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Double-pulse standoff laser-induced breakdown spectroscopy for versatile hazardous materials detection ☆

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Abstract

We have developed a double-pulse standoff laser-induced breakdown spectroscopy (ST-LIBS) system capable of detecting a variety of hazardous materials at tens of meters. The use of a double-pulse laser improves the sensitivity and selectivity of ST-LIBS, especially for the detection of energetic materials. In addition to various metallic and plastic materials, the system has been used to detect bulk explosives RDX and Composition-B, explosive residues, biological species such as the anthrax surrogate *Bacillus subtilis*, and chemical warfare simulants at 20 m. We have also demonstrated the discrimination of explosive residues from various interferents on an aluminum substrate.
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Keywords: LIBS; Double pulse; Standoff detection; Energetic material

1. Introduction

The standoff detection of hazardous materials such as explosives and chemical/biological warfare agents is an important problem for both the military and civilian first responders. Laser-induced breakdown spectroscopy (LIBS) is a spectroscopic analysis technique that uses the light emitted from a laser-induced microplasma to determine the composition of the sample based on elemental and molecular emission intensities. The facility of LIBS for real-time, sensitive remote detection of a wide variety of materials makes LIBS an ideal candidate for hazardous materials detection. LIBS has been successfully demonstrated for chemical [1,2], biological [3–13], and explosive [14–16] materials detection in laboratory close-contact (<1 m) conditions. In December 2004, a group led by the U.S. Army Research Laboratory (ARL) successfully tested standoff LIBS technology using a single-pulse laser source for the detection of residue amounts of explosives on a vehicle at a distance of 30 m at Yuma Proving Ground (YPG) [17]. Subsequent to the successful YPG standoff tests, a standoff sensor based on LIBS (ST-LIBS) has been developed by ARL in collaboration with Applied Photonics, Ltd. and Ocean Optics, Inc. Significant improvements to the system tested at YPG have been made, including the incorporation of a double-pulse laser and full broadband (UV–VIS–NIR) detection.

Double-pulse LIBS uses two successive laser pulses separated by microseconds to improve the sensitivity and selectivity of LIBS, as previously demonstrated by a number of groups ([18], *see ref. therein*). Several recent reviews provide excellent overviews of the success of the double-pulse approach and possible mechanisms for the observed signal enhancements [18–20]. Double-pulse LIBS increases the ablation rate, plasma volume, temperature, and ion density, leading to the enhancement of emission lines. The enhancement is most likely the result of the reduced density environment after the first pulse and the subsequent increase in the plasma volume after the second laser pulse [21–25]. In the context of standoff LIBS, the increase in sensitivity due to double pulsing also results in a longer effective standoff detection range.

As demonstrated in this issue [15], double-pulse LIBS is extremely important for the detection of energetic materials.

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Fig. 1. Photograph of the double-pulse ST-LIBS system developed by ARL in collaboration with Applied Photonics, Ltd. and Ocean Optics, Inc.

Since the identification of explosives depends on determining the relative abundance of nitrogen and oxygen in energetic materials compared to non-energetic materials, the ability of double-pulse LIBS to reduce the amount of air entrained in the plasma event is essential. In this paper we demonstrate the utility of double-pulse ST-LIBS for the detection and discrimination of energetic materials (in bulk and residue amounts), biological agent surrogates, and chemical warfare agent simulants at 20 m.

2. Experiment

2.1. ST-LIBS system

The ST-LIBS system (Fig. 1) incorporates a Quantel Brilliant Twins laser (1064 nm, 10 Hz, 335 mJ/pulse, 5 ns pulse width) and a commercially available 14 in. Schmidt-Cassegrain telescope by Meade (LX200GPS) fitted with UV-coated optics to enable full broadband spectral coverage (UV–VIS–NIR). The combined double-laser pulse is directed along the axis of the telescope by an articulating arm, facilitating a full range of motion on the telescope for ease in targeting the sample. A diode laser (632 nm) coincident with the IR laser illuminates the target spot. The infrared double-pulse beam is expanded with a simple two-lens system and is focused down range by a 3 in. positive lens (f=475 mm). Plasma light collected by the telescope is focused into a fiber optic and sent to a three-channel gated CCD spectrometer (190–840 nm) developed by Ocean Optics, Inc. The Ocean Optics software is used to fire the lasers (single shot) and collect the spectral data. A digital camera and wireless range finder enable remote viewing and measurement of the distance to the target. The entire system is mounted on a wheeled cart and is easily transportable.

Spectra of the materials described in the following section were acquired using the ST-LIBS system at 20 m. The optimal timing of the laser pulses and spectrometer depends primarily on the laser pulse energy and the substrate material. For this experiment the laser pulse energy used was 275 mJ/pulse and the substrate material for the residue samples was aluminum foil. Under these conditions, we have determined the optimal timing for this system as having delay time t_{delay}=2 μs, integration time gate t_{int}=100 μs, and interpulse separation Δt=3 μs.

2.2. Materials

Seven metallic targets (silver, aluminum, gold, chromium, copper, indium and lead) were used to demonstrate the sensitivity of the ST-LIBS system in the UV–VIS–NIR region. The anthrax surrogate *Bacillus subtilis* var. *niger* (commonly known as *Bacillus globigii*, or BG) and mold sample *Alternia alternata* were provided by Battelle. The BG and mold powders were applied directly to double-sided sticky tape, which did not contribute to the LIBS spectra. Explosive samples of RDX (in powder and pellet form) and Composition-B (36% TNT, 63%

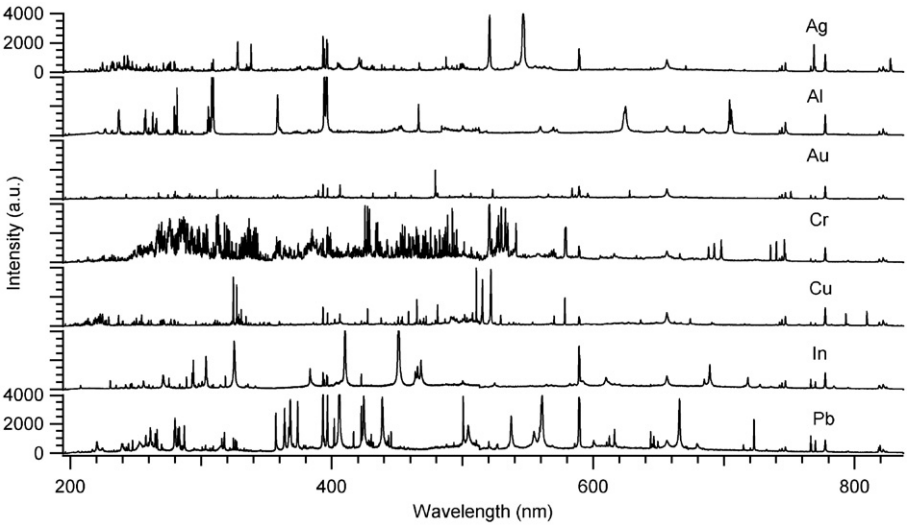

Fig. 2. Single shot spectra of various metals acquired at 20 m using the ST-LIBS double-pulse system (~275 mJ/pulse).