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

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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

Sample Preparation

- Which Equipment is Available?

Sample Measurement

- What Test is Needed?

Destructive vs. Non-Destructive Analysis

- How Much Sample is Available?

Data Analysis

- Are the Results Valid?

Sample Collection

- Is it Urgent?

Information To Customer
Optical Vs. Thermal Techniques

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

**Heat**
- 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

Sample at 25°C

TGA
Furnace

Sample at 1000°C

Pyrolysis
Filament

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

Thermal Analysis
Thermal Desorption
Pyrolysis

Graph showing heat flow and weight percentage against temperature.
The Influence of Temperature Ramp Rates

Slower Ramp ↔ Faster Ramp

Temperature (°C)

Weight (%)
Pyrolysis for GC-MS of Solids

- Sample size is relatively small:
  50 to 200 \( \mu g \) 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: ~20,000°C per sec
- Max Temperature: 1400°C
- Cooling Rate: > 1000°C per sec
- Fast Heating, Fast Cooling

**Microfurnace**
- Heating Rate: ~50°C per min
- Max Temperature: 800°C
- Cooling Rate: 25°C per min
- Slow to Heat, Slow to Cool
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.
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.
The Silicone samples that were nearly identical by FT-IR displayed very different properties by thermal analysis.
Pyrolysis of Silicone Oil at Different Temperatures

Chromatogram Plots

- Heating Rate: 0.5°C per min
- Heating Rate: 1.0°C per min
- Heating Rate: 2.0°C per min
- Heating Rate: 5.0°C per min
- Heating Rate: 10.0°C per min

Flash Pyrolysis
FEP Vs. PTFE Teflon

![Overlaid Chromatogram Plots](image)

![Diagram of FEP and PTFE structures](image)
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.
Many industrial laboratories have only one technique available for characterization of the manufactured product. In many situations, one type of analytical technique is not adequate for assessing the product.
Thermal Analysis of HDPE and LDPE

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

TGA

DSC of HDPE vs LDPE

Pyrolysis-GC-MS

Universal V4.7A TA Instruments

Polyethylene: -CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-CH₂-
Temperature Ramp Pyrolysis

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

- Heating Rate: >1000°C per sec
- Heating Rate: 1200°C per min
- Heating Rate: 600°C per min
- Heating Rate: 300°C per min
- Heating Rate: 180°C per min
- Heating Rate: 120°C per min
- Heating Rate: 60°C per min
- Heating Rate: 30°C per min
Correlating TGA and Pyrolysis Techniques

Pyrolysis at specified temperatures for 20 seconds

Py 440°C
Py 450°C
Py 460°C
Py 470°C
Py 480°C
Py 490°C
Py 500°C
Py 510°C
Py 750°C

Pyrolysis at 440°C for 20 seconds
Pyrolysis at 450°C for 20 seconds
Pyrolysis at 460°C for 20 seconds
Pyrolysis at 470°C for 20 seconds
Pyrolysis at 480°C for 20 seconds
Pyrolysis at 490°C for 20 seconds
Pyrolysis at 500°C for 20 seconds
Pyrolysis at 510°C for 20 seconds

Irganox 1076
Irganox 1010
Thermal Analysis of PE

Pyrolysis at 450°C For Specified Duration

Modification of the thermal parameters at the onset of TGA degradation for PE can provide valuable information about the additives or contaminants.
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.
Under conditions of increasing temperature, the only difference between the two Viton Gaskets was found below 400°C, where the old sample lost a larger percentage of its mass compared to the new sample.
Thermal extraction of the two samples was performed to account for the difference observed in the TGA experiments at temperatures below 400°C. 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).
TGA Analysis of Fluorinated Materials

Krytox 143 AZ

Brayco 815Z
CaCO$_3$ $\rightarrow$ CaC$_2$ or Calcium Bentonite

Travertine

Travertine TGA ashes (Helium or Nitrogen)

Travertine TGA ashes (Air)
The Role of Gaseous Atmosphere During Thermal Decomposition of Travertine

Calcium Carbonate

TGA of Travertine in Air

TGA of Travertine in Nitrogen

Calcium Bentonite

Calcium Carbide
Substances being measured during mass loss near 700°C include CO₂, CO, and O².
Detected Mass Losses of Goethite

At 120°C, Mass losses include:
- \( m/z \) 14 (CH\(_2\)), 16 (O), 32 (O\(_2\))

At 308°C, Mass losses include:
- \( m/z \) 17 (OH), 18 (H\(_2\)O), 32 (O\(_2\))

At 1290°C, Mass losses include:
- \( m/z \) 16 (O), 18 (H\(_2\)O), 32 (O\(_2\))

Goethite \( \alpha \)-FeO(OH)
A sample of Goethite was first pyrolyzed at 750°C to remove all but the pertinent species. The same sample was then pyrolyzed at 1400°C.
TGA Analysis of Kieserite
Detected Mass Losses of Kieserite

At 78°C, Mass losses include: \( m/z \) 17 (OH), 18 (H\(_2\)O), 28 (CO)

At 382°C, Mass losses include: \( m/z \) 16 (O), 17 (OH), 18 (H\(_2\)O), 28 (CO)

At 1136°C, Mass losses include: \( m/z \) 16 (O), 28 (CO), 32 (O\(_2\)), 48 (SO), and 64 (SO\(_2\))

At 1315°C, Mass losses include: \( m/z \) 17 (OH), 48 (SO), and 64 (SO\(_2\))
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