Prof. Eric Cornell to visit WSU

Recipient of the 2001 Nobel Prize in Physics

Two Lectures you may be interested in…

Departmental Colloquium – Wednesday, April 9, 2008, 4:00

"Why is Warm Glass Stickier Than Cold Glass?"

What we think of as "empty" space is really filled with a fluctuating electric field. These tiny electric fields are spooky-seeming but entirely real. They give rise to the stickiness of a perfectly clean glass surface. I'll talk about a set of experiments we did on this so-called Casimir-Polder force; time permitting I'll explore connections to eschatology as well.

Public Lecture – Thursday April 10, 2008, 4:00

"Stone cold science: Bose-Einstein condensation and the weird world of physics a millionth of a degree above absolute zero"

As atoms get colder and colder, they become more and more like waves, and less like particles. When a gas of atoms gets so cold that the "waviness" of one atom overlaps the waviness of another, the result is a sort of quantum mechanical identity crisis, a "condensation" predicted 70 years ago by Albert Einstein. Prof. Cornell will discuss how one reaches the necessary record-low temperatures, and explain why one goes to all the trouble to make this bizarre state of matter.

Undergraduate Interaction

- We are organizing special sessions (of modern physics, biomedical physics seminar, and quantum mechanics I for undergraduates, as well as an “ice-cream social” prior to the Departmental colloquium just for undergrads.
- We are organizing an undergraduate poster session for the hour preceding the public lecture for students to present their research to the public and Prof Cornell.
- http://www.clas.wayne.edu/Physics/

Laser-Induced Breakdown Spectroscopy (LIBS): A Future Super Star of Atomic Spectrometry and Its Application to Rapid Bacteria Identification

University of Windsor, Feb. 21st, 2008

Steven J. Rehse
Department of Physics and Astronomy

WAYNE STATE UNIVERSITY

Our Department

- 29 faculty
- 53 grad students
- 30 undergrad students

My work: Experimental atomic physics

- laser-induced breakdown spectroscopy
- laboratory astrophysics (continuation of work done at UWO with Holt/Rosner)

Outline

1. Introduction to LIBS

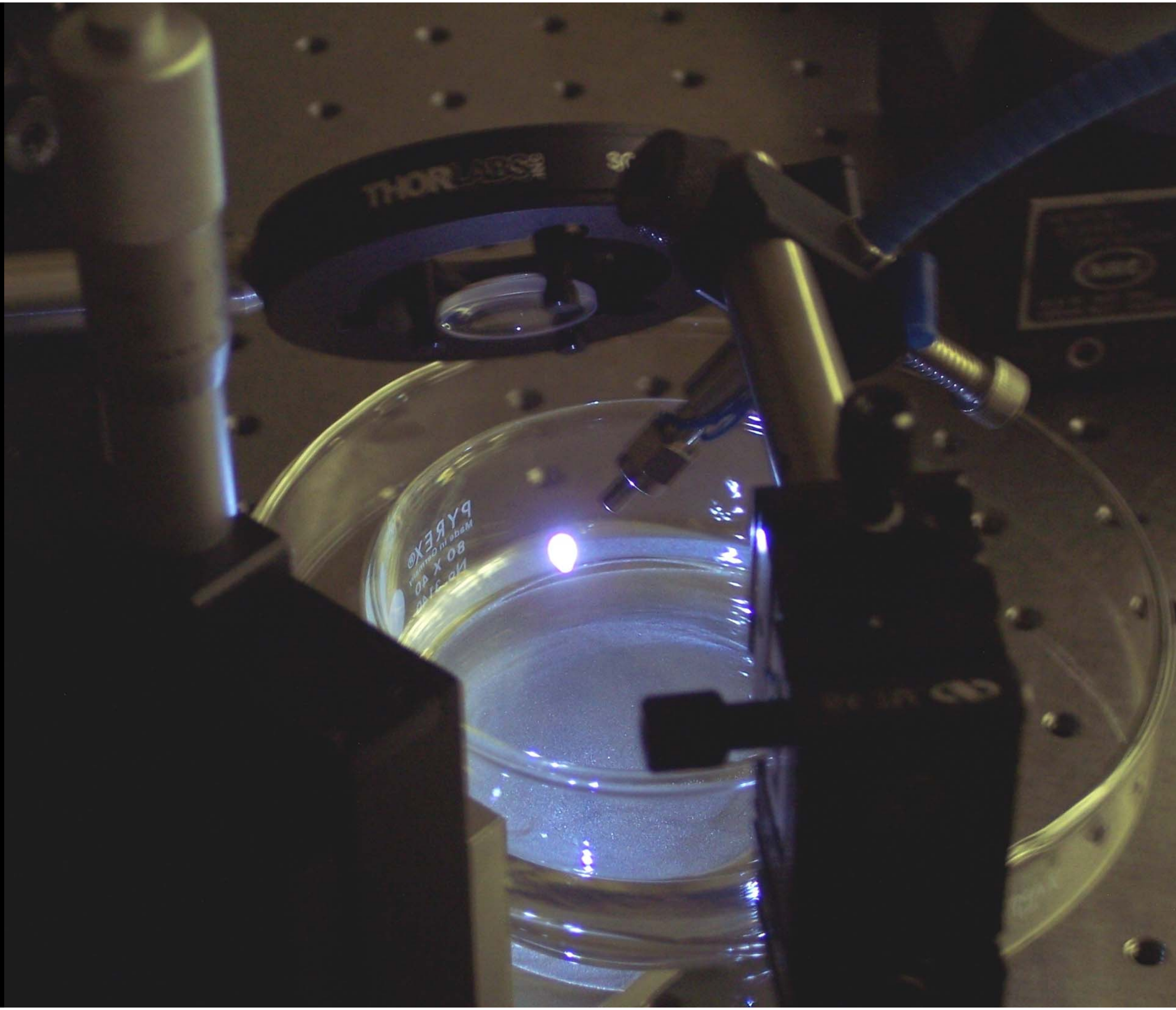
2. Potential Applications

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.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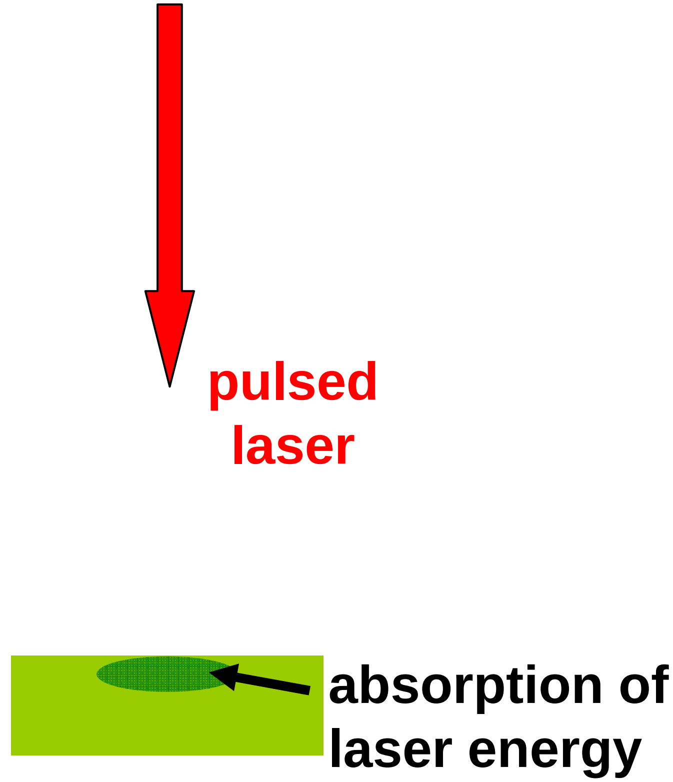
The LIBS Process

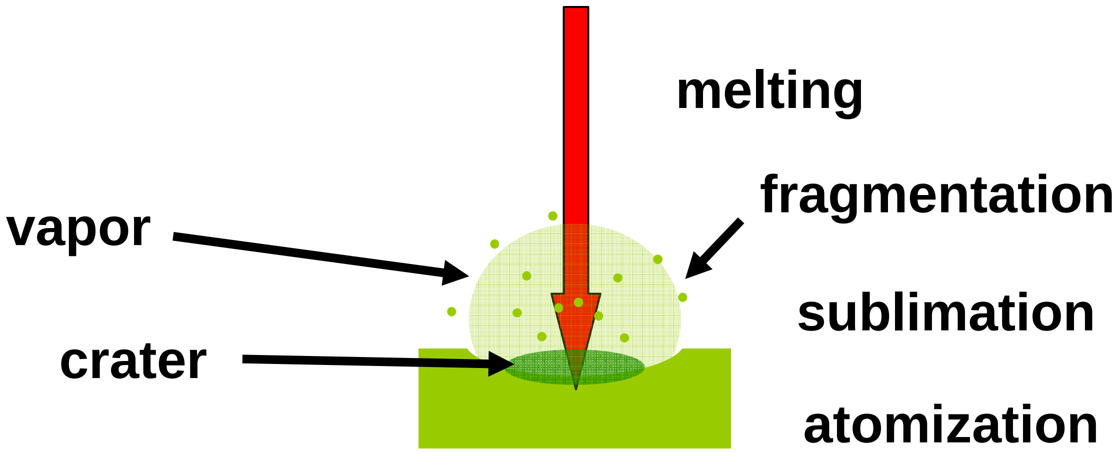
1. laser interaction with the target
2. removal of samples mass (ablation)
3. plasma formation (breakdown)
4. element specific emission

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.

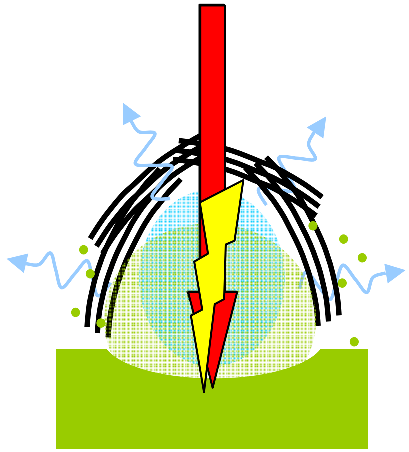
2) removal of samples mass (ablation)



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

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

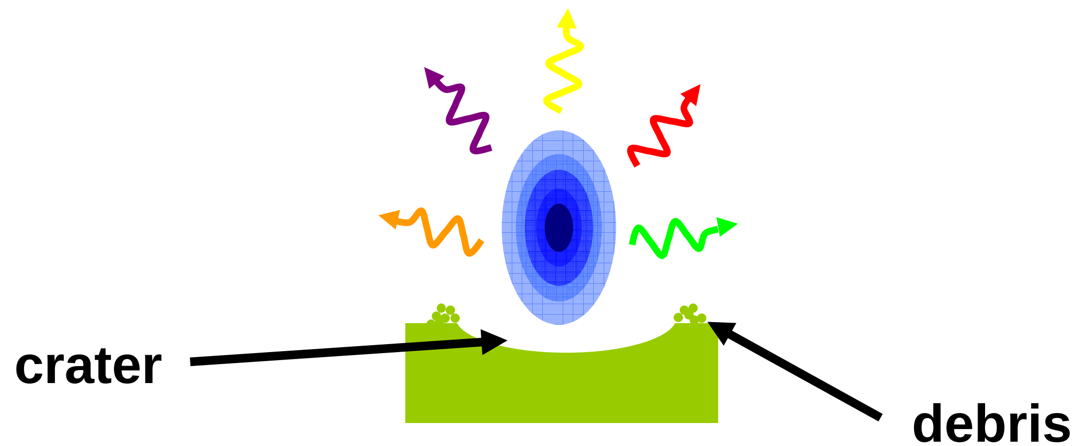
3) plasma formation (breakdown)



- 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.

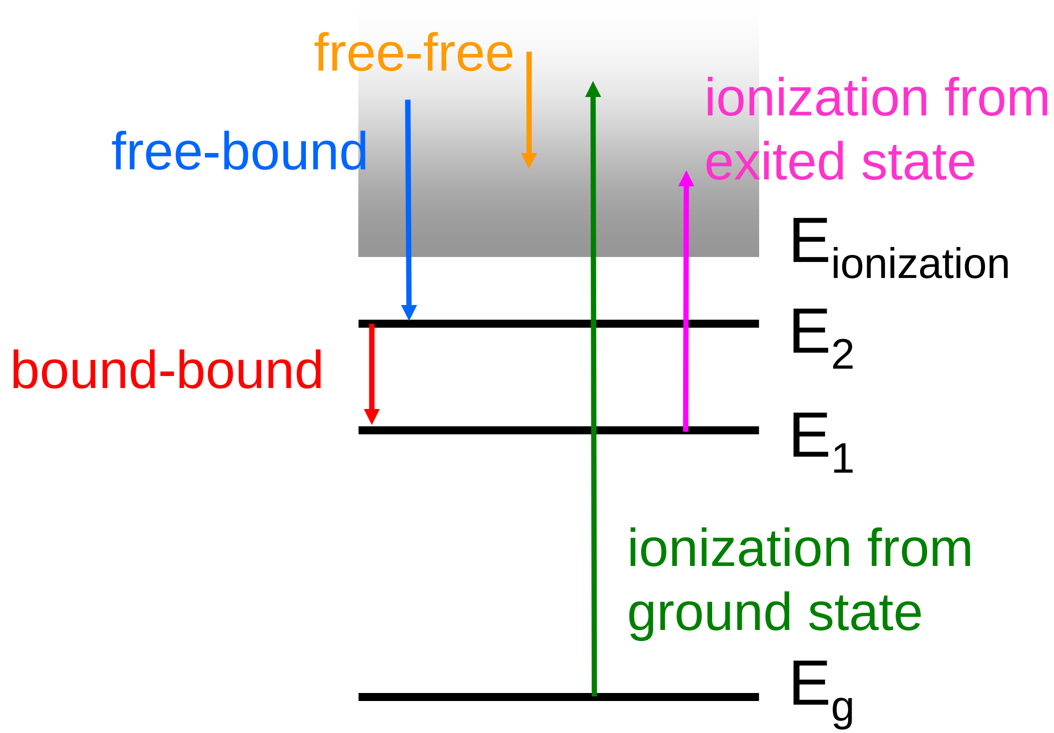
4) element specific emission (atomic or ionic)

spontaneous emission as atoms/ions decay to ground state

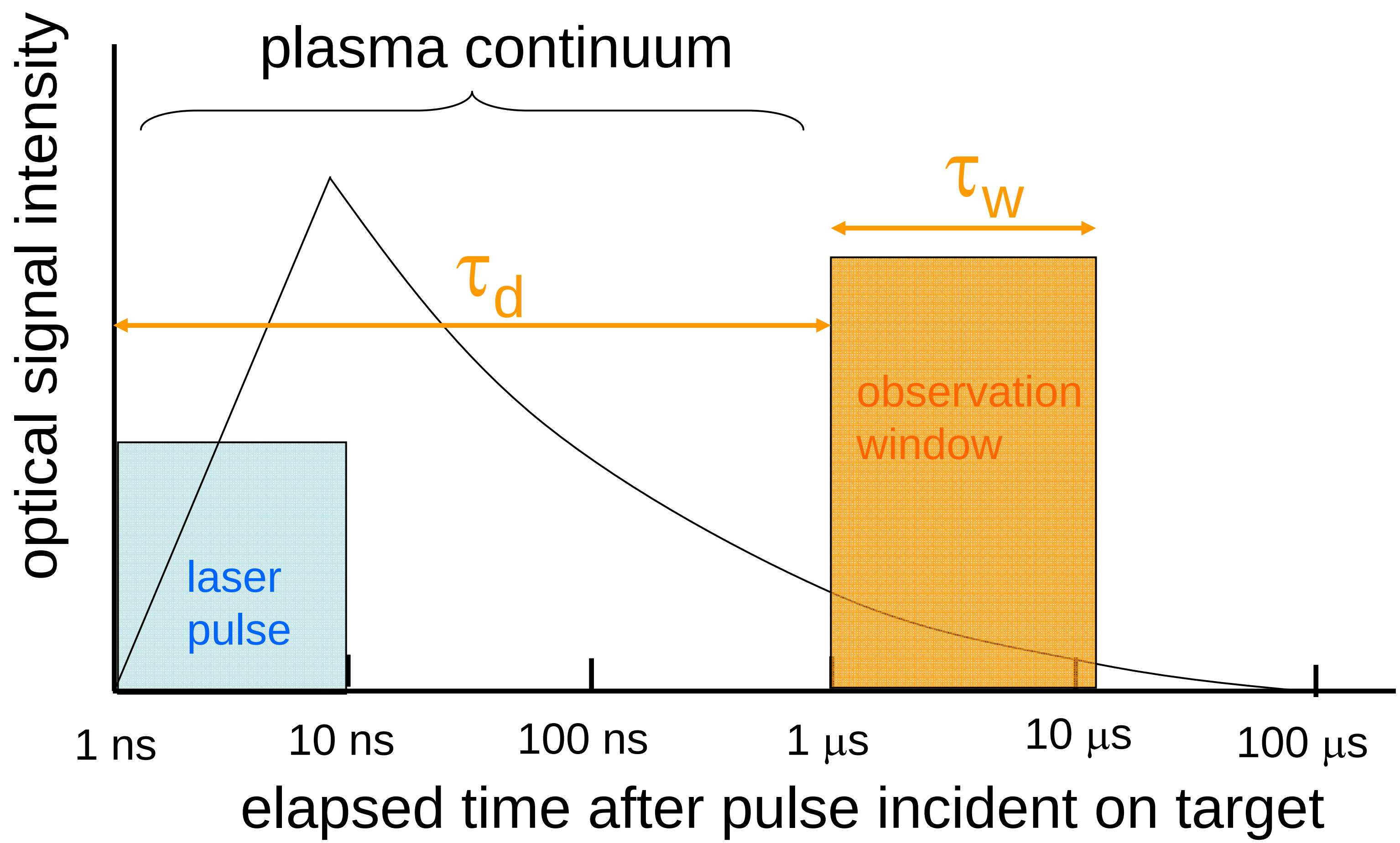


- The dynamical evolution of the plasma plume is then characterized by a fast expansion and subsequent cooling.
- Approximately 1 microsecond after the ablation pulse, spectroscopically narrow atomic/ionic emissions may be identified in the spectrum.

Transitions in an Atom or Ion



Temporal History of a LIBS Plasma



3 Current “Super-Stars” of Atomic Spectroscopy

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

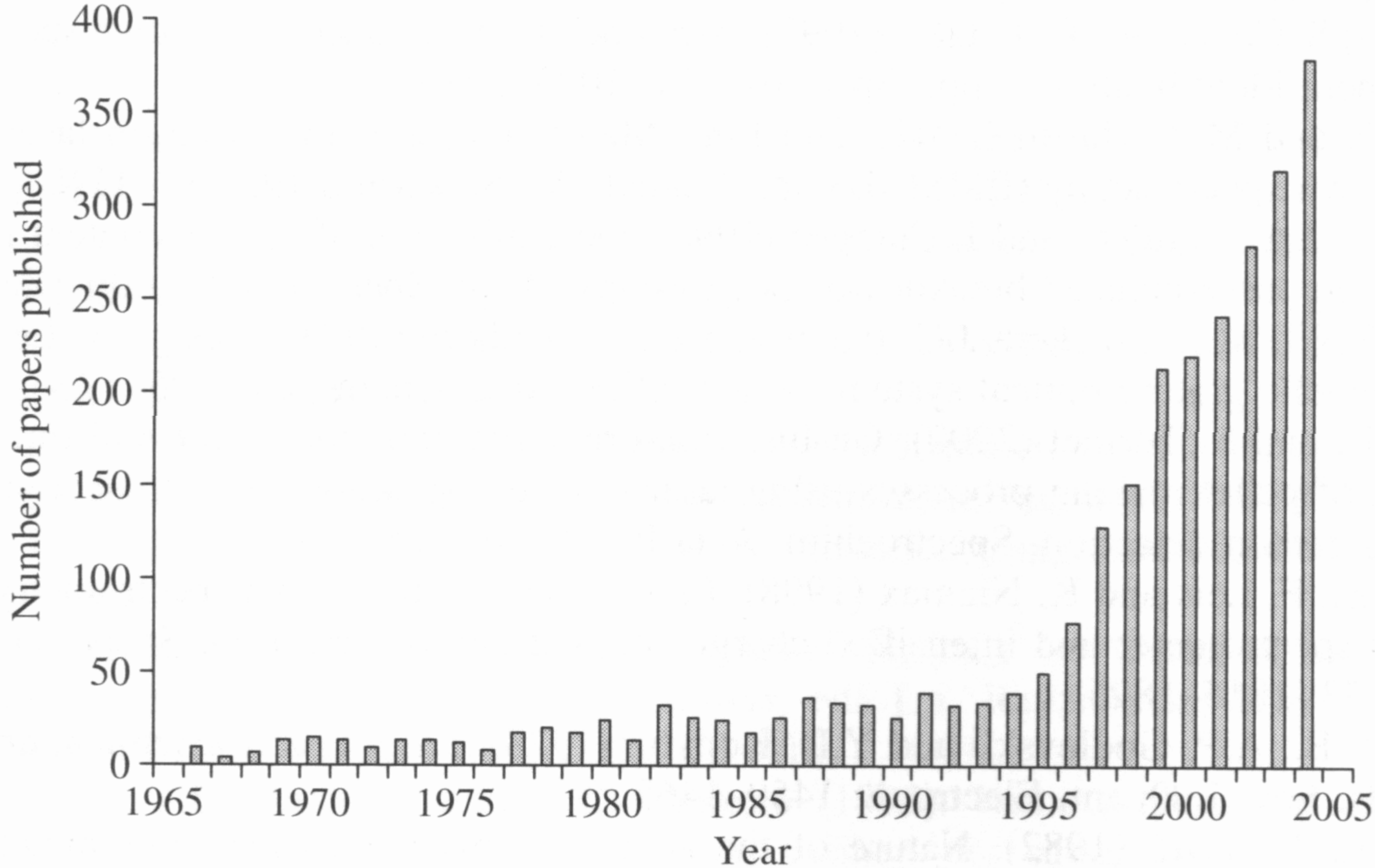
2. inductively couple plasma-atomic emission spectrometry (ICP-AES)

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

Advantages of LIBS

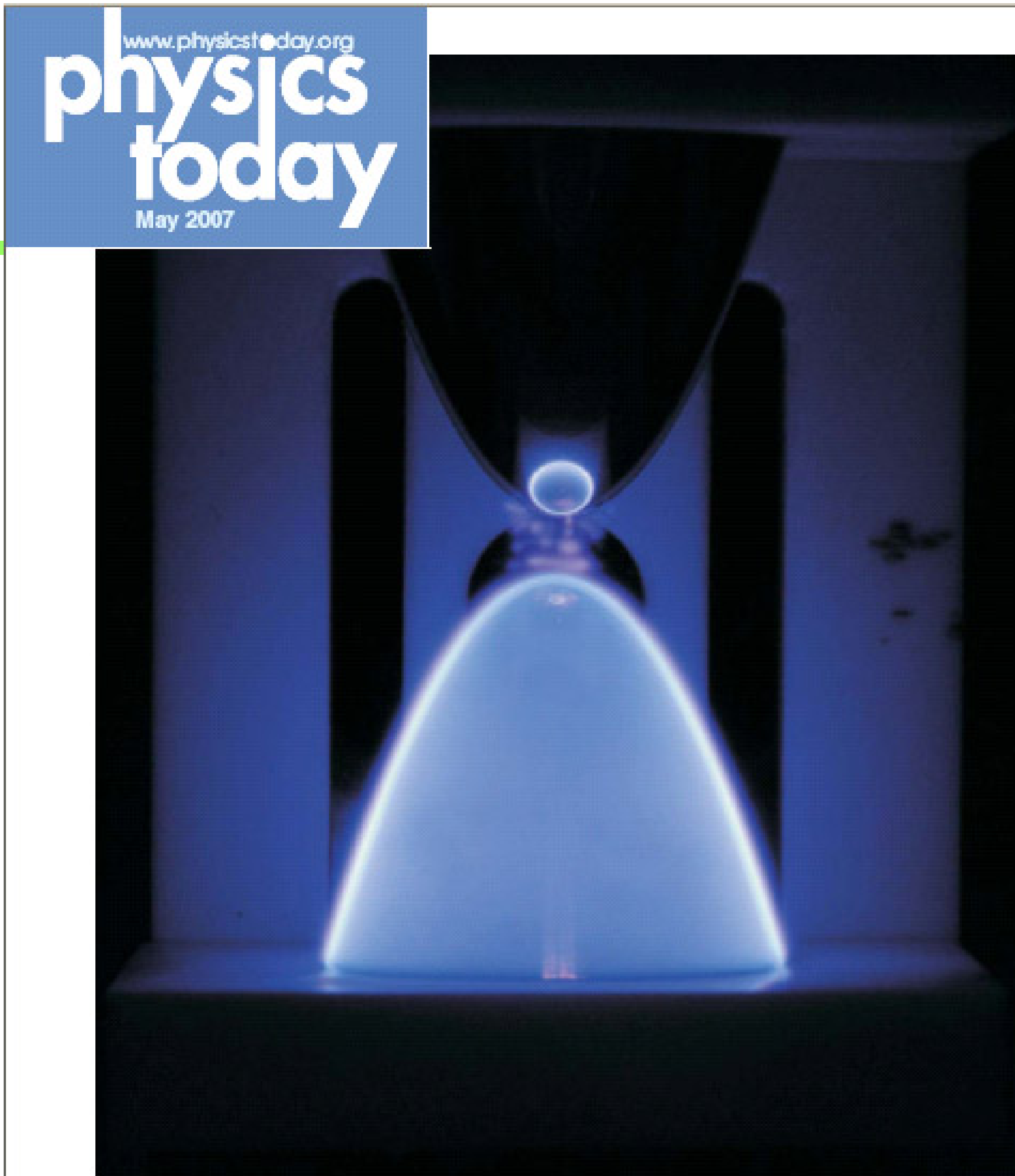
1) extremely fast analysis compared to competing technologies
2) multi-elemental analysis, light from all constituents collected without bias
3) analysis can be performed at standoff distances
4) technique is applicable to all substrates (gas, solid, and liquid)
5) requires minimal or no sample prep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



A Stark look at
plasma breakdown

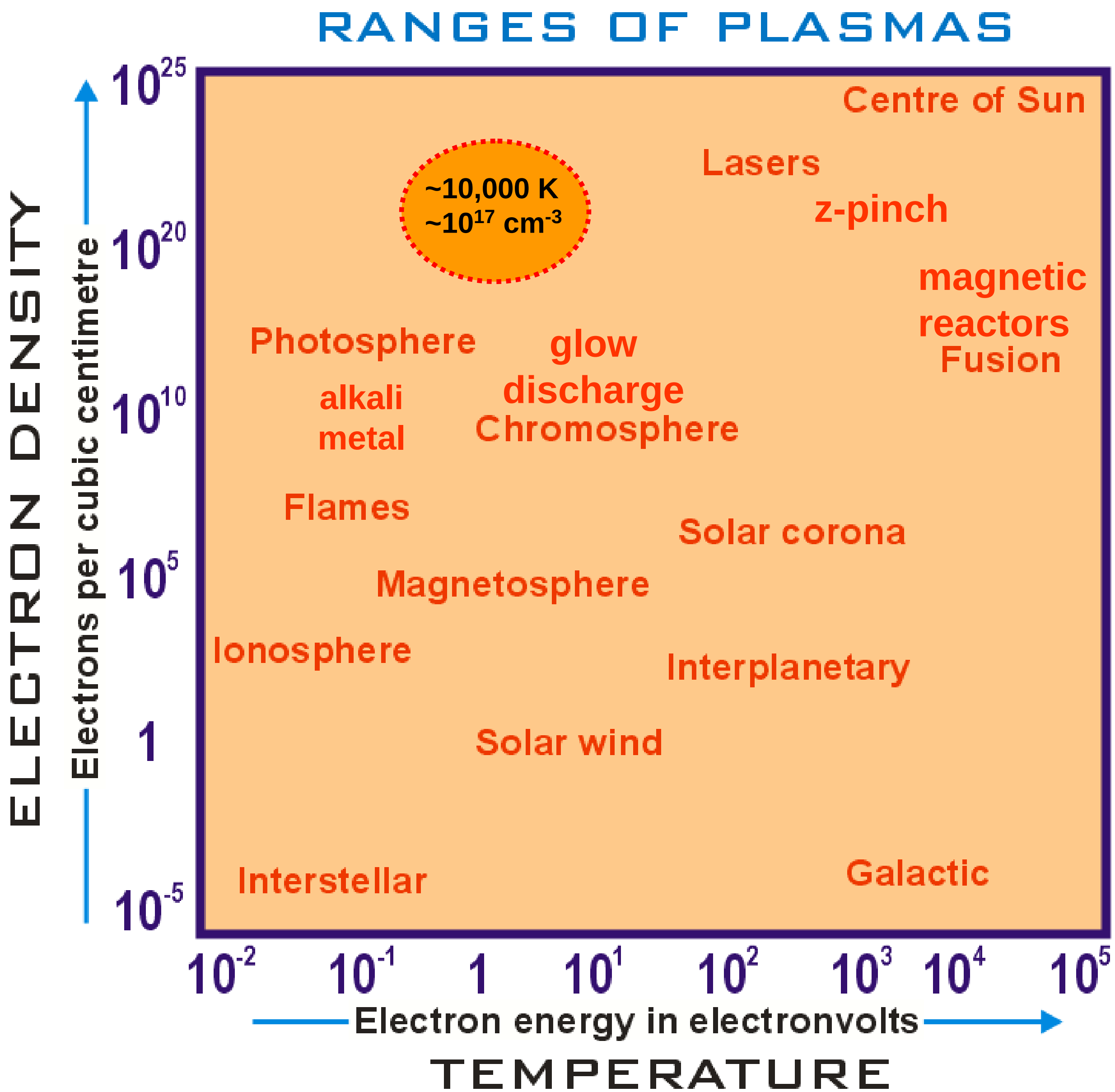
Breakdown

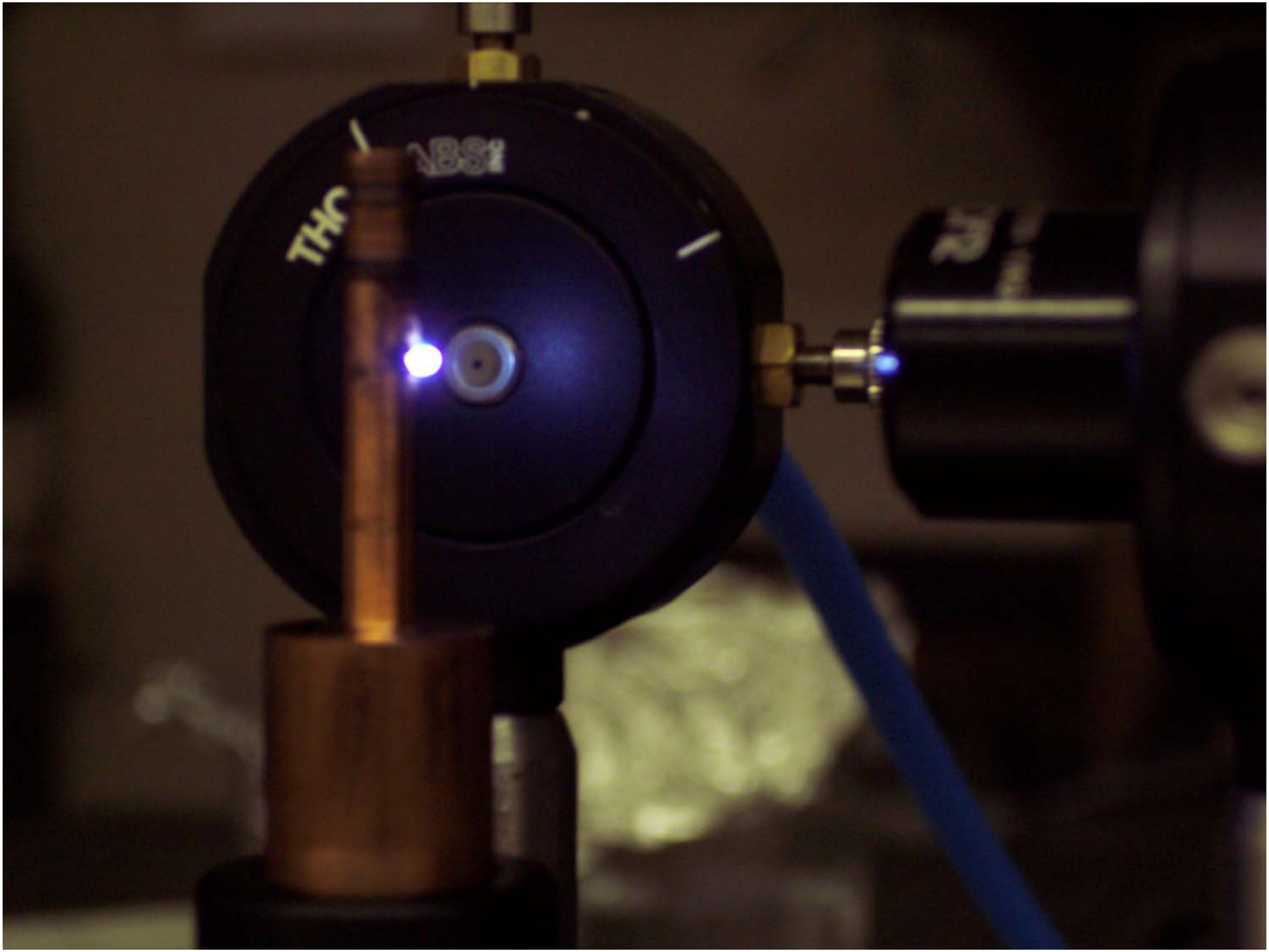
"breakdown" is arbitrarily defined

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


RANGES OF PLASMAS
ELECTRON DENSITY
Electrons per cubic centimetre
10^25
10^20
10^10
10^5
1
10^-5
Centre of Sun
Lasers
~10,000 K
~10^17 cm^-3
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



The Goal of LIBS Plasma Creation

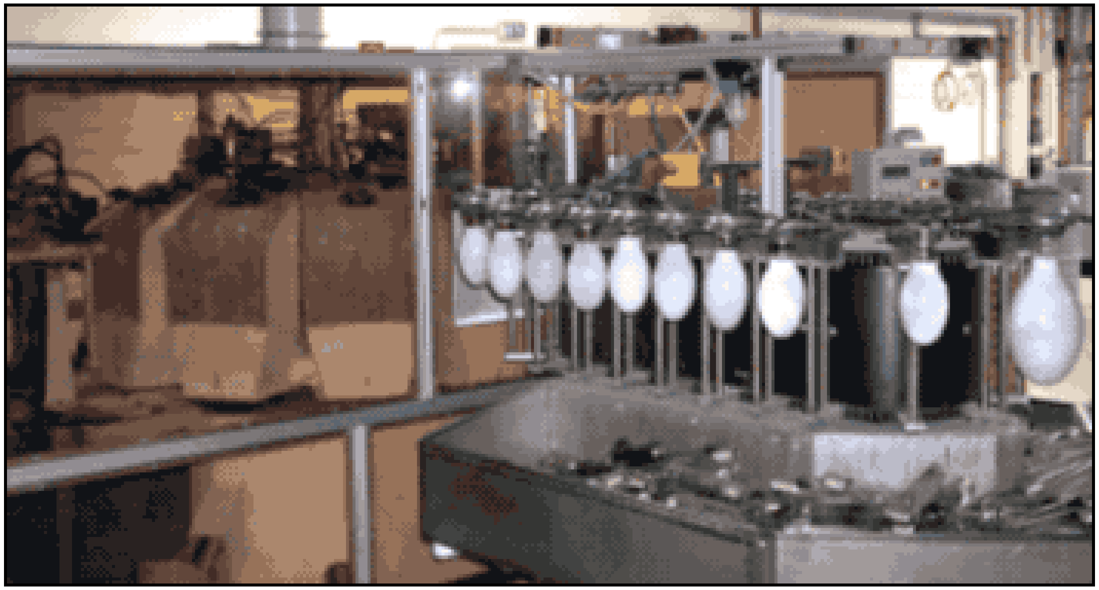
- to create an optically thin plasma which is in thermodynamic equilibrium and whose elemental composition is the same as that of the sample
  - if achieved, spectral line intensities can be connected to relative concentrations of elements
  - typically these conditions are only met *approximately*.

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

Head's-up display

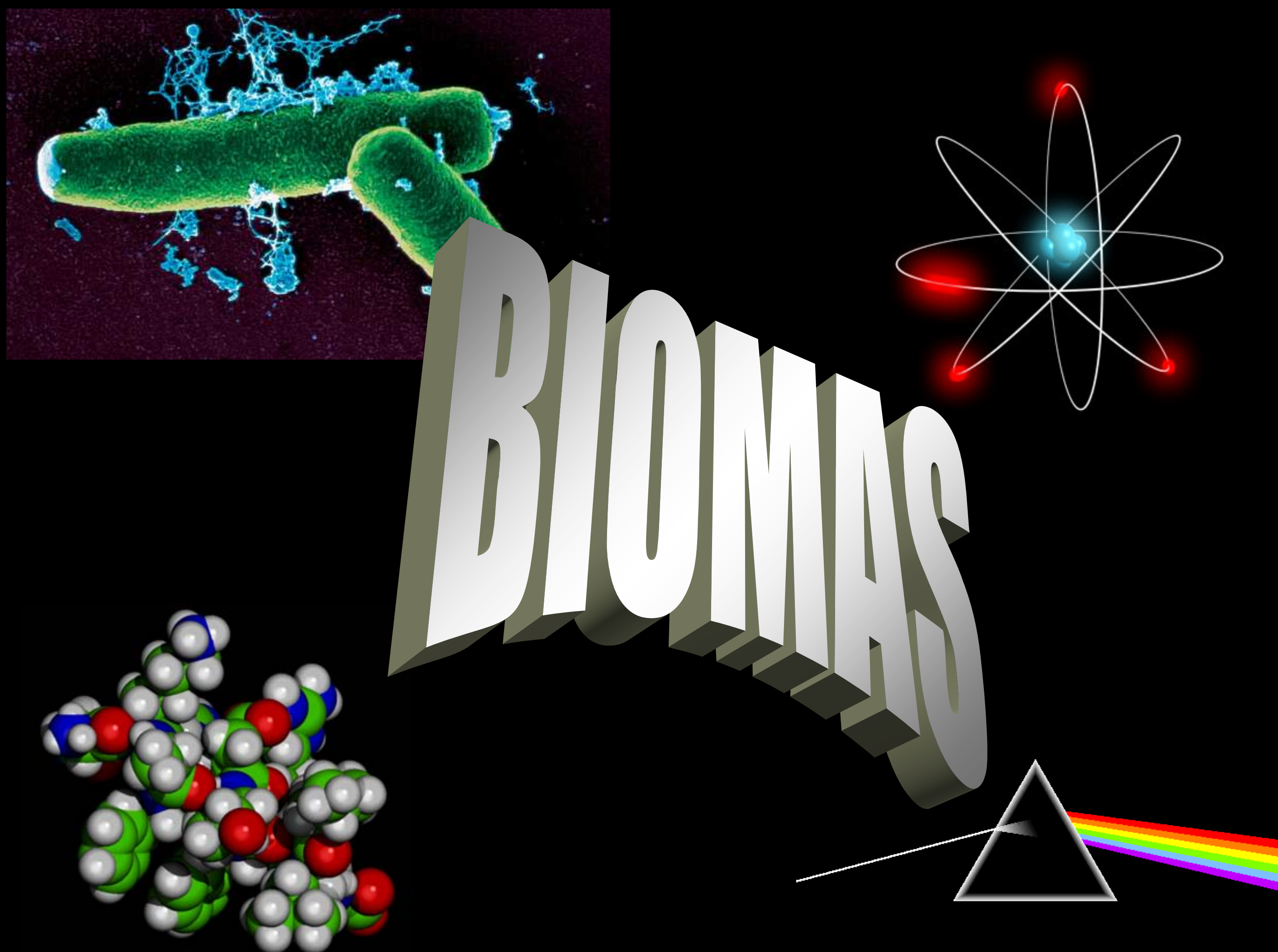
Hand-held probe contains laser, joystick for control, and focus optics

Microplasma/ LIBS Event

courtesy of Ocean Optics.

Identification and Discrimination of Bacteria Strains

The BIOMAS Project:
Bacteria Identification by Optical, Molecular, and Atomic Spectroscopy

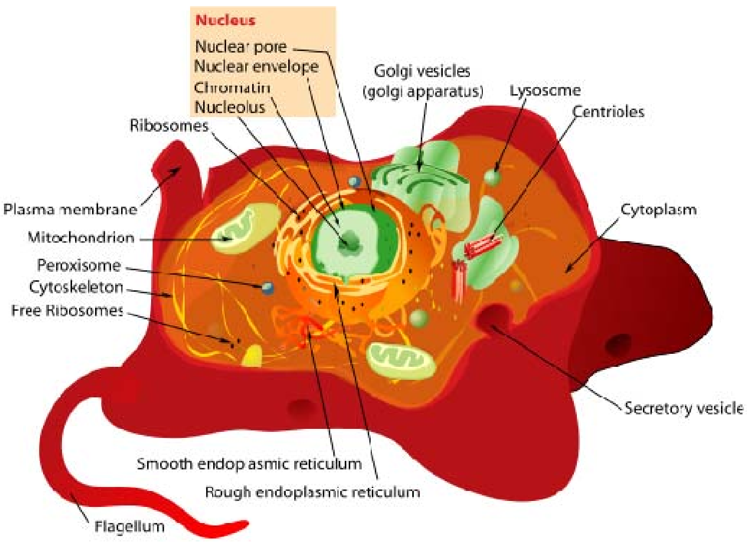


Motivation

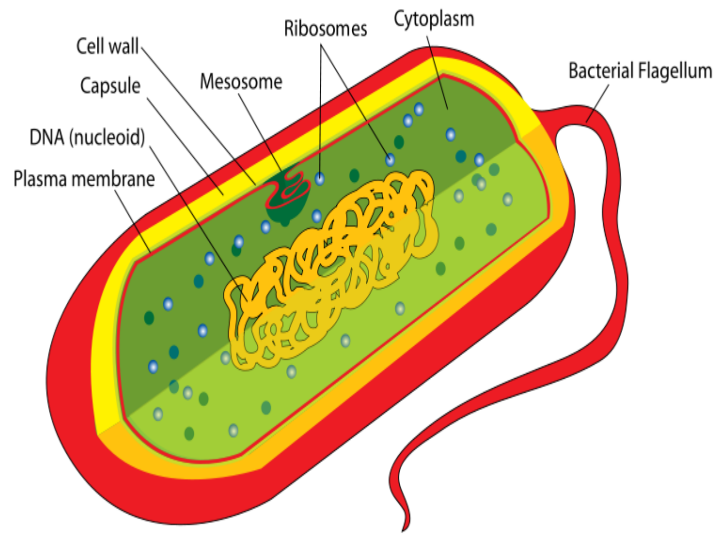
- Require a real-time early-warning detection technology for bio-agents (bacteriological)
  - other applications: EH&S, food inspection, clinical
- Downside of competing technologies:
  - speed
  - target-specific (shelf-life?)
  - expertise required

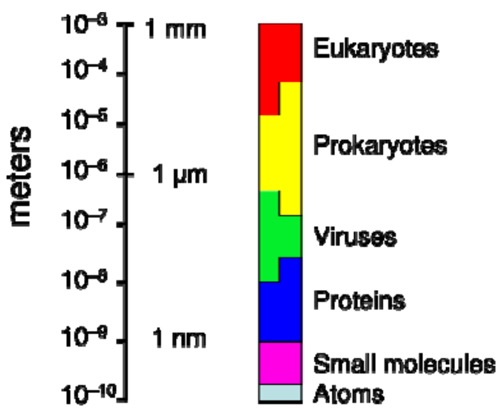
Types of Cells

Eukaryote



Prokaryote





www.en.wikipedia.org

Bacteria

Prokaryote (no nucleus)

Gram-positive

- Thick cell wall
- No outer membrane
- No periplasm

Gram-negative

- Thin cell wall
- Outer membrane
- Periplasm

Example:

•Escherichia coli (Nino C, HF 4714, AB)

•Pseudomonas aeruginosa

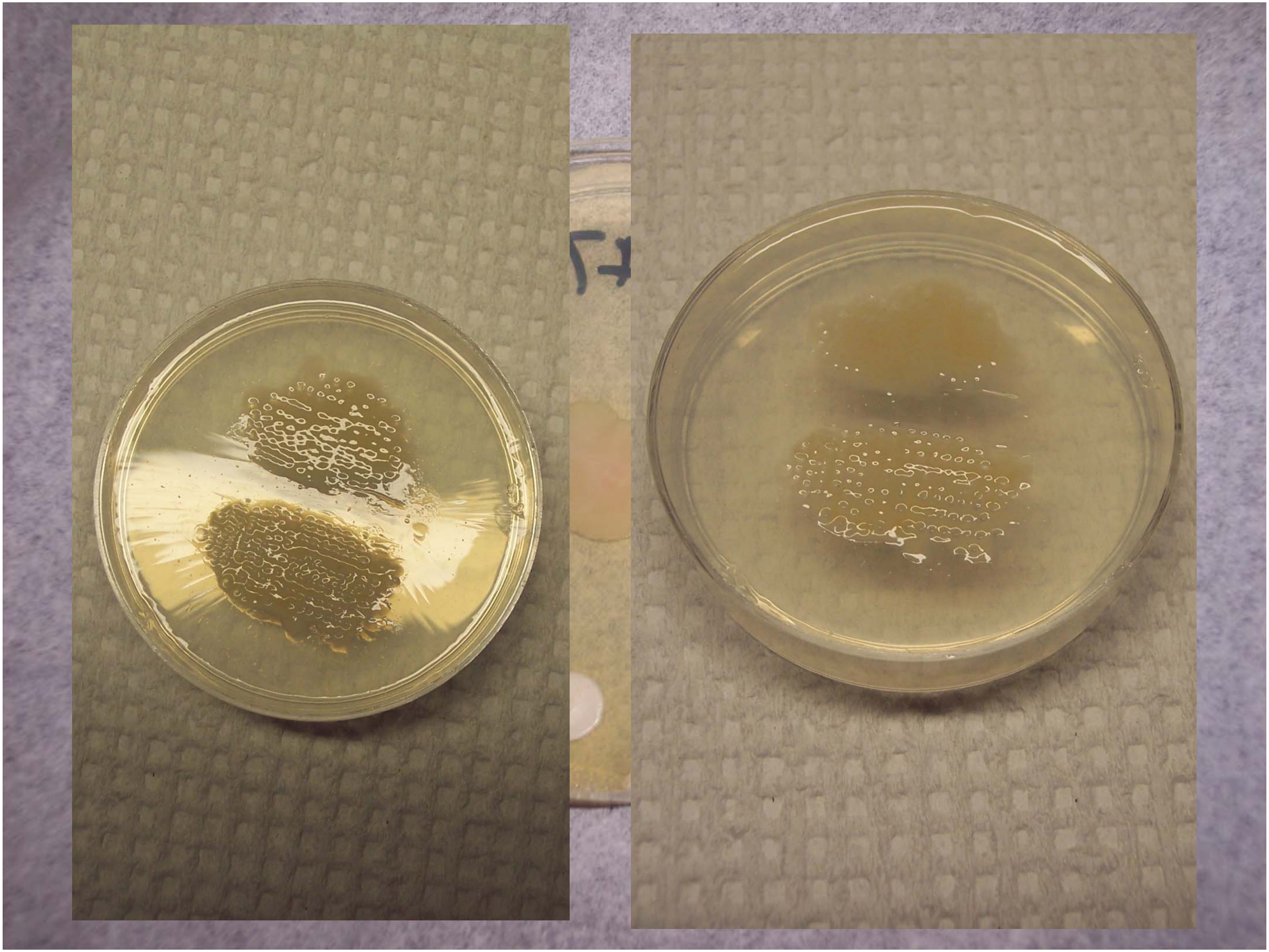
Escherichia coli

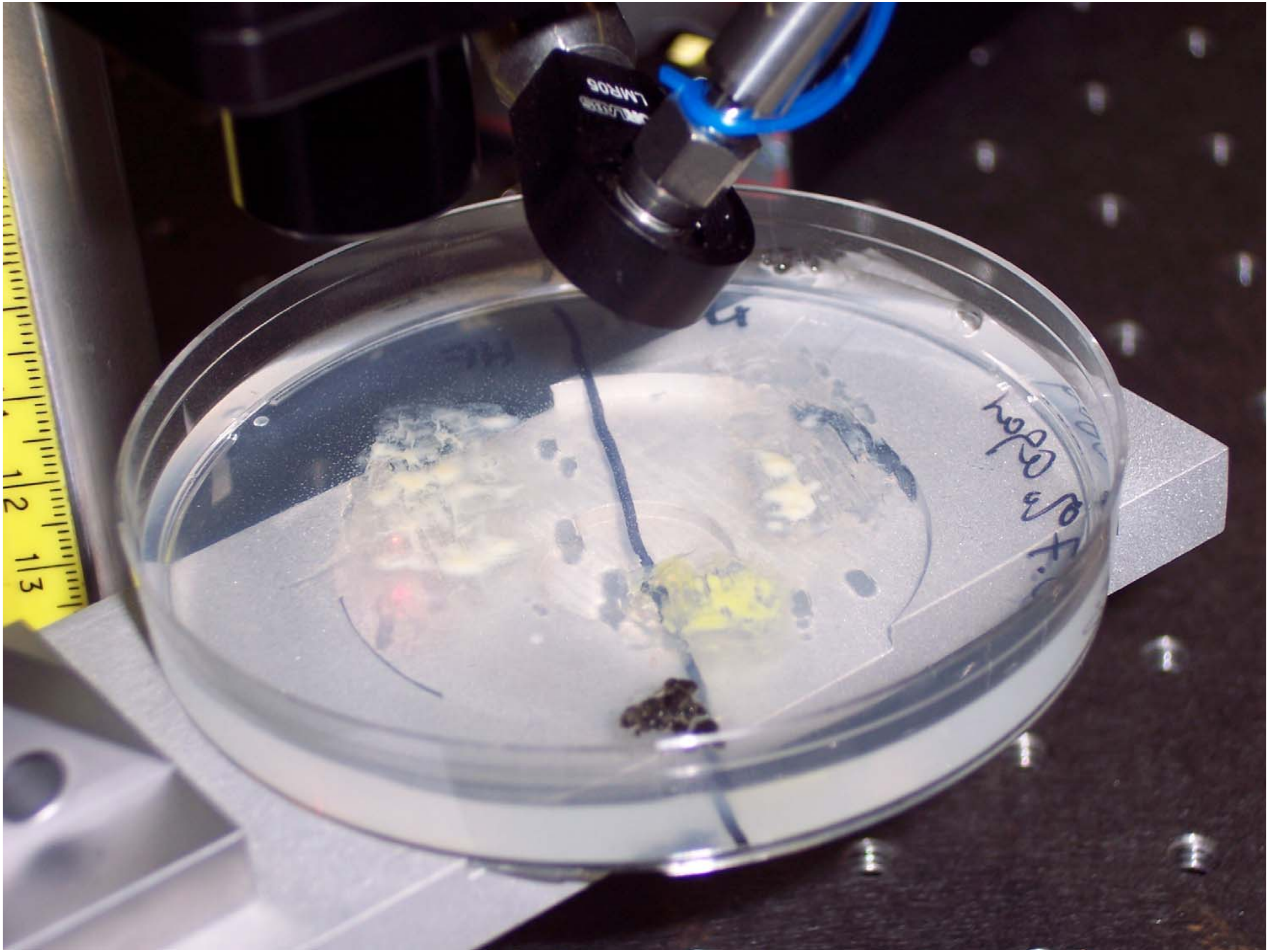
- Very common laboratory micro-organism
- Has many strains, most harmless, some pathogenic
- EHEC or *E. coli* 0157:H7 causes kidney failure in children (hemolytic uremic syndrome)

Inorganic Composition of *E. coli*

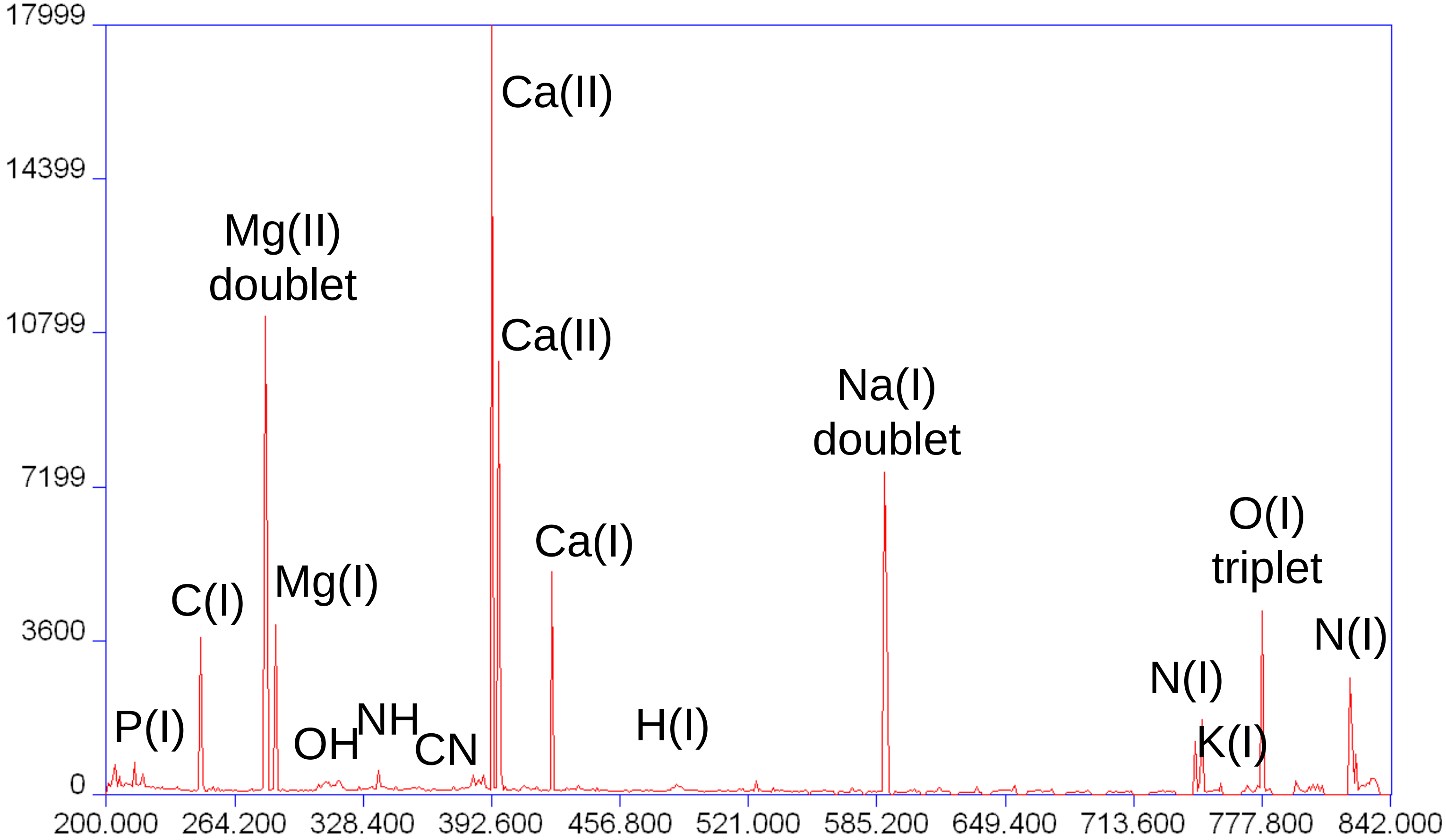
from “*The Bacteria: A Treatise on Structure and Function*” I.C. Gunsalus and R.Y. Stanier, eds

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




LMR05

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)

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

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)

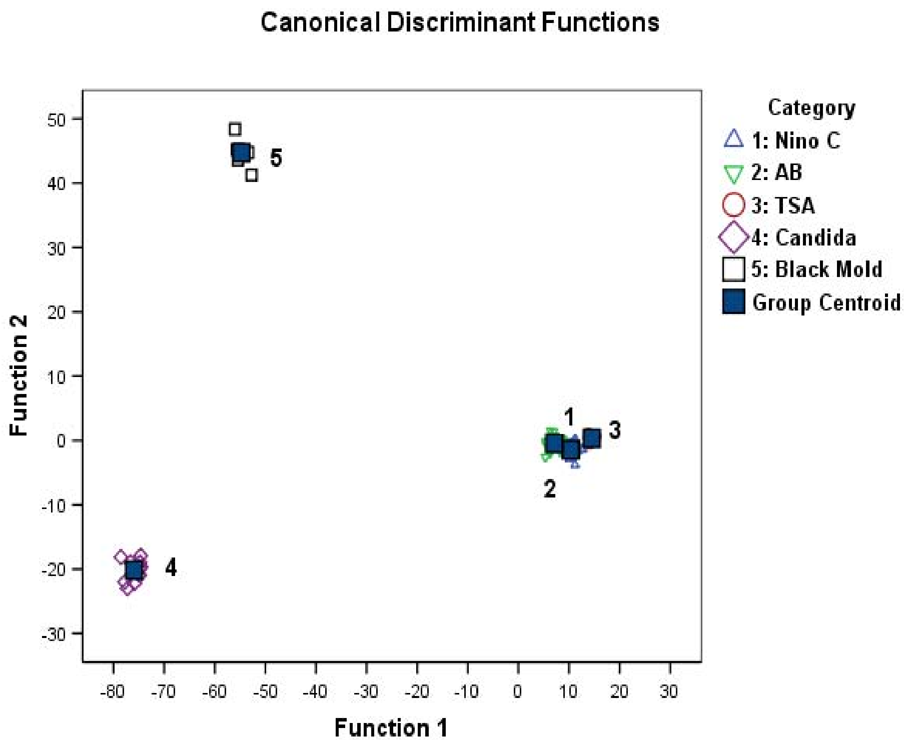
experimental data

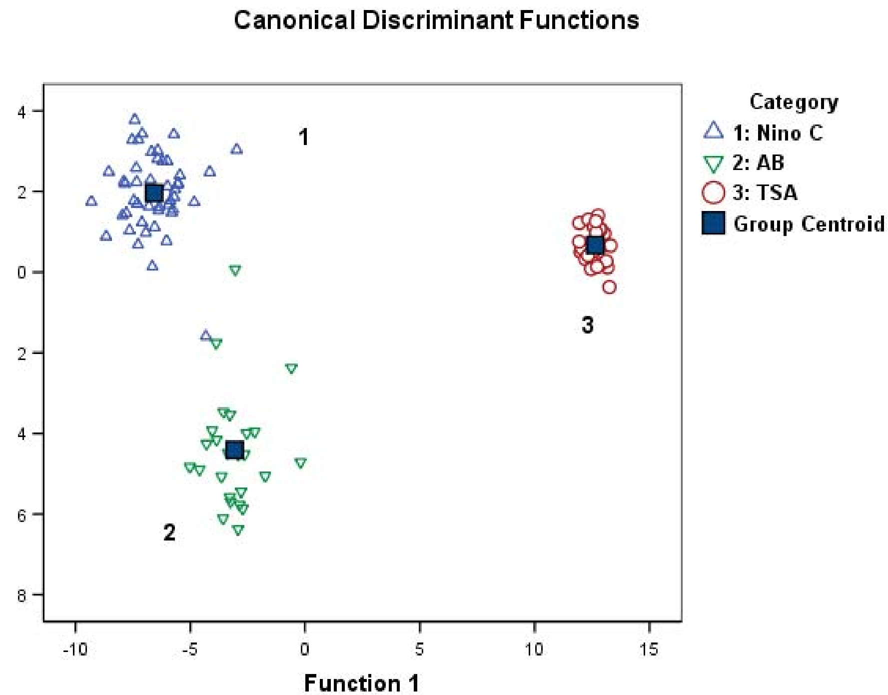
APPLIED PHYSICS LETTERS **90**, 163901 (2007)

Escherichia coli identification and strain discrimination using nanosecond laser-induced breakdown spectroscopy

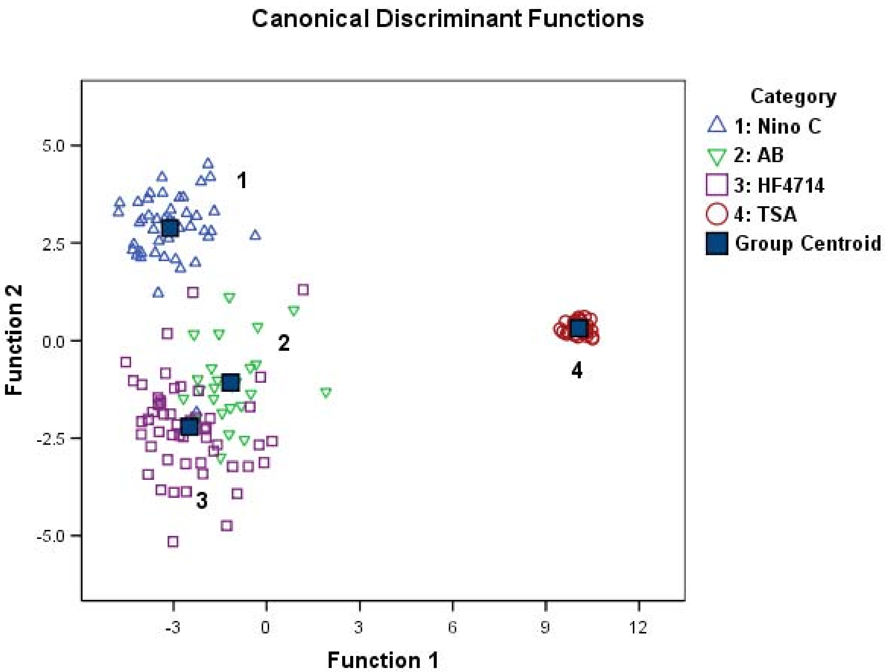
Jonathan Diedrich and Steven J. Rehse[a)]
Department of Physics and Astronomy, Wayne State University, Detroit, Michigan 48201

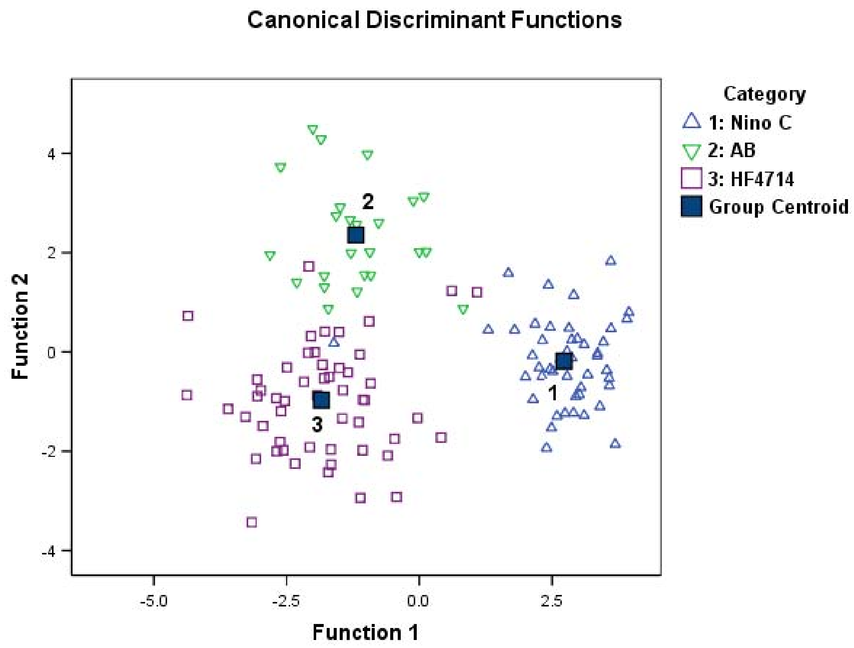
Sunil Palchaudhuri
Department of Immunology and Microbiology, Wayne State University, Detroit, Michigan 48201





E. coli Results





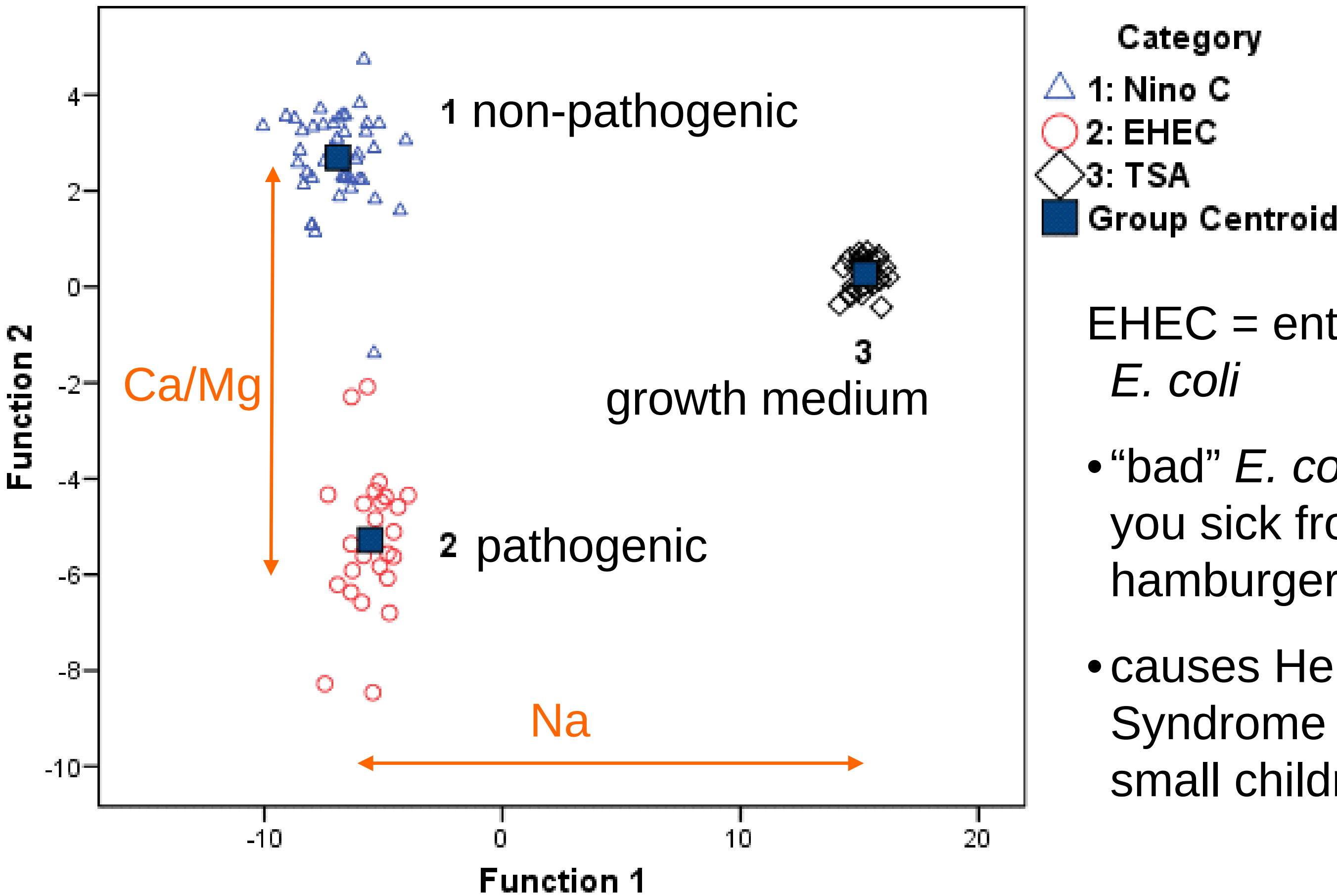
JOURNAL OF APPLIED PHYSICS **102**, 014702 (2007)

Pathogenic *Escherichia coli* strain discrimination using laser-induced breakdown spectroscopy

Jonathan Diedrich and Steven J. Rehse[a)]
Department of Physics and Astronomy, Wayne State University, Detroit, Michigan 48201

Sunil Palchaudhuri
Department of Immunology and Microbiology, Wayne State University, Detroit, Michigan 48201

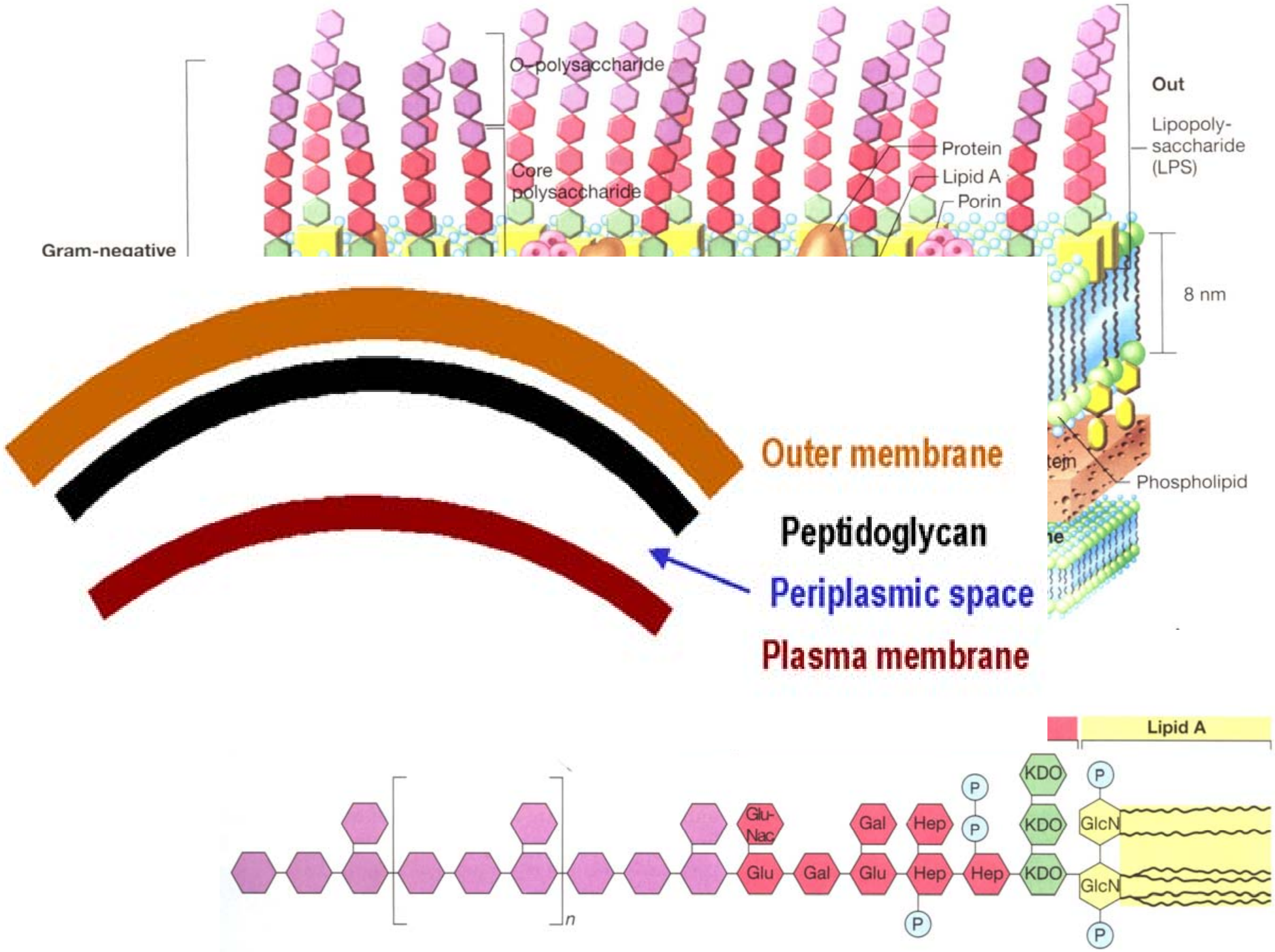
(Received 7 February 2007; accepted 28 May 2007; published online 5 July 2007)



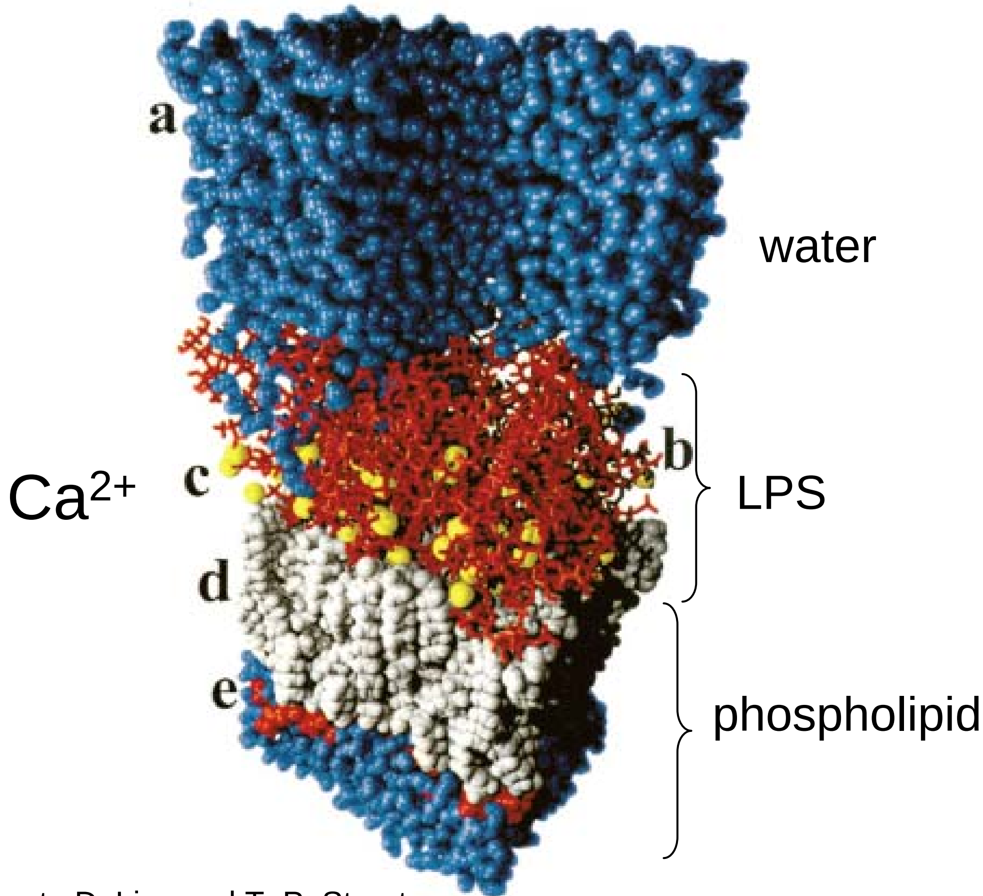
EHEC = enterohemorrhagic *E. coli*

- “bad” *E. coli* which makes you sick from eating raw hamburger.
- causes Hemolytic Uremic Syndrome (HUS) fatal to small children

Why Ca? Why Mg?


O-polysaccharide
Core polysaccharide
Protein
Lipid A
Porin
Out
Lipopoly-saccharide (LPS)
8 nm
Phospholipid
Outer membrane
Peptidoglycan
Periplasmic space
Plasma membrane
Lipid A
KDO
KDO
KDO
P
P
P
P
P
GlcN
GlcN
Glu-Nac
Glu
Gal
Gal
Glu
Hep
Hep
Hep
n

Divalent Cations Regulate Membrane Permeability



Roberto D. Lins and T. P. Straatsma
Biophysical Journal ***81,*** 1037–1046 (2001)

Cation Bio-chemistry

- Increasing concentrations of divalent Ca^{2+} and Mg^{2+} reduced the antimicrobial effect of a standard peptide (protamine).

- Addition of divalent cations to LPS suspensions modified the in-plane packing of LPS molecules from hexagonal to a nonhexagonal lattice (as confirmed by X-ray diffraction).

ELSEVIER

Spectrochimica Acta Part B 62 (2007) 1169 – 1176

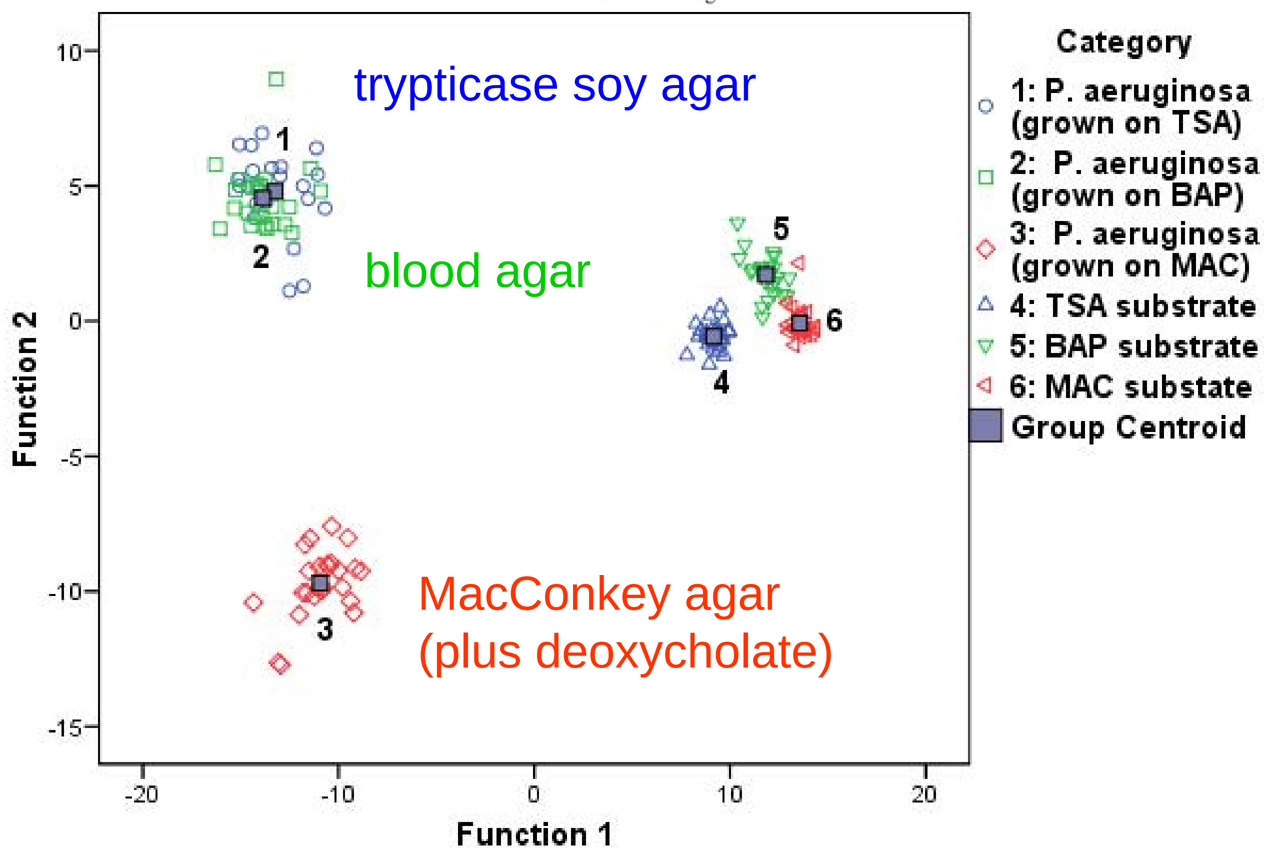
www.elsevier.com/locate/sab

Identification and discrimination of *Pseudomonas aeruginosa* bacteria grown in blood and bile by laser-induced breakdown spectroscopy

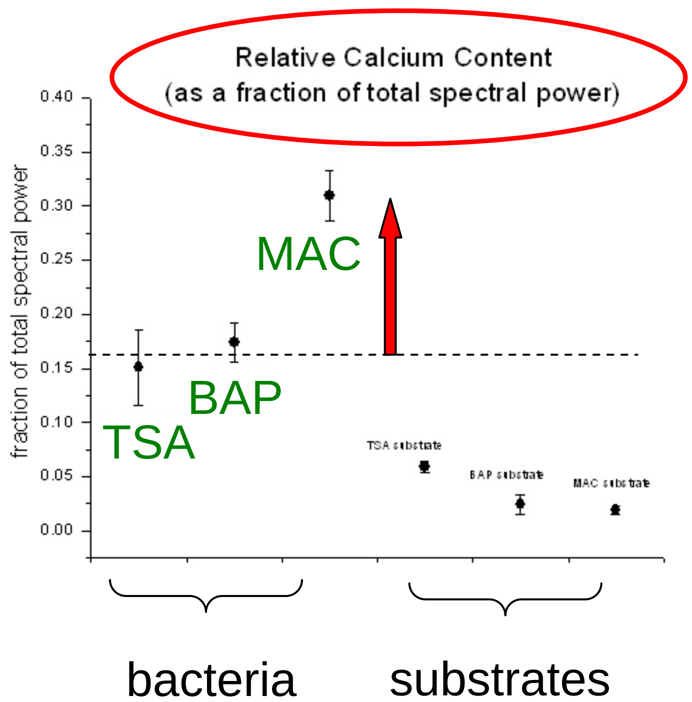
Steven J. Rehse [a,*], Jonathan Diedrich [a,1], Sunil Palchaudhuri [b,2]

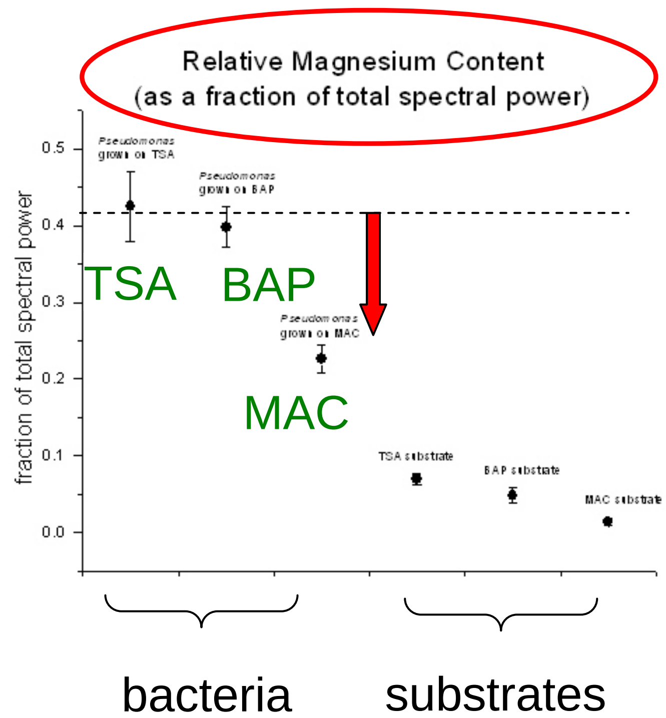
[a] *Department of Physics and Astronomy, Wayne State University, Detroit, MI 48201, USA*
[b] *Department of Immunology and Microbiology, Wayne State University, Detroit, MI 48201, USA*

Received 23 May 2007; accepted 23 July 2007
Available online 1 August 2007

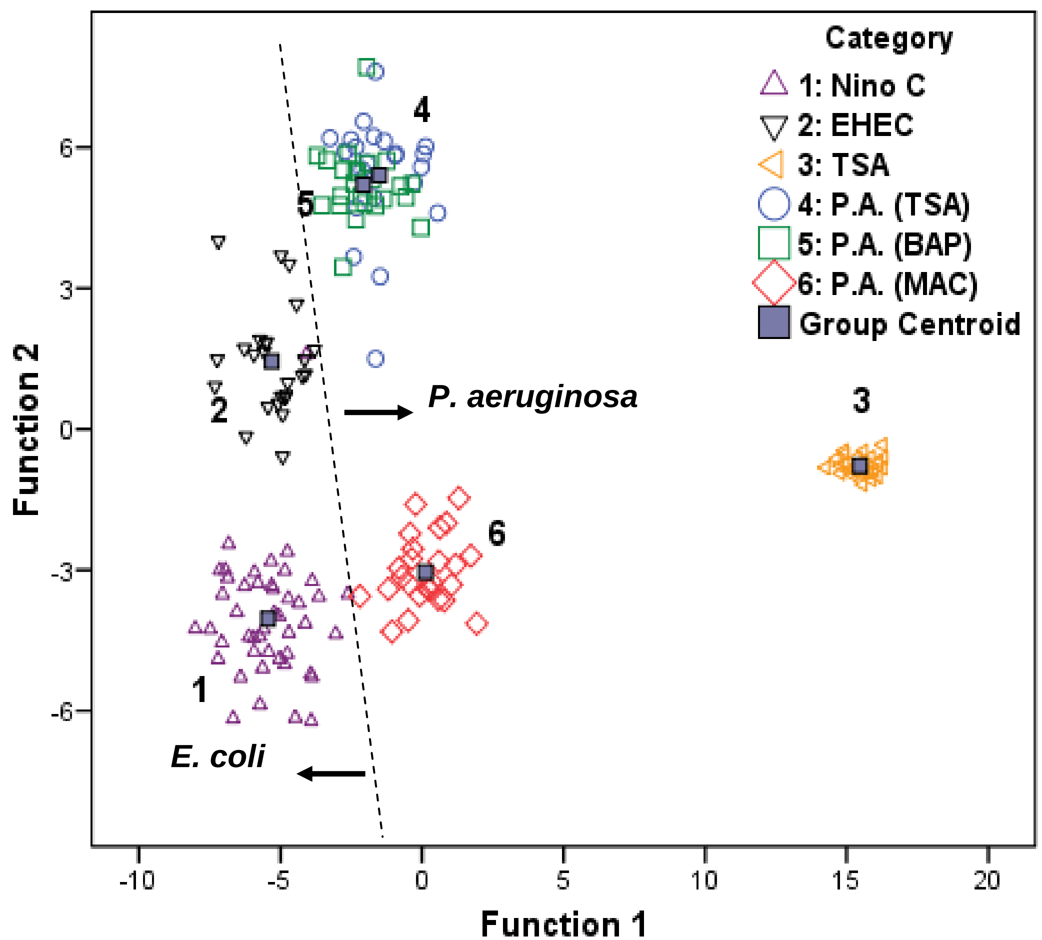


Divalent Cations (Ca^{2+}, Mg^{2+}) Concentrations Are Altered by Environment

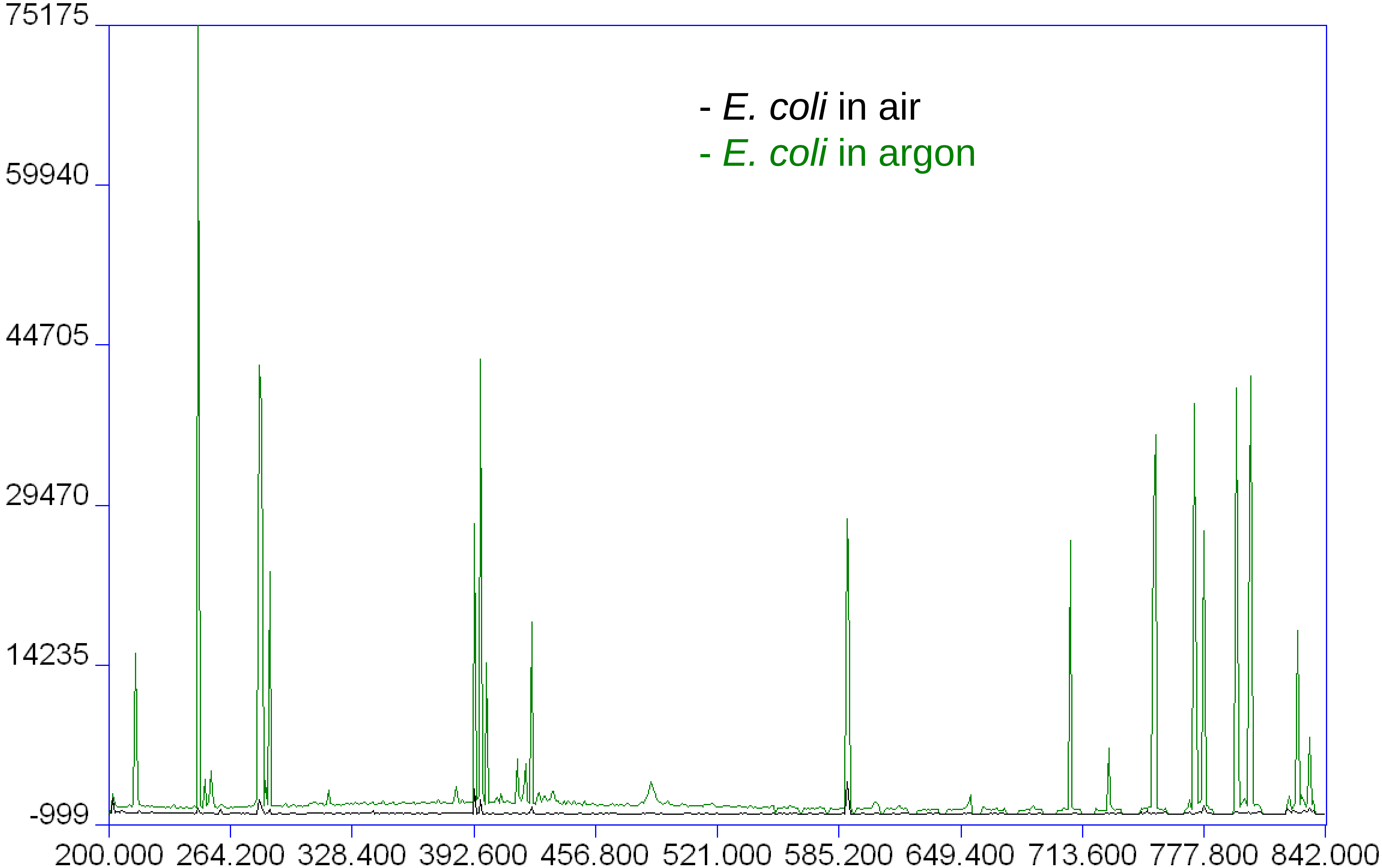


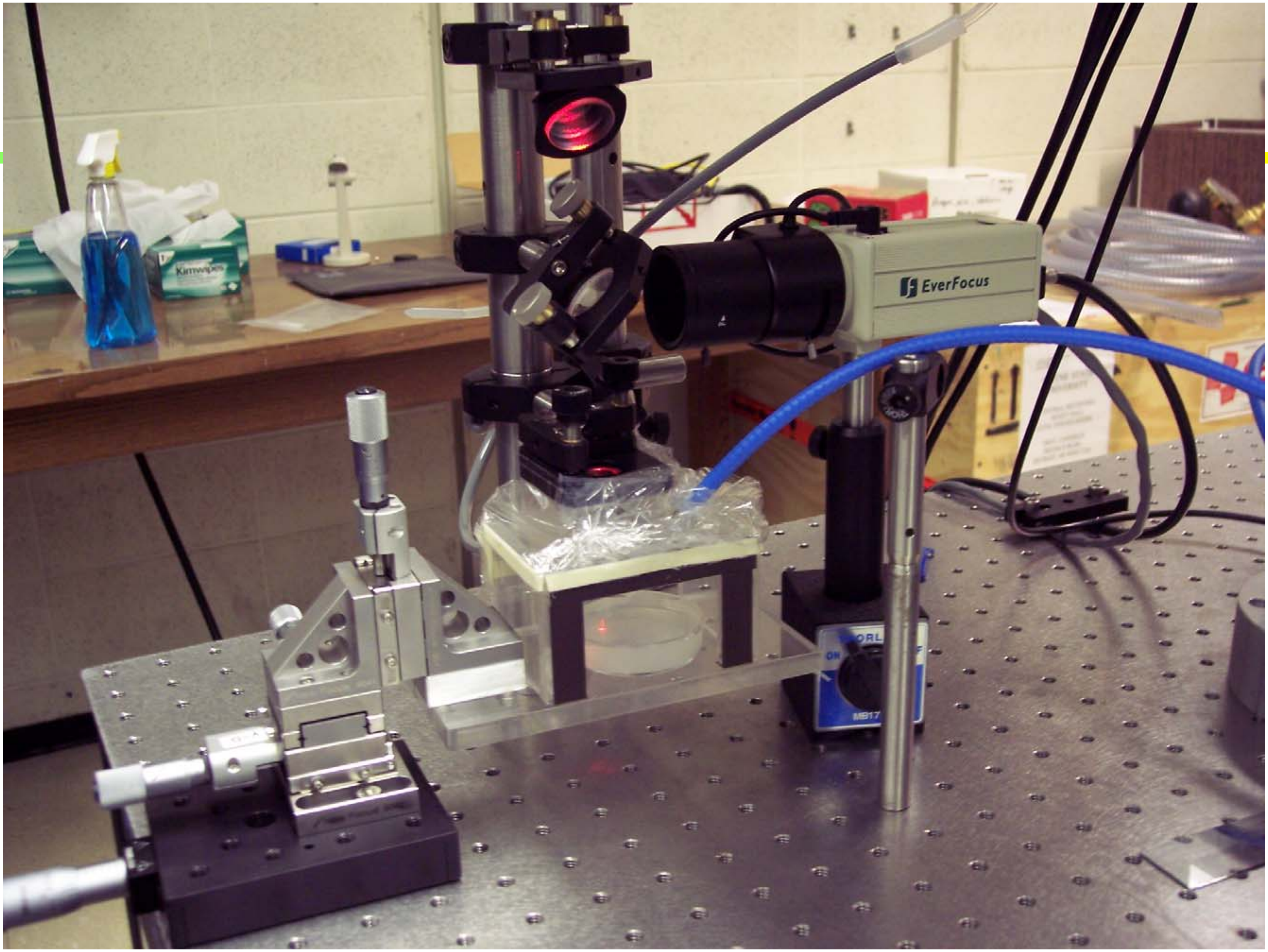


E. coli and *P. aeruginosa*



Improvements




EverFocus
Kimwipes

Improvements

- noble gases (Ar, He)
  - dual-gas environments
- liquid cultures (not colonies)
- different chemometric analysis (PCA)
- Gram-positive bacteria
- Raman spectroscopy

Conclusions

- LIBS a versatile, extremely useful technology
- Many applications in biological systems (and elsewhere)
- Physicists can make valuable contributions in the biological sciences.

Thank you for your attention!

Graduate Students

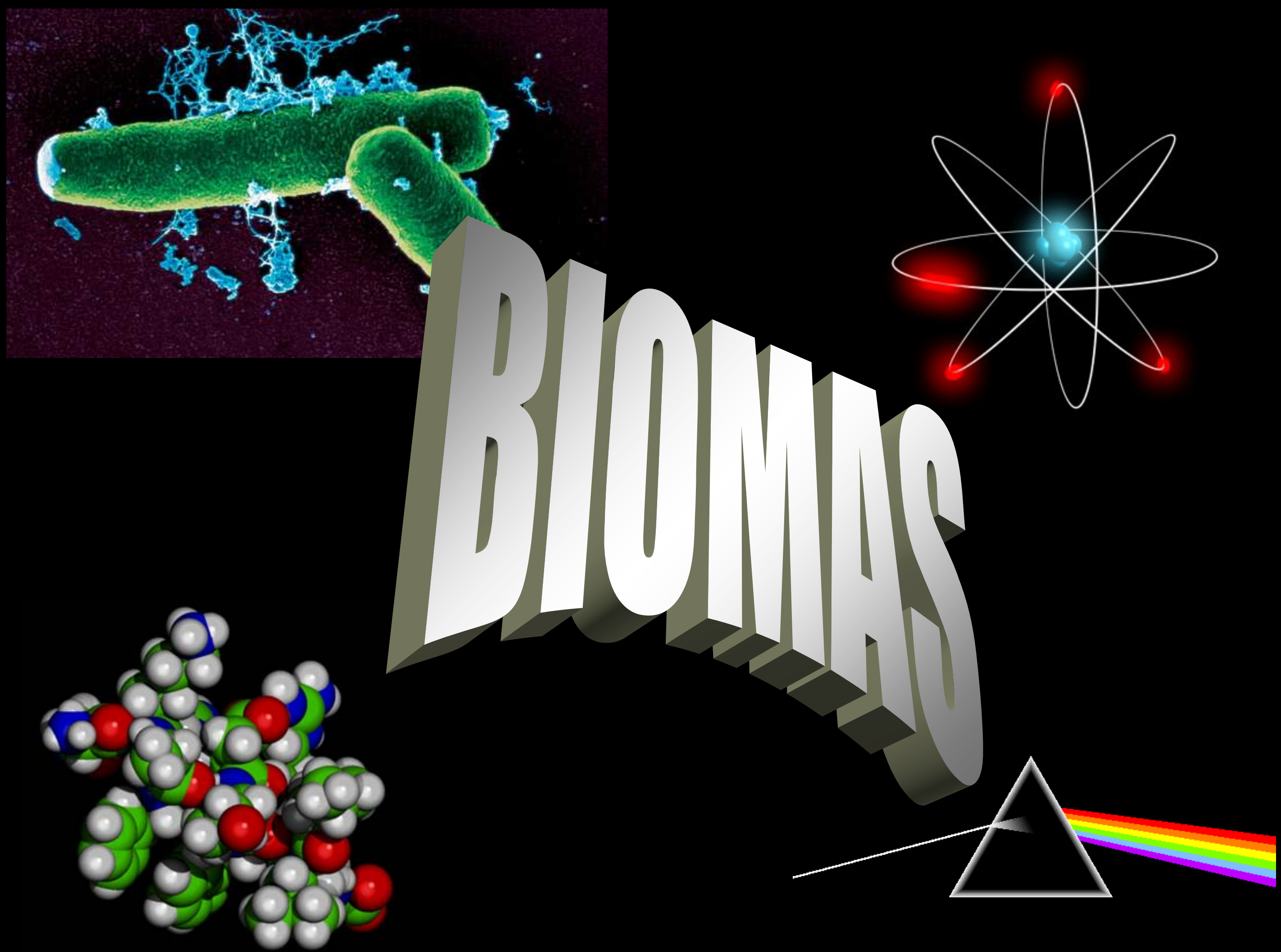
- Jon Diedrich, M.S.
- Narmatha Jeyasingham, M.S.
- Arathi Padhmanabhan
- Caleb Ryder
- Qassem Mohaidat
- Khozima Hamasha

Undergraduate Students

- Marian Adamson
- Emmett Brown
- Garrett Godfrey

The BIOMAS Project:

Bacteria Identification by Optical, Molecular, and Atomic Spectroscopy



Physics of Plasma Formation: breakdown

Problem: 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)

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

- 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

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

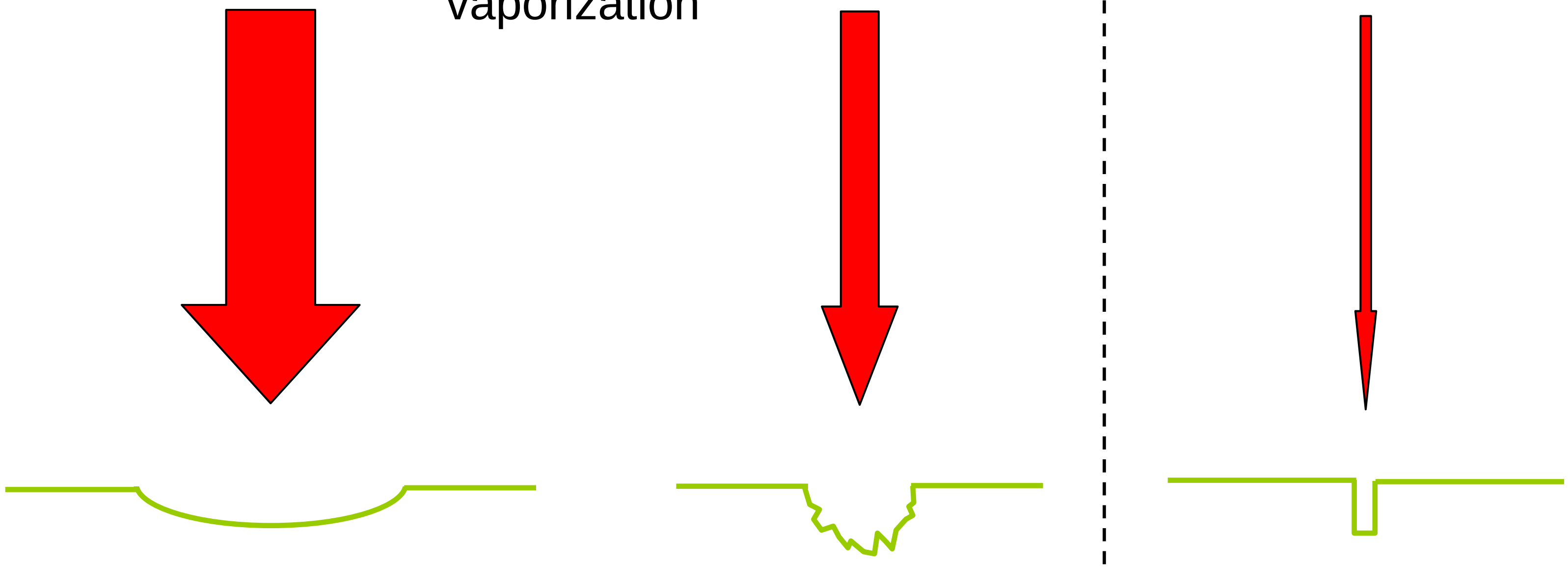
Physics of Plasma Formation: ablation

heating

melting

vaporization

τ_{pulse} < plasma initiation



microsecond nanosecond femtosecond

Physics of Plasma Formation: ablation

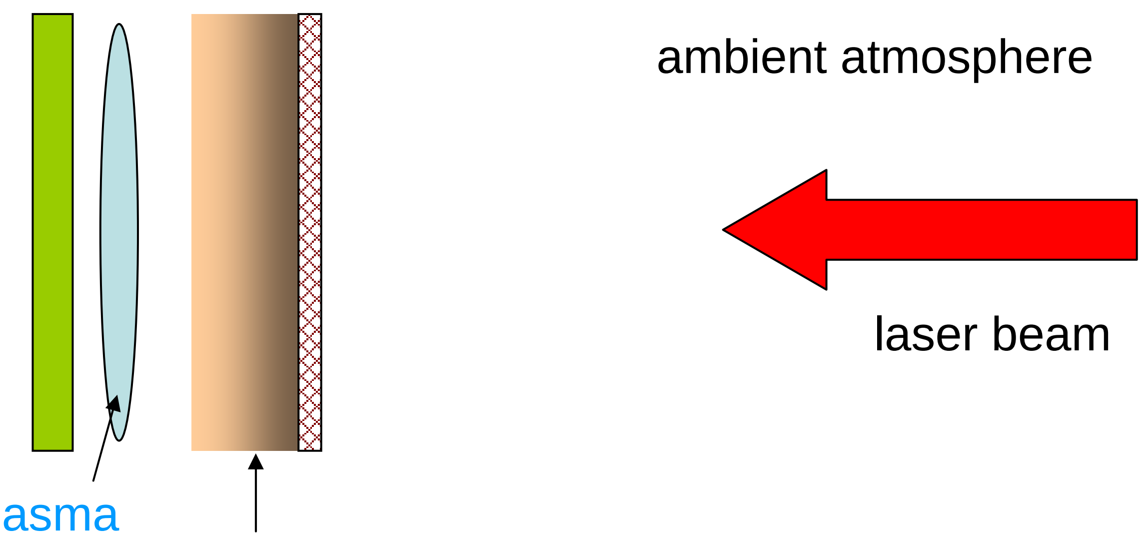
$$I_{\min} = \frac{\rho L_V \kappa^{1/2}}{\Delta t^{1/2}} (\text{W/cm}^2)$$

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

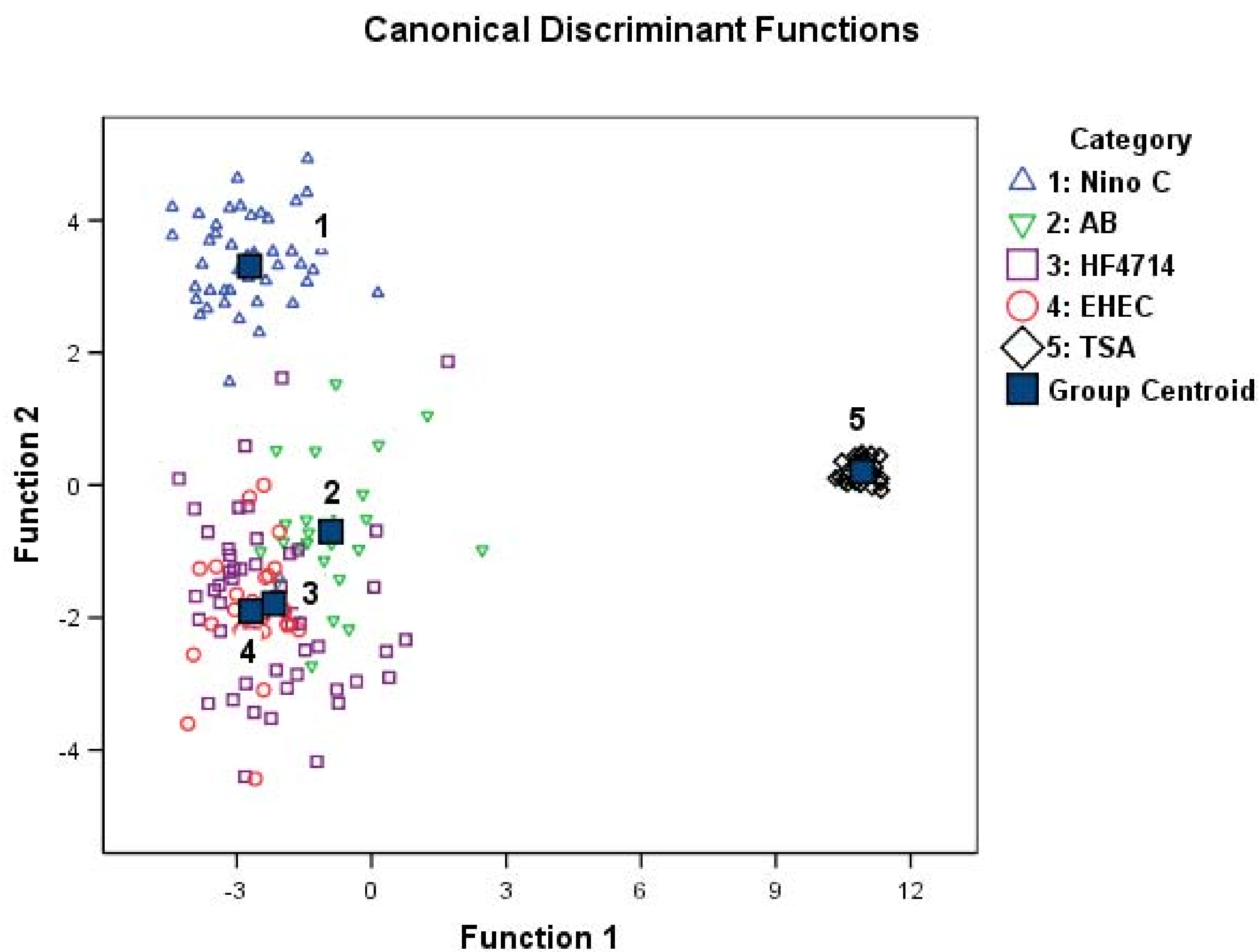
- $I_{\min}$ Al = 1.75 x 10^8 W/cm^2
  - for a 10 ns pulse, focused to a 100 μm spot: ~130 μJ

Physics of Plasma Formation: laser detonation wave

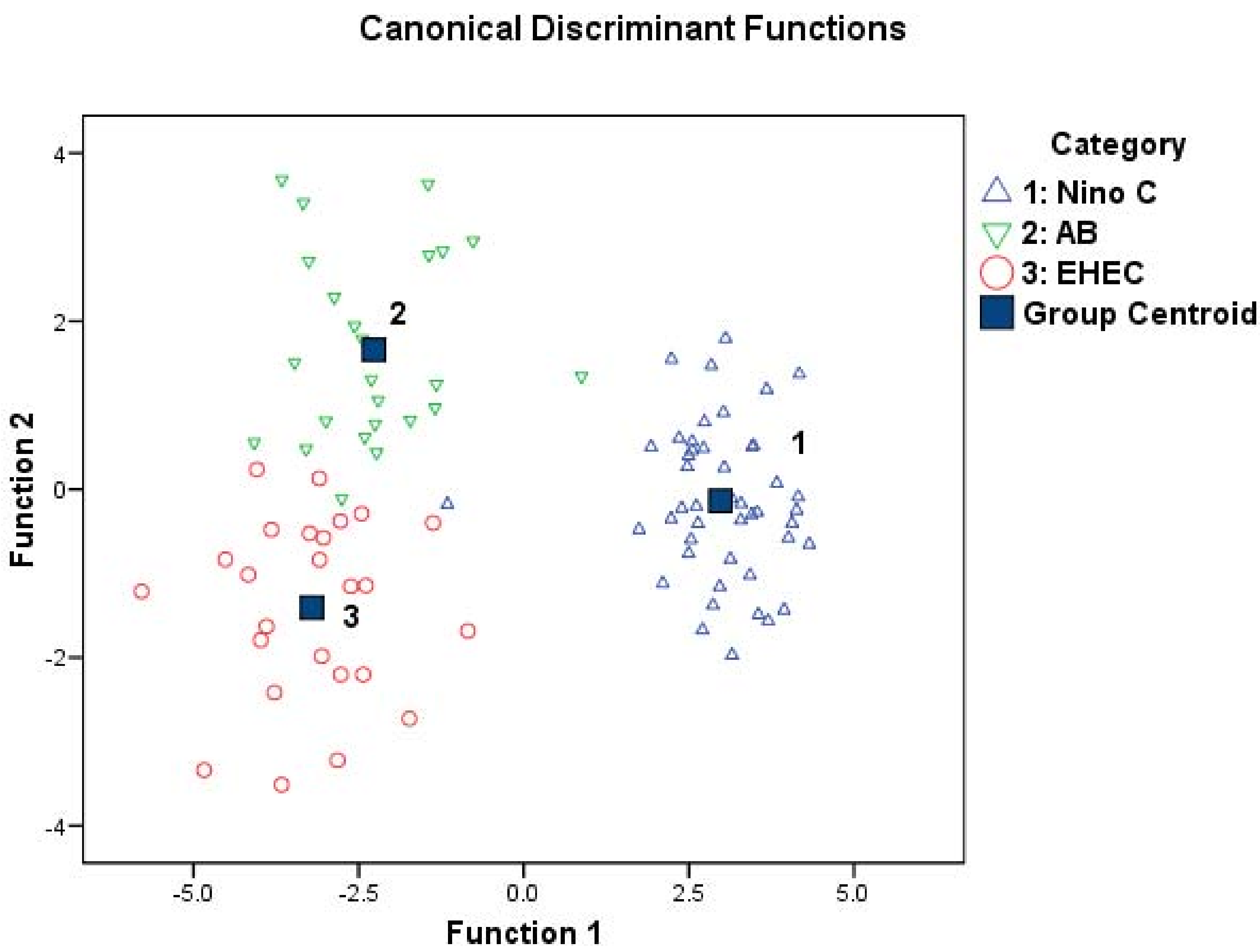
laser-supported detonation wave (LSD or LDW) with a supersonic, rapidly expanding shock-wave front



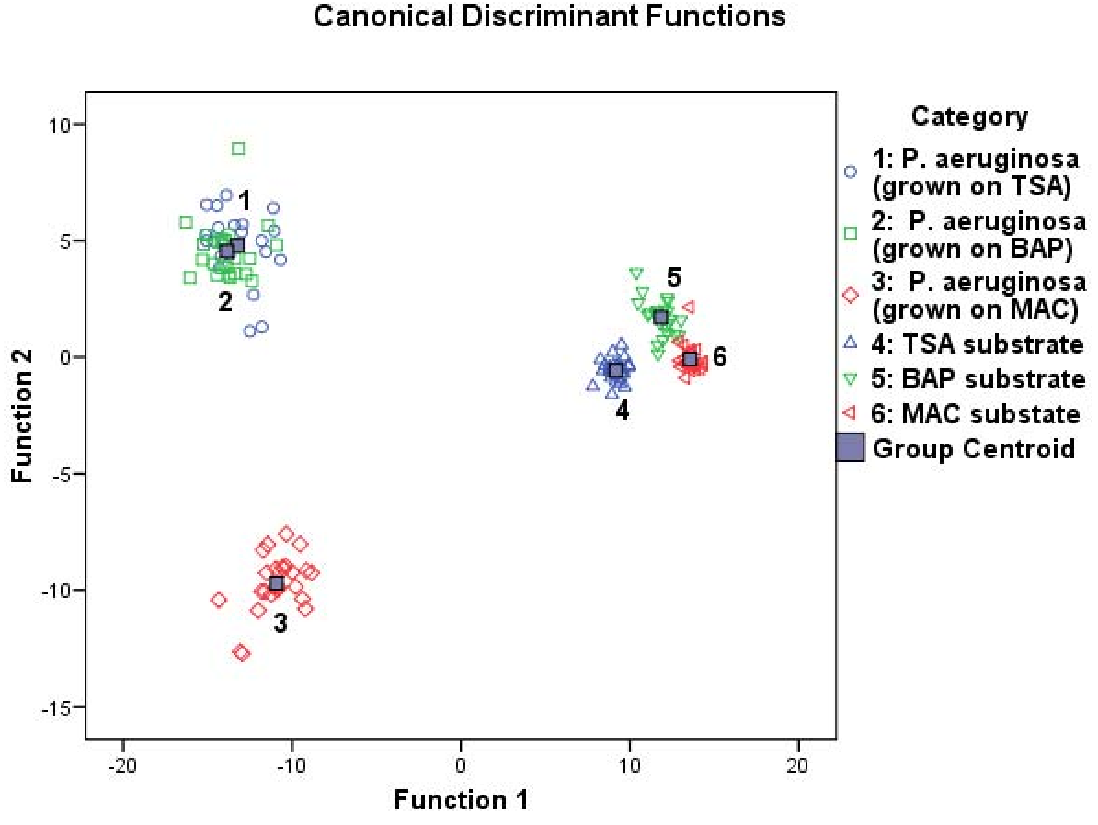
EHEC Results



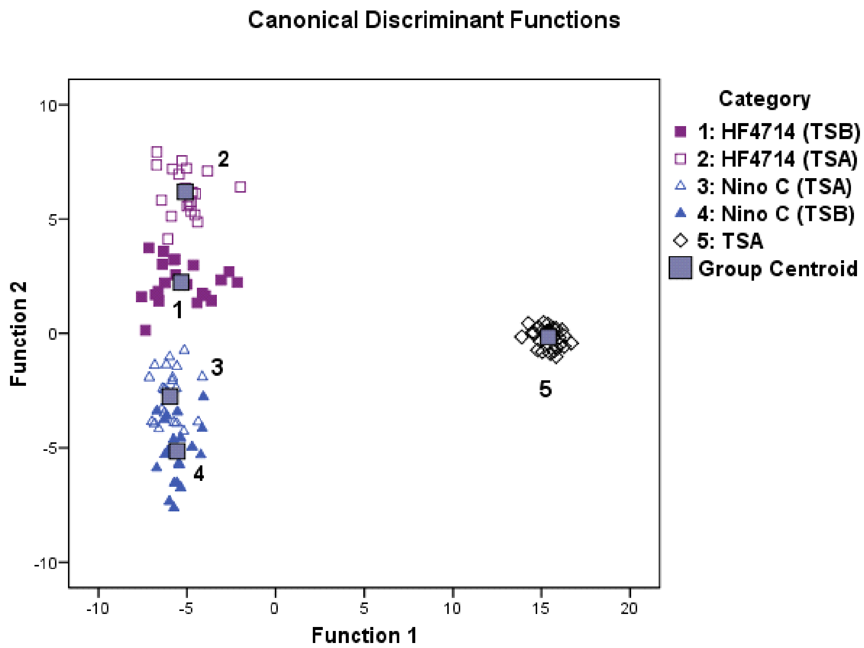
EHEC Results

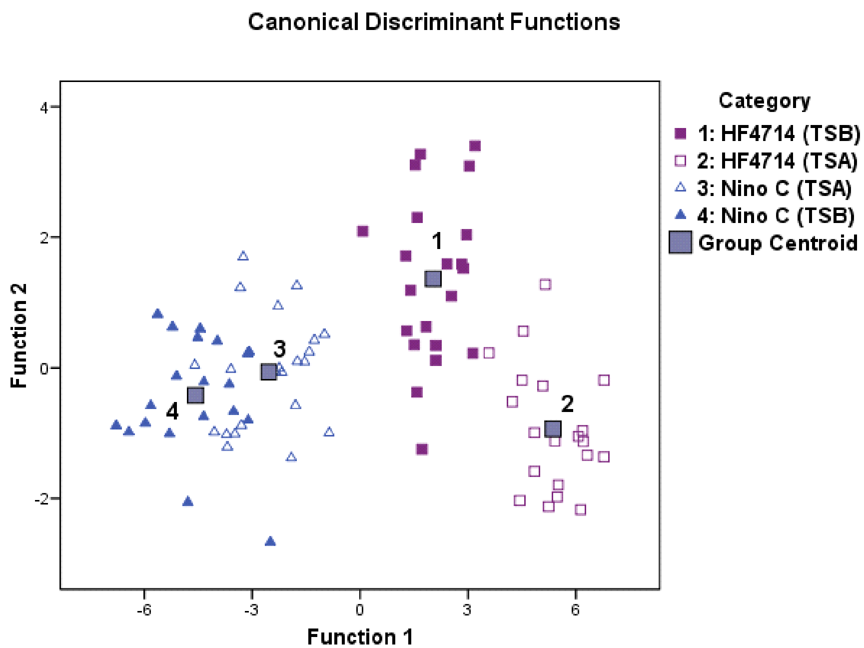


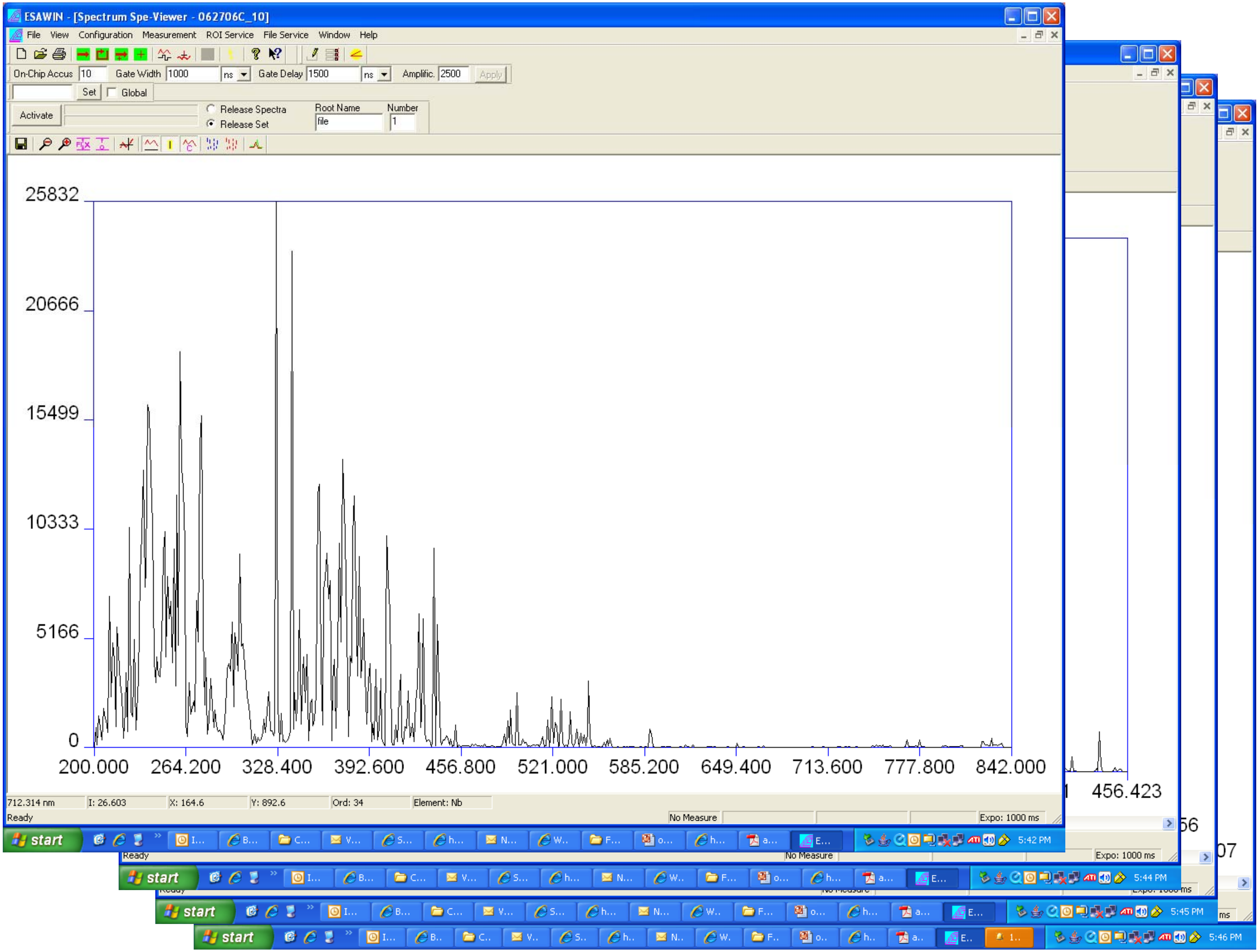
Effect of Growth Environment on *P. aeruginosa*



Effect of Growth Environment on *E. coli*



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Spectral Line Radiant Intensity

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

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

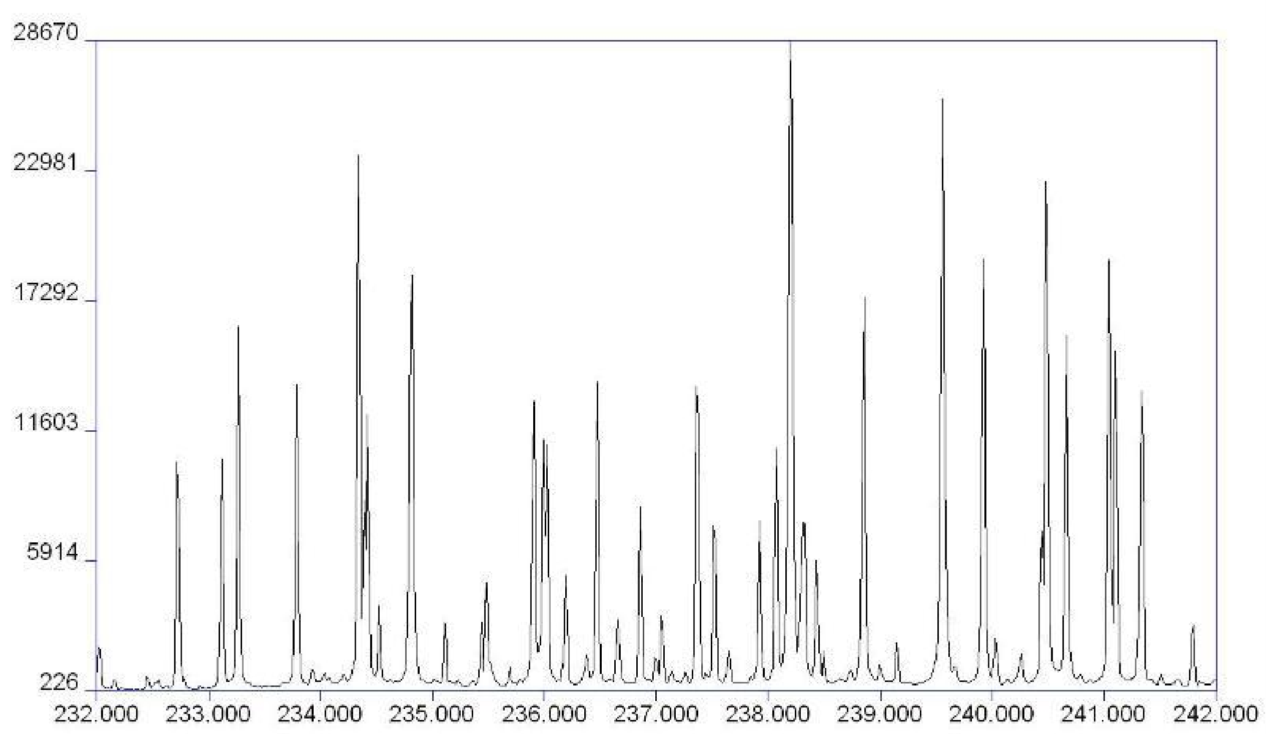
Temperature

- confusing! better to write…

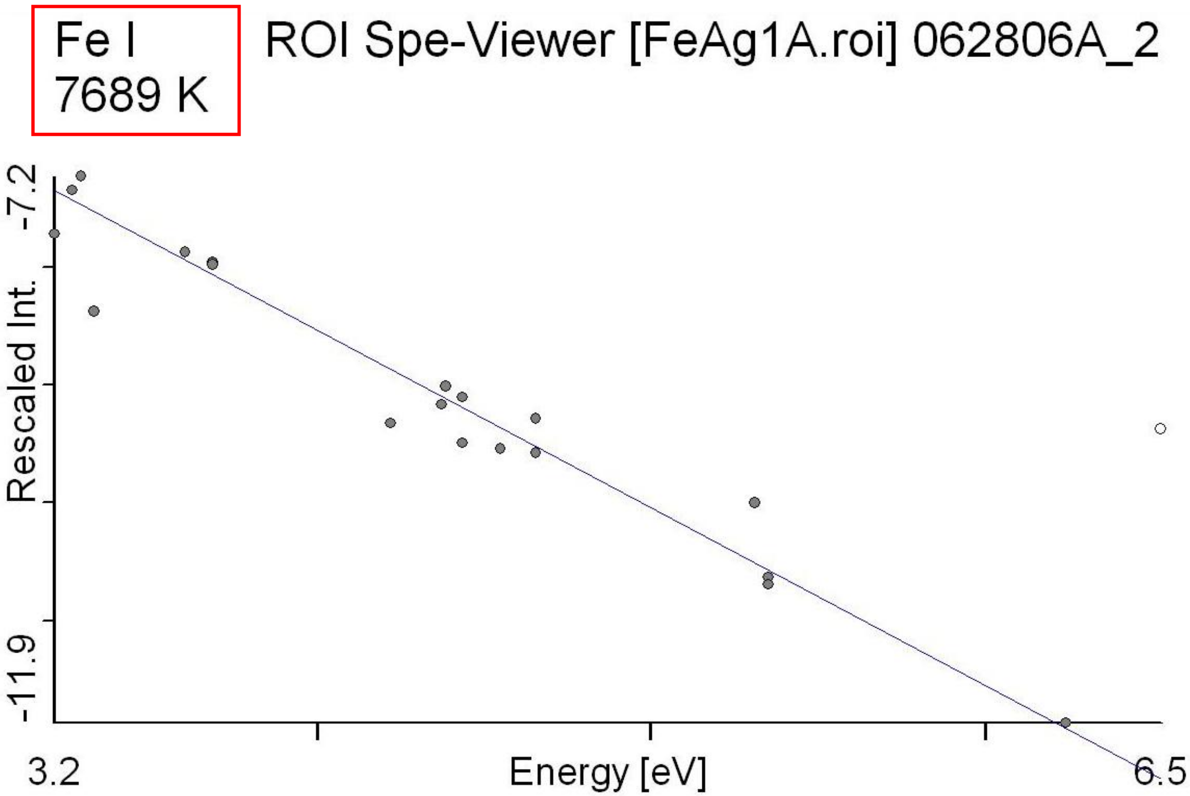
$$\ln\left(\frac{I\lambda}{gA}\right) = -\frac{E}{kT} - \ln\left(\frac{4\pi Z}{hcN_0}\right)$$

- 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

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

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

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

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