

5-10-2011

Using polymer ligand films for rapid radiochemical analyses

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**Water Resources Program
Professional Project**

Using polymer ligand films for rapid radiochemical analyses

by

Crystal L. Tulley-Cordova

LA-UR 11-01496

Committee

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A Professional Project Submitted in Partial Fulfillment of the Requirements
for the Degree of **Master of Water Resources with Hydroscience concentration**

Water Resources Program
The University of New Mexico
Albuquerque, New Mexico
May, 2011

Committee Approval

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Acknowledgements

I want to thank Dr. Bruce Thomson, Dr. Steve Cabaniss, and Dr. Dominic Peterson for their time and efforts to help me succeed. I especially want to thank the people at Los Alamos National Laboratory for their endless support in helping me complete my academic goals.

Special thanks to Dominic Peterson, Edward Gonzales, Claudine Armenta, Hakim Boukhalfa and Jaclyn Herrera. I attribute my success to the support given to me by family and friends.

With heartfelt gratitude, I thank Mom, Dad, Nikki, and Monique for being my biggest support. I want to thank my husband, Victor, for his caring, kind and loving attributes.

Abstract

Existing procedures for radiochemical analysis of environmental samples involves extensive laboratory preparation requires chemical separations that are time consuming, labor intensive to remove interferences and impurities associated with the sample matrix. Technology developed in this project reduces turnaround time, labor and supplies needed to examine radionuclides in water samples. The thin film technique can be used as a screening method. A solution including an extractive ligand and polymer are used to create a thin film to concentrate radionuclides from solution. In this project, several ligands, polymers, solvents, thin film types, and extraction procedures were examined. The polymer ligand thin films were analyzed using alpha spectrometry. Using the polymer ligand thin film method decreased sample preparation time. The thin film extraction and analysis procedure allows rapid and sensitive monitoring of select actinides in tap water with the potential for use with surface and groundwater systems in the field. The thin film method is a proof of concept of polymer ligand film extracting radionuclides; we have demonstrated our capability for detection of Plutonium in laboratory samples at concentrations of 2.5×10^{-1} Becquerels/Liter (Bq/L).

The thin film used for extraction and collection was made using a polymer and ligand solution which was deposited and dried on a stainless planchet. The suitable combination of polymer, ligand and solvent solution included polystyrene, Dipex®, and tetrahydrofuran. After evaporation, polystyrene and Dipex® remain on the stainless steel planchet.

Introduction

There are presently several ways to determine radiological constituents in different environmental media, (water, soil, air). Different agencies suggest different methods for radiological environmental samples. The United States Environmental Protection Agency has methods used for measuring radionuclides in water, EPA 402-R-07-007 (15). ASTM International, also known as the American Society for Testing and Materials, has two methods related to the standard test method related to alpha and beta particles in water; ASTM D1943, and D1890 (16). The Standard Methods for the Examination of Water and Wastewater has a 7000 series that includes multiple methods to examine radioactivity (17).

There are multiple processes to examine and detect radioactivity in environmental samples. The EPA-402-R-07-007 method is extensive, time consuming and requires multiple supplies, reagents, and standards. EPA-402-R-07-007 can examine alpha, beta, and gamma unknown and known samples. The method process requires a sample amount of 20 mL. The disadvantage to this process is it is not ideal for low concentrations of radioactivity. The ASTM processes includes ion exchange and electrodeposition processes. The drawback is the processes are time extensive. Standard Methods examines for Radium, Radon, Strontium, Tritium, radioactive Iodine and Cesium; a disadvantage is it does not include a procedure for Plutonium examination. The mentioned methods conduct sample preparation in a laboratory, and analysis of radionuclides follows the sample preparation process.

Radioactive elements emit radiation, which makes them easy to detect. The detection method depends on the radiation emitted, but is generally either alpha or gamma. Gamma is penetrating, while alpha requires sample preparation to properly present the analyte to the detector and obtain sufficient detection efficiency. Conventional analyses of radionuclides

involve extensive chemical sample preparation prior to analysis by alpha and gamma spectrometry [1]. Sample preparation frequently involves chemical precipitation, chemical extraction, or ion exchange separation. Ion exchange is a process of purifying, separating, and decontaminating an ion containing aqueous solution using polymeric ion exchange (IX) resins. Liquid-liquid extraction is another type separation; it separates, concentrates and purifies radionuclides from aqueous samples.

Standard radioanalytical procedure for alpha spectroscopy (12, 13) for radionuclide extraction from environmental samples includes ion exchange (Figure 2) and liquid-liquid extraction. The ion exchange methods use column formats (Figure 3). Liquid-liquid extraction uses two liquids, usually water and a solution of interest from which the analytes of interest are sought. The organic liquid extractant is stationary in the pores of a polymer material. The success of liquid-liquid extraction is when the analyte of interest is selectively recovered on the resin while other matrix species and interferences are washed away in the mobile aqueous phase. The analyte of interest selectively adheres to the surface of the resin due to Coulombic forces. The resin surface has a negative charge and the analyte has a positive charge (7). After the wash step, the analytes are eluted by an acid or by changing the molarity of the solution (18).

The classical separation methods of ion exchange and liquid-liquid extraction are effective [2], but they are time consuming and labor intensive [18]. For example, a standard analytical method would require sample preparation in a liquid, usually a high concentration of nitric acid [13]. Each analyte would then need to be separated from the solution (in an ion exchange column) and collected [2]. The collected radioactive analyte would then need to be electrodeposited on a stainless steel planchet and counted. A method with a reduced turnaround time, less labor intensive and cost efficient to examine radionuclides in environmental samples is

needed. The need is for a screening method for radioactive isotopes. Ideally this method would be field deployable, so that extraction separation and concentration can occur in the field. Once the analytes are extracted and collected, they can be concentrated in a thin film that can be counted directly without any further sample processing. The thin film is directly counted using an alpha spectrometer. Using a thin film extraction process decreases the labor and time needed for sample preparation.

A method was developed in this project that incorporates a polymeric ligand into a thin film structure. The polymer ligand thin film selectively extracts specific radionuclides from an environmental sample which reduces interferences and concentrates analytes for improved counting. Figure 1 is a diagram of radionuclide extraction from solution to thin film. It shows radionuclides in solution and target radionuclides captured by the ligand onto the active sites of the polymer ligand thin film surface.

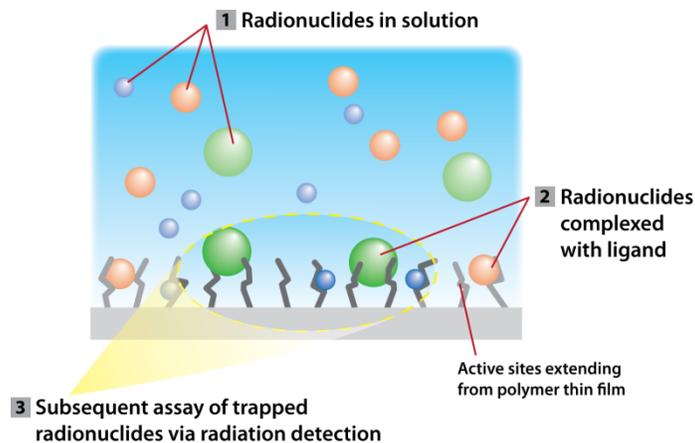


Figure 1 Extraction of radionuclides [3]

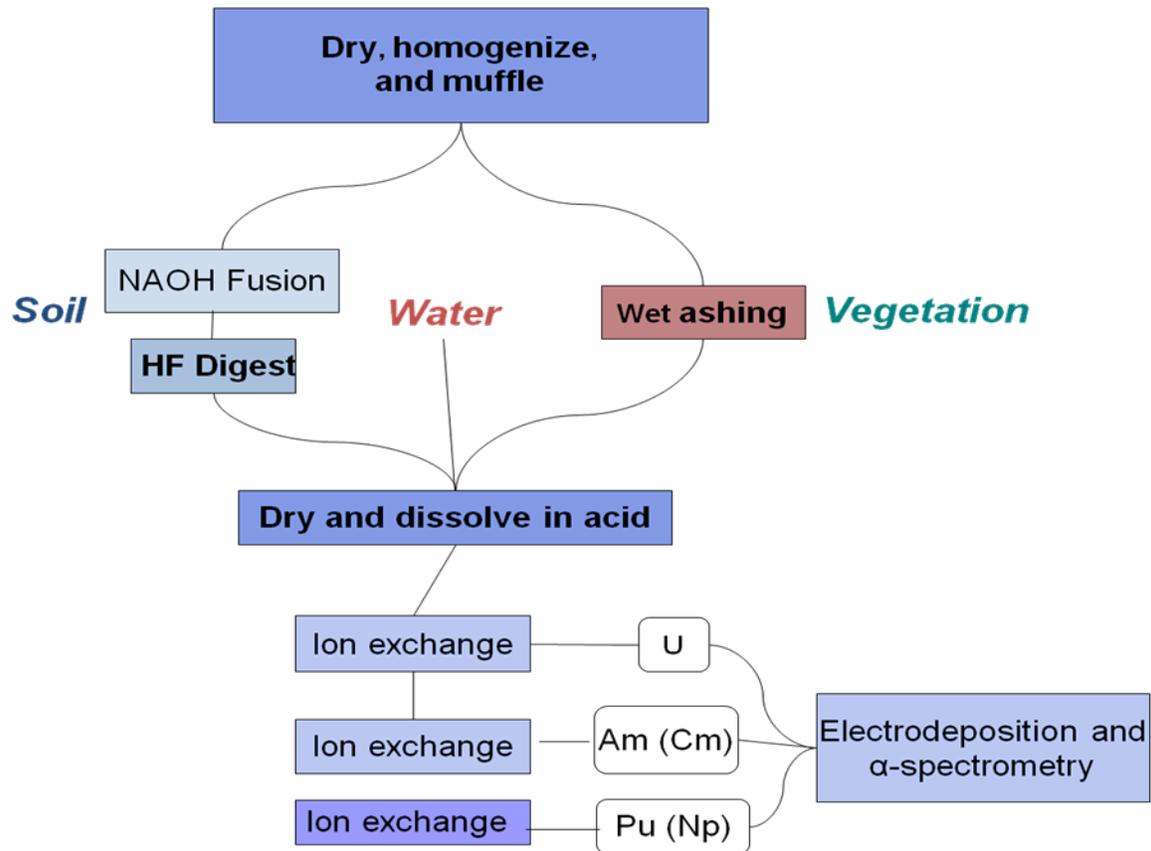


Figure 2 Total sample preparation [3]

After ion exchange or liquid-liquid extraction the recovered radionuclides are transferred onto a surface plate using an electrodeposition method (Figure 3). In Figure 3, the first picture on the left has one resin column and the picture immediately to the right has three resin columns stacked in tandem. The difference is the resin type. Some resins are selective for different radionuclides and others are inclusive of all radionuclides. Resins for concentrating multiple radionuclides are regenerated by changing the molarity concentration using hydrochloric or nitric acids. The resin choice is dependent on the radionuclide(s) of interest. The plated sample of a specific radionuclide is then counted using alpha spectrometry. The total time to process a sample and measure its alpha spectra is approximately one to two days (12). For monitoring

purposes, the radiochemical separation and detection methods must be rapid so that the results will be timely (18).



Figure 3 Ion exchange process, extraction chromatography, electrodeposition, and electrodeposited steel plate

The thin film method is rapid, cheaper, and less labor intensive (13). Direct collection of radionuclides on the surface of a thin film allows the film to be directly analyzed by alpha spectrometry without a prior separation process. This allows rapid sample analysis and isotopic determination. The thin film decreases the labor and supplies cost associated with the separation process. Thin film extraction would facilitate radionuclide sampling and analysis of environmental samples.

The concentration of acid affects the uptake of the radionuclide. At differing molarities different radionuclides are absorbed. For example with Dipex®, a 0.1 M solution retains more Plutonium (IV) than a 10 M solution (see Figure 4). Figure 4 represents data developed by Horowitz using hydrochloric acid (5). The x-axis of Figure 4 is the molarity and the y-axis is representative of amount of actinide able to be absorbed by the Dipex®. The thin film method

uses nitric acid because it is less corrosive for stainless steel, the support used for the thin film. The thin film study uses 0.1 M nitric acid solution to provide an optimal environment for Plutonium extraction.

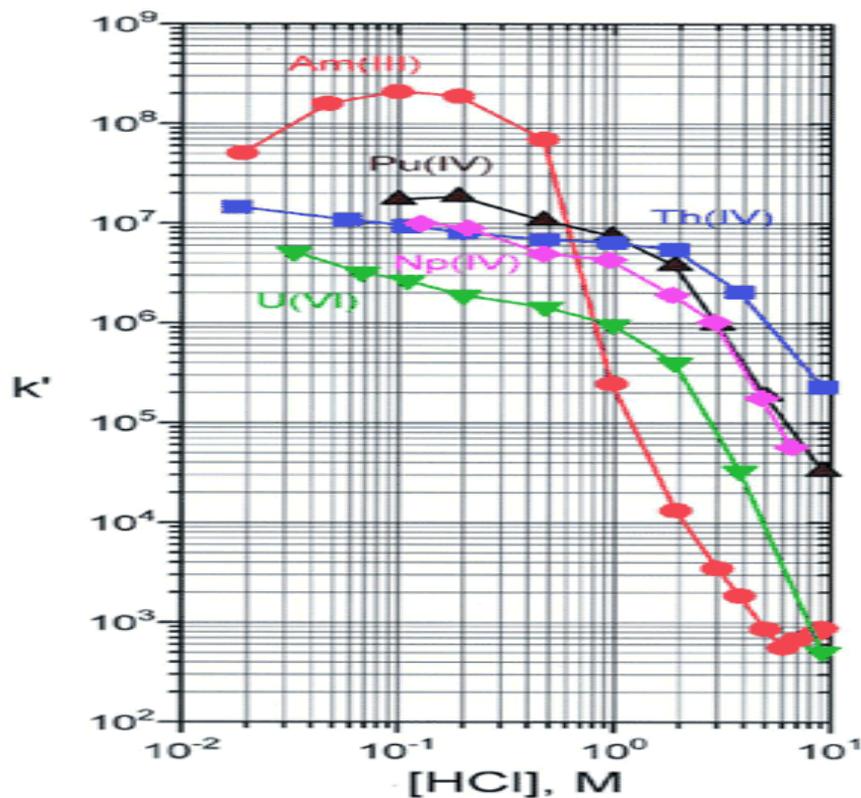


Figure 4 Uptake of actinide elements by actinide resin for ion exchange [5]

In this study, combinations of different types of thin films were evaluated using several different ligands, polymers, and solvents. The polymer ligand solutions were used to create a thin film on the surface of stainless planchets. The polymer ligand thin film solution was deposited, using a pipette, directly onto the planchet. Once the radionuclides were extracted and collected, the polymer ligand thin film was counted directly with no further sample processing.

Literature Review

Polymer Ligand Film Method

Existing radioanalytical methods for determination of alpha emitting radionuclides are based on the separation and pre-concentration of selected elements prior to radiation detection [7, 8]. The current process is labor and time intensive. Each analyte of interest must be individually separated from solution with use of an ion column and collected. The collected analyte would then go through a process known as electrodeposition in which the radioactive analyte is mounted onto a stainless steel plate. Electrodeposition occurs after sample preparation, such as ion exchange. Ion exchange purifies a sample for an analyte of interest. Electrodeposition is also called electroplating, and the two terms are used interchangeably. Electrodeposition is the process of producing a coating, usually metallic, on a surface by the action of electric current. The deposition of a metallic coating onto an object, such as a stainless steel planchet, is achieved by putting a negative charge on the object to be coated and immersing it into a solution which contains the metal to be deposited. The metallic ions carry a positive charge and are thus attracted to the planchet. When they reach the negatively charged planchet, it provides electrons to reduce the positively charged ions to a metallic form. After completion of the process, the metal, radioactive analyte, is deposited on the planchet, and it can then be counted [10, 11].

Rapid sample preparation is possible by direct sample preparation, and counting the polymer ligand thin film directly after radionuclide extraction helps with rapid sample analysis. Some studies have shown selective extraction in polymer ligand thin films for non-radioactive analytes [6]. More recent studies have shown potential for thin films to be used for radioactive analyte extraction. One study used a finely ground IX resin and fixing it with a binder to a flat surface [12]. The binder is the physical structure to which the extractive ligand adheres to a

surface. Another method used a thin film made of magnesium oxide to extract radium from solution and analyzed by alpha spectrometry [13]. Previous methods provide minimal opportunities for improvements in thin film preparation and limited the range of radionuclides extracted for analysis. Constraints in the physical characteristics minimize possible adjustments for performance improvements. A method was introduced to use inorganic ligands to create a thin film structure to extract radioactive analytes [7]. Use of a thin film surface allows for reduction and minimization of interferences. Collection of radioactive analytes on the surface allows the ligand surface to be directly analyzed by alpha spectrometry.

Use of an extractive ligand thin film for extraction of radioactive analytes has advantages. There is a wide variety of possible extractive ligands for uptake of single or multiple radioactive analyte(s). An ideal extractive ligand would be one that has ability to extract multiple radioactive nuclides from solution; however, extraction of radionuclides is also dependent on many other conditions such as the pH of a solution and ionic strength. For our process, an extractive ligand that has rapid kinetics, high exchange capacity, and the potential for surface chemistry manipulations is a good match. Many extractive ligands have been developed and are available commercially. We use Dipex® because of its versatility to be used for different analytes, and its ability to work in different oxidation states. Dipex® is an extractive ligand for extraction of actinides from an aqueous solution (Figure 5) [5]. Dipex® is an actinide resin used for monitoring actinides in aqueous discharges. Dipex® works best with oxidation states in the tri-, tetra-, and hexa-valent states. Dipex® has rapid uptake kinetics for actinides at moderate nitric acid concentrations.

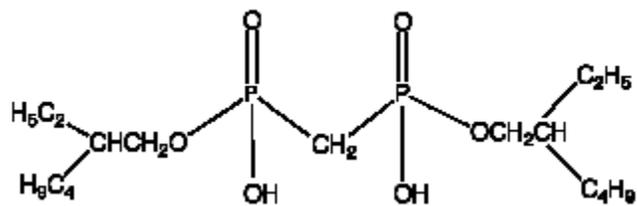


Figure 5 Chemical structure of Dipex®

In this study, five different polymer ligand substrates have been evaluated. All evaluate the extractive ligands Dipex® and B-DGA (Figure 6), an alternative extractive ligand. B-DGA is another actinide resin; it shows high affinity for plutonium and americium. The polymer ligand solutions are created using poly (methyl methacrylate) (PMMA), polyvinyl butyral (PVB), polyvinyl acetate (PVA), polystyrene (PS), and polyvinyl pyrrolidone (PVP), in addition with Dipex® or B-DGA using tetrahydrofuran as a solvent for the polymer and ligand. The prepared polymer ligand solution was then deposited onto a stainless steel planchet to create the thin film. The polymer ligand thin films were then used to extract Plutonium from aqueous solution. After radioactive analytes were collected onto the polymer ligand thin film, the polymer ligand thin film was counted directly using alpha spectroscopy.

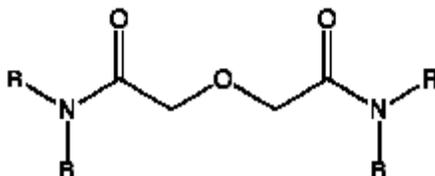


Figure 6 Chemical structure of Branched DGA

Analysis of polymer ligand films

Environmental analysis of actinides using polymer ligand films with counting by alpha spectrometry can require counting times of 24 to 96 hours. The longer count time is required to achieve lower detection limits and better counting statistics. It mainly allows for confidence that

the measured counts are real and above background. For higher concentrations, shorter count times can be used. For example, a sample with 1.67×10^5 Bq would need a few seconds to count.

An alpha spectrometer measures the number of alpha disintegrations per time and the energy associated with these decay events. In most cases counts per minute (CPM) is the measurement unit most used. The CPM is not corrected for detector efficiency or the amount of the actinide recovered from the sample or geometry effects.

The alpha decay rate measured in disintegrations per minute (DPM) is a measure of radioactivity that is corrected for efficiency but not necessarily yield. It is an indicator of the number of radioactive decay events on a counting surface that decay in one minute. The count is directly related to the efficiency of the detector. The decay rate is then referenced back to the radioactive sample and corrected for yield through the sample preparation. Chemical recovery or yield is a measure of the fraction of radioactive material removed from the sample during sample preparation. It is determined by the amount removed from the sample and counted by the alpha spectrometer divided by the true amount in the sample. This is loosely referred to as recovery or yield and expressed as per cent recovery. Fettweis et al. (2003) present a discussion of the theoretical and practical aspects of alpha counting and spectrometry (14).

When talking about detector sensitivity the term used is called the detection limit (DL) and is related to the background counts for the detector. The detection limit of a detector can be calculated many ways and is usually associated with the confidence required for a measured response when measurement is near the background of the detector.

Background radiation is the natural or artificial radiation that will contribute to a false response. This can be controlled to some extent during sample preparation by sample preparation processes that selectively concentrate analytes of interest while preventing

accumulation of interfering constituents. The background measurement in itself does not preclude a good measurement it just limits the sensitivity of the detector. High backgrounds limit the sensitivity of the measurement. Limiting the presence of interfering constituents and reducing background interference is important to achieve low method detection levels.

The DL for the entire sample process is called the Method Detection Level (MDL). The MDL for a sample is based not only on the DL for the counters but also on the yield for the sample preparation process. MDL is different for each analyte and each method because in most cases DL for different detectors is not the same and the yield for each sample process is not identical. MDL is unique to each analytical procedure sample counted because each sample is different. When an MDL is provided for an analytical procedure it is usually the average MDL for the sample process or the MDL for the theoretical best sample process i.e. the best detector, lowest background, highest detector efficiency, and assuming 100% sample processing yield (14).

Experimental

Materials and instrumentation

The polymers, ligands and solvents used were analytical grade. Stabilized tetrahydrofuran (THF), poly (methyl methacrylate) (PMMA), polyvinyl butyral (PVB), and polyvinyl acetate (PVA) were obtained from Acros Organics (Fair Lawn, New Jersey), polystyrene (PS) was obtained from Sigma-Aldrich (Milwaukee, WI), polyvinyl pyrrolidone (PVP), hydrochloric acid, and nitric acid, methanol, ethanol, and isopropanol were all obtained from Fisher Scientific (Fair Lawn, WI and Pittsburgh, PA), Dipex®, CMPO, Aliquat 336, and Branched DGA extractant were obtained from Eichrom Technologies Inc. (Darien, IL). National Institute of Standards and Technology traceable Plutonium-239 was obtained from Isotope Products Laboratories (Valencia, CA). Deionized water was used for solution preparation and rinsing. Stainless steel planchets used were machined on-site at Los Alamos National Laboratory. Analyses were counted on an Ortec (Oak Ridge, TN) Octet Plus Alpha Spectrometer.

Preparation of polymer ligand films

In order to find successful polymer ligand solution different combinations of polymer, ligand, and solvent were tested. The first attempt was to find a suitable solvent. The proposed solvents included methanol, ethanol, isopropanol, and THF. The solvent had to be in a liquid form and be able to dissolve a solid, the polymer and ligand. The method tested two forms of polymers; powder and beads. The ligand was obtained as a viscous liquid or in powder form. Solubility experiments were done using polymers in different solvents. The polymers used

included polyvinyl pyrrolidone (PVP), poly(methyl methacrylate) (PMMA), polyvinyl butyral (PVB), polyvinyl acetate (PVA), and polystyrene. The synthetic polymers selected were used because they are macromolecules composed of repeating chemical structures. They are easy to use, process, and dissolve. The solutions were made using 1g of the polymer and 15g of the solvent. The solutions sat over night, to allow the polymer to dissolve into solution. The polymers that dissolved into THF were PMMA and polystyrene. Isopropanol, methanol, and ethanol did not dissolve the polymers.

The next step after the solvent was found was to create and mix combinations of polymers and ligands in a solvent solution. N-Methyl-N,N-dioctyloctan-1-ammonium chloride (Aliquat®336), N,N,N',N'-tetrakis-2-éthylhexyldiglycolamide (DGA Branched), P,P' di(2-ethylhexyl)methanediphosphonic acid (Dipex®), and Octyl(Phenyl)-N,N-Diisobutylcarbonoylmethyl-Phosphine Oxide (CMPO) were used as ligands in combination with PMMA or polystyrene in THF solvent solution. The ligands were chosen for their high absorption and extraction affinity for radionuclides.

Aliquat®336 has a molecular weight of 404.16; its chemical formula is $C_{25}H_{54}NCl$ (Figure 7). Aliquat®336 can be used for solvent extraction, waste treatment, adhesion promoter and surface curing aid, anti-static agent, discoloration, and deodorization (11).

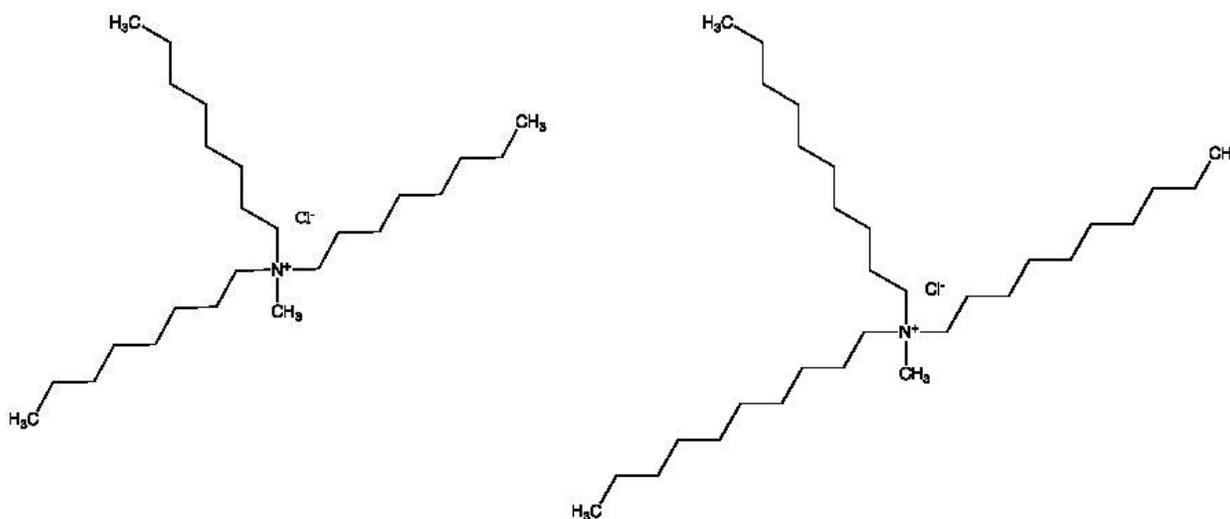


Figure 7 Chemical structure of Aliquat 336

Branched DGA's chemical formula is $C_{36}H_{70}O_3N_2$ (Figure 6); its molecular weight is 578.96. Branched DGA's applications include actinide separation (5). The chemical formula for Dipex® is $C_{17}H_{38}P_2O_6$ (Figure 5); its molecular weight is 400.43 (5). Dipex® is used for analyte extraction in biological and environmental samples (5). The molecular weight of CMPO is 407.57, and its chemical formula is $C_{24}H_{42}NO_2P$. CMPO is used as an extractant ligand (11).

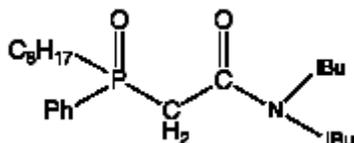


Figure 8 Chemical structure of CMPO

The chosen type of polymer ligand thin film mixture was decided based upon physical appearance of the thin film. The thin film was made of a polymer and a ligand; and plated onto the planchet surface as the solvent evaporated. The success of the thin film was determined by the physical appearance of homogeneity and uniformity of the thin film and the bonding, stability, and strength of the polymer and ligand.

The ideal polymer ligand thin film combination was homogeneous, smooth, and consistent across the surface of the planchet. The results of the different thin film formulations varied. The physical appearance did not determine the reaction when put into solution. For example, Aliquat 336 dissolved when an acidic solution was put onto the thin film. CMPO with two different polymer combinations did not make it to the next step after the thin film was formed; when dried the thin film flaked and did not adhere to the stainless steel surface. Dipex® and DGA Branched ligands worked best to create a thin film with the polymers, PMMA and polystyrene, in THF. It did not flake after trying and it did not dissolve after placement into solution, or when an acidic solution was put on the thin film surface.

There were two polymer ligand thin film possibilities the polystyrene with Dipex® and polystyrene with BDGA; the next step was to determine which worked best to extract radionuclides from environmental samples. Figure 9 depicts the physical appearance of a polystyrene and Dipex® thin film in comparison with an electro-deposited planchet and dime coin.

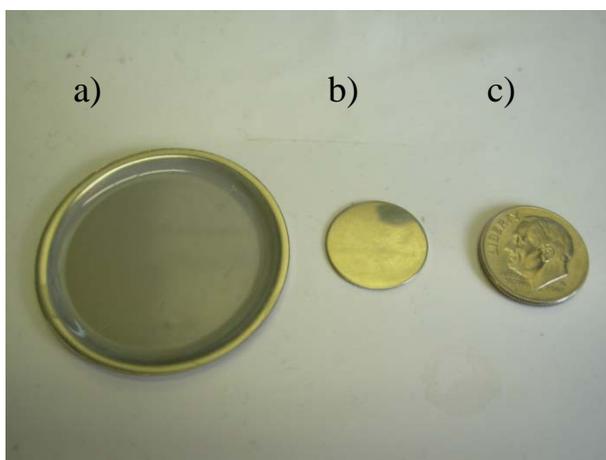


Figure 9 a) thin film planchet, b) electro-deposit planchet, and c) dime

The ratio of concentration of polymer and ligand to THF were 1:1, 1:5, 1:10 (mass/mass). The concentration of Dipex® to polystyrene was 1:1, 1:5, 1:10 (mass/mass). In order to make

the polymer ligand thin film, the solvent solution was deposited onto the 40 millimeter diameter stainless steel planchet surface. The solvent solution was deposited using a 1mL transfer pipette onto the planchet in a chemical hood. The THF evaporated from the polymer ligand thin film at room temperature for 24 hours.

Thin film types

The ligands investigated were Dipex®, Branched DGA, and the possible polymers were PMMA, polystyrene, and THF was the best solvent. The next step was to determine the type of thin film that would have the highest recovery. A thin film has to be homogenous, uniform, and smooth to assure that the radionuclides are spread uniformly across the surface. Homogeneity, uniformity, and texture have an impact on the counting. A detector will not count correctly if one part of the thin film is different from the rest of the thin film. The polymer ligand thin films were generated using various combinations of polystyrene, PMMA, Dipex®, Branched DGA and THF. Using these different combinations produced a thin film that was flat, thin, and homogenous. Different combinations of polymers and ligands were used to make thin films by using spin coating and stippling planchets, filters and membranes.

Spin coating was done using a Chemat Technology spin-coater. A 1mL of the polymer ligand solution was deposited on the spin coater at an initial speed of 5,000 rotations per minute (RPM) for 12 seconds, and then continued on a speed of 3,000 RPM for 20 seconds. The reason for a faster initial speed is because of the rapid drying of the polymer ligand thin film. The difficulty with using the spin coating method for creating thin films is the homogeneity and smoothness of the thin film.

Stippling the thin film onto a planchet works the best. 3mLs of the polymer ligand thin film solution is deposited onto the stainless steel planchet and air dried for a day in a hood. The

stippling method was also used to try and make polymer ligand thin films with filters and creating membranes, but proven to be unsuccessful. A polystyrene filter was dipped into the polymer ligand thin film solution and air dried. The filters curled and made it difficult to count in the alpha counter. The polymer ligand thin film membrane attempts were unsuccessful because a physical structure (a ring) was difficult to adhere to. The bond of the thin film to the ring was weak and would break the polymer ligand thin film apart.

Thin films were made using 2 mL of the polymer ligand solution. The polymer ligand solution was pipetted onto the stainless steel planchet. The polymer ligand thin film solution on the planchet air dried overnight. The diameter of the stainless steel planchet used for the size of the thin film was based on the size of the alpha detector.

Study of extraction mechanisms

Comparison of extraction mechanisms was conducted to determine if mixing would impact the amount extracted. Three different mixing regimes were provided: stir, non-stir, and drip (Figure 10). This study was conducted at time intervals of 0.5, 1, 2, 4, 8, 16, 24, and 48 hour(s). The non-stir study was conducted for 2, 8, 16, 24, 48, 72, and 96 hours. The drip study was conducted for 2, 4, 6, and 8 hours. Mixing does affect the amount extracted by the thin film.

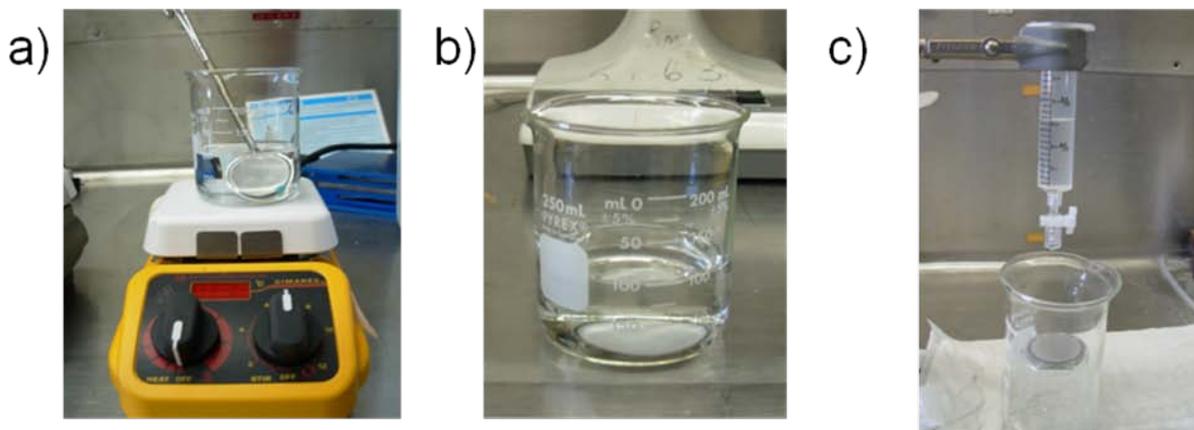


Figure 10 Mechanisms a) stir b) non-stir c) drip

The amount of radionuclide extracted varied with time for the three mixing regimes. The result of mixing regimes is discussed in the results section.

Stir

The stirring mechanism was conducted using a magnetic stirring plate and Teflon coated stirring bar. The experiment was conducted for eight different times; 0.5, 1, 2, 4, 8, 16, 24, and 48 hours. The thin film was in a fixed location and tilted at a 45 degree angle with the thin film facing the vortex. The thin films were fully submerged in the solution. The stirring rod created a vortex and the solution would constantly move past the planchet. After taking the thin film from solution; it was triple rinsed with deionized water and placed on lab bench top to air dry.

Non-stir

The thin film was placed face up in an unmixed beaker. This position was chosen because there was no bulk fluid movement and therefore the thin film did not need to be placed at a forty five degree angle. Seven different times were evaluated; 2, 8, 16, 24, 48, 72, and 96 hours. After completion of the study, the thin film was triple rinsed with deionized water and placed on lab bench top to air dry.

Drip

The drip extraction mechanism can be comparable to a dripping water faucet with a cup catching the dripping water. In this study, a syringe with a luer lock tip was used. Under the tip the thin film was placed to catch the sample. The 100 mL volume consistently rotated onto the

thin film. The thin film planchet has a holding volume of 3 mL, and the remaining amount would flow off the side of planchet and re-circulated to the syringe. Planchets were prepared using drip times of 2, 4, 6, and 8 hours. Once the sample was completed with respect to time; it was triple rinsed with deionized water and placed on the lab bench top to air dry.

Results

Solubility Tests

Several tests were conducted to determine solubility of the ligand supports in the organic solvents. A half gram of polystyrene, PVA, PVP, PVB, PMMA was placed in individual solutions of isopropanol, methanol, and ethanol to determine the best solvent alternative for stabilized THF. Polystyrene, PMMA, PVA, and PVB did not fully dissolve in isopropanol, methanol, and ethanol. PVP dissolved in isopropanol, methanol, and ethanol. See Table 1 for solubility results. PVP solution was stippled onto a planchet to determine dry physical characteristics. The PVP surface was not uniform it had ripples. The second alternative was to test polymer solubility in stabilized THF. See Figure 11 for a comparison of solubility of polystyrene in isopropanol and THF.



Figure 11 Solubility test of polystyrene (polymer) in isopropanol and THF (solvent)

	Isopropanol	Methanol	Ethanol	THF
PVA	no reaction	no reaction	no reaction	Dissolved
PVP	Dissolved	dissolved	dissolved	Dissolved
PVB	no reaction	no reaction	no reaction	Dissolved
PMMA	no reaction	no reaction	no reaction	Dissolved
PS	no reaction	no reaction	no reaction	Dissolved

Table 1 Comparison between polymers and solvents

Preparation of Planchets

Polystyrene and poly (methyl methacrylate) (PMMA) completely dissolved in stabilized THF. The polystyrene and PMMA polymer solvent solutions were deposited onto planchets to determine dry physical characteristics. Polystyrene and PMMA showed similar characteristics. The synthetic polymers are macromolecules composed of repeating chemical structures. Polystyrene is a chain of hydrocarbon with alternating carbons connected to a phenyl group, benzene (13). The chemical formula for polystyrene is $(C_8H_8)_n$. PMMA is an alternating chain of methyl methacrylate. The chemical formula for PMMA is $(C_5O_2H_8)_n$. The polymers selected are easy to use, process, dissolve, and mold. The chemical structures for polystyrene and PMMA are shown in Figures 12 and 13.

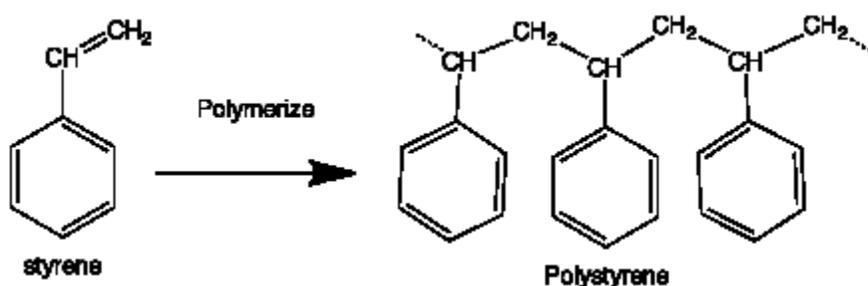


Figure 12 Chemical structure of polystyrene

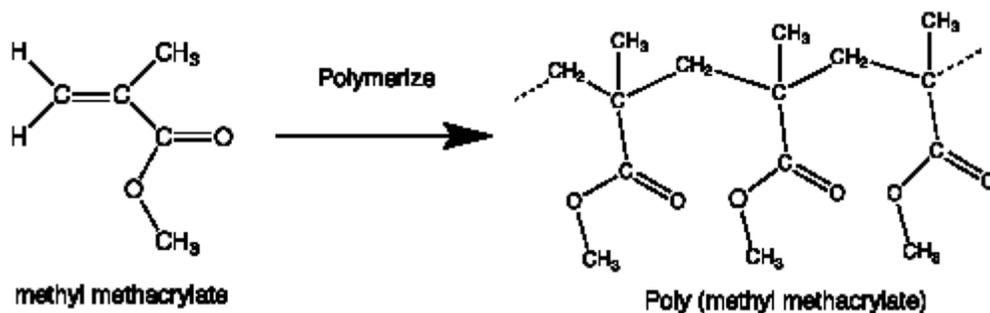


Figure 13 Chemical structure of PMMA

Different ligands were added to the PMMA and polystyrene polymer solvent solutions. The ligands used were Dipex®, Branched DGA, CMPO, and Aliquat 336. The chemical structures of these ligands are shown in Figures 5, 6, 7, and 8..

The THF evaporates which leaves a thin film consisting of the polystyrene and DIPEX on the stainless steel surface. The physical properties changed once immersed in water and taken out to dry. All ligand polymer thin films made with PMMA fell apart after being removed from water.

Planchets prepared with polystyrene as the polymer base with different ligands were more successful. The dry physical characteristics of polystyrene with different ligands were homogeneous and uniform across the surface of the planchets. After immersed in water and dried the Branched DGA and Dipex® was attached to the planchet (see Figure 14).

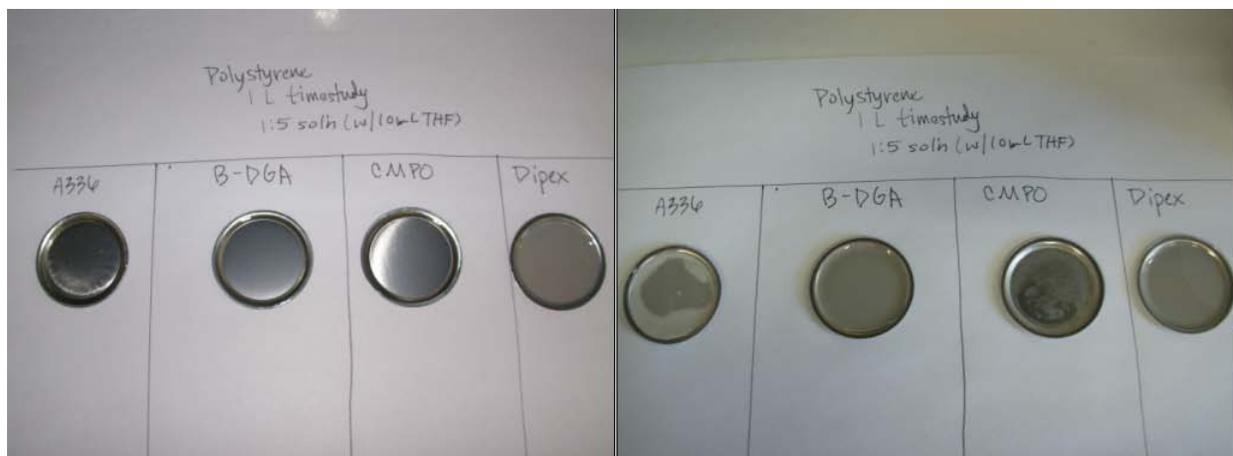


Figure 5 Before and after using different ligands with polystyrene

The use of PMMA with different ligands was unsuccessful because the thin films made with PMMA broke apart; they did not have a homogeneous and uniform surface. If the broken pieces were counted this would damage the alpha spectrometer because the small pieces would be sucked into the system by the instrument's vacuum system. The ligand polymer thin films containing Branched DGA, Dipex®, and polystyrene adhered to the planchet without breaking into pieces and were used for subsequent testing. These Branched DGA and polystyrene and Dipex® and polystyrene coatings had good physical and chemical interactions. When the polymer and ligand were mixed with solvent in solution it did not physically separate; it mixed well meaning if it did not elute off planchet. A solution with fully dissolved polymer and ligand and non-separation of ligand, polymer, and solvent indicates a good chemical mixture and bonding.

Polymer ligand thin film

The chemistry of the thin film is critical to the success of a thin film extraction analytical method and depends on the nature of the ligand. The polymer is important to the thin film process because it is the physical substrate that supports the ligand.

A study was conducted to determine if ligand attraction was the primary cause of radionuclide extraction, and not caused by electrostatic forces. The study conducted included a plain stainless steel planchet, a stainless steel planchet with ligand, a stainless steel planchet with polymer, and a stainless steel planchet with polymer and ligand (Figure 15). The stainless steel planchet's purpose is to mold the polymer ligand thin film. The polymer and ligand used were polystyrene and Dipex®.

The coated planchets were placed in 100 mL solution with 0.1 molar nitric acid tap water spiked with 1 mL of 5 Bq/mL Pu-239. The study was conducted for two hours by stirring on a stir plate. The thin film planchet with ligand dissolved into the solution, and did not stay adhered to the stainless steel planchet. The film planchet with polymer and the film coated with polymer and ligand stayed adhered to the planchet and did not dissolve into solution. The chemical composition of the thin film determines the stability of the thin film in solution. The addition of ligand to the thin film increases the absorption coefficient; this means that the addition of the ligand increases the extraction of radionuclide from solution. The study mentioned proved this to be true; radionuclide extraction from solution occurred because of ligand attraction and not because of electrostatic forces. All thin films were analyzed by alpha spectroscopy, except for the stainless steel planchet with Dipex® ligand. The ligand thin film dissolved in water and did not adhere to the stainless steel planchet. The results (Figure 16) showed the polymer ligand thin film combination with the highest absorption of Pu-239. The plain steel planchet was the lowest; proving electrostatic forces extract only small amounts of radionuclides from solution. The stainless steel planchet with polymer showed slightly higher results than the plain stainless steel planchet. The stainless steel planchet with polymer and ligand showed more than ten times higher absorption than the plain and polymer stainless steel planchets combined (Figure 16).

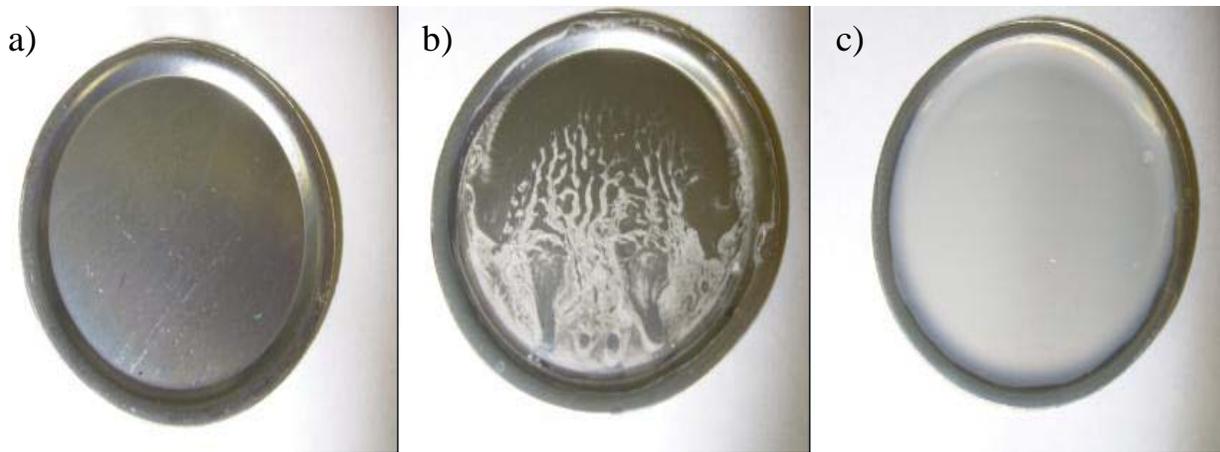


Figure 6 Comparison of a) plain stainless steel, b) polystyrene only, c) polystyrene & Dipex® planchets

This study tested the ligand extraction. It proved that Plutonium bonding to the ligand was successful for the polystyrene supported Dipex®. (The low count rate for the stainless steel disk indicated that the electrostatic force is not the primary cause for radionuclide extraction, but ligand attraction is the primary cause for radionuclide extraction (Figure 16).

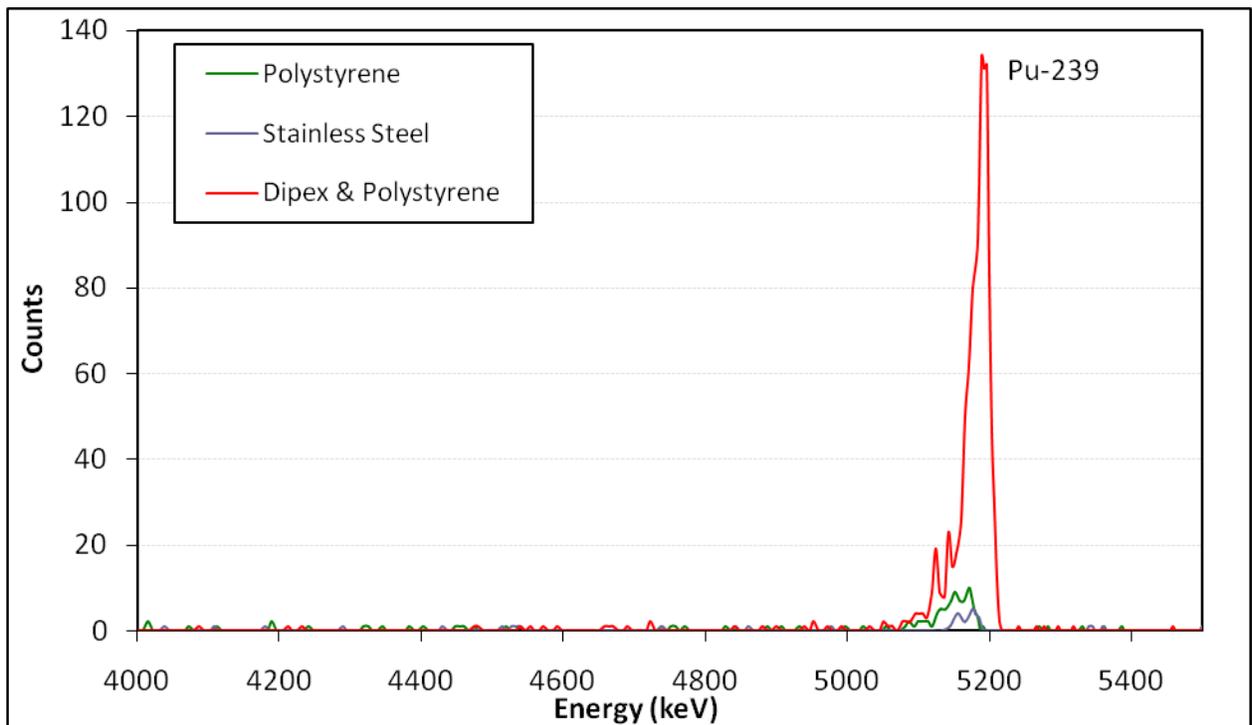


Figure 7 Comparison of stainless steel, polystyrene, Dipex® and polystyrene planchets

Plutonium selectivity

The selectivity of the thin film was tested for different oxidation states of Plutonium. To investigate Plutonium (III) and (IV), 1 M nitric solution was used because Plutonium (III) and (IV) oxidation states are stable in solution with 1 M molarity. For Plutonium (V) oxidation state the solution used had a pH of 2-3. Plutonium (VI) was tested in a solution that had a pH from 5-6. Plutonium (VI) was in this solution otherwise it would reduce to Plutonium (IV). For Plutonium (IV) colloids, the solution was in a neutral state. The results for Plutonium selectivity can be seen in Figure 17. The Dipex® polystyrene thin film showed selectivity for Plutonium (III) and (IV) isotopes.

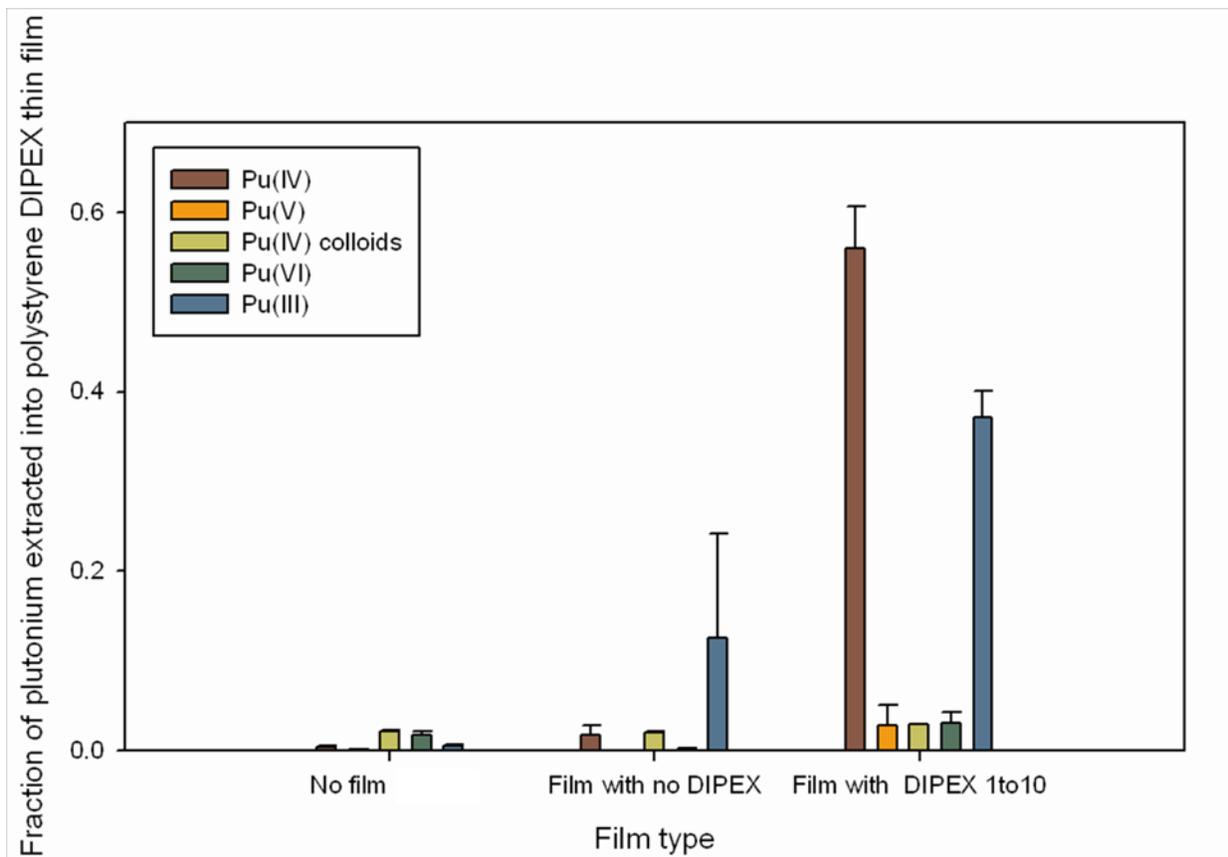


Figure 8 Thin film selectivity of Plutonium

Thin film

A polymer ligand thin film was made using 1:10 ratio of polymer to ligand with a 1:5 ratio of polymer and ligand to solvent. The mass of thin films are 0.0659 ± 0.005 . The thin films were made using polystyrene, Dipex®, and tetrahydrofuran. Other ratios of polymer, ligand, and solvent were used, but durability varied. The 1:10 Dipex® and polystyrene durability was stable over long lengths of time while submerged in water. The other ratios of ligand polymer thin films would break apart within 24 hours.

Effect of Mixing

Three methods of mixing were used to determine if mixing affected the amount extracted (Figure 19). All had the same Plutonium concentrations; 1 mL of 2.5×10^{-1} Bq/mL Plutonium-239 was added to each 100 mL of tap water; the acid molarity was 0.1 M. Concentrated nitric acid was used to decrease the pH. After stabilization of the solution with the Plutonium approximately 5 minutes, the thin film is then put in the solution. The study was conducted running the experiment three times for each mechanism; stir, non-stir, and drip. It was also conducted for limited amounts of time in varying increments of time. The results for each mechanical mechanism varied depending on time. Each experiment and its results will be discussed.

Stir

Stirring will increase mass transfer rate. For the stirring study, six duplicate analyses were carried out for each time increment in order to assure consistency for each sample. The extraction increased significantly from one hour to two hours (Figure 18). The maximum extraction was approximately four percent total recovery and remained constant from two hours to sixteen hours. Six replicates were done simultaneously for each time period; 2, 4, 6, and 8 hours. The repeatability for the stirring method is good for 30 minutes, 4 hours, and 48 hours; the replicate results are closer together. The repeatability for 2, 4, 8, 16, and 24 hours is fair; the replicates' percent recovery results are further apart (Figure 19). When plotted on a graph the Four percent of 2.5×10^{-1} Bq is a small amount, but proves that the polymer ligand film extracts radionuclide from solution.

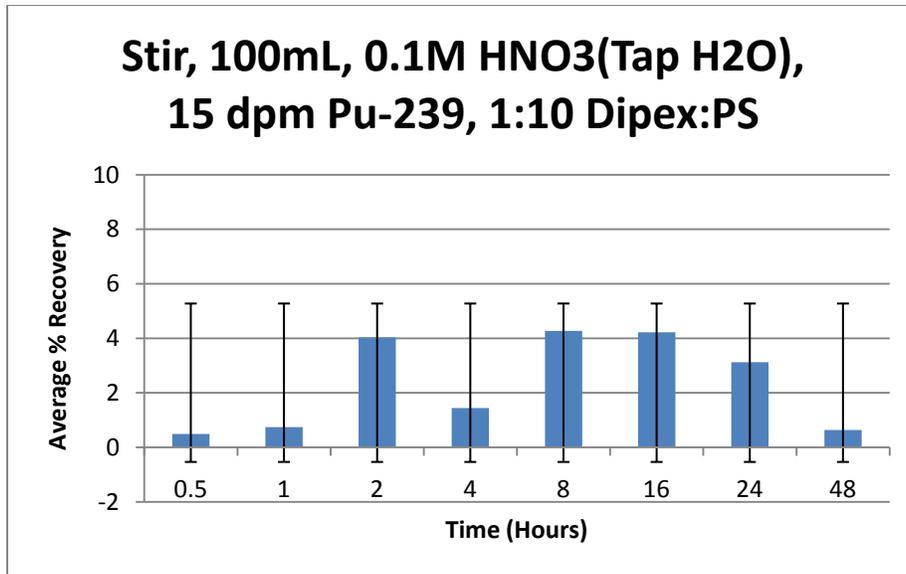


Figure 9 Stirring extraction mechanism results (Std. Dev.=1.71)

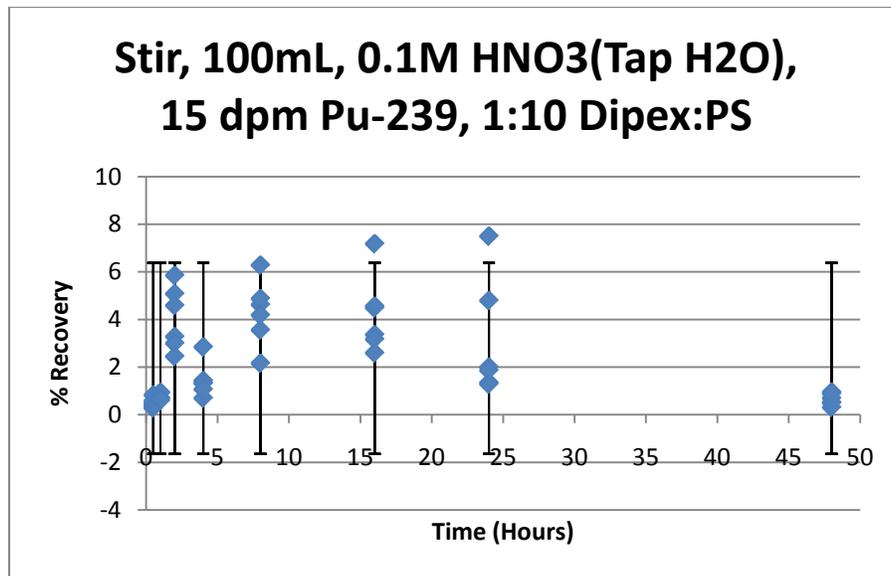


Figure 10 Stirring extraction mechanism replicate results (Std. Dev.=2.00)

Non-stir

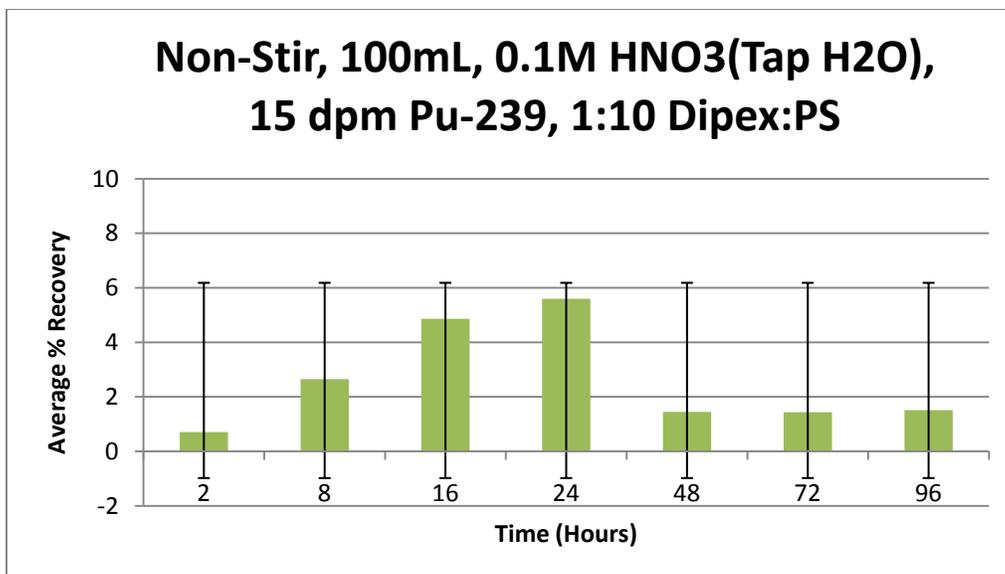


Figure 11 Non-stirring extraction mechanism results (Std. Dev.=1.89)

The results for the non stir experiment differed from the stirring experiment. From time zero to 24 hours there was a gradual increase (Figure 20), with the maximum extraction percent recovery of approximately 5.5 percent. After 24 hours, there was a decrease from 5.5 percent to 1.5 percent at 48 hours. The cause for the decrease could be due to the maximum loading capacity. The decrease in recovery could also be due to a competition of loading sites; the actinides could be competing with matrix interferences over time.

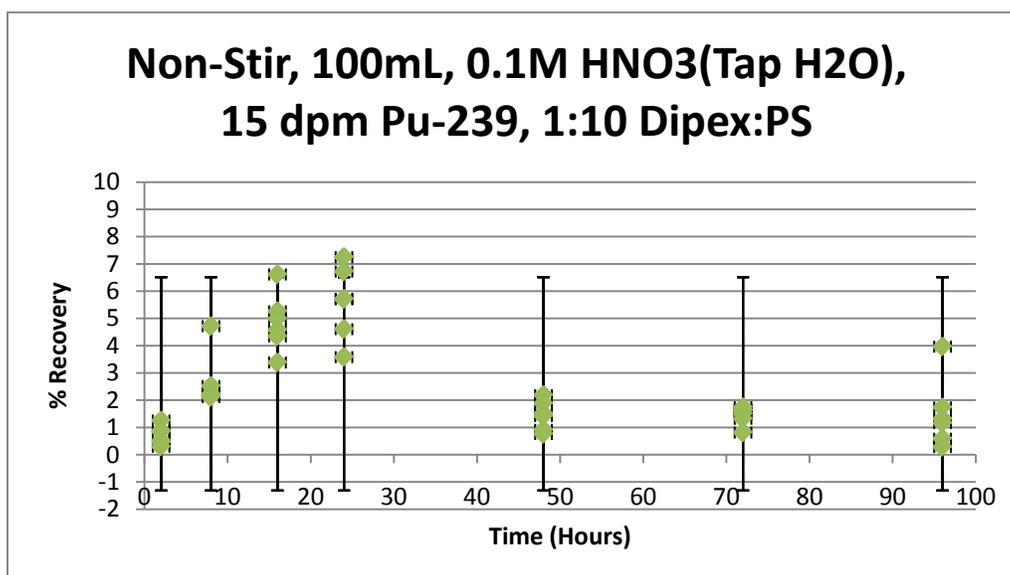


Figure 12 Non-stirring extraction mechanism replicate results (Std. Dev.=1.98)

The replicate results for 30 minutes, 48, 72 and 96 hours had good recovery. Good recovery indicates the replicates were closer to one another when plotted on a graph. Fair recovery, replicate graphed plots further apart, was seen in 8, 16, and 24 hours (Figure 21).

Drip

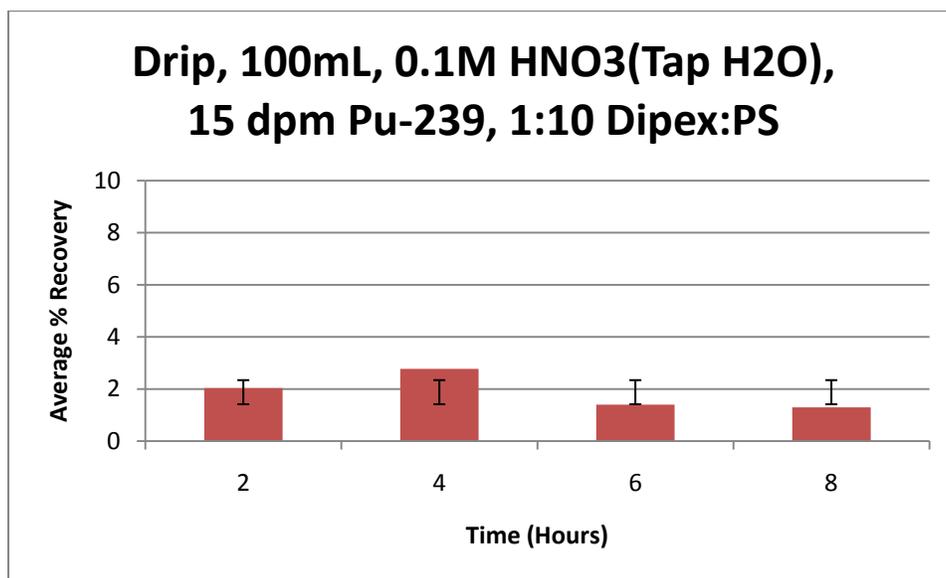


Figure 13 Drip extraction mechanism results (Std. Dev.=0.68)

The drip extraction results do not change significantly from 2 hours to four hours to six hours to eight hours (Figure 22). For the extraction mechanisms, the drip method shows the lowest recovery results. The cause for low recoveries can be related to the inconsistency of the rate of dripping. The system used a luer-lock drip valve, and no measurement of drip was conducted. The drip speed was 1 mL per minute. The speed could have been too fast and the ligand was not able to extract the radionuclide in time.

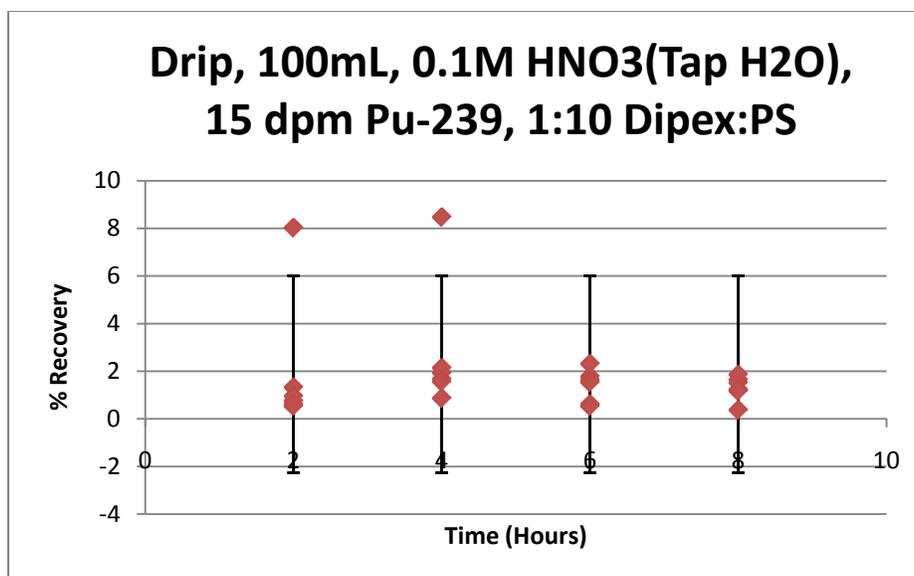


Figure 14 Drip extraction mechanism replicate results (Std. Dev.=2.04)

Conclusions

The thin film method is an alternative method to classical separation methods, namely manual precipitations, solvent extractions, and gravity-feed ion exchange. These processes are slow, labor intensive, and costly. The thin film method can be used as a screening method for radionuclides because it is rapid, less labor intensive, and cost efficient due to direct sample preparation.

Direct sample preparation includes the use of a polymer ligand thin film made from Dipex®, polystyrene, and THF constituents. Other ligands, polymers, and solvents were examined, but a thin film made of Dipex® and polystyrene was the most successful. The success of the thin film was based on the physical characteristics; homogeneity, uniformity, and texture. The success of the thin film was also based on the strength of the thin film after it was submerged in water with varying molarities. The main reason Dipex® and polystyrene was a

success was because the Dipex® polystyrene thin film extracted Plutonium from an aqueous solution.

The polymer ligand thin film can extract Plutonium from solution for subsequent alpha spectroscopic quantitation. Radionuclides were extracted onto the polymer ligand thin film from acidified water solution (Figure 16).

Comparison of electrostatic forces and ligand attraction was tested to determine if the ligand was the primary cause of the radionuclide extraction. The results showed that electrostatic forces or the binding of the Plutonium directly to the stainless steel substrate are not the primary cause of radionuclide extraction; therefore, ligand attraction is the primary cause of radionuclide extraction (Figure 16). The polymer ligand thin film shows high absorption for Plutonium, and the blank stainless steel and polymer coated planchet show less absorption (Figure 16). The polymer ligand thin film chemical characteristics are imperative to the capability of the thin film working properly.

The thin film worked best with a 1:5 ratio of Dipex® and polystyrene in a 1:10 ratio of Dipex® and polystyrene to tetrahydrofuran. A thin film made with this type of solution is durable and does not degrade when put into a 0.1 M or 1M nitric solution and air dried. A homogenous and smooth thin film is best for counting when using an alpha spectrometer because a uniform even surface provides the best counting surface. Also, a stable surface is important because it prevents the detector from being contaminated by small sample particles. The components for producing a thin film are simple; polymer, ligand, solvent, and physical forming mold. The supplies needed are minimal and cost efficient.

Cost efficiency can also be related to the labor needed for sample preparation. Elimination of extraction mechanisms eliminates the tedious and time consuming chemical processing rate. As a result, the thin film process is less labor intensive when compared to classical methods, such as ion exchange and liquid-liquid extraction. The stirring and non-stirring mechanisms are comparable, and showed minimal differences. Dripping shows the lowest recovery of all extraction mechanisms.

The oxidation state of the extracted Plutonium was not known. However, it was shown that the polymer ligand thin film was selective for Pu (III) and Pu (IV) in the acid medium used. More study will be done to determine the plutonium oxidation state extracted by the polymer ligand thin film. The Plutonium oxidation state extractable in solution is dependent upon the molarity or pH of a solution. With this study of extraction mechanism, it is conducted using a 0.1 M nitric solution. The molarity of the solution may be too low and the solution would need to be more acidic in order to extract Pu (III) and Pu (IV). However, further investigation and experiments are needed to test this and could explain the low extraction recoveries.

The explained thin film method is an alternative to classical separation methods. The use of the thin film method is rapid and would decrease labor time, labor and supply costs for sample preparation. The thin film method could be a field deployable method. Once efficiency for the thin film increases, the thin film could be used for emergency situations where fast turnaround time and low levels of detection are desired results.

Future Work

Future tasks include ways of making the current method more efficient and flexible. The recovery rates can improve, but it involves further examining the work done. For example, the stirring method shows the best recovery for two hours. Using a power control could decrease the already low speed on the stir plate. The power supply decreases the voltage the stir plate receives and therefore decreases the power and speed of the stir plate.

Using polystyrene and Dipex® as the polymer and ligand works, but more work could be done using a ligand like B-DGA. B-DGA could be used to extract different analytes with different rinses. Also, finding another polymer would be a future outlook. Currently, the polymer is the structure for the Dipex® to stay attached to the planchet. The planchet is used as support for the thin film. The thin film can continue to be used for stirring, stagnant, and stippling mechanisms, but it could also be used for a different mechanism, as a filter.

Work needs to be done to lift the thin film from the planchet and attach to a peristaltic pump. By detaching the thin film from the stainless steel planchet, a thin film filter can be made by making holes for water to flow through. Without holes, the thin film would prevent water movement from one side of the filter to the other. Using a peristaltic pump allows a larger volume of environmental sample to move through the thin film filter. Larger volumes of sample are ideal for environmental samples with low concentrations. More experiments for lower concentrations, such as 1/60 Bq, of radionuclides are needed. Further research in relation to other radionuclides is needed for uranium and americium.

The main purpose of this project is to suggest a different approach for sample preparation, an alternative for ion exchange. The implementation of using a thin film in the field will decrease lab sample preparation time, labor, and costs. The thin film is versatile and can be

used in the lab or in the field. With increased efficiency and recovery rates, the thin film method can be comparable to the ion exchange and extraction chromatography methods. The thin film method has the potential to compete with the ion exchange method and possibly replace the current ion exchange method due to the benefits of decreased time, labor and costs.

Glossary of Terms

Analyte- a chemical substance that is the subject of chemical analysis

Chromatography- a process in which a chemical mixture carried by a liquid or gas is separated into components as a result of differential distribution of the solutes as they flow around or over a stationary liquid or solid phase

Deionize- To remove ions from (a solution) using an ion-exchange process

Electrodeposition- To deposit (a dissolved or suspended substance) on an electrode by electrolysis

Ion- an atom or group of atoms that carries a positive or negative electric charge as a result of having lost or gained one or more electrons

Ion exchange- a reversible interchange of one kind of ion present on an insoluble solid with another of like charge present in a solution surrounding the solid with the reaction being used especially for softening or demineralizing water, the purification of chemicals, or the separation of substances

Ligand- a substance (atom or molecule) that forms a complex around a central atom

Molarity- the molar concentration of a solution expressed as the number of moles of solute per liter of solution (mole/L), and often denoted by M

Nuclide- a species of atom characterized by the constitution of its nucleus and hence by the number of protons, the number of neutrons, and the energy content

Planchet- a small round metal disk

Polymer- a chemical compound or mixture of compounds formed by polymerization and consisting essentially of repeating structural units

Radioanalytical- relating to radioactive analysis

Radionuclides- an atom with an unstable nucleus, which is a nucleus characterized by excess energy which is available to be imparted either to a newly-created radiation particle within the nucleus, or else to an atomic electron

Stagnant- not flowing in a current or stream

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Peer Reviewed Publications related to the Thin Film Method

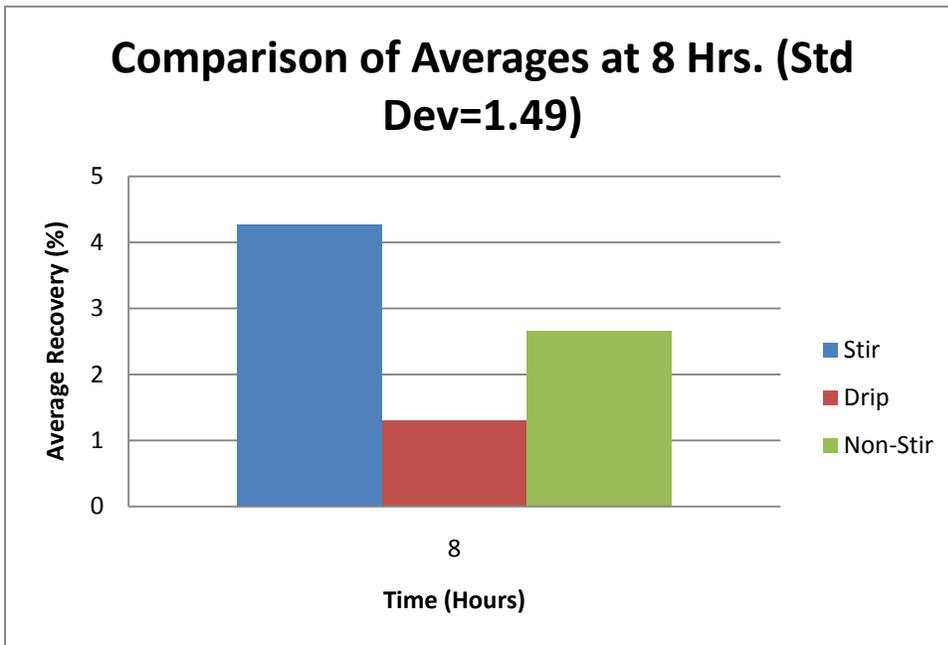
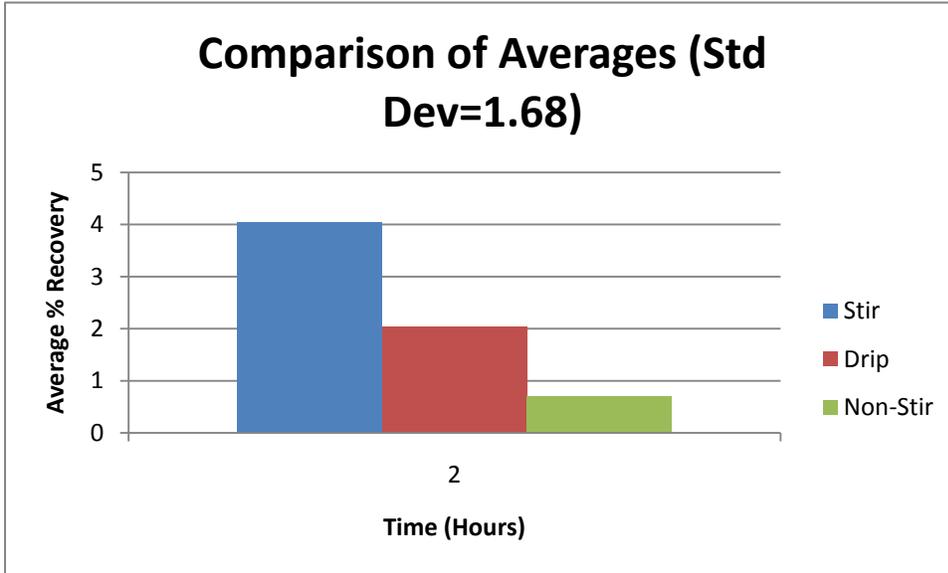
1. Gonzales, E. R., Klingensmith, A. L., Peterson, D. S., “Rapid Separation and Extraction of Radioactive Analytes onto Filters and Surfaces” *Radiochimica Acta*, **in Press**
2. Peterson, D. S., Gonzales, E. R., “Rapid Radiochemical Sample Preparation Using Polymer Thin Films” *Journal of Radioanalytical and Nuclear Chemistry*, **2009**, 282, 543-547.

Conference Presentations related to the Thin Film Method

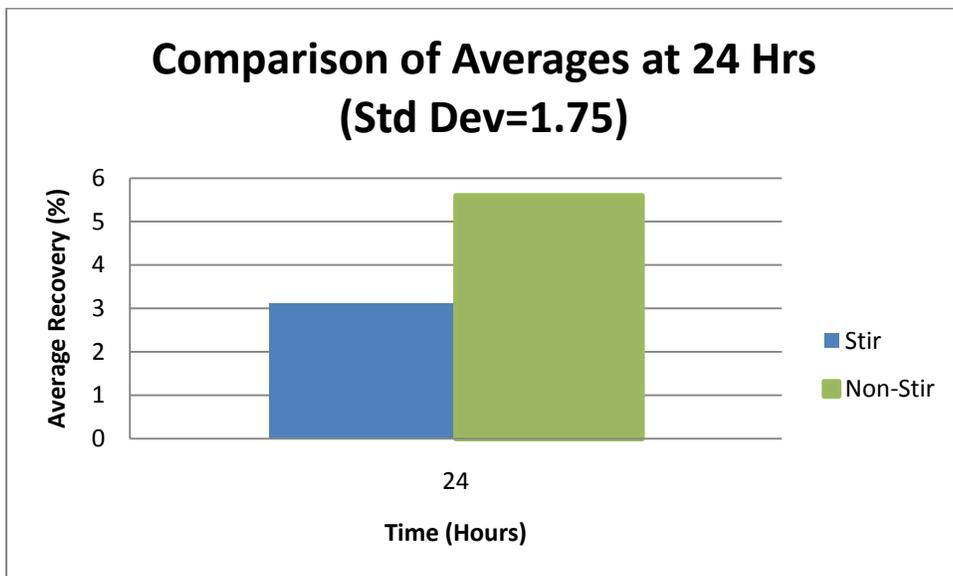
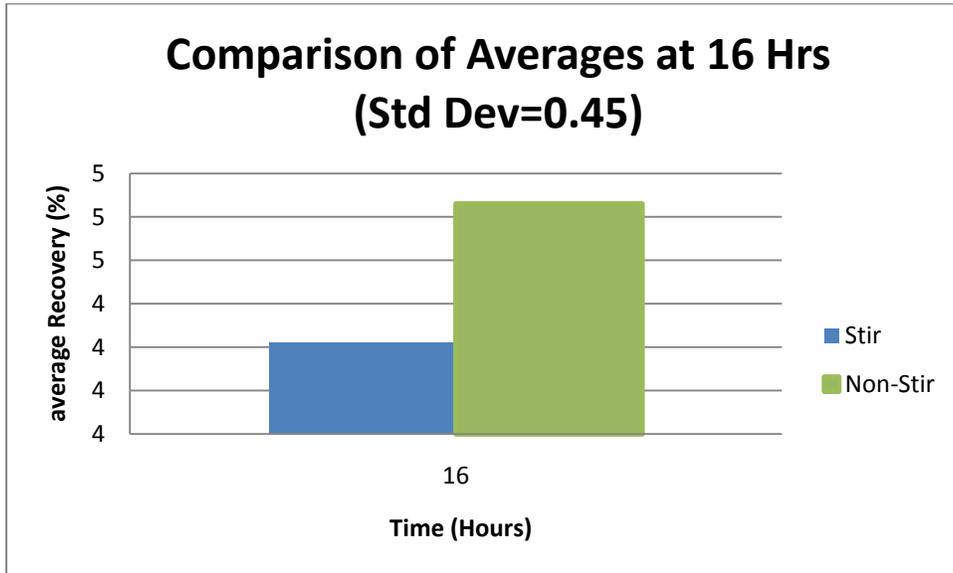
1. Tulley, C. L., Peterson, D. S., Gonzales, E. R., Armenta, C. E., Herrera, J. A., “Rapid radiochemical sample preparation for alpha spectrometry using polymer ligand films” American Chemical Society Joint Northwest/Rocky Mountain Regional Meeting, Pullman, WA, June 22, 2010. LAUR-10-4136.
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8. Peterson, D. S., Gonzales, E. R., Porterfield, D. R., "Polymeric Thin Films for Extraction and Analysis of Radioactive Analytes" American Chemical Society 224th Meeting, Boston, MA, August, 2007.

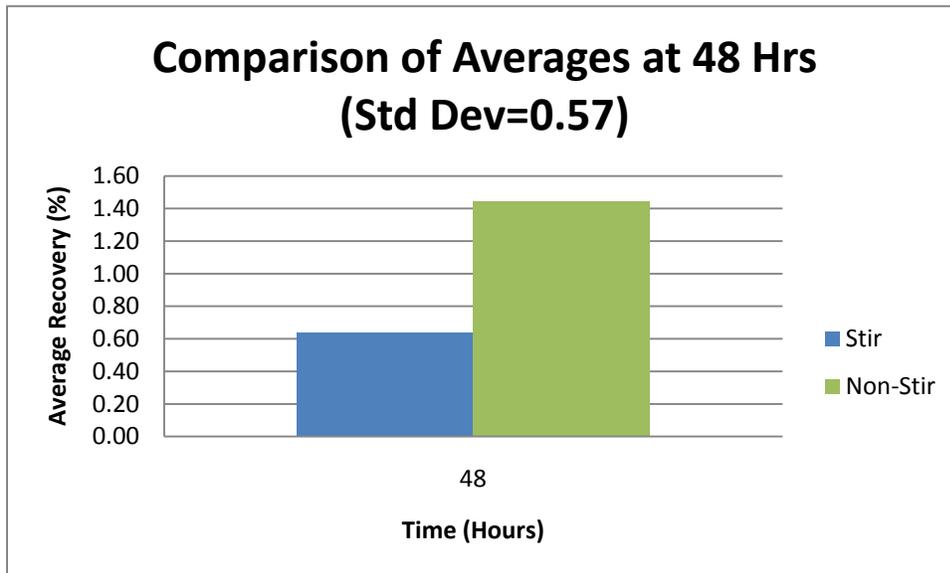
Appendix A



Appendix B



Appendix C



Appendix D

