

R2-A.1: Improved Trap Design for Contact Sensing

I. PARTICIPANTS

Faculty/Staff			
Name	Title	Institution	Email
Stephen P. Beaudoin	PI	Purdue University	sbeaudoi@purdue.edu
Bryan Boudouris	Assistant Professor	Purdue University	boudouris@purdue.edu
Graduate, Undergraduate and REU Students			
Name	Degree Pursued	Institution	Month/Year of Graduation
Sean Fronczak	Ph.D.	Purdue University	12/2017
Darby Hoss	Ph.D.	Purdue University	8/2017
Jennifer Laster	Ph.D.	Purdue University	12/2017

II. PROJECT DESCRIPTION

A. Project Overview

The goal of this project was the development of novel traps with the following characteristics: 1) high affinity for explosives residues; 2) excellent ability to interrogate surfaces of interest; 3) high thermal stability in order to survive multiple trips through an ion mobility spectrometer (IMS); 4) mechanical toughness to avoid breakdown with use; 5) compatibility with electrothermal desorption methods to allow for next-generation, low-temperature use; and 6) low manufacturing cost.

The challenges to be addressed were: 1) limited impact of mechanical and chemical effects on trap performance; 2) high temperatures on the desorber plate in the IMS (well above 250°C); 3) loss of mechanical integrity of the traps as they dry; and 4) optimization of electrothermal methods for low temperature desorption.

It has been shown at Pacific Northwest National Labs (PNNL) and in our lab that changing the surface chemistry of a trap can dramatically change its adhesion behavior towards explosives residues. In our ongoing work outside of this project, we are experimenting with different surface chemistries to identify the ones that most effectively improve the adhesion of the traps to the residue during residue harvesting without impeding the residue release process in the IMS.

The goals of this project were the following:

- Identify surface chemical moieties that influence the adhesion of explosives residues to our polymeric traps, and quantify their effect on the adhesion and the release of residues.
- Transfer the results of this research to a corporate partner who will develop and deliver the traps to the public sector for use in air transportation security settings.

If this project were to have succeeded, the traps would have improved the effectiveness of checkpoint security activities based on contact sampling/IMS at a low cost. These traps would have allowed contact sampling/IMS to be employed in the detection of new and emerging explosives threats that have very low vapor pressures and are not amenable to IMS-based detection using current trap technology. These threats include

inorganic species for which no current methods exist. Because the traps being developed here were expected to operate using a combination of electrostatic potential and thermal effects, we expected to release these residues at such a sufficiently low temperature that trap- and IMS-based sensing would have been possible.

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 IMS detection involve traps 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 traps 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 a focused investigation of mesopatterned polymeric traps with surface structures that are designed for interrogation of surfaces and capture of target residues. These traps are engineered to survive the mechanical and thermal demands associated with contact sampling and IMS detection. In addition, the traps being developed are electrically conductive, which is a unique characteristic compared to all existing traps. This feature allows electrothermal desorption to be employed to remove residues from the trap surfaces in the IMS chamber. This method combines the effects of elevated temperature and applied electrical potential to cause residues to be released from trap surfaces at lower temperatures than in the absence of the applied potential. This enables residues with very high sublimation temperatures, such as inorganic explosives, to be evaluated at lower temperatures that are compatible with existing IMS operation.

To create traps with the desired performance attributes, the shape, size, and spacing of the topographical features on the traps will be designed to increase the van der Waals interaction forces between the traps and residues to the greatest possible degree. For this purpose, a surface element integration method was adapted to create surface contour maps that describe the 3-dimensional adhesion force distribution in the vicinity of the traps [1, 2]. The traps are fabricated using an electropolymerization process to produce mesostructured materials that have strong adhesion towards explosives residues [3-6]. It is possible to modify these materials by grafting different chemical species onto their surfaces, changing the adhesion between the traps and the residues [7]. This is explored in order to create traps that have a very strong adhesion force towards the residue, but which do not adhere so strongly that the residue is not released in the IMS.

C. Major Contributions

Year 5:

- We developed and executed a plan for evaluating the adhesion of explosives vapors (TNT) to our traps, in order to assess the affinity of TNT for polypyrrole films with different terminal (head group) chemistry.
- We determined that the electrothermal method for desorbing residues from traps was driven by joule heating, and not from the electrical potential that was applied. This was a disappointment, but was a key finding regarding the use of these traps for delivering vapor of residues that have very high sublimation temperatures.

Year 4:

- Detailed model for residue adhesion to traps: We finished a three-dimensional model for the van der Waals adhesion between explosive residues and traps.
- Adhesion between different explosives and different chemical species: We created self-assembled monolayers (SAMs) of different chemical species, and measured the change in adhesion between explosives residues and these monolayers.
- Apparatus and method for measuring electrothermal desorption: We developed an apparatus for measuring the change in adhesion between explosives residues and the traps in the presence of the different

chemical species, as a function of temperature and applied electrical potential. Preliminary experiments have begun to quantify the electrothermal desorption effect as a function of the trap, temperature, and residue.

Year 3:

- Continued optimization of trap fabrication: We continued the optimization of deposition/growth conditions for fabrication of new, state-of-the-art traps for contact sampling.
- Continued evaluation of thermal stability of traps: By changing the surfactant used during trap growth, we improved the thermal properties of the traps so that they are stable to temperatures as high as $\sim 250^{\circ}\text{C}$.
- Novel method for measuring the adhesion of explosives residues: Developed a novel, first-in-the-world approach for measuring the adhesion between explosives residues, traps, and surfaces that will allow for the measurement of the adhesion of compounded explosives, such as C-4 and Semtex, with unprecedented accuracy.
- We developed a novel method for measuring the adhesion of an explosives powder or population of explosives residues to a surface based on a modification of the classical centrifuge method.

Year 2:

- Preliminary optimization of trap fabrication: We performed preliminary optimization of deposition/growth conditions for fabrication of new, state-of-the-art traps for contact sampling.
- Thermal stability of traps: By changing the surfactant used during trap growth, we improved the thermal properties of the traps so that they are stable to temperatures as high as $\sim 230^{\circ}\text{C}$.
- Topography of trapped surfaces: We determined the relationship between the number of locations on a surface where one performs topographical measurements and the accuracy of the topography statistics determined. This is the basis for the protocol that will be implemented to determine the trapping challenge on various materials of interest in air transportation security settings.
- Model contaminated surface: We developed and implemented a modeled, highly-engineered surface in combination with fluorescent beads (model contaminants) to create a new "standard" trapping challenge. With this standard challenge, we were able to assess the superior performance of the traps being developed here in comparison to COTS traps.

Year 1:

- Viscosity of binders in compounded explosives: The viscosities of the binders used in C-4 and Semtex H were evaluated. This included the measurement of the shear stress, viscosity, and normal stress values as a function of shear rate. As expected, both binders exhibited non-Newtonian, shear-thinning behavior. There are several important distinctions between each composite. First, the Semtex binder is significantly more viscous than the C-4 binder. The viscosity ranged from 810 to 2030 Pa*s for Semtex compared with 20 to 350 Pa*s for C-4. The C-4 binder is more stable with respect to shear rate, whereas any minute change in shear rate creates a significant change in the viscosity of the Semtex binder.
- Residue failure under load: The dynamic behavior of granulated/compounded materials, including silica particles in C-4 and Semtex binders, was documented. The goal was to assess the process by which the granules deformed and failed under load, as this is a good representation of the way they will behave when they are removed from a surface during contact sampling. We observed many similarities between the behavior of composites made with Newtonian binders (model systems) and those made with non-Newtonian binders, but ultimately learned that it was not possible to make a model out of Newtonian binders that would be a good representation of the real compounded explosive.
- Inverse gas characterization: Cohesive Hamaker constants (the van der Waals force constants in effect for materials adhering to themselves) were evaluated using inverse gas chromatography. Constants were

determined for RDX, PETN, TNT, ammonium nitrate (AN), ammonium nitrate fuel oil (ANFO) at 2, 5, and 10% fuel oil, and ammonium nitrate paraffin (ANPA) at 2, 5, and 10% paraffin. These constants agreed well with those obtained from contact angle measurements and optical constants or Lifshitz's theory (data was available for a limited amount of samples). It should be noted that due to limitations of the theory associated with this method, the constants evaluated in this manner were only lower bounds of the true constants [8-11].

- Trap prototypes: Polypyrrole was electrodeposited in a unique apparatus to create nano-/micro-structured traps for use as advanced contact sampling tools. The windows for material deposition were explored and preliminary progress was made linking the thermal stability of the materials to the deposition conditions.

D. *Milestones*

The following milestones, which were described in the Year 5 Work Plan for this project, are listed below, along with a description of the status of each milestone:

1. "Demonstrate that our traps are reusable many times over, and that they do not liberate any harmful byproducts during IMS processing."
 - a. This was the most important milestone, and despite our best effort, we were unable to deliver. When we made traps using an industrially-viable process, the traps seemed to "dry out" over time, until they eventually crumbled. The traps that were made individually did not suffer from this problem, but hand-made traps were not acceptable for production at scale.
 - b. The traps also had problems in that the surface of the desorber in an IMS is at a temperature substantially higher than 250°C. Our traps were stable up to 250°C, but they broke down at higher temperatures, creating vapors that triggered the IMS as possible nitrate ions. This interferes with the sampling and detection using a drop-in replacement mode.
2. "Develop and perform first generation optimization of a method for affixing functional groups to conductive polymer traps, including identifying the proper functional species to attach and the optimal length of the linker molecule."
 - a. We successfully co-deposited thin films of functionalized polypyrrole over the top of base polypyrrole layers, effectively creating conductive polymers with functional surfaces. We also succeeded in assessing the effectiveness of the various surface groups at influencing the adhesion of a model explosive (TNT).
3. "Demonstrate operational capabilities of electrothermal residue desorption from traps in IMS chamber."
 - a. We had high hopes for this process, but were thwarted because at the potentials where we were comfortable using the traps, the residues were liberated by joule heating, and not due to any electrostatic effect.
4. "Develop a method for improving mechanical stability to the traps, if polymer traps are employed."
 - a. We were unable to improve the stability, in spite of using a variety of different plasticizing agents. We prepared to move to using Kapton, which is a trap with much higher thermal stability than polypyrrole, with the goal of texturing the Kapton surface at the appropriate length scale; however, the project was terminated before we could pursue this.
5. "Demonstrate recovery of threat-levels of residue from target surfaces, and show that the fractional recovery with our traps is higher than with COTS materials."
 - a. We did not attempt this, as all our effort was focused on stability and reuse.

6. "Develop a method for improving the thermal stability of the polymer traps to make them compatible with current IMS protocols."
 - a. This was an extension of #1 above, and we were unable to accomplish #1.

E. Future Plans (Year 6)

As a result of the ALERT Biennial Review conducted in March of 2018, this project has been terminated and will not be funded in Year 6. Despite this, we plan to host Professor Holubowitch from Texas A&M Corpus Christi in lab this summer to work on this project. He is using molecular imprinting of polypyrrole on electrodes to detect residues in a method that is a promising alternative to IMS that will work for organic and inorganic energetic threats.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

If successful, this research could have led to the development of new traps with superior ability to harvest explosives residues allowing for better capture and detection of explosives.

B. Potential for Transition

The use of the traps to replace existing traps with better effectiveness at harvesting residues is not possible. What is possible and will be valuable is that the work has shown that traps textured with features on the length scale of 10 – 20 microns in height and comparable width is superior to the features on existing traps at collecting residues from surfaces of interest in air transportation environments. Also, the method of molecular imprinting into conductive polypyrrole is promising, and may lead to an alternative approach for detecting organic and inorganic residues.

C. Data and/or IP Acquisition Strategy

The IP on the original trap design has been secured.

D. Transition Pathway

The insight from this project is whether the primary result is worth transitioning, since the traps were not sufficiently robust to withstand the IMS. This has been disseminated at TED workshops annually.

E. Customer Connections

- Erin Tamargo, CTTSO/TSWG, quarterly calls, 1000 swabs shipped for testing.
- FLIR, Purdue Research Park, joint development agreement under negotiation
 - Abandoned since project cancelled.
- Cindy Carey, Bruker, testing of traps for potential efficacy and eventual adoption
 - Abandoned since project cancelled.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Student Internship, Job, and/or Research Opportunities
 - a. Trained three PhD students on methods associated with this project.
2. Interactions and Outreach to K-12, Community College, and/or Minority Serving Institution Students or Faculty
 - a. Professor Nick Holubowitch from Texas A&M Corpus Christi and his undergraduate student, Grey Medina, came to my lab for the entire summer to study the use of molecular imprinting to create traps that could work on both organic and inorganic threats.

B. Peer Reviewed Journal Art

1. Laster, J., Ezeamaku, C., Beaudoin, S., & Boudouris, B. "Impact of Surface Chemistry on the Adhesion of an Energetic Small Molecule to a Conducting Polymer Surface." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 551, 74-80 (2018). DOI: <https://doi.org/10.1016/j.colsurfa.2018.04.040>
2. Hoss, D., Boudouris, B., & Beaudoin, S. "Analyzing Adhesion in Microstructured Systems through a Robust Computational Approach." *Surface and Interface Analysis*, 49(11), 1165-1170 (2017). DOI: <https://doi.org/10.1002/sia.6282>

Pending-

1. Hoss, D., Mukherjee, S., Boudouris, B., & Beaudoin, S. "Energetic Microparticle Adhesion to Functionalized Surfaces." *Propellants, Explosives, and Pyrotechnics*. In Press (2018).

C. Other Presentations

1. Seminars
 - a. Beaudoin, S. "Advances in Trace Detection." *The Seventeenth Advanced Development for Security Applications (ADSA17)*, Hosted by DHS-sponsored ALERT Center of Excellence, Boston, MA, November (2017).
 - b. Hoss, D., Mukherjee, S., Boudouris, B., & Beaudoin, S. "Adhesion of Explosive Particles to Functionalized Surfaces." *Annual Meeting of the American Institute of Chemical Engineers*, Minneapolis, MN (2017).
 - c. Laster, J., Boudouris, B., & Beaudoin, S. "Microstructured Conducting Polymer Swabs for Enhanced Trace Explosive Detection." *Annual Meeting of the American Institute of Chemical Engineers*, Minneapolis, MN (2017).

D. Student Theses or Dissertations Produced from This Project

1. Laster, J. "Design of Microstructured Conducting Polymer Films for Enhanced Trace Explosives Detection." PhD, Chemical Engineering, January 2017.
2. Hoss, D. "Adhesion Characterization to Improve Trace Explosives Detection Using Mesostructured Polymers." PhD, Chemical Engineering, January 2017.

V. REFERENCES

- [1] Bhattacharjee, S.; Elimelech, M. J. *Colloid Interface Sci.* 1997, 193, 273–285.
- [2] Bhattacharjee, S.; Ko, C.; Elimelech, M. *Langmuir* 1998, 3365–3375.
- [3] Laster, J. S.; Deom, N. A.; Beaudoin, S. P.; Boudouris, B. W. *Journal Polym. Sci. Part B Polym. Phys.* 2016, 1968–1974.
- [4] Kamperman, M.; Kroner, E.; Del Campo, A.; McMeeking, R. M.; Arzt, E. *Adv. Eng. Mater.* 2010, 12, 335–348.
- [5] Sabouraud, G.; Sadki, S.; Brodie, N. *Chem. Soc. Rev.* 2000, 29, 283–293.
- [6] Martin, C. R. *Acc. Chem. Res.* 1995, 61–68.
- [7] Dong, H.; Cao, X.; Li, C. M. *ACS Appl. Mater. Interfaces* 2009, 1, 1599–1606.
- [8] Greiveldinger, M.; Shanahan, M. J. *Colloid Interface Sci.* 1999, 215, 170–178.
- [9] Kwok, D. Y. *Colloids Surfaces A Physicochem. Eng. Asp.* 1999, 156, 1914–200.
- [10] Kwok, D.; Li, D.; Neumann, A. *Langmuir* 1994, 10, 1323–1328.
- [11] Belgacem, M.; Gandini, A. In *Interfacial Phenomena in Chromatography*; Pefferkorn, E., Ed.; CRC Press, 1999; pp. 42–124.

This page intentionally left blank.