Shaped Femtosecond Laser Pulse Spectroscopy for Nuclear Forensics

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy which utilizes the emissions produced by a laser-produced plasma. A pulsed laser is focused onto a sample with enough energy to ablate the material and generate plasma. Light from the plasma is collected by an optical system and transported to a spectrometer for spectral analysis, which can yield elemental and potentially isotopic composition. The non-destructive, expeditious in situ capability of LIBS can prove instrumental for identifying and attributing the composition of seized nuclear materials, post-detonation analysis, or safeguards verification. We are working on a novel approach to enhance the sensitivity of LIBS spectroscopy by employing optimally shaped femtosecond pulses produced using the Fourier pulse shaping technique. To the best of our knowledge, the use shaped pulses for fs-LIBS analysis is a novel technique and has potential for advancing nuclear forensics science and technology. Advancements in nuclear forensics techniques are needed to address the potential nuclear treats posed by nation states or rogue groups; rapid and accurate LIBS analysis has a potential to make a significant contribution to the effectiveness of deterrence against such threats.

Introduction

LIBS has been identified by the IAEA as a promising novel technique for detection and characterization of nuclear materials. One of the most attractive features of LIBS is the ability to perform rapid, direct sample analysis without the need for time-consuming chemical separations (frequently analysis can be completed in seconds). In LIBS, a pulsed laser beam is focused onto a sample surface. Sufficient laser energy is coupled into the material to ablate the surface and generate plasma. The light from the plasma is collected and resolved by the spectrometer. Based on data acquisition and analysis, the elemental compositions of chemical substances in the sample are identified using a spectral database of known materials [Lee 2004].

Since a single laser pulse both ablates and probes the sample, analysis can be done in situ and without the need for complicated sample preparation. LIBS is a well-established technique, with an application space that has grown over the past few decades. LIBS applications are in areas such as metallurgy, environmental sampling, trace analysis, and remote sensing. Much work has been done to improve the signal-to-noise background (SNB) and resolution by using time-resolved LIBS.
Limitations faced by using plasma emission for spectral analysis are high continuum background, spectral line broadening and self-absorption. The free electrons, excited atoms and ions of the highly energetic plasma emit a continuum of light in the early stages following sample ablation. The continuum emission before the emergence of discrete atomic lines is a source of noise that does not provide spectral information. Numerous studies done to address these limitations include introduction of delay times following sample ablation, and the use of time-resolved LIBS with a gated detection system. Time-resolved spectroscopy is required so that the delay and gate in time related to the laser pulse and plasma generation is optimized in order to maximize the line spectrum.

Studies of LIBS done under various atmospheric conditions (pressured, vacuum, gas compositions such as He, N₂, Ar, and CO₂) have generated interest in recent years. LIBS conducted in non-atmospheric conditions have been shown to affect signal resolution [Effenberger 2010]. Results from LIBS under vacuum show increases in signal to noise ratio and resolution. Spectral enhancement is likely due to prolonged lifetime of plasma emission in vacuum or decreased electron density contributing to background. In low pressures, LIBS helps decrease the effects of Stark broadening which is caused by electron-atom collisions, and Doppler broadening which depends on plasma temperature.

Determination of isotopic ratios have been achieved by LIBS for plutonium 239/240 with an isotopic shift of 0.00625 [Smith 2002] and uranium 238/235, which has an isotopic shift of 0.025 nm [Pietsch 1998]. Improving the sensitivity of isotopic determination will enhance LIBS for nuclear forensics analysis.

**Experimental Description**

The laboratory experiments will be performed using the LIBS setup shown in Fig. 1. The ultrafast laser used in our setup is a Ti:sapphire chirped-pulse amplification laser system (Amplitude Technologies Trident). Pulse shaping is performed using an acousto-optic programmable dispersive filter (Fastlite Dazzler) that is integrated in the laser system. The laser setup used in this experimental work is commercially available. The wavelength of the laser is 800 nm, and the system outputs 30-fs pulses with good beam quality and up to approximately 12 mJ per pulse, at a repetition rate of 10 Hz. The beam is focused onto the target using a 2”-diameter (f=250 mm) lens, and is normal to the target.

The light emitted from the plasma is focused onto the entrance slit of a 55-cm focal length imaging spectrometer (Horiba Jobin Yvon iHR550) equipped with a rotatable turret with three different gratings (1200, 1800, and 3600 groves per mm). Light measurement will be performed using an open-electrode charge-coupled device (Horiba Jobin Yvon Synapse CCD). Our spectrometer system allows up to 0.1 nm spectral resolution when used with 3600 g/mm grating.
Our vacuum target chamber is equipped with a three-axis translation stage and multiple viewports that allow plasma emission light to be collected at multiple angles. A gas feed-through is provided for LIBS experiments to be conducted with different ambient gases and under different ambient pressures.

The experimental approach is based on the hypothesis that the generated arbitrary pulse shapes will optimize laser-plasma interactions in atomic systems to improve the detection of the signal in spectroscopic analysis. Once our sample is ablated inside the target chamber, a collection lens will direct light from the plasma emission to the spectrometer. The sample’s spectroscopic signature will be measured and analyzed. A genetic algorithm will be implemented that will iteratively update our pulse shapes in order to optimize the dynamics of ionization and recombination processes in the plasma.

**LIBS System Modeling**

Considering the solid angle of the plasma source to the chamber port window based on the current setup of our diagnostic, approximately 2% of plasma emission light will be gathered by the collection lens before being transported into the spectrometer (Fig. 2). A laser operating with intensity on the order of $10^{13}$ W/cm$^2$ will ablate most sample materials. The mechanisms for laser-matter interaction and plasma generation depend on the type of material, and include processes such as excitation of conduction-band electrons, thermalization, and heating (metals), or multi-photon ionization and avalanche ionization (dielectrics).

Increasing the amount of light collected from the sample is likely to improve the detectability. Increasing the energy of the laser—and hence the amount of ablated material, increases plasma emission intensity and temperature. However, the energy of
the laser pulse on the sample cannot be increased indefinitely due to nonlinear effects of ultrashort pulses traveling through optics. Models of the optical transport of ultrashort pulses require the effects of dispersion to be taken into account.

![Diagram of optical transport model](image)

**Fig 2.** Model of optical transport of light based on LIBS diagnostic system where $w_{\text{in}}$ is the unfocused beam diameter, and $w_0$ is the focused spot size

The intensity, $I$, at the focal spot is measured in W/cm$^2$ and can be increased by tighter focusing. When the laser light is modeled as a Gaussian beam, the diameter of the beam at its focal spot is

$$w_0 = \frac{M^2 \lambda f}{w_{\text{in}}},$$  \hspace{1cm} (1)

where $M^2$ is a measure of beam quality, $\lambda$ is the wavelength, $f$ is the focal length, $w_{\text{in}}$ is the beam diameter, and $w_0$ is the focal spot diameter.

The intensity is limited by dispersive properties of media through which the pulse propagates, the focusing geometry, the incident beam quality, and the nonlinear effects in focusing optics. One way to assess the effect of nonlinear effects is by calculating the $B$-integral ($B$). Typically, $B$ is desired to be less than 1 to prevent the degradation of beam quality and poor focusing of the laser beam on the sample. $B$ is calculated from

$$B = \frac{2\pi}{\lambda} n_z \int I(z)dz,$$  \hspace{1cm} (2)

where $n_z$ is the nonlinear refractive index ($\sim 2.4 \times 10^{-16}$ cm$^2$/W in glass) and $z$ is the thickness of material that the laser beam passes through in the direction of beam propagation. Based on a numerical model for the LIBS signal output developed to characterize and account for dispersion and nonlinear effects, the focal spot size can be increased by a factor of 4 in our setup before reaching the limits of detrimental nonlinear effects (Fig. 3).
Fig. 3. Operation range of laser beam based on $B$ integral limitation calculations

**Pulse Shaping for Enhancement of LIBS Performance**

An important aspect of our innovative approach is the use of pulse shaping for optimizing the characteristics of plasma emission, thereby improving the detectability and sensitivity of the technique. This is accomplished using a commercial pulse shaper that allows laser pulse waveforms to be defined by computer control. Controlling the temporal shape of ultrafast laser pulses that interact with matter can be used to optimize the magnitude of LIBS signal and signal-to-noise ratios, as suggested by previous studies [Rohwetter 2003]. The experimental approach is based on the hypothesis that the generated arbitrary pulse shapes will optimize laser-plasma interactions in atomic systems to improve the detection of the signal. An adaptive learning algorithm will also be implemented for improving expediency of the pulse optimization process. The future objective is to employ an adaptive learning algorithm based on feedback from data acquisition to automate the process of laser pulse shape optimization.

**References**


