Hyphenated Spectroscopy Techniques

Thermal Analysis and Rheology Short Course
Concord, NH
April 10, 2018

Analytical Instruments Overview

<table>
<thead>
<tr>
<th>Chromatography &amp; Mass Spectrometry</th>
<th>Materials &amp; Structural Analysis</th>
<th>Chemical Analysis Instruments</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Life sciences mass spectrometry</td>
<td>• Electron microscopy</td>
<td>• Portable analytical instruments</td>
</tr>
<tr>
<td>• Liquid, ion, gas chromatography</td>
<td>• Molecular and elemental</td>
<td>• Air-quality monitoring</td>
</tr>
<tr>
<td>• Inorganic(trace) elemental analysis</td>
<td>spectroscopy</td>
<td>• Radiation safety and security</td>
</tr>
<tr>
<td>• Laboratory informatics</td>
<td>• 2D/3D imaging software</td>
<td>• Process instruments</td>
</tr>
</tbody>
</table>

Industry-leading technologies to solve a broad range of complex challenges
The widest range of analytical methods to drive deeper materials insights

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS</td>
<td>Elemental imaging at high spatial resolution</td>
</tr>
<tr>
<td>Raman</td>
<td>Chemical compound identification of both organic and inorganic materials</td>
</tr>
<tr>
<td>FTIR</td>
<td>Identification of both organic and inorganic materials in bulk state</td>
</tr>
<tr>
<td>EDS Bulk</td>
<td>Bulk state elemental composition</td>
</tr>
<tr>
<td>XRD</td>
<td>Structural crystallinity and composition</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Quantitative measurement of reflection or transmission properties of a material</td>
</tr>
</tbody>
</table>

We deliver a full spectrum of analytical tools that enable customers to advance their research, product development, and quality control capabilities.

The Electromagnetic Spectrum

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRF</td>
<td>X-rays</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Infrared</td>
<td>Near-IR</td>
</tr>
<tr>
<td></td>
<td>Mid-IR</td>
</tr>
<tr>
<td></td>
<td>Far-IR</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Range</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-rays</td>
<td>Wavelength (µm)</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Wavelength (µm)</td>
</tr>
<tr>
<td>Infrared</td>
<td>Wavelength (µm)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wavenumbers (cm⁻¹)</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁷</td>
<td>XRF</td>
</tr>
<tr>
<td>10⁶</td>
<td>UV-Vis</td>
</tr>
<tr>
<td>10⁵</td>
<td>Near-IR</td>
</tr>
<tr>
<td>10⁴</td>
<td>Mid-IR</td>
</tr>
<tr>
<td>10³</td>
<td>Far-IR</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wavelength (µm)</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻³</td>
<td>XRF</td>
</tr>
<tr>
<td>0.01</td>
<td>UV-Vis</td>
</tr>
<tr>
<td>0.1</td>
<td>Infrared</td>
</tr>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
The Power of Molecular Spectroscopy

- Work fast…
- Little or no sample prep, rapid screening
- …on a range of samples…
  - Organics, inorganics, films, coatings, paper, fibers, more
- …and answer fundamental questions
  - What is this stuff? How much is in there? In what form?
- Analyze samples from ‘cradle to grave’
  - R & D, process control, QA/QC, failure analysis, waste

Core Molecular Spectroscopy Techniques

- FTIR
  - Chemical fingerprint
  - Fast analysis

- picoSpin NMR
  - Benchtop NMR
  - No cryogens

- Raman Spectroscopy
  - Chemical fingerprint
  - Fast analysis
  - Greater sampling options — microscopy options
General ‘Rules’ for Molecular Spectroscopy

- **Energy** varies along the x-axis
  - Wavelength in nanometers or microns, Wavenumber (cm⁻¹)
- **Response** is along the y-axis
  - Absorbance, transmittance, reflectance
  - Different molecules absorb light differently (“Peaks”)
  - This is what enables spectroscopy to tell us something!

Breaking it Down

Polymer Deformulation Studies using FT-IR Coupled to TGA
Overview

• **Deformation**
  • What is it?
  • Why do it?
  • Common materials

• **FT-IR as a deformation tool**
  • Classical technique
  • TGA coupled with FT-IR

• **Physical property correlation with chemical data**

---

Deformation

• **Reverse Engineering**
  • Unknown material composition

• **Failure Analysis**
  • Known material gone wrong

• Polymers
  • Plastics
    • Fillers
    • Formulation
  • Rubber
    • Carbon Black: O-Rings, Tires

• Epoxies, Resins, Adhesives
• Entrained solvents, Breakdown products
• Fabrics, Paper products
**TGA-IR: The Basics**

Quantitative: How much is coming off?
- T "G" A – Gravimetric Analysis

Qualitative: What is coming off?
- FT-IR – Chemical information

**TGA-FTIR: Experiment**
Experimental Set-up

TGA Conditions
- Sample size: 10 – 15mg
- TGA program: N₂ Purge Isothermal
- Temperature: Ambient up to 650°C

FT-IR Conditions
- Transfer line temp: 300°C
- TGA-IR Module temp: 300°C
- Data Collection: 8 cm⁻¹, 5 scans/spectrum

Low Volume IR Gas Cell

Simple Situation – Calcium Oxalate

- Three weight-loss peaks
- H₂O; CO + CO₂ ; CO₂

[Diagram showing weight-loss peaks and calcium oxalate structure]
Example Applications

- Polymers
- Textiles
- Coatings
- Residual solvent
- Product stability
- Additive analysis

Classic Root Cause Analysis

Gasket analysis

Good

Bad

Subtraction

Search result

<table>
<thead>
<tr>
<th>Index</th>
<th>Mark</th>
<th>Compound Name</th>
<th>Library Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>328</td>
<td>4,4'-Isoniophenonephene</td>
<td>Resolute IR Vap IT</td>
</tr>
<tr>
<td>5</td>
<td>328</td>
<td>4,4'-Isoniophenonephene</td>
<td>Resolute IR Vap IT</td>
</tr>
<tr>
<td>5</td>
<td>328</td>
<td>4,4'-Isoniophenonephene</td>
<td>Resolute IR Vap IT</td>
</tr>
<tr>
<td>5</td>
<td>328</td>
<td>4,4'-Isoniophenonephene</td>
<td>Resolute IR Vap IT</td>
</tr>
<tr>
<td>5</td>
<td>328</td>
<td>4,4'-Isoniophenonephene</td>
<td>Resolute IR Vap IT</td>
</tr>
</tbody>
</table>
Deformulating Nanoparticles

- These nanoparticles are stabilized by ligands
- Heating breaks down the complexes, releasing ligand

Outgassing of Electronic Component

- A critical electronic component, in a sealed chamber, was degrading
- Concern was for outgassing of other materials in the chamber
- The insulation of a wire was found to be the cause
Complete Analysis: Mercury TGA

PC+ABS Characterization

Polycarbonate/Poly(acrylonitrile:butadiene:styrene) (PC+ABS)

Blended Polymer – Complex Matrix
PC+ABS Characterization: Preliminary Evaluation

- OMNIC Mercury TGA software analyzes the complete data set
  - Principle component analysis followed by multi-component search
  - Guides the interpretation and additional searching

Two Wt Loss Areas

PC+ABS Characterization – Early Weight Loss

- Extract data from first weight loss region
  - 420 – 440 °C range
  - Mixture search using OMNIC Specta software
  - Primarily Styrene and related materials
PC+ABS Characterization: Major weight loss

- Extract data from 2nd weight loss region
  - 510 - 540°C range
  - Direct search in OMNIC provides enough information
  - Bisphenol A is the major component

PC+ABS Characterization – Something’s missing

- Nitrile component predicted by structure
  - Not readily pulled out of this complex mixture
  - OMNIC Spectra - Peak Search comes in handy
  - Isocyanic acid – based on nitrile peaks between 2300 & 2200 cm⁻¹
Environmental Stress Cracking (ESC) Investigation

Environmental Stress Cracking is…
the premature embrittlement and subsequent cracking of a plastic
due to the simultaneous and synergistic action of stress and
contact with a chemical agent

ESC Failure Mechanism:
• Chemical agent permeates into molecular structure →
  lower ductility
• Mechanism includes interference with inter-molecular
  forces bonding polymer chains
• Reduces energy required for disentanglement/slippage
to occur producing a shift in the preferred mechanism
from yielding
Environmental Stress Cracking (ESC) Investigation

• Scrape samples with Diamond ATR:
  ➢ Fracture Zone & Intact Area
  ➢ Subtract the two spectra followed by Multi-Component Search
  ➢ Some clues, but overall unsatisfactory result

<table>
<thead>
<tr>
<th>Source</th>
<th>Type</th>
<th>Quantity</th>
<th>Concentration</th>
<th>Component</th>
<th>Spectrum</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture Zone</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intact Area</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Environmental Stress Cracking (ESC) Investigation

• TGA-IR Analysis:
  ➢ Early weight loss area 300 – 360°C
  ➢ Extracted spectrum subjected to OMNIC Specta Multi-Component Search
  ➢ Identified acetic acid and medium-chain length methyl ester

<table>
<thead>
<tr>
<th>Source</th>
<th>Type</th>
<th>Quantity</th>
<th>Concentration</th>
<th>Component</th>
<th>Spectrum</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture Zone</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intact Area</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Environmental Stress Cracking (ESC) Investigation

- TGA-IR Analysis:
  - Main weight loss area 390 – 440°C
  - Extracted spectrum subjected to OMNIC Spectra Multi-Component Search
  - Identified an aromatic alcohol, longer-chain length methyl ester

EPDM Characterization

Poly(ethylene:propylene:diene) (EPDM)

![Poly(ethylene:propylene:diene) (EPDM) molecule structure](image)
EPDM Characterization

EPDM Compounding - Hydrocarbon Plasticizers

- Paraffinic: \[CH_3CH(CH_3)CH_2CH_2-\]
- Naphthenic: \[\text{non-saturated ring structures}\]
- Aromatic: \[\text{benzene structure}\]

EPDM Characterization: TGA Analysis - Quantitative

Sample: EPDM Rubber
Size: 12.7140 mg
Method: Isothermal for TGA
Run Date: 10-Oct-2014 15:40
Instrument: TGA Q5000 V3.15 Build 26

10.88% Plasticizer (1.38 mg)
393°C
486°C
41.26% EPDM (5.25 mg)

Universal V4 TA Instruments
### EPDM Characterization: TGA-IR Results – Qualitative

- **Plasticizer:**
  - Paraffinic hydrocarbon

- **EPDM Breakdown:**
  - Unsaturated hydrocarbon

---

**Textile Example**
Diamond ATR Of Fabrics (Pre-TGA)

- Diamond ATR shows difference between fabrics
- Many unique peaks seen below 1000 cm\(^{-1}\)

NYCO TGA-IR Data

- Temperature (°C) vs. Time (min)
- Weight loss (mg) vs. Time (min)
- Gram-Schmidt (GS)

GS shows total IR response as function of time
- Peaks in GS correlate to sample weight loss and significant off-gassing detected
- For NYCO, 1 major thermal event was observed at ~26 min
- Next slide will show IR spectra in that time region
NYCO Evolved Gas Spectra

- Major evolved gas is CO$_2$ at 26min
- Just before CO$_2$ evolution, small signal observed at ~3000 and ~900 cm$^{-1}$
- See next slide for ID of these peaks

NYCO - 26.37min Detailed Spectral Analysis

- 4 components observed including CO$_2$, CO, methane and ammonia
- Spectral overlay shows peaks that match to each species
FR Fabric TGA-IR Data

Temperature (°C) vs. Time (min)

Weight loss (mg) vs. Time (min)

Gram-Schmidt

For FR Fabric, 3 major thermal event was observed at ~16, 26, 31 mins.
- Next slide will show IR spectra in that time region

FR Fabric Evolved Gas Spectra

345° C
See next slide for library search

542° C
Spectrum matches to CO₂ evolution

650° C
Spectrum matches to CO₂ and CO evolution
Basic Theory and Instrument Design of FT-IR

345° C Linked Spectrum Library Search

- Best match is brominated species
- Species was not seen in NYCO sample

<table>
<thead>
<tr>
<th>Index</th>
<th>Match</th>
<th>Compound Name</th>
<th>Library Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65.0%</td>
<td>Tetrahydrofururum bromide</td>
<td>HR NIOSH Vapor Phase</td>
</tr>
<tr>
<td>2</td>
<td>66.6%</td>
<td>Tetrahydrofururum bromide; 2-Bromomethyltetrahdrofurure</td>
<td>HR Aldrich Vapor</td>
</tr>
<tr>
<td>3</td>
<td>64.4%</td>
<td>1,4-Cyclohexadiene</td>
<td>HR EPA Vapor Phase</td>
</tr>
</tbody>
</table>

Conclusions - Deformulation using FT-IR & TGA

- TGA coupled to FT-IR advances capabilities to break materials down
- OMNIC Series, Mercury TGA and OMNIC Specta software provide tools for analysis of complex mixtures
- Understanding the chemistry of the materials being analyzed is important
Other Applications for Spectroscopy

- **Transmission**
  - Preferred method for quantitative analysis
  - Sample mixed and pressed; good sensitivity

- **Attenuated total reflectance (ATR)**
  - The sample must contact the crystal
  - Simple and fast, generally non-destructive

- **Diffuse reflectance (DRIFTS)**
  - Dilute sample in a matrix (like KBr)
  - Simple, but requires mixing

- **Specular reflectance**
  - Sample must be reflective or on a mirror
  - Signals can be very weak
ATR of Heat Shrink Tubing: Inner Wall

- ATR and OMNIC Spectra reveal two components: Polymer and Mg(OH)$_2$
- Mg(OH)$_2$ is used as a flame retardant

ATR of Heat Shrink Tubing: Outer Wall

- Outer wall shows something else
  - Subtract outer – inner
  - Tyzor 131® is found
  - This is a cross-linker
  - Causes tubing to shrink!
Black Rubber Gasket

- Run on Ge ATR
- Multiple components
- Base polymer
- Silane slip-aid