

# Molecular Spectroscopy In The Study of Wood & Biomass

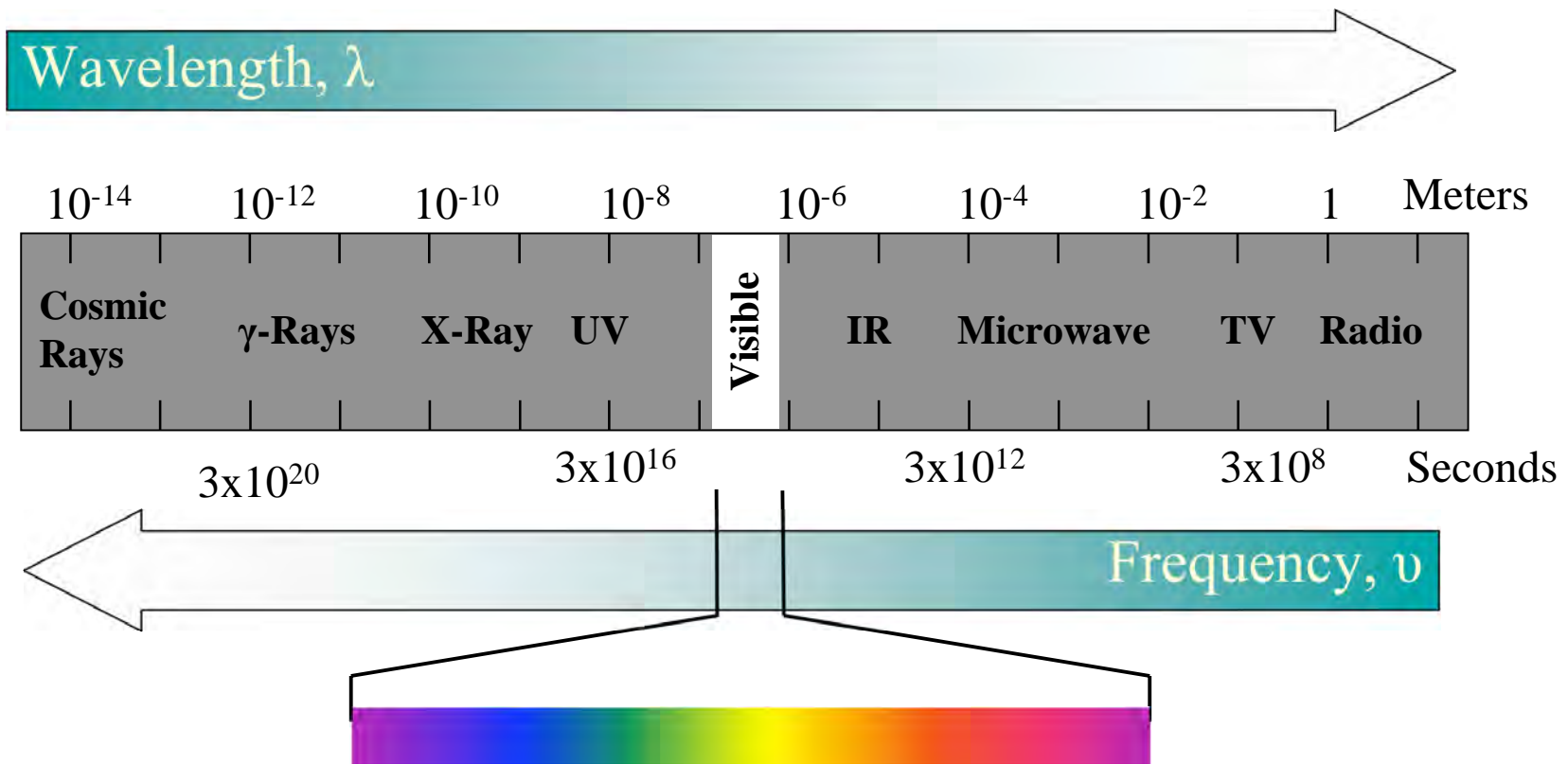
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Society of Wood Science  
and Technology  
50th Annual Convention  
Knoxville, Tennessee  
June 10, 2007

*Timothy G. Rials*  
Forest Products Center  
The University of Tennessee  
Knoxville, TN 37996

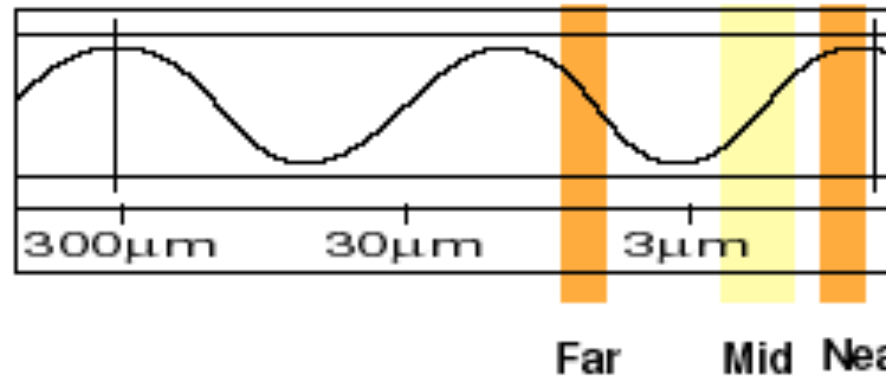


# The Electromagnetic Spectrum

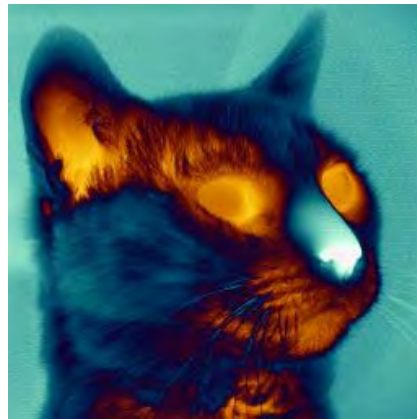


# Everyday Infrared...

Infrared Region of the Electromagnetic Spectrum



Approaching the microwave region; wavelength ca. size of a pinhead (50 – 1000 μ)



2500 - 16000 nm  
4000 – 600 cm<sup>-1</sup>



700 – 2500 nm  
14285 – 4000 cm<sup>-1</sup>

# Beer's Law

The equation that relates absorbance to concentration and takes the form:

$$A_{\lambda} = \varepsilon_{\lambda} l C$$

Where:

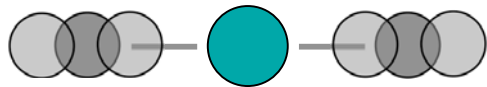
$A_{\lambda}$  = absorbance

$\varepsilon_{\lambda}$  = molar absorptivity (a proportionality constant)

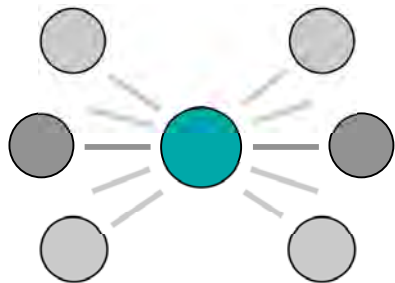
$l$  = pathlength of the sample

$C$  = concentration of the sample

# Spectroscopy Instrumentation



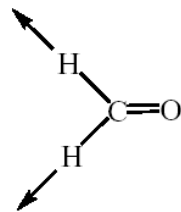
Bond Stretching



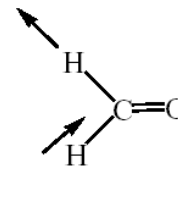
Bond Bending  
& Wagging

Spectroscopy  
measures interaction  
of light with  
materials

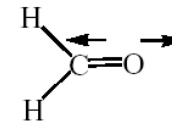
Polyatomic molecule  
with N atoms:  $3N-6$   
vibrations



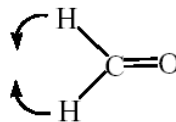
Symmetric C-H stretch



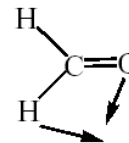
Asymmetric C-H stretch



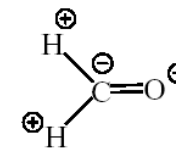
C=O stretch



CH<sub>2</sub> bend



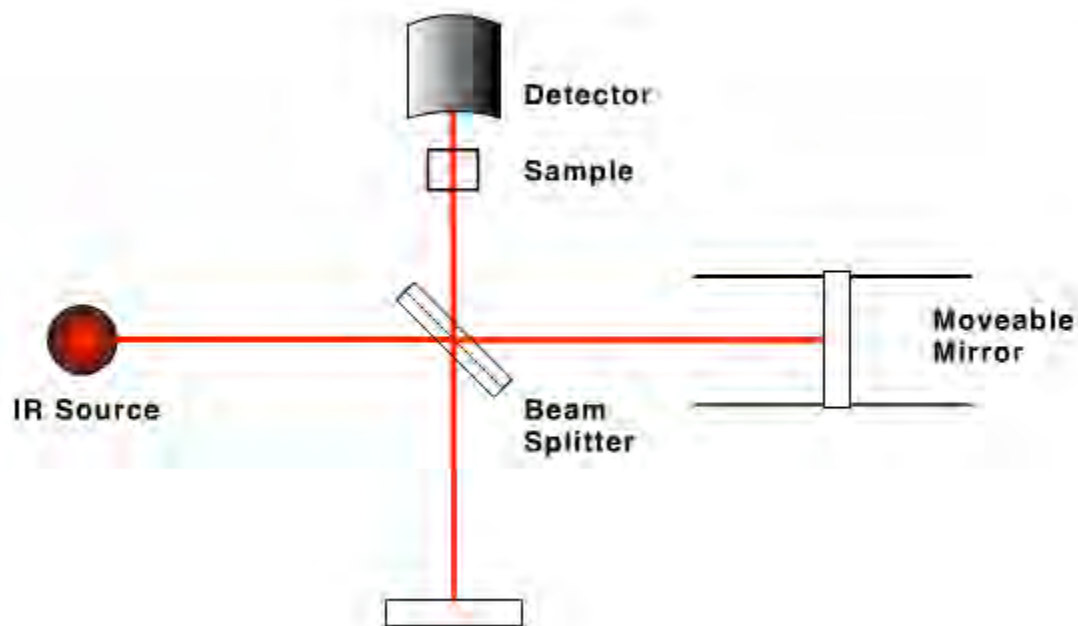
HCO bend



Out-of-plane bend ( $\oplus$  and  $\ominus$  here signify directions of motion not atomic charges)

# Spectroscopy Instrumentation

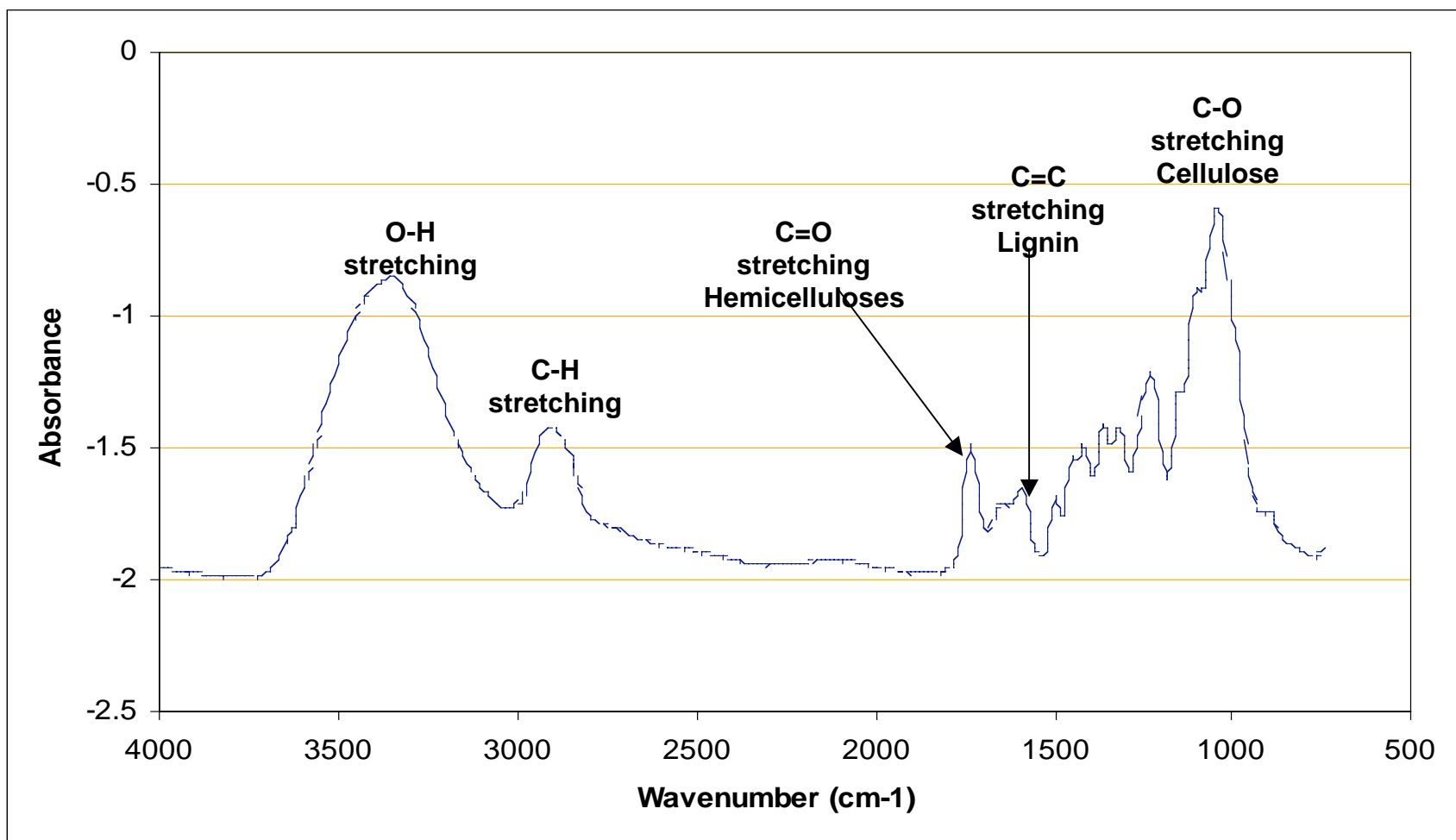
## *Fourier Transform Infrared (FT-IR) system*



- **Advantages**

- Higher signal-to-noise ratio
- Better spectral resolution ( $0.01 \text{ cm}^{-1}$ )
- Faster (seconds instead of minutes)

# Mid-Infrared Spectrum – Aspen



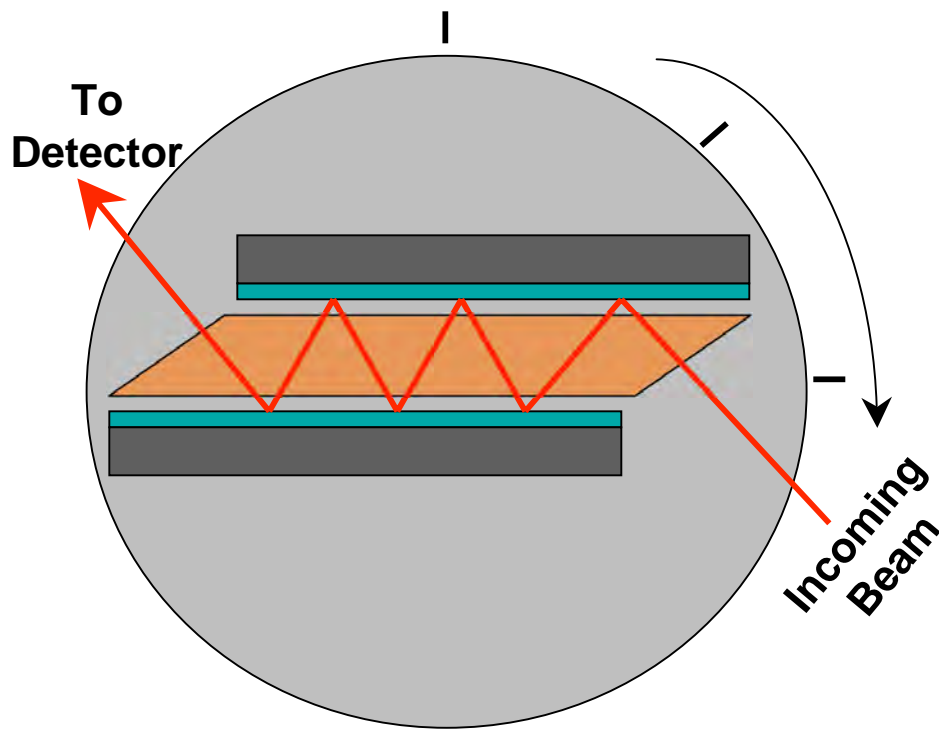
# Sampling Alternatives

- Transmission
  - Thin films, liquids
  - Prepared KBr disc
- Reflectance
  - Diffuse reflectance (DRIFT)
  - Attenuated total reflectance (ATR)
    - Variable angle
    - Single bounce HATR





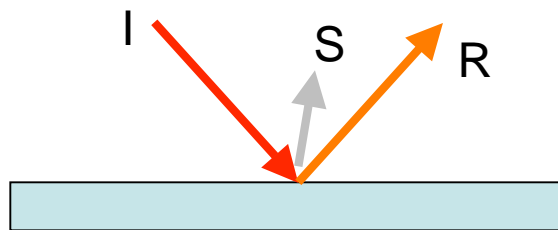
# Attenuated Total Reflectance - IR



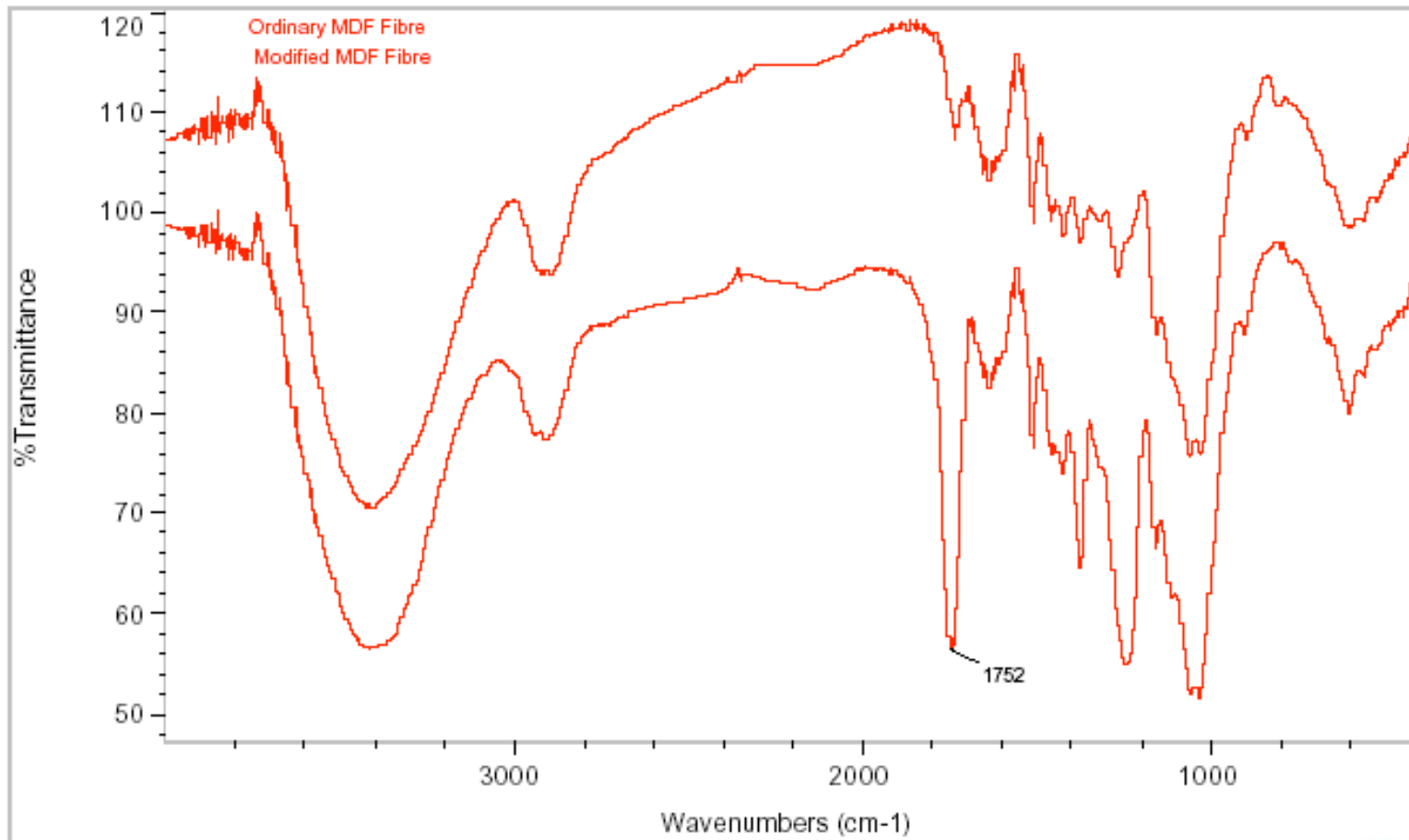
- IR Wavelength
- Penetration Depth
- Incident Angle
- Sample Contact
- Effective Pathlength
- ATR Crystal
  - ZnSe
  - Ge (less efficient)

# Diffuse Reflectance IR (DRIFT)

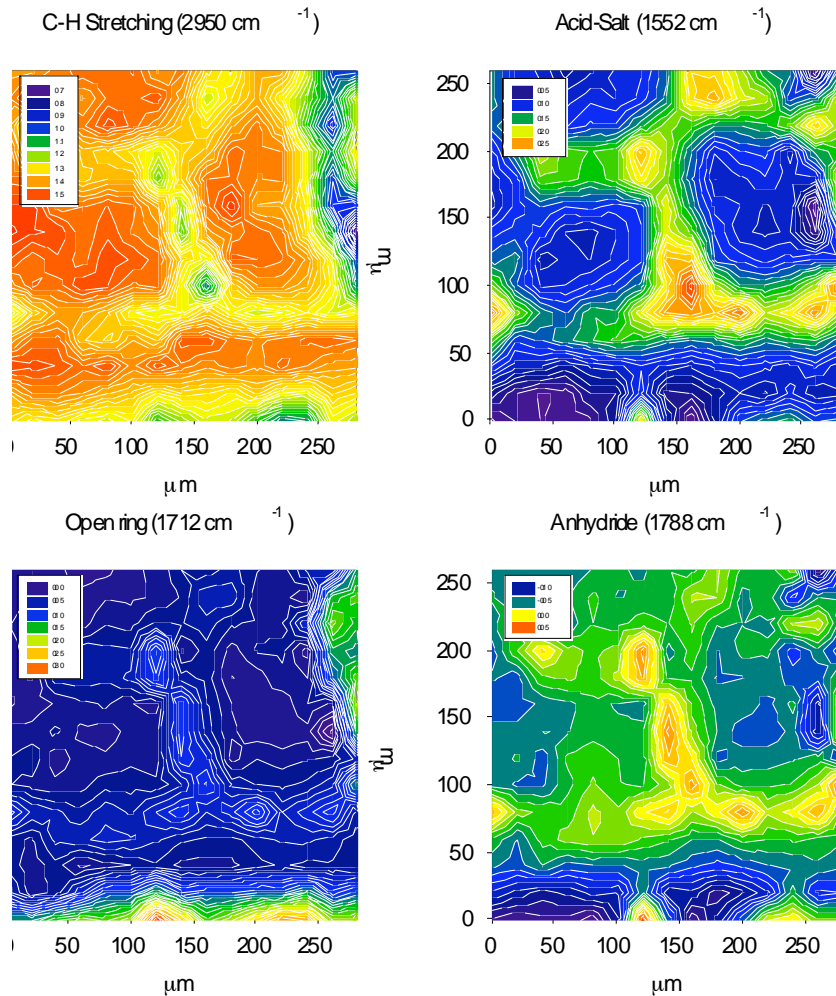
- Minimal sample prep
- Very high sensitivity
- Analyze most non-reflecting materials
- Analyze irregular surfaces/coatings
- Analyze large samples
- Refractive index
- Particle size
- Sample homogeneity and loading
- Concentration
- Uses Kubelka-Munk model for analysis



# Monitoring Chemical Reactions

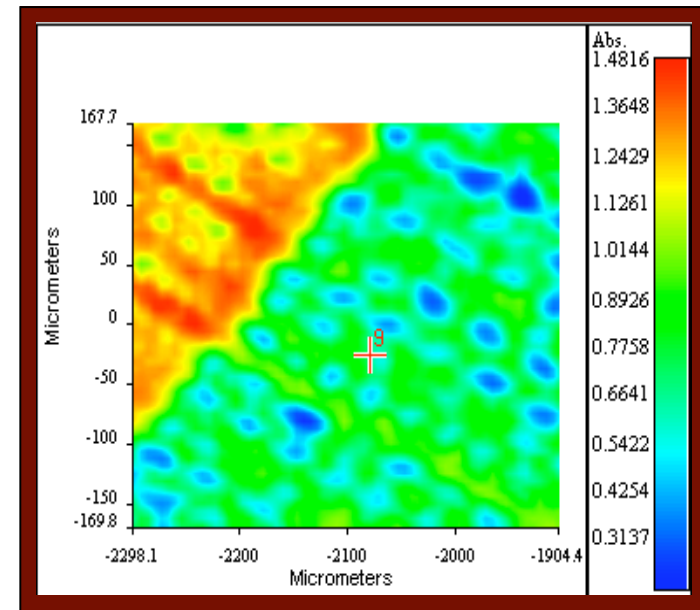


# FTIR Microscopy

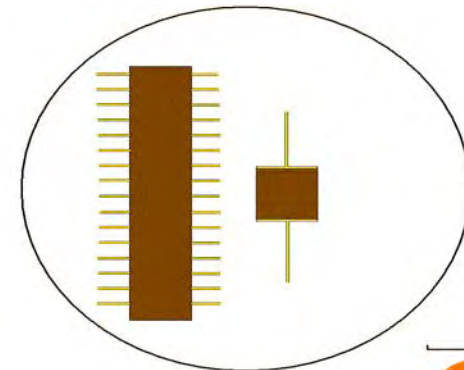


- Very versatile sampling capability
- Sample modes incl.
  - transmission
  - reflectance
  - attenuated total reflectance
- Visual maps available

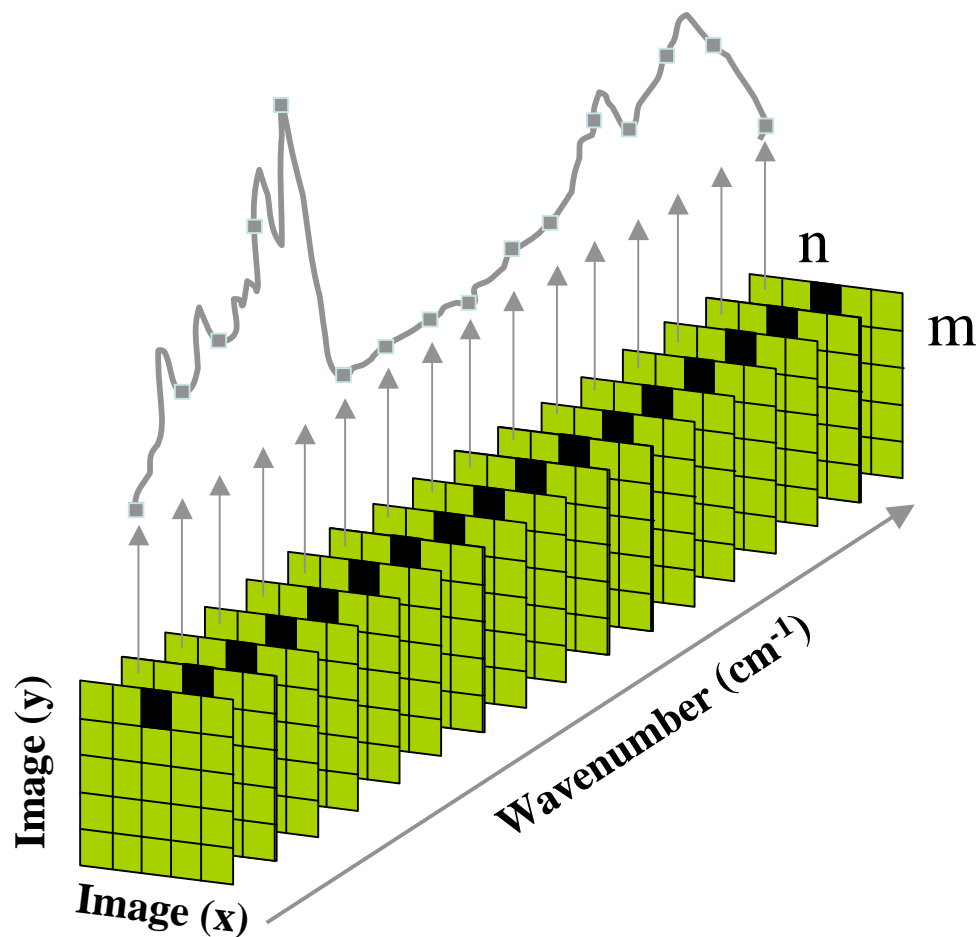
# Spectrum Spotlight Imaging



- Imaging at 6.25 and 25 micron resolution
- Mapping and line-scan modes
- Variable aperture, single-point microscope
- ATR

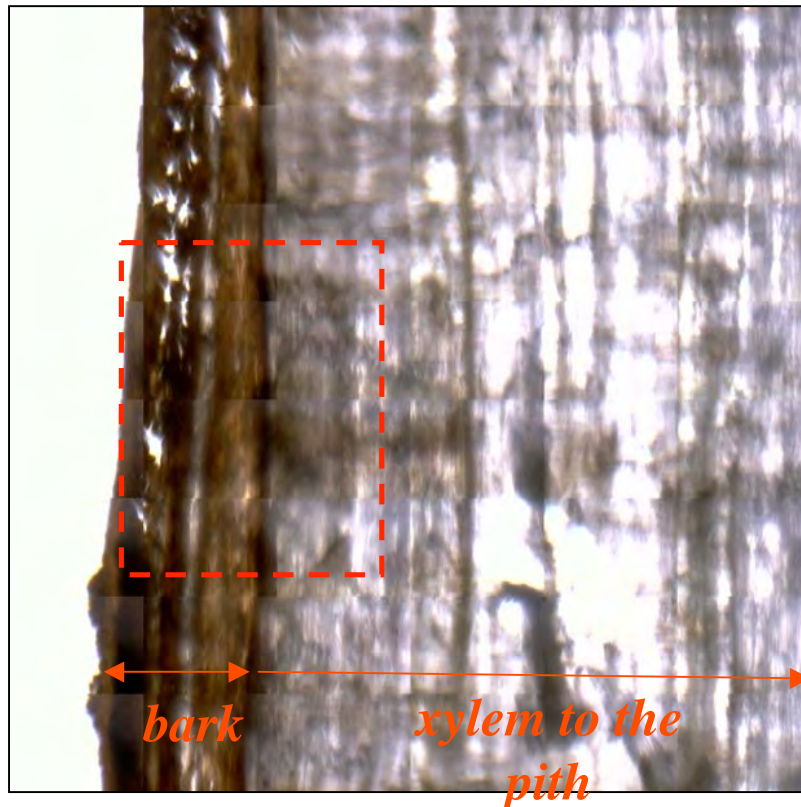


# The FTIR Image Hypercube

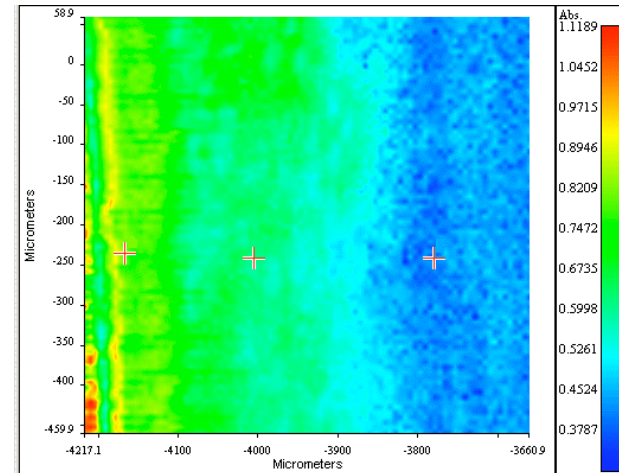


**Chemical images can be created from the total absorbance, and from absorbance data for each wavelength (wavenumber).**

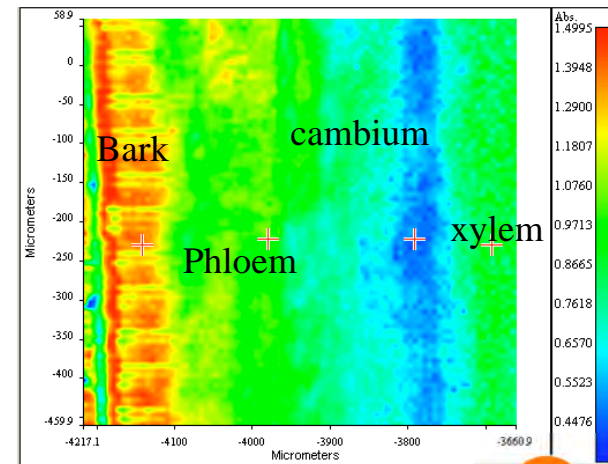
# FTIR Imaging of Wood



*Radial section of the control sample  
2000x2000  $\mu\text{m}$*

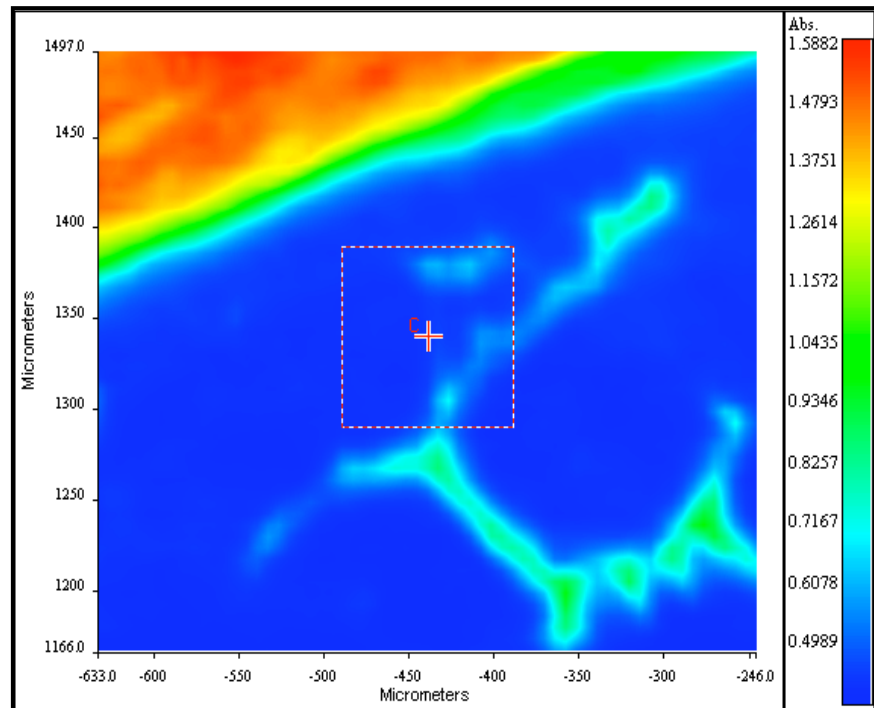
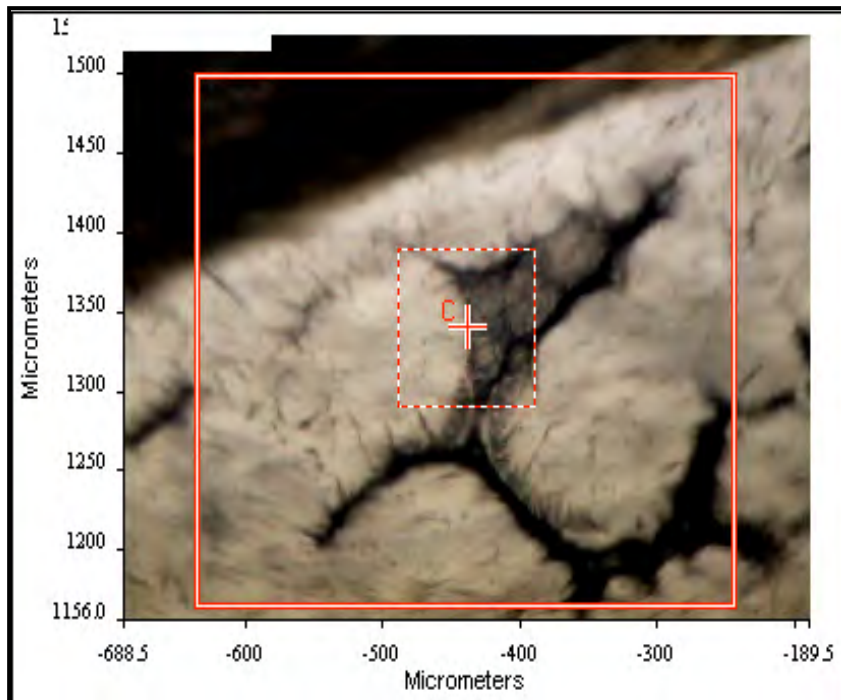


*Total Absorbance*



*Absorbance at 1324  $\text{cm}^{-1}$*

# PP/MAPP/Lubricant ( $1775\text{ cm}^{-1}$ )



*Visible Image:* apparent defect in polypropylene

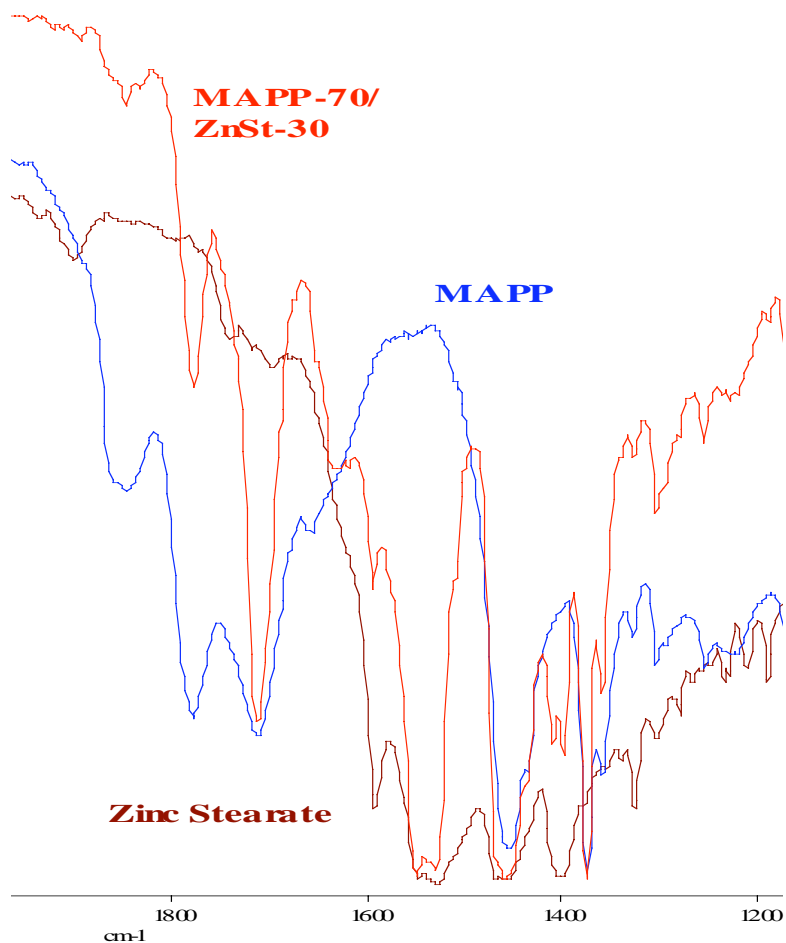
Amorphous zone between crystals nucleated from the wood surface and free crystals in the bulk of polymer.

*Chemical Image:* very strong IR absorption for wood silver; increased absorption in defect region

Concentration buildup of lubricant and coupling agent in the amorphous region

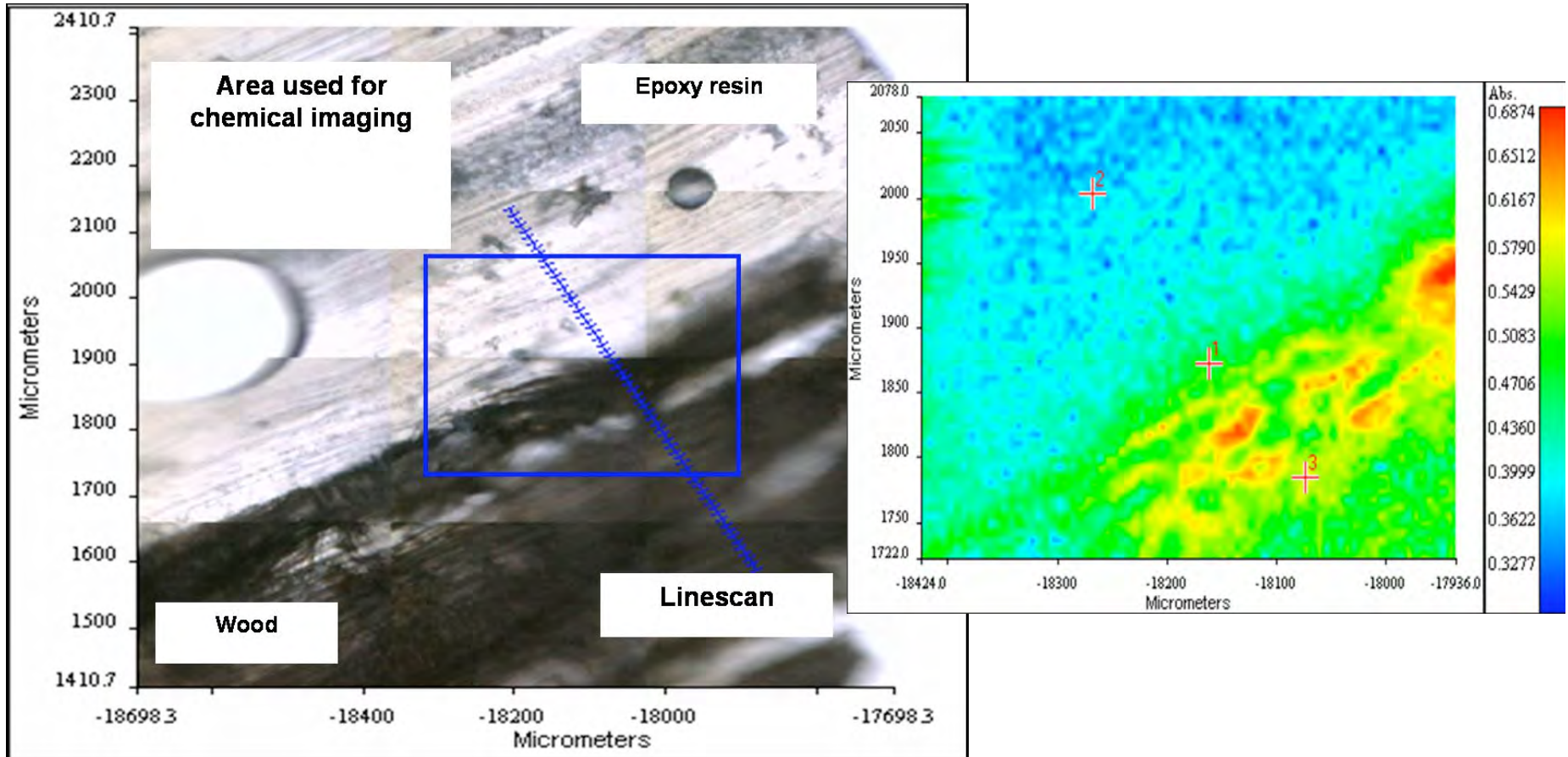


# Chemical Data from Images

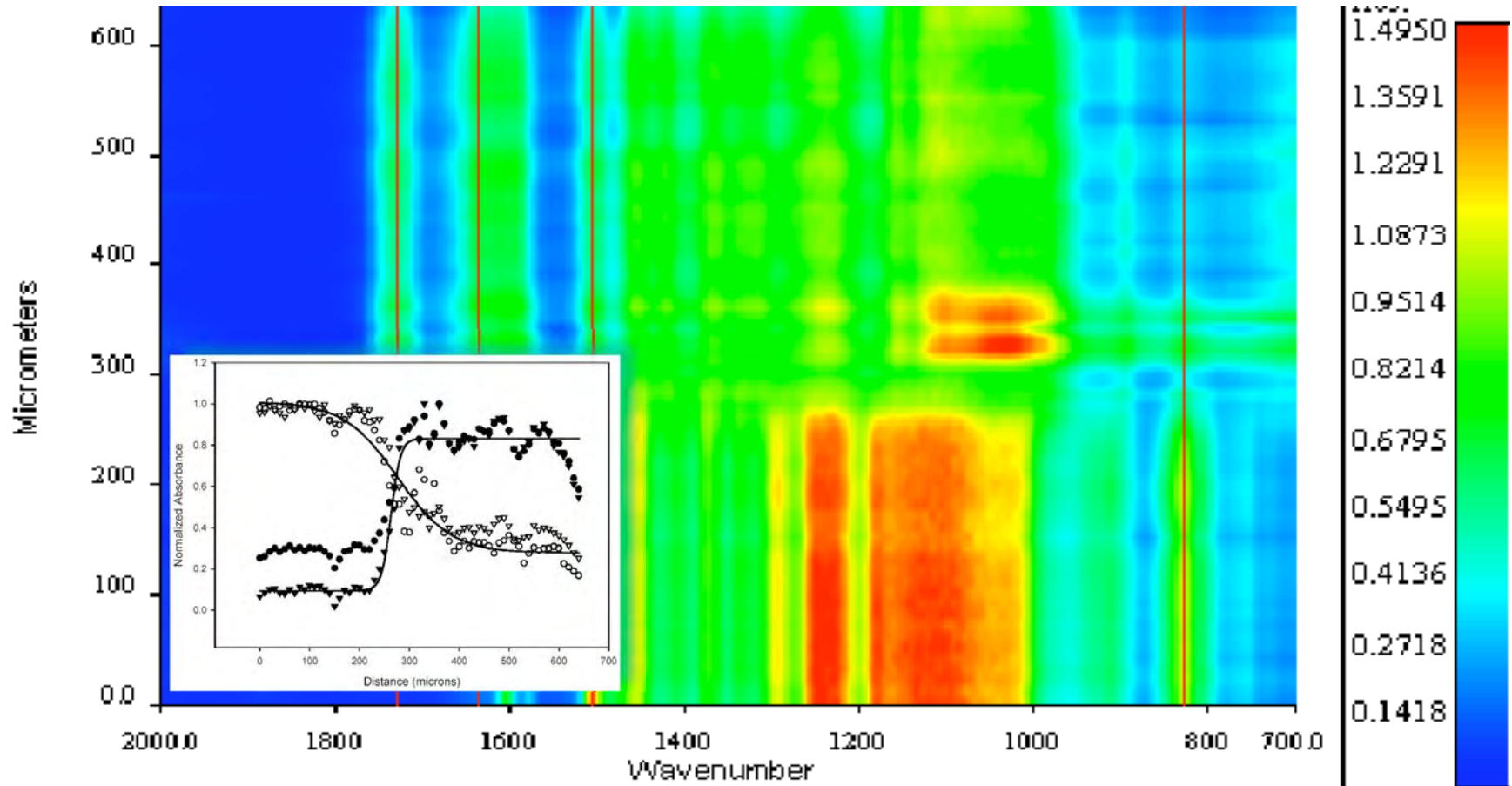


- Point mode
- 2 scan avg.; 8 cm<sup>-1</sup>
- Decrease in C=O anhydride stretch at 1775 cm<sup>-1</sup>
- Increase in C=O stretch of acid at 1712 cm<sup>-1</sup>
- Indicates lubricant interference

# Quantitative Analysis of Wood Bondlines



# Quantitative Analysis of Wood Bondlines



# ATR Imaging System

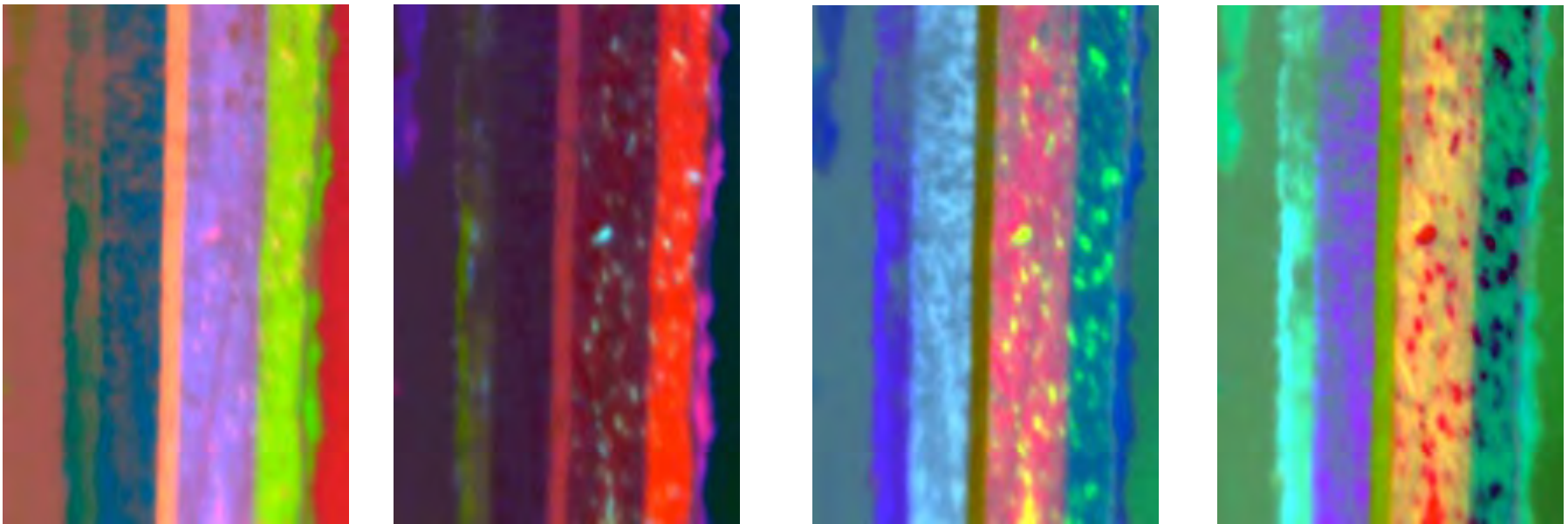
- Spectral performance (S/N)
- Image size and flexibility
- Ultimate spatial resolution
- Ease of use
- Background handling
- Information retrieval from images



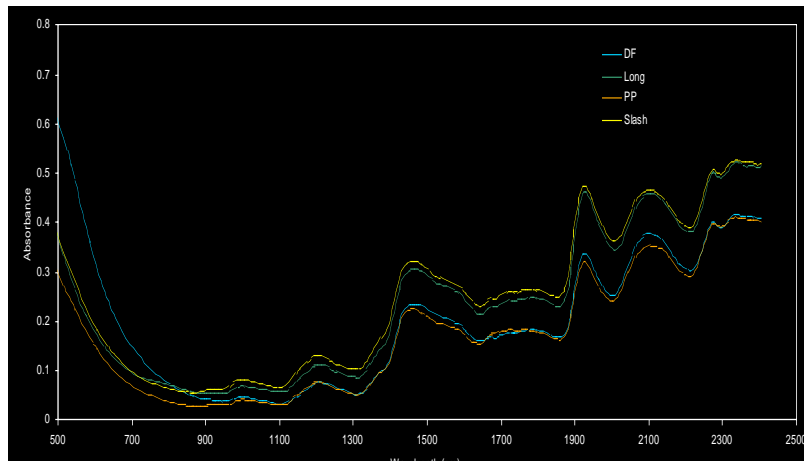
# ATR Imaging/Processing

**Paint Chip Image (200  $\mu\text{m}$  by 300  $\mu\text{m}$ , 1.56  $\mu\text{m}$  pixel 8  $\text{cm}^{-1}$ , 16 scans / pixel)**

**Processing: spectral differential, average subtract, PCA, colour compositing**



# Near Infrared Spectroscopy



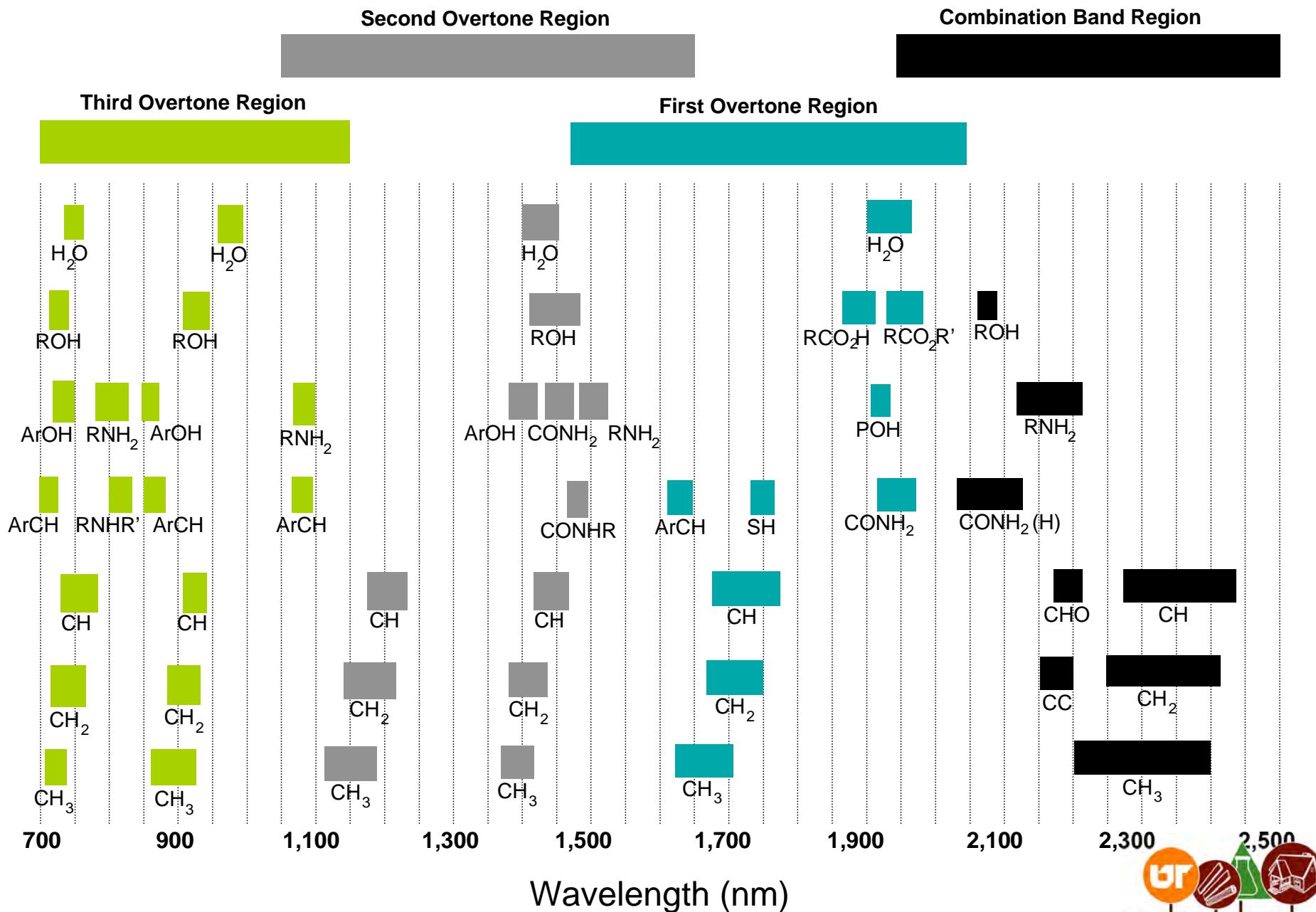
## Advantages

- Fast data acquisition
- Versatile sampling
- Affordable technology
- Raw material information

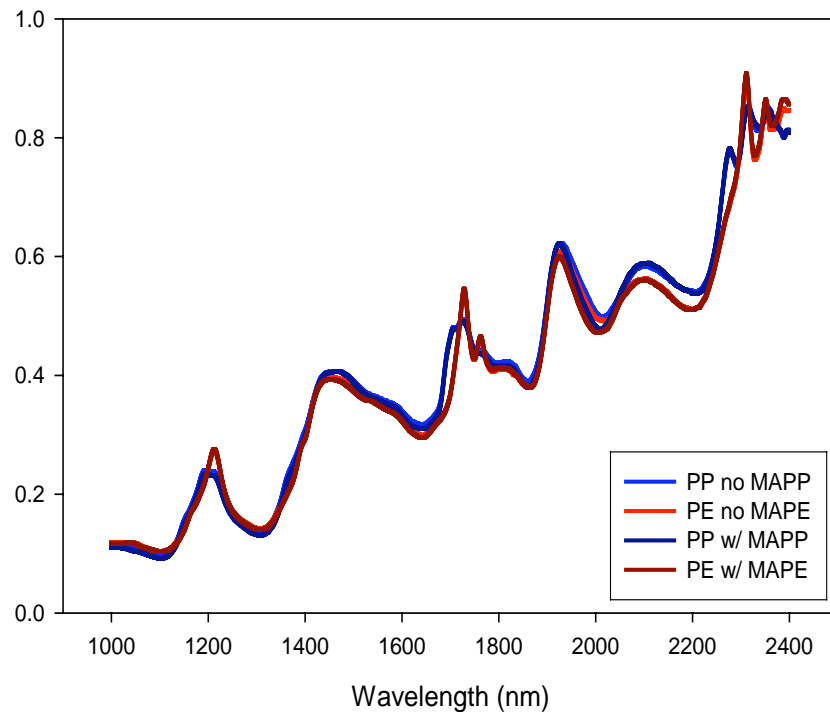
## Limitations

- Difficult visual interpretation
- Too much data!

# NIR Band Assignments



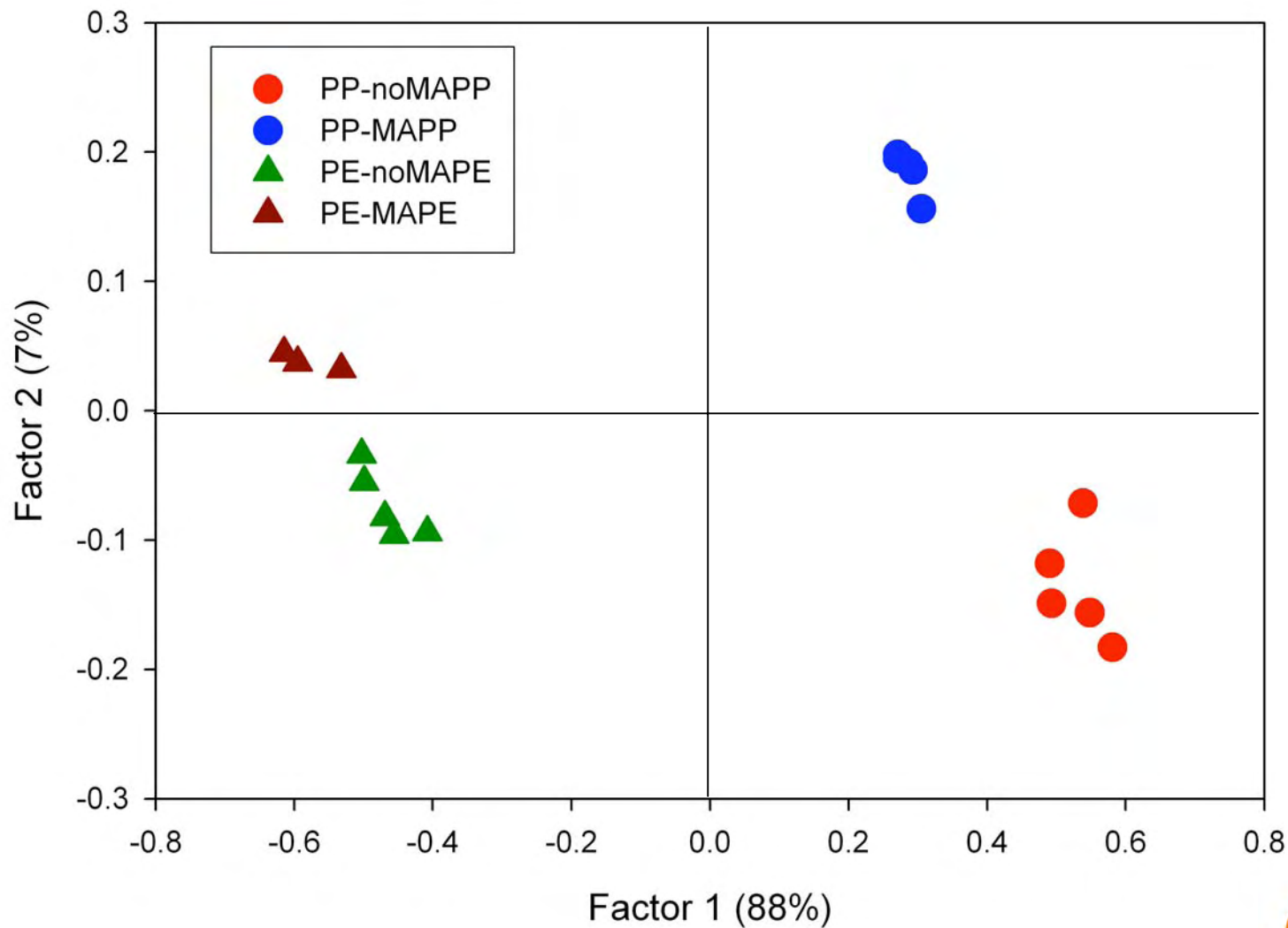
# NIR Spectra of Materials



- Distinctive peaks found at 2280, 1707 and 1215 nm
- Related to  $-CH$  substitution patterns in polyolefins
- No obvious differences with coupling agent addition



# Principal Component Analysis



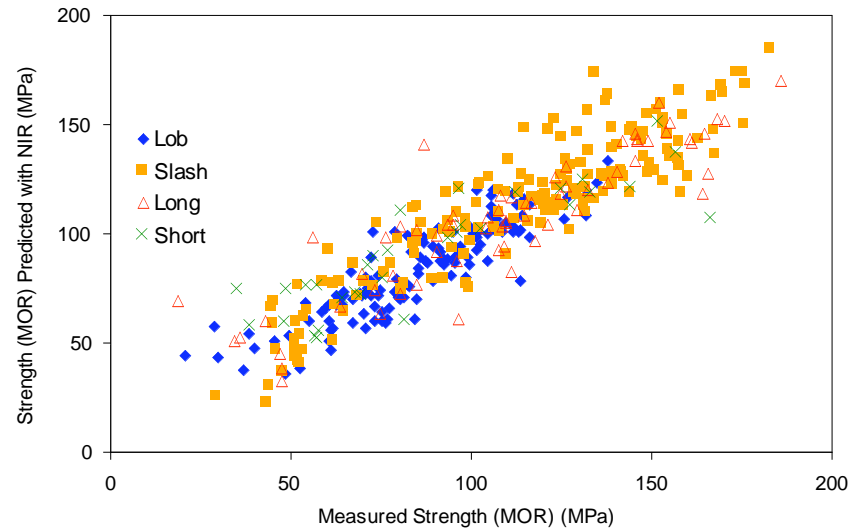
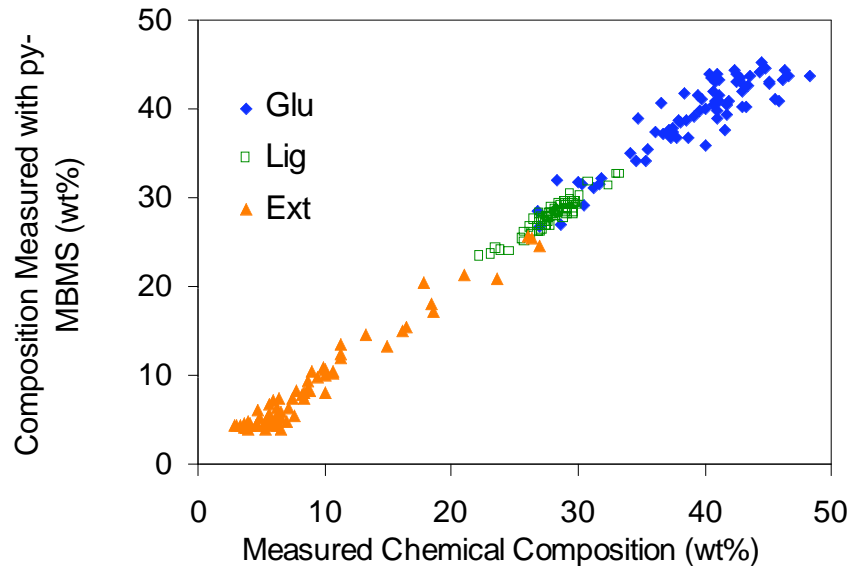
# Projection to Latent Structures

Perform simultaneous extraction of orthogonal latent vectors that “explain” the variance of both matrices

*PLS Model*

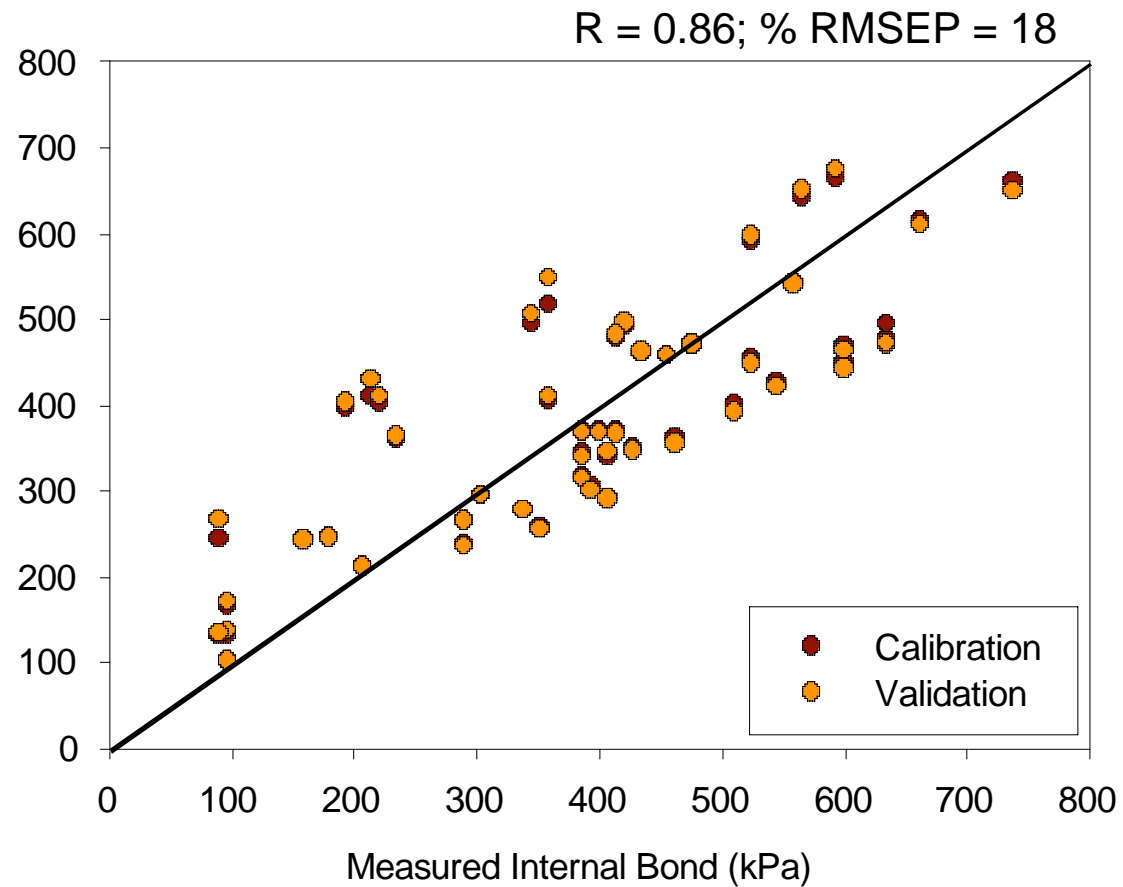


# NIR/MVA Characterization of Wood

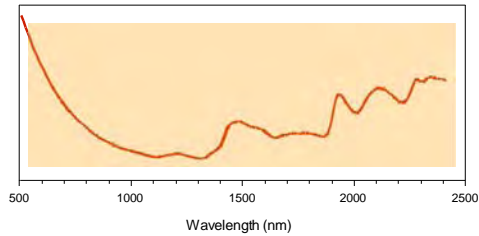


- **Fully cross-validated models for robustness**
- **Utilize calibration and validation set to evaluate performance**
- **Ensure data encompasses the full range of variable space**

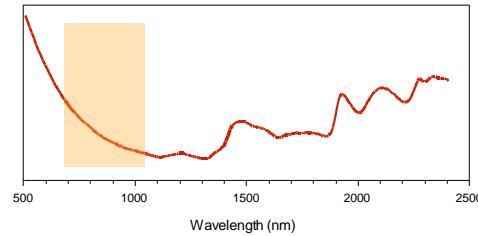
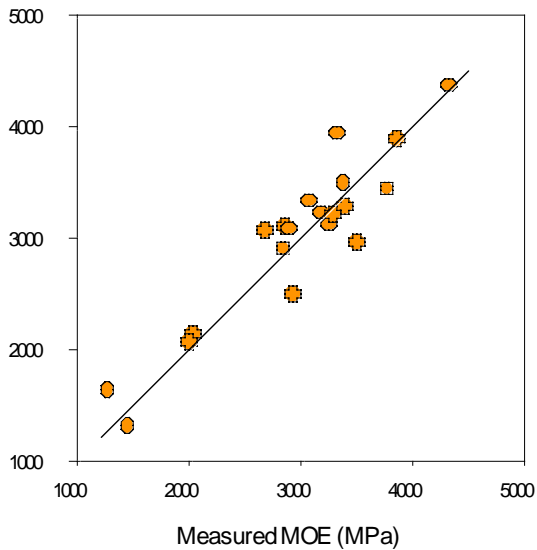
# NIR Prediction of Internal Bond (Interior Spectra)



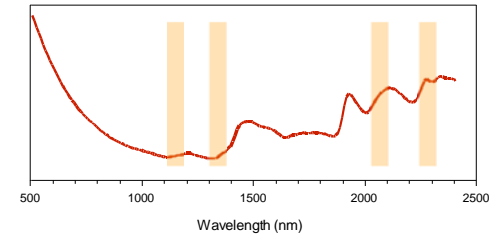
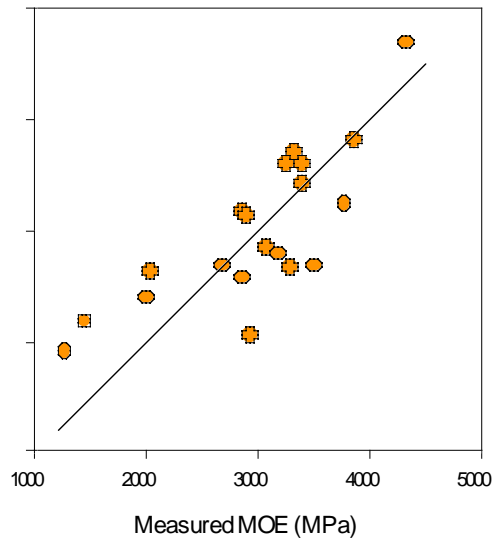
# Reduced Wavelength Models



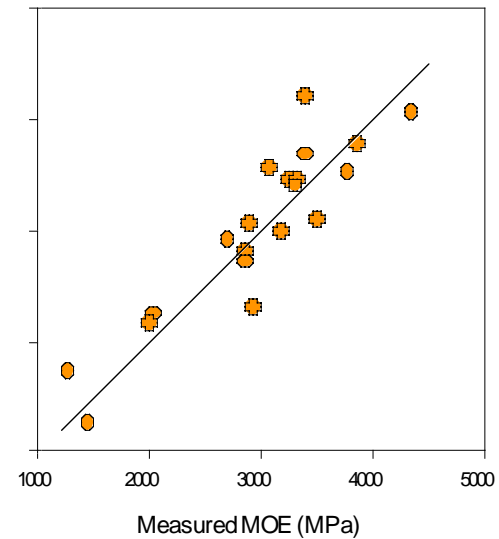
R=0.93  
RMSEP=271.6



R=0.79  
RMSEP=468.5



R=0.91  
RMSEP=325.9



# NIR Sampling Methods



**Field Sampling**



**Process Monitoring**



# Summary Remarks

- Infrared spectroscopy offers unrivaled versatility in sampling
- Advances in technology have expanded access to data/information
- Near infrared has emerged as a valuable analytical instrument for wood products
- Quantitative analysis of IR data expanded using multivariate statistics
- IR is relevant to all stages of wood use: (1) raw material, (2) furnish, (3) QA/QC, and (4) life-cycle or in-service

# For Additional Information

## References

- H. Martens and T. Naes. Multivariate Calibration, Wiley, New York
- Ciurczik, et al. Hdbk. Of NIR Spectroscopy.

## Mfr. Web Sites

- Foss NIR ([www.foss-dk.com](http://www.foss-dk.com))
- Analytical Spectral Devices ([www.asdi.com](http://www.asdi.com))
- Bruker Optics ([www.bruker.com](http://www.bruker.com))
- Ocean Optics ([www.oceanoptics.com](http://www.oceanoptics.com))
- PerkinElmer Instr. ([www.perkinelmer.com](http://www.perkinelmer.com))
- Thermo-Nicolet ([www.thermonicolet.com](http://www.thermonicolet.com))
- Spectral Dimensions ([www.spectraldimensions.com](http://www.spectraldimensions.com))
- Camo ([www.camo.com](http://www.camo.com))