Strategic Study
Workshop Series

Trace Explosives Sampling for Security Applications

Fundamentals and Advances in Trace Sampling and Detection

TESSA02
August 2015 Workshop
Final Report

ALERT
AWARENESS AND LOCALIZATION OF EXPLOSIVES-RELATED THREATS

A Department of Homeland Security Center of Excellence

Northeastern University

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1. Executive Summary

A workshop focusing on three enabling components of future studies of trace explosives detection was held at Northeastern University (NEU) in Boston on August 5-6, 2015. This workshop was the second in a series dealing with the development of a research plan for organizing the community's understanding of contact sampling during trace explosives detection. The workshop was titled Trace Explosives Sampling for Security Applications - 2 (TESSA02).

The topic of key aspects to be considered in performing and evaluating trace explosives detection experiments was chosen for the workshop in order to support the Department of Homeland Security's (DHS) objective of improving the performance of existing technologies. Historically, the trace detection community has devoted substantial resources to the improvement of ion mobility spectrometry (IMS) for residue detection via contact sampling. Each IMS apparatus is optimized for performance with a different type of wipe, and as such, the performance of the spectrometer is coupled with the performance of the wipe in a way that is difficult to separate. However, it is not possible to detect a residue unless that residue is delivered to the IMS. For this reason, the first step in developing a comprehensive understanding of the limitations of IMS-based trace detection is understanding contact sampling. To perform effective and meaningful contact sampling experiments, it can be helpful to understand: 1) how to make and characterize explosives residues, 2) what controls their adhesion and mechanical behavior, and 3) how the various apparatuses that can be used in the study of contact sampling operate. In addition, it can be helpful to understand other orthogonal sampling/sensing methods that are available to augment contact sampling-based detection. For these reasons, these topics were selected for the TESSA02 workshop.

Specifically, the topics that were addressed at the workshop are as follows:

- Module 1: Creating Explosives Residues -
    - Dry transfer of explosives.
    - Inkjet printing of explosives.
    - Synthetic thumb for residue creation.
- Module 2: Fundamentals for Residue Detection -
    - Dynamics of explosives residues.
    - Forces and mechanics of contact sampling.
    - Describing roughness during contact sampling.
    - Open source crockmeters.
- Module 3: Orthogonal Methods for Sampling/Sensing -

  - Orthogonal sensors for explosives vapors.
  - Fluorescence-based sensing of residues.

The key findings from the workshop, per the editors of this report, are as follows:

Creating Explosives Residues -

- Desirable properties:
  - Rough or smooth,
  - Porous or not,
  - Conductive or dielectric,
  - Hard or soft,
  - Complementary to substrates and
  - High or low elastic modulus.
- **Texwipe is the first choice of a model swipe to be studied, due to its chemical reproducibility and claimed purity.**
  - http://www.texwipe.com/products/swabs/
- **Metal mesh is the second choice model swipe due to its unique physical and chemical properties.**

Fundamentals for Residue Detection -

- Properties to be measured or controlled:
  - Surface energy,
  - Roughness,
  - Hardness and
  - Elastic modulus.
- **Acrylonitrile butadiene styrene (ABS) plastic – expensive.**
- **Aluminum with clear coat.**
- **Aluminum with a 'smooth' finish and without clear coat.**

Orthogonal Sampling/Sensing -

- Desirable to work with a residue that deforms on a surface and one that does not.
- Important to consider safety of residues.
- Residues must be easy to detect by orthogonal method.
- Residues must be readily and reproducibly deposited.
- Questions to be answered:

  - Should the residue be deposited at centralized location and distributed already on substrates?
  - Should the residue be shipped and deposited at site using reproducible method?
  - How can we ensure that the residue is reproducible on substrate?

- **Pure RDX is the first residue.**
- **Compounded RDX (with binders) is the second residue.**

This is the last workshop that will focus on contact sampling. A task order to support a comprehensive effort to characterize contact sampling is underway, based on the results of these first two workshops.

2. Disclaimers

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This document summarizes a workshop at which a number of people participated by discussions and/or presentations. The views in this summary are those of ALERT and do not necessarily reflect the views of all the participants. All errors and omissions are the sole responsibility of ALERT.

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3. Introduction

In concert with the Explosive Division (EXD) of DHS Science & Technology Directorate (S&T), the trace explosives detection community (the 'Trace Community') has identified contact sampling effectiveness as an area of critical concern that limits the development of improved detection capability for use in air transportation environments. Capabilities in need of improvement include an ability to assess a larger number of threat categories, lowered false alarm rates, lowered threat masses required for detection, increased throughput and reduced total operating costs, all at a constant or increased probability of detection. The Trace Community has invested heavily in improvements to detection technology, especially IMS technology, with little consideration of the effectiveness of contact sampling at capturing samples to deliver to these improved IMS systems. As a result, it is unclear that the investment in IMS is properly leveraged, and the true limitations to contact-sampling based detection are unknown. By convening the Trace Community in a shared effort focused on understanding the aspects of the swipes, substrates and residues that control sampling effectiveness, it is expected that the community will produce a comprehensive description of our understanding of the state-of-the-art in contact sampling, including specifically identifying the aspects of contact sampling that require additional research. To synthesize this understanding and to enable the necessary research, support in the form of a task order will be pursued through the DHS-sponsored Awareness and Localization of Explosives-Related Threats (ALERT) Center of Excellence. Essential to the success of the task order effort is an appropriate understanding of the behavior of residues in an experimental setting. Without this understanding, experimental results will have limited applicability, and their extension to the field will also be limited. TESSA01 focused on contact sampling fundamentals, and TESSA02, the topic of this monograph, focused on the creation of residues, their dynamics, and alternative methods to perform trace sampling. This last piece, alternative methods, describes complementary technologies that may enhance, improve, or reinforce contact sampling-based methods.

4. Discussion

4.1 Objectives

The objective of the workshop was to explore the fundamentals that surround experimental and theoretical studies of contact sampling in air transportation environments. This will enable the objective of the TESSA Phase 1 effort, which will be: to develop and test (via a round-robin consensus approach) a methodology and processes to measure a baseline of sampling efficiency for fielded commercial off the shelf (COTS) sampling swipes that are used today. The issues that were addressed centered on the following points:

- State of the art in dry transfer of explosives.
- State of the art in inkjet printing of explosives.
- A new method to create explosives residues on surfaces using a synthetic thumb.
- State of the art in explosives adhesion and dynamics during sampling.
- A review of approaches for studying contact sampling.
- Vapor sensing technologies to complement contact sampling-based methods.

The purpose of this section is to synthesize the discussion and recommendations of these topics and the related questions that surfaced during the discussion.

4.2 Creating Explosives Residues

4.2.1 Dry Transfer of Explosives (R. Lareau, TSL)

There are two principle methods for creating sources that can be used in the dry transfer process to create transfer coupons with reproducible residue deposits:

- Explosives powders are raw material -
    - Weigh out known quantity of explosive powder.
    - Dissolve in appropriate solvent.
    - Dilute to desired concentration to create dissolved explosives working solution (DEWS).
    - Perform quality control (QC) on the solutions to assure DEWS with correct concentration has been created.
    - Use calibrated micropipettes (10 or 20 microliter pipettes) to deposit solution on transfer media, which is known as the

System Quality Control check (SQC) strip.

- COTS standards are raw material -
    - Purchase COTS standards and dilute with solvent to obtain DEWS.
    - Perform quality control (QC) on the solutions to assure DEWS with correct concentration has been created.
    - Use calibrated micropipettes (10 or 20 microliter pipettes) to deposit solution onto the SQC strip.

SQC strips are generally Bytac® plastic, although the method can be applied to create SQC strips on other surfaces, as long as those surfaces are non-porous. Following the deposition of the DEWS solution onto the SQC strips, the solvent is allowed to evaporate from the residue overnight, usually in a dry box. Following the creation of the SQC strips, residues can be transferred to surfaces of interest following the method outlined by Tom Chamberlain, PhD (Patent #6470730). Briefly, in this process, the SQC strip is pressed against a surface of interest so that the residue is in contact with the surface. 'Moderate pressure' is applied during this transfer. For these purposes, 'moderate pressure' could be considered 4-8 N. The SQC strip is then wiped a short distance across the surface and removed. It should be wiped over the surface 3 or 4 times, using a back and forth motion (a zig-zag motion in which the SQC strip travels laterally and vertically across the surface). Preparation of dry transferred explosives residues that are similar to actual threats in shape and morphology is accomplished in this manner. Statistical evaluation of the mean particle size of dry transferred C4 and a C4 fingerprint smear, when applied to flannel fabric, revealed very similar mean particle diameters (8.3 micrometers for the dry transfer and 6.3 micrometers for the fingerprint). The method can be applied to transfer residues onto all manner of surfaces. Applying this method to surfaces that are not continuous and non-porous will still transfer residue, but the residue will be embedded (partially or fully) within the surface of interest and not necessarily on top of it.

It is important to perform QC assessments on the SQC strips. Several methods are employed. First, appropriate solvent extraction should be performed to remove all deposit from an SQC strip, and then to perform appropriate quantitative analysis on the extract to validate the quantity of residue deposited. Next, after residue has been deposited onto the test surface, one should perform the same solvent extraction on the SQC strip to assess the quantity of residue remaining on the strip after dry transfer. Finally, it is desirable to deposit the threat in solvent directly into an analytical vial (rather than onto the SQC strip) and to perform QC on that residue in the vial. Each of these methods provides insight into the creation of residues on the SQC strips and their transfer onto the surface of interest. In studies on the effectiveness of

the dry transfer method to transfer RDX residue from Teflon SQC strips to a muslin surface, ~90% of the residue on the SQC strip was transferred onto the muslin. Similar results were obtained when the method was applied to transfer RDX residue onto 5 different COTS swabs, including the Ionscan 400B cloth, the EGIS II Tab, an Itemiser paper swab, an Itemiser MUST surface, and an Itemizer Teflon surface.

In summary, dry transfer is a straightforward, reproducible, and effective tool for transferring residues onto surfaces such that the transferred residues have many properties similar to those of real threats.

4.2.2 Synthetic Thumb for Residue Creation (M. Brookes, DSTL)

Understanding the nature of realistic explosives contamination is fundamental to developing quantitative standards against which to assess detection methods, including those which use surface sampling. Historically, contamination studies have been conducted using bulk explosives in simulated 'bomb-making' trials, or by creating fingerprint depletion series using a contaminated gloved thumb.

These methods were effective for plastic explosives, which are safe to handle, but nevertheless introduced a degree of deposition variability because of inconsistent applied pressure during the fingerprint depletion, or the specific scenario chosen for the 'bomb-making' trials, which are also complex and expensive to conduct. Moreover, some crystalline explosives, in particular primary explosives, are very sensitive to impact and friction, which means that using bulk material to create trace contamination by direct manual manipulation of the bulk is unsafe.

DSTL (Defence Science and Technology Laboratory, UK) has developed a process using a simulated thumb mounted on an automated force testing machine. The simulated thumb (including fingerprint ridges) is cast from a real thumb mold using Dragon Skin®, a high performance platinum cure silicone rubber. Dragon Skin® has mechanical properties that resemble those of a human thumb, and can be stretched and deformed many times and still return to its original form.

The 'thumb force rig' provides a standard baseline to compare trace contamination deposition from different explosives on different surfaces. By applying a standard force (10N for 10s at an approach speed of 5cm/s) onto a surface, multiple deposition series of 50 prints have been produced. The variability in the trace residues will be due to the chemical and physical properties of the explosives, because the deposition mechanism is standardized.

The thumb force rig therefore provides a means to safely characterize the in-

herent variability in trace contamination of different explosives. Explosives particle sizes are measured for prints in the series, and Liquid Chromatography Mass Spectrometry (LCMS) is used to provide quantification. This provides an understanding of the quantity of explosives in a given print; the particle size distribution as a function of print number; how these vary between depletion series for the same explosive; how these vary between different explosives; and how these vary for different surfaces.

This provides crucial information for the development of quantitative standards. It is important to note that the thumb force rig cannot be used to generate quantitative standards; its purpose is to enable characterization of the variability of trace contamination, not to control the mass deposited.

The thumb force rig was used to produce depletion series for up to 50 prints of the following explosives: PE4 (a UK plastic explosive containing 1,3,5-trinitroperhydro-1,3,5-triazine (RDX)); 2,4,6-Trinitrophenylmethyl-nitramine (Tetryl); pentaerythritol tetranitrate (PETN); and hexamethylene triperoxide diamine (HMTD). Triplicate depletion series for each explosive were deposited onto different surfaces, including glass, ABS plastic and metal.

The trace contamination of each explosive on each surface showed a high degree of variability between the replicates. As expected, the general trend was for decreasing levels of contamination at higher print numbers, although contamination mass could increase as print number increased. The mean mass deposited as a function of print number does not fit a simple exponential decay, and this may be in part due to particle sizes changing as the thumb crushes crystals on each contact with the surface.

Crystalline explosives (HMTD, PETN and tetryl) generally produced higher levels of contamination than PE4. Particle size distributions become increasingly weighted towards smaller particles as print number increases. The most common explosives particle size range for the 50^{th} print on glass is 0 - 250μm^2, but much larger particles are also present. A 250μm^2 explosives particle will have a mass of ~5ng, assuming a spherical particle approximation.

Raman chemical mapping was able to clearly differentiate energetic particles from skin oils for realistic residue particles of RDX (~10 microns in diameter), and differentiate between α-RDX (the stable form, present in bulk and deposited by the thumb force rig) and β-RDX (metastable and typically deposited by ink-jet printing). The Raman method clearly identified PETN on polyester-cotton textiles and athletic shoes, and PE4 on cardboard.

DSTL has also developed a method to evaluate swabbing efficiency using a commercial crockmeter to perform automated swabbing at known force loadings. A scoping study was carried out using glass microspheres and thumb-printed C4 and crystalline RDX deposited onto glass and textured ABS surfaces. Linear

interpolation between alternate prints in the 20 – 50 print range was used to estimate explosives mass loading for the scoping study. Mass balance analysis using LCMS will be used for formal quantitative studies. The initial trends observed were that recovery efficiency improved with swabbing force; recovery was more effective from smooth surfaces; and cotton out-performed paper and Teflon-coated glass fiber as a swabbing material.

4.3 Residue Fundamentals

4.3.1 Dynamics (Mechanical Behaviors) of Explosives Residues (M. Sweat, Purdue)

Understanding how compounded explosives behave under wiping loads is important to optimizing contact-based sampling. A model is proposed to describe the compounded residue as containing large 'chunks' of energetic material (e.g. RDX), which has a very thin coating of binder that is intimately and irrevocably attached to its surface. These coated particles move as units through the bulk matrix when a residue is compressed or stretched during the contact sampling process. It is hypothesized that if one creates a synthetic explosive compound that matches the mechanical behaviors of the live residue, then the contact sampling behavior of the two materials will be matched as well. In particular, if the viscosity of the binder, and the size and roughness distributions of the energetic material are matched, then it is hypothesized that the simulant will demonstrate the same behaviors as the live C4.

Small cylindrical compacts of C4 were formed with diameter and height both of roughly 2 cm. These were then subject to a compressive load in an Instron mechanical testing apparatus, and their stress-strain responses were recorded as a function of strain rate. Over a range of strain rates from 1 – 100 mm/s, very similar behavior was generally observed, in that the compact reached a maximum stress (note that stress here is calculated as engineering stress) quickly, at an engineering strain of roughly 0.1, after which the stress fell gradually to a minimum, reaching a plateau at an engineering strain of roughly 0.5. In some cases, there was a mild rise in stress near the end of the test (strain $\sim$ 0.5), but this is an artifact of the measurement technique.

A classic way to evaluate the mechanical behavior of viscous compounds such as compounded explosives is borrowed from the granulation literature, in particular, the aspect of granulation associated with breakage and attrition of the granules. In this process, two terms are defined to characterize the behavior. The first, the Capillary number, is defined as

$$Ca = \frac{\mu \dot{\varepsilon}_a d_{32}}{\gamma cos\theta} \quad (1)$$

where Ca is the capillary number; μ is the viscosity of the granule binder; $\dot{\varepsilon}_a$ is the engineering strain rate; d_{32} is the specific surface mean diameter of the particles in the granule; γ is the surface energy between the binder and the energetic particles; and θ is the contact angle between the binder and the particles. Within Ca, the term $\mu\dot{\varepsilon}_a$ captures the viscous effects in the system, while the ratio $\frac{d_{32}}{\gamma cos\theta}$ captures the interfacial effects. When Ca is very large, the system behavior is dominated by the viscous effects of the granule, and the interfacial effects are irrelevant. When Ca is very small, the behavior is dominated by interfacial effects. The second dimensionless number used in this analysis is the dimensionless strength, which is defined as

$$Str^* = \frac{\sigma_p d_{32}}{\gamma cos\theta} \quad (2)$$

where *Str** is the dimensionless strength, and σ_p is the peak flow stress, which is the maximum stress observed in the stress-strain curve.

For many materials studied in the food and pharmaceutical industries, a plot of Str* as a function of Ca yields a universal curve with 2 regimes of behavior. The first regime, which extends from Ca values ranging from 10^{-10} to 10^{-4} shows basically no change in Str* with changing Ca. A second regime, for values of Ca greater than $\sim 10^{-4}$ shows a monotonic increase in Str* with increasing Ca. Benign compounds were created to mimic C4. These substituted silica particles for RDX and used silicone oil of varying viscosity to represent the C4 binder. They had Ca numbers ranging from 10^{-2} to 10^{2}, and showed behavior consistent with that observed in other studies. This suggests that C4 and other compounded explosives likely deform plastically until they yield under load.

To further characterize compounded explosives, the viscosity of the binder material found in C4 and in Semtex was studied. These both demonstrated non-Newtonian behavior in the shear-thinning regime. This means that the more shear applied to them, the more readily they flow. During contact sampling, a load will be applied to a compounded explosive residue and the material within the residue will have some regions where the binder is under high local shear while others are under lower local shear. A result of this behavior is that the high shear regions are likely to thin and flow preferentially, leading to failure within the binder. Interestingly, when simulated C4 was subject to varying strain rates, its peak flow stress was seen to increase dramatically with increasing strain rate. This is the opposite of what was expected based on the viscous response of the binders. It suggests that the characteristic time over which the load is applied is very short compared to the characteristic

time for the compact to orient itself in a manner that allows flow to occur. As a result, at high strain rates, the peak flow stress is the highest and the material behaves solid-like. At low strain rates, the material flows like a highly viscous liquid.

When viscous effects of simulated C4 binder were studied over a wide range of viscosities, it was seen that the peak flow stress generally increased with increasing viscosity, while the remainder of the stress-strain curve maintained a common shape across all viscosities considered.

As stated earlier, it was hypothesized that a benign surrogate for C4 could be created by matching the viscosity of the C4 binder, and the size and roughness distribution of the energetic particles in the binder. This was demonstrated to be true, as synthetic residue containing benign particles (silica) with size distributions comparable to the RDX in C4 showed the same stress-strain and peak flow stress behaviors as the live C4. For the purpose of contact sampling studies, this benign residue can be used to make sampling studies possible in a wide range of labs without requiring explosives transport and storage.

In summary, the mechanical behavior of compounded explosives is controlled by the mechanical properties of the binder, and the size and roughness distribution of the particles in the matrix. While the binders for C4 and Semtex are shear-thinning, the long relaxation times required to initiate flow in compounds containing these binders makes it very difficult for these granules to flow under load.

4.3.2 Forces and Mechanics of Contact Sampling (S. Beaudoin, Purdue)

The forces that influence the adhesion of explosives to surfaces and to wipes used in contact sampling are electrostatic forces, capillary forces, and van der Waals forces. These forces, in addition to any load that was applied during the deposition of the residue, may allow the residue to make point contact with the surface, or to deform and make more intimate contact with the surface. When a residue is pulled from a surface, it may be released due to adhesive failure (at the point of residue-surface contact), or due to cohesive failure (at some point within the residue or underlying surface). For many compounded explosives consisting of solid particles in a viscous liquid binder, plastic deformation and failure are likely.

In most transportation security environments, any electrostatic forces holding residues to surfaces or wipes will be controlled by Coulomb's law, reflecting the 'dry' environment (no bulk water present at the interface). If adhesion to metals is considered, then the metals are likely to hold no surface charge, as they can conduct away any spare electrons. Most explosives are dielectrics, as are most surfaces of interest in security checkpoint screening. While

these materials are unlikely to originate with a net surface charge, they are subject to charging via contact electrification. Contact electrification involves the transfer of electrons to a surface from a second surface due to rubbing, or other contact between the surfaces. As most materials in security checkpoint screening applications—including residues to be detected and surfaces to be inspected—are dielectric, any charge transferred in this manner will remain fixed on the receiving surface. As such, it is possible to build regions of local charge, which will then be able to participate in Coulombic electrostatic interactions with other charged surfaces. As humidity increases in the security environment, the amount of adsorbed moisture on surfaces will increase. This moisture provides a mechanism for charge to move on a surface, and it helps minimize the effects of accumulated static charge by allowing charges to disperse themselves over a wide area.

At high ambient relative humidity (generally greater than 50%), it is possible for moisture to adsorb on surfaces in the form of liquid droplets. Liquid bridges may then form between surfaces and particles that rest on those surfaces, increasing the particle adhesion force. Generally, this phenomenon is described approximately, using the Kelvin equation. Figure 1 shows the typical geometry that is used for the Kelvin equation development:

$$R_S = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1} = -\frac{V_{m,L}\gamma_{LG}}{RTln\left(\frac{p_g}{p^s}\right)} \quad (1)$$

$$\Delta P = \frac{2\gamma_{LG}}{R_S} \quad (2)$$

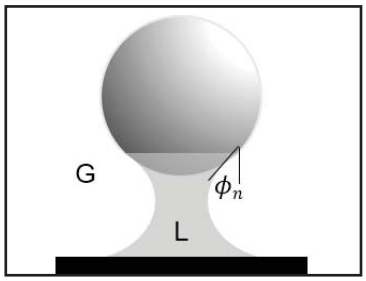


Figure 1: A sphere interacting with a flat surface via a liquid bridge. This is the typical geometry for the Kelvin equation development.

where R_s = Kelvin radius; R_1, R_2 = principle radii of curvature of liquid bridge; $V_{m,L}$ = molar volume of liquid; p_G/p_S = relative humidity; γ_{LG} = liquid-vapor surface tension; ΔP = Laplace pressure; G = gas phase, L = liquid phase. There are a number of shortcomings of this relation that cause it to be only approximate. These are:

- No dependence on surface energy of the solid surfaces between which the liquid bridge is suspended.
- It assumes that the surface tension of the liquid is constant, no matter how small the bridge.
- It assumes that the molar density of water is constant, no matter how little water there may be.
- It predicts that a liquid bridge will form at all humidity levels.

The Kelvin equation is a reasonable approximation at relative humidity (RH) levels above 55 – 60%. Below this limit, it may be off by as much as 50%, and the extent to which the Kelvin equation misrepresents the capillary force increases as humidity drops. At very low RH levels, 15% or lower, the Kelvin equation completely misrepresents the capillary force, as no capillaries of significance will exist at this condition.

The van der Waals (vdW) force is ubiquitous between surfaces separated by less than 30 – 40 nm, and it increases as the surfaces move closer together. This force is proportional to a material-dependent constant that describes the effect of the composition of the two solid surfaces and the intervening medium on the overall vdW force. This constant is generally known as the Hamaker constant, and it varies from 10^{-19} to 10^{-21} J for all materials. If this constant is known and the shape and roughness of the interacting surfaces are known, then the vdW force can be readily predicted. Several methods exist to measure (or estimate) the Hamaker constant for a given system. Direct force measurements, such as those which can be made with an atomic force microscope (AFM), or the surface forces apparatus (SFA), can be used to help determine the Hamaker constant. Inverse gas chromatography (IGC) can also be used, as can surface energy measurements. The last approach is the Lifshitz approach, which calculates the Hamaker constant based on the optical/dielectric properties of the interacting materials. In the AFM or SFA methods, the interaction force between materials is measured directly, and the Hamaker constant is back-calculated based on the size, shape and roughness of the interacting materials, and on the composition of the intervening medium. With the IGC method, a column is packed with a material of interest, and the adsorption of a series of gases of known surface energy to the packed material is measured. The surface energy of the packed material is then estimated. When this is repeated for all interacting materials, the surface energies may be used to estimate the Hamaker constant for the system. Other means to estimate surface energy, such as contact angle measurements, also may be used for this purpose. When the self-Hamaker constants (describing the vdW adhesion of a species to itself) were determined for a number of explosive materials, the constants evaluated by the IGC method were consistently the lowest while those evaluated by the contact angle method were consistently the highest. This is because IGC only considers the non-polar component of the interaction force between the materials, while the contact angle method considers the polar and non-polar components, in addition to hydrogen bonding (which is not a component of the vdW force). The Lifshitz approach, which is intermediate in value in all cases studied, is considered the gold standard, although it is the most challenging to execute.

The effects of surface roughness and contact deformation on vdW adhesion are important to document. Rough features on the order of 5 nm can change

the magnitude of the vdW adhesion force by an order of magnitude, and the significance of this change increases as the magnitude of the roughness increases. Highly rough surfaces will exhibit minimal adhesion compared to the case of smooth versions of the same materials. In the same manner, if a material deforms in contact with a surface, then the extent of intimate contact between the material and the surface will increase. This increases the adhesion force. Compounded explosives are expected to deform in contact with any surfaces on which they deposit. The measurement of the interaction force of compounded explosives against a surface is very difficult to execute due to this deformation.

A new method has been developed to determine the adhesion force of powdered explosives and compounded explosives based on the classic centrifuge method. The advantage of this method is that it yields a distribution of effective Hamaker constants that capture the effects of the size, roughness, and shape distributions of the explosives in an 'effective' Hamaker constant distribution. This allows the adhesion of explosives powders to be described. Prior methods only allowed for the adhesion of individual particles to be described. Similarly, this new approach allows the adhesion of deformable compounded explosives to be estimated.

4.3.3 Describing Roughness During Contact Sampling (L. Miroshnik, Purdue)

It is well known that in order to understand the adhesion between explosives particles and surfaces, one must have an estimate of the roughness of the interacting surfaces. In particular, the ability of opposing surfaces to 'mate' at the nano-scale is very important to the overall adhesion.

From the perspective of the scientist or engineer trying to estimate the adhesion of explosives to surfaces for the purpose of optimizing contact sampling, the prospect of creating a nano-scale roughness map of a large surface is daunting. For example, typical atomic force microscope (AFM) scans of a surface are representative of roughly $2x10^{-5}$% of the surface area of a 1 cm diameter disk.

A method has been created based on a statistical method known as the 'bootstrap,' which can describe the relationship between the number of surface topographical scans made and the accuracy of the description of the surface of interest. To demonstrate the method, three surfaces were evaluated, including Teflon, a silicon wafer with a native oxide, and a stainless steel surface. Nanoscale surface roughness maps were generated using AFM by measuring 40 square regions on each surface with each having a length of 5 micrometers. These were fed into an existing adhesion force simulator at Purdue, which

calculates van der Waals adhesion forces between particles and surfaces of known shape and roughness. The adhesion between a 10 micron diameter particle of silica and a random location on each of the 40 roughness maps for each material (Teflon, silica, and stainless steel) was simulated for 1200 contacts. From the simulated contact data, the mean adhesion for each roughness map can be predicted and then plotted in a histogram called the 'parent' distribution (parent histogram is a distribution of 40 means). The parent distribution is then sampled *n* times, and the *n* samples are averaged. This process of sampling and averaging is repeated many times (in this case, 10,000 times) to create a new distribution, which is called the bootstrap distribution. Repeating this procedure for m different roughness maps yields bootstrap distributions corresponding with results generated from different numbers of locations ($1 \leq m \leq 40$) that could have been selected from the original surface. As a result, a plot of the relative error of the mean adhesion force as a function of the m locations (m varies up to 40) was created. It was seen that the relative error between the bootstrapped mean adhesion force and the mean adhesion force from all 40 locations dropped below 10% when the data from only 10 – 15 regions were included in the determination of the bootstrap mean. From a practical perspective, this implies that no more than 10 – 15 measurements of the topography of a surface (each measurement is over a 5x5 micrometer^2 region) is adequate to describe the expected adhesion force between an explosive particle and a surface with an accuracy, on average, of 10% or less.

To demonstrate the utility of the method, four surfaces of interest to the homeland security community were considered, including smooth and rough ABS plastic, aluminum with a native oxide, and aluminum with a white painted surface. Hamaker constants were estimated to describe the van der Waals adhesion force between three particle types and these four substrates. These particle types included ANFO (5% oil), RDX, and C4 binder. In each case, it was assumed that the particles were smooth and non-deformable, so that the utility of the roughness measurements of the substrate could be demonstrated. An existing van der Waals adhesion simulator was used to estimate the adhesion force between the particles and substrates. Simulated explosives particles were 5 micrometers in diameter, and 1200 adhesion forces were simulated between the particles and the surfaces. In all cases, RDX showed the highest level of adhesion, followed by the ANFO, and then the C4 binder material.

In summary, if the homeland security community wishes to estimate van der Waals adhesion forces between explosives particles and surfaces, they can do so based on a relatively small number of measurements (10 – 15), each of which is itself very small (25 micrometers^2). These estimates should be within 10% of the true values.

4.3.4 Open Source Crockmeter (D. Atkinson, PNNL)

A reproducible method is required to evaluate contact sampling effectiveness when comparing different wipes, residues, and surfaces to be sampled. A crockmeter is a device that moves a stylus of some form over a surface at a set speed, under a set load, and for a set number of repetitions. Crockmeters were developed to determine the colorfastness of textiles to rubbing, but have been adapted to assess scratch resistance and colorfastness of many coatings. They may also be used to assess the removal of explosives residues from surfaces of interest using wipes of interest.

Crockmeters generally retrace a path on a substrate in a cyclical manner, moving back and forth over a linear path under load. Rubbing cloths that are typically employed on crockmeters may be easily replaced by COTS wipes or wipes that are under development.

A range of crockmeters can be purchased from commercial suppliers, ranging from very inexpensive manual crockmeters in which the user moves the wipe over the surface manually to very expensive automated crockmeters, which allow the load, wipe speed, and stroke length to be fixed independently, in addition to making measurements of wiping phenomena, such as the friction at the wipe/substrate surface during the motion.

For the purpose of future contact sampling studies, it is suggested that an 'open source' crockmeter be developed. Such an instrument could be built inexpensively by many labs using off the shelf parts. If an open source crockmeter were created, its blueprints and designs would be readily available to anyone, and improvements could be built into the designs. Using inexpensive parts that are readily commercially available, in conjunction with a 3D printer, it is estimated that an open source crockmeter could be fabricated for less than $100.

4.4 Orthogonal Sampling/Sensing

4.4.1 Orthogonal Sensors for Residue Vapors (O. Gregory, URI)

Detection of explosives vapors is a powerful tool that can be used to complement contact sampling approaches for explosives trace detection (ETD). Unfortunately, many explosives have very low vapor pressures. At 25°C, species like EGDN and TATP have gas phase concentrations in the parts per thousand range, but others like RDX and PETN have concentrations in the parts per trillion range. HMX has a concentration in the parts per quintillion range. As a result, highly sensitive and specific sensors are needed to detect the full range of explosives threats.

A sensing system comprised of six layers (bottom to top): 1) alumina sub-

strate, 2) Ni microheater, 3) sputtered alumina, 4) porous alumina, 5) Ni conductometric electrodes, and 6) metal oxide catalyst has been created. This electronic explosives trace detection, or EETD system simultaneously monitors: 1) the power required to maintain a catalyst coated microheater at the same temperature relative to an uncoated microheater, and 2) the resistivity changes in the same catalyst when explosives vapors adsorb and decompose. The micro-calorimeter based system operates with twin microheaters; one with a metal oxide catalyst present, and one devoid of catalyst. The unreactive probe serves as the control to document temperature changes resulting from the flow environment, while the power required to maintain the catalyst coated probe at the same temperature is measured as the analyte is adsorbed and decomposed. Unique analytes (energetic materials) have unique decomposition signatures, and thus the power required by the microheater comprising the active probe is an indicator of the presence of explosives threats in the vapor phase. At the same time that the power requirements of the probe (thermodynamic signal) are being recorded, the electrical conductivity of the catalyst is also monitored for changes due to analyte adsorption/decomposition. By merging the signals from these two orthogonal sensors, a definitive conclusion can be reached regarding the presence or absence of energetic materials in the vapor stream.

To generate detectable quantities of explosives vapors for use with this sensing system, a pre-concentrator is used. The pre-concentrator utilizes a porous polystyrene coating, and after explosives vapors are captured on its surface, an embedded microheater drives the desorption and sends a pulse of energetic material vapor towards the sensor.

The sensor has been able to detect as little as 1 ppb of TATP, and is readily regenerated via thermal cycling of the microheater. When the metal oxide catalyst is changed, the maximum probe signal shifts with temperature, suggesting that it may be possible to employ an array of sensors with different catalysts, each tuned for a different analyte. Changing the surface area of the catalyst and catalyst support changes the magnitude of the sensor thermal response to the analyte. Moving from a non-porous support to a porous support (with a corresponding change from non-porous catalyst to porous catalyst) dramatically improved the sensor signal. Similarly, moving from porous support to nanowire support improved the sensitivity another two orders of magnitude, from roughly 100 ppb to single digit ppb TATP detection.

4.4.2 Flourescence Based Sensing of Residues (W. Euler, URI)

A promising approach to the detection of explosives vapors is to engineer adsorbent materials that fluoresce upon the adsorption of explosives vapors.

Such materials hold the promise for handheld and/or real time detection of explosives vapors. In the mid-90s, it was established through studies of polyphenylenevinylenes that molecules with a high degree of conjugated C-C bonds amplify fluorescent signals that developed within nearby secondary species. Similarly, a family of inexpensive xanthene dyes, including Rhodamine 560, Rhodamine 6G, Fluorescein 548, Sulforhodamine B, Rhodamine 640, Sulforhodamine 640, Rhodamine 700, and Rhodamine 800 can act as a fluorescence-based sensor for explosives vapor detection. Specifically, sensing stacks were created, comprised of (bottom to top): 1) flat glass substrates; 2) thin transparent commodity polymer films; and 3) fluorescent dye films. These were exposed to broad spectrum light sources (500 – 700 nm wavelength) in the presence of explosives vapors, and the resulting fluorescence signal was recorded. It was discovered that the analyte-fluorophore-polymer combination determined whether or not the emitted fluorescent signal was amplified, quenched, or unchanged compared to the incoming signal. This allows a very large number of 'channels' to be used to develop unique signatures when vapors from any threat adsorb onto the sensor stack arrays. This, in turn, offers the promise of definitive sensing of a wide range of threats.

To optimize and help translate this understanding into a fieldable sensor system, detailed work was conducted to probe the various aspects of the polymers that contributed to this sensing capability. It was determined that the single amplification is in part influenced by the molecular properties of the polymer, and in part by internal reflections within the polymer layer. In addition, the thickness of the fluorophore layer was seen to positively influence the absorbance of light, while the method of creation of the fluorophore layer had little effect on the absorbance. Similarly, as the thickness of the fluorophore increased over the range from 0.5 to 2 nm, both the emission intensity and the wavelength of peak emission increased as well. Finally, mechanistic insight was gained on the effects of the configuration of the film and its emission characteristics. These discoveries suggest that by tuning the thickness of the fluorescent layer, it is possible to tune the absorbance and emission characteristics of the layer to optimize the output in a regime where the presence of explosive analyte is most readily detected.

5. Next Steps

The next steps in this work are as follows:

- Disseminate this report amongst the various community stakeholders.
- Use the results of this study to inform investigations on the mechanism of contact sampling.

6. Acknowledgements

The planning committee would like to thank the following people and organizations for their involvement in the workshop.

- DHS S&T for funding ALERT and sponsoring the workshop.
- Laura Parker, DHS, and Erin Tamargo, CTTSO for their assistance with the workshop activities.
- John Beaty, Teri Incampo, Melanie Smith, Sara Baier, Anne Magrath, Deanna Beirne, and Kristin Hicks of ALERT for their assistance with the logistics, organization, and execution of the TESSA activities.
- Northeastern University for hosting the workshop.
- Richard Lareau (TSL), Matt Brookes (DSTL), Melissa Sweat (Purdue), Steve Beaudoin (Purdue), Leonid Miroshnik (Purdue), Dave Atkinson (PNNL), Otto Gregory (URI), and Bill Euler (URI) for their excellent presentations which provided the intellectual underpinnings of the workshop.
- Dave Atkinson (Pacific Northwest National Labs) and Richard Lareau (DHS S&T) for their vision and leadership in launching and guiding this activity.

The workshop would not have been a success without the participants and the speakers. We extend our heartfelt thanks to them for their contributions.

7. Workshop Planning and Support

The planning committee for the workshop consisted of the following people:

- Steve Beaudoin, Purdue University
- Dave Atkinson, PNNL
- Richard Lareau, DHS S&T
- John Beaty, Northeastern University

The workshop was moderated by:

- Steve Beaudoin, Purdue University

The body of the final report was written by:

- Steve Beaudoin, Purdue University

The final report was assembled by:

- Sara Baier, Northeastern University
- Teri Incampo, Northeastern University

Logistics for the workshop were led by:

- Melanie Smith, Northeastern University

Other logistics, including minute taking and audiovisual assistance, were handled by:

- Sara Baier, Northeastern University
- Deanna Beirne, Northeastern University
- Kristin Hicks, Northeastern University
- Teri Incampo, Northeastern University
- Anne Magrath, Northeastern University
- Melanie Smith, Northeastern University
- Erin Tamargo, CTTSO

The SSI review was performed by:

- Horst Wittmann, Northeastern University

8. Appendix: Notes

This section contains miscellaneous notes about the workshop itself and the final report.

1. The timing in the agenda was loosely followed due to the amount of discussion that took place during the presentations and to allow for additional time for participants to network.
2. Some of the presenters edited their material (mainly redacted information) after the workshop.
3. PDF versions of the presentations from this workshop can be found at the following link: https://myfiles.neu.edu/groups/ALERT/TESSA/TESSA02.

9. Appendix: Agenda

9.1 August 5, 2015

TIME	TOPIC	SPEAKER	AFFILIATION
	INTRODUCTION		
8:00	**Registration/Continental Breakfast**		
8:30	Welcome and Introduction - ALERT	Michael Silevitch	ALERT / NEU
8:35	Welcome and Introduction - DHS	Laura Parker	DHS
8:40	Overview, Goals and Scope	Steve Beaudoin	ALERT/Purdue
	MODULE I: Creating Explosives Residues		
8:50	Dry Transfer of Explosives	Richard Lareau	TSL
9:20	Inkjet Printing of Explosives	Greg Gillen	National Institute of Standards and Technology
9:50	Synthetic Thumb for Residue Creation	Matt Brookes	UK Defence Science and Technology Laboratory
10:20	**Break**		
	MODULE II: Fundamentals for Residue Detection		
10:45	Dynamics of Explosives Residues	Melissa Sweat	Purdue University
11:15	Forces and Mechanics of Contact Sampling	Steve Beaudoin	ALERT/Purdue
11:45	Describing Roughness During Contact Sampling	Leonid Miroshnik	Purdue University
12:15	**Lunch**		
1:15	Pressure/Force Sensitive Sensing	Matthew Staymates	National Institute of Standards and Technology
1:45	Open Source Crockmeter	Dave Atkinson	PNNL
2:15	**Break**		
2:45	Acoustic Insults of Explosives for Vapor Creation	Jeff Rhoads and Steve Beaudoin	ALERT/Purdue
3:15	Orthogonal Sensors for Residue Vapors	Otto Gregory	University of Rhode Island
3:45	Flourescence Based Sensing of Residues	Bill Euler	University of Rhode Island
4:15	**Reception**		

9.2 August 6, 2015 - Leadership Team Meeting

TIME	TOPIC	SPEAKER	AFFILIATION
	INTRODUCTION		
8:00	**Registration/Continental Breakfast**		
8:30	Welcome	Steve Beaudoin	ALERT/Purdue
8:35	ALERT/DHS Task Order Summary	Laura Parker	DHS
	TEAM MEMBER INPUT		
8:45	Summary of Characterization - Part I	Dave Atkinson (Moderator)	PNNL
9:45	**Break**		
10:00	Summary of Characterization - Part II	Dave Atkinson (Moderator)	PNNL
	PLAN TO FINISH		
10:30	Summary of Participant Contributions	Steve Beaudoin	ALERT/PURDUE
11:00	Defining the Round-Robin Characterization Activities	Richard Lareau	TSL
12:00	Wrap Up and Next Steps	Steve Beaudoin	ALERT/Purdue
12:15	**Lunch**		

10. Appendix: Previous Workshops

Information about the previous eleven workshops, including their final reports, can be found at: www.northeastern.edu/alert/transitioning-technology/strategic-studies.

11. Appendix: List of Participants

NAME		AFFILIATION
David	Atkinson	Pacific Northwest National Laboratory
Sara	Baier	Northeastern University
John	Beaty	Northeastern University
Steve	Beaudoin	Purdue University
Deanna	Beirne	Northeastern University
Kurt	Bistany	Morpho Detection
Hacene	Boudries	Implant Sciences Corp.
Matthew	Brookes	Defence Science and Technology Laboratory
Emel	Bulat	Northeastern University
Cindy	Carey	Bruker Detection Corporation
David	Castañón	Boston University
Joseph	Chipuk	Signature Science
Michelle	Clark	MIT Lincoln Laboratory
Allan	Collier	TSA
Kevan	Creppy	Department of Homeland Security
Sonal	Das	Department of Homeland Security
Robert	Deans	FLIR
Reno	DeBono	Smiths Detection
Jayesh	Doshi	GSA
Abiy	Eshetu	DSA Detection
William	Euler	University of Rhode Island
David	Fine	GeNOLLC
Mark	Fisher	FLIR Systems
Noel	Fitzgerald	Enertechnix
Greg	Gillen	National Institute of Standards and Technology
Ilana	Goldberg	Johns Hopkins University
Polly	Gongwer	Department of Homeland Security
Kerin	Gregory	908 Devices, Inc.
Otto	Gregory	University of Rhode Island

NAME		AFFILIATION
Adam	Hall	Northeastern University
Steve	Harden	Leidos
Kristin	Hicks	Northeastern University
Teri	Incampo	Northeastern University
Vladimir	Kekukh	Bruker Corporation
Jude	Kelley	Massachusetts Institute of Technology
Roderick	Kunz	MIT Lincoln Laboratory
Richard	Lareau	Transportation Security Laboratory
David	Lawrence	Johns Hopkins University
Rebecca	Levine	University of Rhode Island
Stefan	Lukow	Morpho Detection
Teresa	Lustig	Department of Homeland Security
Anne	Magrath	Northeastern University
Patricia	McDaniel	Combating Terrorism Technical Support Office and ManTech
Andy	McGill	Naval Research Laboratory
Leonid	Miroshnik	Purdue University
Thoi	Nguyen	Department of Homeland Security
Igor	Novosselov	Washington University
Jimmie	Oxley	University of Rhode Island
Laura	Parker	Department of Homeland Security
Jill	Phillips	NAVTECH EOD
Jay	Postlewaite	Texwipe
Peter	Prodzenko	TSA
Jeffrey	Rhoads	Purdue University
Kenneth	Ribeiro	Bruker Detection Corporation
Susan	Rose-Pehrsson	Naval Research Laboratory
Matt	Rutter	DSA Detection
Anthony	Serino	Raytheon Company
Robert	Shuchatowitz	Reveal Imaging Technologies, Inc.
Michael	Silevitch	Northeastern University
Todd	Silvestri	Implant Sciences Corp.

NAME		AFFILIATION
James	Smith	University of Rhode Island
Melanie	Smith	Northeastern University
Matthew	Staymates	National Institute of Standards and Technology
Devon	Swanson	University of Rhode Island
Melissa	Sweat	Purdue University
Erin	Tamargo	Combating Terrorism Technical Support Office
Patrick	Wen	Massachusetts Institute of Technology
Mark	Witinski	Eos Photonics, Inc.
Ching	Wu	Excellims Corporation

Note: The list of participants reflects those individuals that registered for either Day 1 or Day 2 of TESSA02. Any errors are due to the editors of this report and not to the participants themselves.

12. Appendix: Presenter Biographies

David Atkinson

David Atkinson is a senior research scientist and manages the Chem/Bio/Explosive threat detection R&D portfolio at the Pacific Northwest National Laboratory. Dr. Atkinson holds a Ph.D. in analytical chemistry from Washington State University, under the advisement of Herb Hill. He has worked in trace chemical detector development in the DOE National Laboratory complex over the last 23 years, with a specific emphasis on explosives detection. He has participated in all aspects of R&D on explosives detection, from performing fundamental research, to doing testing/evaluation, to deploying equipment in the field and training end users. He has worked for decades with the Federal Aviation Administration (FAA) and then the Department of Homeland Security (DHS) on applying detection instrumentation to aviation security. He was the co-chair of the 2011 Gordon Research Conference on Detecting Illicit Substances and is a co-founder and co-chair of the annual Trace Explosives Detection Workshop.

Stephen Beaudoin

Stephen P. (Steve) Beaudoin is a Professor in the School of Chemical Engineering at Purdue, where he also serves as the Interim Associate Vice Provost for Academic Affairs. Dr. Beaudoin has won the Faculty Early Career Development Award from the National Science Foundation, and has been named a Purdue University Faculty Scholar and a Purdue University Provost Fellow for Student Success. He has won numerous teaching and mentoring awards, including being the inaugural recipient of the Purdue University Student Government Teaching Excellence Award. Dr. Beaudoin's areas of research interest are focused on particle and thin film adhesion, with emphasis on explosives detection and in microelectronics, food, and pharmaceutical manufacturing. Dr. Beaudoin received his Bachelor of Science degree from MIT in 1988, his Master of Science degree from the University of Texas at Austin in 1990, and his PhD from North Carolina State University in 1995. All of his degrees are in Chemical Engineering.

Matthew Brookes

Dr. Matthew Brookes is the Explosives Detection Group Principal Scientist at the UK Defence Science and Technology Laboratory (Dstl). Prior to joining Dstl in 1998, Dr Brookes completed a DPhil at Oxford University and a post-doc at the National Research Council of Canada, studying high resolution spectroscopy of Van der Waals molecules. Dr Brookes leads the provision of operationally focused science and technology (S&T) to support military and counter-terrorism applications of explosives detection. He deployed to Afghanistan twice as the UK Scientific Adviser, focusing on counter-IED and force protection capabilities, and also working alongside the US Marine Corps S&T branch. He is a Fellow of the Royal Society of Chemistry and a Chartered Chemist, and a previous co-chair of the Gordon Research Conference on Illicit Substance Detection.

William B. Euler

William B. (Bill) Euler is Professor of Chemistry and Chair of the Chemistry Department at the University of Rhode Island. He earned B.S. degree from the University of Wisconsin-La-Crosse, double majoring in chemistry and mathematics, and a Ph.D. degree in Inorganic Chemistry from Florida State University under the supervision of the late Barry Garrett. He then went to Northwestern University as a postdoctoral student working with Brian Hoffman. He served as the co-director of the Sensors and Surface Technology Partnership at URI. Professor Euler has 100 publications spanning topics in solid state chemistry and physics, conducting materials, inorganic chemistry, polymer synthetic chemistry, polymer reaction chemistry, photochemistry, quantum chemical calculations, sensors, thermal analysis, surface chemistry, and IR, NMR, UV-Vis, and EPR spectroscopy. His recent research has focused on developing inexpensive optical detection methods for explosives and other trace analytes.

Greg J. Gillen

Greg Gillen is a Supervisory Research Chemist in the Surface and Microanalysis Science Division at the National Institute of Standards and Technology (NIST). He graduated from the University of California Santa Barbara 1983 with a bachelor's degree in chemistry. He received a PhD in Analytical Chemistry from Arizona State University in 1987 with an emphasis on Secondary Ion Mass Spectrometry (SIMS). He joined NIST

as a Postdoctoral Research Associate in 1988 and became a staff scientist in 1989. He is currently group leader of the Surface and Trace Chemical Analysis Group. He is a technical co-organizer for two yearly scientific conferences focused on trace explosives detection and mass spectrometry. He was the recipient of a Department of Commerce Bronze and two Silver Medals for his research. He is a former co-director of the Chemistry undergraduate research fellowship program at NIST. He is a member and former chairman of the ASTM E42.06 subcommittee on Secondary Ion Mass Spectrometry and has served on the board for the Applied Surface Science Division of the American Vacuum Society.

Otto J. Gregory

Otto J. Gregory is currently Distinguished Engineering Professor in the Department of Chemical Engineering at the University of Rhode Island. He received B.S. degrees in Chemical Engineering and Ocean Engineering from the University of Rhode Island in 1975, a M.S. degree in Chemical Engineering from the University of Rhode Island in 1977 and a Ph.D. degree in Materials Science and Engineering from Brown University in 1983. Prof Gregory has served as Associate Dean of Research and Graduate Studies in the College of Engineering at the University of Rhode Island and Director of the Rhode Island Center for Thin Film and Interface Research, a joint NSF- Brown University - University of Rhode Island Engineering Research Center from 1993-1996. He also founded and co-directs the University of Rhode Island's Sensors and Surface Technology Partnership for Research and Education. Professor Gregory's research over the past 30 years has focused on sensors for harsh environments, thermoelectric materials for energy harvesting, wireless sensors, wide-bandgap semiconductors, and chemical sensors. Prof Gregory hosted the 2007 Joint Propulsion Instrumentation Working Group - European Virtual Institute for Gas Turbine Instrumentation Conference on Gas Turbine Engine Instrumentation in Newport, RI. He received the Major Charles Bassett III Outstanding Paper Award at both the 49th and 56th ISA Symposium (Aerospace Industries Division and Test/Measurement Division) in 2004 and 2010, and the Best Paper Award at the 19th IEEE DASC Conference (Digital Avionics Conference in Philadelphia), in 2000. Prof Gregory currently holds 25 US Patents related to strain, temperature and heat flux sensors, waveguides for carbon dioxide lasers, and wireless sensors for harsh environments.

Richard Lareau

Richard Lareau is the Acting Technical Director and Chief Scientist for the Transportation Security Laboratory, Science & Technology Directorate, Department of Homeland Security. Dr. Lareau holds a Ph.D. in analytical chemistry from Arizona State University. At DHS, he is involved in external and internal explosives detection RT&E programs that span several technology areas, including trace and bulk detection. Additionally, Dr. Lareau is Subgroup Chair for DoD's CTTSO/TSWG CBRNE programs. Previously, Dr. Lareau worked as a senior researcher at the Army Research Laboratory, Electronic Technology & Devices Laboratory, Sensors Division, at Ft. Monmouth, N.J. and Adelphi, M.D., laboratories. As an analytical chemist, Dr. Lareau established and operated DOD's state-of-the-art Advanced Microanalysis Laboratory and materials processing groups. Dr. Lareau is co-Organizer and Scientific Advisor of two scientific workshop series; The Annual Workshop on Secondary Ion Mass Spectrometry and the Annual Workshop on Trace Explosives Detection.

Leonid Miroshnik

Leonid Miroshnik is currently a Graduate Research Assistant pursing his PhD in Chemical Engineering at Purdue University under Stephen Beaudoin. He is studying the dynamic mechanical behavior of simulated energetic material filled granules using Discrete Element Method (DEM) computational models. Leo obtained his bachelor's degree in Chemical Engineering at Drexel University, where he was an Undergraduate Research Assistant. He contributed to the development of a thin-film substrate for Dye-Sensitized Solar Cells (DSSC).

Laura Parker

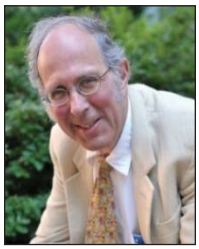
Laura Parker is a Program Manager in the Explosives Division of the Science and Technology Directorate at the Department of Homeland Security (DHS) as well as the Program Manager for the ALERT Center of Excellence, a DHS-sponsored consortium of universities performing research that address explosive threats lead by Northeastern University. She works on multiple projects for trace detection of explosives and algorithm development for improved explosives detection. Previous to her present position at DHS, Laura worked as a contractor providing technical and programmatic support of chemical and biological defense and

explosives programs for several Department of Defense (DoD) offices. She also worked in several DoD Navy laboratories in the field of energetic materials. She obtained her Ph.D. in chemistry from Pennsylvania State University.

Jeffrey F. Rhoads

Jeffrey F. Rhoads is an Associate Professor in the School of Mechanical Engineering at Purdue University and is affiliated with both the Birck Nanotechnology Center and Ray W. Herrick Laboratories at the same institution. He received his B.S., M.S., and Ph.D. degrees, each in mechanical engineering, from Michigan State University in 2002, 2004, and 2007, respectively. Dr. Rhoads' current research interests include the predictive design, analysis, and implementation of resonant micro/nanoelectromechanical systems (MEMS/NEMS) for use in chemical and biological sensing, electromechanical signal processing, and computing; the behavior of electromechanical and thermomechanical systems operating in rich, multi-physics environments; and the fundamental science and engineering associated with energetic and reactive materials. Dr. Rhoads is a member of the American Society for Engineering Education (ASEE) and the American Society of Mechanical Engineers (ASME), where he serves on the Division's Technical Committees on Micro/Nanosystems and Vibration and Sound, as well as the Society's Design, Materials, and Manufacturing Segment Leadership Team. Dr. Rhoads is currently an Associate Editor of the Journal of Vibration and Acoustics, and recently served as the General Chair of the 2015 ASME International Design Engineering Technical Conferences and Computers and Information in Engineering Conference, one of the largest global mechanical engineering focused events. Dr. Rhoads is a recipient of the National Science Foundation's Faculty Early Career Development (CAREER) Award, the Purdue University School of Mechanical Engineering's Harry L. Solberg Best Teacher Award (twice), and the ASEE Mechanics Division's Ferdinand P. Beer and E. Russell Johnston, Jr. Outstanding New Mechanics Educator Award. In 2014, Jeff was selected as the inaugural recipient of the ASME C. D. Mote, Jr. Early Career Award for his contributions to the fields of dynamics and vibration. Dr. Rhoads is a Fellow of the Purdue Teaching Academy, and was recently featured in ASEE Prism Magazine's 20 Under 40.

Michael B. Silevitch



Michael B. Silevitch is currently the Robert D. Black Professor of Engineering at Northeastern University in Boston, an elected fellow of the IEEE, the Director of the Homeland Security Center of Excellence for Awareness and Localization of Explosives Related Threats (ALERT) and the Director of the Bernard M. Gordon Center for Subsurface Sensing and Imaging Systems (Gordon-CenSSIS), a graduated National Science Foundation Engineering Research Center (ERC). His training has encompassed both physics and electrical engineering disciplines. An author/co-author of over 65 journal papers, his research interests include laboratory and space plasma dynamics, nonlinear statistical mechanics, and K-12 science and mathematics curriculum implementation. Prof. Silevitch is also the creator of the Gordon Engineering Leadership (GEL) Program at Northeastern University, a graduate curriculum offered through the College of Engineering, with the mission of creating an elite cadre of engineering leaders. He and the current GEL Director, Simon Pitts, were recently awarded the 2015 Bernard M. Gordon Prize for Engineering Education by the National Academy of Engineering (NAE).

Matthew E. Staymates

Matthew Staymates is a mechanical engineer and fluid dynamicist in the Surface and Trace Chemical Analysis Group at NIST. His research interests focus on improved metrology techniques for the evaluation of trace explosives and narcotics detection technology, as well as computational fluid dynamics, schlieren imaging, high-speed videography, laser light-sheet flow visualization, and other traditional flow diagnostic methods that are used to investigate the performance of current trace detection technology. He is also focused on enhancing non-contact aerodynamic sampling in next-generation trace detection equipment. Matt's other interests include standard explosive microparticle fabrication, particle release mechanisms, and precise material deposition for stand-off explosive detection instrumentation, and additive manufacturing. Matthew serves as the Explosives Safety Officer for the division and oversees the safe handling of high explosives and energetic materials.

Melissa Sweat

Melissa Sweat is a Ph.D. candidate in chemical engineering at Purdue University under Stephen Beaudoin. She has studied small-scale particle adhesion (single particles) to large scale granulation (thousands of particles), with an explosives detection emphasis. Her thesis has focused on the characterizing the dynamic compressive behavior of simulated and live energetic materials. She will be graduating this December, and hopes to obtain a position continuing research on simulated energetic materials as mimetics for live explosives. Previously, Melissa worked as an undergraduate research assistant at Mississippi State University, where she obtained her bachelor's degree in chemical engineering. Her work there focused on the remediation of waste wood contaminated with chromated copper arsenate (CCA).

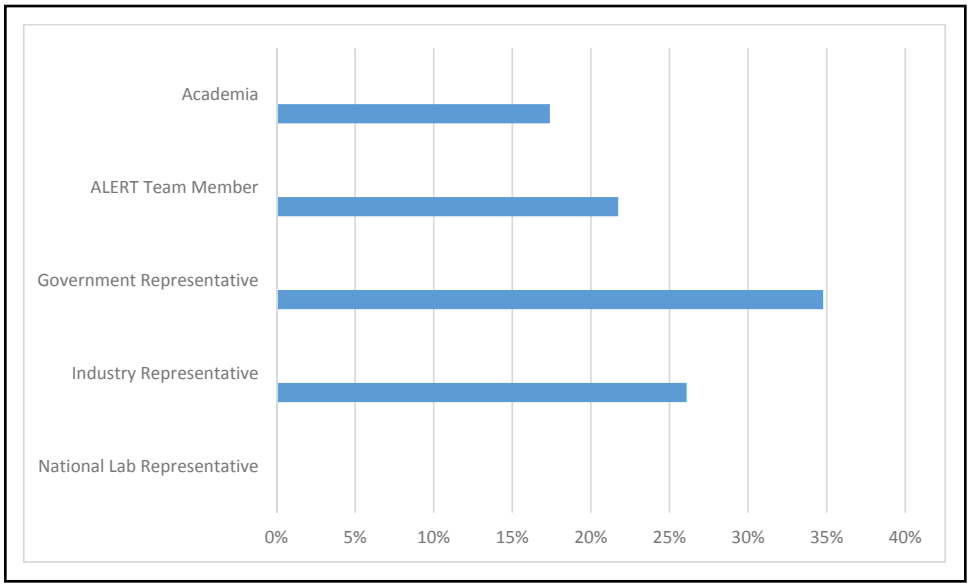
13. Appendix: Questionnaire

Attendees were asked to fill out a questionnaire providing feedback on the workshop. The questions are listed below. The answers appear in the following section with the number of respondents for each question (out of a total of 26 respondents) and their individual comments.

1. What is your current relationship to ALERT?
2. How far did you travel to attend the TESSA02 Workshop?
3. How satisfied are you the format of the TESSA workshops?
4. Would you like to see the workshop expanded to two days?
5. How satisfied were you with the topics and focus of the TESSA02 pre sentations and discussion?
6. Please rate your overall satisfaction with the TESSA02 Workshop.
7. Are there trace explosives sensing technologies that you would like to see discussed at a future TESSA workshop?
8. Do you have suggestions of unmet trace explosives sensing challenges that should be addressed at future workshops?
9. Please provide any other feedback or comments you have.

14. Appendix: Questionnaire Responses

Question 1: What is your current relationship to ALERT?



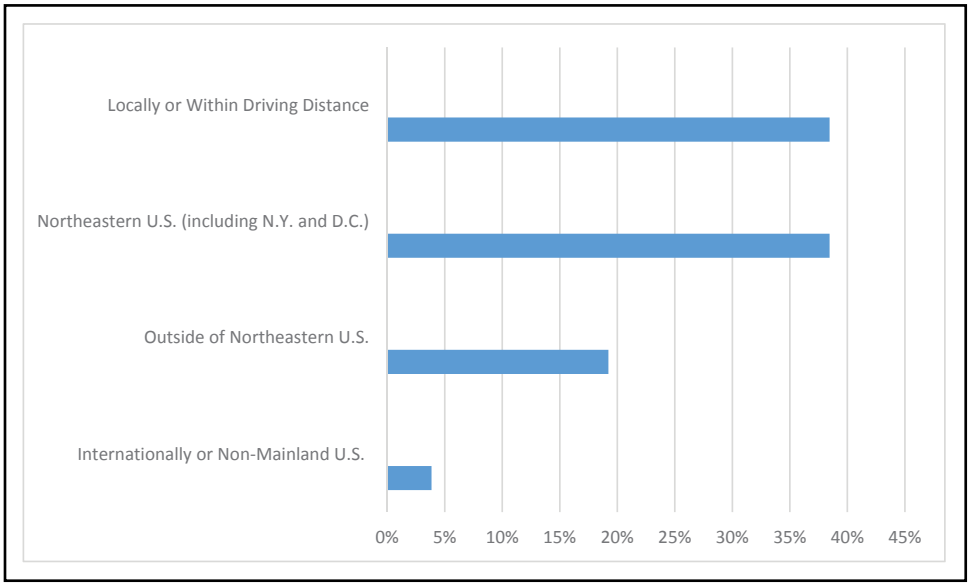
Respondents: 23
Non-Respondents: 3

Academia – 17.39%
ALERT Team Members – 21.74%
Government Representatives – 34.78%
Industry Representatives – 26.09%

Individual Responses for "Other":

- "Contractor supporting Government Representative."
- "Government Contractor."

Question 2: How far did you travel to attend the TESSA02 Workshop?



Respondents: 26

Non-Respondents: 0

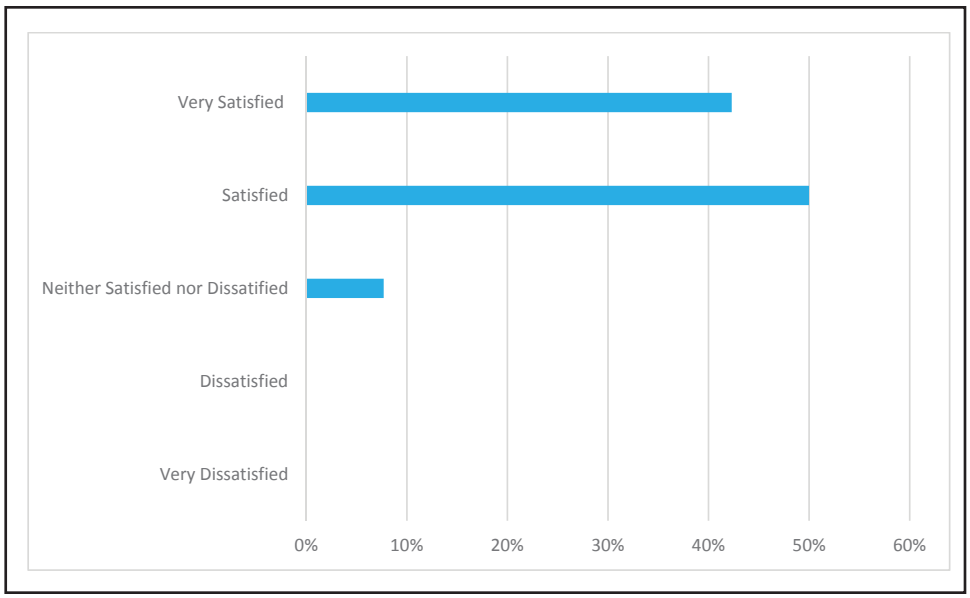
Locally or Within Driving Distance – 38.46%

Northeastern U.S. (including N.Y. and D.C.) – 38.46%

Outside of Northeastern U.S. – 19.23%

Internationally or Non-Mainland U.S. – 3.85%

Question 3: How satisfied are you with the format of the TESSA workshops?



Respondents: 26

Non-Respondents: 0

Very Satisfied – 42.31%

Satisfied – 50%

Neither Satisfied nor Dissatisfied – 7.69%

Dissatisfied – 0%

Very Dissatisfied – 0%

Individual Responses for "Very Satisfied":

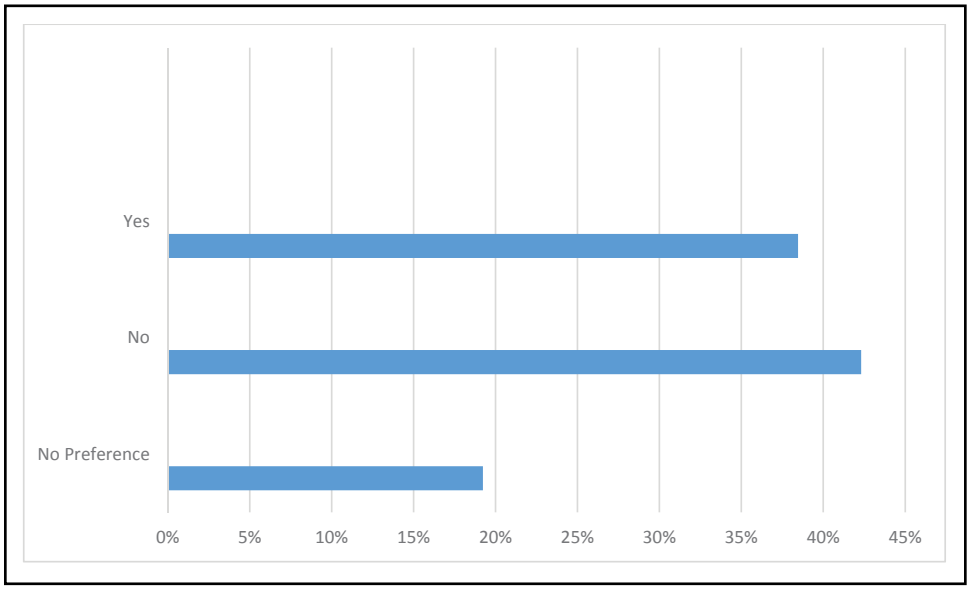
- "The length was just right; the longer breaks allowed us to run a few minutes over without sacrificing time to get snacks and chat so fewer people coming into talks after breaks late."
- "Interesting presentations and good conversation."
- "I enjoyed the free exchange during presentations."
- "I found the format - very precise and efficient."

- "Straight and to the point, great selection of topics and speakers."
- "A wonderful meeting with a good blend of talks on the topic of contact sampling complemented by some interesting work on vapor detection."

Individual Responses for "Satisfied":

- "Earlier invitation-include primary topics of interest for that year. Query invitees to see if they have anything to offer. If not done already, use feedback from TED to amplify sampling and sensing technologies and problems with same."
- "Would benefit from more time for discussion and networking."
- "I think having more time for informal discussion would be nice, without a presentation. An evening networking reception or outing might also work well."
- "Excellent attendance, nice room with tables and good interactions."
- "The information presented was important. However, in comparison to TESSA01, I found that TESSA02 to be far more theoretical and less practical. I also enjoyed how we split up into discussion groups in TESSA01 and the interactive nature of the information generated from the audience."

Question 4: Would you like to see the workshop extended to two days?



Respondents: 26

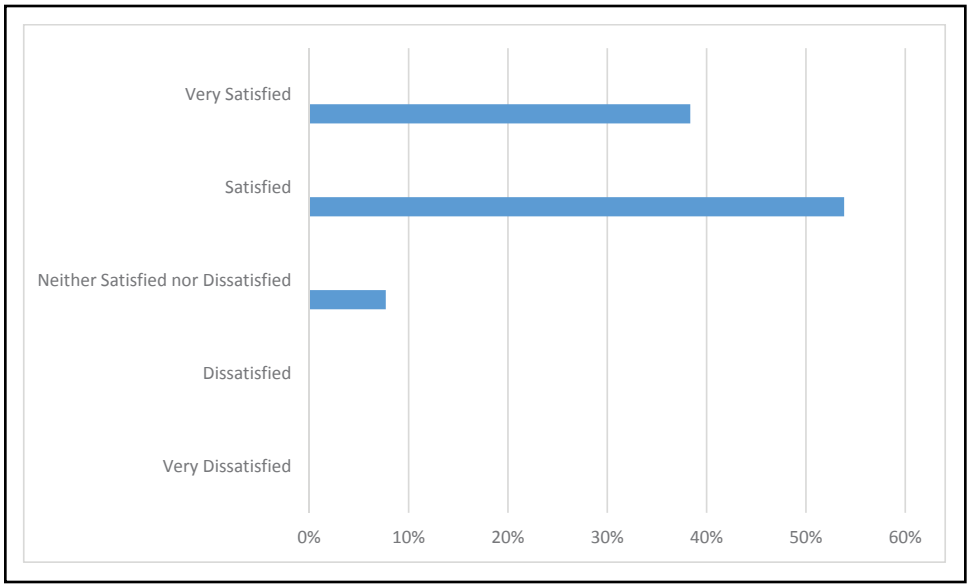
Non-Respondents: 0

Yes – 38.46%

No – 42.31%

No Preference - 19.23%

Question 5: How satisfied are you with the topics and focus of the TESSA02 presentations and discussion?



Respondents: 26

Non-Respondents: 0

Very Satisfied – 38.46%

Satisfied – 53.85%

Neither Satisfied nor Dissatisfied – 7.69%

Dissatisfied – 0%

Very Dissatisfied – 0%

Individual Responses for "Very Satisfied":

- "The focus of the presentations helped lead to the goals of TESSA and the slight variety at the end of the day with new research helped to keep things fresh and interesting."
- "Inkjet printing was great."
- "The different presenters did a good job relaying their respective information."

- "Focusing on the current key issues."
- "Topics presented were focused and pertinent to the topic at hand. I would only extend to two days if there are sufficient talks on the sampling end and how analysis ties into sampling constraints."

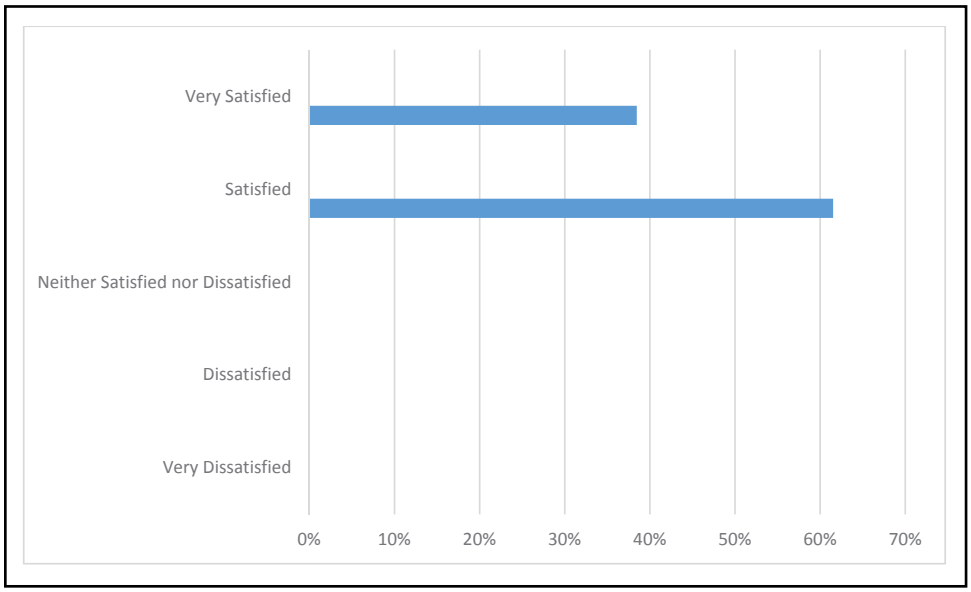
Individual Responses for "Satisfied":

- "Would like to see emphasis on advances in sample acquisition and presentation of samples to various sensor systems to include updates of sampling and sensing technologies from previous workshops."
- "More focused discussion sessions would be valuable."
- "The work being done at Purdue was great. I would have liked to see more about the test plan. I would have liked to have more interaction with the attendees in the first meeting."

Individual Responses for "Neither Satisfied nor Dissatisfied":

- "Several presentations of ALERT team members revealed that their research is fundamental. Not to put down fundamental research, but their research should have a transition plan worked out in advance."

Question 6: Please rate your overall satisfaction with the TESSA02 Workshop.



Respondents: 26

Non-Respondents: 0

Very Satisfied – 38.46%

Satisfied – 61.54%

Neither Satisfied nor Dissatisfied – 0%

Dissatisfied – 0%

Very Dissatisfied – 0%

Individual Responses for "Very Satisfied":

- "Very good workshop!"
- "Pacing and opportunity for interaction and discussion during workshop was very positive."

Individual Responses for "Satisfied":

- "Good venue, good general workshop format. However, this year, it

seemed to be more of a conference than a workshop. Last year was more informative of need for standards and approaches to same along with sampling issues and potential solutions. Small group discussions were helpful."

- "Lunch was excellent."

Question 7: Are there trace explosives sensing technologies that you would like to see discussed at a future TESSA workshop?

Respondants: 10

Non-Respondents: 16

Individual Responses:

- "Sampling issues as applied to specific explosives trace detection methodologies would be of interest (e.g. MS, IR, Raman, IMS, X-Ray, etc.)."
- "Long range trace detection."
- "Not to be specific, but advances in existing technologies would be beneficial."
- "Has TESSA expanded its focus from surface sampling (the original goal) to broader sensing? Need to ensure it does not duplicate talks at TED, which is usually held a month or so before TESSA."
- "Workshops that explain MS, IMS, etc."
- "Not quite the same, but colormetrics?"
- "More stand-off trace technologies should be discussed."
- "Yes. Vapor detection is going to be discussed. There are many opportunities."
- "I liked the idea of having a couple talks on explosives detection technology. Since only a couple of talks are presented in this section, my interest would be on new emerging concepts and ideas. I do not see much value in greatly expanding this area since this is covered by TED. I really like the focus on sampling. Any talks that help to expand the knowledge of the nature of the sample would be helpful. There is definitely an emerging need for non-contact sampling. Areas of interest are both collection and surface ionization techniques, such as low temperature plasma."
- "Mass spectrometry approaches and field portable initiatives in analytical detection."

Question 8: Do you have suggestions of unmet trace explosives sensing challenges that should be addressed at future workshops?

Respondents: 9

Non-Respondents: 17

Individual Responses:

- "Our approach to technology development is more or less "let a thousand flowers bloom" approach. And the company reps attending the workshop are supposed to pick out the best flowers. I don't think it is an efficient way to develop ETD technologies. A more efficient way would be: 1) There are approaches academic researchers/companies developed in the past; 2) This is an issue that may have operational impact; 3) Through discussions (face to face, whiteboard, PowerPoint presentation), ETD community members would settle on a few approaches with the best potential to address that issue; 4) ETD community members would conduct research to convert these approaches into real solutions."
- "There needs to be much better access to past work. Old government funded reports need to be made available to the community. Several studies are repeating work that was done 10 to 30 years ago, unaware of the past studies."
- "Sample acquisition of inorganic explosives samples and generation of airborne explosives (vapors or aerosols)."
- "Vapor detection."
- "Sampling of both particles and vapors have many interesting possibilities."
- "Contamination, matrix effects."
- "Nature of the explosive sample on hands."
- "False IDs by IMS, background interference during sampling and forward thinking past IMS and what the future holds for analytical detection in security applications."
- "Electrostatic forces."

Question 9: Please provide any other feedback or comments you have.

Respondents: 3

Non-Respondents: 23

Individual Responses:

- "I liked seeing the larger number of academics doing research presenting and their students in the audience; this has definitely not been the case in the past."
- "You need to send out dates and agendas for this meeting farther in advance. Also, I would consider having the leadership conference on the day before, so that you can fill the general audience in on what is going on."
- "The food is always great. The location is convenient."

15. Appendix: Acronyms

TERM	DEFINITION
ABS	Acrylonitrile butadiene styrene
AFM	Atomic force microscope
ALERT	Awareness and Localization of Explosives-Related Threats, A Department of Homeland Security Center of Excellence
ANFO	Ammonium nitrate fuel oil explosive
COE	Center of Excellence, a DHS designation
COTS	Commercial off the shelf
CTTSO	Combating Terrorism Technical Support Office
C4	Composition-4
DEWS	Dissolved explosives working solution
DHS	Department of Homeland Security
DHS S&T	DHS Science & Technology division
DSTL	Defence Science and Technology Laboratory, UK
EETD	Electronic explosive threat detection
EGDN	Ethylene glycol dinitrate
ETD	Explosive trace detection
EXD	Explosive detection directorate of DHS
HMTD	Hexamethylene triperoxide diamine
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7 tetrazocine
IGC	Inverse gas chromatography
IMS	Ion mobility spectrometry
LCMS	Liquid chromatography mass spectrometry
NEU	Northeastern University
PETN	Pentaerythritol tetranitrate
PNNL	Pacific Northwest National Laboratory
QC	Quality control
RH	Relative humidity
RDX	1,3,5-Trinitroperhydro-1,3,5-triazine
SFA	Surface forces apparatus
SQC	System quality control
SSI	Sensitive security information
TATP	Acetone peroxide
TBD	To be determined

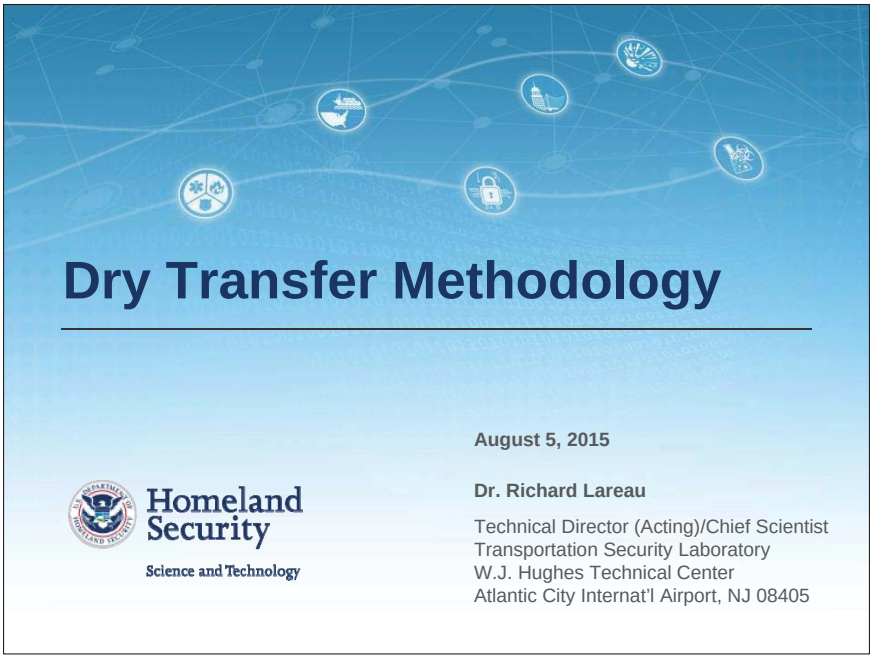
TERM	DEFINITION
TESSA	Trace Explosives Sensing for Security Applications, name of workshops at ALERT
TESSA01	First TESSA workshop held in August 2014
TESSA02	Second TESSA workshop held in August 2015
TNT	Trinitrotoluene
Trace	Synonym of ETD
vdW	van der Waals

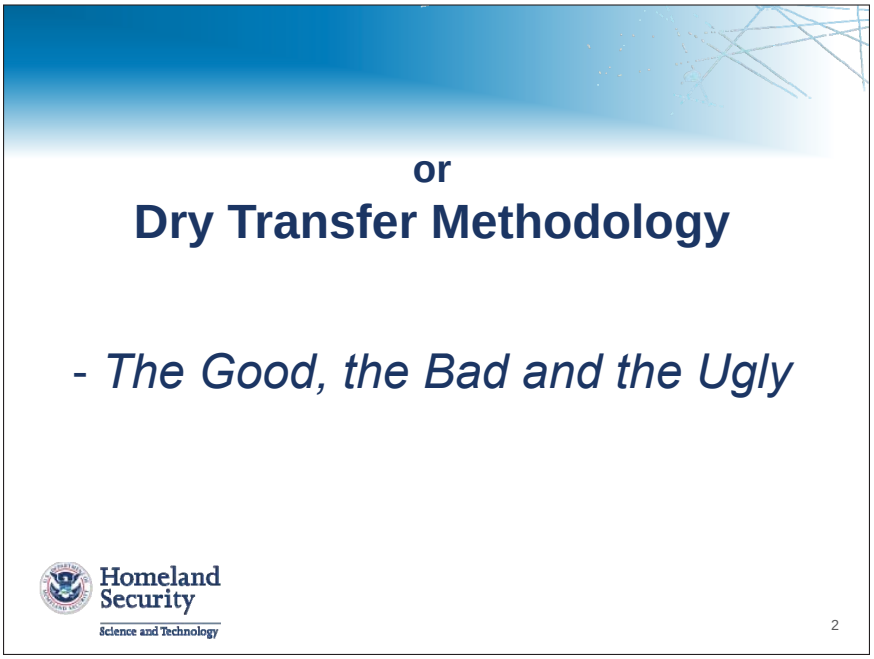
16. Appendix: Presentations

This section contains the slides presented by speakers at the workshop. The slides appear in the order that talks were given as shown on the agenda. Some of the presentation slides have been redacted to ensure their suitability for public distribution.

PDF versions of selected presentations can be found at the following link: https://myfiles.neu.edu/groups/ALERT/TESSA/TESSA02.

16.1 Richard Lareau: Dry Transfer Methodology





Qualitative and Quantitative Analysis of Explosives

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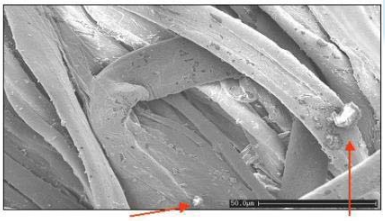
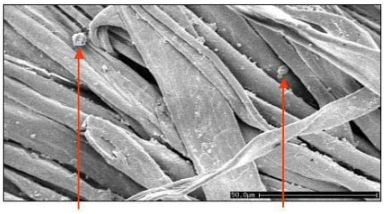
3

Microscopy of Explosives

Fingerprint



Dry Transfer



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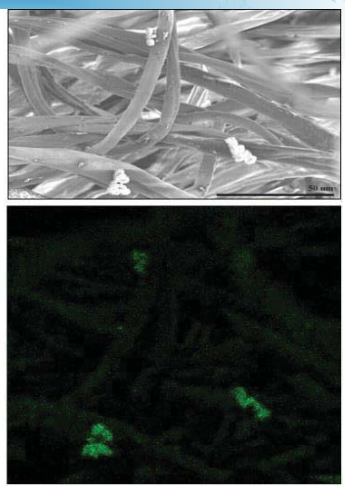
Microscopy of Explosives

X-Ray Mapping
(Dry Transfer)



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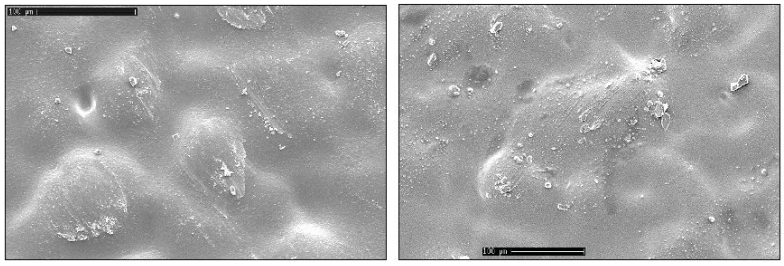
Microscopy of Explosives

Fingerprint

Dry Transfer



SEM of floppy diskette surfaces

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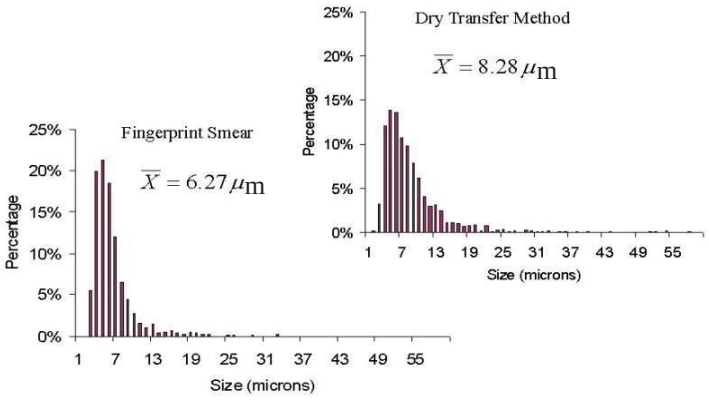
6

Particle Sizing of C-4 on Flannel Patch



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Ref: TSL internal Techn. Report, @1999.

7

Standard Solution Prep;

- TSL prepares each threat standard solution via real explosive particles (powders), weighed and dissolved in carefully chosen solvents. These working solutions are then diluted to the requested concentrations, and QC performed.
- Alternatively, one could use COTS purchased standards and dilute, and perform QC.
- Deposition of standard is performed with calibrated micro-pipettes, carefully controlling the volume desired (e.g., 10 or 20 ul).

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System Quality Control (SQC) Test Kit

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System Quality Control

Dry Transfer Method

- Patent #647030, by Dr. Tom Chamberlain, PhD (retired)
- Secondary transfer of explosives onto a surface
- Rub firmly against the surface 3-4 times (back and forth motion)
- Explosive precipitate is quantitative, stable, and reproducible

Application

- Laboratory setting
  - R&D
  - Pre-certification
  - Certification
  - Acceptance testing of prototype ETDs
  - ***Part of procedures for measuring swipe sampling efficiencies.***

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System Quality Control (cont.)

- Applicable to all surfaces - hard and soft, smooth and rough, solid and porous
  - ABS plastic
  - Vinyl
  - metal
  - Muslin
  - Luggage surfaces
  - ID Badges
  - Boarding Pass
  - Passport
  - Clothing
  - Etc.

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Dry Transfer Methodology;

Direct transfer consists of depositing DEWS (or solvent) onto an SQC strip, allowing the solvent to evaporate, and dry transferring the material on the strip to ETD sampling media. A dry box is used to dry the solvent or explosive doped SQC strips.

- **DEWS = Dissolved Explosives Working Solution**
- **SQC = System Quality Control check**

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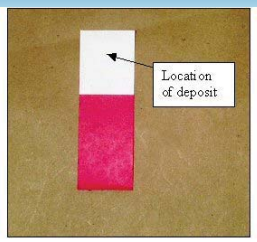
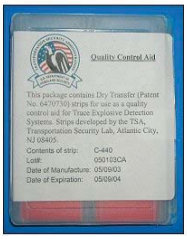
SQC Kit Components; TSL old material



3" x 1"

- Red portion is manila paper
- White portion is Bytac® plastic



Plastic Mailer

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SQC Kit Components – New material

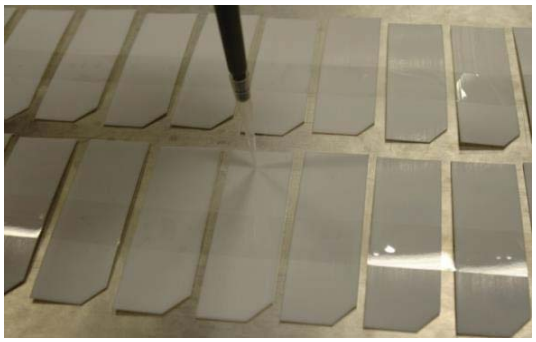

Figure - Depositing onto a SQC Strip

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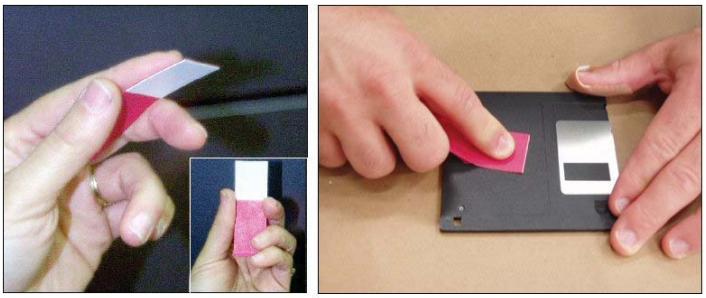
SQC – Application to a Surface



Rub firmly against the surface back and forth 3-4 times.

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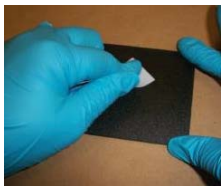
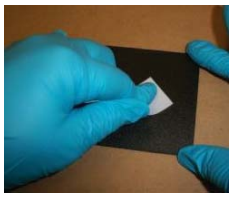
Preparing and Using Dry Transfer Strip

- Deposition Area

- Figure 7. How to properly hold SQC strip prior to dry transfer and location of deposition area.





- Figure 8. Test substrate with dry transfer being performed

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Applying Dry Transfer to a Test Surface

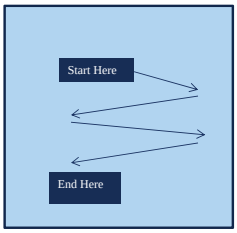

Figure - Example of direction of multi-cycle dry transfer

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Quality Control assessments;

- Solvent extract all deposit from SQC and perform analysis (e.g., GC, HPLC, IC, TD-MS, etc.).
- Solvent extract remaining deposit from SQC, after transfer of deposit onto test substrate; perform analysis.
- Deposit threat/solvent directly into analytical vial, rather than Teflon SQC strip; perform analysis.

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Controlling drying time/environ conditions

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Dry boxes with N2 flow & environmental monitoring

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SQC – Percent Recovery Study

Analytical Instrument: HPLC

C-4 Disks, 100ng	90%
C-4 Disks, 300ng	94%
C-4 Handles, 100ng	106%
Detasheet Disks, 100ng	104%
Detasheet Disks, 300ng	97%
Semtex-H Disks, 100ng (RDX)	105%
Semtex-H Disks, 300ng (RDX)	101%
Semtex-H Disks, 100ng (PETN)	111%
TNT Disks, 300ng	84%
TNT Handles, 300ng	58%
AVERAGE	95%

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SQC – Percent Recovery Study

	Ionscan 400B Cloth	EGIS II Tab	Itemiser² Paper	Itemiser² MUST	Itemiser³ Teflon	AVERAGE (for RDX)
SQC→ swab	97%	83%	98%	96%	70%	89%

Analytical Instrument: GC

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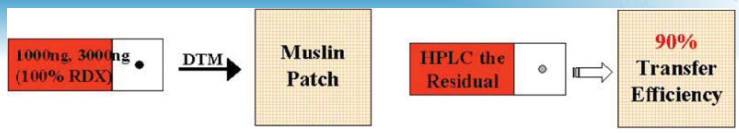
SQC – Percent Recovery Study



1000ng Teflon Strip Residual RDX Analysis

Sample	Solution Conc. (ng/ul)	Residual Qty. (ng)	Transferred Qty. (ng)
T-1	0	0.0	1000
T-2	0.1404	70.2	930
T-3	0.3346	167.3	833
T-4	0.4800	240.0	760
T-5	0.0035	1.8	998
T 6	0.0856	42.8	957
T-7	0.0756	37.8	962
T-8	0.5044	252.2	748
T-9	0	0.0	1000
T-10	0.0471	23.6	976
AVERAGE TRANSFER QUANTITY-->			918

Average Recovery: 92%

3000ng Teflon Strip Residual RDX Analysis

Sample	Solution Conc. (ng/ul)	Residual Qty. (ng)	Transferred Qty. (ng)
T-11	1.285	642.5	2358
T-12	0	0.0	3000
T-13	0.7402	370.1	2630
T-14	1.455	727.5	2273
T-15	1.662	831.0	2169
T 16	0.5026	251.3	2749
T-17	0.4243	212.2	2788
T-18	0.7720	386.0	2614
T-19	0.1649	82.5	2918
T-20	0.5656	282.8	2717
AVERAGE TRANSFER QUANTITY-->			2621

Average Recovery: 87%

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Summary

Use of Dry Transfer;

* developed for specific laboratory use
* reasonable approximation of original threat properties
* quantitative
* transfers approximately 90% from Teflon to substrate (varies per analyte/solvent and environmental conditions

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Recent DHS US Patent Ceremony – Dry Transfer Royalty Check…

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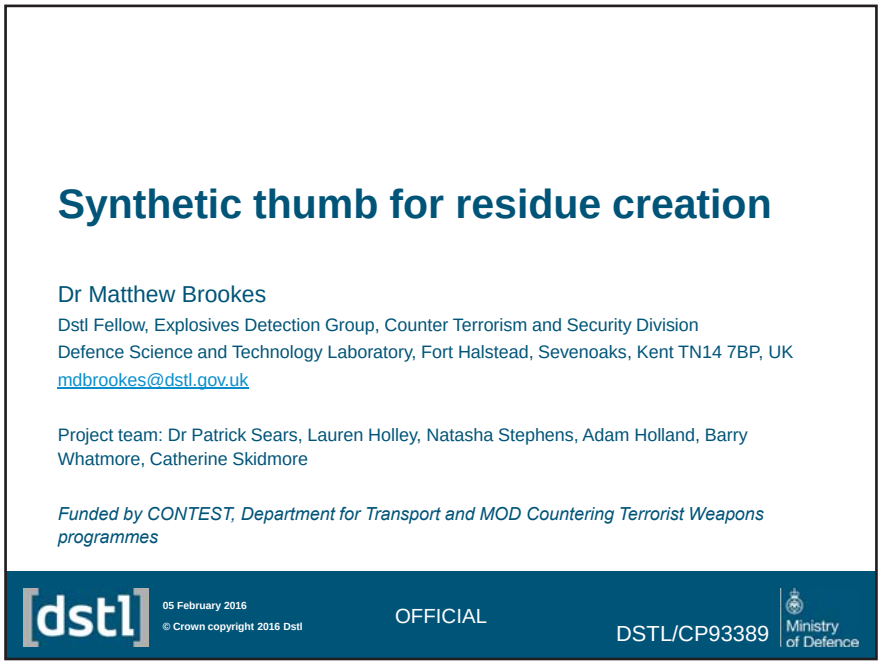
16.2 Greg Gillen: Inkjet Printing of Explosives

Presentation Omitted

16.3 Matt Brookes: Synthetic Thumb for Residue Creation

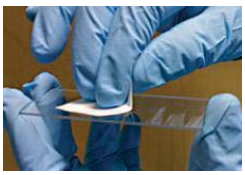


Background

- Detection of explosive traces underpins both high assurance search capability and aviation security screening
- Trace detection is an indirect technique inferring the presence of a larger bulk quantity
- Current swabbing protocols are derived from previous studies based on bomb-making simulations using plastic explosives

Aim

- Develop appropriate operational tools and protocols to detect emerging threats
  - Characterise primary and secondary contamination from a range of explosives on a number of realistic surface types
  - Understand the differences between plastic and crystalline explosives trace deposition, transfer and persistence



So what's with the thumb?

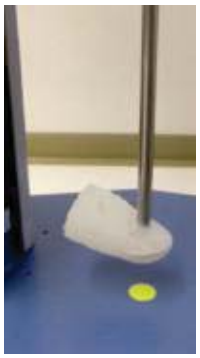
- Some crystalline explosives are sensitive to impact and friction
  - Prohibits working with bulk
  - Prohibits compression by human finger
- A valid comparative study requires a standard deposition method
  - Material, surface profile, force, contact angle etc
  - Variability in deposition is expected
    - but should as far as possible be due to the intrinsic properties of the explosives
- The thumb force rig is designed to deposit residue to enable comparative trace characterisation and aid the development of realistic quantitative standards
- **It is NOT intended to provide a quantitative standard!**

Dragon Skin®

- Dragon Skin® Series silicones are high performance platinum cure silicone rubbers that cure at room temperature with negligible shrinkage
- Cured Dragon Skin® will stretch many times its original size without tearing and will return to its original form without distortion
- Dragon Skin® with Shore Hardness of 10A selected for artificial thumb based on matching size of thumb print to real print under same force
- Not intended to replicate skin in other respects, but can be used with synthetic sebum
- Provides a reference combining ridge properties of fingerprints with dielectric properties of latex/ nitrile glove

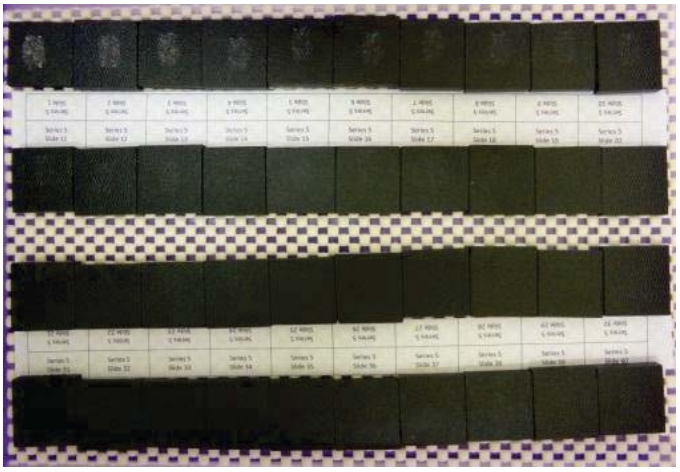
Method

- Dragon Skin® thumb cast from mould of thumb
- Supported by embedded disc attached to stainless steel rod
- Rod attached to Mecmesin force testing rig pressing thumb with 10N of force for 10s an approach speed of 5cm/s
- Initial loading by pressing into bulk
- Depletion series onto clean surface created
- Surface contamination studied by microscopy
- Samples extracted from surfaces and analysed by a validated LC-MS method

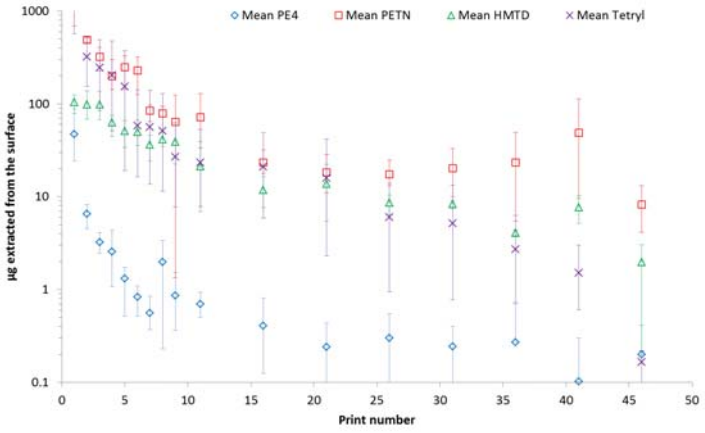


Deposition

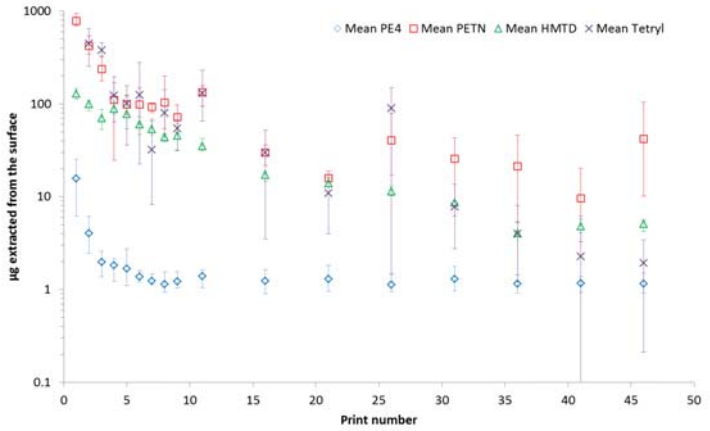
Deposition series



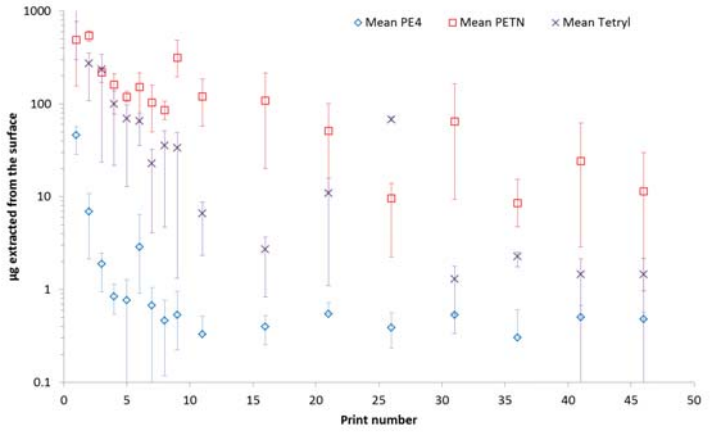
Contamination on glass

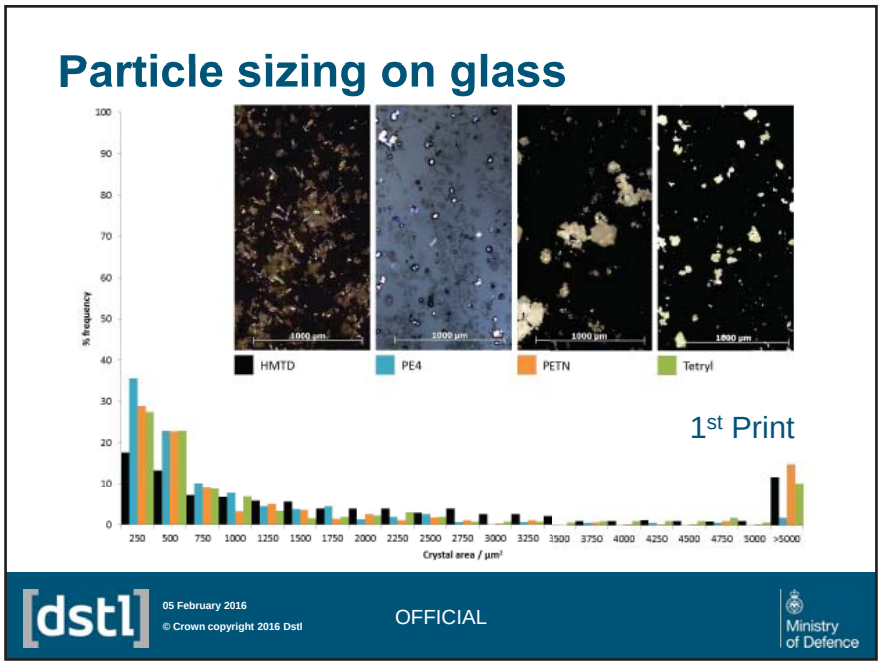


Contamination on ABS



Contamination on metal




Particle sizing on glass
% frequency
HMTD
PE4
PETN
Tetryl
1st Print
Crystal area / µm²
05 February 2016
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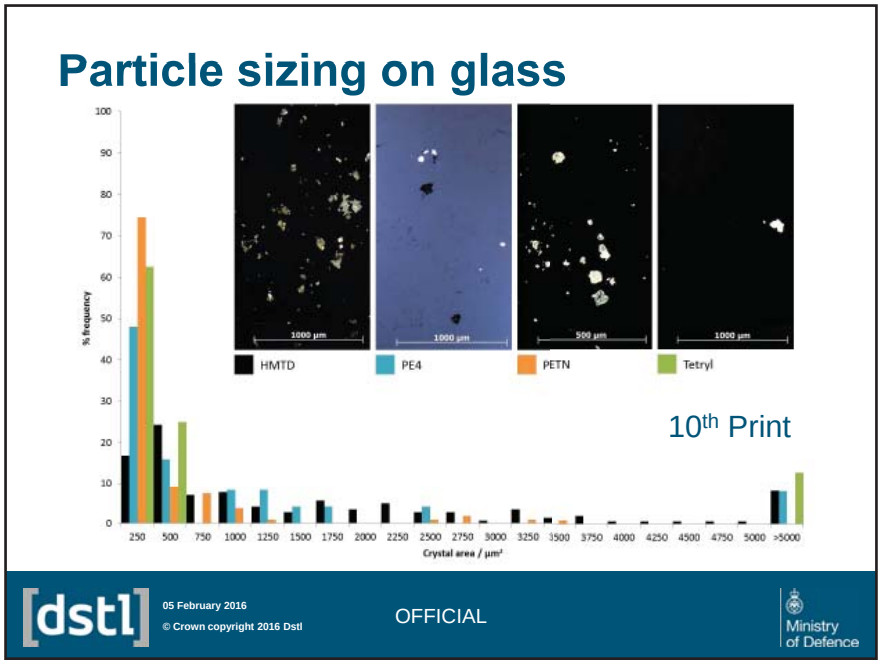
Particle sizing on glass
% frequency
HMTD
PE4
PETN
Tetryl
10th Print
Crystal area / µm²
05 February 2016
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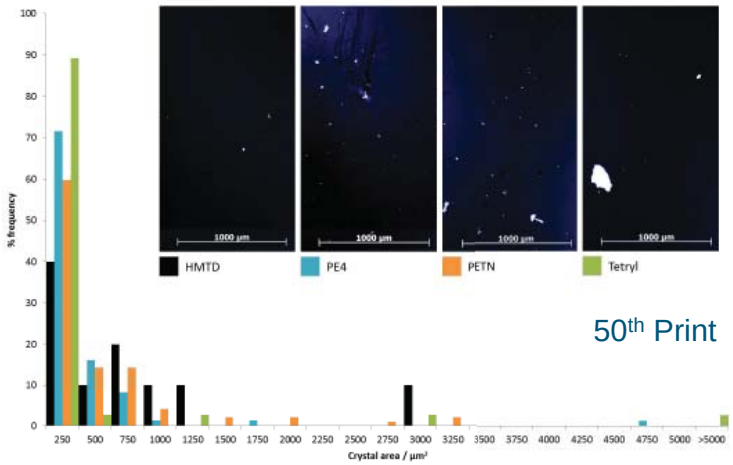
Particle sizing on glass



50th Print

Results

- The crystalline explosives HMTD, PETN and Tetryl generally produce higher levels of absolute surface contamination than the plastic explosive PE4
- The most common particle size distribution for the 50th print for HMTD, PETN, Tetryl and RDX in PE4 is 0 - 250µm², but much larger particles are also present
  - NB Distribution will underestimate 0 – 250 um particles because some will be too small to visualise

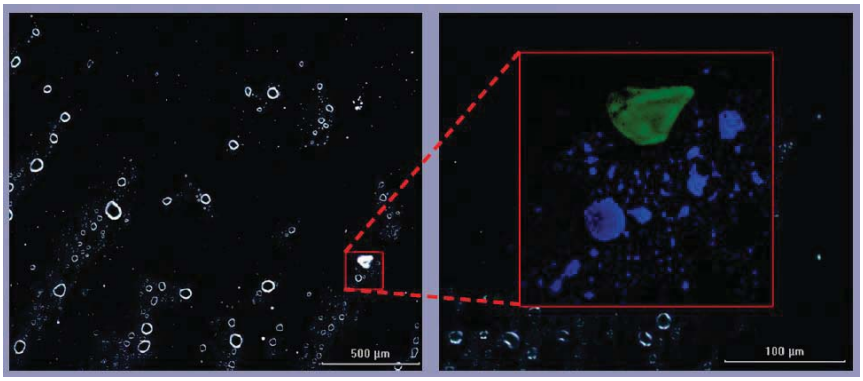
	RDX (PE4)	HMTD	PETN	Tetryl
Density / g cm^{-3}	1.82	1.57	1.76	1.73
1000 µm² particle mass / ng	43.3	37.3	41.9	41.2
250 µm² particle mass / ng	5.4	4.7	5.2	5.1

(Spherical particle approximation)

Raman chemical mapping

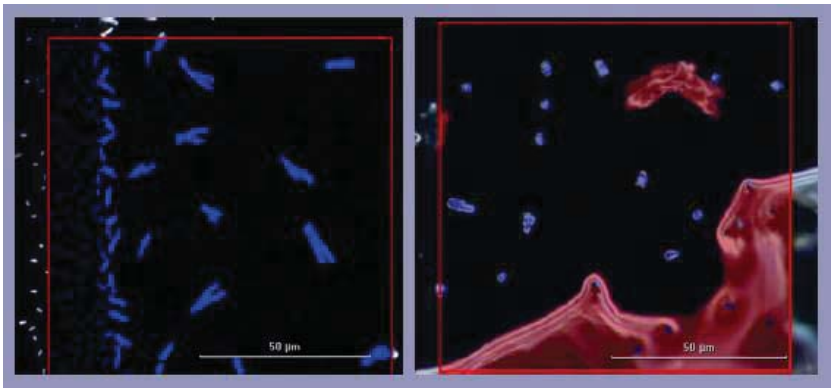
- Provides powerful automated capability to image and map chemical species
- Eg Thermo DXRxi

RDX print using sebum-coated synthetic thumb



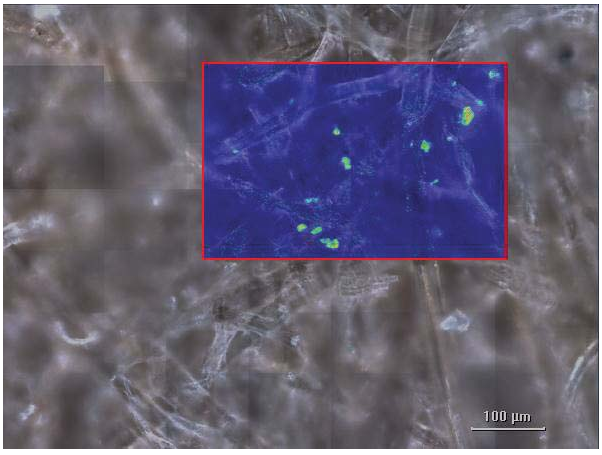
Optical image (left), Raman image (right), α-RDX = green, sebum = blue

Inkjet printed RDX



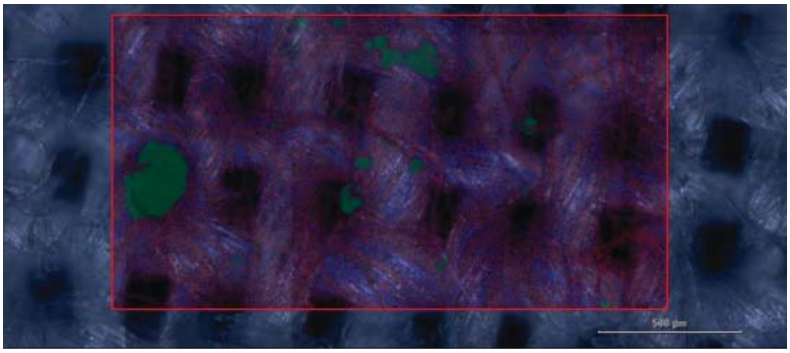
RDX ink showing β-RDX in blue (left), RDX and sebum ink showing β-RDX in blue and sebum in red (right)

PE4 thumb print on cardboard



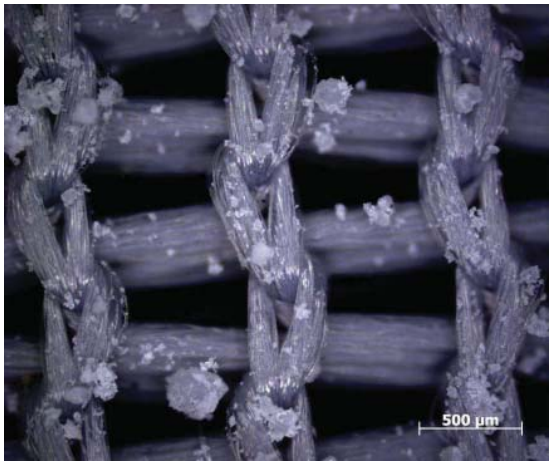
Inset shows Raman mapping of RDX and binder

PETN print on polyester-cotton



PETN = green, cotton = red, PET = blue

PETN thumb-print on sports shoe



Automated swab sampling

- Crockmeter system designed to produce repeatable 'rub' of material across surface
- Range of forces can be applied and swabbing at two speeds
- Develop a protocol for sampling of explosive trace from surfaces

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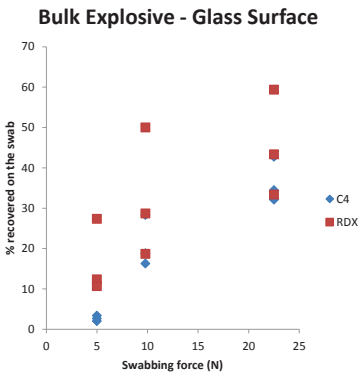
Automated swab sampling

- Crockmeter performed well under test conditions
- Swabbing effectiveness increases with force
- Smooth surfaces >> Rough surfaces
- Natural materials outperformed synthetics
- System mimics 'expert manual user'



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Conclusions

- The synthetic thumb force rig is a powerful characterisation tool
  - Not intended to produce *quantitative* standards, and cannot be used to do so
- Enabled the first comprehensive comparative study of crystalline and plastic explosives contamination
  - HMTD, PETN and Tetryl generally produce higher absolute levels of primary surface contamination than PE4
- Optical microscopy provides crucial insights into particle sampling challenges that quantitative analysis alone cannot
- Raman chemical mapping enables rapid characterisation and validation of printed quantitative standards

Ongoing work

- Additional explosives
  - RDX, TNT, C4 and Semtex
- Wider range of operationally relevant surfaces
  - e.g. cardboard, fabrics etc
- Secondary contamination
- The effects of cleaning
- The effects of transport and agitation
- The effect of moisture and ‘finger oils’


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16.4 Melissa Sweat: Dynamics of Explosives Residues

Dynamics of Explosives Residues

PURDUE CHEMICAL ENGINEERING

Melissa L. Sweat

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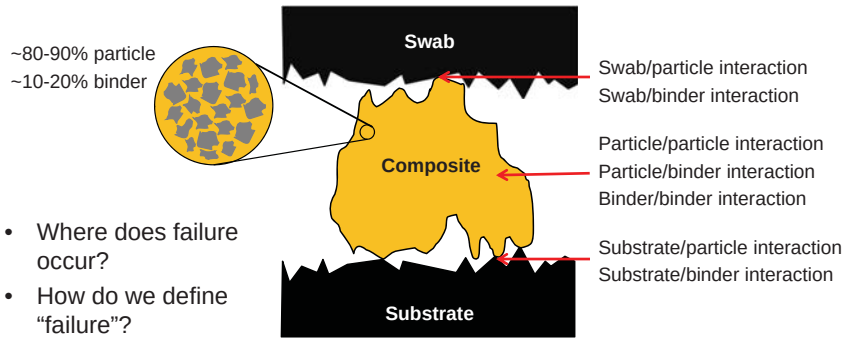
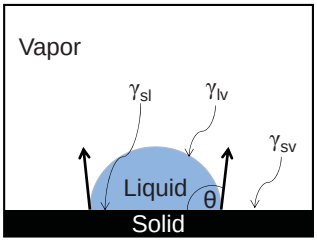
August 5, 2015

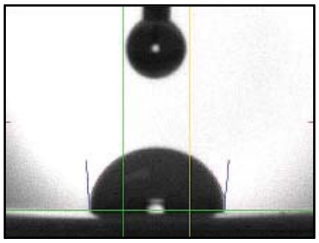
Granular system

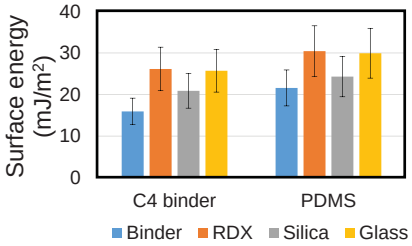


- Where does failure occur?
- How do we define "failure"?

Surface Energies





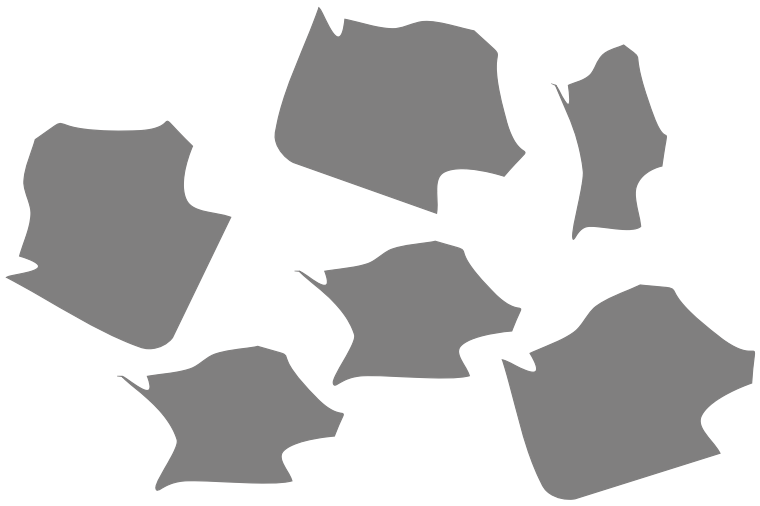


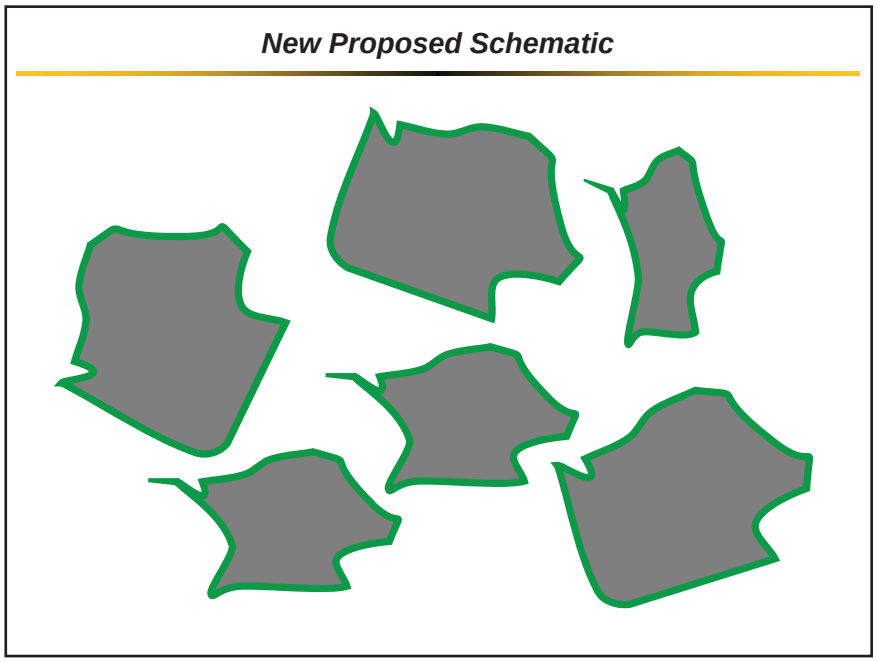
$$\cos\theta\,\gamma_{lv} = \gamma_{sv} - \gamma_{sl} - \pi_e$$

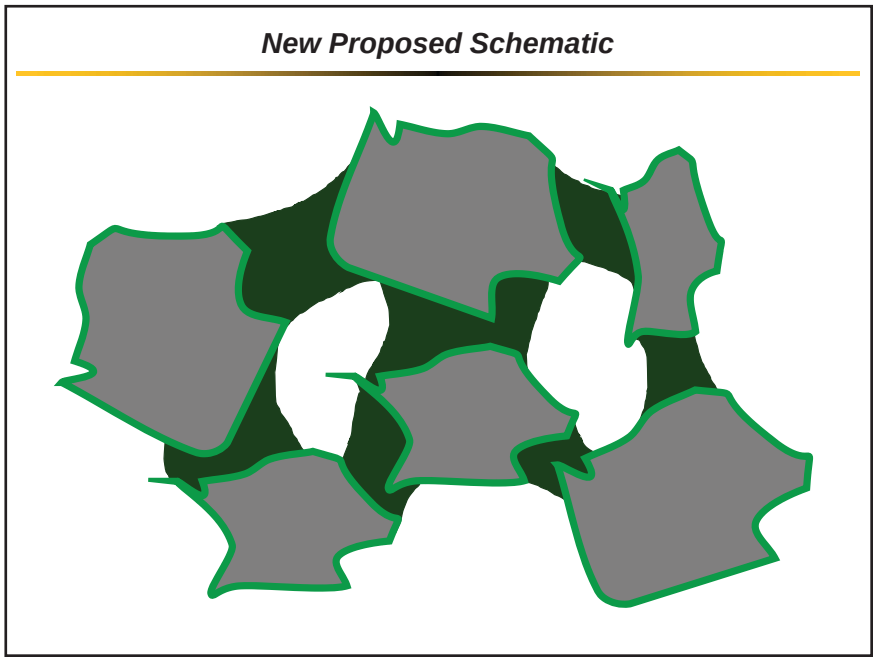
$$\gamma_{ii} = \gamma_{ii}^{d} + \gamma_{ii}^{p}$$

$$\gamma_{ij} = \sqrt{\gamma_{ii}\gamma_{jj}}$$

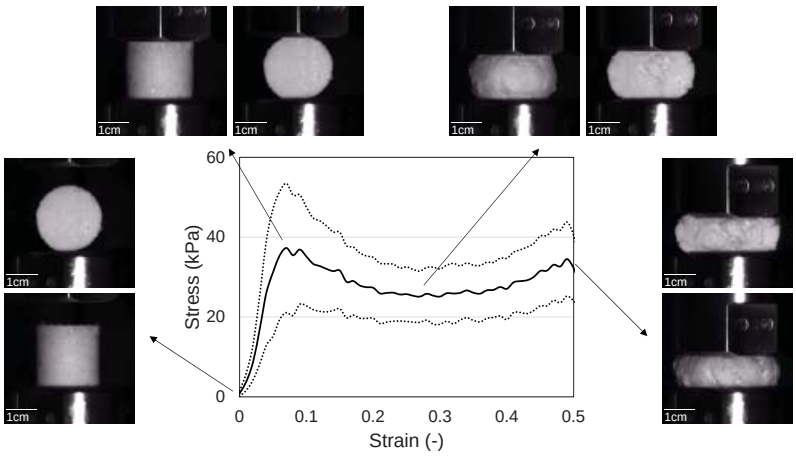
New Proposed Schematic




New Proposed Schematic

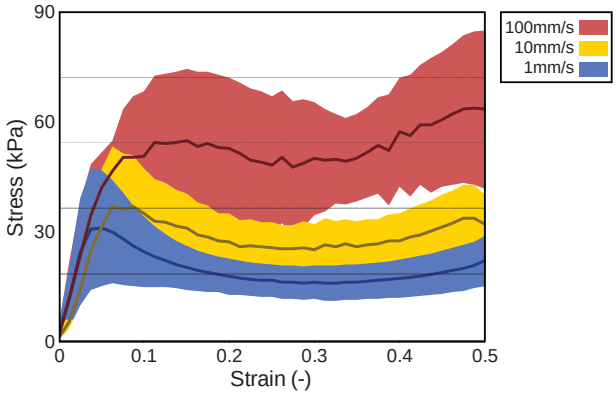

New Proposed Schematic

Stress-Strain Results: Live C4 at 10mm/s



Stress-strain curve (with error regions) live C4 at 10mm/s compression rate. Axial images shown bottom and left; diametrical are top and right.

Live C4 Results

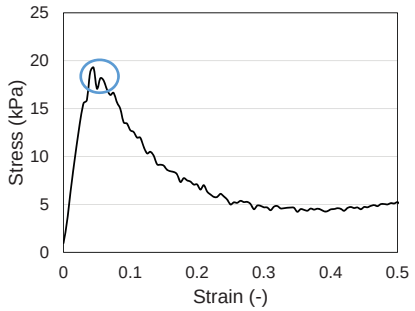


Stress-strain curves (with error regions) live C4 at 1mm/s, 10mm/s, 100mm/s compression rates.

Historical model

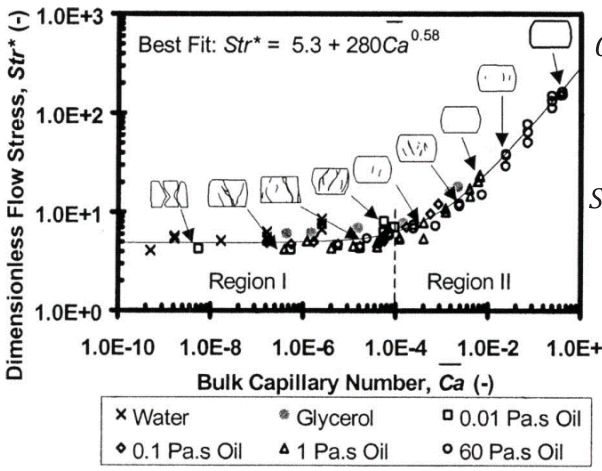
$$Ca = \frac{\mu \dot{\varepsilon}_a d_{32}}{\gamma \cos\theta}$$ Viscous effects; Surface effects

$$Str^* = \frac{\sigma_p d_{32}}{\gamma \cos\theta}$$ Peak flow stress; Surface effects



Stress-strain curve for silica particles (40-150mesh) in PDMS (600,000 cSt viscosity) at 10mm/s compression rate.

Historical model



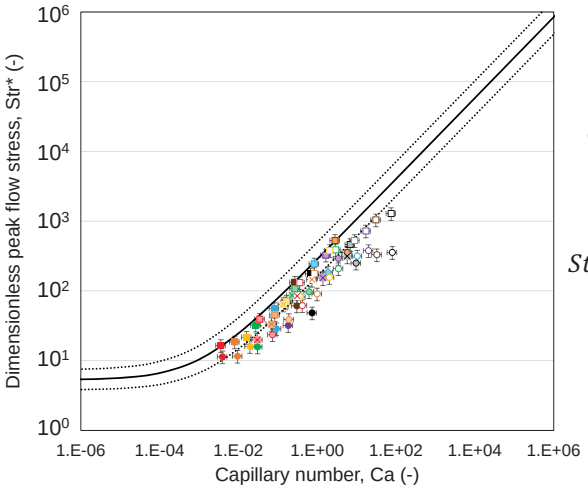
$$Ca = \frac{\mu \dot{\varepsilon}_a d_{32}}{\gamma \cos\theta}$$ Viscous effects; Surface effects

$$Str^* = \frac{\sigma_p d_{32}}{\gamma \cos\theta}$$ Peak flow stress; Surface effects

$$Str^* = k_1 + k_2 Ca^n$$

Iveson, S. M., & Page, N. W. (2004). Brittle to Plastic Transition in the Dynamic Mechanical Behavior of Partially Saturated Granular Materials. *Journal of Applied Mechanics*, *71*(4), 470–475.

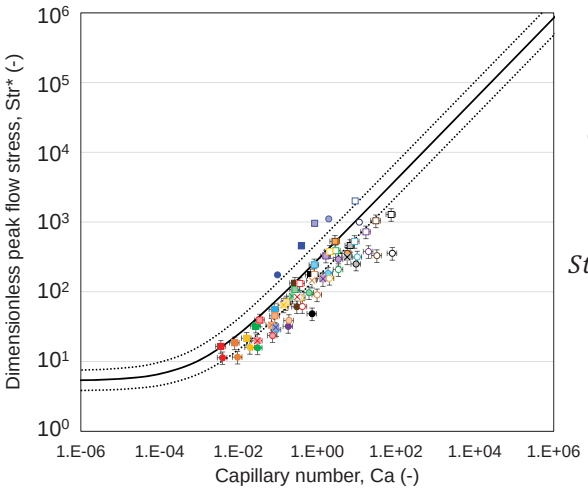
Historical model



$$Ca = \frac{viscous\ effects}{surface\ effects}$$

$$Str^* = \frac{peak\ flow\ stress}{surface\ effects}$$

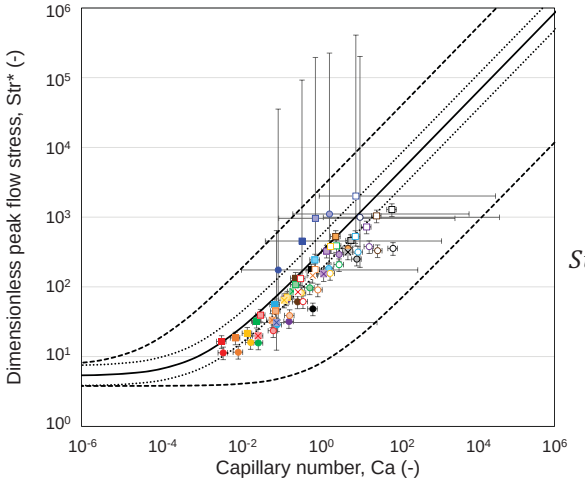
Historical model



$$Ca = \frac{viscous\ effects}{surface\ effects}$$

$$Str^* = \frac{peak\ flow\ stress}{surface\ effects}$$

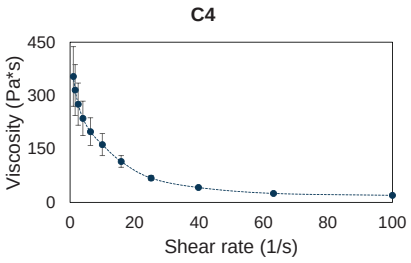
Historical model

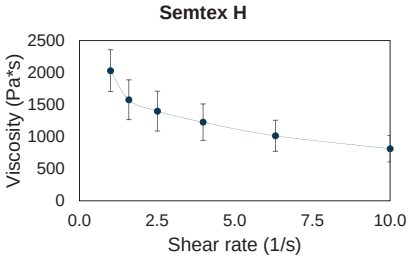


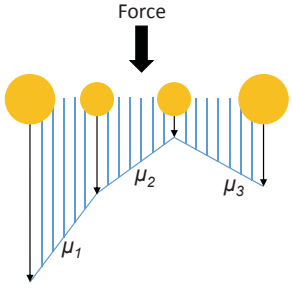
$$Ca = \frac{\textit{viscous effects}}{\textit{surface effects}}$$

$$Str^* = \frac{\textit{peak flow stress}}{\textit{surface effects}}$$

Viscosity profiles

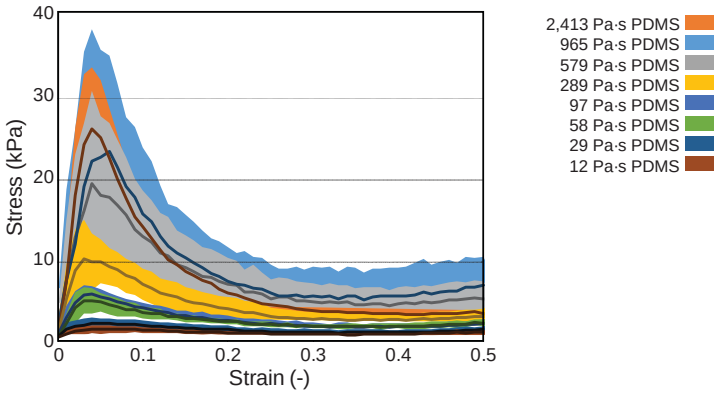






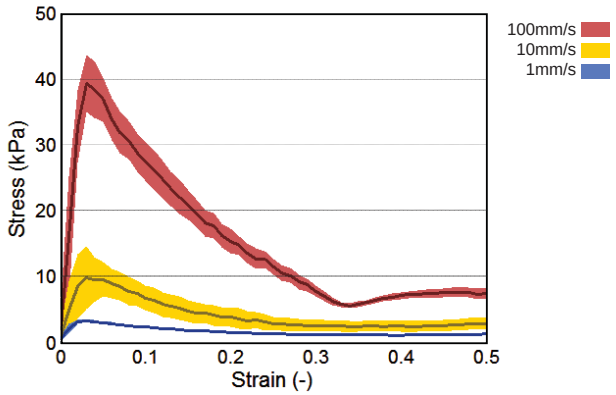
Viscosity profiles for simulated C-4 binder (top left) and simulated Semtex H (bottom left). Top right image is a simple schematics for binder viscosity effects in a granular mixture under applied force.

Viscous effects



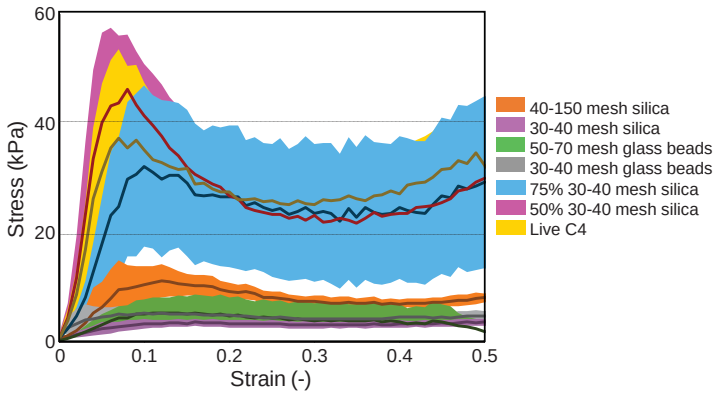
Stress-strain curves (with error regions) for silica particles (40-150mesh) in PDMS at 10mm/s compression rate.

Strain rate effects



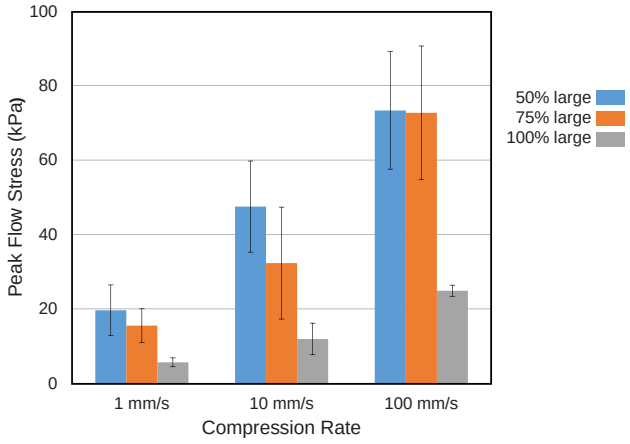
Stress-strain curves (with error regions) for silica particles (40-150mesh) in 289 Pa·s PDMS at 1mm/s, 10mm/s, and 100mm/s compression rates.

Size and shape effects



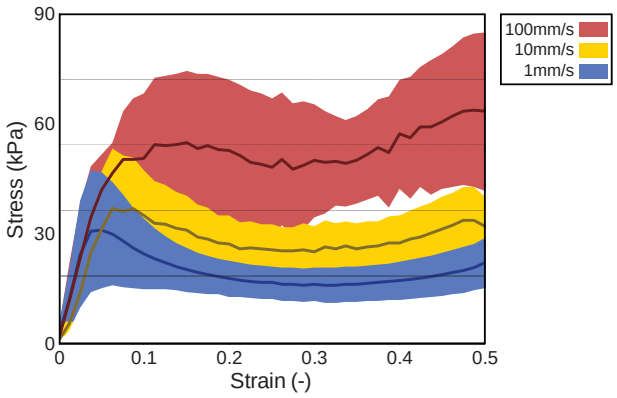
Stress-strain curves (with error regions) for monomodal silica particles (40-150mesh and 30-40 mesh), monomodal glass beads (50-70 mesh) and bimodal silica (75 wt% 30-40 mesh, 25 wt% >230 mesh and 50 wt% 30-40 mesh, 50 wt% >230 mesh) in simulated C4 binder, and live C4 at 10mm/s compression rate.

Peak flow stress



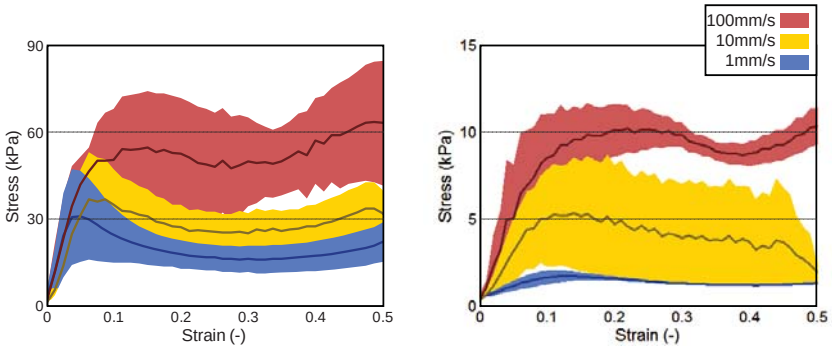
Peak flow stress values for simulated C4 for 1mm/s, 10mm/s, and 100mm/s compression rates. “Large” indicates the percent of granular particulate material from the 30-40mesh silica. The remaining “small” is >230mesh silica.

Live C4 Results



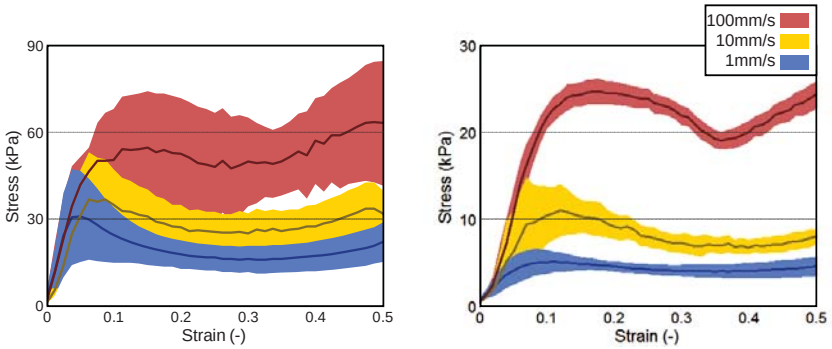
Stress-strain curves (with error regions) live C4 at 1mm/s, 10mm/s, 100mm/s compression rates.

Simulated C4 – effect of particle size



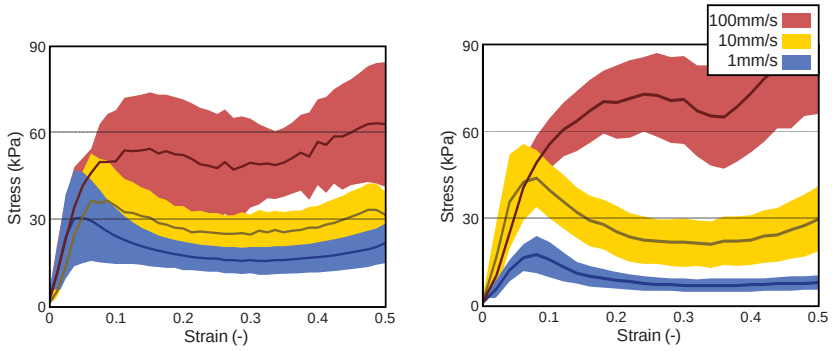
Stress-strain curves (with error regions) for live C-4 (left) and silica particles (40-150mesh) in simulated C-4 binder (right) at 1mm/s, 10mm/s, and 100mm/s compression rates.

Simulated C4 – effect of particle size



Stress-strain curves (with error regions) for live C-4 (left) and silica particles (30-40mesh) in simulated C-4 binder (right) at 1mm/s, 10mm/s, and 100mm/s compression rates.

Simulated C4 – effect of particle size



Stress-strain curves (with error regions) for live C-4 (left) and silica particles (50% from 30-40mesh silica, 50% from >230mesh silica) in simulated C-4 binder (right) at 1mm/s, 10mm/s, and 100mm/s compression rates.

Summary and Next Steps

Comprehensive Approach to Compressive Behavior

- Historical Approach
  - Characterize Granular Behavior
    - Viscous effects
    - Strain rate effects
    - Size/shape effects
  - Live Material Characterization
    - *Complete*
- Benign Analog Development
  - *Complete*
- Evaluation of Slip/Peel Tester: Simulated Residue
  - *Work ongoing*

Acknowledgements

Circled:
- Melissa Sweat
  - Dec. 2015
- Leonid Miroshnik
  - 2018/2019

Not pictured:
- Johanna Smith
  - Grad. May 2014
  - Employed at General Mills
- Chris Browne
  - Grad. May 2017
- Alyssa Bass
  - Grad. May 2017
- Hannah Burnau
  - Grad. H.S. May 2017

Top: Leonid Miroshnik, Sean Fronczak, Jenny Laster, Darby Hoss, Andrew Parker
Bottom: Aaron Harrison, Caitlin Schram, Myles Thomas, Melissa Sweat, Jordan Thorpe

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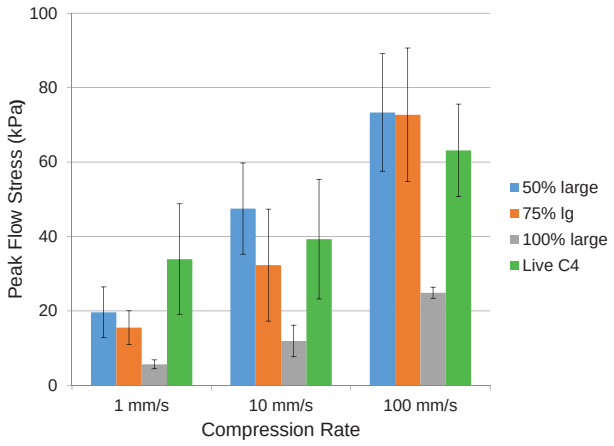
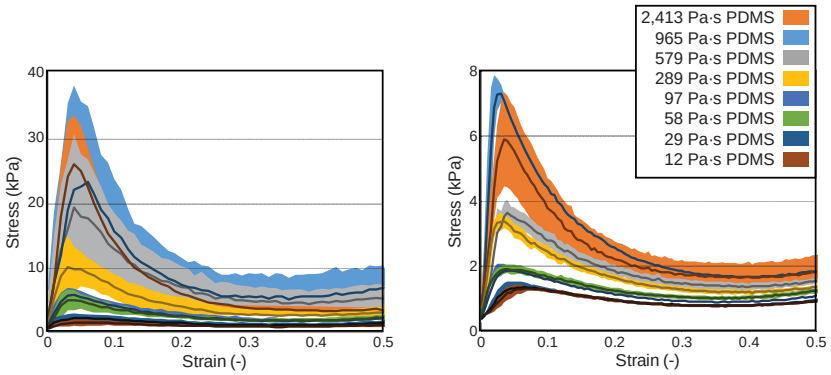
Supplemental slides

Peak flow stress



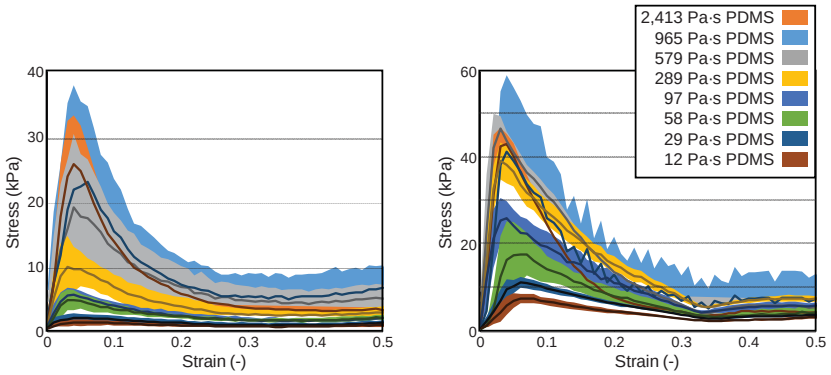
Peak flow stress values for simulated C4 against live C4 for 1mm/s, 10mm/s, and 100mm/s compression rates. “Large” indicates the percent of granular particulate material from the 30-40mesh silica. The remaining “small” is >230mesh silica.

Viscous effects



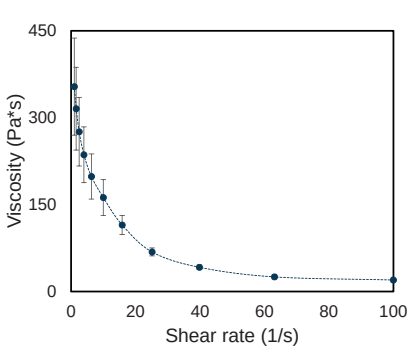
Stress-strain curves (with error regions) for silica particles (40-150mesh) in PDMS at 10mm/s (left) and 1mm/s (right) compression rates.

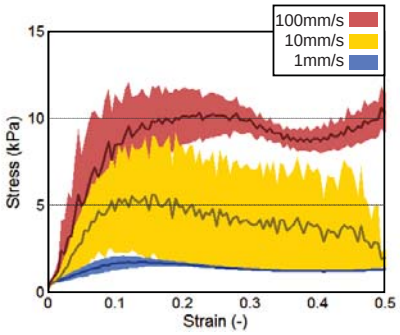
Viscous effects



Stress-strain curves (with error regions) for silica particles (40-150mesh) in PDMS at 10mm/s (left) and 100mm/s (right) compression rates.

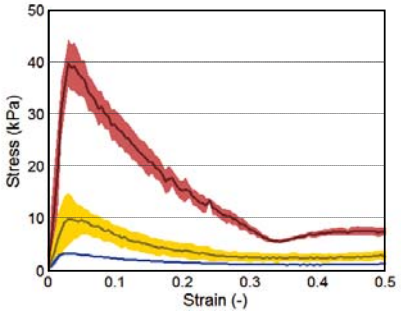
Strain rate effects

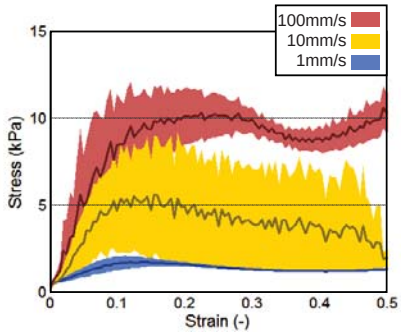




Viscosity of simulated C-4 binder (left) and the associated granular stress-strain curves (with error regions) for silica particles (40-150mesh) in simulated C-4 binder at 1mm/s, 10mm/s, and 100mm/s compression rates (right).

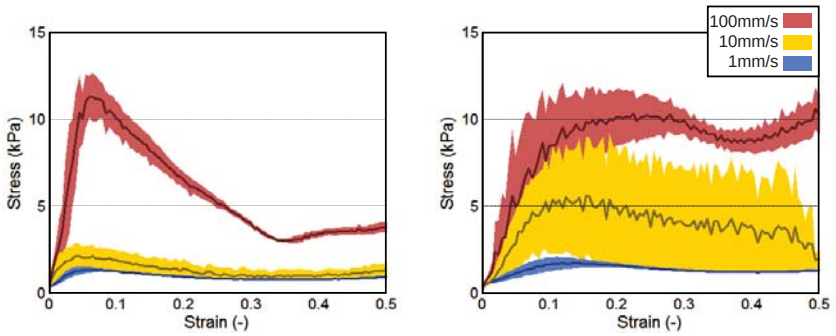
Strain rate effects





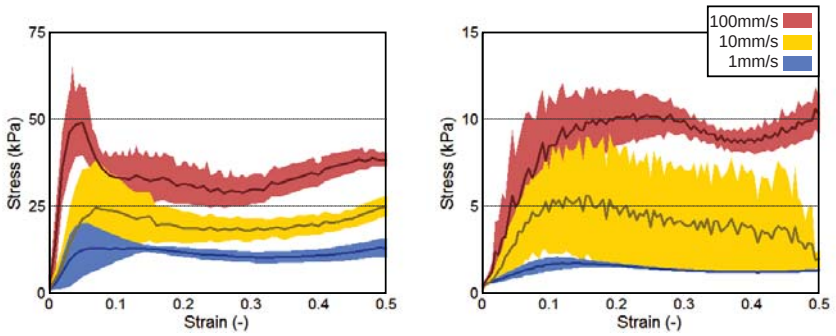
Stress-strain curves (with error regions) for silica particles (40-150mesh) in 289 Pa·s PDMS (left) compared with silica particles (40-150mesh) in simulated C-4 binder (right) at 1mm/s, 10mm/s, and 100mm/s compression rates.

Strain rate effects



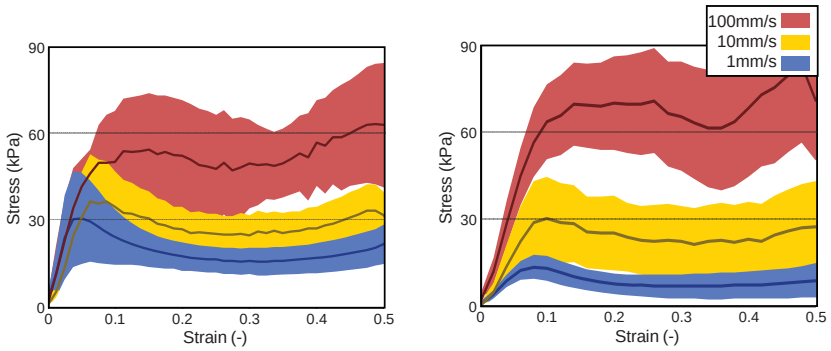
Stress-strain curves (with error regions) for silica particles (40-150mesh) in 29 Pa·s PDMS (left) compared with silica particles (40-150mesh) in simulated C-4 binder (right) at 1mm/s, 10mm/s, and 100mm/s compression rates.

Deformative behavior of C-4



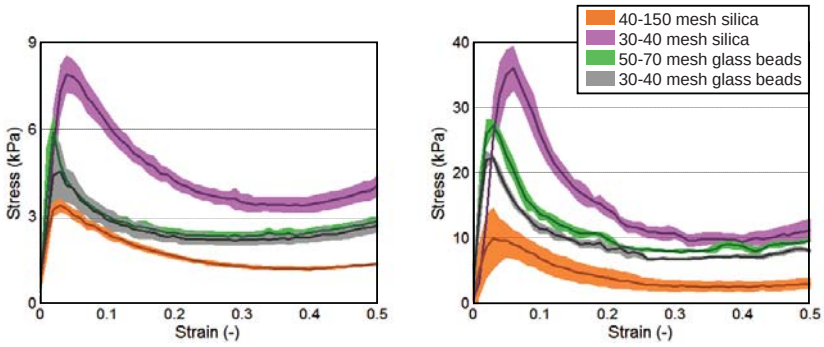
Stress-strain curves (with error regions) for live C-4 (left) and silica particles (40-150mesh) in simulated C-4 binder (right) at 1mm/s, 10mm/s, and 100mm/s compression rates.

Simulated C4 – effect of particle size



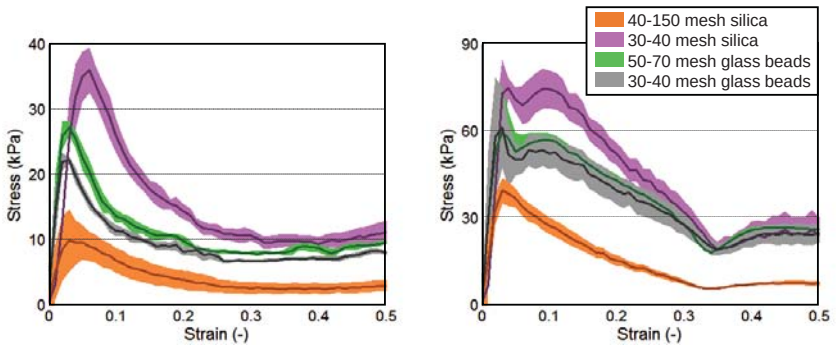
Stress-strain curves (with error regions) for live C-4 (left) and silica particles (75% from 30-40mesh silica, 25% from >230mesh silica) in simulated C-4 binder (right) at 1mm/s, 10mm/s, and 100mm/s compression rates.

Size and shape effects



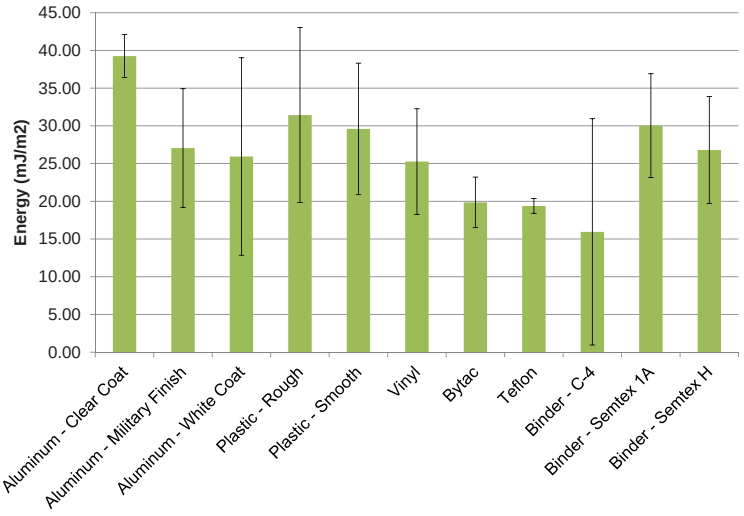
Stress-strain curves (with error regions) for silica particles (40-150mesh and 30-40 mesh) and glass beads (50-70 mesh) in 97 Pa·s PDMS at 1mm/s compression rate (left) and 10mm/s compression rate (right).

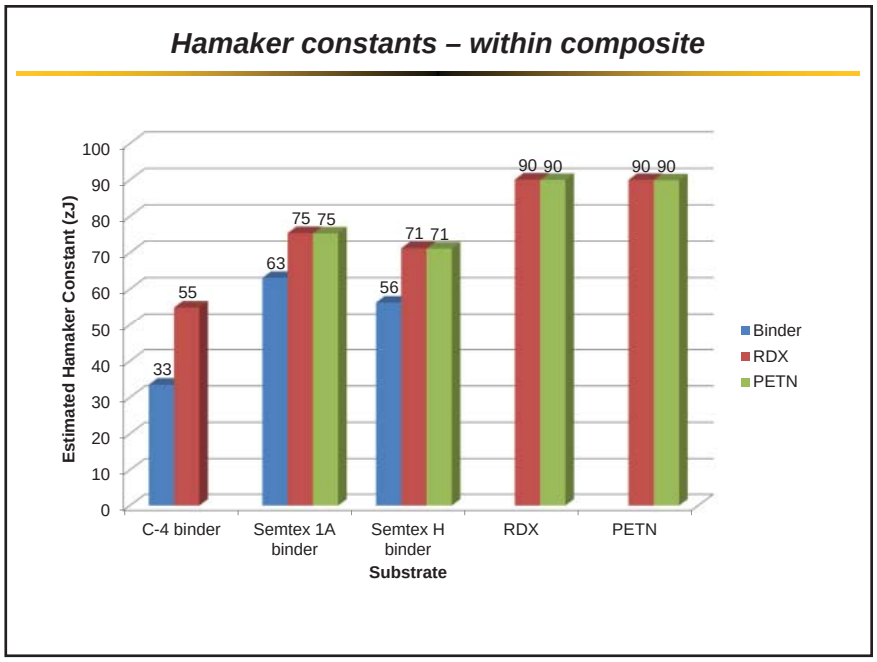
Size and shape effects

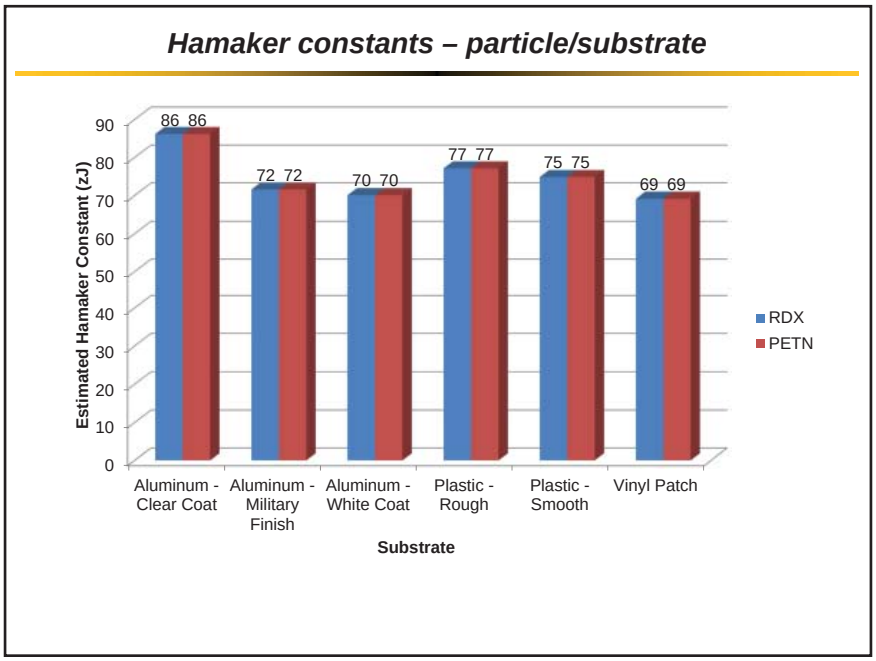


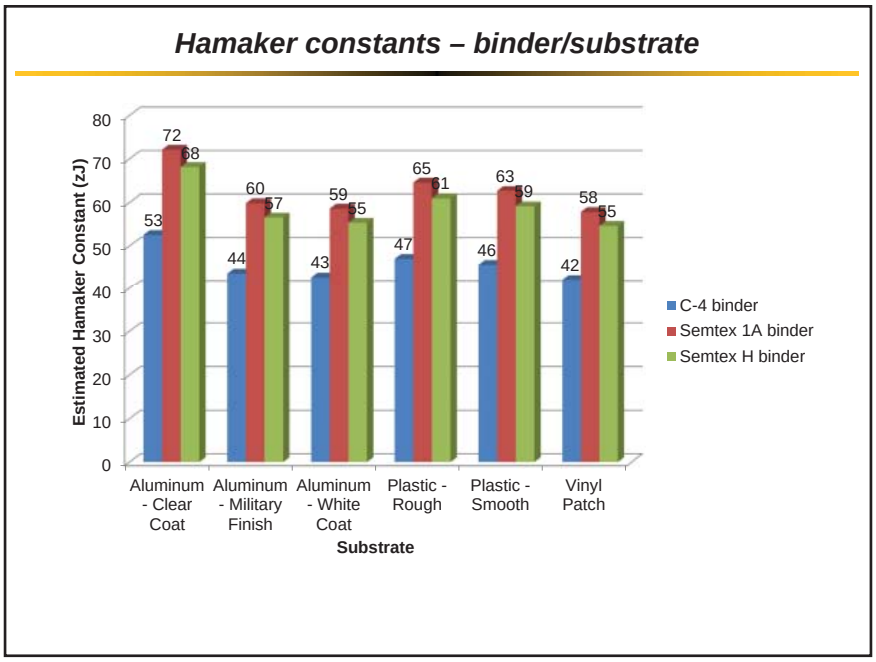
Stress-strain curves (with error regions) for silica particles (40-150mesh and 30-40 mesh) and glass beads (50-70 mesh) in 97 Pa·s PDMS at 10mm/s (left) and 100mm/s (right) compression rates.

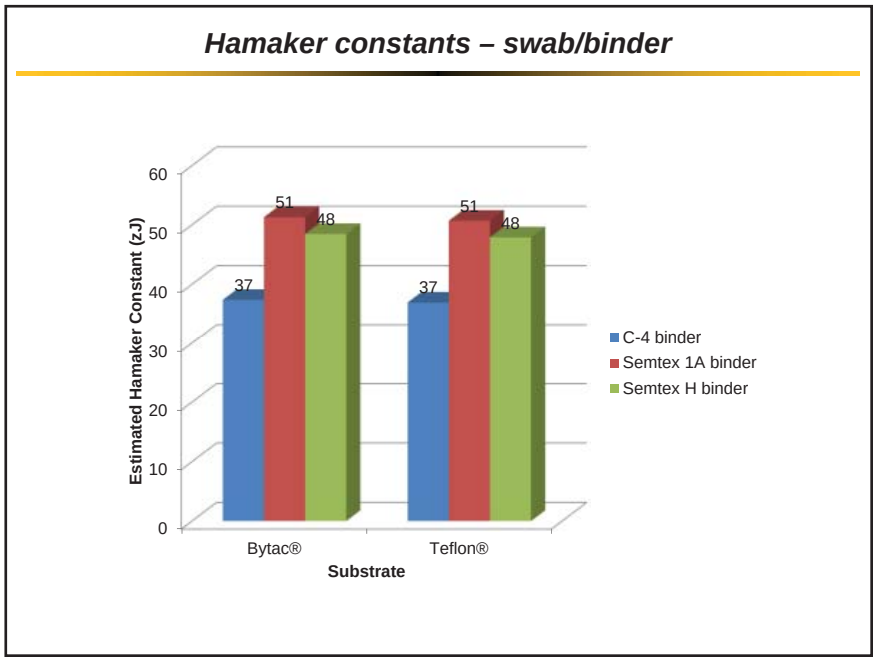
Surface energy

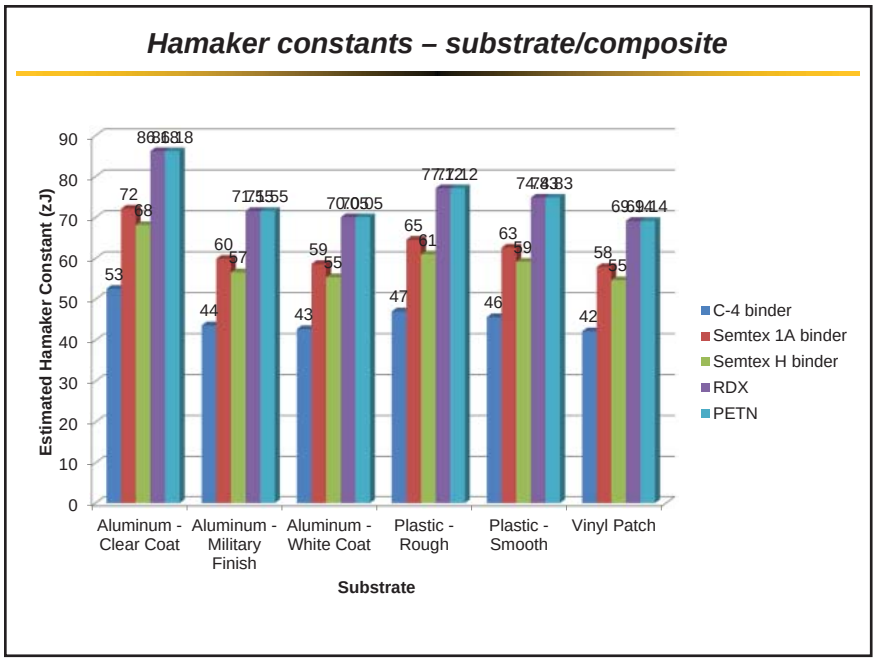


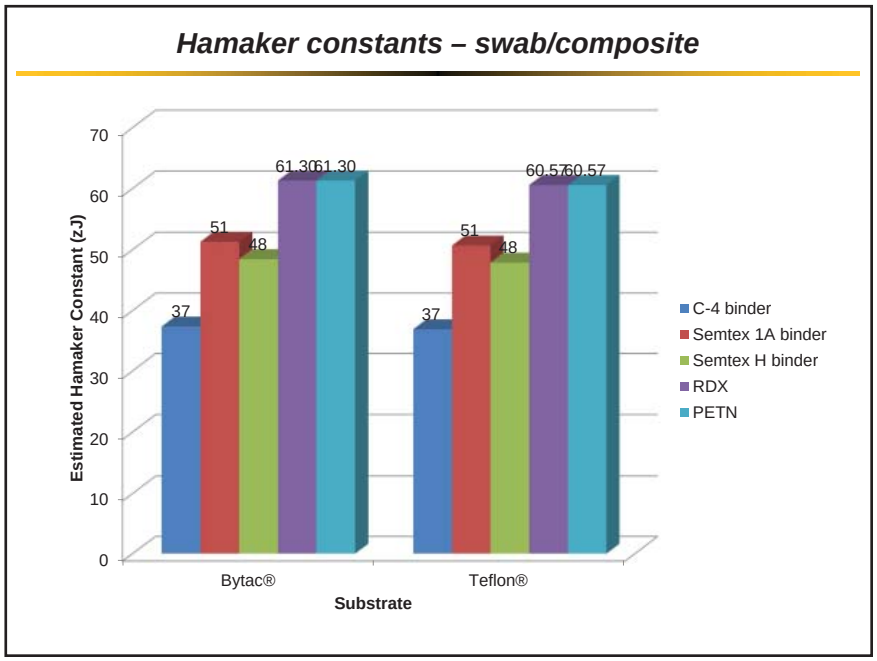

Hamaker constants – within composite
Estimated Hamaker Constant (zJ)
100
90
80
70
60
50
40
30
20
10
0
33
55
63
75 75
56
71 71
90 90
90 90
C-4 binder
Semtex 1A binder
Semtex H binder
RDX
PETN
Substrate
Binder
RDX
PETN


Hamaker constants – particle/substrate
Estimated Hamaker Constant (zJ)
90
80
70
60
50
40
30
20
10
0
86 86
72 72
70 70
77 77
75 75
69 69
Aluminum - Clear Coat
Aluminum - Military Finish
Aluminum - White Coat
Plastic - Rough
Plastic - Smooth
Vinyl Patch
Substrate
RDX
PETN

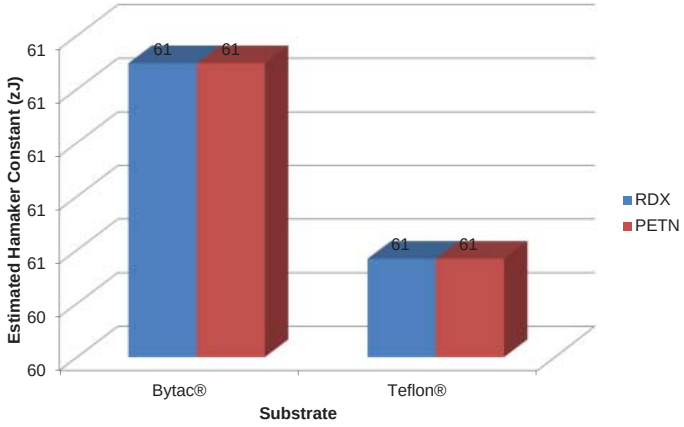

Hamaker constants – binder/substrate
Estimated Hamaker Constant (zJ)
80
70
60
50
40
30
20
10
0
72
68
53
60
57
44
59
55
43
65
61
47
63
59
46
58
55
42
Aluminum - Clear Coat
Aluminum - Military Finish
Aluminum - White Coat
Plastic - Rough
Plastic - Smooth
Vinyl Patch
Substrate
C-4 binder
Semtex 1A binder
Semtex H binder


Hamaker constants – swab/binder
Estimated Hamaker Constant (zJ)
60
50
40
30
20
10
0
51
48
37
51
48
37
Bytac®
Teflon®
Substrate
C-4 binder
Semtex 1A binder
Semtex H binder

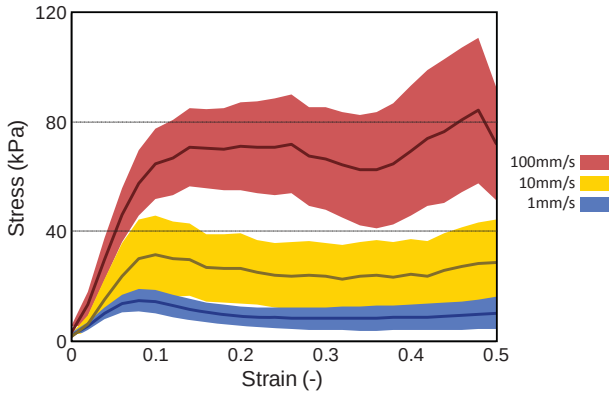

Hamaker constants – substrate/composite
Estimated Hamaker Constant (zJ)
Substrate
Aluminum - Clear Coat
Aluminum - Military Finish
Aluminum - White Coat
Plastic - Rough
Plastic - Smooth
Vinyl Patch
C-4 binder
Semtex 1A binder
Semtex H binder
RDX
PETN


Hamaker constants – swab/composite
Estimated Hamaker Constant (zJ)
Substrate
Bytac®
Teflon®
C-4 binder
Semtex 1A binder
Semtex H binder
RDX
PETN

Hamaker constants – Swab/particle



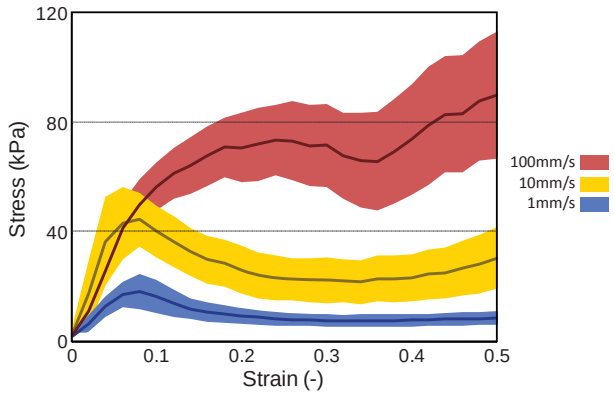
Stress-Strain Results: Bimodal SiO_2 in Simulated C-4 binder



Stress-strain curves (with error regions) for silica particles (75 wt% 30-40mesh, 25wt% >230 mesh) in simulated C-4 binder at 1mm/s, 10mm/s, and 100mm/s compression rates.

MSweat

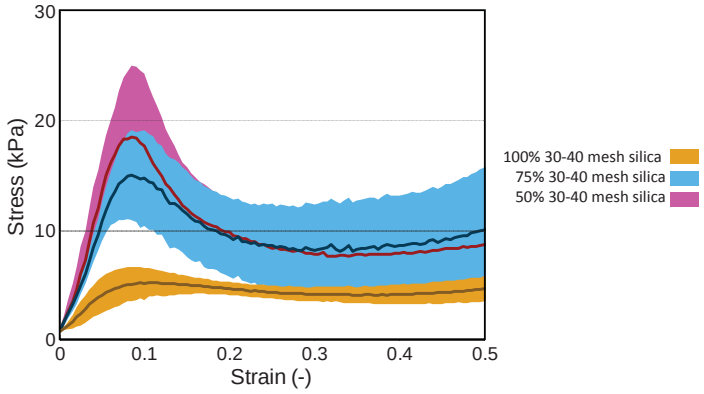
Stress-Strain Results: Bimodal SiO_2 in Simulated C-4 binder



Stress-strain curves (with error regions) for silica particles (50 wt% 30-40mesh, 50wt% >230 mesh) in simulated C-4 binder at 1mm/s, 10mm/s, and 100mm/s compression rates.

MSweat

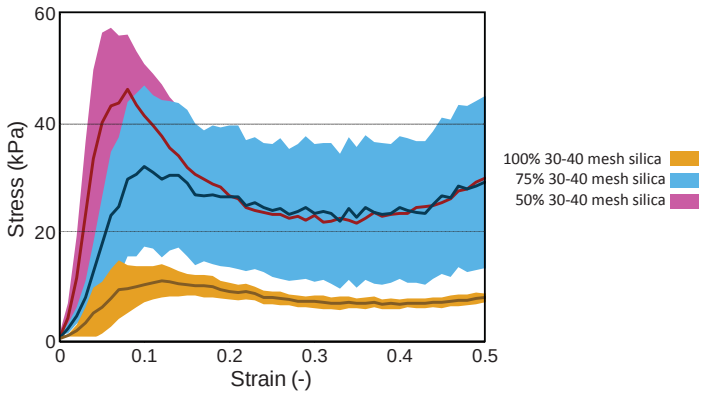
Stress-Strain Results: Bimodal SiO_2 in Simulated C4 Binder



Stress-strain curves (with error regions) for silica particles (100 wt% 30-40 mesh, 0 wt% >230 mesh; 75 wt% 30-40 mesh, 25 wt% >230 mesh; and 50 wt% 30-40 mesh, 50 wt% >230 mesh) in simulated C4 binder at 1mm/s compression rate.

MSweat

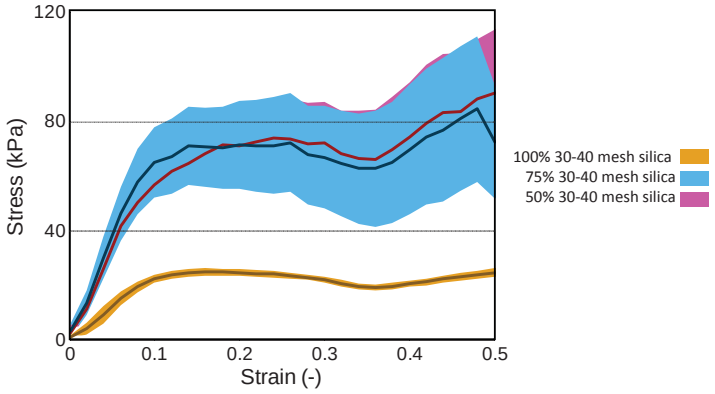
Stress-Strain Results: Bimodal SiO_2 in Simulated C4 Binder



Stress-strain curves (with error regions) for silica particles (100 wt% 30-40 mesh, 0 wt% >230 mesh; 75 wt% 30-40 mesh, 25 wt% >230 mesh; and 50 wt% 30-40 mesh, 50 wt% >230 mesh) in simulated C4 binder at 10mm/s compression rate.

MSweat

Stress-Strain Results: Bimodal SiO_2 in Simulated C4 Binder



Stress-strain curves (with error regions) for silica particles (100 wt% 30-40 mesh, 0 wt% >230 mesh; 75 wt% 30-40 mesh, 25 wt% >230 mesh; and 50 wt% 30-40 mesh, 50 wt% >230 mesh) in simulated C4 binder at 100mm/s compression rate.

MSweat

16.5 Steve Beaudoin: Forces and Mechanics of Contact Sampling

Forces and Mechanics of Contact Sampling

A. Harrison, M. Sweat, D. Hoss, J. Laster, M. Thomas, S. Beaudoin
Purdue University School of Chemical Engineering
West Lafayette, IN 47906

Trace Explosives Sensing for Security Applications – II (TESSA02)
August 5, 2015
Northeastern University

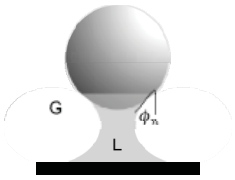
Overview

- Which forces matter in contact sampling?
  - Electrostatics
  - Capillary
  - van der Waals
- How do explosives contact a surface?
  - Point contact
  - Deformation leading to intimate contact
  - Solid-solid or solid-liquid-solid contact
- How do explosives come off surfaces during contact sampling?
  - Plastic deformation followed by internal failure
  - Adhesive failure
  - Cohesive failure
- And now for something completely different!!!

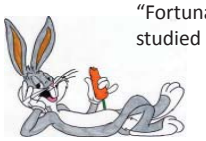
Capillary Forces

- Adhesion forces resulting from adsorbed water
  - Bulk water forms liquid bridges between surfaces
    - Kelvin equation classically used to describe the effect

$$R_s = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1} = -\frac{V_{m,L}\gamma_{LG}}{RT\ln\left(\frac{p_G}{p^S}\right)} \qquad \Delta P = 2\gamma_{LG}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$



- R_s = Kelvin radius; R_1, R_2 = principle radii of curvature of liquid bridge; $V_{m,L}$ = molar volume of liquid; p_G/p^S = relative humidity; γ_{LG} = liquid-vapor surface tension; ΔP = Laplace pressure
  - Limits of the Kelvin equation
    - No dependence on surface energy of the solid surfaces between which the liquid bridge is suspended
    - It assumes that the surface tension of the liquid is constant, no matter how small the bridge
    - It assumes that the molar density of water is constant, no matter how little water there may be
    - It predicts that a liquid bridge will form at all humidity levels
    - Defies laws of physics



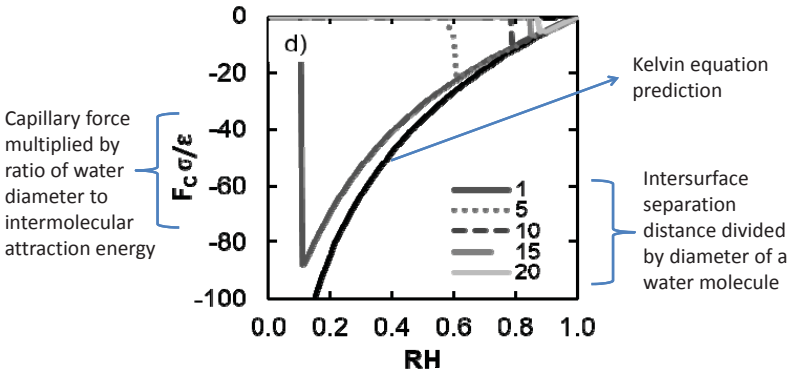
"Fortunately, I never studied law"

Electrostatic Forces

- Dry environments
  - Governed by Coulomb's law
  - As humidity ↑, adsorbed moisture drains surface charge and reduces ES effects
- Materials of our interest expected to have no net charge
  - Metals generally drain charge away – they are usually uncharged
  - Dielectrics and insulators are not manufactured to contain a fixed charge
  - Under certain conditions, charge and non-zero potential on surfaces may emerge
    - Materials may hold small surface charge if surface reactions have created oxides that can hydrolyze in humid environments
- Contact electrification may matter
  - Transfer of charge due to contact
    - For insulating materials, it is prudent to check charge build-up if materials are wiped or rubbed
      - Explosives crystals or powders may become charged due to rubbing
    - Compounded explosives likely will not accumulate charge
- Experiments needed to investigate

Kelvin Equation Limits

- Kelvin equation falls short at conditions most relevant to us
  - Low relative humidity
  - Close contact



Capillary force as a function of humidity for superhydrophilic surfaces

Capillarity: What Does It All Mean

- There will be effects of adsorbed moisture at close separation distances
- Classic laws for prediction of such effects are overestimates at most humidities relevant to indoor environments
- Further study requiring detailed molecular simulation coupled with experimentation can elucidate these effects
- Must consider the following
  - Kinetics of bridge formation
  - How to quantify interfacial separation (our old friend, roughness)
  - How to model
    - Suggest applied model based on correction to Kelvin equation

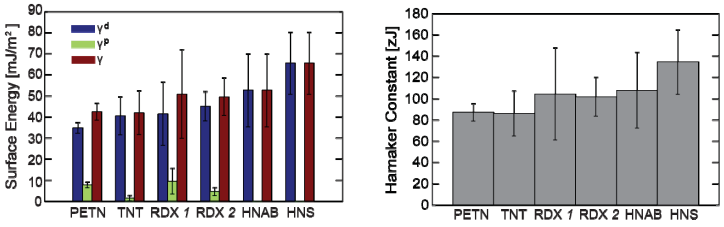
van der Waals Forces

- Result from coupling of dipoles in adjacent surfaces
- Always present
- Generally strongest forces in adhesion when particles (residues) in contact with surfaces
- Substantially influenced by roughness of interacting surfaces
  - Alters the closeness of approach of the interacting surfaces
- Force proportional to
  - Composition-dependent constant (A_{132})
  - inversely proportional to separation distance squared (sphere-sphere, sphere-plate)
  - Inversely proportional to separation distance cubed (cylinder-plate)

van der Waals Forces

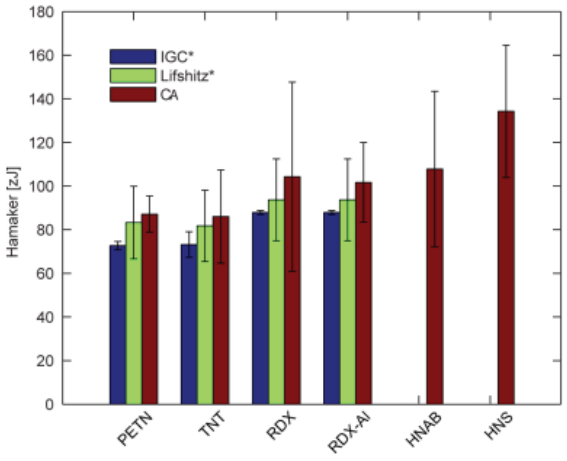
- Challenge: measure or calculate Hamaker constants
  - Range from 10^{-19} to 10^{-21} J for all materials (note: 1 zJ = $1x10^{-21}$ J)
  - Can be determined using atomic force microscopy, centrifuge, inverse gas chromatography (IGC), or surface energy measurements
    - IGC and surface energy both involve quite a bit of approximation

Recent Results of Surface Energy and Hamaker Constant Determination in Collaboration with Sandia National Labs



Based on contact angles of a series of liquids on smooth thin films of explosive

Hamaker Constants Estimated by 3 Methods

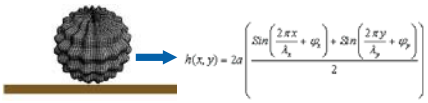


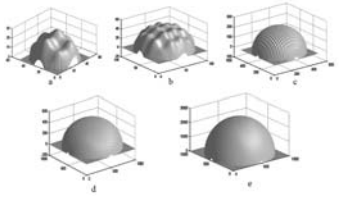
van der Waals Forces, cont'd

- Challenge: consider topographical effects of surfaces on vdW force
  - Total mass interacting within ~ 20-30 nm of point of contact drives vdW force prediction
  - We must accurately understand the roughness (soon) of the interacting surfaces, and we must have a way to model the effect of the roughness
- Modeling roughness effects on vdW forces
  - Simulator in existence
    - Inputs can be in form of topographical map, geometric form
    - Code discretizes the interacting surfaces and calculates vdW force based on separation distance of distinct nodes on each surface
- Modeling deformation effects on vdW forces
  - State of the art assumes equilibrium deformation
  - Does not consider kinetics of deformation in contact

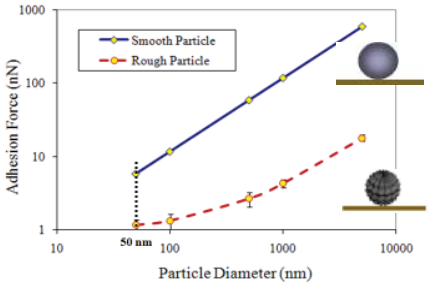
Roughness and van der Waals Forces

- Roughness simulated as 2d-sinusoids
  - Defined by amplitude and wavelengths





Identical roughness parameters
(max. height =5 nm; $\lambda_x = \lambda_y$ =20 nm)
(a) D = 50 nm (b) 100 nm (c) 500 nm (d) 1µm (e) 5 µm

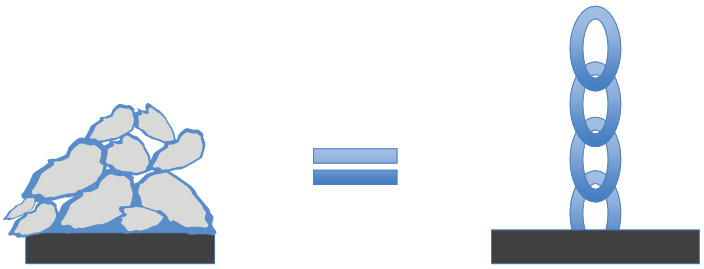


Deformation model still coming…

Explosives Contact with Surfaces

- Crystalline explosives will contact surfaces at distinct points
  - These materials are refractory and will not deform or will undergo only minimal deformation at points of contact
  - Possible to measure the mechanical properties of the crystals and describe the deformation that will occur due to the contact adhesion load
- Compounded explosives contact surfaces via solid-liquid-solid contact
  - Binders (liquids) in compounded explosives wet the crystalline explosives in the granules
  - These liquids flow in contact with surfaces
    - Create intimate contact between explosive and surface
    - An interconnected network of liquid binder completely surrounding all the solid explosives

How Are Residues Removed



Load applied on the residue (left) causes failure in the weak link in the chain (right)

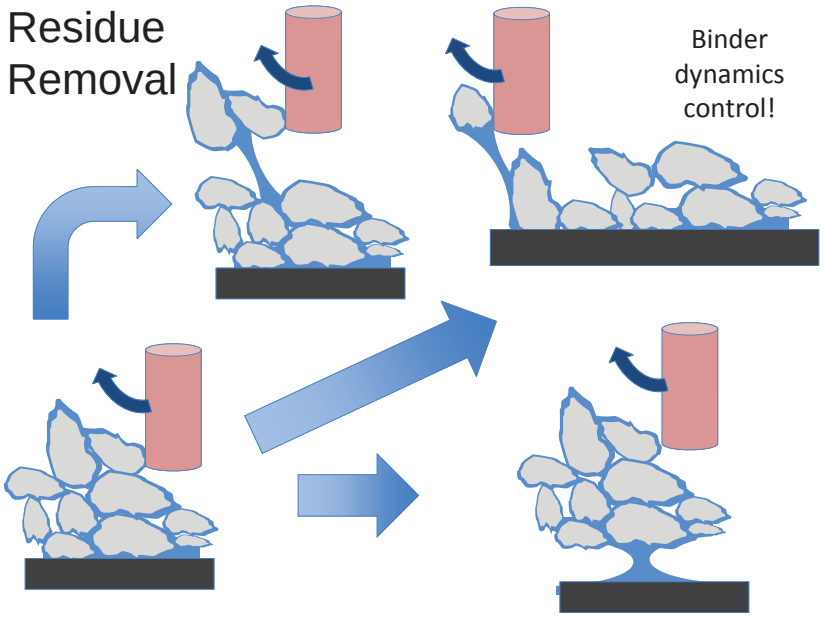
Possible weak links
1) liquid binder – solid surface (adhesive failure);
2) liquid binder – liquid binder (cohesive failure);
3) liquid binder – explosive particle surface (adhesive failure);
4) within explosive particle (cohesive failure)

Key parameter: Capillary number (Ca)

$$Ca = \frac{viscous\ forces}{interfacial\ forces}$$

Ca for compounded explosives ~ 10^{-4} means viscous effects dominate

Residue Removal



A way to measure the adhesion of full residues to any surface!!!

Maybe…

Centrifuge Technique Description

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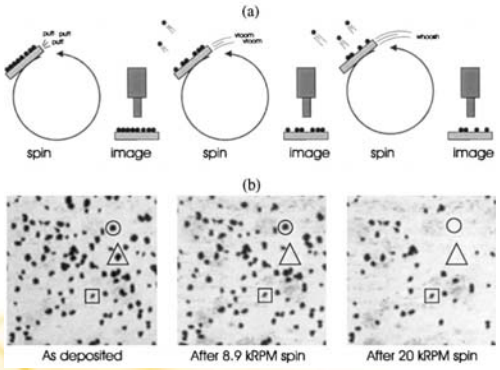

$$F_{ad} = F_{cent} = m\omega^2 r$$

- Deposit particles and count the initial number of particles
- Run in centrifuge
- Capture an image of the surface to determine the number of remaining particles
- Repeat [1]

1. Mizes, "Small particle adhesion: measurement and control," *Colloid Surface A,* May 2000.

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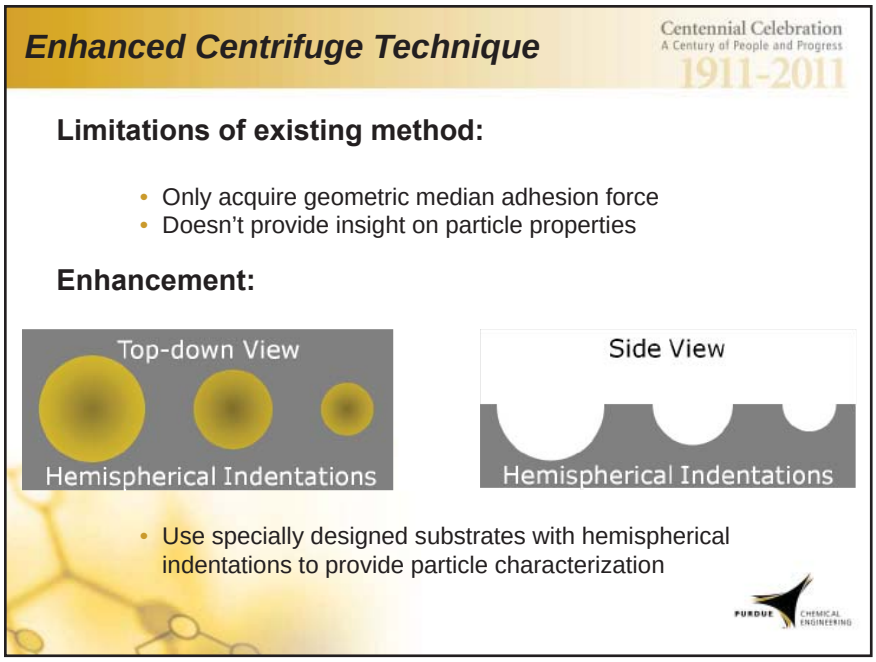
Enhanced Centrifuge Technique
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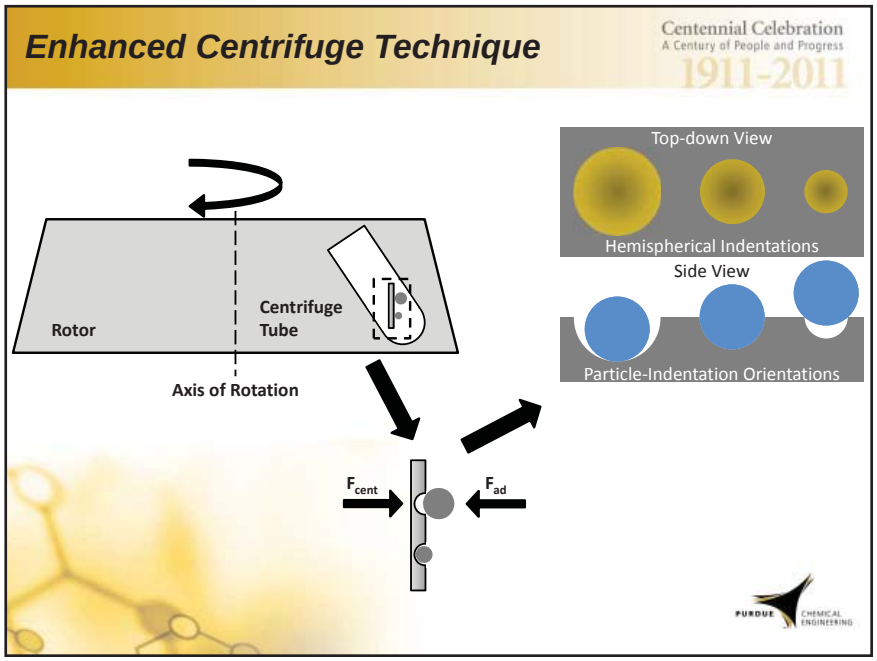
Limitations of existing method:
Only acquire geometric median adhesion force
Doesn't provide insight on particle properties
Enhancement:
Top-down View
Hemispherical Indentations
Side View
Hemispherical Indentations
Use specially designed substrates with hemispherical indentations to provide particle characterization
PURDUE CHEMICAL ENGINEERING


Enhanced Centrifuge Technique
Centennial Celebration
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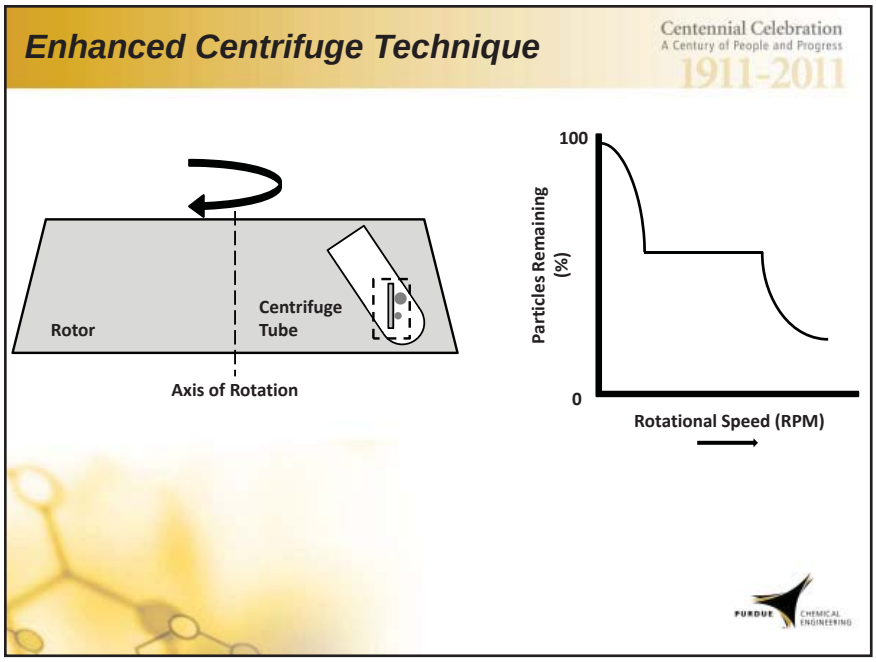
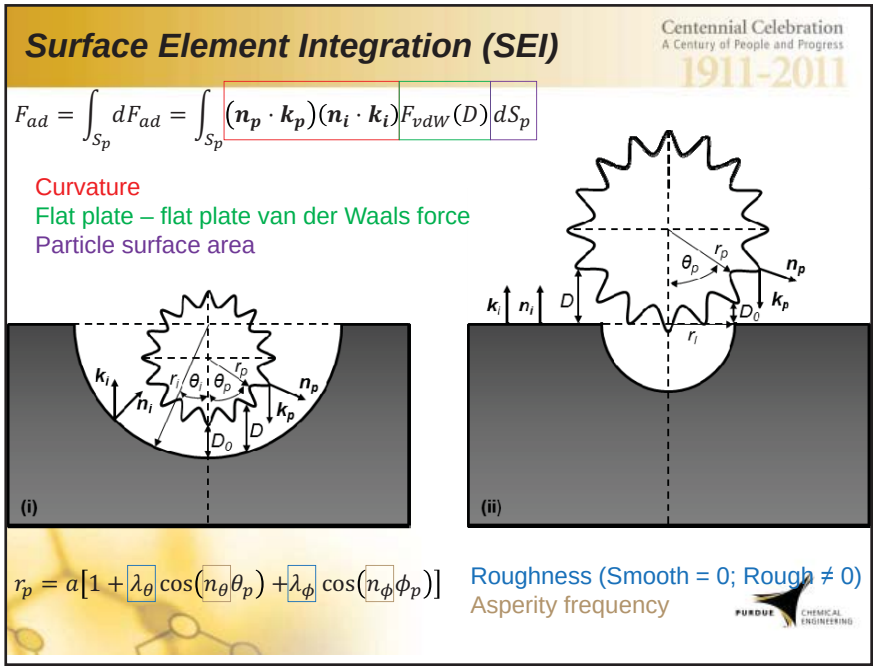
Rotor
Centrifuge Tube
Axis of Rotation
F_cent
F_ad
Top-down View
Hemispherical Indentations
Side View
Particle-Indentation Orientations
PURDUE CHEMICAL ENGINEERING


Enhanced Centrifuge Technique
Centennial Celebration
A Century of People and Progress
1911-2011
Rotor
Centrifuge Tube
Axis of Rotation
100
0
Particles Remaining (%)
Rotational Speed (RPM)


Surface Element Integration (SEI)
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$F_{ad} = \int_{S_p} dF_{ad} = \int_{S_p} (\boldsymbol{n_p} \cdot \boldsymbol{k_p})(\boldsymbol{n_i} \cdot \boldsymbol{k_i}) F_{vdW}(D)\, dS_p$
Curvature
Flat plate – flat plate van der Waals force
Particle surface area
(i)
(ii)
$r_p = a\left[1 + \lambda_\theta \cos(n_\theta \theta_p) + \lambda_\phi \cos(n_\phi \phi_p)\right]$
Roughness (Smooth = 0; Rough ≠ 0)
Asperity frequency

Particle Size Distributions

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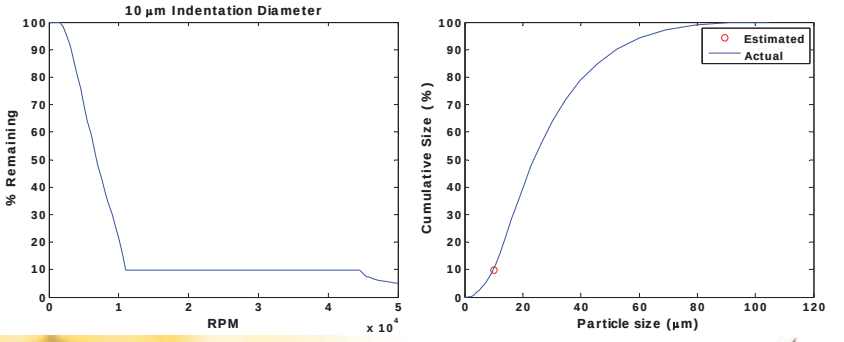
Simulated 10,000 particles of known size distribution adhering to plates with defined indentations

Cumulative size distribution built from Residual Adhering Particle (RAP) curves from each indentation size



PURDUE CHEMICAL ENGINEERING

Particle Size Distributions

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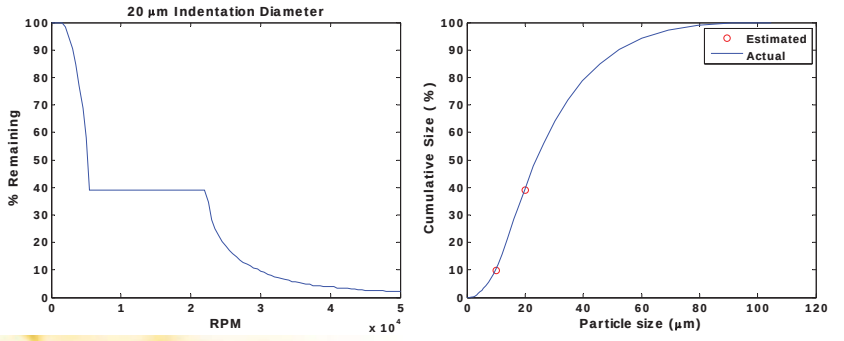
Cumulative size distribution built from RAP curves from each indentation size



PURDUE CHEMICAL ENGINEERING

Particle Size Distributions

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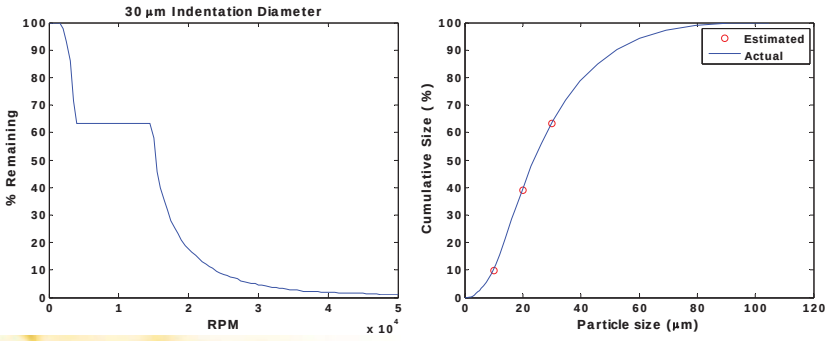
Cumulative size distribution built from RAP curves from each indentation size



Particle Size Distributions

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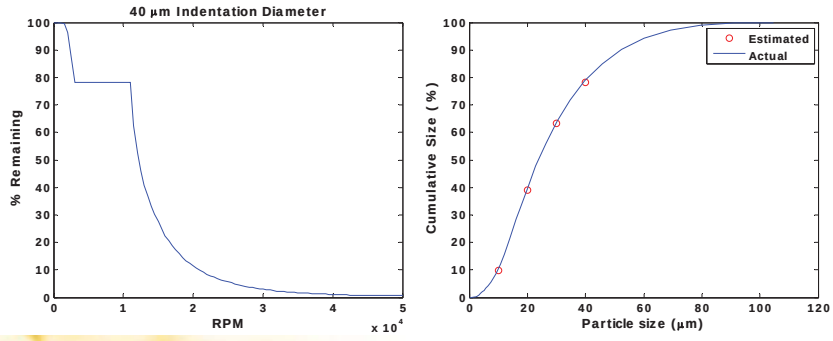
Cumulative size distribution built from RAP curves from each indentation size



Particle Size Distributions

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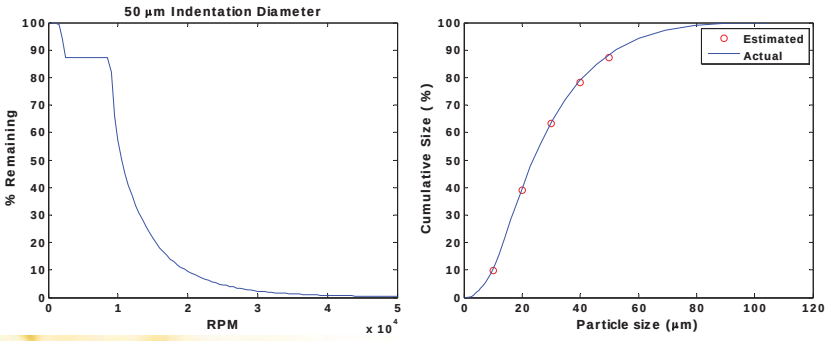
Cumulative size distribution built from RAP curves from each indentation size



Particle Size Distributions

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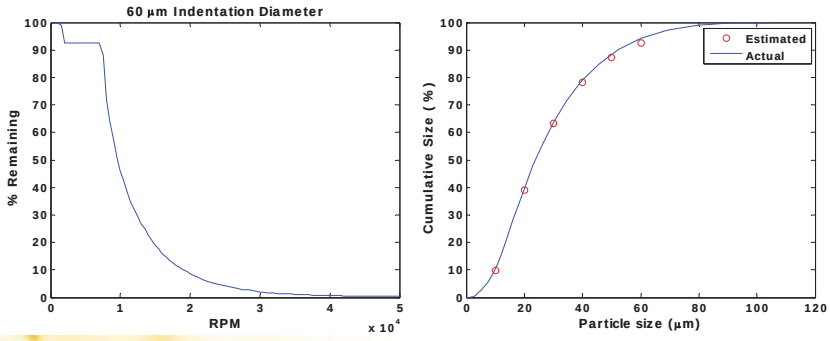
Cumulative size distribution built from RAP curves from each indentation size



Enhanced centrifuge technique developed to discriminate particle size

Simplify Powder Characterization

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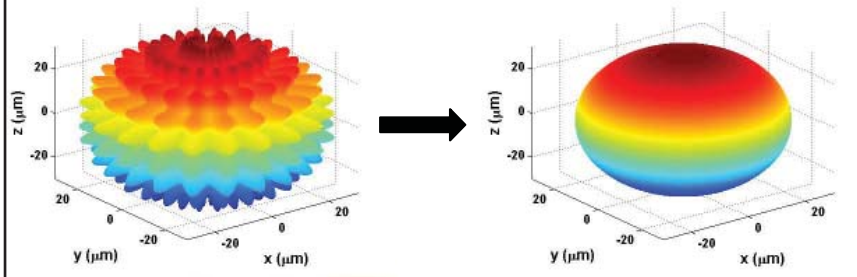

- Size: Known
- A_{132}: Known
- Roughness: ?

- Size: Known
- $A_{132,eff}$: Determine

Effective Hamaker Constants

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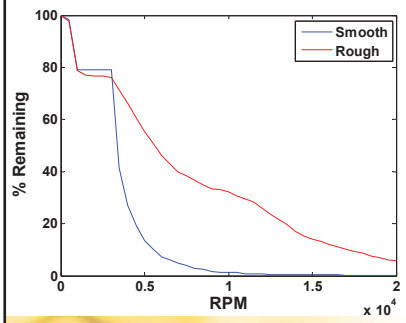
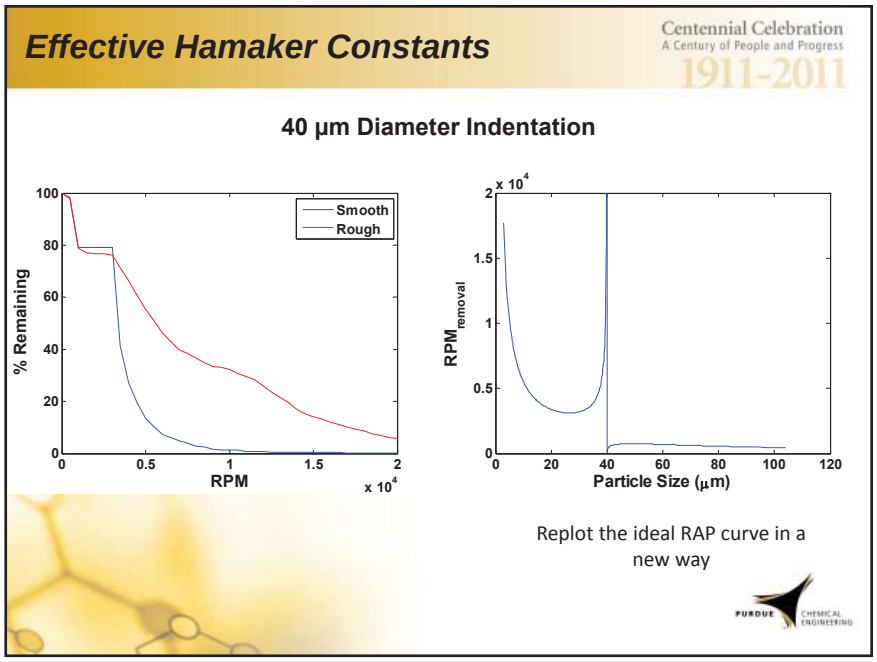
Consider the behavior of particles with same size distribution as before but arbitrary nanoscale roughness…

40 μm Diameter Indentation




Effective Hamaker Constants
Centennial Celebration
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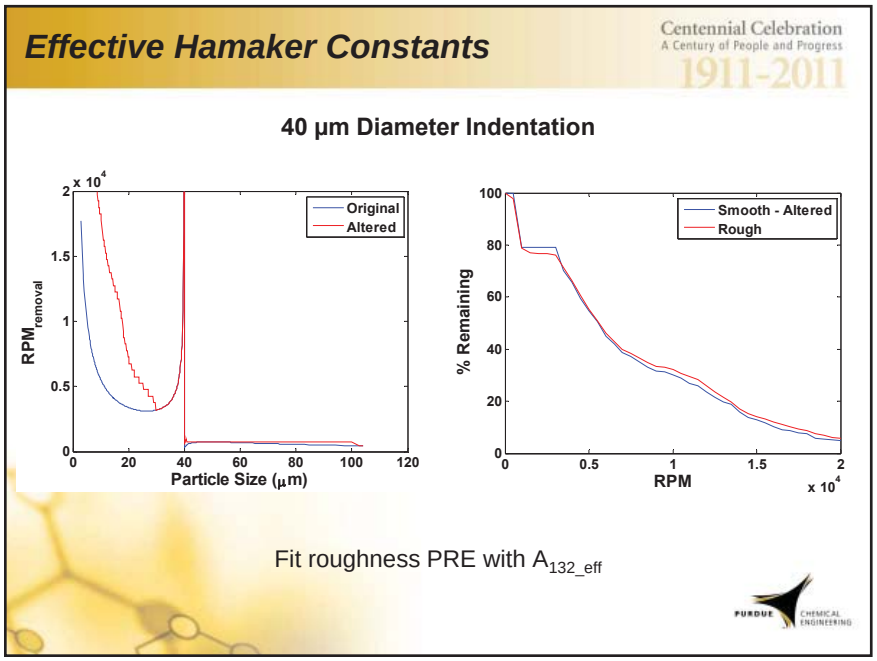
40 µm Diameter Indentation
% Remaining
RPM
x 10^4
Smooth
Rough
RPM_removal
Particle Size (µm)
Replot the ideal RAP curve in a new way
PURDUE
CHEMICAL ENGINEERING


Effective Hamaker Constants
Centennial Celebration
A Century of People and Progress
1911-2011
40 µm Diameter Indentation
RPM_removal
Particle Size (µm)
x 10^4
Original
Altered
% Remaining
RPM
Smooth - Altered
Rough
Fit roughness PRE with A132_eff
PURDUE
CHEMICAL ENGINEERING

Centrifuge Technique – Silica on Steel

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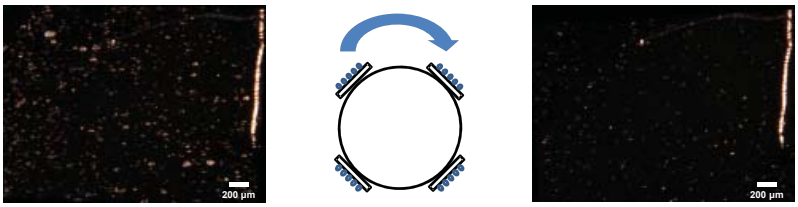
Initial Image | **Centrifugal Rotation** | **After 10500 rpm**



- Silica particles dispersed on stainless steel plates
- Rotate plates in centrifuge
  - 1500 to 10500 rpm
  - One minute run time

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Experimental and Smooth RAP

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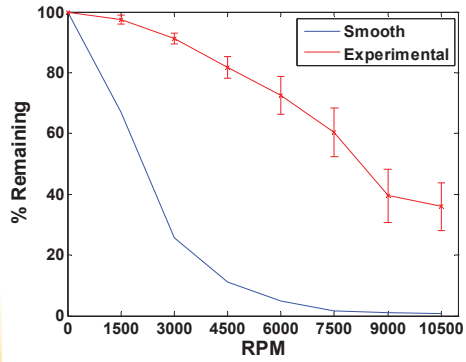
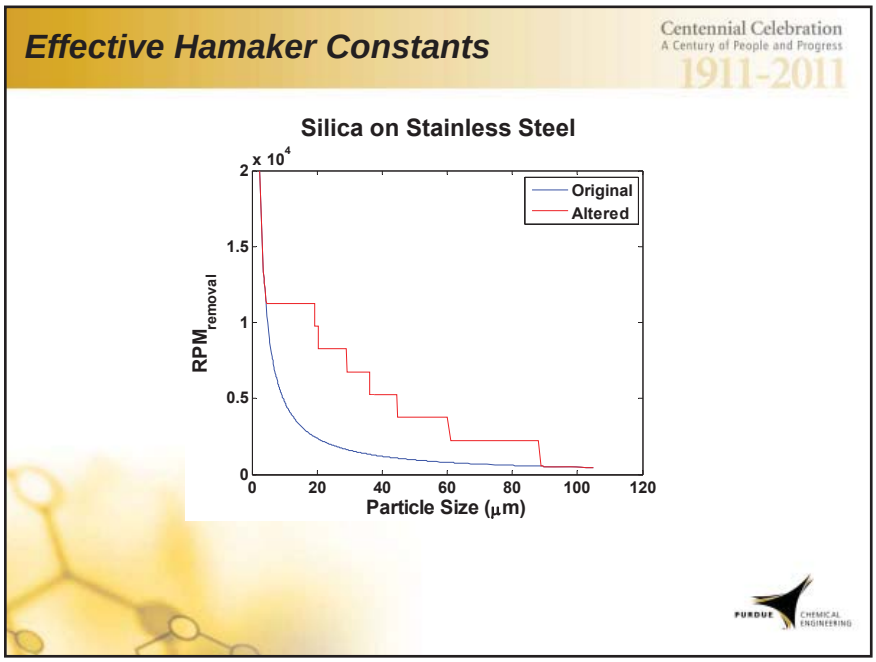
Silica on Stainless Steel



PURDUE CHEMICAL ENGINEERING


Effective Hamaker Constants
Centennial Celebration
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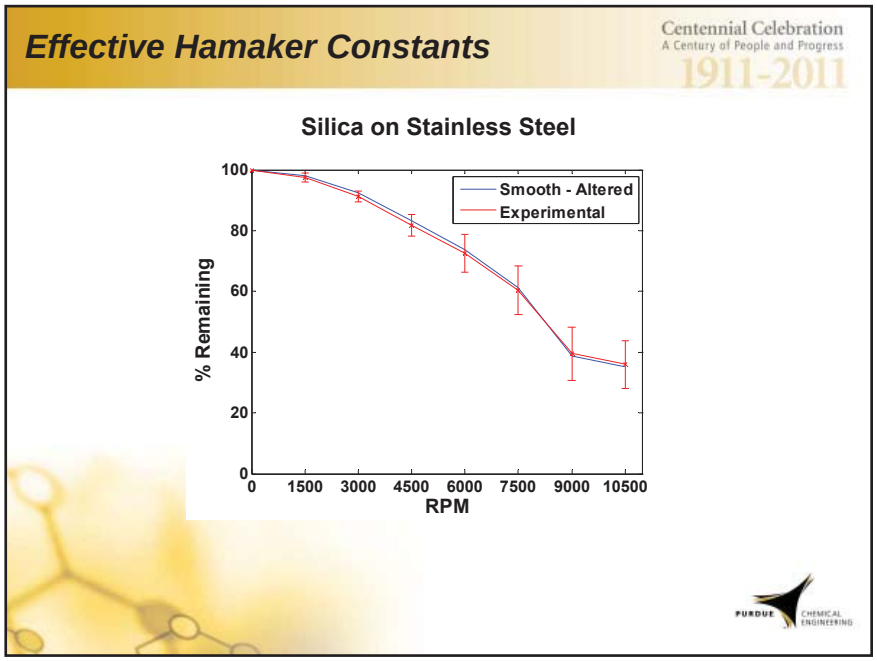
Silica on Stainless Steel
x 10^4
RPM removal
Particle Size (μm)
Original
Altered
0
0.5
1
1.5
2
0
20
40
60
80
100
120
PURDUE CHEMICAL ENGINEERING


Effective Hamaker Constants
Centennial Celebration
A Century of People and Progress
1911-2011
Silica on Stainless Steel
% Remaining
RPM
Smooth - Altered
Experimental
0
20
40
60
80
100
0
1500
3000
4500
6000
7500
9000
10500
PURDUE CHEMICAL ENGINEERING

New Challenge

- Modify the enhanced centrifuge technique to work with compounded residues
  - Proof of concept
  - Quantitative demonstration (including models)
- Deliver effective Hamaker constants to DHS and community
  - Capable of predicting residue adhesion to all substrates of interest using validated constants
  - Models residues as smooth spheres – simple
    - 'Magic' is in the fitted constants

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U.S. Department of Homeland Security, Science and Technology Directorate sponsored this work under agreement 2010-ST-108-LR0003.

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NOTE: This material is based upon work supported by the U.S. Department of Homeland Security, Science and Technology Directorate, Office of University Programs, under Grant Award 2013-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

Acknowledgements

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Circled:
- Melissa Sweat
  - Dec. 2015
- Leonid Miroshnik
  - 2018/2019

Not pictured:
- Johanna Smith
  - Grad. May 2014
  - Employed at General Mills
- Chris Browne
  - Grad. May 2017
- Alyssa Bass
  - Grad. May 2017
- Hannah Burnau
  - Grad. H.S. May 2017

Top: Leonid Miroshnik, Sean Fronczak, Jenny Laster, Darby Hoss, Andrew Parker
Bottom: Aaron Harrison, Caitlin Schram, Myles Thomas, Melissa Sweat, Jordan Thorpe

This material is based upon work supported by the U.S. Department of Homeland Security, Science and Technology Directorate, Office of University Programs, under Grant Award 2013-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security. [10/2013]

16.6 Leonid Miroshnik: Describing Roughness During Contact Sampling

Describing Roughness During Contact Sampling:
Statistical Considerations for Swab Screening Explosive Particulates

PURDUE CHEMICAL ENGINEERING

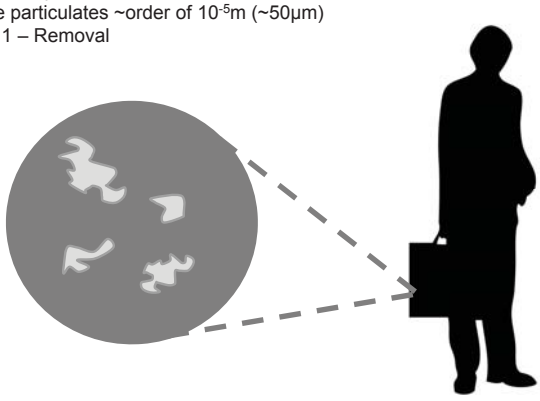
Leonid Miroshnik
Sean Fronczak, Jordan Thorpe, Stephen Beaudoin

Purdue University School of Chemical Engineering
West Lafayette, IN 47906

Trace Explosives Sensing for Security Applications – II (TESSA02)
August 5, 2015
Northeastern University

Swab Sampling

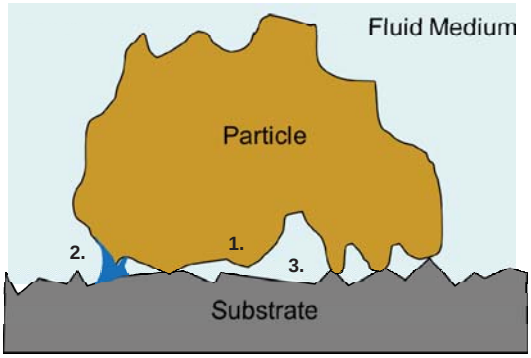
Trace Explosive Sampling
- Ion Mobility Spectrometer (IMS)
- Trace particulates ~order of 10^{-5}m (~50μm)
- Step 1 – Removal



Adhesion

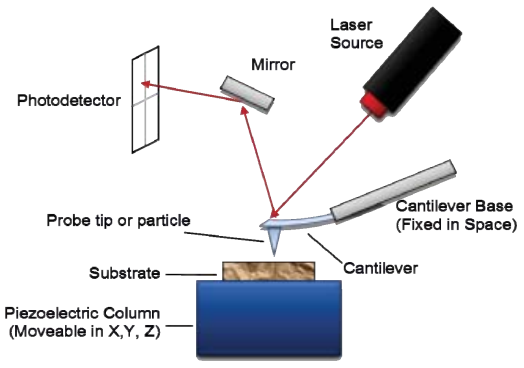
Three Primary Intermolecular Forces

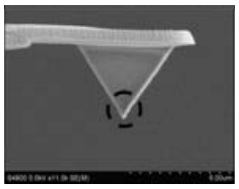
1. van der Waals (vdW)
2. Capillary
3. Electrostatic

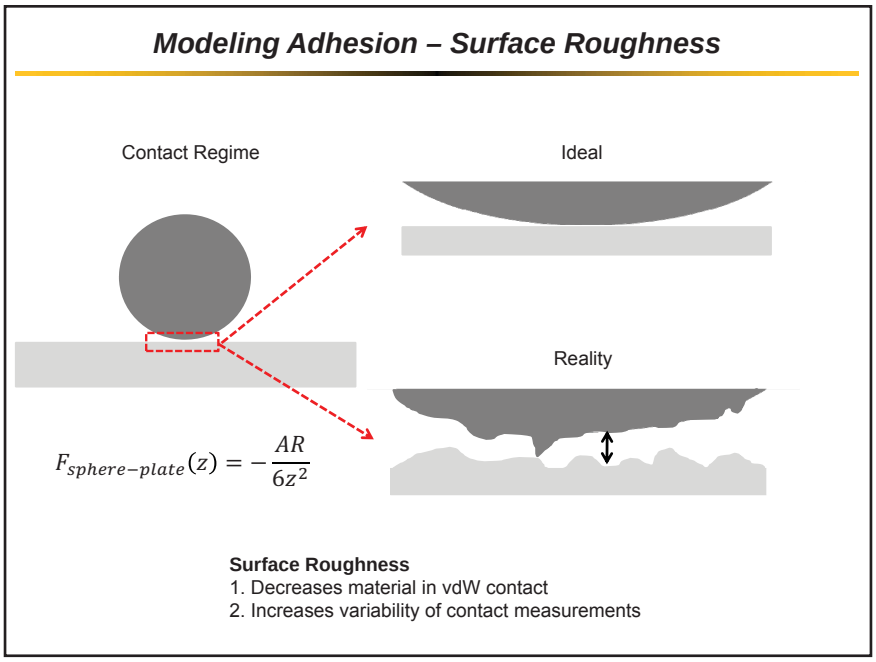


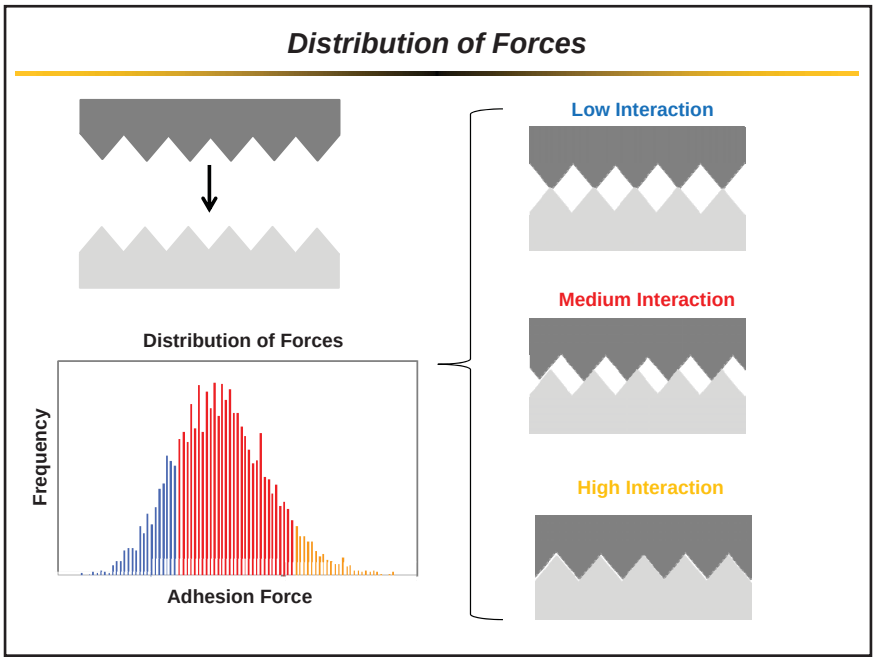
Measuring Adhesion

Atomic Force Microscopy



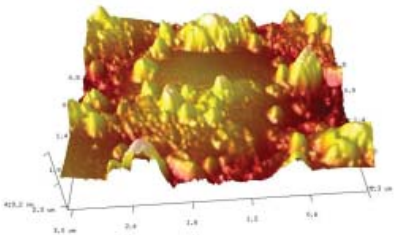



Modeling Adhesion – Surface Roughness
Contact Regime
Ideal
Reality
$F_{sphere-plate}(z) = -\frac{AR}{6z^2}$
Surface Roughness
1. Decreases material in vdW contact
2. Increases variability of contact measurements

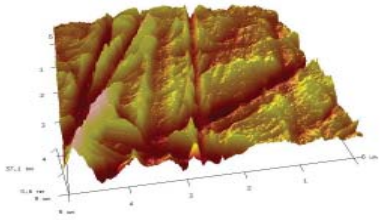

Distribution of Forces
Low Interaction
Medium Interaction
High Interaction
Distribution of Forces
Frequency
Adhesion Force

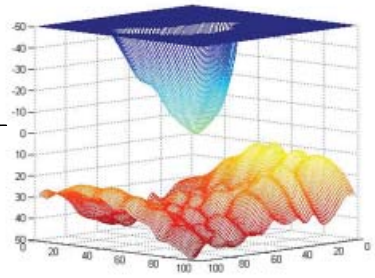
Accounting for Surface Roughness

Topographical Map of Mounted Particle

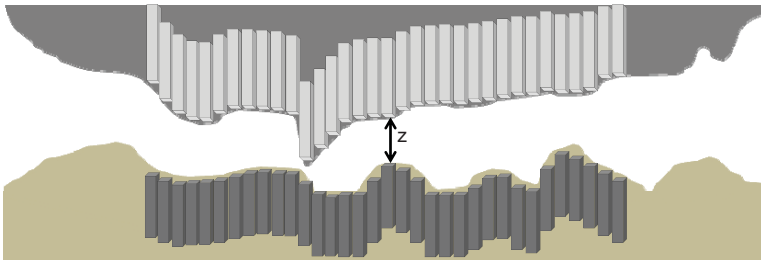


Topographical Map of Substrate

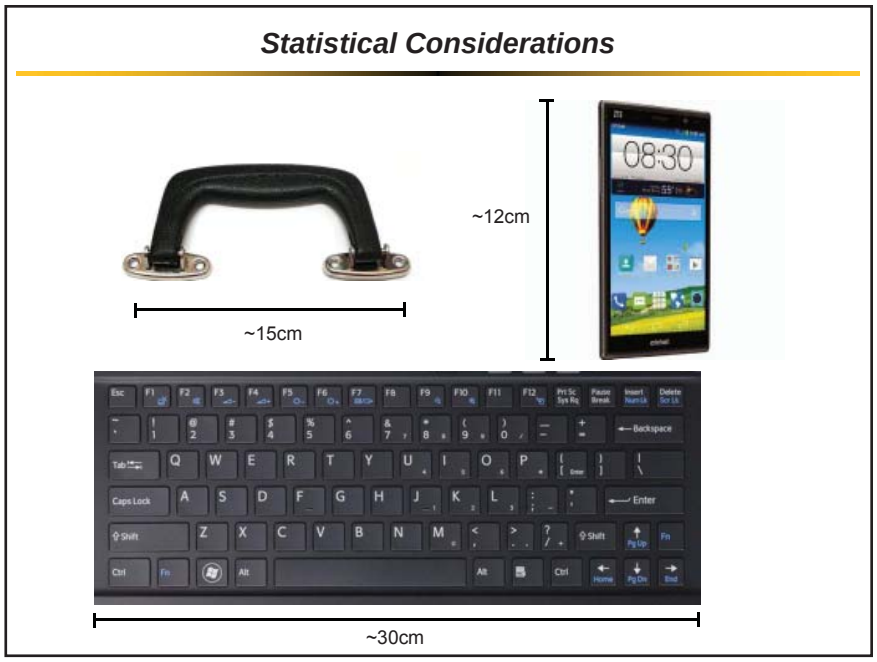


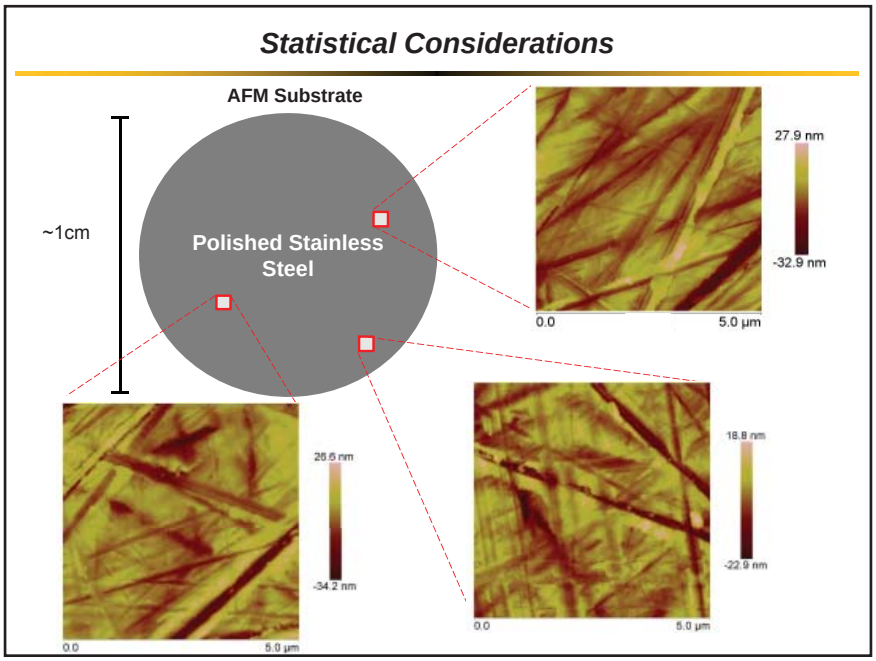


Modeling Adhesion of Rough Surfaces

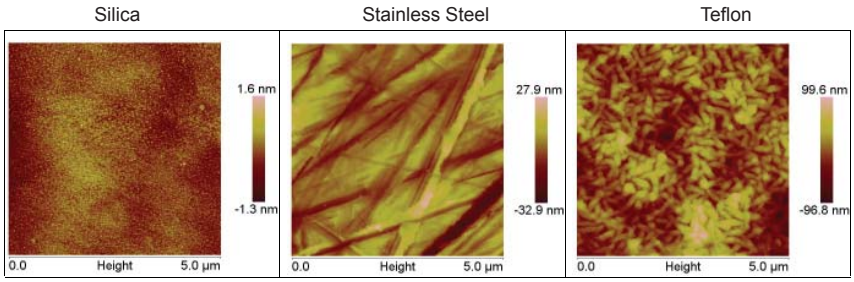


$$F_{plates}(z) = -\frac{A}{6\pi z^3} \times Area \quad \rightarrow \quad F_{total} = -\sum_{i}^{n_x}\sum_{j}^{n_y} \frac{A}{6\pi z_{ij}^3} \times Area_{ij}$$


Statistical Considerations
~15cm
~12cm
~30cm

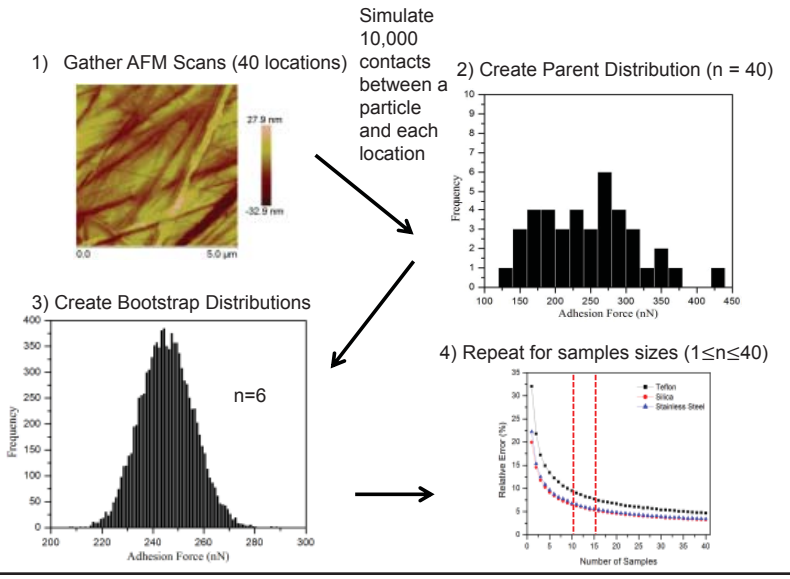

Statistical Considerations
AFM Substrate
~1cm
Polished Stainless Steel
27.9 nm
-32.9 nm
0.0
5.0 µm
26.6 nm
-34.2 nm
18.8 nm
-22.9 nm

Substrates Considered



Substrate	RMS	Pk-to-Pk
Silica	0.63 ± 0.2 nm	12.8 ± 7.9 nm
Stainless Steel	7.4 ± 1.9 nm	65.9 ± 17.9 nm
Teflon	24.3 ± 5.8 nm	181.2 ± 52.7 nm

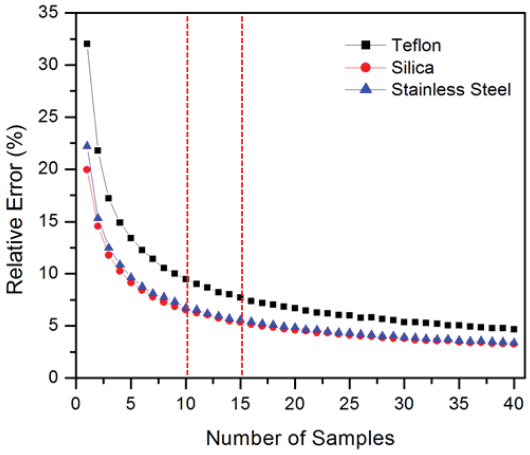
Bootstrap Method



Statistical Results

Determine optimized number of samples required to fully characterize a substrate

$$RE = \frac{1}{k}\sum_{i=1}^{k}\left|\frac{\bar{x} - \bar{x}_i}{\bar{x}}\right|$$



Trace Explosives Application

Surfaces of Interest

Substrate Models

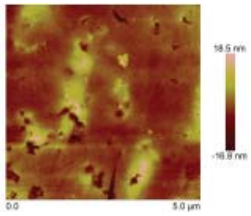
ABS Plastic
- µm-smooth
- µm-rough

Aluminum
- Paint-coated
- With native oxide

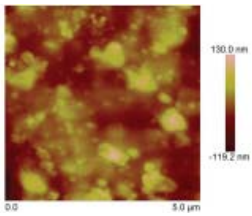
Substrate Roughness Characteristics

Substrate	RMS	Pk-to-Pk
ABS-smooth	66.8 ± 29.9 nm	459.8 ± 134.4 nm
ABS-rough	38.1 ± 20.2 nm	288.6 ± 129.8 nm
Aluminum (native oxide)	60.8 ± 13.1 nm	359.1 ± 120.3 nm
Aluminum (paint-coated)	3.6 ± 0.6 nm	72.6 ± 27.9 nm

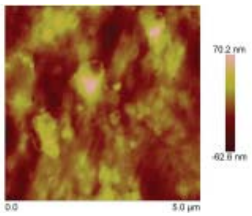
Aluminum (paint-coated)



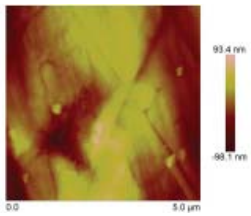
ABS-smooth



ABS-rough

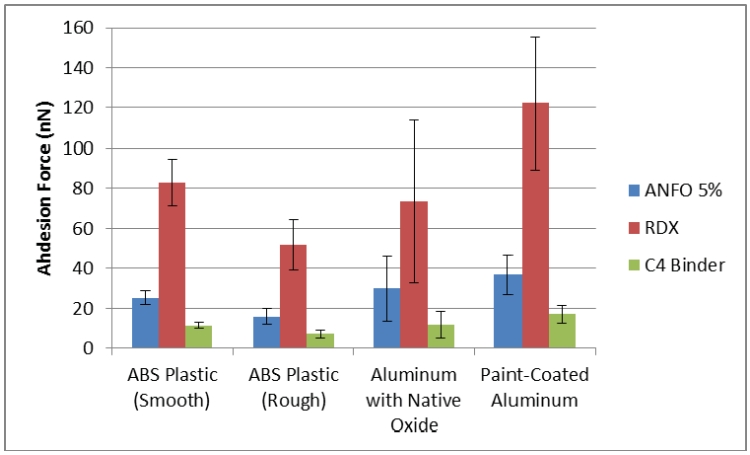


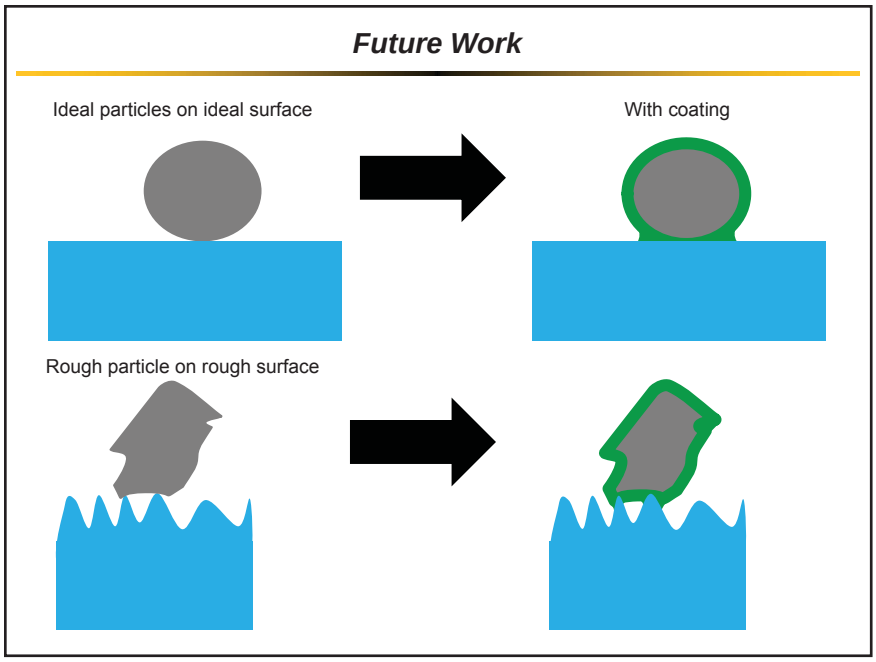
Aluminum (native oxide)

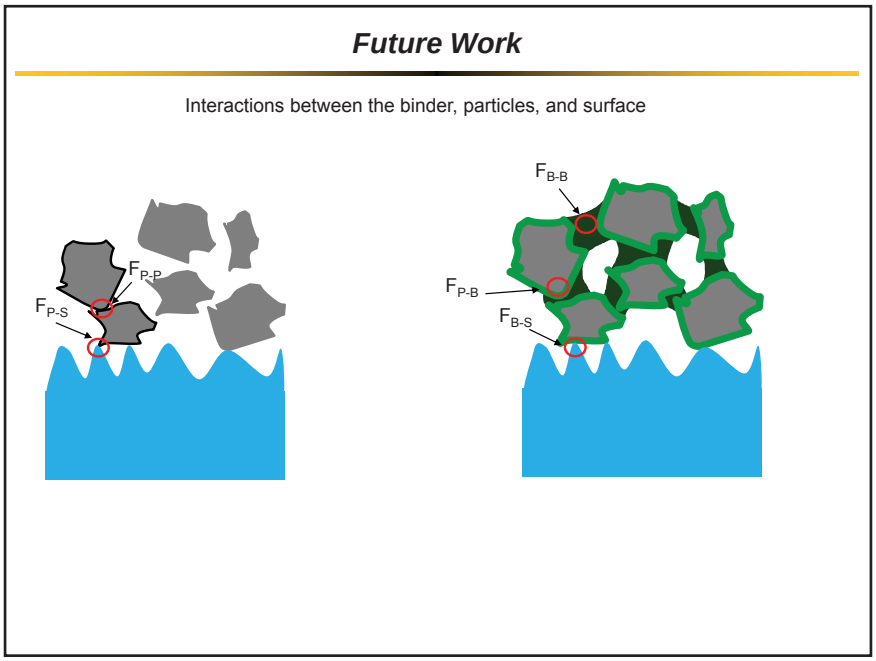


Adhesion Force Predictions

Preliminary results based on 1200 simulated contacts between substrates and 5μm particle

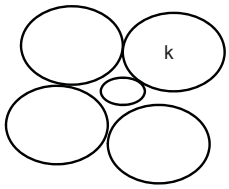


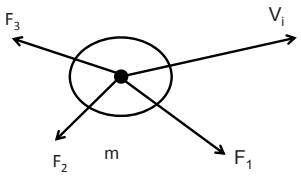

Future Work
Ideal particles on ideal surface
With coating
Rough particle on rough surface


Future Work
Interactions between the binder, particles, and surface
F_{P-P}
F_{P-S}
F_{B-B}
F_{P-B}
F_{B-S}

Future Work

Discrete Element Method (DEM)





$$m\ddot{\mathbf{x}}_i = \sum_{j \neq i} \mathbf{f}_{j \to i}$$

Acknowledgements

Circled:
- Melissa Sweat
  - Dec. 2015
- Leonid Miroshnik
  - 2018/2019

Not pictured:
- Johanna Smith
  - Grad. May 2014
  - Employed at General Mills
- Chris Browne
  - Grad. May 2017
- Alyssa Bass
  - Grad. May 2017
- Hannah Burnau
  - Grad. H.S. May 2017

Top: Leonid Miroshnik, Sean Fronczak, Jenny Laster, Darby Hoss, Andrew Parker
Bottom: Aaron Harrison, Caitlin Schram, Myles Thomas, Melissa Sweat, Jordan Thorpe

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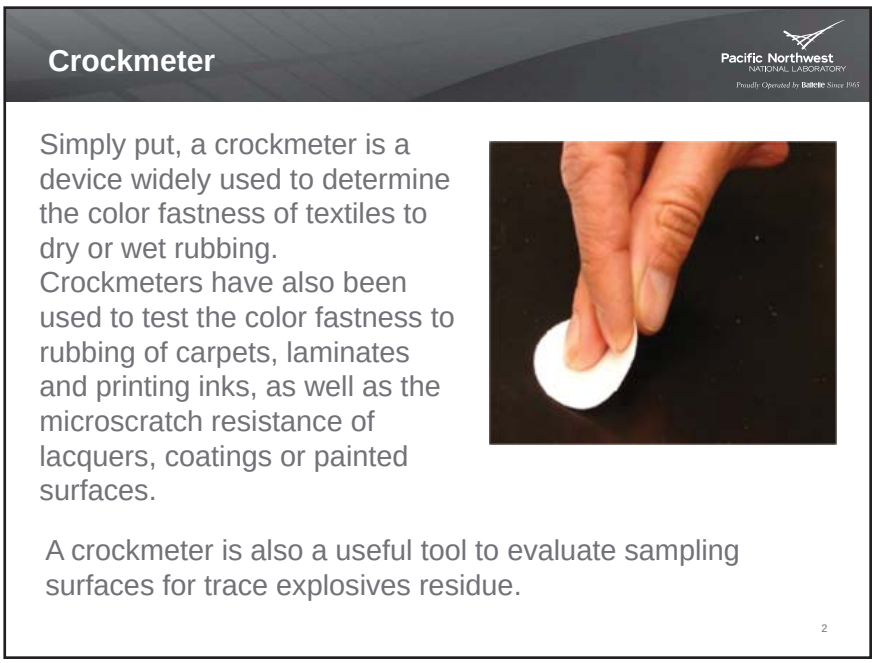
16.7 Matthew Staymates: Pressure/Force Sensitive Sensing

Presentation Omitted

16.8 Dave Atkinson: Open Source Crockmeter



Crockmeter

Pacific Northwest NATIONAL LABORATORY
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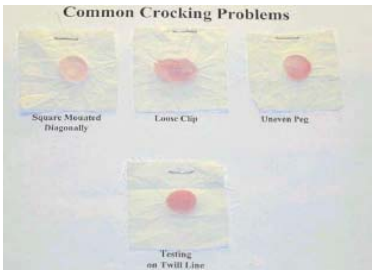
Standard cotton fabric is rubbed against the surface of colored textile specimen to check the transfer of color.



A crockmeter essentially allows two surfaces to be rubbed against each other repeatedly with a known force.

3

Crockmeters

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Crockmeter Electronic
$4,356.00 from Summit Measurement
Crockmeter Electronic

Crockmeter Manual
$1,160.00 from Summit Measurement
Crockmeter Manual

These somewhat simple test instruments fill an textile industry niche and are not cheap.

Trace Explosives Sampling

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It would be useful for trace sampling studies (e.g. our TESSA studies) to have a standardized methodology so that data sets can be directly compared.

A crockmeter in each lab would be optimal, but the price of the commercial units is prohibitive for many labs for such a specialty item.

We propose the development of a low cost, open source crockmeter.

Open Source

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Open source promotes a universal access via a free license to a product's design or blueprint, and universal redistribution of that design or blueprint, including subsequent improvements to it by anyone.

This approach should allow for an inexpensive and uniform crockmeter design to be available to the trace sampling community.

Pearce, Joshua M (2012). "**Building Research Equipment with Free, Open-Source Hardware**". *Science* **337** (6100): 1303–4. doi:10.1126/science.1228183. PMID 22984059. open access

Open Source Crockmeter

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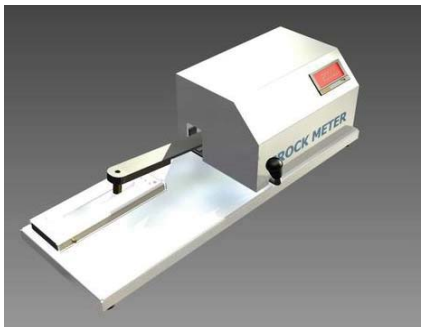
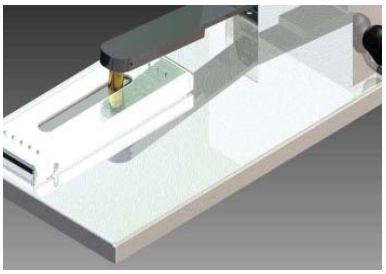
http://www.grabcad.com/library/crockmeter-1





Crockmeter Automation

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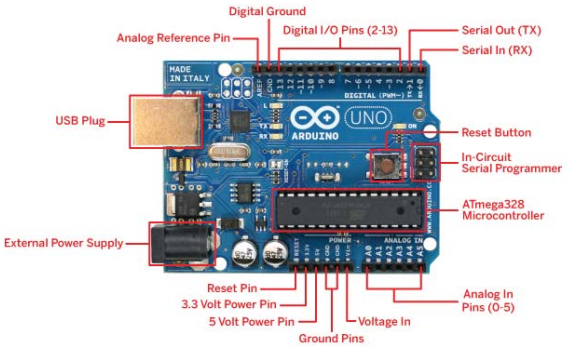
If we would like to further remove variables from the crockmeter operation across organizations, an open source controller could be easily designed using the Arduino platform. This is a $25 microcontroller board with extensive I/O.



Add some low cost servo motors, and an entire low cost automated crockmeter can be built for less than $100.

Open Source Crockmeter

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- It makes sense to provide the community with a uniform, low cost approach for round robin sampling studies
- A open source crockmeter design would be standardized by a consensus and units could even be produced from one source
- A university engineering student with access to a 3D printer and some arduino building/programming skills should be able to build an automated crockmeter at low cost (<$100) – this is likely any undergraduate mechanical engineering laboratory

16.9 Jeff Rhoads and Steve Beaudoin: Acoustic Insults of Explosives for Vapor Creation

Presentation Omitted

16.10 Otto Gregory: Orthogonal Sensors for Residue Vapors

R2-B.1: Orthogonal Sensors for Trace Detection

Orthogonal Sensors for Residue Vapors

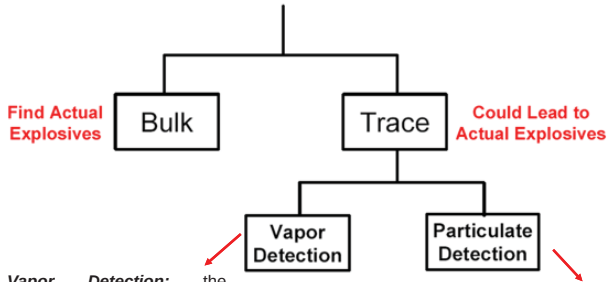
Zach Caron, Vivek Patel. Dylan Meekins, Michael J. Platek and Otto J. Gregory

Sensors and Surface Technology Partnership
Chemical Engineering Department
University of Rhode Island
Kingston, RI 02881

August 5, 2015

Detection of Residue Vapors

Explosives Detection*



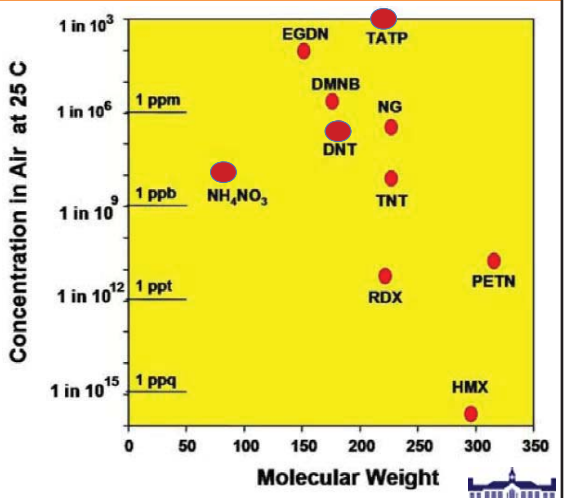
Vapor Detection: the concentration of explosives in the vapor phase is related to its vapor pressure and other factors such as, packaging, air circulation in the location, etc. all are critical for continuous monitoring of threats.

Particle Detection: techniques such as Ion Mobility Spectrometry (IMS) and colorimetric based detectors are typically used but require samples obtained by swabbing and thus cannot be used for continuous monitoring of threats.

**U.S. Department of Justice, November 2004*

Residue Vapors…….Concentration in Air?

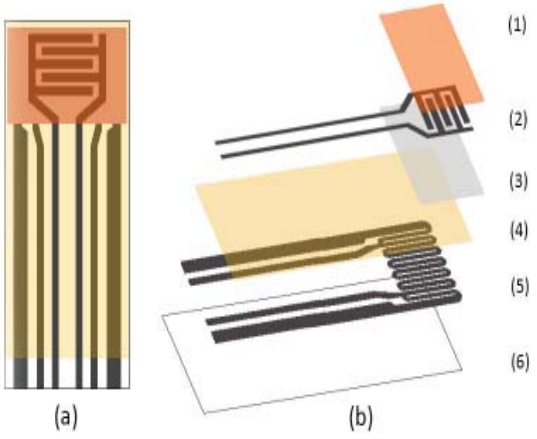
Vapor pressure determines residue concentration in vapor phase; TATP, DNT and ammonium nitrate can be detected in vapor phase ……conc. in the ppm to ppb range; PETN and RDX are not readily detected in vapor phase…….conc. in the ppt range



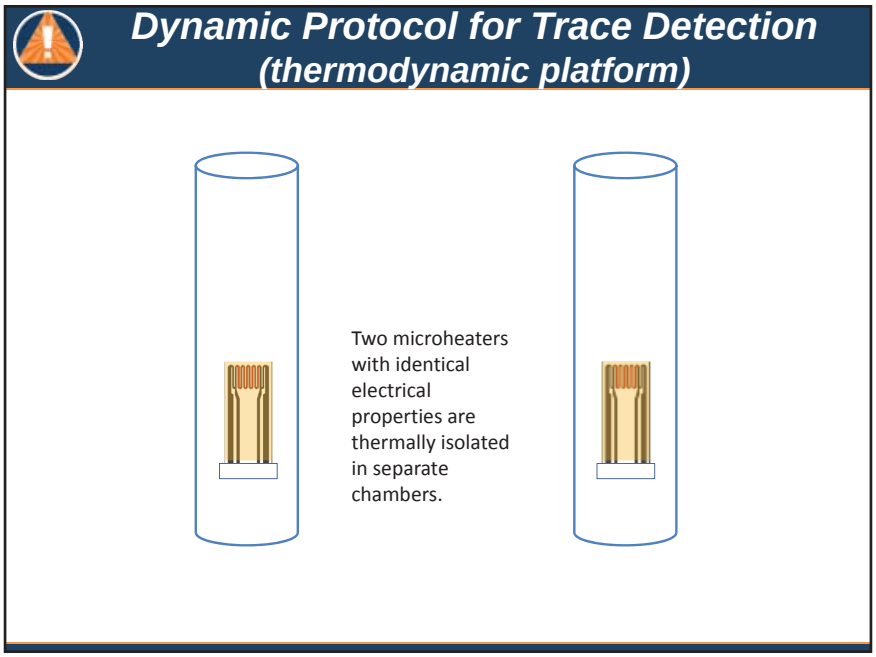
*U.S. Department of Justice, November 2004

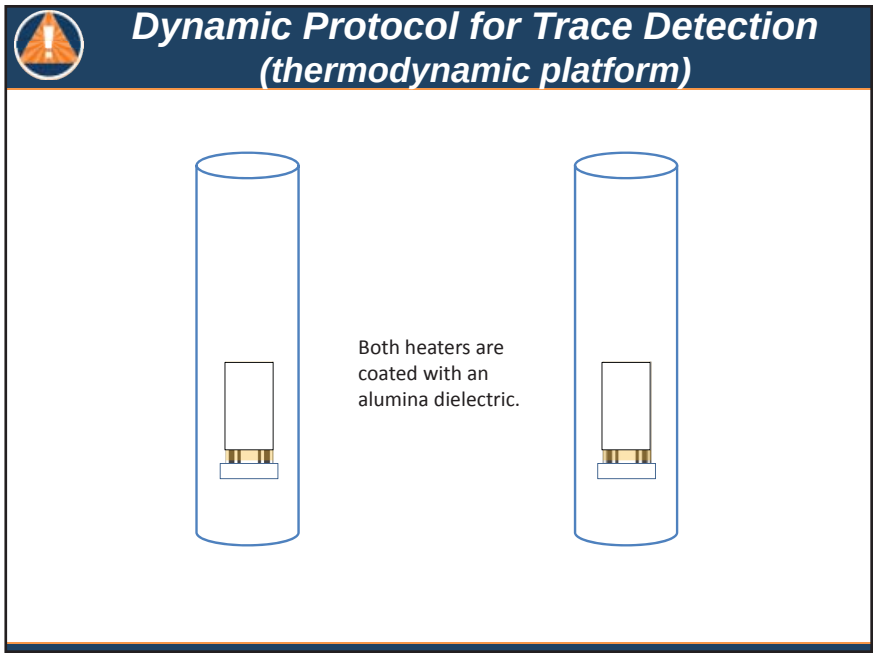
Components Comprising Orthogonal Sensors (thermodynamic and conductometric)

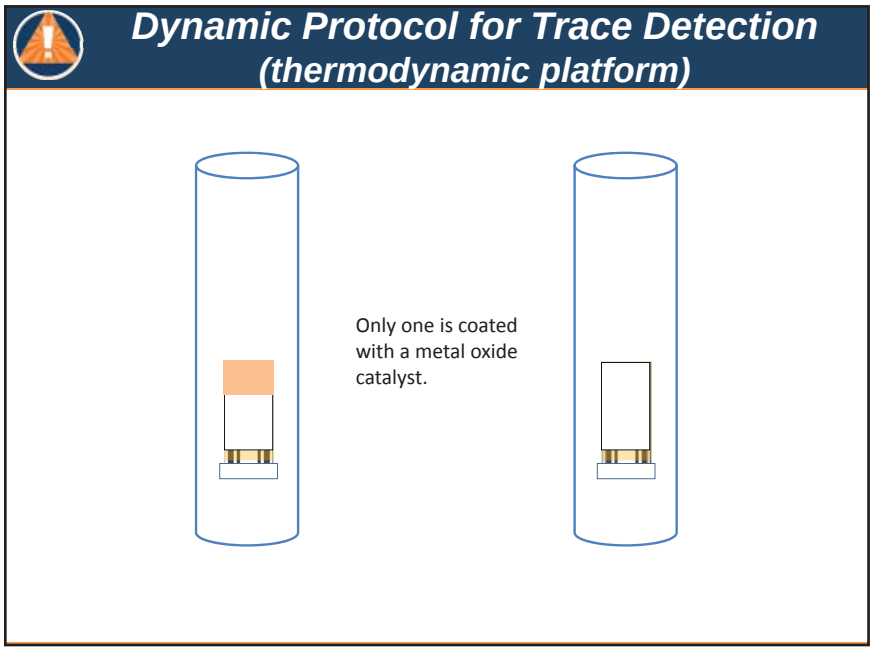
(1) Metal Oxide Catalyst
(2) Ni Conductometric Electrodes
(3) Alumina (porous)
(4) Sputtered Alumina
(5) Ni Microheater
(6) Alumina Substrate

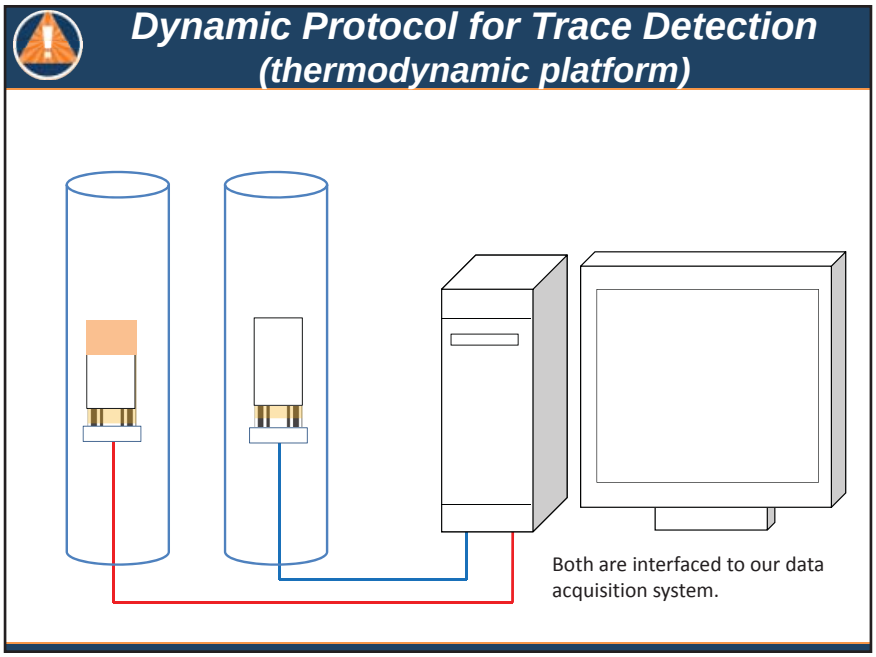


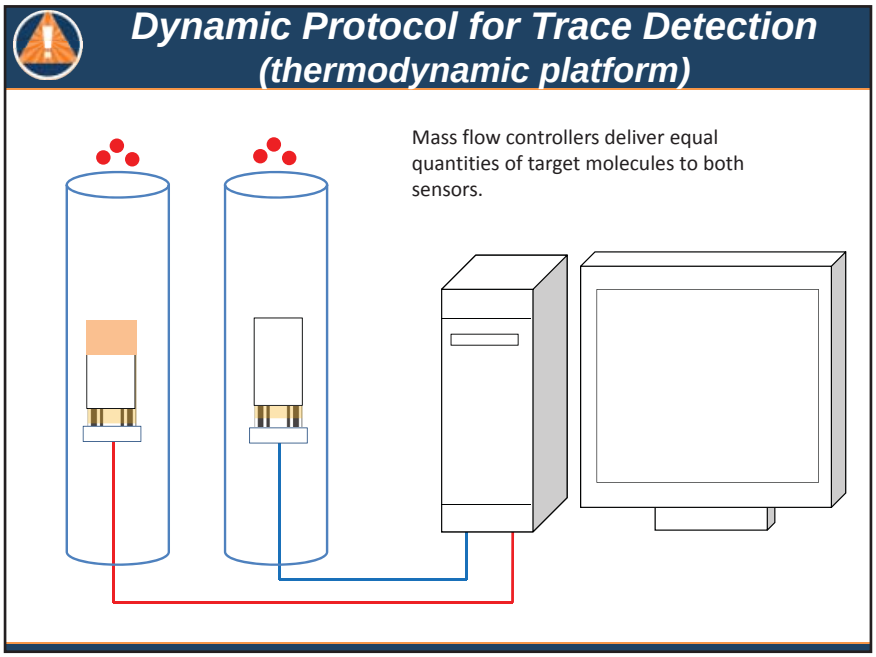
August 5, 2015

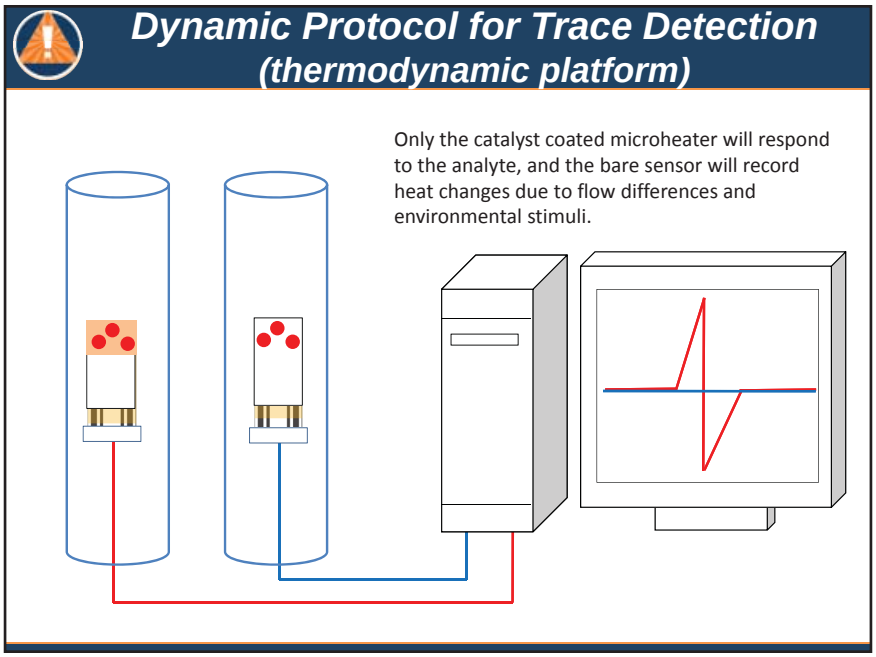

Dynamic Protocol for Trace Detection
(thermodynamic platform)
Two microheaters with identical electrical properties are thermally isolated in separate chambers.


Dynamic Protocol for Trace Detection
(thermodynamic platform)
Both heaters are coated with an alumina dielectric.


Dynamic Protocol for Trace Detection
(thermodynamic platform)
Only one is coated with a metal oxide catalyst.

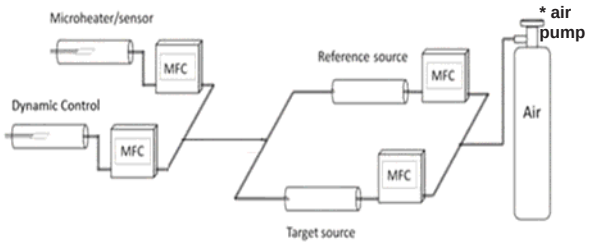

Dynamic Protocol for Trace Detection
(thermodynamic platform)
Both are interfaced to our data acquisition system.


Dynamic Protocol for Trace Detection
(thermodynamic platform)
Mass flow controllers deliver equal quantities of target molecules to both sensors.


Dynamic Protocol for Trace Detection
(thermodynamic platform)
Only the catalyst coated microheater will respond to the analyte, and the bare sensor will record heat changes due to flow differences and environmental stimuli.

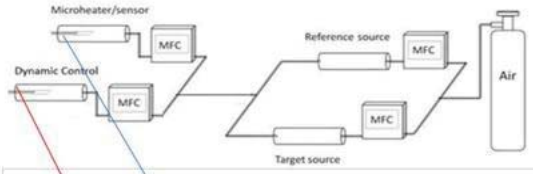
Dynamic Protocol for Trace Detection* (thermodynamic platform)

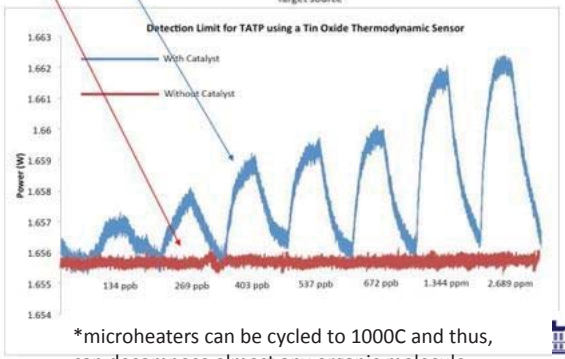
Dynamic (2 sensor) approach employs sensors with and without catalysts to eliminate sensible heat effects……



*microheaters can be cycled to 1000C and thus, can decompose almost any organic molecule

Dynamic Protocol for Trace Detection* (thermodynamic platform)



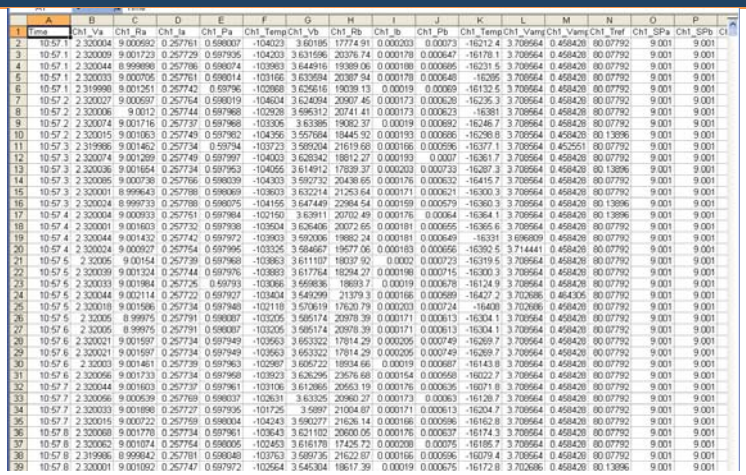


the only heat effect remaining is due to catalyst-analyte interaction;

*For sampling purposes, a small air pump is used to draw the incoming air over the sensor

*microheaters can be cycled to 1000C and thus, can decompose almost any organic molecule

Data Collection/Compilation (7 sec)



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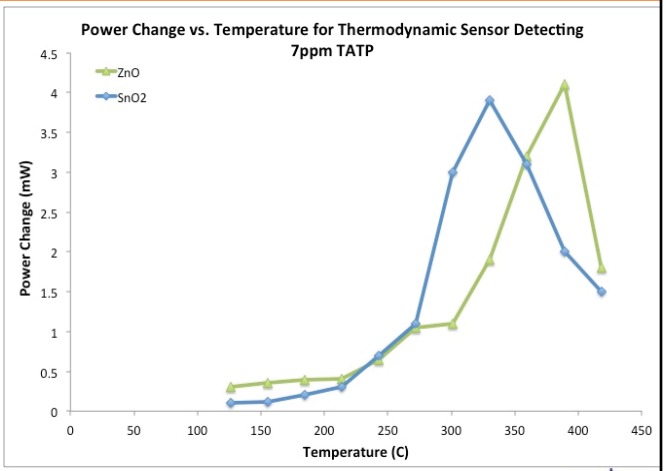
Catalyst Selectivity for Residue Vapors (thermodynamic platform)

Response of orthogonal sensor to TATP using different metal oxide catalysts…….. different peak temperatures for each oxide catalyst are observed…… translates into cat selectivity



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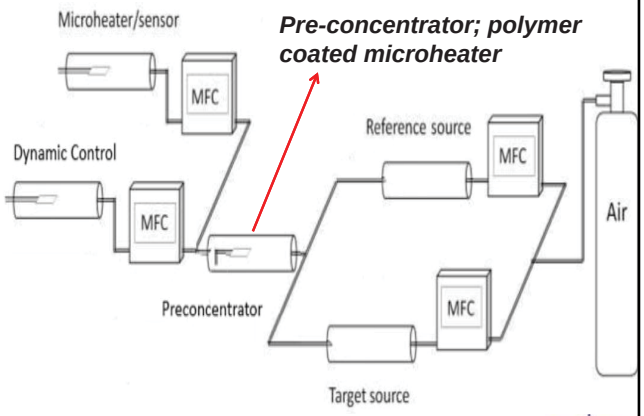
Pre-concentration of Residue Vapors

Pre-concentration employs an additional microheater upstream from active sensor that is coated with a polymer……. polystyrene possesses the desired adsorption/ desorption charact-eristics for con-centrating analyte in the vapor phase



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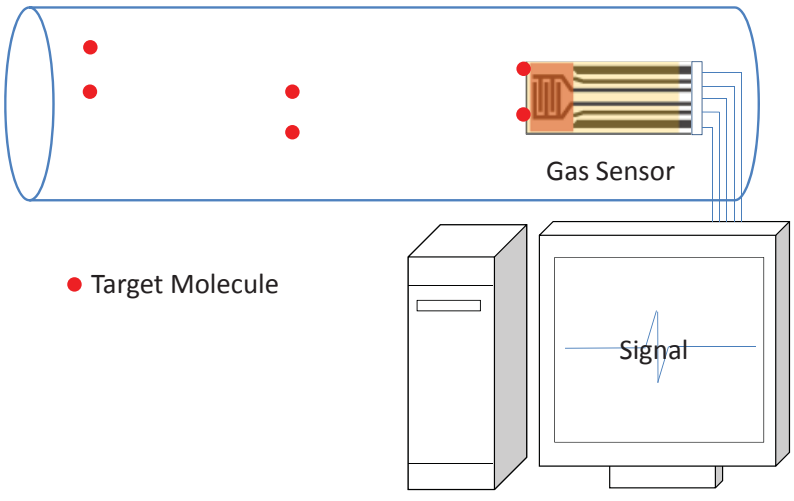
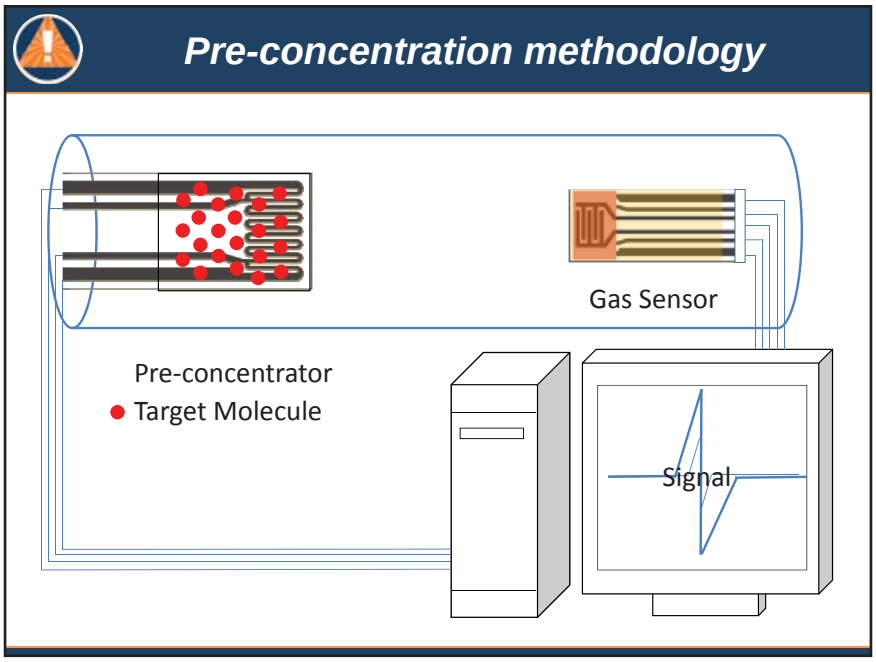
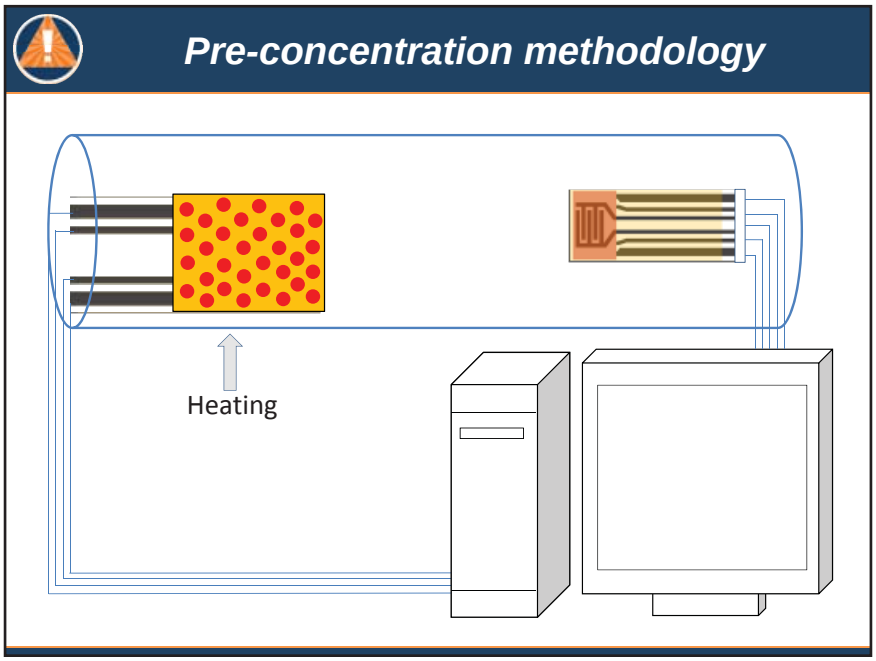
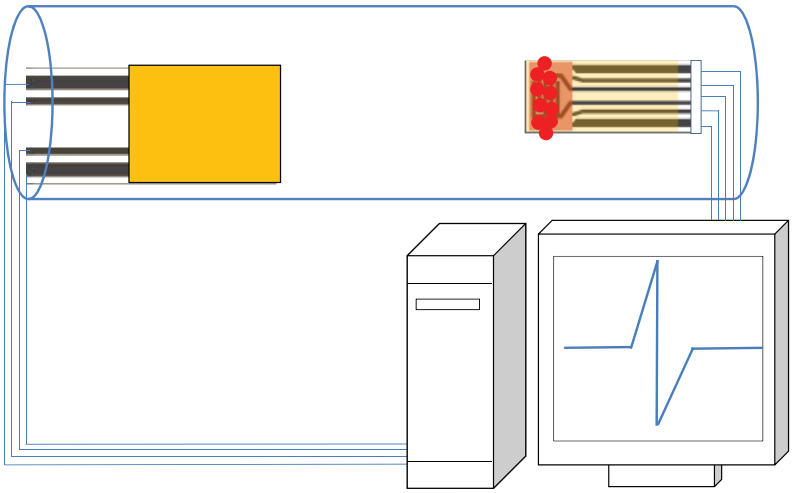
Pre-concentration methodology




Pre-concentration methodology
Gas Sensor
Pre-concentrator
Target Molecule
Signal


Pre-concentration methodology
Heating

Pre-concentration methodology



Pre-concentration of Residue Vapors

Desorption Efficiency of TNT at 120C°

Sample	Total Amount Adsorbed	Total Amount Desorbed	% Desorbed
Tenax	12	0.13	1%
Poly(2,6-dimethyl-1,4-phenyline oxide)	4.7	0.16	3%
Polystyrene	6.3	0.70	11%
Nomex	2.4	2.0	83%

Desorption Efficiency of TNT at 170C°

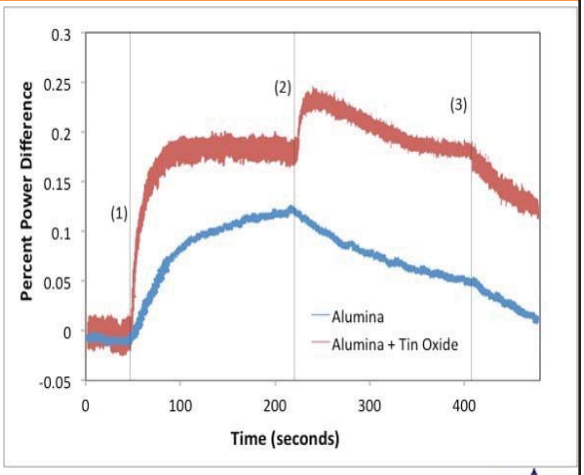
Sample	Total Amount Adsorbed	Total Amount Desorbed	% Desorbed
Poly(ethylene terepthalate)	2.40	0.11	5%
Tenax	7.88	0.50	6%
Poly(2,6-dimethyl-1,4-phenyline oxide)	6.60	0.46	7%
Poly(4-vinyl phenol)	10	0.80	8%
Polystyrene	6.22	3.61	58%
Teflon	2.32	2.48	107%

*Data courtesy of Dr. Jimmy Oxley *et al,* Dept of Chemistry, University of Rhode Island

Pre-concentration of Residue Vapors

Duty cycle used for pre-concentration: (1) introduction of DNT target gas. (2) thermal desorption of pre-concentrator (3) reference gas is re-introduced to the system

The pre-concentrator yields a 47% increase in sensor response with only minimal surface area for contact. With further surface modifications to increase surface area, a more concentrated burst of analyte is anticipated

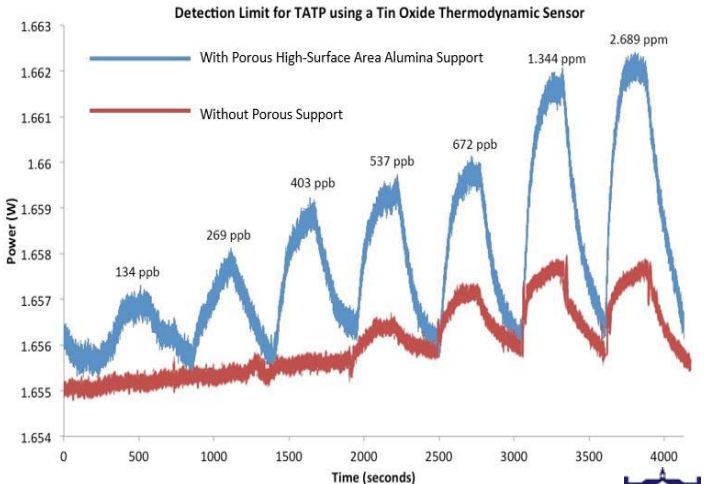


August 5, 2015

University of Rhode Island

Effect of Catalyst Surface Area on Response

Porous catalyst and/or catalyst support yields a much larger signal than a sensor without porous catalyst and/or catalyst support

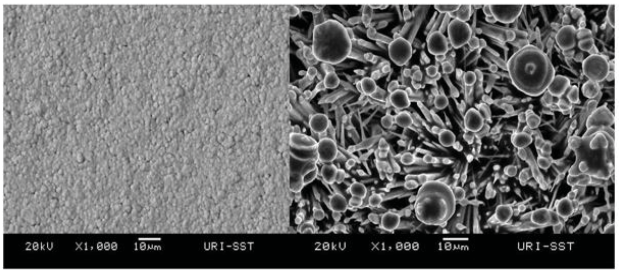


August 5, 2015

University of Rhode Island

Oxide Nanowires as Catalyst Support for Detection of Residue Vapor

High surface area catalyst and catalyst support achieved with ZnO nanowires

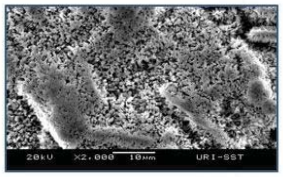


August 5, 2015

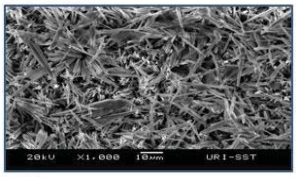
Oxide Nanowires as Catalyst Support for Detection of Residue Vapor

High surface area catalyst and catalyst support achieved with ZnO nanowires

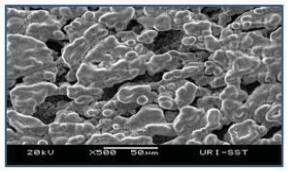
ZnO nanowires grown using a hydrothermal process



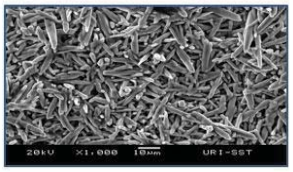
2 HOURS



10 HOURS



6 HOURS



8 HOURS

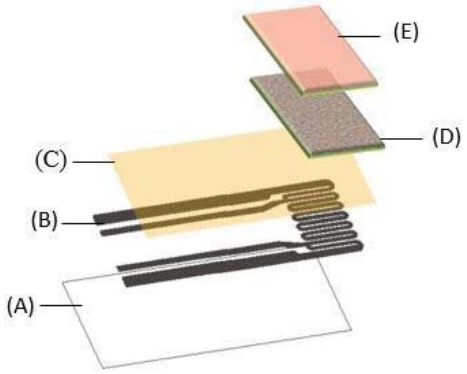
August 5, 2015

Oxide Nanowires as Catalyst Support for Detection of Residue Vapor

High surface area catalyst and catalyst support achieved with ZnO nanowires

ZnO nanowires grown using a hydrothermal process

Sputtered oxide catalyst were deposited over ZnO nanowires

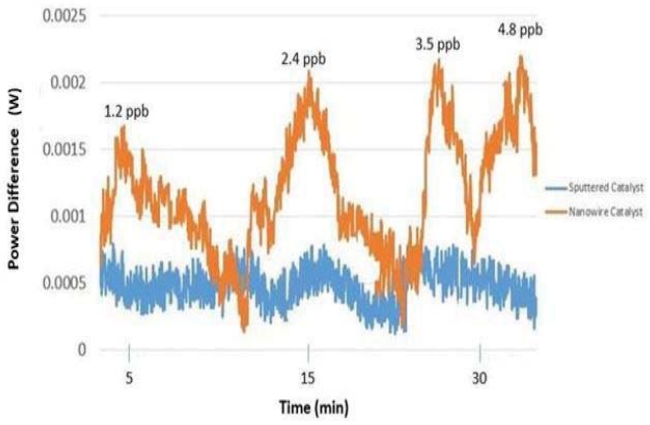


August 5, 2015

Effect of Catalyst Surface Area on Sensor Response

Nearly a 300% increase in sensor response to DNT using ZnO nanowires

Single PPB range can now be detected for DNT

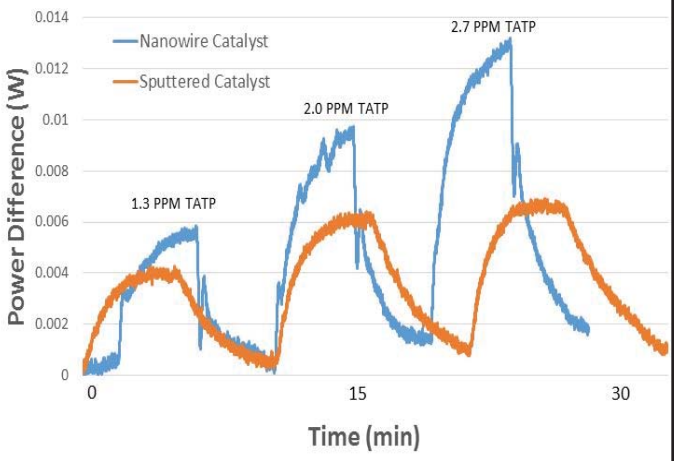


August 5, 2015

Effect of Catalyst Surface Area on Sensor Response

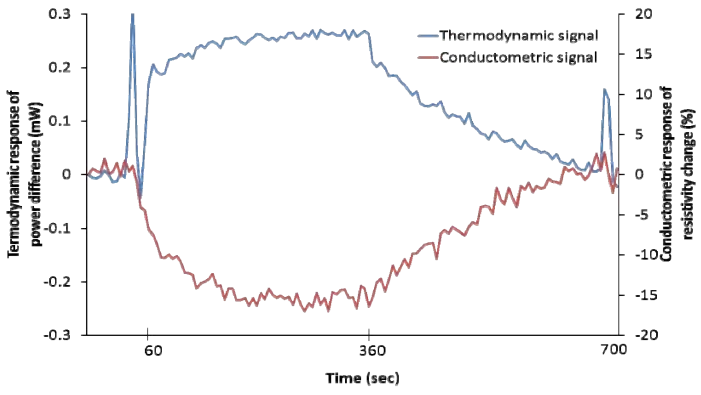
Comparison of sensor response to TATP using ZnO catalyst

At the highest level, nanowires increased the response by nearly 100%



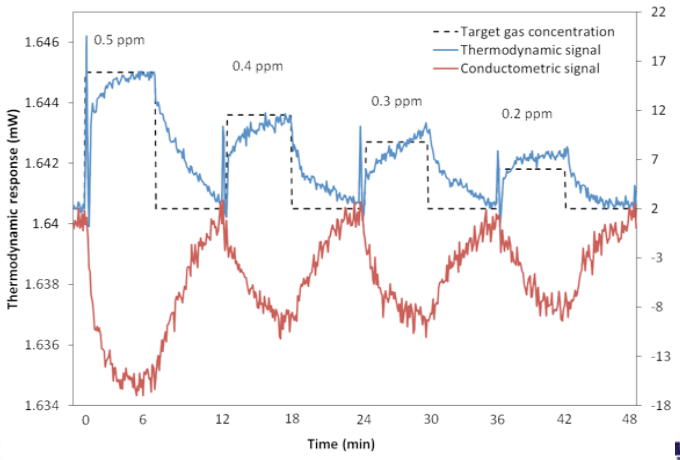
August 5, 2015

Thermodynamic and conductometric sensor response to 2, 6-DNT at 410 ℃ (SnO catalyst)



August 5, 2015

Thermodynamic and conductometric sensor response to 2, 6-DNT at 410 ℃ (SnO catalyst)

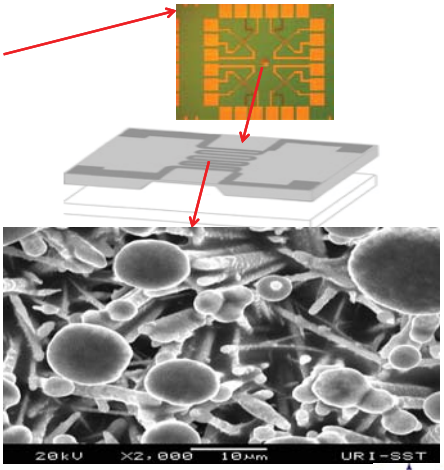


August 5, 2015

A small footprint, handheld sensor for residue vapor……based on a MEMS platform

MEMS quadrant sensor (diaphragm 0.5mmx0.5 mm) was fabricated that has all of the attributes of our orthogonal solid state sensor. We envision multiple catalysts on a single MEMS device for the continuous monitoring and identification of a wide range of unknown threats.

ZnO nanowires were prepared on the microheater surface to enhance the catalytic activity for the MEMS based vapor detection system.



August 5, 2015

Summary

Dynamic (two sensor) approach was used to measure the heat effect due to analyte-catalyst interactions……can detect TATP, AN and 2-6 DNT at the "single" ppb level

Using orthogonal sensor modalities, the metal oxide catalyst is simultaneously interrogated using two different sensing protocols; thermodynamic and conductometric protocols are combined to mitigate false positives and false negatives

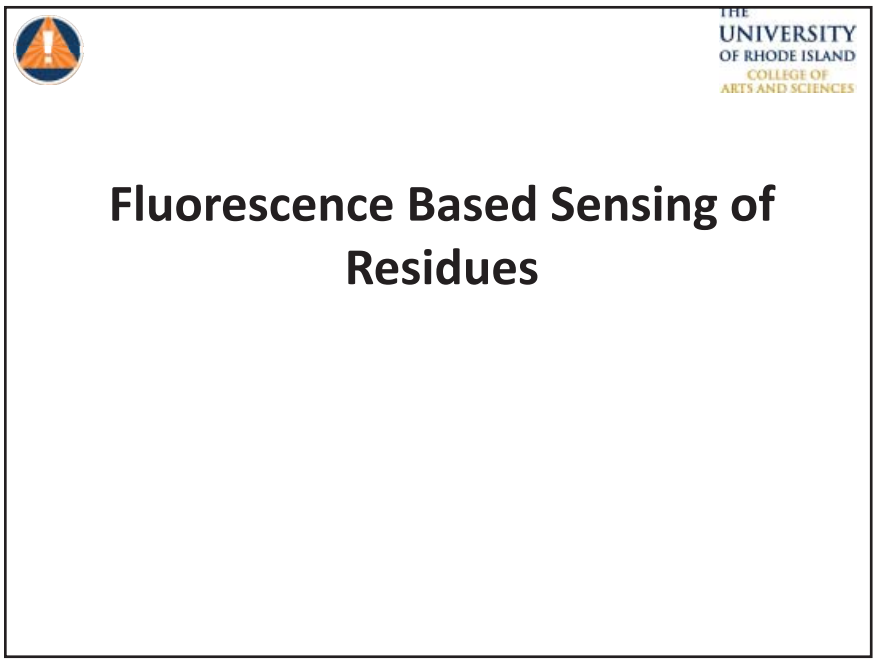
Pre-concentration techniques produce a highly concentrated burst of analyte that is efficiently delivered to the sensor in an optimized duty cycle that lowers the detection limit by an order of magnitude

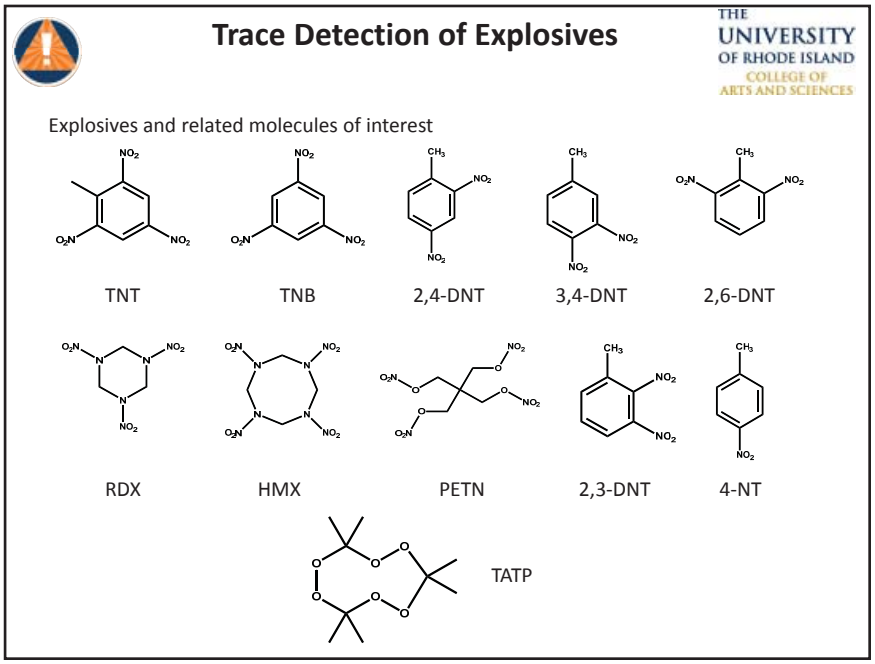
Metal oxide nanowire catalysts and/or catalyst support lowered the detection limit for residue vapors to the "single" ppb level

Acknowledgements

These materials are based upon work supported by the U.S. Department of Homeland Security, Science and Technology Directorate, Office of University Programs, under Grant Award 2013-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

16.11 Bill Euler: Flourescence-Based Sensing of Residues





Trace Detection of Explosives Conjugated Polymers

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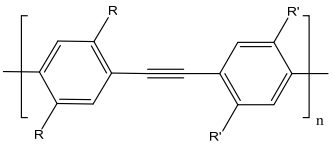
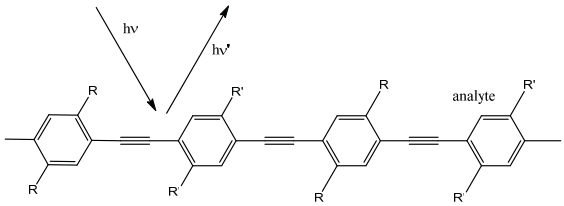
Swager, ca. 1995

Introduced the use of polyphenylenvinylenes as sensors



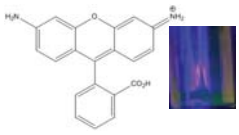
The conjugation amplifies the signal response because the analyte can cause quenching even if it is physically located a long distance from the excitation



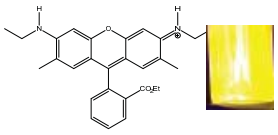
Q. Zhou, T. M. Swager, *J. Am. Chem. Soc.*, **1995**, *115*, 7017 – 7018.

Trace Detection of Explosives Xanthene Dyes

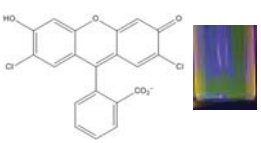
THE UNIVERSITY OF RHODE ISLAND COLLEGE OF ARTS AND SCIENCES



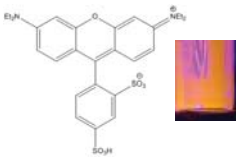
Rhodamine 560 (Rh560)



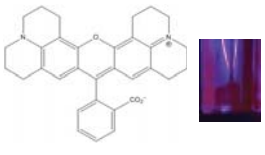
Rhodamine 6G (Rh6G)



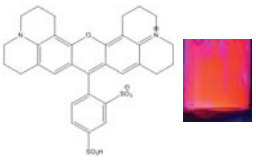
Fluorescein 548 (Fl548)



Sulforhodamine B (SRhB)



Rhodamine 640 (Rh640)



Sulforhodamine 640 (SRh640)

Trace Detection of Explosives Reaction of Xanthene Dyes in Solution

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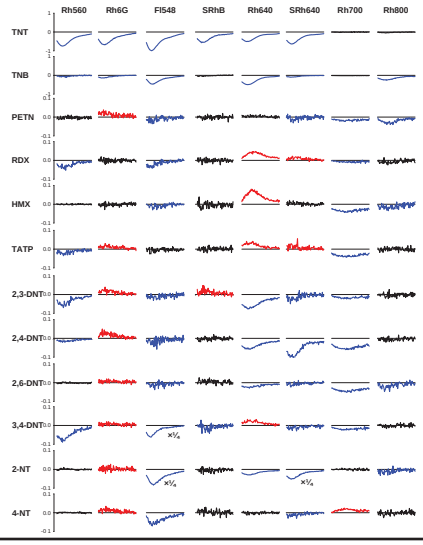

Difference spectra of each dye:

Dye + analyte → product

Blue: the analyte decreased the intensity (quenched) the spectrum

Red: the analyte increased the intensity (enhanced) the spectrum

Black: the analyte had no effect on the intensity of the spectrum

C. L. Latendresse, S. C. Fernandes, S. You, H. Q. Zhang, W. B. Euler, *Anal. Methods*, **2013**, *5*, 5457 – 5463.

Trace Detection of Explosives Reaction of Xanthene Dyes in Solution

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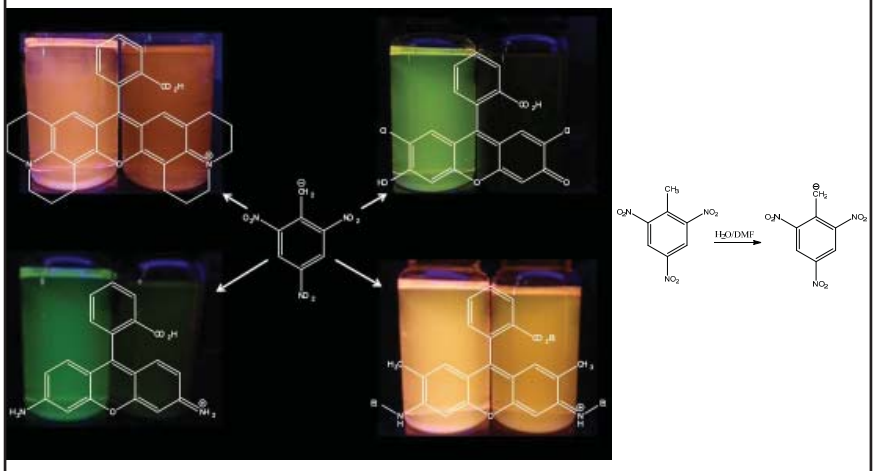

C. L. Latendresse, S. C. Fernandes, S. You, H. Q. Zhang, W. B. Euler, *Anal. Methods*, **2013**, *5*, 5457 – 5463.

Amplification of Fluorescence Emission

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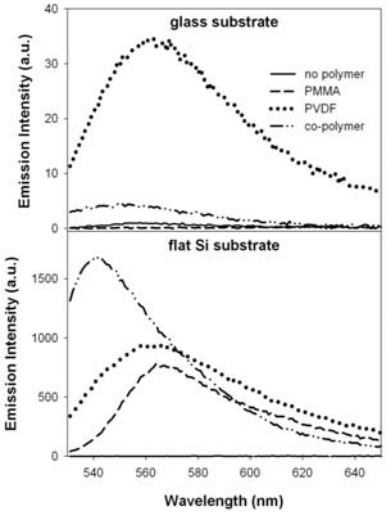

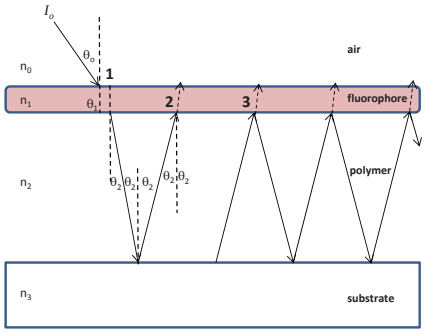

At least some portion of the fluorescent enhancement arises from internal reflections in the polymer layer.

M. A. Matoian, R. Sweetman, E. C. Hall, S. Albanese, W. B. Euler, *J. Fluoresc.*, **2013**, *23*, 877 – 880.

Trace Detection of Explosives Gas Phase Detection

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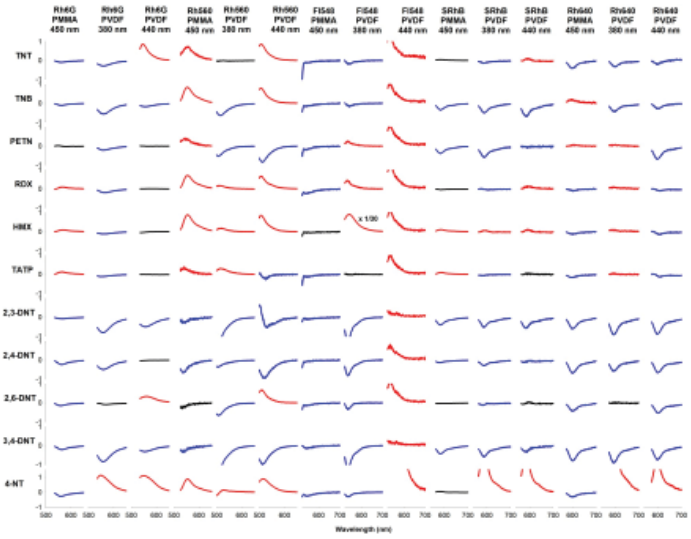

H. Q. Zhang, W. B. Euler, submitted to *Anal. Chem.*, **2015**.

Rh6G on a Glass Substrate

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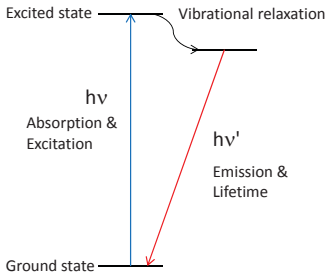
Investigate the fundamental photophysics of one fluorophore – Rh6G – thin film in detail

- Measure the absorption spectrum as a function of thickness
- Measure the excitation spectrum as a function of thickness
- Measure the emission spectrum as a function of thickness
- Measure the excited state lifetime as a function of thickness



Rh6G on a Glass Substrate
Molecular Dimensions

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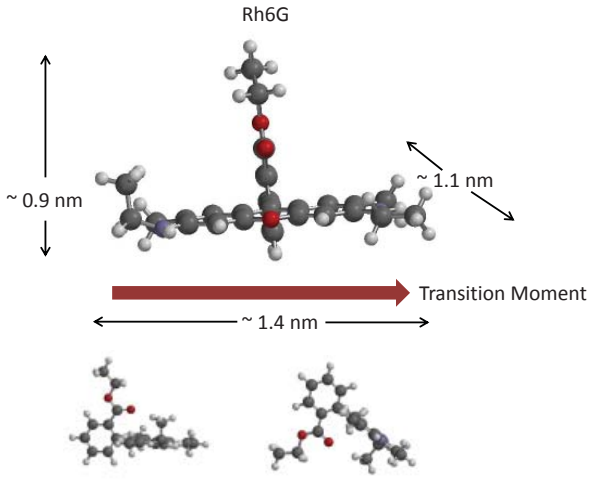

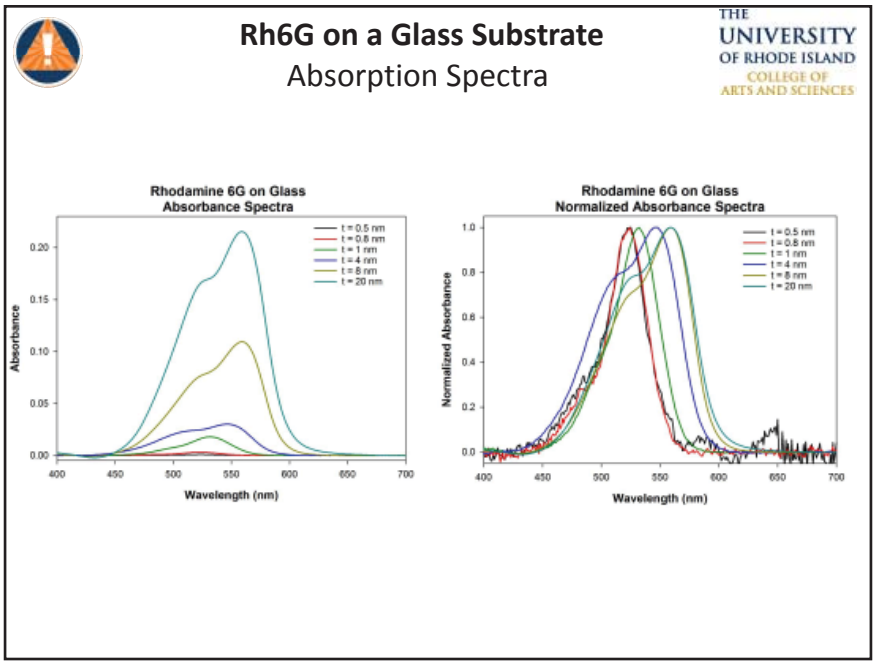
Rh6G on a Glass Substrate
Absorption Spectra
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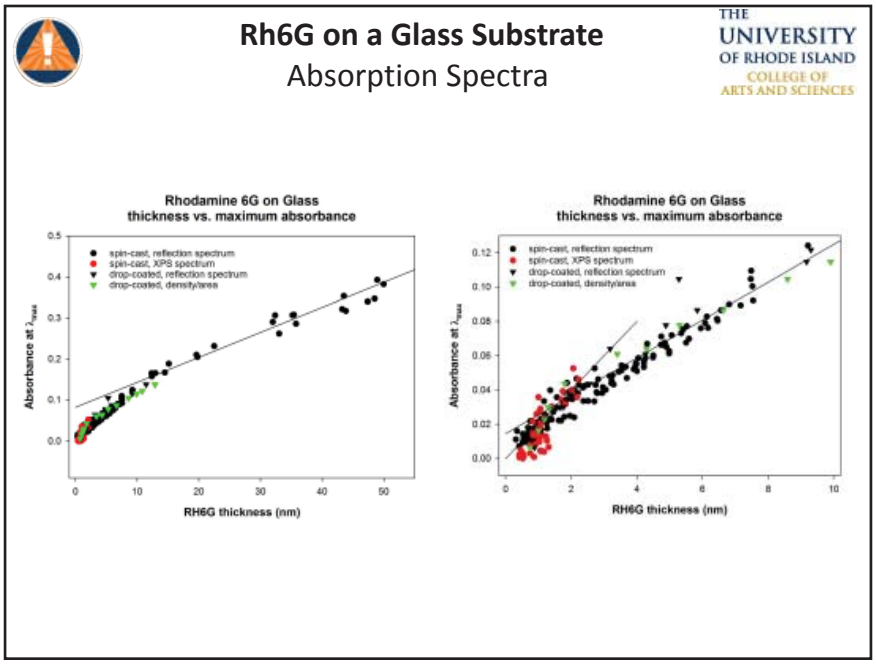
Rhodamine 6G on Glass
Absorbance Spectra
Absorbance
Wavelength (nm)
t = 0.5 nm
t = 0.8 nm
t = 1 nm
t = 4 nm
t = 8 nm
t = 20 nm
Rhodamine 6G on Glass
Normalized Absorbance Spectra
Normalized Absorbance
Wavelength (nm)


Rh6G on a Glass Substrate
Absorption Spectra
THE UNIVERSITY OF RHODE ISLAND
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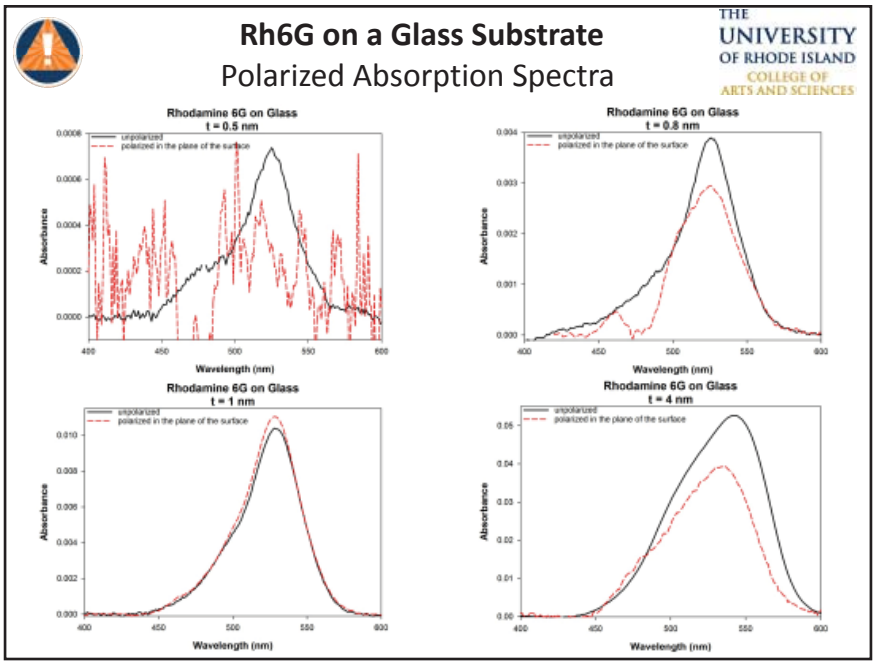
Rhodamine 6G on Glass
thickness vs. maximum absorbance
spin-cast, reflection spectrum
spin-cast, XPS spectrum
drop-coated, reflection spectrum
drop-coated, density/area
Absorbance at λmax
RH6G thickness (nm)
Rhodamine 6G on Glass
thickness vs. maximum absorbance
Absorbance at λmax
RH6G thickness (nm)


Rh6G on a Glass Substrate
Polarized Absorption Spectra
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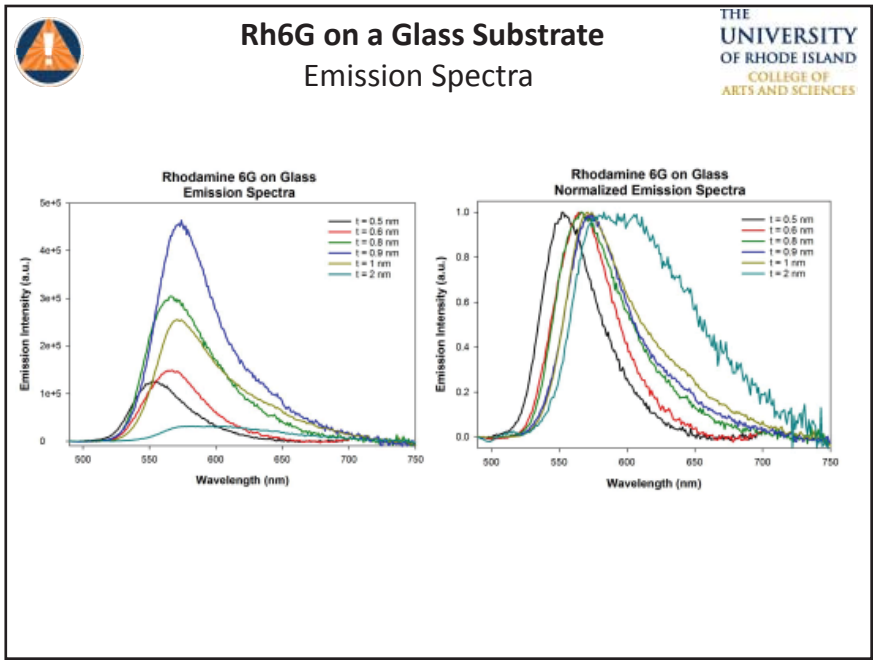
Rhodamine 6G on Glass
t = 0.5 nm
Rhodamine 6G on Glass
t = 0.8 nm
Rhodamine 6G on Glass
t = 1 nm
Rhodamine 6G on Glass
t = 4 nm
unpolarized
polarized in the plane of the surface
Absorbance
Wavelength (nm)


Rh6G on a Glass Substrate
Emission Spectra
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Rhodamine 6G on Glass
Emission Spectra
Rhodamine 6G on Glass
Normalized Emission Spectra
t = 0.5 nm
t = 0.6 nm
t = 0.8 nm
t = 0.9 nm
t = 1 nm
t = 2 nm
Emission Intensity (a.u.)
Wavelength (nm)

Rh6G on a Glass Substrate

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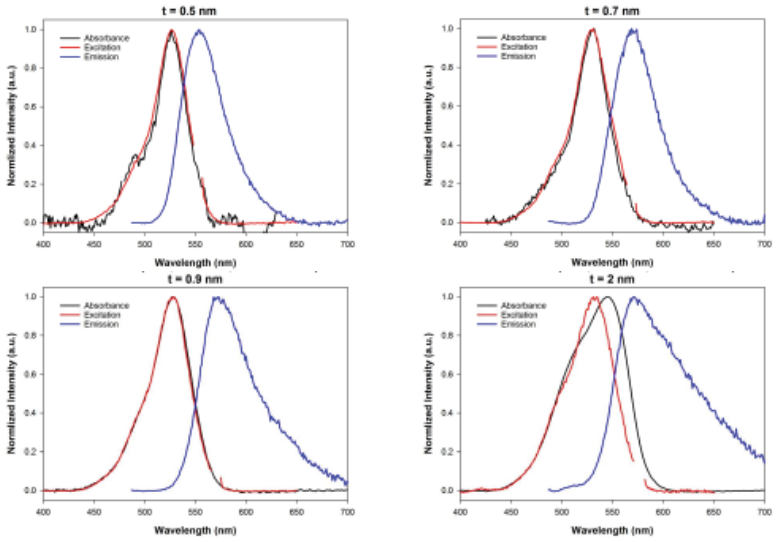
Normalized Absorption, Excitation, & Emission Spectra



Rh6G on a Glass Substrate

Spectral Deconvolution

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Peak	Absorbance (λ, Γ)	Thickness (nm)	Concentration (M)	Emission (λ, Γ)
1	(490, 18)	0.5 – 1.3	$6\times10^{-7} – 4\times10^{-5}$	(562, 18)
2	(510, 28)	1.2 – 60	$8\times10^{-6} – 1\times10^{-2}$	(562, 18)
3	(525, 18)	0.5 – 1.2	$6\times10^{-7} – 7\times10^{-6}$	(552, 18)
4	(533, 18)	1.2 – 60	$8\times10^{-6} – 1\times10^{-2}$	(580, 29)
5	(552, 18)	1.5 – 4.0	$4\times10^{-4} – 1.2\times10^{-3}$	(625, 38)
6	(564, 18)	4.0 – 60	$1.2\times10^{-3} – 1\times10^{-2}$	

Rh6G on a Glass Substrate
Structural Assignments

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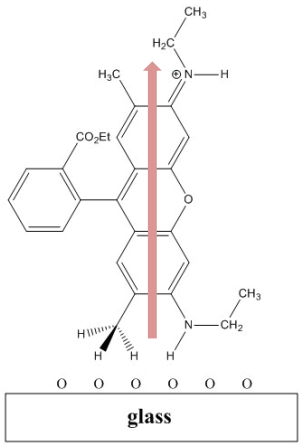

- Monomer
- Perpendicular to the surface at low coverage
- λ_{max} (absorption) = 525 nm
- λ_{max} (emission) = 552 nm

Rh6G on a Glass Substrate
Structural Assignments

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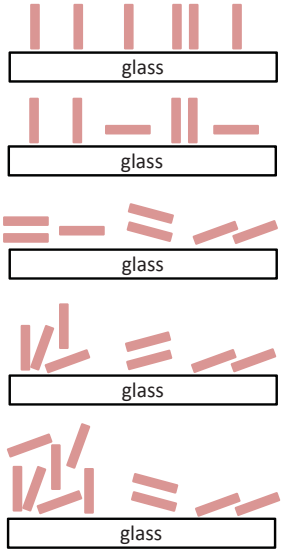

Very low surface coverage < 0.5 nm
perpendicular monomers λ_{max} = 525 nm
perpendicular H-dimers λ_{max} = 490 nm

Low surface coverage ~0.5 – 1.1 nm
perpendicular & parallel monomers λ_{max} = 525 nm
perpendicular H-dimers λ_{max} = 490 nm

Approximately monolayer coverage ~1.2 – 1.5 nm
parallel monomers λ_{max} = 525 nm
perpendicular H-dimers λ_{max} = 490 nm
tilted H-dimers λ_{max} = 510 nm
tilted J-dimers λ_{max} = 533 nm

2- 3 layer coverage ~1.5 – 4 nm
tilted H-dimers λ_{max} = 510 nm
tilted J-dimers λ_{max} = 533 nm
small aggregates λ_{max} = 552 nm

high coverage > 4 nm
tilted H-dimers λ_{max} = 510 nm
tilted J-dimers λ_{max} = 533 nm
large aggregates λ_{max} = 564 nm

Lessons for Sensor Design and Optimization

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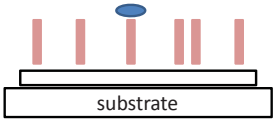
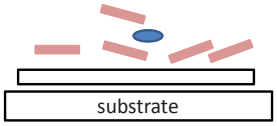
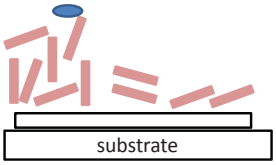


- Low coverage leads to a high emission signal
- Polymer layer provides signal amplification
- Analyte interacts with a high percentage of surface molecules, which leads to a large signal change



- Near monolayer coverage leads to an intermediate emission signal
- Polymer layer provides signal amplification
- Analyte interacts with a small percentage of surface molecules, which leads to a small signal change
- Analyte may break up dimers, which can lead to signal enhancement



- Thick coverage leads to a low emission signal
- Polymer layer provides signal amplification
- Analyte interacts with an insignificant percentage of surface molecules, which leads to no signal change

Conclusions

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- Xanthene dyes interact with explosive analytes to give measurable changes to their fluorescence spectrum
- The absence of a change in the absorption spectrum indicates that the dye/analyte interaction is with the excited state
- For Rhodamine 6G the thickness of a thin film has significant effects on the absorption and emission properties
- Thinner films of Rhodamine 6G have a higher emission intensity, which allows for more sensitive detection of analytes

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Awareness and Localization of Explosives-Related Threats

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