Synthesis and Characterization of Functionalized Surfaces for Rapid Determination of Alpha Particle Emitting Radionuclides

Mary Ann Williford
Clemson University

Follow this and additional works at: https://tigerprints.clemson.edu/all_theses

Recommended Citation
https://tigerprints.clemson.edu/all_theses/2496

This Thesis is brought to you for free and open access by the Theses at TigerPrints. It has been accepted for inclusion in All Theses by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.
SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED SURFACES FOR RAPID DETERMINATION OF ALPHA PARTICLE EMITTING RADIONUCLIDES

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 Earth Science
Environmental Radiochemistry

by
Mary Ann Williford
December 2014

Accepted by:
Dr. Brian Powell, Committee Chair
Dr. Timothy DeVol
Dr. Glenn Fugate
ABSTRACT

To fulfill a need for rapid, simple, and inexpensive ways to identify alpha emitting radioisotopes (i.e. primarily actinides), a method has been developed for the analysis of plutonium by combining concentration and source preparation into a single step using functionalized or coated substrates. Two substrates were utilized in this work 1) glass slides functionalized using polymerized aspartic acid and 2) glass discs coated with graphene oxide (GO) prepared by spin coating. Uptake of plutonium on both substrates was low, on the order of 1% of the total activity in the system. However, GO was found to have superior resolution. As a practical demonstration of the utility of this approach, GO coated glass discs were used to concentrate plutonium from up to 3.7 liters of water and then assayed directly. No pretreatment or separation of the spiked water was required and the procedure can be complete within 24 hours (allowing for a 12 hour count time). Due to the thin layer of sorbent, self-absorption was kept to a minimum and full width half maximum values were commonly seen between 17 keV and 39 keV at 5.6 MeV. However, the requirement for this thin layer causes a reduction in uptake efficiency due to the low mass of GO on the substrate.
ACKNOWLEDGEMENTS

I would like to express my appreciation for the support that I have received throughout my time at Clemson. I would like to start by thanking my advisor, Dr. Brian Powell, for his understanding and guidance throughout this research project and my coursework. Among many other things, Dr. Powell has taught me that the presentation of research results is just as important as the experimental design and analysis of the data. His commitment to my development and understanding of this concept has made me a better scientist and will have a positive impact on my future projects.

I would also like to express gratitude to Dr. Timothy DeVol for his knowledge, patience, and kindness. He taught me the importance of questioning everything, even peer reviewed literature and published textbooks. He pushed me to trust my knowledge and to break overwhelming projects into manageable parts. Most of all I would like to thank him for taking the time to help me understand concepts, in the midst of his busy schedule.

I would also like to thank my committee member Dr. Glenn Fugate for agreeing to add his expertise and opinions to this project.

I have enjoyed being a part of the Powell Research Group. The feedback and suggestions pertaining to my projects have been invaluable and I have enjoyed learning from the group’s research experiences.
None of this would be possible without the funding that I received from Department of Homeland Security – Nuclear Forensics Junior Faculty Award. I am grateful for the opportunity to contribute to this field.

I would like to recognize my family for their love, support, and understanding. Not only did they encourage me to follow my dream, but they also understood the sacrifices that had to be made. They graciously understood the missed vacations, birthdays, weddings and other family events. A special acknowledgement to my mother who has always believed in me and taught me that perseverance will pay off.

Most of all I would like to thank my husband and best friend Stas for taking this journey with me. Through the many late nights, early mornings, and stressful days he has been only loving and supportive and I could not have done this without him.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>viii</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. BACKGROUND</td>
<td>4</td>
</tr>
<tr>
<td>Alpha Particle Decay</td>
<td>4</td>
</tr>
<tr>
<td>Alpha Particle Detection</td>
<td>5</td>
</tr>
<tr>
<td>Alpha Particle Source Preparation</td>
<td>6</td>
</tr>
<tr>
<td>Advantages</td>
<td>8</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>8</td>
</tr>
<tr>
<td>Alpha Spectroscopy with Coated or Functionalized Surfaces</td>
<td>9</td>
</tr>
<tr>
<td>Fundamental Considerations for Experimental Design</td>
<td>9</td>
</tr>
<tr>
<td>Graphene Oxide</td>
<td>13</td>
</tr>
<tr>
<td>Previous Studies Examining Radiouclide Sorption to GO</td>
<td>14</td>
</tr>
<tr>
<td>Previous Studies Examining Thin Films as Alpha Spectroscopy Substrates</td>
<td>17</td>
</tr>
<tr>
<td>III. EXPERIMENTAL GOALS AND TASKS</td>
<td>20</td>
</tr>
<tr>
<td>Task 1</td>
<td>20</td>
</tr>
<tr>
<td>Task 2</td>
<td>20</td>
</tr>
<tr>
<td>IV. MATERIALS AND METHODS</td>
<td>Page</td>
</tr>
<tr>
<td>---------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Functionalization of Glass Slides with Polymeric Amino Acids</td>
<td>21</td>
</tr>
<tr>
<td>Sorption of Actinides to Large Flakes of Graphene Oxide</td>
<td>24</td>
</tr>
<tr>
<td>GO Plating with Sonicated GO</td>
<td>24</td>
</tr>
<tr>
<td>GO Dilution</td>
<td>25</td>
</tr>
<tr>
<td>GO Percent Uptake</td>
<td>25</td>
</tr>
<tr>
<td>Spin Coating GO</td>
<td>26</td>
</tr>
<tr>
<td>Equilibrium Uptake Studies</td>
<td>27</td>
</tr>
<tr>
<td>Optimization of pH</td>
<td>27</td>
</tr>
<tr>
<td>Distribution Coefficient (K_d) Determination for GO Coated Discs</td>
<td>27</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>V. RESULTS AND DISCUSSION</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mica</td>
<td>30</td>
</tr>
<tr>
<td>Functionalized Glass</td>
<td>30</td>
</tr>
<tr>
<td>Equilibrium time &amp; pH</td>
<td>34</td>
</tr>
<tr>
<td>Graphene Oxide</td>
<td>37</td>
</tr>
<tr>
<td>Type of surface &amp; particle morphology</td>
<td>37</td>
</tr>
<tr>
<td>Percent uptake</td>
<td>40</td>
</tr>
<tr>
<td>Uptake studies using GO spin coated onto glass discs</td>
<td>43</td>
</tr>
<tr>
<td>Examination of uptake kinetics and the influence of pH</td>
<td>45</td>
</tr>
<tr>
<td>Characterization of GO spin coated discs</td>
<td>48</td>
</tr>
<tr>
<td>Influence of GO mass on spin coated discs</td>
<td>52</td>
</tr>
<tr>
<td>Demonstration of Pu uptake on GO coated discs from dilute solutions</td>
<td>57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>VI. CONCLUSIONS AND FUTURE WORK</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPENDICES</td>
<td>67</td>
</tr>
<tr>
<td>Appendix-A</td>
<td>67</td>
</tr>
<tr>
<td>Appendix-B</td>
<td>68</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>70</td>
</tr>
</tbody>
</table>
**LIST OF TABLES**

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Table 2.1</strong></td>
<td>A brief description of the advantages and disadvantages of the three most widely used methods of source preparation for alpha spectroscopy.</td>
<td>8</td>
</tr>
<tr>
<td><strong>Table 5.1</strong></td>
<td>Concentrations used in a batch sorption experiment of GO and $^{239}$Pu in which uptake was measured using LSC data.</td>
<td>42</td>
</tr>
<tr>
<td><strong>Table 5.2</strong></td>
<td>Comparison of alpha spectra features due to uptake of $^{238}$Pu onto GO spin coated discs at pH 2.88 with variation in time. Results were compared for reproducibility within samples.</td>
<td>44</td>
</tr>
<tr>
<td><strong>Table 5.3</strong></td>
<td>Comparison of alpha spectra features due to uptake of $^{238}$Pu onto GO spin coated discs with variation between samples due to pH values of Pu solution.</td>
<td>47</td>
</tr>
<tr>
<td><strong>Table 5.4</strong></td>
<td>Comparison of alpha spectra features due to uptake of $^{238}$Pu and $^{233}$U onto GO coated discs created by spin coating at varying RPMs to create coatings of varying mass.</td>
<td>56</td>
</tr>
<tr>
<td><strong>Table 5.5</strong></td>
<td>Comparison of alpha spectra features due to uptake of $^{238}$Pu onto GO coated discs after a 12 hour suspension in 3.7 L of pH 5 solution. A Kd was also calculated based on results using a GO mass of 33 µg.</td>
<td>58</td>
</tr>
<tr>
<td><strong>Table 5.6</strong></td>
<td>Kd’s calculated from $^{238}$Pu uptake on GO coated discs submerged in pH 2.88 solution assuming 33 µg of GO.</td>
<td>62</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Figure 2.1</td>
<td>Theoretical calculation of fraction aqueous per mass of sorbent in grams.</td>
<td>13</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Conceptual image of graphene oxide complete with functional groups.</td>
<td>14</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>A functionalized glass disc composed of a glass layer, a GOPS intermediate and an amino acid layer which can be used to selectively sorb to actinides. Figure was modified from Strakosas et al., 24</td>
<td>22</td>
</tr>
<tr>
<td>Figure 5.1</td>
<td>Alpha spectra of PLAA and PDAA functionalized glass discs as well as a blank glass disc after submersion in $^{239}$Pu.</td>
<td>32</td>
</tr>
<tr>
<td>Figure 5.2</td>
<td>Alpha spectra of triplicate PDAA and PLAA coated glass slides. Slides submerged in 10 mL of solution with 46 dpm $^{238}$Pu for 1000 minutes.</td>
<td>33</td>
</tr>
<tr>
<td>Figure 5.3</td>
<td>LSC results of $^{238}$Pu fraction remaining in aqueous solution vs time in hours for removal by functionalized disc submerged in ~50dpm/mL $^{238}$Pu solution.</td>
<td>35</td>
</tr>
<tr>
<td>Figure 5.4</td>
<td>Alpha spectra of Pu amended PLAA functionalized slides producing the most counts from a triplicate batch when suspended in 6000 dpm/mL $^{238}$Pu solution for 24 hours at varying pH values.</td>
<td>36</td>
</tr>
</tbody>
</table>
Figure 5.5 Alpha spectroscopy results of graphene oxide flakes and sonicated particles submerged in $^{239}$Pu solution for 24 hours, dried at 50°C and counted. The GO sonicated particles were concentrated via centrifugation then pipetted onto a stainless steel planchet to prepare the source for alpha spectroscopy.

Figure 5.6 Similar activities of $^{239}$Pu (225 dpm) were combined with similar concentrations of GO and the solutions were centrifuged, resuspended in varying volumes (indicated by the legend) then 100 $\mu$L aliquots were pipetted on stainless steel planchets for alpha spectroscopy. The 300 $\mu$L is the most concentrated GO suspension and 1200 $\mu$L is the least concentrated.

Figure 5.7 Alpha spectra results of GO spin coated discs submerged in 80 mL of ~50 dpm/mL $^{238}$Pu solution at pH value 2.88. Samples 14 and 15 equilibrated for one hour, while all other samples were equilibrated for 30 minutes, triple rinsed with DI H$_2$O, dried at 50°C and then counted on the alpha spectrometer for 2000 minutes.

Figure 5.9 The percent uptake and percent resolution calculated for GO spin coated discs submerged in 30 mL of ~54 dpm/mL $^{238}$Pu solution for one hour at varying pH values.

Figure 5.10 SEM of GO spin coated disc showing full coverage of sonicated flakes.
Figure 5.11 SEM of GO spin coated disc showing shallow height differences... 49

Figure 5.12 Left image shows phase shift of GO coated disc with channels present. Right image shows thickest GO prepared disc with flakes attributing to height difference........................................................................ 51

Figure 5.13 Left image shows phase shift of glass with fairly uniform phases present. Right image of height difference of glass shows uniform height. Lines in images are artifacts of AFM capture............................................. 51

Figure 5.14 Alpha spec results of three GO spin coated discs of varying thickness, where thickness was controlled by variation in RPM, submerged in ~100 dpm/mL $^{238}$Pu solution.......................................................... 54

Figure 5.15 Alpha spec results of three GO spin coated discs of varying thickness, where thickness was controlled by variation in RPM, submerged in ~100 dpm/mL $^{235}$U solution..................................................... 55

Figure 5.16 GO spin coated disc (sample 41 from Table 5.5) suspended for 12 hours in 3.7 liters of tap water spiked with ~100 dpm of $^{238}$Pu then counted by alpha spectroscopy for 12 hours.................................................. 58

Figure 5.17 GO spin coated disc (sample 52 from Table 5.5) suspended for 12 hours in 3.7 liters of tap water spiked with ~500 dpm of $^{238}$Pu and then counted by alpha spectroscopy for 12 hours................................................. 59
CHAPTER ONE
INTRODUCTION

In 2008 the House Committee on Homeland Security supported a bill that found the threat of nuclear attack to be “one of the most serious threats to the national security of the United States”. The Nuclear Forensics and Attribution Act, submitted by US Representative Bennie Thompson to support HR2631, recognized the importance of the field of nuclear forensics as a vehicle for timely attribution after a detonation or interdiction of nuclear material. The Defense Threat Reduction Agency, along with several other government agencies, agree that there is a threat of nuclear terrorism and acknowledge that developing and utilizing faster analytical techniques is essential to the logical and strategic analysis of future nuclear events.¹

Advances in technology, long histories of regional conflict, and instability of world leadership make the possibility of smaller more clandestine nuclear facilities a grave threat.² In response, the International Atomic Energy Agency’s (IAEA) Nuclear Safeguards Additional Protocol is concerned with verifying the absence of nuclear programs or nuclear facilities in countries or areas where none are declared. The concern of weaponization steers the focus of this protocol toward plutonium and uranium discovery, consequently making the identification of alpha emitters a central aspect of this process. Current IAEA methods for alpha detection of nuclear facilities consist mostly of swipes. However this is limited to analysis of solid surfaces and does
not address the need for sampling of nearby waters. Due to dilution, alpha emitting isotopes in water may be present in much lower concentrations making them difficult to detect. IAEA’s current response is to collect samples of water to send back to their lab for separation and radiochemical analysis. This process can be time consuming, requiring days to weeks depending upon processing time, and expensive with both variables directly related to the complexity of the matrix. These difficulties lead to the need for development of rapid and robust methods for the quantification of actinide concentrations and isotope ratios. Such methods should include a convenient way to concentrate nuclides in situ from large volume (>1 L) water samples into a small, convenient form while still preserving pertinent isotopic ratios.

The primary objective of this work is to develop proof of concept for a reliable method of alpha analysis that is timely and cost effective. Addressing some of the challenges of current techniques, this method will require little to no radiochemical preparation while delivering acceptable resolution and maintaining valuable isotopic ratios. Two types of functionalized surfaces will be examined to achieve this objective 1) polyamino acid functionalized glass slides and 2) graphene oxide coated glass discs

The challenge in developing a new sampling method for alpha spectroscopy lies in the difficulty of alpha particle detection, given the high linear energy transfer of alpha particles, resulting in a very short range in air and/or solid media. Due to self-absorption, a good spectrum can only be achieved using as close to a thin source as possible. Self-absorption occurs when alpha emitting isotopes must pass through a
portion of the solid source material which causes energy loss of the particle and results in a broadening of the spectrum. These interactions can cause low energy tailing in the spectrum and, as a result, isotope discrimination becomes more difficult if not impossible. This phenomenon rules out most porous materials, including many crystalline metal oxides, as sorbents since they would produce spectra with excessive tailing.

Another consideration is the ability of the functionalized substrate to sorb actinides. The affinity of actinides for a solid phase can be described using a distribution coefficient, $K_d$, which is the ratio of the solid phase concentration of the actinide (moles of actinide per kg of sorbent) to the aqueous phase concentration (moles of actinide per liter).

$$K_d = \frac{[\text{Actinide}]_{\text{solid}}}{[\text{Actinide}]_{\text{aqueous}}} \quad (1)$$

If the $K_d$ is too low then percent uptake from solution will be too low to produce a statistically significant spectrum or assay time will be too long to be practical. The $K_d$ expression can be rearranged to represent sorption affinity in terms of the fraction of the actinide remaining in the aqueous phase ($f_{\text{aqueous}}$) as:

$$f_{\text{aqueous}} = \frac{1}{1+K_d[SS]} \quad (2)$$

The term [SS] is the concentration of suspended solids which can be expressed as the mass of absorbent divided by the volume of solution.
CHAPTER TWO
BACKGROUND

Alpha Particle Decay

Alpha particles are a type of ionizing radiation in which an unstable isotope undergoes spontaneous radioactive decay and results in the emission of an alpha particle which consists of 2 protons and 2 neutrons (i.e. a He-4 nucleus). Equation 3 shows the decay process where X is the unstable parent, Y is the daughter, He nucleus is the resultant alpha particle, A is the atomic mass, and Z is the number of protons in each nucleus.\(^6\)

\[
\frac{A}{Z}X \rightarrow \frac{A-4}{Z-2}Y + \frac{4}{2}\text{He}
\]  

(3)

Although an ejected alpha particle has relatively high energy (compared with other forms of radiation such as x-rays and beta particles), it is also relatively large and has a high charge resulting in high linear energy transfer. As a result, alpha particles lose energy rapidly when passing through almost any media (including air) and have very little penetrating capability. The dead outer layer of skin, or even a few centimeters of air is enough to stop most alpha particles.\(^6\) Coulomb forces primarily control alpha interactions with matter because the positively charged particle reacts with electrons of an absorbing medium and causes decrease in kinetic energy until it eventually stops. Rutherford scattering and other interactions with nuclei are also possible but rare.\(^5\)
**Alpha Particle Detection**

Silicon diode detectors are currently the most prevalent choice for alpha particle detection and quantification. This semiconductor technology is advantageous in areas of resolution, stability, lack of drift, simplicity of operation, and lack of attenuation due to window thickness. Limitations include limited size of sample, incomplete vacuum and possibility of incomplete hole-pair interactions. When using silicon semiconductors, the approximately highest possible resolution is 10 keV for a 5.49 MeV energy particle. However it is not uncommon for detectors to have resolutions ranging from 17 to 80 keV. This resolution, generally defined as the full width of the alpha particle peak at half of the maximum height (FWHM), is affected by noise contributions from equipment, window thickness, energy transfer to recoil nuclei instead of electrons, air pressure within the detection chamber, and self-absorption.

The largest cause of poor resolution is also the only controllable variable; therefore it is important that care is taken when preparing an alpha emitting source. During preparation, the radioactive particles must be placed in very thin layers near the surface of the source. If a source is too thick, and radioisotopes are located throughout the source, then self-absorption will occur. Self-absorption is the attenuation of the alpha particle energy within the source material which results in a decreased energy of the particle when it reaches the detector. Self-absorption differs from absorption in that absorption occurs when an alpha particle interacts with electrons in a medium such as air, tissue, or clothing. Absorption can be managed by ensuring the detector has a
thin window which is as uniform as possible. Also, a high vacuum will reduce the pressure inside the detection chamber and minimize attenuation in air. Depending on the thickness of the source relative to the range of the alpha particle, the self-absorption could result in peak tailing to the complete loss of particle kinetic energy. The particles that lost kinetic energy will not reach the detector resulting in decreased efficiency and the slowed particles will have lower energy which will broaden the peak and decrease the resolution.\textsuperscript{5,7} If a source is monolayer and all alpha emitting particles lie on top of the source, then the particles emitted away from the source (i.e. not directly back into the source) will not be attenuated.

The results of absorption and self-absorption on the alpha spectrum are somewhat different. Absorption leads to more uniform energy loss, especially in the case of window thickness, and the spectrum will show a shift to a lower energy due to the loss of energy outside the detector. Absorption also causes peak broadening due to varied angles of incidence, causing the alpha particle to traverse a slightly greater thickness of window media. Self-absorption causes a broadening of the peak but not uniform shifting.\textsuperscript{5} Tailing is the result of partial loss of energy of a fraction of the incident alpha particles (from partial absorption within sample) which results in broadening of the alpha peak and can yield poor resolution spectra.\textsuperscript{5,7}

**Alpha Particle Source Preparation**

Pretreatment and separation of isotopes of interest are common precursors to alpha particle source preparation. When starting with a bulk sample the first step is a
preliminary pretreatment which could include homogenizing, pre-concentration, dissolution, drying or sieving. Next the isotope of interest must be separated from the bulk sample and some common methods include organic extraction, liquid/liquid extraction, ion exchange and extraction chromatography.

Following separation, the isotopes are generally dispersed into a thin layer over a backscatter resistant backing with a typical maximum diameter of 2.5 cm. There are numerous ways to prepare sources of alpha emitting radioisotopes each of which have advantages and disadvantages as discussed below. The Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP) notes that "... measurement is only as good as the sample preparation that has preceded it." and provides an overview of commonly used methods for alpha source preparation in section 15.3. Evaporation, electrodeposition, and microprecipitation are three of the most widely used methods. A brief description of each method is provided (in Table 2.1) below along with notable advantages and disadvantages.

Evaporation uses heat to remove a liquid phase from the sample, leaving concentrated radionuclides on a planchet after the solution has evaporated. Planchets with varying geometries and various organic solvents can be used to help disperse the sample and minimize "coffee ring" effects where radionuclides accumulate at the edges of a drying liquid.

Electrodeposition electrochemically deposits metallic radionuclides from an electrolyte solution onto a suitable metal cathode surface. Typically a platinum anode is
suspended in solution and an electrolyte solution is used in accordance with a stainless-steel cathode planchet with constant current and low voltage. The one to two hour process results in a fairly uniform, non-selective, ultra-thin layer of metal ions on the surface.

Microprecipitation involves coprecipitation of a soluble ion within an insoluble compound, followed by filtration onto a smooth, small pore size filter. Actinides are usually coprecipitated with a lanthanide in the form of a lanthanide fluoride solid.

**Table 2.1** A brief description of the advantages and disadvantages of the three most widely used methods of source preparation for alpha spectroscopy.

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation</td>
<td>simple, rapid, can occur directly from an aqueous solution, high yield</td>
<td>difficult to achieve uniform distribution, evaporation from solvent is more complex (requires a chemically separated sample, extraction from solvent, then evaporation from extracted phase), dissolved matter in water sample may result in attenuation⁵,⁷,⁸</td>
</tr>
<tr>
<td>Electrodeposition (Electroprecipitation)</td>
<td>durable, produces superior resolution, can accommodate multi-isotopic mixtures</td>
<td>time consuming, labor intensive, interference by other metals, does not resolve well with high mass samples⁵,⁷,⁸</td>
</tr>
<tr>
<td>Microprecipitation</td>
<td>rapid, high yield, economical, acceptable energy resolution</td>
<td>thicker source leads to more self-attenuation, uses hazardous chemicals such as hydrofluoric acid, may require additional handling of source (filter) because of curling when drying⁵,⁷,⁸</td>
</tr>
</tbody>
</table>
**Alpha Spectroscopy with Coated or Functionalized Surfaces**

Alpha spectroscopy analysis of bulk liquid samples is difficult because of time involved in preliminary treatment and chemical separation from other nuclides or metals. Also, the balance between preparation time and source quality often results in poor resolution alpha spectra. The elimination of particulate residue and filters, inherently found in coprecipitation and evaporation methods, would lead to more resolved peaks in alpha spectra. While electrodeposition has many of the qualities needed for successful alpha assay, the complication of assembly, interference by other metals and cost exclude it from being a routine choice.

An ideal method would have the same thin surface as electrodeposition, but with a surface charge that could be manipulated by pH adjustments, attracting ions without the need for current. A selective surface could not only eliminate the need for the separation process but could also be used to target specific ions and be resistant to organic interferences. This could be accomplished by functionalizing or coating a surface with negatively charged groups that facilitate electrostatic attraction of cationic actinides present at neutral or low pH values. ⁹,¹⁰

**Fundamental Considerations for Experimental Design**

The focus of this work was to develop coated and functionalized surfaces which were capable of concentrating actinides from an aqueous phase. The surface would also serve as the source material for subsequent alpha spectroscopy. Polyamino acid functionalized glass slides and graphene oxide coated glass discs were selected for these
tests. The key factors involved in this design were type of surface, pH, mass of sorbent with respect to number of functional groups, equilibrium time, and particle morphology. The primary criteria used to evaluate the performance of the selected materials were energy resolution and uptake of the actinides from aqueous solutions.

The pH of the actinide containing solution plays a vital role in the uptake of the metal of interest. In natural waters, plutonium can exist in oxidations states III, IV, V, and VI. The oxidation states profoundly influence actinide mobility and solubility. Following the trend for sorption affinity and complexation actinides tend to sorb following effective charge.\textsuperscript{5,11,12}

\[
\text{An}^{4+} > \text{AnO}_2^{2+} \approx \text{An}^{3+} > \text{AnO}_2^{+}
\]

+4 +3.2 +3 +2.2

Therefore the behavior of the actinide is heavily dependent on the redox conditions system in which it exists. Each of the Pu oxidation states will be present as cationic species at most circumneutral pH conditions. Therefore the substrate of interest for concentrating Pu would need to carry a negative charge at or near neutral pH.\textsuperscript{5}

Plutonium complexes more readily as Pu(IV), which is important for uptake, but acidic or reducing conditions are required for stability of this oxidation state. In more neutral pH environments, such as natural waters, Pu(V) is the more stable oxidation state. It important to realize that even though Pu may enter a system as Pu(IV), the pH of its environment as well as exposure to oxygen will affect its oxidation state. The
result of a Pu(V) oxidation state in natural waters will result in less sorption to most substrates. (source)

Uranium can also exist in a range of oxidation states but typically exists in a tetravalent or hexavalent oxidation state in environmental conditions. Similar to Pu(IV) and Pu(V/VI), U(IV) and U(VI) will persist as cations and will be attracted to negatively charged groups on a functionalized surface at neutral pH.

The particle morphology must also support adsorption instead of absorption by lending itself to small ligands or small flakes. Thick, porous materials that absorb nuclides will not produce a good resolution spectrum and should be avoided. If a surface is functionalized with ligands, then the ligands must be small and uniform so that sorption is even and single layered. If the surface is coated with a sorbent, then the sorbent should consist of very small thin flakes of material that can be laid flat in single layers.

A sufficiently thin sorbent however, will not be completely reactive. Consequently the number of reactive functional groups to the mass of sorbent is very relevant to percent uptake. This ratio at a given thickness will be necessary for a complete $K_d$ calculation. The thin layer surface functionalization will result in an extremely low number of reactive sites in comparison to atoms of actinide in solution therefore uptake will be too low for quantification to occur. However, the relative ratios of isotopes will be preserved and uptake should be sufficient that isotope ratios can identify the source.
The drawback of this method will be low uptake. Calculations can quantify a correlation between mass of sorbent (or number of functional groups on a surface) and the theoretical uptake. Another drawback is that this method would be unable to quantify the activity concentration in the bulk sample.

In order to calculate theoretical uptake vs sorbent mass, a relationship can be established between $K_d$, sorbent mass and uptake. When used as a surface coating, the $K_d$ of the surface sorbent will give a quantification of amount of removal of ions from the bulk sample by the sorbent. The relationship follows Equation 4 (rewritten from Equation 2 using plutonium as an example).\[^{13}\]

\[
\frac{1}{K_d \cdot \frac{m}{V} + 1} = \frac{[^{239}\text{Pu}]_{aq}}{[^{239}\text{Pu}]_{tot}} = \text{fraction aqueous} \tag{4}
\]

Where $m$ is mass of total sorbent, $v$ is total volume of system, $[^{239}\text{Pu}]_{aq}$ is free Pu in the system and $[^{239}\text{Pu}]_{tot}$ is the total amount of Pu in the system.

By assuming a range of masses possibly deposited onto a substrate and assuming a volume of 100 mL (representative of the uptake experiments described below), a range of $K_d$’s from 1 to 10,000 can be used to calculate the fraction aqueous for plutonium in a system after equilibrium using Equation 4 (Figure 2.1). These calculations indicate that unless the $K_d$ value is high or unless sufficient mass of the adsorbent is on the substrate, uptake will be limited. Thus, there is an inherent limitation on using a coated or functionalized surface to both concentrate and detect radioisotopes from liquid samples. Additional mass can be added to the substrate to increase uptake if
absorption is occurring. However, that added mass may come at the cost of decreased spectral quality due to self-absorption.

**Figure 2.1** Theoretical calculation of fraction aqueous per mass of sorbent in grams.

**Graphene Oxide**

Graphene is a one atom thick layer of pure carbon bonded in a hexagonal honeycomb lattice. Graphite is made of stacked layers of graphene. Oxidation of graphite will produce carboxyl, epoxide, and phenol functional groups to produce graphite oxide. The functional groups make graphite oxide hydrophilic and therefore dispersible in water. This layered material can then be sonicated to induce layer delamination and ultimately few-layered flakes and monolayer flakes to form graphene oxide (GO).
Currently GO is being studied by many different disciplines because of its potential uses in the fields of bioengineering, energy storage, water purification, and materials science. GO is an ideal material for environmental applications because it is nontoxic, can be incinerated, and has been shown to have remarkably high capacity for removing heavy metal ions from water. GO’s remarkable high sorption properties are due to carboxyl, epoxide, and phenol functional groups on the surface and edges, as shown in Figure 2.2. It is also relatively inexpensive and usually has increased radiation and thermal stability relative to organic exchange resins and other inorganic sorbents.

**Figure 2.2** Conceptual image of graphene oxide complete with functional groups.

**Previous Studies Examining Radionuclide Sorption to GO**

Romanchuk *et al.*, have studied GO for use in radionuclide removal and reported that at slightly acidic pH’s Pu(IV), Th(IV) and Am(III) sorb to GO within 5
minutes with almost 100% sorption and approximately 50% U(VI) is sorbed. At neutral pH values, all of the above mentioned are essentially 100% sorbed. Romanchuck et al.\textsuperscript{16} reported that in sulfate, citrate, carbonate, and acetate rich solution, actinides had strong affinity for GO despite their tendency to form strong complexes with these competing ions.

Bai et al.\textsuperscript{20} studied Th(IV) removal by GO and found that complete sorption occurred at pH 4 but there was some dependency on the solid sorbent to volume of liquid ratio. The effect of temperature was also studied and results concluded that sorption capacity of Th(IV) increased with temperature. The work did conclude a high capacity for Th(IV) sorption with a maximum of 214.6 mg\textsubscript{Th}/g\textsubscript{GO} at low pH values and fast kinetic sorption of Th(IV) with an equilibrium time of about 10 min.\textsuperscript{20}

Sun et al.\textsuperscript{10} studied the interaction mechanism between Eu(III) and graphene oxide. The graphene oxide existed as graphene oxide nanosheets (GONS) that randomly aggregated and appeared as ~5 nm sheets. Fourier Transform Infrared Spectroscopy (FT-IR) analysis indicated large amounts of carboxyl, epoxide, and phenol functional groups present on the surface of the GONS. Eu sorbed to sheets at pH 2-6 with the main species existing as Eu\textsuperscript{3+} and Eu\textsubscript{2}(OH)\textsubscript{4}\textsuperscript{4+}, and was not affected by ionic strength of solution. Using a surface complexation modeling approach where >SOH represents an amphoteric surface site, SOEu\textsuperscript{2+} and (SO>)\textsubscript{2}Eu\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{2+} were the dominant surface species above pH 5 and 8, respectively. In this modeling effort, >SOH represents the average functional
group on the surface with a surface site density of 18.1 sites/nm². Results concluded that GONS is an excellent sorbent for trivalent lanthanides and actinides.¹⁰

Li et al.,¹⁸ also studied the sorption of Th(IV) to GONS and described it as a two processes that reached equilibrium within minutes. The first process is described as a fast process with a reaction occurring with the functional groups. The second process involves mass transfer through surrounding liquid film and diffusion through the particle pores. The effect of pH on sorption was tested and between pH 1 to 3, sorption increased from 30% to 100%.

Li et al.,¹⁸ also reported a point of zero charge (pzc) for GONS of 2.09. Thus as the pH rises above the pzc of GO and the surface becomes more negative, the sorption of cationic Th(IV) increases. The study also reported the sorption edge of Th(IV) was much lower in the presence of fulvic (FA) and humic acid (HA).¹⁸ This change in sorption edge is a result of the FA and HA forming soluble Th(IV) complexes resulting in less GO-Th(IV) sorption. Also, HA can occupy active sites on GO and decrease Th(IV) sorption because of competition for available sites.¹⁸

Zhao et al.,¹⁵ studied the sorption of metal ions onto GONS in the presence of humic substances. The distribution of surface sites was determined to be 18.6% for C-O, 9.8% for C=O, and 0.2% for COOH.¹⁵ The pzc was determined to be 3.9. Results show that HA and FA had some effect on sorption of Cd(II) and Co(II), particularly below pH 6, however at pH 9.1 over 90% of Cd(II) had adsorbed onto GONS. The data was approximated using a Langmuir model and the $Q_{max}$ values (the maximum amount of
target ions in mg adsorbed per gram of GO), for Cd(II) and Co(II) were 68.2 and 106.3 mg/g, respectively at pH 6.15. Similar conditions produced $Q_{\text{max}}$ values of 50.0 and 30.8 mg/g for Cd(II) with activated carbon cloth oxide and granular activated carbon oxide, respectively. Graphene oxide had the highest sorption capacity of the 14 materials studied.15

**Previous Studies Examining Thin Films as Alpha Spectroscopy Substrates**

Polymeric thin films and filters can be used to bind to radioisotopes and then immediately analyzed by alpha spectroscopy. Several authors have reported attempts on this procedure using varying ligands which are selective for specific radioisotopes. Gonzales *et al.*22 deposited two polymer ligand films (PLF), poly(styrene)/Dipex® and nitrocellulose/Dipex®, directly on a stainless steel planchet. A third PLF, Poly(vinylpyrrolidone)/Dipex® was directly deposited onto a poly(propylene) filter. The alpha spectroscopy results indicated resolutions with FWHM (keV) values of 25 to 251 keV for $^{241}$Am and $^{242}$Pu, along with uptake values ranging from 7 to 54%, respectively.22 These experiments were not performed as a “typical” uptake experiment. Rather a solution containing the radioisotope was pipetted directly onto the surface as a small volume and left for 2 hours. Then the surfaces were rinsed, dried, and counted. Broad peaks with significant tailing were seen in several spectra but the tailing was not quantified. Using these same substrates, a soil sample was also digested and the solution was directly deposited as described above. The results indicated 5 to 6% recovery, FWHM values of 27 to 60 keV, and less tailing.22 In a separate study, Gonzales
et al., 23 studied the polymer ligand Dipex® and its ability to remove actinides from aqueous solutions and urine. Results showed ~20% recovery from the 0.25 pCi/mL solution of 238Pu with acceptable FWHM values of 30 to 98 keV. There was some problem with reproducibility in spectra quality, but the ability to selectively extract certain nuclides in the complex matrix of urine by varying conditions was promising.

Oldham et al., 24 functionalized glass substrates with carbamoylmethylphosphate (CMP) ligands and then exposed the surface to droplets of 239/240Pu. Results showed a high recovery of ~30% of the dissolved Pu within 5 to 10 minutes. The resultant alpha spectrum produced good resolution with a FWHM of 22 keV for 242Pu tracer, however no value was reported for the 239/240Pu peak.

Rim et al., 25 studied a commercially available metal cationic selective ligand, di(2-ethylhexyl) orthophosphoric acid (HDEHP), incorporated into a polystyrene matrix that was used as a thin film for extracting 239Pu and 241Am. Digital autoradiography analysis showed that the coating successfully extracted Pu but showed higher concentrations closer to the middle and edges of the discs. The unexpected hot spots could have been the result of surface defects detected by SEM imaging or localized high concentrations of ligands, which was cause for future study of the coating technique. The most successful sample showed little tailing, a respectable FWHM of ~15 keV and a maximum of ~60% recovery (though the usefulness of this number is limited as the authors did not list the total activity used in the uptake experiments).25
The functionalization of a surface for the explicit purpose of radioisotope removal and assay is a well-developed idea which numerous groups are currently exploring. Advances have been made in the selection and utilization of specific ligands for actinide removal and assay but almost all are based on polymer ligand films. Graphene oxide is also emerging as a sorbent with great affinity for actinides at low to neutral pH values. This work takes advantage of the sorption capacity of GO concentration of alpha emitting radionuclides and the sheet-like structure of GO to produce relatively flat surfaces useful for alpha spectroscopy. Similar to commercially available polymer ligands, GO has promise of use in this application with the ability to be produced in bulk quantity with less environmental impact.14
CHAPTER THREE  
EXPERIMENTAL GOALS AND TASKS

The primary goal of this thesis is to develop proof of concept of a quick and inexpensive procedure utilizing a coated or functionalized surface that is capable of both concentrating actinides from solutions and also serving as an alpha spectroscopy source with no further modification. The desire is to produce materials that will yield an alpha spectrum with acceptable energy resolution that could be used for isotope ratio analysis of uranium. This goal will be met through two primary tasks which utilize different sorbents.

**Task 1:** Mica and silica surfaces were tested as suitable actinide sorption sites using functionalization of the surfaces with GOPS [(3-Glycidyloxypropyl)-trimethoxy-silane] and amino acid ligands.

**Task 2:** Flakes and sonicated particles of graphene oxide were used to sorb actinides. The flakes were dried and directly counted and the graphene oxide particles were either spin coated or pipetted directly onto glass surfaces.

The performance of each material is evaluated below in terms of alpha spectroscopy resolution, tailing, and percent uptake.
CHAPTER FOUR
MATERIALS AND METHODS

An experiment was designed to exploit the formation of Pu(IV)-citric acid ternary complexes, which optimally occur at pH 3.5 to 4, on mica surfaces for rapid alpha spectroscopy analysis. Mica was selected because with simple removal of the surficial layer with tape, a clean and atomically flat surface could be obtained. Two solutions of 100 cpm/mL each $^{238}$Pu(IV) and $^{14}$C-labeled citric acid were prepared in 20 mL volumes with equal activity concentrations of each isotope. The pH values were adjusted to 3.7 so that the $^{238}$Pu and citric acid could complex. Mica slides and Fisherbrand glass slides were added to the solutions and equilibrated 24 hours. The slides were removed and counted approximately 4 mm from the detector on an Ortec Octete PC Alpha spectroscopy system equipped with 450 mm$^2$ detectors. The alpha detector energy calibration was performed using NIST traceable electrodeposited alpha standards. The initial and remaining aqueous concentrations of $^{238}$Pu and $^{14}$C were monitored using pulse shape discriminating liquid scintillation counting (LSC) on a Hidex 300SL with Optiphase HiSafe 3 cocktail.

**Functionalization of Glass Slides with Polymeric Amino Acids**

An amino acid functionalized surface was synthesized by starting with an glass disc base, cleaned with acetone, and using a GOPS intermediate to bind to the oxygen rich glass surface. The amine from an amino acid was then attached to the GOPS
intermediate to create a uniformly layered amino acid surface. Figure 4.1 shows the layers in detail.

**Figure 4.1** A functionalized glass disc composed of a glass layer, a GOPS intermediate and an amino acid layer which can be used to selectively sorb to actinides. Figure was modified from Strakosas et al.,26

To prepare the surface, a 5% v/v solution of silane GOPS [(3-Glycidyloxypropyl)trimethoxy-silane, >98% Sigma Aldrich] in hexane (ACS grade, BDH) was heated to 40 °C and stirred in a glass beaker. Glass discs (Deckglaser Cover Glasses 25mm), mica plates, and glass slides were suspended in solution and the beaker was covered with a watch glass. The experiment was performed in triplicate and the solution was stirred for 2 hours, with hexane added every 15 min as-needed to keep a constant volume. After 2 hours, the discs were removed from solution and triple rinsed with acetone by inserting each disc into a gentle stream of solution for 1 second per side for each rinse. Amino acid solutions of ~0.02 g of Poly-L-aspartic acid (PLAA) (Pfaltz and Baur) or Poly-(α,β)-DL-aspartic acid solution (PDAA) were prepared and equilibrated with the epoxide functionalized discs for 24 hours then triple rinsed with water adjusted to pH using HCl. The functionalized discs, mica plates and glass slides (samples)
were removed from solution, placed in 50 mL Falcon tubes containing ~10 mL of 109 dpm/mL $^{239}$Pu solution and placed on a shaker for 3 days. The oxidation state of this solution was not determined. The samples were then removed, allowed to air dry and counted on the alpha spectrometer for 16 hours.$^{27}$

Due to the low uptake observed in the previous experiment, the oxidation state was fixed as Pu(IV) and the total aqueous concentration was increased for future experiments with ligand functionalized discs. A Pu(IV) working solution was fixed as Pu(IV) by evaporation of an aliquot of a $^{238}$Pu stock solution in 4M HNO$_3$ under low heat followed by dissolution in 0.1 M HCl with the addition of a few crystals of NaNO$_2$. The solution was 90% $^{238}$Pu(IV) as verified using solvent extraction and lanthanum fluoride coprecipitation.$^{28}$ This working solution was then diluted and pH adjusted to prepare the three pH solutions used in this experiment. Next, influence of pH on uptake to the functionalized surfaces using batch uptake experiments at fixed pH values of 3, 5, and 7. Glass discs were prepared as described above using PLAA and then placed in 13 mL of ~6000 dpm/mL $^{238}$Pu(IV). Samples were prepared in triplicate then shaken on an orbital mixer and aliquots were removed for LSC after t=0, 1, 3, 6, 8, 12, 24, and 48 hours. The fraction of aqueous $^{238}$Pu was determined using LSC by diluting the 1 mL aliquot in 4 mL of Optiphase HiSafe 3 cocktail and assaying on a Packard Tri-Carb 1900CA LSC. Following the 48 hour uptake step, the discs were counted on the alpha spectrometer.
**Sorption of Actinides to Large Flakes of Graphene Oxide**

A graphene oxide (Alpha Aeser) flake was selected, trimmed for uniformity, to a 1 cm x 0.5 cm flake, and then taped on one side with Scotch® tape to keep the flake intact during the uptake experiment. The flake was then placed in a 2.4 dpm/mL $^{238}$Pu(IV) solution at pH 1.87 and shaken gently for 24 hours. The flake was removed, placed on a stainless steel smooth bottom planchet and counted on the alpha spectrometer (Ortec Octete PC Alpha Spectrometer) for 45 hours. The $^{238}$Pu concentration in solution following uptake was determined using LSC.

**GO Plating with Sonicated GO**

A small amount of suspended GO was mixed with a small volume of $^{239}$Pu(IV) solution to determine the extent of radionuclide uptake by GO and also to prepare a suspension of $^{239}$Pu amended GO to determine if the material could be plated on a planchet to prepare an alpha spectroscopy source. The intent of this experiment was to get a preliminary idea of the resolution of the alpha spectrum that would be produced by hand pipetting a GO suspension onto a flat non-reactive surface. Samples were prepared by mixing 0.1 mL of a 1 mg/mL sonicated GO was deposited with 0.1 mL of 109.0 dpm/mL $^{239}$Pu solution into a microcentrifuge tube and vortexed. Next, the mixture was centrifuged for 5 min at 5000 RPM then 38 min at 7000 RPM to form a more solid pellet. The supernatant was drawn off and the wet GO was resuspended in 0.10 mL H$_2$O. Then the full resuspension was pipetted onto a 51 mm stainless steel planchet and dried. The resulting samples were measured on an alpha spectrometer.
**GO Dilution**

An experiment was designed to see if the alpha spectrum produced by hand pipetting a $^{239}$Pu sorbed GO suspension would be affected by the concentration of $^{239}$Pu sorbed GO in the solution. To determine this, three solutions of 2.1 mL of 109.0 dpm/mL $^{239}$Pu were combined with 3 mL each of 1 mg/mL GO suspension. The exact volume of each solution was determined gravimetrically. The pH was not measured but based on the 0.01 M HCl Pu working solution and the low pH of the GO suspension (~4), a pH of approximately 2.5 to 3.0 was likely. The suspensions were equilibrated for 24 hours then centrifuged for 4 hours at 8000 RPM. The supernatant was removed and GO was resuspended in 300, 700, and 1200 $\mu$L of 0.01 M HCl. Approximately 100 $\mu$L of each suspension was then plated onto a stainless steel planchet, allowed to air dry, then counted on the alpha spectrometer.

**GO Percent Uptake**

An experiment was designed to determine if the ratio of GO to $^{239}$Pu had any effect on uptake or alpha spectra resolution. This was performed by combining 0.52 mL of 108.97 dpm/mL $^{239}$Pu with 0.10, 0.51, and 1.0 mL of 1 mg/mL GO suspension for three separate Pu/GO ratios. The experiment was performed in triplicate for a total of nine separate mixtures. Mixtures were shaken for 24 hours, centrifuged at 8000 RPM for 5 hours, resuspended in 0.01 M HCl, then pipetted onto aluminum planchets. Approximately 0.5 mL of the supernatant was drawn off for LSC analysis. The exact
volume of each supernatant suspension was determined gravimetrically. Planchets were counted on an alpha spectrometer for 20 hours.

**Spin Coating GO**

To combat inconsistencies of hand pipetting Pu/GO mixtures onto planchets, an idea was developed to coat GO on a glass disc. The GO coated disc could then be dipped into a Pu solution, equilibrated, dried, and counted on an alpha spectrometer. This method would eliminate the problems of varying GO and Pu concentrations and “concentration” of GO on the surface leading to poor quality, unreproducible spectra. To prepare these discs a Chemat Technology Spin Coater (KW-4A) was used to spin coat a 2 mg/mL Sigma Aldrich GO suspension (lot #MKBP8837V) onto 25 mm Deckglaser glass discs. Approximately 200 µL of the GO suspension was evenly spread over the discs and then spun for 9 sec at ~630 RPM then for 60 seconds at ~3560 RPM. (Many attempts were made, varying the initial and final RPM’s, to ensure a visibly thin, even, and streak-free GO coating on the discs. These attempts are summarized in Appendix A. The above mentioned setting was chosen as the standard due to visual appeal.) Discs were carefully removed and dried in an oven for 1 hour at 50 °C. Coated discs were suspended in a beaker containing ~80 mL of a ~50 dpm/mL $^{238}$Pu solution. Four discs were allowed to equilibrate for 30 minutes each and two discs were allowed to equilibrate for 1 hour each. LSC samples were taken before and after each equilibration to monitor changes in the aqueous phase Pu concentration. Discs were dried in 50 °C oven for 20 minutes then counted on alpha spectrometer.
Equilibrium Uptake Studies

Two spin coated discs were each submerged in 86 mL of pH 5.47 $^{238}\text{Pu}$ solution (~50 dpm/mL). After disc one was submerged, LSC samples were taken at t = 0, 1, 3, 5, 10, 30, 45, and 60 min and then the disc was removed. The experiment was replicated with the second disc except that it was equilibrated for a total of 180 minutes. Following the uptake experiments the discs were triple rinsed by inserting each disc into a gentle stream of Deionized (DI) H$_2$O for one second per side per rinse, then dried at 50 °C and counted on the alpha spectrometer.

Optimization of pH

To determine the optimal pH for GO uptake of $^{238}\text{Pu}$, six solutions at pH values of 2.13, 2.72, 3.09, 3.90, 4.48, and 5.00 were made and all spiked with $^{238}\text{Pu(IV)}$ to a concentration of 54 dpm/mL. Approximately 30 mL of each solution was transferred to a 50 mL Falcon centrifuge tube to which a GO coated glass disc was added. All solutions were shaken for one hour then the discs were removed, triple rinsed with DI H$_2$O (using the same method as above), dried at 50 °C and counted on the alpha spectrometer for 2022 minutes. LSC samples to determine the aqueous $^{238}\text{Pu}$ concentration via LSC were taken at t=0 and 1 hour.

Distribution Coefficient ($K_d$) Determination for GO Coated Discs

In order to explain the percent uptake of actinides by GO coated discs, an experiment was designed to help determine the $K_d$ for $^{238}\text{Pu(IV)}/$GO and $^{233}\text{U(VI)}/$GO discs under specific conditions. The experiments with $^{233}\text{U(VI)}$ were performed to
determine if actinyl ions may exhibit different uptake behavior. A $K_d$ determination for actinide/GO discs needed to be performed because the mass of GO on each disc was small compared to the mass of GO in suspensions used in previous experiments. This difference in mass would most likely result in drastically reduced uptake due to the linear nature of a $K_d$.

First, a 200 mL of a pH 5 solution was placed in beaker with stir bar and a 1 mL aliquot was taken for LSC analysis. The solution was spiked to 10 dpm/mL with $^{238}$Pu(IV) then another aliquot was taken for LSC. A disc was then placed in solution (suspended from above) and allowed to equilibrate for 30 minutes. After the disc was removed, another aliquot was taken for LSC analysis. Additional aliquots of a $^{238}$Pu(IV) stock were added stepwise to reach concentrations of 20, 50, 75, and 100 dpm/mL with a 30 minute equilibration between additions. The experiment was repeated using a pH 7 solution and $^{233}$U. All discs used were counted on the alpha spectrometer.

Next, blank 25 mm glass discs were weighed on a Mettler Toledo MX5. The spin coater was used to coat the discs, making sure to maintain consistent RPMs for uniform mass and thickness on each disc. This was performed at three RPM settings, creating three groups with varying thickness and mass. The RPM settings for all groups started with a 9 second ~690 RPM cycle and then ramped up to a top speed. Three groups of discs were prepared with maximum RPMs of 8800, 6700, and 4700.

The microbalance was used in an attempt to determine the masses of the third group (4700 RPM) which should have the thickest coating of GO due to the low spin
rate. Using the microbalance to weigh such small masses was not reliable and some measurements gave negative weights. However, the average of 19 discs was useful as an approximation of the mass for calculations of a $K_d$ from uptake experiments discussed below.
CHAPTER FIVE
RESULTS AND DISCUSSION

Mica

Based on afore mentioned criteria, mica was a consideration for a sorption surface because of its atomically flat naturally occurring structure.\textsuperscript{29} It is a fairly rugged mineral whose very thin layers do not stop alpha particles, which would be beneficial to prevent absorption.\textsuperscript{30} Despite initial potential, mica was quickly ruled out as a suitable surface because alpha spectroscopy results showed no uptake of \textsuperscript{14}C labeled citric acid or plutonium.

Functionalized Glass

Functionalized glass surfaces were created using a GOPS base in which an amino acid, or other nitrogenous based molecule, could attach. The nitrogenous based ligands can vary, but two enantiomers of polymerized aspartic acid were chosen for this experiment. The PLAA form along with the racemic mixture PDAA were used and compared to decide which would produce the best results.

The results of the PLAA and PDAA functionalized slides indicated that when exposed to similar activities of \textsuperscript{239}Pu (46 dpm) for 24 hours, the counts registered by PLAA coated slide via alpha spectroscopy were 0.129 ± 0.011 cpm (with uncertainty from counting error) compared to PDAA with 0.161 ± 0.012 cpm (Figure 5.1). Even though PLAA had fewer counts, the resolution was 43 vs 136 keV for PLAA and PDAA, respectively. The detector was energy calibrated, however, an efficiency calibration
standard was not available for the geometry of the functionalized substrates (i.e. rectangular glass slides), as a result PLAA and PDAA substrates were kept as similar in activity and size as possible and results were compared against each other. Figure 5.2 shows the consistency of the alpha spectra of $^{239}$Pu sorption onto PDAA and PLAA functionalized discs under similar conditions and the data are reasonably reproducible. The net counts per minute (cpm) from all spectra were compared with that of a bare glass slide with no functionalization which yielded 0.044 ± 0.006 cpm (Figure 5.1). The resolution of the blank glass slide was 110 keV at the peak, but had significant tailing that resulted in an unreliable spectrum. PDAA functionalized disc in Figure 5.1 had approximately 364% more counts than the bare glass disc. Thus, it appears the increased activity counted was due to uptake by functionalization of the glass disc, not the silanol groups on the glass disc itself.
Figure 5.1 Alpha spectra of PLAA and PDAA functionalized glass discs as well as a blank glass disc after submersion in $^{239}\text{Pu}$. 
Figure 5.2 Alpha spectra of triplicate (a) PDAA and (b) PLAA coated glass slides. Slides submerged in 10 mL of solution with 46 dpm $^{238}$Pu for 1000 minutes.
**Equilibrium time & pH**

Kinetic uptake experiments with PLAA functionalized slides at varying pH values were performed to determine the optimal pH and time for equilibration of the slides. Figure 5.3 shows LSC results of percent uptake vs pH for times of 1 hour to 48 hours and pH values 3, 5, and 7. LSC results showed that after 8 hours virtually no removal was seen with counts of fraction left in solution 1.006 ± 0.008 for pH 2.95, 0.990 ± 0.006 for pH 5.04, and 0.987 ± 0.005 for pH 6.96. After 12 hours in solution some removal occurred, the most significant at pH 5 where fraction left in solution dropped from 0.990 to 0.957 ± 0.006. At 24 hours, the fraction of $^{238}$Pu remaining in the aqueous phase was 0.931 ± 0.008, 0.913 ± 0.005 and 0.947 ± 0.009, at pH 3, 5, and 7, respectively. After 48, no additional uptake was observed; there actually appears to be a slight increase in the aqueous phase concentration of Pu at all three pH values. This could be due to oxidative dissolution of Pu to less strongly complexing Pu(V) or leaching of the functional groups. To minimize the potential impact of this, 24 hours appears to be the optimal time for removal for samples with volumes of 15 mL or less. These results indicate that the optimal uptake is at low to slightly acidic pH values where uptake of 7.09 ± 0.12% and 4.57 ± 0.07% was observed for pH 3 and pH 5, respectively, as compared with 1.98 ± 0.02% at pH 7. However, due to the relatively low uptake the LSC data has a high signal to noise ratio. Thus, the slight change in aqueous activity expected based on the uptake will be difficult to detect and the samples will be very sensitive to background fluctuations and volumetric errors. Therefore, the results based on comparison of the
alpha spectroscopy data are proposed to be more reliable. In that case the activity removed from solution is being directly measured rather than inferred based on loss of concentration from the aqueous phase.

**Figure 5.3** LSC results of $^{238}$Pu fraction remaining in aqueous solution vs time in hours for removal by functionalized disc submerged in 6000 dpm/mL $^{238}$Pu solution.

The experiment was performed in triplicate and the best alpha spectrum from each experiment is shown in Figure 5.4. It should be noted that the spectra collected at each pH were fairly consistent and the counts were confined to one peak with no scattering. The alpha spectra confirmed the trends identified from LSC measurements of the aqueous uptake with respect to time and pH. However since no efficiency standard was available, activity uptake onto slides could only be compared against each other.
Alpha results showed that PLAA functionalized slides submerged at pH 5 had the most counts with $32.15 \pm 0.10$ cpm followed by pH 7 with $27.32 \pm 0.10$ cpm and pH 3 had the least counts with $9.01 \pm 0.05$ cpm. The percent resolution from alpha spec was best for pH 5 with 45/67 keV followed by pH 7 with 52/74 keV and the worst resolution belonged to pH 3 with 60/97 keV. Although these slides all showed acceptable uptake, the tailing present in each spectra was sufficient to cause problems when using this substrate for determining isotopic ratios of uranium.

![Alpha spectra of Pu amended PLAA functionalized slides producing the most counts from a triplicate batch when suspended in 6000 dpm/mL $^{238}$Pu solution for 24 hours at varying pH values.](image)

**Figure 5.4** Alpha spectra of Pu amended PLAA functionalized slides producing the most counts from a triplicate batch when suspended in 6000 dpm/mL $^{238}$Pu solution for 24 hours at varying pH values.
Graphene Oxide

Type of surface & particle morphology

Previous work has demonstrated that GO has a high sorption capacity for actinides and other charged metals.\textsuperscript{15,16} Based on these observations, this work has examined the use of GO to both concentrate actinides then use the GO as a substrate for subsequent alpha particle detection. The hypothesis of these measurements is that the flat surface of GO sheets will provide an ideal charged surface for sorption at mid to low pH and minimal self-absorption of the alpha particle during detection. As a result, the alpha spectra would produce distinct peaks with acceptable resolution.

The spectra were compared using uptake, resolution, and tailing as metrics. Similar to the PDAA and PLAA samples on glass slides, in some cases no calibration standard was available. Therefore, results had to be compared using cpm from the alpha spectra between samples with similar activities and uptake conditions. Alpha spectra results showed that when subjected to similar activities of \textsuperscript{239}Pu (12 dpm in 5 mL) for 24 hours, the cpm for large GO flakes were 0.672 ± 0.016 cpm. The resolution at FWHM was not always a good indicator of an acceptable spectrum due to tailing. As a result the resolution will be reported as a FWHM and full width fifth max, respectively. The resolution of the GO flakes was 80/230 keV. Results for sonicated GO particles showed 0.863 ± 0.033 cpm with 45/102 keV resolution. Although counts and resolution appear to be similar, Figure 5.5 shows the GO flake tailing to be so extensive that it could not be
used as a reliable alpha spec sorbent. Multiple trials supported this conclusion. The sonicated GO results produced a much cleaner peak with almost no tailing and as a result sonicated GO was chosen as the preferred sorbent.

Figure 5.5 Alpha spectroscopy results of graphene oxide flakes and sonicated particles submerged in $^{239}$Pu solution for 24 hours, dried at 50 °C and counted. The GO sonicated particles were concentrated via centrifugation then pipetted onto a stainless steel planchet to prepare the source for alpha spectroscopy.

Since sonicated particles produced a clear spectrum with little tailing, an experiment was run to see if the concentration of graphene oxide had any effect on the spectrum. Similar activities of $^{239}$Pu (225 dpm in 5 mL) were combined with similar concentrations of GO and the solutions were centrifuged. After centrifugation, the $^{239}$Pu sorbed GO particles were resuspended in 300, 700, and 1200 µL of solution and then 100 µL of each dilution was pipetted onto a stainless steel planchet. The alpha spectra indicated the most concentrated GO solution had the highest with $7.11 \pm 0.08$ cpm, the
middle concentration produced 5.13 ± 0.07 cpm, and the most dilute had the least with 4.03 ± 0.06 cpm. This is consistent with the increasing amount of GO and sorbed Pu transferred to the planchet as the resuspension volume was decreased (resulting in a higher GO/Pu concentration). The resolution increased from 140/202, 68/119, and 55/95 keV for the GO suspensions resuspended in 300, 700, and 1200 µL, respectively. The increased GO mass added from the sample resuspended in 300 µL appears to have caused some self-absorption. The tailing also follows a similar trend with concentration, suggesting that in order to get a well resolved spectrum with little tailing then the amount of GO on the planchet must be reduced and uniformly plated.
Figure 5.6 Similar activities of $^{239}$Pu (225 dpm) were combined with similar concentrations of GO and the solutions were centrifuged, resuspended in varying volumes (indicated by the legend) then 100 $\mu$L aliquots were pipetted on stainless steel planchets for alpha spectroscopy.

**Percent uptake**

Based on the low uptake observed above, further analysis of sorption behavior of Pu on GO particles was required. A batch sorption experiment was run in which the concentration of sonicated GO was varied while keeping the Pu activity constant. The sample volumes ranged from 0.62 to 1.53 mL with GO concentrations ranging from 160 to 657 mg/L (Table 5.1). A constant volume of 0.52 mL of 109 dpm/mL $^{239}$Pu solution was added to each sample. After a 48 hour equilibration time, the GO was removed via centrifugation and the supernatant was removed for Pu determination via LSC. The
pelleted GO was resuspended in 200 µL of 0.01 M HCl, and then pipetted onto planchets and the alpha spectrum of each planchet was collected as previously done. LSC results showed good uptake with the lowest at 60.3 ± 1.6%, corresponding to the least amount of GO, and the highest at 100.0%, corresponding to the highest amount of GO.

$K_d$ values for the first 6 planchets were also calculated from LSC data, for later comparison, and the average was 21,364 ± 18,009 L/kg (Table 5.1). The last three planchets presented 100% uptake and $K_d$ was calculated by using the MDA of the LSC detector (0.003 dpm) as the aqueous concentration and were not included in the average above. The high error reported was based on variation in the individual $K_d$’s and LSC data with very low activities. The difference in just 1 cpm/mL had an effect on the $K_d$ value, however enough counts were present that the data could be used as an approximation of $K_d$. 
Table 5.1 Concentrations used in a batch sorption experiment of GO and $^{239}\text{Pu}$ in which uptake was measured using LSC data.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Volume of $10^9$ dpm/mL $^{239}\text{Pu}$ added [mL]</th>
<th>Volume of 1 mg/mL GO suspension added [mL]</th>
<th>Total Volume of Combined $^{239}\text{Pu}$ and GO in Solution [mL]</th>
<th>Percent Uptake</th>
<th>Kd [L/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>0.520</td>
<td>0.099</td>
<td>0.619</td>
<td>60.35 ± 1.56</td>
<td>9.5 x 10^3</td>
</tr>
<tr>
<td>6.2</td>
<td>0.518</td>
<td>0.099</td>
<td>0.617</td>
<td>66.73 ± 1.94</td>
<td>1.2 x 10^4</td>
</tr>
<tr>
<td>7.2</td>
<td>0.519</td>
<td>0.099</td>
<td>0.618</td>
<td>64.45 ± 1.80</td>
<td>1.1 x 10^4</td>
</tr>
<tr>
<td>8.2</td>
<td>0.511</td>
<td>0.511</td>
<td>1.032</td>
<td>96.51 ± 29.22</td>
<td>5.6 x 10^4</td>
</tr>
<tr>
<td>9.2</td>
<td>0.513</td>
<td>0.513</td>
<td>1.035</td>
<td>85.91 ± 7.33</td>
<td>1.2 x 10^4</td>
</tr>
<tr>
<td>10.2</td>
<td>0.515</td>
<td>1.013</td>
<td>1.533</td>
<td>92.99 ± 14.70</td>
<td>2.7 x 10^4</td>
</tr>
<tr>
<td>11.2</td>
<td>0.520</td>
<td>1.013</td>
<td>1.533</td>
<td>&gt;99%</td>
<td>1.9 x 10^7</td>
</tr>
<tr>
<td>12.2</td>
<td>0.519</td>
<td>1.014</td>
<td>1.533</td>
<td>&gt;99%</td>
<td>1.9 x 10^7</td>
</tr>
<tr>
<td>13.2</td>
<td>0.522</td>
<td>1.016</td>
<td>1.538</td>
<td>&gt;99%</td>
<td>1.9 x 10^7</td>
</tr>
</tbody>
</table>

The alpha source prepared by pipetting a portion of the GO suspension onto a planchet revealed inconsistent peaks and resolution ranged from 884 to 3280 keV. This experiment verified good sorption ability of GO for actinides but showed inconsistencies which were attributed to manually pipetting the GO suspensions onto the aluminum planchet. The droplets would disperse in irregular patterns which resulted in varying thicknesses of the GO on the planchet. Data also indicated that at higher GO concentrations, it was difficult to obtain a sufficiently thin layer to prevent self-absorption of the alpha particles. Though potentially biased due to the batch sorption experiments, these results also indicated that sonicated GO seemed to have much better uptake than the functionalized slides.
Uptake studies using GO spin coated onto glass discs

To address the issue of plating spin coat technology was utilized. Sonicated GO was spin coated onto glass discs and the thickness of the coating was varied using the rotations per minute (RPM) during spin coating. The coated discs were submerged into 80 mL of a 50 dpm/mL $^{238}$Pu solution at pH 2.88. Four discs were allowed to equilibrate for 30 minutes each and two discs were allowed to equilibrate for 1 hour each. Alpha spectroscopy results (Figure 5.7) showed consistent well resolved peaks with most resolutions ranging from 29 to 81 keV. This corresponded to low counts ranging from 3.940 ± 0.068 dpm to 10.390 ± 0.0982 dpm. The percent uptake ranged from 0.099 ± 0.002 to 0.333 ± 0.003 and a full list of values can be seen in Table 5.2. The consistency in these results led the decision that even though the counts were very low, the alpha spectra's resolution was good enough to qualify unknown samples.
Figure 5.7 Alpha spectra results of GO spin coated discs submerged in 80 mL of ~50 dpm/mL $^{238}$Pu solution at pH value 2.88. Samples 14 and 15 equilibrated for one hour, while all other samples were equilibrated for 30 minutes, triple rinsed with DI H$_2$O, dried at 50 °C and then counted on the alpha spectrometer for 2000 minutes.

Table 5.2 Comparison of alpha spectra features due to uptake of $^{238}$Pu onto GO spin coated discs at pH 2.88 with variation in time. Results were compared for reproducibility within samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Equilibrium Time [min]</th>
<th>Percent Uptake</th>
<th>Resolution [keV]</th>
<th>1/5 Resolution [keV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>60</td>
<td>0.126 ± 0.002</td>
<td>65</td>
<td>122</td>
</tr>
<tr>
<td>15</td>
<td>60</td>
<td>0.191 ± 0.003</td>
<td>81</td>
<td>130</td>
</tr>
<tr>
<td>16</td>
<td>30</td>
<td>0.197 ± 0.002</td>
<td>65</td>
<td>105</td>
</tr>
<tr>
<td>17</td>
<td>30</td>
<td>0.333 ± 0.003</td>
<td>29</td>
<td>87</td>
</tr>
<tr>
<td>18</td>
<td>30</td>
<td>0.099 ± 0.002</td>
<td>32</td>
<td>70</td>
</tr>
<tr>
<td>19</td>
<td>30</td>
<td>0.297 ± 0.004</td>
<td>72</td>
<td>104</td>
</tr>
</tbody>
</table>
Examination of uptake kinetics and the influence of pH

An experiment measuring equilibrium time was performed by placing 2 discs in 86 mL of a ~50 dpm/mL $^{238}$Pu solution at pH 5.47. Disc one was submerged for one hour and disc two was submerged for three hours, taking LSC samples periodically. LSC results showed no uptake on disc one after one hour. Disc two indicated an initial activity in liquid of 40.76 ± 1.88 cpm and 34.82 ± 1.77 cpm after 5 min. However, after 3 hours, LSC results showed an activity of 38.73 ± 1.84 cpm. The fluctuation in the LSC data is believed to be due to variations in background and volumetric efforts from sample to sample. However, they indicate a slight decrease from the initial concentration as soon as 5 minutes indicating rapid uptake kinetics. This is consistent with the lack of change in uptake between 30 and 60 minutes for the data shown in Table 5.2 and is supported by other literature showing almost instantaneous sorption of actinides to GO.\textsuperscript{16} Alpha spectroscopy results for disc one showed a clear peak with little tailing with a low activity of 0.482 ± 0.029 dpm, an uptake of 0.013 ± 0.001%, and a resolution of 49/84 keV. Disc two was damaged in the experiment and the alpha spec results were not reliable. Results showed that in less than 100 mL of $^{238}$Pu solution, equilibrium time for uptake was very fast and could be achieved in minutes at pH 5.47.

Due to the relatively low uptake observed at pH 5.47, experiments were conducted to determine the influence of pH on Pu uptake in order to determine the optimal pH. Plutonium uptake across the pH range 2 to 5 was examined and alpha spectroscopy results indicated the highest activity for pH 3.09 with 11.308 ± 0.167 dpm
and second highest at pH 3.90 with 4.855 ± 0.090 dpm. Resolution was 21/52 keV and 23/54 keV for pH 3.09 and 3.90, respectively. These values corresponded to percent uptake values of 0.707 ± 0.010 and 0.303 ± 0.006% for pH 3.09 and 3.90, respectively.

The alpha spectra results for each disc are shown in Figure 5.8. The slight variation between uptake and resolution values can be seen in Table 5.3. These data indicate that while the results were very similar, pH 3.09 yielded the best resolution and uptake values for the GO coated discs based on a plot of the uptake and resolution simultaneously (Figure 5.9)

![Alpha spectra results of GO spin coated discs submerged in 30 mL of ~54 dpm/mL $^{238}$Pu solution for one hour, triple rinsed with DI H$_2$O, dried at 50 °C and then counted on the alpha spectrometer for 2000 minutes.](image)

**Figure 5.8** Alpha spectra results of GO spin coated discs submerged in 30 mL of ~54 dpm/mL $^{238}$Pu solution for one hour, triple rinsed with DI H$_2$O, dried at 50 °C and then counted on the alpha spectrometer for 2000 minutes.
Table 5.3 Comparison of alpha spectra features due to uptake of $^{238}\text{Pu}$ onto GO spin coated discs with variation between samples due to pH values of Pu solution.

<table>
<thead>
<tr>
<th>pH Values</th>
<th>Uptake [%]</th>
<th>Resolution [keV]</th>
<th>1/5 Resolution [keV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.13</td>
<td>0.337 ± 0.007</td>
<td>57</td>
<td>87</td>
</tr>
<tr>
<td>2.72</td>
<td>0.071 ± 0.003</td>
<td>42</td>
<td>63</td>
</tr>
<tr>
<td>3.09</td>
<td>0.707 ± 0.010</td>
<td>21</td>
<td>52</td>
</tr>
<tr>
<td>3.90</td>
<td>0.303 ± .0006</td>
<td>23</td>
<td>54</td>
</tr>
<tr>
<td>4.48</td>
<td>0.242 ± 0.006</td>
<td>43</td>
<td>71</td>
</tr>
<tr>
<td>5.00</td>
<td>0.117 ± 0.004</td>
<td>100</td>
<td>178</td>
</tr>
</tbody>
</table>

Figure 5.9 The percent uptake and percent resolution calculated for GO spin coated discs submerged in 30 mL of ~54 dpm/mL $^{238}\text{Pu}$ solution for one hour at varying pH values.
Characterization of GO spin coated discs

Attempts were made to examine the GO coating on glass discs using FTIR. However, FTIR spectra only showed silanol peaks from the glass slide indicating that the surface coating was not sufficiently thick to yield a signal. Therefore, the surface coating was examined using scanning electron microscopy. Figure 5.10 shows a GO coated disc after being submerged in H₂O at pH 2.72 for 45 minutes then dried for 20 minutes in a 50 °C oven. The image was taken to examine the GO coverage of the disc after equilibration with an aqueous phase. The image shows full coverage of the imaged area, with shallow grooves thought to be the result of the spin coating technique and the roughness of the glass disc surface. Figure 5.11 shows another area of the same disc where full coverage is also present and the surface shows shallow dips and grooves. It is not possible to determine the depth of these grooves from the SEM image. However, based on the relative heterogeneity of the surface, the grooves may have enough of a difference in height from each other to cause mild tailing in the alpha spec but not deep enough to cause drastic differences in the path length of the alpha particle. This is consistent with the observed quality of the spectra shown above. These images, along with similar images not shown, provide assurance that the spin coating technology was successful and that the disc appears to have complete coverage.
Figure 5.10 SEM of GO spin coated disc showing full coverage of sonicated flakes.

Figure 5.11 SEM of GO spin coated disc showing shallow height differences.
An atomic force microscope (AFM) was also employed to help quantify the thickness of GO on the disc. The AFM was used in contact mode and the surfaces of several discs were examined and topography recorded. Results showed that the surfaces were relatively flat and the difference between the highest peaks and deepest well of the surface was measured at ~30 nm, though since no measurements were taken from the bare glass, the total thickness of the coating could not be acquired. The phase changes suggested that each disc was thoroughly coated except in a few spots that were attributed to the area that a clamp was used to hold the discs. AFM images were taken of discs thought to have varying thickness. Although the AFM could not identify the total thickness of the coating, the information obtained confirmed the conclusions drawn from the SEM images, indicating that there was full, fairly uniform GO coverage on the discs (Figure 5.12). The images of a glass disc only, as seen in Figure 5.13, were added for comparison. There is a clear difference in texture, height variance, and phase shift between the glass discs and the GO coated discs. The phase shift of the GO disc shows a pattern within the phase shift mimicking channels present in SEM. The height differences show crisp lines that could be attributed to layering of flakes. The glass slide phase changes show that the majority of the imaged area remains in the same phase, which indicates uniformity. This uniformity can be contrasted against the phase shift that was seen on the GO particulate coated surface. The height difference in the glass is also fairly uniform. The blemishes and striping in the images in an artifact of the AFM atmosphere and the relatively large size of region being examined.
Figure 5.12 Left image shows phase shift of GO coated disc with channels present. Right image shows thickest GO prepared disc with flakes attributing to height difference.

Figure 5.13 Left image shows phase shift of glass with fairly uniform phases present. Right image of height difference of glass shows uniform height. Lines in images are artifacts of AFM capture.
Influence of GO mass on spin coated discs

To examine the potential for self-absorption, theoretical calculations were performed that used the range of an alpha particle in graphene oxide. Variations in oxidation of GO, size of particles and layering of particles will all affect the thickness and uniformity of the GO coating. To perform alpha particle range calculations, a density of 2.3 g/cm³ was assumed. For the calculation, $^{238}$Pu was chosen because it had a higher energy than the other isotopes used throughout the experiment. The alpha particle range in air was calculated using:

$$ R(cm) = 0.322 \cdot E^{-1.5} $$

where $E$ is energy in MeV (5.593) and $R$ is the range of an alpha particle in air in cm. Solving for $R_{Air}$, the range of $^{238}$Pu in air is 4.26 cm. Adjusting for the density of the material, the range of an alpha particle in GO will be:

$$ R_{Air}(cm) \cdot \rho_{Air} \left( \frac{g}{cm^3} \right) \cdot A_{Air}^{0.5} = R_{GO}(cm) \cdot \rho_{GO} \left( \frac{g}{cm^3} \right) \cdot A_{GO}^{0.5} $$

Where the range of $^{238}$Pu in air is 4.26 cm, and the density of air is $1.293 \times 10^{-3}$ g/cm³, and the atomic mass of air is 14.4 g. A density of 2.3 g/cm³ was used for GO as well as an atomic mass of (35% Carbon and 65% Oxygen) 14.6 g. From this information, the range of the alpha particle in GO was calculated to be $2.38 \times 10^{-3}$ cm.

Using 25 mm disc, thickness of 0.136 µm of GO and a density of 2.3 g/cm³, the mass of GO on a disc possible of stopping an alpha particle emanating at the glass-GO
interface was calculated to be 0.0268 grams. This represents the range of the alpha particle in GO on a 25 mm diameter disc. Since relatively high quality spectra with apparently little self-absorption were observed above, this calculation is meant to give an upper limit of the amount of GO loading possible on a disc.

In order to examine the impact that the mass of GO spin coating had on absorption and resolution, an experiment was designed to vary the mass of GO coatings on 25 mm discs. This mass was indirectly affected by varying the maximum RPMs for the discs. Three distinct maximum values were used, and the result was three groups of GO spin coated discs each thought to have similar masses within each group. A microbalance was used in an attempt to quantify the mass added to each disc, but results were inconsistent. Although the microbalance readability, as defined by Mettler, is 1 µg, the practical detection limit may be much closer to 30 µg. Environmental conditions such as air flow, static, humidity, and balance stability likely contributed to drift and attributed to inconsistencies in masses weighed.

The discs were divided into three groups, based on the RPMs, and the expectation was that the fastest rotations would cause the liquid GO suspension coating to spread out the thinnest. Once dry the process would result in a uniformly thin, reproducible layer of GO. One disc was taken from each group (groups categorized as highest, medium, and lowest RPM with relative correlation to thinnest, medium, and thickest coating) and suspended in 200 mL of a $^{238}$Pu solution at pH 5. Through spiking at 30 minute intervals, the concentration of $^{238}$Pu in solution gradually increased to 100
dpm/mL. The discs were allowed to equilibrate for a total of 2.5 hours. An alpha spectrum was taken of each disc and the resultant spectra are shown in Figure 5.14. The experiment was repeated for $^{233}\text{U}$ at pH 7.5 (Figure 5.15).

![Graph showing alpha spectra for different RPM settings](image)

**Figure 5.14** Alpha spec results of three GO spin coated discs of varying thickness, where thickness was controlled by variation in RPM, submerged in $\sim$100 dpm/mL $^{238}\text{Pu}$ solution.
Figure 5.15 Alpha spec results of three GO spin coated discs of varying thickness, where thickness was controlled by variation in RPM, submerged in ~100 dpm/mL $^{233}$U solution. A trend could be seen in both the $^{233}$U and $^{238}$Pu spectra where the thickest coating corresponded to the most counts; similarly, the thinnest coating produced the fewest counts. Due to the similarity in surface area coating, if Pu interacted with GO as only adsorption, then all three coatings of GO would have been expected to have similar uptake. However, Table 5.4 shows a trend of increased uptake with increasing mass which could be explained by Pu absorption in to the GO coating. This absorption would result in actinide sorption to more than just surficial layer of GO. The diffusion of actinides into the GO coating may cause some self-attenuation and cause a decrease in resolution as the mass of GO increased. The trend of decreased resolution with increased uptake can be seen with the thinnest GO coating reporting a $^{238}$Pu uptake of 0.063± 0.001% and a resolution of 53 keV, while the middle GO coating reports uptake
at 0.443 ± 0.001% with a resolution of 68 keV, and the thickest coating reporting the highest uptake at 1.359 ± 0.005% with the worst resolution at 75 keV. Results could not be confirmed by LSC due to virtually no change as a result of low percent uptake.

Appendix B shows the data from LSC that was not used.

Table 5.4 Comparison of alpha spectra features due to uptake of $^{238}\text{Pu}$ and $^{233}\text{U}$ onto GO coated discs created by spin coating at varying RPMs to create coatings of varying mass.

<table>
<thead>
<tr>
<th>Relative Thickness of GO Coating Based on RPM</th>
<th>Isotope</th>
<th>Percent Uptake</th>
<th>Resolution [keV]</th>
<th>1/5 Resolution [keV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thinnest Coating (Highest RPM)</td>
<td>$^{238}\text{Pu}$</td>
<td>0.063 ± 0.001</td>
<td>53</td>
<td>82</td>
</tr>
<tr>
<td>Thinnest Coating (Highest RPM)</td>
<td>$^{233}\text{U}$</td>
<td>2.063 ± 0.001</td>
<td>56</td>
<td>95</td>
</tr>
<tr>
<td>Medium Coating (Medium RPM)</td>
<td>$^{238}\text{Pu}$</td>
<td>0.443 ± 0.001</td>
<td>68</td>
<td>102</td>
</tr>
<tr>
<td>Medium Coating (Medium RPM)</td>
<td>$^{233}\text{U}$</td>
<td>5.943 ± 0.001</td>
<td>58</td>
<td>94</td>
</tr>
<tr>
<td>Thickest Coating (Lowest RPM)</td>
<td>$^{238}\text{Pu}$</td>
<td>1.359 ± 0.005</td>
<td>75</td>
<td>102</td>
</tr>
<tr>
<td>Thickest Coating (Lowest RPM)</td>
<td>$^{233}\text{U}$</td>
<td>4.147 ± 0.005</td>
<td>47</td>
<td>82</td>
</tr>
</tbody>
</table>

The trend breaks down in GO uptake of $^{233}\text{U}$ where the thinnest coating had a 2.063 ± 0.001% uptake with 56/95 keV resolution, the middle coating had a 5.943 ± 0.001% uptake with 58/94 keV resolution, and the thickest coating had a 4.147 ± 0.005% uptake with 47/82 keV resolution. The resolution appeared to be approximately the same for the lowest and highest amount of uptake. The medium thickness GO coating disc reported the highest uptake with the lowest resolution. The inconsistencies in the

56
GO coating thicknesses could cause the breakdown of the trend of increase uptake with increased thickness. The differences in the mechanisms of interaction between Pu and U(VI) could have resulted in higher uptake for the U(VI) in comparison to Pu. The higher pH of the U(VI) uptake experiment (pH 7 versus pH 5 for Pu) may have limited interactions of U(VI) only to the surficial GO. Alternatively, it is noteworthy that plutonium was initially added as Pu(IV). However, oxidation of trace levels of Pu to form Pu(V) in natural waters has been observed by a number of researchers.32-36 If oxidation to Pu(V) occurred, sorption should decrease as Pu(V) is expected to exhibit weaker sorption than both Pu(IV) and U(VI) based on the effective charge of the ion.12

**Demonstration of Pu uptake on GO coated discs from dilute solutions**

A final experiment was conducted to demonstrate the ability of these GO coated surfaces to concentrate Pu from large aqueous volumes with relatively dilute concentrations. Tap water (3.7 L) was spiked with either 100 dpm or 500 dpm of $^{238}$Pu(IV) and adjusted to pH 5 with HCl. A GO spin coated disc was suspended in each solution for 12 hours and then counted for 12 hours on the alpha spectrometer. The first two trials were performed on disc samples 41 and 58 (Table 5.5) with an activity of $\sim$100 dpm $^{238}$Pu. Results produced activities of $0.018 \pm 0.005$ dpm and $-0.002 \pm 0.008$ dpm with calculated uptakes of $0.018 \pm 0.005$ and $-0.002 \pm 0.008$, respectively. Despite a low activity, the alpha spectrum from disc sample 41 produced a clear peak with acceptable tailing as shown in Figure 5.16.
Table 5.5 Comparison of alpha spectra features due to uptake of $^{238}$Pu onto GO coated discs after a 12 hour suspension in 3.7 L of pH 5 solution. A Kd was also calculated based on results using a GO mass of 33 µg.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Activity in Solution [dpm]</th>
<th>Percent Uptake</th>
<th>Resolution (%)</th>
<th>Kd [L/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>100</td>
<td>0.018 ± 0.005</td>
<td>0.82</td>
<td>2.04 x 10^4</td>
</tr>
<tr>
<td>58</td>
<td>100</td>
<td>-0.002 ± 0.008</td>
<td>0.95</td>
<td>-2.31 x 10^3</td>
</tr>
<tr>
<td>45</td>
<td>500</td>
<td>0.012 ± 0.006</td>
<td>0.53</td>
<td>2.45 x 10^4</td>
</tr>
<tr>
<td>52</td>
<td>500</td>
<td>0.039 ± 0.009</td>
<td>1.08</td>
<td>4.43 x 10^4</td>
</tr>
<tr>
<td>59</td>
<td>500</td>
<td>0.013 ± 0.007</td>
<td>1.66</td>
<td>1.49 x 10^4</td>
</tr>
</tbody>
</table>

Figure 5.16 GO spin coated disc (sample 41 from Table 5.5) suspended for 12 hours in 3.7 liters of tap water spiked with ~100 dpm of $^{238}$Pu then counted by alpha spectroscopy for 12 hours.
When submerged for 12 hours in ~500 dpm $^{238}$Pu solution, disc samples 45, 52, 59 (Table 5.5) had an average activity of $0.124 \pm 0.037$ dpm with the uncertainty arising from the standard deviation of three disc samples. Using an electrodeposited standard with similar geometry for approximate detector efficiency, the average uptake was approximately $0.020 \pm 0.009\%$, with the highest $0.039 \pm 0.009\%$ and the lowest $0.012 \pm 0.006\%$. Since activities were extremely low, it was decided to use an approximate standard for efficiency in order to see if results produced were significant. The alpha spectrum of disc sample 52 reveals significant tailing and a somewhat indistinct $^{238}$Pu peak (Figure 5.17).

![Figure 5.17](image-url)

**Figure 5.17** GO spin coated disc (sample 52 from Table 5.5) suspended for 12 hours in 3.7 liters of tap water spiked with ~500 dpm of $^{238}$Pu and then counted by alpha spectroscopy for 12 hours.
In many cases, the observed uptake values were approaching the minimum detectable activity (MDA) as calculated using the Currie equation. This equation takes into account both false-positive errors (Type I) and false-negative (Type II) and represents the minimum level of activity that can be detected at a 95% confidence level. This variation of the equation that presents results as MDA instead of critical limit is as follows:\n\[
MDA = \frac{2.71 + 4.65\sqrt{B}}{ft\varepsilon}
\]  

where \( B \) is the number of background counts, \( f \) is the branching ratio, \( t \) is the counting time, and \( \varepsilon \) is the absolute efficiency of the detector. An average MDA for all detectors used was found to be 0.0034 ± 0.0014 dpm (Note each detector had slightly different background levels and efficiencies; where efficiencies were between 19 and 22% for electroplated disc standards with similar geometries to discs). The 0.0034 dpm MDA can be compared to the average activity of discs submerged in 3.7 L of 500 dpm \(^{238}\text{Pu}\) solution (disc samples 45, 52, 59 from Table 5.5) calculated at 0.124 ± 0.039 dpm. This low MDA gives confidence that even with the large uncertainty, activity was present. 

\( K_d \) calculations show the relationship between mass of GO, volume of contaminated liquid and actinide uptake potential. Based on the observed fractional uptake, \( K_d \) values were calculated using the equation below.

\[
K_d = \frac{[Pu]_{total} - [Pu]_{aq} \times \frac{\text{volume of solution}}{\text{mass of GO}}}{[Pu]_{aq}}
\]  

60
$K_d$'s were calculated from disc samples 14-19 from the uptake experiments in 80 mL solution volumes (disc samples 14-19) and 3.7 L volumes (disc samples 41, 45, 51, 52, and 59) were calculated using Equation 4, assuming 33 $\mu$g of GO was deposited on each disc. This is much less than the value calculated for the maximum thickness above. This value was based on data from multiple attempts to determine the mass of GO on the glass discs using a microbalance. An average mass of $33.2 \pm 45.8 \mu$g was determined after weighing 19 dried, GO coated glass discs which were prepared using the slowest RPM during spin coating (i.e. that would yield the greatest GO mass on the disc). This mass was used with the understanding that it was an approximation of mass and should not be used as a dependable quantitative value. The average $K_d$ value for all discs from Table 5.5 with observed uptake was $26028 \pm 12780$ L/kg. Disc sample 58 was excluded since no uptake was detected.

The $K_d$ values, calculated from disc samples 14-19 which used an 80 mL total volume were calculated assuming a 33 $\mu$g GO coating on each disc, were averaged and results gave a final $K_d$ of $5022 \pm 2244$ L/kg (Table 5.6). The discs were chosen because they all had similar GO spin coating parameters, activity concentration of solution, and a pH of 2.88.
Table 5.6 $K_d$’s calculated from $^{238}$Pu uptake on GO coated discs submerged in pH 2.88 solution assuming 33 µg of GO.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$K_d$ [L/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>$3.07 \times 10^3$</td>
</tr>
<tr>
<td>15</td>
<td>$4.56 \times 10^3$</td>
</tr>
<tr>
<td>16</td>
<td>$4.79 \times 10^3$</td>
</tr>
<tr>
<td>17</td>
<td>$8.10 \times 10^3$</td>
</tr>
<tr>
<td>18</td>
<td>$2.41 \times 10^3$</td>
</tr>
<tr>
<td>19</td>
<td>$7.21 \times 10^3$</td>
</tr>
<tr>
<td><strong>Average ± Standard Deviation</strong></td>
<td>$5.02 \times 10^3 ± 2.24 \times 10^3$</td>
</tr>
</tbody>
</table>

This average $K_d$ of $5022 ± 2244$ L/kg can be compared with the batch sorption values mentioned earlier, from Table 5.1, where the average $K_d$ was $21364 ± 18009$ L/kg. Thus the uptake values from the batch experiments in 80 mL volumes are within a factor of 5 of the batch uptake experiment where graphene oxide was present as a suspension (i.e. not coated onto glass surface). Both $K_d$ values from batch suspensions or uptake onto coated discs in 80 mL solution correlate well to the average $K_d$ of $26028 ± 12780$ L/kg based on the data from the uptake experiments in 3.7 L volumes. The 3.7 L experiments are a rather extreme test of the $K_d$ concept since there was relatively little GO in the system and the volume was relatively large. Even under extreme circumstances, the $K_d$’s remain within an order of magnitude of each other.
Looking back to the theoretical plot seen in Figure 2.1, and assuming a 33 μg mass of GO, the percent uptake falls around 20% for a 1000 K_d solution and approximately 80% for a 10,000 K_d solution. Although the expected uptake does not agree with the results obtained there are variables not accounted for in the figure. First, the volume of solution was 100 mL, which is much smaller than the 3700 mL used in the large volume experiments. Also, more importantly, the K_d calculated was based on sorption occurring; which in the case of Pu, would require Pu(IV) to be present instead of Pu(V). After time in solution, it is likely that at least some of the Pu(IV) oxidized to Pu(V). However, the experiment performed is much more likely to represent uptake of Pu by GO in natural systems.

The results of this study can be compared to a K_d calculated from a paper by Gonzales et al., using Dipex® as an extractive ligand.\textsuperscript{23} Using reported values of 70% fraction aqueous, 0.089 g of Dipex®, and 100 mL of solution, the K_d was calculated to be 1604 L/kg. This is much lower than the K_d from the final experiment suggesting that GO is a suitable material for actinide uptake but limited by its mass loading. The calculated K_d from the Gonzales experiment was a result of ligand submersion into a small volume of liquid. In comparison, other previously reviewed studies reported sorption after pipetting small droplets of radioactive solution directly on the ligand of interest and rinsing after a designated period of time.\textsuperscript{22-25} Although it would increase preparation time, the GO spin coated discs could be used in a similar manner and potentially produce alpha spectra with the spectral qualities similar to an electrodeposited source.
CHAPTER SIX
CONCLUSIONS AND FUTURE WORK

The preceding set of experiments focused on developing a single surface that could be utilized for actinide removal and assay via alpha spectroscopy. Using GOPS as an intermediate, PLAA and PDAA functionalized glass slides were created. When placed in a $^{238}$Pu solution, sorption occurred and alpha spectra showed clear peaks and resolution as low as 12 keV. However, tailing was significant enough that it would be problematic when determining isotopic ratios of uranium. Also, the counts were low but due to lack of an available standard, the uptake could not be determined via alpha spectroscopy. LSC results showed uptake as much as 9% and although results looked promising, it was difficult to obtain reproducibility throughout the experiment.

In an attempt to find a coating that would be uniformly thin and selective for actinides, graphene oxide was considered as a logical choice due to recent studies highlighting its sorption capacity to nuclides such as Eu(III), Th(IV), Pu(IV), and U(VI). GO was spin coated onto 25 mm glass disc at various thicknesses by varying the spin rate until the desired thickness was reached. The difference in thickness showed a trend of increased actinide uptake with increased mass of GO, at the expense of degraded energy resolution. This trend was not an absolute trend for U(VI) and the lack of certainty in mass was problematic for analysis. Overall very low uptake was seen ranging from ~0.06 to ~1.4% and percent resolution was acceptable with ranges from 16 to 136 keV. The most significant drawback to the method described is the low uptake.
With such a low uptake it would be difficult to quantify an activity in solution due to the high uncertainty that comes with such a low count rate. However, the low count rate would not inhibit the ability to identify an isotope based on energy or identify a suite of isotopes and report their relative percentages. This would be useful for discerning between natural uranium or enriched uranium.

Future work should include quantification of number of functionalized sites of graphene oxide. This is important because although the K_d calculations done to date with this experiment are based on mass, the variation in the number of functionalized groups will also greatly affect the calculations. If one batch of GO has twice the functionalized groups, the K_d’s will not remain constant even if the mass does. Quantification of thickness of GO load on discs would be useful when performing uptake calculations, since it seems probable that absorption is occurring. Currently the variation in RPM during spin coating can only measure relative thickness, and that has not been quantified. A more systematic examination of the influence of pH is needed to definitively determine the optimal pH for uptake. This should be done with discs proven to have similar masses and with variation in activity concentration in hopes to verify the work performed in these experiments. Additional variable pH experiments using actinides in different oxidation states are also needed for further method development. The variations in pH with respect to oxidation state may yield a method for selective actinide uptake based on the pH of the uptake solution.
Experiments involving multiple actinide species in natural waters containing various inorganic ions and natural organic matter are needed to test this theory for more real world applications. Although efforts were made using tap water and low concentrations of actinides, varying concentrations of natural organic matter in the solution would identify what impact, if any, it would have on the resultant percent uptake and percent resolution.

The development of a verification method that would quantify uniformity among discs would be vital for standardization of results. This could possibly include some form of absorbance spectroscopy using rectangular pieces of the spin coated disc, where the percent transmittance would correlate to thickness of coating; although this too would be a relative comparison. The lack of verification of uniformity of the mass of GO on the spin coated discs was potentially a very large variable in the above experiments. In order to prove any correlation between uptake and mass or tailing and thickness, the mass and thickness need to be verifiable, not just relative.

Last would be the creation of a series of experiments varying the concentration of actinide in solution, volume of water used, and equilibrium time. These experiments would be needed to give real world limitation and approximate time frames relevant to activity.
APPENDICES

Appendix-A

Table A-1. List of variations in duration of RPM cycle’s one and two and maximum RPM’s during each cycle. Volume of GO suspension and number of depositions per volume were also altered. Visual appearance of streaks, excess droplets of GO suspension, and color of disc were used to narrow down optimal setting parameters.

<table>
<thead>
<tr>
<th>Volume of GO solution deposited [µL]</th>
<th>Max volume deposited per deposition</th>
<th>RPM 1 Duration of first RPM [sec]</th>
<th>RPM 2 Duration of second RPM [sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>50</td>
<td>1000</td>
<td>9</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>1000</td>
<td>9</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>600</td>
<td>9</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>600</td>
<td>9</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>600</td>
<td>9</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>600</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>600</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>630</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>630</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>520</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>540</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>560</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>580</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>630</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>660</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
<tr>
<td>200</td>
<td>100</td>
<td>590</td>
<td>10</td>
</tr>
</tbody>
</table>
Table B-1 LSC results not used due to low uptake corresponding to Figure 5.14

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Count</th>
<th>Time in min</th>
<th>CPMa</th>
<th>BS CPMa</th>
<th>Fraction aqueous per 30 min spike</th>
</tr>
</thead>
<tbody>
<tr>
<td>238Pu</td>
<td>8.1</td>
<td>20</td>
<td>5</td>
<td>background</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>18</td>
<td>13</td>
<td>sample after spike</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>18</td>
<td>13</td>
<td>Sample after 30 min submersion</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>29</td>
<td>24</td>
<td>sample after spike</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>29</td>
<td>24</td>
<td>Sample after 30 min submersion</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>69</td>
<td>64</td>
<td>sample after spike</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>69</td>
<td>64</td>
<td>Sample after 30 min submersion</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>98</td>
<td>93</td>
<td>sample after spike</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>96</td>
<td>91</td>
<td>Sample after 30 min submersion</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>132</td>
<td>127</td>
<td>sample after spike</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>132</td>
<td>127</td>
<td>Sample after 30 min submersion</td>
<td>1.00</td>
</tr>
<tr>
<td>Bkgd</td>
<td>29.1</td>
<td>20</td>
<td>3</td>
<td>background</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>15</td>
<td>12</td>
<td>sample after spike</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>15</td>
<td>12</td>
<td>Sample after 30 min submersion</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>27</td>
<td>24</td>
<td>sample after spike</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>28</td>
<td>25</td>
<td>Sample after 30 min submersion</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>63</td>
<td>60</td>
<td>sample after spike</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>63</td>
<td>60</td>
<td>Sample after 30 min submersion</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>87</td>
<td>84</td>
<td>sample after spike</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>84</td>
<td>81</td>
<td>Sample after 30 min submersion</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>119</td>
<td>116</td>
<td>sample after spike</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>119</td>
<td>116</td>
<td>Sample after 30 min submersion</td>
<td>0.97</td>
</tr>
<tr>
<td>Bkgd</td>
<td>49.1</td>
<td>20</td>
<td>4</td>
<td>background</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>18</td>
<td>14</td>
<td>sample after spike</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>15</td>
<td>11</td>
<td>Sample after 30 min submersion</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>27</td>
<td>23</td>
<td>sample after spike</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>24</td>
<td>20</td>
<td>Sample after 30 min submersion</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>62</td>
<td>58</td>
<td>sample after spike</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>63</td>
<td>59</td>
<td>Sample after 30 min submersion</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>87</td>
<td>83</td>
<td>sample after spike</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>82</td>
<td>78</td>
<td>Sample after 30 min submersion</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>112</td>
<td>108</td>
<td>sample after spike</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>110</td>
<td>106</td>
<td>Sample after 30 min submersion</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Table B-2 LSC results not used due to low uptake corresponding to Figure 5.15

<table>
<thead>
<tr>
<th>$^{235}$U Sample ID</th>
<th>Count Time in min</th>
<th>$^{235}$U CPMa</th>
<th>BS CPMa</th>
<th>Fraction aqueous per 30 min spike</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bkgd 8.1</td>
<td>20</td>
<td>5</td>
<td>0</td>
<td>background</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>13</td>
<td>8</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>11</td>
<td>6</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>21</td>
<td>16</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>19</td>
<td>14</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>49</td>
<td>44</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>46</td>
<td>41</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>70</td>
<td>65</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>68</td>
<td>63</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>92</td>
<td>87</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>88</td>
<td>83</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td>Bkgd 29.1</td>
<td>20</td>
<td>8</td>
<td>0</td>
<td>background</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>17</td>
<td>9</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>17</td>
<td>9</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>28</td>
<td>20</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>24</td>
<td>16</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>54</td>
<td>46</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>51</td>
<td>43</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>69</td>
<td>61</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>70</td>
<td>62</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>96</td>
<td>88</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>89</td>
<td>81</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td>Bkgd 49.1</td>
<td>20</td>
<td>6</td>
<td>0</td>
<td>background</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>16</td>
<td>10</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>15</td>
<td>9</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>25</td>
<td>19</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>22</td>
<td>16</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>51</td>
<td>45</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>46</td>
<td>40</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>67</td>
<td>61</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>61</td>
<td>55</td>
<td>Sample after 30 min submersion</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>84</td>
<td>78</td>
<td>sample after spike</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>81</td>
<td>75</td>
<td>Sample after 30 min submersion</td>
</tr>
</tbody>
</table>
REFERENCES


