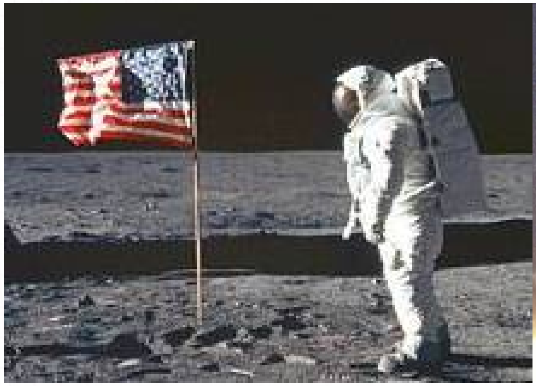
Precise Heat Control: What Every Scientist Needs to Know About Pyrolytic Techniques to Solve Real Problems

Rodrigo Devivar, Ph.D.
Jacobs Technology / NASA-Johnson Space Center
ES4 Materials Analysis Laboratory
Houston, Texas



Controlling Heat in Aerospace

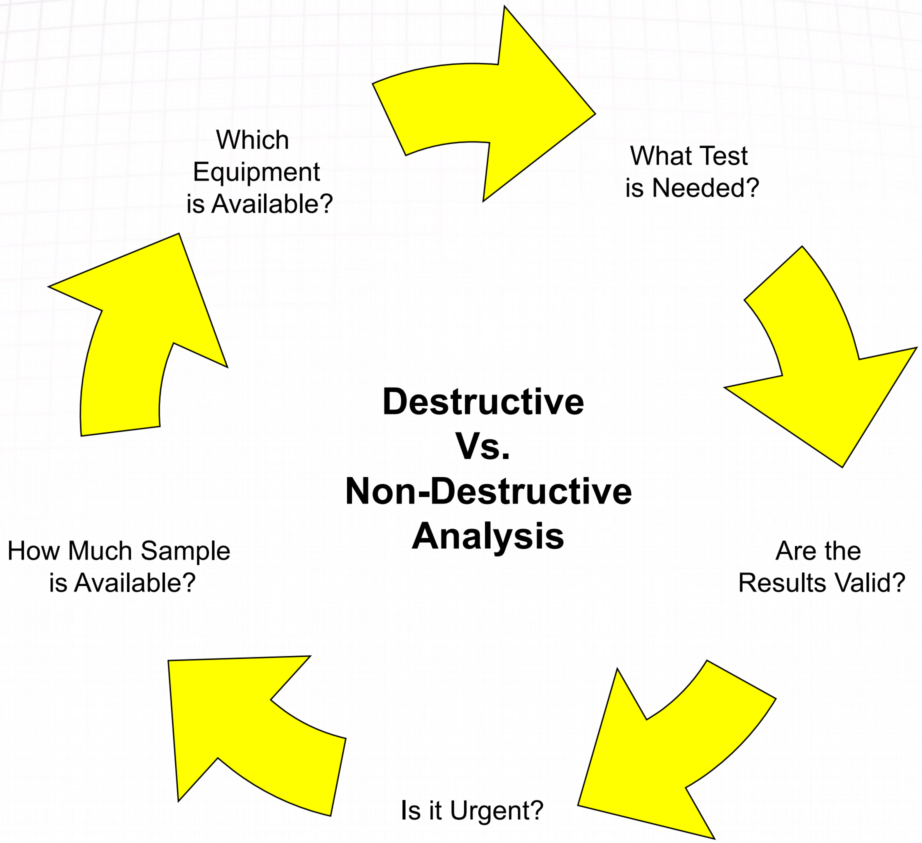
Picture of Space Shuttle During Atmospheric Re-entry
taken from ISS

Analytical Chemistry Laboratory Equipment

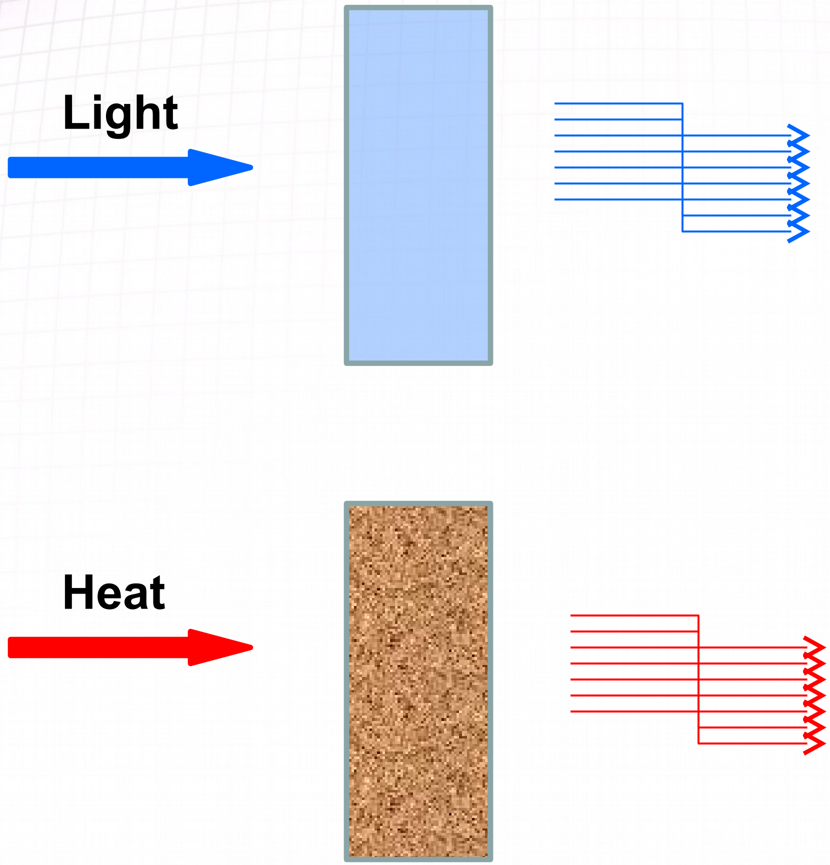
Key Laboratory Equipment

- Optical Instrumentation
  - UV-Vis, Fluorimeter, Solar Reflectance, Infrared Emittance, Raman
- Thermal Analysis Instrumentation
  - DSC, DMA, TGA, TMA, LFA, Rheometer
- Chemical Analysis Instrumentation
  - FT-IR, Ion trap GC-MS, Py-GC-MS, TGA-MS, TGA-IR

The Analytical Chemistry Cycle



Optical Vs. Thermal Techniques



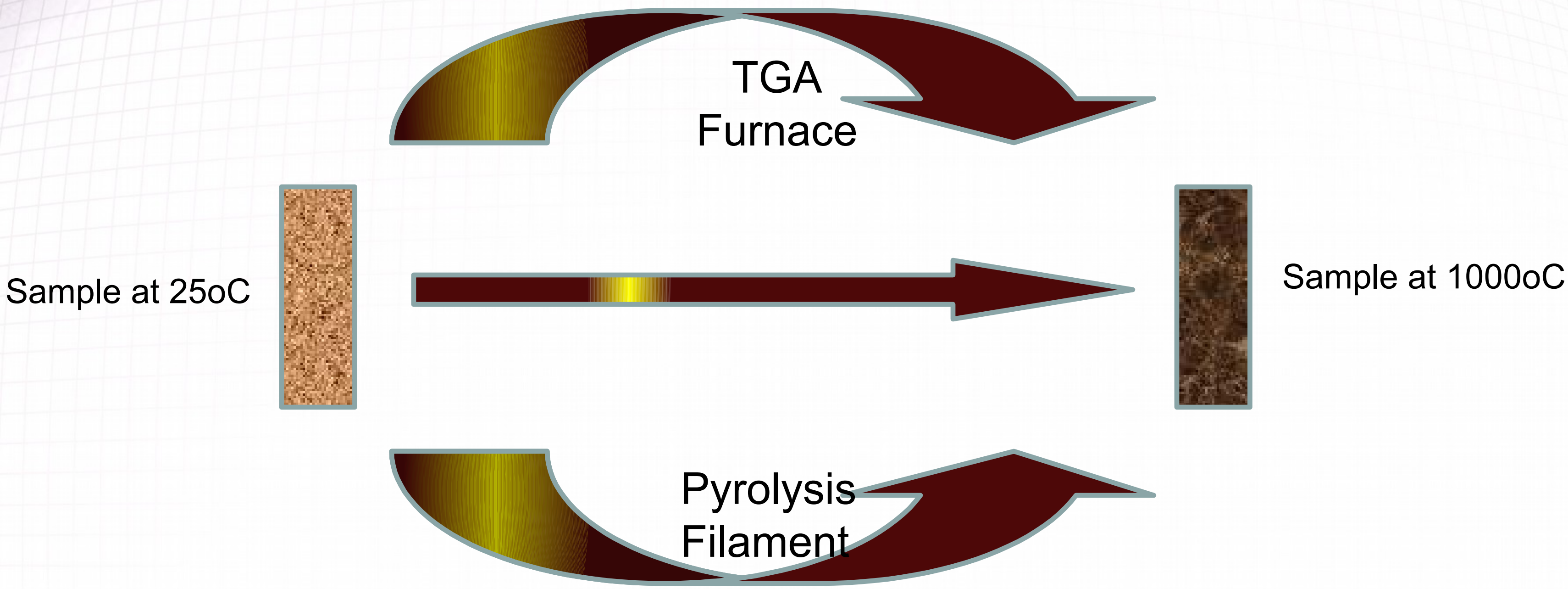
Reflectance
Emittance
Absorbance/Transmission
Fluorescence
UV-Vis Absorbance
FT-IR Analysis
Raman Analysis

Material Curing
Thermal Transition-Tg
Melting Point/ Boiling Point
Residual Solvent
Identification of additives
Material Decomposition
Elimination of labile functional groups
Identification of Material Components
Identification of Inorganic Components

Controlling Heat Exposure

Thermal Analysis

Slow: minutes to hours

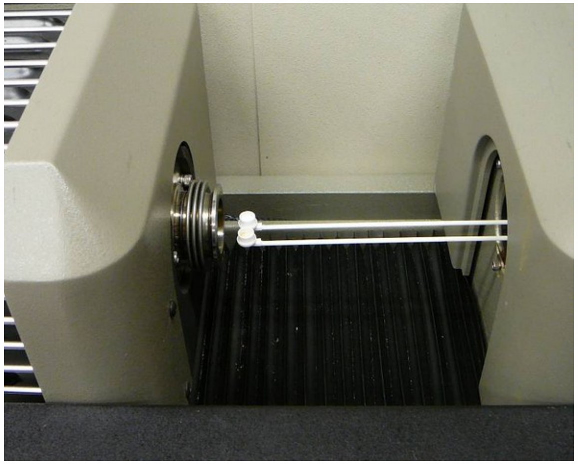


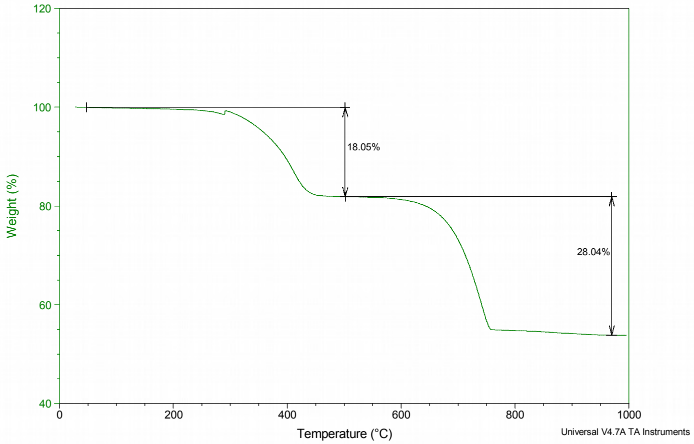
Fast: microseconds to seconds

Thermochemical Analysis

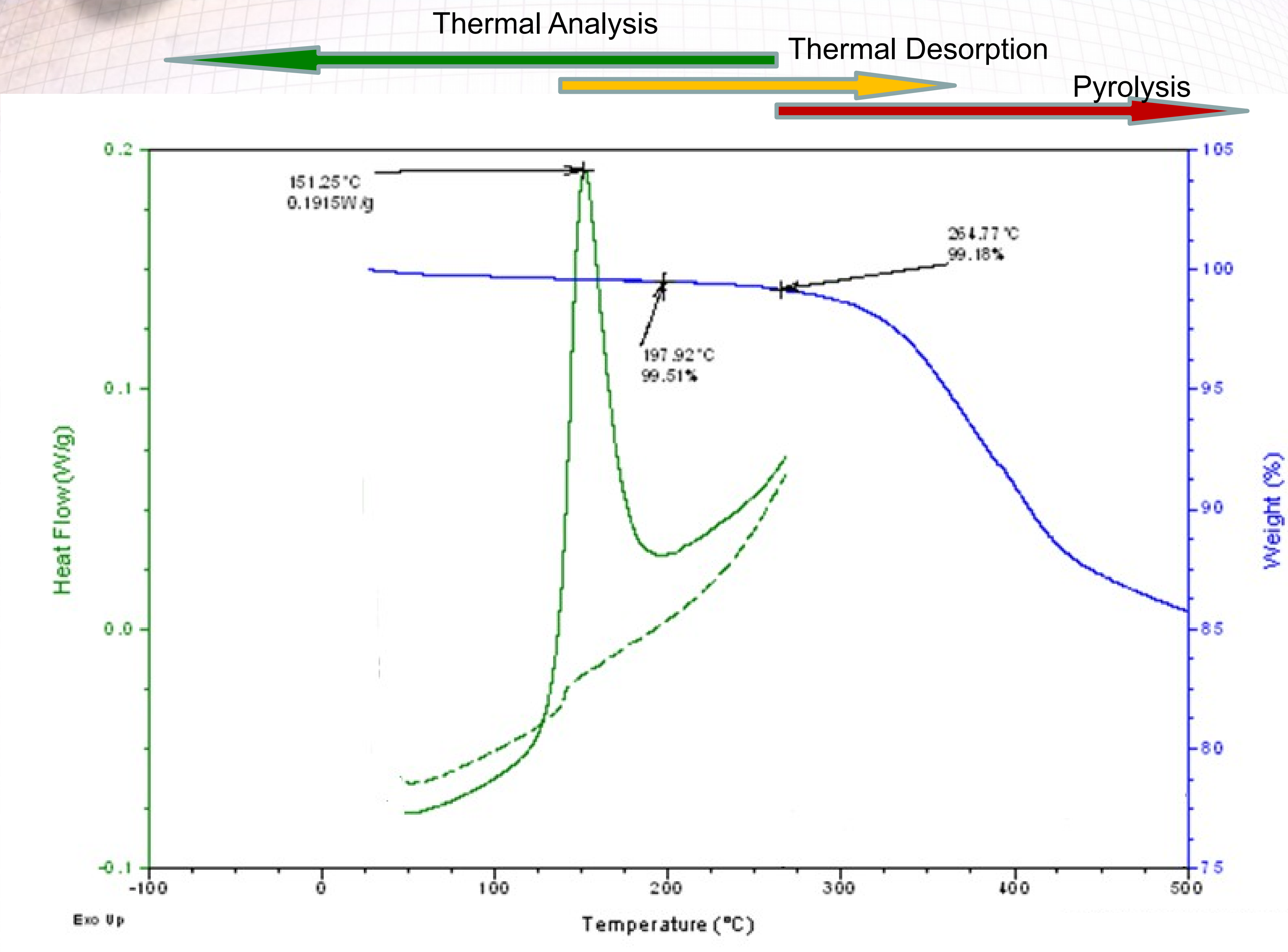
Thermogravimetric Analysis (TGA)

- A TGA instrument consists of an analytical balance and a furnace.
- A small sample of material is heated and its change in mass is measured as a function of temperature.
- Experiments can be conducted under inert or oxidizing atmospheres.
- Information gained from TGA includes:
  - Thermal stability for conducting additional thermal analysis
  - Identification of the number of components in the sample if the decomposition temperatures are different
  - Residual mass for assessing the extent of inorganic additives

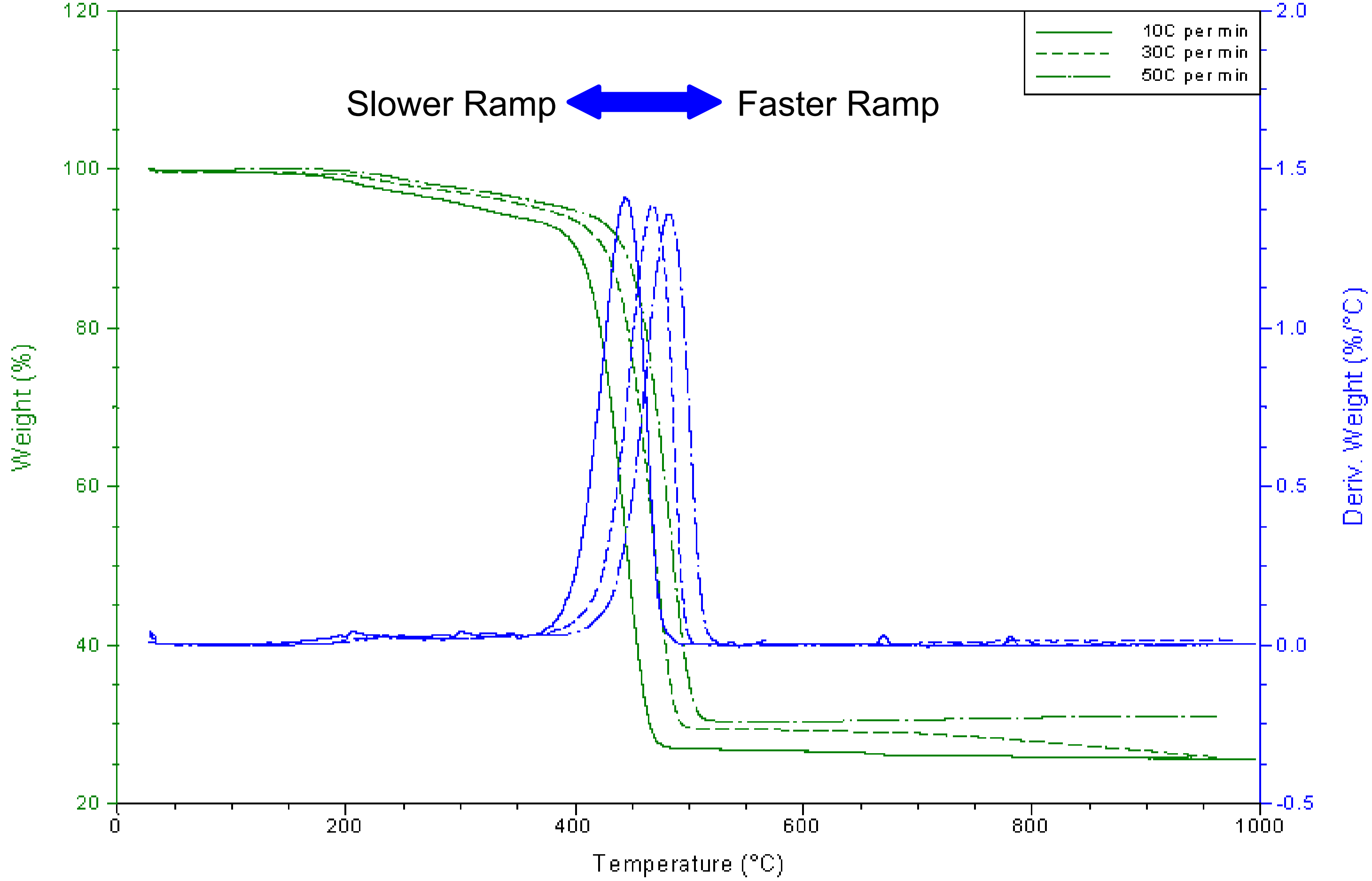




Thermal Analysis of Composite

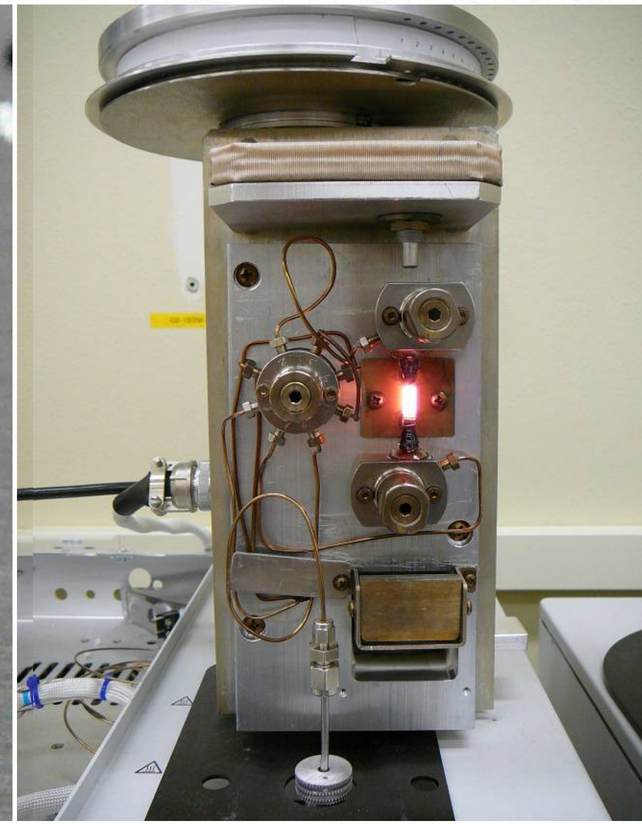


The Influence of Temperature Ramp Rates



Pyrolysis for GC-MS of Solids

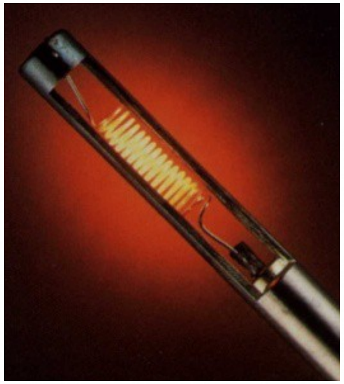
- Sample size is relatively small:
  - 50 to 200 mg is sufficient for solids
  - 50 to 200 nL is sufficient for liquids
- Sample preparation is easy: Place sample inside 1.5 inch quartz tube containing filler tube and plug with glass wool.
- Samples can be solids, gels, viscous liquids, greases, crystalline, emulsions, foams, fabrics
- Pyrolysis temperatures are almost instantaneous
- Sample components can be quantified with the use of software



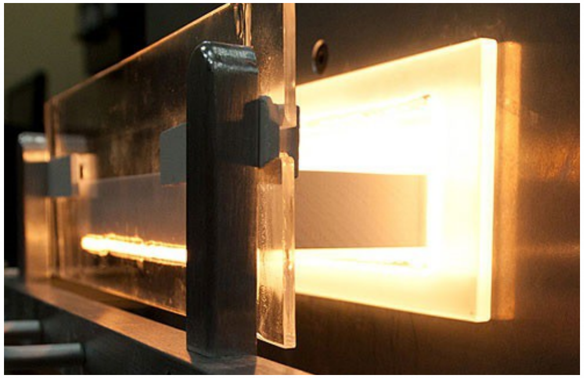
Pyrolysis is the thermal degradation of any substance through the fast application of heat.

Pyrolyzers: Filament Versus Furnace

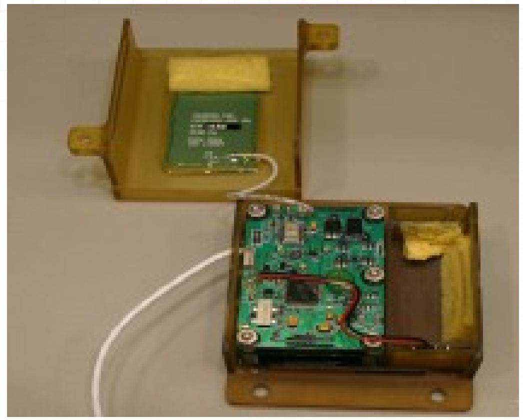
- CDS Platinum Filament
  - Heating Rate: ~20,000oC per sec
  - Max Temperature: 1400oC
  - Cooling Rate: > 1000oC per sec
  - Fast Heating, Fast Cooling

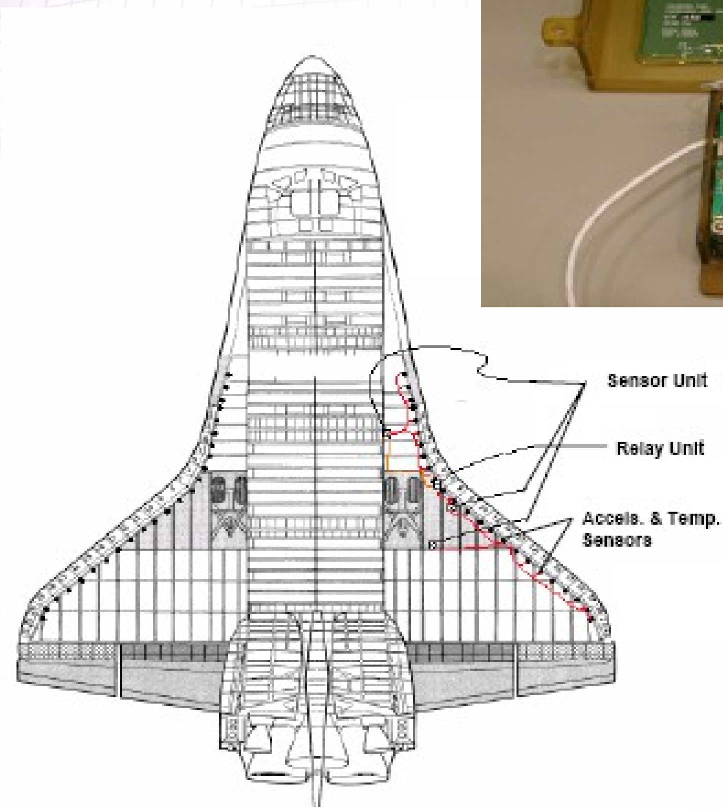


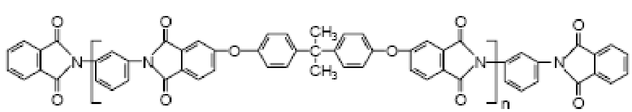
- Microfurnace
  - Heating Rate: ~50oC per min
  - Max Temperature: 800oC
  - Cooling Rate: 25oC per min
  - Slow to Heat, Slow to Cool



Flash Pyrolysis-GC-MS of Ultem 1000

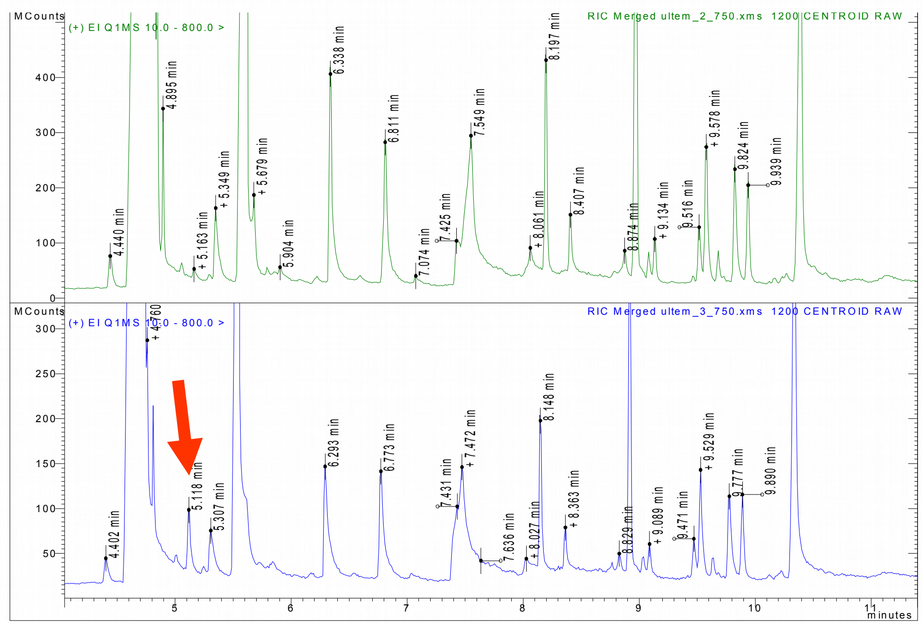




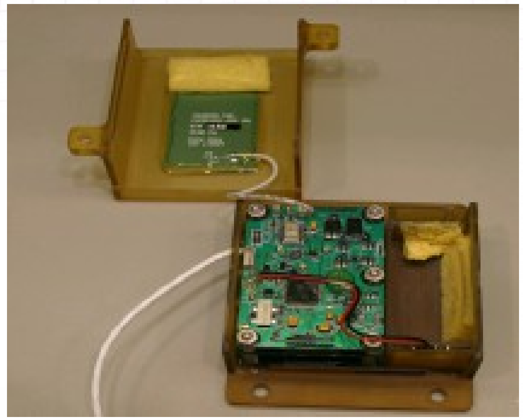


Ultem 1000®

- Relay sensor boxes along the shuttle's wing leading edge were composed of Ultem 1000.
- One lot used to make these relay sensor boxes had failed
- Various manufacture lots of sensor boxes were analyzed by Py-GC-MS and an extra peak was noted in one of those lots. The extra peak was due to dichlorobenzene, a solvent used during manufacture of Ultem 1000.

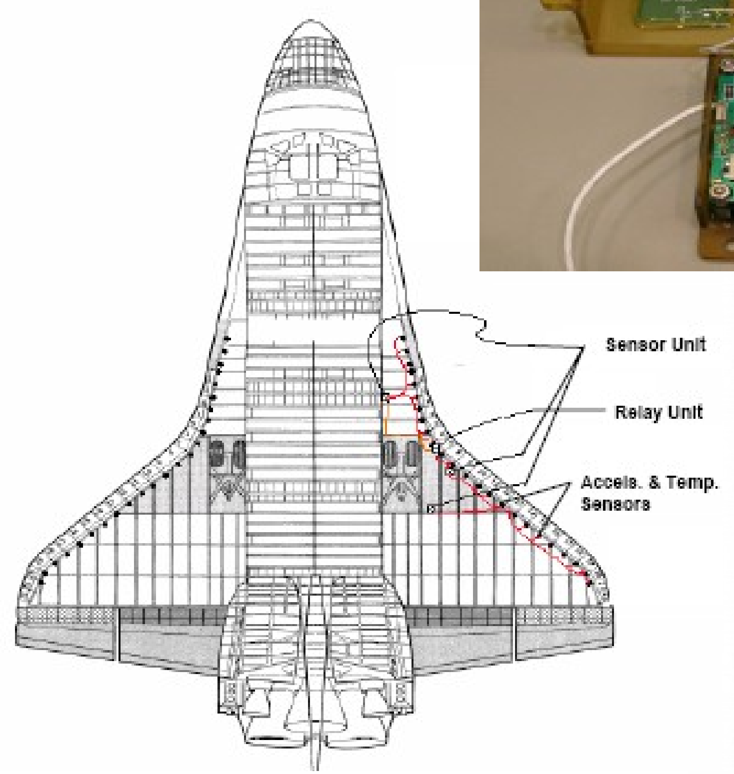


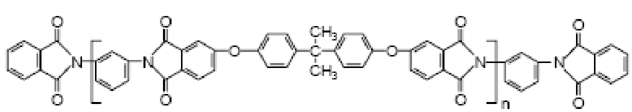
Thermal Extraction of Ultem 1000



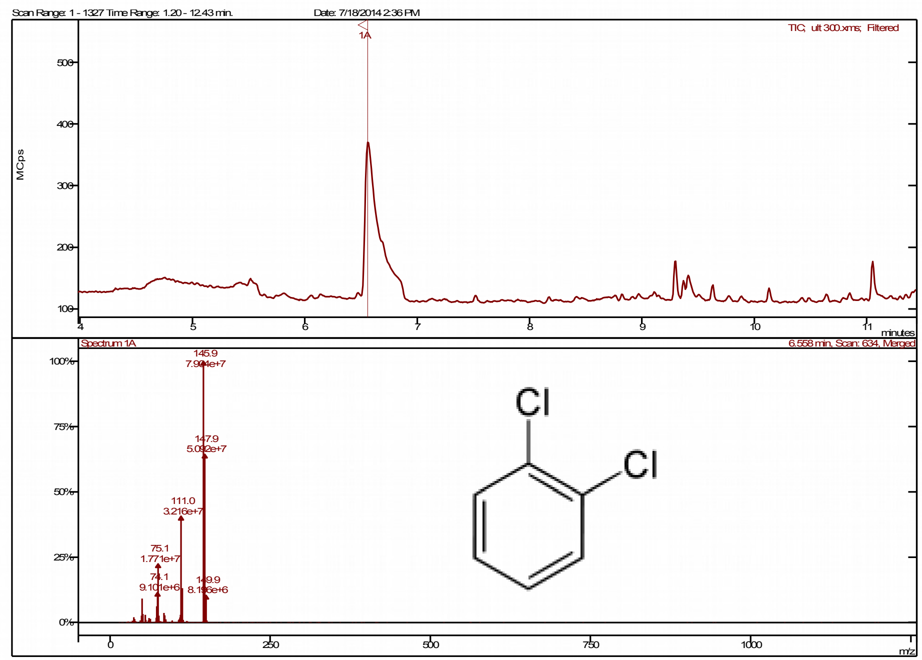
Instead of Flash Pyrolysis at 750oC, The sample could be desorbed at a temperature above the Tg and below the decomposition temperature of Ultem 1000.

This approach facilitated the detection of the trapped solvent, dichlorobenzene.

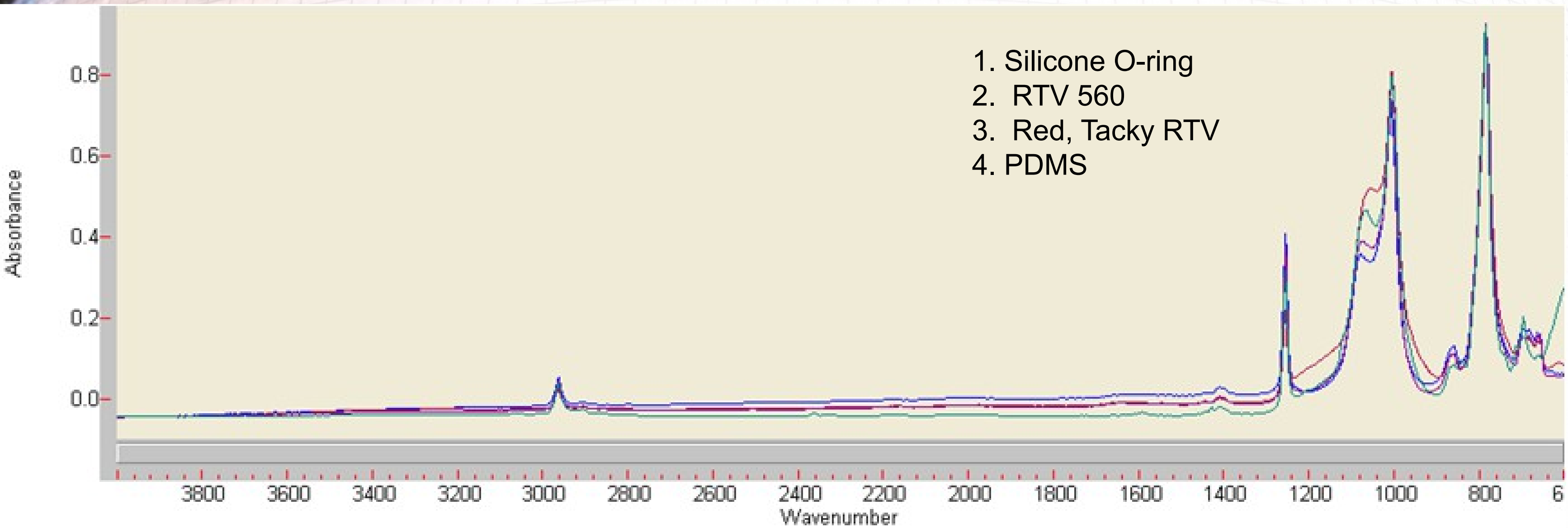




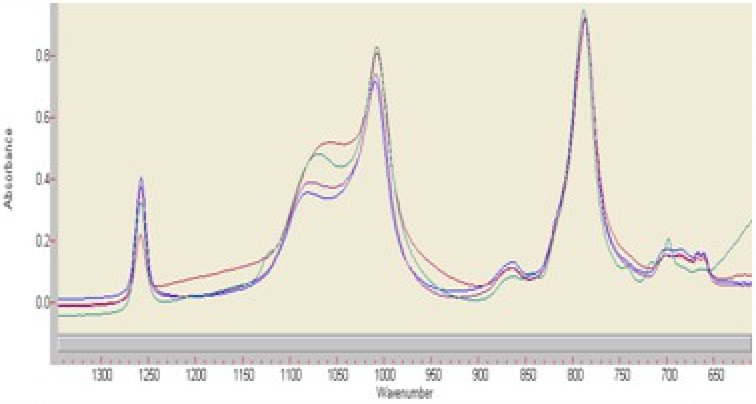
Ultem 1000®



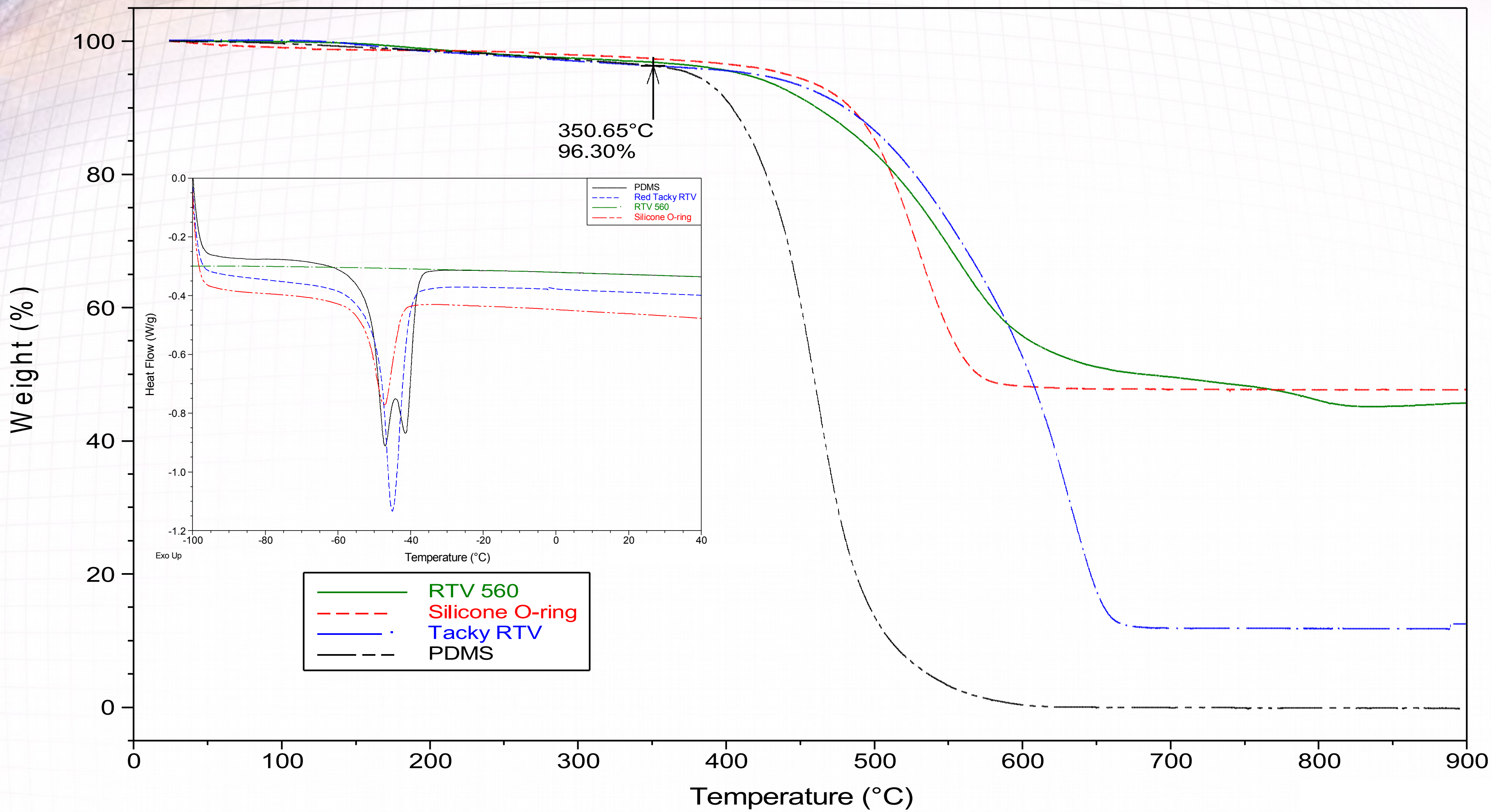
FT-IR Analysis of Silicone Materials



FT-IR is a non-destructive technique that is very diagnostic. However, if infrared light cannot penetrate the sample, any signal obtained through reflectance is only valid for the external surface of a sample.

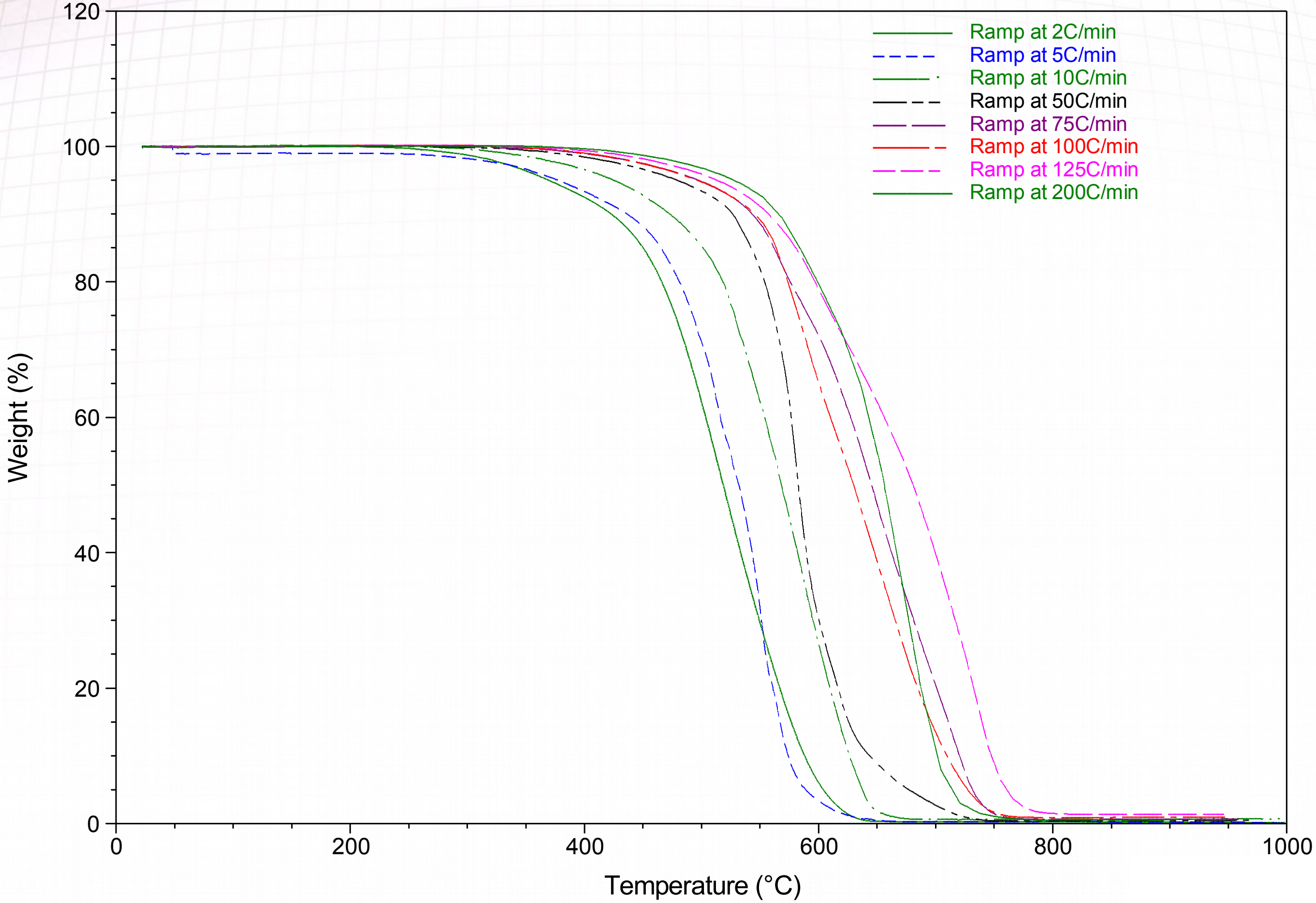


Thermal Analysis of Silicone Materials



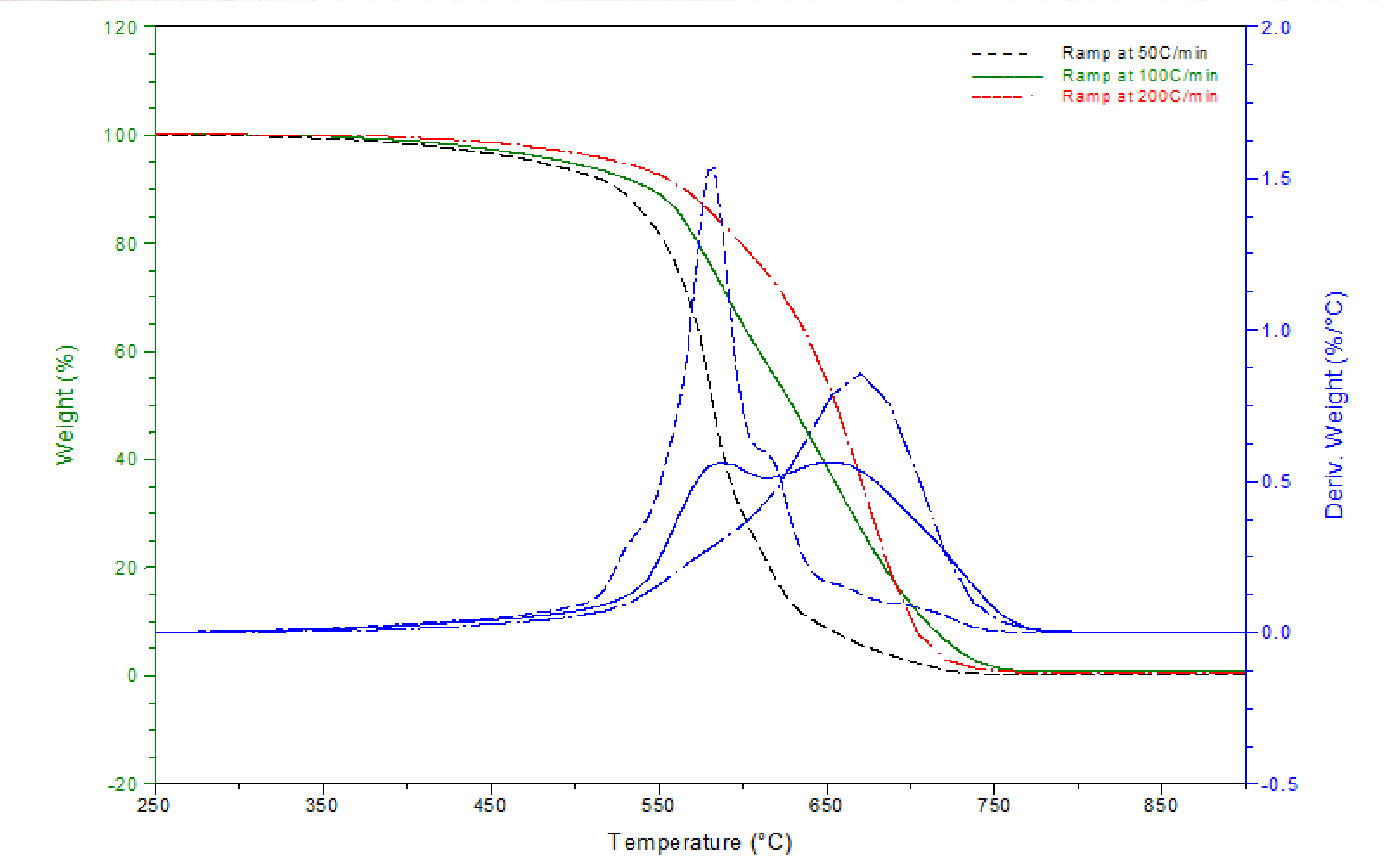
The Silicone samples that were nearly identical by FT-IR displayed very different properties by thermal analysis.

TGA Analysis of Silicone Oil



The thermal profile of silicone oil at different ramp rates indicates the complexity of thermal analysis

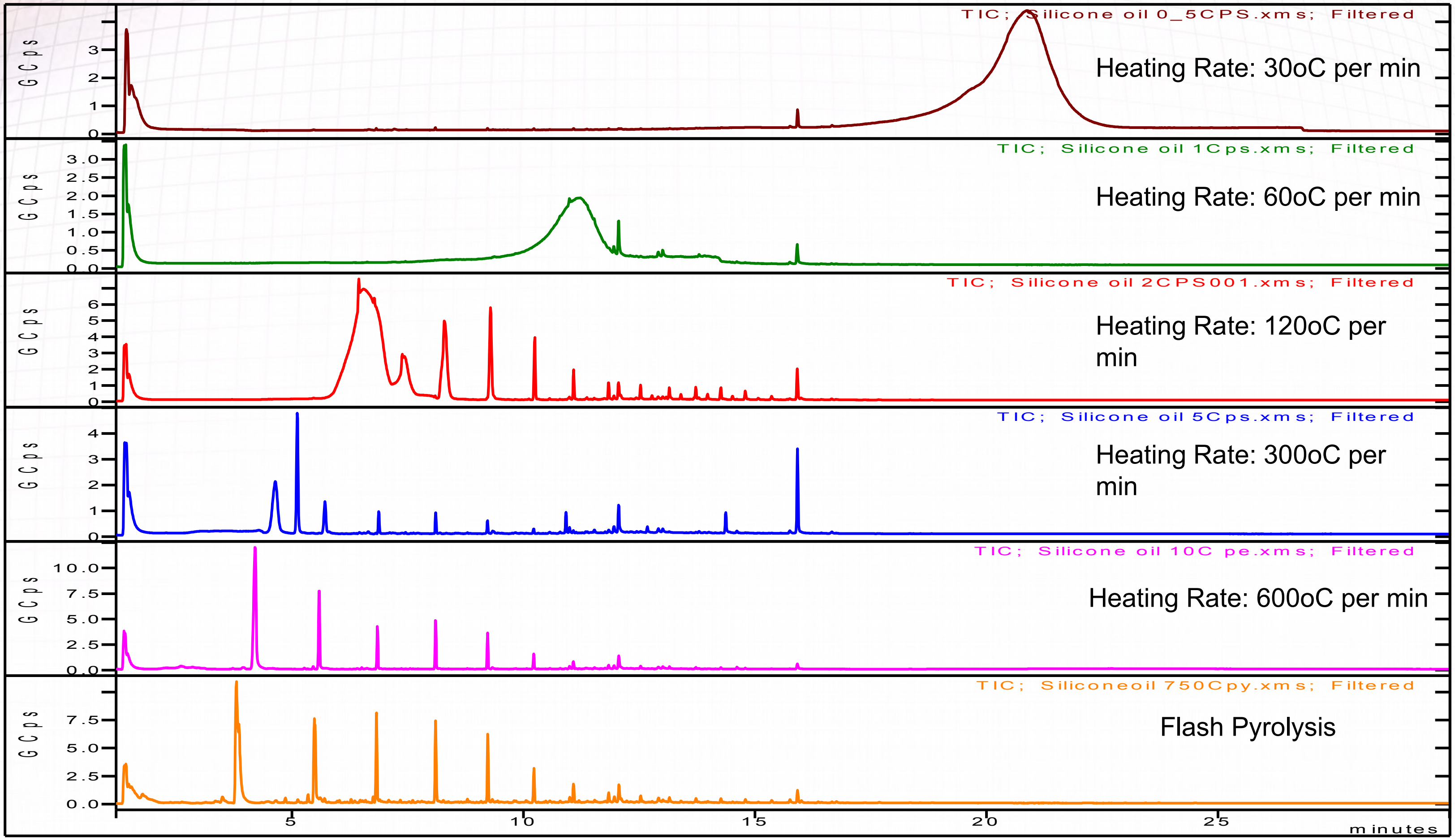
High Temperature Ramp Rates Increases Molecular Fragmentation



At high temperature ramp rates, silicone oil undergoes two types of processes detected by TGA analysis, evaporation through boiling and molecular fragmentation.

Pyrolytic Analysis of Silicone Oil at Different Heating Rates

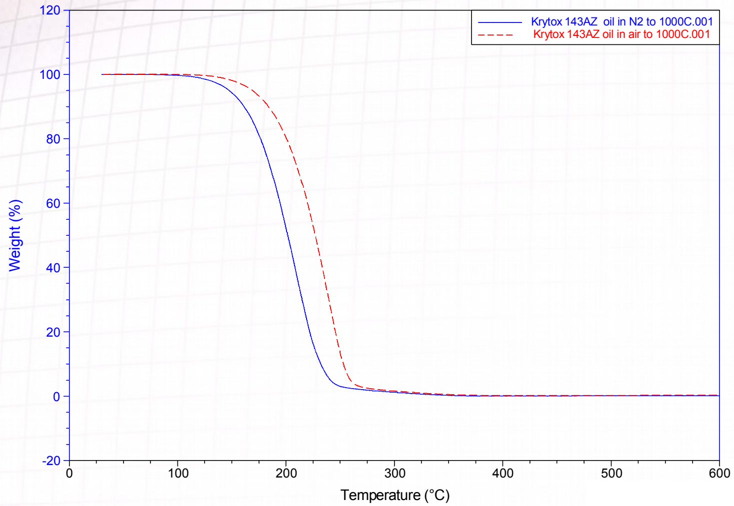
Chromatogram Plots



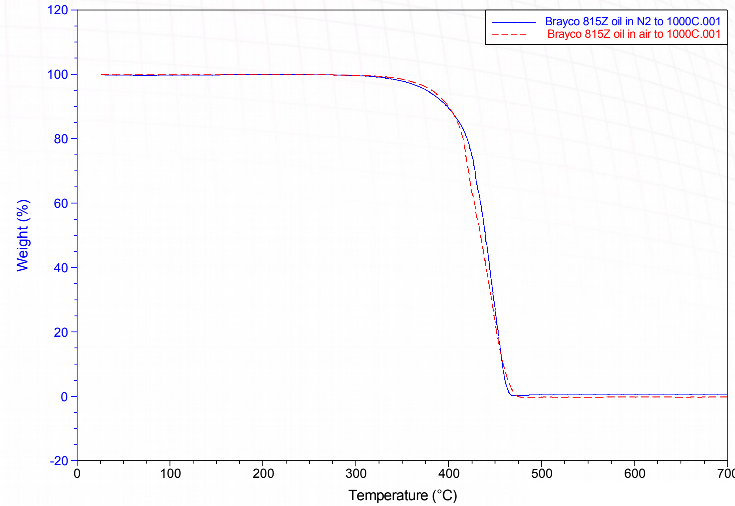
Pyrolysis provides insight into the TGA data. Pyrolysis indicates that silicone oil stays intact and simply boils off at heating rates of 30oC/min. The oil starts to display substantial fragmentation at 120oC

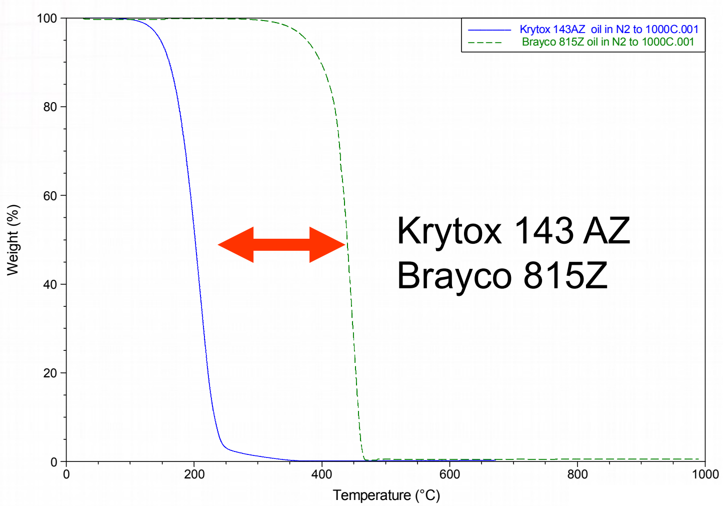
TGA Analysis of Fluorinated Materials

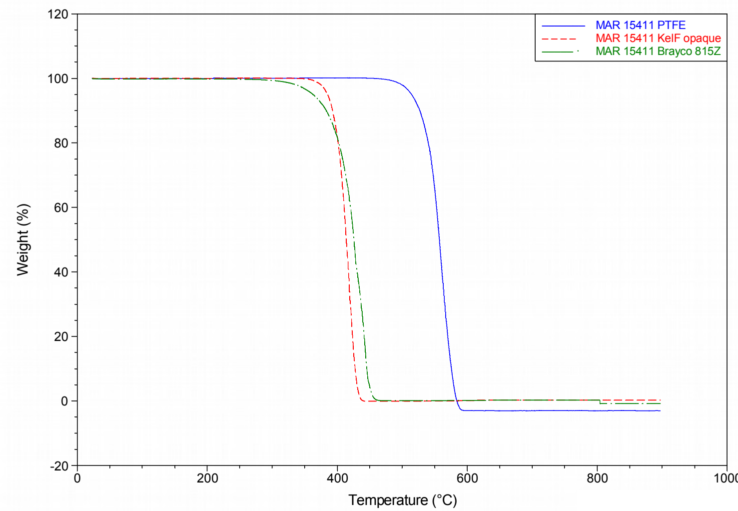
Krytox 143 AZ



Brayco 815Z

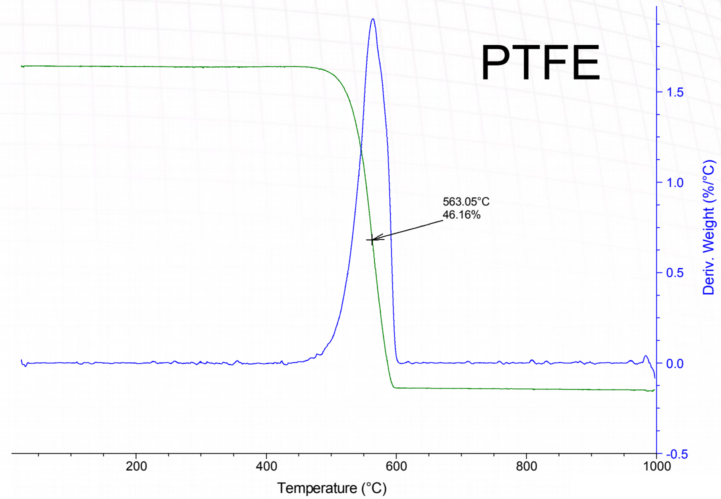


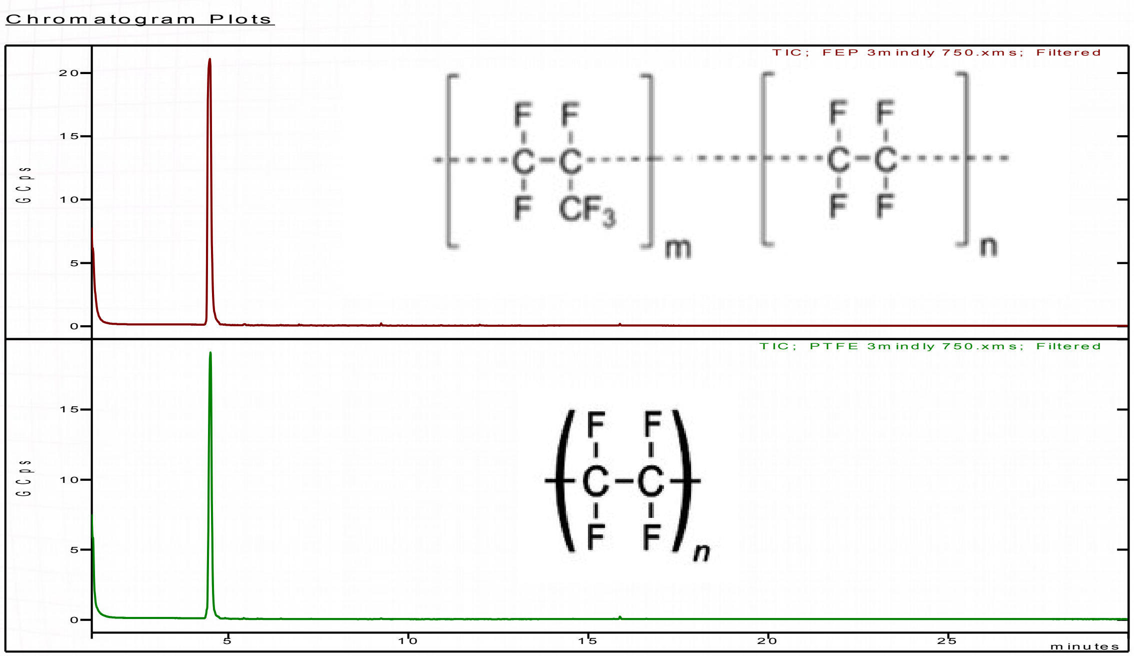


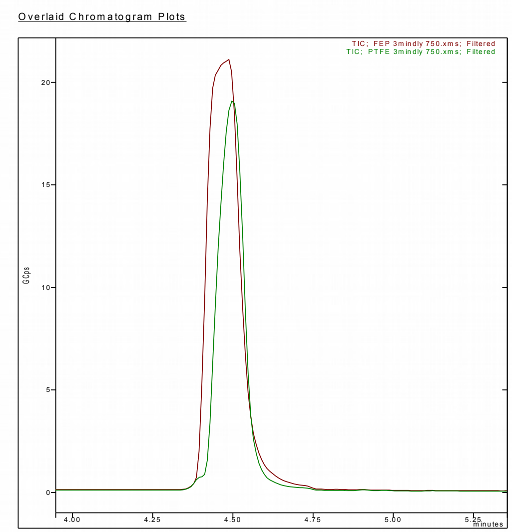


FEP Vs. PTFE Teflon

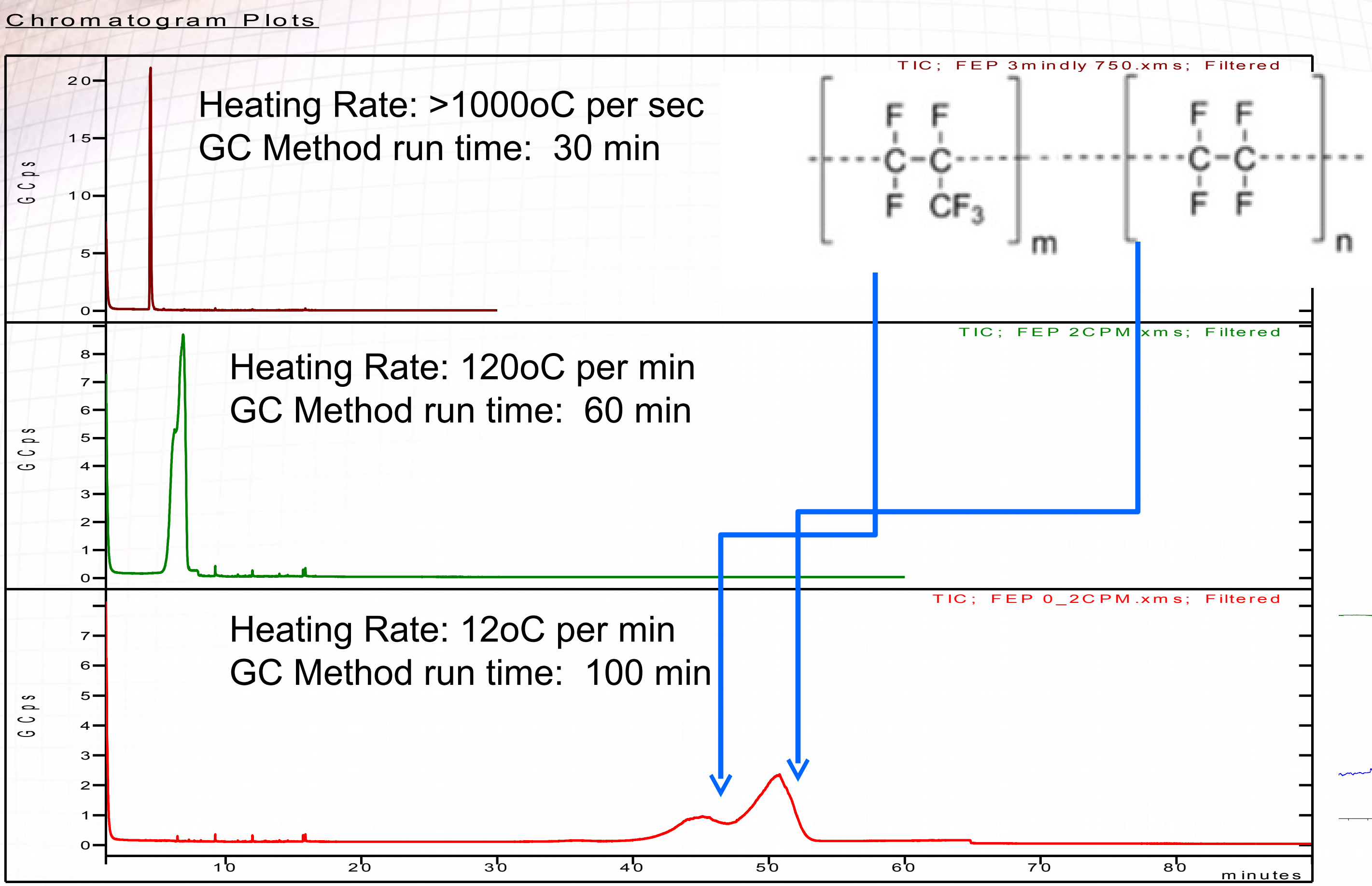
FEP Teflon



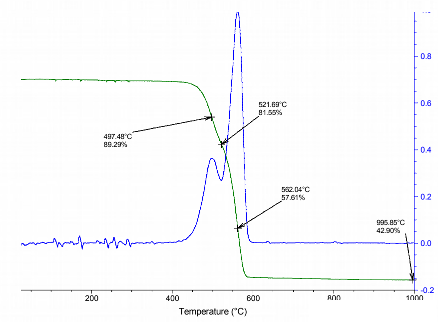




FEP Teflon Heated at Different Rates



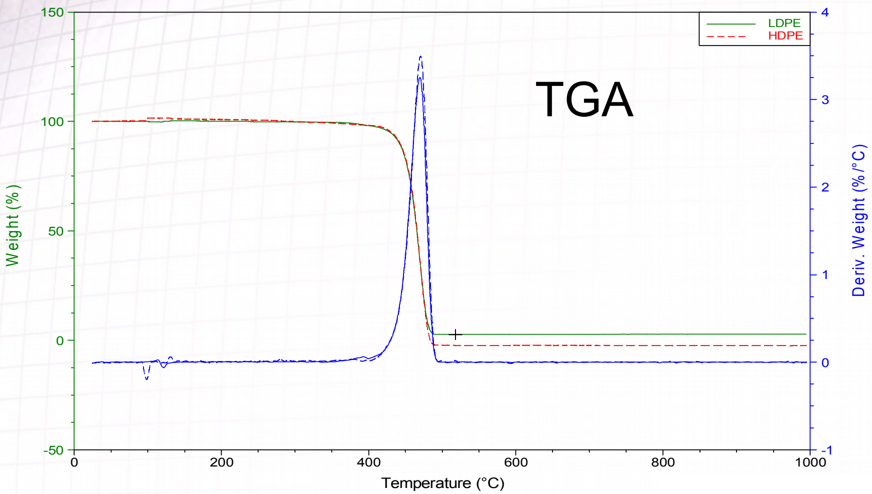
TGA

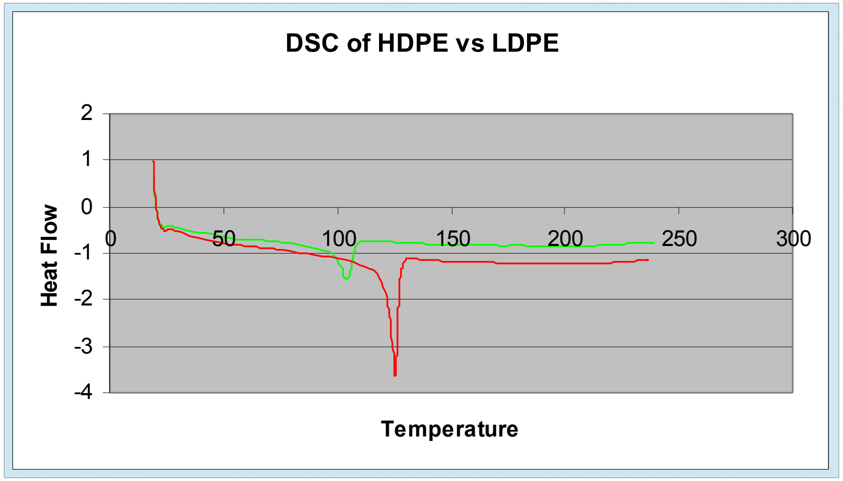


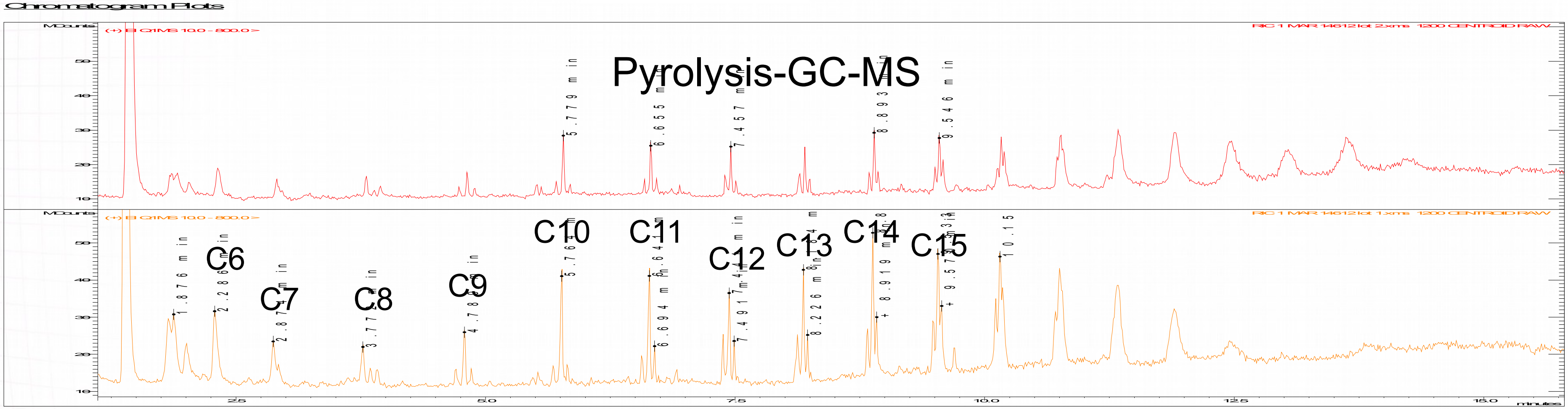
During pyrolysis, materials undergo thermal degradation via chemical pathways dictated by the thermal stability of the components. When pyrolysis is slowed to simulate TGA conditions, a thermal response pattern similar to what was observed with TGA first derivative plot is observed.

Thermal Analysis of HDPE and LDPE

Polyethylene: -CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-CH2-

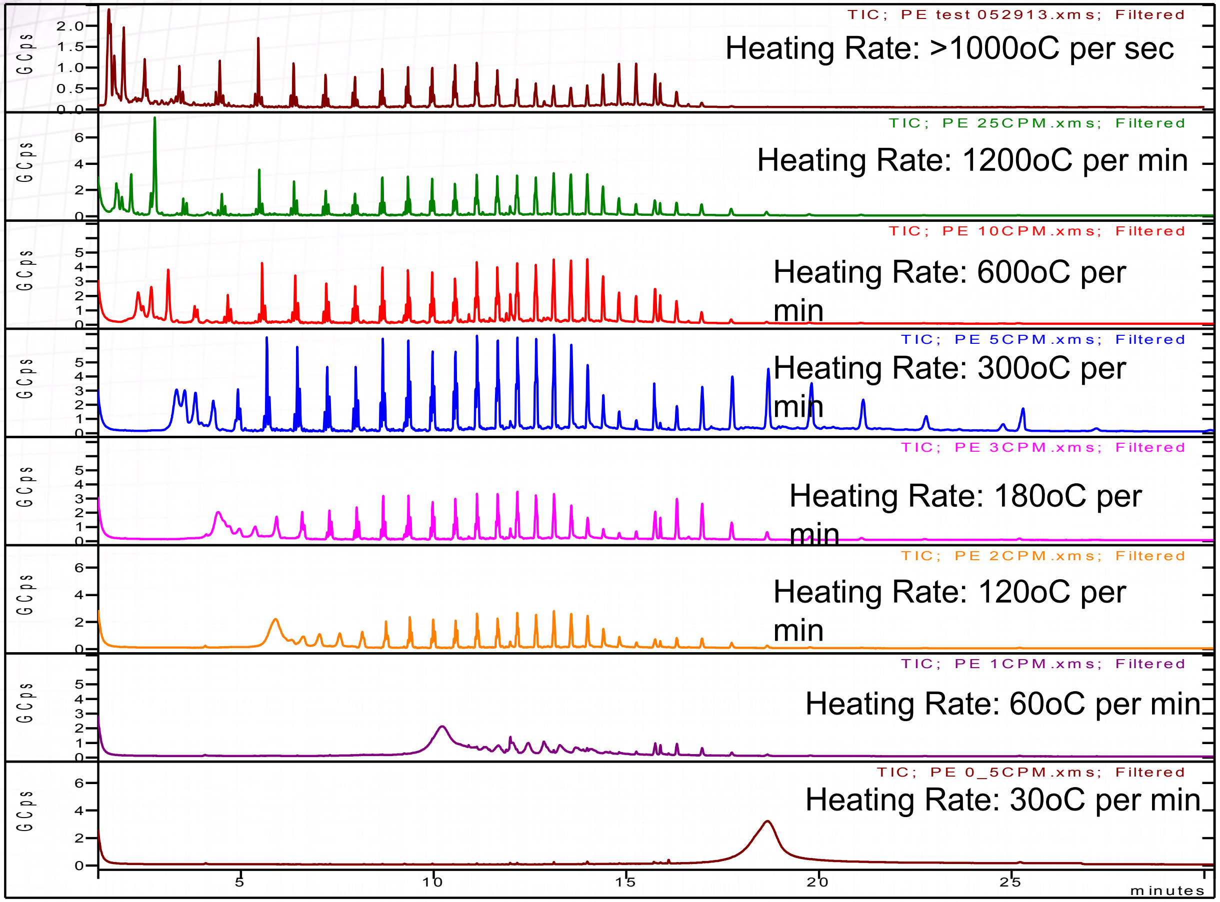






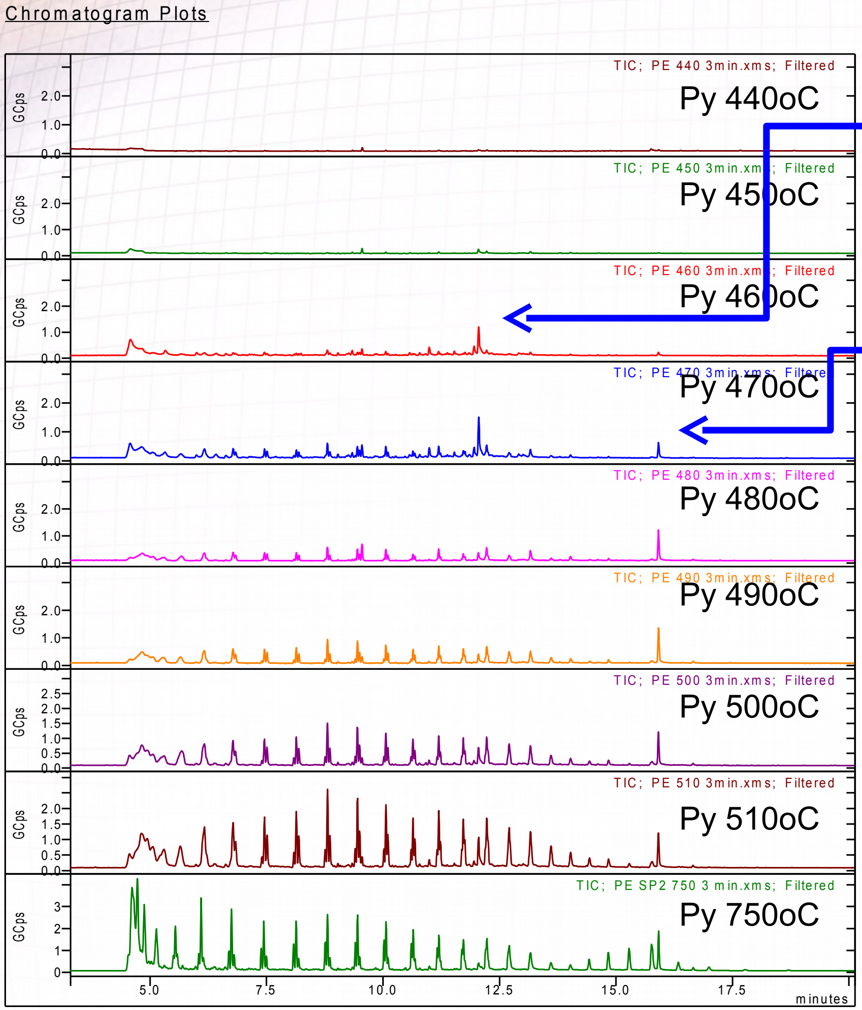
Temperature Ramp Pyrolysis

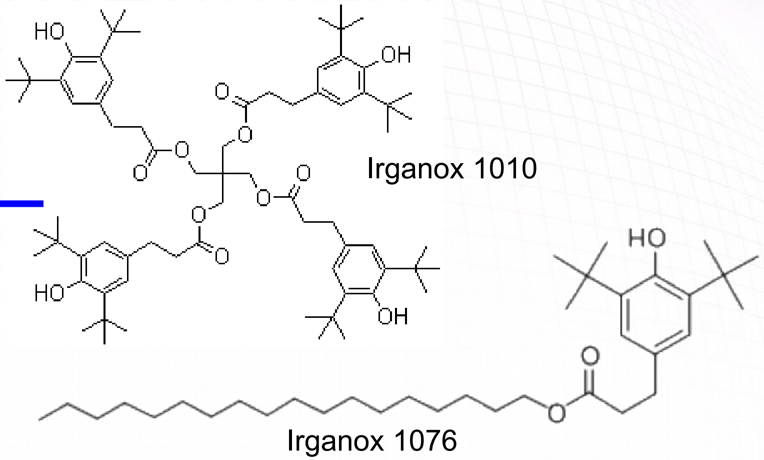
Heating PE in Pyrolysis chamber from 25oC to 750oC at different rates

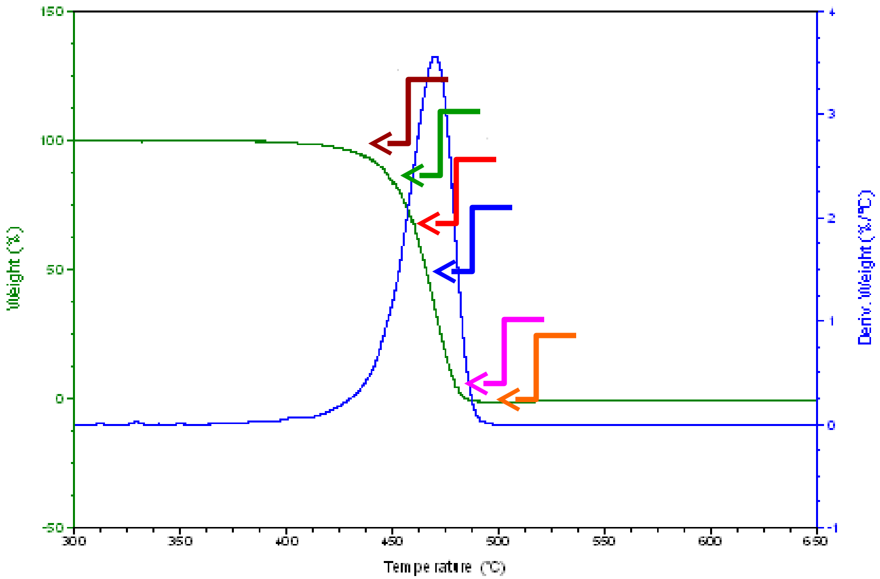


TGA
Heating Rate: 5oC per min

Correlating TGA and Pyrolysis Techniques





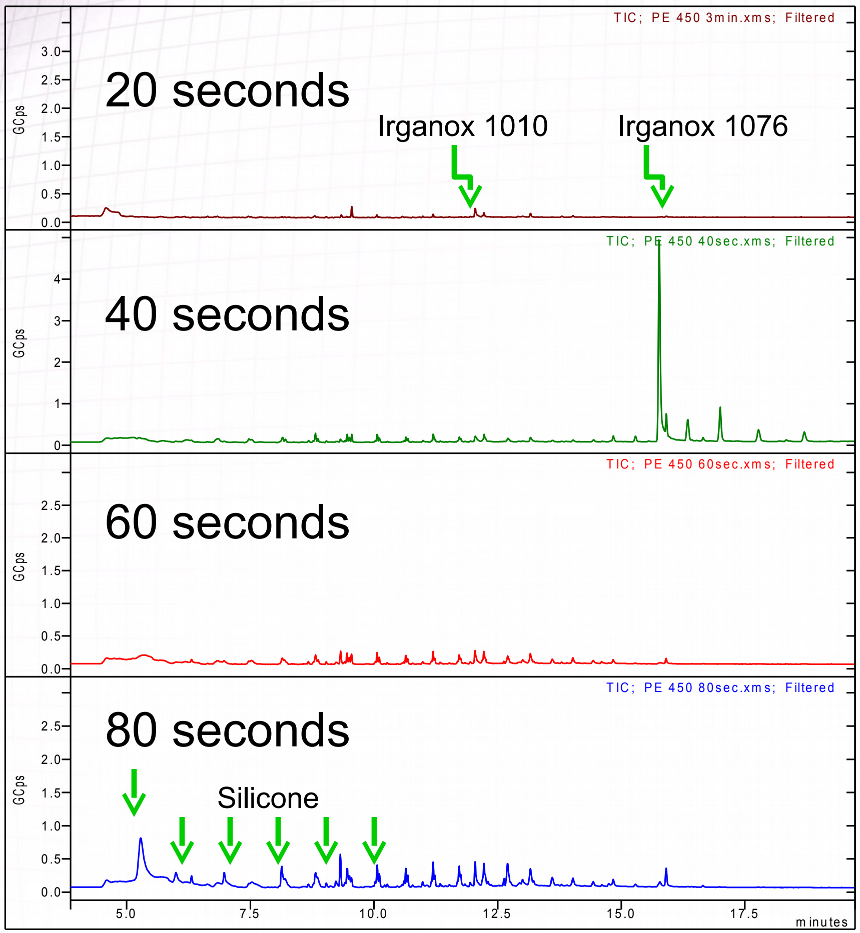


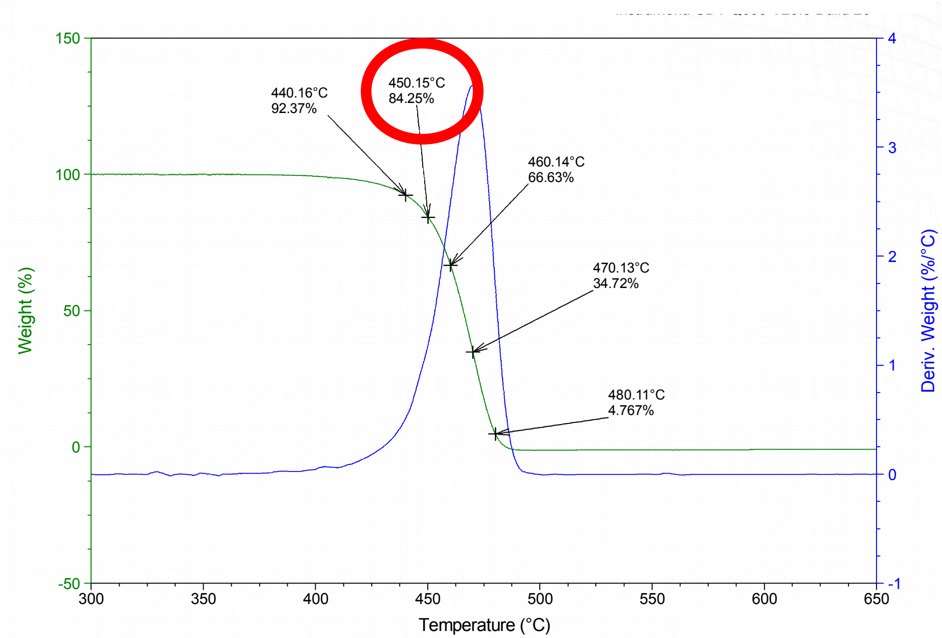
Pyrolysis at specified temperatures for 20 seconds

Thermal Analysis of PE

Pyrolysis at 450oC For Specified Duration

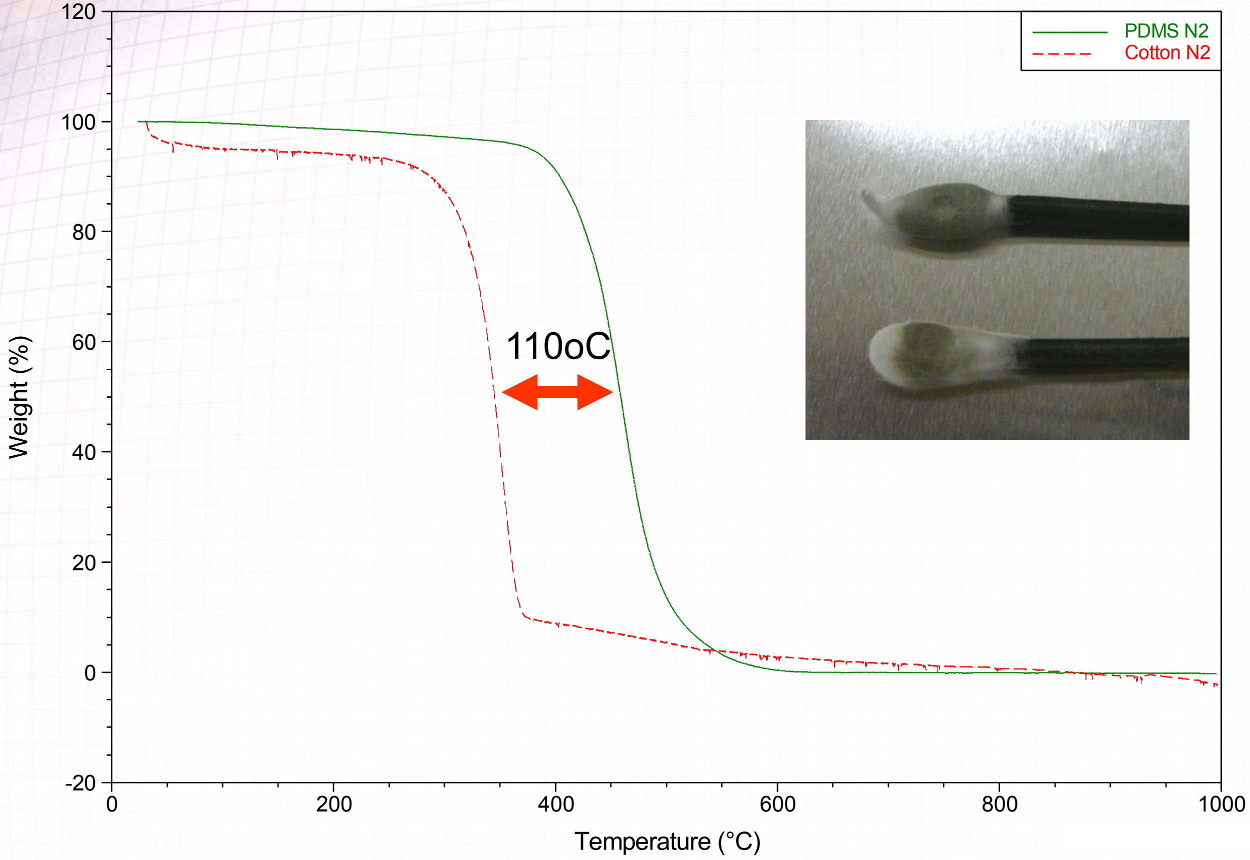
Chromatogram Plots





Modification of the thermal parameters at the onset of TGA degradation for PE can provide valuable information about the additives or contaminants.

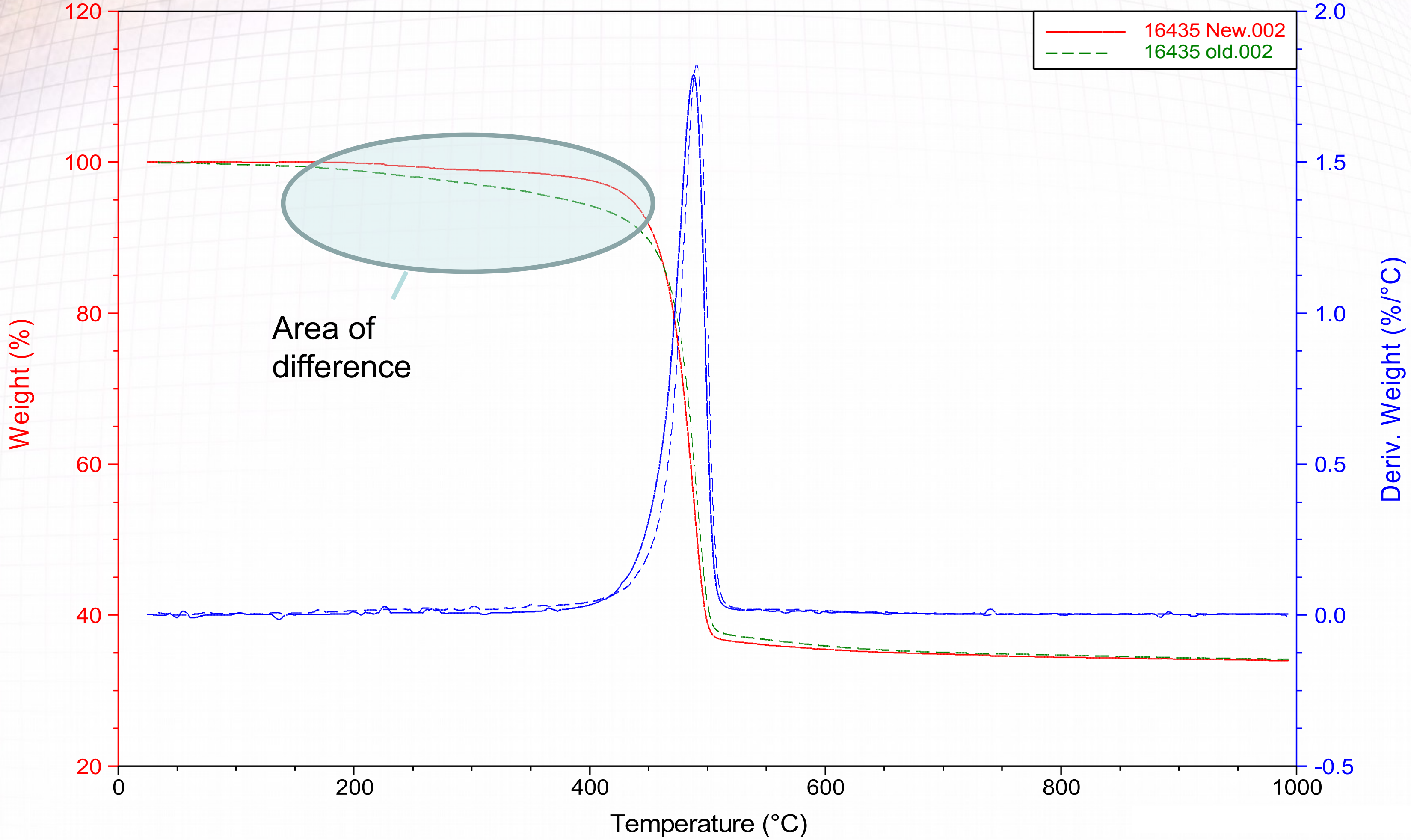
Cotton Vs. Silicone



The large difference in thermal stability between cotton and silicones can be used to easily characterize the silicone sample collected on a cotton swab.

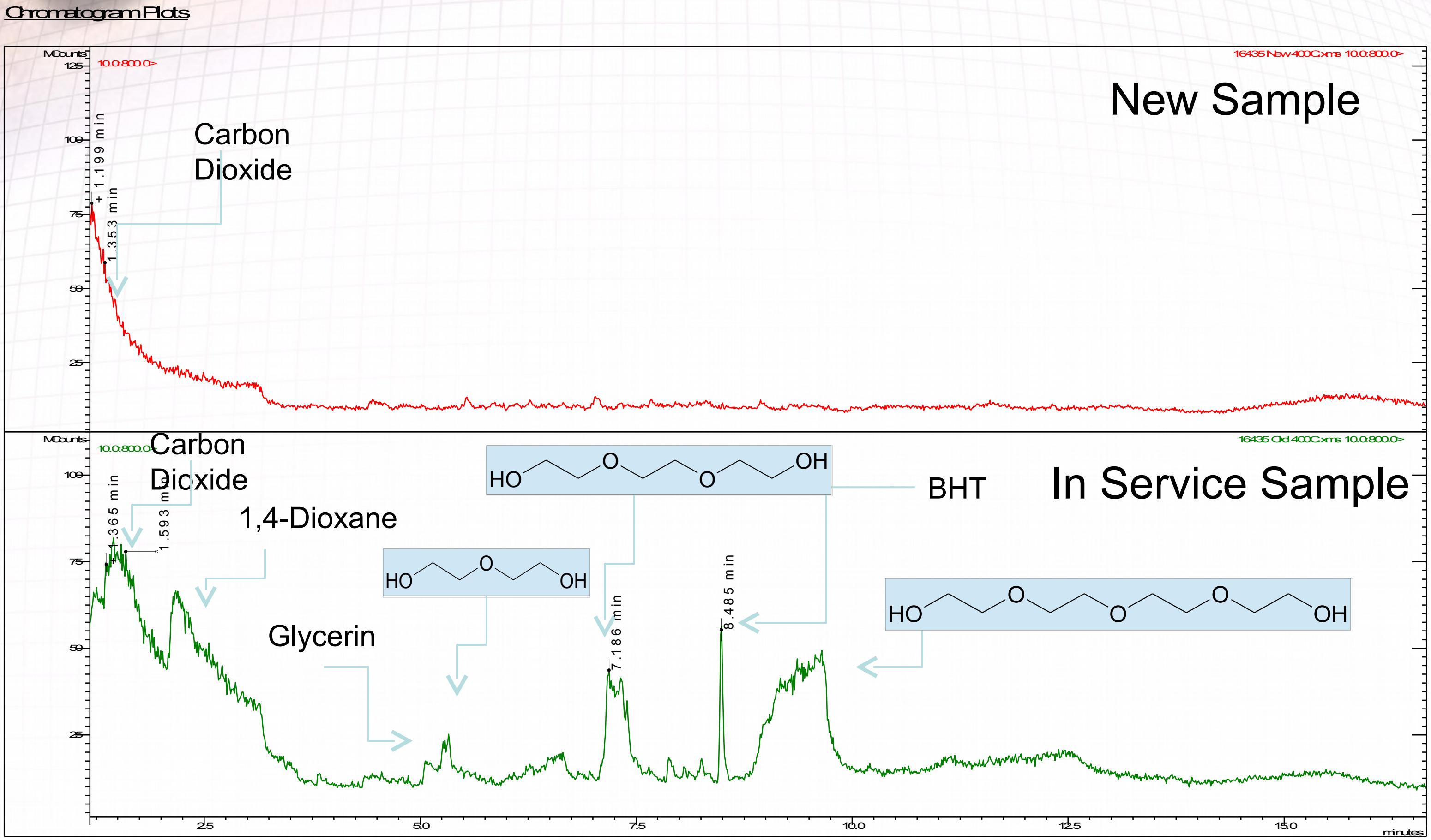
The cotton may be completely decomposed by application of heat without adversely affecting the silicone.

TGA Comparison of Gaskets



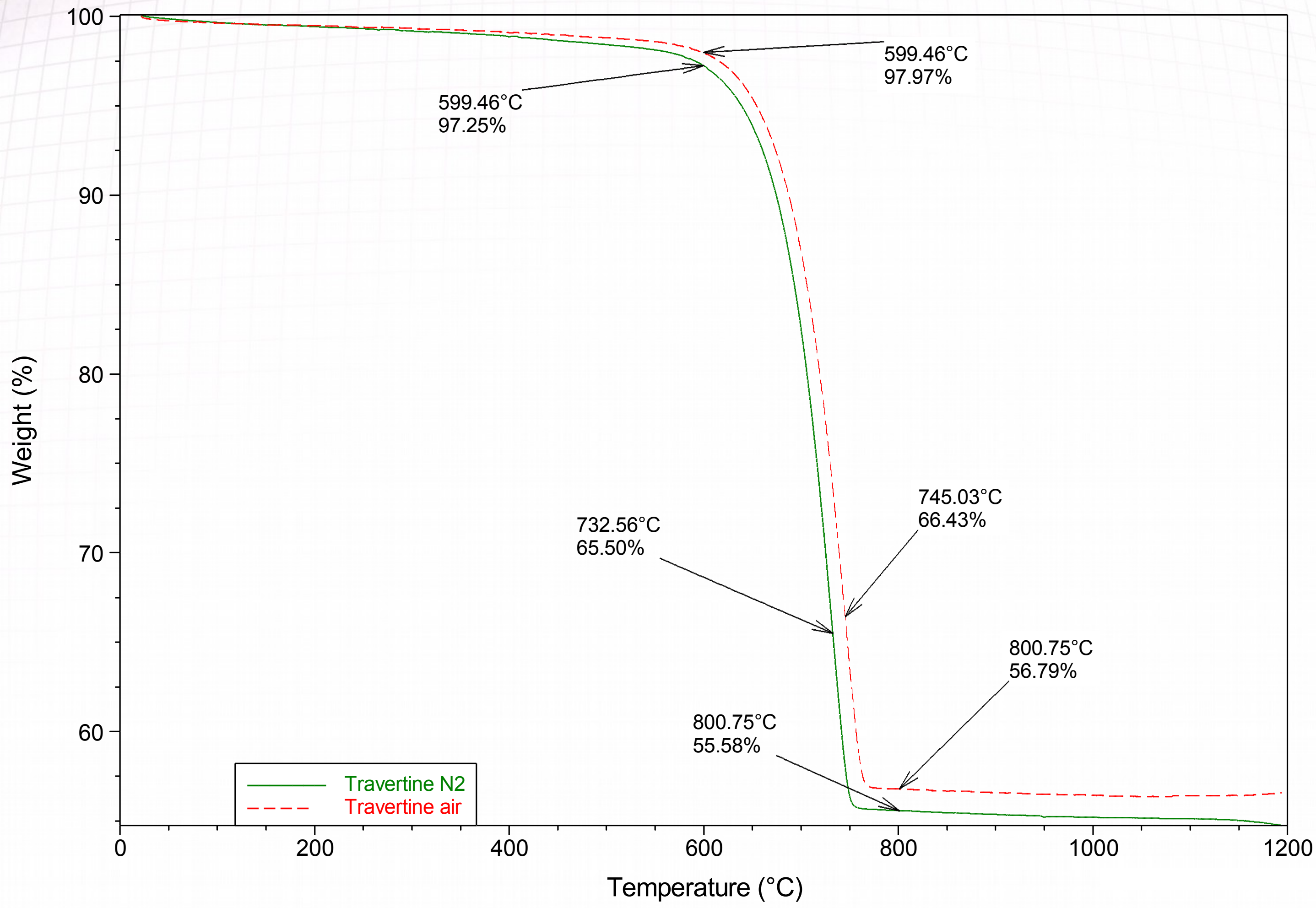
Under conditions of increasing temperature, the only difference between the two Viton Gaskets was found below 400oC, where the old sample lost a larger percentage of its mass compared to the new sample.

Thermal Extraction of Samples

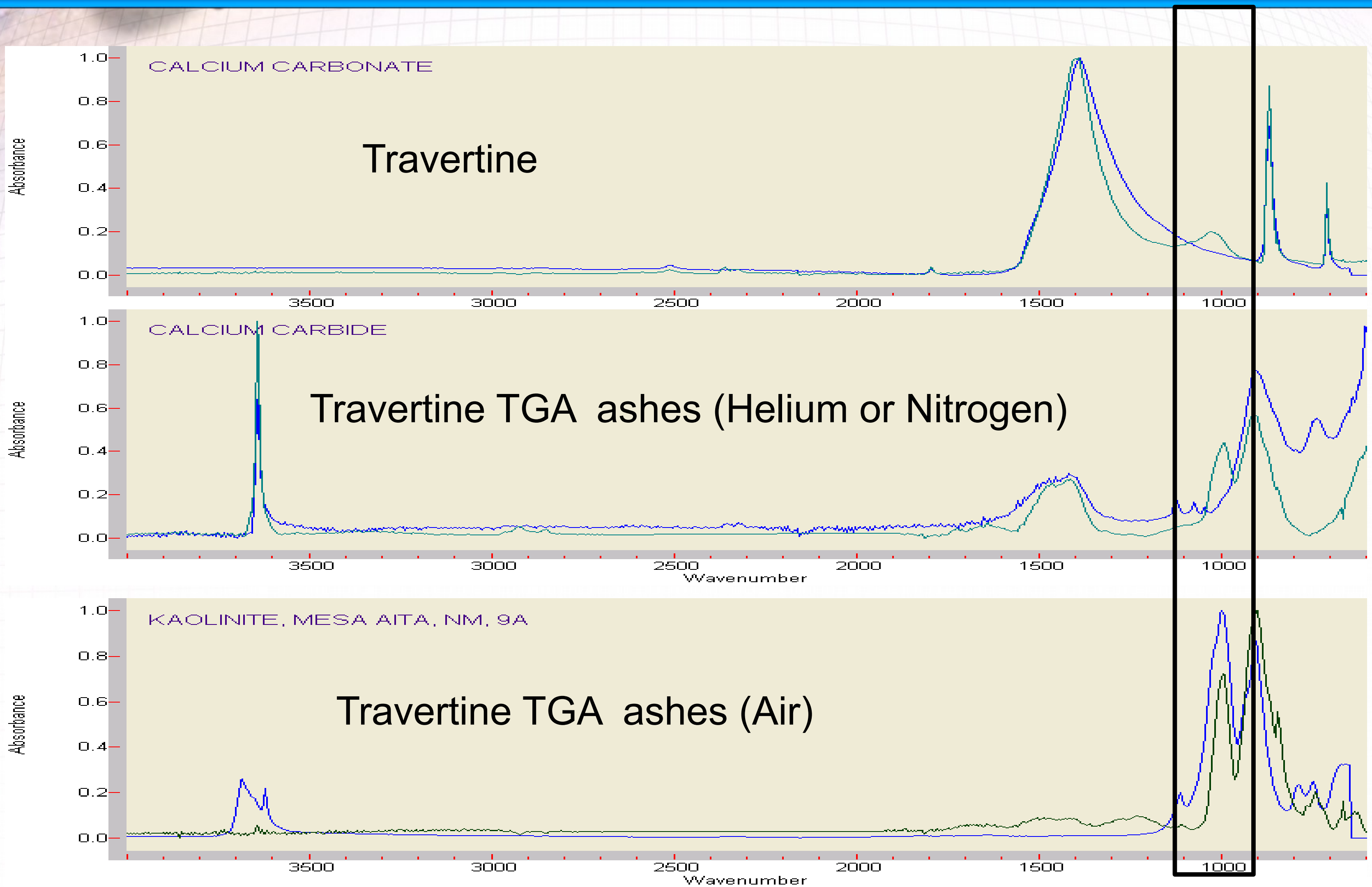


Thermal extraction of the two samples was performed to account for the difference observed in the TGA experiments at temperatures below 400oC. Such an experiment indicated the Old sample contained various fragments that are attributed to polyethylene oxide. Other substances found included Glycerin and Butylated hydroxy toluene (BHT).

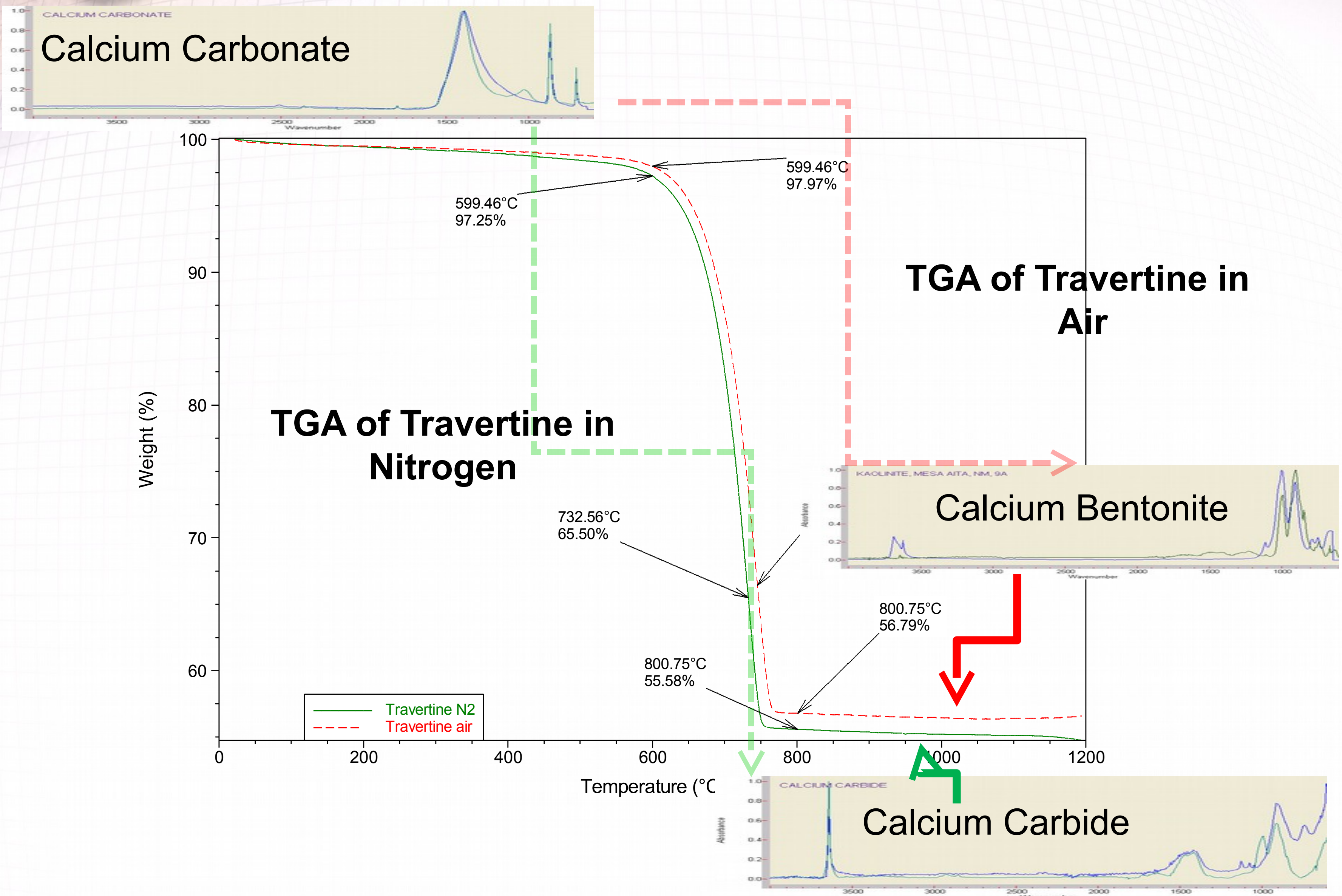
Thermal Response of Travertine in Different Atmospheres



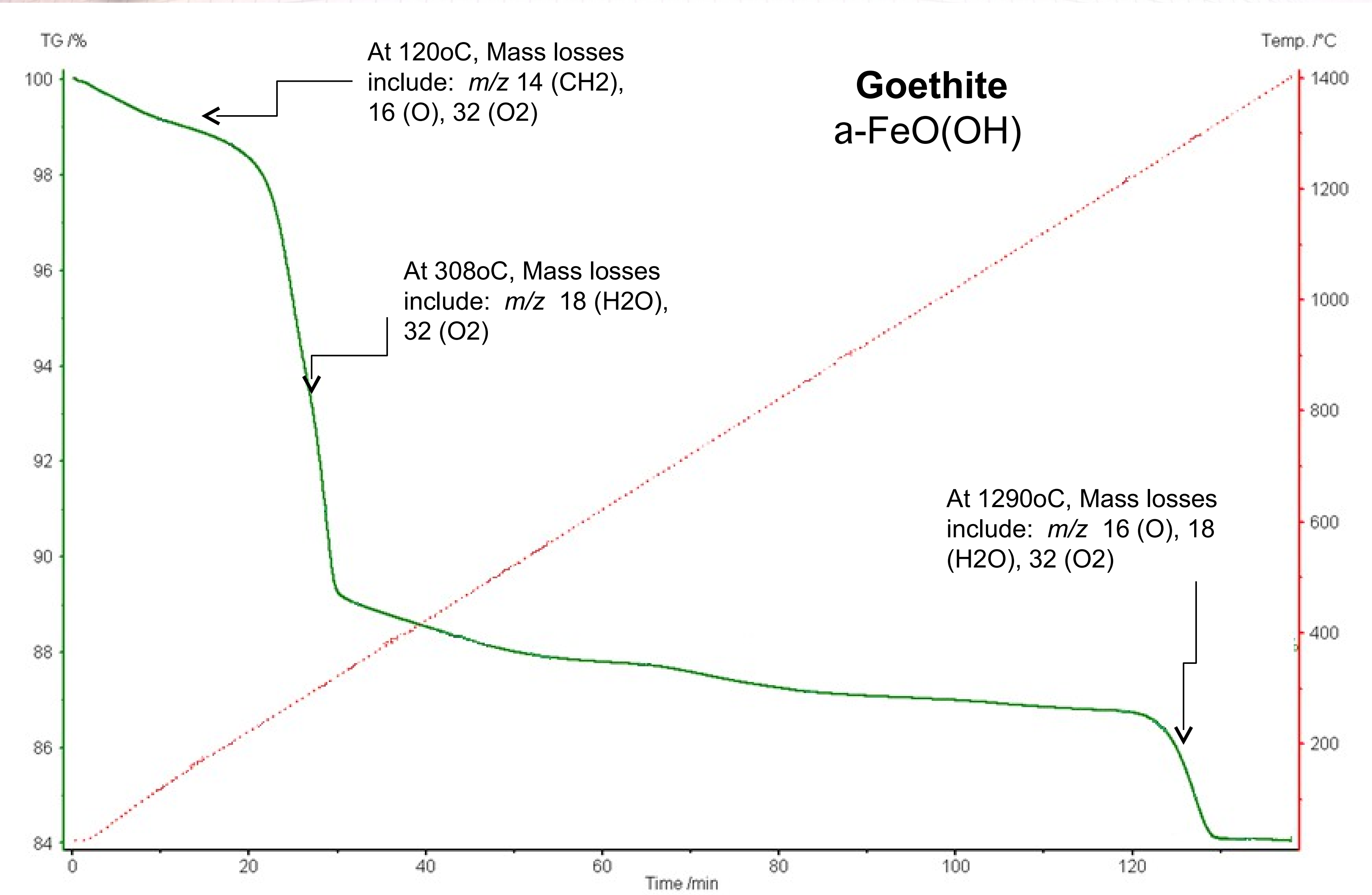
CaCO3 → CaC2 or Calcium Bentonite



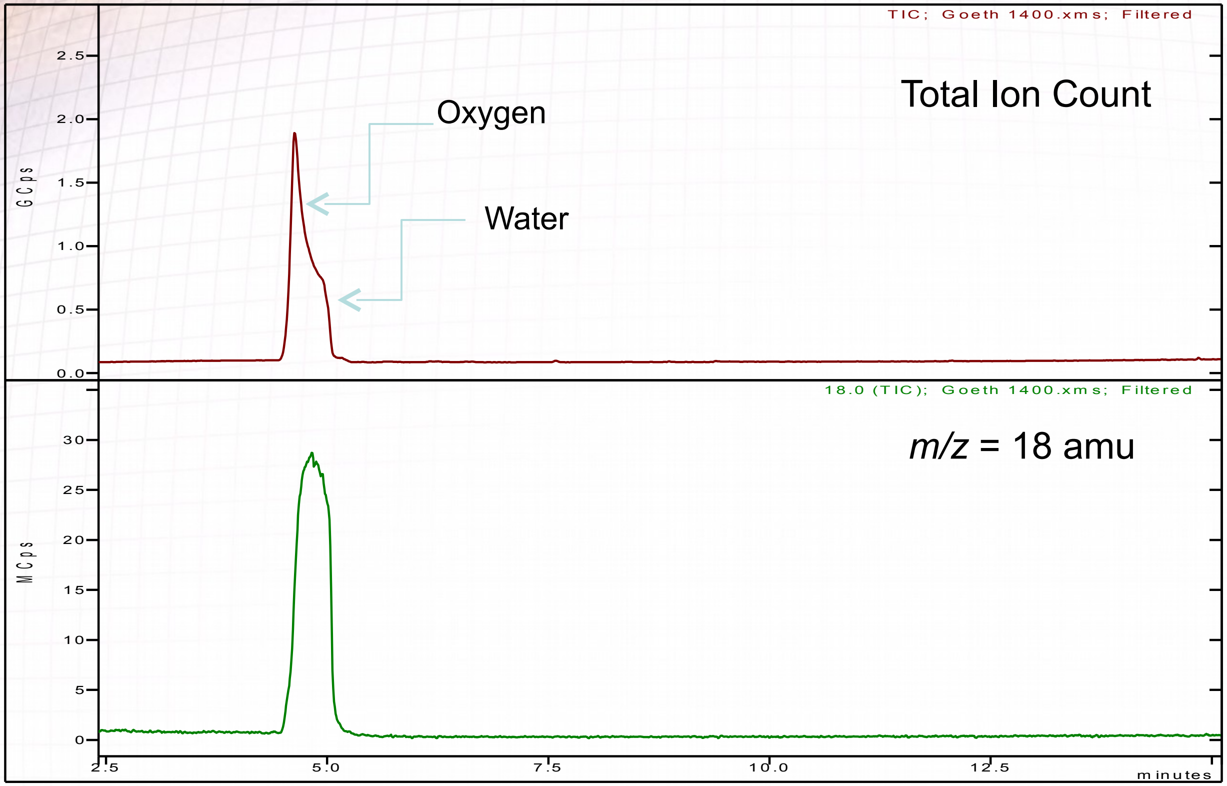
The Role of Gaseous Atmosphere During Thermal Decomposition of Travertine



TGA Analysis of Geothite in Helium

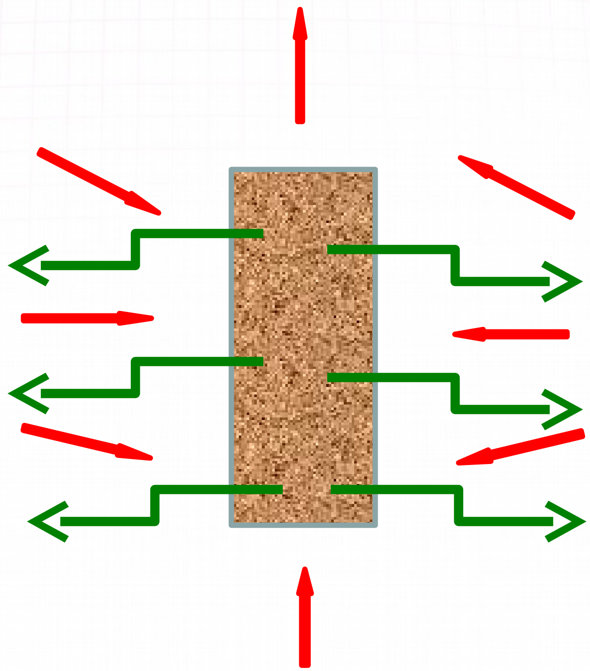


Goethite Analysis by Py-GC-MS at 1400oC



A sample of Goethite was first pyrolyzed at 750oC to remove all but the pertinent high temperature species. The same sample was then pyrolyzed at 1400oC to reveal two key molecules, oxygen and water. Since Goethite has been detected on the surface of Mars by Spirit, the NASA rover, we essentially have a source of water and oxygen waiting on Mars; we just have to heat it under the proper conditions to release these vital substances.

Applying Thermal Energy to Extract Chemical Information



Using Thermal Energy:

- How much Thermal Energy do we add
- How fast do we add the Thermal Energy
- How long do we maintain the Thermal Energy
- What atmosphere do we use
- How much sample do we use

Chemical Information

- Trapped solvent
- Organic additives
- Contaminants
- Labile Functional Groups
- Monomer identification
- Off-gassing information
- Inorganic additives

TGA **Pyrolysis-GC-MS** **TGA-MS-IR**