

Nd:YAG-CO₂ double-pulse laser induced breakdown spectroscopy of organic films

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Abstract: Laser-induced breakdown spectroscopy (LIBS) using double-pulse irradiation with Nd:YAG and CO₂ lasers was applied to the analysis of a polystyrene film on a silicon substrate. An enhanced emission signal, compared to single-pulse LIBS using a Nd:YAG laser, was observed from atomic carbon, as well as enhanced molecular emission from C₂ and CN. This double-pulse technique was further applied to 2,4,6-trinitrotoluene residues, and enhanced LIBS signals for both atomic carbon and molecular CN emission were observed; however, no molecular C₂ emission was detected.

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1. Introduction

An interest in detection of hazardous materials, such as chemical, biological, or explosive compounds, has become increasingly widespread over the last decade [1–8]. Remote sensing by laser spectroscopy, such as laser-induced breakdown spectroscopy (LIBS), is one solution to the detection of potentially hazardous materials. LIBS is an optical analytical technique that works on practically any material and is appealing for its potential as a stand-off detection technique that requires minimal sample preparation [9–11]. LIBS suffers from plasma irreproducibility that is caused by laser instabilities, ablation irreproducibility and sample non-homogeneity, all resulting in a relative standard deviation (RSD) on the order of 5–10% [12, 13]. A double-pulse approach, first reported in 1969 [14], has been investigated by many groups [13, 15–24] as a method of improving the sensitivity and selectivity of the LIBS

technique, as well as providing better reproducibility [25]. Double-pulse LIBS using both collinear [17, 18, 21–24] and orthogonal [15, 16, 26] irradiation of either single [15–18, 21] or multiple wavelength [18, 22–24] laser pulses has been demonstrated.

Recently, LIBS emission enhancements with a factor of 25–300 (depending on the emitting species) have been reported using a multi-wavelength (1.064 $\mu\text{m}/10.6 \mu\text{m}$) approach on an alumina ceramic sample [22]. In this scheme, a second laser pulse in the mid-infrared region is likely absorbed by inverse Bremsstrahlung processes and heats the existing plasma, leading to an enhanced emission of its constituents. A potential advantage to using a second pulse at 10.6 μm (rather than 1.064 μm) is that longer wavelengths are more easily absorbed at lower electron densities by inverse Bremsstrahlung process. Laser absorption by inverse Bremsstrahlung processes has been described in the form of a simple model by Mora et al. [27]. An increase in plasma temperature can also result in greater excitation of the surrounding gaseous environment or enrichment of the plasma by new chemically formed compounds in the hot medium [28]. For analysis of organic compounds, sample identification can be complicated by a surrounding atmosphere of nitrogen, oxygen, water vapor, and dust. This intrusion of the surrounding atmosphere during sample analysis can be manifested by excited nitrogen and oxygen ions and atoms, as well as the formation of molecular species resulting from reactions between the native carbon from the analyte and the nitrogen of the air [29, 30].

This study evaluated 1.064 $\mu\text{m}/10.6 \mu\text{m}$ dual-pulse LIBS as a possible method of improving the signal-to-noise ratio (with respect to a single Nd:YAG pulse) from organic materials. Two different samples were studied: a polystyrene film with controlled thickness and trace amounts of 2,4,6-trinitrotoluene (TNT), both in an ambient air atmosphere.

2. Experimental

The experimental setup for dual-pulse LIBS (Fig. 1) was similar to that reported by Weidman et al. [31]. It utilized two lasers: a Q-switched Nd:YAG laser (Brilliant — Quantel) operated at the fundamental wavelength of 1064 nm and capable of producing over 300 mJ of pulse energy in a 5 ns FWHM pulse duration and a TEA CO₂ laser (Lumonics) operating at a wavelength of 10.6 μm , with 100 mJ of pulse energy in a 100 ns pulse followed by a 1 μs long tail (Fig. 2).

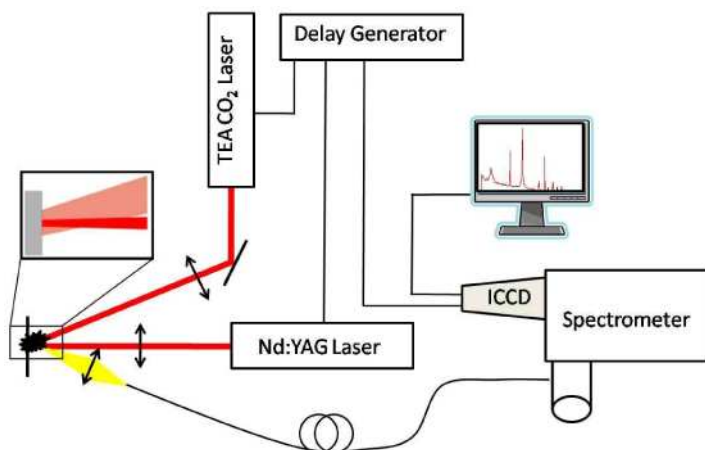


Fig. 1. The double-pulse experimental setup

The pulse energy of the Nd:YAG laser could be varied using a half-wave plate before a polarizing beam-splitter and was set to 17.5 mJ per pulse as measured using a pyroelectric energy meter (QE-25/Solo2 — Gentec). A 10 cm focal length lens was used to focus the Nd:YAG beam to a waist with a diameter of 400 μm , as determined using the knife-edge scan technique, giving an irradiance of 2.8 $\text{GW}\cdot\text{cm}^{-2}$. The pulse energy from the CO₂ laser could

be varied using a set of polarizers and the energy was adjusted to 63 mJ per pulse, measured using the same pyroelectric energy meter. A 25 cm focal length germanium lens was used to focus the CO₂ laser on the sample that was 21 cm from the lens. A defocused spot diameter of 1.2 mm, also determined using a knife edge scan, provided an irradiance of 5 MW·cm⁻² on the target. The chosen power distribution on target was based on work presented by Killinger et al. [22], in which the CO₂ spot was seven times larger than the Nd:YAG spot. A larger CO₂ spot allowed greater energy to be delivered for a given target irradiance. In the case examined here, the CO₂ laser alone did not create a plasma. The CO₂ laser beam was at an angle of approximately 15° with respect to the surface normal and the Nd:YAG was normally incident. Timing synchronization between both lasers was accomplished using two pulse-delay generators: a DG-645 (Stanford Research Systems) set as the master clock and a DG-535 (Stanford Research Systems) to control the delay between lasers and detector gate. The experiment was run at 0.3 Hz repetition rate, as limited by the CO₂ laser. The interpulse delay was measured between the rising edge half-maxima of the two pulses. The detector gate delay was measured with respect to the rising edge half-maximum of the second pulse (Fig. 2).

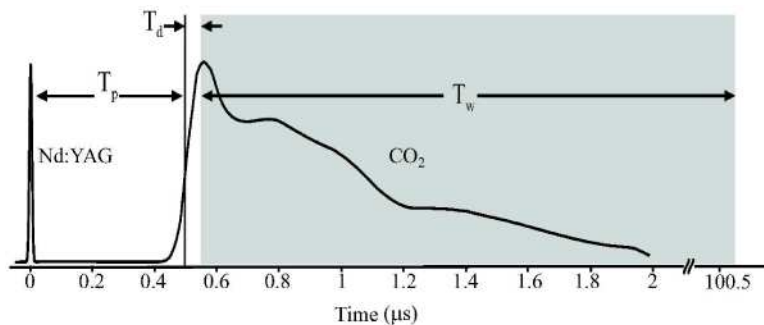


Fig. 2. The CO₂ pulse was delayed with respect to the Nd:YAG pulse by T_p and the detector gate was delayed with respect to the CO₂ pulse by T_d . The duration of the detector gate (T_w) was 100 μs for all cases studied

Light was collected using an f/2 UV grade fused silica lens (1 inch diameter and 2 inch focal length) and focused onto a round-to-line UV grade fiber bundle that was f-matched to a 0.5 meter Czerny-Turner spectrometer (Acton 2500 — Princeton Instruments). The collection optics were positioned at approximately 45° to the sample surface normal and provided a field-of-view of approximately 800 μm, as limited by the diameter of the fiber bundle. The spectrometer was equipped with a 600 line/mm grating and provided 0.08 nm spectral resolution at 400 nm. Light was detected using a UV sensitive Gen II ICCD camera (iStar — Andor Technology) with 1024 x 256 pixels. All reported spectra were corrected for the wavelength dependent sensitivity of the detection system

The polystyrene sample (M_w 280000, dilution of 100 mg/ml in toluene — Sigma Aldrich) was spin coated on a silicon wafer to provide a 3 ± 0.3 μm thick uniform layer and approximate surface concentration of 30 μg/cm². The thickness was determined using a profilometer (Veeco—Dektak 150). The TNT sample was dissolved in acetonitrile (1 mg/ml) and deposited on a silicon wafer. The solvent was allowed to evaporate leaving an approximate surface concentration of TNT corresponding to 7 μg/cm². After each laser event (one shot for single pulse or two shots for double pulse), the spectrum was acquired and the sample was translated. To compute the statistical variation, this process was repeated 30 times.

3. Results and discussion

3.1 Polystyrene

A typical double-pulse LIBS spectrum of polystyrene spin coated on silicon (Fig. 3) contains atomic emission lines from carbon at 247.9 nm, nitrogen 742.4 nm, 744.2 nm and 746.8 nm

and oxygen at 777.2 nm, 777.4 nm, and 777.5 nm as well as molecular emission from CN and C₂ molecules at 388.3 nm (violet (0-0) band head) and 516.5 nm (Swan (0-0) band head), respectively. The 2nd order of the CN violet (0-0) band head emission appears at 776.6 nm. The other spectral lines are mainly due to silicon emission resulting from the substrate. The thickness of the polystyrene film is much less than the 1/e penetration depth due to absorption by polystyrene; therefore, the laser pulse can be absorbed by the substrate [32]. This spectrum was obtained using double-pulse excitation with the CO₂ laser pulse following the Nd:YAG pulse by 500 ns (Fig. 2). To reduce the background radiation, the signal was acquired after a 50 ns gate delay. In all cases, this delay was measured with respect to the rising edge (half maximum) of the second pulse. To acquire maximum signal, a 100 μs acquisition window was used to integrate over the complete decay time of the emitting species.

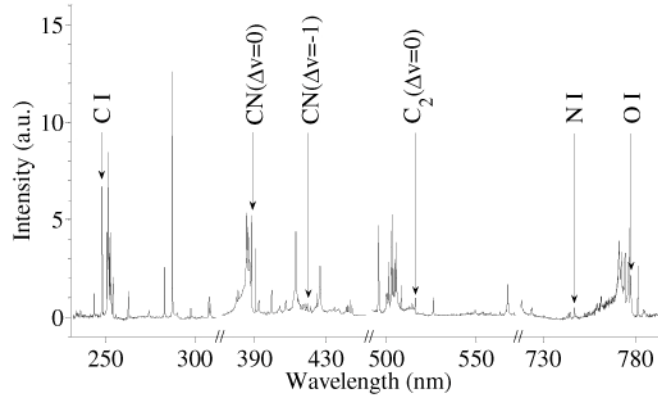


Fig. 3. Double-pulse LIBS spectrum for polystyrene on silicon. The second order of the CN violet band system appears at 776.6 nm. There are silicon lines present as a result of the substrate. The CO₂ pulse followed the Nd:YAG pulse by 500 ns, gate delay of 50 ns and 100 μs acquisition.

This study has focused mainly on carbon emission: atomic carbon ($2s^22p^2\ ^1S - 2s^22p(^2P^o)3s\ ^1P^o$ line at 247.9 nm), CN violet band system ($B^2\Sigma^+ - X^2\Sigma^+$, with (0-0) band head at 388.3 nm) and C₂ Swan band system ($d^3\Pi_g - a^3\Pi_u$, with (0-0) band head at 516.5 nm). The optimal signal from these emitters resulted from a separation time between laser pulses of approximately 100 ns (Fig. 4). Triggering the CO₂ laser before the Nd:YAG resulted in less signal from these three emitters. When the Nd:YAG pulse was delayed with respect to the CO₂ pulse (detector gate is now delayed with respect to the Nd:YAG pulse), a gradual decrease in signal was observed until the two pulses were no longer overlapped in time, in which case, emission similar to that for Nd:YAG-alone was observed.

Emission from the CN violet band system was likely resulting from a plasma reaction between atmospheric nitrogen and carbon species from the sample since neither polystyrene nor toluene contains nitrogen in their composition. Similarly, molecular CN formation has been reported from graphite plasmas [29, 33–35] as well as from polymers [29, 36].

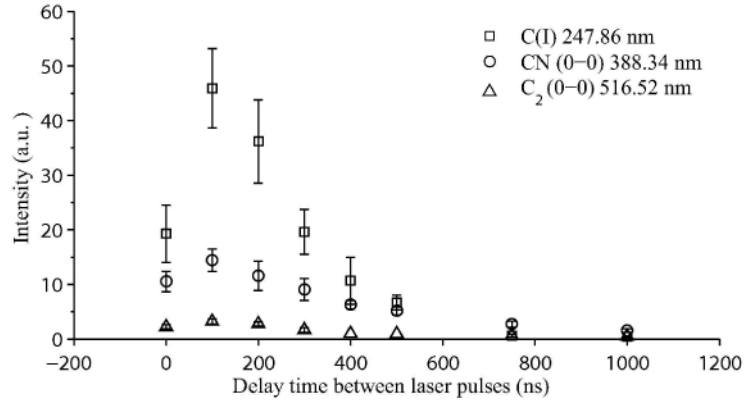


Fig. 4. LIBS emission from polystyrene as a function of the delay between laser pulses—Nd:YAG preceding CO₂. Triggering the CO₂ laser before the Nd:YAG resulted in less signal from these three emitters.

A comparison between single-pulse (Nd:YAG only) and double-pulse (Nd:YAG followed by CO₂) LIBS on polystyrene (Fig. 5) was made using the optimal interpulse delay of 100 ns (Fig. 4). The acquisition delay of 50 ns and gate width of 100 μs was not changed. Excitation with only the CO₂ laser resulted in no observed spectral lines.

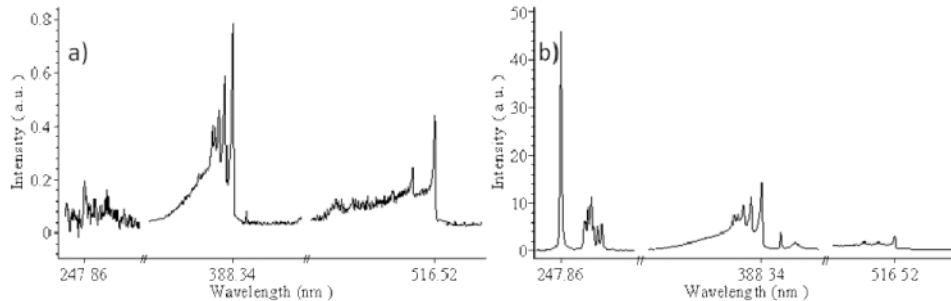


Fig. 5. Polystyrene on silicon: a) Nd:YAG single pulse, b) Nd:YAG/CO₂ double-pulse

An increase in signal was observed for double-pulse compared to single-pulse excitation. The ratio of line intensities between double- and single-pulse excitation was approximately 230 for atomic carbon, 20 for CN and 7 for C₂. Since the sample was a uniform film and the crater diameter was ~300 μm for both single- and double-pulse irradiation, as determined using an optical microscope (BX52—Olympus), the calculated amount of ablated polystyrene remained constant (within the shot-to-shot fluctuations) to approximately 20 ng. Therefore, the observed increase in signal suggests that the plasma is heated by the CO₂ laser, which is consistent with the greater atomic emission enhancement compared to molecular emission enhancement. An increase in the temperature will lead to an increased rate of molecular dissociation and hence to a lower molecular mole fraction. For graphite plasmas, atomic carbon emission was reported as having an I^{2.8} dependence on irradiance [29] while molecular emission remained roughly constant.

The figure-of-merit used for evaluating the analytical usefulness of this double-pulse technique was the signal-to-noise ratio (SNR), defined as the background subtracted peak intensity divided by the standard deviation of this peak value. Double-pulse excitation improved the SNR: an increase from 1 to 11 for atomic carbon emission, from 7 to 15 for CN and an increase from 5.6 to 9.3 for C₂ molecular emission. The uniformity in both thickness and concentration of the polystyrene film allowed the SNR to be calculated based on spectra obtained at different locations on the sample without considering sampling heterogeneity.

Statistics were based on spectra obtained from 30 independent locations on the sample —30 single-pulses or 30 double-pulses.

Single pulse Nd:YAG irradiation using greater energy also resulted in more signal. For example, an Nd:YAG pulse with an energy of 330 mJ resulted in atomic carbon emission approximately half of that obtained with double-pulse. For this more energetic Nd:YAG pulse, the signal-to-noise ratio was 2.6. Therefore, simply increasing the energy of the Nd:YAG pulse yields a SNR of approximately one-quarter of that obtained for double-pulse. This interesting characteristic of double-pulse LIBS led to its evaluation on an explosive residue.

3.2 Application to 2,4,6-trinitrotoluene residues

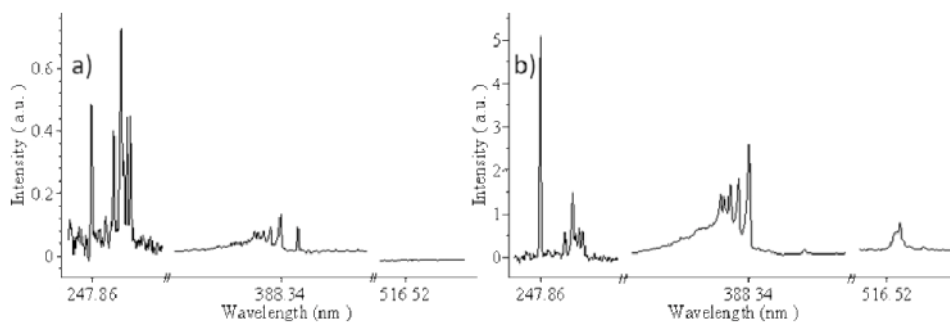


Fig. 6. TNT on silicon: a) Nd:YAG single pulse, b) Nd:YAG/CO₂ double-pulse

An enhanced emission spectra of 2,4,6-trinitrotoluene (2,4,6-TNT) was obtained (Fig. 6) using the same optimal acquisition parameters used for polystyrene. However, there was no C₂ emission (Swan system) observed for either single or double-pulse excitation. The atomic carbon emission is enhanced by a factor of 10 while CN emission is enhanced by a factor of 30. For atomic carbon, the signal-to-noise ratio is 1.5 and 2, and for CN the signal-to-noise ratio is 1.9 and 3.2 for single and double-pulse respectively. The evaporative deposition of TNT resulted in non-uniformity, as observed with an optical microscope (BX52—Olympus), and likely caused sampling heterogeneity that led to a reduced SNR.

Molecular C₂ emission has been detected from polystyrene (Fig. 5); however, no C₂ molecular emission was observed from 2,4,6-TNT (Fig. 6). At first glance, the surface concentration of TNT was significantly less than the surface concentration of polystyrene. The 7 μg.cm⁻² surface concentration of TNT over the 240 μm diameter crater (measured with the optical microscope) yields ~98 x 10⁻¹² moles of carbon atoms in the plume if all TNT was ablated and atomized. Likewise, complete ablation and atomization of the polystyrene would produce ~1.8 x 10⁻⁹ moles of carbon atoms — two orders of magnitude greater than for TNT. Moreover, the oscillator strength of the C₂ Swan band (0-0) transition (0.005) is 6 times weaker than the CN violet band (0-0) transition (0.032) [37, 38].

Furthermore, there is different chemistry within the plasma for TNT and polystyrene. A molecule of 2,4,6-TNT is formed of toluene with three attached nitro-groups. The necessary elements to form CN are present in the original molecular structure; yet, at temperatures of 3500 K and above, the most favorable path for thermal decomposition is the detachment of the -NO₂ groups around the aromatic ring, producing a 2,4,6-tolyl triradical [39]. The lack of C₂ emission observed in the case of TNT suggests that the presence of the extra nitrogen in the NO₂ groups provided an additional mechanism for consumption/removal of carbon which would otherwise be available to form C₂.

4. Conclusion

This preliminary study evaluated 1.064 μm/10.6 μm dual-pulse LIBS as a possible method of improving the signal-to-noise ratio (with respect to a single Nd:YAG pulse) from organic

materials. For a film of polystyrene on silicon, ~10-fold improvement in SNR were observed for atomic carbon emission and ~2-fold improvements for molecular C₂ and CN emissions. This technique was further applied to the analysis of 2,4,6-TNT residue on silicon; however, there was less than a 2-fold SNR improvement for atomic carbon and molecular CN, and no C₂ emission was observed for single or double-pulse excitation. The lack of observed C₂ emission could be attributed to the low surface concentration of TNT (residue), as well as the chemistry in the plasma that provides additional mechanisms for consumption/removal of carbon which would otherwise be available to form C₂.

For polystyrene, the enhanced SNR for the atomic carbon signal is noteworthy; however, the small SNR improvement seen from TNT residue is exceeded by the increased experimental complexity of this double pulse approach. Further experiments must be performed to fully characterize this approach for a more diverse set of organic samples, and to fully characterize the effects of changing the laser pulse parameters, such as pulse energy and duration.

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