

Stand-off detection of organic samples using filament-induced breakdown spectroscopy

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ABSTRACT

As an alternative to focusing nanosecond pulses for stand-off LIBS detection of energetic materials, we use self-channeled femtosecond pulses from a Ti:Sapphire laser to produce filaments at 12 meters and create a plasma on copper, graphite and polyisobutylene film. We show the possibilities of this Laser-Induced Breakdown Spectroscopy configuration for thin organic sample detection on a surface at a distance.

Keywords: Filamentation, Laser-induced breakdown spectroscopy, Stand-off detection, organic materials, surface analysis

1. INTRODUCTION

Laser Induced Breakdown Spectroscopy (LIBS) is a field of intense study due to the vast amount of available applications. LIBS provides a means of conducting real-time analysis and multi-elemental spectroscopy on samples that require minimal to no sample preparation. The laser pulse intensity needs to be high enough to produce a plasma on the target. The pulse duration usually comprised between the microsecond and the femtosecond range. [1] LIBS is used in the detection of trace compounds, ranges data are collected ordinarily a few centimeters from the sample. Having the capability to remotely detect plasmas provides a means of conducting experiments where samples are difficult to access or may be positioned in hazardous environments [3-6].

To use LIBS in a stand-off detection scenario, we use the properties of self-channeling of high-intensity laser pulses. The nonlinear effects induced by the intensity of the laser pulse in the air cause these laser pulses to self-channel, thus producing a filament [2], which is used to induce a plasma on the target sample. Self-channeling of the beam allows propagation of the beam up to kilometer ranges while producing a stable, high-intensity source (10^{14} W/cm²) at a distance. The combination of LIBS and self-channeling (or filamentation) leads to what is called Filament-Induced Breakdown Spectroscopy (FIBS) [7]. Several previous studies have shown how useful can be FIBS for remote detection of metallic, organic and biological targets up to 180 meters [7-13]

Our motivation for this research is to provide a means for stand-off detection of trace organic materials. For the purpose of this experiment, we use a CPA femtosecond laser system as a laser source to produce the filaments. The light is collected by a parabolic mirror (diameter 316 mm, focal length 1900mm) and is analyzed by an imaging spectrometer coupled to an iCCD camera. We used bulk copper and graphite samples initially, and then organic thin films.

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2. EXPERIMENTAL SETUP

2.1 Laser

In this experiment, a Chirped Pulsed Amplified Ti:Sapphire laser is utilized to produce the filament. The laser delivers 45 fs pulses centered at 800 nm at a 10 Hz repetition rate. The oscillator (Tsunami – Spectra Physics), pumped by a doubled Nd:YVO₄ laser (Millenia – Spectra Physics), delivers sub-35 fs pulses with a spectrum centered at 800 nm. After being shaped through an acousto-optical programmable dispersion filter (Dazzler – Fastlite) to pre-compensate the dispersion inside the amplifying chain, the pulses are stretched and seed a regenerative amplifier pumped by a Nd:YLF laser (Evolution – Spectra Physics). The amplified pulses are then further amplified in a double-pass amplifier pumped by a Nd:YAG laser (Quanta-Ray – Spectra Physics) at 10 Hz. Then the pulses are compressed to 45 fs with an energy of 20 mJ centered around 800 nm.

The filamentation process is forced by a 1 meter focal length lens in order to stabilize the spatial position of the filament inside the beam. The plasma is created on the target 2 meters away from the lens, 12 meters from the detection optics.

2.2 Detection

The emission signal from the stand-off plasma is collected by a 316 mm diameter, 1900 mm focal length parabolic mirror mounted on homemade support. This mirror was extracted from a Newtonian designed telescope to decrease the obstruction due to the secondary mirror in the tube assembly. The mirror is coated with UV-aluminum in order to detect signal down to 200 nm.

The signal is then focused on a round-to-line UV-transmissive fiber bundle connected to a 0.3 meter spectrometer (2300i – Acton Princeton Instruments). The spectrum is then recorded on an iCCD camera (PIMAX2 – Princeton Instruments) to allow fast triggering of the detection time after the laser pulse. In Figure 1, our typical stand-off LIBS experimental setup is shown.

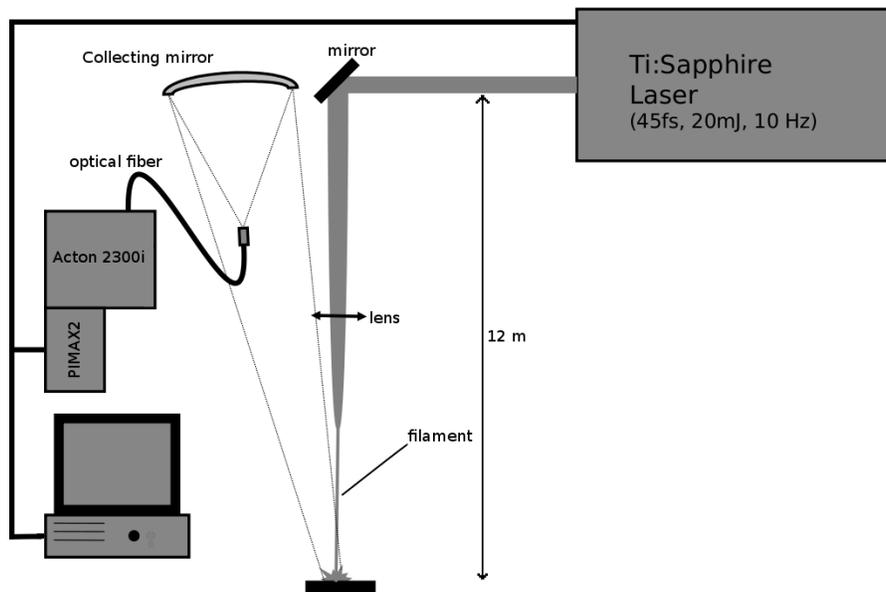


Figure 1. Experimental setup.

3. RESULTS AND DISCUSSION

The main purpose of this study is to test our facility and show the possibility of detecting an organic film in a single-shot configuration. The samples we decided to analyze in this experiment were a copper sheet, a graphite disk, and a polyisobutylene thin film.

3.1 Trace surface detection on copper

Initially, we tested our system by analyzing a sheet of copper. The spectrum obtained by a single shot analysis (delay time = 94 ns, integration time = 1 μ s) is shown in Figure 2. We observed the expected atomic copper lines at 510.6 nm, 515.3 nm, 521.8 nm, 570 nm and 578.2 nm, in addition to atomic sodium at 589 nm and atomic calcium line at 560.2 nm. Sodium and calcium are known to be common pollutants that are adsorbed onto the surface.

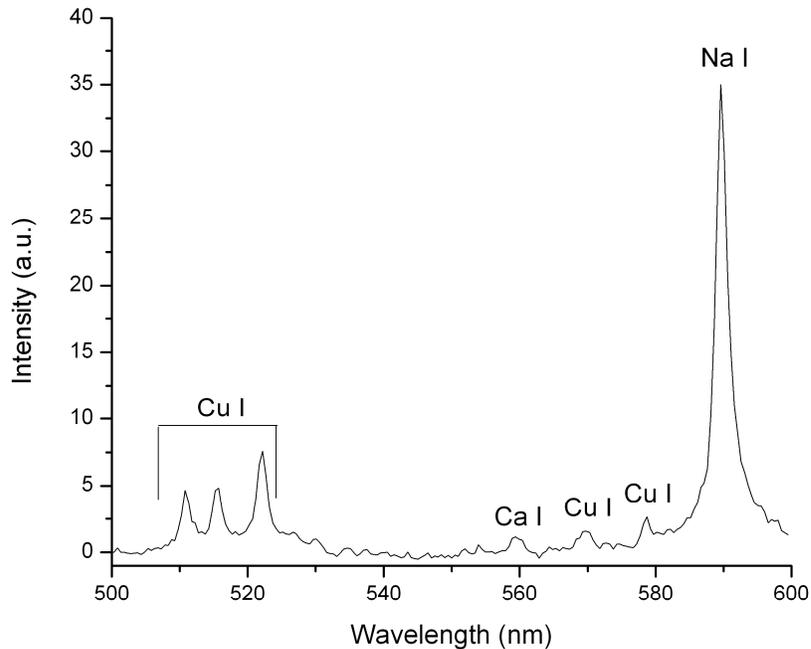


Figure 2. Single shot spectrum of the surface of a copper sample.

By ablating the sample without moving it and so drilling into it, we are able to visualize one shot after another the spectrum for each ablated depth. Figure 3 shows a spectral depth map of a hole we drilled in the copper sample with the filament. We can see that copper lines remain at a relatively stable intensity throughout the drilling after the first shot where the sodium signal is prominent; however, the surface pollutants disappeared after the initial two shots. This observation proved that Filament-induced breakdown spectroscopy is able to give a spectral signature in a single shot basis of an adsorbed compound at the surface of a metallic sample.

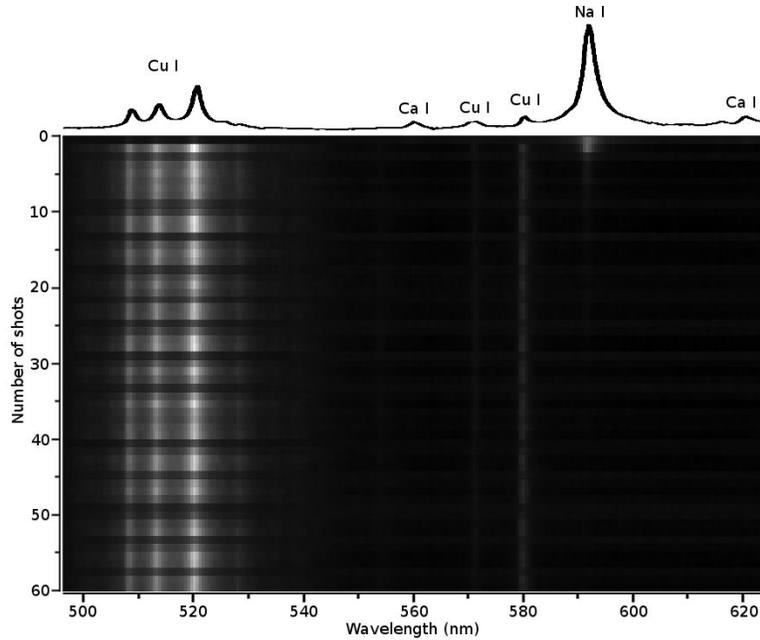


Figure 3. Spectral depth map of copper resulting from drilling the sample on the same spot

3.2 Molecular signal from graphite

As previously mentioned, the purpose of this study is to provide a means to detect trace organic materials. Moving towards that goal, we decide to analyze graphite as it is a carbon-based sample. Figure 4 shows two parts of the spectrum from graphite: (a) the ultraviolet region centered on the emission of atomic carbon at 247.9 nm and (b) the visible region where emit the of molecules C_2 (Swan System) and CN (Violet System) occurs.

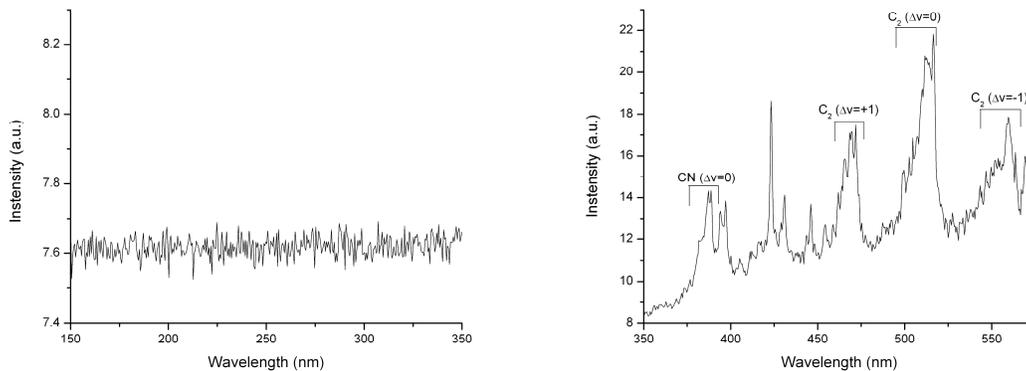


Figure 4. Single shot spectrum of graphite showing (a) no emission from atomic carbon and (b) molecular emission from CN and C_2 bonds

We were unable to observe any atomic carbon at 247.9 nm in our spectra, however, we were able to detect molecular signals from CN and C_2 . C_2 is expected from the graphite sample, since this material is composed of carbon only. But

CN comes from recombination between the carbon (atomic and molecular) ablated from the sample and the nitrogen in the surrounding atmosphere (air in our experiment) [ref] Furthermore, this examination shows the molecular signal can be a signature for carbon-based samples, with the precaution of the interpretation of the CN molecular bands.

3.3 Organic film detection

In the third part of this study, we analyze an organic thin film. Polyisobutylene (PIB) was chosen as it is a common polymer as well as a prime example of an organic material. Its chemical composition (Fig. 5) shows that there is only carbon and hydrogen in its structure, which tells us there is no CN bonds that can emit as a signature of the sample. The sample is prepared by spin-coating a PIB solution on a silicon wafer to approximately 3 μm thickness. This method of preparation provides us with a uniform sample in order to conduct systematic and reproducible experiments. In addition, the thickness of the PIB moves us towards more realistic samples which are sub-micron in scale.

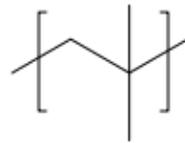


Figure 5 Chemical composition of Polyisobutylene

By ablating the PIB, we obtain the spectrum shown in Figure 6. Once again, we observe molecular carbon signal centered at 516.5 nm from our sample, but we also see the singly-ionized silicon signal around 462 nm and an atomic silicon signal around 505 nm ablated from the substrate. This shows the pulse passes through the film on the first shot. As in the case of graphite, the atomic carbon is not present in the spectrum. However, this also shows we are able to detect the signature of an organic sample on the first shot with the molecular signal.

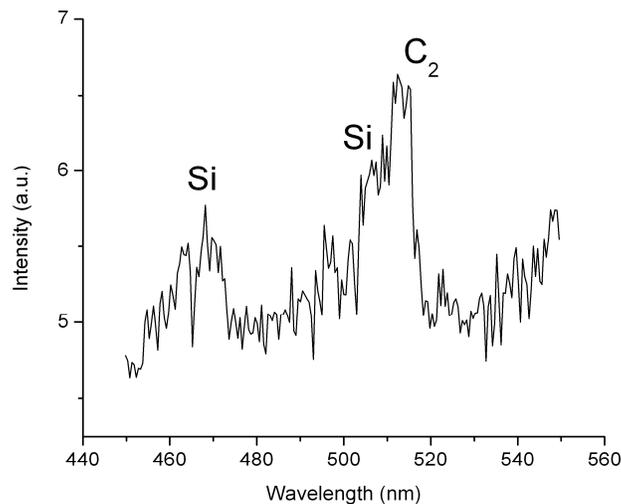


Figure 6. Single shot spectrum of PIB film on a Silicon substrate

This situation is very similar to the circumstances we experienced earlier with sodium on the copper sample. In this instance, however, we are instead detecting an organic film on a silicon substrate. By drilling into the sample, we are able to determine the initial shots are ablating polyisobutylene, while subsequent shots are hitting only silicon.

A simple way of showing this phenomenon is to compare the wavelength of the maximum intensity in the spectral range from 480 nm to 540 nm that contains the atomic Si lines (504.1 nm and 505.6 nm) and the band head of the $\Delta v=0$ transitions of the C_2 Swan system (516.5 nm) by the number of shots. Figure 6 shows that it is clearly evident the initial shots are centered about the molecular carbon signal from the organic film but then the signal is dominated by the atomic silicon emission from the substrate. This behavior proves that the detection of trace organic materials in a single shot basis is possible by filament-induced breakdown spectroscopy when the drilling is monitored spectrally

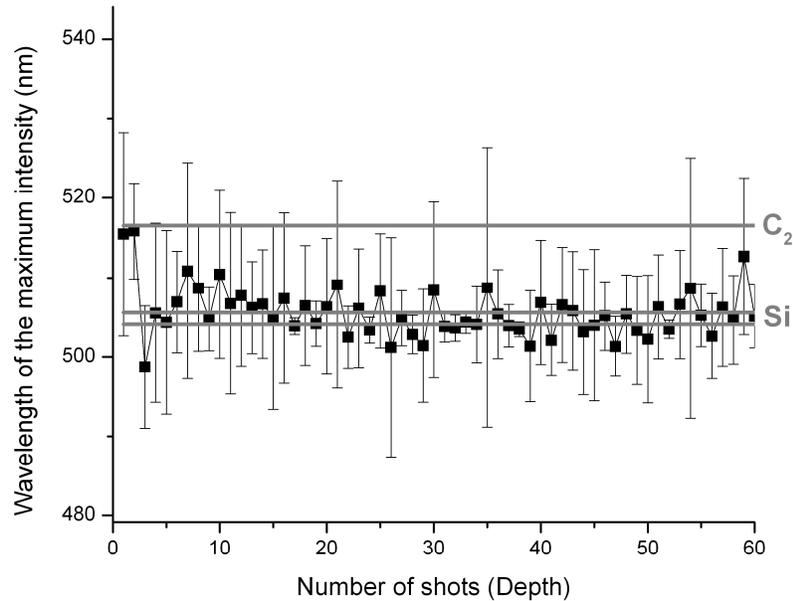


Figure 7. Wavelength of the maximum intensity in a single shot spectrum of a $3\mu\text{m}$ film of PIB on a silicon wafer as a function of depth

4. CONCLUSION

In conclusion, our results support the concept of stand-off detection of trace organic materials. In our experiment, we were able to prove surface analysis of trace materials is possible using filament-induced breakdown spectroscopy by detecting sodium on our copper sample. We determined that molecular C_2 and CN signals are spectral signatures for carbon-based samples and not atomic carbon emission. By using a spectrally monitored drilling method with a filament, it is possible to detect organic thin films based on the C_2 molecular signal. This provides a systematic method for trace materials detection on micron-scale samples.

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REFERENCES

- [1] Cremers D., Radziemski, L., [Handbook of Laser-Induced Breakdown Spectroscopy], John Wiley (2006)

- [2] Couairon A., Mysyrowicz, A., "Femtosecond filamentation in transparent media", *Physics Reports* 441, 47-189 (2007).
- [3] Knight A.K., et al, "Characterization of laser-induced breakdown spectroscopy (LIBS) for application to space exploration", *Applied Spectroscopy* 54, 331-340 (2000)
- [4] Palanco S., et al, "Open-path laser-induced breakdown spectroscopy for remote analytical measurements on solid surfaces", *Spectrochimica Acta Part B* 57, 591-599 (2002)
- [5] Vadillo J.M., et al, "Remote, real-time, on-line monitoring of high temperature samples by non-invasive open-path laser-induced plasma spectroscopy", *Anal. Bioanal. Chem.* 375, 1144-1147 (2003)
- [6] Palanco S., et al, "Design, construction, and assessment of a field-deployable laser-induced breakdown spectrometer for remote elemental sensing", *Spectrochimica Acta Part B* 61, 88-95 (2006)
- [7] Stelmaszczyk K., et al., "Long-distance remote laser-induced breakdown spectroscopy using filamentation in air", *Applied Physics Letters* 85, 3977-3979 (2004)
- [8] Rohwetter P., et al., "Filament-induced remote surface ablation for long range laser-induced breakdown spectroscopy operation", *Spectrochimica Acta Part B* 60, 1025-1033 (2005)
- [9] Xu H.L., et al., "Remote time-resolved filament-induced breakdown spectroscopy of biological materials", *Optics Letters* 31, 1540-1542 (2006)
- [10] Liu W., et al., "Efficient non-gated remote filament-induced breakdown spectroscopy of metallic sample", *Spectrochimica Acta Part B* 62, 76-81 (2007)
- [11] Daigle J.-F., et al., "Multi-constituents detection in contaminated aerosol clouds using remote-filament-induced breakdown spectroscopy", *Optics Communications* 278, 147-152 (2007)
- [12] Daigle J.-F., et al., "Long range trace detection in aqueous aerosol using remote filament-induced breakdown spectroscopy", *Applied Physics B* 87, 749-754 (2007)
- [13] Judge E.J., et al., "Discrimination of composite graphite samples using remote filament-induced breakdown spectroscopy", *Analytical Chemistry* 81, 2658-2663 (2009)