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IS - 5177

Detection of Substituted PAH Residues by SPME in Arson Debris Analysis

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Final Report: October 1, 2004 – September 30, 2005

December 14, 2005

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Ames, Iowa 50011

Prepared for
The U.S. Department of Energy
Under Contract W-7405-Eng-82

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1. **Detection of Substituted PAH Residues by SPME in Arson Debris Analysis**
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4. **Abstract**

This project addresses the need for method development in the recovery of ignitable liquid residues from a variety of matrices outlined in *Forensic Sciences: Review of Status and Needs* (1) by assessing novel screening applications of SPME in the analysis of polyaromatic compounds (i.e. naphthalene) from gasoline residues. Project objectives include:

- 1) development of optimal SPME protocols for assessing the aromatic analogs of interest,
- 2) comparison of SPME methodologies with activated carbon strip (ACS), and
- 3) a partnership with Wisconsin State Crime Laboratory – Madison to assess the effectiveness of SPME in detecting gasoline residue in complex arson debris matrices.

5. **Project Description**

This proposal offers an in-depth assessment of SPME's usefulness in bridging the gap between the forensic community's capabilities in detecting gasoline accelerants in arson residues by current methods and the need for a reliable, inexpensive, readily available technology with improved sensitivity for aromatic compounds in an environment containing pyrolytically degraded polymers.

SPME is a widely accepted technique in the analytical community and is accepted by ASTM as a screening analysis for accelerants in arson debris. The focus of this research proposal is the assessment of SPME capability in three specific hypotheses. The first hypothesis is that SPME can accurately and reliably detect / C1-substituted naphthalene / C2-substituted naphthalene ratios in gasoline, evaporated gasoline, and a wide variety of complex arson matrices that includes polymeric material with high concentrations of aromatic monomers such as polystyrene and reproducibly distinguish these samples based on the ratio of these polyaromatics. The second hypothesis is that SPME can provide reliable detection of heavier semi-volatiles in gasoline such as anthracene as well as more highly substituted aromatics such as C5 alkylbenzenes. The third hypothesis is that a hybrid solvent extraction-fiber immersion SPME technique provides an optimal recover of heavier polyaromatics

from complex matrices. These experiments represent three potential windfalls in advancing the trace evidence community's ability to detect aromatic compounds associated with gasoline in very difficult matrices.

6. Project Objectives

The primary practical objective of this project is to provide an enhanced detection of gasoline residues in arson debris that may contain contaminants due to the pyrolytic decomposition of polymeric materials. The goal of this research project is to bridge the gap between the current status of techniques used in the analysis of arson residues and the need of the forensic community for method development for recovery of ignitable liquid residues from a variety of matrices as described in *Forensic Sciences: Review of Status and Needs* (1). This project bridges this gap by thoroughly assessing the applicability of a highly sensitive, pre-concentration technique known as solid-phase microextraction (SPME) for determining the presence of gasoline residues in a complex matrix of arson debris that includes high levels of pyrolytically degraded polymeric materials.

7. Procedures

The experiment began with the purchase of SPME fibers, holders, and related equipment Supelco. The 7 μm and 100 μm polydimethylsiloxane (PDMS) fibers were evaluated for best extraction parameters. The 100 μm PDMS fiber methodology was developed further because it was the more promising substrate for SPME of the polyaromatic hydrocarbons of interest.

A variety of 87-octane gasolines (non-winterized formulations) were evaporated to varying levels of residue to simulate weathered gasolines. SPME pre-concentration parameters were optimized with respect to fiber adsorption and desorption based on the analysis of headspace vapors using a Shimadzu GC 17A – QP5050S GC-MS.

Charcoal strips (100 mm^2) were obtained from Albrayco Technologies Inc., and activated charcoal strip (ACS) protocols from the Wisconsin State Crime Laboratory – Madison were followed in the use of ACS. Comparisons of ACS and SPME methods were performed by simultaneously hanging an ACS and exposing a 100 μm SPME fiber in the headspace of a wide variety of samples and standards for varying lengths of time. The variety of matrices used in the comparison of ACS and SPME included evaporated standards simulating weathered gasoline, building materials such as pine wood, asphalt shingles, drywall, carpeting, and carpet padding.

In addition, SPME fiber coatings were tested in a variety of solvent immersions. Solvents selected for testing were GC-MS grade or Optima grade. A SPME fiber was immersed in acetone, benzene, ethyl alcohol (100%), or carbon disulfide and subjected to the heating cycle of the desorption and GC inlet liner temp (225°C). This process was repeated until the fiber background began to show signs of

decomposition in order to observe the maximum potential number of trials with a single fiber in an organic solvent immersion. Following this experiment, 20. mL samples of CS₂ were spiked with 50 µL of 87-octane gasoline and extracted with 100-µm PDMS fibers.

8. Results/ Discussion

In a comparison of SPME and ACS on two manufacturer's GC-MS units, there are desirable utilities in each technique. The SPME is much more sensitive than the ACS method as previously reported in the literature. This sensitivity is compromised however by the relatively rapid saturation of the SPME fiber with aromatic and polyaromatic hydrocarbons. After initial experiments demonstrated that the optimal desorption time was 1.0 minutes in a GC inlet at 250°C, SPME fibers were optimally "loaded" with 1.0 hour headspace exposure. Longer periods of time such as "overnight" resulted in a loss of resolution caused by fiber saturation. Subsequent experiments demonstrated that the 100 µm PDMS fiber was better suited than the 7 µm PDMS ($p < 0.05$) for detection of polyaromatic compounds which ran contrary to one previous report in the literature.

There was an observed tendency for heavier aromatic compounds displacing lighter aromatic compounds with increased exposure times; however, at 1.0 hour fiber exposure there was no loss of the classic "crown" of alkylbenzenes with SPME. It should also be noted that the crown remains and there is a detection of C2, C3, and C4-naphthalenes (Figure 1) by SPME that is not present using ACS and overnight exposures (Figure 2). A similar phenomenon was observed with anthracene and C1-anthracene.

With respect to polyaromatic (PAH) peak ratios, the increased sensitivity of SPME did not carry over into better defined peak ratios (i.e. C1-naphthalene to C2-naphthalene) in a consistent manner. Sample to sample variability was high when comparing the evaporated series of gasoline standards, and the introduction of a burn matrix further complicated straightforward attempts at quantification. As part of these experiments a wide variety of polymer standards were burned under various conditions (i.e. varied air intake). While these burns produced pyrolysis products that were chromatographic interferences, the mass spectral identification of these compounds did not indicate the formation of naphthalene, anthracene, or simple alkyl derivatives of either PAH.

Perhaps the most significant, encompassing result of this project is the potential for SPME to augment the trace evidence toolbox for arson debris analysis. The results of the SPME analysis of gasoline residue in various building material matrices demonstrated that in a vast majority of trials SPME did produce the "key" structural elements (i.e. "the crown" of alkylbenzenes in gasoline) **and** reliably detected more highly substituted forms of PAH in all spiked samples and many control burns.

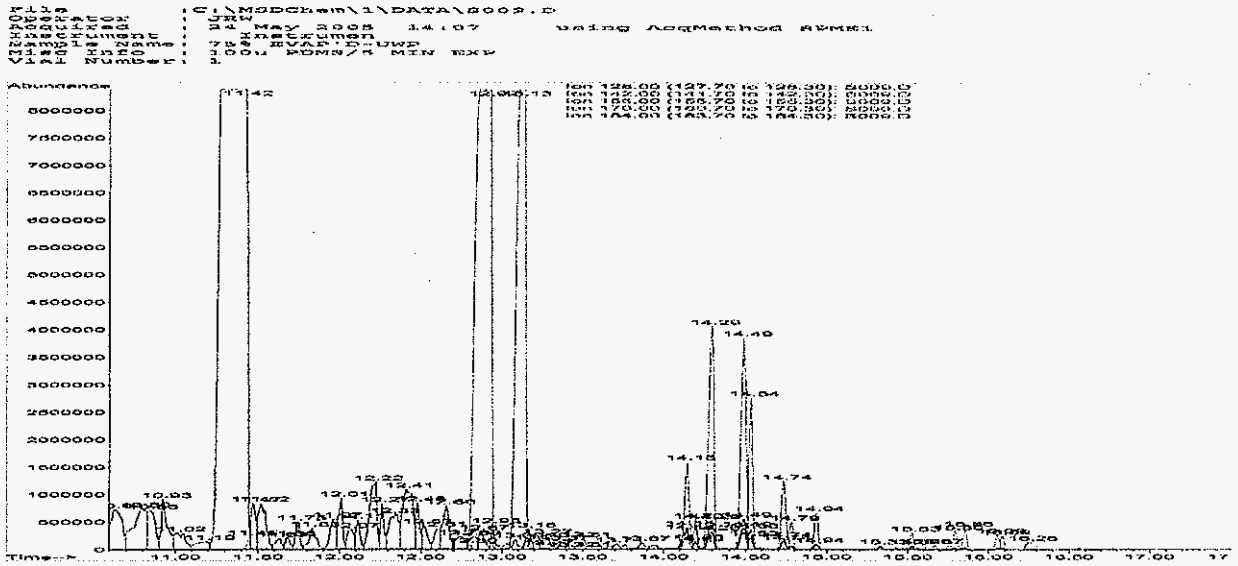


Figure 1. Naphthalene Detection and Resolution Via SPME (naphthalene at 11.42 minutes, C1-nap. At 12.00 min., C2-nap at 14.29 min, and C3-nap at 15.53 min)

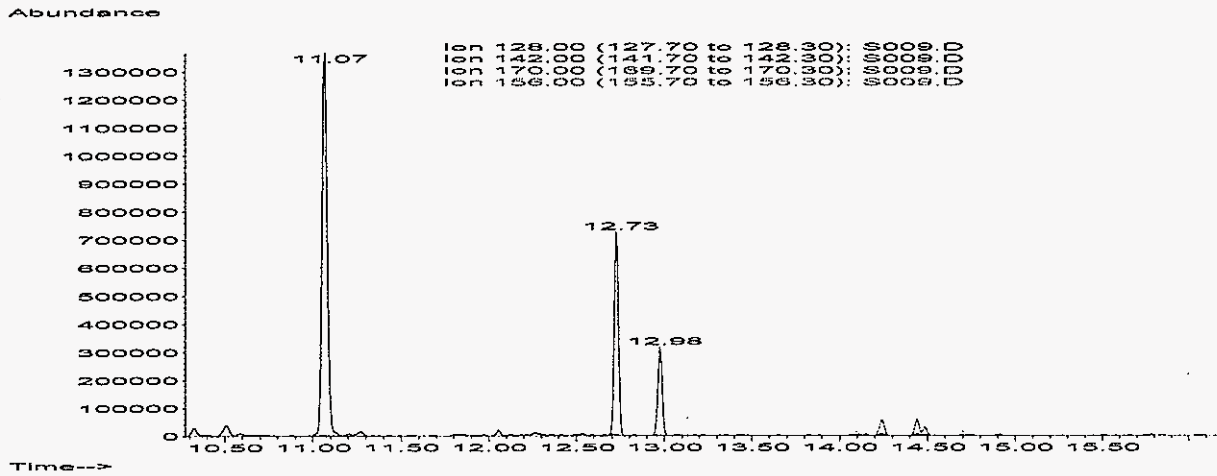


Figure 2. Naphthalene and C1-Naphthalene Detection and Resolution Via ACS

One of the significant arguments against the use of SPME in crime laboratory validations is the cost of the fiber vs. the need to archive a sample. ACS method provides a rather inexpensive, easy-to-store archival sample (part of the strip or the strip itself). If SPME were to replace ACS, the cost of using a SPME fiber for one analysis would be impossible to meet; however, if SPME methodologies were validated and used as a screening/analytical tool specifically for PAH, SPME could provide a relatively affordable method to obtain potentially vital information in a portion of the difficult cases. Because samples falling under these criteria (confounded or inconclusive ACS analysis) may only be between 5-10%, the cost of archiving a fiber becomes less of an impact on the budget of a laboratory.

Figures 3 and 4 illustrate the usefulness of SPME in a complex matrix. These mass spectra clearly show C2-naphthalene in the gasoline (75% evaporate standard) containing asphalt shingle matrix whereas the compound is not present in the asphalt shingle matrix alone (n = 10). The ACS method (n = 8) could not provide sufficient analyte to detect the presence of gasoline in this environment.

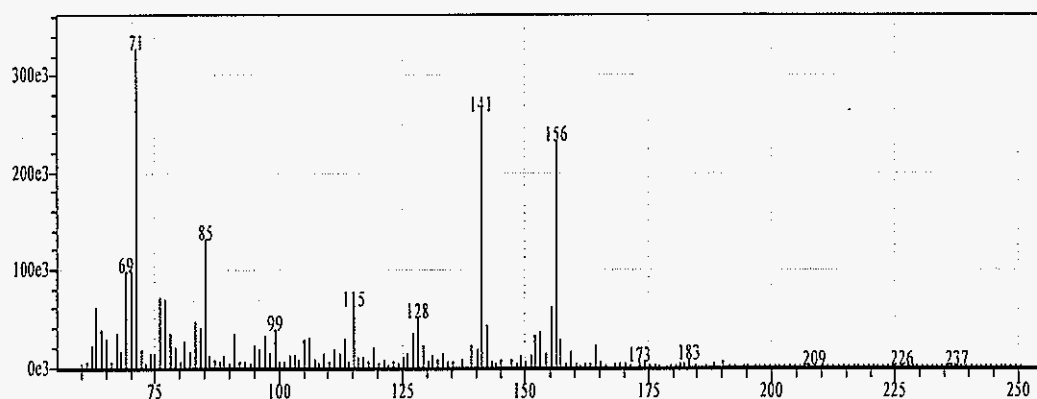


Figure 3. Mass spectrum of 16.65-minute retention compound from the analysis of gasoline and asphalt shingle pyrolyzate

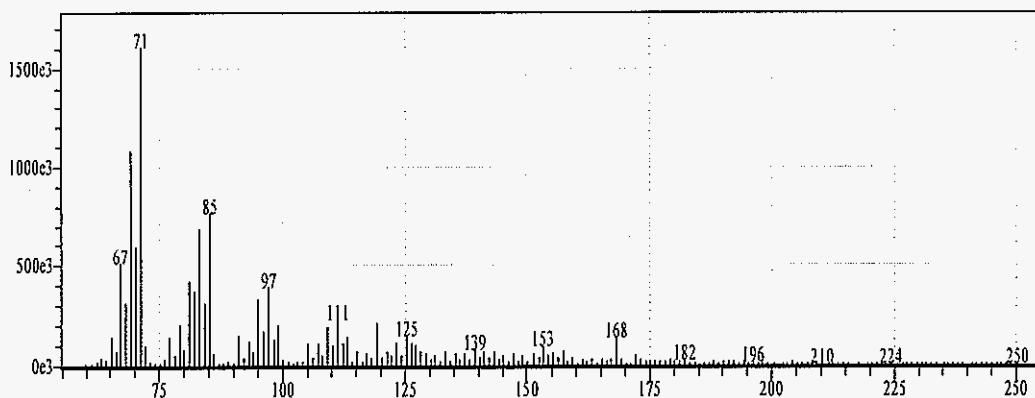


Figure 4. Mass spectrum of 16.65-minute retention compound from the analysis of asphalt shingle pyrolyzate

Thus the primary conclusion of this work is that SPME can be used to effectively augment ACS methods employed in the vast majority of crime laboratories today. Further work needs to be done to ascertain the percentage of cases where this method would yield useful data, to search for a fiber coating that provides a more uniform retention of all molecular mass PAH, and to automate the technology.

9. Dissemination Discussion

Dissemination to date has included an oral presentation and undergraduate poster presentation at the Midwest Association of Forensic Scientists annual meeting October 5-7, 2005 in St. Louis, MO. Further dissemination plans include accepted abstracts at the Pittsburgh Conference March 13-17, 2006 in Orlando, FL. In addition, a manuscript is in progress; this article will be submitted to the Journal of Forensic Sciences for peer-review.