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Tailored Ultrafast Pulses for Selective Energetic Residue Sampling

by Frank De Lucia, Jr., and Jennifer Gottfried

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14. ABSTRACT

Femtosecond pulses offer several advantages over more conventional nanosecond pulses for laser-induced breakdown spectroscopy applications. These advantages include improved ablation, lower breakdown threshold, more efficient energy deposition, and less thermal damage to surrounding areas. The scope of this work is to determine if femtosecond laser-induced breakdown spectroscopy offers advantages for detecting trace explosive residues. Also, additional laser pulses, focused and nonfocused, were used to enhance the emission signal. It was determined that the lower breakdown threshold was the most important characteristic of the femtosecond pulse for explosive residue detection. Enhancement of the plasma becomes more critical if lower-energy pulses are used since emission intensity is sacrificed.

15. SUBJECT TERMS

LIBS, double pulse, femtosecond, explosives detection, plasma

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1. Objective

The authors have investigated the use of ultrafast laser pulses for explosive residue detection. The initial setup and collection of data with the U.S. Army Research Laboratory (ARL) femtosecond (fs) system represents some of the first explosive and explosive residue laser-induced breakdown spectroscopy (LIBS) spectra collected using ultrafast laser pulses. A comparison with conventional nanosecond (ns) LIBS was performed in order to determine any fs LIBS advantages for residue detection. In addition, two methods for enhancing the LIBS emission were investigated using additional laser configurations.

2. Approach

LIBS is an atomic emission spectroscopy technique used for real time minimally destructive material determination. Conventional LIBS is performed with a Nd:YAG ns laser pulse that is focused onto a sample creating a microplasma. At ARL, LIBS was used to study explosive residues (*1*). One consequence of interrogating explosive residues with a ns laser pulse is the inclusion of substrate material in the laser-induced plasma. Instead of using ns laser pulses, fs laser pulses were substituted to see if the amount of substrate entrained in the plasma could be reduced. Plasmas formed from an ultrafast laser pulse, ~100 fs, are generated by a different mechanism than plasmas formed from longer laser pulses (*2*); fs laser pulses deposit energy into the sample surface more efficiently (*3, 4*). The use of laser pulses from the fourth harmonic of the Nd:YAG (266 nm) was also studied. Organic material absorbs ultraviolet (UV) radiation more efficiently than 1064 nm radiation (*5*). Thus more of the UV laser energy may be deposited into the organic residue instead of the substrate, decreasing the amount of substrate interference.

The authors set up an fs LIBS system as shown in figure 1. Briefly, a Ti:Sapphire (Ti:S) oscillator (Coherent, Vitesse) generates an fs pulse that is used to seed the Ti:S amplifier (Coherent, Hidra-25). An Nd:YLF pump laser (Coherent, Evolution-15) is used to amplify the output energy of the fs laser pulse. The output of the Ti:S amplifier is a train of 1 mJ, 120-fs pulses at a 1-kHz rep rate. An additional Nd:YAG laser (Continuum, Powerlite Precision II 8000) can be used to amplify the fs pulse energy even further. The output from the Ti:S amplifier using an additional Nd:YAG laser is a train of 25 mJ, 120-fs pulses at a 10-Hz rep rate. Typically, fs LIBS spectra were collected using a single 1- or 10-mJ fs pulse. The fs laser pulses passed through a convex-focusing lens (100-mm focal length) in order to generate a plasma. A parabolic mirror collects the plasma emission and focuses the light onto a 600-µm fiber optic.

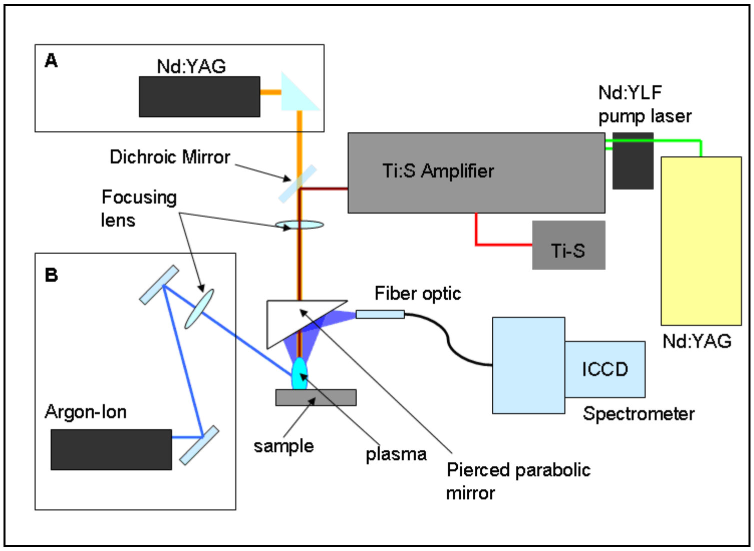

Figure 1. ARL fs LIBS experimental setup: (a) additional Nd:YAG for double-pulse LIBS fs/ns setup and (b) argon-ion laser for resonant enhancement LIBS setup.

The light is delivered into an echelle spectrometer (Catalina Scientific, SE200) or a Czerny-Turner spectrometer (Andor, SR-163 Series) through a 25-µm pinhole or a 50-µm slit, respectively. An intensified charge-coupled device (ICCD) (Apogee Alta or Andor iStar) was used to record the LIBS spectra. The spectra collected from the Czerny-Turner spectrometer were collected with a 5-µs gate and covered the wavelength range from 230 to 410 nm. The spectra collected from the echelle spectrometer covered the wavelength range from 200 to 850 nm.

Femtosecond LIBS spectra were collected from bulk explosives RDX, C-4, and Composition-B, as well as a residue of RDX on a metal (aluminum) substrate. The residue was prepared by one of two methods. A small amount of RDX was dissolved into acetone (~1 mg/ml) and then deposited onto the metal substrate in microliter quantities. The second method involved depositing a small amount of RDX (~1 mg) onto the metal substrate directly. The RDX was then crushed and rubbed onto the surface. Excess RDX was knocked off the substrate so only residue that adhered to the metal substrate was left behind.

The authors also investigated two methods for enhancing the LIBS signal obtained from a plasma created by an fs pulse. For the first method, a focused ns laser pulse was added to the plasma generated by the fs laser pulse. Double-pulse LIBS, i.e., adding two collinear pulses separated by hundreds of nanoseconds, has been shown to increase signals (*6*). The reasons for the enhancement are not entirely understood but are thought to be a combination of several factors, including a decrease of atmospheric gas density in the plasma (*7*). An Nd:YAG laser (Big Sky, CFR200) was integrated with the fs laser system to study double-pulse LIBS. As seen in figure 1a, the Nd:YAG laser pulse passes through a dichroic mirror so it is collinear with the fs laser pulse. Several experiments were performed on materials such as aluminum, plastic, bulk

RDX, painted car panels, and RDX residue on an aluminum substrate. These fs-ns double-pulse spectra were compared to conventional ns-ns double-pulse spectra taken with similar energies, 10 mJ for the first pulse and 100 mJ for the second pulse unless otherwise noted.

For the second method, the continuous wave 50-mW argon-ion laser (Jarrell Ash) output was added to a LIBS plasma that was generated on a sample bathed in argon as shown in figure 1b. In theory, the enhancement will occur due to the interaction of the argon-ion laser lines with the argon bath gas inside the plasma. The absorption of the argon-ion laser energy will reheat the plasma, extending its lifetime, thus increasing the amount of light emission. Argon gas was blown across the surface of the aluminum substrate, and the argon-ion laser was aimed onto the spot where the plasma would be formed.

3. Results

Using the ARL fs LIBS system, the authors collected fs LIBS spectra of a variety of explosive materials, both in bulk and residue form. Each spectrum from an explosive, either bulk or residue, contains the expected key elemental lines carbon, hydrogen, oxygen, nitrogen, and the molecular fragment CN. Aluminum elemental emission lines are also present in the residue due to the substrate. The focus is on using fs LIBS for explosive residue detection. To that end, LIBS spectra of RDX residue (70 $\mu g/cm^2$) were collected on an aluminum substrate. We used 10-mJ and 95-mJ ns pulses at 1064 nm, 10-mJ ns pulses at 266 nm, and 10-mJ fs pulses at 800 nm to interrogate the residue. The echelle spectrometer was used to collect broadband spectra. The ICCD integration gate time was 1 µs for each spectrum collected. Each spectrum displayed in figure 2 is an average of 20 single shot spectra. The LIBS spectrum of RDX residue collected from the 10-mJ fs laser pulse is compared to the spectra obtained by using the 10-mJ UV and infrared (IR) laser pulse in figure 2. The carbon and hydrogen atomic emission line intensities are greater for the fs LIBS spectrum compared to the 10-mJ IR and UV spectra. There does not appear to be much difference between using UV and IR laser radiation when comparing the two wavelengths. The carbon-to-aluminum atomic emission line ratio is larger, 0.29 ± 0.08 for the fs LIBS spectra vs. 0.10 ± 0.07 for the IR spectra, indicating less aluminum substrate is sampled relative to RDX residue. By using the Boltzmann equation, the plasma temperature can be calculated for each individual spectrum (*1*). The temperatures calculated from the plasmas generated by the fs laser pulses are higher than those generated by the IR ns pulses (8500 ± 660 K vs. 5800 ± 700 K). The line widths of the atomic emission lines are broader in the plasmas generated by the fs pulses, indicating a higher electron density. Also, several ionized aluminum (Al II) atomic emission lines appear in the fs spectrum. These features indicate an increased emission will occur in an fs LIBS spectrum when compared to an ns LIBS spectrum generated from similar laser pulse energies.

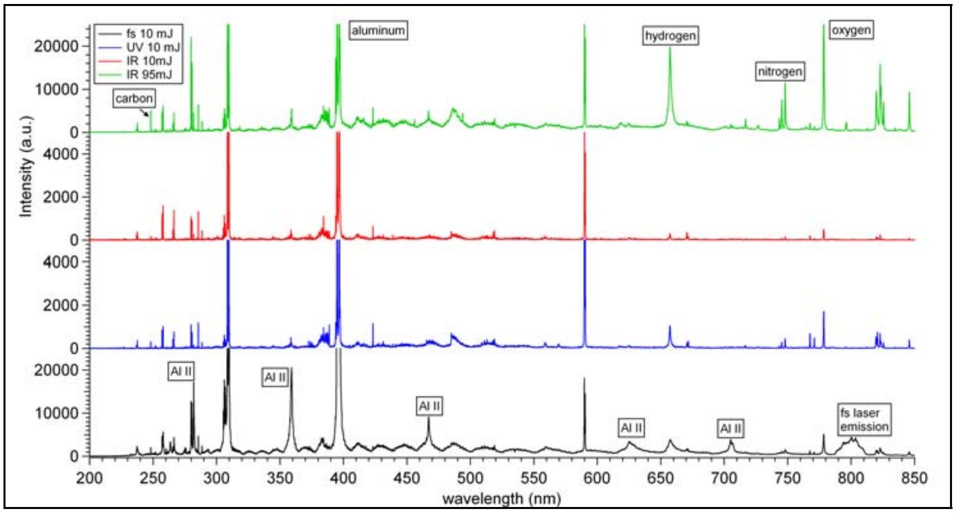

Figure 2. Broadband LIBS spectra of RDX residue on aluminum obtained from plasmas generated by fs laser pulses at 10 mJ and UV and IR ns laser pulses at 10 mJ and 95 mJ. Note the y-axis scale is larger for the 10-mJ fs spectrum and the 95-mJ ns spectrum.

Next, the authors attempted to increase the emission signal from the LIBS plasma by adding an additional laser pulse to the plasma a few hundred ns after the initial plasma is formed from the fs pulse. Overall, there does not appear to be significant enhancement with the fs/ns double-pulse configuration compared to higher-energy (>50 mJ) ns single-pulse or ns/ns double-pulse LIBS. In figure 3, LIBS spectra generated by two laser pulses separated by 500 ns are displayed. The top spectra was collected using a 10-mJ fs pulse followed by a 100-mJ ns pulse. The bottom spectra was collected from a plasma generated by a 10-mJ ns pulse followed by a 100-mJ ns pulse. The insets are expanded regions of the broadband spectra focusing on the carbon and aluminum atomic emission lines. There are several differences between the two spectra. The atomic emission line widths are broader in the fs/ns double-pulse spectrum, indicating a higher electron density. Another indication of higher electron density is the increase in intensity of Al II lines at 281 and 358 nm. A larger carbon atomic line intensity is seen in the fs/ns double-pulse spectrum. One could also argue that the double pulse increases substrate emission as seen in figure 3. The initial fs pulse ablates better than the initial ns pulse. However, the other pertinent lines H, O, and N do not appear to be enhanced significantly. LIBS spectra were collected from several materials using the fs/ns double-pulse method at various times between pulses. There did not appear to be a significant increase in elemental emission intensities from the explosive residue. The second ns pulse energy was probably too high (~100 mJ). The second ns pulse creates a larger plasma that overwhelms the lower-energy (10 mJ) fs pulse. In addition, the larger plasma will leave a larger imprint in the substrate because the plasma from the fs pulse is too small to shield the second pulse from interacting with the substrate.

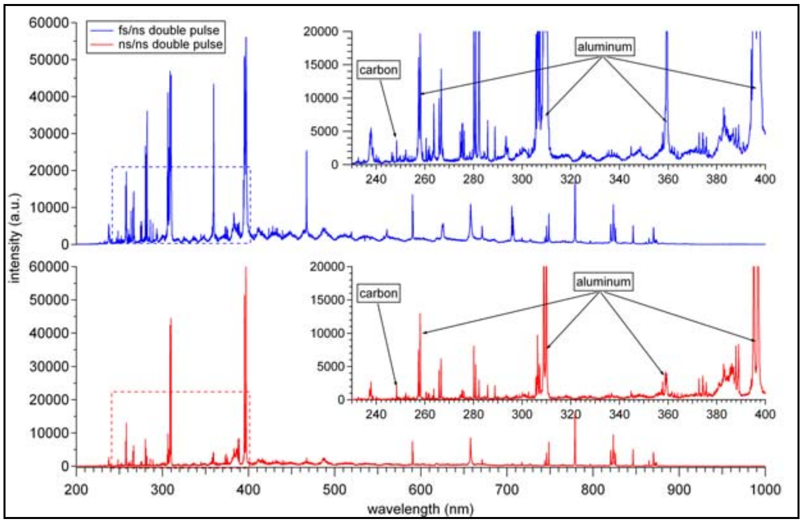

Figure 3. Double-pulse LIBS of RDX residue on aluminum using fs/ns pulses and ns/ns pulses. Insets: expanded regions of broadband LIBS spectra highlighting carbon and aluminum atomic emission lines.

Another method to enhance the LIBS plasma is to use an unfocused laser that will reheat the plasma. This method is called resonance-enhanced LIBS when the wavelength is specifically chosen to excite a species in the plasma, typically the substrate (*8, 9*). In this case, an argon bath gas was used on the sample surface. The plasma is formed in the argon atmosphere. A continuous wave (CW) argon-ion laser is directed toward the plasma. The wavelengths of the argon-ion laser are shown in figure 4. The laser energy will be absorbed by argon within the plasma, enhancing all of the elements in the plasma by collisional energy transfer, thus extending the plasma lifetime. Figure 4 shows aluminum atomic emission lines from a sample collected in an argon bath gas with and without the added argon-ion laser. A slight enhancement can be seen, but it is minimal.

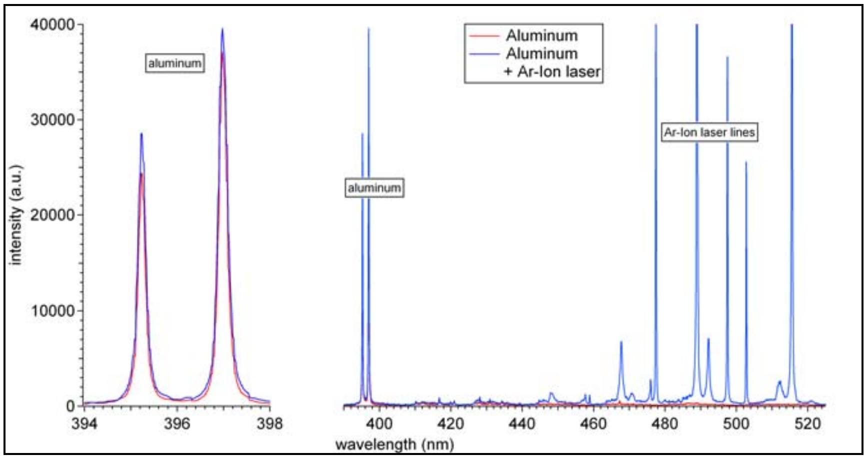

Figure 4. LIBS spectra of aluminum in argon bath gas collected with and without the addition of argon-ion laser radiation. Expanded region (left) shows aluminum enhancement due to resonance enhancement.

4. Conclusions

Fs LIBS potentially provides several advantages, such as improved ablation, better signal-to-noise (with smaller pulse) energy, less damage to the sample, and less interrogation of the surrounding material (substrate or atmospheric gas). While fs pulses showed improved performance compared to ns pulses, the two enhancement methods demonstrated only minimal success. Before fs pulses become a viable replacement to ns pulses, several other characteristics of the fs pulse need to be taken into account. While the fs pulse provides several advantages, there are also disadvantages. One disadvantage is that the plasma generated by an fs pulse is much shorter-lived than a plasma created by an ns pulse. Less emission time means less light for the spectrometer to collect, thus a reduced signal-to-noise ratio (SNR). In addition, while a 10-mJ fs pulse generates a usable spectrum, a 30-mJ ns pulse generates a superior spectrum. In figure 5, RDX residue LIBS spectra collected from a Czerny-Turner spectrometer/ICCD are displayed. The LIBS spectrum of RDX collected from a 30-mJ ns pulse compared to the LIBS spectrum collected from a 10-mJ fs pulse is better. This is demonstrated by the increase in carbon atomic emission line SNR. Current technology required to generate a 10-mJ fs pulse is far more costly than a Nd:YAG laser capable of delivering 30 mJ. The imprint left by the 10-mJ fs pulse is an improvement over a 30-mJ ns pulse, but that improvement must be weighed against the reduced SNR.

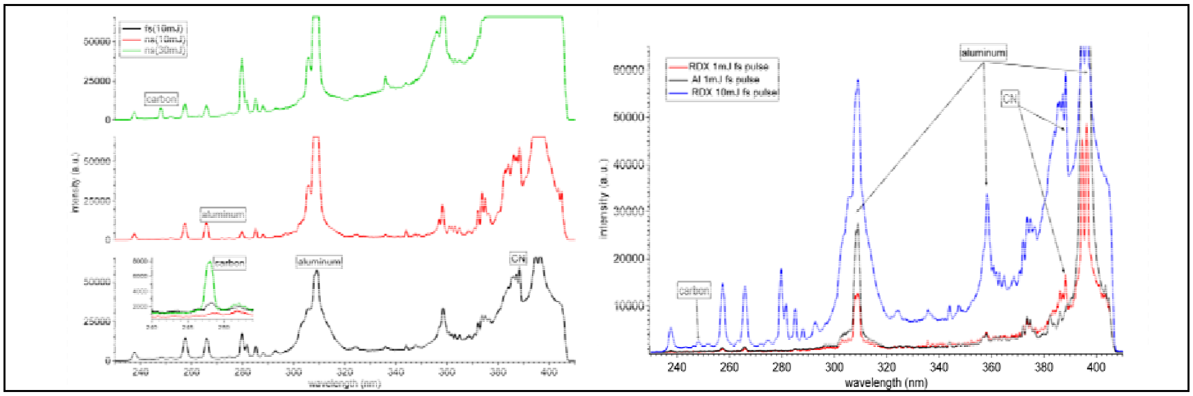

Figure 5. LIBS spectra collected using a high-light throughput spectrometer. Both fs and ns LIBS spectra of RDX residue were collected. Left: comparison of 10-mJ fs LIBS spectrum with 10-mJ and 30-mJ ns LIBS spectra. Right: comparison of a 1-mJ fs LIBS spectra of RDX on aluminum, a 1-mJ fs LIBS spectrum of clean aluminum, and a 10-mJ fs LIBS spectrum of RDX residue on aluminum.

One area explored was the use of low-energy fs pulses (<1 mJ) with a higher light throughput spectrometer (Czerny-Turner)/ICCD. At lower laser pulse energies, a ns pulse will not form a plasma with the current focusing optics. There is simply not enough energy density for a LIBS plasma to form. However, spectra can be obtained from a plasma generated by a 1-mJ fs pulse. The low-energy pulse interrogates the residue and leaves a small imprint. In figure 5, the spectrum from a 1-mJ fs pulse is shown. There is a CN peak at 388 nm indicative of RDX residue. There is no carbon signal at that low energy, but the amount of aluminum in the spectra is much smaller than in the spectrum collected from a 10-mJ fs pulse. A spectrum collected from a 1-mJ aluminum blank is also provided. The amount of aluminum emission is much larger without the residue on it. The imprint from the 1-mJ fs pulse is not observable with the eye.

Future studies would involve enhancing the 1-mJ fs pulse. The first step is to use a second ns pulse at much lower energies than used in this study. A lower-energy ns pulse will not overwhelm the fs plasma and create a large imprint. The second study would involve using a tunable nonfocused ns pulse laser. The initial resonant enhancement experiment relied on a CW 50-mW laser. A pulsed laser will provide more peak power to reheat the plasma. New equipment recently installed will allow the laser wavelength to be tuned from 200 to 1700 nm in order to enhance different elements within the plasma with a higher-energy pulsed laser. For example, the laser could be turned to 247 nm to interact with the carbon that is atomized within the plasma. Since the laser energy is not focused, it will not leave an imprint on the substrate.

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