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

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II. PROJECT DESCRIPTION

A. Project Overview

The goal of this project is the development of novel swabs 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 that must be addressed include: 1) limited impact of mechanical and chemical effects on swab performance; 2) high temperatures on the desorber plate in the IMS (well above 250°C); 3) loss of mechanical integrity of the swabs 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 (shown below) that changing the surface chemistry of a swab can dramatically change its adhesion behavior towards explosives residues. In our ongoing work, we are experimenting with different surface chemistries to identify the ones that most effectively improve the adhesion of the swabs to the residue during residue harvesting without impeding the residue release process in the IMS.

It is generally accepted that electrothermal methods (the application of an elevated temperature combined with a strong electrostatic potential) will allow residues to desorb from surfaces at lower temperatures than in the absence of the potential. However, because existing swabs are not electrically conductive, the method has not been applied to the desorption of explosives residues in IMS chambers. The conductive swabs developed here do not suffer from this limitation, and therefore have the potential to deliver the electrothermal process. As such, this provides a means by which to employ a new tool for enhanced detection of current difficult-to-detect threats as well as future materials of interest.

The goals of this project are as follows:

- Identify surface chemical moieties that influence the adhesion of explosives residues to our polymeric
swabs, and quantify their effect on the adhesion and the release of residues.

- Demonstrate the effectiveness of electrothermal desorption on altering the thermal profile of residue release from our conductive polymeric swabs, including the swabs with modified surface chemistry.
- Transfer the results of this research to a corporate partner who will develop and deliver the swabs to the public sector for use in air transportation security settings.

When this project succeeds, the swabs that we deliver will improve the effectiveness of checkpoint security activities based on contact sampling/IMS at a low cost. These swabs will allow contact sampling/IMS to be employed in the detection of new and emerging explosives threats that have very high vapor pressures and are not amenable to IMS-based detection using current swab technology. These threats include inorganic species for which no current methods exist. Because the swabs being developed here can operate using a combination of electrostatic potential and thermal effects, we expect to release these residues at such a sufficiently low temperature that swab- and IMS-based sensing will be possible.

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

The strengths of the project were as follows:

- “If the growth and optimization of the meso-structured swabs can be accomplished, this will be very promising.”
- “The approach is sound.”
- “The swab has the promise for detecting other agents besides explosives, and could benefit other agencies, and this should be explored” (this comment appeared twice).
- “Reusable swabs should be cost competitive.”

The project weaknesses were as follows:

- “Swabs that are optimal for sampling some surfaces, such as nylon, will not be optimal for sampling other surfaces, like plastic.”
- “The community may migrate to non-contact sampling, rendering this work obsolete.”
- “If the swabs are reused, they will not be valuable for the prosecution of criminals.”

The weaknesses identified include two concerns that would be relevant for all technologies being employed for contact sampling. First, if the community abandons contact sampling, then all research along these lines is unnecessary. The community has shown no movement in that direction, although there has been a stated desire to go to standoff methods. For the foreseeable future, however, contact sampling is the main tool in the toolkit, and for this reason we are moving forward with our work. Next, whether the swabs are reused or not is a decision made by the Transportation Security Administration (TSA), not by the PI; this decision affects the swabs being developed and existing commercial-off-the-shelf (COTS) swabs. We are working to make swabs that offer superior performance at the lowest possible cost so that single use can be financially viable. If we are successful, this will obviate the need for multi-use. Specifically, COTS swabs that were to be reused would incur the same chain of evidence concerns as our swabs, and COTS swabs would face the same obsolescence as ours if the community can successfully perform non-contact sampling.

In Year 4, we worked on improving the thermal stability of the swabs. We modified the growth conditions by changing the surfactant/supporting electrolyte composition during the electropolymerization process to make the swabs. We identified a surfactant that caused the swabs to be thermally stable up to 250°C in our labs. We found that our swabs tend to ‘age’ poorly if left out in air for an extended period of time. This is because water trapped in the polymer tends to diffuse out of the polymer and evaporate, reducing the plasticity of the polymer. By storing the swabs in a sealed environment (like a plastic bag), we believe that this effect is minimized. We have developed a method to describe the topography of large surfaces using a small number
of measurements. This allows us to characterize the topography of a wide range of surfaces in silico, which will then allow us to optimize the topography and mechanical properties of the swabs so that a single swab can operate effectively on a broad range of surfaces.

C. 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 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 a focused investigation of mesopatterned polymeric swabs with surface structures that are designed for interrogation of surfaces and capture of target residues. These swabs are engineered to survive the mechanical and thermal demands associated with contact sampling and IMS detection. In addition, the swabs being developed are electrically conductive, which is a unique characteristic compared to all existing swabs. This feature allows electrothermal desorption to be employed to remove residues from the swab surfaces in the IMS chamber. This method combines the effects of elevated temperature and applied electrical potential to cause residues to be released from swab 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 swabs with the desired performance attributes, the shape, size, and spacing of the topographical features on the swabs will be designed to increase the van der Waals interaction forces between the swabs 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 swabs [1, 2]. The swabs 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 swabs and the residues [7]. This is explored in order to create swabs 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.

D. Major Contributions

Year 4:

1. Detailed model for residue adhesion to swabs: We finished a 3-dimensional model for the van der Waals adhesion between explosive residues and swabs.

2. 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. The method and materials are shown in Figure 1 on the next page, including the structure of the atomic force microscope (AFM) tip with the attached particles, the structures of the explosives molecules used, and the structures of the thiol-based SAM species immobilized on the gold for the purpose of these measurements. The results are shown in Figure 2 on the next page. In this graph, the force was normalized by the adhesion between the explosives particles and the bare gold, thus removing effects of the shape, size, and topography of the particles.
3. Apparatus and method for measuring electrothermal desorption: We developed an apparatus for measuring the change in adhesion between explosives residues and the swabs 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 swab, temperature, and residue.

Year 3:

1. Continued optimization of swab fabrication: We continued the optimization of deposition/growth conditions for fabrication of new, state-of-the-art swabs for contact sampling.
2. Continued evaluation of thermal stability of swabs: By changing the surfactant used during swab growth, we improved the thermal properties of the swabs so that they are stable to temperatures as high as \( \sim 250^\circ C \).

3. Novel method for measuring the adhesion of explosives residues: Developed a novel, first-in-the-world approach for measuring the adhesion between explosives residues, swabs, and surfaces that will allow for the measurement of the adhesion of compounded explosives, such as C-4 and Semtex, with unprecedented accuracy.

4. 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:

1. Preliminary optimization of swab fabrication: We performed preliminary optimization of deposition/growth conditions for fabrication of new, state-of-the-art swabs for contact sampling.

2. Thermal stability of swabs: By changing the surfactant used during swab growth, we improved the thermal properties of the swabs so that they are stable to temperatures as high as \( \sim 230^\circ C \).

3. Topography of swabbed 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 swabbing challenge on various materials of interest in air transportation security settings.

4. Model contaminated surface: We developed and implemented a modeled, highly-engineered surface in combination with fluorescent beads (model contaminants) to create a new ‘standard’ swabbing challenge. With this standard challenge, we were able to assess the superior performance of the swabs being developed here in comparison to COTS swabs.

Year 1:

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.

2. 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.

3. 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].

4. Swab prototypes: Polypyrrole was electrodeposited in a unique apparatus to create nano-/micro-structured swabs 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.

E. Milestones

Milestones accomplished in Year 4:

• Completed Generation 1 optimization of the size and shape of the fingers on the swab to help them be more effective in the field. For the bilayer swabs that are compatible with IR assessment in the field, we will first demonstrate an ability to make the films of interest.

Milestones to be achieved in Year 5:

• Demonstrate recovery of threat-levels of residues from target surfaces in realistic swipe conditions (using slip/peel tester), and show that the fractional recovery with our swabs is higher than with COTS materials.
• Demonstrate that our swabs are reusable many times over, and that they do not liberate any harmful byproducts during IMS processing.
• Develop and perform first generation optimization of a method for affixing functional groups to conductive polymer swabs, including identifying the proper functional species to attach.
• Develop a method for improving mechanical stability of the swabs, that is if polymer swabs are employed.
• Develop a method for improving the thermal stability of the polymer swabs to make them compatible with current IMS protocols.
• Demonstrate operational capabilities of electrothermal residue desorption from swabs in the IMS chamber.

F. Future Plans

In the next year, it is proposed to complete the proof-of-concept of the electrothermal desorption from our polymeric swabs, demonstrating that residues can be desorbed from our swabs at lower temperatures in the presence of an applied electrical potential than in its absence. This will be performed with at least one explosive material (likely TNT). Samples of our electrothermally-capable swabs will be shared with industry and government partners, including 908 Devices, CTTSO/TSWG, TSL, Bruker, and Smiths/Morpho for testing. We will also document the details of this work at the Trace Explosives Detection workshop in Salt Lake City in April 2018, to further enhance the transition possibilities. Preliminary results show that there should be no problems with completing this work; the process seems to work. It is now a question of simply documenting the magnitude of the effect of the electrical potential on the desorption. The technology will be protected once the preliminary results are complete, to facilitate licensing. In addition, we will complete the work demonstrating the effect of the SAMs on the adhesion between explosives and the swabs, and will make swabs with and without the most effective SAMs. These will be distributed to the same companies and government labs for testing as in the case of the electrothermal work. Preliminary results show that surface treatment has an effect on the adhesion, so we are confident this will work. All that remains is to quantify the magnitude of the effect. When both of these aspects are finalized, the work can sunset in Year 6. The only exception to this projection is if the thermal stability remains inadequate for the modified swabs, even with the electrothermal enhancement. If this is the case, then we will move to metal swabs, aluminum (Al) or copper (Cu), with SAMs present. These can be grown inexpensively with soft, flexible surface topography that would
be highly stable both thermally and mechanically. With appropriate engineering, these can support the electrothermal approach, can be modified by SAMs, and can be reused many times.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

1. Develop new swabs with superior ability to harvest explosives residues:
   a. Metric 1. The swabs will recover at least the same quantities of residue as existing swabs in swipe tests.
   b. Metric 2. The swabs will release residue at lower temperatures than existing swabs when electrical potential is applied.
   c. Metric 3. The swabs will survive multiple uses without a degradation in performance.
   d. Metric 4. The swabs will be implemented in checkpoint security applications.

2. Quantify the effects of the topography, surface chemistry, and electrical potential on the swab performance:
   a. Metric 1. Swab/IMS manufacturers will develop conductive swabs and IMS desorber chambers that support the employment of this understanding.
   b. Metric 2. Swab/IMS manufacturers will develop SAM coatings for existing swabs.
   c. Metric 3. Swab/IMS manufacturers will develop swabs with new textures to optimize residue recovery.

B. Potential for Transition

First generation swabs have been sent to CTTSO/TSWG for testing. We also are pursuing a joint development agreement with FLIR. If preliminary work is successful, we will pursue joint development with these partners.

C. Data and/or IP Acquisition Strategy

A patent application is pending on this technology (see Section IV.D).

D. Transition Pathway

Technical results documenting swab performance have already been shared. During Year 5, the swab performance will be compared side-by-side with existing COTS swabs using a slip-peel tester, which will replicate the swiping environment encountered at checkpoints. The results of these tests will be shared at the annual Trace Explosives Detection workshop in April, 2018. Swabs have been distributed to several commercial partners for testing, and a substantial number have been provided to CTTSO/TSWG, and they are helping to commercialize the swabs.

E. Customer Connections

• Erin Tamargo, CTTSO/TSWG, quarterly calls, 1000 swabs shipped for testing.
• FLIR, Purdue Research Park, joint development agreement under negotiation.
IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities
   1. Student Internship, Job, and/or Research Opportunities
      a. Trained 3 PhD students on methods associated with this project.

B. Peer Reviewed Journal Articles

Pending –

C. Other Presentations

   1. Seminars

D. Technology Transfer/Patents

   1. Patent Applications Filed (Including Provisional Patents)

V. REFERENCES