## A90 Development of PAH-SPME Phases for the Forensic Science Application of Selective Absorption of Nitroaromatic Explosives

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After attending this presentation, attendees will have a better understanding of solid phase microextraction (SPME) and the unique selectivity that polyaromatic hydrocarbons (PAH) have for nitroaromatic explosives. This presentation will also discuss the development of homemade SPME fibers, sampling and analysis techniques. Lastly, the presentation will project the future integration and impact this technique will have on the forensic science community.

This presentation will impact the forensic science community by demonstrating the there is an increasing need for a cost efficient, environmentally friendly technique that can detect a broad range of explosive compounds effectively to ensure the future safety of the American people. With the events of September 11 and the increase of national threats, the homeland security agency has developed a series of scientific devices to hinder and absolve these types of events in the future. The current security explosive detection methods, such as ion mobility spectrometry and canine detection units, are tuned to only a small band of compounds.

Solid-phase micro-extraction (SPME) has found widespread use in the extraction of volatile and semi-volatile compounds from environmental matrices. SPME is a rapid, re-usable, environmentally- benign and a cost-effective, field sampling technique when compared to liquid-liquid extraction and solid phase extraction. The basis for SPME is the use of a small- diameter, fused silica fiber coated with a polymer that has strong affinity of the target analytes. Commercially-available polymers include polydimethylsiloxane (PDMS), polyacrylate, and carbowax among others. Once the analytes are adsorbed onto the surface of the coating, removal requires chemical or thermal desorption. As such, SPME is typically coupled with either gas chromatography or high- pressure liquid chromatography for the separation, identification and quantitation of adsorbed analytes. The development of efficient and sensitive analytical methods to detect and quantify trace amounts of explosives and explosive residues is significant both for environmental protection and public security agencies.

**Phase I: Explosives Selectivity –** The initial work of this project focuses on developing new pyrene-, phenyl- and phenoxy- based stationary phases bonded to silica substrates. The commercial Supelco phase, Ascentis Butylphenyl, synthesized for high pressure liquid chromatography columns is particularly selective toward aromatic analytes that have electron withdrawing groups attached to the aromatic ring. This is believed to be caused by strong p-p interactions between the phenyl phase and the analytes. The enhanced selectivity of the phenyl phase may provide unique applicability for HPLC as well as SPME applications for components of explosive mixtures that contain nitro aromatics. Extending the stationary phase chemistry to include poly aromatics will potentially yield the same selectivity advantage, or better, but with the added benefit that poly aromatic compounds are fluorescent.

**Phase II: SPME Extraction –** The fiber coating process begins with the addition of a platinum catalyst to a linear polymer, PDMS. This will then start a reaction that will crosslink the PDMS with the PAH phase that has been added simultaneously. This process creates a three dimensional polymer with a high molecular weight. Also, the platinum catalyst induces a hydrosilation reaction to remove any double bonds within the polymer chain and increase the dimensions. The poly-aromatic phases are covalently bonded to the oxygen group on the surface of the fused silica fibers through a coating process. Once the fiber is evenly coated with the PDMS/PAH phase, the high molecular weight of the polymer will give the coating the ability to withstand the degradation of the organic solvents that the fiber may be subjected to during sampling or analysis. This characteristic will allow the fiber to have an indefinite lifetime and increase the recycling aspect of the fiber after complete chemical or thermal desorption.

**Phase III: Explosives Detection –** It is a well known verity that nitro aromatics quench the fluorescence of poly aromatic compounds. However, the mechanism for fluorescence quenching is not completely understood. The high degree of selectivity of the synthesized poly aromatic silanes towards nitro aromatic compounds translates into a corresponding unique fluorescence (or fluorescence quenching) signature. This study will collect the emission spectra of the synthesized poly aromatic silanes in the absence, and in the presence, of nitro aromatic compounds.

The PAH silane-based SPME fibers serve a dual purpose: (1) fluorescence quenching of the PAH silane by nitro-aromatics can be monitored by attaching the fiber to a field-portable fluorimeter allowing real-time quantitative detection of nitro aromatics in ambient air; and, (2) the analytes can be thermally or chemically desorbed from the fiber upon return to the laboratory and undergo “normal” chromatographic analysis.

The principal goal of the research is to develop a suite of silane coatings with a high-degree of selectivity towards specific nitro aromatics and/or develop a mixed-mode phase (PDMS/PAH) with broad selectivity and use multiple component analysis to recover individual analyte species. The forensic application of these PAH fibers could lead to future validation studies confirming accelerant canine detection alerts and aid in the screening process by airport security agencies.

**Nitroaromatic Explosive Compounds, Solid Phase Microextraction, Public Security**

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