Application of handheld laser-Induced breakdown spectroscopy (LIBS) to develop quantitative calibration curves for the analysis of heritage copper alloys

Elizabeth Coquillette[1], Richard Hark[1,2], Anikó Bezur[1]

[1] Yale University Institute for the Preservation of Cultural Heritage, New Haven, CT; [2] Juniata College, Huntingdon, PA

Background

- Handheld laser-induced breakdown spectroscopy (LIBS) is well suited for analysis of archaeological artifacts in the field because it is portable, requires little or no sample preparation, has good spatial resolution, consumes only micrograms of sample, and can be used to remove surface corrosion to provide depth profiling for a variety of materials.
- LIBS excels at qualitatively identifying all elements (H through U) in a sample, with the level of detection for higher Z elements comparable to or lower than portable XRF. However, quantitative analysis is a more complex undertaking.

Research Objectives

The goals of this study were to:

1. determine optimal data collection parameters for the LIBS instrument
2. determine optimal data normalization method
3. create and evaluate calibration curves for several elements

with the ultimate aim of enhancing the utility of handheld LIBS for analysis of copper-containing artifacts.

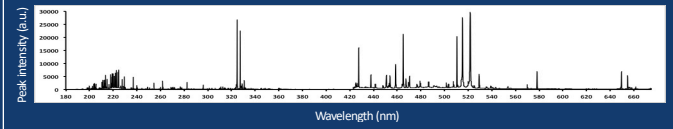
Materials

- LIBS unit used was handheld SciAps Z-500, with wavelength 1064 nm; spectral range 180-675 nm; beam size 50-100 μm; pulse duration 1-2 ns; power per pulse 5-6 mJ; sampling rate set at 10 Hz
- Primary sample material was 14 copper-alloy standards in the Cultural Heritage Alloy Reference Material (CHARM) Set

Methods

- Data collected with 3 cleaning shots and 10 data shots per location, averaged into a single spectrum for analysis
- Five locations tested on each sample, using a 1x5 grid pattern with 500 μm spacing
- Spectral lines were chosen for analysis based on both data observation and literature precedent

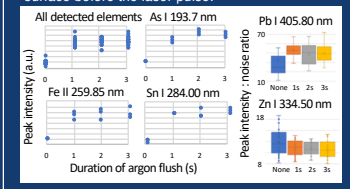
LIBS spectrum for CHARM sample 36XCUAS4, 180-675 nm, averaged of 10 data shots from a single location



Results Part 1: Parameter Optimization

1. Argon flush

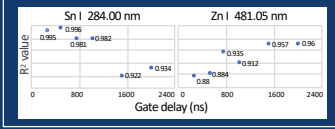
The usage and duration of argon purging of the surface before the laser pulse.



- Argon usage improved both peak intensity and signal : noise ratio
- Extending flush duration had negligible impact on overall results
- **Conclusion:** argon flush should be used, and a 1s duration is sufficient to optimize results

2. Gate delay

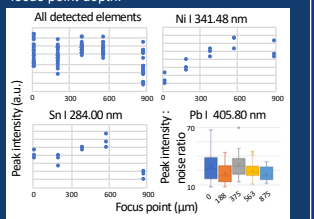
The length of time between the laser pulse and the activation of the spectrometer detector.



- Results varied among individual elements
- Best compromise was 750 ns
- Optimal results might be better obtained by adjusting gate delay to target specific elements
- **Inconclusive**

3. Laser focus

Distance of laser focus above maximum focus point depth.



At value 0 µm, the laser focus is at its maximum depth below the surface (~0.5mm). At larger values the laser focus is closer to the laser source.

- Increasing focus point value (decreasing focus depth) caused variation in peak intensity but not in signal : noise ratio
- **Conclusion:** optimal focus depth is around 560 μm

Results Part 2: Calibration Curves and Normalization

1. Linear regressions

Relates measured signal magnitude and known element content, with the intent of getting quantitative information from otherwise qualitatively analyzed spectra.

- Used 24 wavelengths, covering 10 total elements.
- 10/10 elements had at least one valid (R^2>0.85) line
- 5/10 elements had at least one very good (R^2>0.95) line

Element	Line (nm)	R^2
Ag I	328.07	.814
	338.29	.926
Al I **	394.40	.947
	396.15	.958
As I *	189.00	.819
	193.70	.851
	278.00	.556
Bi I	306.77	.953
Fe I	358.12	.883
Fe II	259.85	.467
Mn I *	259.50	.886
	403.40	.929
	482.35	.704
Ni I *	341.48	.941
	352.45	.925
Pb I	364.00	.967
	368.35	.962
	405.80	.960
	560.90	.980
Sn I	270.65	.664
	284.00	.980
	286.33	.989
Zn I	334.50	.992
	481.05	.936

1.0 > R^2 > .95 N= 9
.95 > R^2 > .90 N= 6
.90 > R^2 > .80 N= 5
.80 > R^2 > .50 N= 4

* Highest content value omitted
** Two highest content values omitted

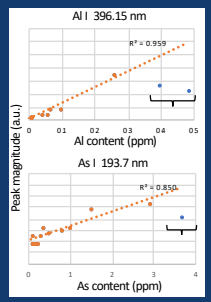
Sorted by wavelength:

Element	Line	R^2
As I *	189.00	.819
As I *	193.70	.851
Mn I *	259.50	.886
Fe II	259.85	.467
Sn I	270.65	.664
As I *	278.00	.556
Sn I	284.00	.980
Sn I	286.33	.989
Bi I	306.77	.953
Ag I	328.07	.814
Zn I	334.50	.992
Ag I	338.29	.926
Ni I *	341.48	.941
Ni I *	352.45	.925
Fe I	358.12	.883
Pb I	364.00	.967
Pb I	368.35	.962
Al I **	394.40	.947
Al I **	396.15	.958
Mn I *	403.40	.929
Pb I	405.80	.960
Zn I **	481.05	.936
Mn I *	482.35	.704
Pb I	560.90	.980

- Six lowest wavelengths (<280 nm) were in bottom 7 R^2 values
- Single ionic line tested (Fe II 259.85) had worst result
- Suggests limiting choices to atomic lines above 280 nm

2. Region of linearity

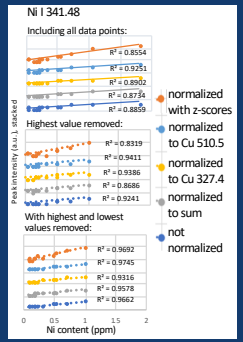
- Peak intensity often began to decrease at highest content levels
- Attributable to self-absorption at high levels of signal



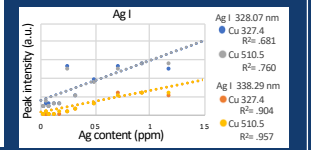
- **Conclusion**: many lines only apply within limited region of linearity
- For 3 elements (Al, As, Mn), a valid regression line could only be achieved with the highest 1-2 content values removed (shown in blue on the graphs)

3. Normalization methods

- LIBS signal strength can vary between shots, necessitating data normalization



- **Conclusion**: normalizing to the Cu 510.5 line gave the best overall results
- Cu-based normalizations were always the most accurate and stable
- Z-score normalization gave particularly poor and inconsistent results
- The Cu 510.5 line was consistently equivalent to or better than the Cu 327.4 line



4. Testing on external samples

Calibration lines were tested using

- 9 additional copper-alloy reference samples (CDA & NIST)
- 18 ancient Peruvian metal fragments, with compositions previously determined using electron microprobe analysis

Conclusion:

- External comparisons were inconsistent at best
- Indicates that the calibrations lose validity when testing outside CHARM Set

Example regression test results:

Key
Within +/- 10%
Within +/- 20%
Within margin of error
Outside margin of error

Ni I 341.48 nm
R^2 .925
Margin of error +/- 0.13 ppm

SRM I.D.	Known (ppm)	Predicted (ppm)
C1253a	0.049	0.186
C1101	0.013	0.042
C1252a	0.013	0.193
C1251a	0.002	0.270
CDA 510	bdl	0.163
CDA 260	bdl	0.128
CDA 110	bdl	0.049
CDA 464	bdl	-0.005
CDA 360	bdl	-0.065

Zn I 334.50 nm
R^2 .992
Margin of error +/- 0.80 ppm

SRM I.D.	Known (ppm)	Predicted (ppm)
CDA 464	36.7-40.2	41.762
CDA 360	32.95-37.15	31.354
C1101	30.300	33.515
CDA 260	27.38-31.38	43.365
C1253a	0.033	-0.705
CDA 510	0.30 max	0.144
C1252a	0.007	-0.720
C1251a	0.002	-0.620
CDA 110	bdl	-0.020

Bi I 306.77 nm
R^2 .953
Margin of error +/- 0.067 ppm

Artifact I.D.	Known (ppm)	Predicted (ppm)
NP26	0.165	0.081
NP13	0.090	0.004
NP25	0.082	0.086
HS11	0.076	0.332
NP10	0.071	0.069
NP11	0.059	0.074
NP12	0.051	0.041
S1	0.014	0.078
HS12	bdl	0.077
HS13	bdl	0.076
Pun394	bdl	0.073
NP24	bdl	0.054
HS7	bdl	0.041

Results summary

1. Optimized LIBS instrument parameters (argon flush, gate delay, and laser focus)
2. Compared four normalization methods
3. Developed and tested calibration curves for 10 elements

Future directions

1. Incorporate instrument's ability to break through a corrosion layer to sample material underneath (particularly important for studying archaeological artifacts)
2. Explore calibration-free LIBS, which takes into account the sample matrix

Acknowledgements: The authors express thanks to Yale and IPCH for support and to SciAps, Inc. for use of the LIBS instrument.

Primary author contact: elizabeth.coquillette@yale.edu

References:

Connors, B., Somers, A. & Day, D. (2016). Application of handheld laser induced breakdown spectroscopy (LIBS) to geochemical analysis. *Applied Spectroscopy, 70*, 810-815.

Heginbotham, A., et al. (2014). The Copper CHARM Set: A new set of certified reference materials for the standardization of quantitative x-ray fluorescence analysis of heritage copper alloys. *Archaeometry, 57*.

Harmon, R., et al. (2017). Geochemical fingerprinting by handheld laser-induced breakdown spectroscopy. *Geostandards and Geoanalytical Research, 41*, 563-584.