Laser-Induced Breakdown Spectroscopy (LIBS): a future super star of atomic spectrometry and its application to biological systems

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Outline

1. Introduction to LIBS
2. Potential Applications
3. My Applications
   - trace contaminants in simulated tissue
   - identification/discrimination of bacteria

LIBS Defined

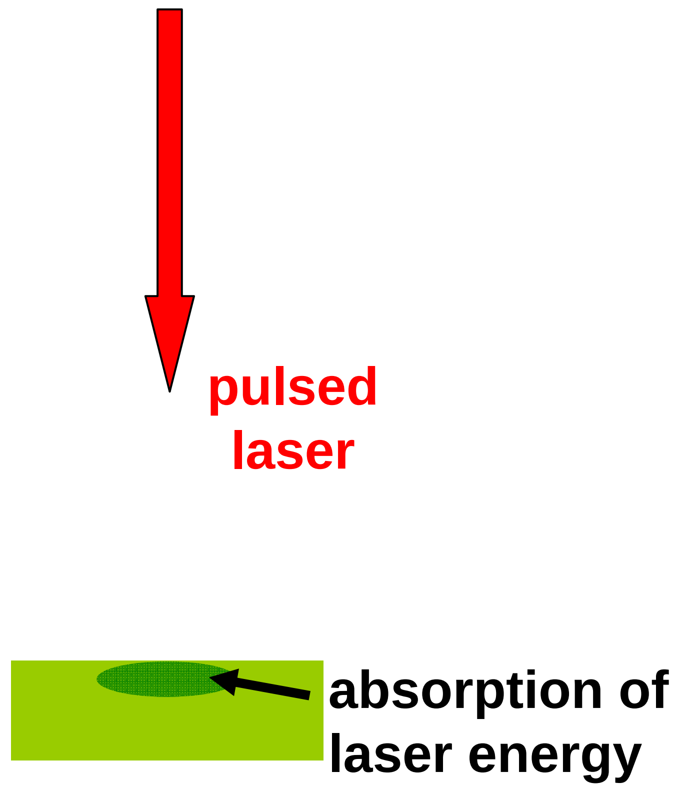
One sentence?

A spectrochemical technique which utilizes an intense laser pulse to determine the atomic/elemental composition of a sample via generation of a high-temperature micro-plasma followed by time-resolved optical spectroscopy.

The LIBS Process

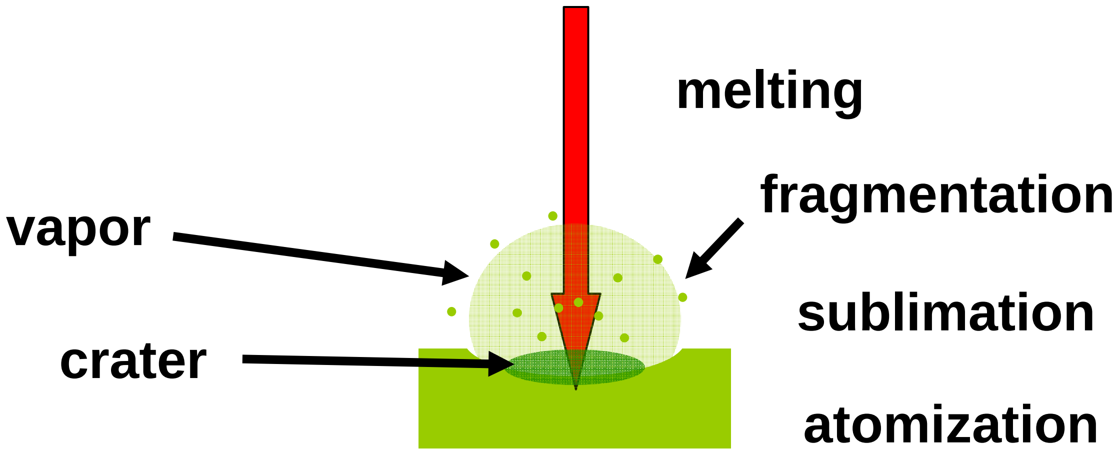
1. laser interaction with the target
2. removal of samples mass (ablation)
3. plasma formation (breakdown)
4. element specific emission

1) laser interaction with the target



- initiated by absorption of energy by the target from a pulsed radiation field.
- pulse durations are on the order of nanoseconds, but LIBS has been performed with pico- and femto-second laser pulses.

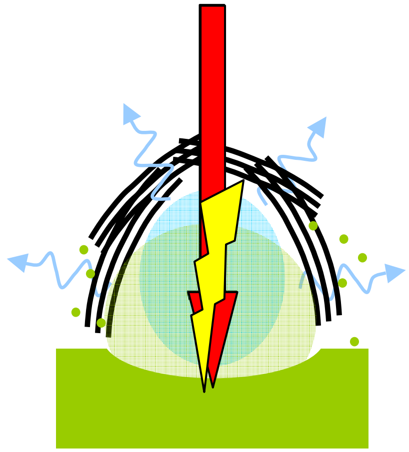
2) removal of samples mass (ablation)



- The absorbed energy is rapidly converted into heating, resulting in vaporization of the sample (ablation) when the temperature reaches the boiling point of the material.

- The removal of particulate matter from the surface leads to the formation of a vapor above the surface.

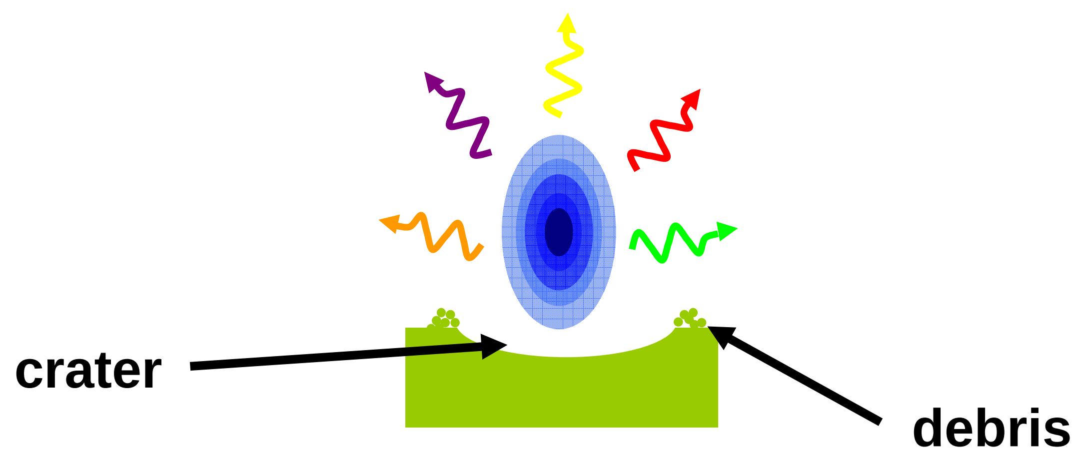
3) plasma formation (breakdown)



- The laser pulse continues to illuminate the vapor plume.
- The vapor condenses into sub-micrometer droplets that lead to absorption and scattering of the laser beam, inducing strong heating, ionization and plasma formation.

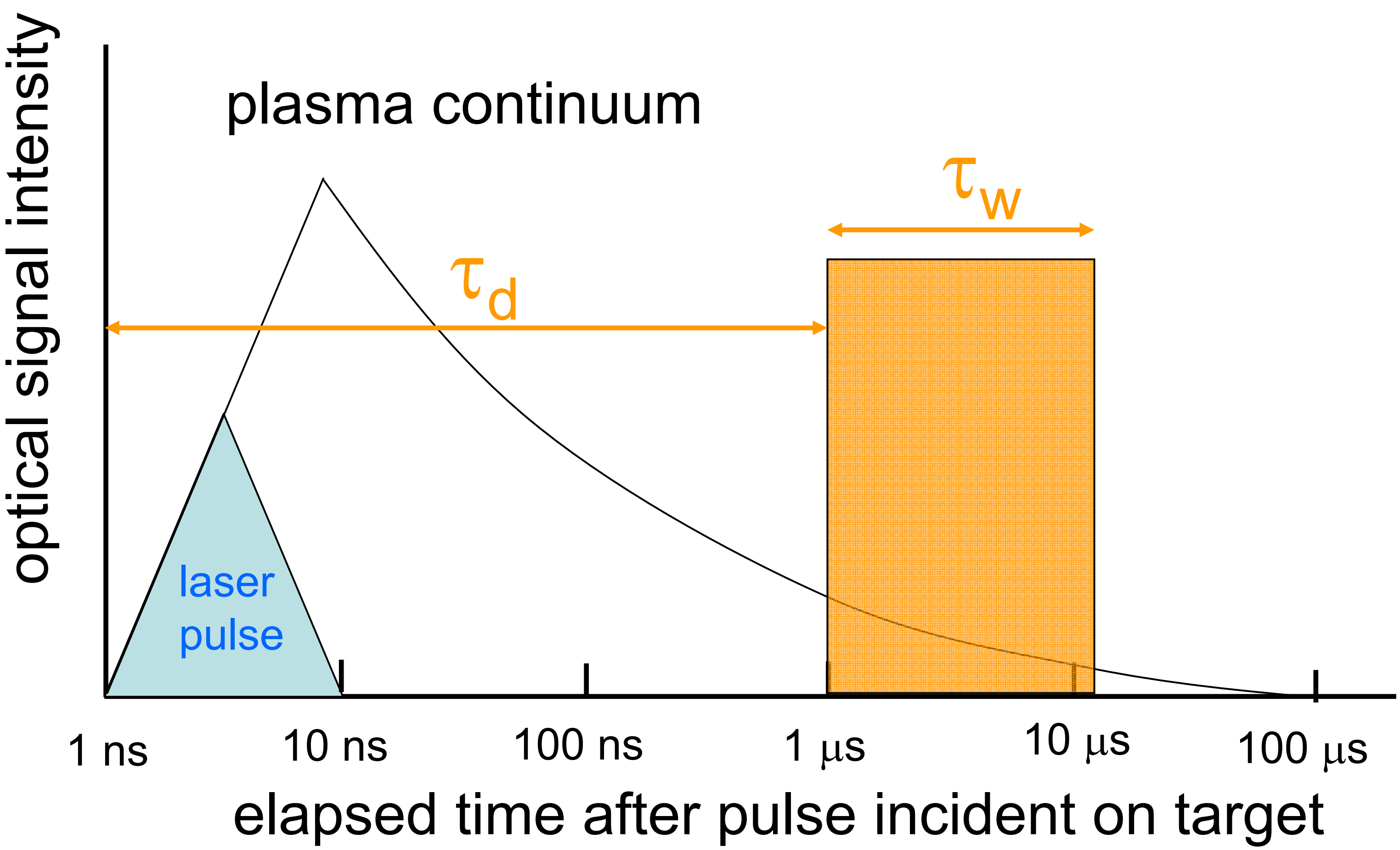
4) element specific emission (atomic or ionic)

spontaneous emission as atoms/ions decay to ground state



- The dynamical evolution of the plasma plume is then characterized by a fast expansion and subsequent cooling.
- Approximately 1 microsecond after the ablation pulse, spectroscopically narrow atomic/ionic emissions may be identified in the spectrum.

Temporal History of a LIBS Plasma



3 Current “Super-Stars” of Atomic Spectroscopy

1. electrothermal atomization-atomic absorption spectrometry (ETA-AAS)

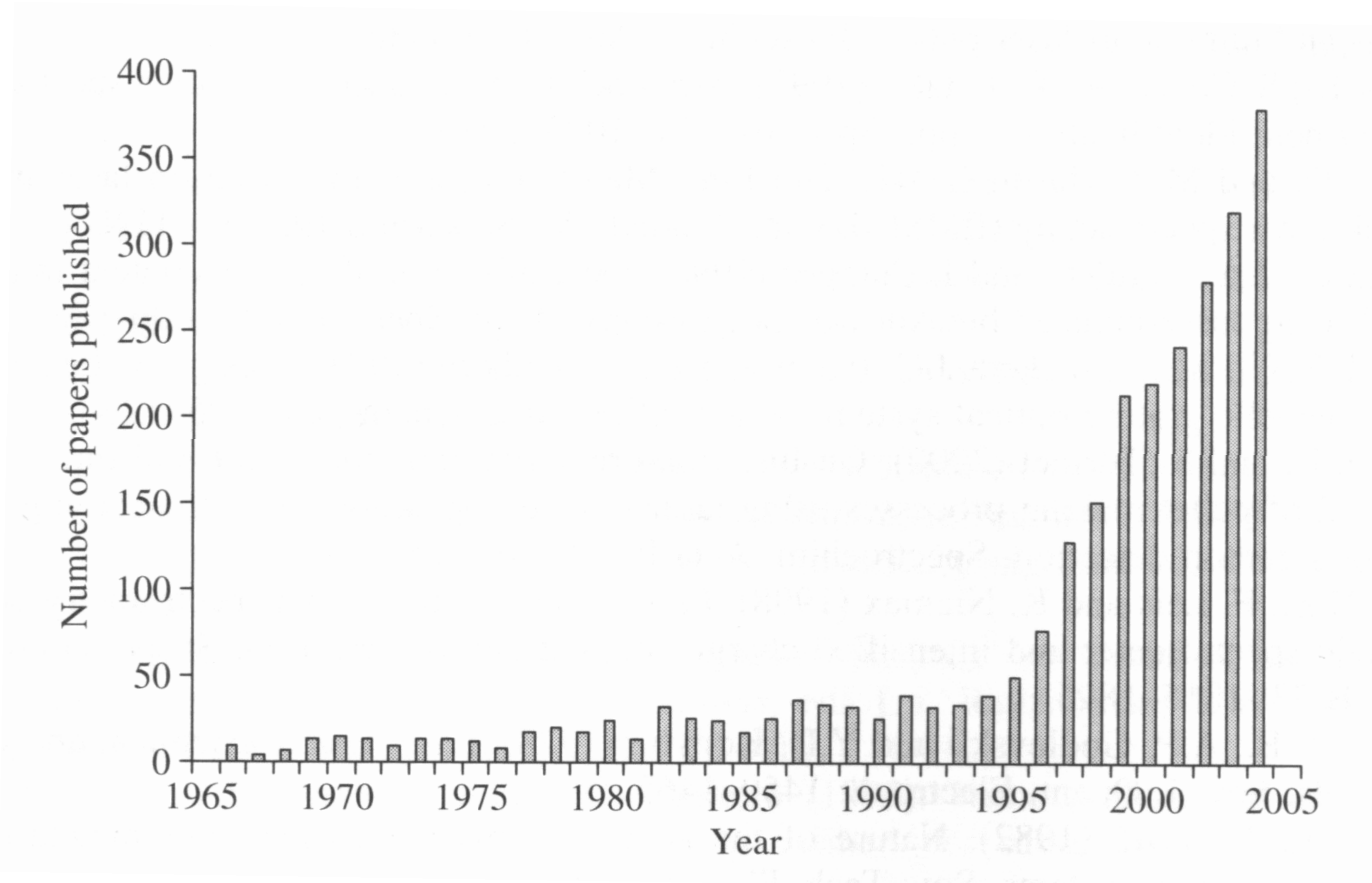
2. inductively couple plasma-atomic emission spectrometry (ICP-AES)

3. inductively coupled plasma-mass spectrometry (ICP-MS)

Advantages of LIBS

1) extremely fast analysis compared to competing technologies
2) multi-elemental analysis, light from all constituents collected without bias
3) analysis can be performed at standoff distances
4) technique is applicable to all substrates (gas, solid, and liquid)
5) requires minimal or no sample prep
6) exquisite spatial resolution, ~1 μm

LIBS Publications



What’s Driving the interest in LIBS?

- mid-80’s: reliable, small, inexpensive lasers
- mid-80’s: intensified charge-coupled devices (ICCD)
- 90’s – 00’s: femtosecond pulsed lasers
- 90’s – 00’s: broadband spectrometers and Echelle spectrometers
- 00’s: microchip lasers

Physics of Plasma Formation: breakdown

<u>Problem</u>: how do photons of relatively low energy, 1-2 eV, (compared to ionization threshold of common gases) generate a breakdown?

Three distinct but overlapping stages:

1. plasma ignition
2. plasma growth (electron avalanche or cascade) and interaction with laser pulse
3. plasma development accompanied by shock wave generation and propagation (“breakdown”)

Physics of Plasma Formation: breakdown

1. cascade or avalanche requires an initial electron
   - multiphoton absorption/ionization

$$M + mh\nu \rightarrow M^{+} + \mathrm{e}^{-}$$

   - local radioactivity
   - cosmic rays

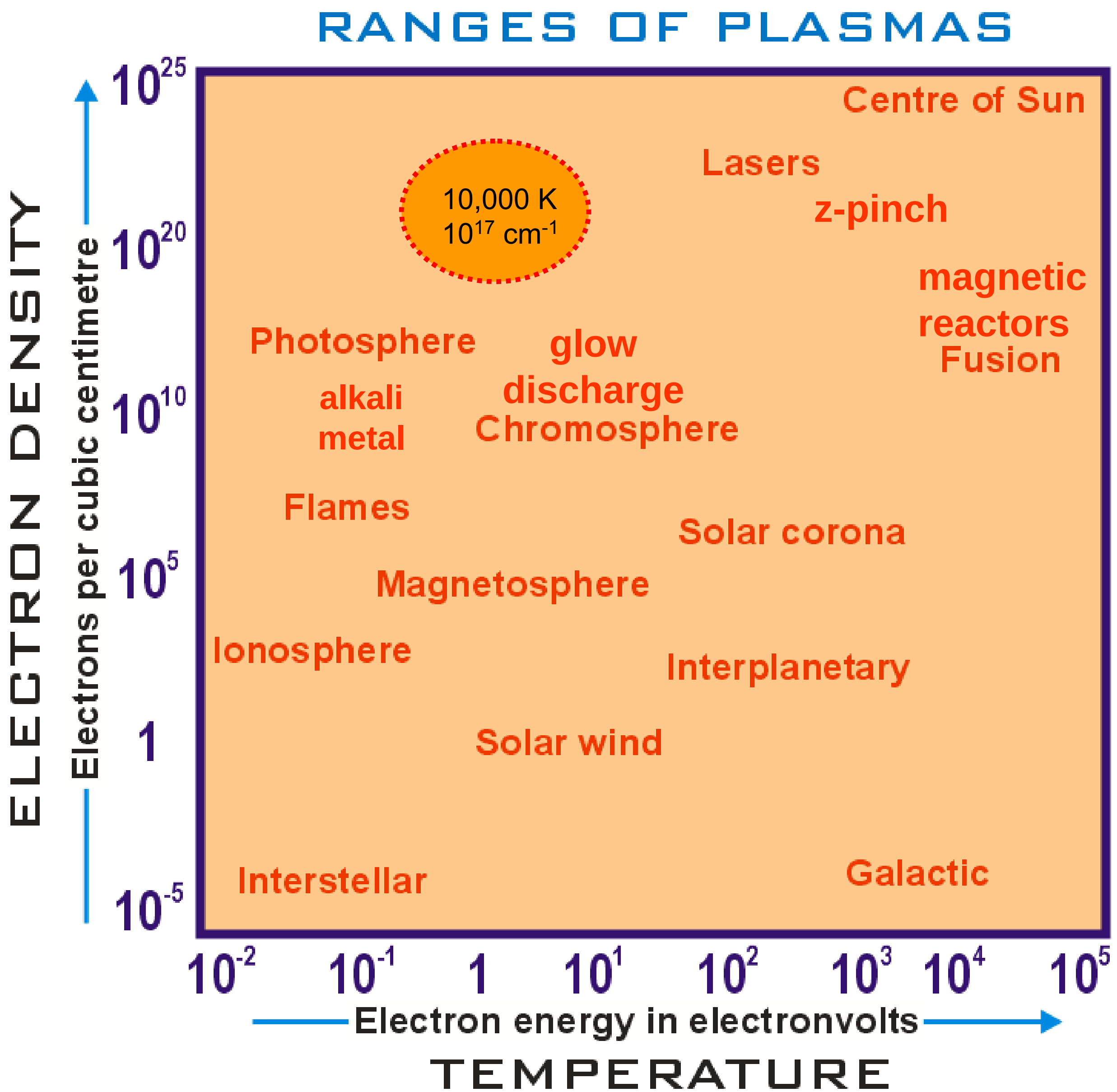
Physics of Plasma Formation: breakdown

2. electron cascade or avalanche occurs by inverse bremsstrahlung (free-free absorption)

$$\boxed{e^{-}(\text{slow}) + h\nu \rightarrow e^{-}(\text{fast})}$$

- electrons absorb photons from laser field (in the presence of gas) for momentum transfer between collisions with neutral species
- acquire sufficient energy for collisional ionization of gas atoms
- electron density increases exponentially via cascade

$$n_e\text{~}1\text{-}10\ \text{cm}^{-3} \rightarrow 10^{17}\text{-}10^{20}\ \text{cm}^{-3}$$


RANGES OF PLASMAS
ELECTRON DENSITY
Electrons per cubic centimetre
10^25
10^20
10^10
10^5
1
10^-5
10,000 K
10^17 cm^-1
Centre of Sun
Lasers
z-pinch
magnetic reactors
Fusion
Photosphere
glow discharge
alkali metal
Chromosphere
Flames
Solar corona
Magnetosphere
Ionosphere
Interplanetary
Solar wind
Interstellar
Galactic
10^-2
10^-1
1
10^1
10^2
10^3
10^4
10^5
Electron energy in electronvolts
TEMPERATURE

Physics of Plasma Formation: breakdown

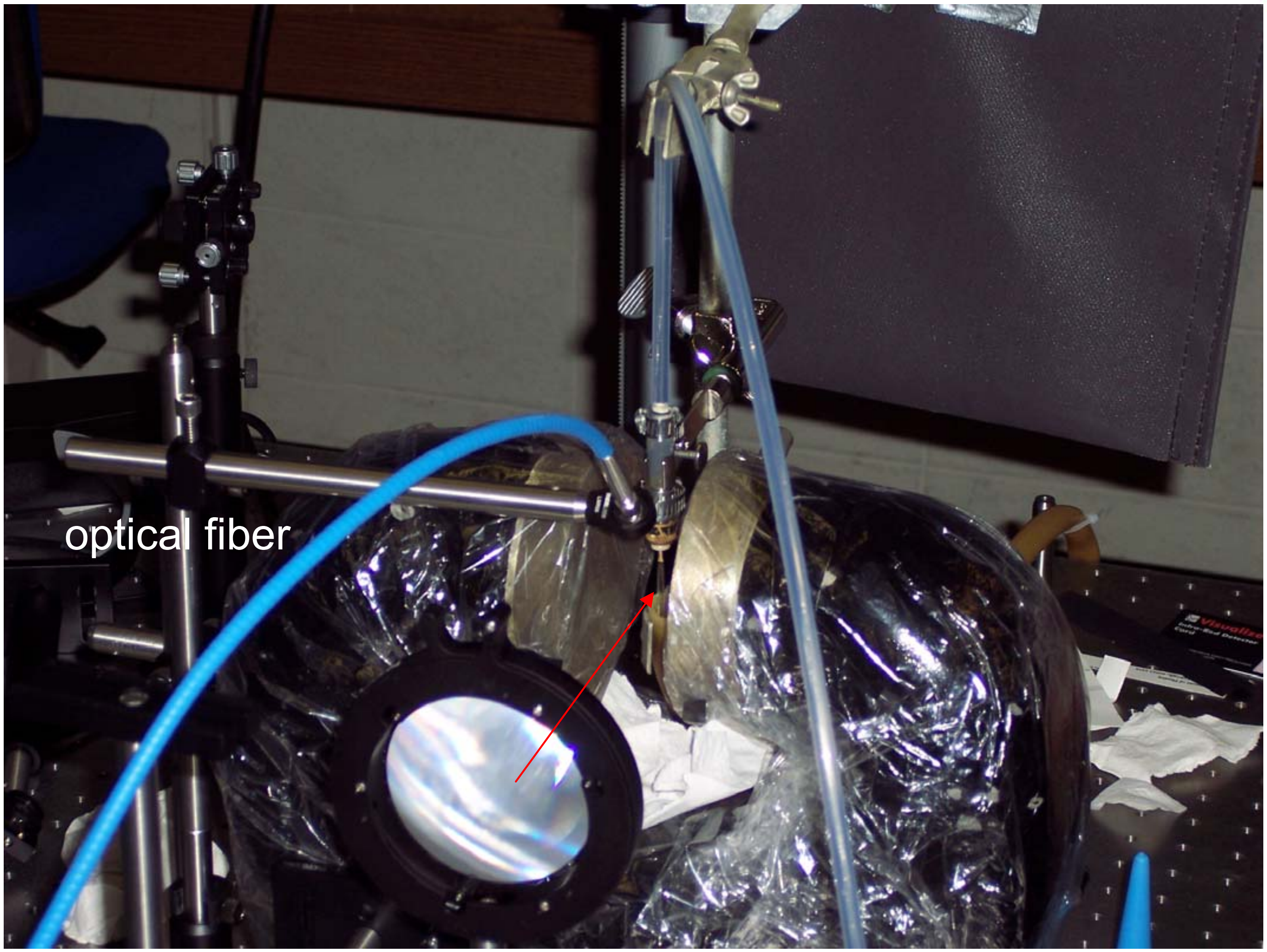
3. "breakdown" is arbitrarily defined

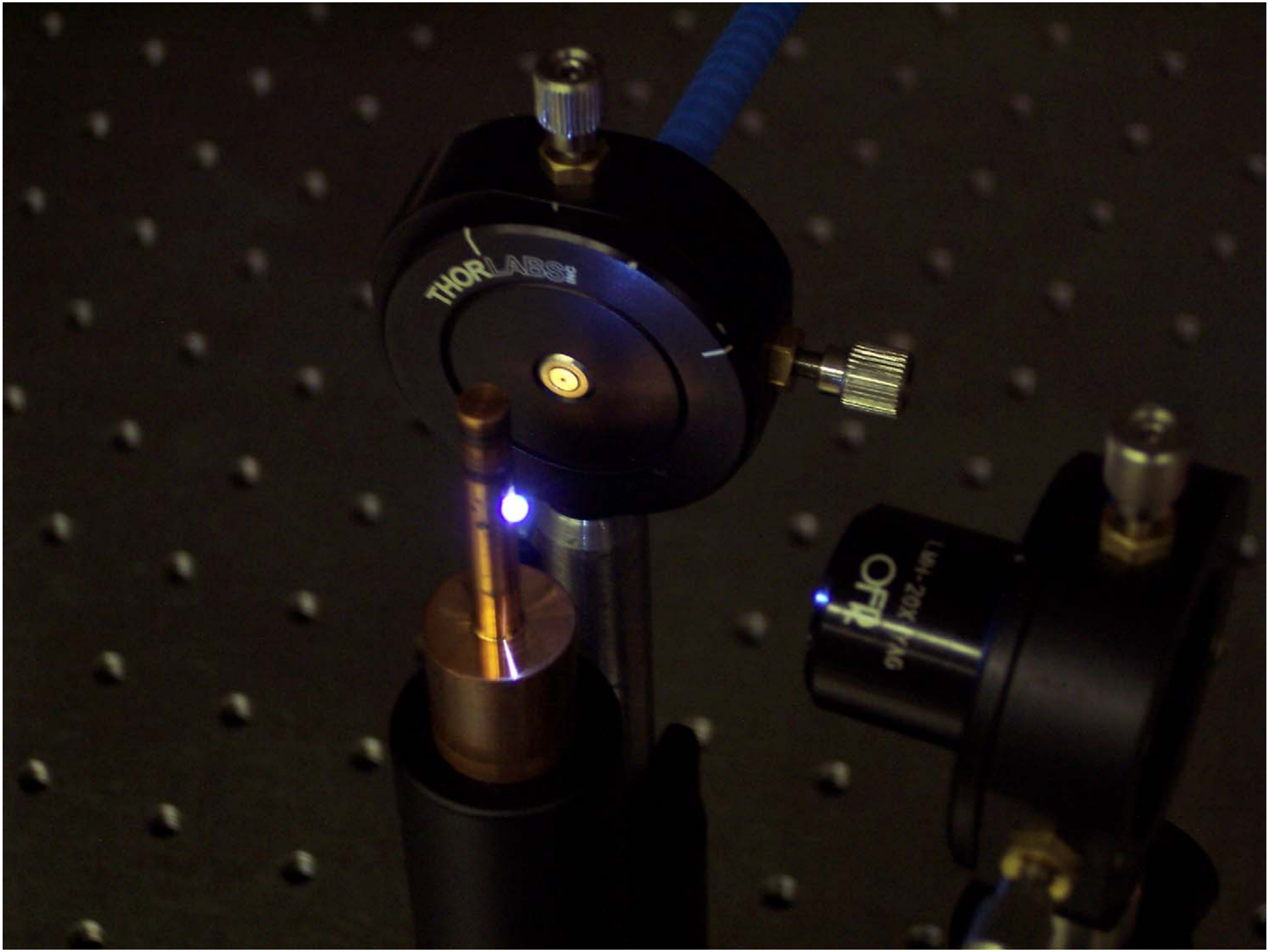
$n_e \sim 10^{13}$ cm^{-3} or degree of ionization of 10^{-3}

permits significant absorption and scattering of incident laser beam leads very fast to a fully developed plasma and shockwave

10 cm^{13} $\rightarrow$ 10^{17}-10^{20} cm^{-3}

What It Looks Like




THORLABS
OFR

Physics of Plasma Formation: plasma shielding

eventually, the plasma becomes opaque to the laser beam and the target is shielded

occurs when plasma frequency becomes greater than the laser frequency

$$\omega_p \approx \omega$$

or when

$$n_e \sim \left(10^{21} / \lambda^2\right) \mathrm{cm}^{-3}$$

The Goal of LIBS Plasma Creation

- to create an optically thin plasma which is in thermodynamic equilibrium and whose elemental composition is the same as that of the sample
  - if achieved, spectral line intensities can be connected to relative concentrations of elements
  - typically these conditions are only met *approximately*.

Plasma diagnostics

- temperature (excitation and ion)
- electron density
- species density

Spectral Line Radiant Intensity

$$I = {h\nu gAN}/{4\pi} = \left({hcN_0 gA}/{4\pi\lambda Z}\right)\exp\left({-E}/{kT}\right)$$

I = intensity (given in units of W/sr)

g = statistical weight of level

A = Einstein A coefficient

N_0 = total species population

Z = partition function (statistical weight of ground state)

E = Energy of upper state of transition

Temperature

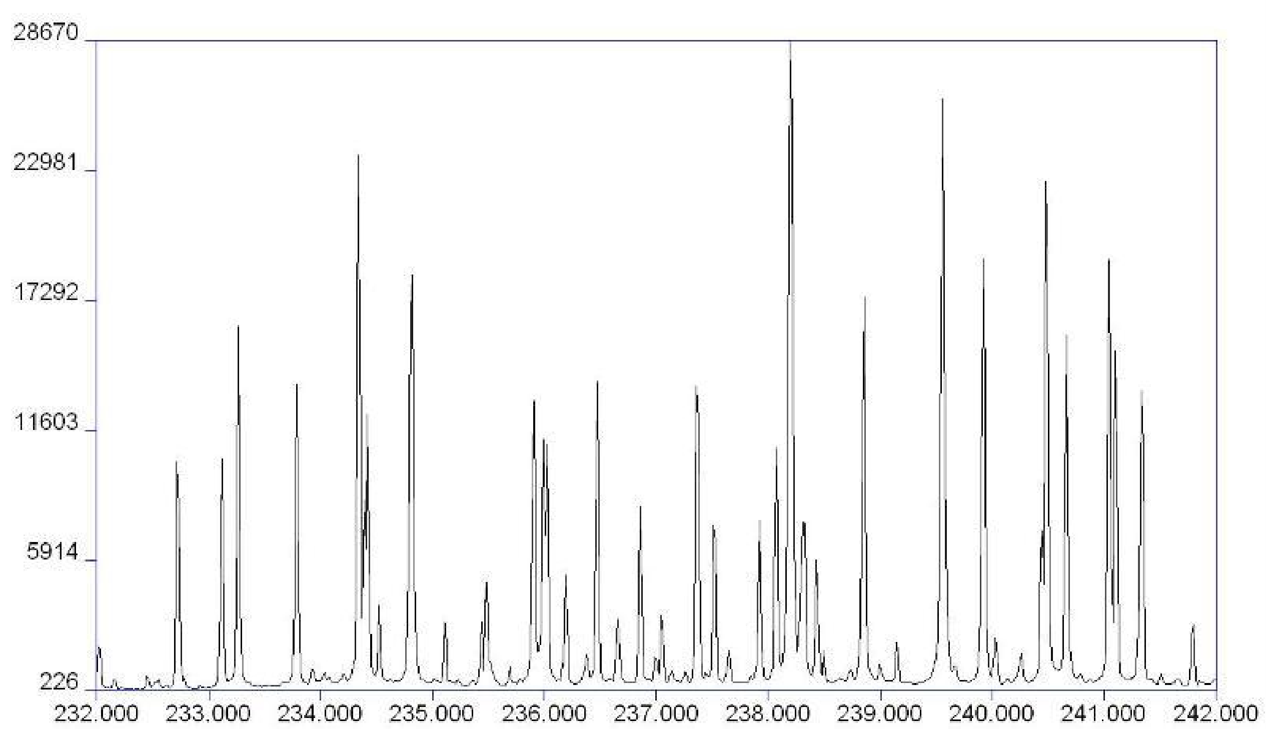
- confusing! better to write…

$$\ln\left(\frac{I\lambda}{gA}\right) = -\,{}^{E}\!/_{kT} - \ln\left(\frac{4\pi Z}{hcN_0}\right)$$

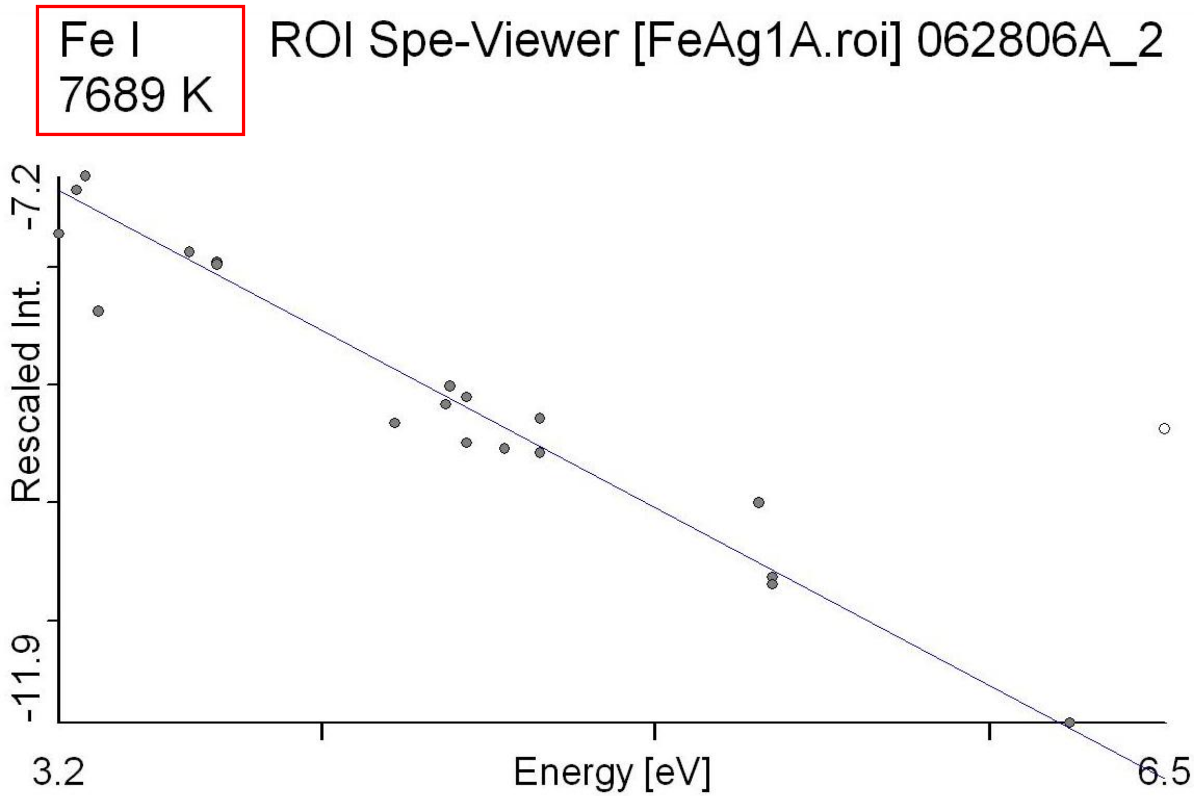
- This is a straight line with slope of -$1/kT$!

- So if we plot the adjusted measured line intensity vs. the upper state energy of transitions we can measure T of our plasma.

Fe_2O_3 / Ag Mixture



Fe Temperature



Boltzmann plot for 22 Fe transitions

Plasma Diagnostics

Temperature

plasma on water surface

Temperatures calculated from H_β / H_γ intensity ratio using Boltzmann equation:

$$\frac{I_1}{I_2} = \frac{g_1 A_1}{g_2 A_2} \frac{\lambda_2}{\lambda_1} \exp\left(-\frac{|E_1 - E_2|}{kT_e} \right)$$

Plasma Diagnostics

electron density

FWHM of Stark-broadened lines used to calculate electron density N_e

$$\boxed{N_e = C\left(N_e, T\right)\Delta\lambda_{FWHM}^{3/2}}$$

- N_e must be $> N_{e,crit}$

The Uses of LIBS

- industrial processes
  - analysis of steam generator tubes in nuclear power stations
  - grading of powered pellets for glass melts
  - analysis of treated wood in recycling centers
  - grading of iron-ore slurry prior to pelletizing

- environmental analysis
  - quantification of heavy metal content in soils, sand, and sludge
  - measurement of lead content in paint
  - waster quality assessments
  - hazardous waste remediation
  - atmospheric sampling

- biology
  - hair and tissue mineral analysis
  - identification of trace metals in teeth
  - spectral fingerprinting of bacterial strains
  - identification of bacterial spores, molds, pollens and proteins

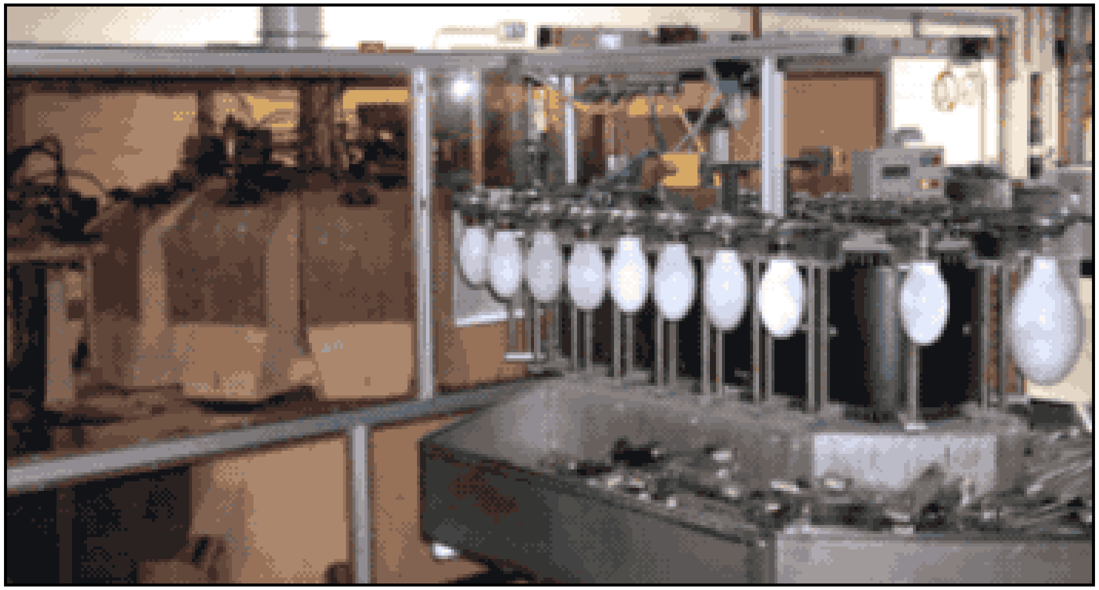
- defense/homeland security
  - detection of uranium in material,
  - high sensitivity detection of chemical and biological agents
  - *in situ* detection of land mines

- forensic science
  - identifying gunshot residue on hands
  - pen ink characterization

- art conservation
  - identifying pigments in paintings
  - dating/cleaning ancient marble

Pharma-LIBS
for pharmaceutical slurry
analysis

on-line iron ore slurry additive
measurement



recycling of lamp glasses at WEREC GmbH

courtesy of LLA Instrumetns GmbH

courtesy of Applied Photonics Ltd, U.K.

MP-LIBS A full laboratory High-Resolution Broadband LIBS system in a portable backpack

Backpack contains broadband high-resolution spectrometer, laser power supply, computer, and battery

courtesy of Ocean Optics.

Head's-up display

Hand-held probe contains laser, joystick for control, and focus optics

Microplasma/ LIBS Event

Detection of Trace Metal Contaminants in Simulated Human Tissue

NSF-REU SSIM Project

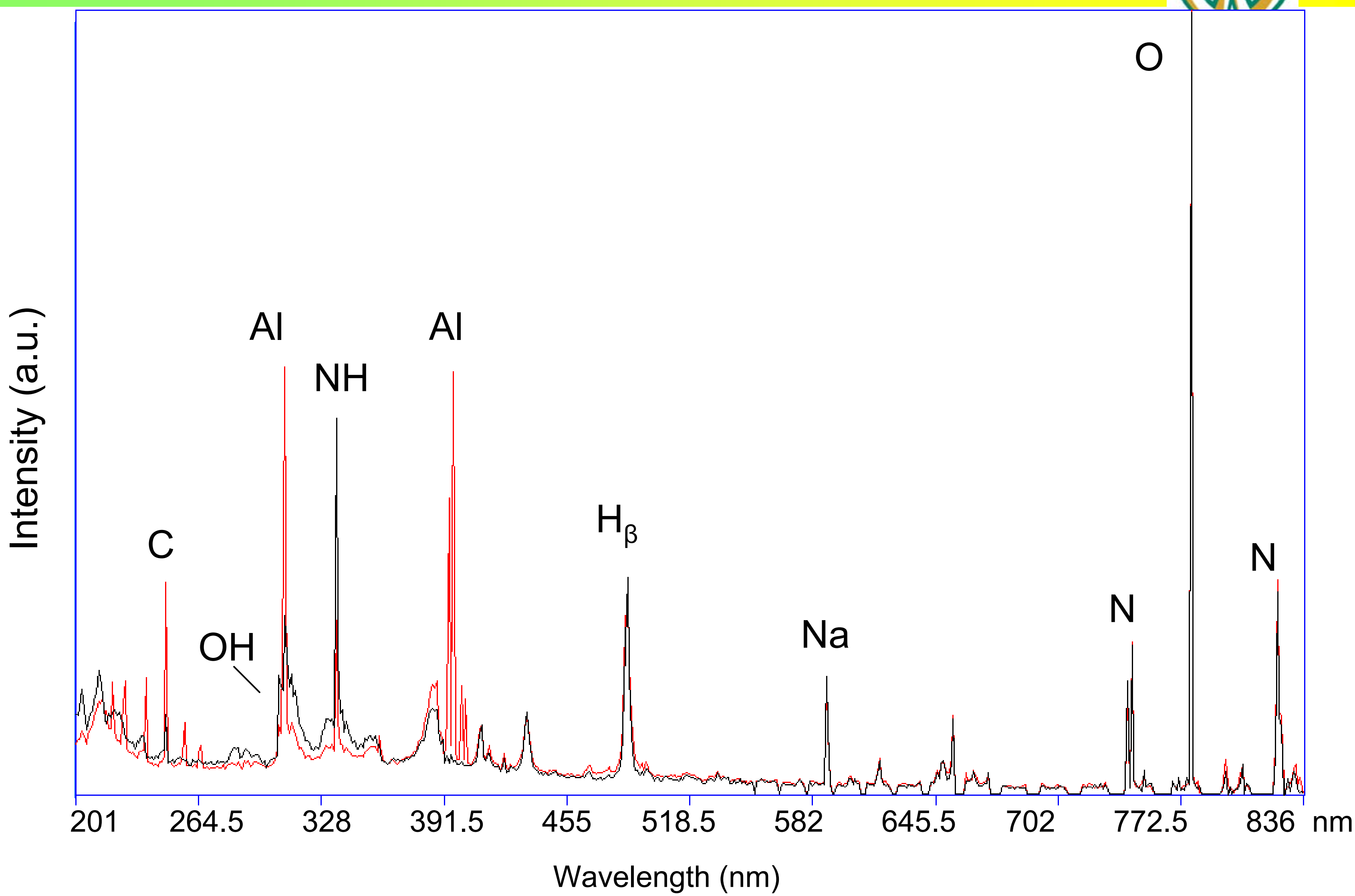
The Problem

- Retinal implants are possibly leaching aluminum contaminants into tissue.

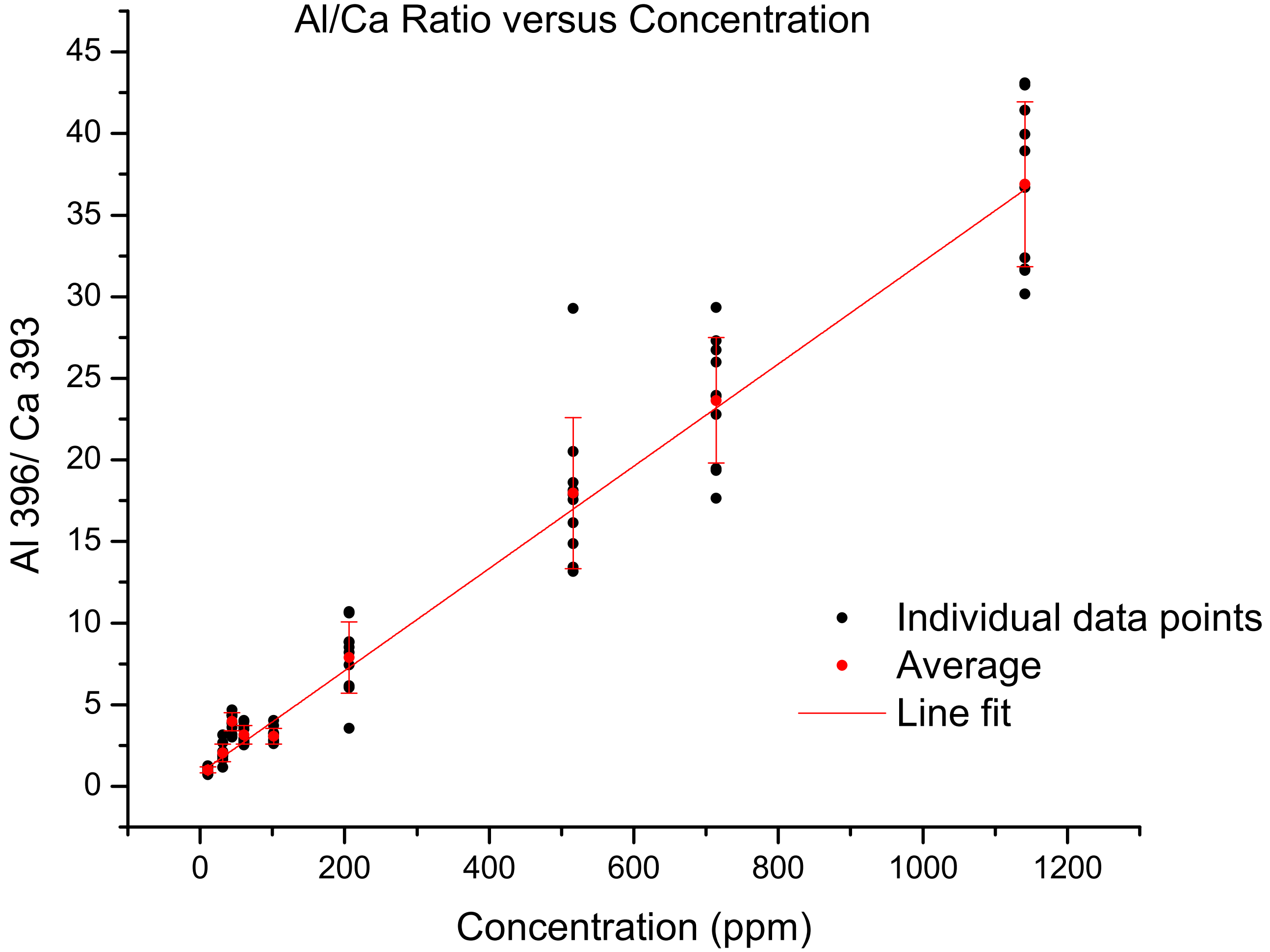
Our Solution

- Use LIBS on tissue to determine if and how much aluminum is there.

A sample spectrum



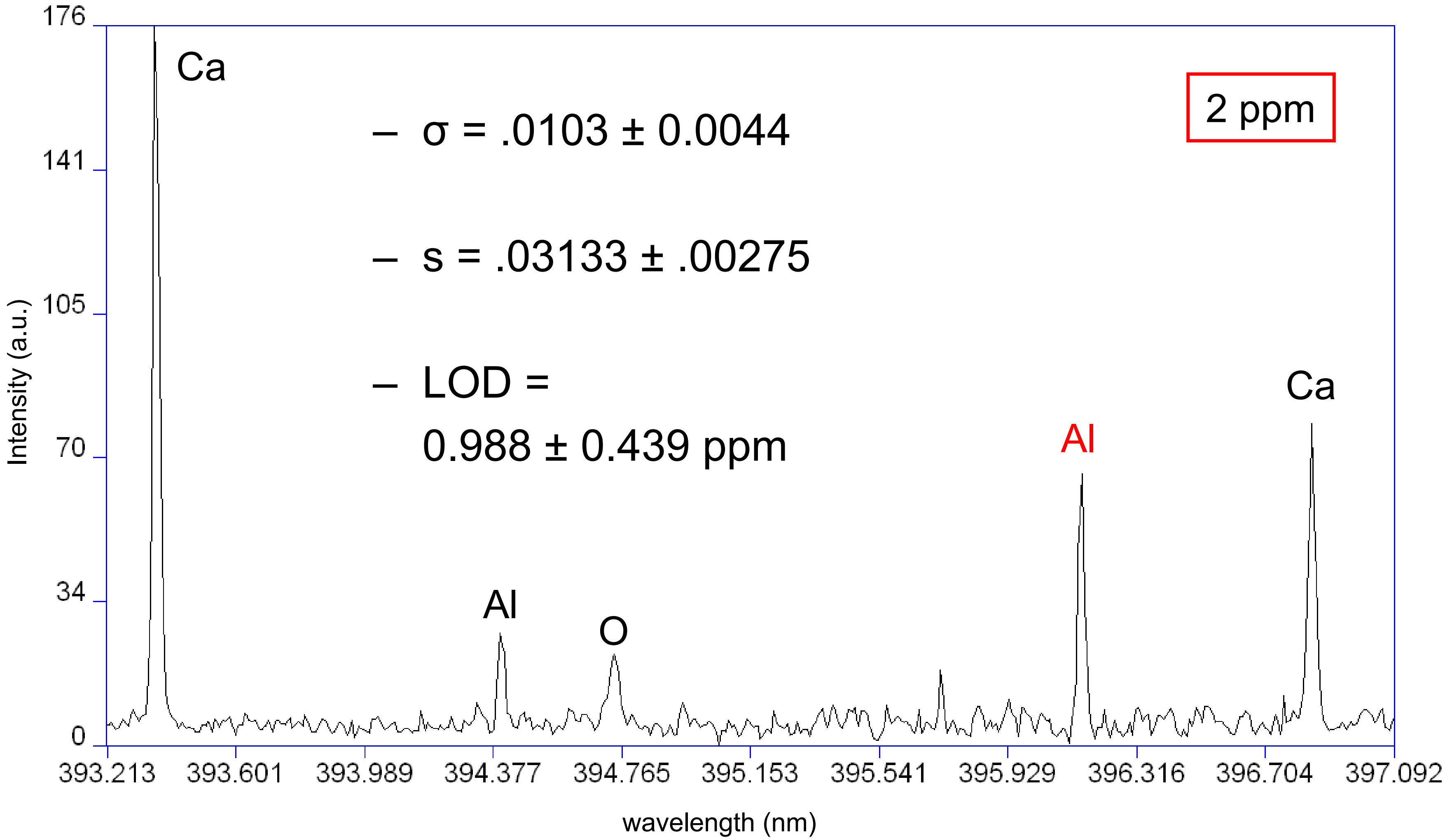
Concentration Curves



$R^2 = 0.89$

$s = 0.0313$

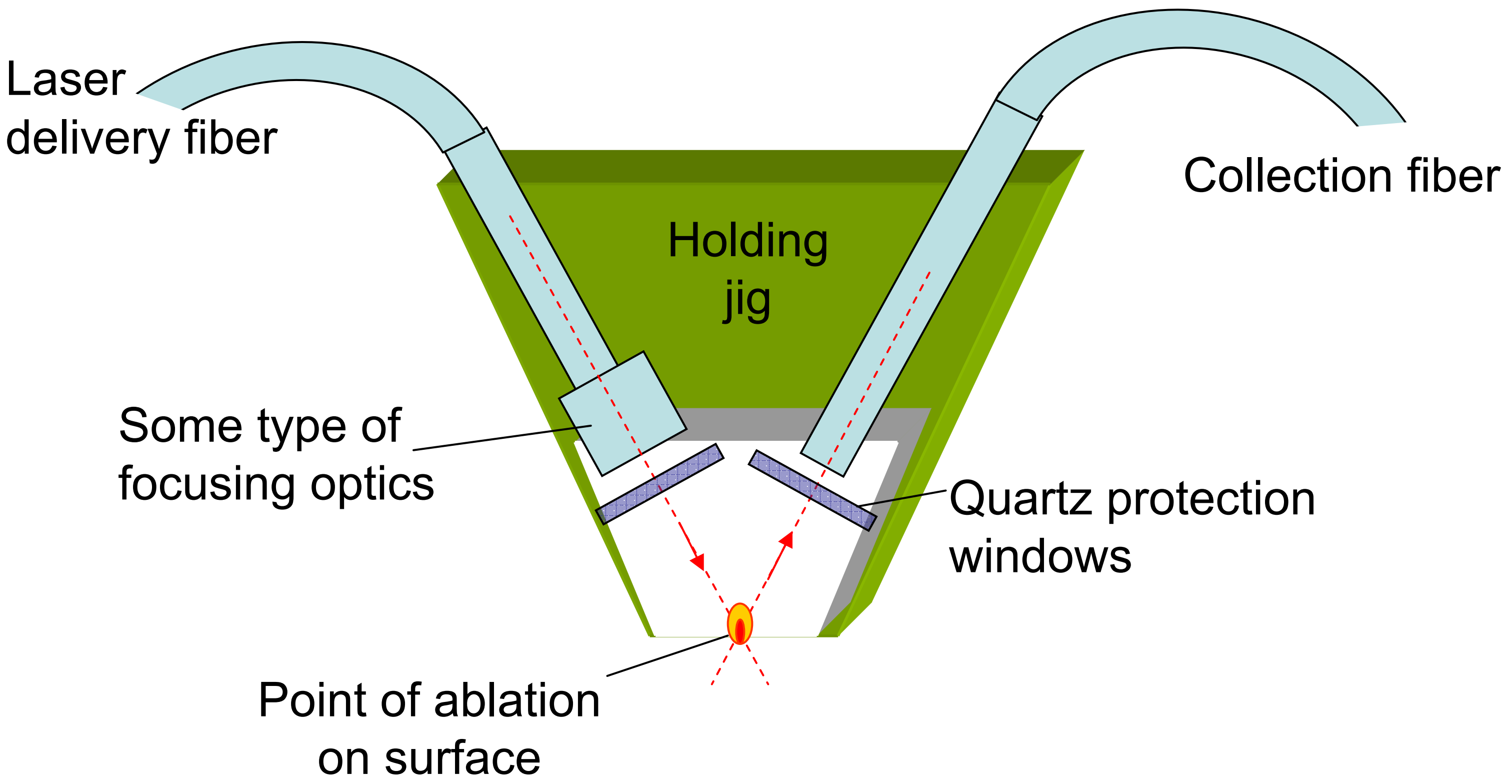
Limit of Detection



- σ = .0103 ± 0.0044
- s = .03133 ± .00275
- LOD = 0.988 ± 0.439 ppm

Future Work

- Fiber Delivery



Detection and Discrimination of Bacteria Strains

Motivation

- Require a real-time early-warning detection technology for bio-agents (bacteriological)

- Downside of competing technologies:
  - speed
  - target-specific (shelf-life?)
  - expertise required

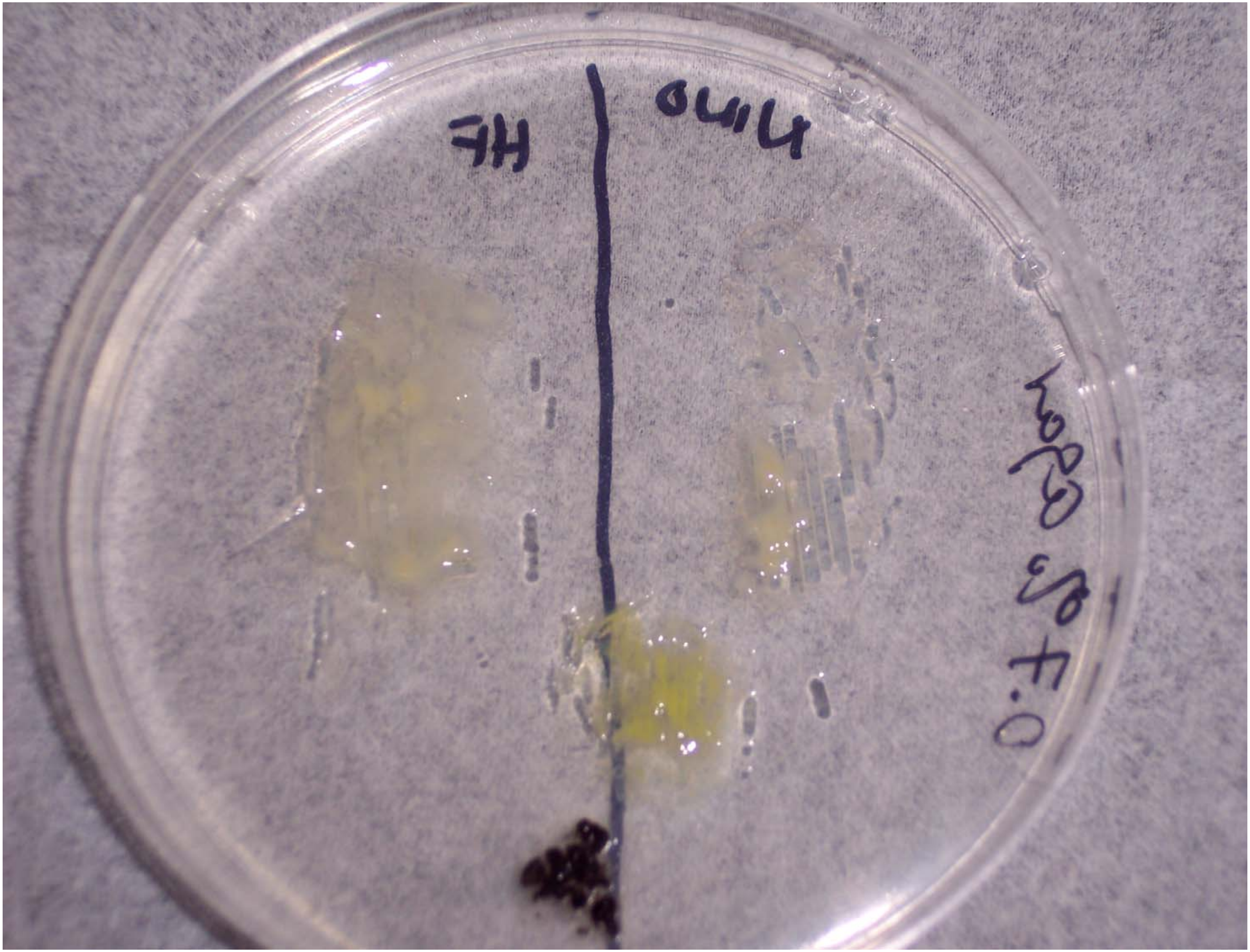
Escherichia coli

- Very common laboratory micro-organism
- Has many strains, most harmless, some pathogenic
- EHEC or *E. coli* 0157:H7 causes kidney failure in children (hemolytic uremic syndrome)

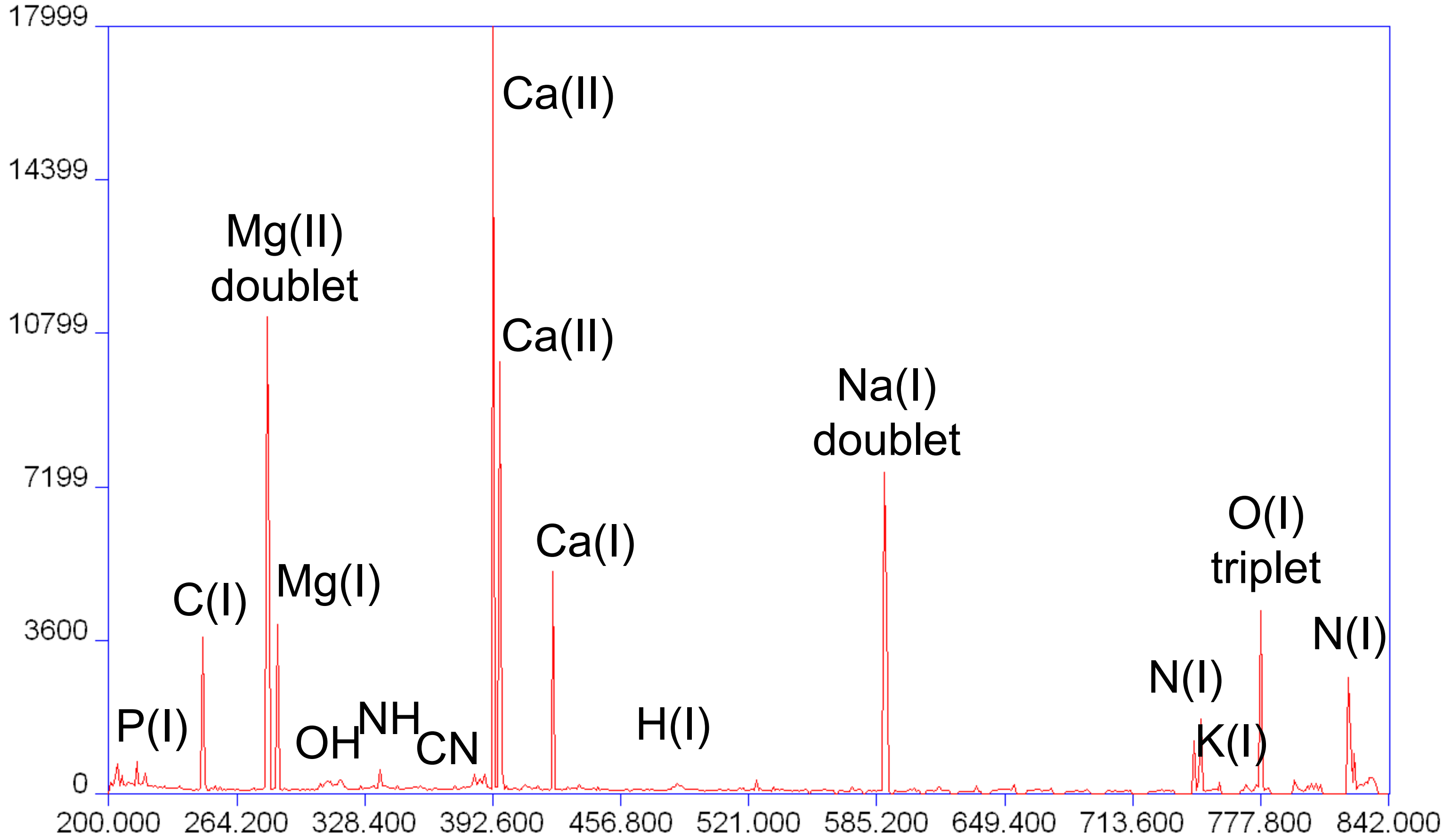
Inorganic Composition of *E. coli*

from "*The Bacteria: A Treatise on Structure and Function*" I.C. Gunsalus and R.Y. Stanier, eds

Element	% of fixed salt fraction
Sodium	2.6
Potassium	12.9
Calcium	9.1
Magnesium	5.9
Phosphorus	45.8
Sulfur	1.8
Iron	3.4



E. coli Spectrum



Spectral Fingerprint

The intensities of 19 spectral lines from 6 elements provides a *spectral fingerprint*

wavelength (nm)	line identification	Fraction of total spectral power	Wilks' Lambda
213.618	P I	0.034	.619
214.914	P I	0.040	.492
247.856	C I	0.099	.521
253.56	P I	0.007	.771
279.553	Mg II	0.202	.040
280.271	Mg II	0.113	.061
285.213	Mg I	0.109	.037
373.69	Ca II	0.002	.909
383.231	Mg I	0.015	.782
383.829	Mg I	0.005	.588
393.366	Ca II	0.099	.034
396.847	Ca II	0.037	.060
422.673	Ca II	0.033	.062
430.253	Ca I	0.002	.803
518.361	Mg I	0.004	.773
585.745	Ca I	0.000	.920
588.995	Na I	0.124	.020
589.593	Na I	0.067	.022
769.896	K I	0.012	.931

Discriminant Function Analysis

- The relative strengths of the 19 emission lines forms the basis of an identification
- A statistical analysis called Discriminant Function Analysis (DFA) looks for similarities and differences in spectra from different strains

Discriminant Function Analysis

- We want to see the difference between *N* groups (*N* strains), each group composed of spectra containing 19 independent variables (predictor variables)

$$X = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ \ldots \\ x_{19} \end{bmatrix}$$

one entire LIBS spectrum reduced to this

Canonical Discriminant Functions

- DFA constructs *N*-1 "Canonical Discriminant Functions"
  - essentially the eigenvectors of the system
  - use the eigenvalues to rate the importance of the canonical discriminant functions

$$DF^{1} = \left[b_1^1 b_2^1 b_3^1 \ldots b_{19}^1 \right]$$

$$DF^{N-1} = \left[b_1^{N-1} b_2^{N-1} b_3^{N-1} \ldots b_{19}^{N-1} \right]$$

decreasing importance to the overall discrimination.

Discriminant Functions Scores

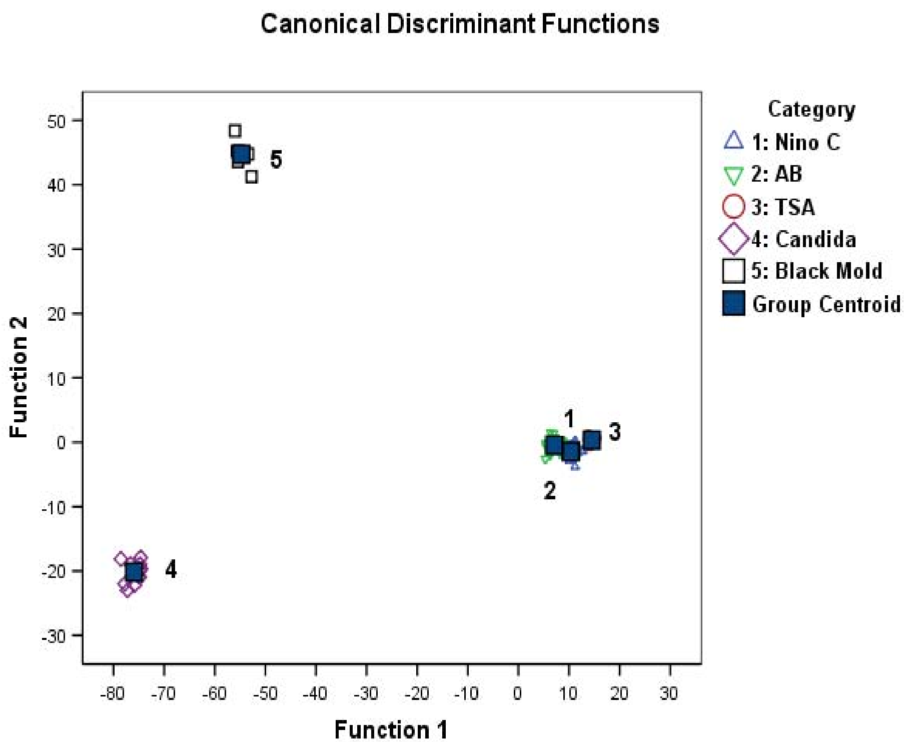
- Using the *N*-1 Canonical Discriminant Functions, *discriminant function scores* are constructed

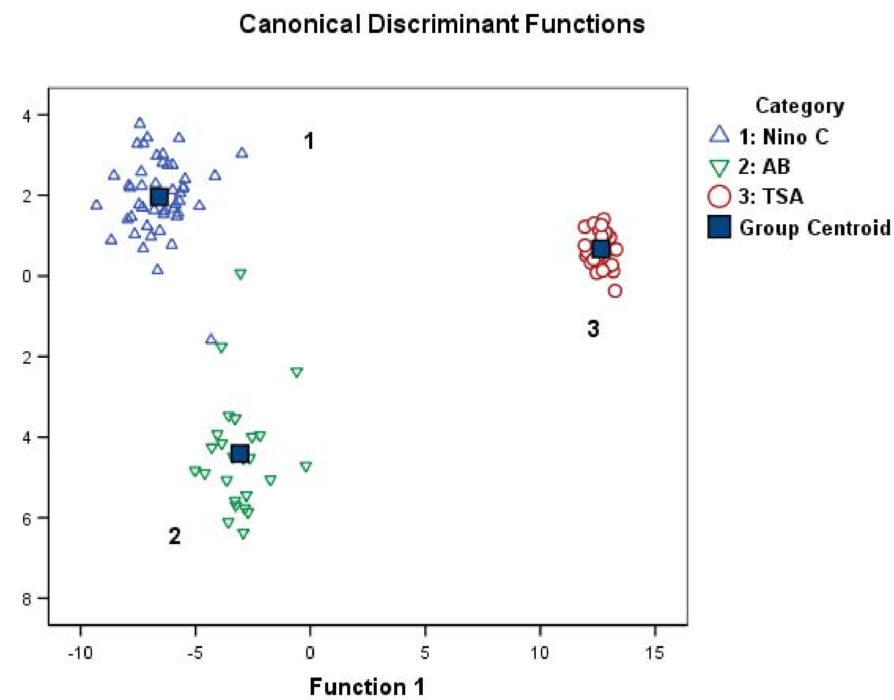
$$DF^{j} = b_0^j + \sum_{k=1}^{19} b_k^j x_k = b_0^j + \left[b_1^j b_2^j \ldots b_{19}^j \right] \begin{bmatrix} x_1 \\ x_2 \\ \ldots \\ x_{19} \end{bmatrix}$$

discriminant function (eigenvector)

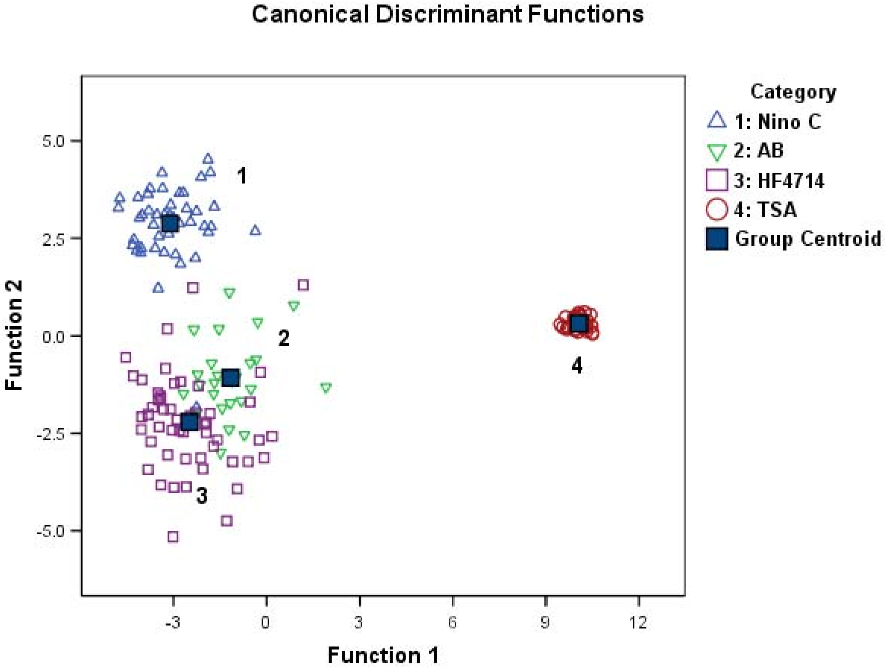
experimental data

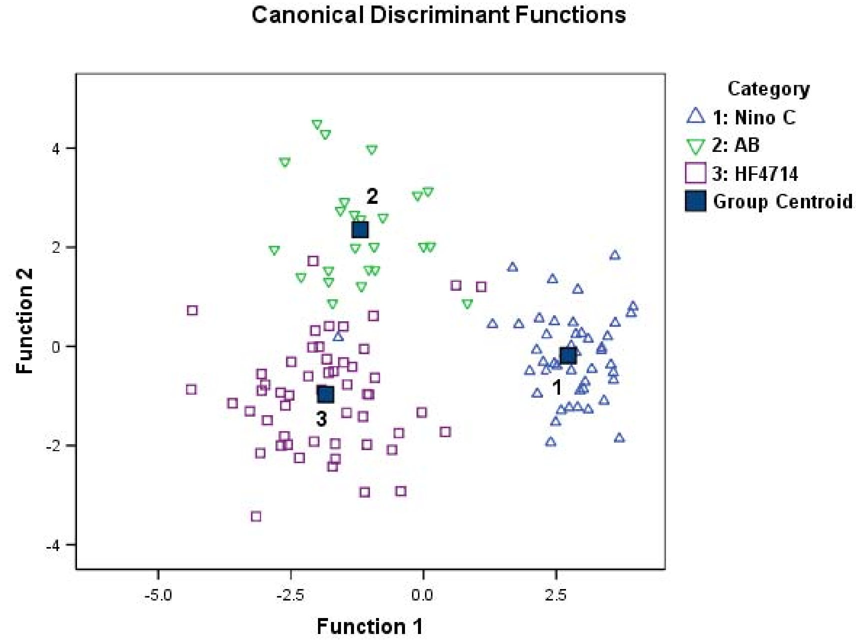
E. coli Results



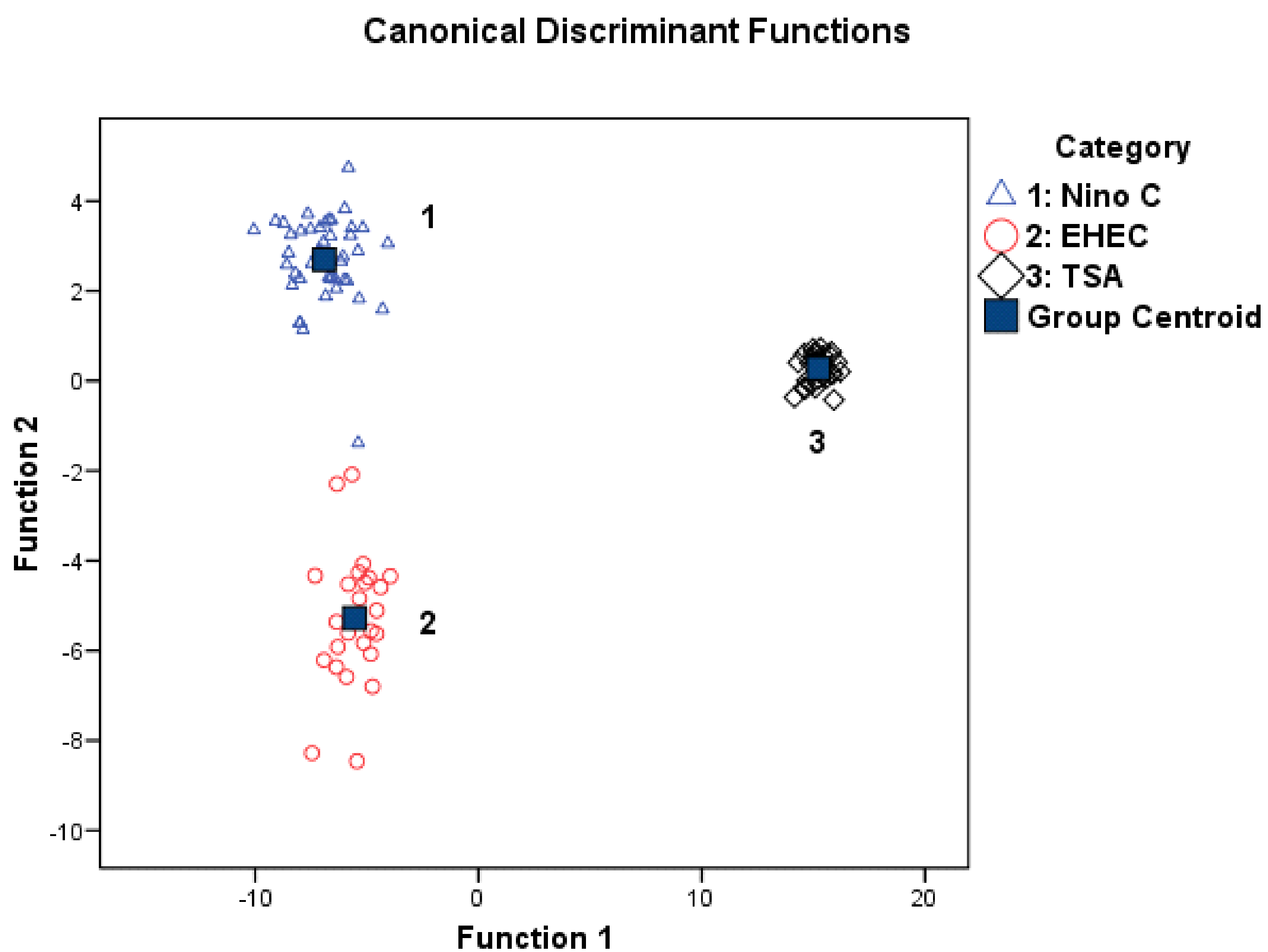


E. coli Results

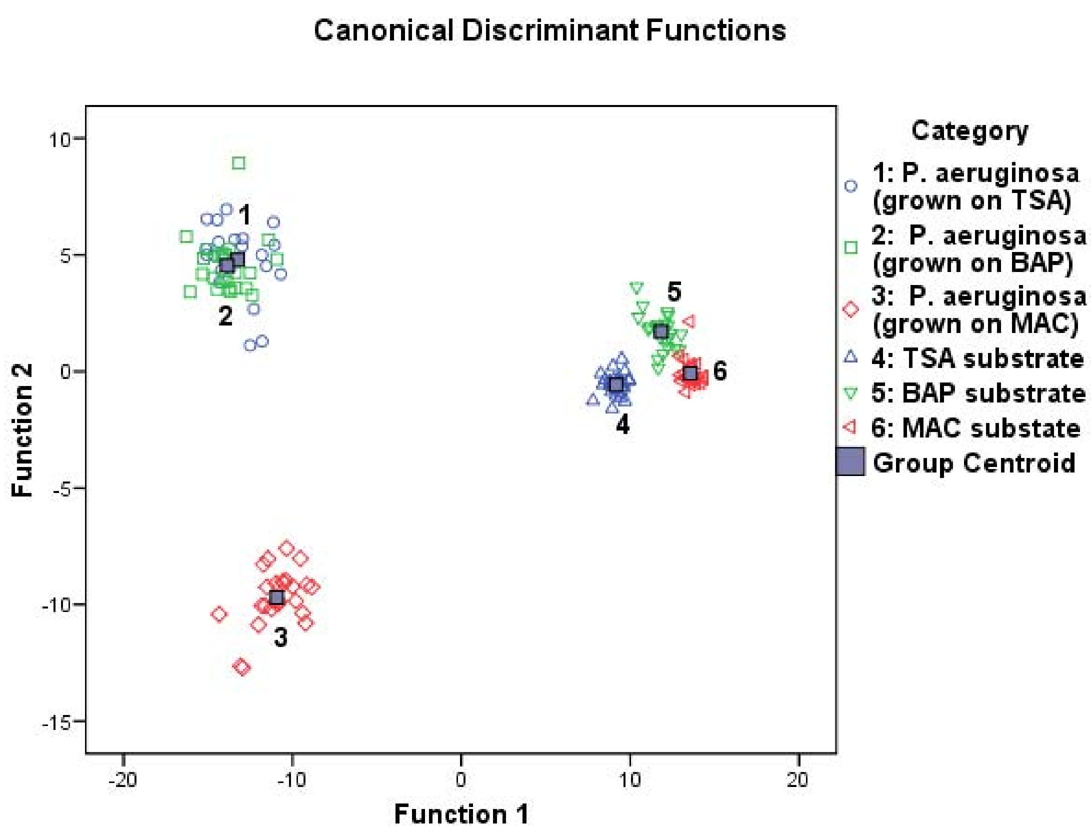




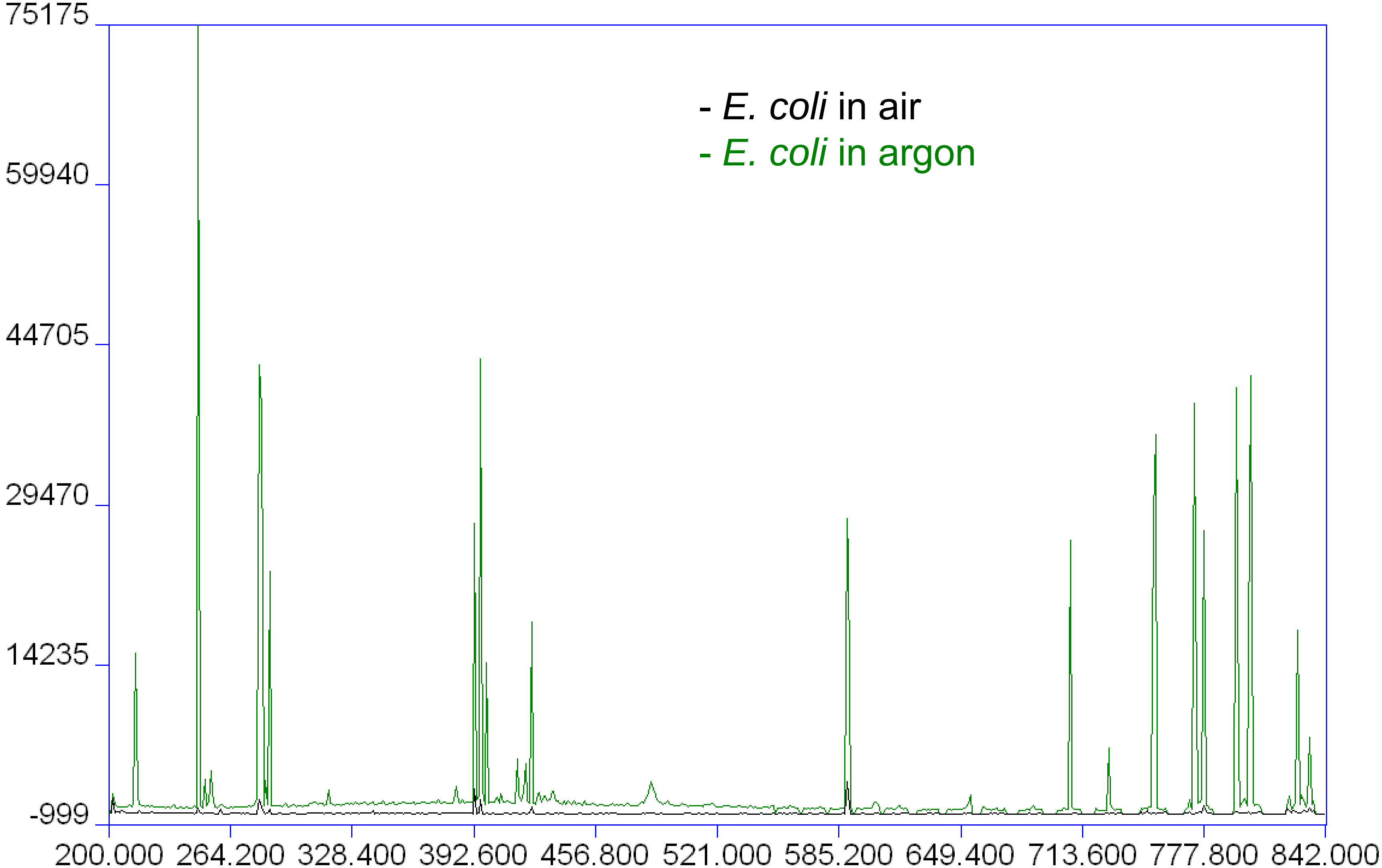
EHEC Results



Effect of Growth Environment on *P. aeruginosa*



Improvements



Conclusions

- LIBS a versatile, extremely useful technology

- Many applications in biological systems (and elsewhere)

Thank you for your attention!

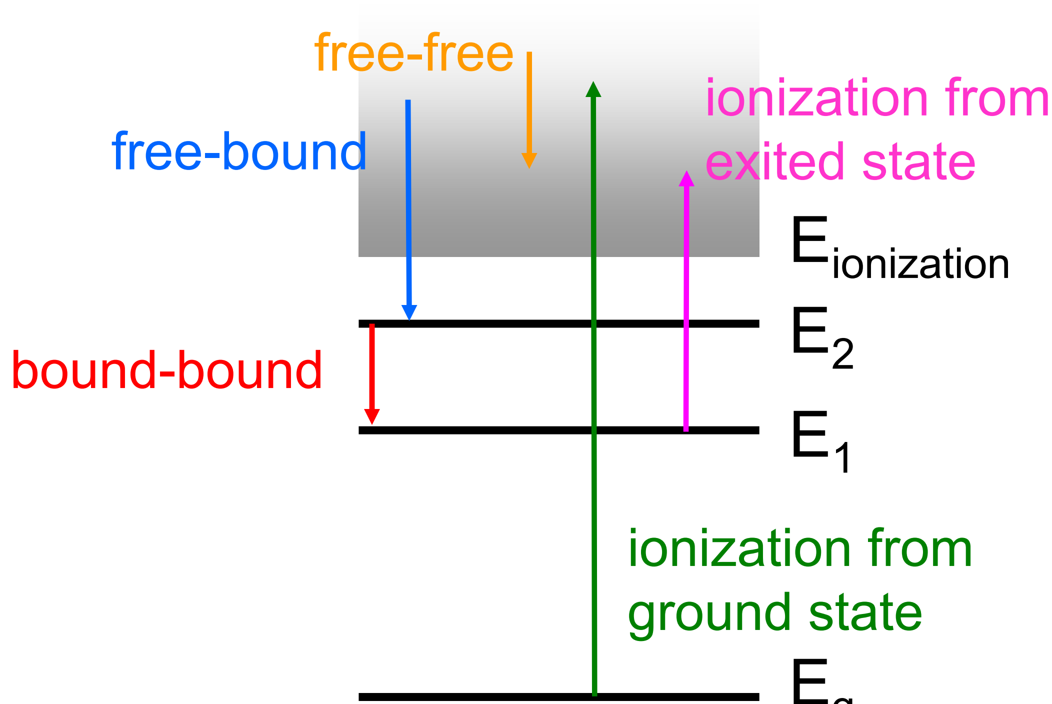
<u>Graduate Students</u>

- Jon Diedrich
- Arathi Padhmanabhan

<u>Undergraduate Students</u>

- Marian Adamson
- Emmett Brown
- Garrett Godfrey

Transitions in an Atom or Ion



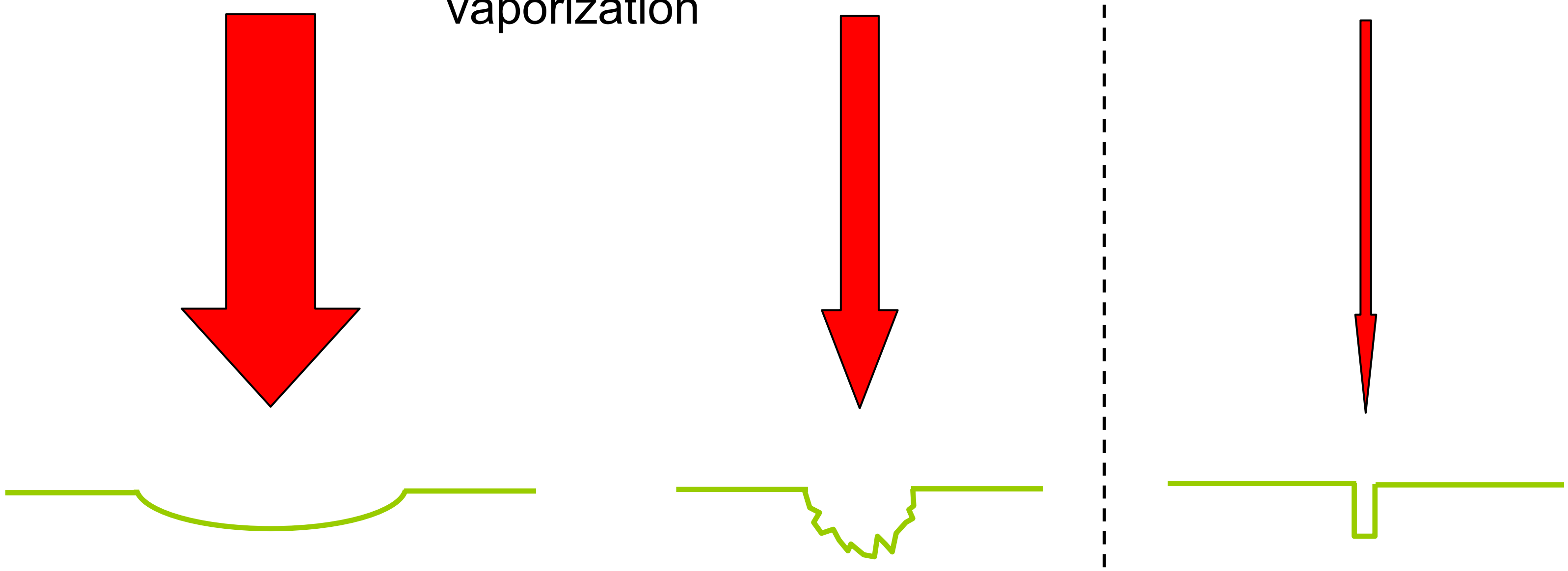
Physics of Plasma Formation: ablation

heating

melting

vaporization

τ_{pulse} < plasma initiation



microsecond   nanosecond   femtosecond

Physics of Plasma Formation: ablation

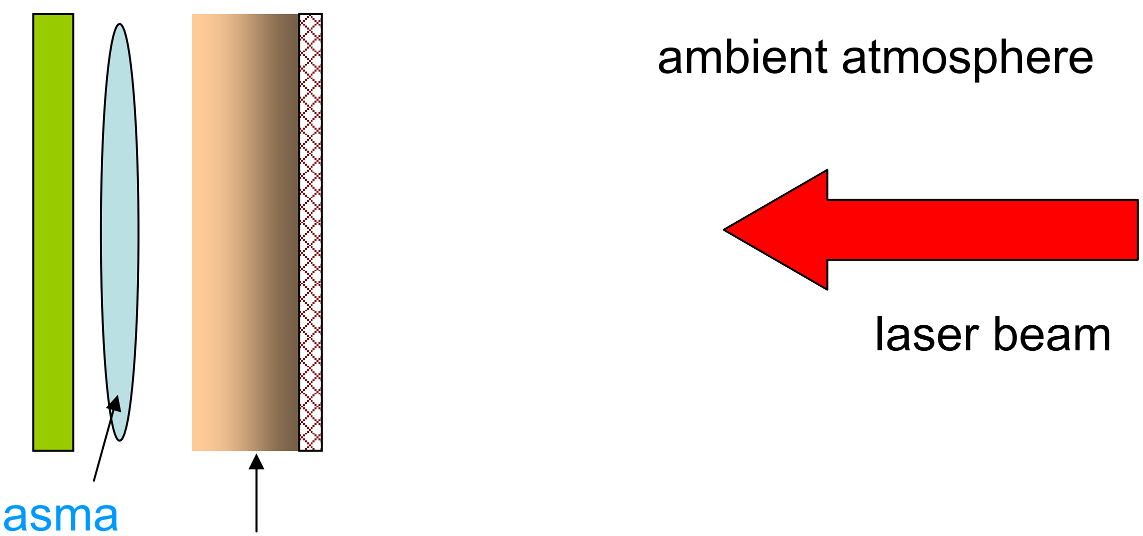
$$I_{\min} = \frac{\rho L_V \kappa^{1/2}}{\Delta t^{1/2}} (\mathrm{W/cm^2})$$

- ρ = density
- L_V = latent heat of vaporization
- κ = thermal diffusivity
- Δt = laser pulse length

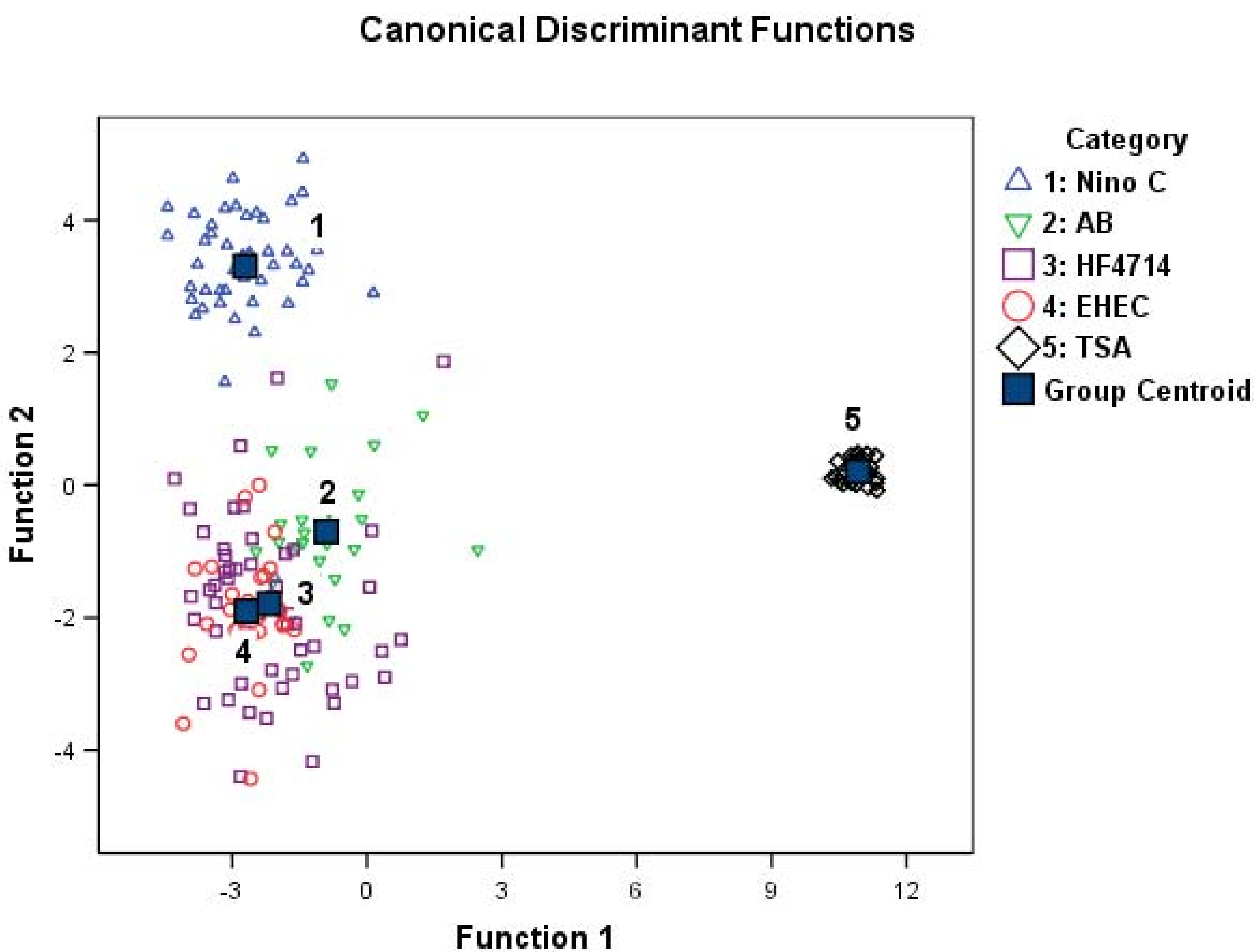
- $I_{\min}$ Al = 1.75 x 10^8 W/cm^2
  – for a 10 ns pulse, focused to a 100 μm spot: ~130 μJ

Physics of Plasma Formation: laser detonation wave

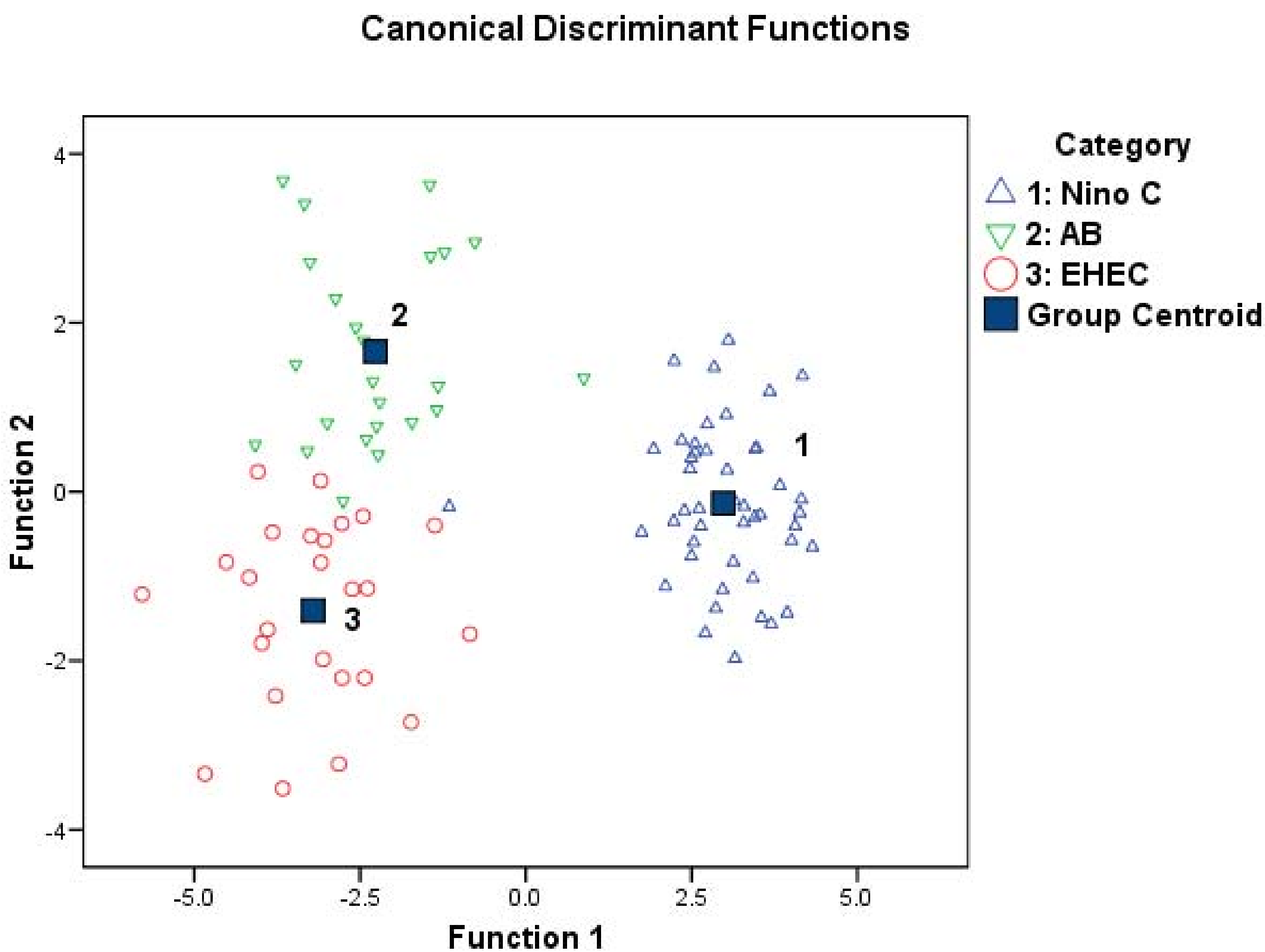
laser-supported detonation wave (LSD or LDW) with a supersonic, rapidly expanding shock-wave front



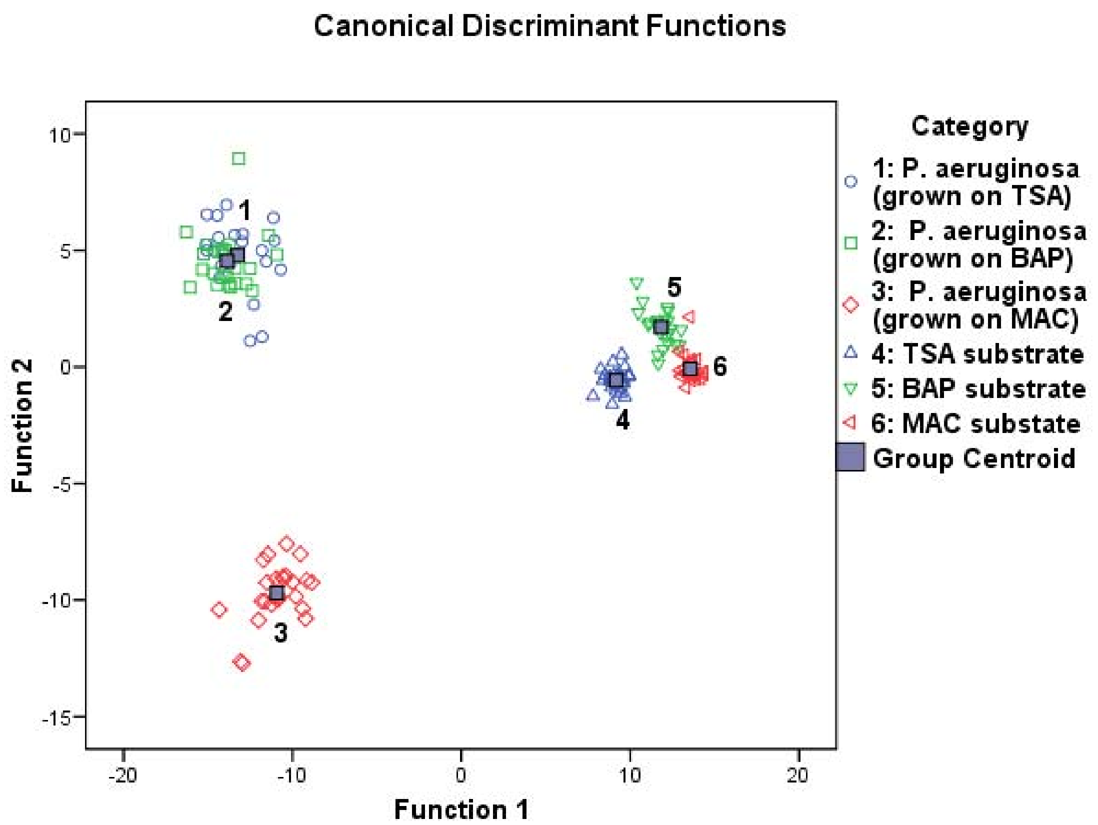
EHEC Results



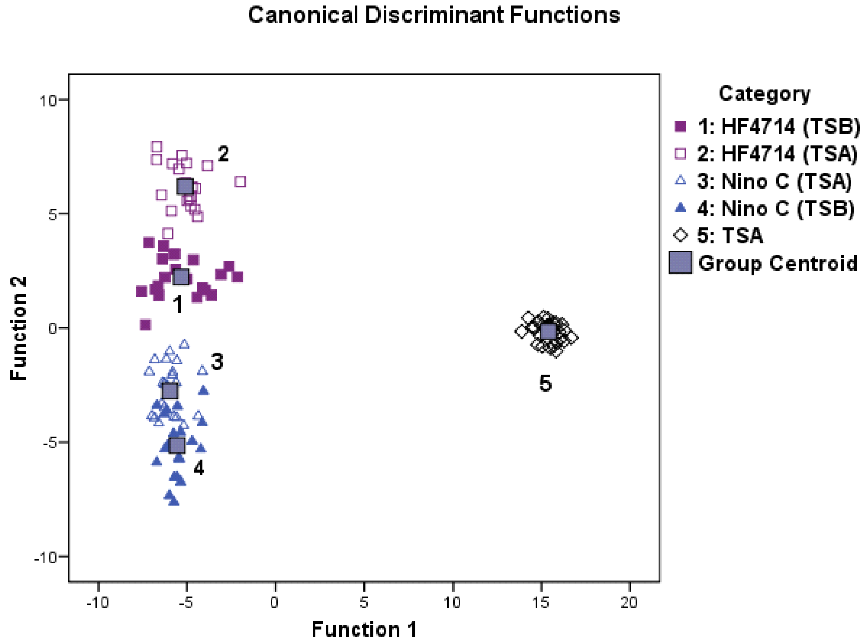
EHEC Results

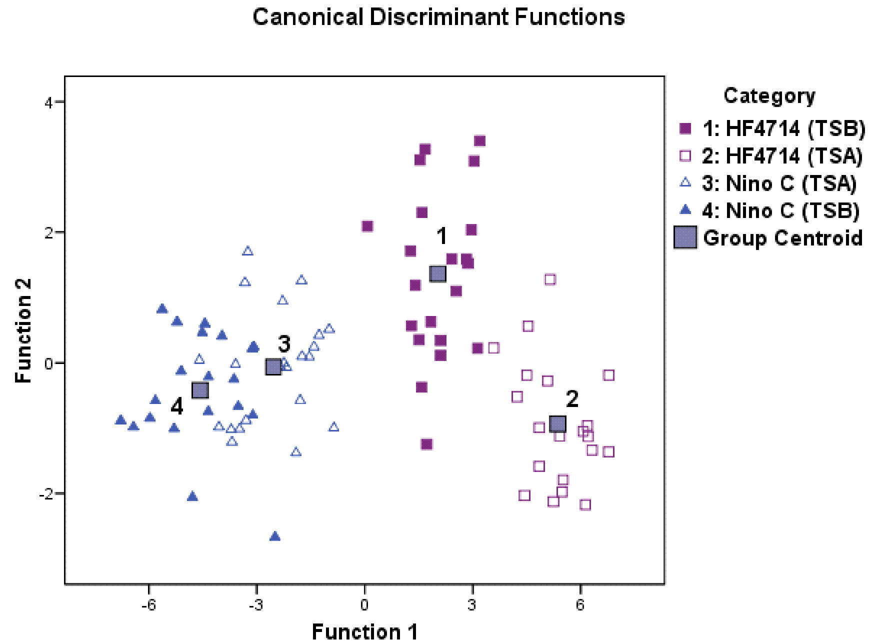


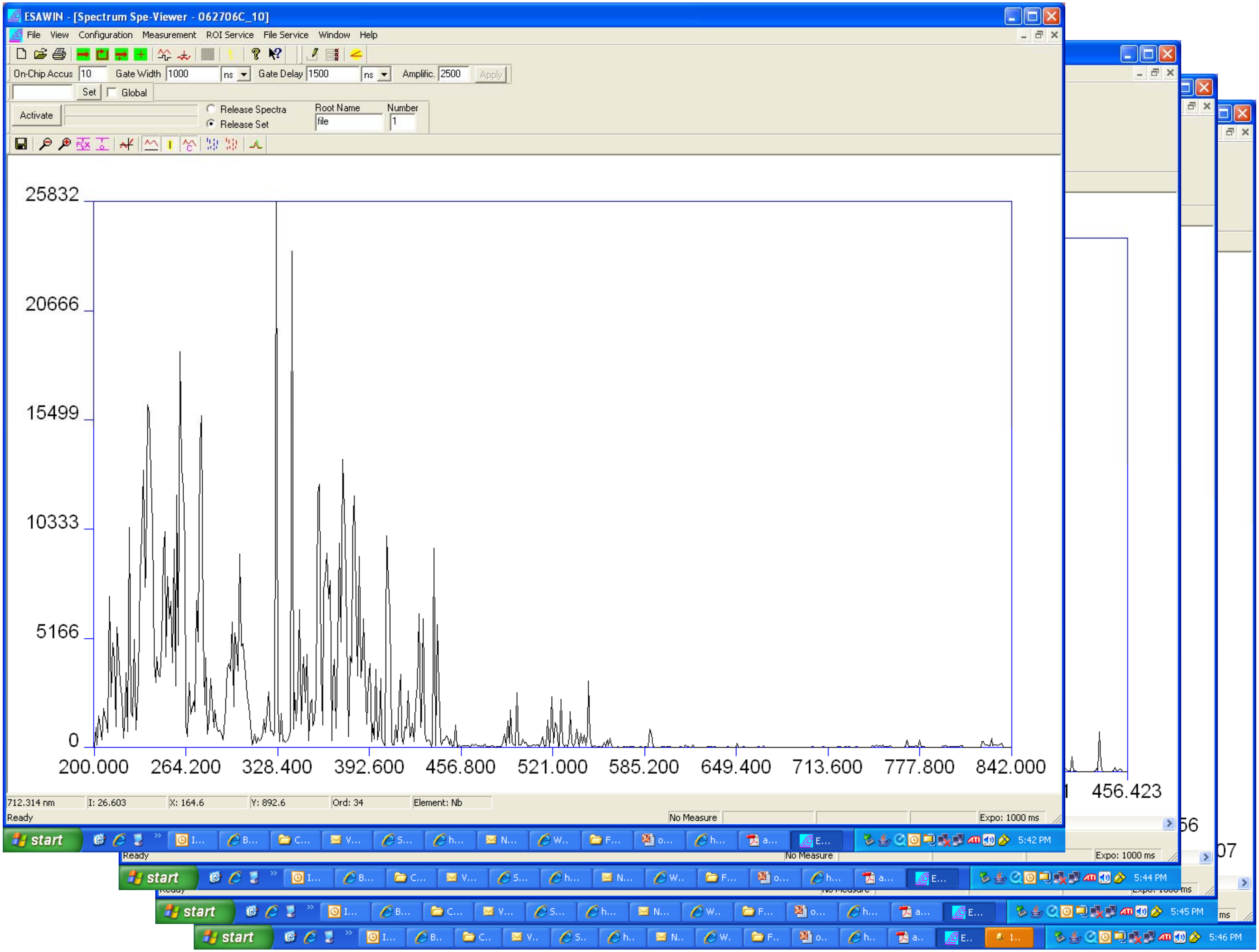
Effect of Growth Environment on *P. aeruginosa*



Effect of Growth Environment on *E. coli*



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15499
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328.400
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585.200
649.400
713.600
777.800
842.000
712.314 nm
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X: 164.6
Y: 892.6
Ord: 34
Element: Nb
Ready
No Measure
Expo: 1000 ms
start
5:42 PM
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Expo: 1000 ms
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5:45 PM
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