

Prototype LIBS Sensor for Monitoring Subsurface Water Quality Impacts from Geologic Carbon Storage

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Abstract

A Laser Induced Breakdown Spectroscopy (LIBS) based sensor is developed for sub-surface water quality monitoring and characterization. The prototype sensor head was constructed using off the shelf components and a custom, passively Q-switched (PSQW) laser. The sensor head is fiber coupled to a pump laser and a time-gated spectrometer, a design that will allow the expensive and fragile components to remain at the surface while only the low-cost sensor head needs to enter the hostile downhole environment. Ongoing testing has demonstrated the validity of the fiber coupled design and has shown the prototype's performance matches or exceeds that of traditional benchtop LIBS systems. Applications of this novel sensor technology include carbon dioxide (CO₂) leak detection for Geologic Carbon Storage (GCS) and Rare Earth Element (REE) source characterization. Leakage of CO₂ from GCS can potentially contaminate the groundwater aquifers with metals originating either from the high salinity brines or acid leaching of the formation rocks. Detection of the elevated level of these proxy metals (e.g., Ca, Sr, K) can be used to provide an early detection of the CO₂ leak. Measurements of aqueous solutions of Ca, Sr, and K showed good calibration linearity with R² values over 0.99 and provided excellent Limits of Detection (LODs) between 10 and 100 ppb. The LOD for REE (Eu and Yb) ranged between 1 and 10 ppm for liquid and solid samples respectively.

Laser-Induced Breakdown Spectroscopy (LIBS)

- LIBS is an atomic emission spectroscopy-based analytical technique to obtain qualitative and quantitative elemental information of the materials.
- High energy laser pulse creates a 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.

Prototype Design

System Overview

- A rugged LIBS based sensor head is build around a custom, PQSW laser for sub-surface applications.
- The sensor head is fiber coupled to a spectrometer and pump laser. The fiber coupled design allows these fragile and expensive components to remain on the surface while only the low-cost sensor head needs to be exposed to the harsh downhole environment.

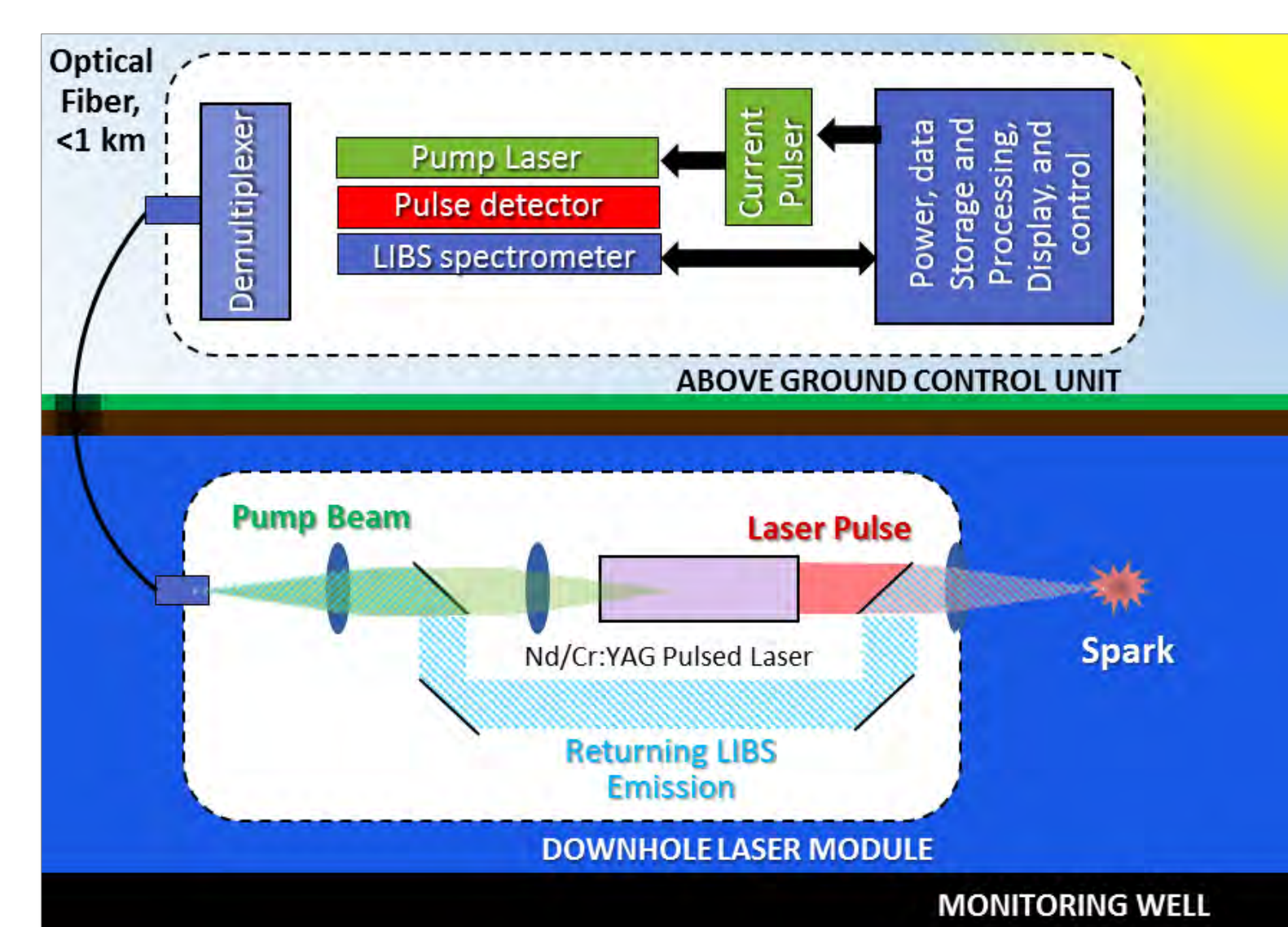


Figure 1: System concept. Pump laser, spectrometer, and other electronics remain on the surface while the all optical sensor head enters the sub-surface.

Prototype Design

Pill Laser

- The Pill laser is a custom PQSW laser 16 mm in length and 5 mm in diameter, the size of a pill. Laser performance parameters are listed in Table 1.
- Monolithic design consisting of a Nd:YAG laser crystal diffusion bonded to a Cr:YAG passive Q-switch (Fig 2).

Table 1: Laser Performance

Parameter	Value
Beam Quality (M ²)	X-axis = 1.04 Y-axis = 1.55
Pulse Length	3.3 ns
Pulse Energy	4.8 mJ

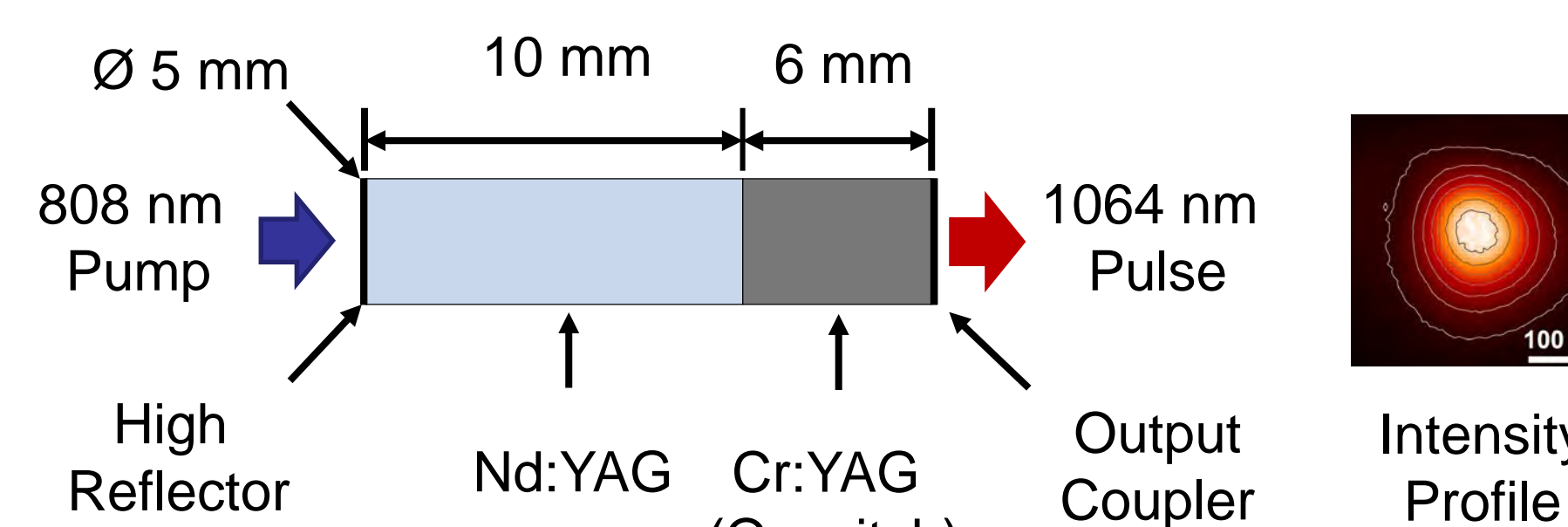


Figure 2: Pill Laser design and beam cross-section

Sensor Head

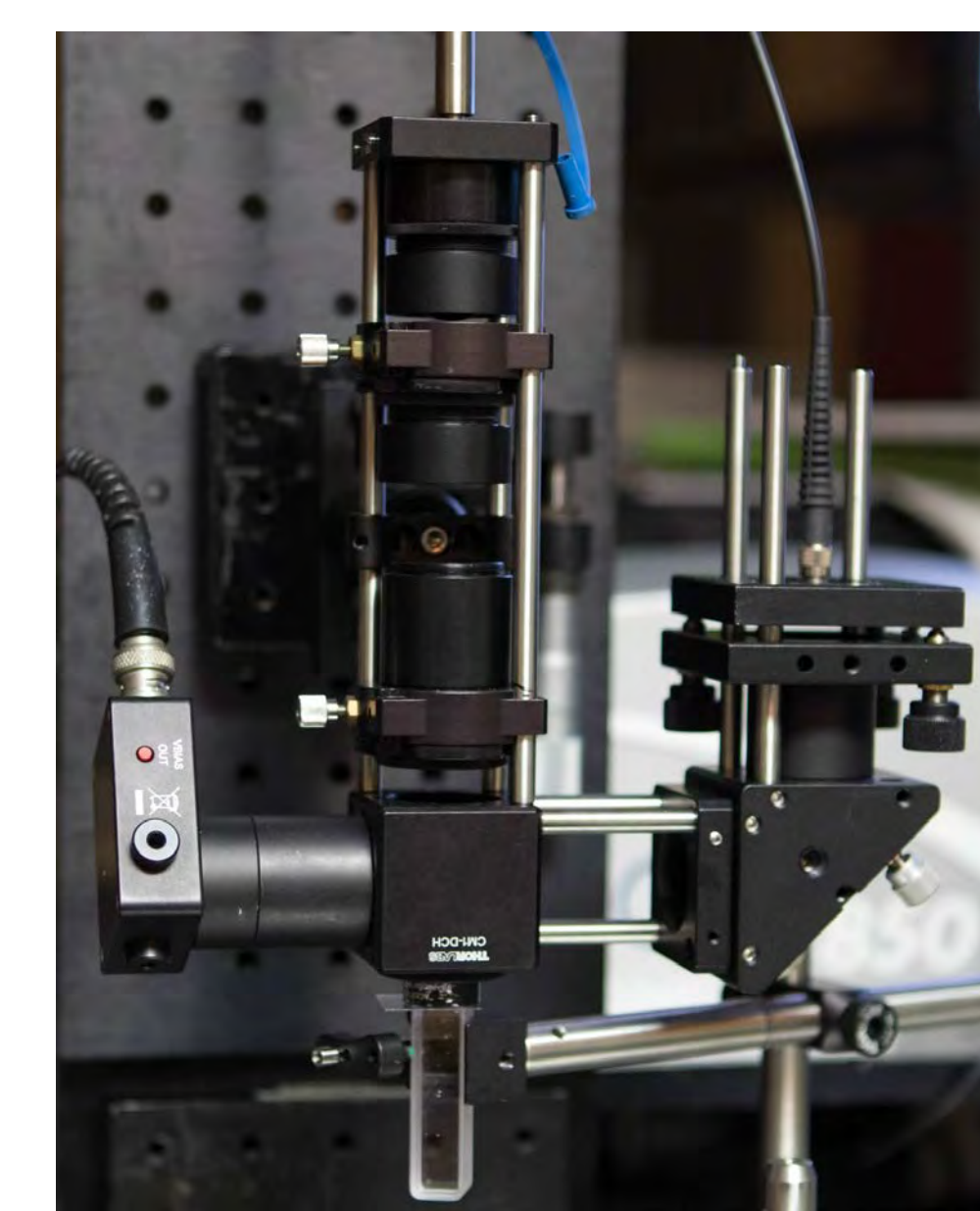


Figure 3: Prototype Sensor Head and Schematic

Sensor Optical Design

- Telescope (L1 & L2) couples 808 nm pump into Pill Laser.
- Beam Expander (L3 & L4) expands Pill Laser output 3X.
- Aspheric Lens (L5) focuses Pill Laser and collects plasma emission.
- Long Wave Pass Dichroic Mirror (DCM) reflects plasma emission wavelengths < 900 nm while passing the 1064 nm pulse.
- Lens L6 couples plasma emission into fiber.
- Photodiode (PD) generates timing signal for the spectrometer from weak 1064 nm reflection off back surface of DCM. A bandpass filter (BP) removes residual 808 nm light

Laser Induced Plasma (LIP)

- To produce a LIP, the irradiance / power density at the focal point (Fig 4A) must be high enough to exceed the breakdown strength of the sample.
- Multiple factors influence the focused power density such as pulse energy, pulse length, and focal spot size (i.e. the beam waist 'w₀') which itself depends on multiple factors including the incident beam radius "R" (Equation 1)

$$w_0 = M^2 \frac{\lambda f}{\pi R}$$

Equation 1: Beam waist ('w₀') dependence on beam quality ('M²'), lens focal length ('f'), wavelength ('λ'), and the incident beam radius ('R').

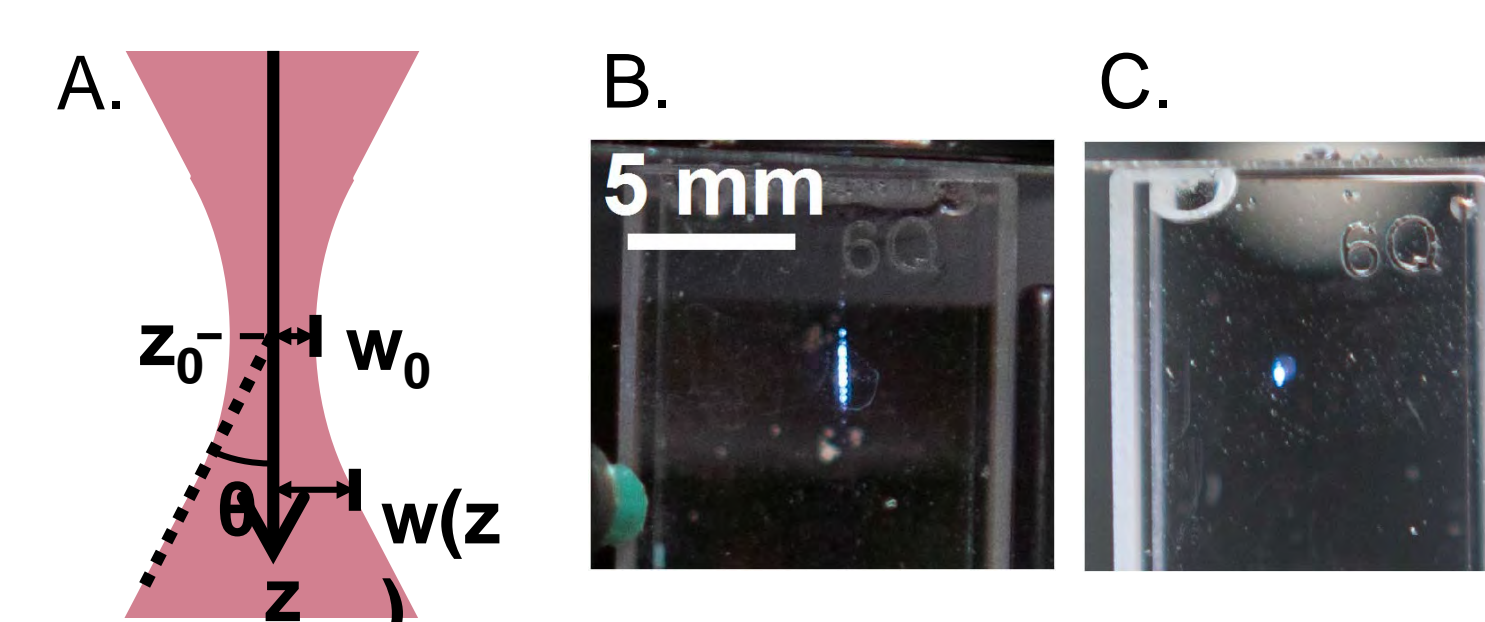


Figure 4: A – Beam radius ('w') as a function of position ('z') near the beam waist ('w₀'). B – LIP in water without 3X beam expander (Fig 3). C – LIP in water with 3X expander.

Prototype Performance

Ca, Sr, K aqueous solutions

Figure 5: Calibration data for three elements relevant to GCS leak detection. Good linearity was observed for all elements across the concentration ranges investigated. Error bars are ±3σ of eight measurements.

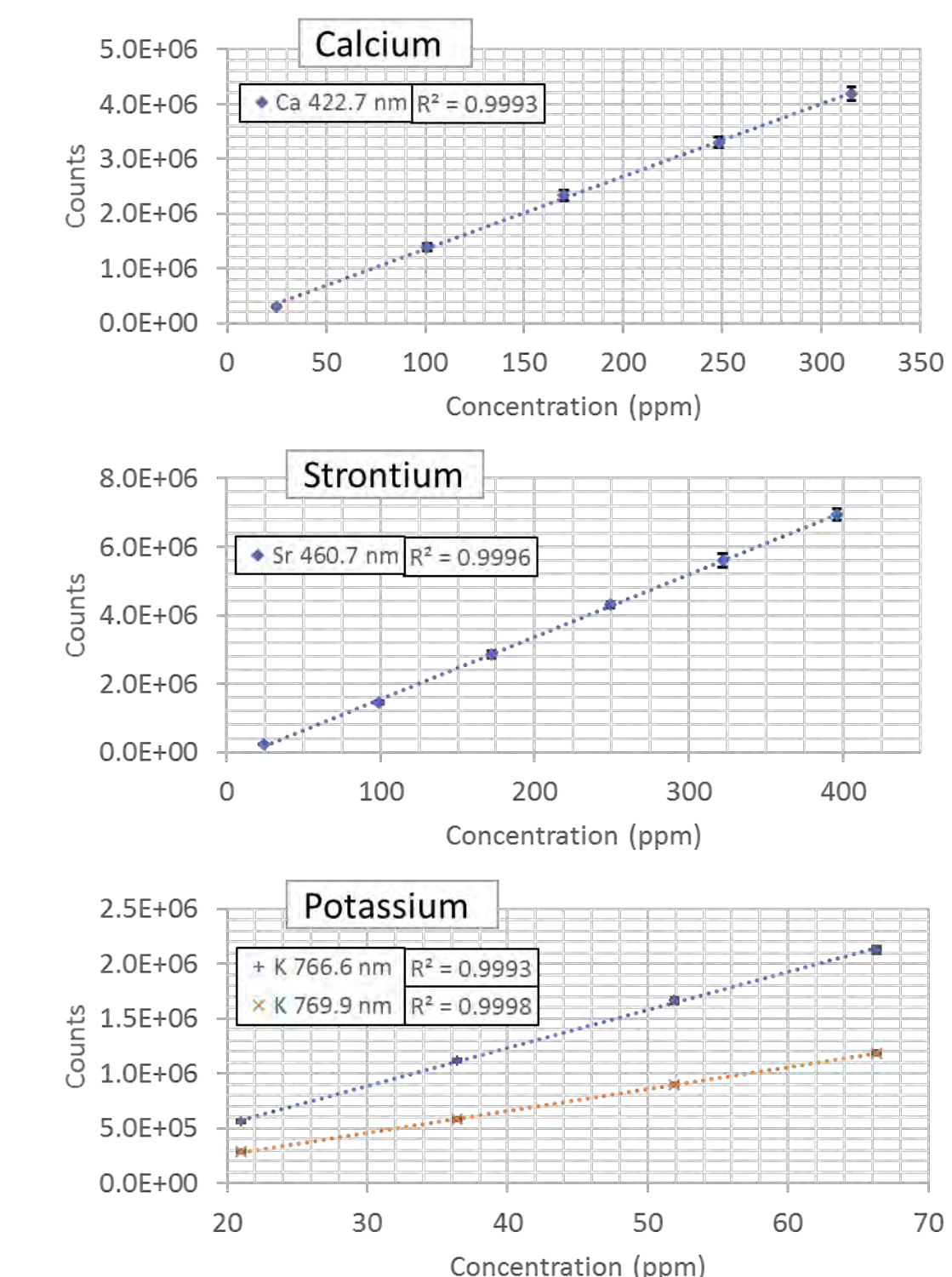


Table 2: Limits of detection for Ca, Sr, and K.

Element	Line (nm)	LOD (ppm)	Literature LOD (ppm)
Calcium	422.7	0.10 ⁽¹⁾	0.94 ⁽²⁾ , 0.047 ⁽³⁾ , 0.13 ⁽⁵⁾
Strontium	460.7	0.04 ⁽¹⁾	2.89 ⁽²⁾
Potassium	766.6	0.009 ⁽¹⁾	0.03 ⁽²⁾ , 1.2 ⁽⁴⁾
	769.9	0.069 ⁽¹⁾	

REE aqueous solutions and solid pellets

Figure 6: Calibration data for aqueous solutions of Eu and Yb. Only the atomic (i.e. neutral) emission lines were analyzed as the ionic lines showed self absorption. Error bars are ±3σ of eight measurements.

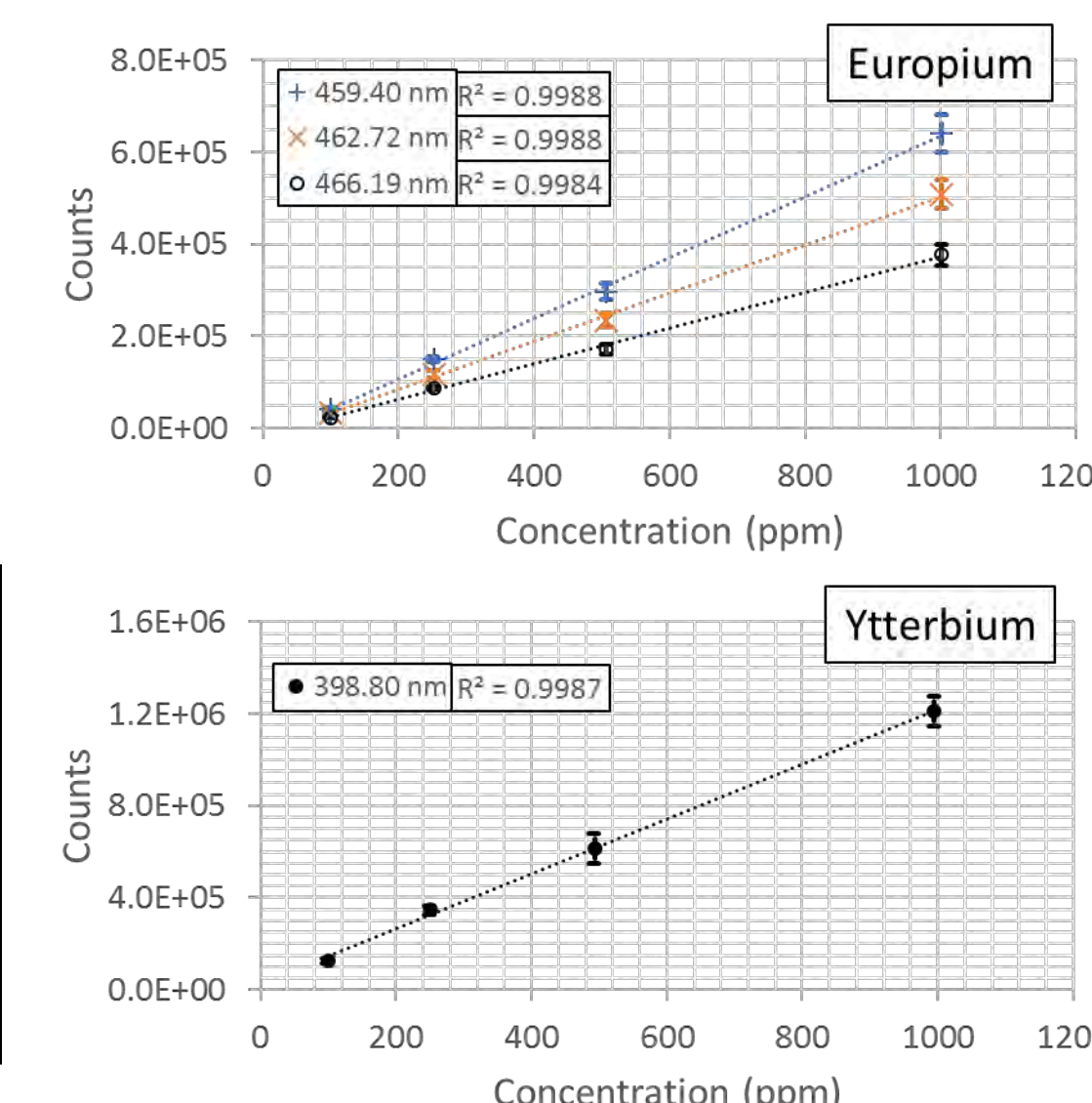


Table 3: Eu & Yb aqueous solution LODs

Element	Line (nm)	LOD (ppm)	Literature LOD (ppm)
Europium	466.19	1.54 ⁽⁶⁾	5.0 ⁽⁹⁾
	462.72	1.05 ⁽⁶⁾	5.0 ⁽⁹⁾
	459.40	0.85 ⁽⁶⁾	256 ⁽⁶⁾ , 5.0 ⁽⁹⁾
Ytterbium	398.80	1.15 ⁽⁶⁾	156 ⁽⁶⁾

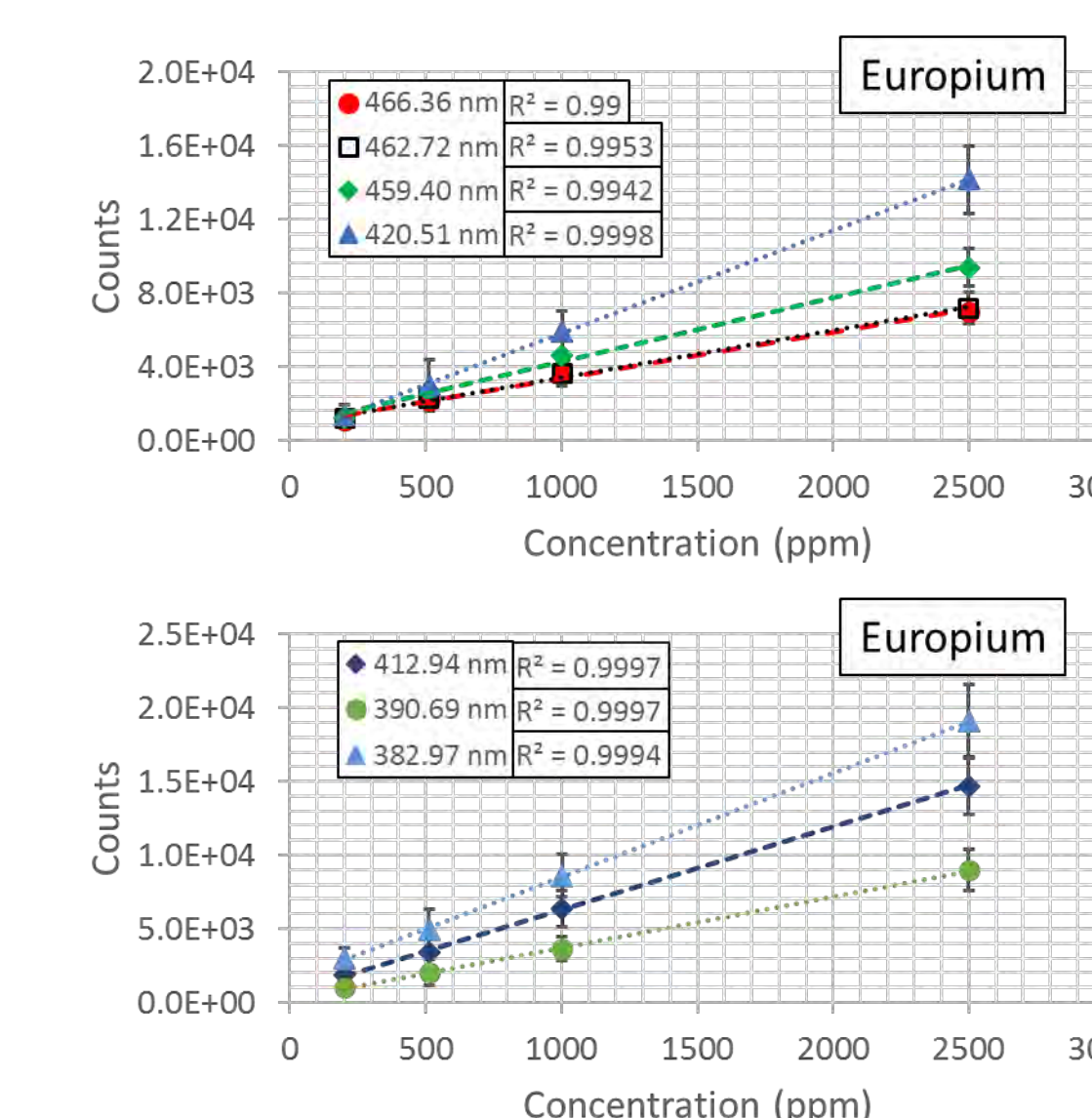


Figure 7: Calibration data for Europium oxide containing solid pellets. Both atomic and ionic lines showed good linearity (i.e. no self absorption). Error bars are ±1σ of eight measurements.

Species	Line (nm)	LOD (ppm)	Literature LOD (ppm)
Eu I	466.36	38.6 ⁽⁶⁾	80 ⁽¹⁰⁾
	462.72	24.7 ⁽⁶⁾	
	459.40	22.4 ⁽⁶⁾	2.4 ⁽¹¹⁾
Eu II	420.51	10.7 ⁽⁶⁾	100 ⁽¹⁰⁾
	412.94	9.9 ⁽⁶⁾	120 ⁽¹⁰⁾
	390.69	26.1 ⁽⁶⁾	
	382.97	14.3 ⁽⁶⁾	

Table 4: Solid Eu oxide containing pellet LODs.

Conclusions

- This work validates the design of the downhole LIBS based sensor.
 - A fiber coupled prototype sensor head was developed (Fig 2 & 3) and tested.
 - Spectral data were successfully collected and analyzed for selected elements relevant to GCS and REE source characterization (Fig 5, 6, & 7).
 - LODs are comparable or better than traditional bench top systems (Table 2 & 3).
- Future work:
 - Continue optimization of system performance for other elements relevant to GCS and the remaining REEs.
 - Develop a miniature, pressure resistant prototype for downhole testing.

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