

Improved design and field deployment of laser induced breakdown spectroscopy (LIBS) in-situ groundwater trace element analyzer

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Additional Declarations: Competing interest reported. The United State Department of Energy has been granted patents on the design of the sensor head, microchip laser, and triggering mechanisms described in this manuscript, Patent Numbers US8786840B1, US9297696B2, and US11451004B2. D.M. is listed as a co-inventor on US8786840B1 and US9297696B2. D.M. and D.H. are listed as co-inventors on US11451004B2, which is based on select design elements described in this work. C.B. and C.U. declare no competing interest.

Abstract

The present work describes the deployment activities of the updated side facing miniaturized laser induced breakdown spectroscopy (LIBS) subsurface deployable liquid sensor. Previous work illustrated prototype development with laboratory work validating the system operation as well as deployment of the initial sensor probe with data collection and lessons learned. The probe design was modified to turn the laser focal spot 90 degrees to shoot out of the side of the sensor housing instead of straight down. This was done to eliminate data variability introduced due to bubble production and coalescence within the optical deliver and collection pathway. The new design was tested in the subsurface for 7 weeks continuously with daily data collection. The collected data showed improved performance of the sensor system including lower data variability. The overall design and data collection is described and discussed and future work and avenues of research as well as application areas are listed.

Introduction

Reinjection of wastewater/produced water from oil and gas operations can be a significant source of potential contamination and leakage in areas where substantial exploration and production activities occur. Class II wastewater injection rates are approximately 2 billion gallons/day across the US but primarily limited to Texas, California, Oklahoma, and Kansas [1]. Other areas do permit this type of reinjection for disposal purposes, and all areas are required to provide some level of monitoring so that this activity does not cause problems with sources of water that the public and industry rely on. The reason for reinjection is to eliminate the costs of water treatment, lack of appropriate infrastructure for transmission once treated, and the lack of demand that would satisfy the cost of treatment for use in other applications.

Loss of containment at a wastewater reinjection site can cause subsurface brines to migrate upward through the strata into aquifers and soils, potentially contaminating groundwater, a critical resource that millions in the United States rely on for drinking, agriculture, and industry. If leaking subsurface brines reach these aquifers, they are expected to contaminate the groundwater, increasing total dissolved solids (TDS) and, potentially, trace toxic metals [2–5].

Rapid measurement of key elements from trace to percent level is desirable to ensure that permanent storage of injected fluids (wastewater) is not leaking and negatively impacting the total dissolved solids (TDS), salinity, alkalinity, acidity, etc. of the native fluids. Even when local fluids are produced and require treatment prior to use the significant upset of the known conditions can provide additional cost and or treatment which is undesirable for end-users.

Two commonly used techniques for material trace element analysis are inductively coupled plasma mass spectrometry (ICP-MS) and ICP atomic emission spectroscopy (ICP-AES), both of which are highly sensitive, multielement techniques with large dynamic ranges [6–8]. Disadvantages of ICP-MS / AES include high equipment cost, significant infrastructure, operator training requirements, limits to TDS for ICP-MS, and a lack of portability, requiring samples to be collected in the field and transported to a

laboratory for analysis [7, 8]. Depending on the type of analytical lab used (i.e., in-house or 3rd party), results can take hours to weeks before being returned.

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission technique for elemental analysis. In LIBS, an intense pulsed laser is focused into or onto a sample, breaking down the target material into a plasma. As the plasma cools, its atomic emission spectrum is measured, permitting the elements present to be identified and quantified based on the wavelength and intensity of their characteristic emission lines [9 – 2]. While not as sensitive as ICP-MS/AES, major advantages of LIBS include (1) little to no sample preparation needed, (2) sensitivity to both light and heavy elements, and (3) potential for miniaturization and ruggedization for continuous, in-situ measurements in hostile environments.

This project aims to build on prior work and further improve an in-situ subsurface probe for high-frequency/real-time elemental analysis. This study describes work to add turning optics to prevent bubble production interference and data collection and test the modified fielded prototype system. Lessons learned from prior deployment of the unmodified prototype were applied to this next design iteration to improve data production and collection fidelity.

While the intended purpose of this system is to monitor wastewater injection sites for leakage, what has been developed is a general-purpose elemental analyzer for hostile environments that could be applied as an on-line sensor in applications that traditionally use off-line elemental analysis or could benefit from the speed and automation capability of a fluid-based LIBS system. Potential application areas include real-time industrial process monitoring and control, separations and filtering, and environmental field monitoring for produced water, acid mine drainage, and wastewater injection [13–15].

Prior work

Underwater LIBS (i.e., laser spark submerged in the bulk fluid) has been used to investigate aqueous solutions for several decades and has even been deployed on underwater remotely operated vehicles (ROVs) to the ocean floor at depths of up to 1400 m to investigate hydrothermal vent fluids [16–31]. For instance, the ChemiCam system [28] is enclosed in a 300×1300 mm (11.8×51") cylindrical vessel and draws 140 W of electrical power, while the LIBSea II system [29] enclosure is 190×588 mm (7.5×23").

While the environment near deep ocean hydrothermal vents bares some similarities to the subsurface environment [32–35], sensor size is a major constraint for subsurface use. For example, downhole logging tools used in the oil industry are typically cylindrical and designed to operate in boreholes with minimum internal diameters of around 2–6" (~ 5–15 cm) [36].

With ground water monitoring wells, one can expect a complex matrix containing significant amounts of dissolved salts, and other minerals and gases at pressures of many atmospheres/bar (1 atm ≈ 1 bar). It has been demonstrated that both the pressure and matrix effects from dissolved materials can have a significant effect on the strength of the analyte atomic emission. How the signal is affected can be

complex and depends on several factors such as the analyte of interest and the specific matrix composition.

Influence of fluid pressure, gas pressure, and chemical properties of the dissolved constituents is discussed at length in a prior publication outlining the previous design and deployment and the issue encountered [37–39].

Progress Review

Previous work on this project has progressed the concept from proof of principle to benchtop prototypes, through to a field-deployable prototype system [37–42]. Each stage of testing has identified design changes needed to optimize system performance and to correct design flaws.

Initial benchtop testing demonstrated the feasibility of the split-system concept [38], though, this testing revealed the need to modify the concept from a single fiber design (i.e., one optical fiber for pump delivery and signal return) to a dual fiber design, allowing each fiber and their associate coupling optics to be optimized for a single task. This change eliminated complexity and compromises that caused loss of pump power and signal strength. However, it's likely that a single fiber design is feasible with an optimized design and custom optics. Additionally, shaping of the output beam was investigated during this round testing, resulting in a smaller, hotter laser spark.

Initial subsurface testing revealed a critical flaw where the downward facing design of the sensor head allowed gas bubbles to accumulate on the sensor window, scattering the excitation laser and plasma emission signal. It was known from laboratory testing that the laser induced plasma could cause gas bubbles to form, possibly the result of the plasma decomposing water or the associated shockwave releasing dissolved gasses similar to ultrasonic degassing [43–44], that would accumulate at the top of the cuvette (see Fig. 1). Thus, the sensor head was designed such that the optical window was flush with, to slightly past, the front surface of the enclosure with the belief that the gas bubbles would dissipate into the unconfined volume of water surrounding the sensor head (as opposed to the confined volume of the cuvette). Unfortunately, it appears this was not the case as drops in signal strength were observed during data collection, particularly on days where heavy rain occurred a few hours before data collection.

New design

To address the accumulation of gas bubbles on the probe window, it was decided to turn the laser output by 90 degrees and have it exit the side of the probe, permitting gas bubbles to rise away from the output window. Instead of redesigning and fabricating a new prototype, a bolt on adapter for the existing prototype was made (see **Fig. 2**). The 90-degree adapter was 3D printed out of 316 stainless steel and included a mount for a turning prism and a lens that served as the final focusing element and output window. The prism was epoxied to a seat designed to slide into a receiving socket that was printed onto

the adapter baseplate and held in position by an integral band clamp (see **Fig. 2A.2, A.3, and A.4**). This arrangement permitted linear and angular movement of the prism along the probe axis for alignment with the lens (**Fig. 2A.7**). Two drawbacks of the specific design used is that it introduced additional (uncoated) optical surfaces and restricted the light collection aperture, resulting in loss of laser and signal power. However, since the primary goal of the adapter was to test if redirecting the laser out the side of the probe would result in more stable operation, this loss of signal strength is not considered important.

Materials and methods

The LIBS probe upon which this work is based has been described previously (see[39]), and the only modifications made to the existing prototype was to remove the output window and lens. The optical design of the sensor head and 90-degree adapter is show in **Fig. 2B**. Briefly, pump light (808 nm, **Fig. 2B** (light red)) is delivered to the sensor head via an optical fiber, the pump energy is coupled into the passively Q-Switched (PQSW) microchip laser by lenses L1-L3, the PQSW laser output (~ 4 mJ / 1064 nm / ~ 3 ns / 10 Hz repetition rate, **Fig. 2B** (dark red)) is expanded 3X by L4 & L5 before entering the adapter and being turned by a prism 'P', and being focused by lens L6 into the surrounding medium. Plasma emission (**Fig. 2B** (light green)) is collected by L6 and directed to, and coupled into, the signal return fiber by a longwave pass dichroic mirror (DCM), aluminum mirror 'M', and lens L7. Adapter optics consisted of an uncoated, 10 mm right prism (Esco Optics: ZI41010M, 'P' in **Fig. 2B**) and a 10 mm diameter x 10 mm focal length, MgF2 anti-reflective coated lens (Edmund Optics: 63-484, 'L6' in **Fig. 2B**) which also served as the output window.

The sensor head is connected to a surface control unit by a 30 m fiber optic umbilical consisting of a pair of 600 μ m core fibers (pump and signal return fibers) in a protective sheath. The control unit consisted of a 600 W, 808 nm, quasi-continuous-wave (QCW) fiber-coupled diode laser (Lumibird: PDBX0397) and laser driver (Northrup Grumman: eDrive), a gated spectrometer (Andor: iStar ICCD DH320T-25F-03 and Shamrock 303i), computer, and chiller. Triggering of the ICCD was accomplished by detecting a pulse of residual 1064 nm traveling up the signal return fiber. This arrangement allows precise synchronization of the camera to the subsurface PQSW laser. For details of these subsystems, see Hartzler et. al. 2019 and 2023 [38, 39].

Calibration

Calibration samples were prepared by making a stock solution and then diluting to lower concentration levels with DI water. Five analytes of interest, chlorides of Ca, Mn, Na, Li, and K, (Fisher Scientific) were dissolved together in DI water to make a stock solution which was further diluted to make a set of six calibration samples (S1-S6) with concentration ranging from 1.2 to 60 ppm of Ca, 3 to 150 ppm of Mn, 0.12 to 6 ppm of Na and Li, and 0.6 to 30 ppm of K as shown in Table 1. To develop the calibration

curves, LIBS spectra collected from samples with lower range of concentration at the optimized experimental parameters were used as signal saturation occurred at higher analyte concentration.

Table 1
Multielement calibration solutions

Sample	Element Concentration (ppm)				
	Ca	Mn	Na	Li	K
S1	60	150	6	6	30
S2	30	75	3	3	15
S3	12	30	1.2	1.2	6
S4	6	15	0.6	0.6	3
S5	3	7.5	0.3	0.3	1.5
S6	1.2	3	0.12	0.12	0.6

The spectrograph was configured with a 100 µm entrance slit and 600 l/mm, 500 nm blaze grating, resulting in a spectral range of about 130 nm, while the ICCD camera was configured with a gate time delay of 200 ns and gate width / integration time of 3 µs. Calibration spectra were collected by immersing the LIBS probe sensor head into a beaker containing 150 mL of the sample solution. The strong emission lines of Ca at 422.6 nm, Mn at 403.2 nm, Na at 588.9 nm, Li at 670.8 nm, and K at 766.5 nm were used for detection and quantification and spectra were recorded over four wavelength ranges; Range 1: 360–490 nm (for Mn and Ca emission lines), Range 2: 485–615 nm (for Na emission lines), Range 3: 600–730 nm (for Li emission lines) and Range 4: 710–840 nm (for K emission lines). Ten spectral acquisitions, each with 100 laser shots, were collected from all calibration samples. Background subtracted peak intensity of the emission signals at the wavelengths mentioned above was averaged for 10 acquisitions and plotted against the analyte concentration to obtain calibration curves. Linear relationship between background subtracted signal intensity and the analyte concentration was observed for all the selected emission lines with R^2 values close to 1 as shown in Fig. 3. These calibration curves were used for determining the detection limits and estimating groundwater analyte concentration in the test well. Limits of detection (LODs) were calculated as follows[45]:

$$LOD = \frac{1.96\sigma}{m}$$

Where 'm' is the calibration curve slope, and 'σ' is the standard deviation of the background. See Table 2 for values.

Table 2
Limits of Detection (LOD) and Quantification (LOQ).

Limit (ppm)	Ca	Mn	Na	Li	K
LOD	0.31	0.82	0.015	0.017	0.11
LOQ	1.0	2.7	0.05	0.057	0.37

Test site

Subsurface testing was performed at a monitoring well located on site at the NETL Morgantown, West Virginia campus. The monitoring well is PVC lined with an internal diameter (ID) of 4 inches / 10 cm and a depth of approximately 30 ft / 9.1 m (perforated at the bottom) with groundwater beginning at a depth of approximately 12 ft / 3.7 m. All measurements were performed at a well depth of 27 ft / 8.25 m, corresponding to a water depth of 15 ft / 4.6 m.

Subsurface measurements were performed daily (excluding weekends, holidays, and site closures) over a 49-day period from June 10th to July 29th, 2024, for a total of 34 days of measurements. Prior to the beginning of the test period, the LIBS probe was lowered into the test well on Friday, June 7th, to allow any disturbed sediment to settle over the weekend, with measurements beginning the following Monday, June 10th. The probe was left submerged for the entire 49-day period and only retrieved once on Friday, June 28th to inspect for leakage.

Daily measurements were collected across all four spectral ranges (defined above), with 40 spectral acquisitions, each with 100 laser shots, collected for each range. At a repetition rate of 10 Hz, data collection took 400 s (6.7 min.) to complete for each spectral range. Note that, due to the relation between the standard deviation (σ) and standard error of the mean ($\sigma_{\text{mean}} = \sigma/\sqrt{N}$), we expect our detection limits to improve by a factor of 2 when collecting 4 times the number of spectra used to determine with LODs in Table 2.

Emission signals of Ca, Na, K and Mn were detected in the daily spectra and, using the calibration curves developed above, their concentrations were estimated, see Fig. 4. Three of the five elements, Ca, Na, and K were consistently at concentrations above their quantification limits (0.5, 0.025, 0.185 ppm respectively), while the Mn concentration fell below the LOQ (1.35 ppm) for most days. Note that these LOQs have been adjusted for the fact that 4x more data was collected for each daily spectrum as compared to the calibration spectra used to create Table 2.

Discussion

Compared to testing performed in 2022, with the downward pointing design (see[39]), the new 90-deg. / sideways pointing design did not show the same decay in signal strength (see **Fig. 5**). While the 90-deg. adapter reduced the overall signal strength due to increased reflection losses and a more restricted

aperture, the primary goal of this round of testing was to investigate stability improvements of the sideways pointing design. Redesigning the entire sensor head, as opposed to adding an adapter to the existing design, would allow this signal loss to be minimized by optimizing the optical layout.

Additionally, a redesign would allow the sensor head to be reduced in size, most critically in its maximum cross-sectional dimension, to permit operation in 2-inch (50.8 mm) ID well bores commonly used for monitoring wells. The current sensor head with the adapter is slightly larger than 2-inches in outer diameter (OD) and exactly 2-inches OD without the adapter. There is nothing inherent in the design that requires this cross-sectional size, and it could easily be adapted to a sub-2-inch OD design.

Also of note, when all the daily spectra were averaged together (34 days total), a weak Li signal at 670 nm was observed, see Fig. 6. With 40 spectra of 100 laser shots each being collected for each daily spectrum, this represents 136000 individual laser shots or 3.7 hours of data collection (at a sample rate of 10 Hz). While this may be an excessive length of data collection for most applications, the result demonstrates the adaptable sensitivity of systems of this type.

Conclusion

Ongoing development has identified design changes necessary to optimize performance of the subsurface LIBS probe. Each stage of testing has led to significant improvements, such as moving from a single to a dual fiber design, resulting in improved pump delivery and signal collection, and introducing a beam expander into the output beam-path to reduce the eventual focal spot size, resulting in a smaller, hotter laser spark [38]. In the current work, it was successfully demonstrated that turning the path of the output beam by 90 degrees eliminated the issue of fine bubbles collecting on the sensor head output window, reducing signal intensity by scattering. This issue, potentially caused by groundwater outgassing due to the laser induced shockwave, was identified during the previous round of testing [39] and had caused significant performance degradation. Its successful resolution has resulted in a more stable and more reliable measurement system. Future work will look to further miniaturize, simplify, automate, and commercialize the current system into something more amenable for rapid fluid monitoring as it relates to the previously mentioned applications as well as downhole applications.

Declarations

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Competing interests

The United State Department of Energy has been granted patents on the design of the sensor head, microchip laser, and triggering mechanisms described in this manuscript, Patent Numbers US8786840B1, US9297696B2, and US11451004B2. D.M. is listed as a co-inventor on US8786840B1 and US9297696B2. D.M. and D.H. are listed as co-inventors on US11451004B2, which is based on select design elements described in this work. C.B. and C.U. declare no competing interest.

Data Availability Statement

All data generated or analyzed during this study are included in this published article [and its supplementary information files].

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Figures

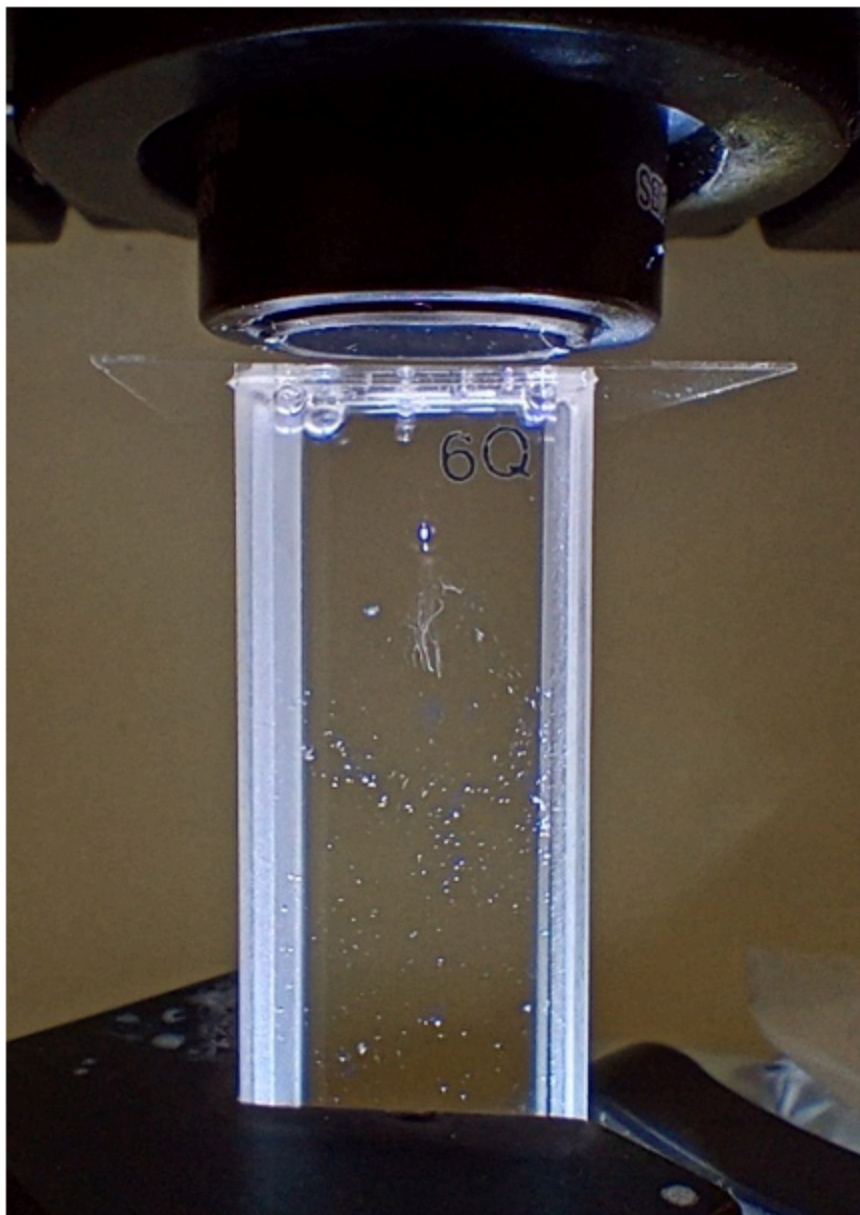


Figure 1

Laser induced plasma in water and associated gas bubbles. Note the motion blur of the newly created bubbles just under the plasma, gas bubbles created by previous laser shots in the middle of the cuvette, and accumulated gas bubbles at the top of the cuvette. Also note that when the coverslip was placed (see top of cuvette), there were no bubbles in the cuvette.

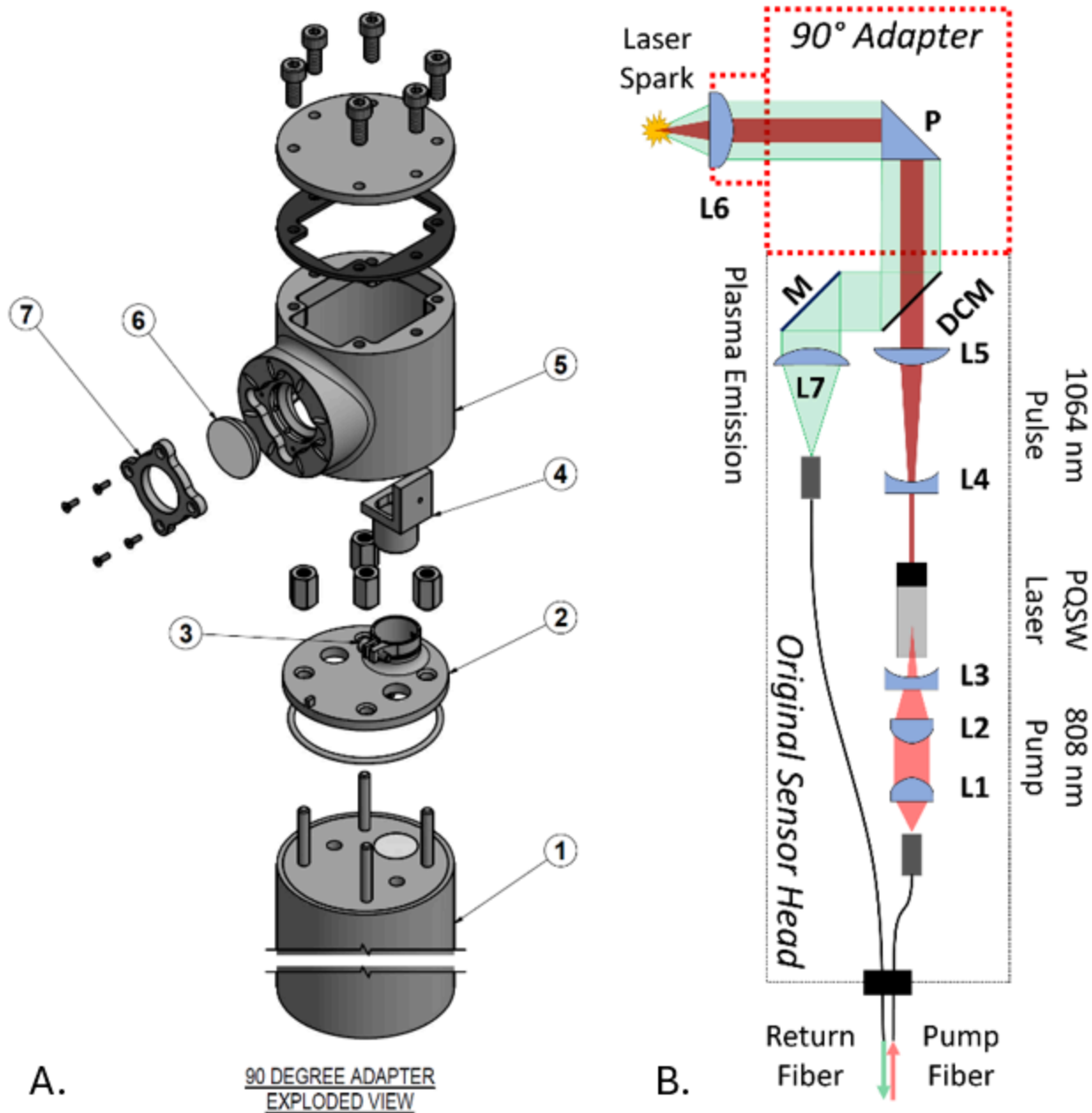


Figure 2

A - Exploded view of 90-degree adapter. 1 – Original prototype. 2 – Adapter baseplate. 3 – Prism mount receiving socket and band clamp. 4 – Prism seat. 5 – Main body of adapter. 6 – Lens / output window. 7 – Lens safety retainer. Note that the original output window (visible on '1') was removed. **B** – Optical design of the sensor head and 90-degree adapter.

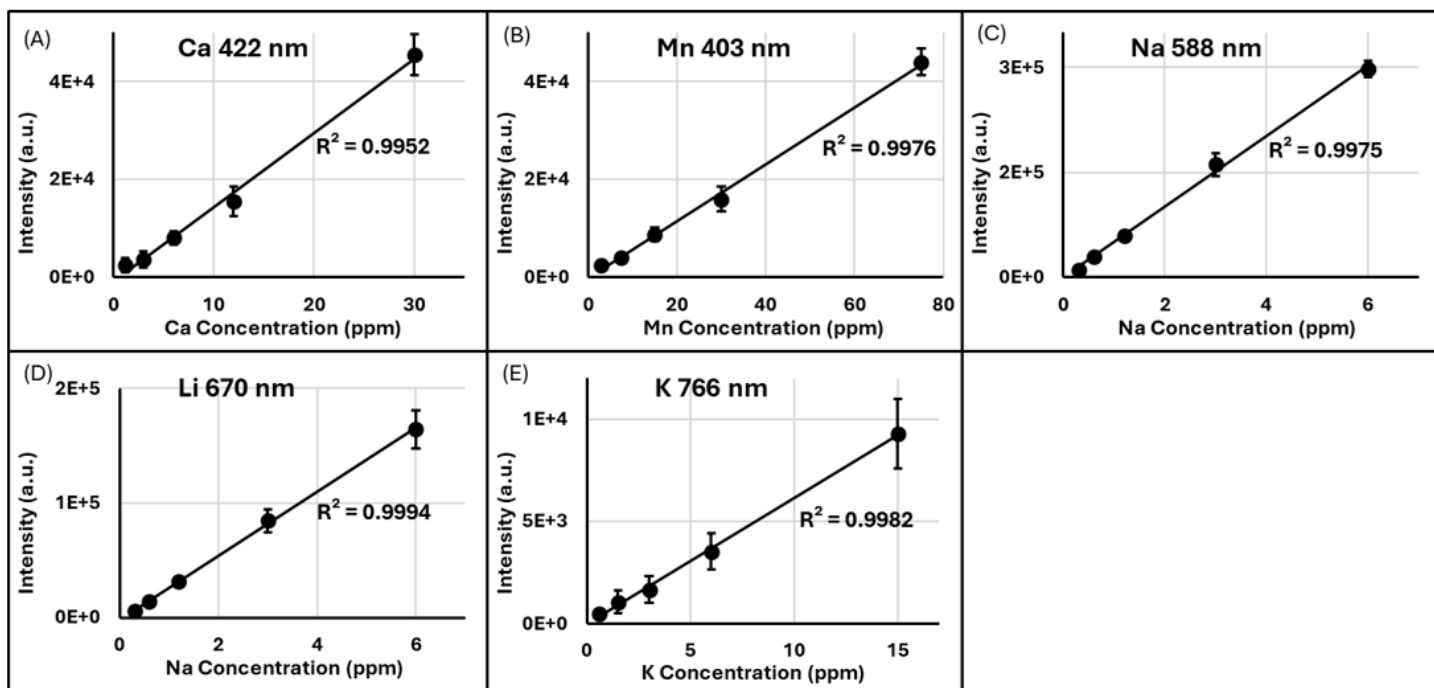


Figure 3

Calibration curves for the determination of (A) Calcium (Ca), (B) Manganese (Mn), (C) Sodium (Na), (D) Lithium (Li), and (E) Potassium (K). Each graph displays the selected emission line intensity) versus analyte concentration (ppm). Error bars show $\pm \sigma$ (standard deviation) of ten replicate measurements of 100 laser shots each.

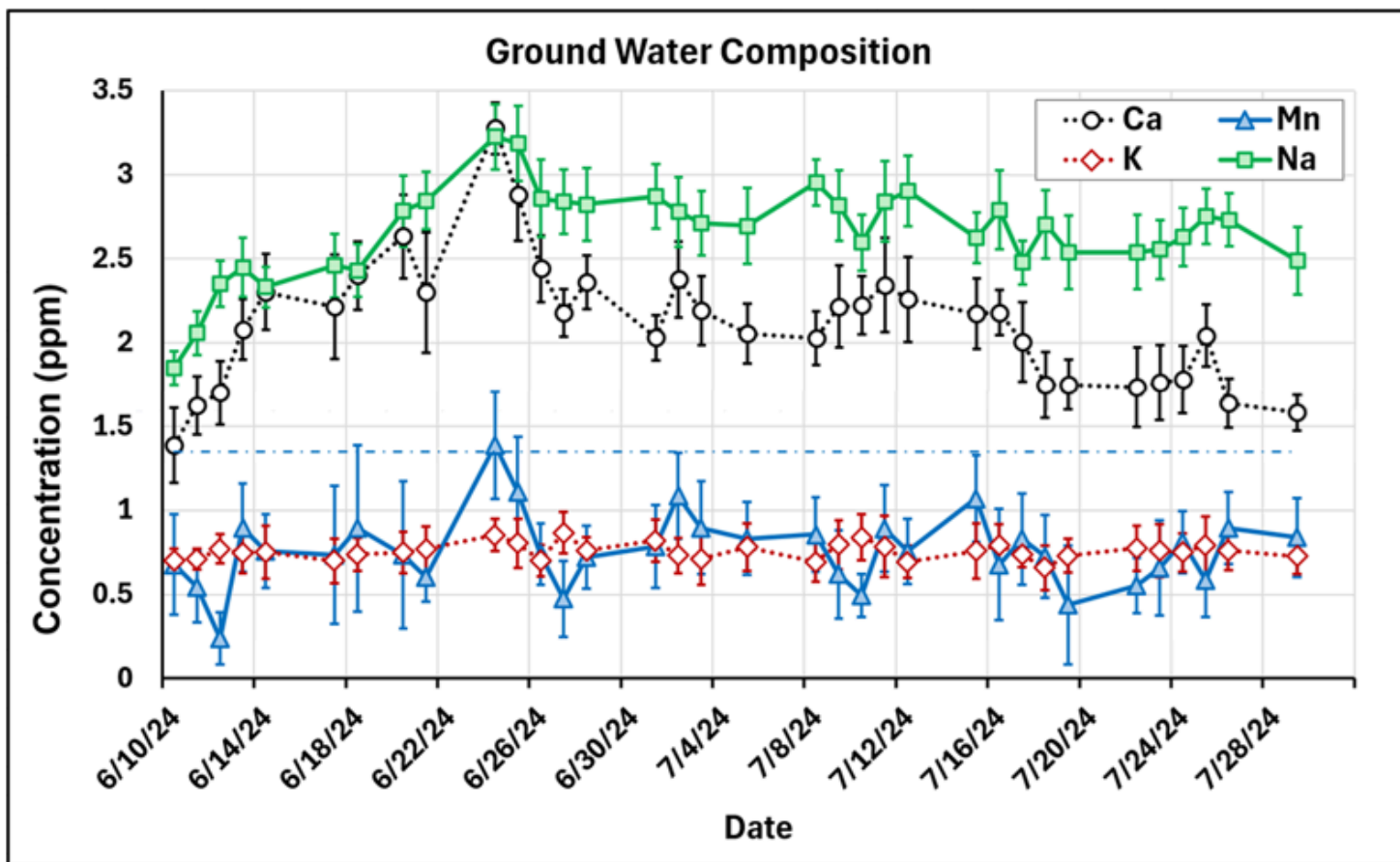


Figure 4

Daily concentration of Ca, Mn, K, and Na. Note that the concentration of Mn was below the LOQ (blue dash-dot line) for most days while a signal from Li (data not shown) was not observed on any day.

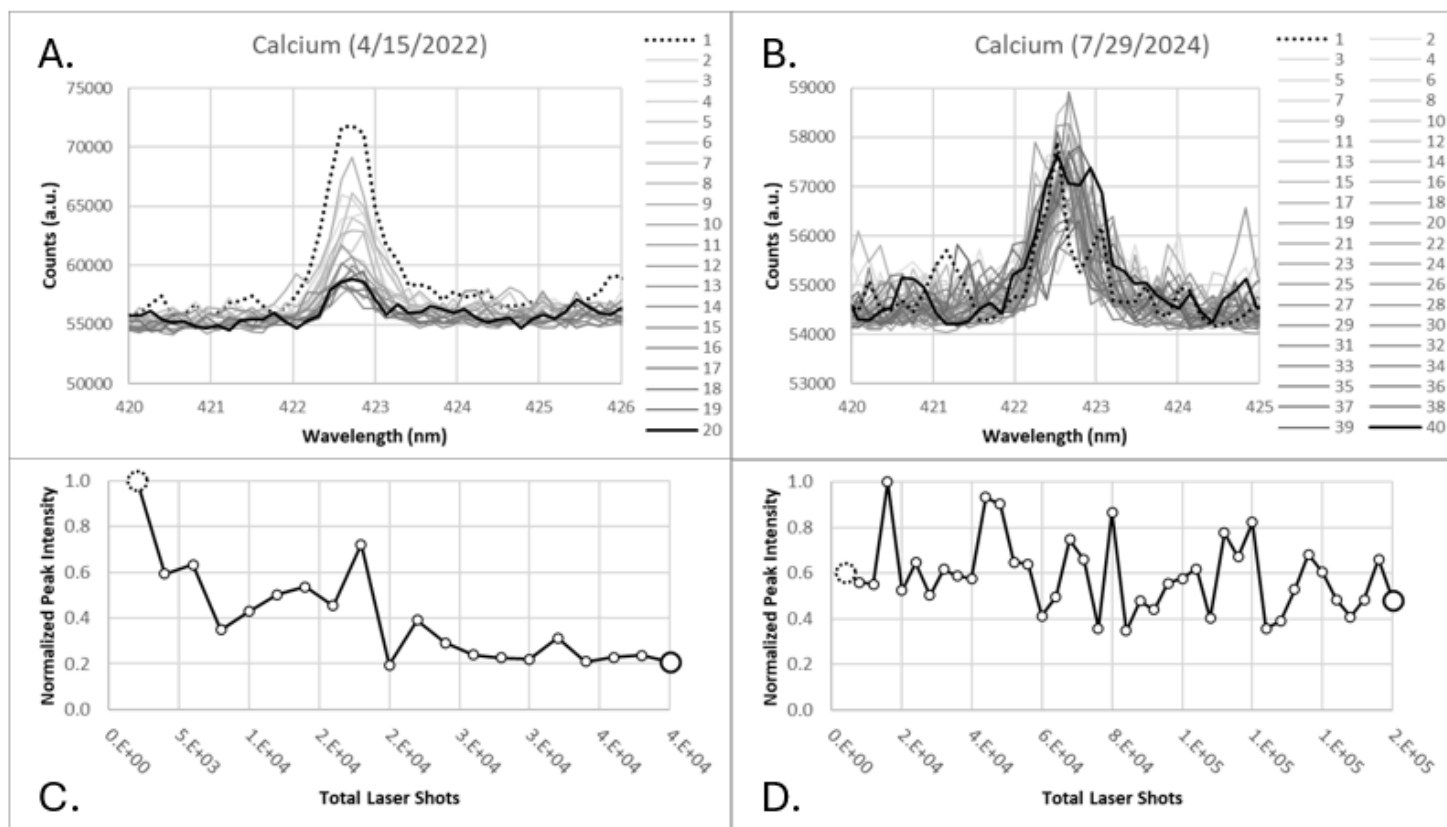


Figure 5

Sequential spectra collected during testing in 2022, **(A)**, with the downward pointing, and 2024, **(B)**, with the 90-deg. pointing design. **C** – Average (background subtracted) peak intensity demonstrating the signal decay observed with downward pointing design. Likely caused by accumulation of bubbles on the output window. **D** –The 90-deg. turned design does not show signal decay. **Note:** the first and last spectrum is highlighted in each figure, with the first being dashed.

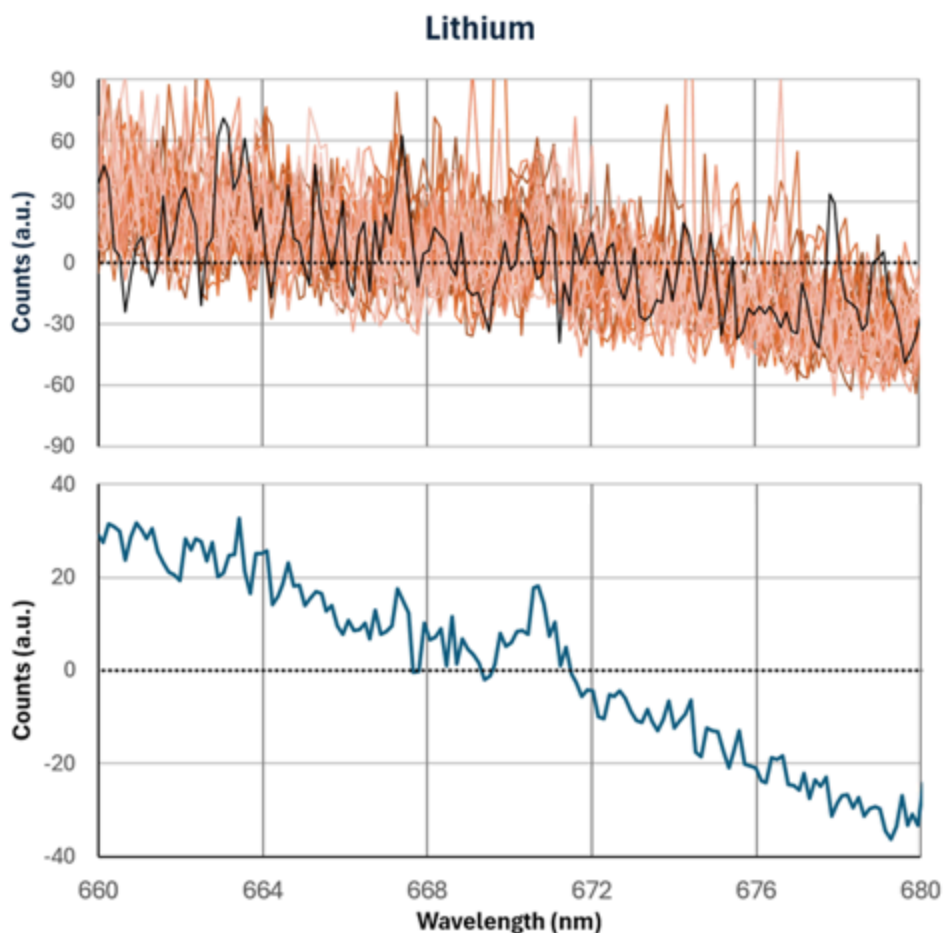


Figure 6

Lithium emission spectra (background subtracted). **TOP** – All 34 daily spectra. Note, the last day, 7-29-2024, is highlighted (BLACK) to demonstrate the magnitude of the Li signal observed in the daily spectra. **BOTTOM** – Average of all 34 daily spectra with Li emission visible at approx. 670 nm.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Dailyaveragespectra.txt](#)