



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

**Madhavi Z. Martin,
Oak Ridge National Laboratory
and**

**Nicole Labbé, Nicolas André, and Timothy G. Rials
University of Tennessee**

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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 timely knowledge of process parameters, including accurate measurement or estimation of key variables.”

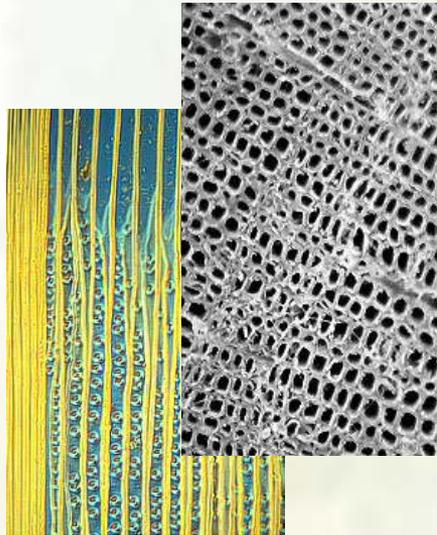
DOE/OIT (2003)

Crosscutting sensors and controls – “Focus is on control systems, chemical and physical property measurements, numerical 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

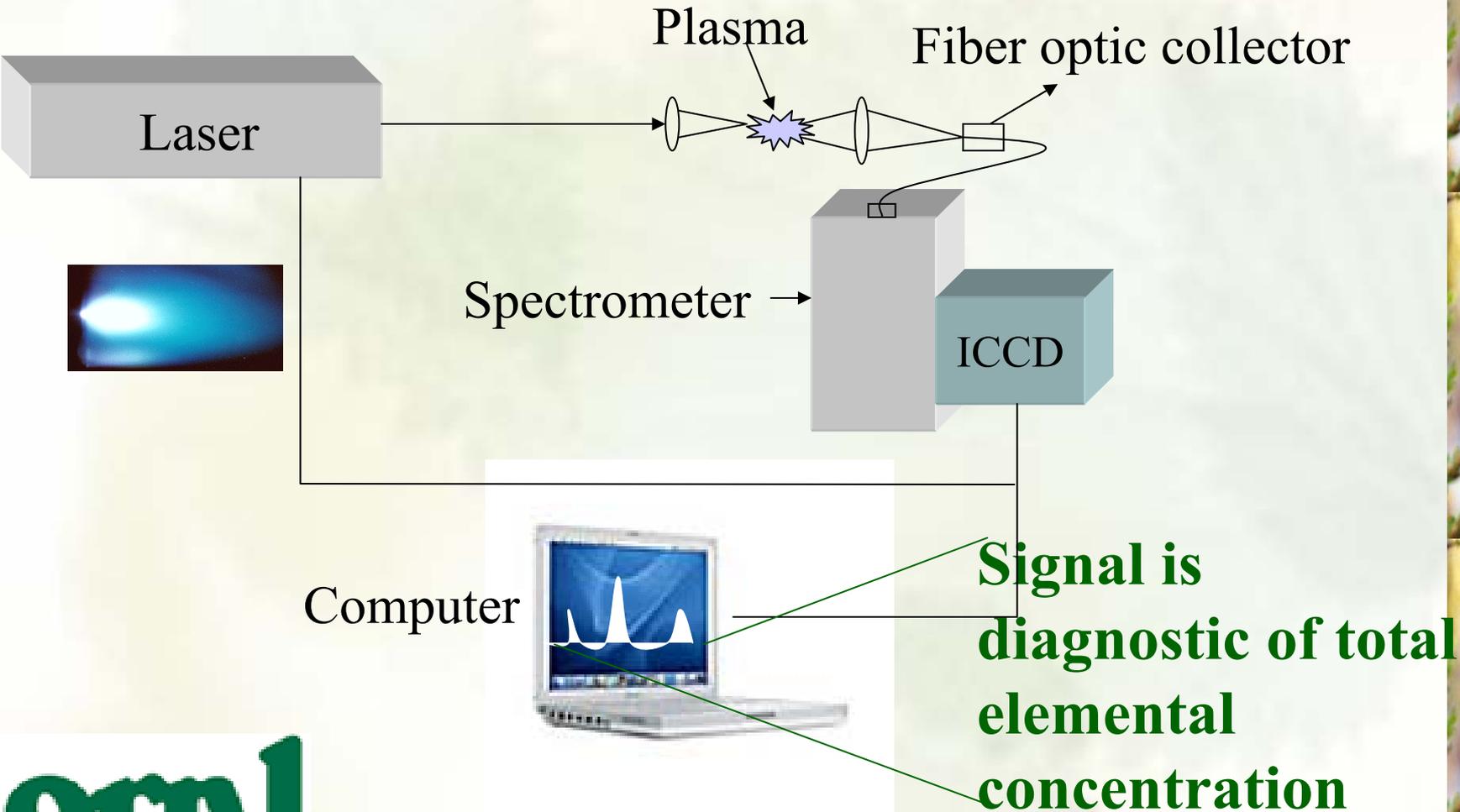


We believe that an opportunity exists to complement this focus by now examining the inorganic or elemental composition of wood in environmental events



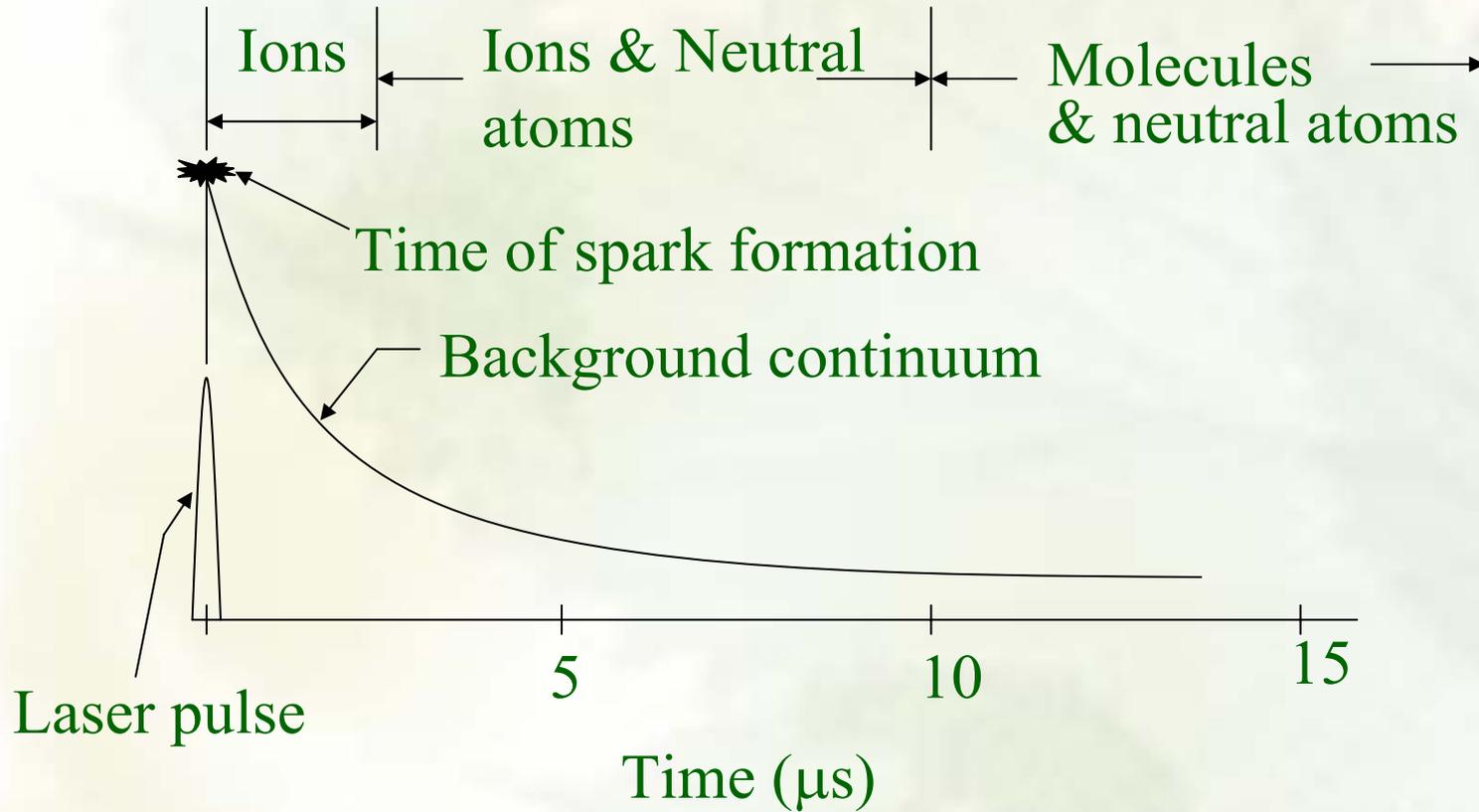
Experimental Setup for LIBS

LIBS = Laser-Induced Breakdown Spectroscopy





Temporal Resolution of a Laser Spark



Periodic Table for LIBS



Periodic table of the elements

1 H Hydrogen 1.00794																	2 He Helium 4.003				
3 Li Lithium 6.941	4 Be Beryllium 9.012182															5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050															13 Al Aluminium 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulphur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80				
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29				
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)				
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114								
			58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967					
			90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)					

Typical detection limits for LIBS



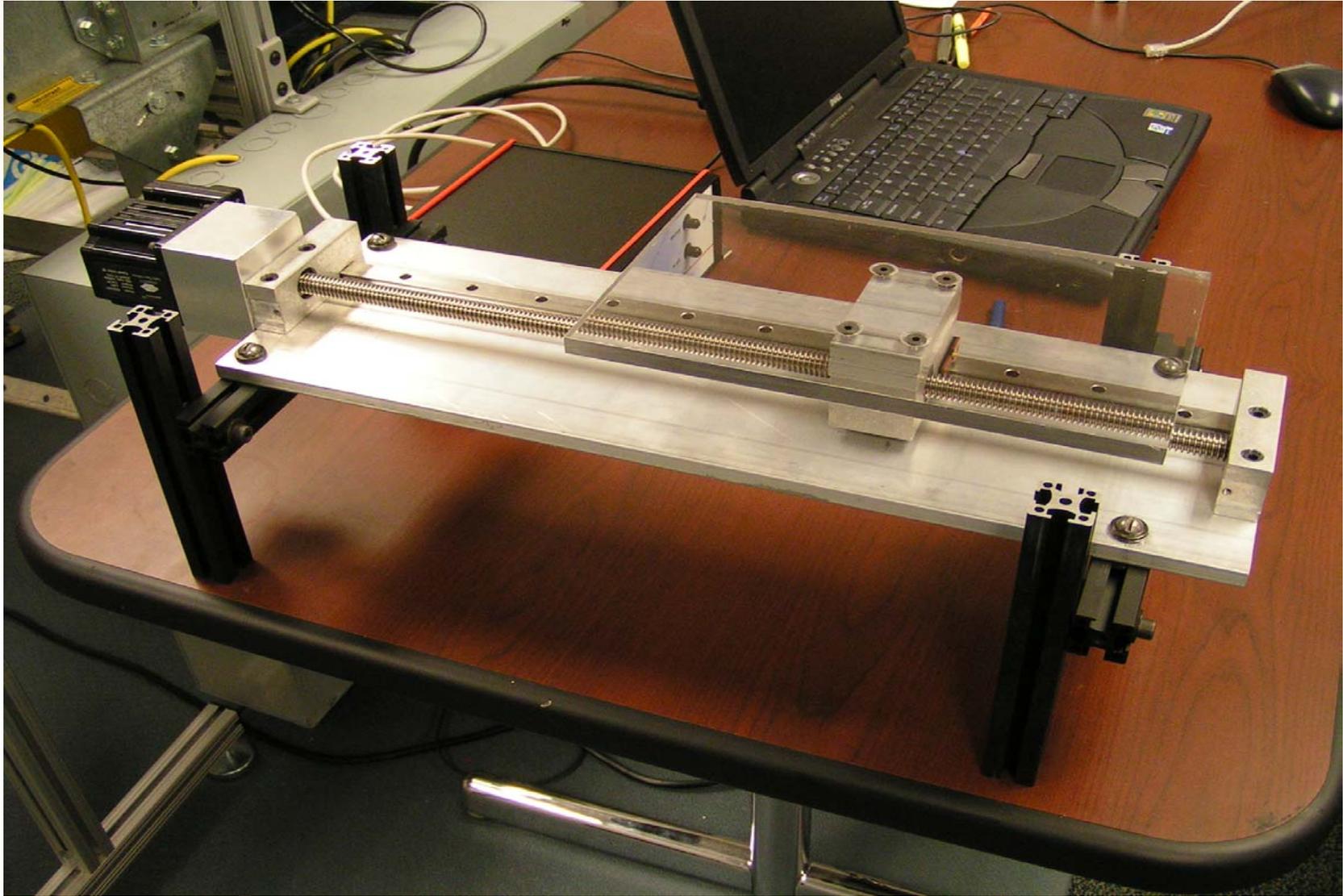


Advantages of LIBS

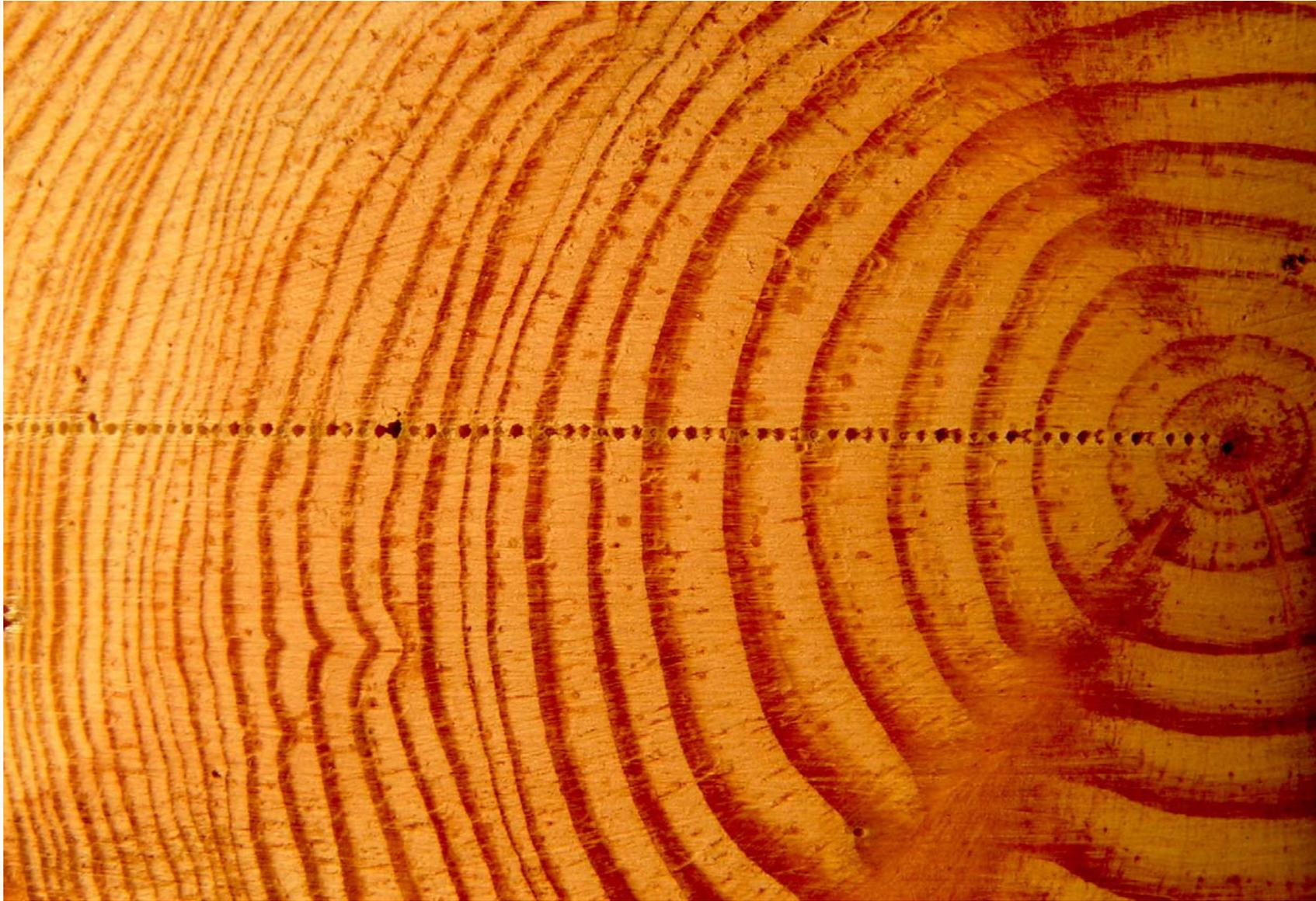
- ***High throughput detection.*** Identification of metals and non-metals in a second.
- ***Multi-elemental analysis.*** Simultaneously detect all elements with high spectral resolution from solids, liquids, gases, and aerosols.
- ***Remote analysis.*** Fiber optics permit instrument operation away 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



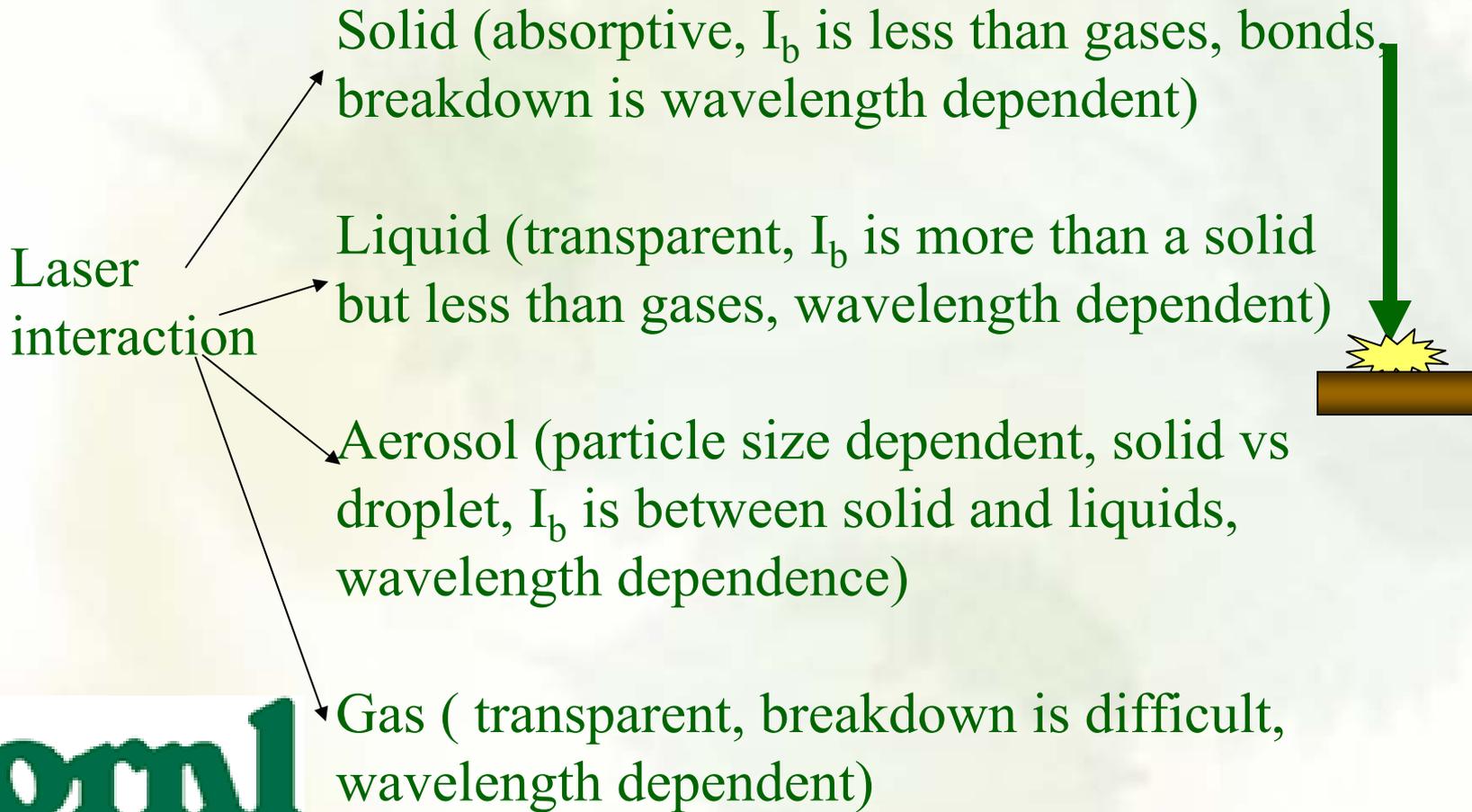
Dendrochemistry using LIBS





Laser Interaction with Matter

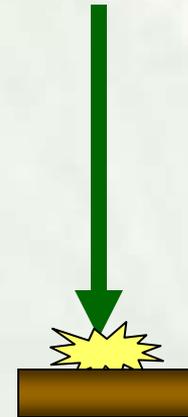
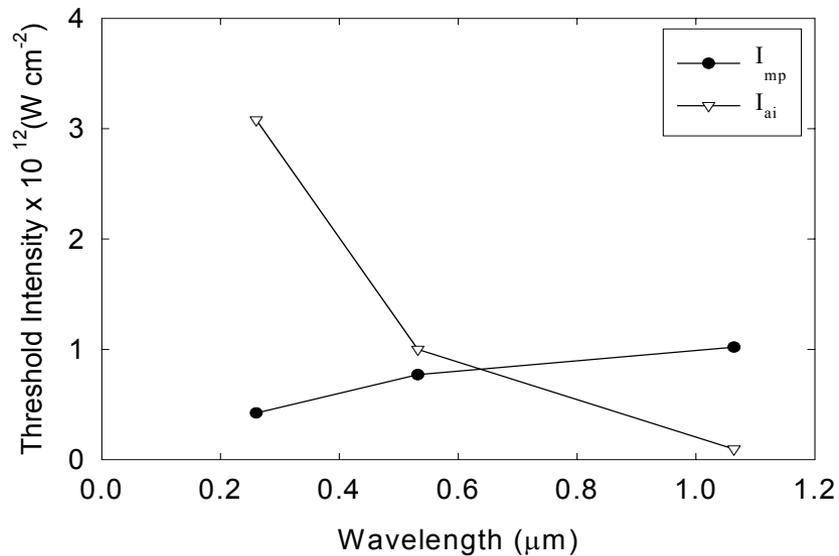
Laser interacts with the different states of matter differently:



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:

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

where n_{ad} is the neutral atom density,

g_g the gas-dependent parameter,

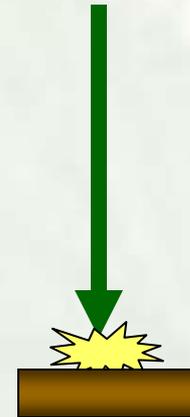
ϕ the laser frequency,

τ_e duration of laser pulse,

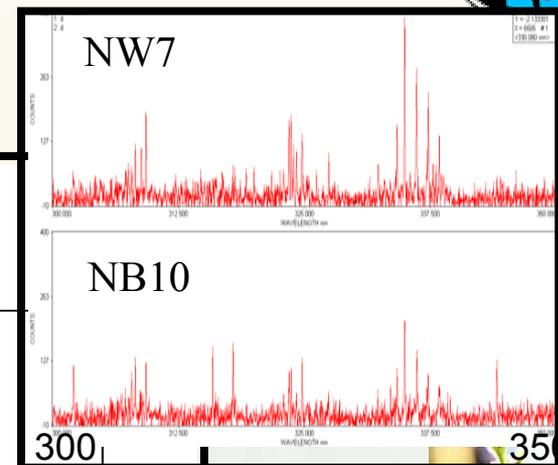
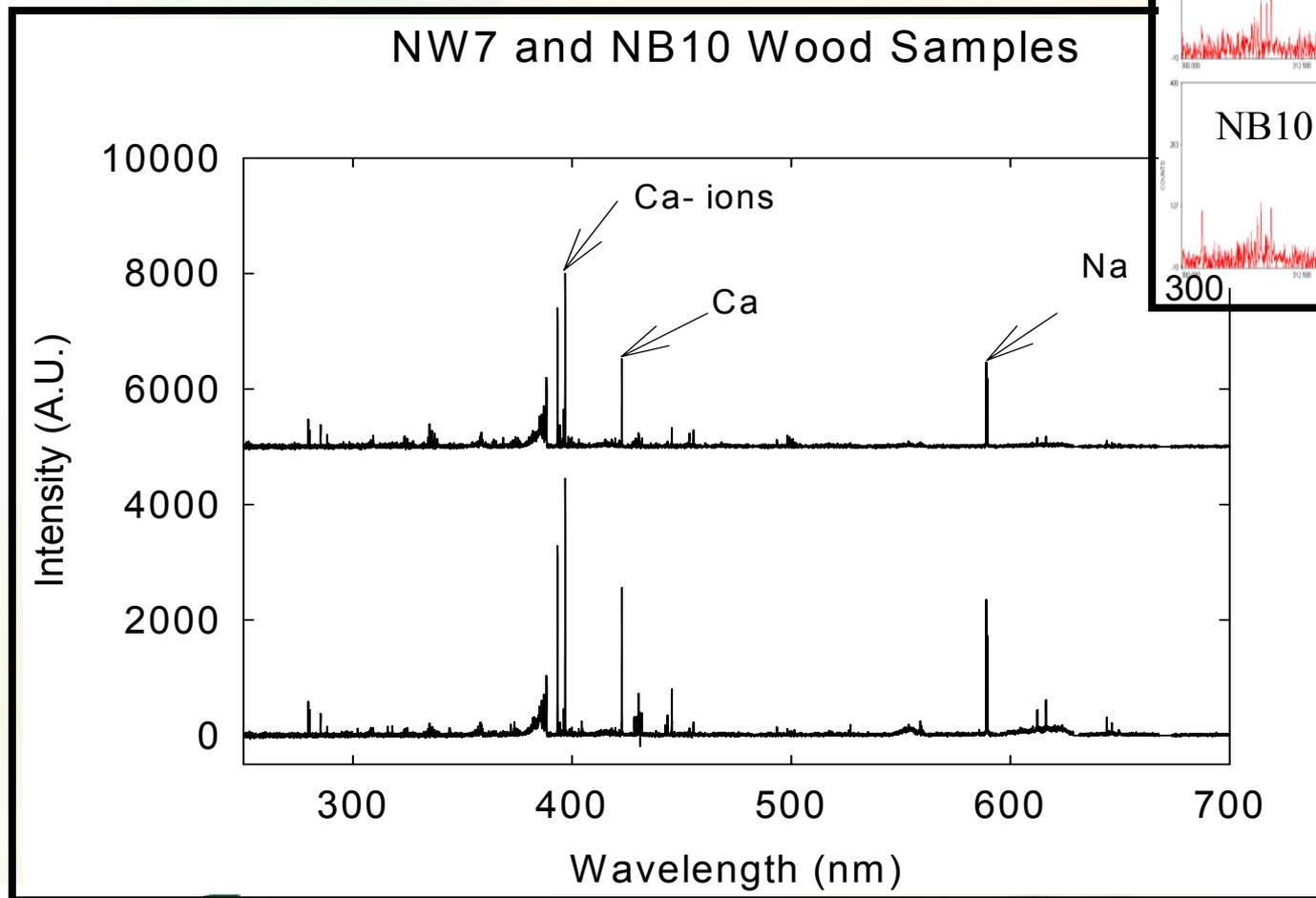
n_e electron density,

v_{ca} the neutral atom collision frequency,

V_v the focal volume of the laser beam.

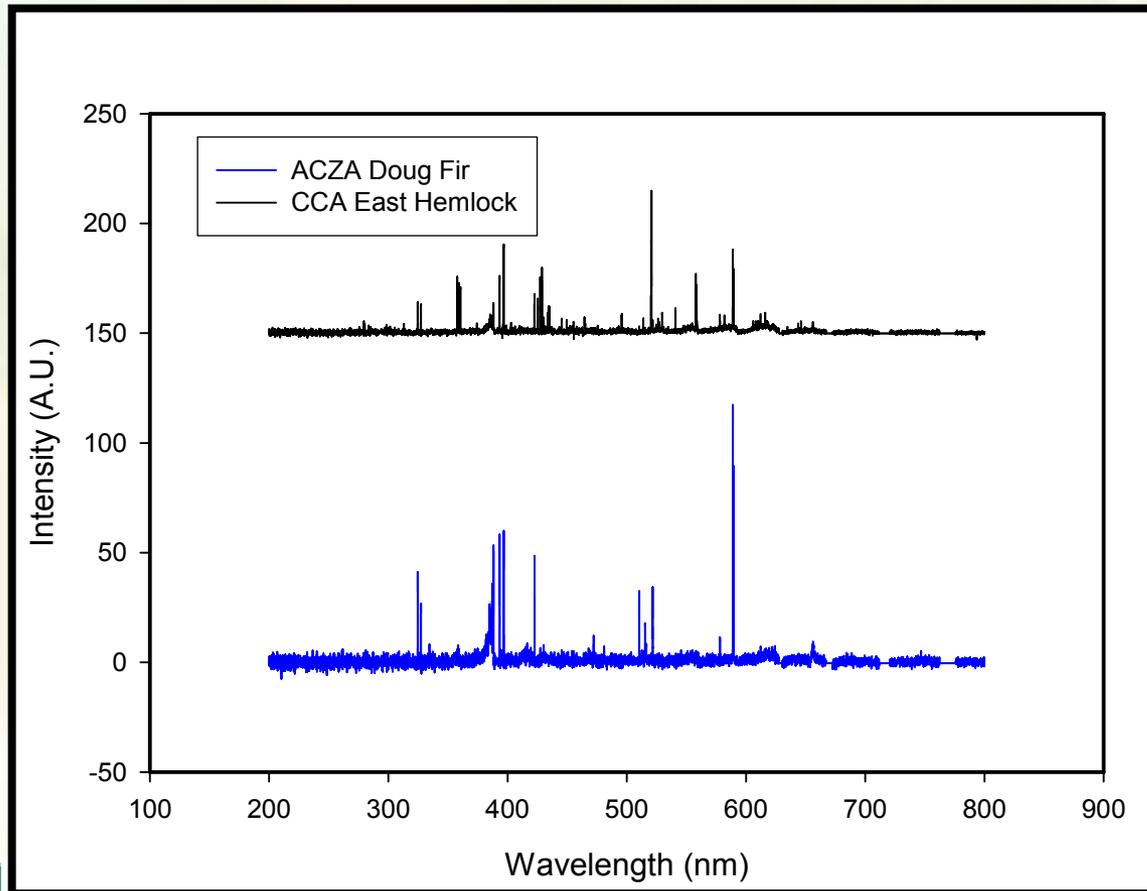


Comparison of LIBS spectra for two different natural woods.



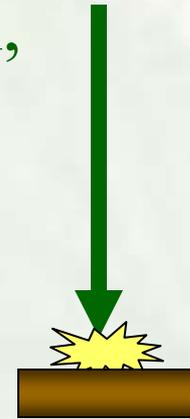
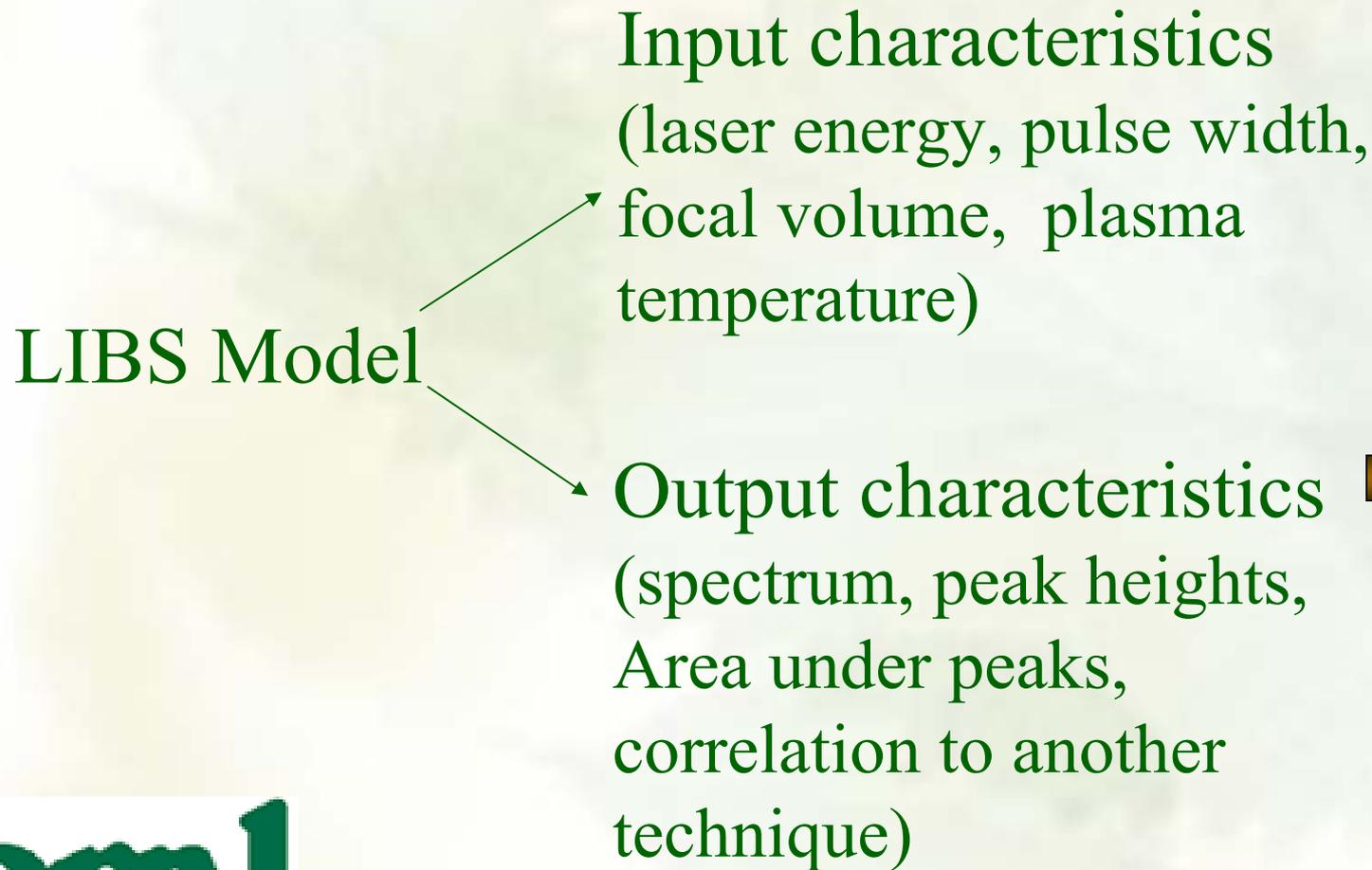


Comparison of LIBS spectra for two different treated woods.



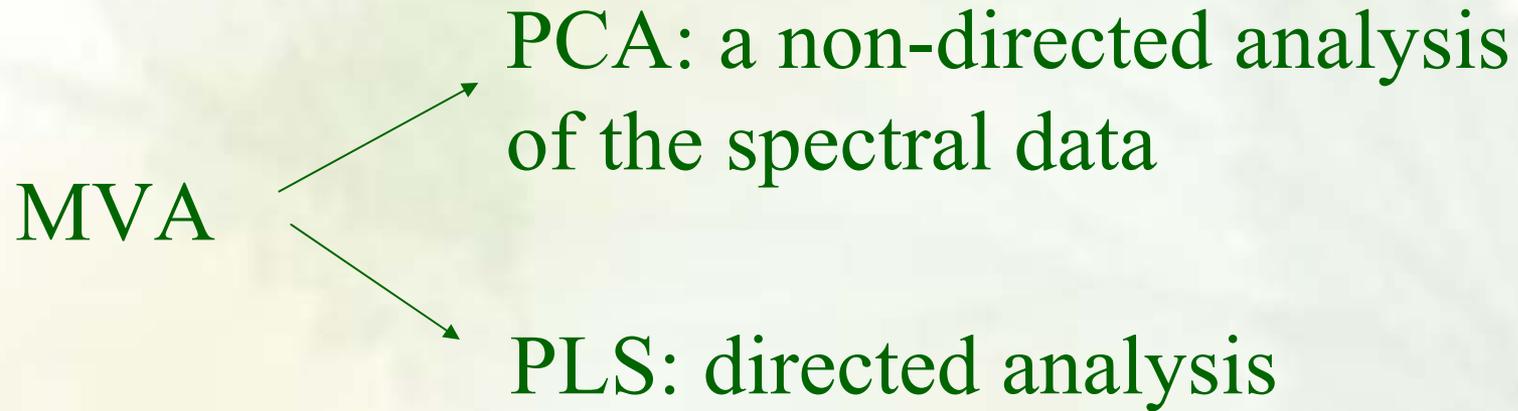


Quantification of LIBS Data





Multivariate Analysis.



Construction of Regression Model



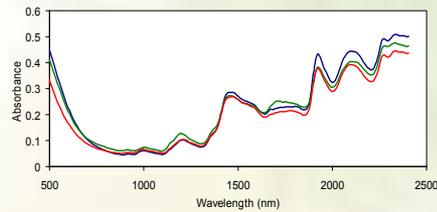
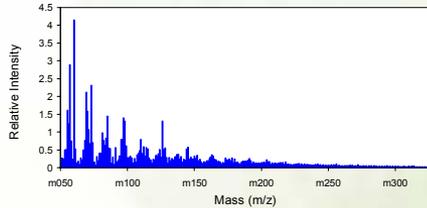
Properties of Interest

Process variable

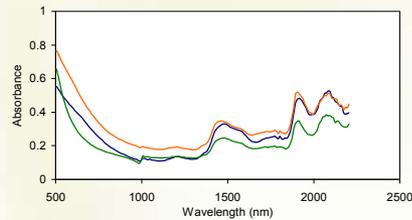
Strength, Stiffness

Elemental content

Calibration set



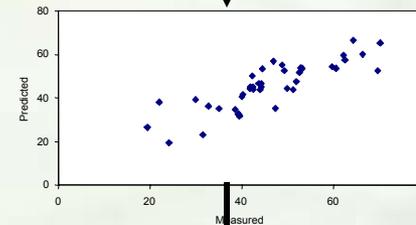
Test set unknowns



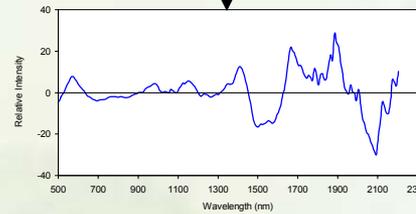
Spectral data

0.751408	0.148209	0.300433	0.220004	0.040444	0.282529	0.131109	0.102851	0.020410	0.000855	0.000000	0.282529	0.131109	0.102851	0.020410	0.000855	0.282529	0.131109	0.102851	0.020410	0.000855
0.132889	0.130288	0.171333	0.020470	0.010404	0.282529	0.131109	0.102851	0.020410	0.000855	0.282529	0.131109	0.102851	0.020410	0.000855	0.282529	0.131109	0.102851	0.020410	0.000855	0.282529
0.516028	0.281121	0.00	0.00	0.00	0.282529	0.131109	0.102851	0.020410	0.000855	0.282529	0.131109	0.102851	0.020410	0.000855	0.282529	0.131109	0.102851	0.020410	0.000855	0.282529

Spectral data



Correlation Model

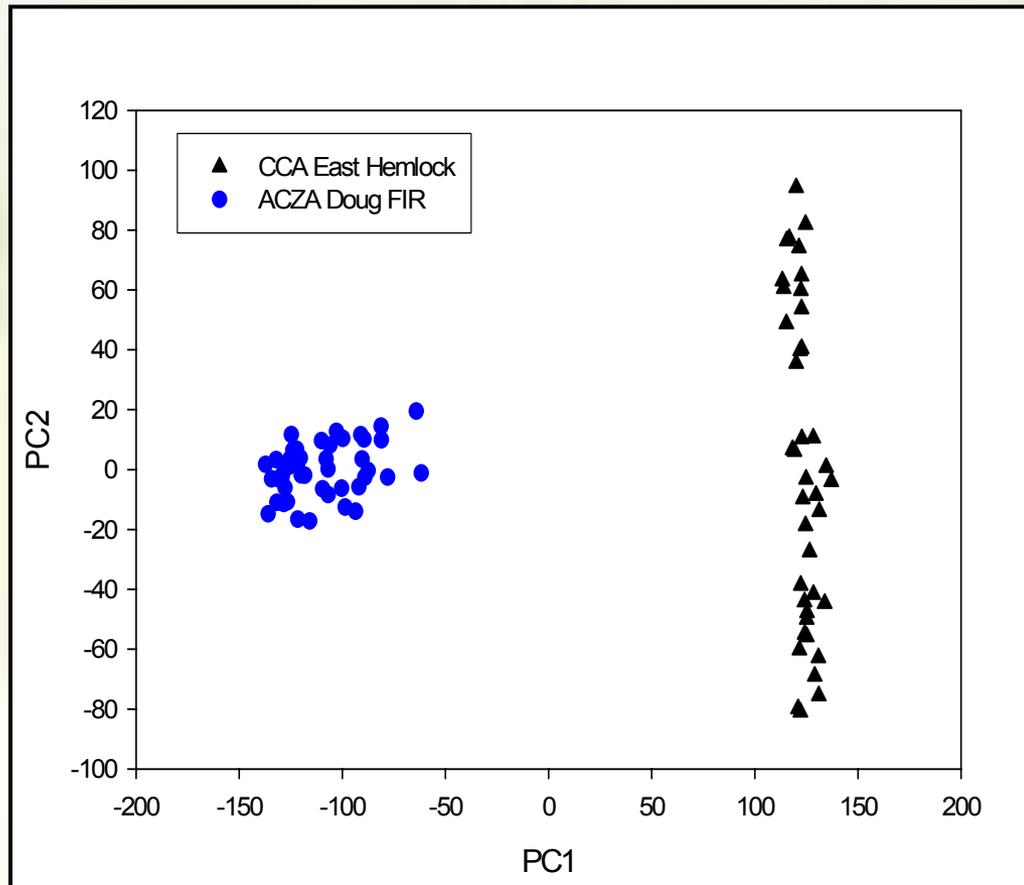


Regression Coefficients

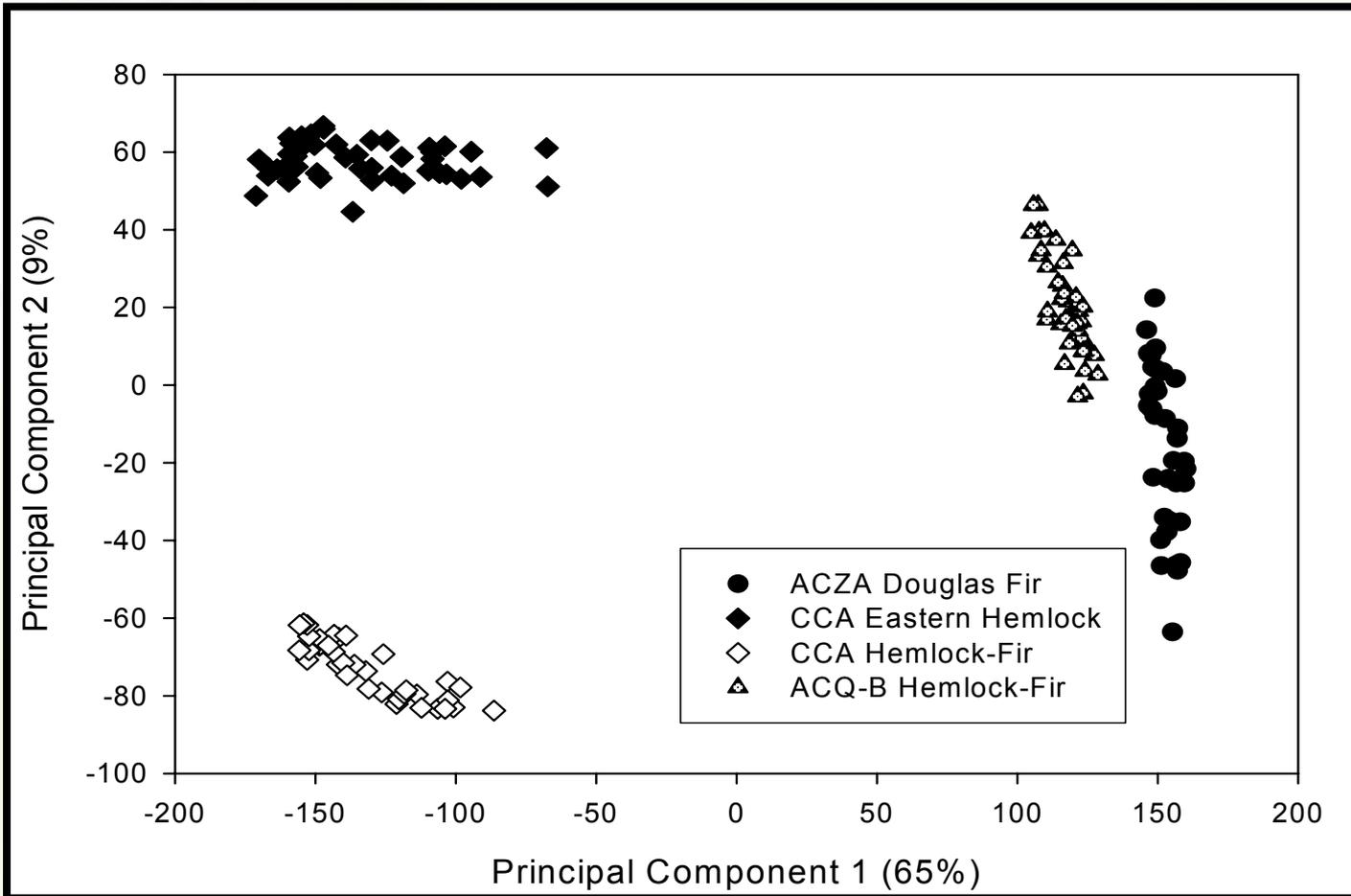
Predicted Properties



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



Principal component analysis for four different treated woods



Regression statistic



Set	Element	Calibration		Validation	
		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

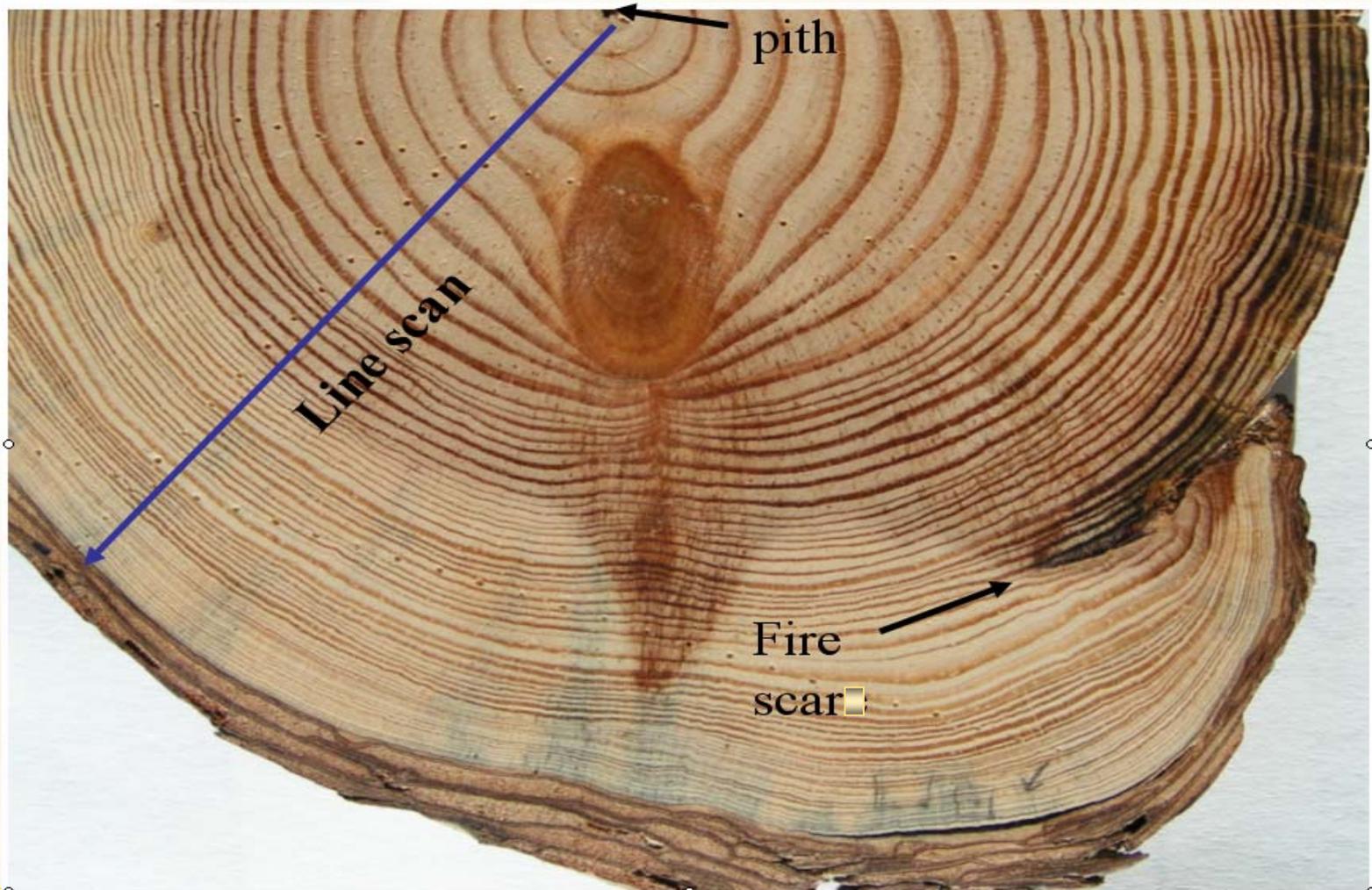
Nature fire regimes



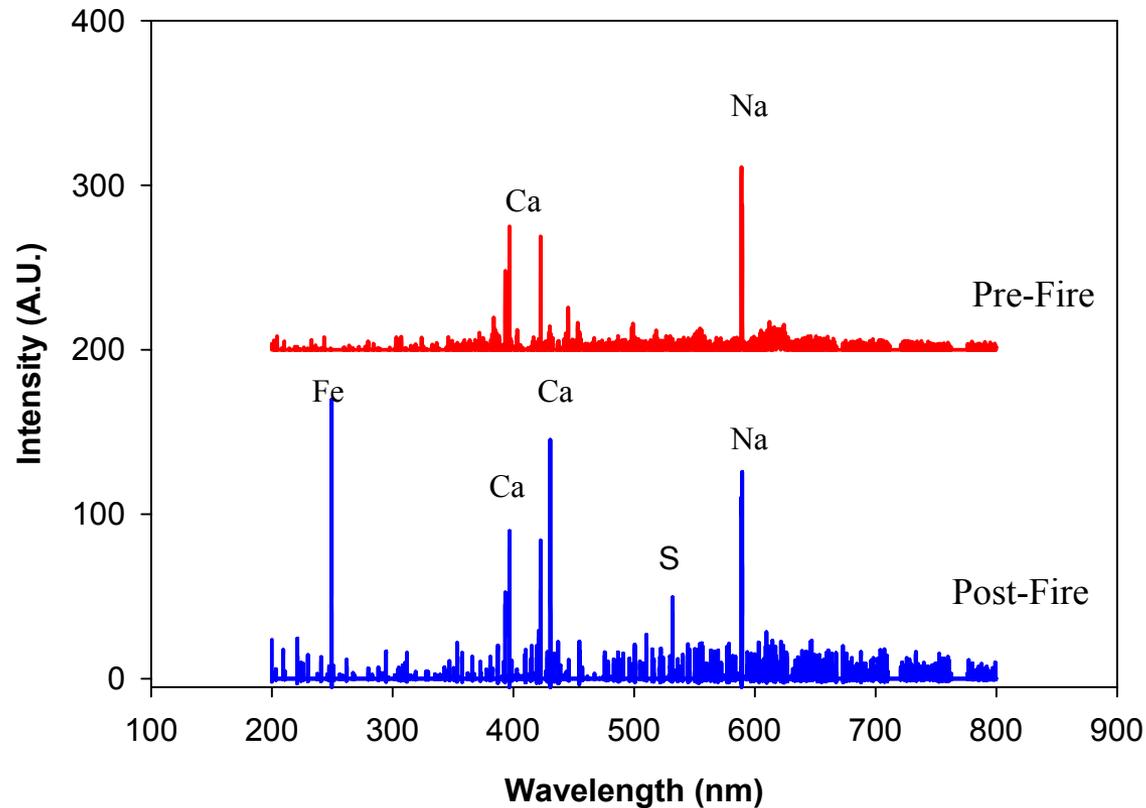
Hunting,
ceremonies,
clearing maize
fields



Line Scan

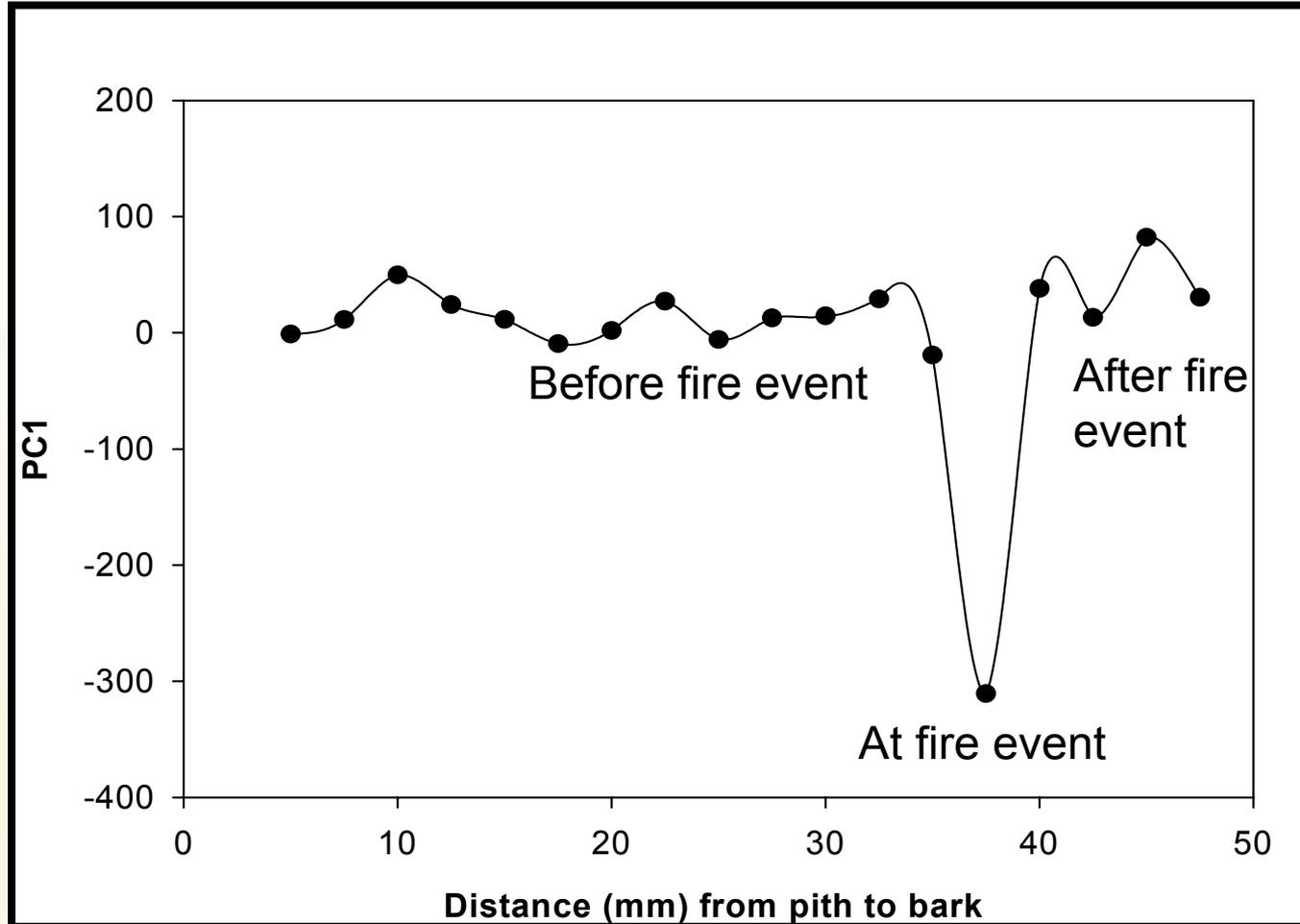


LIBS spectra on pine xylem before and after a fire

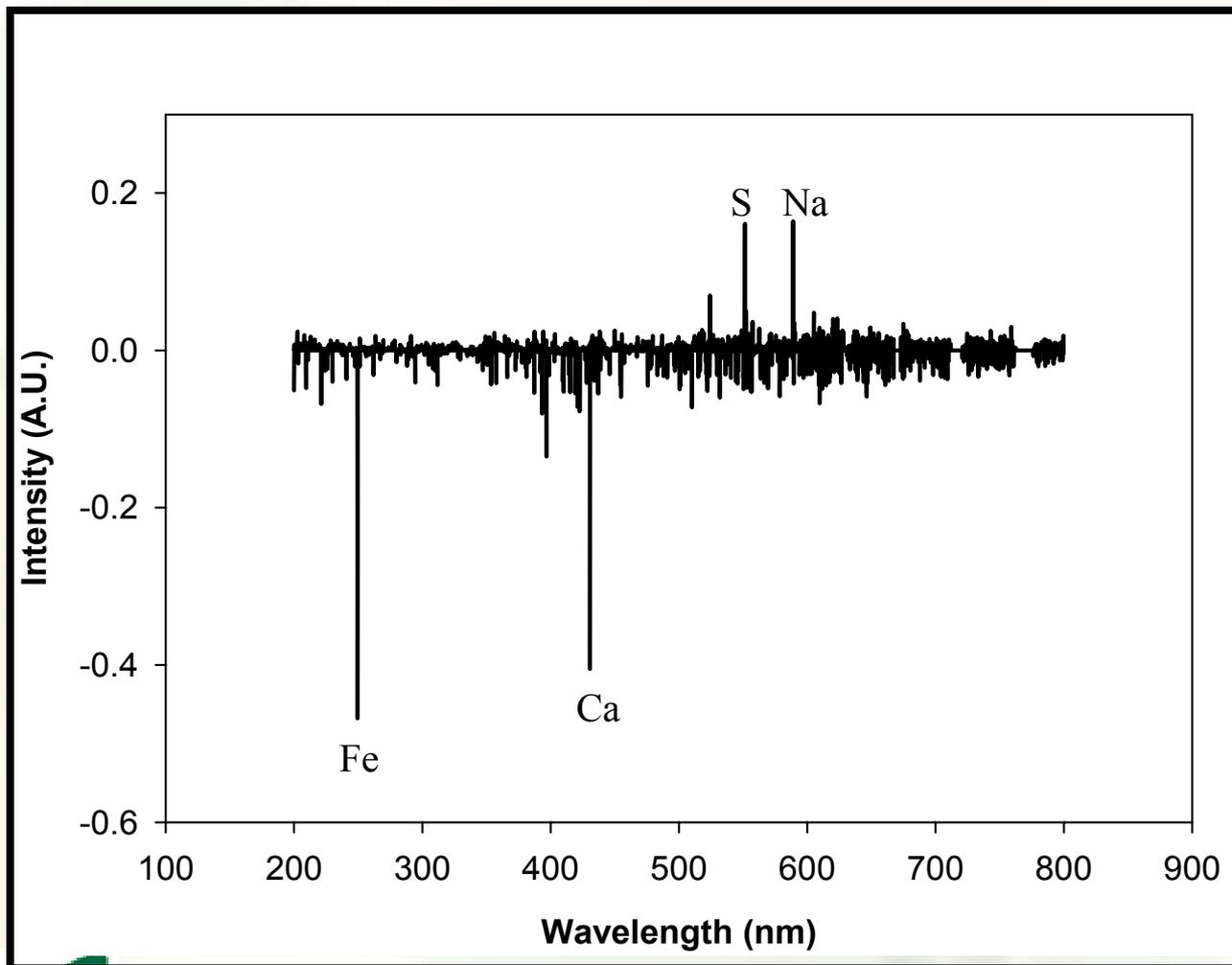




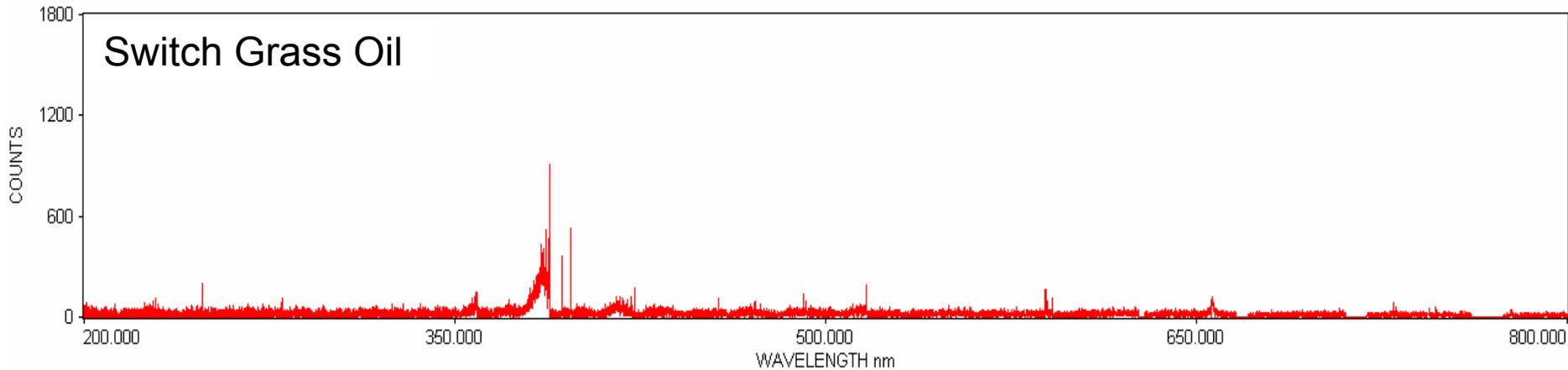
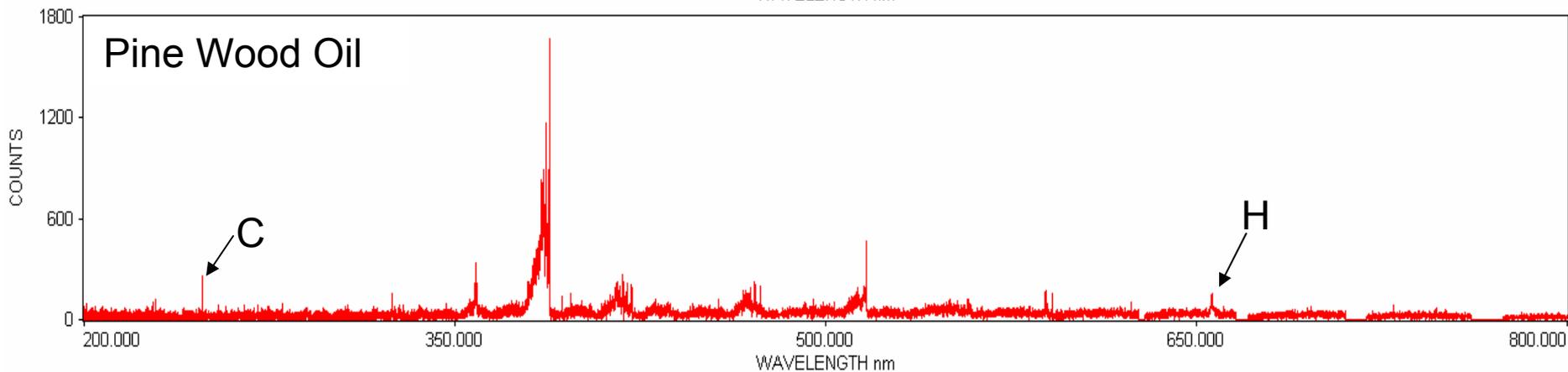
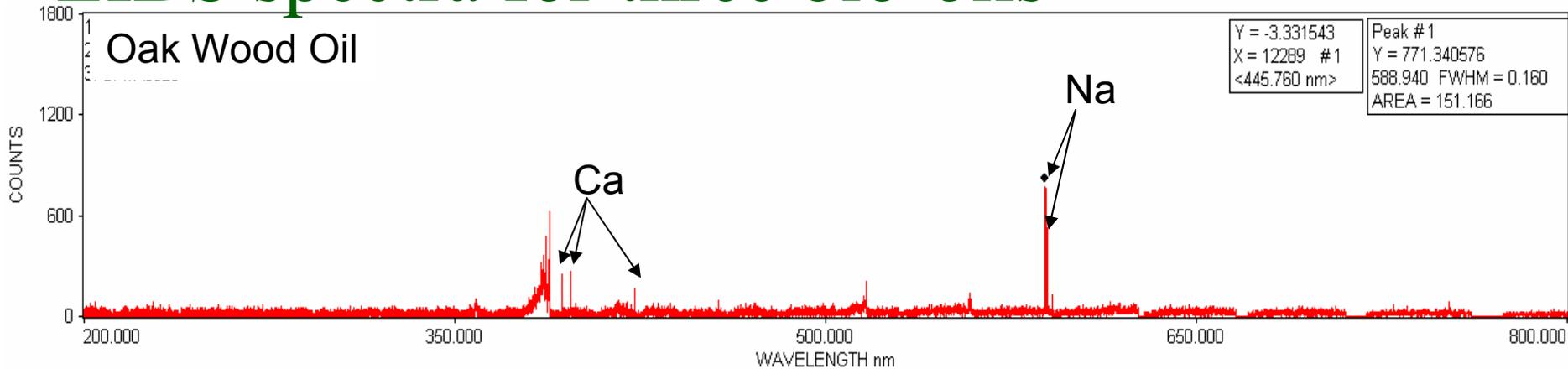
Score of PC1 versus spectrum number



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





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