Solid Phase Microextraction Sampling of High Explosive Residues in the Presence of Radionuclides and 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 high explosive (HE) evidence while maintaining evidentiary value. One experimental method for the isolation of HE residue involves using solid phase microextraction or SPME fibers to remove residue of interest. Due to their high affinity for organics, SPME fibers should have little affinity for most metals. However, no studies have measured the affinity of radionuclides for SPME fibers. The focus of this research was to examine the affinity of dissolved radionuclide ($^{239/240}$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) for SPME fibers at the exposure conditions that favor the uptake of HE residues. Our results from radiochemical and mass spectrometric analyses indicate these metals have little measurable affinity for these SPME fibers during conditions that are conducive to HE residue uptake with subsequent analysis by liquid or gas phase chromatography with mass spectrometric detection.

Disclaimer: This was a feasibility study for demonstration of method and not a final product. The methods used for the analyses of the HE are not those used by the FBI, and it should not be implied that the data shown for GC/MS or LC/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 the 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 high explosive (HE) residue materials in various matrices typically require a concentration step to isolate the residue from its host matrix. These methods are typically dependent on host matrix type (solid, liquid, gas). Some of the methods used to recover and concentrate HE (organic) residue are solvent extraction, membrane separation, solid phase extraction (SPE), supercritical CO_2, and solid phase microextraction (SPME).[1,2,3,4,5,6,7] Several types of commercially available SPME fibers have an affinity for HE and 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 HE recovery methods such as column plugging and their usage does not require large volumes of (potentially mixed and highly flammable) organic solvent wastes, which could potentially interfere with the radionuclide decontamination (if the solvents also have an affinity for the radionuclide). Additionally, the SPME fibers offer high sensitivity during gas or liquid chromatographic analyses and the fibers can be quickly analyzed radiometrically to determine their level of radioactivity after exposure to HE residue.

For this work, several radioactive isotopes were identified (as listed in the methods section) that could be present in radioactively-contaminated evidence. When in a dissolved form, these radionuclides could potentially adsorb to the SPME fibers during HE extraction from aqueous solutions. For experimental purposes, this list was often modified to allow for substitutions of radionuclide surrogates—to limit worker radiation dose during testing. For example, stable Cs was substituted for radioactive ^{137}Cs. Due to their 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. However, no studies have examined the affinity of radionuclides for SPME fibers at the exposure conditions that favor HE uptake. One minor goal of this work was to examine the application of SPME fibers for radioactive decontamination of HE residue.

We performed these studies with as little change to the FBI protocol as possible, with the exception of using SPME fibers, the introduction of potential radionuclide metals (using surrogates) and a setup that was appropriate for remote operations in a shielded radioactive hot cell. The overall goal of this study was to examine the use of SPME fibers for HE residue uptake (and decontamination) from aqueous solution under conditions that are most conducive to radioactive shielded cell operations in the presence of radionuclide metal surrogates.

Methods

For the HE decontamination, we examined a variety SPME fibers and solution conditions for HE decontamination. We tested five commercially-available SPME fibers (listed **Table 1**): the PA, the PDMS fiber with a DVB polymeric coating (PDMS-DVB) the PDMS, the PDMS fiber with a carboxen coating (CBX-PDMS) and the carbowax fiber with a DVB coating (CW-DVB) series for their affinity for radionuclides and radionuclide surrogate metals. In general, we used two pH conditions (pH 2 and 9.5) and two salt concentrations [0.0 and 0.23 M Na$_2$SO$_4$]. The first set of experiments performed with SPME fibers was conducted to screen a large number of radionuclides and radionuclide surrogates (in pH 2 and 9.5 solutions, at two known salt concentrations) for their affinity for the several types of SPME fibers. For the first set of experiments, two tests were conducted in the same manner, one with solutions that contained

non-radionuclide metals and the second with solutions that contained only radionuclide metals. A second set of tests (commonly referred to as the "second set of tests") was performed to determine the affinity of the SPME fibers for *very low* levels of dissolved radionuclides. A third set of tests was performed with non-radioactive surrogates in the presence of HE residue using SPME liquid phase sampling. A set of SPME tests were performed to demonstrate the analysis of the five thermally labile HE analytes by LC/MS. These analyses of RDX, HMX, Tetryl, NG, and PETN were conducted because all of these analytes responded poorly or not at all when analyzed by GC/MS.

For these studies, several radionuclide metals were targeted for testing: [americium (^{241}Am), cobalt (^{60}Co), curium (as $^{244,\,245}$Cm), iridium (^{192}Ir), cesium (as $^{134,\,137}$Cs), neptunium (^{227}Np), nickel (as $^{59,\,63}$Ni), plutonium (as $^{239,\,240,\,241}$Pu), radium (^{226}Ra), strontium (^{90}Sr), technetium (^{99}Tc), and uranium (as $^{235,\,238}$U)]. Most of these isotopes are the products of nuclear fission reactions. Many of them have commercial uses. Some of these isotopes such as ^{192}Ir are used in hospitals for chemotherapy. Others like ^{241}Am are used to help detect smoke in smoke detectors. There are also naturally-occurring isotopes (e.g., ^{226}Ra and ^{238}U) that can be found in geologic ore deposits. To limit the radiation exposure to the workers during the experiments to a level as low as reasonably possible, surrogate radionuclide elements (when possible) were selected for use in this study. For $^{59,\,63}$Ni, ^{60}Co, ^{90}Sr, $^{134,\,137}$Cs, and ^{192}Ir, we used the stable isotopes of the elements. Some of the elements that we selected did not have stable isotopic forms so surrogates were selected (listed in **Table 2** along with the rationale for their selection). All isotopes of the elements of U, Np and Pu are radioactive and these three radioactive elements are part of the larger elemental "actinide" group. Some actinide isotopes (such as ^{238}U) are less radioactive than other actinide isotopes (such as ^{235}U). Relative to the high activity isotopes, these lower activity isotopes present less of a hazard to the radiation worker. Therefore, we selected the isotopes of the actinides based on activity levels and on radioisotope availability at our facility.

Methods for First Set of SPME Tests

The solutions used during the SPME exposure test were made to have the approximate dissolved metal and salt concentrations that are listed in

Table 3 and **Table 4**. The target concentrations of the radionuclide and radionuclide surrogate elements were selected after performing calculations to determine what dissolved concentrations of these 11 metals would be completely dissolved and not supersaturated or saturated (or prone to precipitation) in the solutions. The solution speciation computer program called MINTEQA2 was used to perform these equilibrium-based calculations.[8] We used this aqueous geochemistry program to calculate the solubility of metals of a known valence in waters of known pH and salt concentrations. The calculations were performed based on the test solution constituents (such as pH and 0.23 M Na_2SO_4 concentration) in addition to targeted concentrations of the metals of interest. When the model predicted the metals would be supersaturated with respect to a precipitating phase, the modeling was repeated using a lower initial metal concentration until the results predicted that there was at least one order of magnitude lower concentration of metal than that required for precipitation. In all cases, the dissolved metal concentrations that we used (based on the modeling) were less than 1 mg L^{-1}. When thermodynamic data were available in the MINTEQA2 database for the metals we intended to study, we used that data for our calculations. In some cases, we had to use analog data. For Re(+VII), we used thermodynamic data in the MINTEQA2 database for Tc(+VII) and for Nd(+III), we used the thermodynamic data for Am(+III). Thermodynamic data for Am(III) (in MINTEQA2) was used because the dataset was more complete than that for Nd(III). No thermodynamic solubility data were available in the MINTEQA2 database for the noble metal Ir. However, water solubility data for Pt, which is also a noble metal with a similar +IV charge and size were used for comparison to Ir(+IV).[9] The modeling was conducted for two groups of metals. Those metals in solutions that were radioactive (i.e., actinide-containing, with U, Pu and Np) and for solutions that were not radioactive (i.e., with stable radionuclide surrogates). Therefore, as noted in **Table 3** and **Table 4**, the two types of solutions that were modeled with MINTEQA2 were also prepared and tested separately—a radioactive actinide-containing solution and a non-radioactive metal-containing solution.

Stock solutions of the selected metals were made in 0.01 or 1.0 M trace metal grade nitric acid (Optima Grade) using reagent grade chemicals: $Nd(NO_3)_3•6H_2O$, $Co(NO_3)_2•6H_2O$, $CsNO_3$, $Sr(NO_3)_2$, $BaCl_2•2H_2O$, $Ni(NO_3)_2•6H_2O$, ReO_2, and high purity solutions of: Ir(IV) (10 mg L^{-1}),

^{239,240}Pu(IV) (0.972 mg L^{-1}, with approximately 94% ^{239}Pu and 6% ^{240}Pu), ^{237}Np(V) (2.68 mg L^{-1}) and ^{238}U(VI) (10,000 mg L^{-1}). A salt solution containing 0.23 M Na$_2$SO$_4$ (using reagent grade material) was made and treated with 0.2 g L^{-1} of monosodium titanate (MST) solids to remove "tramp" metals (such as non-radioactive Sr, Co and Cs ions by sorption on the MST particles) that were associated with the reagent grade Na$_2$SO$_4$.[10] All stock and diluted stock solutions were prepared in Teflon™ bottles to help limit container adsorption by the metals.

For the pH 2 tests, 1 M nitric acid stock solutions containing the target metals were diluted 1:100 using de-ionized water or 0.23 M Na$_2$SO$_4$ to give the approximate dissolved elemental concentrations listed in **Table 3** and **Table 4**. For the pH 9.5 tests, the 0.01 M stock solutions were diluted 1:100 using de-ionized water or 0.23 M Na$_2$SO$_4$ and the pH was adjusted by the stepwise addition of 0.01 M NaOH until the pH was near 9.5.

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. The SPME fiber exposure times were 30 minutes. Fifteen milliliter (mL) volumes of test solution were placed in 20-mL plastic high-density polyethylene vials (with Teflon™ lined caps). The SPME fibers were immersed in the solutions at equal heights so that the SPME fibers were immersed at equal depths in the solutions. The radionuclide and surrogate solutions were stirred (rapidly) by magnetic stir plates using trace metal grade nitric acid-washed Teflon™ mini-stir bars during SPME exposure. 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.

After the rinse solution was added to the exposure solution, the solution was acidified to pH 2 with trace metal grade nitric acid (when required) and sent for analysis by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). We analyzed these aqueous solution samples by ICP-MS for the metals of interest. Internal standards with 0.050 mg L^{-1} of bismuth and indium were used

in all measurements. Due to isobaric interferences and the high ionic strength "background" from the 0.23 M Na_2SO_4 salt, matrix matching for some solutions was required. Therefore, the standards used for the analyses of the 0.23 M Na_2SO_4 SPME test solutions were made using a 0.23 M Na_2SO_4 solution that had been acidified to pH 2 with trace metal grade nitric acid.

The SPME fibers from the pH 2 and pH 9.5 (high salt) radionuclide studies were saved for radiometric counting (gamma counting of ^{237}Np and alpha counting for ^{238}U, ^{237}Np and $^{239,240}Pu$). The five types of SPME fibers that were exposed to the pH 2 and pH 9.5 solutions (one set of five fiber types for each test pH) were gamma counted simultaneously in the old Whole Body Counting Facility (WBC) at SRNL by high resolution gamma-ray spectrometry. This WBC is surrounded by 0.46 m of pre-World War II battleship steel and 0.65 cm of low background lead to reduce the background inside the counting chamber. A 30% [relative to a 5 by 5 cm^2 NaI (sodium iodide) detector] efficient high purity germanium (HPGe) gamma-ray spectrometer is located inside the counting chamber. All five fibers from each set of pH 2 and 9.5 tests were initially counted together in their metal sheaths by placing the bagged fibers, still in the fiber sheath, directly on top of the HPGe crystal. Spectra were acquired for 24 hours.

These gamma counting results provide information on whether the samples had low enough levels to be counted in our low-level facility. However, these counting measurements do not provide information on whether the counts were coming from the metal sheath or from the SPME fiber inside the metal sheath. To determine if the contamination was on the SPME fiber itself or on the fiber sheath the pH 2 fibers were separated from their protective metal sheaths and the separated fibers were counted individually in the Underground Counting Facility (UCF); the sheaths were re-counted in the WBC. The UCF has a 90% efficient HPGe spectrometer which is shielded by more than 12 m of overburden and surrounded by 1.2 m of specular hematite (Fe_2O_3) and pre-World War II battleship steel. Further background reduction in the UCF is obtained by removing particles in the air with high-efficiency particulate air filters (HEPA filters), by displacing radon (^{222}Rn) gas near the detectors using the liquid nitrogen boil-off, and by preventing contamination using clean room controls. The five separated SPME fiber

samples were individually counted in an HPGe well type detector overnight (85,000 seconds). The data were analyzed using customized software for low-level counting. [11]

For the alpha spectrometric analyses, the unsheathed fibers were also counted for alpha-particle radioactivity. Low-level alpha spectrometry surface scintillation barrier detectors are located in the Ultra Low-Level Counting Facility (ULLCF). The radiological counting background in the ULLCF is minimized using clean room techniques and HEPA filtered air supply. The SPME fiber samples were mounted on 1.905 cm stainless steel planchets with double-sided stick tape. The ^{238}Pu and $^{239+240}$Pu activities on the mounted fibers were determined by alpha spectrometry. Samples were counted for approximately 6 days in an Ortec Octet™ alpha spectrometer equipped with Canberra 450 mm^2 passive ion implanted (PIPs) detectors. Because the fibers were of a nonstandard geometry (i.e., they were not infinitely flat), the detector efficiency was approximated using a standard 1.90 cm electrodeposited source.

Second Set of SPME Experiments

A second set of tests were conducted to determine the affinity of low levels of radionuclides for the SPME fibers to confirm the earlier results. A standard solution was prepared that contained 2000 to 5000 pCi each of ^{137}Cs, ^{85}Sr, ^{133}Ba, ^{226}Ra and ^{60}Co in a 0.01 M nitric acid solution. Tests were only performed at pH 2 and concentrated salt solutions were not used. Fifteen mL aliquots of this solution were poured into 22-mL scintillation vials and exposed to the SPME fibers for 15 minutes using a magnetic stirrer and mini-stir bar. The height of the SPME fibers was the same as in previous tests. Tests with the PDMS, CW and PDMS-DVB were done in triplicate. Tests with PA and CBX-PDMS fibers were done in duplicate. For the radiometric analysis of the SPME fibers and test solutions, a known aliquot of the starting solution, and the residual solutions after the SPME exposures were counted in the WBC—as previously described. Test and control solutions were counted for several thousand seconds. For improved counting statistics, some of the sheathed fibers were counted for longer periods (i.e., overnight).

Third Set of SPME Experiments

A third set of tests was performed to evaluate non-radioactive metal uptake in the presence of dissolved HE residue. The HE equilibrations were performed using 500 ng quantities of HE

residue [specifically 2, 4, 6-trinitrotoluene (TNT), *p*-nitrotoluene, ethylene glycol dinitrate (EGDN), nitroglycerin (NG), pentaerythritol-tetranitrate (PETN), 2, 4-dinitrotoluene, tetryl, octagen (HMX), hexogen (RDX)] and a taggant called 2, 3-dimethyl-2, 3-dinitrobutane (DMDNB). The HE originated by custom order through Restek Corp. (Bellefonte, PA). In duplicate, two items [5.0 g of a sandy-loam soil from Alabama and a ~2 cm by 2 cm by 0.5 cm pipe bomb fragments (supplied by the FBI)] were spiked with the 500 ng of HE residue in water (a 100 μL volume). The soil and pipe bomb fragments were allowed to dry in air for one hour. After the drying period, a 5 and 15 mL volume of a pH 5 solution containing approximately 5 to 20 μg L^{-1} of (non-radioactive) Co, Zr, Nb, Ru, Cs, Ba, Nd and Ir was added to the soil and pipe bomb fragment (respectively). These quantities of solution permitted complete immersion/ saturation of the soil and roughly 50% immersion of the pipe bomb fragment in sealed glass vials. The mixtures were sonicated in perforated tray that was suspended in a water bath. The pipe bomb fragments were turned over after the first hour of sonication so that the other sides of the fragments could be sonicated in the added metal solution for another hour. The soils were sonicated for no less than one hour. After the sonication, the solution in contact with the soil was filtered using a 0.2 μm Anotop filter. The pipe bomb solution was not filtered. The resulting solutions were exposed to pre-conditioned PDMS-DVB SPME fibers for 25 to 30 minutes in glass vials of a geometry that permitted complete immersion of the SPME fibers. The volume of water resulting from the soil sample exposure was too low to allow stirring during SPME exposure. In contrast, the 15-mL volume of water from the pipe bomb fragment was large enough to permit stirring during SPME exposure. Similar SPME studies in the absence of the non-radioactive metals were performed using cell phone and circuit-board fragments. These studies with the cell phone and circuit board fragments were performed with five of the analytes (NG, HMX, RDX, PETN and tetryl).

To confirm the uptake of HE in the presence of non-radionuclide metals, the SPME fibers were analyzed using GC 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.

Detection of the HE was performed using a Hewlett Packard 5973 mass selective detector and selective ion monitoring. The mass spectrometer tuning was confirmed within 24 hours prior to each HE and FD measurement using perfluorotributylamine. For the HE analyses, the injector temperature was 220 ºC. The flow rate of helium was 24.1 mL minute^{-1}. The initial oven temperature was 50 ºC, which was held for one minute upon SPME addition. The oven was then ramped to 240 ºC at a rate of 12 ºC min^{-1} and held at 240 ºC for 9 minutes. The SPME fiber was desorbed in the injector for a period of 5 minutes and the solvent delay was 4 minutes. This method was adapted from Furton et al. (2000) [12]. Mass ranges of the scan were between 25 and 250 mass units.

The liquid chromatograph / mass spectrometer (LC/MS) used with SPME for detection of selected (thermally-labile) HE analytes was an Agilent 1100 binary pump with a Micromass Quattro LC triple quadrupole mass spectrometer. The LC column consisted of a Chromegabond WR C18 column (15 cm by 2.1 mm) with 5 μm particles and 120 Å pore size from ES Industries. The ionization mode was electrospray in negative ion mode. For the HE analysis, a mobile phase of 60:40 methanol:water with 1.25 mM ammonium nitrate was used in isocratic mode at 200 uL/min. Fibers were prepared as above, except that LC compatible fibers were used and an SPME-HPLC interface was used for the fiber desorptions.

Results

First Set of SPME Fiber Studies with Radionuclide and Non-Radionuclide Surrogates

The solutions from these studies were analyzed by ICP-MS. The results of the analyses for the non-radioactive and actinide elements are listed in **Table 5** and **Table 6**. These tables list the percentage of metal in solution after the SPME exposure relative to that of the controls. **Table 5** and **Table 6,** the percentage of metal in solution after SPME exposure compared well with that of the control. Hence, the difference between the treatments and the controls is within the error of the measurements, which was usually about a few percent. The Re measurements by ICP-MS have greater error associated with them. This is due to the low level of Re used in these tests (near 10 μg Re L^{-1}) because there is always more error in the measurement of elements at low concentrations than at higher concentrations. The results in **Table 6** are similar to that of **Table**

5. The coefficient of variation (which is a unit-less value) was calculated so that the error could be shown as a percentage.   In general, the results are similar to that of the previous SPME tests with the non-radionuclide metals in that minimal radionuclide uptake is observed. In all cases, there was good agreement between the control and the treatments and the measurements within each triplicate set were in good agreement—as indicated by the low coefficient of variation (complete data set not shown).

In general, the ability of the ICP-MS instrument to measure concentrations of dissolved metals in the treatments and controls was acceptable and highly reproducible. The measurements usually had less than a few percent in standard deviation of the mean for triplicate analyses (data not shown). However, if the value of the standard deviation for these ^{238}U measurements were converted to a mass of ^{238}U, the amount of contamination would be low—a few hundred disintegrations per minute (dpm). If the value of the standard deviation in the Cs measurements were converted from mass of Cs to dpm of ^{137}Cs, the value for the ^{137}Cs would be over 10^7 dpm (and be a radiation dose exposure concern). This amount of ^{137}Cs would be too high for decontamination purposes, but the level of U may be more acceptable for decontamination (although the acceptable levels for decontamination have not been determined). This difference in dpm for Cs and U is primarily because the specific activity of ^{137}Cs is several thousand-fold greater than that of ^{238}U.

The SPME fibers have a low affinity for the radionuclide and radionuclide surrogate metals but the error in the measurements was too large to conclude that a complete or near complete radioactive decontamination of the HE can be provided by the SPME method. Additional low level studies were performed to obtain more information about radionuclide uptake. The results of the ICP-MS analyses indicate that low levels of actinides could be on the SPME fibers. To better evaluate the actinide levels, the fibers were taken to a low contamination and low dose level facility for radiometric gamma ray and alpha-particle counting to determine the levels of Np, Pu and U on the SPME fibers and their protective metal sheaths. Five intact SPME fibers (one of each type as listed in **Table 1**) from the low ionic strength pH 2 tests were initially counted together in the WBC to obtain a rough estimation as to the sample radioactive

contamination levels. The gamma ray spectrum of the five background corrected SPME fibers (exposed to the pH 2 actinide solutions) is shown in **Figure 1**. As seen in the background corrected spectrum, there are two peaks that are identified in red at 312 keV and 661 keV. The 312 keV peak is due to ^{233}Pa, the short-lived radioactive decay daughter of ^{237}Np. Although we added Pu and U, no gamma peak was identifiable at 129 keV (^{239}Pu) or 1001 keV (^{238}U). The Pu and U isotopes that we added are not strong gamma X-ray emitters so at low loadings, large gamma peaks from these isotopes were not expected. The spectrum for the five SPME fibers from the pH 9.5 exposures (data not shown) was nearly identical to the pH 2 spectrum shown in **Figure 1**. The peak at 661 keV is due to ^{137}Cs decay. Although ^{137}Cs was not added to the test solutions during these equilibrations, it was present in the spectra. The high activity radioactive hood that was used for these equilibrations has a history of use with ^{137}Cs. The ^{137}Cs contamination is most likely tramp contamination on the outside of the fiber sheath (from contact with contaminated gloves while handling the SPME fiber sheaths during testing). Count rates for ^{233}Pa and ^{137}Cs were approximately 0.85 and 0.3 counts per minute (cpm) (respectively).

After separation from the metal sheaths, each of the five fibers from the pH 2 exposure was found to contain approximately 1 pCi of ^{233}Pa per fiber (data not shown). The WBC HPGe recount of the five fiber sheaths found ^{233}Pa (from ^{237}Np decay) and ^{137}Cs on the sheaths at a count rate of 0.25 and 0.3 cpm respectively (data not shown). These results indicate that some of the ^{237}Np is attached to the SPME fiber while the tramp ^{137}Cs is found only on the fiber sheath. The amount of Pa atoms that correspond to 1 pCi of ^{233}Pa is approximately 124000 atoms. The level of ^{237}Np is nearly equal to that of the ^{233}Pa because the ^{237}Np stock solution is greater than a half-year old and is in secular equilibrium with the ^{233}Pa.

Figure 2 shows the gamma-ray spectrum for the separated PA SPME fiber that was counted in the UCF. The peaks associated with the short-lived ^{233}Pa daughter of ^{227}Np decay are indicated in these two figures. The major peak at 312 keV is highlighted in the original WBC composite spectrum shown in **Figure 2**. With the reduced background in the UCF the ^{233}Pa X-ray peaks below 111 keV are clearly visible as are the minor peaks just below and just above the major 312 keV peak (**Figure 2**). The peak at 351 keV is due to ^{214}Bi in the air from the decay of naturally

ocurring ^{222}Rn. No peaks due to ^{235,238}U (^{235}U peaks are at 144 keV and186 keV and the ^{238}U peak is at 1001 keV) are not visible in this or any of the other spectra.

The alpha particle counting results indicate that the separated (un-sheathed) fibers contain a minute, but measureable amount of Pu. As shown in **Figure 3**, the PA fiber contained the greatest amount of Pu. The mass of the Pu in the PA fiber is 280 picograms (pg), which is about 10^{11} Pu atoms. **Figure 3** shows the alpha particle spectrum from the PA fiber. The low-energy peak tailing is due to the non-standard geometry of the fibers. When samples are typically prepared for alpha spectrometry they are electroplated in a thin film deposit. These samples were counted as is. The peak energy maximums are used to identify the isotopes present in the sample. The small amount of ^{237}Np determined indirectly by gamma spectrometry at 4.7 keV and any ^{238}U at 4.2 keV was not readily visible under the larger $^{239+240}$Pu-tail. The spectrum is dominated by the Pu alpha particle spectrum. However, we estimate the ^{238}U and ^{237}Np amounts (which if present are within the background noise) to be less than 1 % of the Pu counts.

Uptake of the very low levels of Pu (determined by alpha counting) and Np (determined by gamma counting) by the PA fiber is potentially attributable to the fiber being made of a solid as opposed to a liquid (as with the other four fibers). Relative to liquid coatings, solid coatings like PA tend to have slower uptake of materials.[13] A more thorough rinsing after exposure to the actinide-containing solutions may lower the amount of entrained Pu and Np.

Second Set of SPME Fiber Studies with Radionuclide Metals

We performed a series of similar tests of a more limited scope with SPME fibers and trace levels of radionuclides. By using low levels of dissolved radionuclides, we could increase our ability to observe low levels of metal uptake because there will be a larger amount of SPME fiber surface area relative to metal available for radionuclide sorption. Additionally, by testing with very low but measurable quantities of radionuclides, we can increase our sensitivity to detect sorption from solution and on the SPME fibers by using radiometric methods as opposed to ICP-MS methods. **Figure 4** is a background corrected gamma ray spectrum of the control solution and **Figure 5** is a background corrected gamma ray spectrum of the of the CBX-PDMS residual solution. All the peak areas from the gamma ray counting for the SPME test solution were

ratioed to the starting control solution and plotted in **Figure 6**. The test solutions and control were counted for approximately 3000 seconds in the WBC. As shown in the **Figure 6** both PA fibers show a low level of ^{226}Ra remaining in solution relative to the control solution based on the 186 keV photopeak. The other radionuclides (^{137}Cs, ^{85}Sr, ^{133}Ba, and ^{60}Co) remained at similar levels to that of the control solution after SPME exposure and if any uptake of these radionuclides occurred during these studies, the amount of radionuclide that was removed by the SPME fibers was within the error of the instrumental measurement.

To obtain better counting statistics for the PA SPME test, the solutions were re-counted and the individual PA SPME fibers were counted. The results of the overnight PA solution counting are shown. A typical spectrum from the PA1 SPME fiber is shown in Figure 7. No detectable activity above background was found on the un-sheathed fibers. With the longer count time and smaller counting error, the results indicate that the added ^{226}Ra is present in the residual solution and not on the fibers. In conclusion, none of these radioisotopes in this study appear to sorb to the SPME fibers—in the absence of HE residue.

SPME Fiber Studies with Non-Radionuclide Metals

Our next set of SPME tests were performed with non-radioactive metals in the presence of HE residue. The HE tests were performed with soil and pipe bomb fragments. The SPME exposures to the solutions from the sonication of HE-loaded materials resulted in the uptake of most of the HE compounds at levels that were detectable by GC-MS. However, we observed with direct solvent injections that not all of the added HE compounds could be detected (at low hundred μg total quantities) with our GC analytical method. An example chromatogram with a direct solvent injection is shown in **Figure 9a**. Due to the thermal instability of some of the HE compounds such as RDX, tetryl and the NG-like compounds (EGDN, NG and PETN), these compounds were difficult to detect at lower levels. An example chromatogram with 500 μg of HE mix by solvent injection is shown in **Figure 9b**. For our GC-MS instrumentation setup, we could more readily detect RDX, tetryl, and the NG-like compounds at total initial exposure amounts of a few μg of HE. The HMX, which is thermally labile in the GC-MS, was not detected by direct solvent injection or SPME technique.

Liquid chromatography / mass spectrometry (LC/MS) was used to analyze five of the thermally-labile HE analytes, including RDX, HMX, tetryl, NG, and PETN. Using this chromatographic method with SPME sampling, these analytes were readily detected, although NG had a higher limit of detection. Exemplary chromatograms from the LC/MS analysis of these analytes are shown in **Figures 10a** and **10b**.

Discussion

Although this analytical approach does not answer the question of whether there was residue decontamination, we anticipate that there is significant decontamination during the SPME exposure process to dissolved HE residue. We obtained HE recovery at low (ng) levels in the presence of the non-radioactive metals, which indicates that they do not have a large negative effect on HE recovery during these treatments. 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 HE residue from radionuclides in aqueous solution. The use of SPME fibers holds several advantages over solvent extraction in that use of the SPME fibers can produce lower detection limits.[12] When a high level of decontamination is most needed due to high radiation levels in the specimens and flammable solvents are a safety concern, the use of the SPME fibers may be most amenable. This is 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.

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Fiber Coating Type	Coating Stability	Polarity	Coating Porosity	Coating Thickness (μm)
Polydimethylsiloxane (PDMS)	Non-bonded	Nonpolar	Non-porous	100
Polyacrylate (PA)	Cross-linked	Polar	Non-porous	85
Carbowax-Divinylbenzene (CW-DVB)	Cross-linked	Polar	DVB has mesopores	65
Carboxen- Polydimethylsiloxane (CBX-PDMS)	Cross-linked	Bipolar	Carboxen has macro-, meso- and micro-pores for small molecules	75
Polydimethylsiloxane - Divinylbenzene (PDMS-DVB)	Cross-linked	Bipolar	DVB has mesopores	65

* Some of these SPME fibers are known to exhibit marginal uptake of HE (such as the PDMS).[13] However, we tested the PDMS (only) fiber because PDMS is a component of the more effective SPME fibers that are recommended for use in HE extraction (such as the PDMS-DVB, which is a PDMS fiber with a DVB polymeric coating). By studying the sorption properties of the select components of the fibers, we intended to isolate which coating (if any) exhibits significant radionuclide uptake. This information could then be used to select alternative fibers for testing if need be.

Table 2 Selection of radionuclide surrogates for initial SPME testing. The isotopes of U, Np and Pu (called "actinide") are radioactive and not listed below. We did not select stable analogs for these elements because low specific activity isotopes were available.

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)[14] and Shannon (1976)[15]
^{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)[14] and Shannon (1976)[15]
^{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)[14] and Shannon (1976)[15]

Table 3 Target test conditions for the first set of tests with the SPME fibers with pH 2 solutions.

	Non-radioactive pH 2	Radioactive pH 2	Non-radioactive pH 2	Radioactive pH 2
		Target Species Concentration [mg L^{-1}]		
Na$_2$SO$_4$*	none added	none added	2300	2300
Nd	0.34	none added	0.43	none added
Co	0.52	none added	0.59	none added
Cs	0.74	none added	0.78	none added
Sr	0.30	none added	0.30	none added
Ba	0.23	none added	none added	none added
Ni	0.59	none added	0.59	none added
Ir	0.10	none added	0.10	none added
Re	0.15	none added	0.01	none added
Np	none added	0.54	none added	0.38
Pu	none added	0.12	none added	0.12
U	none added	0.48	none added	0.34

* Na$_2$SO$_4$ concentrations are in moles L^{-1}.

Table 4 Target test conditions for the first set of tests with the SPME fibers with pH 9.5 solutions.

	Non-radioactive pH 9.5	Radioactive pH 9.5	Non-radioactive pH 9.5	Radioactive pH 9.5
		Target Species Concentration [mg L^{-1}]		
Na$_2$SO$_4$*	none added	none added	0.23	0.23
Nd	none added	none added	none added	none added
Co	0.58	none added	0.02	none added
Cs	0.66	none added	0.75	none added
Sr	0.30	none added	0.31	none added
Ba	0.42	none added	0.01	none added
Ni	none added	none added	none added	none added
Ir	none added	none added	none added	none added
Re	0.09	none added	0.09	none added
Np	none added	0.18	none added	0.18
Pu	none added	none added	none added	none added
U	none added	0.01	none added	0.01

* Na$_2$SO$_4$ concentrations are in moles L^{-1}.

Table 5 Percentage of each added radionuclide surrogate element remaining in solution after the SPME fiber exposures--ICP-MS data for the treatments without Na$_2$SO$_4$.

pH	SPME Type*		Ni	Co	Sr	Cs	Ba	Nd	Re	Ir	Np	U	Pu
2	1	Average (Mean)	98.7	97.3	106.9	102.8	97.5	101.0	116.0	101.2	106.4	107.5	109.2
		Coefficient of Variation	2.6	1.7	4.6	1.7	4.2	1.7	7.7	2.7	1.2	1.2	5.3
2	2	Average	102.6	101.1	100.8	101.1	95.7	104.0	115.5	100.2	102.2	102.4	111.7
		Coefficient of Variation	1.7	0.7	0.3	0.7	0.8	3.2	21.7	0.4	3.9	3.9	8.0
2	3	Average	98.1	98.3	92.6	98.1	94.2	98.7	91.4	95.1	91.6	92.6	93.2
		Coefficient of Variation	2.4	1.7	0.7	2.2	8.7	2.6	9.5	2.2	1.6	1.8	10.0
2	4	Average	99.2	101.0	100.1	99.8	106.9	100.9	98.0	100.4	106.7	106.4	124.7
		Coefficient of Variation	1.3	1.1	1.5	1.5	6.6	0.8	6.3	1.1	2.2	1.8	7.2
2	5	Average	101.1	100.5	98.3	98.3	92.2	97.4	118.4	94.8	99.6	100.1	102.6
		Coefficient of Variation	3.4	2.5	2.9	2.2	7.9	1.9	9.2	2.0	0.7	0.7	8.5
9.5	1	Average	NT**	99.3	100.0	100.1	98.9	NT	NT	NT	98.8	122.9	NT
		Coefficient of Variation		0.4	1.1	0.7	4.2				0.5	16.1	
9.5	2	Average	NT	100.3	100.0	100.5	103.9	NT	NT	NT	99.6	101.8	NT
		Coefficient of Variation		0.3	0.9	0.7	5.7				2.7	4.1	
9.5	3	Average	NT	100.3	97.4	106.4	92.9	NT	NT	NT	100.1	90.1	NT
		Coefficient of Variation		0.9	0.9	0.7	3.2				1.7	6.6	
9.5	4	Average	NT	99.1	97.8	94.4	98.7	NT	NT	NT	101.9	101.9	NT
		Coefficient of Variation		0.8	2.5	3.1	2.0				1.1	3.9	
9.5	5	Average	NT	100.8	100.7	100.9	98.8	NT	NT	NT	100.1	103.4	NT
		Coefficient of Variation		0.9	0.8	1.1	1.4				0.4	2.5	

* Fiber type: 1 = Polydimethylsiloxane/divinylbenzene; 2 = Carboxen; 3 = Divinylbenzene/Carbowax; 4 = Polydimethylsiloxane; 5 = Polyacrylate

** NT = Not Tested

Table 6 Percentage of each added radionuclide surrogate element remaining solution after in the SPME fiber exposures--ICP-MS data for the treatments with 0.23 M Na_2SO_4.

pH	SPME Type*		Ni	Co	Sr	Cs	Ba	Nd	Re	Ir	Np	U	Pu
2	1	Average (Mean)	132.0	121.1	121.1	110.3	100.7	105.1	94.5	87.5	99.0	99.5	94.1
		Coefficient of Variation	1.5	1.5	1.4	0.7	12.1	1.1	8.5	1.6	1.6	1.4	3.6
2	2	Average	112.7	101.1	98.6	97.5	82.3	131.4	104.3	112.2	96.8	97.2	98.7
		Coefficient of Variation	11.9	1.7	0.9	1.0	8.7	29.5	18.9	11.9	1.0	0.8	3.3
2	3	Average	98.0	97.7	96.9	96.8	112.1	96.7	100.0	97.6	100.5	98.4	105.4
		Coefficient of Variation	1.4	1.0	3.0	1.4	32.1	1.4	0.0	1.4	2.0	1.6	2.3
2	4	Average	104.4	106.1	104.8	101.6	99.6	103.1	103.7	101.1	100.4	100.1	98.1
		Coefficient of Variation	1.8	2.2	0.9	1.2	20.0	0.8	11.1	0.9	1.40	1.6	3.0
2	5	Average	94.6	95.3	96.0	99.1	128.2	96.4	145.4	101.4	99.8	91.1	99.8
		Coefficient of Variation	3.6	3.2	2.4	2.8	25.8	2.3	18.1	1.2	1.3	1.2	3.5
9.5	1	Average	NT**	108.9	97.5	98.1	100.7	NT	NT	NT	106.1	99.4	101.5
		Coefficient of Variation		2.8	0.4	1.1	11.5				9.8	1.4	3.1
9.5	2	Average	NT	96.1	105.0	99.8	78.2	NT	NT	NT	124.7	101.2	100.2
		Coefficient of Variation		11.4	2.2	2.8	16.2				14.8	1.4	2.6
9.5	3	Average	NT	95.1	79.2	99.1	110.1	NT	NT	NT	56.7	95.9	95.6
		Coefficient of Variation		5.3	2.1	1.2	17.7				15.4	0.7	2.3
9.5	4	Average	NT	116.8	103.0	102.6	93.6	NT	NT	NT	123.5	95.7	93.9
		Coefficient of Variation		7.1	2.2	1.0	13.5				15.4	2.1	3.1
9.5	5	Average	NT	87.3	113.2	113.3	130.7	NT	NT	NT	99.0	98.9	87.2
		Coefficient of Variation		2.7	5.4	7.4	3.6				14.3	1.6	9.9

* Fiber type: 1 = Polydimethylsiloxane/divinylbenzene; 2 = Carboxen; 3 = Divinylbenzene/Carbowax; 4 = Polydimethylsiloxane; 5 = Polyacrylate

** NT = Not Tested

Table 7 Alpha particle counting results for the five SPME fibers from the pH 2 exposures. An overall uncertainty of 20 % was applied to account for the geometry difference between the fibers and the standard, and the excessive peak tailing caused by self absorption of alpha particles by the fibers.

SPME Fiber	^{238}Pu (pCi)[1]	$^{239+240}$Pu (pCi)	^{238}Pu (pg)*	$^{239+240}$Pu (pg)
CBX-PDMS	0.27	7.4	0.016	105
PDMS-DVB	0.27	8.8	0.016	125
CW-DVB	0.15	4.7	0.009	67
PDMS	0.22	7.4	0.013	105
PA	0.65	19.9	0.038	282

*Although we did not purposely add ^{238}Pu, the low levels of this Pu isotope in the ^{239,240}Pu that we used were detectable. These results indicate that our source of the ^{239,240}Pu was not entirely pure. However, the high specific activity of ^{238}Pu makes its detection at low levels much more possible than similar concentration levels of the other two ^{239,240}Pu isotopes in the sample.

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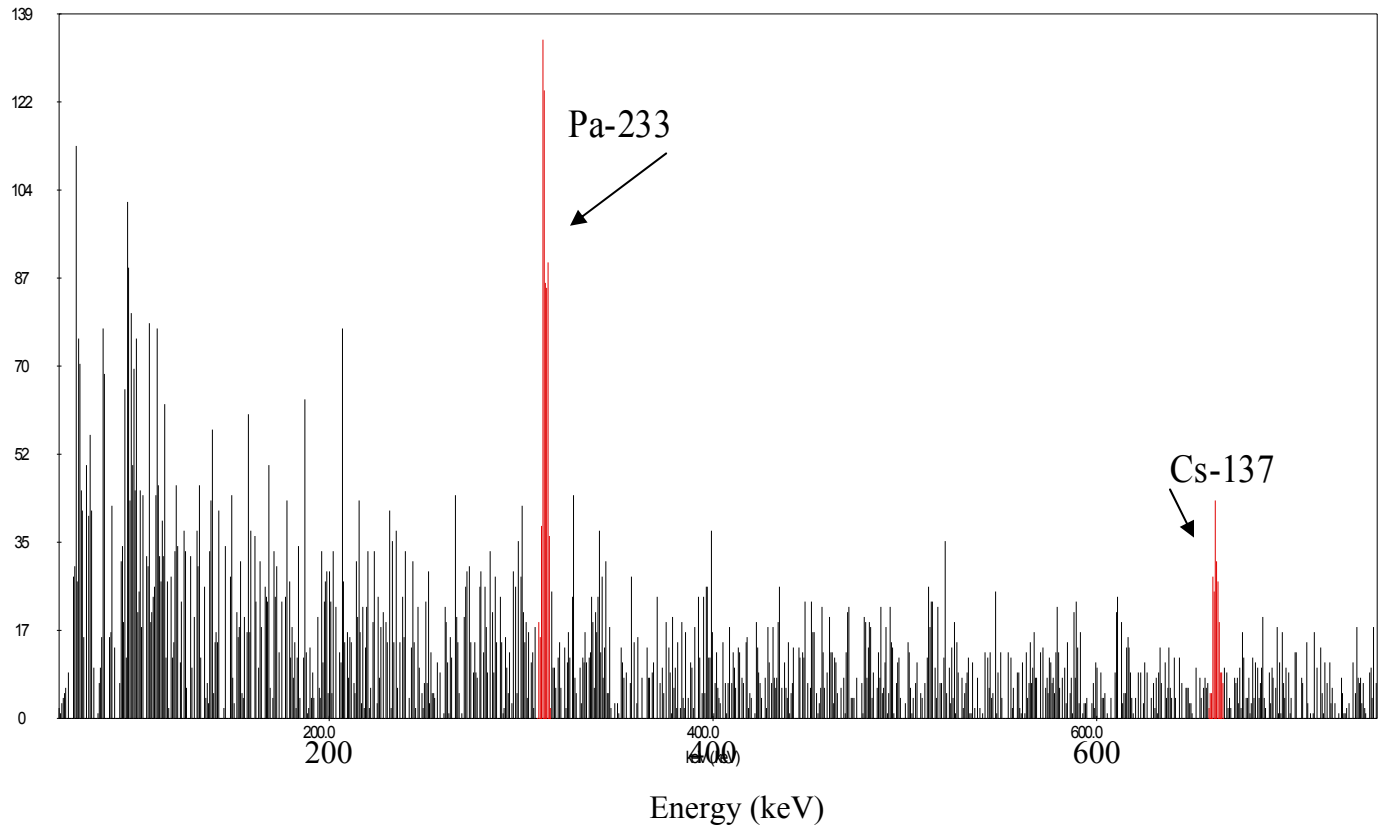
Figure 1 Gamma X-ray spectrum for the bag of five SPME fibers, which contained one of each SPME fiber from the pH 2 exposures.
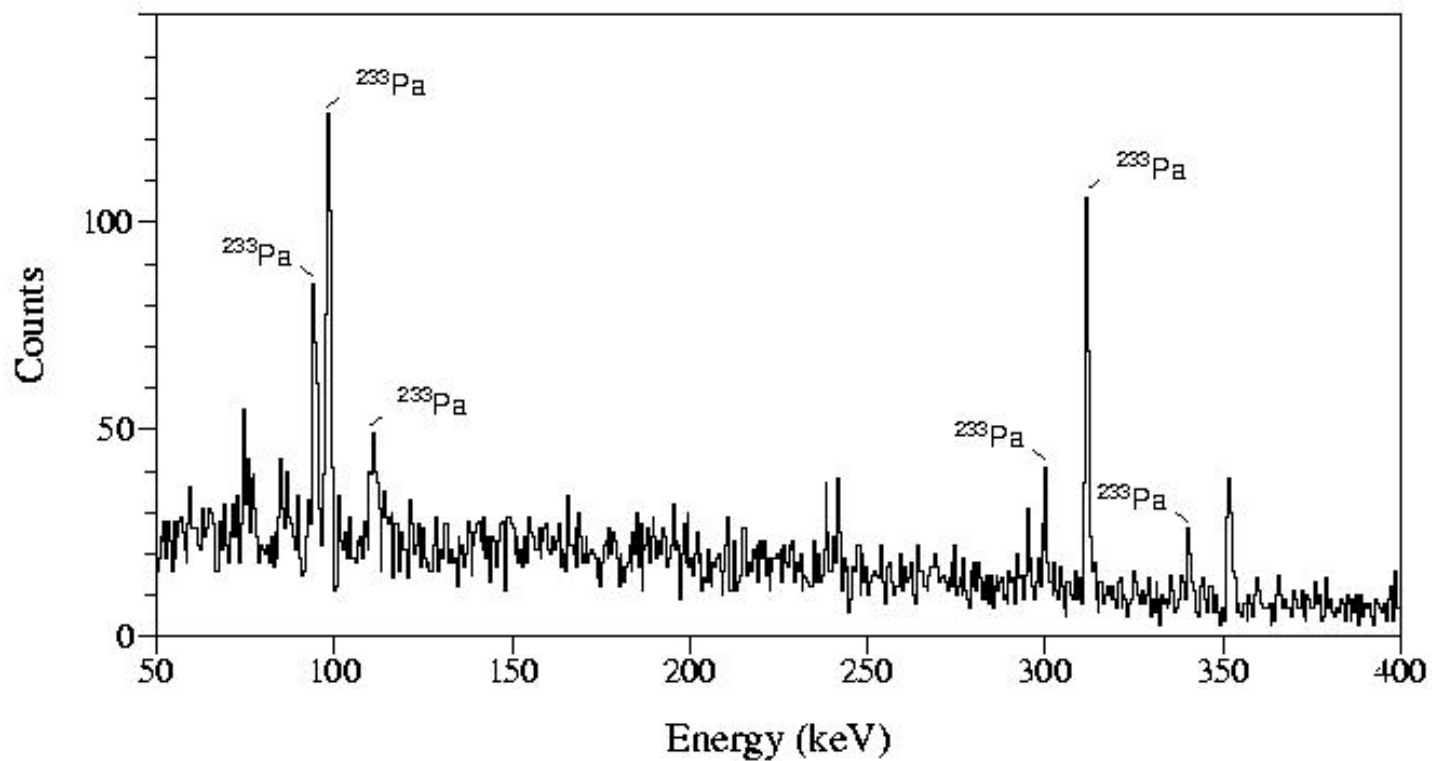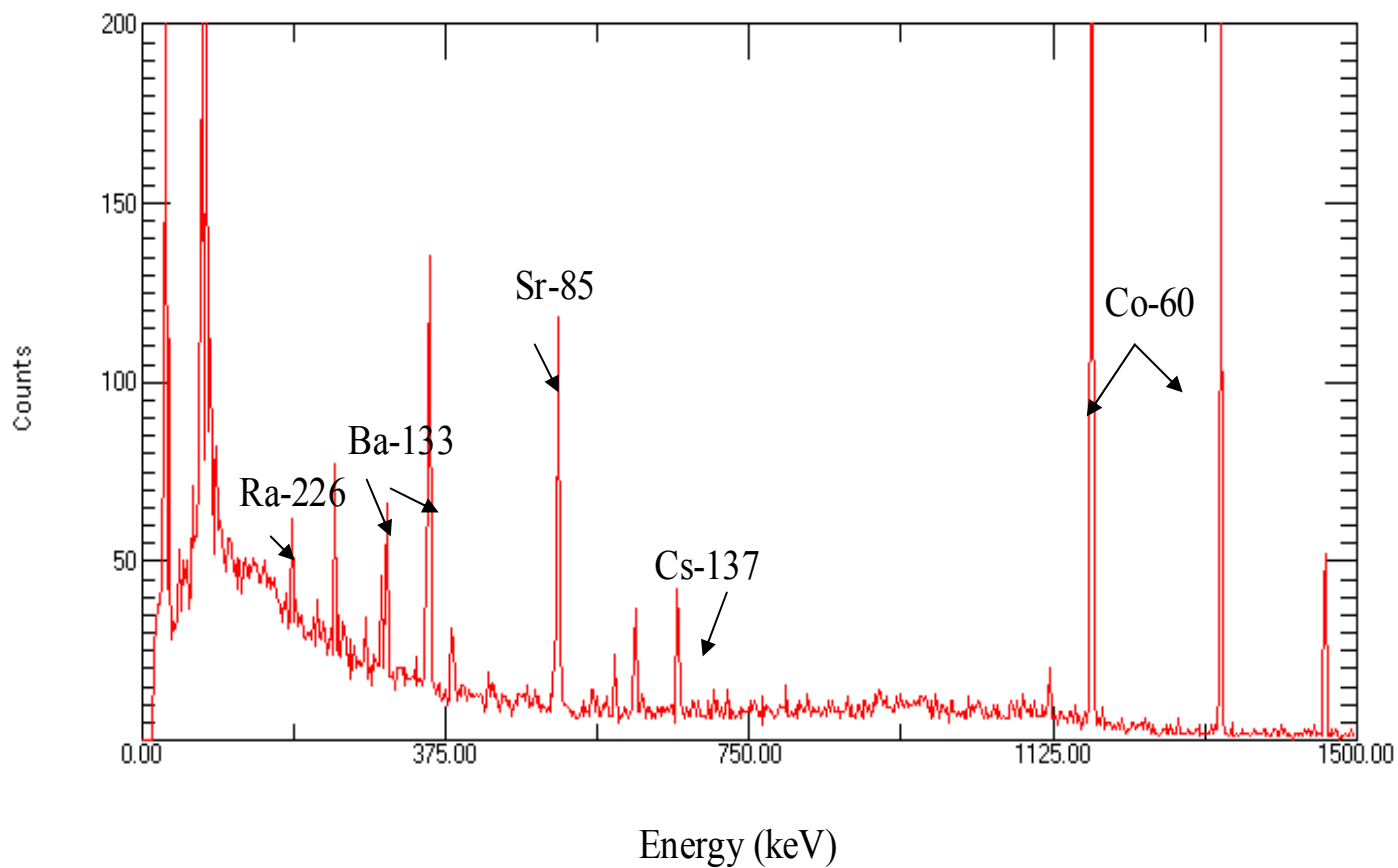
**Figure 2** Gamma X-ray spectrum for a polyacrylate (PA) SPME fiber from the pH 2 exposures.
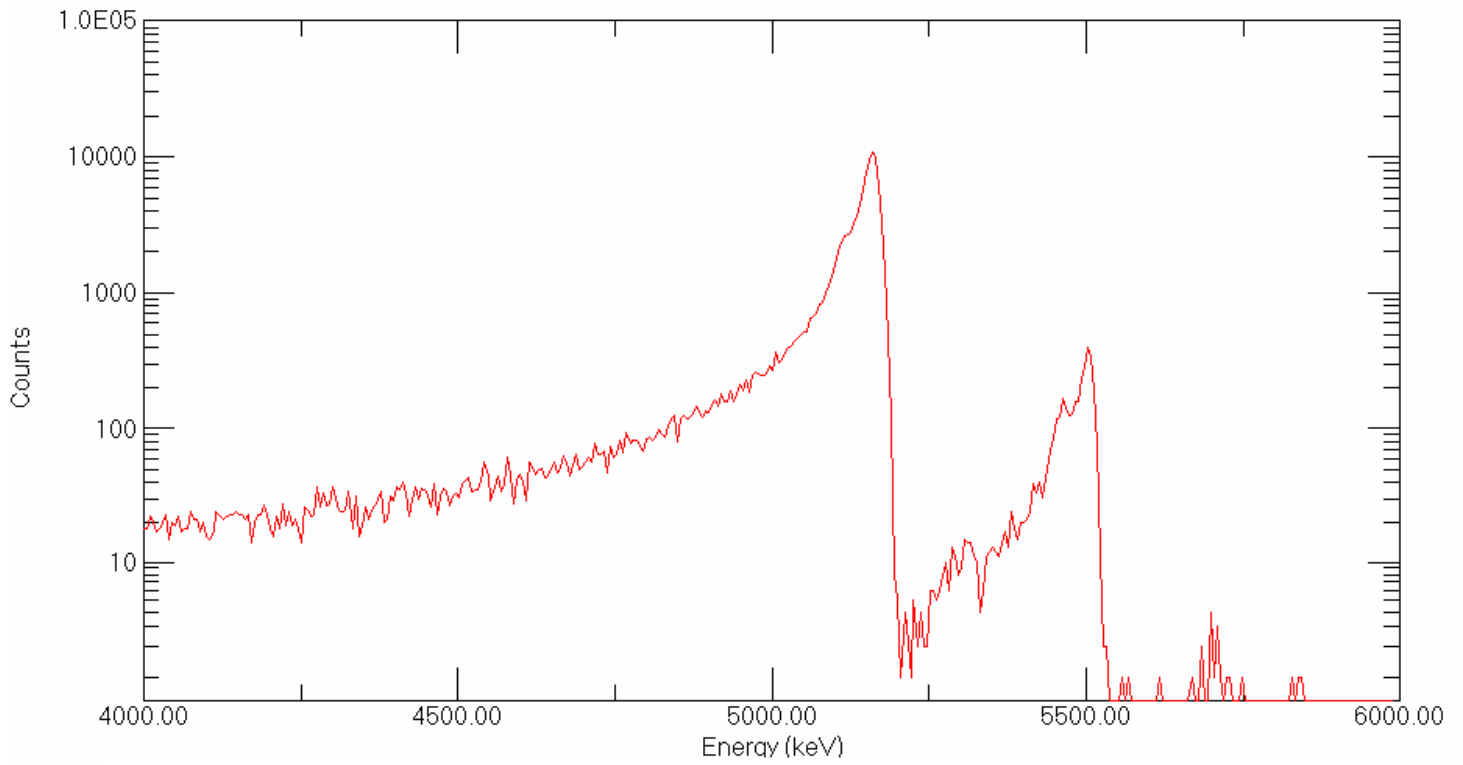
Figure 3 Example of the alpha counting spectrum for the PA SPME fiber (pH 2 low ionic strength solution exposure).
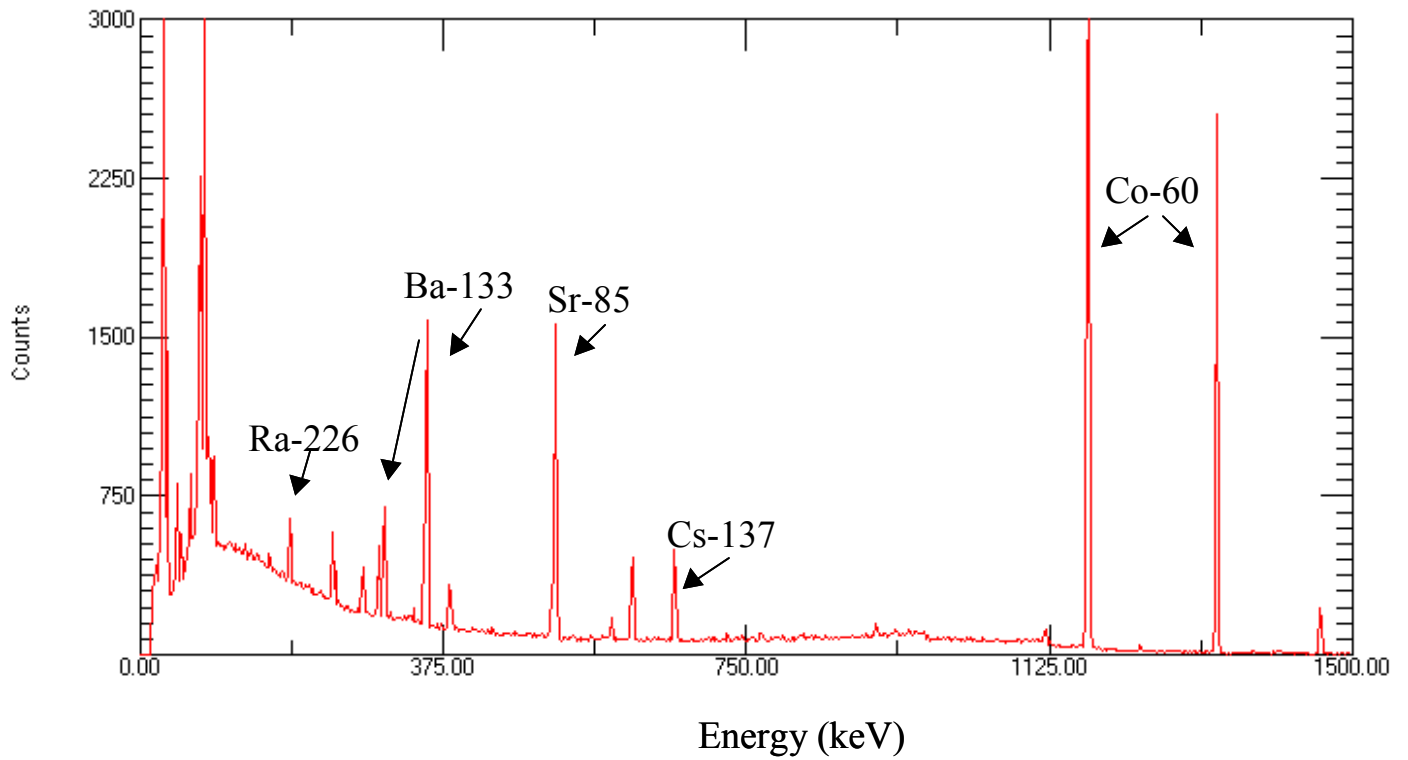
Figure 4 Gamma energy spectrum for the radionuclide control (starting) solution used in the low-level radionuclide exposures with the SPME fibers.

Figure 5 Gamma energy spectrum of the low level radionuclide solution after exposure to a CBX-PDMS SPME fiber.
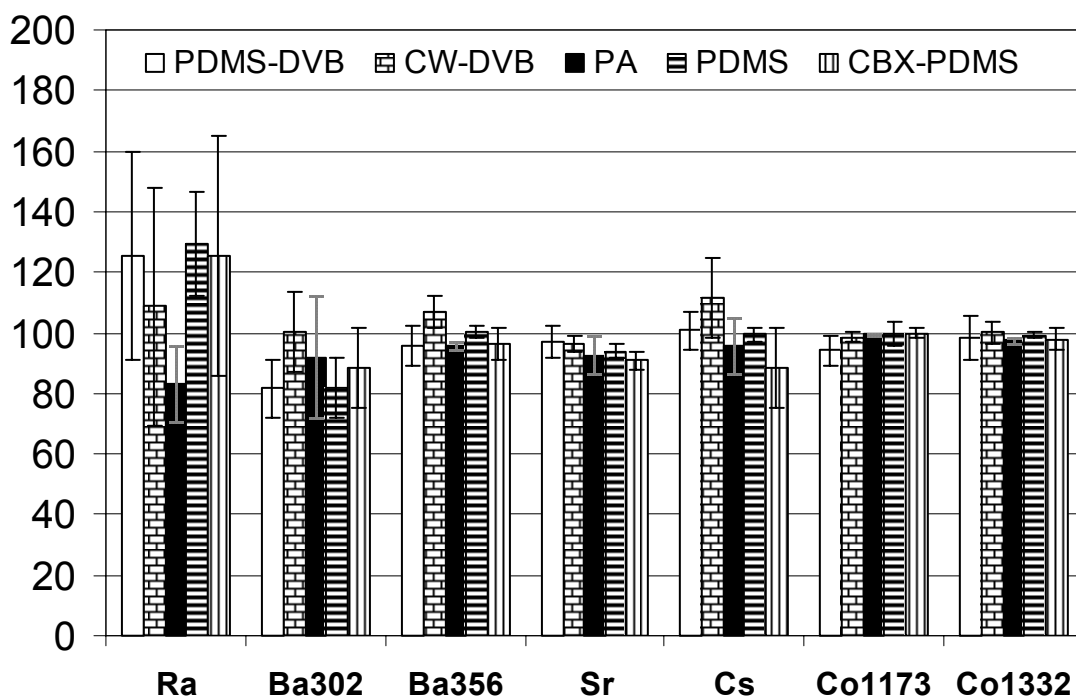
Figure 6 Plot of the gamma counting data showing the percent radionuclide remaining in individual solutions after SPME exposure.   The numbers after the chemical symbols (for Ba and Co) in the legend represent the gamma ray energies (in keV) that were counted. For Ra, Cs and Sr, one gamma ray energy was monitored during counting.
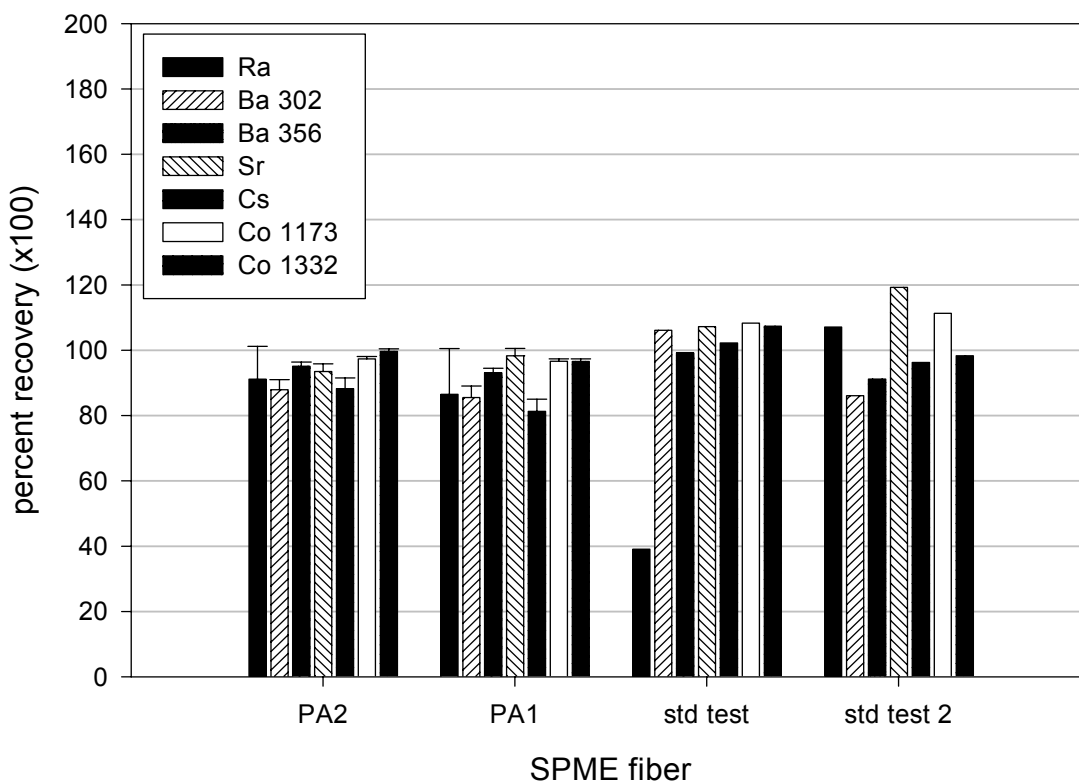
Figure 7 Overnight counting results of the polyacrylate (PA) SPME fibers that were exposed to low levels of radionuclides—in addition to duplicate analyses of the control solution.

The numbers after the chemical symbols in the legend represent the gamma X-ray energies (in keV) that were counted. For Ra, Sr and Cs, only one gamma X-ray energy was used for counting.
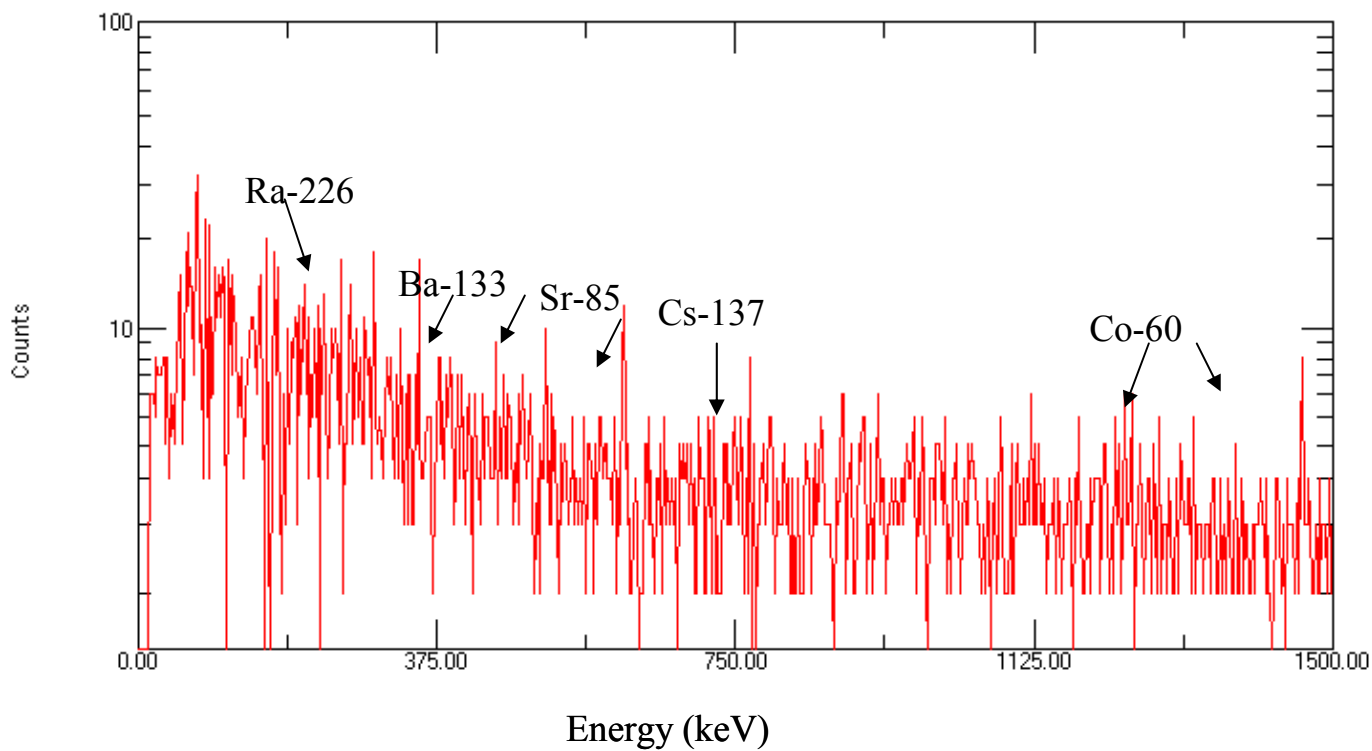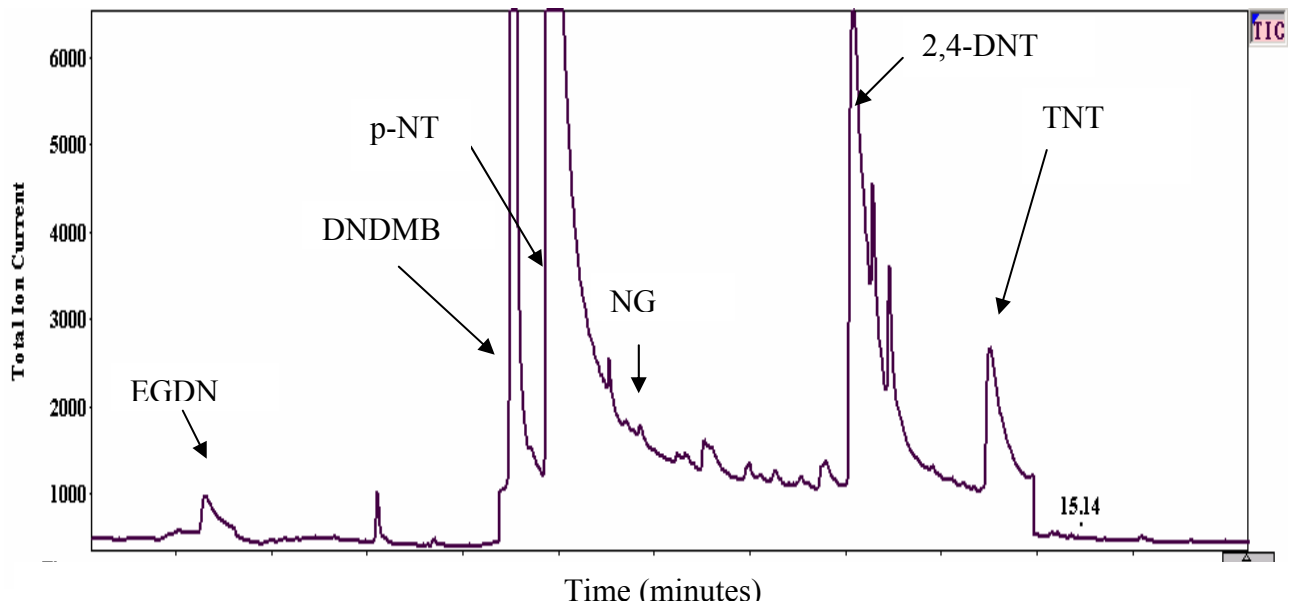
Figure 8 Gamma X-ray spectrum for the polyacrylate (PA) SPME fiber that was exposed to the low level radionuclide solution. The peaks for the labeled radionuclides are nearly within the background noise of the low level counting instrument.
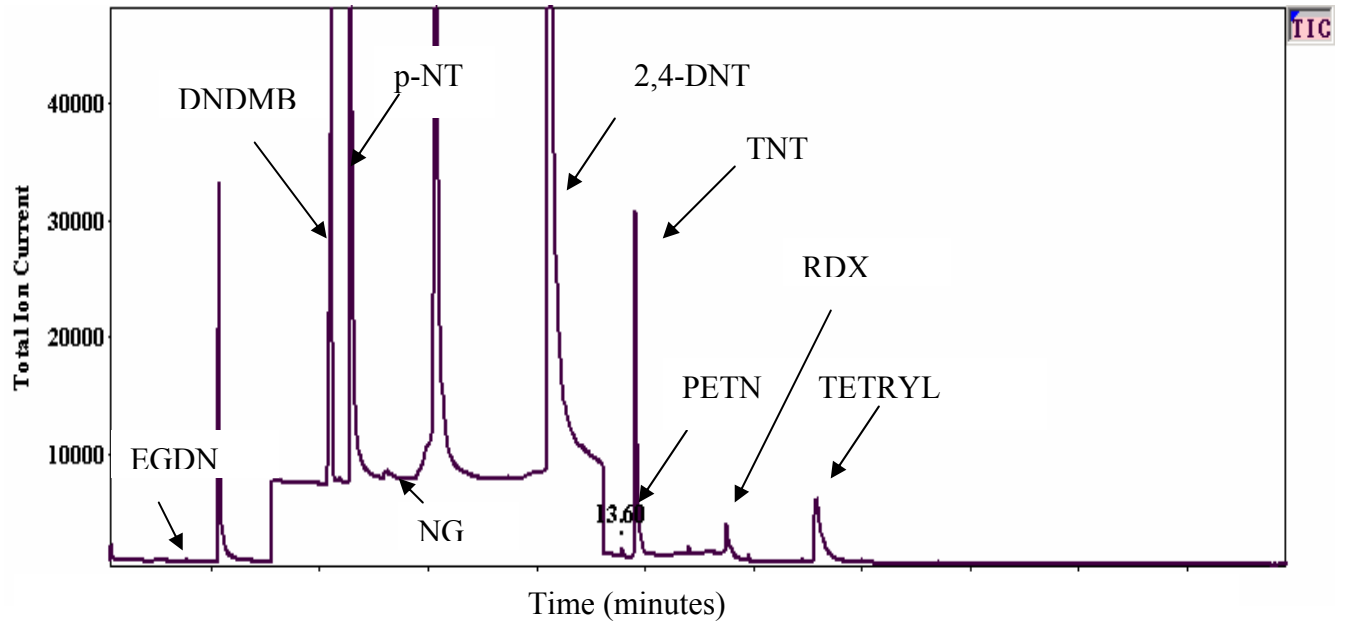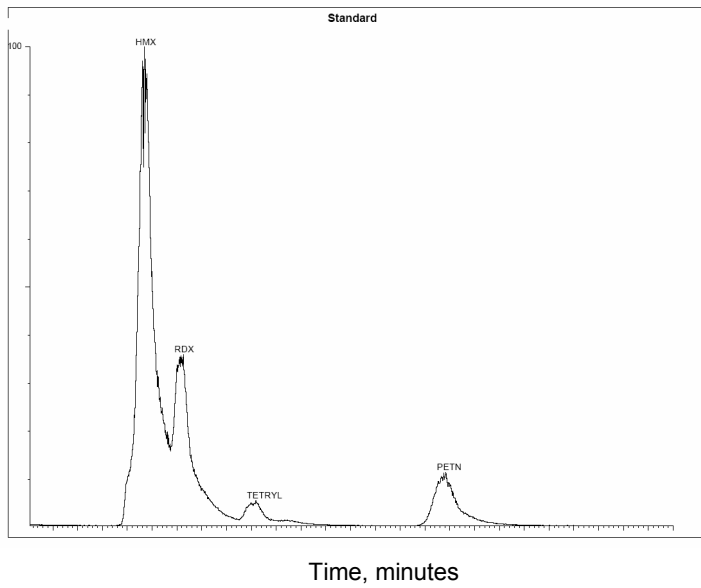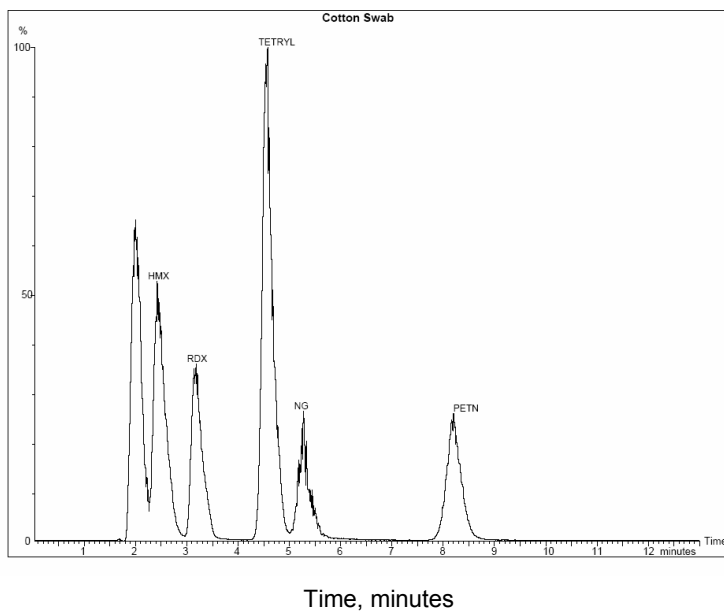
Figure 9 The results from the selective ion monitoring analyses of **a**) direct solvent injection of the HE standard (1 µl of 50 mg L^{-1} HE standard in acetone) showing the presence of the thermally-unstable RDX and NG-type compounds and **b**) the results of a 500 ng amount of (initially added) HE residue from one of the soil exposures.

A)

Time, minutes

B)

Time, minutes

Figure 10 LC/MS analysis of five selected HE analytes which were too thermally labile for GC-MS analysis. Trace (A) is a blank spiked with analytes, and Trace (B) is a matrix spike of cotton swab spiked with analytes, then extracted in aqueous sodium sulfate. Both were extracted with SPME fiber (PDMS/DVB) and solvent desorbed by LC/MS. The shoulder on the tetryl peak in trace (A) is nitroglycerin. The first peak in Trace B is an artifact of the matrix.

References

[1] Yinon J; Zitrin S. Modern methods and applications in analysis of explosives. West Sussex, England: Wiley, 1993.

[2] Psillakis E; Kalogerakis N. Solid-phase microextraction versus single-drop microextraction for the analysis of nitroaromatic explosives in water samples. J Chrom A, **2001**, *938,* 113.

[3] Hennion MC. Solid-phase extraction: method development, sorbents and coupling with liquid chromatography. J. Chrom A **1999**, *856*, 3.

[4] U. S. Environmental Protection Agency (1989). Nitroaromatics and nitramines by high performance liquid chromatography (HPLC). Method 8330. SW-846. Rev. 1, Jan. 1998.

[5] Crockett A.B; Craig HD; Jenkins TF (1999). Field sampling and selecting on-site analytical methods for explosives in water. U. S. Environmental Protection Agency Technology Support Project EPA/600/S-99/002. May 19, 1999.

[6] Jenkins TF; Miyares PH; Myers KF; McCormick EF; Strong AB. Comparison of solid phase extraction with salting-out solvent extraction for preconcentration of nitroaromatic and nitramine explosives from water. Analytica Chimica Acta **1994**, *289*, 69.

[7] Halasz A; Groom C; Zhou E; Paquet L; Beaulieu C; Deschamps S; Corriveau A; Thiboutot S; Ampleman G, Dubois C; Hawari J. Detection of explosives and their degradation products in soil environments. J Chrom A. **2002,** *963*, 414.

[8] U. S. Environmental Protection Agency (1991). MINTEQA2 and PRODEFA2 Versions 3.10 and 3.11. Center for Exposure Assessment Modeling (CEAM), U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, College Station Road, Athens, GA 30613-0801.

[9] Azaroual M, Romand B, Freyssinet P, Disnar JR. Solubility of platinum in aqueous solutions at 25°C and pHs 4 to 10 under oxidizing conditions. Geochim Cosmochim Acta **2001**, *65*, 4453.

[10] Duff MC, Hunter DB, Hobbs DT, Fink SD, Dai X, Bradley JP. Mechanisms of strontium and uranium removal from high-level radioactive waste simulant solutions by the sorbent monosodium titanate. Environ. Sci. Technol. **2004**, *38*, 5201.

[11] Winn WG. Ultra-sensitive examination of environmental samples by SRL Underground Counting Facility. Trans. Amer. Nucl. Soc. **1987**, *54*, 34.

[12] Furton KG, Wu L, Almirall JR, Optimization of solid-phase microextraction (SPME) for the recovery of explosives from aqueous and post-explosion debris followed by gas and liquid chromatographic analysis. J. Forensic Sci. **2000**; *45*, 857.

[13] Solid phase microextraction: A practical guide. (1999). S.A.S. Wercinski (editor). Marcel Dekker, Inc. New York, New York.

[14] Dean JA. Lange's handbook of chemistry. New York: McGraw-Hill, Inc. 1999.

[15] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cryst **1976**, *A32*, 741.