Deconvolution of the Matrix Effect in Laser-Induced Breakdown Spectroscopy for Nuclear Forensics and Verification

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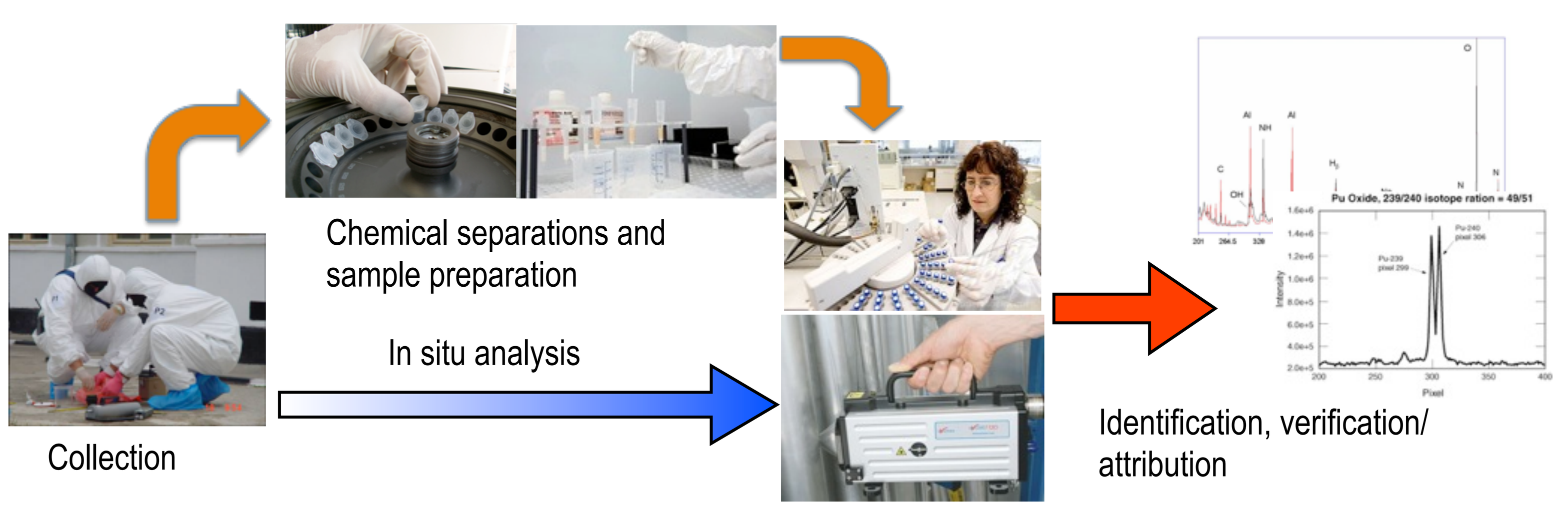
Of particular utility to the goal of reliably verifying that signatories are meeting their disarmament and nonproliferation obligations are technologies that make it possible to perform rapid measurements of elemental and isotopic composition of materials at a considerable standoff. Laser-induced breakdown spectroscopy (LIBS) can be used to perform rapid in-field elemental and isotopic measurements with little or no sample preparation. LIBS measurements have been shown to depend on not only the amount of analyte present but also on the specific makeup of the bulk matrix. We use both *ab initio* modeling and experimental diagnostics to elucidate the origins of the matrix effect observed in complex nuclear verification relevant materials. Future work involves spatially resolving the emission and quantifying the mass and energy diffusion rates of each element within the plasma.

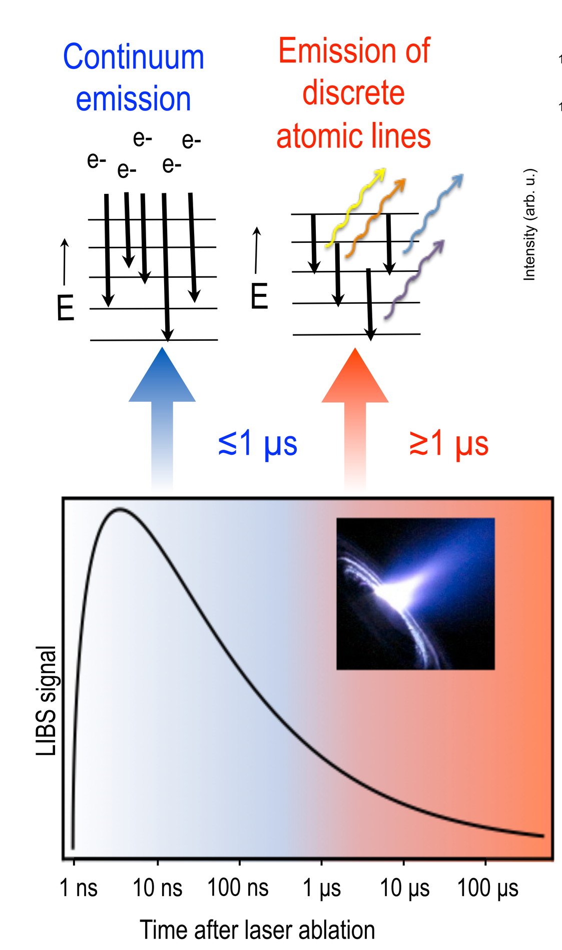
Material Verification: Sample Preparation vs *In Situ* Analysis

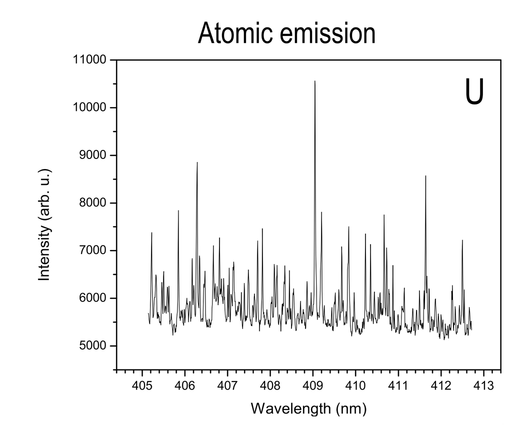
The goal of nuclear material verification is to obtain information about an interdicted or remotely interogated sample or material that can be used to verify that signatory states are meeting their disarmament and nonproliferation obligations.

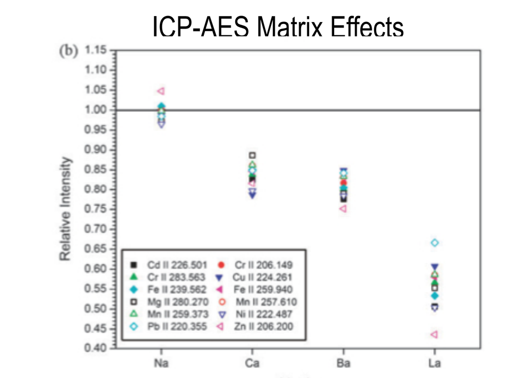


Sample preparation	*In situ* analysis
+ High sensitivity - Destructive - Time consuming - Generates toxic waste	+ Rapid + No sample preparation + Stand-off capabilities - Lower sensitivity

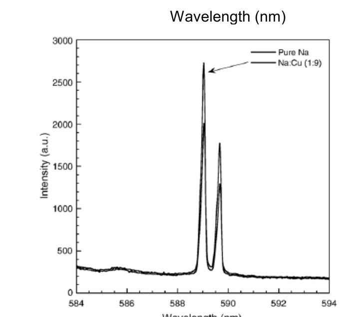
LIBS Emission and Matrix Effects



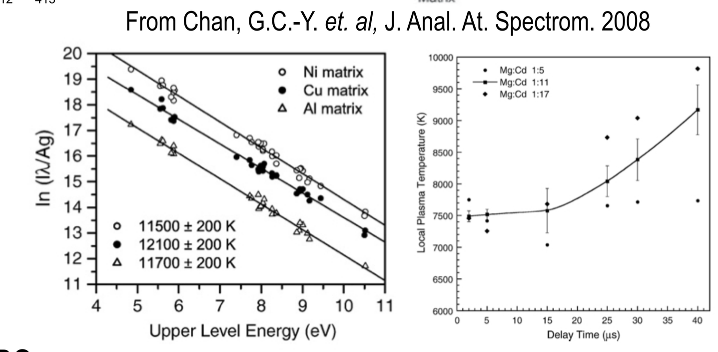




From Chan, G.C.-Y. *et. al*, J. Anal. At. Spectrom. 2008



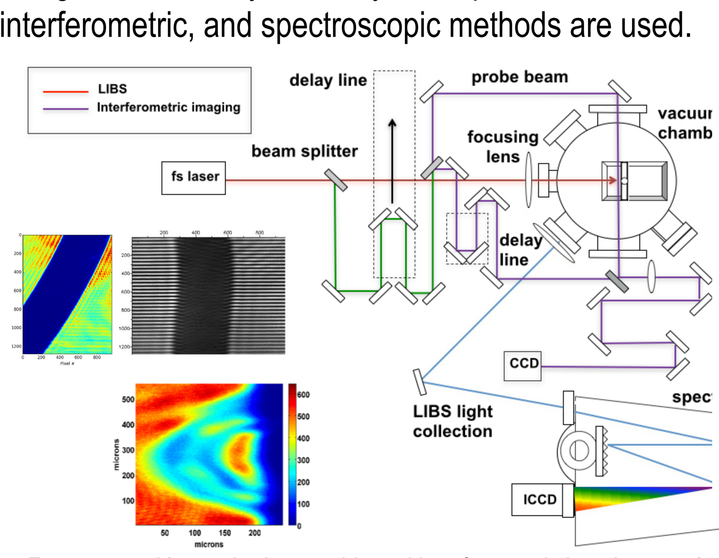
The intensity of Na LIBS emission increases in the presence of a bulk matrix element compared to a pure Na sample. From Diwakar *et. al.* 2010.



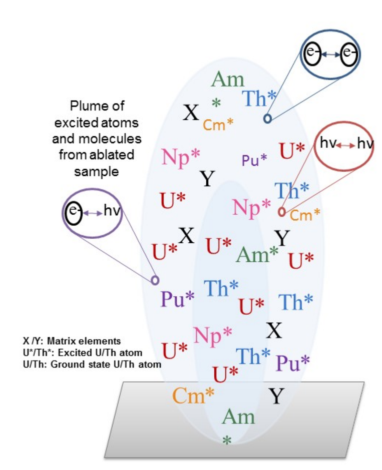
The properties (temperature, density, lifetime, etc.) of the laser induced plasma have been observed to depend on the bulk matrix element. From Aguilera *et. al.* 2009 and Diwaksar *et. al.* 2010.

Experimental Infrastructure for LIBS Measurement

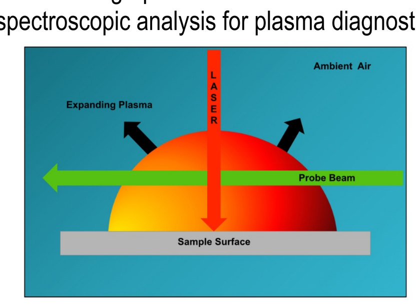
In order to elucidate the origin of the matrix effect for mixed samples and complex samples an experimental set-up is being built to study not only the optical emission but also the complex plasma dynamics. Ultrafast shadowgraphic, interferometric, and spectroscopic methods are used.



Femtosecond laser shadowgraphic and interferometric imaging coupled with spectroscopic analysis for plasma diagnostic



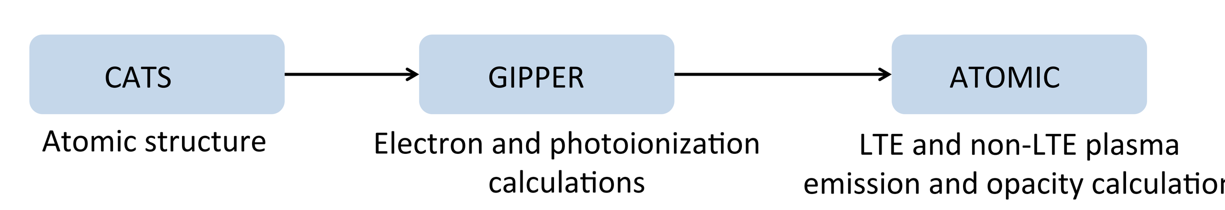
It is well understood that the resulting LIBS plasma exhibits a complex spatio-temporal evolution that leads to a number of plasma- and photo-dynamic interactions.



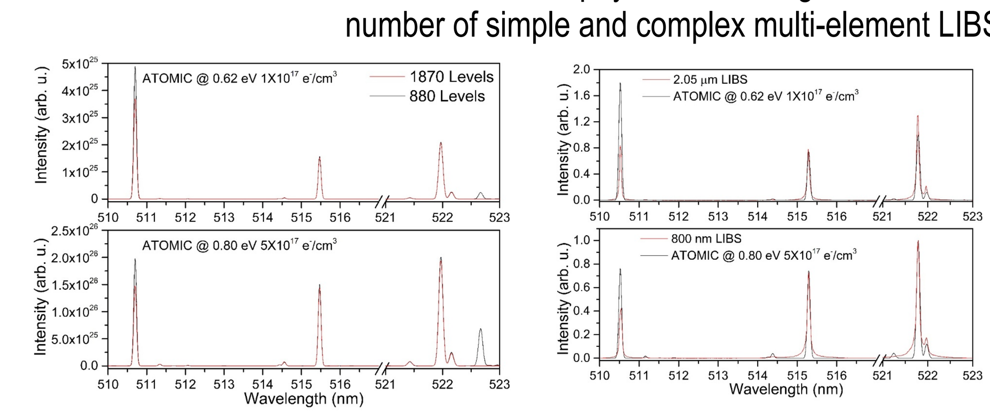
Experimental setup for LIBS utilizing ultrashort pulses

Ab initio Modeling

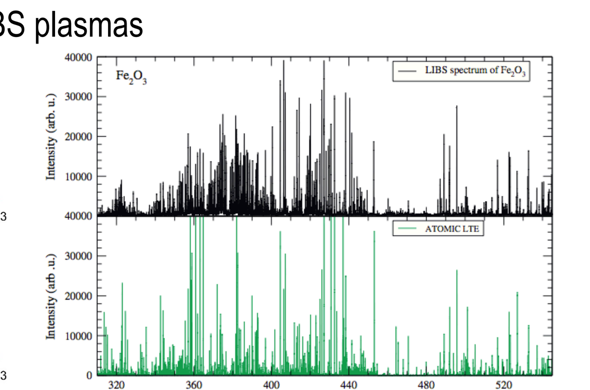
The LANL suite of atomic structure and plasma emission calculation codes based off of Cowan's atomic codes is used to model the complex plasma- and photo-dynamics of simple and complex samples with up to 16 different elemental constituents.



Ab initio atomic physics modeling has been used to model a number of simple and complex multi-element LIBS plasmas



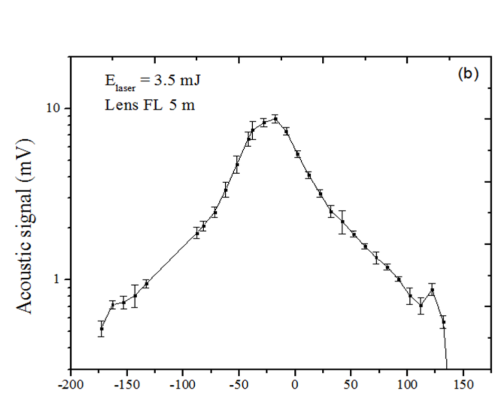
A strong configuration interaction and plasma temperature sensitivity for Cu LIBS emission lines of interest has been observed.



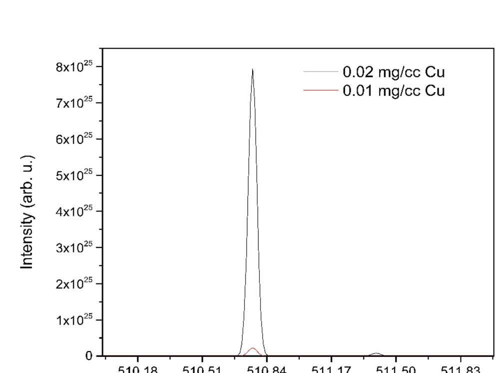
Ab initio modeling has been implemented and verified against complex samples like iron oxide.

Preliminary Results

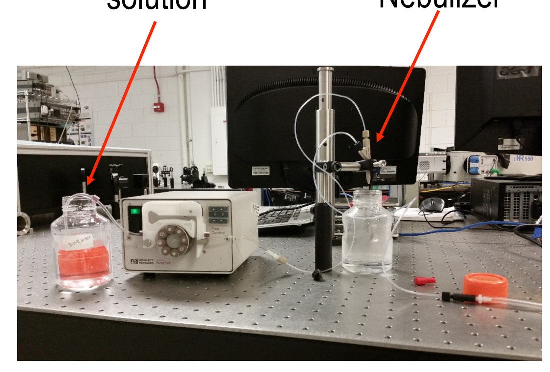
Ab *initio* modeling has been applied to simple samples with varying plasma properties following ablation by both ns and fs laser pulses and of different ablation wavelengths. We have studied the profile of filaments produced by focusing fs laser pulses in air through measurement of the acoustic signal generated by ionization of air within the filament. Through measurement of both the acoustic signal of the filament and the emission spectrum of the LIBS plasma a set of optimal laser parameters for filament formation can be found to enhance the remote sensing of material using R-FIBS.



With onset of filamentation marked by the measurement of an acoustic signal above the ambient noise level and the end of the filament marked by the acoustic signal dropping to the ambient noise, we obtain about 300 cm long filament



In the presence of an Ar ambient atmosphere the electron density and number density of Cu atoms is increased leading to an increased emission intensity.



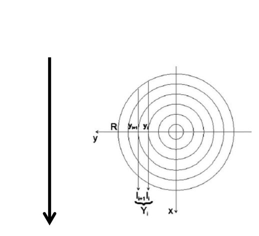
Nebulizer setup for use in generating aerosol particles of known elemental concentration from ICP-MS elemental standards.

Future work

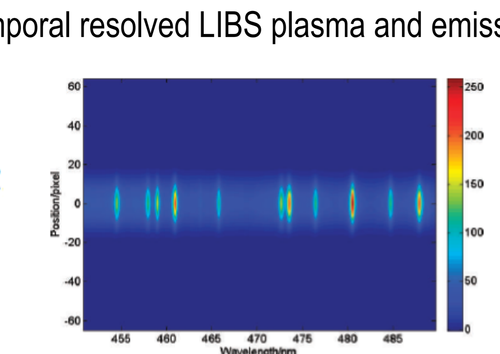
As there is a spatio-temporal dependence in both the LIBS plasma and the resulting optical emission, we will combine Abel inversion with traditional spectroscopic measurements to resolve the spatial emission of the plasma. This will allow for an improved understanding of where the LIBS emissions for each neutral and ion originates from. We have also begun work with our collaborators on spatio-temporal resolved LIBS plasma and emission models.

$$I(y) = 2\int_y^R \frac{\epsilon(r)rdr}{\sqrt{r^2-y^2}}; 0<r<R$$

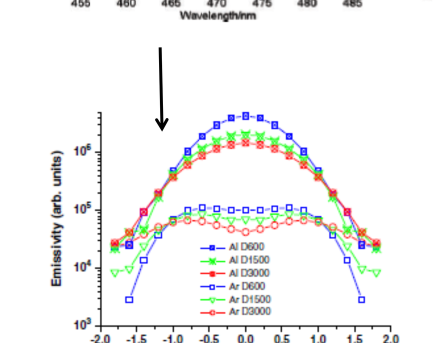
Abel inversion



$$\epsilon(r) = -\frac{1}{\pi}\int_r^R \frac{dI(y)}{dy}\frac{dy}{\sqrt{y^2-r^2}}$$



Ar LIBS emission spectrum imaged at a 1.3 magnification onto the ICCD, such that the y direction of the spectral image represents the y-axis of the plasma.



Ma *et. al. Sprectrochimica Acta B* 2010

Following Abel inversion of the measured spectral image a radial profile for each emission line can be found.

The rate and spatial distribution at which the energy and mass diffuse for each element within the plasma over its evolution is postulated to be responsible for the observed matrix effects and will be studied using this technique.

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National Nuclear Security Administration