A High Resolution Laser-Based Technique for Quantifying the Elemental Composition of Wood: Applications in Biomass Characterization

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Outline

- Rationale
- Experimental Setup
- Advantages of LIBS
- Results:

  Natural and treated wood

  Forest fire affected wood
- Multivariate Model

  LIBS model approach

Sensors and controls are important components of the forest industry

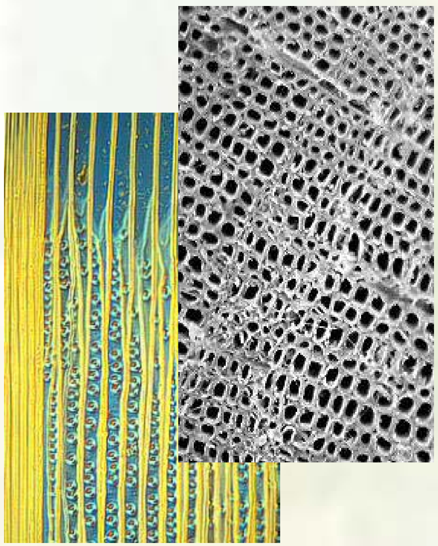
American Forest & Paper Association (1999)

Sensors & Control Task Group *- "Good control requires* *<u>timely knowledge of process parameters</u>, including <u>accurate measurement</u> or estimation of key variables."*

DOE/OIT (2003)

Crosscutting sensors and controls *– "Focus is on control systems, <u>chemical and physical property measurements, numerical</u> processing, imaging, and emissions measurement."*

Measurement focus of forest product industry has been on organic constituents of wood – cellulose, hemicellulose, lignin, fiber properties, strength, stiffness, etc.

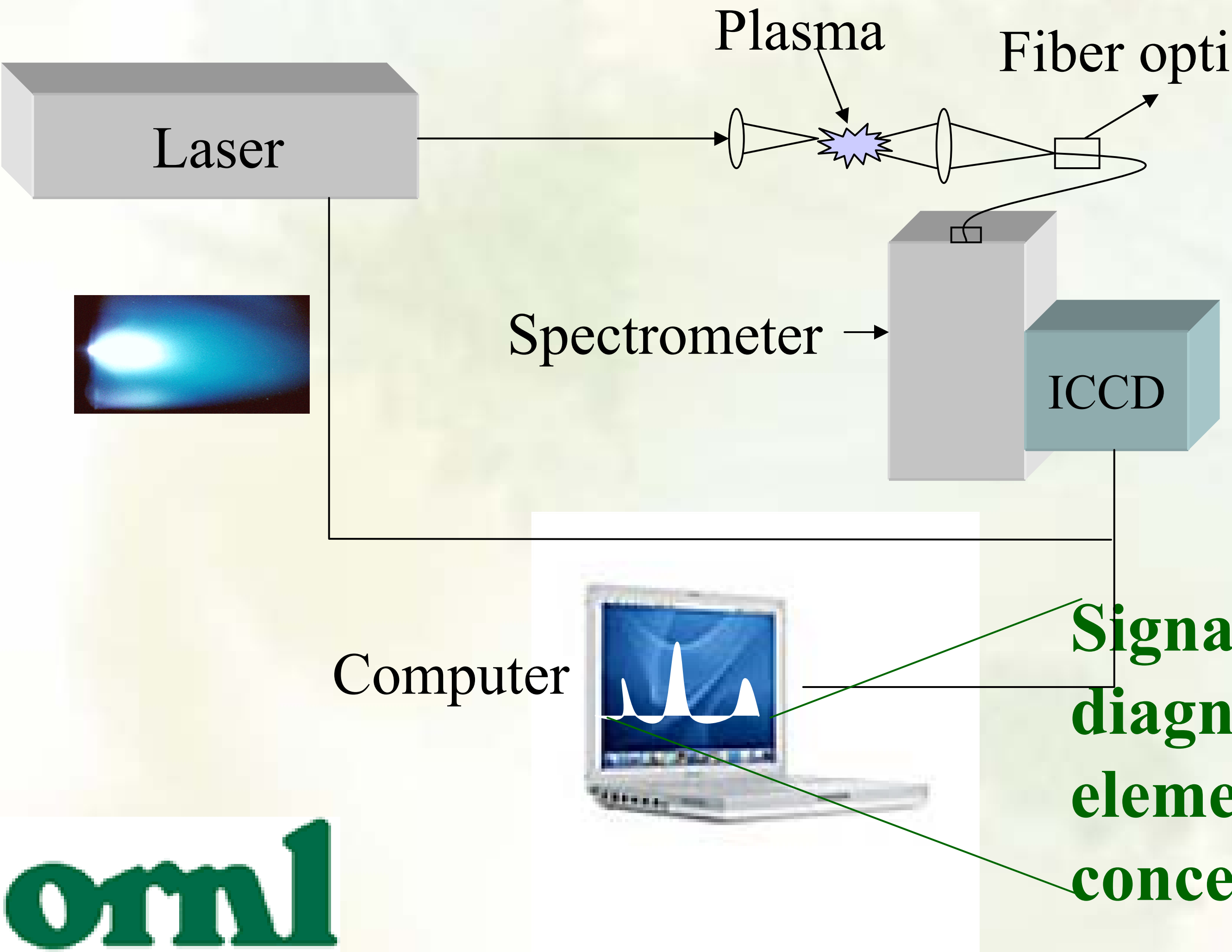


^{13}C-NMR
Raman
NIR
Densitometry

We believe that an opportunity exists to complement this focus by now examining the inorganic or elemental composition of wood in environmental events

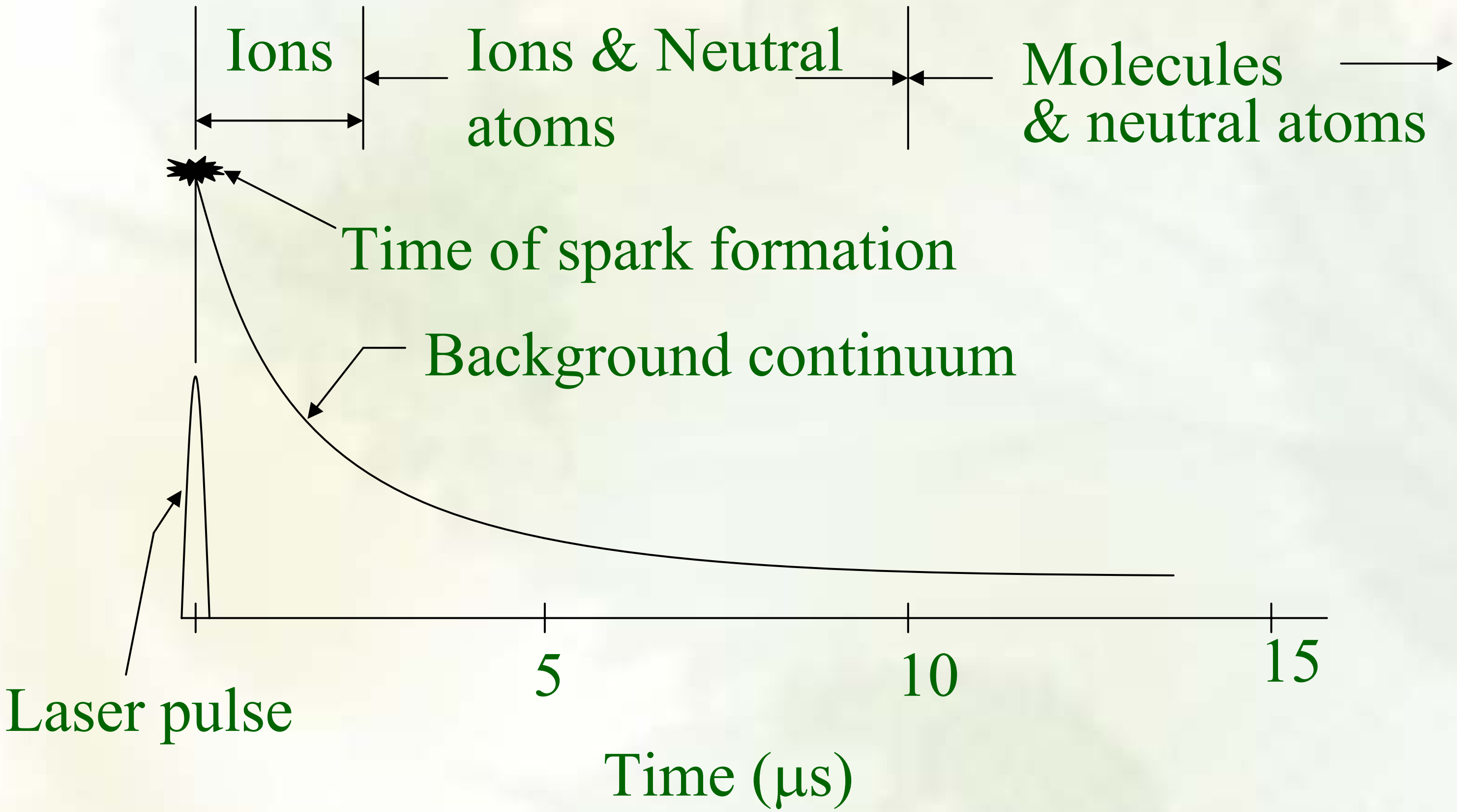
Experimental Setup for LIBS

LIBS = Laser-Induced Breakdown Spectroscopy

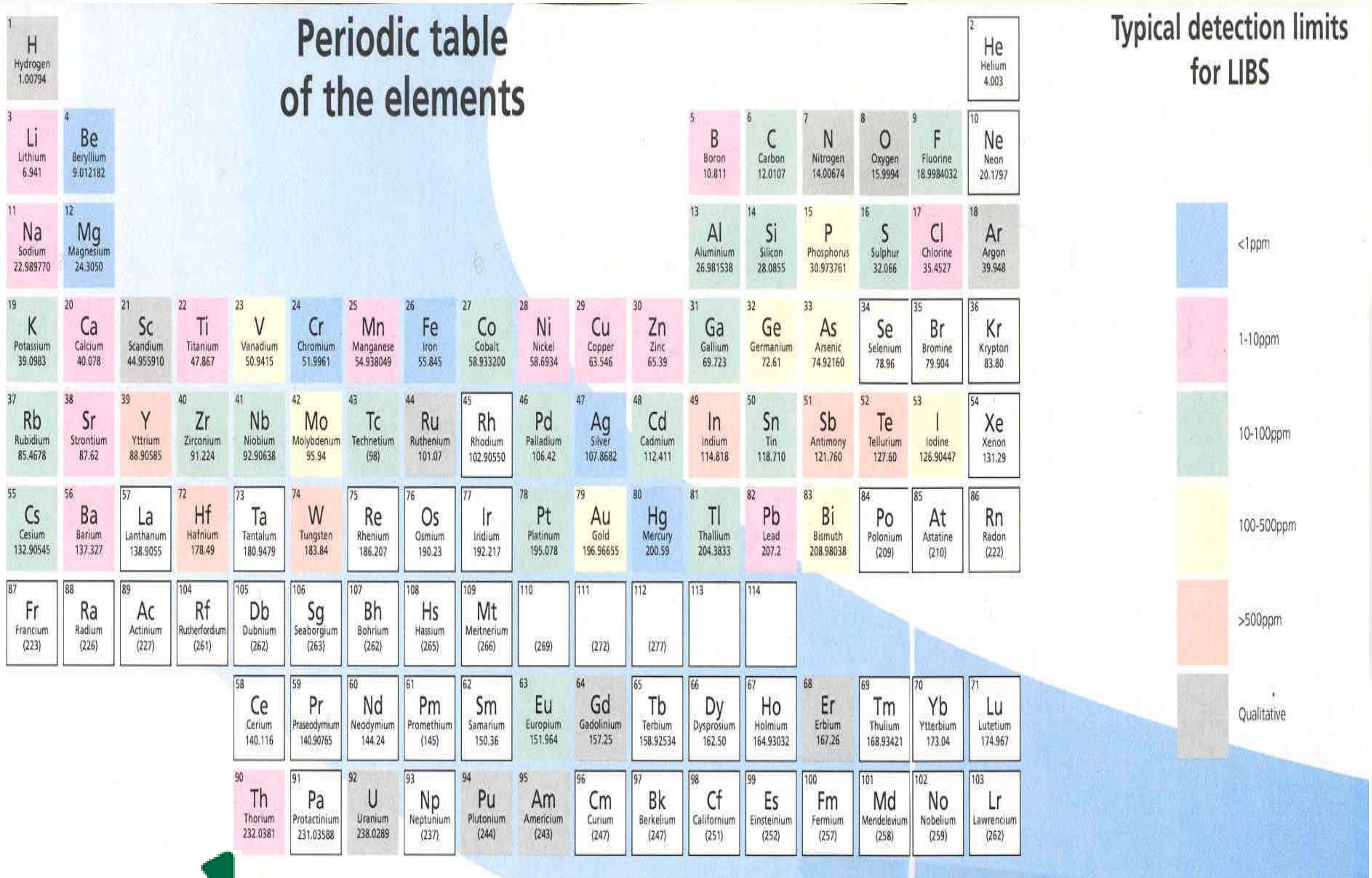


Signal is diagnostic of total elemental concentration

Temporal Resolution of a Laser Spark



Periodic Table for LIBS



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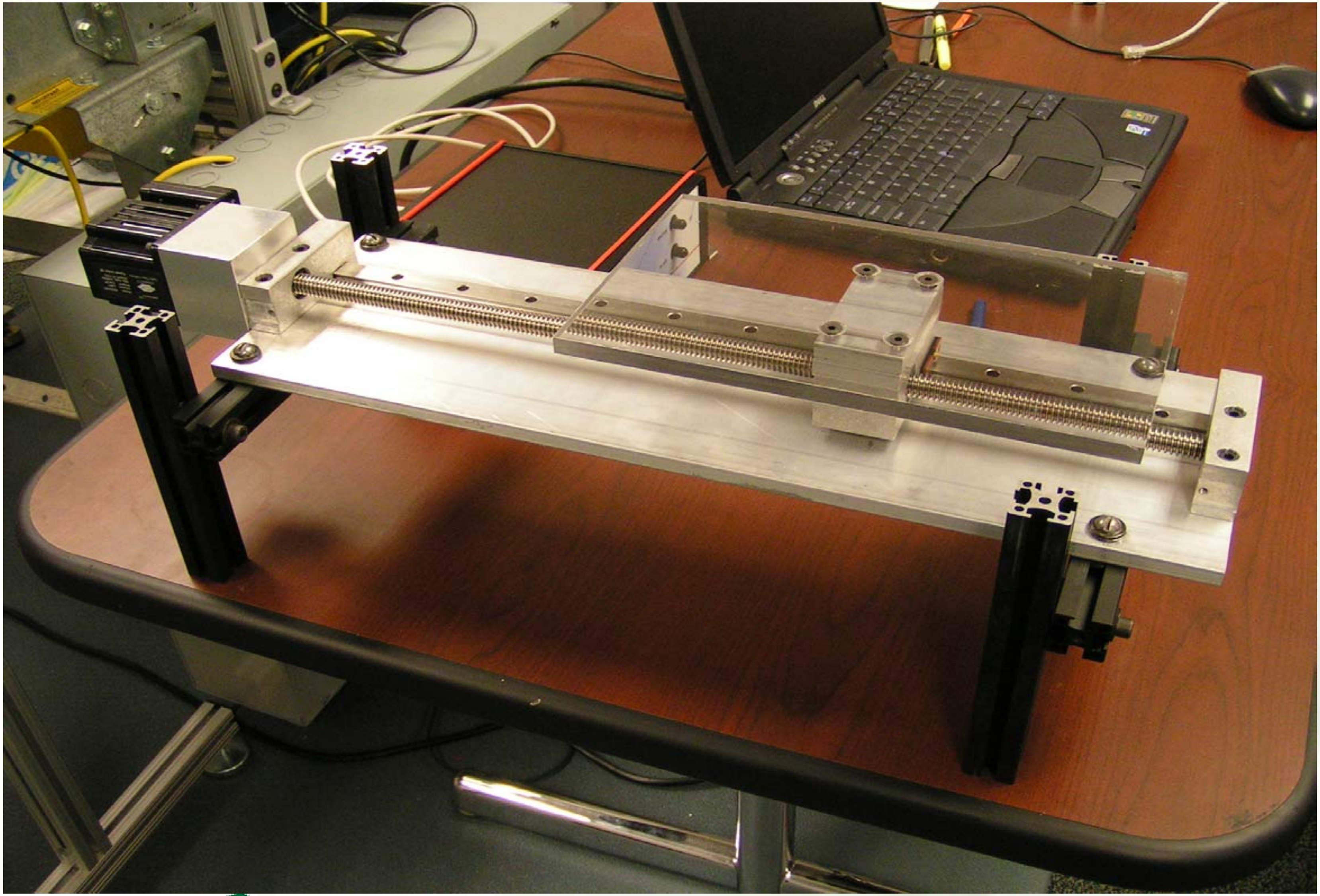
Advantages of LIBS

- ***High throughput detection***. Identification of metals and non-metals in a second.
- ***Multi-elemental analysis***. Simultaneously detect all elements with high spectral resolution from solids, liquids, gases, and aerosols.
- ***Remote analysis***. Fiber optics permit instrument operation away from a hazardous/industrial site.
- ***Minimal sample preparation*** and no waste generation.
- ***Continuous monitoring capability***. Depth profiling and mapping can be accomplished.
- ***Robust instrumentation.*** No moving parts in the instrument.

Translational Stage-High Spatial Resolution Data



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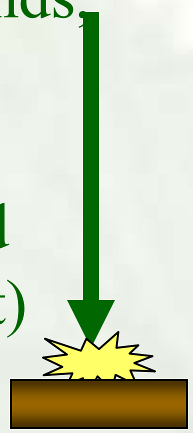
Dendrochemistry using LIBS

Laser Interaction with Matter

Laser interacts with the different states of matter differently:

Laser interaction

- Solid (absorptive, I_b is less than gases, bonds, breakdown is wavelength dependent)



- Liquid (transparent, I_b is more than a solid but less than gases, wavelength dependent)
- Aerosol (particle size dependent, solid vs droplet, I_b is between solid and liquids, wavelength dependence)
- Gas (transparent, breakdown is difficult, wavelength dependent)

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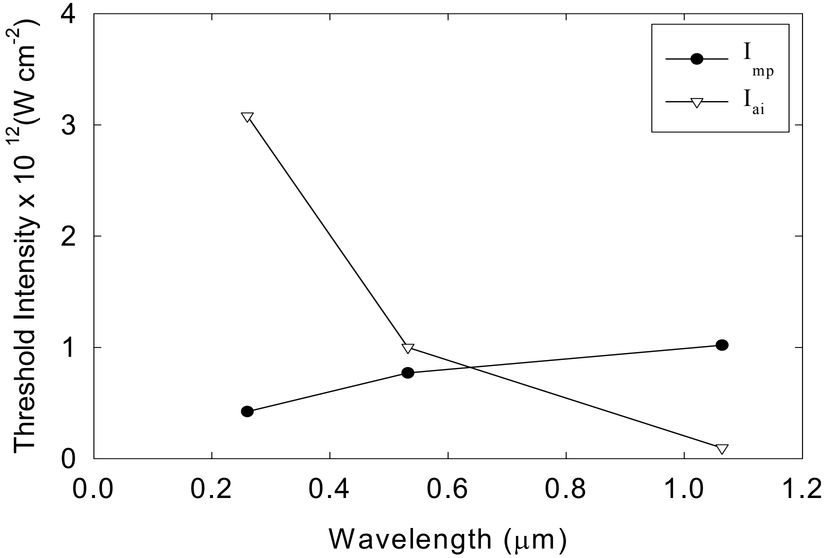
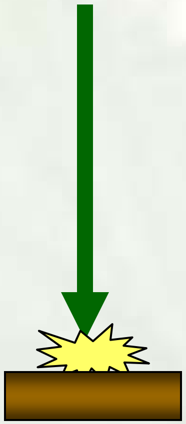
Dependence of Laser Wavelength on Threshold of Breakdown

—●— Multiphoton Breakdown Thresholds

—▽— Avalanche Breakdown Thresholds





Understanding the Parameters in LIBS

The breakdown threshold, I_b, of a gas is given as:

$$I_b = (n_{ad}/g_g)\,[\phi/v_{ca}]^2\,(1/\tau_e)\,\ln(n_e V_\nu)$$

where n_{ad} is the neutral atom density,

g_g the gas-dependent parameter,

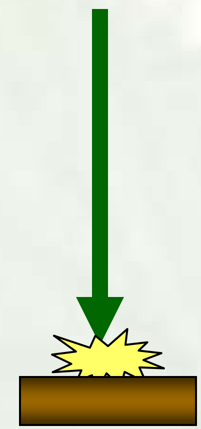
ϕ the laser frequency,

τ_e duration of laser pulse,

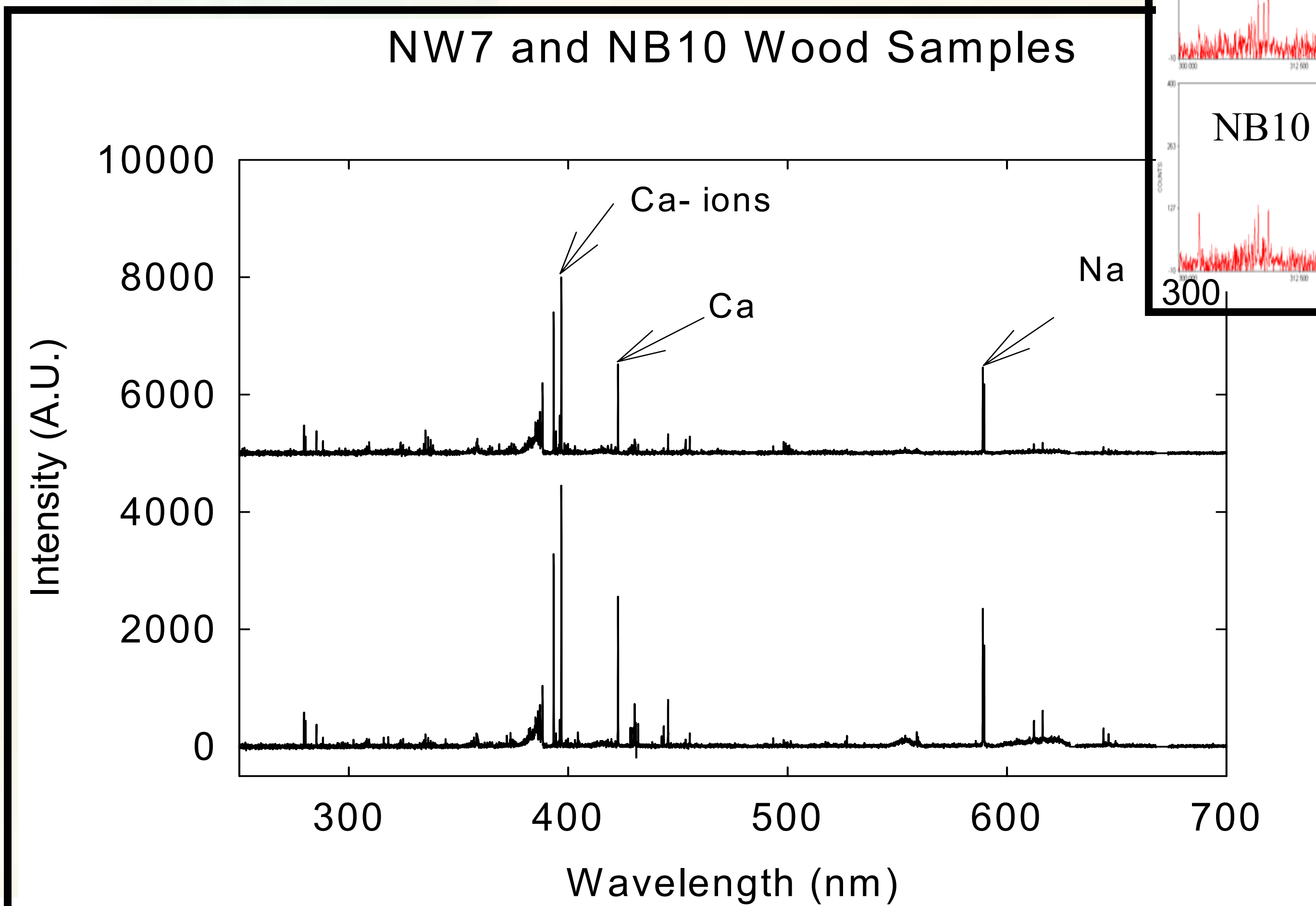
n_e electron density,

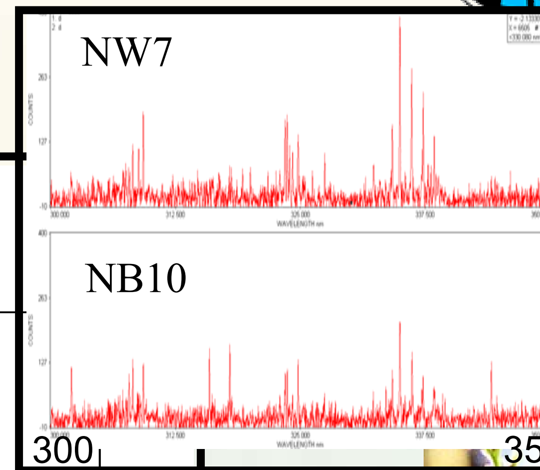
v_{ca} the neutral atom collision frequency,

V_ν the focal volume of the laser beam.

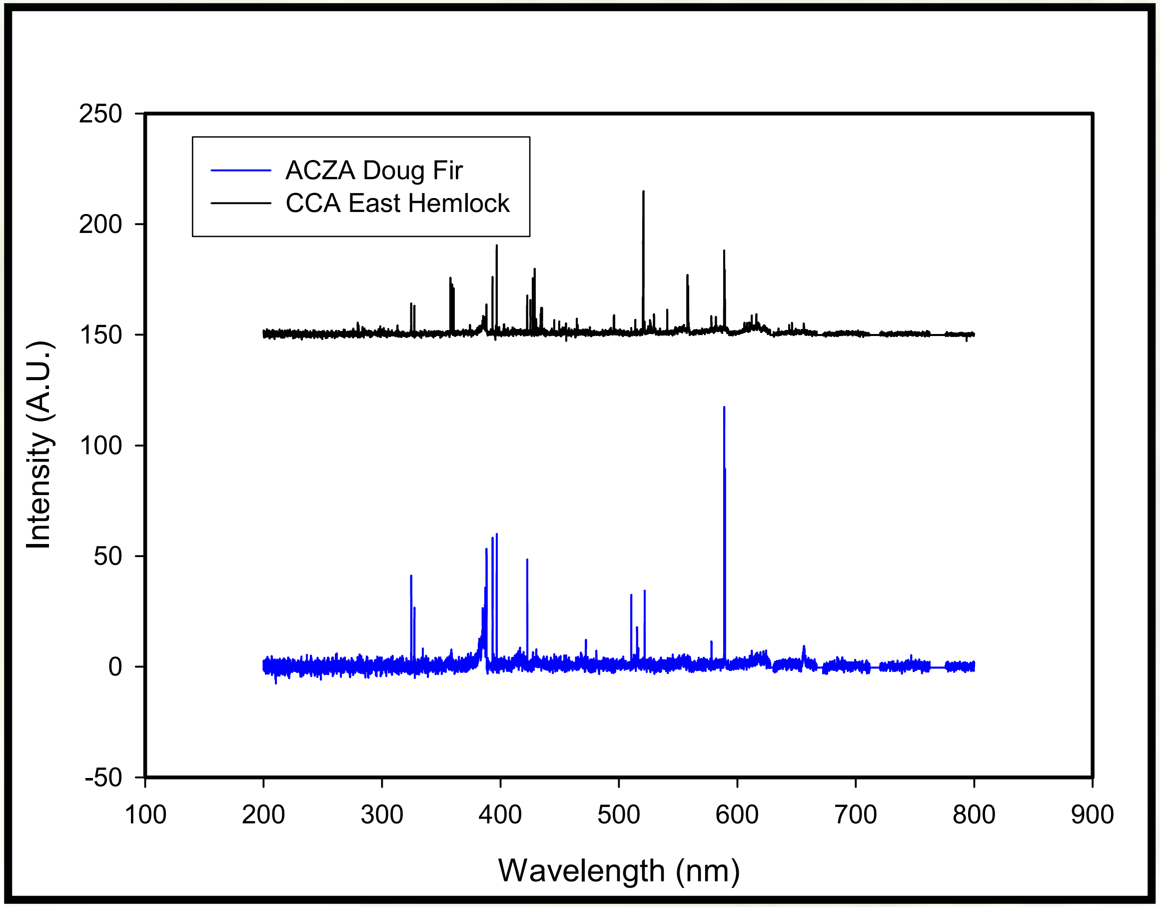


Comparison of LIBS spectra for two different natural woods.





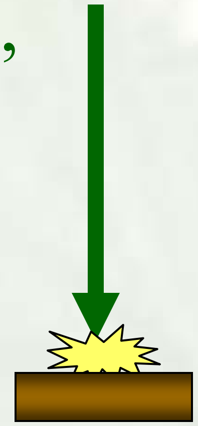
Comparison of LIBS spectra for two different treated woods.



Quantification of LIBS Data

LIBS Model

Input characteristics
(laser energy, pulse width, focal volume, plasma temperature)



Output characteristics
(spectrum, peak heights, Area under peaks, correlation to another technique)

Multivariate Analysis.

MVA

PCA: a non-directed analysis of the spectral data

PLS: directed analysis

Construction of Regression Model

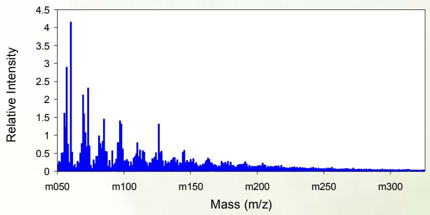
Properties of Interest

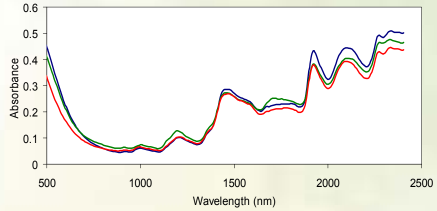
Process variable

Strength, Stiffness

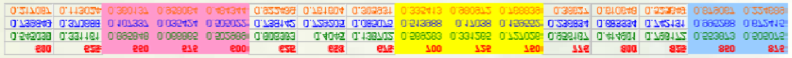
Elemental content

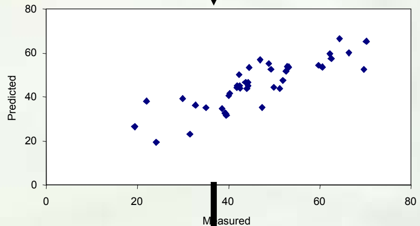
Calibration set





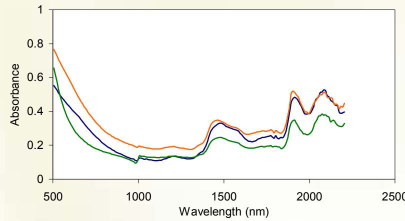
Spectral data



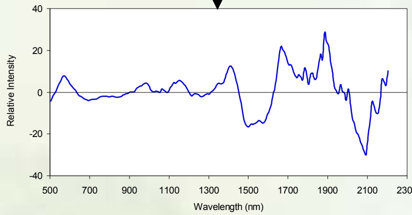


Correlation Model

Test set unknowns



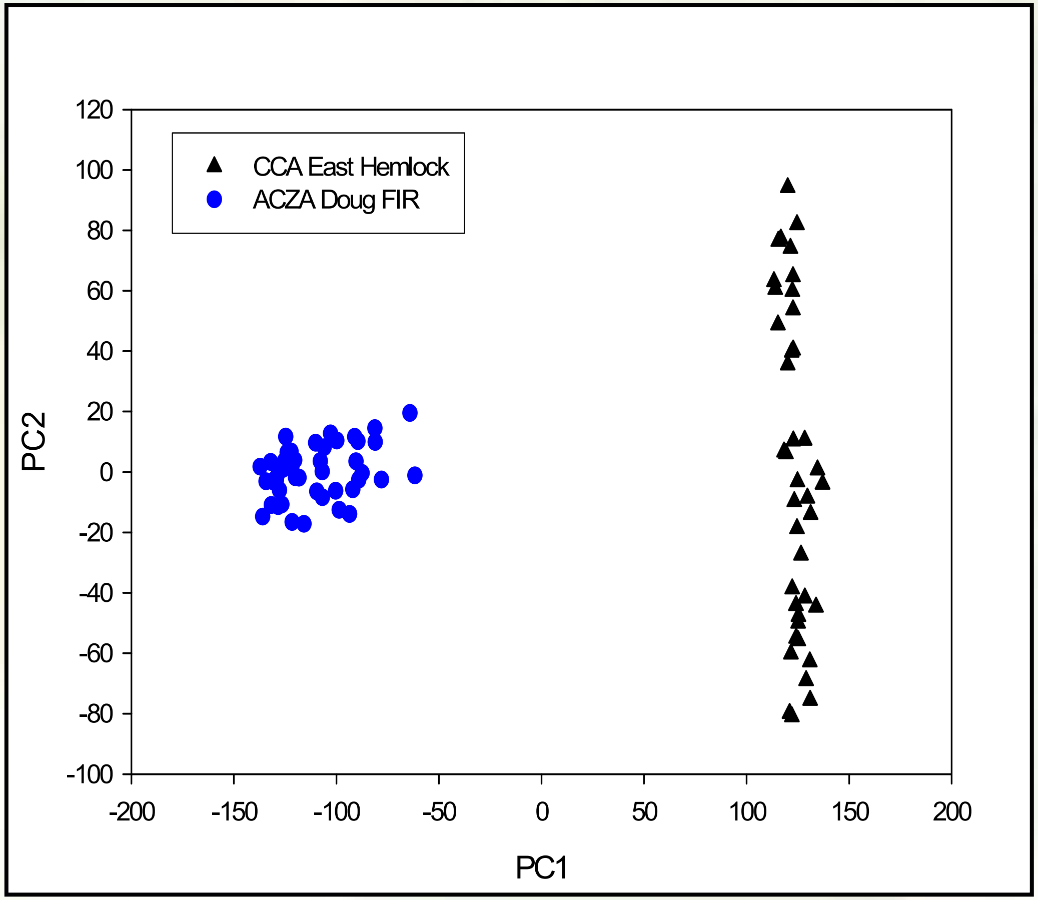
Spectral data



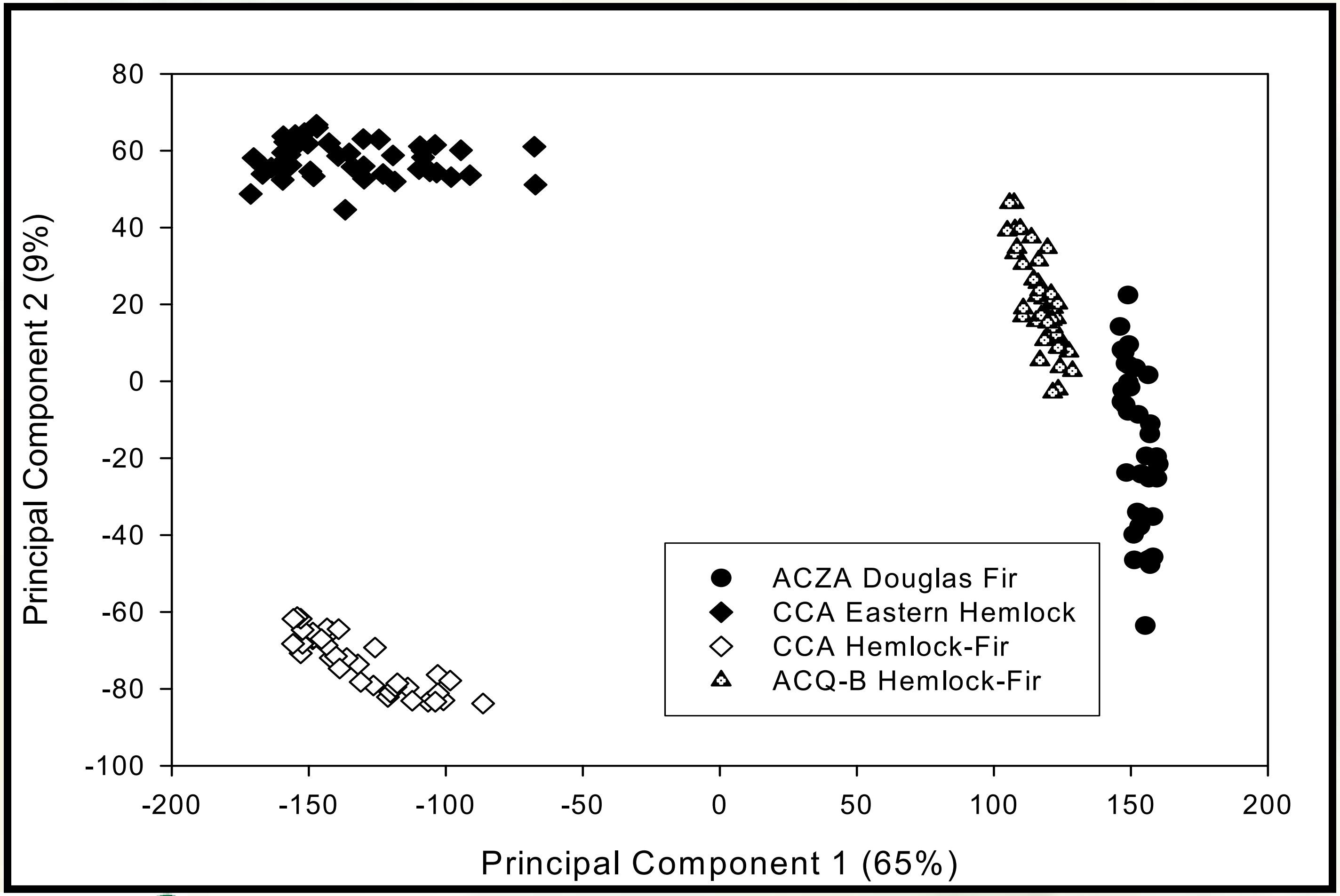
Regression Coefficients

Predicted Properties

Principal component analysis used to observe any clustering or separation in the sample sets.



Principal component analysis for four different treated woods



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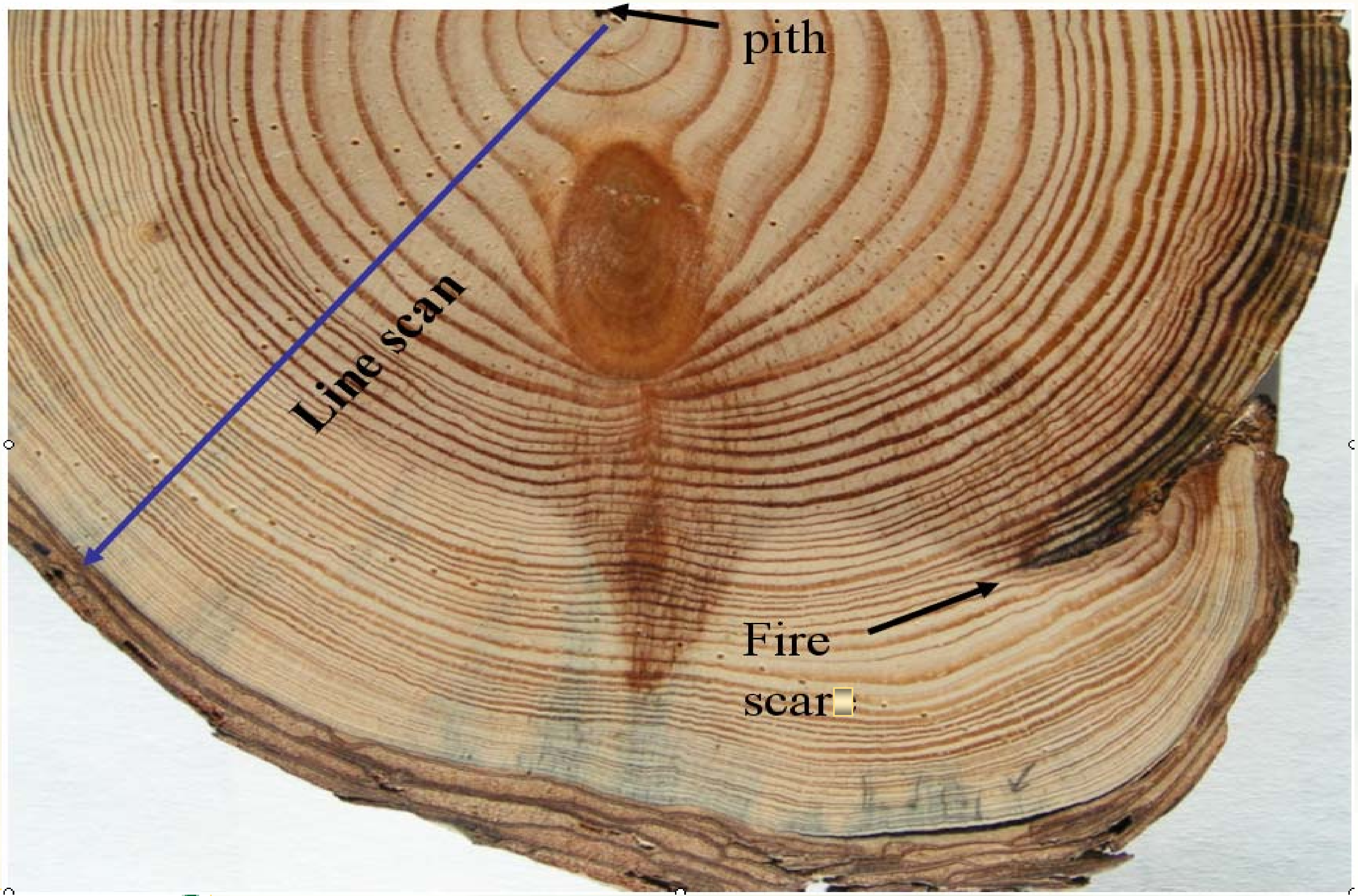
Regression statistic

		Calibration		Validation	
Set	**Element**	**r**	**RMSEC**	**r**	**RMSEP**
ACZA Douglas Fir 4 Principal Components	Cu	0.99	0.352	0.97	0.913
	Zn	0.99	0.224	0.90	0.673
	As	0.98	0.240	0.90	0.769
CCA Eastern Hemlock 4 Principal Components	Cu	0.99	0.080	0.91	0.272
	Cr	0.99	0.224	0.88	1.089
	As	0.99	0.192	0.88	0.897
CCA Hemlock-Fir 2 Principal Components	Cu	0.98	0.144	0.97	0.272
	Cr	0.97	0.416	0.97	0.625
	As	0.92	0.497	0.91	0.593
ACQ Hemlock-Fir 3 Principal Components	Cu	0.98	0.593	0.89	1.057

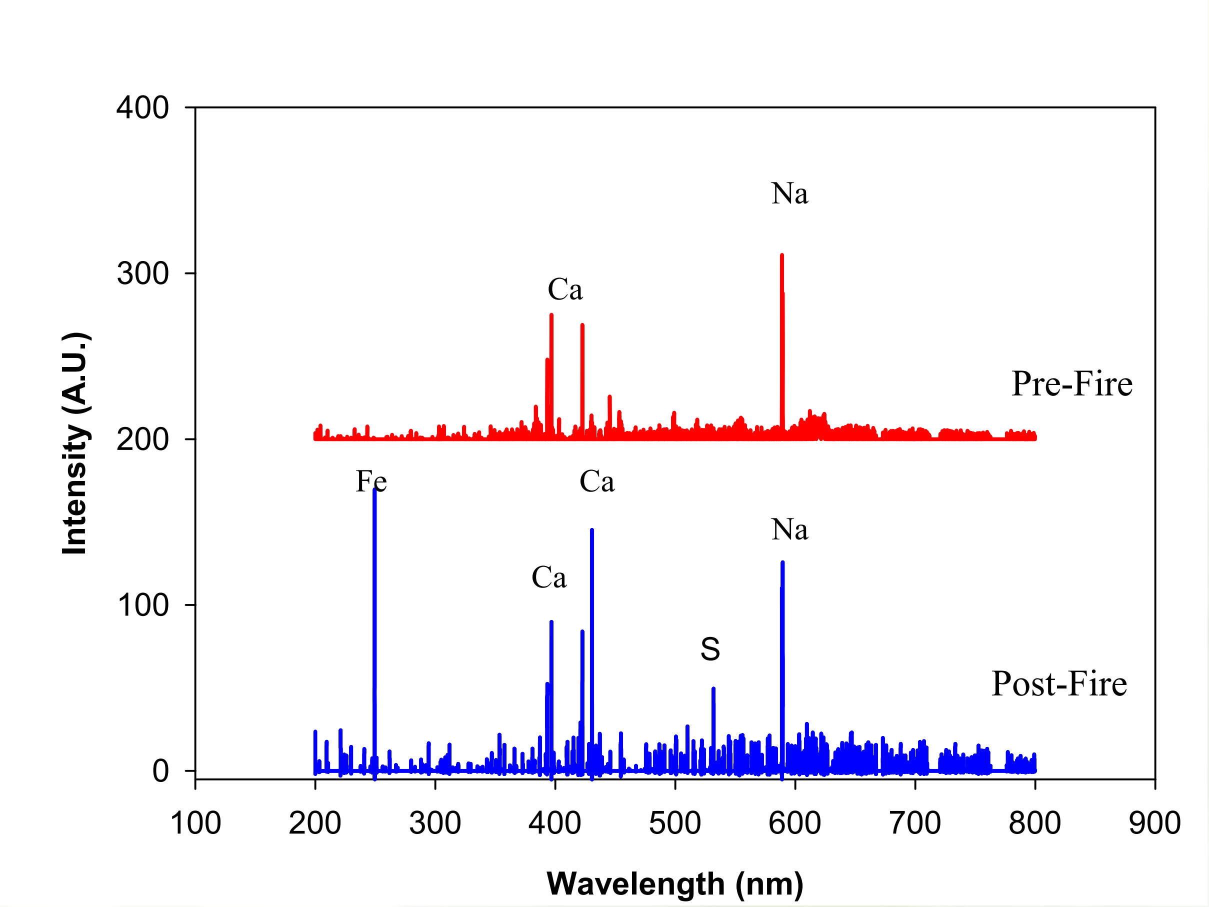
Fire maintains ecosystem
Study fire and its role in nature
Nature fire regimes

Hunting, ceremonies, clearing maize fields

Line Scan

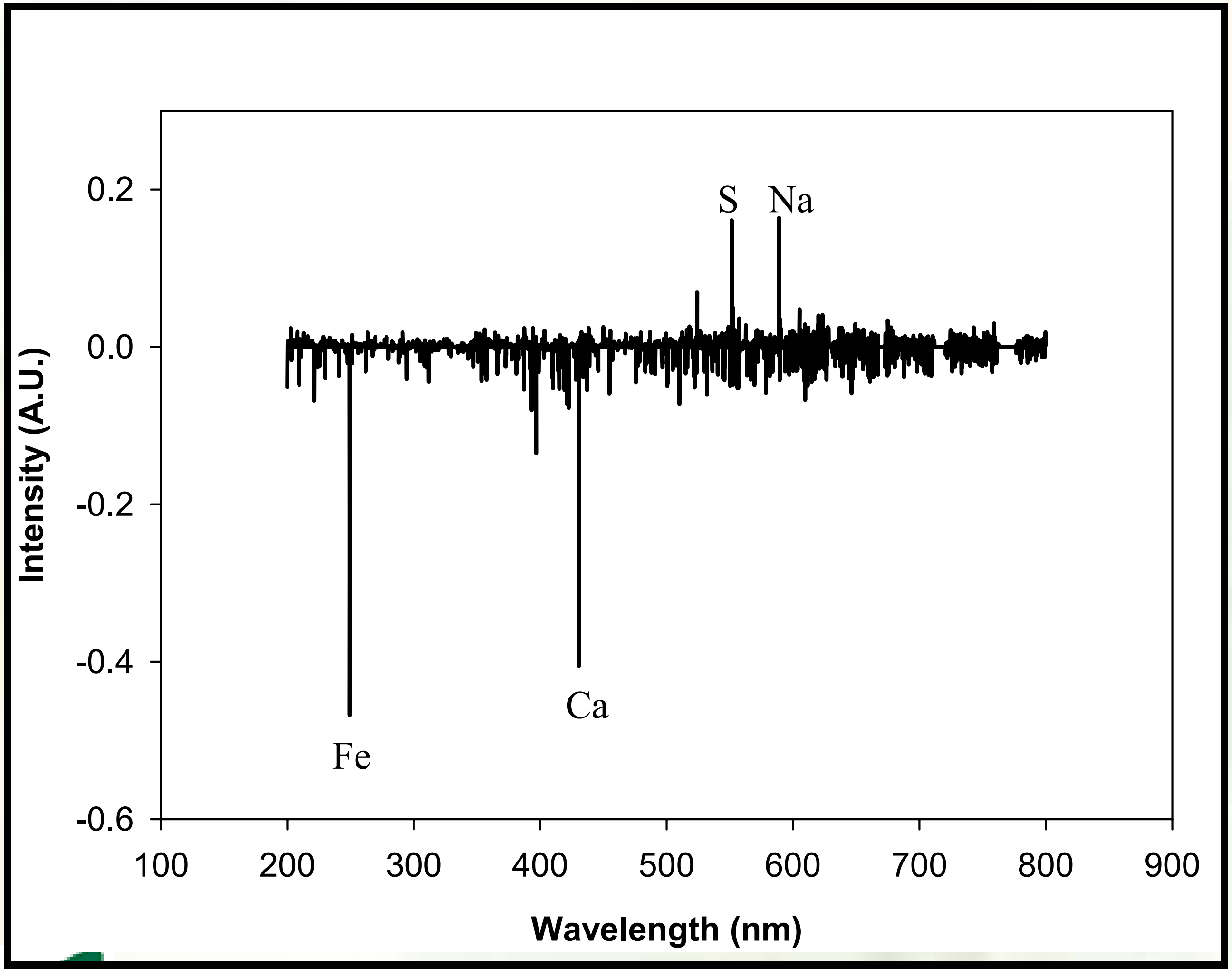


LIBS spectra on pine xylem before and after a fire

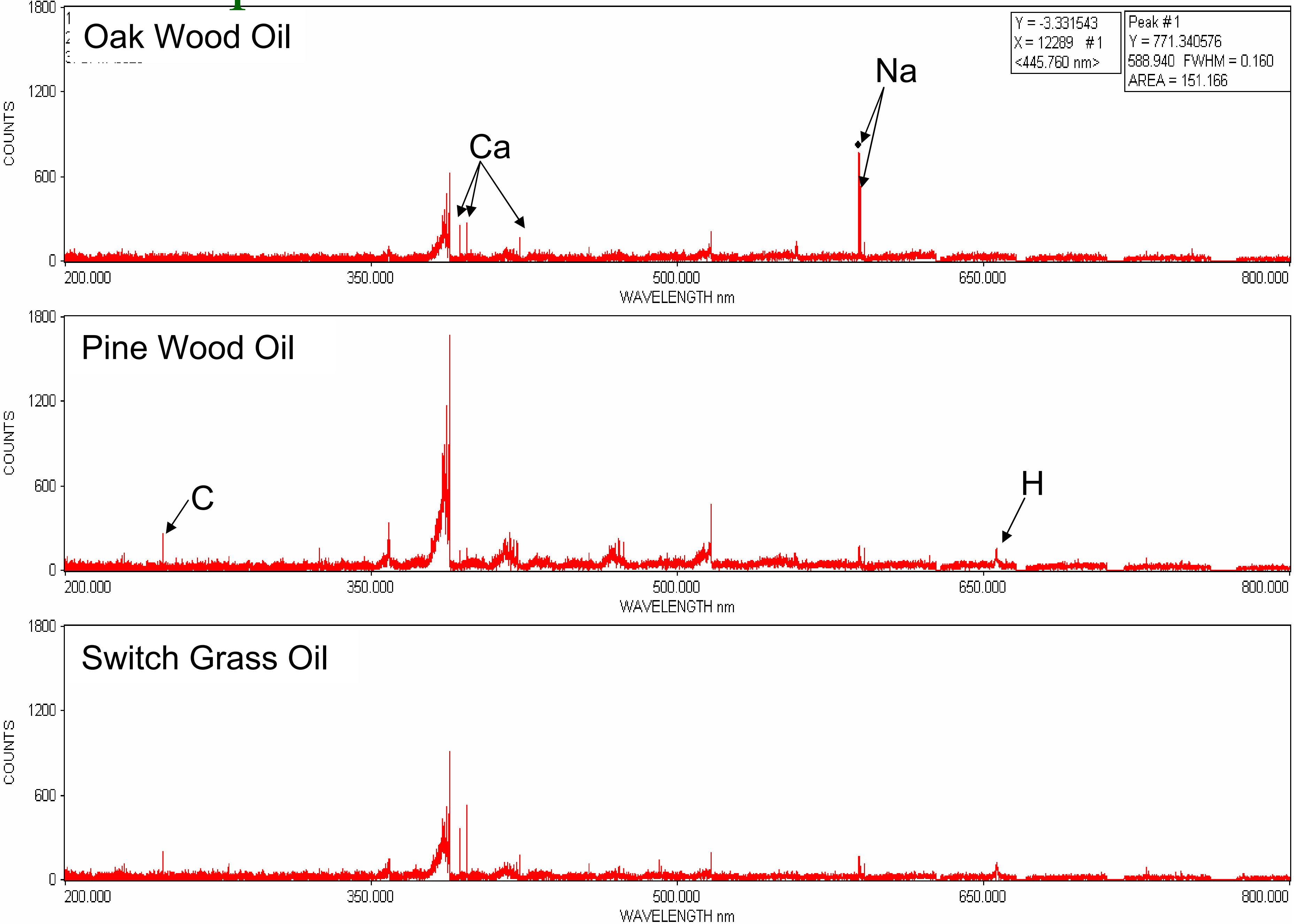


Score of PC1 versus spectrum number

Loading of the PC1 of the LIBS spectra



LIBS spectra for three bio-oils



Future Work

LIBS on Chestnut Oak for understanding fire events:

- Low intensity fire
- Medium intensity fire
- High intensity fire

Direction of fire

- Uphill
- Downhill

LIBS will also be performed on the roots of the same trees

LIBS on bio-oils and bio-diesels will also be performed

Acknowledgements

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