

Laser Induced Breakdown Spectroscopy (LIBS): Rapid Screening of Beryllium Surface Contamination

4th International Symposium on Beryllium Particulates and Their Detection
Wednesday October 3rd 2012

Mark Sutton, PhD



Co-authors:

Greg Klunder, LLNL

Rick Russo, Applied Spectra Inc., Fremont CA

LLNL-PRES-584153

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC



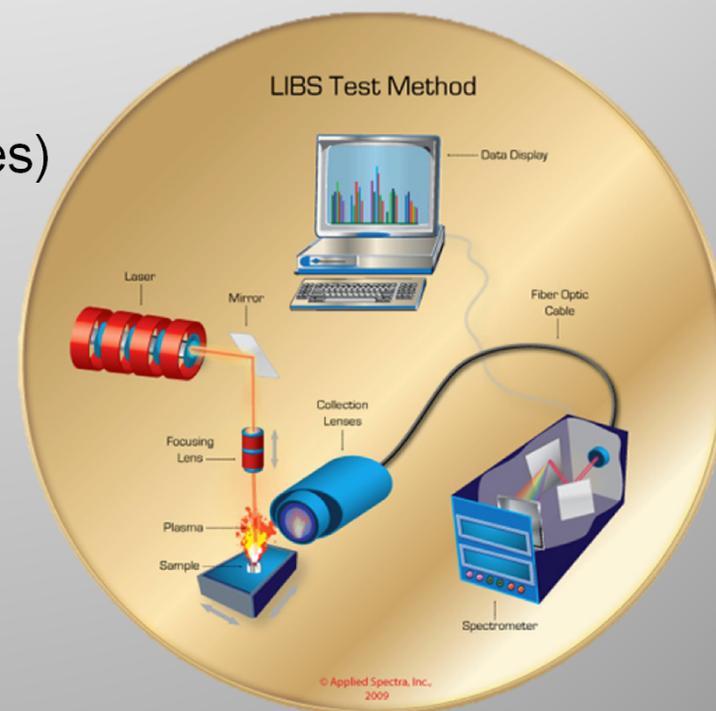
Laser Induced Breakdown Spectroscopy

- LIBS:

- High power laser pulse produces plasma at the analyte surface
- Analyte materials are vaporized and atomized/ionized
- Atomic/ionic optical emissions are measured with spectrometer

- Advantages:

- Discrete solid sampling (particles, swipes)
- Surface and depth profiling
- Direct solid multi-element analysis
- No sample digestion, no acid waste
- No additional wastes from operation
- Minimum sample mass (pg)
- Rapid throughput (10 sec/swipe)



LIBS Analysis of Be and IH Metals

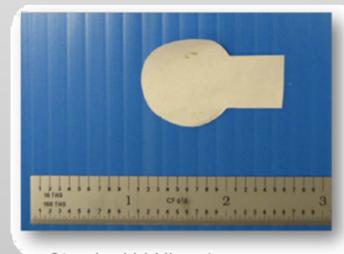
- This is nothing new:
 - Radziemski et al. (1983) first investigated beryllium analysis using LIBS with a LOD of 5 ng/g and a linear range of 0.5 to 20,000 ng/g.
 - LIBS systems have also been used to perform continuous emission monitoring of metals including beryllium (Lemieux et al. 1998).
 - Recently, LIBS has been used to demonstrate analysis of material collected on surface swipes (Chinni et al. 2010 and Klunder et al. 2010) typically with a detection limit of 2 ng per swipe.

LIBS Recent Improvements

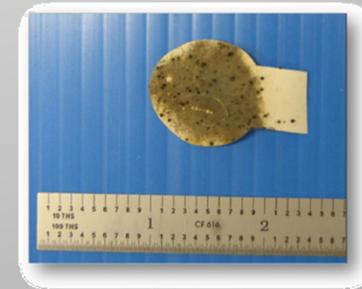
- Recent improvements to the commercial LIBS systems include:
 - Emission database/library
 - Auto focus for uneven/rough sample surfaces
 - Reduction in background/interference
 - Portability

LLNL 2010 Study

- A recent study included a collection of 17 blind facility swipes and 60 beryllium-spiked swipes, subjecting them to LIBS analysis using the Applied Spectra Inc RT-100HP and compared the data to on-site ICP-AES analysis of dissolved swipe material



- Standard LLNL swipe
- # 6144078
- LIBS and ICP-OES confirm negative for Be



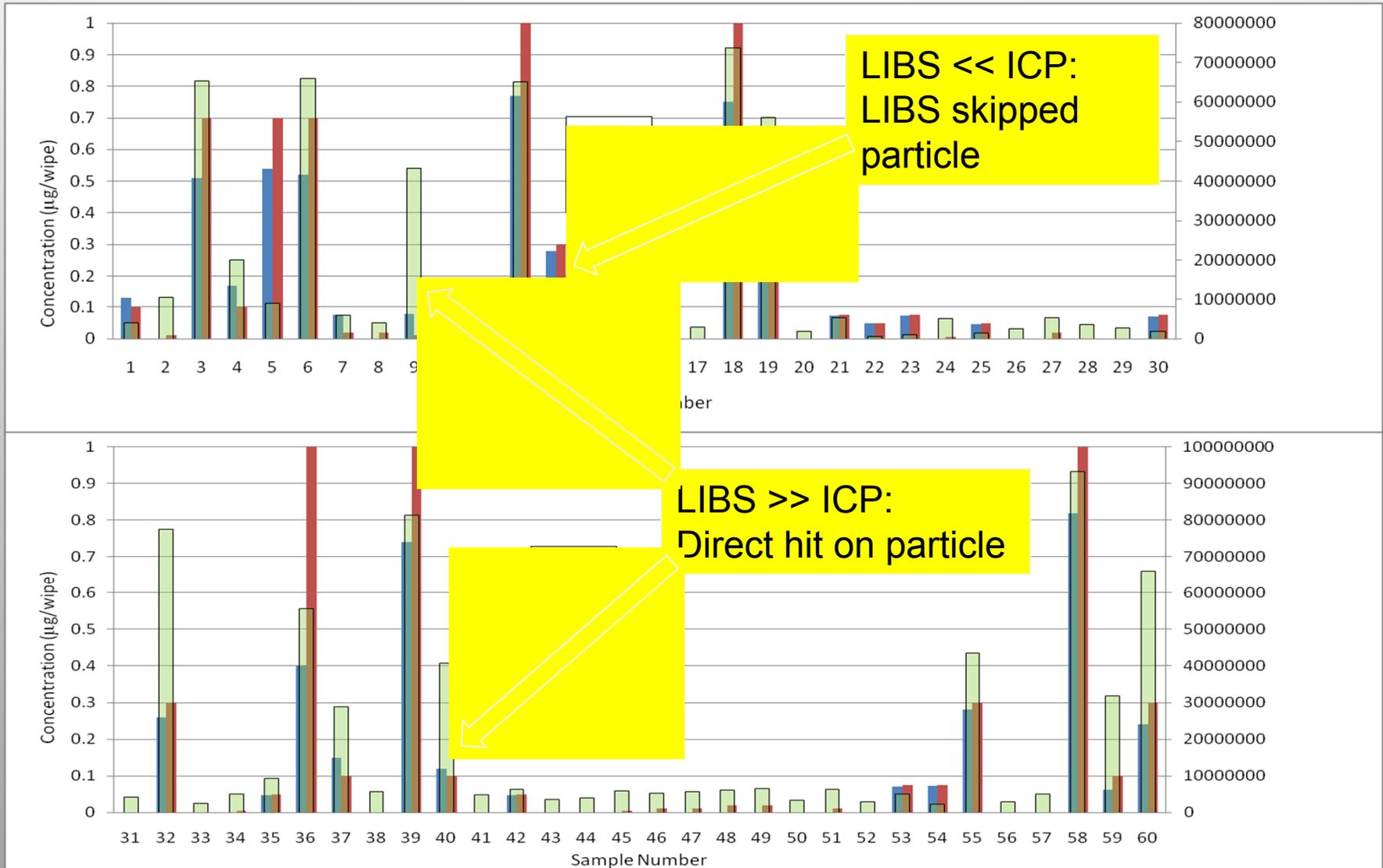
- Sample # 6144070
- LIBS and ICP-OES confirm positive of Be

LLNL 2010 Blind Tests

Sample Group	Locations Sampled	Positive Be Locations	Positive LIBS Be	ICP-AES Result, ug/cm ²
1	9	9	Yes	0.0026
2	10	10	Yes	0.00085
3	10	10	Yes	0.0026
4	9	6	Yes	<0.0002 (0.000038)
5	10	7	Yes	<0.0002 (0.000085)
6	3	3	Yes	0.0069
7	7	7	Yes	0.14
8	3	3	Yes	0.0028
9	3	3	Yes	0.018
10	18	9	Yes	<0.0002 (0.00016)
11	15	0	No	<0.0002
12	9	9	Yes	0.052
13	10	10	Yes	0.24
14	10	0	No	<0.0002 (0.000074)
15	5	3	Yes	0.0021
16	10	10	Yes	0.0071
17	15	0	No	<0.0002

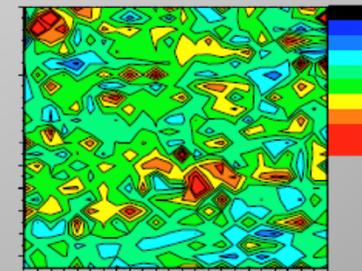
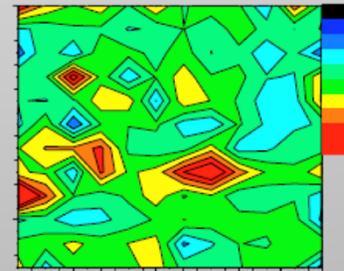
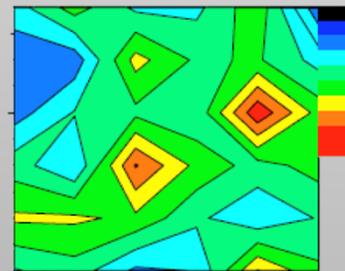
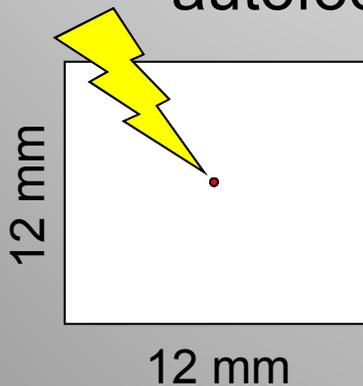
ASI and LLNL blind tests show 100% correlation between positive Be locations and positive LIBS Be signal

LLNL 2010 Be Spike Results



Laser Spatial Resolution

- As seen in the previous figure, small particles can be missed if the spatial resolution of the laser on the surface is not fine enough
- This becomes a trade-off between sampling completeness and analysis time
- For 300 μm diameter spot, 3 pulses/location, autofocus on, 144 mm^2 swipe area:



Determining Spatial Resolution

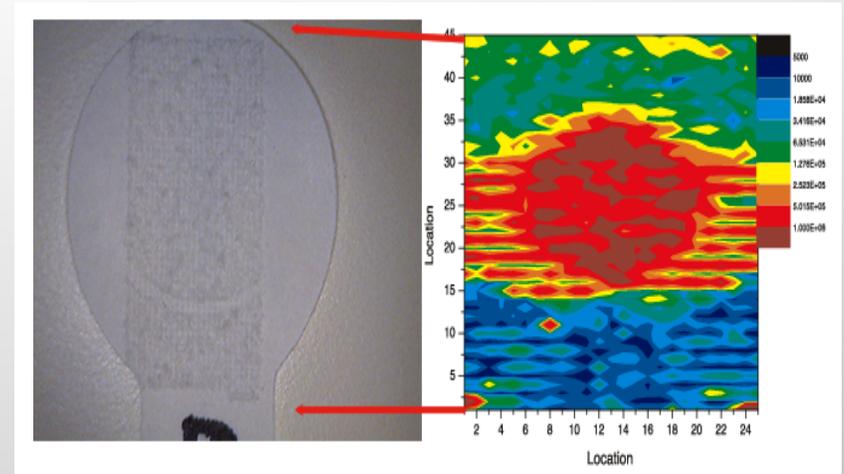
- For bulk samples with little concern of beryllium in the respirable range (larger debris), the spatial resolution may be such that minimizes analysis time
- For samples from facilities with likelihood of beryllium particles in the respirable range (e.g. BeO powder), the spatial resolution may be such that micron-sized particles are visible to LIBS
 - However, if resolution is too high, no Be remains for ICP
 - Statistical analysis is needed to determine optimum resolution
- LIBS can be used to screen samples in IH lab, reducing workload on ICP systems that require complete digestion of swipe and debris

Beryllium Particle Example

- Hoover (1989) BeO particles max 4.6 microns had density of 1.9 g/cm³
- Simplistic calculation (best case scenario):
 - Radius: 2.3 μm; therefore volume of a particle: 5.10E-11 cm³
 - Mass of particle: 97 pg; compare to RC of 0.2 ug/100 cm²
 - Number of particles/100 cm² needed to exceed RC: 2,065
 - Assume all particles are transferred from the 100 cm² surface to a 100 mm² wipe: 2,065 particles on wipe surface; assume even, monolayer distribution
 - Equates to 1 particle every 220 microns; Beam spot size diam: 300 microns
 - Should see at least 1x particle per shot if > RC and if LOD < 0.1 ng Be
- However, clumping and multi-layer particles (which are realistic) make hitting with laser Be less likely.
- Need bigger spot size – mapping Be on surface is not important, finding Be on surface is important!

Pattern/Grid Evaluation Study

- Comprehensive LIBS analysis of BeO spiked wipes
 - ‘Truth’, analysis of entire wipe area
 - 300 micron spot size
 - Minimal spacing
- Enables any pattern/array to be evaluated
- Evaluate 3 different concentrations
- Spot Size
 - Currently use 300 micron diameter, laser 1064 nm 90mJ
 - 200 mJ lasers available 500 micron spot size achievable



Interferences and Alternate Lines

- Spectral resolution
 - Bandwidth of detection 0.08 nm
 - Overlap from saturated channels
- Alternate Be (I) line, 332.134 nm
 - 10% of primary line, 313.042 nm
 - Extend dynamic range

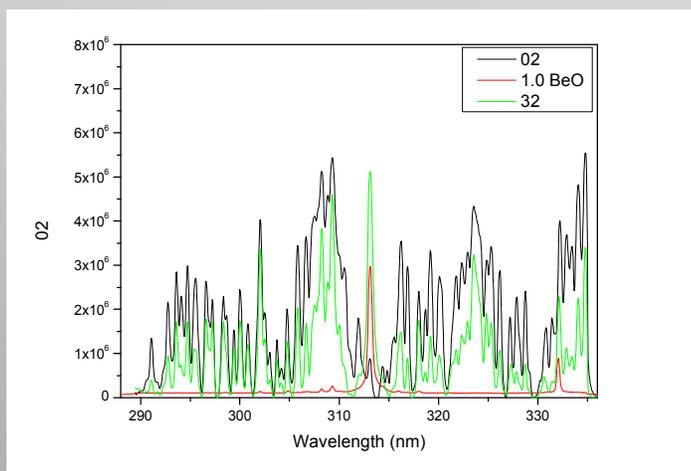


Table 1
Potential spectral interferences for Be determination by ICP-AES^a

Analyte	Peak (nm)	Intensity
U	312.879	6.0
Zr	312.917	400.0
Nb	312.964	22.0
U	312.973	15.0
Zr	312.976	550.0
Th	312.997	10.0
V	313.027	1020.0
Ce	313.033	50.0
U	313.056	6.0
U	313.073	0.0
Nb	313.079	2200.0
Ti	313.079	150.0
Ce	313.087	65.0
Th	313.107	27.0
Tm	313.126	Not listed
U	313.132	8.0
Hf	313.181	20.0
U	313.199	15.0
Cr	313.206	1000.0
Zr	313.207	7.0
Th	313.226	5.0
Mo	313.259	1800.0
Ce	313.259	30.0

^a As listed in PerkinElmer WinLab32 software v.2.0.

^b Commonly used peaks for determining beryllium by ICP-AES.

Cost Benefit

- ICP-AES analysis at LLNL
 - 4 full time operators, 3 instruments
 - 40,000 samples per year
 - Sample prep
 - Total swipe digestion
 - 25 mL acid per sample (1000 L/year)
 - Argon to run the instrument
- LIBS
 - 10 samples/hour for 1 operator and 1 instrument
 - 400 samples/week, 20,000 sample/year
 - No additional waste
 - No sample prep
 - Reduce ICP workload by 50% = save \$160,000/year (\$80/sample)

Observed Problems

- Gain provides low-end sensitivity but also results in high-end saturation
- Samples need to be dried before analysis
- Standard acetate wipes perforated by one laser pulse
- Matrix effects complicate quantitation based on calibration curves

Summary

- LIBS can detect Be on wipe samples at the levels required
- Analytical protocols can address more comprehensive wipe sampling
- Matrix effects can effect the background signal
- LIBS analysis does not consume all the sample
- Essentially non-destructive
- Subsequent ICP analysis for confirmation
- LIBS can be an effective screening tool to reduce costs, waste and improve surveillance

References:

- Chinni et al. (2010) “Analysis of materials collected on swipes using laser-induced breakdown spectroscopy” *Applied Optics* 49 (13): C143-152
- Lemieux et al. (1998) “Results of the September 1997 DOE/EPA demonstration of multimetal continuous emission monitoring technologies” *Waste Management* 18: 385-391
- Klunder et al. (2010) “Analysis of Beryllium Wipe Samples by Laser-Induced Breakdown Spectroscopy (LIBS) – An Update” LLNL presentation to BHSC meeting, November 4th, 2010
- Radziemski et al. (1983) “Detection of beryllium by laser-induced-breakdown spectroscopy” *Spectrochimica Acta* 38B (1/2): 349-355

