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14. ABSTRACT New instrumentation including an eye-safe laser and a mercury cadmium telluride (MCT) array detector-spectrometer system were purchased and tested for infrared laser-induced breakdown spectroscopy (IR-LIBS) experiments. Conventional LIBS is limited to atomic type transitions in the UV-VIS-NIR region (~0.2-1 µm). It is well known, however, that molecules exhibit spectroscopic signatures in the long-wavelength IR region. In this project, the IR LIBS (2-12 µm) facility at HU was extended to include an eye-safe laser operating at ~1.5 µm for comparative studies using a conventional 1.064 µm Nd:YAG laser. In addition, a MCT array detector with 128					
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## Report Title

Final Report: Development of IR Laser Induced Breakdown Spectroscopy employing a Mercury Cadmium Telluride Array Detector

### ABSTRACT

New instrumentation including an eye-safe laser and a mercury cadmium telluride (MCT) array detector-spectrometer system were purchased and tested for infrared laser-induced breakdown spectroscopy (IR-LIBS) experiments. Conventional LIBS is limited to atomic type transitions in the UV-VIS-NIR region (~0.2-1  $\mu\text{m}$ ). It is well known, however, that molecules exhibit spectroscopic signatures in the long-wavelength IR region. In this project, the IR LIBS (2-12  $\mu\text{m}$ ) facility at HU was extended to include an eye-safe laser operating at ~1.5  $\mu\text{m}$  for comparative studies using a conventional 1.064  $\mu\text{m}$  Nd: YAG laser. In addition, a MCT array detector with 128 elements was incorporated into the IR LIBS setup for atomic and molecular IR LIBS of solid-state samples relevant for CBE sensing applications. In comparison to the single element MCT detector, the new MCT array system allowed the rapid detection of IR LIBS emission signatures from several potassium compounds (incl. KCl, KClO<sub>3</sub>, KClO<sub>4</sub>). Time-resolved IR LIBS studies, however, revealed that the longer-lived molecular emissions exhibited rather weak signal strength. Comparative LWIR LIBS studies of several solid-state samples were performed using a Nd:YAG laser at 1.064  $\mu\text{m}$  and the new eye-safe laser operating at 1.574  $\mu\text{m}$ . Under the same experimental conditions, the IR LIBS emissions using an eye-safe laser exhibited nearly identical LIBS signatures but with slightly reduced intensity compared to 1.064  $\mu\text{m}$  laser excitation.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
12/19/2016	2 E. Brown, C. S. Yang, U. Hommerich, F. Jin, S. B. Trivedi, A. C. Samuels. Comparative studies of long-wave laser induced breakdown spectroscopy emissions excited at 1.064 $\mu\text{m}$ and eye-safe 1.574 $\mu\text{m}$ , Optics Express, ( ): . doi:
<b>TOTAL:</b>	<b>1</b>

**Number of Papers published in peer-reviewed journals:**

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**(b) Papers published in non-peer-reviewed journals (N/A for none)**

<u>Received</u>	<u>Paper</u>
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**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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**(c) Presentations**

1. E. Brown, U. Hommerich, C.S.C. Yang, F. Jin, S.B. Trivedi, Infrared Molecular Emission Signatures from Solid-State Materials using Laser Induced Breakdown Spectroscopy, presented at the 7th international conference on optical, optoelectronic and photonic materials and applications (ICOOPMA 2016) June 12-17, 2016, Montreal, Canada.
2. Keith Tukes, E. Brown, U. Hommerich, "Laser-Induced-Breakdown Spectroscopy of Potassium-Based Energetic Materials Deposited on Substrates in the UV-VIS and MIR", presented at the Emerging Researchers National (ERN) Conference in STEM, Febr 24-27, 2016, Washington, DC.

**Number of Presentations:** 2.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

<u>Received</u>	<u>Paper</u>
10/27/2016	1 EiEi Brown, Uwe Hommerich, Clayton C Yang, Feng Jin, Sudhir B. Trivedi, Alan C. Samuels. Eye-Safe Infrared Laser-Induced Breakdown Spectroscopy (LIBS) Emissions from Energetic Materials, SPIE Defense 2016. 17-APR-16, Baltimore, MD. : ,
<b>TOTAL:</b>	<b>1</b>

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

<u>Received</u>	<u>Paper</u>
<b>TOTAL:</b>	

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**(d) Manuscripts**

<u>Received</u>	<u>Paper</u>
<b>TOTAL:</b>	

Number of Manuscripts:

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**Books**

Received      Book

**TOTAL:**

Received      Book Chapter

**TOTAL:**

**Patents Submitted**

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**Patents Awarded**

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**Awards**

none

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**Graduate Students**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

**Names of Post Doctorates**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Faculty Supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Names of Under Graduate students supported**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... 0.00

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**Names of Personnel receiving masters degrees**

<u>NAME</u>
<b>Total Number:</b>

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**Names of personnel receiving PHDs**

<u>NAME</u>
<b>Total Number:</b>

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**Names of other research staff**

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

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**Sub Contractors (DD882)**

## **Inventions (DD882)**

### **Scientific Progress**

see attachment

### **Technology Transfer**

Faculty and students from Hampton University (HU) collaborated with researchers from Battelle (Dr. C. Yang), Edgewood Chemical Biological Center ECBC, (Dr. P. Snyder), and Brimrose Corporation (Dr. S. B. Trivedi, Dr. F. Jing) on the development of combined UV-VIS and Infrared Laser-Induced Breakdown Spectroscopy (LIBS) for chemical sensing related to DOD applications. HU provided basic spectroscopy results to researchers at Brimrose and ECBC for comparative time-resolved IR LIBS studies of several energetic materials under 1.064  $\mu\text{m}$  and 1.5  $\mu\text{m}$  laser excitation. In addition, researchers from Brimrose visited HU for joint IR LIBS experiments under eye-safe excitation using a new 1.5  $\mu\text{m}$  pulsed laser.

**Final Report for Award: W911-NF-15-1-0050**

***Development of IR Laser Induced Breakdown Spectroscopy  
employing a Mercury Cadmium Telluride Detector***

**Time period covered: 02/01/2015 until 09/30/2016**

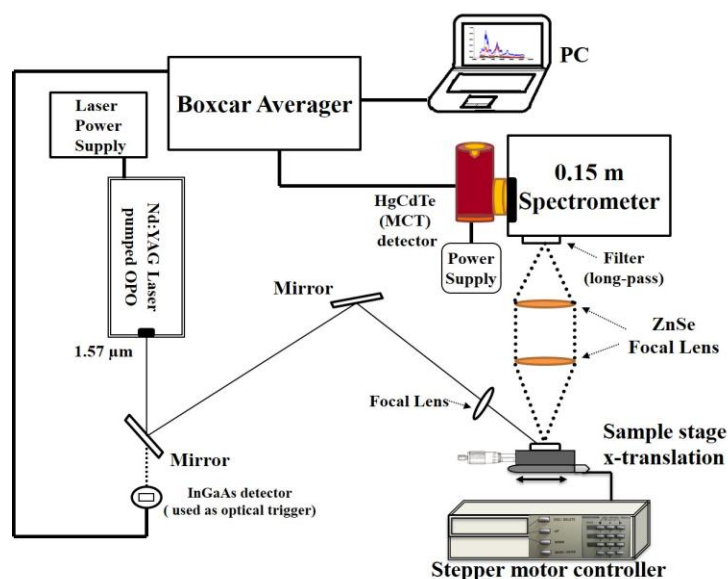
**Summary:**

During the time-period of this award, new instrumentation including an eye-safe laser and a mercury cadmium telluride (MCT) array detector-spectrometer system were purchased and tested for infrared laser-induced breakdown spectroscopy (IR-LIBS) experiments. LIBS has shown great promise for sensing of chemical, biological, and energetic (CBE) hazardous materials of relevance to DOD and Homeland security applications. Conventional LIBS is typically limited to atomic type transitions in the UV-VIS-NIR region (~0.2-1  $\mu\text{m}$ ). It is well known, however, that molecules exhibit spectroscopic signatures in the long-wavelength IR region. In an effort to augment the atomic emission spectra of conventional LIBS and to provide an increase in selectivity, researchers from HU, along with collaborators at Brimrose Corporation and Edgewood Chemical Biological Center (ECBC), demonstrated the first IR LIBS emission signatures in the 2-12  $\mu\text{m}$  IR region. Atomic and molecular fingerprints of several energetic materials (e.g. ammonium nitrate, potassium chlorate) were identified using a standard 1.06  $\mu\text{m}$  Nd: YAG pump laser and a single element MCT detection system. In this project, the IR LIBS facilities at HU were extended to include an eye-safe laser operating at ~1.5  $\mu\text{m}$  for comparative studies using a conventional 1.064  $\mu\text{m}$  Nd: YAG laser. In addition, a new multi-element MCT array detector with 128 elements was incorporated into the IR LIBS setup for atomic and molecular IR LIBS spectroscopy of solid-state samples relevant for CBE sensing applications. In comparison to the single element MCT detector and scanning spectrometer, the new MCT array system allowed the rapid detection of broad spectra of atomic and molecular IR LIBS emission signatures from several potassium compounds (incl. KCl, KClO<sub>3</sub>, KClO<sub>4</sub>). Time-resolved IR LIBS studies, however, revealed that the longer-lived molecular emission signatures exhibited rather weak signal strength using the MCT array and suffered from poor signal to noise ratio. Comparative LWIR LIBS studies of several potassium and ammonium containing compounds were performed using a conventional Nd:YAG laser at 1.064  $\mu\text{m}$  and the new eye-safe laser operating at 1.574  $\mu\text{m}$ . Under similar experimental conditions, the IR LIBS emissions using an eye-safe laser exhibited nearly identical LIBS signatures but with slightly reduced intensity compared to 1.064  $\mu\text{m}$  laser excitation.

## 1. Development of eye-safe infrared laser-induced breakdown spectroscopy (IR-LIBS)

Most LIBS studies reported in the literature have been carried out using a Nd:YAG laser operating at 1.064  $\mu\text{m}$ , which has an extremely low threshold for eye-damage [1-6]. Therefore, the development of eye-safe LIBS systems is of critical importance for many applications such as standoff detection of chemical, biological, and explosive (CBE) materials, laser radar, remote sensing, range-finding, and laser countermeasures [1-6]. Laser wavelengths longer than  $\sim 1.4 \mu\text{m}$  are often called “eye-safe” or particularly “retina-safe” since they are not well transmitted within the ocular media and are poorly absorbed by the retina [7]. In this work, comparative LWIR-LIBS emission studies using conventional 1.064  $\mu\text{m}$  pumping and a new eye-safe laser operating at 1.57  $\mu\text{m}$  were performed on several potassium compounds (e.g.  $\text{KClO}_3$ ,  $\text{KClO}_4$ ) and ammonium compounds (e.g.  $\text{NH}_4\text{SO}_4$ ,  $\text{NH}_4\text{ClO}_4$ ). The investigated potassium and ammonium compounds are major ingredients used in many improvised explosive devices. Bulk samples as well as thin films deposited on different background substrates (e.g. aluminum, cement, asphalt) were employed in the IR LIBS studies. For both pump wavelengths, sample specific atomic and molecular emission signatures in the 4-12  $\mu\text{m}$  spectral regions were observed.

Figure 1 and 2 shows the experimental setup developed at HU for performing eye-safe IR LIBS studies in the 4-12  $\mu\text{m}$  spectral region. The 1.574  $\mu\text{m}$  output of a pulsed (11 ns pulses, 10 Hz) Nd:YAG pumped Optical Parametric Oscillator (OPO) system and the 1.064  $\mu\text{m}$  output from a Q-switched Nd:YAG laser (pulse width of 5 ns and 10 Hz repetition rate) were employed for the IR LIBS studies. The energy per laser pulse on the sample was  $\sim 70 \text{ mJ}$  for both laser sources.



**Figure 1:** Schematics of eye-safe (1.57 $\mu\text{m}$ ) IR LIBS system developed at HU employing a single element MCT detector and scanning spectrometer. A conventional 1.064 $\mu\text{m}$  Nd: YAG laser was used in comparative IR LIBS studies.



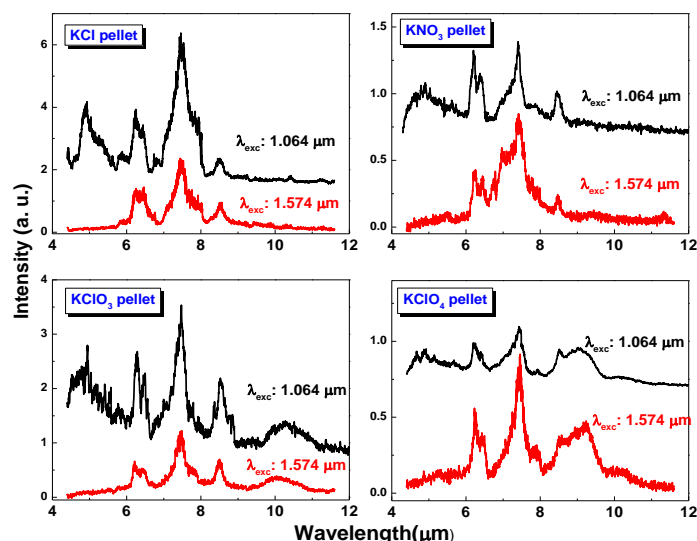
**Figure 2:** Picture of the eye-safe IR LIBS system (left), pump laser systems (1064nm & 1570nm), and associated control and data acquisition equipment (right).



The samples were mounted on a linear translation stage which was attached to a stepper motor with a motion controller. The laser beam was focused with a lens (focal length = 7.5 cm) onto the sample surface leading to a beam diameter of ~0.2 mm. Two ZnSe lenses (focal length = 10 cm) were employed as the collection optics to focus the sample LIBS emission onto the entrance slit of a 0.15 m spectrometer. The spectrometer was equipped with 150 grooves/mm and 75 grooves/mm reflective grating blazed at 4  $\mu\text{m}$  (MIR) and 8  $\mu\text{m}$  (LWIR), respectively. Long pass filters for corresponding spectral regions were utilized to block laser scattering and the shorter emission wavelengths. The emission spectra were recorded using a liquid-nitrogen cooled HgCdTe (MCT, 2-12  $\mu\text{m}$ ) detector. Each emission scan took 720s covering a wavelength range of 1200 nm. The emission signals were averaged using a boxcar average with a gate width of 16  $\mu\text{s}$  and delay time of 30  $\mu\text{s}$ .

### 1.1 Comparative IR LIBS studies on potassium containing compounds in bulk pellets

Commercially available powders of potassium chloride (KCl), potassium chlorate ( $\text{KClO}_3$ ), potassium perchlorate ( $\text{KClO}_4$ ), and potassium nitrate ( $\text{KNO}_3$ ) materials were pressed into bulk pellets for IR LIBS measurements using a hydraulic press. The pressed pellets had a size of ~15 mm diameter and 5 mm thickness. Comparative IR LIBS studies using laser wavelengths at 1.574  $\mu\text{m}$  and 1.064  $\mu\text{m}$  were performed for all samples at ambient atmospheric condition. Figure 3 shows the IR LIBS spectra of KCl,  $\text{KClO}_3$ ,  $\text{KClO}_4$ ,  $\text{KNO}_3$  pellets over the spectral range 4.4-12  $\mu\text{m}$ . No significant IR LIBS emission signatures were observed from air under nearly identical experimental conditions.



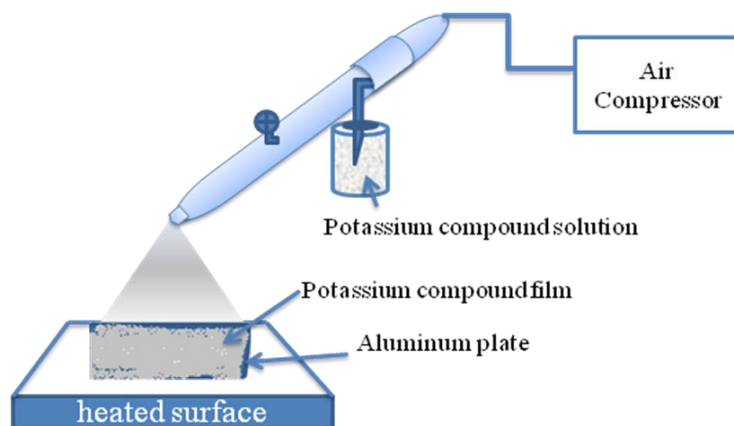
**Figure 3:** Comparative IR-LIBS emission spectra of KCl,  $\text{KClO}_3$ ,  $\text{KClO}_4$ , and  $\text{KNO}_3$  pellets under 1.064  $\mu\text{m}$  and 1.574  $\mu\text{m}$  laser excitations.

For both pump wavelengths (1.064  $\mu\text{m}$  and 1.574  $\mu\text{m}$ ), IR LIBS signatures for K atomic emissions as well as the asymmetric stretching bands of the  $\text{ClO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  anion were observed [8-13]. Evidence of a NO stretching mode at ~5.2  $\mu\text{m}$  was also noticed in the LIBS spectra of all K compounds under 1.064  $\mu\text{m}$  excitation, while this spectral feature was not noticeable under 1.574  $\mu\text{m}$  laser pumping. Furthermore, the overall background in the LIBS spectra was less under eye-safe 1.574  $\mu\text{m}$  pumping.

### 1.2 Comparative IR LIBS studies of potassium compounds deposited as films on aluminum

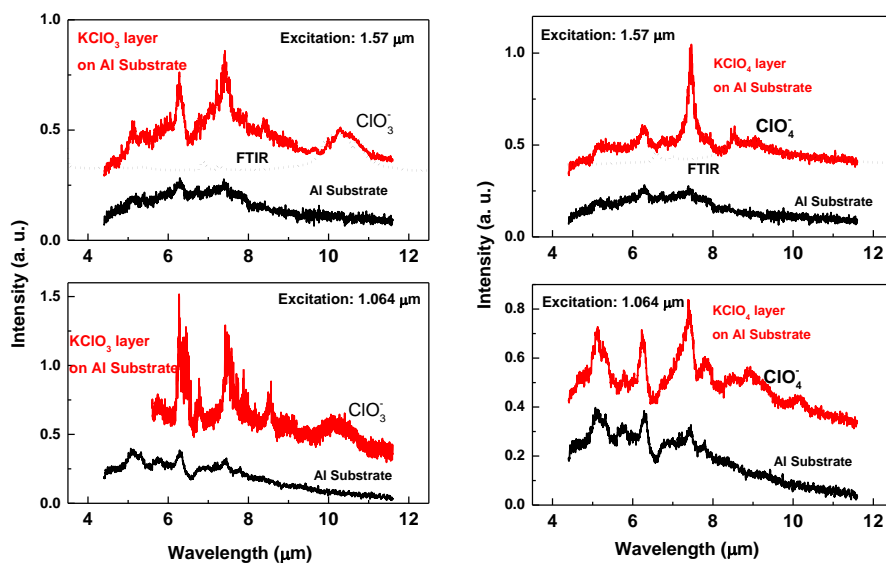
Samples of  $\text{KClO}_3$  and  $\text{KClO}_4$  films (< 1 mm thickness) were deposited on aluminum (Al) substrates for comparative IR LIBS studies using 1.064  $\mu\text{m}$  and 1.57  $\mu\text{m}$  laser pumping. The K films were air-sprayed as a thin film on Al plates using an air spray systems as shown in Figure 4. First, a desired amount of potassium containing powder was dissolved in distilled water while the Al plate was heated to ~60°C. The prepared potassium solution was then air-sprayed onto the heated Al plate for several minutes. Eventually, the water was evaporated leaving a potassium containing thin film on the Al plate. The size of the Al plate was

approximately one square inch. Samples of ammonium containing compounds were also deposited on Al substrates using a similar procedure.



**Figure 4:** Schematic diagram for air-spraying potassium or ammonium compounds on aluminum substrates for IR LIBS studies.

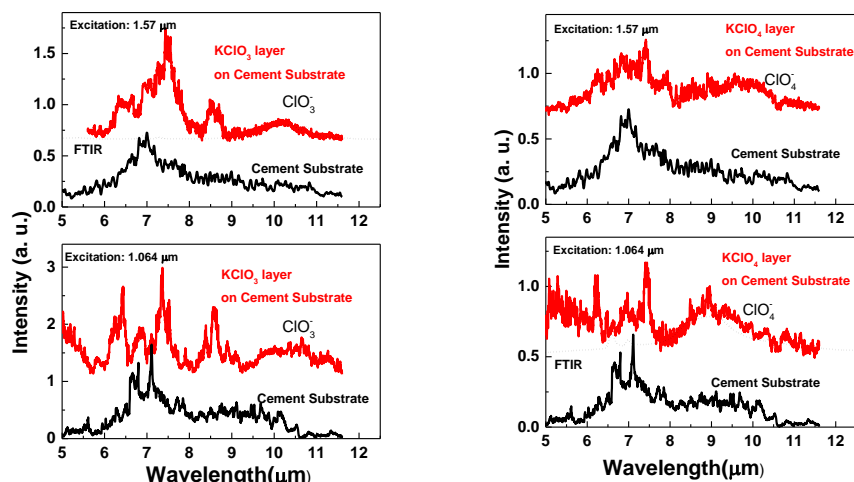
Figure 5 shows the IR LIBS spectra of  $KClO_3$  and  $KClO_4$  films deposited on Al substrates over the spectral range 4.4 to 11.6  $\mu\text{m}$  using 1.064  $\mu\text{m}$  and 1.574  $\mu\text{m}$  pump lasers. Similar to IR LIBS studies on bulk pellets, potassium emission signatures as well as the asymmetric stretching bands of the  $ClO_3^-$ ,  $ClO_4^-$  anion were observed [8-13]. The Al substrate only provided minor interference with the IR LIBS signatures from the potassium compounds.



**Figure 5:** IR-LIBS spectra of  $KClO_3$  and  $KClO_4$  films deposited on Al substrates under 1.064  $\mu\text{m}$  and 1.574  $\mu\text{m}$  laser excitations.

### 1.3 Comparative IR LIBS studies of potassium compounds deposited as films on cement

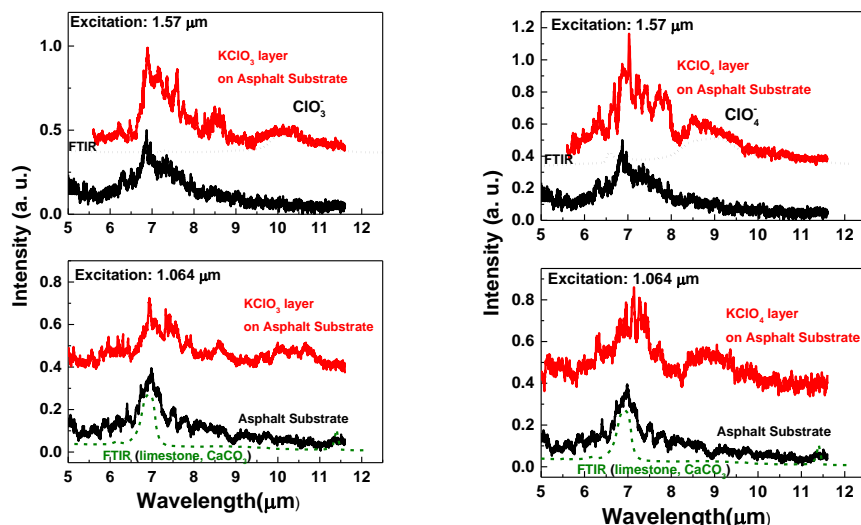
Samples of  $KClO_3$  and  $KClO_4$  films were also deposited on cement substrates using the air-spray system described under 1.2. IR LIBS (4.4–11.6  $\mu\text{m}$ ) measurements were performed for all samples using eye-safe laser excitation at 1.57  $\mu\text{m}$  and compared to LIBS studies under 1.06  $\mu\text{m}$  pumping as shown in Figure 6. Despite the fact that the cement substrate yielded significant IR emission under both pump wavelength, characteristic K emission signatures as well as the asymmetric stretching bands of the  $ClO_3^-$ ,  $ClO_4^-$  anion [12,13] were observed under both laser pumping schemes.



**Figure 6:** IR-LIBS spectra of  $KClO_3$  and  $KClO_4$  films deposited on cement substrates under 1.064  $\mu m$  and 1.574  $\mu m$  laser excitations.

#### 1.4 Comparative IR LIBS studies of potassium compounds deposited as films on asphalt

Samples of  $KClO_3$  and  $KClO_4$  films were also deposited on asphalt substrates for IR LIBS studies. Since asphalt is heat sensitive, depositing K compounds on asphalt using air-spray method was not successful. Instead  $KClO_3$  and  $KClO_4$  powders were manually deposited on low-heated asphalt. First, asphalt was heated to 30-40  $^{\circ}C$  for a few minutes and then removed from the heated surface. The investigated K compounds were then distributed evenly over the slightly heated asphalt with a spatula and slightly pressed against the surface. After cooling for  $\sim 30$  minutes the sample powder stuck to the asphalt as a thin film layer. Figure 7 shows the comparative IR LIBS spectra of  $KClO_3$  and  $KClO_4$  films deposited on asphalt substrates for 1.064  $\mu m$  pumping and eye-safe laser excitation at 1.574  $\mu m$ .

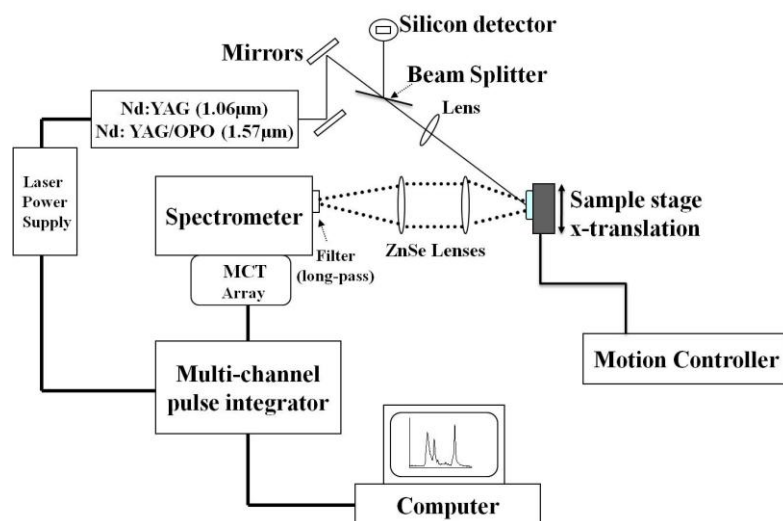


**Figure 7:** LWIR-LIBS spectra of  $KClO_3$  and  $KClO_4$  films deposited on asphalt substrates under 1.064  $\mu m$  and 1.574  $\mu m$  laser excitations.

Both K emission signatures as well as the asymmetric stretching bands of the  $ClO_3^-$ ,  $ClO_4^-$  anion [12] were observed for both pumping schemes. As described in earlier report, a broad band ranging 6.2-8.0  $\mu m$  corresponds most likely due to the asymmetric stretching of  $CO_3^{2-}$  from the limestone and C-H bending from the bitumen (FTIR spectrum of limestone ( $CaCO_3$ ) is included) [14,15].

## 2. Integration of Mercury Cadmium Telluride Array Detector into current IR-LIBS setup

A schematic and pictures of the IR LIBS setup developed at HU using the new MCT array detector are shown in figures 8 and 9. The MCT array-spectrometer system was purchased from Infrared Systems Development [16]. The detector consists of a linear MCT array with 128 elements in a single row configuration. The element size is 0.2 mm horizontal by 0.5 mm vertical on a 0.25 mm horizontal pitch. The MCT detector array is attached to a 0.19 m Horiba spectrograph (TRIAX 190) utilizing a 3 grating turret (see figure 9). With the standard detector size this yields a spectral resolution of  $\sim 21$  nm/pixel when employing a 50 line/mm grating. For a 150 line/mm grating the spectral resolution increases to 7nm/pixel. Two grating turrets with interchangeable gratings were purchased to cover the spectral range from 2-12  $\mu\text{m}$ . The signal from MCT array is processed with a multi-channel pulse integrator, which includes detector bias and preamplifier, box-car type integrator, and analog digital converter. All components are combined as a turn-key system that includes Labview control and data acquisition software. The experimental setup in the IR-LIBS studies also included a Q-switched Nd: YAG laser operating at 1.064  $\mu\text{m}$  or a Nd: YAG/OPO operating at 1.57  $\mu\text{m}$  (pulse width: 5-10 ns, repetition rate 10 Hz) as the excitation source. Similar to the setup described in section 1, the laser beam was focused onto the sample using a convex lens ( $f=5-10$  cm) resulting in a beam size of  $\sim 1$  mm diameter. The laser energy reaching the sample typically varied between  $\sim 50-70$  mJ per pulse. The IR emission was collected with two ZnSe lenses and imaged onto the spectrometer entrance slit. The sample was mounted onto a linear translation stage attached to a stepping motor with controller. The sample was translated at speeds of 1-2 mm/min during LIBS experiments so that the laser beam would always hit a fresh sample spot.



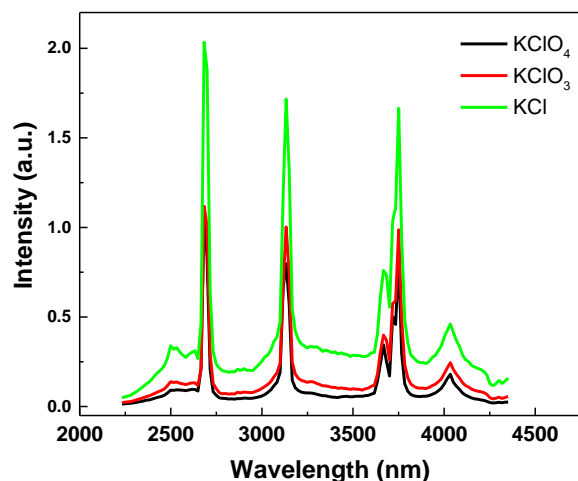
**Figure 8:** Schematics and picture of IR LIBS setup using a multi-element, linear MCT array detector attached to an imaging spectrometer.



**Figure 9:** Picture of IR LIBS setup at HU employing an MCT array-spectrometer system (left). Close up picture of spectrometer with attached MCT array detector (right).

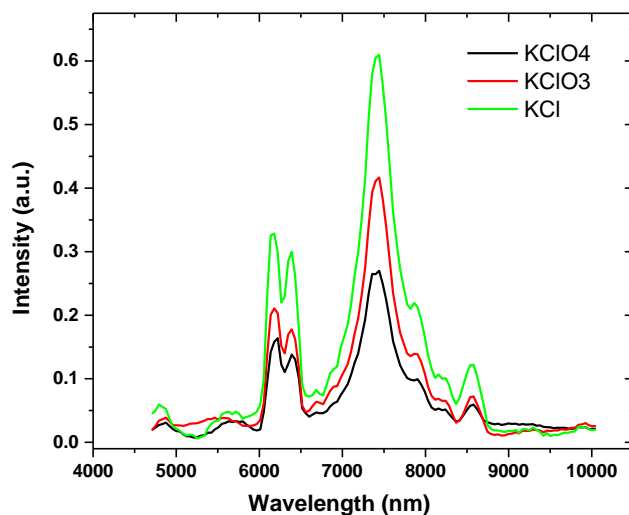
(Infrared Systems Development: <http://www.infraredsystems.com/Products/spectrometer.html>)

The LIBS systems employing the MCT array system was capable of recording a wide range of LIBS emission spectra rapidly, covering the spectral range from 2-12  $\mu\text{m}$  using a turret with interchangeable gratings blazed at 4  $\mu\text{m}$ , 6  $\mu\text{m}$ , and 8  $\mu\text{m}$ . Following 1.064  $\mu\text{m}$  excitation, initial testing of the MIR LIBS spectra using the MCT array detector were carried out for potassium compounds including KCl,  $\text{KClO}_3$  and  $\text{KClO}_4$  pellets (Fig. 10). As mentioned before,  $\text{KClO}_3$  and  $\text{KClO}_4$  are major ingredients used in many improvised explosive devices. A 75 grooves/mm reflecting grating blazed at 4  $\mu\text{m}$  was selected for the MIR spectral region. LIBS spectra were collected with an integration time of 15  $\mu\text{s}$  and a gate delay of 1.5  $\mu\text{s}$ . A 2  $\mu\text{m}$  long pass filter was placed in front of the spectrometer to block laser scattering. The spectrometer was set to a monitor wavelength of 3.3  $\mu\text{m}$  and a slit width of 0.25mm, which allowed the observation of LIBS emission features over a spectral bandwidth of  $\sim 2$   $\mu\text{m}$ . Figures 10 shows the atomic emissions from neutral potassium atoms centered at  $\sim 2.7$ , 3.1, 3.7, and 4.0  $\mu\text{m}$ , which were obtained by averaging the emissions resulting from a few laser shots (5-10 pulses). The observed LIBS emission features exhibited similar K atomic spectra as collected using a MCT single element detector and scanning spectrometer [9]. Similar spectra with slightly higher signal to noise ratio were also obtained for single shot measurements.



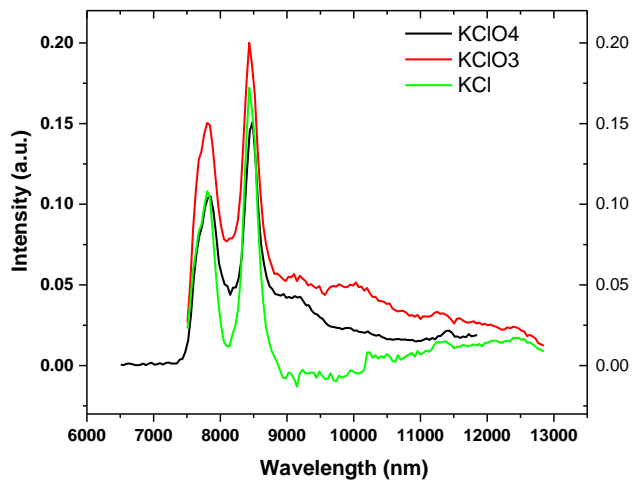
**Figure 10:** Mid-IR LIBS emission (2-4.5 $\mu\text{m}$ ) spectra of potassium compounds pellets recorded using the new MCT array detector system at HU.

The longer-wavelength IR LIBS emissions extending from  $\sim 5$ -10  $\mu\text{m}$  from several potassium compounds are shown in Fig. 11. The spectra were recorded using a grating blazed at 8  $\mu\text{m}$ , a monitor wavelength of 7.5  $\mu\text{m}$ , and a slit width of 2mm. The spectra were with a gate delay of 5  $\mu\text{s}$  and gate width of 15  $\mu\text{s}$ . LIBS emission signatures were observed from all samples at  $\sim 6$   $\mu\text{m}$ , 7.4  $\mu\text{m}$ , and 8  $\mu\text{m}$  [11,12].



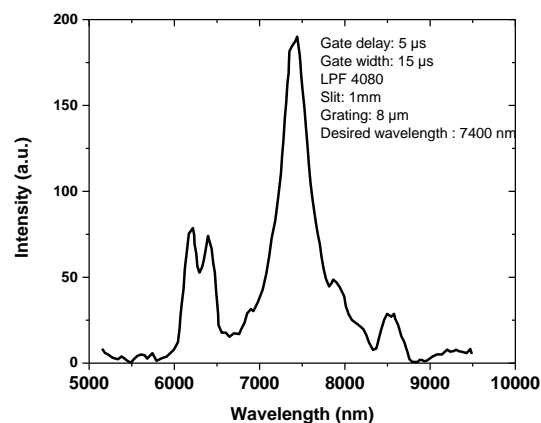
**Figure 11:** Long-wavelength IR LIBS (5-10  $\mu\text{m}$ ) emission spectra of potassium compounds pellets recorded by a MCT array detector system and integrated over only 5-10 laser pulses.

Figure 12 shows results of IR LIBS measurement with a monitor wavelength of  $\sim 10.2 \mu\text{m}$ , which extended the maximum observed emission bandwidth to  $\sim 12.5 \mu\text{m}$ . The spectra were recorded using a  $7.4 \mu\text{m}$  long pass filter blocking laser scattering and lower wavelength LIBS emissions. The spectrometer slit width was adjusted to 1 mm and a gate delay of  $5 \mu\text{s}$  and gate width of  $15 \mu\text{s}$  were selected. LIBS emission signatures were observed from all samples at  $\sim 6 \mu\text{m}$ ,  $7.4 \mu\text{m}$ , and  $8 \mu\text{m}$ . In addition, a weaker molecular emission signature from  $\text{ClO}_3^-$  at  $\sim 10.5 \mu\text{m}$  and from  $\text{ClO}_4^-$  at  $\sim 9.5 \mu\text{m}$  was clearly observed in the  $\text{KClO}_3$  and  $\text{KClO}_4$  sample, respectively [12]. The observed molecular emissions from  $\text{KClO}_3$  and  $\text{KClO}_4$  samples are unique LIBS feature critical for identification of these compounds. It was noticed, however, that observation of the broad molecular bands with long-lived emission contributions was very sensitive to laboratory vibrations impacting the mechanical stability of the array detector with its attached wiring. Further improvements in the detector stability needs to be achieved in order to extend the observation of molecular emission bands into the LWIR region.



**Figure 12:** Long-wavelength IR LIBS (7-13  $\mu\text{m}$ ) emission spectra of potassium compounds pellets recorded by a MCT array detector system. Atomic and molecular emission features were observed from  $\text{KClO}_3$  and  $\text{KClO}_4$  samples.

Figure 13 shows an attempt to measure the IR LIBS emission from a thin film of  $\text{KClO}_3$  on an aluminum substrate. The characteristic IR LIBS emission features from neutral potassium ions was clearly observed with emission signatures at  $\sim 6.2 \mu\text{m}$ ,  $7.5 \mu\text{m}$ , and  $8.5 \mu\text{m}$  [11,12]



**Figure 13:** Long-wavelength IR LIBS (5-10  $\mu\text{m}$ ) emission spectra of a  $\text{KClO}_3$  film deposited on an aluminum substrate using a MCT array detector system. The atomic MIR emission features of neutral potassium atoms at  $\sim 6.2 \mu\text{m}$ ,  $7.5 \mu\text{m}$ , and  $8.5 \mu\text{m}$  were clearly observed.



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