

Novel Method for Rapid Extract of Radionuclides Using Polymer Ligand Film for Nuclear Forensics Applications

J. Rim^{*†}, D. Peterson[†], E. Gonzales[†], C. Armenta[†], and K. Ünlü^{*†}
*Pennsylvania State University, [†]Los Alamos National Laboratory

Introduction

Accurate and fast determination of radionuclides activity in a sample is critical for nuclear forensics analysis. Radioanalytical techniques are well established for radionuclides measurement; however, they are slow and labor intensive, requiring extensive radiochemical separations and purification prior to analysis. With these limitations, there is great interest for a new technique to rapidly process samples. This poster presents a development of Polymer Ligand Film (PLF) for rapid extraction of plutonium and uranium. PLF is a thin polymer medium with ligands incorporated onto its structure to enable selective extraction of analytes from a solution. The PLFs developed in this research were designed to facilitate fast isolation of radionuclides from solutions for screening samples. The main focus was to shorten and simplify the procedure for separating radionuclides from solutions onto a surface appropriate for radiometric counting. To achieve this goal, PLFs were synthesized to perform direct sorption of analytes onto its surface for direct counting using radiometric techniques. A diagram comparing the classical method and PLF technique is shown in Figure 1. The new technique combines column chromatography and electrodeposition into a single step for samples.

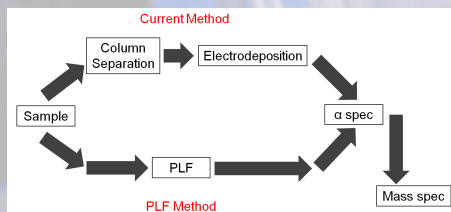


Figure 1 Diagram comparing conventional sample preparation method and PLF method

Method

Materials

- Bis(2-ethylhexyl) methanediphosphonic acid ($H_2DEH[MDP]$) was obtained from Eichrom Technology Inc
- Polystyrene beads were obtained from Sigma-Aldrich.
- Tetrahydrofuran (THF) was obtained from Acros Organics.

Alpha Spectroscopy

- An Octet Plus system from Ortec, equipped with 900 mm² ion implanted silicon detectors.
- Each detector was for calibrated energy and efficiency using a secondary NIST traceable source.

PLF Preparation and Experimental Conditions

- Polymer ligand films were prepared by incorporating $H_2DEH[MDP]$ in the polystyrene structure.
- The stock solution was prepared by dissolving the ligands and the polystyrene beads in Tetrahydrofuran (THF).
- The solution was directly deposited onto a 40 mm diameter stainless steel substrate then dried.
- 1:5, 1:10, 1:15, 1:20, and 1:25 (wt/wt) $H_2DEH[MDP]$ PLFs were tested over 0.01 to 8M nitric acid solutions.
 - 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 (w/w) ratio.
- The physical appearance of the PLFs changed depending on the amount of ligand in the film.
- ²³⁹Pu tracer was directly stippled on the PLF surface, allowing the analyte to equilibrate for 3 hours before removing the solution.
- The plutonium activity of each sample was measured by direct alpha counting to quantify the plutonium recovery by $H_2DEH[MDP]$ PLF.

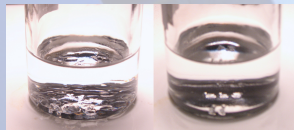


Figure 2 PLF stock solution (A) with un-dissolved polystyrene, (B) with polystyrene completely dissolved



Figure 3 PLF prepared with solvent casting method

Acknowledgements

This research was performed under the Nuclear Forensics Graduate Fellowship Program which is sponsored by the U.S. Department of Homeland Security, Domestic Nuclear Detection Office and the U.S. Department of Defense, Defense Threat Reduction Agency. This material is based upon work supported by the U.S. Department of Homeland Security under Grant Award Number, 2012-DN-130-NF0001-02. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

Results

Pu Sample Recovery

- 1:10, 1:15, and 1:20 PLFs were all effective in plutonium extraction from 0.01 to 1M nitric acids.
- The highest recovery for these PLFs all occurred at 1M tracer solution.
- The percent recoveries were 50.44 ± 8.27 and 47.61 ± 7.17 for 1:10 and 1:20 PLF, respectively.
- The plutonium recovery for 1:5 PLF was noticeably lower than the other PLFs from 0.01 to 1M.

U Sample Recovery

- The uranium extraction behavior was entirely different than the plutonium extraction.
- Neither 1:10 nor 1:20 PLF was effective in uranium extraction over all nitric acid ranges tested.
- 1:5 PLF showed the highest recovery of ~30% with 1M nitric acid and 22.5% with 0.1M nitric acid.
- 1:5 PLF, uranium can be co-extracted along with plutonium at 0.1 or 1M nitric acid. At the same nitric acid concentration, 1:20 PLF can be used to extract plutonium over uranium.

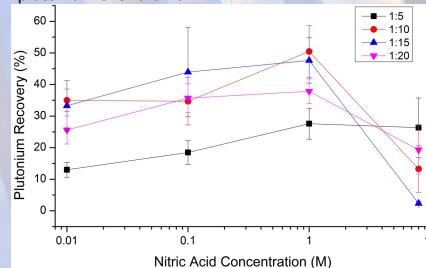


Figure 4 Plutonium recovery

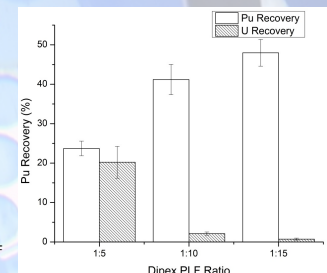


Figure 5 Pu & U recoveries with PLF

Mass spectroscopy Analysis

- Analyte + ligand complexes were removed from PLF with isopropanol.
- Hydrogen peroxide and sodium vanadate were added to destroy the plutonium complexes.
- The ²⁴⁰/²³⁹Pu ratio measured with TIMS were accurate when compared to the known values.

Environmental Sample Analysis

- Analytes from soil samples were first leached with nitric acid.
- Nitric acid solution was filtered then stippled directly onto PLF to extract plutonium.
- Water samples were first treated with nitric acid, then plutonium was extracted with PLF.
- PLF was able to extract Pu from environmental samples with minimal sample preparation.

Conclusions

The PLF technique simplified the procedure and offered considerably reduced sample analysis time. The entire sample preparation to analysis was done within one to two days. The classical method takes two days to a week in comparison. The technique also requires minimal chemicals and it is also field deployable. The reduction in time and simplified procedure make this technique ideal for post-detonation nuclear forensics. Sample processing procedures for alpha spectroscopy and mass spectroscopy were established. Environmental samples were effectively processed with the PLF system using the established procedure.