2018年TA技術講座

TGA操作與應用技術研討會

日期	地　　點
2018年5月31日(四)	集思台大會議中心　米開朗基羅廳

許炎山

TA Instruments, Waters LLC

美商沃特斯國際股份有限公司台灣分公司

TA Taipei office: 104臺北市長安東路1段23號4F之5

Tel: 02-25638880　　Fax: 02-25638870

C/P: 0928-168676　E/M : jhsu@tainstruments.com

PART I

A Practical Approach To Thermal Analysis

An Overview of Thermogravimetric Analysis (TGA)

A Practical Approach to Thermal Analysis
An Overview of TGA

- **What is TGA?**
- Considerations with instrument hardware and accessories
- Calibration and verification
- A guide to experimental design

What is Thermogravimetric Analysis (TGA)?

- Thermogravimetric Analysis (TGA) measures weight/mass change (loss or gain) and the rate of weight change as a function of temperature, time and atmosphere.
- Measurements are used primarily to determine the composition of materials and to predict their thermal stability. The technique can characterize materials that exhibit weight loss or gain due to sorption/desorption of volatiles, decomposition, oxidation and reduction.

Thermogravimetric Analyzers

- A TGA must accurately:
  - control heating rate (furnace)
  - measure the change in temperature (thermocouple)
  - measure the mass of a sample and the change in mass as it is heated or held at an isothermal temperature (balance)

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TGA Applications

- Thermal stability of materials
- Oxidative stability of materials
- Composition of multi-component systems
- Decomposition mechanism when coupled with evolve gas analysis techniques (FTIR, MS)
- The effect of reactive or corrosive atmospheres on materials
- Moisture and volatiles content of materials
- Estimated lifetime of a product
- Decomposition kinetics of materials

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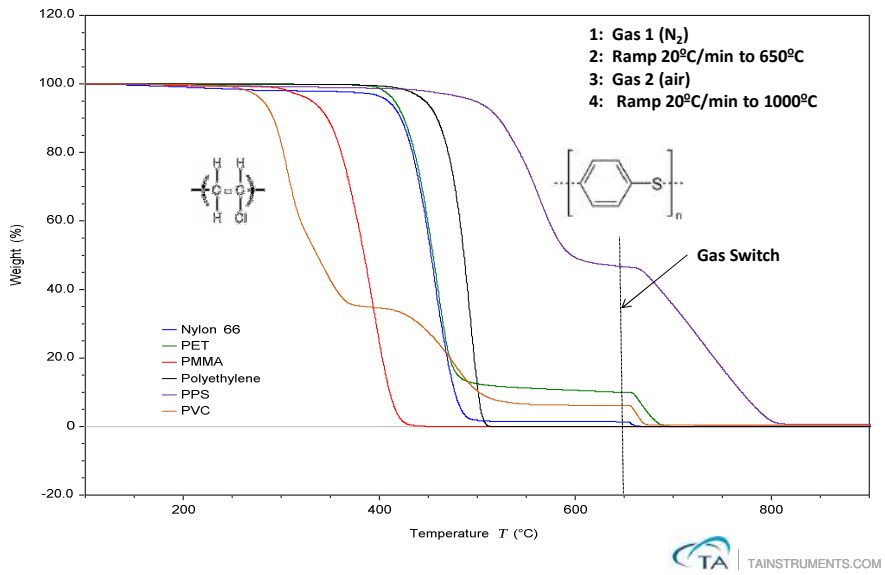
Thermal Stability of Polymers



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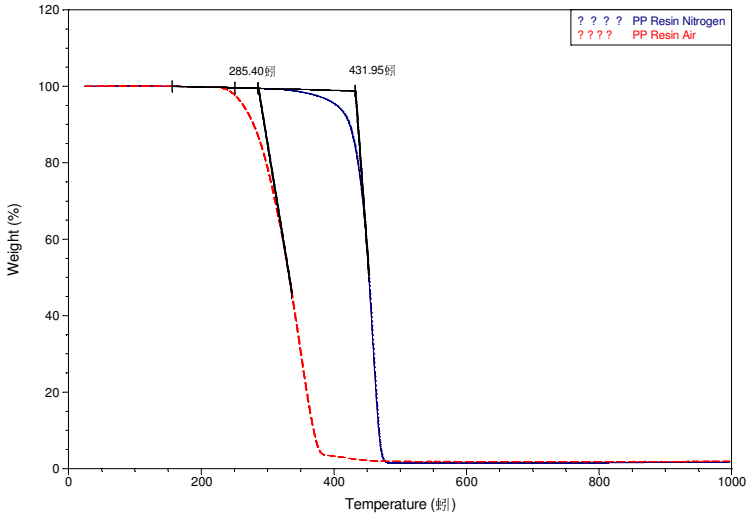
Oxidative Stability (Polypropylene)



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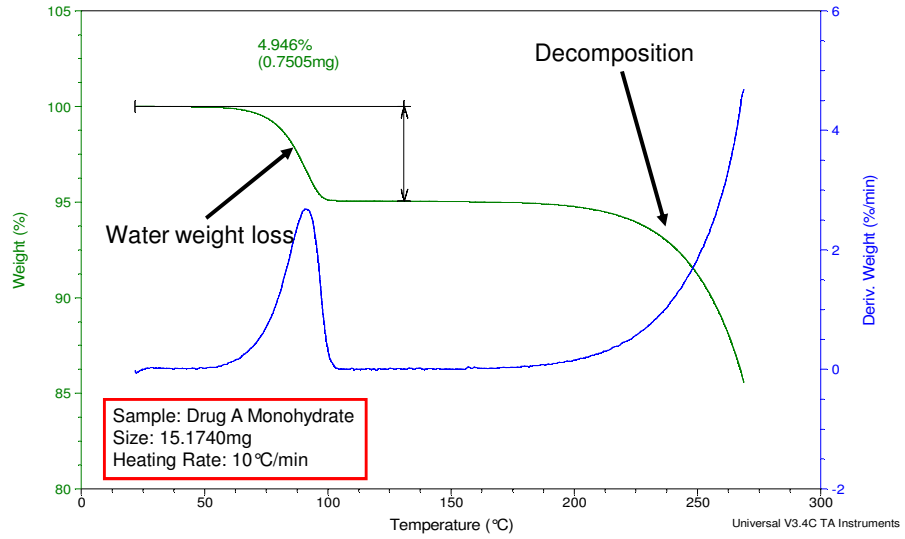
TGA of Drug A Monohydrate



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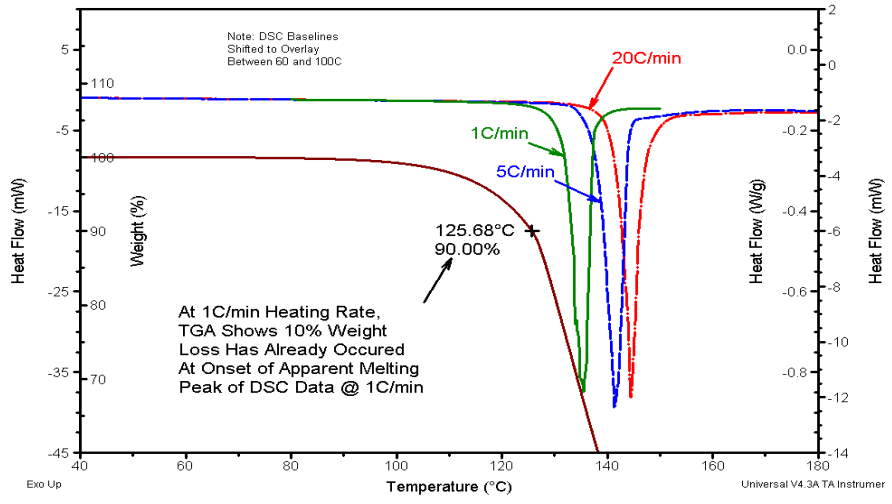
TGA Data Shows That Acetylsalicylic Acid is Decomposing Prior to Apparent Melting Point



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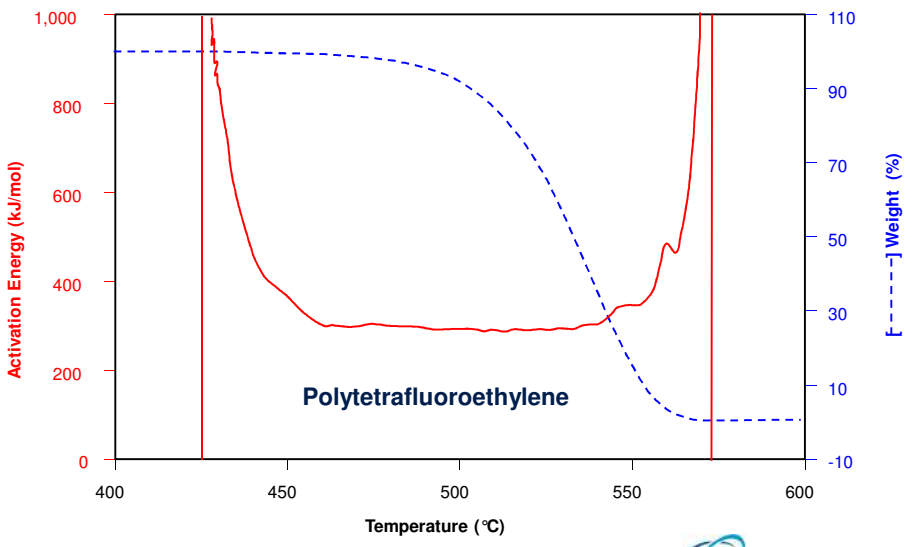
Modulated TGA – Decomposition Activation Energy and Lifetime Kinetics



A Practical Approach to Thermal Analysis An Overview of TGA

- What is TGA?
- **Considerations with instrument hardware and accessories**
- Calibration and verification
- A guide to experimental design

Instrument Hardware and Gas Selection Considerations

Evolve Gas Analysis (EGA) techniques

- Heated adapter on the exhaust port
- Turnkey solutions for FTIR or Mass spectrometer integration
- Allows for chemical identification of the decomposition gases/off-gas
- Derivation of decomposition mechanism

Gas Delivery Module

- Nitrogen - inert, inexpensive and readily available
- Helium - inert, commonly used when performing TGA-MS
- Air/Oxygen - used when studying oxidative stability of materials
- Gas mixing for specific atmospheres – hydrogen, carbon dioxide and other gases

TGA Pan Options

- Aluminum: max. temperature of 600°C, ability to seal prior to testing followed by pan punching at start of test (great for volatile content of samples while using the autosampler)
- Platinum: reusable, easily cleaned, non-porous; 50,100 µl volume options
- Alumina; high temperatures, 100, 250 and 500 µl volume options

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A Practical Approach to Thermal Analysis An Overview of TGA

What is TGA?

Considerations with instrument hardware and accessories

Calibration and verification

A guide to experimental design

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TGA Calibration and Verification

- A TGA measures the change in mass of a material with respect to temperature, time and atmosphere.
- A TGA is calibrated for mass (user), temperature (user) and gas flow rate control (manufacturer).
- A calibration is affected by
  - Purge gas and flow rate
  - Type of specimen pan
  - Heating rates

International Standards

- American Society of Testing and Materials, ASTM
  - www.astm.org
- International Organization of Standards, ISO
  - www.iso.org
- Deutsches Institut für Normung/German Institute for Standardization, DIN
  - www.din.de/en

ASTM/ISO Standards for TGA Temperature and Mass/Weight Calibration

- ASTM E 1582 - Standard Practice for Calibration of Temperature Scale for Thermogravimetry
- ASTM E 2040 - Standard Test Method for Mass Scale Calibration of Thermogravimetric Analyzers
- ISO 11358 – Thermogravimetry (TG) of Polymers

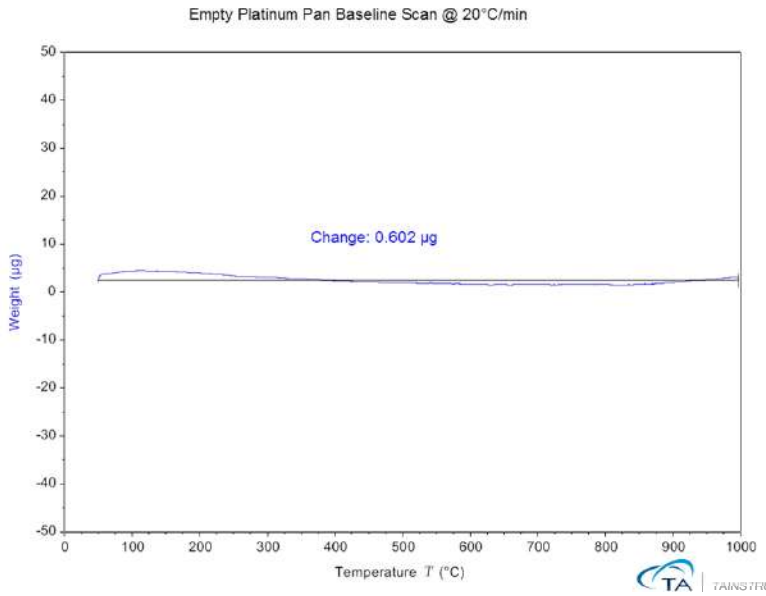
Requirements Prior to Calibration

- The TGA pan should be cleaned prior to calibration procedures. If using platinum or alumina pans, a flame torch can be used to burn off organic residue.
- The purge gas flow rate setting should be set (flow rates differ depending on furnace design and internal volume). The flow rate should not deviate by more than +/- 5ml/min.
- Use high purity reference materials with traceability for calibration

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 thermogravimetry analysis 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.
- TA Instruments uses a zero tare, then a 100mg and 1000mg mass standard to calibrate the TGA.

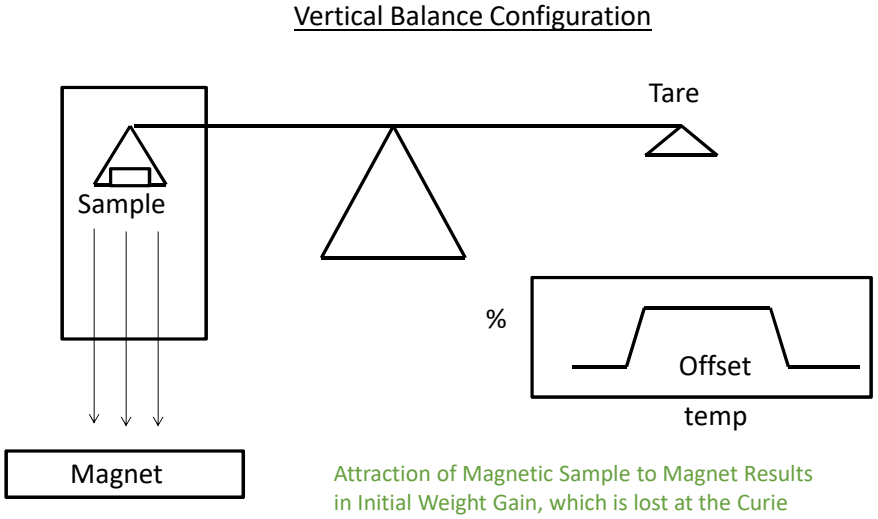
TGA Baseline Performance



ASTM E 1582 - Calibration of Temperature Scale for Thermogravimetry

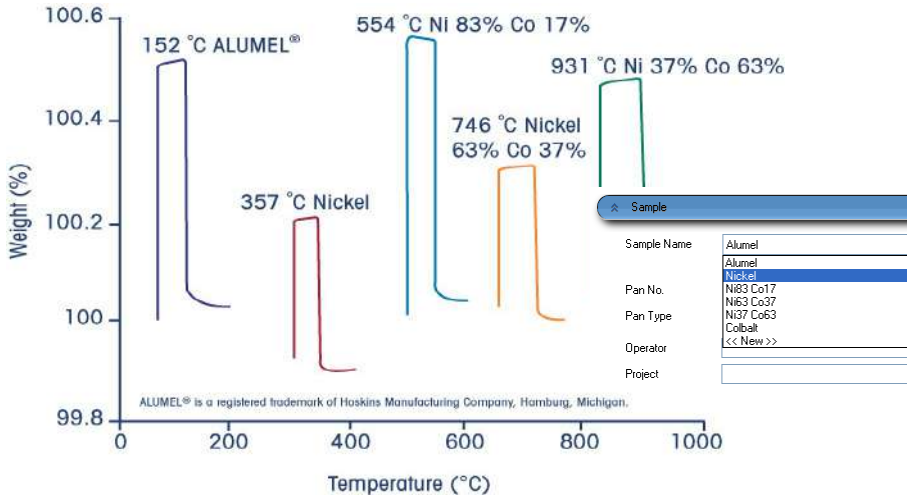
- The standard describes two methods by which the TGA can be calibrated for temperature; by melting point or magnetic transition. The most common approach for a TGA would be the magnetic transition approach.
- Curie Point Temperature - that temperature where the material loses its magnetic susceptibility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

TGA: Temperature Calibration

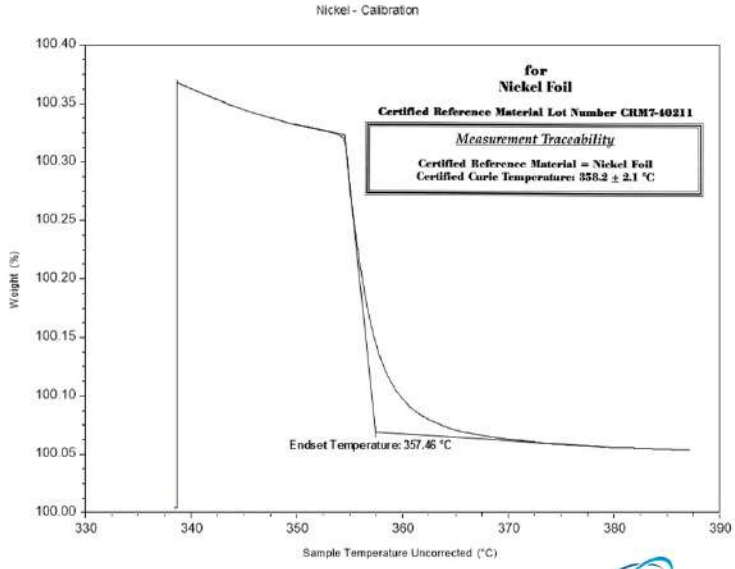


Attraction of Magnetic Sample to Magnet Results in Initial Weight Gain, which is lost at the Curie Transition Temperature

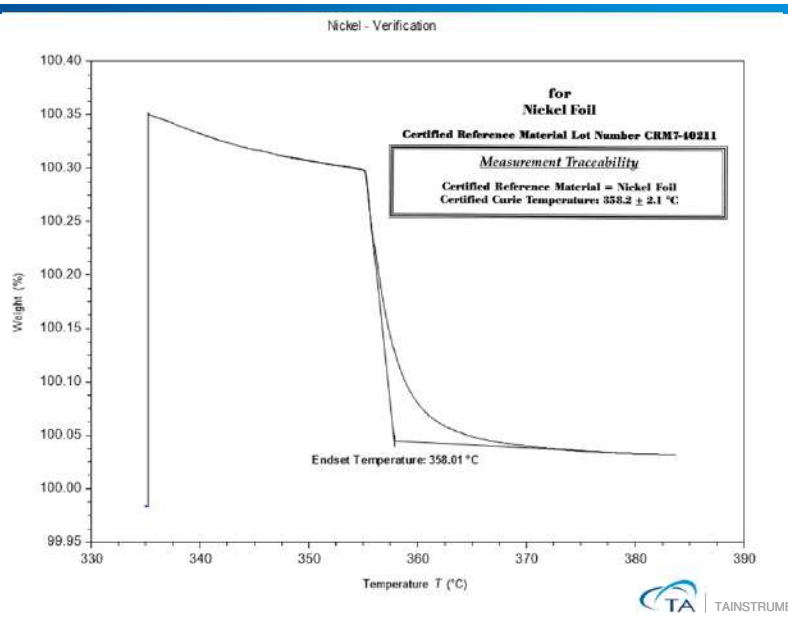
Curie Standards with ICTAC traceability



TGA – Temperature Calibration



TGA – Temperature Verification



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A Practical Approach to Thermal Analysis
An Overview of TGA

- What is TGA?
- Considerations with instrument hardware and accessories
- Calibration and verification
- **A guide to experimental design**

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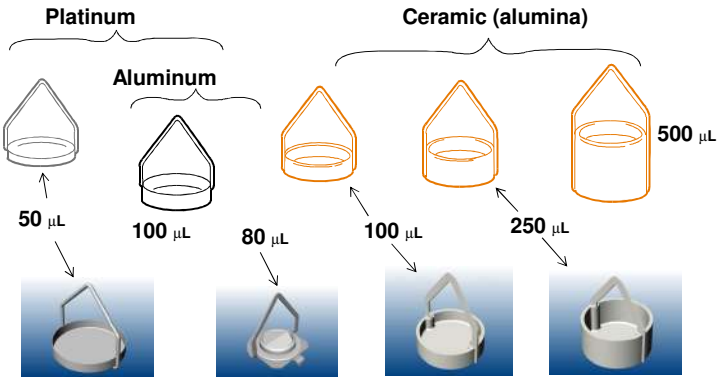
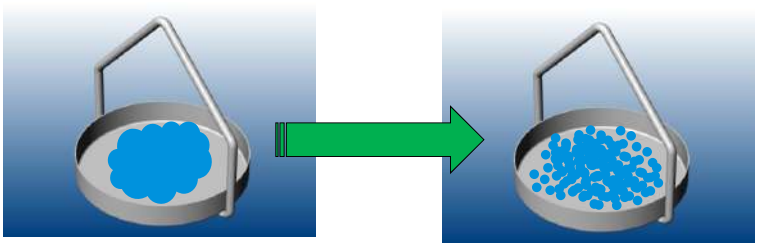
TGA: Sample Pans - Types/Sizes



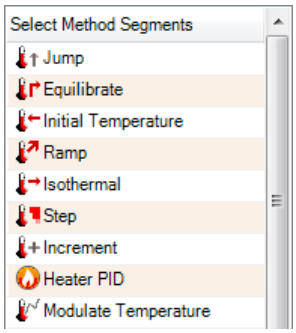
Deep-walled pans are good for larger mass and low-density materials but may impact the decomposition profile

TGA: Sample Preparation



- Sample mass
  - 10-20mg for most applications
  - 50-100mg for measuring volatiles
- Most TGA instruments have a baseline drift of +/-25µg which is 0.25% of a 10mg sample

Method Design: DSC 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.

Method Development

A controlled, linear heating rate method

1) Ramp 10℃/min to 700℃ (inert gas)
2) Select gas: 2 (air or oxygen)
3) Ramp 10℃/min to 1000℃

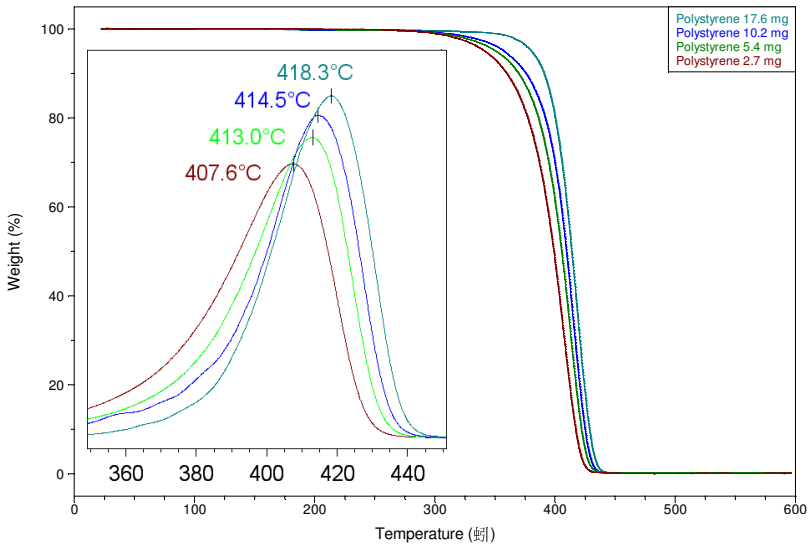
A heat, then isothermal method

1) Ramp 20℃/min to 200℃
2) Isothermal for 100.00 minutes (with option to switch gases)

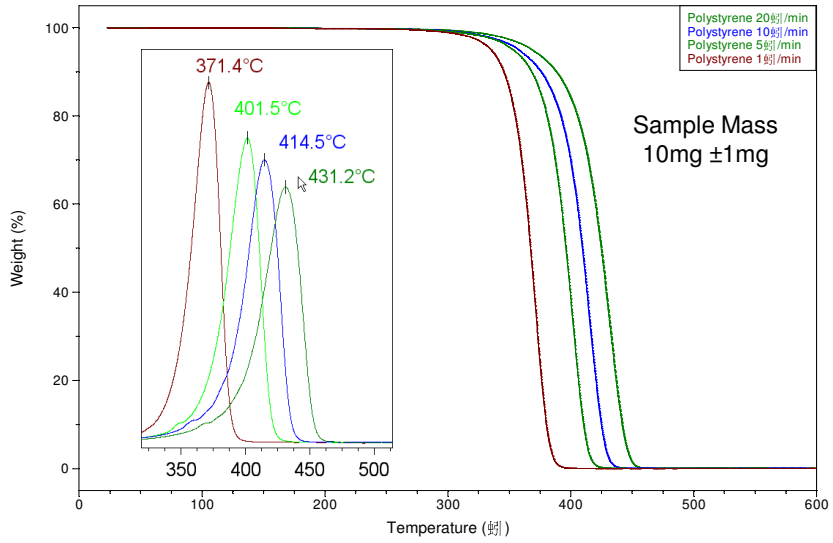
TGA Curves are not 'Fingerprint' Curves

- As events that occur in a TGA are ***kinetic*** in nature (meaning they are dependent on absolute temperature and time spent at that temperature), the experimental parameters can affect the reaction rate will change the shape and transition temperatures of the TGA profile.
- Influencing factors include;
  - Sample mass, surface area
  - Heating rate
  - Purge gas
  - Sample shape and morphology

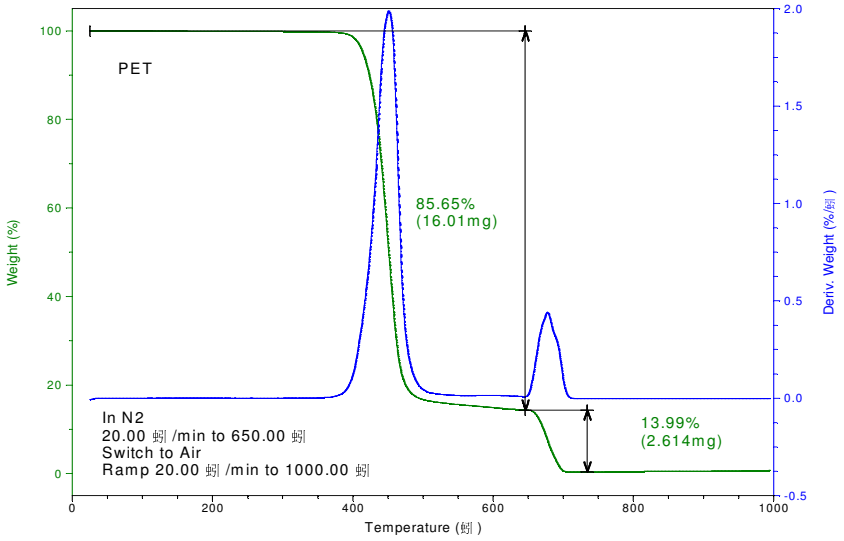
Larger sample mass increases the observed decomposition temperature



Higher heating rates increase the observed decomposition temperature



PET Polymer Without Filler



Summary

- TGA is an analytical technique used to determine the change in weight of a material with respect to time, temperature and atmosphere.
- Influential factors:
  - Instrumentation
    - Calibration of mass and temperature
    - Gas selection
  - Sample
    - Specimen mass and preparation
    - Heating rate
  - Method design
    - Linear temperature ramp
    - Isothermal tests
    - Gas switching

A Practical Approach to Thermal Analysis Thermogravimetric Analysis

- **An Overview of Thermogravimetric Analysis (TGA)**
- Methods to improve resolution of complex TGA weight loss profiles – An introduction to HiRes™ TGA and Stepwise Isothermal TGA
- Determining Decomposition Activation Energy by Modulated TGA
- Evolve Gas Analysis – An Introduction to TGA-Mass Spectrometry

PART II

A Practical Approach To Thermal Analysis

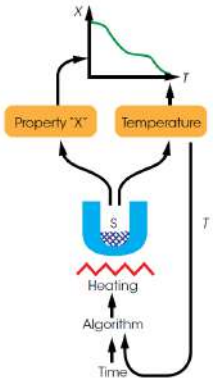
Methods to improve resolution of complex TGA weight loss profiles – An introduction to Hi-Res™ TGA and Stepwise Isothermal TGA

Hi-Res™ is the trademark of TA Instruments-Waters LLC

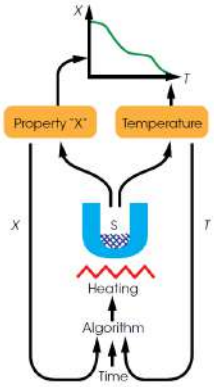
Agenda

- **Introduction: Methods to change temperature in a TGA experiment**
- Improving resolution in Standard (constant heating rate) TGA experiments
- Hi-Res™ TGA
- Automated Stepwise isothermal TGA

Temperature-controlled TGA (standard TGA) vs sample-controlled TGA



Temperature-controlled thermal analysis

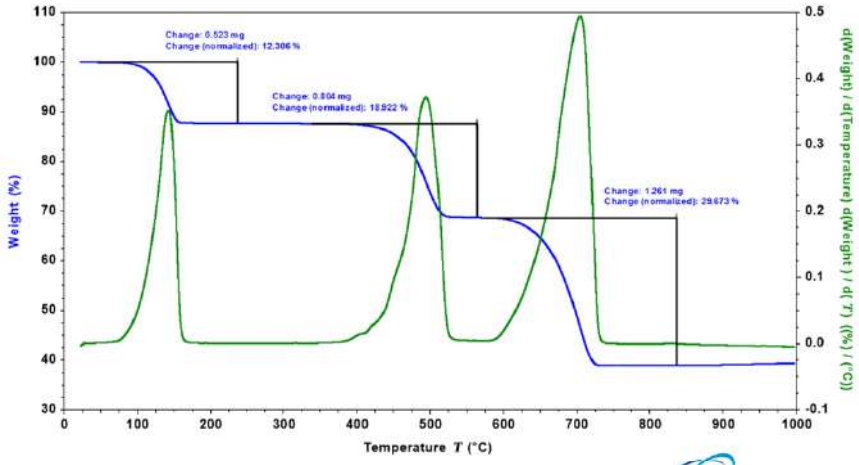


Sample-controlled thermal analysis

Ref:
O. Toft Sørensen and J. Rouquerol (2003). Sample Controlled Thermal Analysis: Origin, Goals, Multiple Forms, Applications and Future. Kluwer Academic Publishers, Netherlands

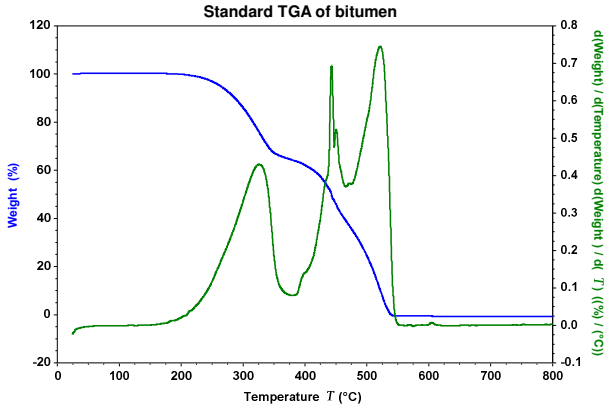
Standard TGA: advantages

- Easy to set up
- When the individual decomposition steps occur at well-separated temperatures, quantitative information for each step can be obtained



Standard TGA: limitations

- Complex thermal scans with broad weight losses
- Overlapping weight losses
  - Multiple peaks/shoulders



Ref:
J-F. Masson, S. Bundalo-Perc, Thermochimica Acta, 436 (2005), 35–42

A Practical Approach to Thermal Analysis: Agenda

Introduction: Methods to change temperature in a TGA experiment

Improving resolution in Standard TGA experiments

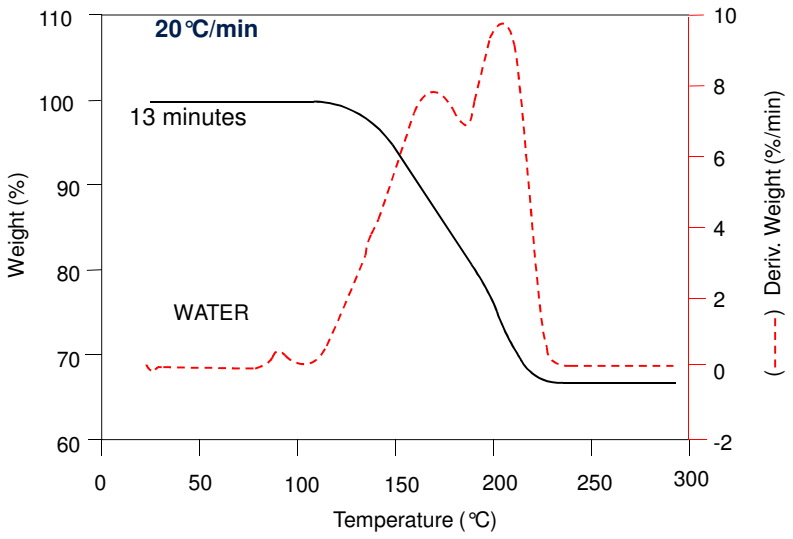
Hi-Res™ TGA

Automated Stepwise isothermal TGA

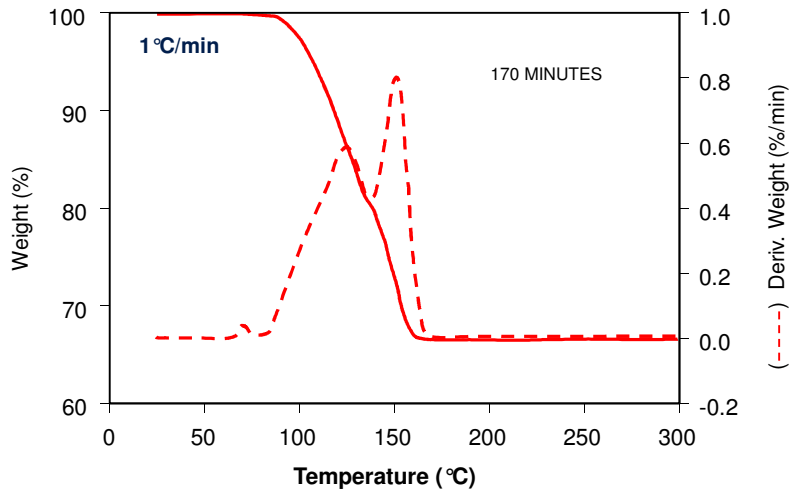
Improving resolution in Standard TGA experiments

- Means of Enhancing Resolution
  - Slower heating rate
  - Reduced sample size
  - Pin-hole hermetic pans (self-generating atmosphere)

Impact of heating rate on resolution: 20°C/min



Impact of heating rate on resolution: 1°C/min



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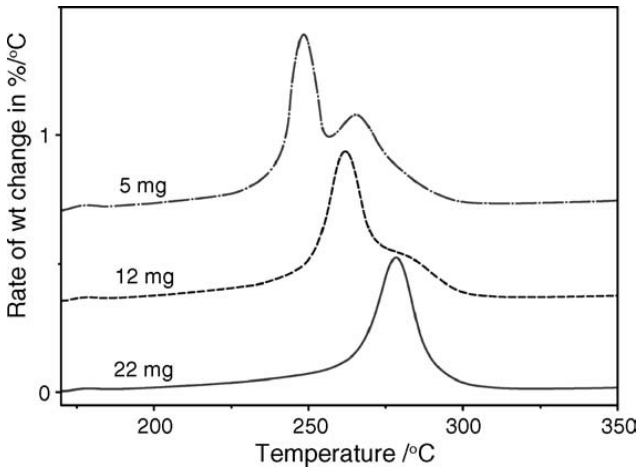
Effect of sample mass on resolution: bitumen

Overall magnitude of weight change is lesser



Ref:
J-F. Masson, S. Bundalo-Perc, Thermochimica Acta, 436 (2005), 35–42

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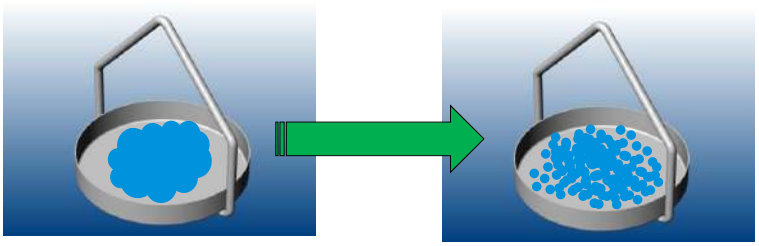
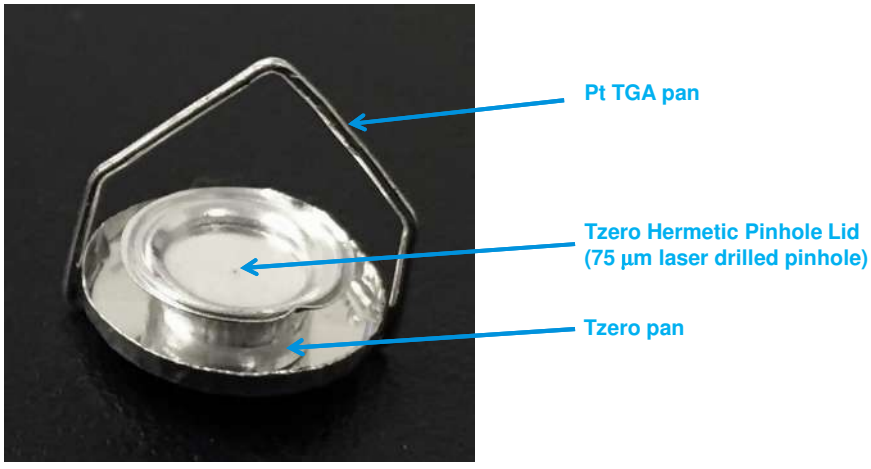
TGA: Sample Preparation



- Sample mass
  - 10-20mg for most applications
  - 50-100mg for measuring volatiles
- Most TGA instruments have a baseline drift of +/-25µg which is 0.25% of a 10mg sample

Resolution enhancement using a pinhole hermetic DSC pans



Resolution enhancement using a pinhole hermetic DSC pans: gypsum

- Heating gypsum between 100°C and 150°C (302°F) partially dehydrates the mineral by driving off exactly one and a half moles of the water contained in its chemical structure.
- The partially dehydrated mineral is called calcium sulfate hemihydrate or calcined gypsum ($CaSO_4 \cdot ½H_2O$).

$$CaSO_4 \cdot 2H_2O + \text{heat} \rightarrow CaSO_4 \cdot ½H_2O + 1½H_2O \text{ (steam)}$$

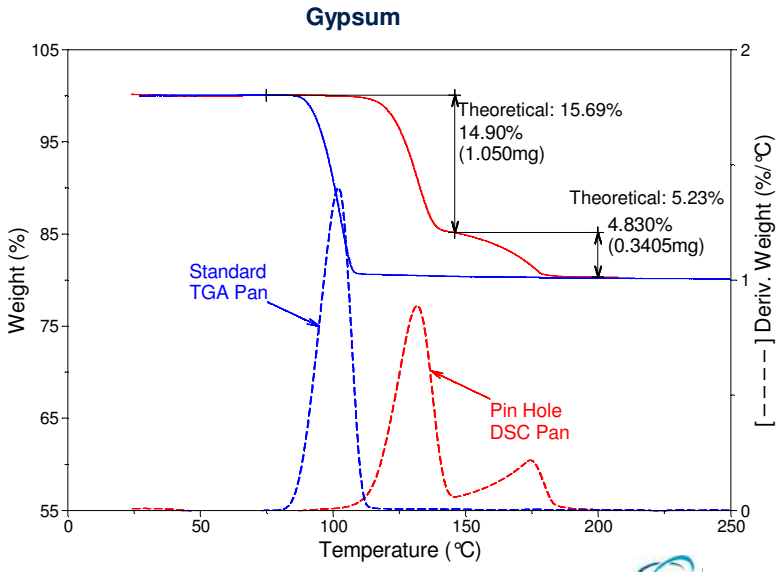
- As heating continues, the anhydrite, $CaSO_4$, is then formed.

$$CaSO_4 \cdot ½H_2O + \text{heat} \rightarrow CaSO_4 + ½H_2O$$

Theoretical Mass Losses of Gypsum

- $CaSO_4 \cdot 2H_2O + \text{heat} \rightarrow CaSO_4 \cdot ½H_2O + 1½H_2O$
  A loss of $1½H_2O$ = 100*(MW. $1½H_2O$/ MW. $CaSO_4 \cdot 2H_2O$)
  = 15.69%
- $CaSO_4 \cdot ½H_2O + \text{heat} \rightarrow CaSO_4 + ½H_2O$
  A loss of $½H_2O$ = 100*(MW. $½H_2O$/ MW. $CaSO_4 \cdot 2H_2O$)
  = 5.23%
- Total weight loss = 15.69% + 5.23% = 20.92% (2 mols H_2O)

Effect of DSC Pinhole pans on TGA resolution



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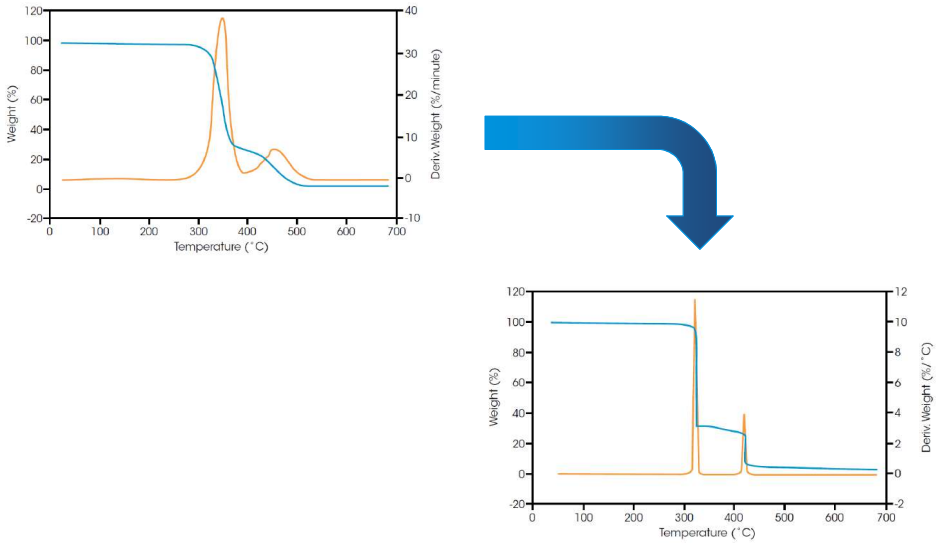
Sample-controlled TGA to improve TGA resolution



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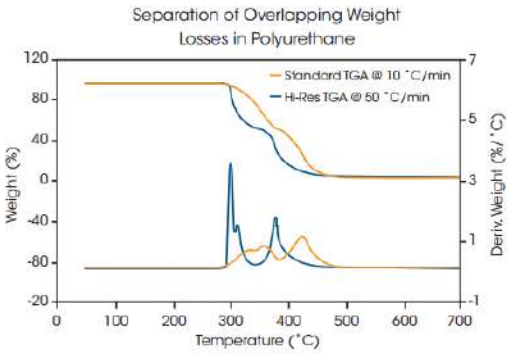
A Practical Approach to Thermal Analysis: Agenda

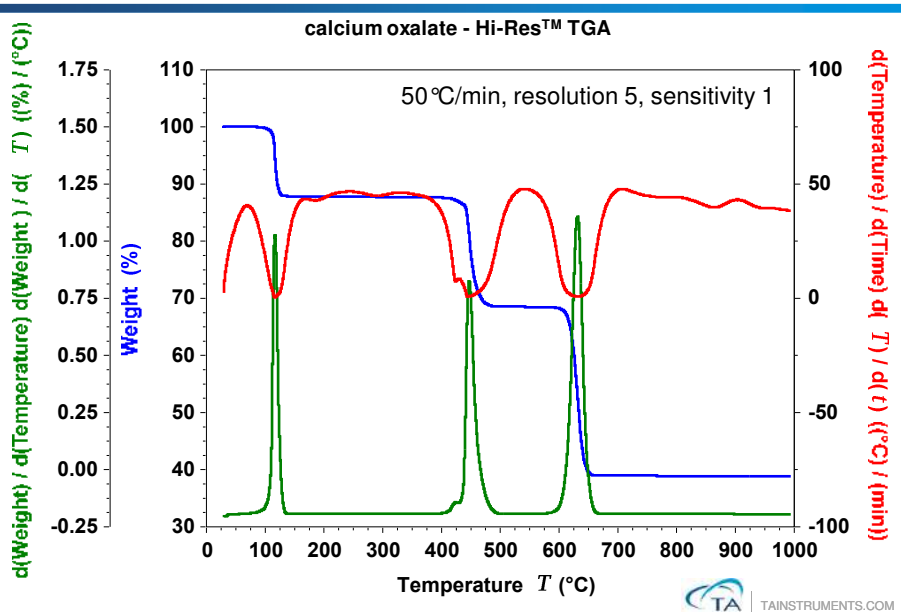
- Introduction: Methods to change temperature in a TGA experiment
- Improving resolution in Standard (constant heating rate) TGA experiments
- **Hi-Res™ TGA**
- Automated Stepwise isothermal TGA

Hi-Res™ TGA

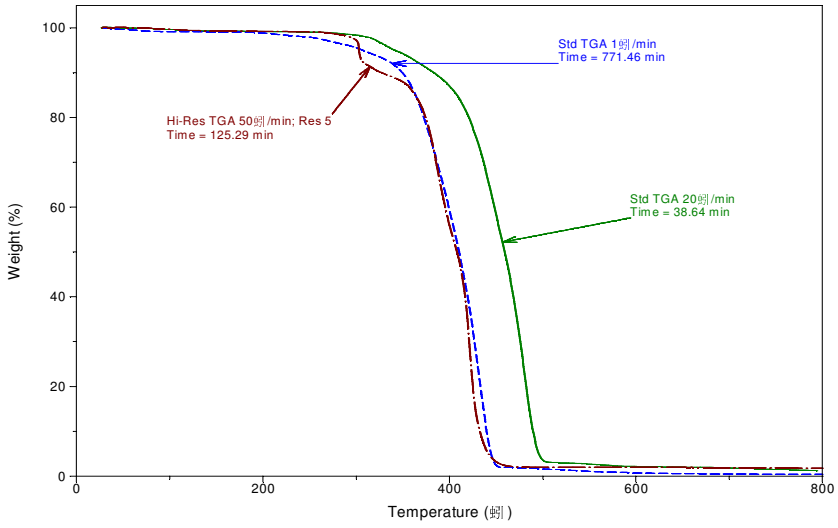
- In a Hi-Res™ TGA experiment the heating rate is controlled by the rate of decomposition.
- Faster heating rates during periods of no weight loss, and slowing down the heating rate during a weight loss – therefore not sacrificing as much time
- Hi-Res™ TGA can give better resolution or faster run times, and sometimes both



Hi-Res™ TGA of Calcium oxalate



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



Programming a Hi-Res™ TGA experiment – sensitivity number

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

Sensitivity : typically varies from 0 to 8.0

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

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Programming a Hi-Res™ TGA experiment – resolution number

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

Resolution : typically varies from -8.0 to 8.0

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

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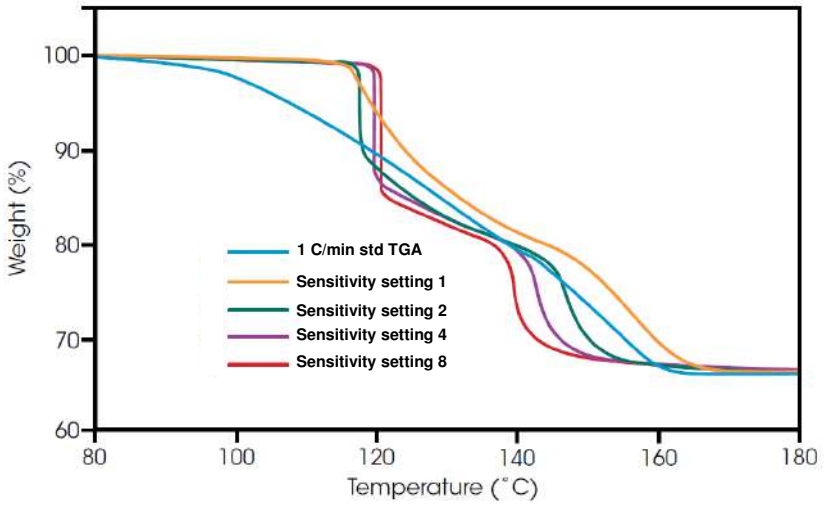
Effect of sensitivity settings on TGA data

Res = 5 for all Hi-Res experiments



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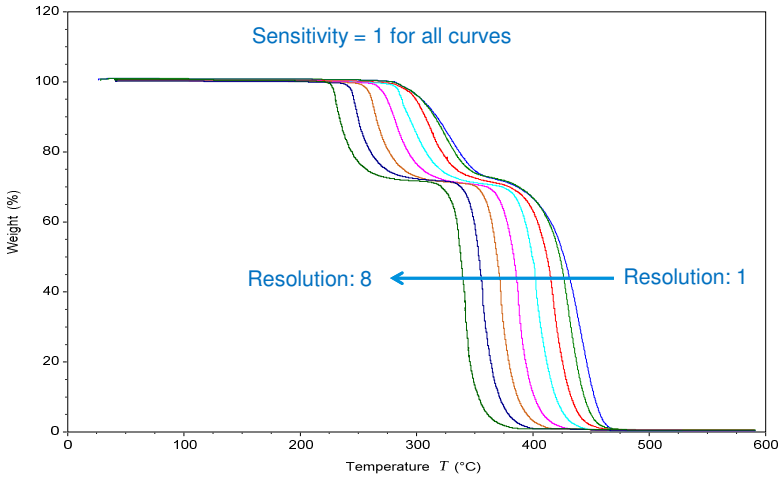
Effect of resolution settings on TGA data

Hi-Res TGA on ethylene-vinyl acetate copolymer



Note that increasing resolution setting increases the resolution of each transition and simultaneously reduces the transition temperature.

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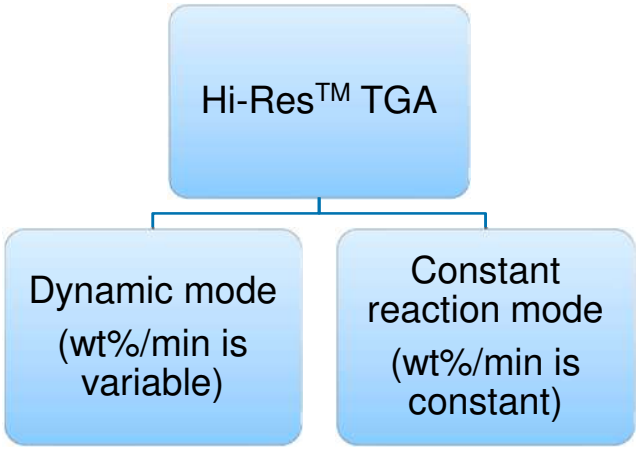
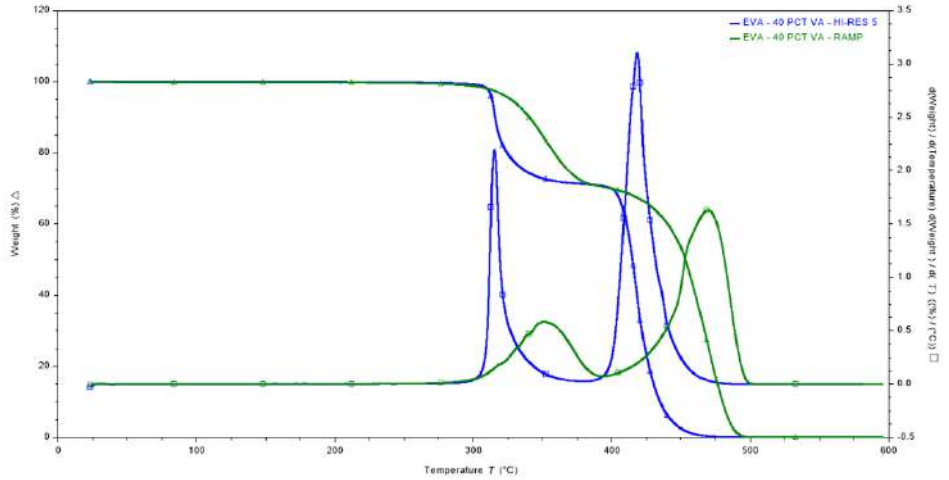
Optimizing the Hi-Res™ TGA settings

- Sensitivity of 1 and resolution of 4 are good starting points. Higher resolution number means slower heating rate.
- Increasing the resolution number if you need further separation of derivative peaks

Two modes of Hi-Res™ TGA

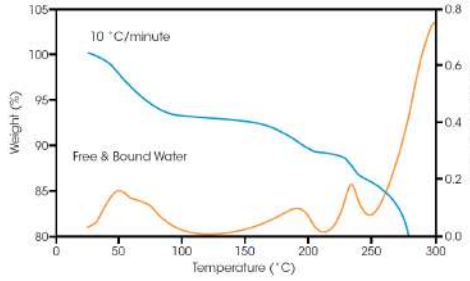


Compare Hi-Res™ TGA vs. standard TGA at 10°C/min – Ethylene Vinyl Acetate copolymer

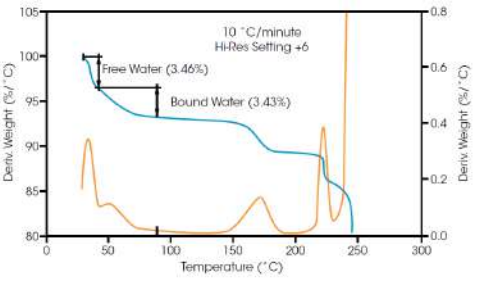


Use of Hi-Res™ TGA for determination of free and bound water in pharmaceuticals

Standard TGA



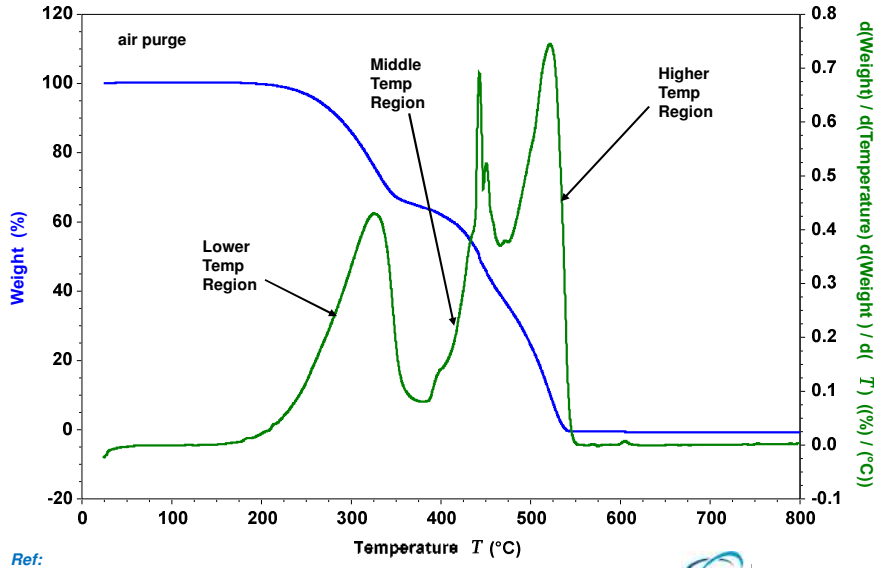
Hi-Res™ TGA



Note the use of 10 C/min heating rate in the Hi-Res™ TGA as the sample loses mass rapidly

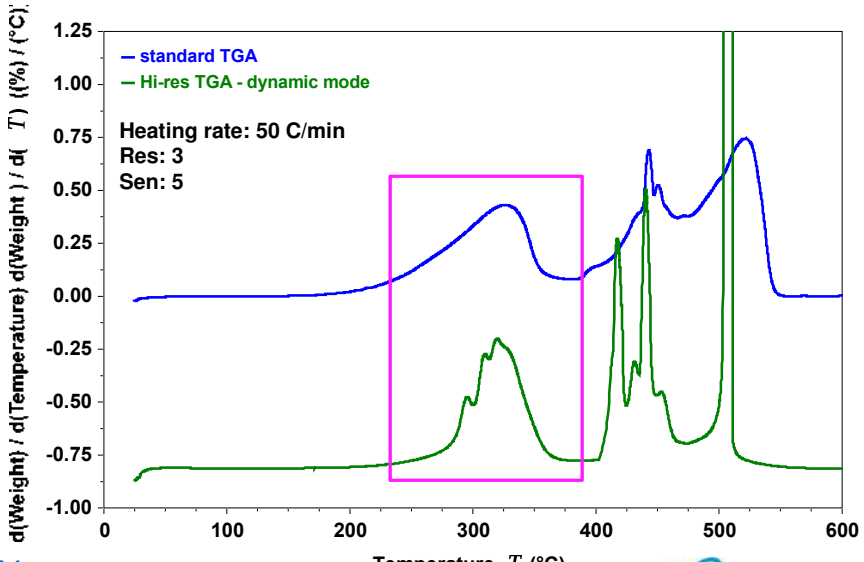
Ref:
TA Instruments application note TS17

Standard TGA 10°C/min of bitumen sample



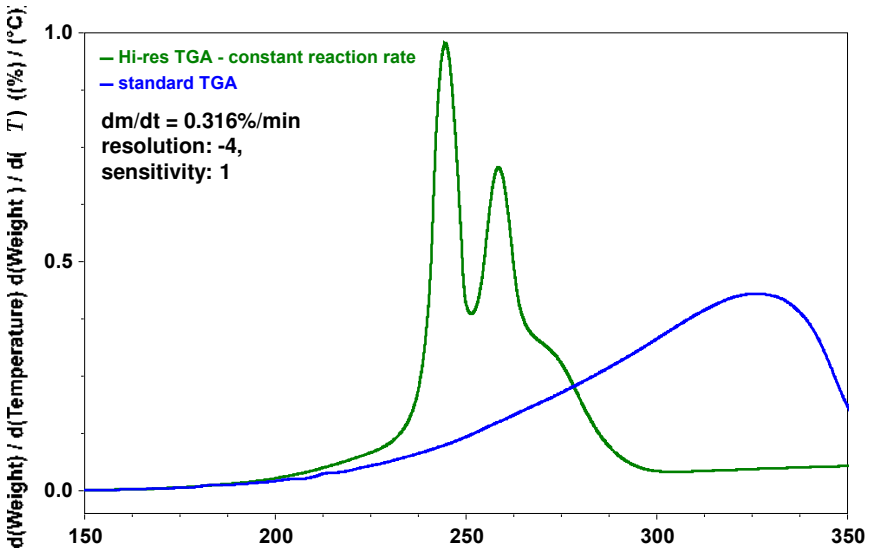
Ref:
J-F. Masson, S. Bundalo-Perc, Thermochimica Acta, 436 (2005), 35–42

Standard TGA vs Hi-Res TGA (dynamic mode) of bitumen sample



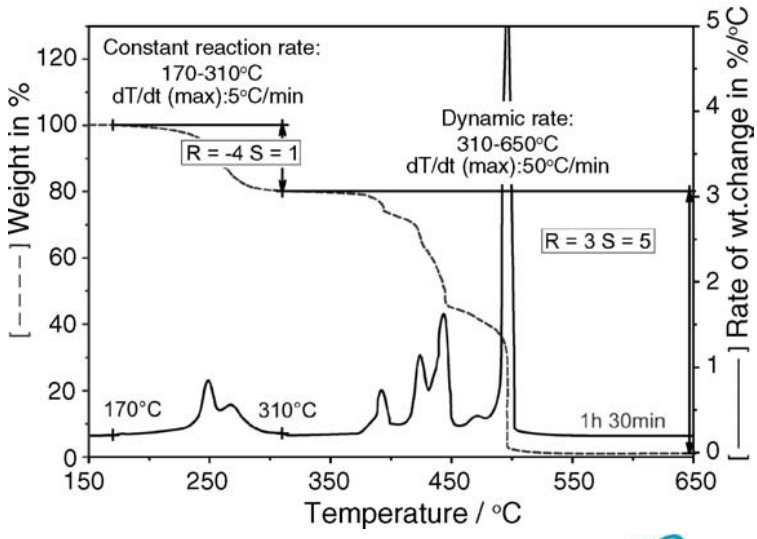
Ref:
J-F. Masson, S. Bundalo-Perc, Thermochimica Acta, 436 (2005), 35–42

Constant Reaction Rate TGA of bitumen sample



Ref:
J-F. Masson, S. Bundalo-Perc, Thermochimica Acta, 436 (2005), 35–42

Combining the dynamic and constant reaction rate Hi-Res™ TGA



Ref:
J-F. Masson, S. Bundalo-Perc, Thermochimica Acta, 436 (2005), 35–42

Hi-Res™ TGA- Advantages

- Relatively simple to develop method
- Rapid survey over wide temperature range with excellent resolution
- High resolution with equal/better productivity, even on unknowns

A Practical Approach to Thermal Analysis: Agenda

Introduction: Methods to change temperature in a TGA experiment

Improving resolution in Standard (constant heating rate) TGA experiments

Hi-Res™ TGA

Automated Stepwise isothermal TGA

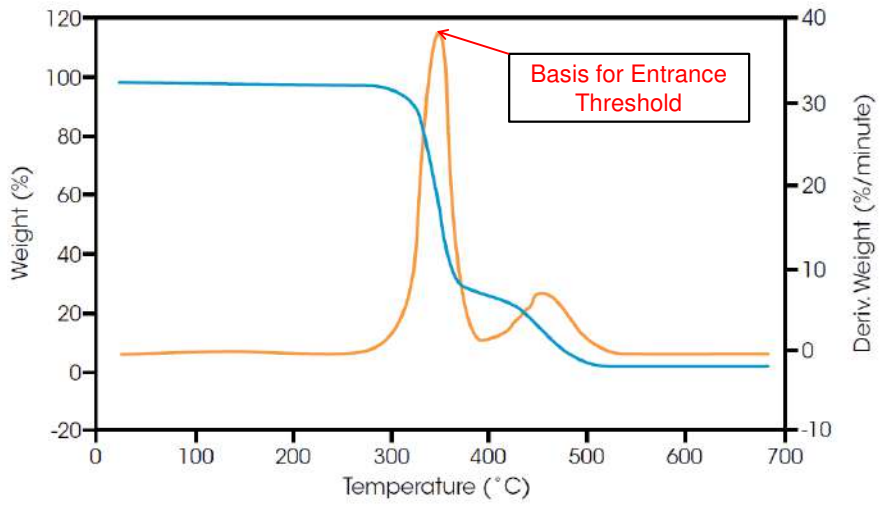
Automated Stepwise Isothermal TGA (SWI)

- Heating stops (goes isothermal) when a certain rate of weight loss is reached, then resumes after this rate falls below a second defined value
- Operator defines the values for the rate of weight loss
- Incorrect values can cause artifacts that appear as 'additional' mass losses
- Correctly set up, can give excellent resolution, but takes quite a bit longer

Automated Stepwise Isothermal TGA (SWI)

- Advantages
  - Sample held isothermal until transition completed - thus excellent resolution of overlapping transitions
  - Permits careful control of reaction environment
  - Programmable on any TGA
- Disadvantages
  - Requires method development. May require several scans to optimize run conditions
  - Inappropriate parameter choices may produce artifacts
  - Long run times

Standard TGA of Polyvinyl Acetate

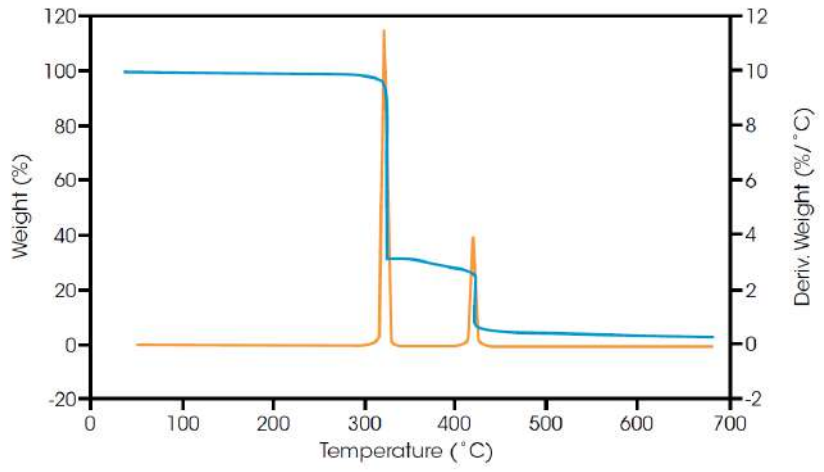


Ref:
Thermal Applications Note TN40 – Optimizing Stepwise Isothermal Experiments in Hi Res TGA

Typical SWI Thermal Method

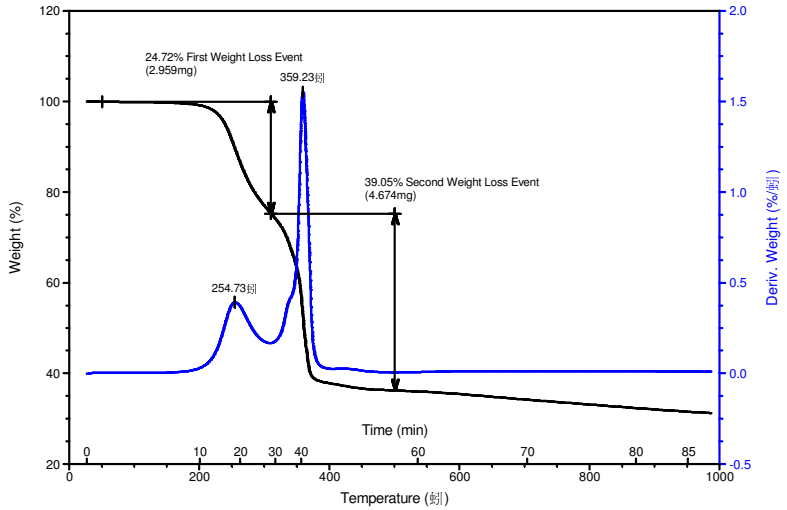
1. Abort next segment if %/min > 4
2. Ramp 10°C/min to 1000°C
3. Abort next segment if %/min < 0.4
4. Isothermal 1000 min
5. Repeat 1 until 1000°C

SWI of Polyvinyl Acetate

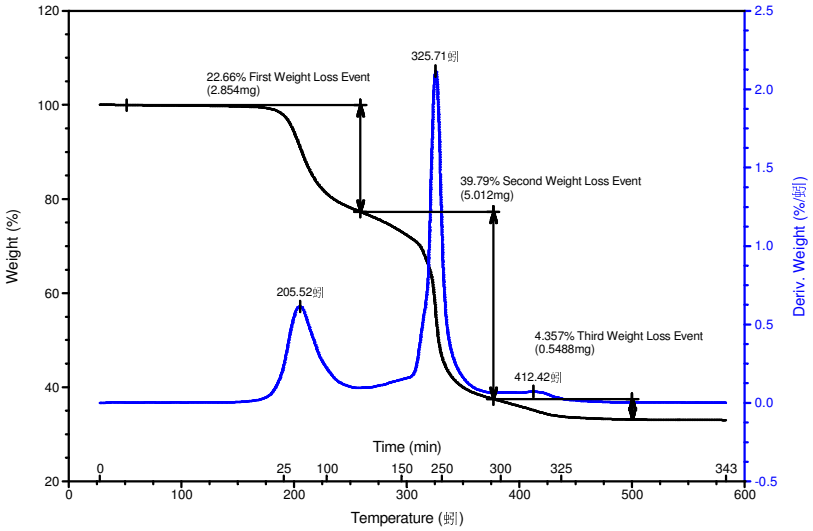


Ref:
Thermal Applications Note TN40 – Optimizing Stepwise Isothermal Experiments in Hi Res TGA

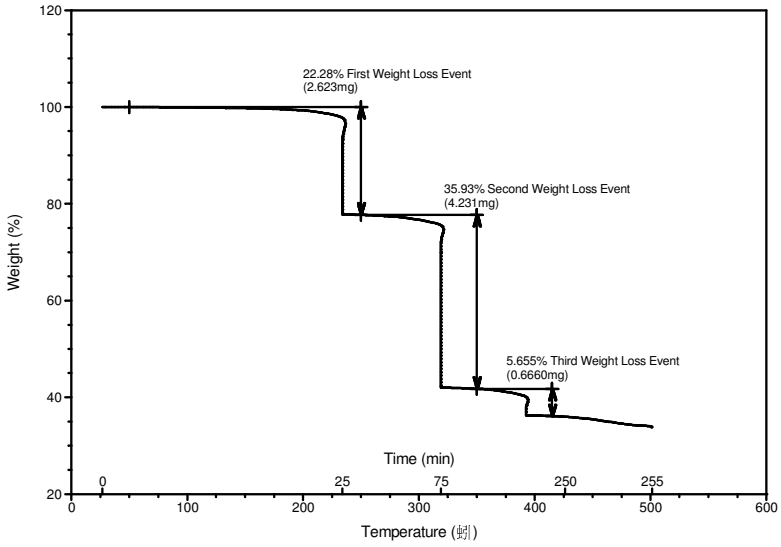
Hi-Res™ TGA of lubricating oil (Res. 4)



Hi-Res™ TGA of lubricating oil (Res. 6)



Stepwise Isothermal TGA of lubricating oil



Summary

- Resolution in a TGA experiment is the process of separating decomposition steps closely spaced in temperature.
- A lower sample mass and a slower heating rate improves the resolution of a TGA thermogram
- Hi-Res™ TGA dynamically modifies the heating rate in response to the rate of decomposition of the sample.
- Stepwise isothermal TGA heats the sample at a constant heating rate until the onset of decomposition, and holds it isothermally until the decomposition is complete.

A Practical Approach to Thermal Analysis Thermogravimetric Analysis

- **An Overview of Thermogravimetric Analysis (TGA)**
- **Methods to improve resolution of complex TGA weight loss profiles – An introduction to Hi-Res™ TGA and Stepwise Isothermal TGA**
- Determining Decomposition Activation Energy by Modulated TGA™
- Evolved Gas Analysis – An Introduction to TGA-Mass Spectrometry

PART III

Determining Decomposition Activation Energy by Modulated TGA (MTGA™)

材料分解動力學與熱壽命預測的最佳途徑

Decomposition Activation Energy by MTGA™

- How is decomposition kinetics measured by TGA?
- Conventional method for Activation Energy
- A guide to Modulated TGA
- Applications of MTGA for Decomposition Kinetics

Kinetic Analysis

- The rate at which a kinetic process proceeds depends not only on the temperature the specimen is at, but also the time it has spent at that temperature.
- Typically kinetic analysis is concerned with obtaining parameters such as
  - activation energy (E_a),
  - reaction order (n), and
  - generating predictive curves for conversion (α).

Kinetics by TGA

$$Conversion:\ \alpha = \frac{w_{in} - w_T}{w_{in} - w_f}$$