Cp = \text{Sample Heat Capacity; J/°C}$$

$$= \text{Sample Specific Heat (J/g°C) x Sample Weight (g)}$$

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

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

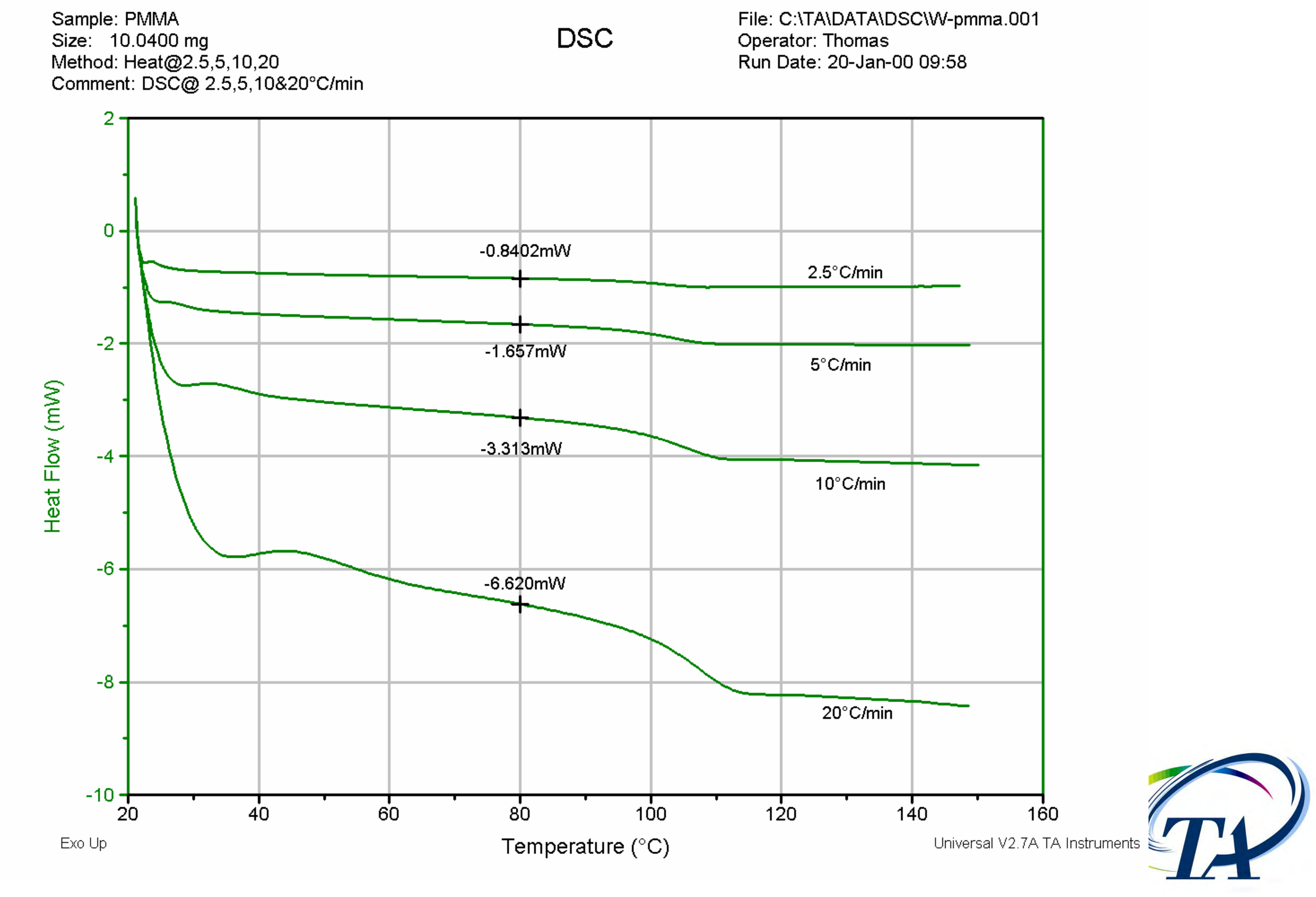
DSC Heat Flow (cont.)

- For a given sample, the rate of heat flow (J/sec) due to heat capacity is linearly proportional to heating rate; Figure 1.
- At a heating rate of zero, the heat flow due to heat capacity is also zero.

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

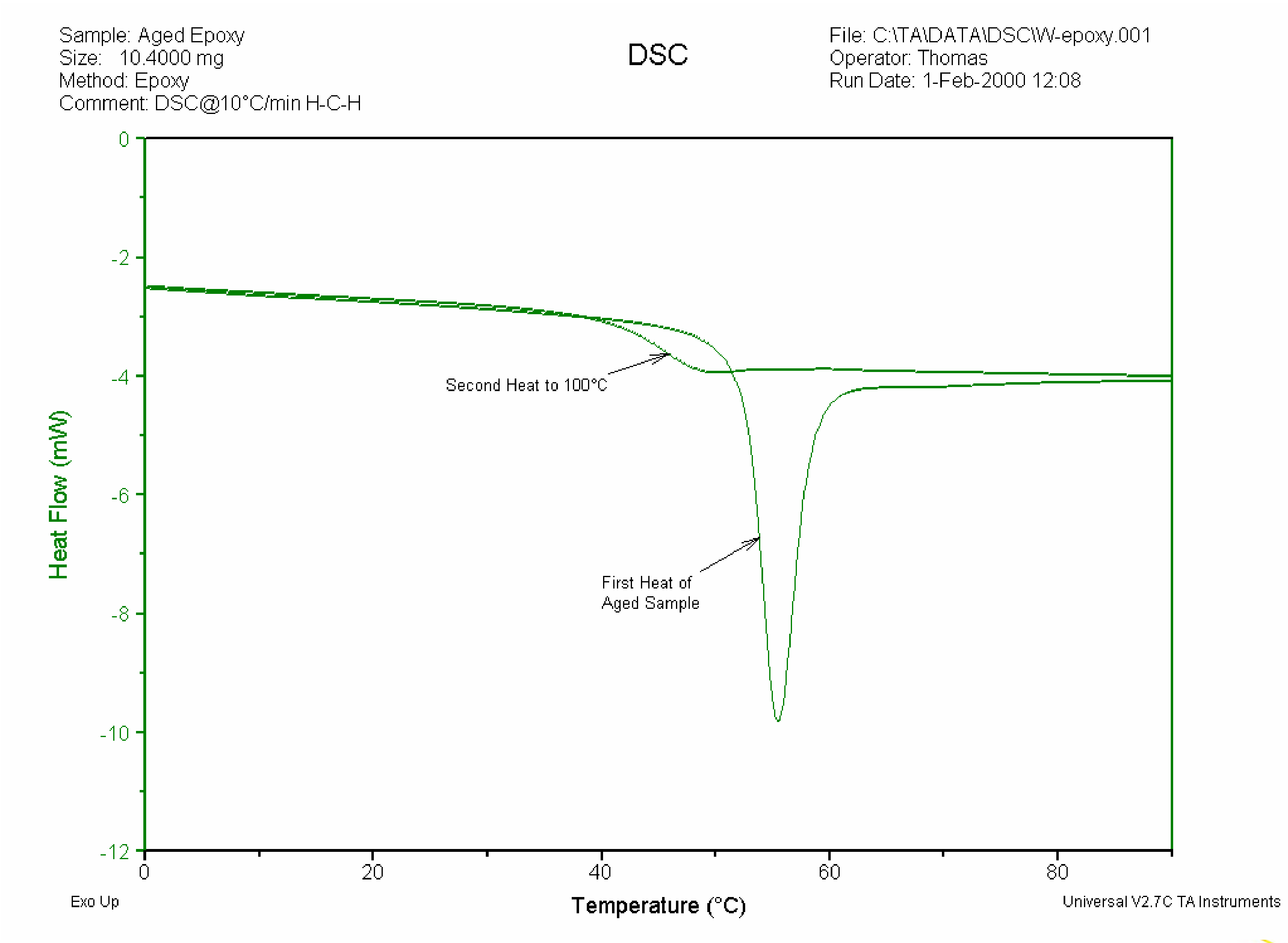
- Any heat flow detected at a zero heating rate must be due to kinetic processes f(T,t) in the sample; Figures 2 – 4.
- The purpose of MDSC is to separate the total heat flow into the part that responds to heating rate and the part that responds to absolute temperature; Figures 5 – 6 .

Figure 1



Sample: PMMA
Size: 10.0400 mg
Method: Heat@2.5,5,10,20
Comment: DSC@ 2.5,5,10&20°C/min
DSC
File: C:\TA\DATA\DSC\W-pmma.001
Operator: Thomas
Run Date: 20-Jan-00 09:58
2
0
-2
-4
-6
-8
-10
Heat Flow (mW)
-0.8402mW
2.5°C/min
-1.657mW
5°C/min
-3.313mW
10°C/min
-6.620mW
20°C/min
20
40
60
80
100
120
140
160
Temperature (°C)
Exo Up
Universal V2.7A TA Instruments

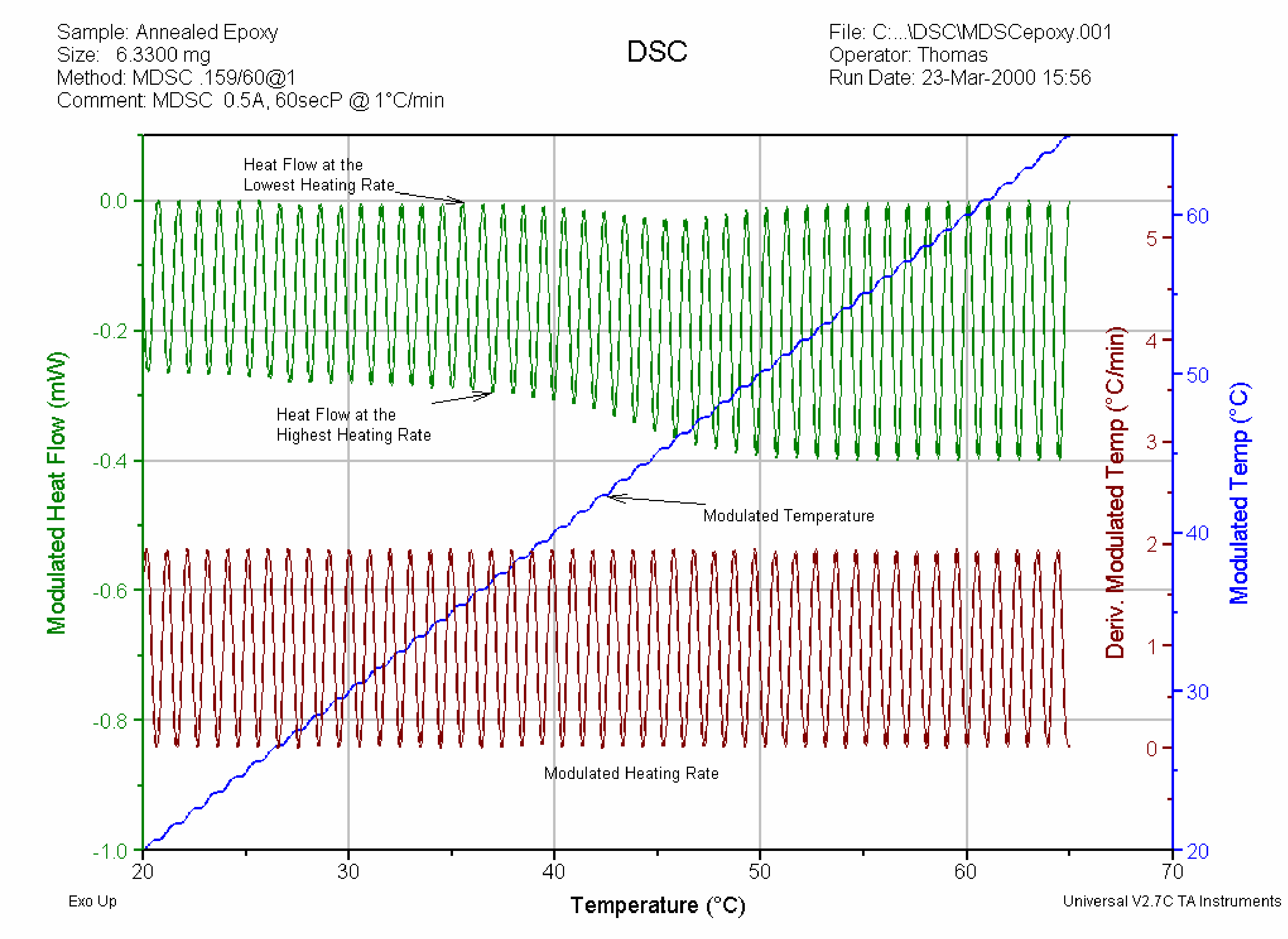
Figure 2



Sample: Aged Epoxy
Size: 10.4000 mg
Method: Epoxy
Comment: DSC@10°C/min H-C-H

File: C:\TA\DATA\DSC\W-epoxy.001
Operator: Thomas
Run Date: 1-Feb-2000 12:08

Figure 3



Sample: Annealed Epoxy
Size: 6.3300 mg
Method: MDSC .159/60@1
Comment: MDSC 0.5A, 60secP @ 1°C/min

DSC

File: C:...\DSC\MDSCepoxy.001
Operator: Thomas
Run Date: 23-Mar-2000 15:56

Figure 4

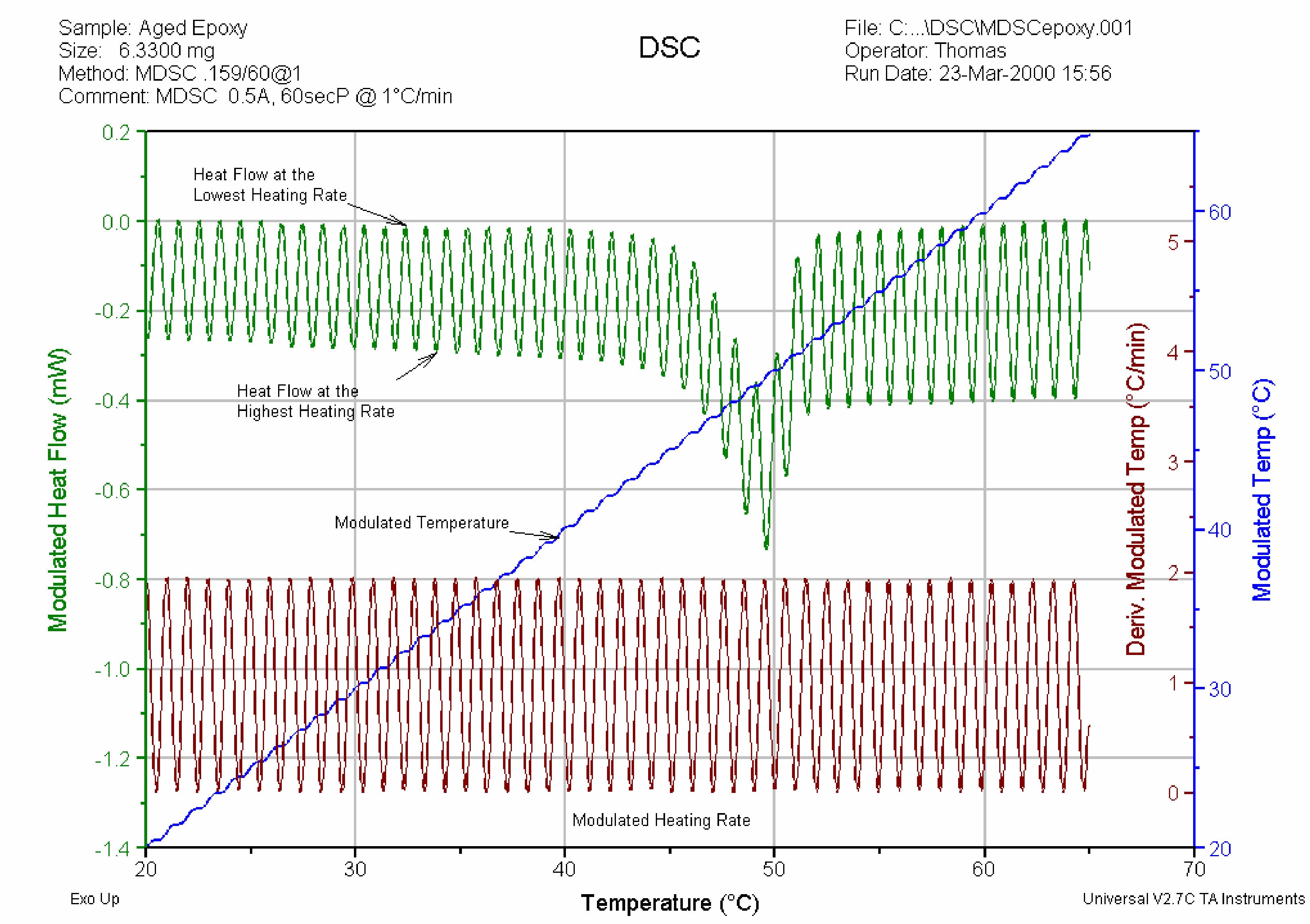
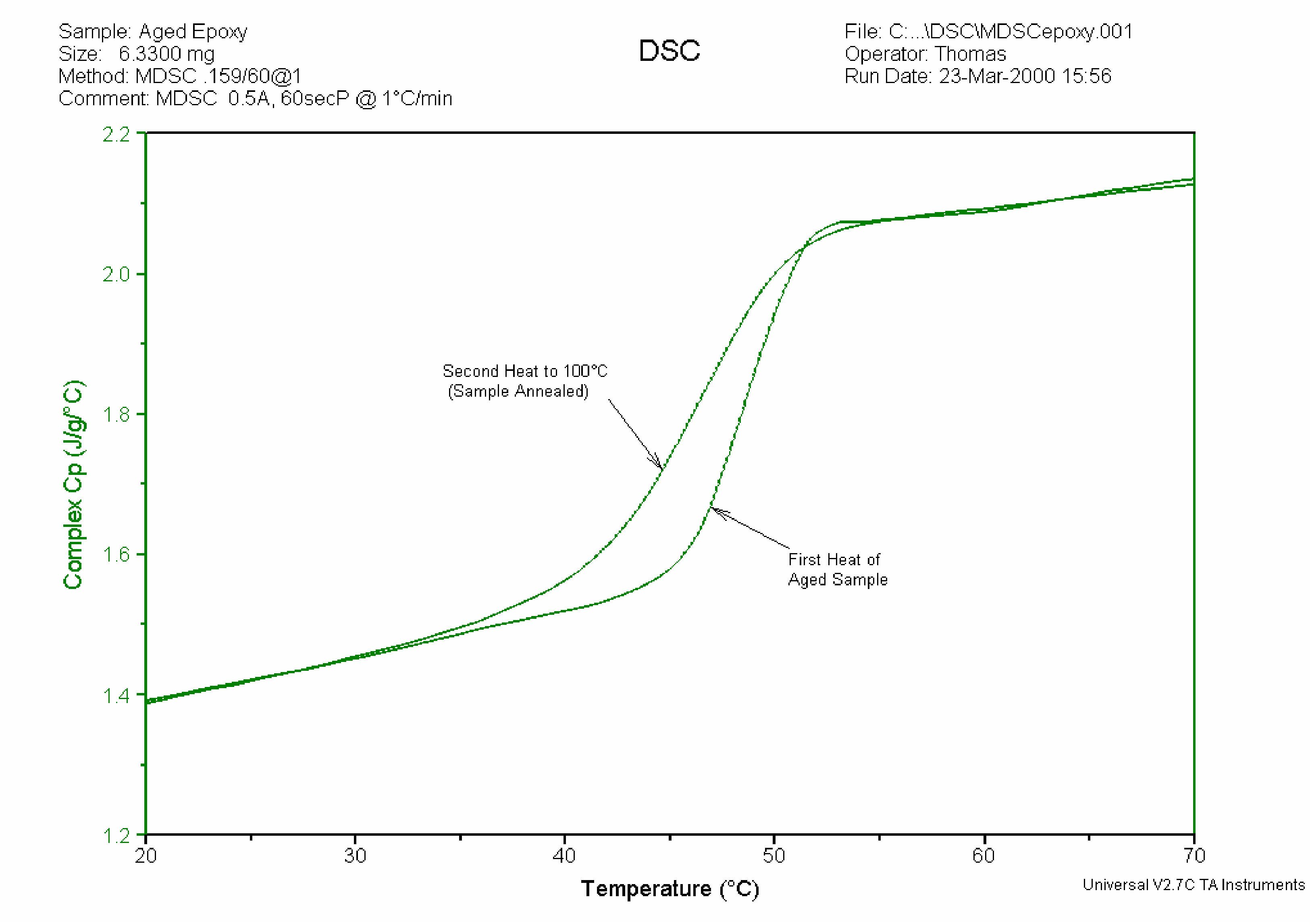

Sample: Aged Epoxy
Size: 6.3300 mg
Method: MDSC .159/60@1
Comment: MDSC 0.5A, 60secP @ 1°C/min
DSC
File: C:...\DSC\MDSCepoxy.001
Operator: Thomas
Run Date: 23-Mar-2000 15:56
Heat Flow at the Lowest Heating Rate
Heat Flow at the Highest Heating Rate
Modulated Temperature
Modulated Heating Rate
Modulated Heat Flow (mW)
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Deriv. Modulated Temp (°C/min)
5
4
3
2
1
0
Modulated Temp (°C)
60
50
40
30
20
20
30
40
50
60
70
Temperature (°C)
Exo Up
Universal V2.7C TA Instruments

Figure 5

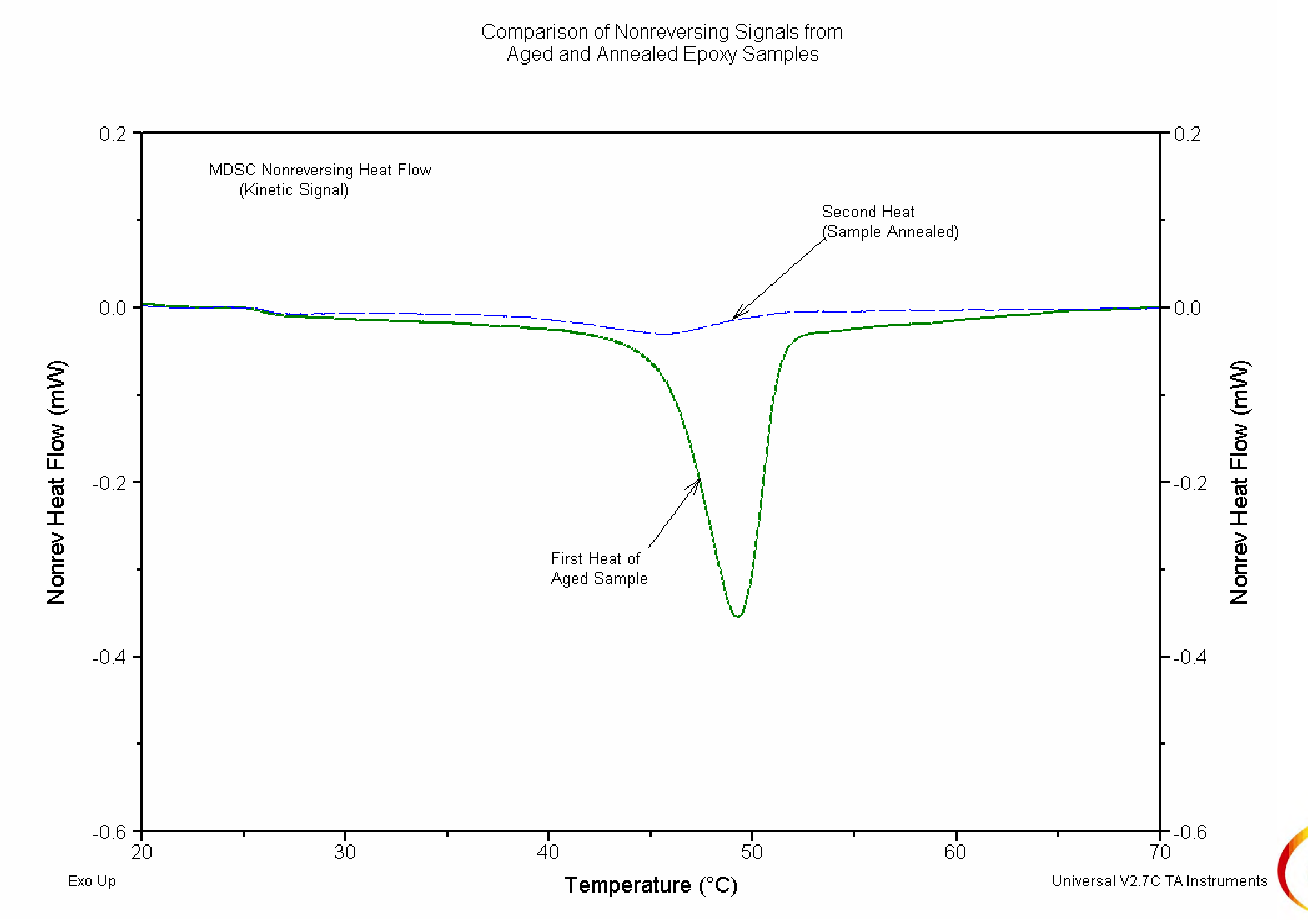


Sample: Aged Epoxy
Size: 6.3300 mg
Method: MDSC .159/60@1
Comment: MDSC 0.5A, 60secP @ 1°C/min

DSC

File: C:...\DSC\MDSCepoxy.001
Operator: Thomas
Run Date: 23-Mar-2000 15:56

Figure 6


Comparison of Nonreversing Signals from
Aged and Annealed Epoxy Samples
MDSC Nonreversing Heat Flow
(Kinetic Signal)
Second Heat
(Sample Annealed)
First Heat of
Aged Sample
0.2
0.0
-0.2
-0.4
-0.6
Nonrev Heat Flow (mW)
20
30
40
50
60
70
Temperature (°C)
Exo Up
Universal V2.7C TA Instruments

Section 2: The Natural Limitations of DSC and How They are Solved by MDSC

1. It is not possible to optimize both sensitivity and resolution in a single DSC experiment.

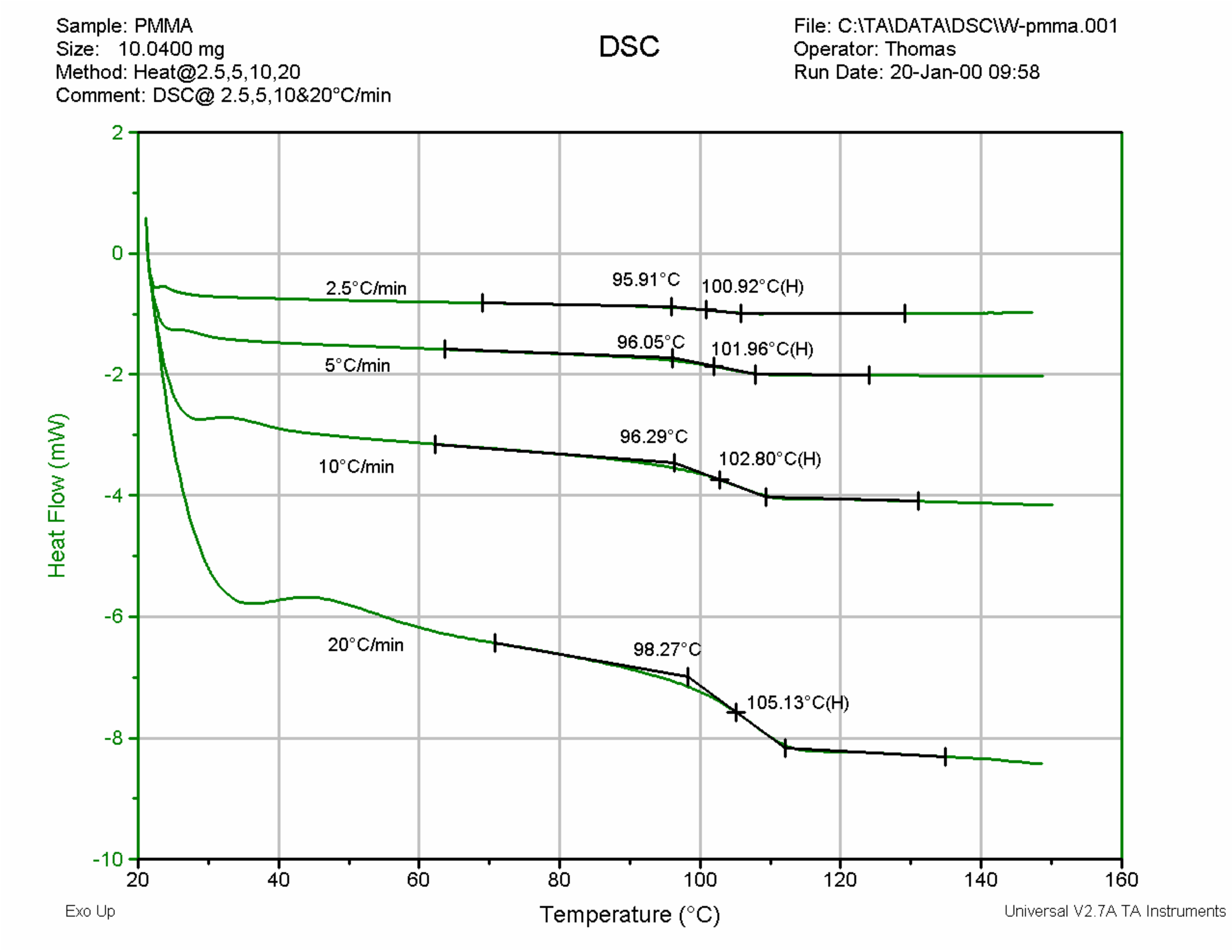
   - In order to increase the sensitivity of DSC, where sensitivity is defined as the ability to detect transitions in the sample, it is necessary to increase sample size, heating rate or both.

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

   - Although increased sample size or heating rate improves sensitivity, they decrease resolution by causing a larger temperature gradient within the sample (see Figure 7 and Table 1).

   - MDSC solves this problem because it has two heating rates: the average heating rate can be slow to improve resolution, while the modulated heating rate can be high to improve sensitivity (Figure 8).

Figure 7



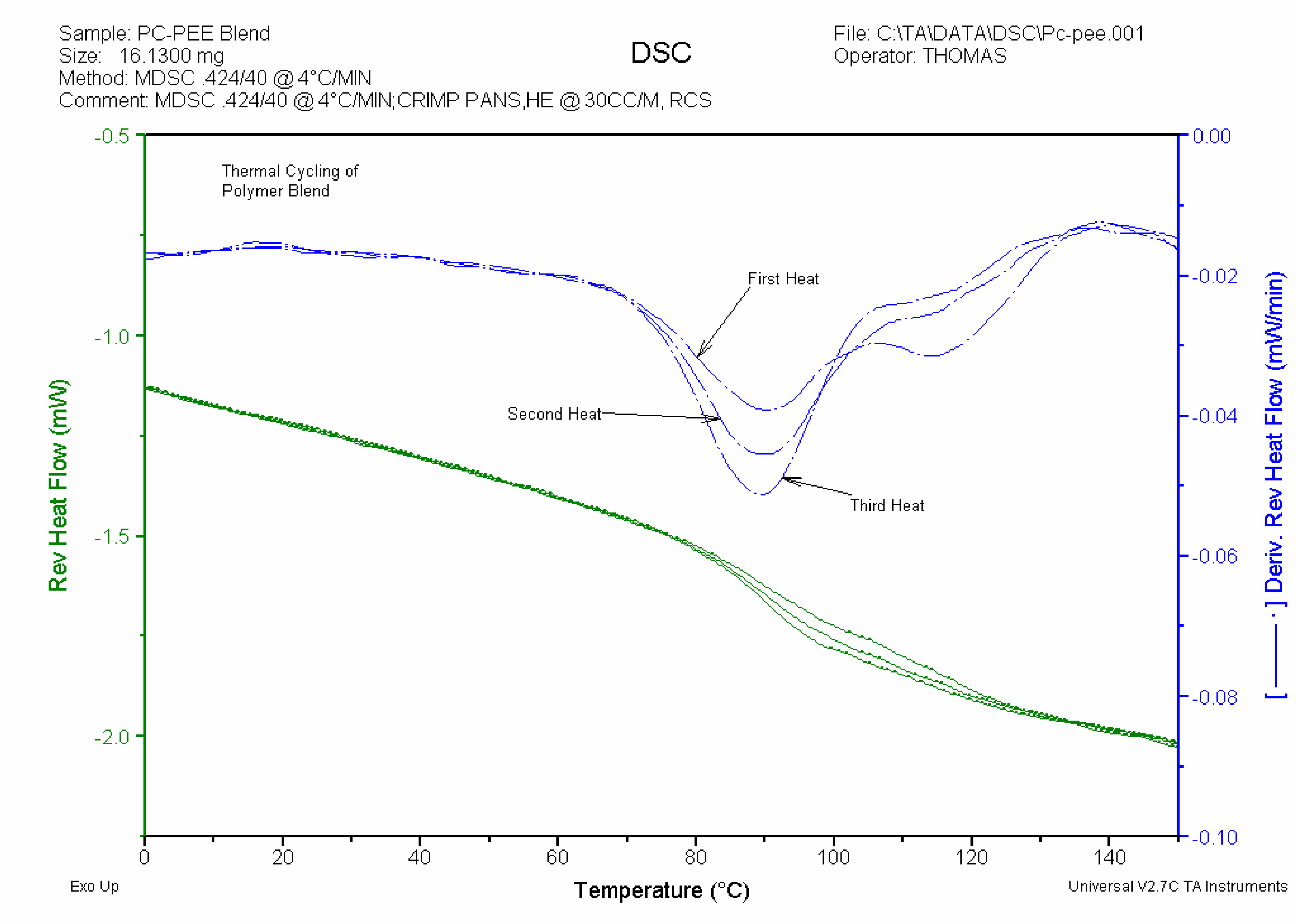
Sample: PMMA
Size: 10.0400 mg
Method: Heat@2.5,5,10,20
Comment: DSC@ 2.5,5,10&20°C/min

File: C:\TA\DATA\DSC\W-pmma.001
Operator: Thomas
Run Date: 20-Jan-00 09:58

Table 1

Heating Rate (°C/min)	Heat Flow @ 80°C	Tg Onset (°C)	Tg Midpoint (°C)	½ Width of Tg (°C)
2.5	-0.84	95.9	100.9	5.0
5.0	-1.66	96.0	102.0	6.0
10.0	-3.31	96.3	102.8	6.5
20.0	-6.62	98.3	105.1	6.8

Figure 8



Sample: PC-PEE Blend
Size: 16.1300 mg
Method: MDSC .424/40 @ 4°C/MIN
Comment: MDSC .424/40 @ 4°C/MIN;CRIMP PANS,HE @ 30CC/M, RCS

File: C:\TA\DATA\DSC\Pc-pee.001
Operator: THOMAS

Natural Limitations of DSC (cont.)

2. Baseline curvature and drift limit the sensitivity of DSC for detecting weak transitions (Figure 9).

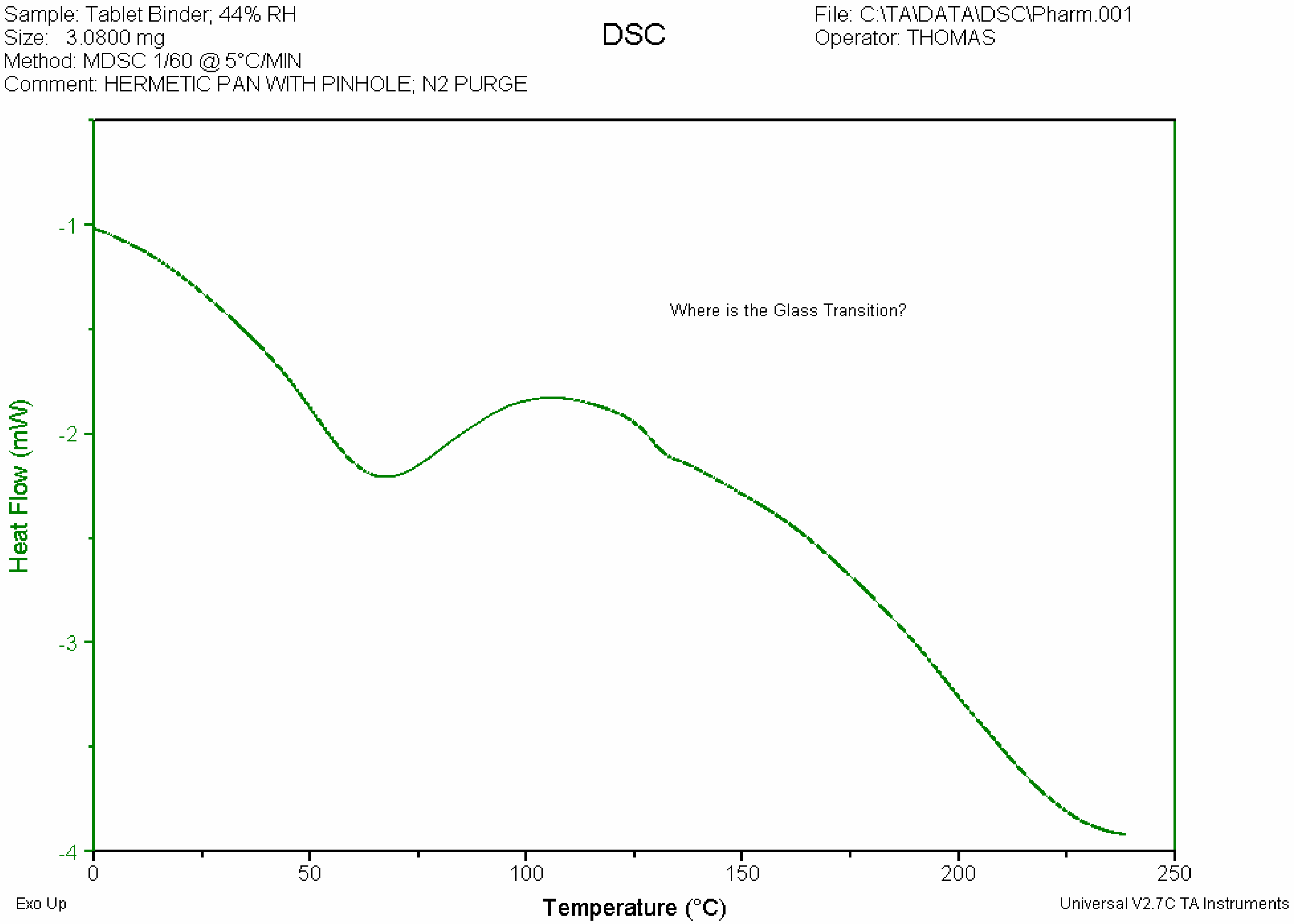
   - MDSC eliminates baseline curvature and drift in the Heat Capacity and Reversing signals by using the ratio of two measured signals rather than the absolute heat flow signal as measured by DSC.

$$Cp = \frac{\text{Amplitude Mod Heat Flow}}{\text{Amplitude Mod Heating Rate}} \text{ x K}$$

$$\text{Reversing} = \text{Cp x Avg Heating Rate}$$

[See Figure 10]

Figure 9



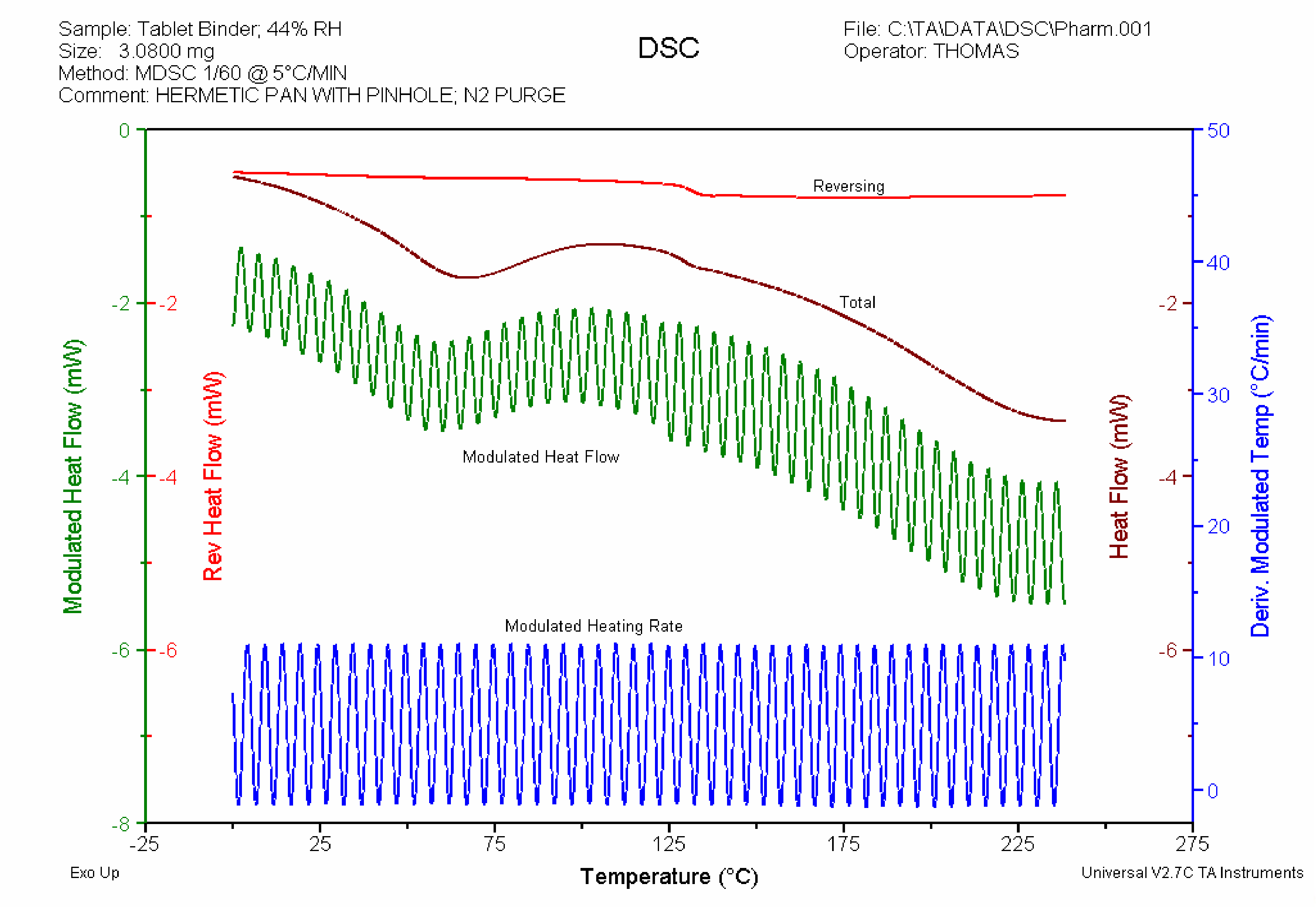
Sample: Tablet Binder; 44% RH
Size: 3.0800 mg
Method: MDSC 1/60 @ 5°C/MIN
Comment: HERMETIC PAN WITH PINHOLE; N2 PURGE

DSC

File: C:\TA\DATA\DSC\Pharm.001
Operator: THOMAS

Where is the Glass Transition?

Figure 10



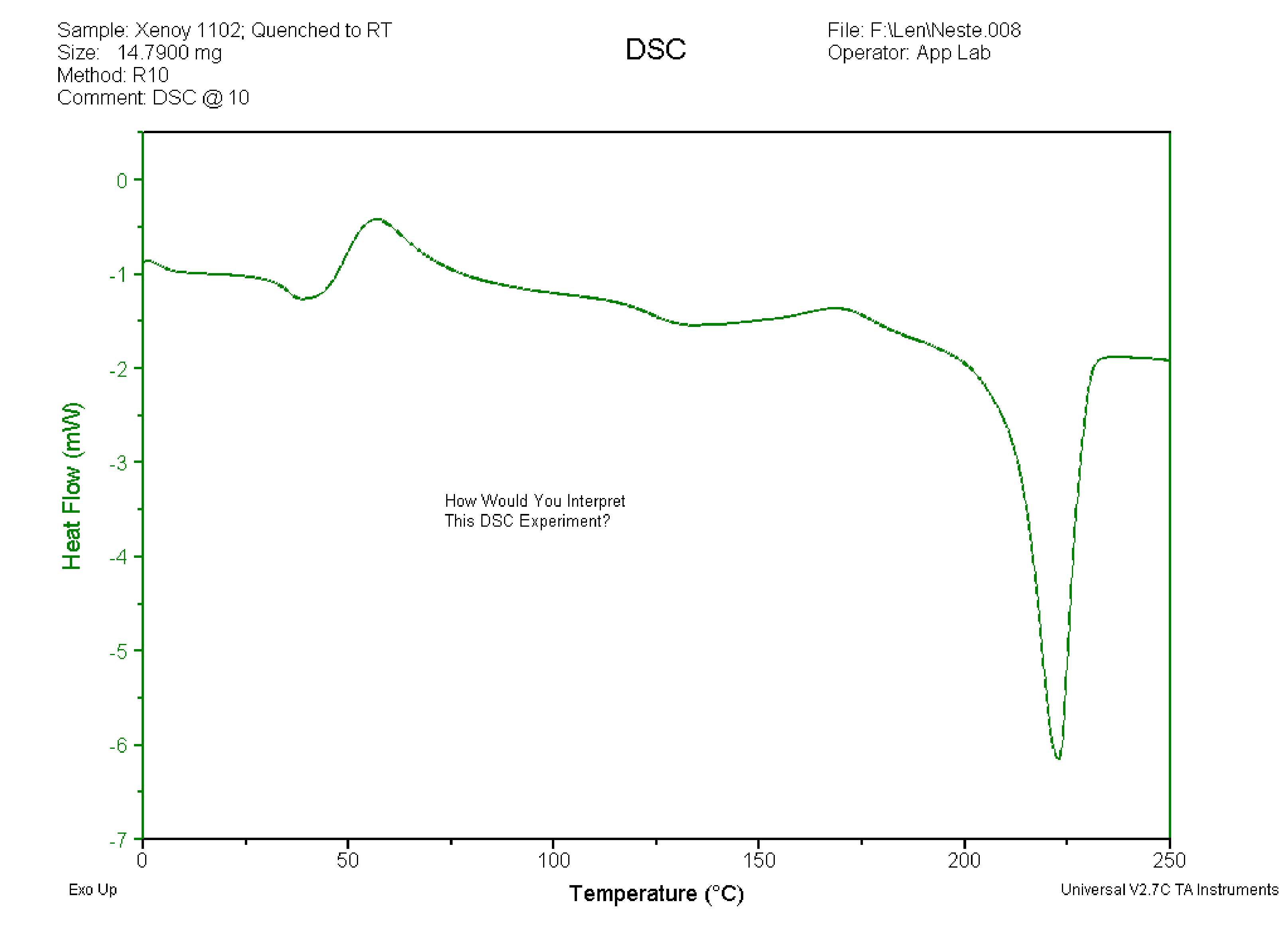
Sample: Tablet Binder; 44% RH
Size: 3.0800 mg
Method: MDSC 1/60 @ 5°C/MIN
Comment: HERMETIC PAN WITH PINHOLE; N2 PURGE
DSC
File: C:\TA\DATA\DSC\Pharm.001
Operator: THOMAS
Reversing
Total
Modulated Heat Flow
Modulated Heating Rate
Modulated Heat Flow (mW)
Rev Heat Flow (mW)
Heat Flow (mW)
Deriv. Modulated Temp (°C/min)
0
-2
-4
-6
-8
-2
-4
-6
-2
-4
-6
50
40
30
20
10
0
-25
25
75
125
175
225
275
Exo Up
Temperature (°C)
Universal V2.7C TA Instruments

Natural Limitations of DSC (cont.)

3. Transitions are often difficult to interpret because DSC can only measure the <u>Sum</u> of Heat Flow within the Calorimeter (Figure 11).

    - MDSC minimizes this problem by providing not only the Total Heat Flow signal but also the heat capacity and kinetic components of it (Figure 12).

Figure 11

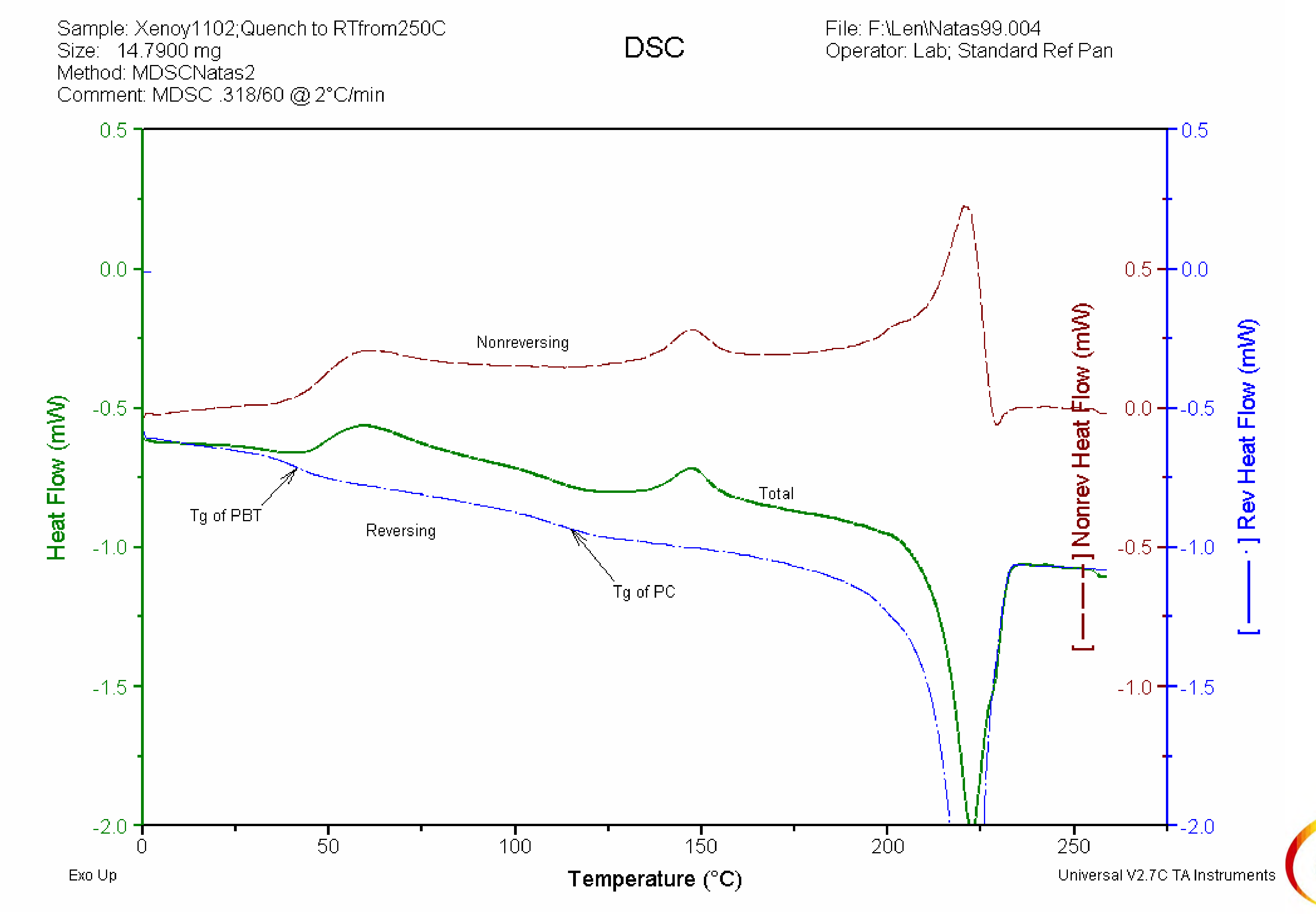


Sample: Xenoy 1102; Quenched to RT
Size: 14.7900 mg
Method: R10
Comment: DSC @ 10

File: F:\Len\Neste.008
Operator: App Lab

How Would You Interpret This DSC Experiment?

Figure 12


Sample: Xenoy1102;Quench to RTfrom250C
Size: 14.7900 mg
Method: MDSCNatas2
Comment: MDSC .318/60 @ 2°C/min
DSC
File: F:\Len\Natas99.004
Operator: Lab; Standard Ref Pan
Nonreversing
Total
Reversing
Tg of PBT
Tg of PC
Heat Flow (mW)
[– – –] Nonrev Heat Flow (mW)
[—— ·] Rev Heat Flow (mW)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
0.5
0.0
-0.5
-1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
0
50
100
150
200
250
Exo Up
Temperature (°C)
Universal V2.7C TA Instruments

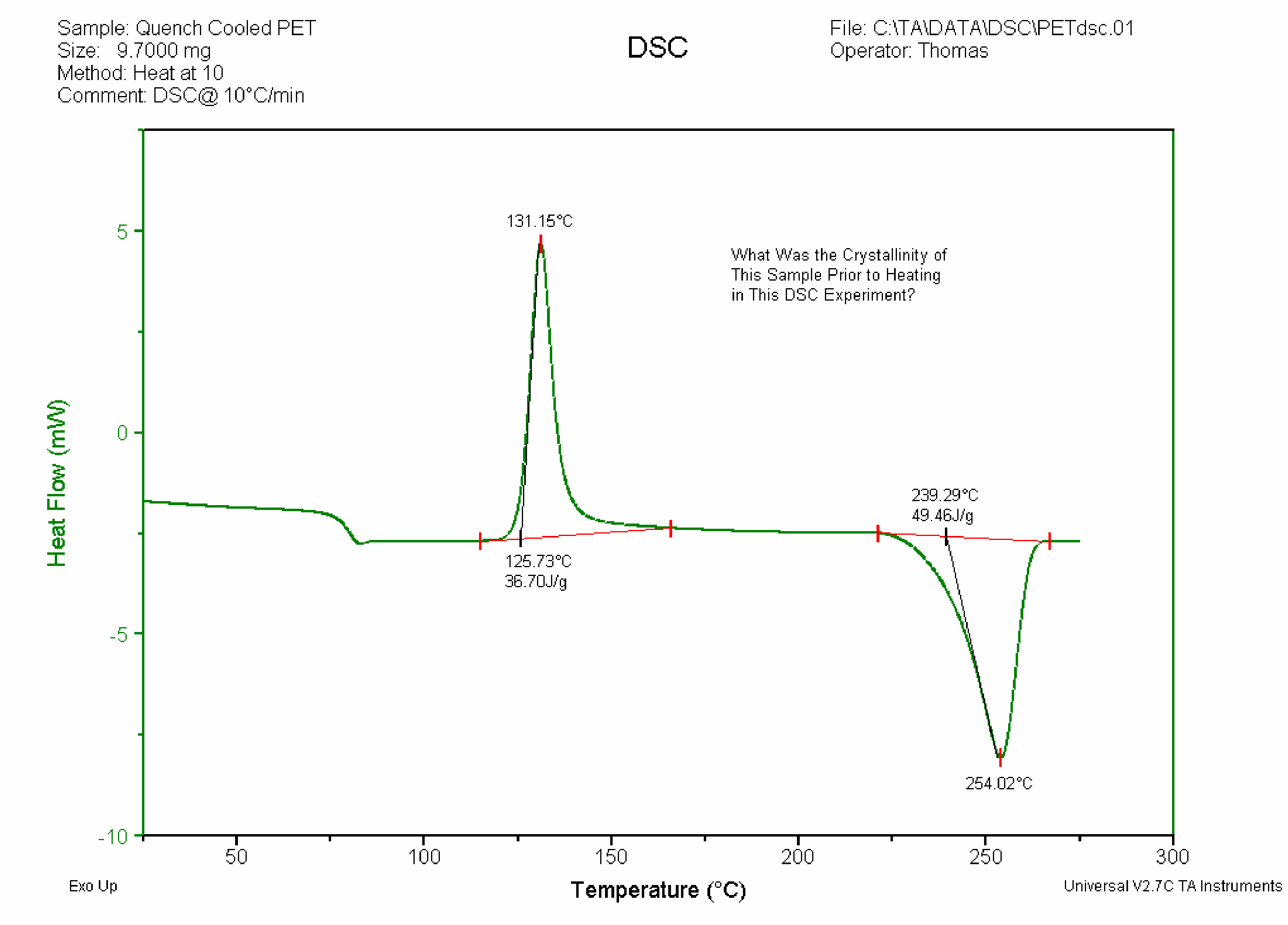
Natural Limitations of DSC (cont.)

4. The DSC measurement of polymer crystallinity is often wrong because it fails to detect the formation of crystalline structure as the sample is heated (Figure 13).
    - MDSC minimizes this problem by providing signals that are proportional to the amount of crystal structure forming as the sample is heated (Nonreversing) and the amount of melting occurring (Reversing). The sum of the Reversing and Nonreversing signals is used to calculate crystallinity (Figure 14).

Reversing + Nonreversing = Crystallinity

86.4 J/g + (-85.2 J/g) = 1 J/g

Figure 13



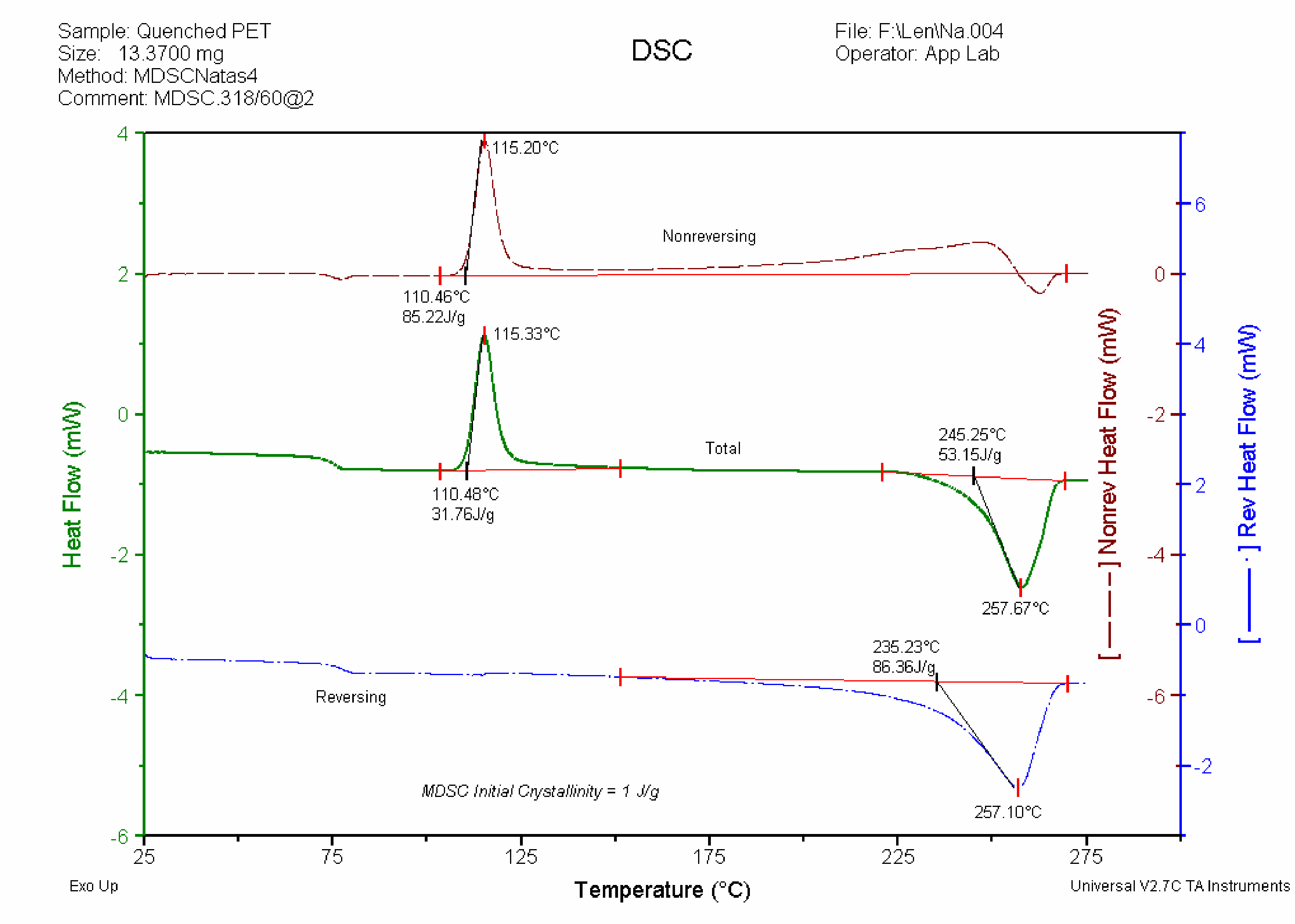
Sample: Quench Cooled PET
Size: 9.7000 mg
Method: Heat at 10
Comment: DSC@ 10°C/min

DSC

File: C:\TA\DATA\DSC\PETdsc.01
Operator: Thomas

What Was the Crystallinity of This Sample Prior to Heating in This DSC Experiment?

Figure 14


Sample: Quenched PET
Size: 13.3700 mg
Method: MDSCNatas4
Comment: MDSC.318/60@2
DSC
File: F:\Len\Na.004
Operator: App Lab
115.20°C
Nonreversing
110.46°C
85.22J/g
115.33°C
Total
245.25°C
53.15J/g
110.48°C
31.76J/g
257.67°C
235.23°C
86.36J/g
Reversing
MDSC Initial Crystallinity = 1 J/g
257.10°C
Heat Flow (mW)
4
2
0
-2
-4
-6
[– – –] Nonrev Heat Flow (mW)
0
-2
-4
-6
[——·] Rev Heat Flow (mW)
6
4
2
0
-2
25
75
125
175
225
275
Temperature (°C)
Exo Up
Universal V2.7C TA Instruments

Natural Limitations of DSC (cont.)

5. DSC cannot measure Heat Capacity under isothermal conditions.

   - Since MDSC has two independent heating rates (average and modulated), the average heating rate can be zero (isothermal) while the actual temperature is modulated higher and lower than the average. This permits the measurement of the sample's heat capacity and an analysis of how structure in the sample is changing as a function of time at that temperature.

[Figures 15 – 17]

Figure 15: MDSC Quasi-Isothermal Heat Capacity of Quench Cooled 40% Sucrose Solution

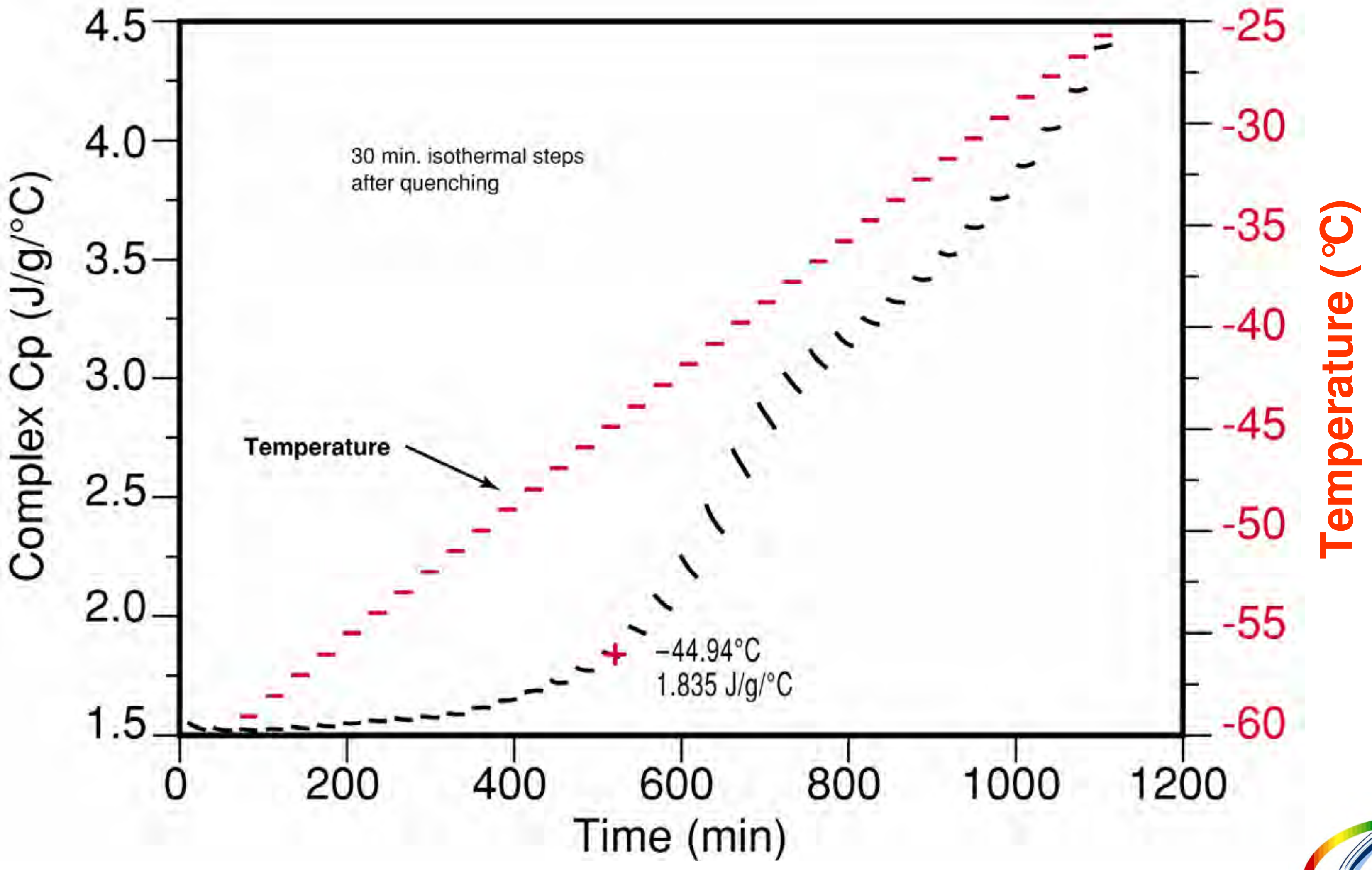
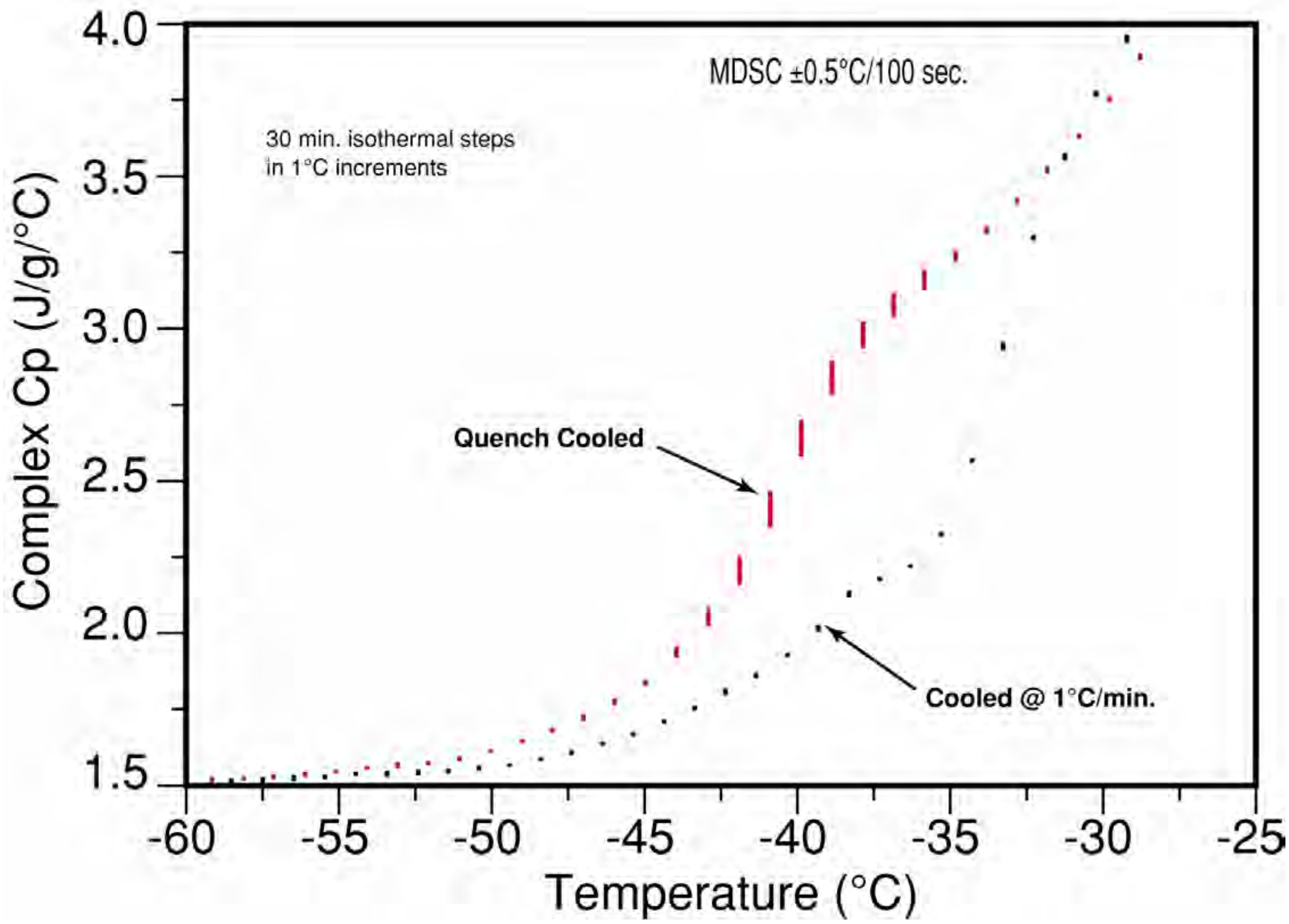


Figure 16: MDSC Quasi-Isothermal Heat Capacity of Quench Cooled and Slow Cooled 40% Sucrose Solution



MDSC Theory

Heat Flow Equation

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

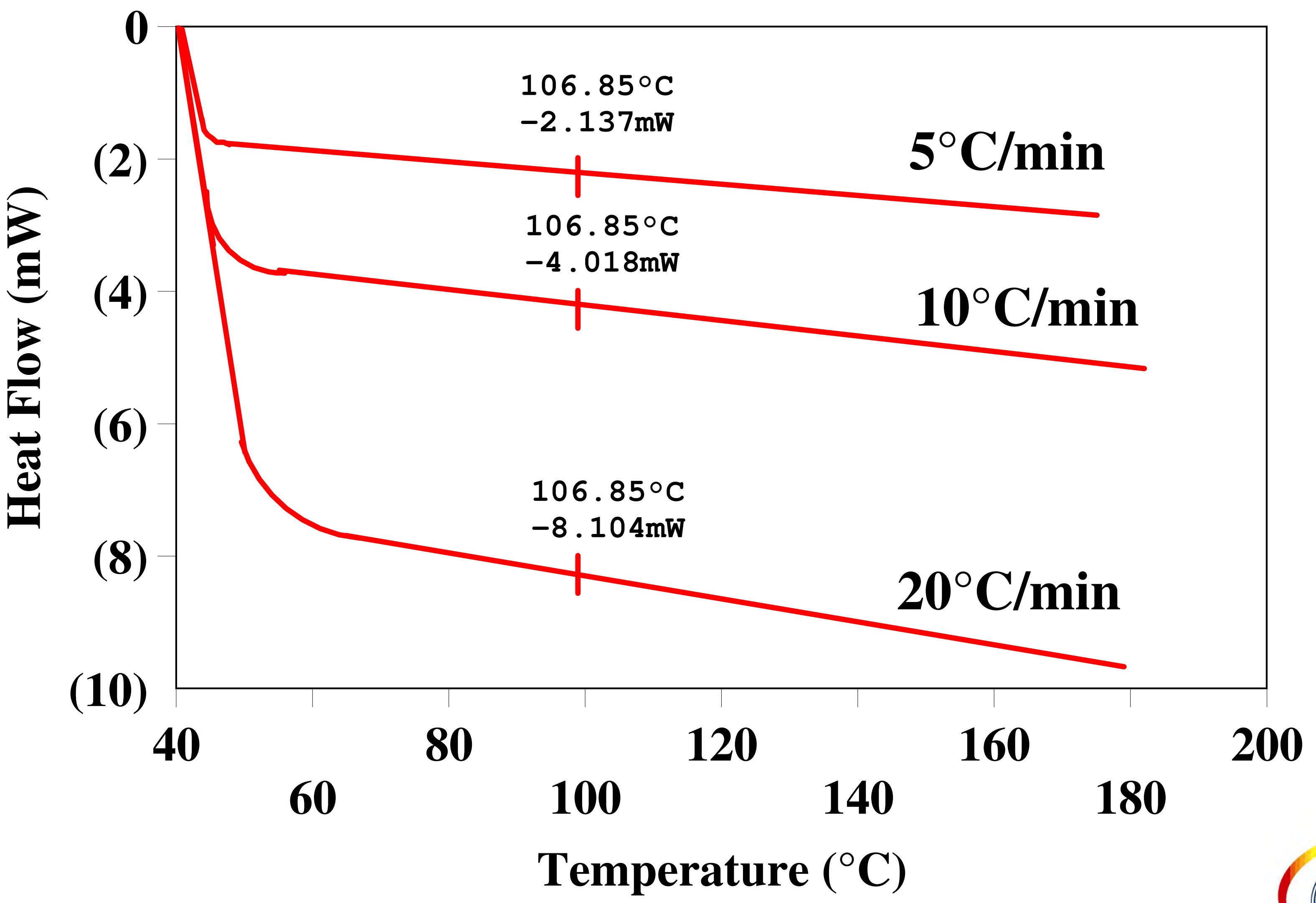
$\frac{dH}{dt}$ = Total Heat Flow measured by the calorimeter

Cp = Specific Heat Capacity

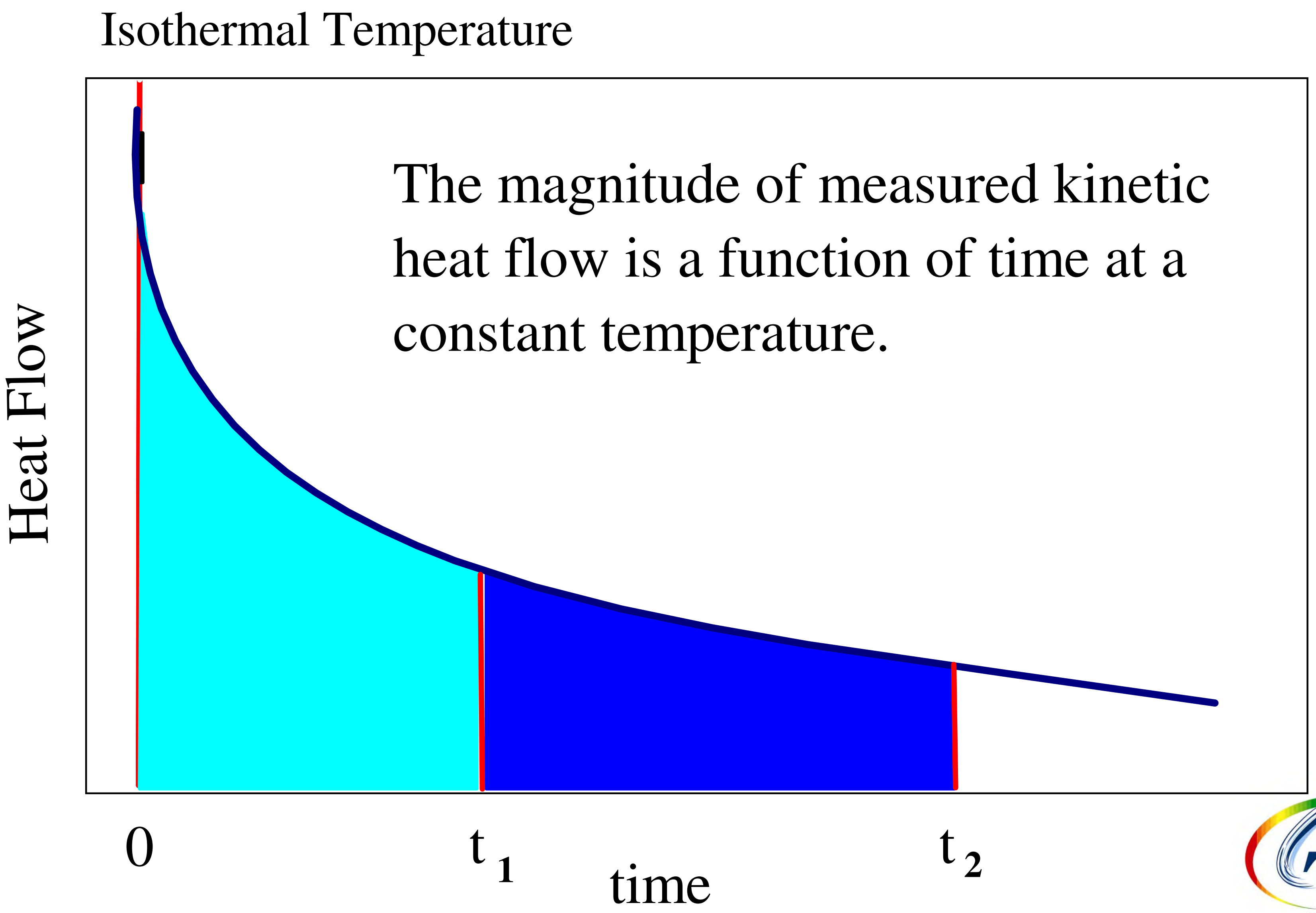
$\frac{dT}{dt}$ = Underlying Heating Rate

$f(T,t)$ = kinetic response of sample

Heat Flow Due to Heat Capacity

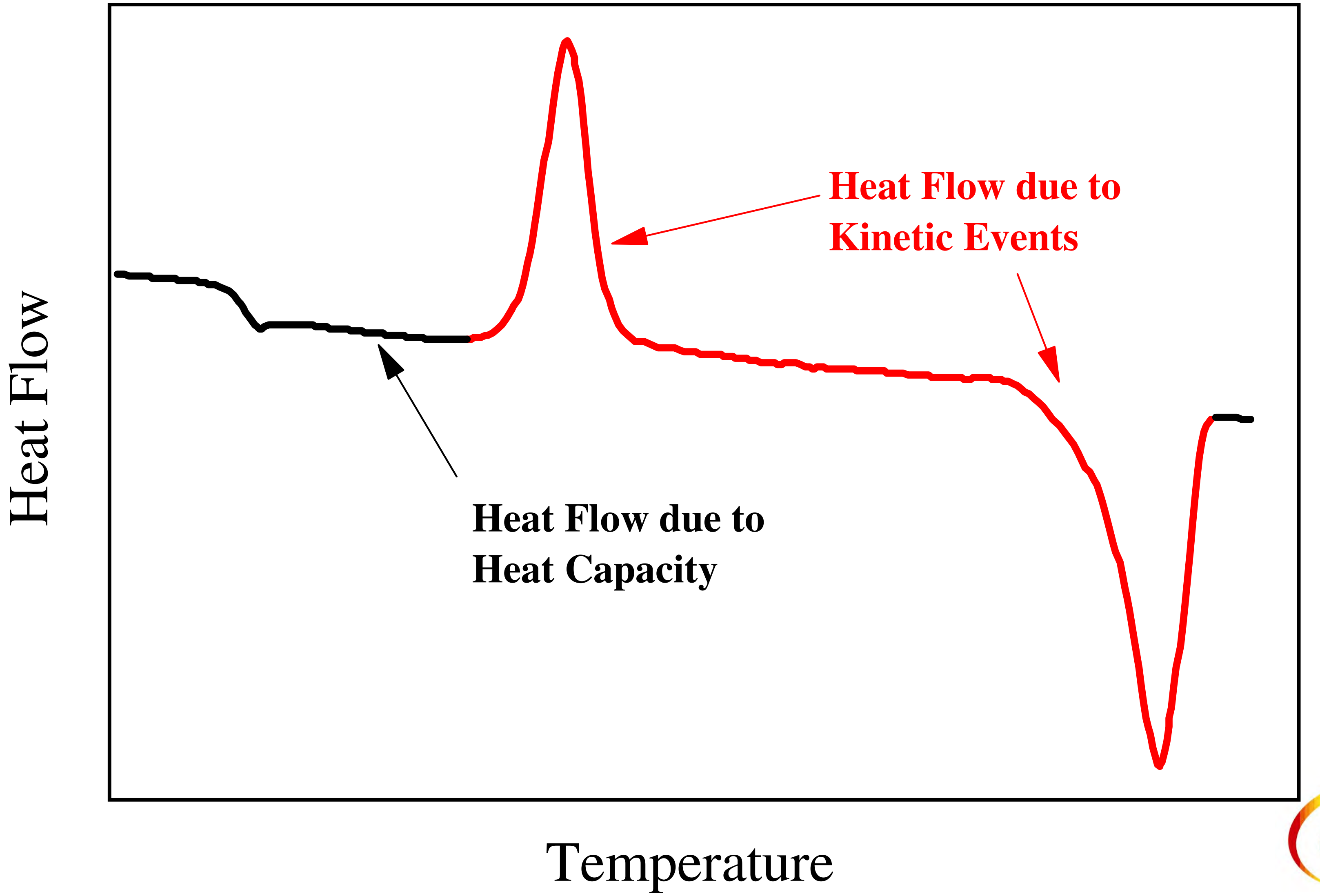


Kinetic Heat Flow

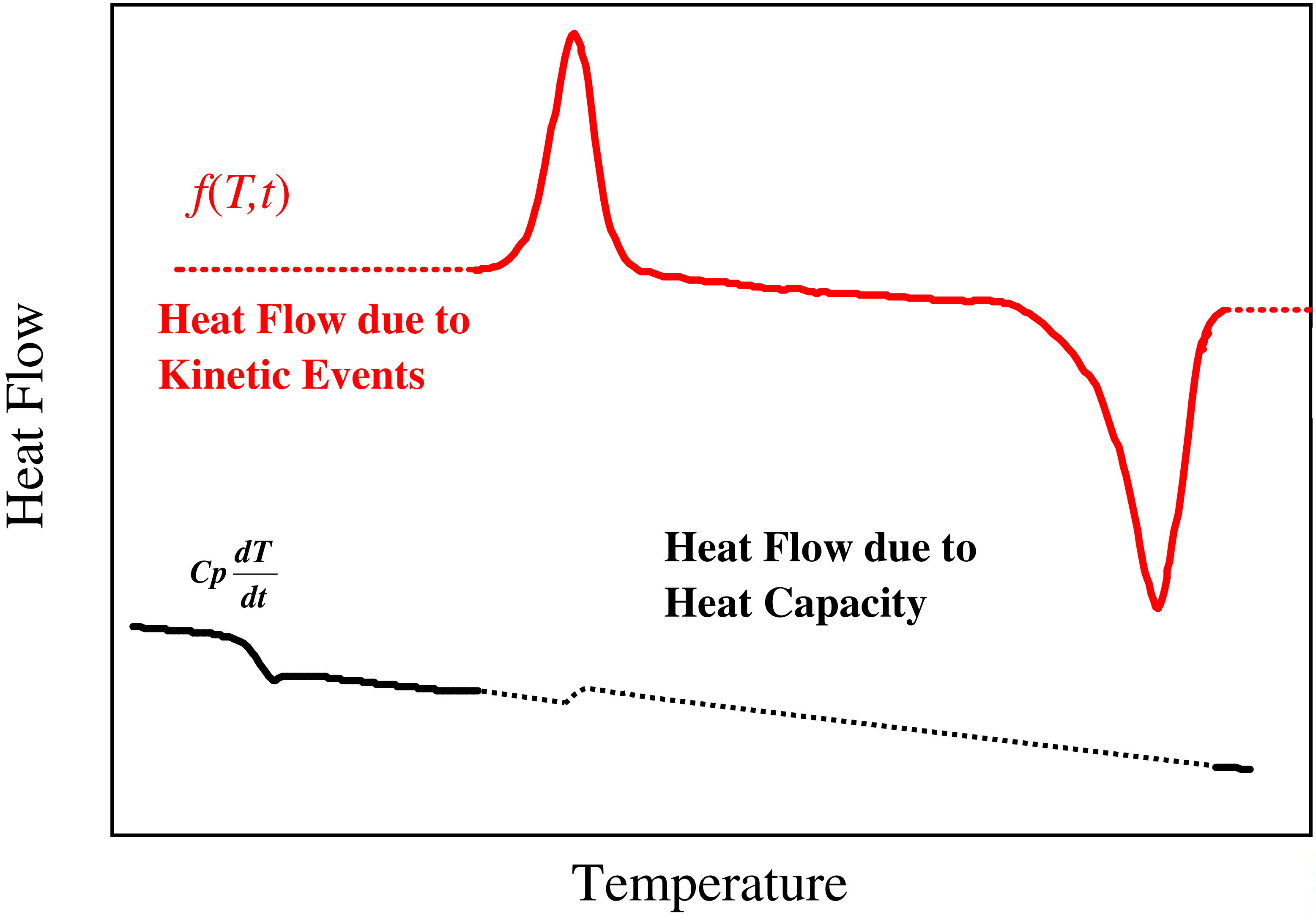


The magnitude of measured kinetic heat flow is a function of time at a constant temperature.

Standard DSC Measures the Sum of Heat Flow



Heat Flow Can Be Separated



General Theory of MDSC

Heat flow from DSC experiments is composed of two parts but DSC can only measure the sum of the two.

dH/dt	**=**	**$Cp\ (dT/dt)$**	**+**	**$f\ (T,t)$**
Total Heat Flow (DSC)	**=**	**Heat Capacity Component**	**+**	**Kinetic Component**
	=	**Heating Rate Dependent**	**+**	**Time Dependent**
	=	**MDSC Reversing**	**+**	**MDSC Nonreversing**

Distribution of Transitions in MDSC Experiments

Total = Heat Capacity Component + Kinetic Component

= Reversing Heat Flow + Nonreversing Heat Flow

- glass transition
- melting (some)

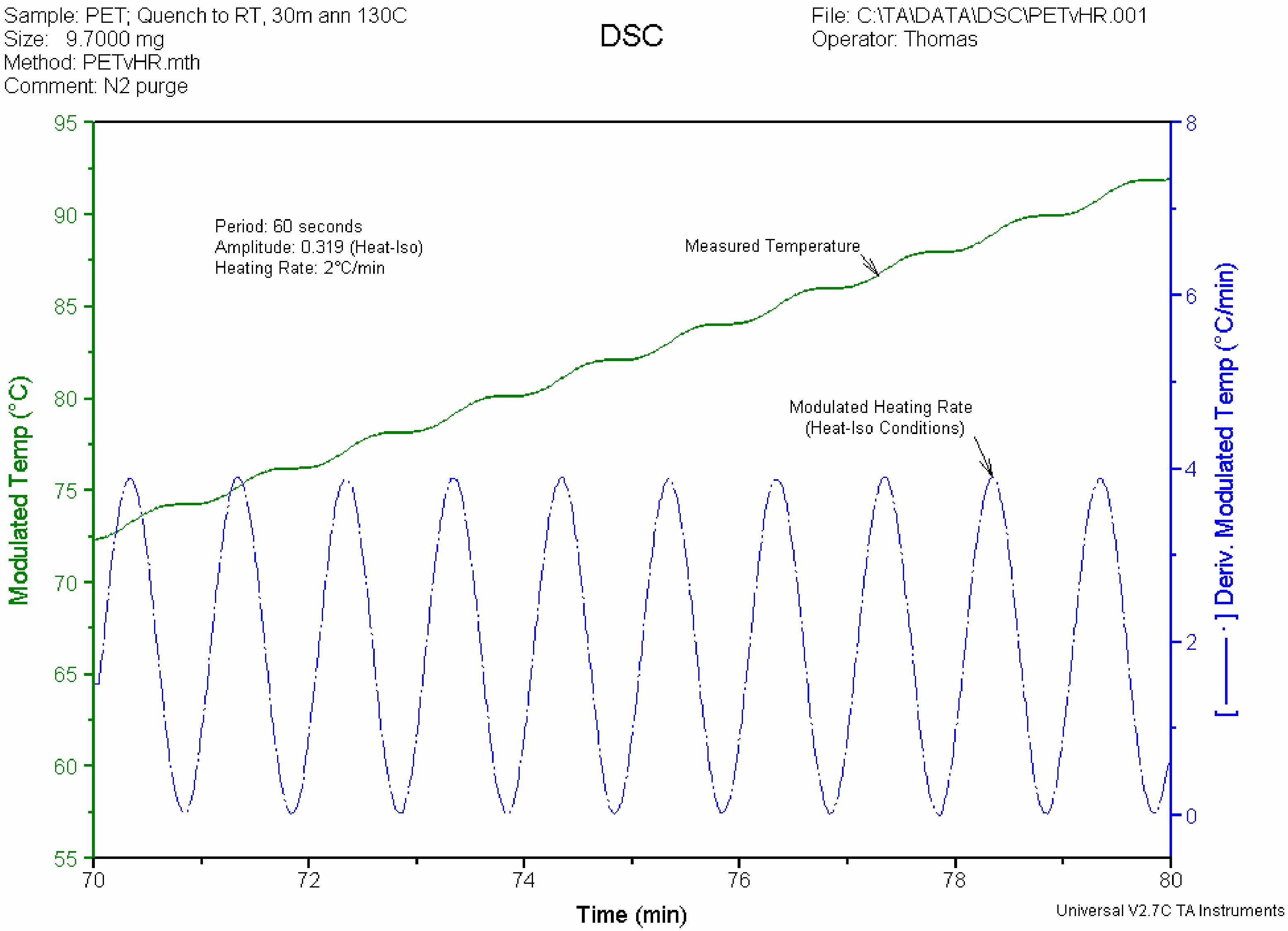
- enthalpic relaxation
- evaporation
- crystallization
- decomposition
- cure
- melting (some)

Physical Measurement Technique

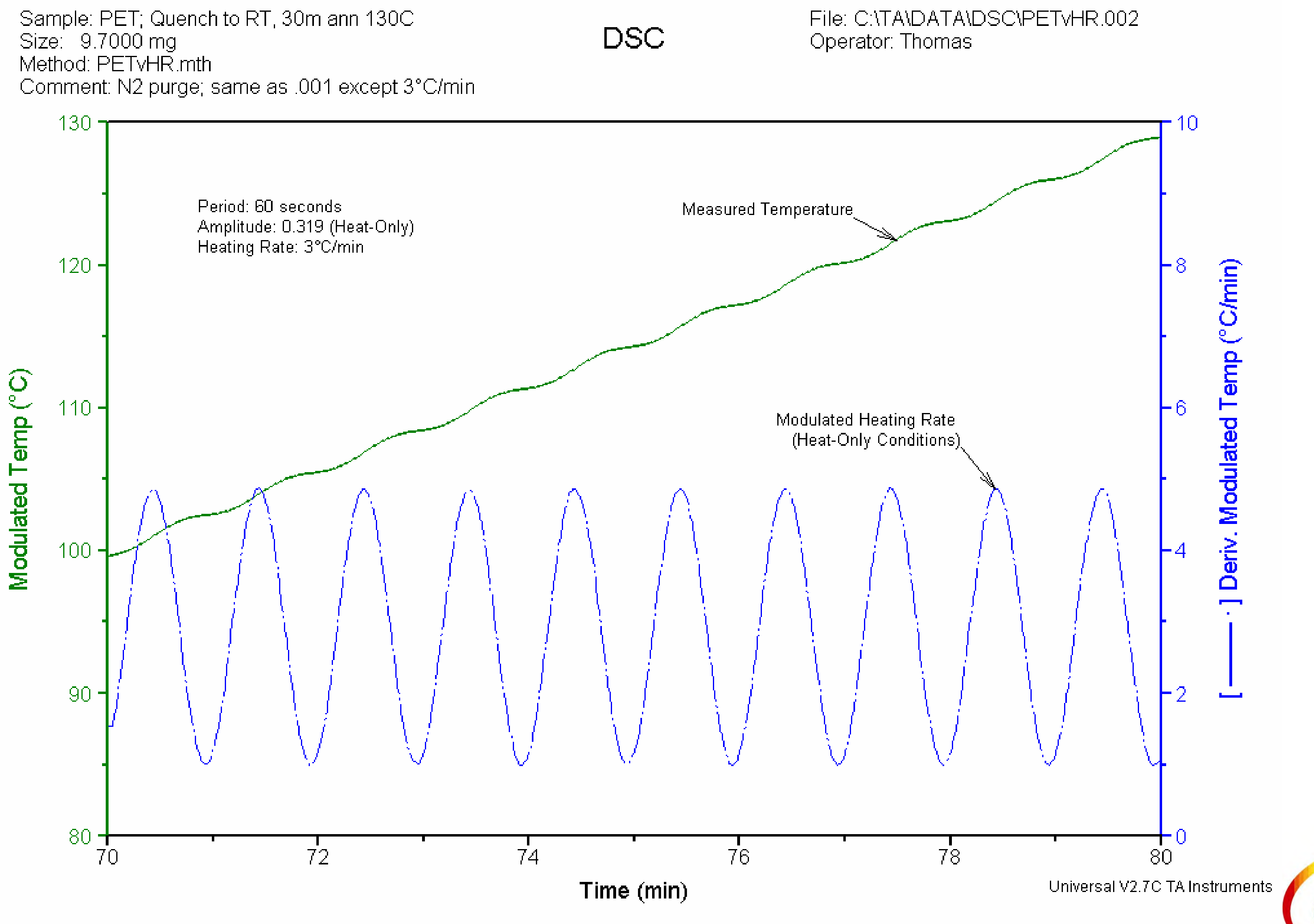
Apply Stimulus → Measure Response

	Stimulus	Response
FTIR	IR Radiation	Absorbance Wavelength
NMR	Magnetic Field	Resonance Frequency
X-Ray Diffraction	X-Ray Radiation	Angle of Diffraction
MDSC	Sinusoidal Heating Rate	Amplitude of Heat Flow

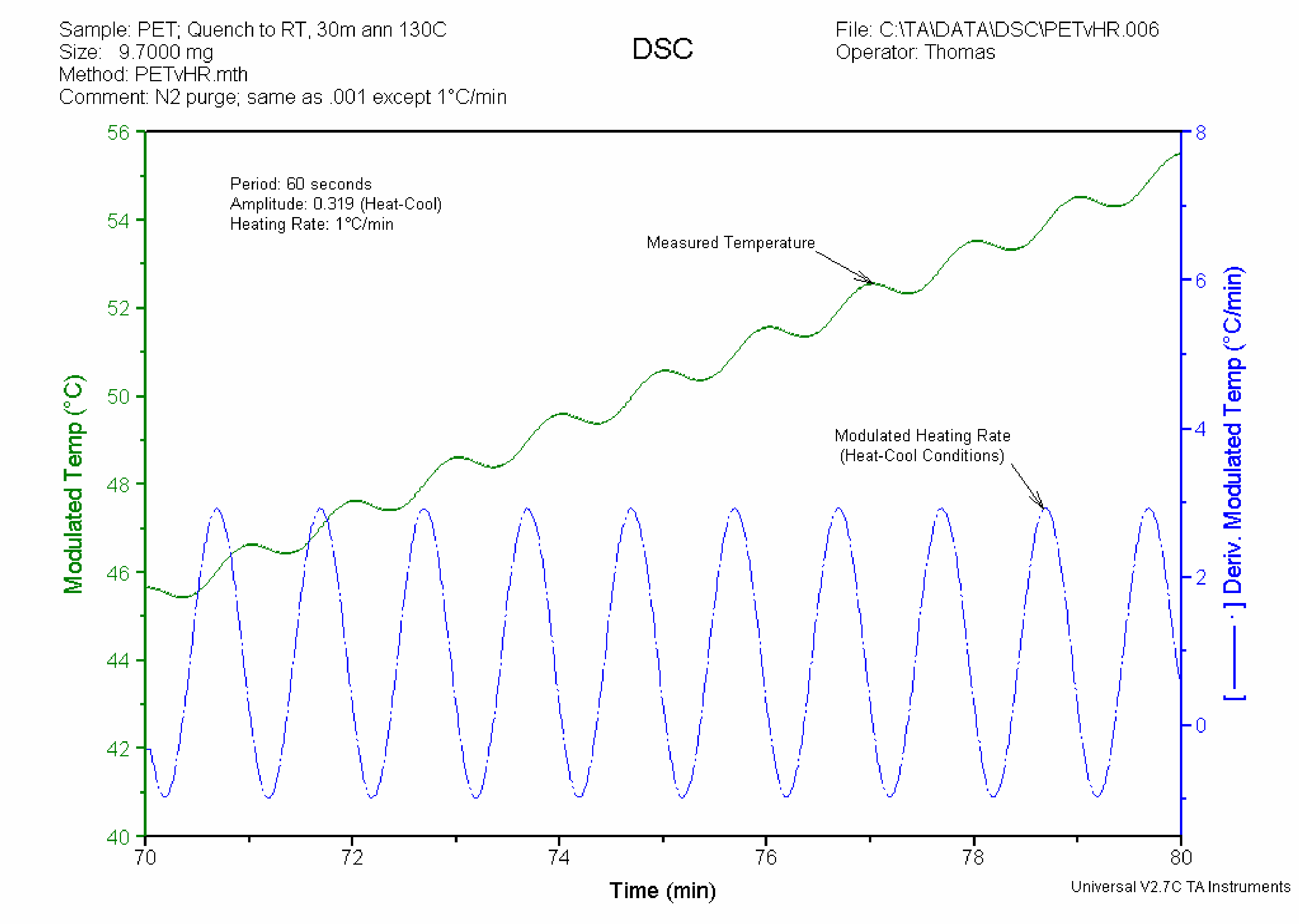
MDSC Temperature Profile – Step-Iso



MDSC Temperature Profile – Heat Only



MDSC Temperature Profile - Conventional

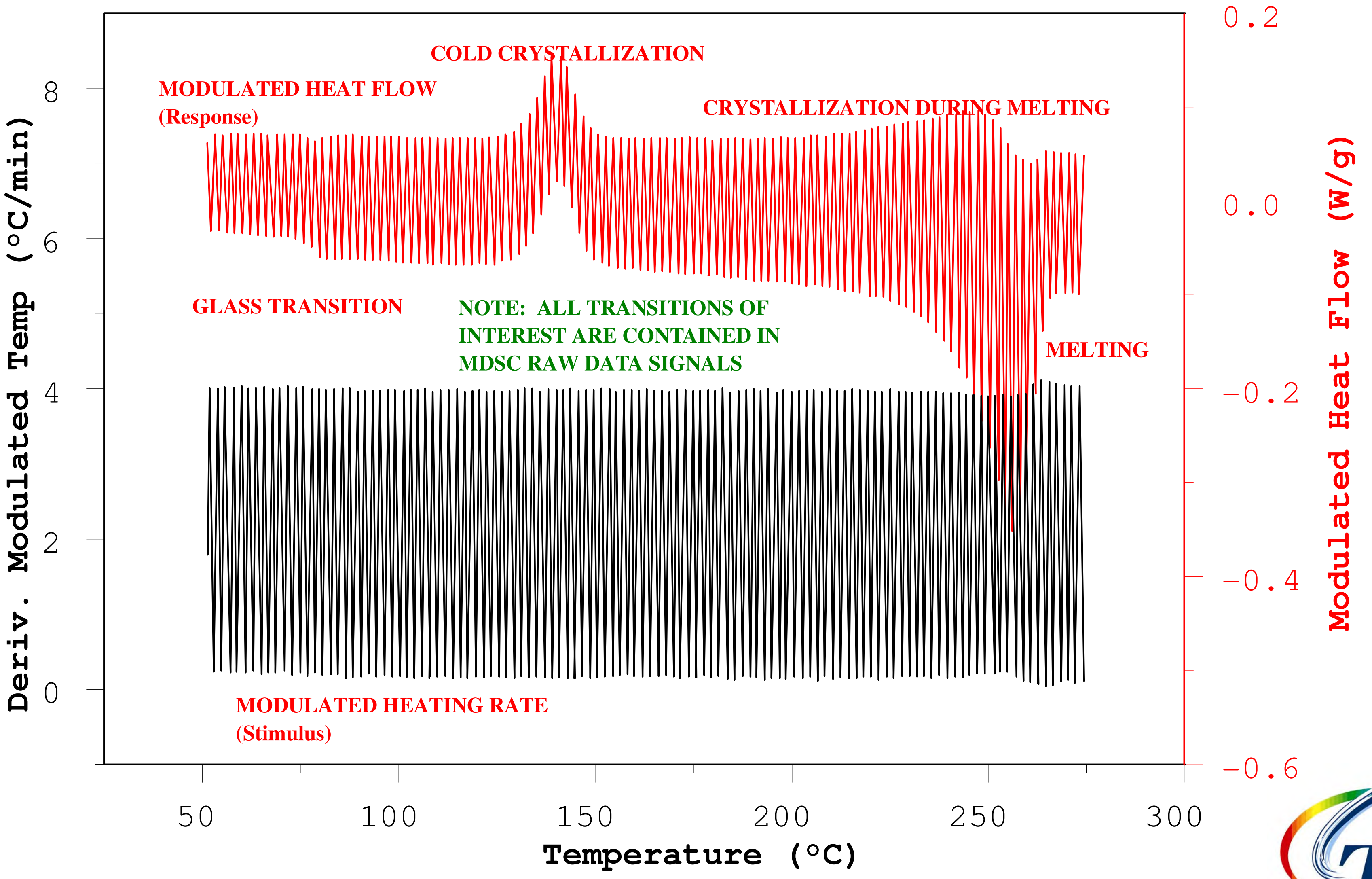


Raw Signals in MDSC

All Modulated DSC Signals are derived from three measured parameters.

- **Time**
- **Modulated Temperature (Stimulus)**
- **Modulated Heat Flow (Response)**

MDSC Raw Signal



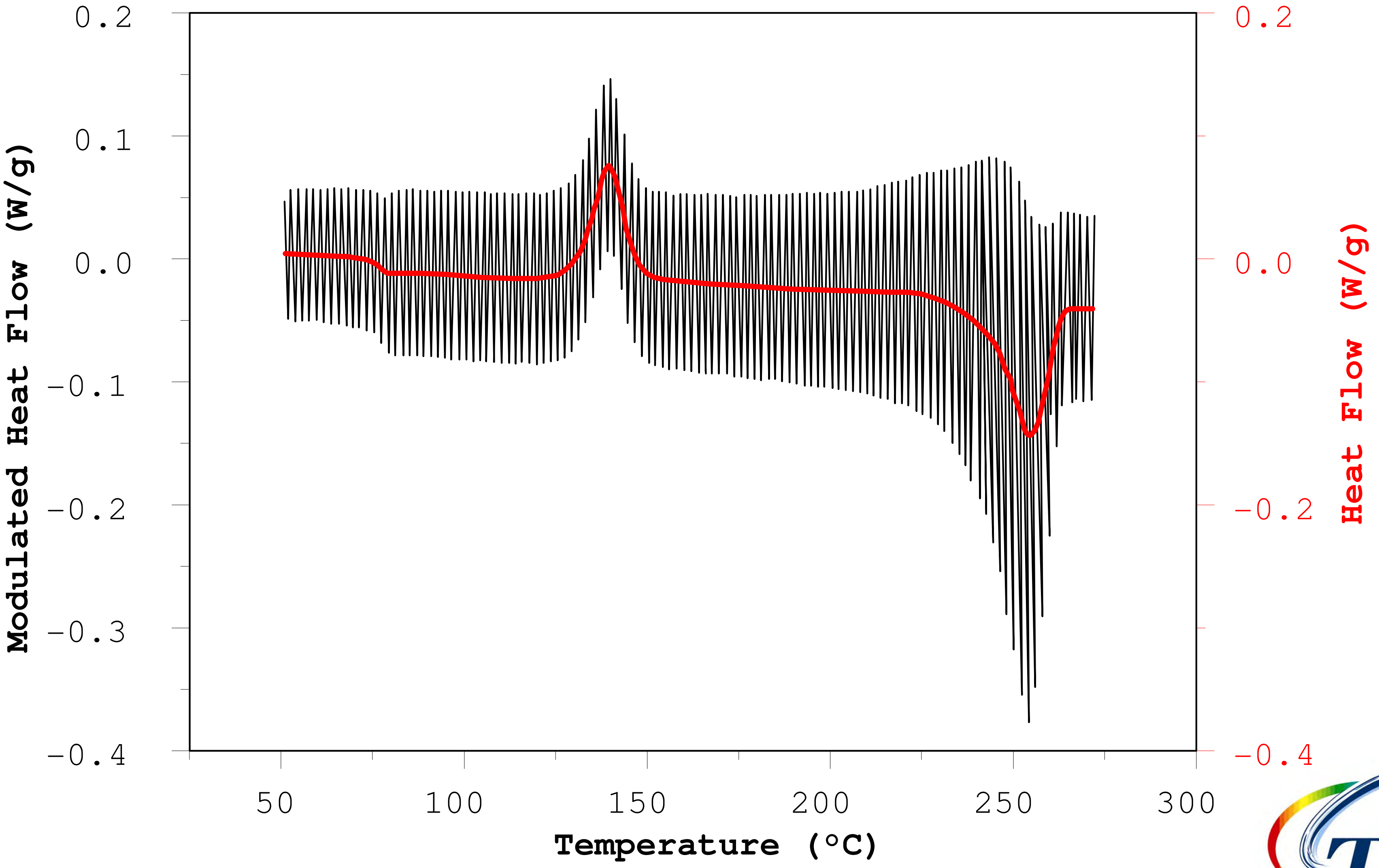
MDSC Signals: Total Heat Flow

The average value of the modulated heat flow signal. This signal is qualitatively and quantitatively equivalent to the heat flow signal from conventional DSC at the same average heating rate.

Definition: The sum of all thermal events in the sample

Calculation: Fourier Transformation analysis of the modulated heat flow signal is used to continuously calculate its average value

Total Heat Flow: Average of Modulated Heat Flow Signal



MDSC Signals: Heat Capacity

$$\boxed{Cp = \frac{A_{MHF}}{A_{MHR}} \text{ x } K}$$

Where:

A_{MHF} = Amplitude of Modulated Heat Flow
A_{MHR} = Amplitude of Modulated Heating Rate
K = Heat Capacity Calibration Factor

Definition: The amount of heat required to raise the temperature of a material 1°C.

Calculation: The basis for making the heat capacity measurement in MDSC can be explained from a series of conventional DSC experiments at different heating rates.

Conventional DSC Cp Measurement

$$Cp = K \times \frac{HF_S - HF_{MT}}{\text{Heat Rate} \times wt}$$

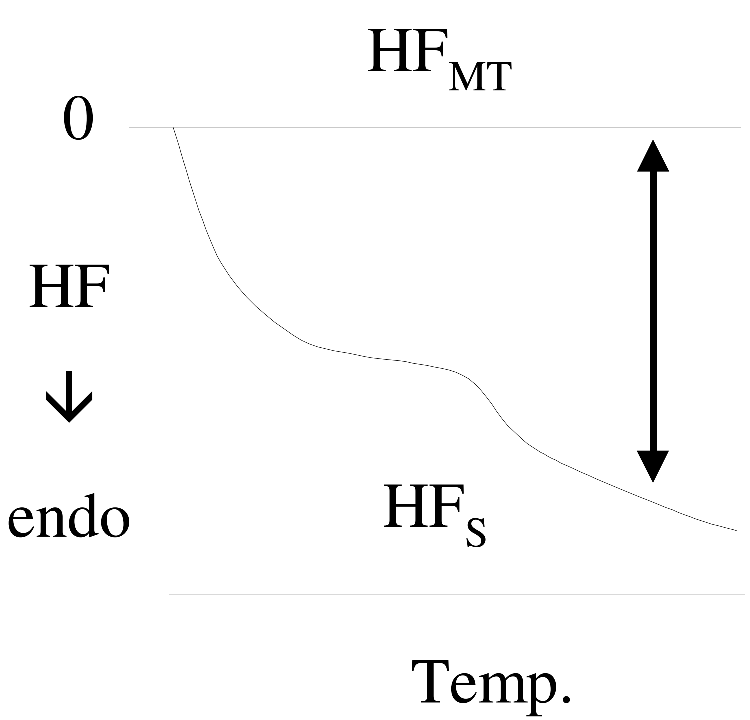
Where:

K = Calibration constant

HF_S = Differential heat flow with sample

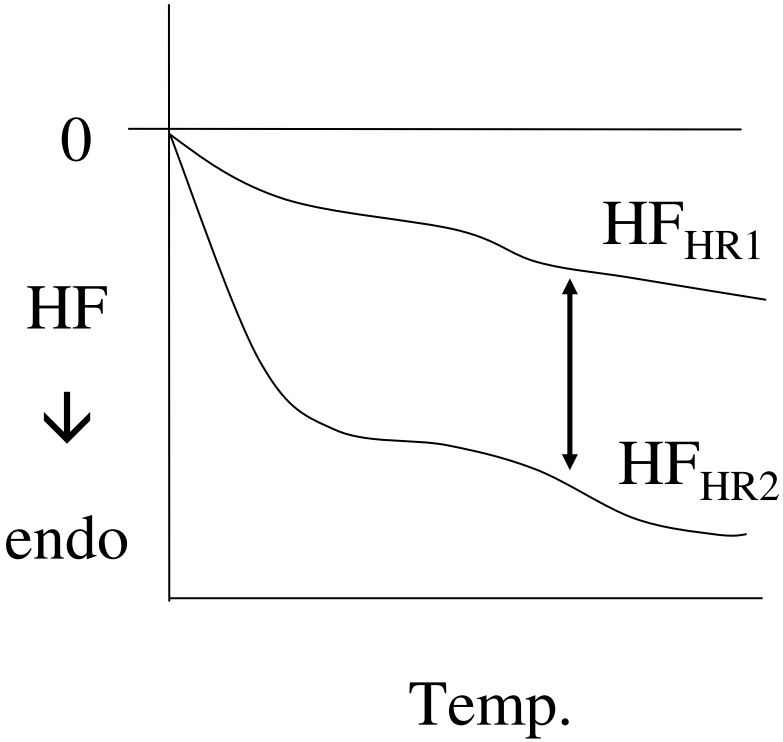
HF_{MT} = Differential heat flow with empty pans

wt = weight of sample



Alternative DSC Cp Measurement

$$Cp = K \times \frac{HF_{HR2} - HF_{HR1}}{(HR_2 - HR_1)\ wt}$$



Where:

K = Calibration constant

HF_{HR1} = Differential heat flow of sample at HR_1

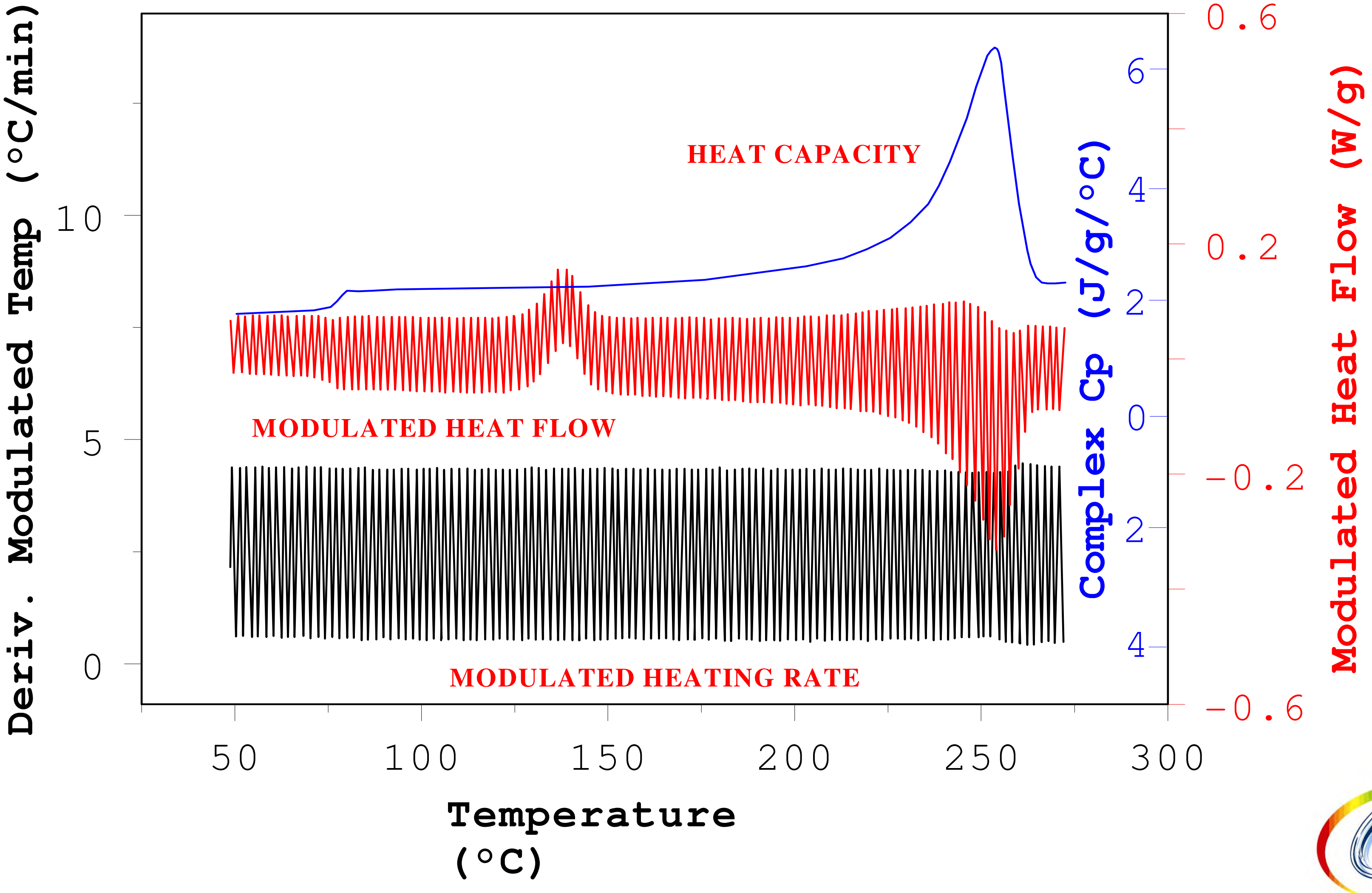
HF_{HR2} = Differential heat flow of sample at HR_2

HR_2 = Heating rate 2

HR_1 = Heating rate 1

wt = weight of sample

Heat Capacity from MDSC Raw Signals



MDSC Signals - Reversing Heat Flow (Heat Capacity Component)

Reversing Heat Flow is the heat capacity component of the total heat flow. It is calculated by converting the measured heat capacity into a heat flow signal using the classical heat flow equation as a theoretical basis.

$$\boxed{\text{Reversing Heat Flow} = -\text{Cp x Avg. Heat Rate}}$$

Basis for Calculation

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

Where :

$\frac{dH}{dt}$ = total heat flow

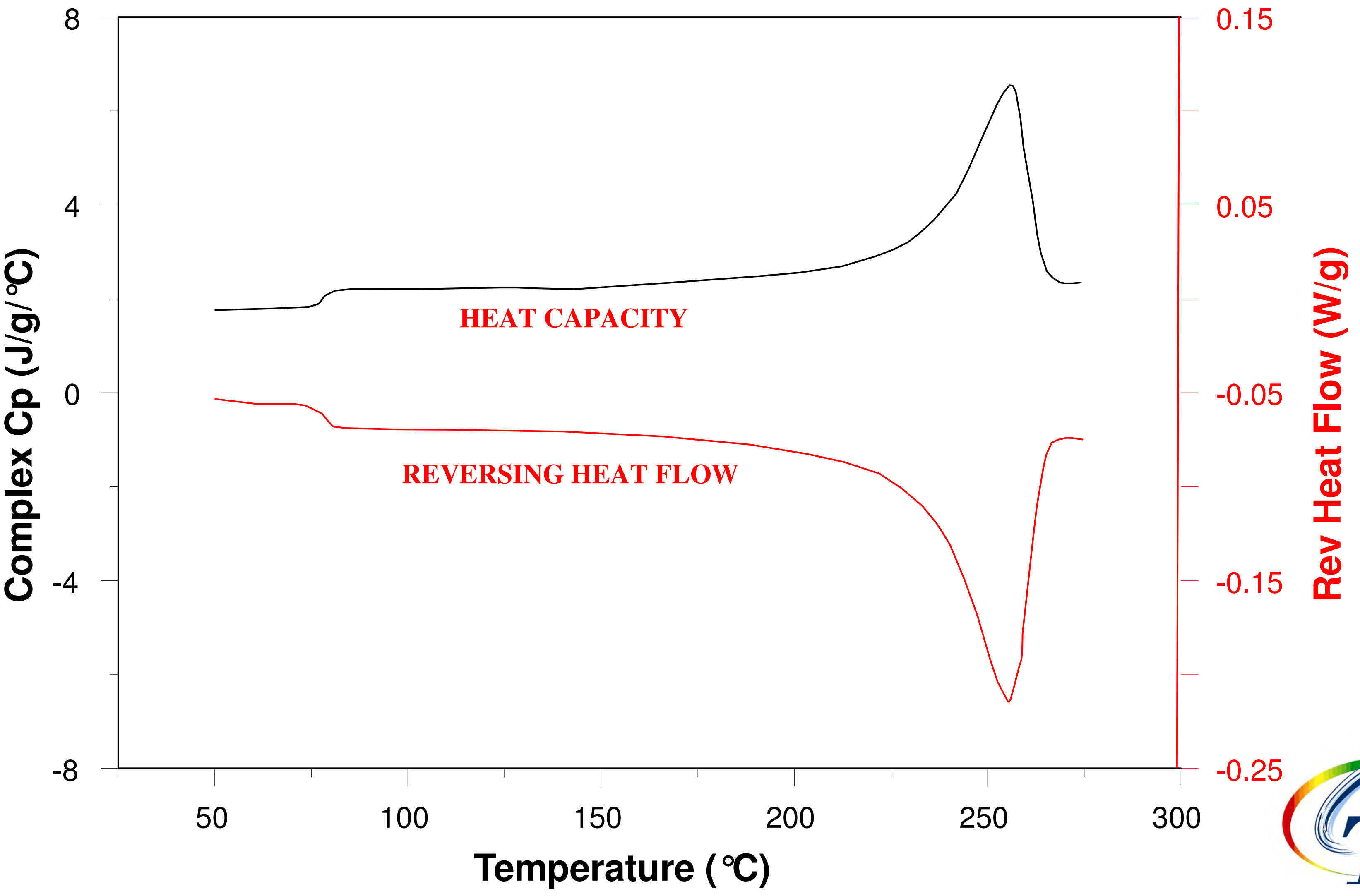
Cp = measured heat capacity

$\frac{dT}{dt}$ = average heating rate

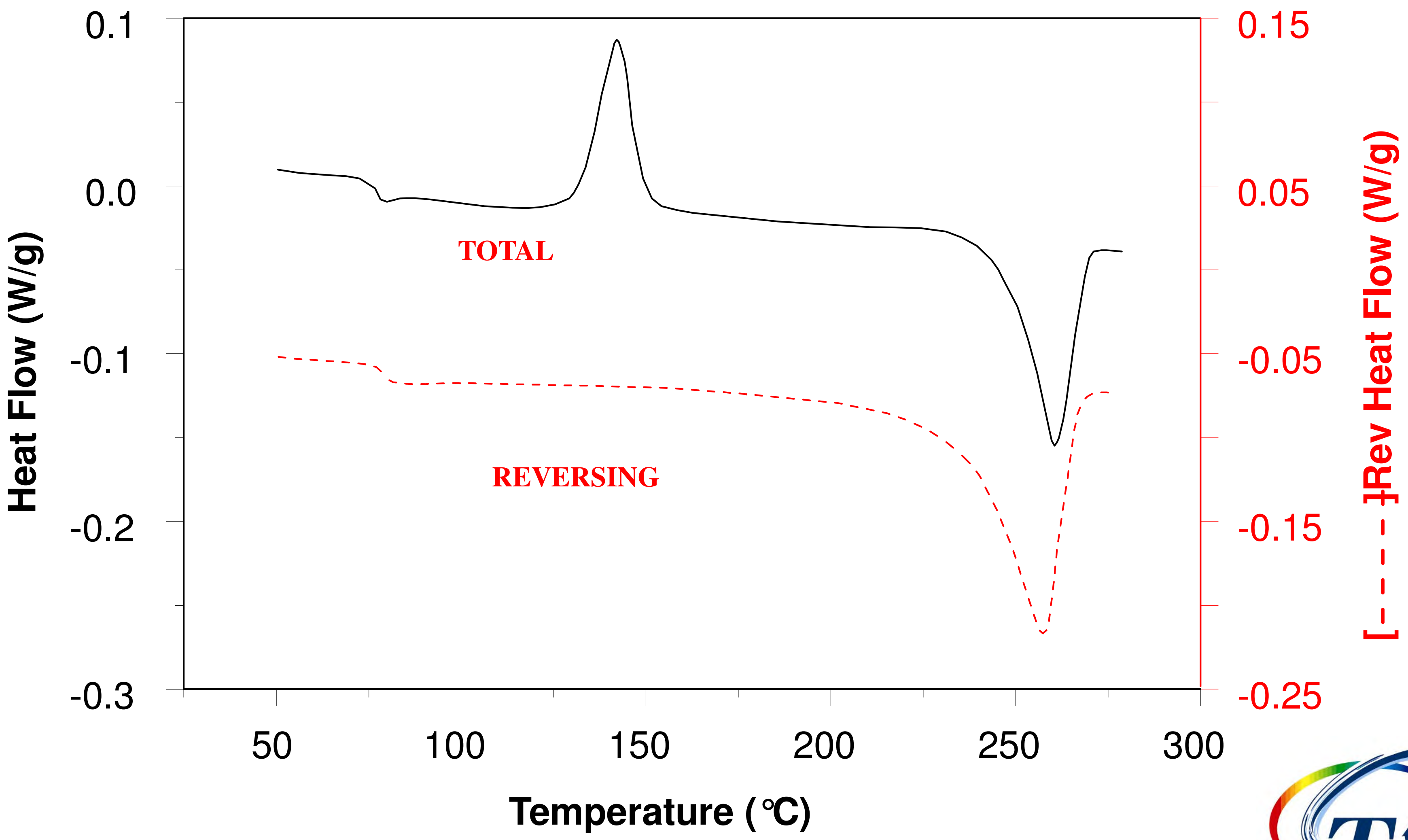
$Cp\frac{dT}{dt}$ = heat capacity component (Reversing)

$f(T,t)$ = heat flow from kinetic process (Nonreversing)

Reversing Heat Flow from MDSC Raw Signals



Quench Cooled PET: Total vs. Reversing Heat Flow



MDSC Signals - Nonreversing Heat Flow (Kinetic Component)

Nonreversing Heat Flow is the kinetic component of the total heat flow. It is calculated by subtracting the heat capacity component from the total heat flow using the classical heat flow equation as a theoretical basis.

Nonreversing = Total – Reversing

Basis for Calculation

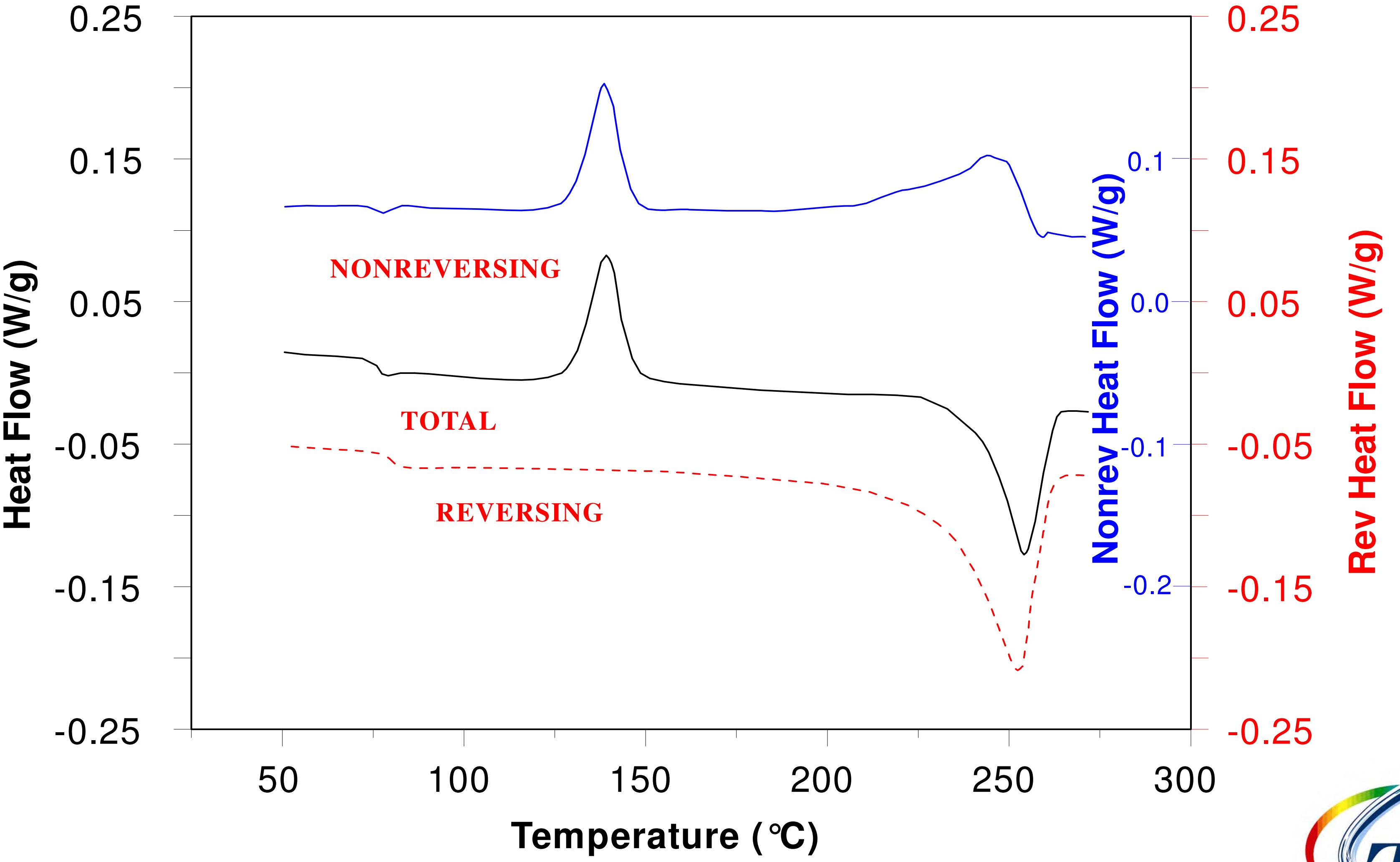
$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T,t)$$

$$\frac{dH}{dt} = \text{total heat flow}$$

$$Cp\frac{dT}{dt} = \text{heat capacity component (reversing)}$$

$$f(T,t) = \text{kinetic component (nonreversing)}$$

Quench-Cooled PET: Deconvoluted Signals



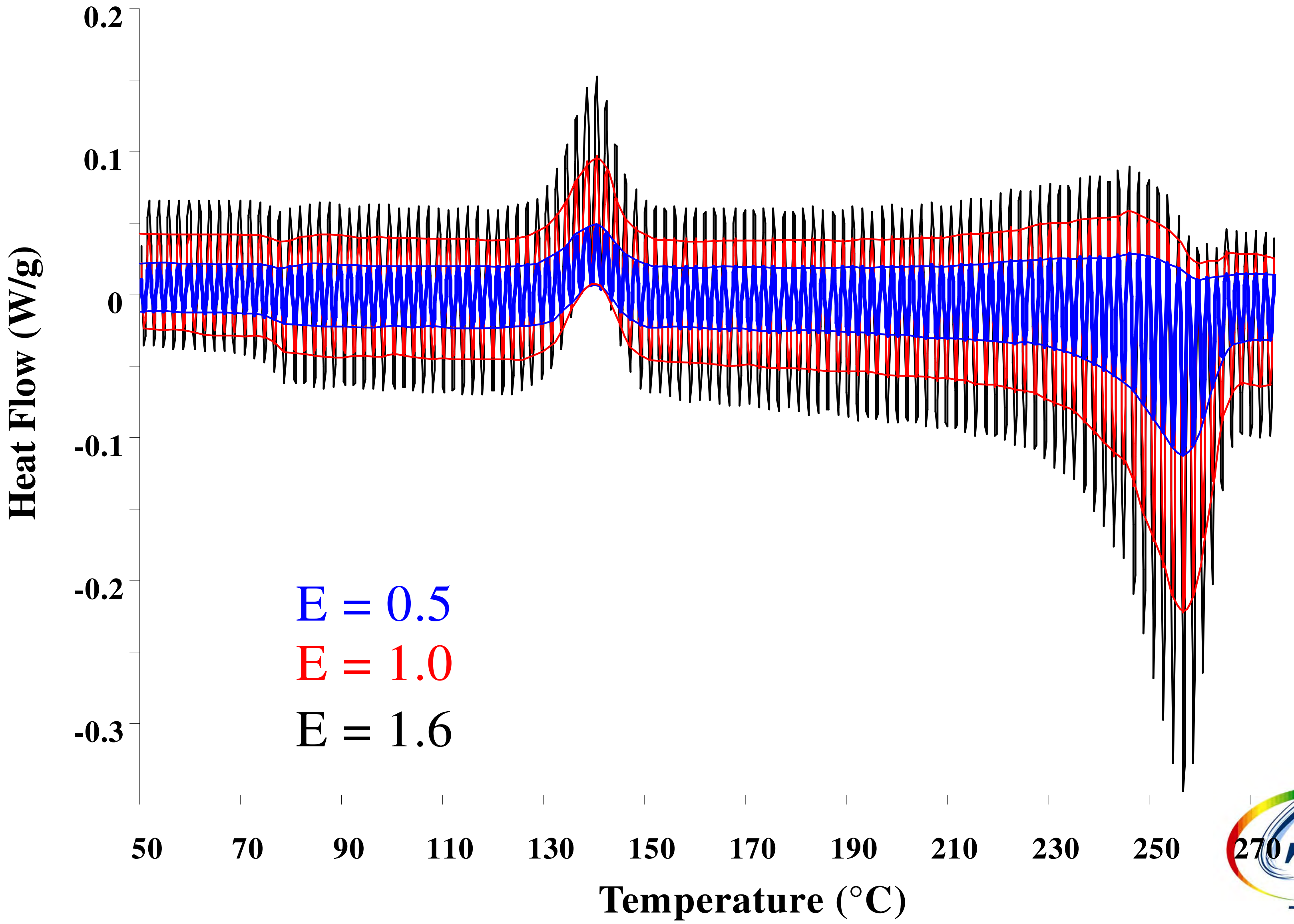
Calibration

Calibration for MDSC

There are three calibration steps necessary to produce accurate and precise MDSC results.

- Baseline Calibration
- Heat Flow Calibration (Cell Constant)
  - Melting temperature provides temperature calibration
- Heat Capacity Calibration

Cell Constant Effect on Modulated Heat Flow



Heat Capacity Constant: K

$$\frac{A^{MHF}}{A^{MHR}} \text{ x } K = Cp$$

The heat capacity calibration constant, K, is a multiplying factor which provides for the quantitative measurement of heat capacity by MDSC.

Measuring K

$$K = \frac{Cp^{\mathrm{Theo.}}}{Cp^{\mathrm{Meas.}}}$$

The heat capacity calibration constant, K, is calculated as the ratio of the theoretical heat capacity of a standard material, to the measured heat capacity of the material.

Calibration - Conclusions

- Nitrogen provides for the greatest stability of the heat flow & heat capacity measurements.
- K is stable to changes in conditions above a 50-second period.
- Periods below 50 seconds may be used.
  - Use thin samples to minimize gradients.
  - Calibrate at the same conditions for the best accuracy.

Analyzing Glass Transitions by MDSC

What is the Glass Transition?

"... reversible change in an amorphous material or in amorphous regions of a partially crystalline material, from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one."

ASTM E 1142

Why is the Tg Important?

Why important?

Region of dramatic & rapid property changes

Thus critical to:

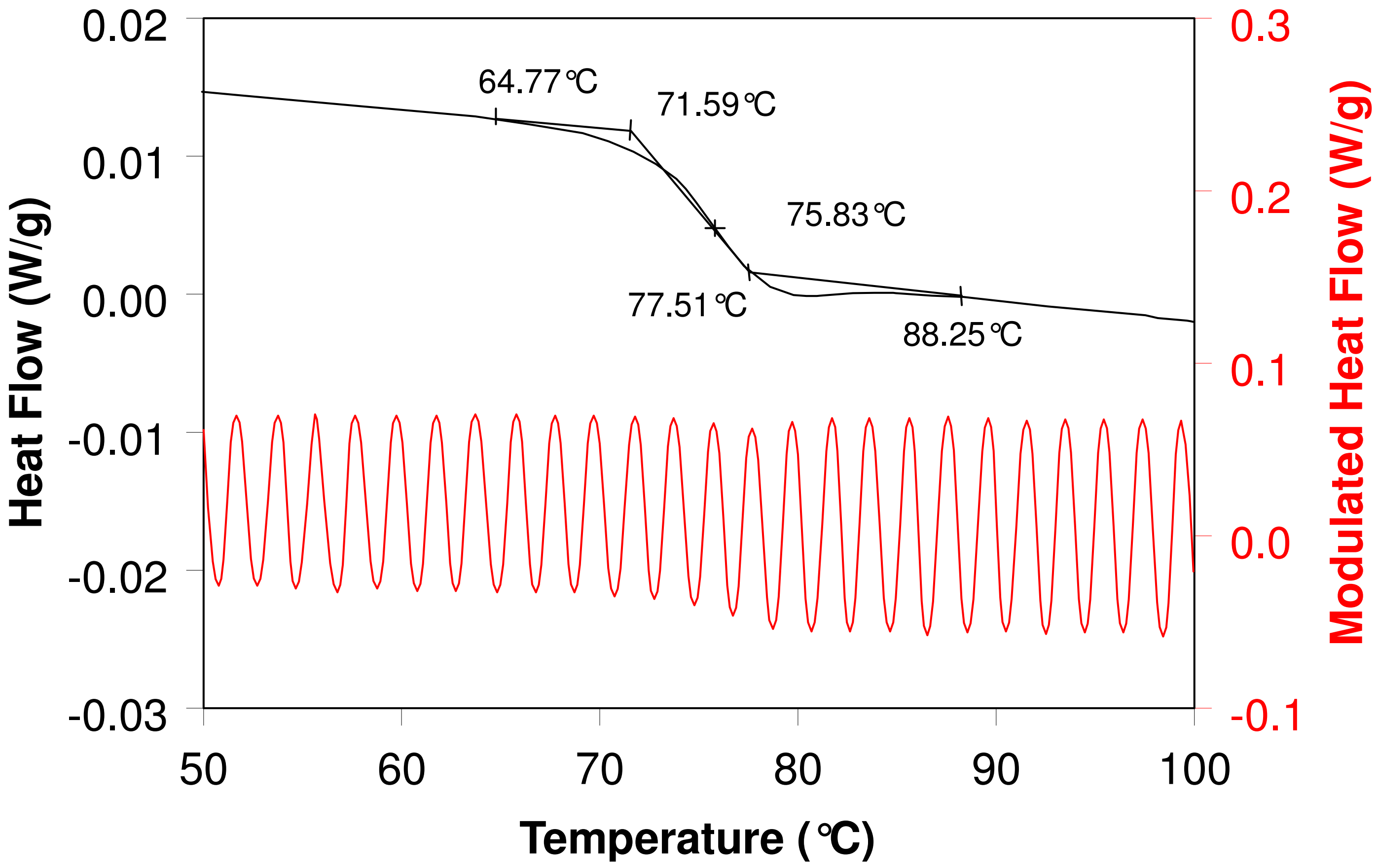
- **Processing**
- **Storage**
- **Use**

Some Properties Affected at Tg

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

Measuring Width of Tg

- **Make sure there are at least 4-6 cycles across the step change in the total heat flow.**



Choosing the Period/Heating Rate Combination

If the transition is 12°C wide, and you wish to use a 60 second period.

$$\frac{12°\mathrm{C}}{6\ \mathrm{cycles}}\ \mathrm{x}\ \frac{1\ \mathrm{cycle}}{60\ \mathrm{sec}}\ \mathrm{x}\ \frac{60\ \mathrm{sec}}{\mathrm{min}} = \frac{2°\mathrm{C}}{\mathrm{min}}$$

If the transition is 3°C wide, and you wish to use a 40 second period.

$$\frac{3°\mathrm{C}}{6\ \mathrm{cycles}}\ \mathrm{x}\ \frac{1\ \mathrm{cycle}}{40\ \mathrm{sec}}\ \mathrm{x}\ \frac{60\ \mathrm{sec}}{\mathrm{min}} = \frac{0.75°\mathrm{C}}{\mathrm{min}}$$

Measuring the Width of Enthalpy Recovery

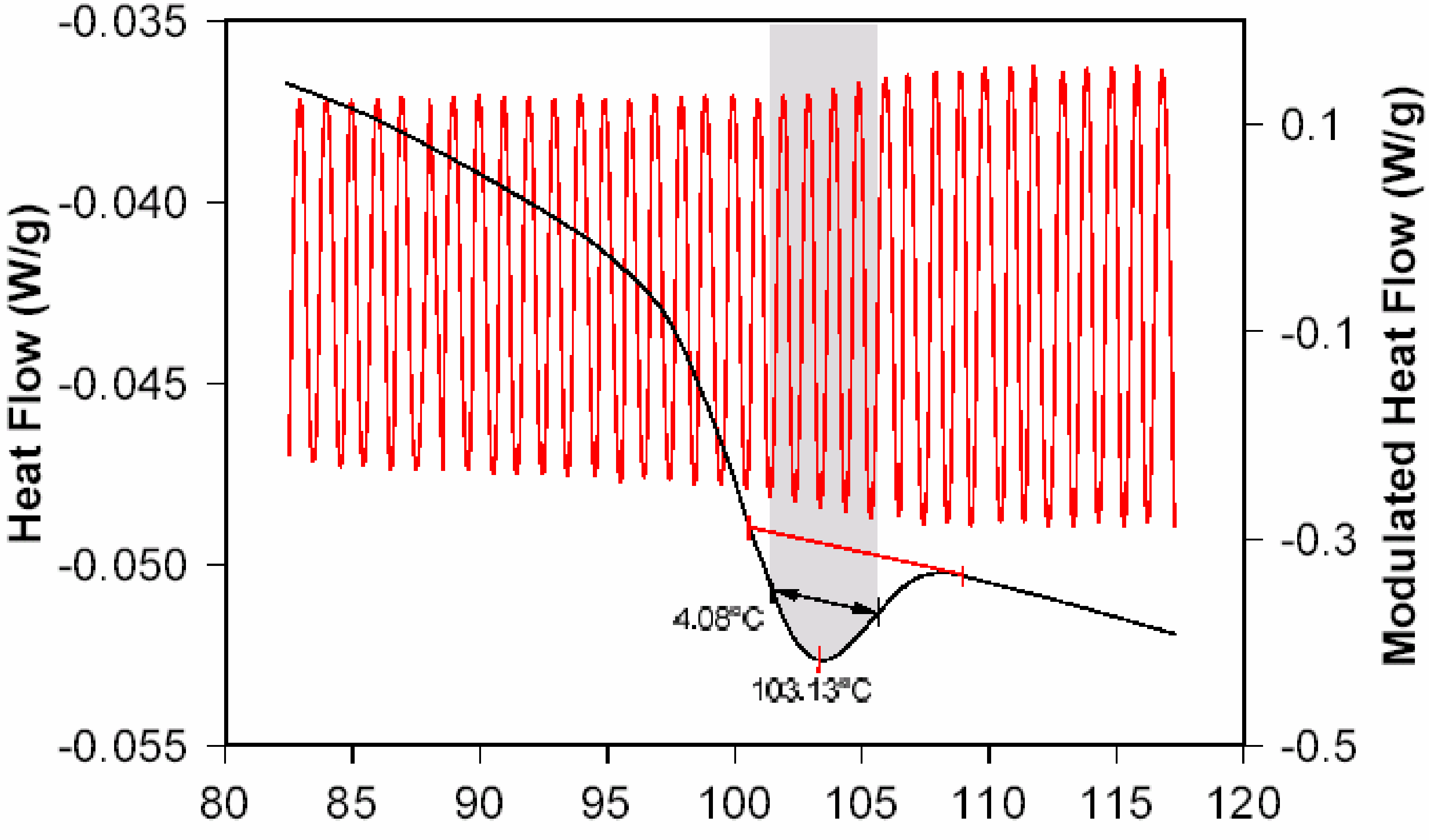
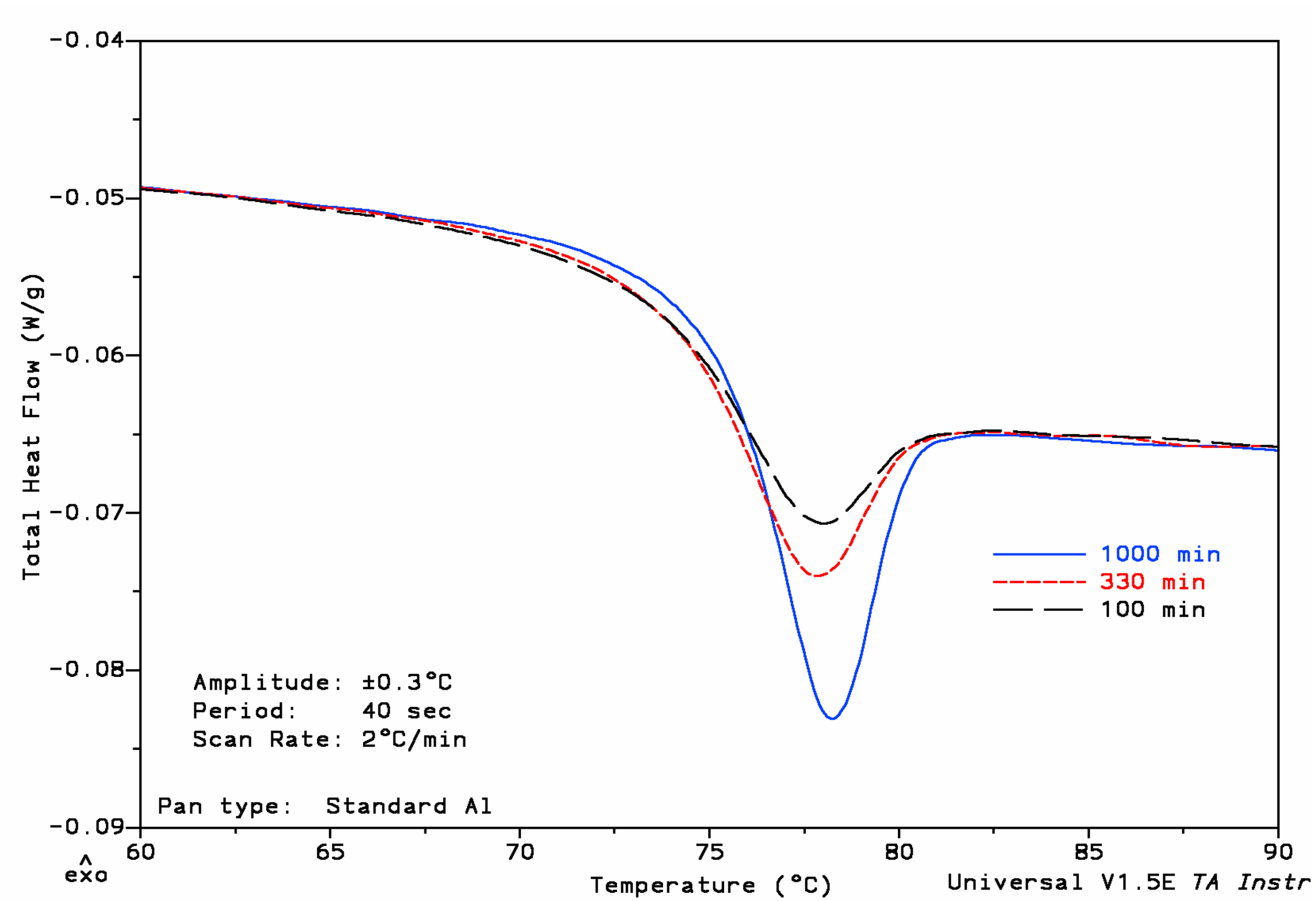
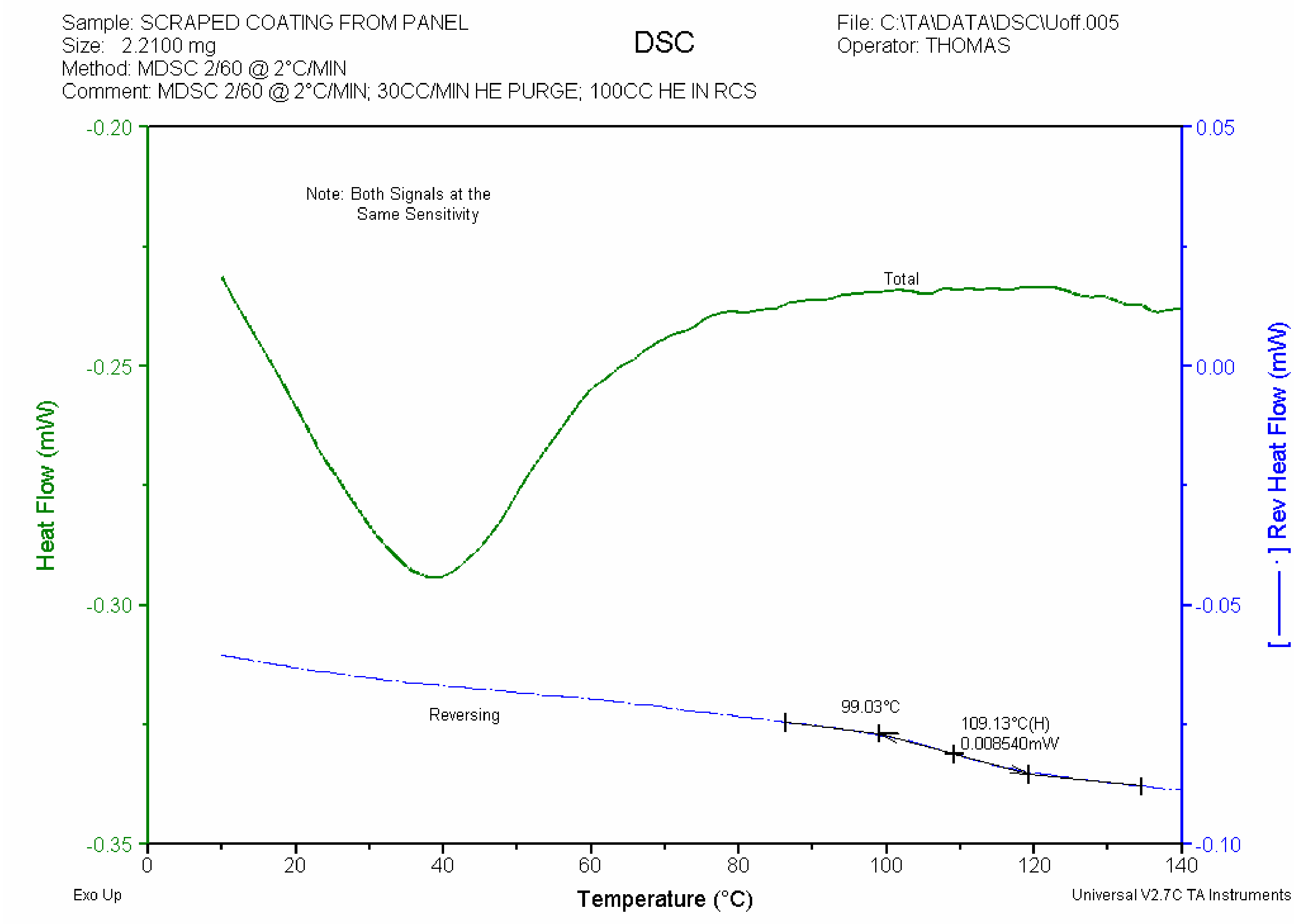


Figure 6

Physical Aging of PET



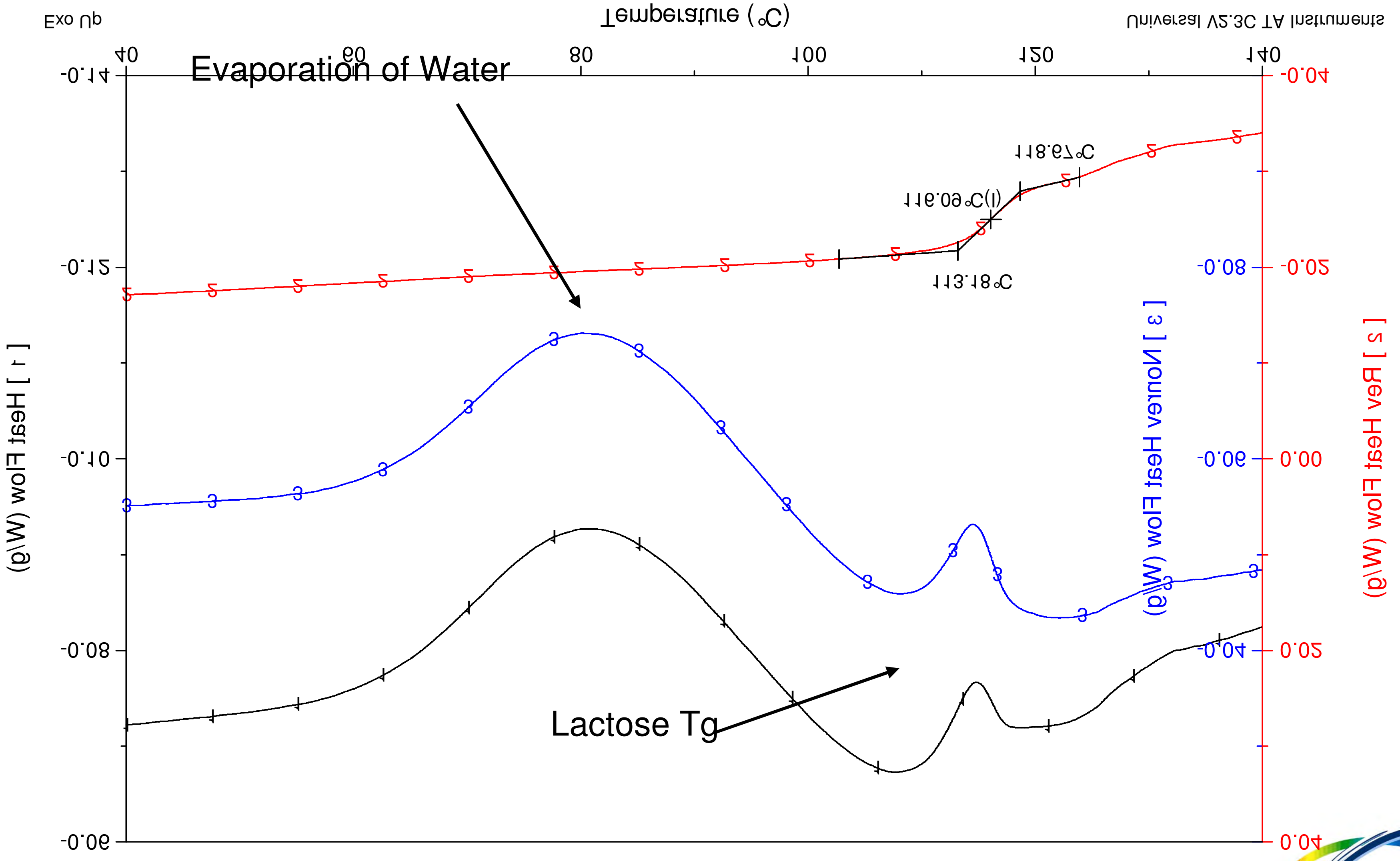
Panel Coating



Sample: SCRAPED COATING FROM PANEL
Size: 2.2100 mg
Method: MDSC 2/60 @ 2°C/MIN
Comment: MDSC 2/60 @ 2°C/MIN; 30CC/MIN HE PURGE; 100CC HE IN RCS

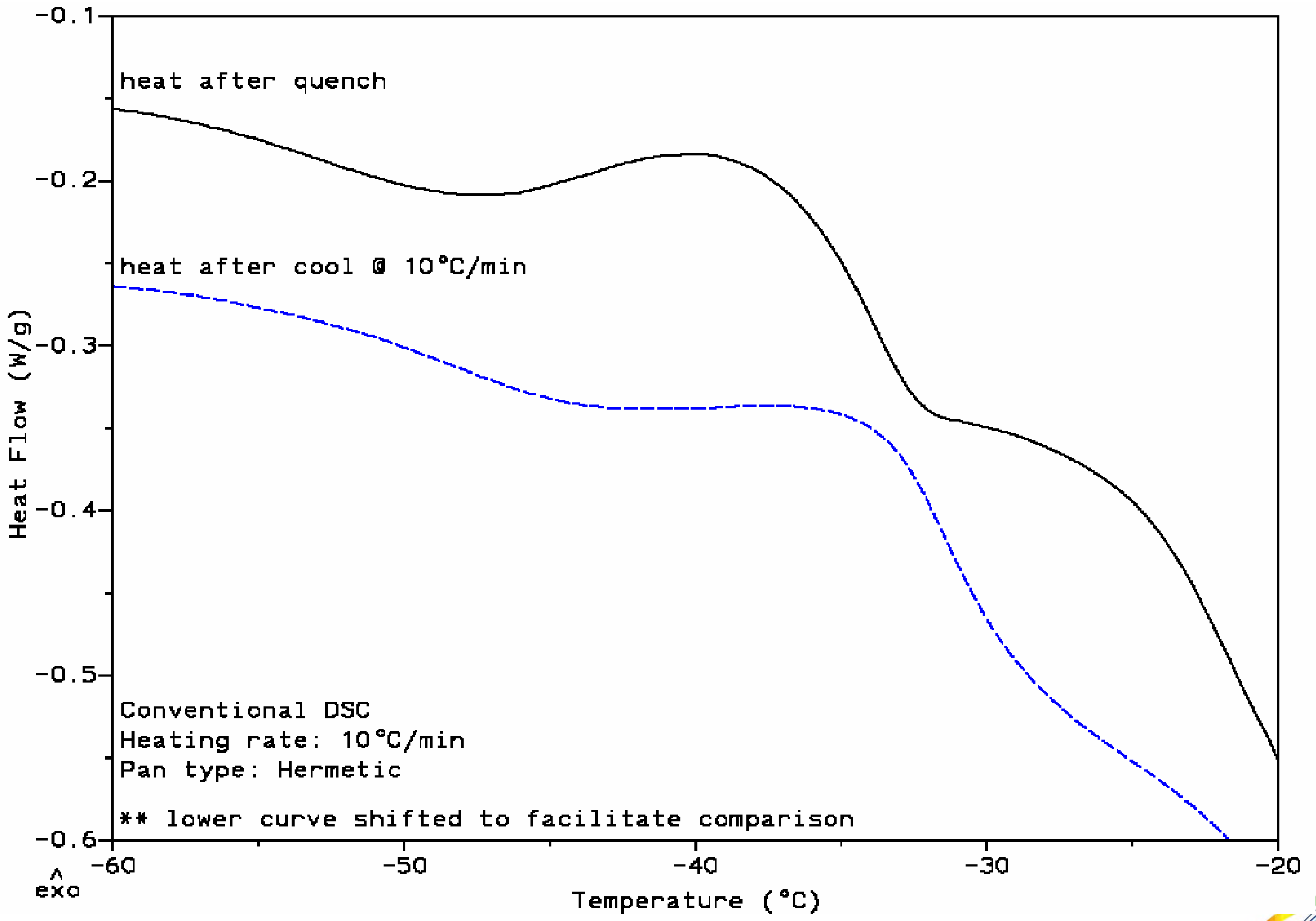
File: C:\TA\DATA\DSC\Uoff.005
Operator: THOMAS

Spray-Dried Lactose


Evaporation of Water

Lactose Tg

Standard DSC of Sucrose/Water (40% w/w)



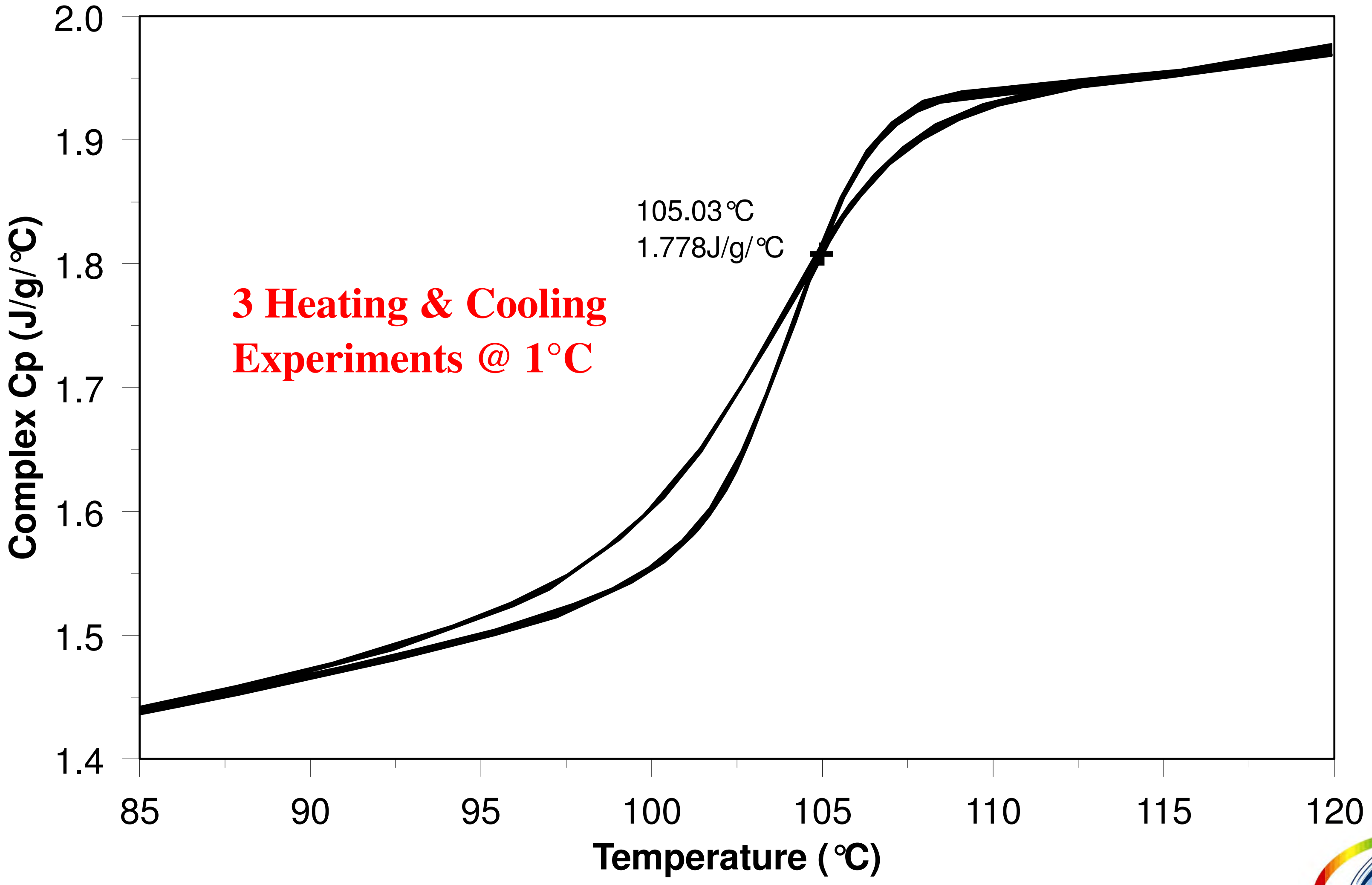
Special Operating Conditions

Special Operating Conditions:
Stepwise Quasi-Isothermal MDSC

Modulated DSC provides the unique ability to measure heat capacity under quasi-isothermal conditions, i.e., isothermal with the exception of the small temperature modulation.

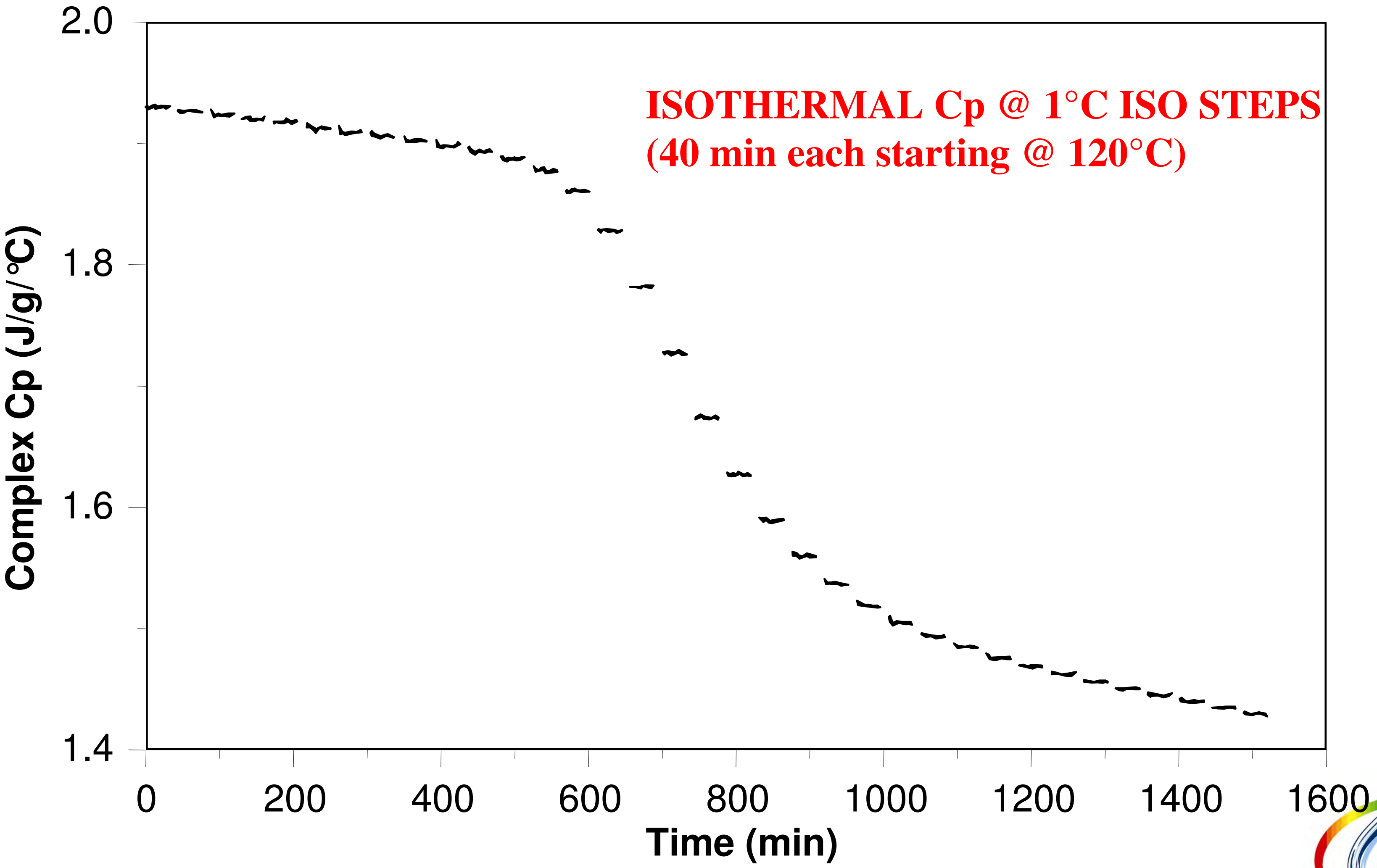
Stepwise quasi-isothermal MDSC provides for the ultimate in resolution in that the underlying heating rate is essentially zero. In addition, time-dependent effects in the measured Cp can be eliminated, allowing for the measurement of the true, temperature-dependent heat capacity across a transition.

Hysteresis (Time-dependence) at the Tg



3 Heating & Cooling Experiments @ 1°C

Quasi-Isothermal Measurement



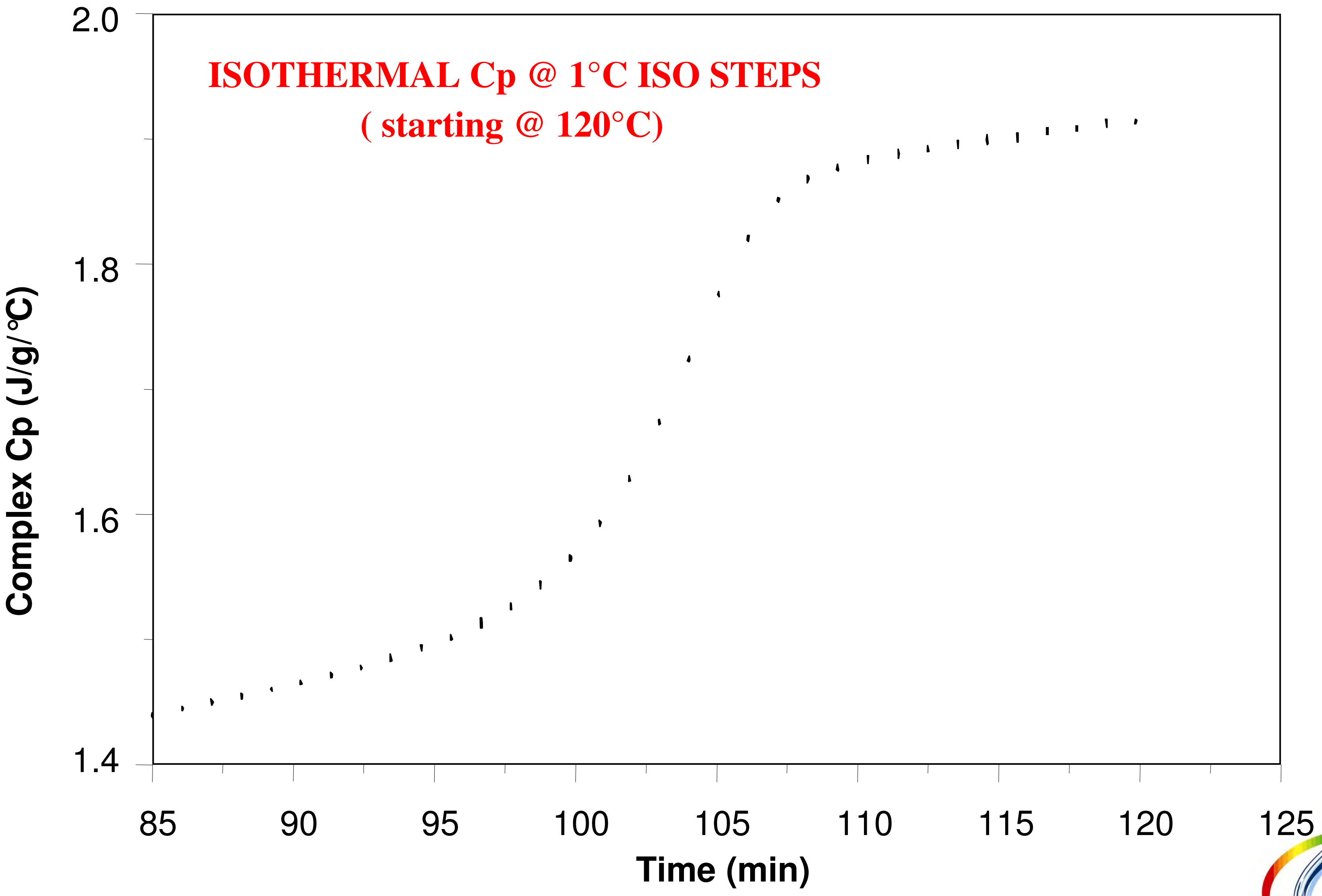
Constructing the Quasi-Isothermal Measurement

1) Equilibrate @ 100°C
2) Data Storage OFF
3) Modulate ±0.5°C every 80 seconds
4) Isothermal for 10 minutes
5) Data Storage ON
6) Isothermal for 5 minutes
7) Data Storage OFF
8) Increment (-)1°C
9) Repeat Segment 4 <u>30</u> times

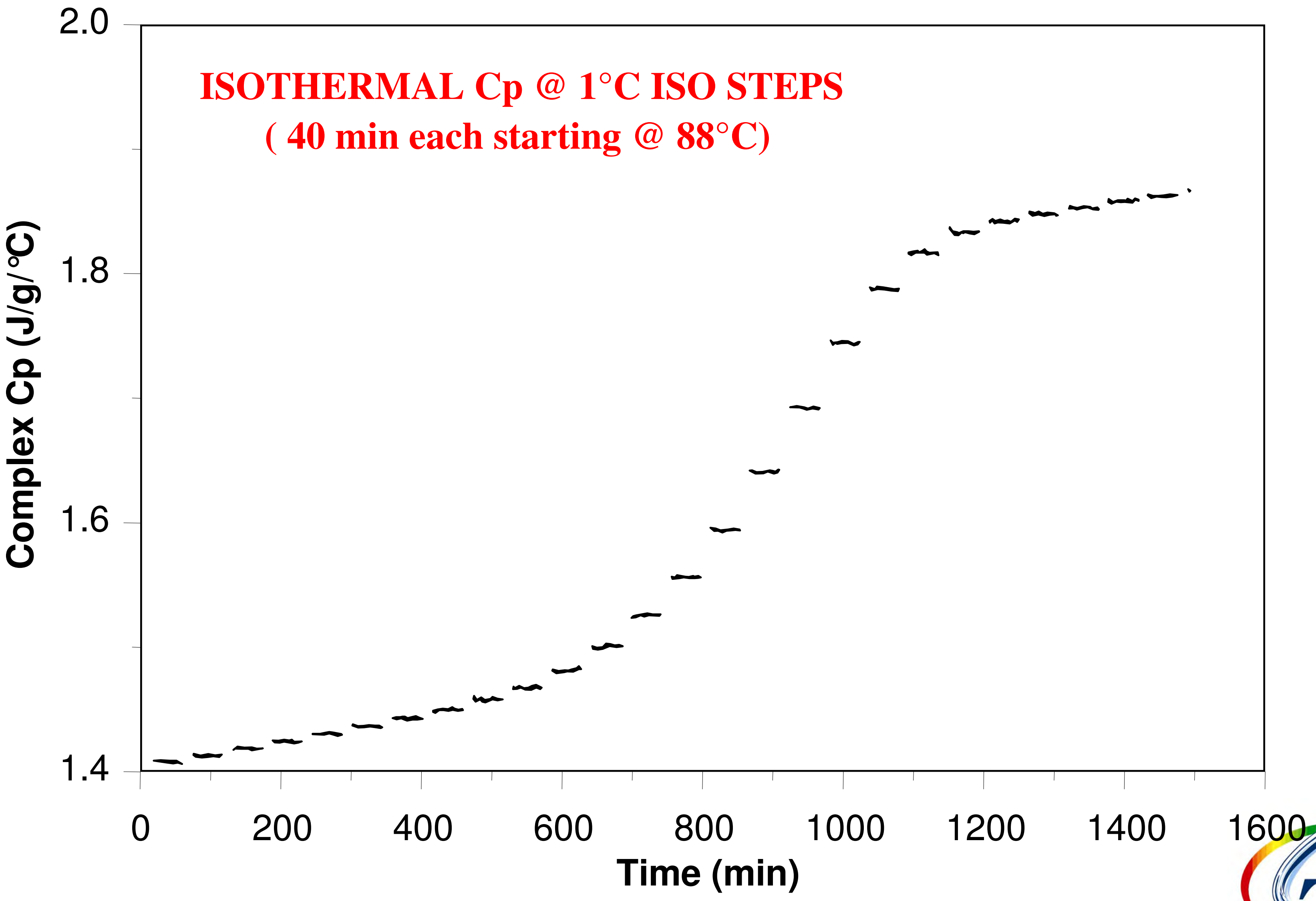
or

9) Repeat Segment 4 until 130°C

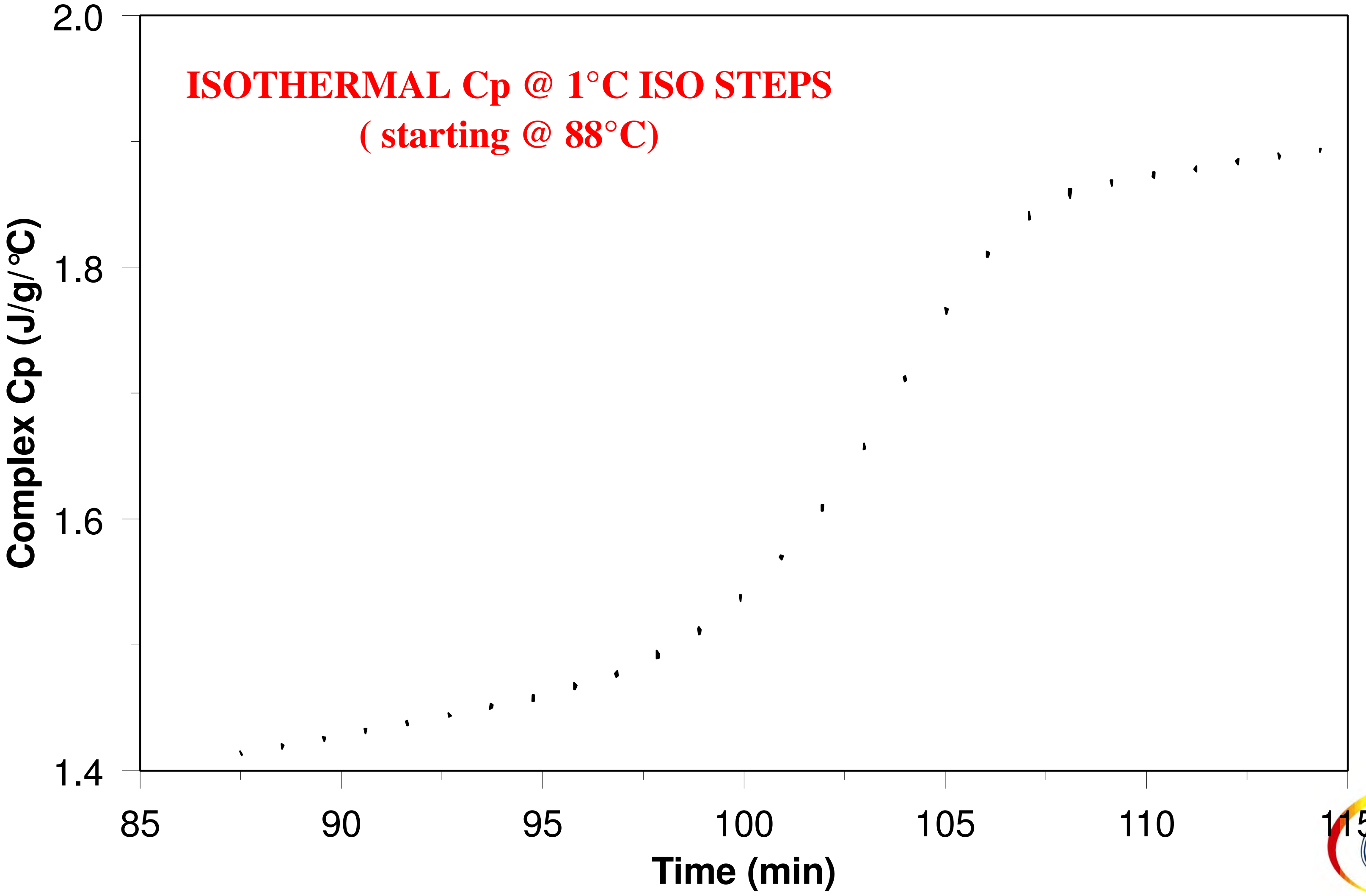
Quasi-Isothermal as a Function of Temperature (stepping down)



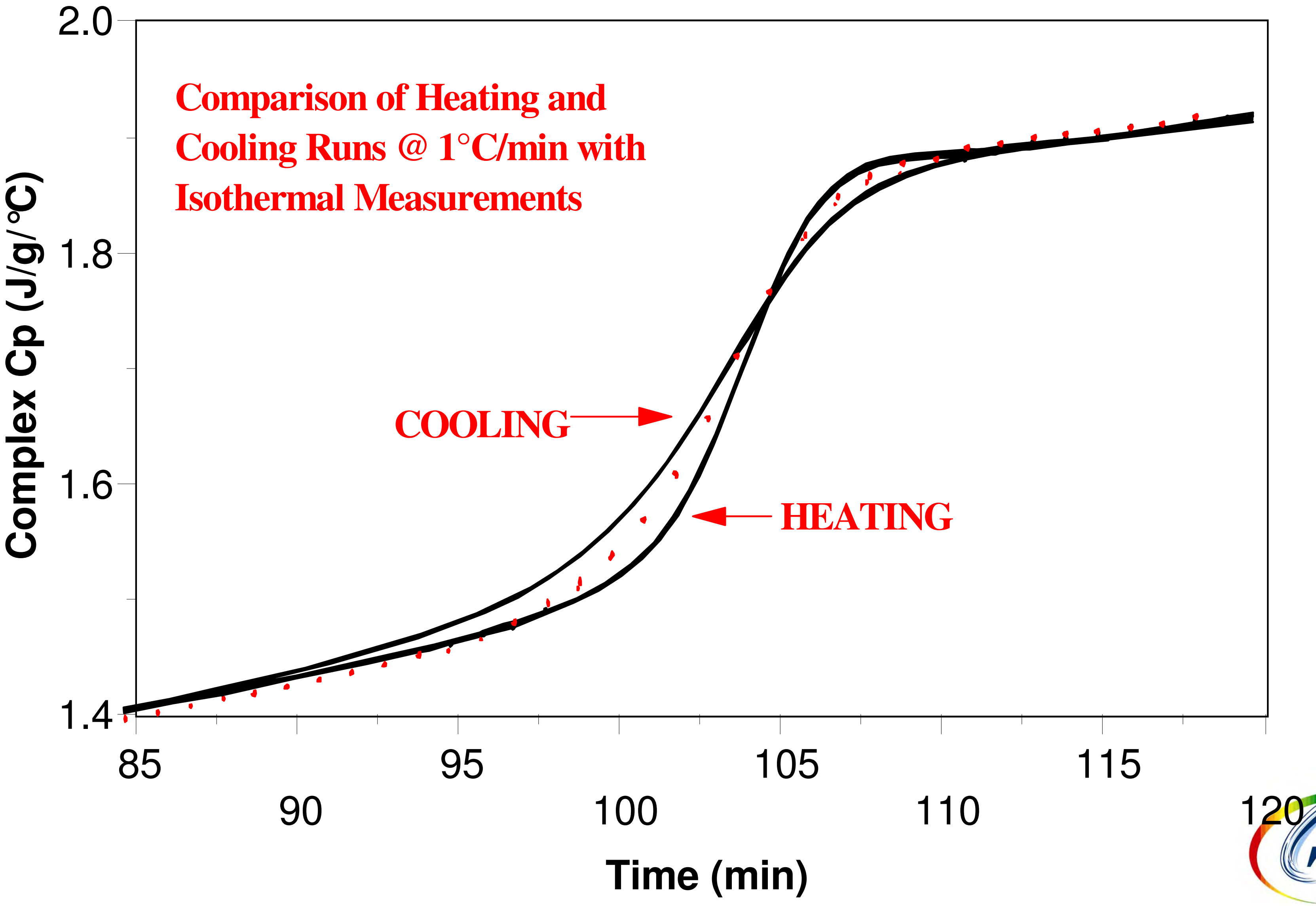
Quasi-Isothermal (stepping up)



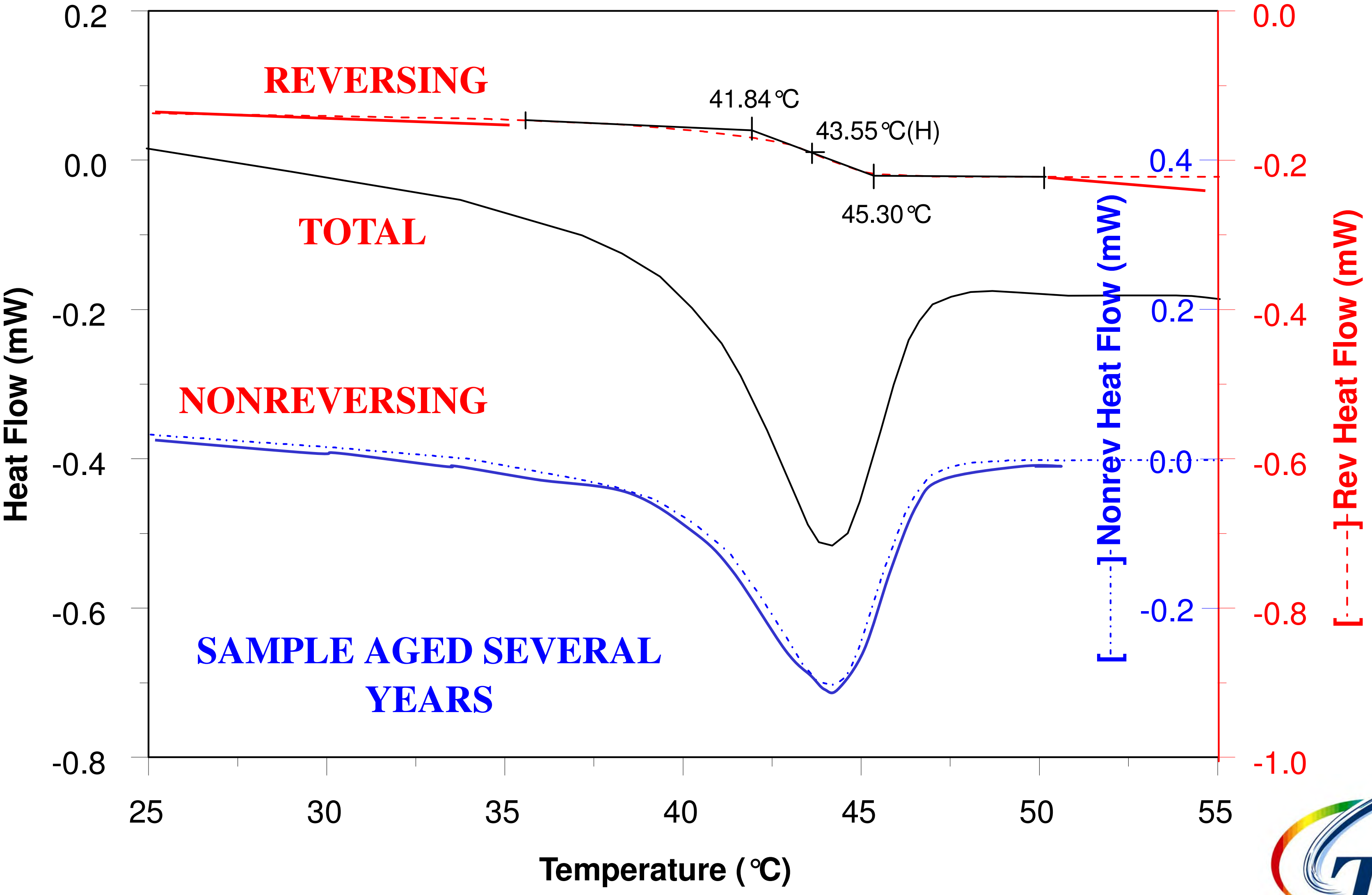
Quasi-Isothermal as a Function of Temperature (stepping up)



Comparison of Heating, Cooling & Quasi-Isothermal Measurements



Aged Sample


REVERSING
TOTAL
NONREVERSING
SAMPLE AGED SEVERAL YEARS
41.84℃
43.55℃(H)
45.30℃
Heat Flow (mW)
0.2
0.0
-0.2
-0.4
-0.6
-0.8
Temperature (℃)
25
30
35
40
45
50
55
Nonrev Heat Flow (mW)
0.4
0.2
0.0
-0.2
Rev Heat Flow (mW)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0

Characterization of Polymer Melting and Crystallization by MDSC®

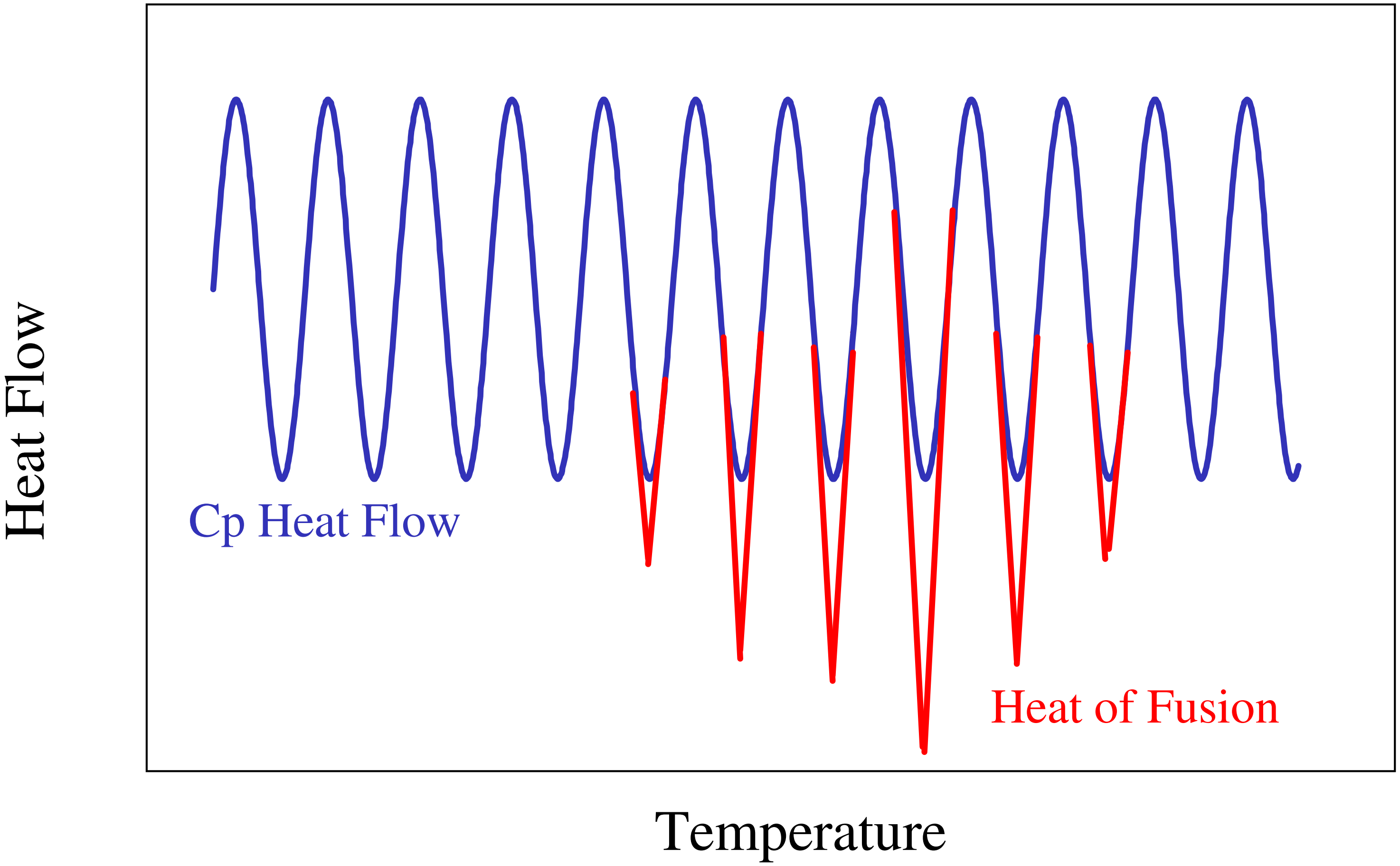
Background

1. What is being measured during melting?
   Total Heat Flow; like DSC, the Total signal from MDSC® is the average value of all heat flows and is qualitatively and quantitatively equivalent to DSC heat flow at the same average heating rate the Total signal is unaffected by the choice of MDSC® experimental conditions

   Reversing Heat Flow or Heat Capacity Component; this signal is calculated from the amplitude of the modulated heat flow which has at least two components in the melting region, heat capacity and latent heat of fusion
   [Figures 1 and 2]

Melting Region

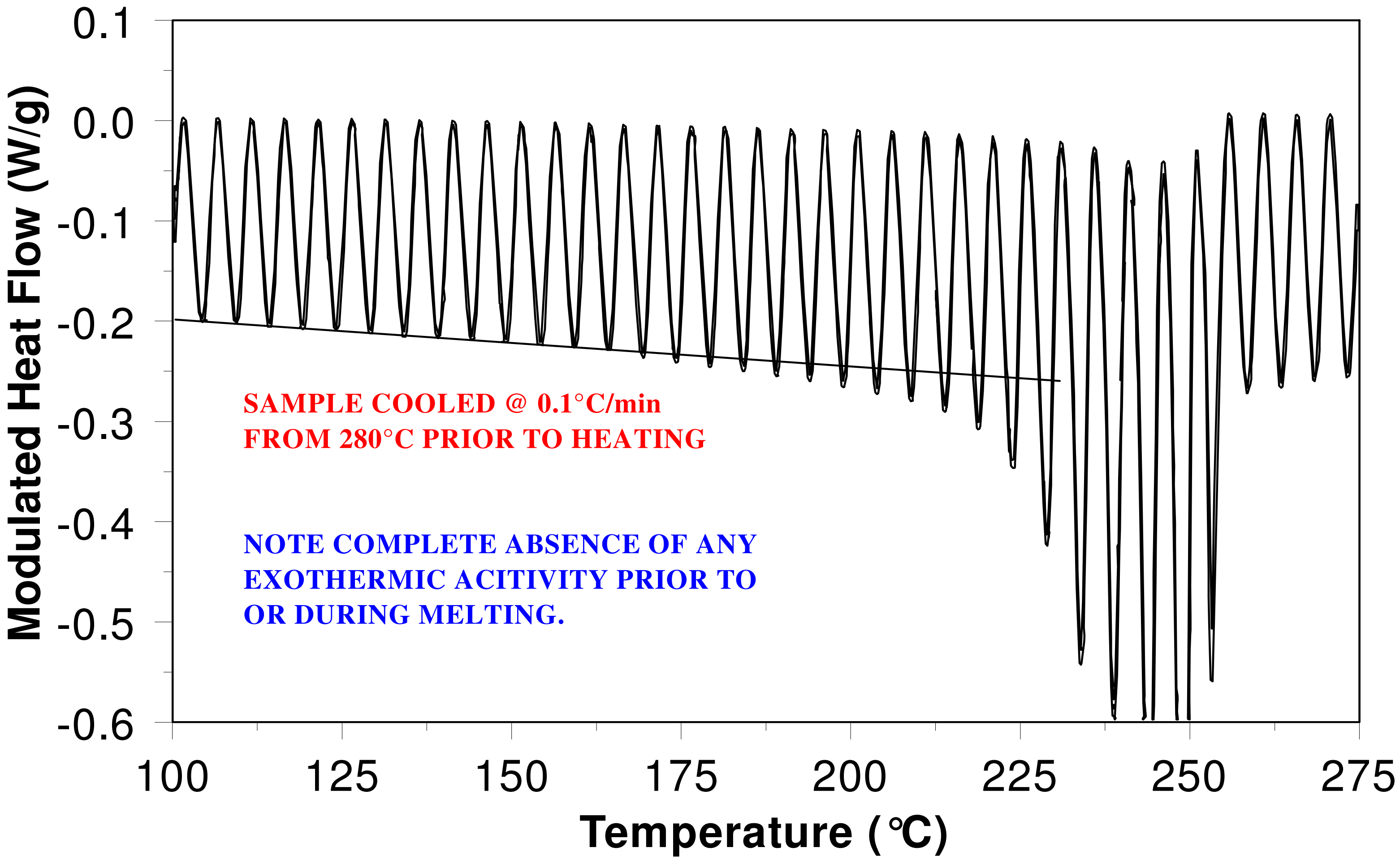
Figure 1



In the melting region, there are two processes which require energy: heat capacity & heat of fusion.

Crystalline PET Melt

Figure 2



SAMPLE COOLED @ 0.1°C/min
FROM 280°C PRIOR TO HEATING

NOTE COMPLETE ABSENCE OF ANY
EXOTHERMIC ACITIVITY PRIOR TO
OR DURING MELTING.

The peaks crossing below the superimposed line represent the heat of fusion of the material.

Quantification of Signals

Nonreversing Heat Flow; there is no independent measurement of this signal. It is calculated by subtracting the Reversing signal from the Total signal. This is important in the melting region because the Total signal is quantitative and independent of modulated conditions, therefore any error (plus or minus) in the Reversing signal will also occur in the Nonreversing signal but opposite in Sign.

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

$$\text{Total} = \text{Reversing} + \text{Nonreversing}$$

$$\text{Nonreversing} = \text{Total} - \text{Reversing}$$

Since the Total signal is quantitative and the Nonreversing signal is simply the difference between the Total and Reversing signals, the sum of the Reversing and Nonreversing signals (Initial Crystallinity) must also be quantitative.

Selecting Optimum Experimental Conditions for Analysis of the Melting Transition

Selecting Experimental Conditions

Modulation Period

- The period must be slow enough for the sample to follow the temperature modulation.
- DSC 2900 Series: 60-second periods for samples up to 15mg.
- Q Series: 30-second periods for samples up to 15mg.

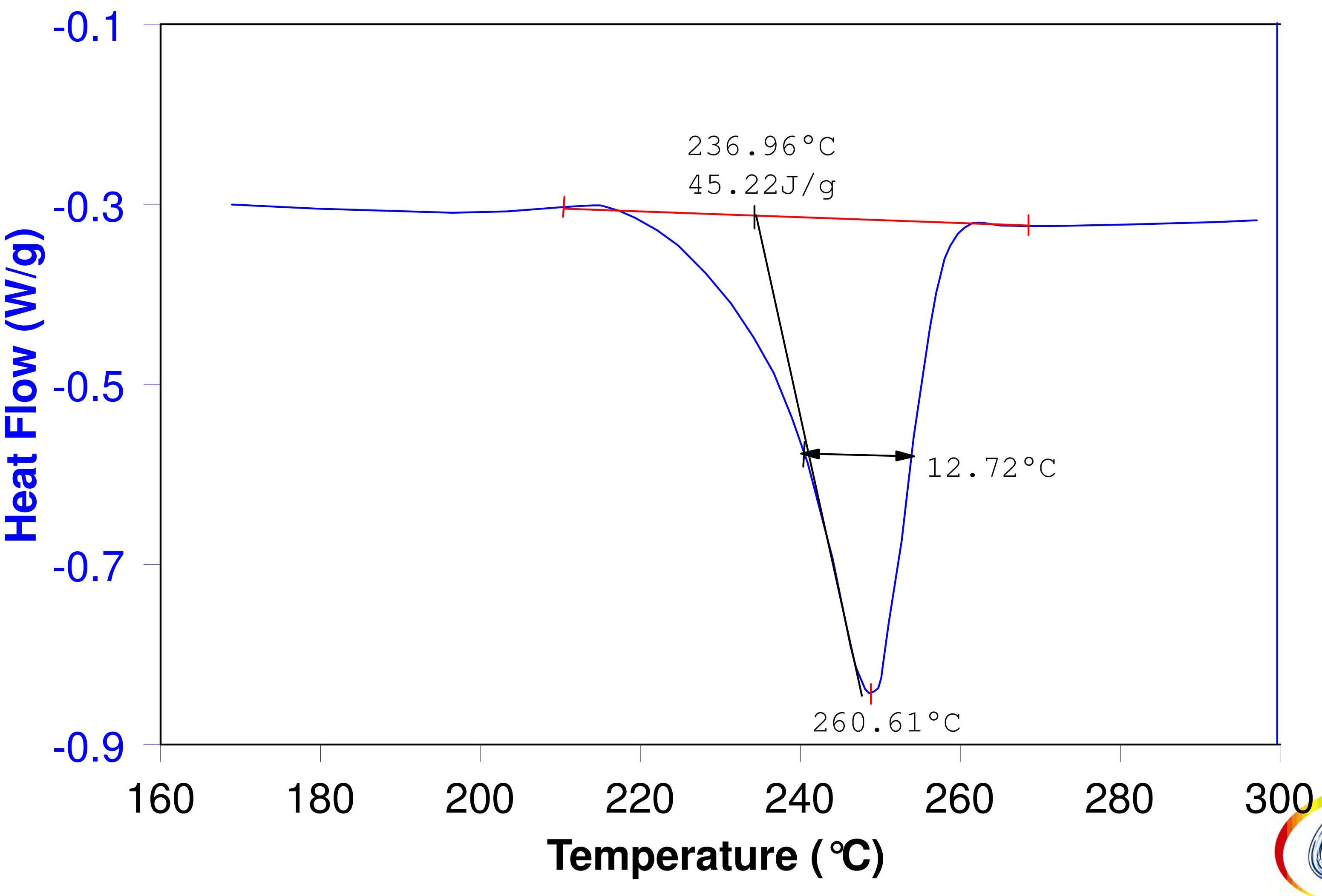
Heating Rate

- In order to property separate the Total heat flow into its components, it is necessary to have a minimum of 4-5 cycles over the critical region of the Transition. For melting, this region is at half-height of the melting peak [Figures 6 - 7].

Choosing the Underlying Heating Rate

Figure 6

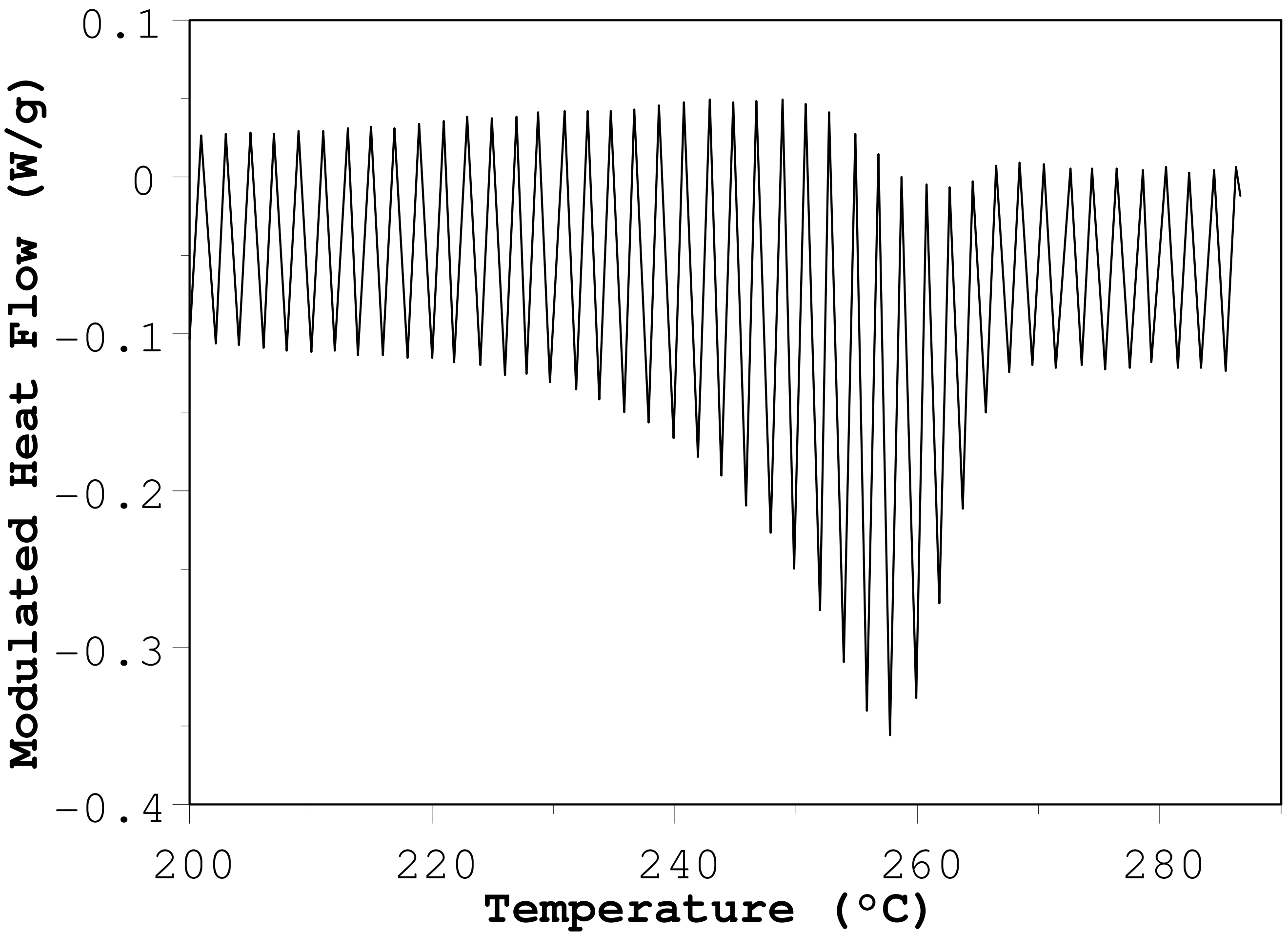
- Calculate the width of the transition



Choosing the Period/Heating Rate Combination

Figure 7

- Choose Heating Rate / Period such that there are 4-6 cycles across the width of the transition (see previous page).



Selecting Experimental Conditions (cont.)

Modulation Amplitude

- The modulation amplitude is the most important parameter from the viewpoint of interpreting the data with confidence.
- There is absolutely no need to guess which amplitude to use. It should always be selected from the table in the manual [Figure 8].
- Why specific amplitudes should be used for characterization of the melting transition:
    1. The recommended amplitudes result in the heating rate going from 0°C/min to a value that is double the average heating rate. These "Heat-Iso" Amplitudes result in no cooling of the sample during temperature modulation [Figure 9].

       Note: This is a psychological reason since the results are essentially the same with and without cooling.

Figure 8

Heat-Iso Amplitude

Period (sec)

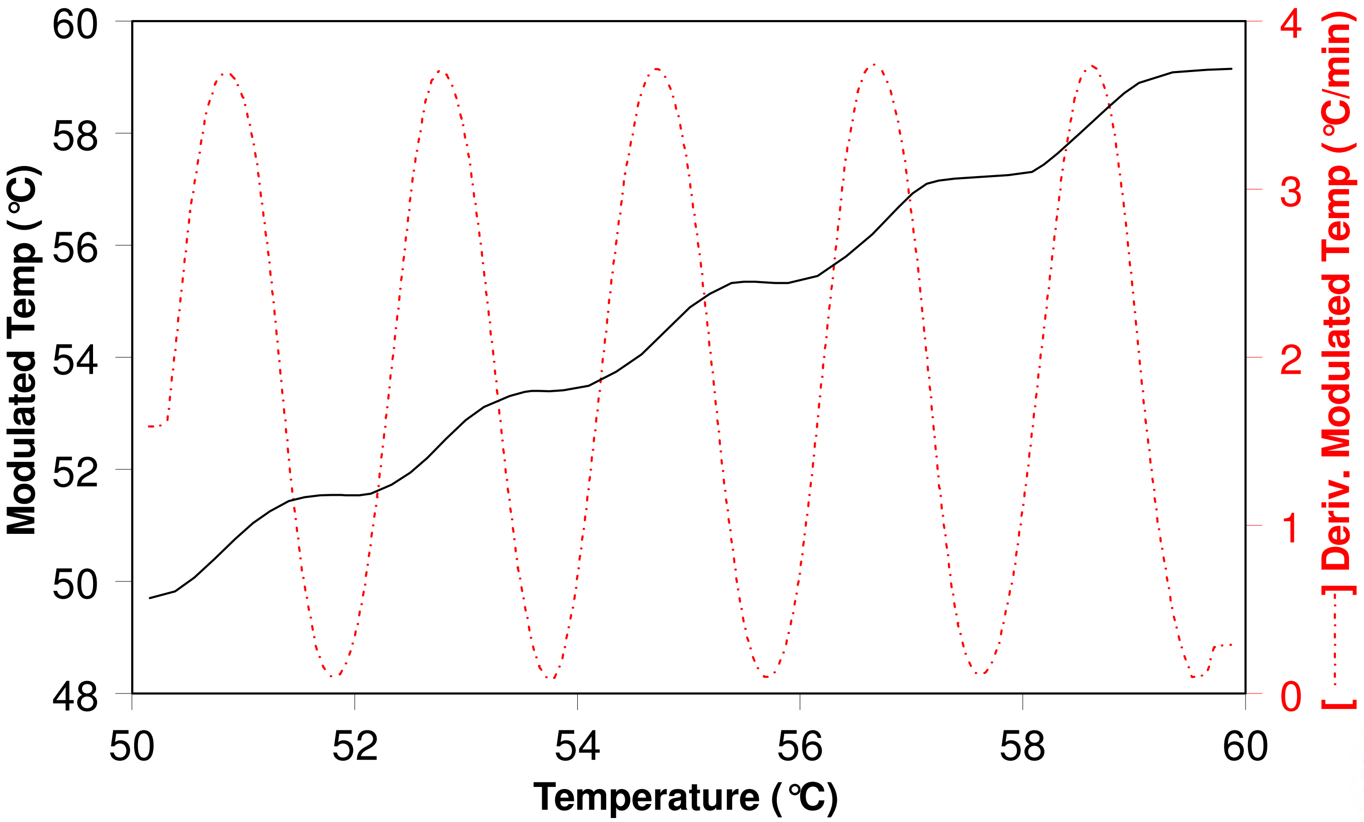
	40	50	60	70	80	90	100
0.1	0.011	0.013	0.016	0.019	0.021	0.024	0.027
0.2	0.021	0.027	0.032	0.037	0.042	0.048	0.053
0.5	0.053	0.066	0.080	0.093	0.106	0.119	0.133
1.0	0.106	0.133	0.159	0.186	0.212	0.239	0.265
2.0	0.212	0.265	0.318	0.371	0.424	0.477	0.531
5.0	0.531	0.663	0.796	0.928	1.061	1.194	1.326

This table is additive, i.e. the heat only amplitude for a period of 40 sec and heating rate of 2.5°C/min. is the sum of the values for 2.0°C/min and 0.5°C/min:

<u>Amplitude (40s, 2.5°C/min) = 0.212 + 0.053 = ±0.265°C</u>

Heat-Iso Amplitude

The "heat-iso" amplitude means that the modulated heating rate never becomes negative. In other words, the sample is always heated - never cooled.



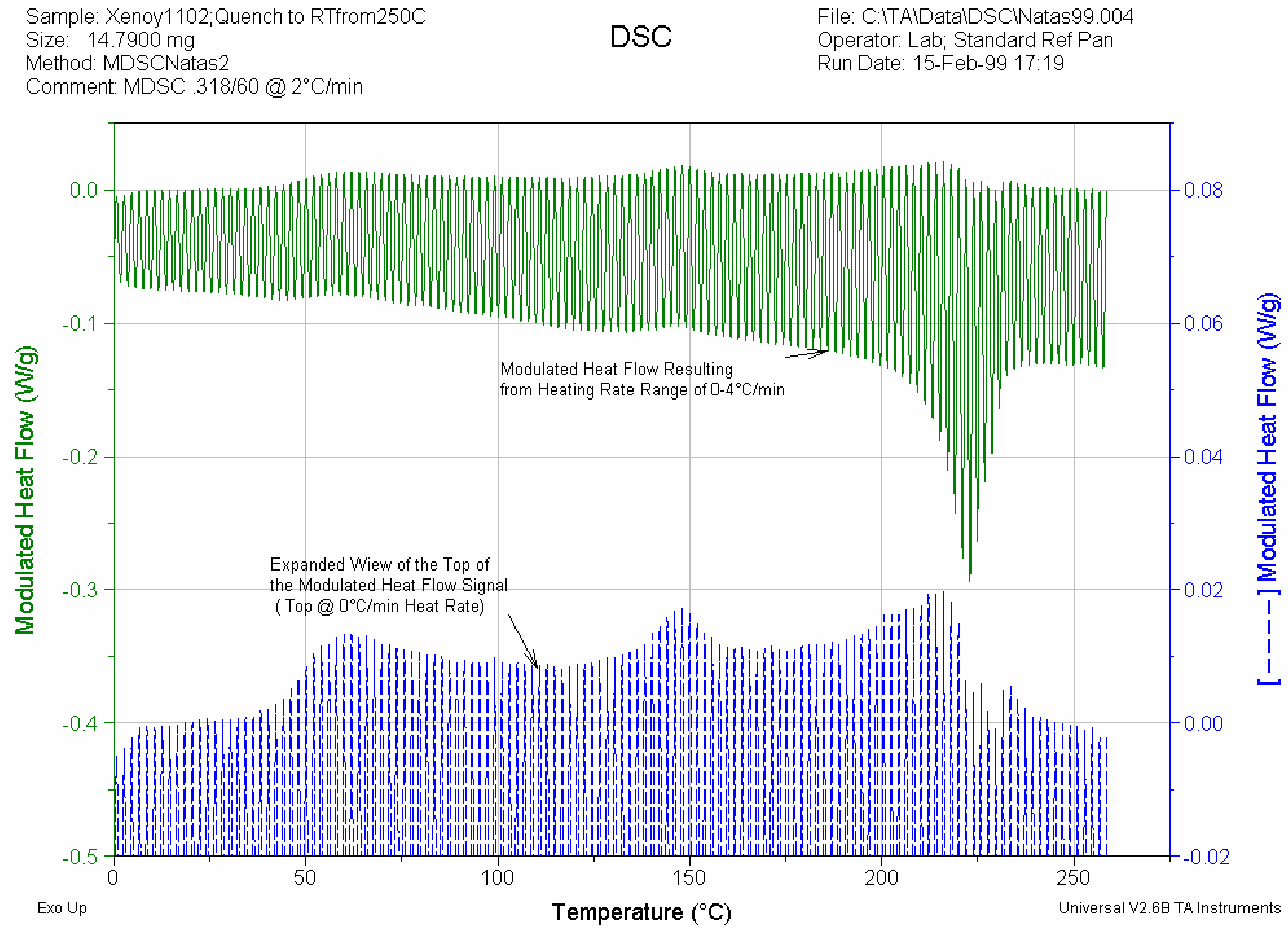
Selecting Experimental Conditions (cont.)

Heat-Iso Amplitudes (cont.)

Since the top of the raw Modulated Heat Flow (MHF) signal is the heat flow at lowest heating rate, or 0°C/min with the recommended amplitude, its shape should be identical to the calculated Nonreversing signal except in the center of the melting region.

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

$$\frac{dH}{dt} = f(T,t) \text{ when } \frac{dT}{dt} = 0$$



Sample: Xenoy1102;Quench to RTfrom250C
Size: 14.7900 mg
Method: MDSCNatas2
Comment: MDSC .318/60 @ 2°C/min

File: C:\TA\Data\DSC\Natas99.004
Operator: Lab; Standard Ref Pan
Run Date: 15-Feb-99 17:19

Modulated Heat Flow Resulting from Heating Rate Range of 0-4°C/min

Expanded Wiew of the Top of the Modulated Heat Flow Signal (Top @ 0°C/min Heat Rate)

Special Operating Conditions

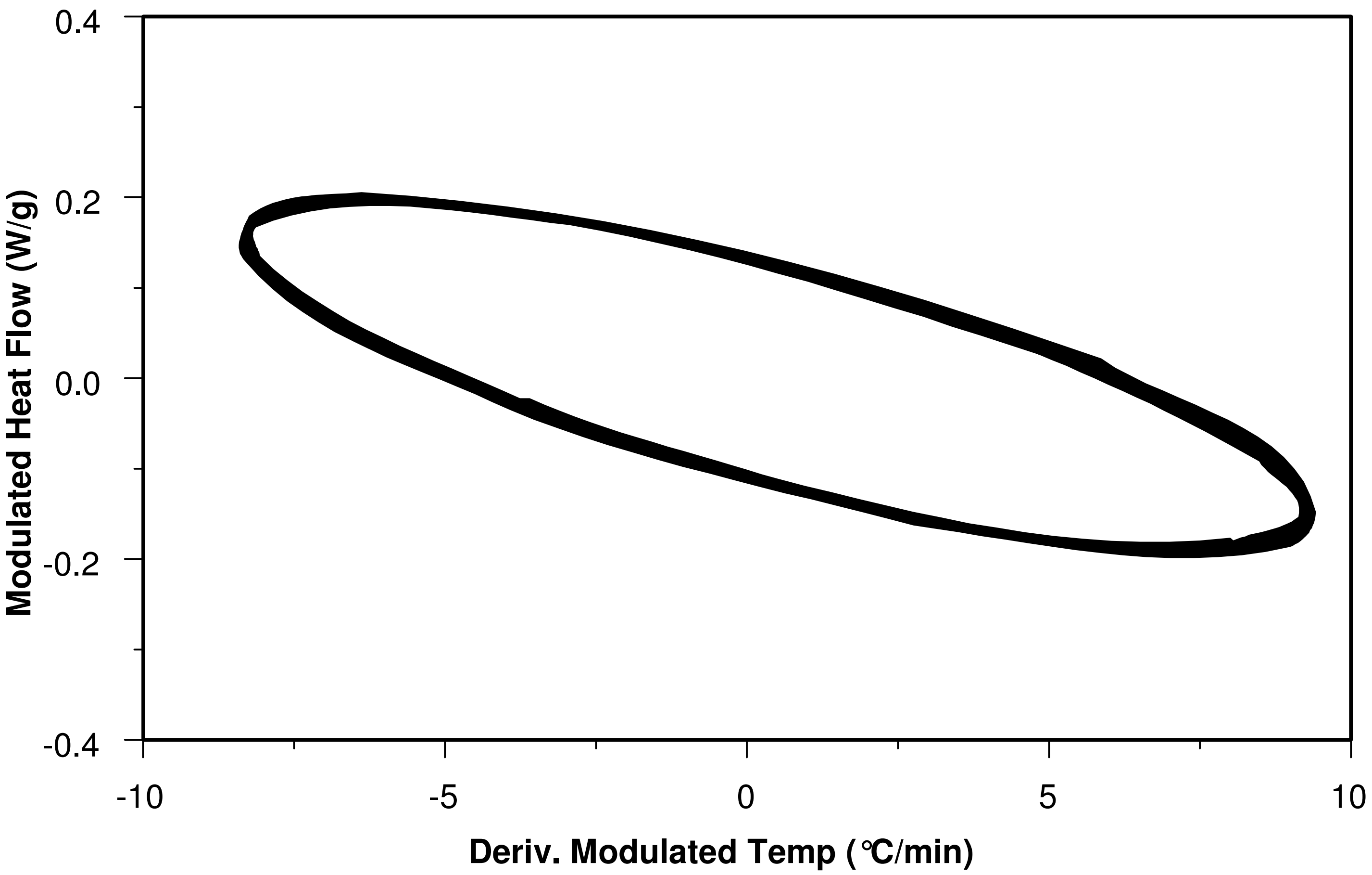
Lissajous Figures

Special Operating Conditions: Lissajous Plots

The ability to perform a Modulated DSC measurement also provides for an additional utility: Lissajous plots.

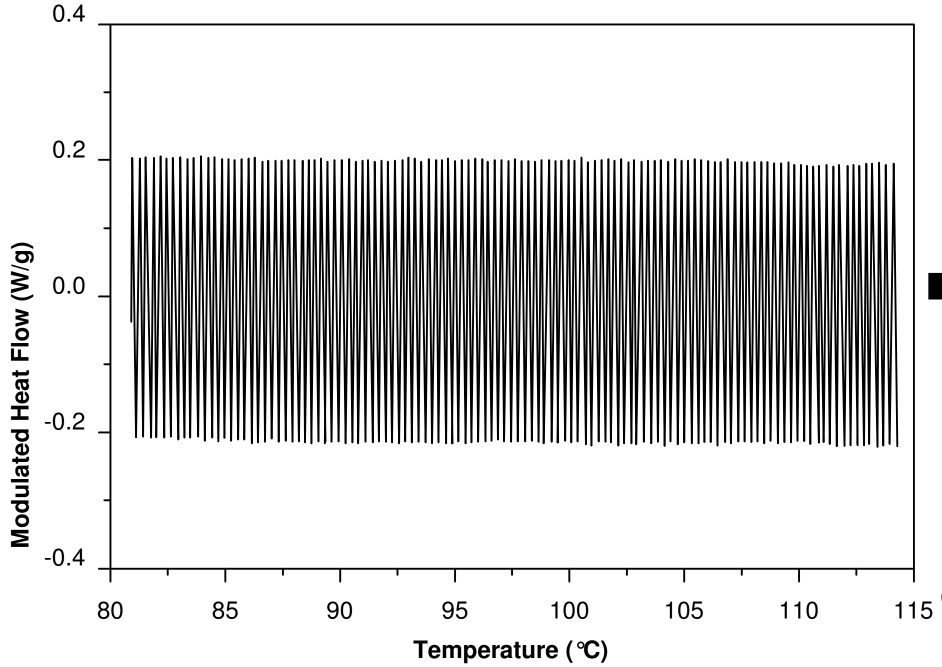
The Lissajous plot is useful in that it can provide diagnostic information concerning the stability of the MDSC measurement. In addition, Lissajous analysis can lend more information into the study of phase-equilibria before and during phase transitions such as the Tg or melting of materials.

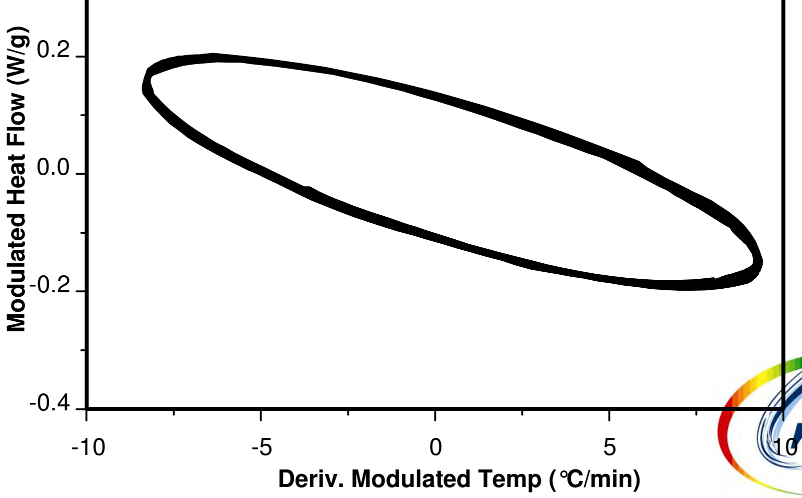
Lissajous Figure



Lissajous Figure: Any of an infinite variety of curves formed by combining two mutually perpendicular simple harmonic motions.

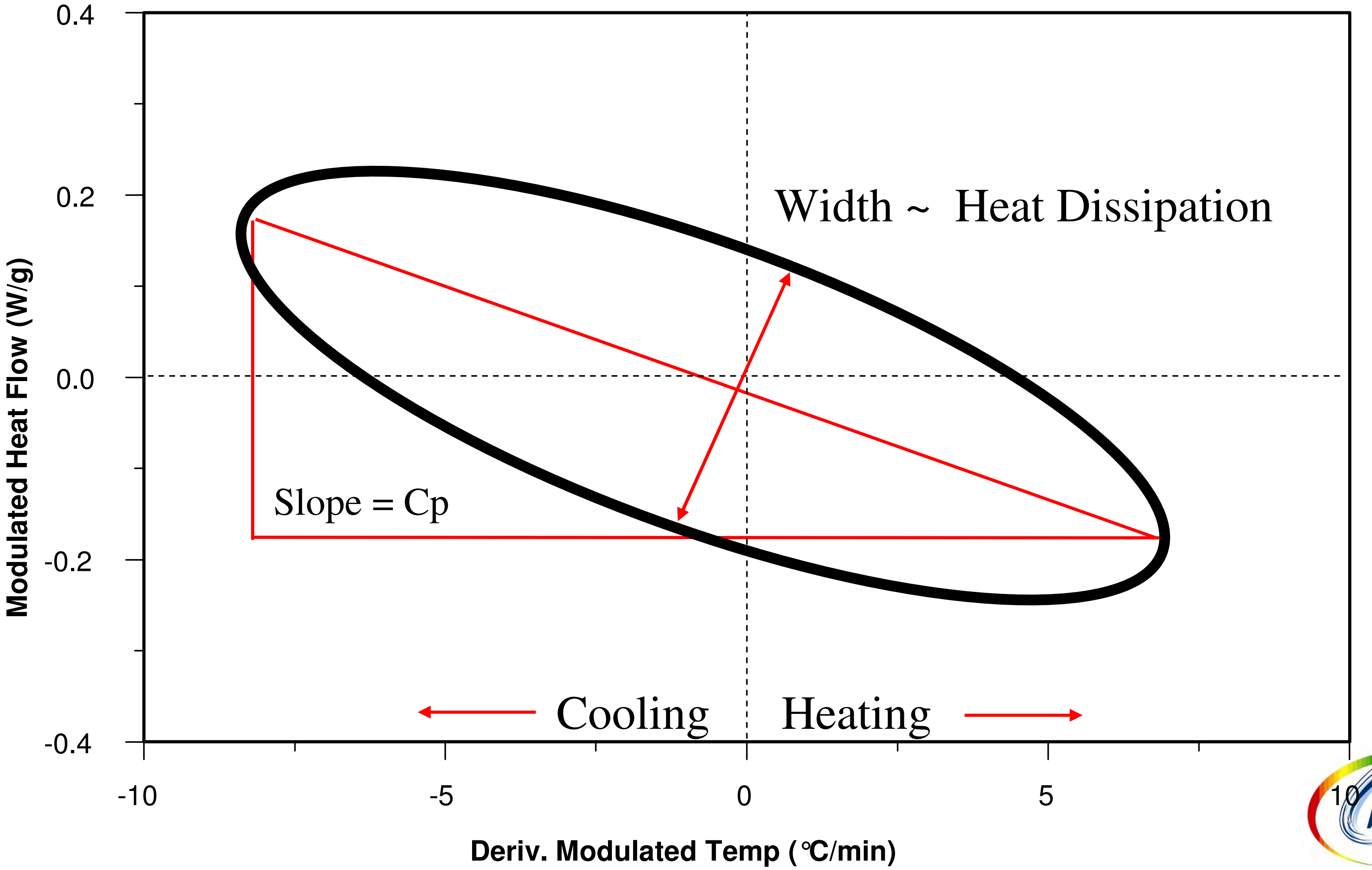
Lissajous Figure (cont.)



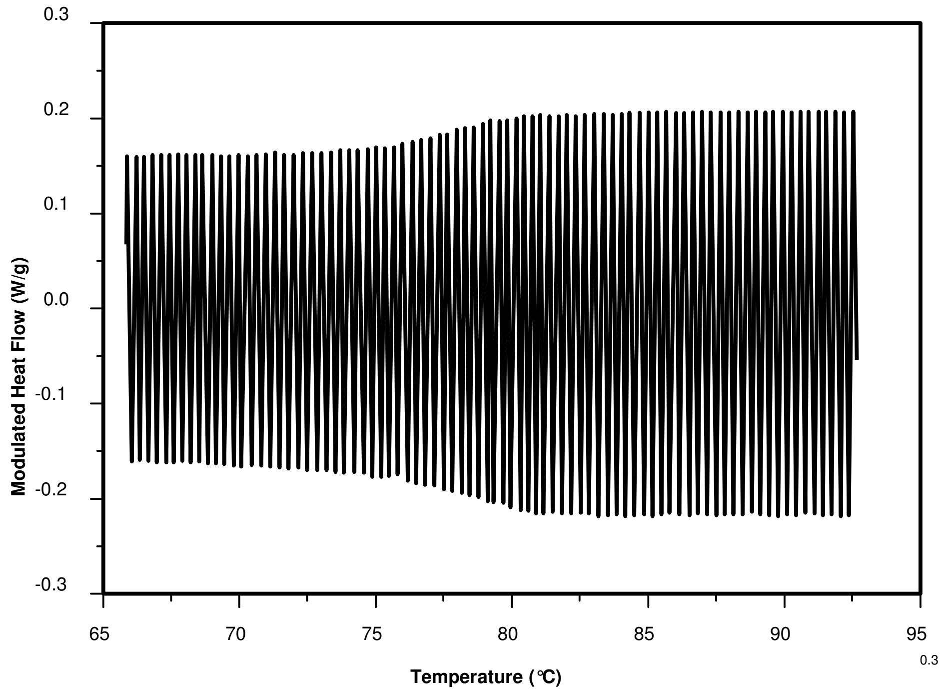


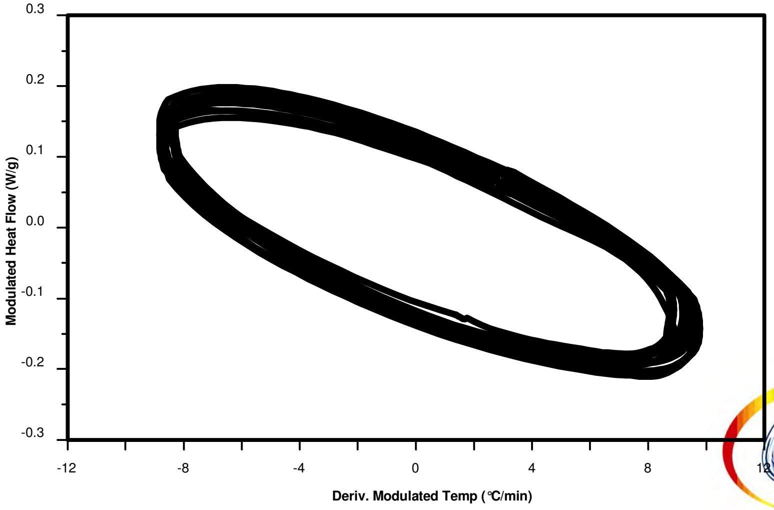
If the system is under control, the ellipse should retrace.

Interpreting the Lissajous Figure

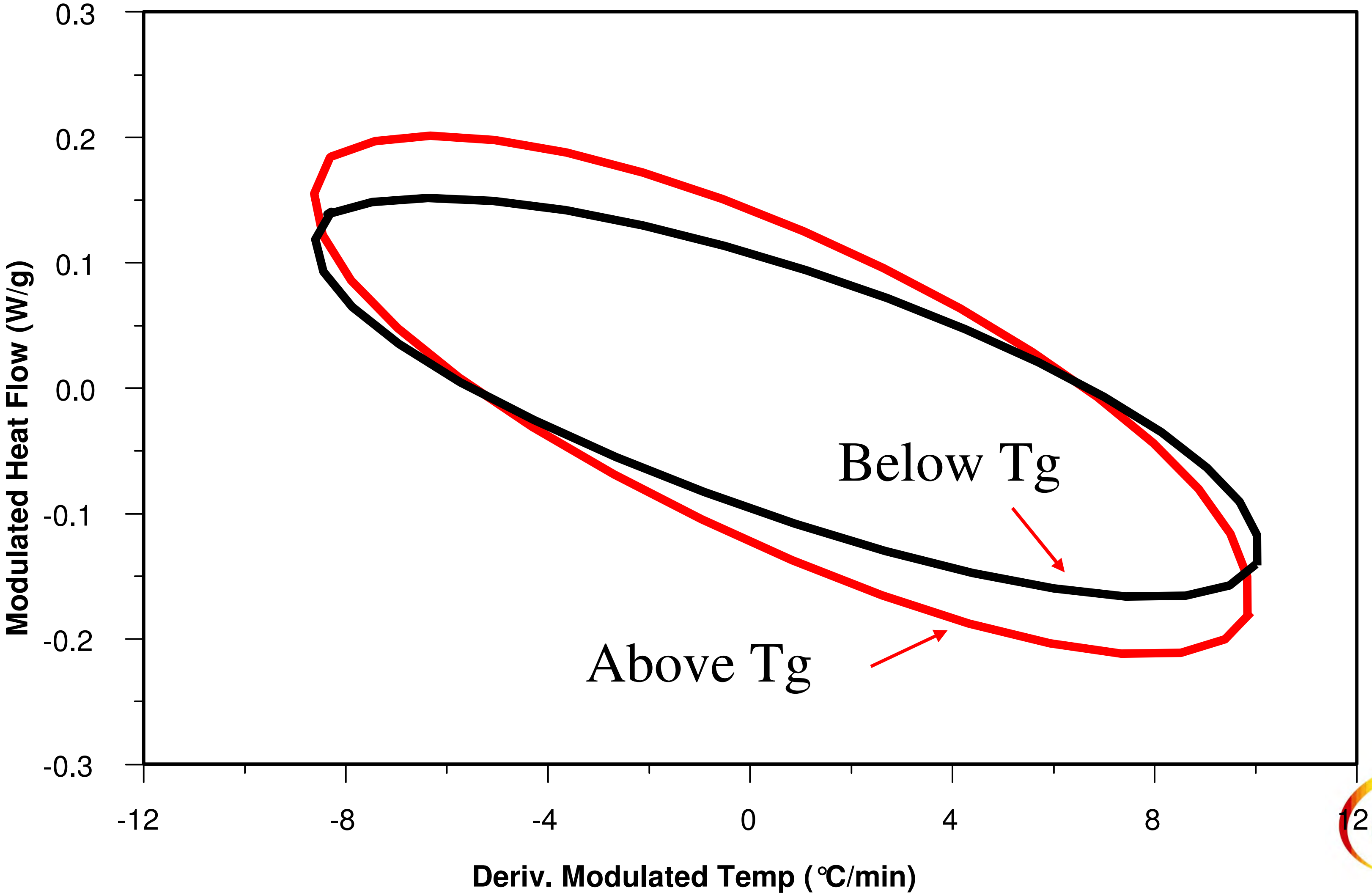


Glass Transition





Glass Transition (cont.)



Special Operating Conditions

Thermal Conductivity

Special Operating Conditions: Thermal Conductivity

Thermal conductivity is a measurement of the rate at which heat energy can be transferred through a material. It is an important factor in materials engineering and design.

Thermal conductivity and heat capacity are related properties. Since MDSC has the ability to directly measure heat capacity, it can be used to measure thermal conductivity through a series of calibrations and heat capacity measurements.

Conclusions

Once understood and properly used, Modulated DSC provides significant advantages over traditional DSC for characterization of semicrystalline materials. These advantages include the ability to:

1. Interpret complex, overlapping transitions.
2. Better determine the true melting onset temperature.
3. Detect changes in the sample as it is heated which affect both the qualitative and quantitative interpretation of results.
4. More accurately measure the “Initial Crystallinity” which is closer to the real crystallinity of the sample prior to the DSC experiment.