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#### A Comparison of Handheld Field Chemical Sensors for Soil Characterization with a Focus on LIBS

Jay Clausen, Richard Hark, Russ Harmon, John Plumer, Sam Beal and Meghan Bishop February 2022

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#### A Comparison of Handheld Field Chemical Sensors for Soil Characterization with a Focus on LIBS

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#### Preface

This study was conducted for the U.S. Army Corps of Engineers with funding under Army Direct Project T15, Program Element 633734, Task 2.

The work was performed by the Biogeochemical Sciences Branch (Mr. Nathan Lamie, Chief) of the of the Research and Engineering Division (Dr. George Calfas, Chief), U.S. Army Engineer Research and Development Center, Cold Regions Research Engineering Laboratory (ERDC-CRREL); North Carolina State University; Yale University; JR Plummer & Associates, and the Oak Ridge Institute for Science and Education. At the time of publication of this paper, the deputy director for ERDC-CRREL was Mr. Bryan E. Baker and the director was Dr. Joseph Corriveau.

This material was originally presented at the *SCIX 21 Conference* on 17 September 2021.

The commander of ERDC was COL Teresa A. Schlosser and the director was Dr. David W. Pittman.

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Prepared by Jay Clausen USACE, ERDC-CRREL, Biogeochemical Sciences Branch SCIX2021

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# **Objective**

- Sensors capable of characterizing/monitoring the environment
  - o Proximal distances
  - o Battlefield or military training ranges
    - Environmental awareness
    - Environmental characterization
    - Exposure
- Evaluate hand-held LIBS for characterization of metals (Sb, Cu, Pb, W, and
  Train and compare with XDE and ICD AEC
  - Zn) in soil and compare with XRF and ICP-AES
  - $\circ~$  Soils from military training ranges and other sites
  - Standard reference materials
  - o Certified reference materials
- Ascertain precision, accuracy, sensitivity, and reproducibility of hand-held LIBS technology

Go (Green), Slow-Go (Yellow), No-Go (Red) suitability map for a given sensor modality in a given region of the world at relevant spatial resolutions

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#### What Does the Soldier Want

#### FOB Environmental Characterization





#### Countermine Detection



# Environmental Awareness

# Occupational Exposure

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#### What Does the Soldier Want

#### FOB Environmental Characterization



#### Countermine Detection





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#### What Does the Soldier Want

#### FOB Environmental Characterization



Countermine Detection





Tricorder



Environmental Awareness Occupational Exposure

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# **Conventional Analytical Approach**

- Analysis in fixed-based laboratory
  - ICP/AES-MS, HPLC, LC/MS, GC/MS
  - Metals, energetics, VOCs, SVOCs, pesticides, herbicides, dioxins, PCBs, perchlorate, cyanide, nutrients, etc.





- In-field analysis with hand-held XRF
  - Metals





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#### Next Generation Technology: Laser Induced Breakdown Spectroscopy (LIBS)

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- a) Laser ablation of material of interest
- b) Development of plasma field
- c) Collection of resulting spectra with optical spectrograph
- d) Software based analysis of spectral data
- e) Results

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#### **XRF and LIBS Measured Values vs Certified Values**



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## LIBS versus XRF



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## **Instrument versus Sample Variability**



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#### **Particle Size Issue**



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#### **LIBS Intensity as Function of Particle Size**



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### Conclusions

- Copper and zinc LIBS measurement in agreement with known value of analytical NIST standards
- Lead data, not shown, in poor agreement
- LIBS appears to underpredict copper and zinc concentrations as compared to XRF and known quantity
- Poor agreement between XRF and LIBS measurements of same sample for copper and zinc
- Variability as measured by percent Relative Standard Deviation appears to be due to sample heterogeneity
- Another issue contributing to LIBS variability is particle size
- Particle size differences are analyte specific, and outcomes can be diametrically opposed



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Commercially available ha systems from multiple ven (FTIR) spectroscopy, and a and potential applications of focus on soils from militar elimination of transport of technologies have the capa evaluated results from the plasma atomic emission sp Raman spectroscopy for de The soil samples contained (TNT), hexahydro-1,3,5-tr of the handheld field senso suitability for field charact	Indheld chemical analyzers for forens dors can perform X-ray fluorescence recently laser-induced breakdown spe- of a multisensor system consisting of y ranges. Handheld sensors offer the samples back to the laboratory and la bility for extremely rapid analysis, or analysis of several hundred soil samp ectroscopy (ICP-AES) for metals ev- etection and characterization of energe 1 antimony, copper, lead, tungsten, ar iazine (RDX), nitroglycerine (NG), a or technologies were compared agains erization leading to decisional outcom	sic applications ha (XRF) spectrosco ectroscopy (LIBS) XRF, Raman, and potential to substa abor-intensive san n the order of tenss oles using convent aluation and high- getic materials aga and zinc as well as and dinitrotoluene st conventional lab	ve been availab ppy, Raman spe . Together, we d LIBS for envi- antially increase uple preparation of seconds or l ional laboratory performance lic inst handheld X energetic comp isomers (DNT) poratory instrum	ble for over a decade. Portable ctroscopy, Fourier transform infrared have been exploring the development ronmental characterization with a e sample throughput through the n procedures. Further, these less. We have compared and y bench top inductively coupled quid chromatography (HPLC) and KRF, LIBS, and Raman analyzers. ounds such as 2,4,6-trinitrotoluene . Precision, accuracy, and sensitivity nentation to determine their	
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