Evaluation of Laser Induced Breakdown Spectroscopy (LIBS) for the Forensic Discrimination of Copper Metal

Chase J. Notari, B.S.[1] and Brooke W. Kammrath, Ph.D.[1,2]

[1]Department of Forensic Science, University of New Haven, Connecticut, USA

[2]Henry C. Lee Institute of Forensic Science, Connecticut, USA

Introduction

The purpose of this research was to evaluate LIBS to determine if it has the ability to perform comparative analysis of copper, specifically the jacketed metal on different bullets. Copper metal has great potential as forensic evidence due to its presence in a range of cases from thefts of copper wiring and pipes, the use of copper wiring in IEDs, and its common function as bullet jackets. Excellent discrimination of copper metal has been demonstrated through trace element profiles collected using solution-based ICP-MS. Although ICP-MS has many advantages for elemental analysis, including its low detection limits, high accuracy and excellent precision, alternative methods that are faster, require less (or no) sample preparation, and require smaller sample sizes are being investigated. LIBS is an advantageous tool for elemental profiling due to the fact that it is rapid, requires no sample preparation, is able to simultaneously provide information on multiple elements at once, and is less expensive than other instruments used for elemental analysis. LIBS has proven value for the analysis of glass, paint, soil, ink, and other samples of forensic interest, and this research investigated its capabilities for the discrimination of copper. The ability of LIBS to perform comparative elemental analysis on copper-jacketed bullets has the potential to provide a novel method for forensic scientists to use in comparing ballistic evidence. These results that can be extended to other sources of copper, such as pipes and wiring, thus expanding the utility of LIBS instrumentation in forensic laboratories to alternative evidence items.

Methods

- Method development resulted in the following optimal LIBS parameters for Copper: 0.3 µs gate delay, 100% energy, 100 shots, & 125 µm spot size.
- 5 spectra were collected from the copper jacketing of each bullet

Figure 1: Image of LIBS J200 instrument, Applied Spectra, Inc.

Materials

Bullet #	Bullet Type
1	Remington 44 Magnum
2	Armscor Precision
3	Federal Premium Hunting
4	Remington Express
5	Smith & Wesson 40 Caliber
6	Ultramax Ammunition
7	Winchester 38 Special
8	Winchester 303 British
9	Winchester 357 Magnum
10	Winchester Government

Table 1: Ten (10) copper jacketed bullets used in experiment

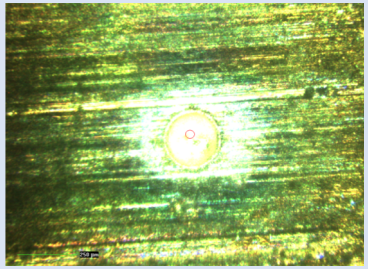

Figure 2: Image of laser ablation divot on copper jacketing.

Results

Table 2: Table of 9 elements (and their LIBS peaks) evaluated for discrimination of Copper

Element & Peak (nm)	Variable #	Element & Peak (nm)	Variable #
Zn 206	1	Zn 334	9
Sb 218	2	Sc 402	10
Bi 223	3	V 438	11
Cd 226	4	Zn 468	12
Zn 256	5	Zn 472	13
Fe 260	6	Zn 481	14
Pt 270	7	Ba 553	15
Zn 303	8	Zn 636	16

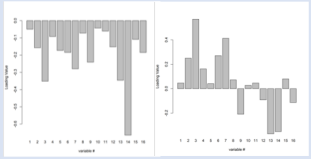

Figure 3: Loading plots for PC1 (left) & PC2 (right)

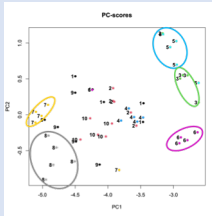

Figure 4: 2D scores plot of data with ellipses added to show clustering.

Results & Conclusions

Multivariate Statistics:

- Principal Component Analysis (PCA) was used to orthogonalize the data for Canonical Variate Analysis (CVA), with Hold-One-Out Cross-Validation (HOO-CV) used to estimate classification error rate.

Group	HOO-CV Predicted Group										Classification	Error Rate
1	2	1	1	2	1	3	of 5 correctly classified	40%
2	2	2	2	1	2	4	of 5 correctly classified	20%
3	5	3	3	3	3	4	of 5 correctly classified	20%
4	6	4	4	4	4	4	of 5 correctly classified	20%
5	3	5	5	5	5	4	of 5 correctly classified	20%
6	7	6	6	6	6	4	of 5 correctly classified	20%
7	10	7	7	8	7	3	of 5 correctly classified	40%
8	7	7	8	8	8	3	of 5 correctly classified	40%
9	10	9	9	9	7	3	of 5 correctly classified	40%
10	10	10	9	10	10	4	of 5 correctly classified	20%
							AVERAGE	28%

Table 3: Table of misclassifications and error rates of HOO-CV PCA-CVA

Overall Error Rate = 28%		Actual Class									
		1	2	3	4	5	6	7	8	9	10
Predicted Class	1	60%	20%	0	0	0	0	0	0	0	0
	2	40%	80%	0	0	0	20%	0	0	0	0
	3	0	0	80%	0	20%	0	0	0	0	0
	4	0	0	0	80%	0	0	0	0	0	0
	5	0	0	20%	0	80%	0	0	0	0	0
	6	0	0	0	20%	0	80%	0	0	0	0
	7	0	0	0	0	0	0	60%	40%	20%	0
	8	0	0	0	0	0	0	20%	60%	0	0
	9	0	0	0	0	0	0	0	0	60%	20%
	10	0	0	0	0	0	0	20%	0	20%	80%

Table 4: Confusion matrix for bullet class prediction

- All samples had at least 1 replicate incorrectly classified, possibly due to micro-inhomogeneity of the copper or precision of method.
- No sample had more than 2 replicates incorrectly classified, thus if 5 (or more) replicates from a sample are considered together, the correct classification would be made for all 10 bullets.
- Not yet able to source identify from the copper, but can be used for exclusions. For the discrimination of bullets, it may have value when combined with elemental analysis of bullet lead
- Future research will include investigating other statistical models and data pre-treatments. Also, other sources of copper metal (i.e., wires & pipes)

References

- Koons, R. D., & Buscaglia, J. (Mar, 2005). Forensic Significance of Bullet Lead Compositions. Journal of Forensic Science, 50(2).
- Applied Spectra. (n.d.). What is LIBS? Retrieved May 09, 2021, from https://appliedspectra.com/technology/libs.html
- Bush, L. (april, 2011). LIBS in Forensics. Spectroscopy, 26(4), 34-35.
- Applied Spectra. (n.d.). Building Confidence for Forensic Glass Analysis with Applied Spectra's J200 LIBS.
- Spiegelman, C., & Tobin, W. A. (n.d.). Comparative/Compositional Bullet Lead Analyses (CBLA): An Autopsy.
- Dettman, J. R., Cassabaum, A. A., Saunders, C. P., Snyder, D. L., & Buscaglia, J. (2014). Forensic Discrimination of Copper Wire Using Trace Element Concentrations. Analytical Chemistry, 8176-8182.

Acknowledgements

This material is based upon work supported by the National Science Foundation under 1827839.

Questions? Email Chase Notari at cnota1@unh.newhaven.edu