I. PARTICIPANTS

### Faculty/Staff

<table>
<thead>
<tr>
<th>Name</th>
<th>Title</th>
<th>Institution</th>
<th>Email</th>
</tr>
</thead>
<tbody>
<tr>
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### Graduate, Undergraduate and REU Students

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<th>Degree Pursued</th>
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<th>Month/Year of Graduation</th>
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<tr>
<td>Nataly Galán</td>
<td>Ph.D.</td>
<td>UPRM</td>
<td>6/2016</td>
</tr>
<tr>
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<td>Ph.D.</td>
<td>UPRM</td>
<td>6/2017</td>
</tr>
<tr>
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<td>UPRM</td>
<td>6/2016</td>
</tr>
<tr>
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<td>Ph.D.</td>
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<td>6/2017</td>
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<tr>
<td>Amanda M. Figueroa</td>
<td>BS/MS</td>
<td>UPRM</td>
<td>6/2016-6/2018</td>
</tr>
<tr>
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<td>BS</td>
<td>UPRM</td>
<td>6/2017</td>
</tr>
<tr>
<td>Jorge L. Rosa</td>
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<td>UPRM</td>
<td>6/2017</td>
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<td>Michael Siberón-Guzmán</td>
<td>BS</td>
<td>UPRM-Ponce</td>
<td>12/2017</td>
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<tr>
<td>Juan E. Tió-Pagán</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2018</td>
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<td>Axel R. Rivera Larrieux</td>
<td>BS</td>
<td>UPRM</td>
<td>6/2017</td>
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<tr>
<td>Luis A. Blanco-Riveiro</td>
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<tr>
<td>Carrie M. Maymon-Baco</td>
<td>BS</td>
<td>UPRM</td>
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<tr>
<td>Ariana Vega-Galichet</td>
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<td>UPRM</td>
<td>6/2017</td>
</tr>
<tr>
<td>Emy R. Mina-Barzola</td>
<td>HS</td>
<td>Immaculate Conception High School</td>
<td>6/2017</td>
</tr>
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</table>

II. PROJECT DESCRIPTION

A. Project Overview

This project deals with the use of infrared spectroscopy (IRS) in standoff (SO) mode, and coupled with laser sources operating in the mid-infrared (MIR), to develop confirming (orthogonal chemical) sensors for detecting explosives residues on clothing, travel bags, personal bags, laptop bags/cases, skin, and other substrates. The main hurdle to overcome is discriminating the nitro- or peroxy-based explosives from highly interfer-
ing, MIR-absorbing substrates (matrices) in which explosives are found. Quantum cascade lasers (QCLs) will be used as energy sources. QCLs have revolutionized MIR spectroscopy applications. The techniques evaluated will provide either a positive/negative or a confidence-level indication to the operator for the presence of explosives within 1 min (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.

A main objective of the tasks performed by the ALERT research and education components at the University of Puerto Rico at Mayaguez (UPRM) is to lay the foundation for the SO detection of explosives on highly MIR-absorbing substrates, including natural and synthetic fibers, cardboard, wood, and plastics. The second objective is to generate a library of adaptable infrared absorbance/reflectance spectra for a variety of highly energetic materials (HEMs) on various substrate surfaces. An addressable library of HEMs will be constructed, tested, and made available. 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 can include as many as 30 HEMs and seven or more substrate types. Target chemicals will include high explosives, explosives formulations, non-nitrogen-based homemade explosives (HMEs), and co-indicator compounds and precursors of these various chemicals. Substrates could be metals or non-metals and could have high infrared transmittance of reflectance or absorbance; they could also have low infrared transmittance, reflectance, or absorbance. The concentration of a given dilute solid on a surface can be 1 μg/cm² or lower. Single target chemicals can represent as little as 0.1% of the overall residue. Mixtures can have as many as 5 to 10 target components plus 15 or more additional background chemicals, with a given target component representing as little as 1% of the overall amount of residue on a surface. 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 UPRM will make use of several spectroscopic measurement instruments available, including an FT-IR spectrometer, tunable QCL sources, and photodetectors.

B. Biennial Review Results and Related Actions to Address

The Biennial Review panels have 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 the investigation of more complex clothes and 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.
- The technique is capable of “providing forensic evidence” by analysis of post-blast residue. The term “forensic” should not be used in this instance until it has been verified and validated fully.

Plans for addressing the Biennial Review panels’ concerns:

- Our research group has demonstrated that it is possible to translate MIR reflectance spectra of explosives deposited on complex substrates using multivariate analysis techniques. This was not possible before due to low signal to noise ratios (S/N) when using conventional thermal MIR sources. QCLs and other
tunable laser sources have led the way to much higher S/N, creating the opportunity to do the analysis. This is described 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. Appl. Spectrosc. 69(9) 1023-1035.

<table>
<thead>
<tr>
<th>Fabrics</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lycra</td>
<td>84% Polyester, 16% Spandex</td>
</tr>
<tr>
<td>White A</td>
<td>65% Polyester, 35% Cotton</td>
</tr>
<tr>
<td>White B</td>
<td>45% Polyester, 55% Cotton</td>
</tr>
<tr>
<td>Basketball Short</td>
<td>100% Polyester</td>
</tr>
<tr>
<td>Sweater</td>
<td>55% Cotton, 29% Rayon, 16% Nylon</td>
</tr>
<tr>
<td>Pink Shirt</td>
<td>100% Cotton</td>
</tr>
<tr>
<td>White-Pink shirt</td>
<td>100% Polyester</td>
</tr>
<tr>
<td>Gray shirt</td>
<td>65% Polyester, 25% Rayon, 10% Spandex</td>
</tr>
<tr>
<td>Swimsuit</td>
<td>(82% Nylon, 18% Spandex)</td>
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<tr>
<td>Green shirt</td>
<td>50% Cotton, 50% Polyester</td>
</tr>
<tr>
<td>Violet shirt</td>
<td>52% Cotton, 48% Modal</td>
</tr>
</tbody>
</table>

Table 1: List of fabric that this project intends to use in future substrate experimentation.

- Our research efforts will expand to include more fabrics, including dyed ornaments. Table 1 details the fabrics we intend to use.
- 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 UV light, lasers required to build such a system are not totally eye-safe.
- The approach is very transferable to field applications.
- Transition plans are discussed in Section III. 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.
- The term “forensic evidence” will be deleted.

C. State of the Art and Technical Approach

Vibrational spectroscopy consists of two main techniques: IRS and Raman scattering (RS). Spectra obtained by means of these techniques 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 [1-5]. The two techniques are, in general, complementary in the information they provide. When coupled with multivariate chemometrics routines, IRS and RS can be used for discriminating between interfering substrates and other analytes, even when the target analyte is in very small quantities [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 has gradually developed all of its major modalities: absorption/transmission, reflection, and emission spectroscopies, has and benefited from technological developments in spectral sorting capabilities (gratings in lieu prisms; interferometers in lieu of dispersive spectrometers), improvements in detection technologies, in development of water resistant optical elements, and in fast processing data analysis: Fourier transformation [1-5]. However, one area that has lagged in incremental developments and improvements until recently has been in the energy sources 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 enables 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 [8-17]. 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 has the ability to produce varying wavelengths and to operate at various temperatures, this type of laser has various advantages over other types of lasers [19-23]. QCLs are capable of producing 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 and 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, the majority of 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 s. 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.
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 spectroscopy-least squares detection of HEMs on cotton

QCL spectroscopy was used to discriminate for the presence of HEMs on cotton. The identification of vibrational signals was accomplished via a simple and fast spectral evaluation using the capabilities of the classical least squares (CLS) method, which strives to minimize the difference of a real spectrum and a calculated spectrum. A model to obtain the calculated spectrum involves obtaining a linear combination of the HEM spectrum, the cotton spectrum, and a bias was proposed. Three experiments considering binary, ternary, and quaternary combinations of components such as cotton, TNT, RDX, and PETN were performed. The parameters calculated for the linear combination of the calculated spectrum were used to generate a discriminant analysis in order to determine the sensitivity and specificity. In addition, the extracted spectral signals of several amounts (> 0.02 mg) of RDX on cotton were used to calculate the limit of detection (LOD) from the measured S/N. The S/N was determined from different spectra of cotton with different amounts of RDX in decreasing order until the S/N was 3. The LOD for RDX was 22 ± 6 μg.

The HEMs samples were deposited on cotton by direct download of the solid. Two types of procedures were used for HEM deposition. First, an amount of HEM was deposited on glass, then the fabric was placed in contact with the HEM/glass and the HEM was forced to be transferred using a thumbprint. In the second procedure, a metallic tip was pressed against a deposit of HEM and a small amount of the HEM (particles) were transferred to the tip; next, these particles were deposited on the fabric. The fabric was weighted before and after the deposition in order to determine the amount of HEM deposited. The weighing was done using two weighing scales (see Figure 2). The first scale had a precision of ± 0.1 mg. This scale was used for depositions of 3 to 0.1 mg. The second scale had a precision of ± 0.01 μg (thermogravimetric analysis, TGA) for the smallest samples. This procedure was used for deposition of HEM samples of masses ≤ 0.1 mg.

![Figure 2: (a) Photo of cotton fabric from jeans used in the experiments; (b) weighing of samples in TGA balance.](image)

A linear model based on CLS analysis was proposed, as shown in the following equation:

\[
f(\phi, \beta) = \beta_0 + \beta_1 \phi_1(\omega_i) + \cdots + \beta_j \phi_j(\omega_i)
\]

where \(f(\phi, \beta)\) are the \(i\) normalized intensities of the spectrum calculated for a mixture of different components, \(\phi_j(\omega)\) is the normalized intensity for each wavenumber \(\omega\) of the net spectrum of a component, and \(\beta\) is a parameter that indicates the fraction of net spectrum of a component in the spectrum mixture. This
model assumes that there are no interactions between the mixture components, and that the intensities are additives. The $\beta_i$ parameters were found by minimizing the least squared of the difference between the real spectrum ($y_i$) and calculated spectrum:

$$d_i = y_i - f(\psi_i, \beta_i)$$

(2)

The minimum value of the sum of squares was found by setting the gradient to zero. Since the model contains $n$ parameters, there are $n$ gradient equations:

$$\frac{\partial \sigma^2}{\partial \beta_j} = -2 \sum d_i \frac{\partial f(\psi_j, \beta_i)}{\partial \beta_j} = 0, j = 1, 2, \ldots, n$$

(3)

It is possible to extract the signals-of-interest component from the model. For example, if the component of interest is 1, the extracted spectrum ($\psi$) is

$$\psi_1(\omega) = y_i - \beta_0 - \beta_2 \psi_2(\omega_i) - \cdots - \beta_j \psi_j(\omega_i)$$

(4)

The obtained spectra were converted from reflectance units to the negative of logarithm of reflectance because these units are proportional to the concentration. Normalization was generated by standard normal variate (SNV) pre-processing, which was applied to the complete spectral region for the analyses in order to eliminate the baseline generated by light scattering due to the differing particle size and topology of the fabric.

Three classes of models were generated: binary, ternary, and quaternary. The binary model consisted only in spectra of cotton and TNT. The equation is following:

$$f = \beta_0 + \beta_{cotton} \psi_{cotton}(\omega_i) + \beta_{TNT} \psi_{TNT}(\omega_i)$$

(5)

TNT samples were deposited on cotton with nominal amounts of 3, 1, 0.5, 0.1 mg, and $\beta_{TNT}$ was calculated from five replicas (20 spectra) and the probability was estimated, as shown in Figure 3. Similar models were generated for RDX and PETN. The three explosives have high sensitivity and specificity in the amount range of 0.1 to 3 mg. In Figure 3b, the spectrum of 0.1 mg TNT on cotton is shown together with the predicted spectrum from Eq. 5 and the QCL cotton spectrum. The cotton subtracted TNT spectrum calculated from Eq. 4 is also shown. Spectra were compared with the solid TNT spectrum (reference) in order to verify the presence of the important vibrational signatures of the target HEM.

![Figure 3: (a) Probability of detection and (b) spectra of TNT/cotton, cotton, cotton subtracted TNT/cotton, predicted, and solid TNT (reference).](attach:image)
A second model for the three component mixtures was based on the following:

\[ f = \beta_0 + \beta_{cotton}\varphi_{cotton}(\omega_i) + \beta_{\text{TNT}}\varphi_{\text{TNT}}(\omega_i) + \beta_{\text{RDX}}\varphi_{\text{RDX}}(\omega_i) \]  

(6)

Different amounts of TNT, RDX, and a mixture of 50% TNT and RDX (134 samples) were deposited on cotton from 0.1 to 3 mg, and \( \beta_{\text{TNT}} \) and \( \beta_{\text{RDX}} \) were calculated. Then the distribution of each sample was plotted for the values calculated of \( \beta_{\text{TNT}} \) and \( \beta_{\text{RDX}} \) by means of Eq. 7 (see Fig. 4a).

A third model for four components was tested:

\[ f = \beta_0 + \beta_{cotton}\varphi_{cotton}(\omega_i) + \beta_{\text{TNT}}\varphi_{\text{TNT}}(\omega_i) + \beta_{\text{RDX}}\varphi_{\text{RDX}}(\omega_i) + \beta_{\text{PETN}}\varphi_{\text{PETN}}(\omega_i) \]  

(7)

Various amounts of TNT, RDX, PETN, a mixture of 50% TNT and RDX, a mixture of 50% TNT and PETN, a mixture of 50% PETN and RDX, and a mixture of 33.3% TNT, PENT, and RDX (252 samples) were deposited on cotton from 0.1 to 3 mg. \( \beta_{\text{TNT}} \), \( \beta_{\text{RDX}} \), and \( \beta_{\text{PETN}} \) were calculated and the distribution of each sample was plotted for the values calculated of \( \beta_{\text{TNT}} \), \( \beta_{\text{RDX}} \), and \( \beta_{\text{PETN}} \) by Eq. 7 (see Fig. 4b).

In order to evaluate statistically the discrimination power of the \( \beta \) parameters, a discriminant analysis was carried out. Two statistically significant discriminating functions (F1 and F2) were obtained. These functions contained nearly all of the statistically relevant information as they contributed to 95.3% of the discrimination capability. As shown in Table 2, the eigenvalues for the discriminant functions were highly significant (p < 0.0001). According to the canonical correlation coefficient, which is indicative of the ability or effectiveness for the discrimination capability of new samples, the functions have excellent capacities for determining group differences 93% and 87%, respectively (see Fig. 5 on the next page).

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<th>Discriminant function</th>
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<tr>
<td>Eigenvalue</td>
<td>6.2</td>
<td>3.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Relative %</td>
<td>63%</td>
<td>32%</td>
<td>5%</td>
</tr>
<tr>
<td>Canonical Correlation</td>
<td>0.93</td>
<td>0.87</td>
<td>0.56</td>
</tr>
<tr>
<td>Wilks Lambda</td>
<td>0.02</td>
<td>0.16</td>
<td>0.68</td>
</tr>
<tr>
<td>Chi-squared</td>
<td>901.9</td>
<td>431.7</td>
<td>90.6</td>
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<tr>
<td>p value</td>
<td>&lt; 0.0001</td>
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Table 2: Values of statistical parameters of functions derived from the \( \beta \) parameter.
Function three (F3), which had 77% capacity for determining group differences, was not as effective as F1 and F2 in the sought discrimination model, and was not used. The LOD was calculated from different spectra of RDX at low amounts (< 0.1 mg). Eq. 4 was applied to the spectra, and the signals of RDX were validated (see Fig. 6a). Next the S/Ns were calculated for two signals (1040 and 1463 cm\(^{-1}\)) (see Fig. 6b). An S/N of 3 was found for a mass of 22 ± 6 μg. Based on the IUPAC definition, this is the LOD.

The discrimination ability of the CLS method for binary, ternary, and quaternary mixtures of HEMs deposited onto non-ideal, non-reflective substrates, such as cotton, was demonstrated. The use of the least-square concept in combination with remote sensing (QCLs) is an effective alternative in the detection of HEMs and mixtures of explosives. In addition, if the spectra for the neat components can be included in the calibration set, in this case RDX, TNT, and PETN, the discrimination on any surface is possible with just by updating the model with the spectrum of the new surface where detection will be performed, in this case, different types of fabrics. The concept of CLS facilitates interpreting the remote detection on highly MIR interfering substrates making possible visual spectral control of the signal of interest.

D.2. QCL spectroscopic library of explosives

Spectral signatures of explosives were recorded by MIR spectroscopy using a QCL system. Explosives samples were deposited on aluminum (Al) and on real-world substrates such as travel baggage (TB), cardboard, and others. Explosives used in this stage of the project were RDX, PETN, and 2,4-DNT. The deposition method utilized was sample smearing. An addressable QCL spectral library was started by measuring vibrational
signatures of explosives samples deposited on Al using QCL spectroscopy. QCL reflectance spectra were compared with reference spectra acquired in KBr matrices in transmission mode. The reagents used include DNT, RDX, and PETN, synthesized at the micro scale in the lab. Acetone was used to deposit explosives samples with different surface concentrations on to a TB and on Al used as substrates. Detection of PETN, RDX, and DNT deposited on selected substrates was carried out using a QCL spectrometer. All spectra were taken with five co-adds and four cm$^{-1}$ resolution. In addition, five spectra were taken for each sample. The spectral range was 1600 - 1000 cm$^{-1}$. Table 3 contains the list of chemicals that have been used to build the QCL library of 46 common (and not so common) explosives. RDX, PETN, and TNT have been measured on all substrates: Al (highly reflective metal surface; M), wood (plywood; W), cardboard (CB), and TB materials (plastic polymer, black polyester). Their spectra have been included in the QCL spectral library.

<table>
<thead>
<tr>
<th>#</th>
<th>Status</th>
<th>Explosive</th>
<th>#</th>
<th>Status</th>
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<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>RDX</td>
<td>24</td>
<td>M</td>
<td>3,5 dinitro-4-methylbenzoic acid</td>
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<td>A</td>
<td>PETN</td>
<td>25</td>
<td>M</td>
<td>4-nitroresorcin</td>
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<td>3</td>
<td>A</td>
<td>2,4,6-TNT (TNT)</td>
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<tr>
<td>4</td>
<td>M</td>
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Table 3: Explosives included in QCL spectral library; status: all substrates (A); metal substrate (M); not measured (N).

Figure 7a on the next page shows the QCL spectrum of PETN deposited on Al. Samples were prepared by the smearing deposition method. The most prominent signal is at 1280 cm$^{-1}$, which corresponds to one of the vibrational signatures of the -NO$_2$ group. Figure 7b on the next page shows the QCL spectra of PETN/TB and TB without explosives. Samples with PETN were also prepared by the smearing method. Higher signals were achieved by the PETN/TB samples. -NO$_2$ group vibration at 1280 cm$^{-1}$ can be clearly distinguished on top of synthetic fibers of TB. The PETN/TB spectrum reveals to have higher intensities than TB without explosives. The spectra were subjected to various preprocessing steps such as baseline correction and smoothing.
Difference spectrum (PETN/TB - TB) should result in the clear identification of targeted explosives, even in reflectance mode.

Sample smearing deposition proved to be an effective sample transfer method on TB and Al substrates. QCL identification was demonstrated to be effective in explosives detection, even in the presence of highly interfering substrates such as TB. In summary, QCL-MIR spectroscopic detection of explosives samples on common substrates such as TB and Al was demonstrated. Explosives compounds such as PETN, 2,4-DNT, and RDX were detected at significant vibration regions at 1300 to 1500 cm$^{-1}$ and identified at near trace level quantities.

![Figure 7: (a) MIR spectra of PETN: Blue trace reflectance QCL; red: transmittance FT-IR. (b) QCL spectra of PETN. Red: Explosive on TB; blue: TB without explosive.](image)

E. Milestones

The following milestones were met or addressed in Year 3:

- Achieved < 1 μg/cm$^2$ detection limit of PETN, RDX, and TNT on CB, W, and TB.
- Continued refining the QCL library of explosives on various targets.
- Nearly completed Al metallic substrates.
- Began addressing discriminating mixtures of explosives and highly interfering background (i.e. rag material).

The following milestones are expected for Year 4 and reflect the relevance to the DHS Enterprise:

- Simulated field detection experiments on static targets at distances of 1-10 m.
- Study effects of real-world samples, including non-uniform coverage and fingerprints, on substrates.
- The addition of synthetic skin as part of the substrates targeted.

Sensing at off-normal incidence geometries is in preparation for whole body scanning.

F. Future Plans

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

1. As part of the invention disclosure: coupling of thin layer chromatography (TLC) with MIR tunable laser sources (such as QCLs), several substrates will be investigated for Surface Enhanced Infrared Absorption (SEIRA) spectroscopy for enhanced explosives detection.
2. Development of a grazing angle probe coupled to MIR tunable laser sources (such as QCLs). At or near the grazing angle can lead to reflection-absorption infrared spectroscopy (RAIS), which is one of the most sensitive spectroscopic technique for thin films and traces analysis.

3. Plans for next year also include continuing to build the addressable library of HE/HEM independent of substrate type.

4. Year 4 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 the first months of Yr.-4.

5. The anticipated end date of the project is June 2018.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

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

1. Having access to improved/fieldable QCL systems:
   - Higher power QCL systems: current ~ 5 mW; sought: 50 – 200 mW.
   - Wider spectral coverage: current 600 cm\(^{-1}\): 1000-1600 cm\(^{-1}\); sought 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).

The results of ongoing studies demonstrate that the preceding experimental setups can be used in many applications for the detection of explosives and other threat chemicals and biological threat agents. These set ups and applications have already resulted in transition to other US defense and security agencies, as is the case with the collaborative effort with Hughes Research Labs (HRL) to address IARPA's needs. The results of this study indicates that explosives, as well as illegal drugs, can be detected even if they are strategically mixed with innocuous compounds with similar chemical and physical properties, purposely attempting to disguise them from security personnel and using them for criminal or terrorist acts.

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 of thumbprints of HEMs/HMEs that simulate finger prints 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

This project is already transitioning to industry. A collaborative proposal was submitted together with potential commercialization partners, Hughes Research Labs (HRL), Malibu, CA, and Exelis Geospatial Systems, Rochester, NY (now part of Harris Corp, Melbourne, FL). Unfortunately, though the project was targeting an IARPA BAA, it was not funded. Collaborative efforts will transition into another application of QCL detection
of explosives and other hazardous chemicals and drugs. Another IARPA BAA has been targeted and a proposal will be sent soon.

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

We have targeted the results of our research at the development of tools accessible to checkpoints in airports, government buildings, large gathering facilities (stadiums, big events, etc.), and, in particular, for first responders and soldiers.

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.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. 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. Peer Reviewed Journal Articles


Pending-

C. Other Conference Proceedings


D. Student Theses or Dissertations


E. New and Existing Courses Developed and Student Enrollment

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</table>

F. 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: S.P. Hernández-Rivera and John R. Castro-Suarez. 13 April 2016.

2. Patent Applications Filed (Including Provisional Patents)

V. REFERENCES

copy: Methods and Applications” Edited by Schrader, B., VCH, Weinheim, Germany.


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