R1-B.1: Metrics for Explosivity, Inerting, & Compatibility

I. PARTICIPANTS INVOLVED FROM JULY 1, 2019 TO JUNE 30, 2020

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Graduate, Undergraduate and REU Students			
Name	**Degree Pursued**	**Institution**	**Month/Year of Graduation**
Ryan Rettinger	PhD	URI	5/2019
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Rachael Lenher	BS	URI	5/2021

II. PROJECT DESCRIPTION

A. *Project Overview*

To reveal detonability/initiability with small-scale tests was our ultimate goal. There has been no precedent for this type of test, but the goal is of such value to the homeland security enterprise (HSE) that it was worth the effort. To double our chances of achieving this goal, two very different approaches were pursued: (1) detonation studies, which require a special facility where explosives can be tested, and (2) using a research-grade mass spectrometer found in many chemical laboratories. A mass spectrometric technique, termed "survival yield," has been adapted to our purpose. We employed energy-resolved mass spectrometry (ERMS), a similar technique to monitor and collect the energy required to "break down" a species using a linear ion trap mass spectrometer.

In working with mass spectrometry and delving into issues of ionization, we examined a technique termed paper spray ionization. Because of the known difficulty with nonvolatile species entering the IMS, we decided to attempt a similar transfer technique. The technique involved using the swab as the platform for ionization and adduct formation, if necessary. Presently, it is performed on commercial swabs, which are shaped after swabbing and treated with solvent, and exposed to high voltage. This approach both ionizes the sample and drives it from the swab, making both thermal desorption and subsequent ionization sources unnecessary. It has been demonstrated to allow detection of high melting inorganic species as well as the current IMS library of threat materials. Voltage requirements are no higher than currently available internal to IMS instruments, and solvent requirements are minimal (a few microliters).

B. *State of the Art and Technical Approach*

B.1. Approach 1: Detonation Studies

Studies developing new small-scale detonability tests are underway and will be continued through the no-cost extension period provided to ALERT through May 2021. Characterizing detonation behavior for subcritical diameters of non-ideal energetics is extremely challenging. A material may fail to detonate because it is below its critical diameter or because it has no explosive character at all. We are attempting to probe the explosivity of materials labeled "nonexplosive" but possessing fragmentation energies similar to explosive materials. We have developed a small-scale test using photon Doppler velocimetry where less than a pound of the material of interest is impacted by a shock wave from a booster and the profile of shock wave structure through that material is captured at early times before edge effects become important. Evaluation of such profiles will reveal whether a material is detonable but failed to detonate due to its small charge size or whether the material's chemical contribution is too slow and low energy ever to grow to detonation. We have demonstrated visualization of the detonation wave, but now we find that the curvature of the input shock is too great to allow use of a flat flyer plate required for these small-scale detonation tests with hydrogen peroxide. Creating a flat input wave could be accomplished with a gas gun, which we and many HSE facilities do not have. Therefore, our approach is to develop an inexpensive, simple plane wave. This development was of interest to the US Army; thus, the project has transitioned to their funding.

B.2. Approach 2: MS and IMS Studies

In pursuing methods of evaluating potential detonability, we examined the detailed workings of our liquid chromagraph-mass spectrometer (LC-MS). We have previously reported development of the ERMS technique by which we hope to understand detonability or at least stability. The LC-MS ionizes the analyte-solvent mix by a number of methods; one common one is ESI (electron spray ionization). By this route the laboratory-grade LC-MS can analyze chlorate salts. This is something the fielded IMS cannot do. We took on this challenge.

Unlike the MS, the IMS requires no high vacuum or special gases. Its versatility, speed, and portability has made the IMS a common tool for explosive detection, and it is widely used in airports, border security, and controlled check-points screenings. Because of these characteristics, there are many commercially available IMS devices. The Transportation Security Administration groups these devices as explosives trace detection (ETD). Standalone IMS systems are widely used at a variety of security checkpoints; however, they suffer from a number of limitations (e.g., high rate of false positive detection, missing true alarms, and inability to detect nonvolatile compounds). To improve the operation of the IMS (i.e., lower false alarm rate and increase the number of detectable species), we have developed ambient desorption ionization (ADI). ADI offers a new way to introduce the analyte into the IMS. Instead of relying on heat to drive the analyte into the instrument to be ionized, ADI performs the ionization first; this facilitates the introduction of the analyte into the IMS. In ADI the swab containing the analyte is treated with both high voltage and solvent to create an environment somewhat analogous to that created in electrospray ionization (ESI) used in many mass spectrometers. In other words, ionization, volatilization, and possibly adduct formation are all performed as part of the process of introducing the sample into the IMS. This novel approach allows normally nonvolatility species to be moved into the instrument. This improved detection of nonvolatile species might be compared to the improved detection offered by the liquid chromatography-MS compared to the gas chromatography-MS. Use of ADI with an IMS adds detection capability not attainable with commercial desorbers; perchlorate, chlorate and nitrate salts—all major parts of threat explosive compositions—can be added to the libraries of IMS instruments. ADI effectively eliminates the use of radioactive or any other type of ionization source that is required under current instrumentation configurations. Additionally, the high voltage required is no more than IMS instruments already have included in the components, and solvent requirements are a few microliters. The solvent eliminates the need for added dopants (presently part of the IMS consumable list), while providing potential adducting species. We believe use of ADI can mitigate many of the IMS shortcomings, but we need to be able to directly compare IMS ionization to that of an MS. If we can combine IMS and an MS, we will be able to characterize the manner in which ADI ionizes fragments species.

ADI can be used on a variety of benchtop MSs. In fact, a high resolution MS was used to prove that the proposed technique results in proper compound ionization. IMS on its own lacks the specificity, precision, and accuracy of molecular identification, solely relying on time-space separations. The benchtop MS, on the other hand, possesses these important attributes and adds confidence to the results. Unfortunately, an MS with these capabilities lack the IMS mobility and field deployability. (We believe ADI can add detection capabilities to the present handheld MS.) We have a provision patent on ADI and are applying for a full patent. We have teamed with Smiths Detection and have been promised DHS funding to create a prototype.

B.3. Advantages of ADI Versus Existing Sources

- ADI allows volatilization and ionization of low volatility materials (e.g., chlorates, perchlorates, sulfides, phosphides, and cyanides) without the need of heat or chemical reaction.
- Power needed to operate the ADI source utilizes high voltage supply already incorporated in the ETD.
- The ADI source obviates the need for any other ionization approach.
- The ADI requires a small amount of aqueous buffer, which may also act as a dopant to aid ionization.

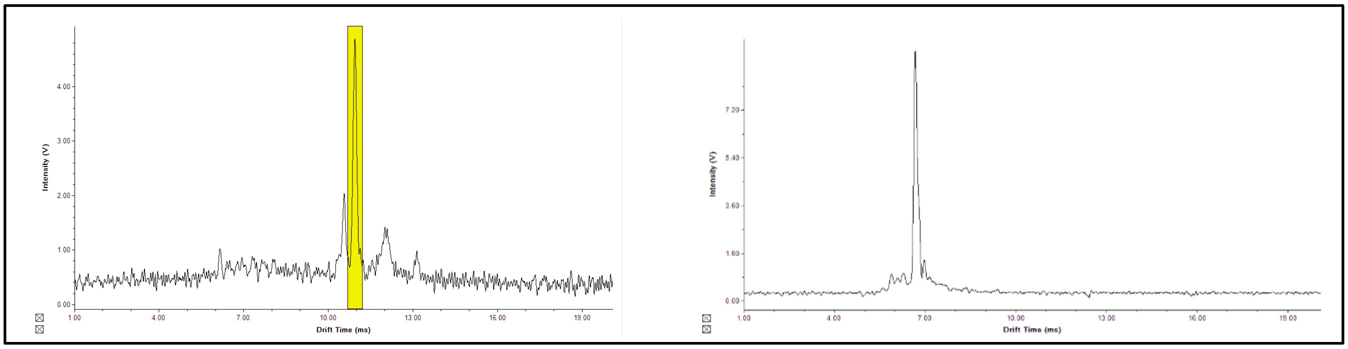

Figure 1: ADI used to detect PETN (acetonitrile solvent; left) and potassium perchlorate (methanol/water solvent; right). Floating voltage is 3 kV.

C. Major Contributions

- Extensive triacetone triperoxide (TATP) characterization—safe-scent aids, gentle destruction (Years 1–4)
- The limitations of certain oxidizers in terms of terrorist use (Years 1–6)
- Baseline information about hexamethylene triperoxide diamine (HMTD) chemical properties and reactivity (Years 1–7)
- Identifying the hazards of humidity to HMTD (Years 2–3)
- Formation mechanism of HMTD initiated (Years 2–3)
- Gentle destruction methods for HMTD (Years 3–4)
- Safe-scent aids for HMTD (Years 3–4)
- Revealing modes by which peroxide explosive signature can be masked by solvent (Years 3–4)
- Canine training aids for TATP and HMTD (Years 3–4)
- Determining best practices in analyzing peroxide explosives (Years 5–6)
- An extremely reliable standard for HMTD quantification work has been developed (Year 5)
- Examination of ETN, tracking synthesis routes, and attribution (Years 6–7)

- Creating new methods of "neutralizing" any small-scale (1-lb. scale) hazard SCHMOO (Safe Control of Hazardous Materials or Others Onsite) & SCHMOO II (Years 6–7)
- Examination of toxicity issues for canines (Years 5 and 7) and humans (Years 6 and 7)
- Development of a new method for "injecting" nonvolatile explosives (e.g., chlorate) into an IMS (Year 7)

D. Milestones

A major milestone was the examination of the six-carbon sugars. This study is close to complete. We expect to submit a paper by the end of the summer.

HMTD transformations required laboratory study, and that student has not been able to come into the lab due to COVID-19.

The book chapter(s) are still in progress. Cover and foreword have been submitted.

E. Final Results at Project Completion (Year 7)

- Thirty-five papers on HME (TATP, HMTD, ETN, AN, UN), one full patent (safe-scent training aids), two full patents in process (SCHMOO and ADI), and one provisional patent (sheet pyrotechnics) in process.
- Nine PhD, three master's degree students, and numerous BS students have graduated, and many have entered the homeland security enterprise.
- Safe-scent explosive training aids are on the market and have recently been suggested for authentication aids for TSA.
- SCHMOO has received a great deal of free publicity, and we expect to find a vendor for it shortly.
- Ambient desorption ionization (ADI), with an additional task order from DHS S&T, is being integrated into the Smiths 6000 ETD.
- Explosive database has over a thousand subscribers.

It is difficult to separate these projects by project number. The basic chemical characteristic had to be established in R1-A.1 before any work could progress on other projects.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

Characterization of HMEs is an ongoing research effort within DHS, involving vendors and associated researchers. It impacts the entire HSE. In many cases, our methods of analysis led the way for other members of the HSE. Our studies on the extreme sensitivity of HMTD to moisture and acidity may have prevented mishandling in a number of laboratories. Many vendors of explosives detection instrumentation have requested access to the explosives database, or asked for help in working with various materials characterized in this project. The characterization of these materials is published on our database (URI Explosives Database), which is subscribed to by over a thousand people, about a quarter of which are from US government agencies. Furthermore, our work is cited in the DHS HME Safety Protocols Handbook, and we were invited to participate in the DHS Chemical Security Analysis Center & Explosives Division 1st Inter-agency Explosives Terrorism Risk Assessment Working Group. We have worked directly with ten vendors of explosive detection instrumentation.

B. Status of Transition at Project End

Safe-scent aids have been licensed to Detectachem. ADI is moving forward with Smiths Detection. Many papers on HME are available in the open literature.

C. Transition Pathway and Future Opportunities

The ADI-Smiths project is ongoing with a task order through Northeastern.

D. Customer Connections

The connections to DHS (central), TSL, and TSA are strong. To date the FBI is the major agency outside of DHS that is aware of the details of this project.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Course, Seminar, and/or Workshop Development
   a. Since June 2019 we have held seven classes with 105 attendees. The new class was CTH.
   b. Dr. Oxley gave an invited lecture at the International Pyrotechnic Symposium in Tours, France, summer 2019.
2. Student Internship, Job, and/or Research Opportunities
   a. Five graduate students who were supported by ALERT and graduated are now at Signature Science supporting TSL (two students), the Navy Research Lab (two students), and Los Alamos National Laboratory (one student).
3. Interactions and Outreach to K–12, Community College, and/or Minority Serving Institution Students or Faculty
   a. We ran two 2-week workshops introducing high school students to chemical analysis. This program will end with the end of ALERT.
4. Training to Professionals or Others
   a. Since June 2019 we have held seven classes with 105 attendees. The new class was CTH.

B. Peer Reviewed Journal Articles

1. Bezemer, K., McLennan, L., van Duin, L., Kuijpers, C.J., Koeberg, M., van den Elshout, J., van der Heijden, A., Busby, T., Yevdokimov, A.V., Schoenmakers, P., Smith, J., Oxley, J., & van Asten, A. "Chemical Attribution of the Home-Made Explosive ETN—Part I: Liquid Chromatography–Mass Spectrometry Analysis of Partially Nitrated Erythritol Impurities." *Forensic Science International*, 307(110102), December 2019. https://doi.org/10.1016/j.forsciint.2019.110102.
2. Rettinger, R.C., Porter, M., Canaria, J., Smith, J.L., & Oxley, J.C. "Fuel-Oxidizer Mixtures: A Lab and Field Study." *Journal of Energetic Materials*, *38*(2), 23 October 2019, pp. 170–190. https://doi.org/10.1080/07370652.2019.1679282.

Pending –

1. Bezemer, K., McLennan, L., van Duin, L., Kuijpers, C.J., Koeberg, M., van den Elshout, J., van der Heijden, A., Busby, T. Yevdokimov, A.V., Schoenmakers, P., Smith, J.L., Oxley, J.C., & van Asten, A. "Chemical Attribution of the Home-Made Explosive ETN—Part II: Use of Isotopic Ratio." *Forensic Science International*, in preparation.
2. Gonsalves, M.D., Colizza, K., Smith, J., & Oxley, J.C. "In Vitro Metabolism and Enzyme Phenotyping of Triacetone Triperoxide (TATP) in Humans." *Forensic Toxicology*, submitted.

C. Peer Reviewed Conference Proceedings

b. Oxley, J.C., Smith, J.L., Colizza, K., & Gonsalves, M. "In Vitro Metabolism of TATP." *NTREM*, April 2020, meeting proceedings, meeting canceled.

D. Seminars

1. Oxley, J.C. "Evaluation of Explosive Characteristics via Energy-Resolved MS." *ISADE*, April 2020 canceled.
2. Yevdokimov, A.V. "A Novel Approach to IMS Sampling and Analysis." Student Award Winner, *ISADE*, April 2020 canceled.

E. Poster Sessions

1. Gonsalves, M. "Metabolism of TATP." *ISADE*, April 2020 canceled.

F. Interviews and/or News Articles

1. CBS News. "'Innovative Checkpoint' and 'digital dog nose': TSA tests new security technology." *CBS News*, 25 November 2019. https://www.cbsnews.com/news/tsa-testing-advanced-airport-security-technology-digital-dog-nose-innovation-checkpoint/.

G. Other

1. Jimmie Oxley is an on-call American Chemical Society (ACS) expert. Consulted on July 2019 script for Gunpowder & Moon Smell and January 2020 on Explosive Vapor Detection.

H. New and Existing Courses Developed and Student Enrollment

New or Existing	Type	Title	Description	Enrollment
Existing	Short course	Explosive Stability	Analysis and safety of explosives	3
Existing	Short course	Propellants	Propellants	12
Existing	Short course	Fundamentals of Explosives	Fundamentals of explosives	26
Existing	Short course	Explosive Components	Device design	17
Existing	Short course	Explosive Components	Device design	17
Existing	Short course	Dynamic Diagnostics	Instrumentation and analysis	17
New	Short course	CTH for China Lake	Sandia computer code	13

I. Patent Applications Filed (Including Provisional Patents)

1. Oxley, J.C., Smith, J.L., Yevdokimav, A.V., & Colizza, K. “Apparatus and Methods for Explosive Trace Detection Sample Preparation and Introduction into an Ionizing Detection System.” Provisional Patent 62/816,253, 11 March, 2019.
2. Oxley, J.C., Smith, J.L, Ichiyama, R., & Kagan, G. “Safe Control of Hazardous Materials or Others Onsite.” US 62/837,520, April 2019.
3. Oxley, J.C., Smith, J.L., Kominia, A., Busby, T., & Stubbs, V. “Plasticized Flexible Pyrotechnic Material and Methods of Using the Same.” Provisional Patent 62/993,992, 24 April, 2020.

J. Requests for Assistance/Advice

1. From DHS
    a. Oxley is part of the DHS-formed Inter-Agency Explosive Terrorism Risk Assessment Working Group (IExTRAWG). In addition to group meetings, a representative was sent to URI for two days in August 2018, so that we could finalize the metric for selecting threat materials.
    b. On call for a variety of TSA TSS-E personnel.
2. From Federal/State/Local Government
    a. The URI bomb dog and his trainer rely on our lab for advice and explosives.