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Polymer Analysis from Raw Material to Formulation

Using the Thermo Scientific Nicolet iS50 FT-IR Spectrometer

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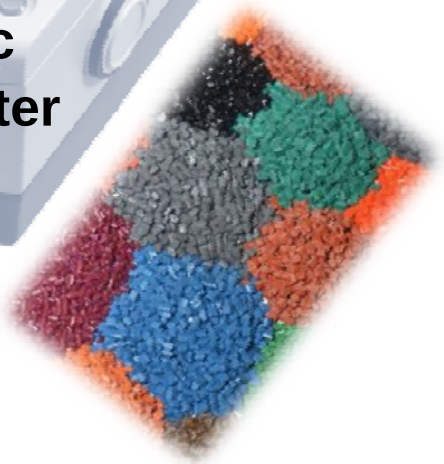
Product Manager, FT-IR Products



Cutting Edge Tools Across the Spectrum

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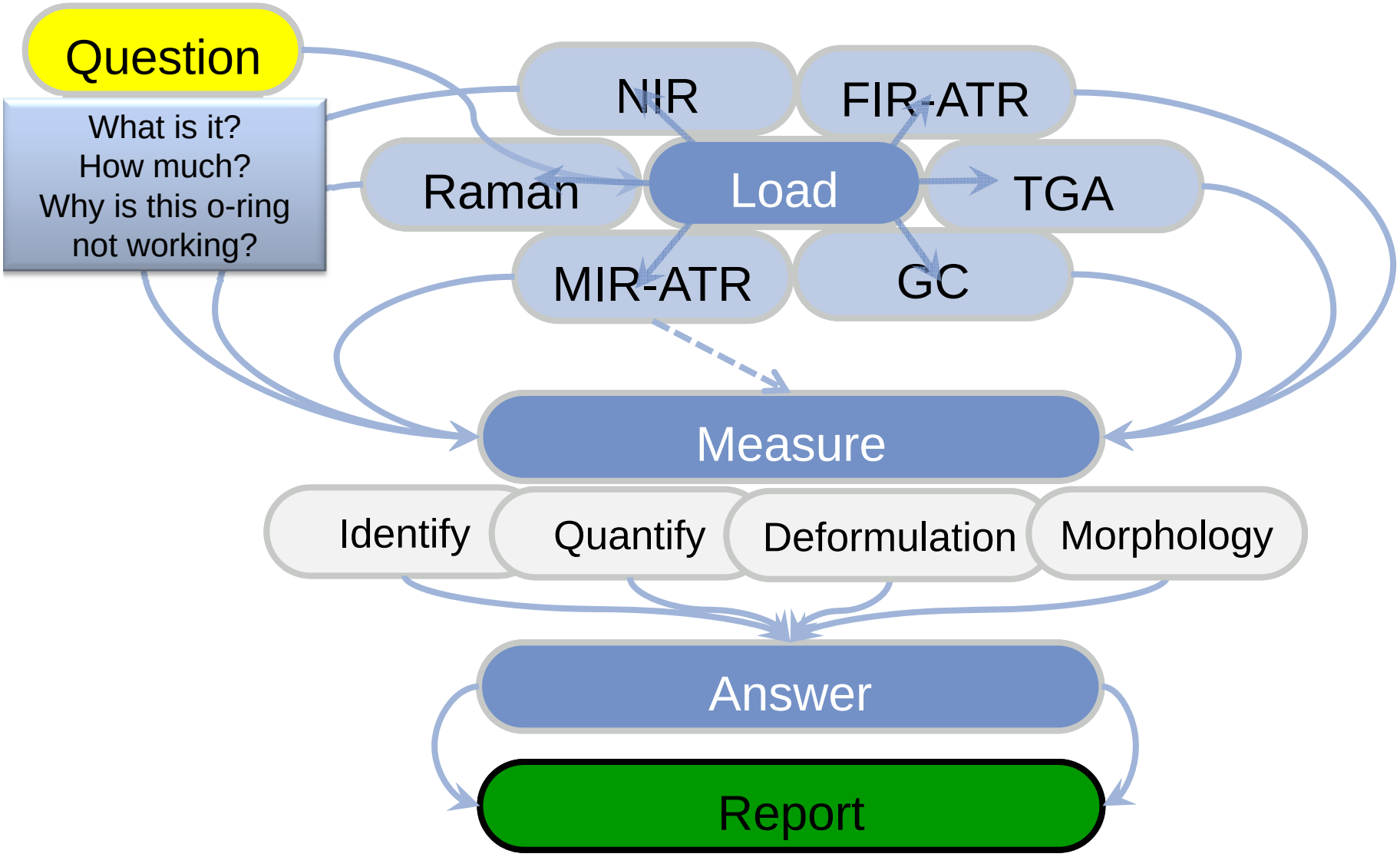
We are the leading provider of analytical instruments, equipment, reagents and consumables, software and services for research, analysis, discovery and diagnostics.

The Polymer Laboratory Workflow



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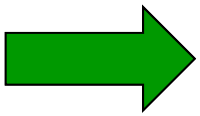
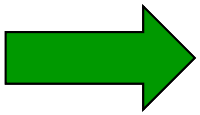
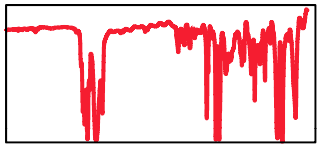
Modes of Analysis with Molecular Spectroscopy



NIR

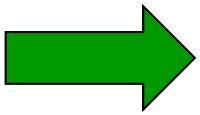
- Common in industrial applications
- Deeply penetrating light

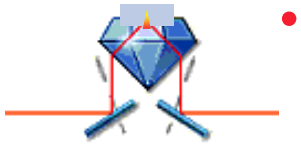




Mid-IR

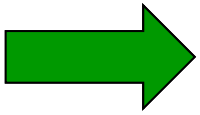
- Most common type of molecular spectroscopy
- Useful for most organic compounds

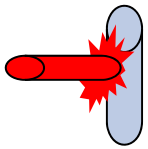




Far-IR

- Provides more information that mid-IR
- Useful for inorganics and some organics





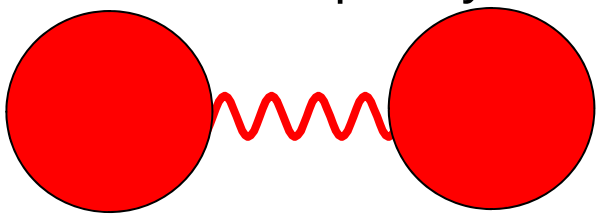
Raman

- Complementary to infrared
- Provides information when IR isn't suitable

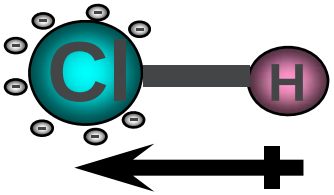
When Does a Material Absorb Infrared Light ?

- The frequency of the light must be identical to the frequency of the vibration (resonance)
  - Higher Frequency

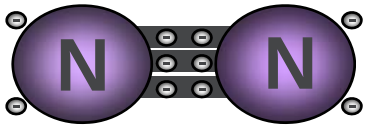
  - Lower Frequency



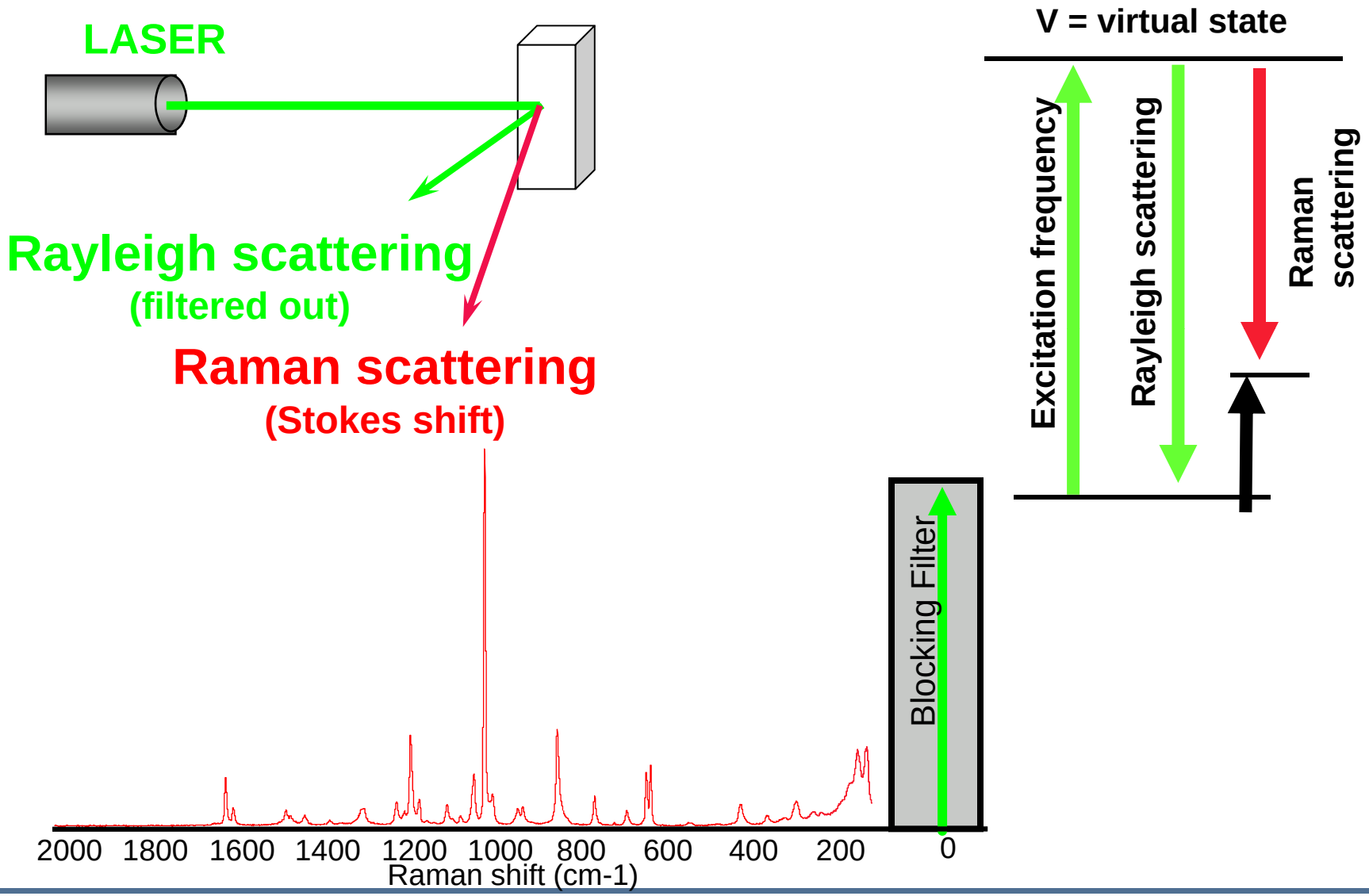
- The dipole of the molecule must change during the vibration
  - Strong Absorbance



  - No Absorbance



Raman Spectroscopy – The Raman Effect



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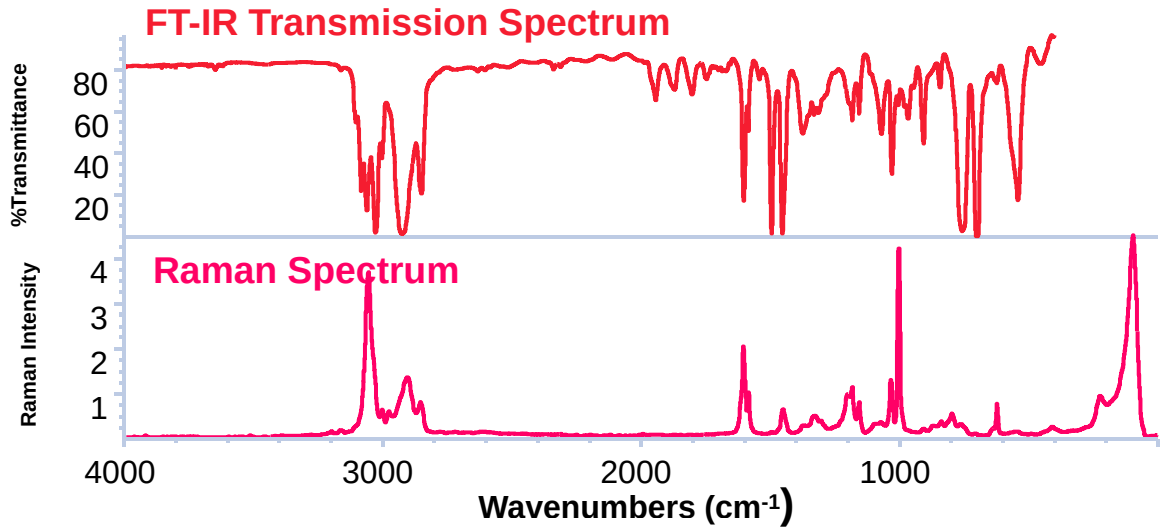
Raman Compared with Infrared

- Complementary information
  - Functional groups dominant in Infrared spectrum
  - Molecular backbone dominant in Raman spectrum
    - Raman often useful for characterizing morphology
  - Weak IR absorbers often strong Raman emitters and vice versa
    - Aqueous solutions pose fewer challenges with Raman



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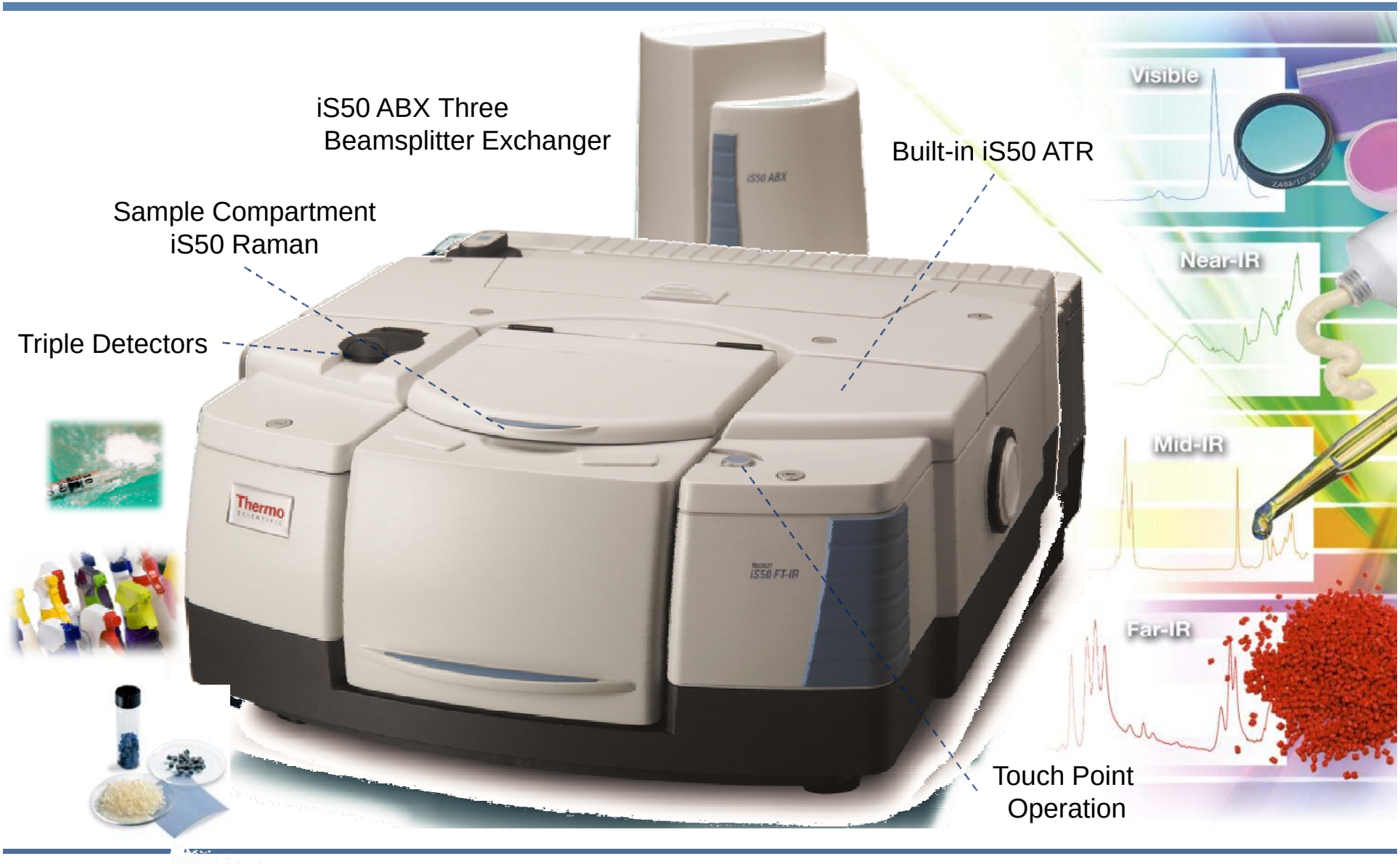
The Nicolet iS50 FT-IR



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Flexibility

Hyphenation

- FT-IR microscope
- iS50 NIR Module
- TGA-IR Module
- iS50 GC-IR module

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Polymer Orientation Studies

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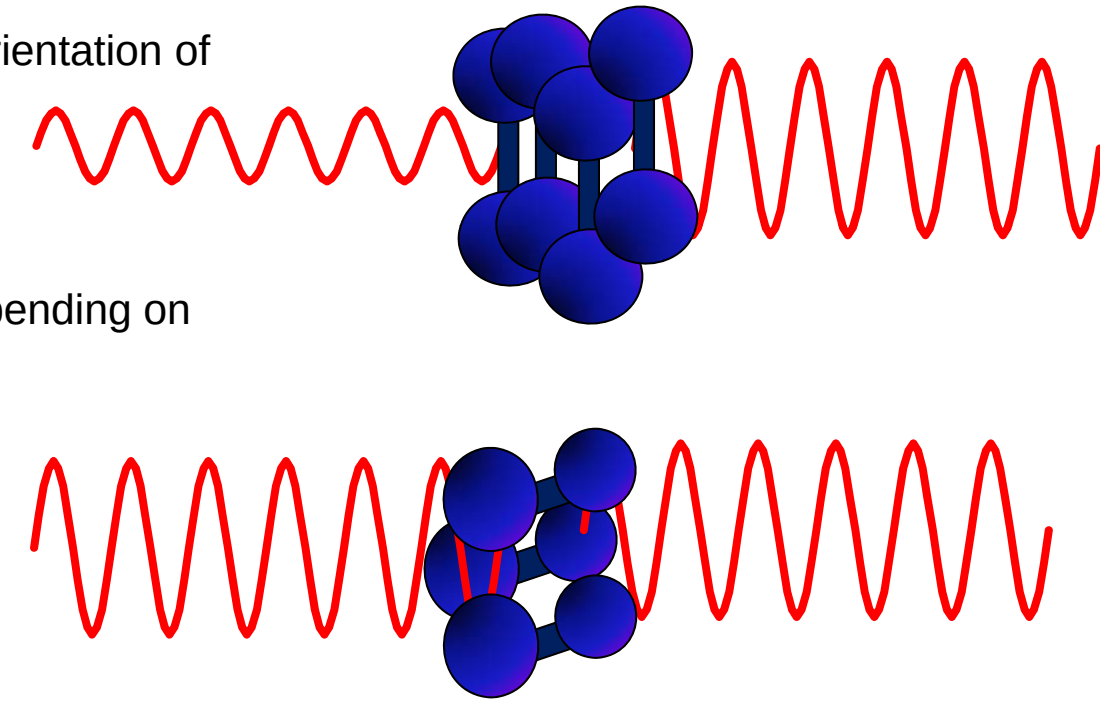
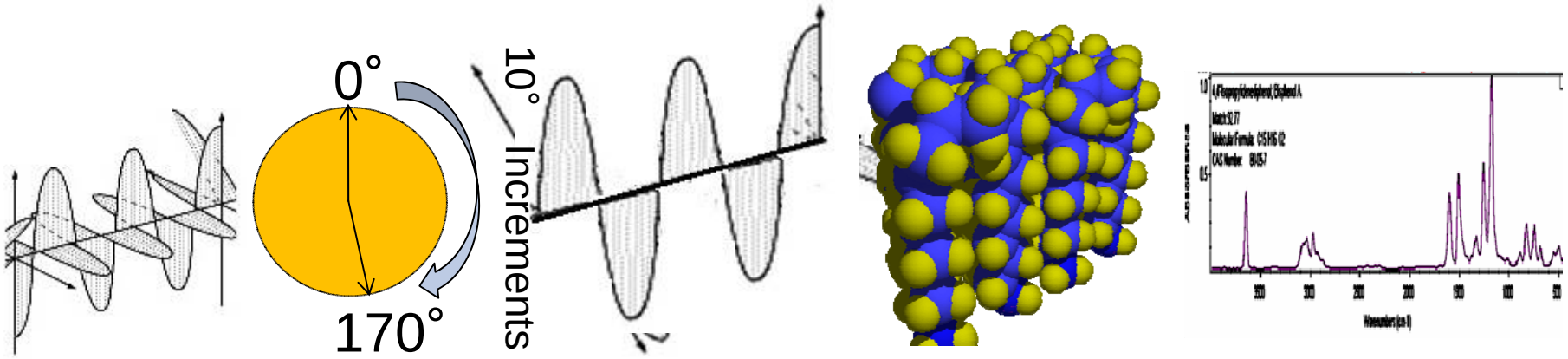
Polymer Orientation Studies

- Polymers are often stretched along an axis
  - IR absorption is sensitive to the orientation of the molecules
  - Different spectra are obtained depending on molecular bond orientation

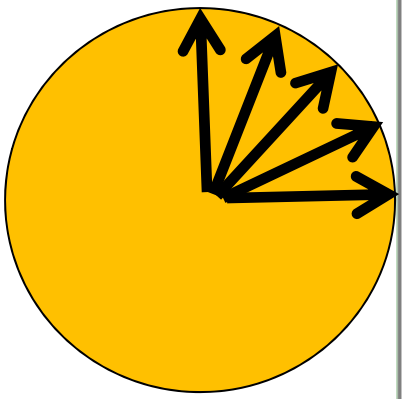


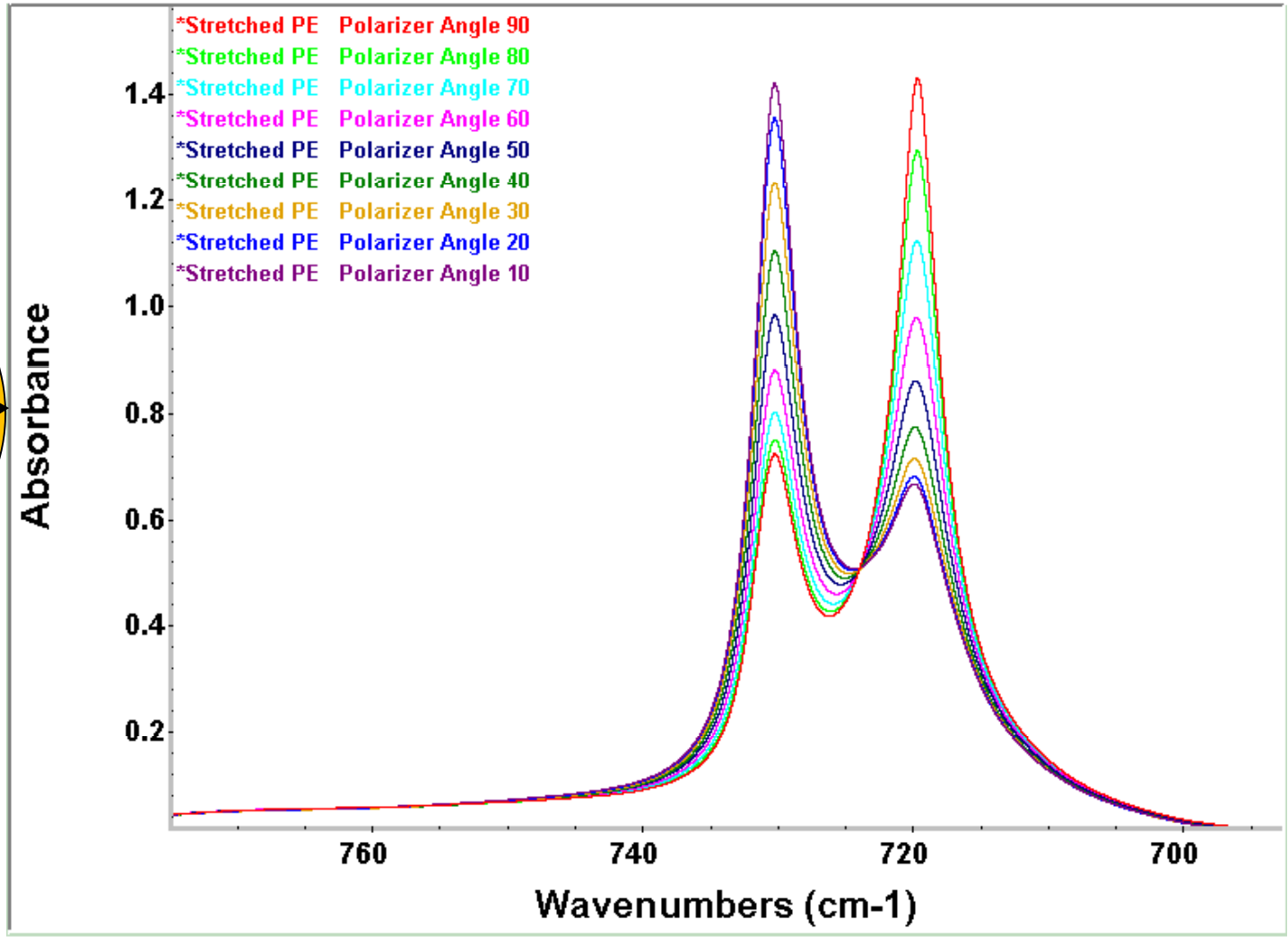
Polymer Orientation Studies

- Stretched Polyethylene film placed in instrument
- Polarizer automatically moved into beam path and rotated during data collection
- Series of spectra show changes in absorption as polarizer is rotated



Polymer Orientation Studies (FT-IR)





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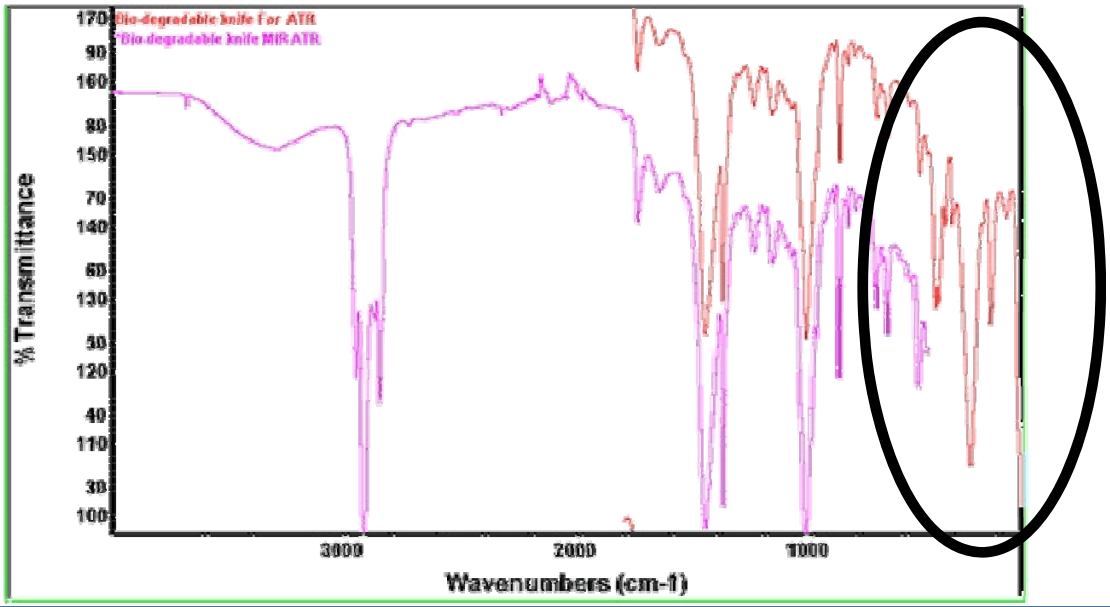
Far-IR: Extended Range

When Mid-IR isn't enough

Far-IR: Extended Range

- Infrared Spectroscopy
  - Generally encompasses 4000cm^{-1} to around 600cm^{-1}
    (wavelength 2.5 microns to 20 microns)
  - Limited by the detector, lens and window material

- Far Infrared ATR
  - Down to ~150cm^{-1} (<50 micron wavelength)
  - Diamond ATR crystals and windows allow Far IR



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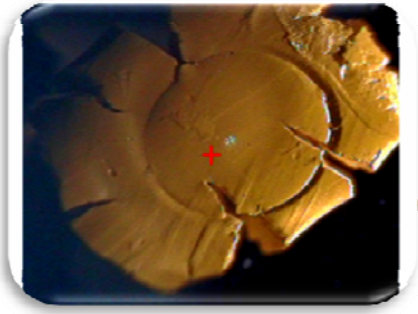
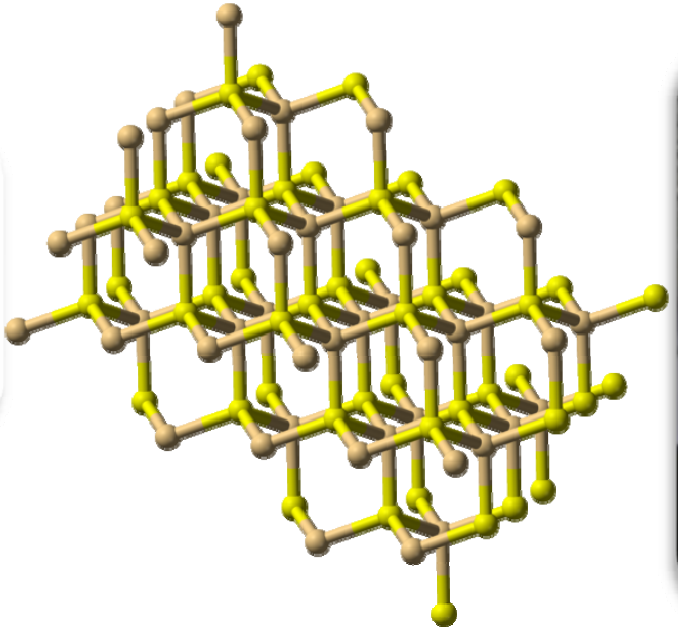
Far-IR: Extended Range

- Polymer additives and pigments are scrutinized for safety
  - Some pigments are banned because they are heavy metals (lead, cadmium)
  - Often these pigments have no mid-IR signature
  - Can be detected with Far-IR

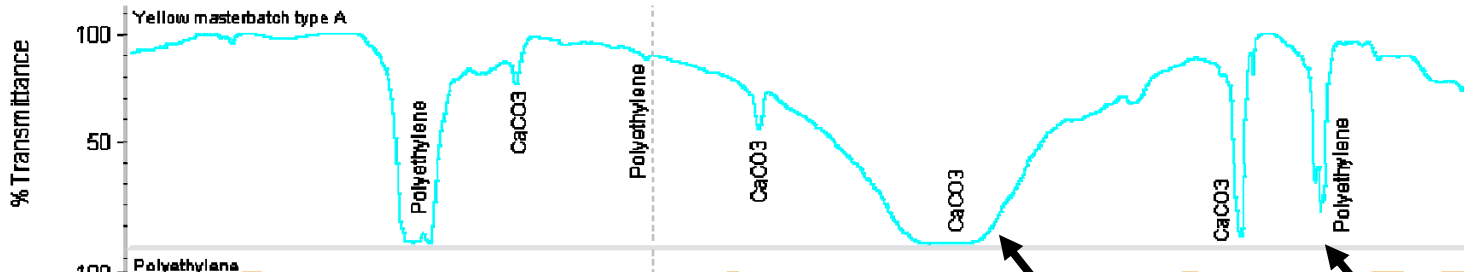
- Yellow pigmented polymer was obtained from a supplier
  - It was suspected to contain the banned pigment CdS
  - Mid-IR analysis using an ATR didn't show anything unusual





Far-IR: Extended Range

- Mid IR analysis
  - The spectrum shows spectral features of polyethylene and carbonated materials
  - There is <u>not enough information</u> to identify the yellow pigment composition



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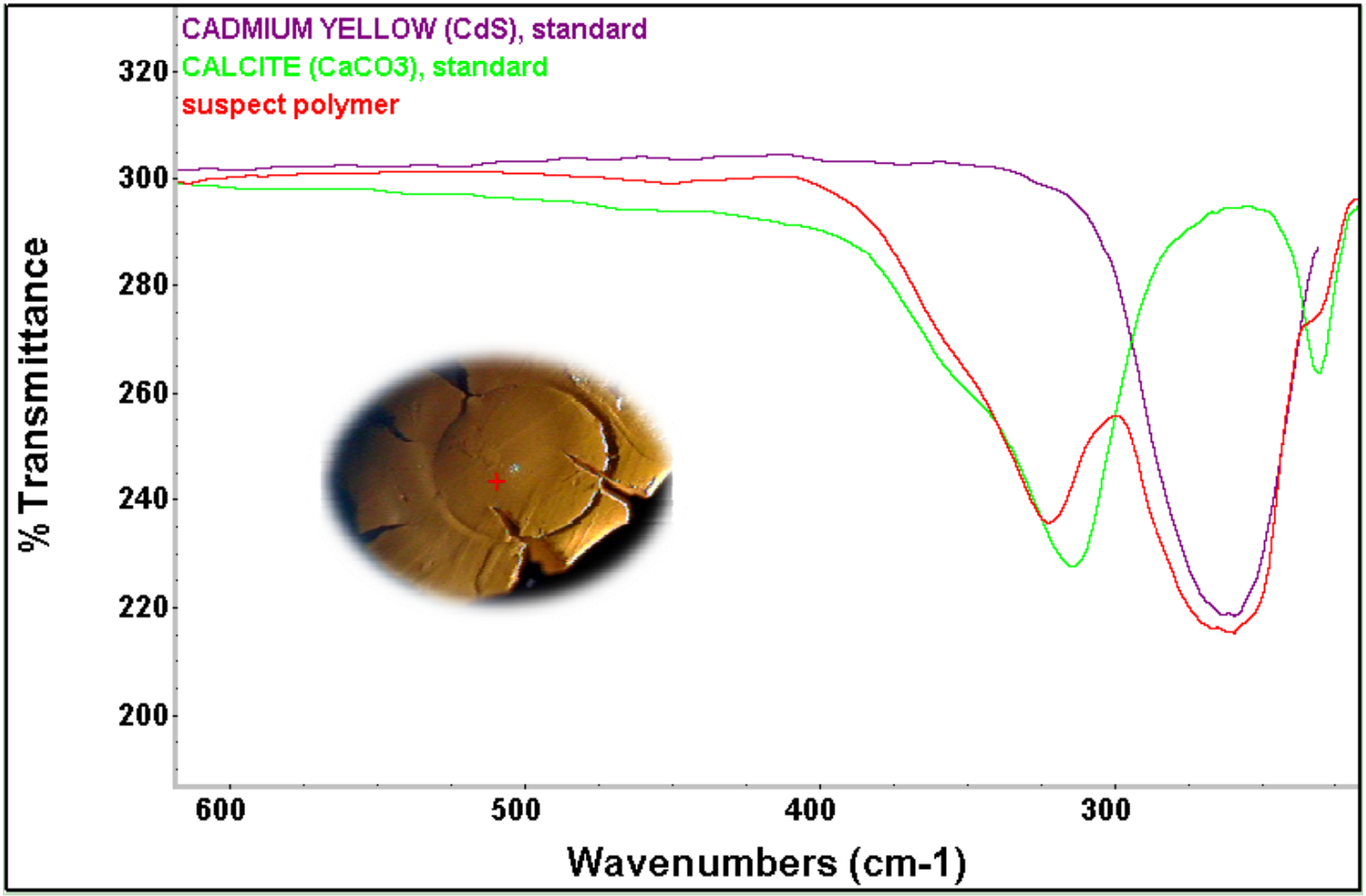
Far-IR: Extended Range

- Far IR using the diamond ATR
  - Shows that it contains cadmium pigment



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Raman in Conjunction with FT-IR

Raman complements infrared information with crystallinity, density and inorganics ID

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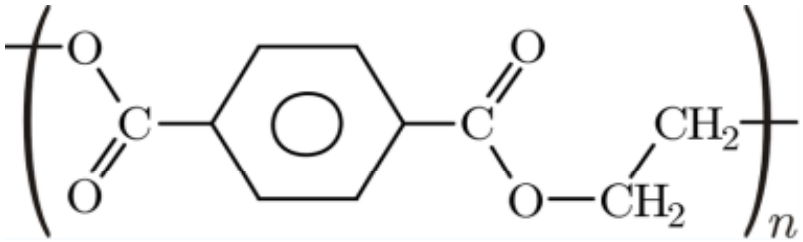
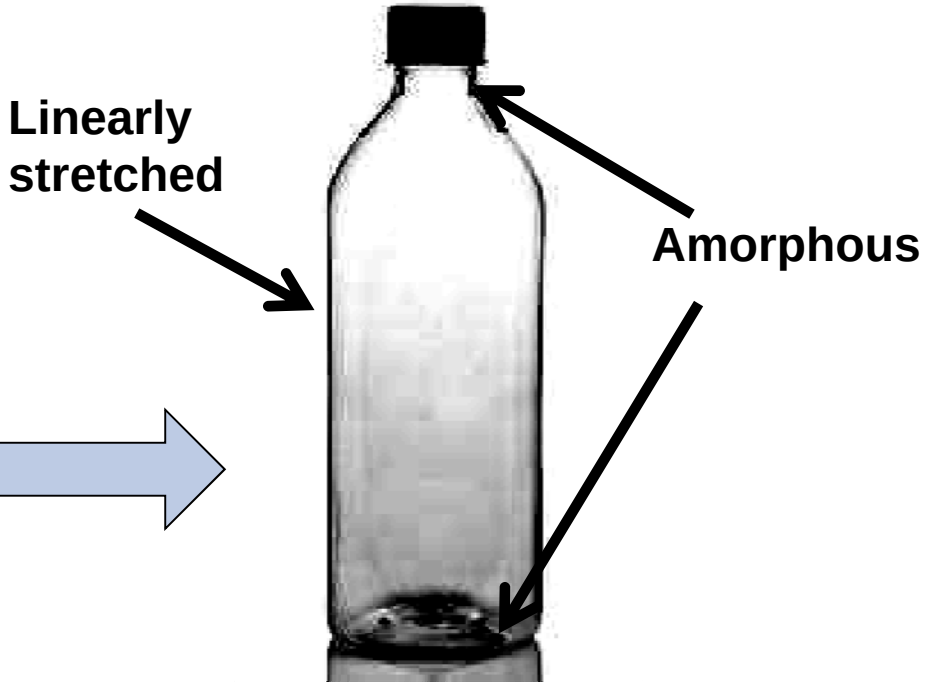
Polymer Orientation Studies

- Polyethylene terephthalate (PET) used in making bottles

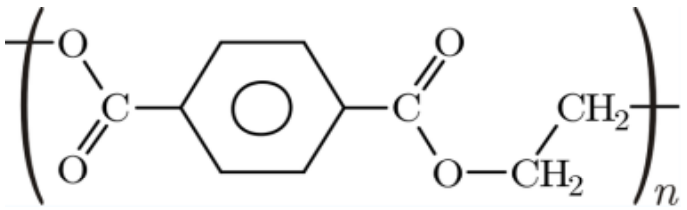


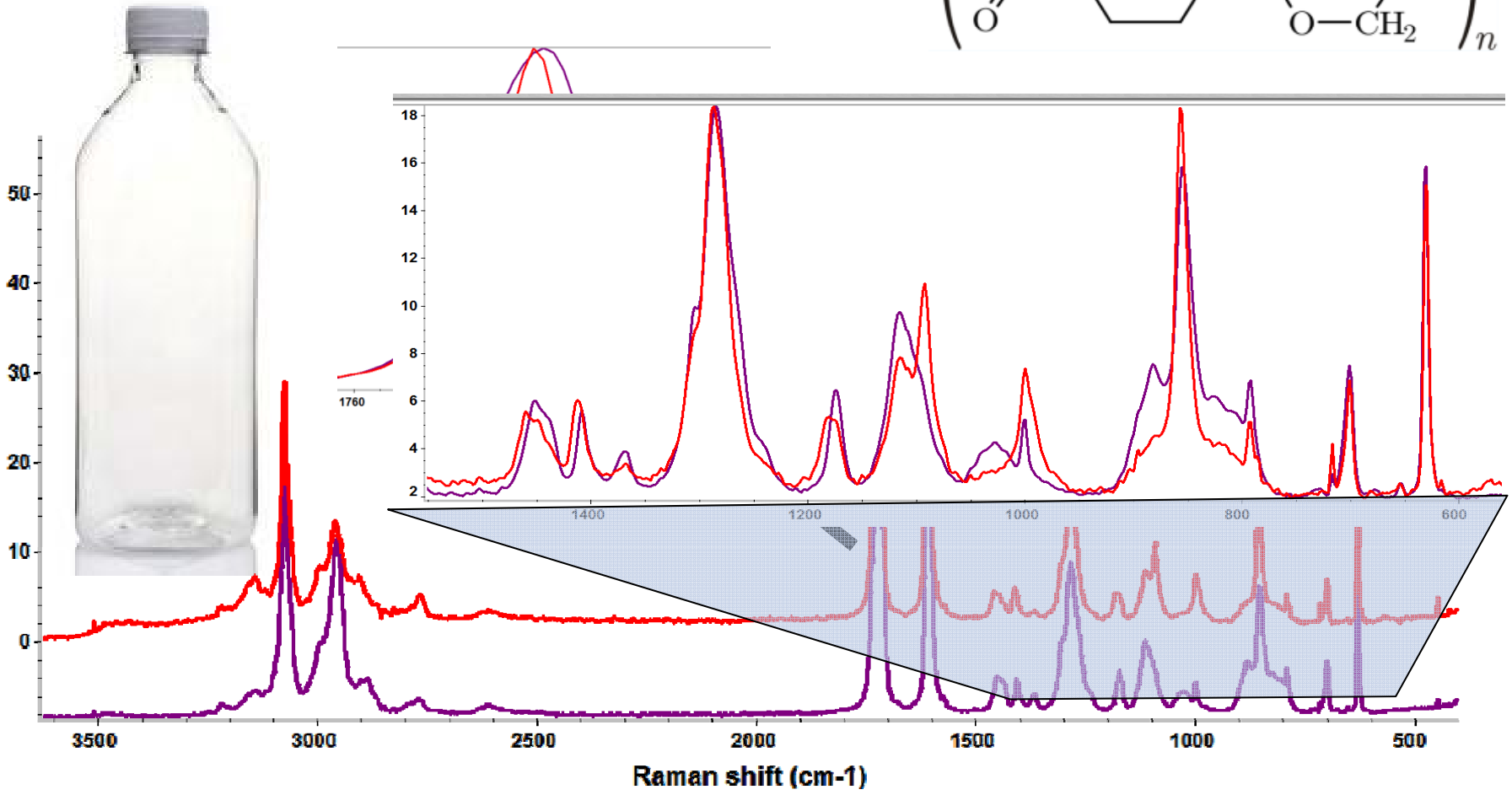
- Thick walled blanks are heated and blown into a mold
- The PET molecules in the sides of the bottle become stretched and linearly aligned



Polymer Orientation Studies (Raman)

Bottle side: Crystalline (PET)
Bottle Top: Amorphous (PET)





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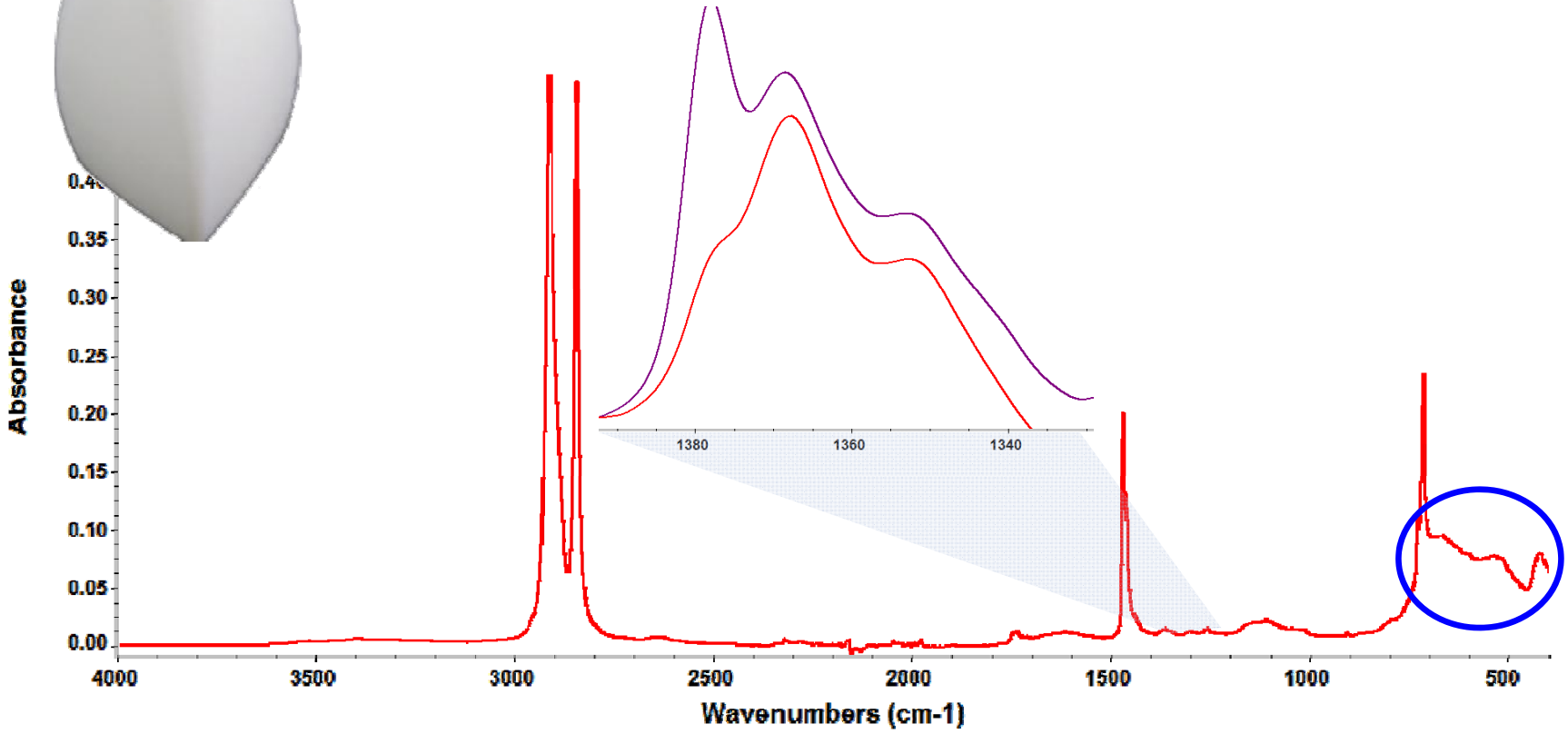
Raman complements FT-IR

- Mid infrared ATR
  - …high density polyethylene, with “inorganic filler”



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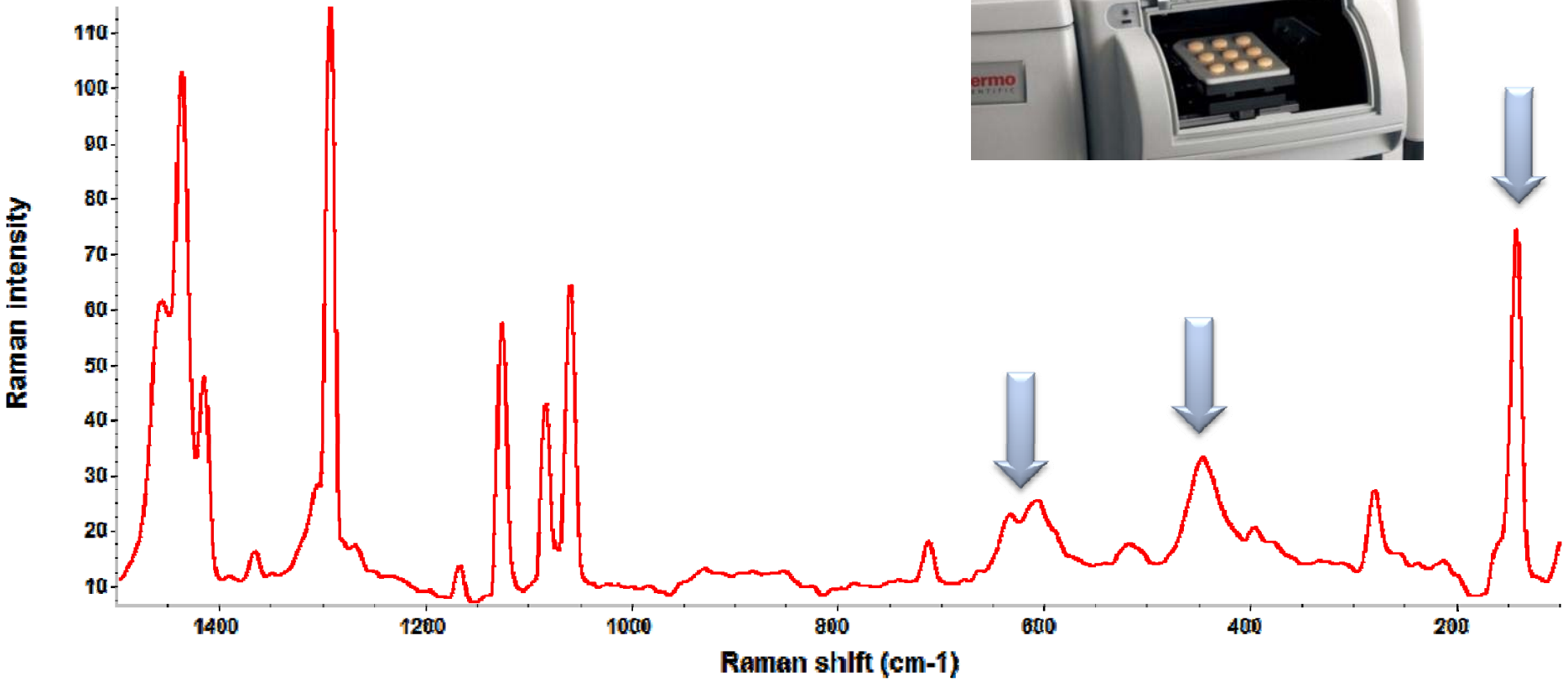
Raman complements FT-IR

- Same sample in Raman module
  - Unique peaks show information on additives
  - Data combined with FT-IR gives a more complete picture of the material



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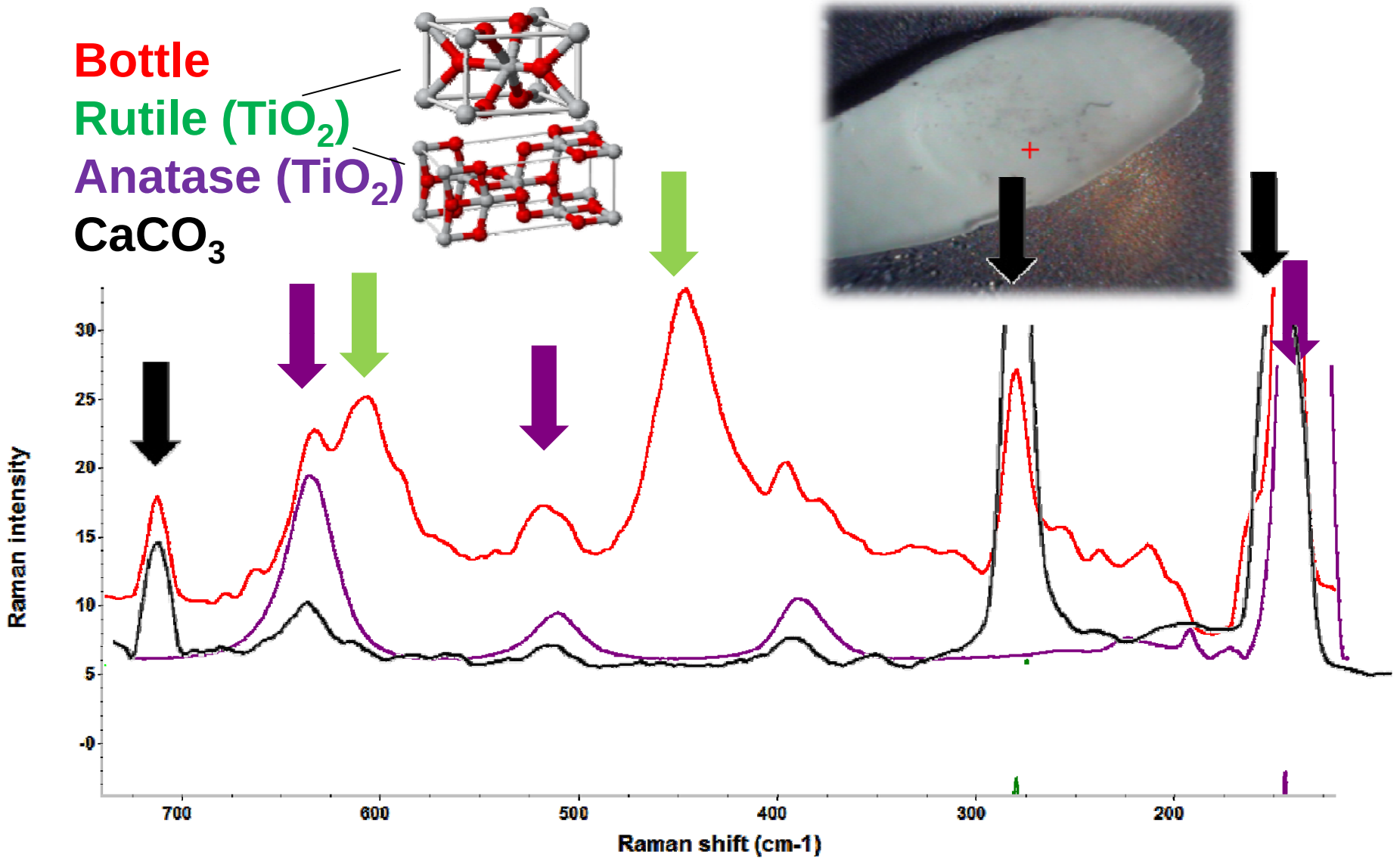
Raman complements FT-IR



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Nicolet iS50 NIR Dedicated Module

Method Development Tool

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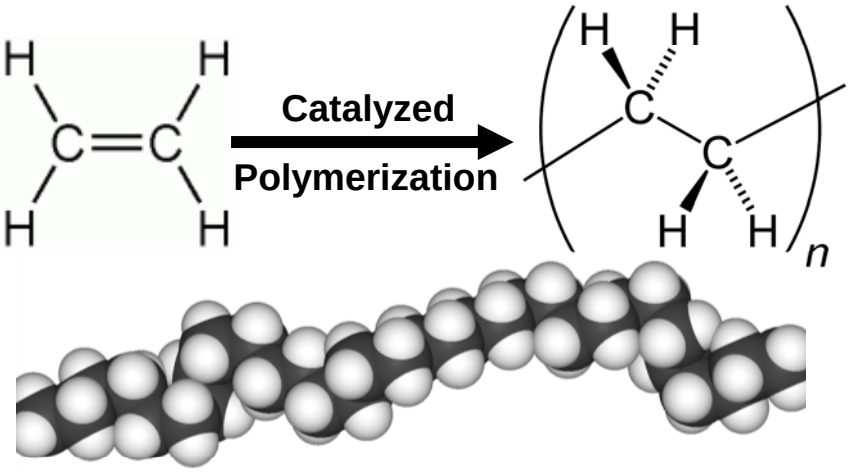
NIR for Raw Material Identification

Polyethylene is often classified according to density, which in turn depends on numbers and size of side branches.

- Linear Low Density (LLDPE)
  - •Large numbers of short branches
  - • 0.915 – 0.925 g/cm^3
- Medium density (MDPE)
  - •0.926 – 0.940 g/cm^3
- High density (HDPE)
  - •Very few branches
  - • greater than 0.941 g/cm^3



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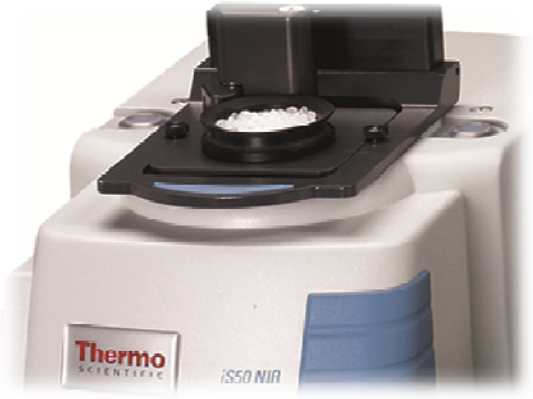
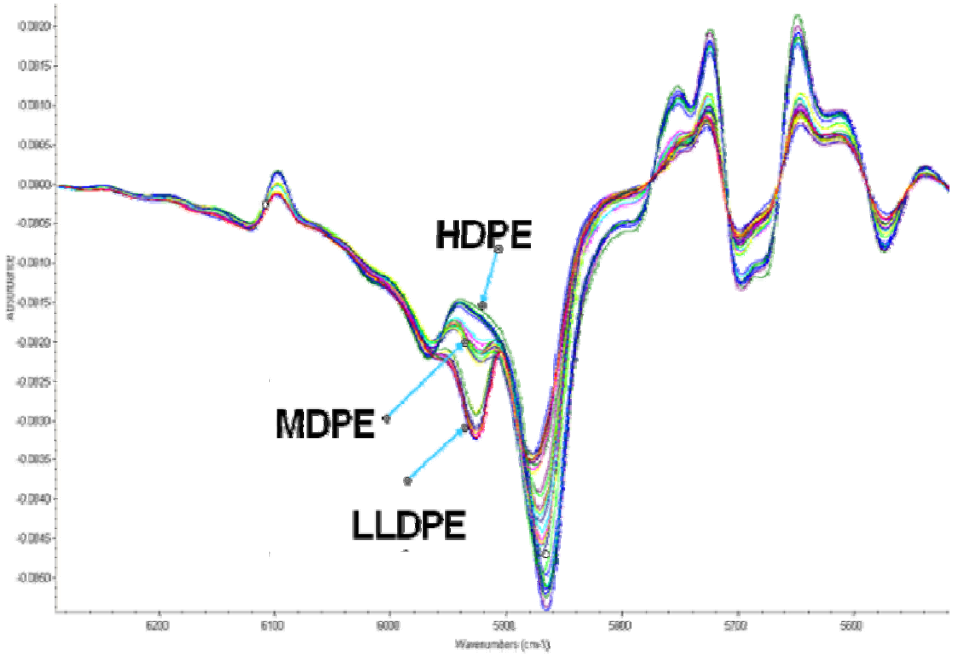
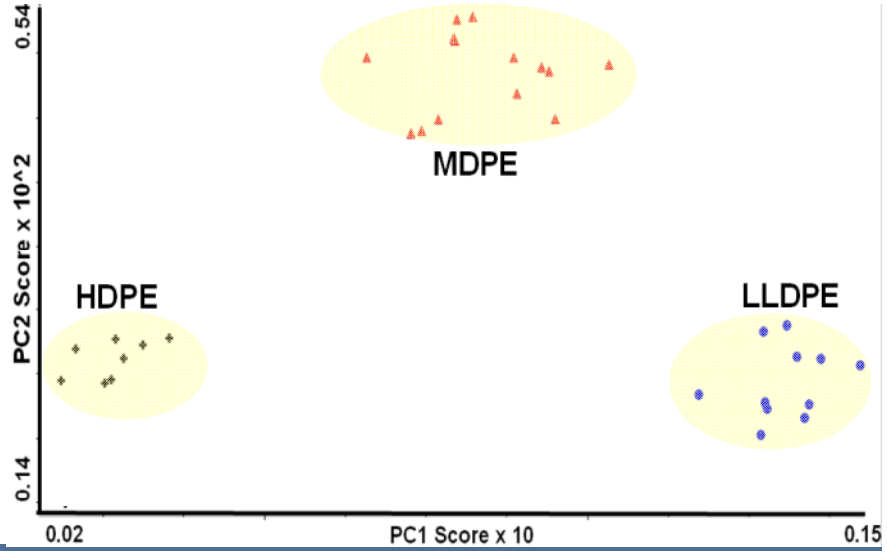
NIR for Raw Material Identification

- NIR used for chemometric method development
- No sample preparation required







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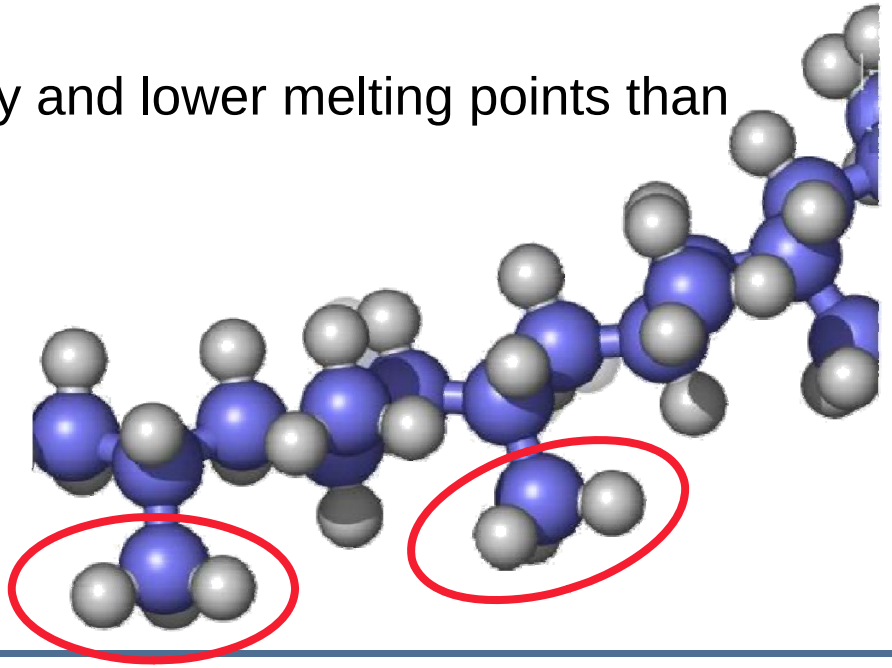
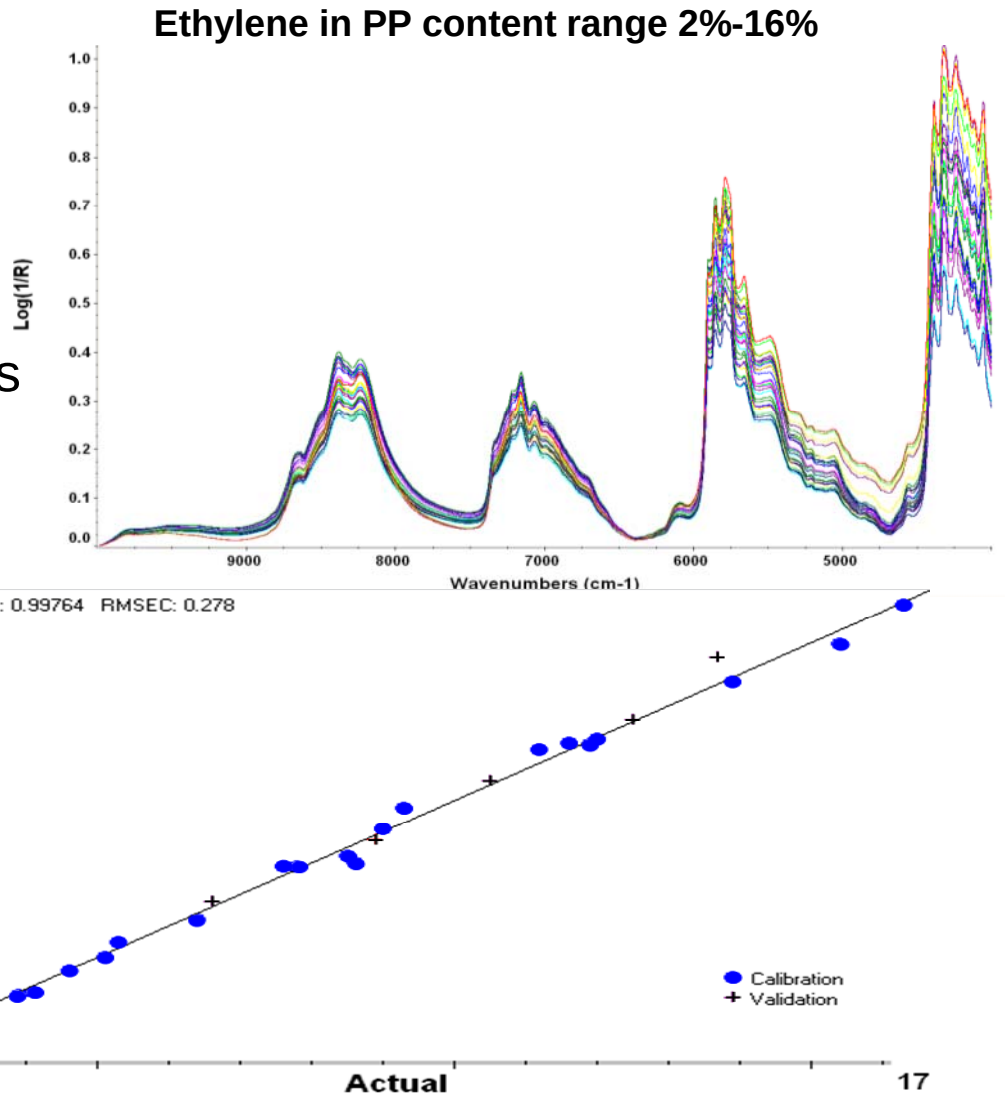
NIR for Raw Material Identification

- Ethylene/Polypropylene Copolymers
  - Ethylene may be added in various amounts to propylene to form copolymer material
  - These copolymer materials exhibit high stiffness and impact strength
  - Additionally they have better clarity and lower melting points than polypropylene alone.



NIR for Raw Material Identification

- Quantitative results based on analyzing standard materials
- Method deployed into process plants using process instruments



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Nicolet iS50 TGA-IR

Identify residual solvent and decomposition products

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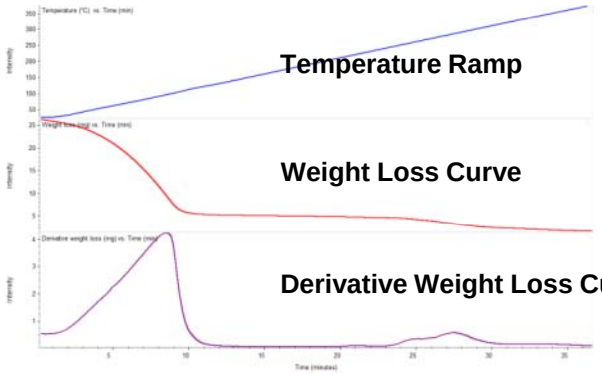
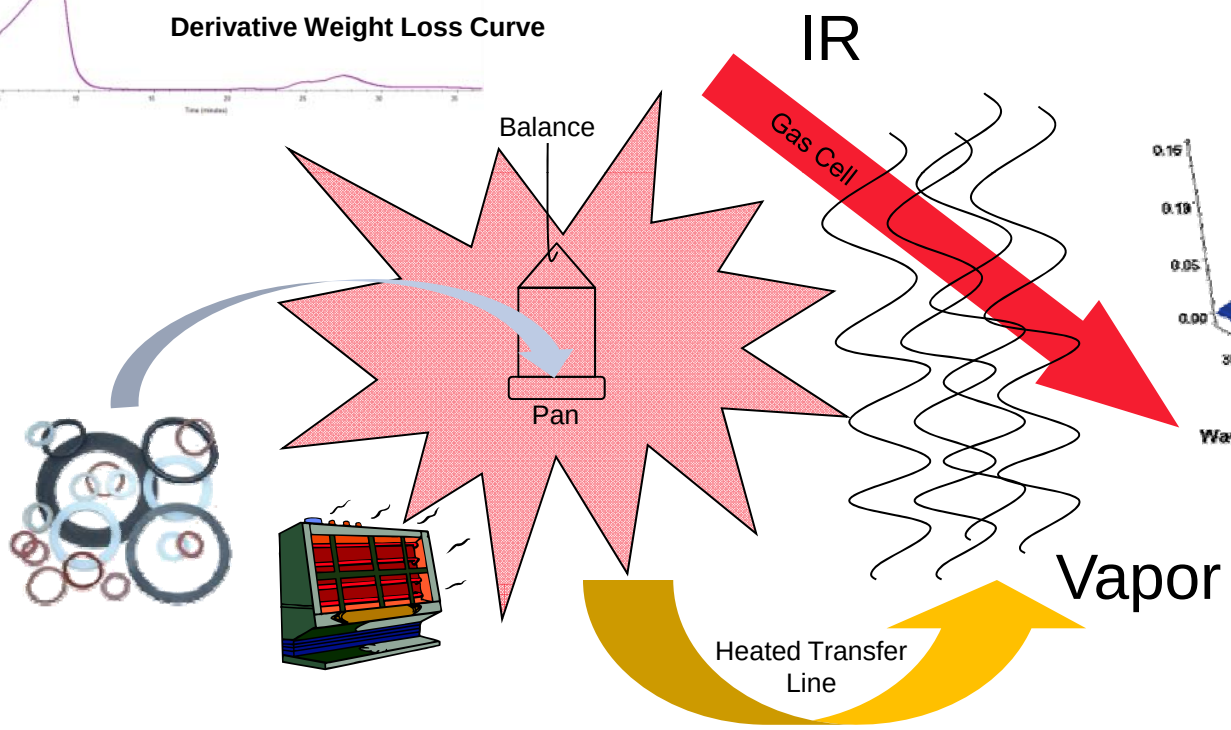
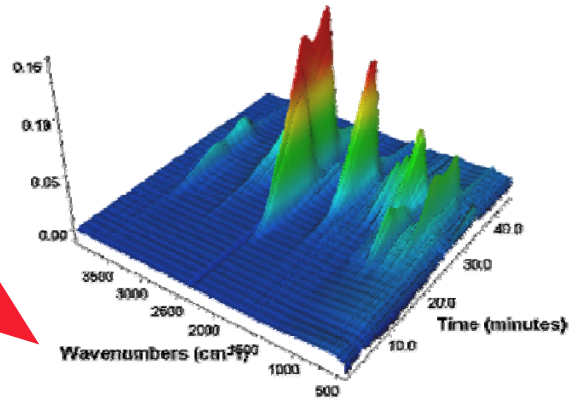
TGA-IR: The Basics







Infrared Series File

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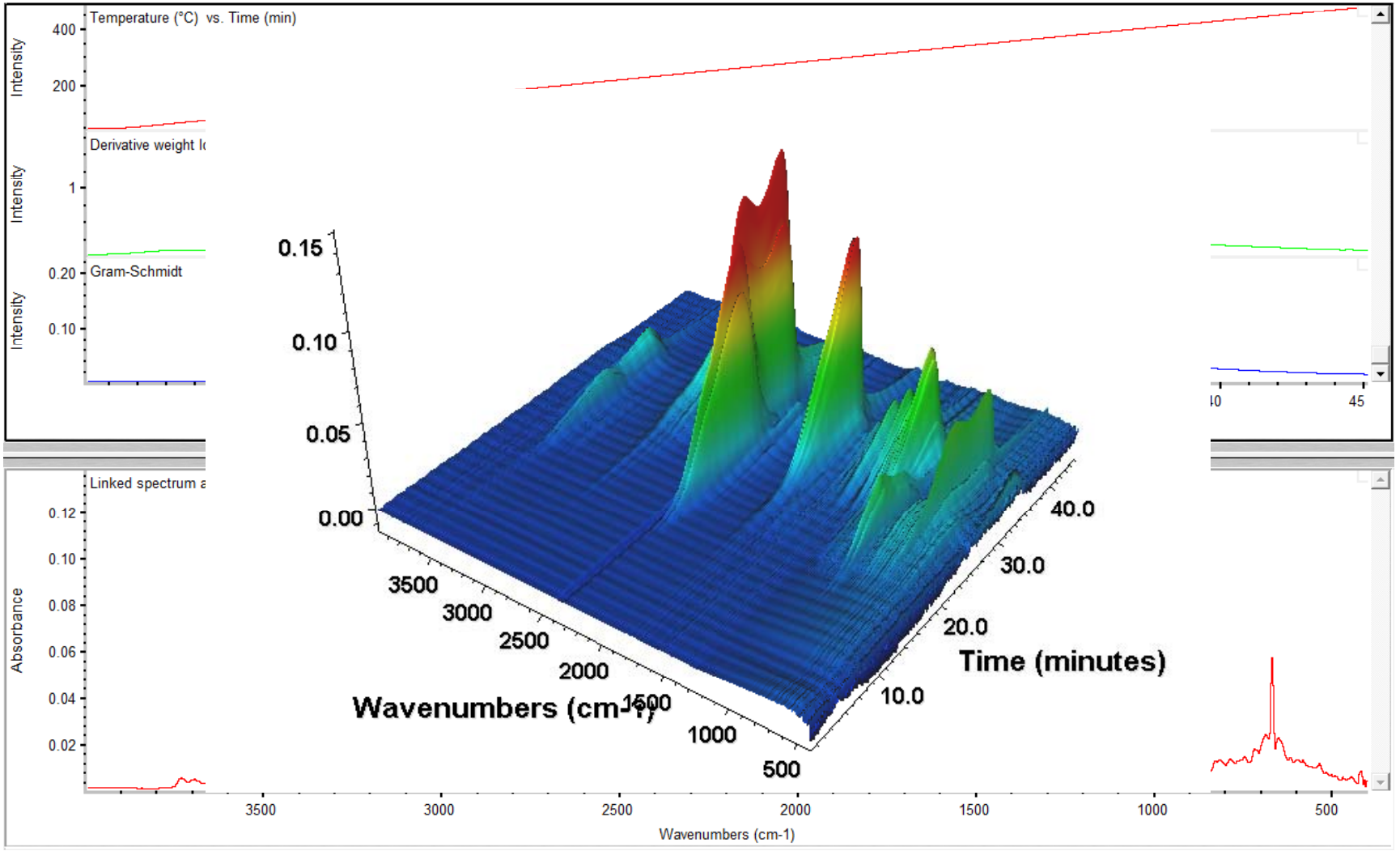
Deformulation

- Reverse Engineering
- Failure Analysis
- Material Analysis

- Polymers
  - Plastic
    - Fillers, formulation
    - Biopolymers
  - Rubber (!)
    - Carbon Black: O-Rings, Tires
- Epoxies, Resins, Adhesives
- Pharmaceuticals
    - Entrained solvents, breakdown products
- Fabrics, Paper products

TGA-IR: 3-D Data Sets



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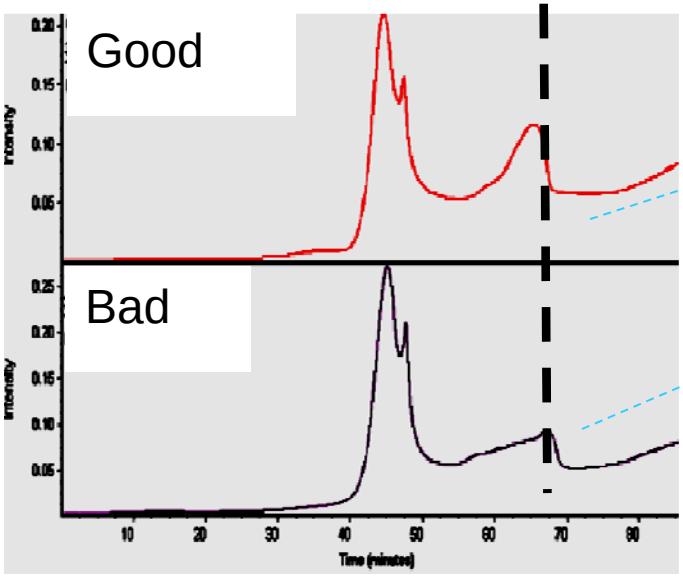
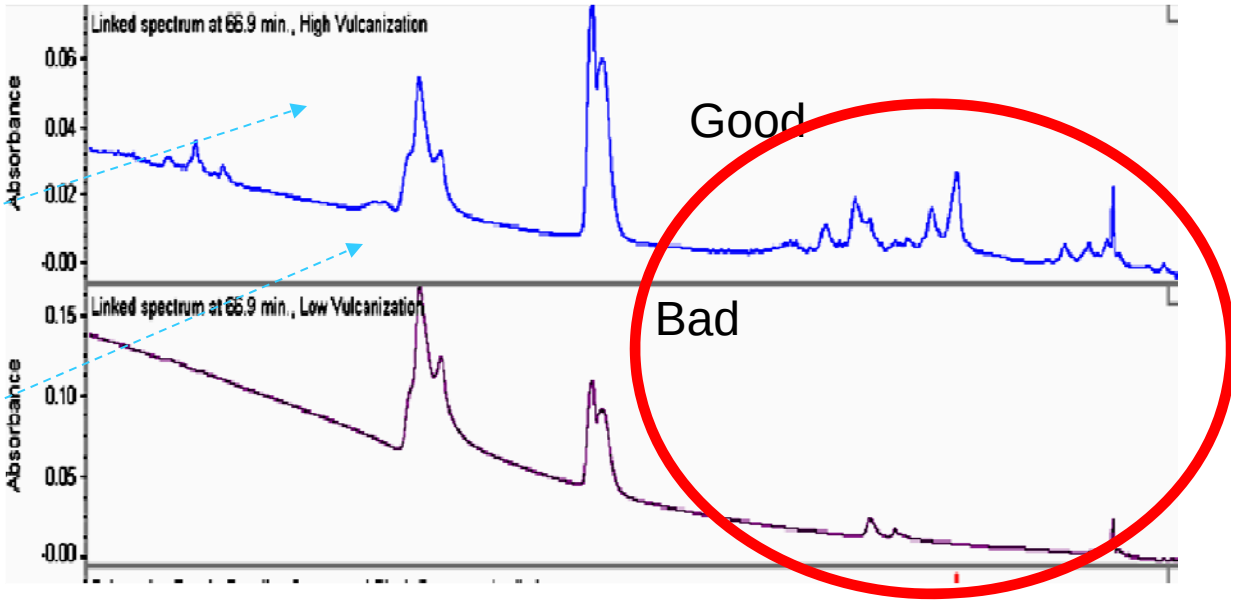
TGA IR

- Deformulation and Failure Analysis
  - Rubber gaskets were failing
  - TGA analysis shows incorrect formulation

TGA



IR of vapor at 67 min



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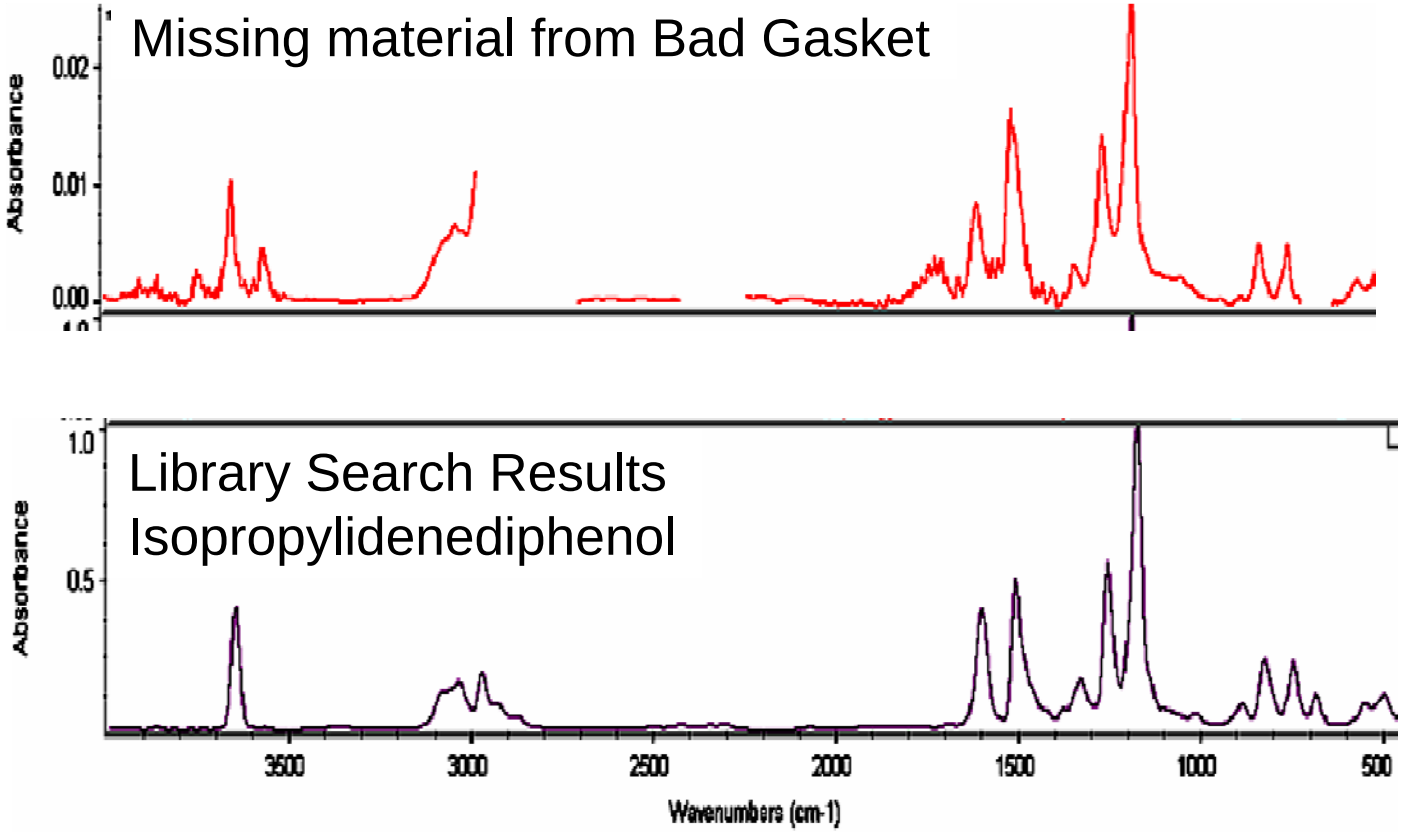
TGA IR

- Deformulation and Failure Analysis
  - Library search on the IR spectra
  - Missing ingredient: Bisphenol A



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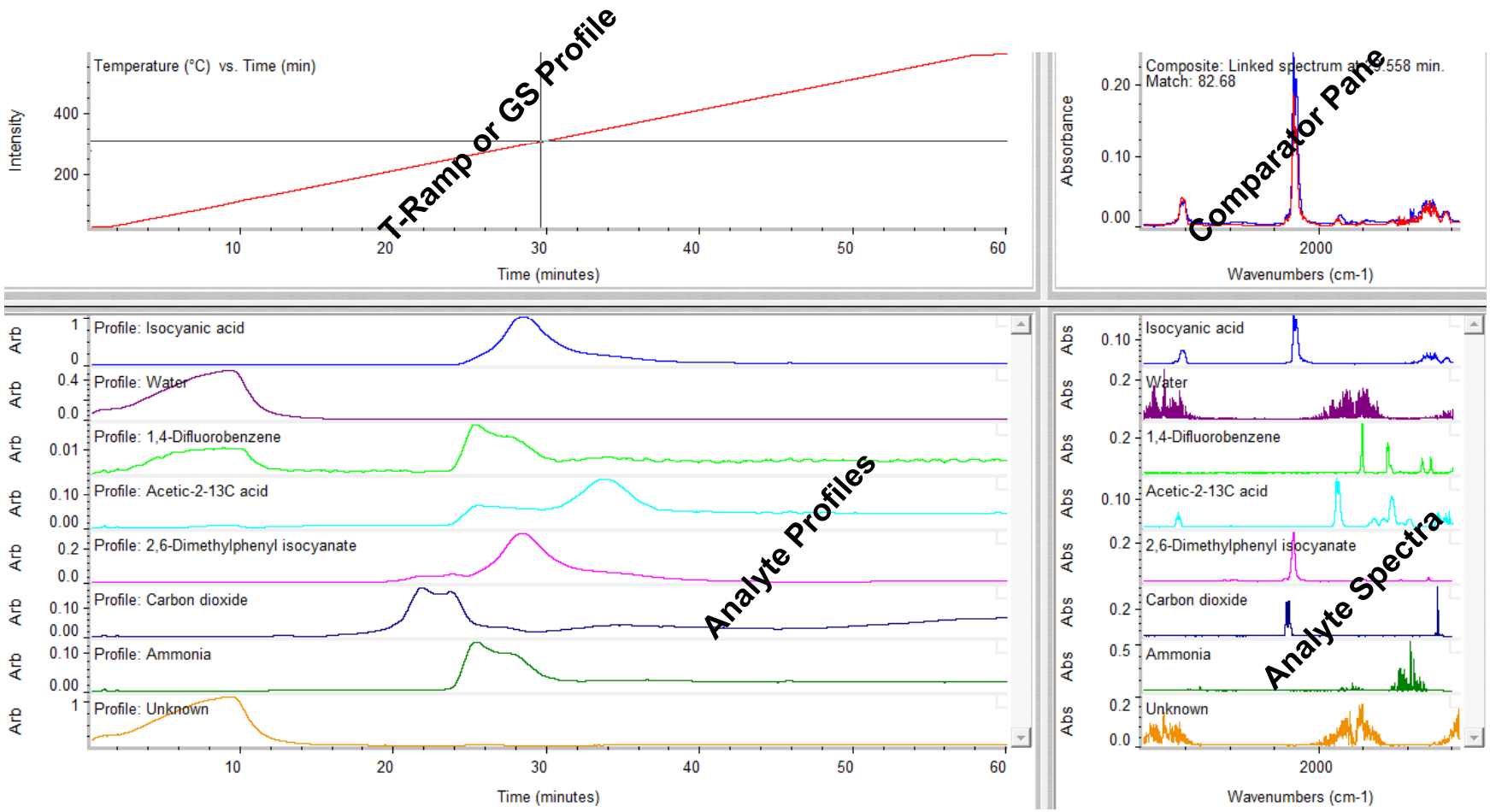
Complete Analysis: Mercury TGA



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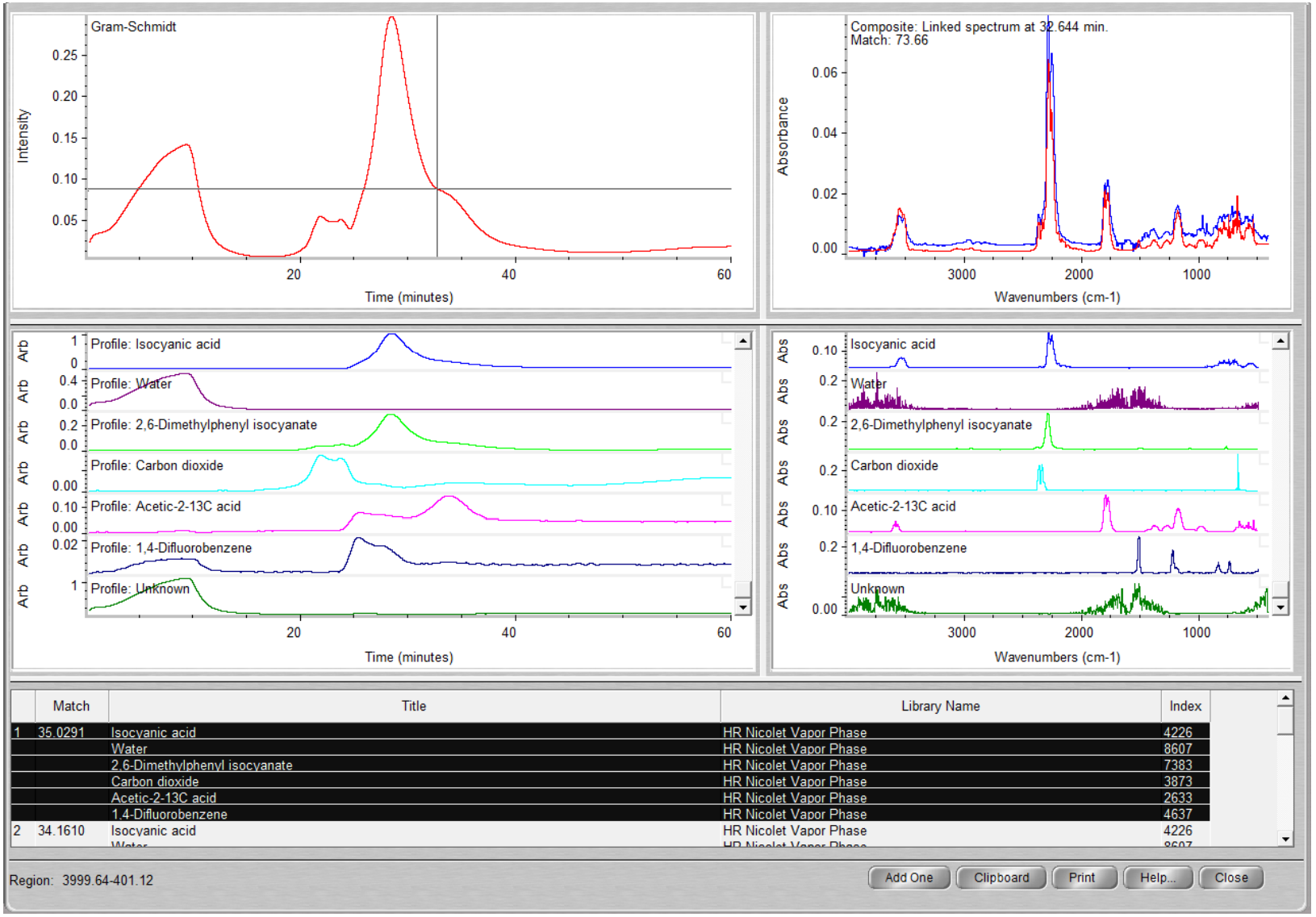
How Many Components?



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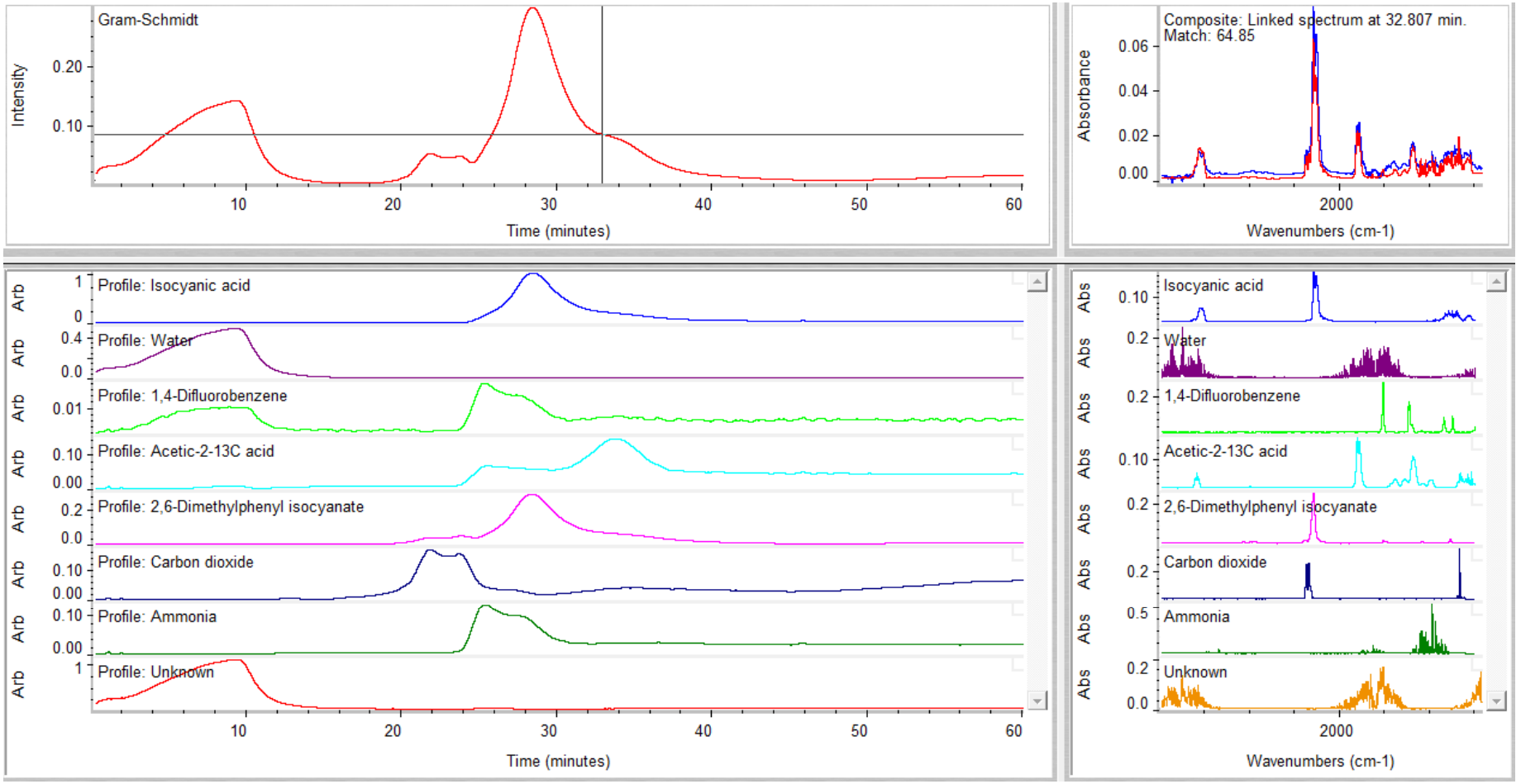
Full Deformulation: 7 Components



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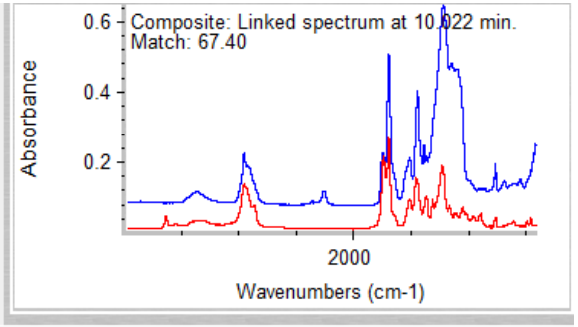
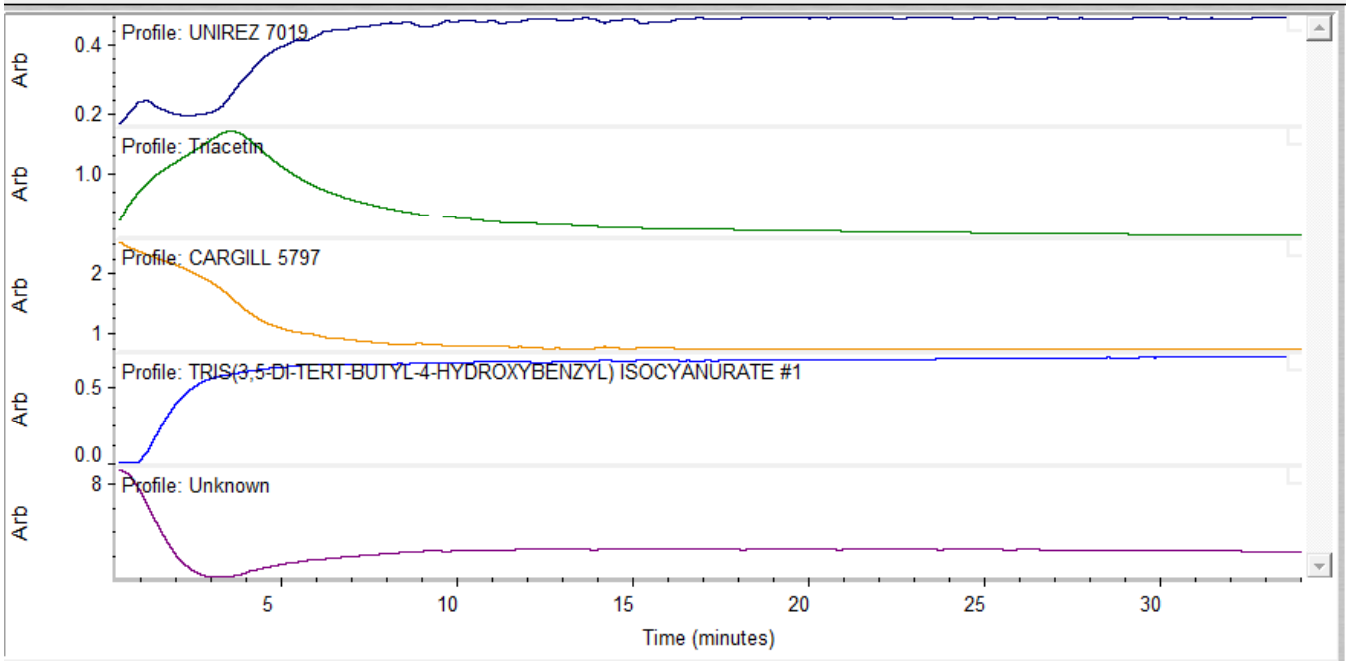
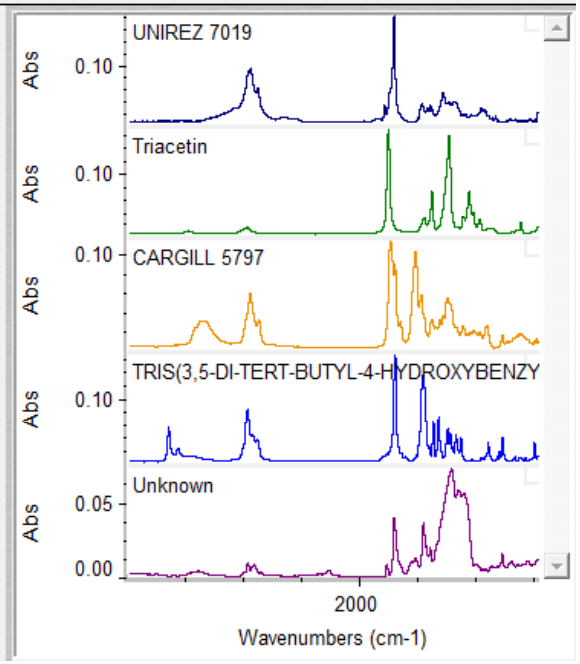
Mercury TGA Also Works for Kinetics!

- Reaction of urethane







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FT-IR to Get Your Job Done

- Bulk Polymer / Copolymer Analysis
- Inorganic fillers
- Crystallinity
- Raw Materials Method Development
- Deformulation

Upcoming Events

Trade Shows

- ANTEC, Booth #523
  Cincinnati, OH, April 22-24
  - Attend our live, on-booth presentations:
    - "Bringing More to the Material Characterization Party – Coupling Raman and IR"
    - "Taking a Good Look Inside – IR Deformulation Studies"
    - "Putting it Out There - On-line IR Analysis"
    - "Characterizing Multi-Layer Materials – IR and Raman Microscopy"
    - "A New Angle on Rheology – Simultaneous FT-IR and Rheometry"
    - "The Right Stuff – Extrusion and Polymer Processing"
    - "What went wrong – Failure Analysis" *special guest speaker, Jeff Jansen, the Madison Group*

- ChinaPlas, Guangzhou, PR China, May 20 – 23
- Nordic Polymer Days, Helsinki, Finland, May 29-31
- K-Show International Trade Fair for Plastics and Rubbers, Dusseldorf, Germany, October 16 – 23

See other webinar offerings for FT-IR, Near-Infrared, Raman or UV-Vis at www.thermoscientific.com/spectroscopywebinars

- **To contact our presenter, please email him at mike.bradley@thermofisher.com**