Development of laser induced breakdown spectroscopy sensor to assess groundwater quality impacts resulting from subsurface activities

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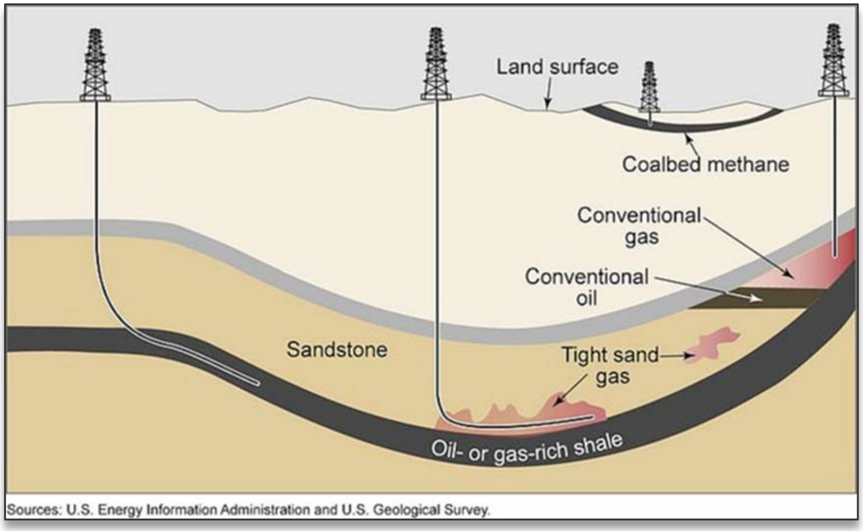
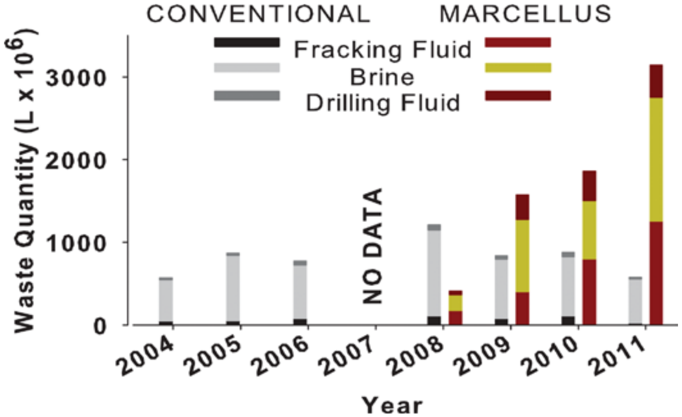
Outline

- **Subsurface activities**
  - Oil and gas production
  - Carbon sequestration
- **Ground water monitoring**
- **LIBS Technology**
- **Conclusions**



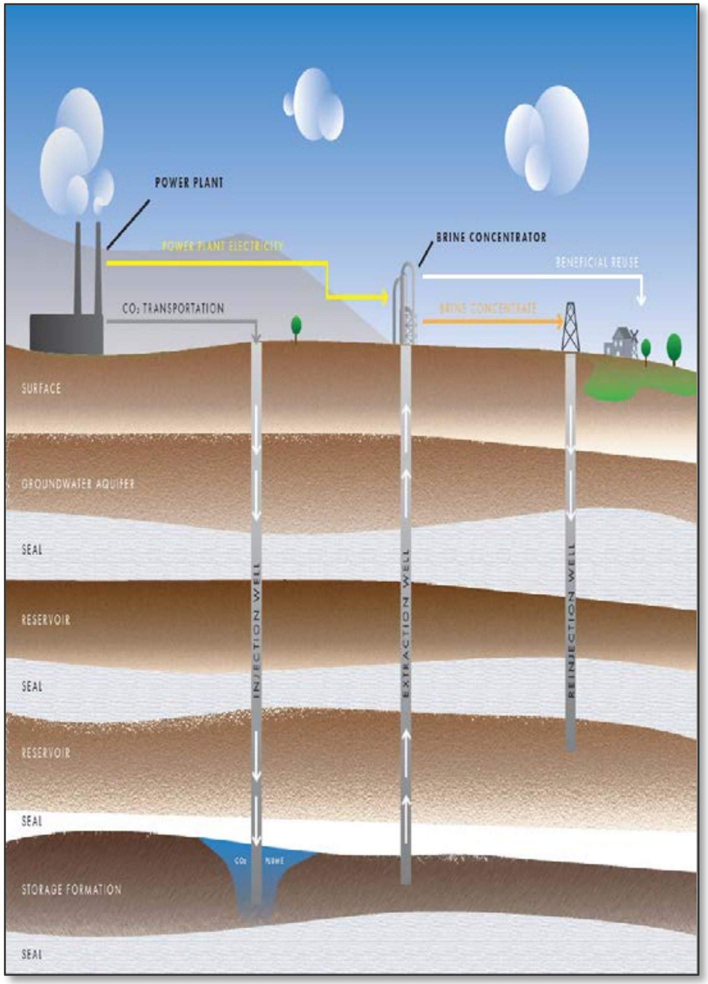
Produced water

- Water from underground formations brought to the surface during oil and gas production
- About 15-20 billion barrels per year or 1.7-2.3 billion Gallons per day (ANL Report 2009)
- Water from conventional and Marcellus wells is given in the figure (Lutz et al., Water Resour. Res., 49, 2013)
- It contains dissolved and dispersed oil compounds, formation minerals, production chemicals, production solids, and dissolved gases

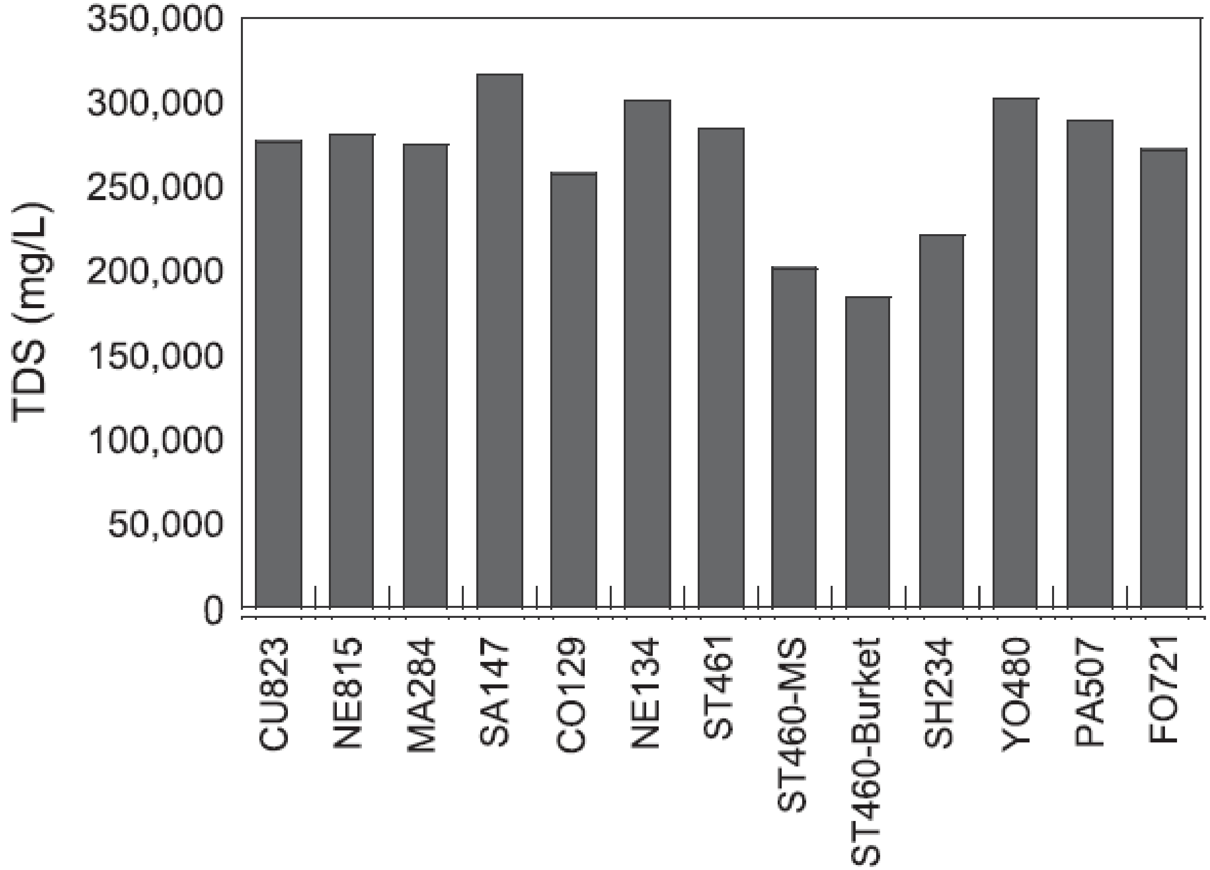


Carbon Management

- Capturing CO2 and storing it in such a way that it does not enter the atmosphere
- Compression and injection into deep geological formations
- Pressure build-up particularly in saline storage formations has risk of brine leakage

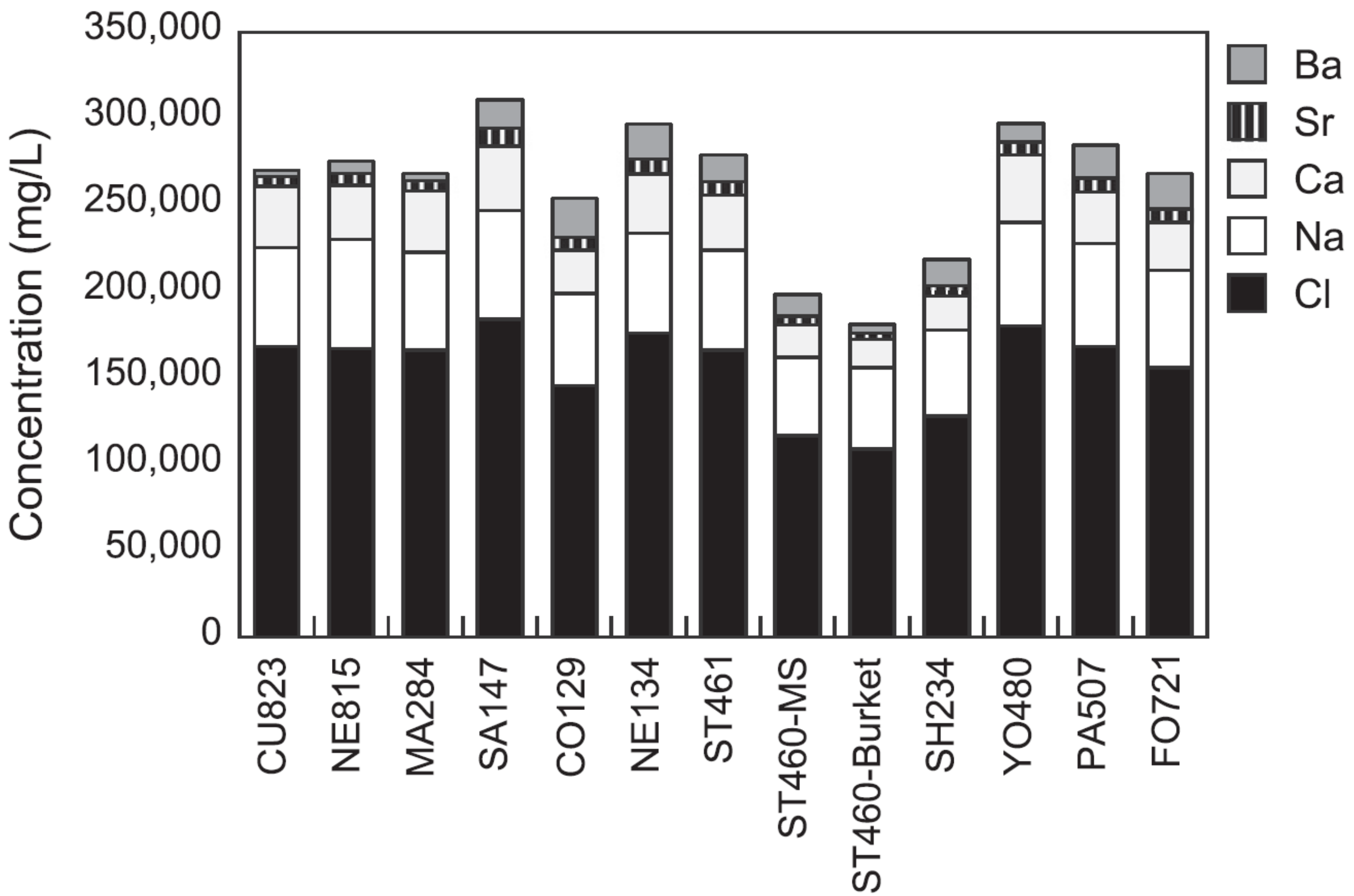


Marcellus Shale Produced Water Composition



Akob et al., Applied Geochemistry, 2015

Marcellus Shale Produced Water Composition



Akob et al., Applied Geochemistry, 2015

Marcellus Shale Produced Water Composition

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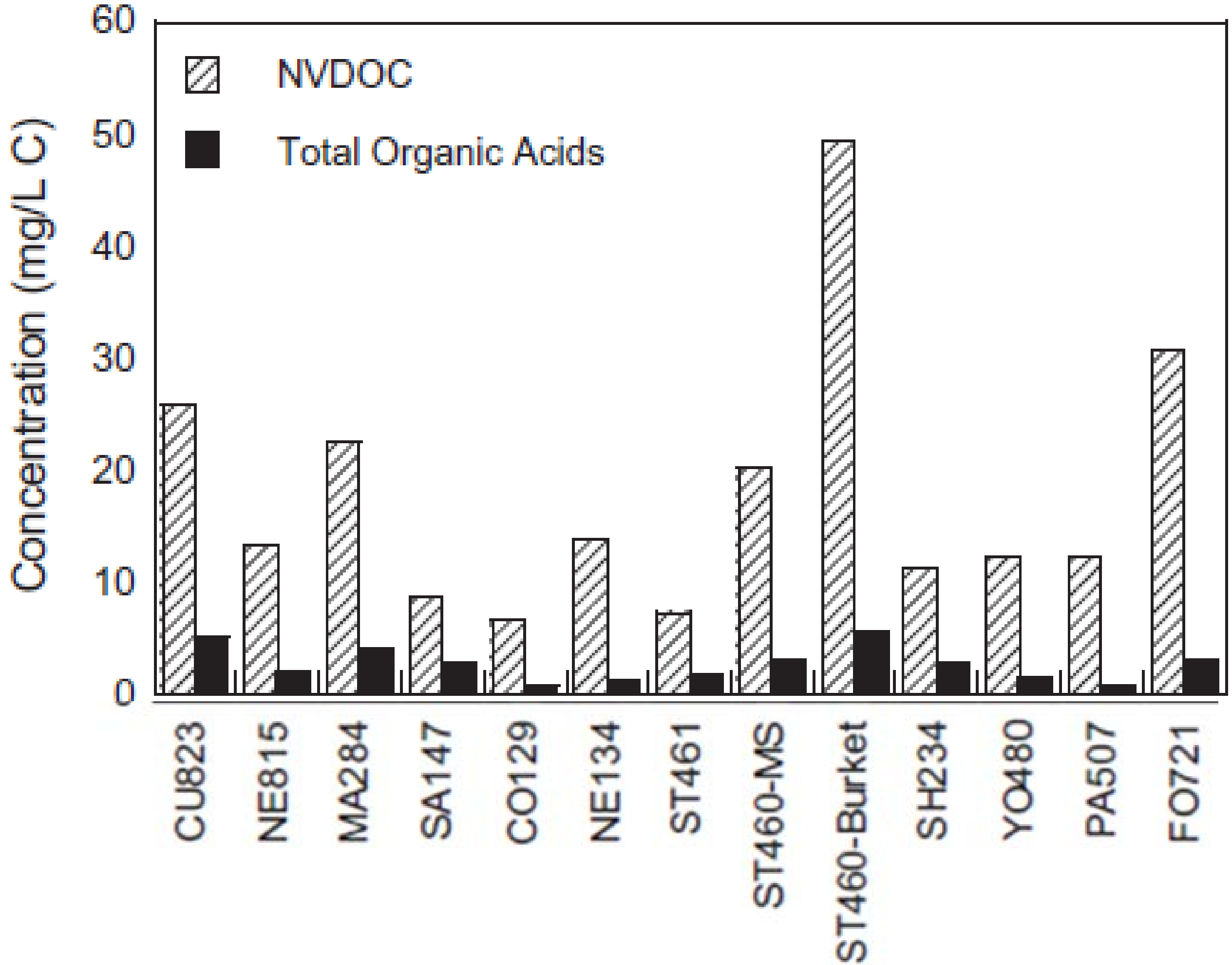

Akob et al., Applied Geochemistry, 2015

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Groundwater Contamination

- The sub-surface activities can potentially impact the deep aquifers and affect the quality of groundwater supplies if leakage were to occur by adding contamination from the injection formation or fluids.

- Detection of entrained contaminants that migrate into shallow groundwater aquifers is important to evaluate impacts on water resources.

- Produced water Management and groundwater monitoring are essential part of oil and gas production

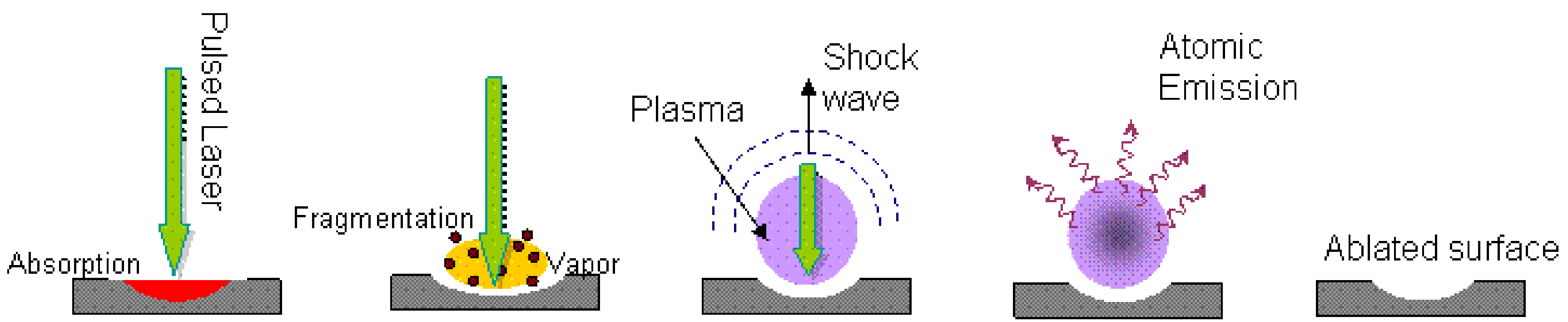
- Laser induced breakdown spectroscopy (LIBS) technique is an emerging techniques for groundwater monitoring.

Laser Induced Breakdown Spectroscopy

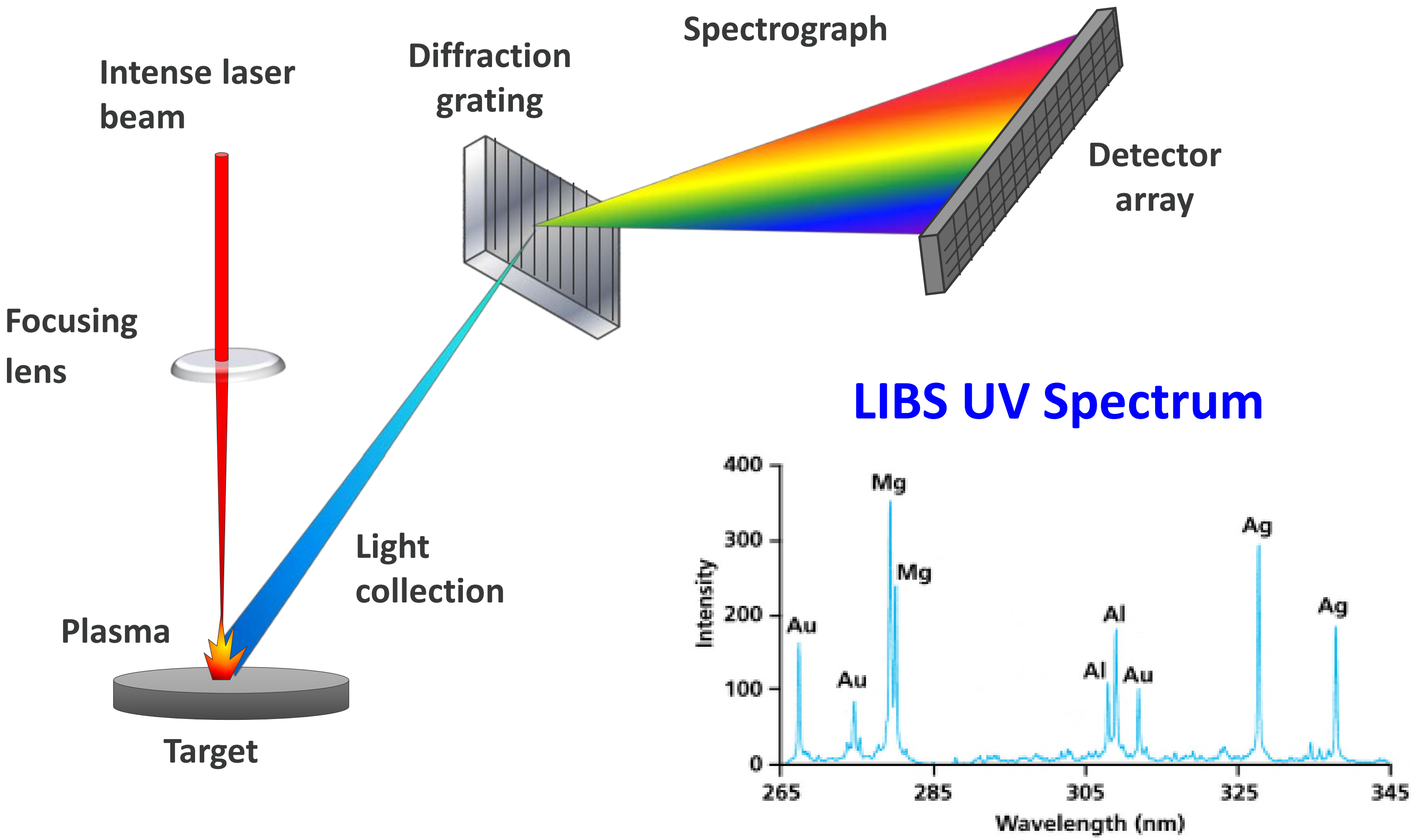
- Laser is fired upon a given sample and laser energy focused to a small spot
- A hot luminous plasma vaporizes the material, and leads to atomization and excitation of elements
- As plasma cools, emission occurs and the emitted light can be collected
- Every element in the Periodic Table gives off light at a distinct wavelength
- LIBS can perform in-situ elemental and isotopic analysis of liquid samples and is capable of making underwater measurements
- Flexibility of probe design, and use of fiber optics make it a suitable technique for real-time and stand-off measurements in harsh conditions and at hard to reach places.

Laser Induced Breakdown Spectroscopy

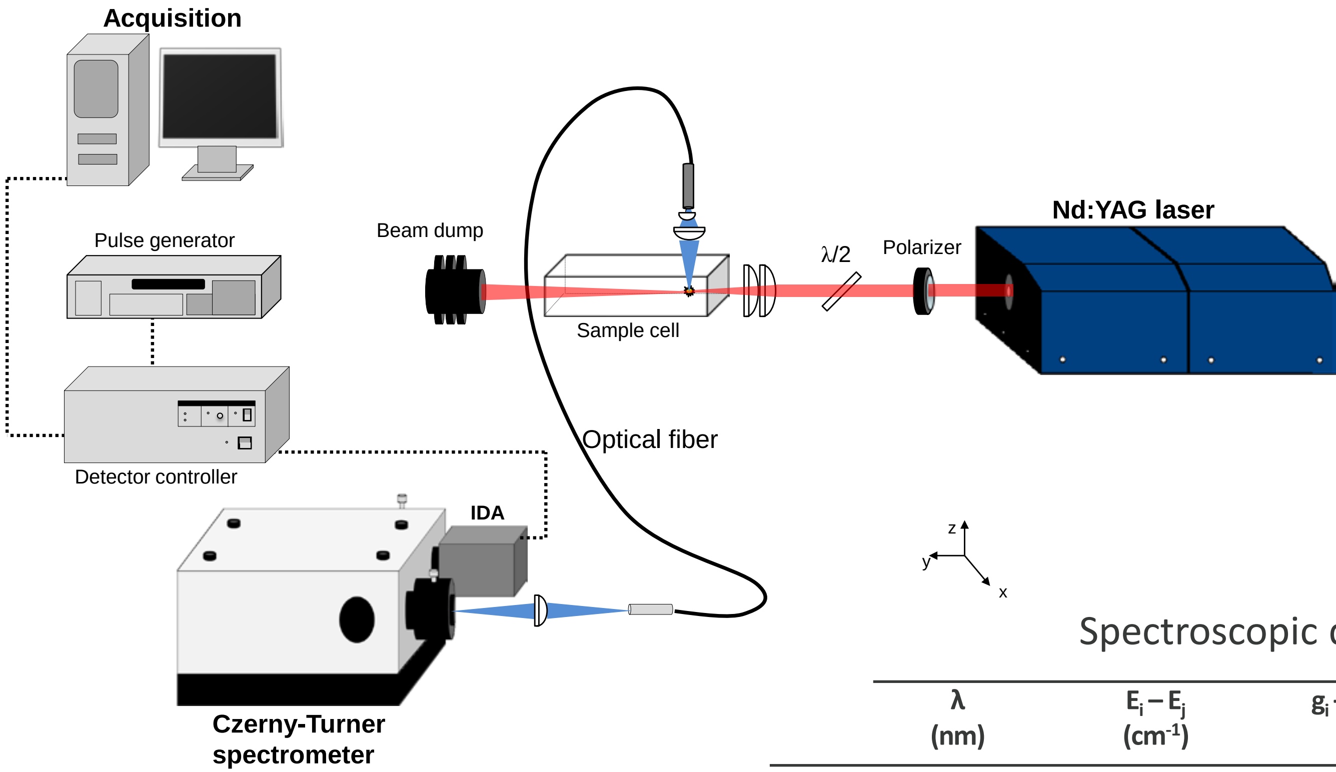
- High energy laser pulse creates micro plasma plume on the sample. It ablates a very small amount of material
- The ablated material dissociates into excited ionic and atomic species
- The excited atoms/ions present in the plasma emit light at their characteristic wavelengths
- Spectral analysis of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

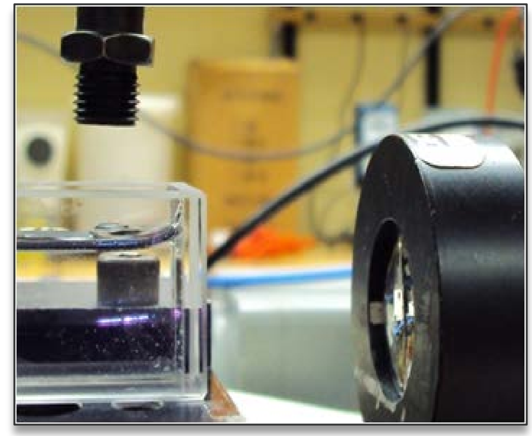


Principle of Laser Induced Breakdown Spectroscopy



Underwater LIBS Analysis of Metal Ions





Spectroscopic data

	λ (nm)	$E_i - E_j$ (cm^{-1})	$g_i - g_j$	A_{ij} ($10^8\ s^{-1}$)	Ioniz. energy (eV)
Ca	422.67	0 – 23652.30	1 – 3	2.18	6.11
Sr	460.73	0 – 21698.45	1 – 3	2.01	5.70
Li	670.78	0 – 14904.00	2 – 4	0.37	5.39
	670.79	0 – 14903.66	2 – 2	0.37	
K	766.49	0 – 13042.90	1 – 4	0.39	4.34

Pulse Energy and Acquisition Delay Optimization

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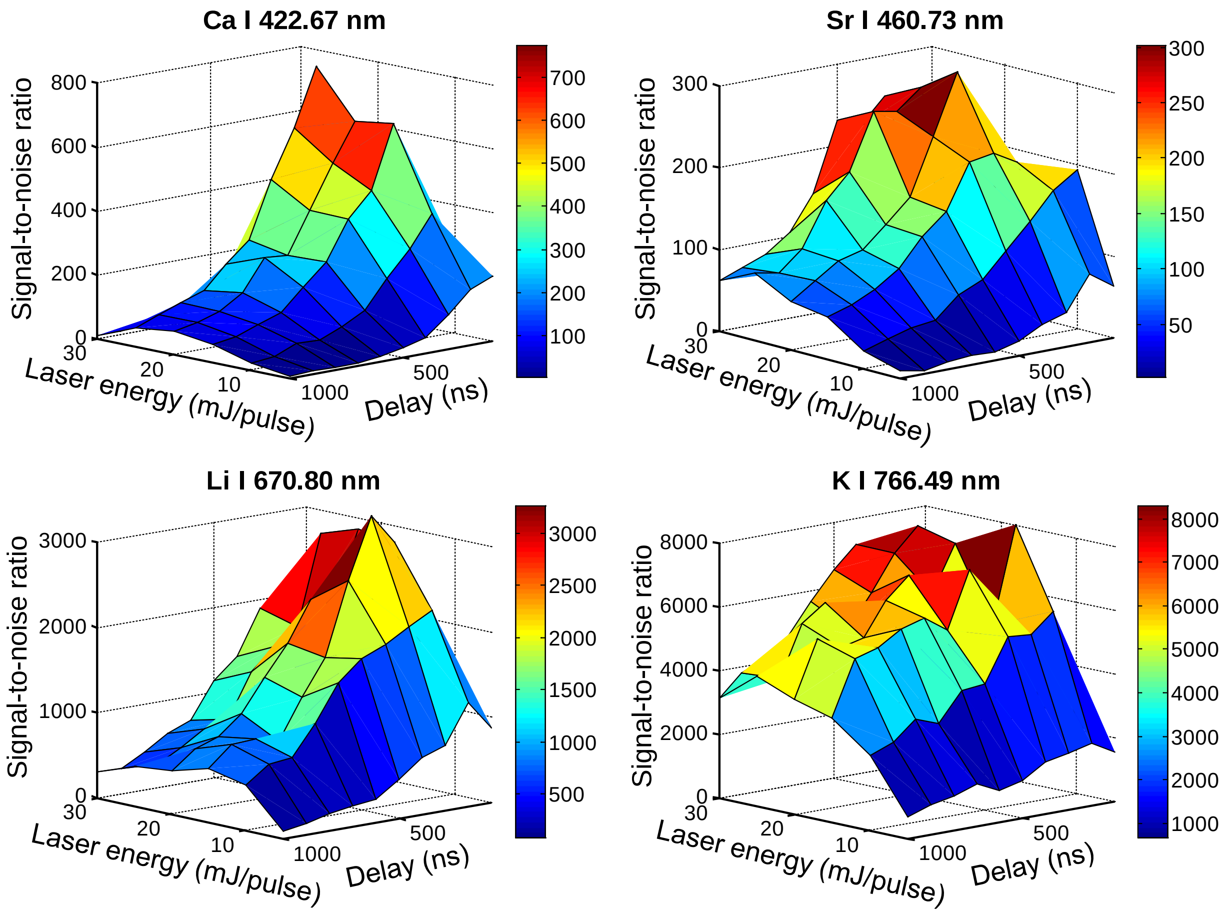
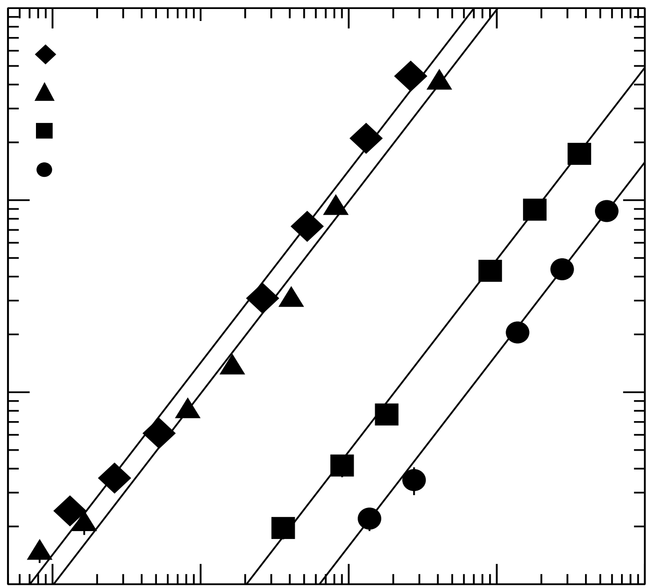


Optimal parameters: 20 mJ/pulse, 200 ns delay

C. Goueguel, D.L. McIntyre, **J. Jain**, A.K. Karamalidis, C. Carson, *Appl. Optics*, 54(19), 6071-6079 (2015)

Calibration Curves, Detection Limits, and Quantification Limits of K+, Li+, Ca2+, and Sr2+

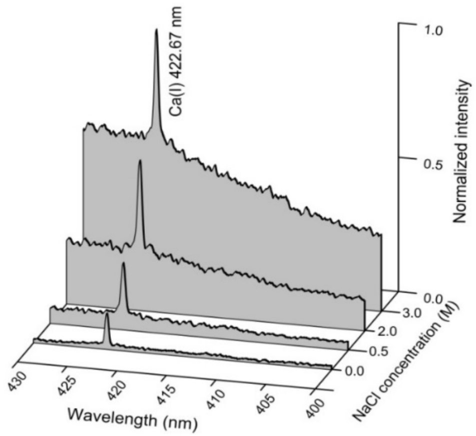


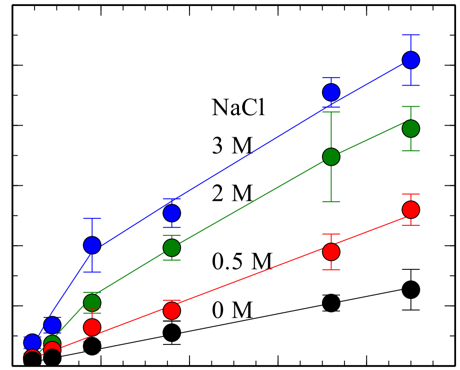
	R^2	DL	QL
Sr^{2+}	0.9990	2.89±0.11 ppm	9.63±0.39 ppm
Ca^{2+}	0.9997	0.94±0.14 ppm	3.11±0.07 ppm
Li^{+}	0.9988	60±2 ppb	0.19±0.01 ppm
K^{+}	0.9977	30±1 ppb	80±4 ppb

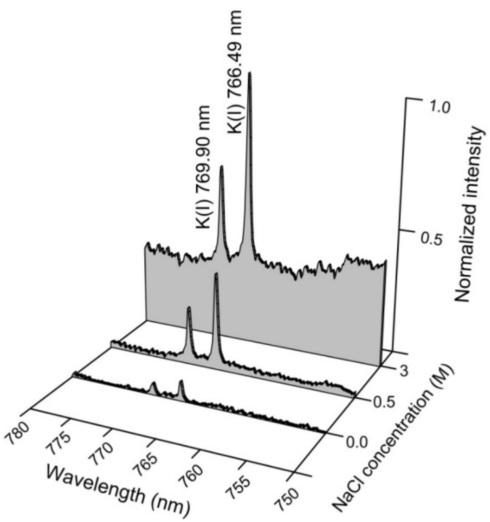
Easily ionized elements were detected in the ppb range, whereas elements with emission originating at higher energy levels were detected in the low ppm range

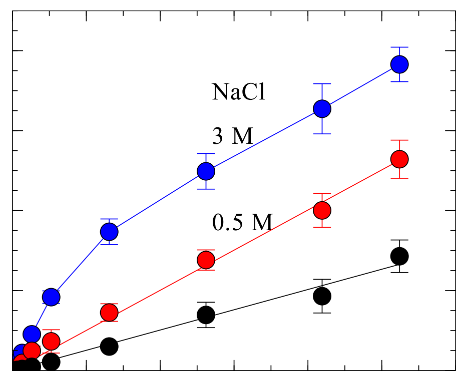
C. Goueguel, D.L. McIntyre, **J. Jain**, A.K. Karamalidis, C. Carson, *Appl. Optics*, 54(19), 6071-6079 (2015)

Evaluating NaCl-induced Matrix Effects









C. Goueguel, J.P. Singh, D.L. McIntyre, J. **Jain,** A.K. Karamalidis, *Appl. Spectrosc.*, 68(2), 213-221 (2014)

Comparing Matrix Effects Induced by Common sodium compounds: NaCl, Na2SO4, and Na2CO3

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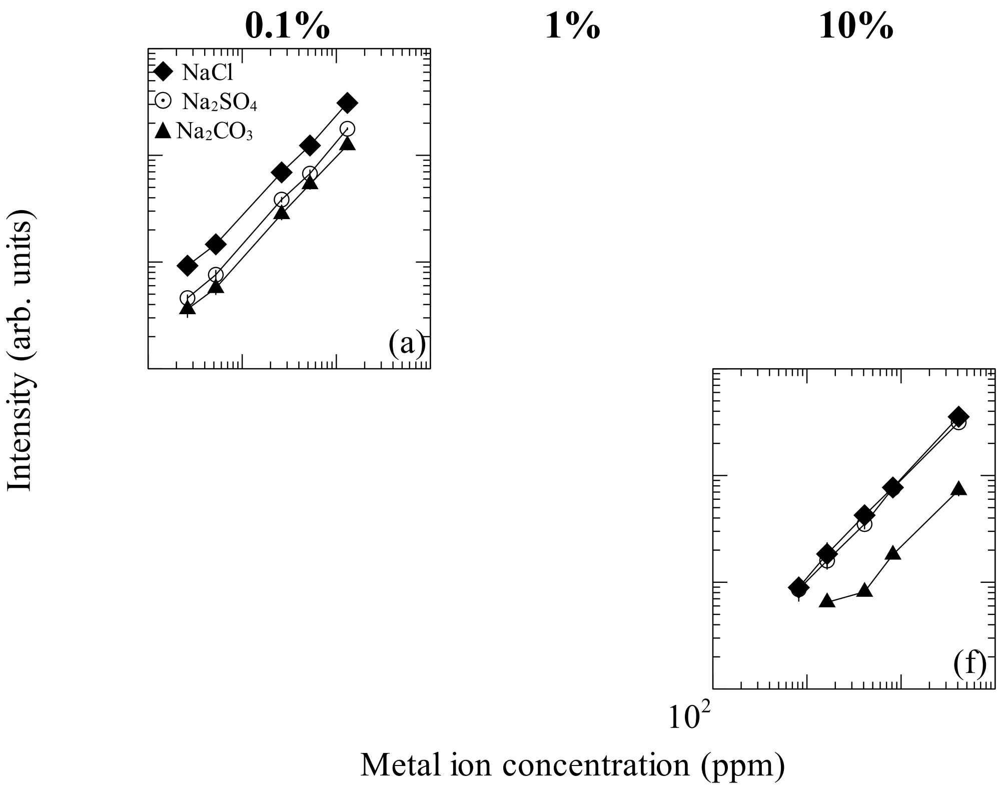
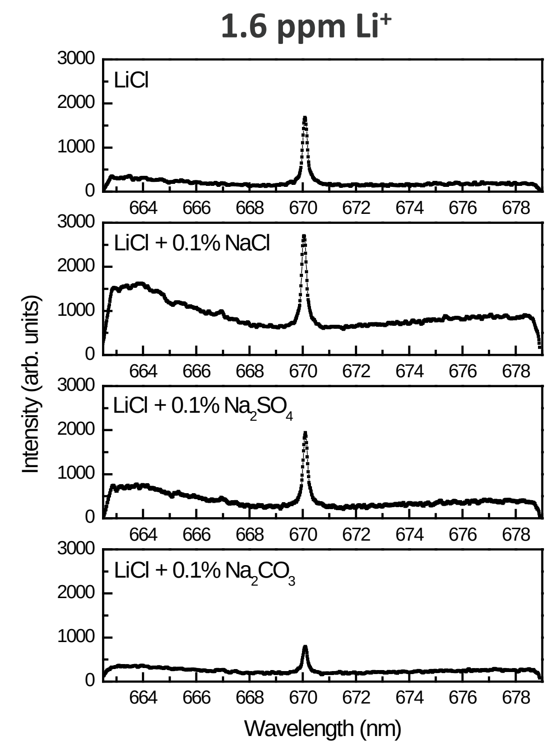
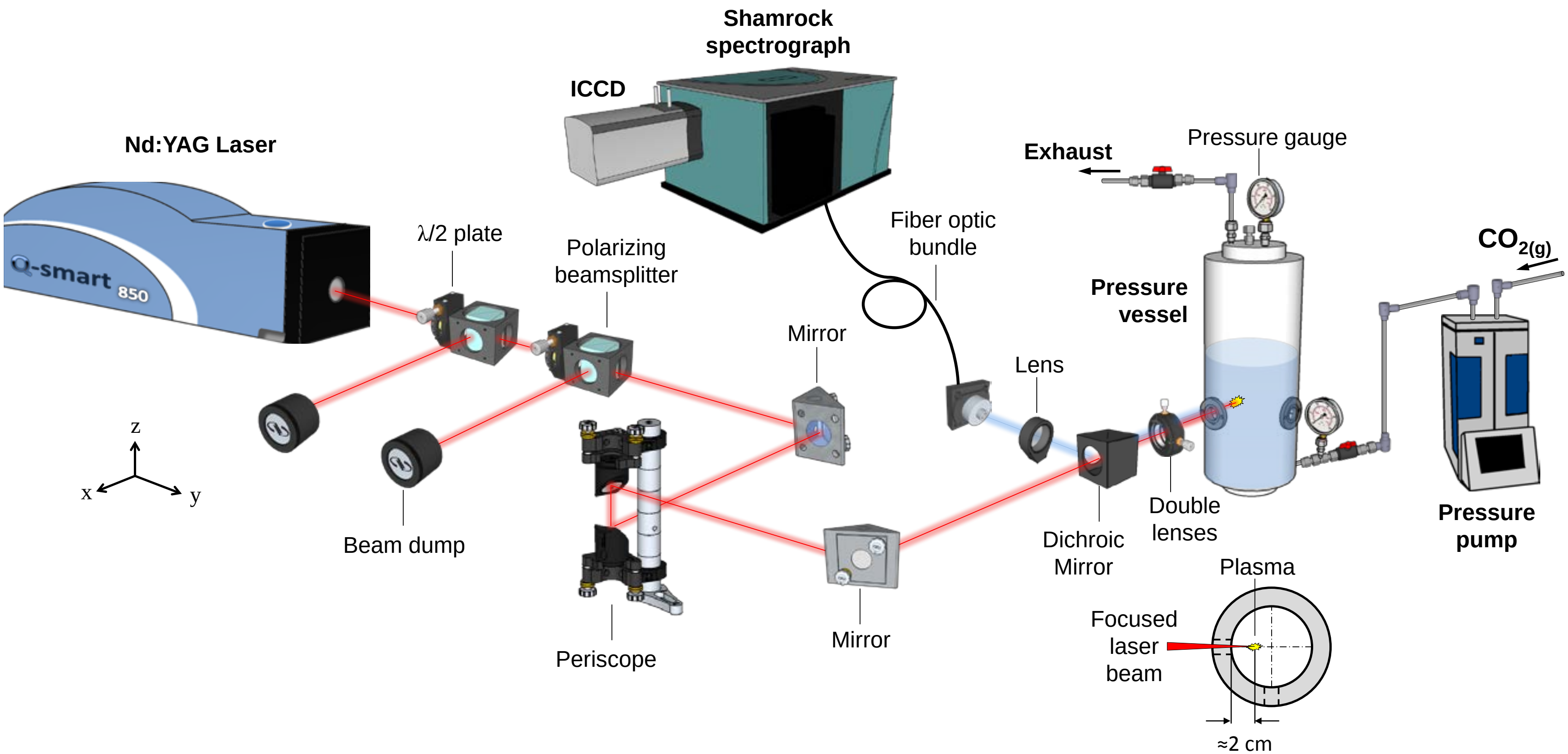




- Increase in sodium compounds (from 0.1, 1, to 10 wt.%) affect detection of the elements
- Must be accounted for with all measurements (Example: use of an internal standard)

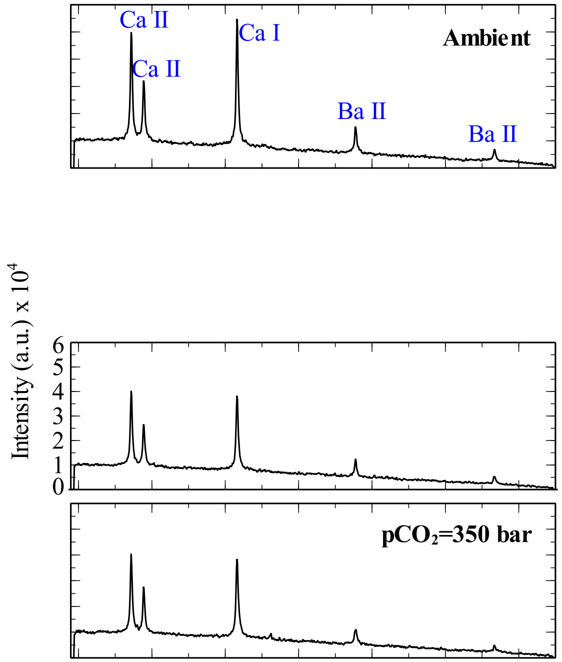
C. Goueguel, D.L. McIntyre, **J. Jain**, A.K. Karamalidis, C. Carson, *Appl. Optics*, 54(19), 6071-6079 (2015)

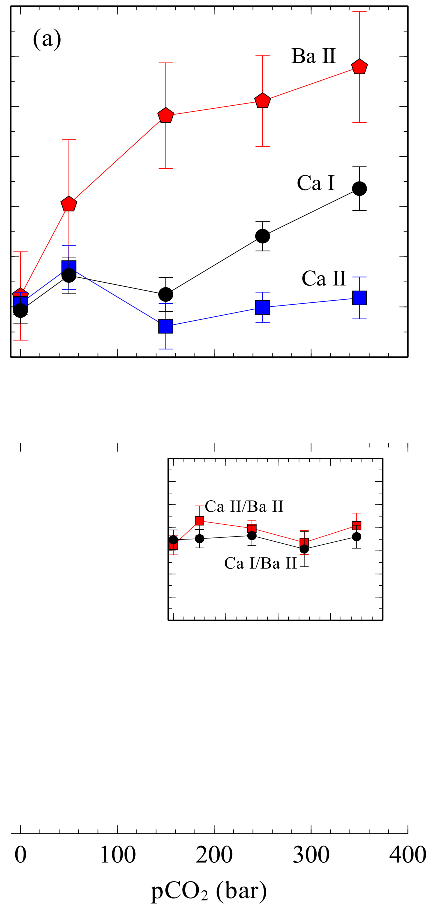
LIBS Benchtop Experiment



- Optically accessible pressure vessel (0.5 liter), 6,000 psi – 300 F
- Experimental conditions: 20 mJ/pulse; 160 ns gate delay; 400 ns gate width; 500 accumulations; 5 replicates

Effects of CO_2 Pressure on LIBS Spectra





Pressure-induced line broadening:

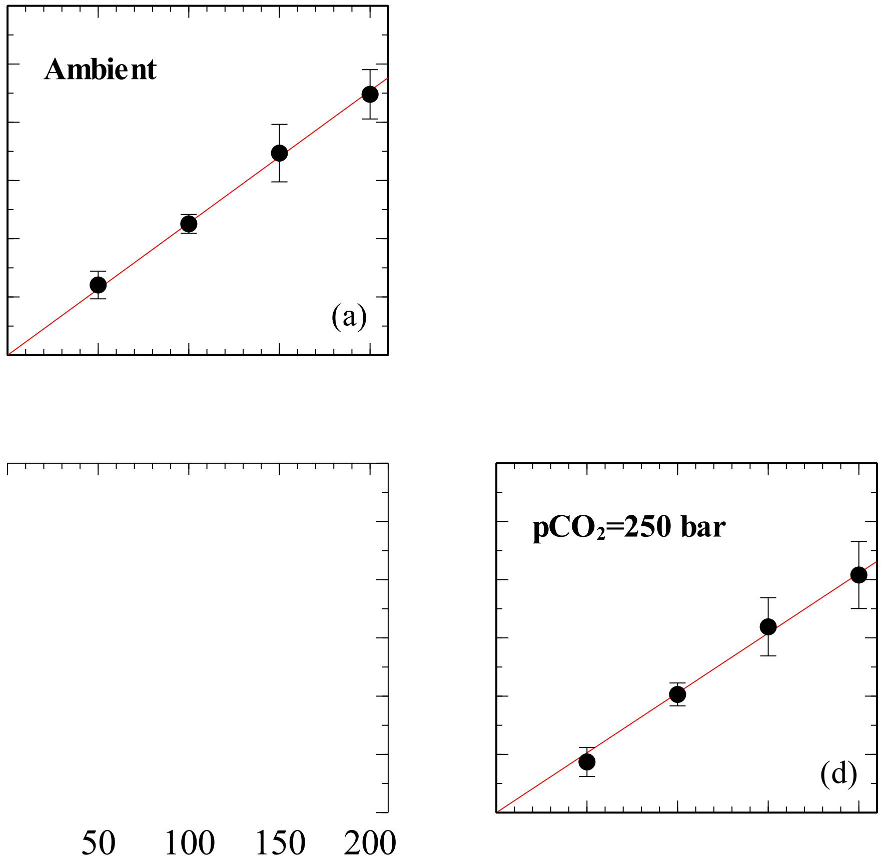
20–37% increase of the full at width half maximum (FWHM) for Ca I and Ba II lines

CO_2 pressure has minimal adverse effects on the signal-to-background ratio (SBR), other than a small decrease at 350 bar

Strong and well-resolved spectral lines of Ca^{2+} and Ba^{2+} cations obtained in CO_2-saturated water over 50–350 bar

C.L. Goueguel, **J.C. Jain**, D.L. McIntyre, C.G. Carson, H.M. Edenborn, Submitted to *J. Anal. At. Spectrom*. (April 2016)

Calcium Calibration Curves and Detection Limits



pCO_2 (bar)	R^2	DL (ppm)
Ambient	0.9997	7.35 ± 0.4
50	0.9977	9.21 ± 0.3
150	0.9962	9.37 ± 0.5
250	0.9988	9.03 ± 0.8
350	0.9994	9.58 ± 0.3

Increasing CO_2 pressure over the range 50–350 bar has little effects on calcium detection limit (DL), which was **estimated to be about 9 ppm**.

C.L. Goueguel, **J.C. Jain**, D.L. McIntyre, C.G. Carson, H.M. Edenborn, Submitted to *J. Anal. At. Spectrom*. (April 2016)

Application: In-situ Measurements of $CaCO_3$ Dissolution as a Function of Rising CO_2 Pressure

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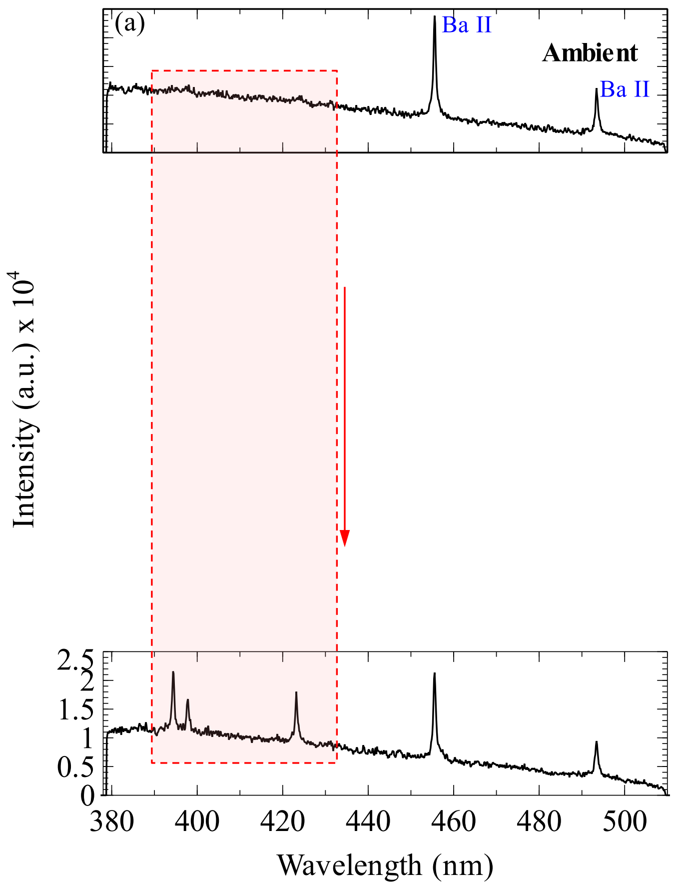
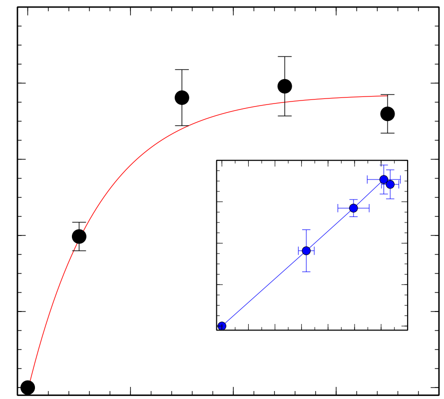
Pressed pellet of CaCO3 powder (99.999%, trace metals basis) was introduced into a solution of 1 mM BaCl2·2H2O

Measurements are based upon mass transport of dissolved Ca2+ by diffusion away from the liquid–carbonate boundary

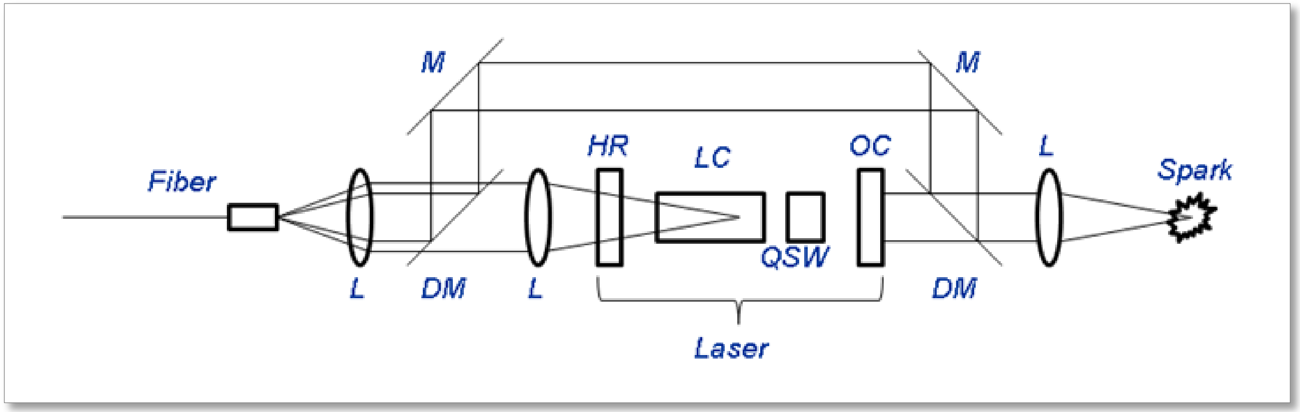




Ca2+ released in water increases with pCO2 up to 150 bar but remains nearly constant when pCO2 was further increased to 350 bar, which may be related to lesser effects on the pH of the solution.

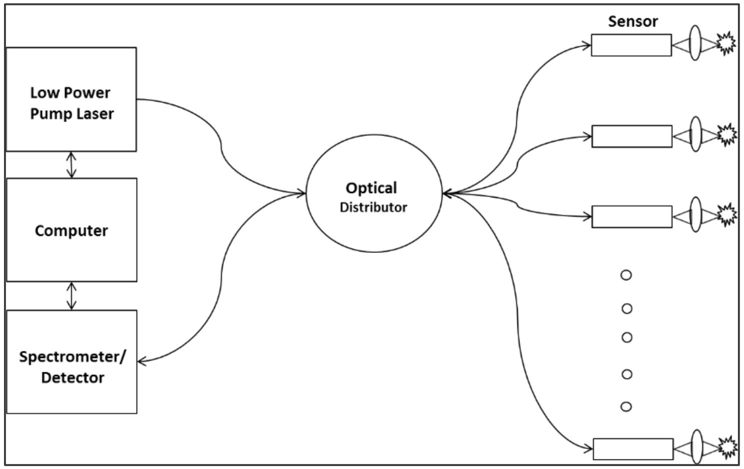
Fabrication of Laser Unit

- **Method and Device or Remotely Monitoring An Area Using a low Peak Power Optical Pump, US Patent 8786840 B1**



  - Fiber delivers pump pulse and returns spectral signature
  - Laser can be designed to perform either LIBS or RAMAN excitation
  - Laser is approximately 1 inch long
  - Entire optical setup can be sealed to withstand pressure and temperature
  - Laser operation is dictated by selection of optical element parameters and tailoring of input pump pulse

LIBS Sensor

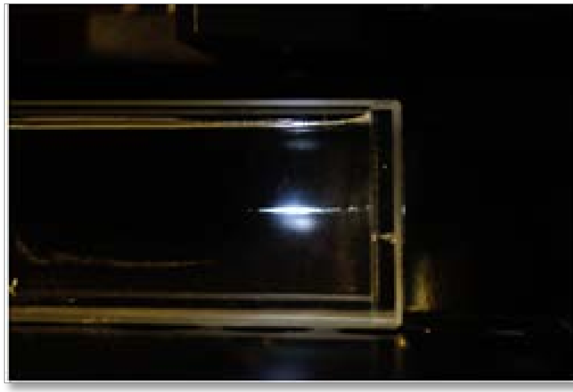


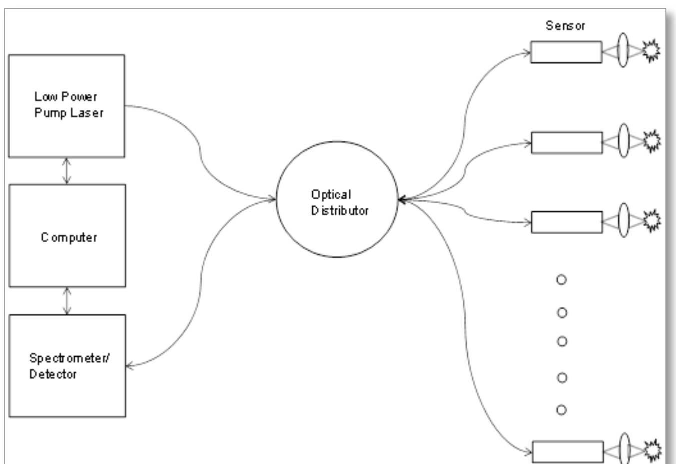
- Working prototype now in operation
- Fiber coupled to CW laser diode
- Remotely End Pumped
- Nd:YAG Gain Medium (green)
- Cr:YAG Passive Q-switch (brown)
- 1064nm 3mJ 1.2ns 10 Hz
- Sensing head can be distributed

J.C. Jain, D.L. McIntyre, K.K. Ayyalasomayajula, V. Dikshit, C. Goueguel, F. Yu-Yueh, J.P. Singh, *Pramana - Journal of Physics*, 83,179-188 (2014)

D.L. McIntyre**, J.C. Jain**, C. Goueguel, J.P. Singh, *in "Spectroscopic Techniques for Security, Forensic and Environmental Applications"* Nova Publication, USA, pp 25-52 (2014)

LIBS Sensor





- Laser Diode coupled Fiber
- Nd:YAG Active Media
- Cr:YAG Q-switch
- Remotely End Pumped
- 1064nm 8mJ 4ns 15Hz

J.C. Jain, D.L. McIntyre, K.K. Ayyalasomayajula, V. Dikshit, C. Goueguel, F. Yu-Yueh, J.P. Singh*, Pramana - Journal of Physics*, 83,179-188 (2014)

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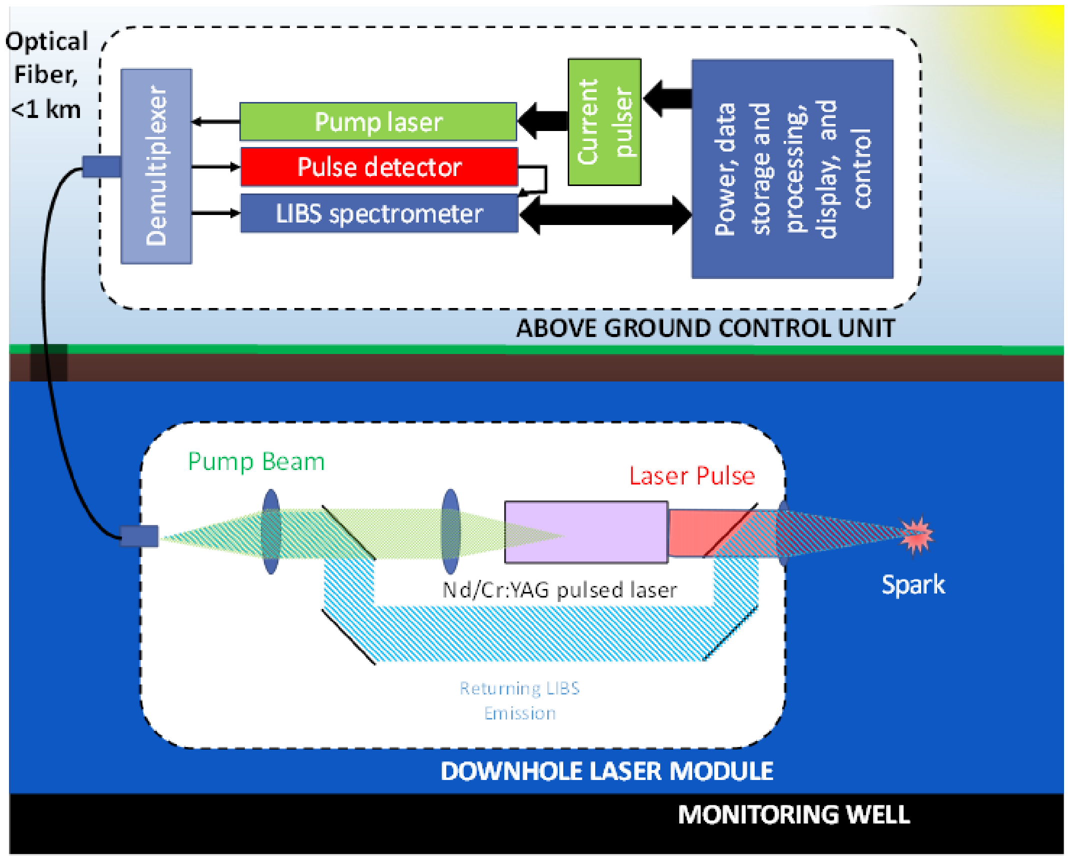
Field Deployable Unit



CG. Carson., C. Goueguel, **J. Jain**, D. McIntyre., *Proc. SPIE 9467, Micro- and Nanotechnology Sensors, Systems, and Applications VII*, 94671K (May 22, 2015)

Conclusions

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- **Laser induced Breakdown Spectroscopy (LIBS) can provide mineral composition of aqueous samples**
- **Measurements in high pressure conditions makes it suitable for down hole conditions**
- **Use of fiber optics can aid the analysis at hard to reach places**
- **LIBS can provide a robust sensing device to determine long term ground water quality**
- **Development of a field deployable LIBS sensor is in progress**
  - Component integration toward field scale studies
  - Laser and optical design for harsh environments
  - Fiber optics Coupling

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