Evaluating HDEHP and HEH[EHP] Ligands for use in Polymer Ligand Films (PLFs) for Plutonium Extraction

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Introduction

There is great interest in developing new, field deployable alpha analysis techniques for nuclear forensics applications [1–4]. The current techniques are well established for radionuclide measurement; however, they are slow and labor intensive, requiring extensive radiochemical separations and purification prior to analysis. This paper describes a new analyte extraction technique using Polymer Ligand Film (PLF). PLFs were synthesized to perform direct surface sorption of analytes for direct counting using alpha-particle spectroscopy. The main focus of the new technique is to shorten and simplify the procedure for chemically isolating radionuclides for determination through a radiometric technique. Di(2-ethyl hexyl) phosphoric acid (HDEHP) and 2-ethylhexylphosphonic acid (HEH[EHP]) were examined for plutonium extraction. HDEHP PLFs were more effective in plutonium extraction than HEH[EHP] PLFs.

Background and Related Work

A thin film extraction method has been used by several authors to selectively extract analytes from a liquid medium [1–8]. This technique is similar to resin based extraction, where ligands are coated or fixed to a polymer to separate analytes from the solution. With this technique, what is typically a two-step process of column separation and electrodeposition can be combined into a single step, which greatly reduces the overall analysis time. The difference between the two methods is illustrated in Figure 1. Surbeck has reported the possibility of using MnO_2 thin film to extract radium from a water sample with a six-hour exposure time and directly measuring radium with alpha-particle spectroscopy [7]. The resolution of the alpha-particle spectrum was similar to the energy resolution of a typical electrodeposited source. Surbeck also prepared thin films out of commercially available resin beads for uranium extraction. The films were prepared by fixing finely ground resin beads onto a flat surface. Fifty percent of uranium was recovered within 4 hours, and 80% was extracted in about 20 hours [7]. The alpha-particle spectroscopy energy resolution was, however, poor in these samples; probably due to the unevenness of the film surface.

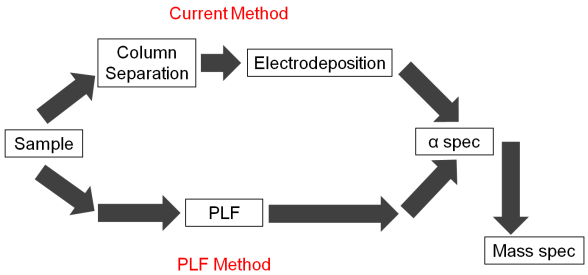

FIGURE 1: Diagram comparing conventional sample preparation method and PLF method

Our research group has demonstrated and reported the possibility of rapid separation of radionuclides using polymer ligand films (PLFs) [1–3]. An H_2DEH[MDP] based PLF has shown effectiveness in extracting plutonium from nitric acid solution [1–3]. Plutonium and americium were also effectively extracted using H_2DEH[MDP] based thin polymer film with an extraction time of only two hours [2,3]. In previous H_2DEH[MDP] studies, several extraction conditions were examined to find an optimal condition for plutonium and americium extraction. The first experiment indicated strong absorption of plutonium and americium by H_2DEH[MDP] based PLFs in a 0.1 M nitric acid solution [2]. The second study determined that out of several polymers, a polystyrene structure gave the best combination of analyte recovery and alpha-particle spectra resolution [3]. These ligands are commercially available and manufacture information shows high uptake of plutonium and uranium [9]. In addition to previously tested ligands, our research group has investigated the possible use of HEH[EHP] for plutonium extraction. HEH[EHP] is mainly designed for lanthanide separation; however, due to its similarity to HDEHP, it has great potential to be also effective for plutonium separation in PLF form.

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Experimental

The PLFs were prepared by incorporating ligands in a polystyrene structure. The stock solution was prepared by dissolving the ligands and polystyrene in tetrahydrofuran (THF). The films were prepared with a solvent casting method using a 40 mm diameter stainless steel substrate with a thickness of 2.0 mm. 1 mL of a stock solution was deposited to prepare a thin film. The deposited solution was dried at room temperature for at least 12 hours to evaporate THF and form a solid film. The PLF composition is described as the ratio between ligand and the entire solid mass. For example, PLF with one part ligand and one part polystyrene was assigned 1:2 (wt/wt) ratio. A detailed PLF preparation method had been published in previous works [1–3].

The PLFs were tested over 0.01 to 8M nitric acid solutions for analyte extraction capability. 2.5 to 3mL ^{239}Pu tracer solution was directly stippled on the PLF to cover the entire surface with an equilibration time of 3 hours before removing the solution. After 3 hours, the solution was removed and the PLF was thoroughly rinsed with deionized water to remove any nitric acid left on the surface. The PLF was then air dried to remove any water that may have been left on the polymer medium. The plutonium activity of each sample was measured with direct alpha counting to quantify the plutonium recovery by PLF.

Materials

HDEHP and HEH[EHP] were obtained from Eichrom Technology Inc. No further purification was done to the ligands. Aqueous solutions were prepared using nitric acid from Fisher Scientific, and ultrapure deionized water was obtained from a Barnstead Fi-Stream II Glass Still purification system. Tetrahydrofuran (THF) was obtained from Acros Organics. Polystyrene beads were obtained from Sigma-Aldrich. Polystyrene beads were not cross linked and the average molecular weight was 35,000. The ^{239}Pu tracer was obtained from Eckert & Ziegler Isotope Products Inc.

Alpha Spectroscopy

An Octet Plus system from Ortec, equipped with 900 mm^2 ion implanted silicon detectors, was used in the entire experiment performed in this study. The manufacturer's rated resolution for the detectors was 27 keV FWHM for ^{241}Am at 5.486 MeV energy. Each detector was calibrated for energy and efficiency using a secondary NIST traceable source.

Results and discussion

1:2, 1:5, 1:10, and 1:20 HEH[EHP] PLFs were prepared for the study but the 1:2 PLF was excluded from the experiment due to its film instability. The large mass of ligand hindered the polymer from solidifying, and the ligands were easily washed away from the film structure. The plutonium recovery by HEH[EHP] PLF showed some dependency both on the nitric acid concentration and the composition of the polymer film. Plutonium extraction was most effective with 1:10 PLF in all nitric acid solutions tested in the experiment. The plutonium recoveries by HEH[EHP] PLFs are plotted in Figure 2. The plutonium percent recoveries by 1:10 PLF range from 17 to 25%, but these were all within the standard deviation except for the 1M samples. One noticeable plutonium recovery characteristic of HEH[EHP] PLF is that the performance does not decrease at 8M nitric acid. All other ligands examined in previous experiments showed significant decrease in plutonium recovery at 8M nitric acid [1,10].

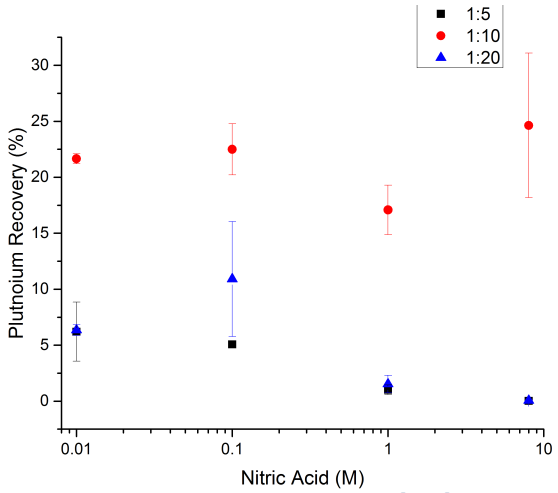

FIGURE 2: Plutonium recoveries by HEH[EHP] PLF in varying nitric acid concentrations

HDEHP PLFs were prepared in several different compositions from 1:2 to 1:20. The 1:5 PLF had given the best combination of plutonium recovery and resolution. The next closest PLF composition, 1:10, was ineffective in all nitric acid concentrations. The complete drop down of recovery was unexpected and the behavior of HDEHP was further studied by preparing PLFs with smaller ratio increments over and under the 1:5 PLF. A total of four new PLF compositions were prepared: 1:3, 1:4, 1:6, and 1:7. These ratios were selected to provide finer detail between 1:2 and 1:5 and between 1:5 and 1:10 to see whether the change in plutonium extraction is a sudden or gradual change.

The 1:6 and 1:7 PLFs showed slight improvement in plutonium extraction over 1:10 or 1:20 PLF in all nitric acid concentration. The plutonium recoveries were still low, below 10%, even with an increase in HDEHP ligand in PLF. Both the 1:3 and the 1:4 PLFs had similar spectrum tailing issues observed with the 1:2 PLF. The alpha-particle spectrum region of interest was adjusted accordingly to encompass the all of the counts from ^{239}Pu. The long peak tailing is undesirable in alpha analysis due to possible peak convolution caused by the tail. For the case of 1:3 and 1:4 PLFs, plutonium

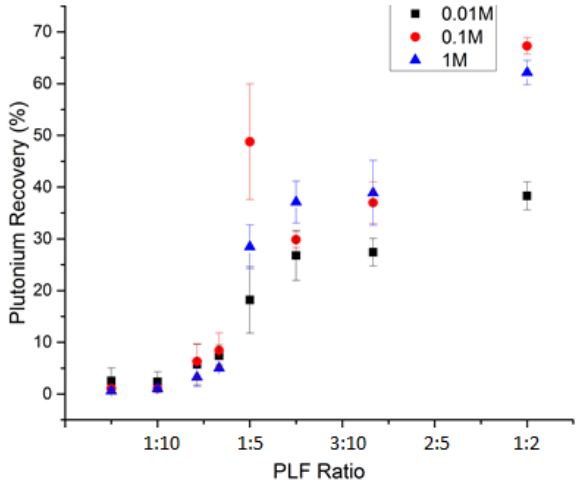

FIGURE 3: Plutonium recovery by HDEHP PLF as function of PLF composition

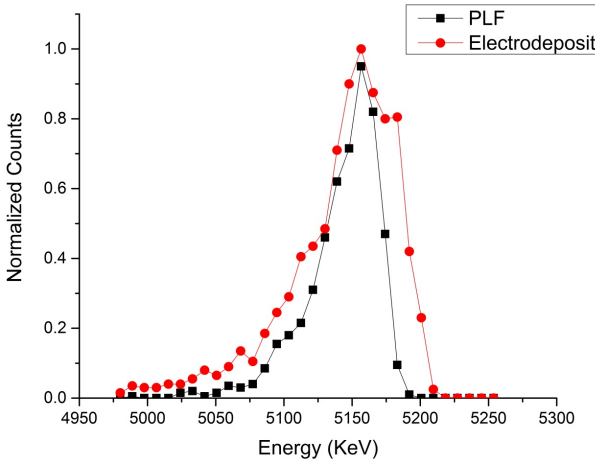

FIGURE 4: PLF and electrodeposition sample alpha spectra comparison

recoveries generally fell between 1:2 and 1:5 in all nitric acid concentration except for 0.1M.

In 0.1M nitric acid, 1:5 still had higher plutonium recovery than either 1:3 or 1:4 PLF. The plutonium recoveries were plotted as function of PLF ratio in Figure 3 to better show the recovery transition as the function of PLF ratio.

There was a sudden plutonium recovery efficiency change from 1:6 and 1:5 PLF. It seems to be that 1:5 is a transitioning point from low to high recovery. This greatly suggests that ligands have to reach a certain mass compared to the polymer to become available for analyte extraction. The behaviors were similar for all three nitric acid concentrations shown in Figure 3. In 0.01 M and 1 M nitric acid, the plutonium recovery reached a plateau between 1:3 and 1:4 PLF before achieving the highest plutonium recovery with 1:2 PLF. In 0.1M nitric acid, however, plutonium recovery spiked at 1:5 PLF then significantly decreased at 1:4 PLF. Plutonium recoveries then start to linearly increase from 1:4 to 1:2 PLF. The 1:5 PLFs consistently had large standard deviations with 0.1 M nitric acid. The standard deviation could be a result of slight inconsistency in the PLF composition. The 1:5 PLF is right at the transition point and a slight change in ratio may dramatically change the plutonium recovery.

The PLF alpha spectra showed similar resolution as the samples prepared through electrodeposition method. The similarity between the PLF and the electrodeposition sample spectra can be also seen in a visual inspection of the plotted data. Figure 4 was plotted with normalized count data from PLF and electrodeposited samples.

Conclusions

HDEHP PLF plutonium extraction was higher than HEH[EHP] PLF. The highest recovery for HEH[EHP] was only about 25% compared to 49% for HDEHP. However, HEH[EHP] was more consistent in plutonium recovery over the entire nitric acid concentration studied. The PLF method greatly saved analysis time in a laboratory setting, combining column separation and electrodeposition steps into a single step. The overall analyte recoveries by PLFs were lower than typical electrodeposited samples. However, the new method has a great potential to be deployed as a screening tool to decrease the number of samples required for more extensive analysis. The reduction in time and simplified procedure make this technique ideal for post-detonation emergency response.

Future work is planned to perform more detailed studies with respect to elimination of interference of other alpha-emitting radionuclides, such as ^{241}Am, to show the effectiveness of PLF in selectively extracting plutonium over other interferences.

Acknowledgements

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