R3-C: Standoff Detection of Explosives: Infrared (IR) Spectroscopy Chemical Sensing

1. PARTICIPANTS

<table>
<thead>
<tr>
<th>Faculty/Staff</th>
<th>Name</th>
<th>Title</th>
<th>Institution</th>
<th>Email</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Samuel P. Hernández-Rivera</td>
<td>PI</td>
<td>UPRM</td>
<td><a href="mailto:samuel.hernandez3@upr.edu">samuel.hernandez3@upr.edu</a></td>
</tr>
<tr>
<td></td>
<td>Leonardo C. Pacheco-Londoño</td>
<td>Research Associate</td>
<td>Simón Bolívar Univ. Colombia</td>
<td><a href="mailto:leonardo.pacheco@upr.edu">leonardo.pacheco@upr.edu</a></td>
</tr>
<tr>
<td></td>
<td>Nataly J. Galán-Freyle</td>
<td>Research Associate</td>
<td>Simón Bolívar Univ. Colombia</td>
<td><a href="mailto:nataly.galan@upr.edu">nataly.galan@upr.edu</a></td>
</tr>
<tr>
<td></td>
<td>Joaquín A. Aparicio-Bolaño</td>
<td>DHS MSI-SRTP-Follow On Grant 2016</td>
<td>UPR-Ponce</td>
<td><a href="mailto:joaquin.aparicio@upr.edu">joaquin.aparicio@upr.edu</a></td>
</tr>
<tr>
<td></td>
<td>Ricardo Infante-Castillo</td>
<td>DHS MSI-SRTP-2017</td>
<td>UPR-Arecibo</td>
<td><a href="mailto:ricardo.infante1@upr.edu">ricardo.infante1@upr.edu</a></td>
</tr>
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<tr>
<th>Graduate, Undergraduate, and REU Students</th>
<th>Name</th>
<th>Degree Pursued</th>
<th>Institution</th>
<th>Month/Year of Graduation</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>José L. Ruiz-Caballero</td>
<td>PhD</td>
<td>UPRM</td>
<td>6/2017</td>
</tr>
<tr>
<td></td>
<td>Nelson Granda-Paz</td>
<td>PhD</td>
<td>UPRM</td>
<td>6/2018</td>
</tr>
<tr>
<td></td>
<td>Vladimir Villanueva-López</td>
<td>PhD</td>
<td>UPRM</td>
<td>6/2019</td>
</tr>
<tr>
<td></td>
<td>Amanda M. Figueroa-Navedo</td>
<td>MS</td>
<td>UPRM</td>
<td>6/2017</td>
</tr>
<tr>
<td></td>
<td>Juan E. Tió-Pagán</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2018</td>
</tr>
<tr>
<td></td>
<td>Luis A. Blanco-Riveiro</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2019</td>
</tr>
<tr>
<td></td>
<td>Carrie M. Maymón-Bacó</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2018</td>
</tr>
<tr>
<td></td>
<td>Adriana Vega-Galichet</td>
<td>BS/REU Summer 2016</td>
<td>UPRM</td>
<td>6/2017</td>
</tr>
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<td></td>
<td>Joel A. Gutiérrez-Torres</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2018</td>
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<td></td>
<td>Diego G. Rivera-Campos</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2018</td>
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<tr>
<td></td>
<td>Natalie López-Rodríguez</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2019</td>
</tr>
<tr>
<td></td>
<td>Miguel A. Hernandez-Rovira</td>
<td>BS/REU Summer 2017</td>
<td>UPRM</td>
<td>6/2020</td>
</tr>
<tr>
<td></td>
<td>Marializ Nieves-Maldonado</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2019</td>
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<td></td>
<td>Alexandra Quiñones-Meléndez</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2019</td>
</tr>
<tr>
<td></td>
<td>Isaac A. Ramírez-Marrero</td>
<td>BS/REU Summer 2017</td>
<td>UPRM</td>
<td>6/2019</td>
</tr>
<tr>
<td></td>
<td>Sixto A. Ramírez-Vega</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2018</td>
</tr>
<tr>
<td></td>
<td>Josué A. Rivera-Ramos</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2019</td>
</tr>
<tr>
<td></td>
<td>Víctor F. Rivera-Santana</td>
<td>BS</td>
<td>UPRM</td>
<td>12/2017</td>
</tr>
<tr>
<td></td>
<td>Norberto Valladares-Bonilla</td>
<td>BS</td>
<td>UPRM</td>
<td>12/2017</td>
</tr>
<tr>
<td></td>
<td>Blanca M. López-Pagán</td>
<td>BS/REU Summer 2017</td>
<td>UPRM</td>
<td>6/2020</td>
</tr>
<tr>
<td></td>
<td>Emy R. Mina-Barzola</td>
<td>HS</td>
<td>Immaculate Conception High School</td>
<td>5/2017</td>
</tr>
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II. PROJECT OVERVIEW

A. Project Overview

This project centers on applications of standoff (SO) infrared spectroscopy (IRS) coupled to laser sources operating in the mid-infrared range (MIR) to develop confirming chemical sensors for detecting explosives residues on clothing, travel bags, personal bags, laptop bags/cases, skin, and other substrates. Quantum cascade lasers (QCLs) are used as excitation sources. QCLs have revolutionized IRS applications since these sources are much brighter than thermal sources (globars) and even brighter than synchrotron sources. The secondary or confirming chemical sensors can be used in an orthogonal sensing scheme after remote detection of anomalies/devices under clothing and within human bodies by millimeter wave sensing. Multivariate analysis routines are then coupled with the detection step, providing target identification and discrimination from substrates and other interferences, and even quantification of highly energetic materials (HEMs).

The main obstacle to overcome is the discrimination of nitroexplosives from highly interfering, MIR-absorbing substrates (matrices) on which explosives residues are found. The techniques evaluated provide either a positive/negative result or a confidence-level indication to the operator for the presence of explosives within 1 minute (in most cases, a few seconds), while operating effectively in a field environment at multiple distances with varying levels of relative humidity, air particulates, temperature, light, and wind.

The vibrations in nitroexplosive compounds are remarkably insensitive to differences in the local chemical environment and these could therefore be used as detection tags. The presence of nitro group bands evidenced by signatures at 760 cm⁻¹, ~1350 cm⁻¹ (symmetric -NO₂ stretch) and ~1600 cm⁻¹ (asymmetric -NO₂ stretch) can be used as markers within nitrocompounds. These signatures can be universally used to detect these compounds from a distance. The requirements for remote detection of these signatures include the following characteristics:

• Capability of detecting explosives at a distance under non-contact conditions.

• Universality – the techniques should detect all types of explosives.

• Specificity – the techniques should be able to detect and identify explosives and formulations (including explosive mixtures) with relatively few false positives.

• Rapid – The technique should be capable of providing results in a short time (~ few sec).

• Sensitivity – the techniques should be capable of detecting samples with sufficient sensitivity.

A second objective is to generate a library of adaptable infrared absorbance/reflectance spectra for a variety of HEMs on various substrate surfaces. An addressable library of HEMs is being created, tested, and will be made available to the Homeland Security Enterprise (HSE). The spectra in the library will be able to be modified or morphed according to models that consider the spectroscopic measurement conditions, the physical features of the HEM residues, and the characteristics of the substrate surfaces. This library is intended to be useful for both the identification of single target chemicals that are combined with many clutter species as well as the discrimination among multiple target chemicals that are mixed with each other and with additional clutter species. The library will contain more than 30 HEMs and seven or more substrate types. Target chemicals will include high explosives, explosives formulations, explosives mixtures, non-nitrogen based explosives (such as cyclic organic peroxides) ammonium nitrate/fuel oil and other homemade explosives (HMEs), as well as precursors of some of these chemicals. Substrates could be metals or non-metals. The concentration of a given solid on a surface can be 1 μg/cm² or lower. Single target chemicals can represent as little as 0.1% of the overall residues. Development of this library will include the preparation of samples comprising chemical residues on the surface of a substrate, spectroscopic characterization of samples like the ones prepared and the investigation and modeling of various measurement effects and residue/substrate effects. The measurements performed at the University of Puerto Rico at Mayagüez (UPRM) will make use of several available spectroscopic measurement instruments, including an FT-IR spectrometer, tunable QCL...
The specific aims of the research include:

- Detection of explosives on metallic and mate substrates at close distances (∼ 15 cm).
- Discrimination of explosives from interferences, including highly MIR absorbing substrates.
- Detection of explosives on substrates at mid-range distances (∼ 1-10 m).

The challenges/obstacles encountered, which the research intends to address, include the following:

- Establish the differences between real samples vs. lab prepared samples in detection of explosives with MIR laser spectroscopy.
- Detection of explosives traces with MIR lasers at off-normal incidence geometries in preparation for whole body scanning.
- Detection of explosives with MIR laser spectroscopy of moving targets.

Overcoming these challenges requires transitioning from a commercially available MIR laser spectrometer operating at close distances (∼ 15 cm) to a homebuilt system with the following characteristics:

- Highly collimated laser beams with capabilities for sensing at mid-distances (1-10 m) and long distances (10-30 m).
- Higher power QCL systems: 50 – 200 mW.
- Wide spectral coverage: 1000 cm⁻¹: 830–1850 cm⁻¹ (5.5 – 12 µm).
- Fast scanning system: 5 s (or less).

Three optical setups are currently being evaluated and compared for developing methodologies for SO detection of HEM:

- Direct detection mode, in which detection is accomplished using QCL spectrometers (2) without modifying the output beam (∼ 2 mm x 4 mm) of the available spectroscopic systems.
- Coupling the output beam of spectrometers to MIR beam expanders to achieve a nominal expanded sensing area of 12 mm x 24 mm.
- Coupling the output beam of our QCL spectrometers to a specially designed, compact grazing angle probe (GAP) mount to enable reflection-absorption infrared spectroscopy (RAIS) measurements at 82° from the surface normal.

This work is different from other groups in that it addresses detection of explosives residues of mass range from milligram to picogram that are deposited on real world substrates: bare and painted metal parts, clothing, travel bags, personal bags, laptop bags/cases, automobile parts, skin, and other relevant substrates. MIR laser spectroscopy signatures obtained in this mass range allow for the identification and quantification of explosives.

B. Year Two (July 2014 through June 2015) Biennial Review Results and Related Actions to Address

The Biennial Review panel identified the following weaknesses for the project:

- Does the approach described in the project fill the technology gap of translating MIR reflectance spectra of explosives on complex substrates into a detection methodology?
- Can the research team pursue investigation of more complex clothes/fabrics (including colored fabrics)?
- Can the approach be extended to the ultraviolet (UV) region?
- Can the approach be transitioned to field-type applications?
- There is no evidence of an understandable agreement between these parties describing a realistic vision/
plan for how results will be transitioned.

Plans for addressing the weaknesses identified by the Biennial Review panel:

- Demonstration that MIR reflectance spectra of explosives deposited on complex substrates using multivariate analysis (chemometrics) techniques can transform into practical explosives detection techniques. Low signal to noise ratios (S/N) are obtained when using conventional thermal sources. MIR laser sources have led the way to much higher S/N, leading to the opportunity of achieving the project goal. This has been documented in “Castro-Suarez, J.R., Hidalgo-Santiago, M., Hernández-Rivera, S.P. ‘Detection of highly energetic materials on non-reflective substrates using quantum cascade laser spectroscopy,’ 2015, Applied Spectroscopy, 69(9): 1023-1035.” Other similar contributions have more recently been published (Castro-Suarez, J.R., Pacheco-Londoño, L.C., Aparicio-Bolaño, J., Hernández-Rivera, S.P. “Active Mode Remote Infrared Spectroscopy Detection of TNT and PETN on Aluminum Substrates,” 2017, Journal of Spectroscopy, 2017: 2730371). Other works have also been submitted for publication.

- Our research efforts will expand to include more fabrics, including dyed ornaments.

- The way to extend the research to the UV region would be to use an UV-Raman Telescope; however, although the eye does not focus the UV light, lasers required to build such a system are not eye-safe.

- The approach is very transferable to field applications. Year 5 will focus on this.

- Transition plans are discussed in the next sections. An invention has recently been disclosed for patent filling on the coupling of thin layer chromatography (TLC) with QCL spectroscopy for the separation, identification, and quantification of explosives present in dirt and soils. More recently, the coupling of QCL sources with a grazing angle mount have also been described for filing of another invention disclosure. With this setup, reflection absorption infrared spectroscopy (RAIRS) measurements of thin explosives deposits on metallic and non-metallic substrates have been carried out.

C. State of the Art and Technical Approach

Vibrational spectroscopy can be used for identifying and quantifying samples in complex matrices because each substance has a unique spectrum in the fingerprint and fundamental vibrations regions of the MIR region and corresponding Raman shift regions [1-6]. IRS is a well-established discipline within science and technology fields, and it has continuously evolved over the past 200 years [1-3]. Throughout this time, IRS gradually developed all of its major modalities: absorption/transmission, reflection, and emission spectroscopies; it has benefited from technological developments in spectral sorting capabilities (gratings in lieu of prisms; interferometers in lieu of dispersive spectrometers), improvements in detection technologies, development of water resistant optical elements, and in fast processing data analysis: Fourier transformation [1-6]. However, one area that has lagged in incremental developments and improvements, until recently, has been in the energy sources used for excitation of infrared spectra. Only polychromatic thermal sources (globars) have been traditionally available [3].

The difference in inherent strength of the photonic mechanisms that enable IRS and RS as dominant techniques of molecular spectroscopy limits their capabilities and use in applications of SO detection of threat chemical compounds. IRS being a photonic absorption process is a much stronger process than the inelastic scattering of photons in a Raman event. This enables SO-IRS with the capability of near trace detection of target chemicals up to tens of meters. On the other hand, RS is supported by important properties of lasers, which enable SO ranges as long as 1 km, but is limited to bulk amounts of samples (as low as several mg) and gaseous molecules of small molecules due to the weakness of the scattering event. Both IRS and RS, in their various modalities, have been shown to be useful for characterization, detection, identification, and quantification of threat chemicals, among them HEMs and HMEs [6-17]. Over the past 25 years, the techniques have frequently been used in SO mode to deter terrorist threats by providing the basis for the required countermeasures to prevent explosives events. Fundamental and applied research in areas of interest to national
defense and security focusing on remote detection of HEMs and HMEs that could be used as weapons of mass destruction has been reviewed regularly [7-17].

The need to develop more powerful MIR sources that enable detection at longer distances when a target hazardous threat chemical is located on a substrate in the form of a residue at trace or near trace levels suggests the use of collimated, coherent, and polarized sources. These sources were first developed in 1994 at Bell Labs with the invention of QCLs [18]. A QCL is a unipolar semiconductor injection laser based on sub-interband transitions in a multiple quantum-well heterostructure. As a semiconductor laser that can produce varying wavelengths and to operate at various temperatures, this type of laser has various advantages over other types of lasers [19-23]. QCLs can produce from a few tens to hundreds of milli watts of continuous mode or pulsed power under ambient conditions, are commercially available, and have enabled the development of ruggedized systems for the detection of hazardous chemical compounds. The increase in output power has enabled the use of QCL-based spectrometers in long distance (range) applications, making the detection of chemical and biological threat agents possible at tens of meters from the source [24-25].

Furthermore, QCLs can be operated in field conditions, allowing for the sensitive detection of HMEs such as triacetone triperoxide (TATP), of aliphatic nitrate esters such as pentaerythritol tetranitrate (PETN), of aliphatic nitramines such as RDX, and of nitroaromatic HEMs such as 2,4-dinitrotoluene (2,4-DNT) and 2,4,6-trinitrotoluene (TNT) in the vapor phase using photoacoustic spectroscopy [26-28]. The detection of TATP and TNT in the vapor phase has also been achieved using IRS with satisfactory results [28-29]. Moreover, the use of QCL sources has been useful for the remote detection of HEMs deposited on surfaces using photoacoustic and traditional infrared absorption spectroscopies [30-35]. Thundat’s group recently reported that nanomechanical IRS provides high selectivity for the detection of TNT, RDX, and PETN without the use of chemoselective interfaces by measuring the photothermal effect of the adsorbed molecules on a thermally sensitive microcantilever [36].

However, most of the previous investigations focused on the detection of HEMs deposited on nearly ideal, highly-reflective substrates such as highly polished metallic surfaces [33]. There are few published reports on the effects of non-ideal, low-reflectivity substrates on the spectra of the analyzed target HEM [35]. The work by Suter and collaborators (2012; PNNL), in which they measured the spectral and angular dependence of MIR diffuse scattering from explosives residues deposited on a painted car door using an external cavity QCL (EC-QCL), laid the foundation for part of the work that this research group pursues [34]. However, our approach is significantly different because it comprises detection, identification, and discrimination of explosives on highly interfering backgrounds such as a cotton shirts or pants, nylon and black polyester from laptop bags or travel cases, simulated human skin, and other compacted solid mixtures [35]. The work also centers on using robust chemometrics techniques for “on-the-fly” pattern recognition and discriminant analysis, with an expected turnaround response time from a few milliseconds to less than 1 second. The main difference between the expected contributions of this research and the current state of the art is in bridging the gap between lab experiments under well-controlled conditions and the real-world detection of explosives residues [36]. Angular dependence of source-target-detector in active mode SO-IRS [37], and dependence of detection limits on angular alignment, substrate type, and surface concentration in active mode SO-IRS [38], using globars both modulated and non-modulated, have also been measured as part of the group contributions.

D. Major Contributions

D.1. QCL-GAP RAIRS measurements of explosives residues

In situ trace level detection and identification of pollutants, threat chemical residues, and biofilms (films containing microorganisms) on surfaces is important for rapid and effective screening in different fields such as homeland security, defense, environmental sampling, clean validation in pharmaceutical and biotechnol-
ogy industries and others. In homeland security applications, fast trace detection of chemical and biological threat agents on contaminated surfaces is fundamental in the prevention, rapid performance, and execution of security protocols. Mid infrared (MIR) spectroscopy practiced at or near grazing angle of incidence is probably the most powerful technique for surface analysis of monolayers of chemicals and microorganisms deposited on surfaces. At high incident angles of a polarized MIR source, the phenomenon known as RAIRS takes place. However, to fully take advantage of the power within RAIS experiments, since the samples are so optically thin, to obtain spectra with good S/N, relatively long analysis times (from 5 to 120 min of integration) are typically required. This is because the absorbance of monolayers is low due to the low number density of molecules (microorganisms) present in the path of the MIR beam. Moreover, typical MIR sources have inherently low optical powers as is the case for thermal sources such as globars. The integration time can be reduced by multi reflection passes because the absorbance increases as is the case in multi pass cells used for phase gas analysis. However, there are significant light intensity losses with MIR mirrors, which do not have the high reflectivity that can be achieved in visible and ultraviolet coated mirrors. Moreover, scattering by imperfections of the substrates that contain the samples, MIR beam divergence, and absorption by substrates, samples and mirrors cause even more light losses. The need to develop more powerful MIR sources that enable RAIS data when a target chemical or microorganisms is deposited on substrates at trace levels suggests the use of collimated, coherent, and polarized sources. The ideal solution to many of these problems is to use a MIR tunable laser. These sources were first developed in 1994 at Bell Labs with the invention of the most well-known of these devices: quantum cascade lasers (QCLs) [18]. A QCL is a unipolar semiconductor injection laser based on sub-interband transitions in a multiple quantum-well heterostructure. As a semiconductor laser that can produce varying wavelengths and to operate at various temperatures, this type of laser has various advantages over other types of lasers [19]. QCLs can produce from a few tens to hundreds of milliwatts of continuous or pulsed modes power under ambient conditions. A QCL is an ideal source for RAIS experiments due to its properties such as the high brightness (six orders of magnitude larger than those of conventional thermal sources (globar)), portability, high optical power output, the room temperature operation, low energy consumption, long-term power stability, and ability to fine-tune the output frequency [39]. The central idea in this development is to design and build a two reflection passes optical probe mount operating as close as possible to the grazing angle and coupling it to a widely MIR laser source. This new prototype reduces the time analysis and improves S/N of RAIS spectra allowing for very low limits of detection of explosives and microorganisms. Further signal enhancement by applying powerful multivariate chemometrics routines allows for discrimination from vibrational signals originating from MIR absorbing substrates (such as plastics, including Teflon® and polyacrylate plates), interferences (such as dirt, and other components), other chemicals in mixtures (such as C-4 and Semtex-H), and other microorganisms in mixes of potential biothreats.

MIR spectroscopy operating at the grazing angle of incidence is the most sensitive optical absorption technique available for measuring low chemical concentrations on surfaces such as metals [4,40]. In addition, QCL spectroscopy can be used outside the confinement of the sample compartment, making it available for fieldwork. Thermal source (globar) fiber optic coupled grazing angle probe reflection absorption infrared spectroscopy (FOC-GAP-RAIRS) has been investigated before as a powerful tool to develop techniques for detection of explosives residues on surfaces. The methodology is remote sensed, in situ and can detect nanograms of the compounds. It is solvent free and requires no sample preparation. Samples with surface concentrations (Cₙ) ranging from micrograms/cm² to nanograms/cm² of explosives (DNT, TNT, PETN, nitroglycerine (NG) and triacetone triperoxide (TATP)) were studied on stainless steel plates with excellent results yielding 10-100x lower limits of detection (LODs) for explosives than for active pharmaceutical ingredients, for which the setup was originally developed. Recently, the first setup for coupling a QCL spectrometer to a home built grazing angle probe has been successfully tested for explosives detection on substrates. The complete setup is illustrated in Figure 1 (on the next page).
The limitation imposed by the available QCL spectrometer is related to the instrument design in which the MIR detector is located within the spectrometer and that the system operates only collecting the back reflected light. Preliminary results on detection of explosives residues on stainless steel plates with the unoptimized setup illustrated in Figure 1 are highly encouraging: 460 pg/cm² for ammonium nitrate, 73 pg/cm² for RDX, and 35 pg/cm² for PETN. These values are ~ $10^{-2}$-$10^{-3}$ times lower than currently reported LOD values for these explosives. In the (proposed) next generation design, the MIR detector will be placed at the plane of the second gold-coated mirror and placed at $82^\circ$ from the surface normal. Preliminary results are included in Figures 2 and 3 (on the next page).

**Figure 1:** Grazing angle probe mount for existing QCL spectrometer.
Figure 2: Reflectance spectra of RDX as function of the surface concentration using QCL-GAP setup.

Figure 3: Plot of signal/noise (S/N) as function of reciprocal of surface concentration to determine the value of the detection limit (DL).
D.2. Removal QCL-GAP Interference Fringes in RAIS Spectra of HEM

The proposition of using a QCL coupled to a GAP setup was evaluated for monolayer analysis of HEM residues. Principal component analysis (PCA) and partial least squares (PLS) multivariate routines of chemometrics were employed to verify the effect of preprocessing options for the MIR RAIS spectra obtained. Fast Fourier transform (FFT) analysis was also evaluated as a pre-processing method to evaluate reflectance spectra obtained for monolayers of RDX. Sensitivity and specificity values of 1.000 were obtained for quantitative models of the HEM by optimizing FFT parameters. This setup provides portability, low detection limits (DL) and facile coupling with QCL with multivariate analysis. The LOD for the RDX model was 7 ng/cm².

In-situ and non-destructive spectroscopic methods available for measuring low explosives concentrations on surfaces are methods based on reflectance mode grazing-angle spectroscopy in the near infrared (NIR) and MIR. An advantage of NIR spectroscopy is that the light can be back reflected off the sample without sample preparation. In comparison to MIR spectroscopy, the NIR technique does not work in the fingerprint region. This means that signals from functional groups such as C=O and C-N, among others, that do not include hydrogen, are not identifiable. In addition, in the NIR, observed overtones and combination bands are very broad and overlapped which makes it difficult to distinguish between signals. Conventional MIR grazing-angle spectroscopy has the disadvantage of sample positioning into the spectrometer, evidencing a lack of portability for the methodology. However, MIR grazing-angle spectroscopy coupled to fiber optic cable solves this problem, making it possible to move the fiber optic cable into the reactor for in-situ analysis [41-44]. The MIR region, working at the grazing angle of incidence (~ 80-82° from the surface normal), is considered one of the highest sensitive optical absorption techniques. This is able to measure low concentrations of chemical compounds deposited on the surfaces such as metals, glasses, and plastics [44]. Low limits of detection (LOD) from 10 to 50 ng/cm² of single analyte have been obtained [42].

This technique promotes the analysis of monolayers on surfaces. To obtain spectra with good S/N, it is necessary to apply a longer time of analysis (5-120 min of integration). This is due to the low absorbance of the monolayer. The integration time can be reduced by a multi-reflection pass because the absorbance is increased as well as in cell multi passes for gas analysis. For this reason, it is necessary to have an infrared high power source. With multiple reflections, the light is lost by phenomena such as scattering due to substrate, sample, and mirror imperfections. The divergence of beam and absorption by substrate, sample, and mirror are also factors that affect scattering.

For security applications, a variety of optical sensing methods including the current Quantum Cascade Laser (QCL) spectroscopy, Raman, FTIR, remote infrared spectroscopy (RIRS) and Laser-Induced Thermal Excitation of Infrared Emission are desirable for the detection of explosives [15, 22-23, 25, 39, 41-51]. The fast trace detection of chemical and biological threat agents on contaminated surfaces with high selectivity and specificity is fundamental in the prevention of terrorist attacks, and rapid performance and execution of security protocols. Ideally, analyte sensing on surfaces would be a rapid, in-situ, economic, portable, highly sensitive, and able to discriminate between components. Despite the challenges faced during sensing, a new set-up with multi reflection pass by a grazing angle probe using a QCL source was employed to improve the in-situ detection of organic contaminants on a surface. This new prototype reduced the time analysis and improves the spectra S/N ratio.

Therefore, the main objective of this study is to assess the QCL-GAP back-reflection grazing angle probe, which is suggested as a viable method to validate detection of explosives on metallic surfaces. A QCL-GAP was designed to obtain measurements in our laboratory. Back-reflectance spectra of RDX samples deposited on aluminum (Al) plates were obtained for a remote sensing modality.

Figure 4 (on the next page) shows the spectra of substrate clean (SS), the SS with the analyte loading (SS-RDX) at 16 ng/cm² of RDX and the spectra of the standard concentrated of RDX acquired with the conventional diffuse-reflection system of QCL for bulk samples (90° with respect to the surface normal). Interference patterns were observed (see Figure 4) in the spectra of substrate clean and with the analytes loading. These
patterns are due to the interference by multiples reflections in the system. The variation of interference patterns depending on whether the substrate is clean or loaded with the analyte can also be noticed. In the RDX spectra, some signals were observed with difficulty such as NO\textsubscript{2} symmetric stretch at 1275 cm\textsuperscript{-1} and N-N symmetric stretch at 1352 cm\textsuperscript{-1} [47,48].

To explain how the presence of the analyte in the surface change the interference pattern and discriminate between both, analytes and clean surfaces, the interference signals of each sample were transformed and exploited. Fast Fourier Transform (FFT) was applied as preprocessing to the data as shown in Figure 5. Figure 5a shows a sketch of the wave behavior when the surface is clean or where it has an analyte. Here, a single reflection representation is observed when the surface is clean. Multiple reflections are generated by the semi-transparent analytes when low concentrations are deposited. This interaction of the light with the surface causes a modification of the interference patterns depending on the analyte and the concentration deposited. Figure 5b shows the representation of the preprocessing FFT, which was created through a MATLAB code. The transformation of the data with the FFT preprocessing produces a complex function as a Fourier transform—this function consisting of an imaginary part (Im), another real part (Re), and the magnitude of the function expressed as the absolute value of z(n). These parameters will be used for the analysis to have a good model.

Figure 4: Spectra comparison of Al substrate, RDX/Al (~16 ng/cm\textsuperscript{2}), and the reference RDX standard.

Figure 5: FFT preprocessing assembly: (a) fringes from metallic substrate; and (b) fringes from analyte/substrate.
Figures 6a-c show the spectra transformation for substrate SS clean (none), SS contaminant with RDX, and IRBS. Basically, the FFT shows each frequency or modes that generated the interferences in the spectra. A detailed analysis of Figures 6a-c, shows that modes for RDX and IRBS are similar to clean SS and these differ in small modifications of these modes. These small modifications are due to the nature of the layer, shown as absorbance, homogeneity, refractive index, size of particle, and thickness of the layer. The Re function has a mode with a higher intensity than the others modes. This mode should be the principal interference which is generated between the lens and the mirror in back reflection. Basically, each transformation and other preprocessing were used for a principal component analysis (PCA) to verify the differences between the analytes and the clean surface. A complete separation of spectra without analytes, with RDX and IRBS was archived with the real part Re of FFT (see Figure 7d on the next page). The loadings for the analysis are shown in Figure 6d. Two components were necessary for a complete separation with Re FFT preprocessing. In comparison to other parameters of FFT and other preprocessing algorithms, the separation was not complete. The preprocessing used were standard normal variate (SNV), first derivative (FD), second derivative (SD), extended scatter correction (EMSC), multiplicative signal correction (MSC), Im and |z(n)|. Figures 7a-d show the correlation between the scores of PC1 and PC2 for the SNV, |z(n)|, Im and Re. A visualization of the separation between the classes using Re is clear and complete; the maximum separation was achieved with PC2.

Partial least squares coupled to discriminant analysis (PLS-DA) was employed using Re(FFT) as a preprocessing step and this analysis was done to measure the discriminant capacity. The number of points in FFT was changed to select the better resolution for the analysis. The sensitivity and specificity for leave one out
cross validation (LOOCV) were also calculated for different number of points for FFT. The PLS-DA models performance was evaluated through parameters of the confusion matrix such as sensitivity and specificity of the validation. The validation was initially evaluated in terms of LOOCV. Sensitivity is the number of samples predicted to be in the class divided by the actual number per class, and specificity is the number of samples predicted not to be in the class divided by the actual number not in the class. The sensitivity and specificity were calculated according to Equations 1 and 2, respectively:

\[
\text{Sensitivity} = \frac{TP}{TP + FN} \quad (1)
\]
\[
\text{Specificity} = \frac{TN}{TN + FP} \quad (2)
\]

where TP, FN, TN, and FP represent the number of True Positives, False Negatives, True Negatives, and False Positives, respectively. The best models were generated using 75 and 100 # of points in the FFT preprocessing (see Table 1 on the next page). These models present very high sensitivity and specificity. The parameters of cross validation for all models are shown in Table 1 with two latent variables. In addition, a model for quantification for RDX was generated.

Figure 7: PCA with (a) SNV preprocessing, (b) absolute values for FFT, (c) an imaginary part for FFT, and (d) a real part for FFT.
E. Milestones

Of the original proposed Year 4 milestones, the following were achieved:

- Study on effects of real-world samples, including non-uniform coverage and fingerprints on substrates.
- Synthetic skin was incorporated as one of the target substrates for explosives for detection.

The following additional milestones were also achieved:

- Three deposition methodologies were developed:
  - Spin coating deposition for smooth texture substrates, including metals, painted metals, plastic sheets, and others.
  - Thumb printing deposition for rough and porous surfaces, and for fabrics, cardboard, wood, and others. This deposition method was also used for transferring explosives crystalline particles to any substrate type.
  - Inkjet printing deposition for standards and samples for trace level MIR laser detection.
- Study of effects of polymorphism of RDX in sample distribution and in MIR laser signatures detected.
- Study of optical properties of RDX in the MIR for gold and stainless steel substrates.

The overall final goal of this project is to be able to detect explosives residues on substrates of moving targets, independent of the incident angle of the MIR beam. In order to achieve this goal, the following milestones proposed in Years 4 and 5 will be carried over for completion during Year 5:

- Simulated field detection experiments on static targets at distances of 1-50 m.
- Sensing at off-normal incidence geometries is in preparation for whole body scanning.

<table>
<thead>
<tr>
<th># points</th>
<th>Sensitivity</th>
<th>Specificity</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>substrate</td>
<td>RDX</td>
</tr>
<tr>
<td></td>
<td>substrate</td>
<td>RDX</td>
</tr>
<tr>
<td>10</td>
<td>0.900</td>
<td>0.893</td>
</tr>
<tr>
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</tr>
<tr>
<td>1000</td>
<td>1.000</td>
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</table>

Table 1: Sensitivity and specificity for leave one out cross validation for two latent variables.
Achievement of these goals depends on transitioning to the homebuilt QCL spectrometer described before. All the parts required were acquired during Year 4. Assembly of the first optical layout has been tested. The remaining work is to program the data acquisition routines in LabView (NI).

F. Future Plans

Several projects have been planned as a continuation of the efforts in the vibrational-spectroscopy-based chemical detection of explosives:

1. Continue coupling of TLC with QCLs. Several substrates will be investigated for Surface Enhanced Infra-red Absorption (SEIRA) spectroscopy for enhanced explosives detection.

2. Continue development of a grazing angle probe coupled to MIR tunable laser sources (such as QCLs). At or near the grazing angle leads to RAIS, which is one of the most sensitive spectroscopic techniques for thin films and trace analysis.

3. Continue building the addressable library of HEM/HME independent of substrate type.

4. Year 5 of this project also contemplates the transition to a higher power QCL source that will be used for remote sensing measurements at much longer distances. Work on the LabView based interface and data acquisition and analysis module will be completed during Summer 2017.

5. Anticipated end date of several objectives of the project is June 2018. However, recent developments within our research group related to two grazing angle probe setups (two invention disclosures in preparation for subsequent filing for patent applications) promise to result in even lower detection limits for threat chemicals and explosives resulting in more applications, transferable to remote detection of explosives.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

The overall final goal of this project is to detect and discriminate explosives residues on substrates of moving targets, independent of the incident angle of the MIR beam. To achieve this goal, the following obstacles must be circumvented:

1. Having access to improved/fieldable QCL systems:
   a. Higher power QCL systems: current ~ 5 mW; sought: 50 – 200 mW.
   b. Wider spectral coverage: 1000 cm\(^{-1}\): 830–1800 cm\(^{-1}\) (12-6 µm).

2. Faster scanning system: current ~ a spectrum (3 averaged acquisitions) in 15 s; sought: 5 s (or less).

This project also intends to expand the knowledge in the field of preparation and characterization of samples and standards based on thin films and islands of HEMs/HMEs for both basic and applied research. Depositing traces of target analytes on substrates of high interest using spin coating technology develops the mentioned assemblies and thumbprints of HEMs/HMEs that simulate fingerprints of explosives on substrates. A Confocal Raman-AFM-SNOM Imaging Spectroscopic System will be used for characterization studies.

The following specific deliverable is relevant to the DHS Enterprise: The development and use of a QCL MIR portable standoff detection system coupled with multivariate analysis routines capable of detecting, identifying, and discriminating for HEMs/HMEs. The main use of this system is as confirming sensors for explosives residues on cloth, luggage, and other substrates down to ng/cm\(^2\). This system should provide first responders with a highly-versatile tool for explosives detection at close range.
B. Potential for Transition

The ultimate transition products/outcomes of the research endeavors include:

- Dissemination of research and development efforts via research reports, discussion of data with potential transition partners, presentations at national and international meetings, publications, and submission of invention disclosures (2 recent; 4 in total).
- Methodology based on MIR laser spectroscopy for detection of explosives in “direct pointing” mode on reflective and mate substrates.
- Methodology based on MIR laser spectroscopy coupled to thin layer chromatography for separation, detection, and quantification of explosives with detection limits to 70 ng.
- Methodology based on coupling MIR laser spectroscopy to grazing angle probe for detection of traces of explosives (< 100 pg) on reflective and mate substrates.
- Libraries of MIR laser spectroscopy signatures for HE/HEM using all of the methodologies developed and any substrate type: reflective and mate. The libraries are based on “intelligent” routines that have the capability of incorporating signatures for new explosives threats “on the fly” using adaptive routines.

C. Data and/or IP Acquisition Strategy

Possible IP and disclosures are in the area of spectral libraries. Our research group has been very active in protecting IP with three invention disclosures and one patent awarded in recent years.

D. Transition Pathway

- Commercialization through Pendar Tech and other QCL manufacturers
- Planning of a joint venture with VERLUZ, LLC (Humacao, PR), a division of Pacific Advanced Technology, Corp. (Solvang, CA); Michele Hinricks (Founder and CEO)
- DHS: Jim Jensen & Adolfo Negrón at DHS in Edgewood Chemical Biological Center
- DTRA and other DOD divisions

Engagement with potential customers will begin as soon as testing of QCL-GAP capabilities and building of libraries have been completed.

E. Customer Connections

A partnership with Pendar Technologies (formerly Eos Photonics) was directed at the development of a hand-held explosives detection system based on QCL arrays. We anticipate that our facilities will serve as a beta-test site for some of the technologies and applications under development, and that we will eventually become commercialization partners with this and other companies. Another targeted partnership is with VERLUZ, LLC for development of a QCL-Imaging MIR Camera detection system.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Student Internship, Job, and/or Research Opportunities
   a. Amanda M. Figueroa-Navedo, Summer 2017, Research Internship at Transportation Security Labs, Atlantic City International Airport, Atlantic City, NJ.
b. Sebastián Pérez-Orozco, Summer 2017, BioREU Program, Johns Hopkins University, Baltimore, MD.

c. Carrie M. Maymón-Bacó, Summer 2017, Pre-Medical Training Program, Dr. García-Rinaldi Foundation, Mayaguez, PR.

2. Interactions and Outreach to K-12, Community College, and/or Minority Serving Institution Students or Faculty

a. Served as host for 2 high school students and 1 junior high school student participating in Science Fair projects.

b. Served as collaborator and host for Follow-On Project of DHS SRTP-MSI Grant of Dr. Joaquín A. Aparicio-Bolaño, University of Puerto Rico-Ponce Campus ($50,000/1 year).

c. Served as host for DHS-SRTP-MSI-2017 Visiting Professor Dr. Ricardo Infante-Castillo and two Summer Research Undergraduate Students.

3. Training to Professionals

a. Puerto Rico Chemists Association Continued Education Program, Course in Chemistry of Explosives, November 2016, Southeastern Section, Aguadilla, PR, 65 attendees.

b. Puerto Rico Chemists Association Continued Education Program, Course in Spectroscopic Stand-off Detection of Chemical Threats, August 2016, Annual Convention, 72 attendees.

4. Other Outcomes that Relate to Educational Improvement or Workforce Development

a. Jorge Castellanos, hired as Research Scientist, Naval Surface Warfare Center – Indian Head Division, Indian Head, MD.

B. Peer Reviewed Journal Articles


Pending -


C. **Student Theses or Dissertations Produced from This Project**


D. **New and Existing Courses Developed and Student Enrollment**

<table>
<thead>
<tr>
<th>New or Existing</th>
<th>Course/Module/ Degree/Cert.</th>
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<th>Student Enrollment</th>
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<td>Existing</td>
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<td>For students of Chemistry and Chemical Engineering</td>
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<td>Existing</td>
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<td>CHEM 5175: Explosives Detection &amp; Analysis</td>
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E. **Technology Transfer/Patents**

1. Inventions Disclosed
   a. “Coupling of thin layer chromatography (TLC) to quantum cascade laser spectroscopy (QCLS) for qualitative and quantitative field analyses of explosives and other pollutants.” Inventors: Samuel P. Hernández-Rivera and John R. Castro-Suarez. Serial No.: 62/346,145. Filing Date: June 06, 2016. Docket No.: UPR-16253

2. Patent Applications Filed (Including Provisional Patents)

F. **Software Developed**

1. Algorithms: Fast Fourier Transform pre-processing programmed in in MATLAB® 8.6.0.267246 (R2015b; Math Works Inc. Natick, USA). This algorithm is being used to remove interference fringes from thin HEM films generated by GAP-QCL RAIS measurements.

V. **REFERENCES**


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