Center of Excellence in Explosives

For the period of July 1, 2017 – June 30, 2018

I. ABSTRACT A1

Project A1 seeks to determine the physical properties, synthesis, and destruction mechanisms of improvised explosives, often called homemade explosives (HMEs). The overall objective of this project is to make the detection, handling, and transport of these materials by the Homeland Security Enterprise (HSE) as safe as possible, while obstructing the manufacturing of HMEs by terrorists. Additionally, the signatures of HMEs must be accurately characterized to allow for reliable detection. In the case of explosives, complete characterization is a matter of safety as well as performance. Most HMEs are not new, many having been reported in the late 1800s; however, "routine" handling of these explosives and resulting accidents by those involved in the homeland security enterprise (HSE) requires a thorough understanding of their properties.

To detect, destroy, handle safely, or prevent the synthesis of HMEs, complete understanding of the following aspects is required:

- How an HME is formed and what accelerates or retards that formation;
- How it decomposes and what accelerates or retards that decomposition;
- How it crystallizes;
- What is its vapor pressure and its headspace signature;
- What is its density;
- What is its sensitivity to accidental ignition as well as purposeful ignition; and
- What is its performance under shock and fire conditions?

Characterization of HMEs is an ongoing research effort at the Department of Homeland Security (DHS) including vendors and associated researchers—it affects the entire HSE. In many cases, our methods of analysis have lead 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 explosive detection instrumentation have asked for our help in working with materials characterized in this project, or requested access to the explosives database we have developed. Currently, the explosives database is subscribed to by over 1000 people, including members of DHS, and other government agencies.

Given the large scale of this mission, we have chosen areas considered most urgent or reachable by our present experience and instrument capabilities. Having examined triacetone triperoxide (TATP) in detail, Project R1-A.1 is now examining hexamethylene triperoxide diamine (HMTD), erythritol tetranitrate (ETN), and other nitrated sugars and fuel/oxidizer (FOX) mixtures.

I. PROJECT DESCRIPTION

All new materials require characterization; in the case of explosives, complete characterization is a matter of safety as well as performance. Most HMEs are not exactly new, having been reported in the late 1800s. However, their common handling and resulting accidents by those involved in the HSE demand a thorough understanding of their properties. Admittedly, this mission is too big to cover without more researchers, funding, and time; we have chosen areas considered most urgent or reachable by our present experience and instrument capabilities. We have examined a number of homemade explosives (HME): triacetone triperoxide (TATP), in detail. Presently, we are examining hexamethylene triperoxide diamine (HMTD), erythritol tetranitrate (ETN) and other nitrated sugars, and fuel/oxidizer (FOX) mixtures.

Characterization has included a detailed study of the thermal decomposition of erthyritol tetranitrate (ETN). Our work highlighted a hazardous operation that many in the HSE perform. Because ETN melts at 60^{o}C and *appears* unchanged to over 100^{o}C; sometimes melt-casing this material is included in HME training. In the U.S. alone, a number of training accidents have occurred. We examined the thermal decomposition of ETN, both through experimental and computational methods. In addition to ETN kinetic parameters, decomposition products were examined to elucidate its decomposition pathway. As a result of increased terrorist use of ETN, we were invited to team with researchers at the Netherlands Forensic Institute (NFI) to examine the key characteristics which might identify how, where, and possibly who made the HME. Work was recently presented at the DHS Centers' of Excellence Summit (May 2018, DC) and at the 47th International Symposium on High Performance Liquid Separations.

Also examined were sugar nitrates contain more than the four nitrate groups found in ETN. We are examining the synthesis of mannitol and sorbitol hexanitrate under a number of conditions. Under no experimental conditions attempted was either sugar totally nitrated. Furthermore, sitting at room temperature, the amount of hexanitrate in the sample decreased relative to the amount of pentanitrate, suggesting facile decomposition. This information needs to be included in the characterization of these materials.

Development of analytical protocols was necessary to allow us to quantify TATP and HMTD at levels as low as 25 ppm. This work supported task R1-C1 allowing quantification of the signature released (from the safe-scent aids) and of the pickup attributable to the enhanced swabs of R1-C1. As part of this work it was discovered that the reason that often low concentrations of TATP and HMTD were not observed was the use of acetonitrile (ACN) as a solvent. Further advances in their detection resulted in a lower detection limit for TATP of 25 μg/ml and for HMTD of 10 μg/mL. Five papers resulted each providing methods of improving detection of these HME peroxides.

A. State of the Art and Technical Approach

A major strength of our project is that in many cases we have introduced the best ways to approach these hazardous materials. The instrumentation used (infrared (IR), Raman, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry) is commercially available. Thus, we introduced the laboratories serving the HSE to certain safe approaches. We participated in the review of the DHS

HME safety book.

With terrorists using peroxide explosives for initiating bombs, a number of scientists are involved in analysis and detection of these materials. However, there are a number of difficulties in the execution of their efforts. The vapor pressure of triacetone triperoxide (TATP) (4.1 to 7.0 Pa) is extremely high for a solid so that storage must be in sealed containers [1-3]. This even applies to storage of TATP solutions. When aqueous solutions of TATP (100 µM) were held at 37 °C for 60 minutes in an open, polypropylene Eppendorf tube, the TATP concentration dropped about 40% every 15 minutes (Fig. 1). This effect was still quite significant at low TATP concentration samples (<10 µM kept in closed 1.5 mL tubes) where periodic opening of the tube to remove aliquots resulted in evaporative loss of approximately 3% per sampling. [1]

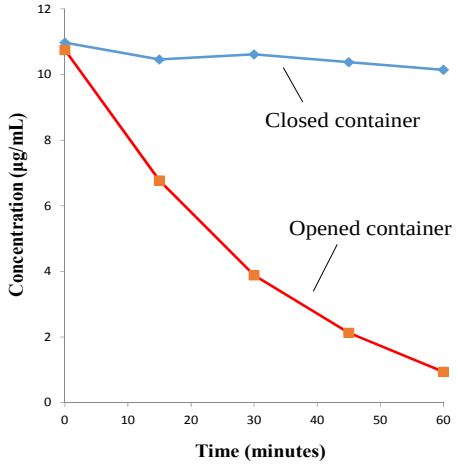


Fig. 1 TATP (100 µM) in 10mM potassium phosphate buffer incubated 37°C, 60 min in 1.5 mL Eppendorf snap-cap tube [1]

We have previously reported attempts to understand and inhibit the formation of TATP from acetone and hydrogen peroxide [4-9] as well as introduced methods for gentle destruction and detection [10-13]. Although as soon as acetone and hydrogen peroxide are mixed, they instantly form 2,2-hydroxy hydroperoxy propane (Fig. 2, I) which eventually dimerizes on its route to diacetone diperoxide (Fig. 2, DADP). Under high acid and water content, 2,2-hydroxy hydroperoxy propane converts to 2,2-dihydroperoxy propane (Fig. 2, II) which eventually makes TATP. We find hydrochloric acid the best catalyst for TATP synthesis. Without acid catalyst TATP formation requires weeks. TATP formation is favored over DADP formation at low temperature and high water content [5]. Preparation of DADP uncontaminated by TATP is best done in non-aqueous media [14,15]. Acid not only aids TATP formation but can be used to initiate its violent or gentle decomposition. We have gently digested a pound of pure TATP by first moistening it with aqueous isopropanol and then slowly adding hydrochloric acid, ceasing when a rapid temperature rise was observed [6].

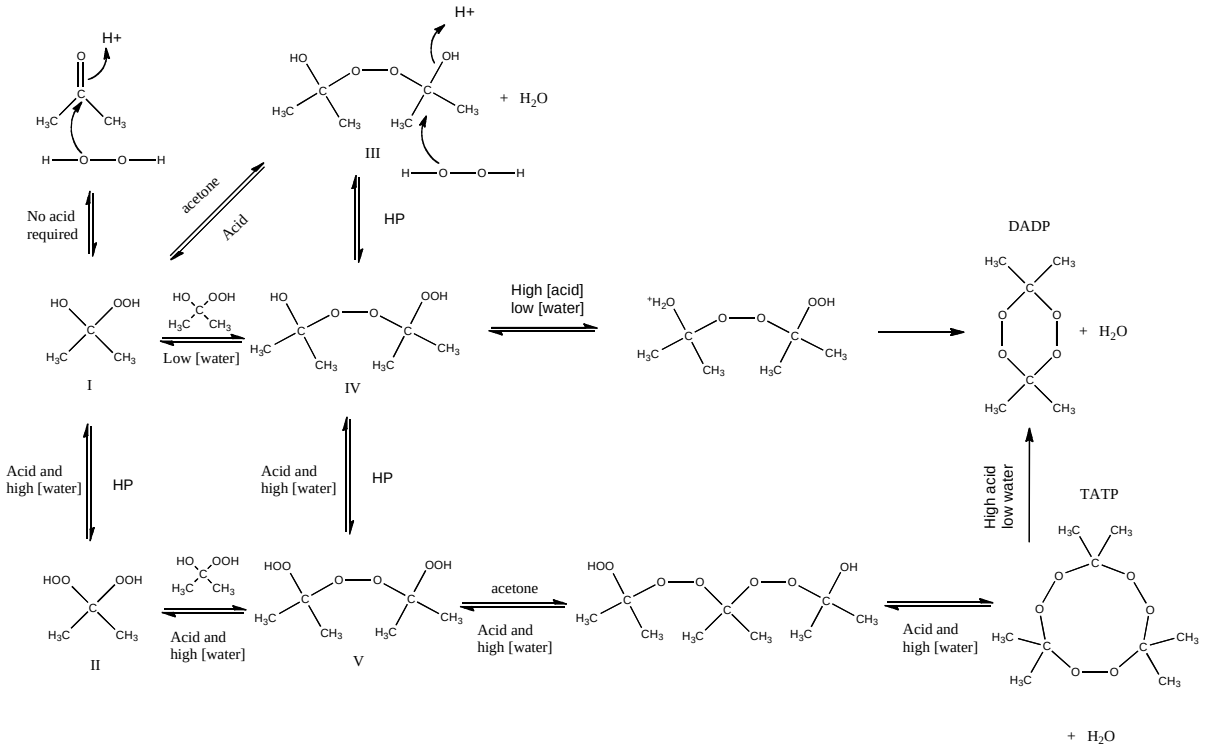
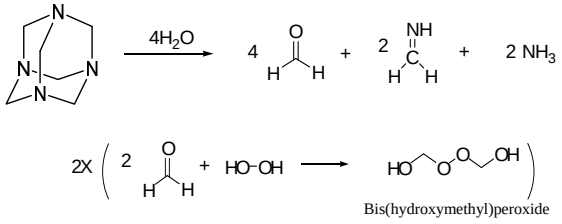


Fig. 2: Proposed mechanism for DADP and TATP formation [5]

Similarly we examined HMTD formation and its compatibility with a number of compounds. We found that it rapidly degraded in the presence of moisture; and, in under an hour, at ambient conditions, a fishy odor characteristic of its decomposition produces could be noted [16-18]. With no added acid catalyst, HMTD formed more rapidly (under a week) than TATP did without the catalyst; it preferred a multi-protic acid catalyst, e.g. citric acid. A series of labeling studies were employed in an attempt to understand its formation. When a 50/50 mixture of hexamine and ^{15}N-labeled hexamine ($C_6H_{12}{}^{14}N_4$ and $C_6H_{12}{}^{15}N_4$) was treated with hydrogen peroxide and citric acid, the1:2:1 distribution of the label $C_6H_{12}{}^{14}N_2O_6$: $C_6H_{12}{}^{15}N^{14}NO_6$: $C_6H_{12}{}^{15}N_2O_6$ indicated that hexamine dissociated during the synthesis. Figure 3 shows a tentatively proposed formation mechanism [16].



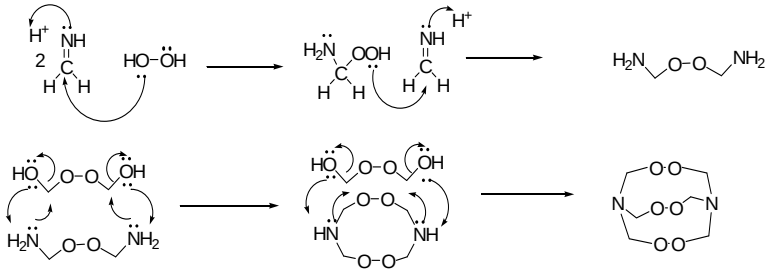


Fig. 3 Tentative proposed mechanism for HMTD formation [16]

In an attempt to lower the limits of detection for TATP and HMTD using liquid chromatograph-mass spectrometric (LC-MS) analysis, we found that choice of mobile phase and ionization source were crucial. In both electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) use of acetonitrile in the mobile phase extensively reduced the ionization efficiency of these and other peroxides and ketones (Fig. 4) [19]. However, use of acetonitrile as a storage solvent is not a problem since this solvent is chromatographically separated from the analytes prior to ionization. Acetonitrile actually has lower proton affinity than the species it suppresses. Therefore, we proposed that polar interaction between the nitrile and the analyte causes the formation of a neutral aggregate. This would further suggest that the ion suppression effects due to acetonitrile (observed in both APCI and ESI) occur prior to the ionization step. The conformation of the analyte can also dramatically affect the acetonitrile suppression effect. For example, cyclic peroxides, where the peroxide bond is forced into a polar, cis configuration, were susceptible to the nitrile neutralization, whereas large linear peroxides with non-polar, trans conformations escaped this effect [19].

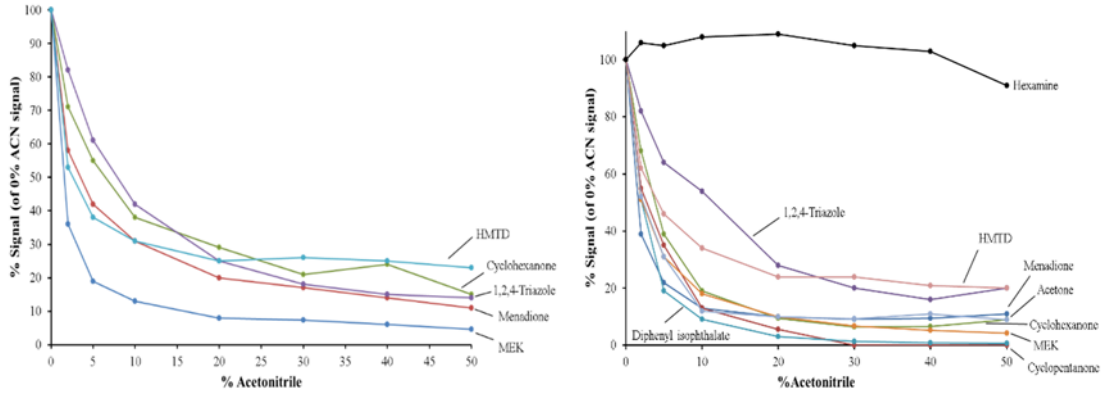
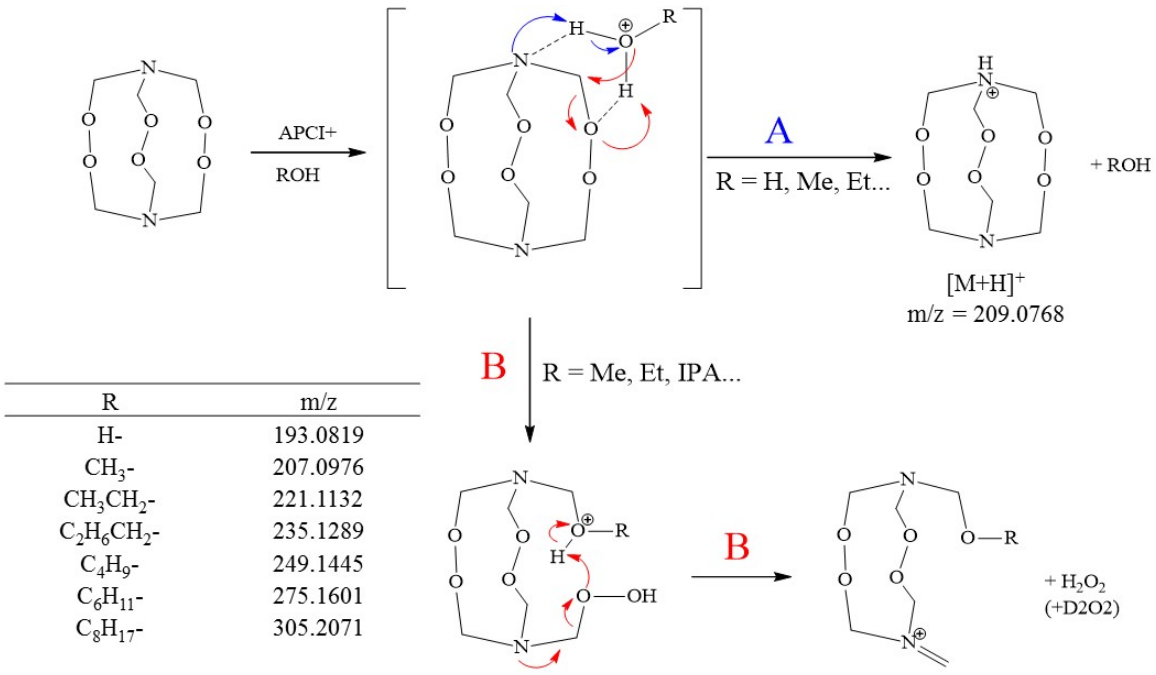


Fig. 4 Flow injection analysis a) in APCI (left); b) in ESI (right) [19]

While the above discovery may elimiate the use of acetonitrile in the mobile phase, use of an aqueous methanol mobile phase is not without consequences. Using APCI and a mobile phase of ammonium acetate/methanol, detection limits for HMTD of 1 ng on-column were achieved for the $[M+H]^+$ (m/z 209.0768) ion. Use of any alcohol with HMTD in the APCI source resulted in a chemical reaction that produced the alcohol incorporated product $[HMTD+ROH_2\text{-}H_2O_2]^+$ [m/z 207.0975 ($C_7H_{15}N_2O_5^+$) when the alcohol is methanol]. This reaction does not negatively affect the HMTD signal intensity, and it can be used as confirmation of the presence of HMTD along with commonly observed in-source fragments, e.g. 191.0662, 179.0662, 145.0608 and 88.0393, depending on source conditions (Fig. 5) [20].



R	m/z
H-	193.0819
CH_3-	207.0976
CH_3CH_2-	221.1132
$C_2H_6CH_2$-	235.1289
C_4H_9-	249.1445
C_6H_{11}-	275.1601
C_8H_{17}-	305.2071

Fig 5. Proposed mechanism for formation of (A) protonated molecular ion; (B) various alcohol adducts [20].

In the LC-MS analysis of TATP in methanol/aqueous ammonium acetate, a fragment of m/z 89.0597 is frequently observed. This ion has an exact mass of m/z 89.0597, which corresponds to the molecular formula $C_4H_9O_2^+$. Since each TATP ring is composed of three C_3H_6 units separated by peroxide linkages, a four carbon fragment is rather unlikely. When observing the deuterated analog of TATP, $[d^{18}TATP + NH_4]^+$, m/z 258.2571, the major fragment shifted from m/z 89.0597 to m/z 95.0974 which corresponded to $C_4H_3D_6O_2^+$. Further experimentation showed that the source of the non-deuterated methyl groups was the addition of methanol solvent to TATP [21], such as we noted for HMTD [20]. Furthermore, fragments indicating the addition of two methanol molecules/ions ($C_4H_6D_3O_2^+$) were also observed along with fragments at m/z 91.0390, 75.0441 and 74.0368 (Fig. 6).

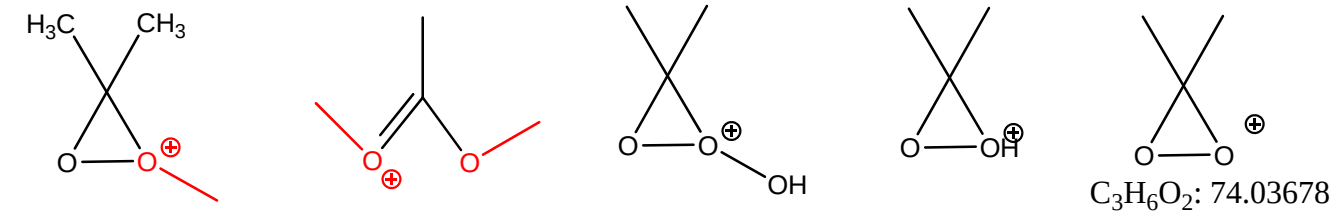


Fig. 6: TATP methanol gas phase reaction products in LC-MS with APCI (red indicates solvent incorporation)

During the LC-MS analysis of HMTD in methanol/aqueous ammonium acetate, the fragment m/z 224 was frequently observed. When chromatographically separated, two peaks with the same m/z 224 were seen. One peak eluted early with a major ion m/z 224.08826 $[HMTD+NH_2]^+$ and a minor one

m/z 207.0611 [HMTD-2H+H]$^+$. The second peak was observed where HMTD eluted with all its associated fragments. The former, we believe is tetramethylene diamine diperoxy dialdehyde (TMDDD), an oxidation product of HMTD. Preparation of an authentic TMDDD sample [21] and further experimentation indicated that our HMTD sample was contaminated with about 1% TMDDD and TMDDD contained about 1.5% HMTD. Furthermore, temperature-dependent formation of TMDDD in the gas phase during APCI was significant, but not to such an extent that it could be exploited to quantify HMTD. Experiments showed that TMDDD formation increased with increasing temperatures, up to the point (350^{o}C) where both HMTD and TMDDD begin to decompose [22]. Interestingly, TMDDD had significantly better signal in ESI than APCI, but HMTD did not convert to TMDDD to any appreciable extent under ESI conditions. Attempts to form TMDDD in the heated electrospray ionization (HESI) source failed. HMTD (as with all other cyclic peroxides) has a stronger signal in APCI than ESI.

Since both HMTD and TMDDD formed ammonium adducts, we attempted to enhance the mass spectral response by use of basic, organic amines. A variety of amines at 1 mM concentration were infused with HMTD into either an APCI or ESI source. With all the primary or secondary amines, HMTD formed a new reaction product, typified in Figure 7 with isopropyl amine. Collision induce dissociation (CID) of this product formed clearly identified fragments shown in Figure 7. Like alcohols, the gas-phase attack was on the methylene carbon, but unlike with alcohols, the addition of amines did not improve the detection limits of HMTD. Interestingly, products indicating the loss of a methyl group from HMTD and the transfer of a methyl group to the amine were frequently observed. TMDDD formed adducts, rather than products, with these same amines [22]. TATP did not react with amines under the same conditions.

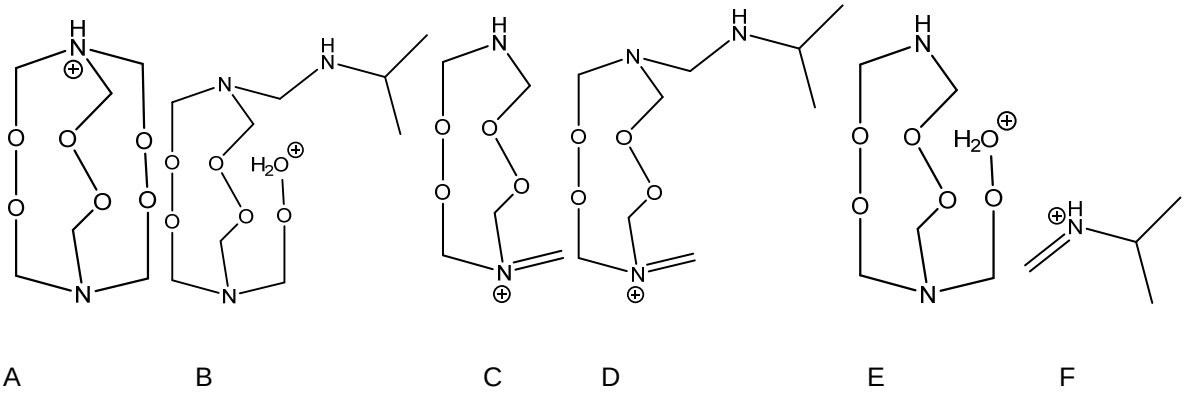


Fig. 7: Structures of Products observed from source reaction of HMTD & i-propyl amine; A:[HMTD+H]$^+$; B: [iPrNH$_2$-HMTD]$^+$; C: major fragment ion; D: [HMTD+iPrNH$_2$ -H$_2$O$_2$]$^+$; E: [HMTD -CH$_3$]+ F: [methylated iPrNH]

It is important to recognize that because peroxide explosives may interact with both alcohol and acetonitrile solvent systems, signal response may vary if a gradient solvent method is employed for LC-MS analysis. Control of temperature and pressure must also be considered. Optimized TATP detection employed a C18 column with an ammonium acetate/ methanol mobile phase. For optimal analysis of intact TATP or related compounds, a mobile phase containing 10 mM NH_4OAc and 210^{o}C were used to favor m/z 240 production, while for low level quantification, m/z 89.0597 was targeted using conditions of 300^{o}C and almost no ammonium ion (200 μM NH_4OAc). Currently, we detect TATP at 1 ng on column for m/z 240.1442 and 200 pg on column for m/z 89.0597. For HMTD, use of a polyfluorinated phenyl (PFP) column (t_R HMTD ~ 4.8 min.) over the C18 column (t_R HMTD ~ 3.5 min) favors the formation of m/z 207.0975 [HMTD+MeOH$_2$-H$_2$O$_2$]$^+$. Optimum conditions appeared to be

250°C with sheath and auxiliary gasses set to 15 AU. Using these conditions, HMTD has been detected as low as 100 pg on column with a robust analysis of 300 pg on column. Of course, it is necessary to optimize conditions for each LC/MS instrument.

II. Abstract B1

The goal of Project R1-B1 is to narrow the range of potential explosives threats that concern the Department of Homeland Security (DHS) and Homeland Security Enterprise (HSE). For example, not every oxidizer/fuel (FOX) mixture is a potential explosive. This project is aimed at determining which are and assessing at what point threat mixtures have been successfully "inerted." Because the number of potential threats is large and highly diverse, it is essential that a quick, safe method of determining detonability be established—a method not requiring the formulation of large amounts of material to determine if it is an explosive hazard. We have taken multiple approaches to this problem, including:

- Using homemade explosives (HMEs) that are FOX mixtures. We have characterized their responses to small-scale tests and are in the process of seeking a correlation to modest-scale detonation testing;
- Applying fundamental tandem mass spectrometric (MS) techniques to discover possible relationships between collision-induced fragmentation energies and specific properties of explosives;
- Developing a new way to characterize the shock/detonation front using unique probes to aid in the examination of the growth to detonation vs. shock attenuation at small-scale; and
- Soliciting other groups to join the effort due to the difficulty of the task (see projects R1-A2, R1-B2, and a funded project with LANL).

There are potentially hundreds of explosive threat materials. Distinguishing between actual threats and benign chemicals is of high interest to the HSE. This effort also extends to the question of concentration (e.g. absolute safe concentrations of hydrogen peroxide). These are the types of questions coming from Transportation Security Administration (TSA) and explosive trace detection (ETD) vendors. When the proposed tests are developed and executed, they will be available as screening tools for producing the answers to these problems.

II. PROJECT DESCRIPTION

To reveal detonability/initiability with small-scale tests is our ultimate goal. There is no precedent for this type of test, but the goal is of such value to the HSE that it is worth the effort. To double our chances of achieving this goal, two very different approaches are being made. First, an approach using a research-grade mass spectrometer in a typical chemistry laboratory. Second, detonation studies which require a special facility where explosives can be tested. A mass spectrometric technique, termed "survival yield," has been adapted to our purpose. We are employing Energy Resolved Mass Spectrometry (ERMS), a similar technique to monitor and collect the energy required to "breakdown" a species using a linear ion trap mass spectrometer.

A. State of the Art and Technical Approach

In pursuing methods of evaluating potential detonability, we must differentiate between characterizing the relative ease with which a detonation is initiated and the tendency to detonate. Over the decades the military has developed a number of tests to characterize stability of energetic

materials (EM). Drop weight impact, electrostatic discharge, and friction testing are routinely performed as soon as a few grams of a new energetic material are available. Yet, the results of these tests are subject to the machine they are tested on and even the operator who tests them. The results with precisely produced military explosives vary widely from facility to facility and operator to operator. Needless to say, attempts to characterize homemade explosives in this manner have failed despite all efforts to use standardized materials. An "intrinsic" stability test is needed.

Molecular stability can be used to predict chemical and physical properties of a material, and that may include its potential to be explosive. In order to elucidate stability of existing and emerging materials, we are attempting to combine the power of mass spectrometry and calorimetry. Mass spectrometry is one of the major tools in structural elucidation and quantification, while calorimetry can be used to measure the energy change for a chemical reaction or transition.

It is often speculated that overall stability of a compound can be related to the ease of loss of its first functional group. Although, no applications in mass spectrometry exist which directly measures this phenomenon, we believe that Energy Resolved Mass Spectrometry (ERMS) can be employed to investigate molecular stability via resonance frequency fragmentation.

LC-MS (liquid chromatography with a mass selective detector) is a gentler method of separating materials and examining their fragmentation pattern than GC-MS (gas chromatography with MS detector). However, the solubilized LC-MS sample must be stripped of solvent and ionized before it reaches the interface into the mass spectrometer (MS). One way to accomplish stripping of the solvent is electrospray ionization (ESI), schematic in Figure 1. The ions produced are typically protonated $[M+H]^+$or deprotonated $[M-H]^-$ precursor ions. These ions are guided into a high vacuum region of the MS by an applied voltage. That transition and voltage may sometimes be sufficient to fragment the molecule, but it is generally considered a "gentle" form of ionization (compared to electron impact commonly used in a GC-MS) and effectively produces intact precursor ions even for very sensitive explosives (i.e., HMTD).[2]

While all ions can be monitored by MS, ion trap mass spectrometry allows the user to isolate, trap and fragment selected precursor ions (one nominal mass at a time) and monitor resulted product ions. In the ion trap, the ERMS technique gradually increases the energy imparted onto the precursor ion until the weakest bond(s) breaks. This initiation of fragmentation corresponds to the precursor decomposition. Unique to ion trap MS is the ability to input energy only at a specific resonance frequency, thus fragmenting only the precursor ion.

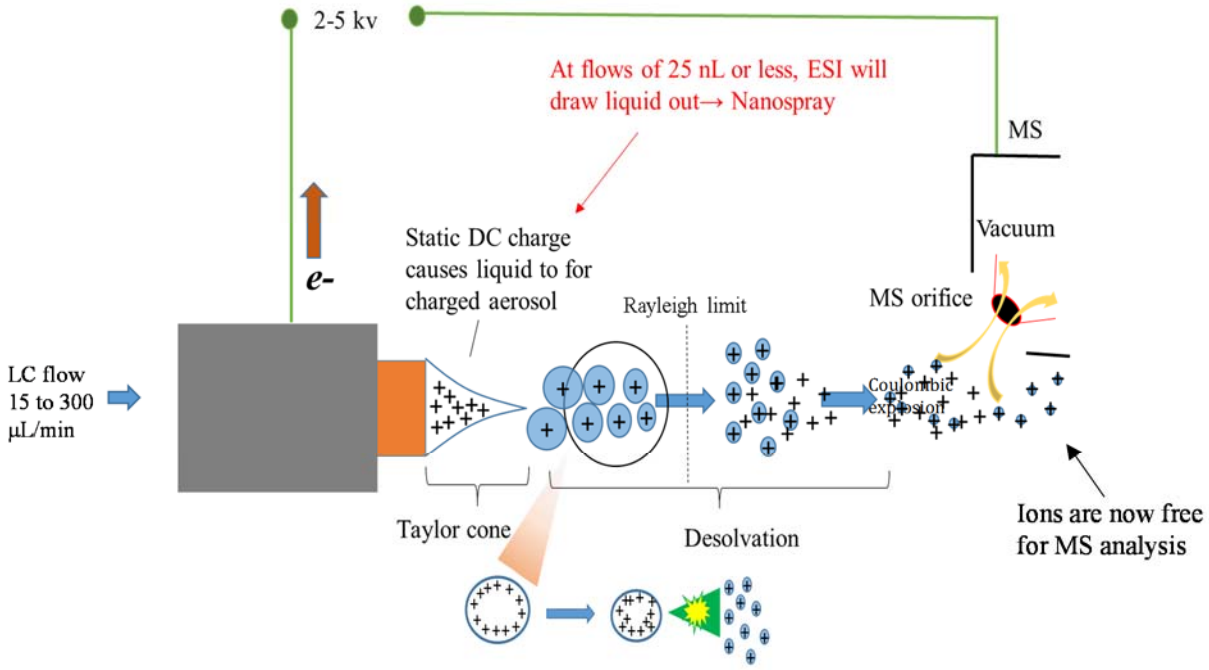


Figure 1: Schematic of electrospray ionization technique

Approach details: The energy ramp in the ion trap produces a breakdown curve for the precursor ion (Figure 2). Increasing the energy in 0.2 eV increments allows observation of the precursor when it is completely (100%) present to completely dissociated (0%). (Maximum normalized collision energy of 50 eV ensures that virtually any ion should be completely fragmented). During this process, all energy levels are recorded and could be used for statistical analysis (Figure 2). There might be a potential to uncover additional chemical and physical properties of molecules; but as the experiment is currently formatted, collision time is fixed for all species and energies. This is somewhat analogous to a thermal scan. (It is also possible to vary collision time at a fixed energy, analogous to an isothermal experiment.) The ERMS experiment relies on the property that in ion trap MS, the resonance excitation will produce and retain the same fragment ions throughout the energy ramp. In the resulting energy scan (Figure 2), the energy change to the onset point in eV represents sensitivity of compounds relative to other species. A common reference point can be established by calibrating a metric in the future (e.g. thermometer ions)[3] or be cross comparison to other sensitivity methods to observe any common trends (e.g. comparing Table 1 to Table 2). The energy change between the onset and offset points (Figure 2) represents molecular stability and can be compared across a wide range of compounds. Survival yield is frequently used in literature,[4–6] where calculations are dependent upon the resultant fragments. This technique is difficult to apply to most explosives as few if any fragments are observed depending on ion type (e.g. sodium adduct vs proton adduct) being observed. Generally, those that are observed usually do not account for the parent loss. To that end, the metric selected that captures most of the information in one data point is coined as the "fragmentation resilience 50" (FR50), the point at which 50% of precursor ion is gone, and 50% of corresponding fragments are formed. This can be based solely on the parent loss.

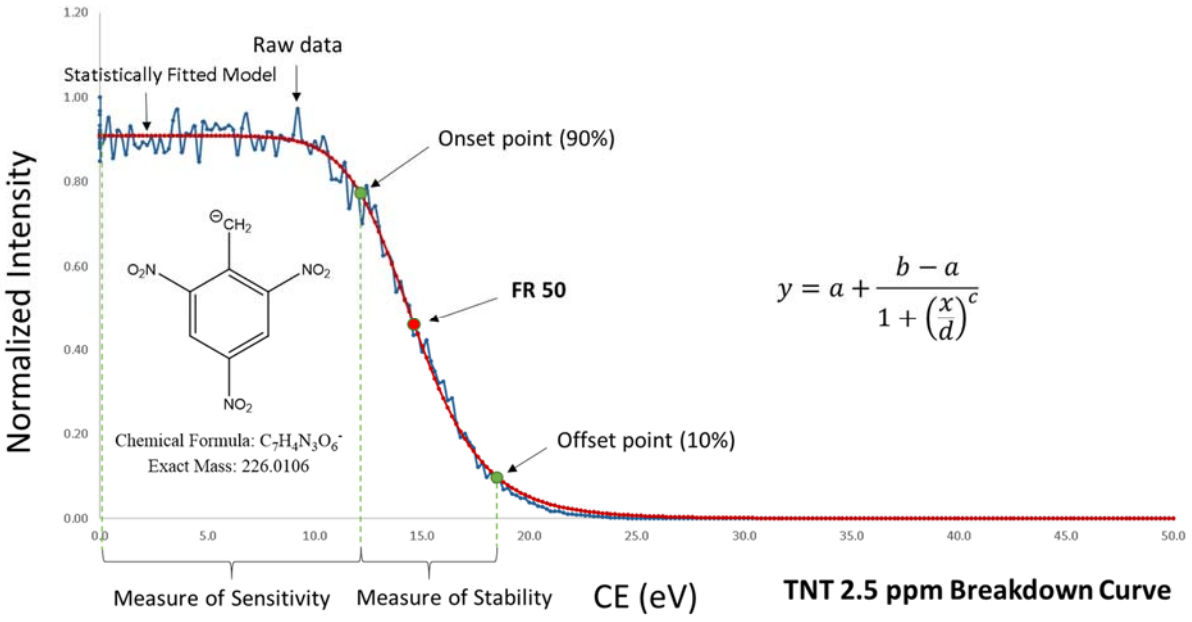


Figure 2. ***Fragmentation resilience (FR50) method*** *for statistical analysis of TNT. Onset point (in eV) indicates relative sensitivity of the compound; FR50 point is a quick metric used for cross comparison between different compounds; the energy (in eV) between onset and offset points indicates compound overall stability.[a = lowest asymptote; b= highest asymptote; c= slope at d; d- inflection point]*

With regards to fragments, the intensities of the observed fragments are indicative of how stable they are, with the most intense being the most stable. The advantage of using the ion trap is that the energy input is specific to the parent ion, in contrast to quadrupole MS fragmentation. This means that the fragments formed from the parent ion persist since added energy is tuned to the resonance frequency of the parent, not the fragment ions. Thus, the intensities of the fragment ions are, indeed, a measure of the statistically favored decomposition pathway (MS2). Additionally, they survive because their energy is absorbed by the helium gas through "collisional cooling" or "dampening". It should be noted, that the fragment ions can be trapped at their resonance frequency and fragmented further (MS3). This latter experiment shows molecular connectivity in large molecules, but explosives do not usually produce strong MS3 signals, provided they do produce MS2 signals.

By comparing the precursor ion signal decrease to the fragment intensity increase, a specific fragment can be associated to the parent molecule. Figure 3 illustrates the manner in which the "cross intersect" method indicates the association of precursor and fragment ions. The assumption of this method is that as precursor ions are being fragmented, the related and corresponding fragments are being formed at the same rate. If both energies are normalized (to either average or maximum intensities), the traces of the breakdown curves can be plotted on the same scale and overlaid. If two fragments overlap at approximately 50% of normalized intensities, then we assume the fragment and the precursor ions are related; otherwise, they are statistically different and presumed to come from different sources. We believe these two methods (FR50 and cross intersect) can provide strong fundamental basis for probing chemical and physical properties of not just energetic materials, but of any type of molecules. Having two independent methods of analysis that provide similar outcomes reinforces the validity of the proposed technique. Additionally, it offers extra versatility if one of the analytical methods cannot be used as mentioned above when no

fragments are present. The FR50 could still be used to analyze the precursor ion trace, but the "cross-intersect method" would not provide data.

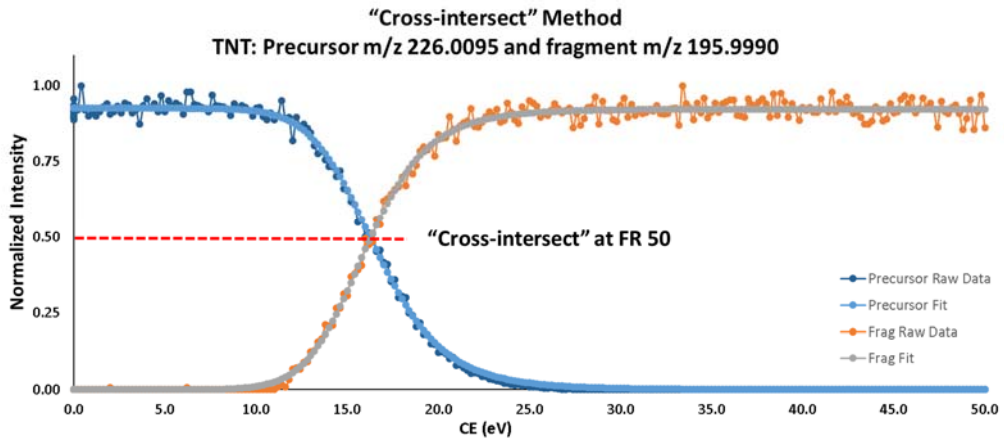


Figure 3. ***Cross-intersect method*** *for assigning correct fragments to TNT ion (m/z 226.0095). The fragment should intersect at approximately half-height of normalized intensity.*

Our instrument (Thermo Scientific LTQ Orbitrap XL) is a linear ion trap interfaced with an Orbitrap high resolution mass detector. It has been used to collect the ERMS data summarized in Tables 1 and 2. In this ion trap MS, the applied resonance energy can be gradually increased to produce precise breakdown curves of the material under investigation; it might be compared to having an ion isolated in a gas-phase test tube. Such ERMS applications have been reported for oligosaccharides[7] and other type of compounds to differentiate among structural isomers.[8] We have run a variety of explosive and non-explosive compounds in this fashion and developed a computer algorithm to assign the point at which fifty percent of the molecules fragment. Our first observations indicate that explosives (Table 1), in general, do not require as much fragmentation energy as the non-explosives (Table 2), although the nitroarene explosives, with the exception of tetryl, require more fragmentation energy than the other explosives. Interestingly, Table 1 shows that fragmentation energy correlates well with the Explosive Hazard Index of sensitivity assigned in a Navy study summarizing impact and shock tests, where the lower the number, the more sensitive the explosive.[9] It also follows thermal trends as represented by differential scanning calorimetric (DSC) results[10, 11].

Table 1: Fragmentation Energy for Explosive Compounds

	Onset	FR 50	Navy	Thermal Stability DSC (°C)		
Compound/Ion +/-H^+	eV	eV	Hazard	peak	onset	difference
PETN	2.3	3.4	10	210	189	21
RDX	0.3	3.6	24	249	224	25
HMX	0.6	3.8	26	279	266	13
Tetryl	3.4	6.8	32	2 peaks		
FOX-7	8.7	12.5		282	278	4
TNT	12.6	16.4	160	322	314	8
Styphnic Acid	12.7	16.9		3 peaks		
TATB	15.6	19.4	233	373	363	10
DNAN	17.8	21.7		379	366	13
AVERAGE	**8.2**	**11.6**				

Navy Hazard Index is attached in appendix. DSC (run at 20°C/min) are from the URI database of explosive properties available online http://expdb.chm.uri.edu/

Several interesting questions arise from the data shown in Tables 1 and 2. (1) Does molecular stability (as established by MS) directly correlate with thermal stability (as determined by calorimetry)? (2) Can thermodynamic parameters be calculated from fragmentation energy? (3) What are the effects of varying the ionization source [ESI vs atmospheric pressure chemical ionization (APCI)], introducing adducts, varying concentration, or enlarging the energy window. (4) Can an ERMS analysis obviate the need for chromatography on the front end of the MS? (5) Are the compounds listed as non-explosives in Table 2 but exhibiting fragmentation energies close to those of the nitroarene explosives potentially detonable? Each of these questions suggests a fruitful line of inquiry.

1. Probing the relationship between molecular and thermal stability we propose to examine select energetic materials by calorimetry. It is already evident from Tables 1 and 2, that use of ERMS alone will not identify an explosive, e.g. oxcarbazepine and phenytoin are incapable of being explosives. DSC is used for initial screening to determine if a compound is exothermic; and, if it is, the appropriate temperature for isothermal calorimetric (ITC) experiments. In Table 1 we have already collected those peak and onset values currently in our database[12]. It should be noted that the fragmentation observed by MS is for a gas-phase reaction. Energetic materials labs use DSC as the first look at thermal stability. Although this is a condensed phase experiment, comparing DSC runs with sealed versus unsealed samples can provide information as to the importance of autocatalytic reactions. Thermal gravimetric analysis (TGA) coupled to an infrared spectrometer can detect and identify evolved gases. However, isothermal calorimetry is the best way to determine decomposition kinetics, and running the sample at different temperatures will, at a minimum, produce universal activation energies (E_a)[13]. For quantifying heat release we use both traditional adiabatic calorimeter and a detonation calorimeter capable of handling the detonation of up to 25 g TNT.

2. Inherent in our ERMS approach is the assumption that each intact precursor ion isolated in the ion trap has the same amount of energy imparted into it when entering the ion trap. This is the case only if space charge effects are minimized since overfilling the ion trap results in more inter-ion repulsions which impact the system. To avoid this well-known problem of overfilling, Thermo designed their instruments with automated gain control (AGC) which counts the number of ions entering the ion trap. In addition, all our ERMS experiments are performed at dilute concentrations. This offers enhanced reproducibility and has the advantage of optimizing our systems to match the trace-level explosives detection of ion mobility spectrometers (IMS), since trace detection is also a research interest of our lab.

   When stating that all ions have the same energy, this is also a statistical argument that the spread of ion energies is rather low compared to when the trap is excessively full. Most ion trap technology is based on this premise[14]. There will be a Boltzmann distribution of ions or molecules with energies very close to the "initial internal energy" in every system (not only in mass spectrometry). This is, of course, related to the number of particles and the temperature (energy) of that system. Since state functions such as internal energy (U) can only be practically measured as change (Δ) to a particular state, at some point, they must have an assigned value of "zero" for comparative purpose[4–6, 15]. With no resonance energy being applied to the precursor ion [Normalized Collision Energy (NCE) = 0], the internal energy (U) can be set at zero for reference. As the NCE is increased to a point where the ion begins to fragment or the parent begins to decrease, this energy should correlate to the internal energy change (ΔU) during the first decomposition step. Using quantum calculations applied to the decomposition of the neutral and ionized forms of these molecules, direct comparisons to the activation energy (E_a) can be made. Other thermodynamic values can also be calculated.

   If a direct correlation exists between mass spectrometric and thermal methods, additional metrics can be sought to establish more direct links between the two. For example, there have been attempts to use so-called thermometer ions, e.g. benzylpyridium,[3–6] to calibrate the internal energy in the ion trap, which, in turn, would provide a metric for the compounds of interest. This will facilitate examination of future materials with the possibility of performing mass spectrometry experiments for prediction of both molecular and thermal stabilities. The advantage of using mass spectrometry techniques over isothermal calorimetry is significantly less time and quantity requirements for sample analysis (minutes and micrograms vs. days and milligrams). However, the disadvantage is that only charged species can be investigated, making direct comparisons difficult. Yet, theoretical studies have shown that ionic species can be predicted and correlated to observed mass spectra,[16] making it a promising technique for predicting which fragment forms first. It is, perhaps, more directly comparable to reaction processes happening during detonation.

3. Researchers have attempted to use the ERMS technique to probe molecular properties based on kinetic interactions with the precursor ion, resulting in production of corresponding fragments [17–19]. In those experiments the control of energy input was course 5 to 10 eV apart, resulting in ill-defined breakdown curves. Our experiments are performed in 0.2 eV increments, providing higher resolution and exceptionally well-defined breakdown curves. Effects of ionization source (ESI vs APCI), adduct formation, analyte concentration, and breadth of energy window will be examined.

Table 2: Fragmentation Energy for Non-Explosives

Compound	Onset (eV)	FR 50 (ev)
ethyl centrilite	7.8	11.4
2,4,6 trinitro-3,5-dihydroxyaniline	10.1	12.6
diphenyl isophthalate	10.8	13.2
oxcarbazepine	11.0	13.9
phenytoin	11.6	14.2
2-amino-4chloro-5nitrophenol	11.5	14.4
hexamine	10.5	14.5
phenolphthalein	13.4	15.9
1,3-dinitrobenzene	12.9	16.8
Sebacic Acid $C_8H_{16}(COOH)_2$	13.3	17.1
2,4,6-trinitroaniline	13.9	17.4
Michler's ketone $[(CH_3)_2N\text{-}C_6H_4]_2\text{-}C=O$	13.8	17.6
2,6-dinitroaniline	14.6	19.0
dimedone	16.9	20.9
2,5-dinitrophenol	17.2	21.0
aleuritic acid	17.5	21.7
3-nitroaniline	16.7	22.5
2-nitrophenol	18.4	23.2
2-nitrophenol	19.5	23.9
3,5-dinitroaniline	19.9	25.4
4-nitrophenol	21.6	26.7
4-nitroaniline	21.9	26.8
3,4 diaminotoluene	23.5	29.2
2,2-bipyridine	24.1	29.2
m-aminophenol	24.3	30.5
2,4-dinitrophenol	24.1	33.3
3-nitrophenol	25.2	33.9
phenol	28.6	35.5
AVERAGE	17.0	21.5

4. ERMS experiments suggested that an improved method exists for assigning fragments to a particular ion based on their breakdown characteristics or cross-intersect, rather than on a chromatographic retention time. Exploitation of this concept would allow one to assign a fragment to a particular precursor with a high degree of certainty, distinguishing it from background and/or unrelated fragment(s). This work can potentially be extremely beneficial to the field of mass spectrometry, even beyond energetic materials. This would be especially true for the work done on nominal mass instruments (e.g. triple quadrupole mass spectrometer, ion-mobility mass spectrometer, etc.). There have been reports of successfully using a similar method, called "survival yield," to distinguish between mixtures of compounds in the same solution, including polyethylene glycols[20] and sugar hemiacetals[21]. The same method has been shown to be useful in structural elucidation of glycosides[22] and oligosaccharides[23] using quadrupole ion trap (a nominal mass instrument), and even discriminated between structural isomers of oligosaccharides using both accurate mass and nominal mass instruments[7, 8, 23, 24].

The drawback of the "survival yield" method is a reliance on the precursor ion to produce distinguishable fragments, and the fact that the analyst must correctly assign precursor and corresponding fragments. Failure of the first assumption results in no quantifiable data; failure of the second, results in skewed data and wrong structural assignments and corresponding chemical and physical characteristics. Using our "cross intersection" methodology (Figure 3) in conjunction with the FR50 assignment we have devised a new analytical method that addresses both pitfalls outlined above. This new statistical analysis tool both inspects and assigns fragments to the precursor ion.

The proposed analytical technique not only allows assessment of molecular stability, but also has the ability to analyze and produce quantifiable data, if the precursor ion fails to produce any fragments in the instrument detection range. Lack of fragmentation is extremely common with energetic materials, which quite often produce only small molecular weight permanent gases (e.g. nitrogen, carbon dioxide, carbon monoxide, water). This feature of highly energetic molecules may also be exploited toward their characterization. ERMS, implemented with our unique analytical technique, could eliminate the need for chromatography and allow rapid advancement in the field of portable MS devices.

While this report has focused in depth on the mass spectrometric approach, studies developing new small-scale detonability tests are underway. Characterizing detonation behavior for sub-critical diameters of non-ideal energetics is extremely challenging. Energetic materials not hereto characterized as detonable (Table 2) may be in this category. 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 "non-explosive" but possessing fragmentation energies similar to explosive materials. We have developed a small-scale test 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. (Figure 4) 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.

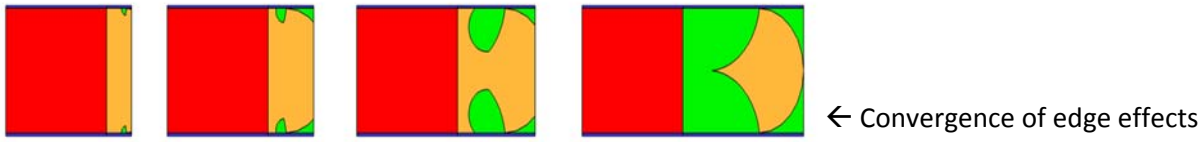


Figure 4: Schematic of initiation by booster (red) of detonation (orange) & its quenching by edge effects (green). Observations must be made before edge effects overtake the front.

III. ABSTRACT C1

The aim of this project is to develop new methods for those involved in the Homeland Security Enterprise (HSE) to collect, handle, and store novel explosives—often called "homemade explosives" (HMEs)—in a safe and effective manner. Because there are many applications where explosives may interact with other materials, a number of approaches have been developed. To date, the applications of this study have included the development of:

- Safe-scent aids that contain trace amounts of explosives encapsulated in polymers, which allows the scent of explosives to be released for safe canine training and electronic instrument calibration.
- Explosive sampling devices (swabs), which are effective at pick-up and release of explosives residues.
- Better methods for analyzing these hazardous materials.

Because of their volatility, explosives are rarely used in their pure form (meaning without plasticizers or other formulating agents) and instead are often mixed with other materials. This includes both military explosives and HMEs, which may be made safer or more hazardous when mixed with other materials. In either case, it is essential that we understand the consequences of combining HMEs with other materials either purposely or accidentally.

III PROJECT DESCRIPTION

Work continues on enhanced swabs using electrostatic charging to improve pickup of explosive particles. Efforts also continue to expand and improve on the range of canine safe-scent training aids. As both the TATP and HMTD aids are being tested in the market, minor improvements become necessary. Both these efforts require that samples with as little as 10 ng/mL (45 nM) be accurately quantified. Many challenging analytical issues were met and successfully surmounted. These are discussed in project R1_A1. This report will focus on an aspect of marketing canine training aids, not previously considered. Is the product harmful to the canine? To answer this question the metabolism of TATP was examined *in vitro* using the liver microsomes of male beagle dogs (DLM). Only one metabolite, hydroxy-TATP (TATP-OH), was identified. Canine CYP2B11 was the only enzyme specifically determined to catalyze TATP metabolism, but the degree to which it metabolized TATP was insufficient to account for observed DLM metabolism. This observation suggests more than one enzyme may be involved. The metabolite disappears over extended incubation times, but no other metabolites were detected.

A. State of the Art and Technical Approach

The ease of production and power of peroxide explosives makes them appealing to those wishing to inflict damage and destruction. [1-3] Therefore, research into the formation and safe destruction of these compounds as well as applications for their trace detection must continue. Currently, canines are being trained to detect trace levels of triacetone triperoxide, TATP and hexamethylene triperoxide diamine, HMTD to mitigate risk of terrorist attack [4]. Therefore, there is significant exposure of both humans and canines to these compounds. While some of the more common, older explosives such as trinitrotoluene (TNT) have been fully investigated for metabolism and subsequently found to have toxic metabolites [5,6], many newer or peroxide-based explosives have never been tested for toxicity. No information on the metabolism or potential toxicity of these easy to produce homemade explosives (HME) currently exists.

Hydrogen peroxide is produced through many endogenous sources including, mitochondrial respiration [7], superoxide dismutase activity [8], and metabolism by P450 [9] or other oxidase

enzymes.[10] While H_2O_2 is necessary for the redox regulation of many physiological processes,[7] it can cause cellular damage, and its destruction by catalase and enzymes like glutathione peroxidase is well known. [11-13] The reactivity and metabolic fate of hydroperoxides has been examined. [14-17]; and there is much work done on the methylation of DNA from exposure to organic hydroperoxides, particularly in the presence of iron(II). [18,19] Although organic hydroperoxides are generally too reactive to be used medicinally, cyclic peroxides are used as anti-parasitic drugs.[20-24] Literature would suggest that cyclic peroxides may be stable in the body and available for systemic circulation. When (and if) there is interaction with ferrous iron or some other agent, significant toxicity or mutagenicity may occur. {It should be noted that TATP was shown to be stable in the presence of iron(II) when solvated in tetrahydrofuran, but not in ethanol.[25]}

While HMTD is not volatile [26] and is most likely detected by the scent of its degradation products,[27] TATP is quite volatile as an intact molecule and is known to sublime.[28] This would make inhalation the most likely route of exposure. Furthermore, with sensitive explosives, using gloves is generally not an acceptable practice as the static associated with nitrile or latex can cause initiation. With these compounds being rather lipophilic (log $P_{o/w}$: TATP = 3.21 and HMTD = 1.99), the risk of exposure due to absorption through the skin is rather high. Investigation of the metabolism of TATP and HMTD may determine if measures should be instituted to mitigate exposure for both animals and humans working with these compounds. We have previously established that TATP vapor in a closed vessel exists at a concentration of about 375 µg/L[29]. With an average dog lung capacity of about 40 mL/Kg[30], a 30 Kg dog (~65 lbs), has a lung capacity of 1.2 L. A full breath would lead to an exposure of 450 µg. For humans, with a vital lung capacity of 4 to 5 L,[31] exposures in a closed room over a short time could lead to very large doses. As a forensic consideration, if TATP and HMTD are not extensively metabolized and are stable in the body, individuals producing large quantities of these materials for nefarious reasons may be identified by the analysis of small amounts of blood.

The analysis of TATP and HMTD by reverse phase liquid chromatography-mass spectrometry (LC-MS) is the most amenable means of separation and detection for aqueous-based samples of these molecules and their potential metabolites. Development of assays for these compounds have presented significant analytical challenges. For instance, LC-MS analysis of peroxides cannot have acetonitrile in the mobile phase solvent due to severe, direct, gas-phase ion suppression by the solvent.[32] While methanol is a better solvent for ionization, both HMTD[33] and TATP[29] react with alcohols in the gas phase depending on the conditions used. Since concentration of TATP solutions cannot be performed due to the volatility of TATP, it is fortunate that the chromatographic peak shape is relatively unaffected by high levels of strong solvent content in the injection plug. Also fortunate is that HMTD is not affected by solvent evaporation since its peak shape and sensitivity are tremendously altered by small changes to the organic content in the sample plug.[34] The fully deuterated TATP and HMTD molecules have been synthesized for use as an internal standards (IS) in their analysis[29][34]. The work presented herein focuses strictly on TATP metabolism.

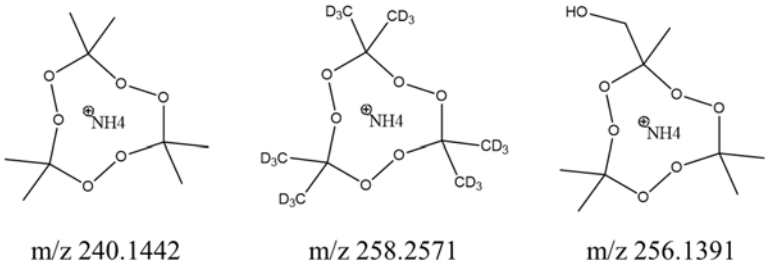


Fig 1. *Structures of TATP, d18-TATP and TATP-OH ammonium adducts.*

TATP Analysis: TATP and d18-TATP were synthesized and their $[M+NH_4]^+$ ions at m/z 240.1442 and m/z 258.2571, respectively, were monitored using a Thermo Electron LTQ Orbitrap XL or Exactive mass spectrometer equipped with an APCI interface. Chromatographic details can be found elsewhere. [35] The same analytical procedure for TATP was used to quantify the synthesized TATP-OH (Fig. 1). Aqueous TATP samples at 37 °C in containers open to the atmosphere showed significant loss of compound due to volatilization.[29] Therefore, microsomal incubations had to be performed in closed containers. Oxygen gas was bubbled through the buffer matrix for several minutes prior to incubations to provide the required atmospheric O_2 for enzymatic reactions. Open and closed incubations of verapamil were used to validate this method.

Microsomal Incubations: Samples were run in triplicate with TATP initiating each reaction. Incubations of 1mL were performed in a shaking reaction block at 37 °C in potassium phosphate buffer, reduced nicotinamide adenine dinucleotide phosphate (NADPH) and 0.5mg/mL of dog liver microsome (DLM) proteins (579 pmol P450/mg protein). Details on condition are given elsewhere.[35] In parallel with each trial, samples of TATP in buffer were incubated and treated identically to account for the headspace evaporative loss associated with opening the tube at each time point (significant at concentration >10 μM). Evaporative loss data was added to each metabolic loss data point to account for non-metabolic loss. Closed containers of TATP in buffer showed no degradation of TATP under the incubation conditions; thus, it was metabolism, rather than decomposition which resulted in TATP loss.

Results: Preliminary work performed at high concentrations of TATP (100 μM in 1 mg/mL DLM) showed only one metabolite, TATP hydroxylated on one of the primary methyl groups (TATP-OH) (Fig). A significant amount of the TATP remained intact. Product formation was NADPH-dependent; this was confirmed by incubation of the fully deuterated TATP. To perform any type of enzyme kinetics, incubations would require detection well below 1 μM (222 ng/mL). With that level being diluted in half with ACN/IS addition and our inability to concentrate the samples by evaporation, significant efforts to lower the detection limit were required. The target LLOQ was 10 ng/mL, approximately 10x less than the required 111 ng/mL needed for 1 μM incubations. Achieving this level was possible by adjusting the mass spectrometric conditions and monitoring m/z 89.0597, the gas phase reaction product of TATP with MeOH.[29] However, to assure that related metabolites could also be detected we chose to look at the intact TATP ammonium adduct at m/z 240.1442 which could now be detected with an lower limit of quantification of 25 ng/mL.

A number of experimental conditions required significant research; [35] yet day to day variability was remained unacceptable. Evaporation in the headspace of the tubes was the prime suspect. On several different days, incubation of two closed, aqueous TATP samples for 1 hour were performed. One sample remained closed the full hour and one was sampled every 15 minutes. Fortunately, there was no detectable substrate degradation, but significant sample loss (frequently greater than 3% depending on concentration) was observed due to the opening of the tubes for sampling. Attempting to perform separate incubations for each time point in individual tubes provided data with even more inconsistency. With many variables to affect specific evaporation at any given time, it was decided that every incubation would have an identical, parallel incubation performed in buffer alone. The concentration loss at each time point from these buffer-only incubations was added to the TATP concentrations from the metabolic incubation to account for non-metabolic TATP loss due to evaporation. Data for a single incubation trial at 50 μM TATP in DLM is shown in Figure 2. For determination of kinetics, three trials were performed at each concentration. Using this method, results improved to an acceptable consistency.

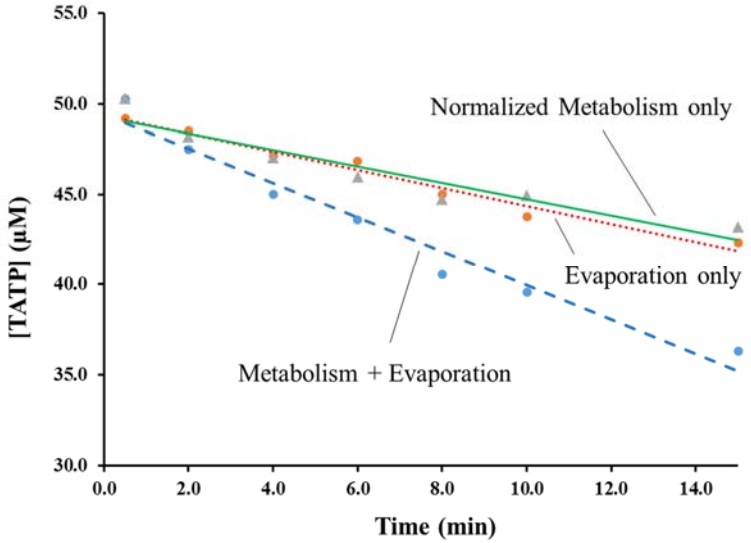


Fig 2. *Incubation of 50 µM TATP in DLM. Each data point is the mean of 2 injections.*

Kinetics were assessed on initial substrate depletion. Several methods of analysis were examined (Fig. 3). The most common, Michaelis-Menten, estimated the non-specific K_m for TATP depletion as 2.21 µM (± 14.8%) with a V_{max} of 1.13 nmol/min/mg protein (± 3.27%). The half-life at 2.5 µM (close to K_m) was graphically calculated to be 3.82 minutes with an intrinsic clearance of 363 µL/min/mg protein. When sampling time was extended past 15 minutes at concentrations of 10 µM or higher, where TATP metabolism would begin to slow, the mono-oxidation product appeared to be further consumed with no secondary metabolite(s) observed. At concentrations of 50 µM or higher where TATP persisted at high levels past 30 minutes, the TATP-OH product response levels appear to be in a steady state (possible balanced between formation and destruction of metabolite) (Fig. 4).

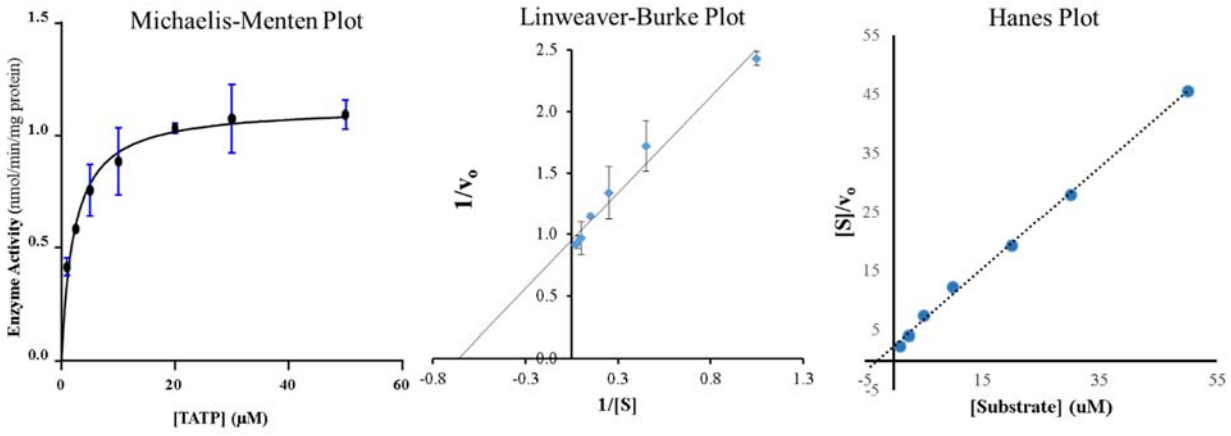


Fig. 3**.** *Michaelis-Menten plot,, Lineweaver-Burke Plot and Hanes Plot for TATP non-specific metabolism in DLM.*

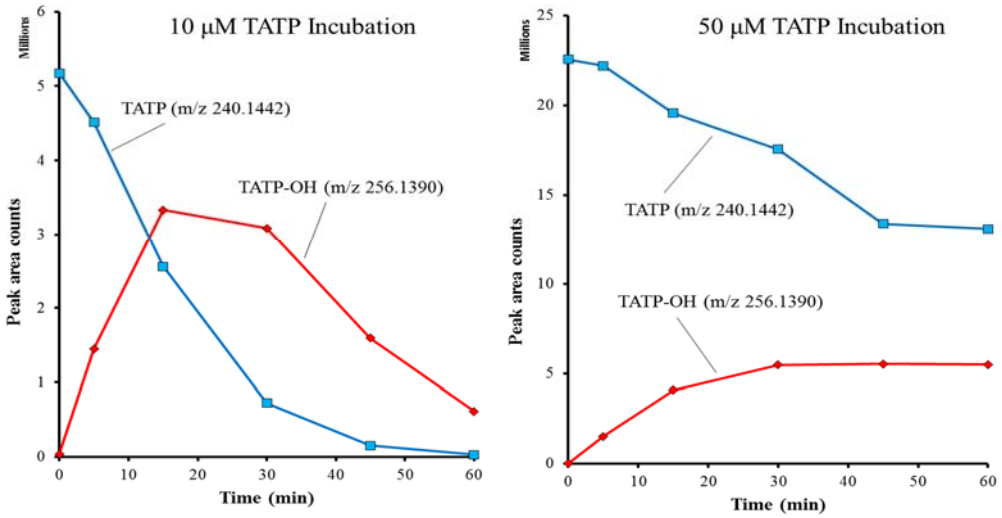


Fig. 4. *Average peak area counts for TATP and TATP-OH incubated at 10 & 50 µM in DLM for 60 minutes at 37 °C. Area counts are in millions.*

Incubations were designed to identify the isoform responsible for TATP metabolism using the commercially available isoforms of recombinant P450 dog liver (rCYP 3A12, 1A2, 2D15, 2C21 and 2B11). This covered about 85% of dog liver P450.[35, 36]. A constant concentration of 2.5 µM TATP (close to the Km) was incubated for 5 minutes in each rCYP as described above. Data shown in Figure 5 suggests that only rCYP2B11 participated in the metabolism of TATP to TATP-OH with only about 15% conversion compared to ~40% turnover in DLM. If we estimate the DLM contain ~18% CYP2B11, this only accounts for about 5-6% of the 40% metabolized.

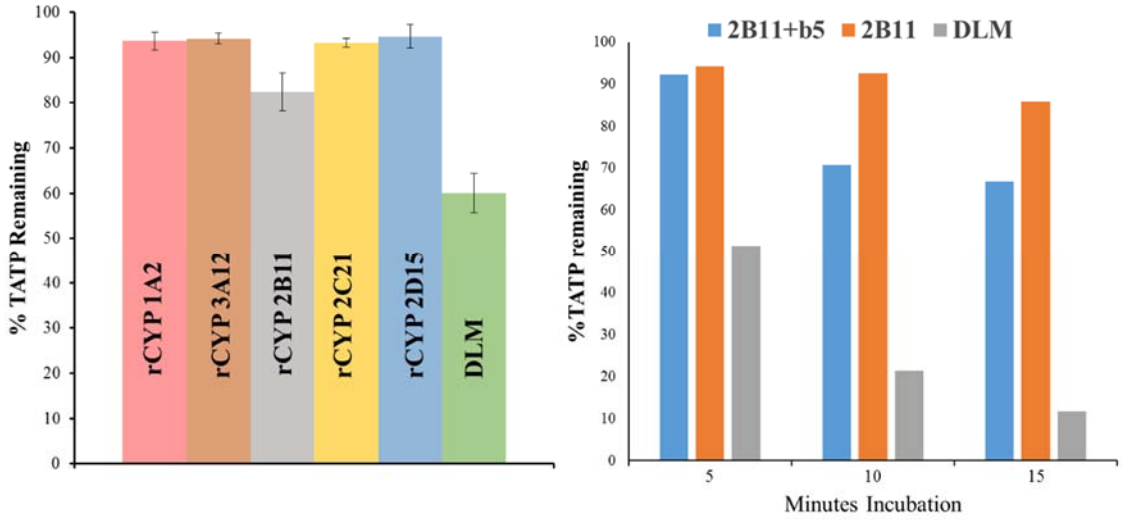


Fig. 5. *Remaining % TATP following 5 minutes incubation of 2.5µM substrate in 100 pmol/mL rCYP P450 or 200 pmol/mL P450 in DLM (left) and rCYP2B11(50 pmol/mL) run with and without cytochrome b5 (250 pmol/mL) and DLM (200 pmol/mL) for 5, 10 and 15 minutes (right)*

To determine if systemic exposure would been issue, dog lung microsomes (DLugM) were incubated with 2.5 μM TATP. Negligible metabolism was observed compared to DLM. Figure 5 compares the formation to the TATP-OH metabolite in dog liver and lung microsomes. The TATP loss is difficult to distinguish from evaporative loss in lung microsomes. This lack of metabolism in the lungs suggests that TATP could have significant systemic exposure in canines.

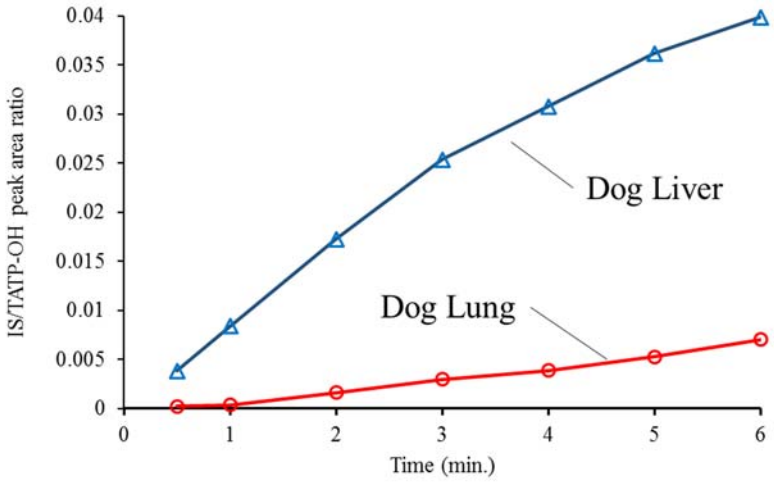


Fig. 5. *Ratio of TATP-OH/internal standard peak area ratios from incubation of 2.5 μM TATP in dog liver (DLM) and lung (DLugM) microsomes.*

B. Conclusions: TATP metabolism was characterized in canine liver microsomes. Only one hydroxylated metabolite was detected. Although the clearance was high, the low capacity of metabolism suggests that large exposure to TATP vapor could lead to significant systemic exposure. This was further evidenced by the lack of lung microsomal activity, since inhalation is the most likely route of exposure. With the assumption that absorption would not be much of a barrier, TATP may be sequestered in cells (and toxic) if its clearance does not progress by other means.

IV. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

Characterization of HME is an ongoing research effort within DHS, including vendors and associated researcher. It impacts the entire HSE. In many cases, our methods of analysis lead 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 explosive 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, which is subscribed to by over 1000 people, about of 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 directly worked with ten vendors of explosive detection instrumentation.

B. Potential for Transition

While we are not building detection devices, we provide essential input to those who build such devices. As we noted above almost a dozen vendors have visited us or sent their instruments to be evaluated by us. We have worked with numerous companies producing explosive detection instruments. We publish results in the open literature and present at the Trace Explosive Detection conference annually. Information is also disseminated via short courses, and we post results on the URI Explosives Database, which has over 1000 users. A National Institute of Standards & Technology (NIST) senior scientist commented on our database of explosive properties, "*It was all we had, in many cases*." This is high praise from the organization that maintains the "Chemistry Webbook." We have also received such compliments from military labs, both in CONUS and OCONUS. There are now over 1000 registered users of the database.

C. Data and/or IP Acquisition Strategy

As data from the program becomes available it will be provided to the community through DHS, publications, and presentations. We have received requests to license the explosive database; however, to date vendors have not offered sufficient security protocols.

D. Transition Pathway

Results will primarily be transferred to the user community by publications, presentations, and classes. (The results of this work reach over 300 HSE researchers annually through classes they request.)

E. Customer Connections

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

V. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Course, Seminar, and/or Workshop Development
2. Student Internship, Job, and/or Research Opportunities

We have had 13 classes on seven different topics which were attended by a total of 275 people—three of those classes were specifically for TSA employees.
In addition four graduate students graduated with DHS ALERT support are now at ARA Tyndal AFB (2 students) working on TSA screening equipment, Signature Science, supporting TSL, and FBI.

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

We hosted people from Netherlands Forensic Institute. They collaborate with us in a European Union examination of methods of ETN production.

B. Peer Reviewed Journal Articles

Sayavur I. Bakhtiyarov, Jimmie C. Oxley, James L. Smith, Philipp M. Baldovi "A Complex Variable Method to Predict a Range of Arbitrary Shape Ballistics" J Applied Nonlinear Dynamics **2017**, 6(4), 521-530.

Oxley, Jimmie C.; Smith James L.; Brown, A.C. "Eutectics of Erythritol Tetranitrate" J Phys Chem **2017**, 121(30), 16137-44

Oxley, J.C.; Furman, D.; Brown, A.C.; Dubnikova, F.; Smith, J.L.; Kosloff, R.; Zeiri, Y "Thermal Decomposition of Erythritol Tetranitrate: A Joint Experimental & Computational Study" J Phys. Chem. **2017**, 121(30), 16145-57.

C. Other Publications

Oxley, J.C.; Smith, J.L.; Porter, M; Yekel, M.J.; Canaria, J.A. "Potential Biocides" Iodine-Producing Pyrotechnics" Propellants, Explosives, Pyrotechnics **2017**, 42(8), 960-73.

D. Peer Reviewed Conference Proceedings

NATAS "Analysis of Peroxide Explosives" Aug 7-9, 2017; U Delaware

E. Other Conference Proceedings

JANNAF Difficulties in Analyzing Peroxide Explosives Dec 5, 2017
Why Study Energetic Materials; Texas Tech University, Nov 13, 2017
ISADE "Adventures in Analyzing Peroxide Explosives" Sept 17-21, 2017; Oxford, UK
"The Future of Energetic Materials" Sept 7, 2017; Bar Ilam University, Israel

F. Other Presentations

Poster Sessions

Student poster for the Centers of Excellence Summit May 2018

1. Webinars -NA
2. Short Courses –13 see above
3. Briefings – see presentations above
4. Interviews and/or News Articles

Kellie Gormly, Pittsburgh Quarterly, about 1862 explosion of Allegheny Arsenal during Civil War, July 2017
Conor Jones, Outrageous Acts of Science, about explosivity of frozen gasoline, Aug 2017
Jyllian Kemsely, ACS C&EN, about explosion of Arkema peroxides after tropical storm Harvey knocked out power, Sept 2107
Lori Hinnant AP about London train bombing, Sept 2017
Andrew Silver, The Register (London), with questions about explosive detection, Oct 2017
Colin Freeman, freelance for Daily Telegraph, research on "master" bomb maker, Oct 2017
Chrstine Mayall, Discovery Canada show Daily Planet, URI did a small-scale model of the Halifax Explosion (100th anniversary) for TV show Nov-Dec 2017
Jon Wellner, former actor & research forf CSI, questions about vapor switches for bombs, Dec 2017
Nick Owen, The Gazette Newpaper (UK), about storage 15 tonnes AN at Sharpness Docks, Gloucestershire, Dec 2017
Dave Mosher, Science & Technology Correspondent, Business Insider, about pipebombs in NYC Dec 2017
Rebecca Wood, Daily Planet, Discovery Canada, about NYC explosion, Dec 2017
Tom Hughes, author about a 1907 murder by bombing, Feb 2018
William Henningan, National Security Correspondent,Time, about forensics of bomb, Mar 2018
Eric Dexheimer Austin american-Statesman, about Austin bombings, March 21, 2018

John Donovan frelance writer in Atlanta, about Austin bombing, Mar 21, 2018

G. Student Theses or Dissertations Produced from This Project

Kevin Colizza Chemistry PhD, May 2018 "Metabolism and Gas Phase Reactions of Peroxide Explosives using Atmospheric Pressure Ionization Mass Spectrometry"

H. Technology Transfer/Patents

J Oxley; J Smith; J Canino "Non-Detonable Explosive or Explosive-Simulant Source" US 9,784,723 B1 Oct. 10, 2017

J Oxley, J. Smith; Alex Yeudakimau; Gerald Kagan "Apparatus & Methods for Explosive Trace Detection Sample Preparation & Introduction into an Ionizing Detection System" Patent Application 62/816,253

I. Software Developed

Over 1000 members in the explosive properties database http://expdb.chm.uri.edu/
About 250 members are with U.S. government agencies.

J. Requests for Assistance/Advice

1. From DHS
2. From Federal/State/Local Government

On call for a variety of TSA TSS-E personnel.

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 2 days in August so that we could finalize the metric for selecting threat materials.

Oxley was a member of the NAS committee on "Reducing the Threat of Improvised Explosive Device Attacks by Restricting Access to Chemical Explosive Precursors" Report issued May 2018 http://dels.nas.edu/Study-In-Progress/Reducing-Threat-Improvised-Explosive/AUTO-7-66-86-I
Oxley is a standing ACS Expert

From Federal/State/Local Government

TSA explosive specialist email in questions weekly and occasionally call.

The new URI bomb dog and his trainer rely on our lab for advice and explosives.

VI. REFERENCES

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