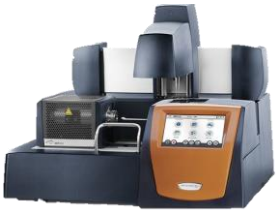
TGA & SDT Theory and Applications Online Courses

Part 1: Theory & Instrumentation



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Agenda

- Understanding TGA and SDT techniques
  - Theory
  - Instrumentation
- Calibration & Verification
- Instrument & Method Considerations
  - Purge gas
  - Sample Pans
  - Sample Preparation
  - Maintenance
  - Experimental Setup
  - Experimental Methods

2

What is Thermogravimetric Analysis (TGA)?

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

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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
- Residue

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Mechanisms of Weight Change in TGA

- Weight Loss:
  - Decomposition: The breaking apart of chemical bonds.
  - Evaporation: The loss of volatiles with elevated temperature.
  - Reduction: Interaction of sample to a reducing atmosphere (hydrogen, ammonia, etc.).
  - Desorption.
- Weight Gain:
  - Oxidation: Interaction of the sample with an oxidizing atmosphere.
  - Absorption.
  - All of these are kinetic processes (i.e. there is a rate at which they occur).

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DSC-TGA (SDT): The Technique

- Simultaneous DSC-TGA measures both heat flow and weight changes in a material as a function of temperature or time in a controlled atmosphere from room temperature to 1500˚C.
- Information obtained allows differentiation between endothermic and exothermic events which have no associated weight change (e.g., melting and crystallization), and those which involve a weight change (e.g., degradation).

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What Simultaneous DSC-TGA Can Tell You

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- The Effect of Reactive or Corrosive Atmospheres on Materials
- Moisture and Volatiles Content of Materials
- Residue
- Transition Temperatures
- Heats of Fusion and Reactions
- Melting and Boiling Points
- Heat capacity

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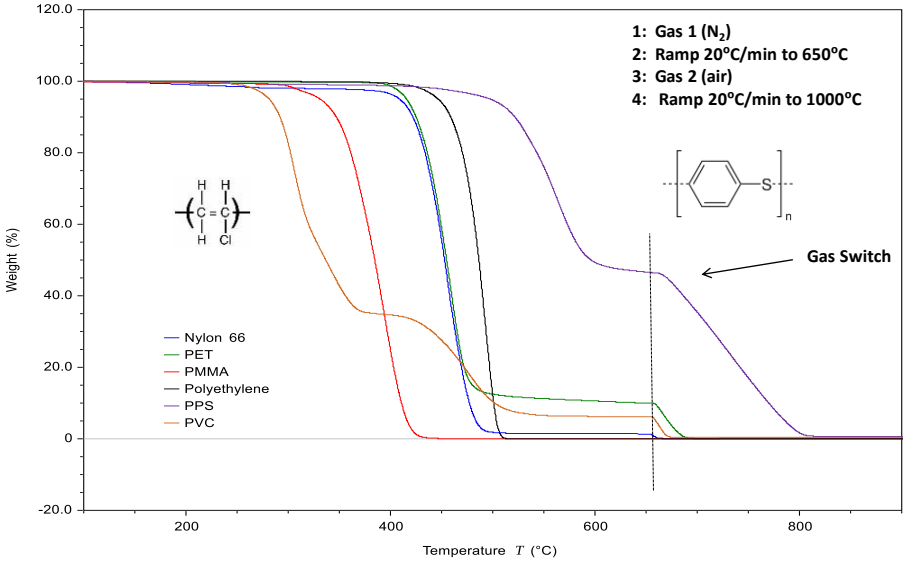
Thermal Stability of Polymers



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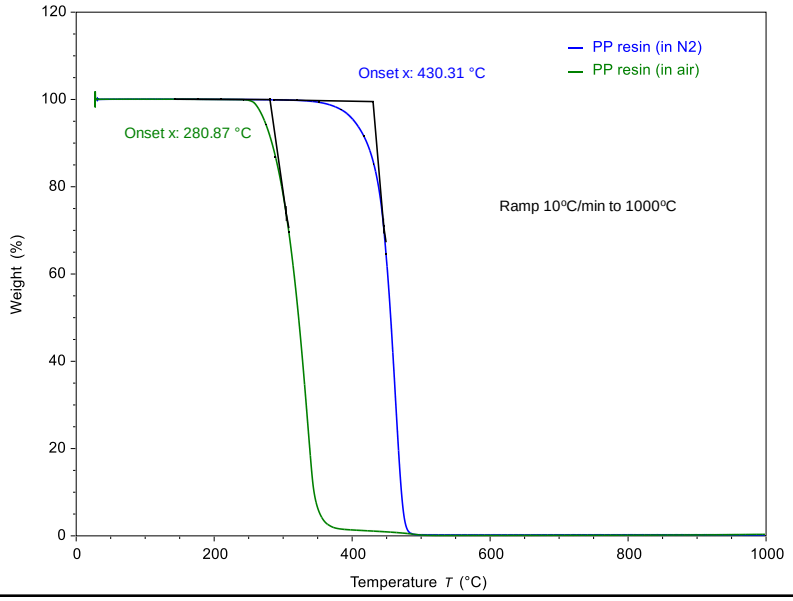
Oxidative Stability (Polypropylene)



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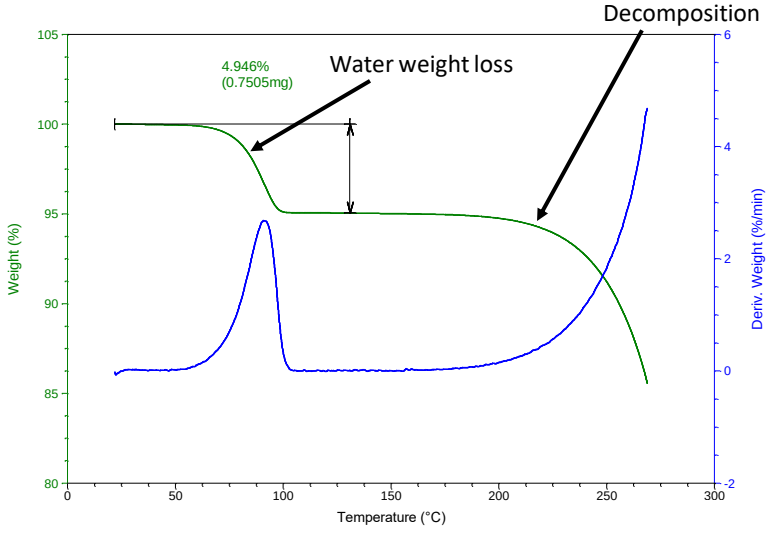
TGA of Drug A Monohydrate



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

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TA Instruments TGA/SDT Models

TGA 55
TGA 550
TGA 5500

Discovery TGA

Q5000 IR

SDT 650

Q600

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TGA Specifications

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

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SDT Specifications

	SDT 650
Temperature Range	Ambient to 1500°C
Heating Rate Range	0.1 to 100°C/min (Linear)
Sample Weight Capacity	200 mg
Baseline Dynamic Drift (50-1000°C) (1000°C t0 1500°C)	 <50 µg <50 µg

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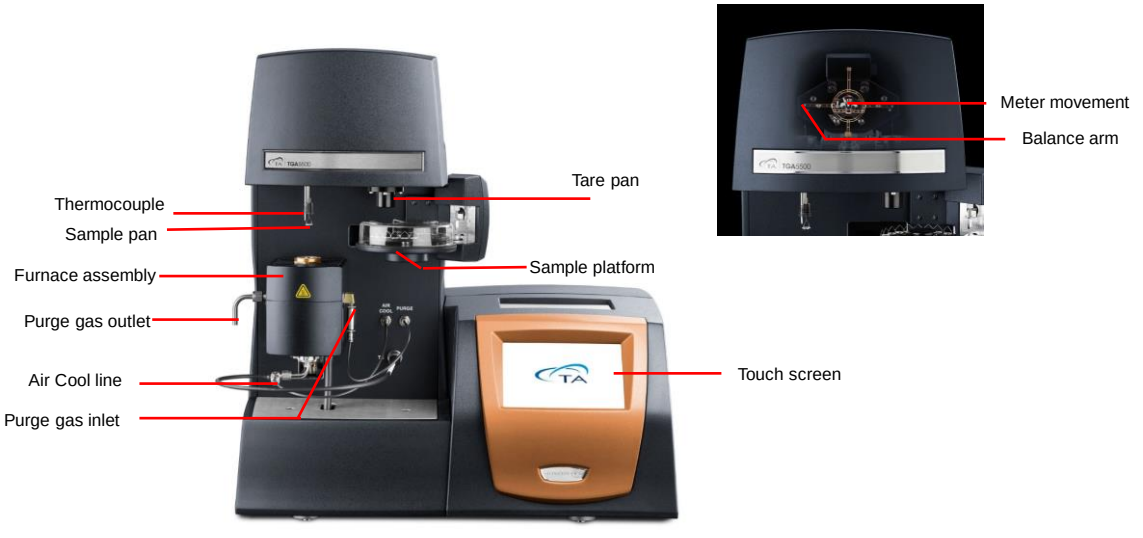
TGA: Schematic Diagram



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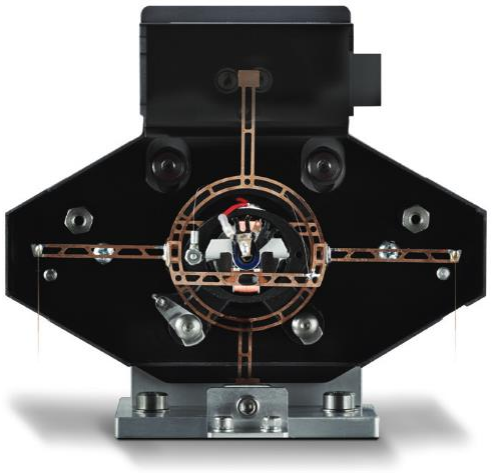
TGA Balance and Operation



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

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TGA Gas Flow Rate Distribution

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TGA Furnace Options: Wire Wound Furnace

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

Wire Wound (Pt/Rh) Furnace

Flow rate Balance/Sample :
40/60 ml/min

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TGA Furnace Options: EGA Furnace

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

EGA Furnace

Flow rate Balance/Sample :
10/90 ml/min

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TGA Furnace Options: Infra Red (IR) Furnace

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

IR Furnace

Flow rate Balance/Sample :
25/25 ml/min

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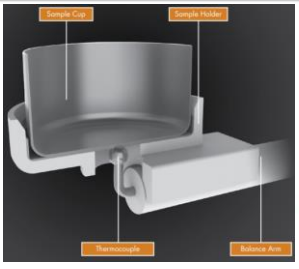
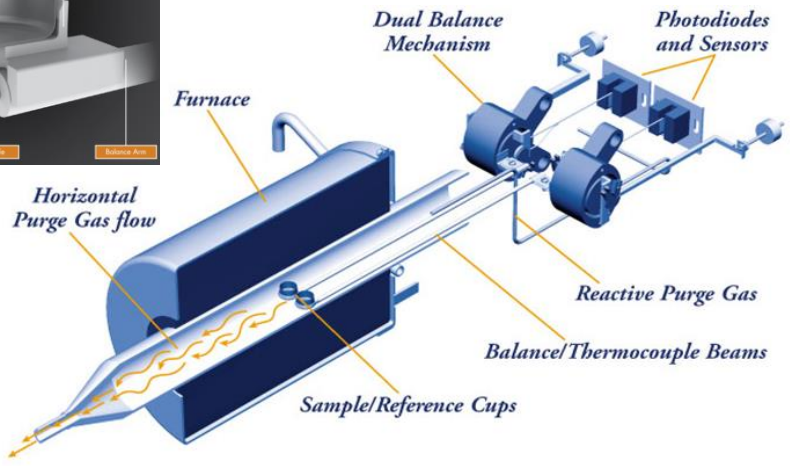
SDT: Schematic Diagram





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Calibration & Verification

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TGA Calibration and Verification

- Two types of calibration are needed:
  - Weight
  - Temperature
- Temperature calibration is affected by:
  - Purge gas and flow rate
    - Thermal conductivity of helium ≠ Thermal conductivity of nitrogen/air/oxygen ≠ Thermal conductivity of argon
  - Pan type
  - Heating rates

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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
  - Re-calibrate if results are out of tolerance

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Requirements Prior to Calibration

- The TGA pan should be cleaned prior to calibration procedures.
- The purge gas flow rate should be set (see flow rates according to furnace type). The flow rate should not deviate by more than +/- 5ml/min.
- Use high purity reference materials (>99.99%) for calibration

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Mass/Weight Calibration

- Weight calibration can be performed:
  - Manual, using an empty pan and calibration weights
  - Automatically, using the three weight calibration fixtures (pans) P/N 957341.901 (on Q5000IR, Discovery, and TGA 55XX).
- The calibration pans may only be used when a platinum reference pan is installed.

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ASTM E 2040 - Mass Scale Calibration of Thermogravimetric Analyzers

- The mass signal generated by a TGA is compared to the mass of a reference material traceable to a national reference laboratory. A linear correlation using two calibration points is used to relate the mass (or weight) signal generated by the TGA and that of the reference material
- This test method calibrates or demonstrates conformity of thermogravimetric apparatus at ambient conditions. Most TGA experiments are carried out under temperature ramp conditions or at isothermal temperatures distant from ambient conditions. This test method does not address the temperature effects on mass calibration

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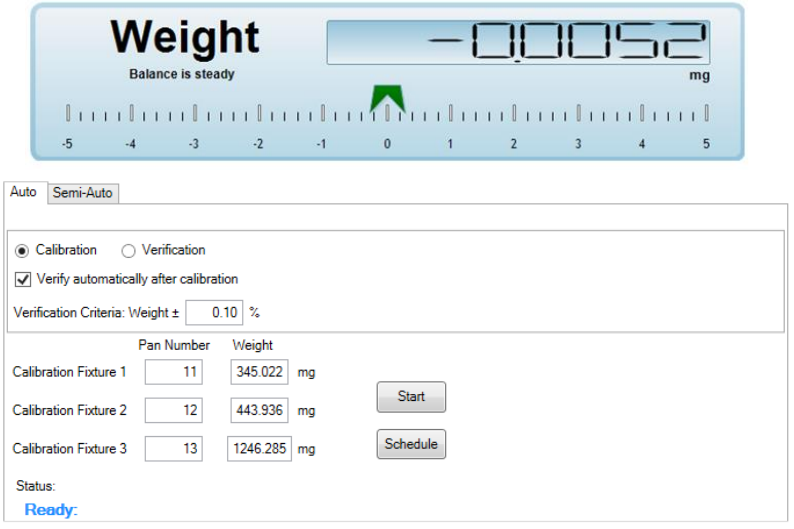
Calibration – Weight (Auto)



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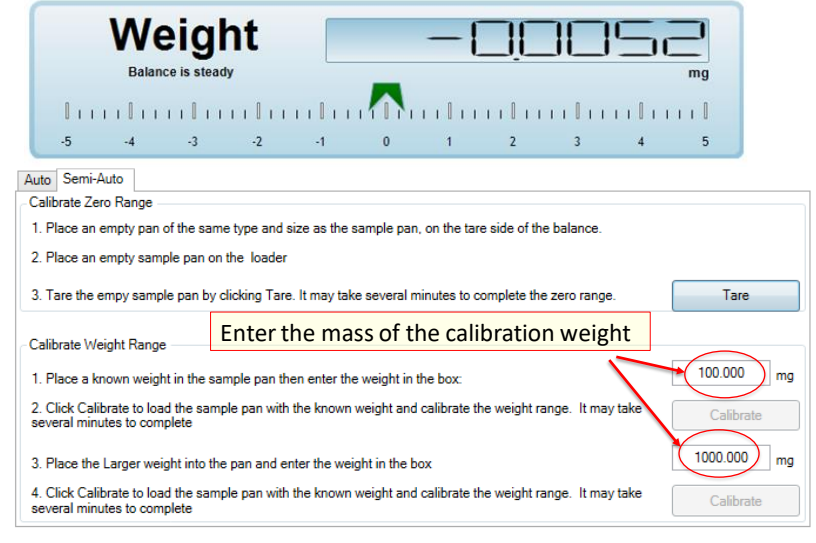
Calibration – Weight (Manual)



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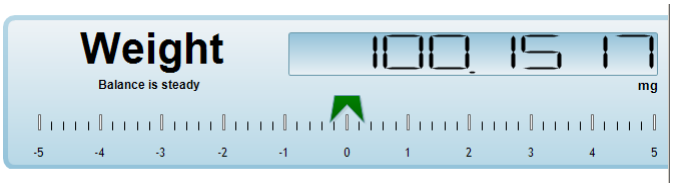
Calibration – Weight (Manual)

Simply reload the mass to verify – mass difference of ~ 0.005%



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ASTM E 1582 - Calibration of Temperature Scale for TGA

- The standard describes two methods by which the TGA can be calibrated for temperature; by melting point or magnetic transition. The most common approach for a TGA would be the magnetic transition approach
- Curie Point Temperature - that temperature where the material loses its magnetic susceptibility - defined as offset point
- Paramagnetic - a material that is susceptible to attraction by a magnet
- Temperature Calibration points are determined by comparing the measured melting onset temperature to the literature value
- TA Instruments software allows for up to 5 temperature calibration points
  - Generally, these should bracket the temperature range of interest for subsequent samples

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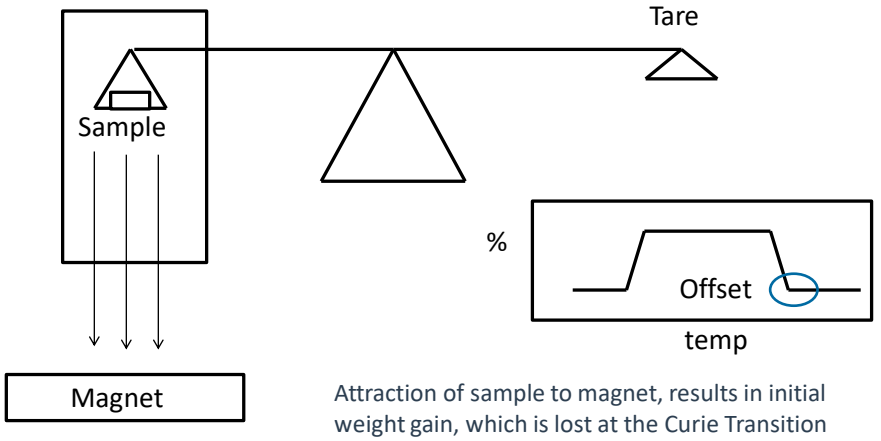
TGA: Temperature Calibration

Vertical Balance Configuration



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

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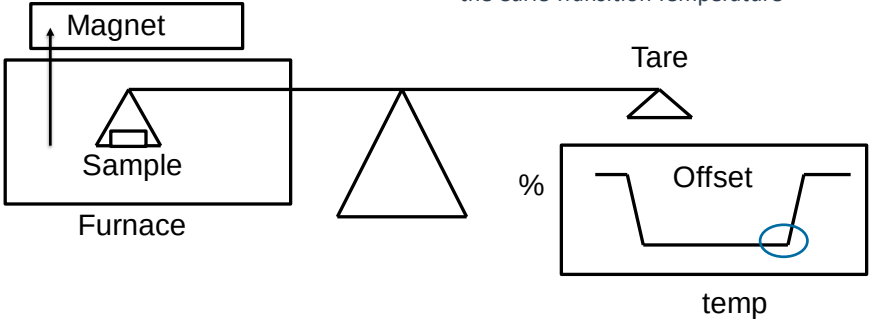
SDT: Temperature Calibration

Horizontal Balance Configuration

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



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Curie Temperature Reference Materials

- International Confederation for Thermal Analysis and Calorimetry (ICTAC) developed a set of six certified and traceable Curie temperature reference materials for the calibration of TGA
  - Alumel 153°C
  - Nickel 358C
  - Ni83Co17 555°C
  - Ni63Co37 747°C
  - Ni37Co63 931°C
  - Cobalt 1116.0°C
- The materials permit temperature calibration in about 200 °C intervals over the range of 150 to 1120 °C
- TA Instruments is the exclusive worldwide distributor for these Curie point materials

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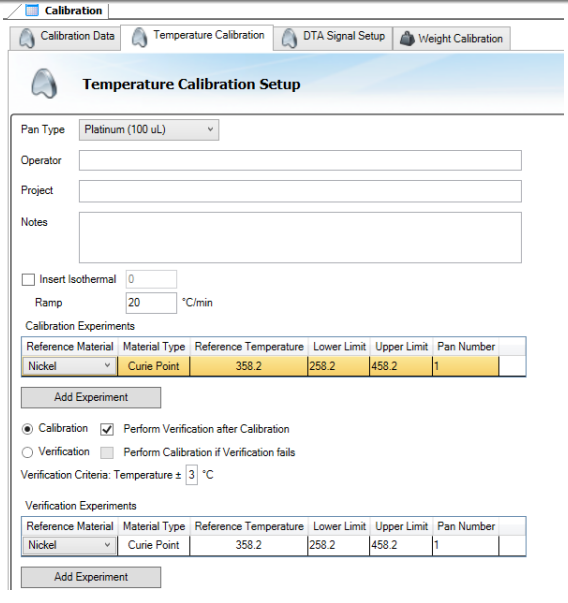
Calibration – Temperature



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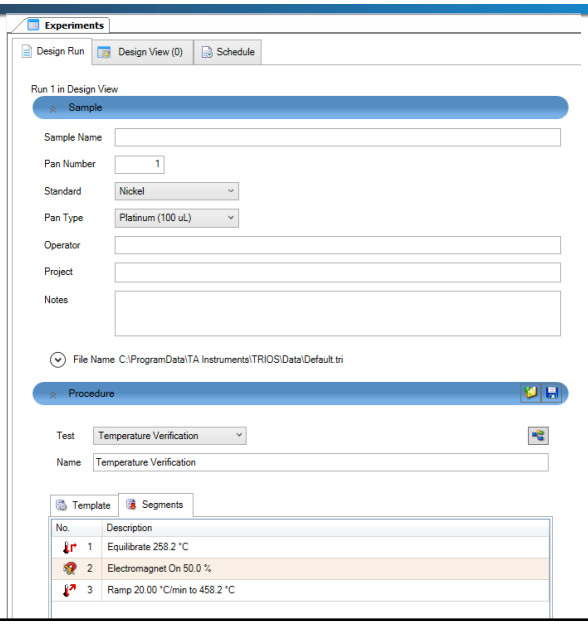
Verification – Temperature



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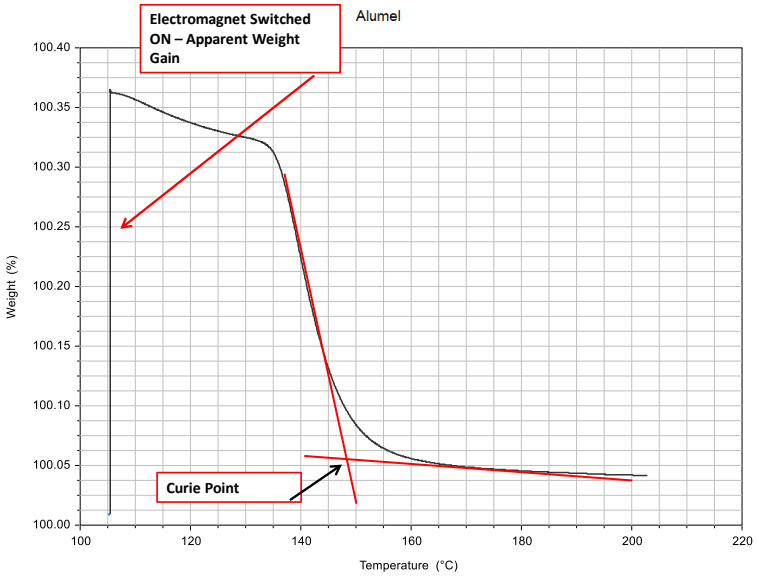
Calibration – Temperature



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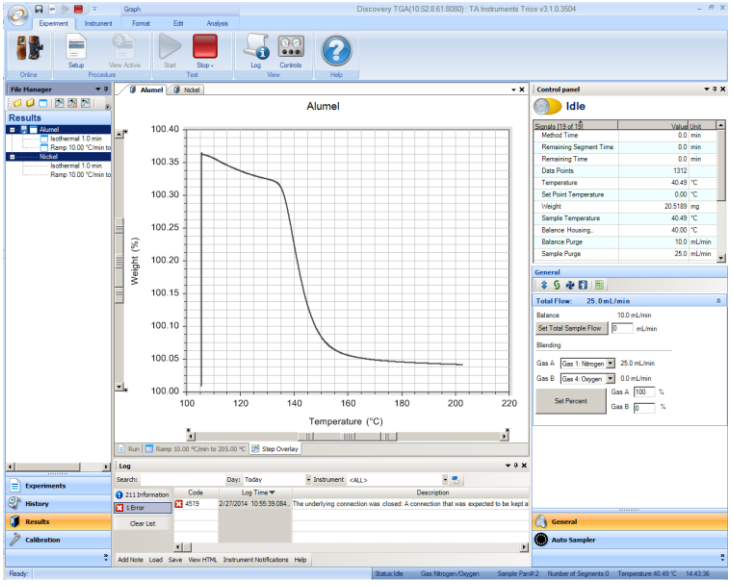
Calibration – Temperature

From the 'Results' Pane, Choose both the Alumel and Nickel Runs



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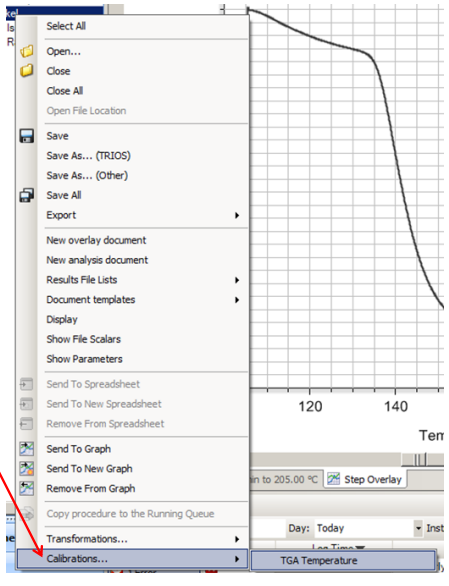
Calibration – Temperature

Choose 'Calibrations' and 'TGA Temperature'



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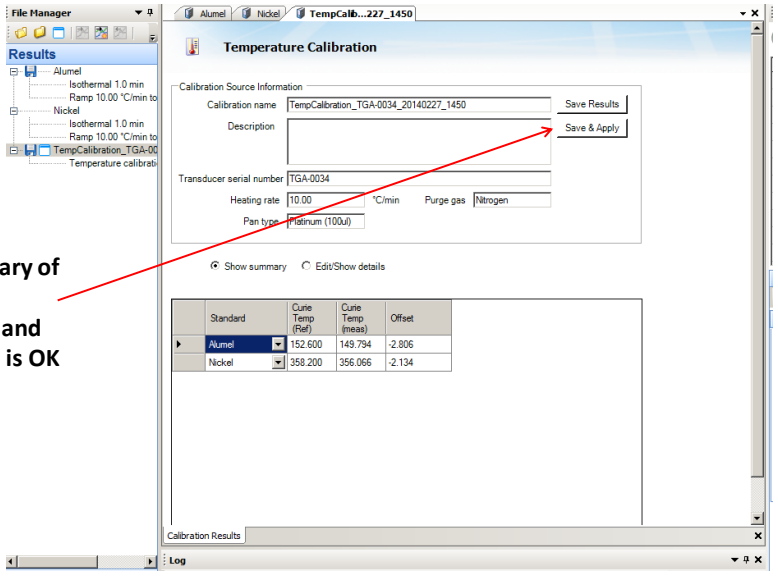
Calibration – Temperature



Dialogue Box Shows Summary of Calibration – Choose 'Save and Apply' if Data is OK

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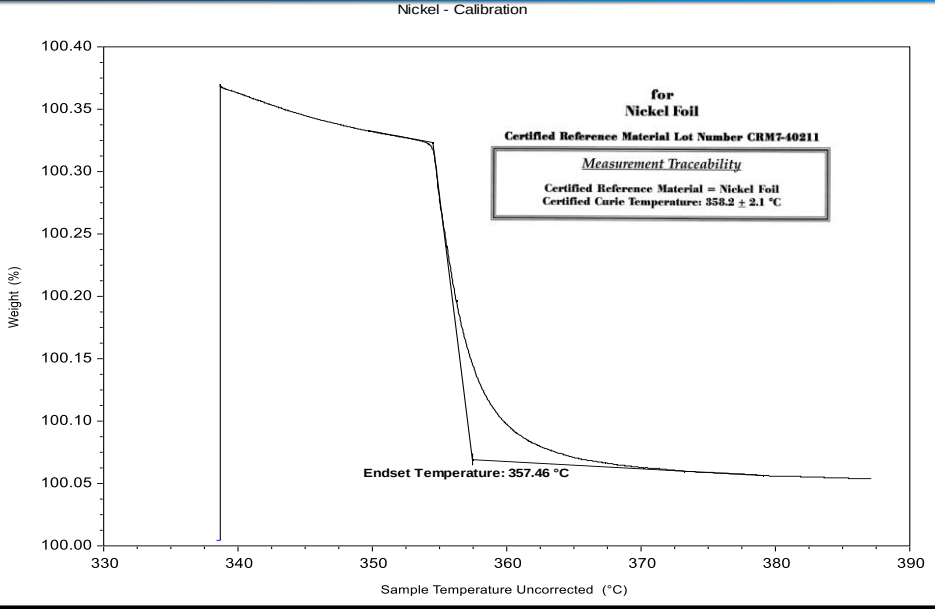
TGA – Temperature Calibration



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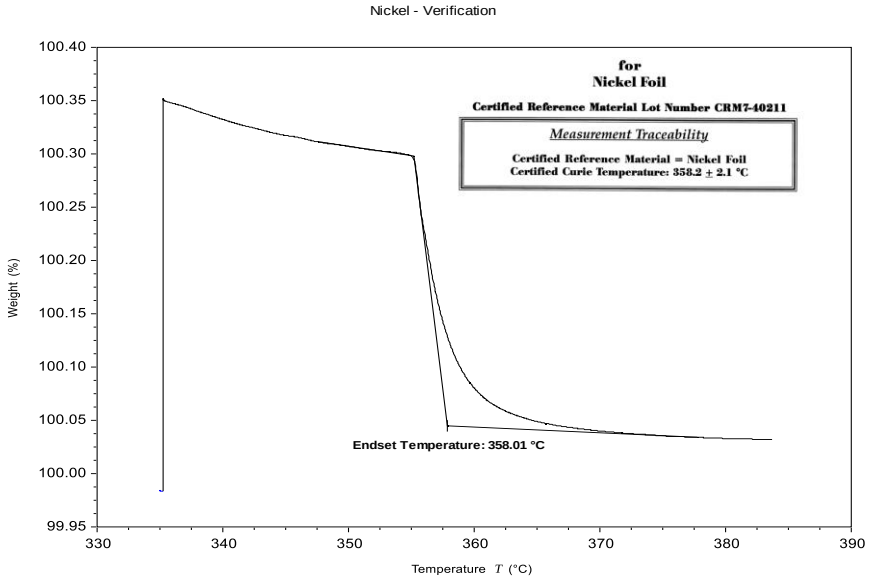
TGA – Temperature Verification



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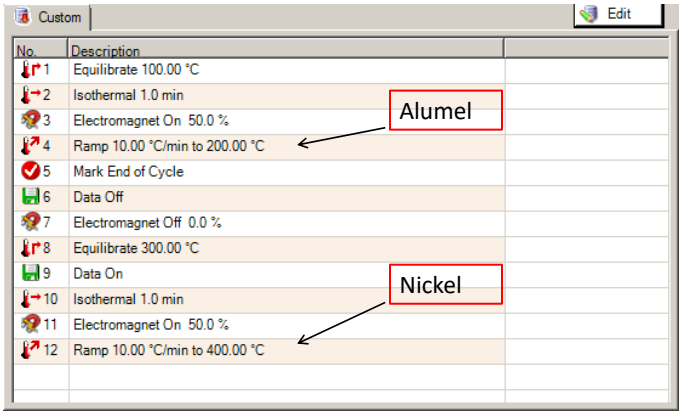
Calibration – Temperature: Verification



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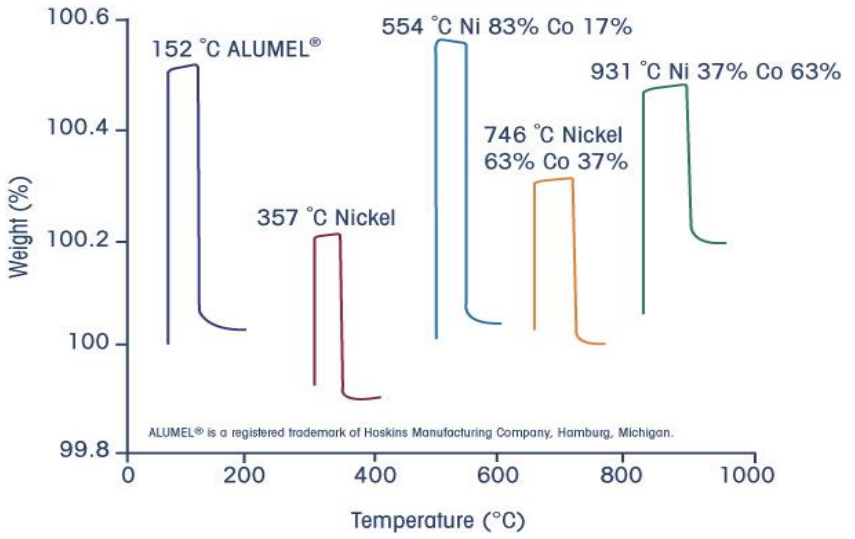
Curie Standards with ICTAC traceability



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Calcium Oxalate "Standard" Analysis

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

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Calcium Oxalate Decomposition

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

Calcium Oxalate Monohydrate — *Calcium Oxalate*

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

Calcium Oxalate — *Calcium Carbonate*

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

Calcium Carbonate — *Calcium Oxide*

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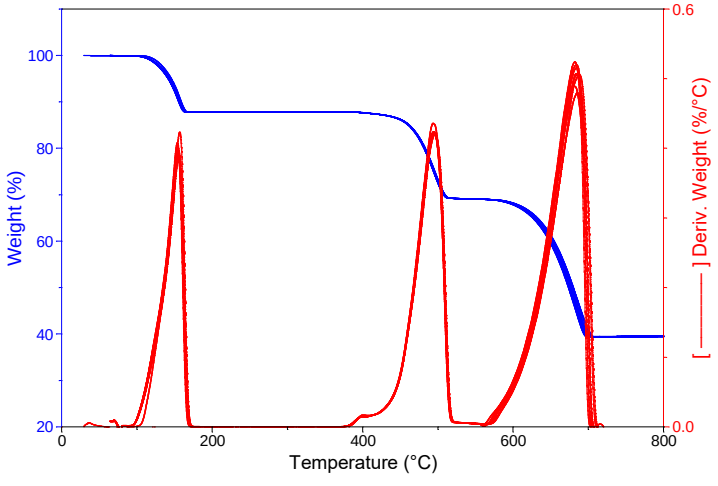
Calcium Oxalate Repeatability

Overlay of 8 runs, same conditions



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Calcium Oxalate Repeatability

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

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SDT Calibration and Verification

- Calibrate upon initial installation
- Re-calibrate anytime the beam set, experimental heating rate, or purge gas is changed
- Types of calibration available:
  - Weight Calibration: (TGA weight signal)
  - DTA Signal Setup: Analyzing the Delta T signal data
  - Temperature (Melting point or curie point standards as in TGA. Commonly use melting point standards)
  - DSC Heat Flow
  - MDSC Reversing Heat Capacity (SDT 650)

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SDT Calibration and Verification

- DTA signal:
  - Not required when using the SDT as a DSC-TGA
    - This run usually utilizes the same baseline run obtained for TGA Weight Calibration
- Heat flow and cell constant:
  - Based on analyzing the heat capacity curve for sapphire over the range 200 to 1500°C. Three experimental runs are required: two runs to generate the heat flow curve and another run to refine that calibration through cell constant calibration using a known metal standard (zinc, for example)
- MDSC Reversing heat capacity:
  - A heat capacity calibration curve is generated by running a sapphire sample over a desired temperature range using appropriate modulated conditions. The collected Reversing Heat Capacity curve is calibrated against the true value of the heat capacity of sapphire over the experimental temperature range

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Instrumental Considerations

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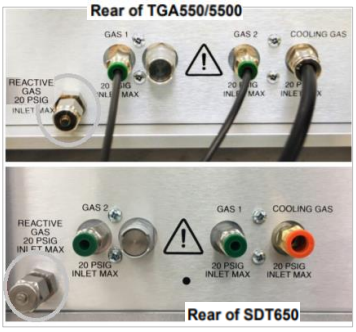
Instrument Hardware and Gas Selection Considerations

- Gas Delivery Module and Mass Flow Controllers
  - The gas 1 port purges both sample and balance areas
  - Gas 1 should be an inert gas (N2, He, Ar)
  - The gas 2 port is used when a different purge gas is required, or gas switching is used
  - Typically this is air or O2
  - Gas type is assigned to Mass Flow Controller in the Instrument section of the control software and chosen before on the setup page.



Gases Typically used on TGA/SDT

• Nitrogen - inert, inexpensive and readily available
• Helium - inert, commonly used on TGA-MS
•Argon - inert
• Air/Oxygen - used when studying oxidative stability of materials, can sometimes improve resolution of weight loss events

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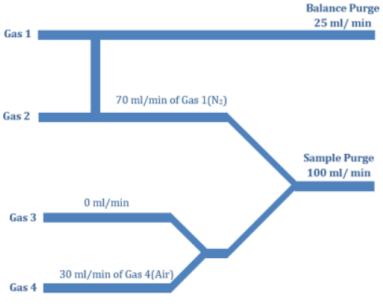
Blending Gas Delivery Module

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



Four gases can be used in a test

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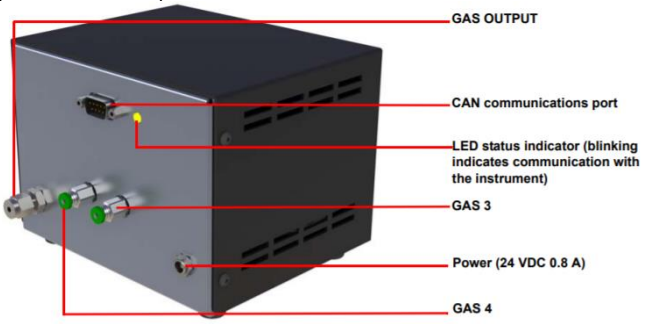
Blending Gas Delivery Module

- Balance and sample purge flow will depend on the instrument:



Back panel of the Blending GDM.

TGA 550	40	60	Balance/Sample
TGA 5500	25	25	
SDT 650	100	100	

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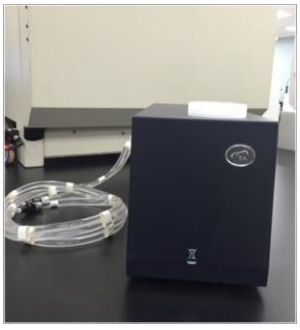
Heat Exchanger - TGA

- The heat exchanger contains a liquid reservoir that supplies the instrument with coolant to dissipate heat from the furnace
- The coolant exits the heat exchanger through the supply line, circulates to the furnace, and returns to the reservoir via the return line
- Check the level and condition of the heat exchanger coolant periodically (about 3 months)
- To clean: empty old water, fill with distilled water
- Add TA Instruments TGA Conditioner
  - (P/N 952377.901) (algae growth suppressor)
- For Q series, after filling, in software

  choose “Control \ Prime Exchanger”



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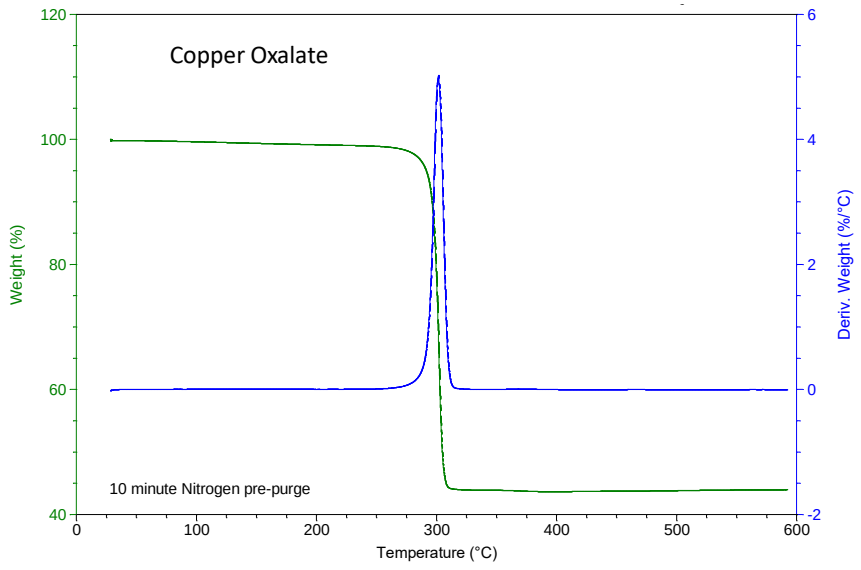
Test for Oxygen Contamination of N2 Purge Gas



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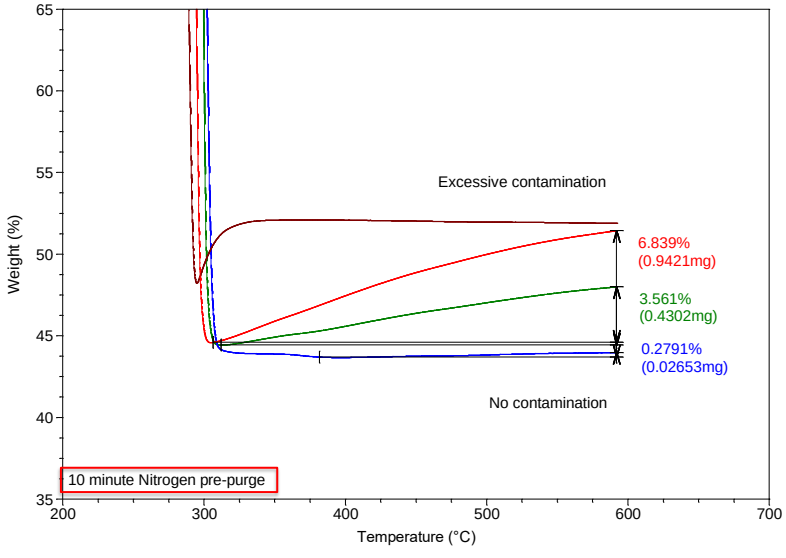
Effect of Oxygen on Copper Oxalate



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Baseline Performance Verification

- A good way to quantify how well the TGA is working
- Especially important for measuring small weight losses associated with volatilization or small amounts of residue
- Run clean, empty, tared pan, over temperature range of interest, at desired heating rate
- Plot weight in µg vs. temperature
- Dynamic drift should be less than 10 µg for the Discovery TGA 5500, and Discovery TGA and less than 50 µg on the Discovery TGA 550/55 & Q Series TGA's when using platinum pans and 20°C/min heating rate

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TGA: Factors Influencing Baseline

- Stability of table
- Hang down wire / beam condition
- Hang down tube condition
- Leveling of TGA
- Cleanliness of the furnace
- Purge gas flow rates

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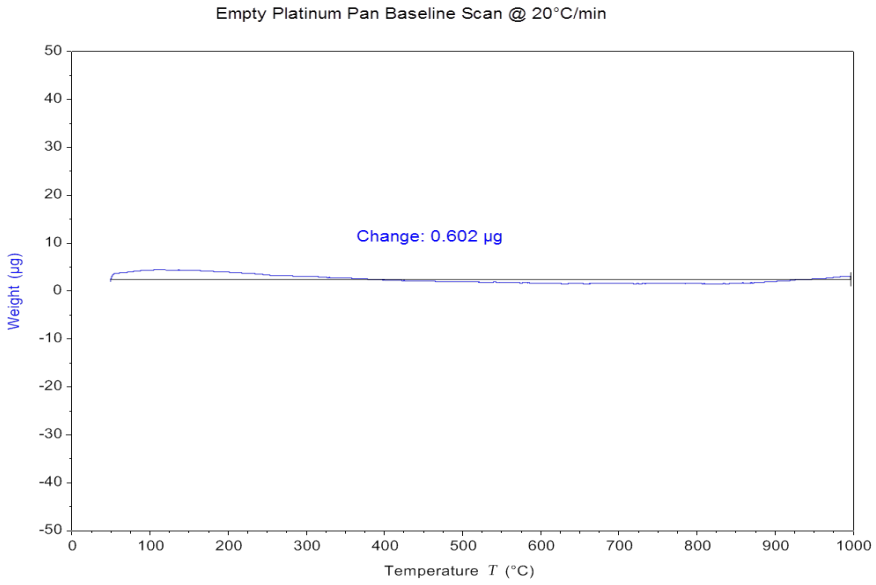
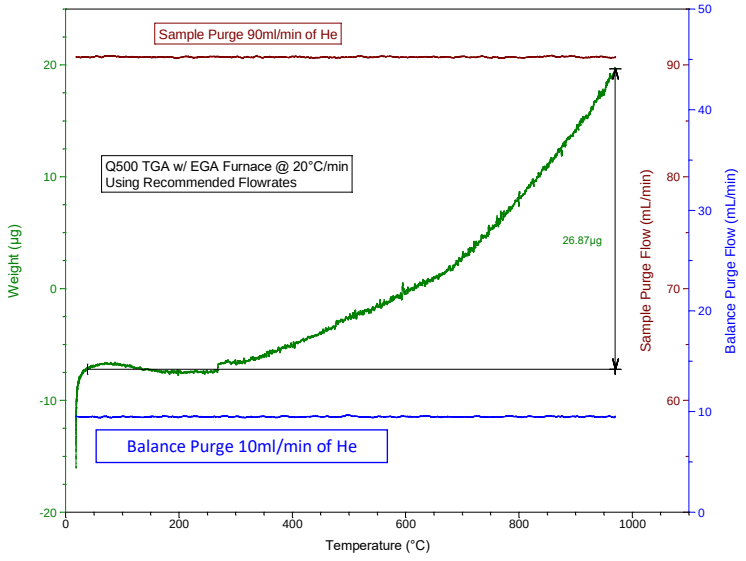
Discovery TGA 5500 Baseline Performance



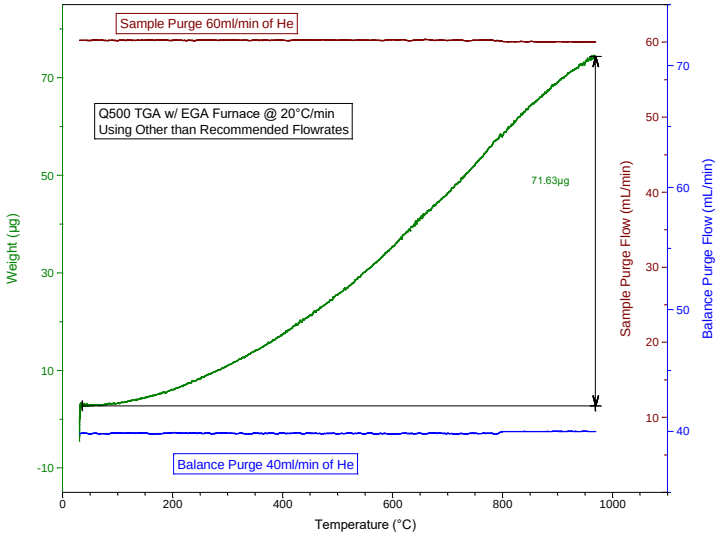
60

Effect of Purge Gas Flowrate on Baseline



61

Effect of Purge Gas Flowrate on Baseline



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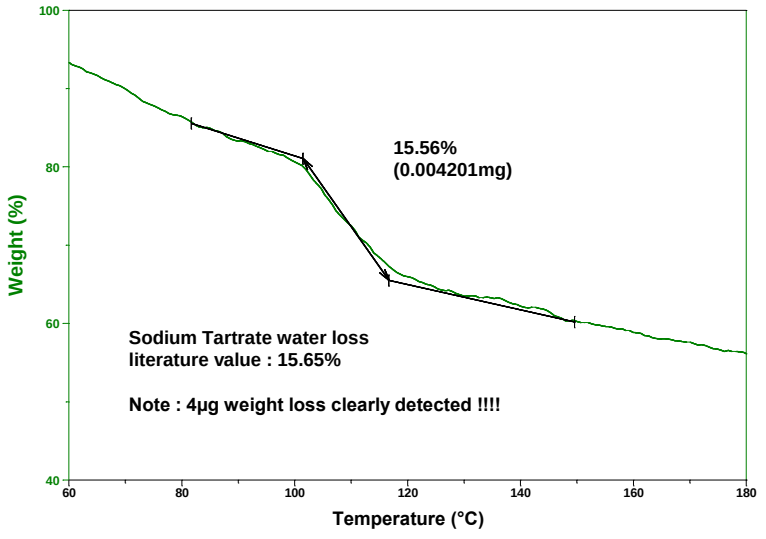
Balance Sensitivity - Sample: 27µg Sodium Tartrate



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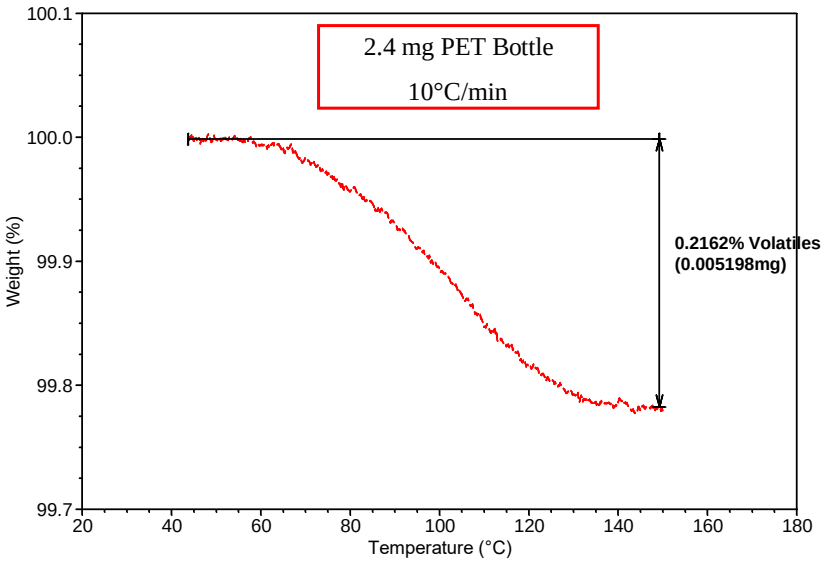
TGA: High Sensitivity Volatiles Analysis



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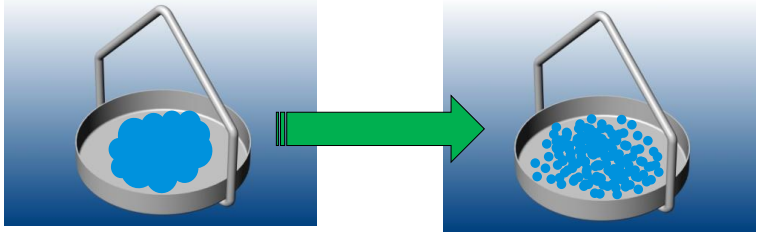
TGA: Sample Preparation

- Sample mass
  - 10-20mg for most applications
  - 50-100mg for measuring volatiles or residues
- If a TGA has a baseline drift of +/-25mg then this is 0.25% of a 10mg sample



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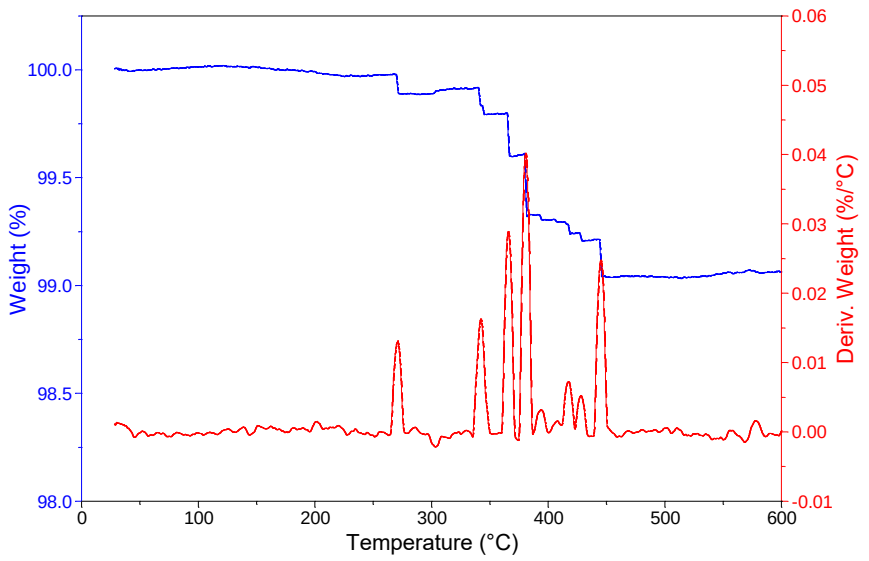
TGA particle size matters, NaCl decrepitation



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TGA: Sample Preparation

- Use brass tweezers to eliminate static effects
- Tare a clean sample pan before every run
- Distribute sample evenly over bottom of pan
- Liquid samples - use hermetic pan with a pin-hole lid

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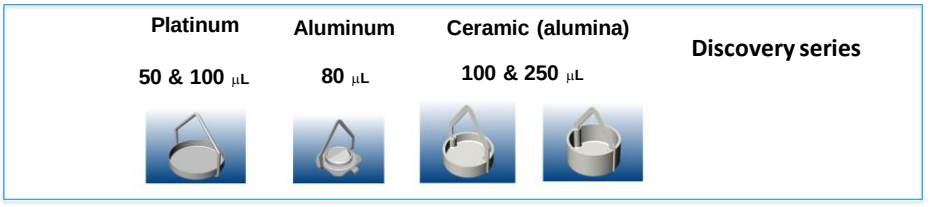
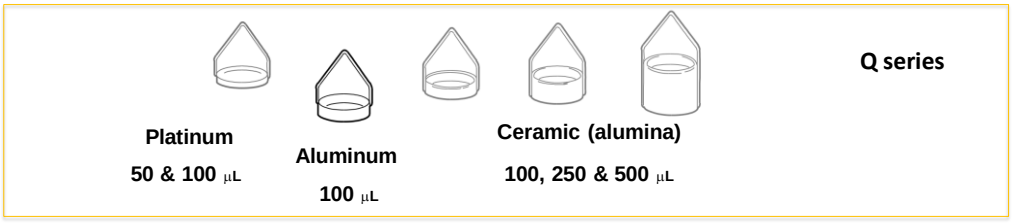
TGA: Sample Pans - Types/Sizes



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



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TGA: Sample Pan Selection

- Platinum (useful for most materials)
  - Easy to clean
  - Nonporous
  - Can alloy with most metals
- Alumina (Ceramic)
  - Corrosives/Inorganics
  - Large samples
  - Porous, can be easily contaminated
- Aluminum (TGA) (designed for one-time use)
  - Lower cost, disposable
  - Lower temperature limit (<=600°C)

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SDT: Sample Pans - Types/Sizes

- Platinum:
  - 40 µL
  - 110 µL
- Alumina:
  - 40 µL
  - 90 µL

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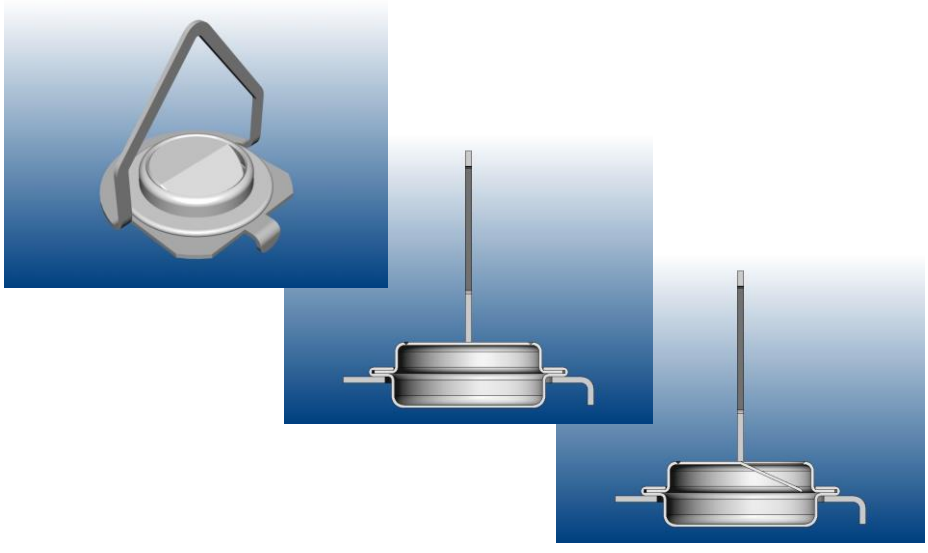
Sealed Aluminum Pans



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Sealed Aluminum Pans and Punching

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TGA: Sample Pan Cleaning

- All sample pans are reusable (except Aluminum)
- If using platinum or alumina pans, a flame torch can be used to burn off organic residue. (do not flame Aluminum pans)
- Scrape off remaining ash (DSC fiberglass brush)
- Swab out with an organic solvent such as acetone or alcohol. Let it dry out before using it

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TGA: Environment Considerations

- Avoid areas near heater or air conditioner ducts
- Avoid tables with drawers or those near a door
- For optimum results, use a marble table

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Experimental Methods

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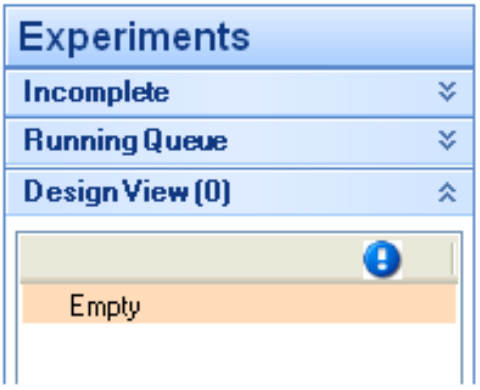
Experiment Setup

- Experiments are created in the Running Queue or the Design View
- They are launched from the Running Queue!



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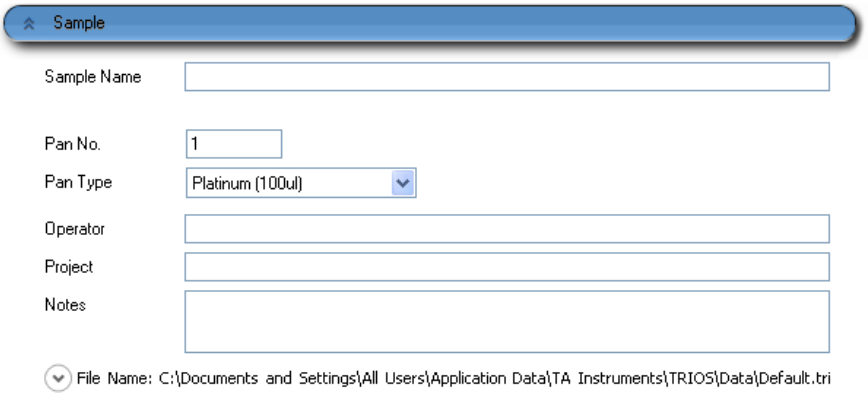
Experiment Setup

- Sample information is entered here



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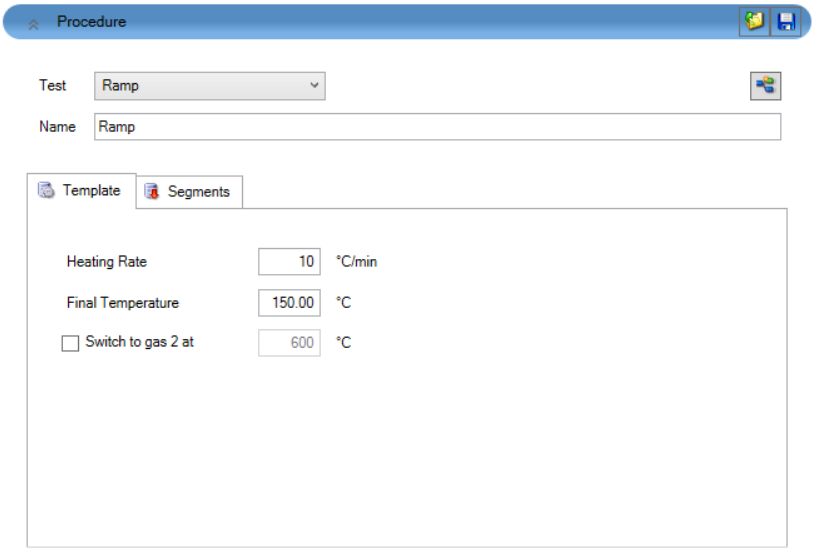
Experiment Setup



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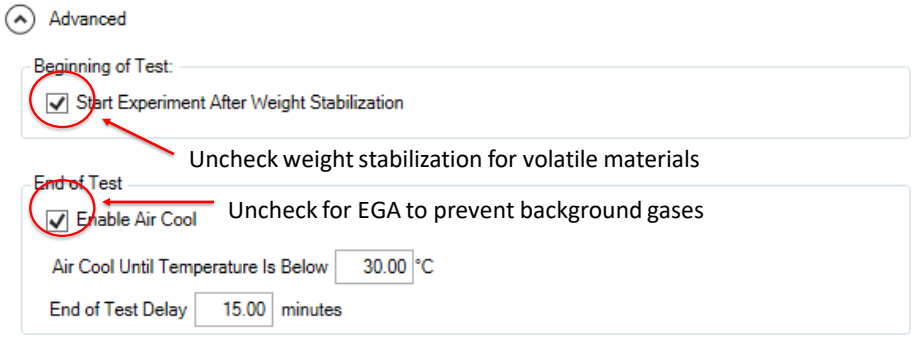
Experiment Setup



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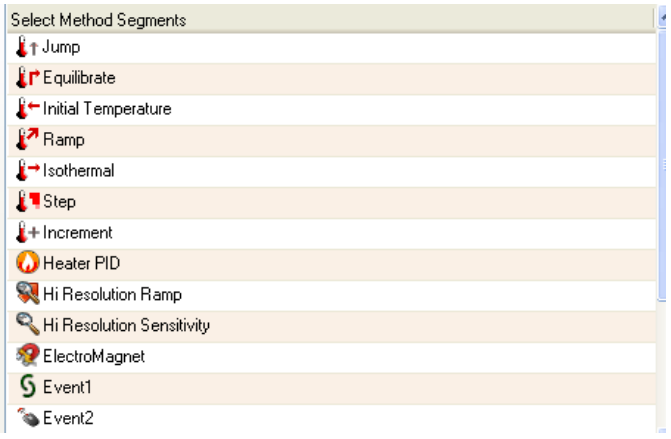
Segment Statements

- The logic of the instrument control software is based upon segment statements which the user enters during the design of the experiment
- These segments are executed during the experiment.



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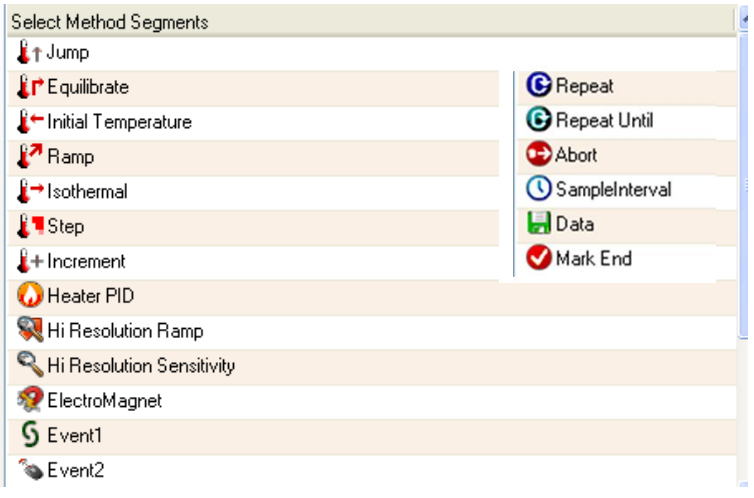
Method Segments



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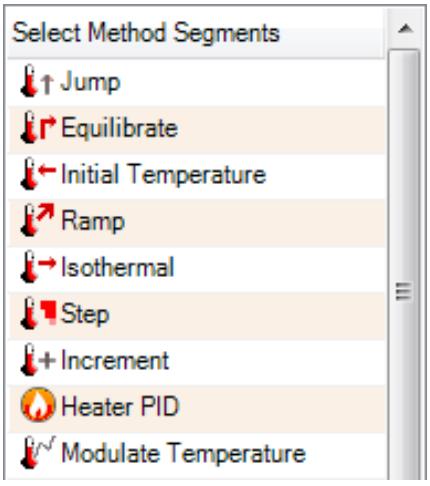
Method Design: TGA Segment List

- The Ramp segment heats or cools the sample at a fixed rate until it reaches the specified temperature, producing a linear plot of temperature versus time
- The Equilibrate segment heats or cools the furnace to the defined temperature, stabilizes the furnace at that temperature, then continues to the next segment
- The Select Gas segment controls the switching of gas between Gas 1 and Gas 2 for an instrument with a gas delivery module. This segment is used to synchronize gas switching at a specific time or temperature in an experiment



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Segments and Descriptions

Segment	Description
Abort **Abort**	The **Abort** segment skips over the next segment when specified limit conditions are met. • If the limit is reached at the beginning of a segment, then that segment is skipped and method execution continues with the next segment. • If the limit is reached during the execution of a segment, then the remaining portion of the segment is skipped. • NOTE: The **Abort** segment is generally followed by a **Ramp** or **Isothermal** segment. Example (DSC): 1. Equilibrate at 200°C 2. Abort next segment if mW>1 3. Isothermal for 100 min

Balance Mass Flow **Balance Flow Rate** (Discovery TGA only)	This segment is used to alter the rate of flow of the selected gas to the balance. Example: Flow rate 50 mL/min
Blend Gas **Blend Gas**	*Applicable to Blending GDM instruments only:* The **Blend Gas** segment allows you to select the input gas for Channel A (Gas 1 or Gas 2), a percentage to blend with Channel B (Gas 3 or Gas 4), and which input Gas to use for Channel B. • NOTE: Minimum controllable flow rate is 5 mL/min. Take this into account when specifying percentage. It may be necessary to increase overall sample flow. Example: Blend Gas 1 at 60% with Gas 3

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Segments and Descriptions

Data 	The **Data** segment controls data collection during the experiment. If a **Data** segment is not used, data storage is automatically initiated by the first **Ramp**, **Isothermal**, or **Step** segment that appears in the method. Example: Data Storage: On
Electromagnet (Discovery TGA only) 	The Discovery TGA has a magnetic coil surrounding the furnace. The **Electromagnet** segment allows you to apply a magnetic field during an experiment so that temperature calibration using Curie point standards may be performed. Example: Electromagnet: On Ramp 10°C/min to 250°C
Equilibrate 	The **Equilibrate** segment heats or cools the furnace to the defined temperature, stabilizes the furnace at that temperature, then continues to the next segment. This segment does not automatically start data collection. Example: Equilibrate at 200°C
Event 1 / **Event 2** 	The **Event** segment controls the external event relay through the event jack on the back of the instrument. This is used to synchronize control of additional hardware through the method. Example: Event 1: On

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Segments and Descriptions

Initial Temperature 	The **Initial Temperature** segment heats or cools the furnace to the defined temperature, stabilizes the furnace at that temperature, then holds the temperature until the experiment is continued by clicking **OK** on the TRIOS dialog box, or by selecting **Start** on the instrument display or instrument keypad. This segment does not automatically start data collection. Example: Initial Temperature 200°C
Isothermal 	The **Isothermal** segment holds the sample at the current temperature (as programmed by the previous segment) for a defined period of time. This segment automatically turns on data collection, except when preceded by a **Data OFF** segment. Example: Isothermal for 10 min
Jump 	The **Jump** segment instantly changes the set point temperature, causing ballistic changes in the sample temperature. This segment then allows the immediate execution of the next segment (which is usually the **Isothermal** segment). Note that large temperature overshoots may result from the use of this segment. This segment does not automatically start data collection. Example: Jump to 200°C
Mark End 	The **Mark End** segment places a marker in the data for use by the data analysis programs. In general, markers provide quick parsing of data to separate experimental segments (i.e., the heat-cool cycle). Example: Mark end of cycle 0
Mass Flow 	The **Mass Flow** segment alters the rate of flow of the selected gas when an instrument is equipped with a Gas Delivery Module (GDM). Example: Mass Flow 50 mL/min
Modulate Temperature	*Available for Modulated Instruments Only:* This segment allows you to enter the modulation temperature amplitude and period (frequency) parameters that will be used with subsequent ramp or isothermal segments. Example:

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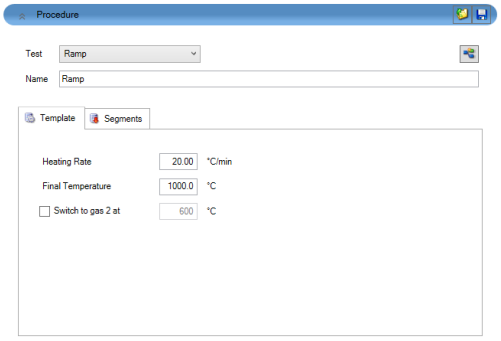
Typical Methods

- Ramp (heating) experiment:
  - Ramp 20°C/min. to 800°C
- Ramp and switch gas (carbon black content, residue)
  - Ramp 20°C/min. to 650°C
  - Select gas: 2
  - Ramp 20°C/min. to 1000°C



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What if I need help?

- TA Tech Tips
  - http://www.youtube.com/tatechtips
- TA Instruments Applications Helpline available from the TA website
  - http://www.tainstruments.com/support/applications/applications-hotline/
- Check out our Website
  - http://www.tainstruments.com/

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- For additional questions:
- Email thermalsupport@tainstruments.com
- Please put Online Training Questions in the subject line
- To download the training course: https://www.tainstruments.com/online-training-course-downloads/

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