Standoff Enrichment Measurements Using Laser-Induced Breakdown Spectroscopy

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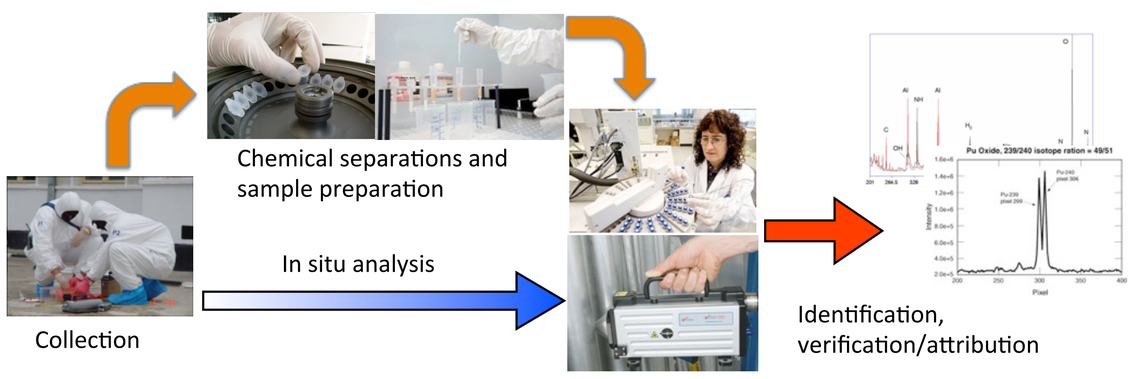
Of particular utility to the goal of reliably verifying that signatories are meeting their disarmament and nonproliferation obligations are technologies that make it possible to perform rapid measurements of elemental and isotopic composition of materials at a considerable standoff. Laser-induced breakdown spectroscopy can be augmented by concurrent spectroscopic measurements of both atomic and molecular emissions following the recombination of laser-ablated plasmas with the ablated sample and the surrounding environment. The use of relatively compact ultrafast, high intensity lasers also opens the possibility of standoff measurements by propagating the laser pulse over laser-induced plasma filaments produced in nonlinear interactions between the laser pulse and the atmosphere. We will experimentally investigate the feasibility of performing standoff isotopic composition measurements of relevance to treaty verification by use of filamentation LIBS.

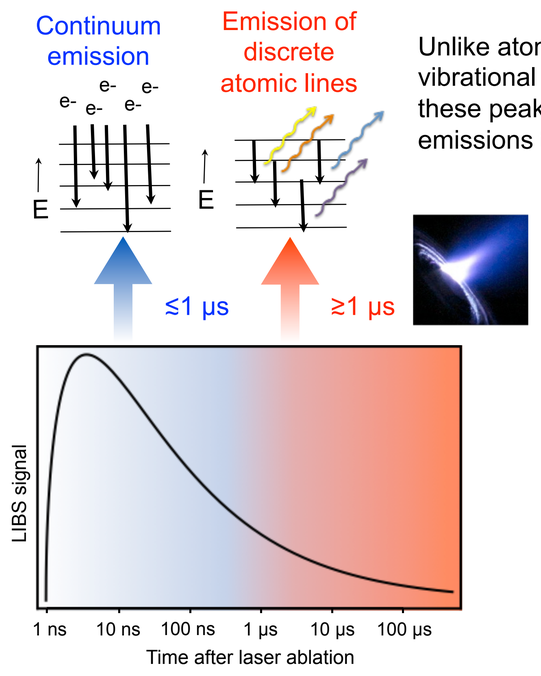
Material Verification: Sample Preparation vs *In Situ* Analysis

The goal of nuclear material verification is to obtain information about an interdicted or remotely interogated sample or material that can be used to verify that signatory states are meeting their disarmament and nonproliferation obligations.

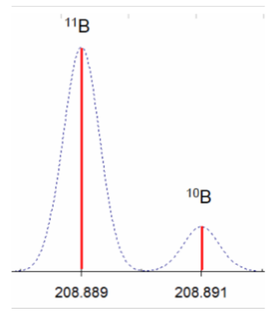


Sample preparation	*In situ* analysis
+ High sensitivity - Destructive - Time consuming - Generates toxic waste	+ Rapid + No sample preparation + Stand-off capabilities - Lower sensitivity

LIBS Emission and Isotopic Shift

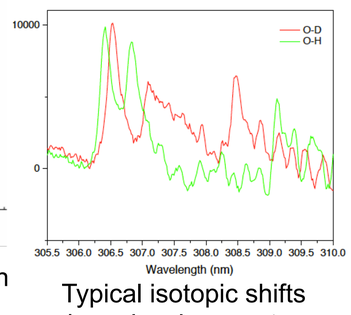


Unlike atoms, molecules emit in "bands" of peaks due to various vibrational and rotational energy changes, and the broadening of these peaks results in the observed bands. LIBS molecular emissions typically occur >2-5 μs following ablation.



Typical isotopic shift in atomic peaks (nm)

Russo, *et al.*, **S**pectrochim. Acta Part B 66 (2011) 99-104

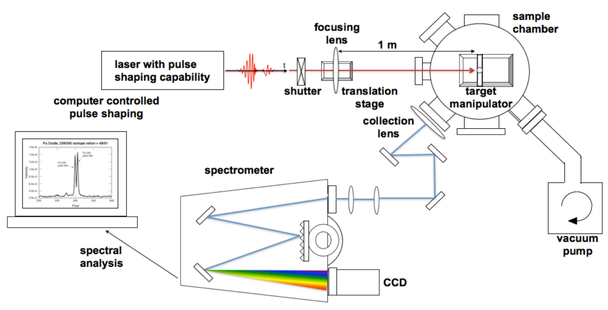


Typical isotopic shifts in molecular spectra

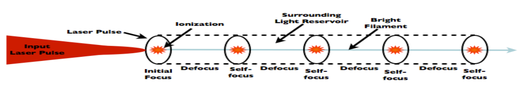
Russo, *et al.*, **S**pectrochim. Acta Part B 66 (2011) 99-104

Experimental Infrastructure for LIBS Measurements

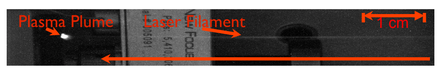
In order to study the response of materials to laser filaments and measure both the atomic and molecular emissions of the plasma the experimental setup below with an acousto-optic pulse shaper was used. The laser filament results from the balance of non-linear Kerr self-focusing and plasma defocusing.



Femtosecond laser and acousto-optic pulse shaper integration



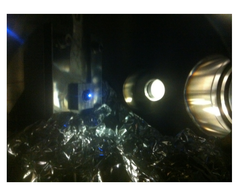
Schematic view of filament formation



Filament propagating into chamber and striking a graphite sample

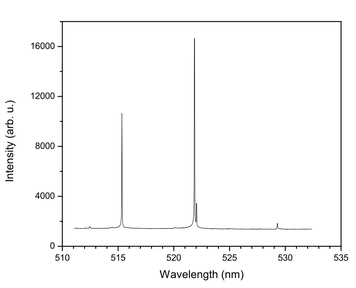
Experimental setup for LIBS utilizing ultrashort pulses and laser filaments

uranium sample mounted to holder

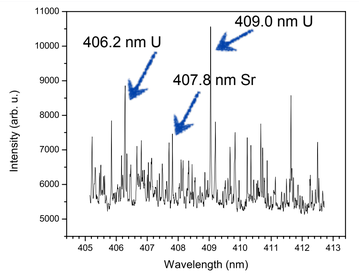


LIBS plasma on uranium in vacuum

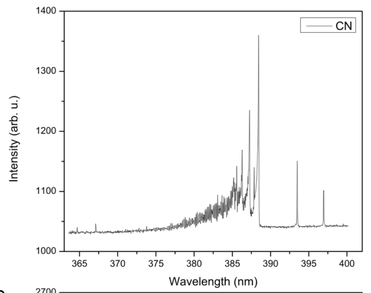
Measured LIBS Spectra

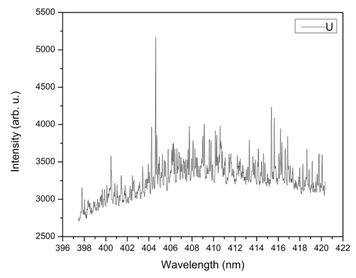


Copper spectrum averaged over 10 measurements for a 45 fs, 2mJ pulse. Intense 521.82 nm and 515.32 nm emission lines are present in the spectrum.

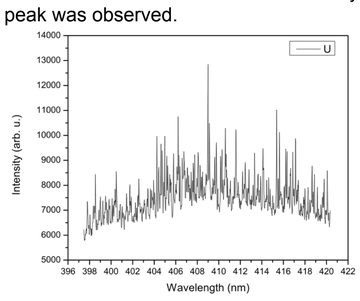


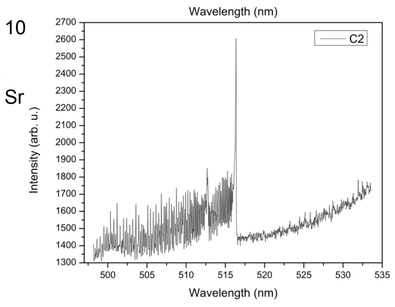
Natural uranium spectrum averaged over 10 measurements for a 45 fs, 2 mJ pulse. 409.01 nm and 406.25 nm emission lines are notable. An additional lower intensity Sr peak was observed.





Uranium emission signal from a 3.0 and 6.0 cm long filament.

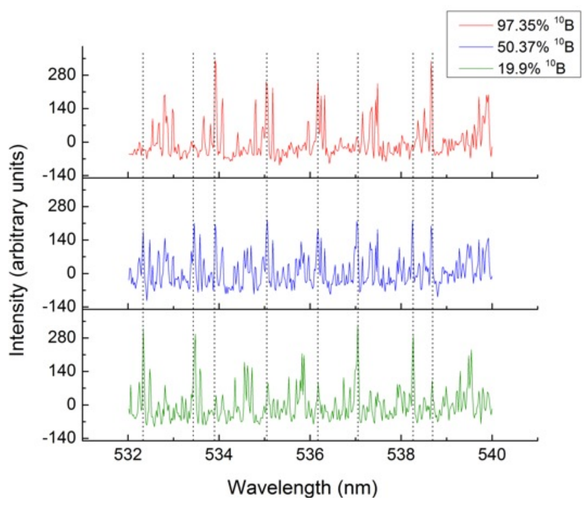




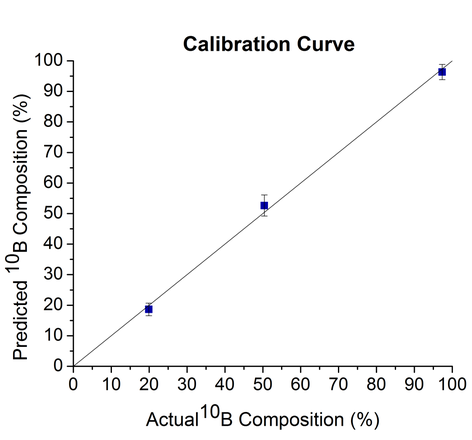
Samples ablated in a gas can undergo plasma-assisted chemical reactions to form exited molecular radicals, as shown above for graphite in air.

Isotopic Results Utilizing B_4C Samples

The spectra of three boron carbide samples were used to calibrate a multivariate model relating emissions to isotopic ratios. Predicted values for the three samples fell within 2% of actual values.



BO Emissions from B_4C samples, 532-540 nm.

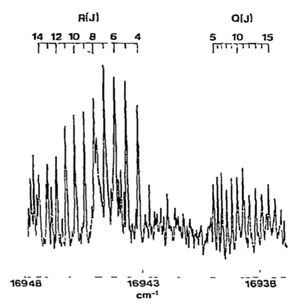


Multivariate regression results from using two known and one unknown sample enrichment.

Future Work

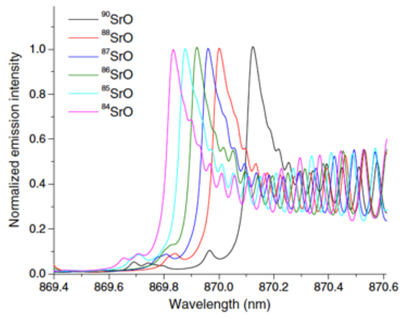
Since most elements form diatomic oxides when ablated in air, we expect that we can extend this method to other elements- specifically enriched uranium. Investigation and Modeling efforts in conjunction with our collaborators will be furthered to understand reported matrix effects from mixed samples.

The observed molecular vibrational and rotational LIBS spectra observed under atmospheric conditions can be used to measure the isotopics of a sample.



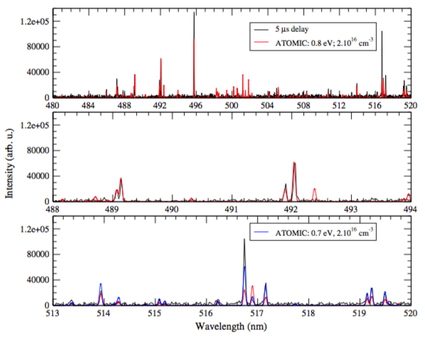
$U^{18}O$ molecular spectra in visible region centered at 595 nm. From Michael C. Heaven, *et al.* Chem. Phys. Lett. 1985.

LIBS spectra of strontium isotopes



R. Russo, *et al.*, Spectrochim. Acta Part B 66 (2011) 767-775

Iron oxide *ab initio* modeling and comparison to experimental ns-LIBS results.



Atomic structure, photoionization and electron cross sections, and plasma emission modeled utilizing LANL's ATOMIC codes.

K.C. Hartig's research was performed under the Nuclear Forensics Graduate Fellowship Program, which is sponsored by the U.S. Department of Homeland Security's Domestic Nuclear Detection Office and the U.S. Department of Defenses Defense Threat Reduction Agency. This project was also performed with support of the Nuclear Forensics Young Faculty Award Program sponsored by the U.S. Department of Homeland Security's Domestic Nuclear Detection Office.

National Nuclear Security Administration