TGA & SDT Theory and Applications Online Courses

Part 2: Applications

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Agenda

- General Experimental Effects
- Thermal & Oxidative Stability
- Improving Resolution
  - Standard TGA
  - Hi Resolution TGA (Hi-Res)
- Decomposition Kinetics and Modulated TGA (MTGA)
- Evolved Gas Analysis

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General Considerations

- Experimental Effects

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TGA Curves are not 'Fingerprint' Curves

- Because most events that occur in a TGA are kinetic in nature (meaning they are dependent on absolute temperature and time spent at that temperature), any experimental parameter that can effect the reaction rate will change the shape / transition temperatures of the curve.
- These things include:
  - Sample Mass
  - Heating Rate
  - Purge gas
  - Sample volume/form and morphology

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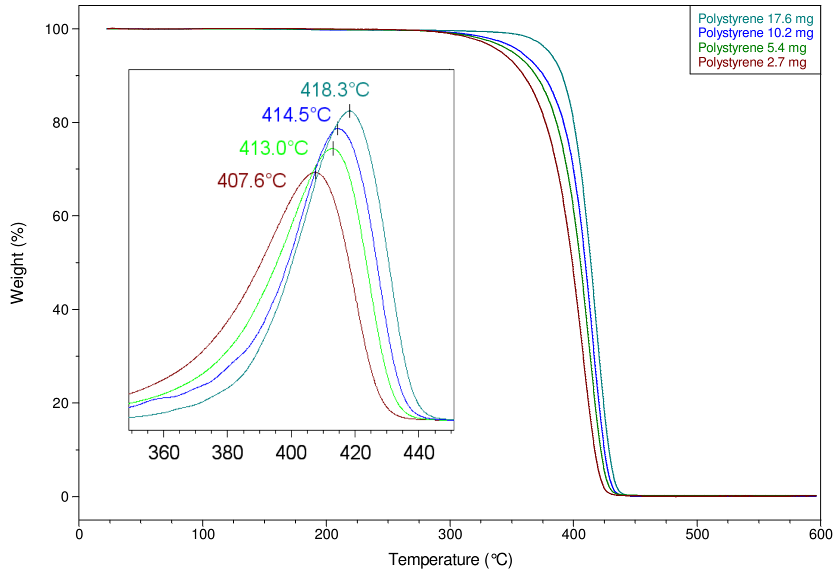
Larger sample mass increases the observed decomposition temperature



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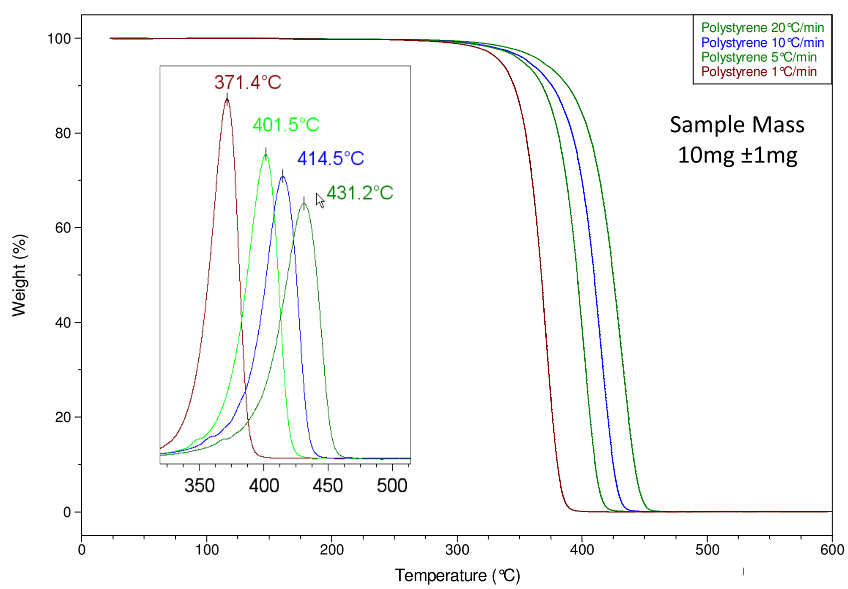
Higher heating rates increase the observed decomposition temperature



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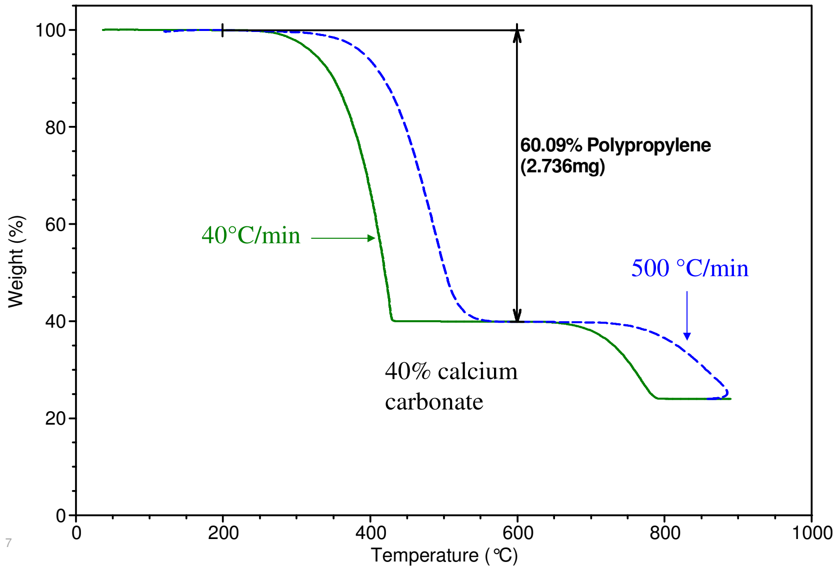
High-Heating Rate TGA Analysis



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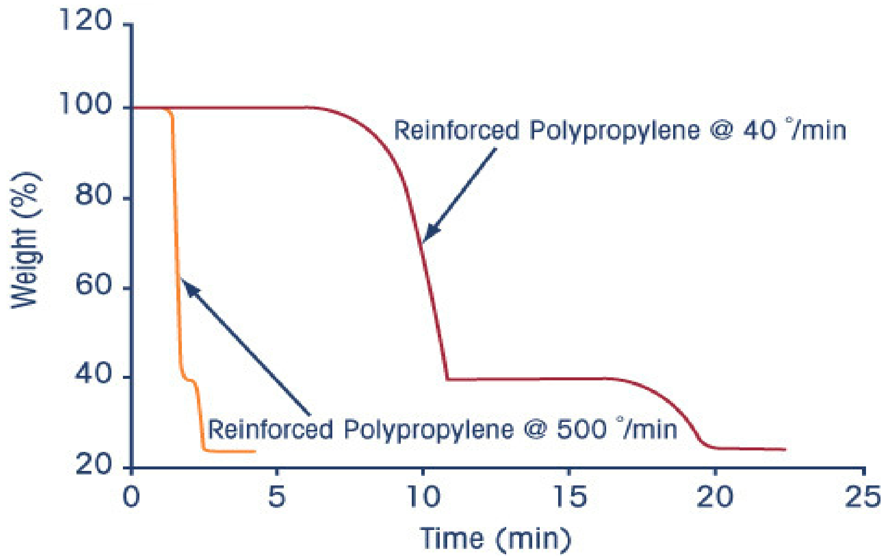
High-Heating Rate TGA Analysis



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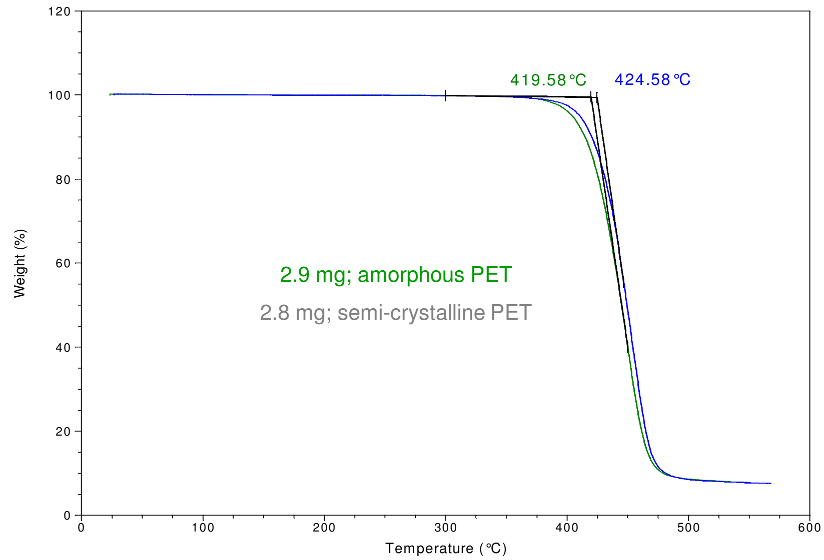
Sample Morphology Effects – PET



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Applications

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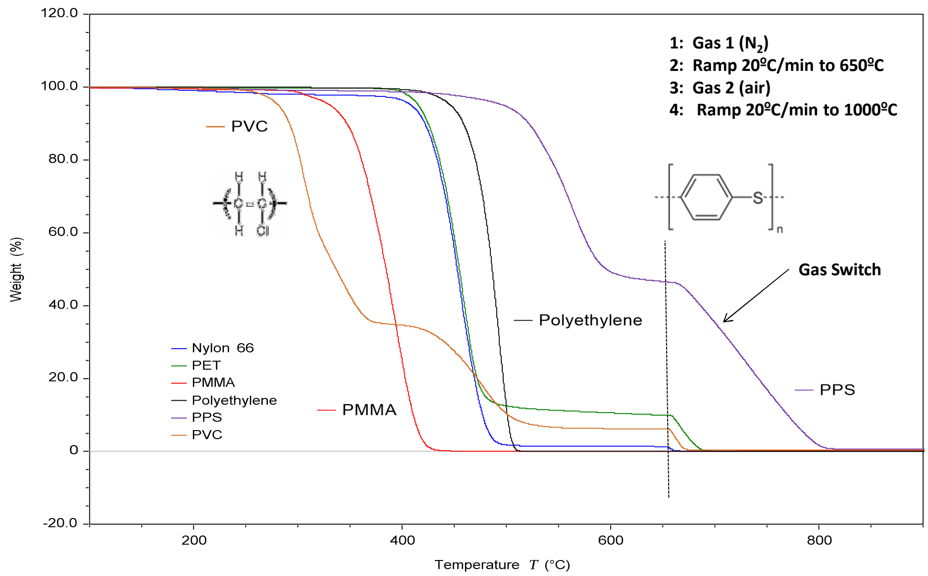
Thermal Stability of Polymers



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TA

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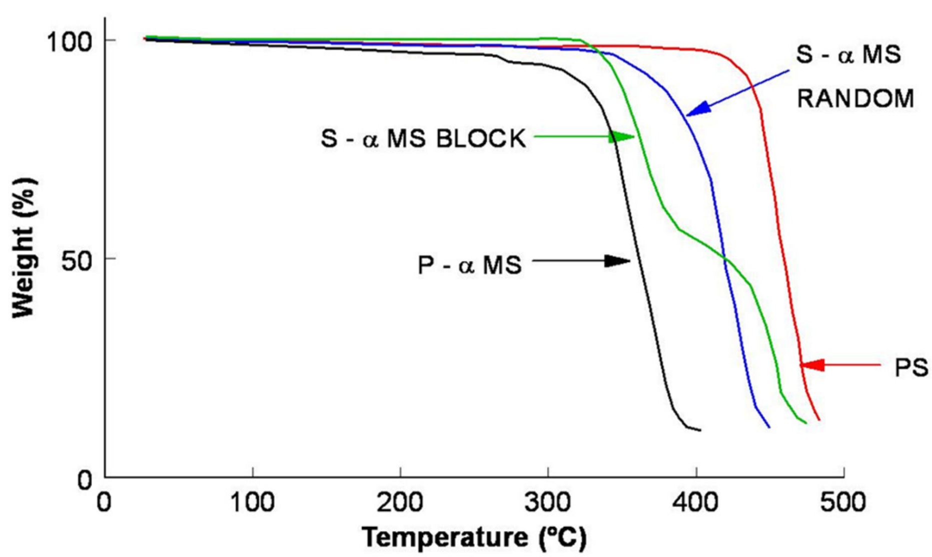
Block versus Random Copolymers



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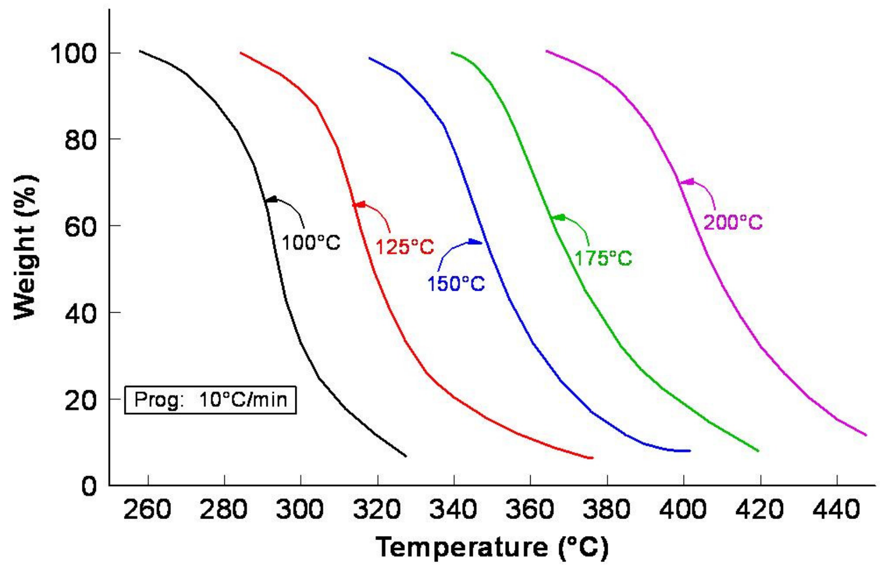
Effect of Epoxy Cure Temperature



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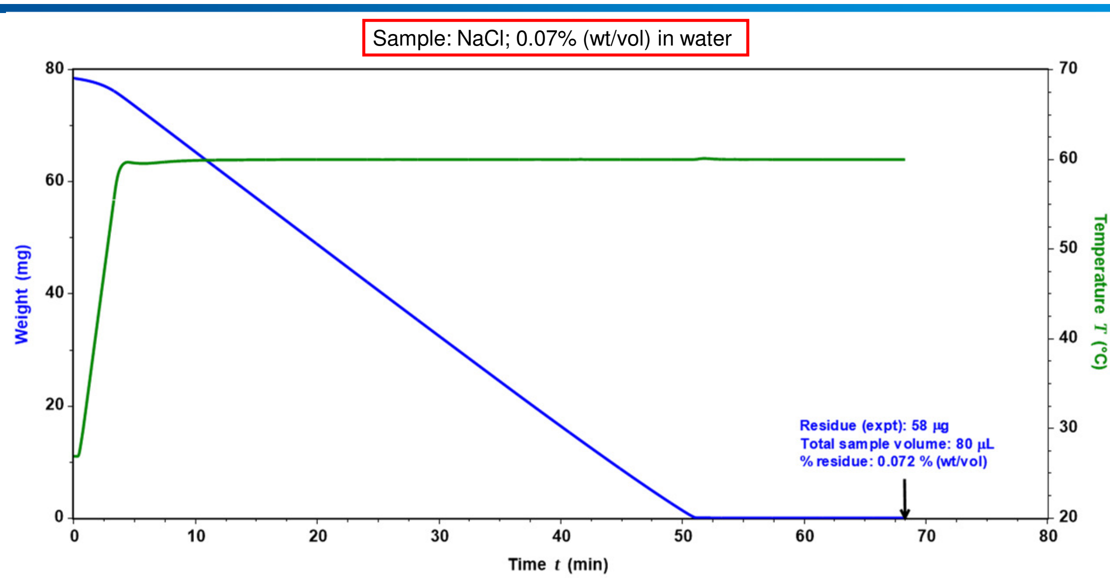
Residue determination using TGA



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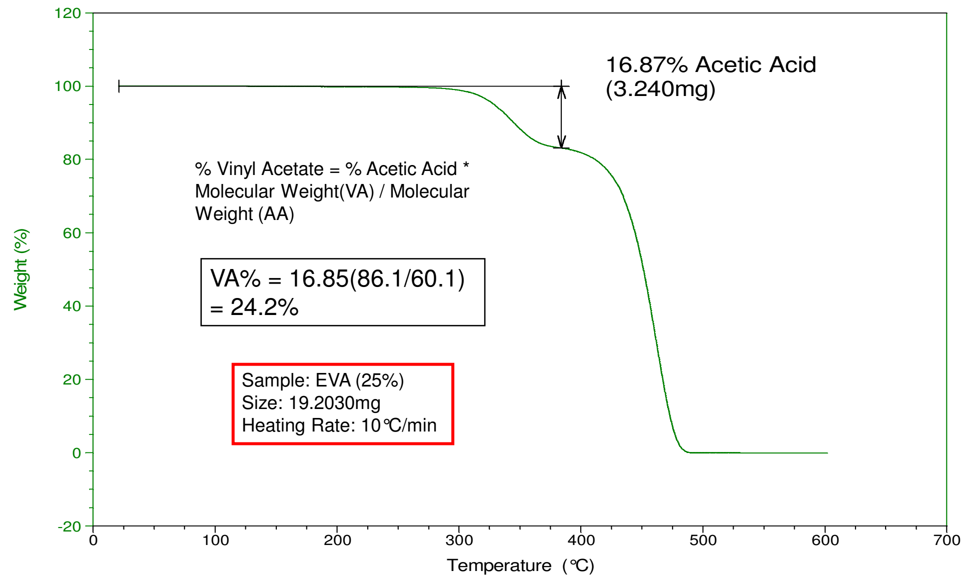
EVA Copolymer



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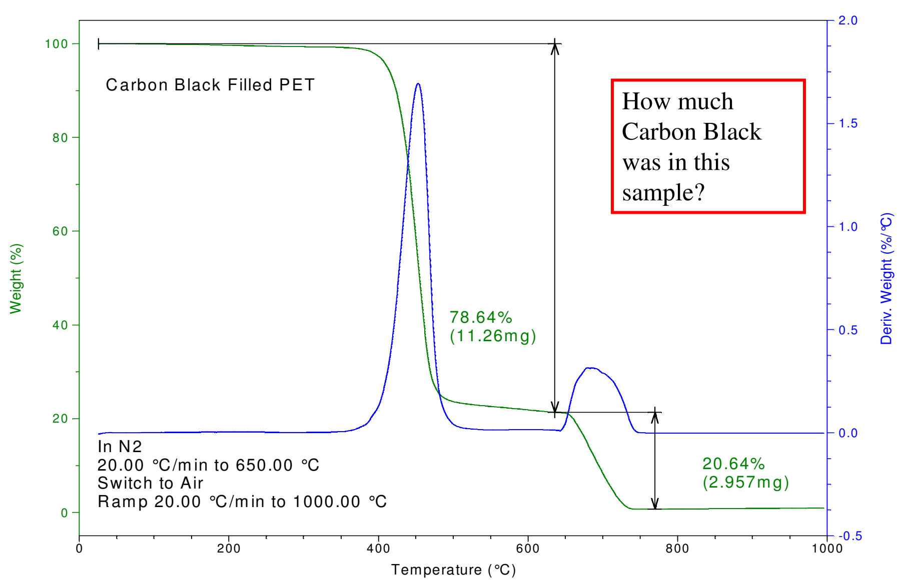
PET w/Carbon Black Filler



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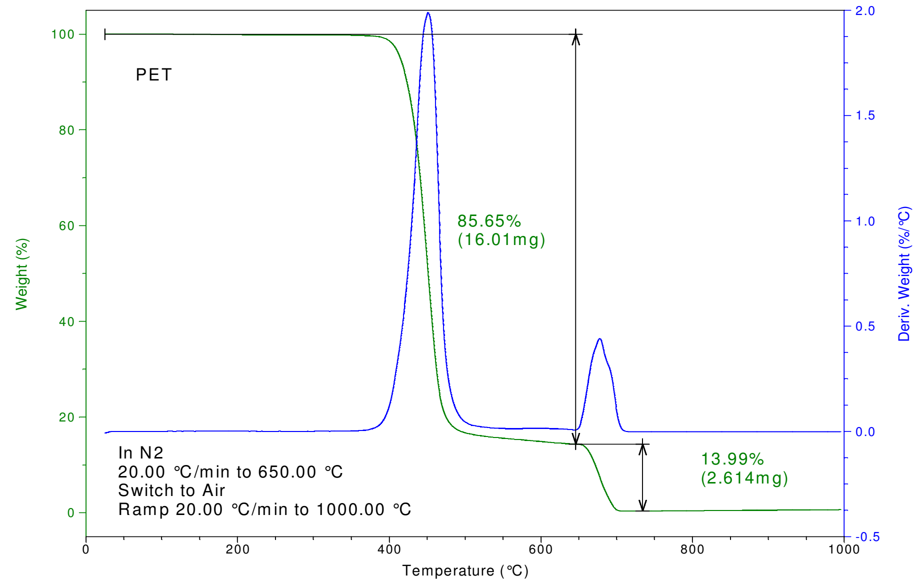
PET Without Filler



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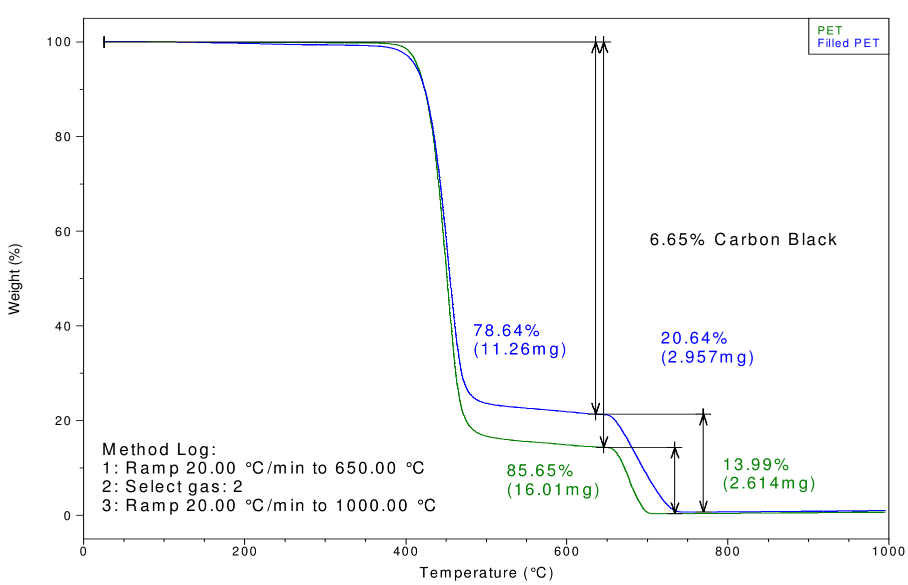
Comparison of Filled & Un-Filled PET



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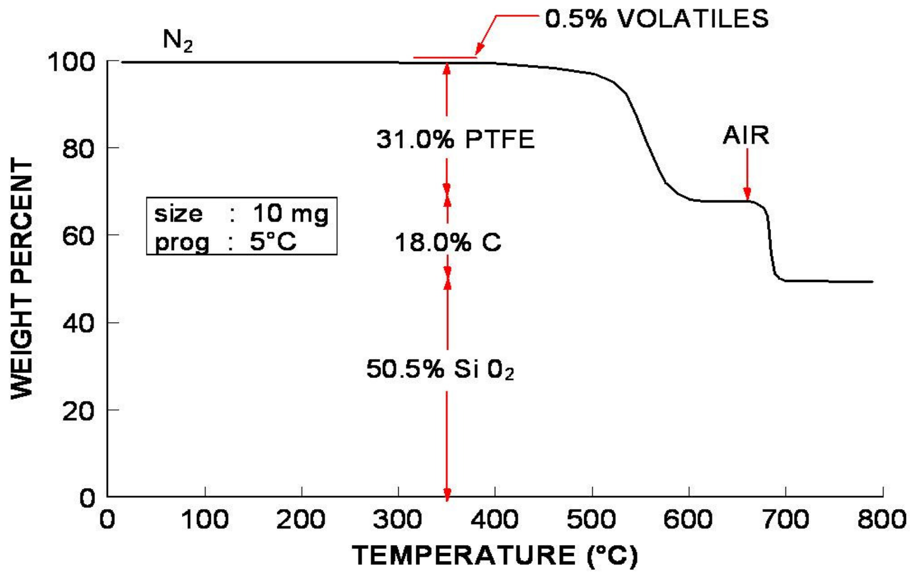
Composite Analysis



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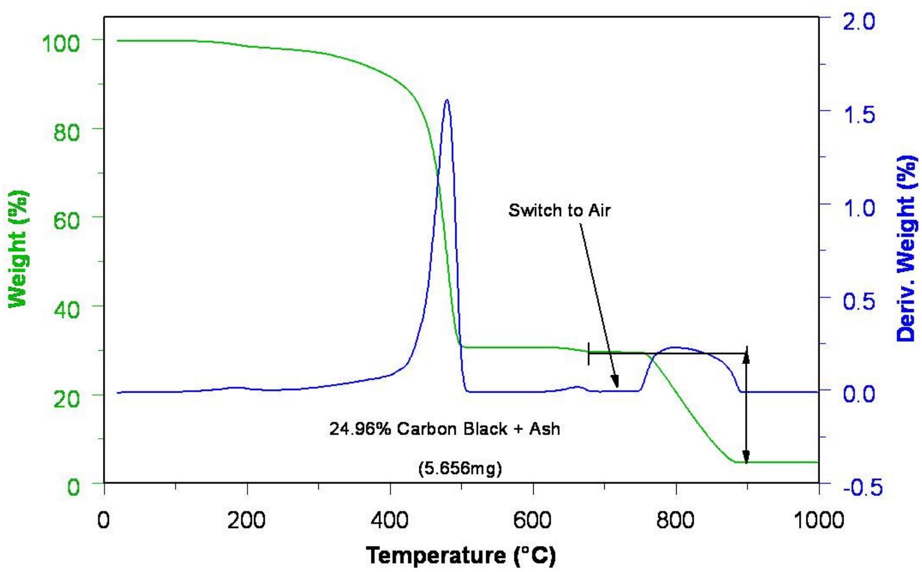
EPDM Rubber Analysis



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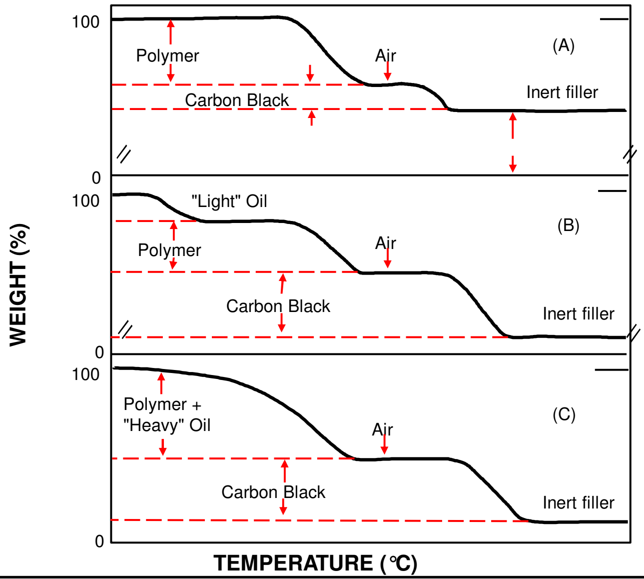
Filled Polymer Analysis



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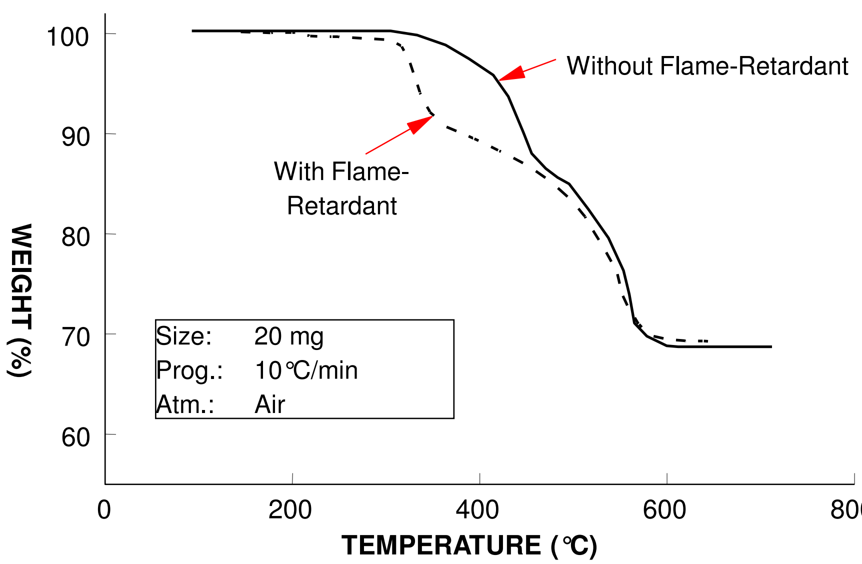
Effect of Flame-Retardant



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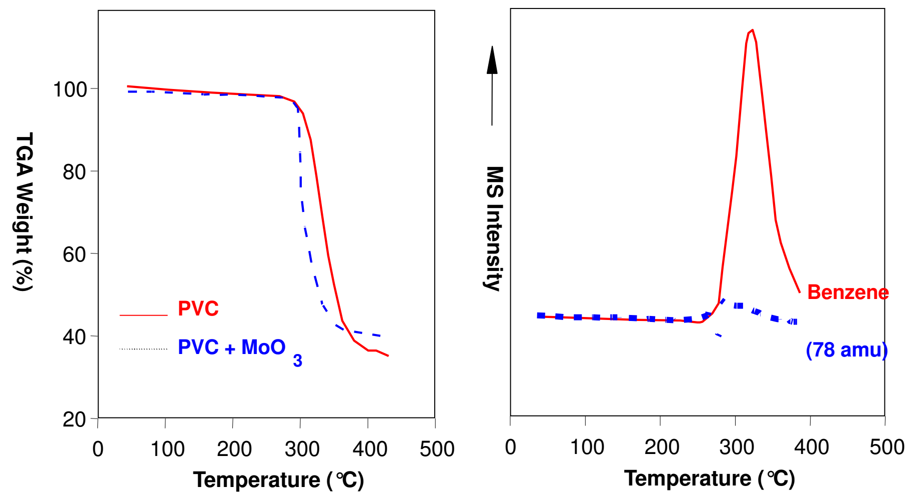
TGA-MS of Flame-Retardant



Benzene is a component of smoke. Much reduced in the flame-retardant sample

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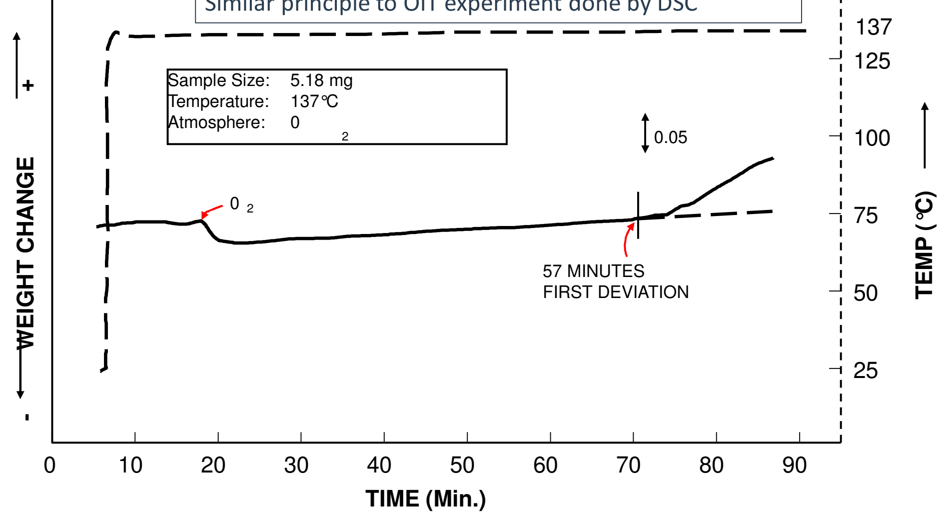
Vegetable Oil Oxidative Stability

Similar principle to OIT experiment done by DSC



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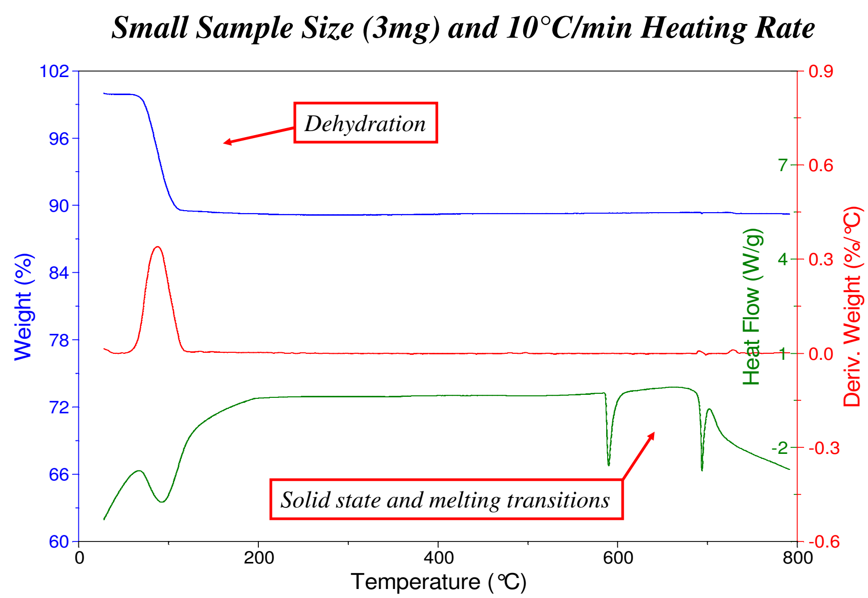
DSC-TGA Sodium Tungstate



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High Resolution TGA

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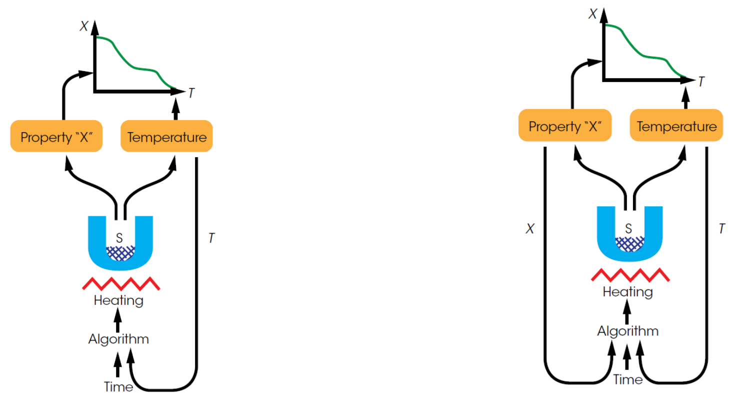
Temperature-controlled TGA (standard TGA) vs sample-controlled TGA



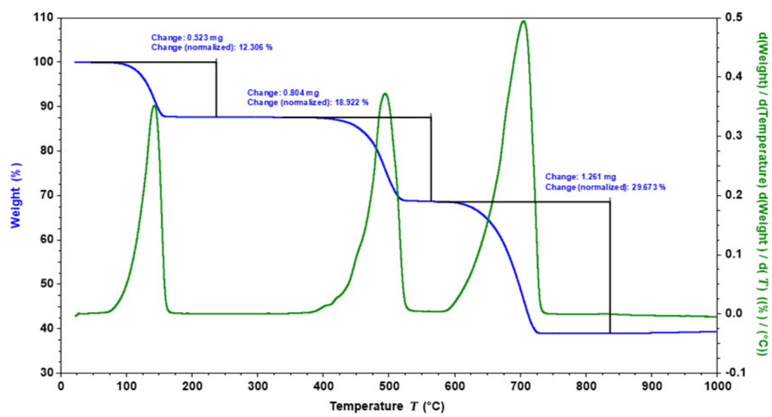
Temperature-controlled thermal analysis **Sample-controlled thermal analysis**

Hi-Res TGA is a sample-controlled TGA method

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

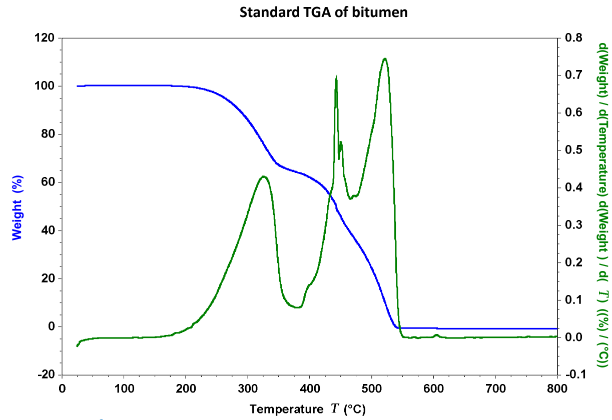
Standard TGA: advantages

- 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

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Improving resolution in Standard TGA experiments

- Means of Enhancing Resolution
  - Slower heating rate
  - Reduced sample size
  - Pin-hole hermetic pans (self-generating atmosphere)
    - Applicable to hydrates & solvates
    - Not applicable to all materials

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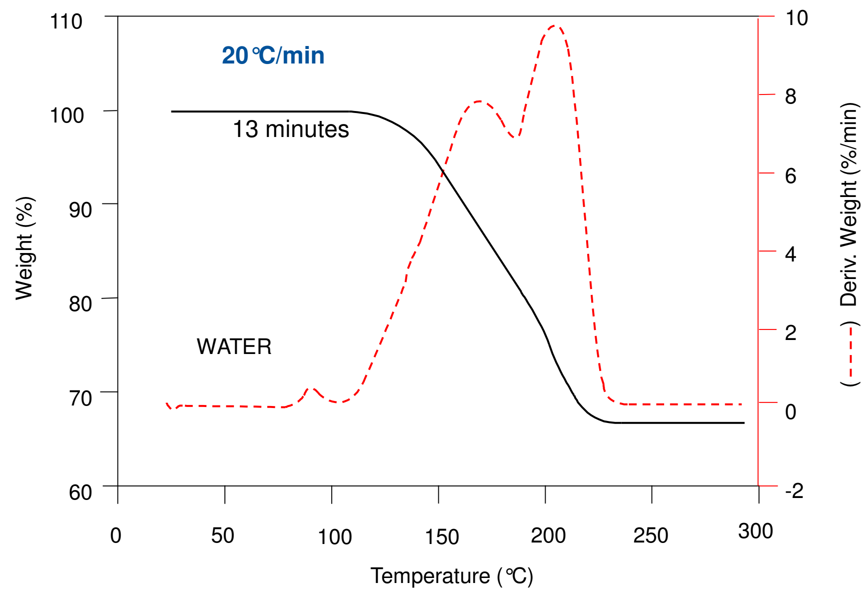
Impact of heating rate on resolution: 20°C/min



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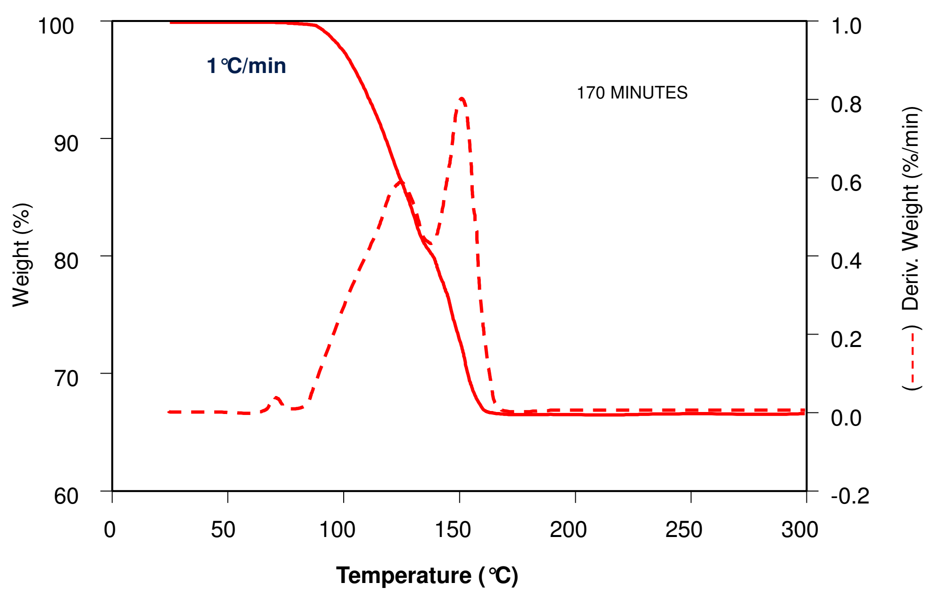
Impact of heating rate on resolution: 1°C/min



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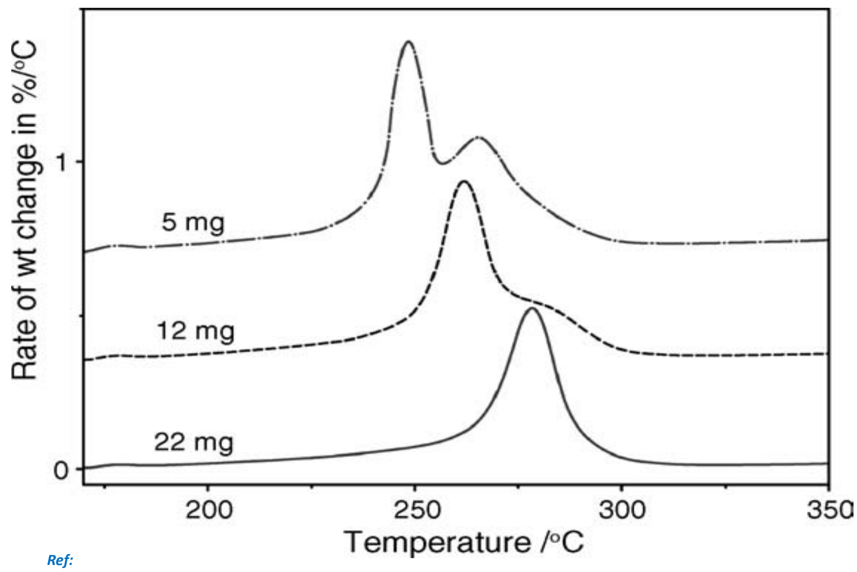
Effect of sample mass on resolution: bitumen



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

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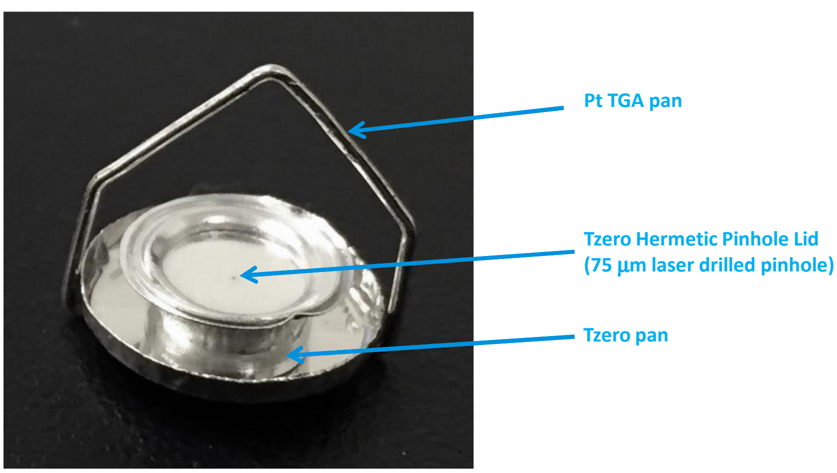
Resolution enhancement using a pinhole hermetic DSC pans



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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 (CaSO4·½H2O)

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

- As heating continues, the anhydrite, CaSO4, is then formed.

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

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Theoretical Mass Losses of Gypsum

- CaSO4·2H2O + heat → CaSO4·½H2O + 1½H2O
  - A loss of 1½H2O = 100*(MW. 1½H2O/ MW. CaSO4·2H2O)
    - = 15.69%
- CaSO4·½H2O + heat → CaSO4+ ½H2O
  - A loss of ½H2O = 100*(MW. ½H2O/ MW. CaSO4·2H2O)
    - = 5.23%
- Total weight loss = 15.69% + 5.23% = 20.92% (2 moles of H2O)

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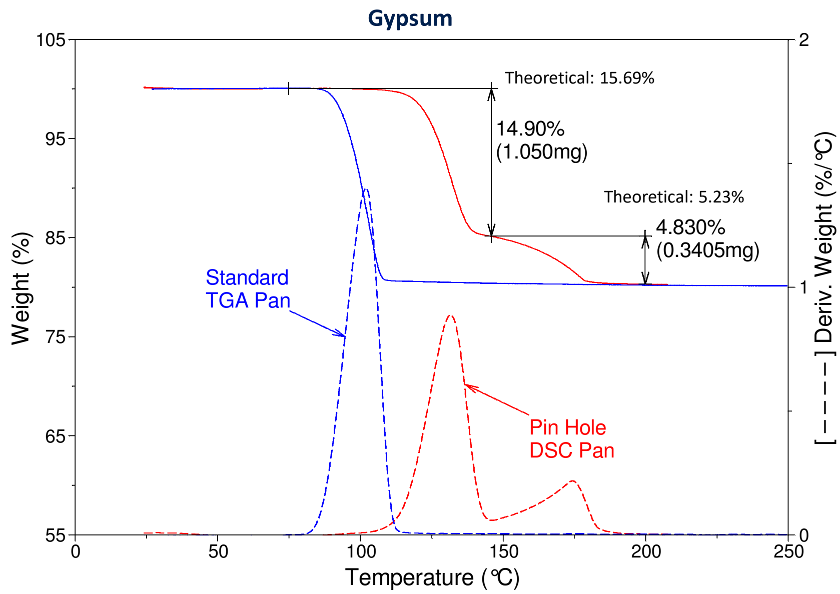
Effect of DSC Pinhole pans on TGA resolution



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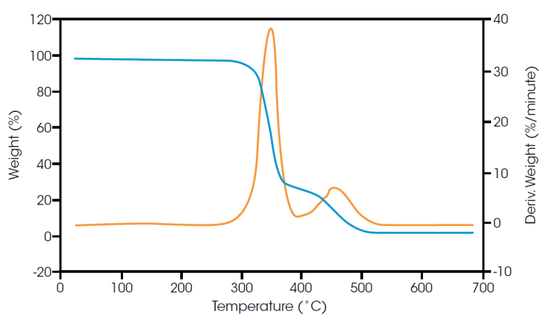
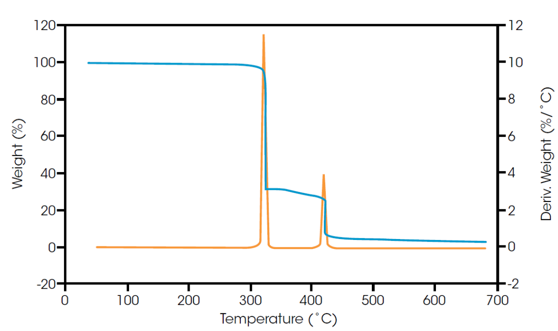
Sample-controlled TGA to improve TGA resolution





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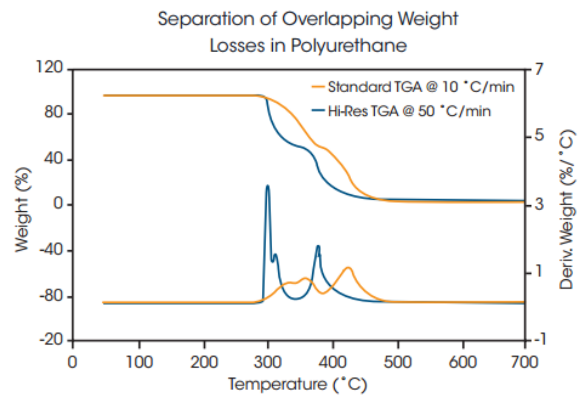
Hi-Res™ TGA

- 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



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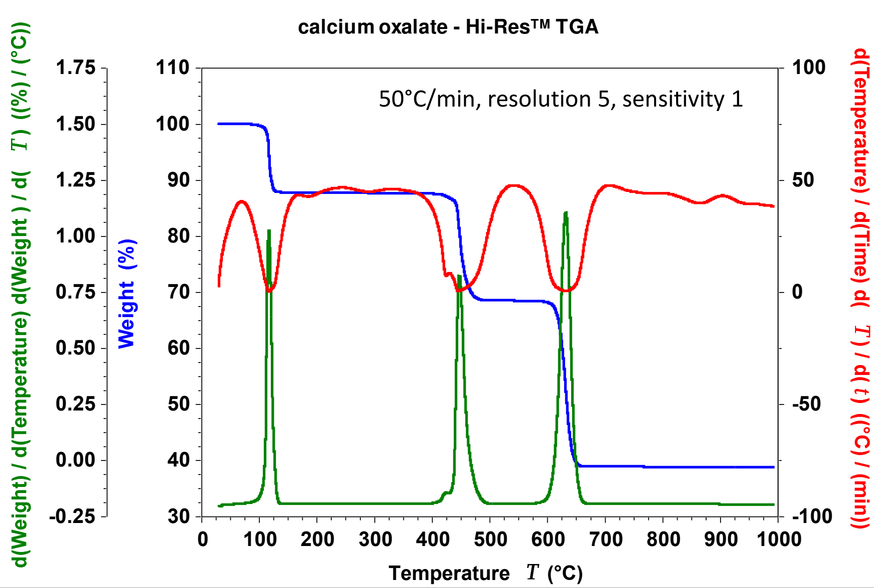
Hi-Res™ TGA of Calcium oxalate



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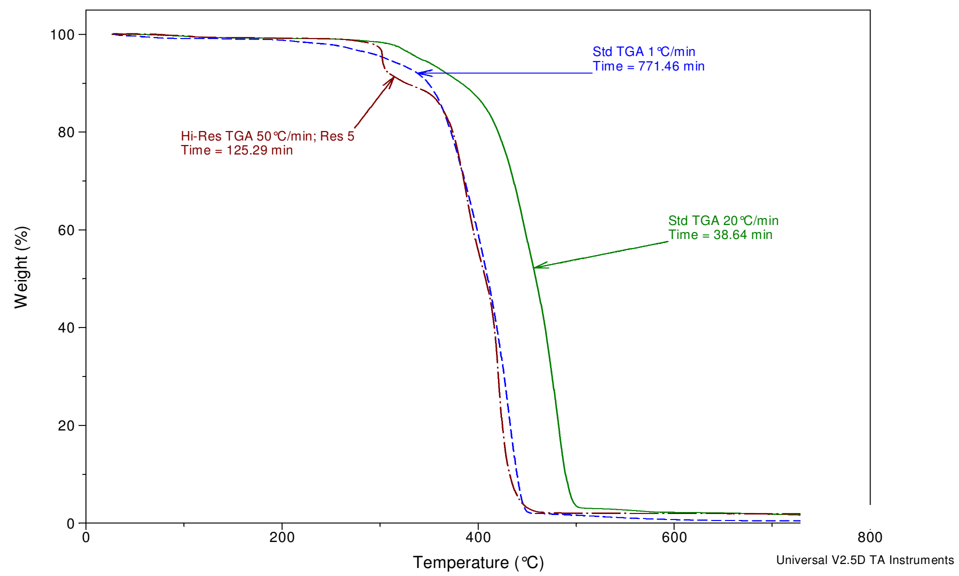
Hi-Res™ TGA vs. Std TGA of Nylon/PE Blend



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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 (D wt%/min)
     - Determines the increase in decomposition rate that warrants a reduction in the heating rate (or vice-versa)
   - Higher sensitivity values increase sensitivity
     - Makes 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

- Sensitivity 1.0
- 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 higher resolution
    - Greater reduction in heating rate at smaller values of wt%/min
    - Also increases the time of the experiment

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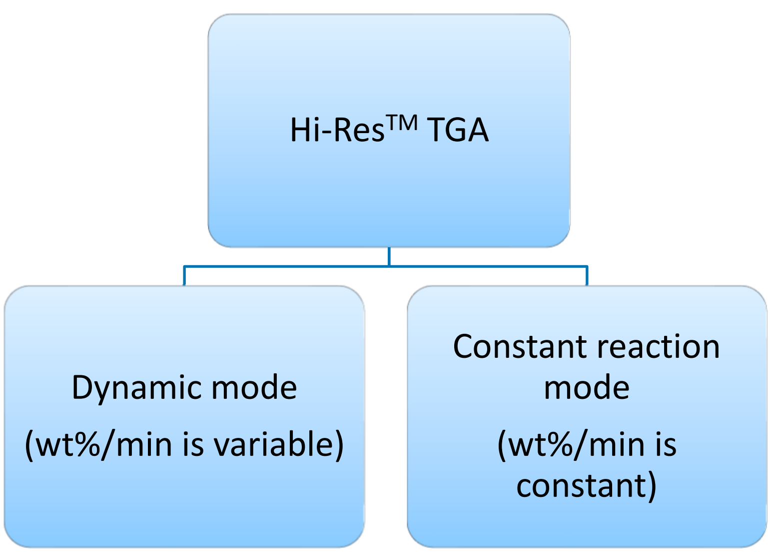
Two modes of Hi-Res™ TGA



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Dynamic Mode

- Positive resolution settings
- Higher heating rate (e.g., 50˚C/min) for most materials
  - Start with 20°C/min for materials with low temperature (under 50-100 °C)
- Heating rate never goes to zero
- Preferred for fast survey scans of unknown samples over wide temperature ranges
- Typically gives better resolution and/or faster time than standard TGA

Constant Reaction Mode

- Negative resolution settings
- Slower heating rate (1-10˚C/min); 5˚C/min is a good start
- Furnace temperature is controlled to maintain a constant preselected rate of weight change
- Preferred for any sample where it is important to limit or control the rate of reaction – may include self-heating reaction, auto-catalyzing reactions, etc

Optimizing the Hi-Res™ TGA settings

- Good starting points
  - Sensitivity of **1**
  - Resolution of **4**
- Higher resolution number means slower heating rate, therefore, longer experiment time
- Increase the resolution number if you need further separation of derivative peaks

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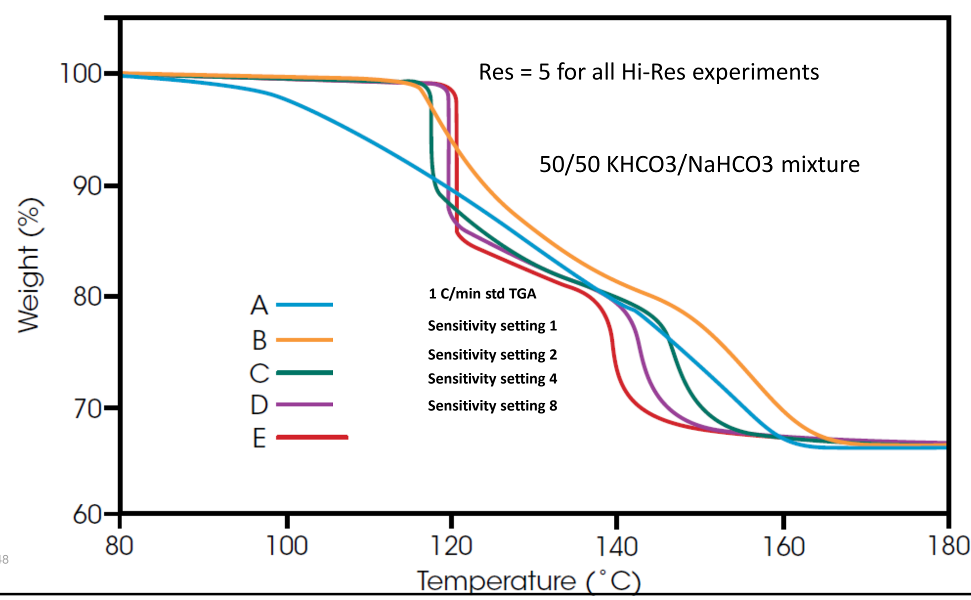
Effect of sensitivity settings on TGA data



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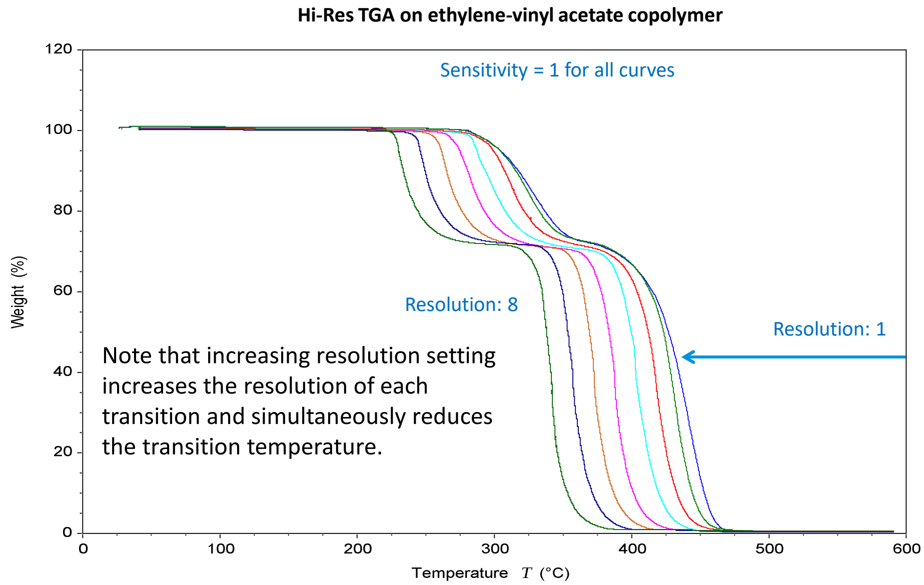
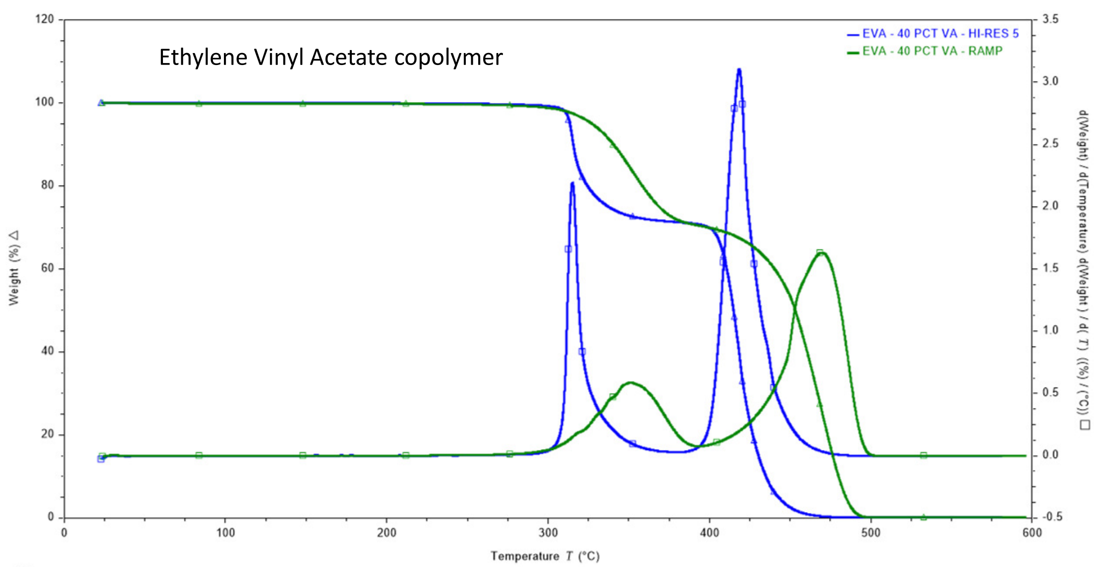
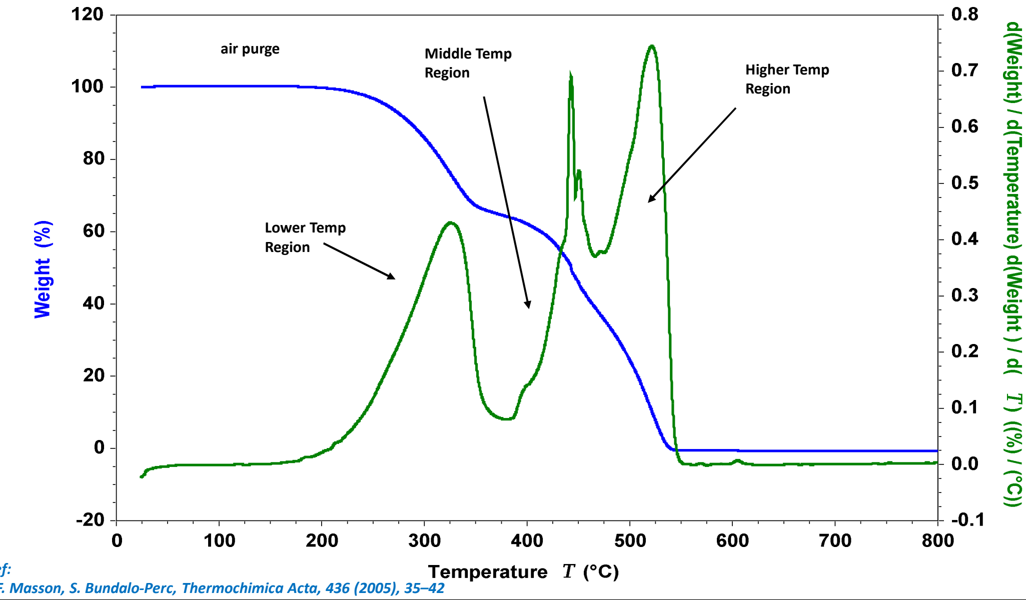
Effect of resolution settings on TGA data



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



Standard TGA 10°C/min of bitumen sample



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

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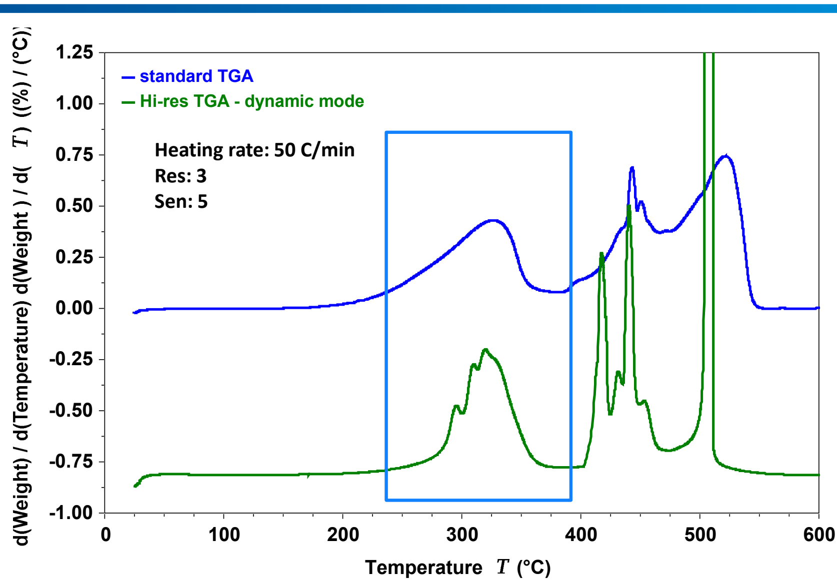
Standard TGA vs Hi-Res™ TGA (dynamic mode) of bitumen sample



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

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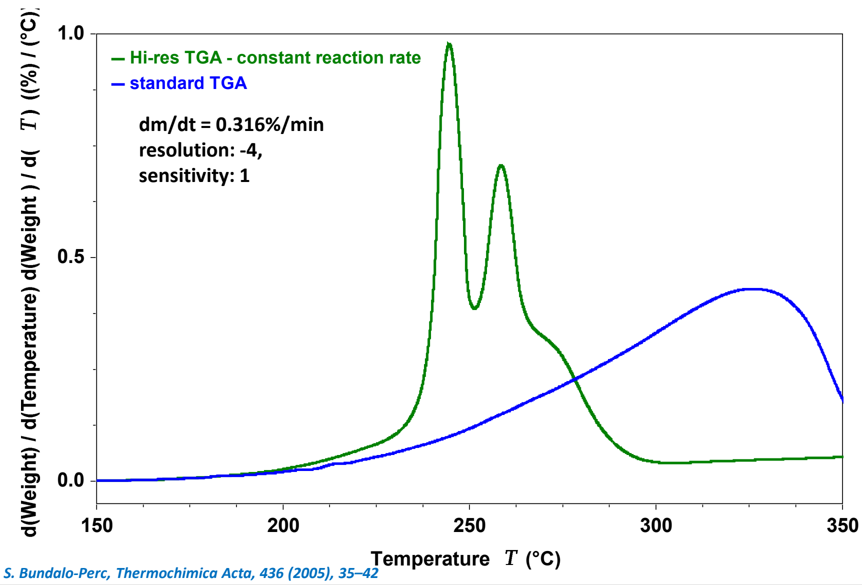
Constant Reaction Rate TGA of bitumen sample



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

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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

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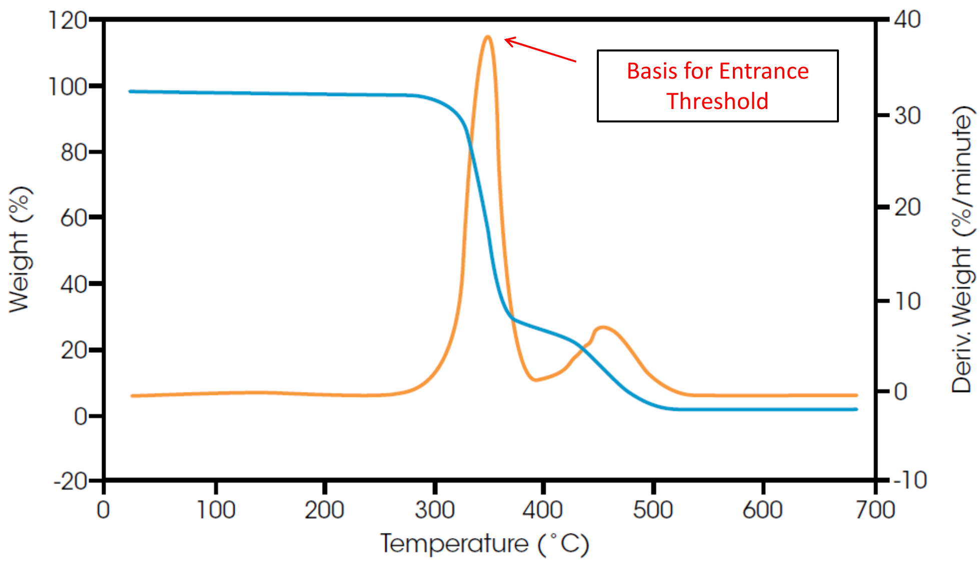
Automated Stepwise Isothermal TGA (SWI)

- 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
  - Available on any TA Instruments 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



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

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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

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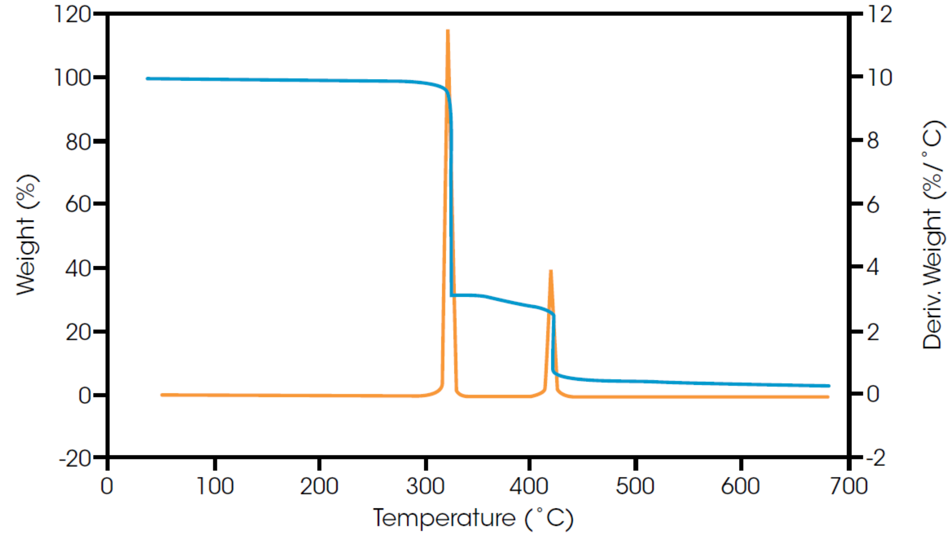
SWI of Polyvinyl Acetate



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

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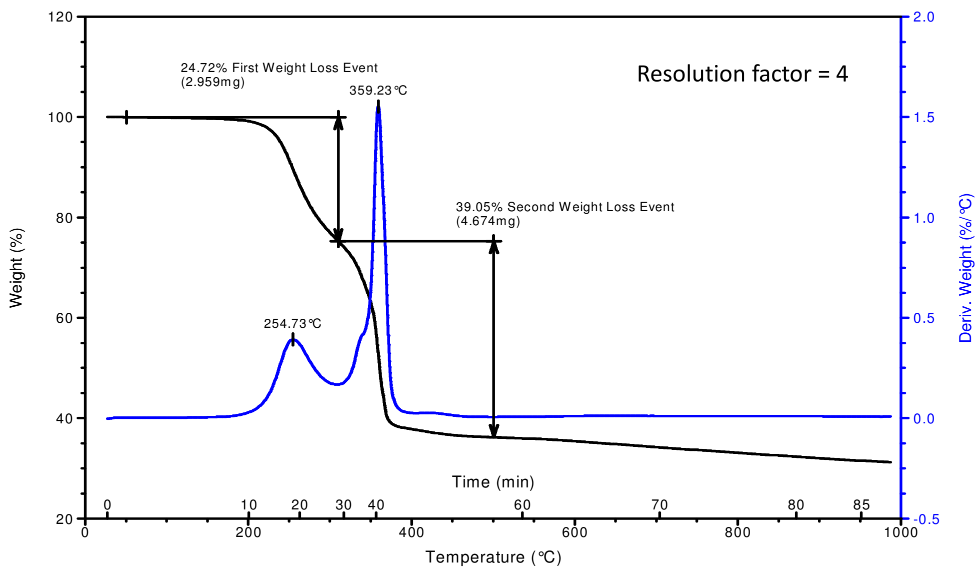
Hi-Res™ TGA of lubricating oil



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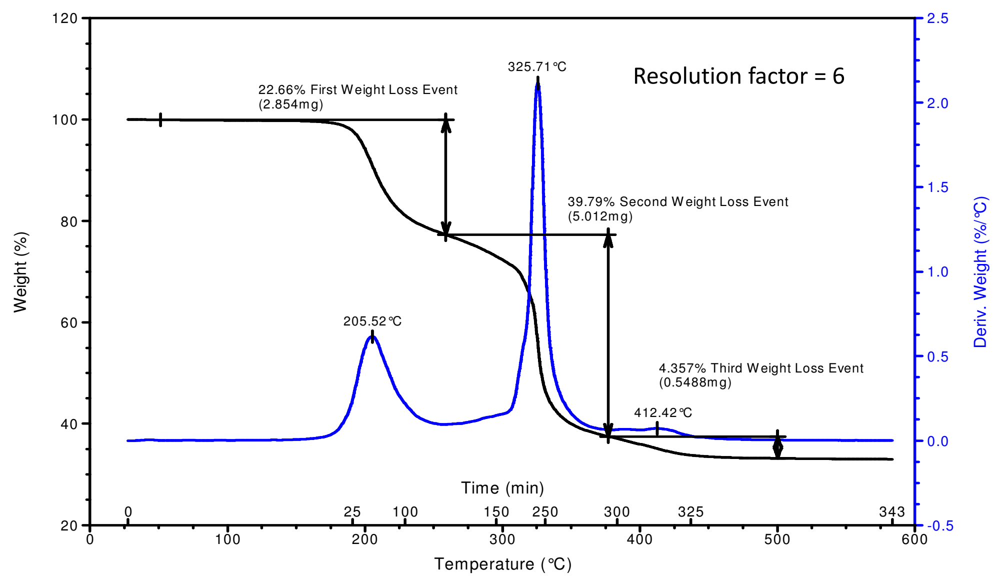
Hi-Res™ TGA of lubricating oil



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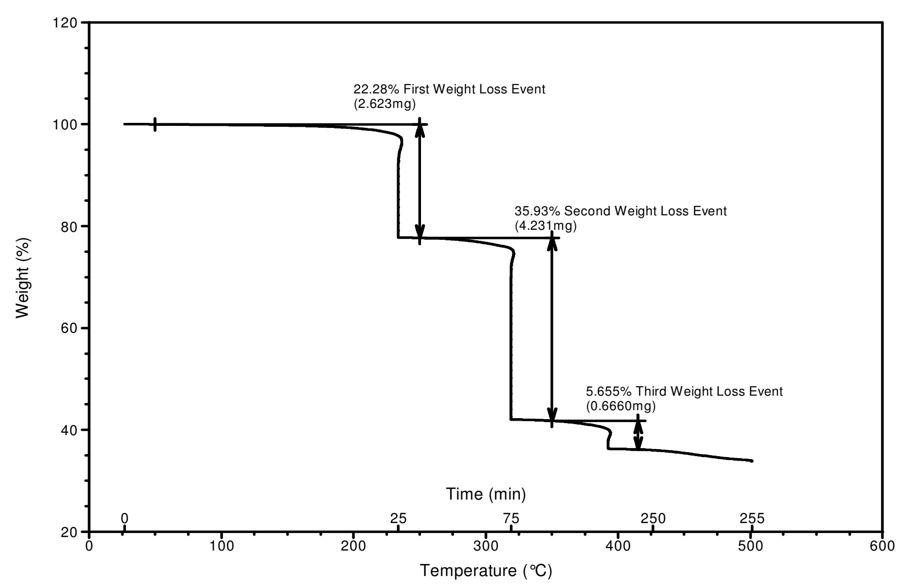
Stepwise Isothermal TGA of lubricating oil



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Decomposition Kinetics by MTGA™

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Decomposition Kinetics Background

- Includes isothermal and constant heating rate methods
- Constant heating rate method is the fastest and will be discussed here
- Ultimate benefit obtained in 'Life-Time' plots
- Requires at least 3 TGA runs at different heating rates or 1 Modulated TGA® run

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Kinetic Analysis

- The rate at which a kinetic process proceeds depends on the temperature the specimen is at, and the time it has spent at that temperature
- Typically kinetic analysis is concerned with obtaining parameters such as
  - Activation energy (Ea),
  - Reaction order (n), and
  - Generating predictive curves for conversion (α)

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Fundamental equation for kinetics

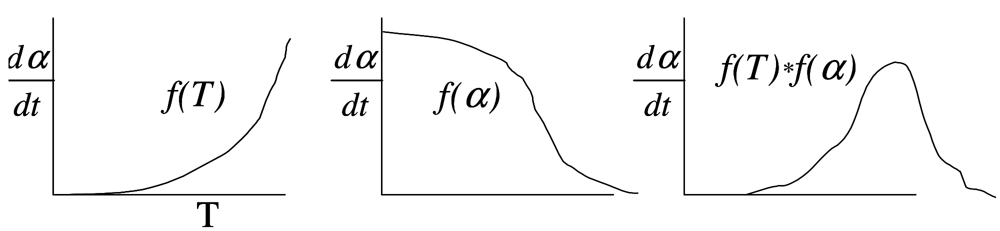
$$\frac{d\alpha}{dt} = f(T) \bullet f(\alpha)$$

α = fraction reacted or converted

$\frac{d\alpha}{dt}$ = reaction rate

$f(T)$ = a function of Temp.

$f(\alpha)$ = a function of α



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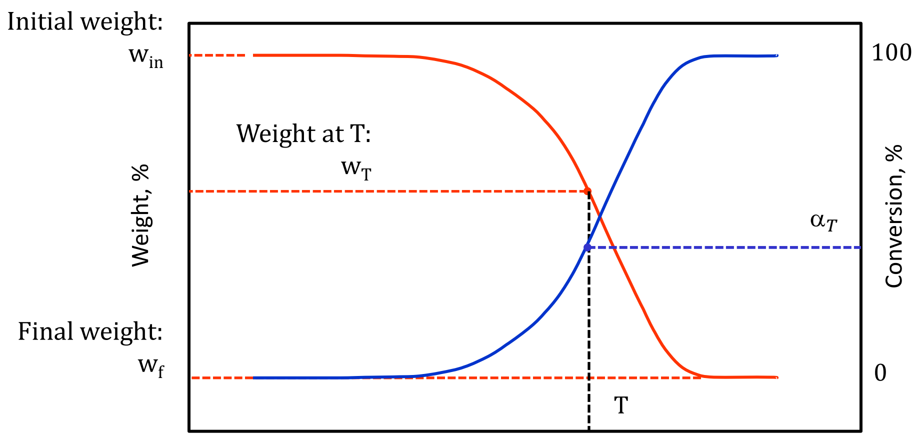
Kinetics by TGA

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



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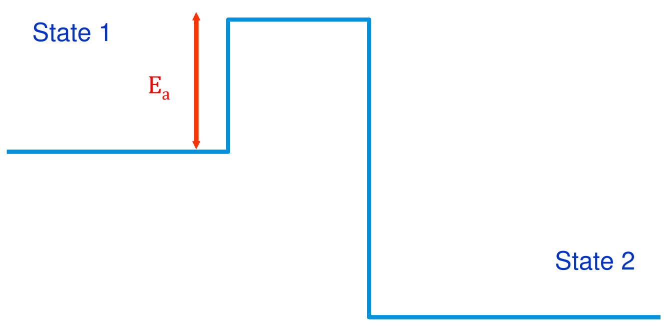
Kinetic Analysis

Activation energy (E_a) can be defined as the minimum amount of energy needed to initiate a chemical process.



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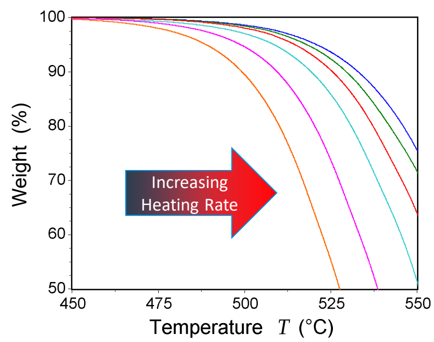
Decomposition Kinetics by TGA

- Traditional methods include isothermal and constant heating rate techniques
- ASTM E1641
  - Based on method of Flynn and Wall – Polymer Letters, 19, 323 (1966). Requires collection of multiple curves at multiple heating rates



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Recipe for Activation Energy by ASTM E1641

- Run TGA experiment on polymer at 4-6 different heating rates
- Obtain a temperature at an isoconversional point – for example 10% weight loss for each heating rate
- Plot the ln of the heating rate (β) versus 1/T (temperature units must be in Kelvin)
- Slope of the line is (-Ea/R). Multiply the slope of the line by –(8.314 x 10-3) to obtain the activation energy in kJ/mol

TA Instruments Application Note TA251
Blaine, R. L. and Hahn, B. K., "Obtaining Kinetic Parameters by Modulated Thermogravimetry," J. Therm. Anal., Vol. 54, 1998, p. 694.

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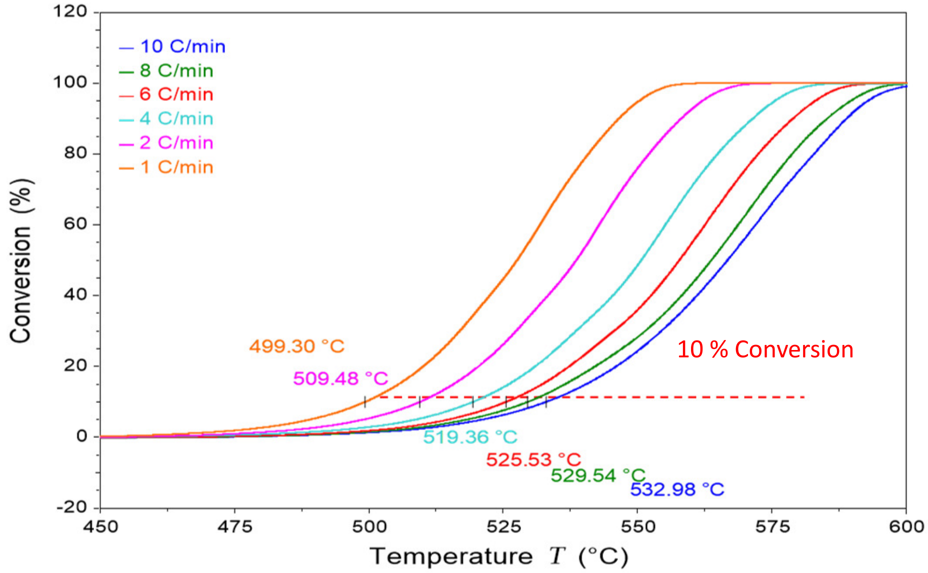
PTFE Decomposition by ASTM E1641



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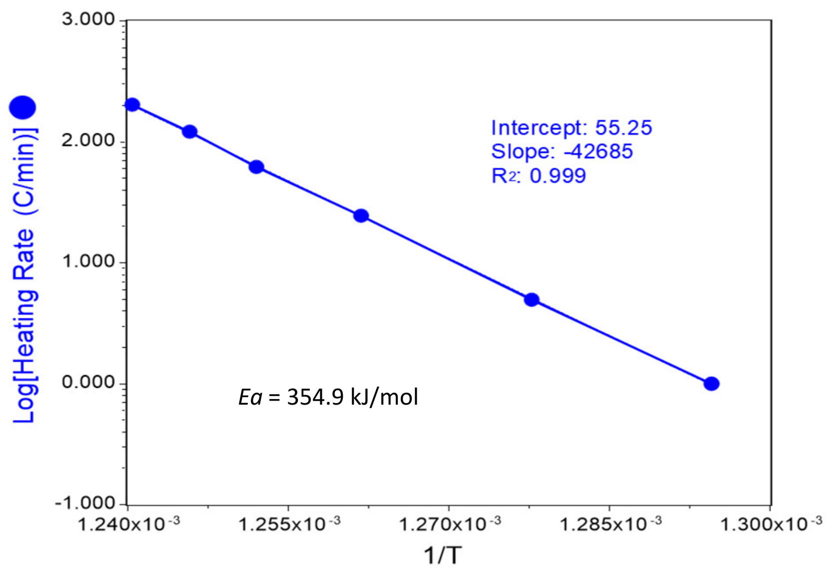
PTFE Decomposition by ASTM E1641



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Advantages of MTGA™

- One run needed to obtain activation energy
  - (ASTM E2958)
- Activation energy is a signal in the data file
- Comparable with Flynn-Wall method for calculated Ea with the benefit of the reduced time
- Method works under quasi-isothermal or ramping conditions
- Activation energy is obtained as a continuous curve and so can be manipulated numerous ways. For example, it can be plotted as a function of conversion
- Can be combined with Hi-Res™ to speed up experiments and more accurately handle multiple weight loss events

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Setting Up MTGA™ Experiment

- Three parameters must be defined:
  - Heating rate
  - Modulation period
  - Modulation amplitude
- What is the effect of these parameters on the data? What are the optimum values?

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Setting Up MTGA™ Experiment - General Guidelines

- Higher amplitudes improve signal/noise and increase precision but require longer periods to make sure the sample is remaining in equilibrium
- Longer periods ensure equilibrium but require slower ramp rates so the minimum 5 cycles per transition can be obtained
- A scouting run at 10 °C/min is useful to determine width of transitions
- Range of consistent results:
  - Period = 200-300 s (practical range: 100 – 500s)
  - Amplitude = 3-5°C (practical range: 1 – 10°C)
  - Ramp Rate = 1 °C/min (practical range: 0.5 – 2 °C/min)

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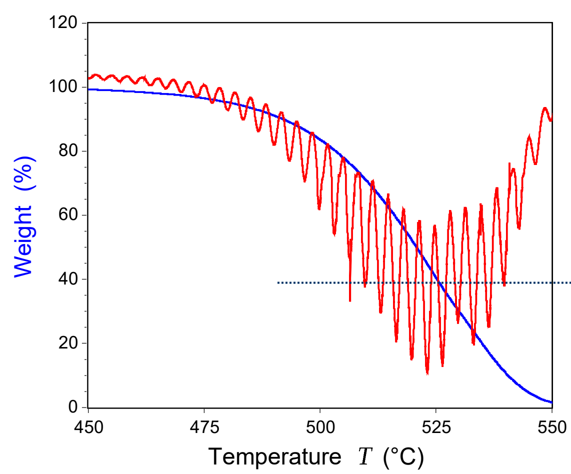
MTGA™ – Typical Values

- Modulation period – 200 seconds
- Amplitude – 5°C
- Heating rate – 1°C/min
- Plot derivative of weight loss and calculate the width at half height of the derivative weight loss peak.
  - Need at least 5 modulation cycles across this region.



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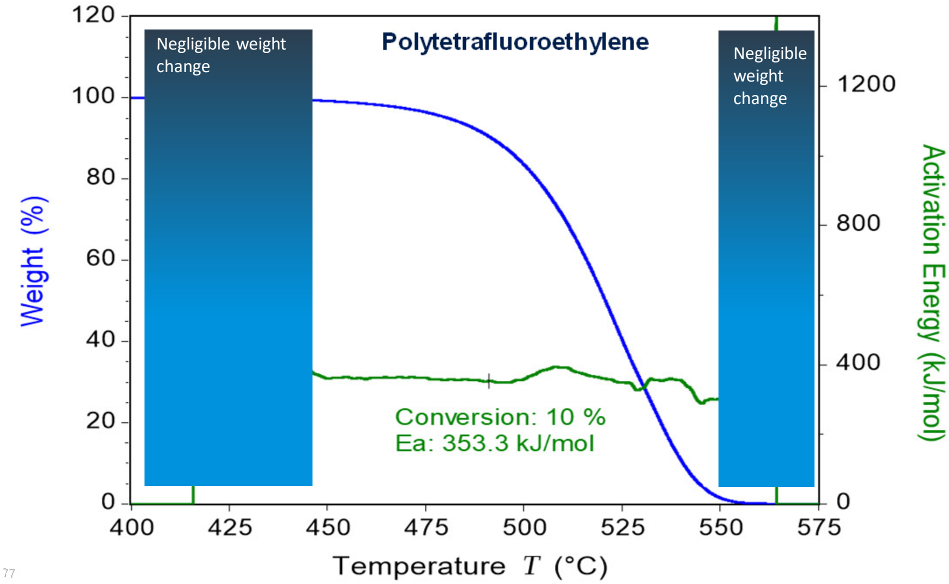
PTFE: Modulated Ramping Experiment



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MTGA Precision: PTFE

Conversion (%)	#1	#2	#3	#4	#5	Average (kJ/mol)	Standard Deviation (kJ/mol)	Relative Stnd Dev (%)
1	333.0	342.4	335.8	345.9	340	339.42	5.14	1.51
2	334.9	329.3	330.8	330.8	327.7	330.70	2.67	0.81
5	319.3	322.6	323.7	319.7	323.1	321.68	2.03	0.63
10	313.1	314	311.9	316.2	318.6	314.76	2.66	0.85

Repeatability = 2.8X Standard Deviation

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C.G. Slough The Accuracy, Repeatability, and Reproducibility of Activation Energy Values Measured by Modulated Thermogravimetry. J of Testing and Evaluation V. 42, N. 6 (2014)

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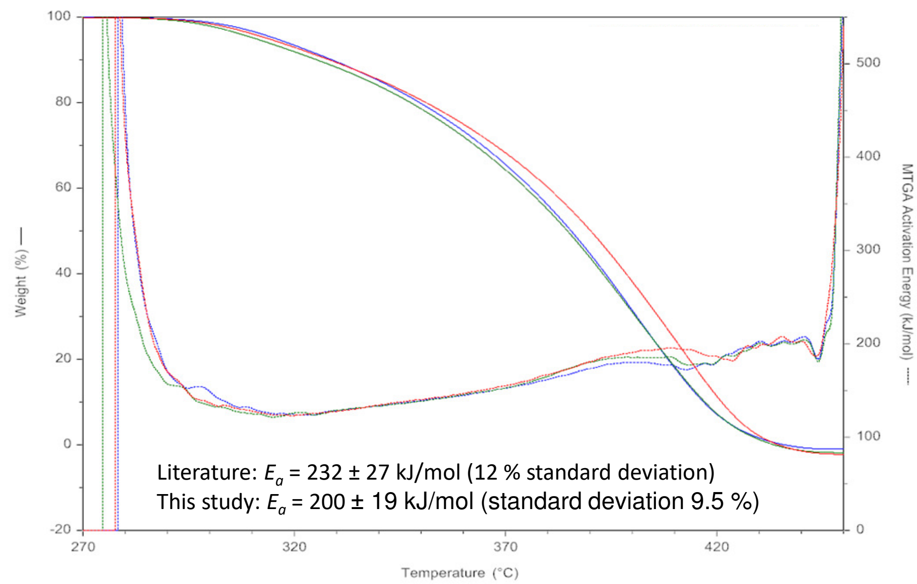
PP: Modulated Ramping Experiment



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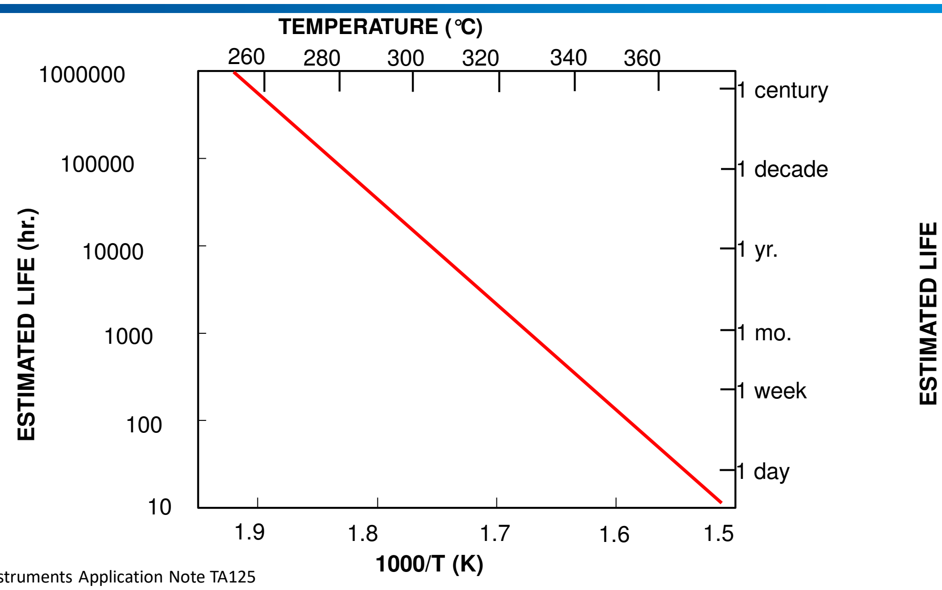
TGA Kinetics - Estimated Lifetime



TA Instruments Application Note TA125
Estimation of Polymer Lifetime by TGA Decomposition Kinetics

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Evolved Gas Analysis

- Identification of Decomposition Products Using TGA/FTIR and TGA/Mass Spec

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Why Use Evolved Gas Analysis?

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

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TGA-EGA: Typical Applications

- Polymers (composition, hazard evaluation, identification)
- Natural Products (contamination in soil, raw material selection {coal, clays})
- Catalysts (product/by-product analysis, conversion efficiency)
- Inorganics (reaction elucidation, stoichiometry, pyrotechnics)
- Pharmaceuticals (stability, residual solvent, formulation)

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TGA-FTIR Advantages

- No solvents
- No sample preparation
- Rugged
- Easy maintenance
- Good sensitivity
- Easy to use
- Excellent for scouting or determining presence of absence of species

- Fast identification of functional groups
- Search capabilities are really good – Thermo Nicolet for example
- Data interpretation can be challenging.
- Generally, with EGA analysis, a strong chemistry and analytical chemistry background is needed

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EGA Example – TGA/FTIR

- The gases produced during thermal breakdown of the sample flow through a heated transfer line into a gas cell where infrared radiation passes through.
- The total infrared absorption and frequency as a function of time is stored in an array as the Gram Schmidt file which is opened with the instrument software (Gram Schmidt Reconstruction)
- The Gram Schmidt reconstruction will typically resemble the derivative with respect to temperature of the weight loss curve in the TGA experiment
- Individual FTIR spectra are displayed by selecting points on the x-axis of the Gram Schmidt reconstruction which has units of intensity as a function of time
- Typically spectra can be searched using vendor supplied spectral data bases and fairly reliable identifications of species can be made

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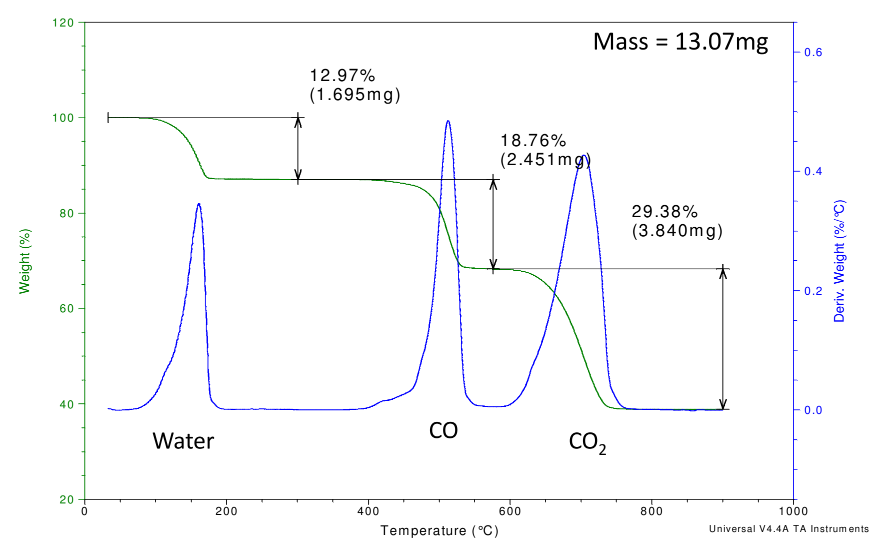
Calcium Oxalate Monohydrate – TGA Data



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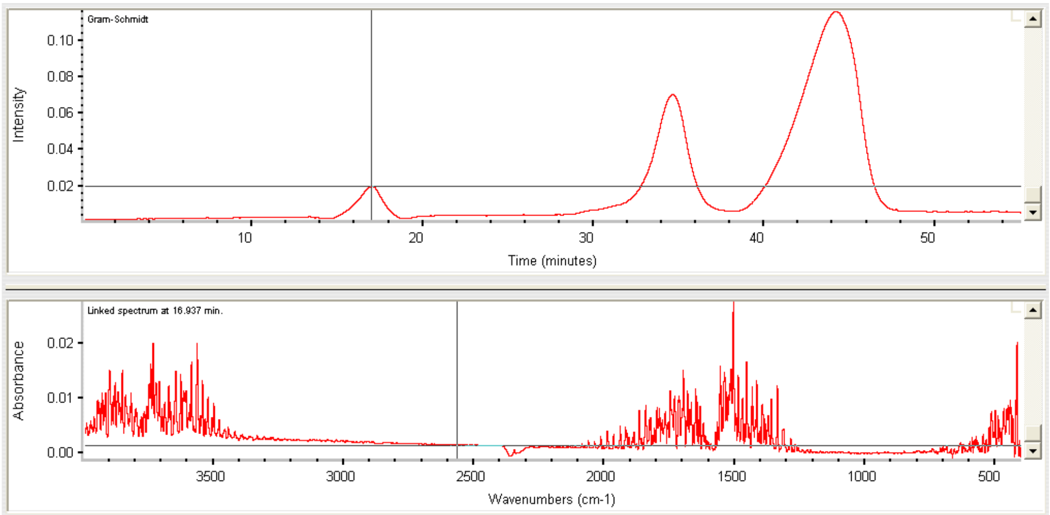
Calcium Oxalate – Water



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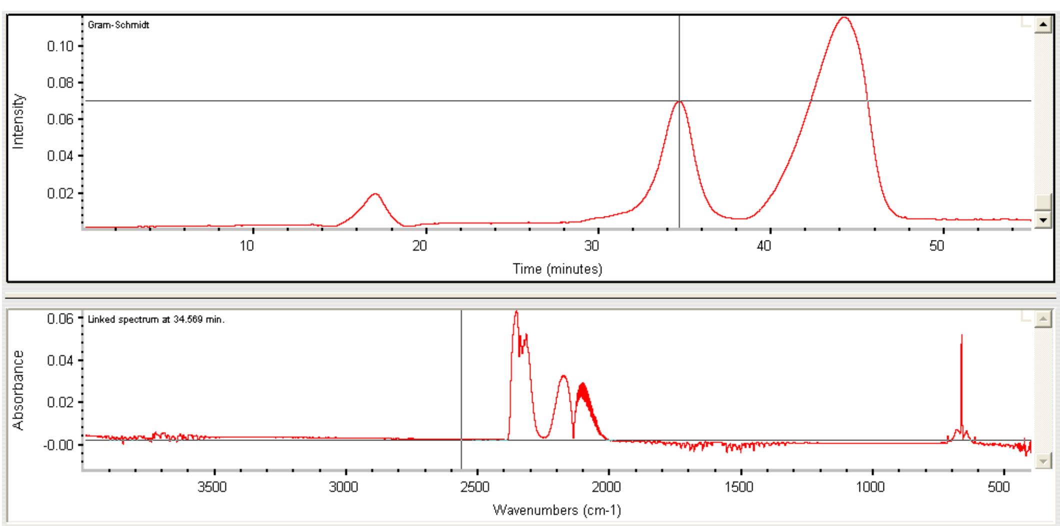
Calcium Oxalate – CO + CO2



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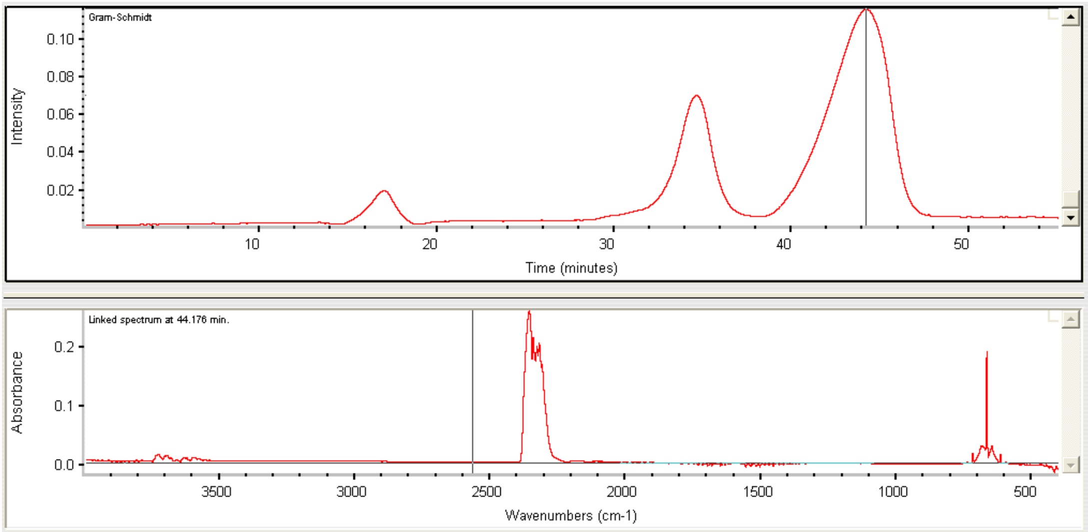
Calcium Oxalate – CO2



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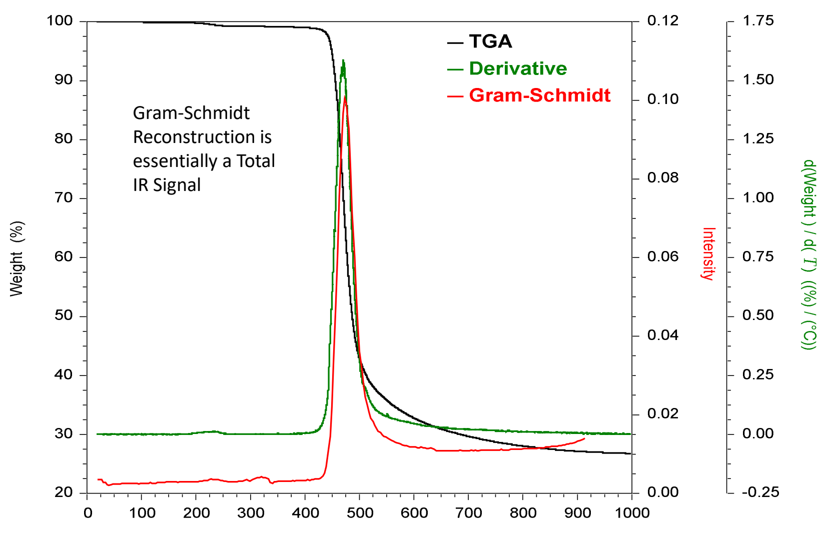
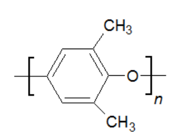
TGA-FTIR: Analysis of Polyphenylene Oxide



Engineering polymer
-Heat resistant
-Good tensile properties



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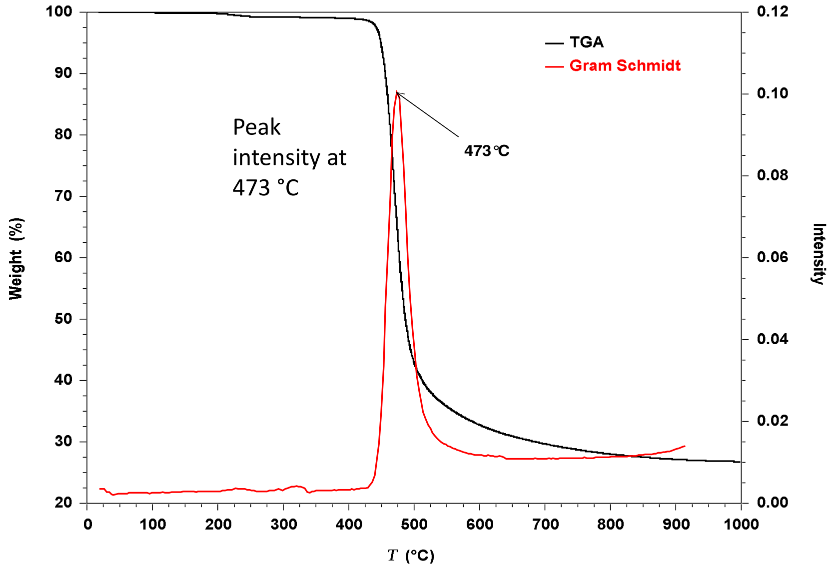
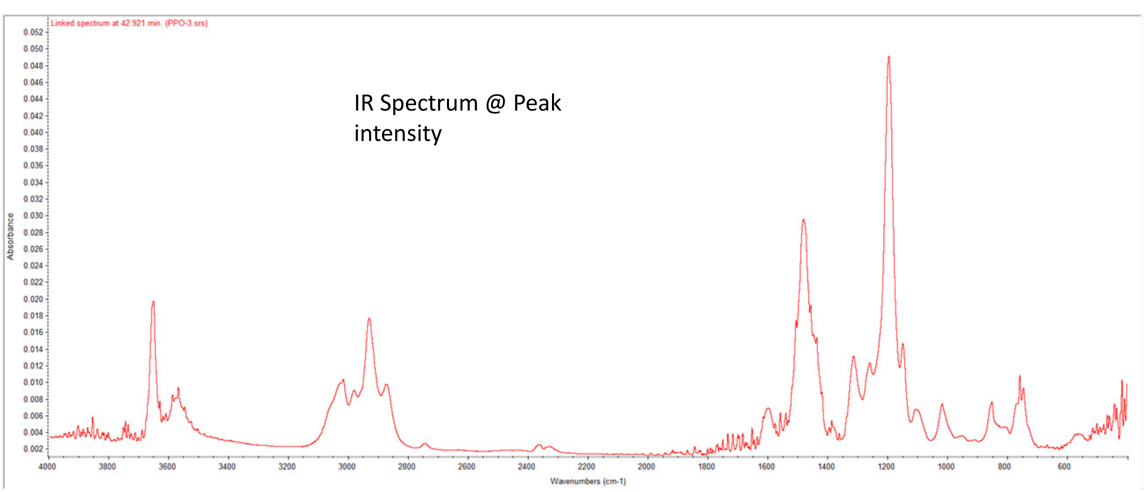
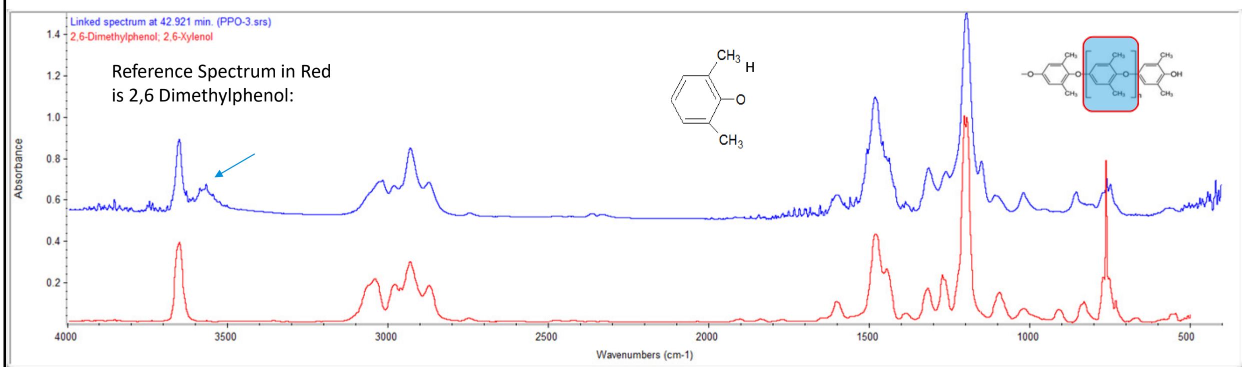
TGA-FTIR: Analysis of Polyphenylene Oxide



TGA-FTIR: Analysis of Polyphenylene Oxide



TGA-FTIR: Analysis of Polyphenylene Oxide



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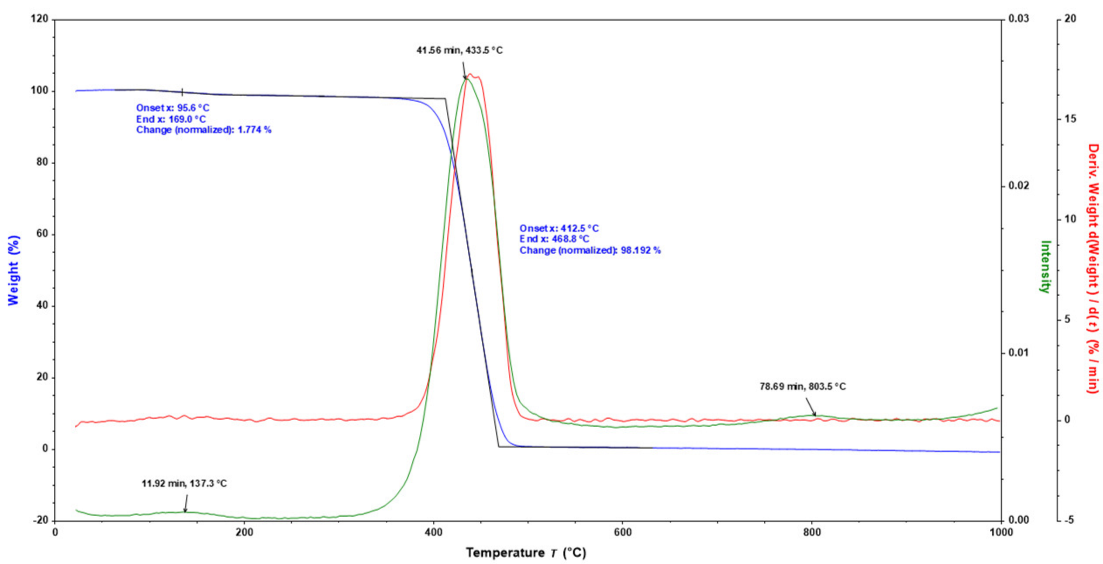
TGA-FTIR: Analysis of Nylon 6,6



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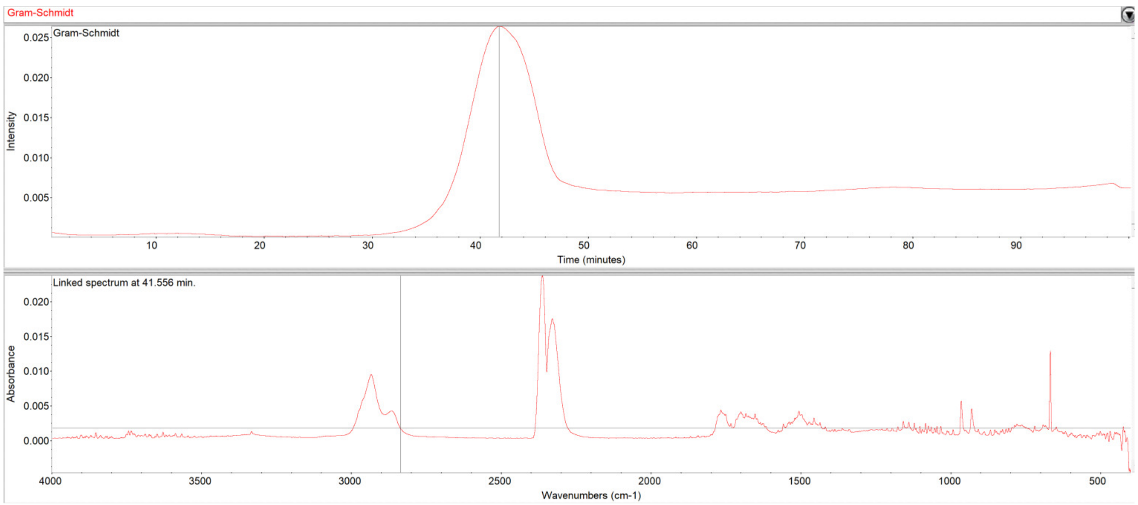
TGA-FTIR: Analysis of Nylon 66



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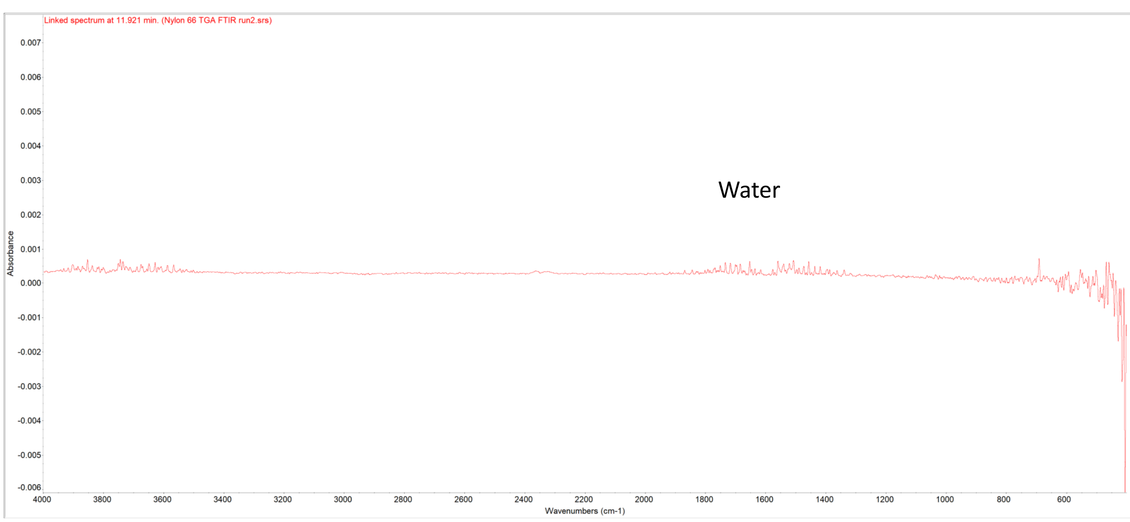
TGA-FTIR: Analysis of Nylon 66



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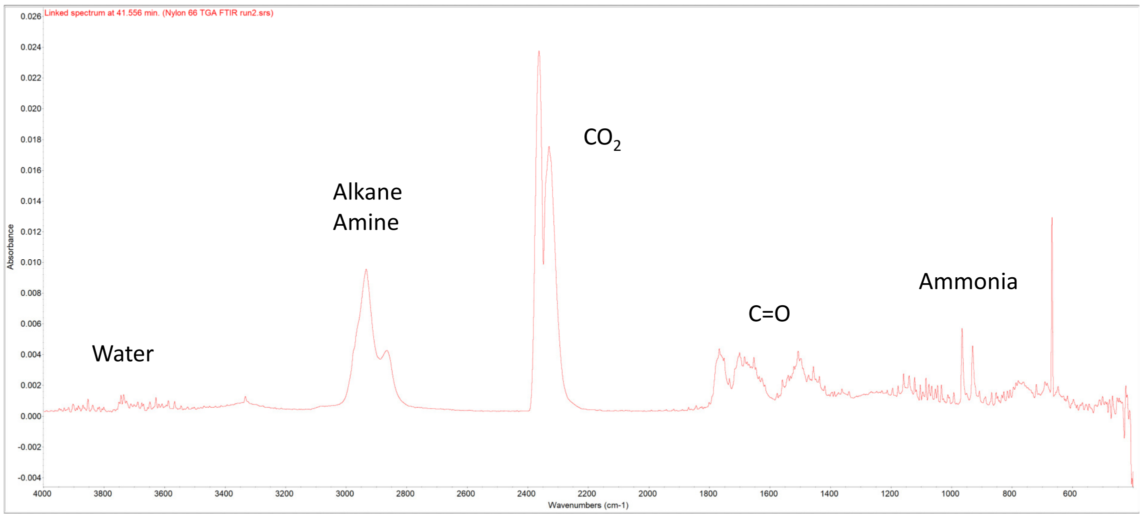
TGA-FTIR: Analysis of Nylon 66



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FTIR Library Search

- Libraries give the best single spectra match to the data presented
- If multiple components are being emitted during a single weight loss event, the spectra will be superimposed upon each other possibly leading to difficulties
- The existence of searchable libraries does not relieve the analytical chemist from critically analyzing the search results
- ThermoNicolet FTIR software can attempt to deconvolute a spectrum to a maximum of four components. Demonstration can be found in this TA Instrument webinar: https://www.tainstruments.com/evolved-gas-analysis-tgaftir/

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TGA Mass-Spectrometry Benefits

- Additional information for the interpretation of the reactions in the TGA results
- Sensitive method for the analysis of gaseous reaction products
- Exact control of the furnace atmosphere before starting and during the experiment

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Discovery Mass Spectrometer – TGA / MS

- Advantages
  - No solvents
  - No sample preparation
  - Rugged
  - Easy maintenance
  - Good sensitivity
  - Easy to use
  - Excellent for scouting or determining presence of absence of species – great complement to GC / MS
- Disadvantages
  - No search capability
  - Data interpretation can be challenging (as with any unit mass spectrometer)
  - Multiple software platforms for data reduction

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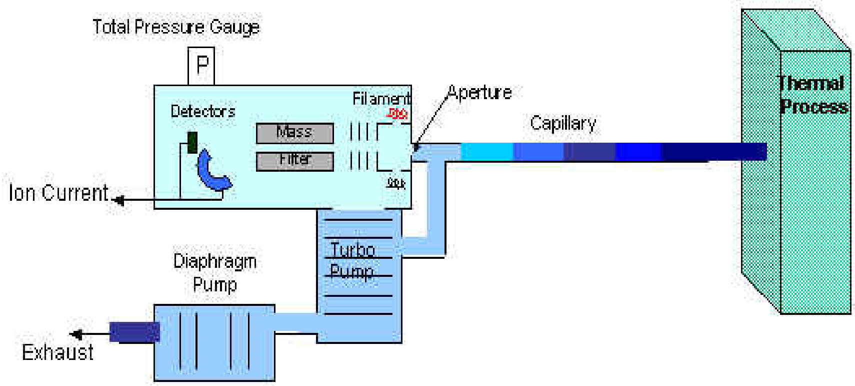
TGA-MS: System Schematic



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The Discovery Mass Spectrometer (DMS)

- Benchtop, unit resolution quadrupole mass spec designed and optimized for evolved gas analysis (EGA)
- Quadrupole detection system includes:
  - Closed ion source
  - Quadrupole mass filter assembly
  - Dual detector system (Faraday and Secondary Electron Multiplier) ensuring excellent sensitivity from ppb to percent concentrations

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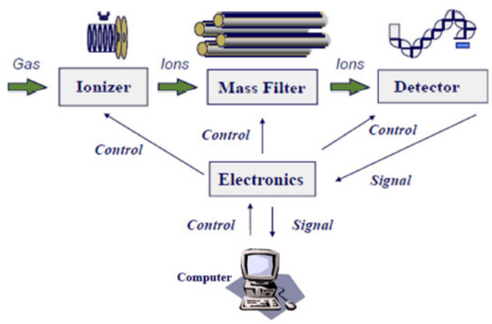
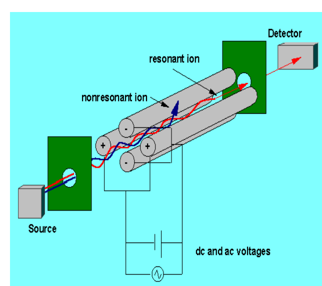
TGA / MS

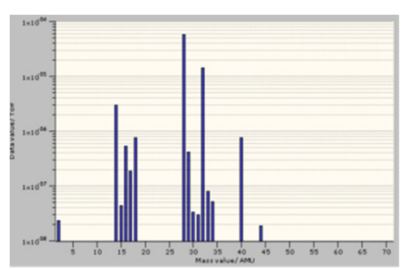
- Gases formed during the TGA experiment are drawn down a heated transfer line into the mass spectrometer where they are ionized by an ion stream from the ion source, sorted by the quadrupole mass filter and ultimately amplified and detected.



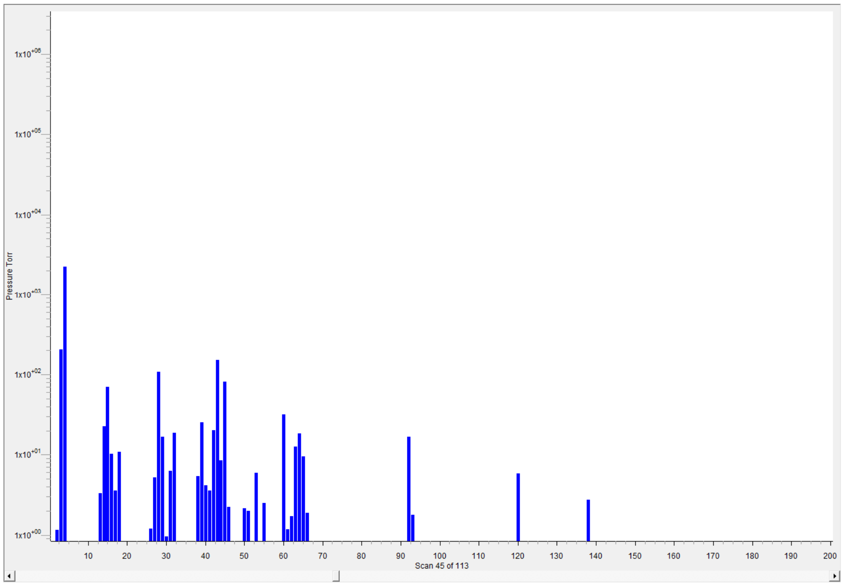
What is a Quadrupole Mass Spectrometer?

- Ionizes gas molecules and atoms
  - Electron impact knocks off an electron and fragments molecules forming positive ions
- Sorts by the mass/charge (m/z) ratio
- Measures the ion current
- Displays ion current vs. m/z ratio
- When calibrated against inlet pressure - can display partial pressure vs. m/z ratio





TGA-MS Example: Aspirin



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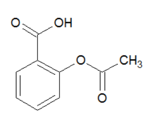
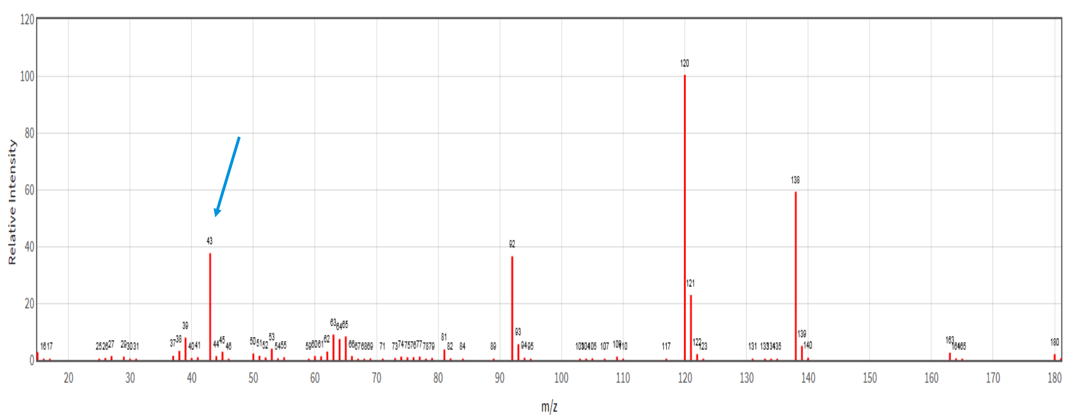
MS Data Presentation

Aspirin

Mass Spectrum





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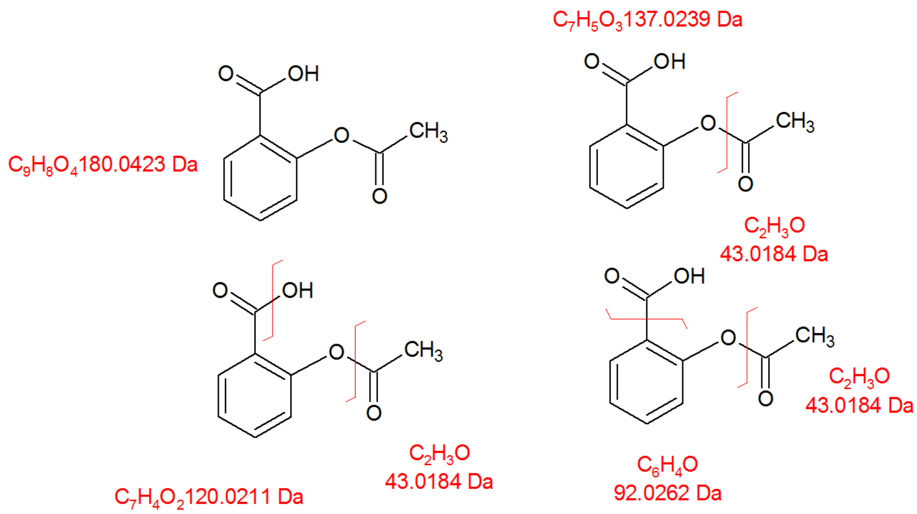
Mass Spectrum of Aspirin



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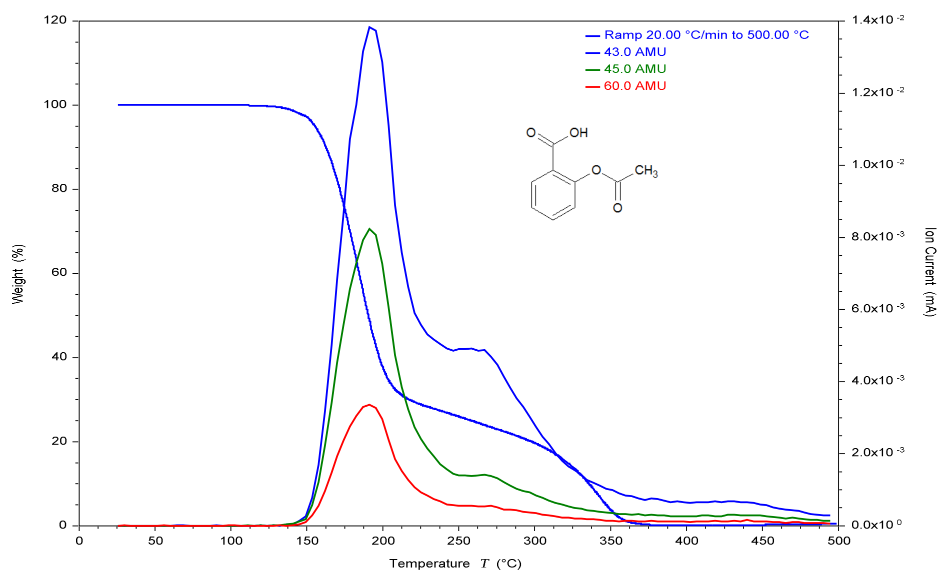
TGA-MS Example: Aspirin



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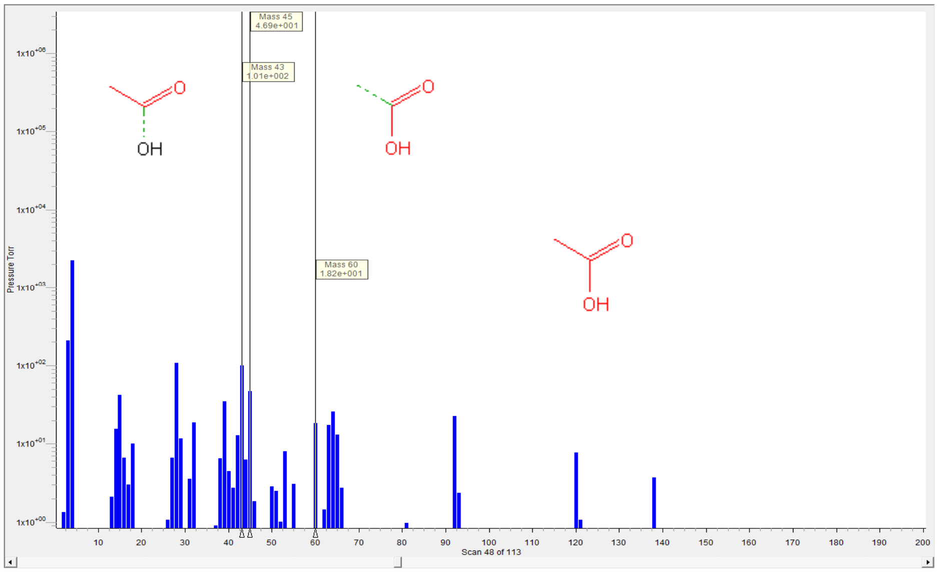
TGA-MS Example: Aspirin



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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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Thank You

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