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

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II. PROJECT DESCRIPTION

A. *Project Overview*

The goal of the R3-C research component at the University of Puerto Rico at Mayagüez (UPRM) was to use mid-infrared (MIR) laser spectroscopy for the detection of explosives. The end-state of this project was to detect residues of explosives on surfaces that could be present due to an explosion or as a threat to citizens at a distance. Our approach was based on using a tunable quantum cascade laser (QCL) source as a chemical sensor for explosive residues left due to terrorist activities. The infrared spectroscopy (IRS) modalities presented in this work were coupled to chemometrics methods of multivariate analysis (MVA) for the classification, discrimination, and prediction of the threats.

The specific aims of the research included:

- Detection of high explosives (HEs) on metallic/matte substrates at close distances using QCL-GAP (QCL grazing angle probe) systems (~15cm)
- Use of MVA routines and an artificial neural network (NN) for the detection of the HEs
- Detection of HE traces at off-normal incidence geometries using a MIR source

The challenges/obstacles that the research intended to address included:

- Establishing the differences between standards and real-world samples for the detection of HEs
- Detection of HEs with MIR laser spectroscopy on moving targets

Overcoming these challenges required transitioning from commercially available laser spectrometers operating at close distances (~15 cm) to a homebuilt system with the following characteristics:

- Highly collimated laser beams using a telescope for sensing at long distances (10–30 m)
- Higher power laser source systems 50–200 mW
- Wide spectral coverage: 1000 cm^{-1}: 830–2000 cm^{-1} (5–12 um)
- Fast scanning systems: 5 s

The work performed under R3-C addressed the detection of HE residues deposited on real-world substrates. The focus is mainly on real-world samples, including bare and painted metal parts, clothing, travel bags, personal bags, laptop bags/cases, and other relevant substrates. Laser spectroscopy signatures obtained for these surfaces allow for the identification/quantification of explosives by coupling the technique to multivariate analysis.

B. State of the Art and Technical Approach

Chemicals in complex matrices can be identified and quantified based on their unique vibrational spectrum [1-6]. IRS and Raman scattering (RS) are the two main branches of vibrational spectroscopy. IRS is a well-established discipline developing constantly. However, energy sources in the MIR have lacked incremental developments, and until now, thermal sources dominated IRS and FT-IR [1-6]. Therefore, remote detection capabilities for IRS and RS are limited by their photonic mechanisms. Both techniques characterize, detect, identify, and quantify threat chemicals, including HEs and homemade explosives (HMEs) [6-17]. Their ability has allowed countermeasures to deter terrorist threats by focusing on remote detection and other interests for national defense [7-17].

There is a need to detect hazardous threat chemicals at trace or near-trace levels on substrates at longer distances. To successfully realize this goal, more powerful MIR sources need to be developed which led to the consideration of collimated, coherent, and polarized sources. A QCL, which is a unipolar semiconductor injection laser based on sub-interband transitions in a multiple-quantum-well heterostructure, was used as QCLs have the following advantages over other types of lasers [18-22]:

- Ability to produce a laser beam from tens to hundreds of milliwatts of pulsed power under ambient conditions
- Commercial availability
- Ability to enable the development of ruggedized systems for detection of chemical/biological (CHES/BIO) threats

Most of the previous investigations to detect HEs at trace levels have focused on the detection of HE residues deposited on ideal, highly reflective substrates, such as highly polished metallic surfaces [23]. There are very few reports published on the effects of nonideal, low-reflectivity substrates on the spectra of the target HEs [24]. The work by Suter and collaborators (which measures the spectral and angular dependence of MIR diffuse scattering from explosive residue deposited on a painted car door using an external cavity QCL (EC-QCL)) is the foundation for part of our research [25]. However, our approach is significantly different because it focuses on the detection, identification, and discrimination of HEs on highly interfering backgrounds. These substrates include wood, natural and synthetic fibers, such as cotton shirts or pants, nylon, and black polyester from laptop bags or travel cases, and simulated human skin [24]. 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 milliseconds to a few seconds. The main difference between the contributions of this research and the current state-of-the-art research is in bridging the gap between lab experiments under well-controlled conditions and the real-world detection of explosives residues [26].

QCL spectroscopy was used previously for sensitive detection of nitroamine, nitroaromatics, aliphatic nitrate, and peroxide-based HEs at long-distances (meters from the source) [23-25,27-33]. Also, it has been used for remote detection of a variety of HEs. However, the implementation of MVA with QCL has been limited, especially with variating deposition techniques. In addition to principal component analysis (PCA) we employed soft independent modeling of class analogies (SIMCA), support vector machines (SVM), Partial least squares coupled to discriminant analysis (PLS-DA) and k-nearest neighbors (KNN). KNN has become a hot topic for discrimination analysis. In this work, HEs were deposited by spray, spin coating, sample smearing, and partial immersion. QCL spectra were acquired and then analyzed using PCA. Also, experiments varying the angle of incidence to determine the optimal source and detector position for acquisition of MIR laser reflectance spectra was implemented. Spectra were then analyzed with KNN to classify each HE.

C. Major Contributions

C.1. Detection of HEs on Reflective Substrate Using MIR laser spectroscopy (Year 1)

The first stage of this project involved confirming the performance of a commercial QCL spectrometer (LaserScan™ Block Engineering) for detecting HEs by validation experiments. The MIR spectroscopic system acquired reflectance spectra of films and deposits of chemicals on substrates. Some of the results obtained with the QCL system are included in Figure 1. The reflectance spectra measured with QCL and FT-IR spectroscopy of nitroaromatic 2,4,6-trinitrotoluene (TNT), aliphatic nitrate ester pentaerythritol tetranitrate (PETN), aliphatic nitramine 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), and triacetone triperoxide (TATP) are shown in the figure [34, 35]. The MIR laser spectra were collected on a smooth aluminum (Al) substrate. These spectra serve the purpose of validating the technique for the detection of HEs, explosive mixtures/formulations, and chemical precursors. The MIR laser spectra were collected in open-air conditions. Thus, water vapor lines were observed on some of the spectra. TATP samples had particularly evident water vapor lines because the samples sublimated rapidly, even at room temperatures. In other cases, the inherent strength of the MIR signatures of the HEs made the water vapor lines imperceptible. There are operational parameters worth discussing: the LaserScan™ was designed for short focal length work (~15 cm). Highly reflective polished metallic substrates (e.g., Al, stainless steel, or gold) required a defocused MIR laser beam since the specular radiation collected in back reflection mode saturated the detector. Alternatively, using an incidence angle of 9–10° avoided detector saturation.

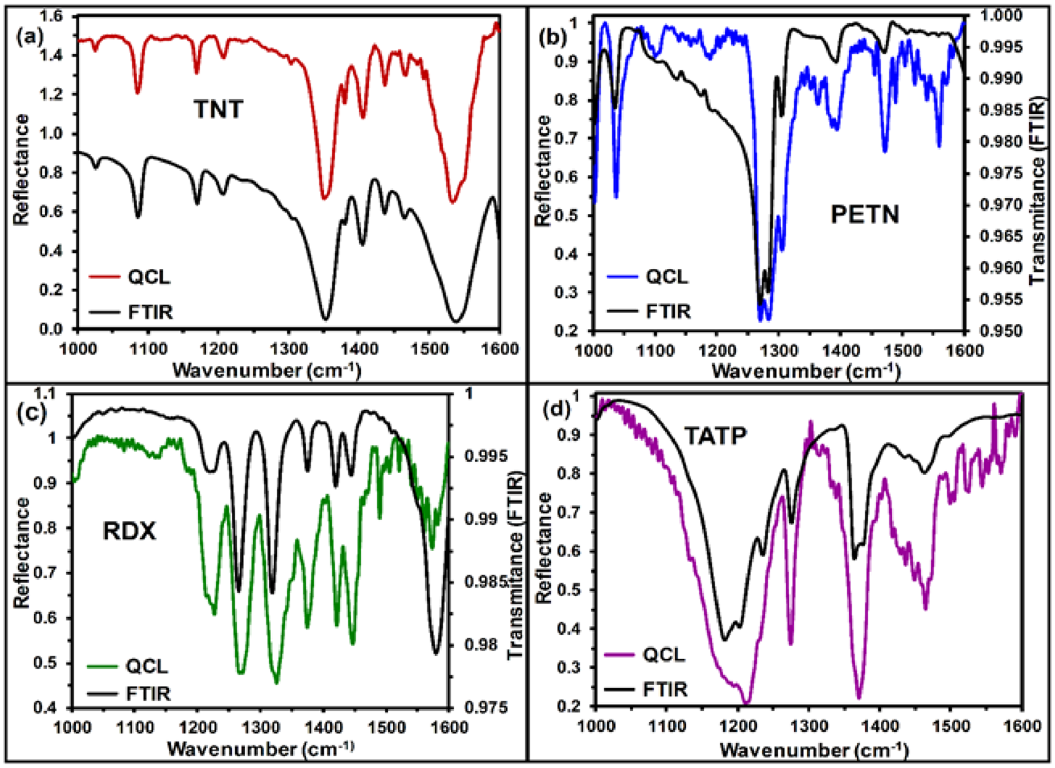

Figure 1: QCL and FTIR (ref.) spectra of HEs deposited on highly reflective polished Al substrates: (a) TNT, (b) PETN, (c) RDX, and (d) TATP. The quality and intensities of the bands are equal or better than those measured by FT-IR.

C.2. Detection of HEs on Nonreflective (Matte) Substrates Using QCL Spectroscopy (Years 1–2)

The spectroscopic system based on QCL was next used to obtain MIR reflectance spectra of HEs deposited on nonideal, low reflectivity matte substrates such as travel bags (TB), cardboard (CB), and wood (W). We tested various deposition methods, including spin coating, sample smearing, partial immersion, and spray deposition for preparing standards and samples used in the study. The HEs used include TNT, PETN, and RDX. Low surface concentrations (1–15 mg/cm^2) of HEs were used in the investigation. Figure 2 shows representative QCL spectra of TNT, PETN, and RDX on Al, CB, W, and TB.

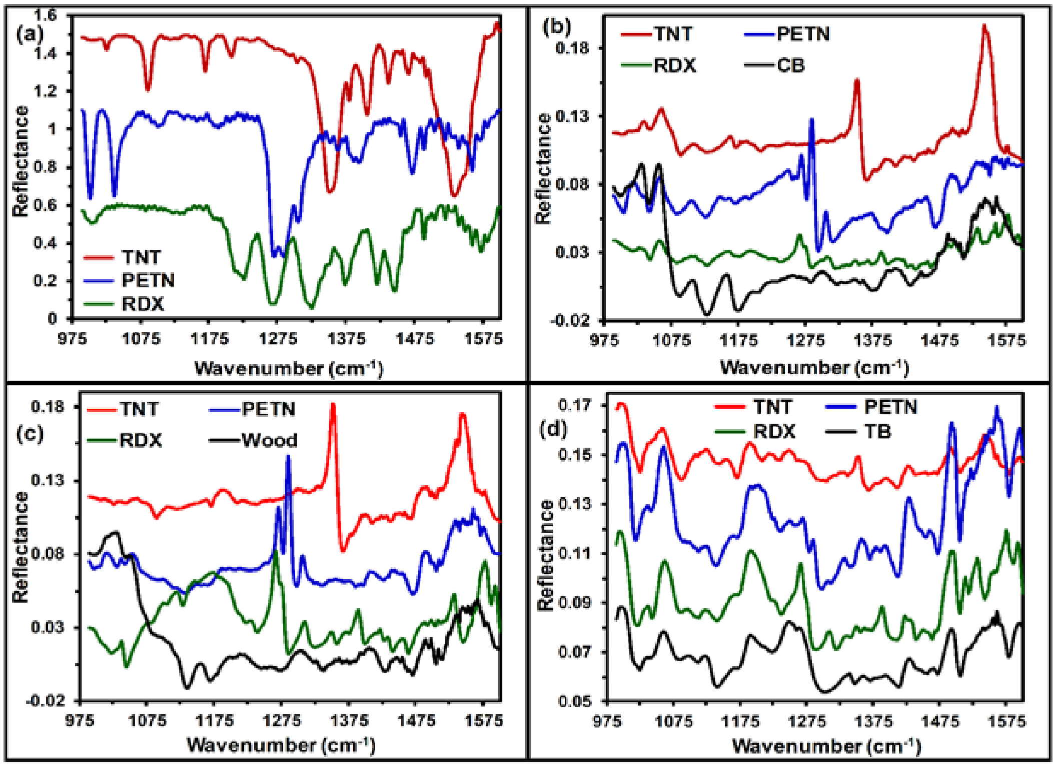

Figure 2: QCL spectra of HEs on substrates: (a) Al, (b) CB, (c) wood, and (d) TB. Surface concentrations were 15 µg/cm2. QCL spectra of substrates are included to establish the degree of spectral interference.

MIR laser reflectance spectra were used for the surface concentration profiles to perform quantitative MVA. A total of nine different surface concentration profiles were assembled: three HEs × three substrates (plus three replicas of each combination). QCL spectra of clean Al substrates were used as backgrounds. Figure 3a shows some of the RDX spectra recorded on wood substrates; Figure 3b shows spectra for TNT on CB at various surface concentrations, and Figure 3c shows measured QCL reflectance spectra for PETN on wood. However, the QCL methodology used for detection of explosives on non-reflective (matte) substrates did not require the use of multivariate analyses (MVA) for identification of HEs, but rather, as illustrated in Figure 3d, a single acquisition (3 s) of CB was subtracted from the corresponding QCL spectrum of PETN on CB to obtain the difference spectrum of PETN. Comparison with the QCL transflectance spectrum of PETN on Al demonstrates that several of the aliphatic nitrate ester signature bands can be readily assigned by comparison with the reference QCL spectrum. The only requirement for this type of remote detection experiment is to be able to acquire a QCL spectrum of a non-contaminated (non-dosed) segment of the substrate. The LaserScan™ spectroscopic system allowed the detection of HEs deposited at low surface concentrations (1–15 mg/cm^2) on three types of nonideal low reflectivity substrates: travel bag fabrics (TB), cardboard (CB), and wood (w). Spectral identification using spectral correlation algorithms were not efficient enough for identifying HEs when present on nonideal low reflectivity, highly mid-infrared absorbing substrates. However, multivariate analyses were efficient enough to attain the goals of this investigation. Finally, PLS models demonstrated the capability of predicting surface concentrations of HEs on the substrates tested using a maximum of eight latent variables (LV) to obtain values of R^2 higher than 0.9 [24, 26].

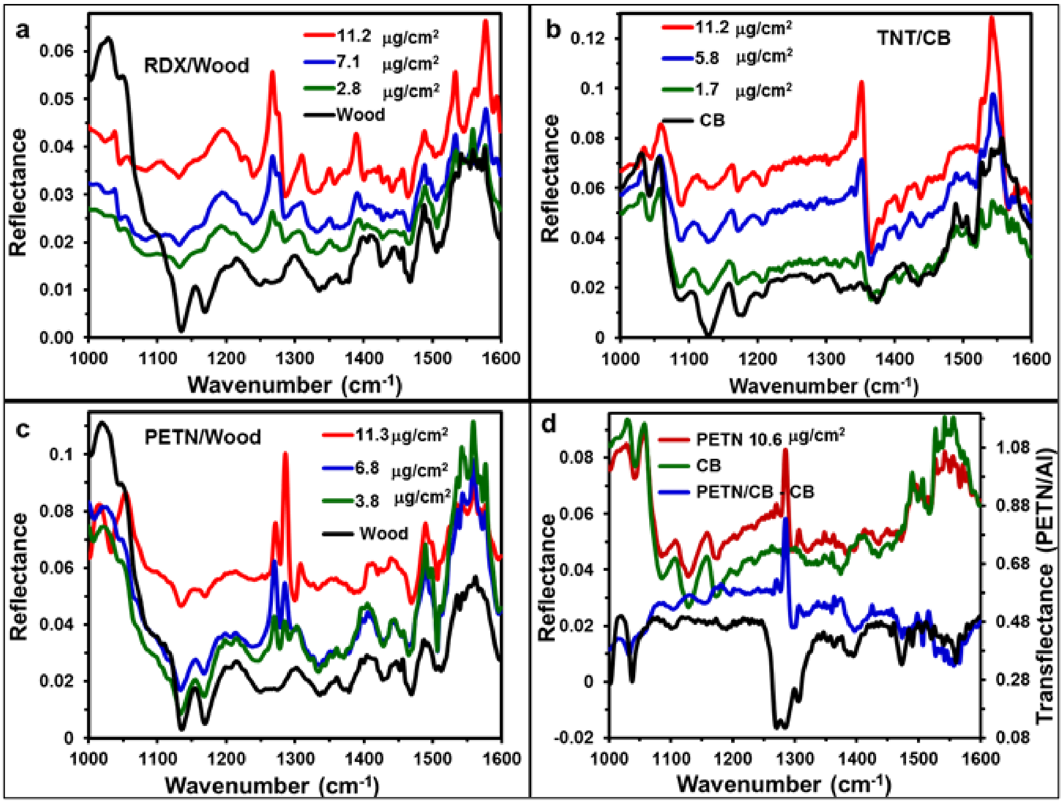

Figure 3: Surface concentration profiles for (a) RDX on wood; (b) TNT on CB; and (c) PETN on wood. Difference spectrum (d): PETN/CB minus CB and comparison with QCL transflectance spectrum PETN/Al (used as reference).

C.3. QCL Spectroscopic Library of Explosives (Year 2)

Spectral signatures of explosives were recorded by MIR spectroscopy using a QCL system. Explosive samples were deposited on aluminum and real-world substrates such as travel baggage, cardboard, and others. Explosives used in this stage of the project were RDX, PETN, and 2,4-dinitrotoluene (2,4-DNT). The deposition method utilized was sample smearing.

C.4. Classical Least Squares–Assisted MIR Laser Spectroscopy Detection of High Explosives on Fabrics (Years 3–5)

MIR laser spectroscopy was used to detect the presence of residues of HEs on fabrics. The discrimination of the vibrational signals of HEs from a highly MIR-absorbing substrate was achieved by a simple and fast spectral evaluation, without preparation of standards, using the classical least squares (CLS) algorithm [36]. CLS focuses on minimizing the differences between the spectral features of the actual spectra acquired by MIR spectroscopy and the spectral features of calculated spectra modeled from linear combinations of the spectra of neat components: HEs, fabrics, and bias. Samples in several combinations of cotton fabrics / HEs were used to validate the methodology. Several experiments were performed focusing on binary, ternary, and quaternary mixtures of TNT, RDX, PETN, and fabrics. The parameters obtained from linear combinations of the calculated spectra were used to perform discrimination analyses and to determine the sensitivity and selectivity of HEs to the substrates and each other. However, discrimination analysis was not necessary to achieve the successful detection of HEs on cotton fabric substrates [37].

C.5. QCL Spectroscopy at Grazing-Angle Incidence Using Fast Fourier Transform Preprocessing (Years 4–7)

A simple optical layout for a grazing angle probe (GAP) mount for coupling to a MIR QCL spectrometer was designed and developed. This assembly enables reflectance measurements at high incident angles. In the case of optically thin films and deposits on MIR reflective substrates, a double-pass effect occurs, accompanied by the absorption of deposited samples in a reflection-absorption infrared spectroscopy modality. The optical system allows MIR light to pass through the sample twice. Applications to the detection of traces of explosives using the QCL-GAP were also developed. They have been published in various peer-reviewed journals. Principal component analysis and partial least squares multivariate chemometrics methods were employed to analyze MIR spectra to evaluate an analytical methodology for confirming the presence of residues of pharmaceutically active ingredients (irbesartan) and of traces of explosives (RDX) that have been deposited on metallic substrates. The performance of spectral preprocessing via fast Fourier transform (FFT) analysis was evaluated for the ability to extract more robust and accurate information from the obtained reflectance spectra. According to the figures of merit or distinguishing attributes of this new technique, FFT with chemometric routines can obtain sensitivity and specificity values of 1.000. The limit of detection obtained for RDX was 7 ng/cm^2. The experimental results demonstrate that the proposed system, when used together with proper chemometrics routines, constitutes a powerful tool for the development of methodologies that have lower detection limits for a range of applications that involve detecting traces of analytes that reside on substrates as contaminants [38].

C.6. Design and Construction of a Homebuilt MIR Laser Spectrometer System (Years 6–7)

Commercial MIR lasers (QCLs) are already predispersive systems: the grating selected wavelength of the output beam can be scanned very fast, maintaining high accuracy and precision. However, coupling to fast detection systems, in our case, was not a trivial problem to solve. The first approach to obtain data acquisition routines based on National Instruments (NI) LabView™ from researchers affiliated with National Labs or from other researchers in the field was not successful. A commercial solution to the problems was not within reach (>$35k). Thus, several members of our research team had to be involved in the solution of the problem. The first successful experiments are reported here. First, the development of an interface using LabView™ to acquire spectroscopic data from a QCL source and a mercury-cadmium-telluride (MCT) cryocooled detector has not been thoroughly discussed in the literature. A few research papers have focused on parts of the algorithms that can be employed [39-41]. However, none fully describes a procedure that can be programmed as a Virtual Instrument (VI) code in LabView, including acquisition and data processing required to interface a fast laser with an equally fast data acquisition board (analog to digital card) and detector. Software developed in LabView to implement the required interface was created for this purpose.

An ultrafast conversion data acquisition card (DAQ; 200 mega samples/s) was used to capture the signals from the preamplifier, which is connected to the MCT detector, as shown in Figure 4. The system can acquire potential difference (volts) as a function of time and performs the signal processing required to obtain the spectroscopic information related to the samples. The advantage of developing this in-house system was that it facilitated coupling QCL systems with traditional IRS and FT-IR techniques to perform studies with the advantages of a laser source. Among these techniques are transmission, absorbance, diffuse reflectance infrared spectroscopy (DRIRS), attenuated total reflectance (ATR), and grazing angle incidence reflectance (GAIR) which enables the most sensitive IRS technique: reflectance-absorption infrared spectroscopy (RAIRS).

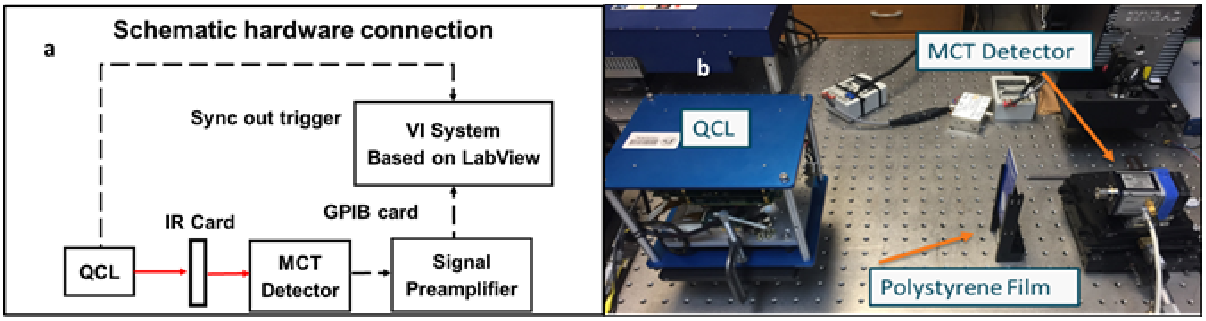

Figure 4: (a) Schematic diagram of the transmission setup using QCL-MCT; (b) calibration of QCL-MCT using a polystyrene film in transmission mode.

C.7. Variable Angle of Incidence MIR Laser Spectroscopy Method for Diffuse Reflectance Measurements (Years 7–8)

The study focused on the development of a MIR laser reflectance method to perform spectroscopic measurements at ten angles of incidence from 12° to 84° for PETN (81.4 μg/cm^2), RDX (47.4 μg/cm^2), and Tetryl 62.7 μg/cm^2. The energetic materials were deposited on substrates with different properties such as the index of refraction, reflectivity (metallic or nonmetallic), and surface roughness. Those differences produce complex infrared spectra, which make it challenging to identify vibrational signatures by sight. Previous results have shown that higher angles of incidence (grazing angle) provide high signal to noise ratios and cover a more extensive sampling area. However, real-life applications could require measurements at an angle of incidence different from grazing angles. QCL has a powerful source of mid-IR that could compensate for the scattering due to the nature of the experiments and still obtain a strong signal. Deep learning emerged as an advanced artificial intelligence method that discovered patterns in the spectra without supervision; therefore, its synergy with QCL spectroscopy leads to the development of more sophisticated detection systems capable of identifying threats in public places by using copius amounts of data collected in airports security checkpoints and laboratories. The algorithm resembles our brain's process of learning. A set of NN layers made of compound nodes "learns" from reliable spectra labeled with its corresponding class. After the learning stage finishes, the algorithm is ready for classification. The goal of the project was to cover a wide range of angles of incidence with respect to the surface normal vector of the substrate using a robust a MIR laser, as shown in Figure 5. The goal was to construct a database that could be coupled with AI algorithms for identification and classification of HEs. The method proposed in this study could be used in airports to inspect surfaces of baggage using diffuse reflectance laser spectroscopy. The acquisition of spectra at several angles of incidence increases the probability of detecting threats independent of the position with respect to the QCL and the detector of the luggage in a conveyor belt.

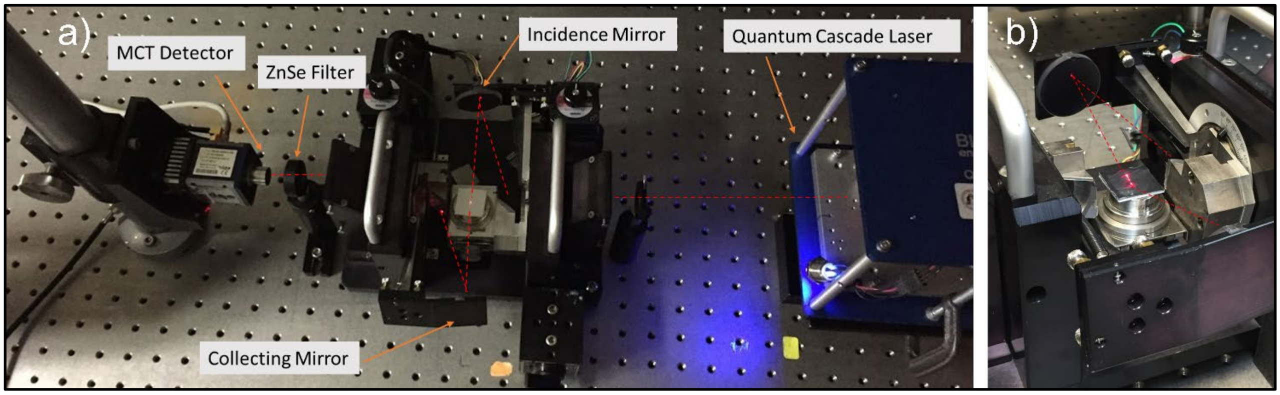

Figure 5: (a) Optical setup for multi-angle incidence diffuse reflectance spectroscopy. (b) Side view.

A total of 450 spectra were collected containing 830 bands from 930 to 1,375 cm^{-1}. A total of 80% of the spectra are separated and labeled with their corresponding class used to train the NN model. A PCA was used as a preprocessing step to select only the most significant bands. Those bands represent the representative features that identify each class. The parameters of the model (the weights) were optimized at each iteration to minimize the percentage of misclassified samples. The training finished when the number of iterations was reached. Afterward, the validation stage began. The remaining 20% of the spectra collected were used to test the model (test set). The results are presented using a confusion matrix. The values in the diagonal of the matrix represent the spectra correctly classified. The overall performance of each stage is shown in the right lower corner of the matrix (shaded in gray), as shown in Figure 6. The green shaded values represent the percentages of the success rate. No additional data was collected for validation. Hence, the values on the validation confusion matrix are zero. Finally, the overall performance of the model is display on the "All Confusion" matrix, which combines the results from the confusion matrix for the training set and the confusion matrix for the test set. Several trials were conducted to find the best parameters of the model, such as the number of classes and if PCA data reduction was applied successfully.

C.7.a. First Trial: Classification Based Only on HEs

A general KNN model, only considering three classes (PETN, RDX, and tetryl), was generated for classification of the samples belonging to these classes. Initially, the NN model was overfitting the data, but it was not generalizing. This conclusion is generated from the training confusion matrix and test confusion matrix. Figure 6 show a 97.2% of overall accuracy. Still, there was only 34.1% of overall accuracy for the testing. These results were computed using three layers arranged as follows: three nodes in the first layer, one node in the second layer, and finally, two nodes in the last layer. The number of iterations was set to 7,000, and only 22% of the data was selected for training.

Training Confusion Matrix

Output Class \ Target Class	1	2	3	
1	117 32.3%	0 0.0%	2 0.6%	98.3% 1.7%
2	0 0.0%	120 33.1%	4 1.1%	96.8% 3.2%
3	3 0.8%	1 0.3%	115 31.8%	96.6% 3.4%
	97.5% 2.5%	99.2% 0.8%	95.0% 5.0%	97.2% 2.8%

Validation Confusion Matrix

Output Class \ Target Class	1	2	3	
1	0 NaN%	0 NaN%	0 NaN%	NaN% NaN%
2	0 NaN%	0 NaN%	0 NaN%	NaN% NaN%
3	0 NaN%	0 NaN%	0 NaN%	NaN% NaN%
	NaN% NaN%	NaN% NaN%	NaN% NaN%	NaN% NaN%

Test Confusion Matrix

Output Class \ Target Class	1	2	3	
1	8 9.1%	9 10.2%	6 6.8%	34.8% 65.2%
2	6 6.8%	6 6.8%	7 8.0%	31.6% 68.4%
3	16 18.2%	14 15.9%	16 18.2%	34.8% 65.2%
	26.7% 73.3%	20.7% 79.3%	55.2% 44.8%	34.1% 65.9%

All Confusion Matrix

Output Class \ Target Class	1	2	3	
1	125 27.8%	9 2.0%	8 1.8%	88.0% 12.0%
2	6 1.3%	126 28.0%	11 2.4%	88.1% 11.9%
3	19 4.2%	15 3.3%	131 29.1%	79.4% 20.6%
	83.3% 16.7%	84.0% 16.0%	87.3% 12.7%	84.9% 15.1%

Figure 6: Preliminary results—confusion matrix of targets (1) PETN, (2) RDX, and (3) tetryl.

C.7.b. Second Trial: Classification Based Only on HEs and Substrates

Improving the prediction capability required the research team to create more classes for the same data, as shown in Table 1. The parameters employed for the second trial were similar to the first trial: three layers arranged as follows: three nodes in the first layer, one node in the second layer, and finally two nodes in the last layer. The number of iterations was set to 4,000, and only 20% of the data was selected for the test set. In this case, an overall accuracy for the training stage was 96.7% as can be seen in Figure 7. For the testing stage, an overall accuracy of 12.2% is shown in Figure 8. This means that the network was training well but the prediction had a low accuracy. The overall true positives of the model were 80% as we can see in Figure 9. However, the model needs to be improved to increase prediction in the testing stage.

1	2	3	4	5	6	7	8	9
PETN Al	PETN Glass	PETN Vinyl	RDX Al	RDX Glass	RDX Vinyl	Tetryl Al	Tetryl Glass	Tetryl Vinyl

Table 1: Classes for training the KNN model.

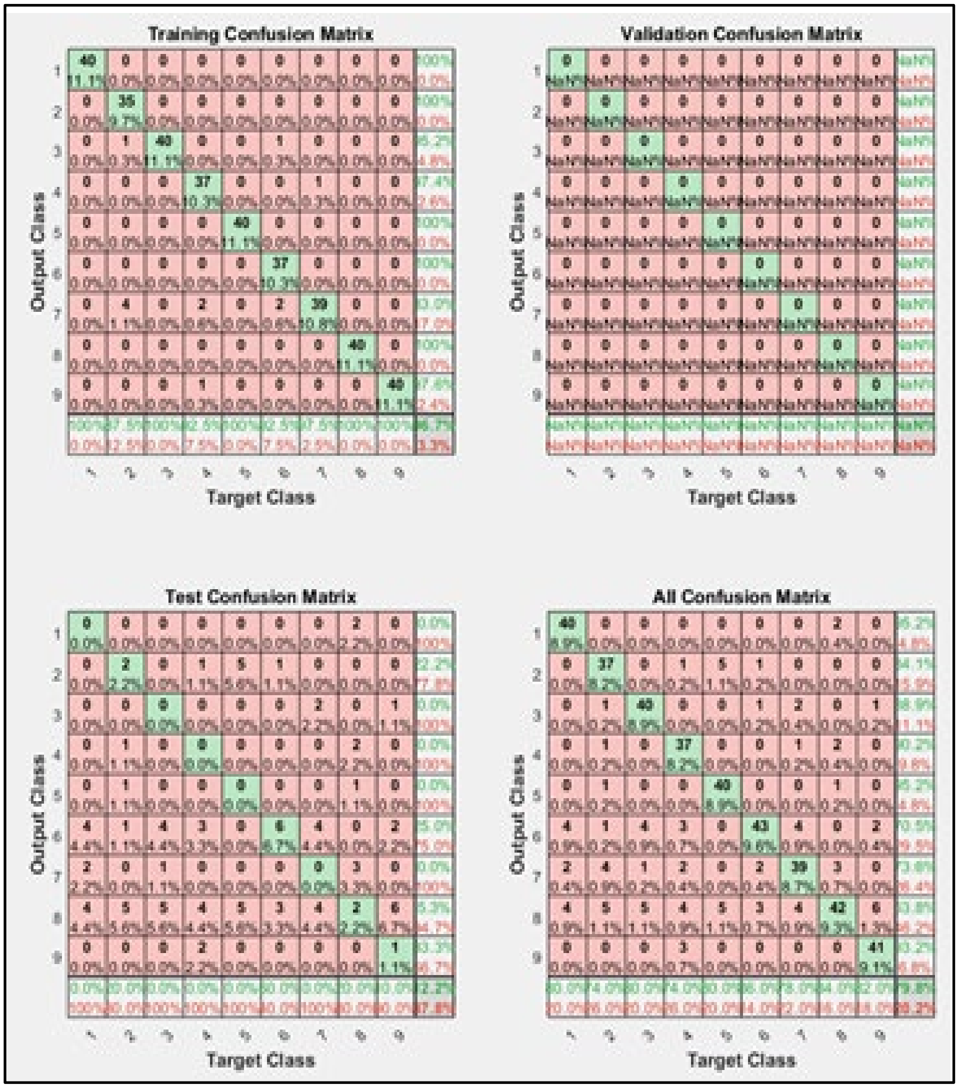

Figure 7: Preliminary results—confusion KNN matrix used to separate nine classes.

C.7.c. Third Trial—Classification Based Only on Energetic Material and Substrate

The same parameters employed in the second trial were used for the third model. The number of contributing bands (vectors) was reduced to twenty using PCA. This reduction retained the twenty most significant bands that contribute more significantly to the spectroscopic data set. The overall accuracy for testing data increased to 27.8% while the overall accuracy for the training data decreased to 56.4%. It is essential to highlight that the comprehensive training time for the 896 bands was around 1 hour. Using 20 bands the model converged in 3 minutes. We are currently working on improving the predictability of the deep learning model by preprocessing the spectra and also by increasing the number of nodes per layer.

C.8. Characterization and Classification of Standards Samples Using QCL-GAP Laser Spectroscopy (Years 7–8)

The use of MIR lasers (QCLs) provides the user with the capability to detect substances that may present interferences even at low concentrations. Our approach entails the signal enhancement of HEs by using the GAP. The results using a Block Engineering, LLC portable system coupled to the GAP mount are presented for the characterization of standards obtained from the Naval Research Laboratory (NRL, Washington, DC) as a part of the SED-V Program: DHS Methods of Optical Detection of Explosives (MODEx). Figure 8 shows the samples first analyzed and used to characterize the HEs, which included: RDX, tetryl, and PETN deposited on acrylonitrile butadiene styrene (ABS) and Al used as matte and reflective substrates as shown respectively. The acquired spectra of the characterization for the HEs are presented in Figure 9a and Figure 9b. The normalized spectra for each HE are shown in comparison to the pure substance synthesized in our laboratory. The IR spectrum of the tetryl was simulated using the OPT + FREQ job setup in Gaussian (Gaussian, Inc. Connecticut, USA) with density functional theory (DFT), 6-311 + G(2d,p) basis set and B3LYP hybrid functional.

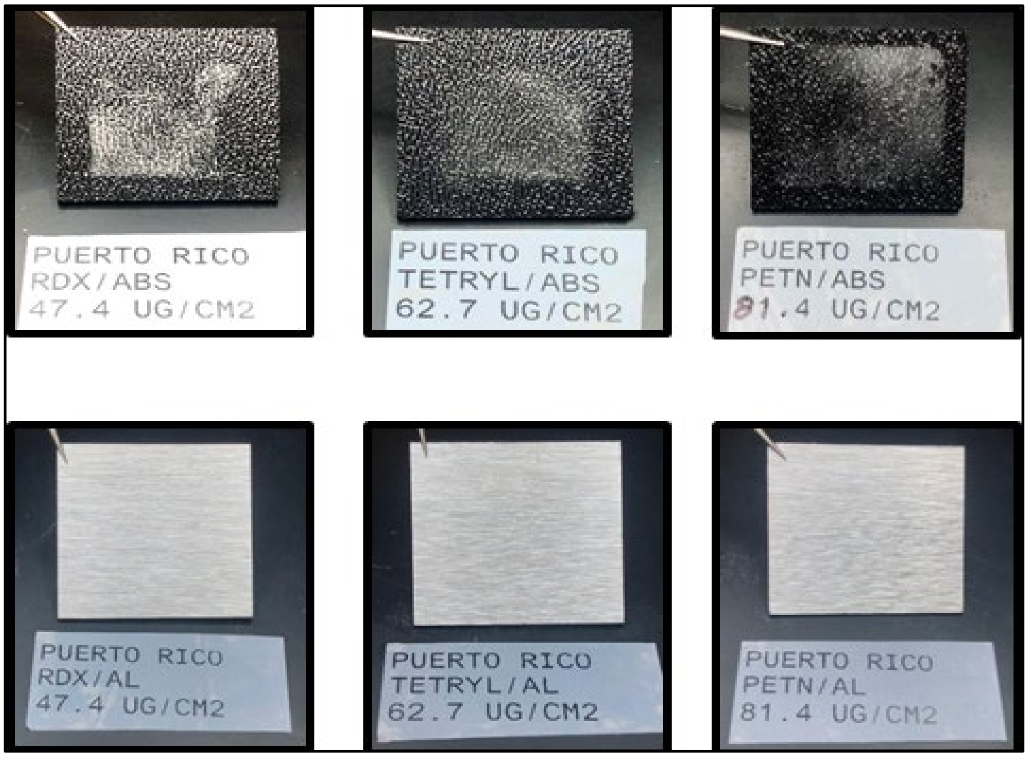

Figure 8: White light micrographs of ABS and Al substrates loaded with HEs used for spectral acquisition.

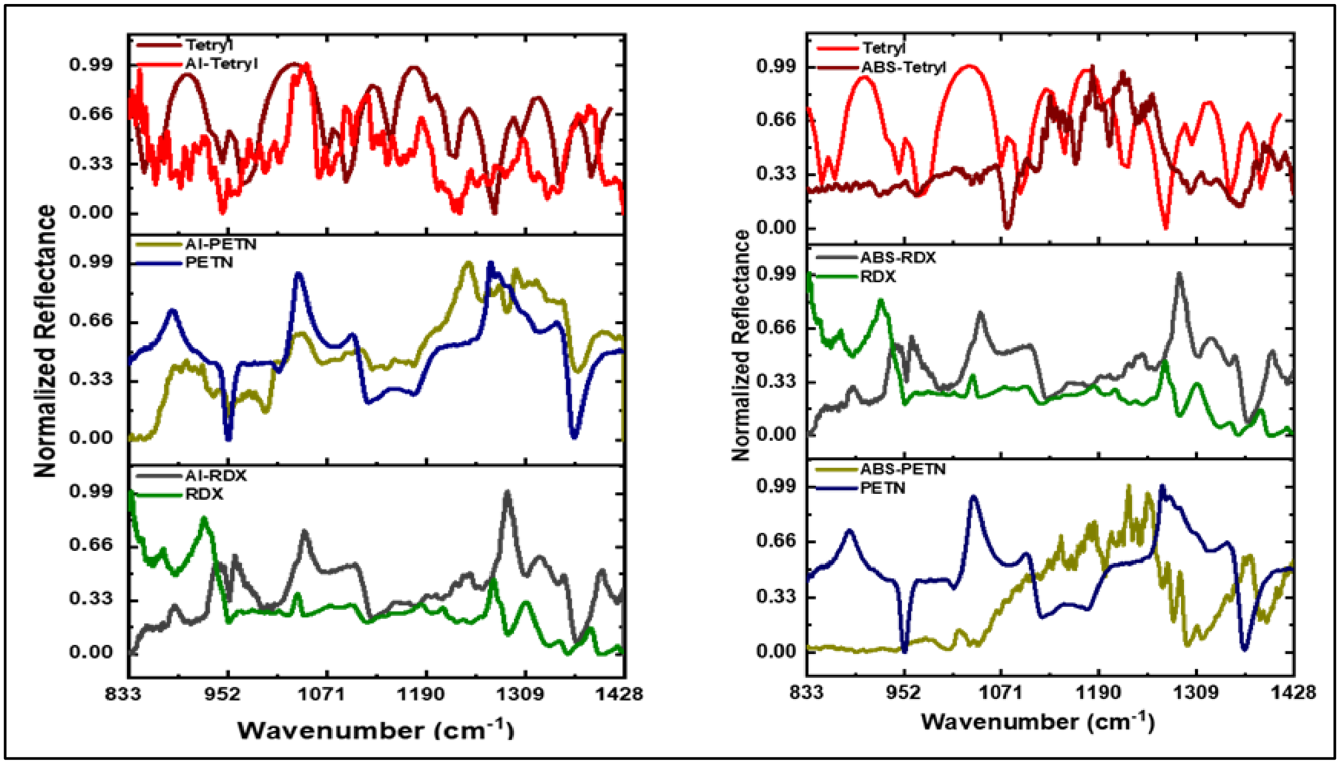

Figure 9: Normalized reflectance spectra of various HEs deposited on the substrates used as standards (a) Al reflective substrate; (b) ABS matte substrate.

PCA models for the standards were generated using MVA routines to differentiate between the explosives deposited and the substrates used for the analysis. The complete MIR spectral region from 833 to 1,428 cm^{-1} was used to investigate these variables. Scores for principal component 1 (PC-1) and PC-2 presented the two most notable variations (percent variance) for the spectra acquired on both substrates. Figure 10 shows the scores plot (PCA plot) for ABS, where PC-1 accounted for 46% of the total spectral variance, and a value of 37% for PC-2. Most of the information contained in PC-1 and PC-2 showed a complete separation between the classes of HEs for both substrates. The classes considered include the substrates with the three types of HEs at different concentrations to identify the variance between the vibrational signatures of the HEs. The percentage of the variance is mainly attributed to the difference in the signals for the HEs. A second score plot, shown in Figure 11, was generated for the samples deposited on Al. The PC-1 score plot shows the main variation in vibrational signatures for the analytes, where the most prominent signals are attributed. In this case, PC-1 explained 46% of the total variance, while PC-2 contributed to 20%. Both PCA scores plots for ABS and Al required the preprocessing steps of the Savitzky-Golay first derivative using a second-order polynomial fit of 15 points followed by minimization of scattering effects by particle-size distribution using standard normal variate (SNV).

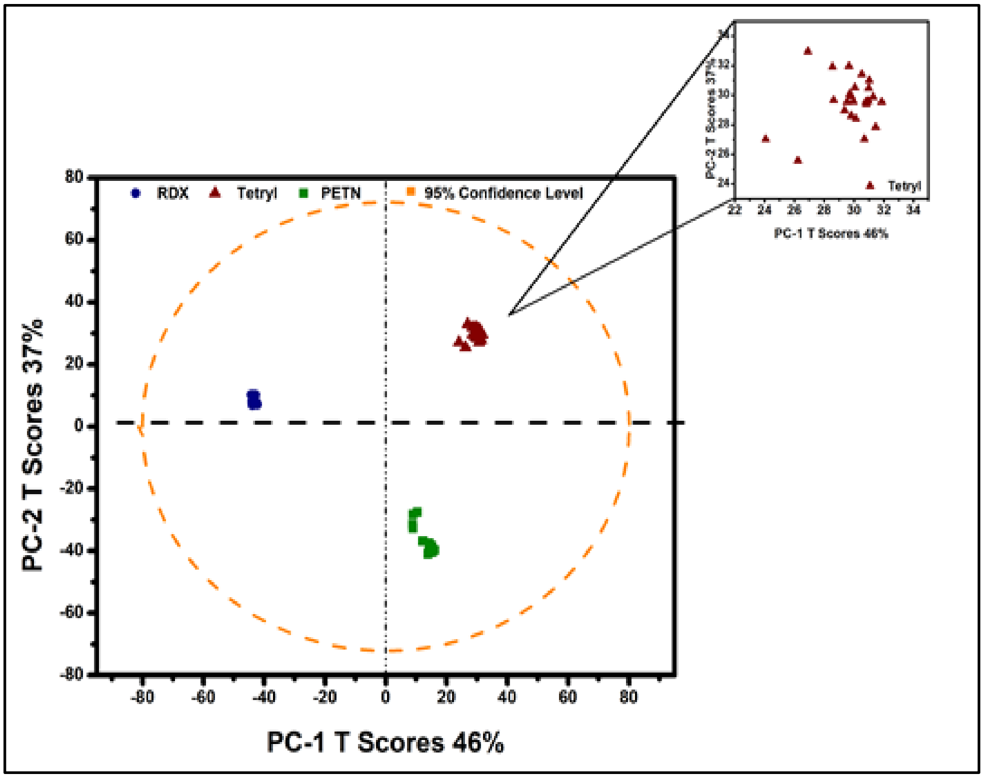

Figure 10: Scores plot for PETN, RDX, and tetryl on ABS substrate in terms of PC-2 versus PC-1. The 95% confidence level used in the analysis is also shown.

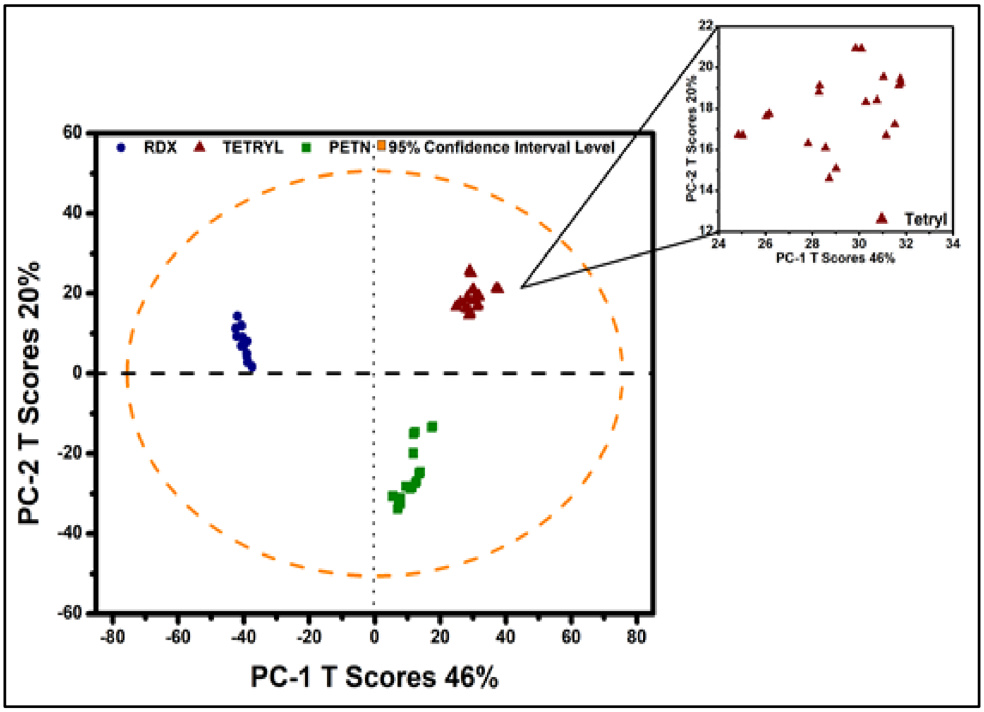

Figure 11: Scores plot for PETN, RDX, and tetryl on Al substrate in terms of PC-2 versus PC-1. The 95% confidence level used in the analysis is also shown.

C.9. PCA Classification of Standards Versus Commercial Aerosol Deposition Samples

Samples representing “real-world” surfaces were prepared by using a Paasche VL series Double Action Internal Mix Airbrush (Harwood Heights, IL, USA), as shown in Figure 12. Samples containing the HE, PETN, were deposited on the surface on reflective substrates stainless steel (SS), aluminum (Al), and Teflon as matte. The MIR spectra obtained from each deposition were characterized and used to classify between the standards and the samples, representing how the HE might be found in a heterogeneous surface.

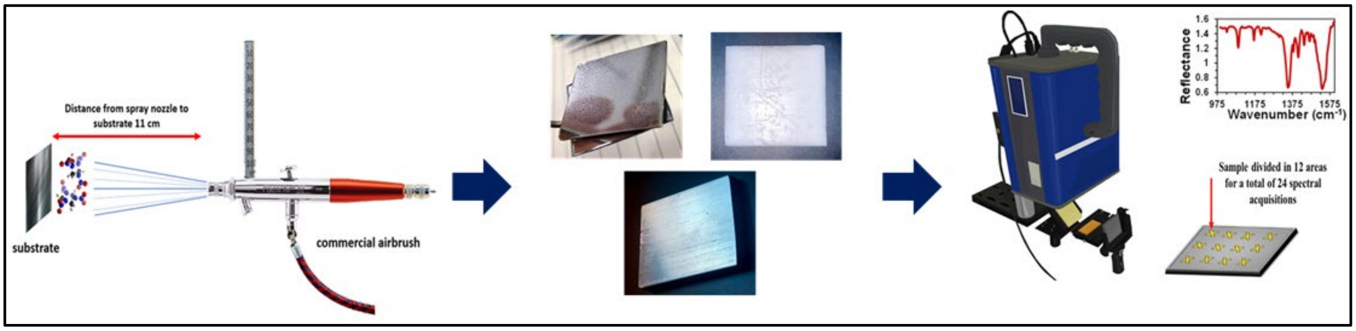

Figure 12: Setup for the MIR QCL-GAP system, including the aerosol deposition on SS, Teflon, and Al substrates.

PCA models were used as a method to validate the HE deposited utilizing the aerosol. The models showed significant variations in the classification of the HE, and it depended on the properties of the substrate. The preprocessing treatment that best classified the HE required Savitzky-Golay first derivative with 2nd order polynomial fit of 15 points followed by SNV. Figure 13 shows the PCA plot generated for the HE in Al, partially reflective standards in comparison to the Al samples with the PETN deposited using the spray. The PC-1 explained 30% of the variance, while PC-2 accounts for 26%. In this case, it was expected that the PETN used for the aerosol deposition samples collided with the PETN standards. The difference in the classification may be attributed to the difference in the Al substrate used in comparison to the standard.

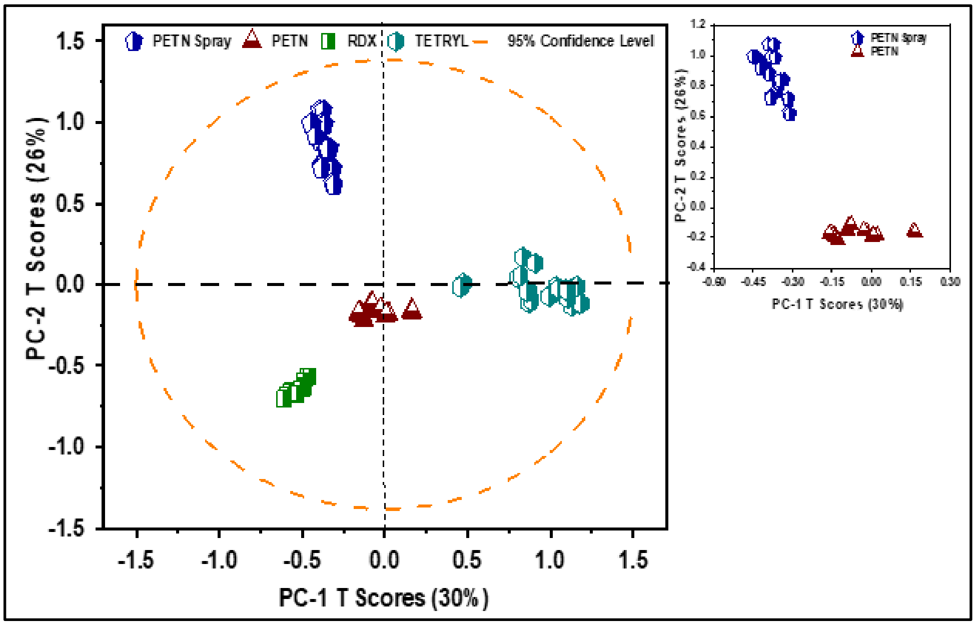

Figure 13: Scores plot PETN, RDX, and tetryl on Al substrates. PETN deposited using aerosol in spray Al is shown for validation of the HE.

A second score plot was generated for the nonreflective (matte) substrates. Teflon with PETN deposited using aerosol was compared to the HE deposited on ABS. These samples were used as the lowest reflective substrates, an essential aspect of the RAIRS experiments. The classification score plot for the HE in ABS standards and PETN in Teflon is shown in Figure 14. The PETN for both samples, standards, and nonstandards were classified with similar scores. PC-1 explained a percentage of 31%, while the PC-2 score explained the variance of 22%. The nitroaromatic compounds, RDX, and tetryl were also classified in this model. This model of the nonreflective substrate was able to fully classify PETN samples deposited on both ABS and Teflon, merging the PETN under one classification. The results for this model prove that the MVA routine used can differentiate between other HEs. The third model for the classification of the data included the highly reflective substrate, stainless steel with the PETN deposited utilizing the spray, and was compared to the partial reflective substrate Al as a standard. The model grouped the different compounds in the score plot but was not able to fully classify the PETN using the spray with the PETN standard. The plot for this model is shown in Figure 15.

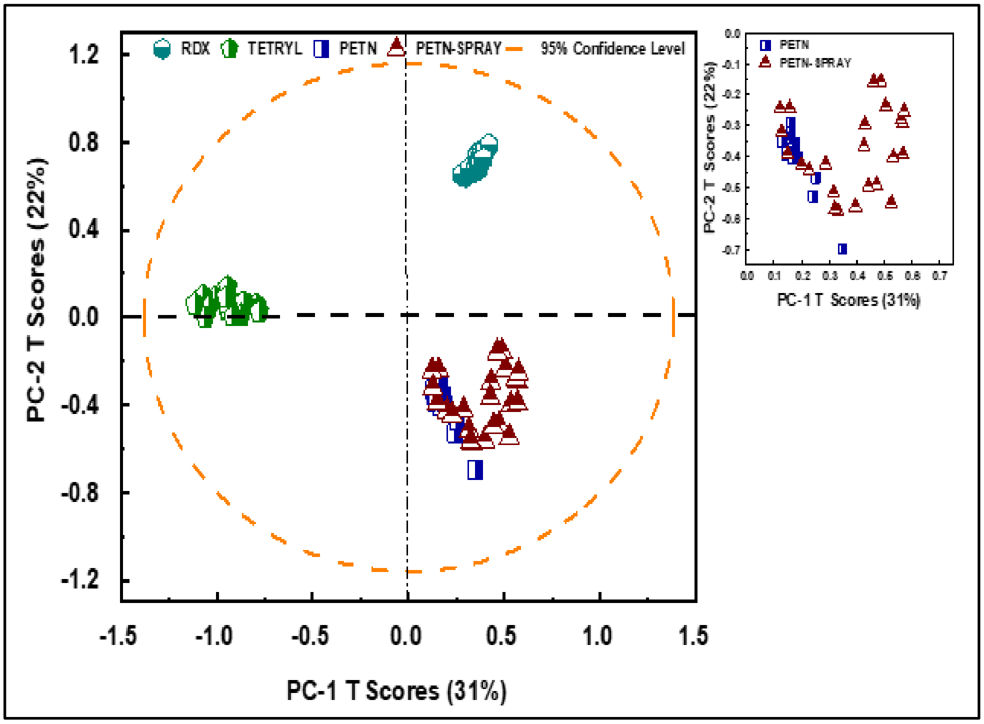

Figure 14: Scores plot for PETN, RDX, and tetryl on the ABS matte substrate. PETN deposited using air spray-on technique on Teflon substrates is shown for the validation of the HE.

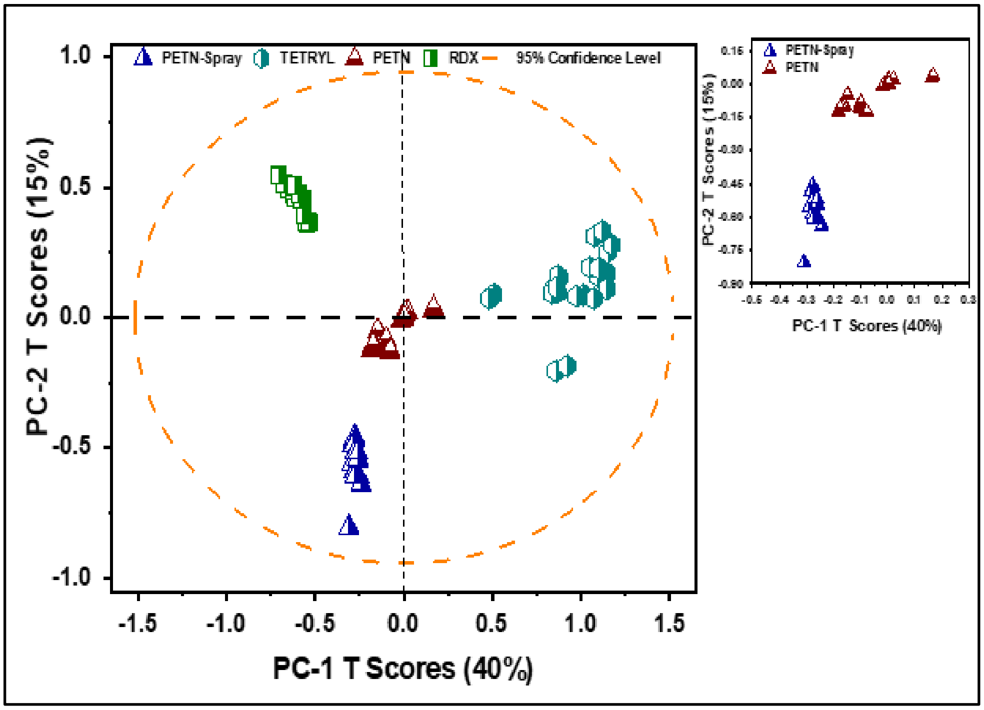

Figure 15: Scores plot for PETN, RDX, and tetryl on Al substrate. PETN deposited using air spray on SS reflective substrate.

The variations in the signals that classified the HEs and created the presented models were evaluated in terms of the loadings for the three models. The difference in the reflectiveness of the substrate may have caused interferences in this model, as well as the deposition method used. The deposition for this analysis plays a significant aspect since it is expected that a homogeneous deposition using a printer or direct deposition is more reliable than spray due to the loss of sample during the sample preparation. The use of other PC scores could aid in the classification of the PETN while varying the preprocessing treatments.

D. Expected Milestones at Project End

The key milestones from this year's project are related to the application of MVA routines for accurate detection using MIR QCL spectroscopy. In line with the no-cost extension provided on the ALERT Year 7 award, we will continue to work towards the completion of the following milestones up to or before May 2021:

- Finish the design of the multipass system (August 2020)
- Couple the setup to MVA routines to evaluate the effectiveness of the system (December 2020)
- Enhance factors: Ag/Au nanoparticles embedded on substrates for creation of materials for detection at lower concentrations: surface enhanced infrared reflectance (SEIRR); project recently started.
- Finish the computational chemistry of target chemicals (December 2020)

E. Final Results at Project Completion (Year 7)

One of the most important outcomes and contributions from this research component is the characterization of trace and near-trace to semi-bulk amounts of HEs. Deposition methods of HEs on substrates of interest to the homeland security enterprise, in general, must be characterized both morphologically and spectroscopically. The project has achieved significant advances related to trace-level HE detection with the coupling of the QCL spectrometer to the GAP (QCL-GAP). The deposition methods were varied by introducing samples that represent real-world heterogeneous surfaces with the HE. Classification models were created using the acquired spectroscopic data containing the vibrational signatures. The validation aspect was achieved by using the NRL standards. The models were able to classify the HEs according to the substrate, and HE deposited.

Another contribution of this project was realized by the variation of the incident angle from 12° to 84° for the HEs under study. The investigation was carried out using the QCL with a neural network analysis algorithm for the sorting of the classes by creating confusion and test matrices. A total of nine classes were analyzed to predict the HEs when using spectra with the variation of the angles. KNN is still under the MVA tool in our lab and is expected to continue providing results based on the training of data to improve the prediction of samples.

III. RELEVANCE AND TRANSITION

A. Relevance of the Research to the DHS Enterprise

Over the years, incidents involving attacks have fortunately decreased due to technological advancements and rigorous security measures; however, threats still exist. The detection, identification, and quantification of HEs, homemade explosives (HMEs), precursors, and new green explosives continue to be a high priority for security agencies.

- Development of a methodology for detection, identification, discrimination, and quantification of explosives in the presence of highly interfering backgrounds
- Mass range from bulk (0.1 g) to trace (10 ng) at close distances (~15 cm) for potential operation at checkpoints and mid to long remote distances
- The methodology under development will provide a positive/negative result or a confidence level indication to the operator for the presence of explosives within (<3 s), with a goal of (1 s)
- The methodology will operate effectively in field environments at multiple distances with varying amounts of humidity, air particulates, temperature, light, and wind
- The methodology will be useful in providing evidence of post-terrorist events by detecting explosives residues on dirt, concrete, wood, cardboard, bricks, and other surfaces
- Two invention disclosures for patent applications on coupling technology under development for robust separation and quantification methodologies
- Neural network analysis, multivariate routines, and partial least squares discriminant analysis for data analysis and generation of prediction models

The impact of developing QCL-GAP technology through this effort is particularly essential to the HE trace detection community in security and defense applications. It is particularly important for development of methods that can determine if individuals have been in contact with HE illicitly. QCL-GAP system operated in standoff mode with chemometrics-based MVA should become a new technological approach for rapid detection of HE traces.

B. *Status of Transition at Project End*

- Will continue to seek partnerships for the ongoing development of methods of detection of explosives and hazardous chemicals with companies that fabricate laser sources for MIR or are involved in explosives detection instruments/methodologies
- Have already shared papers and described the invention disclosures that have resulted from this project to most of the potential partners
- Plan to submit a proposal to DHS Small Business Innovation Research (SBIR) Topic solicitation in the subject area of Research and Development of Countering Biological Weapons of Mass Destruction threats. The first phase of the topic solicitation pitch paper was recommended for competition in two of the topics selected. The proposal was submitted on June 19, 2020.

C. *Transition Pathway and Future Opportunities*

C.1. Sub-Project 1

The sub-project described in Task 1 will be either a “spinoff” small startup with alumni from the UPRM chemistry doctoral program in Applied Chemical Sciences and former ALERT-II R3-C students in the form of a Small Business Innovation Research (SBIR) proposal channeled through the Puerto Rico Science Trust. Another possible mechanism is to apply to DHS, Department of Defense, or the National Science Foundation for an SBIR together with Michele Hinnrichs and VERLUZ, LLC (PAT, Inc.). We have already submitted an invention disclosure for a patent (“Grazing Angle Probe Mount for Quantum Cascade Lasers”; Ser.#: 62/587,557; filing date 11/17/2017). The planned prototype would be a portable explosives detection system (EDS), physically coupled to MIR fiber optics, user friendly, and completely contained in a small frame rugged box.

The goal of Sub-Project 1 is to fully develop QCL-GAP setups coupled to MVA for the detection of HEs on reflective and non-reflective substrates and to transition the technology through an SBIR to build a portable system prototype.

The expected outcomes include:

- Developing portable QCL systems setups for the detection of HEs on non-reflective substrates
- Building a lab-based fiber optics coupled QCL-GAP
- Completing the design and development of the multipass system
- Strengthening our research, education, and training STEM facilities, focusing on explosives sensing concepts and data analysis at the University of Puerto Rico.

This ongoing process is visualized to allow for continuous, sustainable participation of undergraduate students and development of faculty from the BS program focused on Technology in Industrial Chemical Processes at UPR at Arecibo. Students and faculty members will be pipelined into UPRM MS and PhD programs and further into DHS, US government, and private sector internships and work opportunities.

C.2. Sub-Project 2

Planning of a joint venture with Michele Hinnrichs (VERLUZ, LLC; Humacao, PR), a division of Pacific Advanced Technology, Corp. (Solvang, CA), Targeted SBIR: DHS (Jim Jensen, DHS program manager, Edgewood Chemical Biological Center, Aberdeen Proving Grounds, Aberdeen, MD). Other possible sources of funding are DoD-DTRA, other DoD divisions, and NSF.

The goal of Sub-Project 2 is to transition Laser-Induced Thermal Imaging Spectroscopy (LITIS) together with VERLUZ, LLC.

The expected outcomes include:

- Establishing the feasibility of LITIS on reflective and dielectric (i.e., non-reflective) substrates using various HEs/substrates combinations
- Establishing the limits of detection and quantification of the technique
- Establishing a joint venture with an industrial partner (VERLUZ, LLC) for developing an instrument capable of detecting explosive residues at a distance using an active sensing modality.

C.3. Sub-Project 3

Intellectual property stemming from this task will be made available, cost-free, possibly through a mechanism similar to the one used by the University of Rhode Island, with its database of explosives properties.

The goal of Sub-Project 3 is to predict the performance and thermochemical properties of new energetic materials using computational chemistry, from a given molecular structure without using experimental measurements.

The expected outcomes include:

- Predicting the detonation parameters without experimental data for a systematic set of novel green energetic materials with high nitrogen and low carbon content as triazoles, tetrazoles, azidotetrazoles, triazene, nitro-substituted cage compounds, and oxygen-rich organic peroxides
- Training students in computational chemistry to integrate the information provided by different programs of molecular modeling and chemometrics routines for the prediction of explosive properties

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Student Internship, Job, and/or Research Opportunities
    a. Annette M. Colón-Mercado, MS student, summer 2020, research internship, Naval Research Lab, Indian Head division, Washington, DC (canceled due to COVID-19)
    b. Francheska M. Colón González, MS student, summer 2020, research internship, Sandia National Laboratories, Albuquerque, New Mexico (canceled due to COVID-19)
2. Training to Professionals or Others
    a. Raman Spectroscopy Workshop I, October 2019, Society for Applied Spectroscopy (SAS-UPRM)
    b. Raman Spectroscopy Workshop II, November 2019, SAS-UPRM
    c. Raman Spectroscopy Workshop III, March 2020, SAS-UPRM

B. *Peer Reviewed Journal Articles*

1. Pacheco-Londoño, L.C., Galán-Freyle, N.J., Figueroa-Navedo, A.M., Infante-Castillo, R., Ruiz-Caballero, J.L., & Hernández-Rivera, S.P. "Quantum Cascade Laser Back-Reflection Spectroscopy at Grazing-Angle Incidence Using the Fast Fourier Transform as a Data Preprocessing Algorithm." *Journal of Chemometrics*, *33*, 29 July 2019, p. e3167. https://doi.org/10.1002/cem.3167.
2. Pacheco-Londoño, L.C., Ruiz-Caballero, J.L., Ramírez-Cedeño, M.L., Infante-Castillo, R., Gálan-Freyle, N.J., & Hernández-Rivera, S.P. "Surface Persistence of Trace Level Deposits of Highly Energetic Materials." *Molecules*, *24*(19), 26 September 2019, p. 3494. https://doi.org/10.3390/molecules24193494.
3. Galán-Freyle, N.J., Ospina-Castro, M.L., Medina-González, A.R., Villarreal-González, R., Hernández-Rivera, S.P., & Pacheco-Londoño, L.C. "Artificial Intelligence Assisted Mid-Infrared Laser Spectroscopy in situ Detection of Petroleum in Soils." *Applied Sciences*, *10*(4), 15 February 2020, p. 1319. https://doi.org/10.3390/app10041319.
4. Pacheco-Londoño, L.C., Warren, E., Galán-Freyle, N.J., Villarreal-González, R., Aparicio-Bolaño, J.A., Ospina-Castro, M.L., Shih, W.C., & Hernández-Rivera, S.P. "Mid-Infrared Laser Spectroscopy Detection and Quantification of Explosives in Soils Using Multivariate Analysis and Artificial Intelligence." *Applied Sciences*, *10*(6), 31 May 2020, p. 1319. https://doi.org/10.3390/app10041319; https://doi.org/10.3390/app10124178.

Pending –

1. Colón-González, F.M., Perez-Almodovar, L.A., Barreto-Pérez, M., Vargas-Alers, G.L., Santos-Rolón, J.M., & Hernández-Rivera, S.P. "Raman Scattering Detection of High Explosives on Human Hair." *Optical Engineering*, submitted February 2020.
2. Colón-Mercado, A.M., Vázquez-Vélez, K.M., Caballero-Agosto, E., Villanueva-López, V., Infante-Castillo, R., & Hernández-Rivera, S.P. "Detection and Classification of High Explosives Samples Deposited on Various Substrates Types Using a Mid-infrared Laser Grazing Angle Probe Assisted by Multivariate Analysis." *Optical Engineering*, submitted February 2020.
3. Galán-Freyle, N.J., Pacheco-Londoño L.C., Figueroa-Navedo, A.M., Ortiz-Rivera, W., Castro-Suarez, J.R., & Hernández-Rivera, S.P. "Modulated-Laser Source Induction System for Remote Detection of Infrared Emissions of High Explosives Using Laser-Induced Thermal Emission (LITE)." *Optical Engineering*, submitted February 2020.

C. *Other Presentations*

1. Poster Sessions
   a. Caballero-Agosto, E.R., Infante-Castillo, R., & Hernández-Rivera, S.P. "1H, and 13C NMR Chemical Shifts Prediction Models for Peroxi-Based Compounds with Computational Chemistry" [poster]. Industrial Advisory Board Meeting, Awareness and Localization of Explosive-Related Threats, Northeastern University Innovation Campus at Burlington, MA. 4 November 2019.
   b. Colón-Gonzalez, F.M., & Hernández-Rivera, S.P. "Detection of HE's on Human Hair by Raman Spectroscopy" [poster], Industrial Advisory Board Meeting, Awareness and Localization of Explosive-Related Threats, Northeastern University Innovation Campus at Burlington, MA. 4 November 2019.

   c. Colón-Mercado, A.M., López-Pagán, B.M., Ruíz-Caballero, J.L., & Hernández-Rivera, S.P. "Enhanced Detection of High Energetics Materials in Substrates Using Tunable Quantum Cascade Laser-Grazing Angle Probe" [poster], Industrial Advisory Board Meeting, Awareness and Localization of Explosive-Related Threats, Northeastern University Innovation Campus at Burlington, MA. 4 November 2019.

2. Interviews and/or News Articles
   a. Colón-Mercado, A.M. "Meet the ALERT Students." Industrial Advisory Board Meeting, Awareness and Localization of Explosive-Related Threats, Northeastern University Innovation Campus at Burlington, MA. 4 November 2019.
   b. Colón-Mercado, A.M. "Student from RUM Stands Out in DHS Security Challenge." *Primera Hora*, local PR newspaper, 23 November 2019. https://www.primerahora.com/noticias/puerto-rico/notas/estudiante-del-rum-se-destaca-en-competencia-del-departamento-de-seguridad-nacional/.

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

1. Colón-González, F.M. "Detection and Discrimination of High Explosives on Human Hair by Raman Scattering." MS Thesis, University of Puerto Rico at Mayagüez, May 2020.
2. Colón-Mercado, A.M. "Quantum Cascade Laser-Grazing Angle Spectroscopy Detection of High Explosives Deposited on Various Substrates Using Air Spray." MS Thesis, University of Puerto Rico at Mayagüez, May 2020.
3. Padilla-Rivera, G.I. "TNT and MO Photodegradation in Deionized and Salt Waters with Visible Light Assisted by Photoactivation of Modified TiO_2." MS Thesis, University of Puerto Rico at Mayagüez, May 2020.

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

New or Existing	Course/Module/Degree/Cert.	Title	Description	Student Enrollment
Existing	Certificate program course in forensic chemistry	Chemistry of Explosives	For students of chemistry and chemical engineering	15

F. *Technology Transfer/Patents*

1. Patent Applications Filed (Including Provisional Patents)
   a. Hernández-Rivera, S.P., & Castro-Suarez, J.R. "Coupling of Thin-Layer Chromatography (TLC) to Quantum Cascade Laser Spectroscopy (QCLS) for Qualitative and Quantitative Field Analyses of Explosives and Other Pollutants." U.S. Patent 10,379,033 B1, 13 August 2019.

G. *Software Developed*

1. Databases
   a. Ongoing: Library of vibrational spectra of HEs, HMEs, and precursors.

2. Algorithms
   a. Fast Fourier Transform preprocessing programmed in MATLAB 8.6.0.267246 (R2015b; MathWorks Inc., Natick, USA). This algorithm is being used to remove interference fringes from thin HE films generated by GAP-QCL RAIRS measurements. Used in Pacheco-Londoño, L.C., Galán-Freyle, N.J., Figueroa-Navedo, A.M., Infante-Castillo, R., Ruiz-Caballero, J.L., & Hernández-Rivera, S.P. "Quantum Cascade Laser Back-Reflection Spectroscopy at Grazing-Angle Incidence Using the Fast Fourier Transform as a Data Preprocessing Algorithm." *Journal of Chemometrics*, *33*, 29 July 2019, p. e3167. https://doi.org/10.1002/cem.3167.

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