# URI Center of Excellence
# 2017
# R1-A.1: Characterization of Explosives & Precursors

*Abstract (Project description for the web)*

The threat against homeland security often involves explosives. All aspects of the explosive threat must be understood. It is necessary to know how explosives are made, how stable and how sensitive they are, and how to safely destroy them. To enable detection of such materials, their physical properties must be thoroughly defined. These include density, vapor pressure, crystal habit, decomposition products. To allow members of the homeland security enterprise to handle and protect against these materials their compatibilities and performance must also be documented. An equally important aspect of this effort is to develop an "awareness" of possible future threat materials. This latter effort to some extent overlaps and melds with Project R1-B.1.

## Project Overview

All new materials require characterization; but in the case of explosives, complete characterization is especially important due to safety concerns--safety for those who handle the materials and for those who must mitigate its performance. In the case of homemade explosives (HMEs), the materials are not necessarily new (many were reported in the late 1800's). In recent years the capture of terrorist facilities has resulted in "routine" confiscation of HMEs by counterterrorism units. Accidents have been reported that emphasize the importance of safe methods for detection, identification and destruction of HMEs.

To detect, destroy, handle safely or prevent the synthesis of HMEs, complete understanding involves answering the following questions:

- How are the HMEs formed and what accelerates or retards formation?
- How do HMEs decompose and what accelerates or retards decomposition?
- How do the HMEs crystallize?
- What are vapor pressure and headspace signature of HMEs?
- Density?
- Sensitivities to accidental ignition and purposeful ignition?
- Performance under shock and fire conditions?

Answering such questions is overarching to this project, and each year we continue to make progress. Previously, we have examined triacetone triperoxide (TATP). Our detailed examination of TATP has resulted in a dozen publications and led to a method of preparing safe, long-lasting training aids for canine and explosives detection instruments [1-12]. Erythritol tetranitrate (ETN), a compound chemically similar to the well-known explosive PETN (pentaerythritol tetranitrate), has been briefly examined and reported [13]. Characterization will be ongoing in the coming year. We have amassed extensive data of thermal properties of fuel/oxidizer (FOX) mixtures [14]. Building on these results we hope to develop a better understanding the detonability of FOX mixtures. This year we have devoted considerable effort in methods for analysis of peroxide explosives, especially hexamethylene triperoxide diamine (HMTD) [15, 16]. The latter studies are summarized below.

Many laboratories which work directly or indirectly on homeland security issues are not able to purchase or store explosives, especially HMEs. Our database provides a valuable service to those laboratories. Standard chemical properties are measured and uploaded to a database for assessment by registered users. In addition, protocols are available as to how to perform chemical analyses in the laboratory. In some cases, personnel have trained in URI laboratories. Disposal of small quantities of HMEs can also be a concern. Information on chemical digestion of unwanted HMEs is also available. Research on FOX mixtures is a field with little definitive information but much speculation in terms of what "works" and what "ought to work". Our research in this area has two goals: (1) To allow the homeland security enterprise (HSE) to narrow or widen the list of threat oxidizers; and (2) To collect and match sufficient small-scale data to large-scale performance so that small-scale data has greater relevance in predicting magnitude of large scale events.

R1-A.1 is currently focused on HMTD formation, decomposition and vapor composition of headspace. Publications regarding our findings can be found in section IV. One of our first approaches to the study of HMTD was examining analysis methods. HMTD exhibits an unusual gas phase phenomenon in the presence of alcohols, and we used positive ion mode atmospheric pressure chemical ionization (APCI) liquid-chromatography-mass–spectrometry (LC-MS) to examine this behavior. HMTD was infused with various solvents, including $^{18}O$ and $^{2}H$ labeled methanol; and based on the labeled experiments, it was determined that under APCI conditions, the alcohol oxygen attacks a methylene carbon of HMTD and releases $H_2O_2$ [15]. Interestingly, our work this year has found it necessary to further examine our methods of analyzing peroxide explosives. We now report, in a manuscript in preparation, that certain popular solvents suppress ionization of cyclic peroxides by positive ion APCI LC-MS. This finding affects not only researchers in the homeland security enterprise, but those in the field of forensics and possibly (although yet unknown) those involved in detection techniques involving ionization (e.g. ion mobility spectrometry).

Our work continued to study synthesis and decomposition of HMTD in condensed phase. Mechanisms have been proposed based on isotopic labeling and mass spectral interpretation of both condensed phase products and headspace products. Formation of HMTD from hexamine appeared to proceed from dissociated hexamine, as evident from the scrambling of the $^{15}N$ label when synthesis was carried out with equal molar labeled/unlabeled hexamine. The decomposition of HMTD was considered with additives and in the presence and absence of moisture. In addition to mass spectral interpretation, researchers in Project R1-D.1 used density functional theory (DFT) to calculate energy differences of transition states and the entropies of intermediates along the decomposition pathway. HMTD is dramatically destabilized by water and all acids, making purification following initial synthesis essential in order to avoid unanticipated violent reactions [16].

### Biennial Review Results and Related Actions to Address – NEW

Transition via the University of Rhode Island's Explosives Database, an interactive library of continuously updated analytical data for explosive and energetic compounds, is highly regarded. There was a request to track the number of users, which we have already addressed, and the number of hits per a given time frame. The latter feature has been addressed since that review.

One reviewer sought clarification of our strategies to prioritize research topics (i.e. HMEs). It was suggested we directly solicit DHS for selection of our topics. Although that is implied in the submission and approval of work plans, emails were sent to Dr. Laura Parker, our Program Manager, and Ms. Elizabeth Obregan, as suggested in the review. In addition, we have attended the September HMEs meeting organized by CTTSO/DHS and will attend the CTTSO HME meeting occurring in May. The R1 thrust area constantly seeks updates as to threats needing study and is open to suggestions at any time.

The expressed interest in further studies of FOX mixtures as well as on peroxide explosives will be addressed in the coming year.

Coordination with other R1 projects will be enhanced by periodic meetings of R1 members.

## State-of-the-Art and Technical Approach

**Physical characterization includes infrared (IR), Raman, $^1$H and $^{13}$C NMR spectroscopy and mass spectrometry. These properties are measured and made available to the HSE and forensic labs through continuously updated online database. Also available to the users are analytical methods. Other essential properties include thermal stability under various conditions, heats of combustion, decomposition and detonation as well as measurement of destructive outcomes. As discussed below our database has over 950 subscribers and is well-regarded. I**n the last year, we have been asked to review more than 40 papers dealing with explosives and recently one of our principal investigators has been named to the editorial boards of Forensic Chemistry and Central European Journal of Energetic Materials. These activities serve to keep us abreast of the latest explosive work world- wide.

### *C.1 HMTD studies*

### *C.1.a Rationale and approach for HMTD studies*

Several accidents involving counterterrorism personnel handling HMTD (Fig. 1) have motivated studies to better understand its chemistry and, for the purposes of detection, to identify its signature under a variety of conditions [16]. The chemistry and decomposition of HMTD in the presence of a number of chemicals was probed. It was found that moisture and acid enhanced its decomposition. Furthermore, oxidation of hexamine by hydrogen peroxide to form HMTD could be catalyzed by any acid, not just citric acid. This expansion of the potential precursor list may be important to the HSE.

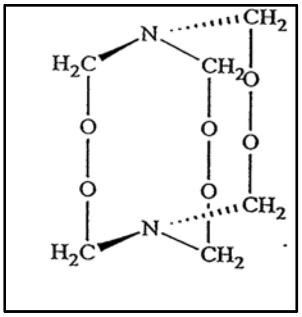


**Figure 1: HMTD structure.**

A mechanism for HMTD formation had been proposed based on data from isotopic ratio mass spectrometry [17]. Because this proposed mechanism involved formation of a triperoxy tertiary amine and protonated methylene imine, both of which we thought unlikely, we looked for alternative mechanistic pathways. Tentative proposals are discussed in Reference 16. Figure 2 illustrates the route most in line with the isotopic label studies. Hexamine is broken into small molecules; and from the formaldehyde/hydrogen peroxide reaction, bis(hydroxymethyl) peroxide (BHMP) is formed, while from the imine/ hydrogen peroxide reaction bis(methylamine) peroxide is formed. The latter reacts with two molecules of BHMP to create HMTD. This mechanism is in line with the fact that the reaction proceeds to HMTD faster in the presence of excess formaldehyde. The key to this proposed mechanism is the formation of BHMP, first synthesized in 1914 by Fenton from hydrogen peroxide and formaldehyde and later studied by Satterfield [18]. It is likely this species was generated *in situ* as reported for syntheses of several caged peroxides having planar bridgehead nitrogen atoms [19]. Once a methylene is lost from hexamine to form formaldehyde, the resulting octahydro-1,3,5,7-tetrazocine would be subject to rapid ring inversion and isomerization, which BHMP can bridge across two nitrogen atoms. To shed light on how HMTD decomposes, density functional theory (DFT) calculations were performed by R1-D.1 team members [16].

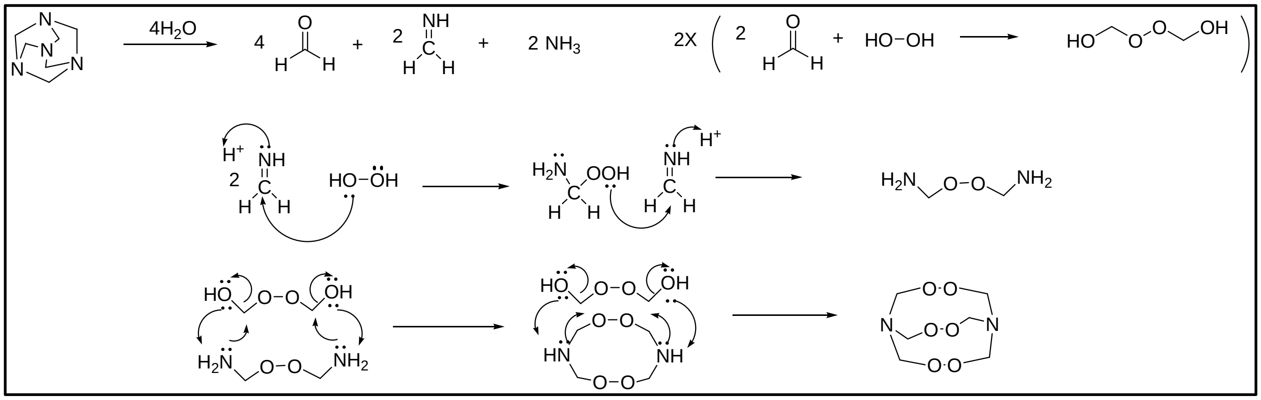
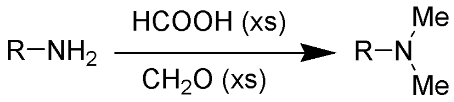


**Figure 2: Formation of HMTD from completely dissociated hexamine.**

*C.1.b HMTD headspace studies*

We had previously reported that HMTD decomposition could be readily observed at 60°C; and we had observed that when HMTD was removed from storage at -15 °C (freezer temperature), it developed a noticeable odor after a couple of hours. Headspace gases were collected using gas-tight syringes or solid phase microextraction (SPME) fibers. The former was used for permanent gases; the latter for volatile amines. When HMTD was heated under a variety of conditions the predominant decomposition products observed in the headspace were trimethylamine (TMA) and dimethylformamide (DMF) with trace quantities of ethylenimine (EN), methyl formamide (MFM), formamide (FM), hexamine and with moisture, 1-methyl-1H-1,2,4-triazole and pyrazine. No oxygen or nitrogen was found, but carbon monoxide and carbon dioxide had evolved in significant amounts. Surprisingly, no HMTD was observed under dry, moist, acidic, or basic conditions. This raised concerns about whether molecular HMTD could be found in the headspace or whether it had decomposed under our analytical protocols. Therefore, we used the same GC/MS conditions to inject a solution of HMTD; the molecular ion was observed, leading us to conclude that if existing in the vapor headspace it was below our methods of detection. However, MIT Lincoln Labs has recently performed experiments which allow its vapor pressure to be estimated at the parts-per-trillion level. [20]

Due to our previous studies on HMTD [21- 24] we were asked to join the Naval Research Laboratory (NRL) in a detailed examination of the vapor headspace of HMTD. Generally, for the sake of safety, we recrystallize (purify) our HMEs before we conduct studies. If we examine the effects of a particular impurity, it is added to the purified material of interest. HMTD is only soluble in polar solvents such as ethyl acetate; and recrystallizing from that solvent, despite herculean efforts, results in the unavoidable appearance of that solvent in the headspace. In our present study we are examining both the crude and the recrystallized HMTD to determine whether there are significant differences. In one experiment HMTD was prepared and allowed to age at room temperature. Within a month, at humid conditions, minor amounts of the decomposition product formamide appeared in the HMTD headspace; in addition, significant amounts of ethyl acetate appeared in the headspace of the recrystallized sample (Fig. 3). The early formation of formamide, rather than the dominant final product dimethylformamide, suggests an Eschweiler-Clarke type reaction where the initially formed amine is methylated in the presence of formic acid and formaldehyde (Scheme 1).



$$\mathrm{R{-}NH_2} \xrightarrow[\mathrm{CH_2O\ (xs)}]{\mathrm{HCOOH\ (xs)}} \mathrm{R{-}N(Me)_2}$$

Scheme 1

A more troublesome observation is that decomposition occurs rapidly at ambient humidity. However, this means that instruments and dogs should readily be able to detect HMTD since major decomposition products are highly odiferous.

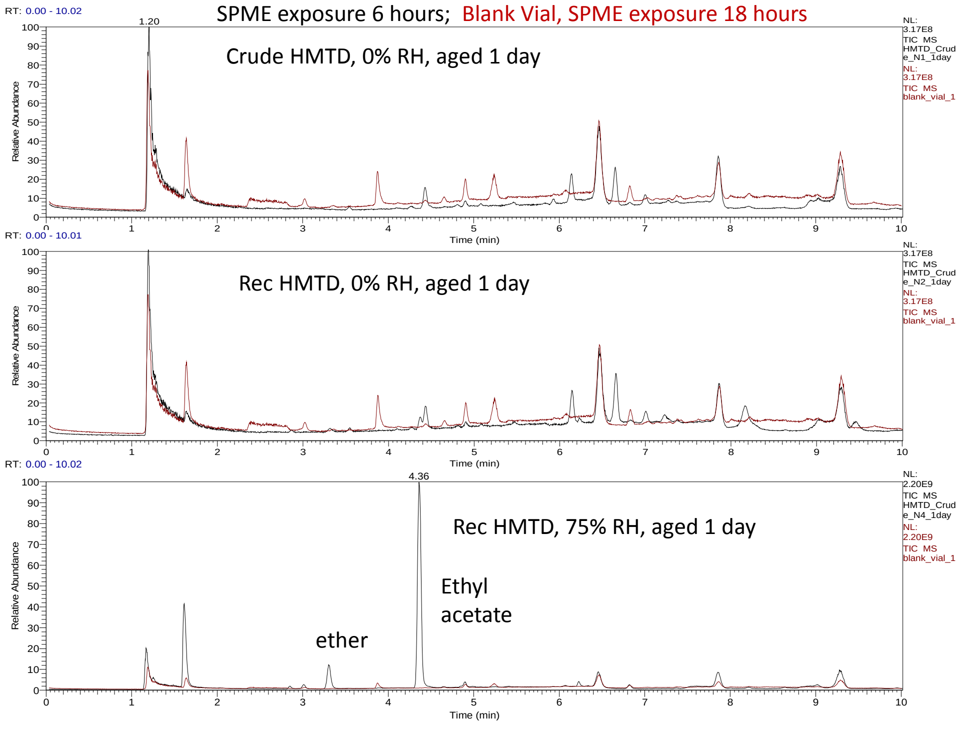


Fig. 3 GC of 1-day old HMTD—crude and recrystallized.

### *C.1.c Mass spectral analysis of condensed-phase decomposition products*

We have examined condensed-phase products of HMTD heated at 60°C under various conditions by gas and liquid chromatography with mass spectrometry; GC/MS and LC/MS, respectively. Figure 4 shows some products formed exclusively under moist conditions; and others only under dry conditions.

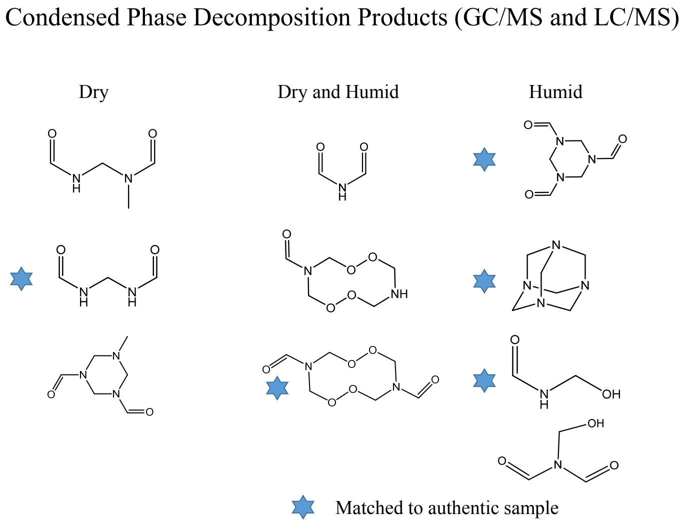
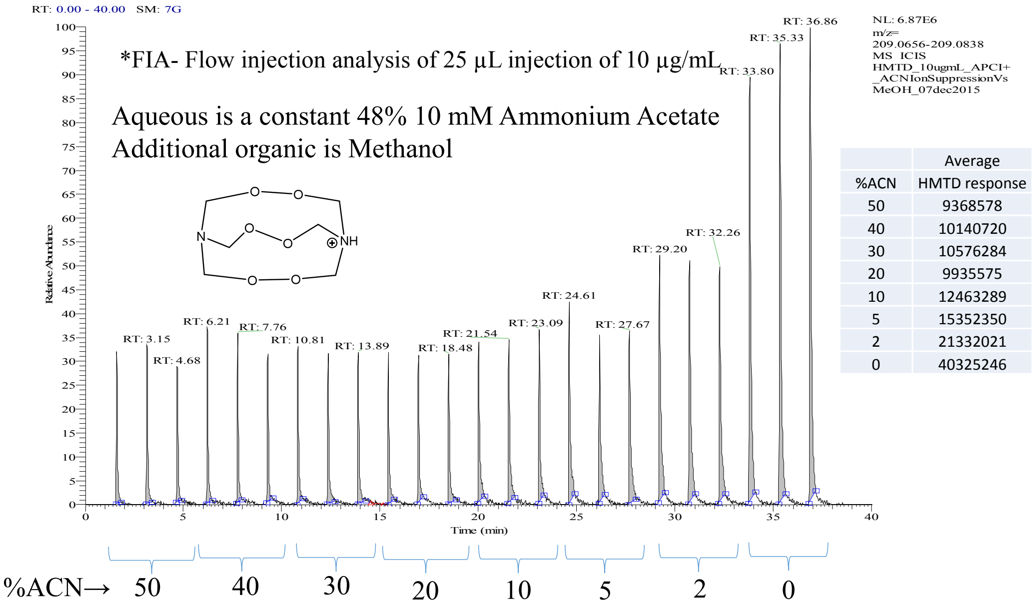


Fig. 4 Condensed-phase decomposition products of HMTD; dry and humid conditions

During efforts to analyze trace levels of cyclic peroxides by liquid chromatography/mass spectrometry we found that even minor amounts (2%) of acetonitrile suppressed ion formation (Fig. 5). Further investigations extended this discovery to ketones, linear peroxides, esters and possibly many other types of compounds including triazole and menadione. Direct ionization suppression caused by acetonitrile was observed for multiple adduct types in both electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI). The addition of only 2% acetonitrile significantly decreased the sensitivity of analyte response. Efforts to identify the mechanism were attempted using various nitriles. The ion suppression was reduced by substitution of hydrogen with an electron-withdrawing group on acetonitrile but was exacerbated by electron-donating or steric groups adjacent to the nitrile. While current theory does not explain this phenomenon, we propose that polar interactions between the various functionalities and the nitrile may be forming neutral aggregates contributing to ionization suppression.

FIA* depicting HMTD $[M+H]^+$ response in APCI with decreasing [ACN]



*FIA- Flow injection analysis of 25 µL injection of 10 µg/mL

Aqueous is a constant 48% 10 mM Ammonium Acetate
Additional organic is Methanol

| %ACN | Average HMTD response |
|---|---|
| 50 | 9368578 |
| 40 | 10140720 |
| 30 | 10576284 |
| 20 | 9935575 |
| 10 | 12463289 |
| 5 | 15352350 |
| 2 | 21332021 |
| 0 | 40325246 |

Fig. 5 Acetonitrile (ACN) suppression of the HMTD cation.

## Major Contributions

In April 2015, we were thanked by a National Institute of Standards & Technology (NIST) senior scientist for allowing them to use our database of explosive properties. They stated: "It was all we had, in many cases." This is high praise from an organization which maintains the "Chemistry Webbook." In the past, we have also received similar acclaim from military labs, both in CONUS and OCONUS. Other forms of outreach include numerous publications as follows:

- Extensive TATP characterization—safe scent aids, gentle destruction (Y -3-1)
- The limitations of certain oxidizers in terms of terrorist use (Y 1-2)
- Baseline information about HMTD chemical properties and reactivity. (Y 1-3)
- Identifying the hazards of humidity to HMTD (Y 2-3)
- Formation mechanism of HMTD. (Y2-3)
- Gentle destruction methods for HMTD. (Y3-4)
- Safe-scent aids for HMTD (Y3-4)
- Revealing modes by which the peroxide explosive signature can be masked by solvent (Y3-4)

We have characterized the headspace over HMTD; the amount of HMTD in the vapor is estimated to be sub-parts-per-trillion [20]. The odor associated with HMTD is due to amine decomposition products. Thus, the amine decomposition products can be used to generate the odor, making canine training aids from non-explosive components feasible. In contrast to early literature [25], HMTD should not be stored under water. It rapidly decomposes in the presence of moisture.

HMTD is thermally unstable. Dry it begins to decompose slightly when isolated; in high humidity, its duration may be as short as one week. This is in strong contrast to all military explosives and most HMEs. A number of decomposition and formation experiments have been performed with HMTD. Most notable were the studies using isotopically labeled species. Among those, the examination of the formation of HMTD using hexamine labeled with $^{15}N$ as well as unlabeled $^{14}N$ hexamine suggested that the formation of HMTD might be accomplished from any source of formaldehyde. While this is not necessarily good news for counterterrorism forces, at least it helps define the magnitude of the problem.

Because HMTD is destabilized by water and citric acid, it is important to purify it after initial synthesis. Ignoring the degrading effects of acid and humidity can lead to unexpected violent reactions. Precautions should be taken to see that HMTD remains dry. The headspace (signature) of HMTD is mainly trimethylamine (TMA) and dimethylformamide (DMF), and these might be used for canine and other vapor detection training instead of the more hazardous HMTD. Further work is underway to clarify mechanisms of HMTD decomposition. Preventing the assembly of formaldehyde into the molecule HMTD will continue as an ultimate research goal.

A dozen FOX mixtures have been examined via both DSC and SDT and, for a few, burn characteristics were determined. This is the start of an initiative to determine the range of the threat in terms of oxidizers for use in FOX explosives. Materials, such as dichromate, appear to have little energy to contribute to an explosion, but other properties are being explored.

Development of analytical protocols for the cyclic peroxides continues. Investigations of the extent to which these materials can be masked by choice in solvent continues.

## Milestones

Studies to thwart the synthesis of HMTD are challenging. Continued mechanistic studies are underway to devise best approaches to this problem. Headspace investigations of HMTD continue to aid mechanistic studies as well as support creation of safe-scent aids for HMTD.

In year 2 studies were initiated to determine those oxidizers considered potential threat materials, which fuels work best with these oxidizers, and what concentrations or FOX ratios are most effective. The completion of this study is a major milestone to be achieved in Years 4 and 5. Characterization will continue, specifically to determine the amount of gas formed. This project will remain a lab study with improved pressure/heat production being the important criteria to move forward to future field tests (see project R1-B.1). Long term commitment to this project is essential to the war against terroristsm. Ultimately, detonation testing, albeit on the small-scale (see project R1-B.1), will be necessary to prove whether or not a FOX formulation is detonable; but we are looking for characteristics observable at the lab-scale that suggest the final outcome. Determining these characteristics is indispensable to the counterterrorism community.

## Future Plans

Greater understanding of HMTD formation and destruction remains a primary goal. Secondary milestones are to prevent its formation and to gently destroy it. Field work continues in an attempt to determine hazards associated with proposed methods of destruction. Work on safe, long-lived canine training aids for HMTD is progressing.

Thermal properties of FOX mixtures have been characterized. Yet, energy release alone does not appear to separate potential explosive precursors from other oxidizers; thus, gas release and rates of reactions measurements (see project R1-B.1) are planned. New methods of assessing oxidizing power are being formulated and links between small-scale laboratory behavior and large-scale field performance are being evaluated.

Erythritol tetranitrate (ETN), a compound chemically similar to more familiar PETN, has been briefly examined and reported upon [13]. It will be further examined in the coming year of this program. Similarly, in a previous year, a study was undertaken of the thermal properties of fuel/oxidizer (FOX) mixtures [14]. In the coming year, work aimed at understanding detonability will build upon those thermal studies.

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

*Abstract (project description for the web)*

It is essential to recognize whether a formulation is detonable as early in its development and at as small a scale (grams vs. pounds or tons) as possible. With insensitive materials this is not easy. Under the Department of Transportation standard tests, which require pounds of material, some materials are classified as oxidizers, yet in industrial situations where tons of material are exposed to an intense fire, detonation occurs. This phenomena occurs because insensitive materials do not release sufficient energy to detonate until significant quantities of them are available to support detonation. The problem is that no one wants to make or handle large quantities (perhaps tons) of a potentially hazardous material until its properties are thoroughly characterized at small-scale (grams), but at that scale some of the poorer explosive formulations, often those employed by terrorists, are not detonable. This makes it difficult to recognize new homemade explosives. It is also makes determining definitively if an explosive formulation has been neutralized or diluted sufficiently to make it safe. The goal of this project is to identify potential explosivity in compounds and formulations at small scale. Nevertheless, we are continuously seeking ways to attack the problem so that at the moment a three pronged effort is underway using tests requiring an explosive range as well as test requiring only a traditional chemistry laboratory.

### Project Overview

Determining if a material or formulation is detonable and determining if an adulterant has inerted a detonable material are extremely difficult problems that cannot be properly addressed unless better metrics are developed. That development is the goal of this project. Because the potential matrix of threatening combinations of fuels and oxidizers is large, we seek to determine the characteristics required for detonability; bounding the problem in terms of oxidizer and its ratio with each fuel. In the laboratory, we probe characteristics such as heat and gas release, and **a full suite of chemical, thermal and sensitivity analyses to correlate to larger scale detonation performance tests.** A method which can successfully determine what formulations are potentially detonable would also reveal if "inerting" of an explosive had successfully made it non-detonable or just "safer". Either question, what is potentially detonable and if adulteration has achieved non-detonability, currently requires **very large-scale testing or a reliable small-scale test. The goal of the R1-B projects is development of the latter-a reliable small-scale test which screens large scale threat combinations quickly and inexpensively. We have taken a number of approaches to this problem. They are discussed below.**

**Approach 1 Calorimetry Plus:** How well an explosive functions is highly dependent on bulk properties, e.g. density, lattice structure, but whether a chemical can detonate at all, requires that the molecule have certain molecular features. To be an explosive, the molecule must be able to react with chemistry that produces heat and gas; and this must happen rapidly enough that the detonation front is supported by the energy release. Examination of the atoms making up the molecule allows prediction of whether heat and gas can be produced. This aspect of the molecule is being investigated under in R1-A.1. Under that task the thermal behaviors of 11 solid oxidizers and combinations of 13 fuels were determined using differential scanning calorimetry (DSC), a technique requiring less than a milligram of material [1]. Their burn rate in air was visually estimated and found to roughly correlate with standard reduction potentials. The thermal studies highlighted the importance of a melt or phase change of one component of the formulation in triggering the reaction. These studies also indicated that the choice in oxidizer, outweighed the choice in fuel, in determining the total energy released. These exciting observations are the first steps in finding behaviors observed on the milligram scale that may correlate with detonability measured on the kilogram scale. Figure 1 is a plot of temperature of decomposition vs heat of decomposition [2, 3]. The fact that explosives clearly group in a different region than non-explosives suggests we can use thermal analysis of small samples as one metric to rate detonability.

We are following up the previous milligram-scale study with gram-scale experiments performed in a adiabatic calorimeter. A modification to the standard instrument allows collection of heat release and pressure rise data versus time as the formulation of interest is burned under a controlled atmosphere. Most explosives will burn under argon atmosphere because they carry their own oxygen. The heat output, peak pressure, and rise time information are employed in predicting propellant performance, but it is unclear whether these parameters will be as effective in predicting explosivity. Heat and pressure reading reflect the production of heat and gas, but pressure-rise vs time in a burn is a function of particle size, pressure, and atmosphere, not parameter of strong importance to energy release in a detonation. Figure 2 shows that certainly some high explosives standout in terms of rise time and pressure. The critical question of whether the reaction can happen fast enough to support detonation is usually found experimentally. Future work includes attempting detonation testing as outlined in Approach 3.

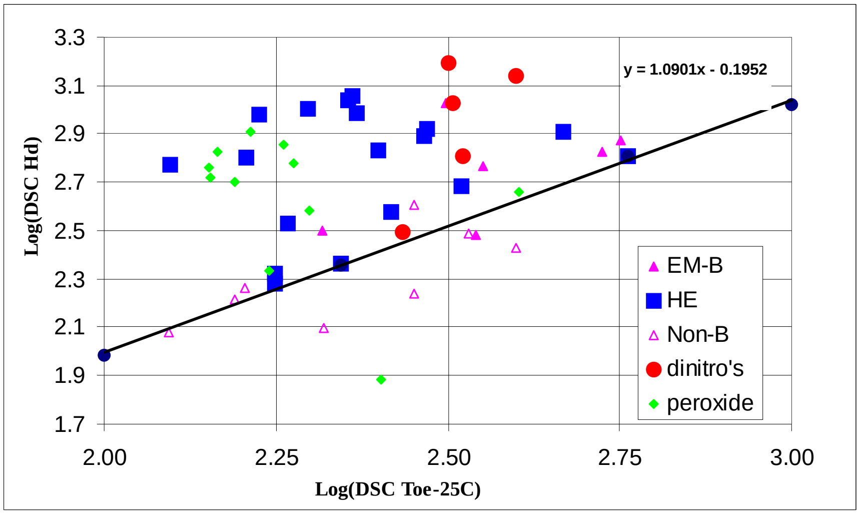


Figure 1: Plotting DSC (differential scanning calorimetric) response for peroxides (green diamonds), high explosives (blue square), dinitroarenes (red circles) and various energetic salts (pink triangles).

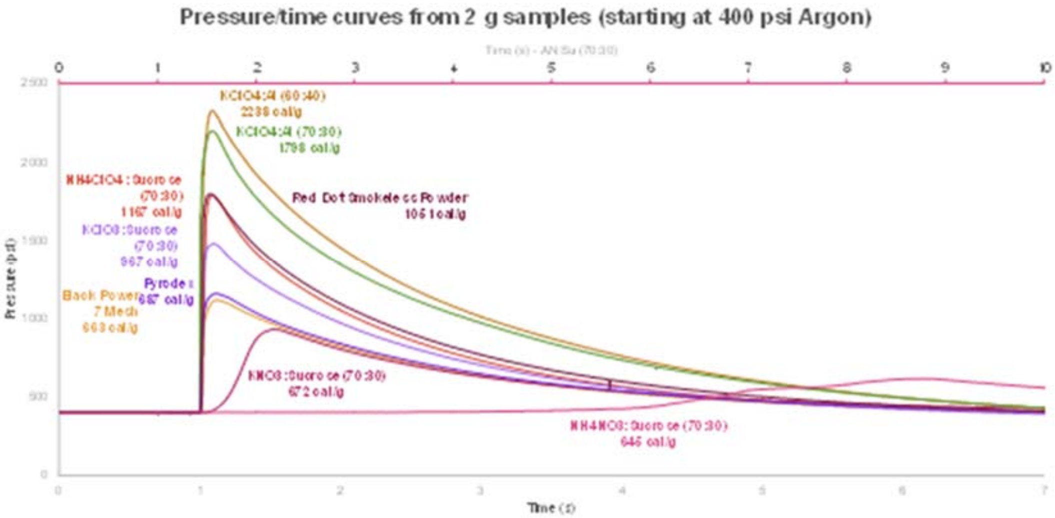
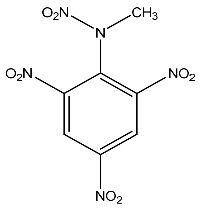


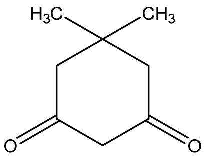
Figure 2. Pressure vs time traces from an adiabatic calorimeter of various FOX mixtures.

**Approach 2** ***Energy Resolved Mass Spectrometry (ERMS)*** is a term used to describe a process of increasing kinetic energy input into a trapped ion to determine the energy required for that material to fragment. ERMS probes one of the fundamental molecular properties--dissociation energies during gas phase ion impact with an inert gas. This technique has been used to distinguish between the fragments of very similar molecules [4] and more recently between isomers of sugar compounds known as oligosaccharides.[5-7] ERMS data results in an s-shaped breakdown curve for the compound of interest as it transforms from intact to completely fragmented. Usually multiple curves are collected and analyzed to gain additional confidence in the reported results (Figure 3). By examining a variety of explosive and non-explosive compounds in an ion-trap or a triple-quadrupole mass spectrometer, a correlation may be observed between ease of fragmentation from the energy input required and the rank order of detonability.

Energy Resolved Mass Spectrometry can potentially be used as a tool for distinguishing explosive materials (EM) from non-explosives (NE). The quick standard procedure for ERMS analysis is outlined below. A compound of interest (the analyte) is first dissolved in appropriate solvent – usually water, methanol, acetonitrile or combination thereof. The analyte solution is infused into mass spectrometer where it is ionized and trapped in an electromagnetic field. One ion mass can be isolated from hundreds based on its mass and charge. Extra energy is applied to that specific mass via radio frequency AC voltage. The energy is gradually increased from 0 to 50 eV in increments of 0.2 eV. At some point during this energy ramp the ion will reach its critical point and begin to break into fragments. Based on the energy at which the molecule starts to fragment and how long it takes to completely breakdown, the molecule can be classed as stable or fragile. We hypothesize that explosive molecules will be more fragile, i.e. requiring less onset energy, than non-explosives, due to the nature of their bonds. Figure 1 shows an example of tetryl, an explosive (EM), and dimedone, a non-explosive (NE) that support this theory. Due to the noisy quality of the raw data, it is hard to distinguish where breaking begins, but tetryl appears to be more fragile than dimedone even by simple visual inspection.



Chemical Formula: $C_7H_5N_5O_8$
Exact Mass: 287.0138



Chemical Formula: $C_8H_{12}O_2$
Exact Mass: 140.0837

EXPLOSIVE: Tetryl

NON-EXPLOSIVE: Dimedone

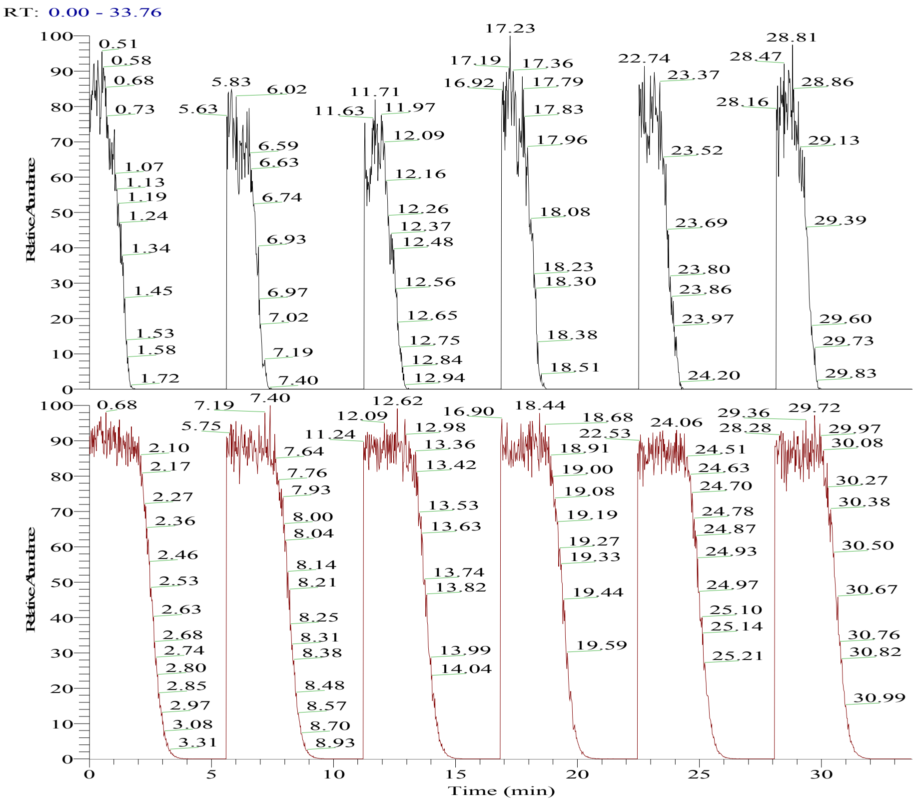


Fig. 3. Energy resolved mass spectrometry--six break down curves from 0 eV to 50 eV, in increments of 0.2 eV. Explosive compound tetryl (ESI-, $[M-H]^-$) (top) vs inert dimedone (ESI+, $[M+H]^+$) (bottom).

**Approach 3 Small-scale Detonation**: Materials characterized as "explosives" release sufficient energy to "support" or "propagate" a detonation. Military explosives have been classified as such using detonation tests of prescribed size and initiating charge [8]. Homemade explosives (HMEs) often fail these tests because they release too little energy to support detonation in the prescribed tests; therefore, they are not recognized as real explosive threats. However, these HMEs will perform as explosive materials if the charge size is increased beyond a material-specific size, the critical diameter ($D_{cr}$). At sizes less than $D_{cr}$, an explosive will not propagate detonation; any conventional explosivity or detonability test performed under the critical diameter of the material will indicate that the material is not an explosive. The critical charge size of many potential threat materials is so large that they are frequently not perceived as threats, when in reality they were simply tested below $D_{cr}$. For example, as dictated by shipping regulations, ammonium nitrate (AN) is not classed as an explosive, rather as DOT 5.1, because it does not propagate detonation at a diameter of 3.65 cm [8]. However, with sufficient AN (e.g. when the diameter exceeds 100 cm) it becomes detonable [9], as was accidentally demonstrated by the explosion in West Texas in April, 2013 [10]. Field testing at large scales is hazardous, expensive and slow. Thus, the goal **of the R1-B projects is to determine whether a material is detonable at any scale by performing experiments with less than a few pounds of the material in question.** A further complication exists in screening a material for explosivity. To confirm that a material is an explosive, traditional testing must be done well above critical diameter and with a sufficient initiating charge [11]. Thus, detonation failure can occur for several reasons including: (1) The material is too small in size; (2) It is insufficiently initiated; or (3) It is not an explosive. Traditional detonability tests do not differentiate.

**For non-ideal explosives, a term which describes most HMEs, small-scale testing necessarily means studying these materials well below their critical diameters ($D_{cr}$). When steady detonation is not possible, conventional metrics, such as detonation velocity, yield little information. New diagnostics must be devised. Several approaches to this problem have been considered. [12]**

**Approach 4 was actively soliciting other groups to join us in this effort. As a result, a group at Los Alamos National Lab (LANL) successfully probed evidence of detonable characteristics using 25 mL samples of hydrogen peroxide aqueous solutions of varying concentrations. While they were successful at that scale, they used instrumentation unique to that lab [13]. It has also been demonstrated by LANL researchers that the reaction zone of detonating nitromethane (NM) can be observed using photon Doppler velocimetry (PDV) [14]. We believe that a similar approach used to characterize a failing detonation can yield useful information about the material's capacity to detonate, i.e. confirming or denying the existence of a critical diameter.**

### Biennial Review Results and Related Actions to Address

From a FCC reviewer at the Biannual Review in December 2015: "Velocimetry (PDV) is by far the most intriguing and offers the highest potential for the introduction of new science into the program…. This is a very high risk, high payoff investment effort and is progressing well into the third year".

Because this is a high-risk, high-payoff project, three different approaches are being taken. It was suggested that "details of the experiments (what works and what didn't work)" be compiled in some fashion. We will make an effort to pass on this information with "this is how to get it to work" or "this is why it didn't work" information. For example, we have just submitted for review "Acetonitrile Ion Suppression in Atmospheric Pressure Ionization Mass Spectrometry" which began as a problem with the chemical analysis of TATP and HMTD decomposition products and synthesis pathways. In this study, we discovered that ion fragments of these energetic peroxides, other peroxides, and ketones may not be detectable if the common LC/MS solvent acetonitrile is present.

## State of the Art and Technical Approach

**Calorimetry Plus:** It has been some years since researchers have attempted to address the question of what chemicals are detonable. Reference 2 is almost thirty years old, and reference 3 which was the only researcher to follow up that work is 14 years old. Recognizing potential detonability on the small-scale is a tough problem. Most researchers in industrial labs do not have the facilities or funding do correlate their lab results with actual detonation testing. Researchers in government labs, who have the facilities and funding, usually do not have the need to do the correlation. The need for them is recent with the terrorist use of such a wide variety of materials that it is impossible to screen all at full-scale. Approach 1 will be novel in providing a direct comparison set of heat, pressure and burn rate data with detonation testing using the identical materials.

***ERMS:*** To resolve the problem in assigning the exact beginning of the breakdown region, we focused our research efforts on finding an algorithm for analyzing such data. The curves shown in Figure 3 can be averaged and analyzed in Microsoft Excel using methods developed in our lab. Figure 4 shows the analysis of tetryl as an example. Here we introduce some important parameters that are utilized for assigning the fragility of the ions. The breakdown onset marked at the top of the graph represents at what energy ions start to break. That value defines their fragility. To distinguish onset of breakdown clearly from noise, the value of 90% ion remaining was assigned as the breakdown onset, and the point for ion destruction was noted as when only 10% of the ion remained. This 90-10 region (boxed in) on the x-axis of Figure 4 represents how long it takes for ion to break. This linear region of the breakdown curve reveals the beginning and duration of the fragmentation as well as a 50 % collision energy (CE50) point, which represents half-life of the ion with regards to energy input. We believe it can be used for quick, cross comparison among different compounds.

We applied the described method of analysis above to a set of explosive and non-explosive compounds in an effort to establish the baseline for our future work. The question was whether the difference between breakdown onset energies between two energetic and non-energetic compounds is significant to pursue our hypothesis. Data in Table 1 illustrates that a significant difference does exist between these compounds. This promising method will be developed further in the next year.

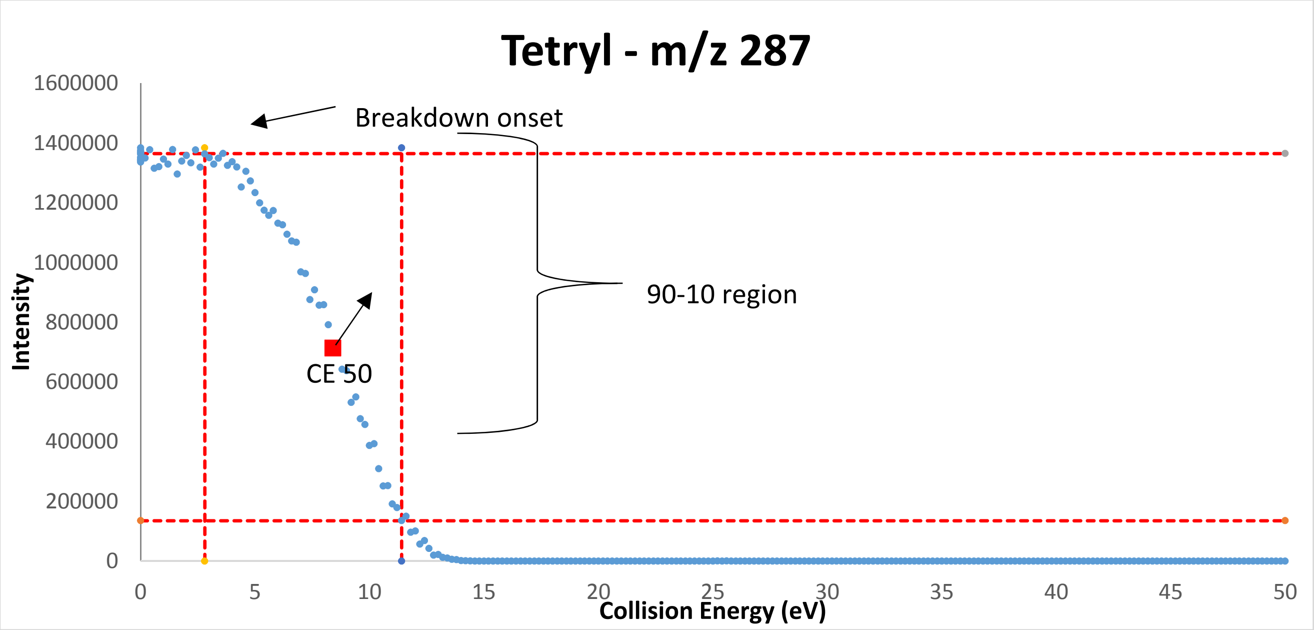


Figure 4. Averaged breakdown graph of the 6 curves shown in Figure 1 for tetryl.

Table 1. Comparison of onset (fragility) & total energies (longetivity) of stable compounds (NE) & explosives (EM)

| Stable compounds | Onset (eV) | Total (eV) |
|---|---|---|
| Oxcarbazepine | 11.0 | 6.6 |
| Phenytoin | 11.6 | 6.0 |
| Phenolphthalein | 13.4 | 5.6 |
| Diphenyl Isophthalate | 10.8 | 5.4 |
| Ethyl Centrilite | 7.8 | 8.1 |
| Michler's Ketone | 13.8 | 8.7 |
| Dimedone | 16.9 | 9.1 |
| Hexamine | 10.5 | 9.0 |
| Average | 12.0 | 7.3 |

| Explosive compounds | Onset (eV) | Total (eV) |
|---|---|---|
| RDX | 0.3 | 7.9 |
| HMX | 0.6 | 7.5 |
| Tetryl | 3.4 | 8.2 |
| TNT | 11.5 | 8.8 |
| FOX-7 | 8.7 | 9.1 |
| average | 4.9 | 8.3 |

**Small-Scale Detonation Testing:**

When a shock travels into an inert material, the peak pressure and wave velocity attenuate in time. This is a familiar phenomenon since we have all seen how sound dies off with distance from the noise source. However, if a shock of sufficient strength transits through an energetic material, the bonds in that material break and reform into new product molecules; this conversion releases energy. If the energy release occurs fast enough, the energy released contributes to the propagation of the shock front, and that shock reaches a stable flow which does not attenuate as long as energetic material remains. Following energy release, the hot product molecules expand and the elevated pressure in the region behind the shock front drops; this region is termed "the Taylor wave". A one-dimensional depiction of this behavior is shown in Figure 5. In three-dimensions, reflections from the charge boundary relieve pressure from the chemical reaction zone at the charge edge, causing detonation front curvature and transferring some of the energy of the explosive into accelerating the charge confinement. These effects are most severe at the charge boundary. At and below some critical diameter ($D_{cr}$), the losses at the edges overpower the energy production, and the detonation wave fails. For diameters larger than the critical diameter, the energy feeding the detonation far outweighs the losses at the edge, and the detonation wave will propagate.

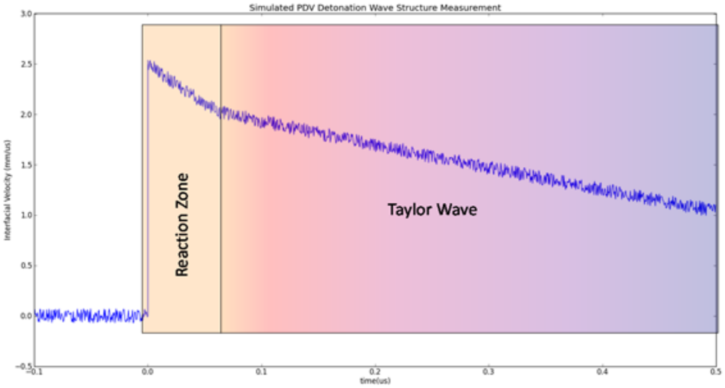


Figure 5: Simulated PDV interfacial velocity of detonation wave structure illustrating the reaction zone and Taylor wave regions.

Characterizing detonation behavior for sub-critical diameters of non-ideal explosives is extremely challenging. **Unless supported by special device design, detonations fail for lack of sufficient and timely energy release from the reaction.** Detonation velocity is used as a measure of explosive performance; high detonation velocities reflect the high rate of energy release of conventional explosives. However, if the energy release lags in time (i.e., the reaction cannot keep up with the shock), the shock wave will decouple from the chemical conversion process, and the detonation will "fail." Thus, an accurate velocity profile gives critical insight into the presence or absence of chemical reaction fast enough to support the detonation front. A versatile array of techniques will enable in-situ monitoring of both ignition and failure of detonation in real time. Using high speed photography and photon Doppler velocimetry (PDV), we may be able to discern phenomena such as the decoupling of the chemistry from the shock front frame-by-frame. **Visualizing the reaction wave should be straightforward with clear liquid explosives, such as nitromethane or hydrogen peroxide because they should be radiating brilliantly while detonating. Our initial successful test of a hydrogen peroxide/ethanol mixture shows this to be the case (Fig. 6).**

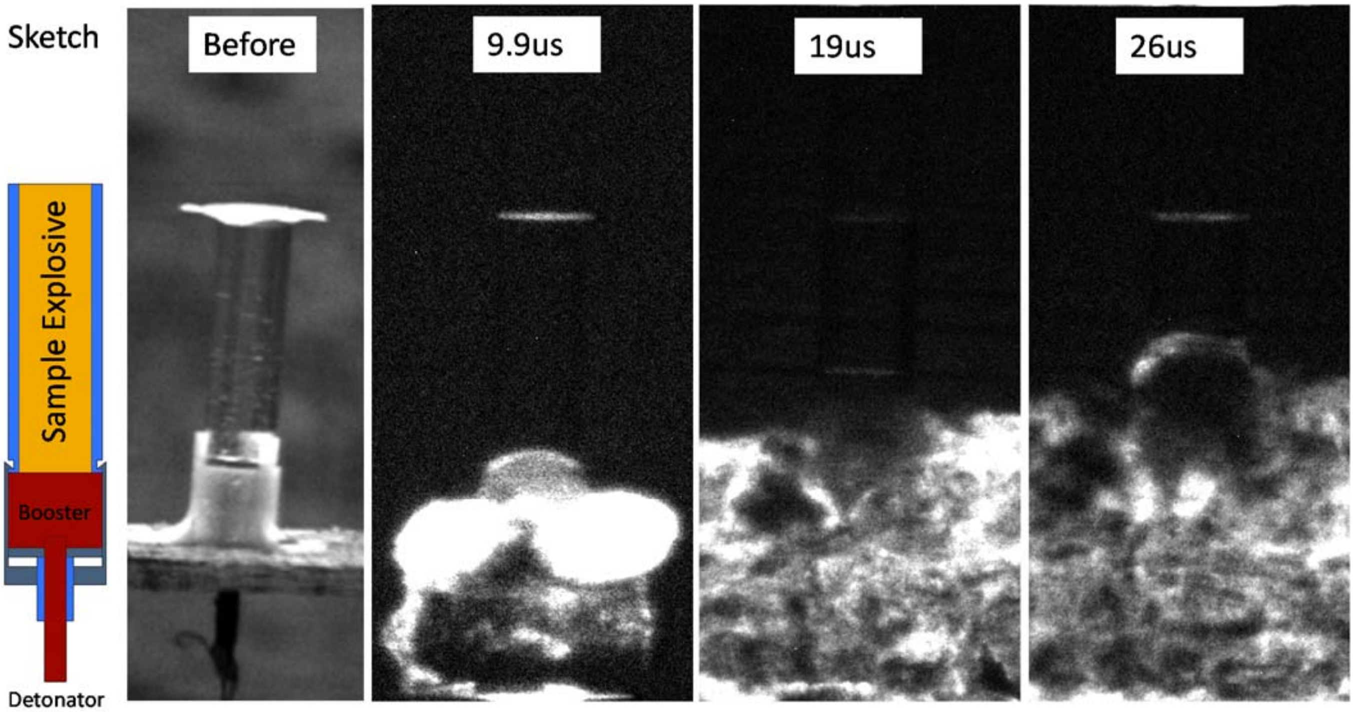


Figure 6.  Development of detonation in hydrogen peroxide/ethanol mix (**13.4%EtOH- balance 70%HP in water solution)**. Time between each frame collected was 3.3 us and each frame exposure = 30 ns. Shock-to-detonation transition is visible at approximately 26us from trigger.

**Our approach is novel because standard diagnostic tools will be used in an unconventional manner to study the transient detonation phenomena for configurations in which stable detonation may not be possible.** We have adapted three independent diagnostic strategies to approach the characterization of non-ideal explosives using conventional diagnostic measurements, namely photon Doppler velocimetry (PDV) and ultra-high speed photography.

Our present experimental configuration is a cylindrical sample material or “acceptor” into which a shock wave is introduced by a cylindrical high explosive booster charge or “donor”.  The time-resolved response of the acceptor to the imparted shockwave characterizes the acceptor as a potential threat by identifying if any detonation-like behavior was observed even if the acceptor is tested below its critical diameter.

The following three strategies will be approached using both diagnostics:

1. ***Over-driven detonation failure***:  A material may fail to detonate because it is below its critical diameter or because it has no explosive character at all.  By measuring detonation wave structure profiles through time, detonable character and failure rates will identify detonable materials whose failure to detonate in conventional tests is simply a problem of charge size rather than those whose chemical contribution is too slow to grow to a detonation.

2. ***Under-driven shock to detonation transition:*** Characterizing the ignition and growth to detonation of a sample already identified to have detonable character (strategy 1) will indicate how easily a particular threat material may be initiated.

3. ***Steady detonation reaction zone structure:*** Direct measurements of reaction zone lengthening and weakening of a known explosive threat as a proposed diluent is added. This strategy will indicate the maximum reaction zone thickness which can grow to a steady detonation and will guide inerting criteria.

In the ***first experimental design***, ***over-driven detonation***: examination of failure profiles), potentially-explosive samples will be subjected to booster conditions which shock it to higher pressures and velocities than the theoretical detonation conditions of that sample material. This ensures that if detonation of that material were possible, it will exhibit detonation-like behavior in the initial (e.g. <5mm) stages of being shocked, i.e. before any sidewall effects can be felt. If detonation of that material is not possible, this test should show it as such and the result is still useful information. In other words, this design distinguishes between detonation failures caused by smallness of charge vs failures due to no explosive chemistry. A shock wave traveling through inert, non-explosive samples will quickly attenuate (decay) at a predictable (using hydrocodes) rate based on its thermodynamic properties; but if the sample exhibits detonable character, even if it is below its $D_{cr}$, the contribution of the chemical reaction can be measured by both PDV and ultra-high speed photography. The PDV record, for this test and all others performed, follows the particle velocity vs. time profile by measuring the interfacial velocity of a sputter-coated, coaxial window in contact with the end of the cylindrical sample. The emitted light from chemical reaction behind the shock front (indicative of detonation) is observed with ultra-high speed cameras. If the sample material exhibits detonable character in the initial stages but is below its critical diameter, the velocity profile (PDV) and the emitted light (cameras) will show the decay and eventual failure of the detonation wave into an inert shockwave. This decay process should indicate how far below $D_{cr}$ the sample being tested is. The Son group, also part of R1 thrust area, has used a similar approach tracking the wave velocity of a decaying, over-driven detonation; however, use of microwave interferometry precluded the study of any microwave-absorbing explosives, e.g. aqueous formulations, or any examination of detonation wave structure [15]. The effect of any shock-induced chemical contributions from a sample, especially one slowly releasing energy, will not be observed by techniques recording only the shock velocity decay, e.g. velocity pins or microwave interferometer, because the chemical contribution of the sample is not released rapidly enough to support the shock front. Late-time reactions will be invisible to these techniques, but the PDV approach we propose will visualize the entire wave profile, including decay, which will indicate the presence of late-time reactions and chemical contributions which did not contribute to the wave velocity attenuation.

In order to track the attenuation of shock into a potential threat sample, we will collect the PDV record of end-on interfacial velocities for various lengths of sample. Comparison of signal attenuation among these samples and a baseline inert material will indicate whether the sample material is contributing energy to the shockwave or whether it is attenuating the shock as in an inert. Only by measuring the entire wave profile (not just the wave velocity) can the nature of chemical energy contribution be determined. The rate and nature of quenching will indicate how far below critical diameter the tested configuration is. The wave profiles of materials for which the critical diameters are known will be correlated to inert materials. The relationship, thus established, will serve as the benchmark for materials for which denotation or $D_{cr}$ is unknown.

The experimental setup requires the use of a polymethylmethacrylate (PMMA) window (see Fig.

7) which is acoustically impedance-matched to the sample so as avoid reflections from that surface thus preserving the accurate particle velocity time history behind the shock front. Accompanying PDV will be high-speed photography. It is expected to show reaction light (directly related to temperature of the sample) in the first stage after the initial shock input, but this will be quenched if the sample is non-detonable or too far below its $D_{cr}$. The first materials chosen for design 1 are mixtures of HP and fuel. These homemade explosives (HME) can be clear liquids, which facilitate photo visualization; and being fuel-oxidizer mixtures, their chemical energy release can easily be tuned by adjustment of the fuel-oxidizer ratio. The experimental configuration for this and the other two experimental designs is diagrammed in Figure 7.

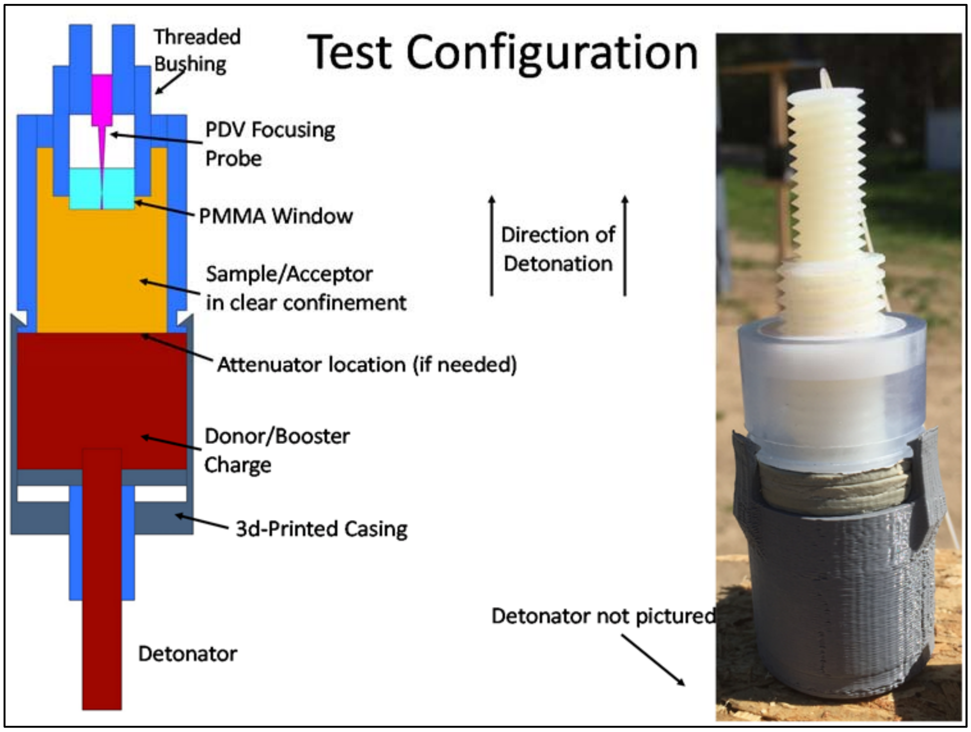


Figure 7: Experimental configuration -- template for all 3 experimental designs. To attenuate the booster shock (design 2), a polymer film is added between the booster charge and the sample. Note: the sample charge length (orange) changes often for designs 1 and 2, but for design 3 should be kept at least 4 charge diameters in length.

The ***second experimental design***, ***under-driven shock to detonation transition or SDT***, attempts to observe an energetic sample transition a weak shock (imparted from the booster) into a pseudo-steady detonation. This test requires that the sample tested has detonable character and is above its critical diameter; otherwise, the detonation will grow into a pseudo-stable state then decay as in design 1. In this experimental design, the shock input by the booster is *below* the theoretical conditions calculated for a stable detonation in the sample material.

This transition begins as the booster-imparted shockwave traverses the sample without causing any chemical change. The sample behaves as an inert material during this period. As the shocked sample remains under pressure loading, the chemical chain reaction begins to grow in the elevated pressures and temperatures behind the initial shock front. After the reaction has been allowed sufficient time to develop, a visibly-bright reaction wave accelerates through the shocked material much faster than the initial shock. This stage is labeled ‘superdetonation’ because it is traveling faster than the steady state shock would. When the superdetonation wave overtakes the initial shockwave, it will decay to its equilibrium value, if the sample is above $D_{cr;}$; or if the sample is below $D_{cr}$ it will be quench at the point where they intersect with the shock rarefactions from the sample. Until this happens, the center of the charge material proceeds as if the configuration were in an ‘infinite diameter’. In other words, the diameter of the charge takes effect only after the rarefaction waves have equilibrated, which takes longer for larger diameters. This window of time for which the charge behaves in an infinite diameter can be simulated with hydrodynamic modeling tools, namely ALE3D from Lawrence Livermore National Laboratory (LLNL) and CTH from Sandia National Laboratory. As long as this process can be completed while the experiment is kept in an infinite diameter state, the steady detonation conditions for that non-ideal material can be directly observed. LANL researchers have reported several SDT observations using magnetic embedded gauges including diluted nitromethane [ref 16 and Fig. 8] and concentrated HP solutions (no fuel added) [17].

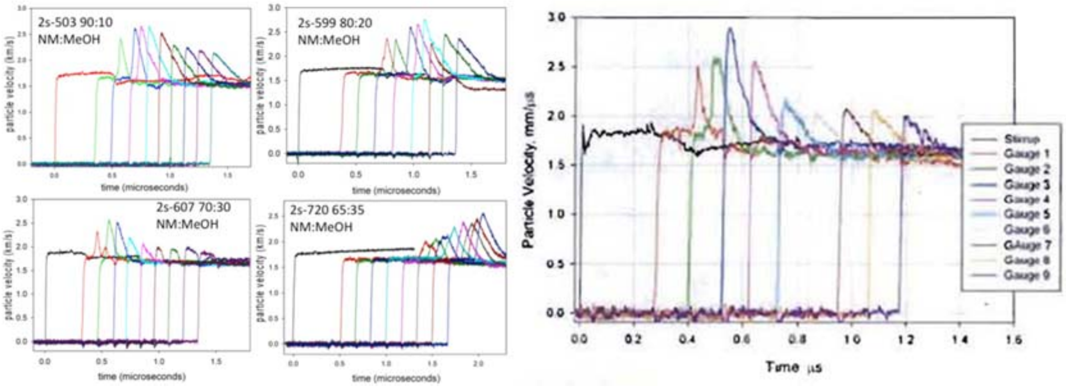


Figure 8: LANL magnetic gauge SDT measurements of nitromethane/MeOH mixtures (left) [16], and hydrogen peroxide/water solutions (right) [17].

This transition to steady-state detonation has not been previously observed with ultra-high speed imaging directly. Our initial tests using this configuration seemingly captured this phenomenon (Figure 6). **Figure 6 was taken using a Specialized Imaging SIMD16 camera, 304,000 frames/second (3.3µs inter-frame). The charge (13.4%EtOH- balance 70%HP in water solution) was contained in a 1” diameter by 4” long clear PMMA (polymethylmethacrylate) pipe equipped with a 1.1” diameter x 1.1” long cylindrical PETN-based booster. The charge was oriented vertically and initiated at bottom by the booster. In frames at 9.9us and 19us the under-driven wave propagates into the explosive. Initially, the shock wave enters the material with flat curvature (not pictured). In the following few microseconds (seen at 9.9us), the wavefront in the sample assumed extreme curvature, channeling light from the booster to the camera. Frame at 19us illustrates the inert shockwave travelling through the sample. The last frame (26us) illustrates the chemical reaction wave, which had been developing within the compressed region behind the shock, accelerating and overtaking the initial shock**

**front in textbook SDT fashion.** While **Figure 6 illustrates our ability to observe some detonation events and is a necessary milestone, this study of the reaction zones will be deferred until after experiments of type 1 and 3 are performed.** Future tests will use PDV to confirm the photographic record interpreted as SDT. Use of PDV will effectively simulate the magnetic gauge experiment of Los Alamos [16, 17] by testing subsequently longer charges to act as 'gauges' embedded in a larger charge [14].

The ***third experimental design steady detonation: reaction zone measurements*** will make direct measurements of the reaction zone length of steadily-detonating, non-ideal explosives. Specifically, it will observed the lengthening and weakening of the reaction zone as a result of dilution of an explosive material with an inert solvent. By measuring the structure of flow in the reaction zone as the material approaches critical diameter, relationships between diluent concentration and the fraction of energy available to support detonation can be drawn. **By comparing these measured values to the theoretical calculations for the maximum energy contribution, the fractional energetic contribution to the detonation will be obtained. This reported value will greatly facilitate the understanding and prediction of the behavior of these materials. Once measured, the dynamic reactivity of these materials can be modeled and simulated in hydrodynamic reactive flow codes.**

**Los Alamos researchers have shown that the steady reaction zone of detonating nitromethane (NM) can be measured using photon Doppler velocimetry (PDV) [ref 18 and Fig. 9]. They interpreted the length of reaction zone by mapping the literature value for the particle velocity at which total reaction *should have* taken place. In the experimental record, the time/special distance to this point was reported as the reaction zone.**

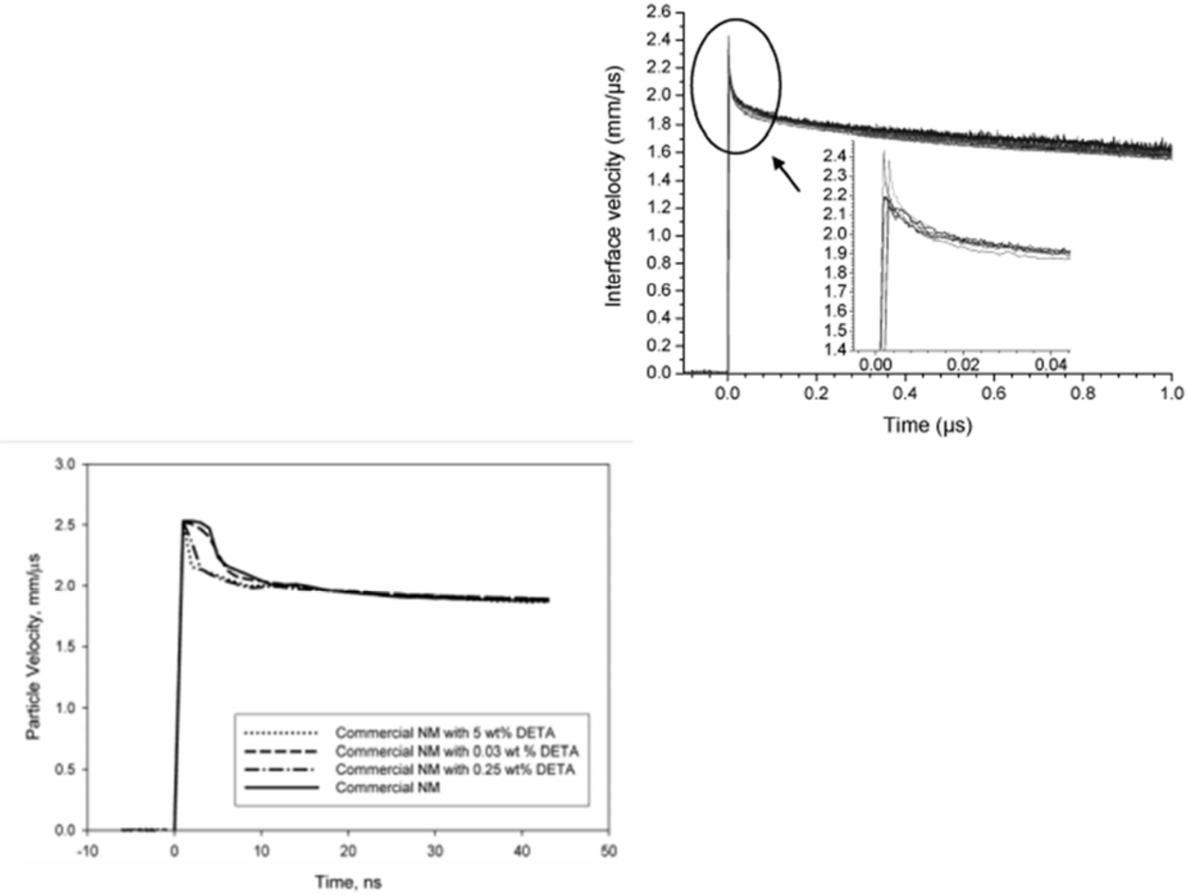


**Figure 9: LANL approaches at studying steady detonation reaction zones with adulterated (sensitized [19] and diluted [18]) nitromethane.**

**A Russian research team uses the steady-state reaction zone assumption to measure the convergence of Taylor wave immediately following the reaction zone, to determine reaction zone length [ref 20 and Figure 10]. If the steady assumption holds, the length of the reaction zone *should be* the same in the PDV record regardless of the charge configuration (e.g. charge diameter, length, or booster size), but the Taylor wave (not steady-state) should diverge. By obtaining two or more PDV records of similar charges which differ only by one of these parameters, the Taylor wave divergence should begin at the end of the steady reaction zone. The figure below illustrates this.**

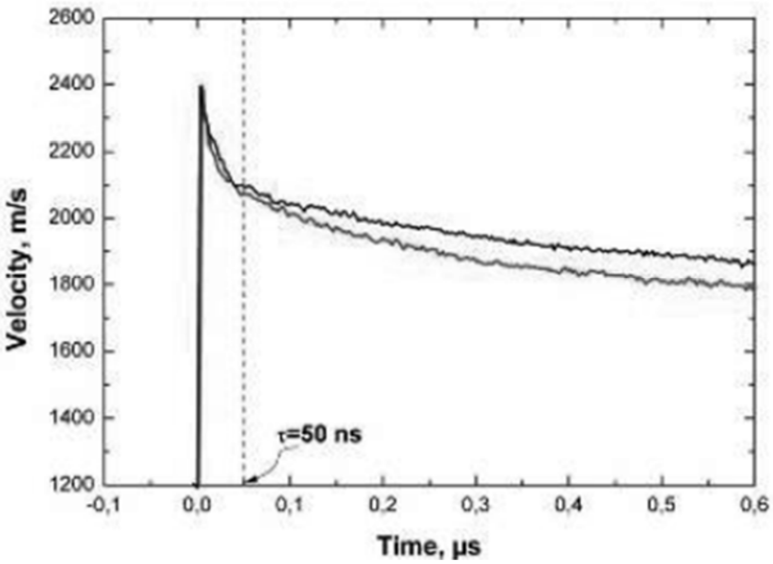


**Fig. 10: Steady detonation wave profiles obtained by Russian scientists [20] for nitromethane illustrating the steady, 1-dimensional reaction zone (0-50ns) and the divergent Taylor wave (50-600ns) as evidence that the flow within the reaction zone remains steady as the charge configuration changes, but the release wave (Taylor wave) diverges.**

**Initial tests will confirm both methodologies by testing nitromethane, which was tested by both groups. This requires two independent tests at different lengths to confirm the steady reaction zone assumption. Successive tests will focus on diluted NM/acetone mixtures. As the adulterant concentration is increased, the reaction zone will begin to lengthen and weaken. At some critical amount, detonation will fail to propagate; this is the critical diameter ($D_{cr}$). The study will examine the failure point of the NM/acetone mixture as well as points of dilution beyond detonation failure.**

**The diagnostic technologies used to characterize a growing (design 2) and failing (design 1 and 2) detonation fronts will also be used to measure the length of the chemical reaction zone. Design 3 does not directly screen questionable materials for detonable character but rather characterizes the nature of reaction zone lengthening as a function of available energy density. For this test, a detonable material must be tested above its critical diameter, and the chemical energy available will be diminished in subsequent tests by dilution until its failure. *This approach will specifically measure what fraction of a non-ideal explosive's energy is supporting the detonation wave.***

## Major Contributions

The thermal studies discussed in Approach 1 highlighted the role that a melt or phase change in a fuel-oxidizer formulation has in triggering its reaction. These studies indicated that the choice in oxidizer, outweighed the choice in fuel, in determining the total energy released. These are significant observations and are the first steps in relating milligram-scale behavior to detonability, measured on the kilogram scale. The fact a plot of temperature vs heat of decomposition clearly groups explosives in a different region than non-explosives suggests we can use thermal analysis of small samples as one metric to rate detonability.

The thermal studies discussed in Approach 1 (Calorimetry Plus) highlighted the role that a melt or phase change in a fuel-oxidizer formulation has in triggering its reaction. These studies indicated that the choice in oxidizer, outweighed the choice in fuel, in determining the total energy released. These are significant observations and are the first steps in relating milligram-scale behavior to detonability, measured on the kilogram scale. The fact a plot of temperature vs heat of decomposition clearly groups explosives in a different region than non-explosives suggests we can use thermal analysis of small samples as one metric to rate detonability.

## Milestones

**Calorimetry Plus: Complete collection of calorimetry and pressure-rise data. Use the Lawrence Livermore code Cheetah to predict detonatbility. Although the FOX mixtures examined in Approach 1 are not new, our observations concerning their fundamental properties should allow correlation with their role as materials used by terrorists. This correlation is a milestone for Year 4.**

**EMRS:** The algorithm for statistical analysis will be refined and a library of known explosives as well as inert materials will be constructed. **Approach 2, mass spectrometry, may fail when truly insensitive explosives are tested. Chemical analysis demands multiple approaches for conclusive identification of threat materials. A further assessment of these approaches is also a Year 4 milestone.**

**Small-scale Detonations: We intend to use a compilation of previous strategies to approach a small scale test suite that can probe potentially explosives materials below what would be their critical diameter. We have three major successes to report this year.**

1. **Our facility and instrumentation have been acquired, set up, and proven fully functional.** The development of an empty field at the URI Alton Jones campus included the planning and construction of a 2200 $ft^2$ building to house office space, lab space, and machine shop. The office is equipped with electricity, AC, heat, and has firing lines buried for the convenience of initiating experiments without having to run cable for each shot. The firing pad is a 20' diameter circle, excavated and back-filled with sand to prevent rock-throw. Immediately adjacent to the pad is a 10' dia x 20' long buried instrumentation bunker. Cutting-edge diagnostics fielded therein allow observation of detonation events.

2. **The first experiment has shown the particle velocity of an RP-501 exploding bridge-wire detonator. This test confirmed the velocimetry record by allowing the reflective surface of an RP-501 detonator to expand into air. A bare fiber probe was used to emit and transmit the incident and reflected light, respectively (Fig. 11).**

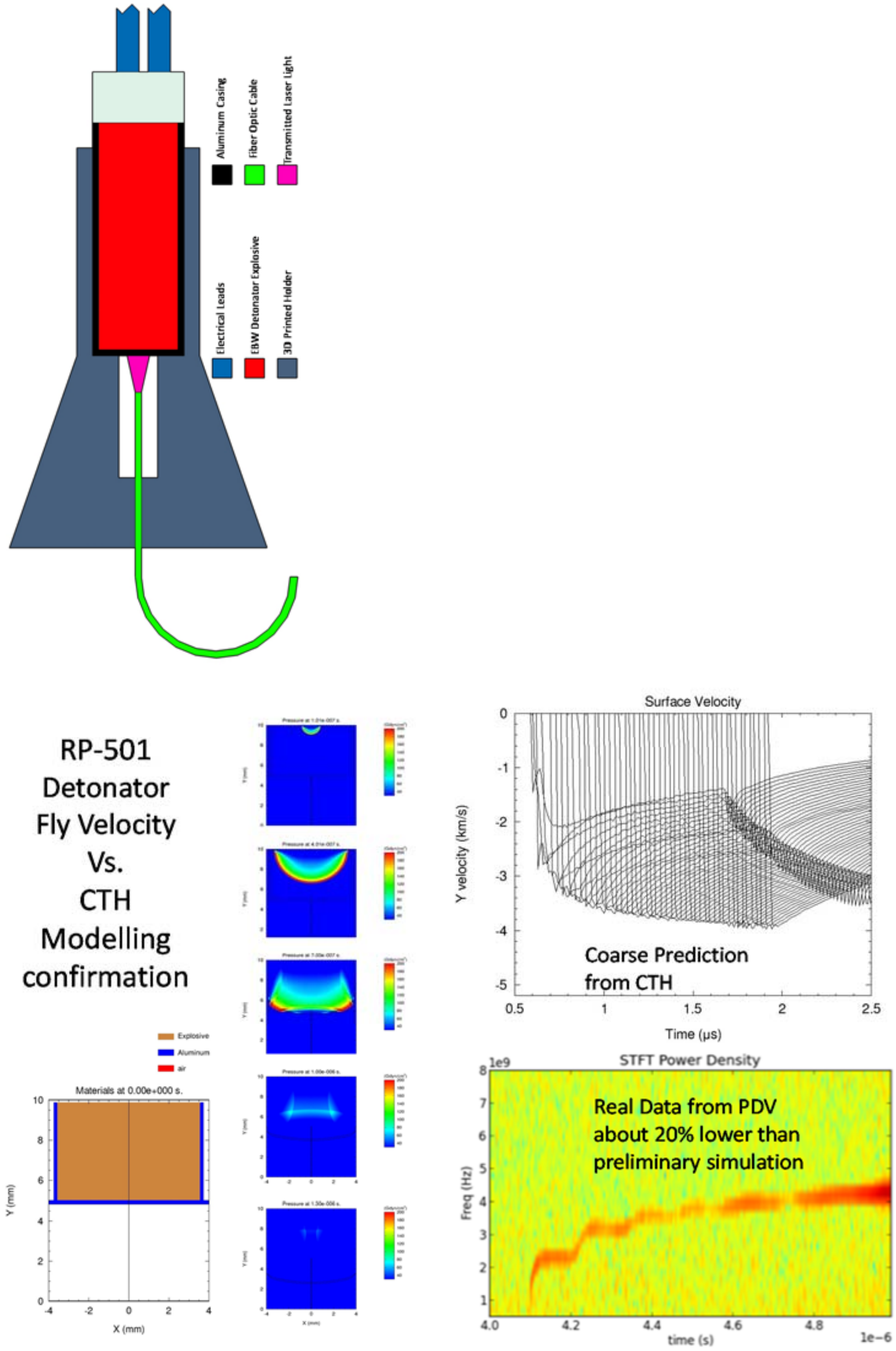


**Figure 11: Sketch and Data obtained from initial PDV tests at URI. The surface velocity was predicted (CTH) and measured via PDV. Predicted CTH calculations employ basic assumptions which can be fine-tuned for more accurate results, but agreeable velocities were obtained for the experiment [21].**

3. **Our PDV configuration was characterized by measuring end-on interfacial surface velocity of a PETN sheet explosive stack of (12) 1" diameter x .080" thick discs which will later serve as the booster explosive for initiating non-ideal explosives. This configuration utilized a 75um aluminum interfacial reflector between the booster and the PMMA window.** Our first surface velocity tests are shown in Figure 12. Using this approach, incremental shots of increasing lengths of sample material will reveal the non-ideal explosive's response to this incident shock pulse as described in experimental design 1. This initial test shows the impulse that will be used to initiate reaction, and the sample materials will respond differently to this booster wave based on how detonable they are.

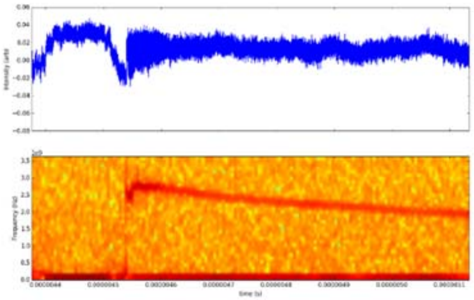


Figure 12: The time-domain (top, blue) and frequency domain (bottom, red) record of PDV-based experiment. The maximum particle velocity pulse correlates to about 1.66mm/μs or 110kbars (11GPa) in PMMA. PMMA has a phase transition above 25GPa above which it is no longer transparent.

**Visualizing the reaction wave with ultra-high speed photography in clear liquid explosives has been demonstrated (Fig. 6). Replicates and repeats with other sample materials are necessary. The premise is that the initial shock wave will be unreactive for some time and the superdetonation wave will be visible as it runs through the shocked sample catching up with the shock front.**

## Future Plans

**Calorimetry Plus:** Completing calorimetry experiments and beginning detonation testing is planned for year 4. The explosive behavior of FOX mixtures will be examined measuring the propagation of a shock wave through the material via high-speed camera and/or PDV or assessing damage to a witness plate. Data from large and small scale experiments will then be compared.

**ERMS:** The algorithm for statistical analysis needs further refinement in order to analyze data in a consistent and independent way. A library of known explosives should be constructed and analyzed using this method to verify the hypothesis. Along with explosive materials, stable compounds with similar functionalities should be analyzed to cross-reference and compare their fragility. Comparison of groups of explosives (nitramines, peroxides, nitroarenes, nitrate esters, etc.) by this method should parallel the sensitivity each explosive has within that group. Various adducts required for the detection of some explosives (eg. $Cl^-$ for ETN), must be compared across that group for consistency. The risk of this approach is that there may not be sufficient differentiation between chemically unstable materials and explosives. Our mitigation strategy is our multiple approaches to studying potential detonability.

### Small-scale Detonability

Using PDV and/or high-speed photography, we hope to develop new ways to examine growth to detonation and failure in samples tested below their critical diameter. The tests outlined will yield information about the capacity to detonate on a scale larger than need be tested. The tests discussed will not necessarily be performed in the order as outlined. Following the development of the detonation front by high speed photography will be optimal for clear liquids; therefore, nitromethane (NM) and hydrogen peroxide (HP) formulations will be used initially.

Once proof-of-concept tests with clear liquid explosives are successfully completed, tests are planned for solid oxidizer-fuel mixtures (FOX). Project R1-A.1 has already begun performing the laboratory characterization of FOX combinations. Characterizing the detonability of these mixtures will confirm or deny the existence of a critical diameter and hint at what scale that may be. Correlation of results with other small-scale tests may indicate that many formulations should be deleted from the threat list. This test will also allow us to assess the effectiveness of a given diluent or adulterant in an explosive mixture. True safe limits for materials can be established, including commercial chemicals being manufactured on the very large (tons) scale. Using these tests, inexpensive and small configurations can be routinely conducted and interpreted to affirm if an explosive threat is warranted. Achievement of these goals would be a breakthrough for the study of all detonation reactions. Our goal is confirming or denying the existence of a critical diameter and establishing the limits of detonability in a material.

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explosive booster charge, but if the sample energetic is below its critical diameter, the chemical reaction will quickly (less than an inch) decouple from the shock front and the shock will propagate as an inert pressure wave through the rest of the non-reacting material, giving the appearance that the material is non-explosive.  This detonation failure phenomenon can be very delicate; many detonations near the critical diameter are very unstable, which means conventional explosive testing must be done well above the critical diameter.

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# R1-C.2: Compatibilities & Simulants: Explosive Polymer Interactions

*Abstract (project description for the web)*

To "secure the homeland" the Homeland Security Enterprise (HSE) must collect, handle and store explosives. Of particular concern are improvised or so-called "homemade" explosives (HME). Often these are materials examined and rejected by conventional militaries as too hazardous to handle, but for HSE there is a high probability that they will frequently encounter such materials. As an outgrowth of characterizing these materials (R1-A), this project is tasked to evaluate the compatibility of various chemicals with HME. The motivation is to provide safe protocols for HSE when they encounter HME and components associated with construction of explosive products. Some questions we have addressed are as follows:

Can HME be packaged to reduce the possibility of an explosive event?

What is the best approach to collection of HME evidence?

Are there ways to improve stability in order to prevent accidental explosive events?

Attempts to answer these questions have generated research resulting in development a product consisting of a trace amount of explosive encapsulated in polymeric material that releases the scent of the explosive for detection by dogs and electronic instruments. The aids are non-explosive, non-toxic and safe to handle. This eliminates the necessity of handling bulk amounts of hazardous even detonable materials. The weak link in any detection method is sample collection. We are studying new approaches to the swab collection of explosives residue. As the HSE continues to deal with these highly hazardous materials, this project aims to provide them with safer more effective methods of performing their tasks.

## I. PROJECT DESCRIPTION

### *A. Project Overview*

The aim of this project is to develop new methods for those involved in the Homeland Security Enterprise (HSE) to collect, handle and store explosives. Because there are many applications where explosives must interact with other materials, a number of approaches have been developed. To date, the applications of this study have been safe trace explosive sources for canine and instrument calibration and training; explosive sampling devices (swabs), which are effective at pick up and release of explosive residue; and better methods for analyzing these hazardous materials.

Military explosives are rarely used pure, meaning without plasticizers or other formulating agents. So, too, homemade explosives (HMEs) may require admixtures with other materials to get a formable formulation or simply conceal the formulation (Figure 1).

Figure 1: TATP Confiscated by the Israeli police

Understanding how HMEs react with other materials addresses a number of applications: safe handling and storage of HME; creation of better swabs; creation of better vapor concentrators; creation of canine training aids; and creation of trace and bulk simulants. This project has focused on finding the most compatible materials for such devices as canine training aids, swab material and pre-concentrators. One successful application of our studies is polymer encapsulation to facilitate handling of volatile, sensitive explosives, e.g. triacetone triperoxide (TATP). It has been received with enthusiasm. We are presently negotiating licensing with a commercial vendor.

Along with the discovery of potential applications, metrics for assessment are being developed. Our studies have employed a closed vapor chamber as a metric for sorption; and we are now working with the Gregory group (R2) on a more reliable way to create vapor. In any case the amount of explosive vapor sorbed is quantified either by exhaustive solvent extraction or heating. Heating with a thermogravimetric analyzer (TGA) coupled with infrared and/or mass spectrometer determines desorption quantity, purity and the presence of decomposition products. Atomic Force Microscopy (AFM) has been used as a way to measure the adhesive forces between the polymer and explosive.

R1-C.2 has resulted in two papers authored at URI [1, 2] and two from our partner at a minority-serving-institution (MSI) [3, 4], as well as a provisional patent [5]. Both our MSI partner and our group have been awarded further Department of Homeland Security (DHS) funding for certain aspects of this research [6, 7]. This work has also resulted in a graduate student award [8] and partnerships with three vendors supporting trace explosive detection.

### *B.* Biennial Review Results and Related Actions to Address

*The HSE and other State and Federal law enforcement agencies consider canines to be the gold* standard for drug and explosives detection. For the canine explosives training aids, there were about 14 users during initial trials supervised by the Transportation Security Laboratory (TSL). The new generation of training aids have been tested by a limited number of users because of a requirement for a specialized heating device to release the scent from a polymeric material used to encapsulate the explosive. With an industrial partner we are working on a compact heating device for use in the field. Once available, the number of users will increase significantly. The prototype heater was on display at the DHS Innovation Showcase (May 19, 2016).

For the swab development, the most obvious user will be the Transportation Security Administration (TSA). This swab development program is benefiting from the direct involvement of DHS personnel from all divisions.

One reviewer noted the diversity of efforts in this project and suggested creating several projects. Should extra funding become available, this may be possible. However, without that, this project will remain in the cradle where new concepts are investigated.

### *C. State of the Art and Technical Approach*

This project uses a variety of tools to determine compatibility of various materials with explosives. In addition to standard laboratory analysis methods, this project has explored the use of reaction and titration calorimetry, AFM, TGA-IR, and various gas and liquid chromatographs as tools to aid this work. This project has also investigated new methods to package sensitive HME and novel ways to collect explosives residues with the goal of an on-off collection methodology. This group produced the first TATP training aids in response to the sudden demand after the attempted shoe bomb. While those initial aids had many drawback, this project has made creation of safe, long-lived canine training aids for peroxide explosives a priority. Scientists at NIST have since reported a similar approach and sent us a congratulatory email after seeing our presentation at the Trace Explosive Detection conference (April 2014). Recently, their paper has been sent to us for review (see reference [10]); in fact in the last year we have been asked to review over 40 papers dealing with explosives that demonstrates our expertise is valued in this field.

### *C.1 Encapsulation and coating of energetics*

Bomb-sniffing dogs and companies manufacturing trace explosive detection instruments must have the pure explosive for testing. However, obtaining, handling, and storing the explosive is a significant obstacle. There is a need for an insensitive, storage-stable source of HMEs, in particular the highly sensitive peroxide explosives. To meet the demand for safe forms of TATP, we have sublimed TATP onto scrupulously clean filter paper. While this approach fulfilled immediate needs of canine trainers and instrument suppliers, preparation was arduous; and the aids were effective for only about 90 minutes. To enhance the work- and shelf-life of the product, we developed a method to encapsulate TATP, creating microspheres which are non-detonable and have long shelf-life.[1] We have now focus on providing non-detonable scent material for hexamethylene triperoxide diamine (HMTD).

HMTD is a highly sensitive explosive which has caused a number of injuries in the counterterrorism community. Unfortunately, since it is readily synthesized from easy to obtain ingredients, like TATP, it is a terrorist threat material. Therefore, we have attempted to create safe-scent aids for this material in a fashion analogous to our TATP training aids. To date we have made microspheres containing the explosive of interest through a solvent evaporation method. The general procedure is as follows: a shell material (polymer) is dissolved in a hydrophobic, volatile solvent with the core material (explosive). This solution of shell and core material is added to a stirring aqueous solution of a surfactant, creating a two phase system. The polymer, being insoluble in water, precipitates around the core material as the volatile solvent slowly evaporates from the solution. The microspheres are collected, washed, and baked at low temperature.

The prerequisite for the solvent is a hydrophobic compound that readily dissolves the polymer and explosive. HMTD has low solubility in most organic solvents but is slightly soluble in chloroform; therefore, chloroform was the first solvent used to dissolve the HMTD and the polymer. Unfortunately, it proved difficult to remove that material from the microspheres. Since, dichloromethane (DCM) was successfully used in the TATP microspheres, as an effective volatile solvent, it was the next choice. Because the solubility of HMTD in DCM was very low, a high volume of solvent was needed (500mg of HMTD was dissolved in 135mL of DCM). The volume ratio of polymer, explosive and solvent solution to surfactant solution required optimization in order to create the two phase system because with the wrong ratio the polymer precipitated from the solution without encapsulating the explosive.

Microspheres of HMTD were synthesized using various polymers and screened using TGA-IR (thermogravimetric analysis with infrared detector) to observe the release of HMTD from the microspheres. In the TGA experiments, about 10 mg of sample were heated at 20°C/min to 300°C by the TGA furnace, and the evolved gases were carried through a transfer line, held at 150°C, to an IR spectrometer for vapor analysis. Many polymers were unsuitable; either they did not encapsulate HMTD, decomposed as HMTD was released or contained difficult to remove impurities.

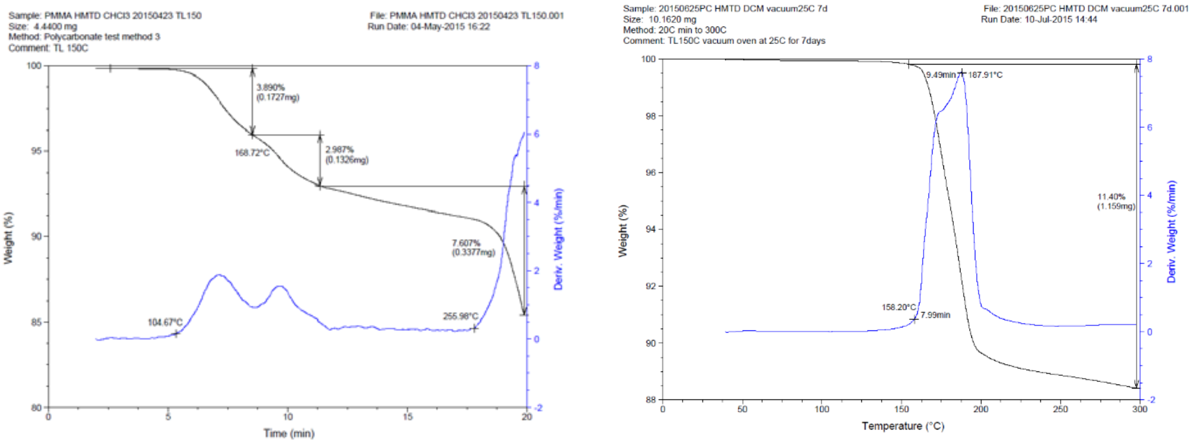


**Figure 2** : TGA of Polymethylmethacrylate (PMMA) HMTD microspheres (left) and polycarbonate HMTD microspheres baked in vacuum 25°C, 7days (right)

Figure 2 (left) shows the thermogram of polymethylmethacrylate (PMMA) microspheres. The first mass loss yields an IR spectrum of chloroform, the solvent used in the synthesis. The second and third mass losses yielded IR spectral library matches (85%) for butyl ester methacrylic acid, suggesting polymer decomposition of heated microspheres. Figure 2 (right) shows the thermogram of polycarbonate (PC) microspheres with only one mass loss starting at 8 min. The IR at 11min, which corresponds to this mass loss, directly matches the HMTD spectrum. Proof of this is shown in Figure 3 infrared (IR) spectral overlay of the polycarbonate HMTD microspheres vapor at 11min with the spectra of HMTD vapor. The polycarbonate microspheres achieved a controllable release of the pure HMTD vapor at 150-160°C. This temperature was selected for further testing. Further examination of the vapor released by the HMTD microspheres showed that the main decomposition products of HMTD are trimethylamine and dimethylformamide. The polycarbonate HMTD microsphere, when heated, also exhibited peaks not associated with HMTD. A great deal of effort went into pre-cleaning the polycarbonate by multiple solvent extraction and supercritical $CO_2$ extraction to remove the impurities. After vacuum drying the HMTD microspheres for 7 days it appeared both the solvent and the impurities were removed. Nevertheless, further examination of our choice in encapsulation polymers will be performed.

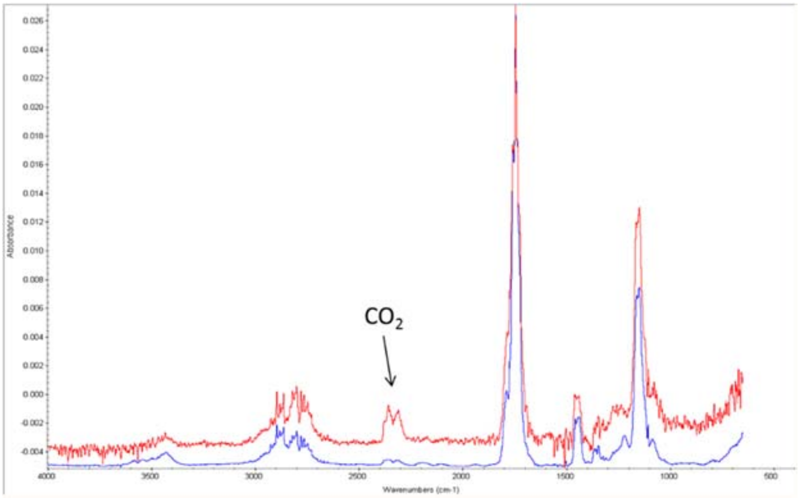


**Figure3**: IR overlay TGA-IR; Polycarbonate HMTD microspheres held in vacuum 25°C, 7days (blue) vs pure HMTD (red)

*

The TATP studies resulted in a paper [9], a student homeland security innovation award of $10,000 [8], and partnership with a vendor desiring to design and market the heating device. Future work includes efforts to further improve the encapsulating polymer for HMTD, working with a vendor to design the heating device for TATP and HMTD heating specification, and rigorously calibrating the heating profiles for releasing TATP and HMTD.

### *C.2 New explosive collection techniques*

Current sampling techniques are inefficient and invasive. To counteract inefficient pickup, swabbing greater surface area may increase the mass of explosive collected but only if there is explosive contamination over the whole surface. Screening of hands, headdresses and medical appliances requires physical contact that can be invasive and may expose passengers and screeners to biohazards. To avoid being intrusive or causing physical harm (medical devices), TSA operators may not swab certain areas otherwise of interest. Swabbing can also damage (scratch) some surfaces. The aim of this work is to create a reversibly switching surface capable of altering adhesive properties. A swab composed of such a material could maximize both pick up and release of analyte particles for introduction to a detector. Modern explosives swabs suffer from the fact that they can only either adhere analyte well and release it poorly, or adhere analyte poorly but release it well. Both aspects are important to adequate delivery of analyte to a detector system. A adhesion tunable surface controlled by a small electric charge (less than that of a 9 V battery) or by thermal stimulus could be a major accomplishment. Three approaches are being considered. Approach 1 and 2 do not required direct contact. While not considered non-contact by the DHS definition (i.e. standoff of greater than 2 inches), the switchable swab would attract explosive particles from about 3 cm away from the contaminated surface. This obviates the need for actual physical contact with a surface, and therefore speeds the sampling process, provides for greater privacy, may increase the overall swab lifetime, and perhaps minimize collection of certain types of interfering compounds. These advantages, coupled with higher pickup and release efficiencies, will make for speedier, more pleasant, and more economical checkpoint operations while improving trace detector performance. Approach 3 involves new material synthesis to improve explosive pickup; a successful material in this area may serve as a pre-concentrator.

### *C.2.a Approach 1*

Non-obtrusive detection of trace amounts of illicit materials has long been a goal of detection companies and security firms. Though detector technology continues to improve, a key challenge remains in collection and release of sufficient analyte, e.g., explosives or precursors, into the detector. In fact, many detection companies choose swabs with the best release profile rather than the best collection profile. Hence, materials such as Teflon, Nomex, and metal mesh have been employed. Our premise is that an electrostatically enhanced swab would improve the collection efficiencies of poorly collecting materials. When the swab is placed in the desorber, the charge is dissipated and desorption occurs. Because the collection is done near-field, there is less wear on the swab material, and therefore the swab has a longer life-time. Furthermore, because the swab does not rely on physical adhesion of particles, the particles are readily released when the static field is dissipated. Thus, more residue can be collected, and more residue can be released, facilitating faster and more accurate identification of threat materials. This method is expected to be insensitive to the type of particles attracted. Electrostatically enhanced swabs have been shown to pick-up sugar, salt, 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5—trinitro-s-triazine (RDX), pentaerythritol tetranitrate (PETN), and ammonium nitrate. On the other hand, a non-contact swab, thus enhanced, is unlikely to pick-up oils and lotions which are pervasive in the environment and often the source of explosive trace detector (ETD) alarms.

This proposed triboelectric enhancement would require no major change in the swabbing materials nor sensor hardware but would allow a change in the technique as the swab would no longer need to be rubbed over a surface. Triboelectric charging, a subset of contact electrification, is a well-known phenomenon, e.g. children rub balloons in their hair to make the balloon stick to the wall. Therefore, it is surprising that so much of the basic theory is subject to debate, even to the point of whether the charge is generated by transferring electrons, ions, or nanoparticles [11]. Nevertheless, static electricity is exploited in applications from laser jet printers to industrial air cleaners [12]. Electrostatic precipitators have been used for many years for dust and other particle collection [13]. Moreover, though there must be a balance of charge between the two neutral surfaces that are rubbed together to create the positive and negative charges, these charges can persist long after the two surfaces are physically separated [12]. However, the electrostatic precipitator imparts a net charge to the particle [13]. In contrast, our technique charges the collector, which temporarily induces a dipole in the particle. This dipole dissipates as soon as the charge on the collector is neutralized. The precipitator charges the particles; the enhanced swab only redistributes charge temporarily so that the particle is attracted to the collector.

The concept is to enhance the pick-up and release efficiency of current swabs used by TSA for the collection of particulate explosives from a variety of surfaces. This enhancement approach can be applied to any swab material of low conductivity, e.g. plastic or cloth. Such a material will be statically charged, e.g., by triboelectric effect or corona discharge. The statically charged swab attracts the explosive particulate through space. However, when the swab is inserted into the inlet of the detection instrument, the static charge is dissipated; thus, it is no longer attractive to the particulate and the analyte is readily released into the inlet. Because the particulate was never pressed into the substrate or the material of the swab by rubbing, it is readily collected and released into the detector. Figure 4 shows that an electrostatically charged (-7 kV) Teflon swab easily picks up a visible amount of PETN. Particle size was not critical; flaked and powdered TNT, and sugar of 150 as well as 800 µm adhered to the swabs.

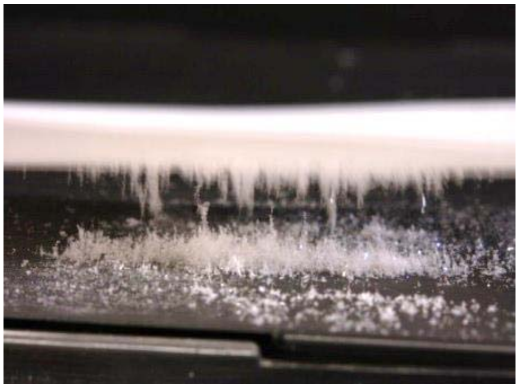


**Figure 4: Bulk PETN attraction to electrostatically charged Teflon.**

While macroscopic tests are more visual, microscopic pickup is the focus of the present study. The technique is effective on substrates such as glass, polymer resin, card stock, rough vinyl, and human hair. (When strands of hair purposely exposed to explosive vapor were swabbed with a charged and an uncharged swab, the charged swab resulted in detection on the FLIR Fido X3 while the uncharged swab did not (see Fig. 5). (Our hypothesis is that the explosive vapor adhered to dust particles which were subsequently attracted to the charged swab.) Additionally, when a C-4 fingerprint was analyzed using a charged swab, it resulted in detection on a Morpho Itemizer IMS (ion mobility spectrometer). It should be noted that all swabbing experiments were performed at 3 mm standoff.

Figure 5: Setup of TNT-exposed hair, depressors for set standoff (left), “No hit” with uncharged (middle left), & “hit” with charged swab (FLIR FidoX3, middle right). Hit with charged swab (Morpho Itemizer, right).

Electrostatically charged swab materials are expected to reduce the introduction of interfering and masking compounds to the detector inlet. Most of these compounds are not very volatile, have high molecular weights, and typically adhere strongly to surfaces, e.g. oils on skin or hair and common plasticizers. During contact sampling, these compounds are collected from the surface along with the explosive particles. Electrostatically enhanced sampling appears to provide some selectivity based on the strength of surface adherence. Loose explosive particles are more likely to be picked up by electrostatically charged swabs than oils.

Under the new DHS funding, COTS swabs are charged both both triboelectric and inductive. Charge degradation due to time and relative humidity was analyzed. Collection efficiency, transfer efficiency, and uncharged swab comparison are assessed by precise quantification of energetic materials via LC-MS techniques.

### *C.2.b Approach 2*

Triboelectric charging of swabs presents a number of challenges. Potential for contamination has been overcome by the use of inductive charging, but long-term retention of charge is a problem. If the TSA protocol were to charge at station before every use, long-term charge retention would not be an issue, but TSA envisions a pre-charged bundle of swabs. That being the case another approach will be investigated. Creating a swab with an electret surface overcomes these difficulties. An electret is defined as a “piece of dielectric material exhibiting quasi-permanent electrical charge" [14]. Quasi-permanence means that a significant decay in charge does not occur in the time scale of the experiments (years). The electret can extend from the surface into layers of the material (10 to 100 microns). Electrets are created by exposing a dielectric material to an electrical field, thus polarizing it. The magnitude of the charge created on the dielectric material is dependent on the resistance and chemical stability of the material. When heated and exposed to a strong electrostatic field, the polar molecules at the surface of the dielectric (polymer) align themselves (see Fig. 6). The dielectric surface molecules solidify and maintain charge on cooling.

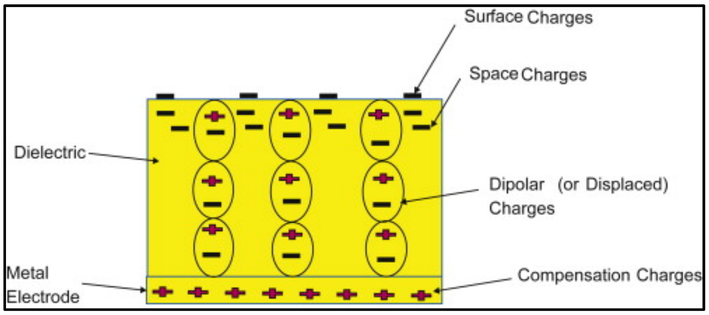


Figure 6: Notional diagram of electrets from [15].

Swabs that are electrets can be created and used in a completely non-contact fashion; thus, reducing the possibility of contamination. The electrets should accept and maintain a charge similar in magnitude to that created by a triboelectric charge (7-12kV). Our initial approach to making electrets would charge Teflon, β-PVDF, or Nomex using an external electric field, e.g., a tip-to-plane corona charging apparatus (see Fig. 7). Charging will be performed at elevated temperatures, just under the glass-transition point of the polymer, in order to increase their thermal stability. The apparatus will be purged with dry nitrogen to ensure low humidity. If higher voltage charging is required (> 30 keV), the chamber would be filled with a high dielectric gas such as $SF_6$; however, need for such high charging is not anticipated.

Swab materials created by Approach 1 (triboelectric charging) will be compared to those created by Approach 2 (electrets). Both of these approaches create a swab that does not require direct contact, and neither approach transfers charge to the operator or the surface being swabbed.

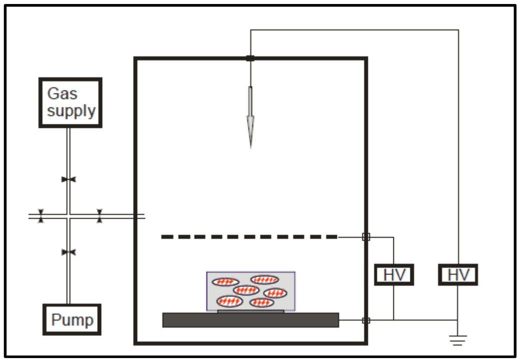


**Figure 7: Charging chamber for creating electrets from [16].**

### *C.2.c Approach 3*

Since the inception of this project we have been interested in preparing molecules with special sorbative properties. These may be used as swabs, pre-concentrators, or even sensors. Therefore, we have investigated molecularly imprinted polymers (MIPs) and considered carbon nanotubes. Now with the aid of an expert organic chemist we will examine metal-organic-frameworks, porphyrins, and supramolecular complexes.

The two most important properties for gas adsorbents are generally considered to be adsorption capacity and selectivity [17]. Adsorption capacity is dependent upon equilibrium pressure and temperature, the nature of the adsorbate, and the nature of the micropores in the adsorbent [17]. The factors which affect adsorption selectivity are not as well understood. Li et al describes that they "seem to be an integrative and process-related issue in practical separation, though it is still related to the operational temperature and pressure as well as the nature of the adsorbent and the adsorbate."[17] When considering chemical sensors, sensitivity, response time, materials stability, and reusability are necessary in addition to selectivity [18].

Porous polymers, e.g. activated carbons and aluminosilicate zeolites, are difficult to tune in terms of specificity. An advanced porous material metal organic frameworks (MOFs) or porous coordination polymers combine sorbative capacity and potential for selectivity which make them promising for preconcentrators or vapor sensors [19] (Fig. 8).

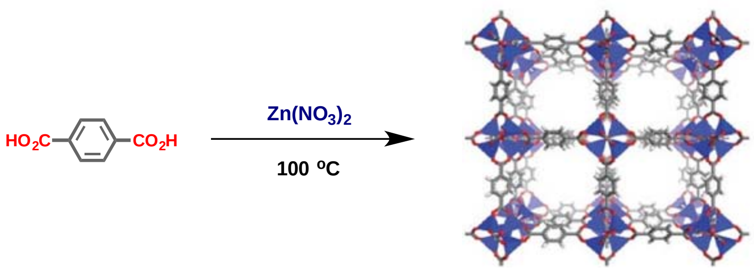
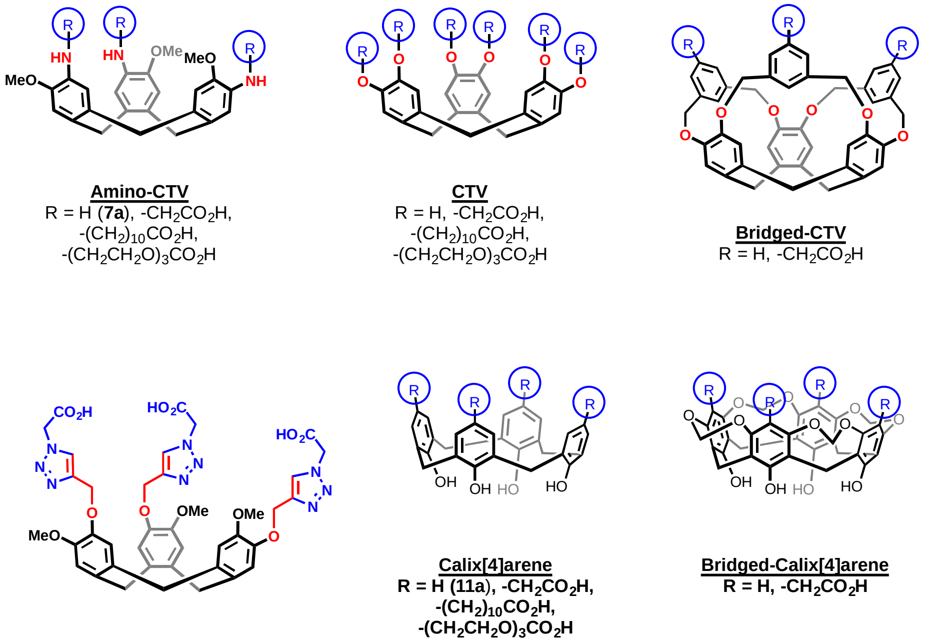


Figure 8. Example of Metal-Organic Framework (reference 20)

An intriguing class of compounds are the cyclotriveratrylenes (CTVs).[21-24] The DeBoef group has specialized in the synthesis and functionalization of these bowl-shaped molecules. We now intend to probe their potential for selectively binding explosives and their precursors. (Fig. 9).



**Amino-CTV**
R = H (**7a**), $-CH_2CO_2H$,
$-(CH_2)_{10}CO_2H$,
$-(CH_2CH_2O)_3CO_2H$

**CTV**
R = H, $-CH_2CO_2H$,
$-(CH_2)_{10}CO_2H$,
$-(CH_2CH_2O)_3CO_2H$

**Bridged-CTV**
R = H, $-CH_2CO_2H$

**Calix[4]arene**
**R = H (11a), $-CH_2CO_2H$,**
**$-(CH_2)_{10}CO_2H$,**
**$-(CH_2CH_2O)_3CO_2H$**

**Bridged-Calix[4]arene**
**R = H, $-CH_2CO_2H$**

Fig 9. Structures of CTVs and related cavitands that may bind explosive molecules.

The chain of atoms defining the cavity can be functionalized to be particularly adept at binding explosives. At this point it is not known whether modifications appropriate for sequestering nitroarenes, e.g. TNT, would also be attractive to nitrate esters, nitramines, and peroxides. In the final application our approach may resemble MIPs in that each explosive requires specific modifications, and a variety of modifications are within synthetic reach. For example, it is possible to covalently join two CTVs to make a molecular capsule, called a cryptophane, which can selectively bind analytes in its cavity based on size.[25] This may be suitable to sequestering small molecules, e.g. methane. When assembled into an array, these supramolecules could be the key component in rapid explosive collection and detection.

### *C.2.d Summary*

The enhancement proposed herein would require no major change in the swabbing materials nor sensor hardware but would require a change in the operational protocol as the swab would no longer need to be rubbed over a surface. Each of the approaches to switchable swabs would require a different operational protocol. Approach 1 would require the swab be charged before each sample collection. Inserting the swab into the detection device would trigger the release of the analyte. In Approach 2, the swab would be permanently charged at the factory, and sample release would be accomplished by heating in a detection device desorber. The swab could be reused immediately. The enhanced swab would attract explosives particles from a distance of about 3 cm from the contaminated surface. This obviates the need for actual physical contact with a surface and, therefore, speeds the sampling process, provides for greater privacy, may increase the overall swab lifetime and may minimize the collection of certain types of interfering compounds. These advantages, coupled with higher pickup and release efficiencies, will make for speedier, more pleasant and more economical checkpoint operations while improving trace detector performance.

This work resulted in a DHS research award under BAA EXD 13-03 (Advanced Swabs for Near-Field Sampling) with subcontractors, FLIR and DSA.

### *D. Major Contributions*

A primary motivation for this research is safety. There must be no unanticipated hazards. Second, most detection instruments contain plastic parts and many ETDs require pre-concentrators or swabs. Not only will this project seek the best way to evaluate the wealth of modern materials available, but it is likely to point to some of the best choices in these areas. This impacts both trace and bulk detection.

TATP has been successfully encapsulated both for canine training aids and for calibration of trace detection equipment. This year HMTD has likewise been successfully tamed.

The concept of a non-contact swab has received additional funding. Initial results suggest it is in most cases more effective than contact swabbing. Furthermore it is less prone to contamination that may cause ETD alarms or malfunction, and it makes some hard to touch areas assessable.

### *E. Milestones*

Our present approach to TATP canine training aids is being adapted to another peroxide explosive, HMTD. Whether this approach can be adapted to the low-melting, erythritol tetranitrate (ETN), is the subject of on-going experiments.

Ongoing, also, is the development of a heater that rapidly attains and maintains desired temperatures. That specific task is the job of an industrial partner; however, we must determine the most optimal heat profile that accommodates both training aids.

We are also examining charged swabs for their pick-up and release capabilities. We have taken a two-prong approach, using electrostatics, a temporary charge, as well as electrets, for a more permanent approach. Both approaches need to be tested for long term viability.

Specific milestones for the coming years include acquiring a patent on the safe scent materials, characterizing the release profiles of TATP and HMTD from the microcapsules so that the commercial heater can be designed, and characterizing the decomposition signature of HMTD. Efforts will be made toward the complete commercialization of the safe scent aids. A method for rapid attribution of HMEs will be investigated. Novel materials/methods for enhanced swabs and vapor concentrators will be investigated. The potential for creating safe simulants of computed tomography (CT) will be probed.

### *F. Future Plans*

The areas outlined above continue to be the subject of active research.

Coating and encapsulation of materials will continue to be of interest. Not only will we investigate encapsulation of energetic materials, but also the encapsulation of potential additives to energetics. For example, we have shown that addition of parts-per-million (ppm) amounts of generally-recognized-as-safe (GRAS) metals to 3% or 12% hydrogen peroxide (HP) prevents its concentration by heating, instead promoting its decomposition. Furthermore, at ppm levels, the metals do not affect the stability of hydrogen peroxide at room temperature. Applying the same approach to 30% HP requires elevated levels of metals which would negatively influence shelf-life. This could be avoided by encapsulating the metals with a coating which can be degraded by heating. Thus, at room temperature, the 30% HP would be stable, but if heated, rather than concentrate the HP, the heat would remove the polymer coating from the metals and expose the HP to their degrading effect. This requires a polymer compatible with both metal and HP and can be removed or softened by heating; hence, the need for metrics.

Work on switchable polymers and swabs begun this year will continue under direct DHS funding. Under Center funding we will explore the possibility that use of electrets as swabs may be more effective than use of electrostatically charged swabs.

Each task requires its own metrics and development of these metrics is an integral part of these projects. We have investigated and reported on use of a vapor chamber exposure. Combining with the Gregory group in R2 we expect to create a vapor generator.

Presently, we are exploring calorimetry for evaluation of explosive interactions; Raman spectroscopy for rapid attribution of HME; novel materials/methods for enhanced swabs and vapor concentrators; and the potential for creating safe simulants of CT will be considered.

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