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

Abstract—The main objective of the ALERT Phase 2 R3-C component is to develop Vibrational Spectroscopy for photonic standoff detection of highly energetic materials (HEMs): explosives and homemade explosives (HMEs). The expected outcomes of the project are to significantly improve the current state of development of vibrational standoff detection of HEMs/HMEs, in terms of: range (target-observer distance); detection limits; quantification; and discrimination capabilities from interferents (background and matrices). During Year 1, significant improvements were made in the development of remote mid-infrared (MIR) sensing of explosives using QCL, thermal and CO2 laser based methods.

I. PARTICIPANTS

<table>
<thead>
<tr>
<th>Faculty/Staff</th>
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<th>Title</th>
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<td>12/2015</td>
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<td>Eduardo Espinosa</td>
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<td>Carlos Ortega</td>
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<td>Amanda Figueroa</td>
<td>BS/REU</td>
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<td>Eric Warren</td>
<td>BS/REU</td>
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II. PROJECT OVERVIEW AND SIGNIFICANCE

The need for rapid detection and identification instrumentation for explosives threats in homeland security and defense applications has become a concern of crucial importance in modern society. For military, secu-
rity and anti-terrorist personnel, to first responders and law enforcing employees, such as police officers, airport screeners and border patrols personnel, to Navy, Army, Air Force and National Guard workforces, the possibility of coming in contact with a chemical or biological threat agent is high. Highly energetic materials (HEMs), including high explosives (HE; nitroaromatic or nitroaliphatic) or homemade explosives (HMEs, organic peroxides, nitrate or perchlorate based) are more often encountered by security personnel and first responders than chemical agents, toxic industrial compounds or biological agents. To achieve the required countermeasures in handling explosives threats and mitigation efforts, vibrational spectroscopic techniques are frequently used. Detection of HEMs resident on substrates at trace levels or airborne remains a subject of great importance. In the past few years, many of the published reports have focused on the detection of these important chemical compounds. However, the majority of them require some type of sampling. Obtaining samples in the field is the principal disadvantage of most explosive detection devices because the person doing the sampling is at risk.

Vibrational spectroscopy based standoff detection has been used for sensing HE and HME, forming an important part of the contributions from the Chemistry research group at the University of Puerto Rico-Mayagüez, as part of the ALERT Phase 1 F2-F component, and now carries on to the DHS COE: ALERT Phase 2 in its new component R3-C. During the past year, research has covered applications at close distances (0.1 m to 1 m) and long ranges (5 to 65 m), in the case of standoff mid infrared (MIR) spectroscopy, not limited by range but rather by source; and up to 140 m, in the case of standoff Raman spectroscopy. Raman spectroscopy based standoff detection still holds a bright future in defense applications (particularly for UV Raman standoff detection) but not for security applications under the DHS/TSA umbrella because of obvious problems with eye safety. On the other hand, MIR spectroscopy coupled with laser sources can provide HEMs detection solutions, both at close range (0.1 – 1 m) and at longer distances from the observer (1-100 m) under totally eye safe conditions for the operators and for target suspects. The need to develop more powerful MIR sources that allow detection at longer distances when a target is present at trace levels deposited on substrates suggests the use of collimated, coherent and polarized sources; i.e.: lasers. These sources were first developed at Bells Labs in 1994 with the invention of quantum cascade lasers (QCLs).

This new project of the R3-C component of ALERT involves evaluating MIR laser sources which are eye safe. Quantum cascade lasers have revolutionized MIR spectroscopy applications. They are capable of producing from tens to hundreds of milliwatts of continuous mode or pulsed power at ambient conditions, are commercially accessible and have made possible the development of a ruggedized system for detection of hazardous threats. Recent developments in QCL technology include size reduction, which has enabled the transition from table-top laboratory instruments to easy-to-handle, portable devices; and design of small instruments that can be used by first responders and military personnel outside the confinement of a sample compartment. Moreover, the increase in output power has enabled the use of QCL-based spectrometers in long distance (range) applications, making detection of chemical and biological threat agents possible at tens of meters from the source. Other Fourier transform IR spectroscopic modalities important to the task of detection, identification and discrimination of explosives range from bulk (few mg) to trace (sub-μg/cm²) @ 0.1 – 20 m. Techniques evaluated must provide positive/negative or a confidence level indication to the operator for presence of explosives within 1 minute (in most cases a few seconds), and must operate effectively in a field environment at multiple distances with varying levels of relative humidity, air particulates, temperature, light and wind.

III. RESEARCH ACTIVITY

A. State-of-the-art and technical approach

Rapid and precise identification of HE and HMEs is at the top of the agenda of National Defense and Security agencies. At the ALERT COE, the interest focuses on all areas related to these highly energetic materials,
including detection, characterization and prevention of terrorist attacks. Instruments that can be used in the field to rapidly and accurately detect and identify explosives and their precursors could form part of checkpoint security stations in airports, seaports and government buildings. Infrared spectroscopy (IRS) in the mid-infrared (MIR) region has played an important role in the characterization of highly energetic materials through persistent characteristic signatures. These signatures can be universally used to detect these compounds from a distance. This project deals with the use of IRS to develop confirming orthogonal chemical sensors for detecting explosives residues on clothing, travel bags, personal bags, laptop bags/cases, skin and other substrates. Confirming orthogonal sensors are envisioned for use after millimeter wave sensing of anomalies/devices under clothing and within human bodies. The main hurdle to overcome is discriminating for the nitro or peroxide based explosives from highly interfering, MIR absorbing substrates (matrices) on which explosives are found. This area is our second most significant contribution to the field.

B. Major contributions

B.1 Detection of highly energetic materials on non-reflective substrates using quantum cascade laser spectroscopy (QCLS)

A spectroscopic system based on quantum cascade lasers was used to obtain mid-infrared spectra of highly energetic materials (HEMs) deposited on non-ideal, low reflectivity substrates such as travel bags (TB), cardboard (CB) and wood (W). Various deposition methods including spin coating, sample smearing, partial immersion and spray deposition were tested for preparing standards and samples used in the study. Figure 1 contains a schematic diagram illustrating the experimental setup, sample preparation and data acquisition and analysis.

The HEMs used included nitroaromatic explosive 2,4,6-trinitrotoluene (TNT), aliphatic nitrate ester pentaerythritol tetranitrate (PETN), and aliphatic nitrime 1,3,5-trinitroperhydro-1,3,5-triazine (RDX). Low surface concentrations (1-15 μg/cm²) of HEMs were used in the investigation. Figure 2 shows representative QCLS spectra of TNT, PETN and RDX on Al (Fig. 2a), on CN (Fig. 2b), on W (Fig. 2c) and on TB (Fig. 2d).

Hit quality index (HQI) values were calculated from a spectral library and used as identification methods through correlation coefficients. Spectral ID using spectral correlation algorithms were not efficient enough for identifying HEMs when present on non-ideal low reflectivity, highly mid-infrared absorbing substrates. The results are shown in Table 1 on the next page.
Two chemometrics algorithms were applied to analyze the spectral characteristics recorded using QCLS; principal component analysis (PCA) was used to identify spectral similarities in a spectral data set and partial least squares (PLS) were used to find the best correlation between the infrared signals and the surface concentration of samples. Multivariate analyses were efficient enough in attaining the goals of this investigation. Several preprocessing steps were used to analyze the obtained infrared spectra of HEMs deposited as contaminants on target substrates. Chemometrics-based multivariate analyses used to detect target HEMs deposited on TB and CB substrates required only first derivative and mean centering as preprocessing steps. Wooden substrates were more challenging for generating efficient PCA models and a third preprocessing step (standard normal variate transformation) was required to achieve the desired discrimination on these substrates. Moreover, classifications according to the type of HEM were achieved. PCA models of the three HEMs studied, TNT, RDX and PETN, on the three substrates tested (general PCA model) allowed discrimination even in the presence of highly interfering and complex substrates, although the model required 12 PCs to account for 80% of the variance. In general, QCL spectroscopy was demonstrated to be useful for detecting HEMs on non-ideal, low reflectivity substrates, and for discriminating the analytes from highly interfering substrates when coupled with chemometric tools such as PCA analysis. Figure 3 illustrates some of the results using PCA models; Figure 3a- PCA for HE investigated on TB; Figure 3b- general PCA regression model for TNT, PETN and RDX on TB, CB and W.

![Figure 3](image)

Finally, PLS models demonstrated the capability of predicting surface concentrations of HEMs on the substrates tested using a maximum of 8 latent variables (LV) to obtain values of R² higher than 0.9. The results clearly demonstrate that the infrared vibrational method used in this study can be useful for the detection of HEMs on real-world low reflectivity substrates. The PLS-DA models resulting from the discrimination of each HEM from the others and from the neat substrate for TB are shown in Figure 4 on the next page. The
class predictions of PETN, RDX, and TNT on TB from the cross validation are shown in Figures 4a-4c. Four LVs were required to obtain the best multivariate classification model with high sensitivity (see Table 2) for the HEMs tested from the calibration, cross validation and prediction data sets. The variance captured was 87.8%, which is sufficient for a good classification of the predicted spectra set on TB. For the multivariate (clustering) analysis of the HEMs on TB, a total of six LVs were necessary to capture 80% of the total variance in the spectral data. As shown in the score plot in Figure 4d two latent variables with 60% of the spectral variance were sufficient to obtain an excellent classification according to the type of HEM deposited and to discriminate from the TB substrate. In this model, spectra from the prediction set (RDX Test, TNT Test, and PETN Test) were well grouped according to chemical characteristics with spectra from the calibration sets.

![Figure 4: PLS model for QCLS detection of HE deposited on TB: (a) PETN test; (b) RDX test; (c) TNT test; (d) Scores Plot for all data.](image)

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Table 2: Statistical parameters of PLS calibrations for QCLS spectra of HEM deposited on substrates.

In summary, a QCL based spectroscopic system allowed the detection of HEM deposited at low surface concentrations (1-15 μg/cm²) on three types of non-ideal low reflectivity substrates: travel bag fabric (TB), cardboard (CB) and wood. Spectral identification using spectral correlation algorithms were not efficient enough
for identifying HEMs when present on non-ideal low reflectivity, highly mid-infrared absorbing substrates. However, multivariate analyses were efficient enough in attaining the goals of this investigation. Finally, PLS models demonstrated the capability of predicting surface concentrations of HEMs on the substrates tested using a maximum of 8 latent variables (LV) to obtain values of $R^2$ higher than 0.9.

**B.2 FT-RAIRS monitoring of ultra-thin RDX films generated by spin coating and modelled by chemometrics multivariate analyses: PLS and PCA**

Ultra-thin films have been prepared by various methods. Their thickness have been estimated with various techniques: profilometry, atomic force microscopy and other sophisticated methods have been employed to measure film thickness and roughness. However, there have been very few studies involving film thickness influence on infrared spectra. Ultra-thin RDX films have been prepared by spin coating on various surfaces. Initially principal component analysis (PCA) findings explain that it is possible to discriminate ultra-thin films prepared by angular speed (rpm) in the spin coating process. Film thickness will be estimated by atomic force microscopy. Calibration curves prepared by partial least squares (PLS) should correlate the measurements, found by atomic force microscopy, to deposition speed (rpm) in the spin coating methodology. Model robustness will be measured with an independent validation set, once the experimental design provides optimized results in principal component analysis. Optical properties for these ultra-thin films will also be measured to examine variations with deposition. The objective of this study is to determine thickness and roughness parameters on the preparation of samples and standards and the concomitant correlation with speed of deposition, film thickness, roughness and the optical properties. This will allow for the generation of samples with a high level of known physical, optical and spectroscopic characteristics.

Principal component analysis was performed on the stainless steel and gold surfaces, spin coated with RDX at 3000 RPM. At a 45° Electric Field Vector angle, there should be little to no response in intensity with thin films. The purpose of carrying out Principal component analysis with this spectra is to compare the responses by EFV angle as the RPM’s increase, assuming that the thickness of the RDX thin film decreases. Figure 6 on the next page shows the change in intensity for the mentioned peaks as the Electric field Vector angle increases, one of them is at 1240 cm-1 and the next one is at 1560 cm-1. The only preprocessing needed was baseline correction, with a Root Mean Squared Error of Calibration (RMSEC) value of 0.0027 (0.27%) and a Root Mean Squared Error of Prediction (RMSEP) value of 0.0054 (0.54%). Variance Captured Percentage for this PCA was calculated as 99.54%. The scores in Figure 7 on the next page show the precision for every spectra taken at each EFV angle, for which we will calculate for every 1000 revolutions per minute, from 1000 to 9000. For one spectrum without polarization, there was more variation and less precision in measurements. The difference noticed on principal component analysis has to do with the intensity of these important peaks. Spectra taken at an electric field angle of 90° are then subjected to principal component analysis, separated by the revolutions per minute when prepared by spin coating. Figure 3 shows that there is a relative decrease in intensity for two peaks at 1265 (NO2 axial) and 1320 cm-1. There is also a slight shift in these peaks as the revolutions per minute decrease.

Partial Least Squares is also to be carried out once PCA shows a clearer distinction per spin velocity. PCA shown in Figure 6 on the next page shows that the first principal component describes a difference per revolution. Looking at Figure 5b on the next page, principal component analysis describes the left-hand side of the principal component as the one with the least amount of revolutions per minute. However, spectra for thin films taken at 9000 revolutions per minute fall right in the middle. In order to corroborate that this behavior is true, a new data set is to be evaluated by PCA, once the homogeneity of the films is established by AFM. This data was only mean centered, with three PCs chosen with 99.97% cumulative variance. With this premise, we assume that thickness is involved in the difference in Fourier transform Infrared Spectra. Figure 7 on the next page shows the scores for the first three principal components. The third component does not add much information to discriminate per spin velocity. Figure 8 on the following page shows loadings per principal component, where the first one explains the most variation per revolution in the spectra. The sec-
ond and third principal component add more noise to the model. The fourth principal component provides additional peaks which will be further studied. Looking at this principal component, one of the most studied peaks of RDX at 1600 cm\(^{-1}\) is appreciated. However, the spectra in this peak are not varying in intensity per revolution per minute as seen in the peak at 1265 and 1320 cm\(^{-1}\). Figure 8 on the next page shows the first loading for the principal component, in which the peaks at 1265, 1320 and 1600 cm\(^{-1}\) are appreciated.

In summary, homogeneity of the films should be established, since there was some variation within the same class. The experimental setup has been modified since the measurements carried out per revolution, so the measurements will be repeated in summer 2014. With Principal Component Analysis, we can deduct that the first principal component explains why there is a difference per spin velocity in the spectra, which is inversely proportional to the thickness. This means that while revolutions per minute increase, the thickness decreases. On the other hand, there is also a marked difference between spectra taken at different electric field vector angle and without polarization. Optical properties will be calculated at these angles for all
revolutions. These measurements will also be carried out in copper, silicon and gold surfaces. The advantages of Fourier Transform infrared spectroscopy to evaluate film thickness is that this method is non-destructive, provides high resolution and it can provide more information when combined with Partial Least Squares (PLS) and PCA, as well as other chemometric methods. Figure 9 shows the initial results for classification with PLS in which more distinct separation of the data are achieved, particularly in 3-dimension score plots as shown in Figure 10 on the next page.

Figure 8: Spectra as function of deposition speed (rpm) showing a decrease of RDX band intensities at 1260 and 1320 cm⁻¹.

Figure 9: PLS results: (a) there are no outliers in this PCA model. (b) Scores show adequate reproducibility within the same classes, particularly at 6000 RPM; (c) Scores on PC 1 are shown in order from left to right from 1000 to 9000 RPM; (d) deposition speeds studied.
C. Future plans

Several projects have been planned as continuation of the efforts in vibrational spectroscopy based chemical detection of explosives. These include MIR spectroscopy based detection of explosives (using thermal and laser excitation sources), and nanotechnology based detection of explosives. Plans for next year include building an addressable library of HE/HEMs independent of substrate type and to start QCLS transmission mode detection of explosives.

Another relevant project deals with characterization of HMEs and their detection and their precursors. Upcoming work will include standoff detection of HEMs/HMEs on other substrates, such as plastic, wood, leather, cloth and other metallic surfaces, in order to quantify and obtain chemometrics models that can be applied in real world environments. Detailed theoretical study of optical processes on these surfaces is required to understand the nature of the results of the experiments and for the transition of standoff laser induced thermal emission (LITE) of explosives to real world substrates using complex matrices, such as sand, plastic, wood, leather, cloth and other metallic surfaces.

Future work will also be performed for detection of HMEs and other harmful substances in vapor phase, combined with statistical analysis in order to obtain a quantification model using chemometrics. In addition, we will be performing research in order to optimize the overall process in the fabrication of our capillary SERS substrate and fully characterize the obtained microdevices.

IV. EDUCATION & WORKFORCE DEVELOPMENT ACTIVITY

The R3-C project has had a strong commitment to education and training at all levels, from high school to post-doc trainees. Table 3 below and continued on the next page illustrates the main factors used to measure productivity and effectiveness.

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During the summer of 2013 the Research Experiences for Undergraduates was extended to host 6 undergraduate students: two (2) from the DHS ALERT-COE; one (1) from DOD HBCU-MI program and two (2) from a recently awarded NSF-REU grant for Metropolitan University. The students are listed in Table 4.

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<th>Name</th>
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<td>1. Eric Warren</td>
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<td>6. Amanda Figueroa</td>
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<td>7. Amanda Figueroa</td>
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Table 4: Summer of 2013 and 2014 REU students hosted by UPR-Mayagüez.

V. RELEVANCE AND TRANSITION

A. Relevance of your research to the DHS enterprise

The results of ongoing studies demonstrate that the experimental setups can be used in many applications for detection of explosives, other threat chemicals and biological threat agents. The results of this study indicate that explosives, as well as illegal drugs, can be strategically mixed with other compounds with similar chemical and physical properties with the purpose of disguising them from security personnel and using them for criminal orterroristic events. Detection of hazardous compounds such as explosives, hazardous chemicals and biological agents employed by terrorists and smugglers is considered an area of high interest for federal government agencies, such as the Department of Homeland Security, Department of Defense, Department of Justice, State Departments of Corrections and Forensic Agencies and others.

This project also intends to expand the knowledge in the field of preparation of samples and standards based on thin films and islands of HEMs, and also HEMs for both basic and applied research by depositing traces of target analytes on substrates of high interest using spin coating technology to develop the mentioned assemblies. The two main goals of this project are related to the study of solid-substrate interactions. The first and primary goal is to develop methodologies capable of producing solid samples deposited on substrates in controlled size and distribution modes deposited on selected surfaces to generate specimens that would reproduce real contamination samples. In a second closely related aim, the prepared samples will be used to characterize analyte-substrate interactions, physical and chemical properties derived from these interactions, including, but not limited to, particle sizes and shapes, polymorphism at the sub-micro range, optical and spectroscopic properties, thermal properties and others. At the micron and sub-micron ranges, the resi-
dence time of these adsorbate-substrate assemblies becomes an important property for study, since behavior at the microscopic scale is very different from bulk phase characteristics. Finally, the applications of these well-characterized samples include use in experiments that require fine control of the distribution of loadings of analytes on surfaces.

B. Anticipated end-user technology transfer

Work on QCLS based detection of explosives is also being pursued in collaboration with Eos Photonics and Thermo-Fisher Scientific (formerly Ahura) for the development of explosives detection equipment. The commercial applications have been envisioned in the standards market for traditional nitroexplosives or high explosives (HE), and for cyclic organic peroxides (CAP) HME, including DADP, HMTD and TMDD.

The technologies under development are useful for gas phase detection of relatively high vapor pressure HMEs (such as 2,4-DNT, TATP and others), for chemical agents, for biological threat agents and for illicit drug detection. They can also be used in Process Analytical Technology (PAT) applications in pharmaceutical and biotechnology industries. The applications for pharma and biotech are in tablet content uniformity verification and for cleaning validation of batch reactors, mixers, filters and dryers. Coupling with multivariate analysis routines in all of these applications will definitively enhance the desired results and drive low limits of detection to the lowest possible values.

In still another application of QCLS coupled to chemometrics, the detection and classification of microorganisms (such as bacteria, viruses and yeasts) can be addressed very successfully, shortening analysis time from hours to seconds. Defense and security, as well as biotech, food industries and public health facilities and hospitals will benefit, to a large extent, from the methods and techniques under development in the R3-C research and development component.

VI. LEVERAGING OF RESOURCES

The NSF Chemical Measurement and Imaging Program supports research focusing on chemically-relevant measurement science and imaging, targeting both improved understanding of new and existing methods and development of innovative approaches and instruments. The primary focus of this research is on development of new instrumentation enabling chemical measurements, likely to be of wide interest and utility to the chemistry research community.

Under the auspices of the Defense Threat Reduction Agency (DTRA) of the DoD and within the program Rapid Investment Funds, Eos Photonics (Lead) and Thermo-Fisher Scientific (Co-Lead) and University of Puerto Rico-Mayaguez (Academic Partner, S.P. Hernández-Rivera) and other companies are also being considered as partners for collaborative and transitioning work.

Grants:
A. Project: Puerto Rico REU: Research Training in Cross-disciplinary Chemical Sciences
   • Program: Research Experiences for Undergraduates (REU)
   • Funding agency: NSF
   • Status: Approved, $450,000 3 years; co-Funded by DOD
   • PI: Dr. Osvaldo Cox
   • Co-PI: Dr. Beatriz Zayas
   • Research Mentors: Dr. Ajay Kumar, Dr. Mitk’El B. Santiago, Dr. Oliva M. Primera-Pedrozo, Dr. Jonathan Friedman, Dr. Shikha Raizada, Dr. Antonio Alegría, Dr. Carlos Cabrera and Dr. Samuel P. Hernández.
   • Description: The goal of this project is to build a cross-disciplinary research community in chemistry to
increase the competitiveness of chemistry majors in Puerto Rico and thereby increase their preparedness and enthusiasm to continue to graduate school. The project will recruit students at Universidad Metropolitana, a Hispanic Serving Institution in San Juan, Puerto Rico and offer a program during the academic year followed by a summer component at four (4) partner institutions which are research intensive institutions.

B. Project: Acquisition of Confocal RAMAN-AFM-NSOM Imaging Spectroscopic System

- Pending: Major Research Instrumentation, NSF 13-517
- Funding agency: NSF
- Status: Pending; Requested: $803,596
- PI: Dr. Carlos Padín-Bibiloni, Chancellor, UMET-AGMUS
- Co-PIs: Dr. Samuel P. Hernández-Rivera', Dr. Oliva M. Primera-Pedrozo, Dr. Mitk'El B. Santiago, Dr. Wilfredo Otaño,
- Researchers: Dr. Francisco Marquez, Dr. Jaime Ramirez-Vick, Dr. Luis F. de la Torre
- Description: Metropolitan University (UMET) and UPR-M proposes the acquisition of equipment capable of performing atomic force microscopy (AFM), near-field scanning optical microscope (NSOM), Raman spectroscopy (RS), surface enhanced Raman spectroscopy (SERS) and material characterization, in general. The objective is to increase the participation of scientists from multiple universities in Puerto Rico in state-of-the-art research and to broadly impact the STEM pipeline education and training in spectroscopic techniques, in fiber optics in scientific instrumentation, and in laser techniques, The requested instrumentation will enable a new network for cutting-edge materials science research that brings together young, competitive researchers and seasoned experienced investigators from four (4) different institutions across the island of Puerto Rico: UMET, University of Puerto Rico-Mayaguez (UPR-M), University of Puerto Rico-Cayey (UPR-C), and Universidad del Turabo (UT).

C. Project: Confocal Raman-AFM-SNOM Imaging Spectroscopic System: An Initiative to Expand Materials Research in Puerto Rico

- Program: Defense University Research Instrumentation Program (DURIP) PA-AFOSR-2013-0001
- Funding agency: Department of Defense – DURIP
- Status: Approved, $225,000
- PI: Dr. Samuel P. Hernández-Rivera
- Co-PI: Dr. Oliva M. Primera-Pedrozo, Dr. Luis F. de la Torre
- Researchers: Dr. Arturo Hernández-Maldonado, Dr. Wilfredo Otaño, Dr. Jaime Ramírez-Vick,
- Description: This proposal is aimed at strengthening research and education infrastructure capabilities at University of Puerto Rico – Mayaguez (UPR-M) aligned with ARO goals and objectives. Equipment acquired through this grant will assist in developing the local workforce by fostering the development of the doctoral program in Applied Chemistry at UPR-M, one of the nation’s leading Hispanic Serving Institutions producing graduates in science, mathematics, and engineering. A second goal is to increase participation of students and scientists in state-of-art research and to impact STEM pipeline education and training in confocal Raman microscopy, atomic force microscopy (AFM), scanning near-field optical microscopy (SNOM), surface enhanced Raman spectroscopy, tip enhanced Raman spectroscopy (TERS) and in materials characterization in general. The requested instrumentation will greatly enhance current research capabilities in National Defense/Security in materials sciences, nanotechnology applications in sensors development, biophysical/cellular studies, regenerative medicine, anticancer drug delivery, and cancer studies, including new protocols for early and non-invasive diagnosis. This equipment will
also enhance the research experiences of graduate and undergraduate students from underrepresented groups by exposing them to research equipment not currently available in any research or educational institution. Computer remote access will provide opportunities for successful sharing and maximizing resources. The project will create a “virtual laboratory” environment including implementation of tools and resources to build necessary infrastructure enabling online instrument access: network connection, multiuser account, instrument registration schedule and multiuser sharing screen.

D. Project: New Approaches to Cleaning Validation in Pharma & Biotech Industries

- Program: Alternate technologies for evaluation of equipment surface samples for Cleaning Validation
- Funding agency: Industry-University Consortium (INDINIV), Government of Puerto Rico
- Status: Pending, $80,000
- PI: Dr. Samuel P. Hernández-Rivera
- Co-PI: Dr. Leonardo C. Pacheco-Londoño, Dr. Pedro M. Fierro-Mercado,
- Researchers: Mrs. Nataly Y. Galán-Freyle, MS; Miss. Amanda Figueroa-Navedo, UGS
- Description: The proposed project focuses on the development, testing and validation of new methodologies for analyzing trace level amounts of APIs, detergents and cleaning agents left as contamination residues on surfaces of batch reactors and handling equipment as part of cleaning protocols. The analytical methodologies to be developed will be robust enough for consistent every-day use and will be of wide capability of implementation in Pharma and Biotechnology industries. The analytical methods will be capable of providing highly cost effective alternatives to established methodologies of cleaning validation in these industries.

For direct examination of equipment surfaces a QCL spectrometer based methodology will be developed, tested and validated to substitute swab/HPLC based sample collection and analysis. Recent developments in QCL technology include size reduction, which has enabled the transition from table-top laboratory instruments to easy-to-handle, portable, and small instruments. Moreover, the augmented output power has enabled the use of QCL-based spectrometers in long-distance applications, making the detection of chemicals possible at several meters from the source. However, the majority of previous investigations are focused on the detection of chemicals deposited on nearly ideal, highly reflective substrates (such as metallic surfaces), and there are no published reports on spectral effects of real-world substrates (such as Teflon, silicones and polymer plastics) on the spectra of the analyzed targets.

For the particular cases for which using a direct, remote sensed methodology is not viable (the field of view of the laser is obstructed), we propose two alternative, in situ, validate-CIP methodologies that will be based on the use of swabs or their equivalent. The first one envisions collecting the sample using swabs and analyzing with CE-QCLS. The other proposed methodology uses gold/silver nanoparticles (Au/Ag NP) coated swabs/filters to capture the APIs/detergents and uses a portable Raman spectrometer and surface enhanced Raman scattering (SERS) to analyze the target chemicals residues.

VII. PROJECT DOCUMENTATION AND DELIVERABLES

A. Peer reviewed journal articles


B. Theses or dissertations produced from this project


C. New courses developed and student enrollment

1. Continued education courses:

VIII. REFERENCES


Appendix A: Project Reports

Thrust R3: Bulk Sensors and Sensor Systems

Project R3-C


2002.


[77] Phelan, J. and Barnett, J., “Solubility of 2,4-Dinitrotoluene and 2,4,6-Trinitrotuluene in Water”, J
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