

LASER AND MICROWAVE INDUCED BREAKDOWN SPECTROSCOPY: BASIS FOR A NEW DETECTION TECHNIQUE FOR CHEMICAL AND BIOLOGICAL AGENTS

**J. Kiel^ξ, B. Rockwell, R. Sutter, J. Williams, D. Hardin, P.
Morales**

*Air Force Research Laboratory, 2503 Gillingham Drive, Bldg. 175E
Brooks AFB, Texas 78235, USA*

D. Eikum, R. Thomas, G. Noojin

*Litton-TASC, 4241 Woodcock Drive, Ste. B-100
San Antonio, Texas 78228, USA*

J. Alls

*Veridian, Inc., 8308 Hawks Rd.
San Antonio, Texas 78235, USA*

R. Seaman, S. Mathur

*McKesson Clinical and Biological Services and United States Army Medical
Research Detachment, 8308 Hawks Rd., Bldg. 1168
Brooks AFB, Texas 78235, USA*

*Abstract**

Laser-induced breakdown in air and solutions is a well-investigated phenomenon. The emission spectra are primarily atomic spectra of gases from air and volatilized metallic and other ions. Microwave-induced breakdown in solution has recently been observed. To accomplish the latter efficiently, a soluble organic semi-conductor must be added to solutions exposed to high power microwave pulses. When these same solutions were exposed to laser and microwave-induced breakdown conditions, peaks associated with atomic spectra and the organics were observed in both. However, some unique peaks were found in the microwave-induced breakdown. Therefore, cavitation generated by either laser or microwave pulses is anticipated to generate spectra analytical for specific chemical and biological agents.

some common indicator of a biological molecule or an added spectral tag (either based on light absorption or fluorescence) [1]. Such indicators limit the interrogation source to a particular wavelength of light. Multiple tags would be difficult to read with a single laser. Also, multiple or more energetic lasers (ultraviolet) place restrictions on the field use of such devices, both because of power and safety concerns. Traditionally, laser-induced breakdown spectroscopy has only been used for atomic analysis [2,3]. Here, we present data that suggest that it can be extended to organics, particularly those of biological origin. Furthermore, we show that microwave-induced breakdown produces similar spectral emissions, but adds highly resolvable peaks not found in the laser spectra [4]. Therefore, the two methods may prove complementary in chemical and biological defense applications.

II. METHODS

Methods for microwave-induced breakdown have been previously described [4,5]. In brief, a FPS-7B radar transmitter, operating at 1.25 GHz provided 6- μ s pulses at 10 pulses per second at a net antenna power of 2 MW. The light emissions from the cavitation events generated by the microwave pulses were recorded with an Ocean Optics' S2000 high-sensitivity fiber optic spectrometer, which is based on the crossed Czerny-Turner optical design and uses a Sony ILX511 linear CCD-array silicon detector. The S2000 interfaces with a PC through Ocean Optics' ADC1000 ISA-bus A/D card. The S2000 has a SMA 905 connector which couples to an Ocean Optics' SMA-terminated fiber optic probe. The spectrometer detects wavelengths from 185.07 to 870.59 nm. The Microsoft

I. INTRODUCTION

Most detection and identification methods used in chemical and biological defense use a spectral signature of

^ξ email: Johnathan.Kiel@brooks.af.mil

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14. ABSTRACT Laser-induced breakdown in air and solutions is a wellinvestigated phenomenon. The emission spectra are primarily atomic spectra of gases from air and volatilized metallic and other ions. Microwave-induced breakdown in solution has recently been observed. To accomplish the latter efficiently, a soluble organic semi-conductor must be added to solutions exposed to high power microwave pulses. When these same solutions were exposed to laser and microwave-induced breakdown conditions, peaks associated with atomic spectra and the organics were observed in both. However, some unique peaks were found in the microwave-induced breakdown. Therefore, cavitation generated by either laser or microwave pulses is anticipated to generate spectra analytical for specific chemical and biological agents.					
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Windows[®] based operating software used with the spectrometer was OOIBase32[™].

The software was setup for time acquisition and an integration time of 500 msec. An ASCII file, which listed the total amount of light detected at each wavelength during the previous 500 msec was created every half second. Then, those files were processed to yield an Excel spreadsheet, which listed each wavelength captured and total amount of light detected over the entire test run for each wavelength. From this data, line graphs were created using the wavelengths as the X-axis and the total light captured as the Y-axis. The length of test runs varied. Therefore, the absolute magnitudes of the Y values had no relationship between runs.

The laser-induced breakdown spectroscopy setups included both aqueous and aerosol samples. The first configuration used a titanium sapphire laser system (800nm;44fs) as the excitation source for aqueous samples. The samples were irradiated in 40mm x 10mm quartz cuvettes with 55uJ energy. The second configuration involved irradiation of aerosol samples using a Q-switched Nd: yttrium-aluminum-garnet (YAG) laser (1064nm; 10ns; 90mJ). The laser beams were focused by a lens to create a laser-induced plasma. Plasma emission was collected and imaged into an Ocean Optics S2000 miniature fiber optic spectrometer. Integration times for both configurations ranged from 100msec to 1.2 sec. The third configuration was identical to the second configuration except that the Ocean Optics spectrometer was replaced by a time resolved spectroscopy system. The time resolved spectroscopy system consisted of a ¼ meter Chromex 250IS spectrograph and a Hamamatsu C1587 streak camera. The time resolved spectroscopy system could record 100nm of spectra for each streak image when the Chromex was configured to use the 100 l/mm grating. Data was acquired for both the 2 µs and 10 µs time scales.

The data reported were from water, physiological phosphate buffered saline, and diazolumelanin (DALM) semi-conductor solutions prepared as previously reported for microwave-induced breakdown [4,5]. The DALM was synthesized in the *E. coli* strain JM109/pIC2ORN1.1 (American Type Culture Collection #69905).

III. RESULTS

Figure 1 shows the side-by-side comparison of pulsed laser and microwave cavitation emissions over a broad spectral range. Similar peaks are noted between the water mist excited by the laser and the DALM solution excited by the microwaves at about 590, 657, and 778 nm. Distinct peaks for the microwave excitation appear around 300 to 350 nm.

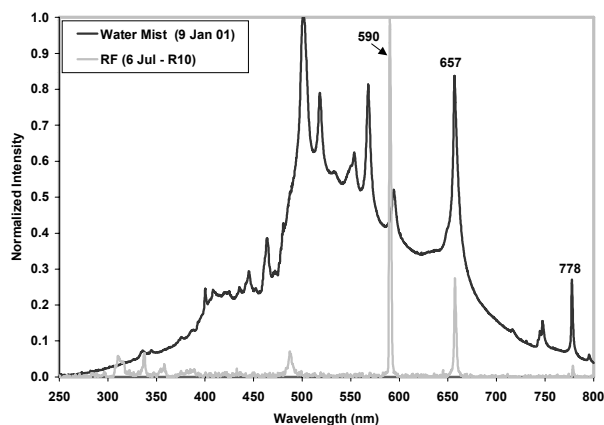


Figure 1. Comparison of nanosecond laser-induced breakdown spectrum of water mist (top curve) with microwave-induced emission spectrum of diazolumelanin (DALM) solution (bottom curve). The peak at 590nm is the NaI doublet. The peak at 657nm is identified as CII, XeII or NeI. The 778nm peak is identified as OI.

Figure 2 shows a closer look at the spectra from 400 to 600 nm. Note that the microwave emission spectra are very reproducible in spite of the fact that intensities of the peaks vary from run to run because of preparation variability. Also, one should note that the microwave spectra are more discrete with less background level noise than the laser spectrum. The microwave peak at 590 nm is near the anticipated sodium doublet at 589 nm. Other very sharp peaks in the spectra are probably metal or gas ionic emissions. The peaks in the 400 nm region are probably related to the organic ions present.

Figure 3 illustrates the discriminatory capability of the laser-induced breakdown method. DALM emissions distinctive from the phosphate buffered saline solvent should be noted at 703 and 729 nm.

Figure 4 displays DALM induced suppression of certain peaks, probably atomic emission lines of air components. Additional data displays this suppression in numerous DALM solutions independent of the solvent. It is possible that such suppression could augment identification of chemical and biological agents. Further, direct investigation in the ambient environment may be possible considering the fact that peaks observed as suppressed might be air components.

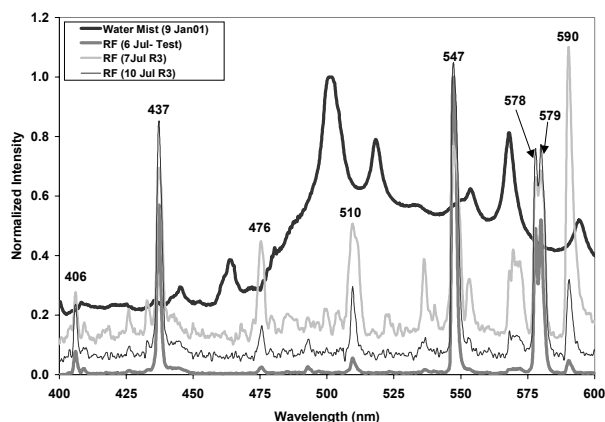


Figure 2. Water mist laser-induced emission spectrum (top curve) compared to microwave-induced spectra of organic semi-conductor (DALM). The peaks and their corresponding elements are as follows: 406nm, NII; 437nm, KrII; 476nm, KrII or NeI; 510nm, XeII; 547nm, XeII; 578nm, NeI or NI; 580nm, NeI; 590nm, NaI. Note that spectra baselines were offset for visualization.

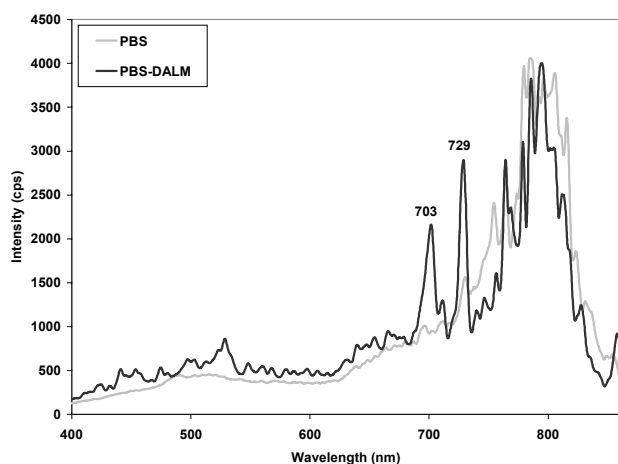


Figure 3. Comparison of 45-femtosecond pulsed laser-induced emission spectra from aqueous phosphate buffered saline (PBS) and PBS with the organic semi-conductor DALM. Peaks at 703 and 729 nm are identified as atomic emission lines of OI and OII, respectively.

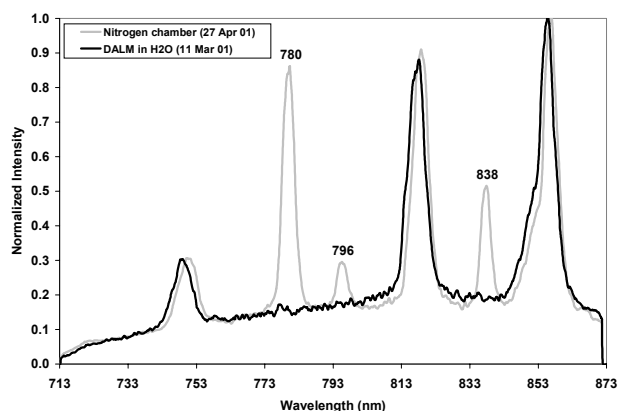


Figure 4. Comparison of streak image profiles of time resolved spectra. Baseline nitrogen filled chamber as compared to water aerosol with the organic semi-conductor DALM. The peaks suppressed by DALM, present at 780nm, 796nm, and 838nm, are identified as OI, ArI and ArI, respectively.

IV. CONCLUSIONS

Based on the example data presented here, we conclude that laser-induced and microwave-induced breakdown spectroscopy have potential as analytical methods for determining the compositions of gases, aerosols, and liquids, including organic compounds. These techniques may form the basis for future detectors and identifiers of chemical and biological agents, both for standoff and near applications.

Future work will include application of time-resolved LIBS and related spectroscopic methods to femtosecond laser pulse LIB and nonlinear broad-band continuum generation in hopes of further improvements in signal discrimination and reduction of background spectrum noise. Experiments quantifying not only spectral content, but also emission lifetime data will be conducted, producing databases for detection probes.

The rapid generation of signature spectra coupled with equally rapid analytical software could generate the next generation “seamless” devices for chemical and biological warfare agent detection and identification.

V. DISCLAIMER

The views, opinions, and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Army or Department of the Air Force position, policy, or decision unless so designated by other documentation.

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