

# Determination of radioisotopes in complex saline matrices using extraction chromatography and liquid scintillation counting

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**Abstract** The retention of <sup>239</sup>Pu and <sup>241</sup>Am on six commercially available extraction chromatographic resins was investigated to determine the effect of matrix constituents commonly found within sea and ocean water on their uptake. It was found that the retention of <sup>239</sup>Pu and <sup>241</sup>Am on almost all of the resins from either nitric acid or hydrochloric acid system was not significantly affected by matrix constituents in artificial ocean water. However, the retention of <sup>241</sup>Am on DGA resin from nitric acid was found to be reduced by over two orders of magnitude in the presence of artificial ocean water.

**Keywords** Ocean water · Extraction chromatography · Liquid scintillation counting · <sup>241</sup>Am · <sup>239</sup>Pu

## Introduction

Nuclear operations conducted over the past seventy years have resulted in the contamination of the environment with potentially hazardous radioactive species. The accidents that occurred in Chernobyl, Ukraine and Fukushima, Japan along with atmospheric testing of nuclear weapons are some of the major environmental contamination sources of anthropogenic radionuclides [1]. These operations have also resulted in a variety of issues concerning the safety of storage and disposal of the nuclear waste that has been

generated. Waterborne discharges from nuclear reprocessing plants, nuclear power plants, and decommissioned nuclear production plants, such as the Hanford Site located along the Columbia River in Washington, are another source of radiological contamination in the environment [2].

Natural waters are the largest recipient of environmental contamination by anthropogenic radionuclides. Sea and ocean waters cover more than two-thirds of the Earth's surface and therefore are the major recipients of radionuclide contamination in the environment through either atmospheric or aquatic pathways [2]. Some of the radioactive species that are associated with nuclear operations possess long half-lives as well as potentially high levels of mobility within the environment. Lanthanides and actinides, for example, adsorb readily to mineral particles, colloids, and natural organic matter [1]. This adsorption has a significant effect on the migration of radionuclides in the environment and complicates the assessment of transport pathways. It is therefore critical to conduct research into the isolation and rapid determination of radioactive species in aqueous environments and in particular in highly saline matrices.

A variety of radioanalytical techniques are commonly employed to determine radioisotopes within a wide array of matrices. Natural waters, however, contain a variety of matrix constituents that can inhibit these techniques. The elevated salinity of sea and ocean water imparts a complex matrix that can affect the isolation, characterization, and determination of the radioisotopes of interest. One of the routine techniques for the determination of the gross activity of alpha-emitting radionuclides in natural water samples requires evaporating 100–1000 mL samples on a planchet followed by subsequent counting by a gas proportional counter. However, this method is limited and has

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a variety of restrictions including: the time required to evaporate the water samples, the amount of solid dissolved in the samples, as well as the decline in efficiency due to solids remaining on the planchet [3].

One of the most common procedures for the determination of anthropogenic radionuclides in natural waters published in the literature is a precipitation technique. The procedure uses a manganese dioxide precipitation to remove plutonium and americium from acidified seawater followed by an ammonium molybdophosphate (AMP) precipitation to remove cesium from the solution [4]. This precipitation technique is often coupled with extraction chromatography, a radioanalytical technique that employs chromatographic resins that are comprised of an extractant system that separates radionuclides from aqueous sample matrices. The precipitation/extraction chromatography technique commonly uses a manganese dioxide and iron hydroxide co-precipitation followed by a two-column extraction [4]. The extraction chromatographic resins that are usually utilized within this technique are UTEVA<sup>®</sup> Resin and TRU Resin, which are manufactured by Eichrom Technologies, LLC. The UTEVA<sup>®</sup> Resin column retains uranium(VI), thorium(IV), and neptunium(IV), while plutonium(III) and americium(III) pass through the UTEVA-Resin and are extracted by the TRU-Resin column.

The precipitation/extraction chromatography technique for the determination of anthropogenic radionuclides in natural waters has a variety of disadvantages; including that the technique is time consuming, a multi-step process, and generates a substantial amount of waste. However, the production of commercially available extraction chromatographic resins has also led to the development of extraction chromatographic resin/liquid scintillation counting (LSC) protocols for the gross alpha determination in water samples that are quick and environmentally friendly. For example, Happel et al. developed an extraction chromatographic resin/LSC method that extracted alpha-emitting radionuclides from four types of water samples: drinking water, mineral water, waste water, and seawater. The water samples were acidified to pH 2 and were extracted utilizing a resin that had a strong affinity for actinides with tri-, tetra-, and hexavalent oxidation states. The gross alpha activity was determined by subsequent counting of the dried resin with an ultra-low-level  $\alpha$ -/ $\beta$ -discrimination LSC. Extraction experiments were conducted to analyze the interference from large amounts of matrix constituents found in natural waters including: calcium, potassium, iron, carbonate, and sulfate [5].

As part of this work the extraction chromatographic resin/LSC protocol is further investigated and a variety of novel extraction chromatographic resins are evaluated in order to determine the effect of matrix constituents, such as

those found within sea and ocean water, on their retention capabilities for radioisotopes of interest.

## Theory

Extraction chromatography is one of the main radioanalytical separation techniques that is currently utilized to separate radionuclides from a wide variety of sample matrices. Extraction chromatographic resin systems are comprised of three main components: an inert support, a stationary phase, and an immiscible mobile phase. The inert support is typically porous silica or an organic polymer bead that ranges in diameter from 50 to 150  $\mu\text{m}$ . The stationary phase is comprised of liquid extractants that adhered to the surface of the inert support. The mobile phase is comprised of an acid solution, normally nitric acid or hydrochloric acid. Additives such as complexants or redox reagents may be added to the mobile phase to enhance the selectivity or facilitate the stripping of strongly retained metal ions on the column [6]. The retention capabilities of the extraction chromatographic resins are typically described by the retention factor,  $k'$ , which corresponds to the free column volumes to peak maximum. The retention factor is measured indirectly by calculating the weight distribution ratio,  $D_w$ , which is the metal ion concentration per gram of resin extracted from a given volume of aqueous solution:

$$D_w = \frac{A_0 - A_s}{A_s} \cdot \frac{\text{mL}}{\text{g}}, \quad (1)$$

where  $A_0$  is the initial activity of the aqueous solution,  $A_0 - A_s$  is the activity adsorbed onto a known weight of resin (g), and  $A_s$  is the activity of the aqueous solution in a known volume (mL).

The retention factor can be directly related to the weight distribution ratio if the free column volume is determined for the specific resin being used [7]. Table 1 provides the factors required to convert from the distribution ratio,  $D_w$ , to the retention factor,  $k'$ , for six resins manufactured by Eichrom Technologies, LLC.

## Experimental

Ultrapure water (18  $\text{M}\Omega \text{ cm}^{-1}$ ) (MilliQ 50, Millipore, Bedford, MA, USA) was used for the preparation of all solutions. All reagents were analytical grade and used as received without further purification. The  $^{239}\text{Pu}$  and  $^{241}\text{Am}$  stock solutions of activities of 100 Bq/mL in 0.1 M nitric or hydrochloric acid and 3000 Bq/mL in 5 M nitric acid were obtained from Isotope Products Laboratories (Isotope

**Table 1** Extraction chromatography resins manufactured by Eichrom Technologies, LLC [7–12]

Resin	Extractant system	Conversion from $D_w$ to $k'$
DGA	<i>N, N, N', N'</i> tetraoctyldiglycolamide (TODGA)	1.75
UTEVA <sup>®</sup>	Diamyl amyolphosphate (DAAP)	1.67
TEVA <sup>®</sup>	Aliquat <sup>®</sup> 336	1.90
TRU	Octylphenyl- <i>N-N</i> -di-isobutyl carbamoylphosphine oxide (CMPO)	1.80
Actinide	DIPEX <sup>®</sup> : bis(2-ethylhexyl) methanediphosphonic acid (H2DEH[MDP])	1.90
Diphonix <sup>®</sup>	Polystyrene/divinylbenzene polymeric support functionalized with diphosphonic and sulphonic acid groups	2.00

Products Laboratories, Valencia, CA). The artificial ocean water was prepared using the American Society for Testing and Materials (ASTM) procedure ASTM D1141-98. Table 2 provides the chemical composition of the artificial ocean water. The artificial ocean water was acidified using ACS reagent grade nitric or hydrochloric acid (Sigma-Aldrich, St. Louis, MO). Reconstituted artificial ocean water was prepared by evaporating an aliquot of the artificial ocean water and reconstituting it in ACS reagent grade nitric or hydrochloric acid. Batch contact studies were performed using 2 mL polypropylene microcentrifuge tubes (VWR International, Darmstadt, Germany). Samples were filtered using Acrodisc<sup>®</sup> PTFE filters (0.45  $\mu\text{m}$ , 13 mm diameter) (Pall Corporation, Port Washington, NY, USA). All measurements were performed using a Perkin Elmer TriCarb<sup>®</sup> 2800 Liquid Scintillation Counter and

analyzed by means of QuantaSmart<sup>™</sup> software (PerkinElmer LifeScience, Boston, MA, USA).

### Batch contact studies

Batch contact studies were conducted with six extraction chromatographic resins in two different mineral acid systems (nitric acid and hydrochloric acid) to determine the retention factors for plutonium and americium in the presence of either a synthetic sodium chloride salt solution or artificial ocean water.

The final acid concentration of each system was chosen based on previously reported retention factors for each Eichrom resin characterized in nitric and hydrochloric acid [7–12]. An acid concentration that resulted in a relatively high retention factor was chosen for each Eichrom resin to ensure that the radioisotope would adsorb onto the resin. For the DGA Resin an acid concentration of 1 M nitric/hydrochloric acid was chosen, while for the remaining five Eichrom resins a concentration of 3 M nitric/hydrochloric acid was selected.

**Table 2** Chemical composition of artificial ocean water prepared using ASTM procedure: ASTM D1141-98

Compound	Concentration ( $\text{g L}^{-1}$ )
NaCl	24.53
MgCl <sub>2</sub>	5.20
Na <sub>2</sub> SO <sub>4</sub>	4.09
CaCl <sub>2</sub>	1.16
KCl	0.695
NaHCO <sub>3</sub>	0.201
KBr	0.101
H <sub>3</sub> BO <sub>3</sub>	0.027
SrCl <sub>2</sub>	0.025
NaF	0.003
Ba(NO <sub>3</sub> ) <sub>2</sub>	0.0000994
Mn(NO <sub>3</sub> ) <sub>2</sub>	0.0000340
Cu(NO <sub>3</sub> ) <sub>2</sub>	0.0000308
Zn(NO <sub>3</sub> ) <sub>2</sub>	0.0000096
Pb(NO <sub>3</sub> ) <sub>2</sub>	0.0000066
AgNO <sub>3</sub>	0.00000049

### Matrix constituent: sodium chloride

Polypropylene microcentrifuge tubes were filled with  $50 \pm 0.05$  mg of the desired resin. The resin was preconditioned with 0.5 mL of the preferred acid concentration. The microcentrifuge tubes were agitated for 1 h using a Labquake Rotisserie shaking table. The tubes were then spiked with 0.5 mL of the synthetic sodium chloride salt solution (0–50 parts per thousand) and 0.5 mL of  $\sim 100$  Bq/mL of <sup>239</sup>Pu in 0.1 M HNO<sub>3</sub>/HCl. The microcentrifuge tubes were agitated for another hour using the shaking table. The solution was subsequently filtered through a 0.45  $\mu\text{m}$  PTFE filter. A 0.9 mL aliquot of the filtered solution was added to 15 mL of LSC cocktail, which was then measured on a Perkin Elmer TriCarb<sup>®</sup> 2800 Liquid Scintillation Counter and analyzed using QuantaSmart<sup>™</sup> software. All batch contact studies were

performed in four replicates (error was calculated by the standard deviation of the replicate measurements).

#### Matrix constituent: artificial ocean water

Polypropylene microcentrifuge tubes were filled with  $50 \pm 0.05$  mg of the desired resin. The resin was preconditioned with 0.5 mL of the preferred solution (acid, acidified artificial ocean water, or reconstituted artificial ocean water). The microcentrifuge tubes were agitated for 1 h using a Labquake Rotisserie shaking table. The tubes were then spiked with 0.9833 mL of the same solution and 0.017 mL of  $\sim 3,000$  Bq/mL in 5 M  $\text{HNO}_3$  of  $^{239}\text{Pu}$  or  $^{241}\text{Am}$ . The microcentrifuge tubes were agitated for another hour using the shaking table. The solution was subsequently filtered through a  $0.45 \mu\text{m}$  PTFE filter. A 0.9 mL aliquot of the filtered solution was added to 15 mL of LSC cocktail, which was then measured on a Perkin Elmer TriCarb<sup>®</sup> 2800 Liquid Scintillation Counter and analyzed using QuantaSmart<sup>™</sup> software. Batch contact studies were performed in four replicates (error was calculated by the standard deviation of the replicate measurements).

Volume correction factors were determined for each resin. For this purpose, polypropylene microcentrifuge tubes were filled with  $50 \pm 0.05$  mg of the desired resin. The resin was preconditioned with 0.5 mL of the preferred acid concentration. The microcentrifuge tubes were agitated for 1 h using the shaking table. The tubes were then spiked with 1 mL of the same preferred acid concentration. The solution was subsequently filtered through a  $0.45 \mu\text{m}$  PTFE filter into a pre-weighted second microcentrifuge tube to determine the amount of solution that was not taken up by the resin. A 1 mL adjustable Eppendorf pipette was calibrated to deliver 0.3 mL based on the density of deionized water at room temperature ( $0.9982 \text{ g/mL}$ ). A 0.3 mL aliquot of the eluted acid was titrated with 0.1 M sodium hydroxide using a 25 mL burette and 0.1 % phenolphthalein as the indicator until a pink endpoint was reached. Titrations of the eluted acid samples were performed in order to determine the change in acid concentration after contact with the resin.

## Results and discussion

#### Matrix constituent: sodium chloride

Batch contact studies were conducted with the six extraction chromatographic resins in two different acid systems (nitric acid and hydrochloric acid) to determine the retention factors of  $^{239}\text{Pu}$  in the presence of a synthetic sodium chloride salt solution. Ocean water contains more dissolved

ions than any other type of natural water with chloride and sodium ions comprising of 85 % of the total salinity (the concentration of sodium and chloride ions in ocean water is 0.459 and 0.536 M respectively). Therefore, batch contact studies focused on the effect that sodium and chloride ions had on the retention of  $^{239}\text{Pu}$ .

The retention of  $^{239}\text{Pu}$  on the six extraction chromatographic resins was not significantly affected by the sodium chloride matrix constituent from either nitric acid or hydrochloric acid system at any concentration (Fig. 1). For a given resin, the retention factors for  $^{239}\text{Pu}$  did not significantly differ with an increase in sodium and chloride ions. A significant change in retention would have been indicated by retention factors that differed by orders of magnitude. Retention factors that were less than one indicated that the radioisotope was not significantly retained by the resin; therefore, any variances of retention factors less than one were attributed to experimental error. In general, for a given resin, the retention of  $^{239}\text{Pu}$  was stronger from nitric acid than compared to the retention from hydrochloric acid, which was expected based upon the retention factors for plutonium in nitric and hydrochloric acid systems reported in the literature [7–12]. The retention of  $^{241}\text{Am}$  on the six extraction chromatographic resins in the presence of varying concentrations of a synthetic sodium chloride salt solution will be examined in future work.

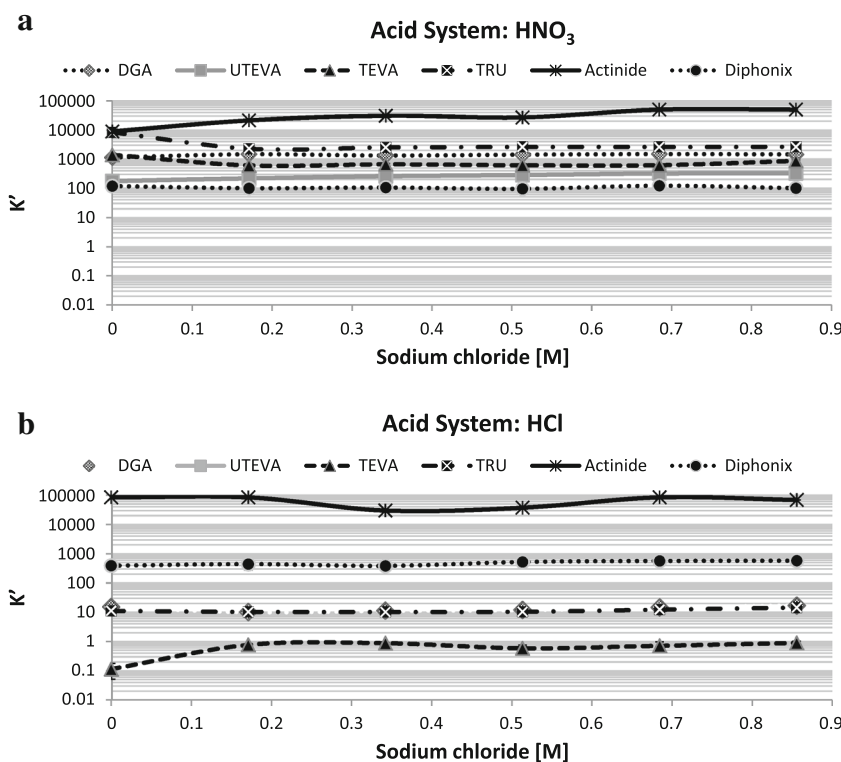
#### Matrix constituent: artificial ocean water

Batch contact studies were conducted with the six extraction chromatographic resins in two different acid systems (nitric acid and hydrochloric acid) to determine the retention factors of  $^{239}\text{Pu}$  and  $^{241}\text{Am}$  in the presence of artificial ocean water. Figure 2 shows the retention factors of  $^{239}\text{Pu}$  on the six extraction chromatography resins in a nitric acid system (Fig. 2a) and in a hydrochloric acid system (Fig. 2b). Figure 3 shows the retention factors of  $^{241}\text{Am}$  on the six extraction chromatography resins in a nitric acid system (Fig. 3a) and in a hydrochloric acid system (Fig. 3b).

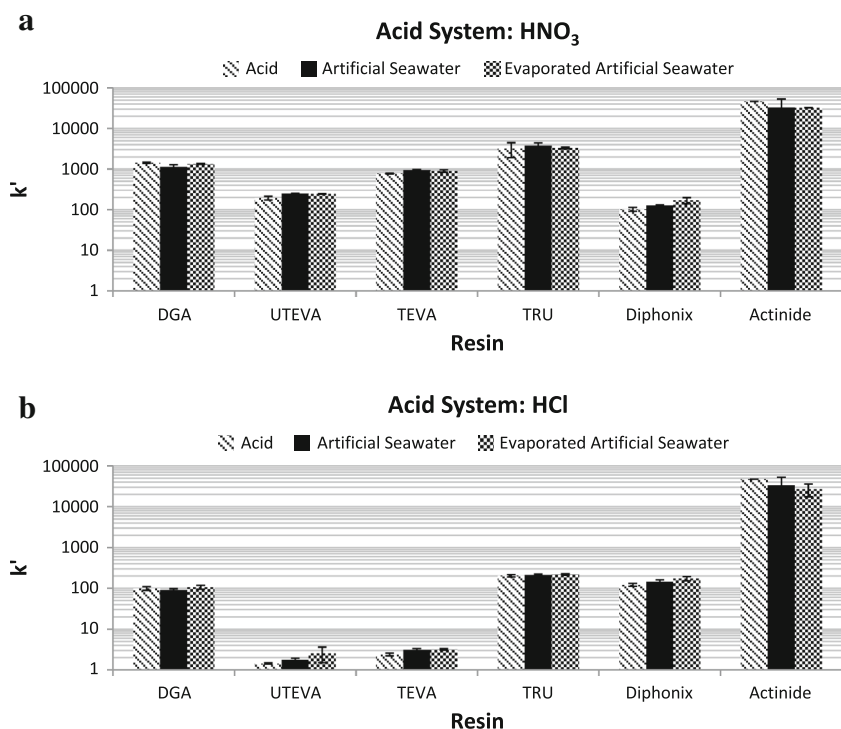
The retention of  $^{239}\text{Pu}$  on the six extraction chromatographic resins from either nitric acid system or hydrochloric acid (Fig. 2) was not significantly affected by the presence of artificial ocean water. For a given resin, the retention factors for  $^{239}\text{Pu}$  did not significantly differ between pure acid, the acidified artificial ocean water system, and the reconstituted artificial ocean water system.

The retention of  $^{241}\text{Am}$  from either nitric acid or hydrochloric acid system (Fig. 3) was not significantly affected by the presence of artificial ocean water for five of the six extraction chromatographic resins investigated. In the case of DGA Resin however, the retention from nitric

**Fig. 1** **a** Retention factors for the absorption of  $^{239}\text{Pu}$  from nitric acid on six extraction chromatographic resins (in the presence of varying concentrations of a synthetic sodium chloride salt solution). *Error bars* are smaller than the individual markers. **b** Retention factors for the absorption of  $^{239}\text{Pu}$  from hydrochloric acid on six extraction chromatographic resins (in the presence of varying concentrations of a synthetic sodium chloride salt solution). *Error bars* are smaller than the individual markers



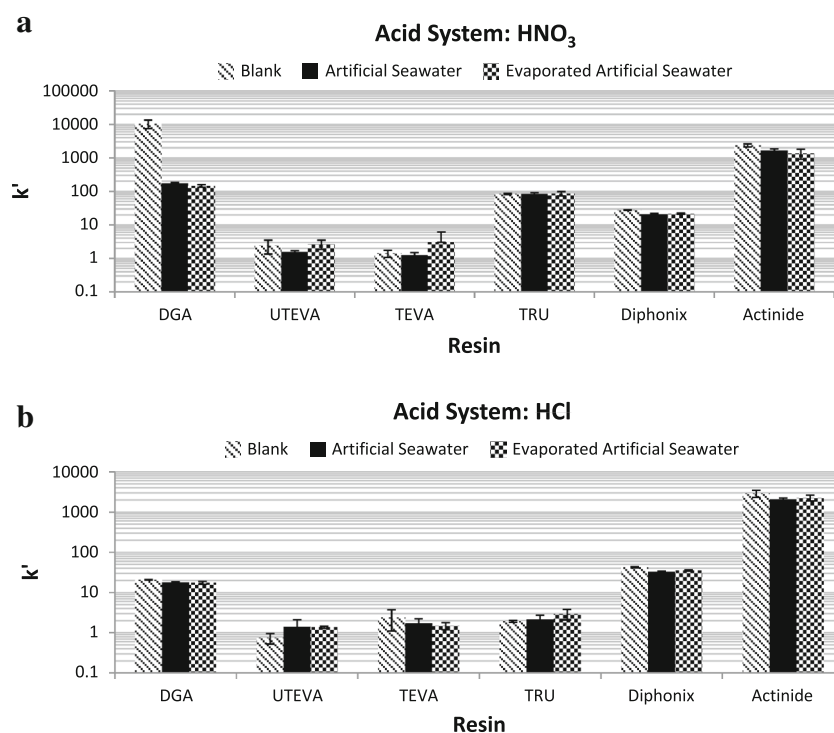
**Fig. 2** **a** Retention factors for the absorption of  $^{239}\text{Pu}$  from nitric acid on six extraction chromatographic resins in the presence of pure acid, acidified artificial ocean water and evaporated reconstituted artificial ocean water. **b** Retention factors for the absorption of  $^{239}\text{Pu}$  from hydrochloric acid on six extraction chromatographic resins in the presence of pure acid, acidified artificial ocean water and evaporated reconstituted artificial ocean water



acid was reduced by over two orders of magnitude in the presence of artificial ocean water (Fig. 3a). The retention factor  $k' > 10^4$  for  $^{241}\text{Am}$  on DGA Resin in a nitric acid system was reduced to  $k' > 10^2$  when artificial ocean water was added to the system (either acidified artificial ocean

water or the reconstituted artificial ocean water). The average salinity of ocean water is around 3.5 % (35 g dissolved inorganic salts/1 L water). The elevated salinity of the ocean water imparts a complex matrix that could have inhibited the extractant system of the DGA Resin

**Fig. 3 a** Retention factors for the absorption of  $^{241}\text{Am}$  from nitric acid on six extraction chromatographic resins in the presence of pure acid, acidified artificial ocean water and evaporated reconstituted artificial ocean water. **b** Retention factors for the absorption of  $^{241}\text{Am}$  from hydrochloric acid on six extraction chromatographic resins in the presence of pure acid, acidified artificial ocean water and evaporated reconstituted artificial ocean water



reducing the uptake of  $^{241}\text{Am}$ . Additional studies are necessary to identify the specific constituent in ocean water that is responsible for reducing the retention of americium on DGA. For the remaining resins, the retention factors for  $^{241}\text{Am}$  did not significantly differ between the acid system, the acidified artificial ocean water system, and the reconstituted artificial ocean water system.

The six extraction chromatographic resins used for the batch contact studies can also have a specific affinity toward the mineral acid used. The amount of liquid that is being adsorbed onto the resin can affect the accuracy of the retention factor values. Therefore, volume correction factors were determined for each resin. The amount of solution that was taken up by the resin was determined by the weight of the filtered eluent and the density of the solution. The volume correction factors for each resin reflected the change of volume induced by contact with the resin. Titrations of the filtered acid samples were performed in order to determine the change in acid concentration after contact with the resin. The titration data indicated that the acid concentration did not statistically change after contact with each respective resin.

## Conclusions

The results of the batch contact studies indicated that the retention of  $^{239}\text{Pu}$  on the six extraction chromatographic resins from either nitric acid or hydrochloric acid was not

significantly affected by the matrix constituents in artificial ocean water or varying concentrations of a synthetic sodium chloride salt solution. In addition the retention of  $^{241}\text{Am}$  from nitric acid and hydrochloric system was not significantly affected by the matrix constituents in artificial ocean water for five of the resins investigated. However, the retention of  $^{241}\text{Am}$  on DGA Resin from nitric acid was reduced by over two orders of magnitude in the presence of artificial ocean water. Additional batch contact studies should be performed to identify which matrix constituent in ocean water is reducing the retention of americium on DGA Resin. Column studies should also be performed with the six extraction chromatographic resins in both acid systems (nitric acid and hydrochloric acid) to determine the effect of ocean water matrix constituents on the elution behavior of  $^{239}\text{Pu}$  and  $^{241}\text{Am}$ .

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