Laser-Induced Breakdown Spectroscopy (LIBS) for Liquids

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Outline

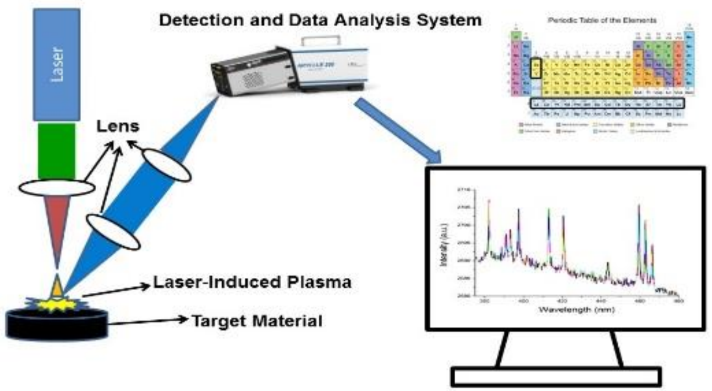
1. Laser-Induced Breakdown Spectroscopy (LIBS)
2. LIBS for Liquids; Recent Trends, Working Mechanism, Challenges
3. LIBS applications:
    - Carbon Sequestration
    - FGD and AMD Wastewaters
4. NETL's LIBS Probe

Laser-Induced Breakdown Spectroscopy (LIBS)

How Does LIBS Work?

LIBS is an atomic emission spectroscopy-based analytical technique to obtain qualitative and quantitative information of the material.

- High energy laser pulse creates micro plasma plume on the sample by ablating a very small amount of material.
- The ablated material dissociates into excited ionic and atomic species.
- The excited atoms/ions present in the plasma emit light at their characteristic wavelengths.
- Spectral analysis of the emission spectrum from the plasma is used to infer the elemental composition of the sample.



LIBS for Liquids

Recent Trends

Plasma Expansion Medium

Underwater and Surface Measurements and Associated Challenges

Our projects: Underwater and Surface Measurements

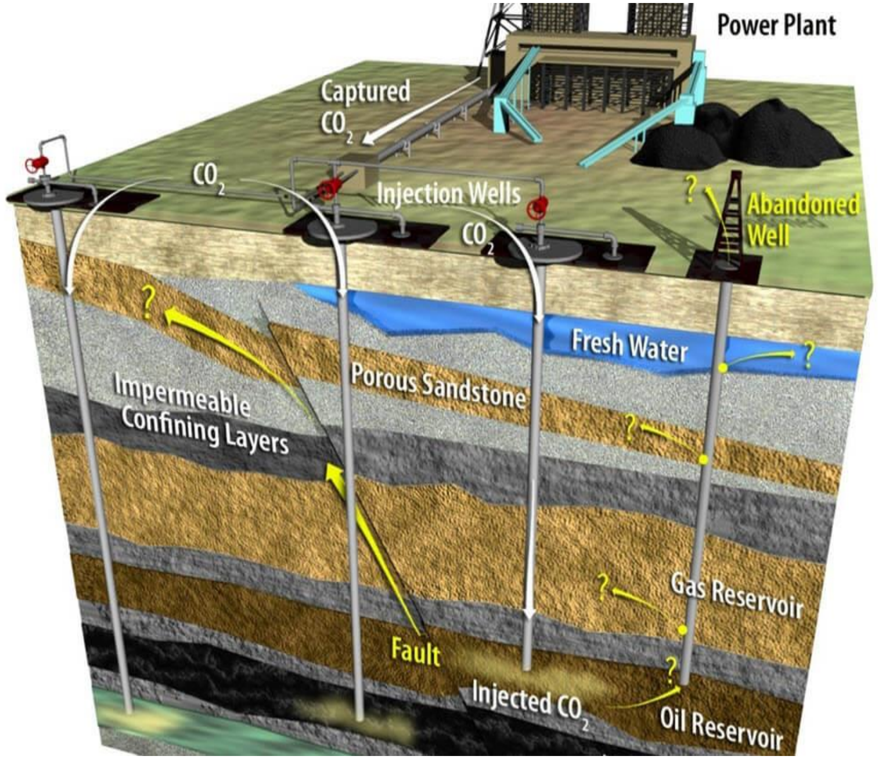
LIBS Application in Carbon Sequestration

- Carbon capture and storage is a big project for the entire world.
- For storage, geological formations (like Sedimentary Basins, Oil Reservoirs, Natural Gas Reservoirs, Unmineable Coal, Saline Formations) are considered as the most promising hosts.
- Deep saline aquifers have been reported to have the highest estimated CO2 storage capacity.
- CO2 leakage detection is critical.
- At NTP, carbonates are almost insoluble.
- As pCO_2 increases, the pH drops, carbonate ions (CO_3^{2-}) are converted into bicarbonate (HCO_3^-) ions.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

$$H^+ + SrCO_3 \leftrightarrow Sr^{2+} + HCO_3^-$$

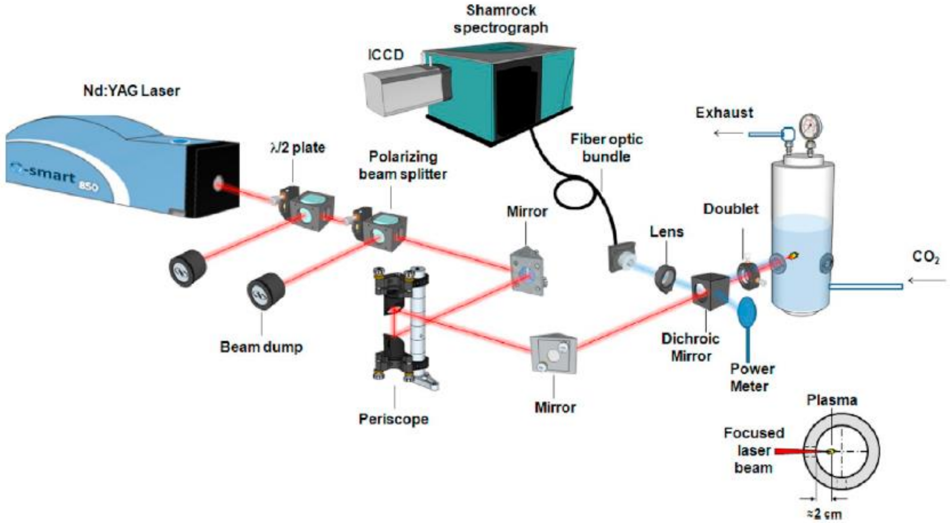
$$H^+ + CaCO_3 \leftrightarrow Ca^{2+} + HCO_3^-$$



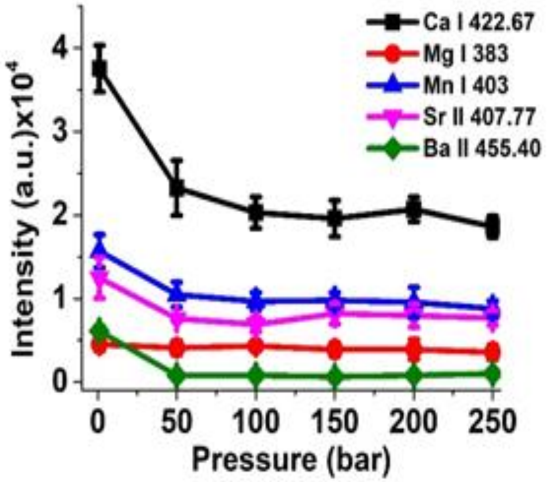
Picture: GoldSim Technology Group, Los Alamos National Laboratory (LANL)

State/ Province	CO_2 Emissions		Oil and Natural Gas Reservoirs Storage Resource			Unmineable Coal Storage Resource			Saline Formation Storage Resource			Total Storage Resource		
	Million Metric Tons Per Year	Number of Sources	Billion Metric Tons			Billion Metric Tons			Billion Metric Tons			Billion Metric Tons		
			Low Estimate	Medium Estimate	High Estimate	Low Estimate	Medium Estimate	High Estimate	Low Estimate	Medium Estimate	High Estimate	Low Estimate	Medium Estimate	High Estimate
North America Total	3,071	6,358	186	205	232	54	80	113	2,379	8,328	21,633	2,618	8,613	21,978

Experimental Set-up, Samples, and Calibration

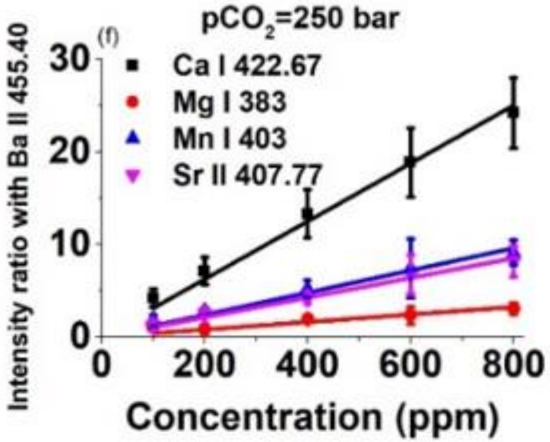


Experimental parameters
Laser: Nd:YAG (Q-smart 850, Quantel), Wavelength: 1064 nm, Pulse duration: 6ns
Gate delay: 100 ns and 160 ns,
Gate width: 400 ns and 800 ns,
Laser energy: 25 mJ with 10 Hz repetition rate



Pressure Effect on Signal Intensity

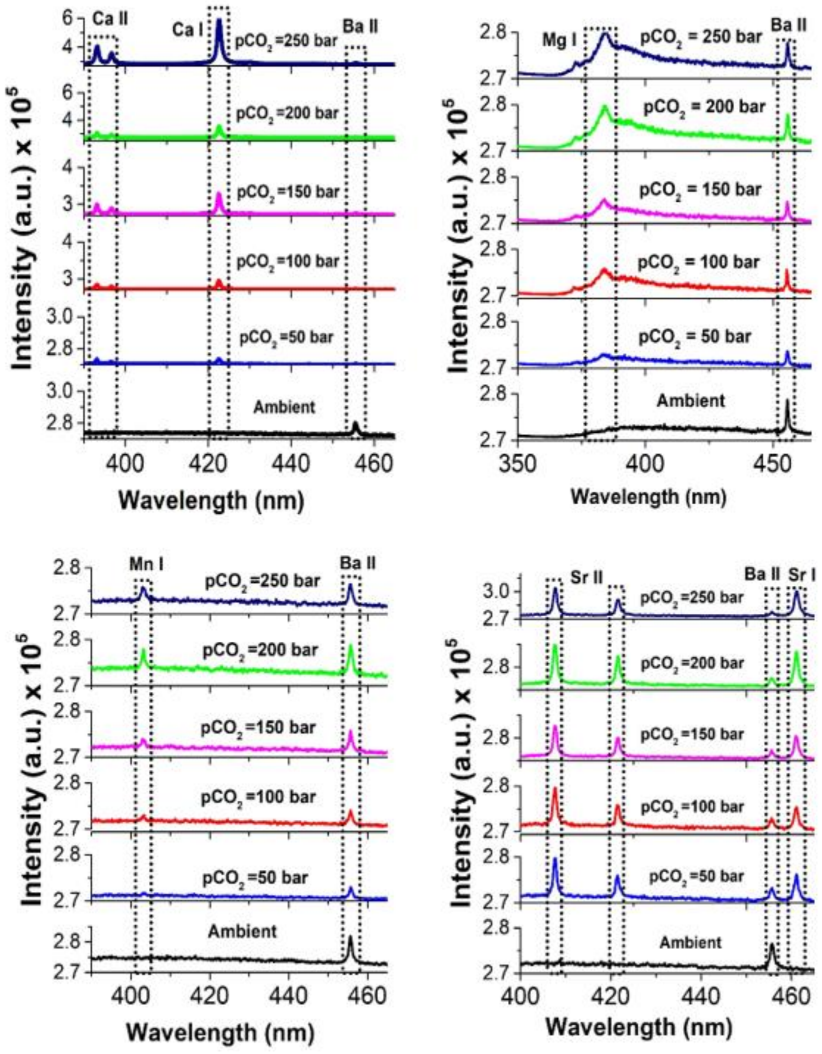
- Samples: $CaCO_3$, $SrCO_3$, $MnCO_3$, $MgCO_3$, Mt. Simon.
- Pellet composition: Carbonate powder and 4% agarose.
- Pellet size and weight: 15 mm diameter, 0.5 g.

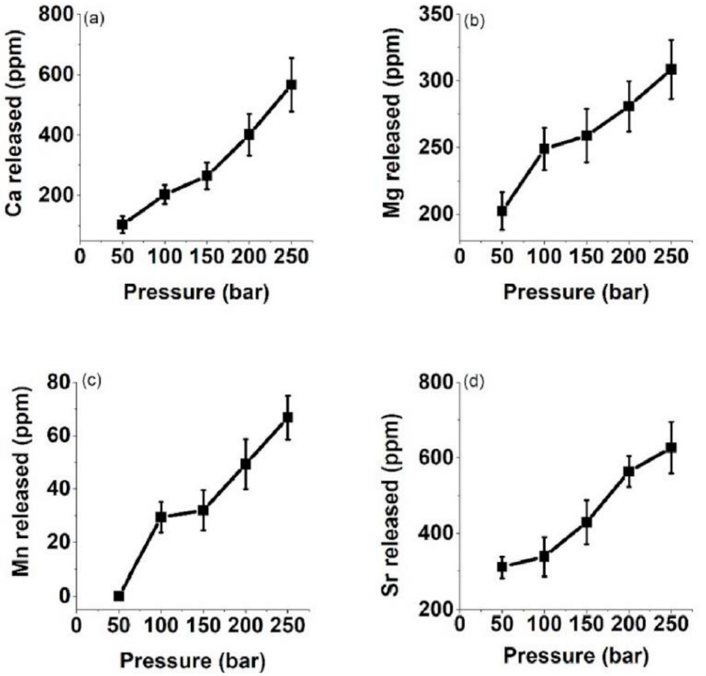


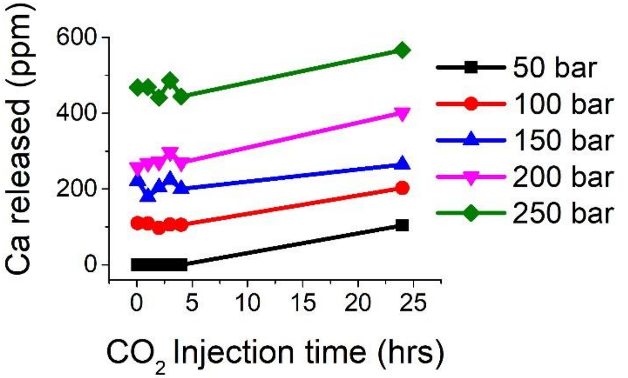
Calibration Curves

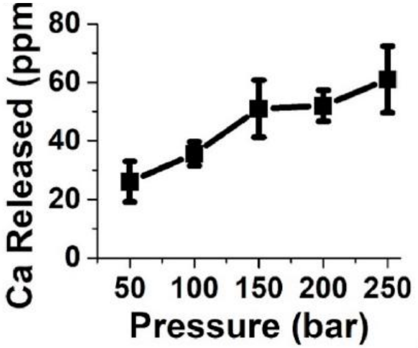
Carbonate Dissolution

- 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 at different pH and at different rate and concentration







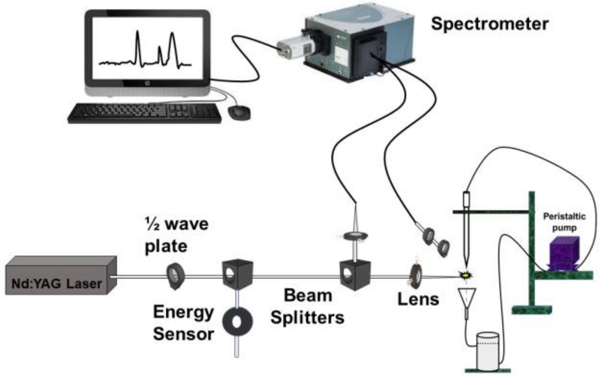


Toxic Elements Detection in Liquids

Motivation

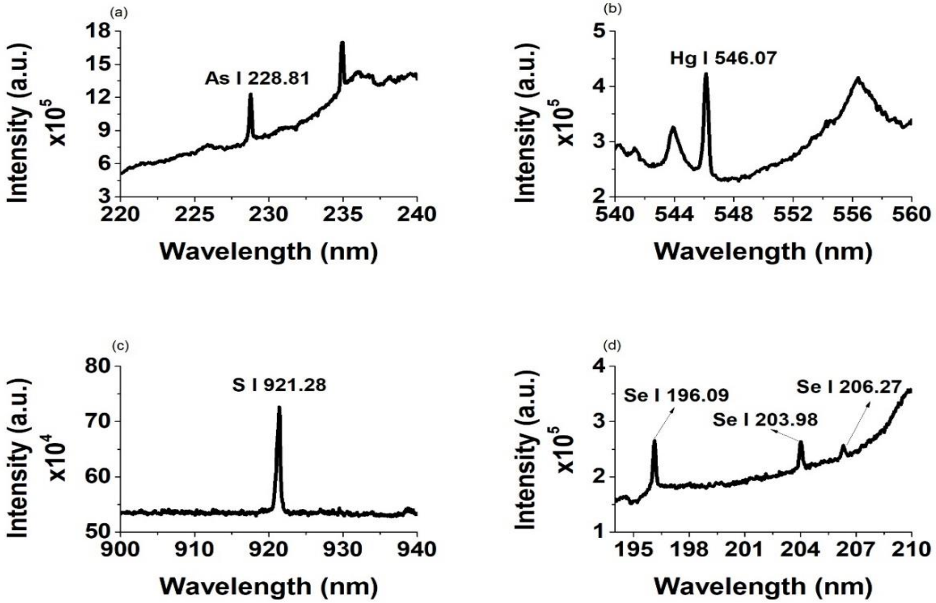
- FGD AMD wastewater
- Importance of toxic elements detection
- Existing practices for detection
- Need for online monitoring tool
- Laser-Induced Breakdown Spectroscopy (LIBS) has potential
- Goal: to develop a LIBS based sensor

LIBS Benchtop SET-UP



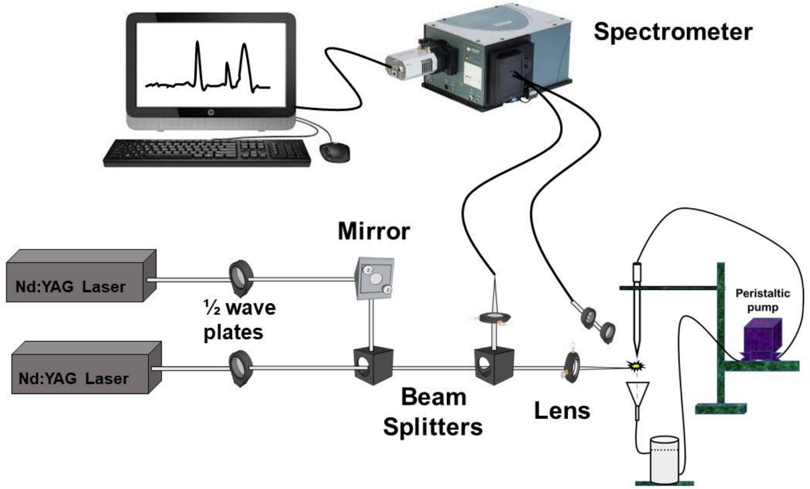
- Samples: As, Hg, S, and Se solution
- Surface ablation
- Underwater LIBS
- Advantages of jet

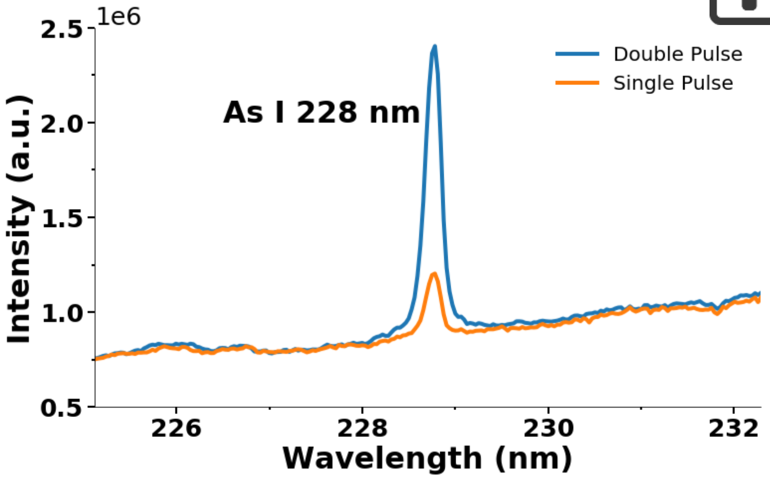
LIBS Spectra

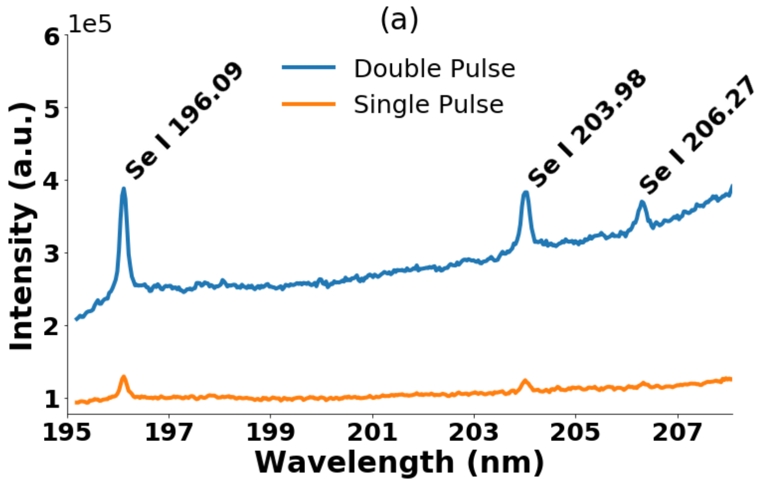


Lasers: Nd:YAG (New Wave Research),
Wavelength: 1064 nm, Pulse duration: 6ns
Spectrograph: Andor Czerny-Turner (190-1000 nm)

Signal Enhancement with DP-LIBS







Spectral lines	LOD(PPM)	
	SP	DP
As I 228.81 nm	2	0.4
Hg I 546.07 nm	16	8
S I 921 nm	16	8
Se I 196.09 nm	29	11

NETL'S LIBS Prototype: System Overview

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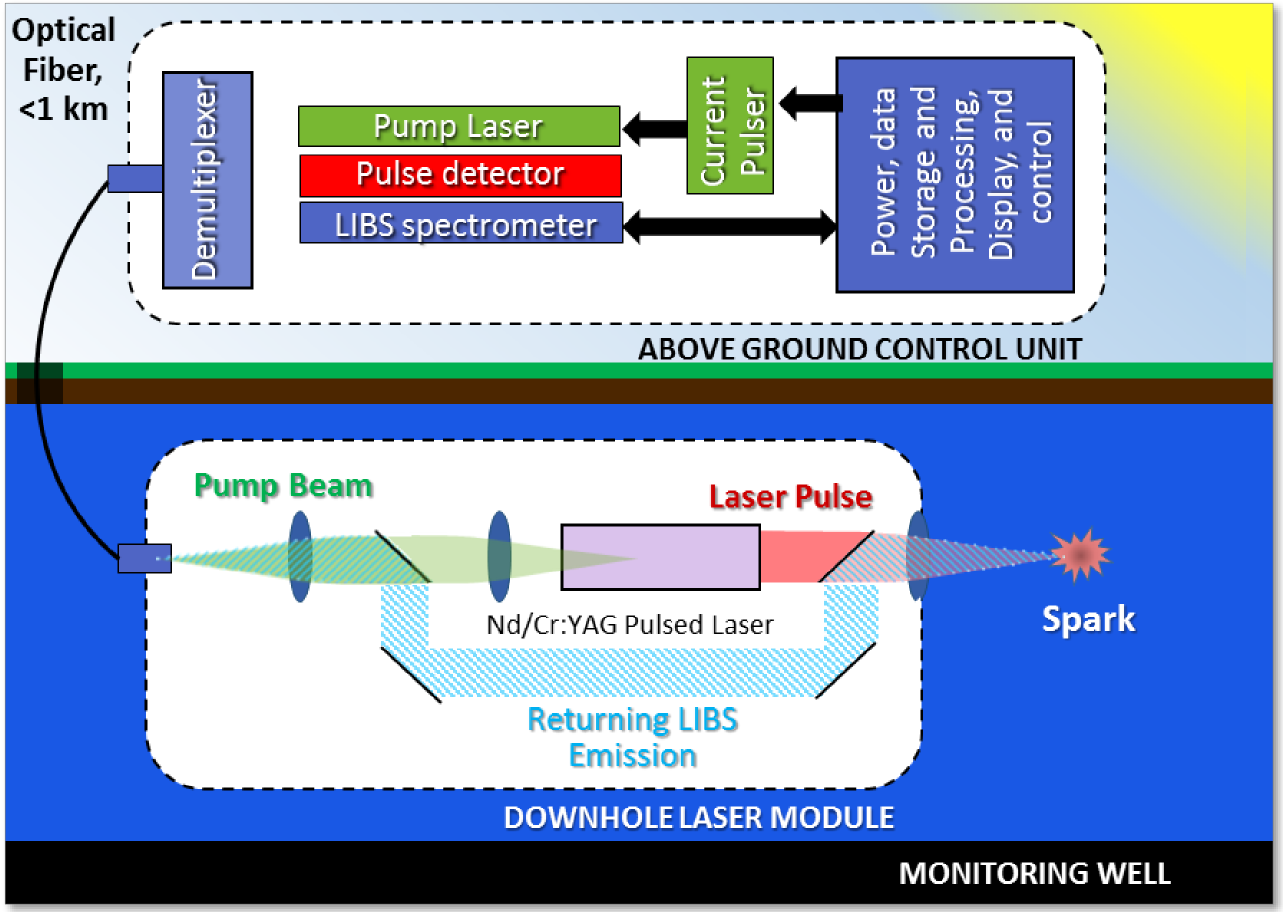
The system splits the traditional Laser Induced Breakdown Spectroscopy (LIBS) into two subsystems

- **Control Unit**: Contains the large and fragile system components such as the spectrometer, pump laser, etc.
- **Sensor Head**: All optical probe built around a Passively Q-Switched (PQSW) laser



The split design allows the control unit to remain in a controlled environment or central location while only the compact, low-cost sensor head needs to enter the hostile environment or remote location

- SD Woodruff, DL McIntyre, JC Jain, U.S. Patent US 8,786,840 (2012)
- SD Woodruff, DL McIntyre, U.S. Patent US 9,297,696 (2013)
- DL McIntyre, U.S. Patent US 10,145,737 (2017)
- JC Jain, DL McIntyre, and CL Goueguel, National Innovation Summit & Showcase (2017)
- CG. Carson., CL Goueguel, JC Jain, DL McIntyre., Proc. SPIE 9467, Micro- and Nanotechnology Sensors, Systems, and Applications VII, 94671K (2015)

Laboratory Prototype

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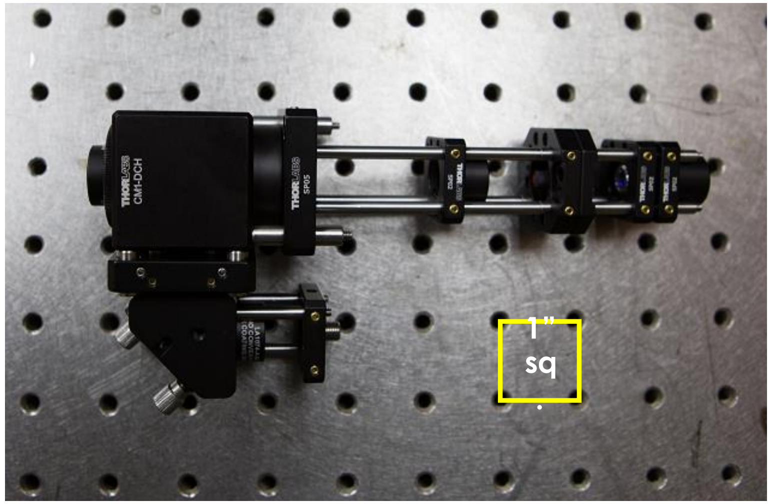
Prototype Sensor – How Does It Compare?
- Limits of Detection (LODs) as good as or better than many benchtop systems

Element	Prototype LOD (ppm)	Benchtop LOD (ppm)		
Calcium	0.10[A]	0.94[B]	0.047[C]	0.13[E]
Strontium	0.04[A]	2.89[B]		
Potassium	0.009[A]	0.03[B]	0.006[D]	1.2[F]



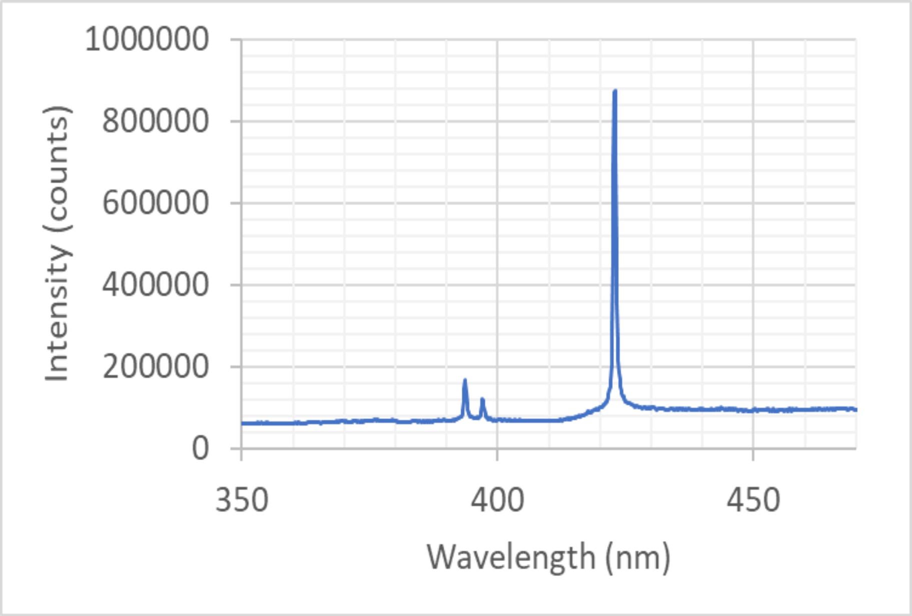
Prototype Sensor – Does it work for REEs?
- Limits of Detection (LODs) comparable to benchtop systems (see Table to right)
- LODs relevant to real world samples [G]

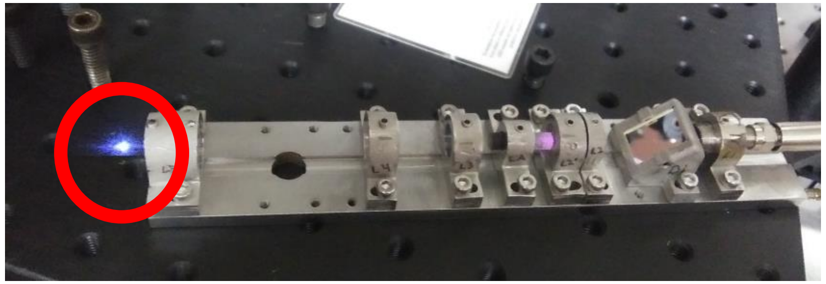
Element	Prototype LOD (ppm)	Benchtop LOD (ppm)		
	Aqueous Solution			
Ytterbium	1.15[G]	156[H]		
Europium	0.85[G]	256[H]	5.0[J]	1.9[K]
	Solid Pellet			
Europium	9.9[G]	2.4[I]		

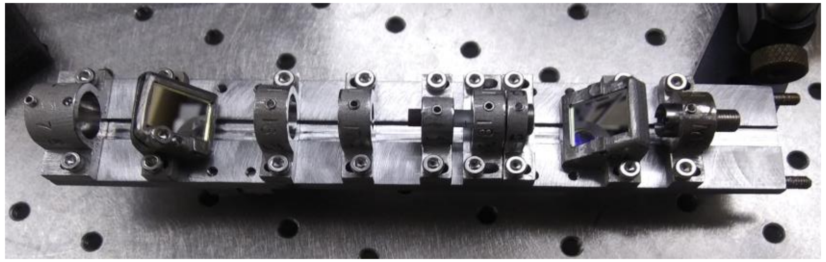
Field Prototype

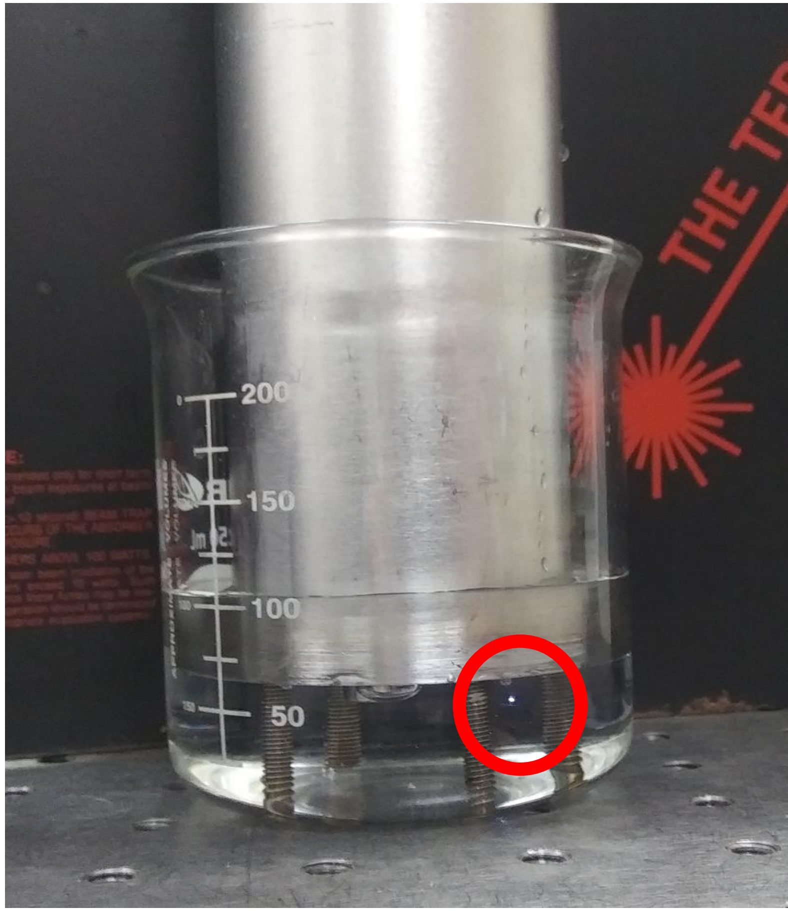
- Construction: <2in diameter
- <8in long watertight
- Operation in Air
- Validation in water

Calcium spectra









System Size – Sensor Head

The main size limitation in the current laboratory prototypes are the use of commercial-off-the-shelf optical components and the inclusion of significant mechanical adjustability in the optical system.

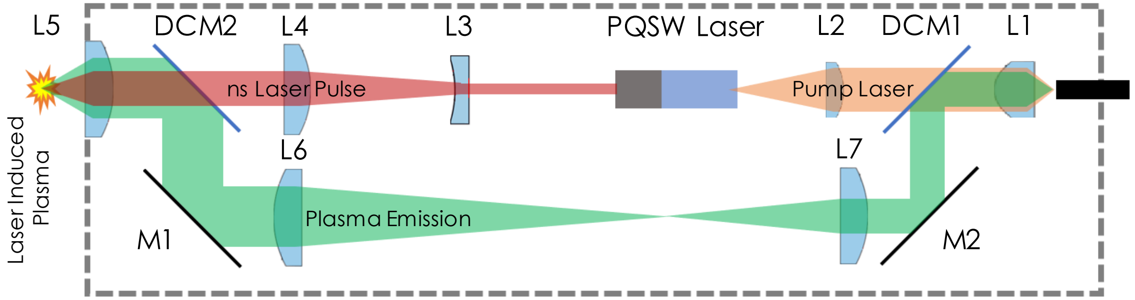
The only limits in the probe cross-section dimensions are the size of the optical components themselves and the minimum separation between the mirrors (e.g. M1 and DCM2) needed to pass the plasma emission around the laser crystal.

The prototype currently under construction have a 2” diameter cross-section and 8” in length.

A fully custom design (optics and mechanics) could easily bring the sensor head cross section < 1”.

A recent NETL DOE patent (US 10,145,737) describes a modification to the original design that eliminates optical components reducing complexity.

- New patented design can reduce device length.



System Size – Control Unit and Power Requirements

Control Unit

The control unit is currently based on general purpose laboratory equipment which is large and heavy.

This equipment can be replaced with light weight miniaturized components.

- Example: gated spectrometer developed for the Mars 2020 Rover
  - doi.org/10.1117/12.2296230
- Example: VCSEL pump laser technology
  - https://www.laserfocusworld.com/home/article/16547957/vcsel-arrays-highpower-vcsels-mature-into-production

Power Requirements

- The sensor head has no electronic components
  - No electrical power needs to be delivered to the head.
- The PQSW laser within the head is powered by an optical pump pulse.
  - A 250 µs current pulse of 50A @ 20V is delivered to the diode pump laser and delivers a 250 µs, 83mJ, 808 nm light pulse via fiber optic to the PQSW laser.

NETL-LIBS Sensor Advantages and Potential Applications

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NETL LIBS sensor advantages

- Fiber coupled design provides flexibility
  - Control unit can be incorporated into platform body while sensor head is deployed into environment or mounted on manipulator
- Compact size saves weight and space
  - Important for mobile platforms like drones and ROVs

Possible Platforms

- Land: Fixed installations (e.g., subsurface, facilities) and Mobile (remotely operated / autonomous vehicles).
- Water: Fixed installations (e.g., pipelines, reservoirs, buoys) and Mobile (remotely operated / autonomous boats or submersibles)
- Air: Fixed installations (e.g., towers) and Mobile (drones, lighter than air)

Potential Applications

Environmental Monitoring

- Nuclear, Biological, Chemical (NBC)
- Water Supply Safety
  - Municipal, Surface, and Subsurface
- Bio-accumulation

Hostile Environments

- High Temperature, High Radiation, Chemical Hazards

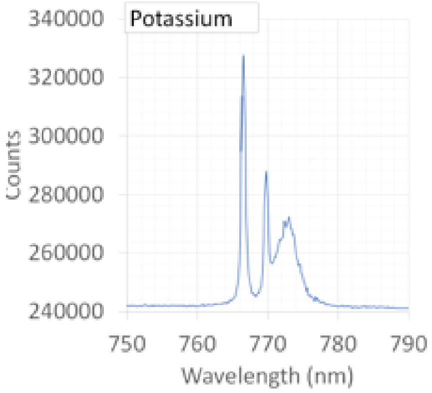
In-situ Sensing

- Operation in Hostile Environments
- Process / Facility Monitoring

Prototype Validation

Element	Line (nm)	LOD (ppm)	LOD (literature) (ppm)		
Calcium	422.7	0.10[A]	0.94[B,†]	0.047[E]	0.13[G]
	393.4[‡]			0.01[E,Δ]	0.6[G]
Strontium	460.7	0.04[A]	2.89[B,†]		
	421.5[‡]		0.34[C,#]		
	407.8[‡]		0.025[D]		
Potassium	766.6	0.009[A]	0.03[B,†]	0.006[E,Δ]	1.2[H]
	769.9	0.069[A]			

Table 2. Room temperature and pressure limits of detection for Ca, Sr, and K. [A]This study, [B]Goueguel *et al.*[22], [C]Fichet *et al.*[24], [D]Popov *et al.*[26], [E]Pearman *et al.*[23], [F]Golik *et al.*[48], [G]Knopp *et al.*[25], [H]Cremers *et al.*[21], ‡Lines showed self-absorption over the concentration ranges used in this study thus these lines were not used for calibration, †NaCl solution matrix, #LIP on liquid surface, Δfs LIBS + LIP on liquid surface.



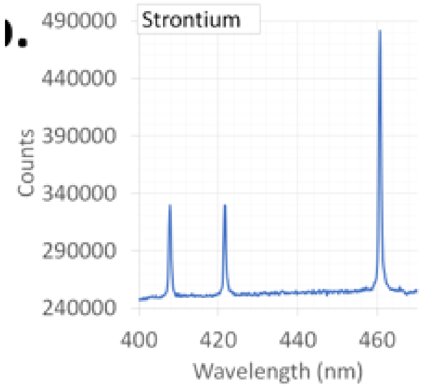
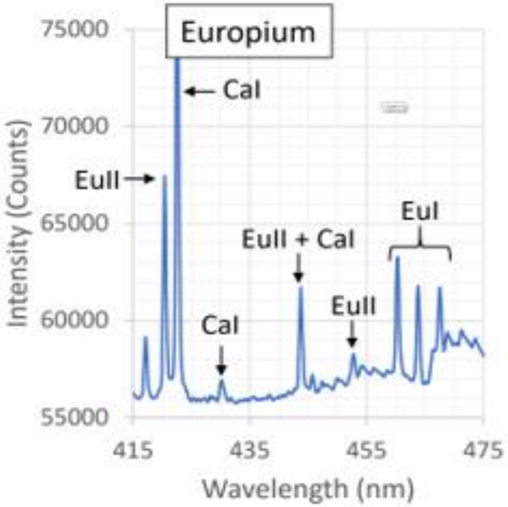


Table 2 Liquid solutions limits of detection for Eu and Yb emission lines

Element	Line (nm)	Calibration curve R^2	LOD (ppm) aqueous solution			Preconcentrate solution
Eu	466.19	0.9984	1.54[a]		5.0[b,c,d]	
	462.72	0.9988	1.05[a]		5.0[b,c,d]	1.9[e,f]
	459.40	0.9988	0.85[a]	256[g]	5.0[b,c,d]	
Yb	398.80	0.9987	1.15[a]	156[g]		

[a]This study.
[b]Yun et al. [24].
[c]Integrated area of all three emission lines used for calibration.
[d]Eu^{3+} aqueous solution.
[e]Alamelu et al. [25].
[f]Evaporation onto filter paper prior to measurement.
[g]Bhatt et al. [23].



Performance Enhancements

Double Pulse LIBS

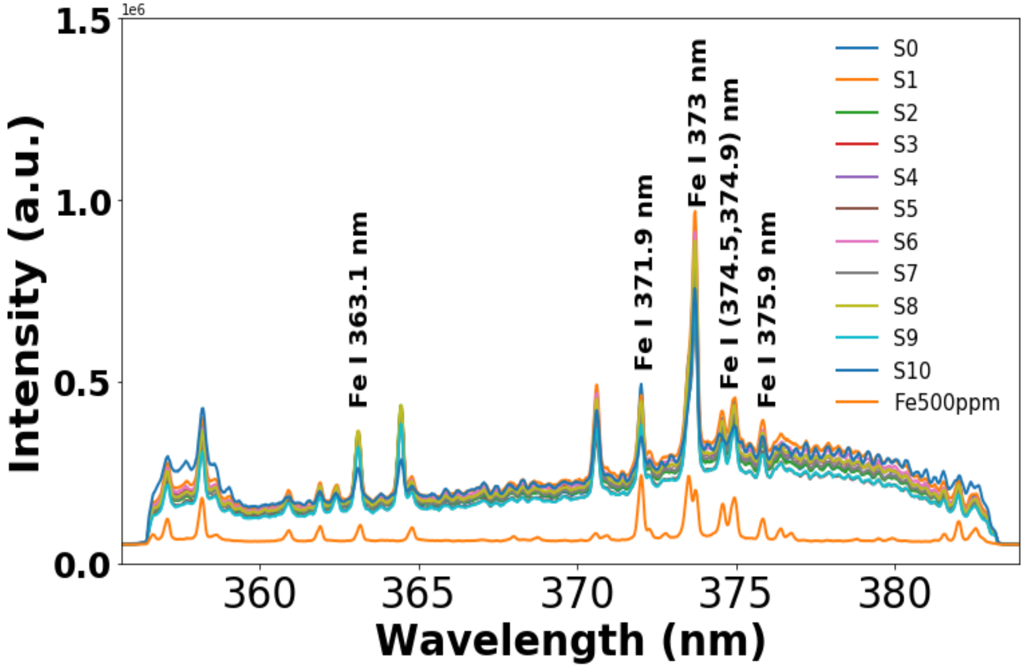
- Up to an order of magnitude improvement in sensitivity to Rare Earth Elements was demonstrated in our lab recently (Bhatt, 2019)
- Incorporation of this technique into a sensor head is planned but **depends on available funds**.

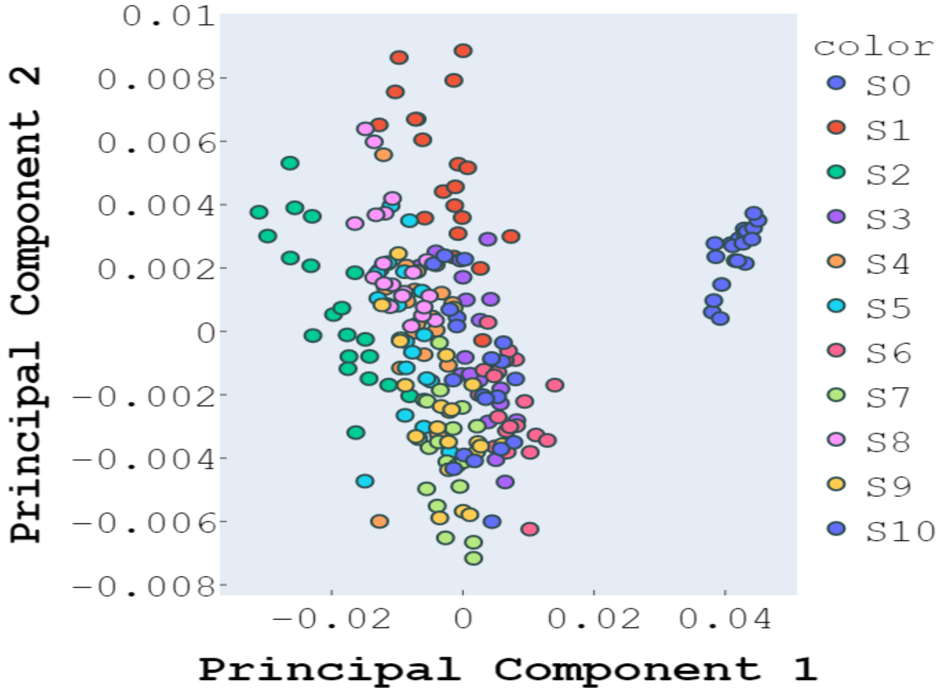
Fluorescence Immune Raman

- Sample fluorescence can completely overwhelm a Raman signal.
- There are known techniques to suppress fluorescence interference (Martyshkin, 2004), however, to the best of our knowledge none have been adapted for field deployment.
  - We are pursuing funding through the Technology Commercialization Fund (TCF) with an industrial partner for the technique described by Martyshkin 2004.
  - An **alternative**, **higher risk / higher benefit** fluorescence gating technique exists. Kerr gating (Johansson, 2013) is a promising technique that has potential for sensor miniaturization and reduction in power consumption. A fiber coupled; all optical **Raman system similar in form factor** to the **NETL LIBS system is possible** using this technique. This approach is not being pursued as part of the mentioned TCF proposal.

Laboratory Measurements

Detection of Iron in Wastewater Outfall





Samples	S0	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	Fe
Water samples collected on	19-Dec-19	29-Sep-20	30-Sep-20	1-Oct-20	2-Oct-20	3-Oct-20	4-Oct-20	5-Oct-20	6-Oct-20	7-Oct-20	8-Oct-20	500 PPM Fe

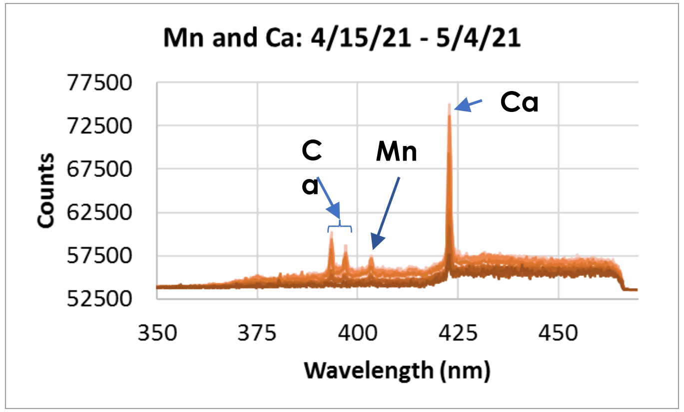
Field Measurements

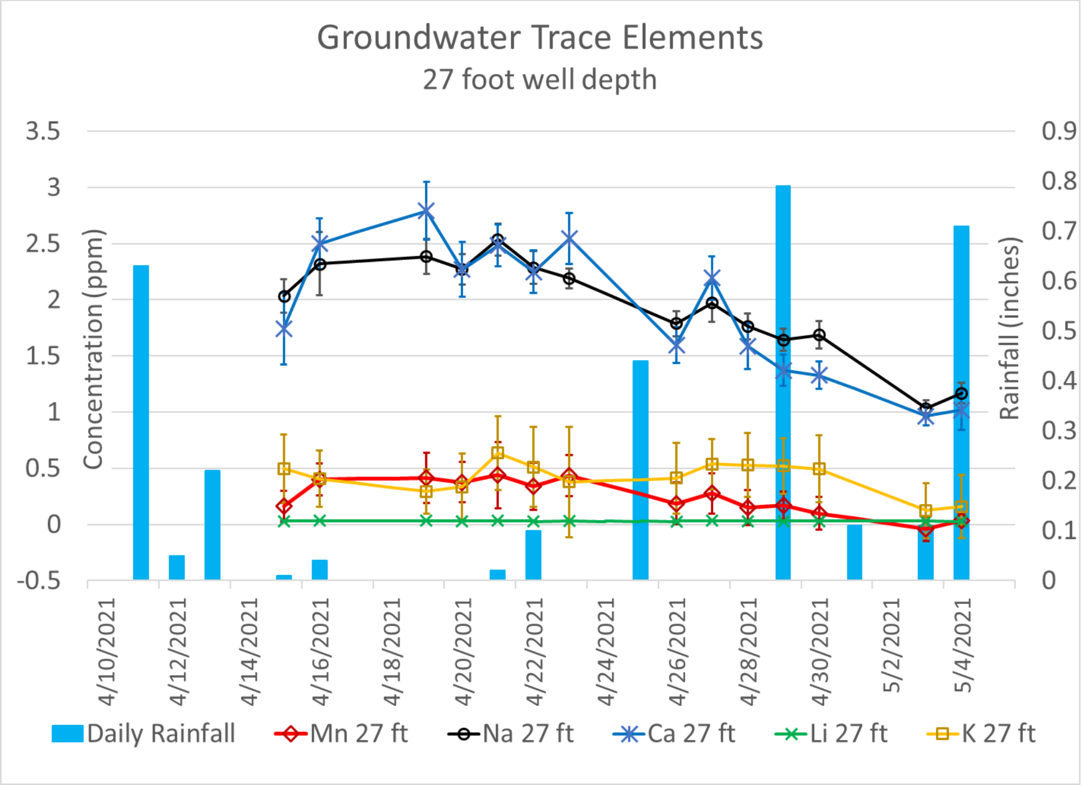
Test parameters

- On site test well: 27 ft well depth / 15 ft water depth
- Data collected daily over a 20-day period (excluding weekends)
- 20 – 40 spectra (100 shots each) were collected for each spectral range

Field Measurements

- Instrument was calibrated for Mn, Ca, Na, Li, and K
  - Li was not observed in the groundwater
- Trace element concentration correlates with local rainfall





NETL'S LIBS Prototype

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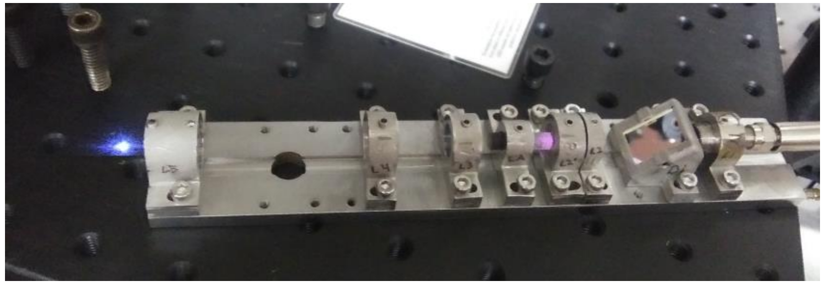

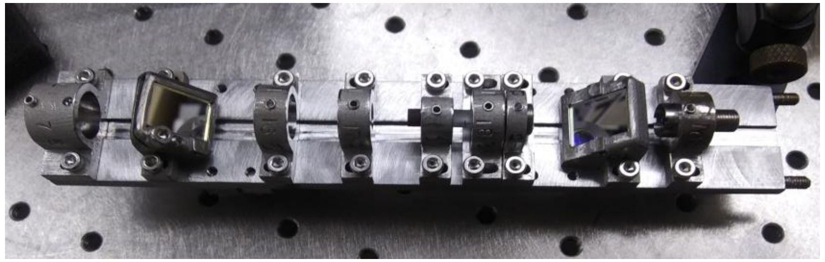

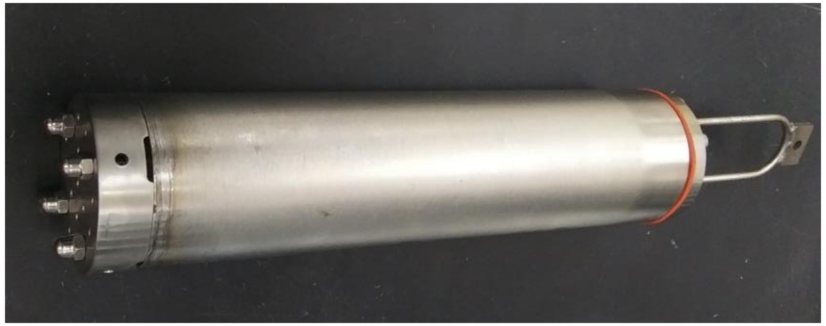

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Huang 2007 - Multisensor Data Fusion for High Quality Data Analysis and Processing in Measurement and Instrumentation

InfraTec - https://www.infratec-infrared.com/sensor-division/fpi-detectors/

Johansson 2013 - Rejection of fluorescence from Raman spectra of explosives by picosecond optical Kerr gating

Martyshkin 2004 – Effective suppression of fluorescence light in Raman measurements using ultrafast time gated charge coupled device camera

Moros 2011 - New Raman–Laser-Induced Breakdown Spectroscopy Identity of Explosives Using Parametric Data Fusion on an Integrated Sensing Platform

Prochazka 2017 - Combination of laser-induced breakdown spectroscopy and Raman spectroscopy for multivariate classification of bacteria

Rammelkamp 2019 - Low-level LIBS and Raman data fusion in the context of in situ Mars exploration

Sciaps - https://www.sciaps.com/libs-handheld-laser-analyzers/z-300/

Sharma 2009 - A combined remote Raman and LIBS instrument for characterizing minerals with 532 nm laser excitation

Thanks for Your Attention!

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