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Polymer Sensors for the Quantification of Waterborne Uranium

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Polymer Sensors for the Quantification of Waterborne Uranium

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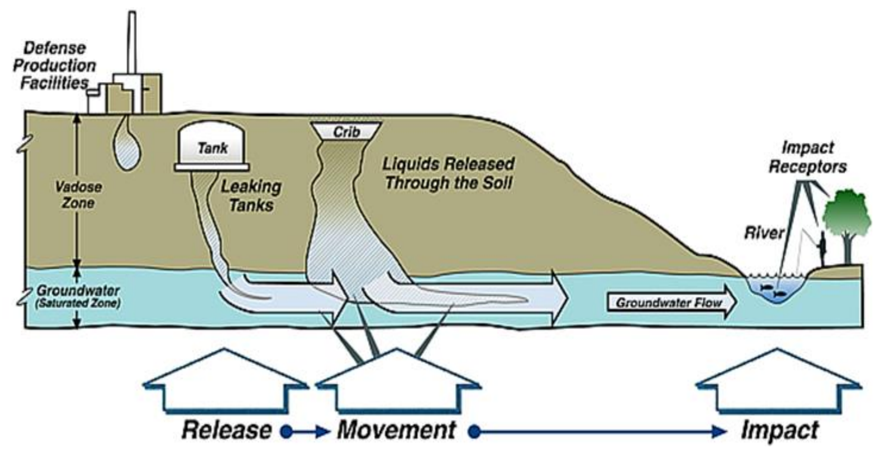
Background and Motivation

❖ Radionuclides can be introduced into the environment through clandestine nuclear activities such as assembly of weapons of mass destruction.

❖ A recent development in environmental sensing is a portable, flow cell detector that utilizes extractive scintillating (ES) resin.



❖ The ES resin serves the dual purpose of (1) concentrating the radionuclide of interest and (2) serving as a radiation transducer.

❖ Nowadays, such resins are produced by physically absorbing the active components into a polymer matrix which yields resins with poor stability as the active components leach from the resin over time.

❖ **Our research objective is to synthesize a new class of stable, extractive scintillating resin for use in flow cell radionuclide detector by incorporating covalently bound active components.**

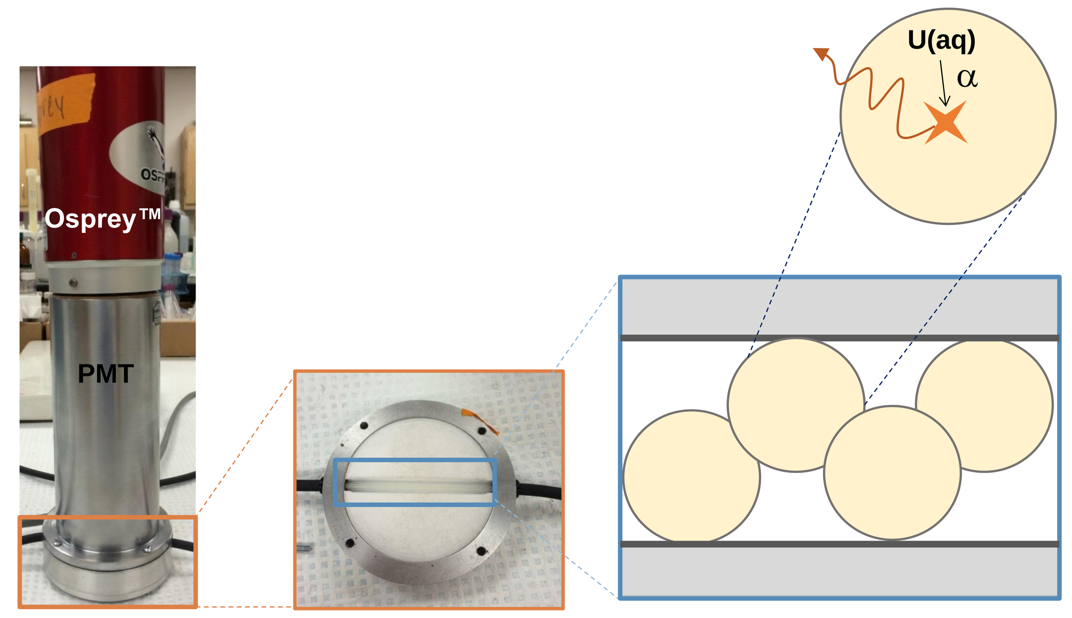


Figure 1: The flow cell detector (left) is 12 inches tall, lightweight and able to connect to a computer over a WIFI. Extractive scintillating resin is packed in the PTFE column (center) which has an inner diameter of 1/16 inch. The sensing mechanism is as follows: uranium binds to the resin and emits an alpha particle during its radioactive decay. The alpha particle deposits its energy into the polymer matrix. That energy is then transferred to the fluorophore which emits a photon. The photomultiplier tube of the detector converts photons to an electrical signal which is transmitted to the computer software.

Design Criteria and Challenges

Desirable Sensor Properties
❖ Rapid Detection
❖ High sensitivity
❖ Linear Response
❖ Robust, stable resin

Desirable Properties for Extraction
❖ High capacity relative to analyte concentration
❖ High quantity of ligand
❖ Selectivity for analyte over competitors

Desirable Properties for Fluorescence
❖ Strong emission signal in visible range
❖ Optically transparent resin

Challenges
❖ Ligands required for extraction can quench the photo signal

❖ Synthetic pathway to selective ligand can be damaging to fluorophore or scintillator

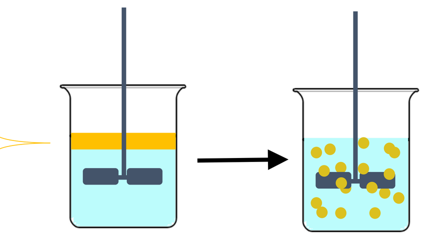
❖ Crosslinking can increase stability but hinder adsorption kinetics

❖ Interplay between experimental conditions needed for rapid analysis and high detection efficiency

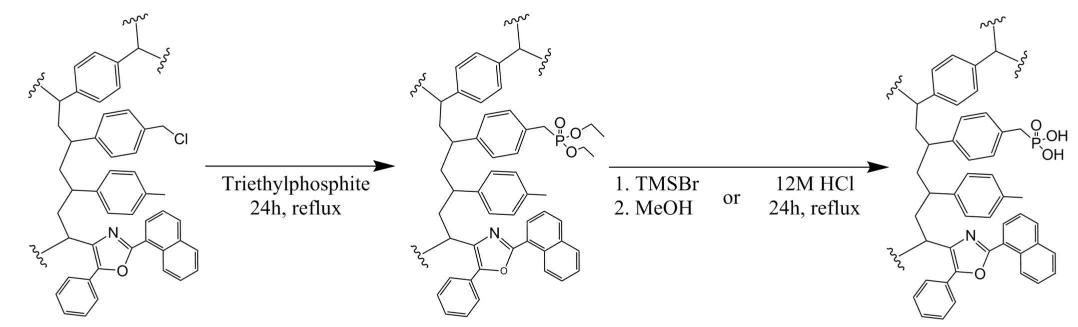
Experimental Methods

Step 1: Suspension Polymerization

Component	Purpose
divinylbenzene	Crosslinker, provides mechanical and chemical stability
4-chloromethyl styrene	Initiator site for functionalization
4-methyl styrene	Scintillator, transfers energy from alpha particles to fluorophore
toluene porogen	Porogen, creates expanded gel network
v-NPO	Fluorophore, emits light signal



Step 2: Solid Phase Synthesize Techniques to Add Functional Groups



Step 3: Resin Characterization

Technique	Purpose
Fourier Transform Infrared Spectroscopy (FTIR)	Support functionalization reactions
Potentiometric Measurements with Ion Selective Electrode (ISE)	Quantify the functional groups attached during functionalization
Spectrofluorometry	Measure emission wavelength and intensity of resin
Static Binding Experiments	Measure maximum resin capacity with U-238
Scintillation Counting	Determine the detection efficiency of the resin

Characterization: Extractive Ligands

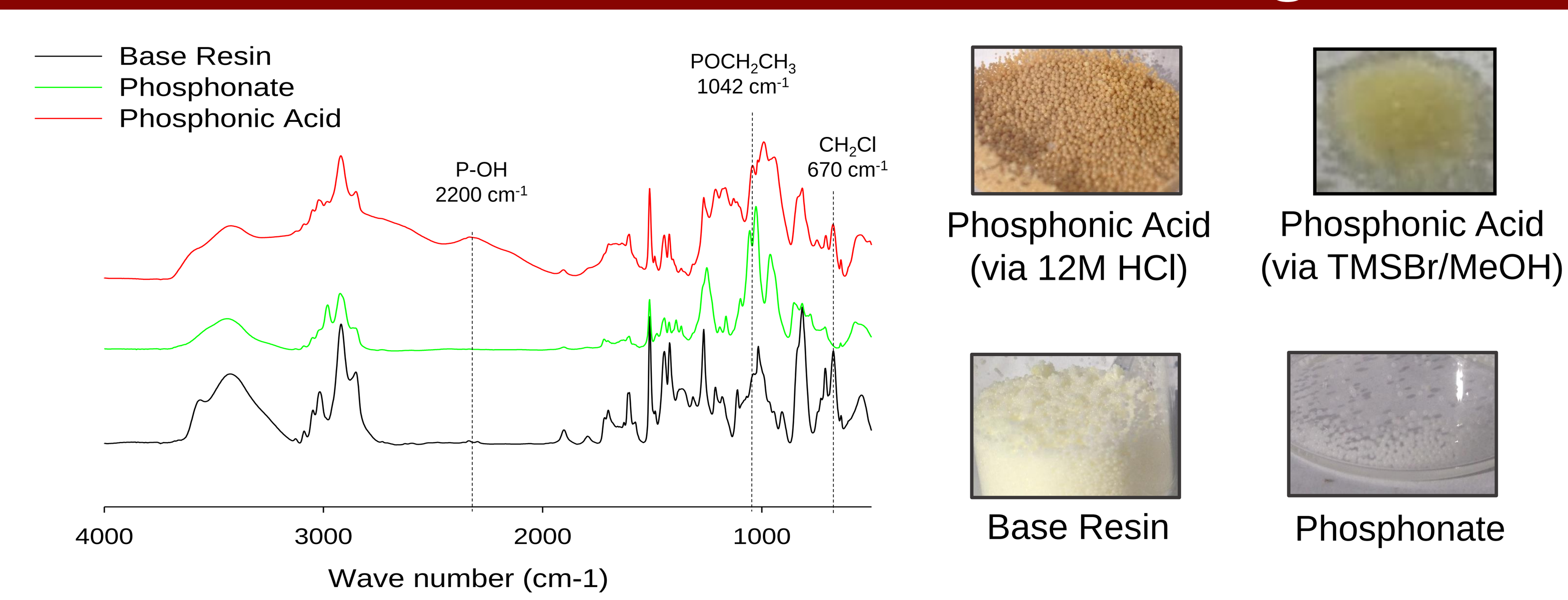


Figure 2: FTIR spectroscopy (left) shows characteristic peaks supporting each step of the synthesis scheme. The phosphonate resin shows characteristic absorbances for P-OEt at 1042cm-1. The phosphonic acid spectrum shows a decrease in the ester peak and the ingrowth of the P-OH at 2200cm-1. Both hydrolysis routes, 12M HCl and TMSBR mediated methanolysis, yield the phosphonic acid moiety; however, they produce resins of different colors (right).

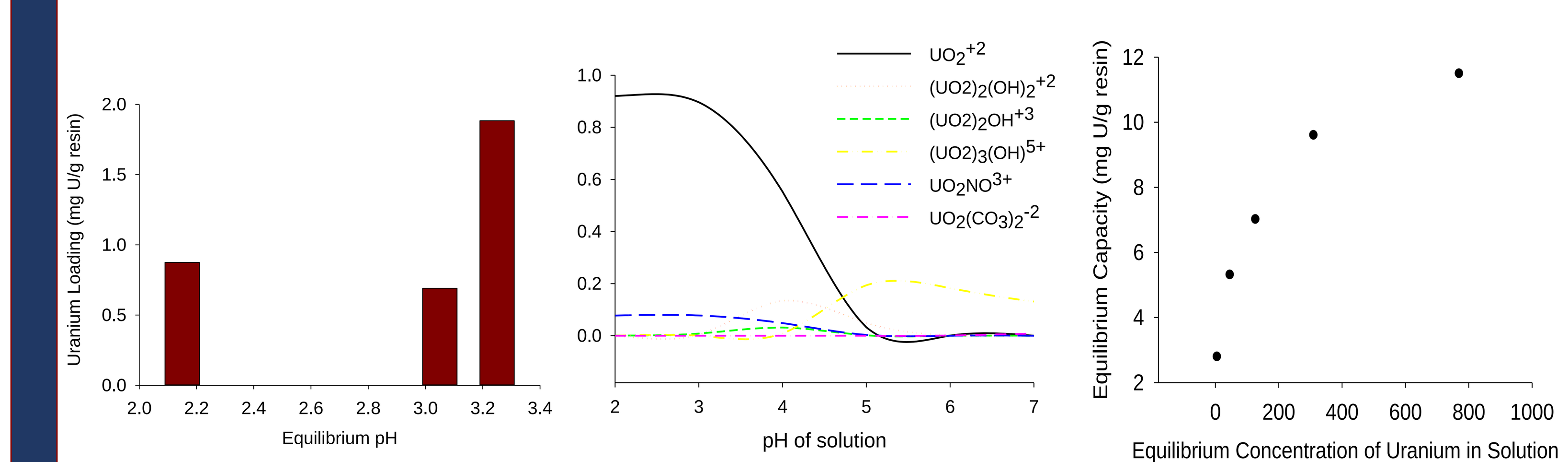


Figure 3: Static binding experiments were performed at varying pH values, well below and near the pKa of phosphonic acid in 100ppm U-238 solution (left). Speciation of uranium(VI) in nitric acid solutions (center) was calculated using Visual MINTEQ software. Langmuir isotherm (right) indicates that the resin has a maximum capacity of 16 mg Uranium/ g resin.

Characterization: Fluorescence

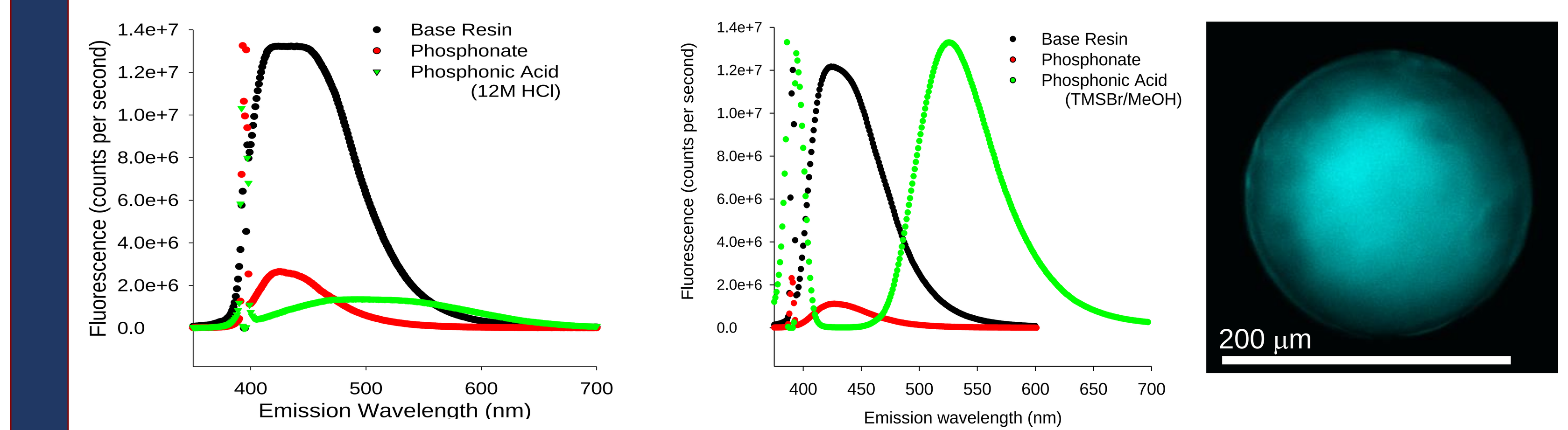


Figure 4: Emission spectrum of the resin which was hydrolyzed by 12M HCl (left). Emission spectrum of the resin which was hydrolyzed by TMSBr/MeOH (center). Confocal image showing the fluorophore distribution within the functionalized resin bead cross-section (right)

Sensor Performance

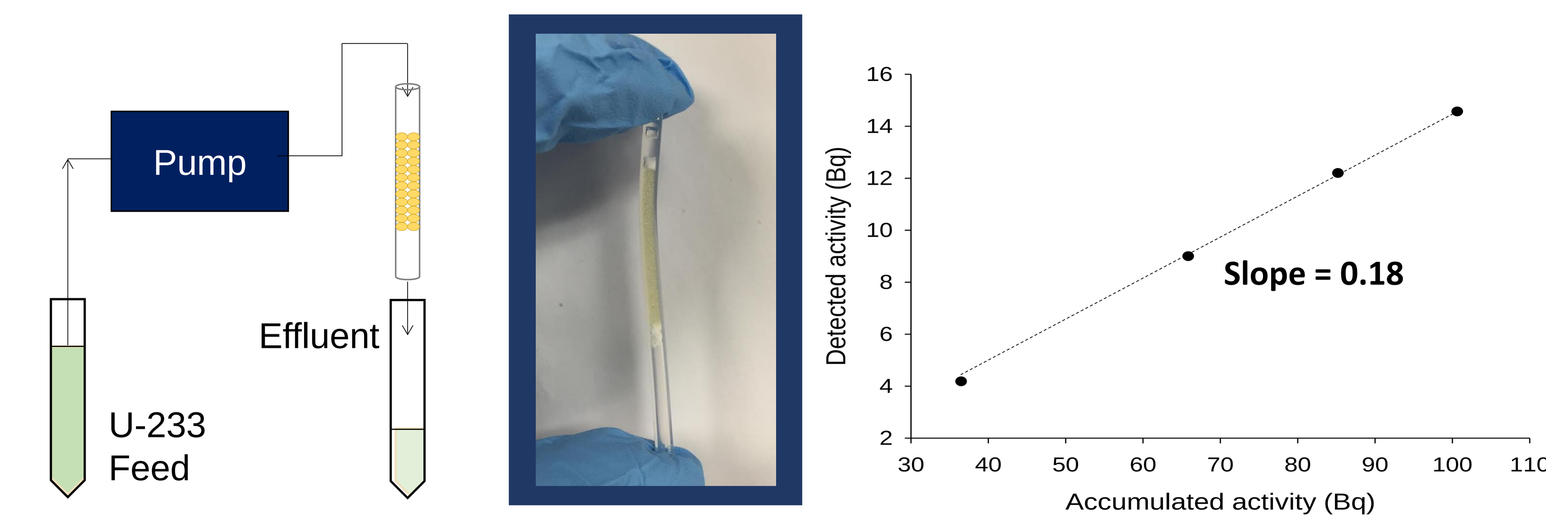


Figure 5: For sensor performance testing, the U-233 feed (4 Bq/L) at pH=4 was pumped through a column packed with phosphonic acid resin (left). The feed, column (center) and effluent were all analyzed by liquid scintillation counting. The detection efficiency of the resin for U(VI) was 18%

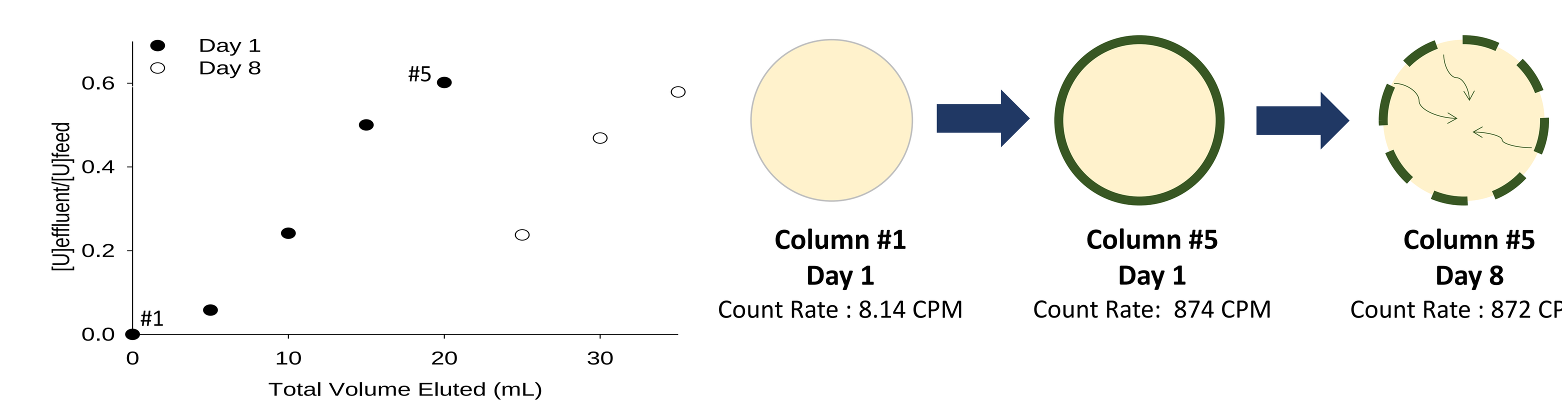


Figure 6: Five successive column loadings were performed at a flow rate of 0.3 mL/min with a feed solution activity of 4 Bq/mL. The column was left for 8 days and counted again before continuing the experiments.

Conclusions

❖ Hydrolysis via TMSBr/MeOH provides a synthesis route that preserves scintillation properties
❖ Resin has an optimum binding pH of 3.3 and maximum capacity of 16 mg U /g resin
❖ Preliminary experiments show detection efficiencies of 18% for U-233 with a linear sensor response
❖ Dynamic binding data implies that uranium is only accessing the surface of the resin

Future Work

Resin Design
❖ Evaluate detection efficiency as a function of ligand/fluorophore ratio
❖ Investigate ligands with high Kd values

Column Conditions
❖ Experimentally determine effect of column diameter, bead size and location of decay event on detection efficiency

Acknowledgements

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