Thermogravimetric Analysis

Advanced Techniques for Better Materials Characterisation

Philip Davies

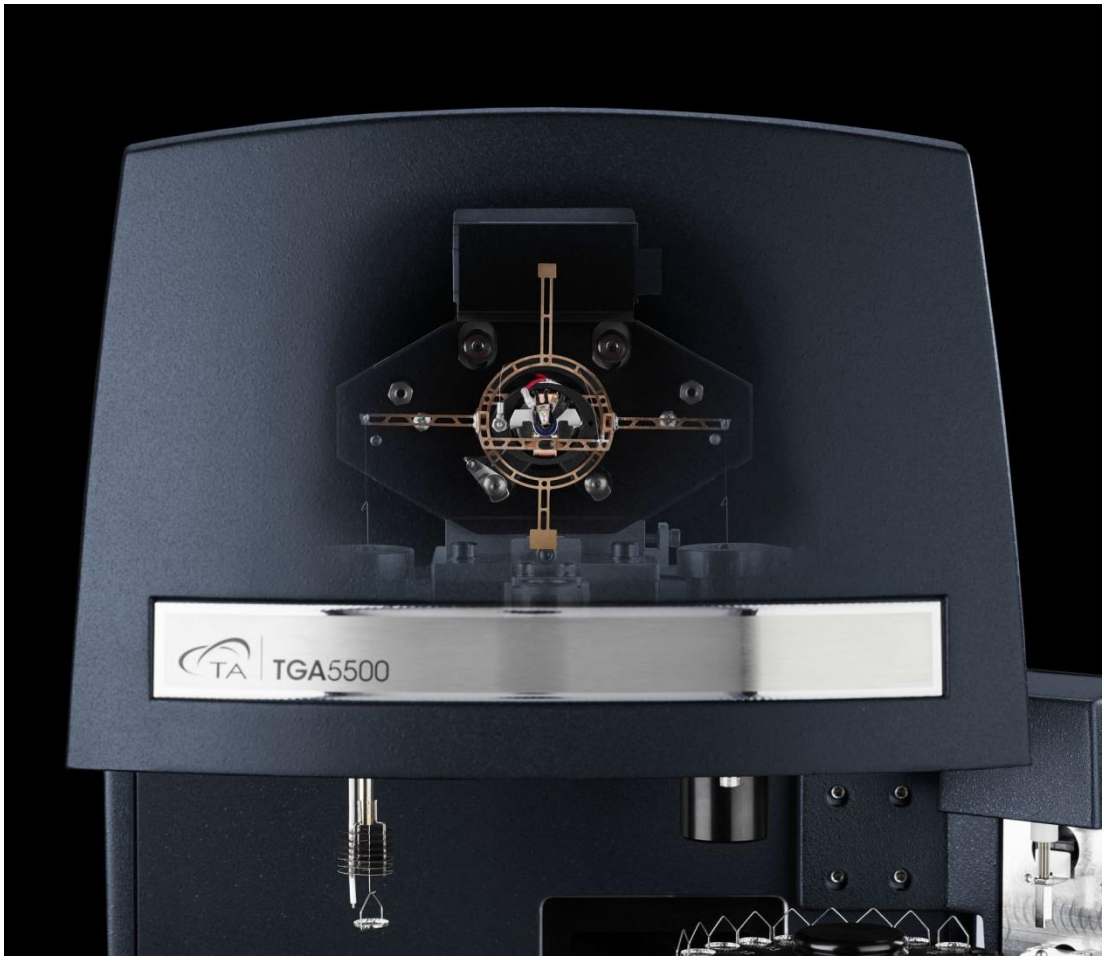
TA Instruments UK

Thermogravimetric Analysis

- Change in a samples weight (increase or decrease) as a function of temperature (increasing) or time at a specific temperature.
- Basic analysis would run a sample (~10mg) at 10 or 20°C/min
- We may be interested in the quantification of the weight loss or gain, relative comparison of transition temperatures and quantification of residue.
  - These values generally represent the gravimetric factors we are interested in.
    - Decomposition Temperature
    - Volatile content
    - Composition
    - Filler
    - Residue
    - Soot
    - ……

Discovery TGA 55XX

Discovery TGA 55XX Null Point Balance



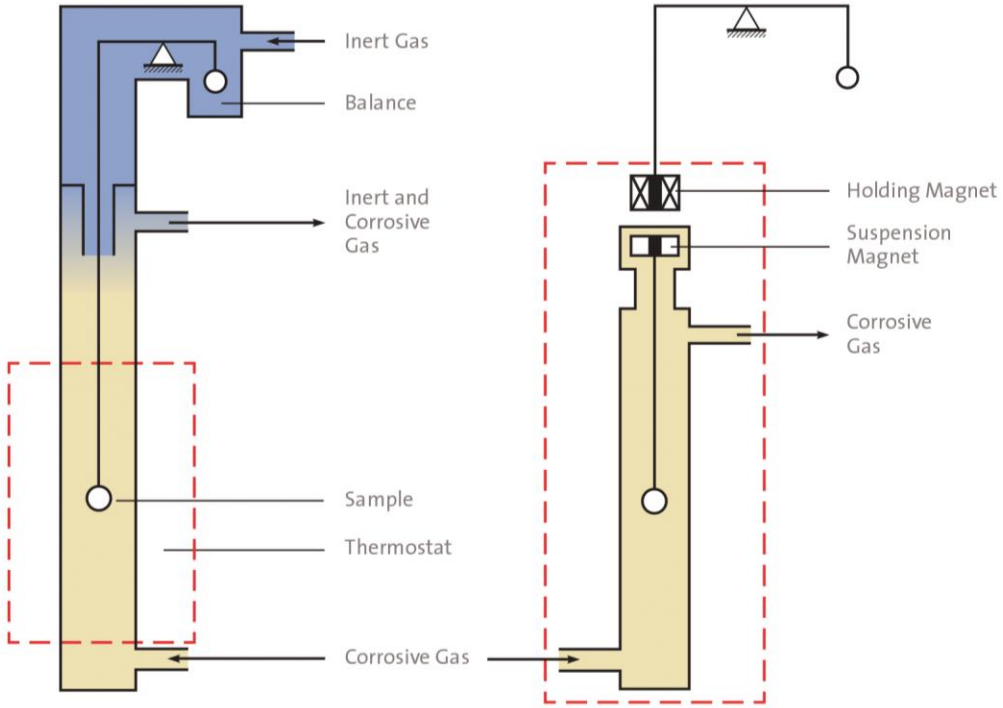
Vapour Sorption

- Technique associated with TGA
- Looking at the sorption and desorption of a vapour species on a material.
- Generally think about water vapour (humidity) but can also look at solvent vapours or other gas species (eg CO, CO_2, NO_x, SO_x)

Vapour Sorption Systems

Rubotherm – Magnetic Suspension Balance

Allowing sorption studies at elevated pressures. Isolation of the balance means studies with corrosive gasses is much easier.

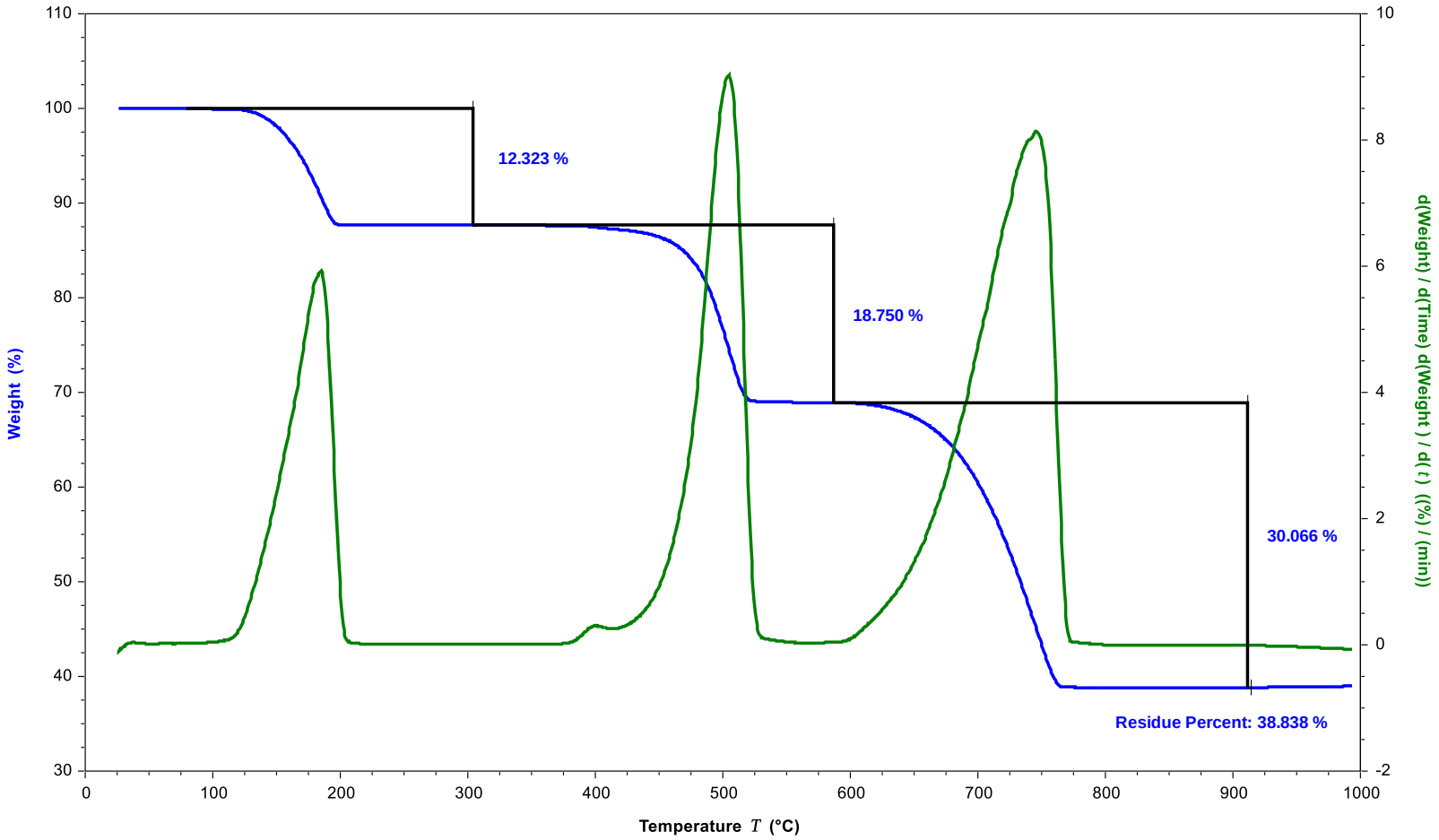


Mechanisms of Weight Change in TGA

- **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).

Typical Data – Calcium Oxalate Monohydrate



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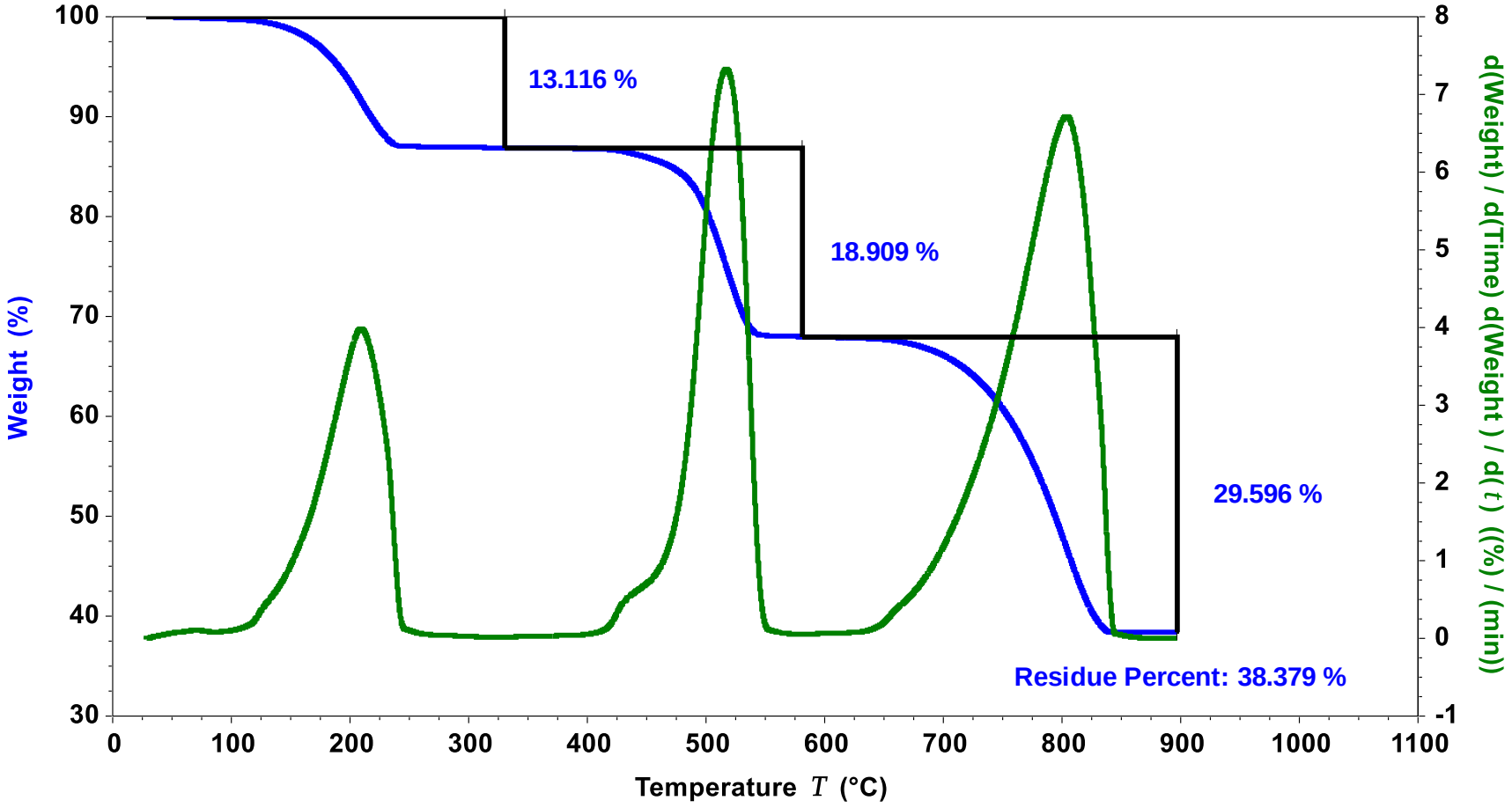
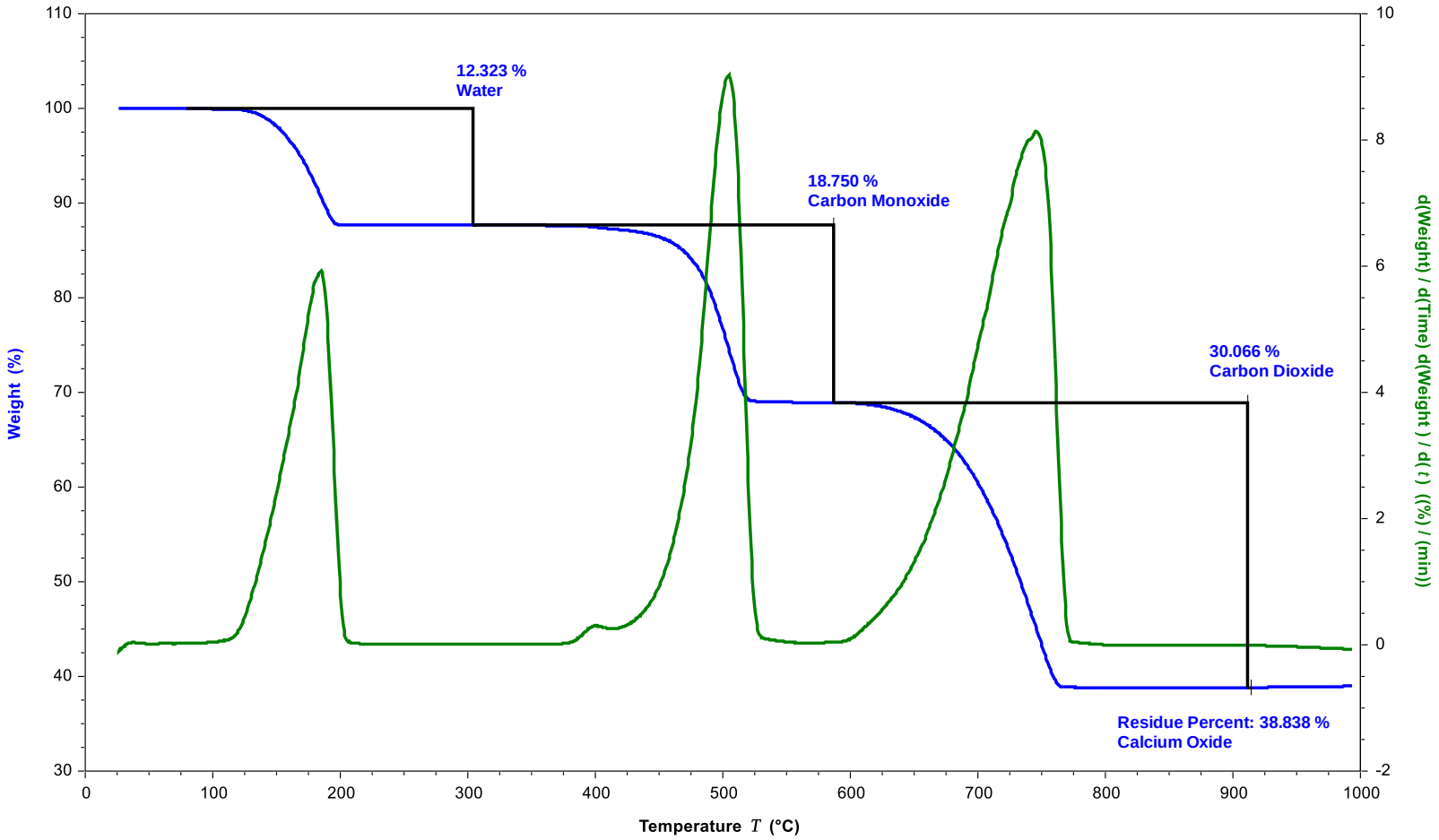


Knowledge of Volatiles



Decomposition Mechanism

$$CaC_2O_4.H_2O\ (s)$$

$$\xrightarrow{\Delta} CaC_2O_4\ (s) + H_2O\ (g)$$

$$\xrightarrow{\Delta} CaCO_3\ (s)\ + CO\ (g)$$

$$\xrightarrow{\Delta} CaO\ (s) + CO_2\ (g)$$

The “nice” samples

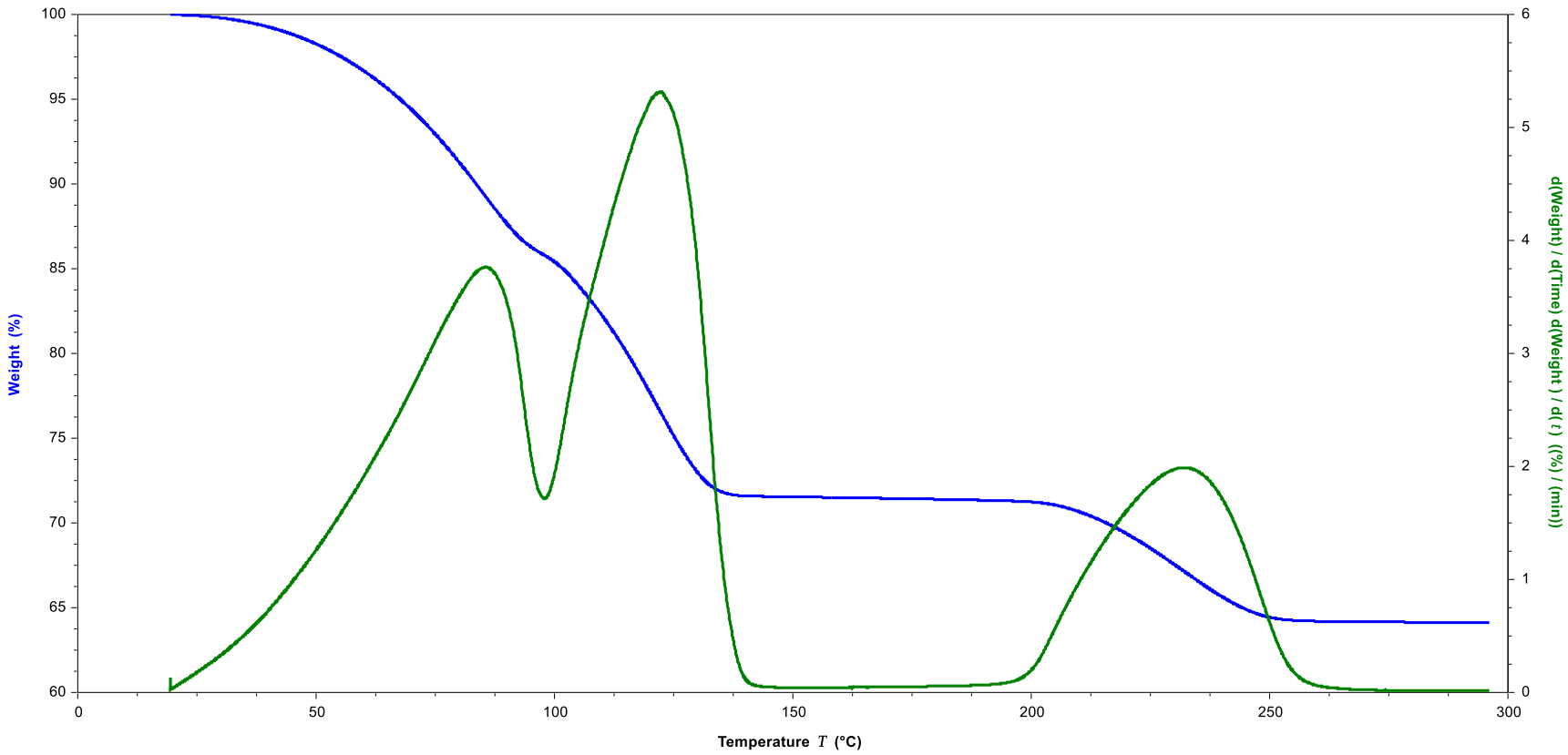
- Calcium Oxalate is one of those nice samples where (for the most part) where the mass losses are separated so analysis of each weight change is achieved easily.

The “not so nice” samples

- Other samples are not so straight forward and weight loss steps may overlap.

- General approaches to increasing resolution include:
  - Slowing down the ramp rate
    - Increase in test time.
  - Reducing sample mass
    - May give issues with sensitivity (sample depending)
  - Reducing particle size
    - Care that sample behaviour is not changed.

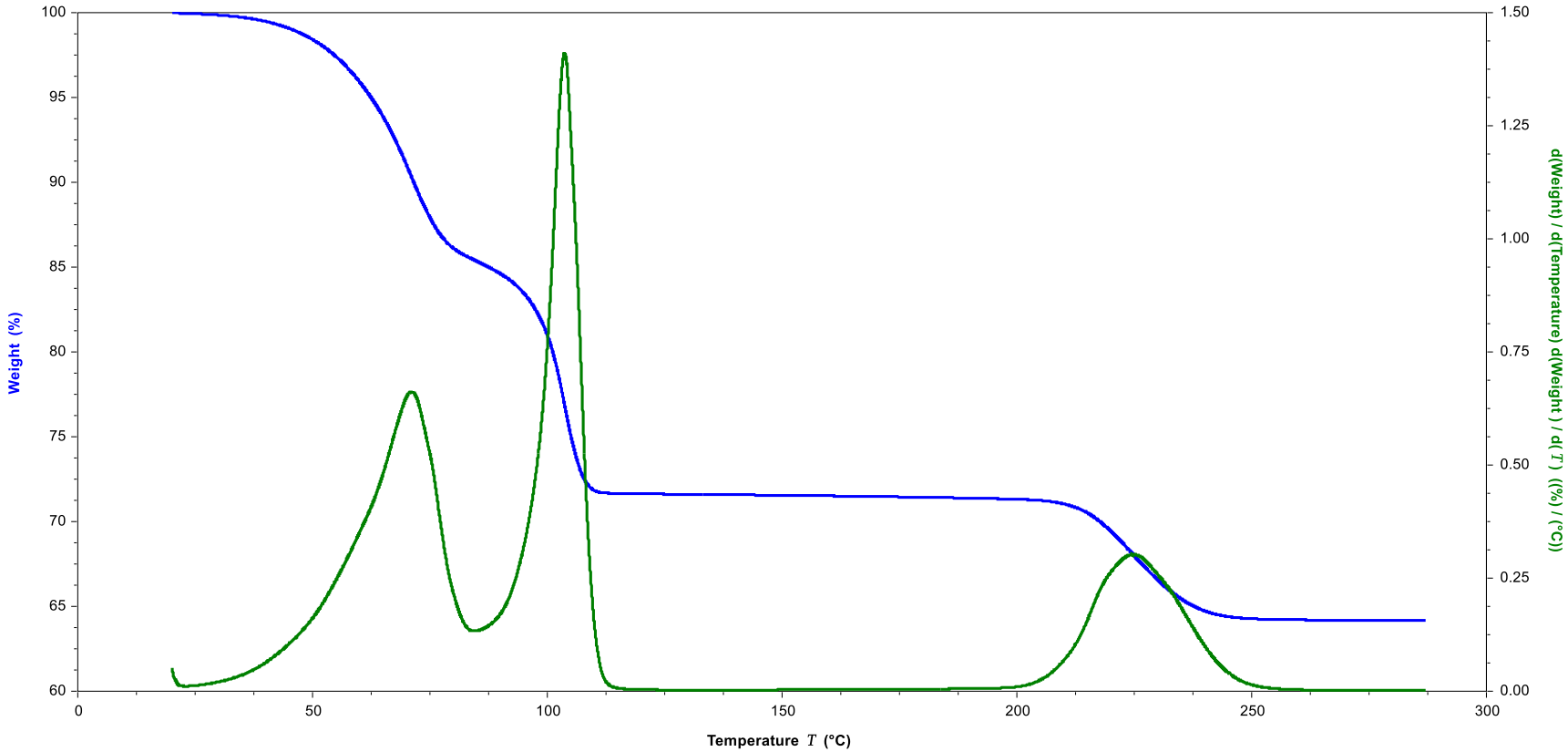
Copper Sulphate Pentahydrate @ 10°C/min



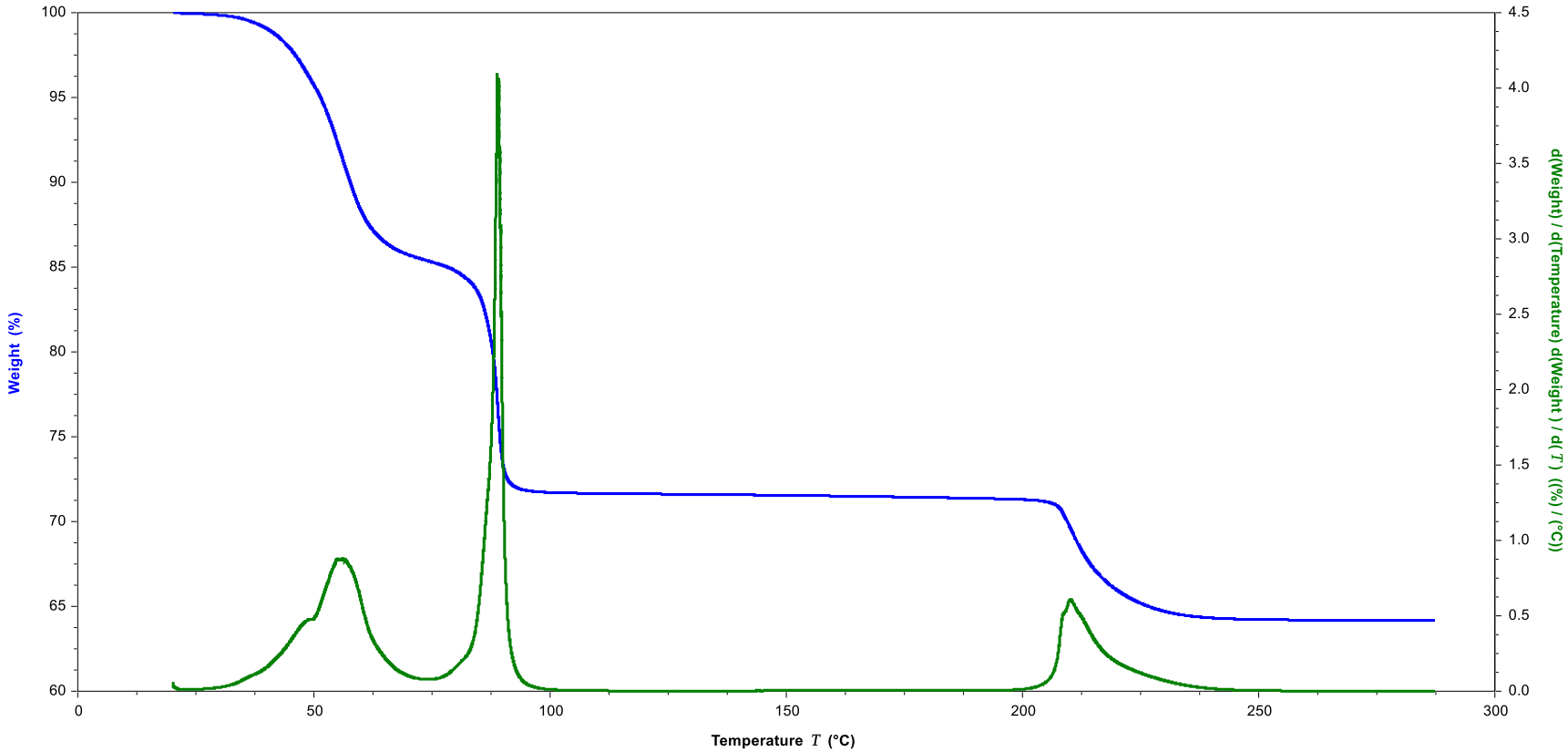
Dynamic Hi-Res TGA

- Part of the sample controlled thermal analysis techniques.
- Heating rate is controlled by the rate of weight loss.
  - Greater the rate of weight loss, the slower the heating rate.
  - Three factors in the experiment
    - Maximum heating rate (M) – heating used with no mass loss.
    - Resolution (R) – at what point in the weight loss is the heating rate reduced.
    - Sensitivity (S) – how quickly the heating rate is reduced.

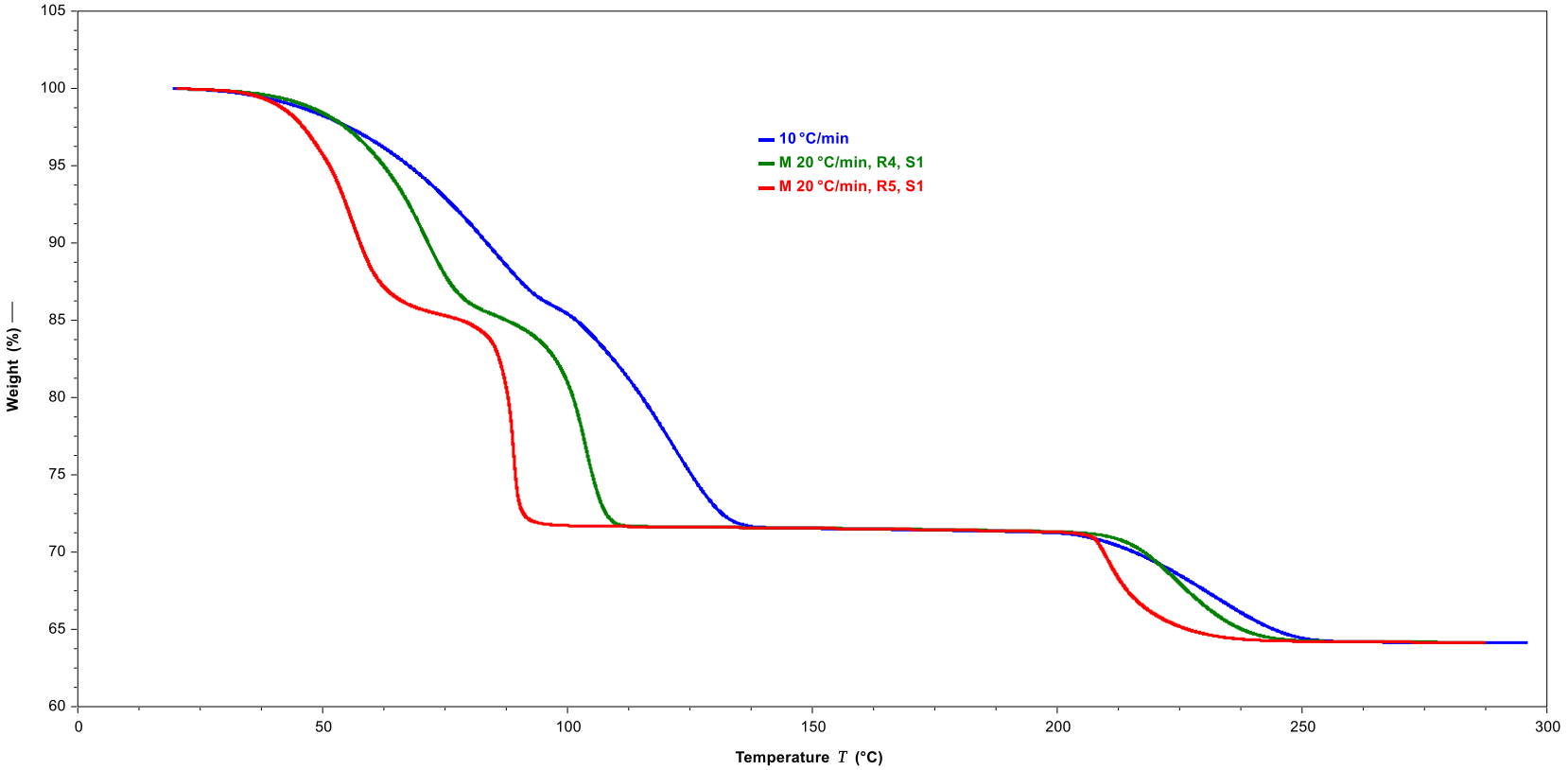
Copper Sulphate Pentahydrate M20,R4,S1



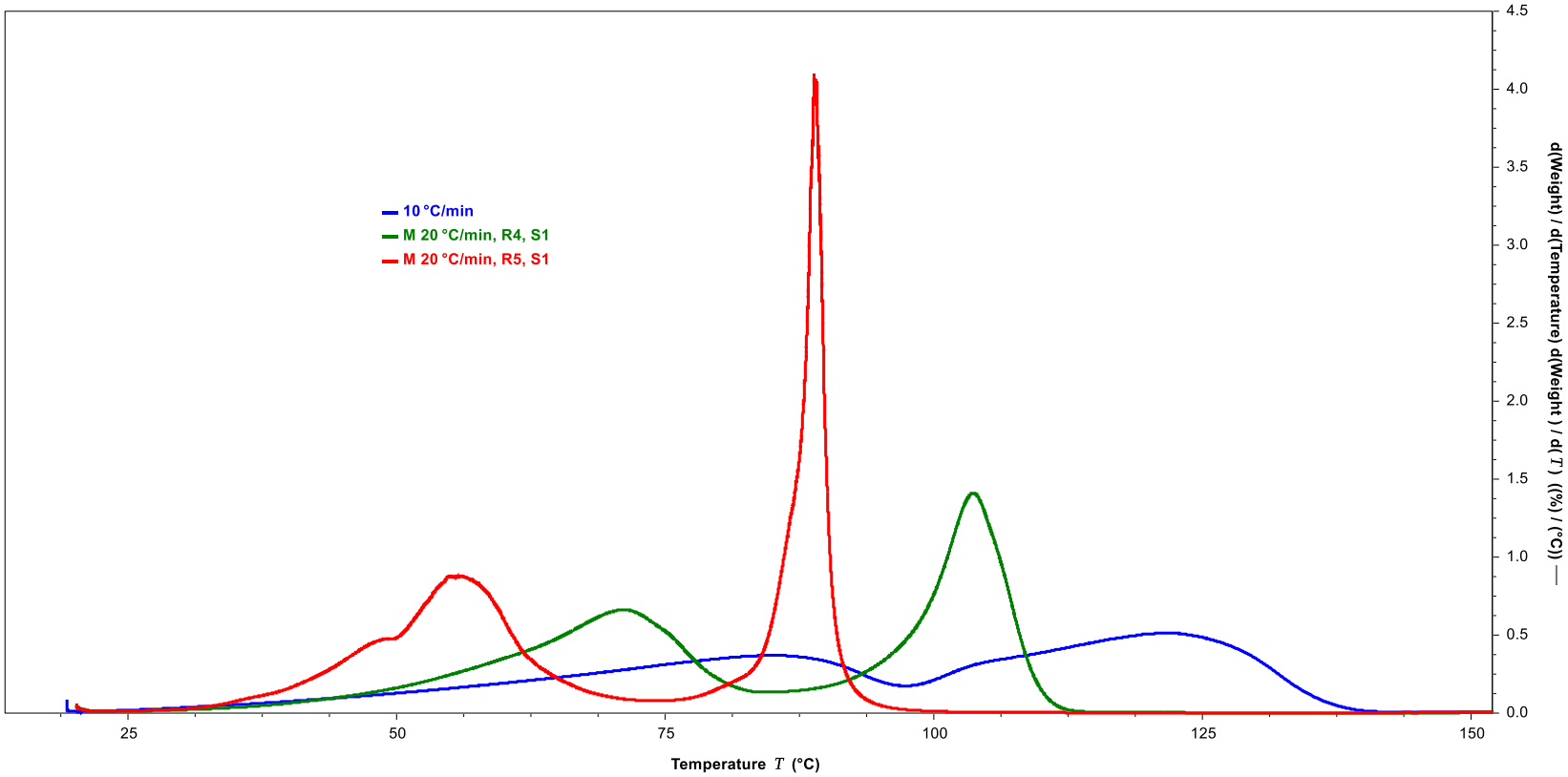
Copper Sulphate Pentahydrate M20,R5,S1



Data Overlay



Derivative Overlay

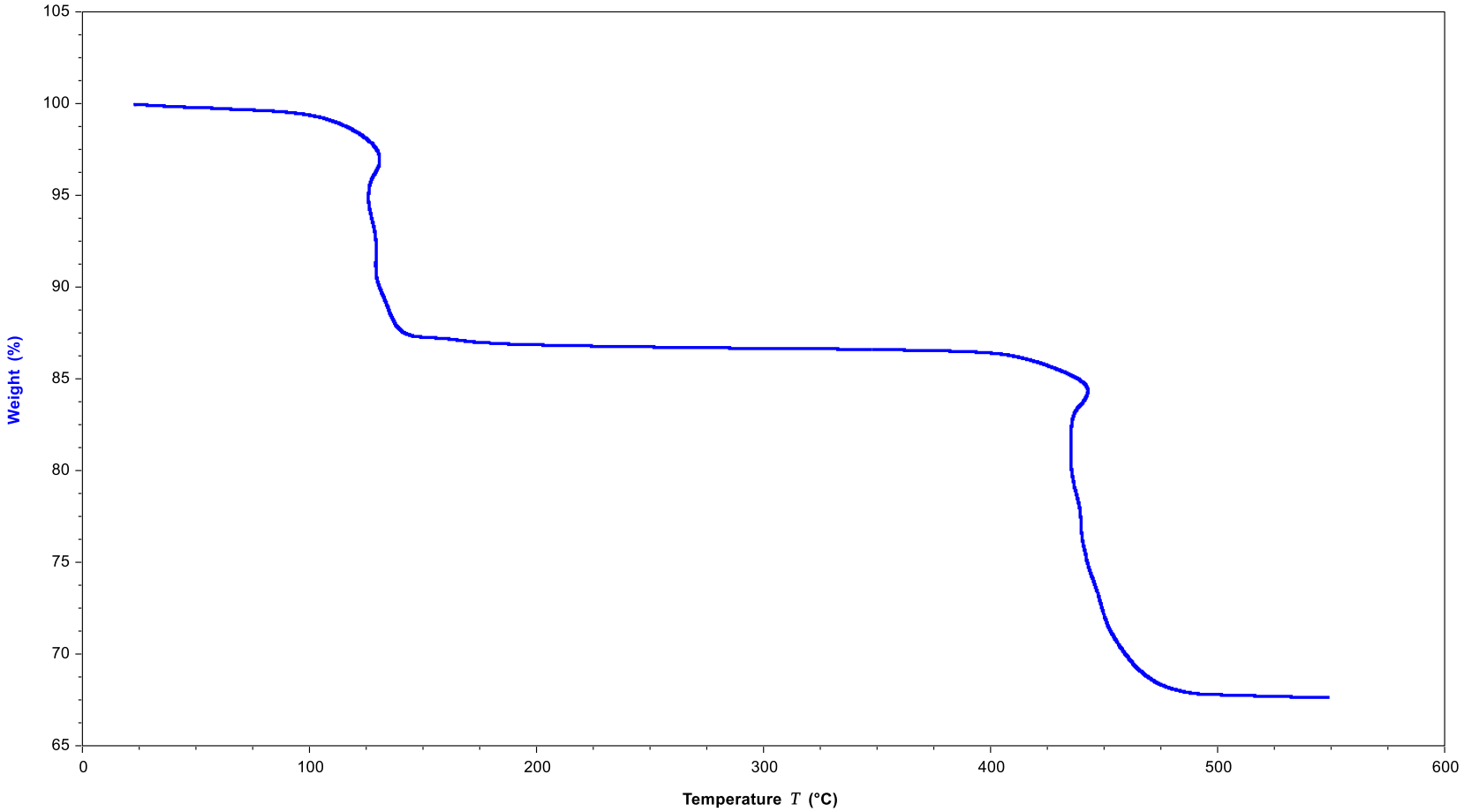


Constant Reaction Rate

- Allow the user to specify the rate of weight loss (or gain) that should be achieved. System can change the heating rate (up to a specified maximum value) or even cool to control the rate of weight loss.

- Three factors in the experiment
  - Maximum heating rate.
  - Resolution – what rate of weight loss / gain should be achieved.
  - Sensitivity – defines at what point the heating rate should reduce. Higher numbers cause the heating rate to decrease earlier in the decomposition and minimize temperature overshoot.

Controlled weight loss requested = 0.316%/min (Calcium Oxalate Monohydrate)



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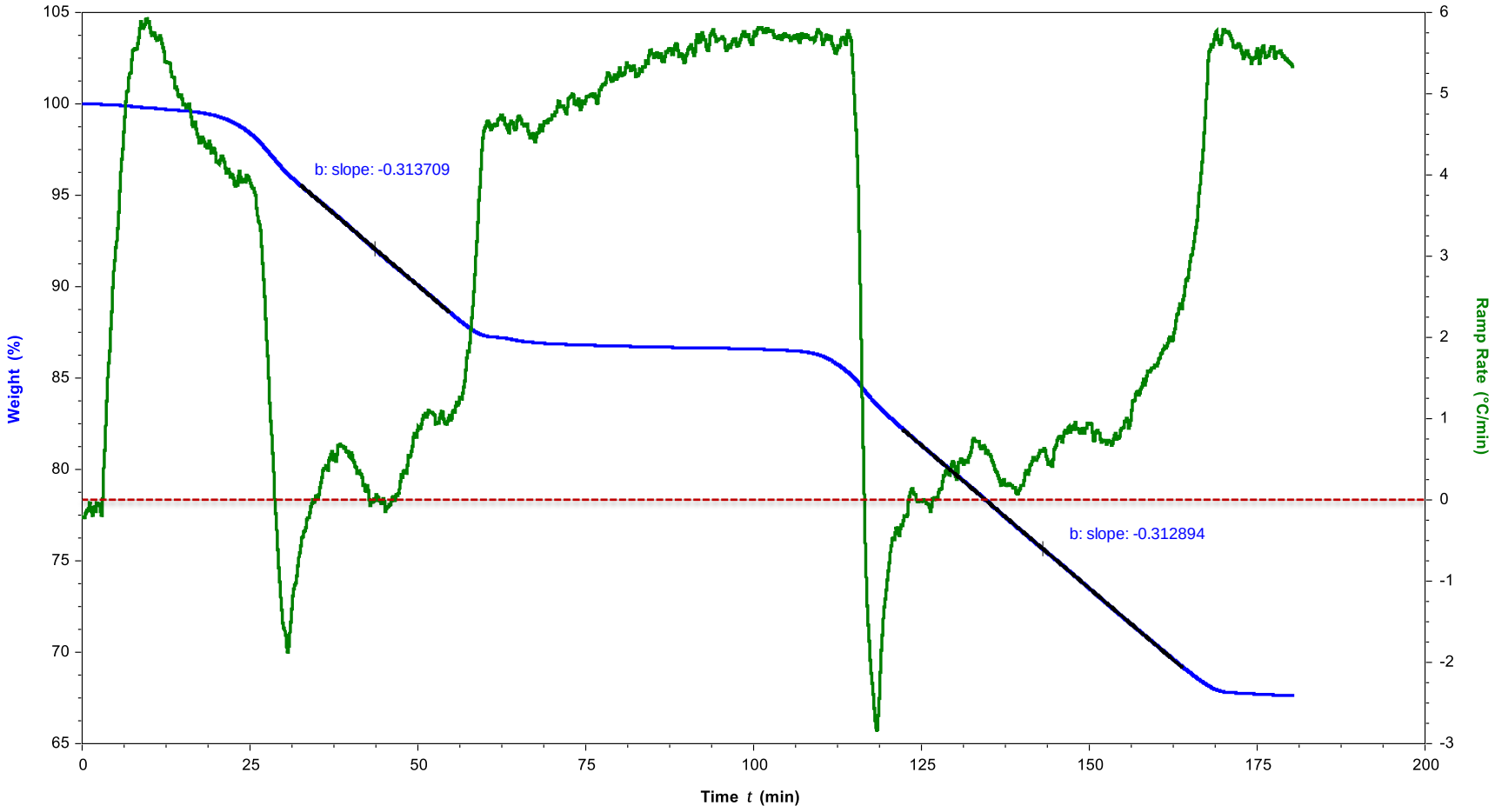


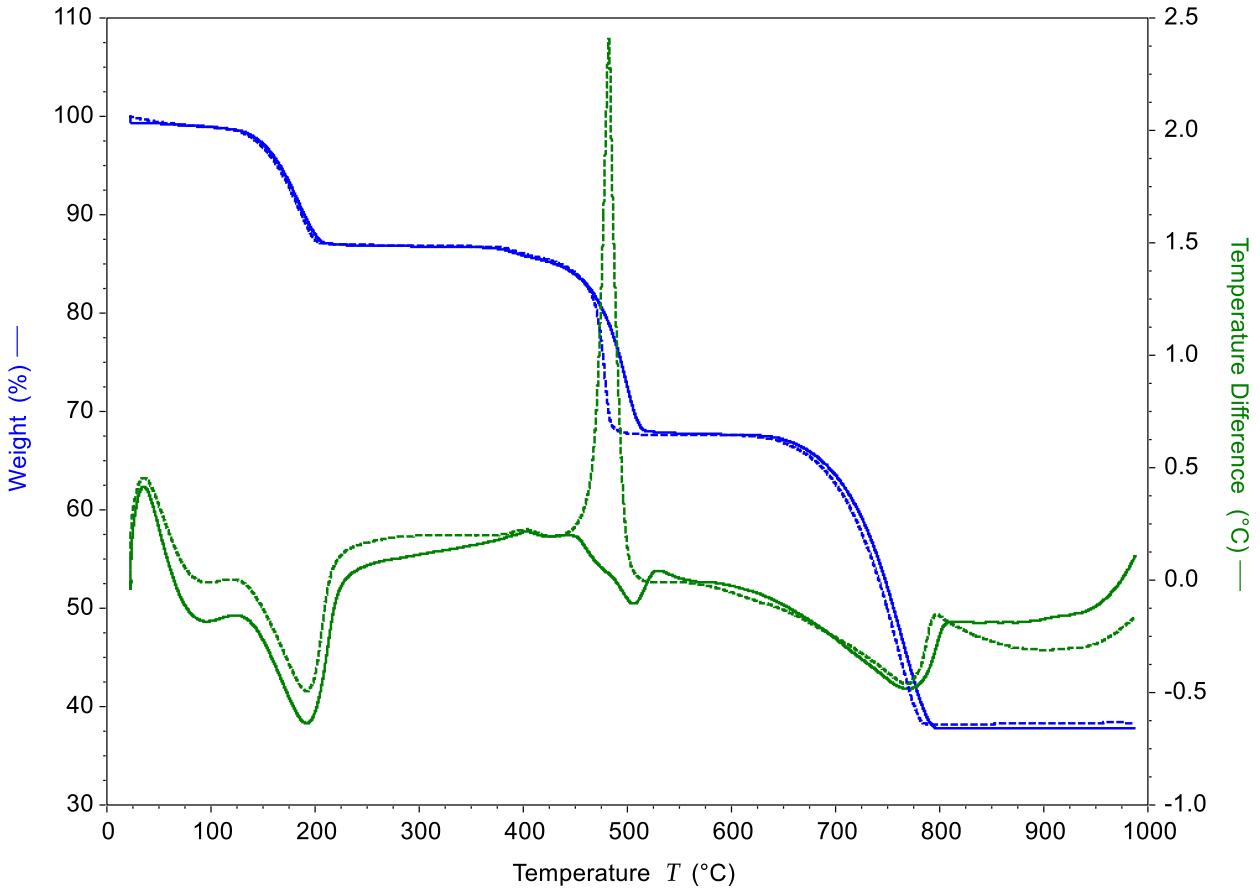
Additional Information

- Gravimetric techniques are giving the information of the weight losses or gains in the material.
- Ability to measure a deviation in the samples temperature from the control temperature (DTA) will allow identification of the endo- or exothermic nature of the transition.
- Analysis of volatiles released (eg via Mass Spectroscopy or Fourier Transform Infrared Spectroscopy) will increase the information or help in following processes.

Differential Thermal Analysis

- Thermocouple positioning allows the temperature response of the sample to be compared against a furnace reference temperature.

Calcium Oxalate – Air and Nitrogen



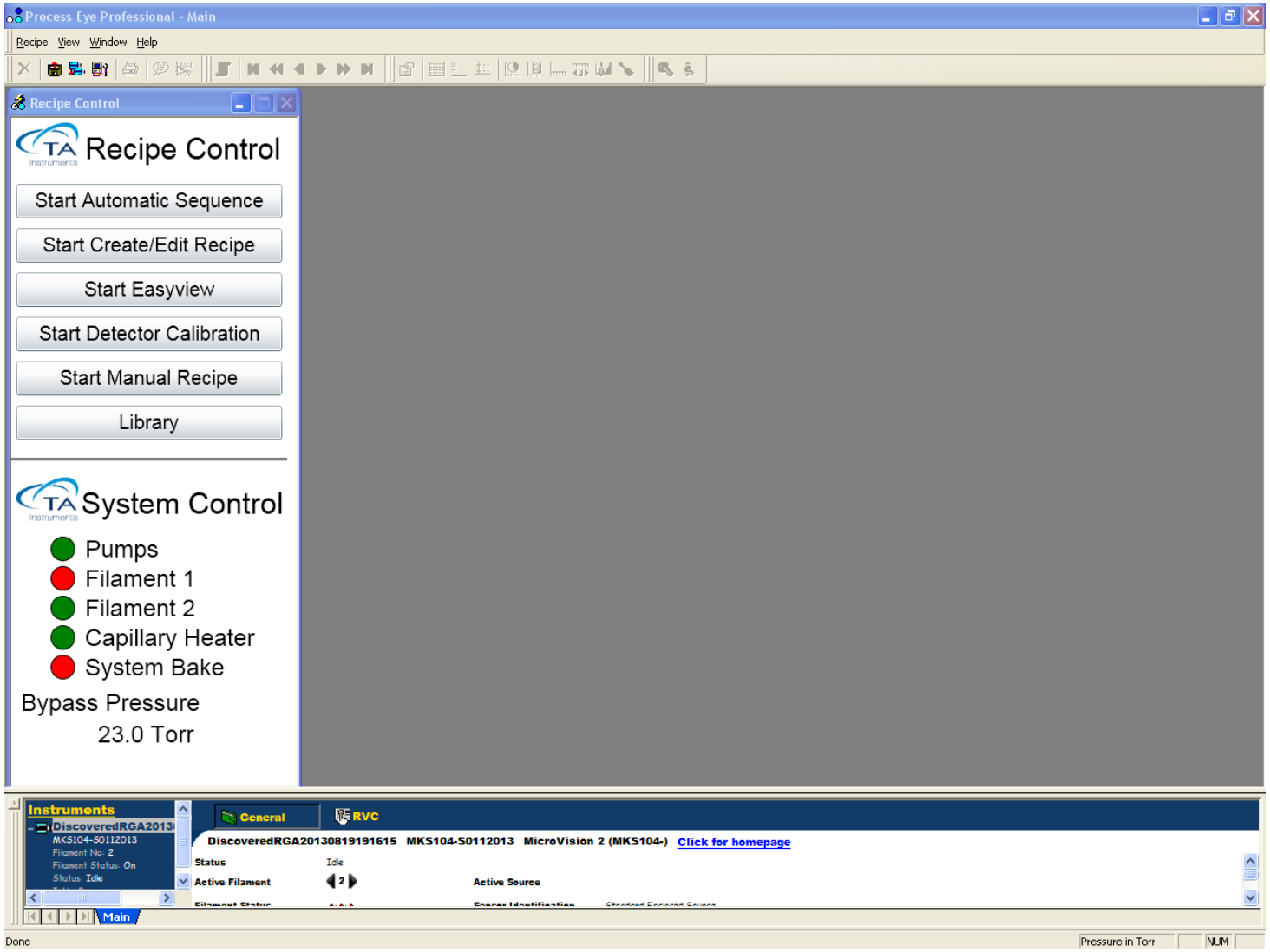
Evolved Gas Analysis

- Volatiles from the TGA process are sampled via a heated transfer line into the spectroscopic process.
- MS & FTIR allow continuous sampling of the gas stream.

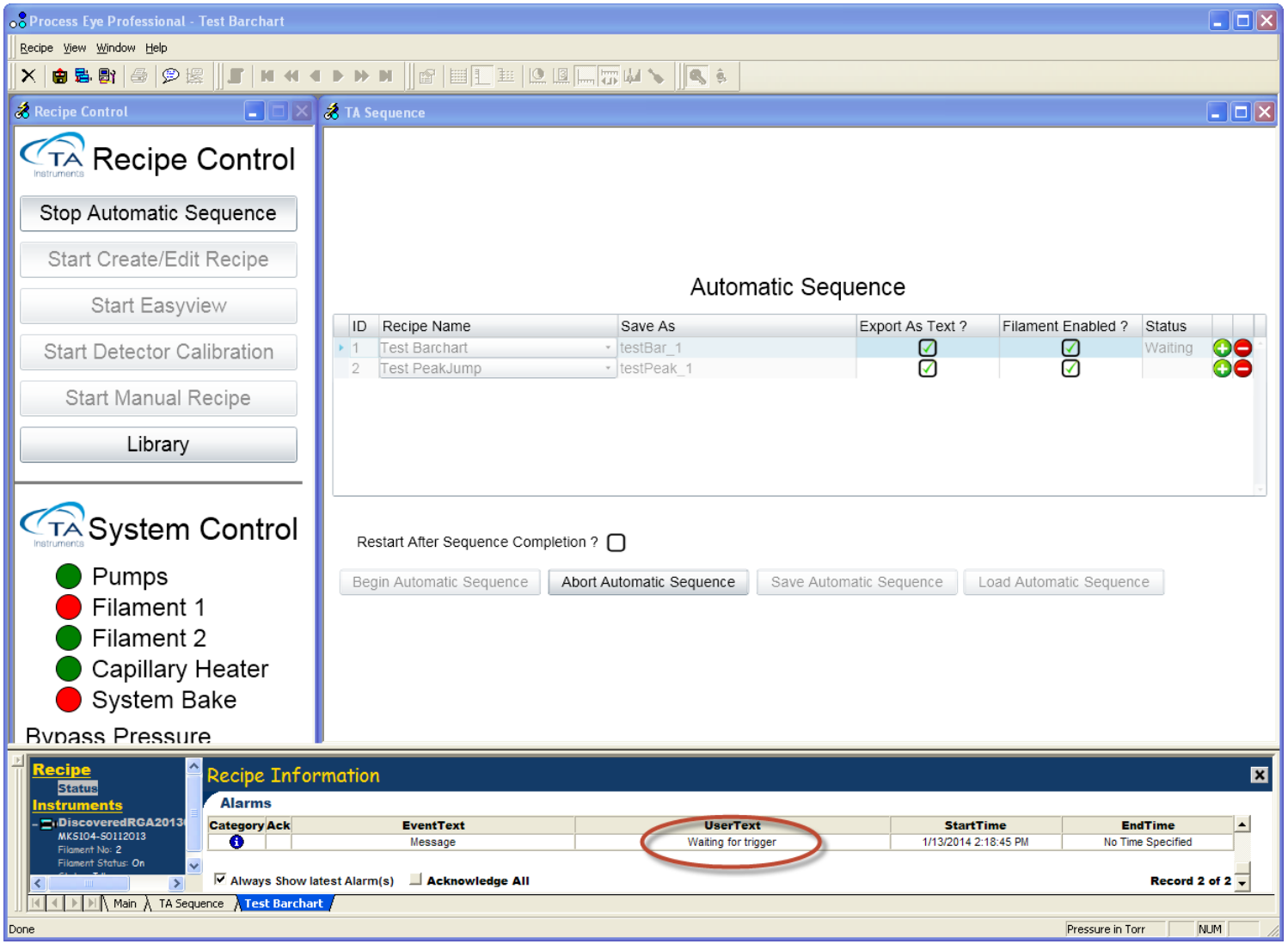
TGA: Why Use Evolved Gas Analysis ?

- TGA measures weight changes (quantitative)
- Difficult to separate, identify, and quantify individual degradation products (off-gases) or reaction products.
- Direct coupling to identification techniques (MS, FTIR) reduces this problem

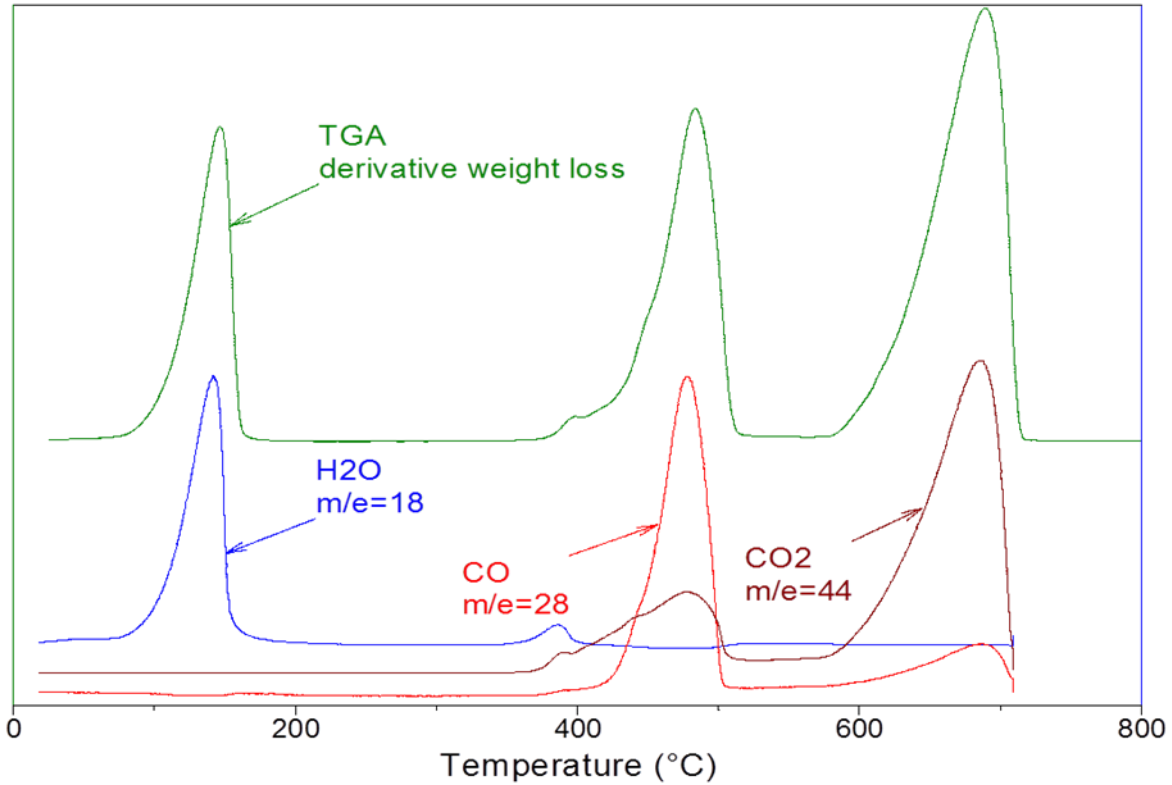
Software – Process Eye Software



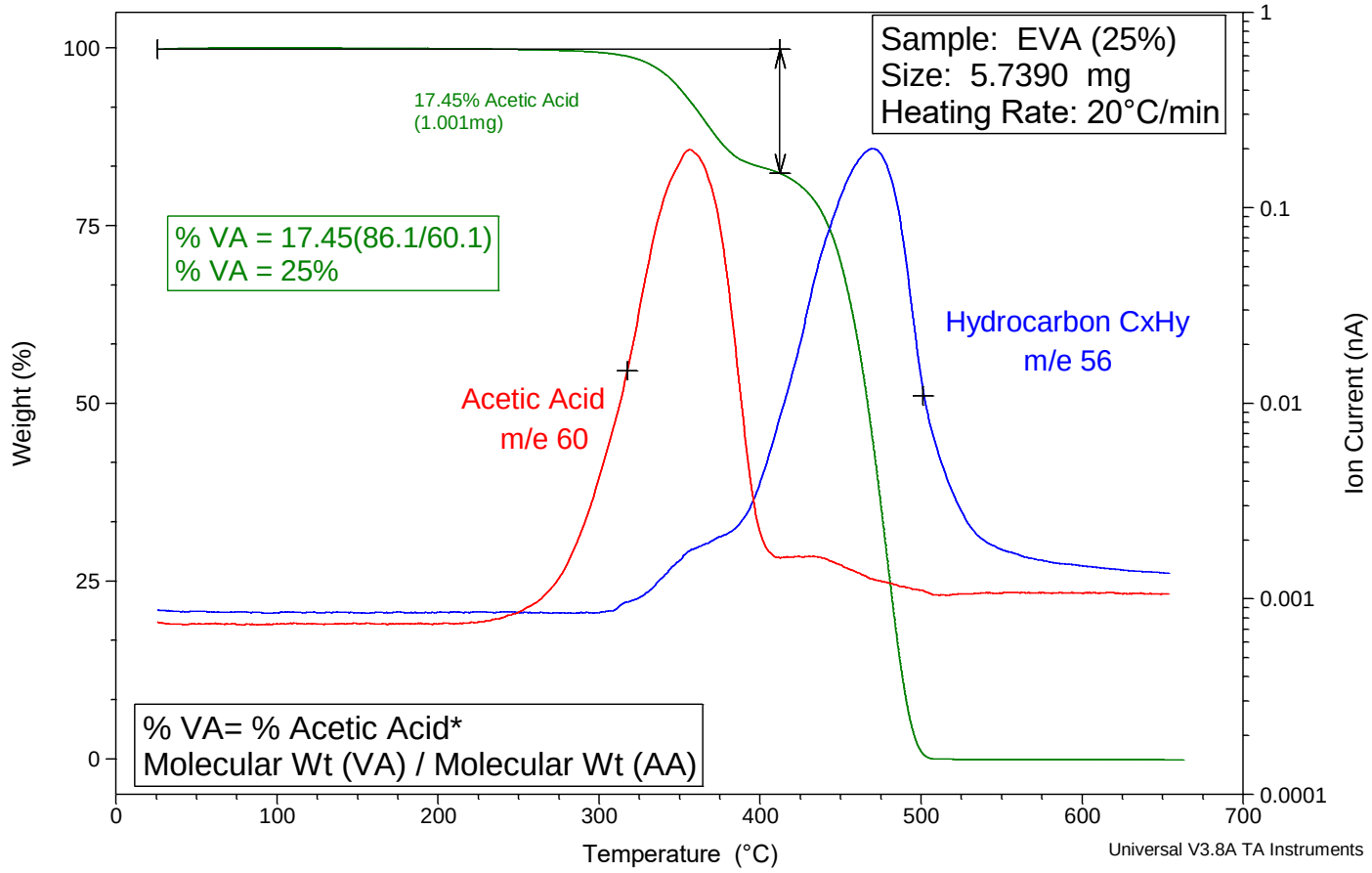
Software – Start Automatic Sequence



TGA-MS Calcium Oxalate

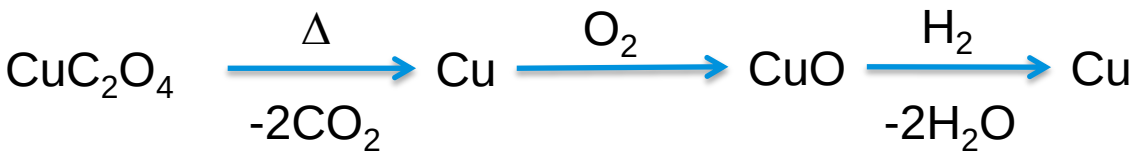


Compositional Analysis by TGA-MS

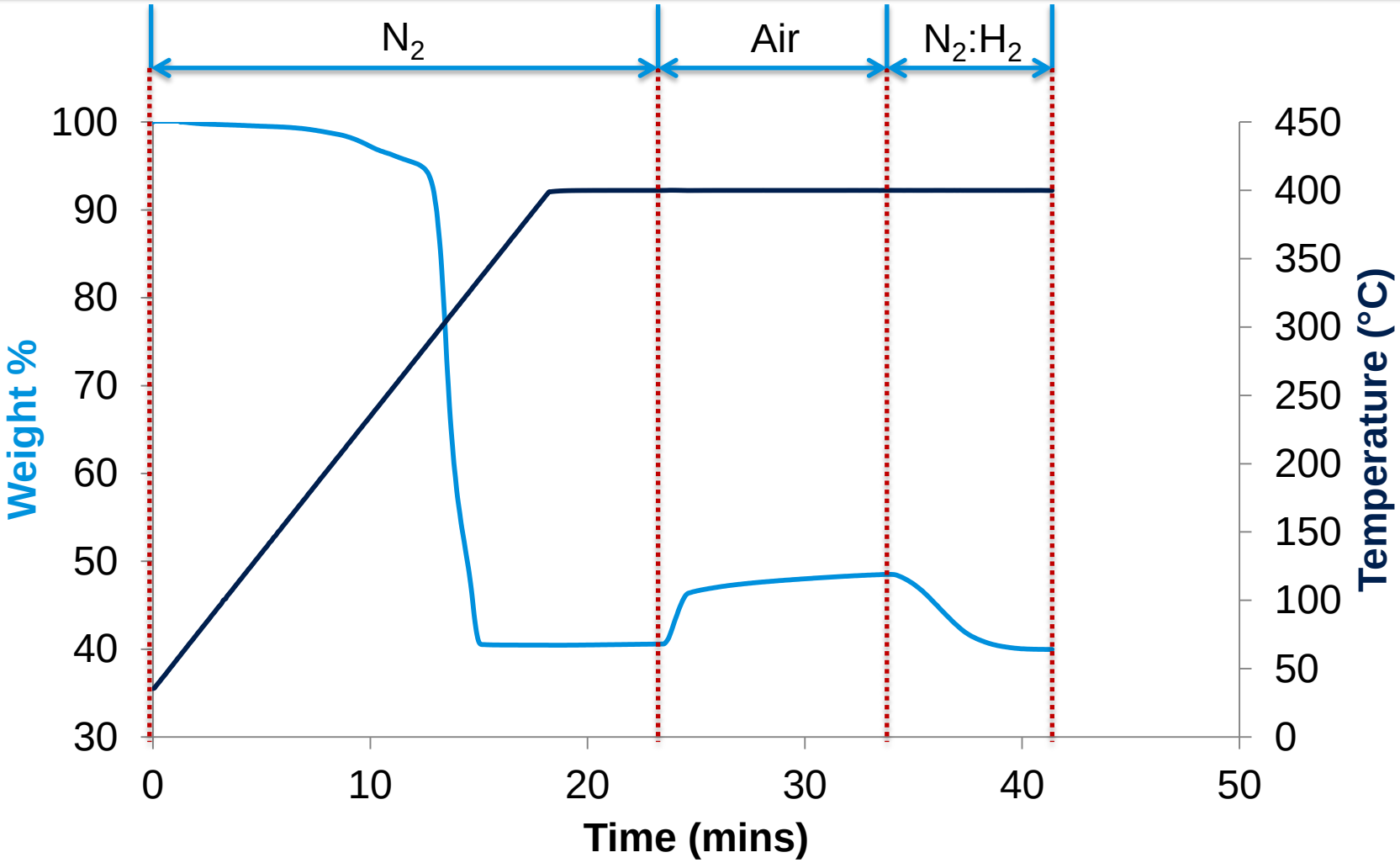


TGA-MS Example – Copper Oxalate

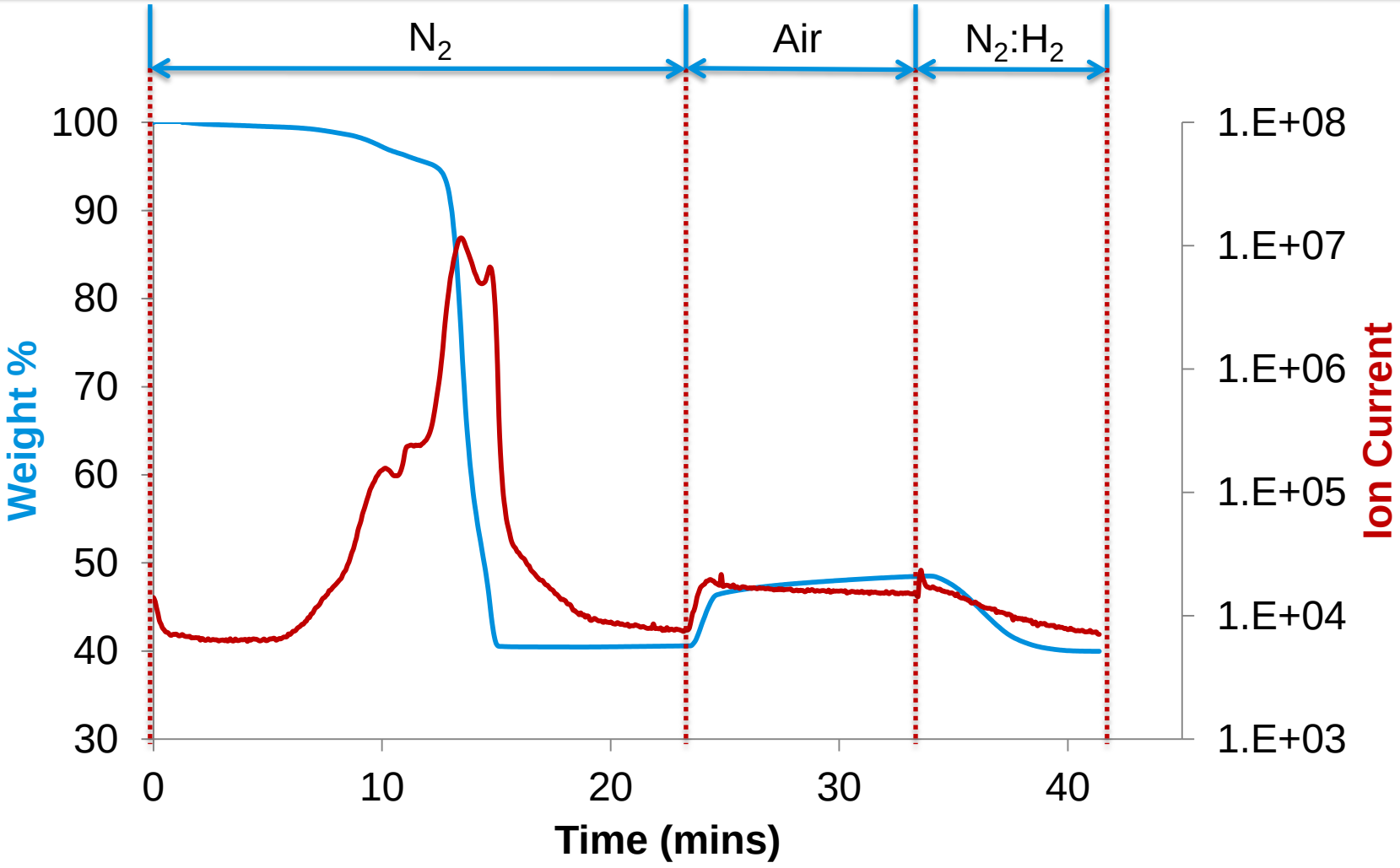
- In the presence of an inert gas Copper Oxalate will decompose to Copper, any oxygen introduced will then result if the formation of copper oxide.
- Use of forming gasses (eg 5% hydrogen in nitrogen) will then reduce the copper oxide back to copper.



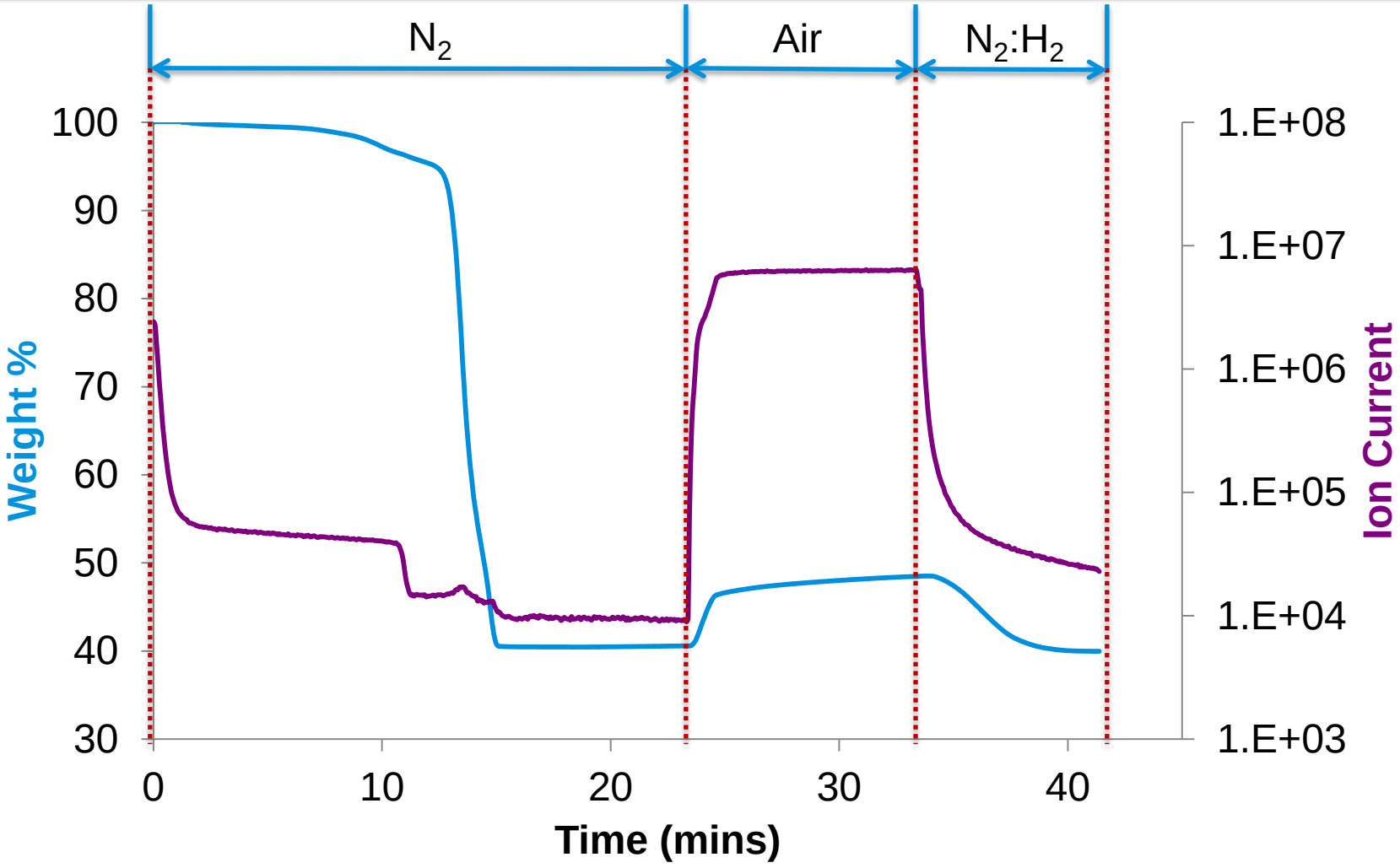
TGA Experiment



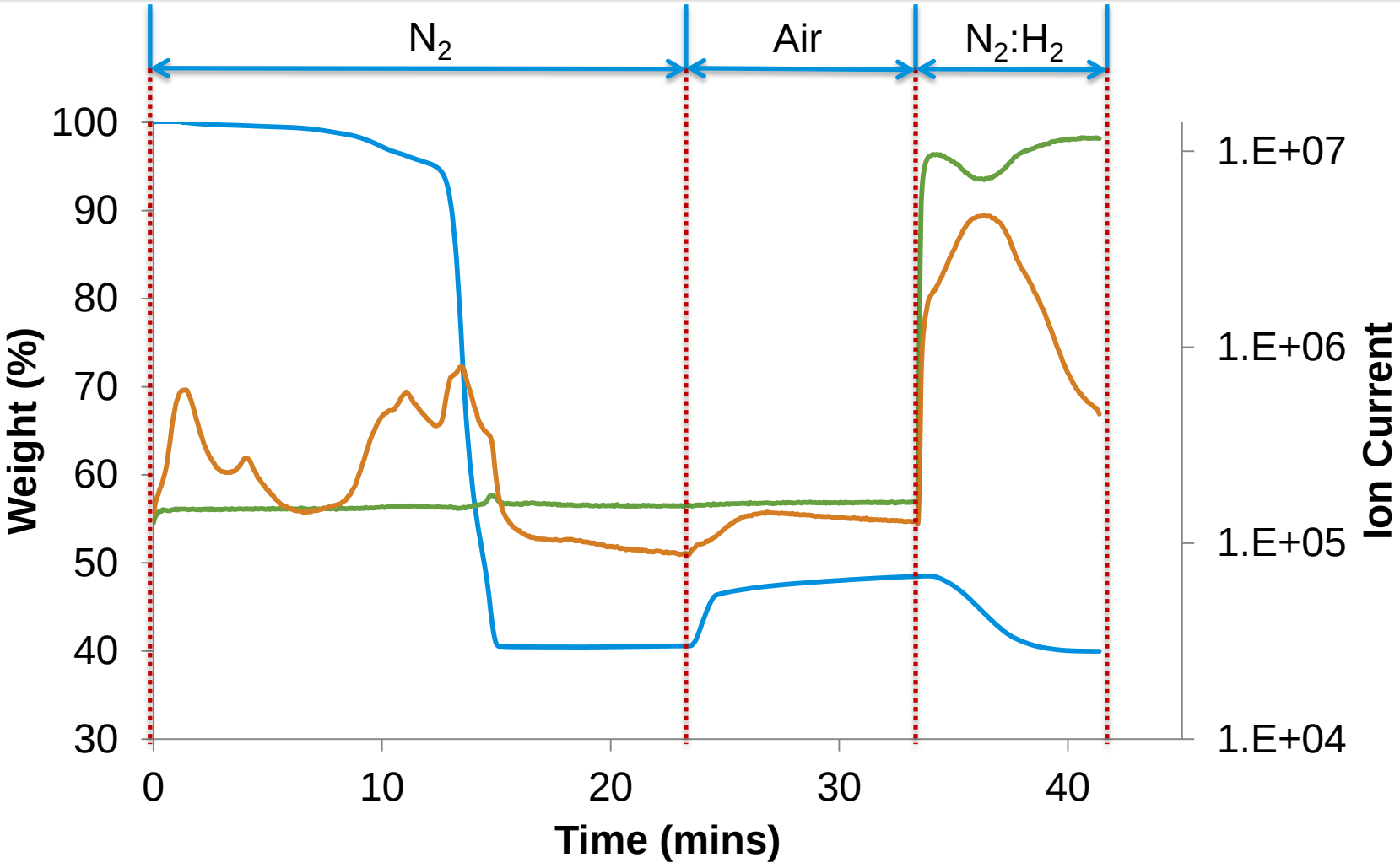
TGA/MS (m/z = 44 (CO_2))



TGA/MS (m/z = 32 (O_2))



TGA/MS (m/z = 2 (H_2), m/z = 18 (H_2O))

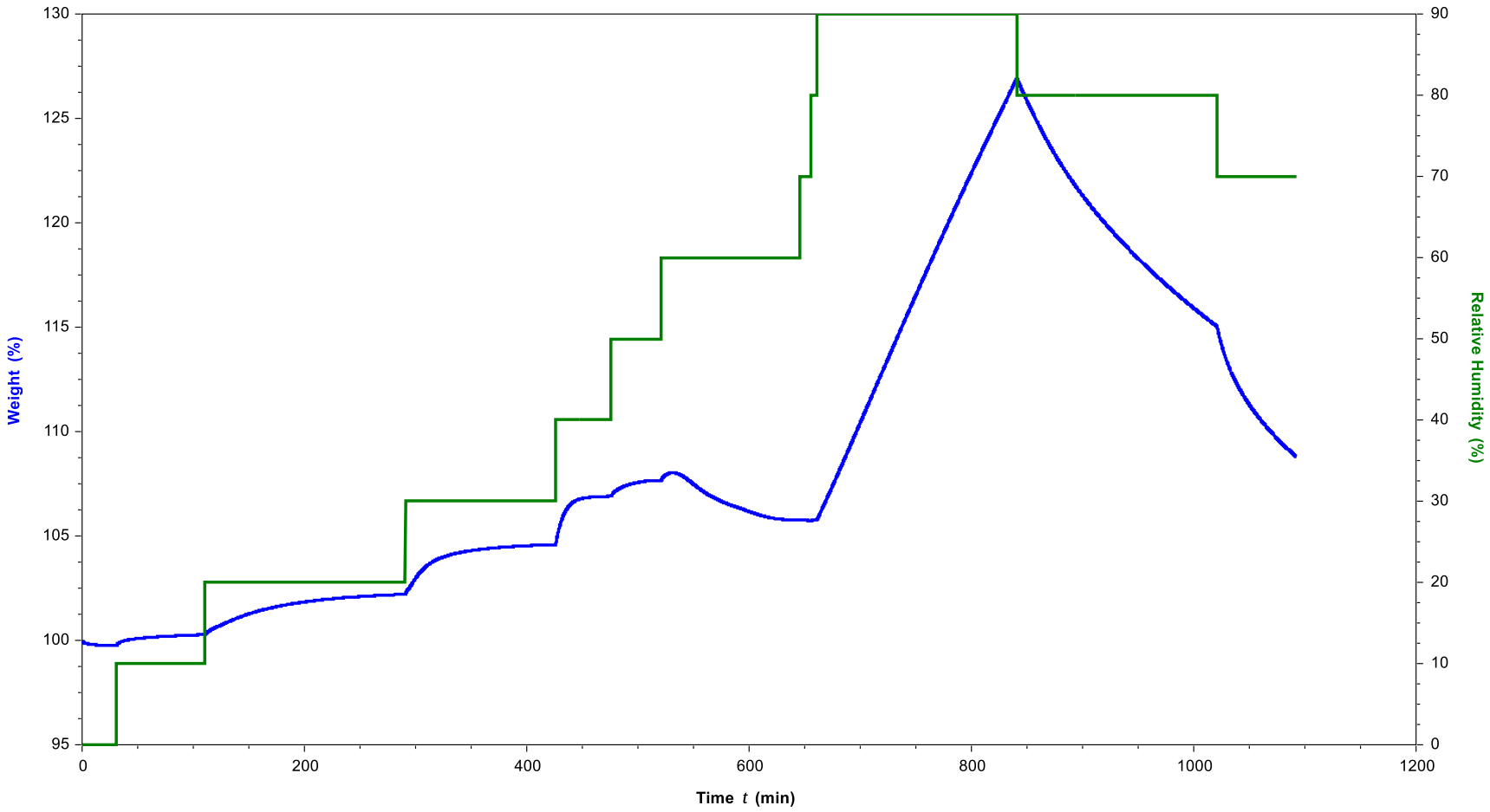


Vapour Sorption

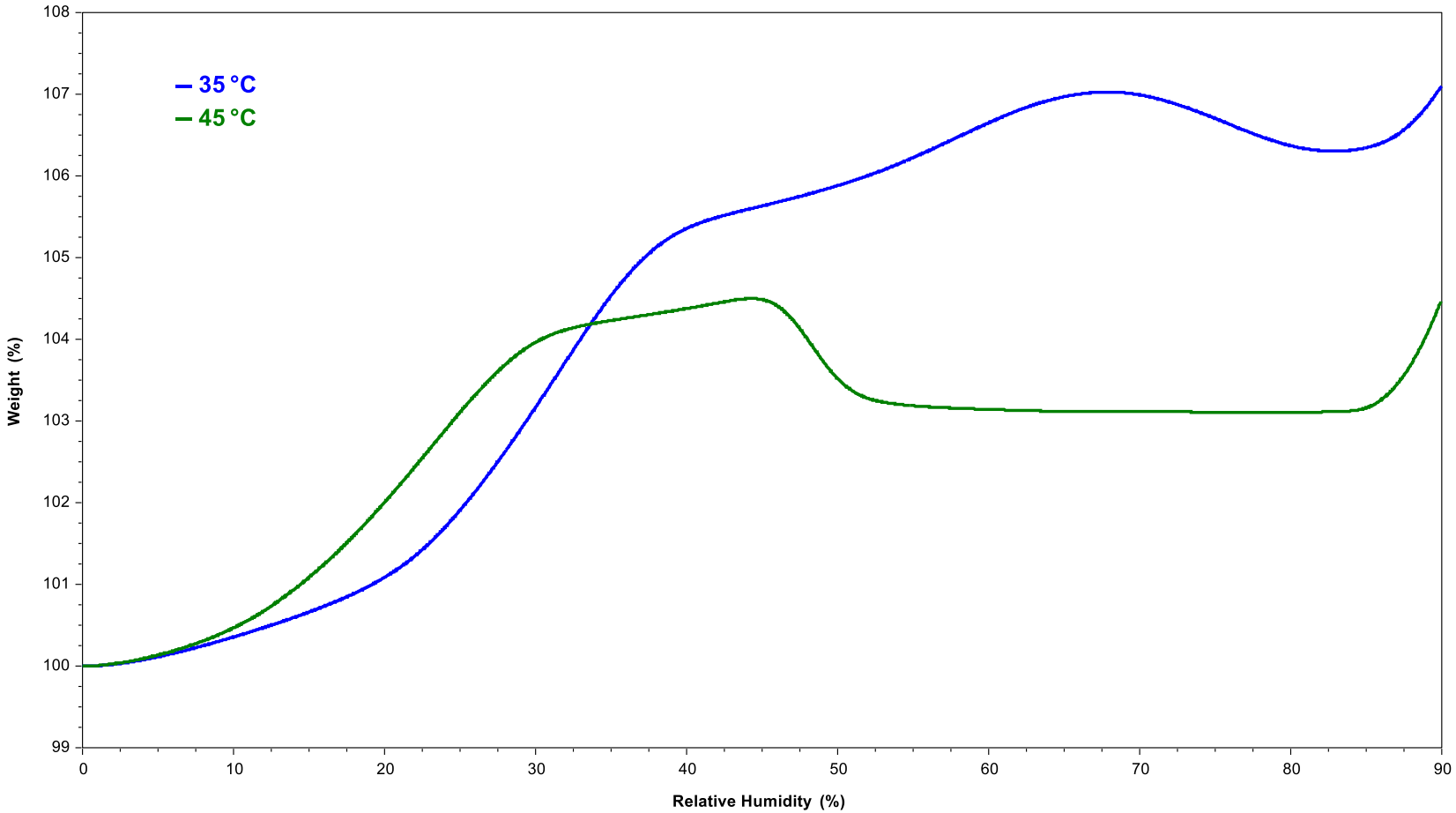
- Typical tests will run isothermally with a stepped humidity, waiting for weight equilibrium at each humidity level.

- Ability to ramp the temperature (constant humidity) or ramp humidity (constant temperature) allow us to make further investigations.

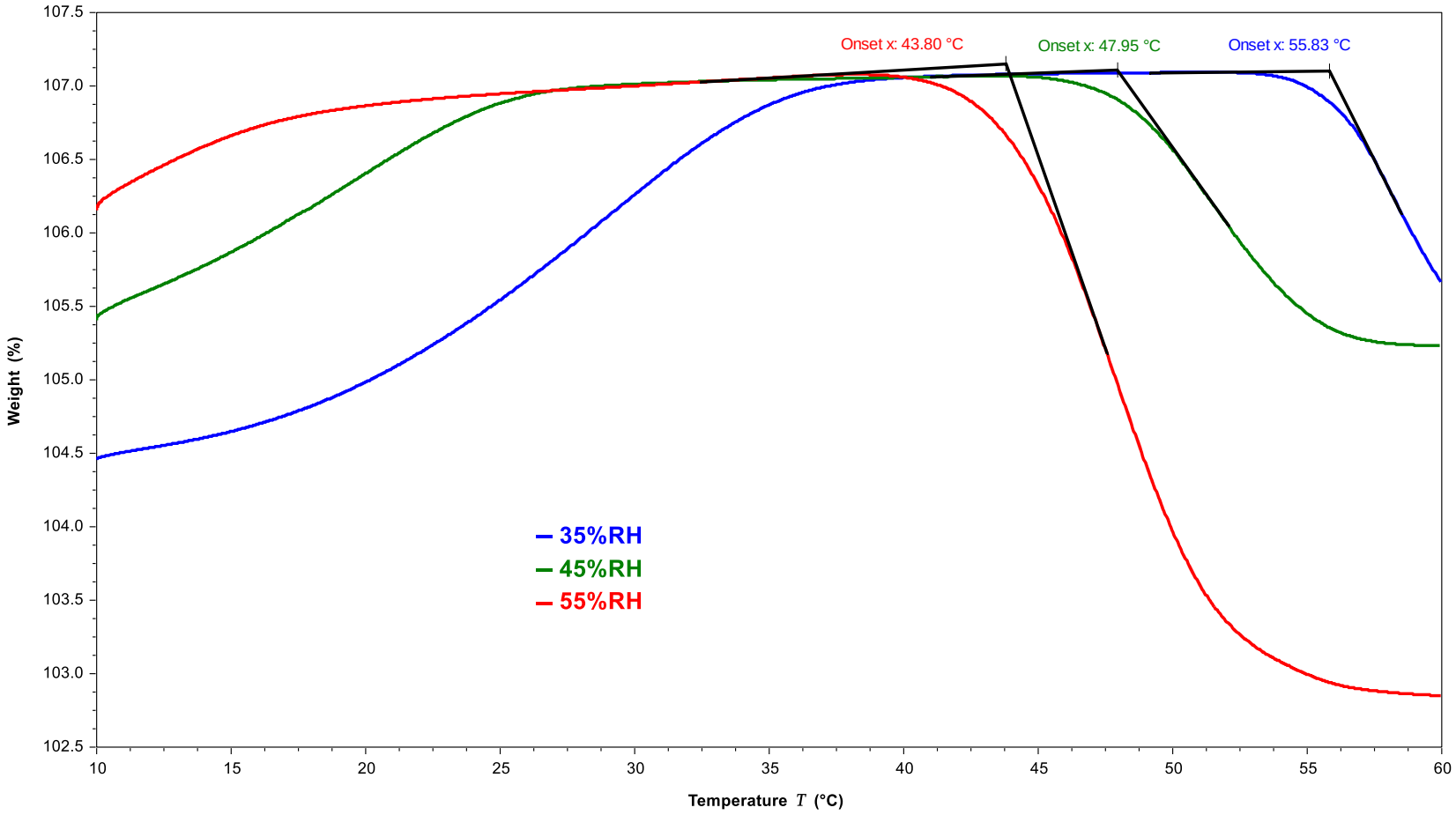
Stepped Test @ 25°C



Freeze Dried Sucrose – Humidity Ramp



Freeze Dried Sucrose – Temperature Ramp



Conclusions

- Thermogravimetric Analysis is a useful tool in our laboratory “toolbox” to look at the decomposition, sorption, desorption characteristics of our materials.
- Depending on the information we require, our analysis approach may be straight forward, however, more complex systems may require more in-depth analysis.
- Use of sample controlled techniques or evolved gas analysis possibly in combination with more complex methods and gas mixing control allow us to generate a fuller picture of our materials behaviour.
- Vapour sorption of materials will provide additional information including sorption and desorption of volatile species at a range of temperatures and pressures.

Thank You

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