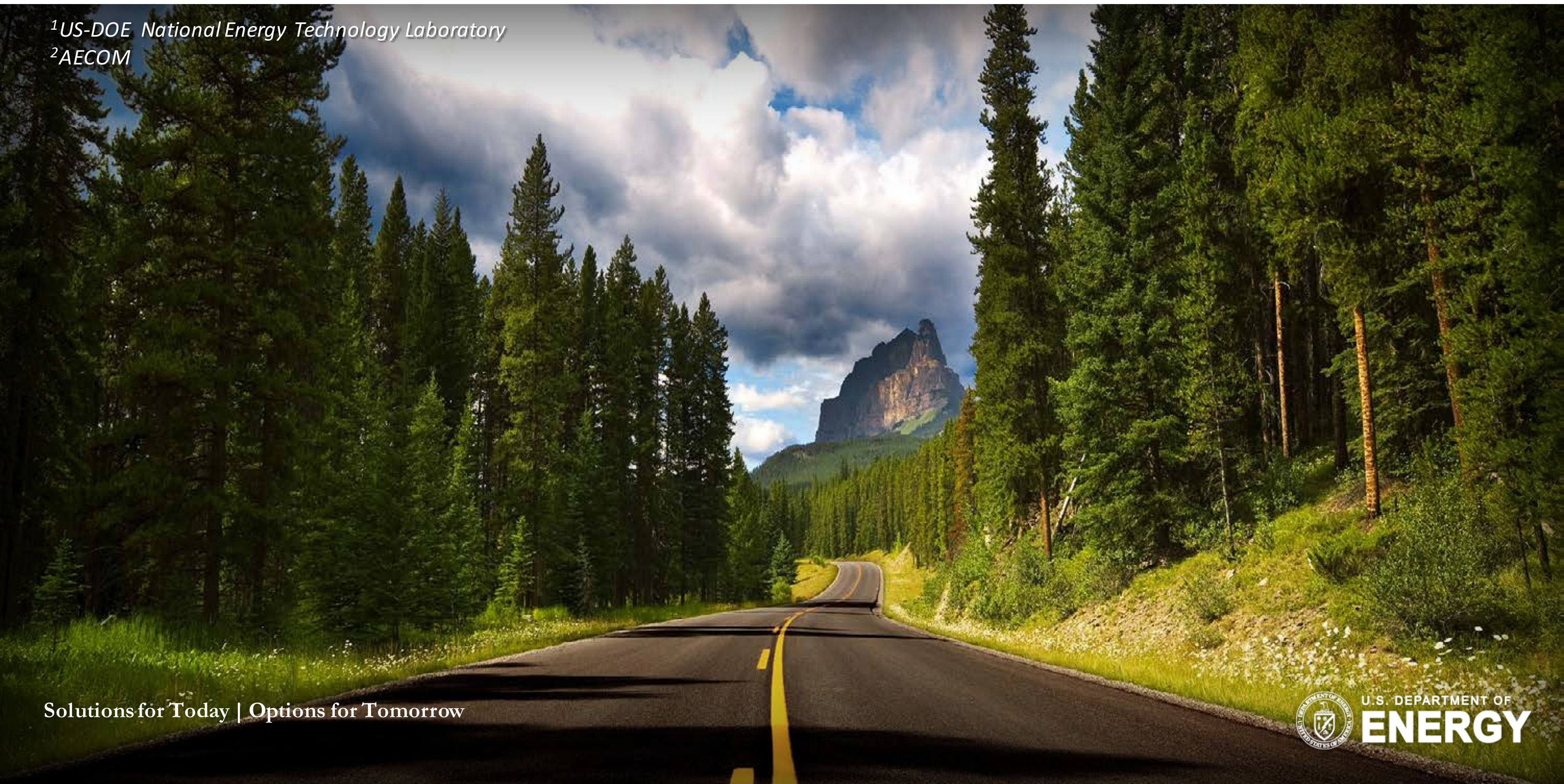
Prototype LIBS Sensor for Sub-Surface Water Quality Monitoring

NATIONAL ENERGY TECHNOLOGY LABORATORY

Daniel Hartzler[1,2], Chet Bhatt[1,2], Jinesh Jain[1,2], and Dustin McIntyre[1]

[1]*US-DOE National Energy Technology Laboratory*
[2]*AECOM*



Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

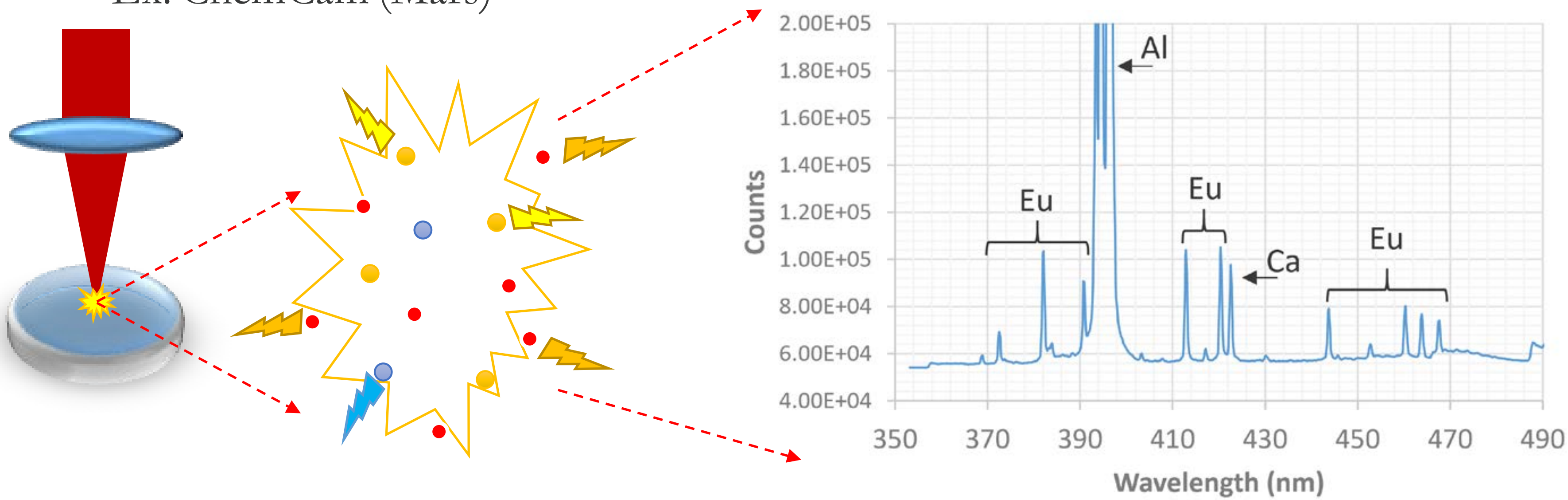
Prototype LIBS Sensor for Sub-Surface Water Quality Monitoring

NATIONAL ENERGY TECHNOLOGY LABORATORY

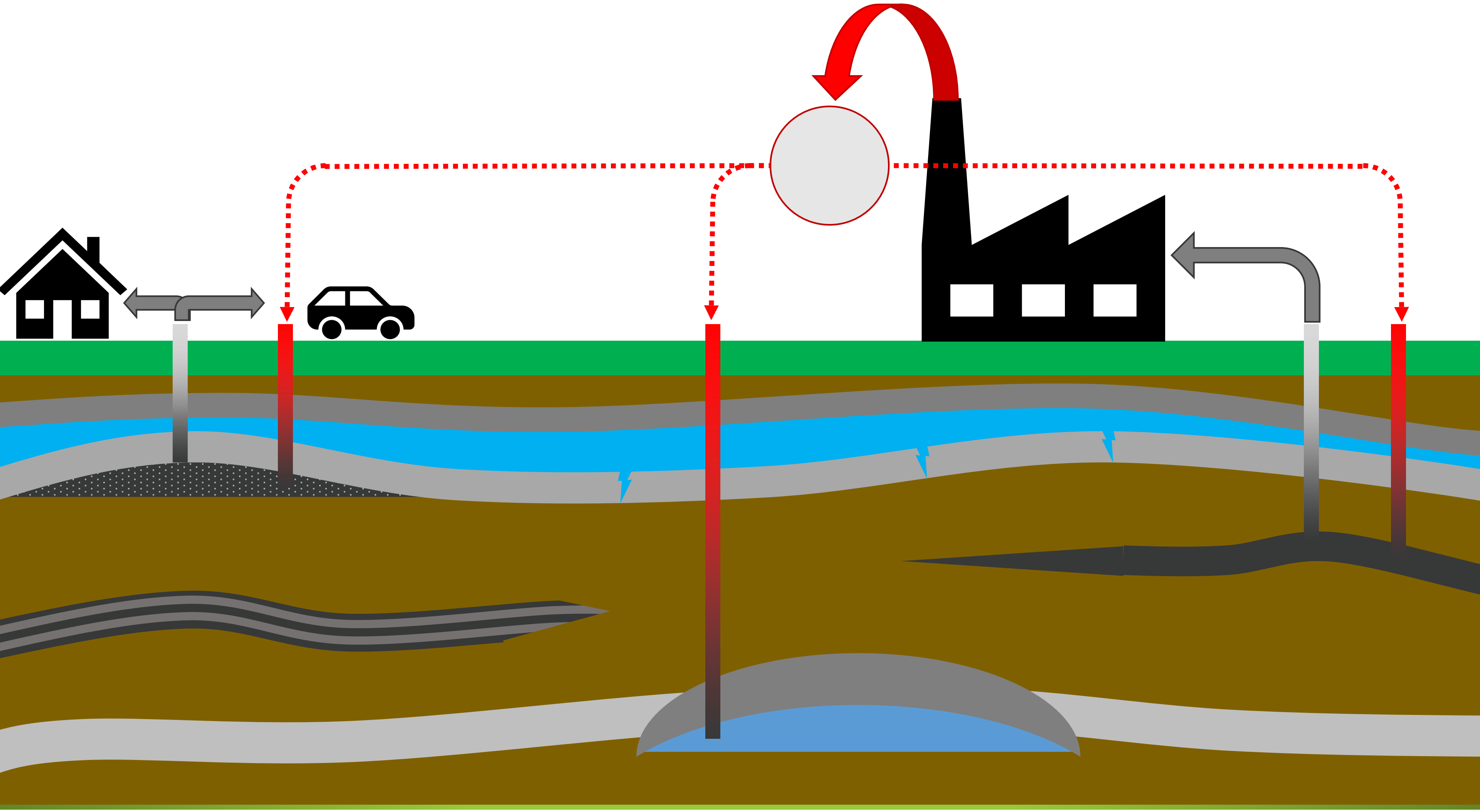
- **Laser Induced Breakdown Spectroscopy (LIBS) Sensor**
  - Limits of Detection (LODs)
    - ppm or sub-ppm
- **Applications**
  - Groundwater monitoring
    - Oil and Gas exploration and recovery
    - Carbon Capture Usage and Storage (CCUS)
  - *Rare Earth Element (REE) source characterization or extraction process monitoring*

Laser Induced Breakdown Spectroscopy

- **Laser Induced Breakdown Spectroscopy (LIBS)**
  - Elemental analysis
  - Rapid
  - Minimal sample preparation is required
  - Versatile (solid, liquid, and gas analysis)
  - Hostile environments
    - Ex: ChemCam (Mars)



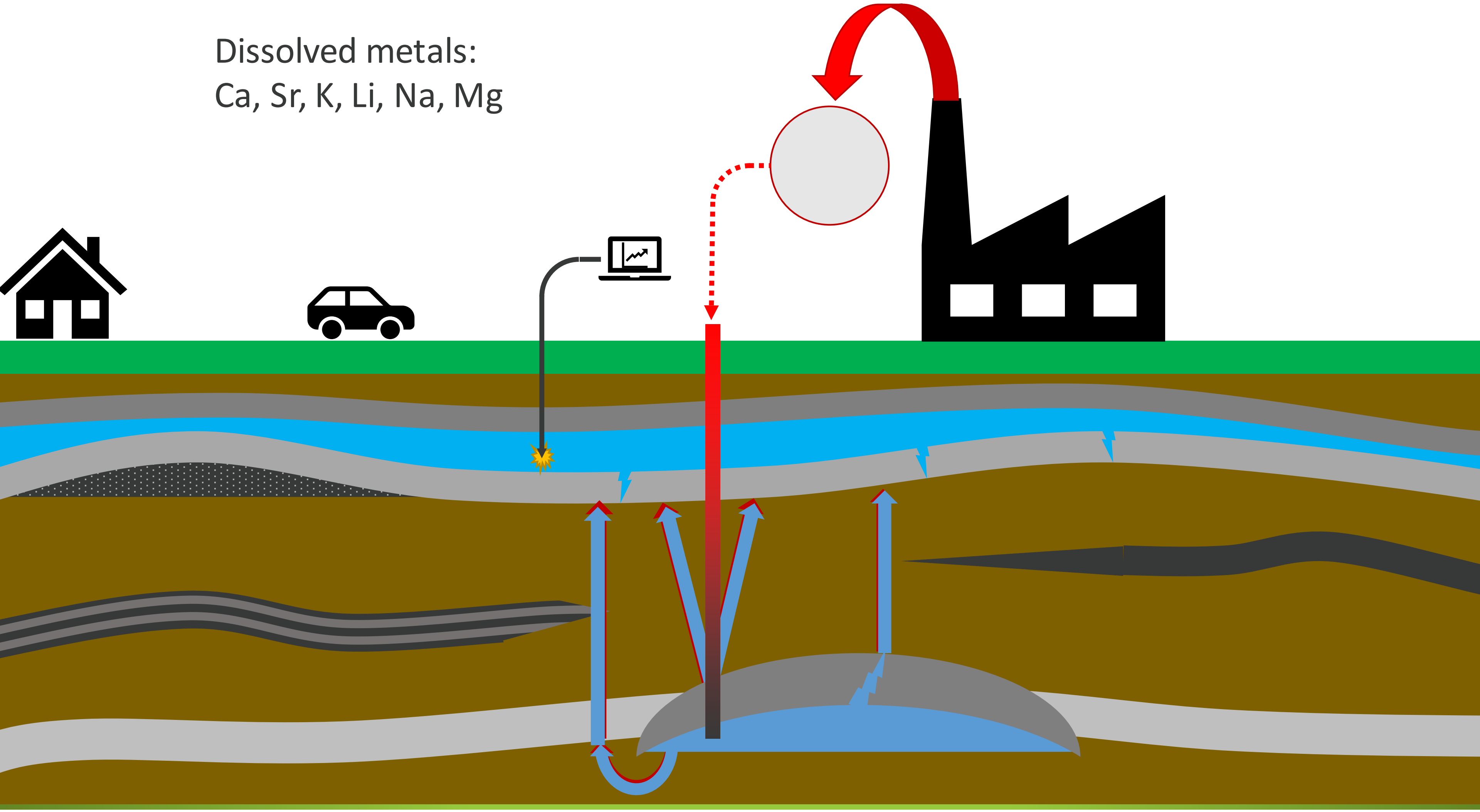
Carbon Capture Usage and Storage



Groundwater Contamination

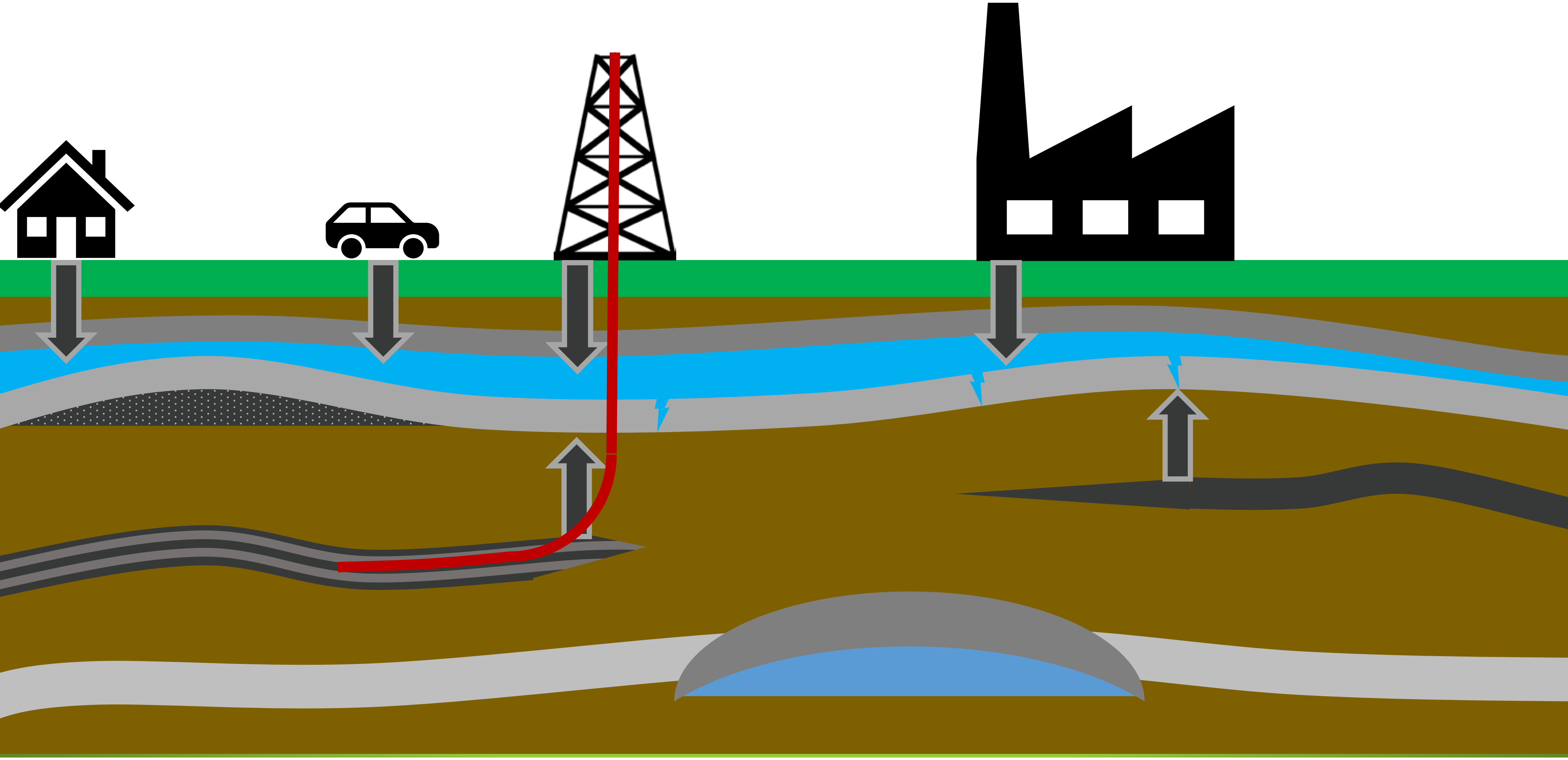
NATIONAL ENERGY TECHNOLOGY LABORATORY

Dissolved metals:
Ca, Sr, K, Li, Na, Mg

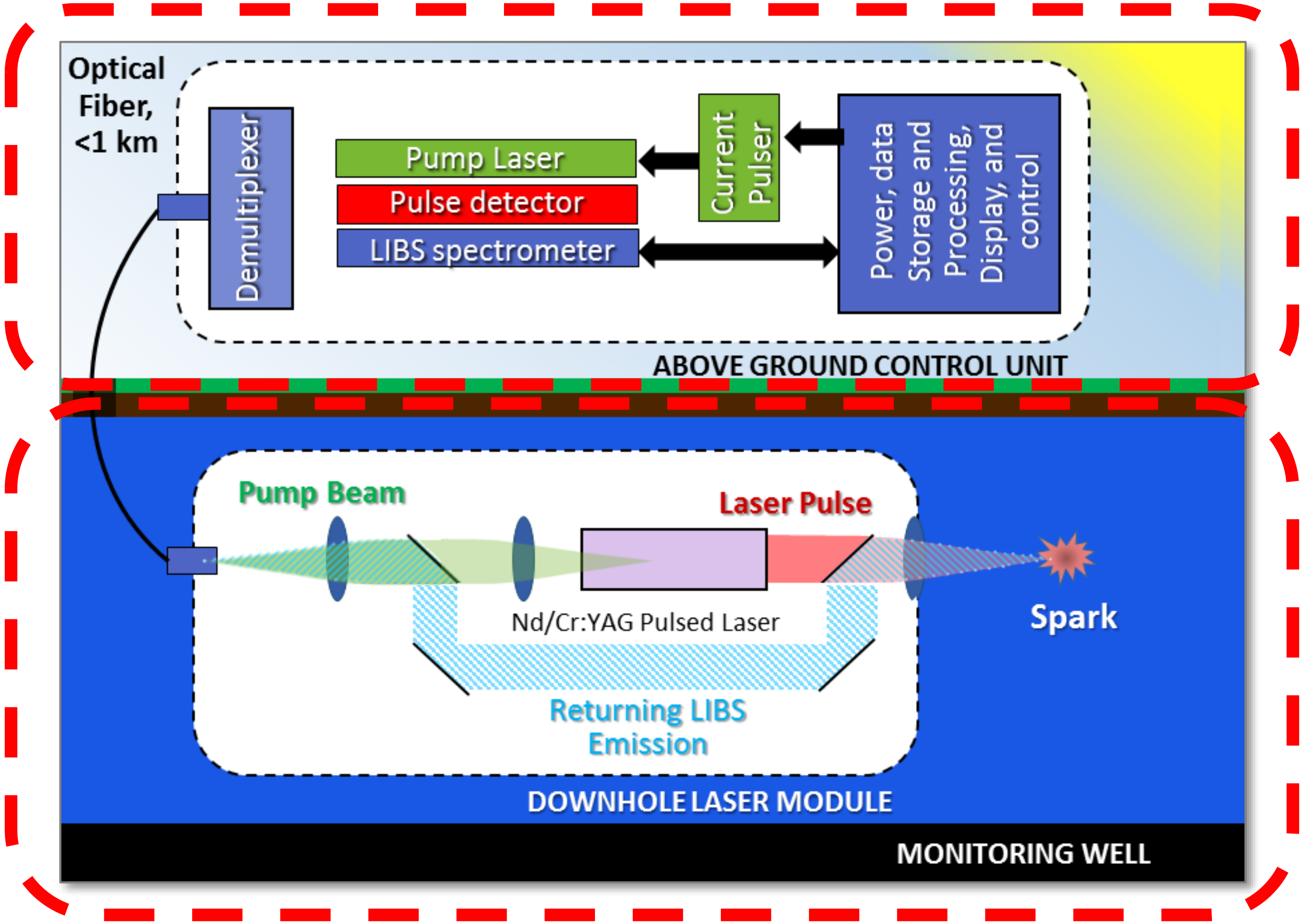


Other Contamination Sources

NATIONAL ENERGY TECHNOLOGY LABORATORY

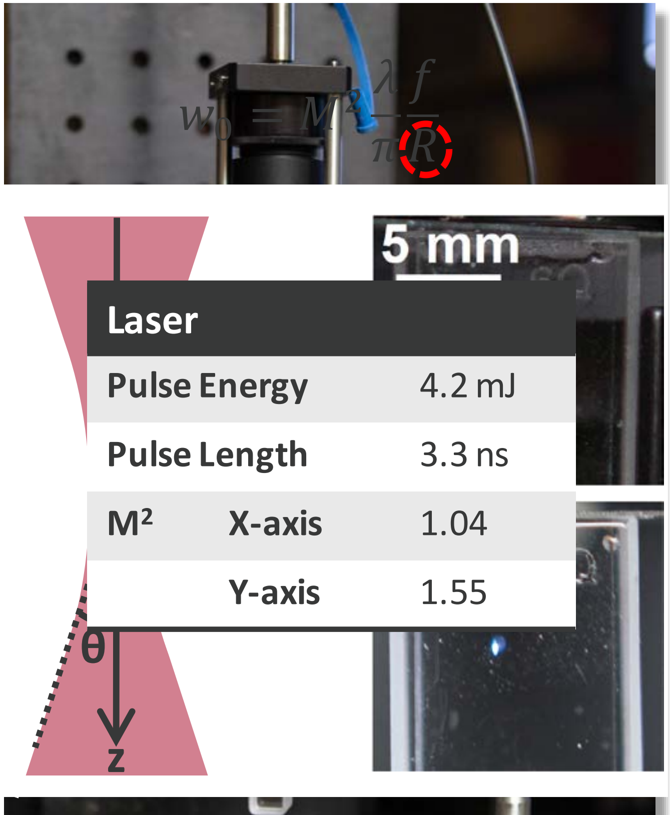


System Concept

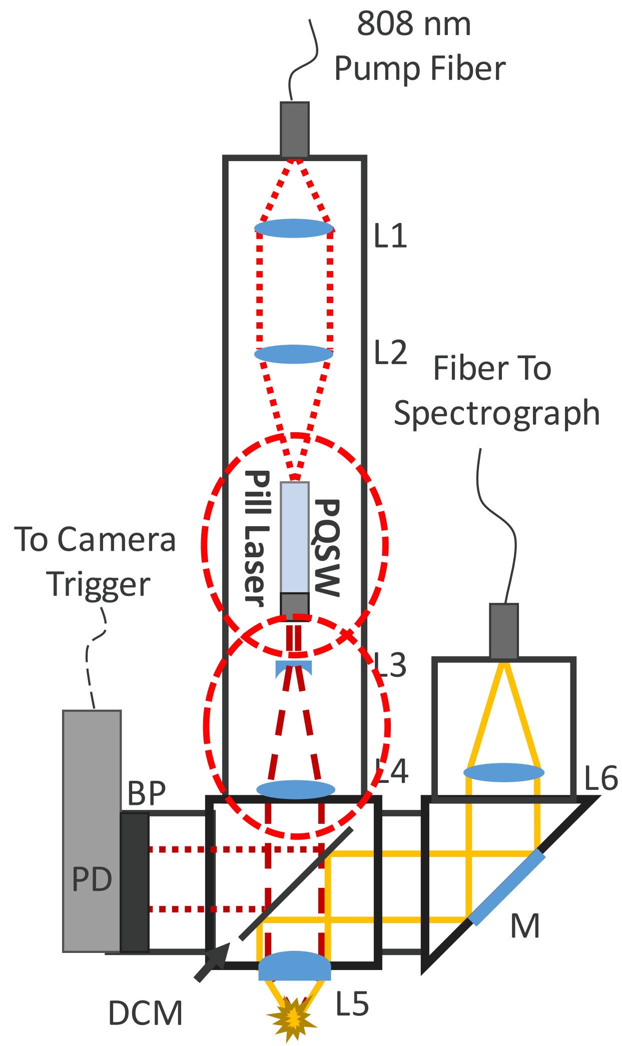


JC Jain, DL McIntyre, and CL Goueguel, National Innovation Summit & Showcase (May 15, 2017)
CG. Carson., CL Goueguel, JC Jain, DL McIntyre., Proc. SPIE 9467, Micro- and Nanotechnology Sensors, Systems, and Applications VII, 94671K (May 22, 2015)
DA Hartzler , JC Jain, DL McIntyre "Development of a subsurface LIBS sensor for in situ groundwater quality monitoring with applications in CO2 leak sensing in carbon sequestration" (submitted)

Prototype Sensor

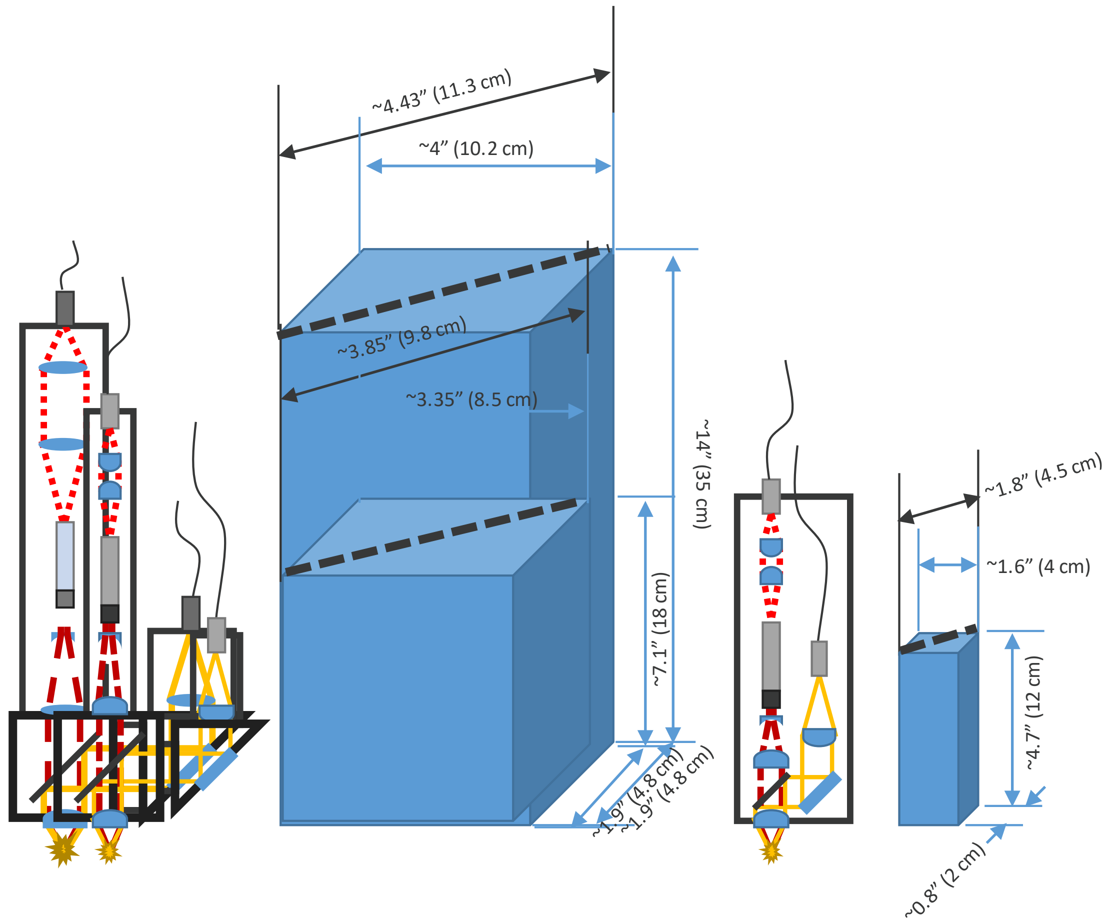


Laser		
Pulse Energy		4.2 mJ
Pulse Length		3.3 ns
M^2	X-axis	1.04
	Y-axis	1.55



DA Hartzler , JC Jain, DL McIntyre "Development of a subsurface LIBS sensor for in situ groundwater quality monitoring with applications in CO2 leak sensing in carbon sequestration", 2018 (submitted)

Sensor Head Size



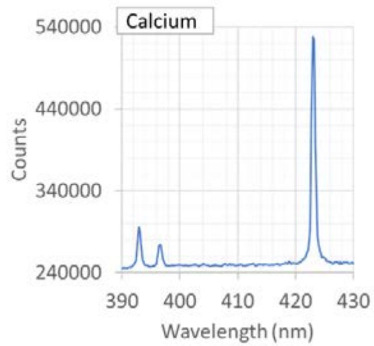
1st prototype
(30 mm cage)

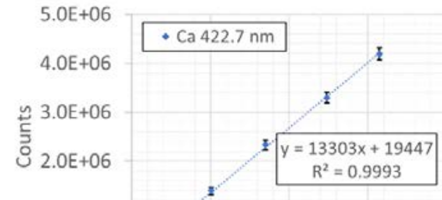
2nd prototype
(16 + 30 mm cage)

3rd prototype
Full custom frame

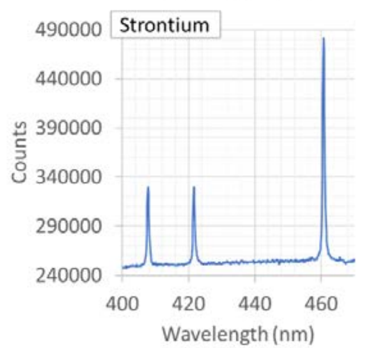
Performance – Alkali / Alkaline Metals

- $CaCl_2$ in DI water
  - 25.1 ppm Ca
  - 450 shots

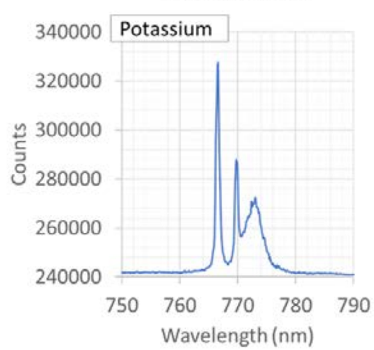




- $SrCl_2$ in DI water
  - 24.1 ppm Sr
  - 450 shots



- KCl in DI water
  - 5.2 ppm K
  - 450 shots



Element	Line (nm)	LOD (ppm)	LOD (literature) (ppm)		
Calcium	422.7	0.10[A]	0.94[B]	0.047[C]	0.13[E]
Strontium	460.7	0.04[A]	2.89[B]		
Potassium	766.6	0.009[A]	0.03[B]	0.006[D]	1.2[F]
	769.9	0.069[A]			

A – Hartzler et. al. **(Submitted),** "Development of a subsurface LIBS sensor for in situ groundwater quality monitoring with applications in CO2 leak sensing in carbon sequestration"

B – Goueguel et. al. **2015**, "Matrix effect of sodium compounds on the determination of metal ions in aqueous solutions by underwater laser-induced breakdown spectroscopy"

C – Pearman et. al. **2003**, "Dual-pulse laser-induced breakdown spectroscopy in bulk aqueous solution with an orthogonal beam geometry"

D – Golik et. al. **2012**, "Determination of detection limits for elements in water by femtosecond laser-induced breakdown spectroscopy"

E – Knopp et. al. **1996**, "Laser induced breakdown spectroscopy (LIBS) as an analytical tool for the detection of metal ions in aqueous solutions"

F – Cremers et. al. **1984**, "Spectrochemical analysis of liquids using the laser spark"

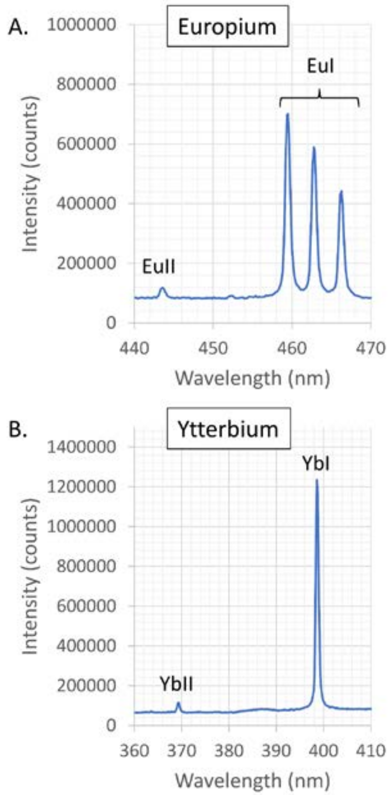
Concentration (ppm)

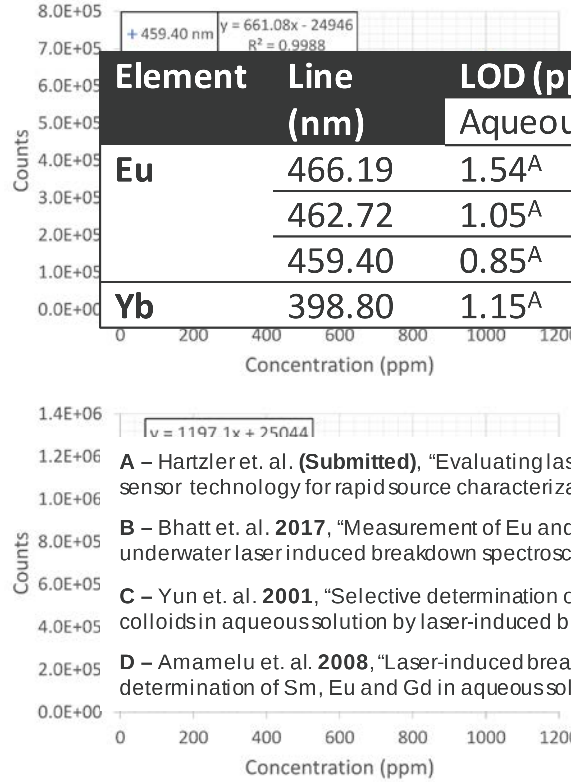
Performance – REE Liquid solution (Eu and Yb)

NATIONAL ENERGY TECHNOLOGY LABORATORY

- Eu in 2% HNO3
  - 1000 ppm Eu
  - 100 shots

- Yb in 2% HNO3
  - 1000 ppm Yb
  - 100 shots





Element	Line (nm)	LOD (ppm) Aqueous Solution			
Eu	466.19	1.54[A]		5.0[C]	
	462.72	1.05[A]		5.0[C]	1.9[D]
	459.40	0.85[A]	256[B]	5.0[C]	
Yb	398.80	1.15[A]	156[B]		

A – Hartzler et. al. **(Submitted)**, "Evaluating laser induced breakdown spectroscopy sensor technology for rapid source characterization of rare earth elements"

B – Bhatt et. al. **2017**, "Measurement of Eu and Yb in aqueous solutions by underwater laser induced breakdown spectroscopy"

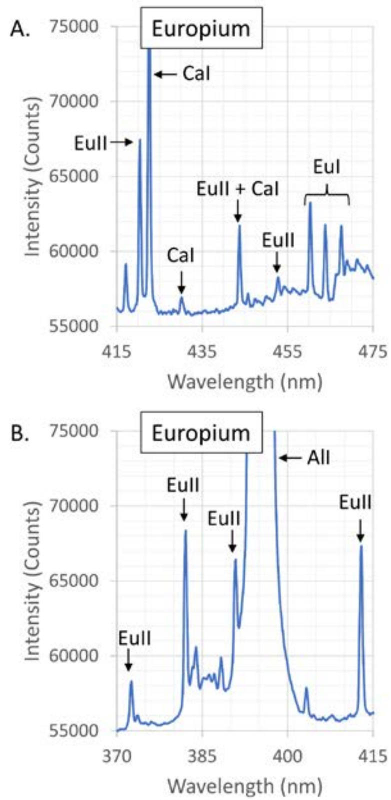
C – Yun et. al. **2001**, "Selective determination of europium (III) oxide and hydroxide colloids in aqueous solution by laser-induced breakdown spectroscopy"

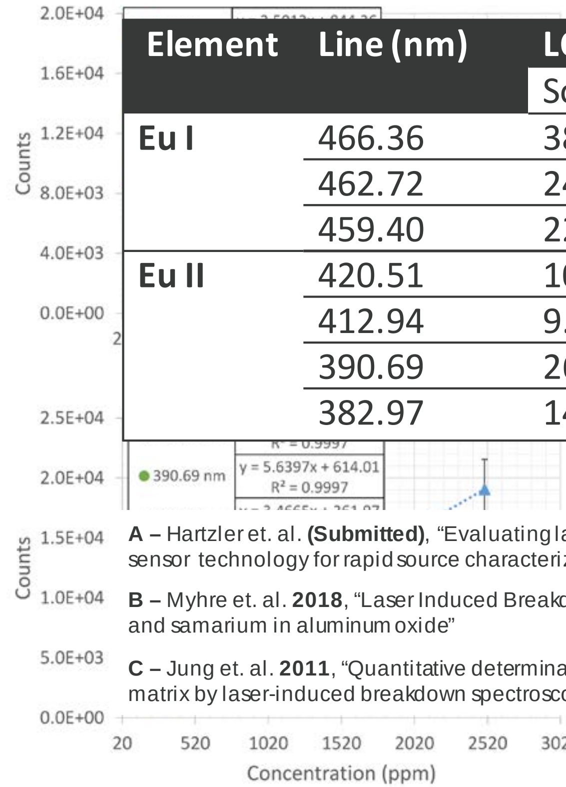
D – Amamelu et. al. **2008**, "Laser-induced breakdown spectroscopy for simultaneous determination of Sm, Eu and Gd in aqueous solution"

Performance – REE Solid Pellet (Eu)

NATIONAL ENERGY TECHNOLOGY LABORATORY

- Eu oxide + (Al_2O_3 + 20 % starch)
    - 2500 ppm Eu
    - 100 shots





Element	Line (nm)	LOD (ppm)	
		Solid Sample	
Eu I	466.36	38.6[A]	
	462.72	24.7[A]	
	459.40	22.4[A]	2.4[C]
Eu II	420.51	10.7[A]	
	412.94	9.9[A]	10[B]
	390.69	26.1[A]	20[B]
	382.97	14.3[A]	

A – Hartzler et. al. **(Submitted)**, "Evaluating laser induced breakdown spectroscopy sensor technology for rapid source characterization of rare earth elements"

B – Myhre et. al. **2018**, "Laser Induced Breakdown Spectroscopy analysis of europium and samarium in aluminum oxide"

C – Jung et. al. **2011**, "Quantitative determination of uranium and europium in glass matrix by laser-induced breakdown spectroscopy"

Acknowledgment

This technical effort was performed in support of the National Energy Technology Laboratory's ongoing research under the RES contract DE-FE0004000.

Disclaimer