Uranium-selective adsorbent materials for environmental radiation sensing

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ABSTRACT

Nuclear nonproliferation efforts and treaty verification require portable, robust radiation detectors capable of detecting trace-levels of radionuclides in environmental matrices. Despite widespread interest, currently, there are no fieldable, radiation detection techniques capable of directly analyzing gross activity or isotopic distributions of uranium in environmental waters. Extractive scintillating resins in flow-cell detectors and alpha spectroscopy are two promising fieldable detection methods; however, the implementation of these detection methods in the field requires novel separation materials capable of isolating uranium from environmental waters. Organophosphorus-derivitized materials are a promising class of materials to fit this need and are reviewed in Chapter 1.

Chapter 2 presents my work understanding the stability of extractive scintillating resins prepared by multiple methods. This chapter characterizes the stability of scintillating resins for ionizing radiation detection that were synthesized with 2-(1-naphthyl)-5-phenyloxazole (α-NPO) or 2-(1-naphthyl)-4-vinyl-5-phenyloxazole (v-NPO) fluorophore in polystyrene (PS) or poly(4-methyl styrene) (PVT) matrices. Leaching studies of the PS and PVT beads with methyl acetate show a 60% reduction in luminosity and 80% reduction in detection efficiency for α-NPO samples; while v-NPO resins retained detection properties. Degradation studies indicate the nitration of PS resins and the fluorophores after nitric acid exposure, resulting in a 100% reduction in optical properties; whereas PVT resins with v-NPO fluorophore maintained 20% detection efficiency. Heuristics are reported for designing stable scintillating resins.
Chapter 3 describes the synthesis and characterization of phosphonic acid derivitized resins for the simultaneous concentration and detection of uranium. Resins in this study were prepared by a two-step procedure: (1) suspension polymerization followed by (2) phosphorylation and hydrolysis. Phosphonate hydrolysis was performed via strong acid or trimethylsilyl bromide (TMSBr)-mediated methanolysis. Fluorophore degradation was observed in the resin hydrolyzed by strong acid, while the resin hydrolyzed by TMSBr-mediated methanolysis maintained luminosity and showed hydrogen bonding-induced Stokes’ shift of ~100 nm. Flow cell detection efficiency of the TMSBr-mediatied methanolysis resin was found to decrease with increasing pH. Trends are discussed in terms of uranium speciation in solution. Experiments performed in pH 4 synthetic groundwater show that the resins can concentrate the uranyl cation from waters with high concentrations of competitor ions at near-neutral pH.

Chapter 4 describes the optimization of design parameters for the implementation of extractive scintillating resin in flow cell detectors. This chapter details the application of extractive scintillating resin with covalently bound fluorophore, v-NPO, and ligand, methyl phosphonic acid, in flow-cell experiments utilizing varying column diameters, resin diameters and diffusion times. The detection efficiency was evaluated by standard offline liquid scintillation counting methods. Diffusion experiments were conducted to determine the effect of the location of the alpha decay on detection efficiency, and the data were compared to a diffusion model to assess the feasibility of relying on diffusion-enhanced detection efficiency in an online measurement.
Chapter 5 describes the synthesis and characterization of phosphonic acid- and alkyl phosphate-derivitized extractive scintillating resins. Organophosphorus-derivitized resins were synthesized by two approaches: (1) synthesis of a 4-vinylbenzyl chloride containing polymer followed by solid-phase synthesis techniques to add the phosphonic acid moiety and (2) one-pot polymerization that directly incorporates an alkyl phosphate moiety. Resins were compared on the basis of capacity for uranium, detection efficiency, and volume to detection. The volume to detection was evaluated in neutral pH simulated ground waters (pH 4-8) using a Shewart-3σ alarm statistic applied to data collected in real-time in a flow-cell detector. Resins exhibited similar binding capacities (0.18 mmol g\(^{-1}\)) and detection efficiencies (~40%); however, the alkyl phosphate resins more rapidly achieved the Shewart-3σ alarm criteria than the phosphonic acid resins. Thermodynamic models in Visual MINTEQ software and the pKa’s of the ligands are used to understand how the binding mechanisms for both functional groups may change as a function of pH. The data imply that as pH increases from 4 to 8, the binding mechanism shifts from ion-exchange to ligand-exchange.

Chapter 6 describes our efforts to develop a high throughput analytical technique for waterborne isotopic analysis by using reactive, functional membranes as alpha spectroscopy substrates. In this work, alpha spectroscopy substrates were prepared by two methods: (1) physical deposition of a uranium-selective, water-soluble polymer film on ultrafiltration membranes and (2) grafting uranium-selective ligands from the surface of ultrafiltration membranes. Uranium was loaded onto the substrates by filtering uranium-contaminated water through the ultrafiltration membranes. The uranium-
selective, water-soluble polymer was prepared by the copolymerization of 2-hydroxylethyl methacrylate and 2-ethylene glycol methacrylate phosphate. The ligand-grafted membrane was prepared by the UV-polymerization of 2-ethylene glycol methacrylate phosphate with N,N-methylene bisacrylimide. Membranes were characterized by Fourier-transform infrared spectroscopy before and after modification to support the deposition or grafting of the polymer on the membrane surface. The capacity for uranium, 1.9 mmol U g$^{-1}$, was determined from equilibrium binding experiments. The effect of membrane preparation method and membrane pore size on peak resolution in the alpha spectrum was investigated for pure uranium containing solutions at pH = 6. To mimic more realistic conditions, the selectivity of the membrane was tested using uranium-233 in simulated groundwater. Both uranium-coated membranes prepared from distilled water and groundwater showed resolutions of 80-100 keV in the alpha spectrum and detection efficiencies of 12% for uranium-233. The membranes showed both high resolution and fast preparation time. The permeability of the polymer-coated, ultrafiltration membranes (MWCO 100 kDa) was determined to be 3.74 LMH kPa$^{-1}$.

Overall, this research demonstrates the ability to synthesize robust, uranium-selective materials for the direct concentration of uranium from ground water. Results from this research are laying the groundwork for the development of robust, portable radiation detection techniques capable of analyzing waterborne alpha-emitting radionuclides.
DEDICATION

To my family.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my advisor, Dr. Scott Husson. Since I arrived at Clemson, he has been incredibly supportive of my research and teaching efforts. He has created a working environment that is both productive and fun to be a part of. I only hope that I can foster those same ideals in a research group of my own.

Dr. Timothy DeVol has been another great influence throughout my graduate career. Since our first meeting, he has shown nothing but patience and understanding. I am forever grateful for such a humble introduction to the field of radiation detection, as it has immensely shaped my career goals and future research interests.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Title</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>DEDICATION</td>
<td>vi</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiv</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION AND OVERVIEW OF DISSERTATION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Real-time, gross alpha activity measurements with</td>
<td>2</td>
</tr>
<tr>
<td>extractive scintillating resins</td>
<td></td>
</tr>
<tr>
<td>1.2 Isotopic analysis with alpha spectroscopy</td>
<td>5</td>
</tr>
<tr>
<td>1.3 Uranium separation materials</td>
<td>8</td>
</tr>
<tr>
<td>1.4 Summary</td>
<td>18</td>
</tr>
<tr>
<td>1.5 Dissertation outline</td>
<td>20</td>
</tr>
<tr>
<td>II. STABILITY OF POLYMERIC SCINTILLATING RESINS DEVELOPED FOR ULTRA-TRACE LEVEL DETECTION OF ALPHA- AND BETA-EMITTING RADIONUCLIDES</td>
<td>23</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>23</td>
</tr>
<tr>
<td>2.2 Experimental</td>
<td>25</td>
</tr>
<tr>
<td>2.3 Results and discussion</td>
<td>29</td>
</tr>
<tr>
<td>2.4 Conclusions and future work</td>
<td>36</td>
</tr>
<tr>
<td>2.5 Acknowledgements</td>
<td>36</td>
</tr>
<tr>
<td>III. EXTRACTIVE SCINTILLATING POLYMER SENSORS FOR TRACE-LEVEL DETECTION OF URANIUM IN CONTAMINATED GROUND WATER</td>
<td>38</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>38</td>
</tr>
</tbody>
</table>
Table of Contents (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 Materials and methods</td>
<td>42</td>
</tr>
<tr>
<td>3.3 Results and discussion</td>
<td>50</td>
</tr>
<tr>
<td>3.4 Conclusions</td>
<td>58</td>
</tr>
<tr>
<td>3.5 Acknowledgements</td>
<td>59</td>
</tr>
<tr>
<td>IV. EVALUATION OF RESIN RADIUS AND COLUMN DIAMETER FOR THE IMPLEMENTATION OF EXTRACTIVE SCINTILLATING RESIN IN FLOW-CELL DETECTORS</td>
<td>61</td>
</tr>
<tr>
<td>4.1 Abstract</td>
<td>61</td>
</tr>
<tr>
<td>4.2 Theory</td>
<td>62</td>
</tr>
<tr>
<td>4.3 Experimental</td>
<td>64</td>
</tr>
<tr>
<td>4.4 Results and discussion</td>
<td>66</td>
</tr>
<tr>
<td>4.3 Conclusions</td>
<td>73</td>
</tr>
<tr>
<td>4.3 Acknowledgements</td>
<td>74</td>
</tr>
<tr>
<td>V. PHOSPHONIC ACID AND ALKYL PHOSPHATE-DERIVITIZED RESINS FOR THE SIMULTANEOUS CONCENTRATION AND DETECTION OF WATERBORNE URANIUM</td>
<td>75</td>
</tr>
<tr>
<td>5.1 Abstract</td>
<td>75</td>
</tr>
<tr>
<td>5.2 Experimental section</td>
<td>76</td>
</tr>
<tr>
<td>5.3 Results and discussion</td>
<td>82</td>
</tr>
<tr>
<td>5.4 Conclusions</td>
<td>91</td>
</tr>
<tr>
<td>5.3 Acknowledgements</td>
<td>92</td>
</tr>
<tr>
<td>VI. RAPID SAMPLE PREPARATION FOR ALPHA SPECTROSCOPY WITH ULTRAFILTRATION MEMBRANES</td>
<td>93</td>
</tr>
<tr>
<td>6.1 Abstract</td>
<td>94</td>
</tr>
<tr>
<td>6.2 Experimental section</td>
<td>62</td>
</tr>
<tr>
<td>6.3 Results and discussion</td>
<td>102</td>
</tr>
<tr>
<td>6.4 Conclusions</td>
<td>113</td>
</tr>
<tr>
<td>6.5 Acknowledgements</td>
<td>114</td>
</tr>
<tr>
<td>VI. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS</td>
<td>115</td>
</tr>
</tbody>
</table>
Table of Contents (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Summary and conclusions</td>
<td>115</td>
</tr>
<tr>
<td>7.2 Recommendations</td>
<td>120</td>
</tr>
</tbody>
</table>

APPENDICES ............................................................................................................. 127

A: Supplementary materials for dissertation chapters ........................................ 128
B: Confocal microscopy ........................................................................................ 137
C: Permissions to reproduce figures and text ................................................... 145

REFERENCES ............................................................................................................ 172
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Half-life and alpha particle energies for selected uranium isotopes</td>
</tr>
<tr>
<td>1.2</td>
<td>Common organophosphorus species for metal ion complexation/ion exchange</td>
</tr>
<tr>
<td>1.3</td>
<td>Summary of selectivity studies performed with organophosphorus ligands</td>
</tr>
<tr>
<td>2.1</td>
<td>Relative luminosity and detection efficiency for PS resins containing α-NPO or ν-NPO after leaching with methyl acetate (MA) for 24 h</td>
</tr>
<tr>
<td>3.1</td>
<td>Typical formulation for the discontinuous phase in suspension polymerization</td>
</tr>
<tr>
<td>3.2</td>
<td>Synthetic ground water composition</td>
</tr>
<tr>
<td>4.1</td>
<td>Order of magnitude analysis for the diffusion coefficient of uranyl ion in the polymer matrix where $M_t$ is the uranyl ion mass in the polymer at time $t$, $M_\infty$ is the uranyl ion mass in the polymer at equilibrium, $[U]<em>{eff}$ is the effluent concentration of uranyl ion and $[U]</em>{feed}$ is the concentration of uranyl ion in the feed solution</td>
</tr>
<tr>
<td>5.1</td>
<td>Composition of the discontinuous phase for EGMP synthesis</td>
</tr>
<tr>
<td>5.2</td>
<td>Summary of acid group speciation</td>
</tr>
<tr>
<td>6.1</td>
<td>Data summary for pH 6 trials of uranium-233 in DDI water and SGW</td>
</tr>
<tr>
<td>6.2</td>
<td>Approximate isotopic composition by mass of various grades of uranium</td>
</tr>
</tbody>
</table>
List of Tables (Continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>119</td>
</tr>
</tbody>
</table>

Summary of detection efficiencies for uranium-binding extractive scintillating resins
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Online sensing of waterborne uranium with extractive scintillating resins in a flow-cell detector</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Pulse-height spectrum collected with a Canberra Model 7401 alpha spectrometer (Canberra Industries, Inc., Oak Ridge, TN) and an electroplated, NIST traceable calibration standard containing uranium-238, uranium-234, plutonium-239 and americium-241 (Eckert &amp; Ziegler, Atlanta, GA)</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>Organo-functionalized mesoporous silica sorbents for uranium sequestration from water and simulated seawater</td>
<td>15</td>
</tr>
<tr>
<td>2.1</td>
<td>Relative luminosity (A) and relative detection efficiency data (B) for PS and PVT resins containing v-NPO exposed to 4M nitric acid</td>
<td>31</td>
</tr>
<tr>
<td>2.2</td>
<td>FTIR spectra of PS before (B) and after (A) nitric acid exposure</td>
<td>34</td>
</tr>
<tr>
<td>2.4</td>
<td>Absorption and emission spectra of α-NPO in ethyl acetate before and after nitric acid treatment</td>
<td>35</td>
</tr>
<tr>
<td>2.5</td>
<td>H NMR spectra of α-NPO before (B) and after (A) nitric acid exposure</td>
<td>36</td>
</tr>
<tr>
<td>3.1</td>
<td>FTIR spectra for a) MS-CMS, b) MS-MP and c) MS-MPA resins</td>
<td>51</td>
</tr>
<tr>
<td>3.2</td>
<td>Fluorescence spectra of MS-MPA resin prepared by (a) TMSBr-mediated methanolysis, (b) acid-catalyzed hydrolysis in 12M HCl and (c) confocal micrograph of the MS-MPA resin produced by TMSBr-mediated methanolysis</td>
<td>53</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3</td>
<td>Loading and elution of the MS-MPA column in the LabLogic Beta-RAM flow-cell detector at pH 4 (a), pH 5 (b) and pH 6 (c). The feed solutions contained uranium-233 concentrations of 500 Bq L(^{-1}) in DI water acidified with nitric acid</td>
</tr>
<tr>
<td>3.4</td>
<td>Chemical speciation of uranium (VI) in solution with nitric acid and atmospheric levels of carbon dioxide. Calculations were performed with Visual MINTEQ 3.0 software at 25 °C and a concentration of 1000 ppm uranium (VI)</td>
</tr>
<tr>
<td>3.5</td>
<td>Simultaneous concentration and detection of uranium-233 at a concentration of 50 Bq L(^{-1}) from groundwater acidified to pH 4 with nitric acid</td>
</tr>
<tr>
<td>4.1</td>
<td>Detection efficiency as a function of inner column diameter and bead radius. Error bars represent standard deviations from measurements made with three different columns</td>
</tr>
<tr>
<td>4.2</td>
<td>Characteristic pulse-height spectra for an 0.16 cm I.D. column loaded with 18.4 Bq uranium-233 with an alpha-peak located at channel 280 (black circles) and an 0.48 cm I.D. column loaded with 20.5 Bq uranium-233 with an alpha-peak located at channel 230 (open squares)</td>
</tr>
<tr>
<td>4.3</td>
<td>Columns exhibit increased detection efficiency after being stored for 2 weeks in sealed containers. Error bars represent standard deviations among triplicate measurements</td>
</tr>
<tr>
<td>4.4</td>
<td>Predicted concentration profiles of the uranyl ion in the polymer resin bead with a radius of 63 μm (left) and 192 μm (right) as function of time</td>
</tr>
<tr>
<td>5.1</td>
<td>FTIR spectra for MS-MPA and EGMP resins</td>
</tr>
</tbody>
</table>
List of Figures (Continued)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>Equilibrium batch ion-exchange data modeled with a Langmuir isotherm</td>
</tr>
<tr>
<td>5.3</td>
<td>Pulse-height spectra of MS-MPA and EGMP resins Loaded with uranium from various pH solutions</td>
</tr>
<tr>
<td>5.4</td>
<td>Representative volume to detection data shown (left) for MS-MPA resin at pH 6 in which $\mu=0.8$ CPS, $\sigma=0.4$ CPS and $\mu+3\sigma=2.1$ CPS (left) and summary of data (right). Negative values correspond to the background spectrum. Activity was introduced at 0 mL.</td>
</tr>
<tr>
<td>5.5</td>
<td>Speciation of uranium (1.4 ppb) in simulated ground water</td>
</tr>
<tr>
<td>6.1</td>
<td>Graphical overview of membrane preparation by (A) physical deposition and (B) UV-polymerization</td>
</tr>
<tr>
<td>6.2</td>
<td>FTIR spectrum (left) of poly(EGMP-co-HEMA with characteristic peaks of EGMP (P-OH, P=O, C-O-C=O) and HEMA (C-O-C=O, -OH). Langmuir isotherm (right) fit to batch equilibrium sorption data</td>
</tr>
<tr>
<td>6.3</td>
<td>ATR-FTIR spectra of unmodified membrane (PES), SEFMs and UVMs</td>
</tr>
<tr>
<td>6.4</td>
<td>Permeability coefficients for all membrane types with MWCOs of 30, 50 and 100 kDa.</td>
</tr>
<tr>
<td>6.5</td>
<td>Alpha spectrum of a UV-polymerized membrane (MWCO 100 kDa) exposed to 10 Bq of uranium-233</td>
</tr>
<tr>
<td>6.6</td>
<td>Pulse-height spectrum 100 kDaUVMs prepared with pH 6 simulated ground water spiked with uranium-238 and uranium-233.</td>
</tr>
<tr>
<td>7.1</td>
<td>Effect of porosity on the adsorption of various metal ions; resin, RSP (DVB 10 mol%). Open circles represent UO$_2$$^{2+}$ (pH 3.3); closed circles represent Fe$^{3+}$ (pH 2.4); Half-filled circles represent Ca$^{2+}$ (pH 5.6).</td>
</tr>
</tbody>
</table>
CHAPTER ONE
INTRODUCTION AND OVERVIEW OF DISSERTATION

1. Introduction

Manipulation of special nuclear material (SNM) for the express purpose of assembling a weapon of mass destruction is likely to contaminate the environment with trace-levels of SNM, (i.e. plutonium, uranium-233, and uranium enriched in the isotopes uranium-233 or uranium-235). The capability to analyze gross-activity or isotopic distributions in the field, directly from environmental samples would be a powerful nuclear forensics tool. A fieldable technique should be portable, robust and minimize consumables. Presently, a major limiting factor is the unavailability of separation materials to prepare samples for analysis directly from neutral pH environmental waters.

Traditional methods of concentrating and purifying alpha- and beta-emitting radionuclides from environmental waters involve time-intensive, batch style analytical techniques that require consumable chemicals. Methods of purification include co-precipitation, purification by ion-exchange resins or liquid-liquid extraction (LLE)—all of which have some drawbacks when considering a fieldable protocol. Co-precipitation is not necessarily a selective process, leading to the deposition of interfering ions that can lower spectral resolution. Actinide selectivity can be achieved with LLE; however, it requires organic solvents, ligands and acid, and it creates mixed radioactive-hazardous waste. Ion-exchange resins produce less waste than LLE; however, commercially available resins often require solutions to be acidified to pH < 2 to achieve uranium-selectivity, vide infra.
After purification, samples can be analyzed by alpha spectroscopy or thermal ionization mass spectrometry to determine the isotopic distribution of the radionuclide. Additionally, the gross-activity or concentration of purified samples can be analyzed by liquid scintillation counting (LSC), gas proportional counting, inductively coupled mass spectroscopy (ICP-MS) or spectrophotometry. Of all the aforementioned techniques, only alpha spectroscopy (isotopic analysis) is considered fieldable due to its small size and robust nature.

1.1 Real-time, gross alpha activity measurements with extractive scintillating resins

Another development in environmental sensing is a flow-cell detector that utilizes extractive scintillating (ES) resin for the online detection of alpha- and beta-emitting radionuclides\(^1\). ES resin serves the dual purpose of (1) concentrating the radionuclide of interest and (2) serving as a radiation transducer. In this detection system, the radionuclide is concentrated by a selective ligand onto the surface of the polymer resin. As the radionuclide decays, ionizing radiation deposits energy in the polymer matrix causing scintillation events that excite the polymer into a higher molecular state. This excitation energy is transferred to nearby fluorophores that subsequently de-excite resulting in the emission of photons of visible light that are counted by a photomultiplier tube. Figure 1.1 provides an overview of the online detection process. The advantages of these materials are that (1) the radionuclide is retained on the radiation transducer for increased sensitivity, and (2) when coupled with modern radiation detection and measurement instrumentation, a real-time signal can be collected for analysis.
Extractive scintillating resins are a modern extension of the scintillating ion-exchange resins that were developed in the mid-1960s by Heimbuch et al. Since, then extractive scintillating resins (sometimes referred to as scintillating microspheres) have been developed for the quantification of various radioisotopes such as strontium-89,90, technetium-99, iodine-129, uranium and actinides.

Three studies have evaluated different resin preparation methods and ligands for the simultaneous concentration and detection of uranium. Roane and DeVol concentrated uranium-233 from a mixture of actinides in 2M nitric acid using an Eichrom TRU-ES® resin impregnated with fluorophores, diphenyloxazole and 1,4-bis-(4-methyl-5-phenyl-2-oxazolyl)benzene and extractant, (octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide in tributyl phosphate, achieving a detection efficiency of 96.6%. While the detection efficiencies were initially high, the system required multiple steps and low pH to achieve simultaneous separation and detection, which can damage the organic fluorophores over time. Hughes and DeVol utilized three approaches: (1) packing a heterogeneous column of scintillating resin and extractive
chromatography resin, (2) diffusing a fluorophore into a polystyrene (PS) resin and then coating it with the Dipex® ligand, and (3) coating a scintillating poly(4-methyl styrene) (PVT) resin with an extractive ligand. All columns were evaluated for recovery and detection efficiency using pH 1 simulated groundwater with 30 ppm natural uranium. In the first approach, the column was packed with equal masses of Eichrom Actinide Resin and BC-400 scintillating microspheres. The columns recovered <5% of the uranium and had a detection efficiencies of 0%. In the second approach, the fluorophore, 2-(1-napthyl)-5-phenyloxazole (α-NPO), was diffused into a PS bead then the bead was coated with Dipex® ligand. This resin design resulted in 100% uranium recovery and a detection efficiency of 52±3%. In the third approach, α-NPO was diffused into a PVT bead then coated with Dipex ligand, which resulted in 52±26% uranium recovery and 58±20% detection efficiency. High errors associated with the third approach were attributed to the degradation of the resin during replicate measurements. Ayaz and DeVol coated a scintillating PVT resin with MnO₂ and achieved uranium recoveries of 25% and detection efficiencies of 17-37% for 102 Bq L⁻¹ natural uranium in pH neutral simulated groundwater. Low uranium recovery was attributed to the use of a non-selective MnO₂ coating. These studies demonstrate the viability of using extractive scintillating resins to simultaneously concentrate and detect waterborne uranium; however, current commercial ligands require strongly acidic feeds to achieve uranium-selectivity and current resin designs are prone to instability.

For flow-cell detectors to be a viable option for low-level radionuclide detection, it is necessary to develop robust ES resins. As discussed, ES resins were produced by
physically absorbing organic extractants and/or fluorophores into a polymer matrix.\(^8\)

While the process of degradation was never fully characterized, it has been hypothesized that the resins produced in this manner exhibit poor stability as the active components leach from the resin over time\(^4,11\). Recently, to mitigate resin instability, new resins have been synthesized with covalently bound extractants and fluorophores for beta-emitting radionuclides like technetium-99\(^5,6\) and strontium-90\(^12\).

1.2 Isotopic Analysis with Alpha Spectroscopy

The isotopes of uranium have an imbalance of protons and neutrons that leads to radioactive decay. The number of protons and neutrons in the nucleus dictate the nuclear force. The difference in nuclear forces between the original nuclei and the fission products will manifest as the kinetic energy of the fission products and any emitted ionizing radiation. Therefore, each isotope of uranium that undergoes alpha decay will emit an alpha particle with a characteristic energy. Table 1.1 lists the properties for selected uranium isotopes.

Table 1.1. Half-life and alpha particle energies for selected uranium isotopes\(^13\)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half Life (years)</th>
<th>Alpha particle kinetic energy (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{238})U</td>
<td>(4.469 \times 10^9)</td>
<td>4.197</td>
</tr>
<tr>
<td>(^{235})U</td>
<td>(7.04 \times 10^8)</td>
<td>4.398</td>
</tr>
<tr>
<td>(^{234})U</td>
<td>(2.46 \times 10^5)</td>
<td>4.776</td>
</tr>
<tr>
<td>(^{233})U</td>
<td>(1.592 \times 10^5)</td>
<td>4.824</td>
</tr>
<tr>
<td>(^{232})U</td>
<td>69.8</td>
<td>5.3203</td>
</tr>
</tbody>
</table>

Alpha spectroscopy is an analytical technique that allows for the identification of different alpha-emitting radioisotopes. In alpha spectroscopy, an alpha-emitting nucleus is positioned near a silicon semiconductor detector. As alpha particles are incident on the
detector, it registers counts in discrete energy channels to form the pulse-height spectrum, shown Figure 1.2. The ideal alpha spectrum would produce vertical lines. Realistically, the alpha particle will lose energy before hitting the detector resulting in broader peaks. Energy losses can result from alpha particle attenuation by other uranium atoms, the sample substrate or air. For alpha spectroscopy, resolution is quantified using the width of the peak at half of its maximum height (FWHM). Resolution is ultimately limited by the detector. For example, in the spectrum below, peak width is primarily attributed to electronic noise in the detector. Like most analytical techniques, the way to produce a well resolved spectrum is through diligent sample preparation.

**Figure 1.2.** Pulse-height spectrum collected with a Canberra Model 7401 alpha spectrometer (Canberra Industries, Inc., Oak Ridge, TN) and an electroplated, NIST traceable calibration standard containing uranium-238, uranium-234, plutonium-239 and americium-241 (Eckert & Ziegler, Atlanta, GA).

Traditional methods of sample preparation for isotopic analysis by alpha spectroscopy require a two-step process: (1) sample isolation and purification followed
by (2) sample mounting. After isolation and purification, samples are mounted onto a substrate for analysis. The state-of-the-art technique for sample mounting is electrodeposition. This technique can achieve a high resolution of ~20 keV in the pulse-height spectrum; however, mounting takes 1-2 hours and requires an expensive platinum anode in an electrolytic cell. Other sample mounting methods for lower resolution needs are evaporation, which yields resolutions of 40-70 keV, and a combination of precipitation and filtration, which yields resolutions of 60-100 keV.

Recent studies have focused on the use of selective polymer films as alpha spectroscopy substrates to avoid the time and expense associated with electrodeposition. These substrates combine the steps of chemical separation and sample mounting while overcoming the poor resolution associated with non-selective films used for complex sample matrices. Pantchev et al. functionalized nylon-6,6 membranes with amidoxime ligands to concentrate uranium from potable water. Spectral resolutions of 40 keV were achieved, but uranium was loaded on the membranes through batch-sorption (not by filtration), which required a lengthy 24-h equilibration time. Surbeck et al. impregnated spin-coated polyacrylonitrile films with MnO$_2$ for the concentration of radium from potable water. After a 20-h equilibration time, resolutions of 40 keV were achieved in the alpha spectrum. Gonzales et al. developed polymer films containing the commercially available Dipex® ligand for the simultaneous separation and mounting of americium and plutonium from urine samples. Despite excellent resolutions of 20-30 keV and a shorter equilibration time (1 h) than Pantchev and Surbeck, sample preparation required the acidification of urine to pH 1 and addition of sodium nitrite. Paul et al. functionalized
polyether sulfone (PES) membranes with a thin phosphonate-sulfate bifunctional layer. Uranium and plutonium were loaded from 3-4 M nitric acid solutions and achieved high resolutions of 20-35 keV from dissolved spent fuel. Membranes were loaded with activity in a batch system (not by filtration) and required an equilibration time of 1 h. While selective polymer films have proven effective in achieving high resolutions, the current designs are not ideal for rapid, field-based measurements due to the need for consumable chemicals and/or long equilibration times.

1.3 Uranium separation materials

At the heart of these analytical methods lies a separations challenge, as the incorporation of analyte-selectivity can enhance the sensitivity of radiation measurements. In gross activity determinations by flow cell measurements, reducing competition between uranium and other metals for binding sites will increase the rate of accumulation on the sensor—leading to lower volumes to detection. For isotopic analysis, excess salts on the surface of the substrate can lead to low energy tailing and poor resolution in the pulse-height spectrum. Introducing uranium-selectivity to the substrate would reduce the amount of other salts on the surface of the substrate.

Uranium solution chemistry has a strong dependence on pH, ionic strength, solution composition (i.e. the presence of other ions) and the redox potential of the system\textsuperscript{27}. Due to its complex chemistry, there is no one material that is universally selective for uranium. Designing a uranium-selective separation material requires a careful consideration of the behavior of both ligand and uranium at a given set of conditions. Common areas of interest for uranium separations are reprocessing spent
nuclear fuel and radioactive waste, analytical chemistry, purifying trace-metal contaminants from phosphoric acid during production, environmental monitoring/remediation and uranium sequestration from seawater.

1.3.1 Uranium separation materials for acidic media (pH < 1)

Solvent extraction processes utilizing organophosphorus ligands to concentrate uranium from acidic media like spent nuclear fuel and radioactive waste have been extensively reviewed elsewhere. Table 1.2 lists commonly used organophosphorus species and their structures. Organophosphorus ligands also have been applied to the field of analytical chemistry through the development of solvent-impregnated resins. One famous example is the Eichrom Actinide resin that is impregnated with the DIPEX® extractant, a gem-phosphinic acid that is used for actinide-selective separations at <1M acid concentrations. Other variations incorporate covalently bound functional groups such as the Eichrom Diphonix® ion exchange resin, which is a polyfunctional cation exchange resin with gem-phosphonic acid and sulfonic acid functional groups.

Table 1.2. Common organophosphorus species for metal ion complexation/ion exchange.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(O)(OH)3</td>
<td>phosphoric acid</td>
</tr>
<tr>
<td>RP(O)(OH)2</td>
<td>phosphonic acids</td>
</tr>
<tr>
<td>R2P(O)(OH)</td>
<td>phosphinic acids</td>
</tr>
<tr>
<td>RP(O)(OR)2</td>
<td>phosphonate</td>
</tr>
<tr>
<td>RO-P(O)(OH)2</td>
<td>alkyl phosphates</td>
</tr>
<tr>
<td>(RO)2P(O)(OH)</td>
<td>dialkyl phosphates</td>
</tr>
<tr>
<td>(RO)3P(O)</td>
<td>trialkyl phosphates</td>
</tr>
<tr>
<td>(OH)2(O)P-C-P(O)(OH)2</td>
<td>gem-phosphonic acids</td>
</tr>
<tr>
<td>(OH)(RO)(O)P-C-P(O)(OR)(OH)2</td>
<td>gem-phosphinic acids</td>
</tr>
</tbody>
</table>
In addition to laboratory analysis, organophosphorus functionalized resins have applications in industrial applications like the removal of trace-level contaminants, including uranium, during phosphonic acid production\textsuperscript{33}. Depending on the end application of the phosphoric acid, it is necessary to remove some of the metal contaminants (like uranium) that were present in the minerals. These separations require uranium selectivity over common impurities like iron, aluminum and lanthanides\textsuperscript{34}. Kabay et al.\textsuperscript{35} evaluated RSPO (styrene phosphonic acid), Diaion CRP2000 (styrene with both phosphonic and phosphinic acids), Purolite (aminophosphonic acid) and Actinide-CU (silica based \textit{gem}-phosphonic acid) resins for uranium selectivity over Fe(II) and Ca(II) at acid concentrations of 0.1M – 3M. Results showed that for all resins, the uranium capacity decreased with increasing acid concentration. Uranium capacity for all resins was negligibly effected by the presence of Fe(II) and Ca(II), demonstrating the selectivity of organophosphorus resins for uranium over competing ions in this application. Zhu and Alexandratos\textsuperscript{34} synthesized five uranium binding resins with different phosphoryl moieties: (1) triethyl phosphate, (2) diethyl phosphate, (3) methyl phosphonic acid, (4) triethylene glycol phosphate diethyl ester and (5) triethylene glycol phosphate ethyl ester. Again, it was observed that resin capacity for uranium decreased with increasing acidity. Across the tested pH range, the triethylene glycol phosphate diethyl ester resin outperformed the other resin designs. The authors attribute the superior performance to lower amount of hydrogen bonding between binding sites compared to the phosphonic acid as well as the synergistic effect of the nearby neutral donor, triethylene glycol. No selectivity studies were performed.
1.3.2 Uranium separation materials for neutral/near neutral pH waters (4 < pH < 8)

More generally, organophosphorous compounds have been explored for uranium removal from waste waters and ground waters in a pH range of 2 < pH < 5.5. Kennedy et al.\textsuperscript{36} first synthesized and evaluated phosphorylated polymers for uranium selective separations in 1958. They evaluated the selectivity of HDAP (acid diallyl phosphate) resin for uranium over a variety of di- and trivalent ions at pH 1 and pH 5.5. At pH 1, a nitric acid solution containing 2 mg mL\textsuperscript{-1} each of the following cations: U(VI), Co\textsuperscript{2+}, Cu\textsuperscript{2+} and Ca\textsuperscript{2+} was passed through the column resulting in quantitative separation of uranium from the other metals. A similar experiment was performed at pH 4 in the presence of 2\% (w/v) ethylenediaminetetraacetic acid (EDTA) in which 100 µg mL\textsuperscript{-1} U(VI) was separated quantitatively from a mixture of Fe\textsuperscript{3+}, Cu\textsuperscript{3+}, La\textsuperscript{3+}, all at a concentration of 500 µg mL\textsuperscript{-1}. The experiment was repeated at pH 5.5 in the presence of 2\% (w/v) EDTA and 250 µg mL\textsuperscript{-1} of each of the following cations: U(VI), Po\textsuperscript{4+}, Bi\textsuperscript{3+}, Sr\textsuperscript{2+}, La\textsuperscript{3+}, Ca\textsuperscript{2+}, Al\textsuperscript{3+}, Fe\textsuperscript{3+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+}. Complete separation of uranium from other ions was achieved in both cases.

Another application involving near neutral pH uranium separations is the sequestration of uranium from seawater as an alternative fuel source for nuclear power. Since the seminal paper by Egawa et al.\textsuperscript{37} in 1979, researchers have explored the use of amidoxime-based sorbents for the sequestration of uranium from seawater. Amidoximes are considered a promising chemistry due to their relatively high capacity for uranium from seawater and have been reviewed in the literature\textsuperscript{38-40}. Surprisingly, these materials are not selective for uranium. In fact, analysis of these sorbent materials after
deployment in seawater shows that uranium only accounts for 6.7 wt% of the total adsorbed species, behind magnesium (32 wt%), calcium (29.3 wt%) and vanadium (21 wt%)\textsuperscript{41}.

Even though another study by Egawa et al.\textsuperscript{42} in 1984 demonstrated the utility of phosphonic and phosphinic acids for uranium sequestration from seawater, they have been a lesser studied class of ligand than the amidoximes. Egawa tested four resin varieties: (1) styrene phosphinic acid (RS), (2) styrene phosphonic acid (RSP), (3) styrene methyl diphosphinic acid (RCSP) and (4) styrene diphosphonic acid (RCSPO). All functionalized resins were prepared from the same polystyrene-\textit{co}-divinylbenzene polymer resins. The resin capacities for uranium in seawater ranked as follows: RCSPO > RCSP > RSPO > RSP. All four resins were regenerable with Na\textsubscript{2}CO\textsubscript{3}. Resins did not lose capacity after loading and regeneration cycles. Selectivity of the resins was not addressed directly in the study; however, the ability of the RCSPO resin to recover 90% of the uranium from 500 bed volumes of real sea water revealed its promise for neutral pH uranium recovery.

In recent years, much attention has been paid to applying commercial (non-selective) resins to environmental remediation. For example, anion exchange resins like Dowex 21K(trimethylamine), Dowex 1-X8 (trimethylamine), Purolite A500 (quaternary ammonium), Purolite A600 (quaternary ammonium), Purolite A520E (triethylamine) and Lewatt K 6367 (quaternary amine) have been shown to remove uranium from solutions having a range of pH values\textsuperscript{43,44}. Cation exchange resins such as Diphonix (\textit{gem}-phosphonic acid and sulfonic acid) also have been tested in both acidic\textsuperscript{45} and near neutral
pH ground waters\textsuperscript{44, 46}. The incorporation of the sulfonic acid group in Diphonix increased the hydrophilicity of the resin and kinetics; however, it renders the resin non-selective. Chiarizia et al.\textsuperscript{46} compared the uptake behavior of Diphonix resin to the Bio-Rad AG MP-50 resin (sulfonic acid) in pH 5-8 water. Distribution coefficients were calculated for Mn\textsuperscript{2+}, Co\textsuperscript{2+}, Zn\textsuperscript{2+}, Pb\textsuperscript{2+} and U(VI) as a function of pH. Diphonix resin exhibits higher distribution coefficients for all tested cations than the Bio-Rad resin; however, the resins are not selective for uranium with affinity series as follows: pH 6 (Zn\textsuperscript{2+} > Mn\textsuperscript{2+} > U(VI) > Pb\textsuperscript{2+} > Co\textsuperscript{2+}) and pH 8 (Zn\textsuperscript{2+} > Mn\textsuperscript{2+} > Co\textsuperscript{2+} = Pb\textsuperscript{2+} > U(VI)).

The chemical modification of mesoporous silica\textsuperscript{47, 48}, mesoporous carbon materials\textsuperscript{49} and commercial Merrifield resins\textsuperscript{50-52} consisting of a lightly cross-linked (2-5\%) poly[styrene-co-(4-vinylbenzyl chloride)] with phosphinic/phosphonic acid ligands has been studied for the preconcentration of uranium(VI) from near neutral pH (4<pH<8) aqueous solutions. Dudarko et al.\textsuperscript{47} synthesized silica-tethered phosphonic acid resins through a one-pot synthesis method. The meso-structure of the silicas and the concentration of phosphonic acid groups were varied. Resins were tested for their uranium capacity in simulated seawater (9 ppb UO\textsubscript{2}\textsuperscript{2+}, 4 ppb NO\textsubscript{3}\textsuperscript{2-}, 65 ppb Na\textsuperscript{+}, 5.5 ppb Cl\textsuperscript{-}, 138 ppb CO\textsubscript{3}\textsuperscript{2-}) at pH 8.3. The authors concluded that larger meso-structures resulted in higher capacities for uranium due to higher accessibility of binding sites. It was also noted that the higher phosphonic acid concentration corresponded to a lower capacity for uranium, for the tested materials. This was rationalized by the propensity of phosphonic acids to form oligomeric structures on the surface of silica, limiting access to the internal pore structure and binding sites.
Chouyyok et al.\textsuperscript{48} functionalized nanofiber and porous column silica materials with (1) \textit{gem}-phosphonic acid, (2) methyl phosphonic acid and (3) ethyl phosphonic acid ligands. Resins were evaluated in real sea water from Squim Bay, Washington, USA that was spiked with 50 ppb of uranium to facilitate analysis. The addition of the uranium spike caused the pH to drop to about 6-7; however, the authors proceeded without adjusting the pH to maintain the nascent composition of the sea water. The results of this research provide a convenient synthetic method for preparing the sorbent materials, but analysis of the materials is lacking. There is no report of resin capacity or selectivity. Additionally, comparisons among materials are made solely on the distribution coefficient (\(K_d\)) which, for the same solution conditions and sorbent to volume ratio, is a function of surface area and ligand density. Since no attempt was made to control either of those parameters, the comparisons are not useful.

In a more comprehensive study, Vivero-Escoto et al.\textsuperscript{53} compared the uranium capacity of sorbents prepared by grafting nine different ligands to mesoporous silica. Ligand grafting density and silica substrate were held constant to provide an equal platform for comparison. Figure 1.3 summarizes the ligands studied.
Figure 1.3. Organo-functionalized mesoporous silica sorbents for uranium sequestration from water and simulated seawater. Reproduced with permission from Elsevier\textsuperscript{53}.

For all distribution coefficient studies, the sorbent mass to volume ratio, pH and initial uranium concentration were held constant. Distribution coefficients were calculated in both DI and artificial sea water (11 ppm Na\textsuperscript{+}, 2.7 ppm SO\textsubscript{4}\textsuperscript{2-}, 0.4 ppm K\textsuperscript{+}, 19.4 ppm Cl\textsuperscript{-}, 1.3 ppm Mg\textsuperscript{2+}, 0.4 ppm Ca\textsuperscript{2+}) at pH 8 with 5 ppm uranium. The results of the analysis show that the trend of uranium affinity follows: MSPh-III (phosphonic acid) > MSPh-II (trialkyl phosphate) > MSPh-I (dialkyl phosphate) = MSPh-IV (gem-phosphonatic acid). In this case, the phosphonic acid resin exhibits a higher affinity for uranium than the other organophosphorus (and amidoxime) resins. This study provides
more reliable evidence that phosphonic derivitized resins exhibit better uranium selectivity than amidoximes.

By far, the sequestration of uranium from seawater has been the most studied application of uranium sorbent materials, inspiring 91 publications in 2016. Smaller focus areas for uranium separation materials are the remediation of contaminated ground waters and separations for nuclear waste streams. These separations typically occur at 2 < pH < 6 and utilize polymer sorbents due their enhanced stability in acidic media as compared to silica. Oftentimes, the literature is limited to the synthesis of new materials with detailed discussions of potential binding mechanisms neglecting resin testing in realistic conditions; however, a few studies have applied organophosphorus functionalized resins to the cleanup of industrial effluents from abandoned mines and other waste streams. Cao et al. grafted dendritic amidoamine structures capped with an aminophenylphosphate moiety and evaluated the influence of coexistent ions like K⁺, Na⁺, Ca²⁺, Fe³⁺, Mg²⁺, CO₃²⁻, Cl⁻ and NO₃⁻ on uranium binding at pH 5. Selectivity studies were performed with single competitor ions and uranium. CO₃²⁻ was the only anion to affect uranium sorption and was explained by the high binding constants for uranyl carbonate complexes. Mg²⁺ and Ca²⁺ only affected uranium sorption when present at 100 times higher concentration than the uranium—reducing sorption by 15-20%. Fe³⁺ reduced uranium sorption by 20% when present at 50 times higher concentration than the uranium. In a different study, Cao et al. investigated the pH dependence of uranium sorption for the same functional group between pH 2 and 10. It was noted that the highest uranium capacity was achieved at pH 5 in aqueous uranium solutions with no
competitor ions. Limited discussion was provided to explain why this trend exists, other than the speculation that the presence of positively charged uranium hydrolysis products facilitates ion exchange and complexation.

Kadous et al.\textsuperscript{51} report the synthesis of polystyrene resins functionalized with an ethylenediamino tris(methyleneephosphonic) acid ligand and its application in uranium sequestration from neutral pH water. Uranium capacity was measured between pH 1.75 and 6 and the maximum capacity was measured at pH 3.4. The influence of competitor ligands, like NO$_3^-$, Cl$^-$ and CH$_3$COO$, were evaluated at pH 3.4 and found to not interfere with uranium binding up to concentrations of 0.1M (uranium concentration 0.5 mM).

Merdivan et al.\textsuperscript{50} functionalized polystyrene-divinylbenzene resins with phosphonic acid and studied the selectivity of the resins for U(VI) over common ions found in radioactive waste solutions. Resin loading with U(VI) and Th(VI) was studied in aqueous solutions at $0 < \text{pH} < 4$. Th(VI) was not retained significantly on the resin ($<$50 mg kg$^{-1}$). The resin exhibited its maximum loading for U(VI) (3000 mg kg$^{-1}$) at pH 4 from an HCl solution. Solutions of 10 mg L$^{-1}$ Th(IV), Ni(II), Cd(II), Cu(II), Zn(II) and Co (III) were pumped through the radiochromatography column at pH 2 to test the selectivity of the resin and none of the ions were retained on the column. Table 1.3 summarizes the conditions used in uranium selectivity studies with organophosphorus ligands at near neutral pH.
Table 1.3. Summary of selectivity studies performed with organophosphorus ligands.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Support</th>
<th>pH</th>
<th>Competitors</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphonic acid</td>
<td>Polystyrene-co-divinylbenzene</td>
<td>2*</td>
<td>Th(IV), Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Co^{3+}</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>Th(VI)</td>
<td></td>
</tr>
<tr>
<td>Phosphonic acid</td>
<td>Meso-porous silica</td>
<td>4*</td>
<td>Ba^{2+}, Cs^{+}, Sr^{2+}, Ag^{+}, Cd^{2+}, Co^{2+}</td>
<td>57</td>
</tr>
<tr>
<td>ethynediamino tris(methylene phosphonic) acid</td>
<td>Polystyrene-co-divinylbenzene</td>
<td>3.4</td>
<td>NO_{3}^{-}, Cl^{-}, CH_{3}COO^{-}</td>
<td>51</td>
</tr>
<tr>
<td>aminophenyl phosphate</td>
<td>Polystyrene-co-divinylbenzene</td>
<td>5</td>
<td>K^{+}, Na^{+}, Ca^{2+}, Fe^{4+}, Mg^{2+}, CO_{3}^{2-}, Cl^{-}, NO_{3}^{-}</td>
<td>52</td>
</tr>
<tr>
<td>Phosphonic acid</td>
<td>Meso-porous silica</td>
<td>8</td>
<td>Na^{+}, SO_{4}^{2-}, K^{+}, Cl^{-}, Mg^{2+}, Ca^{2+}</td>
<td>53</td>
</tr>
<tr>
<td>Trialkyl phosphonate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphinic acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gem-phosphonic acid</td>
<td>Silicas</td>
<td>8.3</td>
<td>NO_{3}^{2-}, Na, Cl^{-}</td>
<td>47</td>
</tr>
<tr>
<td>Acid diallyl phosphate (EDTA in solution)</td>
<td>Polystyrene-co-divinylbenzene</td>
<td>1</td>
<td>Co^{2+}, Cu^{2+}, Ca^{2+}</td>
<td>36</td>
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<tr>
<td>Acid diallyl phosphate (EDTA in solution)</td>
<td>Polystyrene-co-divinylbenzene</td>
<td>4</td>
<td>Fe^{3+}, Cu^{3+}, La^{3+}</td>
<td>36</td>
</tr>
<tr>
<td>Acid diallyl phosphate (EDTA in solution)</td>
<td>Polystyrene-co-divinylbenzene</td>
<td>5.5</td>
<td>Po^{4+}, Bi^{3+}, Sr^{2+}, La^{3+}, Ca^{2+}, Al^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{3+} and Zn^{2+}</td>
<td>36</td>
</tr>
</tbody>
</table>

*Fe^{3+} was found to interfere with uranium binding at high Fe^{3+} concentrations (e.g. 50 times higher than U(VI))

1.5 Summary

This chapter introduced the application of uranium-selective materials to fieldable radiation sensing techniques. Fieldable techniques must be robust, portable and minimize consumables. Analytical tools that are well suited for field analyses are alpha spectrometers and flow-cell detectors that utilize extractive scintillating resins. Extractive scintillating resins can provide a gross-alpha activity measurement, while alpha spectroscopy elucidates the isotopic distribution of a waterborne uranium sample.
The sensitivity of both techniques can be enhanced by the incorporation of uranium-selective ligands to the separation scheme. Furthermore, if ligands are selective at near-neutral pH, both techniques can be truly fieldable while minimizing consumable chemicals.

This chapter also introduced a library of ligands available for near-neutral pH environmental uranium separations. Historically, organophosphorus ligands have been used for uranium separations in acidic media (pH < 1) in applications like nuclear fuel reprocessing and nuclear waste disposal. More recently, in seawater (pH ~8), non-selective amidoxime-based materials have been studied widely for uranium sequestration despite the demonstrated higher selectivity of phosphonic acid derivitized materials at the same conditions. Limited experimental evidence is available for the separation of uranium using phosphonic acid and alkyl phosphate derivitized materials at near-neutral pH and even less is available in real or simulated environmental waters. Two studies\textsuperscript{50,57} evaluated the selectivity of phosphonic acid derivitized resins; however, the resins were evaluated for low pH (2 and 4) with competitor ions (Ba\textsuperscript{2+}, Cs\textsuperscript{+}, Sr\textsuperscript{2+}, Ag\textsuperscript{+}, Cd\textsuperscript{2+}, Co\textsuperscript{2+}, Co\textsuperscript{3+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+} and Zn\textsuperscript{2+}) that are not representative of ground water.

The aim of this dissertation was to fill an existing knowledge gap by studying the selectivity of organophosphorus derivitized uranium-binding separation materials in near neutral pH ground water (4 < pH <8). Materials performance was evaluated through the lens of environmental radiation detection methods.
1.6 Dissertation Outline

The goal of this research was to develop uranium-selective sorbent materials (resins and membranes) for use in fieldable radiation detection devices. For flow-cell detectors that utilize extractive scintillating resins, uranium-selectivity was introduced to the resins through one of two processes: (1) solid phase synthesis techniques or (2) suspension polymerization. The first objective of this work was to synthesize extractive scintillating resins that selectively concentrate uranium from neutral pH ground water. The second objective was to synthesize robust resins that contain all active components covalently bound within the polymer matrix. The third objective was to understand how resin design affects uranium uptake and detection efficiency.

Chapter 2 describes the stability of scintillating resins synthesized with physically incorporated or covalently bound fluorophores. The stability of the resins produced by both methods is characterized by the resistance of the fluorophore to leach from the resin in organic solvents. Additionally, the role of nitric acid in scintillating resin destabilization is explored. Design considerations are presented for the synthesis of stable scintillating resins.

Chapter 3 describes the synthesis of phosphonic acid derivitized extractive scintillating resins that contain covalently bound fluorophores and extractive ligands. Optical properties and resin chemistry are reported throughout the resin synthesis process to determine the optimum synthetic route. Resin performance was evaluated using offline and online detection techniques in near neutral water. Resin selectivity was
probed by analyzing uranium contaminated simulated ground water in the flow-cell detector.

Chapter 4 describes the study of detection geometry for the implementation of extracting scintillating resin in flow-cell detectors. The effect of resin diameter and column width on detection efficiency and luminosity are discussed. Diffusion experiments were performed to understand the timescales of diffusion and characterize the effect of uranium diffusion on detection efficiency.

Chapter 5 describes the one-pot synthesis of extractive scintillating resins with alkyl phosphate functionality. Resin performance was evaluated in terms of detection efficiency and volume to detection in near neutral pH simulated ground water. Proposed mechanisms of binding are discussed considering ligand properties and uranium speciation.

Chapter 6 describes the development of a novel membrane-based, rapid sample preparation technique for alpha spectroscopy. Uranium-selectivity is introduced to alpha spectroscopy substrates through (1) physical coating of the membrane with a uranium-selective polymer layer and (2) grafting the uranium-selective polymer layer from the surface of the membrane. The effect of molecular weight cutoff of the membrane on membrane performance is characterized by permeability, capacity for uranium and resolution in the pulse-height spectrum.

Chapter 7 summarizes the conclusions of the dissertation and presents future work.
Publications that have resulted from this research (at the time of dissertation submission) are as follows:

1) Blyzniuk, VN; Duval, CE; Apul, OG; Seliman, AF; Husson, SM; DeVol, TA. “High porosity scintillating polymer resins for ionizing radiation sensor applications” *Polymer* 2015 (56), 271-279.

2) Duval, CE; DeVol, TA; Husson, SM. "Extractive scintillating polymer sensors for trace-level detection of uranium in contaminated ground water" *Analytica Chimica Acta* 2016 (947), 1-8. **Featured Article on Cover.**

3) Duval, CE; DeVol, TA; Wade, EC; Seliman, AF; Bliznyuk, VN; Husson, SM. "Stability of polymeric scintillating resins developed for ultra-trace level detection of alpha- and beta-emitting radionuclides" *Journal of Radioanalytical and Nuclear Chemistry* 2016 310 (2), 583-588.

4) Duval, CE; DeVol, TA; Husson, SM. “Evaluation of resin radius and column diameter for the implementation of extractive scintillating resin in flow-cell detectors” *Journal of Radioanalytical and Nuclear Chemistry* 2016 (307), 2253-2258.

5) Duval, CE; Ruff, Cody; DeVol, TA; Husson, SM. "Rapid isotopic analysis using ultrafiltration membranes and alpha spectroscopy” *in preparation for Environmental Science & Technology.*

6) Duval, CE; DeVol, TA; Husson, SM. “Phosphonic acid and alkyl phosphate-derivitized resins for the simultaneous concentration and detection of waterborne uranium” *in preparation for Chemistry of Materials C.*
2.1 Introduction

This chapter characterizes the stability of scintillating resins for ionizing radiation detection. Scintillating resins and extractive scintillating resins have shown promise as a tool for the real-time detection of alpha- and beta-emitting radionuclides; however, a limitation of these materials has been that excellent initial sensor performance is followed by declining performance during sequential loading and elution.

The challenge is to develop a material that is both physically and chemically stable enough to elicit reliable and sustained performance under extended field conditions. For the resins to be reusable, they must be durable and able to withstand a harsh acidic environment, needed for loading and eluting the column, while retaining scintillation properties and luminosity. Additionally, in many cases the process of attaching the selective extractant to the surface of the scintillating resin requires contact with organic solvents; hence, the fluorophore must not leach from the scintillating resin during the functionalization reactions.

Next-generation solid-phase extractive scintillating media are being produced to increase physical and chemical stability so that resins can be reused over many cycles. One approach to produce stable resins is called the core-shell arrangement in which a stable scintillating core is coated with a covalently bound outer ‘shell’ of selective
ligands to create high-selectivity sensor materials with permanent surface chemistries and rapid response rates. The fluorophores of these resins are entrapped physically within the polymer matrix and further sealed with the addition of the extractive shell \(^5\). Another approach is to synthesize a stable scintillating core through the copolymerization of a vinyl fluorophore with, for example, styrene, 4-chloromethyl styrene, and divinylbenzene\(^6\).

The goal of this work was to understand how scintillator properties such as fluorophore incorporation method (physical entrapment versus covalently bound) and polymer type influence the stability of porous scintillating resins. Batch leaching experiments were performed with polystyrene (PS) based resins containing either physically entrapped 2-(1-naphthyl)-5-phenyloxazole (\(\alpha\)-NPO), or covalently bound 2-(1-naphthyl)-4-vinyl-5-phenyloxazole (v-NPO), to test the effect of solvent exposure on resin luminosity. PS and PVT resins were characterized by Fourier-transform infrared spectroscopy (FTIR) before and after exposure to nitric acid to determine the effects of the acid on the polymer structure. Finally, the optical properties of \(\alpha\)-NPO were characterized by spectrofluorometry, before and after nitric acid exposure, to test the stability of the fluorophore in oxidizing, acidic conditions. The results of this research will contribute to the rational design of stable extractive scintillating resins for applications in environmental water monitoring.
2.2 Experimental

2.2.1 Reagents

2-(1-Naphthyl)-4-vinyl-5-phenyloxazole (v-NPO) was synthesized according to a previously reported procedure \(^6\). Additional reagents and sources were 2-(1-naphthyl)-5-phenyloxazole (α-NPO, Alfa Aesar, laser grade +99%), 4-methyl styrene (96%, Sigma-Aldrich), chloroform-d (99.8 atom % D, Sigma Aldrich), divinylbenzene (technical grade 80% mixture of isomers, Sigma-Aldrich), ethyl acetate (Sigma-Aldrich), methyl acetate (Acros Organics), nitric acid (Merck), styrene (99+%, Sigma-Aldrich), toluene (HPLC grade, Fisher Scientific).

2.2.2 Resin Synthesis

PVT and PS scintillating resins with 25 wt% crosslinking were synthesized by suspension polymerization according to a previously reported procedure using toluene as the porogen \(^58\). Fluorophores were included in the organic phase during suspension polymerization. The non-polymerizable fluor, α-NPO, was incorporated physically in the poly[styrene-co-divinylbenzene] or poly[4-methyl styrene-co-divinylbenzene] resin. The polymerizable v-NPO was bound covalently within the polymer matrix during suspension polymerization resulting in the terpolymer, poly[4-methyl styrene-co-divinylbenzene-co-(2-(1-naphthyl)-4-vinyl-5-phenyloxazole)]. After synthesis, the dry resin was sieved into multiple size fractions. The resin size fraction with particle diameters of 106-212 microns was used for all experiments.
2.2.3 Resin Characterization

2.2.3.1 Fluorophore Leaching

Experiments were designed to test the stability of the fluorophore within the resin with respect to leaching. To accelerate the leaching process, PS resins with either v-NPO or α-NPO were contacted with methyl acetate for 24 h in an end-over-end mixer. In the true application, the resins may not be exposed to methyl acetate; however, using a good solvent for both the polymer and the fluorophore can provide insight to the long-term stability of the fluorophore in the resin matrix. Luminosity of the resin was measured before and after solvent exposure using an electroplated, alpha-emitting, americium-241 point source with an activity of 37 kBq. The source was positioned at a fixed height of 1 cm above the bottom of a polyethylene scintillation vial. Twenty five milligrams of resin was placed inside the scintillation vial for each measurement and the photopeak was recorded with a Hidex Triathler. Non-linear peak fitting was performed using a Gaussian model to determine the photopeak channel. The Gaussian curves were integrated in the region of interest to calculate the detection efficiency. The region of interest for the peak fitting was determined to be channels 200 and higher to avoid the background region that exists below channel 200. The relative luminosity was calculated by dividing the post-treatment luminosity by the pre-treatment luminosity. The relative detection efficiency was calculated in the same manner. Measurements were performed in triplicate to estimate the error associated with the detection geometry. Slight variations in the distance between the source and the resin or variations in the distribution of resin across
the bottom of the vial could result in differences in peak channel as well as variations in
the calculated detection efficiency.

2.2.3.2 Polymer Degradation

Column experiments were conducted to mimic the application of the resin in a
flow-cell scintillation detector. Whereas the primary focus of this dissertation work is
near neutral pH separations, nitric acid is often used to extract strontium from solution as
a strontium-nitrate complex. Moreover, nitric acid was used by Roane et al.\textsuperscript{10} with
Actinide resin to simultaneously concentrate and detect uranium. These column
experiments were designed to broadly provide insight into potential degradation
pathways for extractive scintillating resins. The effect of acid concentration was not
studied in this experiment, because the objective was to determine whether or not
nitration would occur. Varying acid concentration would provide insight to the kinetics
of the nitration reactions, which is outside the scope of this work. A total of 300 mL of
4M nitric acid was pumped through a resin-packed column at a flow rate of 1.5 mL min\textsuperscript{-1}.
The polytetrafluoroethylene column (0.48 cm inner diameter) was packed with 400 mg of
PS or PVT resin containing v-NPO. Twenty-five milligrams of resin were removed from
the column after 100 mL, 200 mL and 300 mL of acid was eluted from the column. The
resins were washed with ethanol and dried on a Buchner funnel prior to luminosity
measurements. Resin luminosity was characterized in the same manner as the
fluorophore leaching experiments. Measurements were performed in triplicate to
estimate the error associated with the detection geometry.
To decouple the effect of nitric acid on the fluorophore from the effect of nitric acid on the polymer alone, the polymer stability to nitric acid was studied by contacting 25 mg of either PS or PVT resins that did not contain fluorophore with 15 mL of 4M nitric acid for a period of 5 d. The acid concentration and exposure time were chosen to observe whether or not the polymer would be nitrated. Kinetic studies investigating length of exposure or acid concentration were considered outside the scope of this study. The resin was characterized by FTIR before and after acid exposure to monitor changes in the polymer structure. Resin samples were analyzed in KBr pellets using a nitrogen purged Nicolet Nexus 870 FTIR Spectrometer (ThermoScientific, USA) in transmission mode for 64 scans. Resulting spectra were analyzed with Omnic software.

2.2.3.3 Fluorophore Degradation

To study the effect of nitric acid on the optical and structural properties of the fluor, 50 mg of α-NPO was exposed to 15 mL of 4M nitric acid for 24 h in a round-bottom flask and stirred with a magnetic stir bar. The α-NPO was dried by rotary evaporation at 60 °C and then dried to constant weight under vacuum at a pressure of 17 kPa at 25 °C. The dried fluorophore was dissolved in ethyl acetate to create a solution with concentration of 0.03 mM that was used for absorbance and emission measurements. Absorption spectra were measured using a Varian Cary 50 Bio UV-visible spectrophotometer in a quartz cell. Emission spectra of α-NPO in ethyl acetate were measured using a HORIBA fluoroMax-4 spectrofluorometer (Edison, NJ, USA) in a glass fluorometer cell (Starna Cells, Inc., CA) using 1 nm slits, a scanning interval of 5 nm and excitation wavelength of 335 nm. Structural changes to the fluorophore were
characterized by nuclear magnetic resonance spectroscopy (NMR) using a 300 Hz Jeol ECX-300 NMR in proton mode for 32 scans. NMR samples were prepared by dissolving 10 mg of fluorophore in 2 mL of chloroform-d. The fluorophores α-NPO and v-NPO have similar chemical structures and possible sites for nitration (Scheme 1), differing only at position 4 on the 1,3 oxazole; therefore, α-NPO was used as the representative compound for the nitration study.

Scheme 2.1. Possible sites for nitration in α-NPO on (1) ortho, para-nitration of monosubstituted benzene, (2) nitration of 1,3 oxazole at position 4, and (3) α-nitration of 1-methylnaphthalene.

2.3 Results and Discussion

2.3.1 Fluorophore leaching

Table 2.1 compares the relative luminosity and detection efficiency of PS resin containing physically incorporated α-NPO and PS resin containing covalently bound v-NPO before and after contact with methyl acetate for 24 h in a batch experiment. After
methyl acetate exposure, the photopeak of PS resin with α-NPO exhibited a 60% reduction in relative luminosity and 80% reduction in relative detection efficiency, which can be attributed to the fluorophore leaching from the polymer. The photopeak for the covalently incorporated v-NPO increases in channel number from 401 to 474, corresponding to a 15% increase in relative luminosity after methyl acetate exposure. Polymerization inhibitors present in the divinylbenzene and styrene monomers can absorb light emitted by the fluorophore before it reaches the detector thereby quenching the photo-signal. A potential cause for the increased luminosity is the removal of these quenching compounds by leaching with methyl acetate.

**Table 2.1.** Relative luminosity and detection efficiency for PS resins containing α-NPO or v-NPO after leaching with methyl acetate (MA) for 24 h.

<table>
<thead>
<tr>
<th>Fluor</th>
<th>Relative luminosity</th>
<th>Relative detection efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-NPO</td>
<td>0.40±0.03</td>
<td>0.20±0.05</td>
</tr>
<tr>
<td>v-NPO</td>
<td>1.15±0.03</td>
<td>1.06±0.08</td>
</tr>
</tbody>
</table>

**2.3.2 Polymer degradation**

The stability of the polymer to nitric acid was tested by performing column experiments in which 300 mL of 4M nitric acid were pumped through a column packed with PS or PVT resin containing v-NPO. Figure 2.1A shows the relative change in luminosity for PS and PVT resins, which both exhibit a decrease in luminosity as a function of the volume of eluted acid. After 300 mL of eluted acid, the photopeak of the PS resin was below the defined region of interest and therefore was considered to have a 100% loss of relative luminosity. Noticeable yellowing of the PS resin was observed after pumping 300 mL of nitric acid through the column. The PVT resin experienced a
25% reduction in relative luminosity after 300 mL of nitric acid exposure. Figure 2.1B shows the change in relative detection efficiency for both PS and PVT resins. Larger relative errors in the detection efficiency can be attributed to systematic error in the detection geometry. The height of the photopeak influences the integrated area (detection efficiency) under the Gaussian curve. Potential sources of peak height variation can be attributed to a non-homogeneous distribution of resin on the bottom of the scintillation vial, inconsistencies in the distance between the americium-241 point source and the resin or differences in the mass of resin measured for each datum point. The PS resin shows a 100% reduction in detection efficiency after eluting 300 mL of acid from the column while the PVT resin shows an 80% reduction in detection efficiency.

Figure 2.1. Relative luminosity (A) and relative detection efficiency data (B) for PS and PVT resins containing v-NPO exposed to 4M nitric acid.

It is clear from the luminosity data that nitric acid reduced the detection efficiency of the scintillating resin; however, the luminosity measurements cannot identify the source of the quench, i.e. chemical quench, color quench, or polymer degradation. To
decouple the effect of nitric acid on v-NPO from the effect of nitric acid on the polymer, PS and PVT resins were synthesized without the incorporation of a fluorophore and were exposed to 4M nitric acid for 5 d. The resin was analyzed by FTIR before and after contact with the acid. After 5 d, the PS resin showed considerable yellowing. Figure 2.2B shows the FTIR spectrum for the PS resin with a characteristic absorbance band for the monosubstituted benzene of styrene at 1601 cm$^{-1}$. Figure 2.2A shows the FTIR spectrum with strong absorbance bands at 1697, 1631 and 1562 cm$^{-1}$ that are characteristic of NO$_2$ substituents, supporting nitration of the aromatic ring as shown in Scheme 2.2. The discoloration of the PS can lead to the absorption of light emitted by the fluorophore, called color quenching, which decreases the luminosity of the resin. Another mechanism of quenching caused by the nitrated aromatic ring of styrene is charge transfer between the excited fluorophore and the 4-nitrostyrene, which then undergoes nonradiative de-excitation$^{62}$. 
**Figure 2.2.** FTIR spectra of PS before (B) and after (A) nitric acid exposure.

**Scheme 2.2.** Nitration of styrene monomer units.

Since styrene is a monosubstituted benzene ring with a vinyl group that is ortho-para directing in nitration reactions[^59], it was hypothesized that by blocking the para position with a methyl substituent, like in PVT, it would be possible to slow the rate of nitration of the polymer. After exposing PVT to nitric acid for 5 d, the resin was significantly less discolored than the PS resin under the same conditions. The FTIR spectrum of the PVT resin in **Figure 2.3** does not show characteristic NO$_2$ peaks. The
absence of nitro-groups and translucent color of the PVT resin further support that the yelloing of the PS resin can be attributed to the nitration of the styrene monomer units.

Figure 2.3. FTIR spectra of PVT before (B) and after (A) nitric acid exposure.

2.3.3. Fluorophore degradation

To characterize the stability of the \( \alpha \)-NPO in nitric acid, the absorption and emission spectra of the fluorophore were analyzed before and after nitric acid exposure. Figure 2.4 shows that the maximum absorption for \( \alpha \)-NPO in ethyl acetate before and after nitric acid exposure occurs at 335 nm. Upon nitric acid exposure, the absorbance peak for \( \alpha \)-NPO decreases in intensity and broadens such that it overlaps with the \( \alpha \)-NPO emission band.
Figure 2.4. Absorption and emission spectra of α-NPO in ethyl acetate before and after nitric acid treatment.

The optical properties of the fluorophore were essentially destroyed by the nitric acid as seen by the negligible emission spectrum after acid exposure. The overlapping absorption and emission spectra will cause self-quenching, in which the fluorophore reabsorbs the emitted light before it can reach the detector. Another possible cause for the quench could be the color change. Similar to the PS resin, the fluorophore visibly yellowed after nitric acid exposure, suggesting that the nitric acid was chemically modifying the fluor. To test this hypothesis, α-NPO was exposed to nitric acid and analyzed by H NMR. Figure 2.5 shows the H NMR spectra for α-NPO before and after nitric acid exposure. The persistence of the oxazole singlet at 7.26 ppm in both spectra indicates that the oxazole ring was not nitrated. While the proton NMR spectra cannot provide quantitative information regarding the degree of nitration of the fluor, the downfield shift of the proton peaks support the modification of the aromatic rings with an electron withdrawing group, like NO₂. The nitration of monosubstituted phenyl and
naphthyl rings at room temperature with nitric acid has been observed in the literature 59,61,60.

Figure 2.5. H NMR spectra of α-NPO before (B) and after (A) nitric acid exposure.

2.4 Conclusions and Future Work

The stability of scintillating resins was characterized with respect to fluorophore leaching, polymer degradation and fluorophore degradation. Fluorophore leaching can be mitigated by the incorporation of a covalently bound fluorophore (like ν-NPO) in the polymer matrix. The chemical stability of the resin can be improved by utilizing PVT instead of PS due to its resistance to aromatic ring nitration, which disrupts the scintillation energy transfer pathway. Nitric acid also can nitrate the aromatic rings of the fluor, destroying its fluorescence by self-absorption and resulting in a loss of detection efficiency. Since nitration of the resin can be mitigated by using PVT, the primary mechanism for detection efficiency reduction is through fluorophore degradation in nitric acid. Future efforts to synthesize stable, extractive scintillating resins should focus on the
use of a PVT matrix with covalently bound v-NPO as the fluor. Further, alternative acids to nitric acid, such as hydrochloric acid, should be pursued to mitigate the degradation of the fluor. The experiments presented in this work will be combined with parallel studies of resin morphology (surface area and pore distribution) to steer further research into development of the porous scintillating resins for ultra-trace level radionuclide sensing in environmental media.

2.5 Acknowledgements

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CHAPTER THREE

EXTRACTIVE SCINTILLATING POLYMER SENSORS FOR TRACE-LEVEL DETECTION OF URANIUM IN CONTAMINATED GROUND WATER

[As published in Analytica Chimica Acta (947), 1-8 with minor revisions]

3.1 Introduction

The rapid quantification of waterborne radionuclides is of paramount importance for nuclear forensics analyses. To overcome time-intensive, batch style analytical techniques, advances have been made in automated sample preparation and analysis by coupling traditional techniques like precipitation, coprecipitation, liquid-liquid extraction or solid phase extraction with flow analysis techniques to deliver preconcentrated samples to analytical instruments such as alpha spectrometers (AS), liquid scintillation counters (LSC), gas proportional counters, inductively coupled mass spectrometers (ICP-MS) or spectrophotometric instruments.

Horwitz et al.\(^{45}\) physically impregnated an Amberlite XAD-7 polymer support with diamyl amyl phosphonate, now sold commercially as U/TEVA resin from Eichrom Technologies, Inc., to preconcentrate uranium from acid solutions. The developed separation scheme was used to isolate uranium from environmental matrices such as groundwater prior to isotope analysis with thermal ionization mass spectrometry. Turner et al.\(^{64}\) embedded Diphonix™ resin, a commercial actinide-selective resin from Eichrom Technologies, Inc., in diffusive gels to preconcentrate waterborne uranium. The gels were deployed in fresh and saltwater systems in the United Kingdom, collected and transferred to a laboratory where the uranium was eluted with 1M sodium hydroxide and
1M hydrogen peroxide. Concentrated samples were analyzed by ICP-MS. Croudace et al.\textsuperscript{65} employed Actinide\textsuperscript{TM} resin to preconcentrate uranium from seawater that was acidified with nitric acid to pH 0.1 prior to purification. Due to the high affinity of the column for uranium, the uranium could not be eluted and was recovered by digesting the resin. The concentrated uranium solution was prepared for AS by electroplating. The sample preparation steps alone required two full workdays. Oguma et al.\textsuperscript{66} performed an automated analysis of uranium concentration in seawater with polystyrene resin impregnated with dodecylamidoxime ligand. In an automated system, the seawater pH was adjusted to 5.5 prior to preconcentration, and the quantification of uranium was performed with chlorophosphonazo(III) assisted spectrophotometry.

Despite successes in concentrating uranium from complex matrices like seawater, each effort has shortcomings when considering real-time water quality monitoring. The work of Croudace et al.\textsuperscript{65} required lengthy preparation times and strong acids to lower the pH of the seawater sample prior to separation. Turner et al.\textsuperscript{64} required separate steps for concentration, elution and detection, increasing analysis time. Oguma et al.\textsuperscript{66}, while able to automate preconcentration and analysis, produced resins by physical impregnation of a support with the selective ligand, which is known to lead to unstable resins\textsuperscript{11}. Efforts have been made to reduce the analysis timeline by combining concentration and detection. De Sanoit et al.\textsuperscript{67} developed a novel system in which a thin trimethyl boron doped diamond film is fitted to a sample cell. The redox potential of the solution is adjusted to precipitate insoluble hydroxides onto the window. An AS, situated on the opposite side of the window, directly counts the activity of the precipitate. This
technique combines concentration and detection in one sample cell; however, the system will not be able to process large sample volumes due to its batch-style design and has not yet been tested for the effect of interfering ions on detection efficiency and alpha spectrum resolution.

Flow-cell detectors that utilize extractive scintillating resins are an attractive alternative to sample automation because they combine the processes of concentration and detection, reducing sample analysis time. For portable flow-cell detectors to be a viable for low-level radionuclide detection, it is necessary to develop robust ES resins. Historically, ES resins were produced by physically absorbing organic extractants and fluorophores into a polymer matrix. Unfortunately, resins produced in this way exhibit poor stability as the active components leach from the resin over time. Recently, resins have been synthesized with covalently bound extractants and fluorophores for beta-emitting radionuclides like technetium-99.

Synthesis of robust ES resins can be achieved by including fluorophores and solid-phase reactants like 4-vinylbenzyl chloride within the polymer matrix. The synthesis of ES resins with covalently bound active components presents unique design requirements. Resins must maintain their optical properties throughout the course of the functionalization reactions to transduce a detectable light signal. The chemical modifications of mesoporous silica and commercial Merrifield resins consisting of a lightly cross-linked (2-5%) poly[styrene-co-(4-vinylbenzyl chloride)] with phosphonate/phosphonic acid ligands have been studied for the preconcentration of uranium(VI) from near neutral pH (2<pH<8) aqueous solutions. Often, these resins are
synthesized by the addition of a phosphonate moiety followed by a hydrolysis reaction to convert the phosphonate groups to phosphonic acid groups. Typical hydrolysis methods involve long reaction times (~24 h) in either a strong acid or base. These harsh conditions can be damaging to the organic fluorophores if applied to a scintillating resin.

Despite the development of some uranium-binding resins for near neutral pH aqueous solutions, there have been few efforts to develop ES resins for the simultaneous concentration and detection of uranium from near-neutral pH environmental waters. Roane and DeVol concentrated uranium-233 from a mixture of actinides in 2M nitric acid using a TRU-ES resin impregnated with fluorophores, diphenyloxazole and 1,4-bis-(4-methyl-5-phenyl-2-oxazolyl)benzene and extractant, octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide in tributyl phosphate, achieving a detection efficiency of 96.6%. While the detection efficiencies were initially high, the system required multiple steps and low pH to achieve the simultaneous separation and detection, which can damage the organic fluorophores. Hughes and DeVol utilized ES resins as either a heterogeneously packed column with both scintillating resins and extractive resins or by coating Dipex® extractant on a polyvinyl toluene resin impregnated with the fluorophore, 2-(1-naphthyl)-5-phenyloxazole. Detection efficiencies of 51% for natural uranium were achieved with the extractant-coated beads in groundwater samples that were acidified to a pH of 1. These studies show the utility of online-detection of uranium from either mixed actinide or groundwater samples; however, both systems require strongly acidic feeds to achieve the desired separation.
The primary objective of this study was to synthesize ES resin that is both robust and capable of simultaneous concentration and detection of uranium from near-neutral pH groundwater samples. Resins that incorporate covalently bound active components were synthesized and evaluated the flow-cell detection efficiency for uranium while monitoring the activity of synthetic groundwater, in real-time, at varying pH. Resin synthesis occurred in a two-step process: (1) synthesis of a cross-linked polymer containing the covalently bound fluorophore and 4-vinylbenzyl chloride, followed by (2) solid-phase functionalization reactions to add the covalently bound extractive ligand. Consequently, a secondary objective of this work was to determine a synthetic route to add the phosphonic acid moiety that preserved the optical properties of the ES resin.

3.2 Materials and Methods

3.2.1 Reagents

2-(1-Naphthyl)-4-vinyl-5-phenyloxazole (v-NPO) was synthesized according to the literature. Reagents were used as received unless noted otherwise: aluminum oxide (activated, Sigma Aldrich), arsenazo III (spectrophotometric grade, Fluka) benzoyl peroxide (reagent grade >98%, Sigma-Aldrich), trimethylsilyl bromide (TMSBr, 97%, Aldrich), dichloromethane (Acros Organics), divinylbenzene (80% technical grade, Aldrich), ethanol (denatured, reagent grade, Aldrich), hydrochloric acid (HCl, aq. 37%, Sigma-Aldrich), methanol (laboratory grade, Fisher Scientific), 4-methyl styrene (96%, Aldrich), nitric acid (90%, Fisher Scientific), poly(vinyl alcohol) (PVA, 86-89% hydrolyzed, med. molecular weight, Alfa Aesar), potassium bromide (KBr, IR grade 99+, Acros Organics), pyridine (ACS reagent >99%, Sigma Aldrich), sodium chloride
(ACS reagent, Sigma Aldrich), sodium nitrate (ACS reagent, Sigma Aldrich), toluene (99.9%, Aldrich), triethyl phosphite (98% Aldrich), UltimaGold AB liquid scintillation cocktail (PerkinElmer), uranium-233 (Eckert & Ziegler), uranyl nitrate hexahydrate (depleted uranium, PerkinElmer), 4-vinylbenzyl chloride (90%, Aldrich).

3.2.2 Preparation of MS-CMS resin

Poly[(4-methyl styrene)-co-(4-vinylbenzyl chloride)-co-(divinylbenzene)-co-(2-(1-napthyl)-4-vinyl-5-phenyloxazole)] resin (MS-CMS) was synthesized by suspension polymerization. A solution of the continuous phase was prepared in a 1 L volumetric flask by dissolving 1.0 g PVA and 8.33 g NaCl in deionized water. Table 3.1 summarizes the composition of the discontinuous phase. Inhibitors were removed from monomers by passing the monomers through an activated alumina column prior to use. For suspension polymerization, 300 mL of continuous phase was added to a 500 mL glass kettle reactor fitted with a reflux condenser, Caframo model HS12 overhead mechanical stirrer with a paddle blade impeller (5 cm diameter), thermocouple and magnetic stir bar. The reactor was situated in a water bath atop a hotplate-stirrer with temperature control. The reaction vessel was purged with nitrogen for 20 min while heating the continuous phase to 60 °C under mixing with both the overhead and magnetic stirrers at 250 RPM. The discontinuous phase was added to the continuous phase (volumetric ratio of 12:1) at 60 °C and the temperature was increased to 75 °C. The suspension was maintained at 250 RPM stirring at 75°C for 12 h. After synthesis, vacuum assisted filtration was performed using Whatman 54 filter paper, a Buchner funnel and filter flask to remove the resin from the aqueous phase. Soxhlet extraction of the resin in ethanol was performed for 16 h to
remove unreacted monomers from the polymer matrix. Then the resin was stirred in 50:50 (v/v) ethanol/water for 24 h, water for 24 h and finally dried overnight in a vacuum oven at 17 kPa and 60ºC. After drying, the resin was sieved using stainless steel sieves. The fraction of particles with diameters 212-425 microns was used in the functionalization reactions.

Table 3.1. Typical formulation for the discontinuous phase in suspension polymerization

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Purpose</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-methyl styrene</td>
<td>bulk material, primary scintillator</td>
<td>8.6 mL</td>
</tr>
<tr>
<td>4-vinylbenzyl chloride</td>
<td>macroinitiator for functionalization</td>
<td>2.1 mL</td>
</tr>
<tr>
<td>divinylbenzene</td>
<td>crosslinking agent</td>
<td>1.3 mL</td>
</tr>
<tr>
<td>ν-NPO</td>
<td>fluorophore</td>
<td>360 mg</td>
</tr>
<tr>
<td>toluene</td>
<td>porogen (diluent)</td>
<td>12 mL</td>
</tr>
<tr>
<td>benzoyl peroxide</td>
<td>radical polymerization initiator</td>
<td>200 mg</td>
</tr>
</tbody>
</table>

3.2.3 Preparation of MS-MP resin

Scheme 3.1 shows the reaction steps used to incorporate uranium-binding ligands covalently in the resin. To add the diethylmethylphosphonate moiety, an Arbuzov reaction was performed with 1 g of vacuum dried MS-CMS resin refluxed in 20 mL of triethyl phosphate for 24 h. The resin product (MS-MP) was filtered and then stirred in ethanol for 24 h, filtered again, and dried at 60ºC and 17 kPa in a vacuum oven overnight.

2.4 Preparation of MS-MPA resin

Two methods were explored to hydrolyze the diethylmethylphosphonate moiety in the second step of Scheme 3.1. Acid-catalyzed hydrolysis was performed by refluxing 1 g of MS-MP resin in 20 mL of 12M HCl for 24 h. In the second hydrolysis method, 1 g of MS-MP resin was swelled in dichloromethane for 24 h then mixed with 4 equivalents of trimethylsilyl bromide for 24 h at 30 ºC in a nitrogen atmosphere. The resulting
silylated resin was filtered in open air then stirred in methanol for 24 h at room temperature. The resin product (MS-MPA) was filtered and dried in a vacuum oven at 60 ºC and 17 kPa overnight.

\[\text{Scheme 3.1. Reaction scheme for the phosphonic acid-derivitized resin.}\]

3.2.4 Characterization of resin functionality and binding capacity

The step-wise progress of the functionalization reactions was monitored with Fourier-transform infrared spectroscopy (FTIR). All samples were analyzed in KBr pellets in transmission mode for 64 scans at a resolution of 4 cm\(^{-1}\) using a nitrogen purged Nicolet Nexus 870 FTIR Spectrometer (ThermoScientific, USA) with Omnic software.

Potentiometric measurements were used to quantify the conversion of chloromethyl sites to phosphonate sites. In a test tube, 300 mg of MS-CMS resin was swelled in 5 mL of pyridine for 24 h. The test tube was heated in an oven to 100 ºC for 3 h and then cooled in an ice bath. The resin was filtered, washed with acetone, dried on the Buchner funnel and quantitatively transferred to a 125 mL beaker. To the beaker, 90 mL DI water, 6 mL 8M nitric acid and 3 mL ionic strength adjuster (5M sodium nitrate)
were added. The solution was stirred at room temperature for 30 min. A calibrated Accumet™ chloride-selective half-cell electrode (catalog no. 13-620-519, Fisher Scientific) was used in conjunction with an Ag/AgCl reference electrode (catalog no. 13-620-273, Fisher Scientific) and an Accumet™ AB250 meter (catalog no. 13-636-AB250, Fisher Scientific) to measure the activity of the chloride ions in solution. The same procedure was applied to phosphonate-functionalized MS-MP. The difference between the MS-CMS measurement and the MS-MP measurement provides the number of chloromethyl sites that reacted with the ligand. Measurements were made in duplicate.

Static equilibrium binding measurements were conducted at room temperature with solutions prepared from uranyl nitrate hexahydrate to determine the maximum binding capacity for uranium. The equilibrium capacity experiments were performed at pH 4 to provide the maximum theoretical capacity for uranium. At pH 4, the ligand is more than one full pH unit above pKa1, ensuring complete deprotonation of the first acidic hydrogen, and uranium is present at an abundance of >95% as the uranyl cation. Nitric acid solutions with an average pH of 4.00 ± 0.10 were spiked with uranyl nitrate hexahydrate to create solutions of varying concentration. Solution pH was adjusted using 1M nitric acid and 1M sodium hydroxide. The pH was measured with an Orion model 420A pH meter and Orion model 911600 combination semi-micro pH electrode. The concentration of the solution was determined after pH adjustment. Forty milligrams of MS-MPA resin was equilibrated with 2 mL of a uranium-containing solution. The initial and equilibrium concentrations of uranium in solution were analyzed by arsenazo-III assisted spectrophotometry in a VARIAN 50Bio UV-Vis spectrophotomer (Palo Alto,
CA, USA) with Cary WinUV software (version 3.0) according to Khan et al., with the modification of using an HCl/KCl buffer in the current study. Binding experiments were performed in triplicate.

3.2.5 Characterization of resin fluorescence

Fluorescence measurements were made with a HORIBA FluoroMax-4 spectrofluorometer (Edison, NJ, USA) in a solid sample holder with a quartz coverslip. Emission spectra were measured at an angle of 40 degrees, using an excitation wavelength of 390 nm, 1 nm excitation and emission slits and a scanning interval of 2 nm.

Confocal microscopy studies of the spatial distribution of the fluorophore within the resin were performed using a Leica SPE confocal laser scanning microscope (CLSM) in fluorescence mode with a Leica 10x air objective with a numerical aperture of 0.3 and averaging program of 4 scans. The excitation laser was a helium-neon laser with a wavelength of 408 nm. To overcome the limit of depth of penetration of the confocal microscope and obtain unambiguous spatial fluorescence intensity distribution measurements, the resin was sectioned into 8 μm slices prior to imaging. Confocal images were taken 4 μm below the surface of the slice to avoid artifacts associated with the sectioning protocol. To prepare samples for the CLSM, the resin was embedded in TissueTek® O.C.T. Compound 4583 and then sectioned at -20°C into 8 μm slices using a Microm HM 505N Cryostat-Microtome with a diamond coated blade (Fisher Scientific, Edge-Rite™). The resulting slice was mounted on a microscope slide (Fisher Scientific, Fisherbrand™ InkJet), a cover glass (Fisher Scientific, Fisherbrand™ no. 1.5) was
applied to prevent delamination of the resin and the four corners of the cover glass were sealed with clear nail polish.

### 3.2.6 Evaluation of sensor performance

Sensor performance was evaluated using a PTFE column (i.d. 0.16 cm) packed with 30 mg of MS-MPA resin (diameter 212-425 microns) and PTFE frits. Uranium-233, a purely alpha-emitting isotope of uranium, was used for the scintillation studies because the higher specific activity resulted in increased accuracy resulting from better counting statistics. The column was packed with dry resin then conditioned with 5 mL of methanol followed by a 50:50 (v/v) mixture of methanol and water, pure DI water, and pH 4 solution of nitric acid. Uranium-233 was loaded on the column by pumping successive 5 mL aliquots of pH 4, 3800 Bq L⁻¹ solution through the column at a flow rate of 1.5 mL min⁻¹ using a peristaltic pump. After each 5 mL aliquot was loaded, the feed, effluent and column were analyzed by scintillation counting on a PerkinElmer Quantulus 1220 Liquid Scintillation Spectrometer (Waltham, MA, USA) where the differential pulse height spectra were recorded. The feed and effluent samples were prepared for liquid scintillation counting by mixing 4 mL aliquots with 10 mL of UltimaGold AB scintillation cocktail in 20 mL polyethylene scintillation vials. Prior to counting with the LSC, the column was rinsed with 2 mL of pH 4 nitric acid solution to remove unbound uranium. The column was counted without the addition of liquid scintillation cocktail in a standard scintillation vial equipped with a customized cap to maintain the column in a vertical and centered position within the vial. All samples were counted for 60 min. The activity retained on the column was calculated from the difference in activity of the feed
and effluent for each sequential loading. The detection efficiency of the resin was determined from the slope of measured column count rate versus retained activity. Experiments were performed in duplicate.

3.2.7 Online detection of uranium

The online sensor performance was evaluated using a dual photomultiplier LabLogic Beta-RAM Model 5 HPLC detector (LabLogic Systems, Inc., Brandon, FL) with Laura SP3 data acquisition software. Columns were conditioned prior to use as described previously. Uranium feed solutions with 500 Bq L\(^{-1}\) in distilled water with varying pH were pumped through the column at a flow rate of 1.5 mL min\(^{-1}\) and pulse height spectra were collected in 1 s intervals. Solution pH was measured as described previously. Uranium was eluted from the columns using 50 mL of 1M HCl. Loading and elution cycles were performed in triplicate for each column.

Synthetic groundwater was prepared according to the recipe shown in Table 3.2 and adjusted to pH 4 to test the ability of the resin to concentrate and detect uranium from environmental waters. Solution pH was adjusted as described previously. Uranium-233 was spiked into the synthetic ground water solution to raise the activity to either 500 Bq L\(^{-1}\) (1.4 ppb) or 50 Bq L\(^{-1}\) (0.144 ppb), both of which are below the MCL for uranium (30 ppm).
Table 3.2. Synthetic ground water composition\textsuperscript{72}.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca\textsuperscript{2+}</td>
<td>10.4</td>
</tr>
<tr>
<td>Cl\textsuperscript{-}</td>
<td>217.5</td>
</tr>
<tr>
<td>NO\textsubscript{3}\textsuperscript{-}</td>
<td>7.8</td>
</tr>
<tr>
<td>K\textsuperscript{+}</td>
<td>10</td>
</tr>
<tr>
<td>HCO\textsubscript{3}\textsuperscript{-}</td>
<td>744.2</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}</td>
<td>17.5</td>
</tr>
<tr>
<td>SO\textsubscript{4}\textsuperscript{2-}</td>
<td>354.7</td>
</tr>
<tr>
<td>Na\textsuperscript{+}</td>
<td>570.2</td>
</tr>
<tr>
<td>F\textsuperscript{-}</td>
<td>20.1</td>
</tr>
<tr>
<td>Si\textsubscript{4}\textsuperscript{+}</td>
<td>10</td>
</tr>
</tbody>
</table>

The resin was evaluated for its flow-cell detection efficiency in the online detection system by plotting detected activity versus total activity fed. The slope of the line is the flow-cell detection efficiency which is a function of the distribution coefficient of the resin and the detection efficiency of the resin. For example, if the column in the online detection system retained all of the uranium fed to the system then the flow-cell detection efficiency would be equal to the detection efficiency.

3.3 Results and Discussion

3.3.1 Resin functionality and capacity for uranium

The stepwise functionalization of ES resin was tracked using FTIR. Figure 3.1 shows the FTIR spectra with the characteristic peaks supporting each step of synthesis scheme. The phosphonate resin (MS-MP) shows characteristic absorbances for P-OCH\textsubscript{2}CH\textsubscript{3} at 1042cm\textsuperscript{-1}. The phosphonic acid resin (MS-MPA) shows a decrease in the phosphonate ester peak and the ingrowth of the P-OH at 2200cm\textsuperscript{-1}. 

Potentiometric measurements measured the number of 4-chloromethyl sites that had been converted to phosphonate groups and it was found that the yield of the Arbuzov type reaction was quantitative. The phosphonate resin contained 1.5 mmol P (g resin)$^{-1}$.

The resin capacity for uranium was calculated by constructing ion-exchange isotherms (Appendix A, Figure A-1) and modeling the data using the Langmuir-Freundlich model$^{73}$ to calculate a maximum binding capacity of 0.8 mmol U (g resin)$^{-1}$.

### 3.3.2 Resin Fluorescence

Figure 3.2 shows fluorescence spectra for MS-MPA resins prepared by acid-catalyzed hydrolysis and TMSBr-mediated methanolysis. The decrease in fluorescence from the MS-CMS to MS-MP resin is due to the quenching effect of the aliphatic side chains in the phosphonate moiety$^{63}$. The MS-MPA resin produced by TMSBr-mediated methanolysis recovered its fluorescence; however, the emission peak shifted from 424 nm to 525 nm. The Stokes’ shift for a fluorophore depends on factors that include
dissipated vibrational energy, redistribution of electrons in the surrounding solvent in response to the change in dipole of the excited fluorophore, reorientation of solvent molecules around the excited fluorophore and chemical interactions between the fluorophore and the solvents. Stokes’ shifts for fluorophores containing heterocycles, like the di-substituted oxazole group of v-NPO, are especially susceptible to solvation effects. The magnitude of the spectral shift attributed to solvation effects from differences in the refractive index or dielectric constant of solvents generally are smaller than spectral shifts due to chemical interactions (e.g., hydrogen bonding or charge transfer). Fluorophores bound to macromolecules, like polymer resins, can experience analogous solvation effects from nearby groups on the macromolecule. For example, Bulovic et al. observed spectral shifts of 25 to 75 nm for the emission wavelength of heterocycle-based, organic light emitting thin films by varying the concentration of polar dopants. The MS-MPA resin in the current study contains amphoteric P-OH groups. The ability of the P-OH to act as both a hydrogen-bond acceptor and donor, coupled with the susceptibility of the v-NPO to solid-state solvation effects can explain the 100 nm shift between the MS-MP and the MS-MPA emission peaks. Depending on the luminosity this shift may affect sensor performance. Bi-alkali photocathodes that are used for scintillation counting experience ~50% reduction in quantum efficiency with an emission wavelength shift from 424 nm to 525 nm; however, if the luminosity is sufficiently high, the detection efficiency for the scintillation system will be minimally affected.
Figure 3.2. Fluorescence spectra of MS-MPA resin prepared by (a) TMSBr-mediated methanolysis, (b) acid-catalyzed hydrolysis in 12M HCl and (c) confocal micrograph of the MS-MPA resin produced by TMSBr-mediated methanolysis.

The MS-MPA resin produced by acid-catalyzed hydrolysis showed a greater decrease in fluorescence between the MS-MP and the MS-MPA resins when compared to the resin prepared by TMSBr-mediated methanolysis. The observed decrease in fluorescence of the acid-catalyzed sample can be attributed to two possible mechanisms: (1) degradation of the fluorophore or (2) degradation and discoloration of the polymer. The acid-catalyzed resin sample did not show the same peak shift observed for the TMSBr-mediated sample. The lack of peak shift indicates a lack of hydrogen bonding.
between the P-OH groups and fluorophore. Since the FTIR spectrum for the acid-catalyzed sample showed the characteristic absorbances for P-OH groups, the data imply that the fluorophore was altered or degraded during the acid-catalyzed hydrolysis reaction. This acid-catalyzed pathway is not suitable for the synthesis of this uranium-binding ES resin.

To further investigate the fluorescence properties of the MS-MPA resin produced by TMSBr-mediated methanolysis, the resin was analyzed by CLSM. Figure 3.2c shows a cross-section of the center slice of a resin bead with a uniform distribution of fluorophore, indicating that the covalently bound fluorophore is chemically robust and did not leach from the polymer matrix during functionalization reactions or exposure to organic solvents.

### 3.3.3 Sensor performance

The MS-MPA resin produced by TMSBr-mediated methanolysis was used for the scintillation studies due to its favorable optical properties. The detection efficiency of the resin was first investigated by sequential loading of uranium-233 onto a column. A detection efficiency of 40% was calculated by dividing the net count rate of the column by the loaded activity. The sensor showed a linear response to the accumulated activity (Appendix A, Figure A-2) and the pulse-height spectrum (Appendix A, Figure A-3) for each sequential loading of activity on the column shows a characteristic of a mono-energetic alpha peak, which is consistent with previous work.\(^\text{77}\).
3.3.4 Online detection of uranium

Figure 3.3 shows the performance of the MS-MPA resin in the online detection system using DI water acidified with nitric acid to pH 4, 5 and 6. The flow-cell detection efficiency was determined by dividing the detected activity by the total activity in the feed. The average flow-cell detection efficiency was observed to decrease with increasing pH, with flow-cell detection efficiencies of 23%, 16% and 7% for pH 4, 5 and 6. Speciation calculations for uranium (VI) were performed using Visual MINTEQ v3.0 software to understand the decreasing trend. The binding mechanism for hard-donor ligands like phosphonic acid is chelation with the uranyl cation, $\text{UO}_2^{2+}$. Figure 3.4 shows the fractional speciation, which indicates that the free uranyl cation needed for binding is present in water from pH 1 to 5. Furthermore, at pH 5 or higher, the ligand has to compete with hydrolysis of the uranyl cation; and, at pH 6 or higher, the ligand has to compete with further hydrolysis and eventually carbonate complexation. The pKa$_1$ of methylphosphonic acid is 2.38$^{32}$, so the optimum binding pH was hypothesized to exist above 2.38 of the acid but below pH 5. The resin showed highest flow-cell detection efficiency at pH 4, which corresponds to the conditions at which the speciation model predicted the highest relative abundance of free uranyl cation.
Figure 3.3. Loading and elution of the MS-MPA column in the LabLogic Beta-RAM flow-cell detector at pH 4 (a), pH 5 (b) and pH 6 (c). The feed solutions contained uranium-233 concentrations of 500 Bq L$^{-1}$ in DI water acidified with nitric acid.
Figure 3.4. Chemical speciation of uranium (VI) in solution with nitric acid and atmospheric levels of carbon dioxide. Calculations were performed with Visual MINTEQ 3.0 software at 25 °C and a concentration of 1000 ppm uranium (VI).

The flow-cell detection efficiency measured with the online detection system is a function of the efficiency of the energy transfer in the scintillation process and the distribution coefficient of uranyl cation from solution to the resin. Competition for the uranyl cation among inorganic anions (hydroxide, nitrate and carbonate) and the methylphosphonic acid ligand increases with increasing pH, which leads to lower loading of uranyl on the resin and consequently a lower flow-cell detection efficiency. Analogously, choosing a ligand with a higher affinity for the uranyl cation or that can better compete with the interfering inorganic anions should lead to higher partitioning of the uranyl to the ES resin and higher flow-cell detection efficiencies.

The MS-MPA resin also was tested for its ability to concentrate and detect uranium from simulated groundwater. Five hundred milliliters of synthetic groundwater was spiked to 50 Bq L⁻¹, adjusted to pH 4 with nitric acid then pumped through the MS-
Figure 3.5 shows the linear response of the detection system to the accumulated activity with flow-cell detection efficiency of 17%. The similar flow-cell detection efficiencies for uranium in both DI and synthetic groundwater demonstrate the selectivity of phosphonic acid for uranium over competitor ions like calcium, even when the calcium concentration (10.4 ppm) was 4 orders of magnitude higher than the uranium concentration (144 ppt). This contribution provides the first evidence of an entirely covalently bound polymer sensor capable of detecting uranium in environmental waters.

Figure 3.5. Simultaneous concentration and detection of uranium-233 at a concentration of 50 Bq L$^{-1}$ from groundwater acidified to pH 4 with nitric acid.

3.4 Conclusions

Extractive scintillating resin containing uranium-binding methylphosphonic acid ligands for the detection of waterborne U(VI) has been synthesized. The methylphosphonic acid derivitized resin prepared by TMSBr mediated methanolysis
showed both a high capacity for uranium of 0.8 mmol g$^{-1}$ and favorable optical properties for scintillation. Spectrofluorometry revealed a 100 nm Stokes shift after the addition of the methylphosphonic acid derivitized moiety; however, the monoenergetic peak of the pulse-height spectrum indicates that the photon flux is sufficiently high such that the scintillation detection efficiency was not affected. A detection efficiency of 40% was measured in the static detection setup for uranium in DI water. When the resin was tested at the same conditions in the online detection system, the flow-cell detection efficiency was measured as 17%. The difference in efficiencies can be attributed to the affinity of the ligand for uranium. The distribution coefficient of the ligand is low enough such that not all uranium was retained on the column; therefore, the flow-cell detection efficiency was lower than the detection efficiency. Future resin designs should include a ligand with a higher binding affinity than methylphosphonic acid, thus creating a resin with a higher distribution coefficient, which should increase the flow-cell detection efficiency. Finally, the methylphosphonic ligand shows good selectivity for uranium during the online measurements, with respect to common ions found in synthetic groundwater, by competing with Ca$^{2+}$ ions that were 4 orders of magnitude higher in concentration. This contribution provides the first evidence of an entirely covalently bound polymer sensor for real-time monitoring of uranium in environmental waters at near neutral pH.

3.5 Acknowledgements

This work was supported by the Defense Threat Reduction Agency, Basic Research Award #HDTRA1-12-1-0012, to Clemson University. I would like to
acknowledge the Clemson Light Imaging Facility for the use of the Leica SPE CLSM and thank Dr. Terri Bruce for her guidance and patience.
CHAPTER FOUR

EVALUATION OF RESIN RADIUS AND COLUMN DIAMETER FOR THE IMPLEMENTATION OF EXTRACTIVE SCINTILLATING RESIN IN FLOW-CELL DETECTORS

[As published in the Journal of Radioanalytical and Nuclear Chemistry 310 (2), 583-588 with minor revisions]

4.1 Abstract

This contribution details the application of extractive scintillating resin with covalently bound fluorophore, v-NPO, and ligand, methyl phosphonic acid, in flow-cell experiments utilizing varying column diameters, resin diameters and diffusion times. The implementation of this type of flow-cell detection system hinges upon the optimization of resin design, detection geometry and testing conditions. Several detection geometries have been studied including a single photomultiplier tube (PMT), dual PMT continuous flow-cell detector, and a traditional liquid scintillation counter, all of which utilize a resin packed column. Bead and column diameter have been shown to affect the detection efficiency for beta-emitting radionuclides\(^{78-80}\); however, no systematic studies have been conducted to determine the effect of operating parameters on detection efficiency for alpha-emitting radionuclides. The objective of this research was to study the effect of column diameter and bead size on the detection efficiency of uranium for flow-cell detectors. The detection efficiency was evaluated by standard offline liquid scintillation counting methods. Diffusion experiments were conducted to determine the effect of the location of the alpha decay on detection efficiency, and the data were compared to a diffusion model to assess the feasibility of relying on diffusion-enhanced detection efficiency in an online measurement. The results of this research will
provide a foundation for the experimental conditions needed for the detection of alpha-emitting radionuclides in flow-cell detection systems.

4.2 Theory

In fixed-bed adsorption, a feed solution containing an analyte is pumped through a resin-packed column and the analyte diffuses towards the resin surface where binding may occur. Binding to the resin bead can be promoted by the inclusion of analyte selective ligands and by adjusting operating conditions such as the pH, temperature, or ionic strength to maximize the stability constant of the ligand-analyte complex. For the case of a macroporous polymer resin, analyte may diffuse to the outer resin surface or the surface of a pore. If the pores of the resin are not readily accessible, the outer resin surface will become saturated by the radionuclide. Once bound to the surface of the resin, the radionuclide will begin to diffuse through the free volume of the polymer matrix by Fickian diffusion. For resins with inaccessible internal pore structures, the rate of diffusion of the actinyl ion within the free volume of the polymer will dictate whether the alpha particle emitted from the actinide will deposit its energy on the surface of the resin (slow diffusion rate) or inside the polymer matrix (fast diffusion rate) during the time scale of the measurement. For simplicity, we consider the scenario whereby a fixed concentration of uranyl ion is present on the surface of the resin, which is characteristic of a sensor in equilibrium with the feed solution. The radial, unsteady state diffusion in spherical coordinates can be described by the dimensionless form of Fick’s Second Law,

\[
\frac{\partial \Theta}{\partial \eta} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial \Theta}{\partial \xi} \right)
\]  

(4.1)

where \( \Theta, \xi, \eta \) are dimensionless concentration, radial position, and time terms:
\[ \Theta = \frac{C_i - C_o}{C_i - C_0}, \quad \xi = \frac{r}{R}, \quad \eta = \frac{tD_{ij}}{r^2} \]

\( C_i \) is the concentration of uranyl ion at any time \( t \) and radial position \( r \), \( C_o \) is the initial concentration of uranyl ion in the resin, \( R \) is the resin radius, \( C_j \) is the concentration of uranyl ion on the surface, and \( D_{ij} \) is the effective diffusion coefficient of uranyl ion in the polymer. Equation 4.2 gives the initial condition and Equations 4.3 and 4.4 describe the boundary conditions for a resin charged with a fixed concentration of uranyl ion at the surface:

\[ \eta = 0, \quad 0 \leq \xi \leq 1, \quad \Theta = 0 \quad (4.2) \]

\[ \eta \geq 0, \quad \xi = 1, \quad \Theta = 1 \quad (4.3) \]

\[ \eta \geq 0, \quad \xi = 0, \quad \frac{\delta \Theta}{\delta \xi} = 0 \quad (4.4) \]

The general solution to the diffusion equation with these boundary conditions is well known for the concentration profile (Equation 4.5) and mass uptake (Equation 4.6)\(^{81}\):

\[ \Theta = 1 + \frac{2}{\pi} \xi \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin(n\pi \xi) \exp(-n^2 \frac{\pi^2}{2} \eta) \quad (4.5) \]

\[ \frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(\eta n^2 \pi^2) \quad (4.6) \]

\( M_t \) is the mass uptake at time \( t \) and \( M_\infty \) is the equilibrium mass uptake.

Experimental determination of the uranyl ion diffusion coefficient in the polymer will allow for prediction of the time scales needed to position the uranyl ion at any given radial position on the resin bead, which is a key factor in the detection efficiency of the material. Decay events that occur in the free volume of the polymer matrix or the macropore structure are expected to result in higher detection efficiency than events that
occur on the surface of the resin bead due to the higher probability of the alpha particle depositing energy in the bead. The release of an alpha particle from a radionuclide bound to the surface of a spherical resin bead has less than a 50% chance of decaying directly into the scintillator. The other 50+% of particles are released into the interstitial space of the column where they lose some of their energy to the interstitial water in the column before encountering a neighboring scintillating resin bead. The optimization of the online detection systems centers on the interplay between detection efficiency and detection time. This work explores whether or not the detection efficiency gained by allowing the uranyl ion to diffuse into the polymer matrix is worth the time it takes.

### 4.3 Experimental

The base expanded gel poly[(4-methyl styrene)-co-(divinylbenzene)-co-(2-(1-naphthyl)-4-vinyl-5-phenyloxazole)] resin used for this study was synthesized according to a previously reported method\textsuperscript{58}. Phosphonic acid functionality was added to this base resin by first attaching a phosphonate moiety through an Arbuzov type reaction with triethylphosphite (Aldrich, product T61204)\textsuperscript{82}. The phosphonate was hydrolyzed to the phosphonic acid form by a two-step process of silylation with bromotrimethyl silane (Aldrich, 194409) for 24 h followed by methanolysis (Fisher Scientific, A457-4) for 24 h\textsuperscript{69}. After functionalization, the resin was washed with ethanol (Aldrich, 793175) and dried in a vacuum oven overnight. After each step of the functionalization process, the resin was analyzed with a Nicolet Nexus 870 Fourier Transform Infrared (FTIR) Spectrometer (ThermoScientific, USA) to observe characteristic absorbances of the functional groups. All FTIR samples were analyzed using potassium bromide pellets.
(Sigma Aldrich, 221864) in transmission mode for 64 scans. The resins were fractionated by stainless steel sieves to produce two particle diameter fractions, 106-212 μm and 212-425 μm. Resin beads were imaged with a Digital Celestron Microscope (Torrance, CA, USA). The resin images were analyzed in MATLAB version 7.9.0.592 (Natick, MA, USA), which processed the image by filtering noise, enhancing contrast, identifying circles and outputting resin particle radii. At least 30 resin beads were analyzed to estimate the distribution of bead radii in a given size fraction.

To study the effect of resin radius and column diameter on detection efficiency, beads with radii of 63 ± 17 μm and 192 ± 20 μm were dry packed into poly(tetrafluoroethylene) columns with inner diameters (I.D.) of 0.16 cm and 0.48 cm. Each column was packed to a height of 25 ± 1 mm for comparison.

Due to the hydrophobicity of the resin, it was conditioned to properly wet the surface of the resin and promote binding. Columns were conditioned by flowing 10 mL methanol at 0.5 mL min\(^{-1}\), followed by 10 mL of 50:50 (v/v) methanol/water, and then 5 mL of a pH 4 nitric acid (Fisher Scientific, A200C-212) background solution. During detection efficiency tests, a uranium-233 (Eckert & Ziegler) solution with an activity of 3.8 Bq mL\(^{-1}\) and pH 4 was pumped through the column at a rate of 1.5 mL min\(^{-1}\). The column was loaded sequentially with uranyl ion by pumping 5 mL of the uranium-233 solution through the column. After each sequential loading, residual unbound uranyl ion was rinsed from the column by flowing 2 mL of the nitric acid background solution through the column. The column was then counted with a PerkinElmer Quantulus LSC (Waltham, MA, USA) without the introduction of liquid scintillation cocktail by
positioning it within a 20 mL scintillation vial using a customized column holder. The feed and effluent were analyzed by mixing 10 mL of UltimaGoldAB liquid scintillation cocktail (Perkin Elmer, 6013301) with 4 mL of sample and then counted on the same instrument. All samples were counted for 60 min. Columns were regenerated with 15 mL of 1 M HCl (Sigma Aldrich, 320331) between triplicate trials.

To study the effect of location of the alpha decay on the detection efficiency, the columns from the previous experiment were stored in humidified scintillation vials for 14 days. The columns were counted after the 14 d period to determine if the detection efficiency had changed as the uranyl ion diffused from the surface of the resin beads towards their center. A similar study was performed to analyze the change in available surface sites for binding. Two 0.16 cm I.D. columns packed with the 63 μm radius resin were loaded with uranium-233 while monitoring the concentration of uranium-233 in the effluent by LSC. After loading, both columns were stored in humidified containers for 18 or 190 h. After the storage period, the columns were again loaded with activity and the concentration of the effluent was monitored by LSC to achieve an effluent to feed ratio of either 0.5 or 0.8. Data from this experiment were used to calculate the diffusion coefficient.

4.4 Results and Discussion

FTIR spectroscopy was performed on the resin before and after functionalization to support the incorporation of the phosphonic acid groups within the resin. Figure A-4 in Appendix A shows that characteristic absorbance peaks for phosphonate and
phosphonic acid were observed at 1042 cm\(^{-1}\) and 2200 cm\(^{-1}\), respectively, which is consistent with the literature\(^8\).

The effects of column diameter and resin radius on detection efficiency were studied by packing columns with either 0.16 cm or 0.48 cm I.D. with resins of either 63 ± 17 \(\mu\)m or 192 ± 20 \(\mu\)m radius. The detection efficiency was calculated as the ratio of the column count rate to the loaded activity. **Figure 4.1** shows that the detection efficiency of the 4.783 MeV alpha particles from uranium-233 did not change with an increase in mean bead radius from 63 to 192 \(\mu\)m. This result was the same for both column diameters tested. The short diffusion length of the uranyl ion in the resin bead during the timeframe of the measurement (vide infra) explains why the bead radius has no effect on detection efficiency. The detection efficiency decreased with increasing column diameter for both resin sizes.

![Detection efficiency as a function of inner column diameter and bead radius. Error bars represent standard deviations from measurements made with three different columns.](image)

**Figure 4.1.** Detection efficiency as a function of inner column diameter and bead radius. Error bars represent standard deviations from measurements made with three different columns.
Evidence for the reduction in detection efficiency also was observed in the pulse-height spectra (Figure 4.2) for the beads with a radius of 63 \( \mu \)m in the two column diameters. Both columns have similar loaded activities; however the 0.48 cm I.D. column exhibits lower luminosity with the alpha-peak at channel 230 and lower detection efficiency. The lower luminosity indicates that fewer photons per scintillation event are becoming incident on the detector and implies that the resin attenuates photons. In this case, the reduction in detection efficiency with the larger column diameter can be attributed to the attenuation of photons in the column. As the beads scintillate, the photons must traverse the column radius to the detector. In the case of coincidence counting with the Perkin Elmer Quantulus Liquid Scintillation Counter, two photons from the same scintillation event must traverse the column and become incident on both detectors in coincidence to register as a count. If the column diameter is large, then there
is a higher probability that the photons produced in the center of the column will not be incident on the detector surface, resulting in lower detection efficiency. Furthermore, a scintillation event that happens just below the outer layer of a wide column will have a low probability of detection, because while one photon will have a short path length to the first detector, the other must traverse the full column width to the second detector. In summary, increasing the column diameter changes the detection geometry such that some scintillation events are located outside of the detectable region.

Between trials, the columns were regenerated dynamically by pumping 1M HCl through the column at a rate of 1.5 mL min⁻¹. Columns were regenerated to >90% of the original capacity after the first 10 mL of HCl.

To study the effect of time on detection efficiency, the columns packed with 63 ± 17 μm resin used in the previous detection efficiency experiments were stored for 14 d in humidified containers and then counted again with the traditional LSC. Figure 4.3 shows that both columns had an increase in detection efficiency over the tested time period, which was attributed to the diffusion of the bound uranyl ion from the surface of the bead into the polymer matrix. Decay events that occur inside the polymer matrix have a higher probability of depositing energy into the matrix for detection than those bound solely to the surface. Detection efficiency gains of 8-13% were observed when the uranyl ion was allowed time to diffuse into the polymer matrix.
Figure 4.3. Columns exhibit increased detection efficiency after being stored for 2 weeks in sealed containers. Error bars represent standard deviations among triplicate measurements.

To determine whether the time scale for diffusion into the resin bead is comparable to the time scale desired for the online detection of radionuclides, it was necessary to estimate the diffusion coefficient of the uranyl ion in the polymer material for use in the previously developed Fickian transport model. The change in available surface sites for binding can be correlated to the amount of uranium-233 that diffused from the surface to the inner structure of the polymer bead. For diffusion limited systems, the ratio of effluent concentration to feed concentration of uranyl ion gives an indication of the surface coverage of the resin in the column. In both columns, it was observed that the surface sites available for binding had increased during the storage period. During storage, the uranyl ion bound to the surface of the resin was able to diffuse in towards the center of the resin bead, freeing sites on the surface. The amount of uranyl ion needed on day 14 to raise the effluent to feed ratio to the value achieved on day 1 is equivalent to the amount of uranyl ion that diffused into the resin bead during the storage period, $M_t$. 
The equilibrium uranyl ion uptake \( M_\infty \) and the diffusion coefficient, \( D_{ij} \) were solved for simultaneously using Equation 4.6 for Columns A and B.

Without a rigorous study of dynamic binding with various feed concentrations and a method of measuring the internal concentration profile, it is difficult to calculate the true diffusion coefficient; however, an order of magnitude estimate can be made from the current data in terms of mass uptake, which is sufficient for our purpose of estimating the order of magnitude of the diffusion time scales. **Table 4.1** shows the results of calculations.

**Table 4.1** Order of magnitude analysis for the diffusion coefficient of uranyl ion in the polymer matrix where \( M_t \) is the uranyl ion mass in the polymer at time \( t \), \( M_\infty \) is the uranyl ion mass in the polymer at equilibrium, \([U]_{\text{eff}}\) is the effluent concentration of uranyl ion and \([U]_{\text{feed}}\) is the concentration of uranyl ion in the feed solution.

<table>
<thead>
<tr>
<th></th>
<th>( t ) (min)</th>
<th>( M_t / M_\infty )</th>
<th>([U]<em>{\text{eff}} / [U]</em>{\text{feed}} )</th>
<th>( D ) (cm(^2) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column A</td>
<td>11400</td>
<td>0.44</td>
<td>0.5</td>
<td>( 2 \times 10^{-12} )</td>
</tr>
<tr>
<td>Column B</td>
<td>1080</td>
<td>0.18</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>
An effective diffusion coefficient of $2 \times 10^{-12}$ cm$^2$ s$^{-1}$ was estimated for the system and used with Equation 4.5 to predict the concentration profiles.

**Figure 4.4.** Predicted concentration profiles of the uranyl ion in the polymer resin bead with a radius of 63 μm (left) and 192 μm (right) as function of time.

**Figure 4.4** shows the concentration profiles of uranyl ion within the resin bead cross-section. The diffusion model estimates 300 h is needed for the first atom of uranyl ion to reach the center of the resin in the 63 μm bead and 2000 h for the 192 μm bead. Diffusion distances on the order of tens of microns can occur in 45 min. For practical purposes, the time scales for the uranyl ion to diffuse to the center of the expanded gel polymer are too long when a desired measurement time is on the order of minutes to seconds. These slow diffusion times for ions in gel-type polymers also have been observed in absorption studies by Hirotsu et al.$^{83}$ They attributed the slow absorption rate of uranyl ion into the gel-type polymer to difficulty of the large, highly charged uranyl ion diffusing into the hydrophobic expanded gel network of the resin. Based on the current model, uranyl ion is expected to diffuse on the order of 10 μm during the time
scale of detection, which can provide some enhancement in detection efficiency. The location of the uranyl ion just below the surface is consistent with the measured pulse-height spectra, which showed a distinct alpha-peak with minimal interactions recorded in the lower energy channels. Energy deposition less than the full energy is indicative of a decay event originating on the bead surface in which the alpha particle traveled through the interstitial space and lost energy before depositing in a neighboring scintillating bead. The short diffusion length of the uranyl ion in the resin bead also explains why the bead radius has no effect on detection efficiency (Figure 4.1). The uranyl ion is binding primarily on the surface and within the first 10 μm below the surface of the bead and not utilizing the inner polymer structure. The limiting cases for alpha decay in the center of the bead would be that (1) the bead radius is so large that all photons are quenched or (2) the bead diameter is so small that not all of the energy is deposited in the bead. Both scenarios would result in a pulse-height spectrum with a low-energy tail. A low-energy tail in the pulse height spectrum was not observed in this work; therefore, the primary factor influencing the detection efficiency is the column diameter. In this system, the only effect of the resin diameter is the distance between neighboring beads, which is large enough such that an alpha particle released on the surface of one bead does not interact with a neighboring particle.

4.5 Conclusions

Extractive scintillating resins with phosphonic acid functionality were evaluated for their detection efficiency in several detection configurations and conditions. A maximum detection efficiency of 50% was achieved for the 63 μm radius beads packed
in the 0.16 cm I.D. column when the uranyl ion was allowed to diffuse into the polymer for 14 d. The diffusion experiments show that, while the detection efficiency can be increased when the decay event occurs inside the polymer matrix rather than on the surface of the resin bead, the time scales necessary for the uranyl ion to diffuse to the center of the bead (days) are much greater than the time scale for detection (minutes). Thus, the diffusion limitations imposed by the gel-type polymer limit the system to surface binding and render the internal volume of the resin unusable in an online detection system. Future efforts should focus on the synthesis of resins with higher internal porosity and pore size to increase the effective diffusion coefficient of the uranyl ion in the polymer and increase the detection efficiencies during more reasonable time scales.

4.6 Acknowledgements

This work was supported by the Defense Threat Reduction Agency, Basic Research Award #HDTRA1-12-1-0012, to Clemson University. The authors would like to acknowledge the contribution of Shelby Thies for the development of the MATLAB code to analyze the resin particle size.
CHAPTER FIVE

PHOSPHONIC ACID AND ALKYL PHOSPHATE-DERIVITIZED RESINS FOR THE SIMULTANEOUS CONCENTRATION AND DETECTION OF WATERBORNE URANIUM

[As prepared for Chemistry of Materials]

5.1 Abstract

The objective of this study was to develop extractive scintillating resins for the direct, real-time analysis of uranium in neutral pH environmental waters. To attain this objective, two different organophosphorus-derivitized resins were synthesized and evaluated their performance in pH 4, 6 and 8 simulated ground water. In the first approach, a methyl phosphonic acid-derivitized resin was prepared by a two-step process of (1) suspension polymerization to create a cross-linked polymer that contains a covalently bound fluorophore and 4-vinylbenzyl chloride, followed by (2) phosphorylation and hydrolysis to add phosphonic acid functionality—the same process as described in Chapter 3. In the second approach, methyl phosphate-derivitized resin was synthesized in a one-step suspension polymerization reaction resulting in a cross-linked polymer that contains a covalently bound fluorophore and ethylene glycol methacrylate phosphate ligand. Scheme 5.1 shows the ligand structures. Resins were compared on the basis of capacity for uranium, affinity for uranium and detection efficiency. The ability of both resins to detect uranium from neutral pH simulated ground water was evaluated through a Shewart-3σ control statistic applied to real-time data collected in a flow-cell detector. Resins exhibit similar binding capacities (0.18 mmol g⁻¹) and detection efficiencies (~40%); however, the alkyl phosphate resins more rapidly
concentrate uranium from simulated ground water than the phosphonic acid resins. The pH dependence observed for both resins in the volume to detection data are interpreted through changes in uranium speciation and binding mechanism.

![Methyl phosphonic acid (MS-MPA)](image1)

![Ethylene glycol methacrylate phosphate (EGMP)](image2)

**Scheme 5.1.** Ligand structures.

**5.2 Experimental Section**

**5.2.2 Reagents**

2-(1-Naphthyl)-4-vinyl-5-phenyloxazole (v-NPO) was synthesized according to the literature. Reagents were used as received unless noted otherwise: aluminum oxide (activated, Sigma Aldrich), arsenazo III (spectrophotometric grade, Fluka), 2,2’-azobis(2-methyl-propionitrile) (AIBN, 98%, Aldrich), dichloromethane (Acros Organics), divinylbenzene (80% technical grade, Aldrich), ethanol (denatured, reagent grade, Aldrich), hydrochloric acid (HCl, aq. 37%, Sigma-Aldrich), 4-methyl styrene (96%, Aldrich), nitric acid (90%, Fisher Scientific), poly(vinyl alcohol) (PVA, 86-89% hydrolyzed, med. molecular weight, Alfa Aesar), potassium bromide (KBr, IR grade
99+% (Acros Organics), sodium chloride (ACS reagent, Sigma Aldrich), sodium hydroxide (ACS reagent, Sigma Aldrich), sodium nitrate (ACS reagent, Sigma Aldrich), triethyl phosphite (98% Aldrich), trimethylsilyl bromide (TMSBr, 97%, Aldrich), UltimaGold AB liquid scintillation cocktail (PerkinElmer), tri-n-octylamine (Fisher Scientific), uranium-233 (Eckert & Ziegler), uranium nitrate hexahydrate (depleted uranium, PerkinElmer), 4-vinylbenzyl chloride (90%, Aldrich). Water was distilled and deionized by ion exchange resin (DI).

5.2.3 Preparation of MS-MPA resin

Poly[(4-methyl styrene)-co-(styrene phosphonic acid)-co-(divinylbenzene)-co-(2-(1-napthyl)-4-vinyl-5-phenyloxazole)] resin (MS-CMS) was prepared by suspension polymerization and solid phase synthesis techniques according to a previously reported procedure from Chapter 3.

5.2.4 Preparation of EGMP resin

Poly[(4-methyl styrene)-co-(ethylene glycol methacrylate phosphate)-co-(divinylbenzene)-co-(2-(1-napthyl)-4-vinyl-5-phenyloxazole)] (EGMP) was synthesized according to the same suspension polymerization procedure as the MS-MPA resin; however, resin functionality was added by the direct incorporation of the ethylene glycol methacrylate phosphate monomer during polymerization. Table 5.1 summarizes the composition of the monomer (discontinuous) phase for preparation of the EGMP resin. Tri-n-octylamine was included in the monomer phase to complex with the water-soluble ethylene glycol methacrylate phosphate and thereby retain it in the oil phase during suspension polymerization.
Table 5.1. Composition of the discontinuous phase for EGMP synthesis

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Purpose</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-methyl styrene</td>
<td>bulk material, primary scintillator</td>
<td>7.9 mL</td>
</tr>
<tr>
<td>Ethylene glycol methacrylate phosphate</td>
<td>uranium-binding functional group</td>
<td>2.8 mL</td>
</tr>
<tr>
<td>divinylbenzene</td>
<td>crosslinking agent</td>
<td>1.3 mL</td>
</tr>
<tr>
<td>v-NPO</td>
<td>fluorophore</td>
<td>360 mg</td>
</tr>
<tr>
<td>tri-n-octylamine</td>
<td>complexing agent</td>
<td>8 mL</td>
</tr>
<tr>
<td>AIBN</td>
<td>radical polymerization initiator</td>
<td>200 mg</td>
</tr>
</tbody>
</table>

5.2.5 Characterization of resin functionality and binding capacity

Resin functionality was characterized by Fourier-transform infrared spectroscopy (FTIR) using a nitrogen purged Nicolet Nexus 870 FTIR Spectrometer (ThermoScientific, USA) with Omnic software. Samples were analyzed in KBr pellets using transmission mode for 64 scans at a resolution of 4 cm$^{-1}$.

The resin binding capacities for uranium were determined from analysis of equilibrium batch ion-exchange data. Forty milligrams of resin were contacted with 2 mL of 0 – 800 ppm solutions of uranyl nitrate hexahydrate, adjusted to a pH of 4 with 0.1M HCl and 0.1M NaOH solutions using a calibrated Orion model 420A pH meter and Orion model 911600 combination semi-micro pH electrode. The pH was measured with a uranium concentrations in solution before and after contact with the resin were quantified with aresenazo(III)-assisted UV-visible spectroscopy according to a previously reported procedure$^2$. Measurements were performed in triplicate.

5.2.6 Column preparation and conditioning

Radiochromatography columns were prepared by dry-packing 30 mg of either MS-MPA or EGMP resin in a PTFE column (i.d. 0.16 cm). Resins were secured in the column using PTFE frits. Columns were loaded into a dual photomultiplier LabLogic
Beta-RAM Model 5 HPLC detector (LabLogic Systems, Inc., Brandon, FL) with Laura SP3 data acquisition software. Prior to use, columns were wetted by pumping 15 mL of each of the following solutions through the column at a flow rate of 1.3 mL min$^{-1}$: (1) ethanol, (2) ethanol/water (50:50 v/v) and (3) DI water. Then, the columns were conditioned by pumping 40 mL each of the following solutions through the column at a flow rate of 1.3 mL min$^{-1}$: (1) 1M NaOH, (2) DI water, (3) 1M HCl and (4) DI water. Columns were allowed to dark adapt inside the detector for 12 h after conditioning and before use.

**5.2.7 Optical Properties**

Uranium solutions at pH 4, 6, and 8 were prepared by mixing uranium-233 in DI water and adjusting the pH with 0.1M HCl and 0.1M NaOH solutions using a calibrated Orion model 420A pH meter and Orion model 911600 combination semi-micro pH electrode. Conditioned columns were loaded with uranium-233 from pH 4, 6 or 8 solutions of pH adjusted DI water. Column loading was performed by pumping 20 mL of pH adjusted 0.5 Bq mL$^{-1}$ uranium-233 solutions through the column. Uranium-loaded columns were counted for 1 h in a 20 mL glass scintillation vial with a custom sample holder using a PerkinElmer Quantulus Liquid Scintillation Spectrometer (LSC) (Waltham, MA, USA), according to a previously reported procedure$^6$. The pulse height spectrum was extracted for analysis. The data were modeled by non-linear regression with a Gaussian distribution to calculate the peak channel as a function of pH. The peak channel is an indication of the luminosity of the resin.
5.2.8 Radiochromatography

Uranium-233, a pure alpha-emitting isotope, was selected for the characterization of these materials because it has a high specific activity, lending itself to improved counting statistics and lower uncertainty in the measurements. Furthermore, it is an isotope of interest because it is classified as “special nuclear material” by the Atomic Energy Act of 1954. As a fissile uranium isotope, its proliferation is considered a risk for nuclear weapons development.

Simulated groundwater was prepared according to the recipe of Smith et al., with the following composition: 10.4 ppm Ca$^{2+}$, 217.5 ppm Cl$^-$, 7.8 ppm NO$_3^-$, 10 ppm K$^+$, 744.2 ppm HCO$_3^-$, 17.5 ppm Mg$^{2+}$, 354.7 ppm SO$_4^{2-}$, 570.2 ppm Na$^+$, 20.1 ppm F$^-$ and 10 ppm Si$_4^+$. Uranium-containing groundwater was prepared by mixing uranium-233 in the simulated groundwater to create a solution with an activity concentration of 0.5 Bq mL$^{-1}$. Radiochromatography measurements followed the following procedure (1) column wetting and conditioning, as described previously; (2) background measurement; (3) column loading; (4) column regeneration and (5) column post-elution treatment. Background measurements were collected by pumping simulated groundwater through the conditioned column (background solution) and collecting count rate data in 1 s intervals for 30 min. The 30 min collection time was chosen for two reasons. Firstly, it allowed enough time for the column to pH equilibrate with the solution, i.e. the effluent pH was equal to the feed pH. Secondly, it allowed for the accumulation of 1800 data points in the background spectrum to provide sufficient statistical analysis. Column loading was achieved by pumping uranium-233 solutions at pH 4, 6 or 8 through the
column at a flowrate of 1.3 mL min\(^{-1}\). Column regeneration was achieved by pumping 13 mL of 1 M Na\(_2\)CO\(_3\) at the same flowrate. Elution of with the Na\(_2\)CO\(_3\) solution resulted in alkaline conditions in the column and effluent. To return the column to more neutral conditions post-elution, 13 mL of DI water was pumped through the column followed by 6.5 mL of 1M HCl. After such post-treatment, columns could equilibrate with the 30 mL of the background solution.

The role of pH on the ability of the resins to concentrate the uranium from simulated groundwater was evaluated using the volume to detection, which is defined in this study as the volume of uranium-contaminated solution pumped through the column before the column count rate exceeds the control statistic. While a variety of control statistics exist for radionuclide detection\(^{84-86}\), the Shewart-3\(\sigma\) was used for its simplicity. In the Shewart-3\(\sigma\) method, the control statistic (CS) is calculated by **Equation 5.1.**

\[
CS = \mu + 3\sigma
\]

\(\mu\) is the mean background count rate and \(\sigma\) is the standard deviation of the background count rate. All data were binned into 10 s intervals using MATLAB® code developed by Watson\(^{84}\) prior to statistical analysis. The volume to detection for each test condition is reported as the average of triplicate measurements.

The detection efficiency of each resin was measured by pumping 0.5 Bq mL\(^{-1}\) uranium-233 solution at pH 4 through MS-MPA or EGMP radiochromatography columns. After loading, the column was regenerated with 13 mL of 1 M Na\(_2\)CO\(_3\). The column effluent was collected in 6.5 mL fractions, corresponding to 5 min collection intervals, and the effluent activity was analyzed with an LSC. Samples were prepared for
LSC by mixing 5 mL aliquots of effluent with 10 mL of UltimaGold AB scintillation
cocktail in 20 mL polyethylene scintillation vials. All samples were counted for 30 min.
Detection efficiency, $\varepsilon_d$, was calculated according to Equation 5.2.

$$\varepsilon_d = \frac{CR_{net}}{\Sigma_i V_i (C_{feed} - C_i)}$$  \hspace{1cm} (5.2)

$CR_{net}$ is the net column count rate, $V_i$ is volume of effluent fraction $i$, $C_{feed}$ is the activity
concentration of the feed and $C_i$ is the activity concentration of uranium in effluent
fraction $i$. The net column count rate was measured for a 20 min interval after the system
achieved an apparent equilibrium in which the count rate no longer increased with
additional feed solution. Detection efficiencies are reported as the average of triplicate
measurements.

5.2.9 Uranium speciation modeling

The chemical speciation of uranium in simulated ground water was modeled
using VisualMINTEQ software, version 2.0. Speciation was calculated at 25 °C, and pH
was calculated from a mass and charge balance. The thermodynamic data referenced by
the program are included in Appendix A, Table A-1.

5.3 Results and Discussion

5.3.1 Resin functionality and capacity for uranium

Resins were analyzed by FTIR to support the incorporation of the
phosphonate/phosphonic acid moieties in the polymer matrices. Figure 5.1 shows the
FTIR spectra for both EGMP and MS-MPA resins, which exhibit the characteristic
absorbance for P-OH stretching at a wavenumber of 2200 cm$^{-1}$. 
Quantitative determination of the resin capacity for uranium was performed by non-linear regression of the constant-pH batch ion-exchange data using the Langmuir ion-exchange isotherm according to Equation 5.3.

$$q = \frac{b C_{eq} q_{\text{max}}}{1 + b C_{eq}}$$  \hspace{1cm} (5.3)

$q$ is the uranium bound to the resin (mmol g$^{-1}$), $C_{eq}$ is the concentration of uranium in solution at equilibrium (mM), $q_{\text{max}}$ is the maximum capacity of the resin (mmol g$^{-1}$) and $b$ is the Langmuir parameter—a descriptor of binding affinity.

Figure 5.2 shows ion-exchange isotherms for EGMP and MS-MPA resins. The resins have the same maximum binding capacities of 0.18 mmol U (g$^{-1}$ resin), but the difference in the Langmuir parameter ($b_{\text{EGMP}} = 4.9$ and $b_{\text{MS-MPA}} = 3.2$) implies that the EGMP resin has a higher affinity for uranium than the MS-MPA resin.
At pH 4, the solution is one pH unit above pKa of both ligands (pKa$_{1,MS-MPA}$ = 2.38, pKa$_{1,EGMP}$ = 1.60) and below pKa$_{2}$ (pKa$_{2,MS-MPA}$ = 7.74 and pKa$_{1,EGMP}$ = 6.62)$^{87, 88}$. Since the resins exhibit the same binding capacity and degree of protonation, we can infer the resins have similar numbers of accessible binding sites. The difference in binding affinity can be explained by the difference in chemical structure of the two ligands. In two different studies, Alexandratos et al. have shown that the addition of neighboring ether oxygens$^{34}$ and the incorporation of carbonyl moieties$^{55}$ in supported phosphonic acid ligands enhances the metal ion affinity. Since the EGMP resin contains both ether oxygens and carbonyl functionality, the enhancement in uranium affinity over MS-MPA resin is justifiable.

### 5.3.2 Optical properties

The effect of pH on the optical properties of the resins was studied by loading uranium-233 from varying pH solutions and analyzing the pulse-height spectra of the
resins, shown in Figure 5.3. MS-MPA photopeaks appear at lower channels than the EGMP resins due to the attenuation of photons prior to reaching the detector. The MS-MPA resin is an opaque yellow color, whereas EGMP is translucent and colorless. The data indicate that despite minor changes in the peak channel for each resin as a function of pH, the peaks are fully resolved within the spectrum. If pH affected the detection efficiency of the resin, low channel tailing would be observed. Full spectral resolution implies that the alpha particles are depositing their energy in the material and that the emitted light is within the acceptable wavelengths for the photomultiplier tubes. Since the peak channel in the pulse-height spectra for the resins show minimal pH dependence, it can be inferred that the detection efficiency is not affected by a change in pH from 4 to 8.

Figure 5.3 Pulse-height spectra of MS-MPA and EGMP resins loaded with uranium from various pH solutions.
5.3.3 Sensor performance

The detection efficiencies were measured to be 36±4% for MS-MPA and 46±8% for EGMP resins. The volume to detection was measured for both MS-MPA and EGMP resins at pH 4, 6 and 8 in simulated groundwater. Figure 5.4 shows the results of these measurements.

![Graph showing volume to detection data](image)

**Figure 5.4.** Representative volume to detection data shown (left) for MS-MPA resin at pH 6 in which \( \mu = 0.8 \) CPS, \( \sigma = 0.4 \) CPS and \( \mu + 3\sigma = 2.1 \) CPS (left) and summary of data (right). Negative values correspond to the background spectrum. Activity was introduced at 0 mL.

At pH 4, EGMP and MS-MPA resins require 30±9 mL and 27±10 mL to achieve the Shewart-3\( \sigma \) control statistic and show no statistical difference. At pH 6, EGMP resins require 54±6 mL to detection, while MS-MPA resins require 70±4 mL. At pH 8, EGMP resins require 18±6 mL to detection, while MS-MPA resins require 41±5 mL. The volume to detection for both resins is pH dependent. The two factors that contribute to the volume to detection are the detection efficiency of the material and the affinity of the material for the uranyl cation. As previously discussed, the detection efficiency should
not be a function of pH; thus, the more likely cause of the pH dependence is variation in binding affinity. Two phenomena occur in the resin-water system as the pH changes: (1) a change in the surface charge and (2) a change in the speciation of uranium in solution.

The first phenomenon that occurs in the system as the pH increases from 4 to 8 is a change in the degree of protonation of the ligands, described by Equations 5.4 and 5.5.

\[
H_2P \leftrightarrow HP^- + H^+ , \text{ Ka}_1
\]  
\[ (5.4) \]

\[
HP^- \leftrightarrow P^{2-} + H^+ , \text{ Ka}_2
\]  
\[ (5.5) \]

$H_2P$ is the fully protonated, $HP^-$ is the mono-protonated and $P^{2-}$ is the fully deprotonated form of the alkyl phosphate or phosphonic acid. Table 5.2 describes the speciation of the acid groups as a function of pH. At pH 4, EGMP and MS-MPA resins exhibit similar degrees of protonation as well as volumes to detection. At pH 6 and 8, the EGMP resin requires a lower volume for detection than the MS-MPA resin which corresponds to a lower degree of protonation.

**Table 5.2.** Summary of acid group speciation.

<table>
<thead>
<tr>
<th>Solution pH</th>
<th>MS-MPA</th>
<th>EGMP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$P</td>
<td>HP$^-$</td>
</tr>
<tr>
<td>4</td>
<td>2%</td>
<td>98%</td>
</tr>
<tr>
<td>6</td>
<td>0%</td>
<td>98%</td>
</tr>
<tr>
<td>8</td>
<td>0%</td>
<td>35%</td>
</tr>
</tbody>
</table>

Alexandratos et al.\textsuperscript{34} have studied the binding mechanisms of uranium with phosphonate-derivitized resins in 0.01M-6M nitric acid. They concluded that at low pH (i.e. pH $<<$ pKa$_1$) the primary mechanism for uranium binding is direct coordination at the phosphoryl (P=O) oxygen. At pH values near pKa$_1$, the primary mechanism is ion-
exchange with the acidic proton; however, no such studies were performed for pH > pKa$_1$ or pH > pKa$_2$.

**Figure 5.5.** Speciation of uranium (1.4 ppb) in simulated ground water.

The second phenomenon that occurs in the system as the pH increases from 4 to 6 is a change in the speciation of uranium in the bulk solution. Uranium speciation in simulated ground water was modeled in Visual MINTEQ (results shown in Figure 5.5). Without fundamental thermodynamic data describing the uranium-MS-MPA and uranium-EGMP binding constants, we cannot directly explain the difference in uranium uptake; however, several observations can be made based on the uranium speciation in the bulk solution. At pH 4 and 6, uranium speciation in the simulated groundwater is dominated by uranium-fluoride complexes. At pH 4, there is nearly an equal distribution of exchangeable UO$_2$F$^+$ and non-exchangeable UO$_2$F$^-$ ions in solution. The increase in volume to detection between pH 4 and pH 6, which is consistent with a decrease in the
rate of uranium accumulation on the resin, corresponds to an increase in $\text{UO}_2\text{F}_2^{\text{aq}}$ and $\text{UO}_2\text{F}_3^{-}$ concentrations. The data suggest that the MS-MPA and EGMP resins are less able to concentrate uranium when it is present as neutral and negatively charged uranium-fluoride complexes—an observation that is consistent with the mechanism of ion exchange\textsuperscript{89}. At pH 8, uranium speciation is dominated by uranium-carbonate and uranium-calcium-carbonate complexes: $\text{CaUO}_2(\text{CO}_3)_3^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^{\text{aq}}$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$. The data demonstrate that despite the dominance of anionic species, both MS-MPA and EGMP resins are able to concentrate uranium from pH 8 simulated groundwater. The EGMP resin, which is 96% deprotonated at pH 8, exhibits the lowest volume to detection—implying that some mechanism other than ion exchange is causing the rapid accumulation of uranium on the resin.

These observations are not anomalous as phosphonic acid-derivitized resins have been shown to be selective for uranium over common cations like $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{K}^+$ and $\text{Mg}^{2+}$ in pH 8 fresh and seawater matrices in which the uranium speciation is dominated by the same four uranium-carbonate complexes\textsuperscript{53, 90}. Many studies have been performed to elucidate the mechanism of uranium sequestration from seawater using amidoxime-based sorbent materials\textsuperscript{91-94}. Das et al.\textsuperscript{95} have shown experimentally that the rate-limiting step to uranium sequestration by amidoxime-functionalized polymer sorbents is the acid catalyzed decomplexation of the uranium-carbonate species. After decomplexation, the free uranyl cation chelates with the amidoxime functional group. Unfortunately, no such studies have been performed for phosphonic acid-derivitized resins; however, experimental and theoretical analysis have been performed by Tian et
al.\textsuperscript{96} to elucidate the binding mechanism of the hydrated uranyl cation with trimethyl phosphate (the ester of phosphonic acid). The results of experimental analysis and density functional theory (DFT) calculations supported the following binding mechanism: (1) hydrogen bonding of the phosphoryl oxygen to the hydration sphere of uranium; (2) nucleophilic attack on the electrophilic uranium atom by the phosphoryl oxygen; (3) coordinated water moves to outer hydration shell and the uranium atom is coordinated to the phosphoryl oxygen. The mechanism described by Tian et al.\textsuperscript{96} is ligand exchange between a coordinated water molecule and the phosphoryl oxygen—a process which was initiated by the proximity of the phosphoryl oxygen to the uranium atom. An analogous mechanism can be imagined for phosphonic acid derivitized resins; except that the ligand exchange would occur between a coordinated carbonate ion and the phosphoryl oxygen. The criteria for ligand exchange are that the newly formed complex (i.e. uranyl-phosphonic acid) is more stable than the initial complex (i.e. uranyl-carbonate)\textsuperscript{89}. Other variations of the mechanism could include the displacement of multiple carbonate ions resulting in the multi-dentate binding of uranium to the deprotonated phosphonic acid ligand. This mechanism would explain the difference between MS-MPA and EGMP volume to detection at pH 6 and 8; whereby, in the current study at pH \( \geq 6 \), EGMP has more deprotonated acid groups than MS-MPA, resulting in a higher Coulombic attraction between the uranyl cation and the ligand, thusly causing stronger complexation.

Further insight into the binding mechanism is being pursued through the use of the density functional method\textsuperscript{96} with Gaussian 09 (Gaussian, Inc., Wallingford, CT). In
this work, all potential carbonate-phosphonic acid ligand exchange reaction have been defined. Computation calculations are underway to calculate the Gibbs free energy for all possible reactants and products and will be used to subsequently calculate the change in Gibbs free energy for each ligand exchange reaction.

5.4 Conclusions

Extractive scintillating resins containing two types of uranium-binding phosphonic acid ligands have been synthesized and tested for their performance in neutral pH simulated groundwater. After a comparative study, EGMP resins are considered a more promising resin than MS-MPA due to their superior performance by several metrics. Firstly, EGMP resins can be synthesized in a one-step polymerization process; whereas, MS-MPA resins require two subsequent reactions after the initial resin synthesis. Secondly, EGMP exhibited a higher affinity for uranium than MS-MPA due to the presence of neutral-donor (ether oxygen and carbonyl) groups on the ligand backbone. Most importantly, EGMP more rapidly meets the alarm condition to detect uranium in simulated groundwater at neutral pH (i.e., pH 6-8) than MS-MPA resins. The pH dependent trends in uranium binding have been interpreted as a transition in binding mechanism as pH is increased from 4 (ion-exchange) to 8 (ligand exchange). EGMP more efficiently collects uranium at high pH due to its higher degree of deprotonation than MS-MPA, resulting in more opportunities for multi-dentate binding. Both resins are able to bind uranium from simulated ground water at neutral pH despite the fact that competing ions such as Ca$^{2+}$ are present in concentrations 3 orders of magnitude higher than the uranium cation.
5.5 Acknowledgements

This work was supported by the Defense Threat Reduction Agency, Basic Research Award #HDTRA1-12-1-0012, to Clemson University. The authors would like to acknowledge Dr. Ayman Seliman for synthesizing the v-NPO monomer used in this study. The authors would also like to thank Mara Watson for valuable discussions regarding control statistics.
CHAPTER SIX
RAPID SAMPLE PREPARATION FOR ALPHA SPECTROSCOPY WITH ULTRAFILTRATION MEMBRANES

[As prepared for Environmental Science & Technology with minor revisions]

6.1 Abstract

This chapter describes efforts to develop a rapid, fieldable, alpha spectroscopy sample preparation technique that minimizes consumables and decreases the nuclear forensics timeline. In this chapter, functional ultrafiltration membranes are presented that (1) selectively concentrate uranium directly from neutral pH ground water and (2) serve as the alpha spectroscopy substrate. Ultrafiltration alpha spectroscopy substrates were prepared by two methods: (1) physical deposition of a polymer film by size exclusion filtration and (2) ultraviolet (UV)-polymerization to grow polymer chains from the membrane surface. Uranium was loaded onto the prepared substrates by filtering uranium-contaminated water through the ultrafiltration membranes. The uranium-selective, water-soluble polymer was prepared by the copolymerization of 2-hydroxyethyl methacrylate and 2-ethylene glycol methacrylate phosphate. The capacity for uranium, 1.9 mmol U g\(^{-1}\), was determined from equilibrium binding experiments. The ligand-grafted membrane was prepared by the UV-polymerization of 2-ethylene glycol methacrylate phosphate with N,N-methylene bisacrylamide. Membranes were characterized by Fourier-transform infrared spectroscopy before and after modification to support the deposition or grafting of the polymer on the membrane surface. Membrane performance was evaluated using various isotopes of uranium in both deionized and simulated ground water at pH 6. Energy resolutions of 99 ± 12 kDa and recoveries of
85% were achieved for membrane prepared by both methods. Notably, baseline energy resolution was achieved for uranium-238 and uranium-233 with a membrane-based substrate prepared directly from pH neutral simulated ground water. Our porous, uranium-selective substrate designs allow for the filtration of uranium-contaminated groundwater *through* the uranium-binding membrane material, leading to a high throughput separation and sample mounting process.

6.2 Experimental Section

6.2.1 Reagents

2,2’-Azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich), ethanol (reagent grade, Sigma Aldrich), methanol (Fisher Scientific), natural uranium (Eckert & Ziegler), nitric acid (90%, Fisher Scientific), N,N-dimethyl formamide (DMF, Sigma Aldrich), N,N’-methylenebis(acrylamide) (N-MBA, 99%, Sigma Aldrich), ethylene glycol methacrylate phosphate (EGMP, 90%, Aldrich), sodium hydroxide (NaOH, Sigma Aldrich), tetrahydrofuran (THF, Fisher Scientific), UltimaGold AB liquid scintillation cocktail (PerkinElmer), uranium-232 (Eckert & Ziegler), uranium-233 (Eckert & Ziegler), uranyl nitrate hexahydrate (depleted uranium, PerkinElmer). Water was distilled and then deionized with a SuperQ Water System (DDI water, Millipore, Molsheim, France).

6.2.2 Membrane preparation by size exclusion filtration

The first technique for membrane preparation was to filter a solution of uranium-selective polymer through a commercial ultrafiltration membrane and thereby deposit a selective layer on the membrane surface. The polymer was processed such that the
molecular weight was larger than the molecular weight cut off (MWCO) of the membrane.

The first step in membrane preparation was to synthesize a water-soluble, uranium-selective polymer. Poly[(ethylene glycol methacrylate phosphate)-co-(2-hydroxyethyl methacrylate)] (poly[EGMP-co-HEMA]) was synthesized by UV-initiated, solution-phase polymerization. In a 20 mL glass vial, 1.40 g EGMP (uranium binding ligand), 1.00 mL HEMA and 20 mg AIBN (photo-initiator) were dissolved in 10 mL of a 75:25 (v/v) mixture of THF and DMF. The solution was mixed by magnetic stirring for 20 min. Then, while stirring, the mixture was irradiated with 365 nm UV light from an 8 W UVLS-28 EL Series UV lamp (UVP, Upland, CA) for 30 min. The distance between the surface of the UV lamp and the center of the scintillation vial was 7.6 cm. The polymer was precipitated in 100 mL of THF, then the polymer was removed from solution by vacuum assisted filtration using Whatman 54 filter paper, a Buchner funnel and a filter flask. After filtration the polymer was washed by dissolution in 50 mL MeOH. Excess MeOH and dissolved impurities were removed by evaporation under reduced pressure using a BÜCHI Rotavapor R-124 (BUCHI Corporation, New Castle, DE) and a BÜCHI B-481 water bath. The water bath was maintained at 50 °C and vacuum was adjusted manually with a needle valve. Glycol was maintained at 0 °C and recirculated through the condenser cooling coil with a NESLAB RTE-140 chiller (Thermo Scientific, Waltham, MA). The concentrated polymer was converted to the sodium salt form by conditioning in 0.25M NaCl for 12 h. Finally, the polymer solution was dewatered to a volume of 10 mL by ultrafiltration using a Biomax® polyethersulfone
(PES) membrane with a MWCO of 100 kDa (MilliporeSigma, Catalog #PBHK04710) in a 50 mL Amicon ultrafiltration cell (Amicon Bioseparations, Jaffrey, NH) connected to an air cylinder at an applied pressure of 138 kPa. The concentrated polymer solution was dried in a vacuum oven at 17 kPa and 35 ºC overnight.

A stock solution of poly[EGMP-co-HEMA] was prepared in a 250 mL volumetric flask by dissolving 0.2200 g dry polymer in DDI water. Then, the stock solution was diluted in a 500 mL volumetric flask by mixing 35 mL of stock with DDI water. The resulting poly[EGMP-co-HEMA] solution had a concentration of 64 μg L⁻¹.

To prepare the size exclusion filtration membranes (SEFMs), 10 mL of the 64 μg L⁻¹ polymer solution was filtered through a Biomax® PES membrane with a MWCO of 30, 50 or 100 kDa at a pressure of 138 kPa. Membranes were filtered to dryness.

6.2.3 Membrane preparation by UV-initiated polymerization

Poly[(ether sulfone)-graft-(ethylene glycol methacrylate phosphate)-graft-(N,N’-methylenebis(acrylamide))] membranes (UVMs) were synthesized by UV-initiated free radical polymerization. Membranes purchased from MilliporeSigma were rinsed with ethanol to remove any pore fillers prior to functionalization. The polymerization solution was prepared in a 20 mL glass vial by dissolving 0.4 g EGMP, 24 mg AIBN and 0.01 mg of N-MBA in 6 mL of ethanol. Membranes were placed in a petri dish with the active layer (shiny side) face up, and 2 mL of the polymerization solution was pipetted onto each membrane. Then, a second petri dish was placed directly on top of the membrane. Care was taken to assure that there were no visible air bubbles between the membrane surface and the second petri dish. The membrane-containing petri dishes were
positioned underneath an 8 W UV lamp. Membranes were irradiated with 365 nm UV light for 10 min at a distance of 7.6 cm from the UV lamp. After the reaction, the UVMs were rinsed with DDI water, submerged in a 50% (v/v) mixture of ethanol and DDI water, and then placed in a reciprocal shaking bath (Precision Scientific Inc., Winchester, IL) at 100 RPM and 25°C overnight to remove any residual reactants and/or physically adsorbed polymer.

6.2.4 Membrane characterization by infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was used to characterize polymer and membrane samples. Dry poly[EGMP-co-HEMA] samples were analyzed in KBr pellets in transmission mode for 64 scans at a resolution of 4 cm\(^{-1}\) using a nitrogen purged Nicolet Nexus 870 FTIR Spectrometer (ThermoScientific, USA) with Omnic 8.3.103 software (Thermo Scientific).

SEFM\(\'\)s and UVM\(\'\)s were analyzed by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) before and after the addition of the selective polymer layer to support functionalization. Samples were analyzed using the same nitrogen purged FTIR with zinc sulfide ATR crystal for 64 scans at a resolution of 4 cm\(^{-1}\).

6.2.5 Poly[HEMA-co-EGMP] capacity

The capacity of poly[EGMP-co-HEMA] was determined through batch equilibrium binding measurements conducted at room temperature. Uranium nitrate hexahydrate was dissolved in DDI water to create a 1000 mg L\(^{-1}\) solution. A uranium-233 solution was prepared by diluting the uranium-233 as received by Eckert & Ziegler
(37.07 kBq g\(^{-1}\)) with DDI water to a concentration of a 488 Bq g\(^{-1}\). Ten gram samples of the polymer solution (64 \(\mu\)g L\(^{-1}\)) were measured in 15 mL polyethylene centrifuge tubes (VWR, Cat. # 89004-368). The uranium concentration in the polymer solution was varied by adding 0.1–0.5 g of the 1000 mg L\(^{-1}\) uranium nitrate hexahydrate solution to each tube. Then, the polymer solutions were spiked with 28 \(\mu\)L of the 488 Bq g\(^{-1}\) uranium-233 solution. Uranium-233 was used a tracer isotope in this experiment, so the uranium concentration in solution could be analyzed by liquid scintillation counting. The total volume of solution in each tube was brought to 11 mL with DDI water to have the same polymer to solution ratio in all samples. Solutions were adjusted to pH 6 using 0.1M nitric acid and 0.1M sodium hydroxide solutions. The pH was measured with a calibrated Orion model 420A pH meter and Orion model 911600 combination semi-micro pH electrode. The centrifuge tubes were mixed in an end-over-end mixer overnight. Polymer-uranium mixtures were filtered in a 50 mL ultrafiltration cell with Biomax® PES membranes (MWCO 30 kDa) at a pressure of 138 kPa. Control studies were performed by filtering uranium solutions through the membranes without the addition of the polymer solution. The permeate was collected in a single fraction. Uranium concentration in the permeate was analyzed in a PerkinElmer Quantulus Liquid Scintillation Spectrometer (LSC) (Waltham, MA, USA) according to a previously published procedure\(^{77}\). Poly[EGMP-co-HEMA] binding capacity experiments were performed in triplicate.
6.2.6 Membrane capacity

The uranium capacity of the SEFMs was calculated by multiplying the mass of polymer deposited on the membrane by the capacity of the poly[EGMP-co-HEMA] polymer. The mass of polymer deposited is the product of the concentration of poly[EGMP-co-HEMA] in solution and the filtered volume.

6.2.7 Direct-flow water flux measurements

Pure water flux experiments for pristine PES membranes, SEFMs and UVMs were conducted according to a previously described procedure\textsuperscript{97}. In this work, experiments were performed over a pressure range from 34 to 128 kPa using a 50 mL direct flow ultrafiltration cell. Membranes were compressed at 128 kPa for 15 min before data collection. Permeate fractions were collected in 30 s intervals and weighed to determine the mass flowrate through the membrane. Flux data were used to calculate the pure water permeability coefficient of the membranes. Permeability coefficients are reported as the average from triplicate measurements of different membranes.

6.2.8 Simultaneous purification and mounting for alpha spectroscopy

Samples were prepared for alpha spectroscopy by mounting the membranes in a 50 mL Amicon ultrafiltration cell and filtering the uranium-containing solutions at 128 kPa, shown in Scheme 6.1.
**Scheme 6.1.** Alpha spectroscopy substrates were prepared in a 50 mL ultrafiltration cell (left), removed from the cell (center) and mounted in a custom sample holder (right).

### 6.2.9 Alpha spectroscopy

Isotopic analysis was performed by alpha spectroscopy using the ultrafiltration membranes as the substrate for analysis. Immediately after sample purification and mounting, membranes were placed on stainless steel plate, immobilized with a custom 3-D printed sample holder and inserted in a Canberra Model 7401 alpha spectrometer (Canberra Industries, Inc., Oak Ridge, TN). The 3-D printed sample holder positioned the sample under the detector and prevented curling of the membrane edges during measurement. Samples were counted under vacuum, at a distance of 9 mm from the detector surface, and for sufficient time to accumulate a minimum of 1000 counts in the peak of interest. Energy calibrations for the alpha spectrometers were performed using an electroplated, NIST traceable calibration standard containing uranium-238, uranium-234, plutonium-239 and americium-241 (Eckert & Ziegler, Atlanta, GA). Peak energy resolution was quantified by the full width half-maximum (FWHM), which was calculated in the MAESTRO Version 7.01 (AMETEK, Inc., Berwyn, PA) software. Prior to calculation of FWHM values, peaks were smoothed using the “smooth” tool, which
performs a 5 point data binning procedure. Reported FWHMs are the result of triplicate measurements made on different membranes.

6.2.10 Effect of MWCO and sample matrix on resolution

In the first set of experiments, uranium-233 in DDI was filtered through pristine PES membranes, SEFMs and UVMs with MWCOs of 30, 50 or 100 kDa to study the effect of MWCO on resolution in the alpha spectrum for each membrane preparation method. Uranium-233 was used in these studies due to its high specific activity (SA) of 351.5 MBq g\(^{-1}\) to facilitate the rapid characterization of the membrane substrates. Solutions were adjusted to pH 6 using 0.1M nitric acid and 0.1M sodium hydroxide prior to filtration. All experiments were performed by filtering 20 mL of 0.5 Bq mL\(^{-1}\) uranium-233 solution at 138 kPa until membranes were dry. The permeate was collected in a single fraction. Feed and permeate concentrations were determined according to the procedure described in Section 6.3.6. Further experiments were performed to analyze the selectivity of the membranes for uranium over the potential competitor ions found in ground water (e.g. Ca\(^{2+}\)) and evaluate the effect of sample matrix on resolution in the alpha spectrum. For these experiments, 0.5 Bq mL\(^{-1}\) uranium-233 in pH 6 simulated ground water (SGW) was filtered through SEFMs and UVMs. SGW was prepared according to the recipe of Smith et al.\(^72\) with the following composition: 10.4 ppm Ca\(^{2+}\), 217.5 ppm Cl\(^{-}\), 7.8 ppm NO\(_3^-\), 10 ppm K\(^+\), 744.2 ppm HCO\(_3^-\), 17.5 ppm Mg\(^{2+}\), 354.7 ppm SO\(_4^{2-}\), 570.2 ppm Na\(^+\), 20.1 ppm F\(^-\) and 10 ppm Si\(_4^+\). Measurements were performed in triplicate for each membrane type.
6.2.11 Isotope discrimination in SGW

To analyze the ability of the alpha spectrometer to discriminate uranium isotopes mounted on the ultrafiltration membrane substrates, SGW spiked with 5.4 ppm (500 Bq L\(^{-1}\)) depleted uranium and 0.0014 ppm (500 Bq L\(^{-1}\)) uranium-233 was adjusted to pH 6 and filtered through 100 kDa UVMs. Membranes were analyzed by alpha spectroscopy. Reported FWHMs are the results of triplicate measurements made on different membranes.

6.3 Results and Discussion

6.3.1 Membrane preparation and characterization

Ultrafiltration alpha spectroscopy substrates were prepared by two methods: (1) physical deposition of a polymer film by size exclusion filtration and (2) UV-polymerization to grow polymer chains from the membrane surface. Figure 6.1.
Membrane preparation by physical deposition required a two-step process. First, the water-soluble, uranium-binding copolymer poly[EGMP-co-HEMA] was synthesized by UV-initiated polymerization. Figure 6.2 shows the FTIR spectrum of poly[EGMP-co-HEMA] which exhibits characteristic peaks for both EGMP and HEMA, supporting a successful copolymerization. The polymer capacity, 1.1 mmol U g\(^{-1}\) polymer, was
calculated by fitting the batch equilibrium sorption data with a Langmuir isotherm, Figure 6.2.

Next, the poly[EGMP-co-HEMA] was dissolved in water and the solution was filtered with a PES membrane. Figure 6.3 shows the characteristic absorbance at 1725 cm$^{-1}$ (C=O) of the methacrylate repeat in poly[EGMP-co-HEMA], supporting the retention of the polymer on the membrane surface.

Membranes synthesized by UV-polymerization also were analyzed by ATR-FTIR to support functionalization. Figure 6.3 shows the same absorbance peak at 1725 cm$^{-1}$ that is characteristic of the methacrylate polymer, supporting the growth of polymer chains from the surface.
6.3.2 Direct-flow water flux measurements

Membrane permeabilities were calculated from direct-flow pure water flux measurements. A linear fit was applied to the experimental data of water flux versus transmembrane pressure (Appendix A, Figure A-5) according to Equation 6.1.

\[ J_w = A \Delta P \]  

(6.1)

Where \( J_w \) is the pure water flux through the membrane, \( A \) is the permeability coefficient and \( \Delta P \) is the transmembrane pressure. Figure 6.4 shows the results of these calculations with error bars representing 1 standard deviation.
Permeability coefficients for all membrane types with MWCOs of 30, 50 and 100 kDa.

The 30, 50 and 100 kDa pristine PES membranes had permeability coefficients of 290 ± 43, 336 ± 40 and 566 ± 80 LMH/bar. For all three membrane supports, the permeability coefficient decreased for the SEFMs while the coefficients remained unchanged for the UVMs. A lower permeability coefficient is indicative of a higher resistance for water to pass through the membrane. **Equation 6.2** describes the inverse relationship of the permeability coefficient or permeance, $A$, and resistance.

$$A = \frac{1}{\mu R_{tot}} \tag{6.2}$$

Where $\mu$ is the dynamic viscosity of water and $R_{tot}$ is the total resistance to flow in the system. The dynamic viscosity of water was assumed to be 1 Pa s for all subsequent calculations. **Equation 6.3** describes the total resistance to flow through the system using the resistor-in-series model for membranes.

$$R_{tot} = R_{PES} + R_{film} \tag{6.3}$$
$R_{\text{PES}}$ is the resistance of the pristine PES membrane and $R_{\text{film}}$ is the resistance of the polymer film. $R_{\text{PES}}$ was calculated directly from the permeability coefficient of the pristine PES membranes. The total resistance for both SEFMs and UVMs was calculated using the respective permeability coefficients and **Equation 6.3** under the assumption that the $R_{\text{PES}}$ remains constant. The resistance of the polymer film was assumed to scale linearly with thickness according to **Equation 6.4**.

$$\frac{R_{\text{film, UVM}}}{L_{\text{UVM}}} = \frac{R_{\text{film, SEFM}}}{L_{\text{SEFM}}}$$  \hspace{1cm} (6.4)

$L_{\text{UVM}}$ and $L_{\text{SEFM}}$ are the polymer film thicknesses. The thickness of the polymer film on the SEFMs was estimated to be 40 nm based on the mass of polymer filtered and the filtration area. As a result, the thickness of the polymer film on the UVMs were calculated to be <10 nm for MWCO 30, 50 and 100 kDa.

### 6.3.3 Effect of MWCO and sample matrix on peak resolution

To determine the effect of MWCO on peak energy resolution in the alpha spectroscopy measurements, functional membranes were prepared by both methods using PES membrane supports with varying MWCO. Membranes were used to filter pH 6 solutions of uranium-233 in DDI water. Ten Becquerel of uranium-233 was filtered through each membrane before isotopic analysis. **Figure 6.5**, shows a characteristic alpha spectrum for a UV-polymerized membrane and **Table 6.1** summarizes the uranium recovery and resolution for all samples. **Appendix A, Figures A-6 and A-7** show representative alpha spectra for 30 and 50 kDa UVMs and SEFMs.
Figure 6.5. Alpha spectrum of a UV-polymerized membrane (MWCO 100 kDa) exposed to 10 Bq of uranium-233.

Table 6.1. Data summary for pH 6 trials of uranium-233 in DDI water and SGW.

<table>
<thead>
<tr>
<th>MWCO (kDa)</th>
<th>Matrix</th>
<th>SEFMs</th>
<th>UVMs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>DDI</td>
<td>93 ± 17</td>
<td>100 ± 9</td>
</tr>
<tr>
<td>50</td>
<td>DDI</td>
<td>102 ± 20</td>
<td>97 ± 14</td>
</tr>
<tr>
<td>100</td>
<td>DDI</td>
<td>95 ± 15</td>
<td>104 ± 2</td>
</tr>
<tr>
<td>100</td>
<td>SGW</td>
<td>103 ± 12</td>
<td>117 ± 15</td>
</tr>
</tbody>
</table>

The data show that there is no effect of MWCO on resolution or recovery for the tested membranes. Unmodified membranes of all three MWCOs were tested in control studies; however, none retained statistically significant activity (Appendix A, Figure A-8). To understand why membranes were only recovering 80% of the uranium, the capacity of the SEFMs, $7 \times 10^{-5}$ mmol U, was calculated from the mass of the polymer deposited on the membrane and the poly[EGMP-co-HEMA] capacity. At the tested conditions, the concentration of uranium in solution is $6 \times 10^{-6}$ mM U (500 Bq L$^{-1}$). The calculations show that the membranes are not saturated and therefore uranium uptake is
not limited by the capacity. The poly[EGMP-co-HEMA] capacity was derived from an experiment in which the polymer was contacted with uranium in solution overnight. In the filtration experiments, the uranium is contacted with the polymer over the course of minutes during filtration. It is hypothesized that at such low uranium concentrations, the rate of uranium binding is much slower than the rate of transport through the membrane—resulting in a system described by a low Damköhler number.

To study the effect of possible competitor ions found in groundwater on uranium recovery and peak resolution, experiments were performed with uranium-233 in simulated ground water. As shown in Table 6.1, no statistical change in resolution or recovery was observed between the UVM 100 kDa DDI and GW samples—demonstrating the selectivity of the membrane. The consistent recovery demonstrates that the membranes are concentrating uranium (1.4 ppb) selectively over competitors like calcium (10.4 ppm) from neutral pH simulated ground water. The consistent FWHM values imply that only uranium is retained on the surface. Retention of other ions on the membrane surface would lead to attenuation of alpha particles causing peak tailing and lower resolution.

The average resolution achieved from all samples prepared from DDI water was 99 ± 12 keV, which is comparable with mounting methods such as evaporation (40-70 keV) and coprecipitation/filtration (75-100 keV). Resolutions achieved in the current work are lower than those achieved with selective polymer films in the literature (20-40 keV); however, the current sample preparation method offers several advantages over the methods reported in the literature when considering fieldable sample
preparation. Pantchev et al.\textsuperscript{20} and Surbeck et al.\textsuperscript{22} concentrated radionuclides from neutral pH groundwater and achieved spectral resolutions of 40 keV; however, sample mounting required 24 hours. Paul et al.\textsuperscript{26} and Gonzales et al.\textsuperscript{21} achieved a more rapid separation and mounting (1 h); however, the separation occurred in 0.1M HCl and 4M HNO\textsubscript{3} solutions. In the present work, uranium is loaded on the alpha spectroscopy substrate (membrane) directly from neutral pH water—eliminating the use of consumable chemicals. Furthermore, the functional ultrafiltration membranes have significantly shorter sample preparation times than other materials for pH neutral separations. Currently, ultrafiltration alpha spectroscopy substrates are prepared from 20 mL of pH 6 uranium-contaminated water in minutes. Based on the permeability coefficient of the 100 kDa UVMs, 3.6 L h\textsuperscript{-1} of contaminated ground water can be filtered at 400 kPa. While further work must be done to optimize filtration and counting times; this work is promising as a high-throughput technique due to the high permeability of ultrafiltration membranes.

6.3.4 Isotope discrimination in simulated ground water

A mixture of depleted uranium (uranium-238) and uranium-233 was purified and mounted on 100 kDa UVMs from pH 6 simulated ground water. Figure 6.6 shows a representative alpha spectrum. The FWHM for the uranium-233 and uranium-238 peaks were 120 ± 10 keV and 94 ± 2 keV. Baseline resolution was achieved for both isotopes.
Figure 6.6. Pulse-height spectrum 100 kDaUVMs prepared with pH 6 simulated ground water spiked with uranium-238 and uranium-233.

Since uranium is a naturally occurring radionuclide, illicit activities cannot be confirmed based on its presence alone. In the scenario in which a person has contaminated the environment by handling enriched uranium with the intention of assembling a nuclear weapon—the isotopic distribution of uranium is of a critical piece of nuclear forensics evidence. The isotopic distribution of uranium provides insight into the intended use of the material. **Table 6.2** summarizes the isotopic distribution of four common grades of uranium.
Table 6.2 Approximate isotopic composition by mass of various grades of uranium.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Uranium-234 (wt %)</th>
<th>Uranium-235 (wt %)</th>
<th>Uranium-238 (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Uranium(^{98})</td>
<td>0.005</td>
<td>0.72</td>
<td>99.27</td>
</tr>
<tr>
<td>Lowly Enriched Uranium (Fuel Grade)(^{99})</td>
<td>&lt;0.005</td>
<td>3-5</td>
<td>95-97</td>
</tr>
<tr>
<td>Highly Enriched Uranium (Weapons Grade)(^{99})</td>
<td>&lt;0.005</td>
<td>&gt;90</td>
<td>10</td>
</tr>
<tr>
<td>Depleted Uranium(^{98})</td>
<td>&lt;0.005</td>
<td>0.2-0.4</td>
<td>&lt;99.5</td>
</tr>
</tbody>
</table>

Highly enriched uranium will produce a strong uranium-235 peak in the alpha spectrum; however, for trace-level analysis of uranium in the environment, the uranium-238/uranium-234 peak ratio is more commonly used. In naturally occurring uranium, uranium-238 and uranium-234 are in secular equilibrium and therefore have a characteristic peak ratio. The addition of enriched uranium (containing different proportions of uranium-238 and uranium-234) will perturb that ratio and serve as a signature to identify anthropogenic contamination. The current work presented membrane materials that produced baseline resolutions of uranium-238 and uranium-233 in the pulse-height spectrum. In these experiments, uranium-233 can be considered a surrogate for uranium-234 due to their similar alpha-energies (4.824 MeV and 4.776 MeV)—indicating that resolutions of 100 keV are sufficient for isotopic analysis of uranium in nuclear forensics applications.

The benefit of using a uranium-238/uranium-233 isotope mixture, is that ultrafiltration membranes were able to be evaluated as a substrate without concerns of
interference from the daughter products that result from the decay of natural uranium. Alpha-emitting daughter products that may interfere with spectral resolution are thorium-230 (4.770 MeV), radium-226 (4.871 MeV) and actinium-227 (4.95 MeV). Future experiments should mount natural uranium from simulated ground water to assess the selectivity of the functional ultrafiltration membranes for uranium over thorium, radium and actinium.

6.4 Conclusions

Ultrafiltration membrane alpha spectroscopy substrates were prepared by two methods: (1) physical deposition of a polymer film by size exclusion filtration and (2) UV-polymerization to grow polymer chains from the membrane surface. Both preparation methods yielded membranes with high permeability coefficients (> 200 LMH/bar) demonstrating the potential for high-throughput analysis. Additionally, spectral resolutions for membranes prepared by both methods were found to be independent of the MWCO of the membrane and the sample matrix. Future utilize still higher MWCO membranes which may offer higher permeability (reduced sample preparation time) without sacrificing spectral resolution. The 100 kDa UVMs were determined to be the more promising ultrafiltration alpha spectroscopy substrate design due to the facile synthesis and superior throughput. Proof-of-concept experiments with uranium-233 and uranium-238 in simulated ground water demonstrate that the prepared substrates can resolve two isotopes of uranium. The results of this research offer the first evidence of a high-throughput sample preparation method for isotopic analysis with alpha spectroscopy that directly concentrates uranium from pH neutral ground water.
Furthermore, they lay the groundwork for the development of ultrafiltration alpha spectroscopy substrates that can be tailored to target other radioisotopes of interest.

6.5 Acknowledgments

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CHAPTER SEVEN
SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

7.1 Summary and Conclusions

This dissertation describes the synthesis and characterization of phosphonic acid and alkyl phosphate derivitized materials for the rapid concentration and detection of uranium from ground water. Chapter 1 introduced flow-cell detectors that utilize extractive scintillating resins and alpha spectroscopy as two environmental radiation detection techniques that require unique separation materials to increase sensitivity and enable fieldability. It also highlights the need to develop separation materials that are robust and capable of performing selective separations in neutral pH environmental waters to minimize consumables. Organophosphorus chemistries are reviewed and identified as promising ligands for uranium-selective separations; however, little data has been collected for their performance in neutral pH environmental waters.

Chapters 2 and 4 focused on the effect of extractive scintillating resin design and detection geometry on luminosity and detection efficiency. Chapter 2 demonstrated that resins with covalently bound fluorophores are more stable and robust than resins with physically incorporated fluorophores. Additionally, it was shown that nitric acid can nitrate both the polystyrene resin and the α-NPO fluorophore. For a detection event to occur, the kinetic energy from the alpha particle must be transferred by the polystyrene to the fluorophore. Since nitrated polystyrene de-excites non-radiatively, the energy transfer mechanism is interrupted and does not result in a detection event. Nitration of the fluorophore broadened the absorption region for the fluorophore, which led to self-
quenching. These results indicate that the issues of instability presented in previous works\textsuperscript{10} can be attributed to the leaching of the fluorophore out of the polymer matrix and the degradation of both the polymer matrix and fluorophore by nitric acid. While the leaching of extractants was not tested, a logical hypothesis derived from the current work is that physically entrapped ligands will be less stable than covalently incorporated ligands. Chapter 2 highlights the need to develop extractive scintillating resins that effectively concentrate the analyte at near-neutral pH and contain covalently incorporated active components (fluorophores and extractants). Doing so, will eliminate the need for nitric acid and increase long-term resin stability.

In Chapter 4, two criteria were found to affect the detection efficiency of extractive scintillating resins: (1) diffusion time and (2) column diameter. The detection efficiency was unaffected by the resin radius within the range of resins studied. Diffusion experiments support that, during typical measurement time scales, uranium is only concentrated on the surface of the resin. Surface binding limits the resins detection efficiency to <50\% due to the geometry of the system and the isotropic nature of alpha decay. Diffusion data show that detection efficiency can be increased if the uranium is allowed to diffuse further into the resin; however, the timescales needed for diffusion (days) are longer than the timescales needed for rapid detection (minutes). Future resin designs should aim to increase resin porosity and pore volume. Doing so would decrease the effective diffusion coefficient of uranium in the polymer, which may allow for diffusion enhanced detection efficiency on more reasonable time scales.
Chapters 3 and 5 described the synthesis of extractive scintillating resins and their performance in flow-cell detection systems in both DI and simulated ground water. In Chapter 3, resins were synthesized according to a two-step procedure: (1) suspension polymerization to create the base resin, followed by (2) phosphorylation and hydrolysis to create phosphonic acid derivitized extractive scintillating resins. Resins were hydrolyzed by refluxing in strong acid or by TMSBr-mediated methanolysis. The resins hydrolyzed by strong acid experienced a loss in fluorescence properties due to the degradation of the α-NPO fluorophore—an observation consistent with data from Chapter 2. Resins produced by the TMSBr-mediated methanolysis resins were tested in the flow-cell detection system and were found to have pH dependent flow cell efficiencies. The flow cell efficiency is a function of both the detection efficiency and affinity of the resin for uranium. The pH dependence was explained by the change in uranium speciation from the free uranyl cation at pH 4, to the neutral uranyl hydrolysis products at pH 6.

Chapter 5 described the one-pot synthesis of an alkyl phosphate derivitized resin and compared it against the phosphonic acid derivitized resin, as synthesized in Chapter 3. Resins were characterized for their uranium binding capacities, and, since they were similar, they could be compared directly. Flow-cell experiments were performed to analyze detection efficiency and volume to detection for both resins in simulated ground water. Ground water studies proved the ability of phosphonic acid and alkyl phosphate derivitized resins to concentrate uranium in the presence of competitor ions (Ca$^{2+}$, Cl$^-$, NO$_3^-$, K$^+$, HCO$_3^-$, Mg$^{2+}$, SO$_4^{2-}$, Na$^+$, F$^-$, Si$^{4+}$) at neutral pH. Most notably, uranium was
retained on both columns despite the presence of Ca$^{2+}$ at concentrations 3 orders of magnitude higher than uranium. Volume to detection was selected as the method to probe resin affinity for uranium, as it is more statistically driven than the flow cell efficiency. The volume to detection was pH dependent for both resins, which is indicative of pH dependent binding affinities. Binding affinity trends were rationalized through (1) uranium speciation in solution and (2) changes in surface charge as a result of ligand deprotonation. At pH 4, both ligands have similar degrees of deprotonation and exhibit similar uranium affinity. As the pH increases, EGMP resin more readily deprotonates due to its lower pK$a_2$, resulting in a more negative surface charge as compared to the MPA resin. Meanwhile, uranium speciation in solution transitions from containing mostly exchangeable cations to entirely non-exchangeable anions. The combination of these phenomena suggests that the binding mechanism changes from ion exchange (pH 4) to ligand exchange (pH 8).

The extractive scintillating resins developed in this work have comparable detection efficiencies to the best ones previously reported in the literature. Furthermore, they can achieve a selective separation at neutral pH—avoiding the use of consumable chemicals—and they are stable due to the covalent incorporation of the fluorophore and extractive ligand. Table 7.1 compares the present work with those reported in the literature.
Table 7.1. Summary of detection efficiencies for uranium-binding extractive scintillating resins.

<table>
<thead>
<tr>
<th>Separation Scheme</th>
<th>U(VI) Concentration</th>
<th>Matrix</th>
<th>Detection Efficiency</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂ coated PVT resins</td>
<td>102 Bq L⁻¹ Natural U(VI)</td>
<td>Neutral pH ground water</td>
<td>17-37%</td>
<td>9</td>
</tr>
<tr>
<td>Actinide Resin®, BC-400 scintillating beads</td>
<td>30 ppm Natural U(VI)</td>
<td>pH 1 ground water</td>
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<td>8</td>
</tr>
<tr>
<td>Dipex® coated macroporous αNPO-PS bead</td>
<td>30 ppm Natural U(VI)</td>
<td>pH 1 ground water</td>
<td>52 ± 2.6%</td>
<td>8</td>
</tr>
<tr>
<td>Dipex® coated αNPO-PVT scintillating bead</td>
<td>30 ppm Natural U(VI)</td>
<td>pH 1 ground water</td>
<td>58 ± 20%</td>
<td>8</td>
</tr>
<tr>
<td>MS-MPA Resin</td>
<td>500 Bq L⁻¹ ²³³U</td>
<td>pH 4, 6 and 8 ground water</td>
<td>36 ± 4%</td>
<td>present work</td>
</tr>
<tr>
<td>EGMP Resin</td>
<td>500 Bq L⁻¹ ²³³U</td>
<td>pH 4, 6 and 8 ground water</td>
<td>46 ± 8%</td>
<td>present work</td>
</tr>
</tbody>
</table>

In Chapter 7, uranium-binding alpha spectroscopy substrates were synthesized by the modification of commercially available polyether sulfone membranes by two methods: (1) physical deposition of a polymer film by size exclusion filtration and (2) UV-polymerization to grow polymer chains from the membrane surface. Both preparation methods resulted in membranes with high permeability coefficients (> 200 LMH/bar). The molecular weight cutoff (MWCO) of the membrane did not affect the peak resolution in the pulse-height spectrum. Additionally, it was found that membranes selectively retained uranium over the other ions found in simulated ground water (Ca²⁺, Cl⁻, NO₃⁻, K⁺, HCO₃⁻, Mg²⁺, SO₄²⁻, Na⁺, F⁻, Si⁴⁺) — a result consistent with findings from Chapter 6. Alpha spectra produced with the membrane-based substrates were able to. This work provides the initial proof-of-concept work for ultrafiltration as a tool for rapid purification and simultaneous sample mounting of alpha spectroscopy substrates.
7.2 Recommendations

7.2.1 Extractive Scintillating Resin Design

7.2.1.1 Resin Porosity

The diffusion studies from Chapter 4 illustrate that extractive scintillating resins will have higher detection efficiency if the alpha decay event occurs within the internal resin volume rather than the resin surface. Unfortunately, the time scale of uranium diffusion in the current resin design (days) is unreasonably long compared to the time scale of detection (minutes). All extractive scintillating resins studied in this dissertation used toluene as a porogen, which has been shown to produce resins with a high surface area but low pore volume\textsuperscript{58}. The large internal surface area was rendered useless because the large and highly charged uranyl cation could not readily enter the pores. I suggest that future work explore the use of porogens that will create larger pore volumes to facilitate the uranyl cation diffusion into the polymer matrix at a more reasonable rate for online detection measurements. Egawa et al.\textsuperscript{42} prepared poly[(4-chloromethyl styrene-co-styrene-co-divinylbenzene) resins, which were later phosphorylated and hydrolyzed, for the extraction of uranium from seawater using 2,2,4-trimethyl pentane as a porogen. They found that varying the ratio of porogen to monomers affected the capacity of the resin. Figure 7.1 shows the relationship between porogen concentration and resin capacity for different ions.
Based on the results of Chapter 6, the EGMP resin is more promising than the MS-MPA resin due to its facile synthesis and improved uranium affinity. Future EGMP resin designs should utilize 2,2,4-trimethyl pentane as a porogen. Ethylene glycol methacrylate phosphate will have a different solubility parameter than 4-vinylbenzyl chloride; therefore, experiments should be conducted by varying the porogen to monomer ratio to determine the formulation that maximizes uranium capacity.

### 7.2.1.2 Ligand Design

In Chapters 3 and 6, alkyl phosphate and phosphonic acid ligands were shown to be selective for uranium over common ions in ground water. Based on the ion-exchange isotherm data, the EGMP resin (alkyl phosphate) had a higher affinity for uranium than the MS-MPA resin (phosphonic acid) in pH 4 DI water. The difference in affinity was

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**Figure 7.1.** Effect of porosity on the adsorption of various metal ions; resin, RSP (DVB 10 mol%). Open circles represent UO$_2^{2+}$ (pH 3.3); closed circles represent Fe$^{3+}$ (pH 2.4); Half-filled circles represent Ca$^{2+}$ (pH 5.6). Reproduced with permission by John Wiley and Sons Inc. 42.
attributed to the presence of neutral donors in the ethylene glycol methacrylate phosphate monomer (ether oxygens and carbonyl groups), which play a role in synergistic binding and increase metal ion affinity. Alexandratos et al.\textsuperscript{100} studied the role of hydrogen bonding of phosphonic and phosphinic acid ligands on metal ion affinity. In this study, they used Au(III) as a representative soft metal ion and Eu(III) as a representative hard metal ion to probe the binding mechanisms and polarizability of phosphoryl oxygens in different organophosphorus ligands. They found that hydrogen bonding between ligands led to a decrease in metal ion affinity. This effect was more pronounced in the diprotic, phosphonic acid ligand than the monoprotic, phosphinic acid ligand. For future work, it would be interesting to incorporate a dialkyl phosphate or phosphinic acid into the extractive scintillating resin. This may improve metal ion affinity, resulting in lower volumes to detection; however, no studies have been performed to assess whether or not the change in metal ion affinity would affect the selectivity of the functional group.

\subsection*{7.2.2 Density Functional Theory}

In Chapter 6, it was hypothesized that the mechanism of uranium binding to the phosphonic acid and alkyl phosphate ligands shifts from ion-exchange at pH 4 to ligand exchange at pH 8. To support this hypothesis, simulations are being performed with density functional theory in Gaussian 09 software. Density functional theory is a quantum mechanical modelling method that allows for the calculation of ground state energies of molecules. For a given reaction, each reactant and product can be modeled individually in the Gaussian 09 program and each Gibbs free energy can be calculated. Then, the sum of products minus reactants can be used to calculate the Gibbs energy of
complexation. The thermodynamic favorability of the complex is determined by the sign and magnitude of the energy of complexation.

The validity of density functional theory calculation depends on the basis sets chosen to describe the electron density of the atoms in the simulation. Uranium is an f-shell element with delocalized electrons; therefore, electrons near the nucleus are moving at a higher velocity than electrons in the rest of the electron cloud. The difference in electron velocities must be accounted for using the theory of special relativity in order to more accurately model the electron density of the atom. Based on the work of Tian et al.\textsuperscript{96} and with guidance from Dr. Steven Pellizzeri of the Getman Research Group at Clemson University, the Stuttgart quasirelativistic effect core potential and basis sets were used to describe uranium while the 6-31G(d) basis set was used to describe phosphorus, carbon and oxygen. Simulations are underway to elucidate the binding energies for uranyl-carbonate and uranyl-phosphate complexes.

In addition to completing the current set of simulations, future work could include applying this technique to study the binding mechanisms of other special nuclear material, like plutonium, to new ligands. Understanding how ligand structure influences uranium affinity may allow for the rational design of a new class of uranium-selective materials.

7.2.3 Automation of flow-cell detection experiments

Detection efficiency calculations require the collection of all effluent fractions to complete a mass balance on the column. Fraction collection can be automated using the fraction collector in Lab 117 in the L.G. Rich Laboratories. I recommend using the
fraction collector in the “time interval” mode instead of the “drop” mode. The “drop” mode is inconsistent and often cues the next vial prematurely.

Further process automation can be achieved through a program such as LabVIEW and several programmable valves. The following is a typical procedure for a volume to detection experiment: (1) background spectrum collection with a pH adjusted background solution, (2) activity loading using a radionuclide containing solution; (3) column elution with sodium carbonate; (4) pH adjustment with acid; (5) column rinsing with DI water. This procedure requires 5 different feed solutions. Currently, the column operator must be present to move the inlet tubing between solutions manually—which is reasonable for short experiments with high activity feeds; however, more sophisticated statistical analysis often requires longer background collection times and lower activity feeds will induce higher volumes to detection. To enable long-term measurements (possibly 12 hours of data collection), it would be advantageous to develop a protocol in LabVIEW that would allow the user to program a multi-port valve to draw from the various feed solutions in a prescribed order.

7.2.4 Membrane Design

As discussed in Section 7.2.1.2 it would be interesting to incorporate monoprotic organophosphorus ligands onto the membrane surface and evaluate the effect on metal ion affinity and uranium selectivity.

Regarding polymer layer formation, there are several approaches that can be taken to improve the uniformity and thickness of the selective layer that may impact peak resolution. Film thickness for SEFMs can be controlled by simply filtering smaller
volumes of the polymer solution during deposition. A useful study would be to vary the film thickness and quantify the trade-off between gain in spectral resolution due to thin films and losses in uranium recovery due to reduced binding sites. Currently, UVMs are synthesized by an uncontrolled free radical polymerization that occurs on the membrane surface and inside of pores. Utilizing small molecule surface modification techniques, rather than polymer grafting, to modify the surface may reduce attenuation of alpha particles in the polymer film and improve resolution.

7.2.5 Membrane Evaluation

Membranes in the present study were evaluated for their uranium selectivity over common ions found in ground water. The most complicated sample tested involved a mixture of uranium-238 and uranium-233 in simulated ground water. In realistic conditions, the uranium present will be mostly comprised of natural uranium, which is a mixture of uranium-234, uranium-235, uranium-238 and all daughter isotopes in the decay chains. Depending on the age of the sample or the date since its last purification, natural uranium can contain the following alpha-emitting isotopes: actinium-227; astatine-215,218,219; bismuth-210, 211, 214; francium-223; lead-210; polonium-210, 211, 214, 215, 218; protactinium-231; radium-223, 226; radon-219, 222 and thorium-227, 230. Alpha-emitters that are of concern (i.e. may interfere with the alpha peaks for uranium) are: thorium-230 (4.770 MeV), radium-226 (4.871 MeV) and actinium-227 (4.95 MeV). Special attention should be paid to assure the selectivity of the developed membranes for uranium over thorium, radium and actinium. Selectivity of phosphonic
acid for uranium over thorium has been demonstrated in the literature at pH 4\textsuperscript{50}; however, these studies should be expanded to pH neutral ground water.
Appendix A

Supplementary Materials for Dissertation Chapters

Figure A-1. Ion exchange isotherm for depleted uranium on MS-MPA resin (presented in Chapter 3) at pH 4 modeled by the Langmuir-Freundlich isotherm: \( B = \frac{N_i a F^m}{1 + a F^m} \).

- \( B \) is the equilibrium concentration of uranium bound to resin (mmol/g).
- \( N_i \) is the maximum capacity for uranium (mmol/g).
- \( m \) is a heterogeneity index that ranges from 0 (heterogeneous) to 1 (homogeneous).
- \( a \) is a fitting parameter related to the binding affinity of the ligand for uranium.
Figure A-2. MS-MPA resins from Chapter 3 were loaded sequentially with 3.8 Bq mL\(^{-1}\) uranium-233 in pH 4 DI water. The pulse-height spectrum for each column was collected in the Perkin Elmer Quantulus Liquid Scintillation counter for 1 h linear detector response to sequentially loaded uranium-233.

Figure A-3. MS-MPA resins from Chapter 3 were loaded sequentially with uranium-233 from pH 4 DI water solutions. The pulse-height spectrum was collected using the Perkin Elmer Quantulus Liquid Scintillation Counter for 1 h. The pictured spectrum is for a MS-MPA column loaded column with 18.8 Bq of uranium-233.
Figure A-4 FTIR spectra of unfunctionalized resin (bottom) and functionalized resin (top) discussed in Chapter 4. Characteristic absorbance peaks are observed for phosphonate at 1042 cm$^{-1}$ and phosphonic acid 2200 cm$^{-1}$ supporting the successful incorporation of phosphonic acid functionality.
Table A-1. In Chapter 5, uranium speciation calculations are conducted in VisualMINTEQ. This table summarizes thermodynamic data referenced by VisualMINTEQ. The program calculates all possible equilibrium reactions that can occur for uranium in the simulated water. The integers reported in the columns below each ionic species refer to stoichiometric coefficients in each reaction.

<table>
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<th>Species</th>
<th>log K</th>
<th>$\Delta H_{\text{reaction}}$ (kJ/mol)</th>
<th>CO$_3^{2-}$</th>
<th>Ca$^{2+}$</th>
<th>Cl$^{-}$</th>
<th>F$^{-}$</th>
<th>H$^{+}$</th>
<th>H$_2$O</th>
<th>K$^{+}$</th>
<th>Mg$^{2+}$</th>
<th>NO$_3^{-}$</th>
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**Figure A-5.** In Chapter 6, the permeability coefficients are reported for 30, 50 and 100 kDa UVMs and SEFM. This figure provides an example of the pure water flux data used to calculate the permeability coefficient for a 50 kDa UVM. The permeability coefficient, $A$, is the slope of the line.

**Figure A-6.** Alpha spectra of UVMs, described in Chapter 6, with MWCO 30 kDa (left) and 50 kDa (right) exposed to 10 Bq of uranium-233. Spectra were collected for 1 h at a distance of 9mm from the detector surface of a Canberra Alpha Spectrometer.
Figure A-7. Alpha spectra of SEFM s, described in Chapter 6, with MWCO 30 kDa (left) and 50 kDa (right) exposed to 10 Bq of uranium-233. Spectra were collected for 1 h at a distance of 9mm from the detector surface of a Canberra Alpha Spectrometer.
Figure A-8. Pulse-height spectrum of 50 kDa PES membrane after filtering 10 mL of 0.5 Bq mL\(^{-1}\) uranium at pH 6. Spectrum collected for 1 h at 9mm from detector surface. No significant activity was retained on the membrane surface without the addition of a selective polymer film.
Appendix B

Confocal Microscopy

[Excerpts are drawn from Polymer 56, 271-279 with minor revisions]

Introduction

The detection mechanism for extractive scintillating resins is a multi-step process. First, the uranium must bind to the resin. While the uranium is bound to the resin, it is decaying and emitting alpha particles. Those alpha particles transfer their kinetic energy to the bulk 4-methyl styrene polymer matrix. To dissipate that energy gain, the polymer scintillates and emits light in the ultraviolet (UV) region of the electromagnetic spectrum. The fluorophore absorbs the UV light and shifts the wavelength to the visible spectrum such that it can be detected with a conventional photomultiplier tube. In order to maximize the detection efficiency and capacity of the extractive scintillating resin, it is necessary to bind uranium within the entire volume of the polymer matrix and incorporate the fluorophore continuously throughout the polymer sensor. Several factors affect the ability of the uranium to penetrate the polymer matrix such as ligand grafting density and distribution, pore volume and porosity of the resin.

Quantitative fluorescence techniques like spectrofluorometry can be used to measure the emission wavelength and the total fluorescence of a sample; however, it cannot provide information about the spatial distribution of the fluorophore within the polymer sensor. Laser scanning confocal microscopy (LSCM) is an optical microscopy technique that utilizes a pinhole aperture to filter out of plane light before it reaches the
photomultiplier tube detector, shown in Figure B-1. This configuration allows for depth discrimination and optical sectioning of a sample. It is a convenient tool for radiation sensor design because it allows for the imaging of the spatial distribution of the fluorophore within the sensor.

Figure B-1. Schematic of a laser scanning confocal microscope.

**Microscopes**

The Clemson Light Imaging Facility (CLIF) is a user-facility located in the Life Sciences Facility on the main campus of Clemson University. All confocal microscopy studies were performed in this facility after proper training from Dr. Terri Bruce or Ms. Rhonda Powell.

The first imaging protocol in this work utilized the Nikon Eclipse Ti LSCM in fluorescence mode with a Nikon 20x oil immersion objective with a numerical aperture of 0.75 and an averaging program of 4 scans. The excitation laser has a helium-neon
source with a wavelength of 408 nm. Analysis of the confocal images was performed in NIS-Elements Version 3.22.13.

The second imaging protocol in this work utilized the Leica SPE LSCM in fluorescence mode with a Leica 10x air objective with a numerical aperture of 0.3 and averaging program of 4 scans. The excitation laser was a helium-neon laser with a wavelength of 408 nm. Analysis of the confocal images was performed within the Leica LAS Light software.

**Spatial distribution of fluorophore: sample preparation and analysis**

Initially, samples were prepared for confocal microscopy by submerging them in a glycerol in a multi-well plate with a glass bottom. Beads were imaged at 4 μm increments through the Z-plane using the Nikon Eclipse Ti LSCM. Figure B-2 shows the confocal image of the center of the resin. From this image, it appears that the fluorophore is heterogeneously distributed throughout the resin and is concentrated at the outer edges of the resin. Upon further consideration, it was hypothesized that the apparent fluorophore distribution was an artifact of the sample preparation. The resins are >100 μm in diameter meaning that the excitation photons incident on the center of the spherical resin must traverse more of the polymer matrix than the light incident on the outer edges. An analogous process occurs for the emission photons. Therefore, photons either incident or nascent from the center of the resin would have a higher probability of attenuation within the polymer prior to reaching the detector.
Figure B-2. Confocal image of the center of a poly(styrene-co-divinyl benzene) resin with physically incorporated fluorophore, DM-POPOP, and toluene porogen. Sample was not sectioned prior to imaging.

To overcome the limit of depth of penetration of the confocal microscope and obtain unambiguous spatial fluorescence intensity distribution measurements, the resin was sectioned into 8 μm slices prior to imaging. Confocal images were taken 4 μm below the surface of the slice to avoid artifacts associated with the sectioning protocol. To prepare samples for the LSCM, the resin was embedded in TissueTek® O.C.T. Compound 4583 and then sectioned at -20 °C into 8 μm slices using a Microm HM 505N Cryostat-Microtome with a diamond coated blade (Fisher Scientific, Edge-Rite™). The resulting slice was mounted on a microscope slide (Fisher Scientific, Fisherbrand™ InkJet), a cover glass (Fisher Scientific, Fisherbrand™ no. 1.5) was applied to prevent delamination of the resin and the four corners of the cover glass were sealed with clear nail polish

Figure B-3 shows the center of an 8 μm section of poly(styrene-co-divinyl benzene), the same polymer imaged in Figure B-2. The imaged of the sectioned sample shows that the fluorophore is distributed throughout the polymer bead; however, there is a higher concentration at the edges.
Figure B-3. Confocal image of the center of an 8 µm poly(styrene-co-divinyl benzene) resin section with physically incorporated fluorophore, DM-POPOP, and toluene porogen.

The effect of porogen on the spatial distribution of the fluorophore was studied using the improved sample preparation method as part of an overarching work to study the structure, porosity and optical fluorescence properties of scintillating resins by Bliznyuk et al.\textsuperscript{58} Resins were prepared by suspension polymerization and the fluorophore, DM-POPOP, was included in the oil phase during synthesis. The effect of four different porogens (no porogen, toluene, Span-80 and heptane) on the spatial distribution of the fluorophore was studied. Figure B-4 shows representative confocal microscopy images of poly(styrene-co-divinyl benzene) resin cross-sections with the fluorophore incorporated by mixing during the suspension polymerization process and the corresponding normalized intensity profiles.
Figure B-4. Confocal images for poly(styrene-co-divinylbenzene) resin in which DM-POPOP was incorporated by mixing are shown for each porogen type: (a) no porogen, (b) toluene, (c) Span-80 and (d) heptane. Specific pore volumes and surface areas increase from left to right. The corresponding normalized fluorescence intensity distributions are shown below each resin: (e) no porogen, (f) toluene, (g) Span-80 and (h) heptane. Reproduced with permission from Elsevier Ltd.

The images of the nonporous resin and the resin prepared with toluene porogen show a non-uniform radial distribution of the fluorophore. These resins, which have low specific pore volumes (<0.005 cm$^3$ g$^{-1}$), exhibit an intensity maximum at the edges of the resin. The images of the resins synthesized with either heptane or Span-80 as the porogen show a more uniform distribution of the fluorophore. These samples have higher specific pore volumes (>0.016 cm$^3$ g$^{-1}$) and do not exhibit maxima at the center or edges of the resin. The confocal image analysis suggests that the spatial distribution of the fluorophore depends on the pore volume, which is a function of both porogen type and degree of cross-linking.

**Fluorophore leaching studies: sample preparation and analysis**
Poly(styrene-co-divinylbenzene) resins were synthesized using toluene as the porogen and either α-NPO or v-NPO as the fluorophore, as described in Chapter 2. Luminosity measurements were conducted before and after contacting the resins with methyl acetate to assess the stability of the fluorophore within the resin, as described in Chapter 2. The same resins were analyzed by confocal microscopy using the Leica SPE LSCM. To make a direct comparison, the resins were imaged using the same gain and laser power settings. **Figure B-5** shows the confocal images of the resins containing α-NPO and v-NPO, before and after leaching with methyl acetate.

**Figure B-5.** Confocal images of poly(styrene-co-divinylbenzene) resins containing: (a) α-NPO before contact with methyl acetate, (b) α-NPO after contact with methyl acetate, (c) v-NPO before contact with methyl acetate, (d) v-NPO after contact with methyl acetate.
The confocal images imply that not only is the v-NPO resin brighter than the α-NPO resin, but it also maintains its brightness after exposure to methyl acetate. The difference in brightness is attributed to a higher incorporation of vinyl version of the fluorophore in the suspension polymerization reaction than the non-polymerizable version. This reasoning is supported by Seliman et al. who performed total nitrogen measurements to determine the degree of incorporation of each fluorophore in each sample. The vinyl version of the fluorophore (v-NPO) is more stable within the polymer resin because it is bound covalently within the polymer matrix. These observations are consistent with the data presented in Chapter 2.
Appendix C

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<td>Uranium-selective adsorbent materials for environmental radiation sensing</td>
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<td>Clemson University</td>
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