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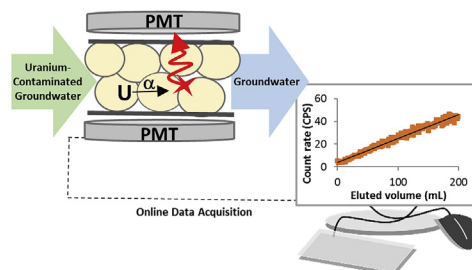
## Extractive scintillating polymer sensors for trace-level detection of uranium in contaminated ground water

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### HIGHLIGHTS

- Extractive scintillating resins synthesized with covalently bound fluor and ligand.
- Methylphosphonic acid-derivitized resins characterized for optical properties.
- Online detection of uranium in ground water demonstrated at near-neutral pH.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This contribution describes the synthesis of robust extractive scintillating resin and its use in a flow-cell detector for the direct detection of uranium in environmental waters. The base poly[(4-methyl styrene)-co-(4-vinylbenzyl chloride)-co-(divinylbenzene)-co-(2-(1-naphthyl)-4-vinyl-5-phenyloxazole)] resin contains covalently bound fluorophores. Uranium-binding functionality was added to the resin by an Arbuzov reaction followed by hydrolysis via strong acid or trimethylsilyl bromide (TMSBr)-mediated methanolysis. The resin was characterized by Fourier-transform infrared spectroscopy and spectrofluorometry. 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. The flow cell detection efficiency for uranium of the TMSBr-mediated methanolysis resin was evaluated at pH 4, 5 and 6 in DI water containing 500 Bq L<sup>-1</sup> uranium-233 and demonstrated flow cell detection efficiencies of 23%, 16% and 7%. Experiments with pH 4, synthetic groundwater with 50 Bq L<sup>-1</sup> uranium-233 exhibited a flow cell detection efficiency of 17%. The groundwater measurements show that the resins can concentrate the uranyl cation from waters with high concentrations of competitor ions at near-neutral pH. Findings from this research will lay the groundwork for development of materials for real-time environmental sensing of alpha- and beta-emitting radionuclides.

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### 1. Introduction

The Environmental Protection Agency regulates drinking water quality in the United States through the Safe Drinking Water Act by setting permissible maximum contaminant levels (MCL) for

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contaminants like radionuclides. For example, the MCL for uranium is 30 mg L<sup>-1</sup> [1].

Traditional methods of quantifying alpha- and beta-emitting radionuclides in environmental waters involve time-intensive, batch style analytical techniques that utilize laboratory-based instruments. 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 pre-concentrated 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. [2] physically impregnated an Amberlite XAD-7 polymer support with diamyl amylphosphonate, now sold commercially as U/TEVA resin from Eichrom Technologies, Inc., to preconcentrate uranium from acid solutions. The separation scheme was used to isolate and concentrate uranium from environmental matrices such as groundwater prior to isotope analysis with thermal ionization mass spectrometry. Turner et al. [3] 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 1 M sodium hydroxide and 1 M hydrogen peroxide. Concentrated samples were analyzed by ICP-MS. Croudace et al. [4] employed Actinide™ resin to preconcentrate uranium from seawater which 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. [5] 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. [4] required lengthy preparation times and strong acids to lower the pH of the seawater sample prior to separation. Turner et al. [3] required separate steps for concentration, elution and detection, increasing analysis time. Oguma et al. [5], 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 [6]. Efforts have been made to reduce the analysis timeline by combining concentration and detection. De Sanoit et al. [7] 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.

Another development in environmental sensing is a flow-cell detector that utilizes extractive scintillating (ES) resin for the on-line detection of alpha- and beta-emitting radionuclides [8]. The 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 which excite the polymer into a higher molecular state. This excitation energy is transferred non-radiatively to nearby fluorophores which subsequently de-excite resulting in the emission of photons of visible light that are counted by a photomultiplier tube. This flow-cell system has the advantage of making measurements in real-time as the activity accumulates on the resin which is distinct from the aforementioned techniques in which the activity is concentrated, eluted and then quantified. For portable flow-cell detectors to be 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 [9]. Unfortunately, resins produced in this way exhibit poor stability as the active components leach from the resin over time [6]. Recently, resins have been synthesized with covalently bound extractants and fluorophores for beta-emitting radionuclides like technetium-99 [10,11].

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 [12] and commercial Merrifield resins [13] 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. These sorbent materials have shown selectivity for uranium over Ba<sup>2+</sup>, Cs<sup>+</sup>, Sr<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup> and Th(IV) at the tested pH values. 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 [14]. These harsh conditions can be damaging to the organic fluorophores if applied to a scintillating resin.

Despite the development of 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 [15] concentrated uranium-233 from a mixture of actinides in 2 M 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 [9] utilized ES resins as either a heterogeneously packed column with both scintillating resins and extractive resins or by coating Dipex® extractant on a polyvinyltoluene 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. In this study, we synthesized a resin that incorporates covalently

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