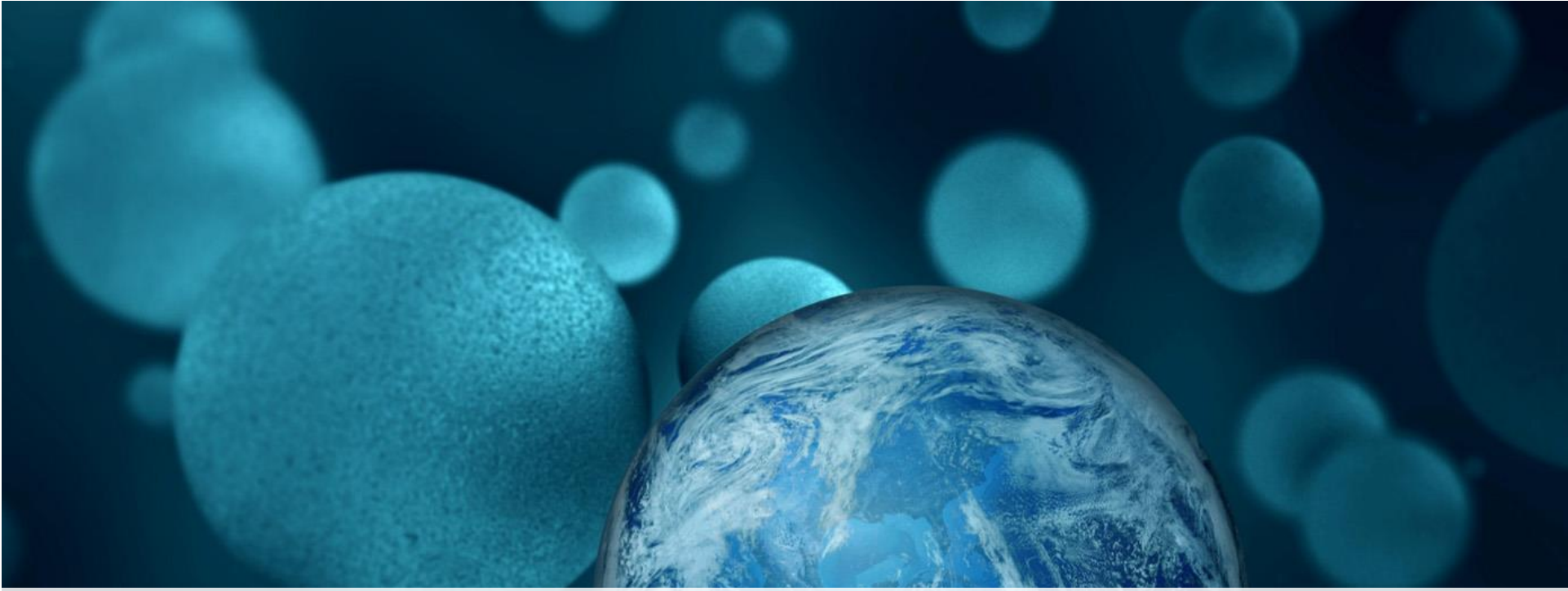

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Contamination Analysis and Identification by Vibrational Spectroscopy

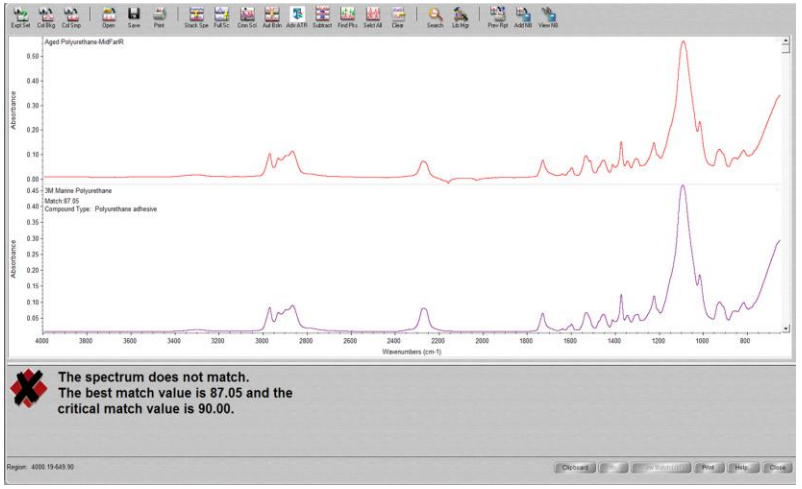
Matt Bartucci

2017 NASA Contamination, Coatings, Materials, and Planetary Protection Workshop
NASA Goddard Space Flight Center

Deformulation and Contamination Analysis via FTIR

- Reverse Engineering
- Failure Analysis
- Material Analysis

- Polymers
  - Plastics
    - Fillers
    - Rubbers (!)
    - Carbon Black: O-Rings



- Epoxies, Resins, Adhesives

- Excellent 1st approach technique

Overview

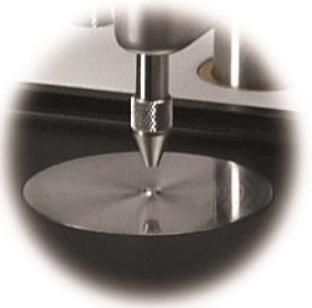
- **ATR-IR**
  - Contamination analysis of organic and inorganic materials
  - Reverse engineering of heat shrink tubing

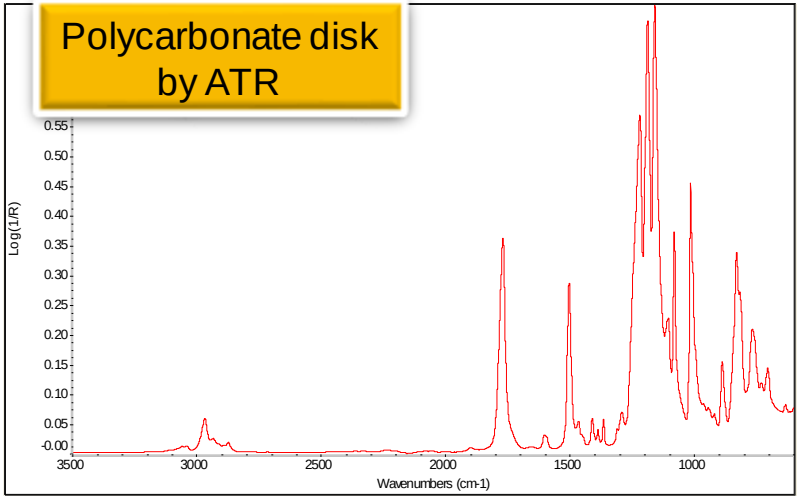
- **TGA-IR**
  - Failure analysis of o-rings

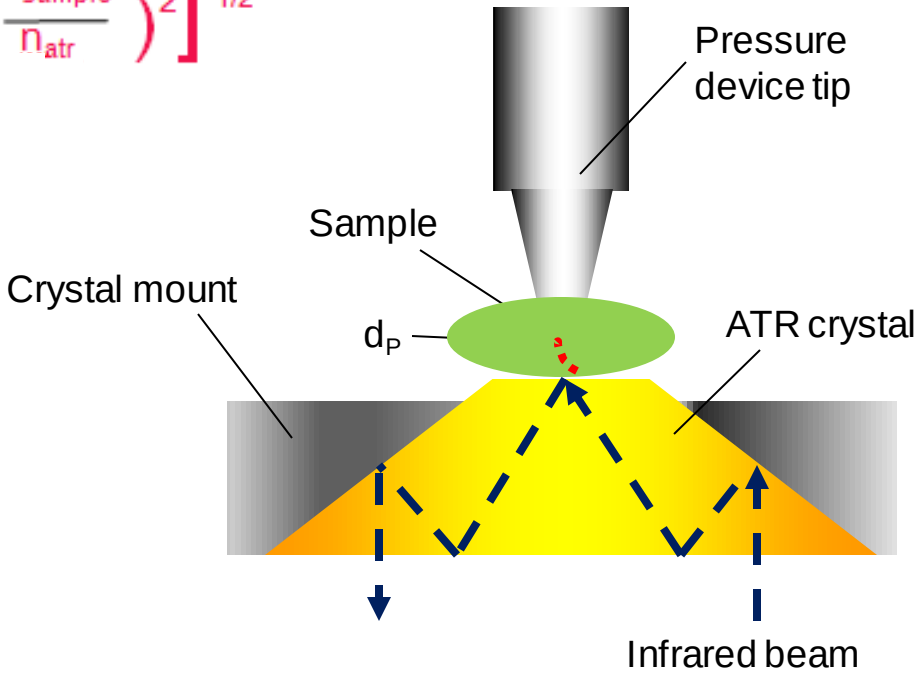
Basics: Depth of Penetration

- Attenuation occurs by sample absorption: A=εlc
- The Evanescent wave probes short distance (~1-2 micron)
  - Measures surface & near-surface only
  - Path Length 'l' characterized by depth of penetration

$$d_p = \frac{\lambda}{2\pi\, n_{atr} \left[(\sin^2\theta) - \left(\frac{n_{sample}}{n_{atr}} \right)^2 \right]^{1/2}}$$







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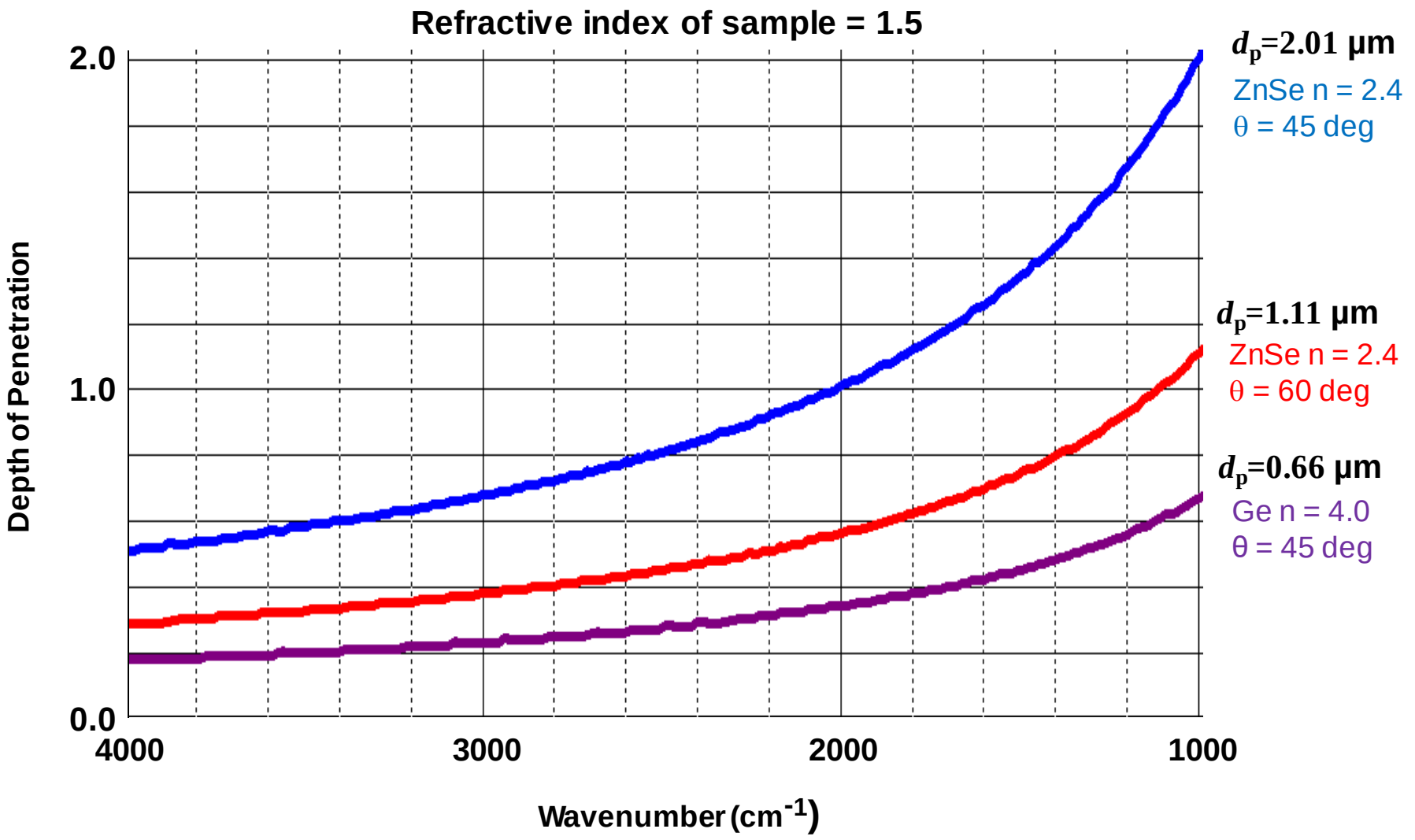
Depth of Penetration with Wavelength



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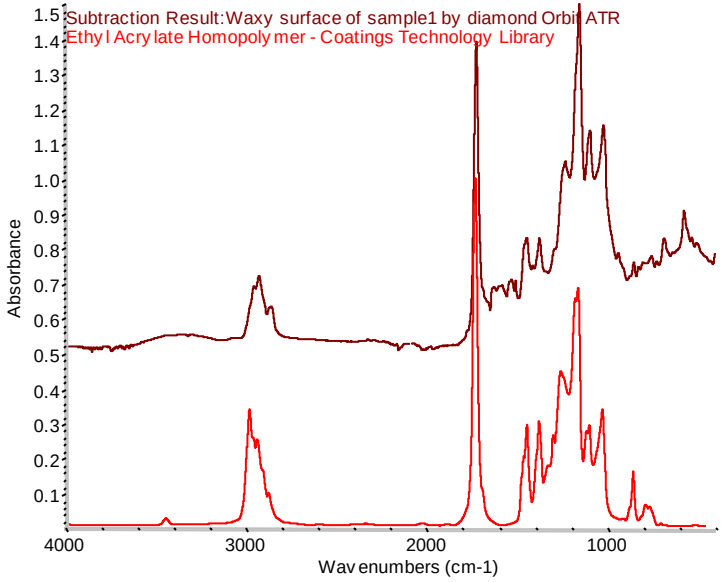
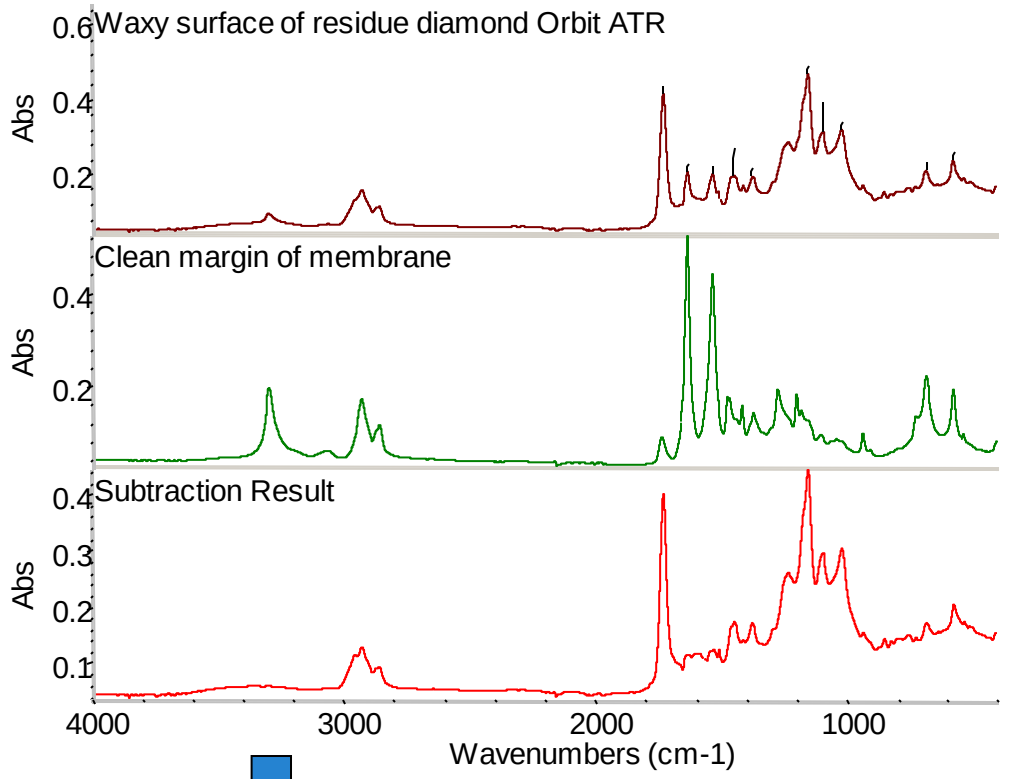
Failure Analysis via ATR

- Residue collected on filter membrane
- Analyzed by direct contact with Diamond ATR
  - Membrane + residue
  - Subtract membrane
  - Search





Ethyl Acrylate Homopolymer
Coatings Technology Library

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Inorganic Residue on Turbine

Small clump
~ 1 mm

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Heat Shrink Tubing

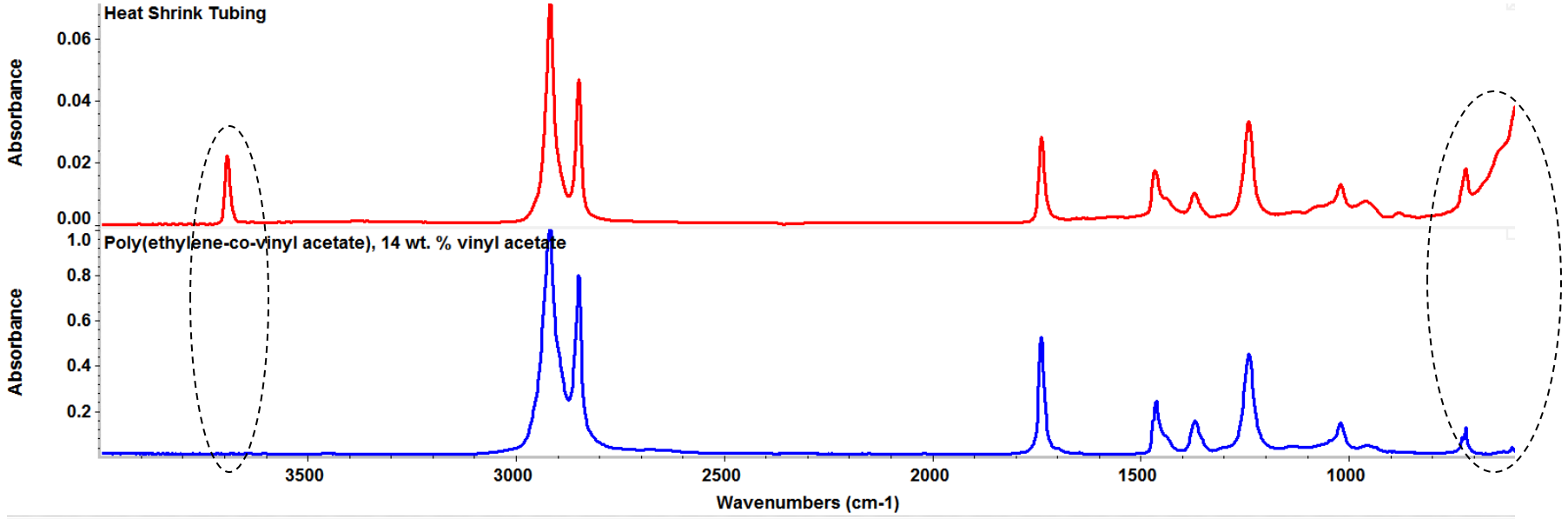
- Attempt to chemically identify and reverse engineer heat shrink tubing
  - Gardner Bender Polyolefin (HST-250)

- Since tubing appears to have a high loading of carbon black, analyze via germanium ATR as it has a lower depth of penetration

Initial Identification of Tubing

- Polyolefin tubing (red) library search result (blue) has strong match value
  - Polymer tubing C-H & C=O stretches appear to be highly correlated

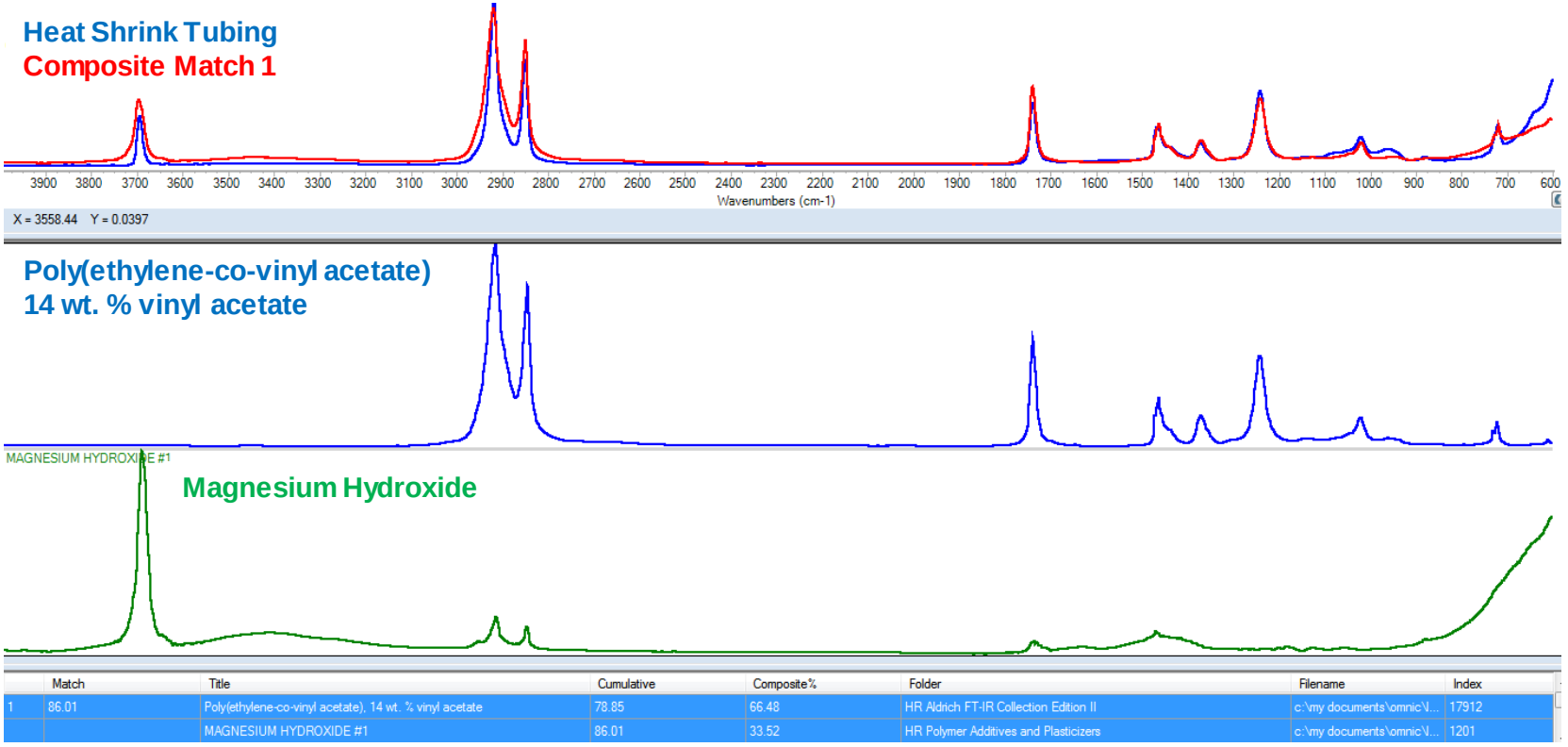
- 3700 cm^{-1} stretch and low wavenumber region do not match well



	Index	Match	Compound Name	Library Name
1	17912	91.07	Poly(ethylene-co-vinyl acetate), 14 wt. % vinyl acetate	HR Aldrich FT-IR Collection Edition II
2	218	91.07	POLY(ETHYLENE-CO-VINYL ACETATE), 14 WT. % VINYL ACETATE	HR Aldrich Polymers
3	232	89.68	ELVAX 360	HR Industrial Coatings
4	119	89.58	ELVAX 420	HR Industrial Coatings

OMNIC Specta Shows Multicomponent Match

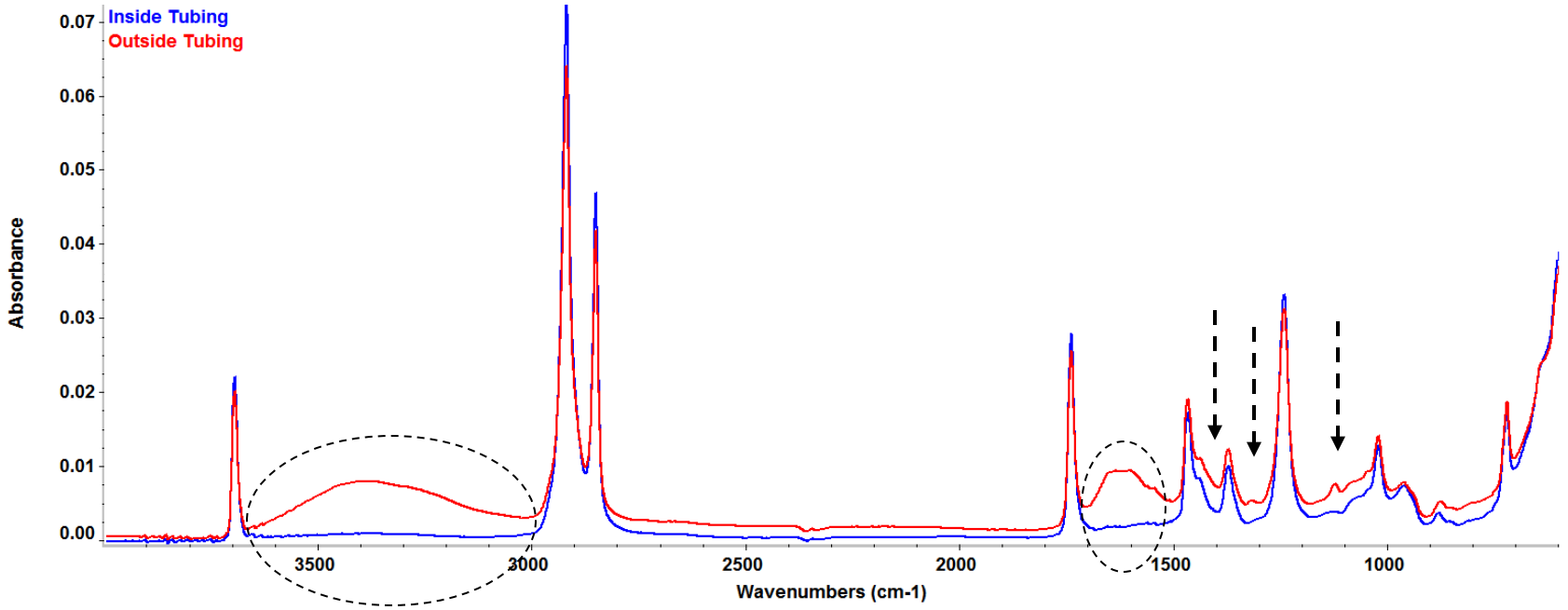
- Peak at 3700 cm^{-1} and low wavenumber tail appears to be from an inorganic filler - magnesium hydroxide
  - MgOH is used as a flame retardant



Outer Tubing

- Spectral changes from inner tubing is different from outside of the tubing

- Why would outside tubing have another chemical coating?
  - What is coating? And what is its purpose?



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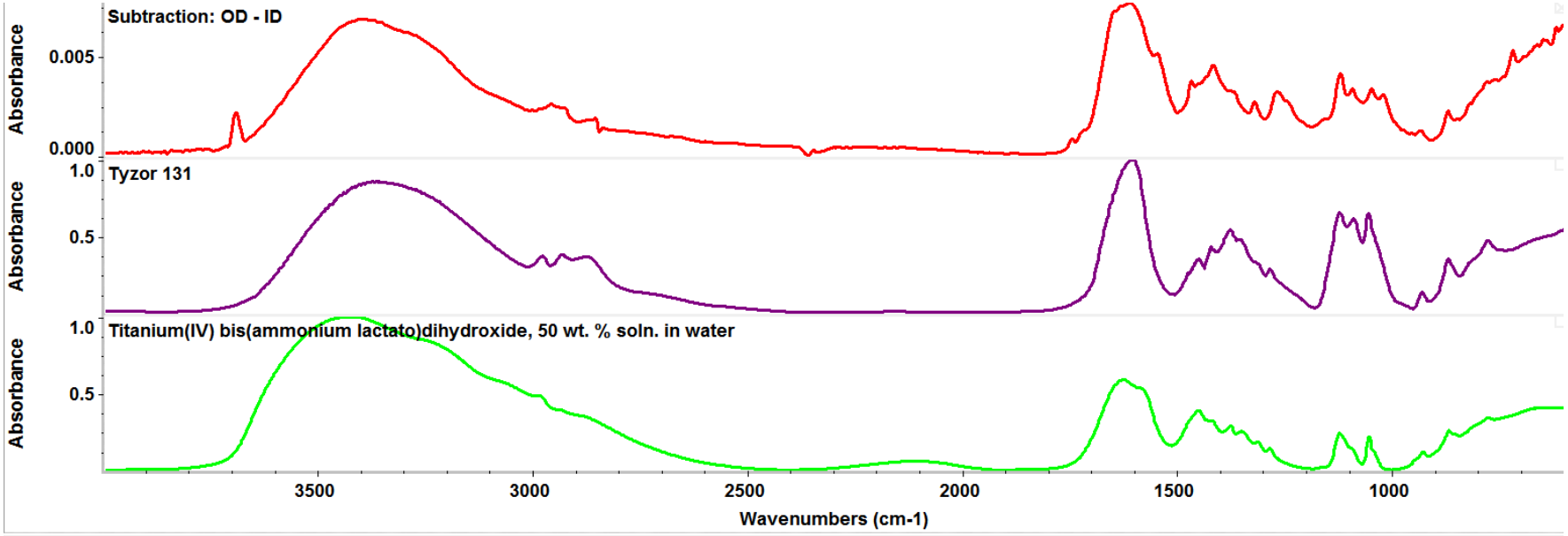
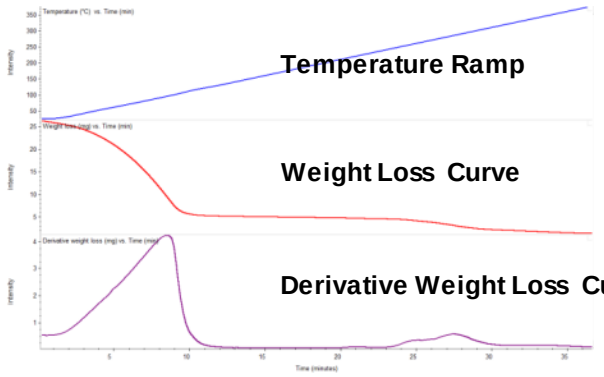
Identification of OD Coating

- Library search of outside coating shows match for Tyzor 131
  - Organic titanium complex made by DuPont as a cross-linking agent
- As polyolefin tube is heated – Tyzor 131 enhances crosslinking causing tube to shrink



	Index	Match	Compound Name	Library Name
1	1671	59.90	Tyzor 131	HR Coatings Technology
2	17487	51.77	Titanium(IV) bis(ammonium lactato)dihydroxide, 50 wt. % soln	HR Aldrich FT-IR Collection Edition II
3	548	47.83	METHYL ALKYL IMIDAZOLINE SODIUM SALT	HR Polymer Additives and Plasticizers
4	573	47.28	Poly(terephthaloyl oxamidrazone)+SrCO3	HR Hummel Polymer and Additives

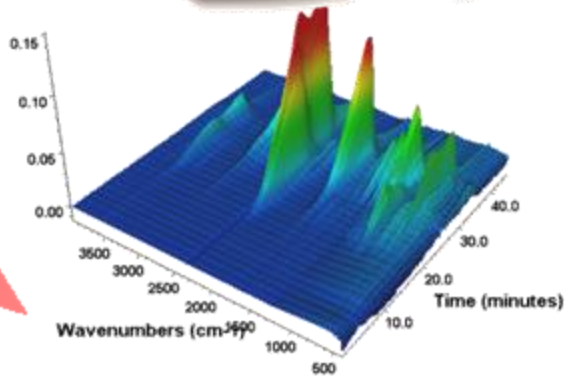
TGA-IR: The Basics



IR

Balance

Gas Cell



Infrared Series File

Pan

Vapor

Heated Transfer Line

Quantitative: T “G” A

Qualitative: FT-IR

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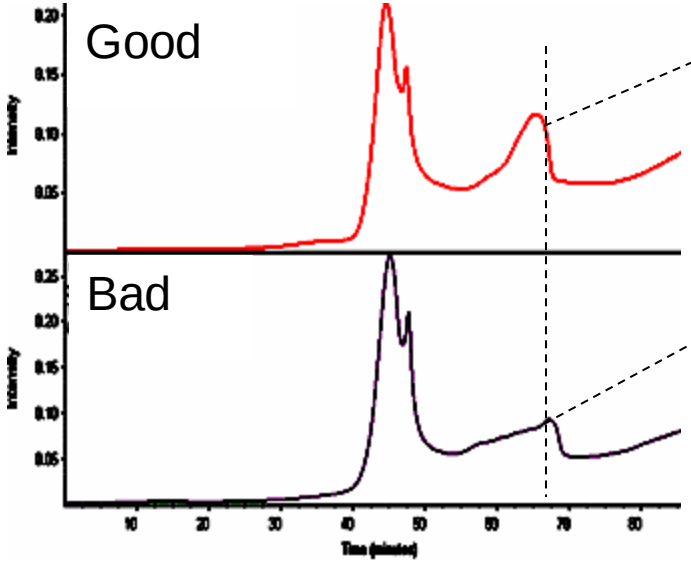
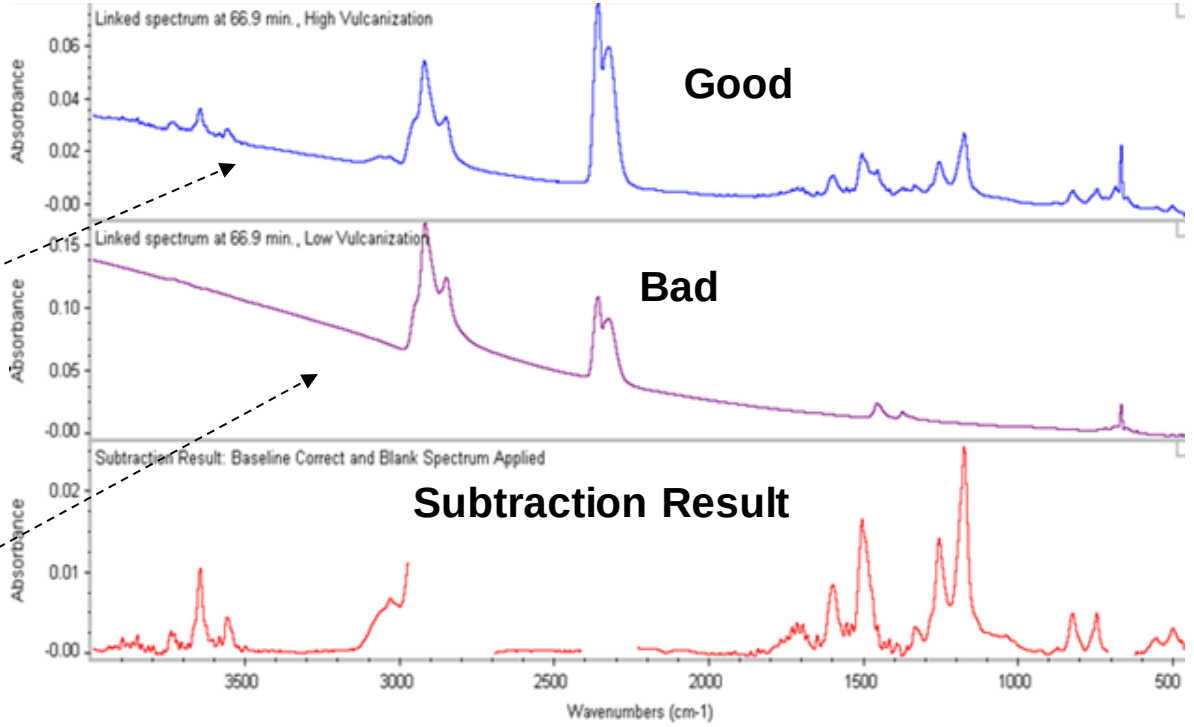
TGA-IR

- Deformulation and Failure Analysis
  - Rubber gaskets were found to be failing in the field
  - TGA analysis of failing gaskets shows incorrect formulation
  - Subtraction result shows chemical differences

Gram-Schmidt Plot



IR of vapor at 67 min



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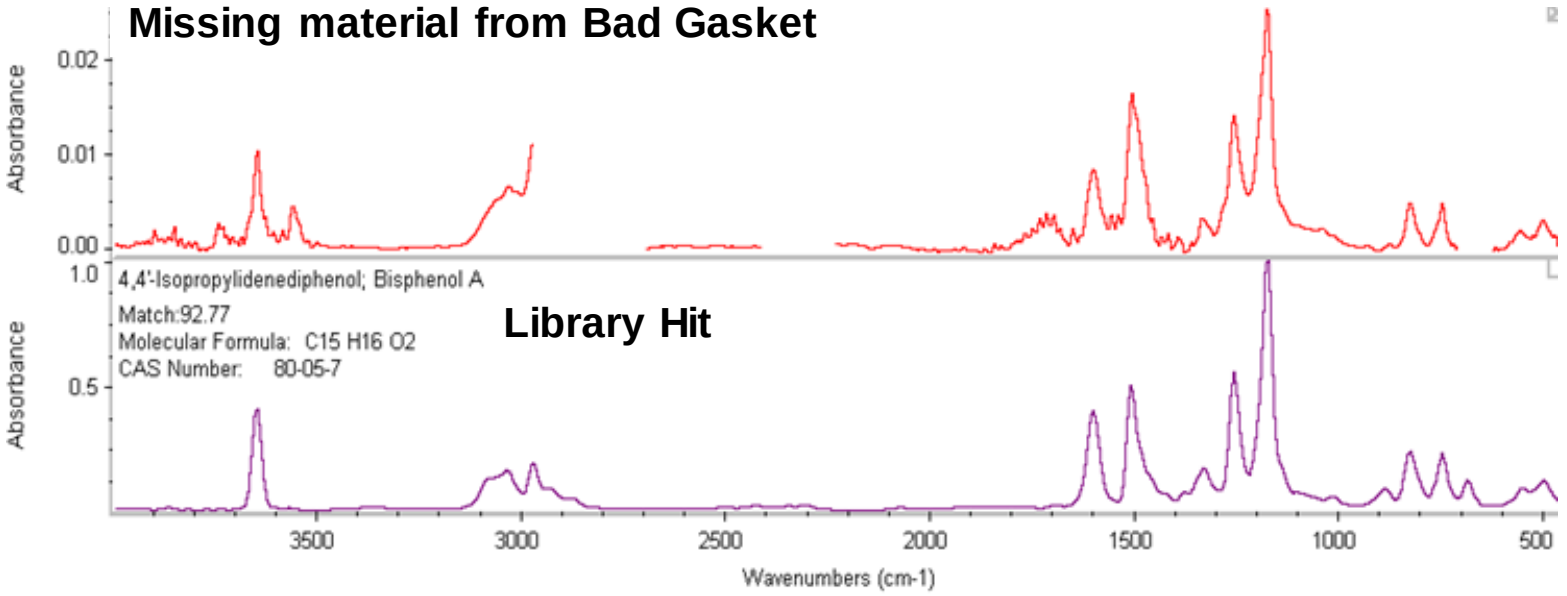
TGA-IR

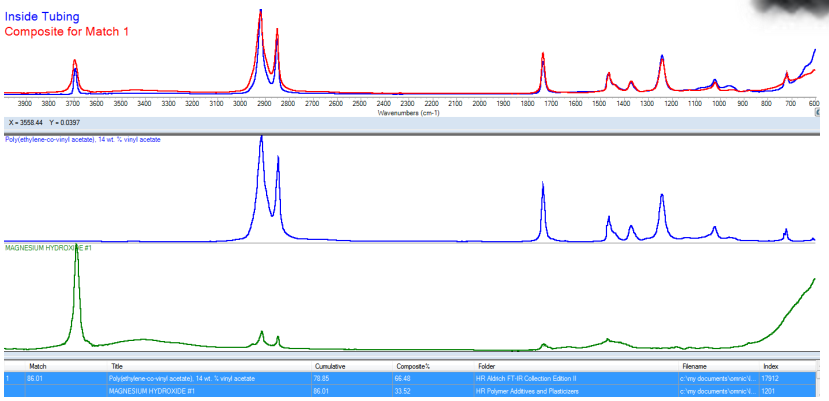
- Bad gasket does is missing bisphenol A
  - Chemical information to support early failure in field
- TGA coupled with IR allows for chemical evidence of failure



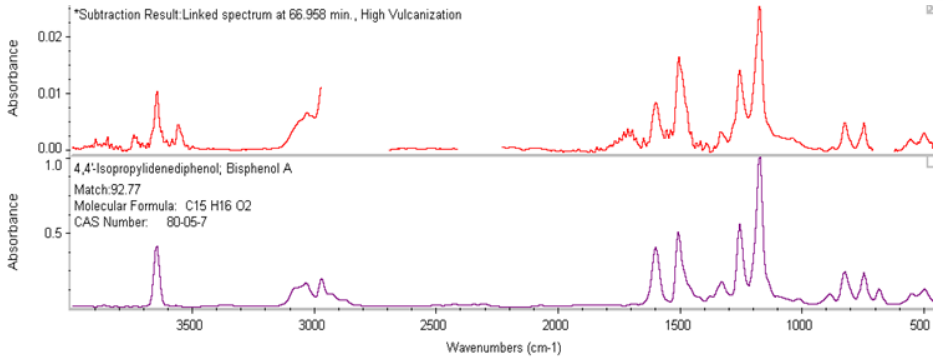
	Index	Match	Compound Name	Library Name
1	3269	92.77	4,4'-Isopropylidenediphenol; Bisphenol A	Nicolet/Aldrich Vapor Phase
2	28	87.20	4,4'-Isopropylidenediphenol; Bisphenol A	Hazardous Chemicals - Vapor Phase Spectra
3	5307	87.17	4,4'-Isopropylidenediphenol; Bisphenol A	Nicolet Vapor Phase
4	407	87.17	4,4'-Isopropylidenediphenol; Bisphenol A	Nicolet TGA Vapor Phase
5	5306	85.83	4-(2-Phenylisopropyl)phenol; 4-Cumylphenol	Nicolet Vapor Phase

Summary

- ATR was used to reverse engineer heat shrink tubing
  - Both organic and inorganic components were identified



- TGA-IR aided in understanding chemical failure
  - Chemical data coupled with physical data aids in understanding failure



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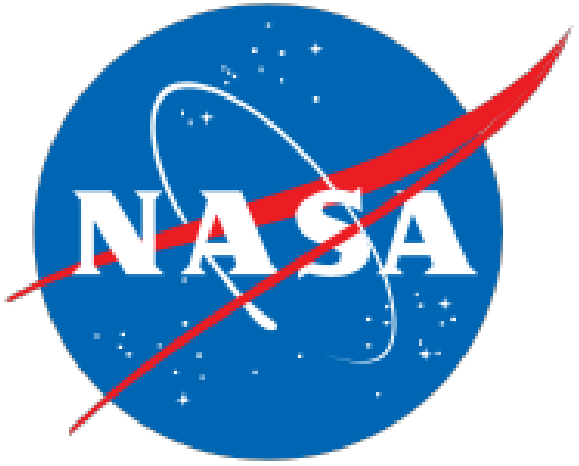
Thanks!



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Questions/Comments?