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

Abstract (project description for the web)

This project seeks to determine physical properties, synthesis, and destruction mechanisms of improvised explosives, often called homemade explosives (HMEs). To detect, destroy, handle safely, or prevent the synthesis of HMEs, complete understanding of the following aspects is required: (1) How an HME is formed and what accelerates or retards that formation; (2) How it decomposes and what accelerates or retards that decomposition; (3) How it crystallizes; (4) What is its vapor pressure and its headspace signature; (5) What is its density; (5) What is its sensitivity to accidental ignition as well as purposeful ignition; and (6) What is its performance under shock and fire conditions? The overall objectives are that detection, handling, and transport of these materials by the Homeland Security Enterprise (HSE) be as safe as possible while obstructing the manufacturing of HME by terrorists. Furthermore, the signatures of the HME must be characterized to allow reliable detection.

I. PROJECT DESCRIPTION

Project Overview

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

Characterization has included a detailed study of the thermal decomposition of erthyritol tetranitrate (ETN). Our work highlighted a hazardous operation that many in the HSE perform. Because ETN melts at 60°C and *appears* unchanged to over 100°C (Figure 1); sometimes melt-casing this material is included in HME training. We examined the thermal decomposition of ETN, both through experimental and computational methods. Our examination revealed that decomposition can occur at its melt; this means cavalier melt-casting may be highly hazardous. In addition to ETN kinetic parameters, decomposition products were examined to elucidate its decomposition pathway. It was found that ETN begins its decomposition sequence by a unimolecular homolytic cleavage of the internal and external O-NO_2 bonds, while the competing HONO elimination reaction is largely suppressed. The global activation energy for decomposition is found to be 104.3 kJ/mol with a pre-exponential factor of $3.72 \cdot 10^9$ s^{-1}. Despite the ability to exist in a molten state, ETN has a lower thermal stability than a similar tetranitrate pentaerythritol tetranitrate (PETN) which is not observed to melt. (see attached publication [1])

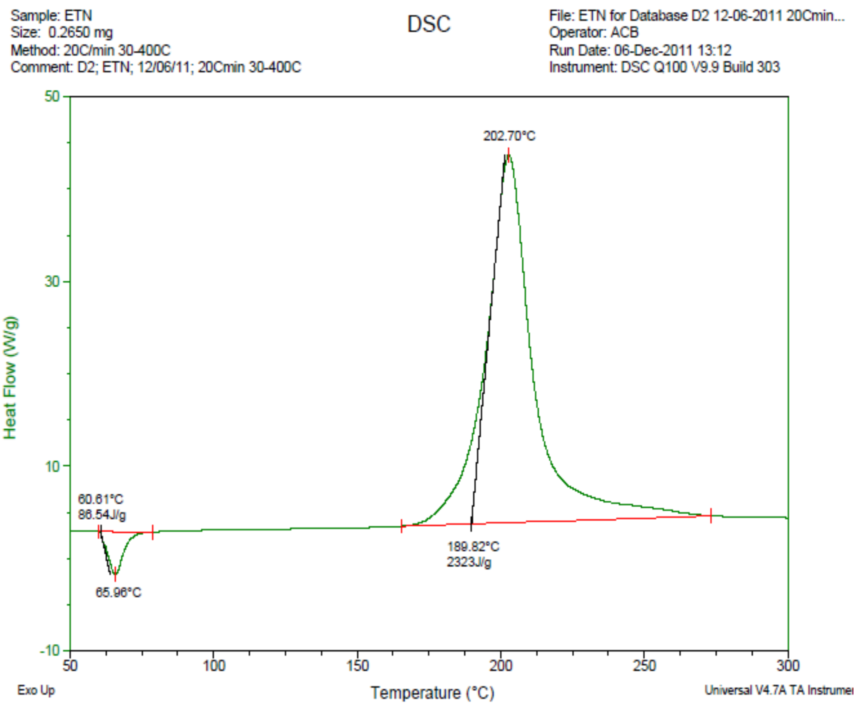


Figure 1: DSC (differential scanning calorimetry) of ETN

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

Development of analytical protocols was necessary to allow us to quantify TATP and HMTD at levels as low as 25 ppm. This work supported task R1-C1 allowing quantification of the signature released (from the safe-scent aids) and of the pickup attributable to the enhanced swabs of R1-C1. As part of this work it was discovered that the reason that often low concentrations of TATP and HMTD were not observed was the use of acetonitrile (ACN) as a solvent. Figure 2 shows the dramatic difference that eliminating ACN made in TATP analysis. This finding was sufficiently important that it was published (see attached paper [2]).

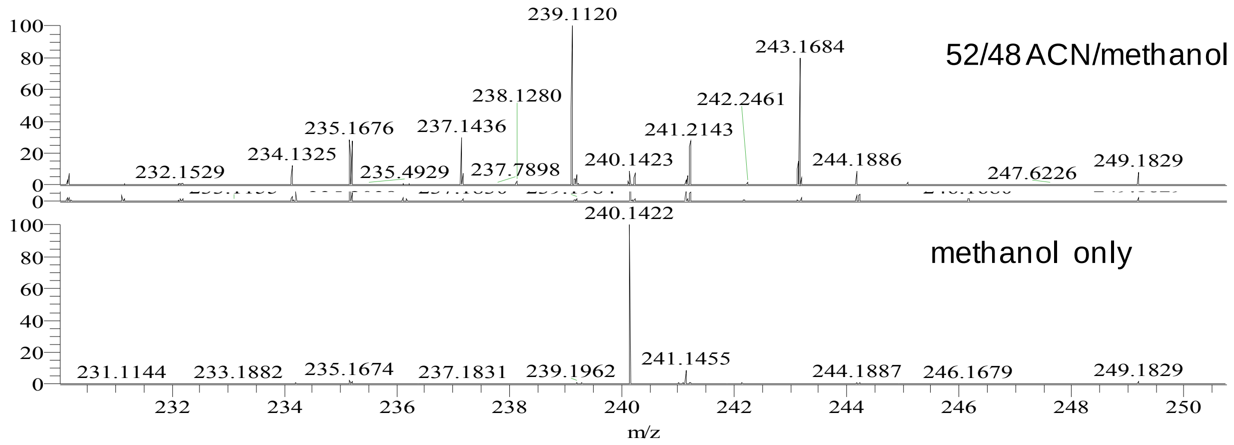


Figure 2: APCI Mass Spectrum of TATP-NH_4^+ (240.1455 m/z)

Because it has become known that we work with these HME and that we are developing safe-scent training aid, we were asked about the toxicity of the peroxide explosives to bomb-sniffing canines. Nitroarene explosives are toxic, and long-term exposure can be fatal to humans. Realizing that no information existed on the toxicity of these compounds that many in the HME community are exposed to, we have initiated a study to determine canine and human toxicity, first, of TATP and then other peroxide explosives. It is essential we obtain this information on TATP because it is high volatile; therefore, anyone working with this material is constantly breathing in its vapors. We must determine to what extent working with TATP is a health threat. Furthermore, we would like to determine if this problem could be used to our advantage. In previous studies we observed that the hair of those handling military explosives is contaminated in as little as 2 hours and the explosive contamination survives in hair overnight despite showering. With contaminated hair we have shown that TATP remains in hair for over two days and is more persistent in hair than the more water-soluble TNT or EGDN (ethyleneglycol dinitrate) (Figure 3).

ug/ g hair Initially	**TATP (48)**	**TNT (648)**	**PETN (5040)**	**EGDN (48)**
Oriental Black	**1300**	**77**	**100**	**21000**
Brown	**55**	**35**	**59**	**7200**
Blond	**80**	**47**	**75**	**6100**
Percent Retained after Standing in Air for 48 hrs				
Oriental Black	**15**	**100**	**nd**	**11**
Brown	**28**	**98**	**nd**	**31**
Blond	**11**	**97**	**nd**	**31**
Percent Retained after 3 washings with 2% SDS				
Oriental Black	**81**	**40**	**5**	**62**
Brown	**59**	**69**	**2**	**10**
Blond	**75**	**43**	**2**	**24**

Fig. 3: Explosive (ug/g) remaining in hair after standing 48 hours or multiple water rinses

We are now examining whether TATP remains in human body fluids long enough to serve as a new source of forensic evidence of illegal activity. Initial results were extremely erratic forcing a more detailed examination of aqueous TATP solutions. It was found that solutions with even low concentrations of TATP experience significant loss of TATP by evaporation (Figure 4). It became necessary to run control experiments where septum-capped vials were punctured with a syringe every time an aliquot was removed from the septum-capped reaction vial. To obtain loss due to metabolism only, as shown in Figure 5, control concentration was taken as baseline at every time point.

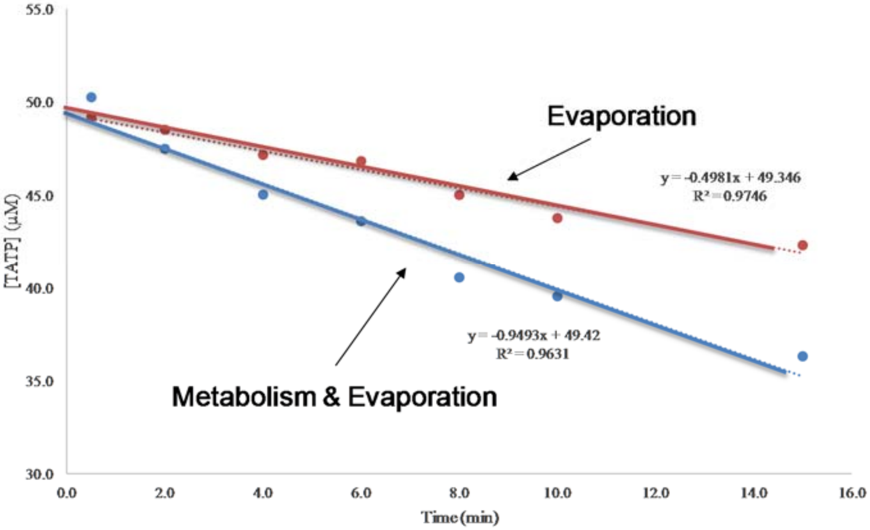


Figure 4: TATP (50uM) in aqueous solution

Figure 5 shows the rapid loss of 10 uM TATP under incubation conditions. Since data was adjusted to account for evaporation, the loss of TATP shown is a result of metabolism. In contrast, the solution containing higher concentrations of TATP (50 uM) with NADPH showed no TATP loss other than that which could be accounted for by evaporation. This is the first suggestion that a) TATP may stay in the body; and b) it may be toxic since it appears possible it builds up at higher concentrations

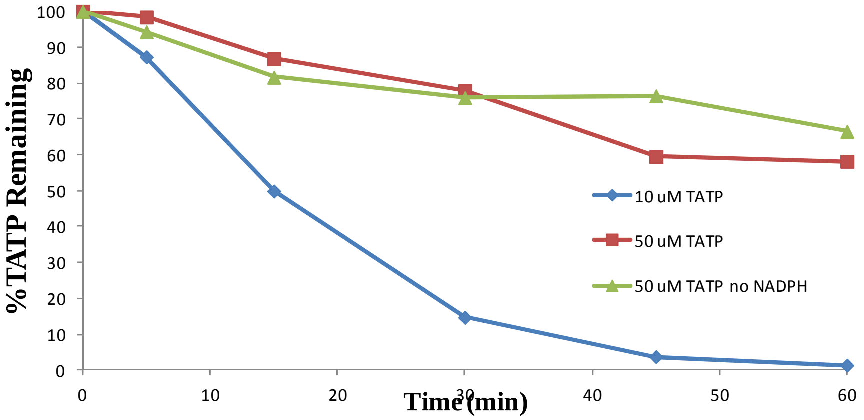


Figure 5: TATP solutions with NADPH (10 uM (blue) 50 uM (red) & 50 uM TATP with no NADPH (green)

Only one metabolite has been observed when aqueous TATP solutions are incubated at 37°C with dog liver microsomes—the hydroxyl-TATP (Figure 6). Interestingly, we have been unable to observe such intermediate species in previous decomposition studies where we attempted to identify early transformation products of TATP.

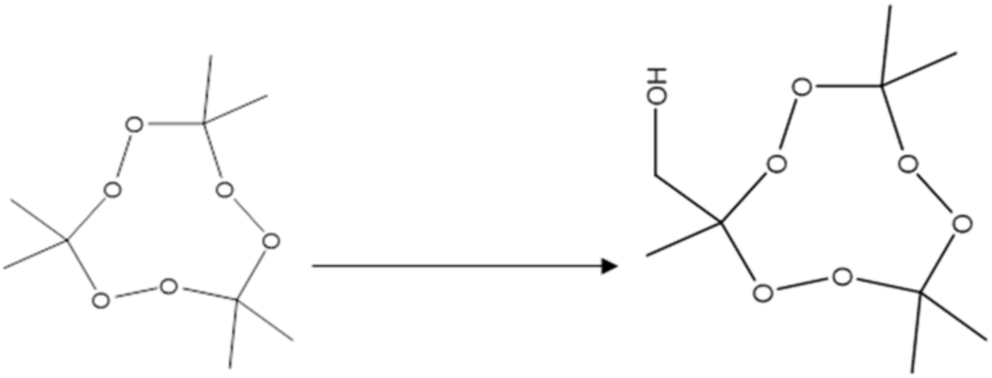


Figure 6: NADPH-dependent biotransformation of TATP in dog liver microsomes at 37°C

Year Two (July 2014 through June 2015) Biennial Review Results and Related Actions to Address

There was a request to track the use, in addition to the number of users, of the University of Rhode Island (URI) Explosives Database, an interactive library of analytical data for explosive and energetic compounds. The appropriate code has been added, and monthly usage was reported at the Year 4 Program Review in January, 2017.

There was a question as to how we made our choice of HMEs to study. We continue to study those listed as of interest by members of the DHS S&T group This includes studies of FOX mixtures, as well as peroxide explosives. This information is shared with other Center projects and especially with other members of Thrust R1.

State of the Art and Technical Approach

A major strength of our project is that in many cases we have introduced the best ways to approach these hazardous materials. The instrumentation used (infrared (IR), Raman, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry) is commercially available. Thus, we introduced the laboratories serving the HSE to certain safe approaches. In fact this year for the third time we offered as a one-day hands-on course "Explosive Analysis." One participant, who works in for the Bureau of Alcohol Tobacco, Firearms and Explosives (BATFE) laboratory, wrote a thank-you note: *"I wanted to thank you for hosting that wonderfully informative short course! Every aspect was exactly what I needed to tie up the loose ends of my new field of study….This note book now serves as a great tool to catch up the other people who hired on with me… Your graduate staff did a great job…."*

Major Contributions

- Extensive TATP characterization—safe scent aids, gentle destruction (Y -1-4)
- The limitations of certain oxidizers in terms of terrorist use (Y 1-2)
- Baseline information about HMTD chemical properties and reactivity. (Y 1-4)
- Identifying the hazards of humidity to HMTD (Y 2-3)
- Formation mechanism of HMTD initiated. (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)

V. REFERENCES

[1] Oxley, J.C.; Furman, D.; Brown, A.C.; Dubnikova, F.; Smith, J.L.; Kosloff, R.; Zeiri, Y "Thermal Decomposition of Erythritol Tetranitrate: A Joint Experimental & Computational Study" submit

[2] Colizza, Kevin; Mahoney, Keira E.; Yevdokimov, Alexander V.; Smith, James L.; Oxley, Jimmie C. "Acetonitrile Ion Supression in Atmospheric Pressure Ionization Mass Spectrometry," *Rapid Communications in Mass Spectrometry* **2016**, 27(1), 1796-1804.

[3] Oxley, J.C.; Smith, J.L.; Porter, M.; Colizza, K.; McLennan, L.; Zeiri, Y.; Kosloff, R.; Dubnikova, F. "Synthesis and Degradation of Hexamethylene triperoxide diamine (HMTD)" Propellant, Explosives, Pyrotechnics **2016**, 41(2), 334-350. DOI 10.1002/prep.201500151
See references within the publications above

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

Abstract (for the web)

Determining if a material or formulation is detonable and determining if an adulterant has made a detonable material inert 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 threat materials is large, we seek to determine the characteristics required for detonability. 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." To answer the questions: “What is potentially detonable?” and “Does adulteration achieve non-detonability?” currently requires large-scale testing or the creation of reliably predictive, small-scale tests. The goal of this project is development of the latter—reliably predictive small-scale tests which reflect large-scale performance quickly, safely, and inexpensively. We have taken a number of approaches to this problem: one of which can be performed entirely in the laboratory with sophisticated analytical instrumentation and two which require an explosive range. In all cases, the outcomes will require benchmarking against larger-scale detonation testing.

PROJECT DESCRIPTION

Project Overview

The goal of this project is to narrow the range of potential explosives threats that need concern the Department of Homeland Security (DHS) and Homeland Security Enterprise (HSE). For example, not every oxidizer/fuel mixture is a potential explosive. This project is aimed at determining which are and assessing at what point threat mixtures have been successfully “inerted.” Because the number of potential threats is large and highly diverse, it is essential that a quick, safe method of determining detonability be established—a method not requiring formulations of tons of material to determine if it is an explosive hazard. We have taken multiple approaches to this problem: 1) Using homemade explosives (HMEs) that are fuel/oxidizer (FOX) mixtures, we have characterized their responses to small-scale tests and are in the process of seeking a correlation to modest-scale detonation testing; 2) We are applying fundamental tandem mass spectrometric (MS) techniques to discover possible relationships between collision-induced fragmentation energies and specific properties of explosives; 3) To aid in the examination of the growth to detonation vs. shock attenuation at small scale, we are developing a new way to characterize the shock/detonation front using unique probes; and 4) Due to the difficulty of the task, we have solicited other groups to join the effort.

This year approach 1 and approach 3 came together. As seen in many cases, including the Boston Marathon bombing, improvised explosives may be as simple as a fuel/oxidizer (FOX) mixture initiated by a hot wire. The knowledge of large scale explosive potential of fuel/oxidizer (FOX) mixtures is incomplete. Predicting this explosive potential from small scale test data is highly desirable. Herein the explosive properties of fuel/oxidizer mixtures (FOX) were measured at both the small scale (2 g) with bomb calorimetry and large scale (5 kg) with high-speed photography and pressure probes. Properties measured at the small scale such as the energy and pressure of reaction were compared to detonation velocity and air blast TNT equivalence measured at the large scale and predictions by Cheetah thermochemical code.

Approach 1: The functionality of an explosive 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: the molecule must be able to react producing heat and gas and be able to do this rapidly enough to support the detonation front. Examination of the atoms making up the molecule allows prediction of whether heat and gas can be produced. This aspect is investigated in the R1-A.1 project. Under that task, the thermal behaviors of 11 solid oxidizers in combinations of 13 fuels were determined using differential scanning calorimetry (DSC), a technique requiring less than a milligram of material [1]. Many are considered FOX (fuel/oxidizer explosives). 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 observations were the first steps in finding behaviors observed on the milligram-scale that may correlate with detonability measured on the kilogram-scale.

In year 3 we followed up the previous milligram-scale study of FOX with gram-scale experiments performed in an adiabatic calorimeter. A modification to the standard instrument allowed 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 readings reflect the production of heat and gas, but pressure-rise versus time in a burn is a function of particle size, pressure, and atmosphere, not parameters of strong importance to energy release in a detonation. Figure 1 indicates that some high explosives standout in terms of rapid production of gas and, thus, heat. The critical question of whether the reaction can happen fast enough to support detonation had to be determined by field testing. (The colors of the pressure traces in Figure 1 indicate the results found in larger-scale detonation testing, red for detonation and blue for non-detonation.)

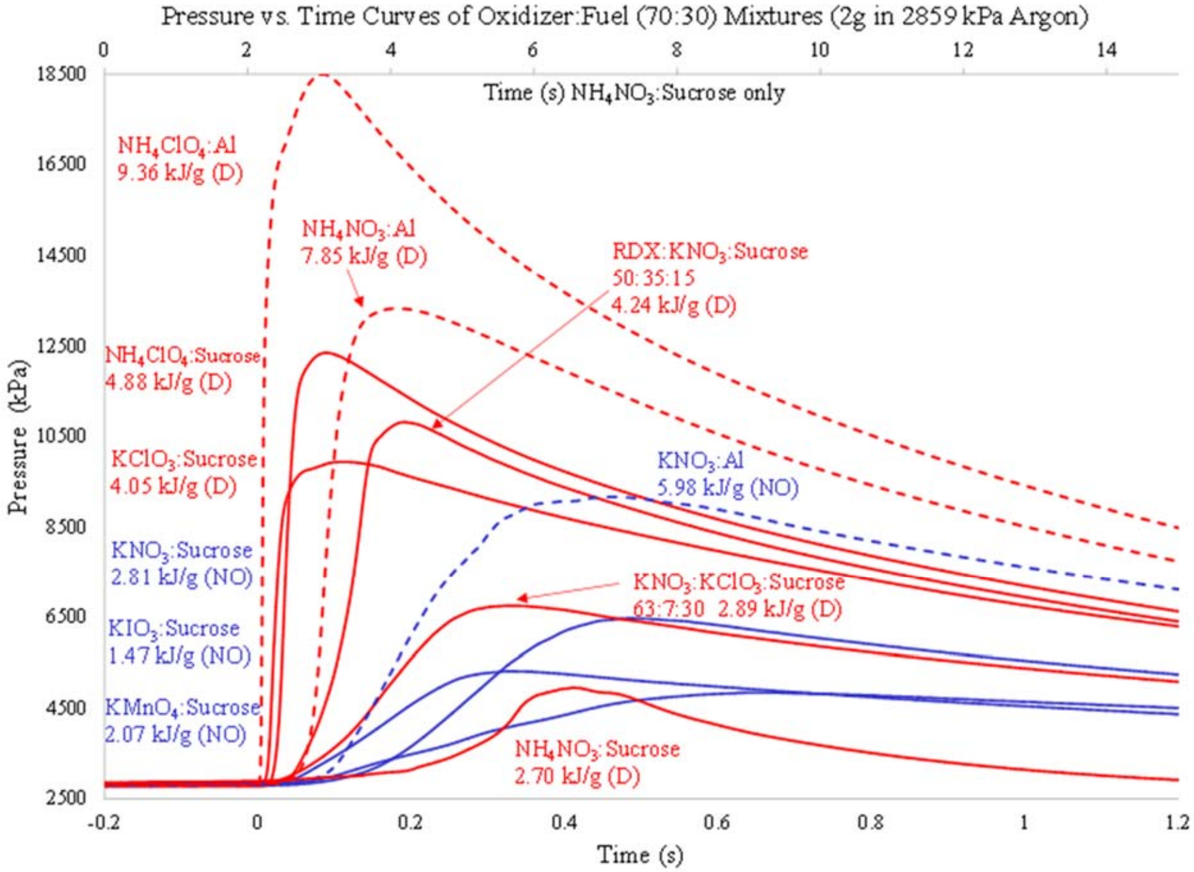
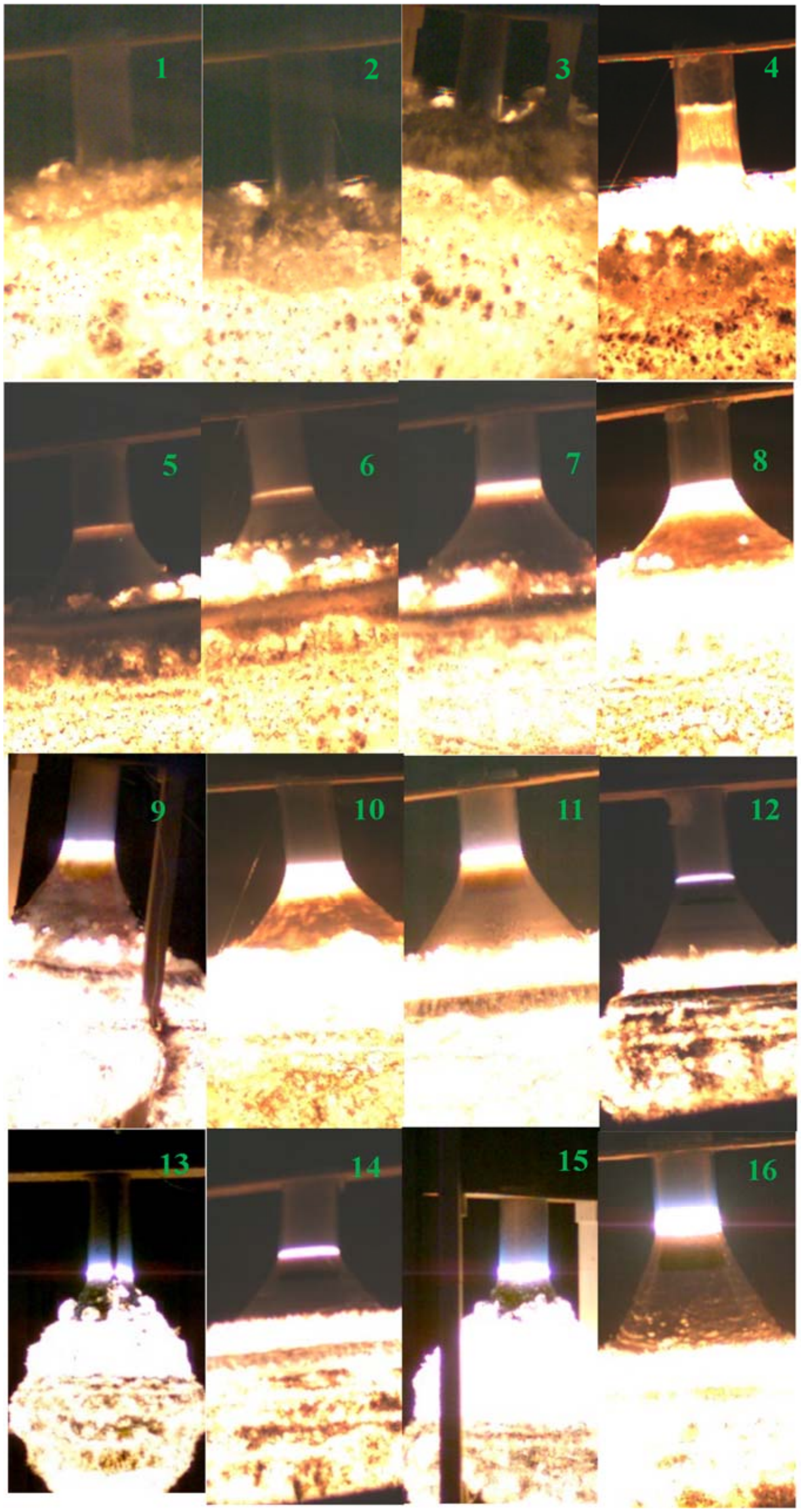


Fig. 1: Pressure production over time (seconds) for 2g FOX mixtures under argon (400 psig)

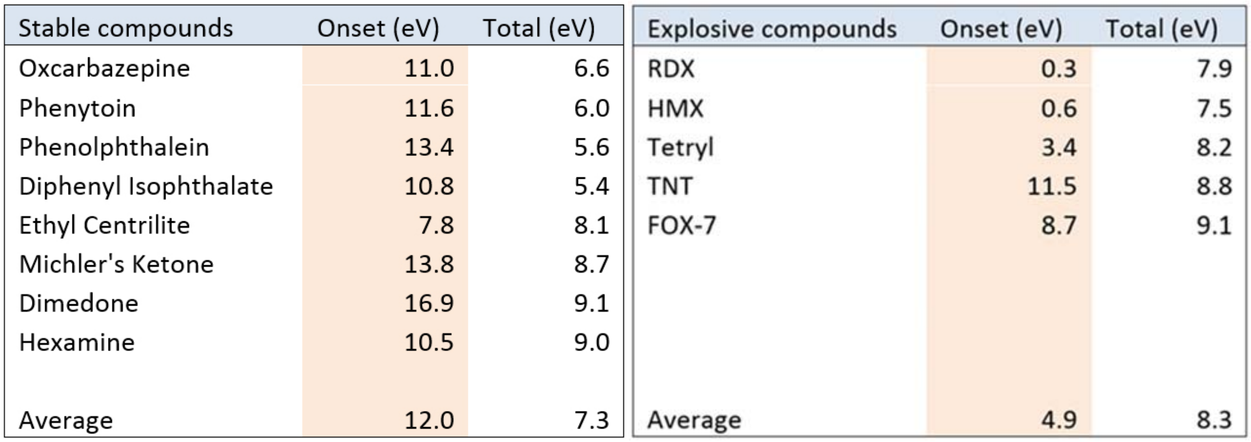
Approach 3: This project aims to characterize non-ideal explosives above and below their critical diameter using high-speed photography which directly observes the non-ideal detonation front and an end-on characterization of the non-ideal detonation front structure using photon Doppler velocimetry (PDV). Many challenges arose in designing the appropriate configuration, chemically isolating the explosive material, tuning the reflector interface, choosing the window material and geometry, and optically characterizing the fiber optic probe/reflection landscape. For 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. The results of high-speed photography are shown in Figure 2. It was decided that pending full implementation of PDV, high-speed photography would be used to obtain data on the FOX mixtures. This in itself presented a number of challenges .



1. KIO_3:Sucrose
   70:30 (NO)
2. $KMnO_4$:Sucrose
   70:30 (NO)
3. KNO_3:Sucrose
   70:30 (NO)
4. KNO_3:Al
   70:30 (NO)
5. $KClO_3$:KNO_3:Sucrose
   7:63:30 (D)
6. RDX:KNO_3:Sucrose
   5:66.5:28.5 (D)
7. $KClO_3$:KNO_3:Sucrose
   35:35:30 (D)
8. NH_4ClO_4:Al
   70:30 (D)
9. $KClO_3$:Sucrose
   70:30 (D)
10. NH_4NO_3:Al
    70:30 (D)
11. $KClO_3$:Sucrose
    70:30 (D)
12. NH_4NO_3:Sucrose
    70:30 (D)
13. TNT (D)
14. NH_4ClO_4:Sucrose
    70:30 (D)
15. TNT (D)
16. RDX:KNO_3:Sucrose
    50:35:15 (D)

Figure 2: High-speed camera images of reaction of 16 FOX mixtures

Approach 2 (Energy Resolved Mass Spectrometry): 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. 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.



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

Table 1: Comparison of onset (fragility) & total energies (stability) of stable compounds & explosives.

Year Two (July 2014 through June 2015) Biennial Review Results and Related Actions to Address

From a FCC reviewer at the Biennial 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 information pertaining to "this is how to get it to work" or "this is why it didn't work." 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

Approach 1 & 3: Predicting this explosive potential from small scale test data is desirable. Herein the explosive properties of fuel/oxidizer mixtures (FOX) were measured at both the small scale (2 g) with bomb calorimetry and large scale (5 kg) with high speed photography and pressure probe. Properties measured at the small scale such as the energy and pressure of reaction were compared to detonation velocity and air blast.

Experimental Details:
The fuels chosen were sucrose from Fisher Scientific, 23 µm flake coated aluminum powder from Obron, and a 5 µm magnesium powder from Firefox. Oxidizers were ground and sieved 100-200 mesh (150-75 µm). Sucrose was ground with a small coffee grinder and sieved 100-200 mesh or 150-75 µm. Fuel/oxidizer (FOX) mixtures were prepared as dry loose powders placed in plastic pop-top containers, for differential scanning calorimetry (DSC) samples in 500 mg batches and for bomb calorimetry as individual 2 g samples. Mixing was then conducted with a Resodyn Lab Ram acoustic mixer at 35 - 40 G acceleration for 2 min. Individual DSC samples ~0.25 mg were taken from the 500 mg batch. Samples for SDT were prepared similarly, using only 4 to 6 mg.

Differential Scanning Calorimetry (DSC) Samples were flame sealed (~0.25 mg) in glass capillaries (borosilicate, 0.06 in. ID, 0.11 in OD) on a metal post cooled by liquid nitrogen to prevent decomposition during sample preparation. Scans were conducted at a ramp rate of 20 °C/min on a TA Q100 DSC. The temperature range was usually 30 °C to 450 °C, and the nitrogen flow rate was set to 50 mL/min. The temperature was calibrated by running indium with a melting point of 156.6 °C. This technique was chosen for oxidizer / sucrose mixtures because exotherms of these mixtures typically fall within the temperature limits of the instrument.

Simultaneous DSC/TGA (SDT): A TA Q600 simultaneous DSC/TGA was used to run samples of 4-6 mg in open aluminum oxide pans, and scanned at 20 °C/min under 100 mL/min nitrogen flow. The temperature was calibrated by running Zinc with melting point of 419.5 °C. The temperature range was usually 50 °C to 1000 °C. Oxidizer / aluminum mixtures were analyzed with this technique due to exotherms appearing at higher temperatures than the DSC limits.

Bomb Calorimetry with Pressure Transducer Heat output and pressure/time curves were determined using a Parr 6200 calorimeter and Parr 1108 bomb, fitted with a pressure transducer (Parr 6976 pressure recording system, including a 5108A Kistler piezoelectric coupler, and a 211B2 Kistler piezoelectric pressure transducer with a calibrated sensitivity of 1.096 mV/psi). The Parr bomb was calibrated (i.e. 10 trials) with benzoic acid ignited with fuse wire (9.6232 J/cm) and cotton string (167.36 J) in 2515 kPa oxygen (ΔH_{comb} = 26434 J/g). In an oxygen atmosphere, the string was in contact with the fuse wire and sample and was ignited by the fuse wire to aid ignition of the sample. The FOX samples (three to six 2 g samples under each set of conditions) were ignited with a fuse wire under argon (2859 kPa, 400 psig). This pressure represented the maximum initial pressure which the regulator could handle. It appeared to be a good balance allowing rapid initiation of burn, and minimizing heat losses with the walls of the Parr bomb [2]. With some energetic materials, it has been observed that there is a critical pressure of ignition associated with a specified input energy [3,4]. Igniting samples at a higher initial pressure is more likely to overcome the critical pressure of the sample. A National Instruments USB-6210 data acquisition card (maximum sample rate of 250 kS/s) and LabView software were used to collect the pressure/time data at a rate of 10 kS/s. This sample collection rate of 100 µs between pressure points was high enough resolution to result in pressure/time plots that appeared continuous on the millisecond time-scale.

Sample Preparation for Detonation: Sucrose and oxidizers were prepared separately by grinding with a Vita-Mix 5000 blender and sieving to 100-200 mesh (150-75 µm). Aluminum flake (23 µm) from Obron was used as received. Fuel/oxidizer samples of ~ kg were manually mixed in a 38 L (10 gal) plastic bag for about 2 minutes (Figure 3). For the detonation studies schedule 40 clear, polyvinyl chloride (PVC) tubes of 4 inch diameter (10.16 cm) were purchased from McMaster Carr in 8 foot lengths and cut to 24 inches (60.96 cm) long. PVC booster cups were assembled by gluing a 4 inch PVC sewer and drain endcap to a 4 inch PVC coupler. Into the booster cup were placed two sheets (30 g) of #2 PETN sheet explosive which had been cut into circle shape to fit tightly into the booster cup. On top of the sheet explosive, C4 (546 g) was packed along with three more circles of PETN sheet explosive. Booster cups (Figure 4) were taped with duct tape directly to the clear PVC tube so that there was direct contact with the sample mixture. The FOX mixture was added by pouring from the plastic mixing bag, using a kraft paper funnel (Figure 3). The test device was placed in a vertical position (booster end down) on a wooden test stand; the bottom of the test device was 91.4 cm (36 in) from the ground. The detonator was inserted last before initiation from a blasting machine.

Figure 3. Photo Showing Preparation of Booster and Assembled Test Device

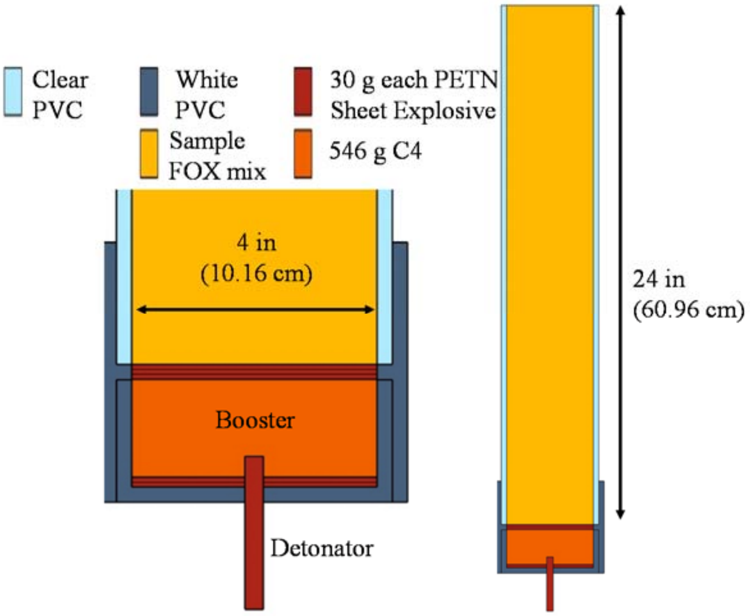
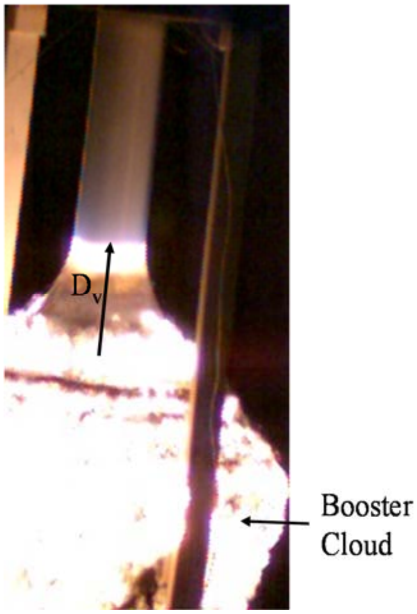


Figure 4: Schematic of Booster Setup

Detonation Diagnostics Detonation velocity was determined visually using a Phantom V7.11 camera with a frame rate of 66,019 fps, interframe time of 15.15 µs, resolution of 160 X 304 pixels, exposure of 0.4 µs (0.29 µs exposure for aluminum mixtures), 1 s of pre-trigger, and 1 s of post-trigger. A twisted pair of duplex wire, taped to the detonator, was used as a falling-edge camera trigger (i.e. "make" trigger). Phantom PCC 2.8 software was used to process the camera data, tracking the detonation front and setting the distance scaling calibration for each file to obtain a detonation velocity. The detonation front was assumed to be the forward most position of the emitted band of light, following the contribution of the booster (Figure 5). Initiation of the booster produces a significant fire ball, present even in samples that did not detonate, and is termed the "booster cloud".



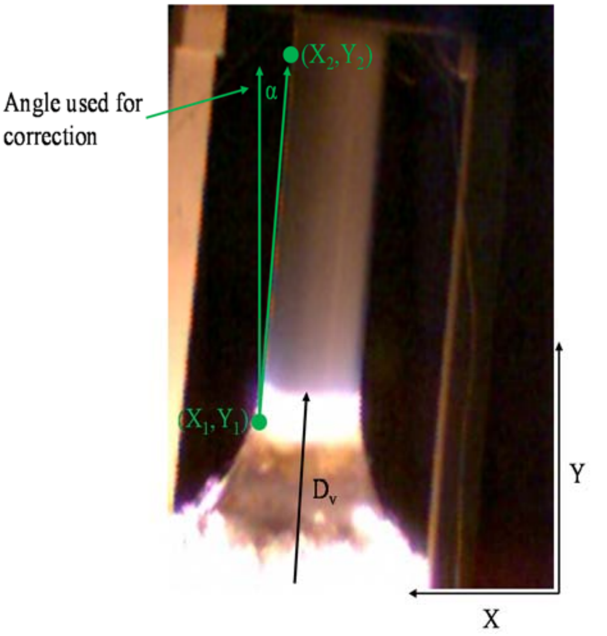


Figure 5. Illustration (70:30 $KClO_3$:sucrose) of how detonation front was used to calculate detonation velocity, D_v

After using the Phantom PCC 2.8 software to track the scaled detonation front (x,y) in time, a correction was made for the angle of incidence (to align the shot to a vertical position). The following equations for rotating the image were used where (X',Y') are the new coordinates:

$$X' = X\cos(\alpha) - Y\sin(\alpha) \qquad (1)$$

$$Y' = X\sin(\alpha) + Y\cos(\alpha) \qquad (2)$$

Where α is the incident angle from vertical, measured by taking the inverse tangent of two points on the side of the pipe (X_1, Y_1) and (X_2, Y_2):

$$\alpha = -\tan^{-1}\left(\frac{X_2 - X_1}{Y_2 - Y_1}\right) \qquad (3)$$

If two points are taken from the calibrated coordinate system (i.e. for 70:30 $KClO_3$:Sucrose) in mm (X_1, Y_1) = (89,30) and (X_2, Y_2) = (68,210), then α = 0.116 rad, and Y'(t) can be plotted for each time point (using equation 2) to find the detonation velocity (the slope in Figure 6). The detonation velocity was taken as the slope of the newly rotated points Y'(t) distance vs. time curve. The distance vs. time curves were linear ($R^2 > 0.99$) for all the samples that detonated.

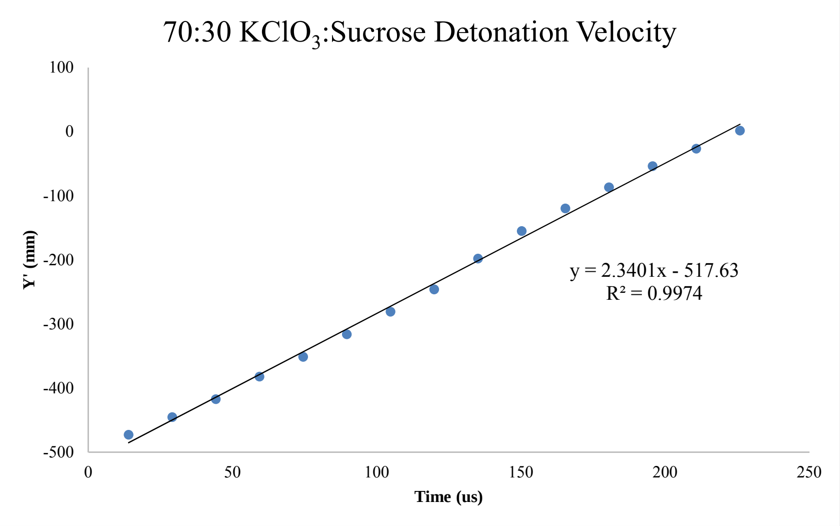


Figure 6. Detonation front tracking of rotation corrected Y' points. The slope is detonation velocity in mm/µs.

A pencil gauge pressure transducer (Kistler 6233A, 25 psi limit, calibrated sensitivity of 200 mV/psi, 5 V limit) with coupler (Kistler 5134B, 0.05 Hz high pass filter, gain of 1) measured blast overpressure. Fifty foot coax cables connected the pencil gauge to the coupler, and coupler to a Tektronix oscilloscope. The pencil gauge was mounted 1.29 m high, positioned 6.096 m (20 ft) from the test device on a wooden stand weighted with sand bags. The Tektronix oscilloscope (model MSO4014B, max bandwidth of 100 MHz) was set with a typical sampling rate between 5-100 MSa/s; it was automatically triggered on the rising edge of the pressure signal. Figure 7 shows the overall test arena.

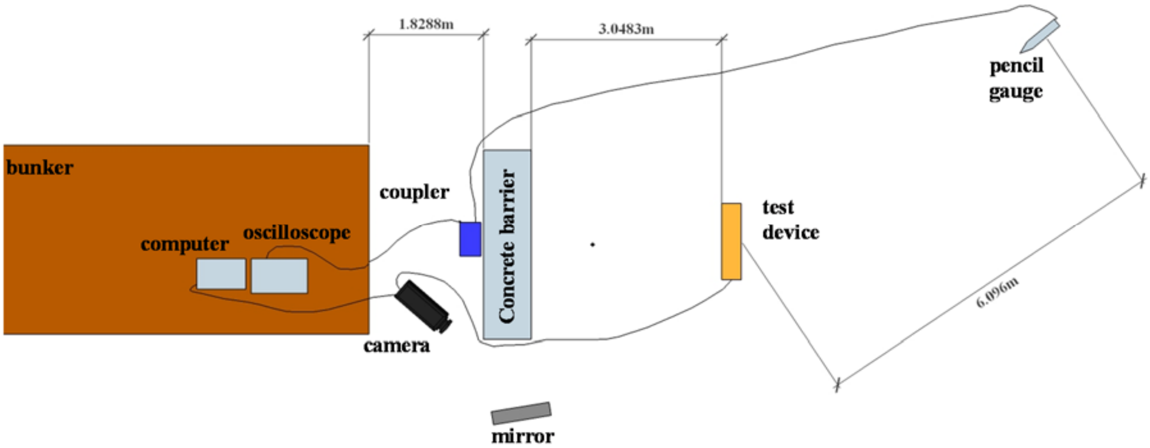


Figure 7. Overall Test Arena Setup

Predictive Tools: Cheetah 7.0 from Lawrence Livermore National Laboratory (product library: sandia, jczs revision 1923) was used to predict detonation velocity, detonation pressure, and total energy of reaction. Each mixture was run with Cheetah using the density that was measured for its large scale test [5]. The blast effects calculator (BEC V5.1) was used to obtain air blast TNT equivalence from the measured peak air blast pressures [6,7,8]. For each experiment, a “goal seek” method was used with the empirical fits for pressure (as a function of scaled distance, $m/kg^{1/3}$) to find the total amount of TNT needed to achieve the same peak pressure. However, the booster also contributed to the air blast pressure. This contribution had to be subtracted in terms of energy or TNT equivalent weight, not in terms of pressure. An experiment with the booster and sand as the sample (no energy contributed from the sand) allowed the TNT equivalent weight of only the booster to be calculated with “goal seek” in the blast effects calculator. The booster TNT equivalent weight from this experiment was subtracted from the total TNT equivalent weight of each test to find the TNT equivalence of the sample (TNT Equivalence = TNT equivalent mass of sample / sample weight).

Results:

Parr Bomb Calorimetry The Parr calorimeter was fitted with a pressure transducer to observe the pressure response as a function of time due to reaction. Closed volume pressure measurement is a common tool for propellant applications. Thus, it was possible to compare the response of a number of common gun propellants (Red Dot, Pyrodex, black powder) to FOX mixtures of interest. In general the propellants exhibit a larger and faster change in pressure, but the FOX mixtures release more heat. Pressure responses of ammonium nitrate and potassium nitrate with sucrose were significantly delayed compared to other FOX (Figure 1). It is interesting to note that KNO_3:sucrose burned slower and with slightly less energy than a similar mixture with added $KClO_3$ (63:7:30 KNO_3:$KClO_3$:sucrose); KNO_3:sucrose did not detonate on the large scale, but mixtures with added $KClO_3$ did.

The change in internal energy of a formulation, as judged by the heat of decomposition measured at the sub-milligram-scale by DSC (far right column, Table 1) and heat of reaction observed in the 2 g Parr bomb samples (penultimate right column, Table 1), differ. Heat of reaction (i.e. Parr bomb data) is greater than heat of decomposition, particularly when the fuel is aluminum. However, the aluminum /oxidizer formulations were tested in open pans by SDT where there were ample opportunities for sample evaporation/sublimation, thus heat loss. A comparison of the same oxidizers with different fuels showed the energy input from the choice of fuel is aluminum > sucrose > sodium benzoate (Table 1). Other fuel/oxidizer mixtures were also examined in the Parr bomb (Table 2). In terms of energy output neither the thermites nor the gun propellants released more energy than the FOX mixtures examined.

Table 1. Bomb Calorimetry Outputs from Fuel:Oxidizer Mixtures Burned 2g 2859 kPa argon

Mixture wt,wt	Δ Time (ms)	RSD	Δ Pressure (kPa)	RSD	Δ P/Time (kPa/ms)	RSD	Δ U (kJ/g)	RSD	DSC/SDT 80:20 Ox:Fuel (kJ/g)
Oxidizer, Sucrose									DSC
K2Cr2O7, Sucrose 70,30	2084	29%	776	2%	0.4	29%	1.14	2%	0.10
AN, Sucrose 70,30	7687	10%	1531	9%	0.2	20%	2.70	1%	1.79
KMnO4, Sucrose 70,30	641	5%	1985	2%	3.1	3%	2.07	0%	1.80
KIO3, Sucrose 70,30	334	13%	2514	3%	7.6	15%	1.47	1%	0.84
KNO2, Sucrose 70,30	509	19%	2702	3%	5.4	20%	2.61	3%	1.69
KNO3, Sucrose 70,30	509	3%	3685	1%	7.2	3%	2.81	1%	0.68
KClO3, KNO3, Sucrose 7,63,30	332	2%	3928	2%	11.8	3%	2.89	2%	
KIO4, Sucrose 70,30	183	10%	3931	3%	21.6	9%	2.11	0%	1.81
RDX, KNO3, Sucrose 5,66.5,28.5	479	4%	4186	1%	8.8	5%	2.93	2%	
KClO3, KNO3, Sucrose 17,53,30	248	13%	4369	3%	17.9	17%	3.04	1%	
RDX, KNO3, Sucrose 10,63,27	401	7%	4509	3%	11.3	6%	3.11	1%	
KClO3, KNO3, Sucrose 35,35,30	148	12%	5580	3%	38.1	10%	3.41	1%	
KBrO3, Sucrose 70,30	78	8%	5873	6%	76.0	13%	2.77	2%	1.72
KClO4, Sucrose 70,30	187	15%	7060	10%	38.5	21%	4.65	0%	0.87
KClO3, Sucrose 70,30	104	21%	7150	7%	72.6	29%	4.05	0%	2.09
RDX, KNO3, Sucrose 50,35,15	212	18%	7852	4%	37.8	15%	4.24	1%	
AP,Sucrose 70,30	97	7%	9289	4%	96.1	10%	4.88	0%	1.36
Oxidizer, Al									SDT
K2Cr2O7, Al 70,30	474	7%	3261	6%	6.9	13%	4.18	1%	0.00
KNO2, Al 70,30	696	21%	4370	14%	6.5	31%	5.20	8%	2.40
KMnO4, Al 70,30	254	8%	5089	9%	20.1	10%	5.31	2%	0.73
KIO3, Al 70,30	241	38%	5682	8%	26.6	46%	4.94	0%	0.49
KNO3, Al 70,30	403	13%	6307	1%	15.8	12%	5.98	3%	1.30
KIO4, Al 70,30	153	30%	8301	5%	58.6	38%	6.32	1%	0.17
KClO4, Al 80,20	75	19%	9578	5%	132.6	26%	5.11	1%	0.80
KBrO3, Al 70,30	105	21%	10215	5%	100.1	23%	6.53	1%	0.45
AN, Al 70,30	195	19%	10367	4%	54.1	14%	7.85	0%	0.64
KClO4, Al 50,50	135	17%	11045	1%	84.0	19%	8.22	1%	
KClO3, Al 70,30	96	11%	11929	5%	126.3	15%	7.18	5%	1.50
KClO4, Al 70,30	78	18%	12272	3%	161.6	20%	7.52	1%	
KClO4, Al 60,40	97	19%	12727	5%	136.4	22%	9.36	2%	
AP, Al 70,30	81	15%	15813	4%	199.7	20%	9.36	1%	1.60
Oxidizer, Na Benzoate									
KNO3, NaBenzoate 70,30	471	7%	3045	2%	6.5	8%	2.25	2%	
KClO3, NaBenzoate 70,30	64	6%	6815	2%	105.8	4%	3.19	1%	
KClO4, NaBenzoate 70,30	65	25%	7636	2%	123.8	30%	3.70	0%	
AP, NaBenzoate 70,30	490	12%	7814	1%	16.1	14%	4.13	2%	

Table 2. Parr Bomb Calorimetry Output for Thermites vs. Gun Propellants

Mixture wt,wt	Δ Time (ms)	RSD	Δ Pressure (kPa)	RSD	Δ P/Time (kPa/ms)	RSD	Δ U (kJ/g)	RSD
Thermites								
Fe3O4, Mg 80,20	1501	9%	424	10%	0.3	19%	2.12	0%
Fe3O4, Mg 70,30	1322	3%	970	7%	0.7	9%	3.22	1%
Fe3O4, Mg 60,40	1043	17%	1539	3%	1.5	16%	3.73	0%
Bi2O3, Al 70,30	288	13%	1810	8%	6.3	4%	1.75	1%
Bi2O3, Al 90,10	210	50%	2277	12%	12.8	46%	1.61	1%
Bi2O3, Al 80,20	113	6%	2704	8%	23.9	13%	1.90	2%
Gun Propellants								
BP Meal	183	6%	4812	9%	26.4	13%	2.83	1%
BP 07 Mesh	139	9%	5000	3%	36.1	6%	2.78	1%
BP 20 Mesh	127	16%	5033	3%	40.4	13%	2.79	2%
Pyrodex	116	8%	5143	1%	44.6	9%	2.87	1%
Red Dot	86	13%	9761	3%	115.1	15%	4.40	0%

Detonation Testing: Table 3 shows FOX mixtures for which initiation to detonation was attempted. Four of the mixtures failed to propagate detonation although the velocity of the burn front is recorded under the column velocity (km/s). Figure 2 provides screen captures of the reactions observed. The detonation front was taken to be the bright line running ahead of the booster debris cloud (bottom). A detonation rather than a burn was judged by the rapid PVC wall expansion immediately behind the front. Figure 8 shows KNO_3:sucrose as an example of a mixture which failed to support detonation. Figure 8 also shows KNO_3:aluminum as an example of a mixture where the detonation failed and transited to a rapid burn. In this case the mixture is more flammable than detonable. Figure 9 shows an enlarged picture of three FOX mixtures known to be improvised explosive mixtures which detonated (NH_4NO_3:sucrose, NH_4NO_3:Al, and $KClO_3$:Sucrose) and one more example of one which did not detonate ($KMnO_4$:sucrose).

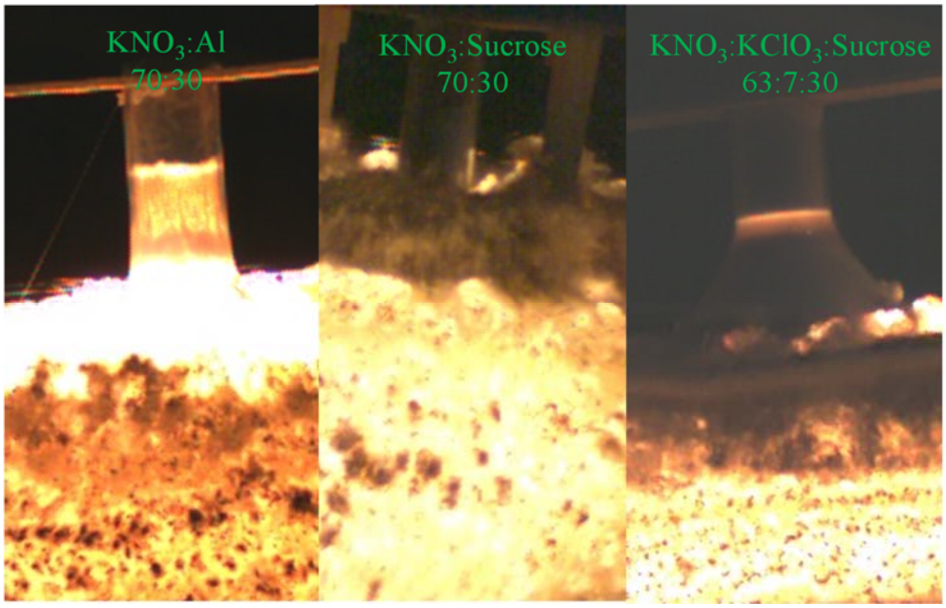


Figure 8. KNO_3:Al transited to burn; KNO_3:sucrose failed to propagate; KNO_3:$KClO_3$:sucrose 63:7:30 detonated.

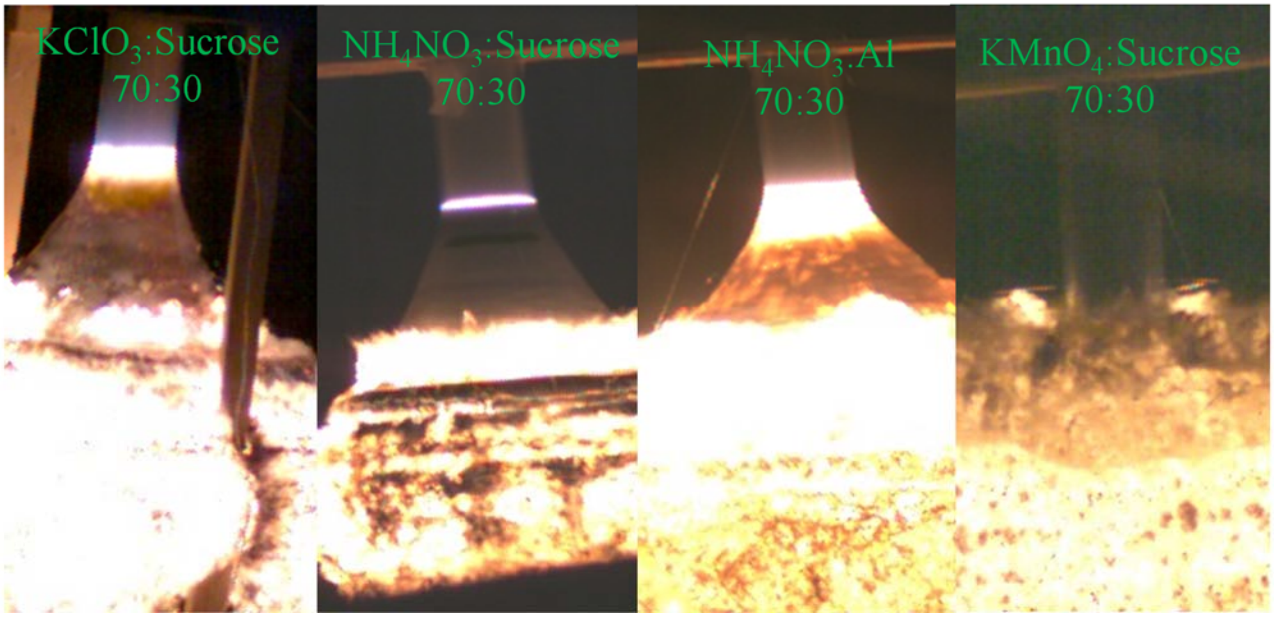


Figure 9. Detonation tests showing three steady detonations (left three) and one which failed to propagate (right).

Table 3: Detonation Testing Summary

Clear PVC pipe Shots (4" Dia x 24" L)			Calorimetry (2g 400 psi Ar)						Detonation		
Mixture	Mass (kg)	Density (g/mL)	Heat (cal/g)	Heat (kJ/g)	ΔP (psi)	ΔP/Δt (psi/ms)	ΔP (kPa)	ΔP/Δt (kPa/ ms)	Phantom V7.11 Det Velocity (km/s)	Peak Airblast ΔP 20ft (psi)	Peak Airblast ΔP 20ft (kPa)
70:30 KIO3:Sucrose (no Det)	6.833	1.49	352	1.47	365	1.11	2517	7.7	0.00	7.90	54.43
70:30 KMnO4:Sucrose (no Det)	5.216	1.10	494	2.07	228	0.45	1572	3.1	0.00	6.47	44.57
70:30 KNO3:Sucrose (no Det)	4.711	0.97	672	2.81	534	1.05	3682	7.2	0.67	8.20	56.54
70:30 KNO3:Al (no Det)	3.636	0.75	1428	5.98	915	2.30	6307	15.8	1.67	13.10	90.32
7:63:30 KClO3:KNO3:Sucrose	4.709	0.97	692	2.89	570	1.72	3928	11.8	1.71	14.54	100.25
5:66.5:28.5 RDX:KNO3:Sucrose	4.254	0.88	701	2.93	607	1.27	4186	8.8	1.77	12.06	83.12
35:35:30 KClO3:KNO3:Sucrose	4.768	1.01	815	3.41	809	5.53	5578	38.1	2.24	14.97	103.18
70:30 NH4ClO4:Al	3.132	0.69	2238	9.36	2293	28.97	15813	199.7	2.24	16.32	112.49
70:30 KClO3:Sucrose	4.788	0.99	967	4.05	1037	10.53	7150	72.6	2.34	16.70	115.14
70:30 NH4NO3:Al	3.140	0.68	1876	7.85	1504	7.85	10367	54.1	2.70	18.60	128.24
70:30 KClO3:Sucrose	5.246	1.10	967	4.05	1037	10.53	7150	72.6	3.07	14.80	102.04
70:30 NH4NO3:Sucrose	4.121	0.87	645	2.70	222	0.03	1531	0.2	3.49	11.87	81.84
Flake TNT	3.663	0.77	1093*	4.57	LLNL	--	--	--	3.84	--	--
70:30 NH4ClO4:Sucrose	4.662	0.98	1167	4.88	1347	13.94	9287	96.1	3.89	19.30	133.07
Flake TNT	4.003	0.81	1093*	4.57	LLNL	--	--	--	4.50	12.73	87.76
50:35:15 RDX:KNO3:Sucrose	4.986	1.05	1013	4.24	1139	5.48	7853	37.7	4.80	13.50	93.08
Booster	--	--	--	--	--	--	--	--	--	5.57	38.40

~23" x 4" charge; C4 booster=0.546kg; PETN = 0.15 kg; (no Det = no Detonation observed); distance Pressure Trans 20 ft

* LLNL Detonation Calorimeter

Discussion

FOX mixtures were chosen to examine three issues: 1) relative detonability of oxidizers as judged from small-scale tests; 2) role of the fuel; and 3) importance of small adjustments in energy input to performance. The FOX mixtures in Table 3 are ordered top to bottom by increasing detonation velocity. Among the FOX mixtures studied, chlorate and perchlorate with sucrose had the highest performance although density variations make it difficult to quantify the extent to which they are superior.

Cheetah, a Lawrence Livermore National Laboratory (LLNL) thermochemical code was used to calculate detonation velocity, Chapman-Jouguet (CJ) pressure, and energies of combustion and detonation at the densities used in the field detonation studies (Table 4). For the FOX formulations with aluminum, the calculated energy of combustion was only slightly higher than that of detonation (Cheetah calculations were run assuming all aluminum reacted.) For the FOX mixtures with sucrose fuel, the combustion energy was about 30% higher than detonation; and for TNT the combustion energy was approximately 4 times as high as the detonation energy. For air blast calculations where TNT equivalence was required, the heat of TNT reaction, rather than combustion, was used. The total heat of detonation calculated from Cheetah correlates linearly with the heat released in the Parr calorimeter (Figure 10). Since it was not feasible to create intact samples of controlled density of the powdery FOX mixtures, it was reassuring that isoperibol bomb calorimetry gave proportional results to detonation calorimetry (heat of detonation of TNT from [9]).

Table 4 Detonation Testing Summary with Analysis

Clear PVC pipe Shots (4" Dia x 24" L)					Detonation		Air Blast Calculations					Cheetah Predictions			
Mixture	Density (g/mL)	Heat (kJ/g)	ΔP (psi)	ΔP/Δt (psi/ms)	Phantom V7.11 Det Velocity (km/s)	Peak Airblast ΔP 20ft (psi)	Mass eq TNT (kg)	TNT Eq	TNT eq booster corrected	Air Blast Energy (kJ/g)	Air Blast Energy Comb (kJ/g)	Det Vel (km/s)	CJ Pressure (GPa)	Energy Detonation (kJ/g)	Heat Combustion (kJ/g)
70:30 KIO3:Sucrose (no Det)	1.49	1.47	365	1.11	0.00	7.90	2.67	0.39	0.18	0.80	2.5	3.60	3.86	1.39	3.92
70:30 KMnO4:Sucrose (no Det)	1.10	2.07	228	0.45	0.00	6.47	1.91	0.37	0.08	0.38	1.2	2.12	1.20	2.83	4.76
70:30 KNO3:Sucrose (no Det)	0.97	2.81	534	1.05	0.67	8.20	2.84	0.60	0.29	1.33	4.2	3.04	1.94	2.69	3.68
70:30 KNO3:Al (no Det)	0.75	5.98	915	2.30	1.67	13.10	5.87	1.62	1.21	5.53	17.5	1.23	0.38	7.24	7.83
7:63:30 KClO3:KNO3:Sucrose	0.97	2.89	570	1.72	1.71	14.54	6.84	1.45	1.14	5.21	16.5	3.08	2.00	2.78	3.79
5:66.5:28.5 RDX:KNO3:Sucrose	0.88	2.93	607	1.27	1.77	12.06	5.19	1.22	0.87	3.99	12.6	2.89	1.67	2.82	3.94
35:35:30 KClO3:KNO3:Sucrose	1.01	3.41	809	5.53	2.24	14.97	7.13	1.50	1.19	5.42	17.2	3.47	3.12	3.14	4.20
70:30 NH4ClO4:Al	0.69	9.36	2293	28.97	2.24	16.32	8.07	2.58	2.11	9.62	30.5	2.75	1.72	10.21	10.41
70:30 KClO3:Sucrose	0.99	4.05	1037	10.53	2.34	16.70	8.34	1.74	1.43	6.55	20.8	3.78	3.19	3.59	4.71
70:30 NH4NO3:Al	0.68	7.85	1504	7.85	2.70	18.60	9.71	3.09	2.62	11.98	38.0	3.58	2.45	9.11	10.32
70:30 KClO3:Sucrose	1.10	4.05	1037	10.53	3.07	14.80	7.02	1.34	1.06	4.83	15.3	4.23	4.99	3.61	4.71
70:30 NH4NO3:Sucrose	0.87	2.70	222	0.03	3.49	11.87	5.07	1.23	0.87	3.99	12.6	4.50	4.65	2.64	5.53
Flake TNT	0.77	4.57	LLNL	--	3.84	--	--		--	--	--	4.34	3.91	3.42	14.48
70:30 NH4ClO4:Sucrose	0.98	4.88	1347	13.94	3.89	19.30	10.23	2.19	1.88	8.58	27.2	4.83	6.13	3.93	5.61
Flake TNT	0.81	4.57	LLNL	--	4.50	12.73	5.63	1.41	1.04	4.74	15.0	4.50	4.45	3.47	14.48
50:35:15 RDX:KNO3:Sucrose	1.05	4.24	1139	5.48	4.80	13.50	6.14	1.23	0.94	4.28	13.5	4.83	6.20	4.02	6.28
Booster	--	--	--	--	--	5.57	1.48	2.12							

~23"x4" charge; C4 booster=0.546kg; PETN = 0.15 kg; (no Det = no Detonation observed); distance Pressure Trans 20 ft

* LLNL Detonation Calorimeter

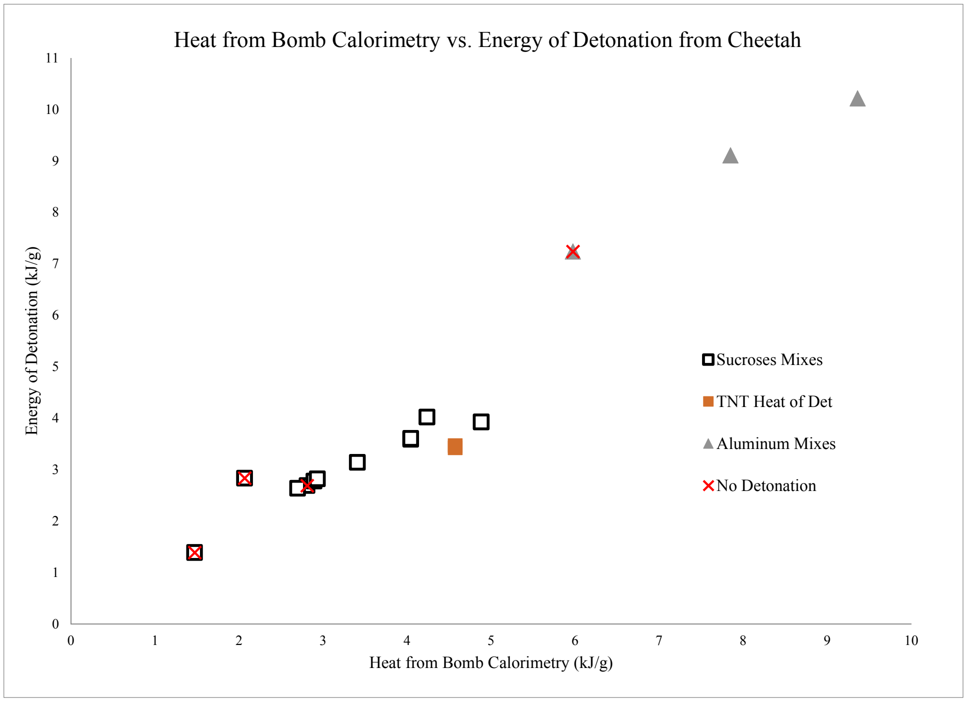


Figure 10. Heat of Detonation from Bomb Calorimeter vs Cheetah Calculation. Error bars on x axis are too small to plot.

Observed detonation velocities tracked with the Cheetah predicted detonation velocities. Figure 11 shows the non-detonations (i.e. potassium nitrate formulations) with an X and separates the shots done with aluminum fuel from those done with sucrose and from those done with formulations including high explosives (in red, two TNT shots and one that was 50% RDX).

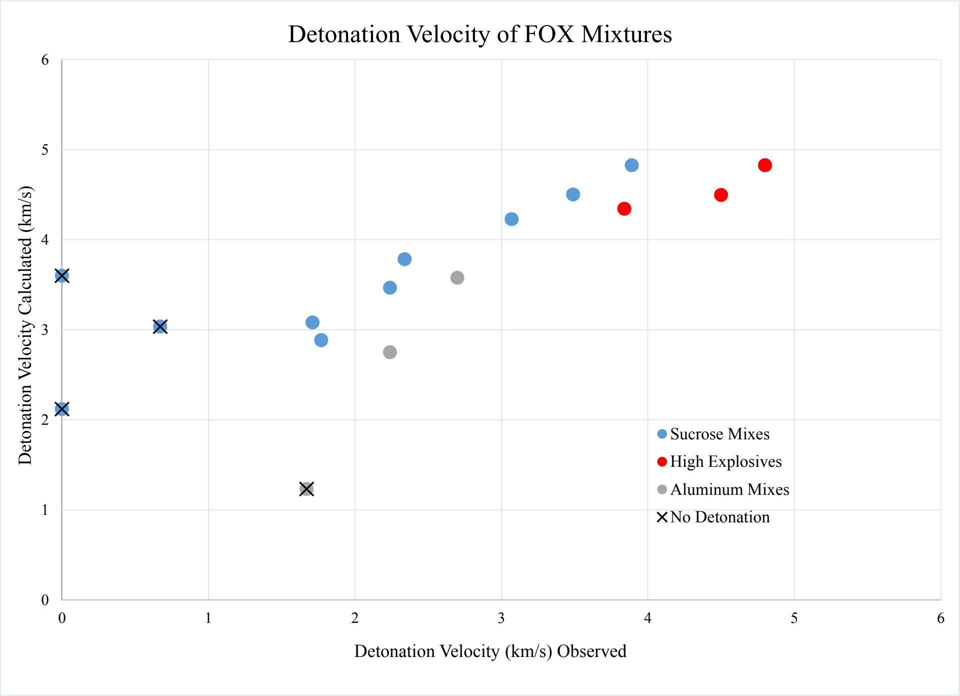


Figure 11. Observed Detonation Velocities (km/s) vs Cheetah Calculation Thereof (X failed to detonate)

Since the heat released measured by calorimetry and detonation velocities measured by camera track with Cheetah predictions, it is not surprising that the measured heat of reaction under argon correlated with observed detonation velocities (Figure 12). Interestingly, the outliers (above the line on both the oxidizer/sucrose and oxidizer/aluminum formulations) are the formulations with ammonium nitrate. Part of this is certainly due to the fact that it is difficult for the sucrose formulation to burn under argon, but this does not explain the AN/Al formulation.

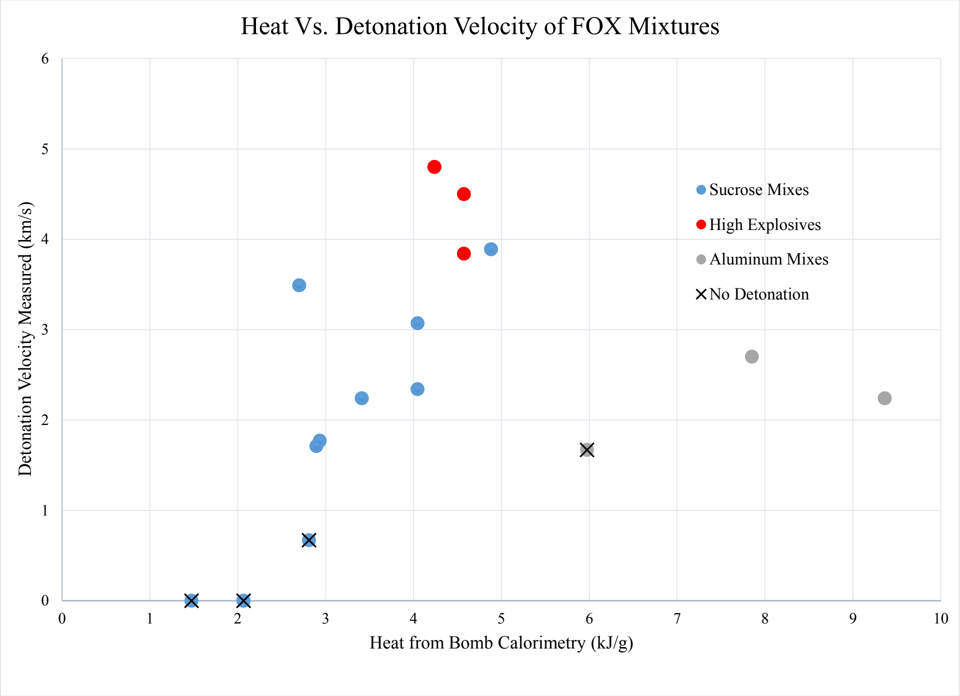


Figure 12. Heat of Reaction measured by calorimetry vs. Detonation Velocity. Error bars in the x axis are too small to be plotted.

Figure 12 suggests there may be a minimum energy (~2.8 kJ/g) needed for detonation. However, the data, as well as detonation theory, dictates that energy alone does not guarantee detonation. The rate of energy release by the formulation must be fast enough to support detonation. If we make the rather speculative assumption that the rates of all the oxidizer/sucrose reactions are similar because the rate of reaction in these low density powders is diffusion controlled, then we might expect a linear relationship between energy of reaction and detonation velocity.

Figure 12 also shows that the aluminum-fueled oxidizers follow a different trend than the sucrose-fueled formulations. Given the idea of minimum energy, it could be speculated that aluminum can provide enough additional energy during its oxidation to push a low-energy formulation to detonation; this was not the case in these studies. Ammonium nitrate and perchlorate sucrose mixtures were detonable; substitution of aluminum for sucrose increased the heat released in the calorimeter, but detonation velocity decreased. We attribute this result to the lower density of the aluminum formulation due to the small aluminum particle size. Not surprisingly, air blast, in terms of TNT equivalence, increased with the addition of aluminum. It is well known that aluminum does not react rapidly enough to contribute all its energy to the detonation front; hence, the provision in Cheetah to make some of the aluminum content "inert." In fact, air blast, in terms of TNT equivalence, is proportional to the heat observed in the Parr calorimeter (Figure 13).

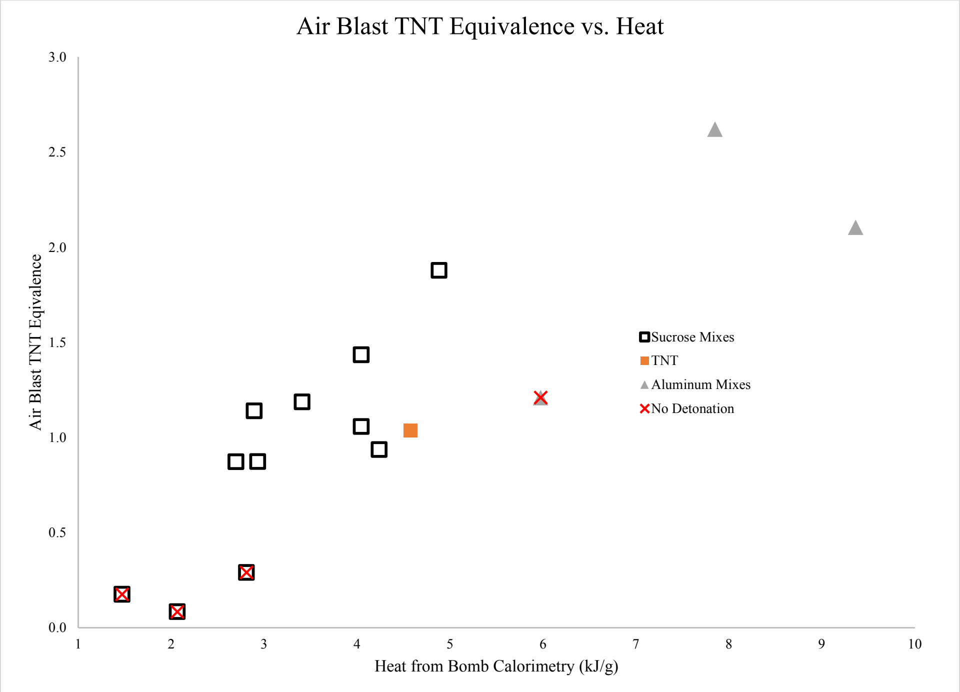


Figure 13. Air Blast TNT equivalence large scale vs. heat from 2g calorimetry. Error bars are too small plot.

Conclusions

Measurement or calculation (Cheetah) of heat of reaction is a useful first step in determining whether a formulation is potentially detonable. It appears there is some minimum energy which a formulation must possess to be detonable. However, examination of Table 4 clearly shows that some materials with high reaction energy (i.e. KNO_3/Al) do not detonate, while others with low reaction energy (i.e. AN/sucrose) do. Clearly any small-scale test or model must take into account the rate of reaction as well as energy. The potassium nitrate/sucrose mixture exhibited low heat release in the Parr bomb, and it did not detonate in the field-scale configuration. The substitution of aluminum for sucrose dramatically increased the energy released (as measured in the calorimeter), but the mixture (KNO_3:Al) still did not detonate in field trials. The rate recorded in Table 3 is a burn, as judged by video record and discussed above. The potassium nitrate/sucrose mixture was prodded into detonation by spiking it with 5wt% RDX or 7wt% potassium chlorate. Both these chemicals were capable of rapidly adding energy to the mixture. However, the total energy released by these potassium nitrate/sucrose mixture with these additives was only a little over half that of potassium nitrate / aluminum. This observation points to the importance of the rate at which the energy is provided. Looking again at small scale tests (Figure 1) we observed that in general FOX mixtures that produce a shorter time to peak pressure in the 2g tests detonated in the 5 kg tests. FOX mixtures which produced long time to peak pressure (> 200 ms) did not detonate at the large scale with the exception of ammonium nitrate and sucrose.

With aluminum mixtures at the large scale, it has already been mentioned that due to the slowness of the reaction only some fraction of the energy released in the aluminum oxidation can support the detonation front [10]. The rest is manifest in the Taylor wave expansion, i.e. air blast. The fuel/oxidizer mixture has as similar problem with reaction rate. Detonation velocity is strongly dependent on density [11]. FOX mixtures are far from dense, and a significant amount of time must be spent in diffusion and compaction of the fuel and oxidizer. High explosives, such as PETN or RDX, have reaction zone lengths of approximately 1-2 mm, reacting rapidly enough so that much of their energy can support the detonation front [12]. This in contrast to a non-ideal explosive, such as ANFO, with a reaction zone length estimated as 8-12 mm [12]. With these FOX mixtures the fraction of energy released to the front must be significantly less. How much less and the role of compaction in these composite materials will be the subject of a number of future studies.

Approach 2: ERMS: We are investigating a technique called energy resolved mass spectrometry (ERMS) for potential detection of energetic materials. This technique was successfully used in the past to distinguish between the fragments of very similar molecules, [13] as well as among isomers of sugar compounds known as oligosaccharides. [14-16] Energy resolved mass spectrometry (ERMS) has a potential to be used as a new technique in distinguishing unknown explosives materials (EM) from non-explosive (NE) stable compounds. The standard procedure for ERMS is outlined below. First, the compound of interest is dissolved in the appropriate solvent (acetonitrile, water, methanol, or combination), then the resulting solvent mixture is introduced into mass spectrometer for analysis. The neutral compounds are ionized into positive or negative ion species, which is a requirement for trapping them in the magnetic field of the mass spectrometer. Once ions are created and trapped, a single ion can be isolated from hundreds of others based on its mass to charge ratio. This particular ion can be further manipulated by increasing its kinetic energy until it starts to fragment. Using radio frequency of AC voltage component we can gradually increase energy from 0 to 50 eV in increments of 0.2 eV in a controlled fashion. At some point in the ramp the ion will become unstable and begin to break apart into smaller ions, called fragments.

We established couple criteria to analyze the resulting breakdown curves shown in Figure 14. The onset point indicates 90 percent of the selected ion isstill intact, and the energy at that point theoretically represents *sensitivity or fragility* of selected ion (i.e. the earlier the onset point, the more sensitive the ion).

The amount of energy that is required to break up the species from 90 to 10 percent represents its *stability or longevity*. We also designated the mid-point of this breakdown (i.e. 50%) curve as a quick metric for cross reference between various molecules under investigation and called it *fragmentation resilience (FR 50).* To minimize the noise associated with collection of raw data, which can be seen in Figure 15, we accumulate six breakdown curves for each compound and then statistically average them to produce a single normalized breakdown curve as shown in Figure 14. We theorized that explosive materials will have tendency to be more fragile upon application of this method, resulting in earlier breakdown onset points. We have evidence that supports this hypothesis, which can be seen from just visual inspection of Figure 15 in which TATP and HMTD (both high explosives) are more fragile and have earlier onset points in comparison to stable compound – hexamine (precursor to synthesis of HMTD).

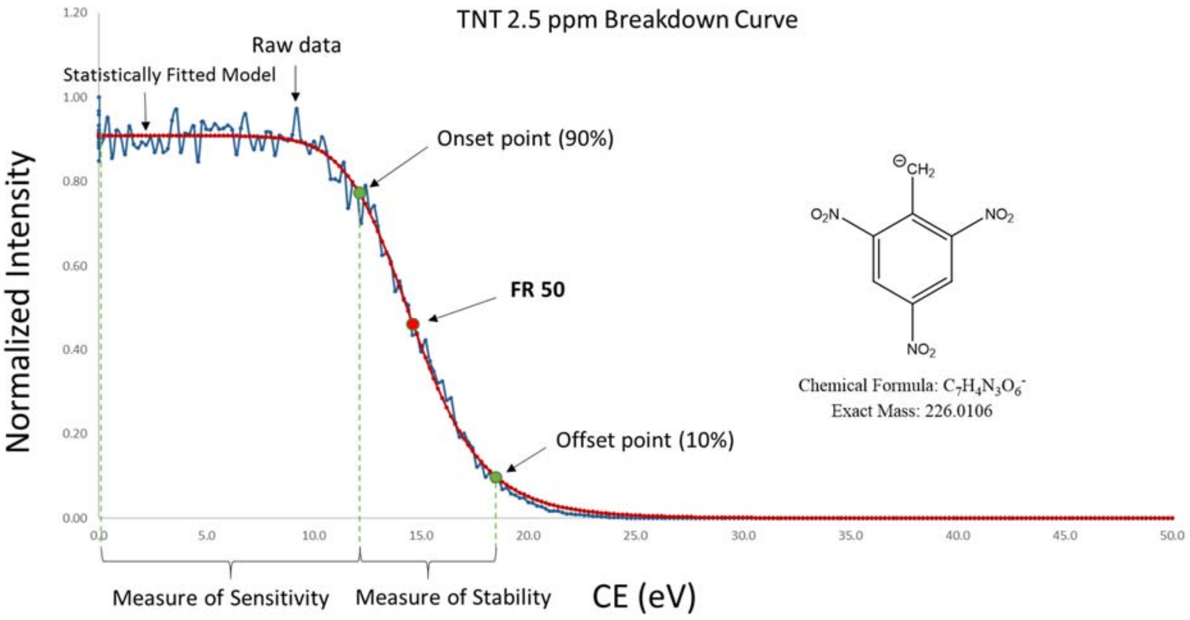


Figure 14. Breakdown graph for trinitrotoluene (TNT) m/z 226.01 averaged over 6 curves

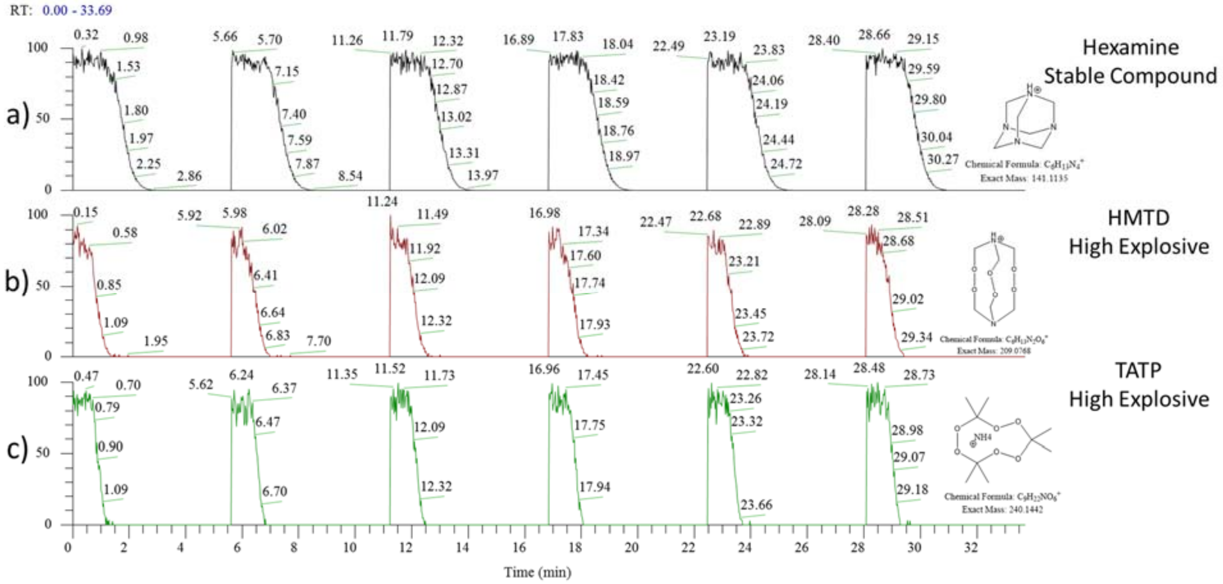


Figure 15. Energy resolved mass spectra comparison of six breakdown curves for a) hexamine (ESI+, [M+H]+, 10 ng/mL), b) HMTD (APCI+, [M+H]+, 10 µg/mL), and c) TATP (APCI+, [M+NH$_4$]+, 10 µg/mL). Each curve is acquired by increasing energy from 0 eV to 50 eV at an interval of 0.2 eV.

In order to compare different compounds to each other, we established a protocol where all mass spectrometer parameters were kept the same. We began our investigation with variety of nitro-aromatic compounds, because TNT, one of the most well-known explosives, belongs to this class. As can be seen from Table 5, TNT indeed has one of the earliest onset points (indicative of sensitivity), as well as smallest amount of energy required for its destruction (indicative of stability). From our initial reported studies last year, TNT was one of the most stable explosives, which means that higher explosive compounds will have even lower onset points. This data directly supports our theory that this method can potentially be used for distinguishing energetic materials from more stable compounds. Some compounds in Table 5 have multiple entries, representing different ionization techniques that the same ion was subjected to. This gave us an insight on how different ionization methods affect the stability of the same molecule, and what steps we need to take to account for that difference.

Table 5. Comparison of onset energies (sensitivity), total energies (stability) and FR 50 for various nitro-aromatic compounds.

Name	Mode	Ion Type	FR 50 (eV)	Onset (eV)	Total (eV)
1,3-dinitrobenzene	ESI-	[M+e]-	16.8	12.9	9.1
2-amino-4-chloro-5-nitrophenol	ESI+	[M+H]+	14.4	11.6	6.6
2-amino-4-chloro-5-nitrophenol	APCI+	[M+H]+	18.2	13.8	10.2
2-amino-4-chloro-5-nitrophenol	APCI-	[M-H]-	21.4	17.6	8.3
2-amino-4-chloro-5-nitrophenol	ESI-	[M-H]-	23.2	18.9	9.7
2-nitrophenol	ESI-	[M-H]-	27.3	22	11.8
3,4-diaminotoluene	ESI+	[M+H]+	29.2	23.5	12.9
3-nitroaniline	ESI-	[M-H]-	26.1	20.9	11.6
3-nitrophenol	ESI-	[M-H]-	34.8	26.2	20.1
4-nitroaniline	ESI-	[M-H]-	26.8	21.9	11
4-nitrophenol	ESI-	[M-H]-	26.7	21.6	11.4
2,4-dinitrophenol	ESI-	[M-H]-	33.3	24.1	21.8
m-aminophenol	APCI+	[M+H]+	29.1	17.5	31
m-aminophenol	ESI+	[M+H]+	27.2	22.4	14.1
m-aminophenol	APCI-	[M-H]-	30.6	24.6	13.4
m-aminophenol	ESI-	[M-H]-	31.3	24.9	14.4
3-nitroaniline	ESI+	[M+H]+	21.9	16.6	12.4

4-nitroaniline	ESI+	[M+H]+	22.6	17.6	11.2
2,4,6-trinitrotoluene	ESI-	[M-H]-	14.5	11.5	7.2

Approach 3:

To determine the tendency of a formulation to detonate and to do so at less than 500g, we are employing two techniques: high-speed photography and photon Doppler velocimetry (PDV). Many challenges arose in designing the appropriate configuration, chemically isolating the explosive material, tuning the reflector interface, choosing the window material and geometry, and optically characterizing the fiber optic probe/reflection landscape.

Configurational challenges:

Test pipe: To improve our ability to visually track the reaction, a new test fixture was created (Figure 16). The thinner wall thickness makes securing the sample fixture more difficult, since the pipe itself is no longer strong enough to affix the rest of the fixture with notches in the pipe wall (the strategy used with the thicker PVC pipes). Therefore, modifications to the booster and PDV probe components were necessary. The sample pipe length will vary depending on the type of test. For steady detonation reaction zone measurements, the pipe length must be varied in order to measure the reaction zone length, while remaining at least 3 diameters long.

Figure 16: Test fixture. Pipe portion has been changed from translucent, schedule 40 PVC (0.114" thickness for 1" diameter up to 0.237" thickness for 4" diameter) to clear high density polyethylene (HDPE) (0.022" wall thickness). The new pipe is quite clear, which provides better light transmission to visualize the ignition and failure of the explosive reaction light. In addition, it is more compatible with nitromethane (NM) than PVC

*Alignment: T*he new fixture with thinner wall pipe is aligned and held together by three threaded rods concentrically compressing the device components into intimate and uniform contact. This method ensures proper and reproducible pressure is applied to all components.

Booster: The booster in the new configuration was a lightly-pressed composition C4 (>90% RDX). For a 1" diameter pipe (1.09" ID, 0.022" wall thickness), the booster section was 1.25" long (L/D > 1). For larger pipe diameters, the booster length would be scaled similarly. An L/D of greater than 1 was required to develop a steady detonation in the booster explosive. [Note: For these experiments, a 1" diameter device was preferred, but larger diameters (1.64", 2.05", and 2.55") are available for compositions which cannot reach a steady detonation in a 1" device. For under and over-driven detonations, larger diameters increase the "infinite diameter time" or 1-dimensionality of the experiment, i.e. larger diameters increase the amount of time that mixture may be probed before the edge effects propagate back into the center and effect the detonation wave structure.]

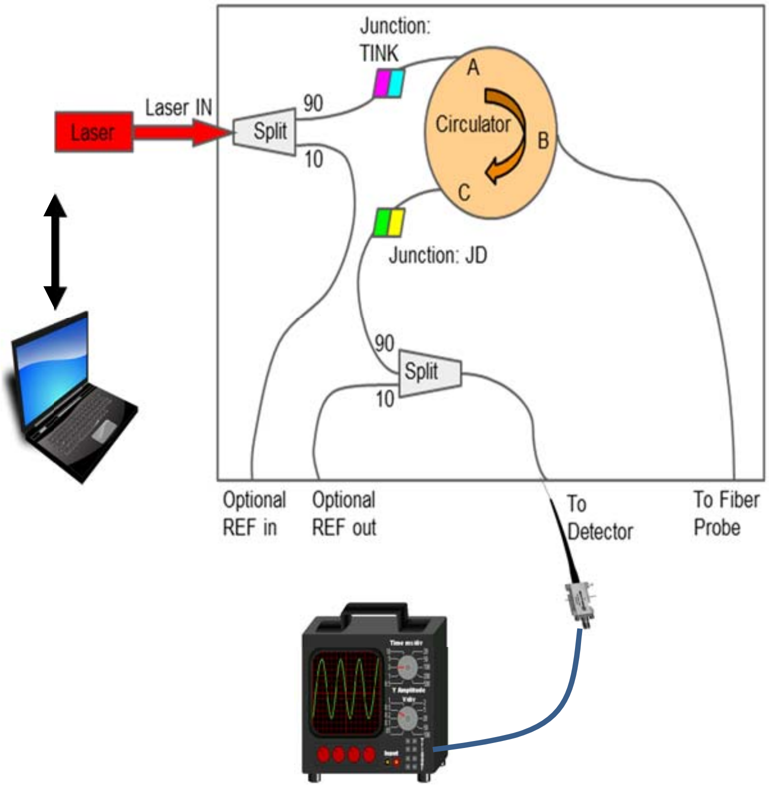


Figure 17: Setup for PDV Measurements

PDV Challenges:

Conventional PDV is often used to measure the expanding wall velocity of a detonating charge by detecting a Doppler-shifted beat frequency proportional to the expansion velocity normal to the probe orientation. By analyzing the frequency-domain time profile, the time-resolved wall velocity can be calculated and used to assess the effectiveness of an explosive at accelerating a finite mass casing through the air. In most PDV experiments, the flow dynamics of the explosion are unseen, and the data is simply a record of the effective drive the explosive had on the surrounding material.

Our Approach: This experimental configuration uses PDV in an unconventional way of interrogating the detonation wave structure of the sample explosive. A few researchers have developed a technique which we find adaptable to our research interests. Because the acoustic impedance of the explosive is matched to an optical window (PMMA), no shock reflections impede the flow of the detonation wave into the inert window material. By sputter-coating a sub-nanometer thick layer of gold on the window at the interface with the explosive, PDV laser light is reflected at the instant the detonation wave interacts with the window. With <10 ns time resolution, the detonation wave is matched onto the PMMA window in real time. (Many configurational and diagnostic constraints affect the time resolution.) The movement of the interface (explosive/gold/PMMA) tracks in step with the particle velocity of the detonation wave, including the chemical transformations in the reaction zone. This entire wave profile is recorded by the PDV system unobstructed until the shock wave transmitted into the window material reflects off its free surface and impacts the explosive/gold/PMMA interface. A schematic is shown in Figure 17.

Optical Window: Our PDV strategy requires an acoustically-matched window abutted to the charge end for two reasons: 1) so that the detonation wave transmits smoothly into the window with no shock reflections (either relief or support) into the reaction zone of the explosive; 2) in order to provide a structural substrate for the sputter-coated gold reflector (otherwise thick foil-type reflectors must be used which will 'ring-up' and attenuate the shock wave). PMMA was chosen as a window material because its shock impedance lies in between that of the unreacted and reaction product shock Hugoniots.

In similar experiments, the back, uncoated side of the window may be machined and polished at an 8° angle to prevent back reflections. In previous configurations, we tried this approach. However, mathematical investigations of the power contributions from each reflection showed that until the back surface began moving after being struck by the shock wave, a reflected light from this surface would be inconsequential in the frequency domain. Therefore, the 8° angle polish was abandoned, and a flat sheet of PMMA was used as the window. The PMMA used transmitted 88.5% of the 1550nm laser light. The PMMA was often simply cleaned, and the reflective surface was sputtered 'as received', rather than polished with abrasive paste.

Reflector Considerations: The explosive contact side of the window was sputter coated with gold (>99.9%pure) in order to reflect the PDV laser light. By keeping this layer thin, <1 nm, its effect on shock attenuation, ringing (the internal reflections inside the metal layer), and shock matching can be effectively neglected. If the reflective layer were thicker (>50 μm), these effects would become significant and possibly prevent the strategy from being effective.

Chemical barriers: Because PMMA is incompatible with nitromethane, a very thin (7.62 µm or 0.0003" thick) Kapton film is placed between the explosive and the gold surface. Without this barrier, the nitromethane compositions would dissolve the PMMA window and gold surface. This thin layer of Kapton also creates a liquid-tight seal between the HDPE pipe and the PMMA window, and as such, is used even when chemical incompatibility is not a problem.

PDV probes: Three types of PDV probes have been used:

1.) Collimators
2.) Focusing probes
3.) Bare Fiber

Collimated lenses are made to project and collect light at a minimal angle, i.e. a small spot size is projected like a laser pointer. The disadvantage to this type of probe is that the reflective surface must be slightly diffuse. Getting the diffusivity of the reflective surface reproducibly correct is difficult; the collimators are costly. The focused probes are more expensive than collimators and can suffer from a similar problem, requiring a delicate diffusive layer to be implemented and characterized. To avoid the need for a diffusive reflector, a simple bare fiber optic cable, cut at a perfect 90° angle was used. Using a bare fiber probe presented many challenges but came at no extra cost or preparation time. Because the numerical aperture of the bare fiber probe spread the light at a large 8° angle, a specular (i.e. as received) reflector was sufficient for this work and did not require the PMMA to be made diffuse. This meant that by using a bare fiber probe with an as-received window required the least amount of sample preparation. The downside of this combination was light loss. Because the numerical aperture was so large, the light was quickly dispersed; over several millimeters it had spread to thousands of times the diameter of the fiber core. The only light which returned back into the system to be detected was that fraction of the light which maps back onto the fiber core. As such, the bare fiber probe and as-is reflector combination was used in the current configuration.

Major Contributions

In **years 1 and 2** the thermal behaviors of 11 solid oxidizers in combinations of 13 fuels were determined using differential scanning calorimetry (DSC), a technique requiring less than a milligram of material [1]. Many are considered FOX (fuel/oxidizer explosives). 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 observations were the first steps in finding behaviors observed on the milligram-scale that may correlate with detonability measured on the kilogram-scale.

In **year 3** we followed up the previous milligram-scale study of FOX with gram-scale experiments performed in an adiabatic calorimeter. A modification to the standard instrument allowed collection of heat release and pressure-rise data versus time as the formulation of interest is burned under a controlled atmosphere. This was also the year that our detonation facility was completed with the acquisition of necessary instrumentation and infrastructure.

This year **(4)** full-scale detonation studies of 16 FOX mixtures were performed. It was found that, in general, FOX mixtures that produce shorter time to peak pressure in the 2 g Parr calorimetry tests detonated at large scale. FOX mixtures which produced longer time to peak pressure did not detonate at the large scale with the exception of ammonium nitrate and sucrose (see Figure 1 and Table 3).

In **year 4** the role of aluminum was dramatically shown. With aluminum mixtures, due to the slowness of the aluminum oxidation, only some fraction of the energy released was provided fast enough to support the detonation front [10]. The rest of the energy is manifest in the Taylor wave expansion, i.e. air blast. The fuel/oxidizer mixtures have as similar problem with slow reaction rate. Detonation velocity is strongly dependent on density [11]. FOX mixtures are far from dense, and a significant amount of time must be spent in diffusion and compaction of the fuel and oxidizer. High explosives, such as PETN or RDX, have reaction zone lengths of approximately 1-2 mm; they react rapidly enough so that much of their energy can support the detonation front [12]. This, in contrast to a non-ideal explosive, such as ANFO, with a reaction zone length estimated as 8-12 mm [12]. With these FOX mixtures the fraction of energy released to the front must be significantly less. How much less and the role of compaction in these composite materials will be the subject of a number of future studies.

Camera protocols devised for Approach 3 allowed Approach 1 to be performed this year (4) with all the accomplishments cited above. This is at least one year earlier than we had expected to be testing the FOX mixtures. In addition a variety of issues were attacked and solved. Year 5 should bring this altogether into a successful small-scale test.

ERMS

In year 4 we successfully improved the statistical algorithm required for the analysis of data obtained from the mass spectrometer. It resulted in significant increase in accuracy of reporting data, due to the limited human interaction and therefore minimized subjectivity. This model lets us automatically predict highest and lowest asymptotes for the breakdown curves, as well as FR 50 without any additional calculations. For evaluation of this algorithm we apply two additional methods of verification. One of them was already used for analysis of oligosaccharides [17] and the other one was developed in our lab for initial studies, which we called the “cross intersection” method. The problem with these two methods is that they rely solely on the existence of fragments, and otherwise cannot be used. With our new algorithm this problem was resolved; now no fragments are required for compound analysis.

In year 4 we created a working program in Microsoft Excel that implements our novel algorithm and analyzes the data in timely and consistent fashion. We established a mass spectrometric protocol where all mass spectrometer parameters were kept the same and began investigations of nitro-aromatic compounds.

Milestones

This year gave us our first look at potential detonability of FOX mixtures. Most interesting was the fact that a 4' diameter the KNO3/Al mixture ***almost*** detonated. This makes this a particularly good formulation to study because it sits on the border of detonability. We have already shown that as little as 5% RDX or 7% $KClO_3$ make the non-detonable mixture detonable. We expect that an increase in the sample diameter would also do so. We hope to examine that possibility in the new year. We face various technical difficulties in doing so.

The data dramatically shows the effect of added aluminum. It important that the HSE realize the hazard is increased blast but not increase brisance from higher detonation rates.

Approach 1: To date, nine fuel/oxidizer explosives or potential explosives (FOX) have been tested at medium scale (~12 lb). Initial review suggests a strong correlation between bomb calorimetry and detonability. A number of shots are planned, although weather and noise considerations dictate only intermittent testing.

Approach 1: We are anxious to examine a formulation which has proved undetonable under certain conditions (size and booster) with the spike of an explosive mixture and determine how close to detonation the formulation is under the set conditions. This would be a better test to conduct with the new small-scale test being developed in Approach 3, but it is a question which requires an immediate answer. The reverse question is how much inertant can be added to an explosive mixture before it becomes non-explosive.

Approach 2 is a novel attempt to classify energetic molecules based on collision-induced dissociation with inert gas using an ion-trap/high mass resolution Orbitrap and a triple-quadrupole mass spectrometer. A computer code aided the assignment of dissociation energy. However, a second mode of analysis is also being explored.

Approach 3 intends to develop a small detonability test which can reveal potential detonability even below the critical diameter. A new test fixture has been developed for these tests. A number of successful Photon Doppler Velocimetry (PDV) end-on measurements have been conducted, but PDV use as a continuous probe has yet to be achieved.

Future Plans

Approach 1 will be extended to more oxidizer/ fuel combinations. Due to limited time and material expense, a relatively small number of combinations can be examined. Specific plans in Approach 1 are to examine KNO_3/fuel mixtures. These failed to detonate on the 4” diameter scale. We will use additives or changes in charge size in an attempt to find the go/no-go point in its detonation.

Approach 2, ERMS, will be looking at the effect of concentration on FR 50 and also the influence of ionization mode.

Approach 3 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. 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). 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.

Approach 2 and 3 are both attempting to achieve something not previously attempted. It is difficult to say whether they will have achieved their goals at the end of Year 5. If either approach does achieve the goals of providing a detonability screening test, then undoubtedly DHS will want us to use it to screen a number of potential detonable formulations. The new techniques developed will be shared via publication so that numerous researchers can become involved in pursuing the goal of this project—identifying what materials are threats and identifying when those threats have been successfully thwarted.

Approach 3: With a configuration decided and proven effective, we plan to implement three techniques to characterize non-ideal explosive detonation wave structure. The first and simplest to interpret is a measurement of the reaction zone of non-ideal explosives which reach a steady detonation. The other proposed tests do not require the explosive to be above its critical diameter. The first of these techniques boosts the sample in an over-driven configuration; and the second, an under-driven configuration. Both tests require the sample explosive to be at least start in an 'infinite diameter' regime, which means that the relief waves originating at the charge boundary must not have sufficient time to relive pressure at the charge center.

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

Abstract (project description for the web)

The aim of this project is to develop new methods for those involved in the Homeland Security Enterprise (HSE) to collect, handle and store novel explosives- the so called "homemade explosives" (HME)- in a safe and effective manner. 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 for instrument calibration and training; explosives sampling devices (swabs), which are effective at pick-up and release of explosives residues; 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 be safer or more hazardous when mixed with other materials. In either case, it is essential that we understand the consequences of combining HME with other materials.

I. PROJECT DESCRIPTION

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, especially homemade explosives (HME), in a safe and effective manner. 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 training; explosive sampling devices (swabs), which are effective at the pick-up and release of explosive residue; and the investigation of X-ray explosive simulants. Explosives are rarely used in their pure form; they are generally mixed with a plasticizer or other formulating agent. Of concern to the HSE is whether components of homemade explosive (HME) compositions interact with each other, thus decreasing stability and increasing sensitivity or the opposite. Of particular importance are the following: (1) Safe handling and storage of HMEs; (2) Creation of better swabs; (3) Creation of better vapor concentrators; (4) Creation of canine training aids; and (5) Creation of trace and bulk simulants. To date, the focus of this project has been explosive/polymer interactions for three purposes—better swabs, safe-scent training aids for canines and instrumentation, and explosive simulants for X-ray. The specific aim depends on which of the specific goals enumerated above is being addressed. In any case, it is essential that explosive and polymer are compatible. Meaning the polymer does not promote the explosive decomposition nor enhance its sensitivity. Furthermore, it is important that no undesirable or unanticipated sorption of the explosive to the polymer occurs.

This year this project has resulted in 2 papers authored at the University of Rhode Island (URI) [a,b], and four papers from our partners at two minority-serving-institution (MSI) [k,l,m,n], as well as a provisional patent [1]. Both our MSI partners and our group have been awarded further Department of Homeland Security (DHS) funding for certain aspects of this research. This work has also resulted in a graduate student award [2], three PhD students (Dec 2014, Dec 2016, May 2017), two working at TSL and Tyndall AFB, and partnerships with three vendors supporting trace explosives detection.

Safe-Scent Aids: One of the first research successes in this project was polymer encapsulation of triacetone triperoxide (TATP), thus, allowing safe handling of a highly sensitive, volatile explosive. Polycarbonate microspheres containing up to 25% TATP have been demonstrated to last for years, yet produce pure TATP vapor when heated at a designated program rate. An appropriate polymer had to be selected, cleaned, and successfully introduced to TATP as the encapsulating material. Similar procedures produced encapsulated HMTD, although residual solvent offered certain challenges. Further characterization was required to make these encapsulated peroxides into useful products. In the case of HMTD, the heating profile required to release the peroxide had to be determined. In the case of TATP, sensitivity characterization was necessary so that Department of Transportation (DoT) approval for shipping these aids could be requested. DoT approval for shipping these aids as non-explosives was received in April 2017. Hopefully, this will remove remaining barriers to successfully marketing these materials.

These encapsulated peroxides provide canine handlers and instrument vendors with safe access to stored hazardous explosives at trace levels for use in the detection, calibration, and validation of instruments as well as the training of explosives detecting canines. The new generation of training aids has been tested by a limited number of users due to the requirement for a specialized heating device to release the explosive scent from the polymer. From law enforcement and instrument vendors who have tested the product, we have received enthusiastic support. A prospective vendor of these training aids has built a compact heating device for use in the field and has made a couple of potential sales. The process of patenting and licensing to a commercial vendor is in progress. *Major milestones this year include performing sensitivity testing and applying for and receiving Department of Transportation (DOT) shipping approval as non-explosives.* Both the TATP and HMTD have been encapsulated and the temperature profiled for released. Once these training aids are made available, and these activities reach a successful conclusion, the number of users will increase significantly. It is apparent that canine trainers and other users of the safe-scent aids require an entire suite of explosives. Efforts this year have focused on encapsulation of erythritol tetranitrate (ETN) and TNT. Furthermore, a new method to encapsulate using supercritical CO_2 was initiated. (Details are in State of the Art and Technical Approach section.)

X-ray Simulants: We have previously reported a way to develop simulants for liquid explosives. The primary x-ray detector used in that study was designed to examine hazardous liquids and was capable of examining materials at two energy levels-above and below 35 keV. This detector analyzed samples based on x-ray scattering rather than attenuation. Surprisingly, this method of making simulants for liquid materials was transferable to other types of X-ray instruments--a computed-tomography (CT) single-energy instrument and on a CT of dual-energy. That being shown initial work was undertaken toward preparing simulants for other solid HMEs. The work with solids has not been particularly successfully due to inhomogeneous packing. However, we believe this approach is a useful way to make simulants of composite materials (explosives made up of more than one compound). Furthermore, it points up potential problems with X-ray analysis of these types of materials. Details are in attached submitted paper (b).

In examining hair as a source of evidence of handling explosives, we were faced with the need of better swabbing materials. Interestingly, vendors who create swabs to accompany their explosive trace detection systems (ETDs) often choose non-sticky materials such as Teflon or Nomex. Presumably, getting the explosive residue to release from the swab into the ETD is a bigger problem than picking up the explosive in the first place. We have taken the approach of putting an electrostatic charge on existing commercial swabs and demonstrating that under most circumstance holding them near explosive residue is more effective in picking up explosive residue than rubbing that area with an uncharged swab. Furthermore, when the swab touches the inlet of the ETD, it is partially discharged, making it significantly less attractive to the swab. The lack of need for vigorous rubbing of the surface of interest means that these swabs are likely to pick up less background interferences and are likely to experience longer life times. A prototype charging station will be constructed. (Details can be found in DHS reports.)

In examining the thermal characteristics of erythritol tetranitrate (ETN) it was decided to make an attempt to stabilize it. It has a relatively long temperature region between melt and violent decomposition—about 120ºC, compared to TNT of 230ºC and PETN of 50ºC. That work is reported here. (Details can be found in attached paper.)

Year Two (July 2014 through June 2015) Biennial Review Results and Related Actions to Address

Of all the R1 projects, this is the one which most closely meets the day-to-day user within the Transportation Security Administration (TSA). It is addressing the requirement for canine training aids of hazardous materials and the need for more efficient swabs.

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 newest generation of training aids has been tested by a limited number of users because of a requirement for a specialized heating device to release the scent from the 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 benefits 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.

State of the Art and Technical Approach

Safe-Scent Aids

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, thermogravimetric analysis with infrared detector (TGA-IR), and various gas and liquid chromatographs as tools to aid this work. This project has also investigated new methods to package sensitive HMEs, 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 failed shoe bomb attempt of December 22, 2001. While these initial aids had many drawbacks, this project has made creation of safe, long-lived canine training aids for peroxide explosives a priority. The encapsulated TATP resulted in a paper [3]; the student author won the National Security Innovation award of $10,000 [2]. Partnering with a vendor to design and market the heating device has built strong industrial ties. Scientists at the NIST sent us a congratulatory email after seeing our presentation at the Annual Workshop on Trace Explosives Detection (April 2014); they had come up with something similar.

Erythritol tetranitrate (ETN) and trinitrotoluene (TNT) microspheres were made using the solvent evaporation method employed for TATP microspheres [3]. The procedure includes a shell material (polymer) and a core material (explosive) which are dissolved in a hydrophobic, volatile solvent. 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.

Polycarbonate (PC) was selected for the ETN and TNT microsphere encapsulant. Thermoplastic polymers were preferred because they soften at their glass transition temperature but do not decompose until higher temperatures. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) were also tested. The chromatogram of the polystyrene heated to 150°C showed peaks, suggesting the need of a cleaning process. Poly(methyl methacrylate) microspheres were abandoned because upon heating the infrared (IR) spectrum showed the release of methacrylate and related molecules, which would have contaminated the explosive vapor. Polycarbonate was chosen because it had been successfully used in TATP microspheres, and a cleaning method had already been developed. The pre-cleaning process consisted of heating the polycarbonate in vacuum oven at 120°C for three days to ensure a clean chromatogram, free of small hydrocarbons.

FTGA-IR (thermogravimetric analysis with infrared detector) was used to determine the success of explosive encapsulation. If the core material (the explosive) was encapsulated within the shell and was released on heating without polymer breakdown, then a single mass loss would be observed in the thermogram. As the temperature of the TGA increased, the polymer would soften releasing the core material as a vapor; simultaneously the sample mass would decrease.

The TGA-IR method consisted of heating about 10 mg of sample at a rate of 20°C/min to 300°C. The evolved gases were carried through a transfer line to an infrared spectrometer for vapor analysis. To compare the vapor released from the spheres, the spectrum of pure ETN was run by the same TGA-IR method used to characterize the microspheres. The temperature of the transfer line, which connects the TGA to the IR, had to be optimized to maintain ETN in the vapor phase but to prevent any further decomposition. Temperatures from 80°C to 160°C were tested, but 120°C was considered the optimum temperature. The transfer line was held at 150°C for TNT, but this requires further optimization.

The thermogram of a polycarbonate ETN microsphere only showed one mass loss around 190°C (Figure 1). The solvent used in the synthesis, dichloromethane (DCM), was completely evaporated during the cleaning/baking process, because no mass loss around the boiling point of DCM (39.6°C) was observed. No mass loss for the polymer should be observed in the TGA analyzed range because polycarbonate does not decompose below 300°C. Furthermore, blank microspheres, made of only shell material (polymer), do not show any mass loss, indicating the cleaning process was effective. The mass loss observed, which correlates to the IR spectrum around 11 min, matches the ETN spectrum. Figure 2 shows the overlaid infrared spectra of polycarbonate ETN microspheres vapor (blue) at 10.974 min and of pure ETN vapor (red), indicating that the spheres are releasing only ETN, the desired result!

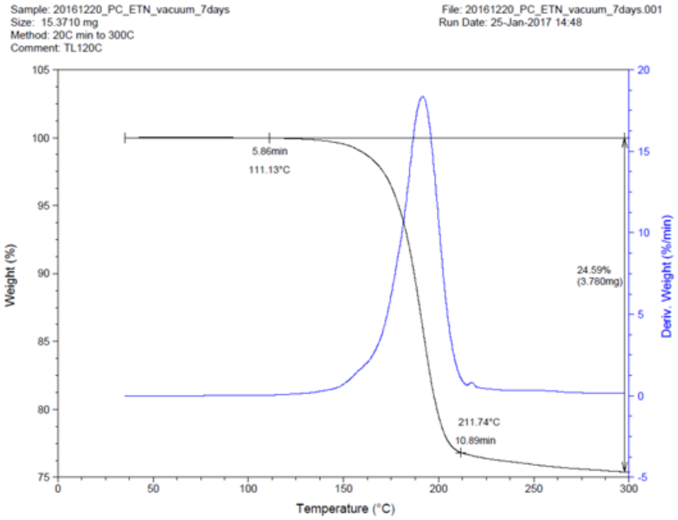

Figure 1: TGA thermogram of a polycarbonate ETN microsphere

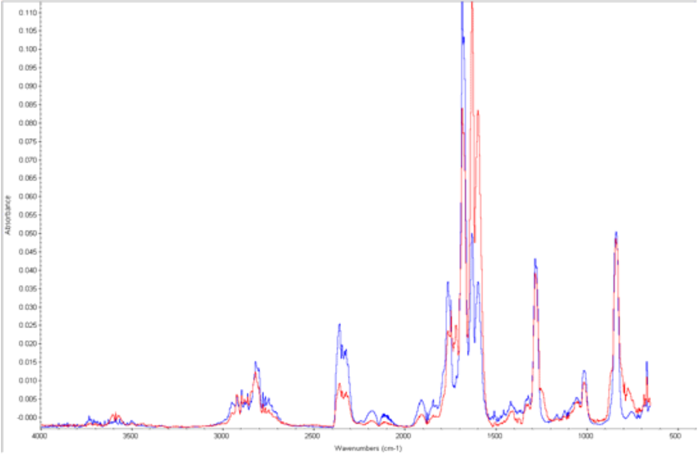

Figure 2: Infrared spectrum of a polycarbonate ETN microsphere

The vapor of the microspheres was further analyzed by mass spectrometry (MS). About 50mg of the polycarbonate ETN microspheres was heated in a sealed headspace vial at 150°C for 1min. The headspace vapor was collected using a 1mL syringe and dissolved in 500uL of a 50:50 mixture of acetonitrile and buffer solution (10mM ammonium acetate, 10mM ammonium chloride, and 0.1% formic acid). The mixture was infused directly into the MS at a flow rate of 10uL/min using ESI- mode. The spectrum collected is shown in Figure 3. The peak at m/z 336.9656 corresponds to the $[ETN+Cl]^-$ adduct. The larger peak at m/z 363.9344 corresponds to the $[ETN+NO_3]^-$ adduct. The data shows that ETN did not decompose during the microspheres synthesis by solvent evaporation, or during the heating process to release the vapor from the spheres, indicating that the polycarbonate microspheres achieved a controllable release of the ETN vapor.

In our lab, gas chromatography mass spectrometry (GC-MS) is usually used to characterize the vapor released by the microspheres, but ETN decomposes in the inlet when it is injected into the GC. For that reason, direct infusion was used to identify the intact molecule of ETN. Although the IR analyzed the vapor released from the microspheres, further tests with chromatographic separation were needed to confirm no other gases were being released with ETN.

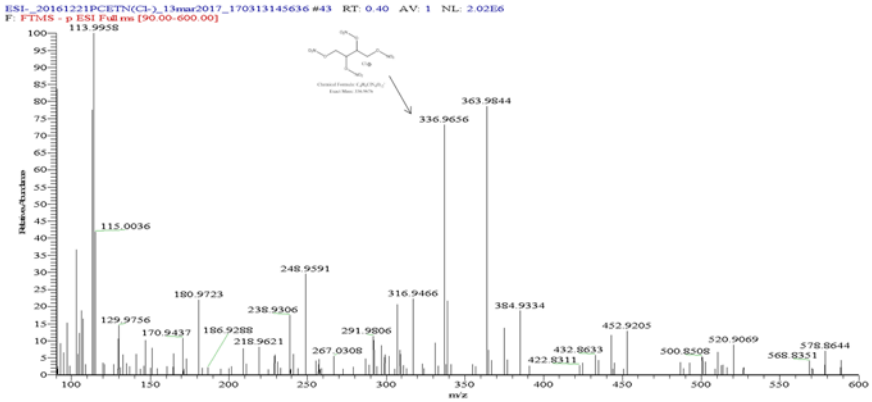

Figure 3: Mass spectrum of a polycarbonate ETN microsphere vapor

The thermogram of a polycarbonate TNT microsphere is shown in Figure 4. The thermogram shows two mass losses. No mass loss for the polymer should be observed in the TGA analyzed range because polycarbonate does not decompose below 300°C. Both mass losses are likely from the core material, which could be degrading during the encapsulation process or contaminated with other synthesis by-product. The IR vapor cell did not collect enough gas for a significant signal to be acquired, so no spectral data to identify the released compounds was obtained.

Dinitrotoluene (DNT) is usually found in TNT and can be considered a permanent contaminated in the headspace. [4] DNT has a higher vapor pressure than TNT; thus, it could be the material being released in the first mass loss. [5] The long mass loss from 150°C to 300°C is questionable. The melting point of TNT is 80.65°C. [6] TNT could be melting and slowly being vaporized throughout the heating range. However, ETN also melts at low temperature, and this issue was not observed. [6]

The synthesis and cleaning process of the TNT microspheres needs further improvement to ensure the presence of only one mass loss in the TGA and a clean TNT odor.

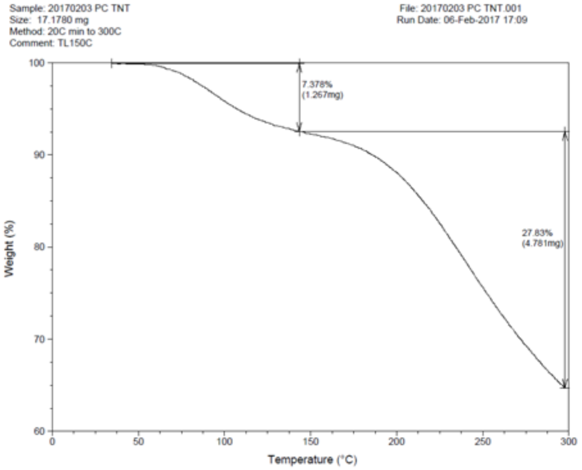

Figure 4: TGA thermogram of a polycarbonate TNT microsphere

Because there was concern about solvent lingering from the emulsion encapsulation technique, supercritical carbon dioxide (CO_2) was examined as an additional solvent to ensure the removal of the encapsulation solvent, e.g. DCM. The Supercritical Anti-Solvent (SAS) procedure consists of dissolving the polymer and explosive in a nonpolar solvent, e.g. DCM. The solution is slowly pumped into a chamber into which supercritical CO_2 is constantly being pumped. As CO_2 pumped through the chamber, the nonpolar solvent exits the chamber dissolved in the CO_2. As the solvent is removed by the CO_2, the polymer explosive sphere precipitates from solution. The adjustable parameters in this process are the concentration of the polymer explosive solution, the flow rate of the solution into the supercritical chamber, the pressure of the CO_2 chamber, and the temperature of the CO_2 chamber. Each of these will have to be optimized to obtain the best results.

Various explosives, e.g. HMTD, TATP, ETN and TNT, have been tested at various concentrations with polycarbonate as the polymer and DCM as the solvent. Figures 5 and 6 shows thermograms of polycarbonate HMTD microspheres made through the SAS method. In both cases, polycarbonate and HMTD were dissolved in DCM and flowed at a rate of 0.5mL/min into the supercritical CO_2 chamber containing 10mL of water. The instrument settings were as follows: CO_2 flow rate was 20g/min; the electric heat exchanger temperature was 80°C; reaction vessel heater temperature was 75°C; cyclone heater temperature was 10°C; and pressure was 150 bar. The thermogram in Figure 5 shows a single mass loss of 6.5%, indicating successful encapsulation, while the thermogram in Figure 6, which should have been identical, shows only mass loss of 1.4% and possibly a two-step loss. Thus, reproducibility is presently an issue.

The use of supercritical CO_2 is a clean method to create microspheres; however, many parameters still need to be optimized to produce a reliable microsphere.

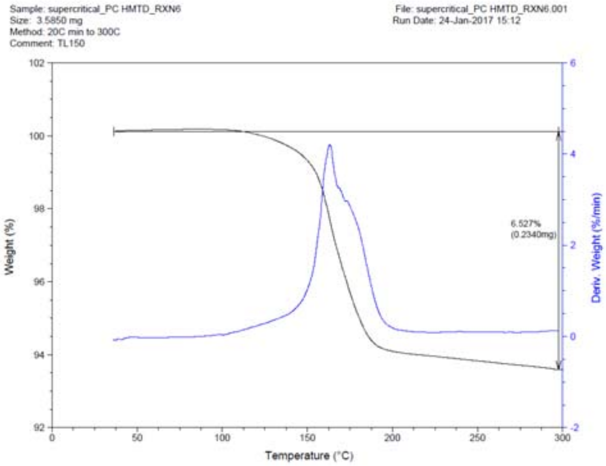

Figure 5: TGA thermogram of a polycarbonate HMTD microsphere made by the SAS method

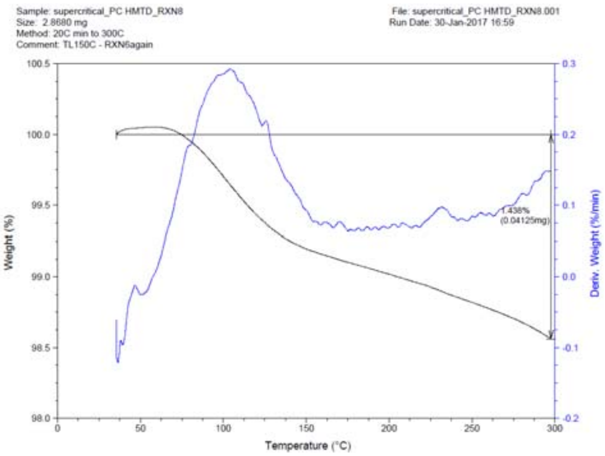

Figure 6: TGA thermogram of a polycarbonate HMTD microsphere made by the SAS method (same procedure used in Figure 5)

Major Contributions

This year has resulted in 2 papers authored at the University of Rhode Island (URI) [a,b], and five papers from our partners at two minority-serving-institution (MSI) [h,k,l,m,n], as well as a provisional patent [1]. Both our MSI partners and our group have been awarded further Department of Homeland Security (DHS) funding for certain aspects of this research. This work has also resulted in a graduate student award, three PhD students (Dec 2016, May 2017, May 2017), two working at TSL and Tyndall AFB, and partnerships with three vendors supporting trace explosives detection.

In developing metrics and tools to judge explosive-polymer compatibility, atomic force microscopy (AFM), and micro-calorimetry were employed. Three papers have resulted from this work (ye**ars 1-3**) as well as a graduated and employed Ph.D student (Dec. 2016). Atomic Force Microscopy (AFM) was used as a way to measure the adhesive forces between 7 polymer and 8 energetic materials. Though Teflon was the least adhesive polymer for every energetic tested, no discernible preference among the other polymers could be established. Furthermore, despite wide chemical variations in the energetic materials attached to the AFM tip, little bias for one energetic over another was observed. The lack of superior adhesion to one polymer over another is attributed to the effect of bulk properties, such as particle size, roughness, and contact orientation/angle, during force curve collection.[7]

Safe-scent aids have progressed over the last four years from learning how to encapsulate TATP and what to encapsulate it with and how to evaluate the results. We have a good product for HMTD and an acceptable, but not perfect one for ETN.

The sampling techniques required by current swabs are inefficient and invasive. To counteract inefficient pick-up, 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 either adhere well and release it poorly, or adhere poorly, but release it well. Both aspects are important to adequate delivery of analyte to a detector system. An adhesion tunable surface controlled by a small electric charge (less than that of a 9V battery) or by a thermal stimulus could be a major accomplishment.

Switchable swab would attract explosive particles from about 3 cm away from the contaminated surface. This prevents the need for actual physical contact with a surface, and therefore speeds up the sampling process; provides for greater privacy; possibly increases the overall swab lifetime; and perhaps minimizes collection of certain types of interfering compounds. These advantages, coupled with higher pick-up 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 pick-up; a successful material in this area may serve as a pre-concentrator.

Our approach to creating CT simulants for liquid explosives proved to be transferable from a system based on X-ray scatter to two different CT-systems. However, a number of issues have been encountered with solid explosives, especially those readily subject to different packing densities. (It should be noted that this is a problem with the actual explosives.) This project resulted in one PhD graduate who will go to the DHS lab at Tyndall AFB to pursue similar projects (May 2017).

Milestones

- Swab work has shown PETN, TNT, RDX pick-up is enhanced by non-contact swabbing with an electrostatically enhanced Nomex swab, regardless of the substrate (about 13 substrates were investigated). Furthermore, we believe the techniques developed in this study offer rigorous protocols for evaluating and comparing swabs. This work has resulted in the completion of a Master’s degree.
- Evaluation of other commercial swabs, such as Teflon-coated fiberglass, is in progress as is evaluation of pickup of the ionic species potassium chlorate.
- TATP safe-scent training aids have received DOT approval for shipping as non-explosive. Patenting and licensing issues remain. Surprisingly, there appears to be demand for similar training aids of more traditional explosives, e.g. TNT, RDX PETN. Year 4 addressed the challenges of creating training aids for TNT and for the homemade explosive ETN (erythritol tetranitriate). ETN and TNT are particularly challenging explosives to encapsulate since they decompose at such low temperatures. (ETN stability was examined under Project R1-A.1.) The use of supercritical CO_2 will be investigated in depth.
- ETN mixtures with a number of other explosives were examined. The idea was that these mixtures might be more stable than ETN itself, or that ETN-TNT mixtures might be more stable than PETN-TNT mixtures. It was shown that ETN-TNT eutectics could be made, but thermal stability has not yet been assessed. One paper has resulted from this work and one PhD graduate (May 2017).
- Our approach to creating CT simulants for liquid explosives proved to be transferable from a system based on X-ray scatter to two different CT-systems. However, a number of issues have been encountered with solid explosives, especially those readily subject to different packing densities. (see paper-reference b).

Future Plans

This year and a subsequent year, will work toward creating a complete suite of canine training aids. This will allow dog trainers as well as vendors of explosive trace instruments the option to work without need of bulk quantities of explosive materials; a huge advantage. Presently vendors must pay exorbitant prices for dilute solutions of explosives or attain an ATF license and purchase storage magazines and the bulk explosives. Canine trainers often travel with their canine partner and bulk explosives in their vehicles. Aside from cross-contamination of explosive types, this is a safety issue, and could be a security one.

- The safe-scent training aids will be extended to cover the entire suite of TSA explosives which must be detected by Explosive Trace Detectors (ETDs). The difficulty will be that each explosive may require a unique polymer and encapsulation method. This year, two of our employees are in the process of attending encapsulation training courses. New instrumentation may also be required if our present emulsion methodology does not apply to the required polymers.
- The enhanced swab idea will be taken to the point that a device for charging is available for use at the check-point, and protocols for use will be documented and tested. Questions to be answered include charge-on-swab versus explosive pickup; what effect touching the surface; to what extent are background contaminants eliminated.
- Our attempts to stabilize ETN for safe transport and storage will continue. Binders and encapsulants will be investigated, not with the idea of use in canine aids, but from the idea of enhanced thermal stability and insensitivity.
- Controlling packing density, we will examine the X-ray characteristics of a few fuel/oxidizer explosives (FOX). The long-term goal is to investigate the potential of simulants; the short term is to assess the flexibility required in CT algorithms to allow detection.
- Coating and encapsulation of materials will continue to be of interest. Not only will we investigate encapsulation of energetic materials, but the encapsulation of potential additives to energetics will be investigated. For example, we have shown that the 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, 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 which can be removed or softened by heating; hence, the need for metrics.

II. RELEVANCE AND TRANSITION

Relevance of Research to the DHS Enterprise

Progress in both the electrostatically enhanced swabs and the canine training aids has advanced sufficiently that their benefit to the Transportation Security Administration (TSA) is obvious. Swabs, which obviate the need for vigorous rubbing of the surface, speed sampling, provide greater privacy, increase swab lifetime, and minimize collection of interfering compounds. These advantages, coupled with higher pick-up and release efficiencies, will make for speedier, more amenable, and more economical checkpoint operations while improving trace detector performance.

The safe-scent aids will allow dog trainers as well as vendors of explosive trace instruments the option of working without needing to maintain bulk quantities of explosive material. This would be a huge advantage. Presently vendors must pay exorbitant prices for dilute solutions of explosives or attain an ATF license and purchase storage magazines and the bulk explosives. Canine trainers often travel with their canine partner and bulk explosives in their vehicles. This is a safety issue and could be a security one. Canine training aids are already in limited use at a number of facilities. The first shipment of these to customers is expected this summer.

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