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Uptake of Plutonium on a Novel Thin Film for Use in Spectrometry

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UPTAKE OF PLUTONIUM ON A NOVEL THIN FILM FOR USE IN SPECTROMETRY

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Science

by
William David Locklair
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Accepted by:
Dr. Brian A. Powell, Committee Chair
Dr. Timothy A. DeVol
Dr. Scott M. Husson

ABSTRACT

Trace elemental and isotopic analysis of actinides via Thermal Ionization Mass Spectrometry (TIMS) is often difficult and time consuming due to intensive sample preparation. Polymer thin films show strong potential for rapid concentration of radionuclides from solution that may prove as suitable substrates for TIMS analyses. In this work, a polymer thin film (~180 nm) was coated onto a silicon substrate and utilized for rapid radioanalytical analysis. The polymer is composed of poly(vinyl benzyl chloride) functionalized with triethyl amine (TEA) to produce an anion-exchange site for concentrating anionic actinide complexes (i.e. PuCl_6^{2-} , $\text{Pu}(\text{NO}_3)_6^{2-}$) from solution. In addition, selectively functionalizing “spots” with TEA creates hydrophilic regions and allows for concentration of an aqueous drop when surrounded by the hydrophobic polymeric backbone. Batch uptake studies were performed using inductively coupled plasma mass spectrometry, liquid scintillation counting and alpha spectrometry to determine uptake kinetics and anion-exchange capacities of the polymer thin film. Results indicated that along with a potential for utilization as a TIMS substrate, the polymer thin film yields high resolution alpha spectra, comparable to samples produced via electrodeposition. An apparent equilibrium constant (K_d) for the functionalized polymer was found to be approximately 9060 L/kg from 9M HCl. The anion exchange capacity of the film was determined using ^{36}Cl uptake studies and found to be $1.25 \times 10^{-1} \pm 1.07 \times 10^{-2}$ meq/g_{polymer}. Thus, the rapid uptake kinetics, good anion-exchange capacity, and high-resolution alpha spectra show good promise for the use of this thin film for rapid radioanalytical analyses.

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TABLE OF CONTENTS

	Page
TITLE PAGE	i
ABSTRACT	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
CHAPTER ONE	
I. INTRODUCTION.....	1
CHAPTER TWO	
II. BACKGROUND.....	7
Plutonium and Actinide Chemistry	7
Thin Film Design	9
CHAPTER THREE	
III. OBJECTIVES AND APPROACH	13
Goal	13
Experimental Tasks	13
CHAPTER FOUR	
IV. MATERIALS AND METHODS	15
Materials.....	15
Substrate Preparation for Coating	16
Dip-Coating.....	16
TEA-Functionalized Polymer Thin-Films.....	17
Batch Kinetic Experiments.....	17
Batch Uptake Kinetics at Higher Total Pu Concentrations	19

Table of Contents (Continued)

	Page
Determination of Distribution Coefficients and Loading	
Capacities	19
Batch Uptake Study Using LSC	20
Alpha Spectrometry	21
Determination of Anion-Exchange Capacity	22
Data Analysis	23
CHAPTER FIVE	
V. RESULTS AND DISCUSSION	25
Batch Uptake Kinetics of ²⁴² Pu	25
Determination of Distribution Coefficients and Loading	
Capacities	26
Batch Uptake Study Using LSC for Determination of	
Distribution Coefficient.....	30
Alpha Spectrometry of Thin Films.....	38
CHAPTER SIX	
VI. CONCLUSIONS AND FUTURE WORK.....	42
Conclusions	42
Future Work	43
APPENDICES	46
REFERENCES	53

LIST OF TABLES

Table	Page
Table 5.1 Representative ICP-MS data for determination of distribution coefficient of PVBC thin film functionalized with TEA.	29
Table 5.2 Mass balance calculated for Pu uptake systems. LSC data were used to calculate aqueous phase Pu and alpha spectrometry data were used to calculate Pu bound to the thin films. ^a LSC data were below the MDC of 0.8 Bq/g of solution. ^b Alpha spectrum did not provide an adequate spectrum or use in calculations.	35
Table 5.3 Alpha spectroscopy analysis of 5% cross-linked, TEA functionalized (5% CL + TEA), 5% cross-linked unfunctionalized (5% CL), and 0% cross-linked (0% CL) unfunctionalized films.	41
Table A.1 List of ICP-MS data and [Pu] calculations for 5% cross-linked, TEA functionalized, 5% cross-linked unfunctionalized, and 0% cross-linked unfunctionalized films.	47
Table B.1 TIMS data for 15% cross-linked functionalized polymer fibers (Sample ID – CU) compared to resin bead (Sample ID –SRNL Bead)	52

LIST OF FIGURES

Figure	Page
Figure 1.1 Rhenium filament used in TIMS analyses.....	4
Figure 2.1 Structure of typical type 1 anion-exchange resin used in bead loading	10
Figure 2.2 Reaction chemistry to incorporate triethylamine (TEA) into Polyvinyl benzyl chloride (PVBC) chain	11
Figure 2.3 Structure of 1,4-diazabicyclo[2,2,2] octane (DABCO) used for cross-linking.....	11
Figure 2.4 Structure of PVBC film functionalized with TEA and cross-linked with DABCO	12
Figure 4.1 Experimental setup for batch kinetic experiments	18
Figure 5.1 Uptake of Pu(IV) versus time from 9M HCl and 8M HNO ₃ onto thin-film coated Si wafers.....	26
Figure 5.2 Theoretical plot of fraction of Pu remaining in aqueous phase versus distribution coefficient (K _d) using a sorbent mass of 0.001 g and a total system volume of 100 mL.....	28
Figure 5.3 Sorption isotherm of ²³⁸ Pu(IV) on 5% cross-linked films with TEA functionalization. The corresponding K _d calculations, R-squared values for each replicate, along with the average K _d and standard deviation are presented as the inset plot on the left	32
Figure 5.4 Sorption isotherm results for ²³⁸ Pu (IV) on 5% cross-linked + TEA Functionalized films, 5% cross-linked polymer films, the unfilled blue diamonds for cross-linked and TEA functionalized films are data from an uptake experiment with CRM 150 (mainly ²⁴² Pu by mass).	34
Figure 5.5 Alpha spectrum of 5% cross-linked, TEA functionalized films submerged in CRM (²⁴² Pu, ^{239/240} Pu, ²³⁸ Pu).....	39

Figure 5.6 Alpha spectrum for 5% cross-linked and 0% cross-linked unfunctionalized films submerged in CRM (^{242}Pu , $^{239/240}\text{Pu}$, ^{238}Pu)..... 40

CHAPTER ONE

INTRODUCTION

Plutonium has been released into the environment, albeit typically at trace levels, primarily arising from atmospheric nuclear weapons testing and disposal of defense related nuclear materials. The resulting global fallout from atmospheric testing has dispersed radionuclides on a global scale. Nuclear accidents from commercial energy production sites such as at Fukushima Daiichi and Chernobyl have resulted in enhanced localized contamination [Chu, 1971; Muramatsu et al. 1999; Skipperud et al. 2004]. Characterization of plutonium and other transuranic contamination are important from a health perspective due to their radiotoxicity and persistence in the environment owing to the long half-lives of many of the transuranic isotopes. Detection and analysis of plutonium samples is critical in health assessments and environmental fate and transport modeling, and provides critical information in nuclear proliferation measurements, nuclear safeguard precautions and national security interests [Bürger et al., 2012]. Isotopic analyses of actinides are essential in verification of declared nuclear stock piles and are used extensively in monitoring enrichment facilities, reprocessing plants, and bioassays of workers who deal with nuclear material.

It has been shown that the isotopic ratio of plutonium provides a “fingerprint” of the contamination and can identify the source of the contamination by delineating among commercial energy production accidents, global fallout, nuclear weapons testing, and weapons grade production and reprocessing of nuclear material [Bürger et al., 2009;

Muramatsu et al., 1999; Skipperud et al. 2004]. The isotopic ratio is sensitive to the neutron flux to which the precursor uranium fuel is subject to during irradiation. Within a nuclear reactor, the intense neutron flux induces fission in uranium fuel. In lieu of undergoing fission, the fissile material may also absorb a neutron resulting in the production of a transuranic element. Subsequent radioactive decay and neutron absorption events can result in the production of varying isotopes. The isotopic composition of plutonium is related directly to the intensity of the neutron flux the nuclear material is subject to as well as the duration of time it is irradiated. As reported by Kersting et al. [2013] the global inventory of plutonium was 1900 t in 2010 and expected to rise by 70-90 t per year.

Plutonium contamination within the environment is often at trace levels, hampering the analysis of environmental samples and inherently increasing the uncertainty of the measurement [Keough and Powers, 1970; Muramatsu et al., 1999]. The trace level contamination of plutonium requires sensitive analytical methods and often lengthy sample preparation to obtain accurate measurements. Alpha spectrometry commonly is used to quantify alpha emitting radionuclides [Inkret et al., 1998]. The $^{239}\text{Pu}/^{240}\text{Pu}$ ratio frequently is used to determine the source of the plutonium. However, the primary alpha energies of these isotopes (5.156 and 5.1685 MeV respectively) are too similar and cannot be readily resolved using alpha spectrometry, making source determination problematic by this method [Muramatsu et al., 1999] The accurate measurement of plutonium and uranium isotopes is necessary in analyzing declared (and undeclared) nuclear materials taken from nuclear production sites and from various

environmental samples for nonproliferation and safeguard purposes. Accurate isotopic information is used to elucidate whether a Pu sample was derived from a commercial nuclear reactor used for power generation or from illicit weapons testing under a nuclear weapons program. Isotopic information is also used to determine the source location, revealing which reactor type produced the plutonium.

Furthermore, in many cases low-level exposures from the workplace or in environmental samples are undetectable using routine radiochemical methods such as liquid scintillation counting and alpha spectrometry. Frequently, Pu contamination is at extremely low levels and must be concentrated from a large sample volume. The accurate determination of isotopic ratios from ultra-trace Pu levels (fg) is essential in verifying illicit weapons testing and in accurate dose and dose risk assessments. Thus sensitive analytical techniques such as thermal ionization mass spectrometry (TIMS) are necessary.

Mass spectrometry is the only analytical technique that can accurately determine the full isotopic composition of a plutonium-bearing sample. TIMS provides the lowest detection limit, on the order of picogram to femtogram (10^{-12} - 10^{-15} g) quantities, and is used extensively in analysis of actinides [Bürger et al., 2012; Bürger et al., 2009; Chu, 1971; Delmore, 2010; Fasset and Kelly, 1984; Inkret et al., 1998; Jakopič et al., 2009]. Although TIMS maintains the lowest detection limit for plutonium analysis, it requires lengthy sample preparation times and has low ionization efficiency. A variety of loading techniques have been developed to increase ionization of the analyte, though efficiencies are frequently still 1% or less. The “bead loading” method is employed commonly for

plutonium analysis as it has shown to give the greatest ionization and lowest detection limit [Fasset, 1984; Kurosaki, Chang, and Inn, 2006]. In this method the purified analyte is loaded manually onto an ion-exchange resin bead and subsequently deposited onto a filament of rhenium metal such as the filament given in Fig 1.1. Anion-exchange beads are utilized for plutonium due to its propensity to form anionic nitrate and chloro complexes [Bürger et al., 2009]. The filament is loaded into the spectrometer and a current is increased linearly across the filament to increase the temperature and volatilize the analyte.



Fig. 1.1 A typical rhenium filament running across two electrodes that is utilized in TIMS analyses

Data from Watrous and Delmore [2009] suggest the formation of analyte-carbide

and rhenium-carbide complexes as intermediate species during TIMS operation. The filaments are subject to heat treatment and carburization to remove impurities on the surface and to aid in the formation of rhenium carbide on the surface [Watrous and Delmore, 2009]. At high temperatures, carbon present on the filament from carburization or from the resin bead itself diffuses into the rhenium filament bringing the analyte into contact with the hot filament surface where it may ionize. Rhenium carbide has a higher work function than the bare metal, resulting in enhanced ionization [Pallmer, Gordon, and Dresser, 1980]. Carbon from the resin bead also aids in scavenging oxygen and suppresses the formation of analyte-oxide species [Watrous and Delmore, 2009]. Despite the apparent advantage of having a carbon source from the resin bead, bead-loading performance often is hindered during operation as the beads are prone to being dislodged from the filament or undergoing catastrophic failure due likely to water trapped within the bead. In one study as much as 20% of the beads were dislodged from the filament during carburization, while an additional 5% were detached during operation resulting in a large loss of time and precious sample [Delmore, 2010].

Considering the current limitations of TIMS analysis, the goal of this research was to develop a robust, reliable, and sensitive TIMS source. The objectives in pursuit of this goal were to (1) produce a thin film of anion-exchange polymer that could be used as the TIMS source, (2) characterize the Pu uptake kinetics and binding capacities of the polymer films, and (3) test the performance of thin-film platform for TIMS analyses. During the course of the research, it was discovered that the polyelectrolyte thin film also is a suitable alpha spectrometry substrate that yields high-resolution spectra. Thus,

objective (4) was to evaluate the thin-film platform for rapid radioanalytical analyses using alpha spectrometry. This thesis details work on objectives (2) and (4).

The polymer thin-film platform utilizes similar chemistry to the Dowex 1 (Sigma Aldrich) anion-exchange resin commonly employed in TIMS bead-loading. It comprises a poly(vinylbenzyl chloride) (PVBC) backbone functionalized with triethylamine (TEA) to produce quaternary amine sites. The quaternary amine functionality provides positively charged sites to bind anionic complexes and has long been used in uranium and plutonium anion exchange, typically as the Dowex 1 resin [Choppin, 1959; Kressin, 1962; Fasset and Kelly, 1984]. Cross-linking by 1,4-diazabicyclo[2,2,2] octane (DABCO), provides structural support to the film without compromising anion-exchange sites due to the production of additional quaternary amine sites from reaction of the DABCO nitrogen atoms with chloromethyl groups of PVBC. This has an advantage over commercially produced Dowex 1 anion-exchange resin, which utilizes divinylbenzene as crosslinker.

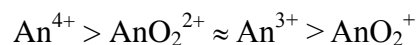
CHAPTER TWO

BACKGROUND

Plutonium and Actinide Chemistry

Plutonium is produced in large quantities as a byproduct from the operation of commercial nuclear power plants. One of the isotopes produced, ^{239}Pu , is fissile and may be used in nuclear weapons once the plutonium is isolated from the host of other elements present in spent nuclear fuel. Upon detonation of a nuclear weapon or other accidental release into the environment, it is important to understand Pu chemistry so as to effectively make analytical measurements for health risk assessments, forensic analyses, and to enact appropriate remediation strategies.

Plutonium chemistry and its mobility in the environment are impacted profoundly by its oxidation state. Plutonium is unique in that it may exist simultaneously in four oxidation states III, IV, V, and VI under environmental conditions due to their similar redox potentials [Cleveland, 1979]. Plutonium (III/IV) are favored under oxidizing, acidic conditions; whereas Pu(V/VI) are favored under reducing, near neutral to basic conditions. Actinide complexation and hydrolysis trends typically follow: $\text{An(IV)} > \text{An(VI)} > \text{An(III)} > \text{An(V)}$. While this trend may seem counterintuitive initially, it should be understood that the complexation and hydrolysis trends follow the effective charge as given below [Choppin, 1983].



+4 +3.2 +3 +2.2

The axial oxygens present on the An(V) and An(VI) actinyl ions (i.e. PuO_2^+ and PuO_2^{2+}) draw electron density away from the central atom resulting in a higher effective charge than the formal charge of the ion.

Several actinide elements including U(IV), Np(IV) and Pu(IV) have been shown to be absorbed by anion-exchange resins from concentrated nitric and hydrochloric acid due to the formation of $\text{An}(\text{NO}_3)_6^{2-}$ and AnCl_6^{2-} species which may undergo exchange onto the resin [Ryan, 1961; Kurosaki, Chang, and Inn, 2006]. These complexes also are formed in concentrated metal nitrate and chloride salts that exhibit larger distribution coefficients than do the mineral acid systems [Ryan and Wheelwright, 1959]. Nevertheless, concentrated acid solutions generally are used due to the faster anion-exchange kinetics compared to the metal nitrate/chloride system. Acidic solutions also aid in maintaining the An^{4+} oxidation state, which tends to bind more strongly than other oxidation states. Moreover, the high acidity sufficiently suppresses hydrolysis of the actinide, which would compete with complexation between nitrate or chloride. This is especially true for Pu(IV), which readily hydrolyzes even at low pH (~1) due to its high charge to ionic radius ratio. The formation of anionic hydrolysis complexes (i.e. $\text{Pu}(\text{OH})_5^-$ and $\text{Pu}(\text{OH})_6^{2-}$) have not been observed and thus Pu would not bind onto the anion-exchange resin if outcompeted by hydrolysis products.

Anion exchange has been utilized in numerous Pu purification and separation schemes [Ryan and Wheelwright, 1959; Ryan, 1961; Choppin, 1959] and can allow for almost quantitative separation from a host of other ions [Kressin and Waterbury, 1962].

Anionic hexachloro and hexanitrate Pu complexes ($\text{Pu}(\text{NO}_3)_6^{2-}$, PuCl_6^{2-}) are known to form when loaded out of concentrated nitric or hydrochloric acid [Ryan and Wheelwright, 1959]. Upon adsorption onto the resin, Pu may be eluted through several techniques. The bound Pu may be displaced by another anion, the oxidation state may be altered to change the affinity of the ion for the resin, or the equilibrium may be shifted through a change in nitrate/chloride concentration [Ryan and Wheelwright, 1959]. The most practical elution method is simply a change in nitric acid/hydrochloric acid concentration to force the bound species off the column and into the eluent. In this research Pu(IV) was loaded from 9M HCl through anion exchange onto a thin film that utilizes similar sorption chemistry as has been demonstrated with the Dowex 1 resin bead for decades. The high chloride concentration present in 9M HCl allows for the formation of the anionic complex necessary for plutonium anion-exchange. The high acidity is also effective in suppressing hydrolysis of Pu(IV), while maintaining a Pu(IV) oxidation state.

Thin Film Design

The thin film design is a modified form of a type 1 anion-exchange resin commonly used in TIMS analysis based on a polystyrene backbone and functionalized with quaternary amine exchange sites as shown in Figure 2.1.

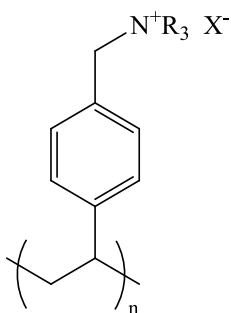


Figure 2.1: Typical type 1 anion-exchange resin used in bead loading method where X represents a singly charged anion.

Cross-linking of the polymer often is done using a compound such as divinyl benzene. Although cross-linking may add physical strength to the resin bead, it removes anion-exchange sites. The modified films used in this research are composed of a poly(vinylbenzyl chloride) (PVBC) backbone functionalized with triethylamine (TEA) to produce quaternary amine anion-exchange sites (Figure 2.2). Cross-linking is done using 1,4-diazabicyclo[2,2,2] octane (DABCO) (Figure 2.3), which provides structural support to the film without compromising anion-exchange sites due to the production of additional quaternary amines from the DABCO molecule (Figure 2.4). The comprehensive synthesis of the polymer films is given in Chapter 4.

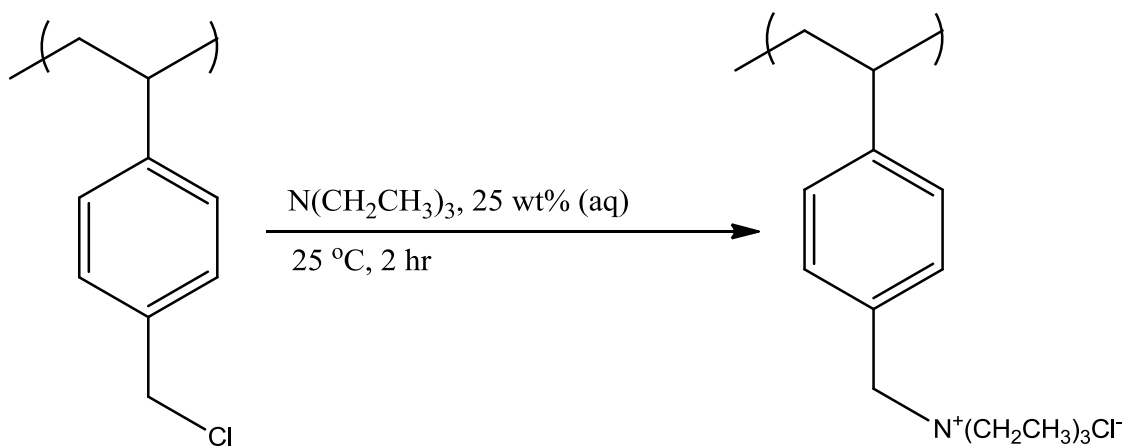


Figure 2.2: Reaction chemistry to incorporate triethylamine into PVBC polymer chain.

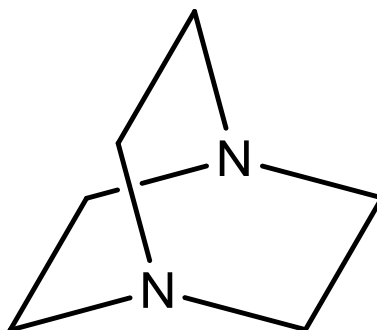


Figure 2.3: 1,4-diazabicyclo[2,2,2] octane (DABCO) used for cross-linking. Quaternary amine groups are created upon nucleophilic addition reactions with chloride groups on the PVBC.

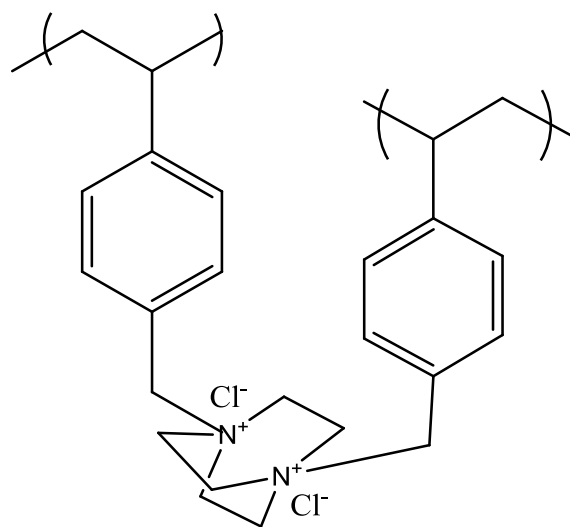


Figure 2.4: PVBC film functionalized with TEA and cross-linked with DABCO. Note that chloride ions or other anionic complex would supply the anionic charge to neutralize the quaternary amine when out of solution

CHAPTER THREE

OBJECTIVES AND APPROACH

Goal

The objectives of this research were to determine the distribution coefficient and sorption capacities of the hexachloro-plutonium complex (PuCl_6^{2-}) to various polymer thin films. The data were quantified in terms of Pu uptake as a function of polymer mass. Batch uptake experiments were used to examine ion-exchange kinetics and anion-exchange of plutonium on polymer thin film coated rhenium ribbons and silicon wafers. The intent was to design and characterize a film that can rapidly concentrate plutonium and serve as more robust and sensitive substrate for TIMS analyses. This work also examined the potential use of the thin films as alpha spectrometry substrates.

Experimental Tasks

- 1) Estimation of anion-exchange capacities of polymer for Pu
 - a. Employ radiolabeled chlorine (^{36}Cl) to quantify the number of anion-exchange sites for the polymer using an ion exchange approach
- 2) Batch uptake experiments
 - a. Determine kinetics of Pu sorption to polymer thin film coated substrates
 - b. Determine anion-exchange capacity of Pu per mass of polymer
 - c. Construct isotherm of anion-exchange behavior to evaluate an apparent equilibrium constant

3) Alpha spectrometry of thin films

- a. Analyze solid state Pu on film with alpha spectrometry and evaluate quality of the spectra

CHAPTER FOUR

MATERIALS AND METHODS

Materials

Polymer thin-film samples were provided by Joseph Mannion in the research group of Dr. Scott Husson in Chemical and Biomolecular Engineering at Clemson University. Reference to materials and methods of the thin-film sample preparation are given here for completeness.

The following materials were obtained from Sigma-Aldrich and used as-received: chloroform (Reagent Plus® $\geq 99.8\%$ with 0.5-1.0% ethanol as stabilizer); 1,4-diazabicyclo[2.2.2]octane (DABCO, Reagent Plus® $\geq 99\%$); hydrogen peroxide solution containing inhibitor (30 wt% in water); poly(vinylbenzyl chloride) (PVBC), 60/40 mixture of 3- and 4- isomers; sulfuric acid (95-98%, ACS reagent grade). Silicon wafers were acquired from Nova Electronic Materials as 4" N/Ph <100> 1-10 Ohm-CM 500-550 μm SSP prime grade Si wafers diced to 1 cm \times 3 cm pieces. Hydrochloric acid (HCl, 37 wt% in water, Ultra trace metal grade) and triethylamine (TEA, 99%, reagent grade) were used as received from Fisher Scientific. NaCl (reagent grade) was obtained from VWR, and NaNO₃ and NaNO₂ (reagent grade) were obtained from Mallinckrodt.

Two sources of plutonium were used in this work. A ²³⁸Pu source was obtained from Eckert and Zeigler Isotope Products (Valencia, CA). For higher Pu mass loading experiments, certified reference material 130 (CRM 130) from New Brunswick Laboratory containing $>99\%$ ²⁴²Pu by mass was used. All solutions were prepared using

ultrapure deionized water from an Elge Purelab Flex system.

Substrate Preparation for Coating

Silicon substrates were cleaned by sonication (Aquasonic 75HT, VWR Scientific) with DI water for 15 min. Next, each substrate was placed in a test-tube with 10 mL of piranha solution and was heated in a water bath to 85°C for 1 h. The piranha wash solution was prepared by slowly adding 1 part 30 wt.% hydrogen peroxide to 3 parts concentrated sulfuric acid. (Caution: To prepare this solution, hydrogen peroxide was poured slowly into the concentrated sulfuric acid under a hood. Piranha solution is a very strong oxidant that may react violently if it comes in contact with organics.) The used piranha solution was collected for safe disposal, and each test tube with silicon wafer substrate was washed with DI water 3 times before 15 min of sonication in DI water. The substrates were washed a final time with DI water and dried with compressed air.

Dip-coating

After cleaning, substrates were dip-coated from solutions of PVBC in chloroform using a Qualtecs Product Industry QPI-128 dip coater. Immediately before dip-coating, DABCO was spiked into the solution to serve as a cross-linker. The molar amount of DABCO added was limited by stoichiometry based on a 1:2 reaction of DABCO to chloride sites along the PVBC chains. A ratio of 18.4 mg DABCO:1 g PVBC was used to prepare films with 5% cross-linking. After casting, films were heated in an oven at 80°C for at least 48 h to complete cross-linking.

TEA-functionalized Polymer Thin-films

Substrates coated by the cross-linked polymer films were submerged in a 5 wt% solution of TEA in chloroform for 24 h at room temperature. After functionalization, the substrates were removed from solution and dried with compressed air.

Batch Kinetic Experiments

Batch kinetic experiments were performed to determine the time needed to reach equilibrium between aqueous PuCl_6^{2-} and sorbed PuCl_4^0 . One-hundred milliliters of 9M HCl were placed in a 250 mL Teflon beaker. A 10 mL spike of 1.11×10^{-10} M (1000 dpm/mL, throughout this document M units will be used for comparison and instrument specific units will be provided in parentheses) ^{238}Pu solution was added to the solution. To ensure Pu was present in a tetravalent state, the spike solution contained 1 mM NaNO_2 . The oxidation state was verified using solvent extraction and lanthanum fluoride co-precipitation [Neu et al., 1994; Nitsche, Lee, and Gatti, 1988]. The beaker was placed on a stir plate with a magnetic stir bar and allowed to stir for 5 minutes to ensure thorough mixing. An initial 1mL aliquot of the solution was taken to determine the exact initial concentration using liquid scintillation counting (LSC, Tri-Carb model 2910 TR). A functionalized film on a silicon substrate was suspended in a stirring acid solution in the Teflon beaker from a Teflon jig to avoid contact between the magnetic stir bar and the substrate (Fig. 4.1). The introduction of the functionalized film initiated time “zero” for the experiment. Additional 1 mL aliquots were taken at time intervals 30s, 1 min, 3 min, 5 min, 10 min, 15min, 30 min, 60 min, and 120 min. All aliquots were monitored

gravimetrically to ensure accuracy in concentration calculations. All samples were placed in individual 7 mL liquid scintillation vials, mixed with 5 mL of scintillation cocktail and counted on a liquid scintillation counter. The decrease in activity of the aqueous phase was attributed to the ion exchange of the plutonium species onto the polymer. The ion-exchange data were plotted considering zero, 1st, and 2nd order reactions to determine if the exchange data follows any of these order reactions. The same experiment also was run out of 8M HNO₃. The experiment was also performed on a bare silicon wafer under the same experimental conditions to determine if any Pu was adsorbing to the bare silicon.

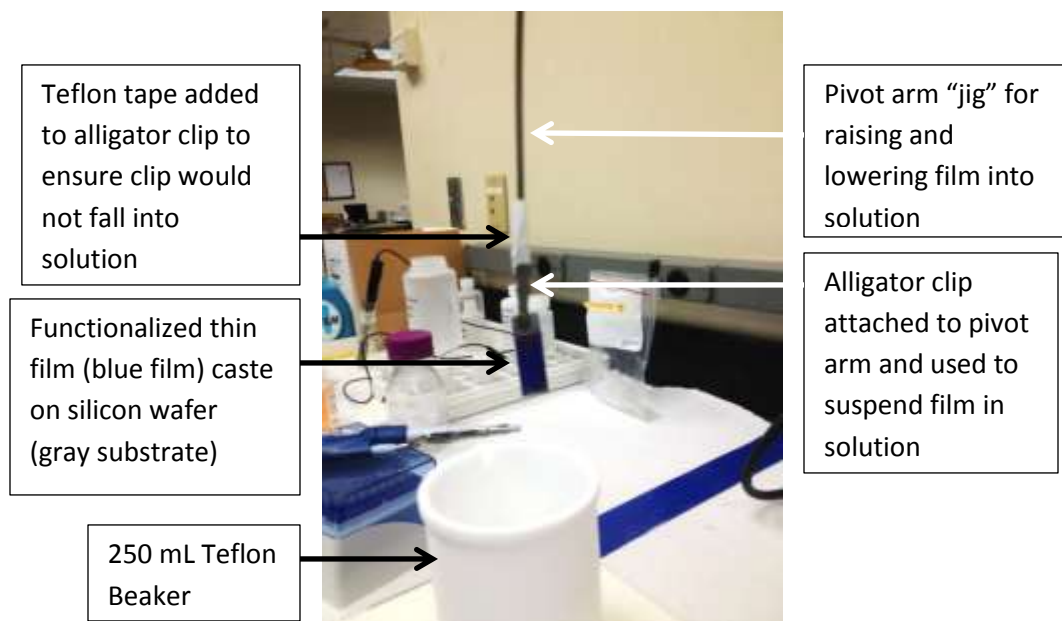


Fig. 4.1 Experimental setup for batch kinetic experiments. A film was suspended in 100mL of 9M HCl containing a 10mL spike of 1000 dpm/mL Pu²³⁸ in a Teflon beaker from an alligator clip connected to avoid contact between the magnetic stir bar and substrate.

Batch Uptake Kinetics at Higher Total Pu Concentrations

A second experiment was designed using ^{242}Pu to monitor the influence of Pu concentration on uptake at higher total Pu concentrations. One hundred milliliters of 9M HCl was placed in a 250 mL Teflon beaker along with 1 mM NaNO₂. A 10 μL spike of 4.13×10^{-6} M (1000 ppb) ^{242}Pu solution was added to the solution and stirred using a magnetic stir bar and stir plate on medium speed for the duration of the experiment. An initial 1 mL aliquot was removed and placed in a 15 mL inductively coupled mass spectrometry (ICP-MS) tube to determine the initial ^{242}Pu concentration. After the initial sample was removed the film was suspended in the beaker to begin the uptake experiment. Additional 1 mL aliquots were removed at similar time intervals as determined by the preliminary experiments and placed in individual ICP-MS tubes. The 1 mL sample solutions were diluted with 9 mL of distilled de-ionized (DDI) water to dilute the high acid concentration and match the ICP-MS standards. The NIST SRM 4334I was used to prepare ^{242}Pu calibration standards for ICP-MS and ^{237}Np was used as an internal standard during analysis. All aliquots and dilutions were monitored gravimetrically to ensure accuracy in concentration calculations. The loss of ^{242}Pu from the aqueous phase provided an indirect measurement of the Pu bound to the thin film in contact with the solution.

Determination of Distribution Coefficients and Loading Capacities

A similar experiment to the one described above was implemented to determine loading capacities for the thin films and functionalized films. A working ^{242}Pu (IV) solution was prepared by removing a given volume from a 4.13×10^{-6} M (1000 ppb) stock. An initial

spike of ^{242}Pu was added to a 100 mL 9M HCl solution (containing 1mM NaNO_2) in a 250 mL Teflon beaker and stirred using a magnetic stir bar and stir plate. A 1 mL aliquot was removed and measured by ICP-MS to obtain the initial Pu concentration at time “zero”. A thin film was then suspended in the solution and allowed to equilibrate with the PuCl_6^{2-} complex. After sufficient equilibration time determined from the earlier uptake kinetics measurements, a 1 mL aliquot was withdrawn for measurement of aqueous Pu concentration. Then an additional ^{242}Pu spike was introduced to the solution to raise the Pu concentration and allowed to equilibrate. This process was repeated to reach aqueous Pu concentrations ranging from 4.13×10^{-9} M to 2.07×10^{-6} (1 to 15 ppb).

Batch Uptake Study Using LSC

After the previous experiment was performed it was noted relatively low uptake of ^{242}Pu was observed. It is believed that this is due to the large volume to sorbent mass ratio used in these experiments. Therefore, an additional experiment was performed using ^{238}Pu to examine behavior at lower total Pu concentration but higher specific activity. Four working solutions of ^{238}Pu were prepared at concentrations of 1, 10, 100, and 1000 dpm/mL by evaporating an aliquot of ^{238}Pu in 4M HNO_3 and reconstituting it in 9M HCl to produce the desired 1000 dpm/mL solution. The reconstituted stock was mixed with enough NaNO_2 to produce a 1mM NaNO_2 solution to ensure a Pu(IV) oxidation state. Oxidation state analysis of the stock solution using solvent extraction and lanthanum fluoride co-precipitation [Neu et al., 1994; Nitsche, Lee, and Gatti, 1988] determined that >99% was Pu(IV). Serial dilutions of the 1000 dpm/mL stock solution were performed to

generate the lower concentration Pu working solutions.

The batch uptake experiments were performed in sets of four, allowing for separate films to be used for each working stock solution. The films were submerged in 10 mL of ^{238}Pu bearing 9M HCl at each ^{238}Pu concentration and allowed to equilibrate for 24 h to ensure equilibrium had been reached. After 24 hr the films were removed and blotted with a paper towel and allowed to air dry. The remaining aqueous phase ^{238}Pu was determined using LSC on a Perkin Elmer liquid scintillation analyzer Tri-Carb model 2910 TR. The ^{238}Pu on the thin-film coated substrates was quantified with alpha spectrometry (described below).

Alpha Spectrometry

Alpha spectrometry was performed on an EG&G ORTEC Octète PC Alpha Spectrometer bank with 450 mm^2 passivated ion implanted planar silicon (PIPS) detectors. A calibration standard for energy efficiency determination was prepared by spotting five 10 μL drops of a 2966 dpm/mL ^{238}Pu solution across a 5% cross-linked, TEA functionalized film that was carefully “smeared” using a pipette tip to cover the area of the film. Films from batch uptake studies were allowed to air dry prior to analysis. Each detector was energy calibrated using a NIST traceable, electroplated ^{238}Pu , ^{241}Am , ^{235}U , ^{238}U bearing source electroplated on a 25mm diameter steel planchet. Differences in geometry between the NIST energy calibration source and the functionalized films did not allow for the NIST source to be used as an efficiency standard. Films that had undergone the aforementioned batch kinetic and uptake experiments were analyzed using

alpha spectrometry.

Determination of Anion-Exchange Capacity

To determine the binding site capacity of the thin-film coated Si wafers, radioactive ^{36}Cl was spiked into a 0.2 M NaCl solution to produce a 10000 dpm/mL (2.28×10^{-4} M ^{36}Cl) working stock solution. A functionalized film was submerged in 10 mL of the ^{36}Cl solution and allowed to equilibrate for 24 h to saturate the binding sites with $^{36}\text{Cl}^-$ and stable $^{35/37}\text{Cl}^-$. The assumption is that the radioactive ^{36}Cl will bind to the polymer with the same molar ratio of chloride ions ($\text{Cl}^{36}:\text{Cl}^{35}+\text{Cl}^{36}+\text{Cl}^{37}$) as is present in the solution. The film was then removed from the solution, blotted dry, and placed in 10mL of a 1M NaNO_3 solution for 24 h. The nitrate effectively displaces the bound chlorine back into solution and saturates the binding sites with nitrate. Then the aqueous ^{36}Cl concentration was determined using LSC. To ensure that all of the bound chlorine was displaced back into solution, the film was placed in a third solution of 1M Na_2SO_4 . Sulfate is a stronger nucleophile than Cl^- and should displace any remaining ^{36}Cl . The aqueous phase concentrations of both solutions were determined and the binding capacity was back-calculated based on the molar ratio of radioactive chlorine to the total chlorine present in the system and corrected to the amount of Cl^- present from the polymer.

Data Analysis

The data were fit to a linear distribution coefficient (K_d) that relates the mass of sorbed Pu per kg of sorbent ($\text{mol}_{\text{Pu}}/\text{kg}_{\text{sorbent}}$) to the aqueous phase concentration ($\text{mol}_{\text{Pu}}/\text{L}_{\text{solution}}$). The concentration of sorbed Pu on the thin-film sorbent ($[\text{Pu}]_{\text{solid}}$) is given by equation 1 where $[\text{Pu}]_{\text{aq}(0)}$ represents the initial plutonium concentration at time zero, $[\text{Pu}]_{\text{aq}(t)}$ is the aqueous plutonium concentration at equilibrium, V is the volume of the solution (L) and m_{sorbent} is the mass of the sorbent (kg). The linear distribution coefficient is defined in equation 2 as the ratio of the concentration on the solid at equilibrium ($[\text{Pu}]_{\text{solid}}$) to the concentration of plutonium in the aqueous phase at equilibrium ($[\text{Pu}]_{\text{aq}(t)}$).

$$[\text{Pu}]_{\text{solid}} = \frac{([\text{Pu}]_{\text{aq}(0)} - [\text{Pu}]_{\text{aq}(t)}) * V}{m_{\text{sorbent}}} \quad (1)$$

$$K_d = \frac{[\text{Pu}]_{\text{solid}}}{[\text{Pu}]_{\text{aq}(t)}} \quad (2)$$

The uptake data were calculated from alpha spectral analysis of the thin films after Pu uptake. A mass balance for the system was established using LSC to quantify the remaining aqueous Pu after uptake. A mass balance was calculated for the Pu systems using the LSC data to calculate the aqueous phase Pu and alpha spectrometry data to calculate the bound Pu. The sum of the LSC and alpha spectrometry data was divided by the known mass of Pu in each system to provide a mass balance on a percent basis. The

lower limit of detection (LLD) for the LSC analysis was determined using equation 3.

$$LLD = 2.71 + 4.65\sqrt{B} \quad (3)$$

where B is the total number of background counts. The minimum detectable activity (MDA) is therefore given by equation 4 where t is the count time. The minimum detectable concentration (MDC) is given in equation 5.

$$MDA = \frac{LLD}{t} \quad (4)$$

$$MDC = \frac{MDA}{EVf} \quad (5)$$

where E is the detection efficiency, V is the volume (or mass) of the sample, and f is the emission fraction. For the LSC analysis for ^{238}Pu it is assumed that the detection efficiency is 1. The emission fraction for ^{238}Pu is also 1.

CHAPTER FIVE

RESULTS AND DISCUSSION

Batch Uptake Kinetics of ^{242}Pu

The batch uptake kinetics were performed on triethyl amine functionalized poly(vinylbenzyl chloride) films cast on silicon wafers. The decrease in activity of the aqueous phase as determined by ICP-MS was attributed to the ion exchange of the plutonium species onto the polymer. Figure 5.1 demonstrates rapid ion exchange under the experimental conditions for both acid systems. Equilibrium between the sorbed Pu species and aqueous Pu was reached within 15 min. The figure is plotted as the fraction of final equilibrium state vs. the duration of ^{242}Pu exposure. The fraction of final equilibrium state was calculated by dividing the aqueous Pu concentration at the designated time by the aqueous Pu concentration at the last data point ($t = 15$ min). It is important to note that the last data point remained essentially constant past 15 min however this data is not plotted for simplicity.

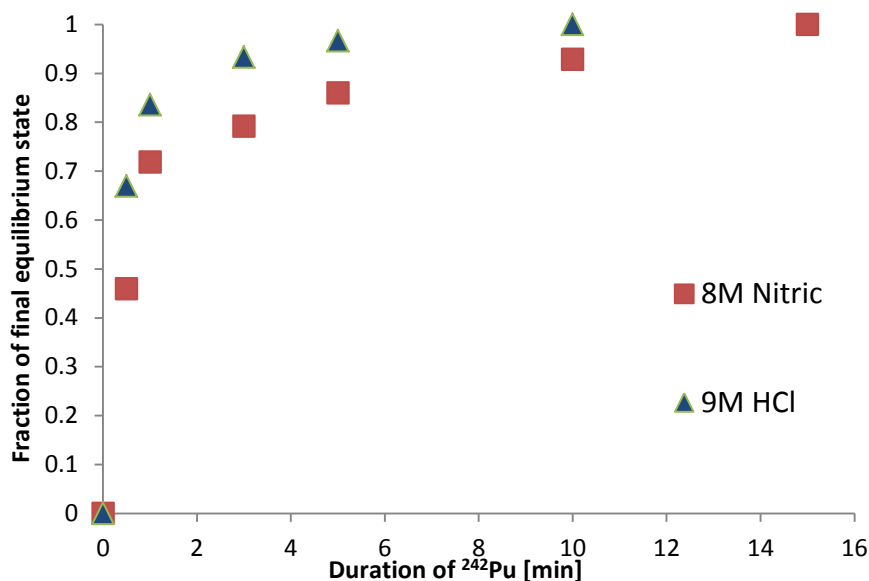


Figure 5.1: Uptake of Pu(IV) versus time from 9M HCl (triangles) and 8M HNO₃ (squares) onto thin-film coated Si wafers. Initial concentration in solution was 4.3×10^{-8} M Pu(IV).

It was later determined that Pu(IV) should exclusively be loaded out of HCl due to the oxidizing nature of HNO₃ and its ability to dissolve rhenium, the filament metal used in TIMS analyses of plutonium. All subsequent experiments excluded the use of 8 HNO₃.

Determination of Distribution Coefficients and Loading Capacities

The initial results of the distribution coefficients determination by ICP-MS were perplexing because relatively low to no uptake was observed, which contradicted previous preliminary uptake experiments. Upon further investigation, several systematic errors were noted that explained the results. The distribution coefficient (K_d) provides a

relationship between the sorbed Pu and aqueous Pu. The K_d equilibrium expression can be algebraically manipulated to provide an equation for the ratio of Pu in the aqueous phase to the moles of Pu on the solid as given below in equation 1.

$$\frac{1}{K_d \frac{m_{\text{sorbent}}}{v} + 1} = \frac{\text{mol Pu}_{\text{aq}}}{\text{Pu}_{\text{Tot}}} = \text{fraction of Pu in aqueous} \quad (1)$$

where m is the dry mass of the sorbent, v is the total volume of the system, K_d is the distribution coefficient, $\text{mol Pu}_{\text{aq}}$ is the moles of Pu in aqueous phase, and Pu_{Tot} is the total moles of Pu in the system. Under the experimental setup, the average mass of the film was 0.001g with a total volume of 100 mL. A *theoretically calculated* plot of the fraction of Pu remaining in the aqueous phase at varying K_d values under these conditions is given in Fig. 5.2.

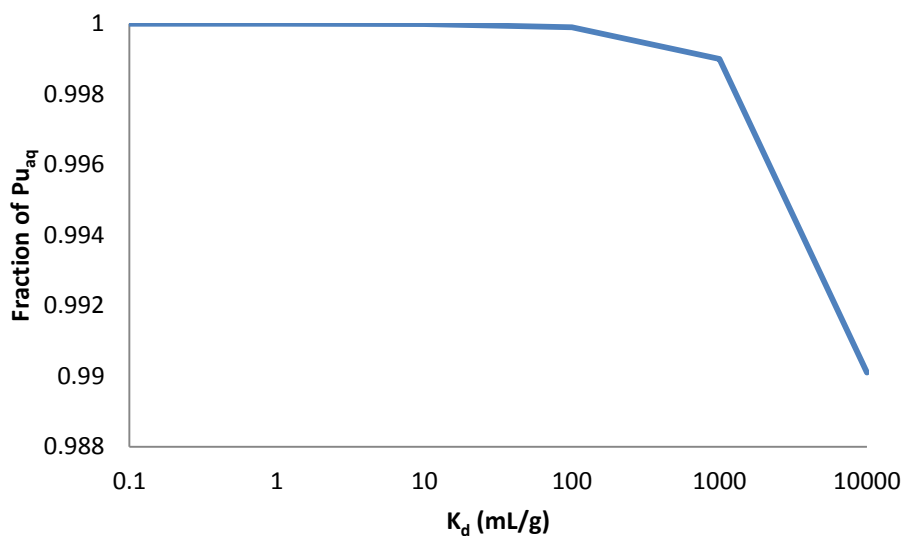


Fig. 5.2: Theoretically calculated plot of fraction of Pu remaining in aqueous phase versus distribution coefficient (K_d) using a sorbent mass of 0.001 g and a total system volume of 100mL.

As Fig. 5.2 demonstrates, the large volume to mass ratio used in the experiment results in minimal uptake from solution. Even with a K_d of 10,000, only 1% of the Pu is sorbed to the film at equilibrium, leaving 99% in solution. The small change in aqueous Pu concentration after sorption hindered the analysis especially at low initial Pu concentrations. The analysis was further plagued by matrix effects as well as Pu adsorbing to the ICP-MS tubing. A representative set of data is given in Table 5.1 to demonstrate the effects of these problems.

Table 5.1: Representative ICP-MS data for determination of distribution coefficient of PVBC thin film functionalized with TEA. A complete set of ICP-MS data is given in Appendix A.

Sample	Time (min)	Cumulative Mass of Pu added (μg)	[Pu] at time given (ppb)	% left in aqueous
Initial Concentration	0.00	0.01	0.10	119.66
A	10.00	0.01	0.10	131.22
B	21.25	0.03	0.31	110.23
C	44.75	0.10	1.05	97.80
D	56.00	0.21	2.09	108.30
E	67.42	0.52	5.22	105.45
F	78.75	1.05	10.39	103.72
G	90.25	1.57	15.51	108.09

It was noted that even after four washes with 1.29M HCl (4.5% HCl by weight) at the end of the ICP-MS analysis, as much as 10-20% of the initial Pu concentration was coming out in the final wash. It was unknown how much the Pu concentration was effected by having Pu removed through sorption to the ICP-MS tubing, or Pu added to the system through desorption of Pu from the tubing into “fresh” Pu solutions. The analysis was further exacerbated by matrix effects, which can profoundly impact the ionization efficiency of the analyte and result in inaccurate results. The standards were prepared in 0.75M (4.5% HNO₃ by weight); however, the samples were run out of 9M HCl which were diluted to ~1.29M HCl. Matrix effects were not considered until much

later into the analysis and thus most of the samples were run using HNO₃ standards which skewed the results. These problems coupled with mechanical problems with the ICP-MS during many of the analyses and the theoretical K_d limitations culminated in data that consistently showed little to no uptake. Plutonium masses higher than the known amount added to the system were even observed as seen in Table 5.1. An alternative experiment was devised to avoid the aforementioned problems using smaller total volumes and liquid scintillation counting for Pu analyses.

Batch Uptake Study Using LSC for Determination of Distribution Coefficients

Functionalized films were prepared by dip-coating PVBC (~180 nm measured by multi-angle ellipsometry) on a silicon substrate. The polymeric film was functionalized with TEA to produce quaternary amine anion-exchange sites for binding PuCl₆²⁻. Chlorine-36 exchange experiments run in triplicate determined the binding site capacity to be $1.25 \times 10^{-1} \pm 1.07 \times 10^{-2}$ meq/g_{polymer}, which is an order of magnitude lower than the Dowex 1 anion-exchange resin capacity of 3.1 meq/g of resin. The full mass of the polymer film was used in the calculations, as the percentage conversion to functionalized anion-exchange polymer is unknown. The binding capacity of the Dowex 1 resin was verified using the same experimental approach as was described for the functionalized films. It was determined that completely drying the resin by heating it at 50°C for 24 hours was necessary to obtain accurate masses as the resin is hydrophilic and the excess water may skew the true mass by as much as 30-40%.

In addition to the TEA functionalization, cross-linking of the films also produces

possible binding sites and so the uptake of Pu(IV) was examined for three sets of films. The first set consisted only of the PVBC backbone. The second set consisted of PVBC with 5% cross-linking by DABCO. The third set was PVBC with 5% cross-linking by DABCO and functionalized with TEA. Figure 5.3 shows a linear distribution between the sorbed and aqueous $^{238}\text{Pu(IV)}$ over the experimental mass loading range of $1.1 \times 10^{-10} \text{ M}$ – $1.1 \times 10^{-13} \text{ M}$ (1000 dpm/mL – 1 dpm/mL) for ^{238}Pu . The R-squared values for the 5% cross-linked + TEA functionalized films demonstrate the strong linearity in equilibrium distribution over the specified concentration range.

The K_d of the 5% cross-linked, TEA functionalized films showed relatively good reproducibility with a range from 7531-10485 L/kg and an average K_d of $9048 \pm 748 \text{ L/kg}$ as determined from the batch sorption studies using direct alpha spectrometry measurements. Furthermore, the calculated K_d is comparable to the approximate value of 10,000 for Dowex 1 anion-exchange resin commonly employed in TIMS measurements. Differences in the K_d value calculated for the functionalized films from the three replicates in Figure 5.3 may be due to slight sample-to-sample variation in the degree of conversion during TEA functionalization. A K_d was not calculated for the 0% cross-linked or 5% cross-linked unfunctionalized films due to the insignificant uptake onto those films. It currently is unknown exactly what conversion was achieved for each of the three replicate samples; therefore, the total mass of the film (polymer + functionalized polymer) was used in the K_d calculation.

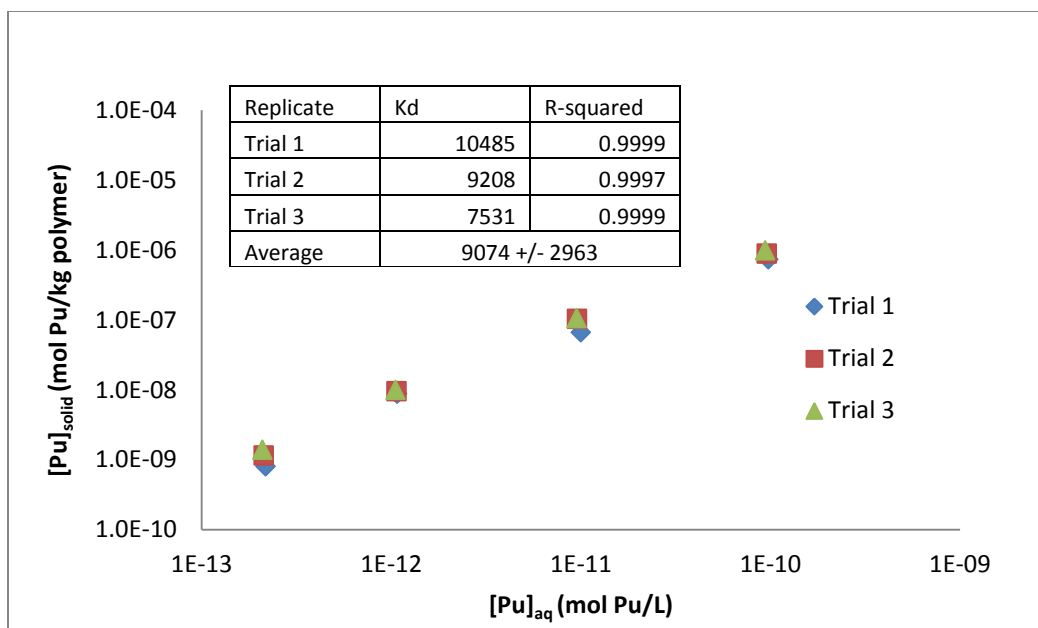


Fig 5.3 Sorption isotherm of ^{238}Pu (IV) on 5% cross-linked films with TEA functionalization. The corresponding K_d calculations, R-squared values for each replicate, along with the average K_d and standard deviation are presented as the inset table

Figure 5.3 shows triplicate measurements for 5% cross-linked, TEA functionalized films. However it does not include the highest aqueous Pu concentration point which is seen in Figure 5.4 obtained from a separate uptake study. The K_d values reported in Figure 5.3 are slightly lower due to the influence of the lowest aqueous Pu concentration points. These points are closer to background and have considerable uncertainty and therefore strongly affect the K_d calculation.

Uptake of Pu(IV) on the unfunctionalized films with 5% cross-linking were examined for comparison and are given in Figure 5.4. The 0% cross-linked films exhibited virtually no uptake and so are not given in the plot. The data are plotted as the

average of triplicate measurements and the uncertainty is given as 2σ of the standard deviation. The data indicate a 10^3 fold increase in uptake for the 5% cross-linked, TEA functionalized films. The data from the highest Pu uptake (4.3×10^{-8} M and 6.3×10^{-8} M Pu) are from an uptake experiment with CRM 130, which contains mostly ^{242}Pu by mass to examine Pu loading at a higher total mass. Re-calculation of K_d values including the higher mass loading shows a dramatic increase in K_d to $19,906 \pm 17.5$ L/kg. The linear model including the largest data point suggested a y-intercept of $-2.9 \times 10^{-7} \pm 1.33 \times 10^{-7}$. This model obviously overestimates sorbed Pu at low aqueous Pu concentration and so a linear regression was performed only on the averaged data points for each aqueous Pu concentration from Figure 5.3. The K_d was calculated to be 9057 ± 66.1 L/kg with a y-intercept of $8.62 \times 10^{-10} \pm 1.59 \times 10^{-9}$. This analysis demonstrates the strong influence of the higher Pu concentration data points. It is important to note that even with the lower K_d value, the model only underestimates the highest Pu concentration data point by a factor of two. A mass balance was calculated for the Pu systems using the LSC data to calculate the aqueous phase Pu and alpha spectrometry data to calculate the bound Pu (Table 5.2). The sum of the LSC and alpha spectrometry data was divided by the known mass of Pu in each system to provide a percent mass balance.

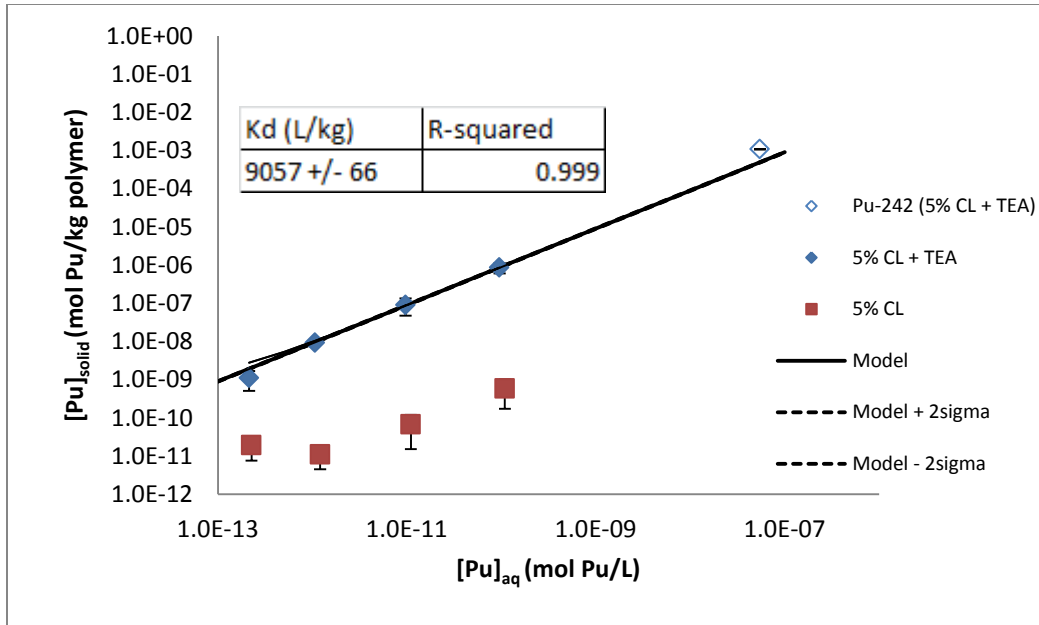


Fig 5.4: Sorption isotherm results for ^{238}Pu (IV) on 5% cross-linked + TEA functionalized films (blue diamonds), 5% cross-linked polymer films (red squares). The unfilled blue diamond for 5% cross-linked and TEA functionalized films are data from an uptake experiment with CRM 150 (mainly ^{242}Pu by mass). All data are the average of triplicate measurements and the uncertainty is represented as 2σ of the standard deviation. The equation for the model fit is given by $[\text{Pu}]_{\text{solid}} = 9057[\text{Pu}]_{\text{aq}} + 8.62 \times 10^{-10}$

Table 5.2 Mass balance calculated for Pu uptake systems. LSC data was used to calculate aqueous phase Pu and alpha spectrometry data was used to calculate Pu bound to the thin films. ^aLSC data was below the MDC of 0.8 Bq/g of solution. ^bAlpha spectrum did not provide an adequate spectrum for use in calculations.

Film	Aqueous Initial Activity (dpm/g)	Measured Aqueous Activity after uptake (dpm/g)	Alpha Spec based Mass (dpm)	Mass Balance (%)
Film 1 5% CL + TEA	946.40	869.35	517.46	96.66
Film 2 5% CL + TEA	95.81	87.11	46.48	95.16
Film 3 5% CL + TEA	10.48	8.68	5.87	87.74
Film 4 5% CL + TEA	2.00	1.14	0.54	a
Film 5 5% CL + TEA	946.40	852.66	602.39	95.65
Film 6 5% CL + TEA	95.81	84.25	67.37	94.08
Film 7 5% CL + TEA	10.48	8.73	6.25	88.54
Film 8 5% CL + TEA	2.00	0.61	0.77	a
Film 9 5% CL + TEA	946.40	849.36	673.55	96.04
Film 10 5% CL + TEA	95.81	84.64	69.45	94.74
Film 11 5% CL + TEA	10.48	8.78	6.85	89.53
Film 12 5% CL + TEA	2.00	0.97	0.92	a

Film	Aqueous Initial Activity (dpm/g)	Measured Aqueous Activity after uptake (dpm/g)	Alpha Spec based Mass (dpm)	Mass Balance (%)
Film 13 5% CL	946.40	949.46	3.08	100.35
Film 14 5% CL	95.81	94.51	0.34	98.68
Film 15 5% CL	10.48	9.37	0.07	89.46
Film 16 5% CL	2.00	1.14	0.11	a
Film 17 5% CL	946.40	944.17	5.83	99.82
Film 18 5% CL	95.81	94.19	0.62	98.36
Film 20 5% CL	2.00	1.23	0.16	a
Film 21 5% CL	946.40	945.55	5.73	99.96
Film 22 5% CL	95.81	94.16	0.78	98.35
Film 23 5% CL	10.48	9.81	0.11	93.68
Film 24 5% CL	2.00	1.06	0.20	a

Film	Aqueous Initial Activity (dpm/g)	Measured Aqueous Activity after uptake (dpm/g)	Alpha Spec based Mass (dpm)	Mass Balance (%)
Film 25 0% CL	946.40	947.52	b	1.00
Film 26 0% CL	95.81	93.96	b	0.98
Film 27 0% CL	10.48	9.41	b	0.90
Film 28 0% CL	2.00	1.14	b	a
Film 29 0% CL	946.40	947.89	b	1.00
Film 30 0% CL	95.81	94.49	b	0.99
Film 31 0% CL	10.48	9.88	b	0.94
Film 32 0% CL	2.00	1.14	b	a
Film 33 0% CL	946.40	928.85	b	0.98
Film 34 0% CL	95.81	92.01	b	0.96
Film 35 0% CL	10.48	9.22	b	0.88
Film 36 0% CL	2.00	0.88	b	a

The binding site capacity studies indicate that significantly more Pu could be loaded onto the functionalized films than was loaded under the experimental conditions given in this paper. The lack of a sorption plateau in Fig. 5.3 and Fig. 5.4 provides further evidence that the anion-exchange sites were not saturated. The unfunctionalized films

showed minimal uptake and uptake remained essentially constant with increasing Pu(IV) concentration. It was hypothesized that the 5% cross-linked films would uptake a greater mass of plutonium due to the formation of quaternary amines during the cross-linking reaction. The results for the 0% and 5% cross-linked unfunctionalized films show little difference in uptake between the films. Due to uncertainty in the measurement, greater uptake by the 5% cross-linked could not be validated. The low uptake that was observed for the 0% and 5% cross-linked, unfunctionalized films is most likely governed by diffusion of PuCl_6^{2-} into the polymer film. While the 5% cross-linked films do provide additional anion-exchange sites, steric hindrance and slower kinetics may result in the low uptake observed.

Alpha Spectrometry of Thin Films

The solid-state ^{238}Pu mass and ^{242}Pu was quantified with alpha spectrometry for comparison to the LSC measurements. The LSC data compared very well with the alpha spectrometry data for the 1000 and 100 dpm/mL solutions. Mass loading ratios based on LSC compared to alpha spectrometry measurements gave ratios of 0.76 – 0.99 for the triplicate trial runs (with a ratio of 1 having the same calculated mass loading). Lower working concentrations of 10 dpm/mL and 1 dpm/mL did not have enough radioactivity to obtain sufficient LSC counts or a reliable enough spectrum to accurately compare the two methods. Figure 5.5 shows an alpha spectrum from the ^{242}Pu batch uptake experiments with the 5% cross-linked, TEA functionalized film. These are high quality alpha spectra with resolutions on the order of 25-30 keV. The significantly lower count

rate and poor spectral quality of the 5% cross-linked and 0% cross-linked unfunctionalized films are demonstrated in Fig. 5.6. Table 5.3 summarizes the alpha spectroscopy data for the 180 nm 5% cross-linked, TEA functionalized, 5% cross-linked unfunctionalized, and 0% cross-linked unfunctionalized films. These data show significantly greater Pu(IV) uptake on the TEA functionalized as observed in Figure 5.4 above. Thus the thin films used in this work showed excellent potential as alpha spectrometry substrates.

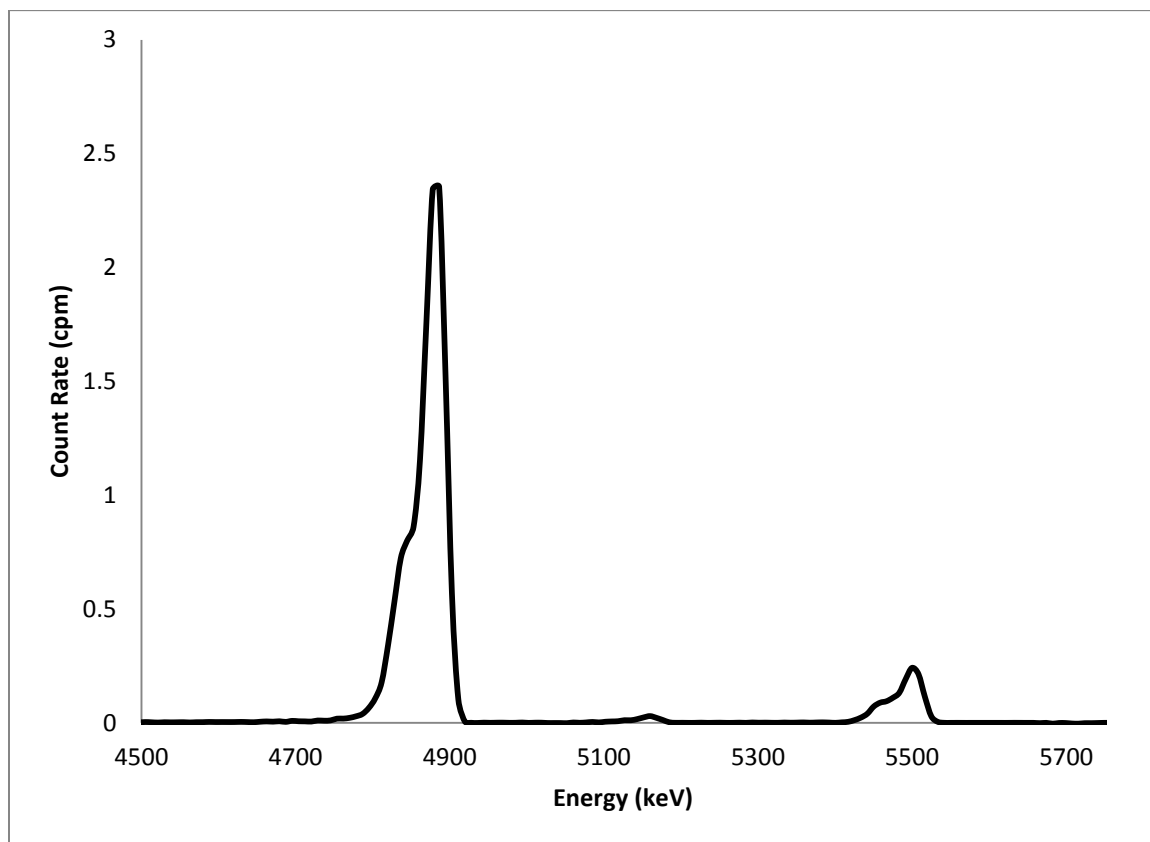


Figure 5.5: Alpha spectrum of 5% cross-linked, TEA functionalized films submerged in CRM (^{242}Pu , $^{239/240}\text{Pu}$, ^{238}Pu).

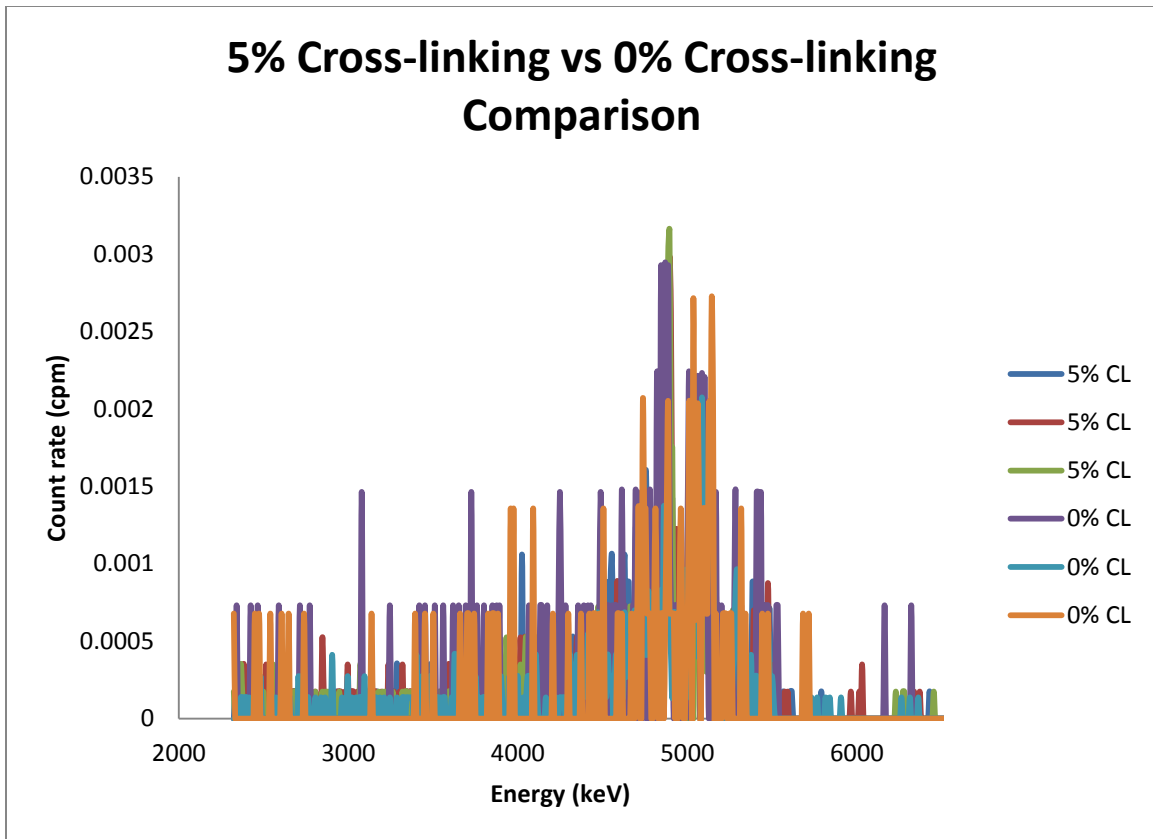


Fig. 5.6 Alpha spectra for 5% cross-linked and 0% cross-linked unfunctionalized films submerged in CRM (^{242}Pu , $^{239/240}\text{Pu}$, ^{238}Pu).

Table 5.3: Alpha spectroscopy based analysis of 5% cross-linked, TEA functionalized (5% CL + TEA), 5% cross-linked unfunctionalized (5% CL), and 0% cross-linked (0% CL) unfunctionalized films. The 5%CL and 0% CL films did not provide an adequate enough spectrum to sufficiently characterize the full width half maximum and so are given as not applicable (NA).

Sample	Measured Mass on Film (ng)	[Pu] in solution at equilibrium [ppb]	Percent Uptake (%)	²⁴² Pu Full Width Half Maximum
5% CL + TEA	25.94	9.65	2.62	30.33
5% CL + TEA	43.12	14.37	2.92	28.25
5% CL + TEA	27.09	14.52	1.83	28.79
5% CL + TEA	38.43	14.41	2.60	26.69
5% CL	0.05	4.97	0.01	NA
5% CL	0.06	6.13	0.01	NA
0% CL	0.06	15.51	0.00	NA
0% CL	0.03	5.88	0.01	NA
0% CL	0.04	5.88	0.01	NA

CHAPTER SIX

CONCLUSIONS AND FUTURE WORK

Conclusions

A thin film of PVBC functionalized with TEA on Si wafers was developed for plutonium ion exchange from 9 M HCl. Preliminary kinetics experiments also indicated extraction from 8 M HNO₃ is possible. However, the intent is to utilize these thin-film coatings on Re filaments for TIMS analysis and Re readily dissolves in HNO₃. Thus experiments were primarily conducted in 9 M HCl. The TEA functionalized thin films demonstrated significantly higher capacity for Pu(IV) compared to the unfunctionalized and/or uncrosslinked polymer thin-film. Anion-exchange experiments showed an anion exchange capacity at $1.25 \times 10^{-1} \pm 1.07 \times 10^{-2}$ meq/g_{polymer} and a K_d value of 9057 ± 66.1 L/kg. The standard deviation in the K_d value is interpreted to be a result of varying degrees of functionalization within the film and the use of the total mass in the calculation in place of the true functionalized mass. Results indicated that the polymer thin film yields high resolution alpha spectra with sharp peaks, comparable to samples produced via electrodeposition. In addition, preliminary data given in Appendix B indicate a strong potential for utilization as a TIMS substrate (Appendix B), as the films were able to increase the total Pu counts 3-4 times over the bead loading method while maintaining accurate isotopic information as determined by thermal ionization mass spectrometry. Thus, the rapid uptake kinetics, high binding capacity, and high-resolution alpha spectra make this thin-film platform an outstanding substrate for rapid

radioanalytical analyses.

Future Work

The films operation within the TIMS is the most critical experiment at the conclusion of this research. Preliminary data not presented in this thesis have shown mixed results. Although several runs using the films for isotopic determination have shown great agreement to isotopic standards, the reproducibility has been poor. In addition, the films consistently show lower overall counts and poorer ionization efficiencies than those achieved using the bead-loading method. The structural integrity of the films during operation has also been problematic as several of the filaments have broken during analysis, most likely due to the high chloride content of the thicker films (~1500 μ m). At the elevated temperatures present in TIMS, the polymer will start to degrade and the chloride may react with the rhenium. At high temperatures, the ReCl_x compounds are a volatile gas and may etch away the thin films and the rhenium filament.

The most recent TIMS analysis however showed vastly improved performance that outperformed the anion-exchange resin beads, producing 3-4 times the total counts with reproducible and accurate isotopic composition analyses (Appendix B). This experiment utilized 15% cross-linked, TEA functionalized fibers of the polymer thin films which were produced by withdrawing a needle from the organic polymer solution which quickly air dried. The fibers were examined under microscope and cut into approximately 0.1" pieces. The fibers were placed into vials containing 10pg of NBL CRM 128 and shaken overnight. The fibers were removed from vials and loaded onto 14

TIMS canoe filaments (seven filaments for each polymer fiber strand). A drop of collodion was added to the fibers to secure the fiber to the filament.

Several experiments have been planned to fine-tune the films in synthesis as well as film operation. The thickness of the film plays a large role in the ionization efficiency. While the carbon content aids in the formation of desirable carbides, a large mass of polymer atop the filament may impede a gaseous ion from reaching the detector. The film thickness should be optimized to obtain the highest ionization efficiency as possible, while maintaining adequate structural and anion-exchange capacities. Alpha spectrometry studies with varying film thicknesses may serve as adequate surrogates by relating spectral resolution to “ease” with which an ion may escape the film. However no experiment would be better than running the films within an actual TIMS system. In lieu of purchasing a thermal ionization mass spectrometer (an expensive endeavor), an ionization chamber is being built to determine the relative ionization efficiency of different film thicknesses, geometries, and changes in polymer synthesis so the films can be optimized prior to its introduction in the mass spectrometer.

To better elucidate whether the Pu is diffusing into the polymer film or present mostly on the surface of the film, the ^{36}Cl anion-exchange capacity experiment reported in this experiment should be run on varying film thicknesses to determine if a linear relationship is observed between the anion-exchange capacity of the films and the thickness.

Additional studies to determine the degree of functionalization and the reproducibility are needed to more accurately characterize the films. One such an

experiment would be to vary the contact time with TEA during synthesis and determine how uptake changes holding all other variables constant. TEA is dissolved in chloroform during the functionalization step to aid in swelling the polymer and homogenizing the functionalization. Changes in chloroform concentration used during synthesis may also sufficiently alter the degree of functionalization and should be considered in synthesis optimization.

Additional uptake studies in the presence of other actinide species and competing ions would be beneficial should the films be used to concentrate actinides from natural waters with little to no sample preparation. The feasibility of this approach has been demonstrated in a series of preliminary experiments by concentrating natural U from well water near Lake Jocassee, South Carolina (Mannion et al., 2015). However, a more systematic study is necessary to determine its applicability.

APPENDICES

Appendix-A

Table A.1: List of ICP-MS data and [^{242}Pu] calculations for 5% cross-linked, TEA functionalized, 5% cross-linked unfunctionalized and 0% cross-linked unfunctionalized films.

Film #27 (5% CL + TEA)	Total Dilution Factor	Time (min)	Calculated Cumulative Mass of Pu added (ug)	Measured [$\text{Pu}_{\text{aq,t}}$] at time given (ppb)	% left in aqueous
Initial Conc.	0.07	0.00	0.01	0.10	119.66
A	0.07	10.00	0.01	0.10	131.22
B	0.07	21.25	0.03	0.31	110.23
C	0.07	44.75	0.10	1.05	97.80
D	0.07	56.00	0.21	2.09	108.30
E	0.07	67.42	0.52	5.22	105.45
F	0.07	78.75	1.05	10.39	103.72
G	0.07	90.25	1.57	15.51	108.09

Film #28 (5% CL + TEA)	Total Dilution Factor	Time (min)	Calculated Cumulative Mass of Pu added (ug)	Measured [Pu _{aq,t}] at time given (ppb)	% left in aqueous
Initial Conc.	0.19	10.00	0.01	0.10	247.38
A	0.19	12.00	0.01	0.10	173.53
B	0.19	25.25	0.03	0.31	121.13
C	0.19	35.00	0.05	0.52	109.07
D	0.19	46.25	0.10	1.05	105.38
E	0.19	57.25	0.21	2.09	101.92
F	0.19	68.15	0.52	5.22	107.04
G	0.19	79.75	1.05	10.39	106.04
H	0.19	91.75	1.57	15.51	101.33

Film # (5% CL)	Total Dilution Factor	Time (min)	Calculated Cumulative Mass of Pu added (ug)	Measured [Pu _{aq,t}] at time given (ppb)	% left in aqueous
Initial Conc.	0.07	0.00	0.01	0.10	145.30
A	0.12	10.00	0.01	0.10	134.60
B	0.12	21.25	0.03	0.31	161.17
C	0.11	32.00	0.05	0.52	122.72
D	0.11	42.75	0.10	1.05	113.66
E	0.11	53.75	0.21	2.09	109.15
F	0.11	68.00	0.52	5.22	146.15
G	0.11	79.00	1.05	10.39	126.21
H	0.11	91.00	1.57	15.51	118.64

Film # 17 (5% CL)	Total Dilution Factor	Time (min)	Calculated Cumulative Mass of Pu added (ug)	Measured [Pu _{aq,t}] at time given (ppb)	% left in aqueous
Initial Conc.	0.12	0.00	0.00	0.04	1549.19
A	0.12	10.00	0.00	0.04	1111.39
B	0.12	20.50	0.01	0.12	375.01
C	0.12	31.00	0.02	0.20	243.69
D	0.12	41.75	0.04	0.40	169.79
E	0.12	52.50	0.08	0.79	135.26
F	0.12	63.25	0.28	2.77	127.15
G	0.12	74.75	0.48	4.72	123.01
H	0.12	90.00	0.68	6.65	119.97

Film # 18 (5% CL)	Total Dilution Factor	Time (min)	Calculated Cumulative Mass of Pu added (ug)	Measured [Pu _{aq,t}] at time given (ppb)	% left in aqueous
Initial Conc.	0.12	0.00	0.00	0.04	876.26
A	0.09	11.25	0.00	0.04	854.28
B	0.12	22.50	0.01	0.12	285.19
C	0.12	33.50	0.02	0.20	193.53
D	0.12	45.00	0.04	0.40	149.30
E	0.12	56.00	0.16	1.59	124.64
F	0.12	71.50	0.36	3.55	122.06
G	0.12	85.00	0.56	5.50	121.54
H	0.12	97.00	0.76	7.42	122.30

Film # 39 (0% CL)	Total Dilution Factor	Time (min)	Calculated Cumulative Mass of Pu added (ug)	Measured [Pu _{aq,t}] at time given (ppb)	% left in aqueous
Initial Conc.	0.11	0.00	0.00	0.04	176.42
A	0.11	12.75	0.00	0.04	176.06
B	0.11	24.00	0.01	0.12	141.06
C	0.11	35.00	0.02	0.20	134.74
D	0.11	46.00	0.04	0.40	131.40
E	0.11	58.00	0.08	0.79	132.13
F	0.11	69.00	0.20	1.98	134.99
G	0.11	80.00	0.40	3.94	135.46
H	0.11	91.00	0.60	5.88	133.30

Film # 40 (0% CL)	Total Dilution Factor	Time (min)	Calculated Cumulative Mass of Pu added (ug)	Measured [Pu _{aq,t}] at time given (ppb)	% left in aqueous
Initial Conc.	0.11	0.00	0.00	0.04	323.03
A	0.11	10.00	0.00	0.04	261.71
B	0.11	21.00	0.01	0.12	156.36
C	0.11	32.00	0.02	0.20	156.97
D	0.12	44.00	0.04	0.40	130.41
E	0.11	55.00	0.08	0.79	123.96
F	0.11	66.00	0.20	1.98	131.48
G	0.11	77.00	0.40	3.94	130.41
H	0.06	89.00	0.60	5.88	131.93

Film # 60 (0%CL)	Total Dilution Factor	Time (min)	Calculated Cumulative Mass of Pu added (ug)	Measured [Pu _{aq,t}] at time given (ppb)	% left in aqueous
Initial Conc.	0.06	0.00	0.01	0.10	144.97
A	0.06	10.00	0.01	0.10	145.76
B	0.06	20.75	0.03	0.31	119.68
C	0.07	31.00	0.05	0.52	122.19
D	0.06	42.00	0.10	1.05	119.87
E	0.07	52.75	0.21	2.09	115.11
F	0.07	63.50	0.52	5.22	112.22
G	0.06	74.25	1.05	10.39	107.03
H	0.06	90.00	1.57	15.51	112.74

Appendix B

Table B.1 TIMS data for 15% cross-linked functionalized polymer fibers (Sample ID – CU) compared to resin bead (Sample ID – SRNL BEAD)

<u>Sample ID</u>	<u>Total counts</u> (<u>Pu242 +</u> <u>Pu239</u>)	<u>Uncorrected</u> <u>Pu239/Pu242</u> <u>ratio</u>	<u>Comments</u>
<u>CU15CL1</u>	-	-	<u>Fiber fell out of filament while loading the filament into the TIMS holder</u>
<u>CU15CL2</u>	-	-	<u>Fiber fell out of filament while loading the filament into the TIMS holder</u>
<u>CU15CL3</u>	<u>25</u>	<u>3</u>	<u>Completed a four hour analysis method/</u> <u>Fiber fell out?</u>
<u>CU15CL4</u>	<u>687376</u>	<u>1</u>	<u>Completed a four hour analysis method</u>
<u>CU15CL5</u>	<u>152739</u>	<u>0.999</u>	<u>Completed a four hour analysis method</u>
<u>CU15CL6</u>	<u>1166718</u>	<u>0.999</u>	<u>Completed a four hour analysis method</u>
<u>CU15CL7</u>	<u>0</u>	<u>0</u>	<u>After the overnight shaking, the polymer fiber was attached to vial wall not in solution</u>
<u>SRNLBEAD</u>	<u>369054</u>	<u>0.999</u>	<u>A good run and good agreement with certified value for Pu239/Pu242 ratio</u>
<u>SRNLBEAD</u>	<u>45125</u>	<u>1</u>	<u>A poor run but good agreement with certified value for Pu239/Pu242 ratio</u>

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