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The Effectiveness of Laser-Induced Breakdown Spectroscopy (LIBS) as a Quantitative Tool for Environmental Characterization

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Cold Regions Research
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Abstract

Laser-induced breakdown spectroscopy (LIBS) is a rapid, low-cost analytical method with potential applications for quantitative analysis of soils for heavy metal contaminants found in military ranges. The Department of Defense (DoD), Army, and Department of Homeland Security (DHS) have mission requirements to acquire the ability to detect and identify chemicals of concern in the field. The quantitative potential of a commercial off-the-shelf (COTS) hand-held LIBS device and a classic laboratory bench-top LIBS system was examined by measuring heavy metals (antimony, tungsten, iron, lead, and zinc) in soils from six military ranges. To ensure the accuracy of the quantified results, we also examined the soil samples using other hand-held and bench-top analytical methods, to include Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and X-Ray Fluorescence (XRF). The effects of soil heterogeneity on quantitative analysis were reviewed with hand-held and bench-top systems and compared multivariate and univariate calibration algorithms for heavy metal quantification. In addition, the influence of cold temperatures on signal intensity and resulting concentration were examined to further assess the viability of this technology in cold environments. Overall, the results indicate that additional work should be performed to enhance the ability of LIBS as a reliable quantitative analytical tool.

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Preface

This study was conducted for the U.S. Army Corps of Engineers, Baltimore District, ERDC T-15 Program under 474428, "Support of US Army Global Military Objectives: LIBS for Military Surveys." The technical monitor was Dr. Jay Clausen.

The work was performed by the Biogeochemical Sciences Branch of the Research and Engineering Division, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (ERDC-CRREL). At the time of publication, Dr. Steven Peckham was Acting Branch Chief; and Dr. M. Andrew Niccolai was Acting Division Chief. The Deputy Director of ERDC-CRREL was Mr. David B. Ringelberg, and the Director of ERDC-CRREL was Dr. Joseph L. Corriveau.

COL Teresa A. Schlosser was Commander of ERDC, and Dr. David W. Pittman was the Director.

1 Introduction

1.1 Background

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy technique that can be used for the rapid detection of heavy metals in soils (Villas-Boas 2015). When sampling with LIBS, the laser ablates a 10-1000 μm in diameter spot on the sample surface. This atomizes and excites a small amount of material, creating a plasma plume that emits light at unique frequencies dependent on the elements present. Atomic and ionic emission lines in the form of ultraviolet, visible, and near-infrared light are collected by the instrument's spectrometer. To date, the primary use of LIBS is as a qualitative tool for forensic analysis. LIBS has known quantitative limitations; including the matrix effects of soil, i.e. issues with soil texture, heterogeneity, and chemical composition (Segnini et al. 2014). However, there are still advantages over traditional quantitative techniques, e.g., inductively coupled plasma – mass spectrometry (ICP-MS), x-ray fluorescence (XRF), or atomic absorption spectrometry (AAS). These techniques are limited in terms of sample preparation and ease of use. LIBS requires little to no sample preparation, limited contamination potential, no hazardous waste generation, and is cost effective. LIBS is also a versatile instrument that is capable of remote material assessment, geological analysis, diagnostics of archaeological objects, metal diffusion in solar cells, and more (Anabitarte 2012). Due to its diverse applications, LIBS has begun to reduce its performance gap in comparison to the more well-known analytical techniques.

The simplicity of LIBS makes it a practical choice as a potential portable, real-time, no-contact analytical tool for users in the field with limited resources and time. The focus of this project was to assess the potential use of LIBS as a quantitative instrument for the analysis of heavy metals (tungsten, antimony, lead, and zinc) commonly found within military training ranges. At high concentrations, these heavy metals are known to be toxic to most organisms, requiring accurate quantification for remediation purposes (In-Sook et al. 2002). Application of this instrument for standoff, rapid quantification of heavy metal contaminants would provide soldiers with a powerful new analytical capability in the field.

1.2 Sample description

The soils used for this project were collected from six different training ranges spread across the United States; specifically Kimama (KTS), Ft. Wainwright (FTWW), Ft. Lewis (FL), Ft. Eustis (FE), Massachusetts Military Reservation (MMR), and Ft. Benning (FB). All soils were used for separate Cold Regions Research and Engineering Laboratory (CRREL) initiatives studying heavy metal contaminants (Clausen et al. 2007, 2012, 2013a, 2013b, 2016). The soils ranged in particle size from silty clay to gravely sands. FTWW, FL, MMR, and FB are currently active ranges, while the ranges sampled at KTS and FE are formerly used ranges last used over four decades ago.

1.3 Instrument description

The LIBS instruments used during this project were the J200 bench-top by Applied Spectra (West Sacramento, California) and the SciApps Z300 hand-held (Woburn, Massachusetts). The J200 bench-top uses a Neodymium-doped Yttrium Garnet (Nd:YAG) laser to ablate samples and the limit of detection for trace elements is in the single-digit ppm levels. The hand-held SciApps Z300 excitation source is a 1064 nm laser with 5-6 mJ per pulse, 50Hz max repetition rate, and has a wavelength range of 190 nm – 950 nm. The XRF used is the Innov-X, with a detection limit in the tens of ppm. The ICP-OES used is the Thermo Scientific iCAP 6000 series, which enables liquid sample analysis of trace elements with a detection capability of < 1 ppb and a wavelength range of 166 to 847 nm.

1.4 Objectives

1. Determine the adequate number of laser shots needed to overcome the variability of soil heterogeneity.
2. Optimize LIBS calibration for increased accuracy in metal concentration determination.
3. Develop calibration curves using a robust standard material representative of samples being analyzed.
4. Verify the LIBS calibration models developed to quantify heavy metal concentrations using hand-held (XRF) and bench-top analytical laboratory methods (ICP-OES).
5. Examine the influence of frozen samples and cold temperature on hand-held and bench-top LIBS systems.

1.5 Approach

Using over 400 different soil samples collected from six military ranges across the United States, we processed and analyzed the samples using both hand-held and bench-top LIBS systems. ICP-OES and XRF were used for validation of the heavy metal measurements obtained using the LIBS calibration model.

1. Compared univariate and multivariate analyses for calibration of military range soils with various concentrations of lead, zinc, antimony, and tungsten.
2. Determined of the number of laser shots required for optimization of prediction accuracy.
3. Values predicted using the univariate and multivariate analysis when compared with XRF and ICP-OES concentrations for assessment of the accuracy of concentrations determined with LIBS.
4. Performed initial assessment of ability of LIBS to perform in cold temperatures (approximately 11˚C).

2 Methods

2.1 Sample pellet preparation

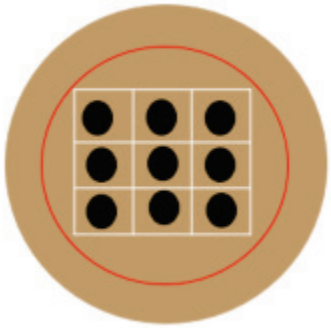
To prepare the soil sample for LIBS analysis, a subsample of each soil was placed into a 6-mm die press under 2,850 lbs of pressure using a hydraulic hand press to create soil pellets. Once the desired pressure was reached, it was maintained for three minutes, after which, the pellet was evacuated from the die and stored in plastic trays.

Of the 400 pellets made, 30 were chosen at random for use in cold trials, which are described in Sections 2.3 and 2.4. Of the 30 samples chosen, 14 were from FTWW and 16 were from FE.

2.2 Bench-top LIBS analysis

Once ready for analysis, individual pellets were placed in a customized acrylic tray and inserted into the holding cell of the LIBS under ambient conditions. A J200 bench-top LIBS by Applied Spectra (West Sacramento, California) was used and contained a 25 mJ Nd:YAG laser operating at 266-nm. Using a micro camera focused on the center of the pellet, the ablation pattern to be shot by the Nd:YAG laser was set as a three-by-three grid to obtain nine different 100 μm shots from the soil. The ablation pattern can be seen in Figure 1, where the black circles represent the 9 laser shot locations on the 3x3 grid layout. No cleaning or warm up shots were used for these samples.

Figure 1. Bench-top LIBS ablation pattern layout on one 3x3 grid.



The Nd:YAG laser parameters of the bench- top LIBS used throughout all bench-top analysis of the investigation can be seen in Table 1. One hundred percent of the 25 mJ laser ablated the pellet with a shot size of 100 μm. Data acquisition had a gate delay (delay time) of 1.3 μs and a gate width (integration time) of 1.05 μs. Gate delay is the length of time between the laser pulse and the detector turning on, and gate width is the length of time the detector remains on. The detector utilized for data acquisition was a 6 channel spectrometer with a wavelength range of 180 nm to 900 nm.

Table 1. Laser parameters of all bench-top LIBS analyses.

Bench-top LIBS Nd:YAG Laser Parameters	
Laser Power (% of 25 mJ)	100
Shot Size (μm)	100
Gate Delay (μs)	1.3
Gate Width (μs)	1.05
Wavelength Range (nm)	180-900

2.3 Cold Bench-top LIBS analysis

A Fisherbrand Traceable Digital Thermometer sensor was placed adjacent to the bench-top LIBS and wired into the holding cell to monitor the internal and external temperatures while preforming analysis. To cool the bench-top LIBS, an Ultra-Pure air tank was stored in a cold room at -15 ˚C for two days before analysis. This air was pumped through copper tubing submerged in a dry ice acetone bath into the LIBS holding cell at 5 psi in order to not disturb the pellet. During analysis, to ensure a consistently cold environment inside the LIBS and limit temperature fluctuations, samples were analyzed on frozen aluminum trays. The average temperature during analysis was 11 ˚C. The operating parameters and ablation pattern of the bench-top LIBS for all cold soil pellets can be seen in Table 1 and Figure 1.

2.4 Cold hand-held LIBS analysis

The hand-held cold tests were conducted using the SciApps Z300 hand-held LIBS. The instrument was bagged with desiccant to help remove any moisture that could freeze inside the instrument 48 hr before testing took place. The analysis was conducted in a cold room set to 10℃ and the soil pellets used for the cold analysis were stored on aluminum trays in a freezer at -20 °C for a month prior to analysis. While scanning the pellets,

the instrument remained concealed in the bag to minimize humidity. However, the nose of the instrument was exposed to allow direct contact with the samples through a small window in the bag. Due to the inherent difference in laser power between the hand-held LIBS (5-6 mJ) and that of the bench-top system (25 mJ), distinct settings were selected in order to optimize the signal to background ratio for the hand-held instrument. The optimized settings can be seen in Table 2.

Table 2. Optimized settings of hand-held LIBS for cold analysis.

SciApps Z300 Optimized Cold Settings	
Step Size (mm)	40
Integration Period (ms)	12
Argon Purge	OFF
Test Rate (Hz)	10
Clean Rate (Hz)	10
Linear	ON

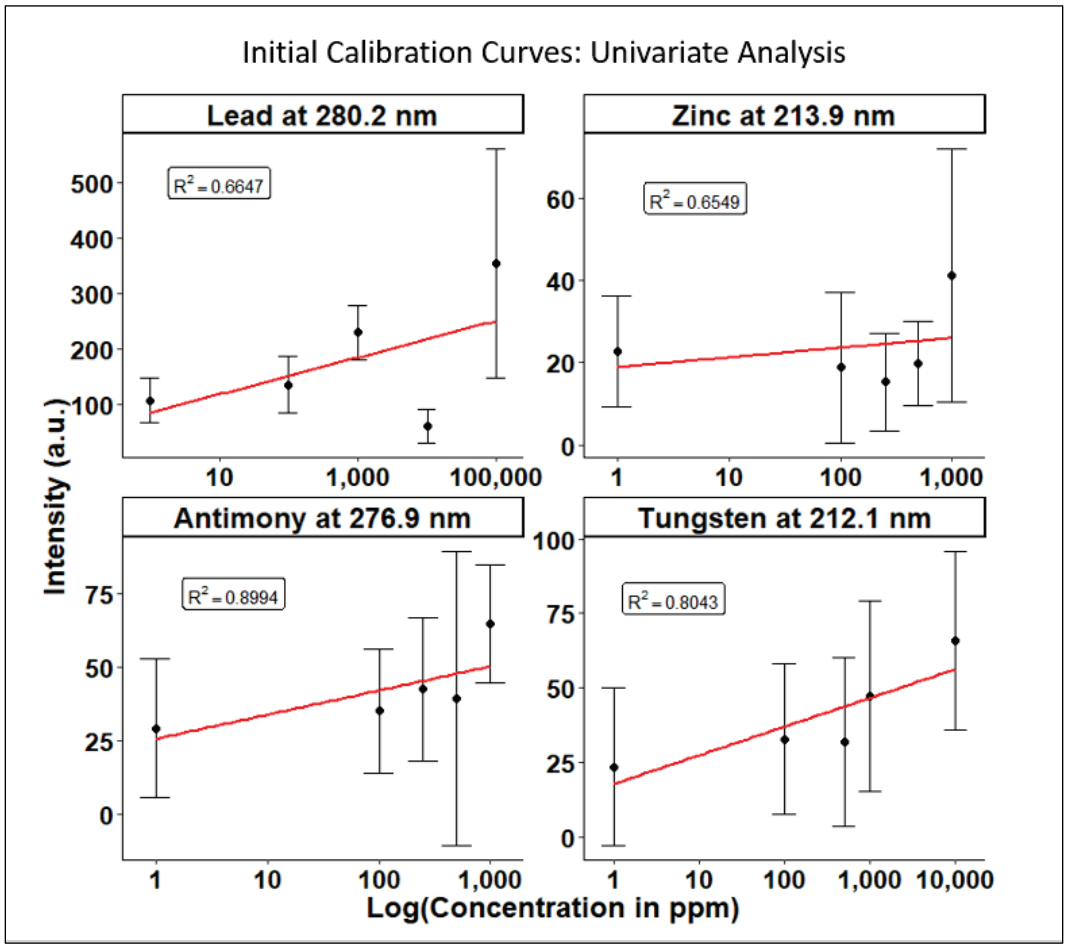
The argon purge option is unique to the Z hand-held LIBS and can be used to boost signals, particularly in the deep UV range. The detector utilized for data acquisition was a 1064 nm with a wavelength range of 190 nm – 950 nm. We continued to use the same ablation pattern as the bench-top analysis as seen in Figure 1, and for hand-held LIBS when shooting the ablation pattern step size is the distance between ablation spots.

2.5 Initial LIBS calibration curve

In order to quantify heavy metal concentrations, a five-point calibration curve was developed for each element using RCT Corps XRF Certified Reference Materials (CRM). Specifically, Antimony (Sb) 1.0 wt% XRF-OX-51, Tungsten (W) in Soil 100 ppm XRF-W-100, Lead (Pb) 0.62 wt % XRF-OX-13, and Zinc (Zn) 0.99 wt % XRF-OX-09 were used. The standard pellets were prepared by mixing the CRM with potassium bromide (KBr) to dilute the standard to the necessary concentration, as well as act as a binding agent to increase pellet stability. The KBr and CRM were ground by hand using a mortar and pestle until smooth. The matrix used to create the varying heavy metal concentrations can be seen in Appendix A. The ground material was placed in a 6 mm die press and pressed for three minutes under 6,613 lbs of pressure. LIBS concentrations were obtained for Pb, Zn, Sb, and W from FB soils (n= 78) using both the univariate and multivariate results from linear model (i.e. y=mx+b) and Partial Least Square Regression analysis respectively.

With the preliminary calibration data using nine shots per pellet, a univariate analysis (Mevik 2007) was performed to calculate the concentrations of Lead, Zinc, Antimony, and Tungsten in the bulk soils. To build the calibration curve, one wavelength was chosen to represent each element (Figure 2). The wavelength for each heavy metal was found by selecting the peak with the highest intensity from the National Institute of Science and Technology (NIST) database. In addition, multivariate analysis was also performed by selecting wavelengths between 200 and 350 nm as a group (not shown) for comparison. The heavy metals used are not seen lower than 200 wavelength or higher than 350 wavelength (Cong et al. 2013). The operating parameters and ablation pattern of the bench-top LIBS for all soil and standard pellets used for this test can be found in Table 1 and Figure 1.

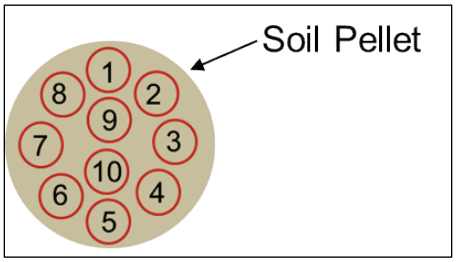
Figure 2. Initial calibration curve results using single element univariate analysis.



2.6 Adequate shots test

To account for the heterogeneous nature of soil, a test was performed to determine the adequate number of shots required until the variation in average intensity stabilized. One pellet from FB and two from FL were shot in 10 different locations. Each of these locations contained a three-by-three grid (9 shots per location). Figure 3 shows the 10 separate three-by-three grid locations, for a detailed diagram of the ablation pattern within a single 3x3 grid, see Figure 1. The total number of shots performed on each pellet was 90 (n = 90) and, every three shots were cumulatively averaged. This average was plotted (Figure 5) in order to see the minimum number of shots needed before the average stabilized (i.e. what number of shots will not affect the prediction accuracy). The standard deviation was also calculated at each step. The operating parameters of the bench-top LIBS for all soil pellets used for the adequate shots test can be found in Table 1, and the ablation pattern can be seen in Figure 3.

Figure 3. Locations of 3x3 grids on 6 mm FB and FL soil pellets for adequate shots test.



2.7 Secondary LIBS calibration curve

Secondary calibration curves were developed on the bench-top LIBS under ambient conditions to improve the quantitative accuracy of LIBS and was based on the information found from the adequate number of shots test described in Section 2.6. A fresh supply of CRM from Sigma Aldrich and NIST were used. Tungsten was excluded from this portion of the experiment due to material availability. The materials were hand ground with a mortar and pestle for three continuous minutes. The ground material was placed in a 13 mm pellet die press and were pressed for five minutes under 15,000 lbs of pressure. The additional time and pressure were needed when pelleting the standard material to reduce the chances of the pellet falling apart due to the coarseness of the material. The list and final pellet concentrations can be found in Appendix B.

The ablation pattern of a secondary standard pellet was 7 locations, and each location contained a three-by-three grid (Figure 4). The layout totaled to 63 shots on the surface of the pellet. Each location received one cleaning shot before the spectra was collected, ensuring there was no surface contamination being included in the plasma. The operating parameters of the bench-top LIBS for all standard pellets used for the secondary calibration can be found in Table 1, and the resulting calibration curves can be seen in Figure 5.

Figure 4. Locations of 3x3 grids on a 13mm secondary calibration pellet.

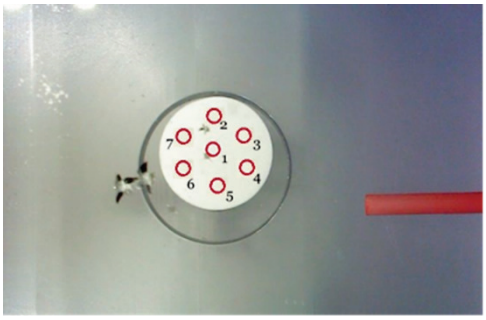
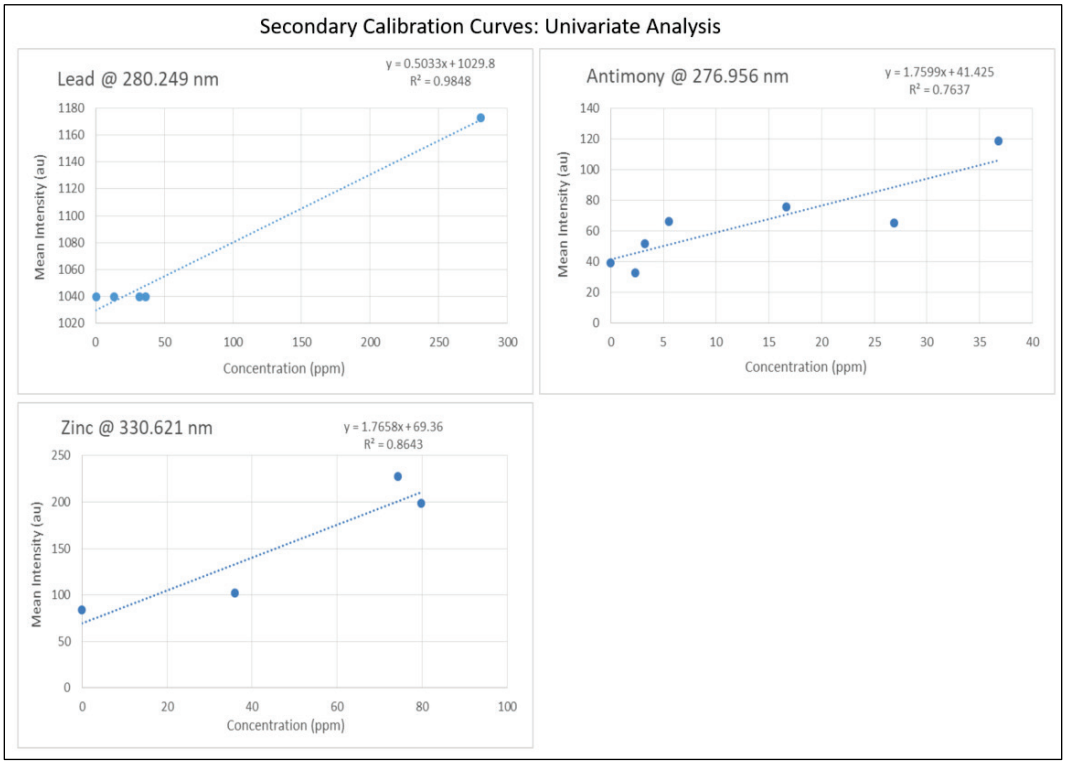


Figure 5. Secondary calibration curve results using single element univariate analysis.



2.8 XRF and ICP-OES analysis

Each soil sample was also analyzed with the Innov-X hand-held XRF device and the Thermo Scientific iCAP 6000 series ICP-OES for assessment of measurements that were made with the LIBS systems.

To perform ICP-OES analysis, one gram of each soil sample was digested in triplicate with a mixture of 2.5 mL nitric acid and 10 mL hydrochloric acid at 95 °C for 4 hr. Digests were allowed to cool and then they were diluted with MilliQ water to a final concentration of 2% and 5 % nitric acid and hydrochloric acid, respectively. Aliquots from these digestates were then analyzed with a Thermo Scientific iCAP 6000 Series ICP-OES followed U.S. Environmental Protection Agency (USEPA) Method 3050B (USEPA 1996).

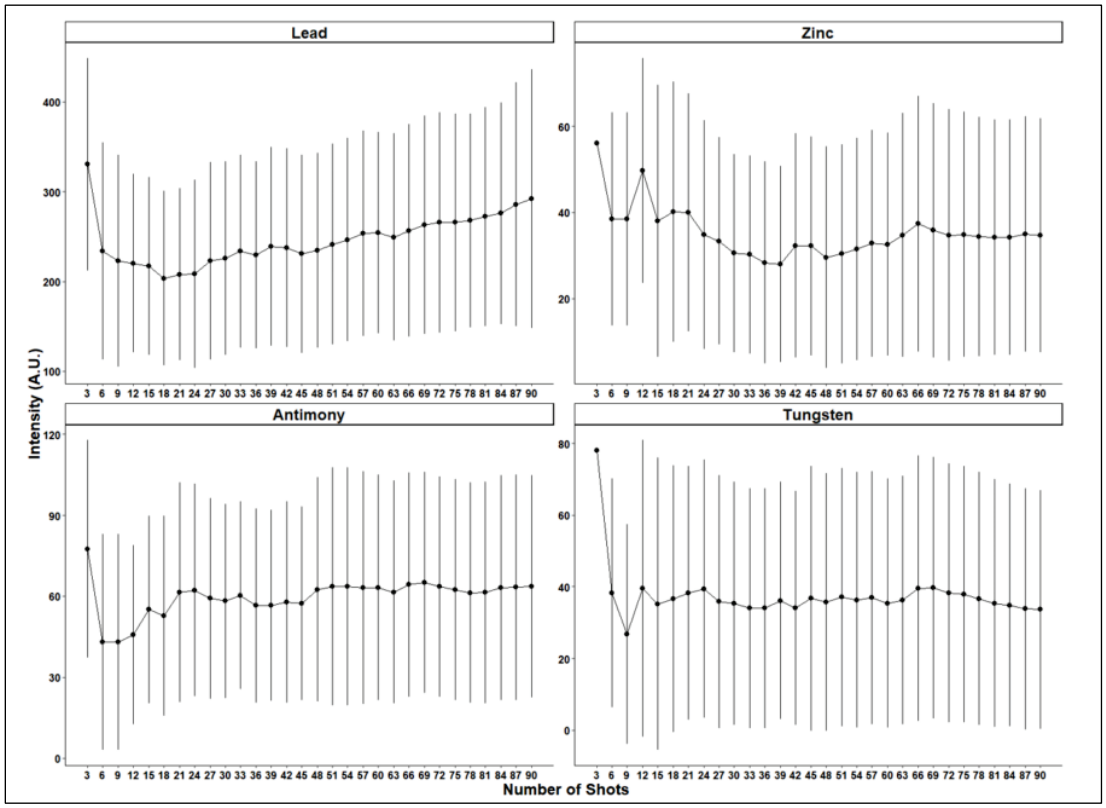
To perform XRF analysis, a subsample of each soil was placed in a clear plastic bag. The subsamples were then analyzed with an Innov-X alpha series XRF by placing the instrument in direct contact with the sample and utilizing a 2-min counting interval.

3 Results and Discussion

3.1 Number of shots to reduce heterogeneity of soil

Of the three soils analyzed for optimal number of shots as described in Section 2.6, we observed the variations in intensity at each designated metals wavelength. The optimal number of shots is determined as the stabilization point in which intensity stops increasing and the variation between shots becomes insignificant. Based on the analysis from the 90 shots taken of each soil (n=90), the majority of the soils stabilized at or around 40 shots, but all the metals stabilized at 60 shots. An example of the analysis from one soil sample, FB 38, is shown in Figure 6. Every soil type behaved differently, as expected due to the heterogeneous nature of the material.

Figure 6. Results from soil sample Ft. Benning 38, examining the adequate number of shots required until stabilization of the concentration of heavy metals.



3.2 Correlation of ICP-OES, XRF, and LIBS heavy metal data

The metal concentrations in this section were obtained from the FB soil samples (n=78), and the LIBS data was calculated using the first calibration effort as described in Section 2.5. When comparing multivariate and univariate calibration curves, univariate analysis performed better due to an improved coefficient of determination value. Herein, examples shown comparing the predicted heavy metal concentrations from ICP-OES, XRF and bench-top LIBS are based on the univariate analysis described in Section 2.5.

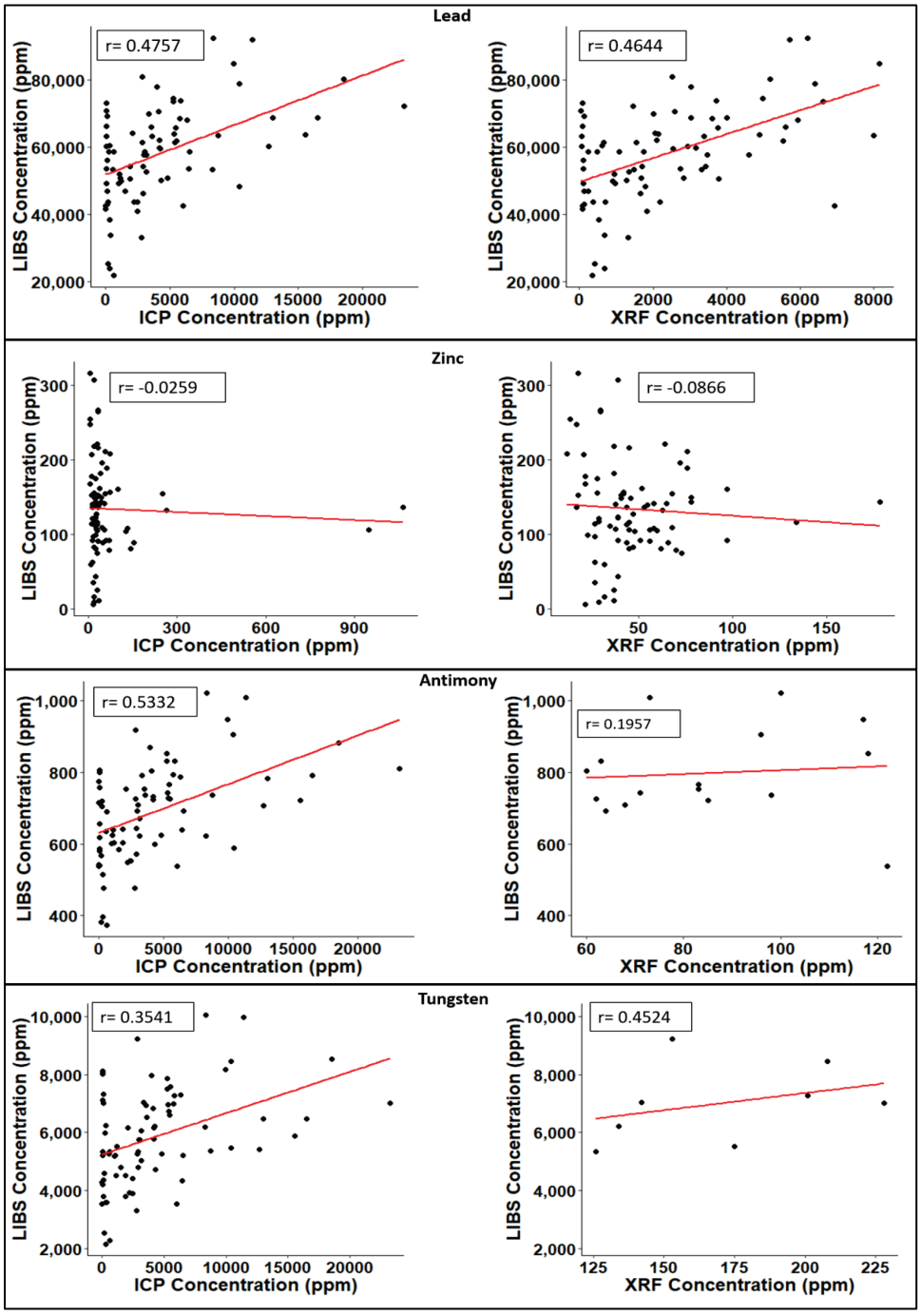
The heavy metals concentration obtained by ICP-OES and XRF were compared to LIBS concentrations using Spearman's Rank-Order Correlation. The Spearman correlation is a nonparametric correlation estimator, which was chosen due to its ability to be robust and resistant to outlying observations. During calculations, some values were under the limit of detection for Sb and W concentration obtained by XRF and ICP-OES, thus those values were left blank. It should be noted that differences in the concentrations measured using XRF and ICP-OES are expected due to the difference in sampling methodologies.

When reviewing the statistical results of this experiment, a high correlation coefficient (r) between XRF or ICP-OES and LIBS data would verify the precision of this tool. Additionally, data about overestimation or underestimation of concentrations by LIBS could be observed. A summary of our statistical results can be seen in Table 3. When using the univariate calibration curve to predict soil concentrations of ICP, XRF, and LIBS, and using the Spearmans correlation to determine a relationship between these predicted soil concentrations, a significant relationship between LIBS and XRF or ICP was not observed due to low correlations coefficients (Table 3). While some of the p-values were significant, the low r-values make the statistical relationship found insignificant. The graphs of each Spearman correlation comparison can be seen in Figure 7. From the four elements we analyzed, Lead performed the best, with the highest r-values (0.4757 and 0.4644) and a significant relationship with both ICP and XRF instrumentation when compared to LIBS ($p = <0.001$).

Table 3. Spearman correlation of Pb, Zn, Sb and W concentrations between LIBS and ICP or XRF.

Lead		
	Analytical Methods Compared	
	LIBS vs ICP-OES	**LIBS vs XRF**
sample number (n)	78	78
correlation coefficient (r)	0.4757	0.4644
p-value	<0.001	<0.001
Zinc		
	Analytical Methods Compared	
	LIBS vs ICP-OES	**LIBS vs XRF**
sample number (n)	78	78
correlation coefficient (r)	-0.0259	-0.0866
p-value	0.043	0.0396
Antimony		
	Analytical Methods Compared	
	LIBS vs ICP-OES	**LIBS vs XRF**
sample number (n)	78	78
correlation coefficient (r)	0.5332	0.1957
p-value	0.787	0.804
Tungsten		
	Analytical Methods Compared	
	LIBS vs ICP-OES	**LIBS vs XRF**
sample number (n)	78	78
correlation coefficient (r)	0.3541	0.4524
p-value	0.438	0.096

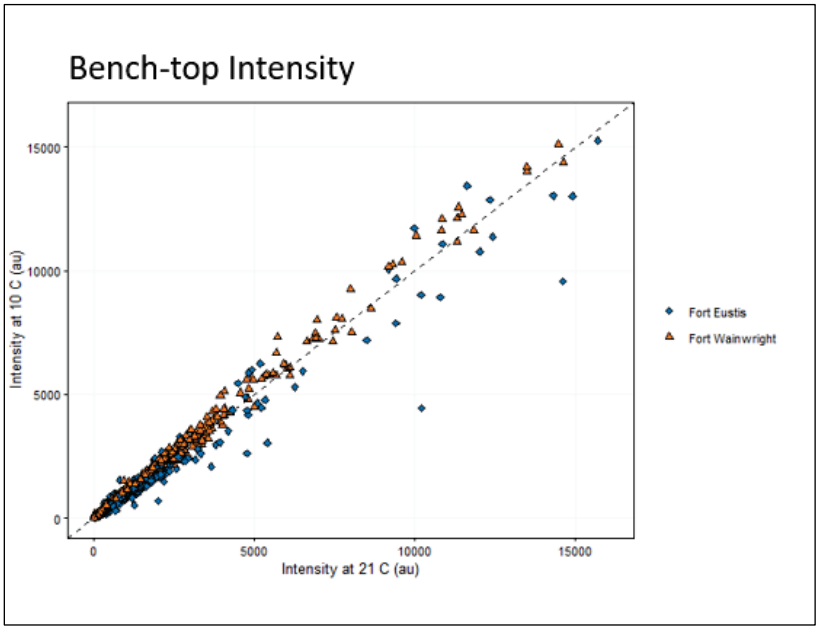
Figure 7. Spearman correlation of Pb, Zn, Sb and W concentrations between LIBS and ICP or XRF.



3.1 LIBS in the cold

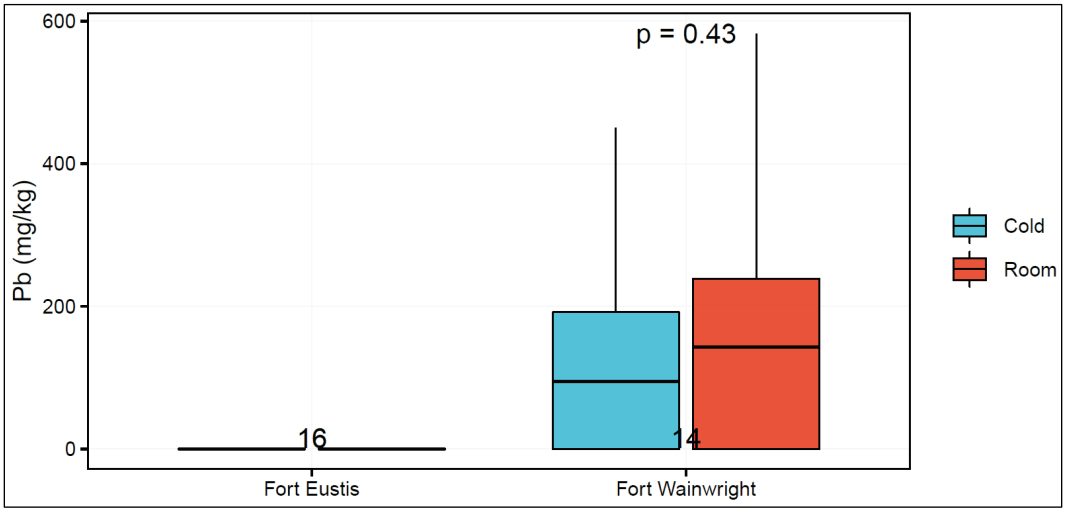
Heavy metal (Pb, Sb, and Zn) concentrations were quantified using the second linear calibration curve explained in Section 2.7. A test was used on the bench-top data (Appendix C) to compare the difference between the calculated concentrations for room temperature and the cold temperature for each metal. The bench-top data has strong unity linear pattern suggesting no temperature influence on the intensity (Figure 8).

Figure 8. Bench-top LIBS intensity in the cold (11 ˚C).



To test this relationship for each site, we used a Wilcoxon test, assuming non-normality, with an alpha of 0.05. The p- values obtained for each element and corresponding site from this test were, (Pb: p=0.0098 (FE), 0.0134 (FTWW), Zn: p= 0.43 (FE), NA (FTWW), and Sb: p=0.12 (FE), 0.33 (FTWW)). The sample size (n) for FE was 16, and 14 for FTWW. From this information, we can conclude that there is a significant relationship between the intensities produced by bench-top LIBS in varying temperatures. For visualization of this signifcant relationship, a box plot comparing the p-values of lead concentrations obtained from both sites can be seen in Figure 9. No hand-held data was reported due to the hand-held LIBS experiencing mechanical faliures in the cold temperatures.

Figure 9. Box plot of bench-top LIBS FE and FTWW Lead p-values.



4 Recommendations for Future Work

LIBS is an excellent analytical tool for the qualitative detection of heavy metals of concern in addition to minimal sample preparation. However, the data presented herein indicates that more work must be performed to optimize this tool for the quantitative analysis of heavy metals in soil.

When building calibration curves, using both univariate and multivariate analysis of LIBS data univariate performed better than multivariate. However, every soil type behaves differently, which indicates different soils cannot be treated the same. Our results support previous studies done on LIBS, whose results also indicated that LIBS quantification is effected by the texture and chemical composition of soil (Segnini et al. 2014).

The LIBS spectra may vary from one shot to another due to plasma instability, which leads to non-reproducible background noise. This appears to contribute to LIBS being difficult to use as a tool for quantitative analysis. To help reduce this issue in the future, an offset of each spectrum should be performed to help reduce the random noise. A digital filter known as Savitsky-Golay could be applied to smooth the LIBS data in order to increase data precision without distorting the signal (Villas Boas et al. 2016). Standards designed for hand-held and bench-top LIBS devices would also be beneficial due to the significant affects grain size has on spectral analysis.

An additional technique that could be applied in the future to help standardize the results achieved from heterogeneous soil samples would be to incorporate in an internal standard for each sample. This would consist of adding a single element with a constant known concentration to every sample. The measured internal standard could then be used to correct the response of the unknown elements in both bench-top and hand-held LIBS analysis (Anabitarte 2012).

Finally, it appears that as temperatures become lower, the hand-held LIBS experiences technical issues. In the future, additional efforts to keep the hand-held warm while measuring cold samples, such as an insulated wrap, could help increase the efficiency of the instrumentation.

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Appendix A: Matrices Used to Create the Varying Heavy Metal Concentrations for the Initial Calibration Curve

0.15 = total pellet mass							
Standard	wt % of standard		standard in ppm	Scaled target	g metal	g KBr	Curve extent (ppm)
Tungsten	0.01		100	0.0001	0.000015	0.149985	0 – 10000
Antimony	1		10000	0.01	0.0015	0.1485	0 – 1000
Lead	0.62		6200	0.0062	0.00093	0.14907	0 – 100000
Zinc	0.99		9900	0.0099	0.001485	0.148515	0 – 1000
			scaled by factor of 10 and then will subsample to make pellets				
		ppm	g standard	g KBr		g metal	g KBr
tungsten:	1	0	0	0.15		0	1.5
	2	100	0.000015	0.149985		0.00015	1.49985
	3	500	0.000075	0.149925		0.00075	1.49925
	4	1000	0.00015	0.14985		0.0015	1.4985
	5	10,000	0.0015	0.1485		0.015	1.485
		ppm	g standard	g KBr		g metal	g KBr
antimony:	1	0	0	0.15		0	1.5
	2	100	0.000015	0.149985		0.00015	1.49985
	3	250	0.0000375	0.1499625		0.000375	1.499625
	4	500	0.000075	0.149925		0.00075	1.49925
	5	1,000	0.00015	0.14985		0.0015	1.4985
		ppm	g standard	g KBr		g metal	g KBr
lead:	1	0	0	0.15		0	1.5
	2	100	0.000015	0.149985		0.00015	1.49985
	3	1000	0.00015	0.14985		0.0015	1.4985
	4	10000	0.0015	0.1485		0.015	1.485

	5	100,000	0.015	0.135		0.15	1.35
		ppm	g standard	g KBr		g metal	g KBr
zinc:	1	0	0	0.15		0	1.5
	2	100	0.000015	0.149985		0.00015	1.49985
	3	250	0.0000375	0.1499625		0.000375	1.499625
	4	500	0.000075	0.149925		0.00075	1.49925
	5	1,000	0.00015	0.14985		0.0015	1.4985

Appendix B: Matrices Used to Create the Varying Heavy Metal Concentrations for the Secondary Calibration Curve

Certified Reference Material Name	Certified Concentration ppm	Metal	Material grams	KBr grams	Pellet Mass grams	pellet concentration ppm
NIST montana soil I 2710a	0.522	Pb	0.525	0.225	0.75	0.37
NIST san joaqiun soil	18.9	Pb	0.525	0.225	0.75	13.23
trace metals- clay 1	45.3	Pb	0.525	0.225	0.75	31.71
trace metals- sandy loam 10	51.9	Pb	0.525	0.225	0.75	36.33
CRREL custom #1	401.00	Pb	0.525	0.225	0.75	280.70
NIST montana soil II 2711a	1400	Pb	0.525	0.225	0.75	980.00
NIST montana soil 2710	5532	Pb	0.525	0.225	0.75	3872.40
trace metals- sandy loam 10	3.28	Sb	0.525	0.225	0.75	2.30
NIST new york waterway sediment	4.6	Sb	0.525	0.225	0.75	3.22
NIST san joaqiun soil	7.9	Sb	0.525	0.225	0.75	5.53
NIST montana soil II 2711a	23.8	Sb	0.525	0.225	0.75	16.66
NIST montana soil 2710	38.4	Sb	0.525	0.225	0.75	26.88
NIST montana soil I 2710a	52.5	Sb	0.525	0.225	0.75	36.75
CRREL custom #1	400.00	Sb	0.525	0.225	0.75	280.00
trace metals- sandy loam 3	4950	Sb	0.525	0.225	0.75	3465.00
Antimony XRF standard	9900.00	Sb	0.525	0.225	0.75	6930.00
Antimony XRF standard	72000.00	Sb	0.525	0.225	0.75	50400.00
trace metals- sandy loam 10	51.3	Zn	0.525	0.225	0.75	35.91
NIST san joaquin soil	106	Zn	0.525	0.225	0.75	74.20
trace metals- clay 1	114	Zn	0.525	0.225	0.75	79.80
NIST montana soil II 2711a	414	Zn	0.525	0.225	0.75	289.80
trace metals- sandy loam 3	546	Zn	0.525	0.225	0.75	382.20
CRREL custom #1	999.00	Zn	0.525	0.225	0.75	699.30
NIST montana soil I 2710a	4180	Zn	0.525	0.225	0.75	2926.00
NIST montana soil 2710	6952	Zn	0.525	0.225	0.75	4866.40
Metals in Soil	7000	Zn	0.525	0.225	0.75	4900.00
Zinc XRF standard	9900.00	Zn	0.525	0.225	0.75	6930.00

Appendix C: Bench-top LIBS 21˚C and 10˚C Heavy Metal Concentrations

Sample	Zinc (ppm)		Antimony (ppm)		Lead (ppm)	
	21˚C	10˚C	21˚C	10˚C	21˚C	10˚C
FE 1	96.57	51.14	3.61	0.07	0.00	0.00
FE 2	63.98	52.46	4.43	0.00	0.00	0.00
FE 3	69.39	90.97	0.00	0.00	0.00	0.00
FE 4	44.98	30.13	0.00	0.00	0.00	0.00
FE 5	74.05	55.17	0.00	0.00	0.00	0.00
FE 6	75.56	57.62	0.77	0.00	0.00	0.00
FE 7	72.79	60.14	0.33	0.00	0.00	0.00
FE 8	67.25	59.07	0.00	0.00	0.00	0.00
FE 9	56.11	39.56	0.00	0.00	0.00	0.00
FE 10	49.95	55.80	0.00	0.00	0.00	0.00
FE 11	69.64	59.57	0.00	0.00	0.00	0.00
FE 12	55.80	56.30	0.00	0.00	0.00	0.00
FE 13	75.12	51.14	0.00	0.00	0.00	0.00
FE 14	60.64	40.38	0.00	0.00	0.00	0.00
FE 15	55.23	0.00	0.00	0.00	0.00	0.00
FE 16	0.00	0.00	54.73	0.00	0.00	0.00
FTWW 1	178.50	175.86	24.95	13.52	122.26	0.00
FTWW 2	150.69	133.07	13.27	24.51	0.00	0.00
FTWW 3	201.47	132.19	45.66	27.47	486.52	76.34
FTWW 4	162.45	136.22	20.47	35.11	293.79	276.80
FTWW 5	162.52	102.55	15.54	18.45	174.36	0.00
FTWW 6	147.16	158.24	1.91	22.11	0.00	121.60
FTWW 7	152.76	121.87	10.37	19.20	0.00	0.00
FTWW 8	223.49	183.91	11.88	18.64	177.89	199.09
FTWW 9	177.81	111.86	25.39	26.28	163.32	169.72
FTWW 10	160.88	140.62	22.36	10.62	103.05	112.55
FTWW 11	148.49	161.26	11.12	4.30	0.00	0.00
FTWW 12	193.16	162.90	11.00	12.13	258.91	0.00
FTWW 13	142.63	169.44	26.34	23.50	0.00	260.24
FTWW 14	173.78	150.62	23.31	34.61	582.33	450.54

Unit Conversion Factors

Multiply	By	To Obtain
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
pounds (force) per square inch	6.894757	kilopascals
pounds (mass)	0.45359237	kilograms
pounds (mass) per cubic inch	2.757990 E+04	kilograms per cubic meter
tons (force)	8,896.443	newtons

Acronyms

AAS	Atomic Absorption Spectrometry
°C	Degree Celsius
CBRNE	Chemical, biological, radiological, nuclear and explosives
COTS	Commercial off the shelf
CRREL	Cold Regions Research and Engineering Laboratory
CRM	Certified Reference Material
DHS	Department of Homeland Security
DOD	Department of Defense
ERDC	Engineer Research and Development Center
FB	Fort Benning
FE	Fort Eustis
FL	Fort Lewis
FTWW	Fort Wainwright
Hz	Hertz
ICP- MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
KBr	Potassium bromide
KTS	Kimama Training Site
ISM	Incremental Sampling Methodology
LIBS	Laser Induced Breakdown Spectroscopy
MD	Munition Debris
mJ	millijoule
mm	millimeter
MD	Munition Debris
MMR	Massachusetts Military Reservation
Nd:YAG	Neodymium-doped Yttrium Garnet
NIST	National Institute of Science and Technology
n Sample Size	
Pb	Lead
Ppb	Part per billion

Ppm	Parts per million
Psi	Pounds per square inch
r	Correlation coefficient
RSL	Regional Screening Levels
Sb	Antimony
µ	micron
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
W	Tungsten
XRF	X-ray fluorescence
Zn	Zinc

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14. ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is a rapid, low-cost analytical method with potential applications for quantitative analysis of soils for heavy metal contaminants found in military ranges. The Department of Defense (DoD), Army, and Department of Homeland Security (DHS) have mission requirements to acquire the ability to detect and identify chemicals of concern in the field. The quantitative potential of a commercial off-the-shelf (COTS) hand-held LIBS device and a classic laboratory bench-top LIBS system was examined by measuring heavy metals (antimony, tungsten, iron, lead, and zinc) in soils from six military ranges. To ensure the accuracy of the quantified results, we also examined the soil samples using other hand-held and bench-top analytical methods, to include Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and X-Ray Fluorescence (XRF). The effects of soil heterogeneity on quantitative analysis were reviewed with hand-held and bench-top systems and compared multivariate and univariate calibration algorithms for heavy metal quantification. In addition, the influence of cold temperatures on signal intensity and resulting concentration were examined to further assess the viability of this technology in cold environments. Overall, the results indicate that additional work should be performed to enhance the ability of LIBS as a reliable quantitative analytical tool.

15. SUBJECT TERMS

Laser-induced breakdown spectroscopy
Soils – Testing
Military bases
Rifle-ranges
Bombing and gunnery ranges
Heavy metals – Detection

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