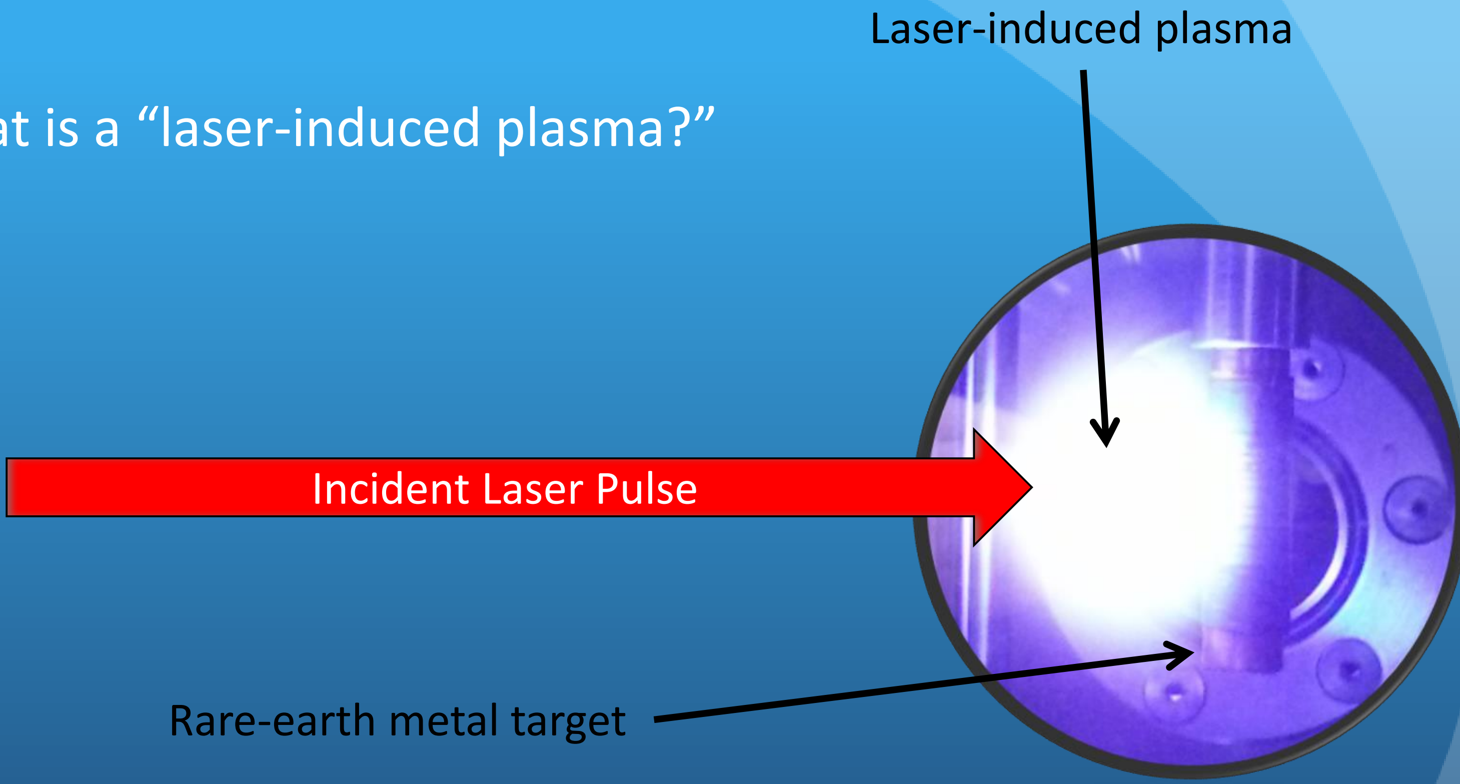
Interdisciplinary Applications of Optical Spectroscopy on a Laser-Induced Plasma

Steven J. Rehse

Department of Physics, University of Windsor, Windsor, ON

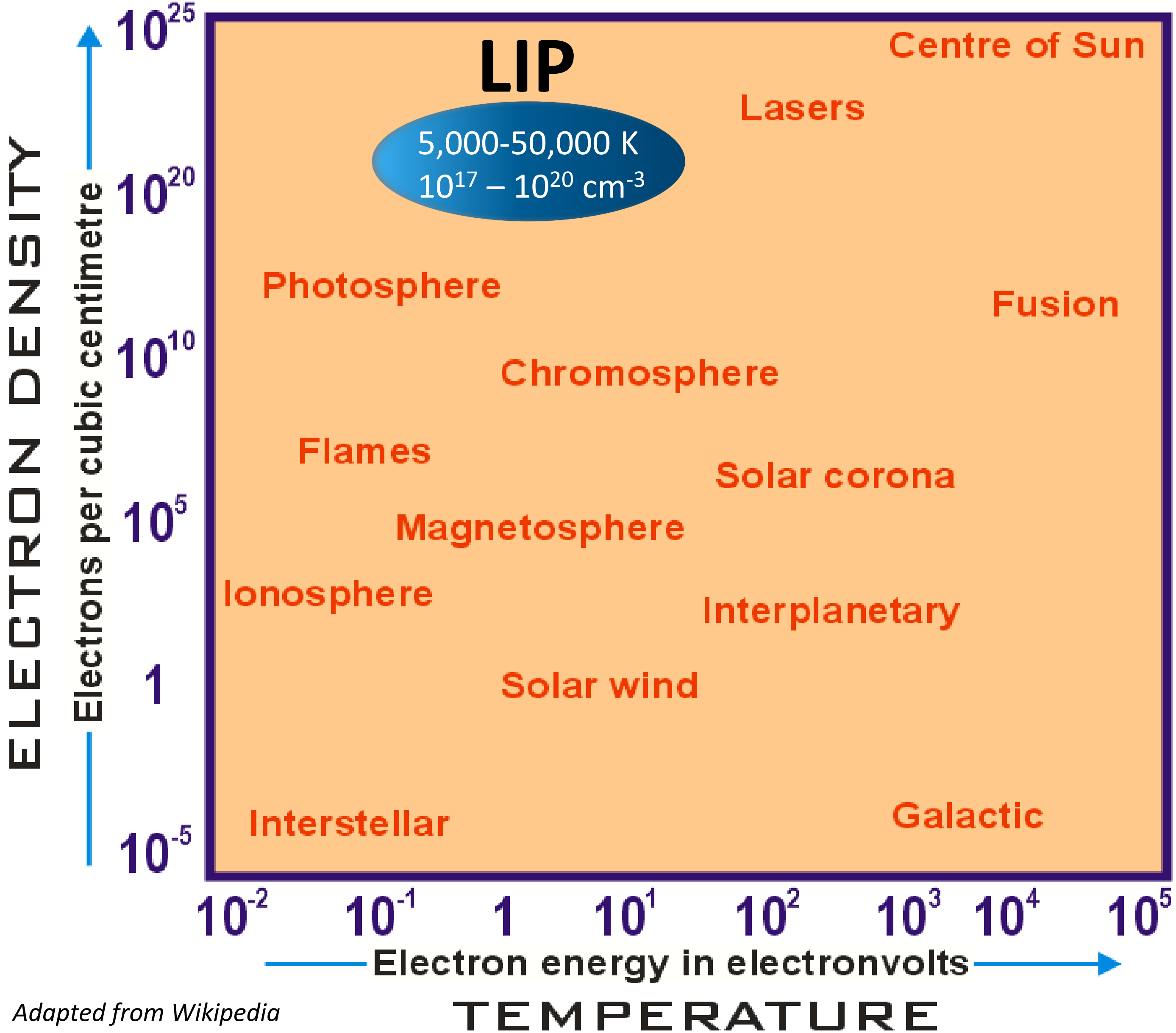
Laser-Induced Plasmas

- What is a “laser-induced plasma?”



- Can be done with ns, ps, or fs lasers
- Threshold irradiance: □ $10^{10} - 10^{11}\ \text{W/cm}^2$

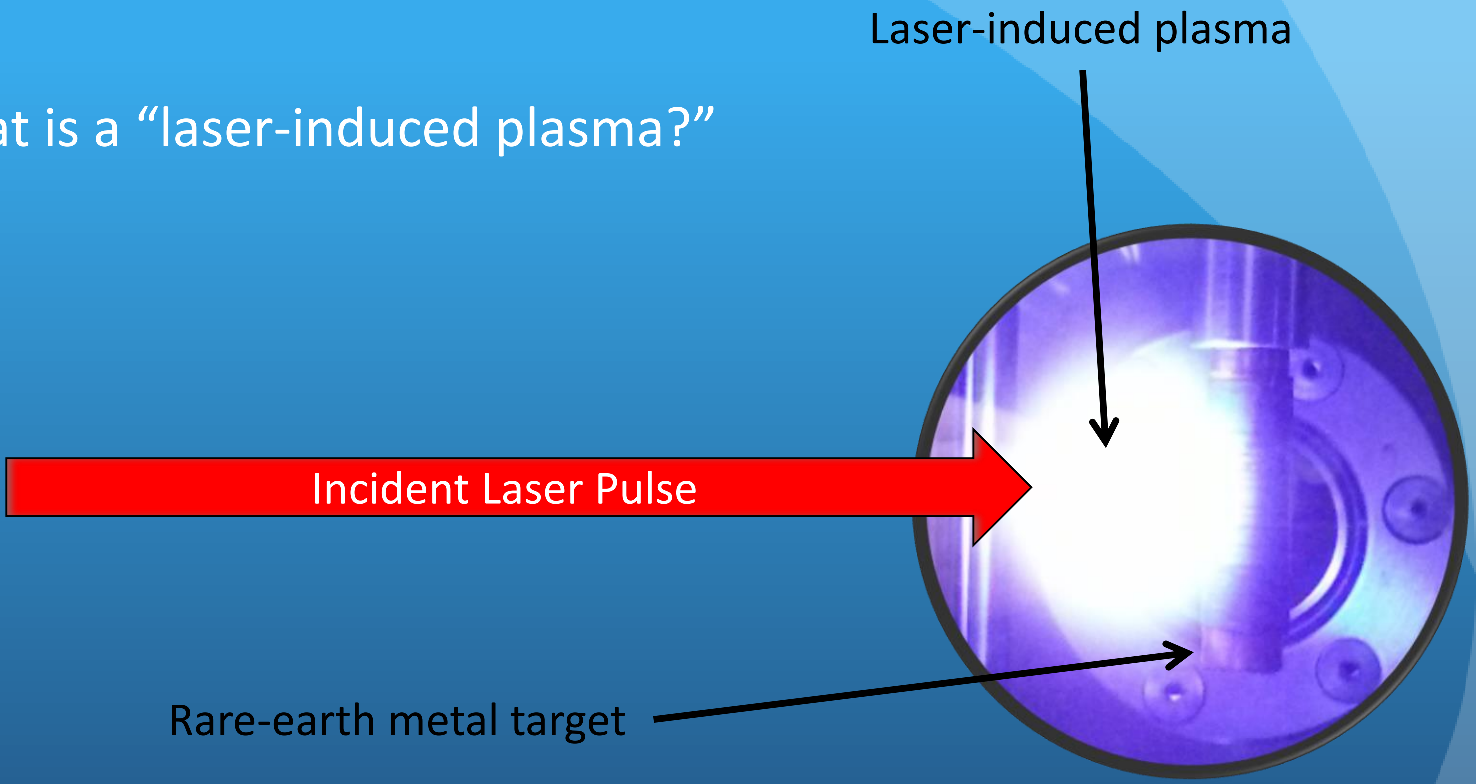
RANGES OF PLASMAS



Adapted from Wikipedia

Laser-Induced Plasmas

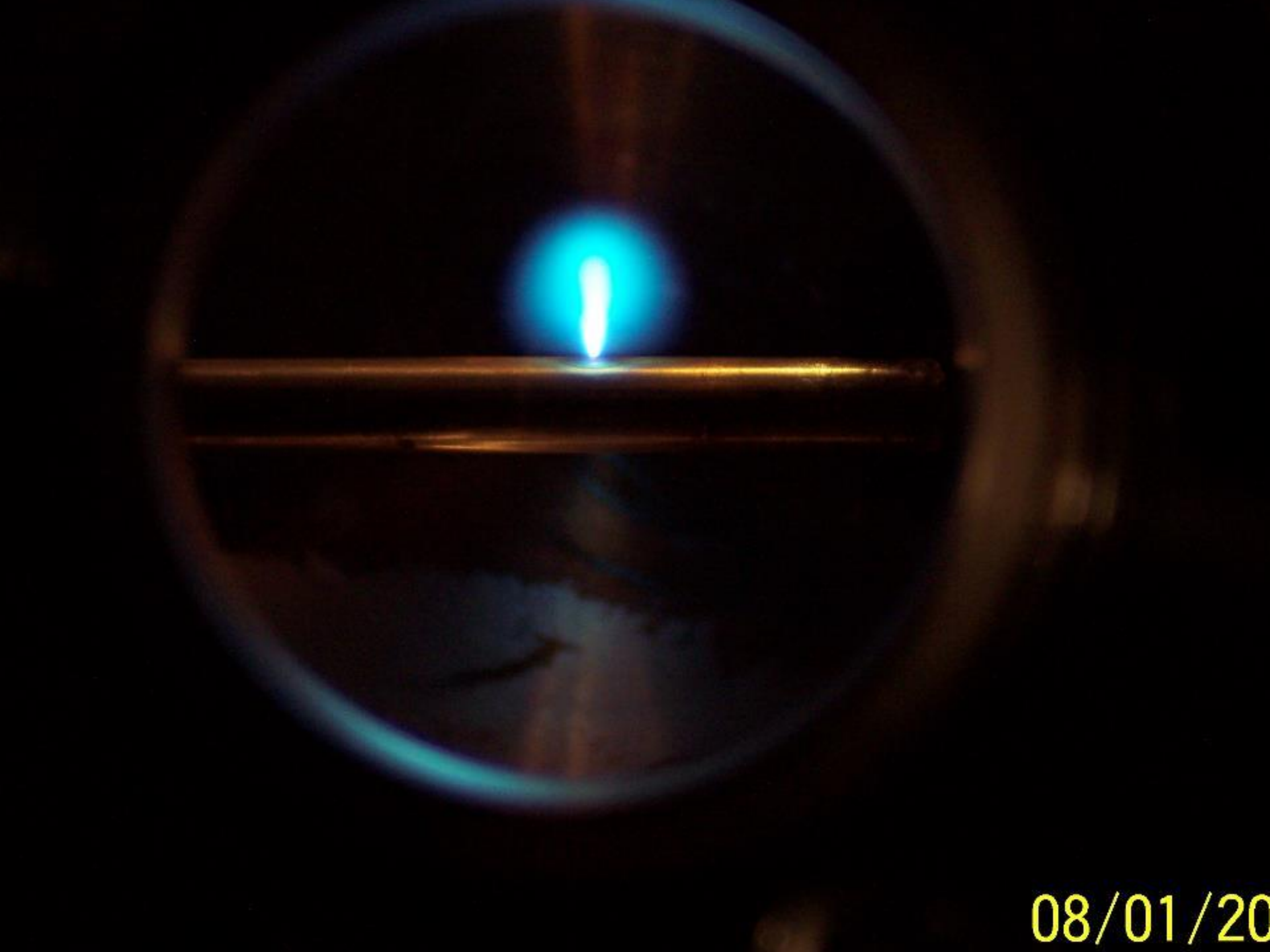
- What is a "laser-induced plasma?"



- Can be done with ns, ps, or fs lasers

We can do spectroscopy on that!

- Threshold irradiance: $\square\ 10^{10} - 10^{11}\ \mathrm{W/cm^2}$

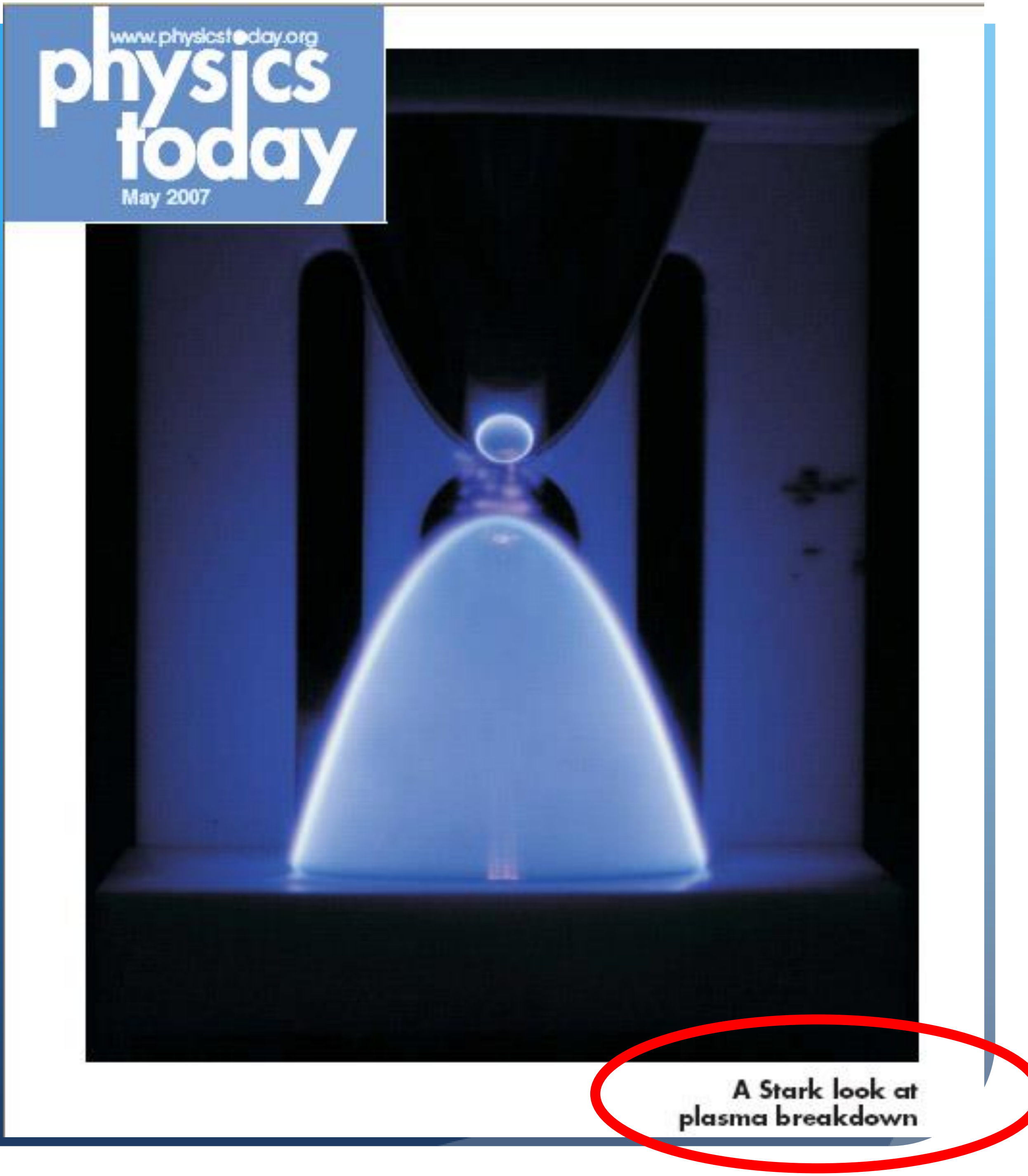

08/01/20

When we do a time-resolved spectroscopy of the plasma, we call it:

“Laser-induced breakdown spectroscopy”

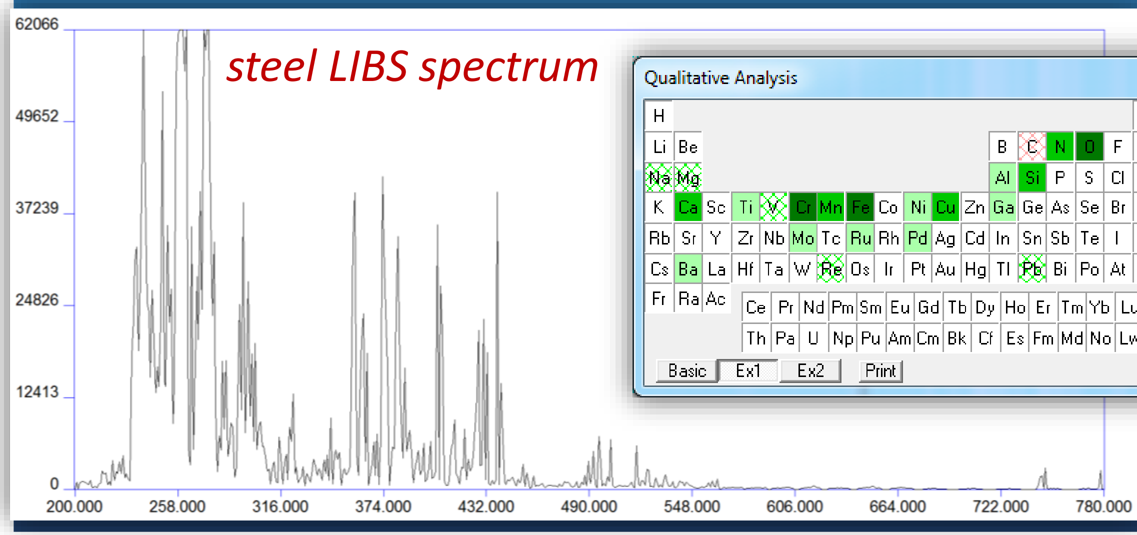
or

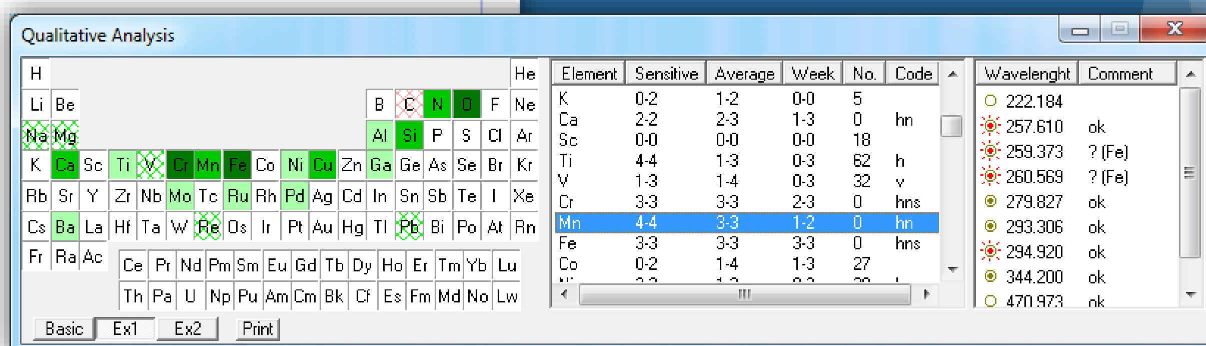
LIBS



The Goal of LIBS Plasma Creation

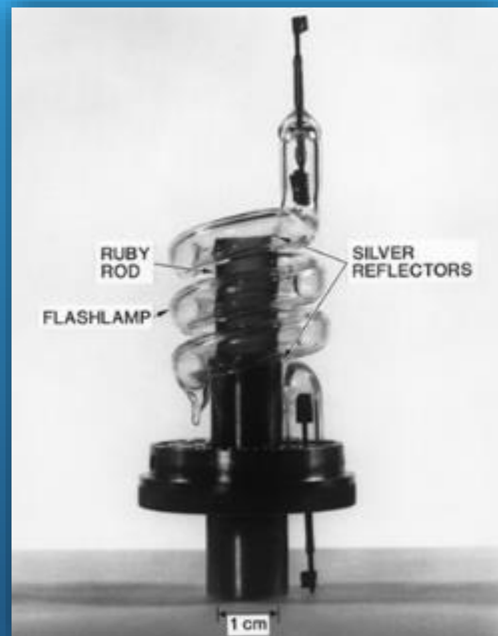
- to create an optically thin plasma which is in thermodynamic equilibrium (or LTE) and whose elemental composition is the same as that of the target/sample
    - if achieved, **atomic emission spectral line intensities** can be related to **relative concentrations** of elements (sometimes absolute concentrations)
    - typically these conditions are only met *approximately*.





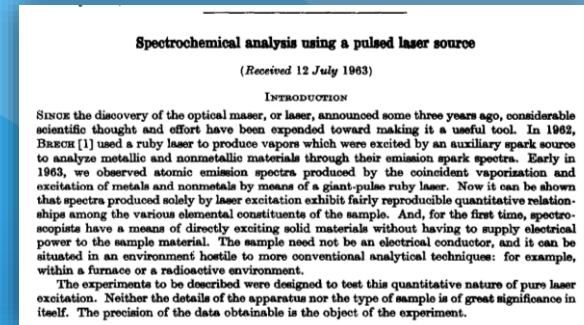
1960

Maiman: first ruby laser



1962

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



Spectrochemical analysis using a pulsed laser source

(*Received* 12 *July* 1963)

INTRODUCTION

SINCE the discovery of the optical maser, or laser, announced some three years ago, considerable scientific thought and effort have been expended toward making it a useful tool. In 1962, BRECH [1] used a ruby laser to produce vapors which were excited by an auxiliary spark source to analyze metallic and nonmetallic materials through their emission spark spectra. Early in 1963, we observed atomic emission spectra produced by the coincident vaporization and excitation of metals and nonmetals by means of a giant-pulse ruby laser. Now it can be shown that spectra produced solely by laser excitation exhibit fairly reproducible quantitative relationships among the various elemental constituents of the sample. And, for the first time, spectroscopists have a means of directly exciting solid materials without having to supply electrical power to the sample material. The sample need not be an electrical conductor, and it can be situated in an environment hostile to more conventional analytical techniques: for example, within a furnace or a radioactive environment.

The experiments to be described were designed to test this quantitative nature of pure laser excitation. Neither the details of the apparatus nor the type of sample is of great significance in itself. The precision of the data obtainable is the object of the experiment.

1964

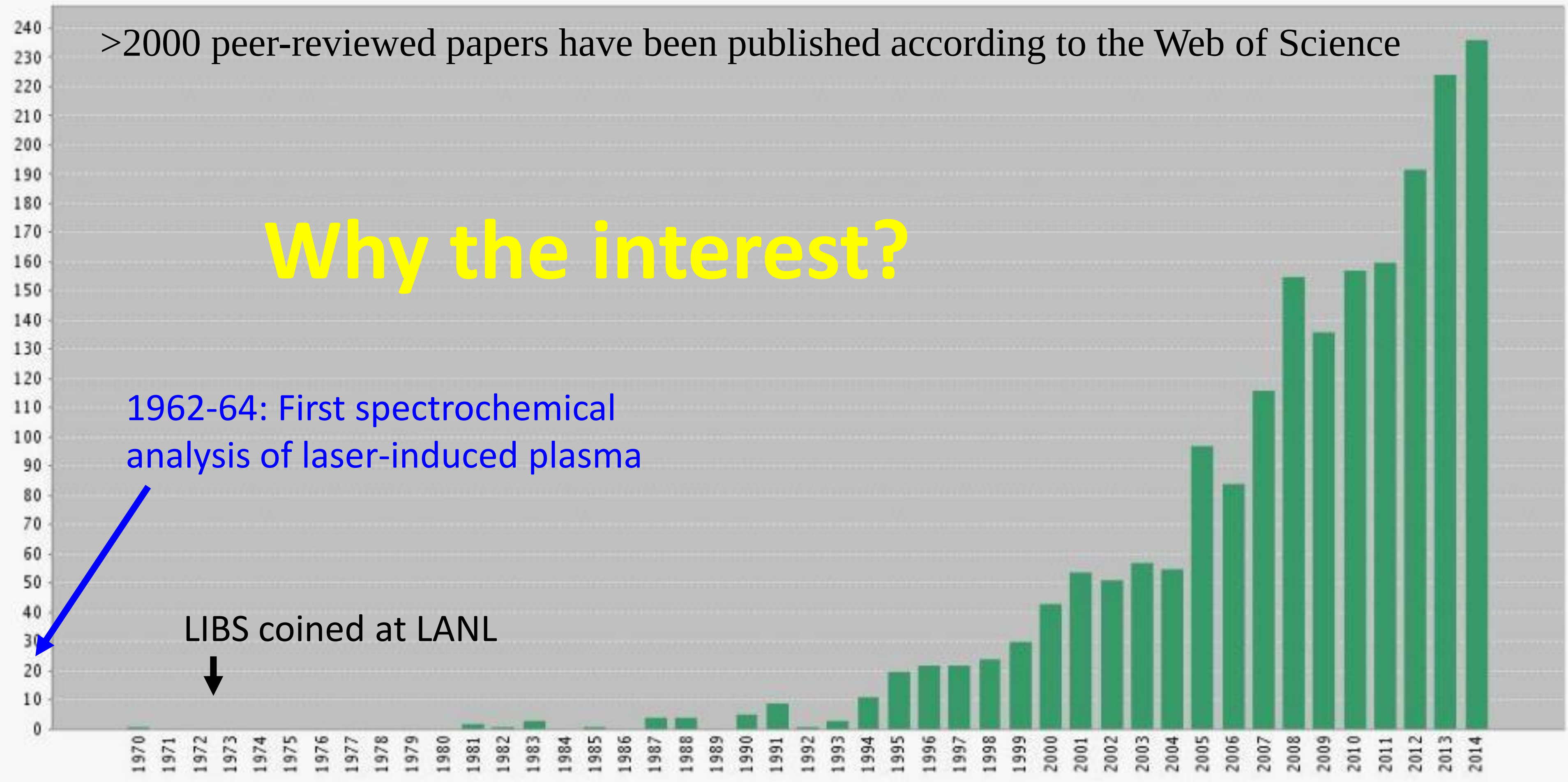
Runger et al. First direct spectro-chemical analysis by LIBS

1965

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

History

“laser-induced breakdown” and/or “laser-induced plasma spectroscopy” @ Web of Science (Thomson Reuters)

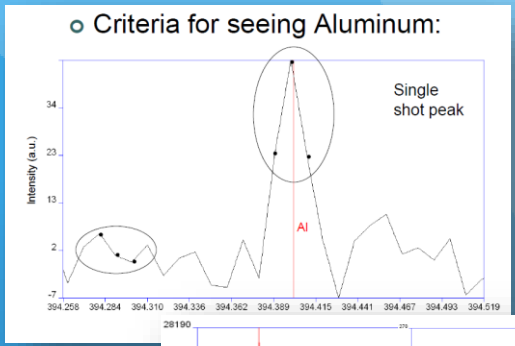


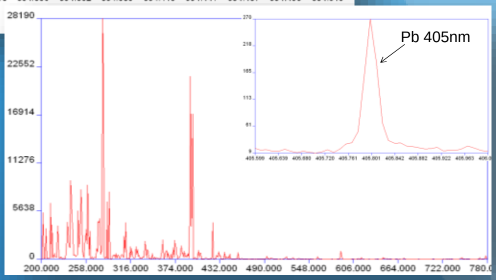
Applications of LIBS

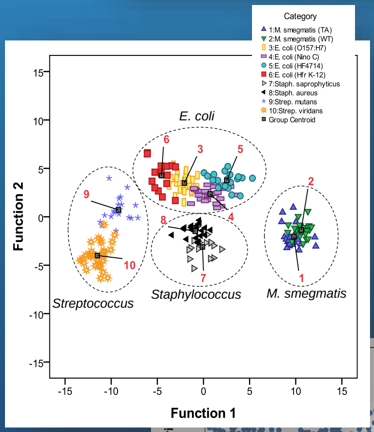
No matter what your application is,
<u>you will be doing one of two things:</u>

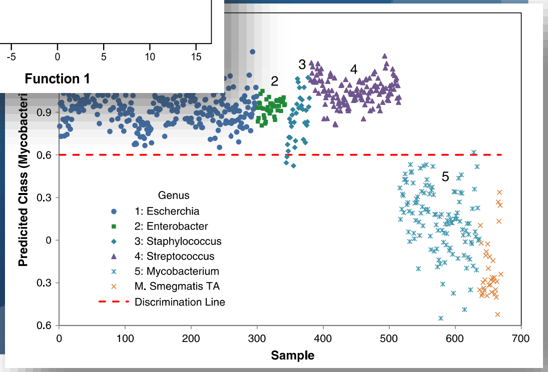
1. Attempting to quantify the amount/concentration of some element by analyzing peak intensities

2. Attempting to identify a target based on its unique elemental composition by analyzing the presence intensity of all/many lines









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

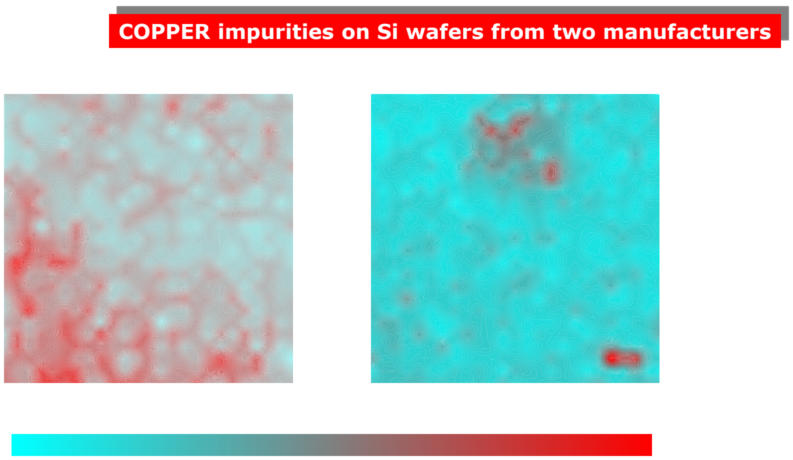
(■ Solids ■ Liquids ■ Gases ■ Artificially prepared)

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

Advantages of LIBS - spatial resolution

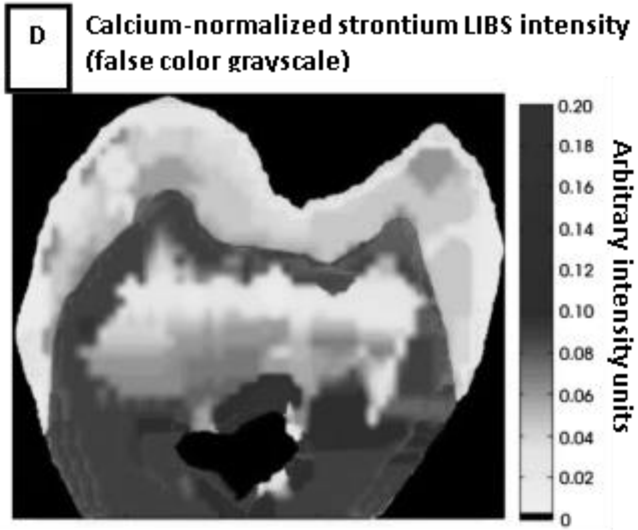
- Laser allows point sampling (1-100 micron)
- Elemental “surface maps” can then be created



Total area imaged: 20 x 20 mm^2
Depth: ≈ 1 μm
Lateral resolution: 750 μm

Nd:YAG @ 532 nm
1 pulse; 5 mJ pulse^{-1}
WD = + 5 mm

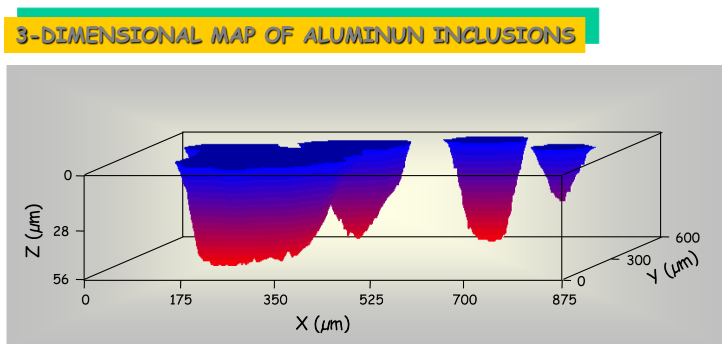
Courtesy of Ben Smith, Javier Laserna



Courtesy of F.C. Alvira et al.

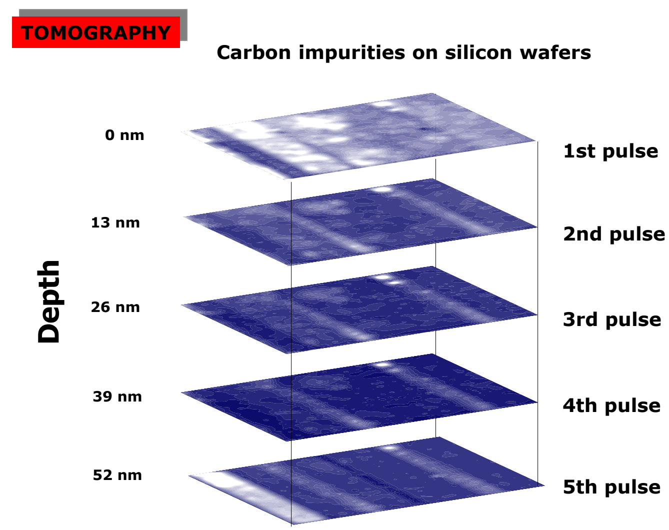
Advantages of LIBS - depth profiling

- Because laser only removes μg to ng of material, ablation crater only microns deep
- Subsequent shots thus sample progressively deeper layers



Courtesy of Ben Smith

- 13 positions
- 100 laser shots in depth
- Mapped volume = 600 x 875 x 56 μm3
- Repetition rate = 10 Hz
- Analysis time = 2 min and 30 s

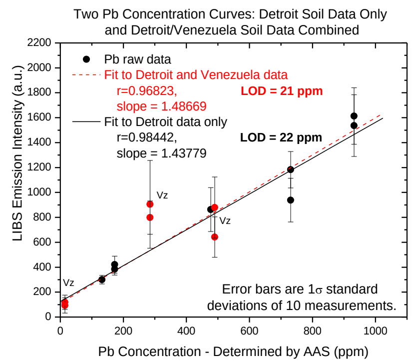


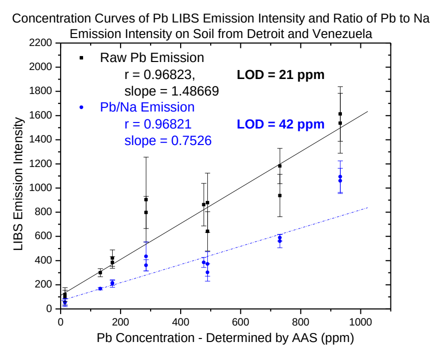
Nitrogen laser; Lateral resolution 15 μm, sampling depth 13 nm

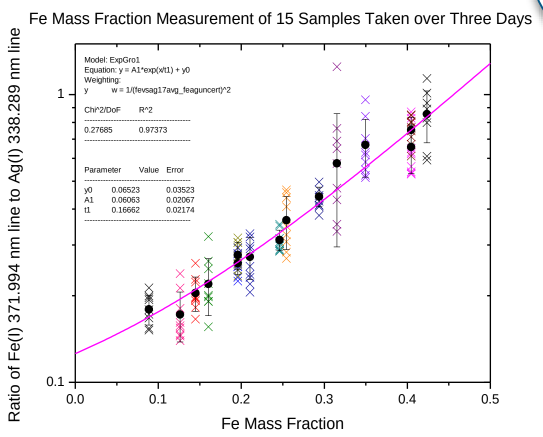
Courtesy of Ben Smith

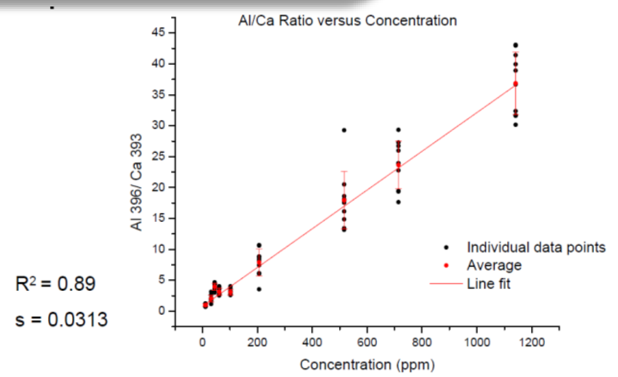
Advantages of LIBS – sensitivity & speed

- Concentrations of 1-100 ppm usually detectable in seconds using a standard LIBS apparatus









Advantages of LIBS - portability / standoff

- Apparatus is compact, low weight; can be made man-portable
- All optical technique, so can be done at a distance "stand-off"

First responder CBRNE prototypes have been built…

Backpack contai
broadband high-
resolution
spectrometer, las
power supply,
computer, and ba

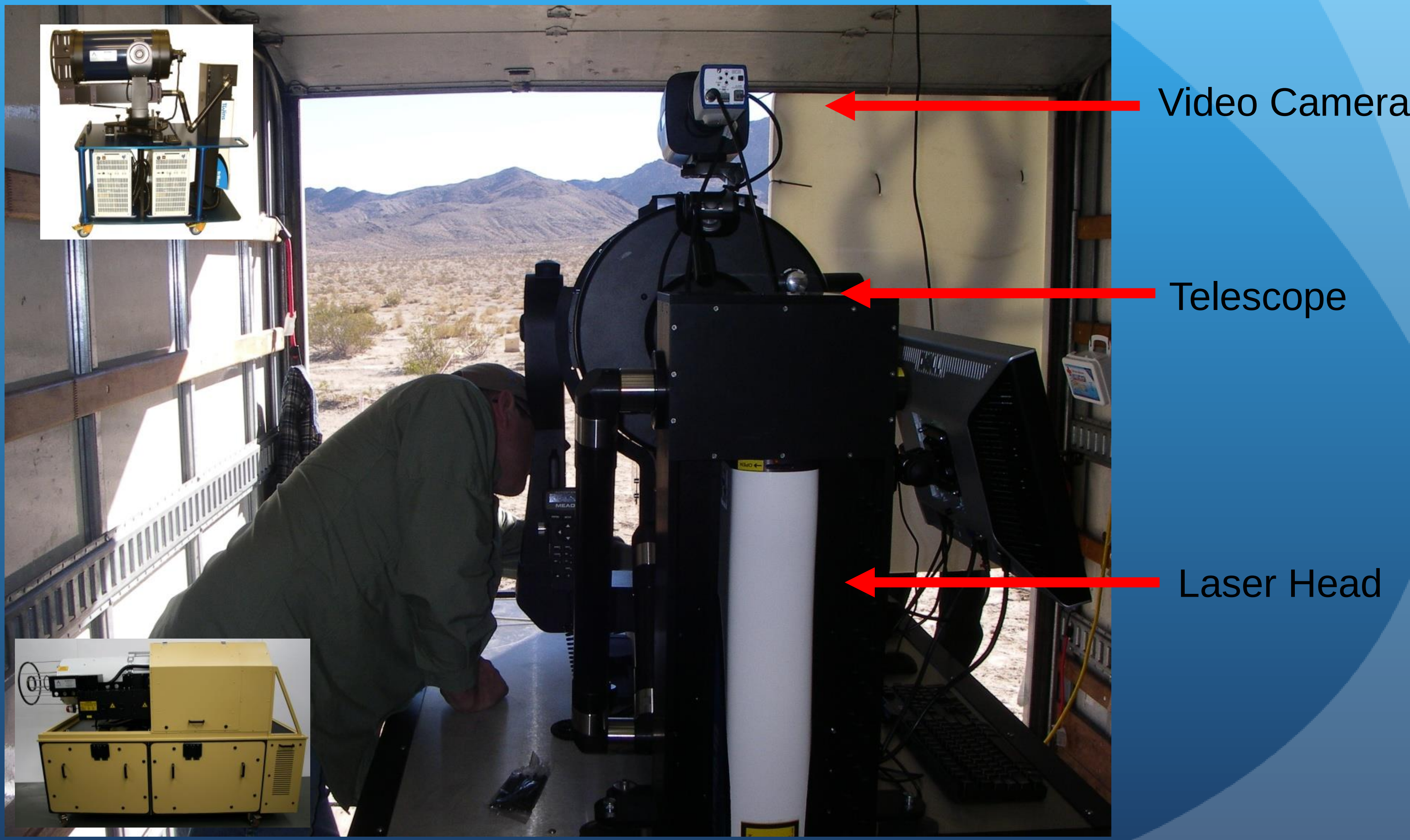
ad's-up display

nd-held probe contains
er, joystick for control,
l focus optics

Microplasma/
LIBS Event

courtesy of Ocean Optics.

High-energy remote systems have been built…



Courtesy of A.J. Miziolek, A. Whitehouse

Hand-held systems have been built…

mPulse – Oxford Instruments

LIBZ – SciApps, Inc

ChemLite- TSI, Inc

Interdisciplinary Applications

- The utility and ease of operation lend themselves to a variety of interdisciplinary applications.
- Four I want to mention:

1. Bacterial identification

2. Biomedical specimens

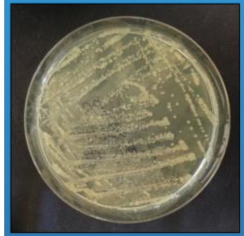
3. Atomic branching ratios

4. Mars exploration

1. Bacterial identification

Our Method of Bacteria Classification

Bacteria is cultured using trypticase soy agar (TSA).



Colonies are removed and placed in 1.5 mL distilled water.

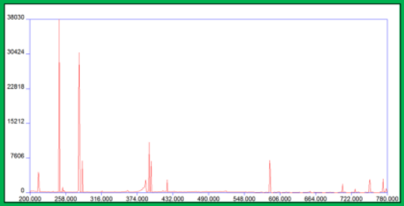
30 μL of vortexed sample are deposited on a standard 0.22 μm cellulose filter in contained wells.

Colloidal solution is dried forming a bacteria lawn on the clinician-friendly filter.

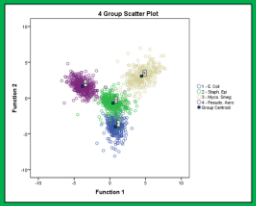
Filter is placed in an argon environment and ablated using a pulsed 1064 nm Nd: YAG laser.

Average time to complete bacterial classification = 1 hour

Échelle diffraction grating spectrometer is used to obtain the atomic spectrum and composition of sample.



Atomic composition is used to discriminate bacteria against pre-existing library.

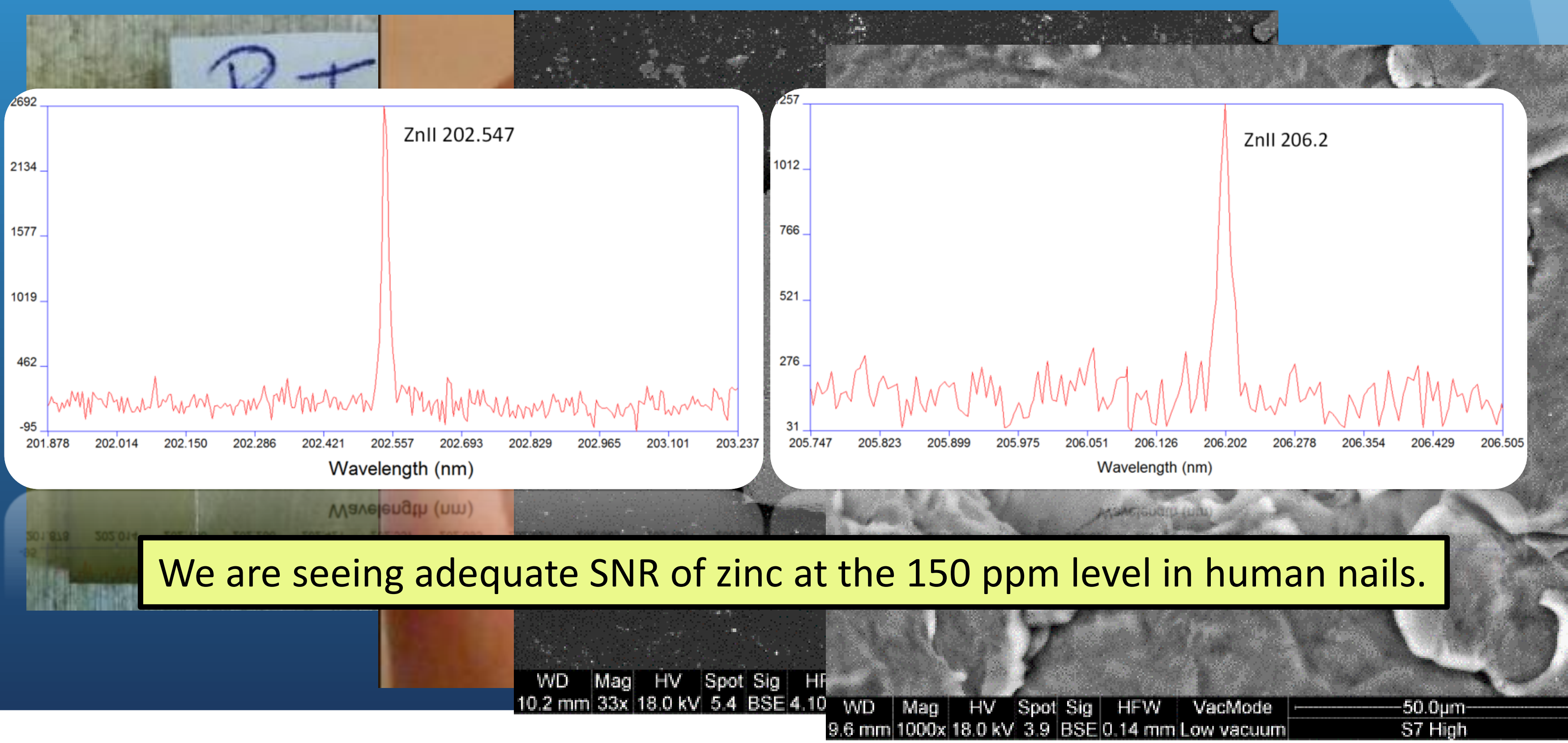


Element	% of fixed salt fraction
Sodium	2.6
Potassium	12.9
Calcium	9.1
Magnesium	5.9
Phosphorus	45.8
Sulfur	1.8
Iron	3.4

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

2. Biomedical specimens

- Zinc in the fingernails has been shown to represent the overall zinc concentration in the body (needed for enzymatic activity, cellular processes, neuron communication.)
- Need a real-time biomedical assay to evaluate zinc content.

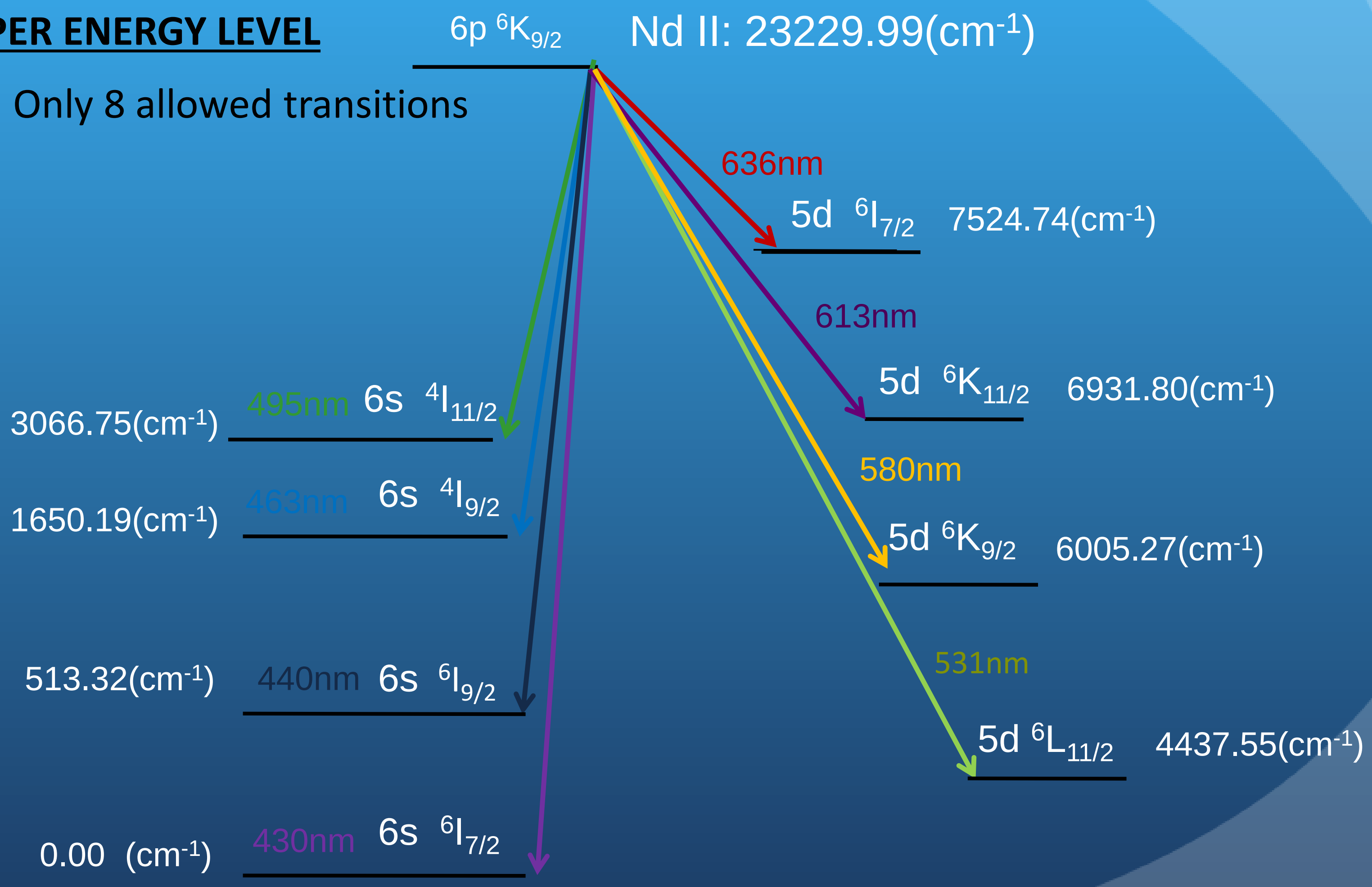


We are seeing adequate SNR of zinc at the 150 ppm level in human nails.

3. Branching Ratios (Fractions)

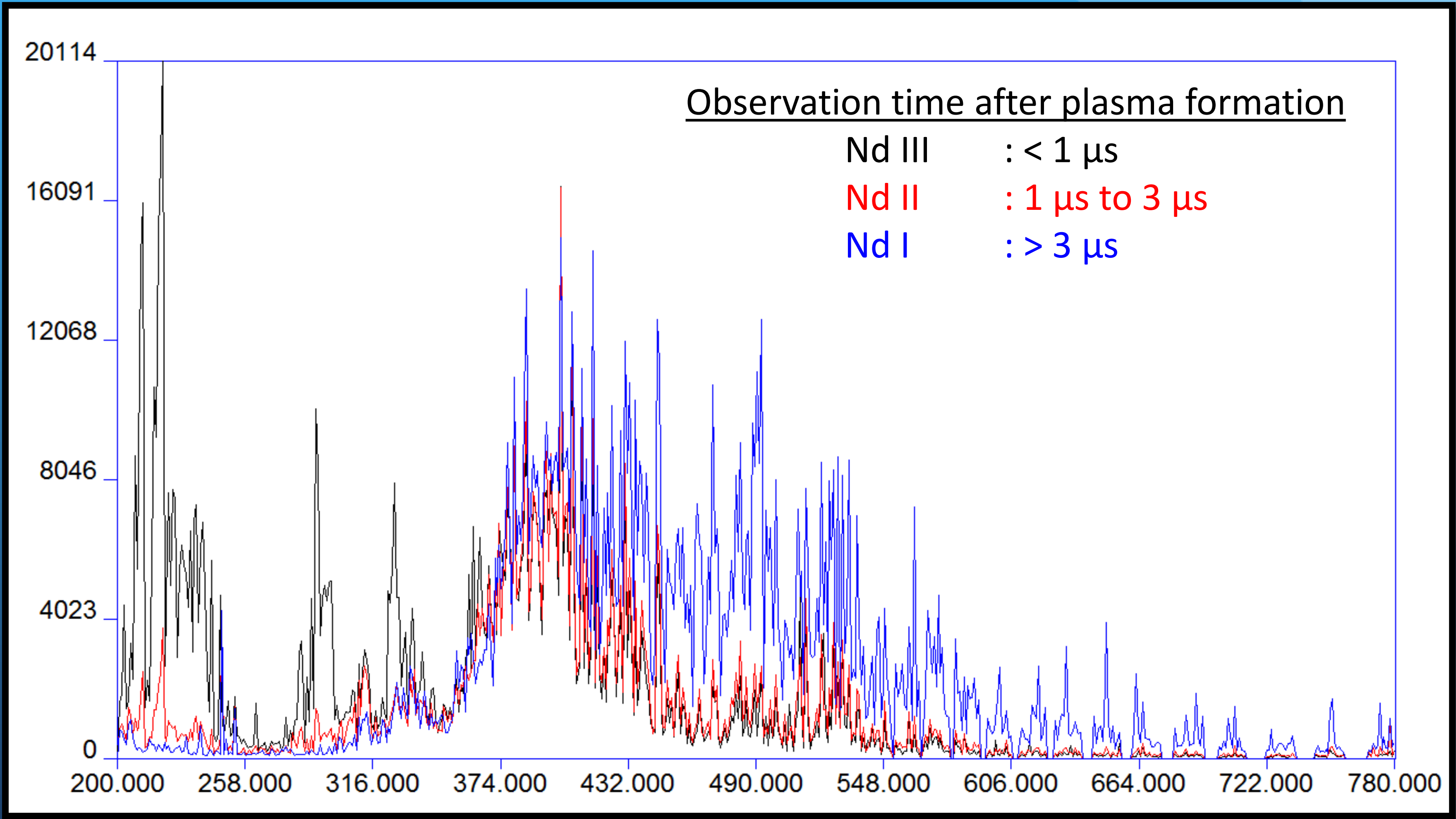
UPPER ENERGY LEVEL

- Only 8 allowed transitions

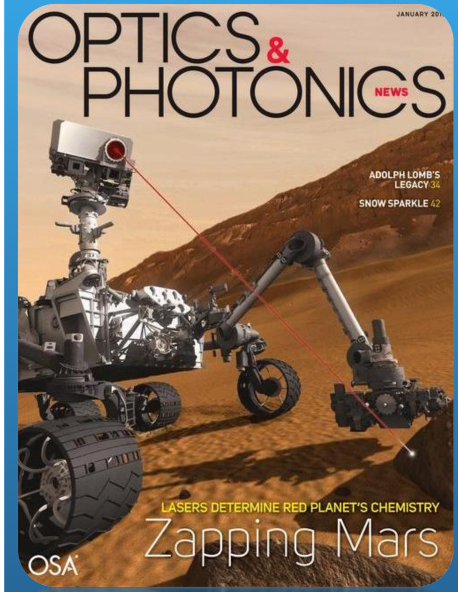


3. Branching Ratios (Fractions)

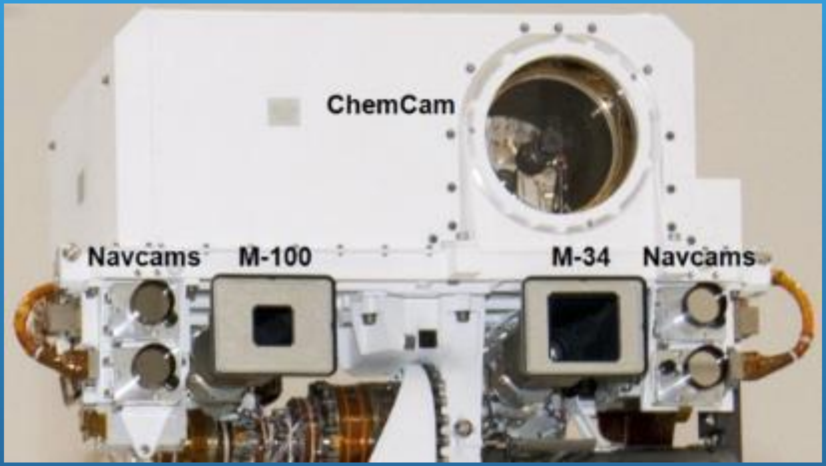
Metallic targets in low pressure Ar atmosphere yield good intensities for BR measurements



4. Mars exploration

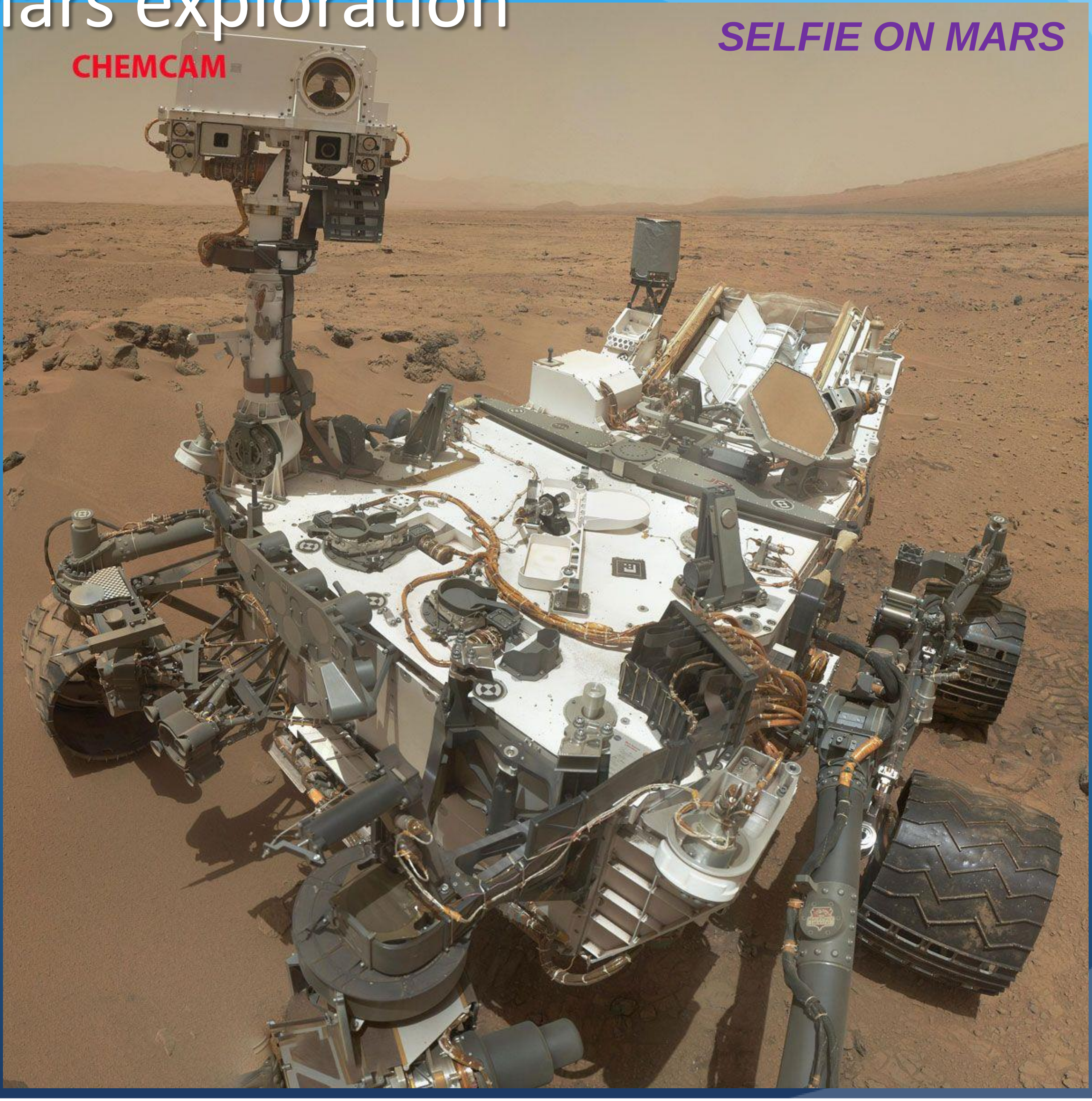


4. Mars exploration



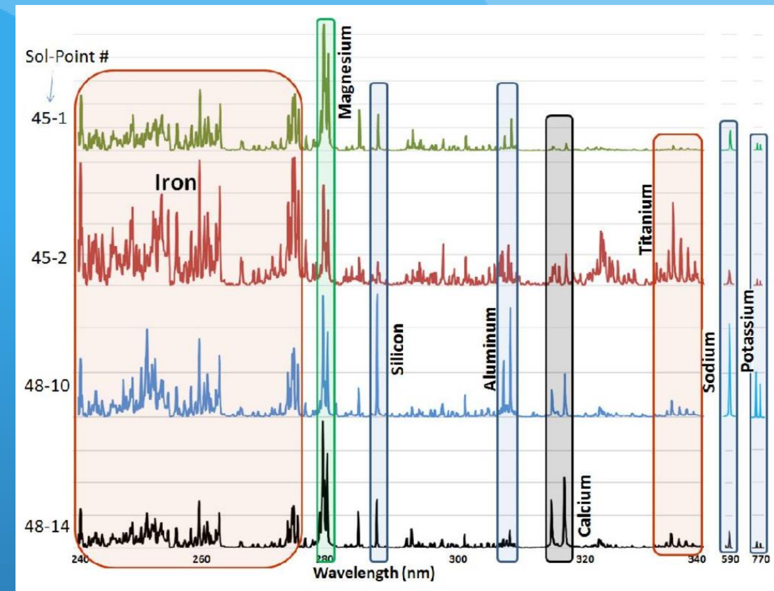
Los Alamos
NATIONAL LABORATORY

4. Mars exploration

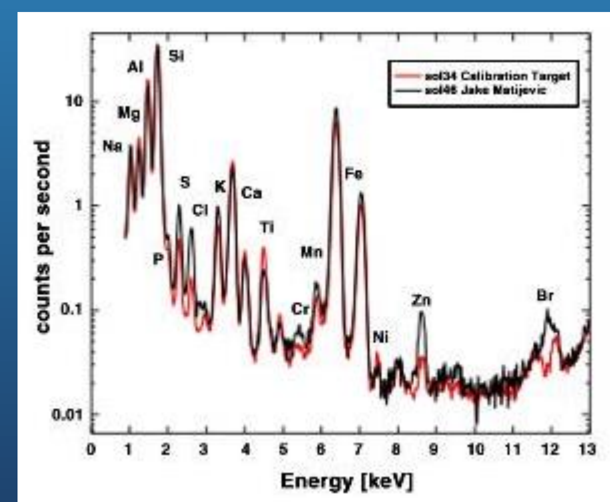


4. Mars exploration

This image shows where NASA's Curiosity rover aimed two different instruments to study a rock known as "Jake Matijevic." The red dots are where the Chemistry and Camera (ChemCam) instrument zapped it with its laser on Sept. 21, 2012, and Sept. 24, 2012, which were the 45th and 48th sol, or Martian day of operations. The circular black and white images were taken by ChemCam to look for the pits produced by the laser. The purple circles indicate where the Alpha Particle X-ray Spectrometer trained its view. This image was obtained by Curiosity's Mast Camera on Sept. 22, 2012, or sol 46. Credit: NASA/JPL-Caltech/MSSS



ChemCam (LIBS)



Courtesy of www.phys.org

Alpha Particle X-ray Spectrometer (APXS)

Conclusions

- LIBS provides an accurate, fast, spatially resolved, remote spectrochemical analysis of almost any type of target (solid, liquid, gas, powder)
- High degree of versatility and robustness suggests its adoption in many different interdisciplinary fields
- Experiments utilizing LIBS involve an exciting mixture of physics, laser science, and analytic chemistry (at a minimum)

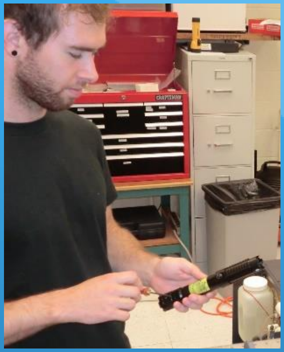
Funding and Acknowledgements

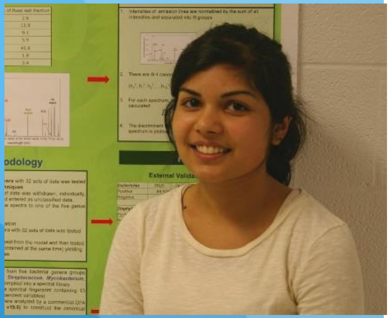
We gratefully acknowledge funding for this project provided by:

- A *Natural Sciences and Engineering Research Council of Canada* Discovery grant and a Research Tools and Instruments grant
- A *Canada Foundation for Innovation* Leaders Opportunity Fund grant
- An *Ontario Research Fund* Small Infrastructure Funds grant
- *University of Windsor* Outstanding Scholars program
- *University of Windsor* Faculty of Science

All Credit to the Students!

Dan Trojand





Khadijia Sheikh

Russell Putnam

Anthony Piazza

Dylan Malenfant

Derek Gillies

Allie Paulick

Andrew Daabous

Vlora Riberdy