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Synthesis and Characterization of Extractive Scintillating Resin for Ultra-Trace-Level Quantification of Uranium in Aqueous Media

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Synthesis and Characterization of Extractive Scintillating Resin for Ultra-Trace-Level Quantification of Uranium in Aqueous Media

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Background & Motivation

The detection and quantification of radionuclides in aqueous media is of interest to both the Environmental Protection Agency, for matters of public health, and international organizations like the Comprehensive Test Ban Treaty Organization, that use environmental samples to investigate claims of illicit nuclear activities.

The current method of quantification involves batch style analytical techniques which utilize bulky instruments. Portable, flow cell detectors utilizing extractive scintillating resin with physically sorbed extractants and fluorophores have been developed; however, this resin shows poor long term stability as the active components leach from the resin over time. There is a need to develop chemically and mechanically stable extractive scintillating resin for flow cell detectors.

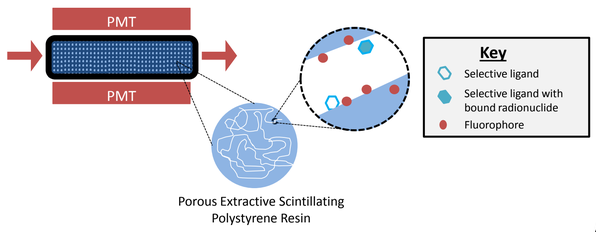


Figure A. Diagram of flow cell detector with physically sorbed fluorophore and extractive ligand within porous polystyrene resin.

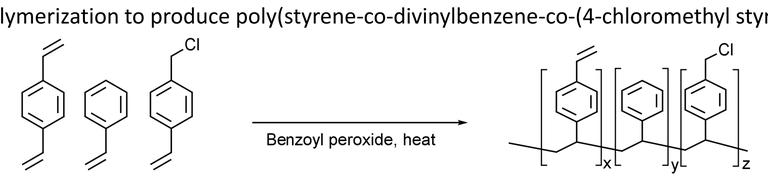
Research Objectives

- ❑ **Synthesize a new class of stable, extractive scintillating resin for flow cell radionuclide sensors**
  - ❑ Physically entrap fluorophore during suspension polymerization
  - ❑ Covalently bind uranium selective ligand to the pore surface
- ❑ **Evaluate resin performance and stability**
  - ❑ Experimentally determine binding capacity of uranium selective resin
  - ❑ Compare the uranium affinity and binding capacity of phosphonate functionalized resin with phosphonic acid functionalized resin
  - ❑ Compare the binding mechanisms of ion exchange and chelation for this system

Experimental Methods

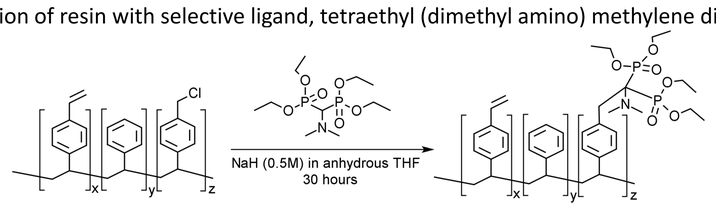
Synthetic Scheme

Step 1: Suspension polymerization to produce poly(styrene-co-divinylbenzene-co-(4-chloromethyl styrene)) resin

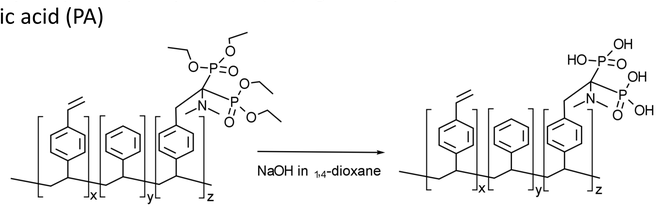


Component	Purpose	Composition by Weight
DM-POPOP	Fluorophore, produces photo signal	1%
Styrene	Spacer, bulk material	64%
Divinylbenzene	Cross-linker, provides mechanical stability of pores	25%
4-chloromethyl styrene	Provides reaction site for functionalization	10%

Step 2: Functionalization of resin with selective ligand, tetraethyl (dimethyl amino) methylene diphosphonate (PE)



Step 3: Base catalyzed hydrolysis of phosphonate (PE) ligand to produce uranium selective ligand, dimethyl amino methylene diphosphonic acid (PA)



Characterization Techniques

Analytical Technique	Purpose
Confocal Microscopy	Analyze fluorophore distribution and intensity profile
ATR-FTIR	Verify the presence of ligands
Silver Nitrate Titration	Quantify accessible chloromethyl groups
pH Titration	Quantify binding sites

Uranium Adsorption: Chelating Resin vs. Ion Exchange Resin

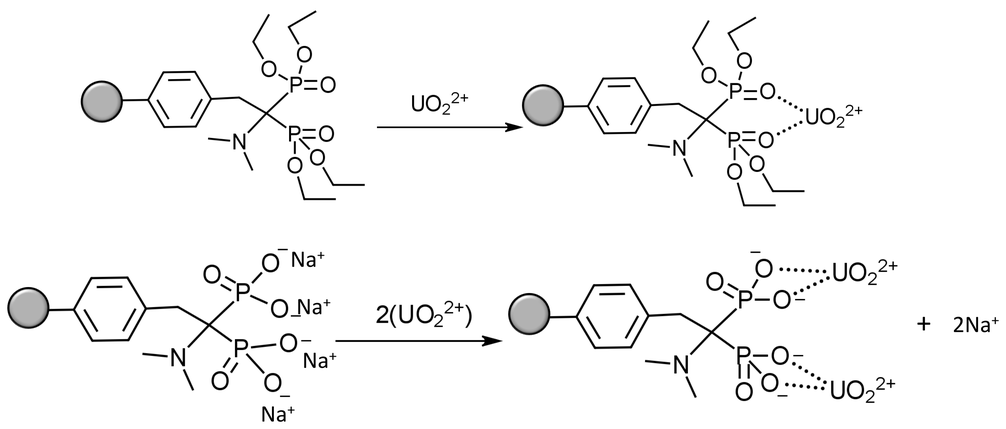


Figure B. The functionalized resin shown in Steps 2 and 3 bind with uranium by two distinct mechanisms at neutral pH. The bisphosphonate functionalized resin chelates with the uranyl cation at the phosphoryl oxygen (top). The bis(phosphonic acid) functionalized resin undergoes cation exchange with a counter cation like Na^+ (bottom).

Results

Characterization of Reaction Products by ATR-FTIR

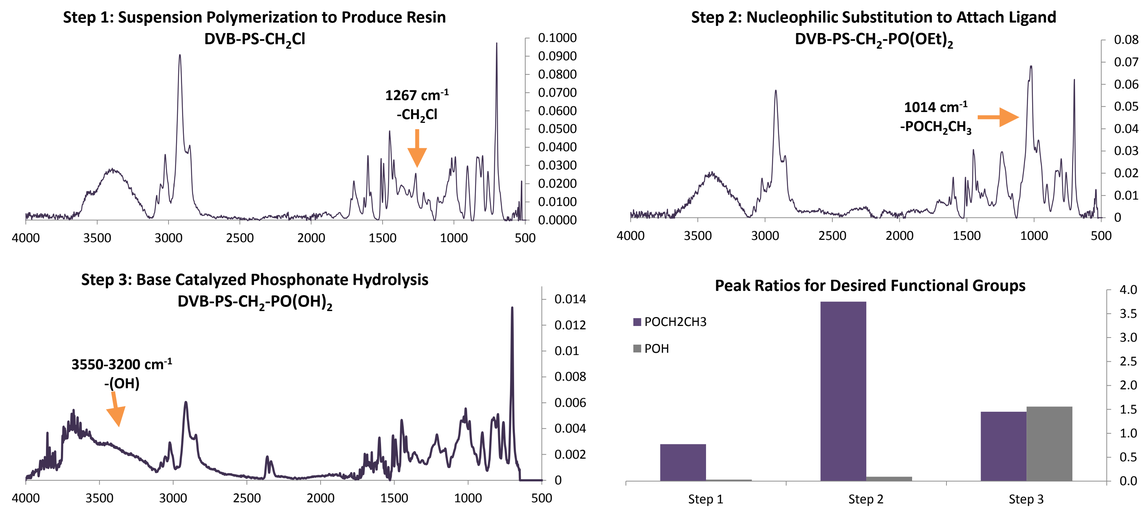


Figure C. ATR-FTIR spectra are shown for each product of synthetic steps 1-3: poly[styrene-co-divinylbenzene-co-(4-chloromethyl styrene)] resin (top left); the tetraethyl (dimethyl amino) methylene diphosphonate functionalized resin (top right); and (dimethyl amino) methylene diphosphonic acid resin (bottom left). Peak ratios were calculated in order to compare spectra with a normalized scale (bottom right).

Analysis of Fluorophore Distribution

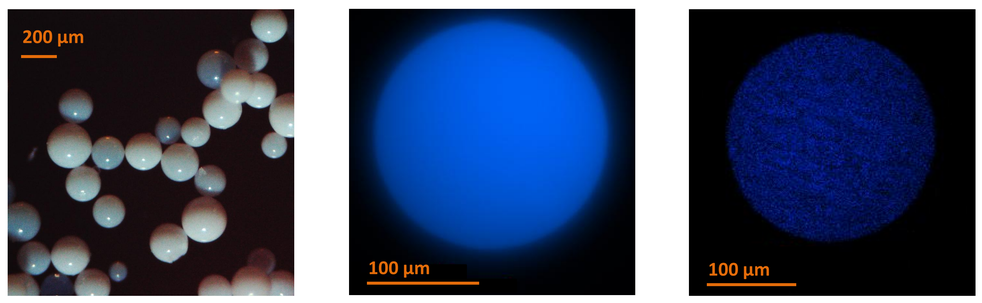


Figure D. The diascopic image of the resin (left) shows the smooth, spherical particles. The episcopic image of the resin (middle) shows the fluorescence of the resin from incorporated fluorophore DM-POPOP. The resin was embedded in TissueTek freezing media and sectioned by CryoSTAT at -20C. The resulting section was imaged by Nikon Ti Confocal Scanning Laser Microscope. The confocal image (right) was taken at the center of the 8µm section.

Uranium Adsorption Experiments

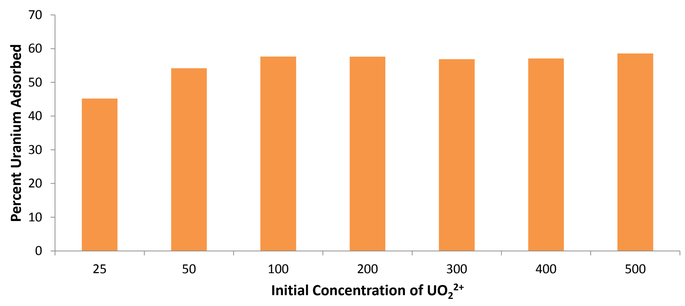


Figure E. Batch uptake experiments were performed for the phosphonic acid functionalized resin neutral pH. The resin consistently adsorbed 50% of uranium out of the solution at varying initial concentrations of uranium.

Conclusions

- ❑ Physical entrapment of the fluorophore during polymerization results in a uniform distribution
- ❑ ATR-FTIR confirms presence of functional groups; however, peak ratios suggest low reaction yield
- ❑ Uranium uptake experiments confirm successful extraction of uranium from solution; however, the constant percent adsorbed across varying concentrations suggests a thermodynamic or kinetic limitation to binding

Future Work

- ❑ Further refine synthesis conditions to improve yield
- ❑ Quantify accessible chloromethyl groups, ligand concentration and hydrolysis yield by titration
- ❑ Continue uranium adsorption experiments
  - ❑ Tetraethyl (dimethyl amino) methylene diphosphonate functionalized resin at neutral pH
  - ❑ Kinetic studies for both functionalized resin

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