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# Chemical and explosive detection with long-wave infrared laser induced breakdown spectroscopy

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## ABSTRACT

Conventional laser induced breakdown spectroscopy (LIBS) mostly uses silicon-based detectors and measures the atomic emission in the UV-Vis-NIR (UVN) region of the spectrum. It can be used to detect the elements in the sample under test, such as the presence of lead in the solder for electronics during RoHS compliance verification. This wavelength region, however, does not provide sufficient information on the bonding between the elements, because the molecular vibration modes emit at longer wavelength region. Measuring long-wave infrared spectrum (LWIR) in a LIBS setup can instead reveal molecular composition of the sample, which is the information sought in applications including chemical and explosive detection and identification. This paper will present the work and results from the collaboration of several institutions to develop the methods of LWIR LIBS for chemical/explosive/pharmaceutical material detection/identification, such as DMMP and RDX, as fast as using a single excitation laser pulse. In our latest LIBS setup, both UVN and LWIR spectra can be collected at the same time, allowing more accurate detection and identification of materials.

**Keywords:** laser induced breakdown spectroscopy, long-wave infrared, chemical and explosive detection, molecular vibrational spectroscopy

## 1. INTRODUCTION

Chemical and explosive materials can be detected by a few methods, such as LIBS, Raman spectroscopy, photoacoustic spectroscopy, hyperspectral imaging, photo-thermal effect imaging [1-13], etc. LIBS is arguably one with simple configuration and short acquisition time [14-25]. Explosive materials function by chemical reactions that release energy stored the chemical bonds. Therefore spectroscopic detection methods targeting these specific bonds are more likely to produce more reliable detection results. Explosive materials can be divided into two groups based on composition – ones that contain nitro/nitrate group (includes most explosives) and ones do not. In both groups, spectral signatures in the Mid-Wave IR (MWIR) and LWIR exist with high specificity.

During the past a few years, LWIR LIBS instrument for chemical and explosive detection has been developed [26-33]. The instrument operates in a similar manner as LIBS, but the detection spectral range is in the LWIR region, instead of the UVN region, as in the regular LIBS setup. It uses high energy Q-switched laser pulse of a few millijoules to excite the material and create micro-plasma. After the plasma expands and cools down, in about 10 to 30us, the emitted LWIR signature is then captured using a MCT linear detector array working with a monochromator, allowing single laser shot acquisition of the spectrum. The switch from UVN to LWIR spectral region is an important one for explosive detection, because UVN signature mainly reveals the elemental composition of the material, whereas LWIR

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emission reveals the types of chemical bonds - the energy-storing mechanism of explosives, between the elemental atoms. Experiments using the LWIR LIBS setup have been performed on a number of chemical and explosive/propellant materials, or components of them, such as DMMP, RDX, HMX, and PETN. The test results showed that the LWIR signature of these compounds are prominent in the spectral region around 8um and can be used to detect their presence in residual amount. The spectral signature can be captured with just four or less laser pulses.

## 2. EXPERIMENTAL SETUP

The experimental setup for LWIR LIBS is shown in Figure 1. A flash lamp pumped actively Q-switched Nd:YAG laser (Quantel CFR400) provides laser pulses with a repetition rate of 10Hz at 1064nm to excite the sample materials. The beam spot size on at the sample is around 60um. Collection optics are a pair of protected gold off-axis parabolic reflectors. The monochromator consists of 0.5mm input slit, 150mm focal length collimating mirror, 30 grooves/mm reflective grating blazed at 8 um, and 50mm focal length focusing mirror, which directs diffracted light onto a liquid nitrogen-cooled MCT linear detector array hybridized with read-out IC (ROIC), which greatly reduces system complicity and interference, and retain highest signal to noise ratio. The linear array contains 332 pixels and captures the spectral range of 5.5 to 10 um with a pixel pitch of 50um. A longwave pass filter is placed in front of the input slit to keep wavelength shorter than 5.5 um from entering the monochromator. Customized electronics is used to control the operation of the detector array, including supplying power, controlling synchronization and timing (including integration delay and duration), and analog to digital conversion. In addition to LWIR linear array, the electronics is also used to trigger a grating and CCD-based spectrometer (Thorlabs CCS200) with separate collection optics to measure UVN LIBS spectrum simultaneously with LWIR LIBS.

During LIBS measurement, the laser pulse energy used is about 70mJ, which usually generates a spark size of a few millimeter. The typical integration time is 42us with a delay of 20us after laser pulse. Spectra are usually obtained by averaging results from four laser pulses for better signal to noise ratio over single laser pulse. The MCT linear detector array with ROIC and actual laboratory setup are shown in Figure 2.

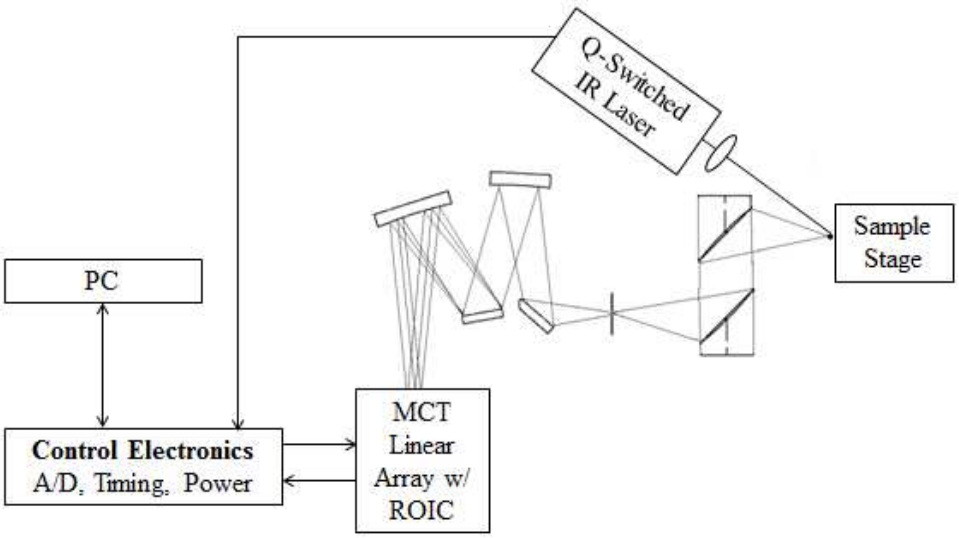


Figure 1. System Diagram of Experiment Setup of LWIR LIBS System with MCT Linear Detector Array.



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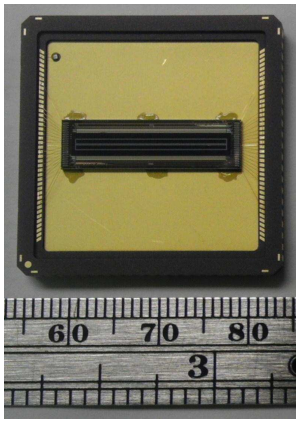
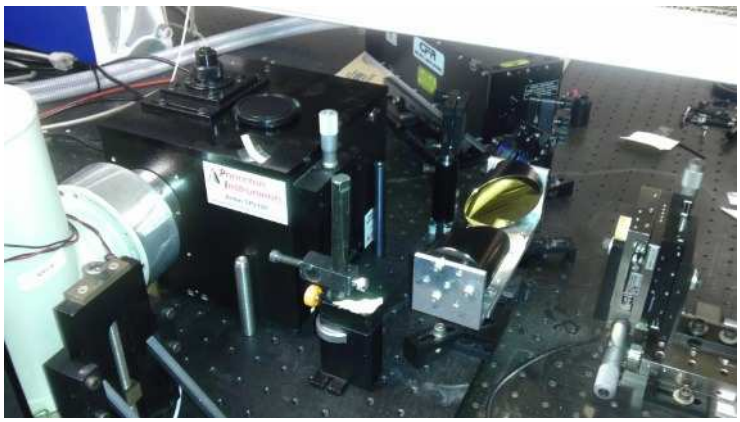


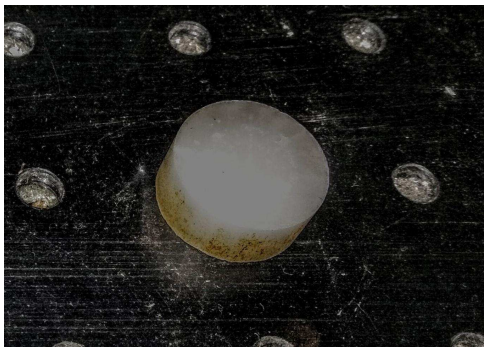



(a) (b)

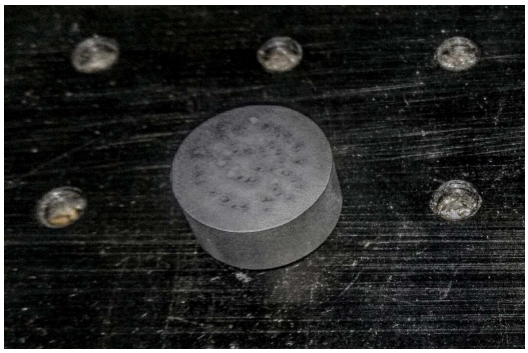
Figure 2. MCT Linear Detector Array with ROIC (a) and Actual Lab Setup (b).

## 3. SAMPLE PREPRARATION

Different methods were used to prepare the sample for test depending on the nature of the material. For inert solid material, such as potassium nitrate (KCl), the material is pressed into tablet. For liquid sample, such as DMMP, it is dripped on to a substrate, such as concrete and asphalt, to form a thin layer of liquid. For energetic materials, such as RDX, the material is dissolved in solvent and then sprayed on to substrate, such as aluminum disc, and let solvent evaporate to form a film. This method also allows the density of the material to be controlled with accuracy. Figure 3 shows a few prepared samples and substrates used in the test.



(a) (b)



(c) (d)

Figure 3. Examples of Prepared Samples/Substrates Used. (a) KCl. (b) Concrete. (c) Asphalt. (d) Al Discs.



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## 4. EXPERIMENTAL RESULTS

### 4.1 LWIR LIBS of KCl Atomic Emissions

KCl sample measured using LIBS emits strong signal in the LWIR region of 5.5 to 10um, mainly from the potassium atoms. Five emission peaks are observed, including 6.23, 6.44, 7.43, 7.89, and 8.53 um, corresponding to K atomic $4D_{3/2}$ to $6P_{1/2}$, $6S_{1/2}$ to $6P_{1/2}$, 5G to 6H, $6P_{3/2}$ to $7S_{1/2}$, and $6P_{3/2}$ to $5D_{5/2}$, respectively. The strong signal from KCl is often used to as the first measurement to check the performance of the setup. Figure 4 shows the measured spectrum fitted with Lorentzian components the aforementioned emission peaks, illustrating good match between the two.

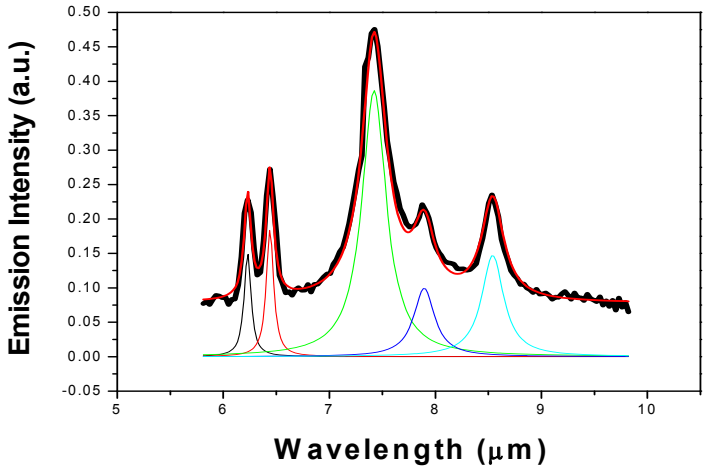


Figure 4. Measured LWIR LIBS of KCl (black) Fitted with Five of K's LWIR Atomic Emission.

### 4.2 LWIR LIBS of Chemical Agent Sarin-Simulant DMMP

Chemical agents are of great interest for LIBS-based detection and identification approach. Dimethyl methylphosphonate (DMMP, $CH_3PO(OCH_3)_2$) is a colorless liquid which is primarily used as a flame retardant. It may be used in the production of chemical weapons and can be used as a sarin-simulant.

The LWIR LIBS spectra of concrete and asphalt substrates without DMMP were measured first with the linear array-based system. Then, two drops of liquid DMMP were dripped onto the surface of each substrate, waited for about 10 minutes and measured with the instrument again. Figure 5 shows the spectra of concrete and asphalt substrates before and after adding DMMP to the substrate surfaces for the spectral region between 5 to 10μm. When DMMP is present on the surface, predominant emission features are at 7 μm from Limestone $CaCO_3$ of the substrates, at 7.8 um from P=O stretching mode of DMMP, and at 9.2 μm from the P-O-$CH_3$ stretching of DMMP. All spectra were collected by averaging of four laser shots.



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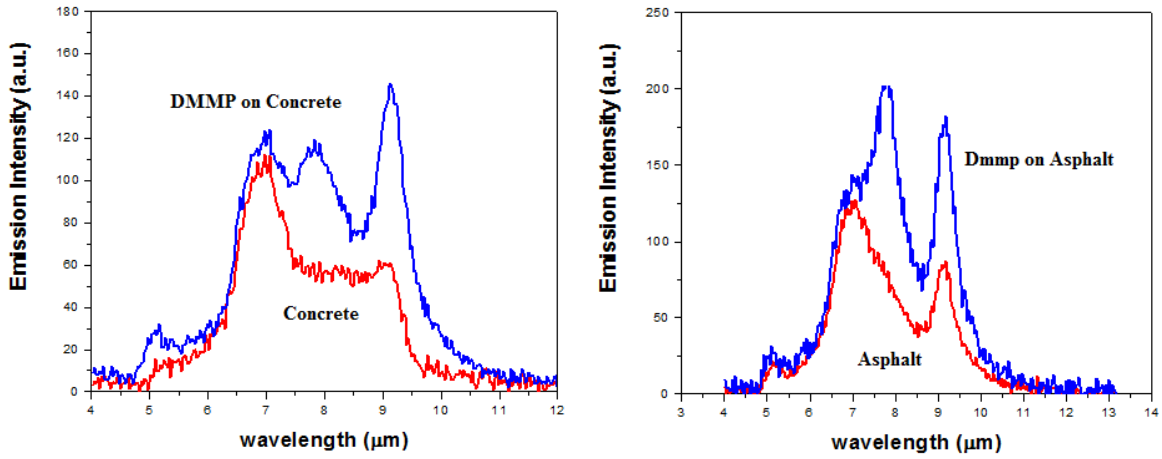


*(a)* *(b)*

Figure 5. Spectra of Concrete (a) and Asphalt (b) Substrates with (blue) and without (red) DMMP.

### 4.3 LWIR LIBS of Energetic Materials RDX, HMX, and PETN

Energetic materials and components of explosives detection is another application for LWIR LIBS technique. Three high explosives, Research Department eXplosive (RDX, $C_3H_6N_6O_6$), HMX ($C_4H_8N_8O_8$), and Pentaerythritol tetranitrate (PETN, $C_5H_8N_4O_{12}$), were measured with the LWIR LIBS setup for 5.5 to 10 um and the results are shown in Figure 6. The obtained spectra (black) show distinct emission patterns that differentiate the three types of materials, and the emission peaks coincide very well with results measured with FTIR instrument.

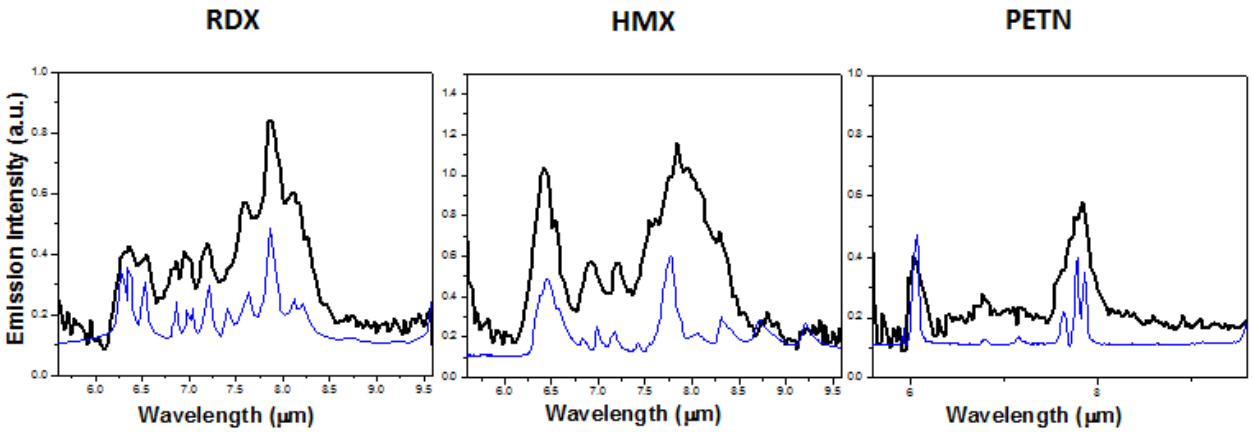


Figure 6. LWIR LIBS Spectra (thick, black) for Three Explosive Materials (RDX, HMX, and PETN), Compared to Absorption Spectra Measured with FTIR (thin, blue).

In addition to LWIR spectral region, UVN LIBS spectra were also collected simultaneously for these materials from 400 to 900 nm (Figure 7). The spectra in this spectral region are practically identical. These results clearly demonstrate the unique contributions of LWIR LIBS in differentiating materials of identical or similar elemental compositions.



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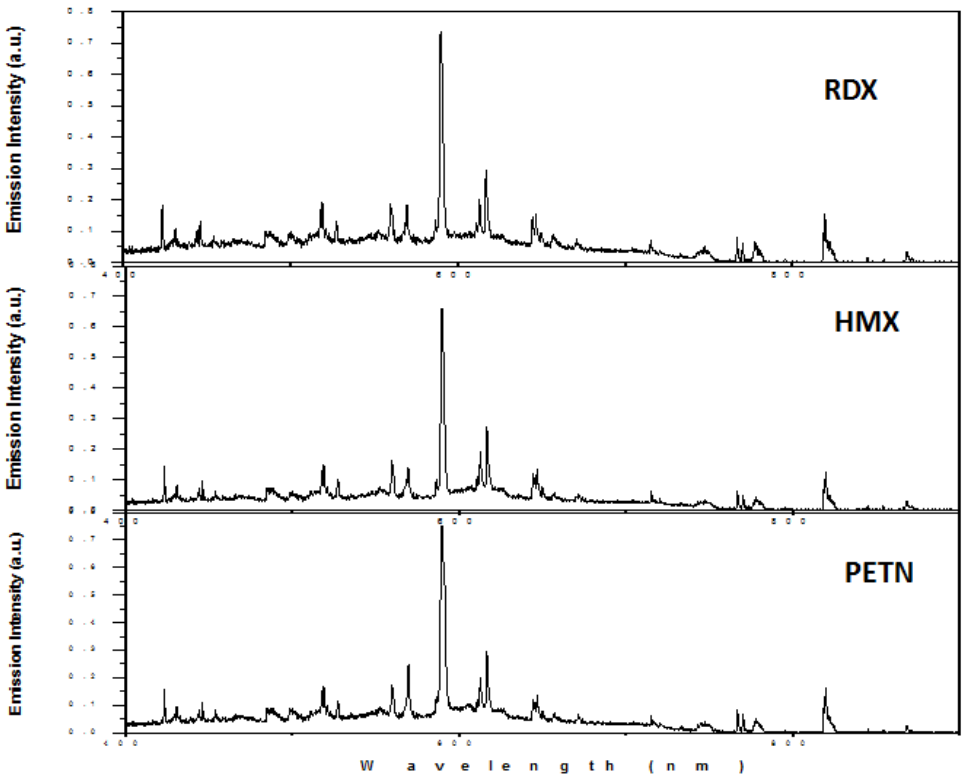


Figure 7. UVN LIBS Spectra for Three Explosive Materials (RDX, HMX, and PETN).

## 5. CONCLUSIONS/ACKNOWLEDGEMENTS

This research program explored the extended spectral range of LIBS into the LWIR region, corresponding to the vibrational and rotational mode of molecules, which reveal the types of bond that exist in the molecules. Experimental results showed that this approach can provide more accurate detection and identification of materials compared to LIBS in the shorter wavelength region.

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