R2-A.3: A Novel Method for Evaluating the Adhesion of Explosives Residues

I. PARTICIPANTS

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II. PROJECT DESCRIPTION

A. Project Overview

The goal of this project is the application of a new interpretation and modeling approach to a traditional experimental method, the centrifuge method, for measuring the adhesion of explosives residues to surfaces. The approach will yield look-up tables containing force constants for the residue-surface systems that are indexed to the particle sizes of a residue. These constants are used in a simple, closed-form algebraic model that can be evaluated on a hand-held calculator to predict the adhesion force of the residues.

Figure 1 shows the configuration of the centrifuge, with emphasis on the orientation of the residues on the surface relative to the axis of rotation. The residues adhere to the surface primarily through van der Waals forces, while the inertial force from the centrifuge’s motion acts to dislodge them. By monitoring the rotational speed required to remove residues of a given size, it is possible to determine the residue adhesion force. From the adhesion force and residue size distribution, the distribution of effective Hamaker constants (the force constants in van der Waals adhesion force descriptions) of model spherical particles against a flat substrate is calculated using the well-established approximate relationship shown in Equation 1 [1]:

$$F_{vdW}(D) = \frac{A_{eff}R}{6D^2}$$  \hspace{1cm} (1)

where $F_{vdW}(D)$ is the van der Waals adhesion force, $A_{eff}$ denotes the Hamaker constant of the system, $R$ is the radius of the particle, and $D$ represents the separation distance between the two surfaces, which is generally regarded to be 0.4 nm for particles or residues in contact with a surface. Figure 2 shows how the modeling and simulation approach developed here can be used to describe the adhesion force distribution of a population of particles against a surface. In this figure, $F_{rad}$ represents $F_{vdW}$ and $F_{cent}$ represents the force to remove particles from the surfaces in the centrifuge. When $F_{cent}$ is just slightly larger than $F_{rad}$, the particles are removed, so by tracking the particles adhering as a function of the rotational speed, we can measure the particle adhesion force.
While this work can be used to identify the force of adhesion holding particulate explosive residues to surfaces, it is also necessary to understand the process by which a compounded residue fails adhesively when a load is applied during the contact sampling process. Adhesive failure can occur when a residue pulls cleanly off the underlying surface, or when the residue fails at some weak plane within itself, leaving some residue adhered to the trap and some to the original surface. For this purpose, we are interested in measuring and modeling the failure of composites that mimic C-4 and Semtex, which are common compounded explosives.

The goals of this project are to:

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**Figure 1:** Schematic of the centrifuge apparatus illustrating how the adhesion and radial forces counteract one another.

![Schematic of the centrifuge apparatus](image1)

**Figure 2:** Observed (●) and simulated (−) effect of centrifuge rotational speed on the percentage of silica particles remaining on a stainless steel plate during the centrifuge experiment. To create the simulated dataset, it was assumed that the particles were smooth and spherical, and an effective Hamaker constant distribution was fitted in Equation 1. This effective distribution linked the size of the particles, the composition and roughness of the particles, and the composition and roughness of the plates to the size-dependent Hamaker constants in the effective Hamaker constant distribution.
• Fully validate the centrifuge method and implement it in order to study the adhesion of particulate explosives, including RDX, TNT, and PETN, to steel, silicon, and ABS plastic surfaces.

• Create look-up tables of effective Hamaker constants that describe the adhesion of particulate RDX, TNT, and PETN to various surfaces in terms of perfect spheres of residue, for use in defining the limiting adhesion forces that must be overcome during contact sampling.

• Develop a deposition method for applying reproducible levels of compounded explosive to surfaces of interest for use in the centrifuge method.

• Develop a quantitative method for measuring the quantity of compounded residue on, and removed from, a surface used in the centrifuge method.

• Completion and dissemination of a Matlab code (Matlab executable) that can be used by commercial and government partners to implement the enhanced centrifuge method to prepare look-up tables of explosive adhesion to surfaces.

• Transfer the results of this research to commercial partners who will use it to develop optimal swabs that most effectively remove residues from surfaces.

When this project succeeds, the knowledge that we generate will be used by swab manufacturers to optimize the design and application of the swabs so that they most effectively remove the residues from the surfaces of interest, facilitating the detection of explosives at checkpoints.

• The first risk associated with this project is that the particulate residues will not be readily detected on rough surfaces due to the optical complexity of the rough surfaces. By varying the lighting, depth of field and angle of lighting applied we hope to solve this problem.

• The second risk is that we will not be able to reproducibly apply compounded residues to the surfaces of interest. We will address this problem by implementing the “Dragon-skin” thumb applicator method developed by DSTL [1].

• The third risk is that we will not be able to detect the presence and removal of compounded residue using a simple optical method. In that case, we will consider radiolabeled residue.

B. State of the Art and Technical Approach

The state of the art in contact sampling is well developed. Virtually all contact sampling protocols used in conjunction with ion mobility spectrometry (IMS) detection involve swabs made of Teflon-coated fiberglass, Nomex, paper, or muslin. These materials are provided by the manufacturers of the IMS equipment, and are designed to be compatible with a specific device. The swabs are optimized to endure repeated exposure to the thermal cycling in the IMS, but not for their effectiveness in removing residues from surfaces. The technical approach pursued here involves fundamental studies of the way that residues deform and yield under the swiping load applied during contact sampling. By developing this understanding, it is possible to elucidate how a swab must contact a residue in order to remove the maximum amount of residue from a surface. With particulate solid residues, this is relatively straightforward to understand: it is necessary to come into contact with the particles. If the adhesion force between the particles and the swab is greater than between the particle and the surface, then it will be collected. In the case of the compounded residues, the behavior is substantially more complex. Specifically, these residues will deform under the sampling load, and it is not clear where they may yield when the swab attempts to lift them from the surface. There have been virtually no studies of this phenomenon, although there has been work on the deformation of compounded, highly-filled composites, primarily for work in granular solids [2–11]. Our goal is to quantify the particulate
residue removed from a surface under inertial load and to develop a method to model this phenomenon. In addition, we wish to develop a method to quantify the compounded residue that stretches and breaks off the surfaces of interest in the centrifuge when the inertial removal force is applied. This will offer the first quantitative study of the residue removal process via applied load. In either case, we will adapt the centrifuge method to evaluate the force required to remove residues of particulate and compounded explosives from surfaces [12–17]. This method allows for the direct measurement of the force required to remove large numbers of particulate explosives, or populations of compounded explosives residues, from surfaces. When these measurements are made, we characterize the adhesion of a sufficiently large number of particles or compounded residues so that the results can be readily generalized to all systems of interest. Moreover, the measurements specifically capture the effects of the topography, shape, and deformation of the explosives particles or residues, as well as the effects of the topography and deformation of the surface to which they adhere. When the two parts of this project are combined, we obtain a comprehensive understanding of the force required to remove residues of explosives, both particulate and compounded, from surfaces, in addition to a first principles understanding of the way that the explosives deform and fail during removal. This understanding enables the development of improved residue sampling protocols and materials.

C. Major Contributions

The outcomes produced in Year 4 include:

1. A first generation model for fluid and particle motion in compounded explosives: We finished a first generation model for the behavior of particles and fluid moving through an array of fixed particles by using particles of the same size scale as those found in energetic materials compacts and fluids with similar mechanical properties to compounded explosives. Note that this thread was abandoned to focus on transition of the centrifuge method described in #2 below.

2. A method for measuring forces required to remove residues from surfaces: We developed and validated a revolutionary interpretation of classical adhesion force measurements using the centrifuge technique. This method allows us to measure the adhesion force of a large population of residues or particles and to include the effects of the size, shape, topography, and deformation of the particles or residues, as well as the shape and deformation of the surface to which they adhere.

The outcomes produced in Year 5 include:

1. We validated the centrifuge method and created a customer-friendly code to interpret the measured adhesion force distributions and developed a method to translate the force distributions into look-up tables that can be readily used to describe residue adhesion. This is essential if the work will be translated to customers in the community.

2. We developed a fluorescent microscopy method for evaluating the removal of residues from surfaces using the centrifuge method.

The outcomes produced in Year 6 include:

1. We developed a fully transferable Matlab executable model, which runs on a personal computer without requiring resident Matlab, which allows members of the community to insert centrifuge data and extract effective Hamaker constant distributions for the adhesion between explosive particles and surfaces. These distributions allow the community members to predict the adhesion force distributions between the particles and the surfaces for particles of any size. The code is configured as a black box with a user-friendly GUI to make it straightforward for users to insert and evaluate their data.
2. We performed experimental and modeling studies to validate the effective Hamaker constant fitting approach for the adhesion between polystyrene spheres and surfaces with significantly varying degrees of roughness. This demonstrates that the experimental and modeling approach allows us to assess the effect of the surface roughness on the particle adhesion.

3. We demonstrated that the effective Hamaker constant distributions vary as a function of the particle size and the topography of the particles and the topography of the surface to which they adhere. This demonstrates the validity of the enhanced centrifuge method.

4. We developed a method for spiking compounded explosive residue with dye, to enable measurement of the amount of compounded residue on a surface using UV-visible spectrophotometry. Unfortunately, when the final calibration was completed, we determined that is was not possible to put enough dye in the compounded explosive to enable measurement of the removal of fingerprint-level quantities of the explosives from surfaces without altering the mechanical properties of the residues.

5. We developed preliminary results for the adhesion of RDX to nominally smooth silica (rms roughness 0.3 nm). Class 5 RDX particles were deposited onto two nominally smooth silica substrates. The adhesion of the RDX particles to the silica was assumed to be due primarily to the vdW force. Each plate contained approximately 1000 particles after deposition and the size distribution of the particles was determined by optical analysis using a Nikon SMZ-1500 camera and ImageJ. The plates were rotated at increasing RPM increments of 2000. The RDX particle count was measured after each increased RPM increment (2000, 4000, 6000, 8000, 10000, 12000, 14000, and 16000). Figure 3 shows the percent of RDX particles that remained on the silica surface as a function of RPM. By 5000 RPM, approximately half of the RDX particles detached from the silica and by 16000 RPM no particles remained on either silica plate. The large standard deviation at 2000 RPM is likely due to initial RDX particle size distribution differences between plate 1 and plate 2. In addition to particle size variability, there is also variability in roughness across the silica plates.

![Figure 3. The total number of RDX particles remaining on silica surfaces as a function of centrifuge RPM.](image)

The enhanced centrifuge technique was executed for each plate using the size distribution of RDX particles specific to the particles on the plate. Each size distribution was sorted from largest to smallest and binned according to the number of RPM increments studied (8 bins in the case of this
experiment). The average particle size in each RPM bin was measured. The effective Hamaker constants were then determined using the average particle size per bin. Figure 4 illustrates the effective Hamaker constants that describe the adhesion of RDX particles to the silica as a function of average particle size. As the particles increase in size, the effective Hamaker constant values decrease. This is in part because all of the particles that come off the plate at a given RPM are considered to be from the same part of the size distribution, which is an approximation. Specifically, when an experiment shows that 30% of the particles have been removed from the plate, it is assumed that the largest 30% have been removed. This is not necessarily true, as some smaller particles may have been removed, depending on their roughness and the roughness of the plates. Similarly, some larger particles may remain depending on how their topography and shape matches that of the surface. This tends to weight each fraction of particles removed towards the larger size particles in the fraction. To match the observation, the resulting fitted Hamaker constants must be smaller than otherwise. By decreasing the RPM intervals (e.g., increasing rotational speeds by 100 RPM steps instead of 2000 RPM steps), this weighting is reduced, at a penalty of having to perform many more experiments. A previous study measured the adhesion of RDX against different materials, including silica, and found a Hamaker constant for this system to be between 400 and 800 zJ [18]. These were intrinsic Hamaker constants, for perfectly smooth systems. The lower effective Hamaker constant values (40 zJ to 200 zJ) in Figure 4 suggest that individual particle shape variation and surface roughness is playing a role in decreasing the adhesion between the RDX powder and the surface.

![Figure 4](image.png)

**Figure 4.** Effective Hamaker constants quantify the effect of the particles’ shape and surface roughness on the adhesion as a function of particle size.

### D. Milestones

Milestones expected for Year 6 included:

- Measurements of the adhesion between fluorescent spheres (model particles) and steel using the enhanced centrifuge method to confirm that the method can be executed properly.
This milestone was modified, and the adhesion between polystyrene latex and silicon with different surface finishes was measured. The efficacy of the enhanced centrifuge method was demonstrated.

- Measurements of the adhesion between particulate explosives and steel.
  - This measurement is in progress, using RDX particles and silicon.
- Preparation of look-up tables demonstrating the adhesion constants that are appropriate for the steel adhesion to the particulate RDX.
  - This work is underway.
- Completion and dissemination of a Matlab code (Matlab executable) that can be used by commercial and government partners to implement the enhanced centrifuge method to prepare look-up tables of explosive adhesion to surfaces.
  - This code will be disseminated to the community following the ALERT Technology Showcase (May 14, 2019).

**Milestones expected for Year 7 include:**

- We will determine adhesion force constants for RDX, PETN, and TNT against common surfaces of interest in air transportation security environments. We also will develop a first order approach for measuring the adhesion forces for compounded explosives against surfaces.

**Programmatic risks and mitigation strategies:**

- It is possible that the wet chemical approach we will take to quantify compounded residue removal will not work. We will consider radiolabeled binder for that purpose.

**E. Future Plans/Project Completion (Year 7)**

We will complete experimentation and prepare and disseminate lookup tables of force constants for the adhesion of particulate explosives to steel and ABS plastic. We will also document the removal of compounded explosives from surfaces and will explain the mechanism of removal to the community.

**III. RELEVANCE AND TRANSITION**

**A. Relevance of Research to the DHS Enterprise**

- Users are constantly seeking better ways to detect particulate explosives on surfaces in air transportation environments. A key part of this is understanding how different explosives adhere to different surfaces and traps. This is especially useful when new explosives threats are considered. We will deliver a method that IMS manufacturers can use to measure adhesion forces to their traps, so that they can make optimal traps.
- The community has no easy way to measure the removal of compounded residues from surfaces. We will develop and demonstrate a new method to measure the removal of such residues from surfaces and will teach the method to the community. They will then be able to assess how effective their processes are at recovering compounded residues.
B. Potential for Transition

The community will use these methods that we will develop to measure residue adhesion to surfaces, so that they can develop better traps. The methods will let them know how much more strongly a new residue will adhere compared to existing ones, so they will know if they need to reengineer their traps.

C. Data and/or IP Acquisition Strategy

All data can be taken in our lab. No data is needed from the community.

D. Transition Pathway

We explained our method to Bruker and Smiths at the ALERT Technology Showcase (May 14, 2019). The results we generate in Year 7 will be shared with the community at the Trace Explosives Detection Workshop in April 2020.

In August 2018, Professor Beaudoin visited Rapiscan in Boston and spent a day there teaching them about particle adhesion in residue detection. This included giving a seminar and spending the rest of the day on site answering questions: Beaudoin, S. “Fundamentals of Explosive Residue Adhesion and Removal.” Workshop for Rapiscan Systems, Boston, MA, August 2018.

E. Customer Connections

- TSL – TSL invited this project to send a PhD candidate to their lab for a 3-month period to teach them the centrifuge method.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Student Internship, Job, and/or Research Opportunities
   a. Four female B.S. students worked in Professor Beaudoin’s lab in Year 6.
   b. Three students graduated and are now employed: Kacie Bradfish (Eli Lilly), Emma Weiglein (Dow), and Molly Baldwin (Rapiscan).
   c. Interactions and Outreach to K-12, Community College, and/or Minority Serving Institution Students or Faculty.
   d. Professor Holubowitch and underrepresented student from Texas A&M Corpus Christi came to my lab in the summer of 2018, and will be returning for the summer of 2019.

2. Training to Professionals or Others
   a. Professor Beaudoin taught a one day workshop on explosive particle adhesion at Rapiscan Systems in August 2018.
B. Peer Reviewed Journal Articles


C. Other Conference Proceedings


D. Other Presentations

1. Seminars

E. Software Developed

1. Models
   a. Matlab code for calculating effective Hamaker constants from centrifuge data.

V. REFERENCES


