Laser-Induced Breakdown Spectroscopy (LIBS)

presented at
Principles of and Recent Advances in Laser Micro/Nano Manufacturing Processes

June 1-4, 2010 - Evanston, IL

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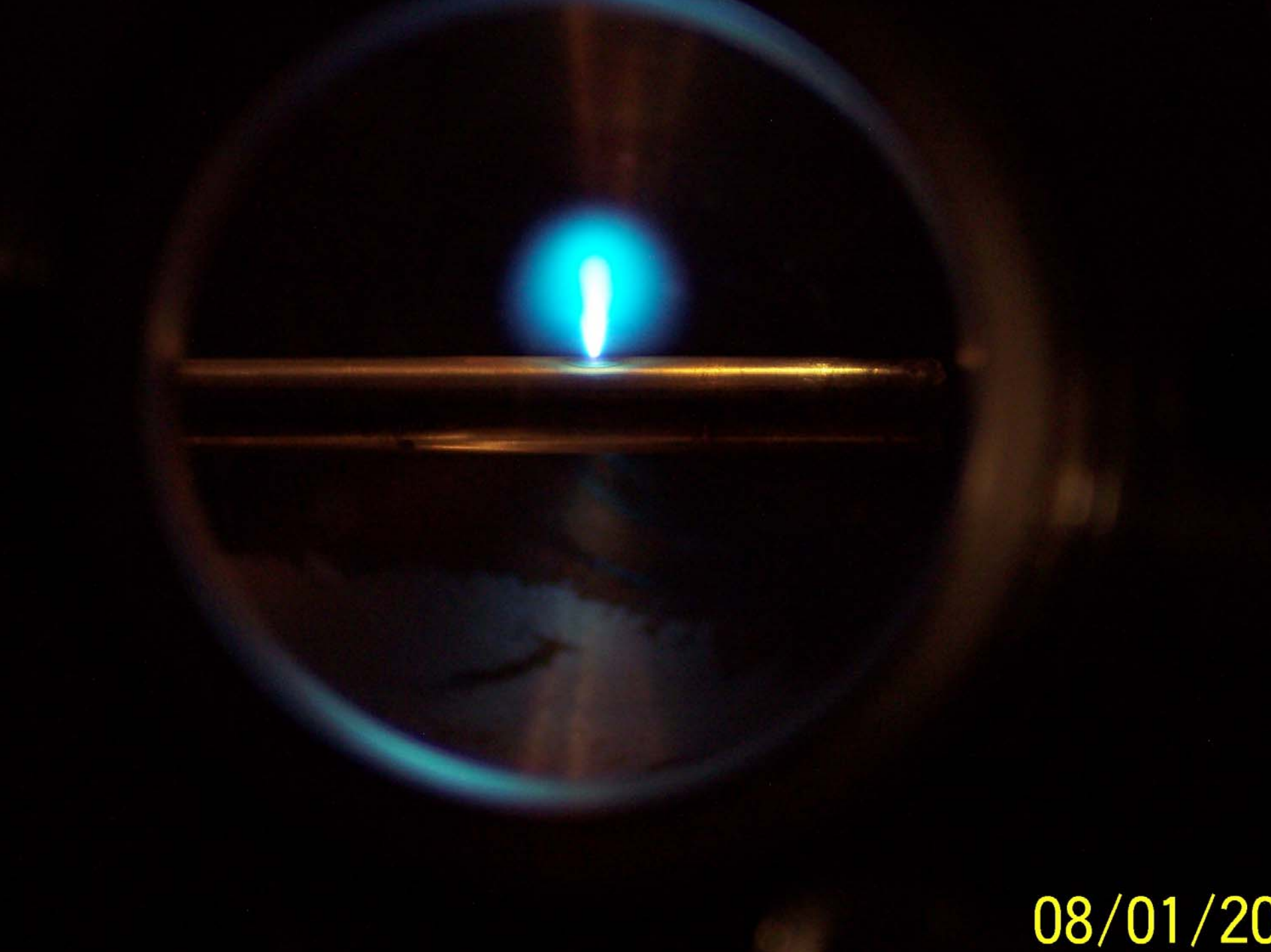
Outline

1. Introduction to LIBS
2. Physics of the plasma formation and observation
3. Instrumentation
4. Advanced techniques

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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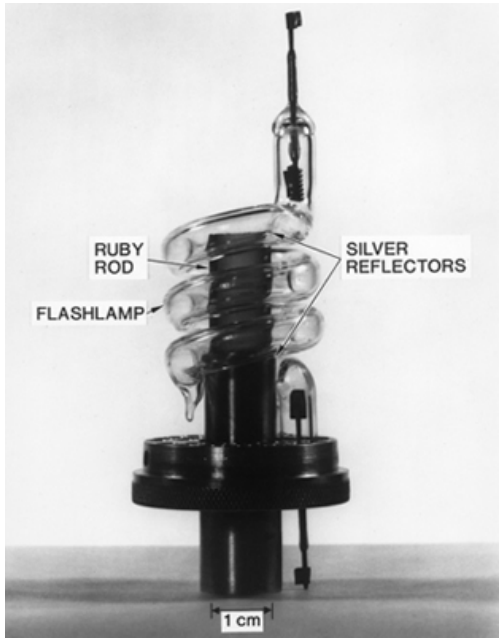
History

1960
Maiman, first ruby laser



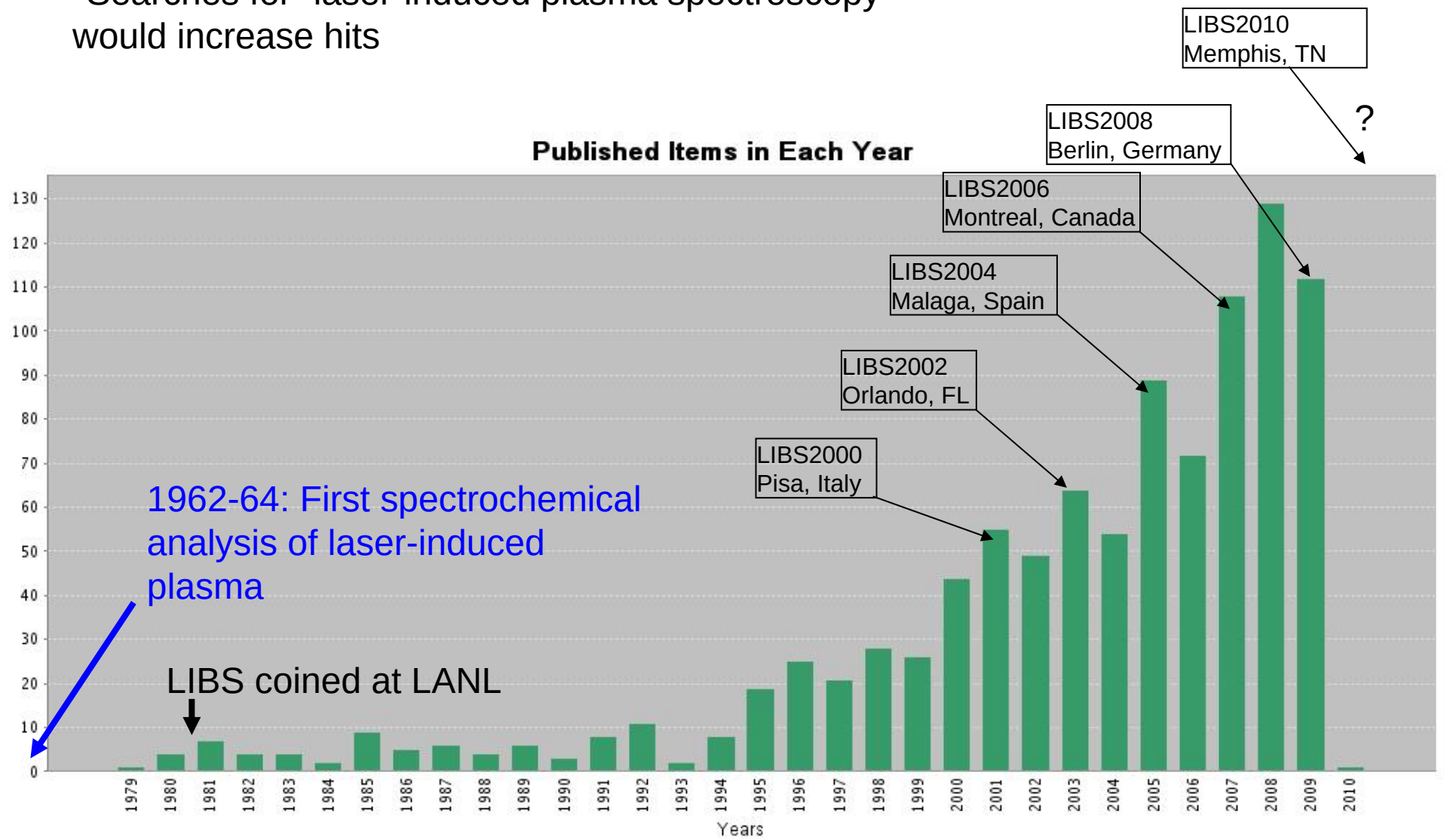
1962
Brech, Cross; Birth of LIBS: detection of spectrum from ruby laser induced plasma

1964
Runger et al. First direct spectro-chemical analysis by LIBS

1965
Zel'dovich, Raizer, First theoretical model for laser breakdown of a gas

History: "laser-induced breakdown"* @ Web of Science

*Searches for "laser-induced plasma spectroscopy" would increase hits



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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
- 00's: portable systems
- 00's: chemometric techniques

LIBS Applications

- 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

3 Current “Super-Stars” of Atomic Spectroscopy

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

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

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

Suggested Reading

Comparing several atomic spectrometric methods to the super stars: special emphasis on laser induced breakdown spectrometry, LIBS, a future super star†

REVIEW

James D. Winefordner, Igor B. Gornushkin, Tiffany Correll, Emily Gibb, Benjamin W. Smith and Nicoló Omenetto

Department of Chemistry, University of Florida, Gainesville FL 32611, USA

J. Anal. At. Spectrom., 2004, **19**, 1061–1083

Review

Characterization of laser induced plasmas by optical emission spectroscopy: A review of experiments and methods

C. Aragón *, J.A. Aguilera

Departamento de Física, Universidad Pública de Navarra, Campus de Arrosadía, E-31006 Pamplona, Spain

Spectrochimica Acta Part B 63 (2008) 893–916

Advantages of LIBS

1) extremely fast analysis compared to competing technologies

2) multi-elemental analysis, light from all constituents collected without bias (see Periodic Table)

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

7) depth resolution (micron or sub-micron)

Keeping Track of the Elemental Inventory
(underlined elements reported in literature)

(■ Solids ■ Liquids ■ Gases ■ Artificially prepared)

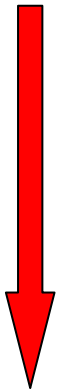
1 H																2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub		114 Uuq		116 Uuh		
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

www.arl.army.mil/wmrd/LIBS

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

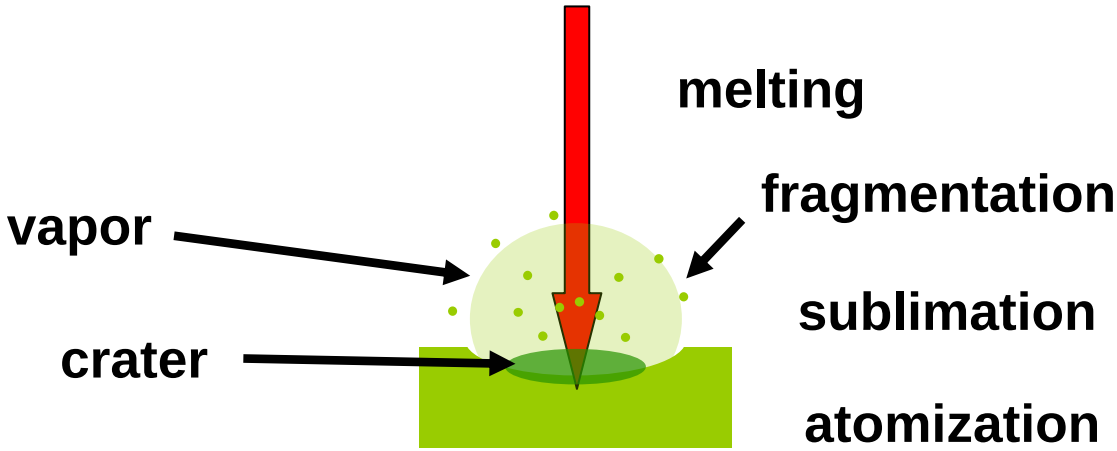


pulsed laser

absorption of laser energy

- 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.

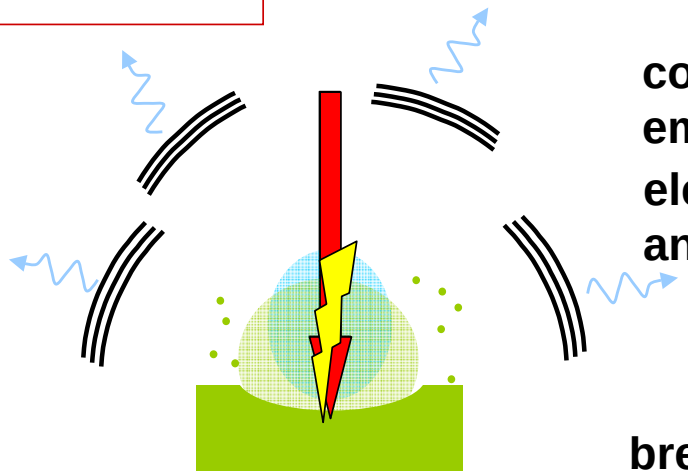
2) removal of samples mass (ablation)



- 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)



absorption of the laser radiation by the vapor

continuum emission

electrical breakdown and plasma formation

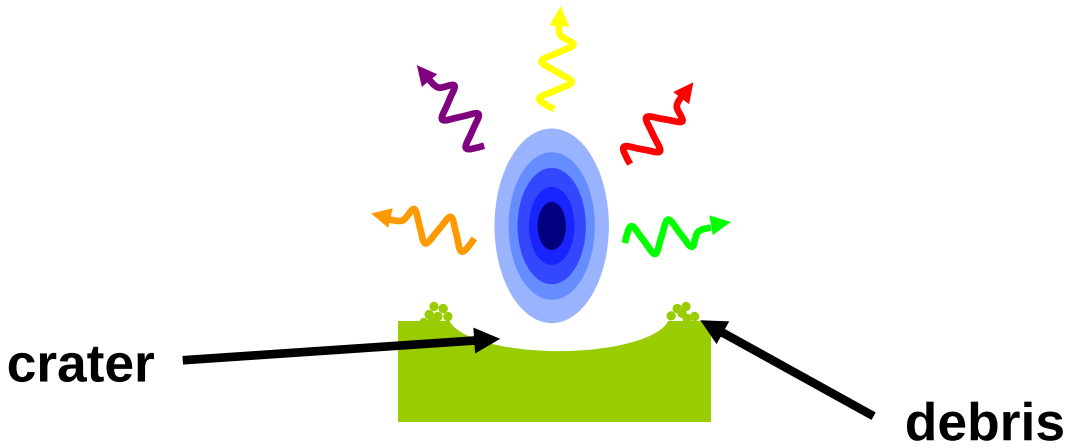
shock wave

bremmstrahlung

- 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) expansion and element specific emission (atomic or ionic)

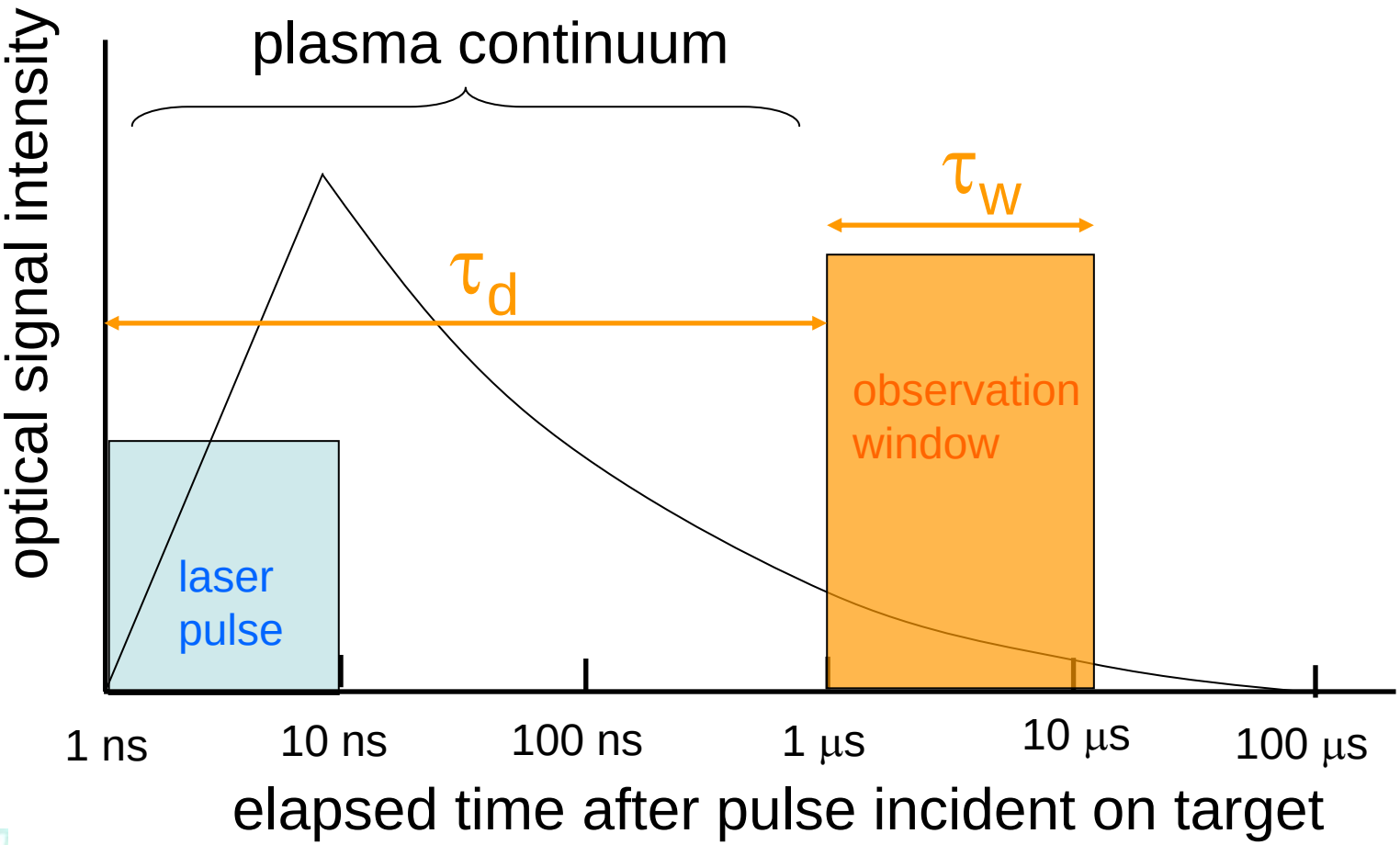
spontaneous emission as atoms/ions decay to ground state



- 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

D.A. Cremers and L.J. Radziemski, in "Handbook of Laser-Induced Breakdown Spectroscopy," (2006) p. 24



Outline

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1. laser interaction with the target

M. Sabsabi, in "Laser-Induced Breakdown Spectroscopy," (2007) p. 159

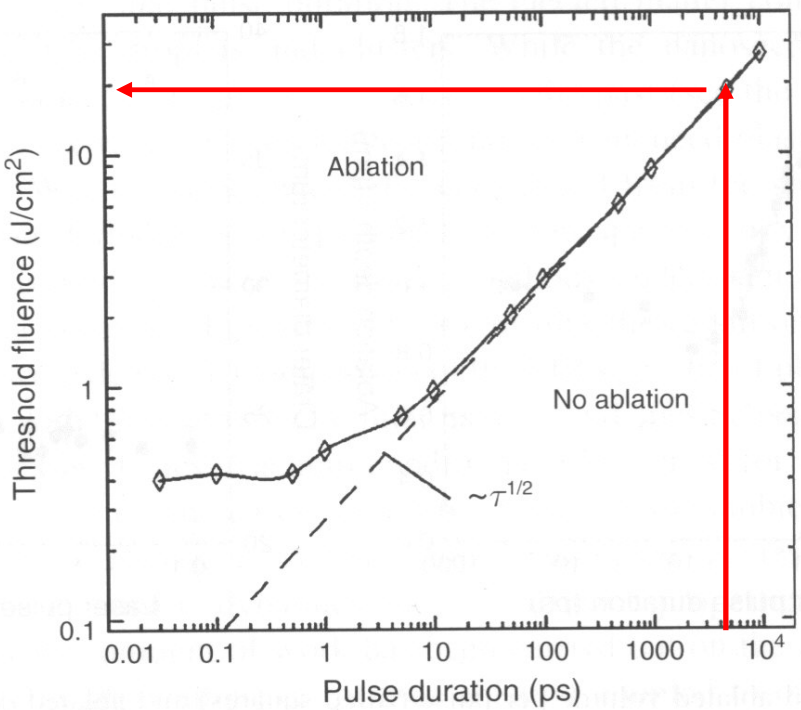


Fig. 5. Threshold fluence for ablation as a function of the pulse duration.

- plot for aluminum
- typical ns lasers
  - assume a 100 micron spot size (modest focusing)
  - requires approximately 1 mJ (modest pulse energy)
  - to be well above ablation threshold, typically 10's of mJ used

1. laser pulse fluence

- so a 1 mJ ns pulse focused to a spot size of 100 μm yields a fluence of ~10 J/cm^2
- assuming a 10 ns pulse (typical) operating at 10 Hz (typical)

$$10\,\frac{\mathrm{J}}{\mathrm{cm}^2}\cdot\frac{1\ \mathrm{pulse}}{10\ \mathrm{ns}}\cdot 10\ \mathrm{pulses}=10\,\frac{\mathrm{GW}}{\mathrm{cm}^2}$$

- so irradiances of 1-10 GW/cm^2 are typical

1. laser irradiance calculation

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

- 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

1. laser pulse wavelength

- all wavelengths have been used / can be used

- different authors have reported different dependence of breakdown threshold fluence with wavelength
  - (some increasing, some decreasing)
  - [see *E. Tognoni et al. Spectrochimica Acta B* ***57*** *(2002) 1115-1130*]

1. laser pulse wavelength

- complexity arises from:
  - the multiple steps required to form a laser-induced plasma
  - the variety of target properties (reflectivity, dielectric constant)
  - what do you want out of it?
    - most mass removed
    - highest intensity
    - best SNR

- "In addition, wavelength is an important factor for the initiation of plasma. Short laser wavelengths aid the ablation process because a good absorption of laser irradiance by the material occurs. Nevertheless, the inverse Bremsstrahlung process is more efficient with IR wavelength than with UV radiation and the laser induced breakdown in ambient air is then favored at larger wavelengths."

  *L.M. Cabalin and J.J. Laserna, Spectrochimica Acta Part B **53** (1998) 723-730*

2. removal of samples mass (ablation)

for solid targets and ns pulses…

HEATING OF SOLID

Free carrier absorption (inverse Bremsstrahlung) ~100 fs

THERMAL PROCESSES

Energy transfer to lattice phonons (few ps)

MELTING

Heat conduction / thermal diffusion into bulk (~10 ps)

10^{-12} – 10^{-9} s timescale

EVAPORATION

Optically thin plasma forms, laser still reaches target (>0.1 ns)

TARGET-LASER DECOUPLING

Optically thick plasma plume, laser no longer illuminates target, ablation ceases (plasma shielding)

2. removal of samples mass (ablation)

for solid targets and fs pulses…

R.E. Russo, in "Laser-Induced Breakdown Spectroscopy," (2007) p. 49

CONDUCTORS

SEMICONDUCTOR OR WIDE BANDGAP DIELECTRICS

free electrons directly absorb laser energy

nonlinear process
- *multi-photon absorption and ionization*
- *tunneling*
- *avalanche ionization*

HOT ELECTRON-HOLE PLASMA

10^{-15} – 10^{-13} s timescale

E-H PLASMA INDUCES EMISSION OF X-RAYS, HOT ELECTRONS, PHOTOEMISSION AND HIGHLY CHARGED IONS (COULOMB EXPLOSION OR NON-THERMAL MELTING)

electron-lattice heating may then occur (10^{-12} s)

Physics of Plasma Formation: ablation

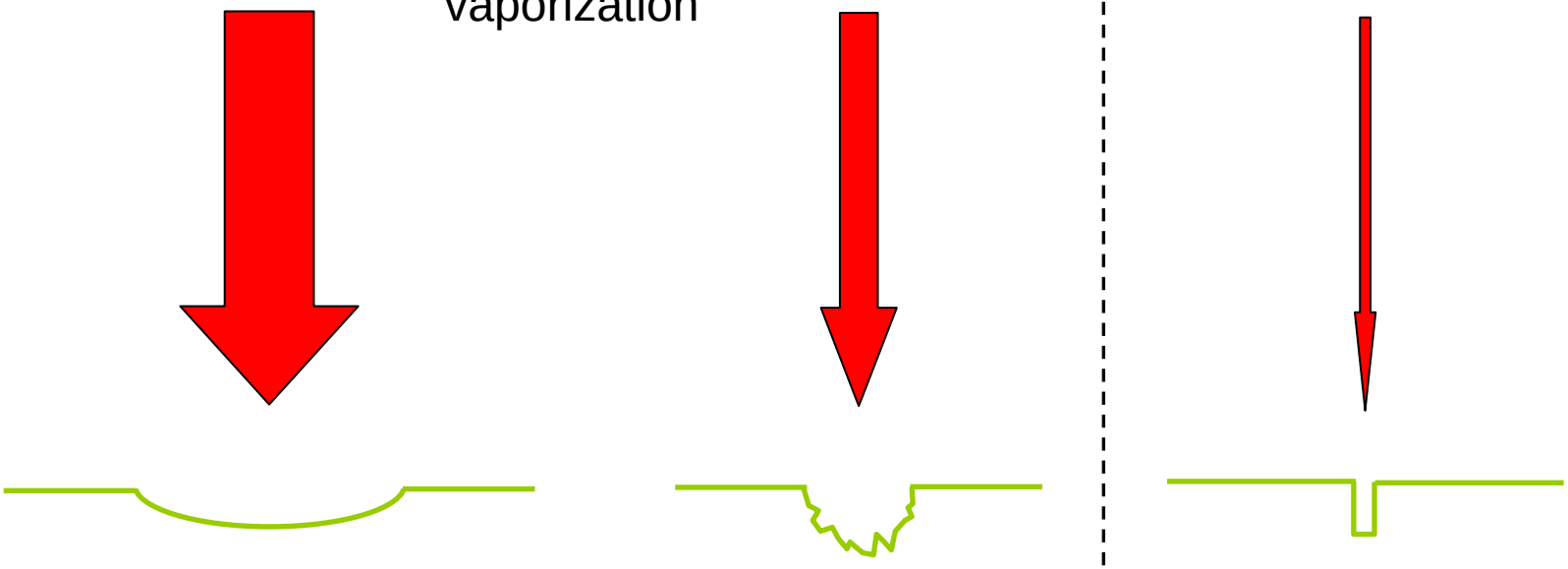
D.A. Cremers and L.J. Radziemski, in "Handbook of Laser-Induced Breakdown Spectroscopy," (2006) p. 45

heating

melting

vaporization

τ_{pulse} < plasma initiation



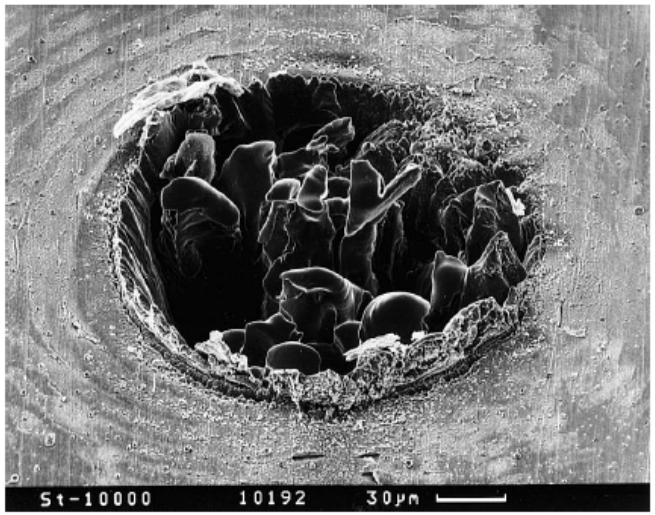
microsecond

nanosecond

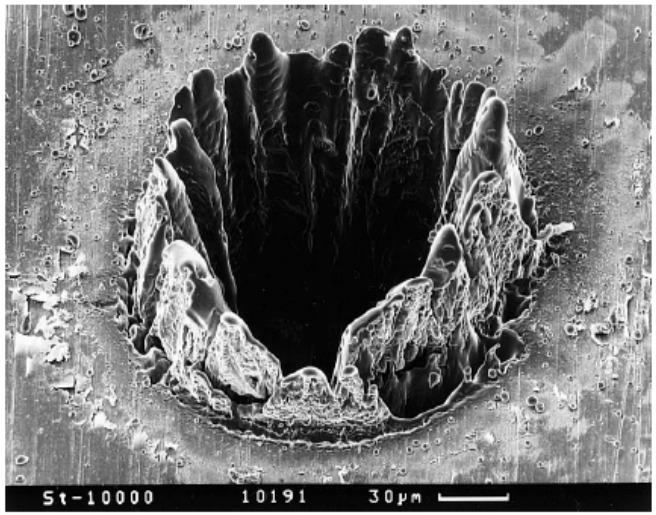
femtosecond

2. removal of samples mass (ablation)

*B.N. Chichkov et al., Appl. Phys. A**63**, 109-115 (1996)*



a



b

Fig. 2a, b. Schematic of nanosecond-pulse laser ablation and holes drilled in a 100 μm thick steel foil with (**a**) 80 ps, 900 μJ, $F = 3.7$ J/cm^2; and (**b**) 3.3 ns, 1 mJ, and $F = 4.2$ J/cm^2 laser pulses at 780 nm

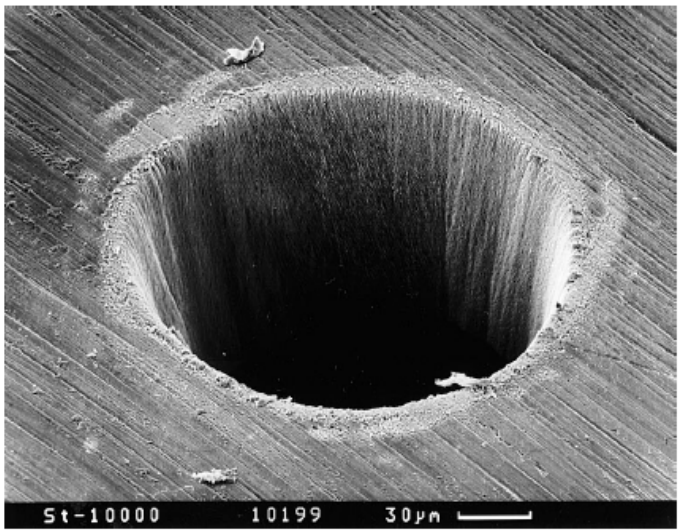


Fig. 1. Schematic of femtosecond-pulse laser ablation and a SEM photograph of a hole drilled in a 100 μm thick steel foil with 200 fs, 120 μJ, $F = 0.5$ J/cm^2 laser pulses at 780 nm

ablation efficiency

e.g., A. Semerok et al., Appl. Surf. Sci. ***311****, 138-139 (1999).*
B. Salle et al., Appl. Phys. A ***69****, S381-383 (1999).*

$$\text{Definition 1} = \frac{\text{volume of matter ablated}}{\text{laser pulse energy}}$$

$$\text{Definition 2} = \frac{\text{crater depth}}{\text{laser fluence}}$$

If the laser intensity distribution corresponds to the crater profile, the two definition are equivalent.

typically ng to μg of material ablated

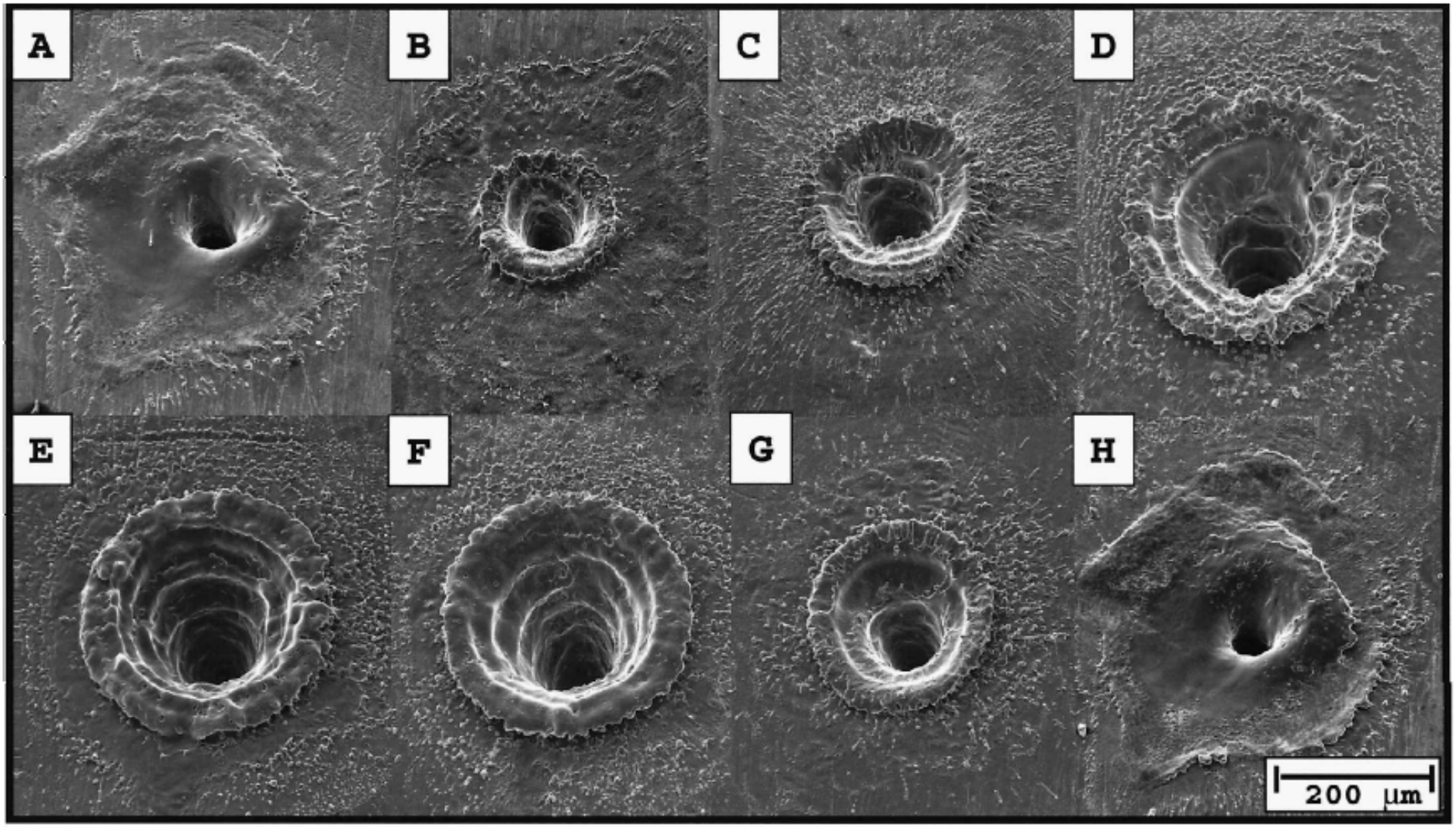
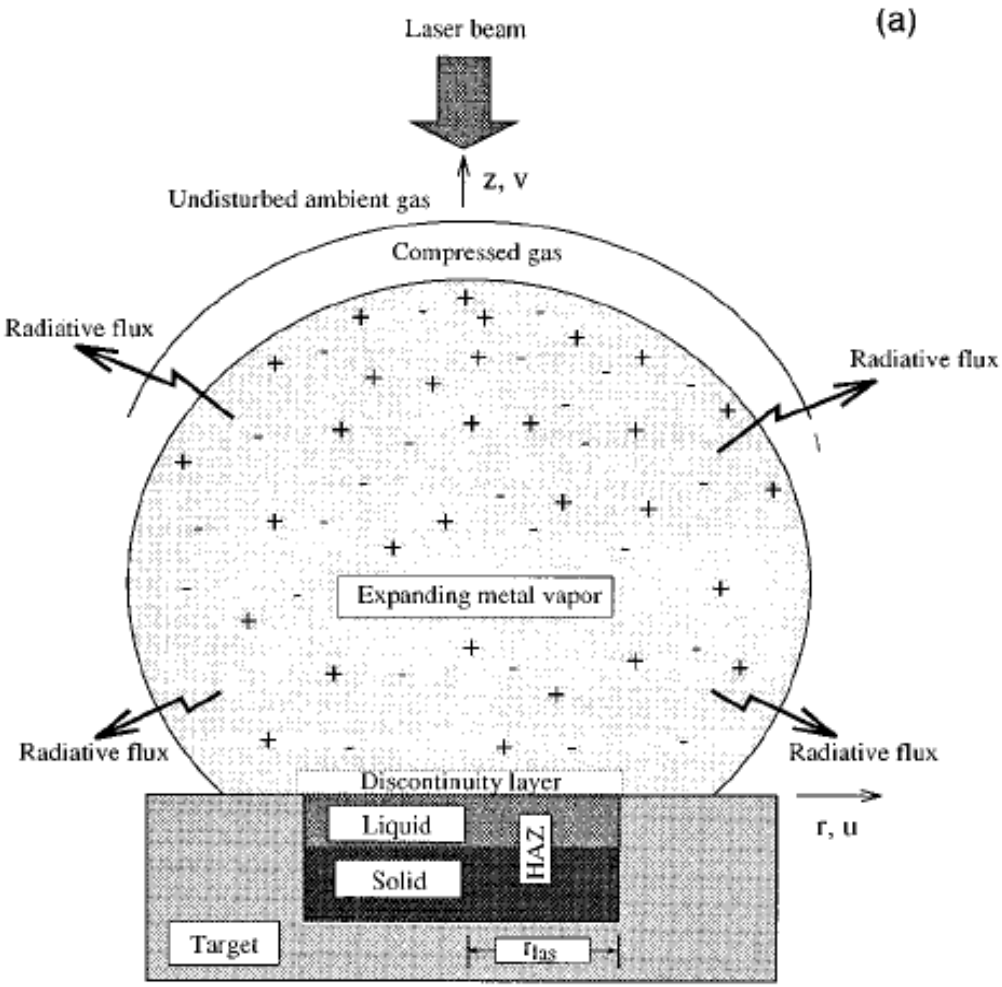


FIG. 4. SEM images of the ablation craters vs. laser pulse delay for a steel sample using (A) single-pulse, and dual-pulse delays of (B) 0.3 μs, (C) 0.5 μs, (D) 2.5 μs, (E) 25 μs, (F) 50 μs, (G) 100 μs, and (H) 300 μs.

D.N. Stratis et al., Appl. Spectrosc. 55, 1297-1303.

3. plasma formation (breakdown)

*J.R. Ho et al., J. Appl. Phys. **79**, 7205-7215 (1996)*



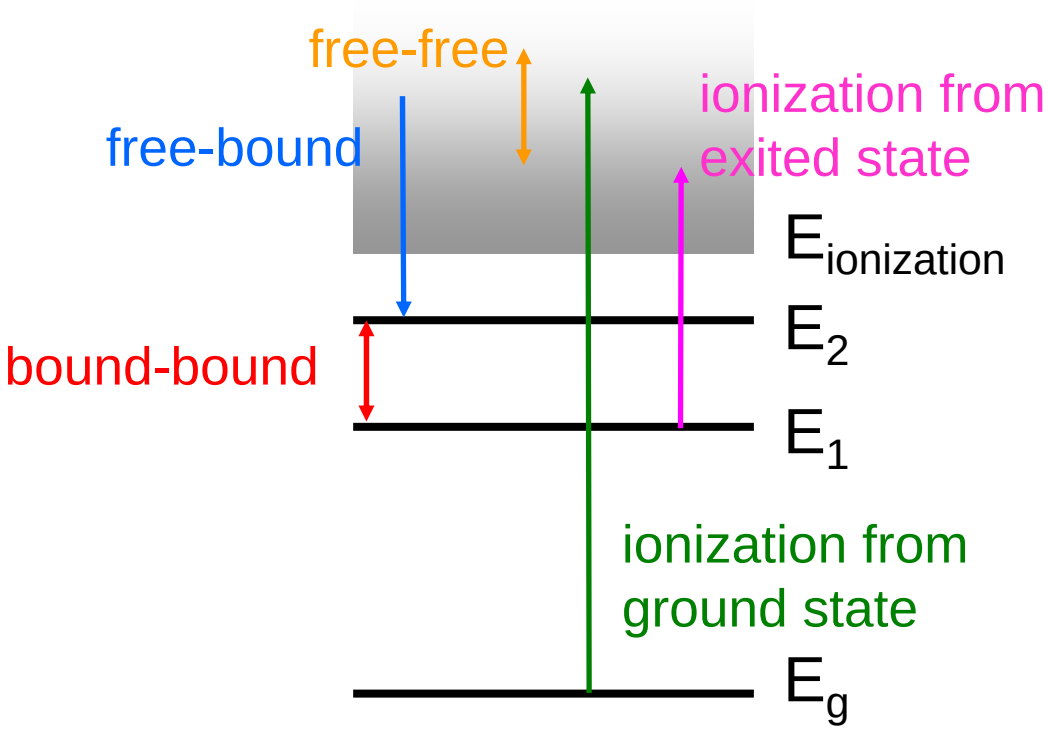
3. plasma formation (breakdown)

Problem: how do photons of relatively low energy, 1-2 eV, (compared to ionization threshold of common gases) generate a breakdown (a plasma at 10,000-50,000K) ?

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”)

Transitions in an Atom or Ion



3. 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
   - local free electron density

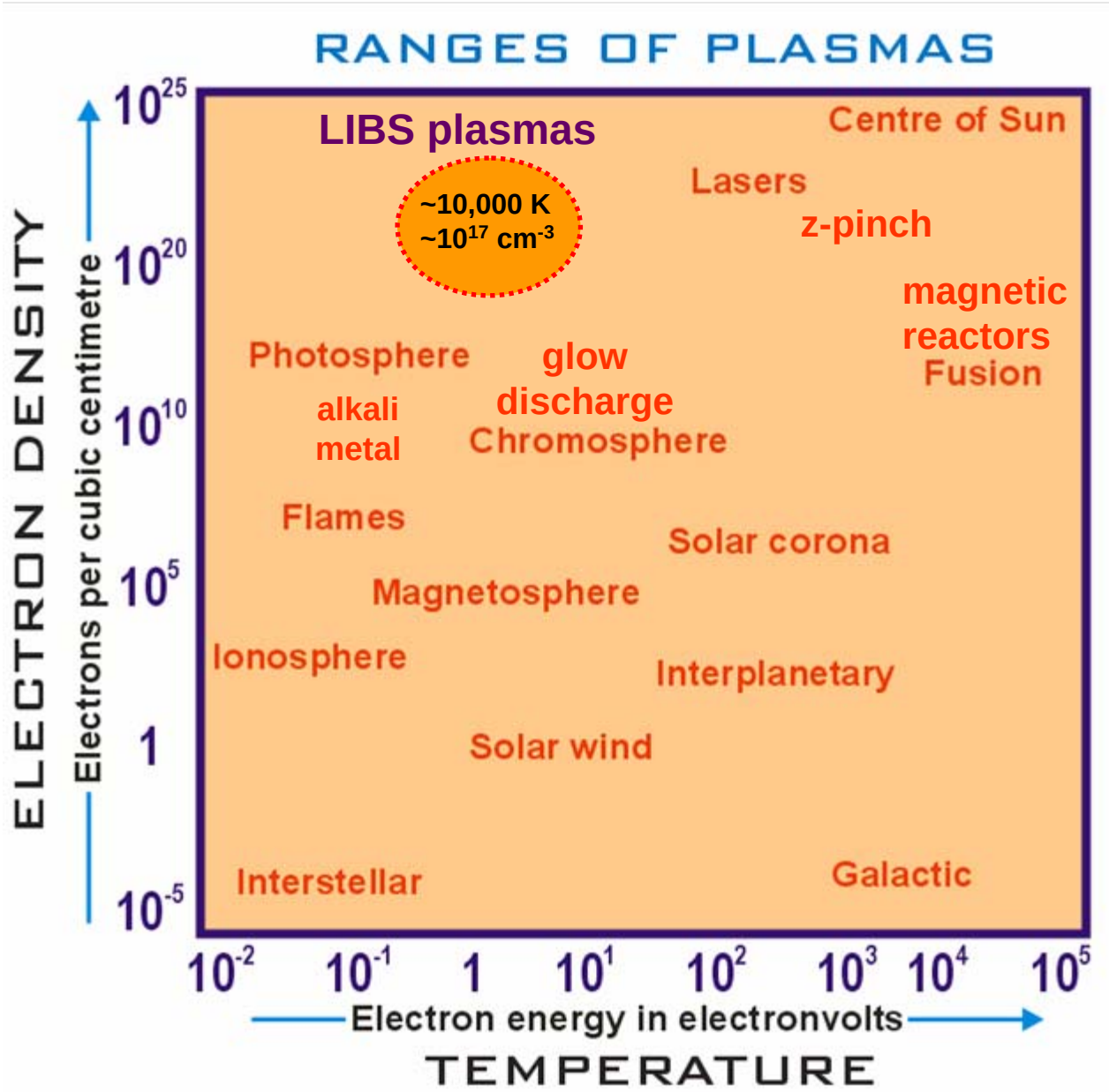
3. plasma formation (breakdown)

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

$$e^-(\text{slow}) + h\nu_{free\text{-}free} + M^+ \rightarrow e^-(\text{fast}) + M^+$$

- 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

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


RANGES OF PLASMAS
LIBS plasmas
~10,000 K
~10^17 cm^-3
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
ELECTRON DENSITY
Electrons per cubic centimetre
10^25
10^20
10^10
10^5
1
10^-5
10^-2
10^-1
1
10^1
10^2
10^3
10^4
10^5
Electron energy in electronvolts
TEMPERATURE

3. plasma formation (breakdown)

3. “breakdown” is arbitrarily defined

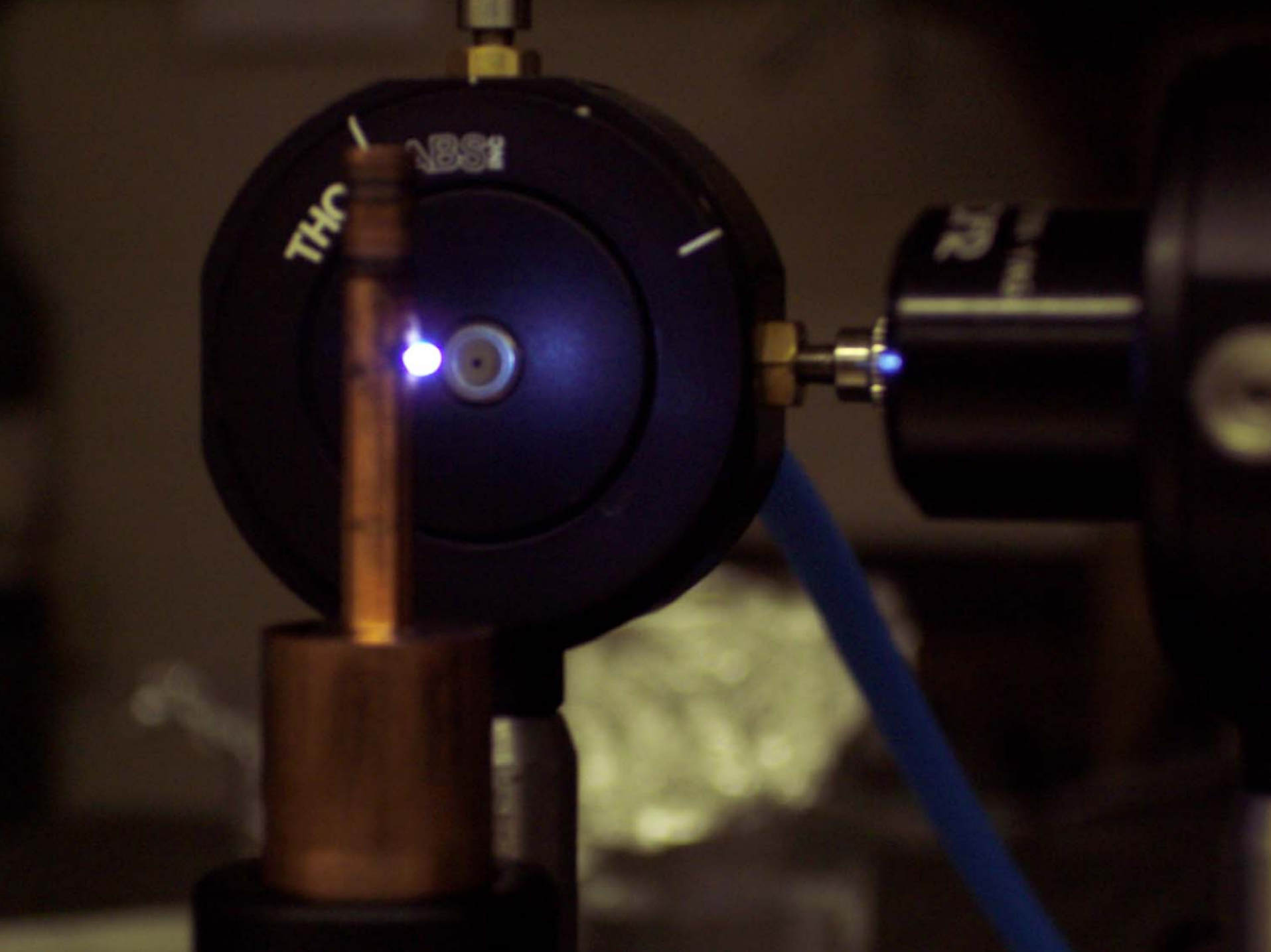
$n_e \sim 10^{13}$ cm^{-3} or degree of ionization of 10^{-3}

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

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

www.physicstoday.org
physics today
May 2007

A Stark look at plasma breakdown



3. 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

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

λ in micron

4. Expansion and Emission

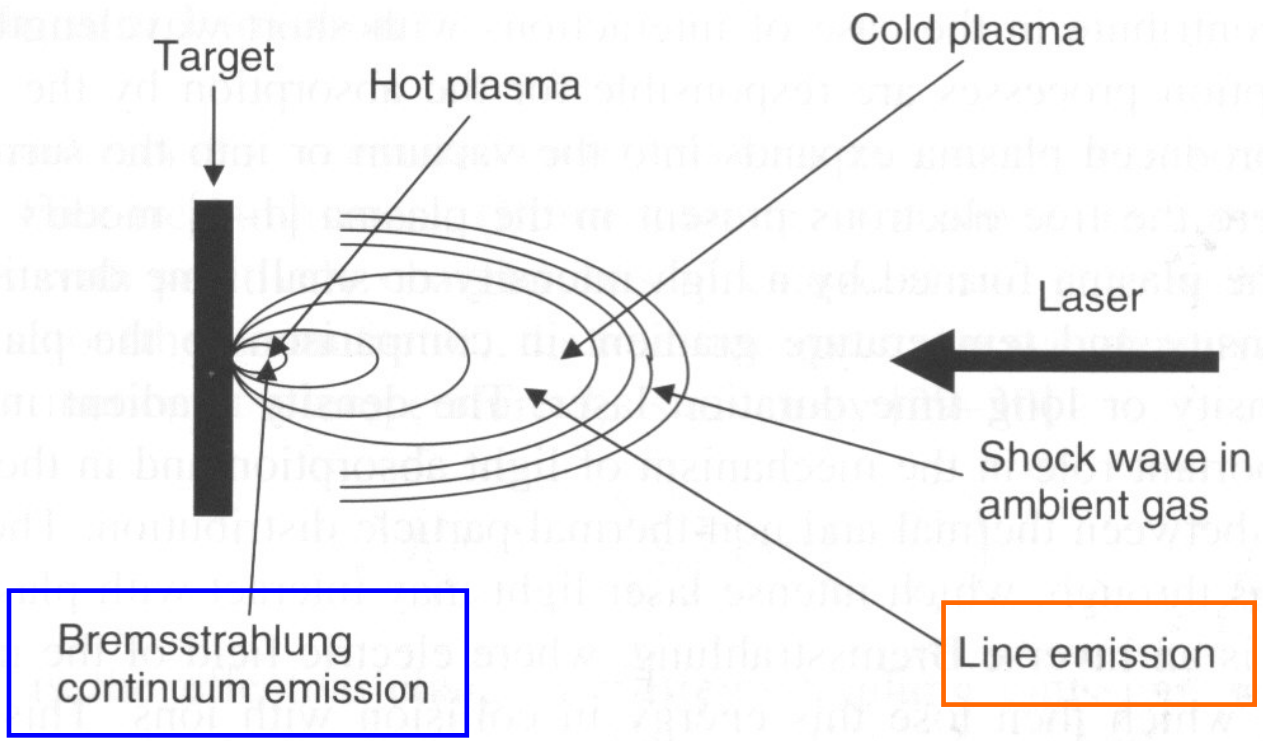
J.F. Ready, "Effect of High Power Laser Radiation," 1971

- laser absorption in the expanding vapor/plasma can generate three different types of waves depending on irradiation intensity
  - laser-supported combustion (LSC)
  - laser-supported detonation (LSD)
  - laser-supported radiation (LSR)

expanding/cooling plasma

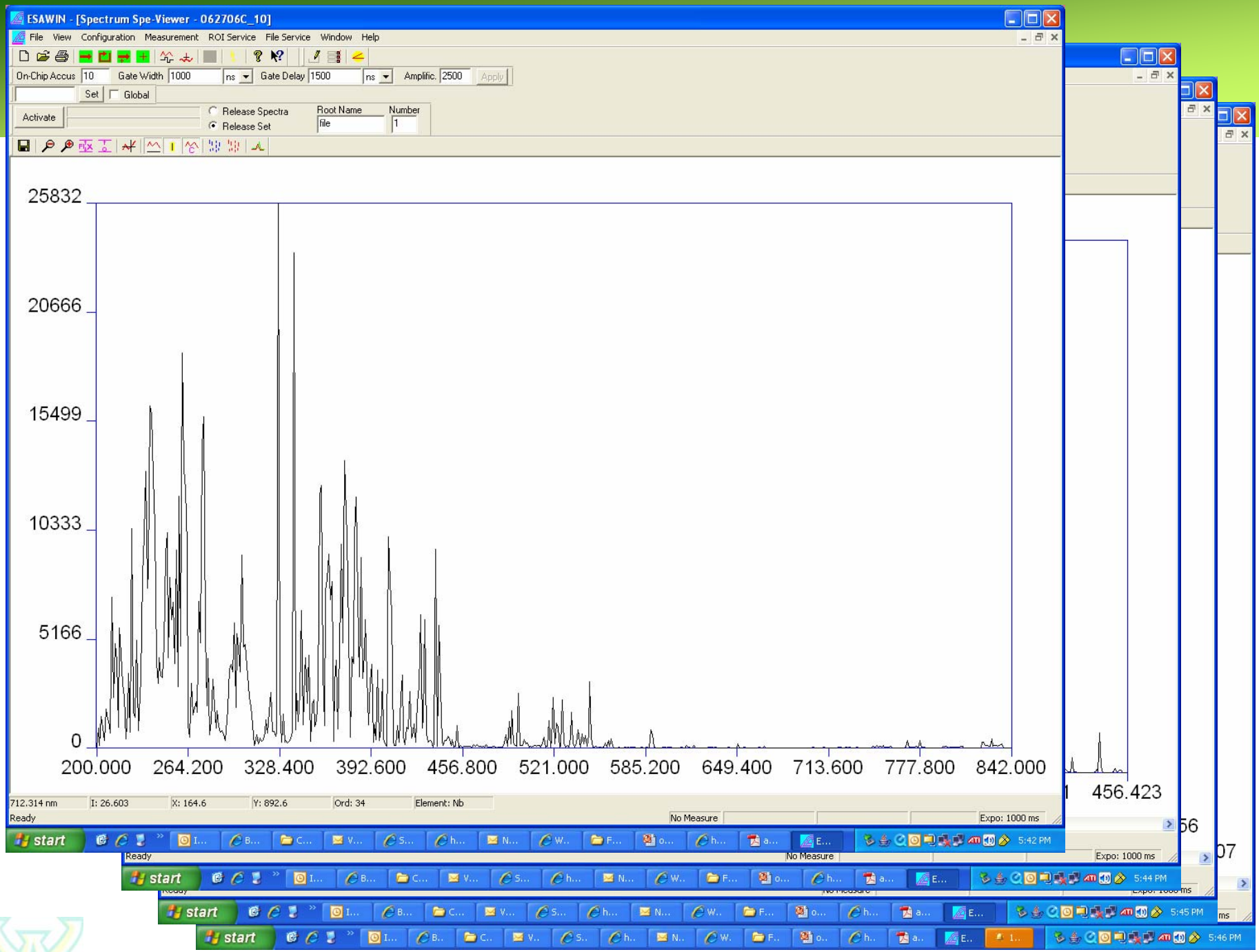
V.N. Rai and S.N. Thakur, in "Laser-Induced Breakdown Spectroscopy,"(2007) p. 85

- the *dynamic* nature of this emission source is why time gating is used



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*.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On-Chip Accus 10 Gate Width 1000 ns Gate Delay 1500 ns Amplific. 2500 Apply
Set Global
Activate Release Spectra Release Set Root Name file Number 1
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10333
5166
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200.000 264.200 328.400 392.600 456.800 521.000 585.200 649.400 713.600 777.800 842.000
712.314 nm I: 26.603 X: 164.6 Y: 892.6 Ord: 34 Element: Nb
Ready
No Measure
Expo: 1000 ms
456.423
start
5:42 PM
5:44 PM
5:45 PM
5:46 PM

Spectral Line Radiant Intensity

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

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)

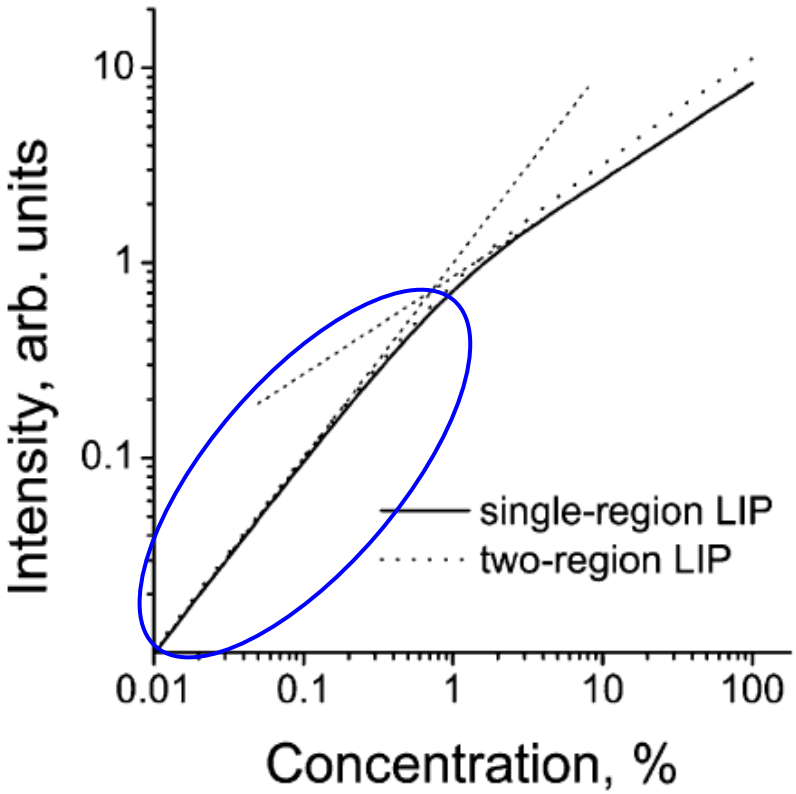
E = Energy of upper state of transition

Low concentrations required

*J.A. Aguilera et al., Spectrochim. Acta B **58**, 221-237 (2003)*

"Curve of growth":

- for weak optically thin lines, I∝N
- as abundance increases the plasma can become optically thick and the curve saturates



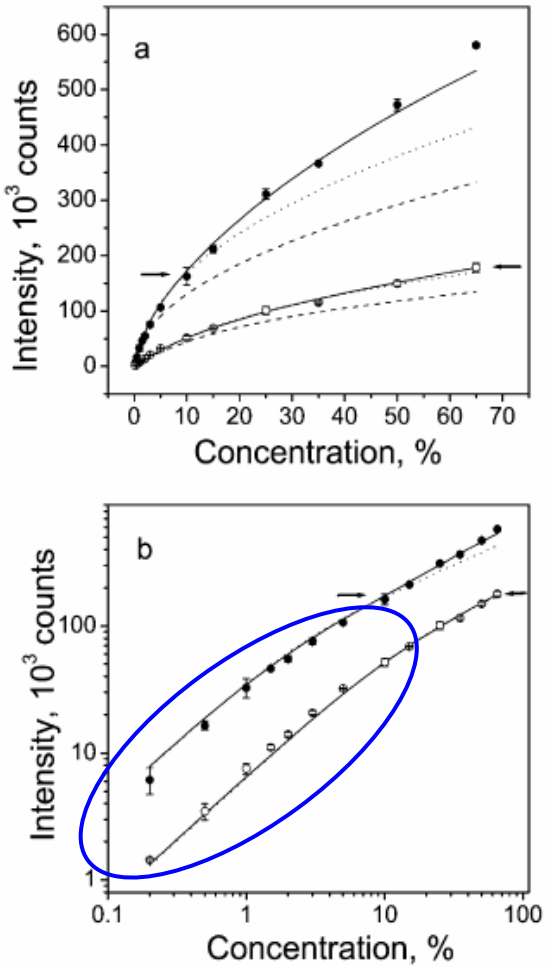


Fig. 4. Experimental and theoretical curves of growth in linear (a) and double logarithmic (b) plots of the Fe I spectral lines A (solid circles) and C (open circles). The theoretical curves have been calculated using the two-region model (solid lines)

Plasma Diagnostics: Temperature

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

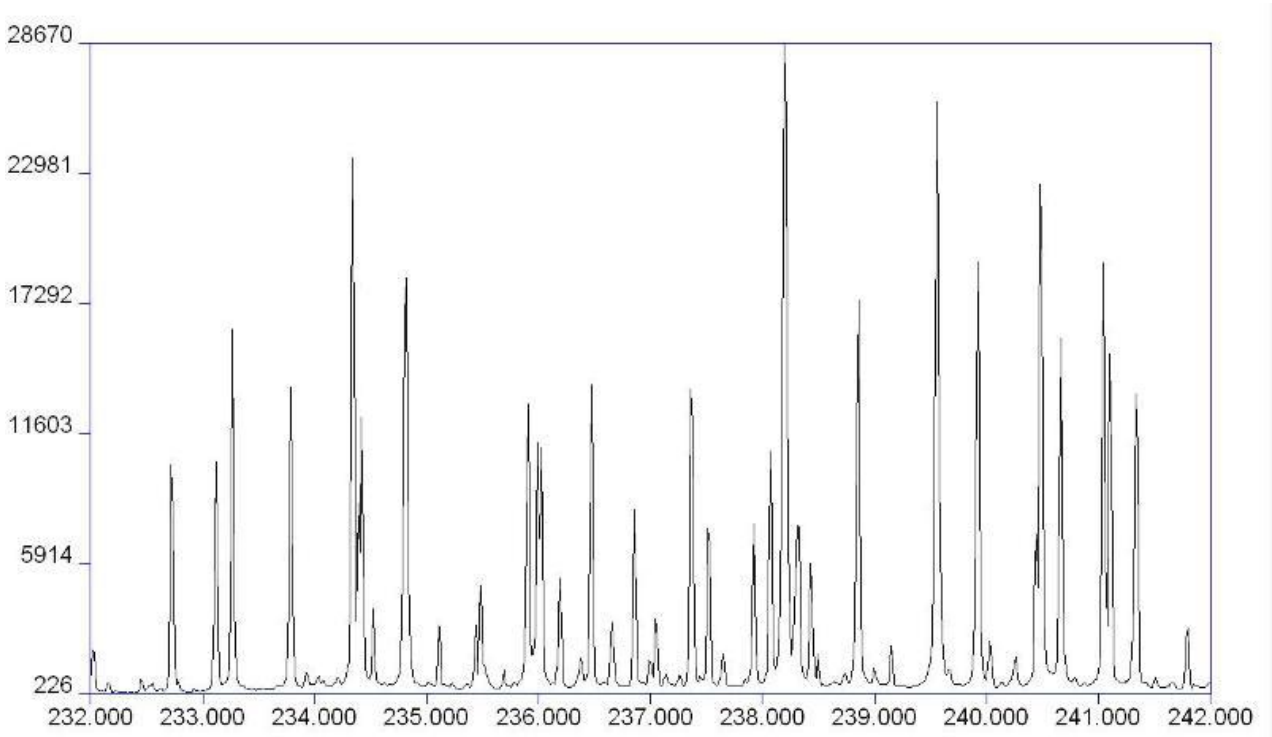
- better to write…

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

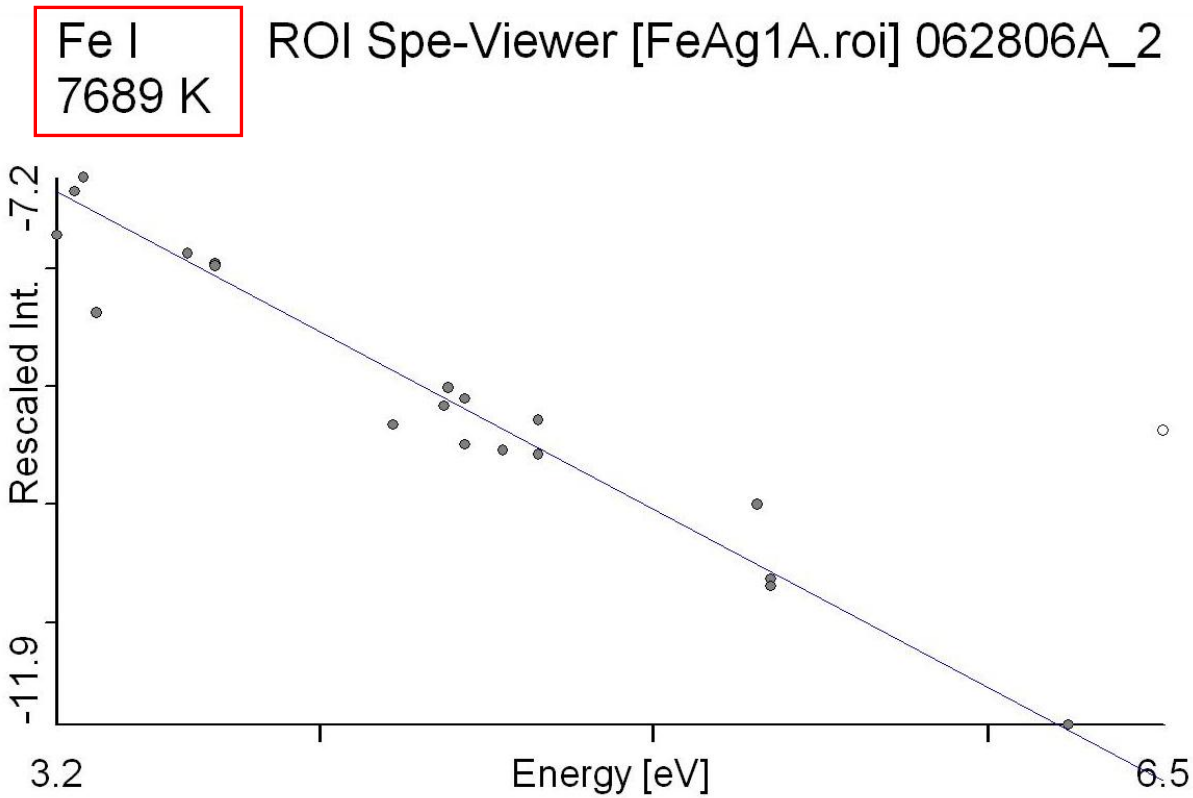
- This is a straight line with slope of $-1/kT$!

- 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:

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

Plasma Diagnostics
electron density

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

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

Local Thermodynamic Equilibrium (LTE) can be assumed if

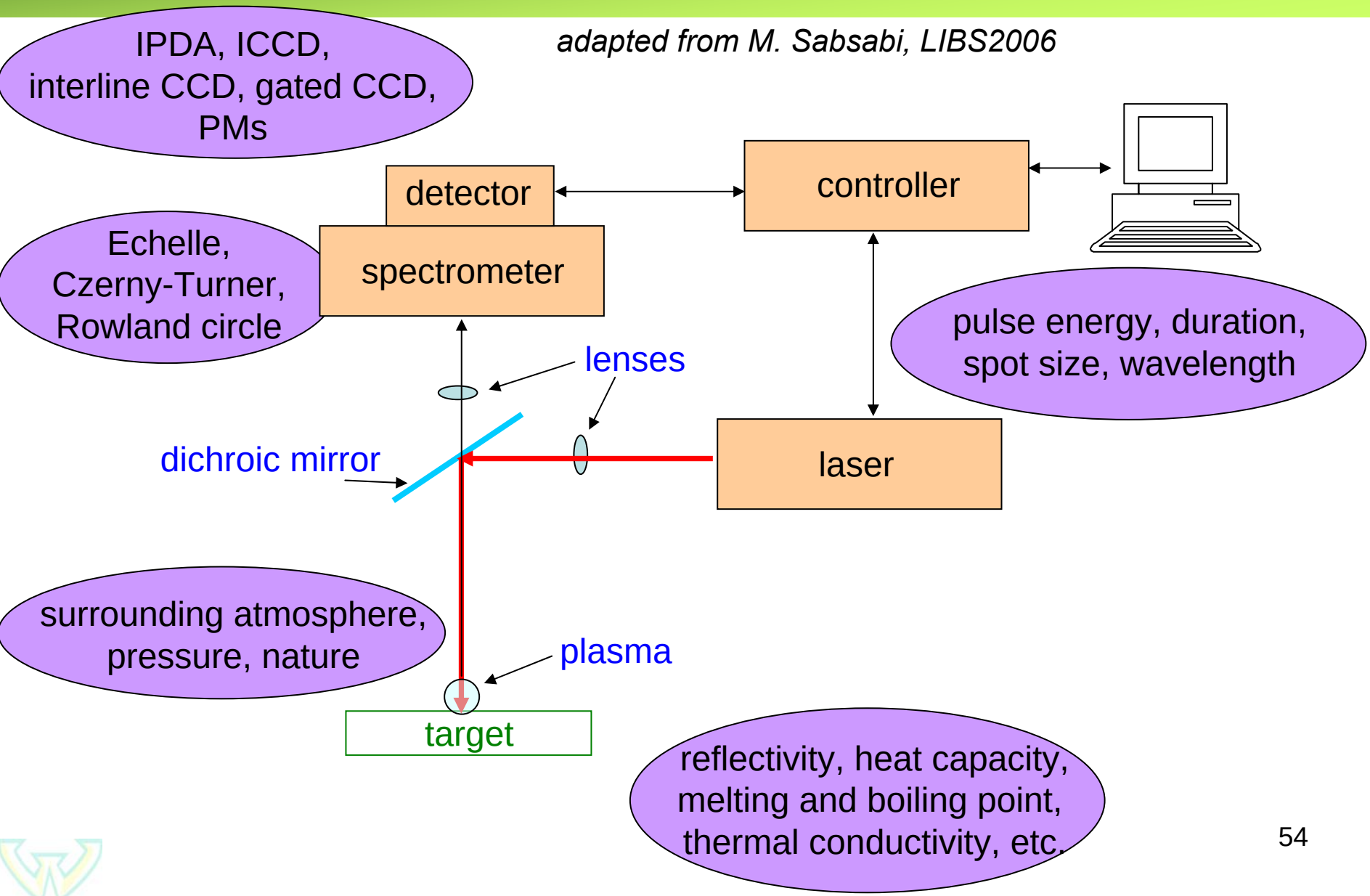
$$N_e\left(\mathrm{cm}^{-3}\right) \geq 1.6\times10^{12}\left(\Delta E\right)^3\left(T\right)^{\frac{1}{2}}$$

ΔE = energy difference with ground level (eV)
T = plasma temperature (K)

Outline

1. Introduction to LIBS
2. Physics of the plasma formation and observation
3. Instrumentation
4. Advanced techniques

LIBS components



Microchip lasers

*K. Amponsah-Manager et al., Microchip laser ablation of metals: investigation of the ablation process in view of its application to laser-induced breakdown spectroscopy, JAAS **20**, 544-551 (2005)*

*A. Freedman et al., Aluminum alloy analysis using microchip-laser induced breakdown spectroscopy, Spectrochim. Acta B **60**, 1076-1082 (2005)*

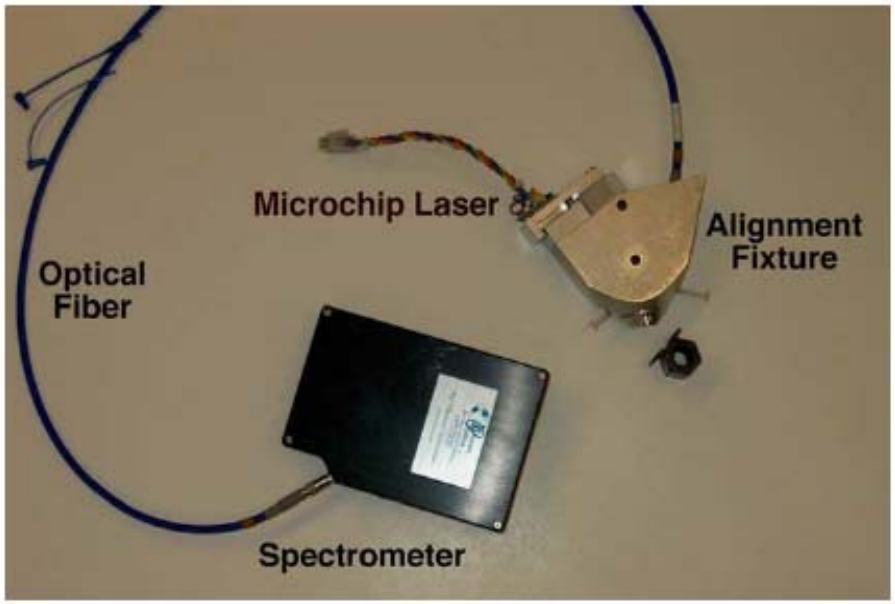
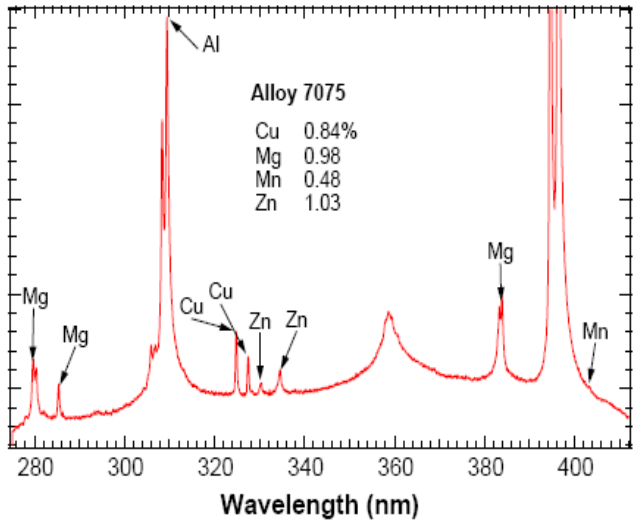


Fig. 1. Photograph of LIBS apparatus.



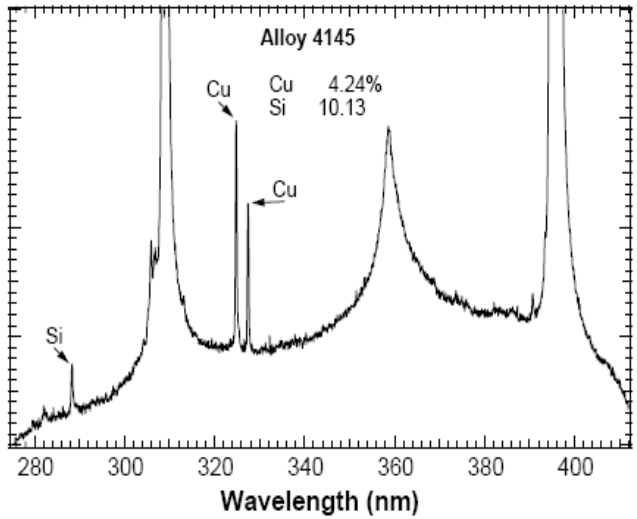
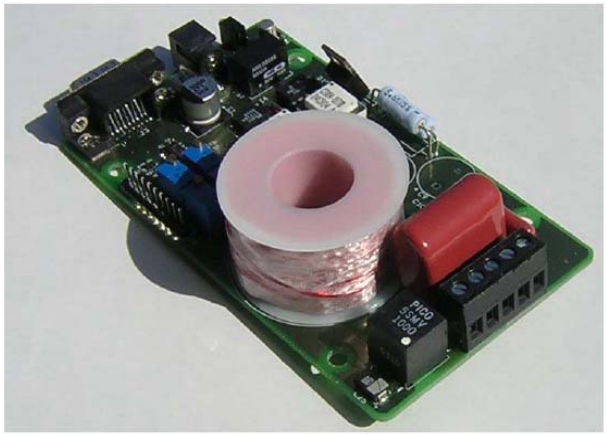
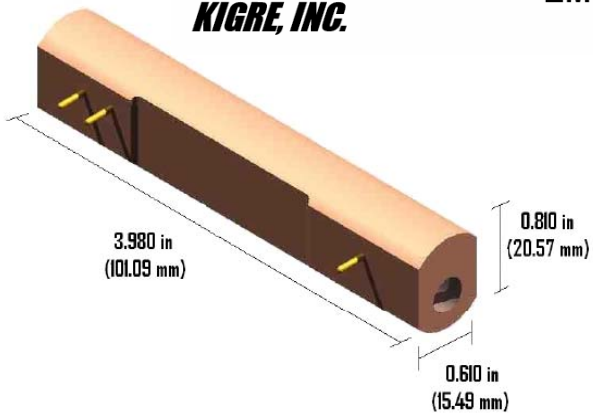


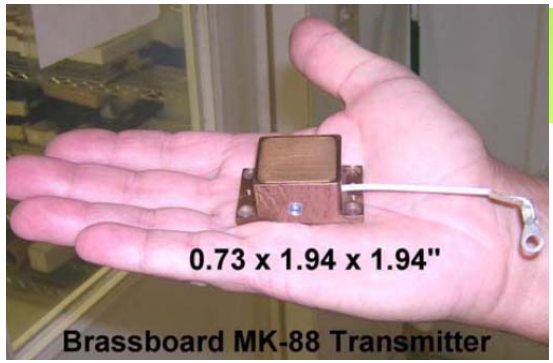
Fig. 3. LIBS spectra of two aluminum alloys.



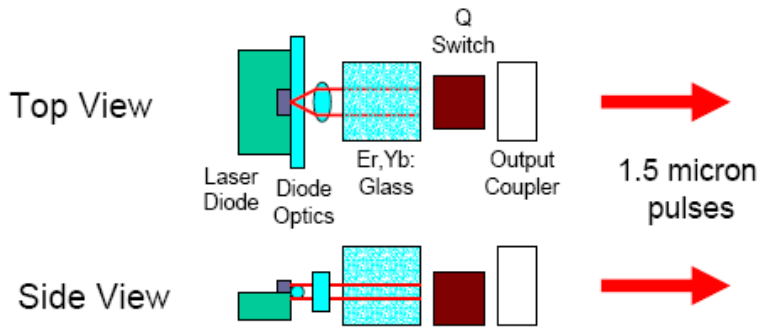
KIGRE, INC.

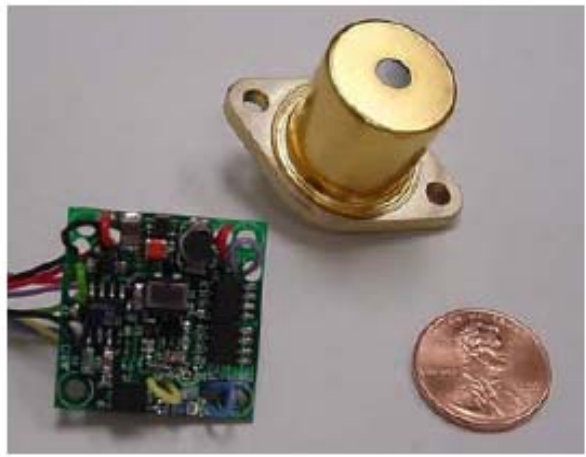


EMK-50 Er:GLASS EYE-SAFE LASER TRANSMITTER



Diode Pumped Er:Yb:glass Micro-laser MegaWatt lasers





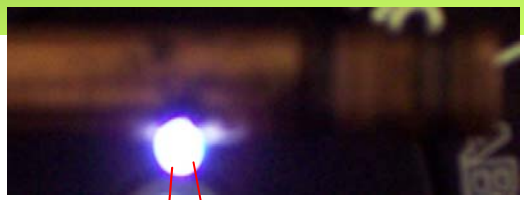
Micro-laser in TO3 package and Diode drive circuit for use with L123 Battery.

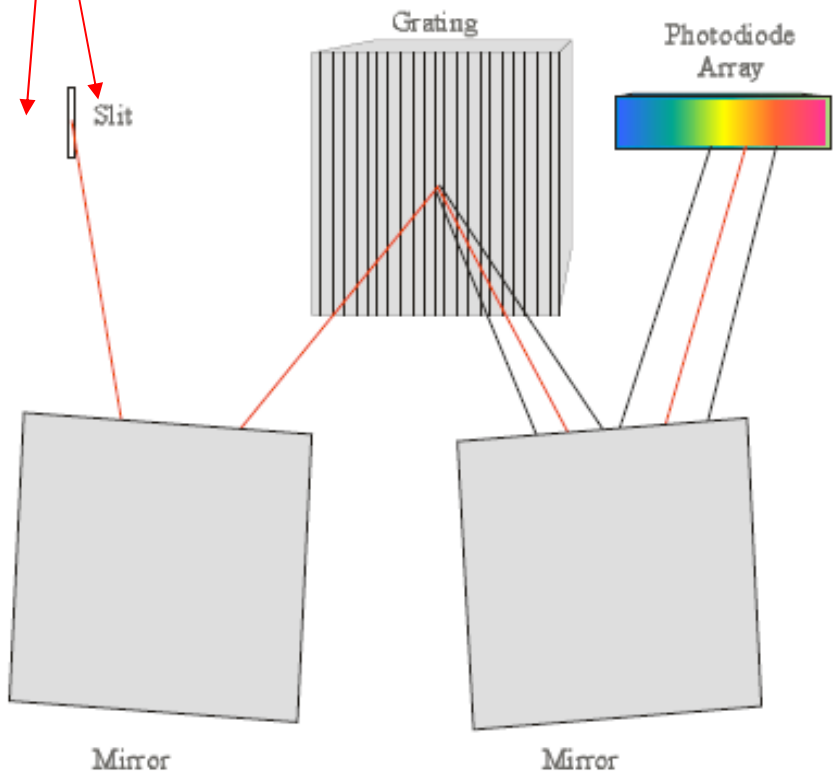
MicroChip NanoPulse, NanoGreen, and NanoEyeSafe OEM Short Package Solid-State Lasers

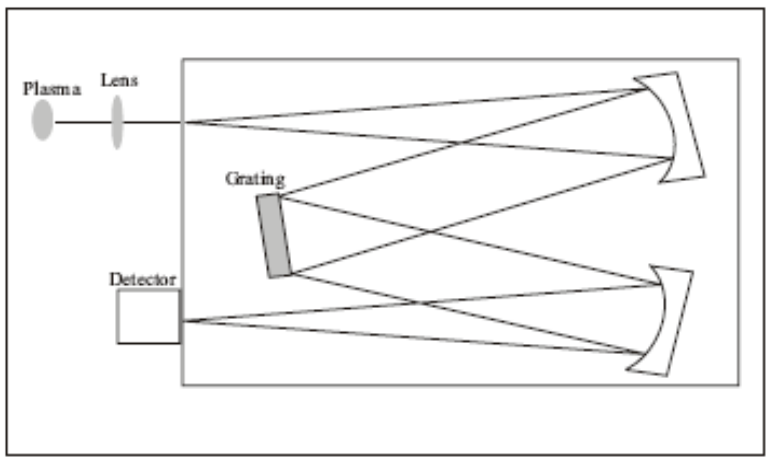
JDS Uniphase

$1K-$10K

Spectrometer: Czerny-Turner







Ocean-Optics USB4000-VIS-NIR Miniature Fiber Optic Spectrometer

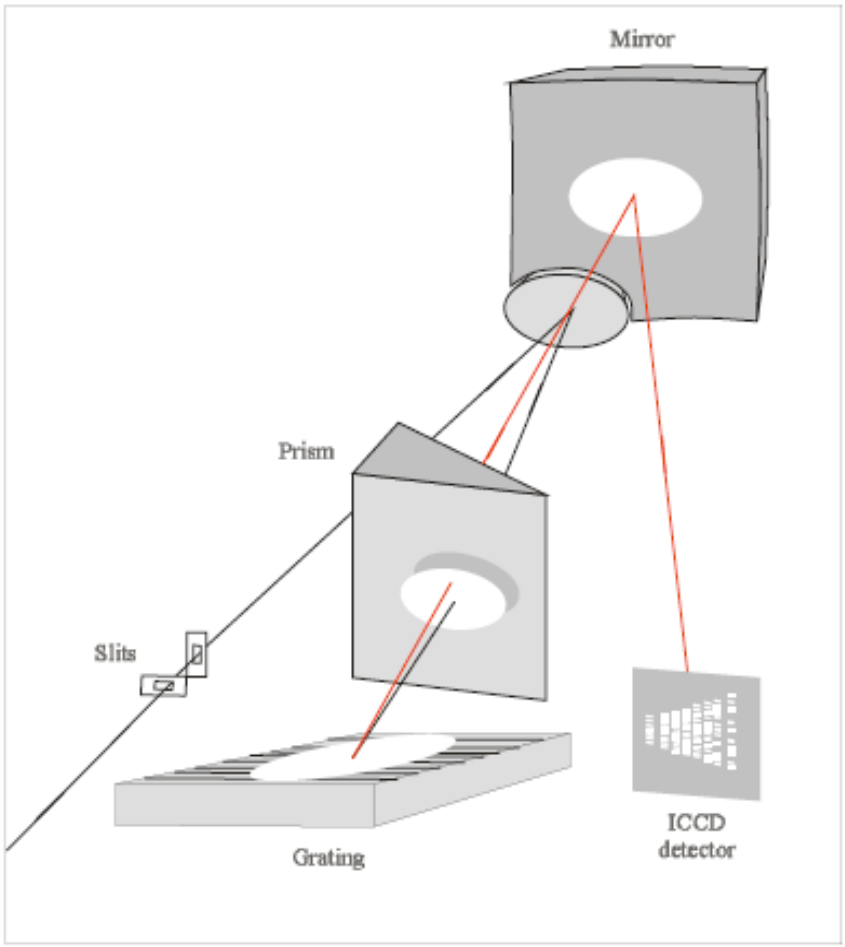
$3000

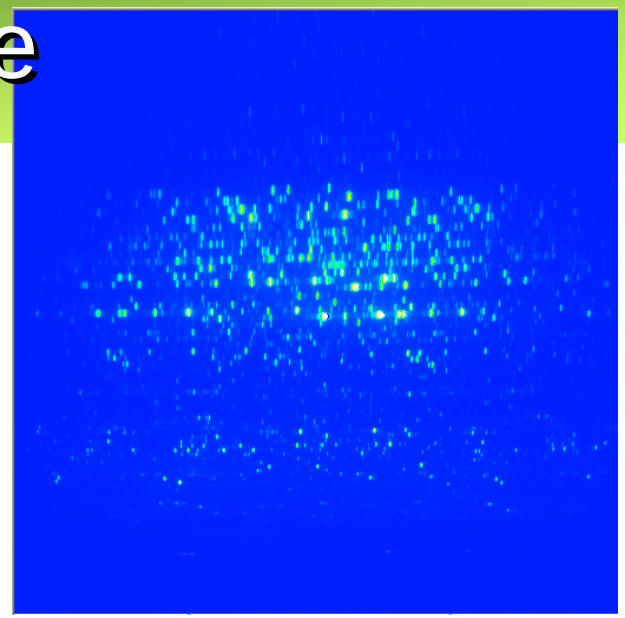
Specifications

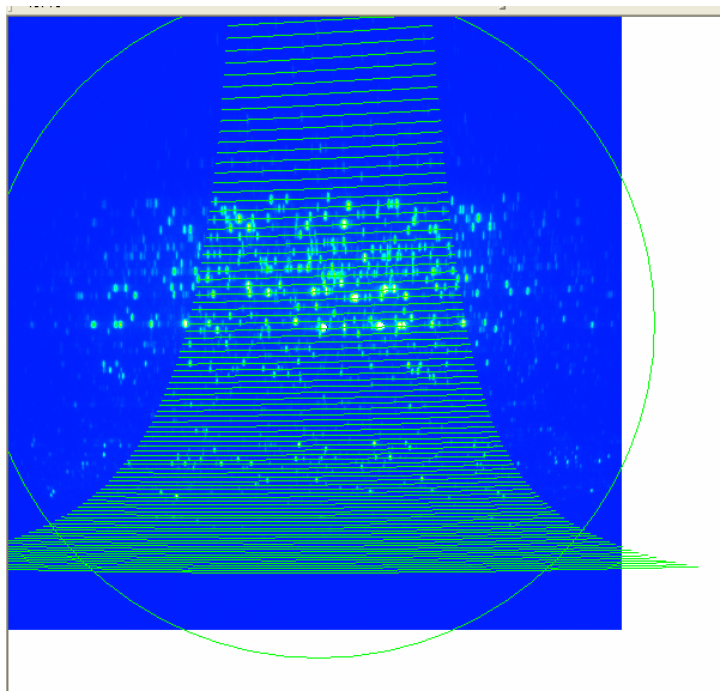
Physical	
Dimensions:	89.1 mm x 63.3 mm x 34.4 mm
Weight:	190 grams
Detector Specifications	
Detector:	Toshiba TCD1304AP Linear CCD array
Detector range:	200-1100 nm
Pixels:	3648 pixels
Pixel size:	8 µm x 200 µm
Pixel well depth:	100,000 electrons
Signal-to-noise ratio:	300:1 (at full signal)
A/D resolution:	16 bit
Dark noise:	50 RMS counts
Corrected linearity:	>99.8%
Sensitivity:	130 photons/count at 400 nm; 60 photons/count at 600 nm
Optical Bench	
Design:	f/4, Asymmetrical crossed Czerny-Turner
Focal length:	42 mm input; 68 mm output
Entrance aperture:	25 µm wide slit
Grating: OFLV filter:	Grating #3 (blazed at 500 nm) OFLV-350-1000
Fiber optic connector:	SMA 905 to 0.22 numerical aperture single-strand optical fiber
Spectroscopic	
Wavelength range:	350-1000 nm
Optical resolution:	~1.5 nm FWHM
Signal-to-noise ratio:	300:1 (at full signal)
A/D resolution:	16 bit
Dark noise:	50 RMS counts
Integration time:	4 ms - 10 seconds
Dynamic range:	2×10^8 (system), 1300:1 for a single acquisition
Stray light:	<0.05% at 600 nm; 0.10% at 435 nm

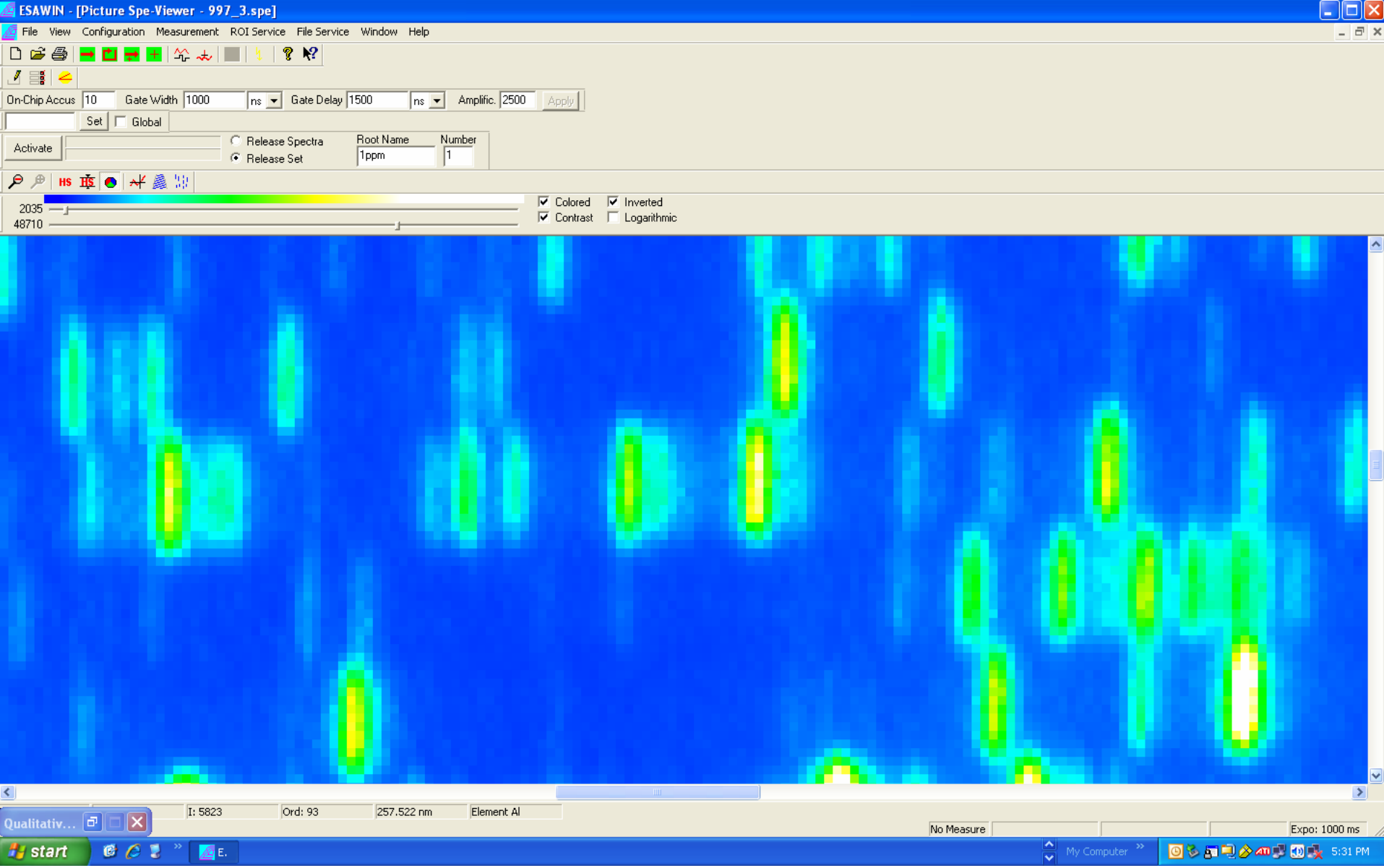
Spectrometer: Echelle

- Échelle Spectrometer





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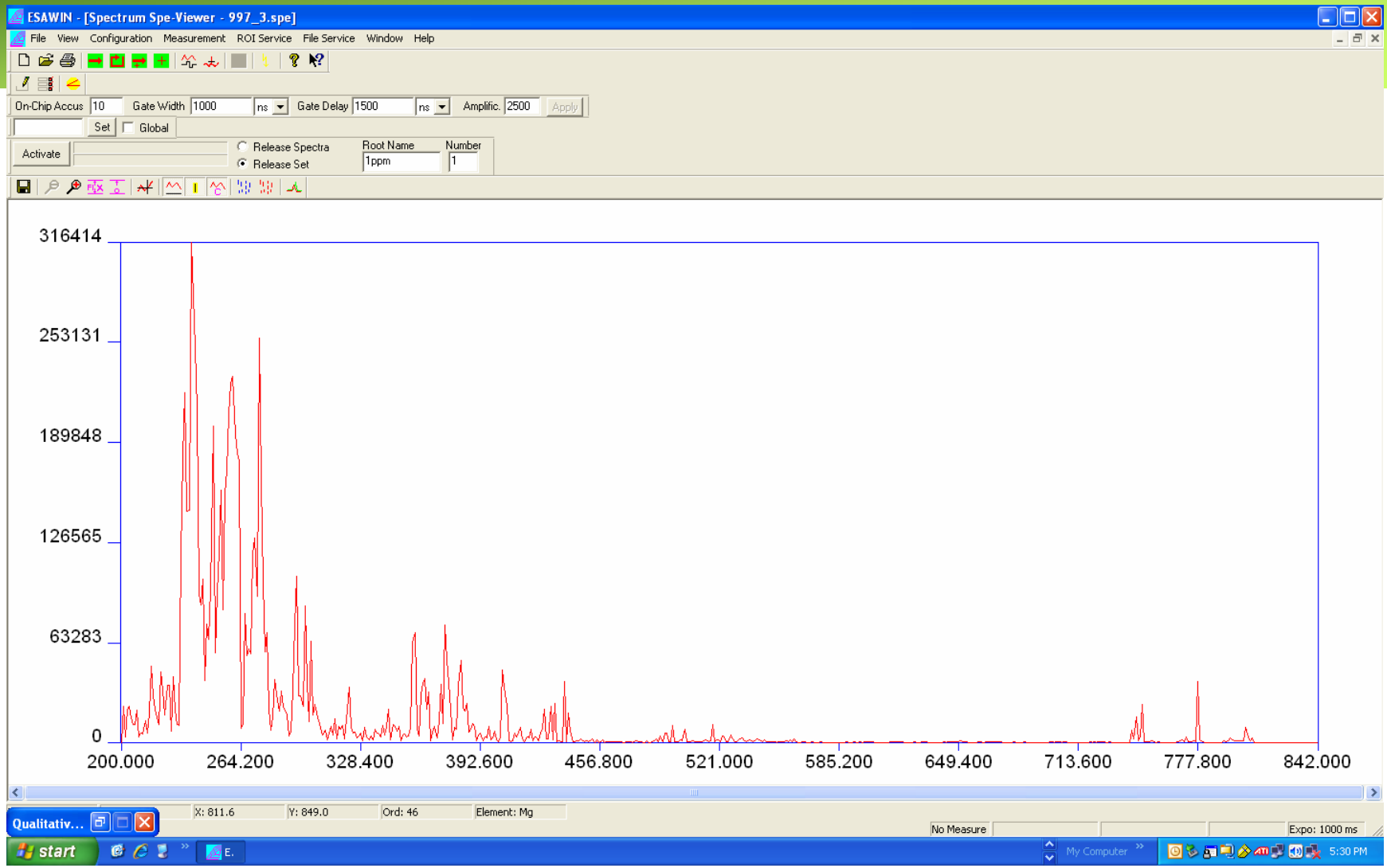
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649.400
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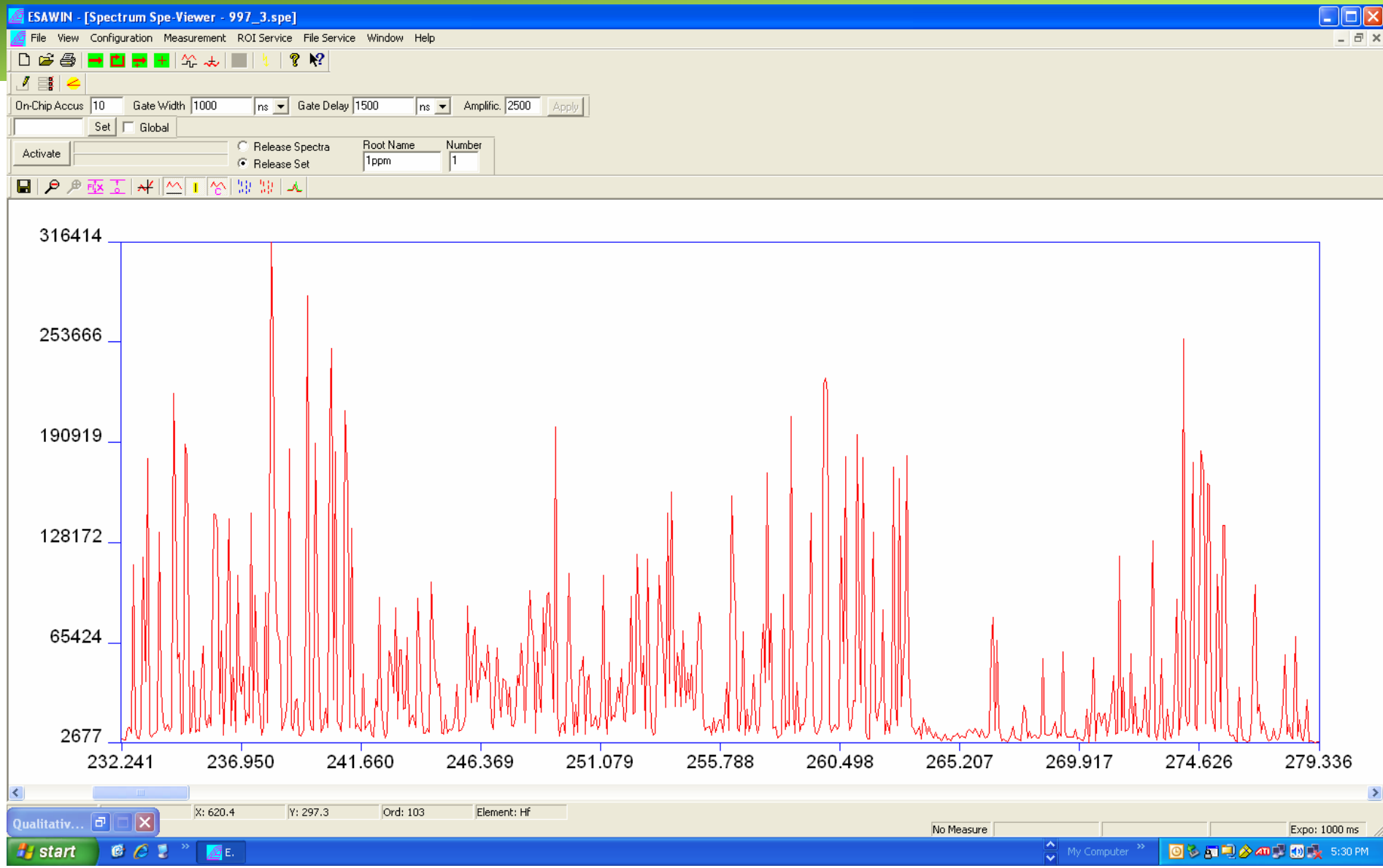
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241.660
246.369
251.079
255.788
260.498
265.207
269.917
274.626
279.336
X: 620.4
Y: 297.3
Ord: 103
Element: Hf
No Measure
Expo: 1000 ms
start
My Computer
5:30 PM

B. Salle et al., Evaluation of a compact spectrograph for in-situ and stand-off Laser-Induced Breakdown Spectroscopy analyses of geological samples on Mars missions, Spectrochimica Acta B ***60,*** *805 – 815 (2005)*

Echelle →

mini-Czerny Turner →

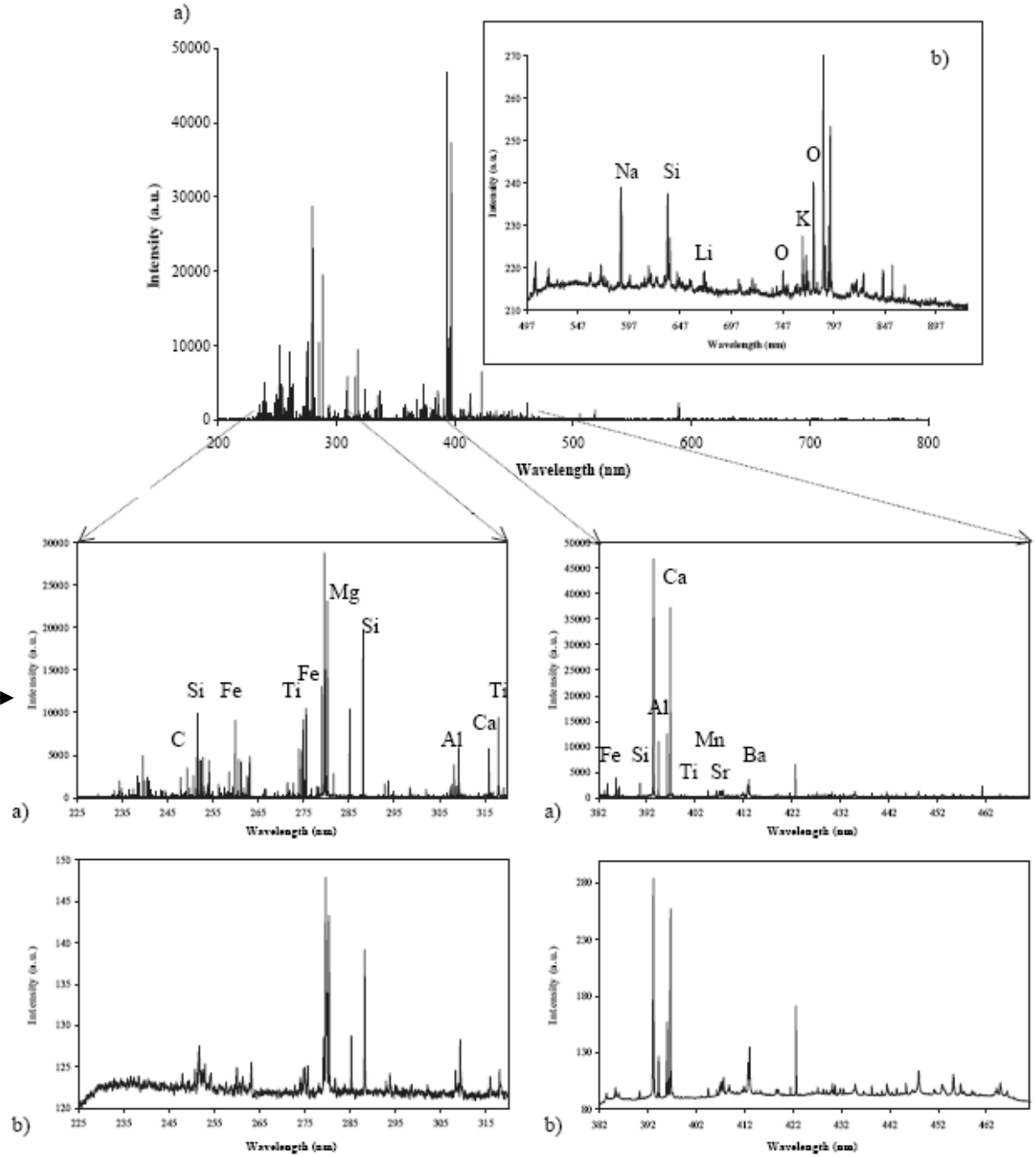


Fig. 3. Comparison of a) LLA ESA 3000 and b) Ocean Optics HR2000 spectra obtained with in-situ LIBS setup and a certified stream sediment sample.

Echelle Spectrometers

LLA Instruments Gmbh ESA 4000

Catalina SE200 with CCD

Andor Mechelle 5000

Aryelle 400 LaserTechnik Berlin LTB

$35K-$100K (Strong Euro)

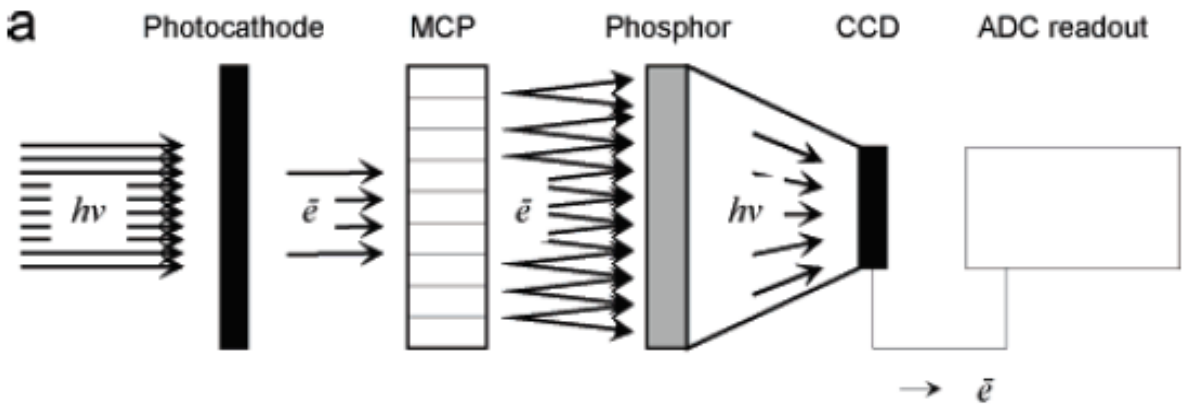
Échelle References

M. Sabsabi et al., An evaluation of a commercial Échelle spectrometer with intensified charge-coupled device detector for materials analysis by laser-induced plasma spectroscopy, Spectrochim. Acta B ***56****, 1011-1025 (2001)*

M. Sabsabi et al., Comparative study of two new commercial Echelle spectrometers equipped with intensified CCD for analysis of laser-induced breakdown spectroscopy, Appl. Opt. ***42****, 6094-6098 (2003)*

ICCD

1-Photocathode: converts photons to electrons
2-Microchannel Plate (MCP): amplifies the photoelectrons
3-Phosphor: converts electron to photons



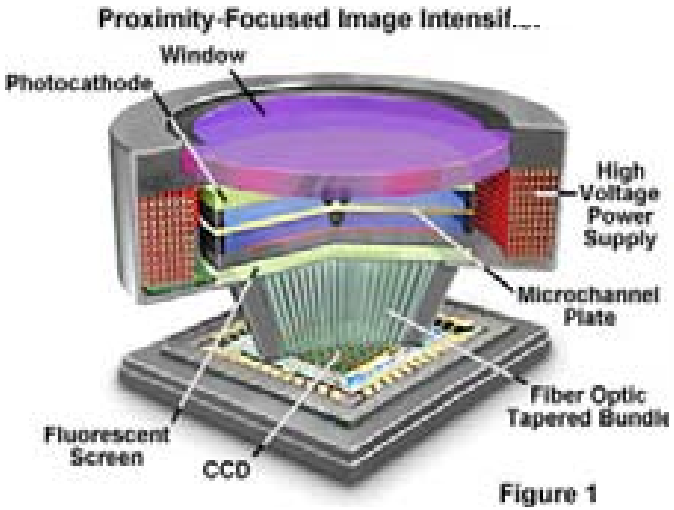
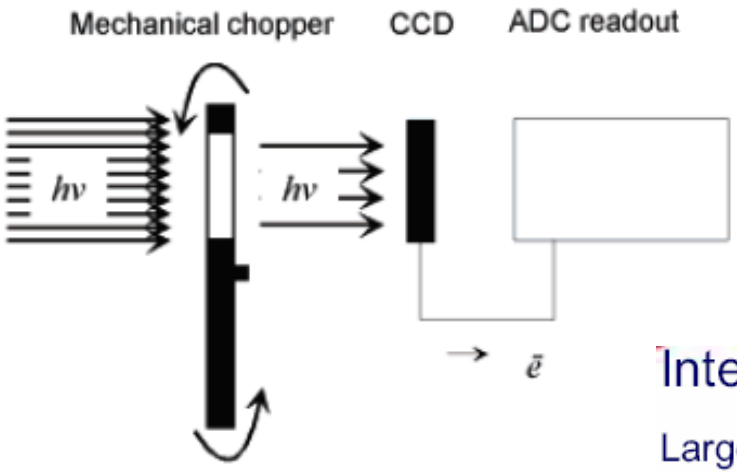


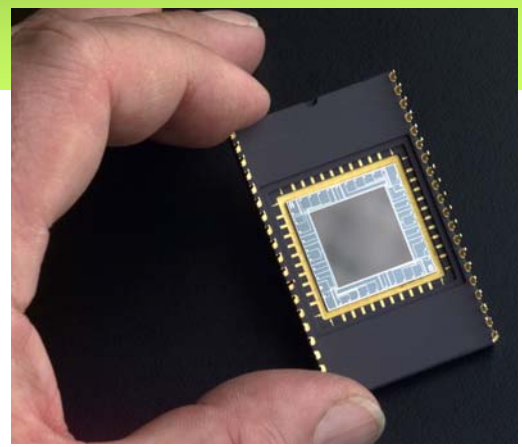
Figure 1

Poor quantum efficiency (below 20%), limited wavelength coverage, high gain, 16 bits dynamic range, simultaneous measurements, high cost.

Cost: 25-50 k$

CCD

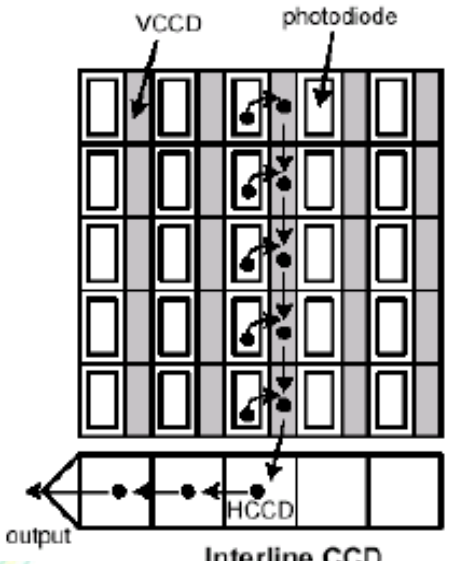




Interline CCD, Gated CCD

Larger wavelength coverage, high quantum efficiency, 12-14 bits dynamic range, less expensive.

Cost: 1-20 k$



Characteristics	Typical Range	Limitations
Full-well capacity	10000-500000 electrons	Defines dynamic range
Pixel dimensions	6-30μm	Dictate spectral or spatial resolution
Array format	Related to pixel size and number	Dictates the active area
Number of pixels	58X512 to 2048X2048	Dictates number of resolution elements and acquisition time
Quantum efficiency	0-80%	Defines ultimate sensitivity limit
Blooming	Present with materials having strong lines in the range 200-900nm	Cannot observe weak lines near strong lines, ghost lines
Read noise	Few electrons	Excess noise limits weak light detection

CCD References

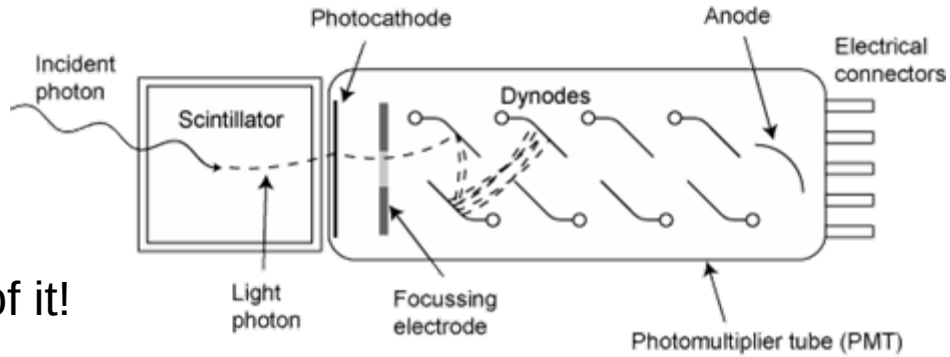
M. Mueller et al., Approach to Detection in Laser-Induced Breakdown Spectroscopy, Anal. Chem. ***79*** *, 4419-4426 (2007)*

J.E. Carranza et al., Comparison of Nonintensified and Intensified CCD Detectors for Laser-Induced Breakdown Spectroscopy, Appl. Opt. ***42****, 6016-6021 (2003).*

M. Sabsabi et al., Critical evaluation of gated CCD detectors for laser-induced breakdown spectroscopy analysis, Spectrochim. Acta B ***60****, 1211-1216 (2005)*

photomultiplier tube

- You may not need a spectrometer! (adds complexity, cost)



put an interference filter in front of it!

Monochromatic, low quantum efficiency, bulky, larger wavelength coverage, high dynamic range, cheap.

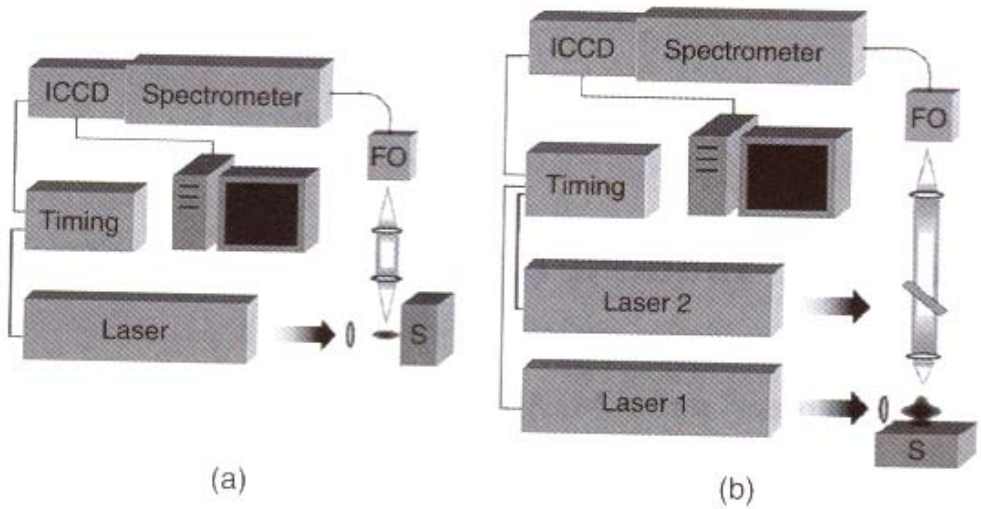
Cost: 1-3 k$

Outline

1. Introduction to LIBS
2. Physics of the plasma formation and observation
3. Instrumentation
4. Advanced techniques

Dual-pulse LIBS

- The use of two non-coincident laser pulses increases emission intensity and SNR
- Variables to be determined
  - pulse geometry
  - pulse order
  - inter-pulse timing
  - energy of pulses



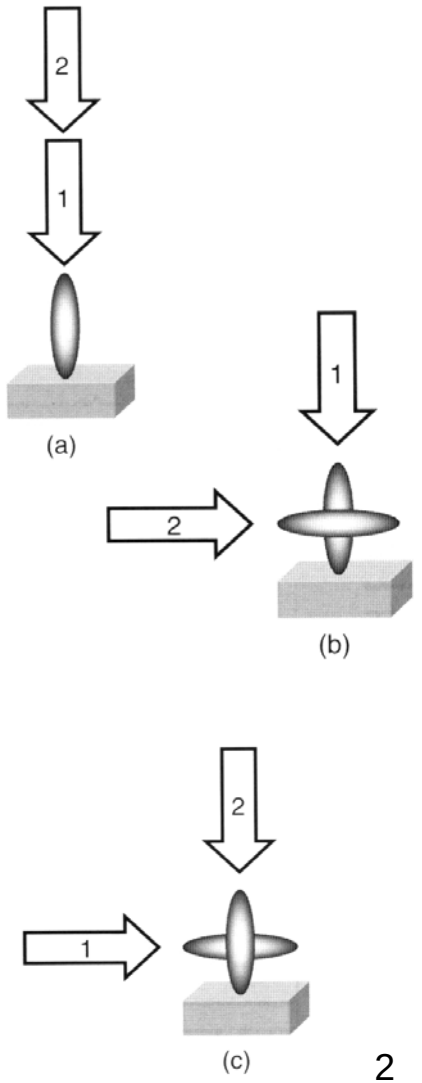
Dual-pulse pulse geometry

J. Scaffidi et al. "Dual pulse LIBS," in Laser-Induced Breakdown Spectroscopy (2007) pp. 137-150

(a) collinear. First and second pulses are both focused onto or into the sample

(b) orthogonal reheating. A single ablative pulse (1) is followed by a post-ablative reheating pulse (2) focused into the plasma plume.

(c) orthogonal pre-ablative spark. A pre-ablative air spark (1) focused up to several mm above the sample surface is followed by a single ablative pulse (2) focused onto or into the sample.



Dual-pulse enhancement

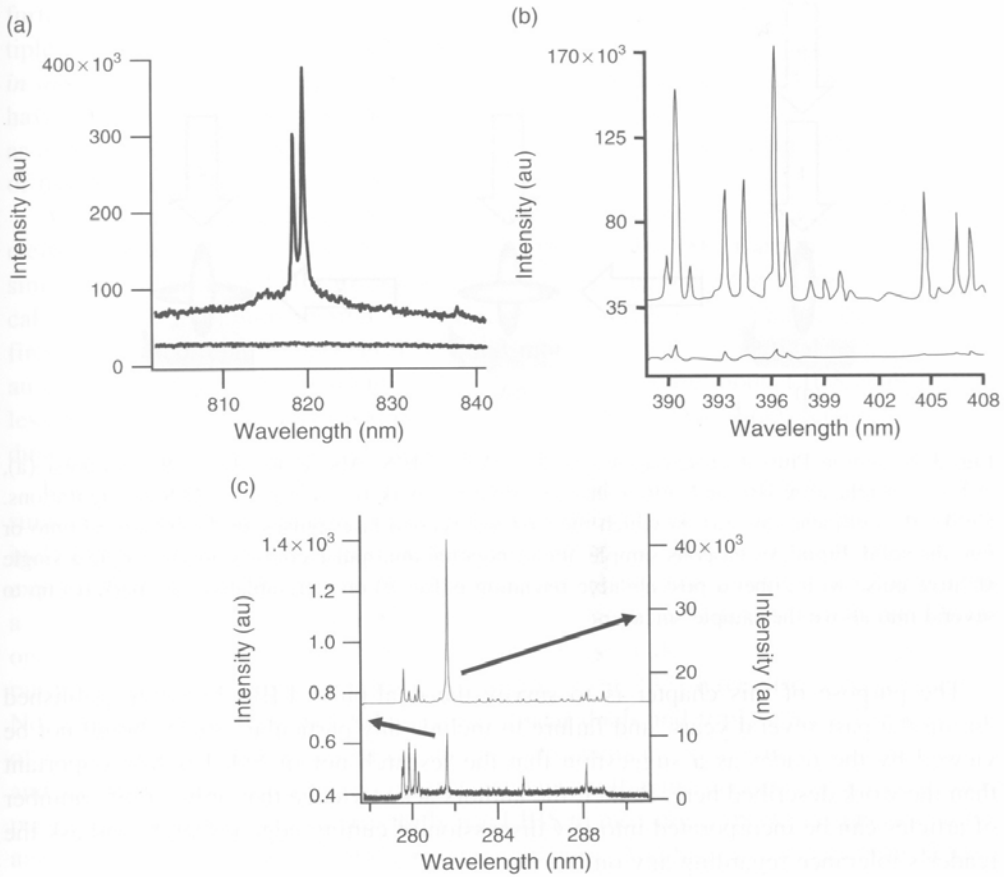
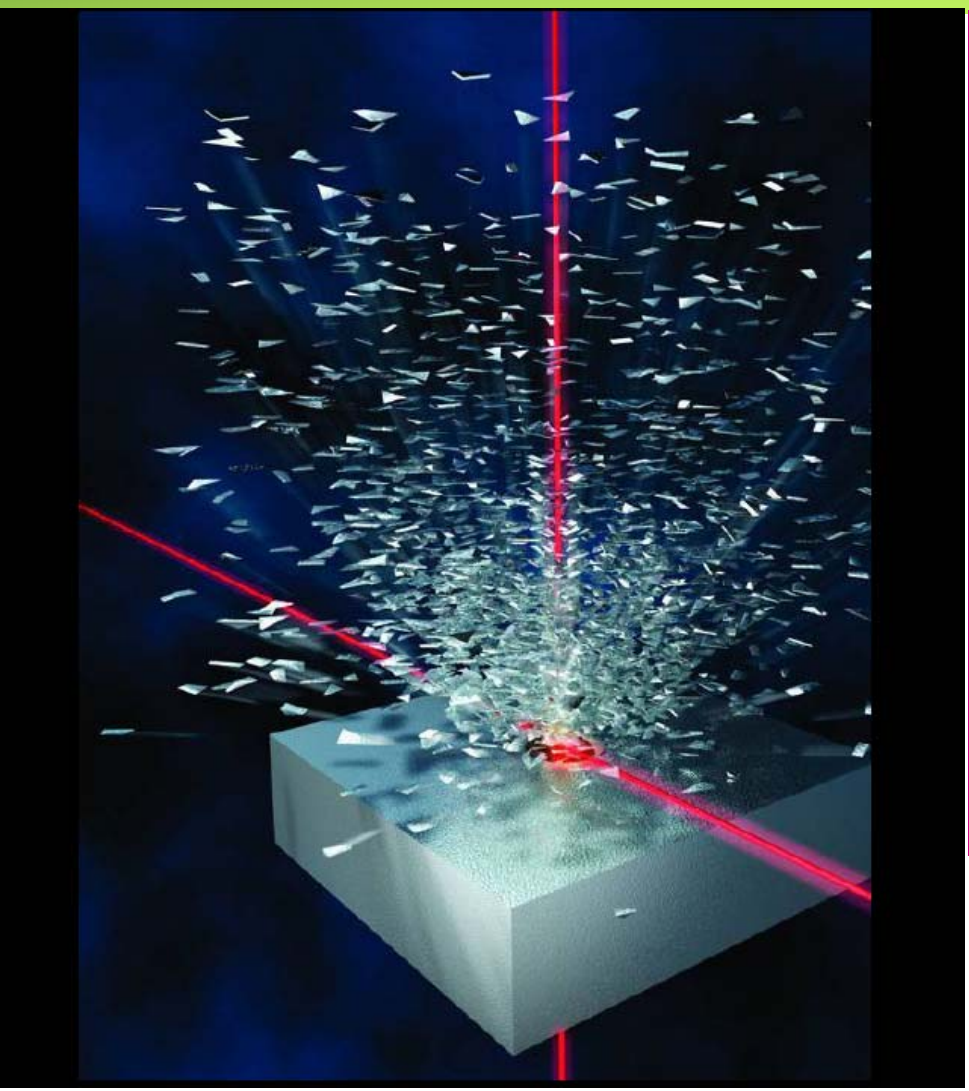


Fig. 2. Dual-Pulse LIBS Atomic Emission and Signal-to-Noise Enhancements. Above are shown sample spectra from Angel, et. al. (a, b) and Sabsabi, et. al. (c) showing the neutral atomic (a, b) and ionic (c) emission and signal-to-noise enhancements possible with orthogonal pre-ablative spark (a, b) and collinear (c) dual-pulse LIBS (top spectra) of dissolved sodium in aqueous solution (a), vitrified glass simulants in air (b), and an aluminum standard in air (c). The lower traces are the corresponding ns single-pulse LIBS (bottom spectra).

- Different pulse configurations suggest the existence of different sources for dual-pulse LIBS enhancements
- Energetic coupling between first LIP and second pulse (reheating/collinear)
- sample heating (pre-ablative)
- reductions in atmospheric pressure or number density effects

Dual-pulse enhancement



Emission Enhancement Mechanisms in Dual-Pulse LIBS

Remote analysis for challenging applications may be possible because LIBS uses only light and collects only photons.

Jon Scaffidi
University of Pittsburgh
S. Michael Angel
University of South Carolina
David A. Cremers
Applied Research Associates

Analytical chemistry **78**, p. 24.

Stand-off LIBS / Remote LIBS

- Not the same
  - Stand-off: the laser is delivered through space to a target. (the target is physically separated, typically 1-100 m, from the laser and light collection optics)
  - Remote: the laser and light collection optics are in physical proximity (contact) to the target but they are remote from the user/operator.

ARL Standoff System Development

Dec 2004: Initial proof of principle test at **YPG**

Feb 2006: 2nd standoff system: Larger telescope, better lasers, broadband

Feb 2010: 5th standoff system installed

Jul 2006: 3rd standoff system delivered (1.54 μm)

2005 2006 2007 2008 2009 2010

Nov 2005: 1st standoff system built for ARL

Nov/Dec 2007: 4th standoff system designed for field tests for JIEDDO project

Dec 2007: 1st field test at **NTC**

May 2008: 2nd field test at **NTC**

Aug 2008: 2nd field test at **YPG**

Standoff LIBS at NTC Testing- December 2007

Appl Phys B (2009) 95: 1–12
DOI 10.1007/s00340-009-3381-7

Applied Physics B
Lasers and Optics

INVITED PAPER

Filamentation "remote" sensing of chemical and biological agents/pollutants using only one femtosecond laser source

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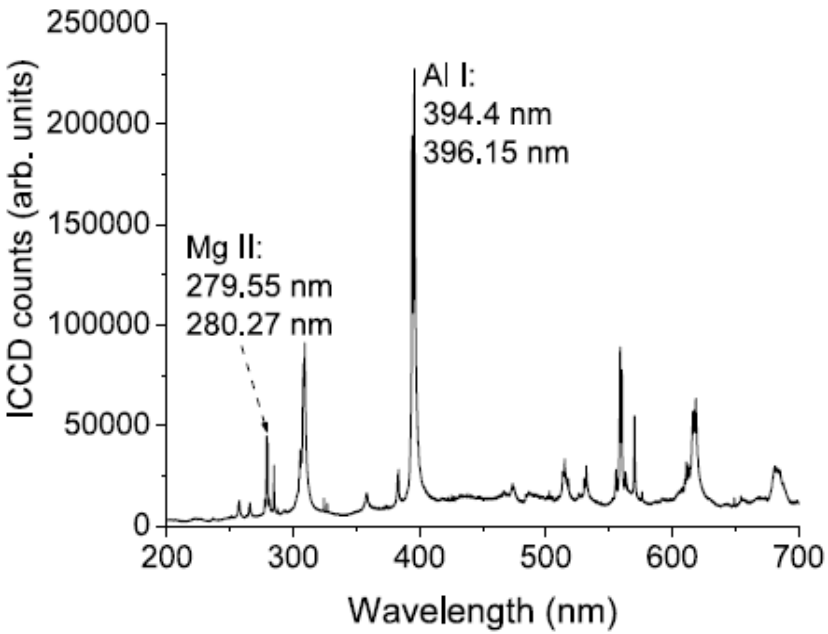

Fig. 9 Filament-induced breakdown spectrum taken for aluminum sample located 50 m away. The laser pulse energy was 108 mJ, and the ICCD gate width was 2 μs with a time delay of $t = -33$ ns with respect to the laser pulse arriving time on the target ($t = 0$)

a

Filament-induced remote surface ablation for long range laser-induced breakdown spectroscopy operation☆

Ph. Rohwetter[a], K. Stelmaszczyk[a], L. Wöste[a], R. Ackermann[b], G. Méjean[b], E. Salmon[b], J. Kasparian[b], J. Yu[b,*], J.-P. Wolf[b]

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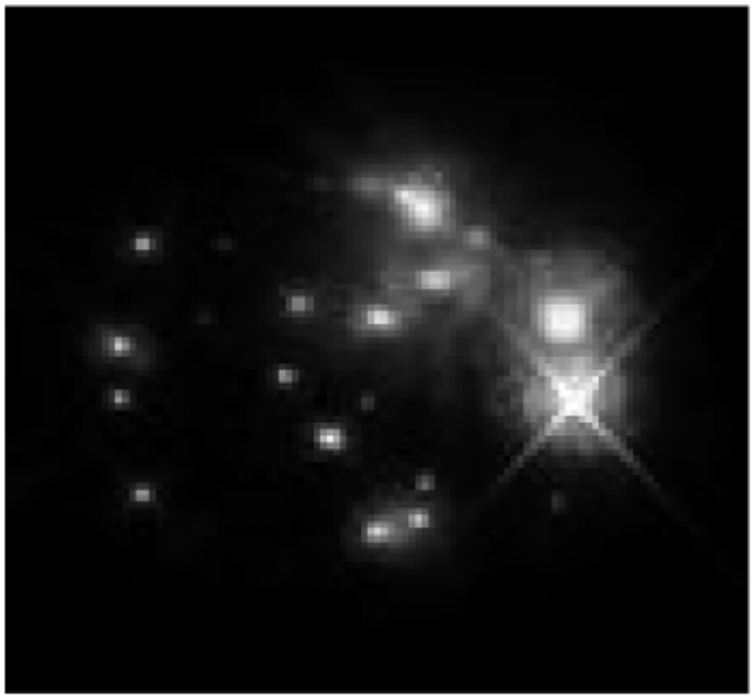
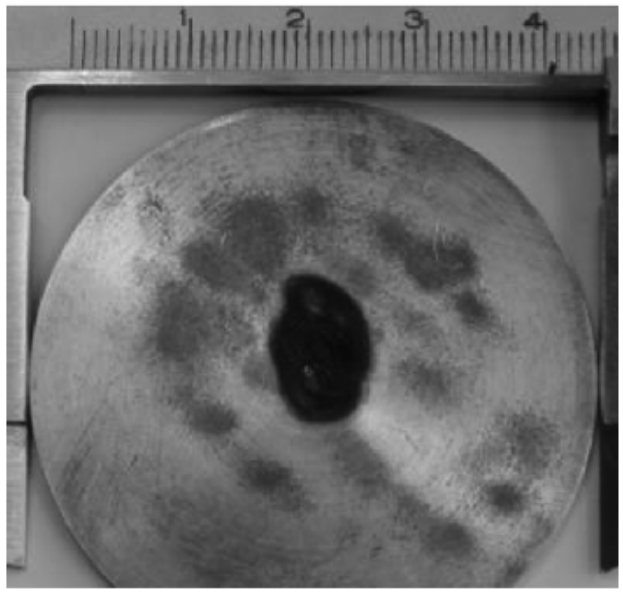
(a)



(b)



. 1. (a) Picture of a typical laser beam profile with many filaments ıgle shot picture). On the picture, filaments appear as bright spots. Notice t each filament is surrounded by a conical emission in the visible range t increases the apparent size of the filaments on the picture to the order of ı. The whole beam had a diameter of 5 cm. (b) Picture of a copper ıple irradiated by a large number of laser pulses. The black spot in the ldle is due to irradiation with a focused beam from a distance of 25 m. ıer grey spots are results of filament irradiation of the sample placed at a tance of 90 m. Random walks of a filament around its mean position due inhomogeneities in air lead to a superficial ablation on a surface much ger than filament diameter. The scale of this picture is indicated by a ruler h a cm graduation in the upper part of the picture.

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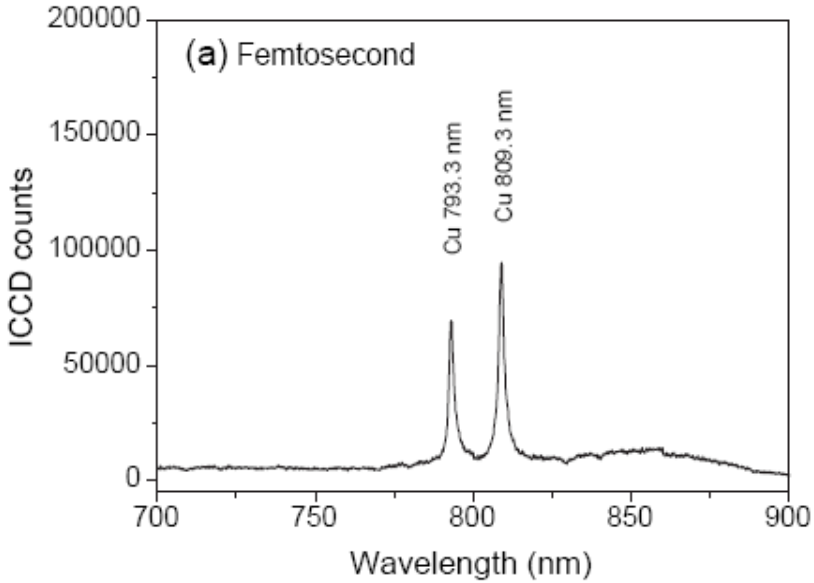


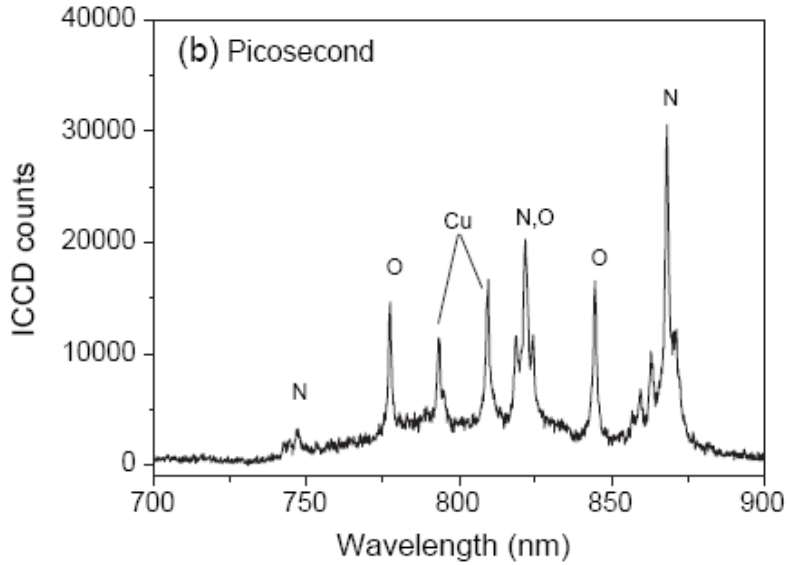
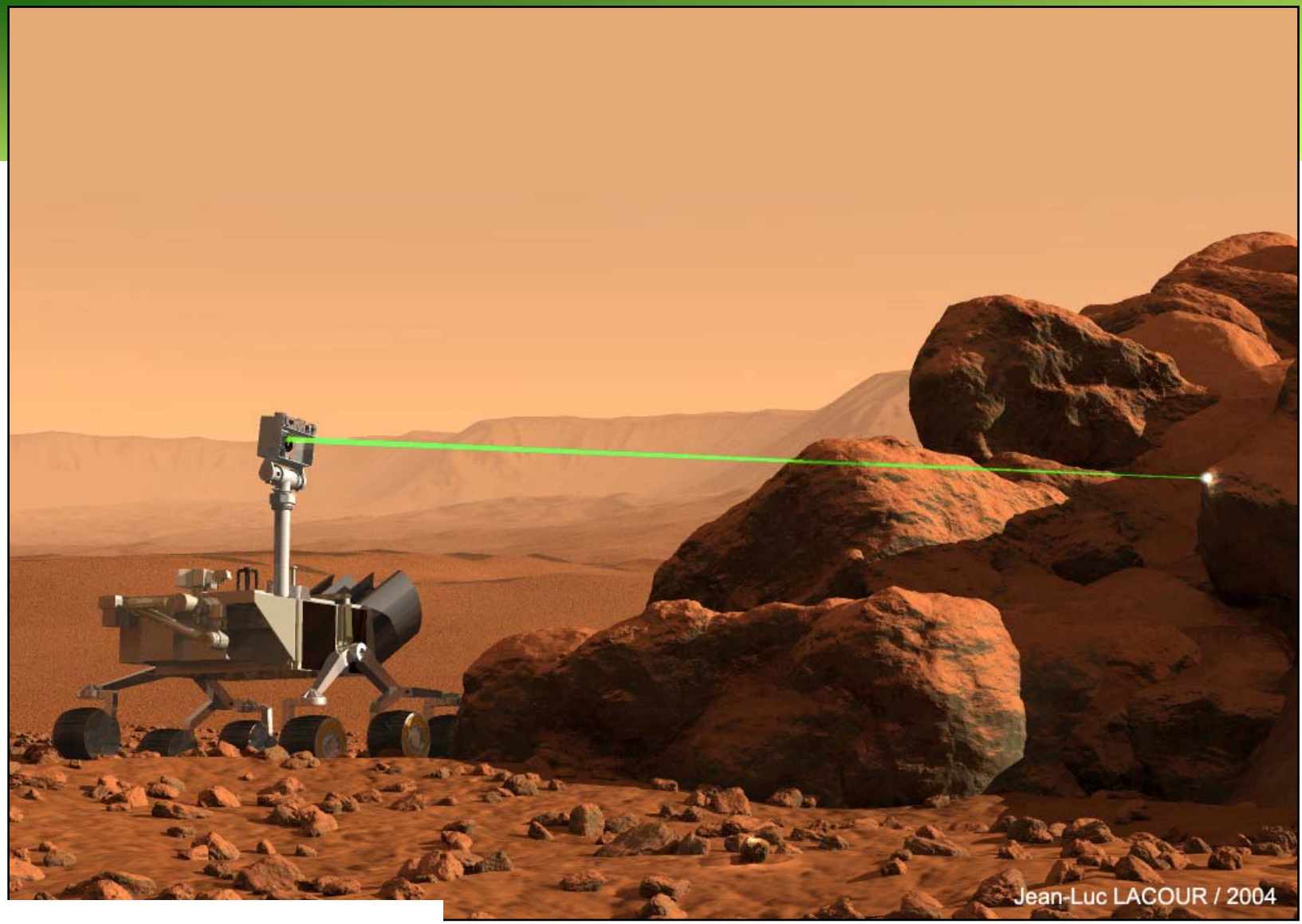


Fig. 3. Plasma line emission spectra from a copper sample excited by femtosecond pulses (a), and by picosecond pulses (b). With femtosecond pulses, two copper atomic lines in the spectral range from 700 nm to 900 nm are observed without any background lines. In contrast, with picosecond (or nanosecond pulses), the copper lines are mixed with background lines from ambient air: atomic oxygen (O) and atomic nitrogen (N) lines.



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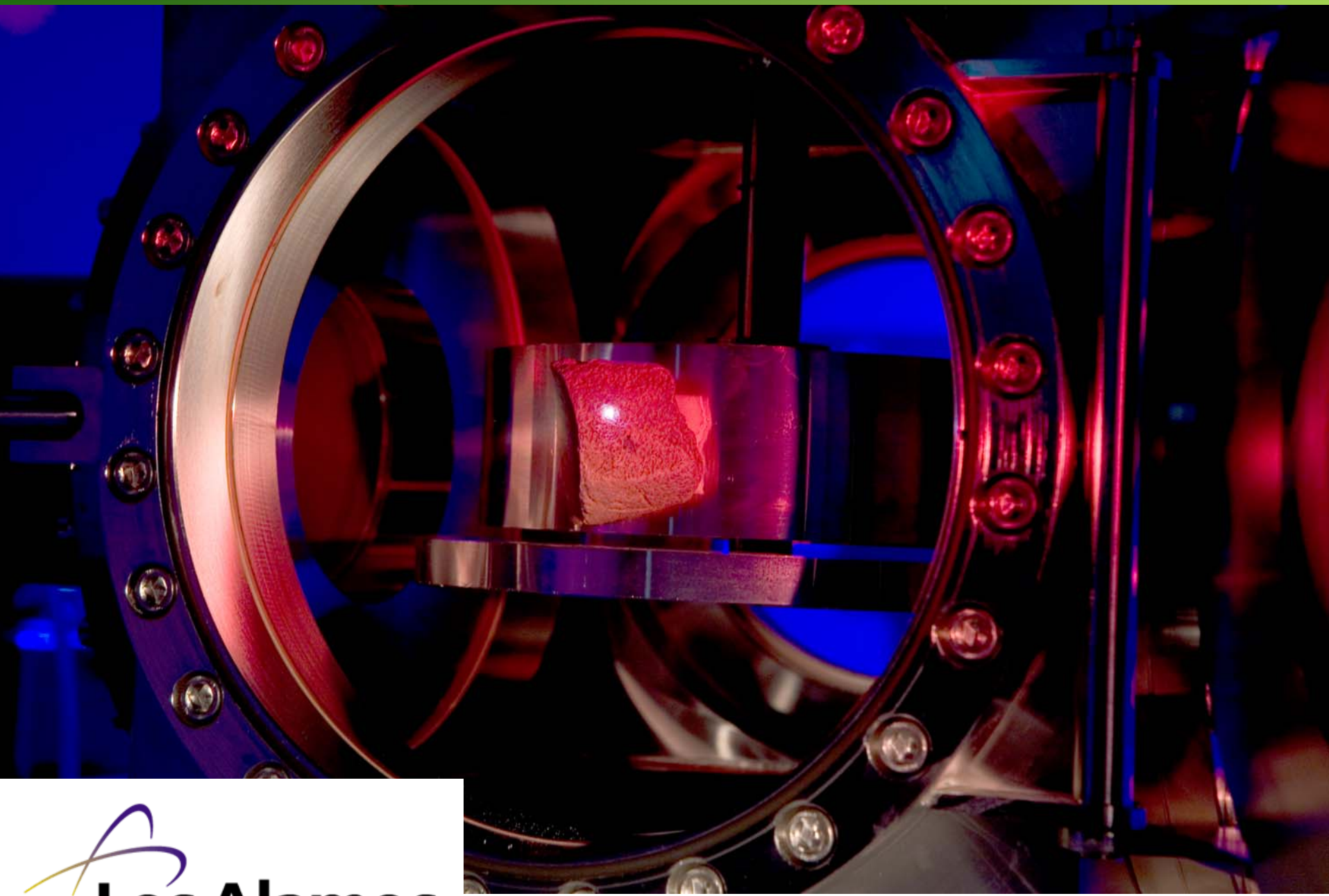

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Chemometrics

- Chemometrics is advanced signal-processing that statistically (mathematically) identifies similarities and differences in LIBS spectra.

- Can express the spectra in a basis set that maximizes the differences for real-time classification and/or identification

Chemometrics

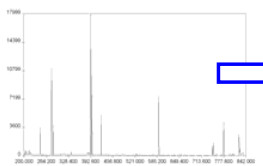
- Intensity of lines, ratios of intensities used in a statistical multi-variate analysis

  - discriminant function analysis (DFA)
  - principal component analysis (PCA)
  - partial least squares – discriminant analysis (PLS-DA)
  - linear discriminant analysis (LDA)

Chemometrics

How a DFA is Performed

(1) The intensities of 13 emission lines are normalized by the sum of all intensities and separated into *N* groups



$$\begin{pmatrix} x_1 \\ x_2 \\ . \\ . \\ . \\ x_{13} \end{pmatrix}$$

(2) "Canonical Discriminant Functions" are constructed from arrays of groups. For discrimination between *N* groups, *N-1* canonical discriminant functions are constructed

$$\begin{pmatrix} b_0^1 & b_1^1 & b_2^1 & . & . & . & b_{13}^1 \end{pmatrix}$$

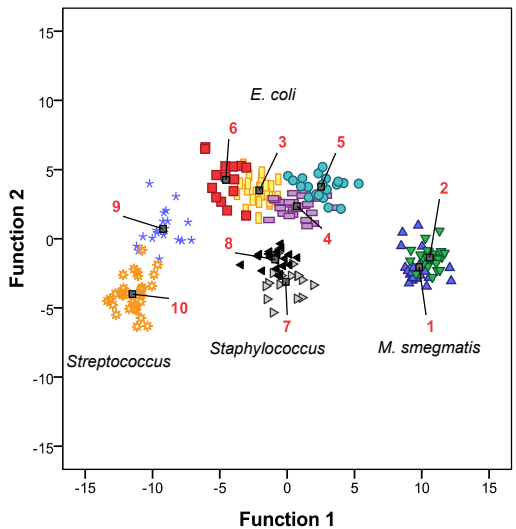
$$\downarrow$$

$$\begin{pmatrix} b_0^{N-1} & b_1^{N-1} & b_2^{N-1} & . & . & . & b_{13}^{N-1} \end{pmatrix}$$

(3) For each spectrum, *N-1* discriminant function scores are calculated

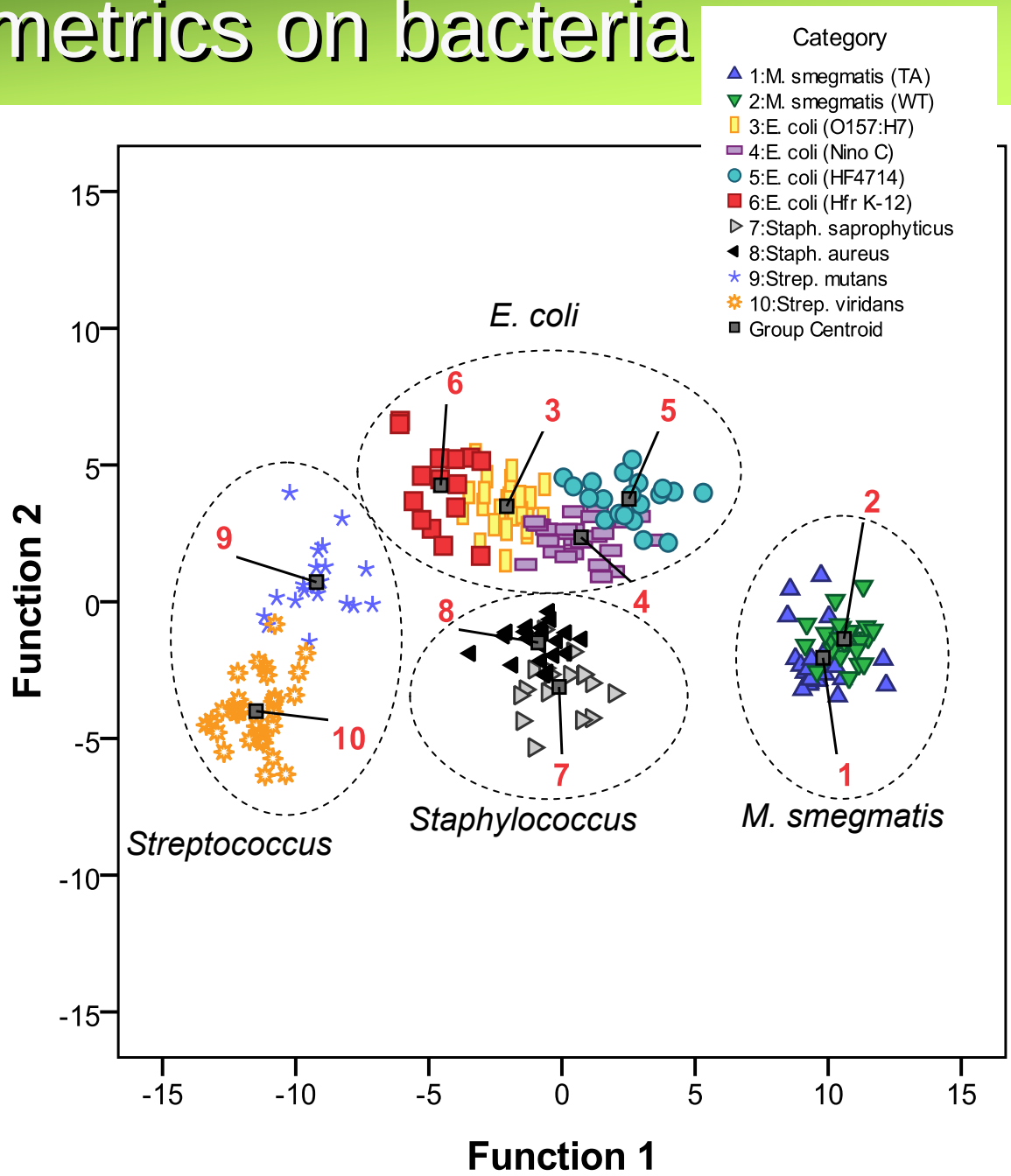
$$DF^{\,j} = b_0^j + \sum_{k=1}^{13} b_k^j x_k$$

(4) Each spectrum is plotted according to its calculated discriminant function scores as a data point on a graph (often 2D).

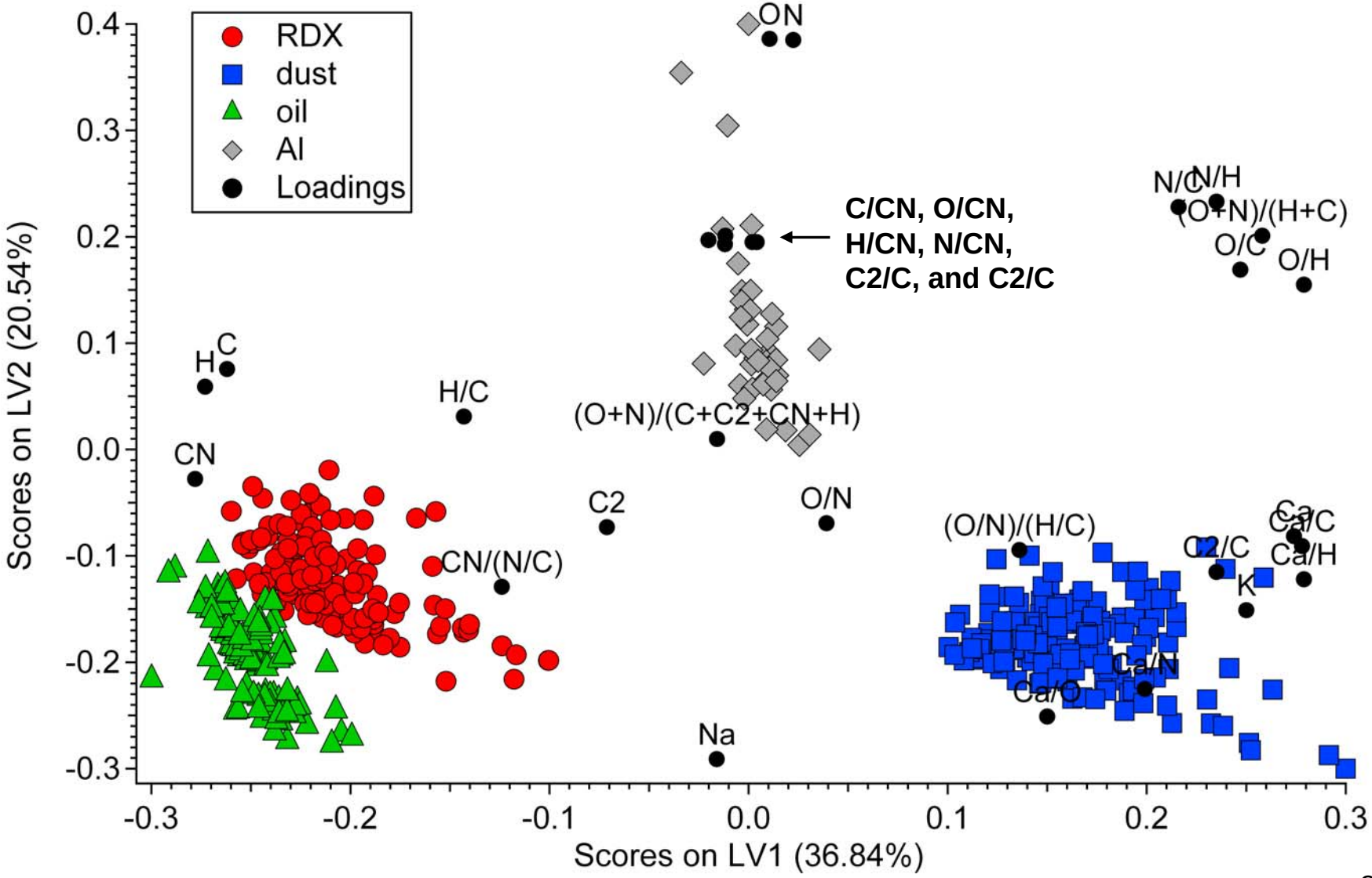


Chemometrics on bacteria

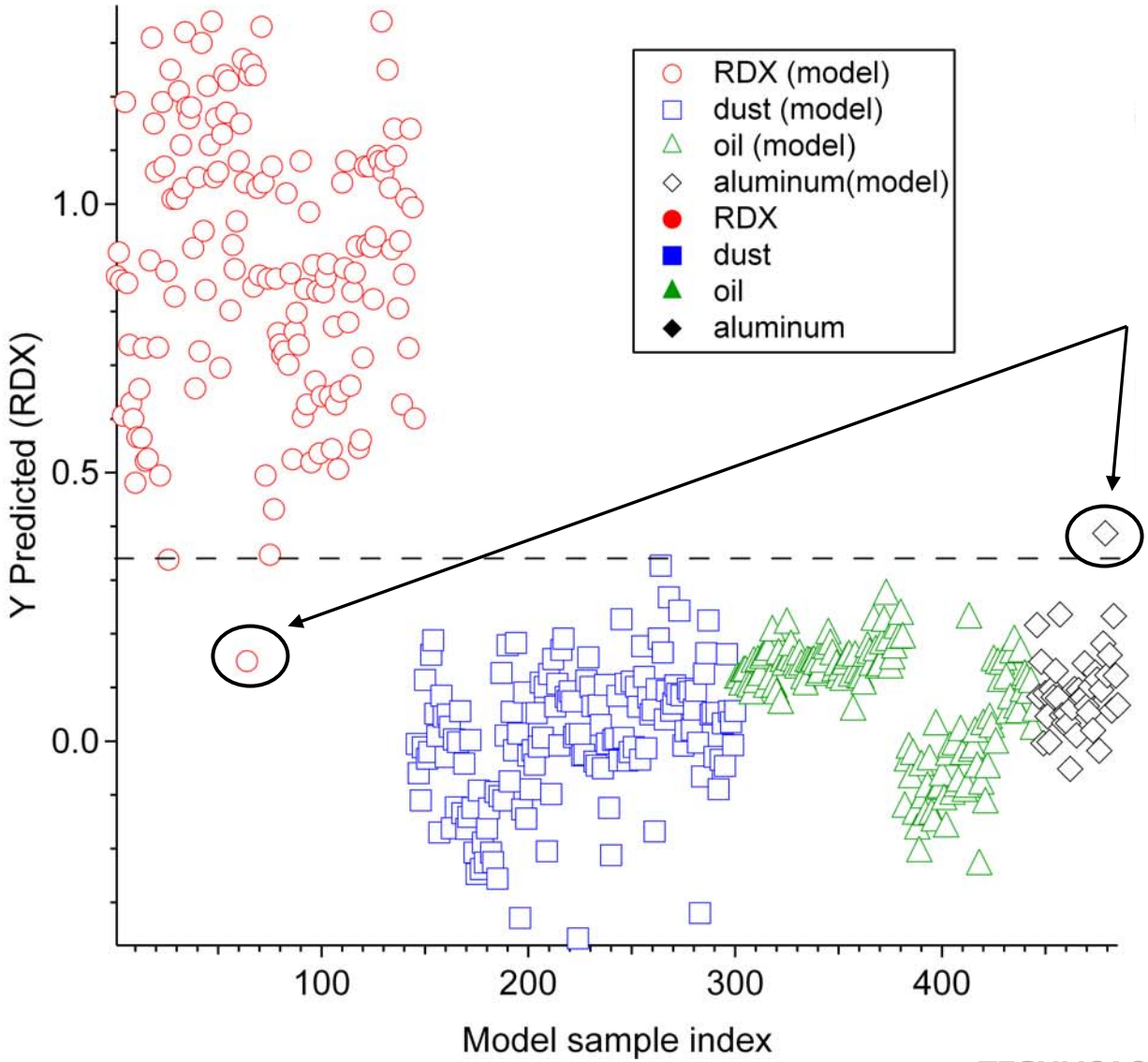
- Each data point is an entire spectrum
- Discriminant function analysis (DFA) performed on 13 LIBS emission lines
- Software was SPSS v18
- Program was only told there were 10 groups of bacteria
- Identification of an unknown sample can be done using this pre-compiled library



Explosive Residues



Explosive Residues - Validation



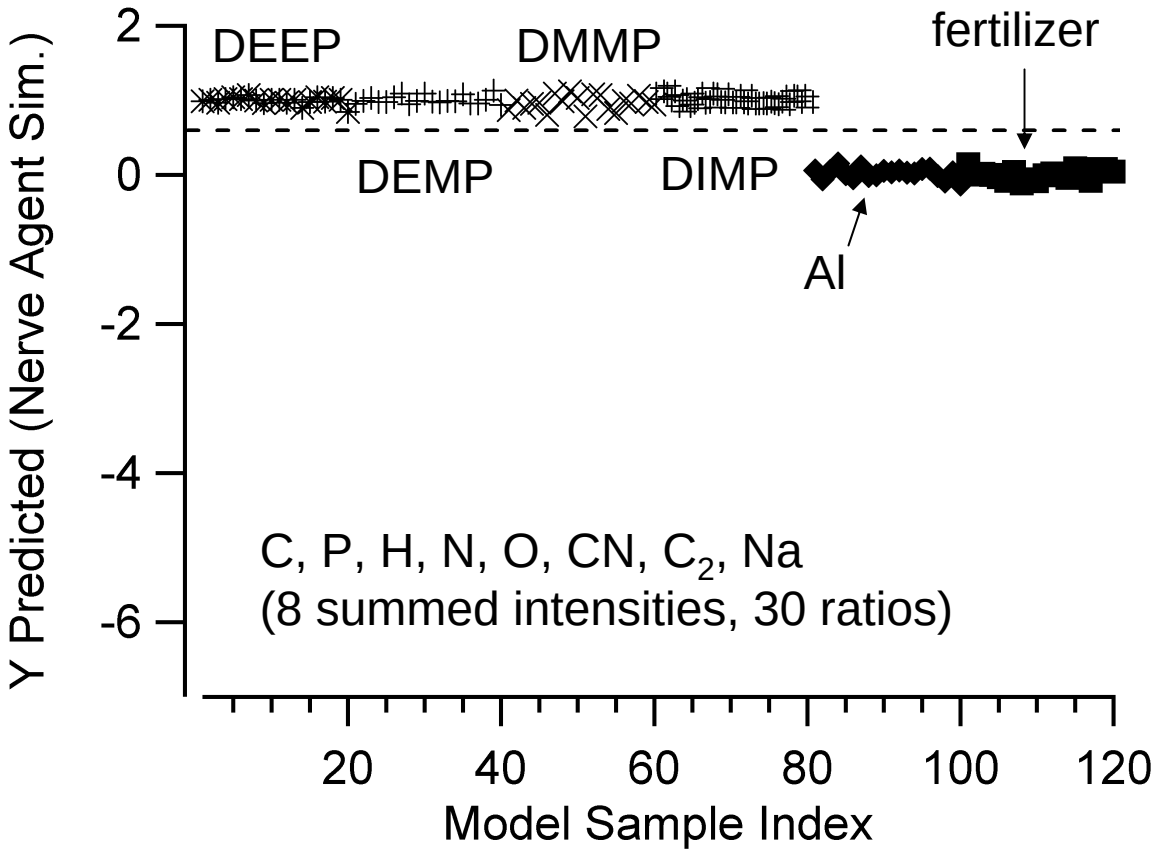
Removing statistical outliers from the model when using single-shot spectra decreases the robustness of the model!

- decreased sensitivity and selectivity

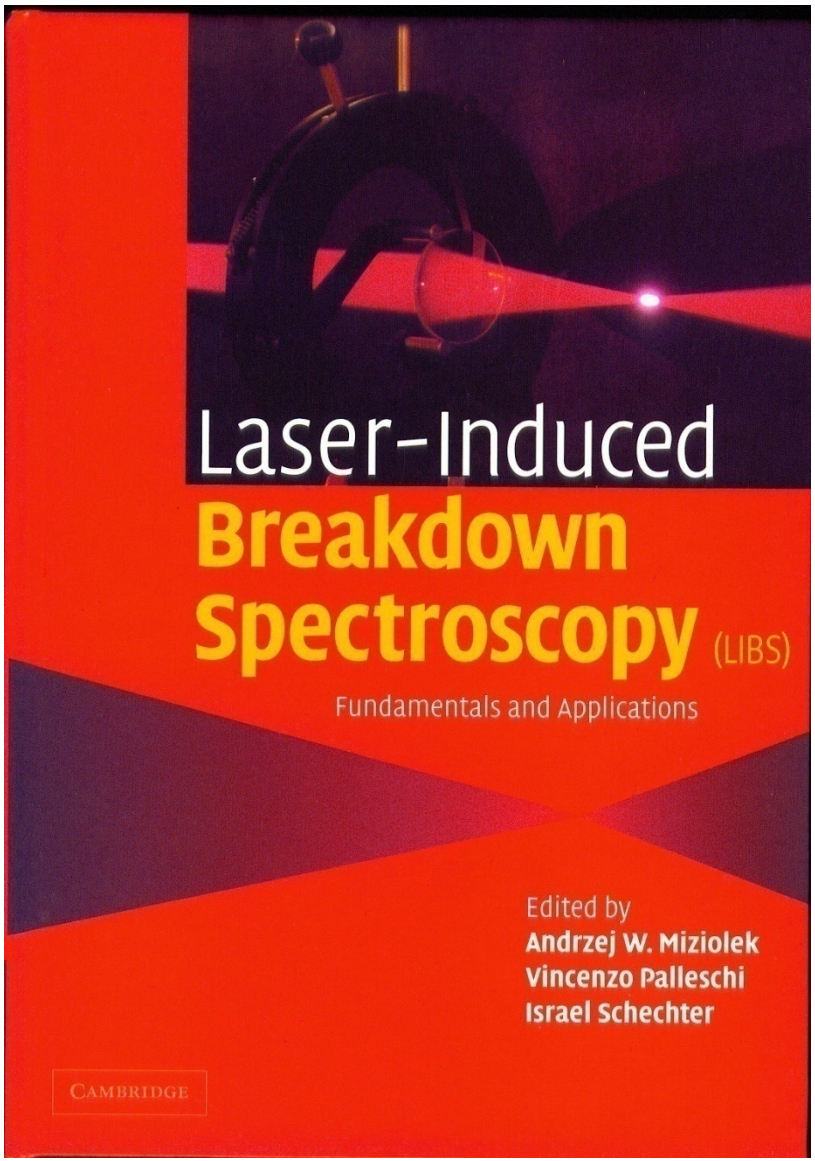
100% true positives with no false negatives

(Model includes data at 20 meters and 30 meters)

Chemical Warfare Agent Simulants



- TEP was correctly identified as a nerve agent simulant (0% false negatives) while none of the interferents registered as false positives



Laser Induced Breakdown Spectroscopy (LIBS)

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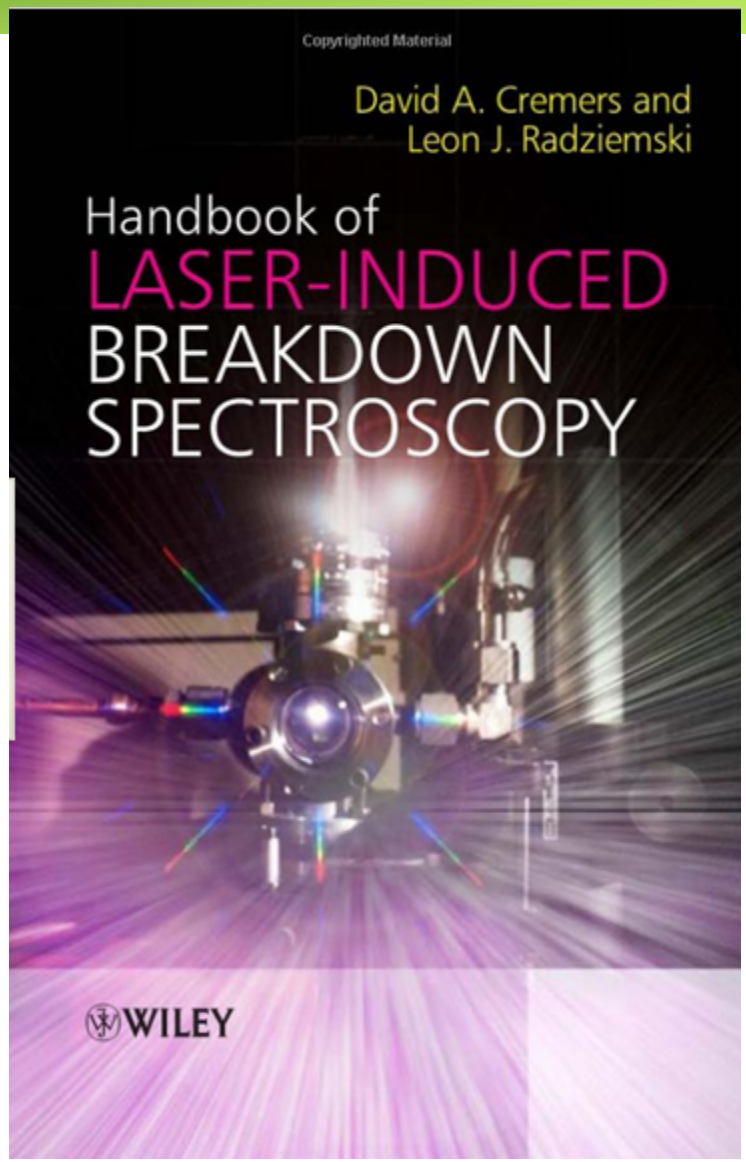

Handbook of Laser-Induced Breakdown Spectroscopy

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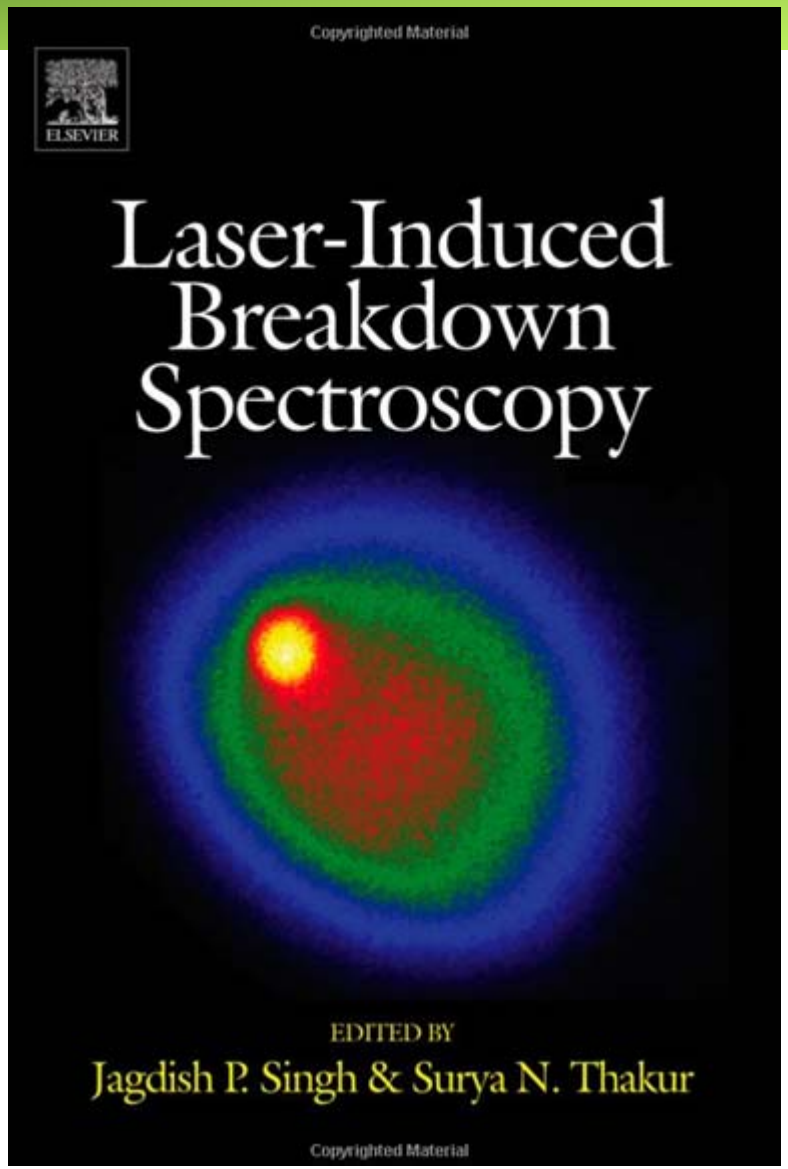

Laser-Induced Breakdown Spectroscopy

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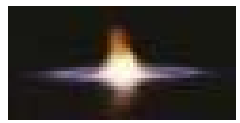
Other Resources

- Progress in LIBS podcast (Dr. Andrzej Miziolek with “Spectroscopy”)
  http://spectroscopyonline.findanalytichem.com/spectroscopy/Podcast/PodcastProgress-in-LIBS/ArticleStandard/Article/detail/666685?contextCategoryId=49103

- Video of real-time LIBS identification of explosive/biological threat (US Army Research Lab)
  http://www.arl.army.mil/www/default.cfm?Action=247&Page=462

- LinkedIn group. Laser-Induced Breakdown Spectroscopy (LIBS)  This group is gathering all the peoples involved in the development and commercialization of the LIBS technique.

- http://www.physics.wayne.edu/~srehse/ My website. I will post this talk there and have some other info about my projects.

Thank you for your attention and the invitation to join you today.

Questions?