# On-line gross alpha radiation monitoring of natural waters with extractive scintillating resins

Lara Hughes*, Timothy A. DeVol

*Department of Environmental Engineering & Science, Clemson University, Clemson, SC 29634-0919, USA*

## Abstract

Extractive scintillating resins, which are used to simultaneously separate and quantify radioactivity in aqueous solutions, were developed for low-level alpha radiation monitoring of natural waters. Resins were investigated with bis(2-ethylhexyl)methane-diphosphonic acid ($H_2$DEH[MDP], Dipex®) extractant, which has a strong affinity for tri-, tetra- and hexavalent actinides in dilute acids. Extractive scintillating resins were manifested (1) as a mixed bed of scintillating resin and extraction chromatographic resin and (2) by diffusing the organic fluor 2-(1-naphtyl)-5-phenyloxazole into macroporous polystyrene chromatographic resin, then coating with $H_2$DEH[MDP], or by coating $H_2$DEH[MDP] on scintillating polyvinyltoluene beads. The scintillation light was detected with a modified Hidex Triathler to allow for continuous flow measurements. The average detection efficiencies were $51.7 \pm 2.6\%$ and $65.8 \pm 10.1\%$ for natural uranium and $^{241}$Am, respectively, for the extractant coated scintillator. The resin was stable for solution flow of up to 1000 ml resulting in rapid real-time quantification of natural uranium in groundwater down to $30 \, \mu g/ml$.
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## 1. Introduction

Anthropogenic radionuclide contamination in soil and groundwater at Department of Energy (DOE) sites is a significant problem requiring remediation and monitoring. The actinides are one group of major concern at these sites. Also, many natural radionuclides which are common in some groundwaters decay by alpha emission. Standard laboratory analysis techniques are expensive, time intensive and typically not suitable for field screening applications.

*Corresponding author. Tel.: +1-864-656-1530; fax: +1-864-656-0672.

*E-mail address:* larad@clemson.edu (L. Hughes).

Quantification of alpha radiation generally requires the separation from the sample matrix followed by radiation detection. Commercially available extraction chromatographic resins are suitable for selective extraction of actinides from aqueous solutions [1]. Bis(2-ethylhexyl)methane-diphosphonic acid ($H_2$DEH[MDP], Dipex®) coated on an inert acrylic polymeric support (Actinide resin) is commercially available from Eichrom Technologies Inc. and is selective for tri-, tetra- and hexavalent actinides from dilute acids [1] and has been applied for actinide separations by several authors [2,3].

Flow cell radiation detection has been generally applied towards quantification of chromatography column effluent. To make a suitable detector, a

heterogeneous flow cell must have a pore volume large enough to achieve a sufficient count time while maintaining chromatographic separation [4,5]. Simultaneous separation and scintillation detection was first realized by producing plastic scintillating beads containing ion exchange groups for non-selective analyte uptake [6]. To date, extractive scintillating sensors have been investigated with on-line flow monitors for real-time quantification [7–9].

The work presented here investigates the feasibility of using extractive scintillating resin for simultaneous preconcentration and radiation detection for alpha activity in natural waters at concentrations at or below those set by the US Safe Drinking Water Act.

## 2. Experimental

### 2.1. Sensor materials and resin preparation

Dipex® was obtained from Eichrom Technologies Inc. in form of the pure $H_2DEH[MDP]$ extractant and as the Actinide resin, which consists of 100–150 μm acrylic resin beads impregnated with 40 wt% extractant. Mixed bed resins were prepared in a ratio of 1:1 by volume with Actinide resin and scintillating plastic beads (BC-400, 100-200 μm, Bicron Inc.) or cerium-doped yttrium silicate (YSO, 75–106 μm, Applied Scintillation Technologies).

Extractive Scintillating (ES) resin was produced by coating 4 wt% Dipex® extractant onto scintillating polyvinyltoluene (PVT), PVT ES, or 40 wt% Dipex® onto scintillating macroporous polystyrene (PS) beads, Actinide ES. Scintillating beads were either synthesized using a modification of a procedure described by Ref. [6], or by diffusing 2-(1-naphtyl)-5-phenyloxazole (αNPO) into the PS resin, Amberchrom CG 300C (TosoHaas) using a modification of a procedure described by Ref. [4]. The Dipex® extractant was coated onto the scintillating beads by dissolving the desired amount in ∼5 ml of isopropyl alcohol, adding the appropriate amount scintillator beads and tumbling the vial for 24 h. The solvent was then allowed to evaporate.

### 2.2. Analytical procedure

The analytical instrument used was a Hidex Triathler Multilabel Tester. Aliquots of collected effluent from the flow cell procedure were quantified for gross alpha activity with a Wallac 1415 LSC using OptiPhase HiSafe 3 as the cocktail.

A flow cell was produced from 11.0 cm of translucent PTFE tubing (3/16 in OD, 1/4 in ID), which was bent to a symmetric U shape and dry packed with resin, forming a reactive zone of 4.0 cm. The flow cell was connected to the top of the sample compartment and positioned in front of the photomultiplier tube (PMT). Data was collected on-line and consists of a series of 100 s counts as the solution is pumped and the radioactivity accumulates on the resin. Pulse height spectra were collected for 600 s before and after radioactivity was loaded onto the ES resin. The sensor material evaluation procedure was typical for extraction chromatography and consisted of conditioning, loading and washing steps, all using 0.1 N $HNO_3$. Radioactive test solutions were $^{241}$Am, $^{237}$Np and natural U standard in 0.1 N $HNO_3$.

Natural groundwater samples (1000 ml) with known uranium concentrations were obtained from private wells in Simpsonville, SC. Samples were acidified to 0.1 N $HNO_3$. Uranium levels were 30, 681 and 8504 μg/l.

## 3. Results and discussion

### 3.1. Resin characterization

Detection efficiencies for the mixed bed resins, Actinide/YSO and Actinide/BC-400 were low and the background count rate relatively high (see Table 1 and Fig. 1). The low detection efficiency is due to poor counting geometry. The limited amount of extractant in a flow cell of fixed volume would result in insufficient preconcentration from natural samples. For these reasons, the mixed bed, although mechanically favorable, was not used to characterize groundwater samples.

The PVT-coated ES resin had the highest detection efficiency and the lowest background of

Table 1
Summary of characterization of ES flow cells

| ES resin | Nuclide | $n$ | % efficiency | % activity loaded |
|---|---|---|---|---|
| Actinide/YSO | $^{237}$Np | 1[a] | 5.6 | 99.4 |
| Actinide/BC400 | $^{237}$Np | 1[a] | 3.7 | 95.5 |
| PVT ES | $^{241}$Am | 3[a] | 65.2 ± 5.6 | 99.8 ± 0.2 |
| PVT ES | Nat U | 3[b] | 57.8 ± 20.0 | 52.1 ± 26.4 |
| Actinide ES | $^{241}$Am | 7[a] | 65.8 ± 10.1 | 99.7 ± 0.4 |
| Actinide ES | Nat U | 3[b] | 51.7 ± 2.6 | 100.0 ± 0 |

[a] $n$ denotes the number of flow cells used in individual trials.
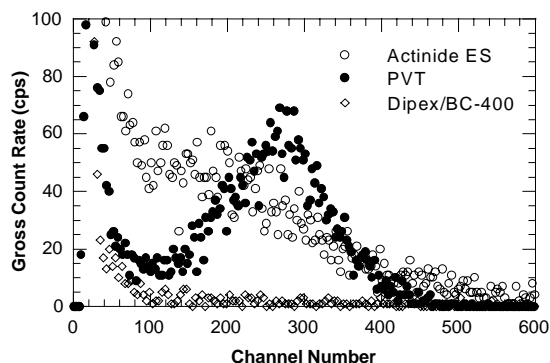[b] $n$ denotes the number of trials on a single flow cell.



Fig. 1. Pulse height spectra of extractant coated and mixed bed resins. Count time was 600 s. Efficiencies were 69.5% for actinide ES, 58.8% for PVT coated and 3.7% for Dipex/BC-400 mixed bed. Data for PVT coated resins was acquired at 725 V, others at 800 V.

the resins investigated. The disadvantage of the PVT-coated resin is that it is not porous and cannot take up large amounts of extractant, thus producing a 'sticky' resin. Also a thick coating on the surface of the bead hinders energy deposition in the scintillator and can reduce the transmission of scintillation light. Detection efficiencies were 65.2 ± 5.6% for $^{241}$Am and 57.8 ± 20.0% for natural U. The high detection efficiency is the result of the radioactivity being sorbed to the scintillator surface. The high variability of the uranium detection efficiency reflects the reduction in the % activity loaded as the flow cell

is reused. The variation for the $^{241}$Am value reflects the variation between flow cells. Higher efficiency for $^{241}$Am was expected due to the higher alpha energy. The detection efficiency for natural uranium only accounts uranium nuclides although there is evidence for the extraction of $^{234}$Th and $^{234m}$Pa.

Fig. 1 shows a comparison of the pulse height spectra of the three resins. The PVT ES resin produces a peak in the pulse height spectrum, indicating partial energy resolution.

The Actinide ES resin appears to have all the chromatographic characteristics of the commercially available counterpart with the additional advantage of also scintillating. The Actinide ES resin contains the same amounts of extractant as the Actinide resin, resulting in relatively higher uptake capacity. Detection efficiencies were 65.8 ± 10.1% and 51.7 ± 2.6% for $^{241}$Am and natural U, respectively. The small variation of the uranium value reflects the higher capacity of this resin; the activity loaded was 100%. The variation between flow cells quantified with $^{241}$Am is higher, because of variation in flow cell production.

Both the PVT ES and the Actinide ES resins were found to be stable scintillators while up to 1000 ml of solution are pumped though the resin bed.

### 3.2. Groundwater tests

On-line counting profiles for the different uranium concentrations are summarized in Table 2 with an example loading profile given in Fig. 2. A clear increase in count rate could be observed even for the lowest concentration. A count rate increase exceeding the 2-σ confidence interval of the background count rate is evident after flowing ∼150 ml of 30 µg/l solution through the cell. Activity breakthrough was observed after ∼200 and ∼670 ml of the 8504 µg/l solution for the PVT ES and Actinide ES resins, respectively. The deviation of the expected capacity and the observed is attributed to the sample and resin not reaching equilibrium for a flow rate of 1 ml/min.

Other constituents in the water sample could also contribute to resin exhaustion.

Table 2
Calculated and detected activity concentrations for groundwater tests, for values given with standard deviation, $n = 3$

| Resin | U (µg/l) | C (Bq/l) | Slope (cps/ml) | C (slope method) (Bq/l) | % difference | Net CR (cps) | C (net CR) (Bq/l) | % difference |
|---|---|---|---|---|---|---|---|---|
| PVT ES | 30 | 0.79 | 7.36E-4 | 1.28 | +62.74 | 0.84 | 1.45 | +84.33 |
| PVT ES | 681 | 17.85 | 1.03E-2 | 17.85 | +0.01 | 9.75 | 16.89 | −5.39 |
| PVT ES | 8504 | 221.40 | 1.25E-1 | 215.82 | −2.6 | 32.66 | N/A | N/A |
| Actinide ES | 30 | 0.79 | 7.04E-4 | 1.36±0.5 | +72.44 | 0.75 | 1.45±0.65 | +84.36 |
| Actinide ES | 681 | 17.85 | 1.09E-2 | 21.0 | +17.6 | 9.51 | 18.4 | +3.07 |
| Actinide ES | 8504 | 221.40 | 1.29E-1 | 249.8 | +12.8 | 85.31 | N/A | N/A |



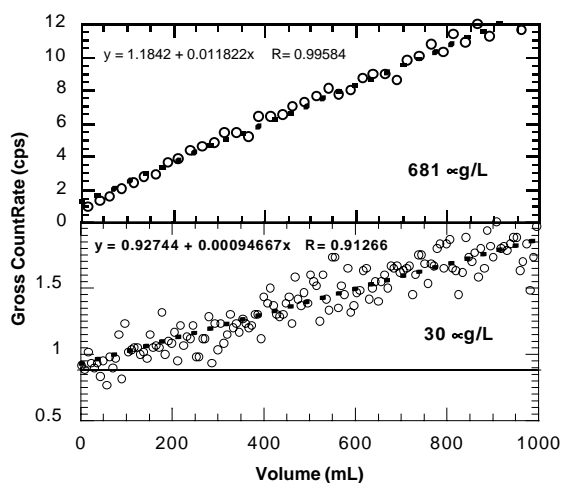Fig. 2. Loading profiles for 30 and 681 µg/l for the Actinide ES resin. Equations present the linear fit of the data. The solid line in the bottom graph represents the background count rate (∼0.8 cpm).

From the slope of the linear data fit lines or the net count rate from the pre- and post-loading pulse height spectra, the detected activities were calculated and compared with the expected values. The flow cell derived values were within <18% of the calculated values for the 681 and 8504 µg/l concentrations and within <85% for the 30 µg/l concentrations, making the resin suitable for groundwater screening applications. If a more accurate analysis is needed, the resin can be stripped with a solvent and the separated radioactivity analyzed by a conventional method.

## 4. Conclusion

Extractive scintillating resins that combine extraction chromatography and scintillation radiation detection with a flow cell approach have been successfully developed. Sufficiently sensitive resins consist of an actinide selective extractant coated onto scintillating beads. Detection efficiencies are >65% for $^{241}$Am and >51% for natural U. The resin can be applied for screening of alpha radiation in natural groundwaters at or below the alpha concentration set forth in the US Safe Drinking Water Act.

## Acknowledgements

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