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Solid Phase Microextraction Sampling of Fire Debris Residues in the Presence of Radionuclide Surrogate Metals*

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Abstract

The Federal Bureau of Investigation (FBI) Laboratory currently does not have on site facilities for handling radioactive evidentiary materials and there are no established FBI methods or procedures for decontaminating highly radioactive fire debris (FD) evidence while maintaining evidentiary value. One experimental method for the isolation of FD residue from radionuclide metals involves using solid phase microextraction (SPME) fibers to remove the residues of interest. Due to their high affinity for organics, SPME fibers should have little affinity for most (radioactive) metals. The focus of this research was to develop an examination protocol that was applicable to safe work in facilities where high radiation doses are shielded from the workers (as in radioactive shielded cells or "hot cells"). We also examined the affinity of stable radionuclide surrogate metals (Co, Ir, Re, Ni, Ba, Cs, Nb, Zr and Nd) for sorption by the SPME fibers. This was done under exposure conditions that favor the uptake of FD residues under conditions that will provide little contact between the SPME and the FD material (such as charred carpet or wood that contains commonly-used accelerants). Our results from mass spectrometric analyses indicate that SPME fibers show promise for use in the room temperature head space uptake of organic FD residue (namely, diesel fuel oil, kerosene, gasoline and paint thinner) with subsequent analysis by gas chromatography (GC) with mass spectrometric (MS) detection. No inorganic forms of ignitable fluids were included in this study.

Disclaimer: This was a feasibility study for demonstration of method and not a final product. The methods used for the analyses of the FD are not those used by the FBI, and it should not be implied that the data shown for GC/MS are acceptable for court admission as presented.

Introduction

Radioactive evidentiary materials present considerable challenges to examiners that need to conduct traditional forensic analyses on them. These types of materials raise worker health and safety concerns due to the risks associated with potential radiation dose, radionuclide uptake and radioactive contamination. Activities of this nature require numerous controls to protect those that work with these hazardous materials. The Federal Bureau of Investigation (FBI) Laboratory does not have an on site capability to permit the examination of radioactively-contaminated evidence. The successful decontamination of evidentiary materials will allow traditional forensic examinations to occur within FBI Laboratories. There are few proven procedures to decontaminate (or “decon”) types of traditional evidence forms that contain radioactive materials. When decontamination is not entirely possible, the partial decontamination of evidence items without compromise to their evidentiary value will help permit examiner handling under lower radiation exposure conditions. These types of traditional examinations of contaminated radioactive evidence could occur at an FBI Partner Laboratory, such as at the Savannah River National Laboratory (SRNL, Aiken, SC) or at Lawrence Livermore National Laboratory (LLNL, Livermore, CA).

Methods for the qualitative and quantitative analysis of fire debris (FD) residue materials in various matrices typically require a concentration step to isolate the residue from its host matrix. These methods are usually dependent on host matrix type (solid, liquid, gas). Some of the methods used to recover and concentrate organic residues are solvent extraction, membrane separation, solid phase extraction (SPE), supercritical fluid extraction (SFE), and solid phase microextraction (SPME).[1,2,3,4,5,6,7] Several types of commercially available SPME fibers have an affinity for organic FD residue under various exposure conditions and they are attractive to use for radionuclide decontamination. The SPME fibers help eliminate some of the disadvantages associated with other organic recovery methods such as column plugging and their usage does not require large volumes of (potentially mixed) organic solvent wastes. Organic solvents may be difficult to work with in areas with high ventilation or behind several feet of glass, such as in highly shielded radioactive cells, which permit work with highly radioactive materials. Due to their flammability, these organic solvents also pose potential nuclear facility safety basis concerns. Finally, the SPME fibers offer high sensitivity during gas chromatographic analyses and the fibers can be quickly analyzed radiometrically to determine their level of radioactivity after exposure to FD residue. For non-radioactive evidentiary examinations of FD evidence, the FBI Laboratory currently uses a protocol for the headspace extraction of organic FD residue using charcoal strips. The residue that is accumulated on the charcoal strips in the headspace after heating the closed paint can is then leached using carbon disulfide (which is extremely flammable).

Several non-radioactive surrogate metals of radioactive isotopes that could be present in radioactively-contaminated evidence were identified. Surrogates were chosen to limit worker radiation dose during testing. For example, a stable isotope of ^{133}Cs was substituted for radioactive ^{137}Cs. Due to the highly selective affinity of SPME fibers for organic and other non-ionic (hydrophobic) species, they should have little affinity for radionuclides, which are inorganic and charged when dissolved in solution and these metals are not likely to be volatile. Our studies examined radionuclide uptake during the SPME headspace sampling of burned materials that contained ignitable fluid residues. Our studies were also performed under conditions that were conducive to work in a radioactively-shielded cell environment and this was mainly done by providing a stable SPME fiber holder and by conducting the SPME exposures at room temperature to avoid the heating of the items. The heating of “unknown” items (in this case fire debris evidence) in a shielded cell environment poses additional safety concerns that can potentially be mitigated by performing the process without heating. We chose to perform our studies with as little change to the FBI protocol as possible, with the exception of using SPME fibers, lower exposure temperatures, the introduction of potential radionuclide metals (using surrogates) and a setup that was appropriate for remote operations in a shielded radioactive hot cell. After exposure, the SPME fibers were directly analyzed for ignitable fluid uptake and characterization after exposure. The primary goal of this study was to examine the use of SPME fibers for headspace FD uptake under conditions that are most conducive to radioactive shielded cells operations in the presence of radionuclide metal surrogates.

Experimental

Manual injection [for gas chromatography (GC) analyses] SPME fibers were procured from Supelco, Inc. (Bellefonte, PA). The conditioned fibers were assembled in the manual sample holders and exposed to the test solutions for 30 minutes. The SPME tests were performed in triplicate. All SPME fibers were rinsed with ~1 mL of de-ionized water after use and the rinse solution was added to the exposure solution. Each set of SPME fiber tests had a control. The control solutions (which were not exposed to the SPME fibers) were tested in triplicate.

For the FD extraction, a specimen container (usually, a new paint can or glass jar with tight fitting lid and septum for SPME) was selected based on the size of the debris specimen and the need to keep the head space as small as possible. The residues of interest were restricted to diesel fuel oil, kerosene, gasoline and paint thinner. The FD specimens typically included roughly 500 cm^3 of charred wooden plywood blocks that were later spiked with a trace amount (10 µl) of diesel fuel #2 or paint thinner and burned 16 cm^2 square carpet pieces that were later spiked with a trace amount (1 µl) of gasoline or kerosene. These FD specimens were spiked with 5 mL of the non-radioactive metal solution and placed into pre-configured containers and the lid to the container secured with a rubber mallet. A pre-conditioned 100 µm PDMS SPME fiber with holder was inserted in the septum on the specimen container. The SPME fiber was exposed in the headspace at room temperature for 20 minutes. The SPME exposure times could differ if the specimen is heated. For example, we have found that specimens that were heated at 45 ºC to 60 ºC for 20 minutes only required a 5-minute SPME exposure. Heating provides typically higher ion abundance and allows for a greater differentiation between higher molecular weight hydrocarbon molecules. However, heating is an additional step that would increase the level of hazard associated with the activity in a shielded cell environment.

The SPME exposures were performed with burned materials that had been spiked with stable isotope surrogates for radionuclides in addition to spiking with FD residue. The radionuclide surrogates that were targeted for testing included the following: fission products [technetium (^{99}Tc), cesium ($^{134,\,137}$Cs)]; activation products [nickel ($^{59,\,63}$Ni), cobalt (^{60}Co), iridium (^{192}Ir), zirconium (^{93}Zr), niobium (^{95}Nb), americium (^{241}Am), and curium (^{244}Cm)]; and the naturally occurring radionuclide [radium (^{226}Ra)]. The criterion used to select the non-radioactive surrogate elements that were used in this study is presented in **Table 1**. For $^{59,\,63}$Ni, ^{60}Co, $^{134,\,137}$Cs, ^{93}Zr, ^{95}Nb and ^{192}Ir, we used the stable isotopes of the elements. To limit the radiation exposure to the workers during the experiments to a level as low as reasonably achievable, stable isotope surrogates (Ba, Co, Cs, Ir, Nb, Nd, Ni, Re, and Zr) for these previously mentioned radionuclides (when possible) were used in this study.

To confirm the uptake of FD in the presence of non-radionuclide metals, the SPME fibers were analyzed using gas chromatography and detection by mass spectrometry (GC-MS). Analytical separations were carried out on a Hewlett Packard 6890 gas chromatograph, equipped with a 30 m DB-5 column, with 0.25 mm diameter and 0.25 μm film thickness. Split/splitless injection was used. (Note that these conditions are not those used by the FBI Laboratory and are not highly optimized for FD analyses.)

Detection of the FD was performed using a Hewlett Packard 5973 mass selective detector and total ion monitoring. For the FD analyses, the injector temperature was 220 ºC using splitless injection. The initial oven temperature was 35 ºC, which was held for two minutes upon SPME addition. The oven was then ramped to 220 ºC at a rate of 10 ºC min^{-1} and held at 220 ºC for 2 minutes. Then, the temperature was increased at a rate of 30 ºC min^{-1} and held at 300 ºC for 5 minutes. The SPME fiber was desorbed in the injector for a period of 5 minutes and the solvent delay was 3 minutes. Mass ranges of the scan were between 29 and 400 mass units.

In duplicate, the SPME fibers from the headspace FD exposures were leached with 5 mL nitric acid (pH 2.5) for 30 minutes. The leach solutions were analyzed by inductively-coupled plasma-mass spectrometry (ICP-MS) to determine the levels of metals that could be leached from the fibers. These values were compared with duplicate measurements of the stock solution used to spike the charred materials and duplicate measurements of the nitric acid leaching solution.

Results and Discussion

Prior tests have shown that the SPME fibers in this study have a low affinity for *dissolved* metals namely $^{239/240}$Pu, ^{238}U, ^{237}Np, ^{85}Sr, ^{133}Ba, ^{137}Cs, ^{60}Co and ^{226}Ra) and stable radionuclide surrogate metals (Sr, Co, Ir, Re, Ni, Ba, Cs, Nb, Zr, Ru, and Nd) (Duff et al., manuscript in preparation; Duff et al. 2003).[8, 9] Given this information, we did not anticipate much uptake of these metal by SPME under headspace sampling conditions. The concentrations of nitric acid leached metal ions that were taken from fibers were in all cases below the levels of the stock solution as shown in **Table 2**. However, the level of Zr in the leached SPME fiber that was exposed to the burned carpet sample had a substantial deviation. The high value for Zr was due to contamination. We did not anticipate much headspace uptake of these metals because these inorganic metals as added are not highly volatile under the experimental conditions. Additionally, other sorption studies with SPME fibers that were exposed to dissolved forms of metals (radioactive or surrogate non-radioactive) in aqueous solutions revealed little uptake by SPME fibers also (Duff et al. 2003; Duff et al., manuscript in preparation).[8, 9]

SPME tests were performed with stable materials in the presence of FD, using burned carpet and charred wood. The SPME exposures to the headspace of the FD specimens resulted in significant uptake of the FD residue at levels that were detectable by the GC-MS. FD specimens that contain higher molecular weight hydrocarbon can be differentiated by heating the specimens at 60 ºC or higher for 20 minutes (i.e. kerosene versus diesel fuel). Example chromatographs that compare kerosene analysis using headspace SPME with gasoline and diesel fuel #2 are shown in **Figure 1a** and **b** respectively.

Conclusion

Although this analytical approach which involves leaching of the fibers does not answer the question of whether there was residue decontamination, we anticipate that there is significant decontamination during the SPME exposure process to headspace FD residue. We obtained FD recovery at low (ng) levels in the presence of the surrogates for radioactive materials, which indicates that they do not have a large negative effect on FD recovery during these treatments. SPME headspace sampling of FD residues offers a number of analytical advantages over traditional forensic techniques. The low affinity of the radionuclides and the radionuclide surrogates for the SPME fibers indicates that SPME fibers show great promise for the separation of FD residue from radionuclides in aqueous solution (Duff et al. 2003; Duff et al., manuscript in preparation).[8, 9] A major advantage of the use of SPME fibers over solvent extraction is the lower detection limits that can be obtained in addition to the other facility and safety-driven advantages as previously mentioned. When a high level of decontamination is most needed due to the presence of high activities of radionuclides in the specimens, the use of the SPME fibers may be most amenable for two reasons: first, because of the potential ease of their use when the residue extraction requires the use of robotics—as is the case in conventional radioactive "hot" or "shielded" cell environments and secondly, the volatility of FD residues makes headspace sampling a useful tool for further reduction of the nonvolatile radioactive contamination.

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Table 1 Selection of radionuclide surrogates for initial SPME testing.

Target Radionuclide	Non-radioactive Surrogate	Reason for Surrogate Selection	Reference
^{99}Tc	Re at natural abundance	Re has a similar ionic radii (~0.70 Å), charge (+7) and electrochemical stability in solution and similar complexation behavior to that of Tc(VII)	Dean (1999)[10] and Shannon (1976)[11]
^{222}Ra	Ba at natural abundance	Ba has a similar ionic radii (~1.42 Å), charge (+2), and coordination behavior in solution to that of Tc	Dean (1999)[10] and Shannon (1976)[11]
^{241}Am, $^{244, 245}$Cm	Nd at natural abundance	Nd has similar ionic radii (~1.0 Å), charge (+3), electrochemical stability, and complexation behavior in solution to that of Cm(III) and Am(III)	Dean (1999)[10] and Shannon (1976)[11]

Table 2 ICP-MS results for the non-radioactive metals used in our tests with FD residue sampling with SPME fibers. The average measurements and their standard deviations are shown below.

Treatment*	**Co**	**Zr**	**Nb**	**Re**	**Cs**	**Ba**	**Nd**	**Ir**
Dilute Nitric Leaching Solution after Contact with Control SPME	0.3 ± 0.1	0.8 ± 0.5	BD	0.4 ± 0.4	0.3 ± 0.3	1.7 ± 0.7	0.2 ± 0.1	0.3 ± 0.2
Nitric Acid Leach Solution after Contact with SPME from FD-Carpet Exposure	1.3 ± 0.8	6.8 ± 8.8	BD	BD	BD	1.0 ± 0.0	0.1 ± 0.0	BD
Nitric Acid Leach Solution after Contact with SPME from FD-Wood Exposure	1.0 ± 0.1	0.4 ± 0.1	BD	BD	BD	0.7 ± 0.4	0.1 ± 0.0	BD
Metal Stock Solution	25.1 ± 5.3	11.2 ± 4.8	15.1 ± 2.7	8.7 ± 1.6	16.3 ± 1.2	6.1 ± 1.2	0.6 ± 0.1	23.8 ± 0.1

* Detection limits for Nb, Re, Cs, and Ir are 0.06, 0.06, 0.5, and 0.1 μg L^{-1} (respectively).
BD: below the detection limit.

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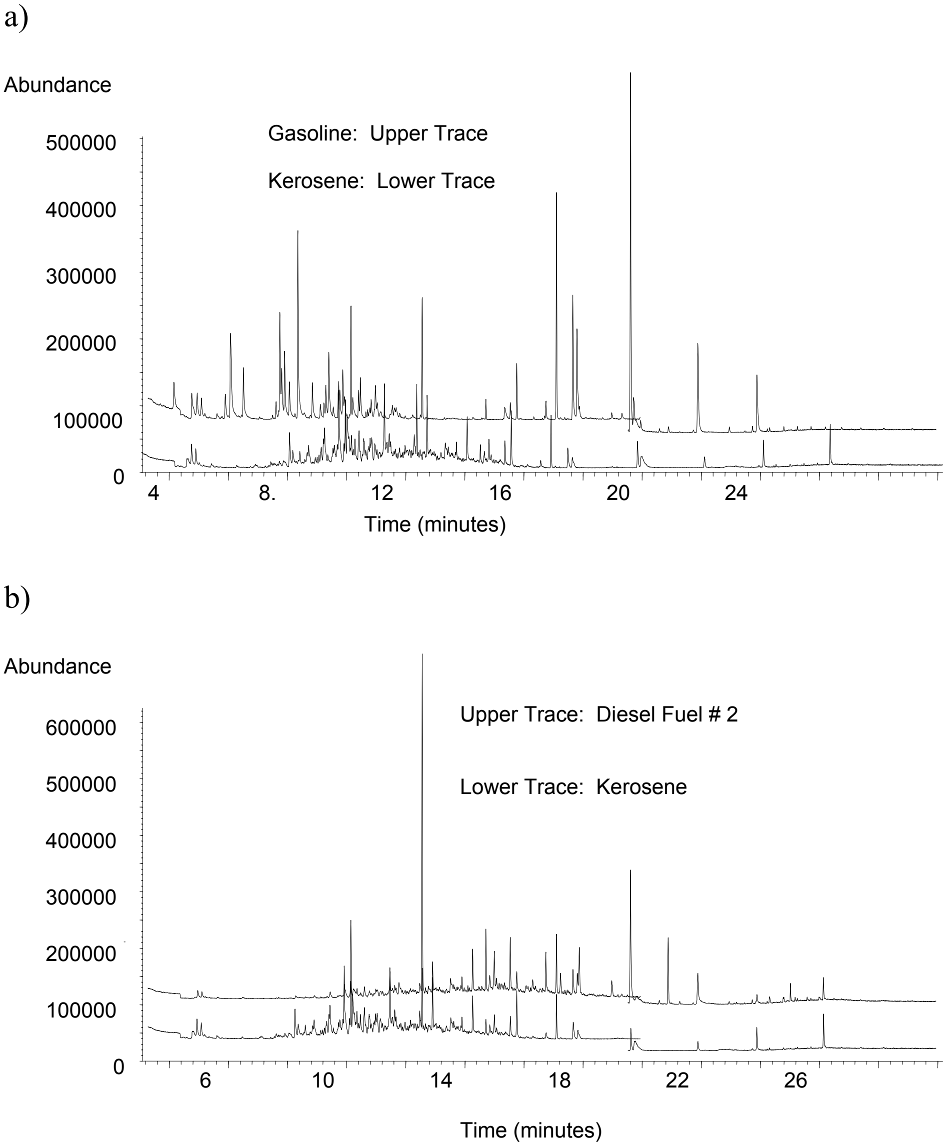

Figure 1 The results from 100 µm PDMS headspace analysis of **a**) gasoline (1 mg L^{-1} standard in sodium sulfate) and kerosene (1 mg L^{-1} standard in sodium sulfate) **b**) diesel fuel #2 (1 mg L^{-1} standard in sodium sulfate) and kerosene (1 mg L^{-1} standard in sodium sulfate). The ambient temperature SPME sampling of the fuel oil samples has led to selective sampling of the oil components.

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