

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

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II. PROJECT DESCRIPTION

A. Project Overview

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

- Approach 1: Using homemade explosives (HMEs) that are FOX mixtures. We have characterized their responses to small-scale tests and are in the process of seeking a correlation to modest-scale detonation testing;
- Approach 2: Applying fundamental tandem mass spectrometric (MS) techniques to discover possible relationships between collision-induced fragmentation energies and specific properties of explosives;
- Approach 3: Developing a new way to characterize the shock/detonation front using unique probes to aid in the examination of the growth to detonation vs. shock attenuation at small-scale; and
- Approach 4: Solicited other groups to join the effort due to the difficulty of the task.

This year, Approaches 1 and 3 came together. As seen in many cases, including the 2013 Boston Marathon bombing, improvised explosives may be as simple as a FOX mixture initiated by a hot wire. The knowledge of large-scale explosive potential of FOX mixtures is incomplete. Predicting this explosive potential from small-scale test data is highly desirable. Herein, the explosive properties of FOX mixtures 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 trinitrotoluene (TNT) equivalence measured at the large-scale as well as 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 features; the molecule must be able to react by 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 us to predict whether heat and gas can be produced. This aspect is investigated in Project R1-A.1. Under that task, the thermal behaviors of 11 solid oxidizers in combinations with 13 fuels were determined using differential scanning calorimetry (DSC), a technique requiring less than a milligram of material [1]. Many are considered FOX 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 for the collection of heat-release and pressure-rise data versus time as the formulation of interest was 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 on the next page indicates that some high explosives stand out 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).

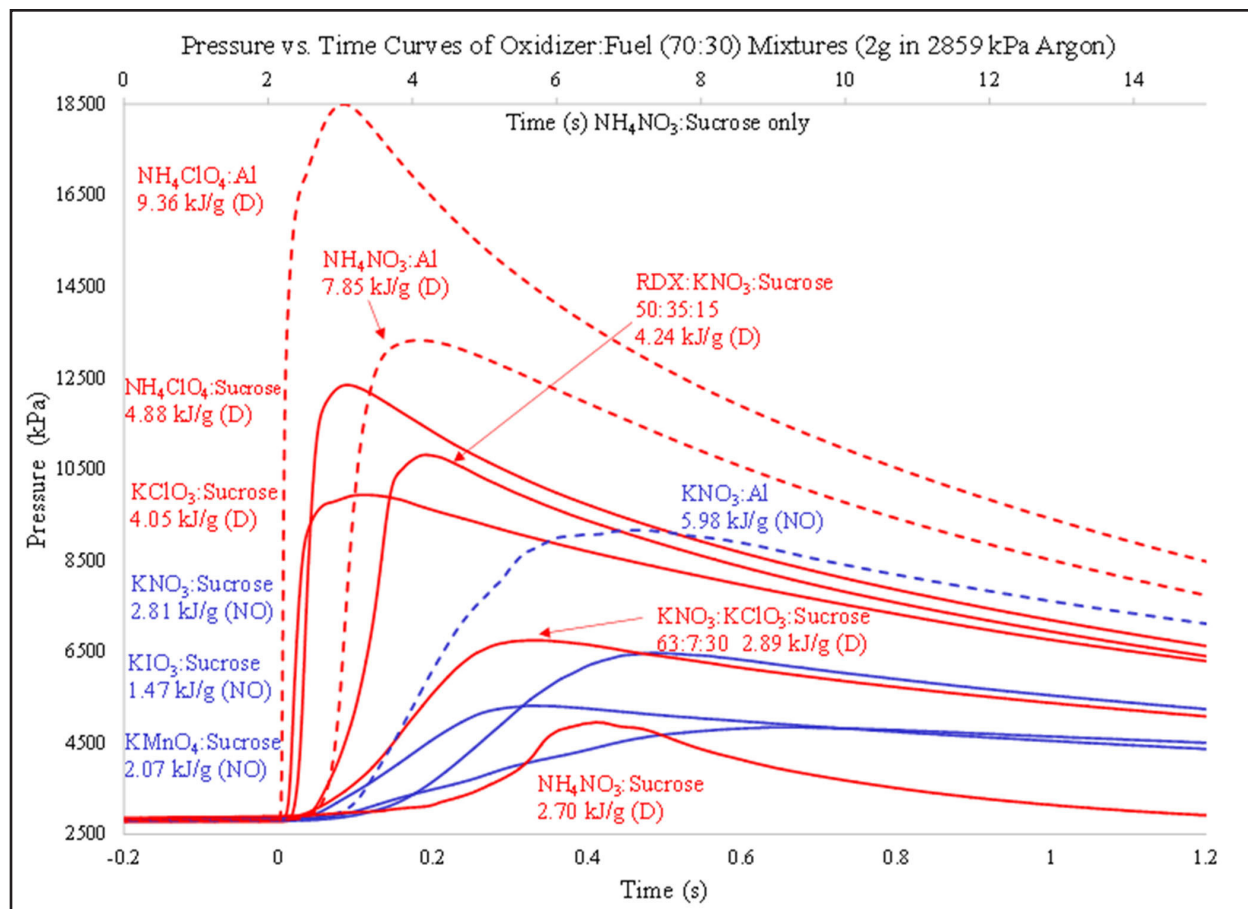


Figure 1: Pressure produced in 2g burn (400 psig argon) of FOX vs seconds with color indicating 5 kg results (red = detonation; blue = no detonation).

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, in addition to 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 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 on the next page. 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.

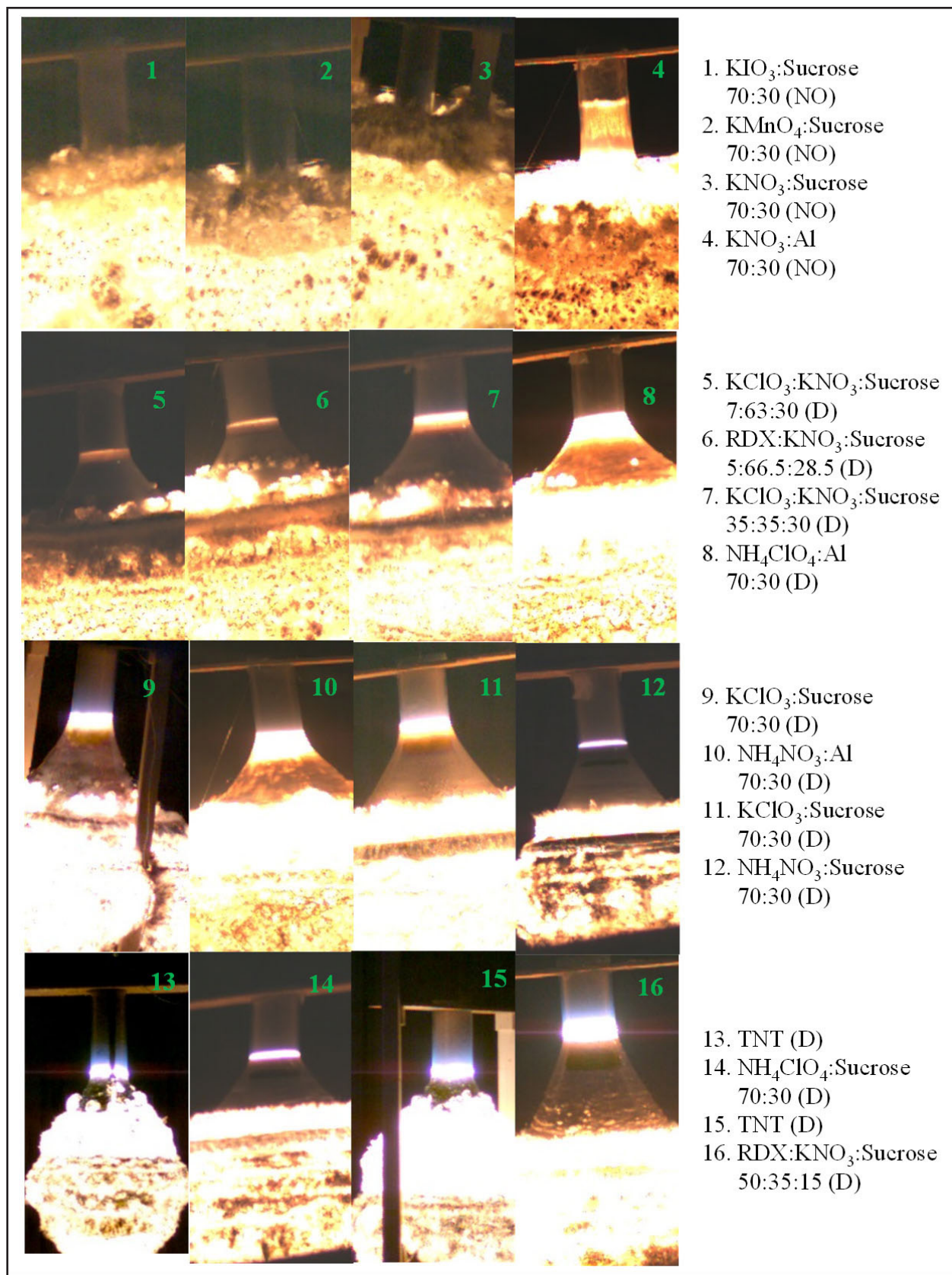


Figure 2: High-speed camera images of reactions of 16 FOX mixtures.

Approach 2: Energy Resolved Mass Spectrometry (ERMS) is a term used to describe a process of increasing kinetic energy input into a trapped ion to determine the energy required for that material to fragment. ERMS probes one of the fundamental molecular properties—dissociation energies during gas phase ion impact with an inert gas. 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 (see Table 1).

Stable compounds	Onset (eV)	Total (eV)	Explosive compounds	Onset (eV)	Total (eV)
Oxcarbazepine	11.0	6.6	RDX	0.3	7.9
Phenytoin	11.6	6.0	HMX	0.6	7.5
Phenolphthalein	13.4	5.6	Tetryl	3.4	8.2
Diphenyl Isophthalate	10.8	5.4	TNT	11.5	8.8
Ethyl Centrilit	7.8	8.1	FOX-7	8.7	9.1
Michler's Ketone	13.8	8.7			
Dimedone	16.9	9.1			
Hexamine	10.5	9.0			
Average	12.0	7.3	Average	4.9	8.3

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

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

The following is a comment we received from an 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 triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (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 liquid chromatography with mass spectrometric (LC/MS) solvent acetonitrile is present.

C. State of the Art and Technical Approach

Approaches 1 & 3: Predicting this explosive potential from small-scale test data is desirable. The explosive properties of FOX mixtures 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 μ m flake coated aluminum (Al) powder from Obron, and a 5 μ m magnesium powder from Firebox. Oxidizers were ground and sieved 100-200 mesh (150-75 μ m). Sucrose was ground with a small coffee grinder and sieved 100-200 mesh or 150-75 μ m. FOX mixtures were prepared as dry loose powders placed in plastic pop-top containers for 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 Simultaneous DSC/thermal gravimetric analysis (TGA) (SDT) were prepared similarly, using only 4 to 6 mg.

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.

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 a 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 ($\Delta H_{\text{comb}} = 26434 \text{ J/g}$). 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 that 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. The sample collection rate of 100 μs between pressure points was a 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 them with a Vita-Mix 5000 blender and sieving to 100-200 mesh (150-75 μm). Aluminum flakes (23 μm) from Obron was used as received. FOX samples of ~ kg were manually mixed in a 38 L (10 gal) plastic bag for about 2 minutes (see Fig. 3 on the next page). 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 pentaerythritol tetranitrate (PETN) explosive, which had been cut into circle shapes 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 (see Fig. 4 on the next page) 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 (see Fig. 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: Preparation of booster and assembled test device.

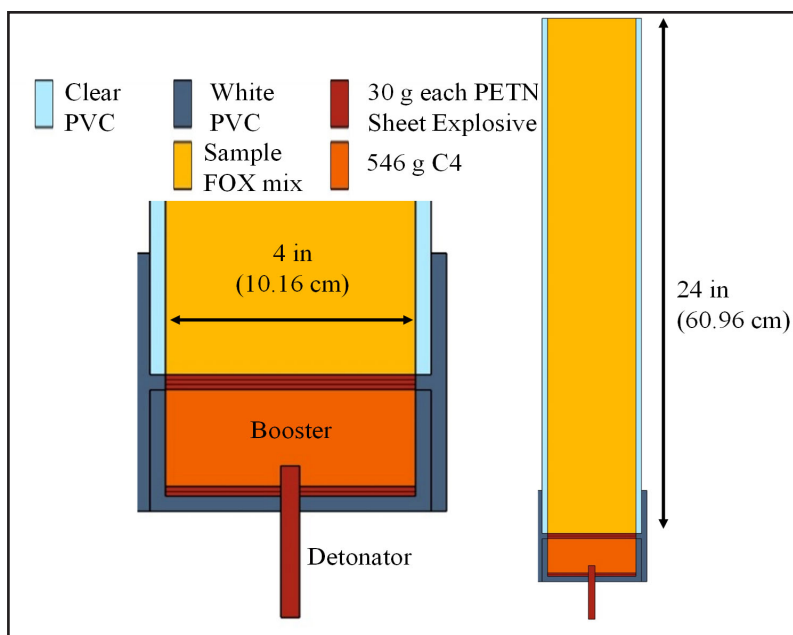


Figure 4: Schematic of booster setup.

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 μ s, resolution of 160 X 304 pixels, exposure of 0.4 μ s (0.29 μ s exposure for aluminum mixtures), 1 s of pre-trigger, and 1 s of post-trigger. A twisted pair of duplex wires, 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 (see Fig. 5 on the next page). Initiation of the booster produces a significant fire ball, present even in samples that did not detonate, and is termed the “booster cloud.”

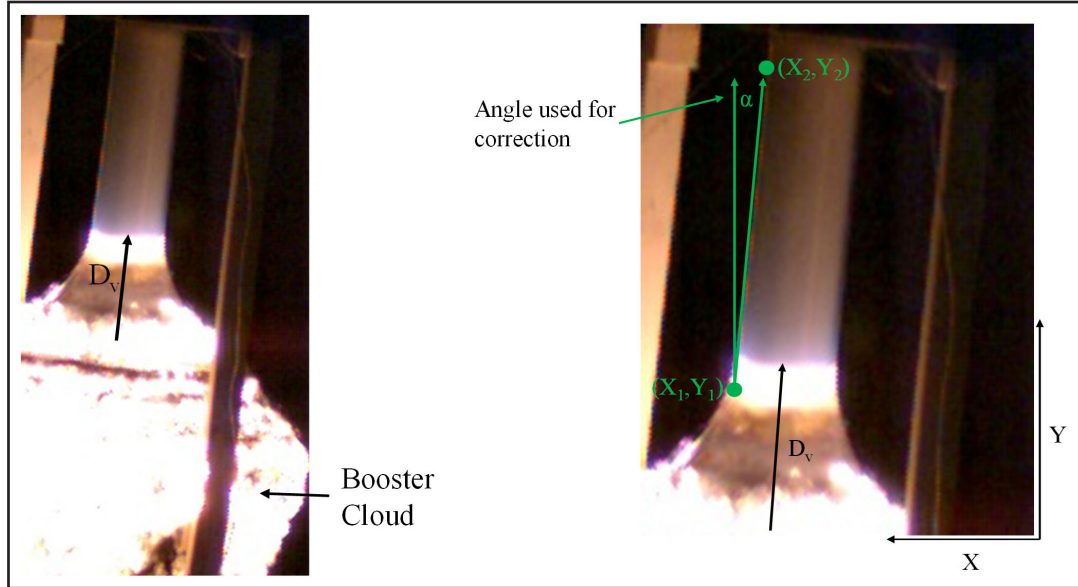


Figure 5: Illustration (70:30 KClO_3 :sucrose) of how the detonation front was used to calculate detonation velocity (D_v).

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:

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

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

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):

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

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 $\alpha = 0.116$ rad, and $Y'(t)$ can be plotted for each time point (using equation 2) to find the detonation velocity (the slope in Fig. 6 on the next page). 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.

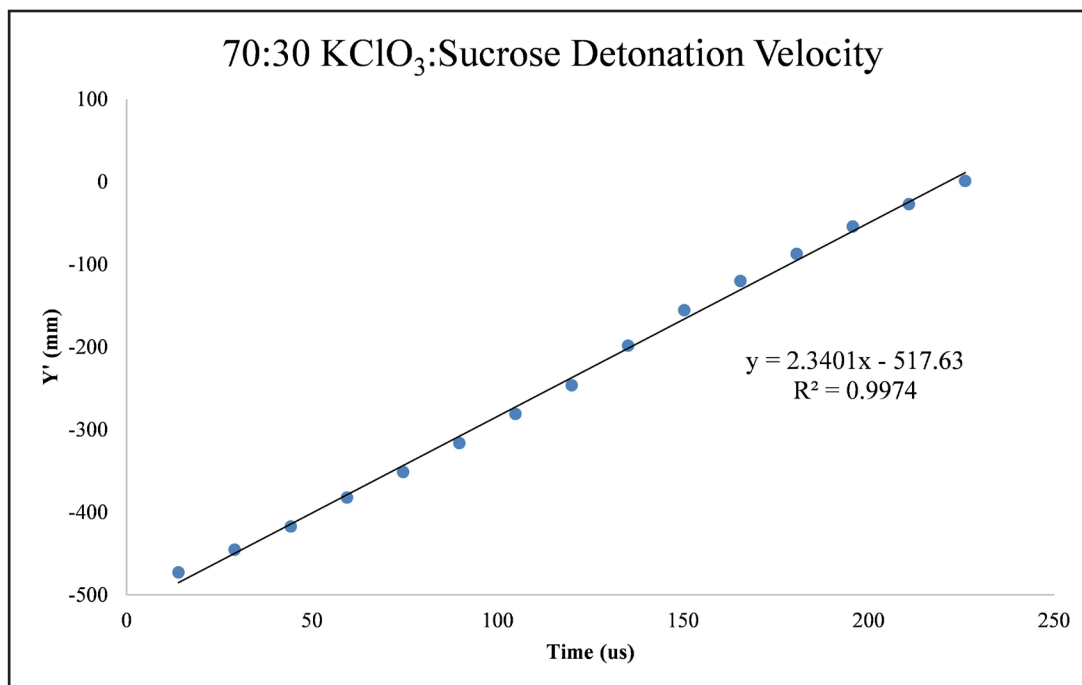


Figure 6: Detonation front tracking of rotation corrected Y' points. The slope is detonation velocity in mm/ μ s.

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, as well as the coupler to a Tektronix oscilloscope. The pencil gauge was mounted 1.29 m high, and was 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.

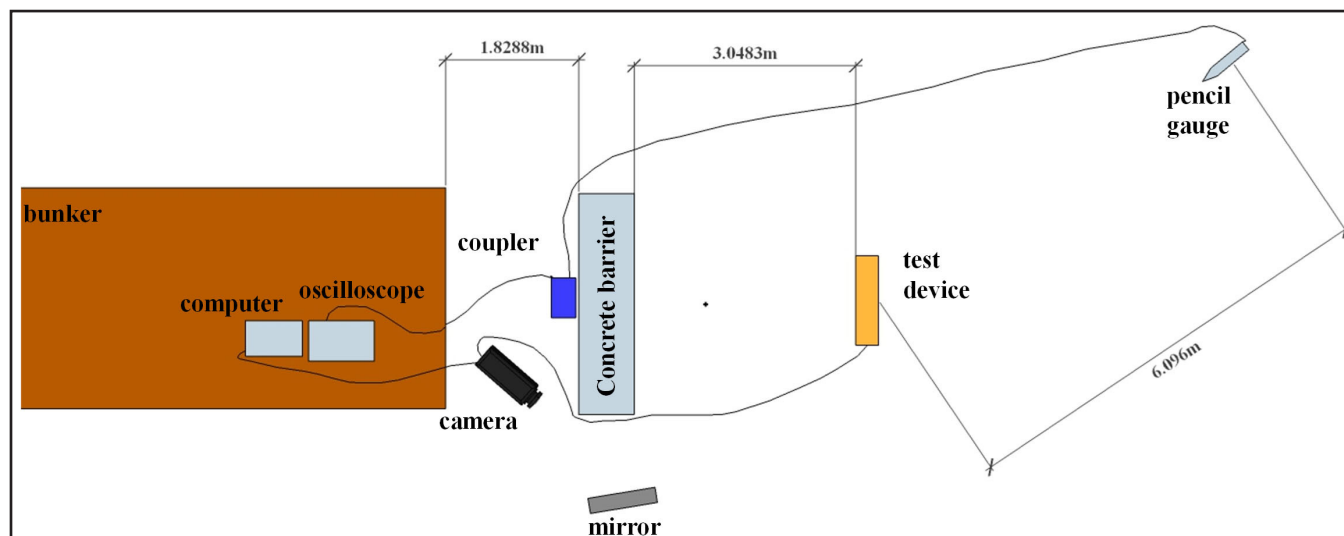


Figure 7: Overall test arena setup.

Predictive tools: Cheetah 7.0 from Lawrence Livermore National Laboratory (LLNL; 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 [6-8]. 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).

C.1. 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 (AN) and potassium nitrate (PN) with sucrose were significantly delayed compared to other FOX (see Fig. 1) explosives. 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 of Table 2 on the next page) and heat of reaction observed in the 2 g Parr bomb samples (penultimate right column of Table 2), 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, resulting in 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 (see Table 3 on the following page). Other fuel/oxidizer mixtures were also examined in the Parr bomb (Table 3). In terms of energy output, neither the thermites nor the gun propellants released more energy than the FOX mixtures examined.

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
K ₂ Cr ₂ O ₇ , 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
KMnO ₄ , Sucrose 70,30	641	5%	1985	2%	3.1	3%	2.07	0%	1.80
KIO ₃ , Sucrose 70,30	334	13%	2514	3%	7.6	15%	1.47	1%	0.84
KNO ₂ , Sucrose 70,30	509	19%	2702	3%	5.4	20%	2.61	3%	1.69
KNO ₃ , Sucrose 70,30	509	3%	3685	1%	7.2	3%	2.81	1%	0.68
KClO ₃ , KNO ₃ , Sucrose 7,63,30	332	2%	3928	2%	11.8	3%	2.89	2%	
KIO ₄ , Sucrose 70,30	183	10%	3931	3%	21.6	9%	2.11	0%	1.81
RDX, KNO ₃ , Sucrose 5,66.5,28.5	479	4%	4186	1%	8.8	5%	2.93	2%	
KClO ₃ , KNO ₃ , Sucrose 17,53,30	248	13%	4369	3%	17.9	17%	3.04	1%	
RDX, KNO ₃ , Sucrose 10,63,27	401	7%	4509	3%	11.3	6%	3.11	1%	
KClO ₃ , KNO ₃ , Sucrose 35,35,30	148	12%	5580	3%	38.1	10%	3.41	1%	
KBrO ₃ , Sucrose 70,30	78	8%	5873	6%	76.0	13%	2.77	2%	1.72
KClO ₄ , Sucrose 70,30	187	15%	7060	10%	38.5	21%	4.65	0%	0.87
KClO ₃ , Sucrose 70,30	104	21%	7150	7%	72.6	29%	4.05	0%	2.09
RDX, KNO ₃ , 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
K ₂ Cr ₂ O ₇ , Al 70,30	474	7%	3261	6%	6.9	13%	4.18	1%	0.00
KNO ₂ , Al 70,30	696	21%	4370	14%	6.5	31%	5.20	8%	2.40
KMnO ₄ , Al 70,30	254	8%	5089	9%	20.1	10%	5.31	2%	0.73
KIO ₃ , Al 70,30	241	38%	5682	8%	26.6	46%	4.94	0%	0.49
KNO ₃ , Al 70,30	403	13%	6307	1%	15.8	12%	5.98	3%	1.30
KIO ₄ , Al 70,30	153	30%	8301	5%	58.6	38%	6.32	1%	0.17
KClO ₄ , Al 80,20	75	19%	9578	5%	132.6	26%	5.11	1%	0.80
KBrO ₃ , 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
KClO ₄ , Al 50,50	135	17%	11045	1%	84.0	19%	8.22	1%	
KClO ₃ , Al 70,30	96	11%	11929	5%	126.3	15%	7.18	5%	1.50
KClO ₄ , Al 70,30	78	18%	12272	3%	161.6	20%	7.52	1%	
KClO ₄ , 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									
KNO ₃ , NaBenzoate 70,30	471	7%	3045	2%	6.5	8%	2.25	2%	
KClO ₃ , NaBenzoate 70,30	64	6%	6815	2%	105.8	4%	3.19	1%	
KClO ₄ , 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: Bomb calorimetry outputs from FOX 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
Thermites								
Fe ₃ O ₄ , Mg 80,20	1501	9%	424	10%	0.3	19%	2.12	0%
Fe ₃ O ₄ , Mg 70,30	1322	3%	970	7%	0.7	9%	3.22	1%
Fe ₃ O ₄ , Mg 60,40	1043	17%	1539	3%	1.5	16%	3.73	0%
Bi ₂ O ₃ , Al 70,30	288	13%	1810	8%	6.3	4%	1.75	1%
Bi ₂ O ₃ , Al 90,10	210	50%	2277	12%	12.8	46%	1.61	1%
Bi ₂ O ₃ , 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%

Table 3: Parr bomb calorimetry output for thermites vs. gun propellants.

Detonation testing: Table 4 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 on the next page shows KNO₃:sucrose as an example of a mixture which failed to support detonation. Figure 8 also shows KNO₃: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 on the next page shows an enlarged picture of three FOX mixtures known to be improvised explosive mixtures which detonated (NH₄NO₃:sucrose, NH₄NO₃:Al, and KClO₃:Sucrose) as well as an example of one which did not detonate (KMnO₄:sucrose).

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)	Δ P (psi)	Δ P/ Δ t (psi/ms)	Δ P (kPa)	Δ P/ Δ t (kPa/ms)	Phantom V7.11 Det Velocity (km/s)	Peak Airblast Δ P 20ft (psi)	Peak Airblast Δ P 20ft (kPa)
70:30 KIO ₃ :Sucrose (no Det)	6.833	1.49	352	1.47	365	1.11	2517	7.7	0.00	7.90	54.43
70:30 KMnO ₄ :Sucrose (no Det)	5.216	1.10	494	2.07	228	0.45	1572	3.1	0.00	6.47	44.57
70:30 KNO ₃ :Sucrose (no Det)	4.711	0.97	672	2.81	534	1.05	3682	7.2	0.67	8.20	56.54
70:30 KNO ₃ :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 KClO ₃ :KNO ₃ :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:KNO ₃ :Sucrose	4.254	0.88	701	2.93	607	1.27	4186	8.8	1.77	12.06	83.12
35:35:30 KClO ₃ :KNO ₃ :Sucrose	4.768	1.01	815	3.41	809	5.53	5578	38.1	2.24	14.97	103.18
70:30 NH ₄ ClO ₄ :Al	3.132	0.69	2238	9.36	2293	28.97	15813	199.7	2.24	16.32	112.49
70:30 KClO ₃ :Sucrose	4.788	0.99	967	4.05	1037	10.53	7150	72.6	2.34	16.70	115.14
70:30 NH ₄ NO ₃ :Al	3.140	0.68	1876	7.85	1504	7.85	10367	54.1	2.70	18.60	128.24
70:30 KClO ₃ :Sucrose	5.246	1.10	967	4.05	1037	10.53	7150	72.6	3.07	14.80	102.04
70:30 NH ₄ NO ₃ :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 NH ₄ ClO ₄ :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:KNO ₃ :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											

Table 4: Detonation testing summary.

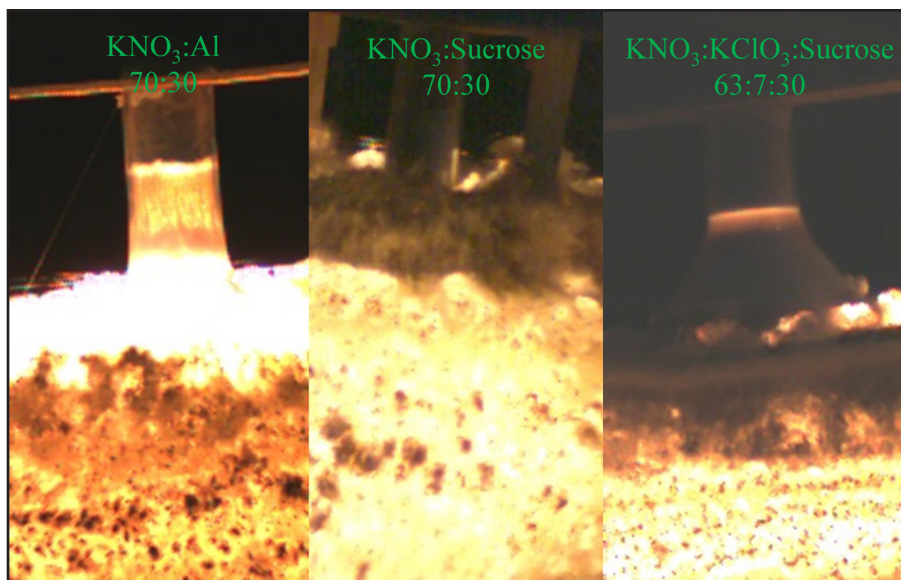


Figure 8: KNO₃:Al transitioned to burn; KNO₃:sucrose failed to propagate; KNO₃:KClO₃:sucrose 63:7:30 detonated.

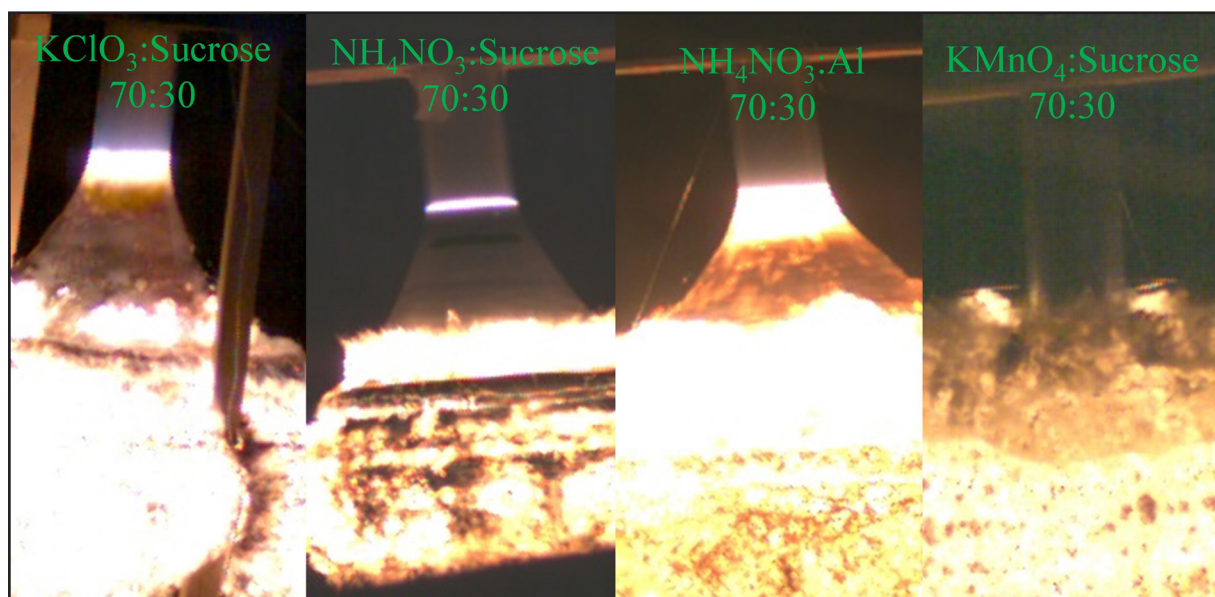


Figure 9: Detonation tests showing three steady detonations (left three) and one which failed to propagate (right).

C.2. 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 5 (on the next page) 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.

Clear PVC pipe Shots (4" Dia x 24" L)					Detonation		Air Blast Calculations					Cheetah Predictions			
Mixture	Density (g/mL)	Heat (kJ/g)	ΔP (psi)	$\Delta P/\Delta t$ (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 KIO ₃ :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 KMnO ₄ :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 KNO ₃ :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 KNO ₃ :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 KClO ₃ :KNO ₃ :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:KNO ₃ :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 KClO ₃ :KNO ₃ :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 NH ₄ ClO ₄ :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 KClO ₃ :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 NH ₄ NO ₃ :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 KClO ₃ :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 NH ₄ NO ₃ :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 NH ₄ ClO ₄ :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:KNO ₃ :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															

Table 5: Detonation testing summary with analysis.

Cheetah, a 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 (see Table 5). 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; 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 (see Fig. 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]).

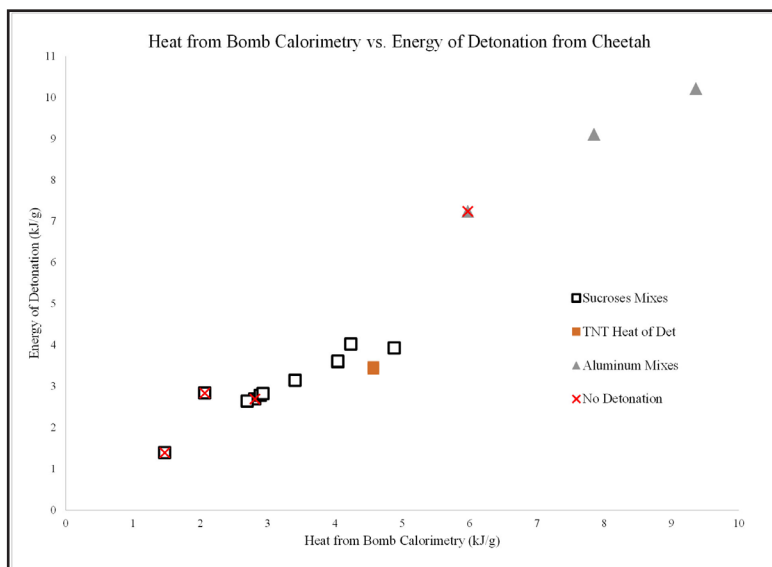


Figure 10: Heat of detonation from bomb calorimeter vs cheetah calculation. Error bars on x axis are too small to plot.

Observed detonation velocities tracked with 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% research department explosive (RDX)).

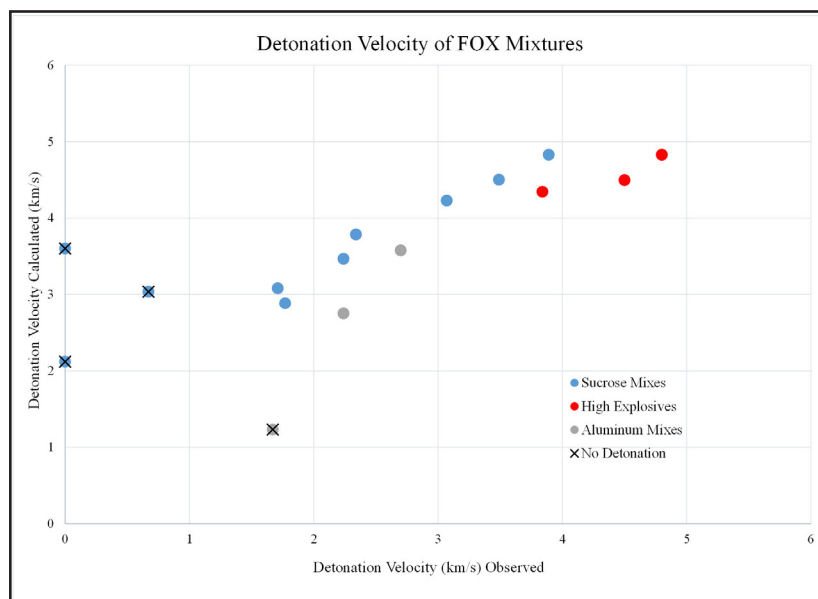


Figure 11: Observed Detonation Velocities (km/s) vs Cheetah Calculation Thereof (X failed to detonate).

Since the heat released was measured by calorimetry and the detonation velocities were measured by camera tracking with Cheetah predictions, it is not surprising that the measured heat of reaction under argon correlated with observed detonation velocities (see Fig. 12). Interestingly, the outliers (above the line on both the oxidizer/sucrose and oxidizer/aluminum formulations) are the formulations with AN. 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.

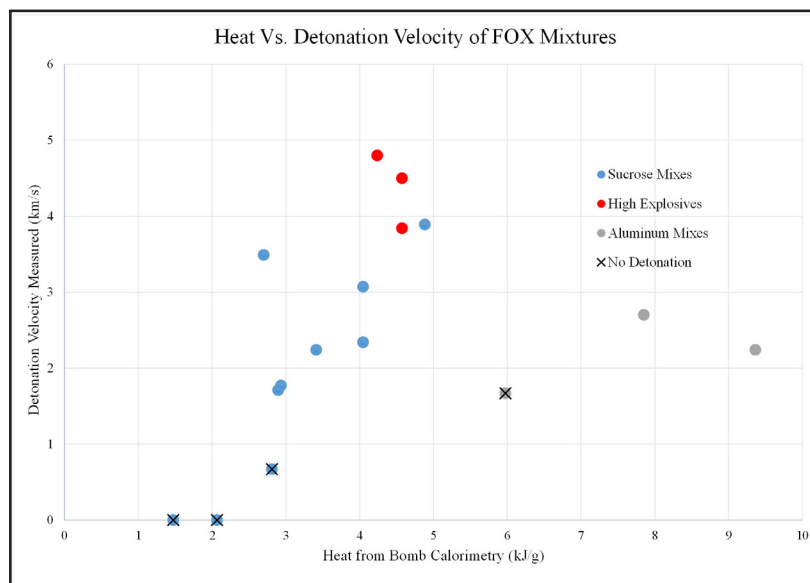


Figure 12: Heat of reaction measured by calorimetry vs. detonation velocity. x axis error bars are too small to be shown.

Figure 12 suggests there may be a minimum energy (~ 2.8 kJ/g) needed for detonation. However, the data and 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. AN 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, there is 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 (see Fig. 13).

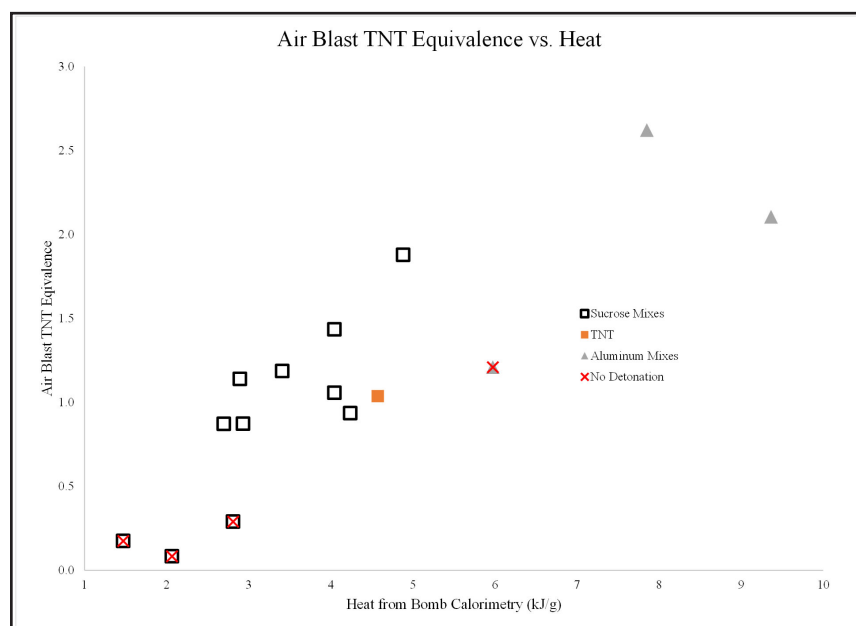


Figure 13: Air blast TNT equivalence large-scale vs. heat from 2g calorimetry. Error bars are too small plot.

C.3. Conclusions

Measurement or calculation (via Cheetah) of heat of reaction is a useful first step in determining whether a formulation is potentially detonable. It appears there is a minimum energy that a formulation must possess to be detonable. However, examination of Table 5 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 PN/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 5 is a burn, as judged by the video we recorded and discussed above. The PN/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 PN/sucrose mixtures with additives was only a little over half that of PN/Al. This observation points to the importance of the rate at which the energy is provided. Looking again at small-scale tests (see Fig. 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 that produced long time to peak pressure (> 200 ms) did not detonate at the large-scale with the exception of AN 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 FOX mixture has a 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 is in contrast to a non-ideal explosive, such as ammonium nitrate/fuel oil (ANFO), with has a reaction zone length estimated at 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.

C.3.a. Approach 2

ERMS: We are investigating ERMS for the 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]. ERMS has a potential to be used in distinguishing unknown explosives materials (EMs) 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 a combination). Then the resulting solvent mixture is introduced into a 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 the radio frequency of the alternating current (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 a couple of criteria to analyze the resulting breakdown curves shown in Figure 14 on the next page. The onset point indicates 90% of the selected ion is still intact, and the energy at that point theoretically represents *sensitivity or fragility* of the 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% represents its *stability or longevity*. We also designated the mid-point of this breakdown curve (i.e. 50%) as a quick metric to cross reference between various molecules under investigation and called it *fragmentation resilience (FR 50)*. To minimize the noise associated with the collection of raw data, which can be seen in Figure 15 on the next page, 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 a tendency to be more fragile upon application of this method, resulting in earlier breakdown onset points. We have evidence that supports this hypothesis, based on a 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 (a precursor to the synthesis of HMTD).

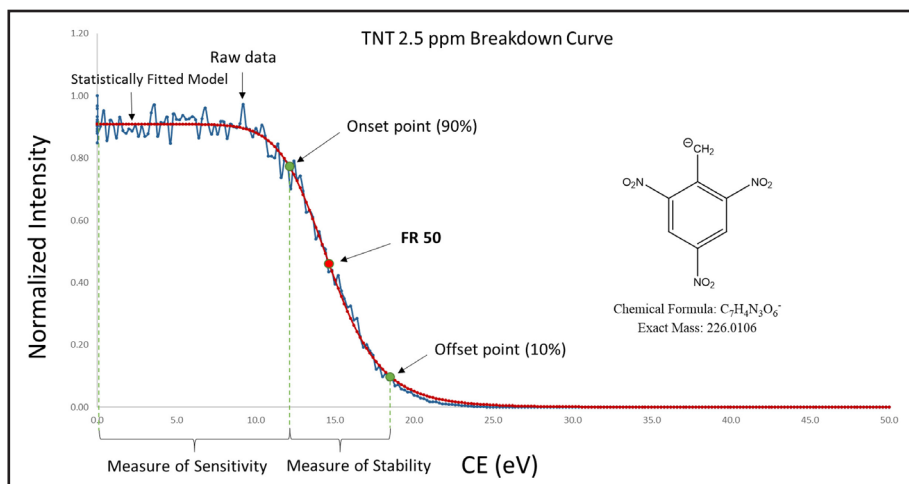


Figure 14: Breakdown graph for TNT m/z 226.01 averaged over 6 curves.

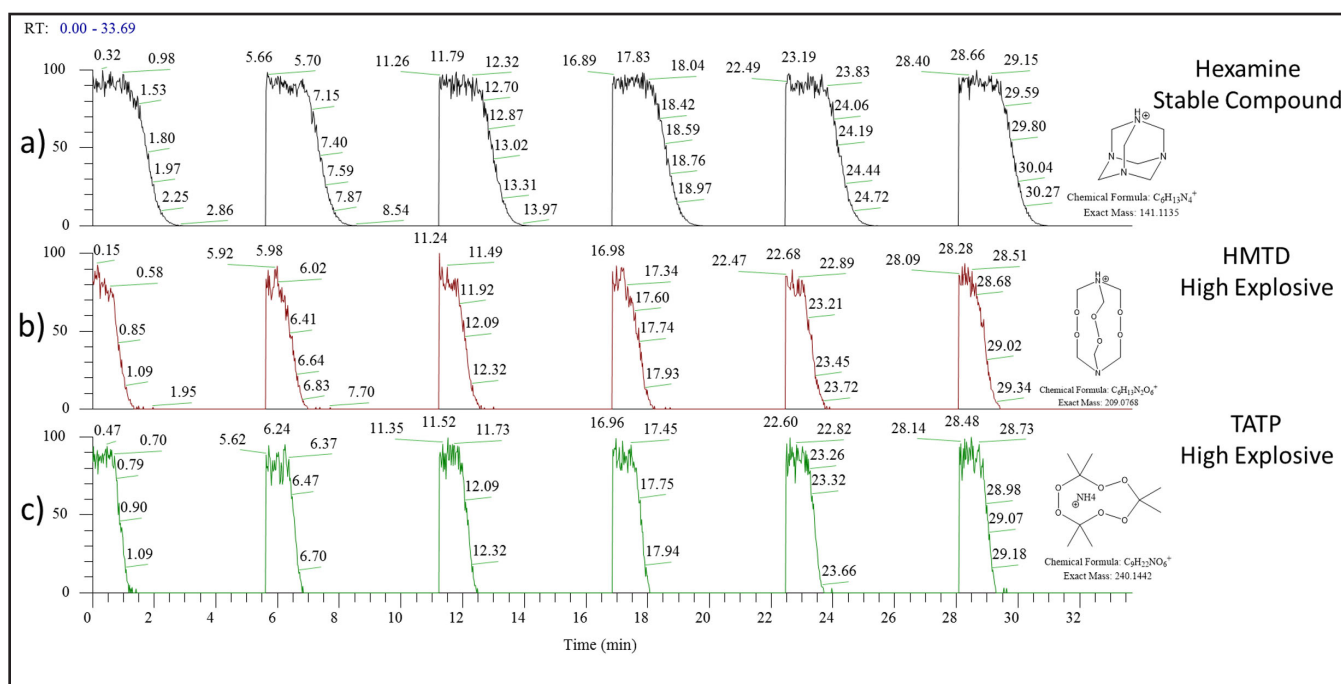


Figure 15: Energy resolved mass spectra comparison of six breakdown curves for a) hexamine (ESI+, [M+H]⁺, 10 ng/mL), b) HMTD (APCI+, [M+H]⁺, 10 µg/mL), and c) TATP (APCI+, [M+NH₄]⁺, 10 µg/mL). Each curve is acquired by increasing energy from 0 eV to 50 eV at an interval of 0.2 eV.

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 a variety of nitro-aromatic compounds because TNT, one of the most well-known explosives, belongs to this class. As can be seen from Table 6 on the next page, TNT indeed has one of the earliest onset points (indicative of sensitivity), as well as the 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 6 have multiple

entries, representing different ionization techniques that the same ion was subjected to. This gave us insight into how different ionization methods affect the stability of the same molecule, and what steps we need to take to account for that difference.

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

Table 6: Comparison of onset energies (sensitivity), total energies (stability), and FR 50 for various nitro-aromatic compounds.

C.3.b. Approach 3

To determine the tendency of a formulation to detonate, and to do so at less than 500g, we are employing two techniques: 1) high-speed photography, and 2) 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.

C.4. Configurational Challenges

Test pipe: To improve our ability to visually track the reaction, a new test fixture was created (see Fig. 16 on the next page). 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: The test pipe 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 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: The new fixture with thinner-walled pipe is aligned and held together by three, threaded rods concentrically compressing the device components into intimate and uniform contact. This method ensures that proper and reproducible pressure is applied to all components.

Booster: The booster in the new configuration was 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 (length/diameter (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. For these experiments, a 1" diameter device was preferred, but larger diameters (1.64", 2.05", and 2.55") are available for compositions that 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 affect the detonation wave structure.

C.5. 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 by 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.

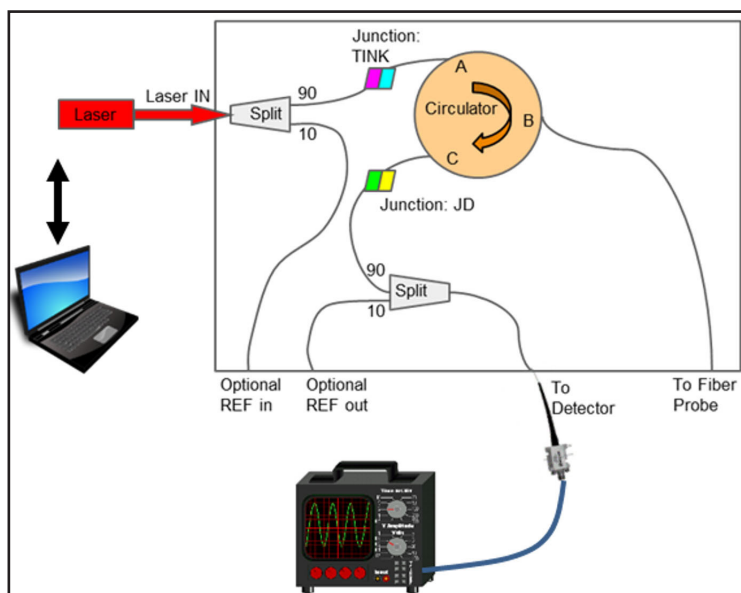


Figure 17: Setup for PDV measurements.

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; and 2) 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 Hugoniot.

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 we 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 neglected. If the reflective layer were thicker (>50 μm), these results 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: Collimators, focusing probes, and 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 diffused. 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 spreads 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 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 that returned back into the system to be detected was the 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.

D. Major Contributions

In Years 1 and 2, the thermal behaviors of 11 solid oxidizers in combinations of 13 fuels were determined using DSC, a technique requiring less than a milligram of material [1]; many are considered FOX 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 for one component of the formulation in triggering the reaction. These studies also indicated that the choice of oxidizer outweighed the choice of 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 (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 AN and sucrose (see Fig.1 and Table 4).

In Year 4, the role of aluminum in improvised explosives was dramatically shown. With aluminum mixtures, due to the slowness of the aluminum oxidation, only a fraction of the energy released was provided fast enough to support the detonation front [10]. The fuel-oxidizer mixtures have a similar problem with slow reaction rate because a significant amount of time must be spent in diffusion and compaction of the fuel and oxidizer. Therefore, the fraction of energy released to the detonation front must be significantly less in FOX mixtures than in military explosives.

Camera protocols devised for Approach 3 allowed Approach 1 to be performed this year, with all the accomplishments cited above. This is at least one year ahead of when we expect to be testing the FOX mixtures. In addition, a variety of issues were attacked and solved. Year 5 should bring this all together 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 a 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 a timely and consistent fashion. We established an MS protocol where all mass spectrometer parameters were kept the same, and we began investigations of nitro-aromatic compounds.

E. Milestones

This year gave us our first look at the potential detonability of FOX mixtures. Most interesting was the fact that, at a 4' diameter, the KNO₃/Al mixture is *almost* detonated. This makes for 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% KClO₃ make the non-detonable mixture detonable. We expect that an increase in the sample diameter would also do so. We hope to examine this possibility in Year 5. However, we face various technical difficulties in doing so. The data dramatically shows the effect of added aluminum. It important that the HSE realize that the hazard is increased blast but not increase brisance from higher detonation rates.

Approach 1: To date, nine FOX explosives or potential FOX explosives 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 to 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 that 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 in 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 efforts. A number of successful PDV end-on measurements have been conducted, but PDV use, as a continuous probe, has yet to be achieved.

F. Future Plans

Approach 1 will be extended to more FOX combinations. Due to limited time and material expenses, a relatively small number of combinations can be examined. Specific plans in Approach 1 are to examine KNO₃/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. Should Year 6 funding become available, azides will be examined.

Approach 2, ERMS, will be looking at the effect of concentration on FR 50 and also the influence of ionization mode. While the approach to date, which will be continued into Year 5, looks at electrical potential, should there be Year 6 funding, the timing will be examined to determine if this is a better method of evaluation.

For Approach 3, using PDV and/or high-speed photography, we hope to develop new ways of examining growth to detonation and failure in samples tested below their critical diameter. The outlined tests 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, 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 FOX mixtures. The 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.

Approaches 2 and 3 are both attempting to achieve something not previously undertaken. It is difficult to say whether they will have achieved their goals at the end of Year 5. If either approach does achieve their goal of providing a detonability screening test in Year 5, it will take at least another year to screen a significant number of potentially detonable formulations. The newly-developed techniques will be shared via publications 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 that 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; for the second, an under-driven configuration. Both tests require the sample explosive to 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 relieve pressure at the charge center.

III. RELEVANCE AND TRANSITION

A. *Relevance of Research to the DHS Enterprise*

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

This understanding of non-ideal detonation is an ongoing security research effort. Due to our efforts in this area, we are the only academic institution invited to join the DHS Chemical Security Analysis Center & Explosives Division 1st Inter-agency Explosives Terrorism Risk Assessment working group meetings. Furthermore, Dr. Oxley is an invited member of the DHS-funded National Academy of Science study on “Reducing the Threat of Improvised Explosive Device Attacks by Restricting Access to Chemical Explosive Precursors.”

The characterization of non-ideal detonation is also of interest to insensitive munitions (IM) research efforts, which require better metrics and diagnostics to track detonation kinetics.

B. *Potential for Transition*

Project R1-B.1 is defining the performance and threat level of many HMEs. Government agencies concerned with security, the security industry, and academics conducting research in security are the audience for the results of this program.

- This project addresses the performance and degree of threat offered by various HMEs. Traditional transition methods, such as publications and presentations, will be used to transmit our new methodologies.

- Potential end-users include any agency concerned with determining actual threat potentials of suspected materials. The protocols developed for evaluating potential detonability will be shared via publications and presentations. In addition to governmental groups in the HSE, this information would be useful to the health/safety of the chemical industry. Information concerning materials revealed as threats will be reported to DHS, allowing that agency to make informed decisions as to further dissemination of the information.

The results from this program will help the explosives security community understand what is important and how to focus their resources to minimize the impact of explosive events.

C. Data and/or IP Acquisition Strategy

As the data from the program becomes available, it will be provided to the community through DHS, publications, and presentations.

D. Transition Pathway

Results will primarily be transferred to the explosives security community by publications and presentations.

E. Customer Connections

Our connections to DHS (central), TSA, and the Transportation Security Laboratory (TSL) are strong. To date, the Federal Bureau of Investigations (FBI) is the only major agency outside of DHS that is aware of the details of this project. The results reported for the first time herein should spark a great deal of interest in the entire HSE.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Course, Seminar, and/or Workshop Development
 - a. We have conducted 13 explosives classes on seven different topics ranging from fundamentals of explosives to safety in handling. Over 350 people attended these courses. See details listed in Section IV.H.
 - b. There is a new course offering in July 2017 called "Safe Handling of Explosives for Technicians."
 - c. Prof. Oxley has given six invited talks and will be giving two more in Summer 2017.
2. Student Internship, Job, and/or Research Opportunities
 - a. We have or will have a number of visitors who come with the express purpose of learning how we handle HMEs and other energetic materials.
 - i. We hosted a young man from the Home Office (United Kingdom) for two days in May 2017.
 - ii. In July 2017, we hosted two students from the lab of last year's MSI award recipient (Dr. Bakhtiyarov, New Mexico Tech) for a week.
 - iii. Having performed TNT equivalence tests for Advanced Technology Research Centre (ATREC), we were asked to host researchers from ATREC and are invited to send students to their facility in Singapore. No dates have been set for this interaction.
 - iv. See also Student Theses in Section IV.G.

3. Interactions and Outreach to K-12, Community College, and/or Minority Serving Institution Students or Faculty
 - a. In Summer 2016, we had a visiting professor, Dr. Bakhtiyarov from New Mexico Tech, as well as one graduate and one undergraduate student from his group. He requested to return in Summer 2017, but decided to accept a DHS follow-on award instead.
 - b. We have done three STEM related magic shows for K-12 students.
 - c. In Summer 2016, we initiated a collaborative learning program where high school teachers along with select high school students spent two 2-week sessions solving an analytical chemistry problem.
4. Training to Professionals or Others
 - a. See details in Section IV.H.
5. Other Outcomes that Relate to Educational Improvement or Workforce Development
 - a. Three PhD students and two Master's students graduated this year and are now employed (see Section IV.G. for details).

B. Peer Reviewed Journal Articles

1. Colizza, K., Mahoney, K.E., Yevdokimov, A.V., Smith, J.L., & Oxley, J.C. 2016. "Acetonitrile Ion Suppression in Atmospheric Pressure Ionization Mass Spectrometry." *Rapid Communications in Mass Spectrometry*, 27(1), pp. 1796-1804.

Pending –

1. Oxley, J.C., Smith, J.L., & Brown, A.C. "Eutectics of Erythritol Tetranitrate." *Journal of Physical Chemistry* (Accepted).
2. 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." *Journal of Physical Chemistry* (Accepted).
3. Oxley, Jimmie C.; Smith James L.; Brown, A.C. "X-ray Simulants." (In preparation).

C. Other Publications

Pending –

1. Bakhtiyarov, S.I., Oxley, J.C., Smith, J.L. & Baldovi, P.M. "Rheological Studies of Functional Polyurethane Composite: Part 1. Rheology of Polyurethane Composite, Its Compounds with and without Solid Additives (Aluminum Flakes)." *Journal of Elastomers and Plastics*, JEP-17-0010.R1 (Accepted).
2. Oxley, J.C., Smith, J.L., Bakhtiyarov, S.I. & Baldovi, P.M. "Rheological Studies of Functional Polyurethane Composite: Part 2. Rheology of Polyurethane Composite with Solid Additives (Calcium Iodate Particles and Aluminum Flakes)." *Journal of Elastomers and Plastics*, JEP-17-0041.R1 (Submitted).
3. Oxley, J.C., Smith, J.L., Porter, M., Yekel, M.J., & Canaria, J.A. "Potential Biocides - Iodine-Producing Pyrotechnics." *Propellants, Explosives, Pyrotechnics* (Accepted).

D. Other Non-ALERT Publications & Conference Proceedings

1. Oxley, J.C., Smith, J.L., Bernier, E., Sandstrom, F., Weiss, G.G., Recht, G.W., & Schatzer, D. 2017. "Characterizing the Performance of Pipe Bombs." *Journal of Forensic Science*. 24 May 2017. DOI: 10.1111/1556-4029.13524.

2. Oxley, J.C.; Smith, J.L; Bakhtiyarov, S.I.; Baldovi, P. M. 2016. "A Complex Variable Method to Predict a Range of Arbitrary Shape Ballistic Projectiles." *Journal of Applied Nonlinear Dynamics* (1), pp. 1-10.
3. Lindsay McLennan. "The Role of Thermal Analysis in Screening and Analyzing Co-crystallization of Energetic Materials." *North American Thermal Analysis Society International Conference*, Orlando, FL, August 14-19, 2016.
4. Rebecca Levine. "Pyrotechnic Foams." *North American Thermal Analysis Society International Conference*, Orlando, FL, August 14-19, 2016.

E. *Other Conference Proceedings*

1. Invited Lecture
 - a. Oxley, J.C. "How to Detect HME." *CBRNe International Conference*, Lyon, Fr, May 29-June 2, 2017.
 - b. Oxley, J.C. "Explosive Analysis." *American Society for Clinical Laboratory Science Central New England*, Providence, RI, May 9-11, 2017.
 - c. Oxley, J.C. "Perspectives on Checkpoint Security." *Advanced Development for Security Applications (ADSA) 15*, Boston, MA, November 15, 2016.
 - d. Oxley, J.C. "What the DHS-CoE does for Law Enforcement." *2016 Texas Special Response Team Conference*, Austin, TX, October 4, 2016.
 - e. Oxley, J.C. "Research into Improvised Explosives (HME)." *5th Australian Symposium on Energetic Materials*, Adelaide, Au, September 27-29, 2016.
 - f. Oxley, J.C. "HMEs." *International Association of Bomb Technicians & Investigators*, Halifax, CA, July 18-22, 2016.
 - g. Oxley, J.C. "Why Study Explosives?" Wesleyan University, April 29, 2016.

F. *Other Presentations*

1. Seminars - See Section IV.D and E for presentations and invited lectures.
2. Short Courses - Listed under Section IV.H (New and Existing Courses).
3. Interviews and/or News Articles
 - a. Mosher, Dave. "What a 'nail bomb' is and why they are terrifying improvised weapons." *Business Insider*, May 23, 2017. <http://www.businessinsider.com/nail-bombs-what-are-they-2017-5>.
 - b. Cross, Ryan. "A look at the explosives used in the New York bombing." *Chemical & Engineering News*, September 26, 2016. <http://cen.acs.org/articles/94/i38/look-explosives-used-New-York.html>.
 - c. Rice, Doyle. "This totally legal product was used to make the NYC bomb." *USA Today*, September 19, 2016. <https://www.usatoday.com/story/news/nation/2016/09/19/tannerite-explosive-bomb/90692338>.
 - d. Greenmeier, Larry. "Chemicals Could Be a Key in Investigating the New York and New Jersey Bombings." *Scientific American*, September 19, 2016. <https://www.scientificamerican.com/article/chemicals-could-be-a-key-in-investigating-the-new-york-and-new-jersey-bombings>.
 - e. Mays, Kelsey. "Which New Cars Still Have Takata Airbag Inflators?" *Cars.com*, August 22, 2016. <https://www.cars.com/articles/which-new-cars-still-have-takata-airbag-inflators-1420689912742>.
 - f. Brown, Jennings. "Land Mines Kill Thousands A Year, But Can This Drone Help?" *Vocativ*, July 22,

2016. <http://www.vocativ.com/342975/land-mine-drone/>.

- g. Kelly Gormly Pittsburgh Quarterly magazine July 21, 2017; interview about 1862 explosion of the Allegheny Arsenal during the Civil War.
- h. Jensen, Alex. *This Morning* (Seoul, South Korea), June 14, 2017, radio interview.
- i. Callimachi, Rukmini. *The New York Times*, May 2017, question.
- j. Schaub, Ben. *Daily Planet*, April 2017, video interview.
- k. Welch, Tom. *Nutopia*, CNN network crime series, February 2017, video interview.
- l. Wellner, Jon. *Rosewood Productions*, January 2017, question.
- m. Jones, Conor. *Outrageous Acts of Science*, December 2016, question.
- n. Rose, Sarah. Journalist writing book on WWII, December 2016.
- o. Recchia, Scott. *The Blacklist* on NBC, September 2016, question.
- p. Jerving, Sara. *Vice New Tonight* (TV), September 2016, question.
- q. Monahan, Kevin. *NBC Universal*, August 2016, question.
- r. Piquet, Caroline. *Le Figaro* (French newspaper), July 2016, interview.
- s. Vallone, Phil. *CBS News*, July 2016, question.
- t. Salahuddin, Chelsea. *CBS National News*, July 2016, interview.

G. *Student Theses or Dissertations Produced from This Project*

1. Swanson, D. "Intermolecular Interactions of Energetic Materials." PhD dissertation, University of Rhode Island, December 2016. *Devon studied improved swabs, AFM, and co-crystalization of explosives. After receiving his PhD, he took a job with ATK in West Virginia.*
2. Porter, M. "Tools to Fight the Terrorist Threat." PhD dissertation, University of Rhode Island, May 2017. *Matt studied FOX from small-scale in project R.1-A.1 to large-scale in project R1-B.2, and also examined HMTD. After receiving his PhD, he took a job with Esterline.*
3. Brown, A. "Improvised Explosives: X-ray Detection & Eutectics of Erythritol Tetranitrate." PhD dissertation, University of Rhode Island, May 2017. *Austin studied ETN decomposition and eutectics as well as X-ray simulants. Austin is working for the Transportation Security Lab run by ARA at Tyndall AFB, FL.*
4. Levine, R. "Interactions of Polymers and Energetic Materials." Masters thesis, University of Rhode Island, May 2017.

H. *New and Existing Courses Developed and Student Enrollment*

New or Existing	Course/Module/Degree/Cert.	Title	Description	Student Enrollment
Existing	Certificate	Fundamentals URI	May 3-5, 2016.	50
Existing	Certificate	Fundamentals Los Alamos	Aug. 1-3, 2016.	43
Existing	Certificate	LANL Fundamentals	Feb. 27-Mar. 1, 2017.	31
Existing	Certificate	LLNL Fundamentals	Mar. 27-29, 2017.	28
Existing	Certificate	Fundamentals ABQ	Aug. 29-31, 2016.	22

Existing	Certificate	Fundamentals VA	Oct. 25-27, 2016.	12
Existing	Certificate	Explosive Analysis URI	May 6, 2016.	21
Existing	Certificate	Advanced Hazards Recognition	May 12, 2016.	12
Existing	Certificate	TSA	June 20-24, 2016.	23
Existing	Certificate	Air Blast	May 16-18, 2016.	36
Existing	Certificate	Detonation & DDT, LANL	Sept. 20-22, 2016.	28
Existing	Certificate	Dynamic Diagnostics, LANL	Nov. 14-15, 2016.	21
Existing	Certificate	Dynamic Diagnostics	Mar. 21-22, 2017.	25
				352 (Total)

I. Technology Transfer/Patents

1. Patent Applications Filed (Including Provisional Patents)
 - a. Oxley, J., Smith, J., & Canino, J. "Non-Detonable Explosive or Explosive-Simulant Source" is in the process of being converted from provisional to full patent.

J. Software Developed

1. Databases
 - a. The Explosives Properties Database: Over 1000 members are registered for the database, of which 250 are associated with U.S. government agencies. <http://expdb.chm.uri.edu/>.

K. Requests for Assistance/Advice

1. From DHS
 - a. On call for a variety of TSA TSS-E personnel.
 - b. Professor Oxley is part of the DHS-formed Inter-Agency Explosive Terrorism Risk Assessment Working Group (IExTRAWG).
 - c. Oxley is a member of the NAS committee on "Reducing the Threat of Improvised Explosive Device Attacks by Restricting Access to Chemical Explosive Precursors." <http://dels.nas.edu/Study-In-Progress/Reducing-Threat-Improvised-Explosive/AUTO-7-66-86-I>.
2. From Federal/State/Local Government
 - a. A TSA explosives specialist emails questions weekly and occasionally calls.
 - b. The new URI bomb dog and his trainer rely on our lab for advice and explosives training aids.

V. REFERENCES

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