FTIR Microscopy & Imaging for Materials Analysis

Sample Preparation Free, Ultra High Spatial Resolution FTIR Microscopy & Chemical Imaging

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FTIR Spectroscopic Imaging: Applications in Polymer Research and Quality Control

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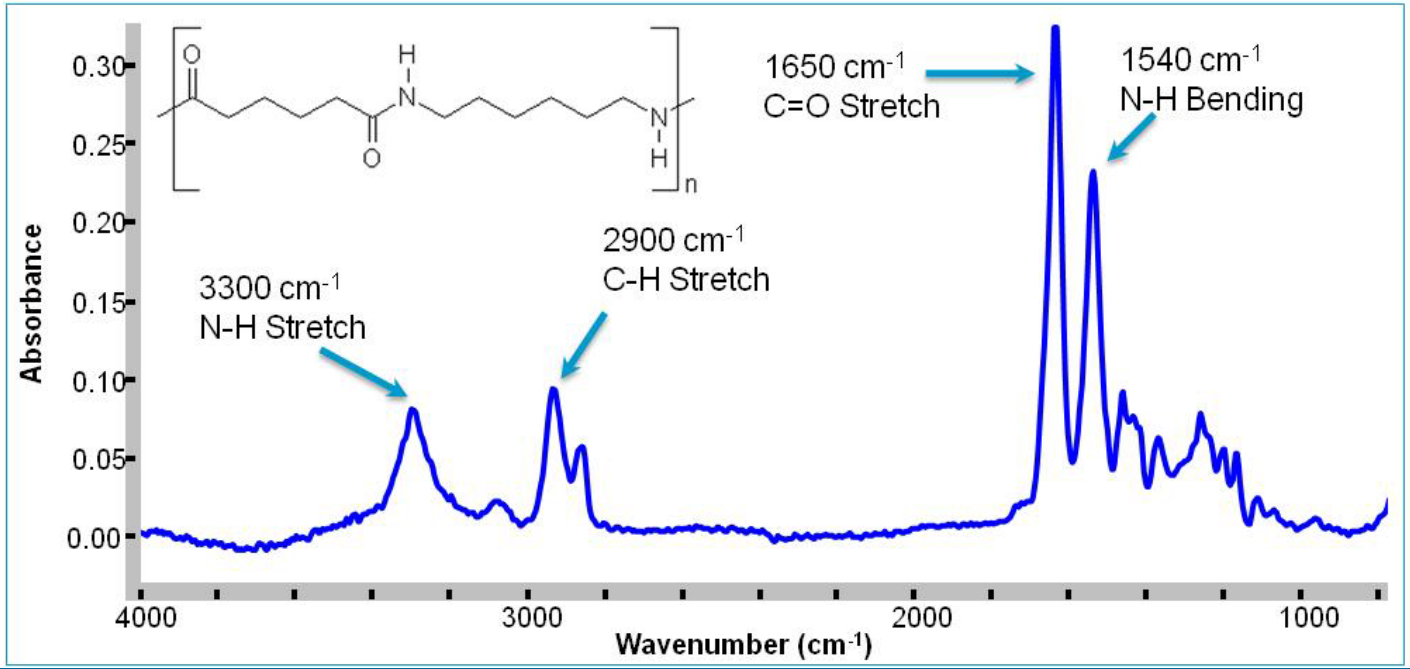
FTIR Spectroscopy - What is it?

- Fourier Transform InfraRed Spectroscopy is the study of the interaction of infrared light with matter.
- The vibrations of bonds between atoms in a molecule are excited by IR light leading to absorbances that are specific to chemical structure specific



FTIR Spectroscopy - Why should I use it?

- *VERSATILE* – Many different sample types & sizes including *SOLIDS*, *LIQUIDS* (organic & water based) & *GASES*
- Often requires very little or *NO SAMPLE PREPARATION* and can be *NON-DESTRUCTIVE*
- Can be *QUALITATIVE* and *QUANTITATIVE*
- *SIMPLE* to perform
- Incredibly *ACCURATE* results
- *FAST* - Results in *SECONDS* to *MINUTES*
- *AFFORDABLE* method

Challenges facing the polymer scientist…

- Troubleshooting production samples
  - Defects, contaminants, degradation etc...
- Reverse engineering competitor samples.
  - Identification of laminate layer and tie (adhesive) composition
- Future demands
  - Needing to measure smaller and smaller samples
  - Higher sample throughput demands
  - User becoming less expert spectroscopists, more routine users

Agilent Cary 600 Series FTIR Microscopes and Chemical Imaging

Simultaneous Chemical & Spatial Information

Why use an FTIR Microscope?

- An FTIR microscope has essentially two main purposes:

  1. To allow users to visually see small (micron) sized samples

  2. Collect accurate FTIR spectra from small samples

- FTIR microscopy can be performed in four data acquisition modes:

  1. Single point

  2. Single point mapping

  3. Linear array mapping

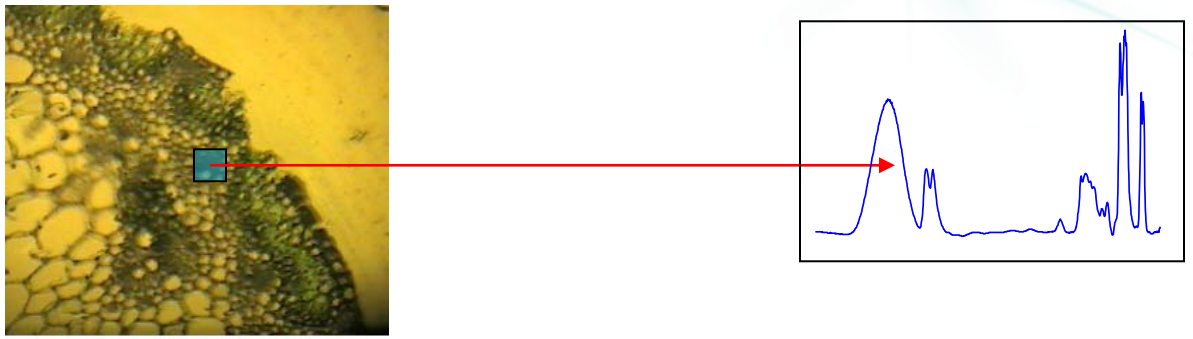
  4. 2-D Focal Plane Array imaging

- FTIR Imaging gives spatial (**WHERE**) and spectral (**WHAT**) information, and FTIR Chemical Imaging with a IR Focal Plane Array (FPA), gives this simultaneously

FTIR Microscope Measurement Modes:

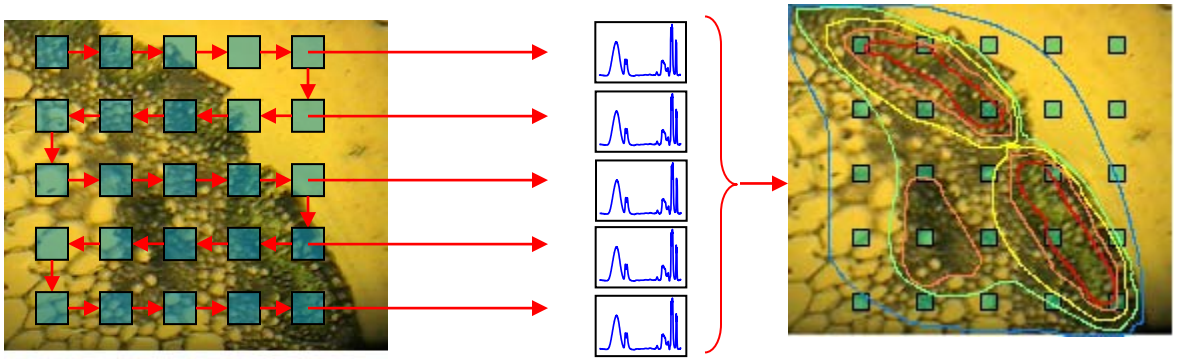
1 : Single Point

Single or multiple spectra of different zones of a sample



2: Single Point Mapping

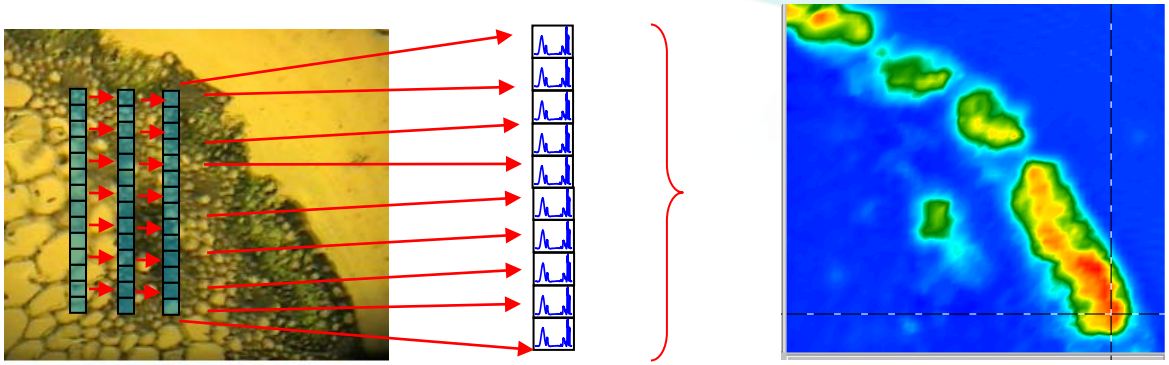
Automated acquisition of spectra (one by one) defined by a grid. A hundred points can take several hours.



FTIR Microscope Measurement Modes:

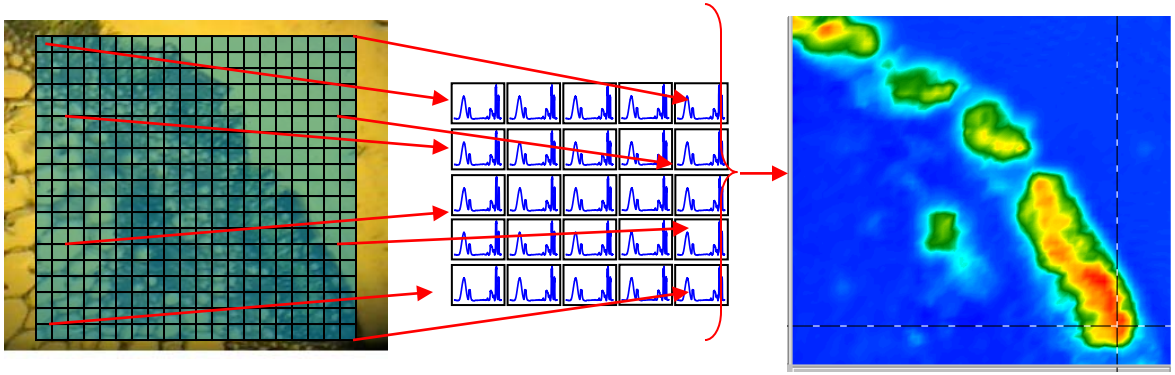
3: Linear array Mapping

Acquisition of spectra by a row (1x16 or 2x14) of detectors. Faster than single point mapping, but still much slower than FPA imaging



4: FPA Imaging

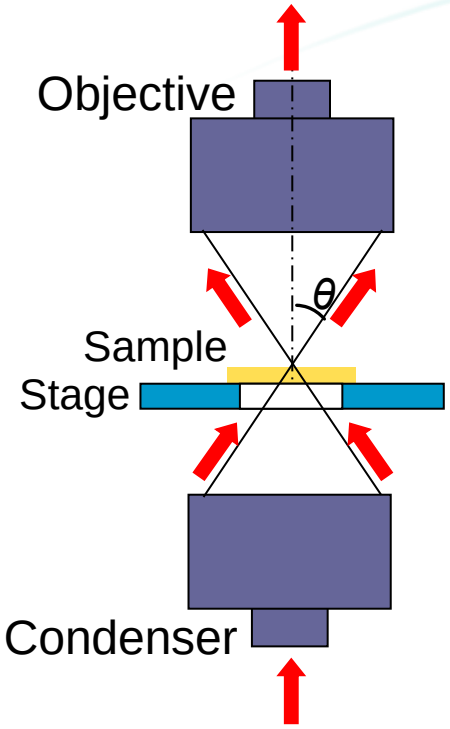
With an FPA detector, up to 16384 spectra can be recorded **simultaneously** in a single measurement



- **FPA based imaging measurements are up to 50x faster than linear array and hundreds of times faster than single point mapping**
- **Much better spatial resolution & sensitivity compared to traditional single point microscopes & linear array systems**

Common Infrared Microscopy Sampling Techniques

Transmission

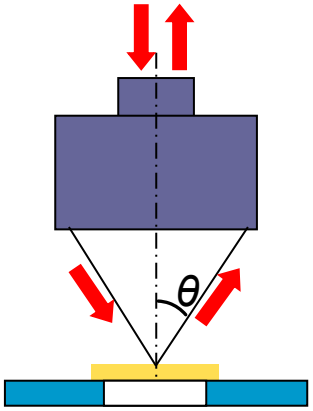


Sample thickness: 10 – 20 μm

Pixel size : 5.5 – 19 μm

Field of View: 700x700 μm to 2.4 x 2.4 mm

Reflectance

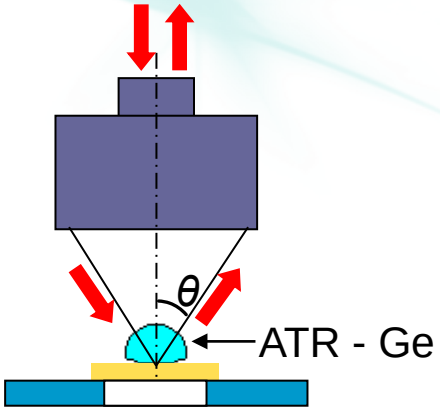


Sample thickness: NA

Pixel size : 5.5 – 19 μm

Field of View: 700x700 μm to 2.4 x 2.4 mm

Micro - ATR



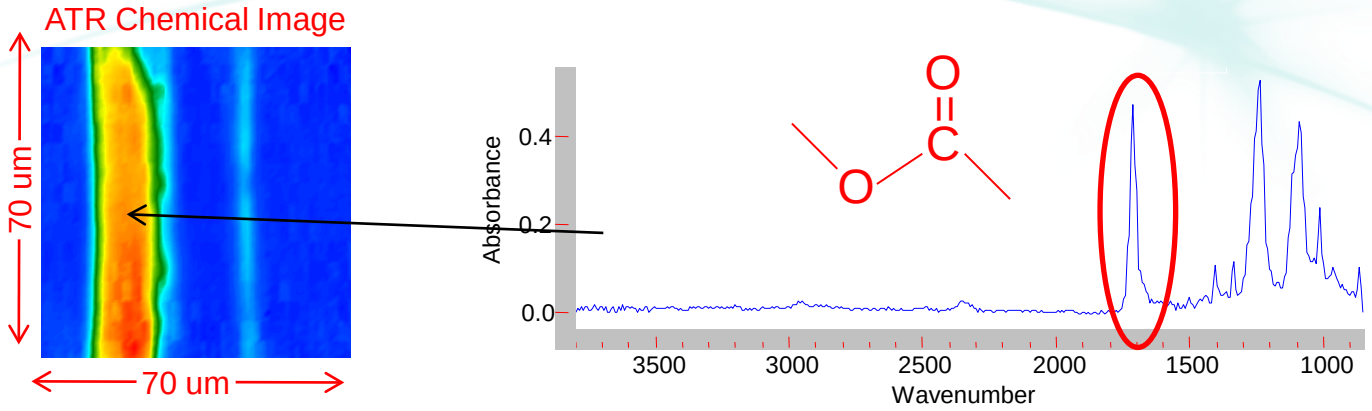
Sample thickness: NA

Pixel size : 1.1 μm

Field of View: 70x70 μm

What do the Coloured Images Mean?

Image @
1724 cm-1
PET



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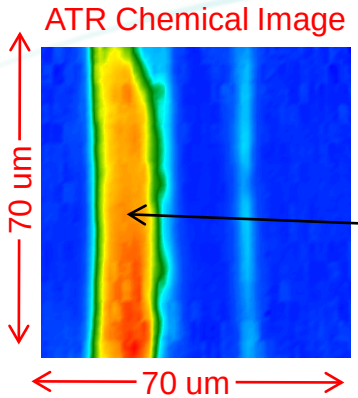


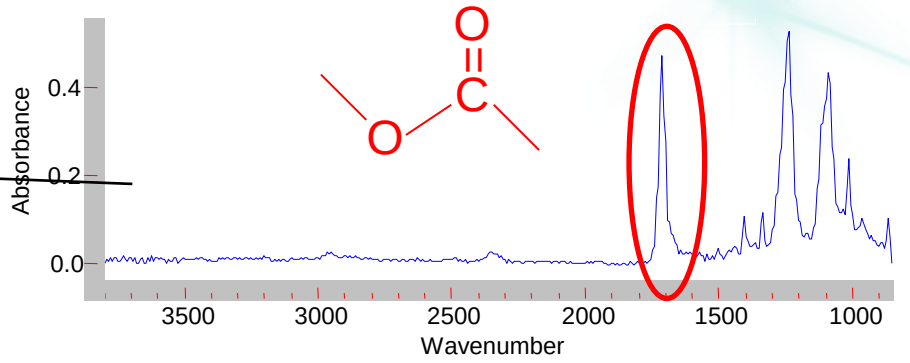
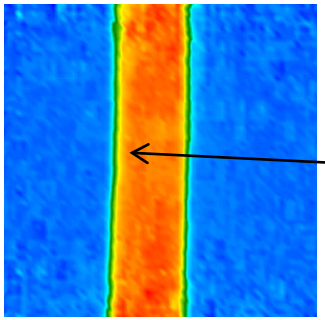
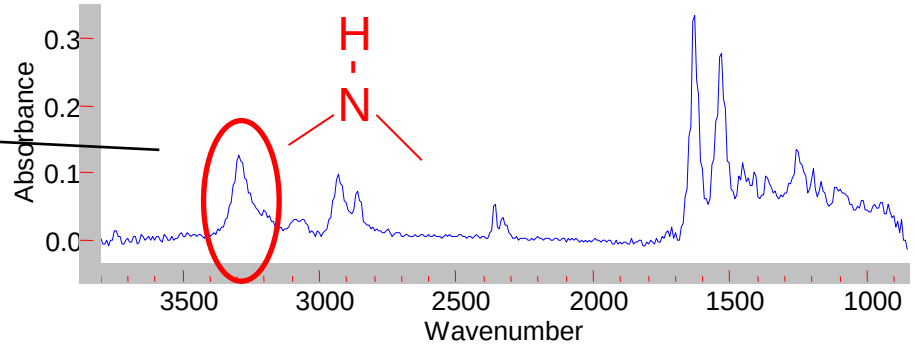


Image @
3295 cm-1
Nylon





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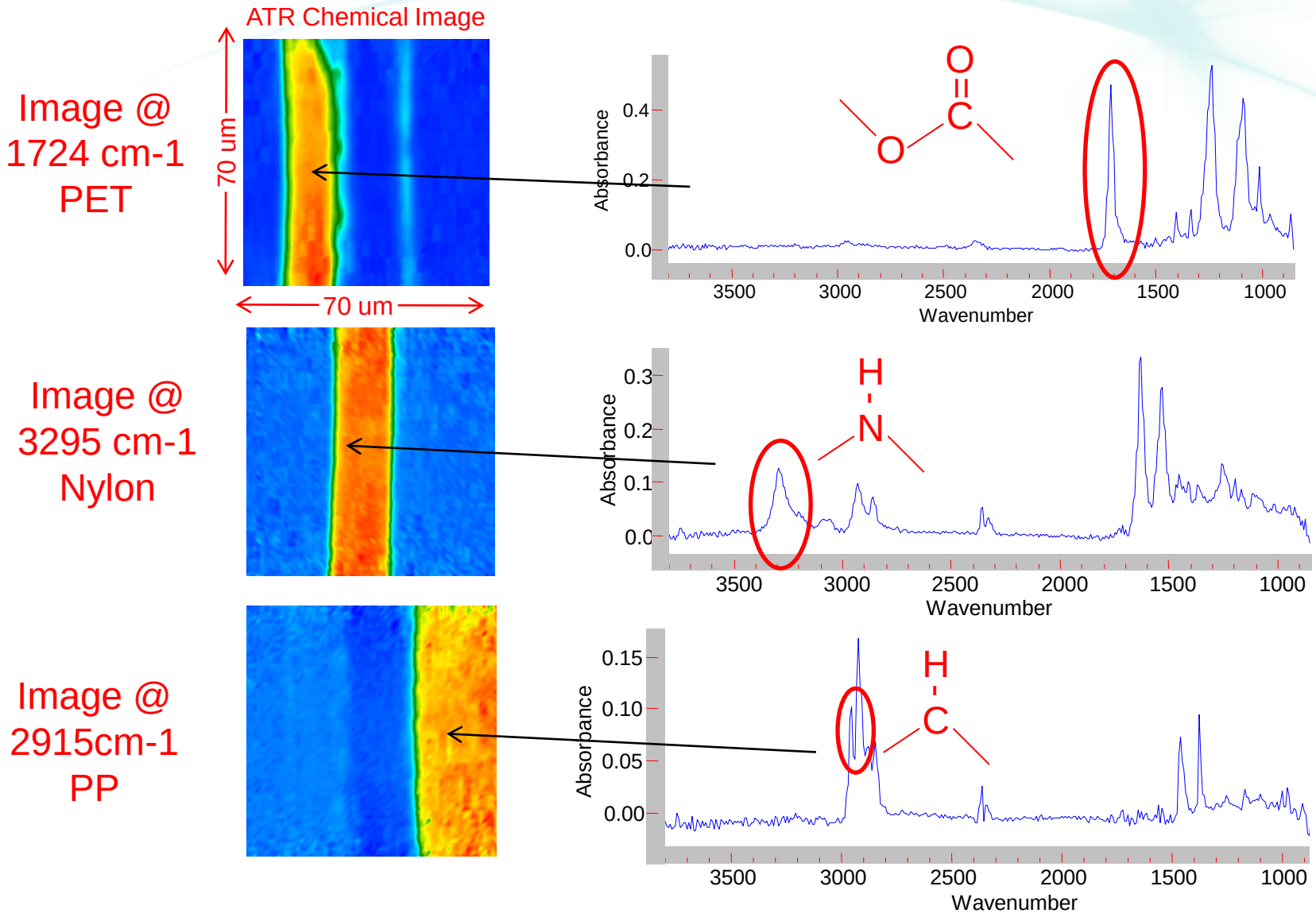

Advantages of micro ATR FTIR Chemical Imaging

Advantages:

1. Reduced sample preparation – thickness is not an issue
2. Increased spatial resolution by factor of 4
3. Almost zero pressure required – eliminating sample deformation
4. Reduces scattering (baseline tilt) and other spectra artefacts

Requirements:

1. Must have good contact (not necessarily high pressure)

Traditional Polymer film/laminate Sample Preparation for FTIR Microscopy/Imaging

1 Cut a small piece of sample and place it vertically in a holding clamp.

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3. Allow resin to cure, typically 12-48 hrs, and then remove the resin-embedded sample from mold.

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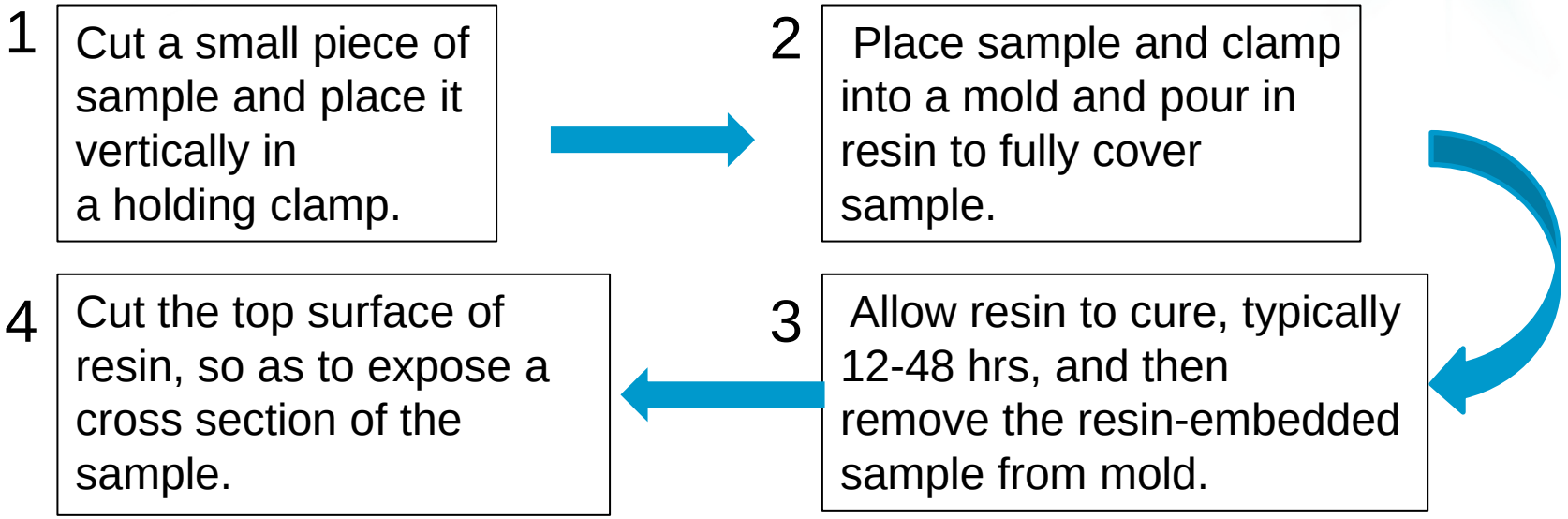

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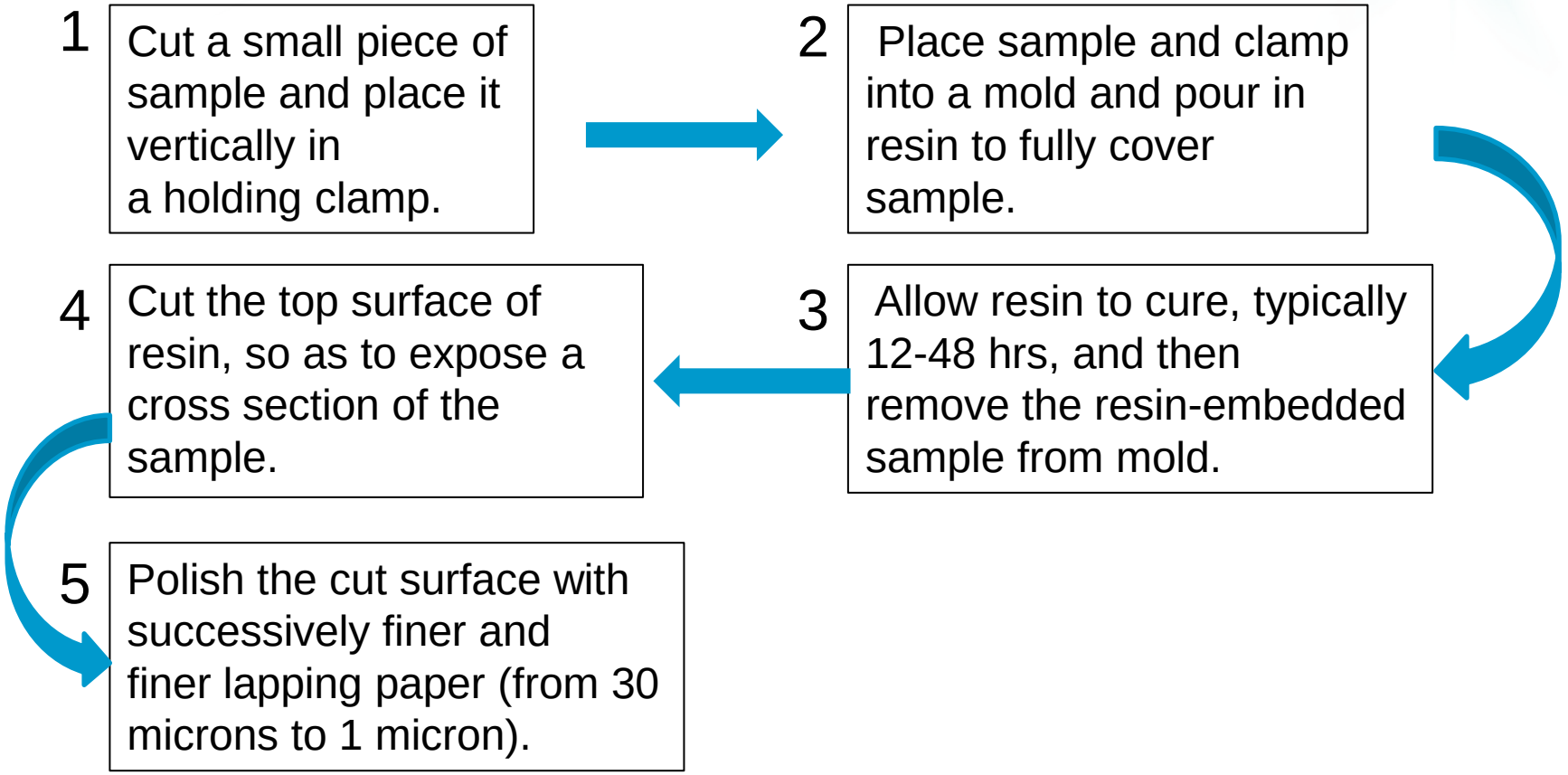
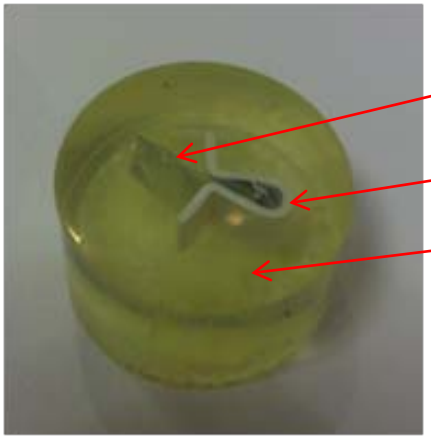


Traditional Polymer film/laminate Sample Preparation for FTIR Microscopy/Imaging

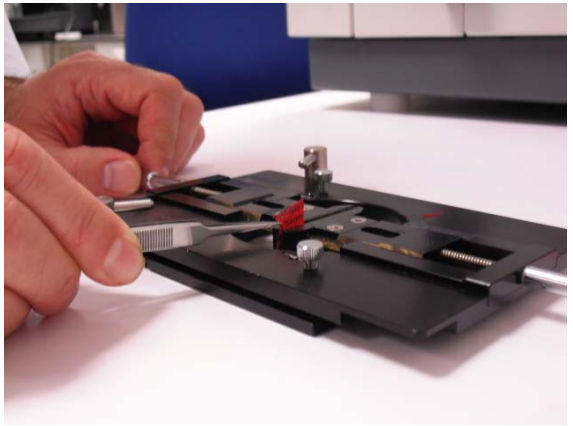
1. Cut a small piece of sample and place it vertically in a holding clamp.
2. Place sample and clamp into a mold and pour in resin to fully cover sample.
3. Allow resin to cure, typically 12-48 hrs, and then remove the resin-embedded sample from mold.
4. Cut the top surface of resin, so as to expose a cross section of the sample.
5. Polish the cut surface with successively finer and finer lapping paper (from 30 microns to 1 micron).



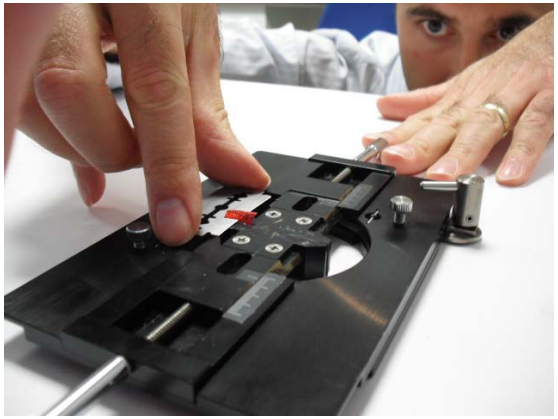
NEW - Sample Preparation Free FTIR Chemical Imaging of Polymer laminates & Films

Step 1. Cut out small piece

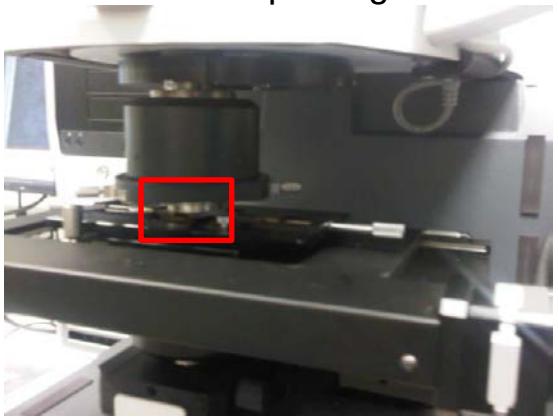
Step 2. Place cut-out piece in micro-vice.



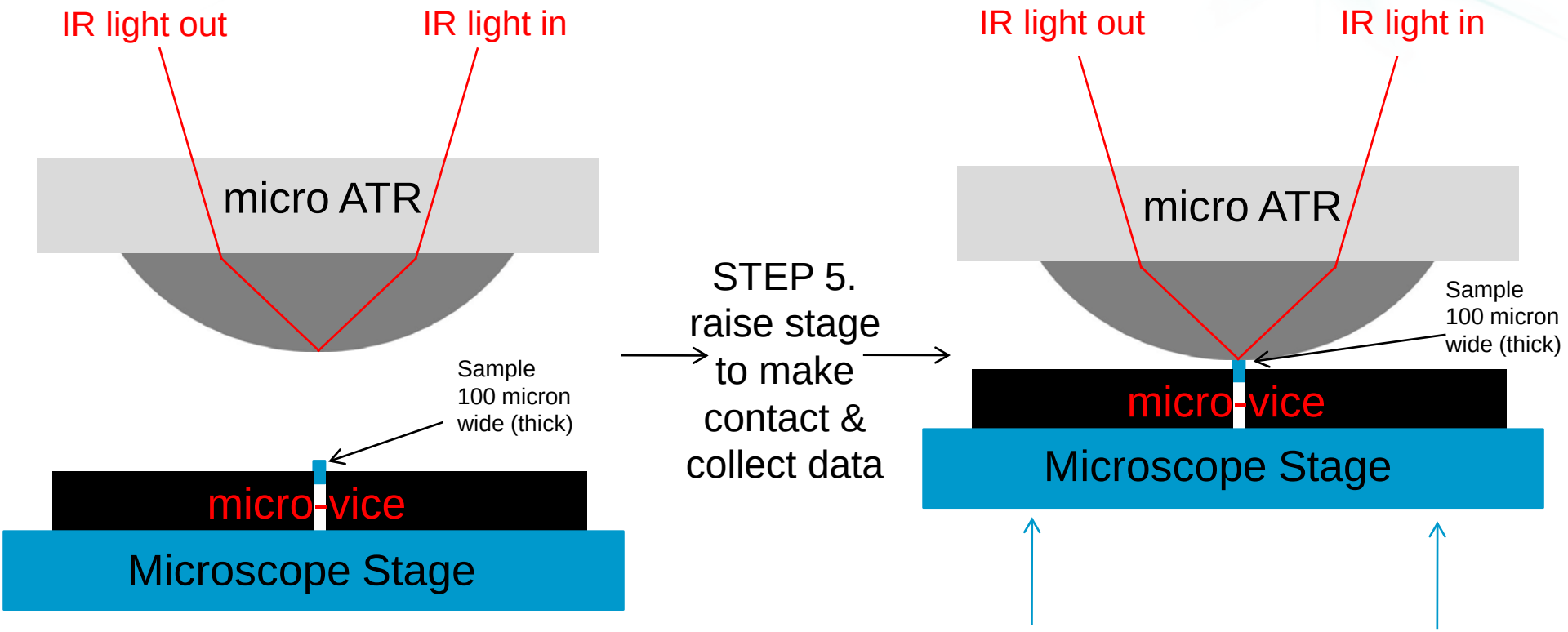
Step 3. Cross-section sample with razor



Step 4. Place micro-vice (with sample) on microscope stage & touch ATR

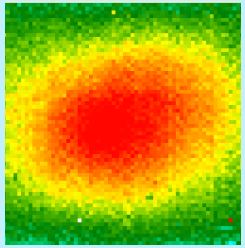


ATR Contact with sample



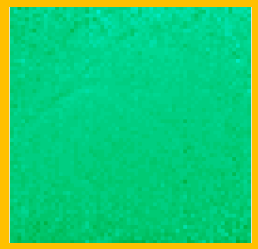
“Live/Real-Time” ATR contact monitoring

Standard Live ATR direct FPA IR Image – without correction



No Pressure
(before contact)

Live ATR direct FPA IR Image with Enhanced Chemical Contrast



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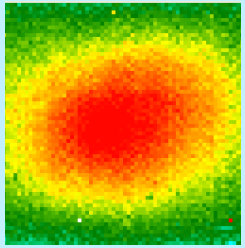
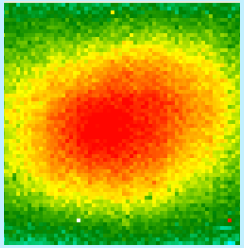


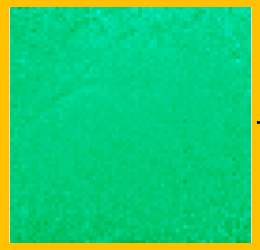
Stage is raised →



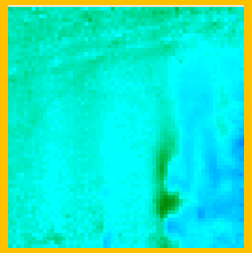
No Pressure (before contact)

First Contact

Live ATR direct FPA IR Image with Enhanced Chemical Contrast



Stage is raised →

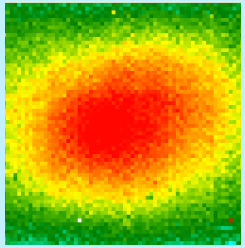


No Pressure (before contact)

First Contact

“Live/Real-Time” ATR contact monitoring

Standard Live ATR direct FPA IR Image – without correction



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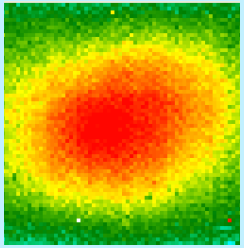
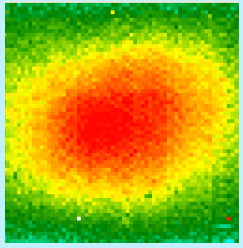


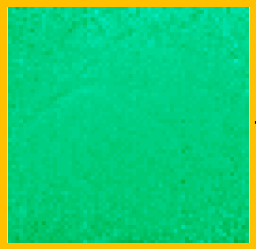


No Pressure (before contact)

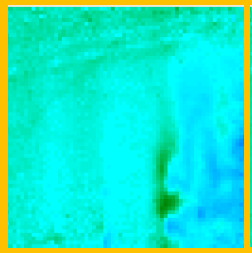
First Contact

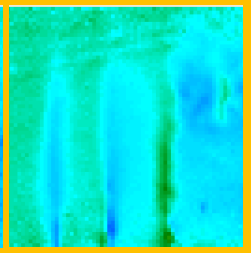
Increasing Pressure

Live ATR direct FPA IR Image with Enhanced Chemical Contrast



Stage is raised





No Pressure (before contact)

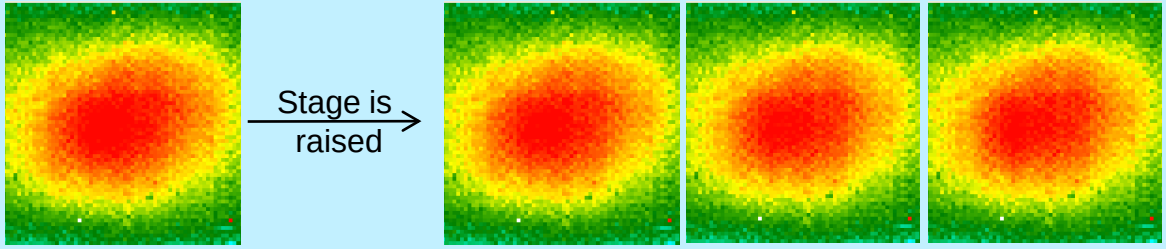
First Contact

Increasing Pressure

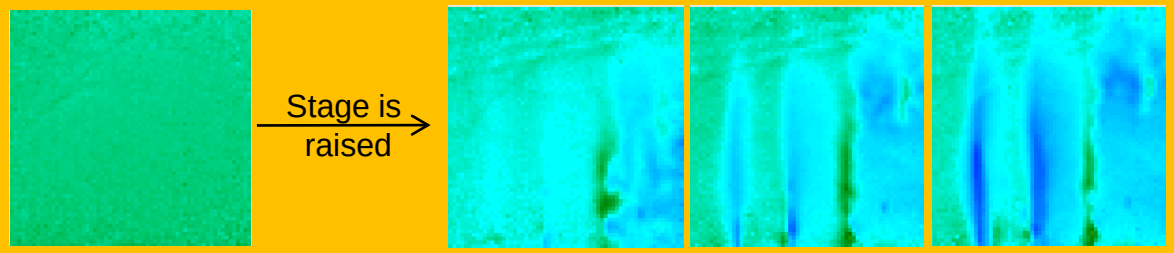
Complete Contact

“Live/Real-Time” ATR contact monitoring

Standard Live ATR direct FPA IR Image – without correction

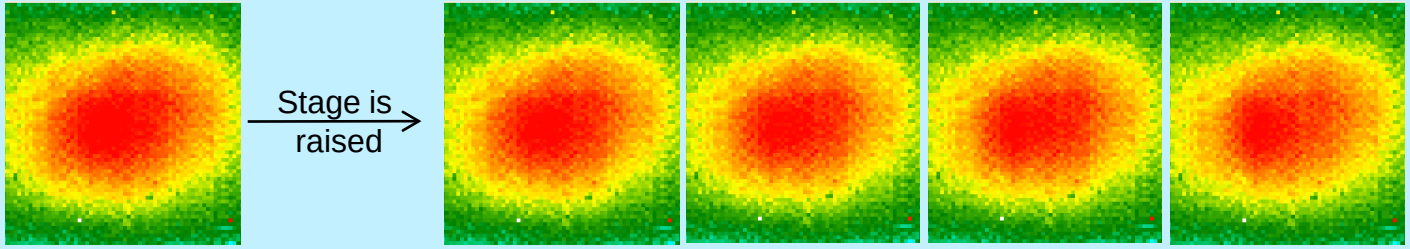


Live ATR direct FPA IR Image with Enhanced Chemical Contrast

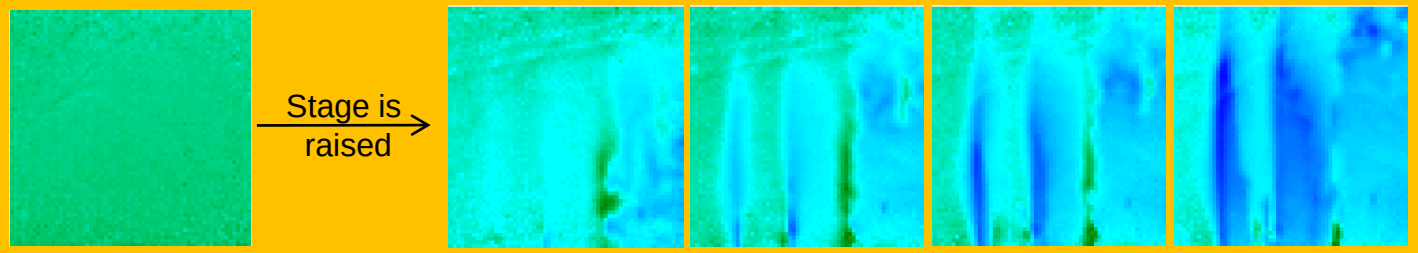


“Live/Real-Time” ATR contact monitoring

Standard Live ATR direct FPA IR Image – without correction



Live ATR direct FPA IR Image with Enhanced Chemical Contrast



“Live/Real-Time” ATR contact monitoring

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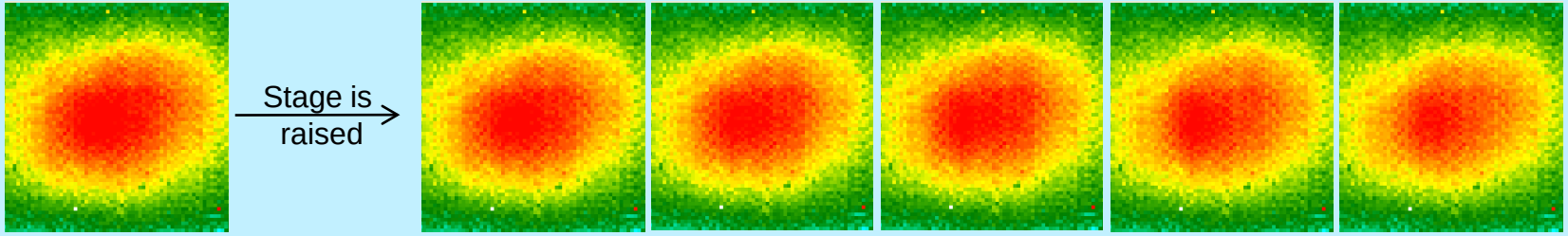
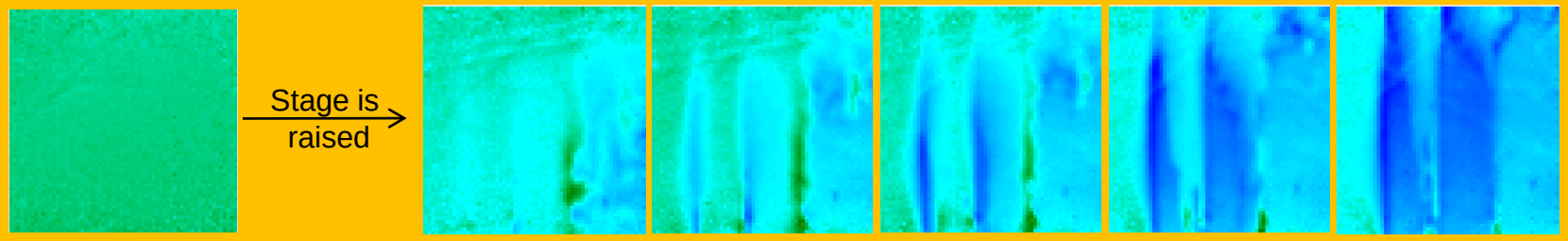


Live ATR direct FPA IR Image with Enhanced Chemical Contrast



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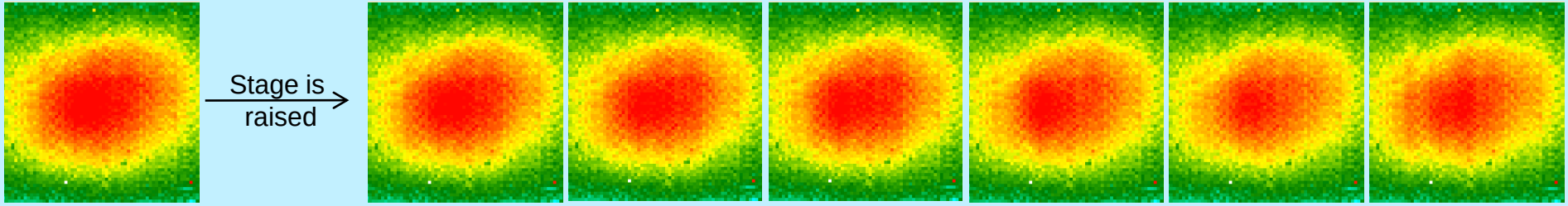
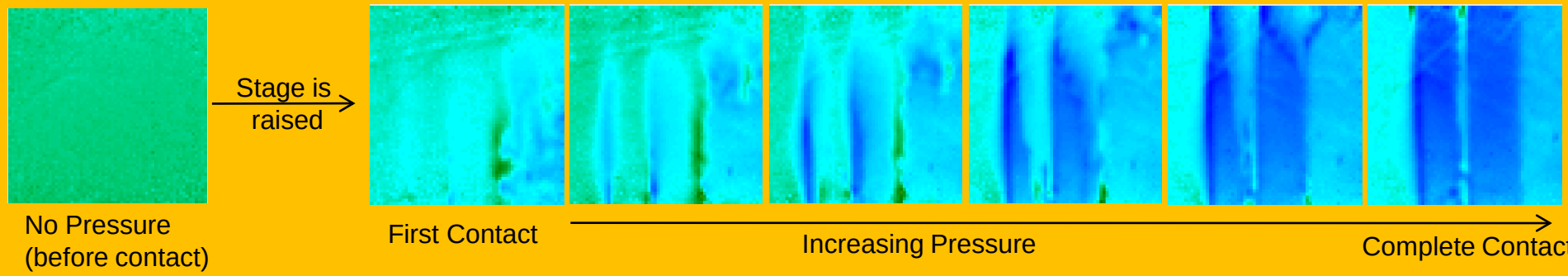
Standard Live ATR direct FPA IR Image – without correction

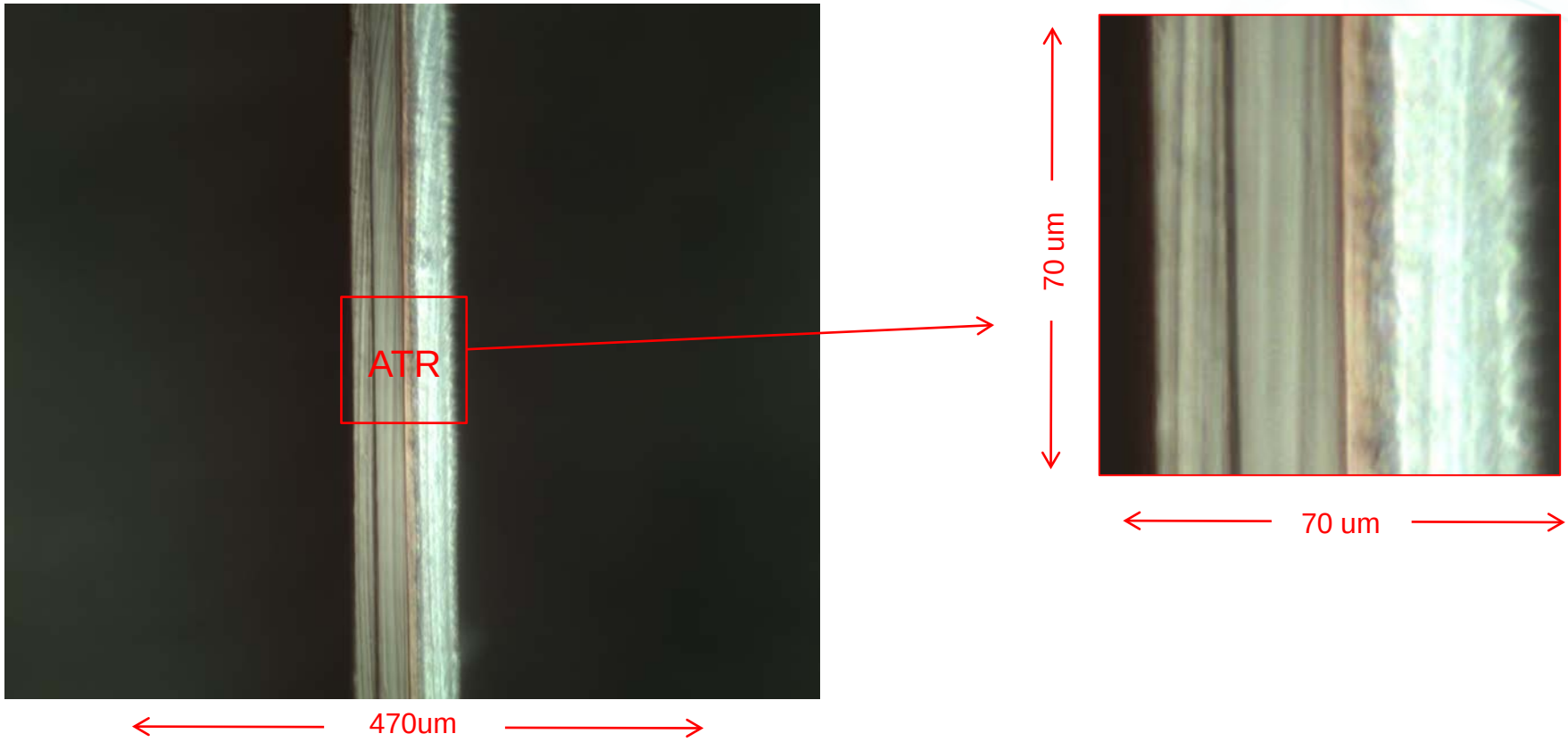


Live ATR direct FPA IR Image with Enhanced Chemical Contrast

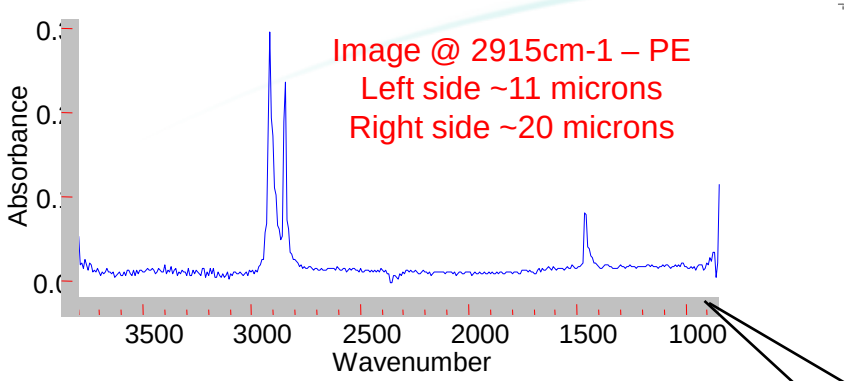


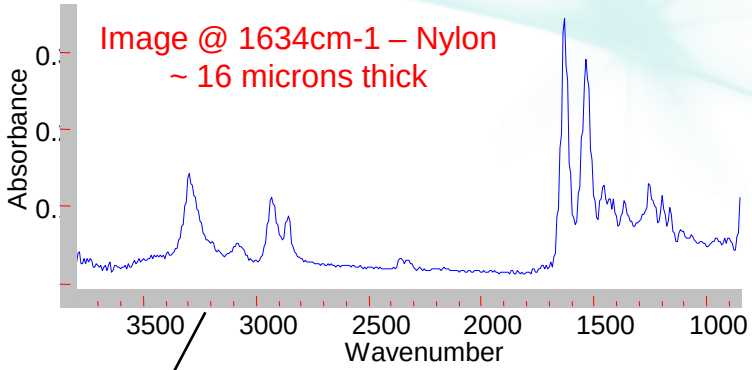
Polymer Laminate #1 - Visible Images & ATR Imaging Sampling Location

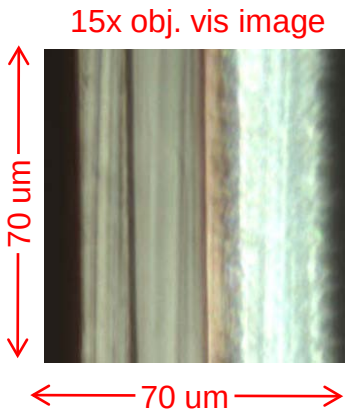
15x obj. vis image –
cross-section view

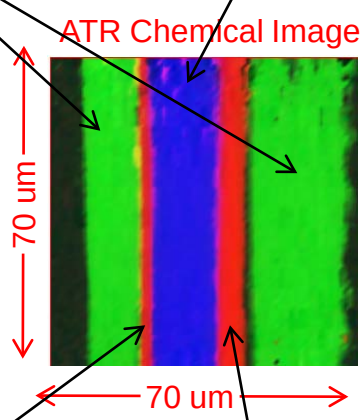


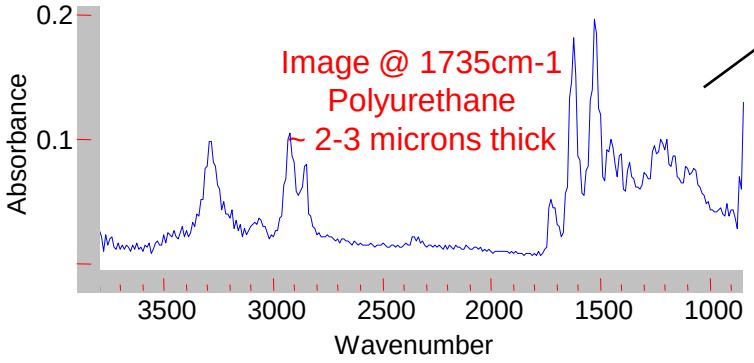
Results Polymer Laminate #1: Chemical Images & Extracted Spectra

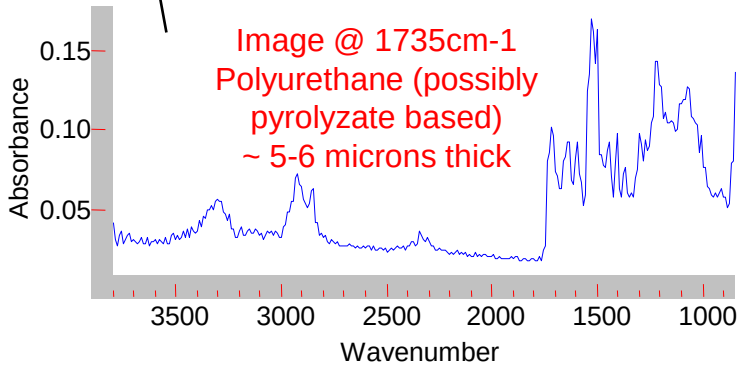






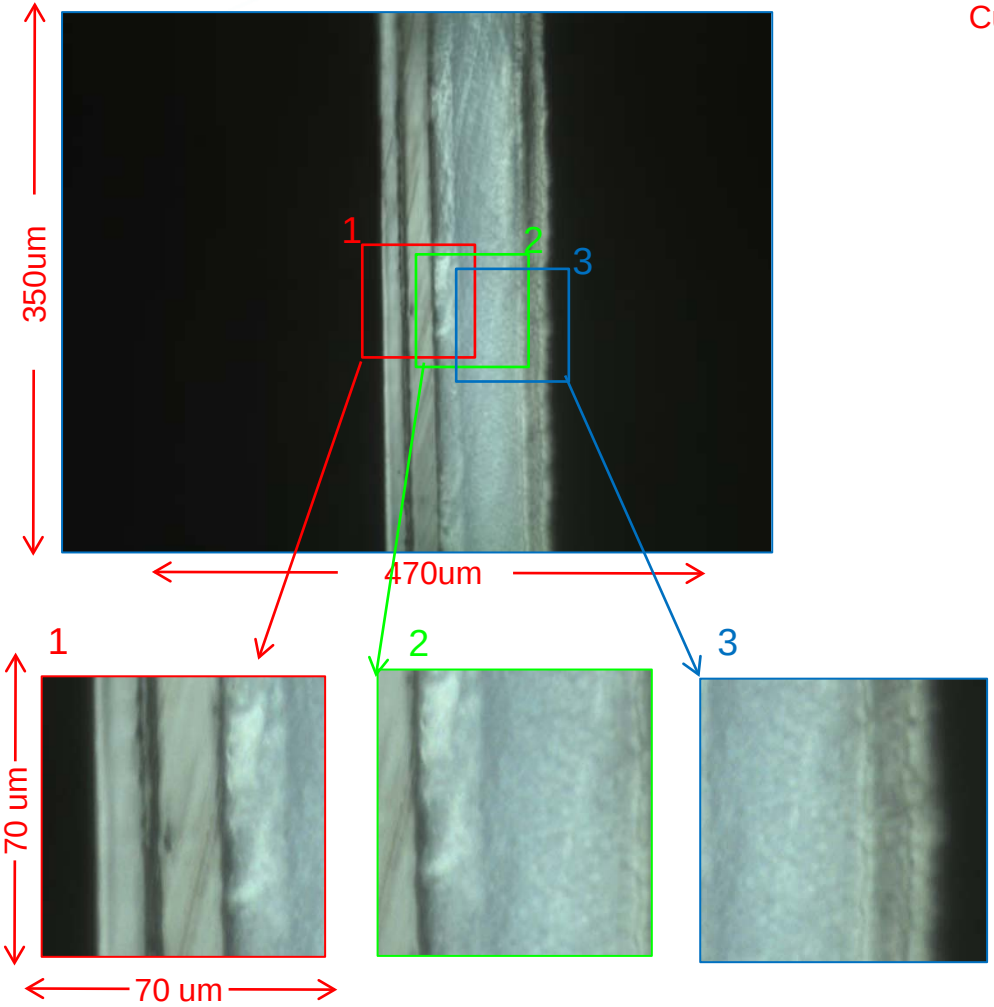




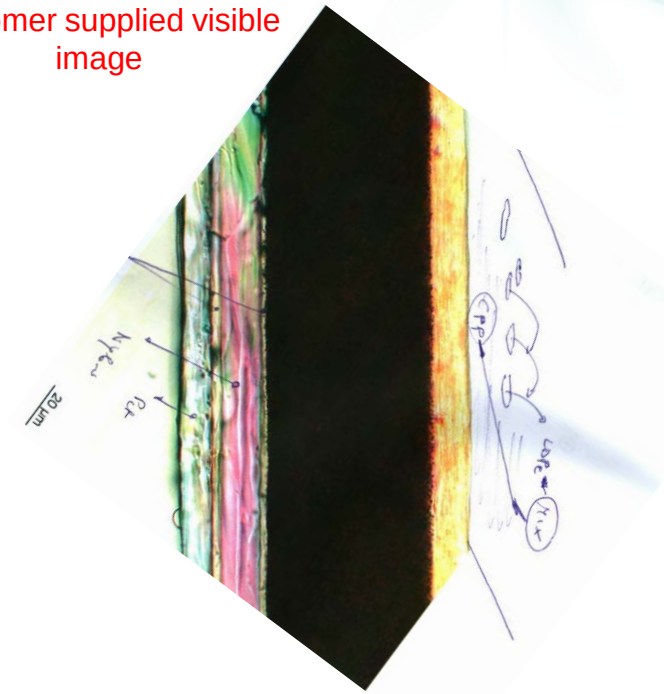


Polymer Laminate #2 - Visible Images & ATR Imaging Sampling Location

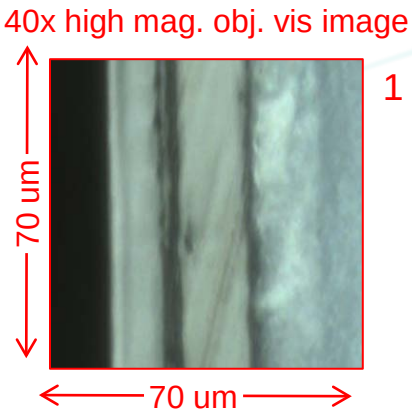
15x obj. vis image – cross-section view

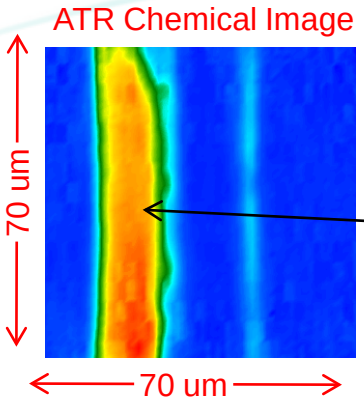


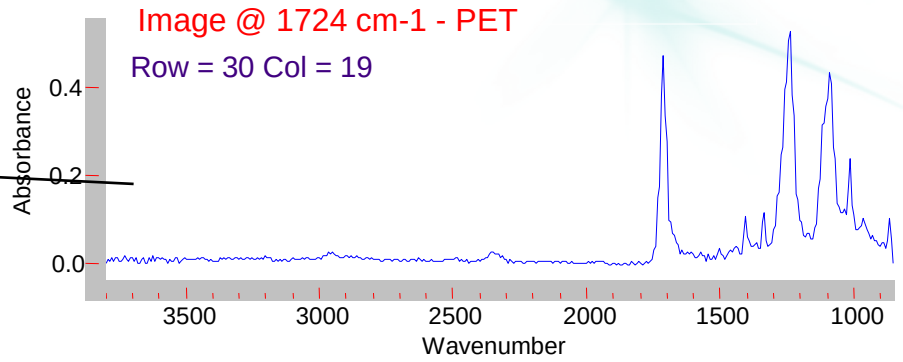
Customer supplied visible image

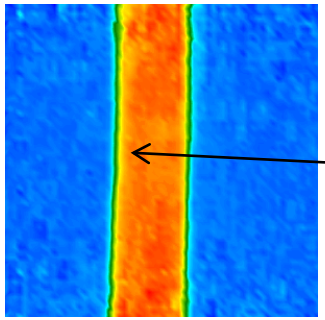


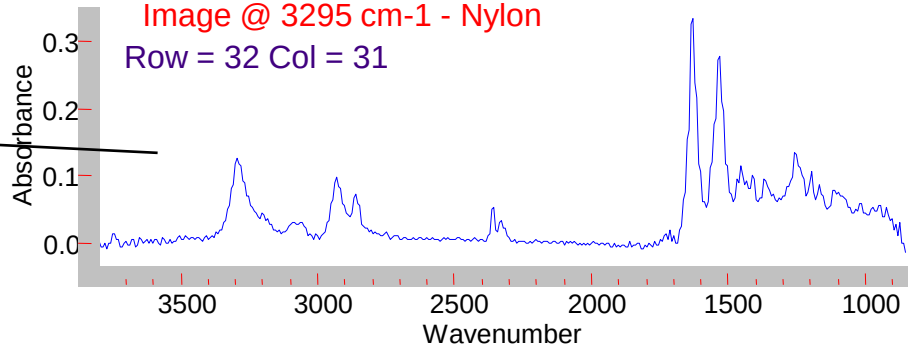
Results Polymer Laminate #2: Chemical Images & Extracted Spectra

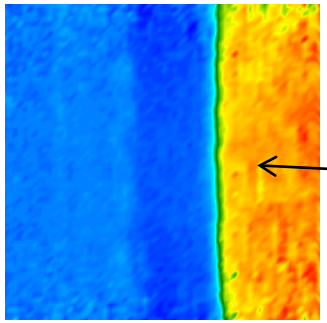


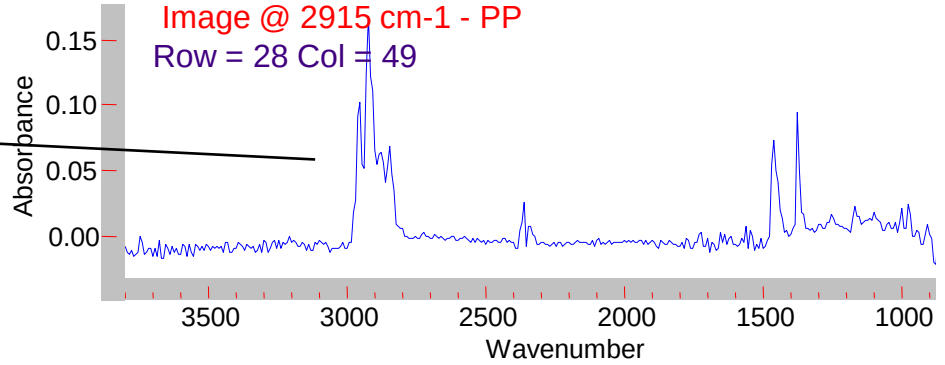






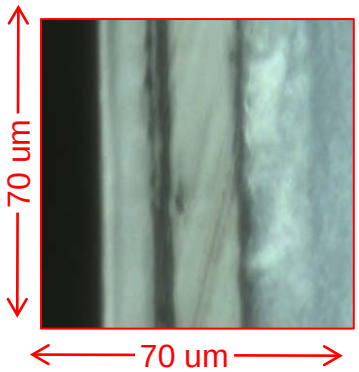






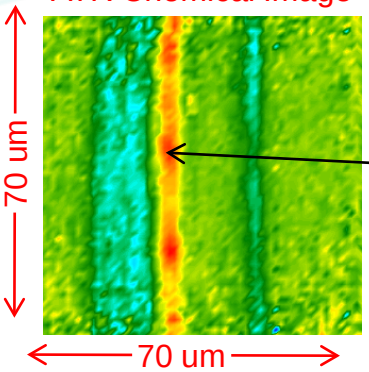
Results Polymer Laminate #2:
Chemical Images & Extracted Spectra of the Tie Layers

40x high mag. obj. vis image



1

ATR Chemical Image



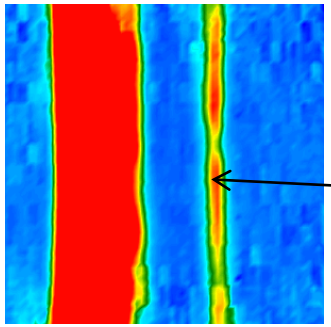


Image @ 1285 cm-1,
poly phthalate, ~4 microns

Tie layer #1

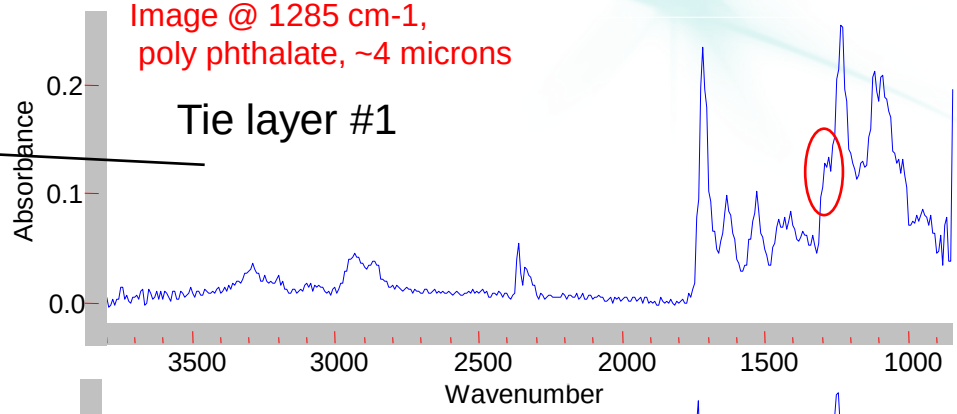
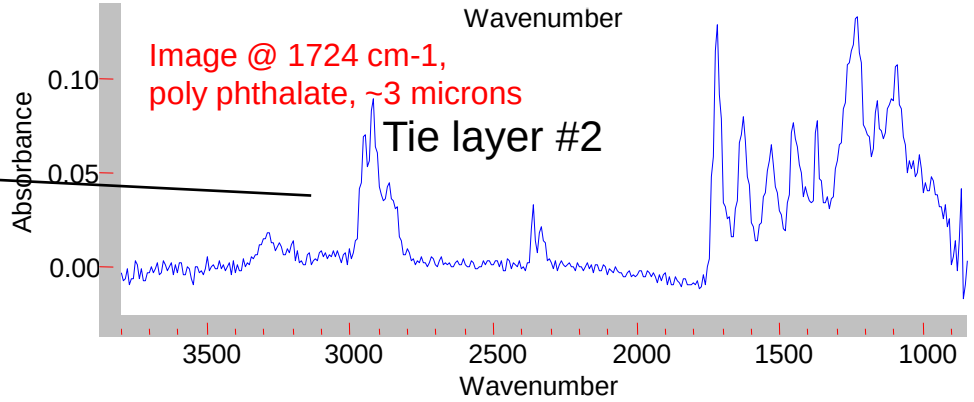


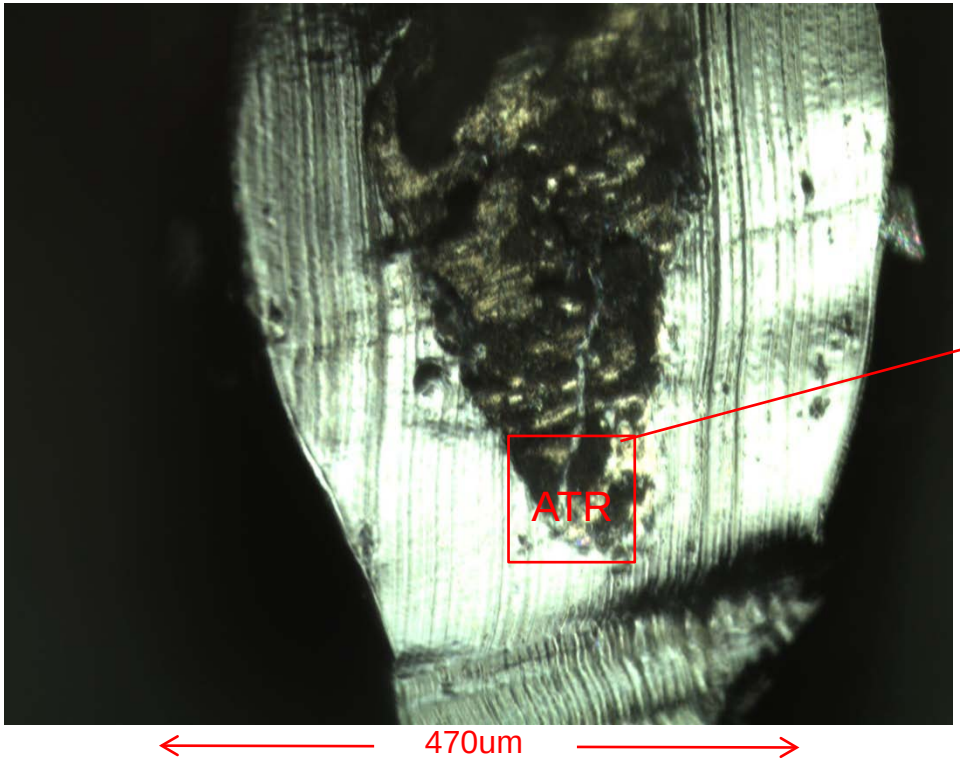
Image @ 1724 cm-1,
poly phthalate, ~3 microns

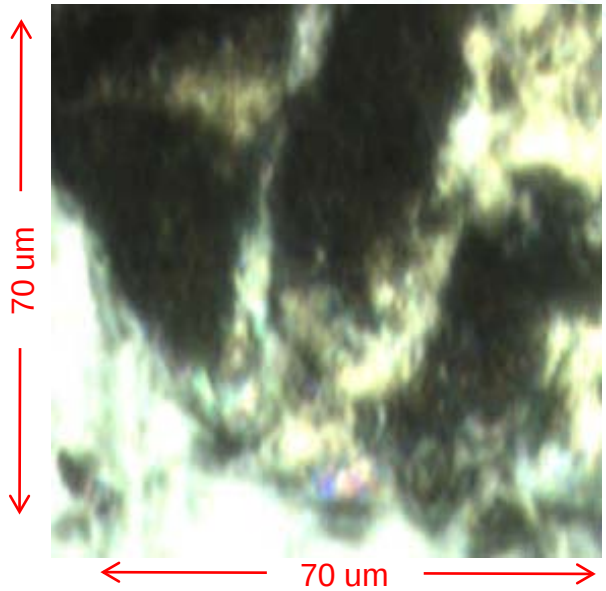
Tie layer #2



Black Rubbish bag - Visible Images & ATR Imaging Sampling Location

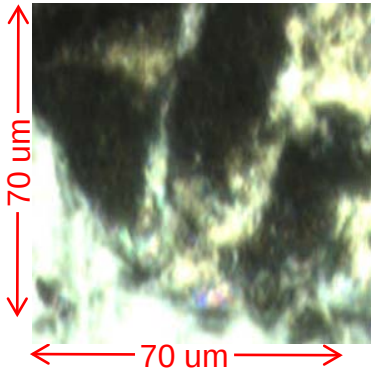
15x obj. vis image –
cross-section view



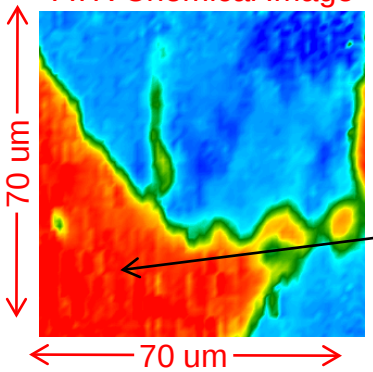


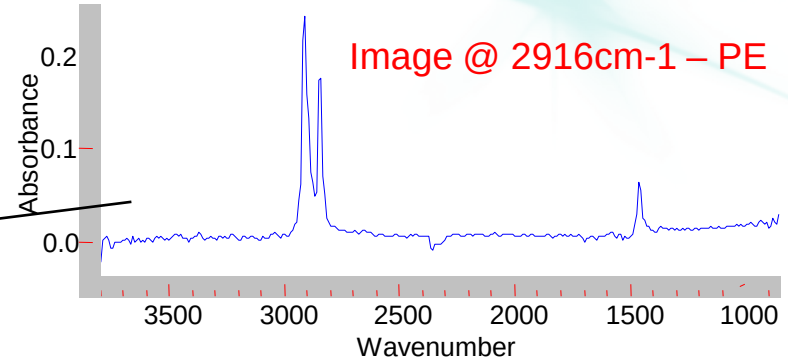
Results Black Rubbish Bag:
Chemical Images & Extracted Spectra of the Tie Layers

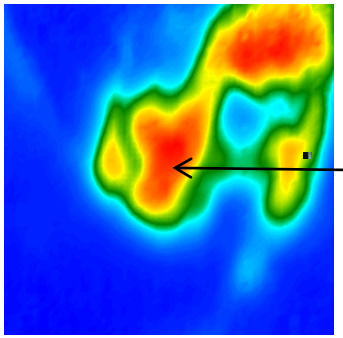
15x high mag. obj. vis image

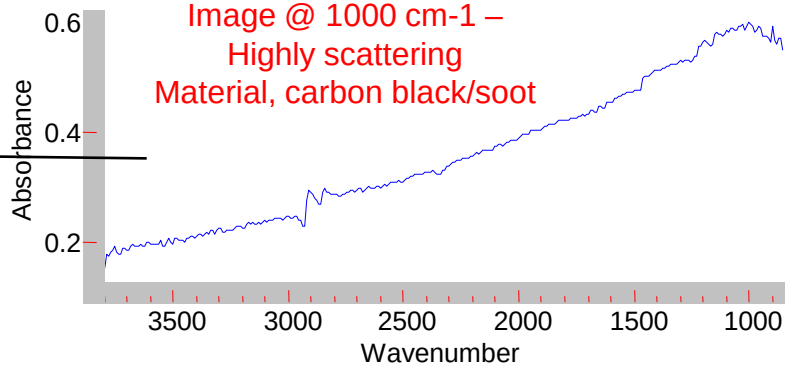


ATR Chemical Image





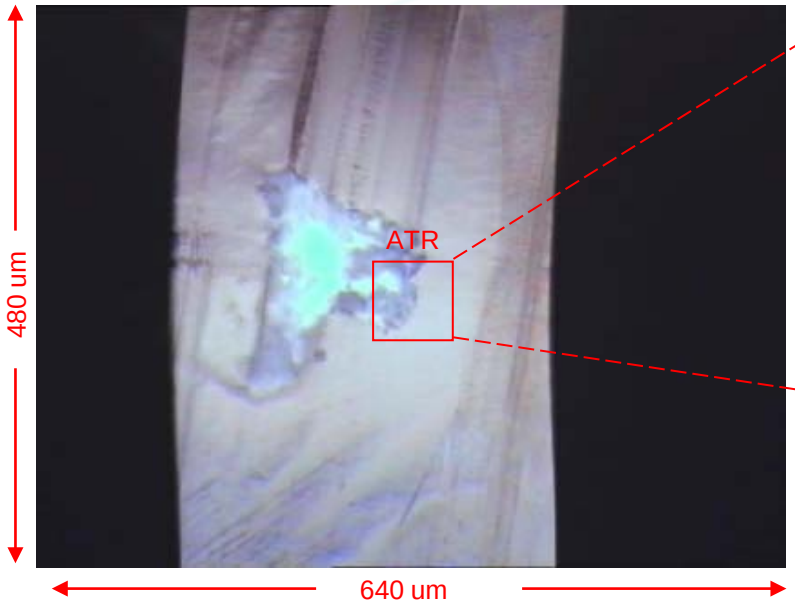




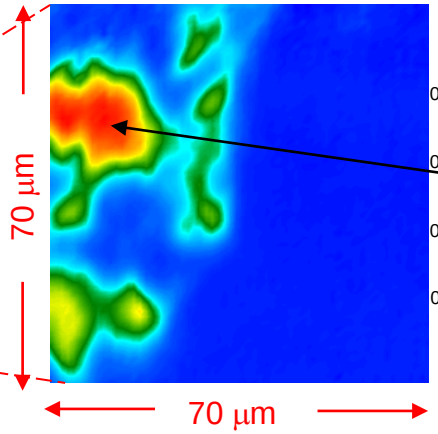
Inclusions show very little spectral features, instead they cause strong baseline tilt effects, typically from scattering.
Material such as carbon black/soot are the likely causes

Polymer Film 1 - Visible Images & ATR Imaging Sampling Location

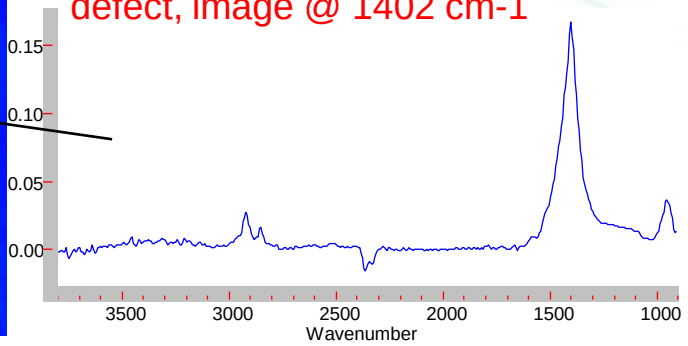
15x obj. vis image – cross-section view

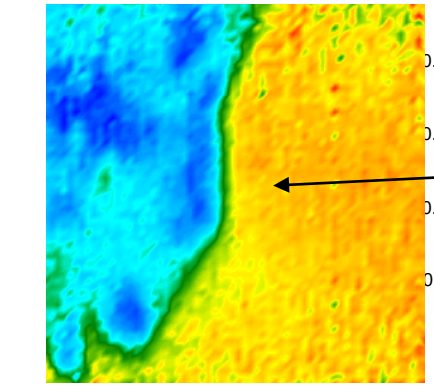


ATR Chemical Image

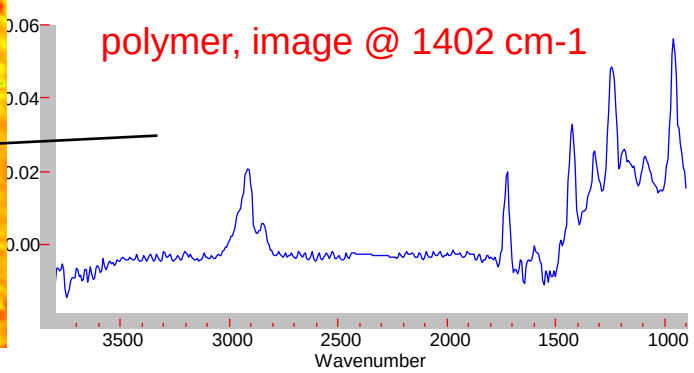


defect, image @ 1402 cm-1

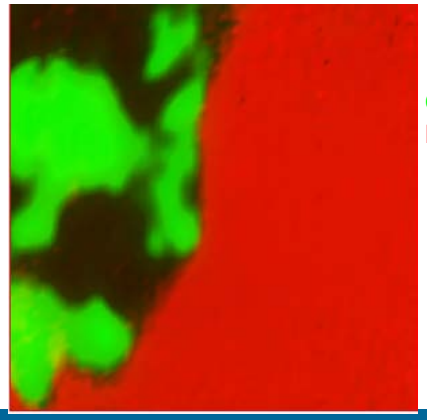




polymer, image @ 1402 cm-1



Composite (Green/Red) image

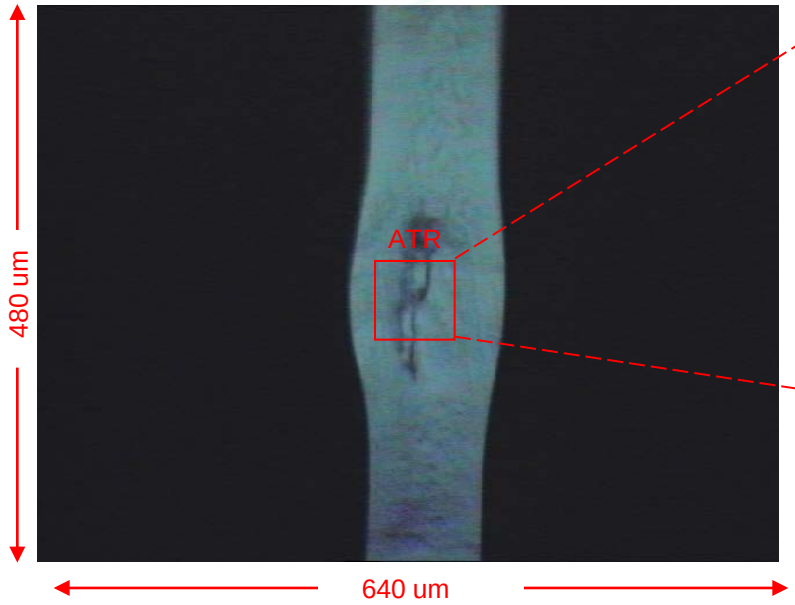


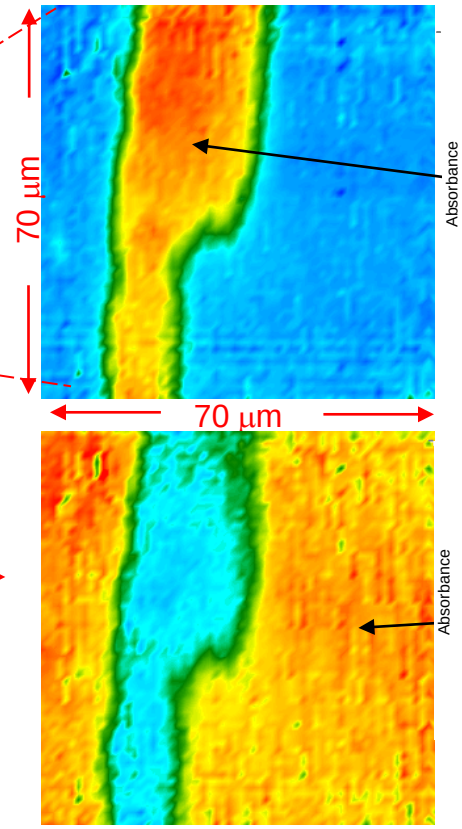
GREEN – DEFECT
RED - POLYMER

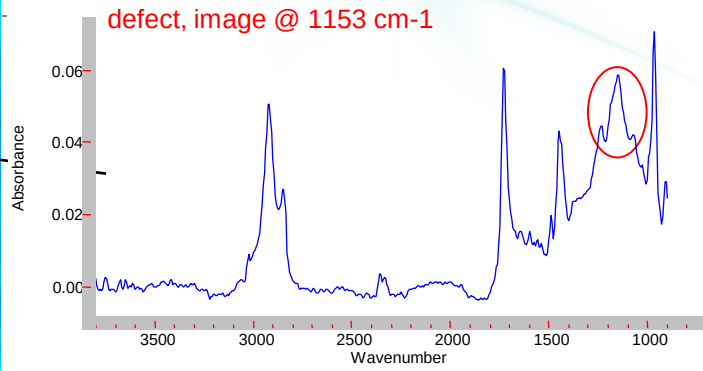
At initial analysis, it appears that the defect is likely to be an Inorganic material, most probably a carbonate, or a carbonate containing mixture

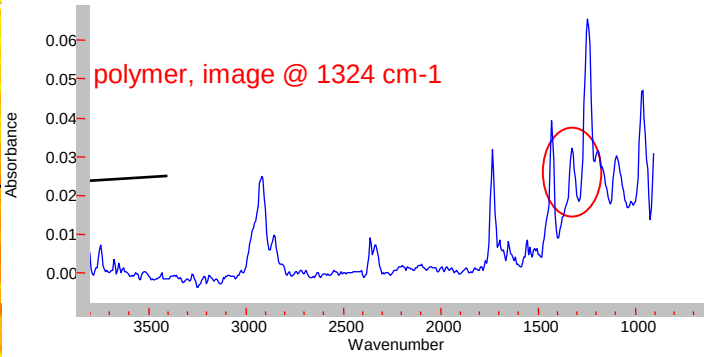
Polymer Film 2 - Visible Images & ATR Imaging Sampling Location

Visible image with 15x objective

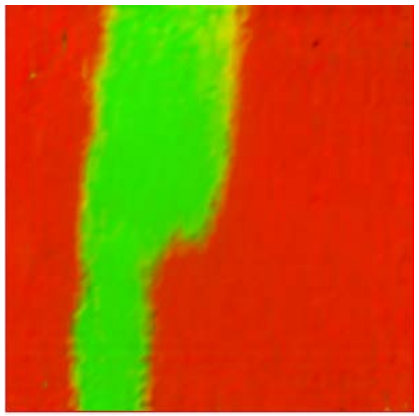








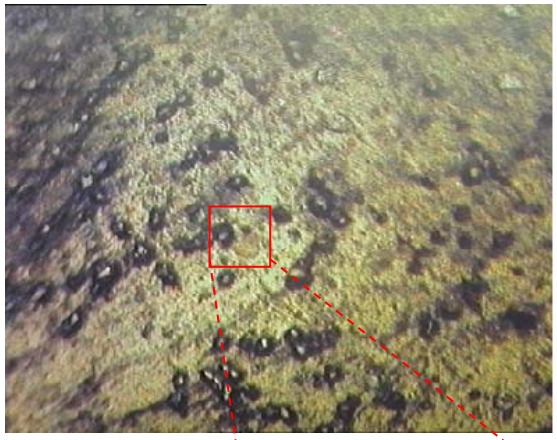
Composite (Green/Red) image



GREEN – DEFECT
RED - POLYMER

Spectral library search confirmed ID as an impact modifier used in the manufacturing process

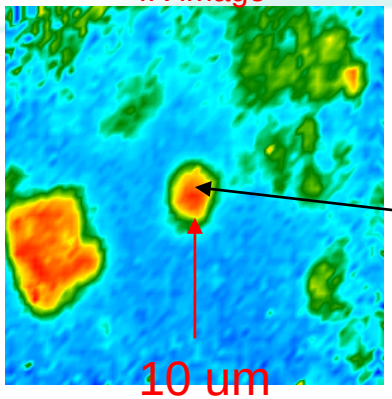
Micro ATR (FPA) imaging of black rubber sample Spot #3



vis image

IR image

Image created at 2848 cm-1



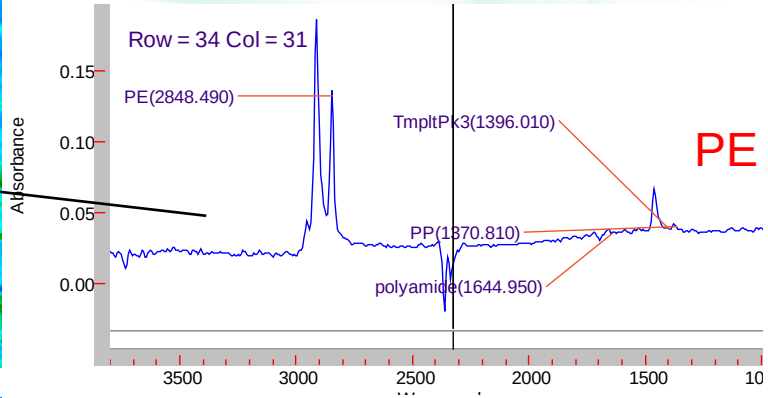
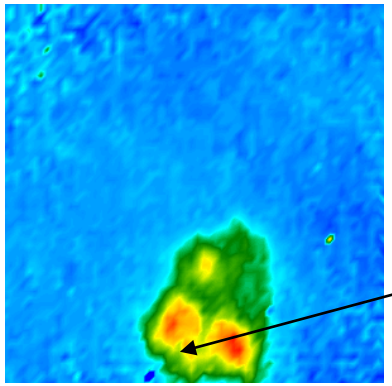
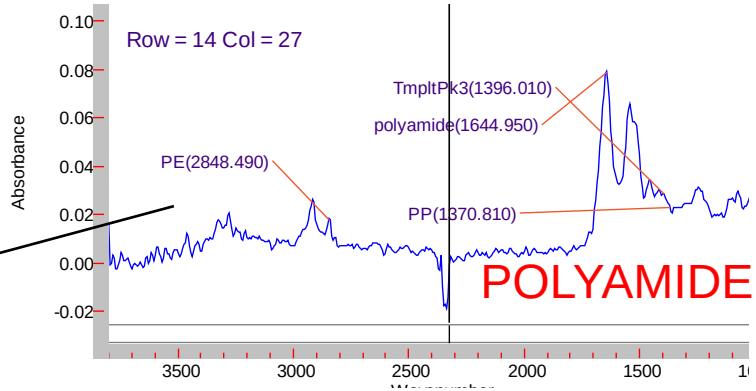
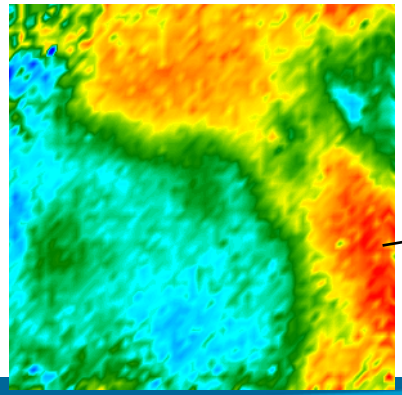
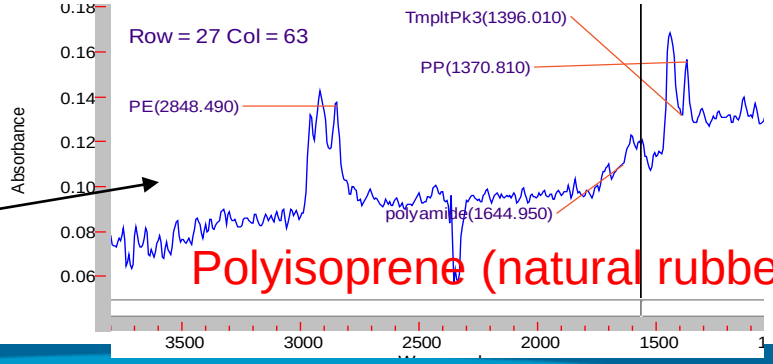


Image created at 1644 cm-1









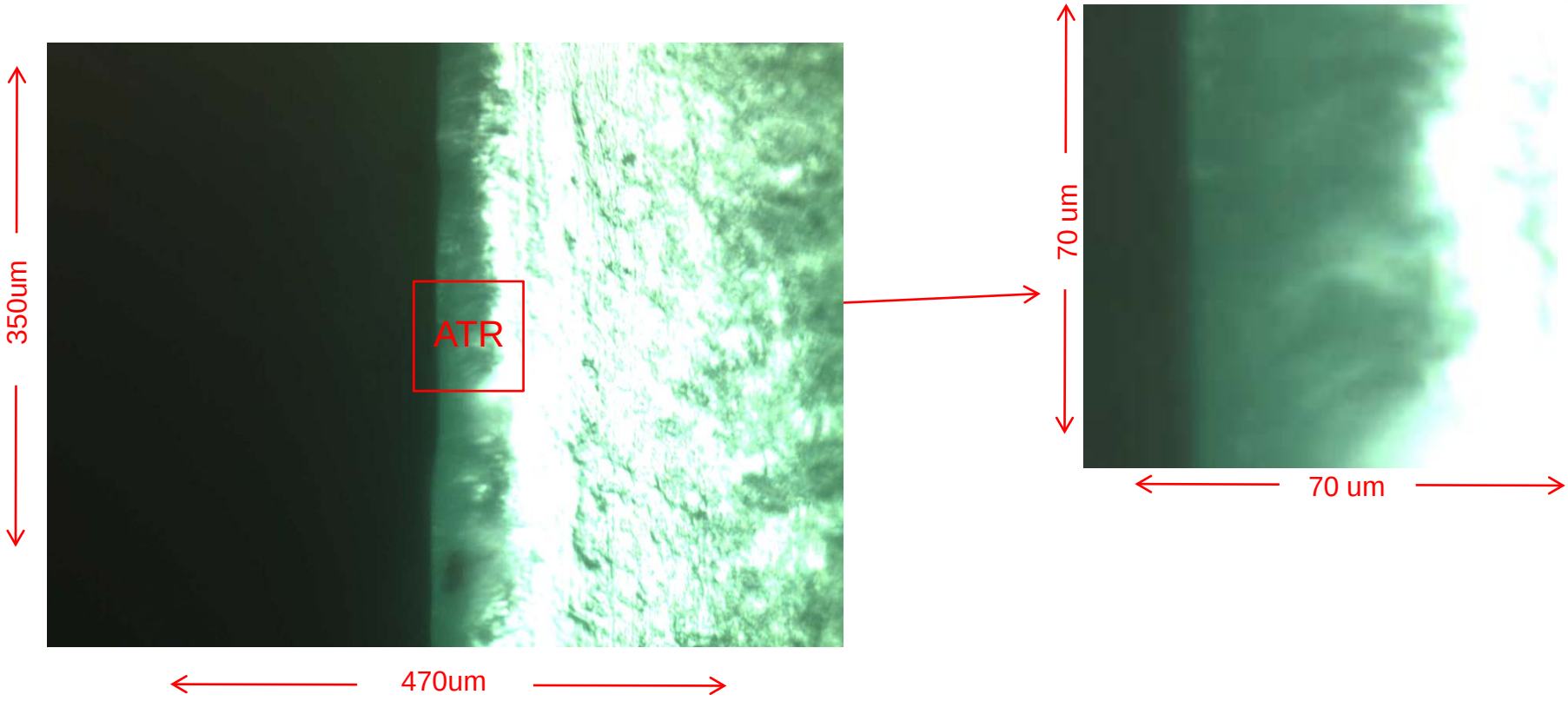
Micro Ge-ATR chemical imaging size 70x70 um.

Each pixel is 1.1 um (diffraction limited)

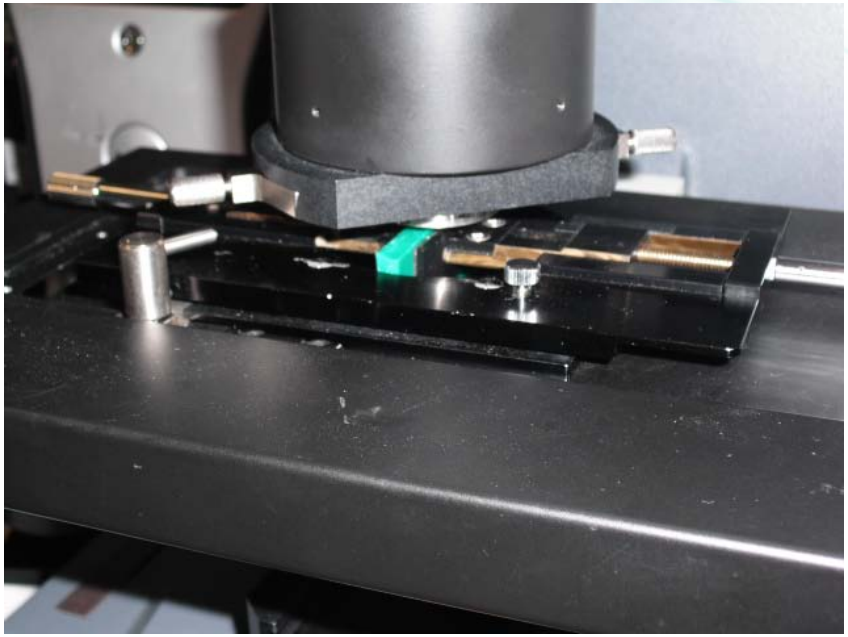
As system is diffraction limited, there is no benefit in having smaller pixel sizes.

Exposed green plastic – Visible images & ATR Imaging Sampling Location

15x obj. vis image

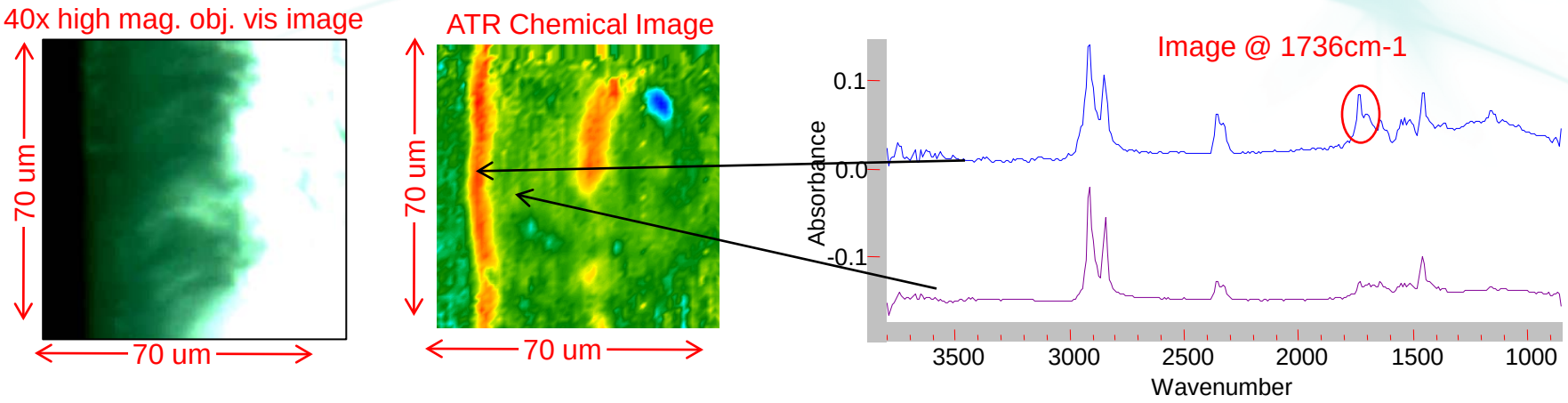


Sample Placement & Measurement



The large green plastic block was placed directly “as-is” into the micro-vice holder, which was then placed on the microscope stage, followed by raising of the stage to make contact with the ATR for data collection.

Results - Exposed Green Plastic



A clear edge containing higher carbonyl content is clearer visible along the expose side edge.

Summary

- Agilent Technologies has developed a method of “sample preparation free FTIR ATR Imaging of polymer films and laminates

- Faster analysis, going from 12-48 hr to 5 mins. Facility to measure multiple locations on the sample or to place multiple samples in mount

- The ATR imaging approach allows for a factor of 4 enhancement in spatial resolution, providing for the ability to measure features as small as 2 microns

- No damage to sample allows for further analysis via other analytical methods

Contacts & Other Information

Email: mustafa.kansiz@agilent.com

Useful Links:

http://www.chem.agilent.com/en-US/Products/instruments/molecularspectroscopy/pages/default.aspx