Miniature subsurface LIBS probe

Advanced Sensors Task 71
Dan Hartzler, Chet Bhatt, Dustin McIntyre
Project Description and Objectives

- Validate complex subsurface LIBS measurements with lab based system
- Improved online high resolution subsurface and/or process sensor based on underwater LIBS
- Show system can rapidly take large complex data sets
- Show system can produce concentration information of multiple elements in-situ
- Determine pinch-points in deployment and document
- Determine best practices for construction, deployment, and calibrations
- Prove system works as described in a relevant environment
- Show that system has potential for subsurface and process applications
  - Critical materials “Securing the domestic supply chain”
  - Environmental Justice
Project Update

What is LIBS?

- Laser Induced Breakdown Spectroscopy (LIBS)
  - Elemental analysis
  - Rapid
  - Minimal sample preparation
  - Hostile environments
    - Ex: ChemCam (Mars)
Project Update

Miniaturized LIBS Probe

Easily Measure Dissolved metals: Ca, Sr, K, Li, Na, Mg, Mn

Carbon Capture Usage and Storage (CCUS)
Miniaturized LIBS Probe

Project Update

Operational Power Plant Applications:
• Coal characterization for blending control

Potential Power Plant Applications:
• Ash and pond in-situ reclamation analysis
• Water inlet and outlet characterization
• FGD measurement and characterization

Additional Applications:
• Geothermal fluid monitoring
• Acid Mine Drainage characterization
• Rare Earth Separations control

Project Update

Carbonate Dissolution

• Simulation of fluids under Carbon Storage Pressure Conditions
• Validation that LIBS can measure multiple components noninvasively
• Validation that LIBS can measure over a wide range of pressures and pH
• Common Carbonates of Ca, Mg, Mn, Sr were measured for dissolution
• Mt Simon Sandstone sample was measured for dissolution
• All elements go into solution a different pH and different rate and conc.

Project Update

Miniaturized LIBS Probe

Split laser system

Benefits

All Optical downhole
Minimize component count and processes downhole
Lower unit cost for deployable component.

Surface

Expensive/Delicate components on surface
Analytical measurement and control

Subsurface

All control and data through optical fiber
All optical rugged components in subsurface
Detachable, can be left in place or continuously interrogated

Prototype validation

- Miniature prototype constructed and validated
- Laser optical parameters were validated
  - Beam Quality ($M^2$)
  - Reproducibility (SNR reduction)
  - Noise Characteristics (Allen Deviation)
- Laser beam shaping to improve performance
- Adjustments for more efficient use of available pump
  - 2 fibers instead of 1

Laser System Characteristics
- Pump wavelength: 808 nm
- Pump pulse width: 300 microseconds
- Pump pulse power: 500 watts
- Output wavelength: 1064 nm
- Output Energy: 4.5 mJ
- Pulse width (FWHM): 3.3 ns
- Beam Quality ($M^2$): 1.04x and 1.55y
Prototype Validation


<table>
<thead>
<tr>
<th>Element</th>
<th>LOD (ppm)</th>
<th>LOD (literature) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>422.7</td>
<td>0.10A</td>
</tr>
<tr>
<td></td>
<td>393.4A</td>
<td>0.04F</td>
</tr>
<tr>
<td>Strontium</td>
<td>460.7</td>
<td>0.04A</td>
</tr>
<tr>
<td></td>
<td>421.5F</td>
<td>0.03F</td>
</tr>
<tr>
<td>Potassium</td>
<td>766.6</td>
<td>0.009A</td>
</tr>
<tr>
<td></td>
<td>769.9</td>
<td>0.069A</td>
</tr>
</tbody>
</table>

Table 2. Liquid solutions limits of detection for Eu and Yb emission lines

<table>
<thead>
<tr>
<th>Element</th>
<th>Line (nm)</th>
<th>Calibration curve R²</th>
<th>LOD (ppm) aqueous solution</th>
<th>Preconcentrate solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>466.19</td>
<td>0.9984</td>
<td>1.54A</td>
<td>5.0¹⁰,0¹⁰</td>
</tr>
<tr>
<td></td>
<td>462.72</td>
<td>0.9988</td>
<td>1.05³</td>
<td>5.0¹⁰,0¹⁰</td>
</tr>
<tr>
<td></td>
<td>459.40</td>
<td>0.9988</td>
<td>0.85³</td>
<td>5.0¹⁰,0¹⁰</td>
</tr>
<tr>
<td>Yb</td>
<td>398.80</td>
<td>0.9987</td>
<td>1.15³</td>
<td>1.9³</td>
</tr>
</tbody>
</table>

a – this study, b – Yun et al. 2001 [24], c – Integrated area of all three emission lines used for calibration, d – Eu³⁺ aqueous solution, e – Alamelu et al. 2008 [25], f – evaporation onto filter paper prior to measurement, g – Bhatt et al. 2017 [23]

Securing the domestic supply chain
Environmental Justice
Project Update

Submersible Prototype

- System Optical modeling
  - Pump laser at 808nm
  - Atomic Spectra Data 300-900nm
- System physical modeling
  - Must fit inside 2in diameter wellbore and be watertight
Additive Manufacturing for complex geometry

Mocking up prototype
- Do all of the parts fit together
- Does the system work as a whole

3D printing of flexible mirror mounts

Complicated geometry
- Time consuming to machine traditionally
Project Update

Submersible Prototype

• Construction: <2in diameter
• <8in long, watertight
• Operation in Air
• Validation in water

Calcium spectra in water
Preparation Project for Next Steps

Advanced Sensors Task 71

Market Benefits/Assessment

- Rapid online measurement of trace elements in liquids or solids. Identification and/or quantification of toxic elements or significant changes due to subsurface activities.

- Does not use X-ray, Isotopic, or high-power radio waves. Laser can be easily shielded and interlocked.

- Deployable device can significantly reduce trips required to collect data over extended periods. [Reduces repeat fluid collection travel and lab delays]

Technology-to-Market Path

- Current industry partners include Applied Spectra Inc (benchtop LIBS) and MetroLaser Inc. (Laser Manufacturer)

- Engineering challenges remain in reduction of size and cost of key equipment. Narrowing device scope and operational characteristics can overcome these challenges in the short term.

- New research includes the addition of Raman spectroscopy to the LIBS measurements
Objective of complementary TTO

- Improve manufacturability
- Decrease size and complexity
- Reduce component costs
- Reduce fabrication costs
- Add Raman Spectroscopy capability
Technology-to-Market Plan
Technology Transfer Opportunity DE-FOA-0002554

Commercialization Effort
• Reduction of complexity
• Innovative spectrometer ideas
• Reduction of cost
• Maintain operability and sensitivity

Confocal Raman using the split laser frame
• Accumulation time: 1 second
• Laser input power: 0.2 W
• Raman shift: 3652 cm\(^{-1}\)
• \(d\sigma/d\Omega\): 1.96\times10^{-30} \text{ cm}^2/\text{sr}
First field deployment

Existing water test well at Morgantown campus, near B23
Laser tight box for sensitive components, laser safe deployment
30 meters of fiber pulled though conduit and available for deployment
Calibrations performed prior to deployment
First Downhole Data

Element calibrations performed prior

Multiple depths interrogated

Each data point is a few hundred spectra

Rainfall dilution indicated for Na and Ca

K appears unaffected

Li too low to measure (LOD = 8ppb in lab)
Average daily values of in-situ spectra
- Outgassing spectra removed
- Potassium affected by broad luminescence
- Spectra colored by collection data
- Lithium was not detected

Bubble production from laser spark
- Buoyancy driven interference
- Interference with light collection
- Interference with spark production
- Design modification to improve data collection

Probe submerged for over two weeks
- No leakage or optical issues encountered
Probe modifications

Design to remove interference from bubble production

- Sealed unit with optics
- Directly coupled to previous unit
- Deliver laser to fluid and collect spectral data
- Use of additive manufacturing for mock-up and fitment
- Use of additive manufacturing for complex geometry
Preparing for next steps

Field validation

Next Steps

- Second field validation in the subsurface at NETL-MGN
  - Sampling well near B23
  - Planned for June 2022
  - Test duration 2-8 weeks
- Plans are being made to validate the device in the subsurface off-site
  - Legacy management sites

The system is split into two subsystems: 1) an above ground control unit that is connected via fiber optics to 2) one or more sensor heads.
Concluding Remarks

Advanced Sensors Task 71

• Next Steps

• Continue seeking intellectual property
• Continue publishing high quality journal papers
• Continue attending international scientific conferences
• Reducing lab scale equipment to more appropriately size and cost components.
• Continue arranging beneficial CRADA’s and applying for TCF and other funding that can help lead to commercialization.