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

I. PARTICIPANTS INVOLVED FROM JULY 1, 2019 TO JUNE 30, 2020

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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 was applied to develop a lookup table containing force constants for the residue-surface systems that are indexed to the particle sizes of a residue. This table is being finalized and will be delivered at the end of the no-cost extension period. The constants are used in a simple, closed-form algebraic model that can be evaluated on a handheld calculator to predict the adhesion force of the residues. The approach was focused on two types of residues: (1) particulate residues such as Royal Demolition eXplosive (RDX), pentaerythritol tetranitrate (PETN), and black powder, and (2) compounded residues such as C4 and Semtex. The work was successful with RDX, but a straightforward, inexpensive, quantitative method for determining the removal of microgram quantities of compounded residues in the centrifuge was not identified.

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. 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]:

$$\textbf{Equation 1:}\quad \boldsymbol{F_{vdW}(D) = \frac{A_{eff}R}{6D^2}}$$

where $F_{vdW}(D)$ is the van der Waals adhesion force, A_{eff} denotes the effective Hamaker constant of the system, R is the radius of the particle, and D represents the separation distance between the two surfaces in contact, which is generally regarded to be 0.4 nm. 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 Figure 1, F_{ad} 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_{ad}, the particles are removed, so by tracking the particles adhering as a function of the rotational speed, we can measure the particle adhesion force. Figure 2 shows three replicates of the removal of RDX powder from stainless steel as a function of rotational speed in the centrifuge. This is the type of dataset from which the model representations of RDX adhesion are developed.

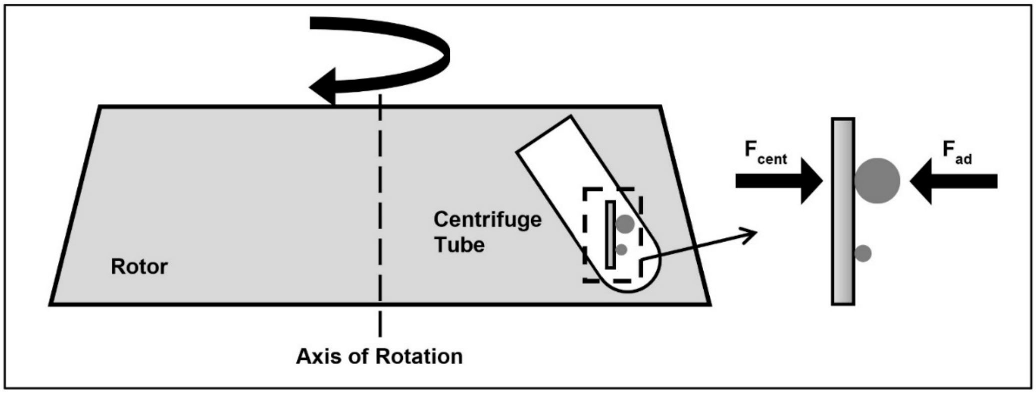

Figure 1: Schematic of the centrifuge apparatus illustrating the adhesion and inertial forces on the particles.

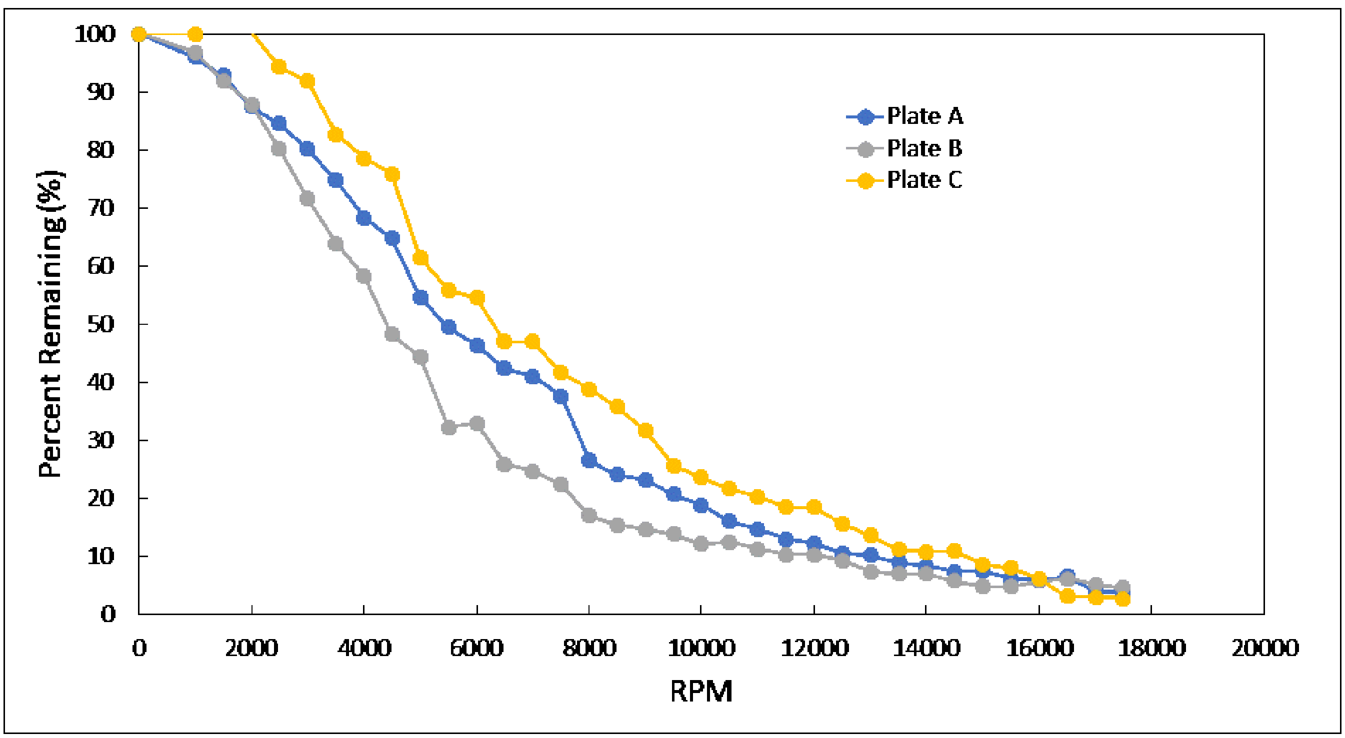

Figure 2: Three replicates of the removal of RDX powder from stainless steel plates during a centrifuge experiment.

The goals of this project were to:

- Fully validate the centrifuge method and implement it in order to study the adhesion of particulate RDX explosive to steel, silicon, aluminum, and acrylonitrile butadiene styrene (ABS) plastic surfaces.

- Create lookup tables of effective Hamaker constants that describe the adhesion of particulate RDX 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.
- Complete and disseminate a MATLAB code (MATLAB executable) that can be used by commercial and government partners to implement the enhanced centrifuge method to prepare lookup tables of explosive adhesion to surfaces.
- Develop a robust model- and simulation-based method to design centrifuge experiments so that the community can quickly and inexpensively determine accurate, effective Hamaker constants. This requires the use of a particle adhesion simulator, which will be disseminated as a MATLAB executable, knowledge of the topography of the surface on which the explosives powder resides, and a modeling framework to relate the size distribution of the particles, the topography of the surface, and the experimental conditions used to develop the effective Hamaker constant distributions.
- Transfer the results of this research to the Transportation Security Lab (TSL), including a series of "how-to" tutorials, so that TSL can apply and disseminate the method as a standard approach in the community.

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 trap 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 has been to quantify the particulate residue removed from a surface under inertial load and to develop a method to model this phenomenon. In addition, we sought 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 was the first quantitative study of the residue removal process via applied load. In either case, we attempted to 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 by this project include:

Year 4

We developed and validated a revolutionary interpretation of classical adhesion force measurements using the centrifuge technique. This enhanced centrifuge technique allows us to measure the adhesion force of a large population of explosive particles and to include the effects of their size, shape, and topography on the adhesion, as well as the effects of the topography of the surface to which they adhere.

We validated the enhanced centrifuge technique, created a customer-friendly code to interpret the measured adhesion force distributions, and developed a method to translate the force distributions into lookup tables that can be readily used to describe residue adhesion.

Year 5

We developed a fully transferable MATLAB executable model that runs on a personal computer without requiring resident MATLAB. It 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.

Year 6

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, and shows the interplay between the length scale of features on the surface, the length scale of the particles, and the adhesion forces.

Year 7

We demonstrated that the adhesion between RDX powder and steel and glass surfaces varies systematically with the topography of the steel or glass, with the size of the RDX particles in the powder, and with the relative humidity. In this case, the key concept identified is that the root mean square (RMS) roughness of the surface is not related to the adhesion of the powder in a straightforward manner. Rather, the adhesion between the explosive powder and the surface is much more closely related to the ability of the roughness on the surface to accommodate the geometry of the particles at the particle scale. In Figure 3, the adhesion between RDX and silica is shown. The adhesion force is represented by the effective Hamaker constants determined using the Enhanced Centrifuge Method. These are directly proportional to the adhesion force. While the smoothest surface adheres to the particles of RDX most strongly, the roughest surface adheres next most strongly, closely followed by the second-smoothest surface. During the no-cost extension period, we will complete similar analysis on stainless steel, aluminum, and ABS plastic surfaces.

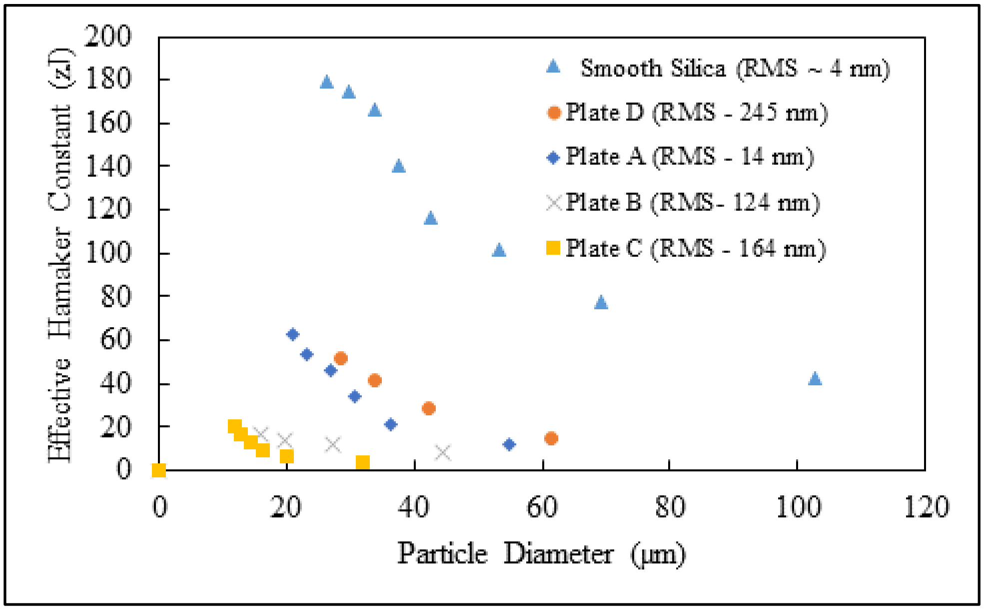

Figure 3: Effective Hamaker constants of RDX against steel and silica surfaces as a function of mean RDX particle diameter.

We developed first generation effective Hamaker constant lookup charts, as shown in Table 1 for RDX adhering to silica and stainless steel. These constants are applied in Equation 1 to determine the adhesion force between the RDX particles and the surfaces listed as a function of particle size and separation distance from the surface.

Silica										Stainless-Steel			
Plate 1 (14 nm)		Plate 2 (245 nm)		Plate 3 (124 nm)		Plate 4 (164 nm)		Pre-polished		Plate 1		Plate 2	
Size (µm)	**Aeff (zJ)**	**Size (µm)**	**Aeff (zJ)**	**Size (µm)**	**Aeff (zJ)**	**Size (µm)**	**Aeff (zJ)**	**Size (µm)**	**Aeff (zJ)**	**Size (µm)**	**Aeff (zJ)**	**Size (µm)**	**Aeff (zJ)**
54.9	12.1	61.5	15.2	44.4	7.9	32.1	4.1	102.8	42.4	59.1	3.5	59.9	8.1
36.4	21.3	42.4	28.9	27.3	12.0	20.1	6.5	69.4	77.3	44.2	4.4	48.3	9.3
30.6	33.8	33.8	41.4	19.8	14.1	16.1	9.4	53.1	101.9	39.7	6.3	44.7	12.5
26.9	46.4	28.4	51.8	15.9	16.3	14.4	13.3	42.6	116.7	32.1	6.5	39.7	14.2
23.1	53.4					13.0	16.8	37.5	140.8	27.7	6.9	35.2	15.2
20.9	63.1					11.8	20.1	33.9	166.4	25.8	8.2	32.1	16.5
								29.8	174.8	24.2	9.4	27.2	15.0
								26.4	179.6	21.2	9.2	24.5	15.0
										18.2	8.3	22.9	15.9
										17.6	9.4	22.0	17.5
										17.3	10.8	19.7	16.5
										16.2	11.1	15.0	11.0
										14.8	10.8	12.7	9.1

Table 1: Lookup table of effective Hamaker constants representing the adhesion of RDX against silica and stainless steel substrates. (Note that "pre-polished silica" had an RMS roughness of ~4 nm.)

We have developed an algorithm to know which rotational speeds to employ in the centrifuge in order to properly implement the Enhanced Centrifuge Method. In particular, during the application of the method, the intervals in rotational speed employed during the powder removal can be tightly coupled to the values of the resulting effective Hamaker constant distribution. When the appropriate rotational speed intervals are employed, this relationship will no longer apply, and the effective Hamaker constant distributions will be only functions of the particle and surface properties. We have developed an algorithm which relates the powder properties (primarily size distribution) and the rotational speed employed in the centrifuge to the distribution of the particles into bins by size. Because each bin has a unique adhesion force, the binning process produces the effective Hamaker constant distributions. The algorithm is shown in Figure 4.

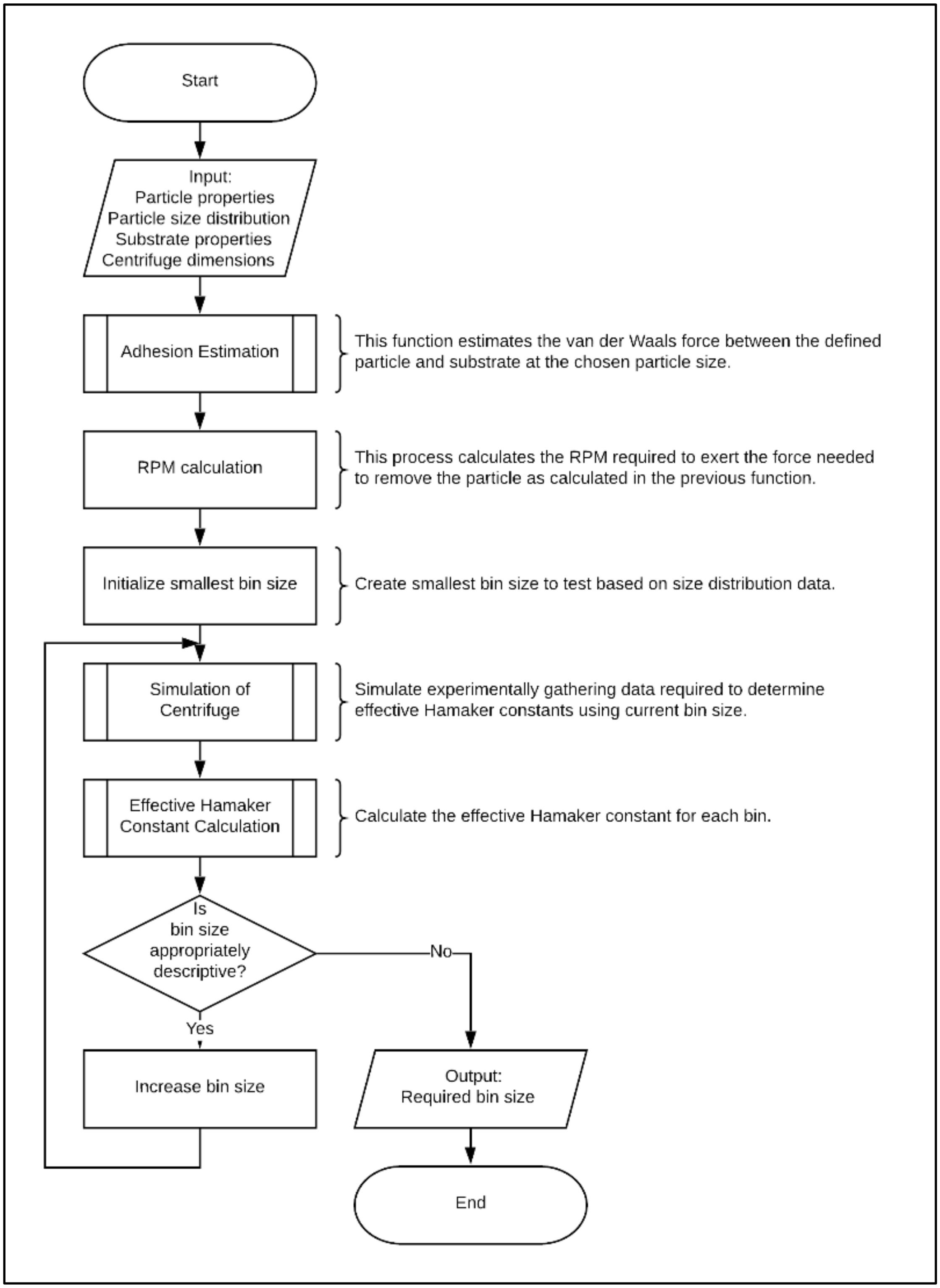

Figure 4: Process flow diagram demonstrating binning algorithm.

D. Milestones

Three milestones were pursued:

1. Determine adhesion force constants for RDX against common surfaces of interest in air transportation security environments;
2. Develop a first order approach for measuring the adhesion forces for compounded explosives against surfaces; and
3. Transfer the enhanced centrifuge method to the community, including a MATLAB-based code to evaluate data, so that the community could design and perform enhanced centrifuge experiments.

The first milestone, determining adhesion force constants for RDX against common surfaces of interest in air transportation environments, was partially achieved, as outlined in Table 1. This was not fully achieved because the lion's share of effort went into the unsuccessful pursuit of milestone 2: develop a first order approach for measuring the adhesion forces for compounded explosives against surfaces.

Milestone 2 was not attained because we could not find a simple, inexpensive, reproducible, and sufficiently sensitive method for quantitatively evaluating trace quantities of a compounded residue on surfaces. We pursued UV spectrophotometry primarily, as an inexpensive and precise approach for measuring residues, but we could not generate the necessary sensitivity.

Milestone 3 was partially achieved. Full completion was prevented because we identified a fundamental challenge in describing surfaces that required solution before the method could be used to design the appropriate operating conditions for experiments.

We anticipate more progress on milestones 1 and 3 during the no-cost extension period.

Programmatic risks and mitigation strategies: In assessing the adhesion forces for powder explosives against surfaces, the topography of the surface to which the explosive powder was adhering was observed to be key to the validity of the determined constants. We explored this phenomenon by systematically varying the surface topography, evaluating quantitatively the resulting force constants, and identifying the topographical features that dominate the adhesion. We also realized that the size of the increments in centrifuge rotational speed had a profound effect on the constants evaluated for particles of any given size. This should not be the case. During the no-cost extension period, we will aim to finalize the relationship between the particle size distribution for the explosive powder and the appropriate rotational speed intervals for the enhanced centrifuge experiments to give ideal experimental results. The goal is shown in Figure 5. As can be seen, for the correct change in rotational speed, the variation in the effective Hamaker constant can be minimized, and thus the intrinsic constant that is influenced only by the topography of the two surfaces and the size and shape of the particles of powder.

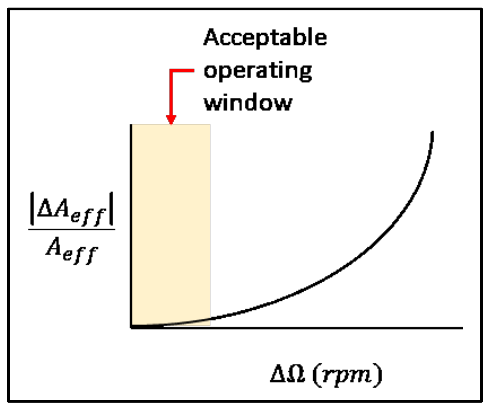

Figure 5: Schematic showing the relationship between the centrifuge rotational speed algorithm and the changes in the effective Hamaker constants.

E. Final Results at Project Completion (Year 7)

We have developed the enhanced centrifuge method to assess the adhesion between explosives powders and surfaces, and to model this adhesion in terms of a simple algebraic model. The model can be readily applied by any member of the community to estimate the range of explosives adhesion to surfaces. We were scheduled to travel to the TSL for the summer of 2020, to transfer the method to the TSL. This was canceled due to COVID-19. Instead, we are preparing a series of YouTube tutorials that will be disseminated to the TSL and other members of the community to walk them through the method from beginning to end. These will be delivered by the end of the no-cost extension period. We have determined that the success of the method depends on a careful understanding of the topography of the surface to which the energetic material adheres, and we will deliver this understanding in an algorithm for surface evaluation by the end of the no-cost extension period.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

Relevance #1/Metrics: Develop a method to measure the adhesion between explosives and surfaces of interest in air transportation environments.

Metric 1: Do look up charts exist for selected powdered explosives?

Yes, look up charts created for RDX against glass and steel.

Metric 2: Does the method work for all surfaces (has it been generalized)?

Not fully. The surfaces of interest to DHS will have a range of finishes. We need to investigate these, evaluate the adhesion force constants, and come back with a range of expected values. This will demonstrate the method, and will be completed during the no-cost extension period

Metric 3: Has a method for measuring adhesion of explosives powders to surfaces been developed and transferred to the community?

Not fully. The method has been developed. There are still details of the method to work out, including the effects of the topography of the surface and an algorithm to design the centrifuge experiments. These will be accomplished by the end of the no-cost extension period.

Metric 3: Is there a simple, accurate, inexpensive method to measure the adhesion of compounded explosives to surfaces?

No. We had to abandon this goal as our attempts with UV / visible spectrometry could never be performed in a sufficiently accurate, sensitive manner

B. Status of Transition at Project End

By the end of the no cost extension period, the community will have a series of videos documenting how to perform every aspect of the method, including how to design the experiments and how to interpret the results. Lookup tables will be presented for one-powdered explosive (RDX) on multiple surfaces (glass, stainless steel, aluminum, and ABS plastic) with different finishes. A manuscript will summarize the results in the refereed literature, and the work will be presented at the Trace Explosives Detection Workshop in spring 2021.

C. Transition Pathway and Future Opportunities

We had scheduled for a student to go to TSL and spend the summer of 2020 working there to transition the method to John Brady, but this was canceled due to COVID-19. Instead we will send a manual, a code, and a series of YouTube videos documenting all aspects of the method so that it may be implemented there. These will be sent at the end of the no-cost extension period.

D. Customer Connections

See above.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Student Internship, Job, and/or Research Opportunities
    a. Three undergraduate students (one female, one Hispanic) performed research in our lab on this project. All three are expected to go on to graduate study. Two will apply to graduate school this fall, while the other has one more year of study remaining.

B. Peer Reviewed Journal Articles

1. Stevenson, M., Beaudoin, S., & Corti, D. "Toward an Improved Method for Determining the Hamaker Constant of Solid Materials Using Atomic Force Microscopy. I. Quasi-Static Analysis for Arbitrary Surface Roughness." *Journal of Physical Chemistry C*, *124*(5), 10 January 2020, pp. 3014–3027. https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.9b09669.

C. Peer Reviewed Conference Proceedings

1. Coultas-Mckenney, C., Norris, C., Roginski, A., Bradfish, K., Weiglein, E., & Beaudoin, S., "Bringing Particle Scale Properties into Descriptions of Energetic Powder Behavior via the Enhanced Centrifuge Technique." *Annual Meeting of the American Institute of Chemical Engineers*, Orlando, FL. November 2019.
2. Stevenson, M., Beaudoin., S., & Corti, D. "Impact of Surface Roughness on Estimating Hamaker Constants through Non-Contact Atomic Force Microscopy." *Annual Meeting of the American Institute of Chemical Engineers*, Orlando, FL. November 2019.

D. Requests for Assistance/Advice

1. From DHS
    a. Request for Jordan Monroe to spend the summer of 2020 at DHS TSL to transfer the enhanced centrifuge technique to the TSL. Jordan was scheduled to spend the summer teaching the method to TSL staff, but the visit was canceled due to COVID-19. We instead are preparing manuals, videos, and computer code to illustrate and assist with the method.

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