

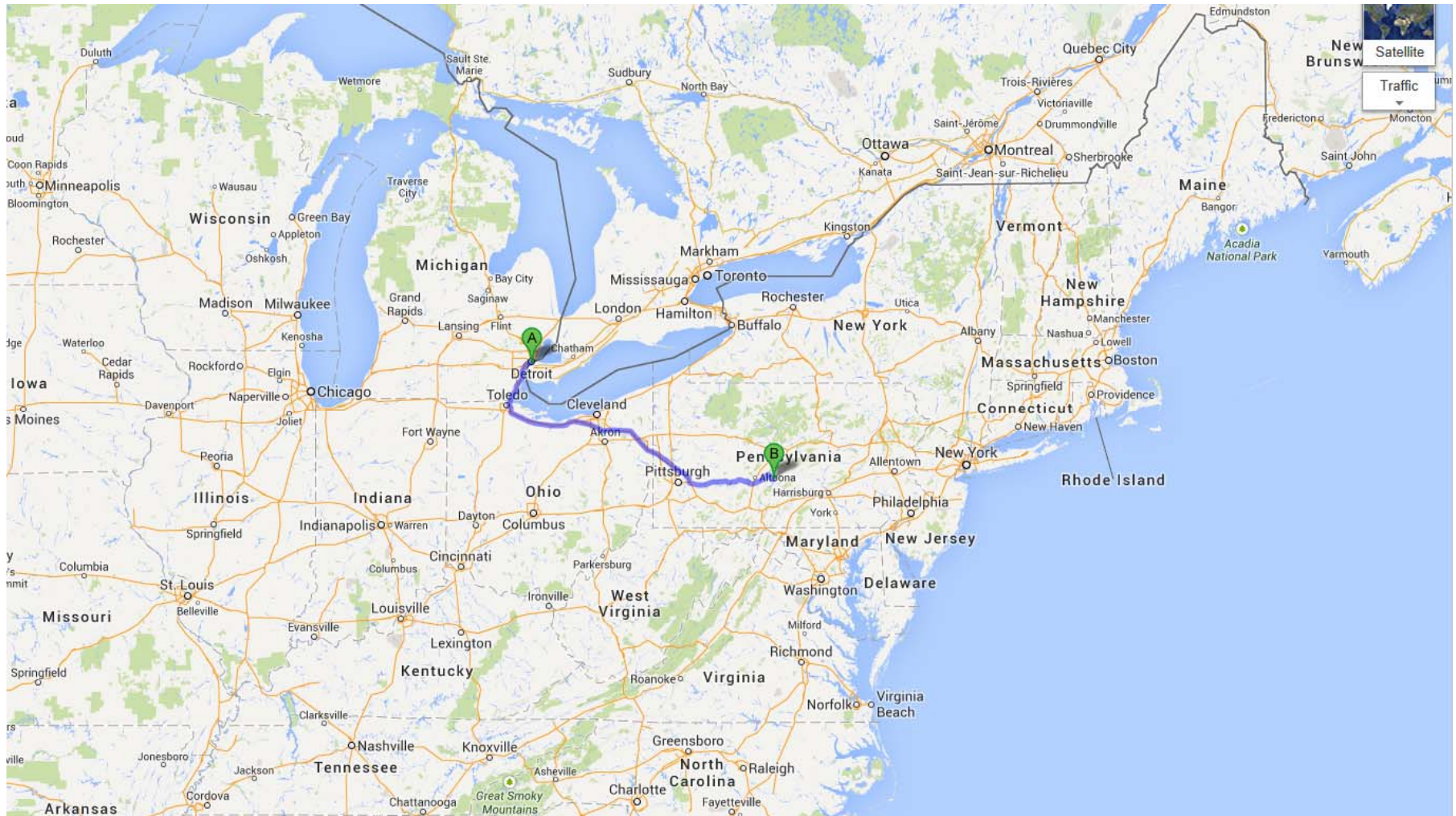
# The “Whys” of Using Laser-Induced Breakdown Spectroscopy

*(advantages and applications)*

Prof. Steven J. Rehse  
*University of Windsor*  
*Windsor, Ontario, Canada*



# Where is Windsor?



# The University of Windsor

## Our History

- In 1857, Assumption College welcomed its first students
- In 1963, it affiliated with Essex College, Canterbury College, Iona College and Holy Redeemer College to incorporate as the University of Windsor, a non-denominational, autonomous degree-granting institution.

## Academics

- The University of Windsor offers 190 undergraduates programs, 65 graduate programs and six professional programs.
- Faculty: 524, Student/faculty ratio: 26:1

## Our Students

- Undergraduates: 14,088 (full and part time students)
- Graduate students: 2,004 (full and part time students)
- International students: 11 percent of student body from nearly 100 countries

## Our Campus

- The University of Windsor is a safe, urban campus covering 51 hectares (125 acres) in Windsor, Ontario.

*The University of Windsor is located on the banks of the Detroit River.*



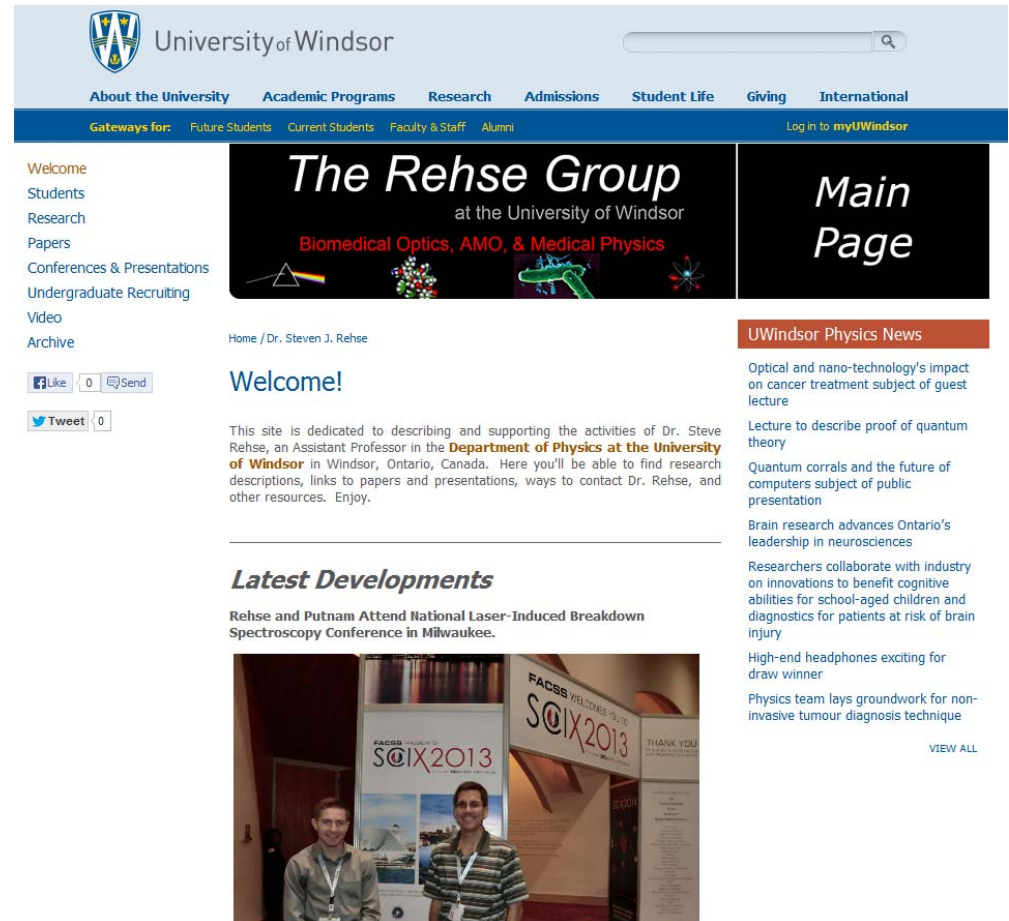
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# Who Am I?

<http://www1.uwindsor.ca/rehse/>

- Assistant Professor of Physics
- Previously at Wayne State University (across river)
- Performing laser-based spectroscopic experiments since 1993 (*LANL*)
- Doing LIBS since 2005 (25 publications, a review, a book chapter)
- Focusing on rapid pathogenic bacterial identification (and biomedical applications)



The screenshot shows the website for Dr. Steven J. Rehse at the University of Windsor. The header includes the University of Windsor logo and name, along with navigation links for 'About the University', 'Academic Programs', 'Research', 'Admissions', 'Student Life', 'Giving', and 'International'. Below this is a 'Gateways for' section with links for 'Future Students', 'Current Students', 'Faculty & Staff', and 'Alumni'. A search bar is located in the top right corner.

The main content area features a large banner for 'The Rehse Group at the University of Windsor' with the subtext 'Biomedical Optics, AMO, & Medical Physics'. To the right of the banner is a 'Main Page' button. Below the banner is a 'Welcome!' message and a 'Latest Developments' section. The 'Latest Developments' section includes a headline: 'Rehse and Putnam Attend National Laser-Induced Breakdown Spectroscopy Conference in Milwaukee.' Below this is a photo of two men standing at a conference booth for 'SOIX 2013'.

On the right side of the page, there is a 'UWindsor Physics News' section with several news items:

- Optical and nano-technology's impact on cancer treatment subject of guest lecture
- Lecture to describe proof of quantum theory
- Quantum corrals and the future of computers subject of public presentation
- Brain research advances Ontario's leadership in neurosciences
- Researchers collaborate with industry on innovations to benefit cognitive abilities for school-aged children and diagnostics for patients at risk of brain injury
- High-end headphones exciting for draw winner
- Physics team lays groundwork for non-invasive tumour diagnosis technique

At the bottom right of the news section is a 'VIEW ALL' link.



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# Outline of Presentation

## 1. Advantages of LIBS

## 2. Applications of LIBS

Too many to list, but there are two broad classes of applications:

- Elemental quantification
- Sample qualification/identification



# Advantages of LIBS

(both for research and teaching)

1. Speed
2. Relative experimental ease
3. Lack of sample preparation – almost anything can be analyzed.
4. Spatial resolution
5. Depth profiling
6. Sensitivity
7. Portability/standoff
8. Lots of teachable entry points



# Advantages of LIBS

## speed

- Primary spectrochemical advantage; almost nothing touches it.
- From firing of laser to spectral data collection is under one second.
- With sample preparation/apparatus calibration, realistically takes about 15 minutes.

This suggests your applications!



# Advantages for teaching speed

- Data easily acquired in time available to undergraduates (for research or during a lab).
  - My students work in 3 hour shifts.
- Spectral analysis can occur “off-line.”





# Advantages of LIBS

relative experimental ease

- Possibility of introduction into industrial / commercial settings (even in harsh environments).



*Courtesy of Andy Whitehouse, Applied Photonic, Inc*

- Apparatus is generally robust / reliable.



# Advantages for teaching

## relative experimental ease

- I have had 2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup> year students running experiments.
- Day-to-day reliability is very good.
- Daily “turn-on” procedures are straight-forward.
- Unsupervised research possible after several training sessions.

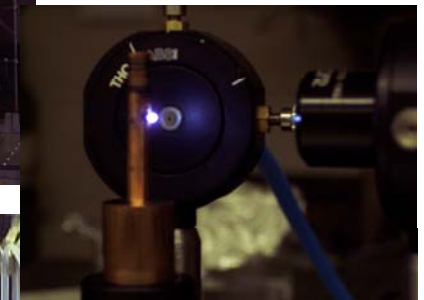
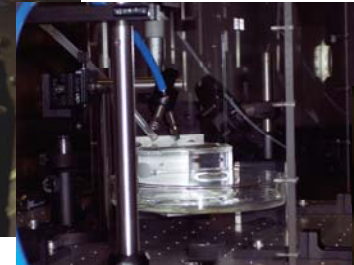
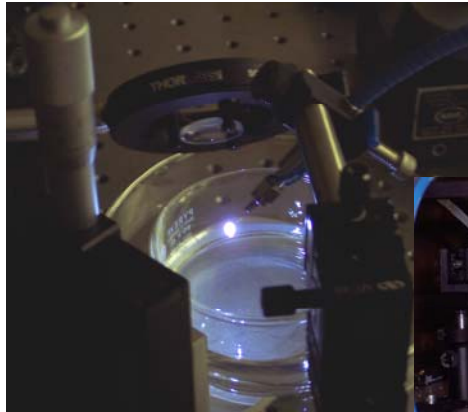


# Advantages of LIBS

lack of sample preparation – almost anything can be analyzed

- Almost unlimited applications and utility
- In my own lab we have tested:

- ✓ Water in bulk and in jets
- ✓ Pressed powders
- ✓ Alloys
- ✓ Gas mixtures
- ✓ Colloids in suspension
- ✓ Bacteria
- ✓ Vegetables
- ✓ Currency
- ✓ Foils and wires
- ✓ Solid metal rods
- ✓ Gelatins





RDECOM

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



(■ Solids ■ Liquids ■ Gases ■ Artificially prepared)

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

[www.arl.army.mil/wmrd/LIBS](http://www.arl.army.mil/wmrd/LIBS)

# Advantages for teaching

lack of sample preparation – almost anything can be analyzed

- Making / characterizing “standard samples” is an excellent undergraduate project



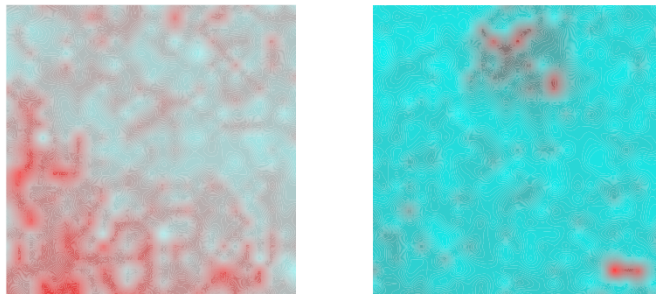


# Advantages of LIBS

## spatial resolution

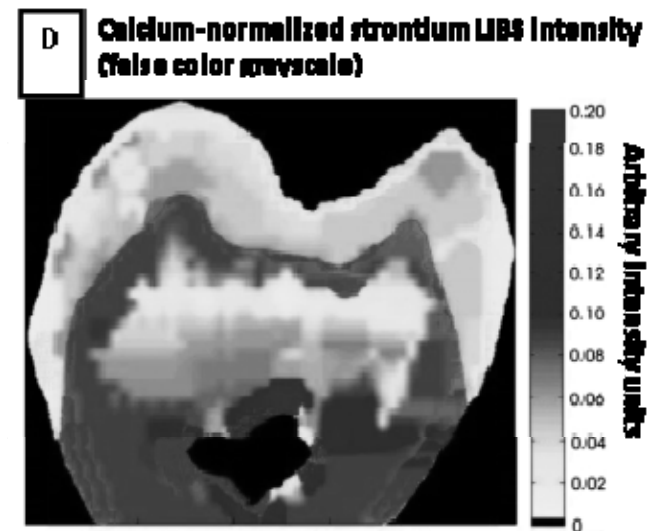
- Laser allows point sampling (1-100 micron)
- Elemental “surface maps” can then be created

COPPER impurities on Si wafers from two manufacturers



Total area imaged: 20 x 20 mm<sup>2</sup> Nd:YAG @ 532 nm  
Depth: ≈ 1 μm 1 pulse; 5 mJ pulse<sup>-1</sup>  
Lateral resolution: 750 μm WD = + 5 mm

Courtesy of Ben Smith, Javier Laserna



Courtesy of F.C. Alvira et al.

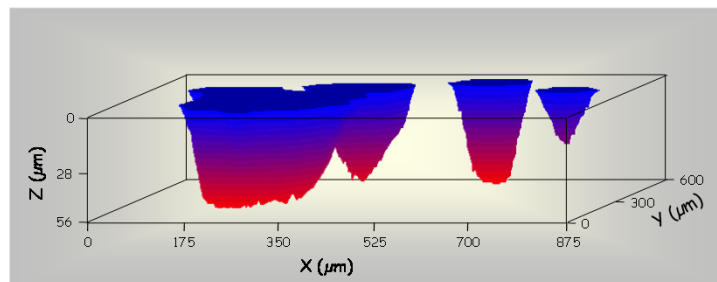


# Advantages of LIBS

## depth profiling

- Because laser only removes  $\mu\text{g}$  to  $\text{ng}$  of material, ablation crater only microns deep
- Subsequent shots thus sample progressively deeper layers

3-DIMENSIONAL MAP OF ALUMINUM INCLUSIONS



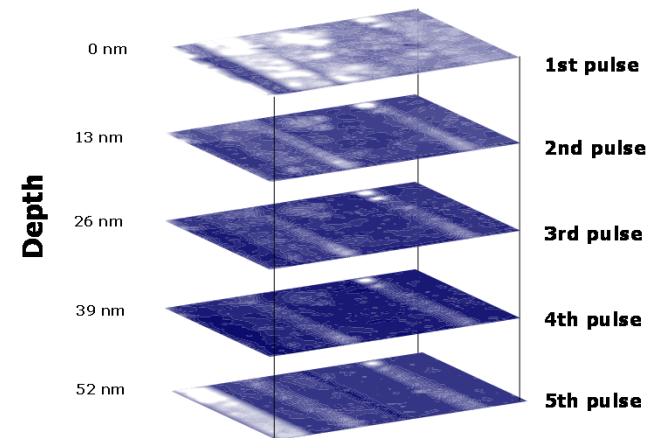
Courtesy of Ben Smith

- 13 positions
- 100 laser shots in depth
- Mapped volume =  $600 \times 875 \times 56 \mu\text{m}^3$
- Repetition rate = 10 Hz
- Analysis time = 2 min and 30 s

## TOMOGRAPHY

Carbon impurities on silicon wafers

Courtesy of Ben Smith



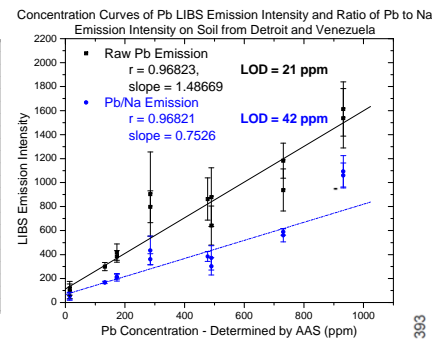
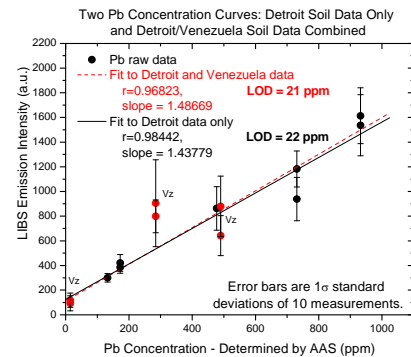
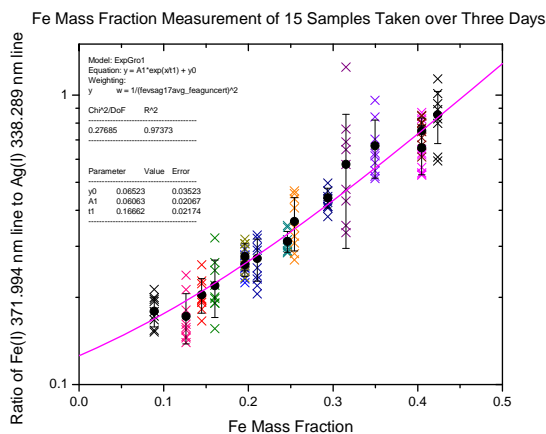
Nitrogen laser; Lateral resolution  $15 \mu\text{m}$ , sampling depth 13 nm



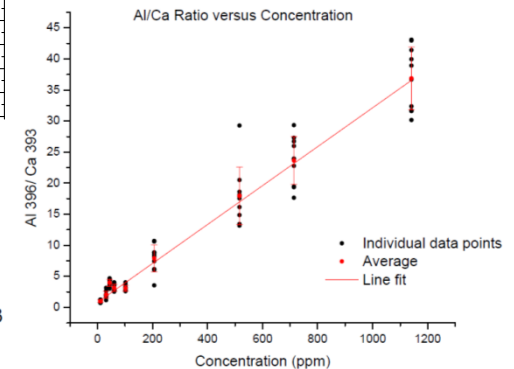
# Advantages of LIBS

## sensitivity

- Concentrations of 1-100 ppm usually detectable using a standard LIBS apparatus
- Other gold-standard techniques usually used to confirm results (ICP-MS, ICP-OES, AAS, etc.)



$R^2 = 0.89$   
 $s = 0.0313$



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



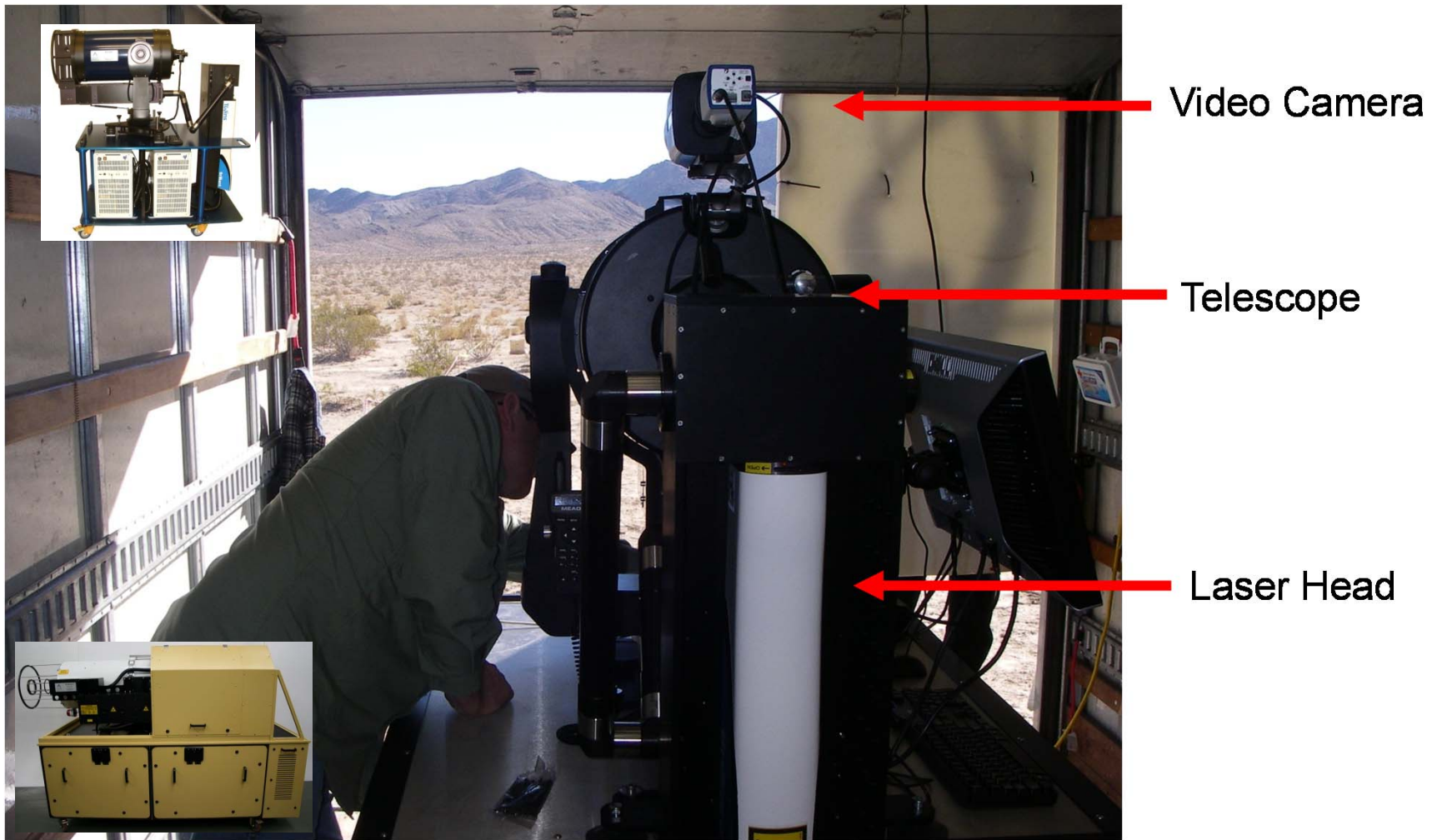
Head's-up display

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

Microplasma/ LIBS Event





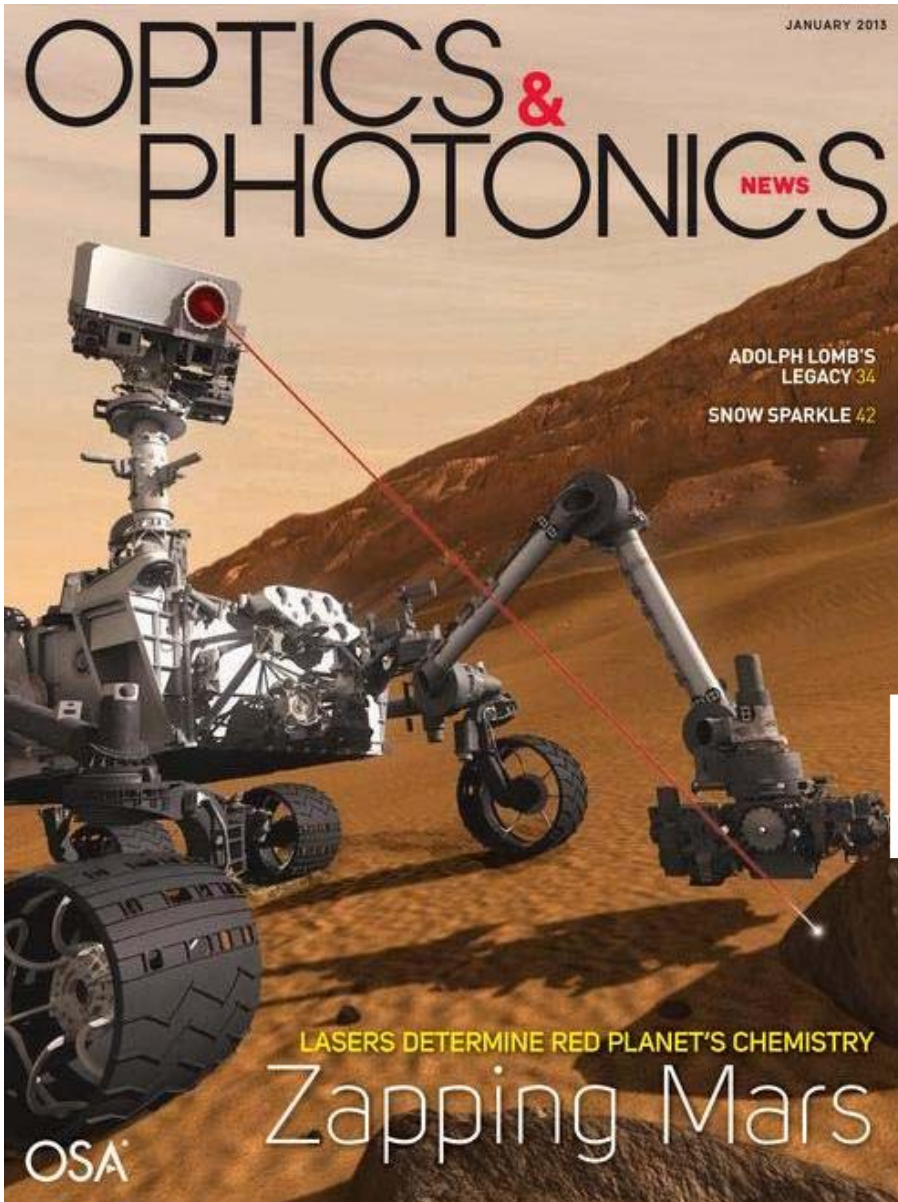


*Courtesy of A.J. Miziolek, A. Whitehouse*



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# The ultimate stand-off...



# Advantages for teaching

## lots of teachable entry points

- **Lasers**: design and operation, stimulated emission
- **Analytical chemistry**: standards, calibration curves, LOD's
- **Spectroscopy**: diffraction, resolution, spectrometers
- **Atomic physics**: ionization, plasmas, spontaneous emission, bremsstrahlung
- **Chemometrics**, data analysis, uncertainty propagation
  - Lots of good commercial computerized algorithms – almost never taught at the undergraduate level.



# Outline of Presentation

## 1. Advantages of LIBS

## 2. Applications of LIBS

Too many to list, but there are two broad classes of applications:

- Elemental quantification
- Sample qualification/identification



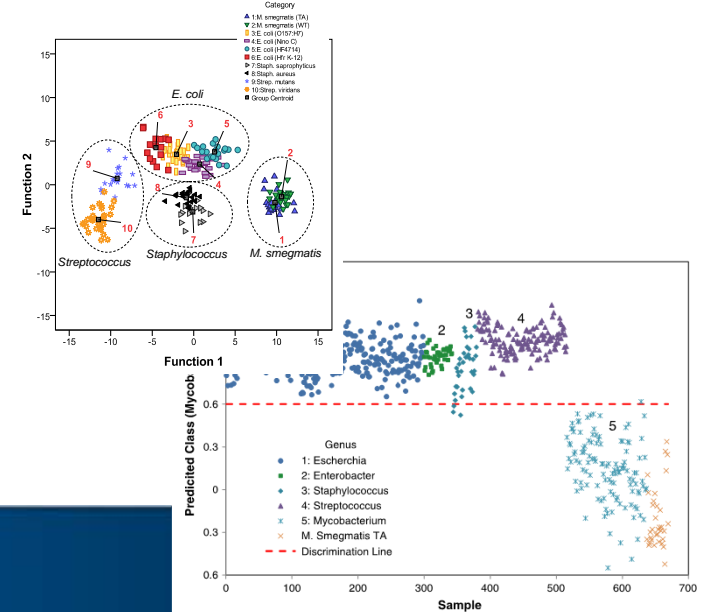
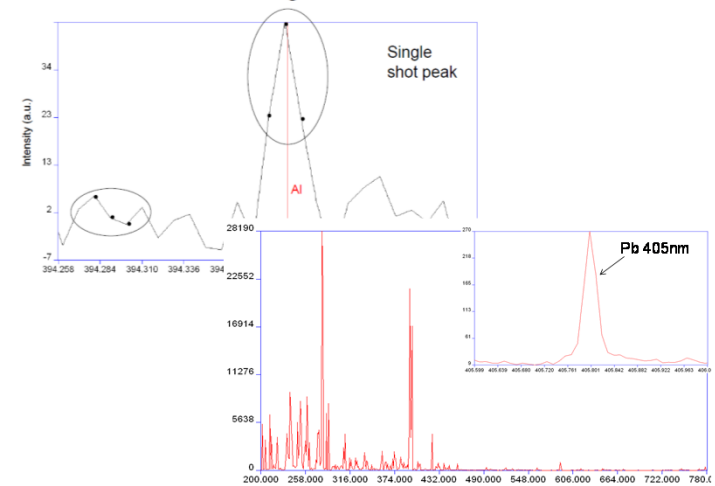


# Applications of LIBS

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

- Attempting to quantify the amount/concentration of some element by analyzing peak intensities
- Attempting to identify a target based on its unique elemental composition by analyzing the presence intensity of all/many lines

Criteria for seeing Aluminum:





# Elemental Quantification

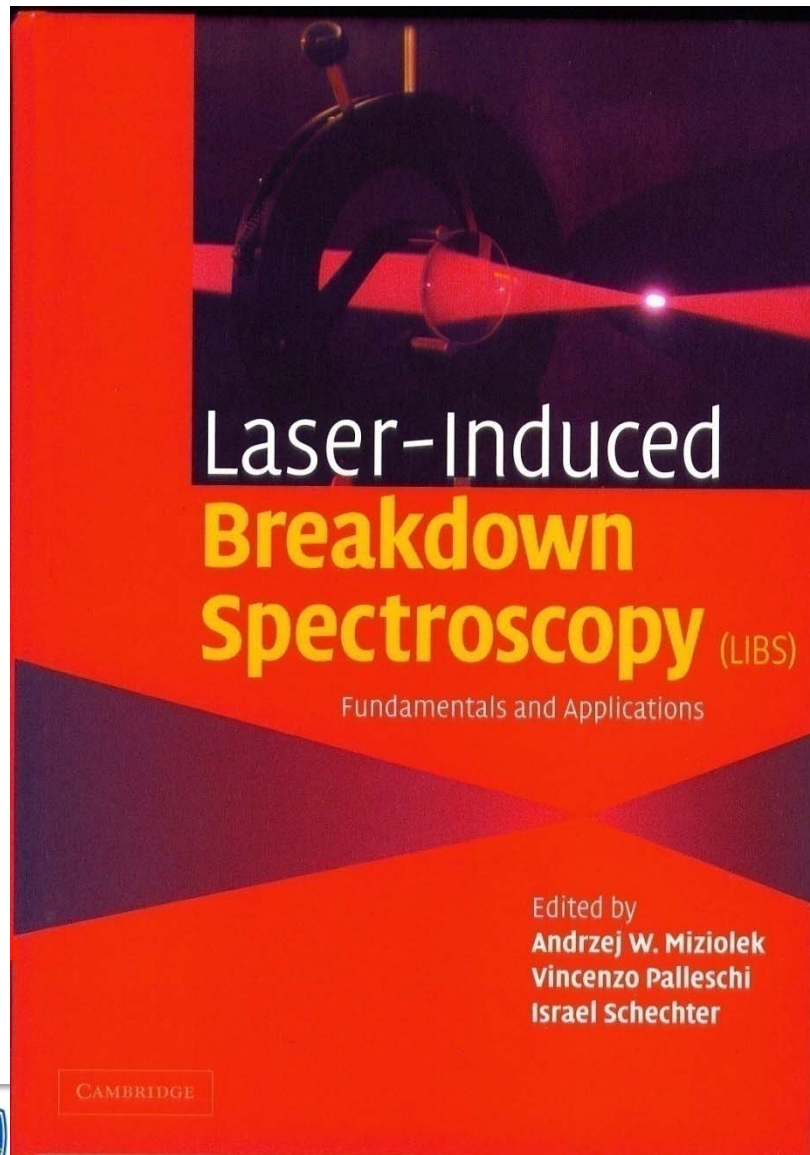
1. Decide on the problem/system to be quantified.
2. Determine if LOD's are appropriate for LIBS.
3. Develop a model system and acquire/construct a series of calibrated samples.
4. Construct calibration curves (identify optimized LIBS parameters, appropriate analytic lines, normalization lines, etc.)
5. Test “unknown” samples.
6. Confirm with gold standard assays.



# Sample Identification

1. Decide on the problem/system to be identified/classified.  
*Is it identification or a yes/no decision?*
2. Acquire/construct a large library of “known” representative samples from every class, with or without interferents.
3. Construct chemometric models (either supervised or unsupervised) based on the library of “known” samples.
4. Test the model with “unknown” samples. **IMPORTANT**, must NOT be part of the library constructed to build models.  
*Preferably not from samples made/acquired at same time as library.*
5. Construct truth tables, calculate sensitivity/specificity, or PPV/NPV.





# ***Laser Induced Breakdown Spectroscopy (LIBS) – Fundamentals and Applications***

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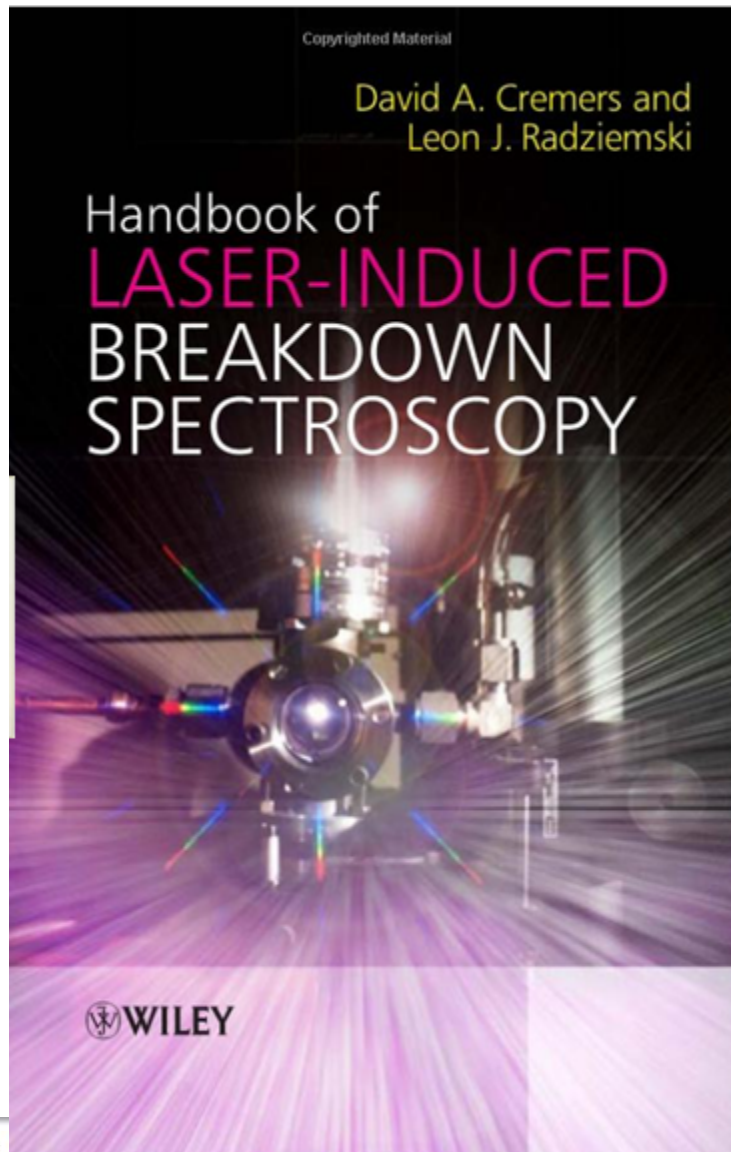
*Hardback (ISBN-13: 9780521852746 | ISBN-10: 0521852749)*

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**Cambridge University Press**



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## ***Handbook of Laser-Induced Breakdown Spectroscopy***

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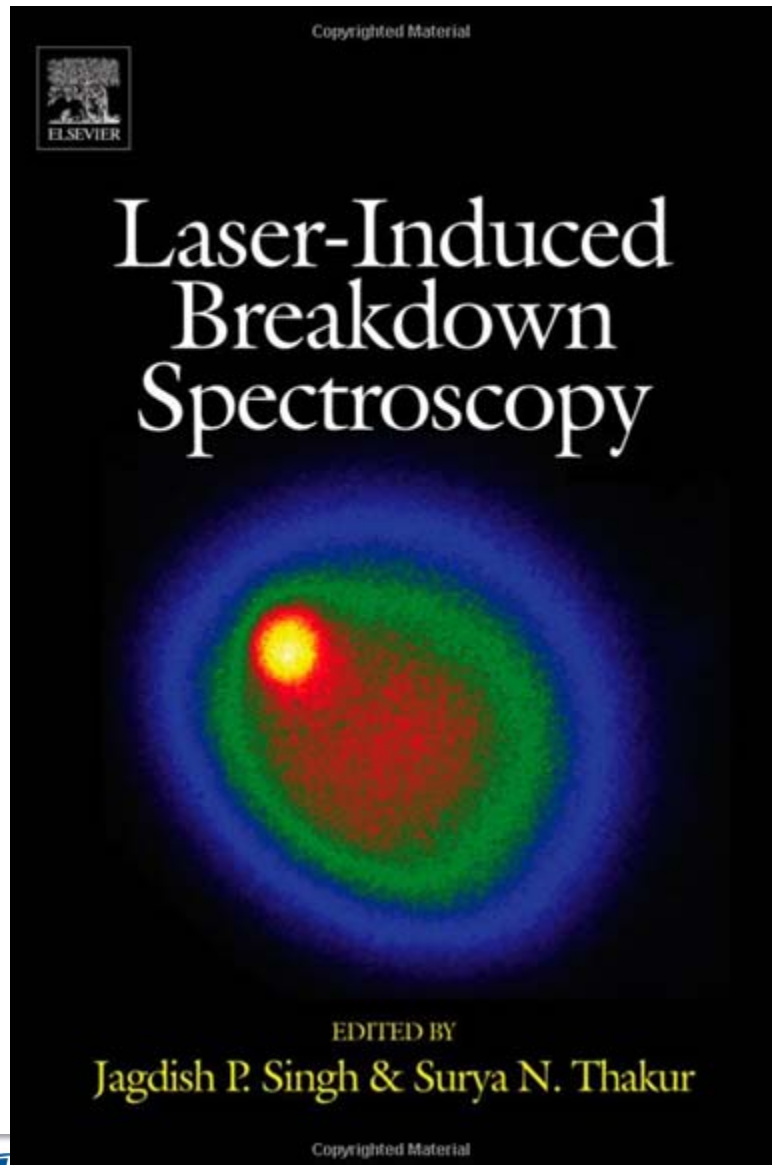
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## ***Laser-Induced Breakdown Spectroscopy***

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