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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

Cold Regions Research and Engineering Laboratory

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

Jay Clausen and Sam Beal

Cold Regions Research and Engineering Laboratory
U.S. Army Engineer Research and Development Center
72 Lyme Road, Hanover, NH 03775

Richard Hark

Yale University
New Haven, CT 06520

Russ Harmon

North Carolina State University
Raleigh, NC 27695

John Plummer

JR Plummer & Associates, LLC
P.O. Box 566, Belmont, NH 03220

Meghan Bishop

U.S. Department of Energy
Oak Ridge Institute for Science and Education
Oak Ridge, TN 37830

Final report

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Under Project T15, Program Element 633734, Task 2

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.

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

A COMPARISON OF HANDHELD FIELD CHEMICAL SENSORS FOR SOIL CHARACTERIZATION WITH A FOCUS ON LIBS





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

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17 September 2021

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- Sam Beal (ERDC-CRREL)
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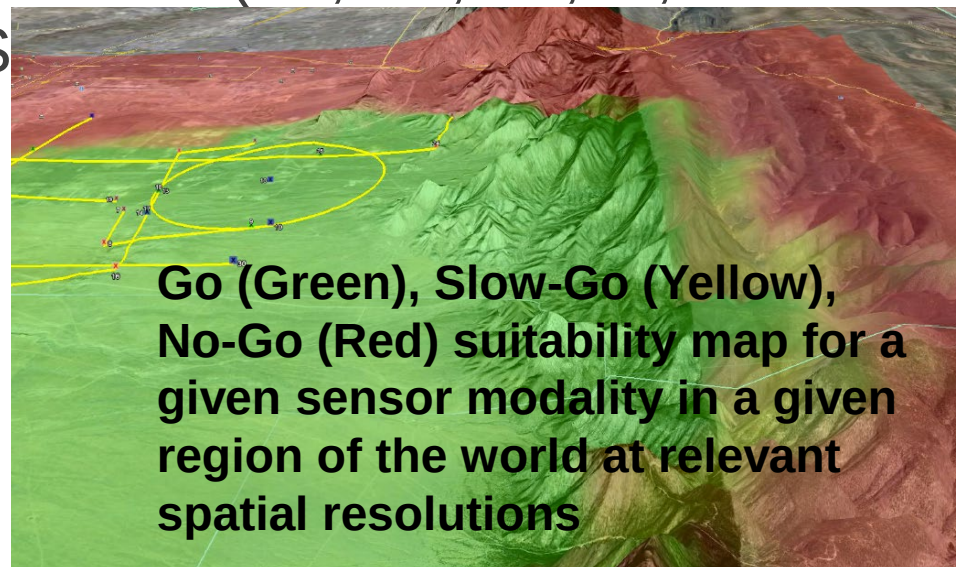
Objective

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



What Does the Soldier Want

FOB
Environmental Characterization

Forensics

Countermine
Detection

Environmental
Awareness

Occupational
Exposure

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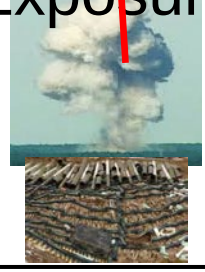
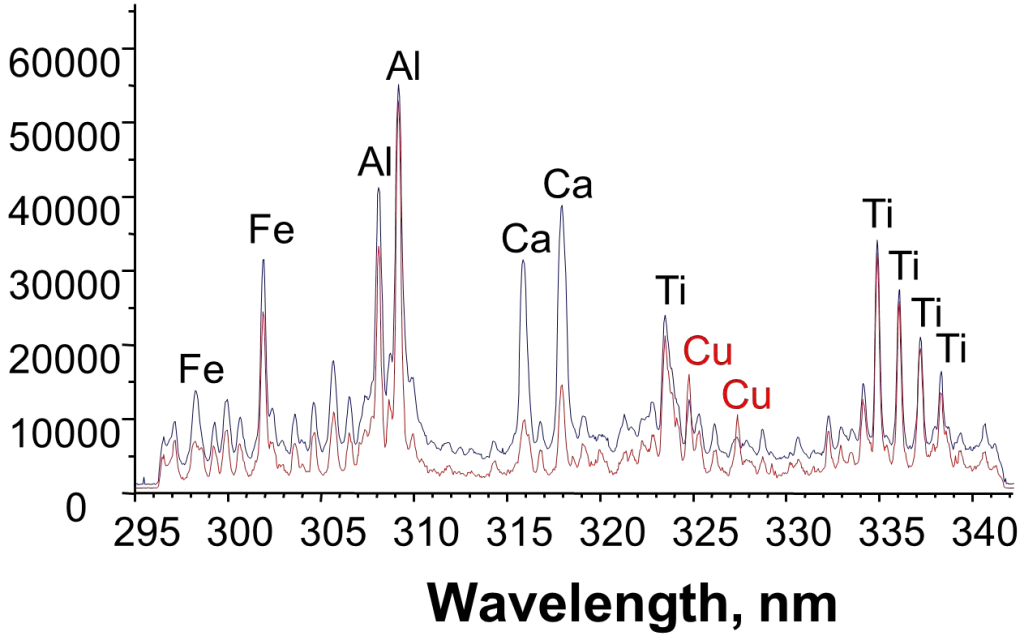


Conventional Analytical Approach

- 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

Next Generation Technology: Laser Induced Breakdown Spectroscopy (LIBS)

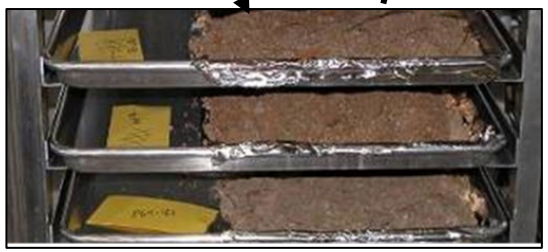


a) Laser ablation of material of interest
b) Development of plasma field
c) Collection of resulting spectra with optical spectrograph
d) Software based analysis of spectral data
e) Results

Methods - Sample Processing

Sampling

Drying



Sieving

Milling

Subsampling

Pelletizing

Digesting
Extracting

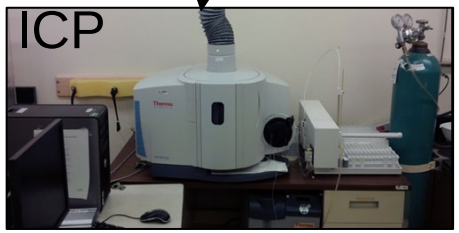
Analysis

XRF

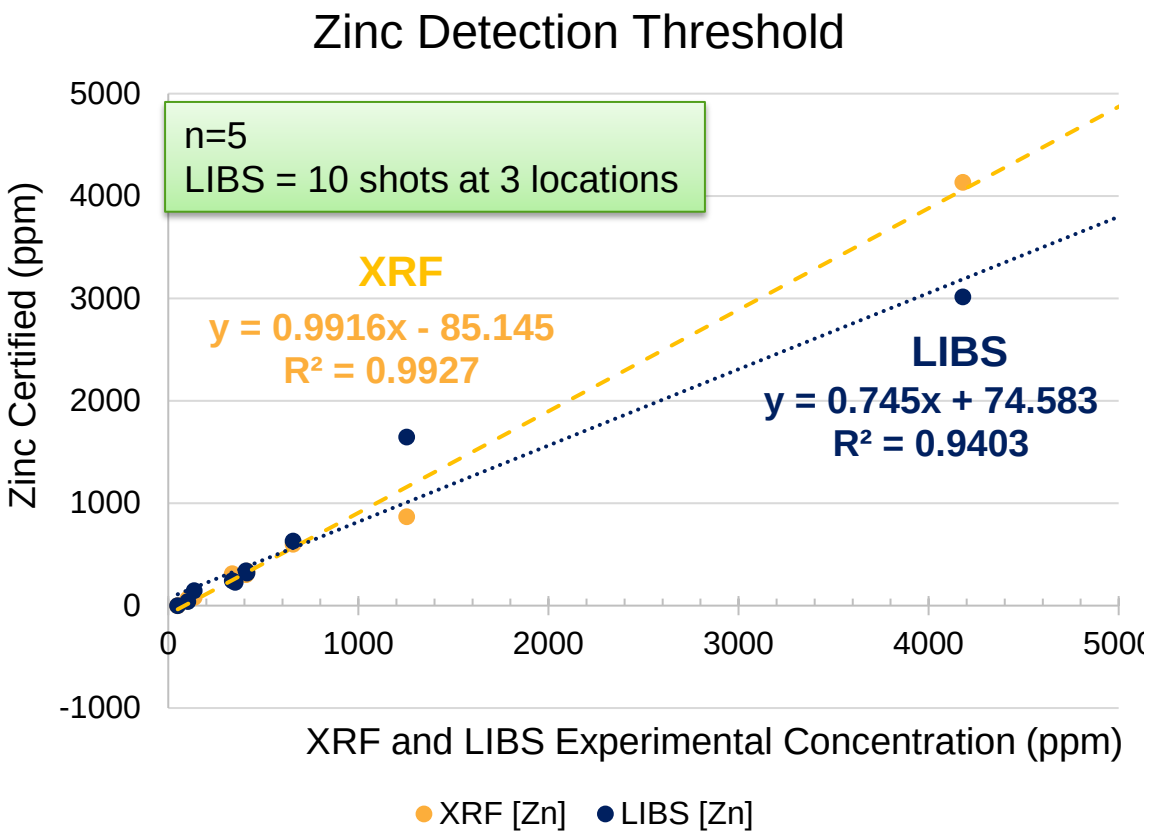
LIBS

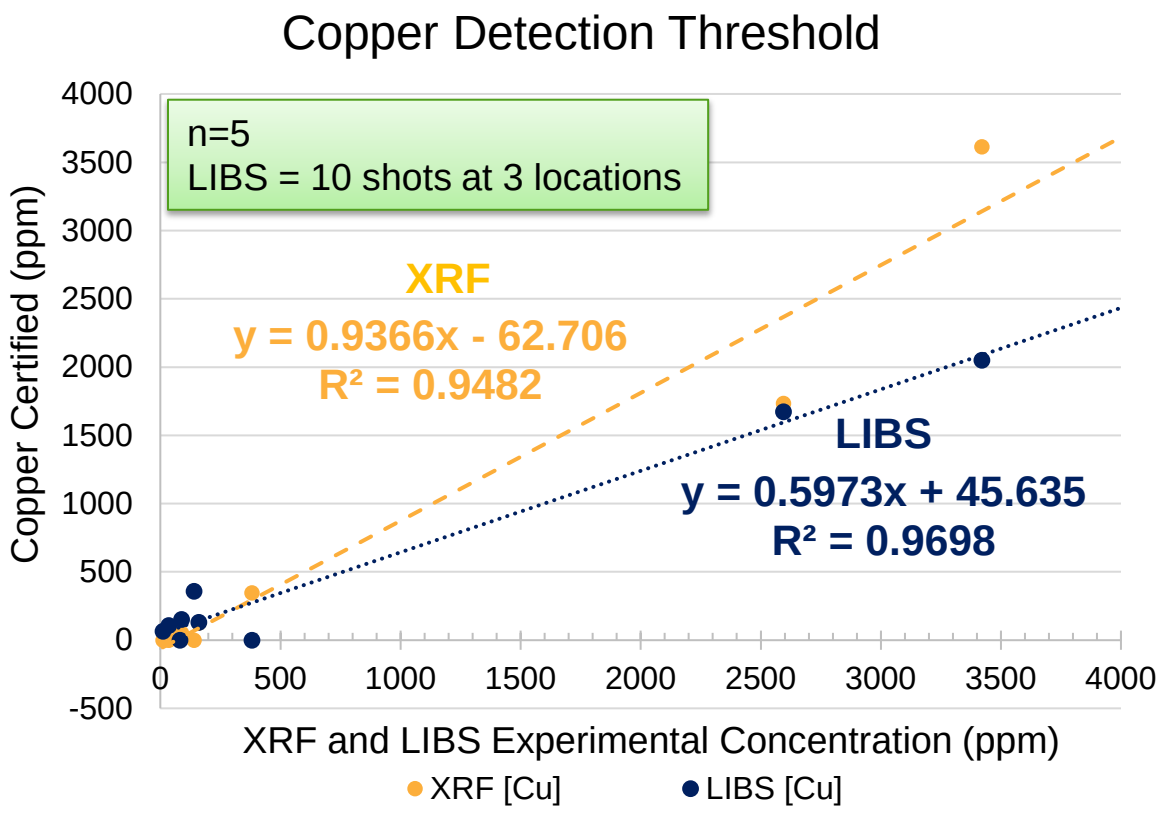
LIBS

ICP

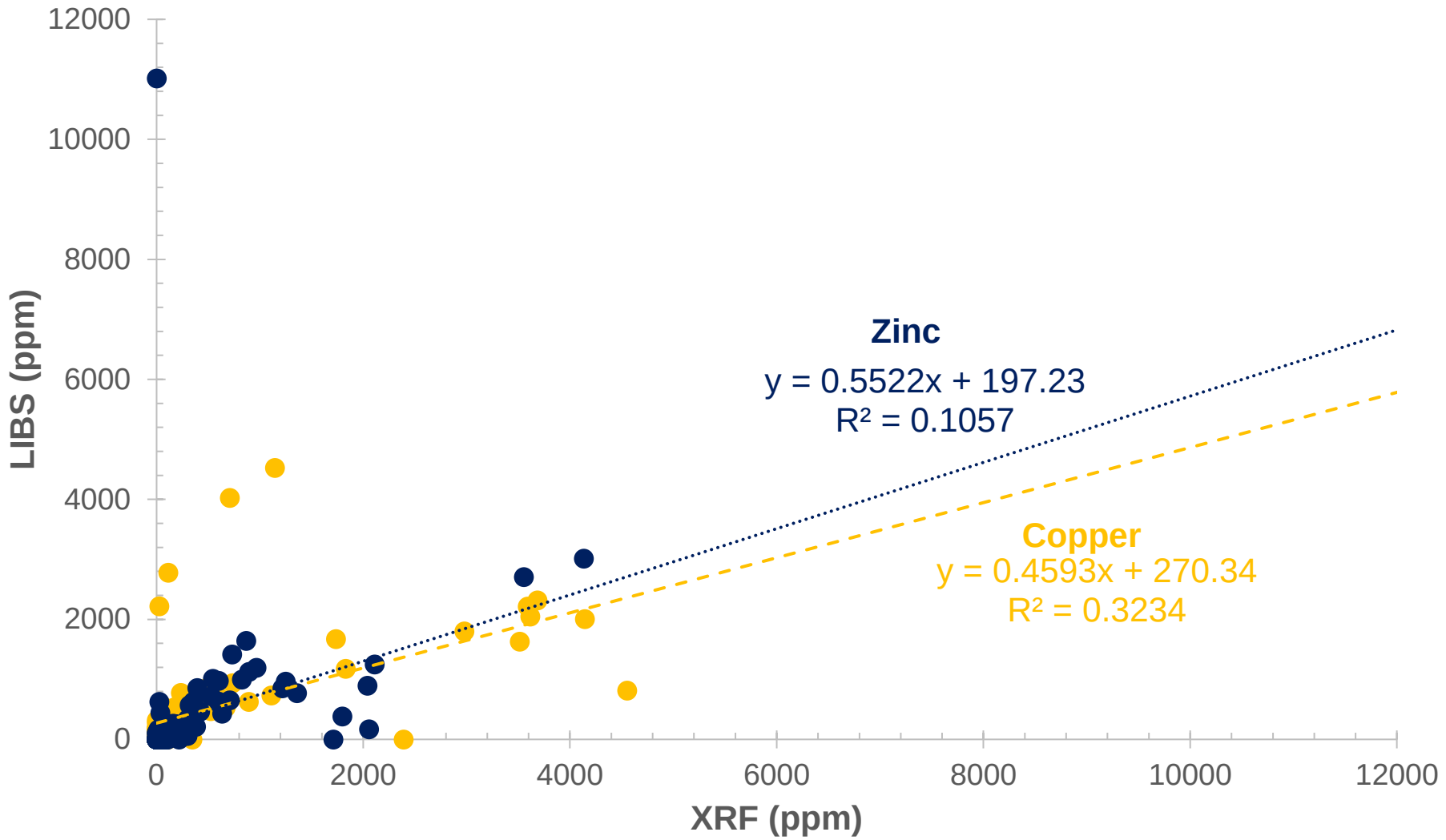


XRF and LIBS Measured Values vs Certified Values

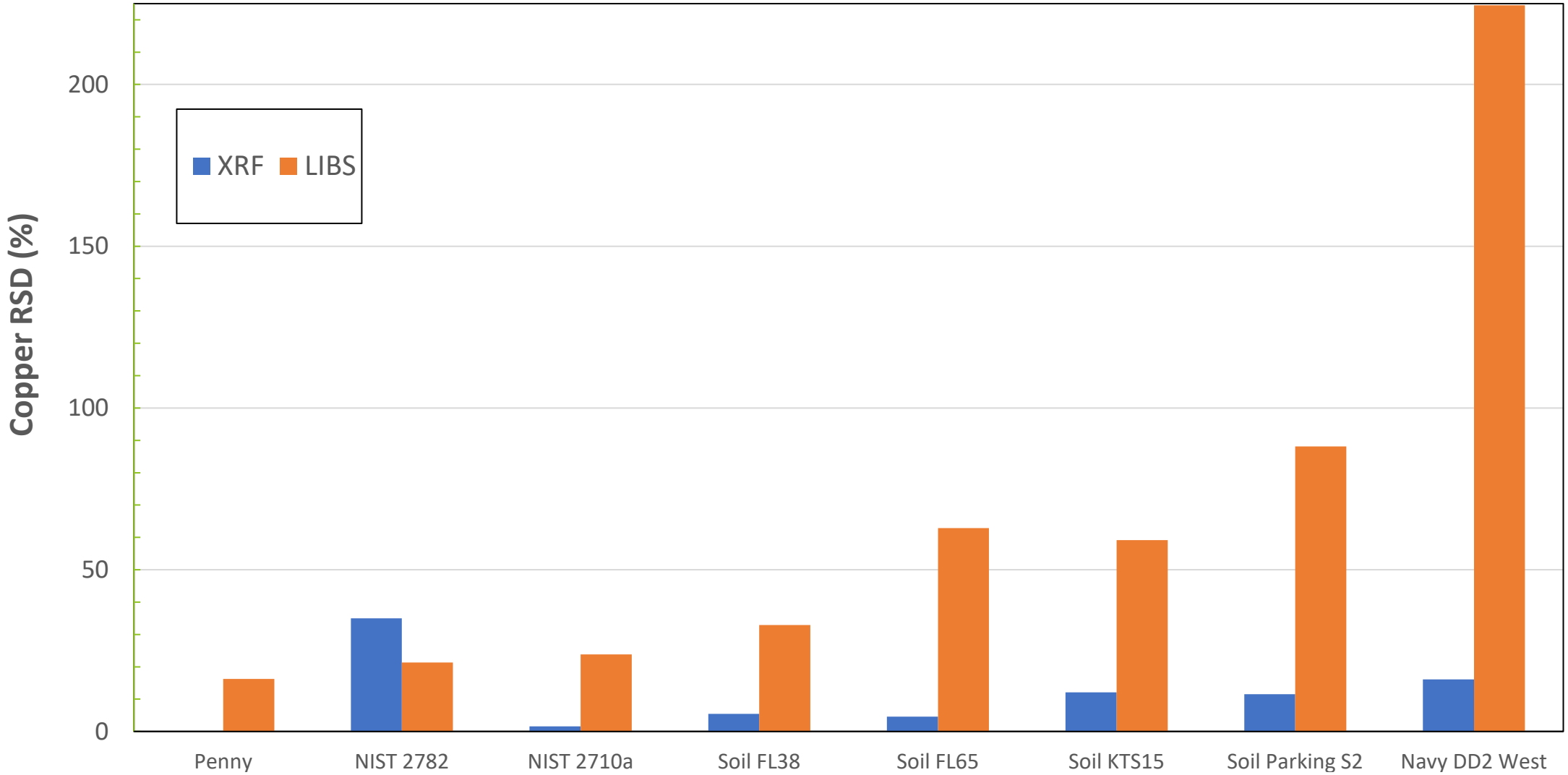




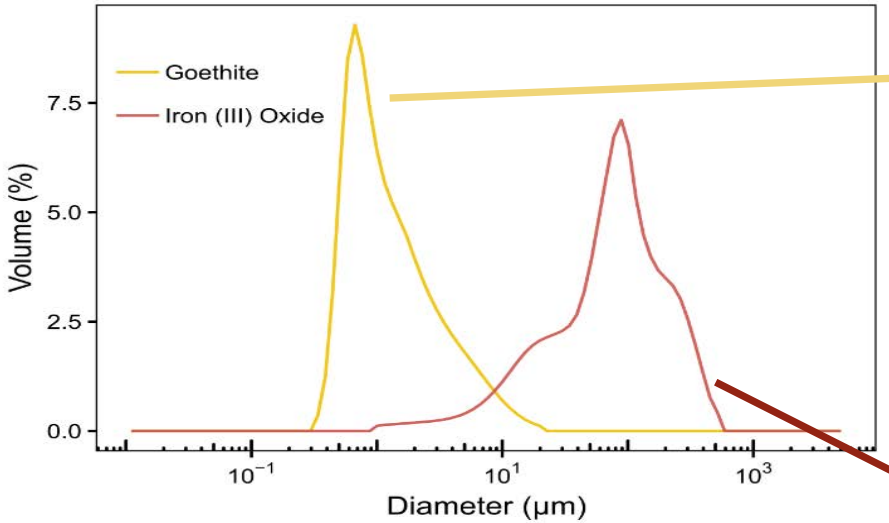
LIBS versus XRF

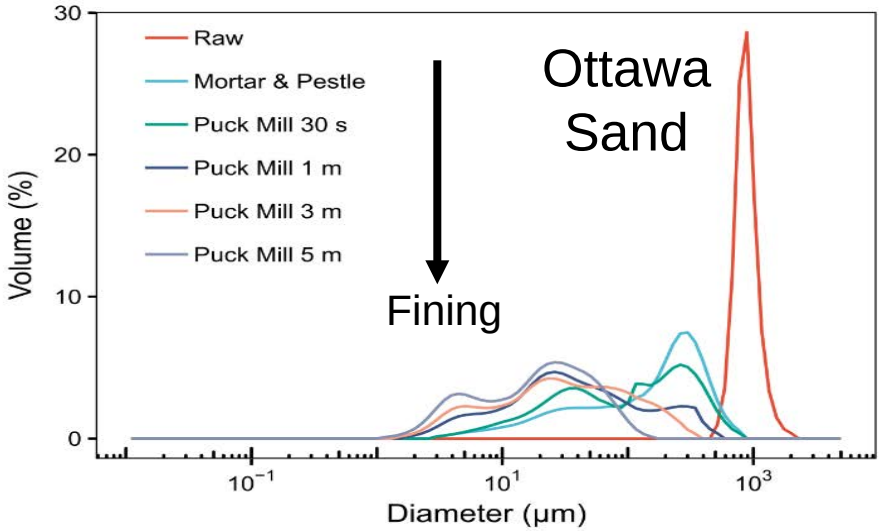


Instrument versus Sample Variability



Particle Size Issue





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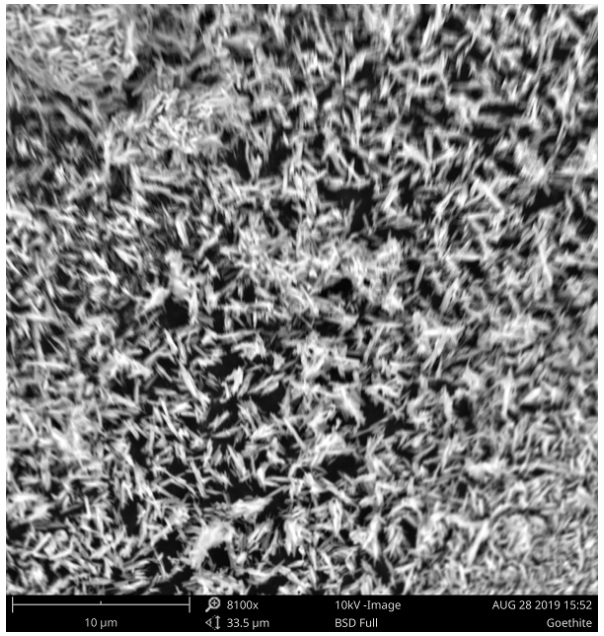
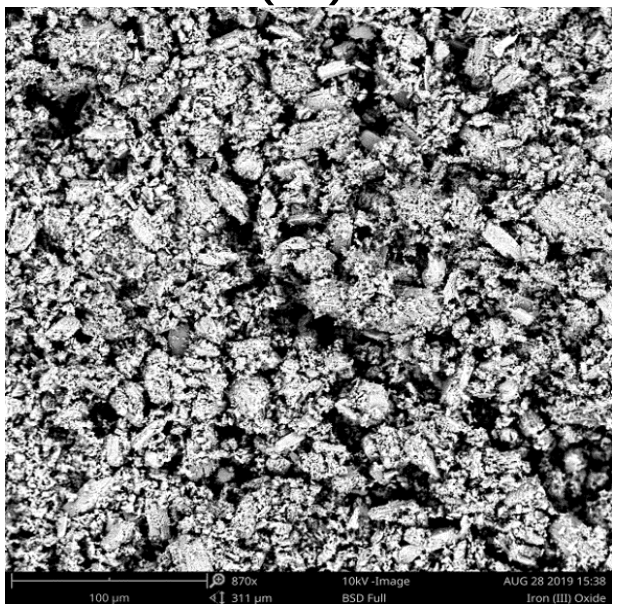
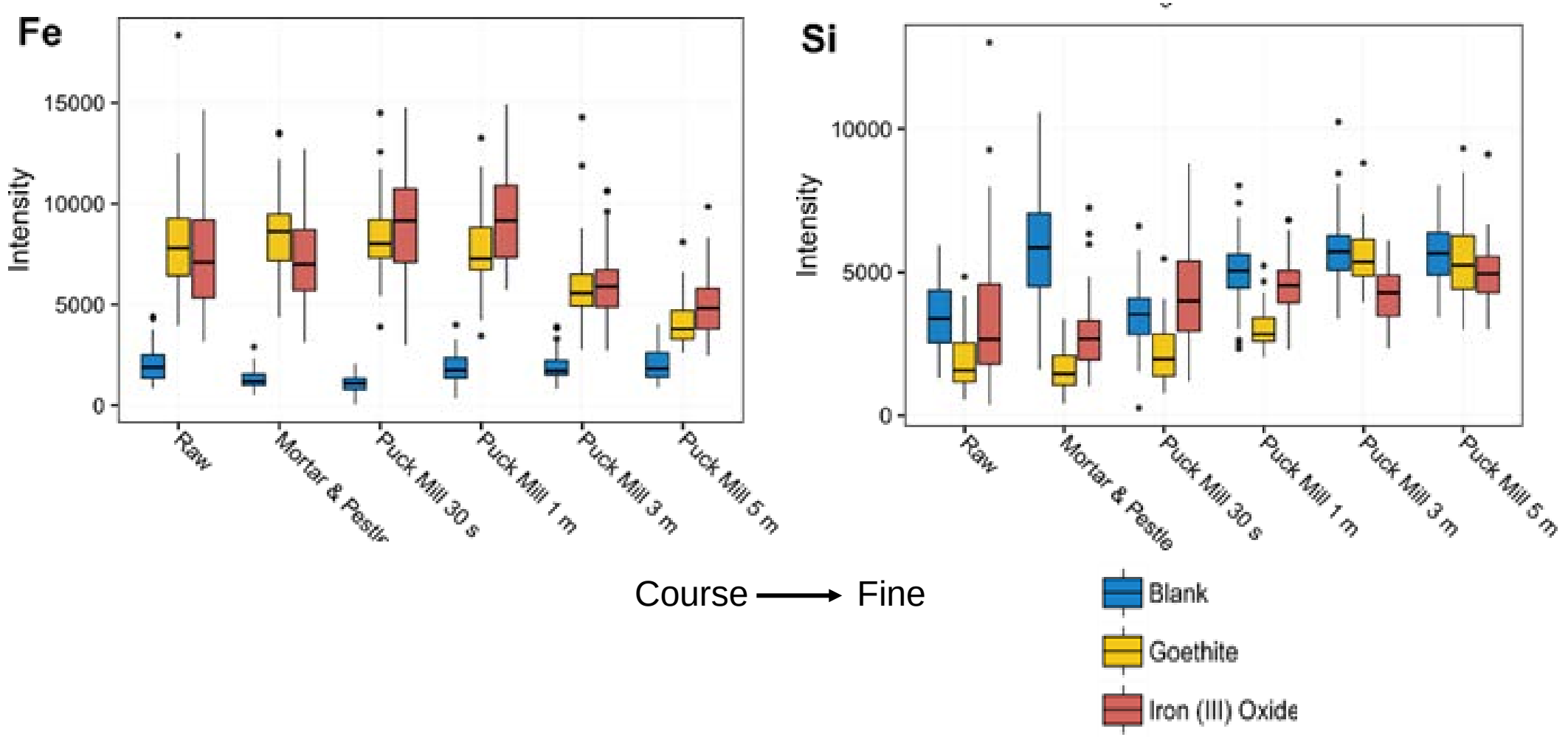


Iron (III) Oxide



LIBS Intensity as Function of Particle Size



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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14. ABSTRACT

Commercially available handheld chemical analyzers for forensic applications have been available for over a decade. Portable systems from multiple vendors can perform X-ray fluorescence (XRF) spectroscopy, Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and recently laser-induced breakdown spectroscopy (LIBS). Together, we have been exploring the development and potential applications of a multisensor system consisting of XRF, Raman, and LIBS for environmental characterization with a focus on soils from military ranges. Handheld sensors offer the potential to substantially increase sample throughput through the elimination of transport of samples back to the laboratory and labor-intensive sample preparation procedures. Further, these technologies have the capability for extremely rapid analysis, on the order of tens of seconds or less. We have compared and evaluated results from the analysis of several hundred soil samples using conventional laboratory bench top inductively coupled plasma atomic emission spectroscopy (ICP-AES) for metals evaluation and high-performance liquid chromatography (HPLC) and Raman spectroscopy for detection and characterization of energetic materials against handheld XRF, LIBS, and Raman analyzers. The soil samples contained antimony, copper, lead, tungsten, and zinc as well as energetic compounds such as 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-triazine (RDX), nitroglycerine (NG), and dinitrotoluene isomers (DNT). Precision, accuracy, and sensitivity of the handheld field sensor technologies were compared against conventional laboratory instrumentation to determine their suitability for field characterization leading to decisional outcomes.

15. SUBJECT TERMS

Scientific apparatus and instruments; Chemistry, Analytic; Soils—Testing; Raman spectroscopy; X-ray spectroscopy; Laser-induced breakdown spectroscopy

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Cold Regions Research and Engineering Laboratory
U.S. Army Engineer Research and Development Center
72 Lyme Road, Hanover, NH 03775

Yale University
New Haven, CT 06520

North Carolina State University
Raleigh, NC 27695

JR Plummer & Associates, LLC
P.O. Box 566, Belmont, NH 03220

Oak Ridge Institute for Science and Education
U.S. Department of Energy
Oak Ridge, TN 37830