The “Whys” of Using Laser-Induced Breakdown Spectroscopy

(advantages and applications)

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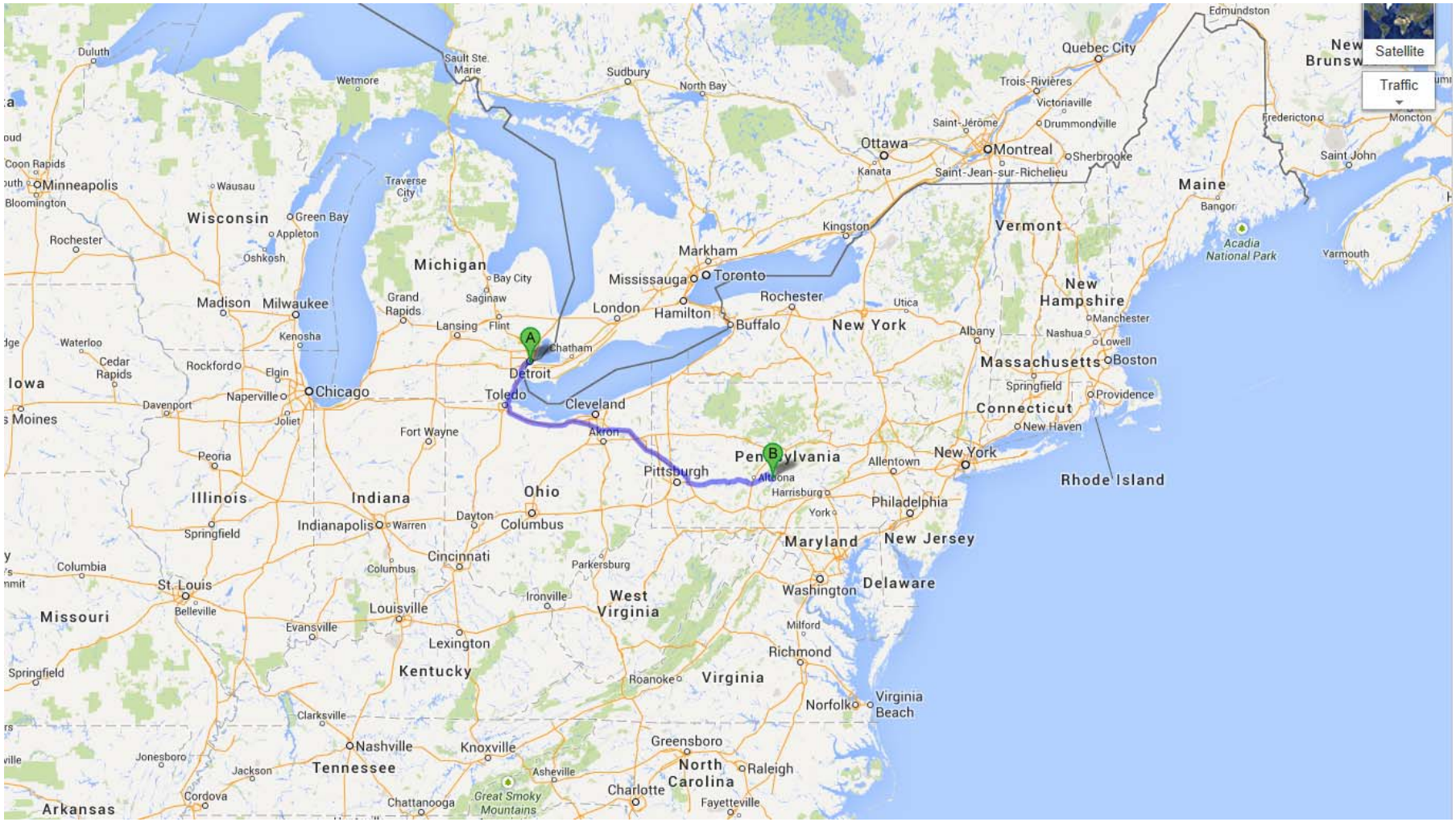
Windsor, Ontario, Canada

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

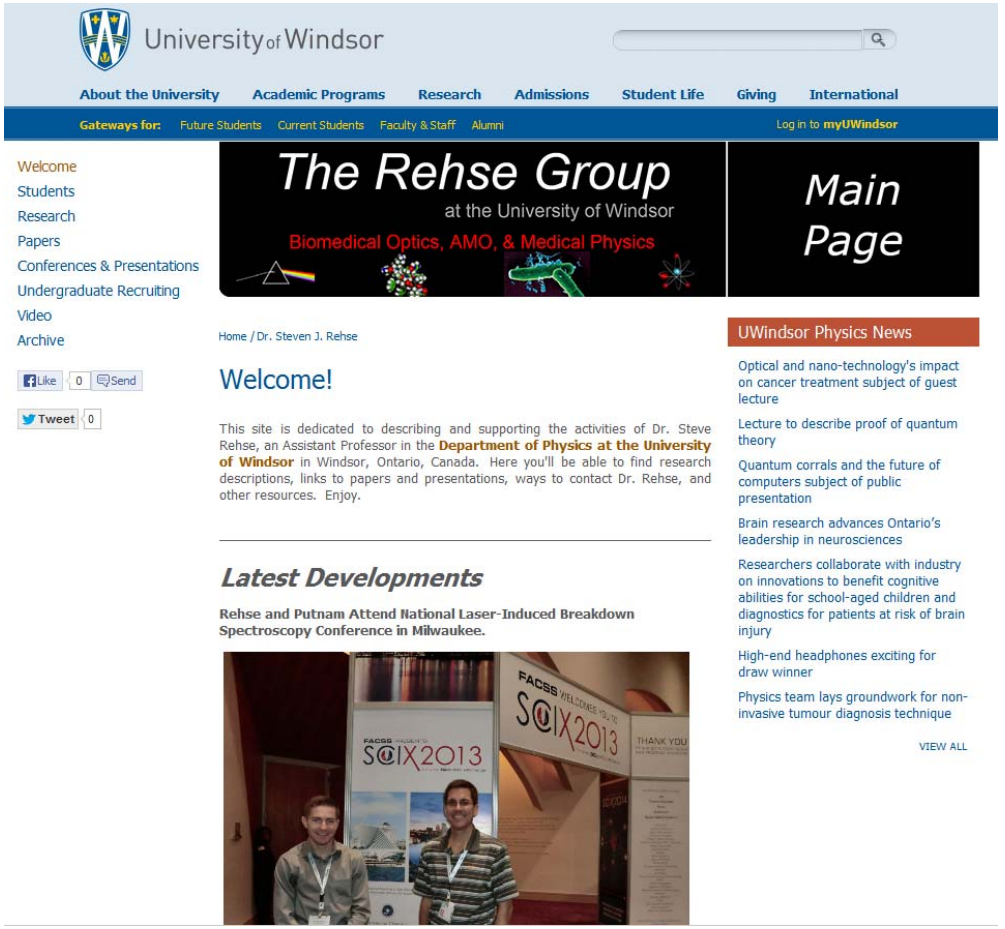
- The University of Windsor is a safe, urban campus covering 51 hectares (125 acres) in Windsor, Ontario.

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

Who Am I?

- 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)

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



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

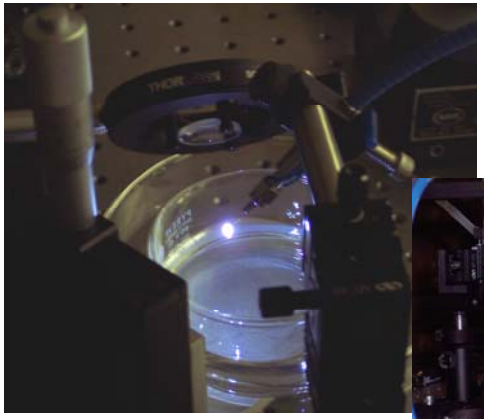
relative experimental ease

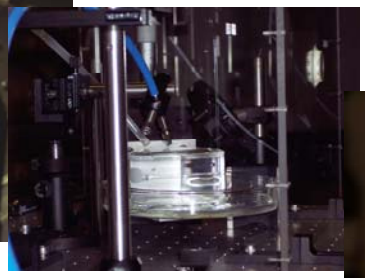
- I have had 2nd, 3rd, 4th year students running experiments.
- Day-to-day reliability is very good.
- Daily “turn-on” procedures are straight-forward.
- Unsupervised research possible after several training sessions.

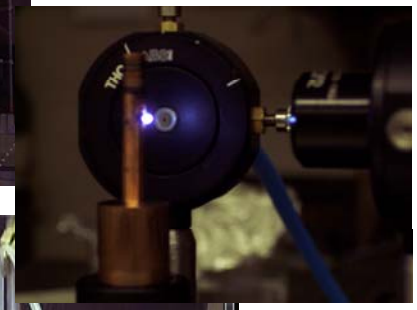
Advantages of LIBS

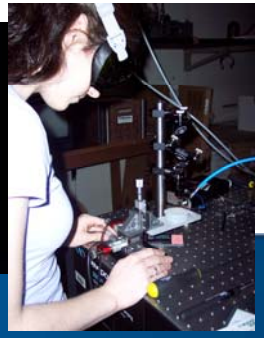
lack of sample preparation – almost anything can be analyzed

- 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









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 for teaching

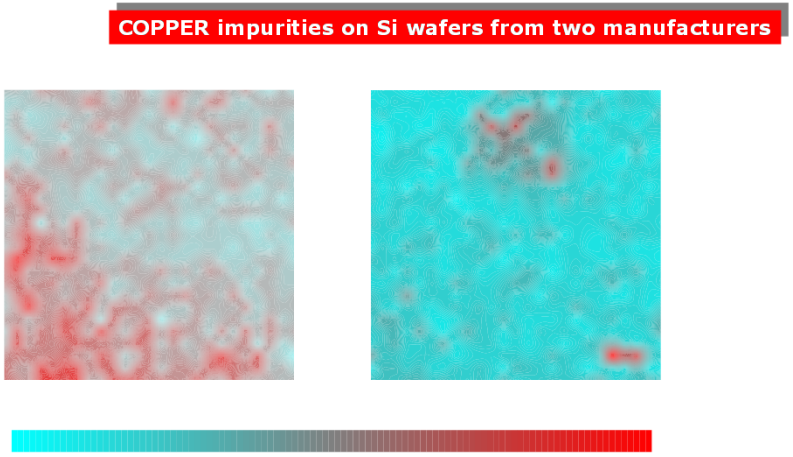
lack of sample preparation – almost anything can be analyzed

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

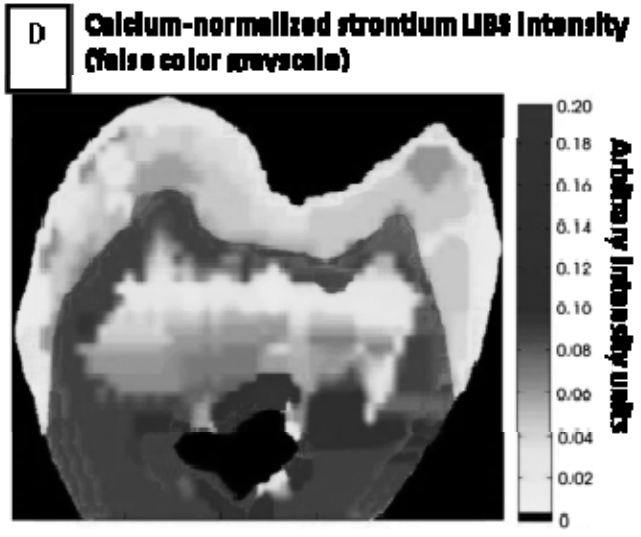
Advantages of LIBS

spatial resolution

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



Courtesy of Ben Smith, Javier Laserna

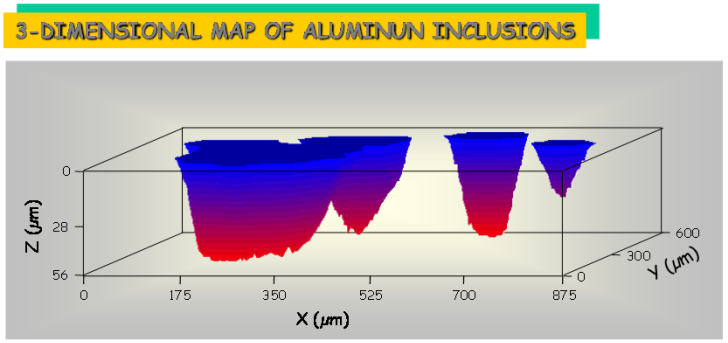


Courtesy of F.C. Alvira et al.

Advantages of LIBS

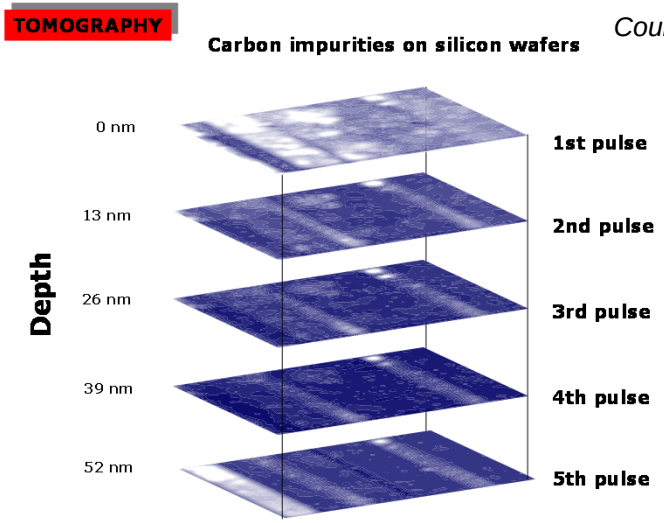
depth profiling

- 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



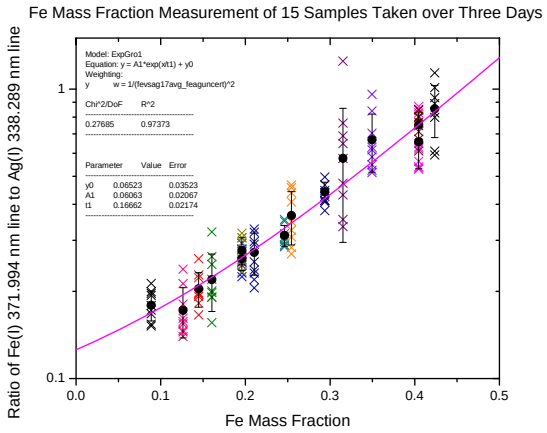
Courtesy of Ben Smith

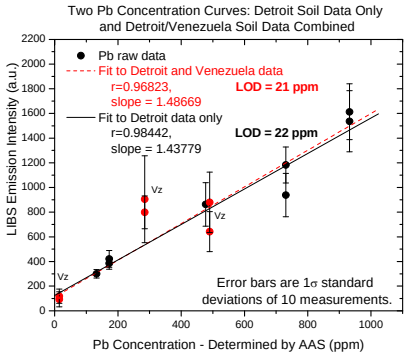
Nitrogen laser; Lateral resolution 15 μm, sampling depth 13 nm

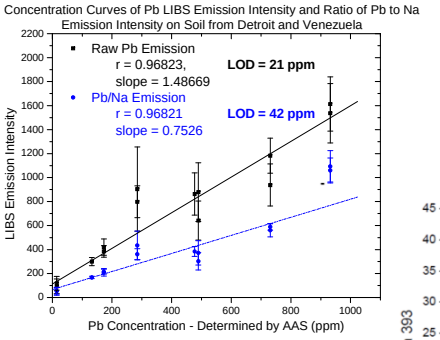
Advantages of LIBS

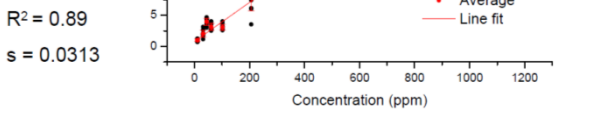
sensitivity

- 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.)









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…

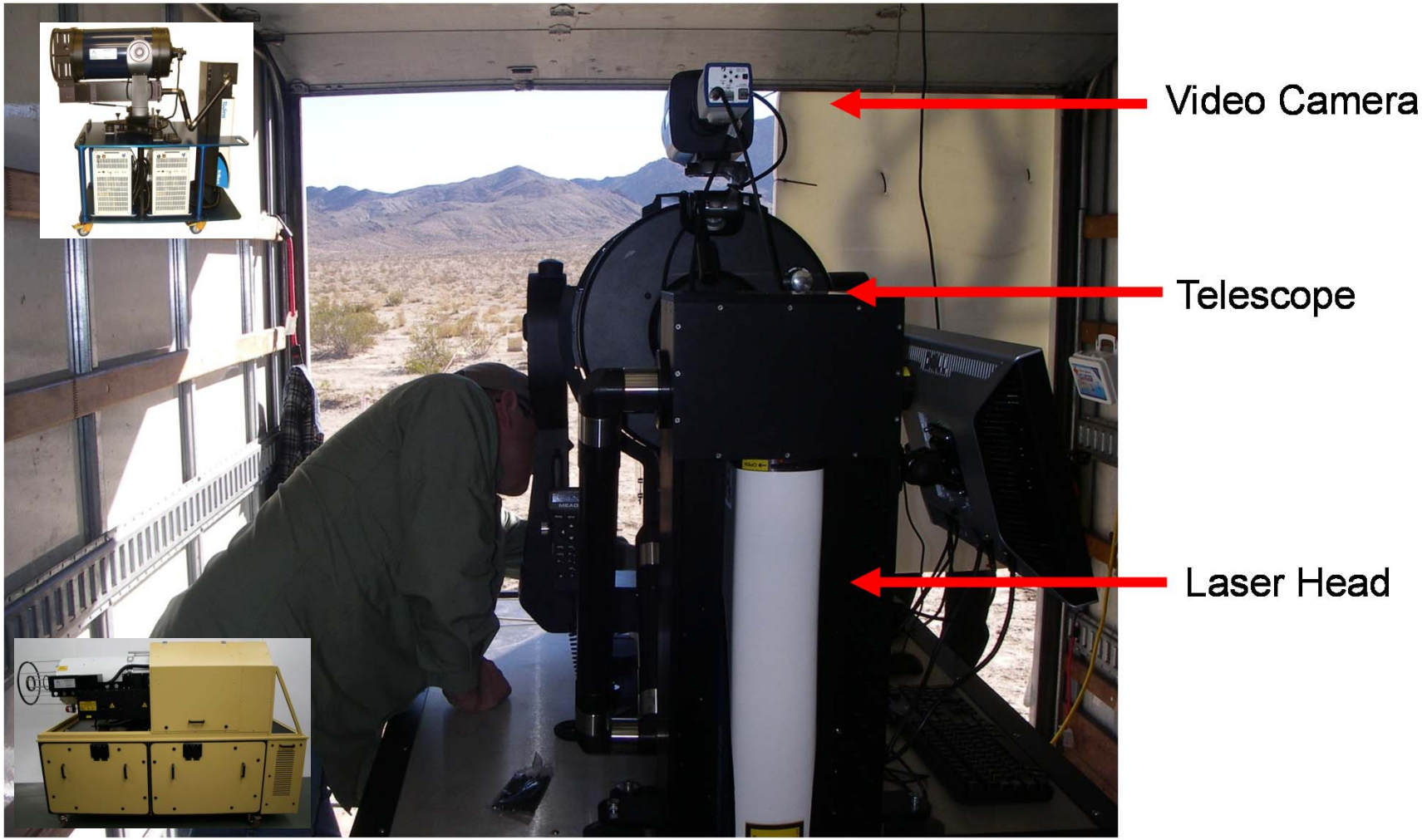
ad's-up display

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

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

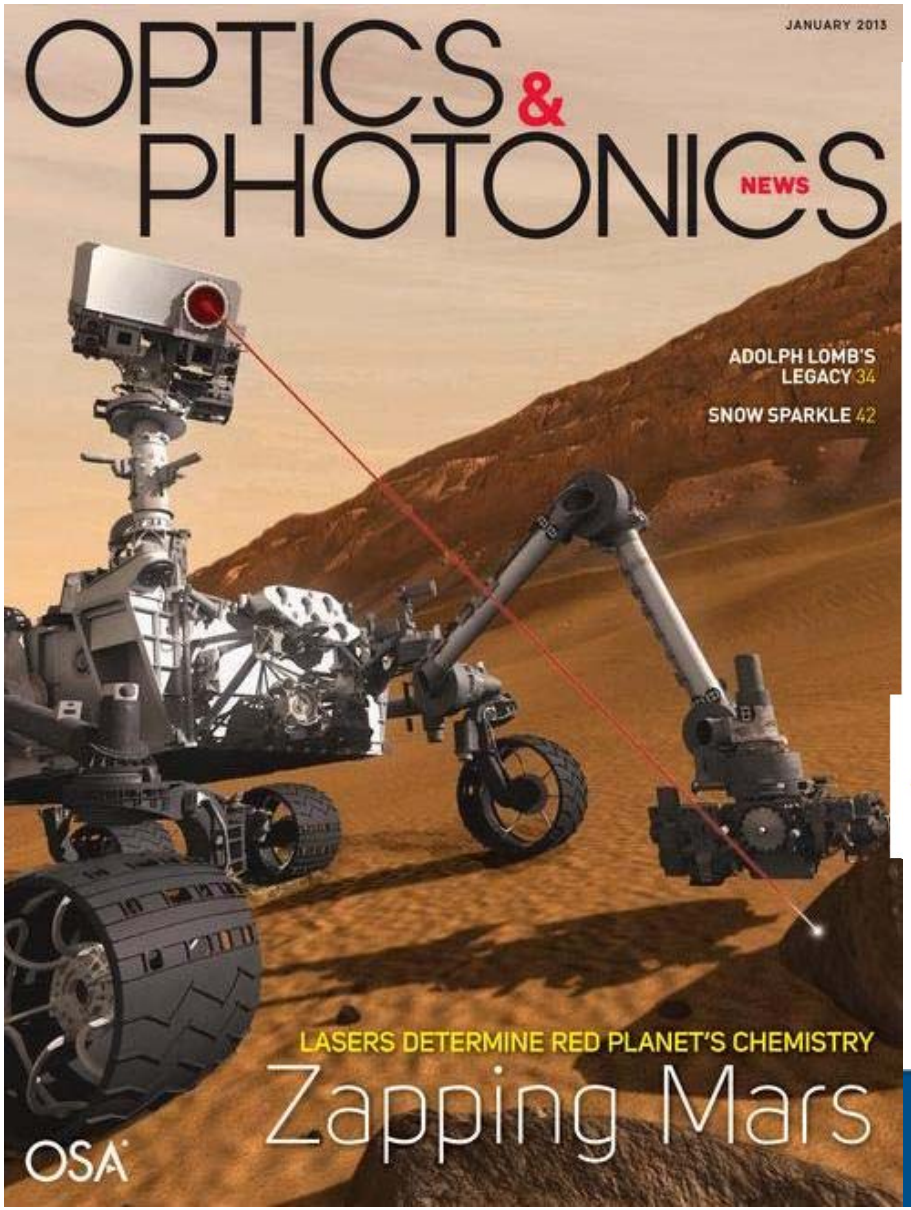
Microplasma/
LIBS Event

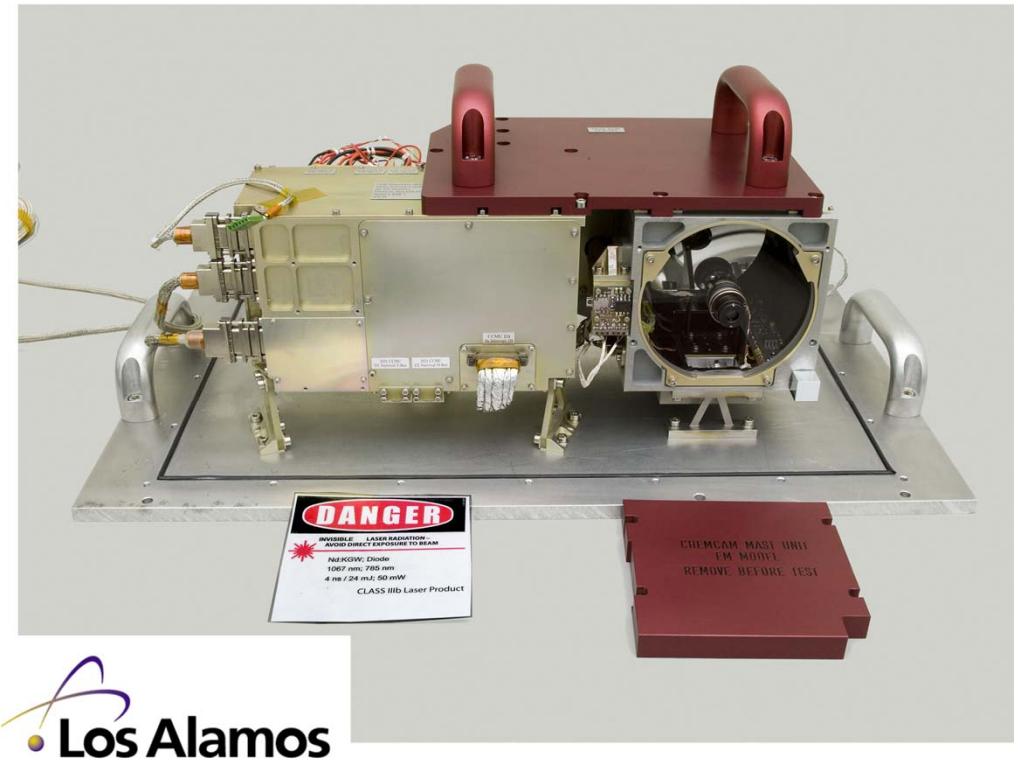
courtesy of Ocean Optics.



Courtesy of A.J. Miziolek, A. Whitehouse

The ultimate stand-off…





Los Alamos
NATIONAL LABORATORY

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

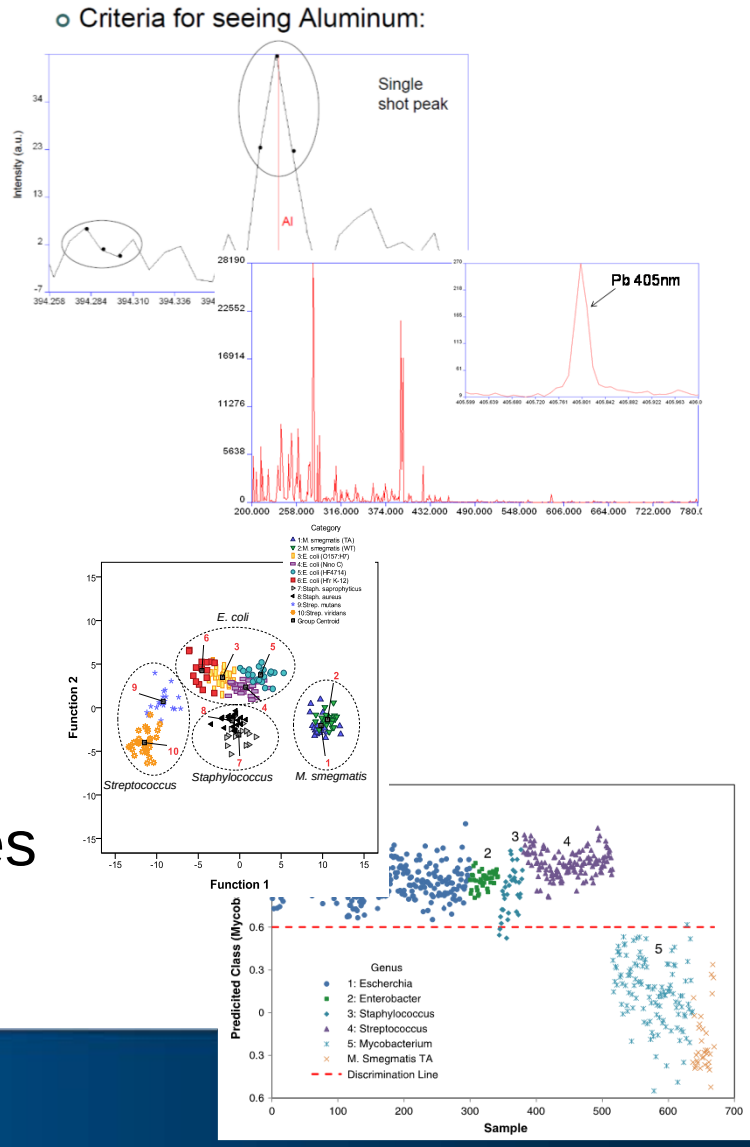
   Too many to list, but there are two broad classes of applications:

   - 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



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

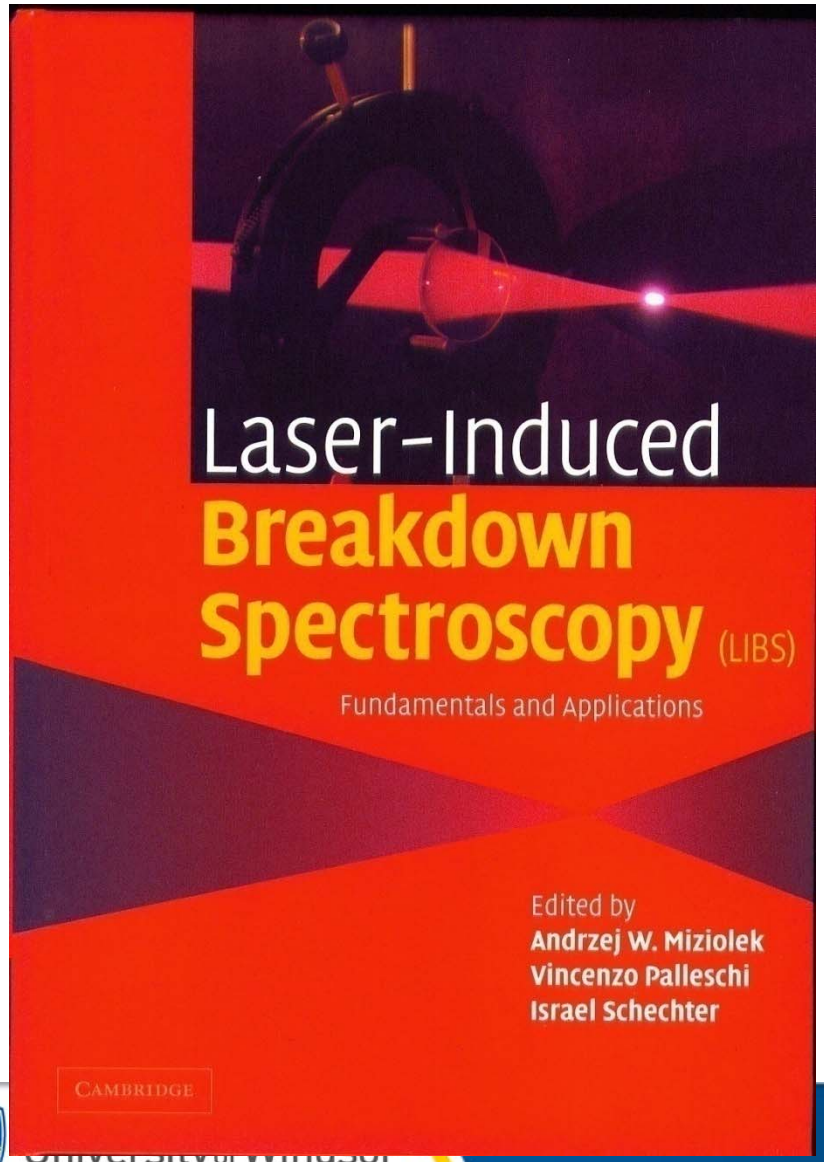
1. Decide on the problem/system to be identified/classified.

   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.



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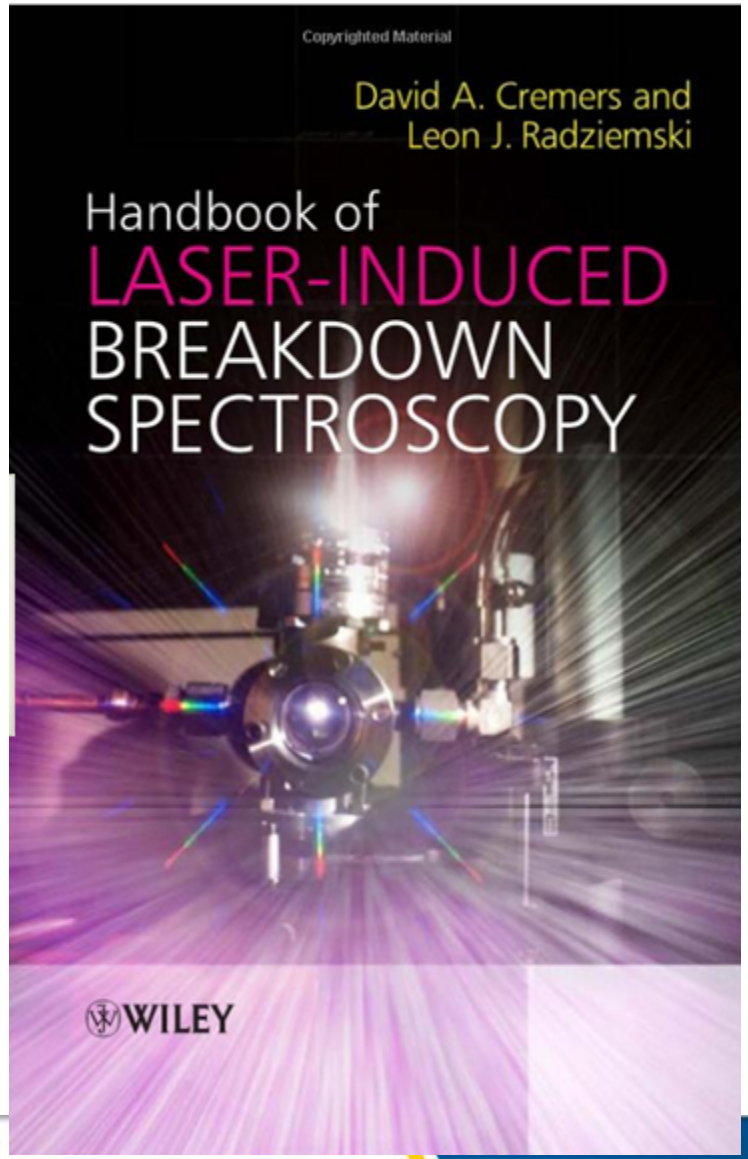

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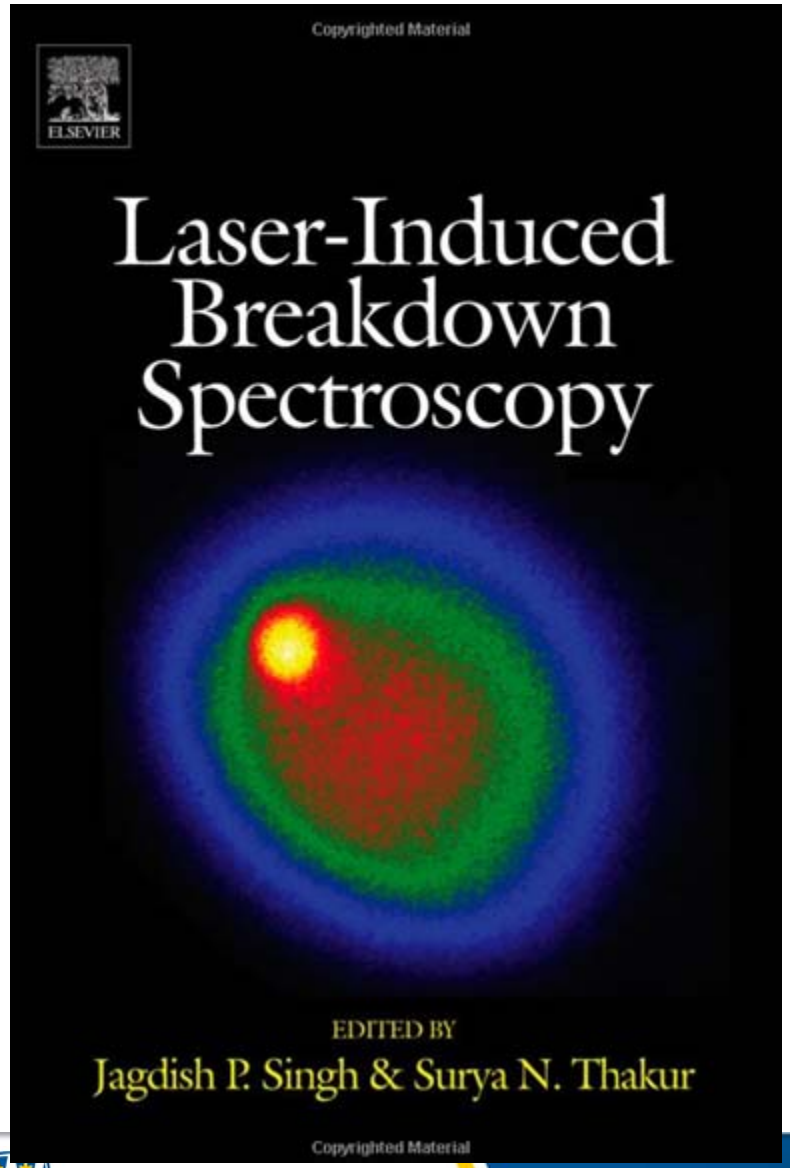

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