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Calcium interference on americium and plutonium uptake on six extraction chromatographic resins

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Abstract

The retention of americium and plutonium on six commercially available extraction chromatographic resins was investigated in the presence of various concentrations of calcium. Results of batch study experiments showed that there was no significant interference due to calcium for the adsorption of plutonium or americium from both nitric and hydrochloric acid on the majority of the extraction chromatographic resins studied. However, the retention of americium on DGA resin from nitric acid decreased by over two orders of magnitude when calcium was introduced into the system. DGA was found to have a capacity for calcium of 4.53 ± 0.08 mg Ca g^{-1} DGA resin.

Keywords Calcium · Actinides · Interference · Extraction chromatography · Liquid scintillation counting

Introduction

A large number of radioanalytical techniques utilizing extraction chromatography have been developed for the determination of radionuclides in a variety of different matrices [1, 2]. However, all of these methods are affected by interfering elements present in the sample. High concentrations of matrix constituents can inhibit the isolation, characterization, and determination of these radionuclides of interest [3]. Calcium, for example, was found to be a major interferent when performing separations using extraction chromatographic resins, particularly DGA resin. Quantitative information of the effects of interferents is however often missing.

Calcium, an alkali earth metal with a + 2 oxidation state and an ionic radii of 100 pm [4], is found within a variety of biological, environmental, and urban samples. Calcium-rich

biological samples include bone and urine. Bone samples are mainly comprised of calcium in the form of the mineral phase hydroxyapatite ($Ca_{10}(PO_4)_6(OH_2)$) [5]. Calcium is typically found at concentrations of ~ 250 mg Ca g^{-1} human bone with a Ca:P molar ratio of ~ 1.7 [6, 7]. The National Institute of Standards and Technology (NIST) provides several Standard Reference Materials (SRMs) for bone samples that contain calcium: SRM 2910b Hydroxyapatite (392.4 mg Ca g^{-1}), SRM 1400 Bone Ash (381.8 mg Ca g^{-1}), and SRM 4356 Ashed Bone Environmental Radioactivity Standard (416 mg Ca g^{-1}) [8–10]. Biological urine samples, on the other hand, contain calcium at concentrations of ~ 163 mg Ca L^{-1} synthetic urine (0.060 w/w%: $CaCl_2 \cdot 2H_2O$) [11]. Radionuclides, specifically actinide elements and strontium that enter the body, can accumulate in bone and the excretion of the radionuclides in urine often needs to be monitored for occupational health as well as in response to radiological emergency situations [12].

Calcium-rich environmental samples include natural waters as well as soil. Calcium is found as a major constituent in natural waters, specifically ocean water, which contains more dissolved ions than most other types of natural waters [13]. Ocean water has an average calcium concentration of 0.416‰ (0.0104 M) with calcium comprising 1.18% of the total salinity [14]. Soil contains a variety of calcium minerals; mainly calcite ($CaCO_3$),

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dolomite $(CaMg(CO_3)_2)$, and aragonite $(CaCO_3)$ [15]. These calcium minerals are also found within sediment samples, which also can contain calcium due to the presence of dead marine creatures that have been deposited in the sediment layers and have a high calcium content from their bones and/or shells [16]. NIST also provides several SRMs for sediment and soil samples that contain calcium: SRM 1646a Estuarine Sediment (5.19 mg Ca g^{-1}), SRM 2709a San Joaquin Soil (19.1 mg Ca g^{-1}), SRM 2710a Montana I Soil (9.64 mg Ca g^{-1}), SRM 4353A Rocky Flats Soil Number 2 (4 mg Ca g^{-1}), etc. [17–20].

The calcium minerals found within soil are also found within a variety of building materials; including concrete, limestone, marble, brick, etc. In the United States, most of the mined limestone is crushed and then used as aggregate which, is a component of concrete [21]. NIST again provides several SRMs for building materials that could be found within urban samples: SRM 1d Limestone (528.5 mg CaO g^{-1}), SRM 88b Dolomitic Limestone (299.5 mg CaO g^{-1}), SRM 1889a Portland Cement (Blended with Limestone) (653.4 mg CaO g^{-1}), SRM 634a Portland Cement (650.7 mg CaO g^{-1}), SRM 198 Silica Brick (27.1 mg CaO g^{-1}), SRM 679 Brick Clay (1.628 mg Ca g^{-1}), etc. [22–27]. These building materials, which are typically found in urban areas, have the potential to be contaminated in the aftermath of a radiation dispersal device (RDD) incident [28].

Matrix constituents, such as calcium, that are found within these biological, environmental, and urban samples could significantly interfere with radiochemical separation techniques. Therefore, robust methods that are not hindered by these interferences are required for the accurate determination of radionuclides within these samples. Extraction chromatography is one of the main radioanalytical separation techniques that is currently used to isolate radionuclides from a wide variety of sample matrices. This technique incorporates the favorable selectivity associated with the organic extractants used in solvent extraction with the multistage character and ease of operation of a chromatographic process [29, 30]. A more detailed description of extraction chromatography and the determination of the retention factors, k', for the six resins (DGA, UTEVA, TEVA, TRU, Diphonix, and Actinide resin) has been published in a previous paper [31]. The six extraction chromatography resins that were examined within this work were chosen (1) based on their commercial availability, (2) for their common use in radioanalytical separation schemes, especially for actinide element isolation and determination, and (3) to expand the elemental inference studies on Am and Pu adsorption that were conducted previously [31]. This work and the studies described in the previous paper focused on these two radioisotopes due to the growing concern of the large risk of internal radiation

exposure, particularly from the ingestion of contaminated agricultural crops and food sources [31, 32].

Three of the extraction chromatography resins (UTEVA, TEVA, and TRU resin) that were examined within this work are expected to show very little affinity for calcium. UTEVA and TRU resin were characterized for Ca(II) adsorption in hydrochloric acid systems and nitric acid systems, respectively [33, 34]. UTEVA resin weakly retained Ca(II) with maximum k' values of 10 at 8 M HCl. TRU resin weakly retained Ca(II) over the entire nitric acid concentration range with k' values below 0.2. Calcium also showed no interference with the uptake of Am(III) in 2 M HNO_3 over a range of salt concentration. The only other published data for these three resins indicated that calcium was eluted off within the first few mL of elution volume from an environmental sample [34–38].

The remaining three resins (DGA, Diphonix, and Actinide resin) were characterized for calcium in nitric acid systems and in hydrochloric acid systems (DGA resin). DGA resin has an affinity for Ca(II) above 0.5 M HNO_3, with k' values reaching a max at $\sim$ 200 at 2 M HNO_3. Calcium could be eluted off using either low (0.1 M) or high (11 M) concentrations of HNO_3. The resin had little affinity for Ca(II) over the entire HCl concentration range studied, with k' less than 10 [39]. Diphonix resin has a strong affinity for Ca(II) at low nitric acid concentrations, with the affinity of the resin for calcium decreasing with increasing acid concentration. Above 1 M HNO_3, the weight distribution, D_W, values were below 10 [40]. The Diphonix resin was also examined for the calcium interference on the uptake of Am(III). The adsorption of Am(III) on Diphonix resin was not hindered by the increasing amounts of calcium up to 5 M HCl. However, even though there was no significant change, the results showed that the D_W values decreased with an increase in salt concentration [41, 42]. Actinide resin weakly retained Ca(II) above 0.1 M HNO_3, with k' values below 20 [43]. Similarly to Diphonix resin, Actinide resin was also examined for calcium interference on the uptake of Am(III) and the affinity of the resin for Am(III) did not significantly change with an increasing concentration of Ca(II) up to 4 M HCl [44].

An extensive literature research into the Ca adsorption/interference on different extraction chromatography resins did not uncover any literature pertaining to the affect of Ca on Pu adsorption. Previous work determined the k' values for Pu(IV), as well as Am(III), on the six extraction chromatography resins from acidified artificial ocean water [31]. The results showed that the adsorption of Pu on the six resins was not influenced by the matrix constituents found within ocean water, including Ca(II) which is found with an average concentration of 0.0104 M. These results were the only reported k' values of Pu on the resins from a

matrix system that contained Ca. The results of this previous work also showed that the adsorption of Am(III) on DGA resin (nitric acid system) was significantly affected by the matrix constituents found within ocean water. The previous research also showed that Na(I), which comprised 30.59% of the total salinity of average ocean water relative to the other major constituents of ocean water, did not inhibit the uptake of Am on DGA resin. Therefore, one of the main motivations of this work was to determine the possible inference of alkali earth metals on both Am and Pu adsorption on the six extraction chromatography resins, particularly DGA resin. Calcium was the next major constituent of average ocean water that showed retention on some of the resins examined.

Consequently, the work described here focused on further examining the calcium interference on Am and Pu adsorption on the six extraction chromatographic resins from both nitric acid and hydrochloric acid. As previously mentioned, the literature has provided some Ca adsorption data as well as some Ca interference studies on Am(III) adsorption on different extraction chromatography resins. However, these results did not examine both nitric acid and hydrochloric acid systems for either the characterization of Ca adsorption or the examination of the Ca interference studies on Am(III), or Pu(IV), adsorption on all six resins. Therefore, this work also aimed to establish a consistent set of data that examined the Ca interference on Am and Pu adsorption with the same methodology over the same Ca concentration range.

Experimental

Ultrapure water (18 MΩ 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. Calcium salt solutions were prepared from $Ca(NO_3)_2 \cdot 4H_2O$ (Sigma-Aldrich, ACS, > 99%) and $CaCl_2 \cdot 2H_2O$ (Fisher Chemicals, ACS, > 99%). Salt solution were diluted to the desired concentration using 1 M HNO$_3$/HCl (DGA resin) or 3 M HNO$_3$/HCl (DGA, UTEVA, TEVA, TRU, Diphonix, Actinide resin). Final calcium salt concentrations ranged from 0 to 1 M (0–40.078‰ Ca).

All resins were used as received without further purification from Eichrom Technologies Inc. (Lisle, IL). Working solutions of ∼ 1000 Bq mL^{-1} ^{241}Am or ^{239}Pu in 1 M HNO$_3$/HCl or 3 M HNO$_3$/HCl were prepared from standard solutions purchased from Eckert & Ziegler Isotope Products Inc. (Valencia, CA). The ^{239}Pu was received in the form of plutonium nitrate in 4 M HNO$_3$ (3.7 MBq/ 5 mL). The ^{241}Am was delivered in the form of americium chloride in 1 M HCl (3.7 MBq/5 mL).

Batch contact studies were performed using using 2 mL polypropylene microcentrifuge tubes (VWR, Denver, CO). Samples were filtered using Acrodisc® PTFE filters (0.45 μm, 13 mm diameter) (Pall Corporation, Port Washington, NY, USA). All radiochemical measurements were performed using a TriCarb® 5110TR Liquid Scintillation Counter (Perkin Elmer, Boston, MA). QuantaSmart software (Perkin Elmer, Boston, MA) was used for all data acquisition and analysis. All stable elemental measurements were performed using an Optima 8000 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (Perkin Elmer, Waltham, MA). Perkin Elmer Syngistix software was used for all data acquisition and analysis.

Batch studies

Batch study experiments were conducted with six extraction chromatographic resins (DGA, UTEVA, TEVA, TRU, Diphonix, Actinide resin) in two different mineral acid systems (nitric acid and hydrochloric acid) in order to (1) determine the retention factors of americium and plutonium in the presence of a calcium salt solution and (2) determine the calcium capacity of the six extraction chromatographic resins for calcium.

The final acid concentration of each resin system was chosen based on previously reported retention factors and an acid concentration that resulted in a relatively high retention factor, without adding significant amount of nitrates or chlorides to the system, was chosen for each resin to ensure that the radioisotope of interest would adsorb onto the resin. A final acid concentration of 1 M HNO$_3$ or 1 M HCl was chosen for DGA resin, while a final acid concentration of 3 M HNO$_3$ or 3 M HCl was chosen for the remaining five extraction chromatographic resins examined [31]. A lower amount of added nitrates and/or chlorides to the system was beneficial, particularly when considering some radioanalytical separation techniques require initial acidification; therefore, a lower volume of acid would be required to acidify certain types of biological, environmental, or urban samples.

Calcium interference studies

Polypropylene microcentrifuge tubes were filled with 50 ± 0.5 mg of the desired extraction chromatographic resin. The resin was preconditioned with 0.45 mL of either 1 M HNO$_3$ or 1 M HCl (DGA resin) or 3 M HNO$_3$ or 3 M HCl (DGA, UTEVA, TEVA, TRU, Diphonix, Actinide resin). The microcentrifuge tubes were then agitated for one hour using a Labquake rotisserie-shaking table.

Following preconditioning, 1 mL of the initial calcium salt solution was added to the sample. The sample solution

was then spiked with 50 μL of $\sim$ 1000 Bq mL^{-1} ^{241}Am or ^{239}Pu in 1 M HNO$_3$, 1 M HCl, 3 M HNO$_3$, or 3 M HCl, depending on the acid system. The total volume of the combined aqueous solutions was 1.5 mL. The microcentrifuge tubes were agitated for an additional hour using the rotisserie-shaking table. The solution was subsequently filtered through a 0.45 μm PTFE syringe filter into a secondary microcentrifuge tube. All batch studies were performed in four replicates.

A 0.9 mL aliquot of the filtered solution was dissolved into 15 ml of Ultima Gold AB cocktail that was contained in a 20 mL HDPE vial for analysis on a Tri-Carb 5110TR. Error was determined by the standard deviation of the replicate measurements. Detection limit was determined based on calculations from the Currie equation.

Calcium adsorption studies

Polypropylene microcentrifuge tubes were filled with 50 ± 0.05 mg of the desired extraction chromatographic resin. The resin was preconditioned with 0.50 mL of either 1 M HNO$_3$ or 1 M HCl (DGA resin) or 3 M HNO$_3$ or 3 M HCl (UTEVA, TEVA, TRU, Diphonix, Actinide resin). The microcentrifuge tubes were then agitated for one hour using a Labquake rotisserie-shaking table.

Following preconditioning, 1 mL of the initial calcium salt solution was added to the sample. Only 0.001, 0.01, and 0.1 M final calcium salt solution concentrations were examined. The total volume of the combined aqueous solution was 1.5 mL. The microcentrifuge tubes were agitated for an additional hour using the rotisserie-shaking table. The solution was subsequently filtered through a 0.45 μm PTFE syringe filter into a secondary microcentrifuge tube. All batch studies were performed in four replicates.

An aliquot of the filtered solution was diluted to 10 mL with 2% HNO$_3$ in a 15 mL polypropylene centrifuge tube for a final concentration of 1–10 ppm and then analyzed on the ICP-OES. The measurement error was again determined by the standard deviation of the replicate measurements.

Results and discussion

Calcium interference studies

Batch study experiments were conducted with six extraction chromatographic resins in two different mineral acid systems (nitric acid and hydrochloric acid) in order to determine the retention factors of americium and plutonium in the presence of a calcium salt solution. Calcium metal ion concentrations examined ranged from 0 to

40.078‰ (0–1.0 M) in order to cover a range of possible concentrations that could be encountered in biological, environmental, or urban samples.

Nitric acid system

The retention factors for americium on the six extraction chromatographic resins from nitric acid that were determined in the presence of varying amounts of calcium are shown in Fig. 1. The retention of ^{241}Am on five out of the six extraction chromatographic resins (UTEVA, TEVA, TRU, Diphonix, and Actinide resin) was not significantly affected by the calcium matrix constituent at any concentration investigated. A significant change in retention would have been indicated by retention factors that differed by orders of magnitude. However, even though there was no significant change in retention, the results indicated that the retention factor for americium on both Diphonix and Actinide resin decreased with an increase in calcium concentration. This slight decrease was attributed to the increased nitrate concentration from the Ca(NO$_3$)$_2$ salt introduced into the system. Literature has shown that the retention of Am(III) on Diphonix resin decreases with increased acid/nitrate concentration after 1 M [41]. Out of these five extraction chromatographic resins, Actinide resin had the greatest affinity for ^{241}Am with k' values around 10^3. The affinity of the five different extraction chromatographic resins for ^{241}Am followed the trend: Actinide > TRU > Diphonix > UTEVA = TEVA. Retention factors that were less than one indicated that the radioisotope was not significantly retained by the resin. UTEVA and TEVA resin showed little affinity for the trivalent Am with k' values around 1, which was expected due to these resins only having an affinity for metal ions that are tetravalent (and hexavalent for UTEVA). These resins were still examined in order establish a consistent set of data with the same methodology as well as to examine any synergistic effects that Ca might have on the adsorption of Am on these resins.

As previously mentioned in the introduction, TRU resin was examined for Ca interference on Am(III) adsorption [34]. The k' values determined in this work matched the trends presented in the literature. Calcium showed no interference with the uptake of Am(III) in 3 M HNO$_3$ (current work) or 2 M HNO$_3$ (literature) over the same range of salt concentration examined. Retention factor values of Am(III) on TRU resin remained constant over the salt concentration range at $\approx$ 100.

The retention of ^{241}Am on DGA resin was however significantly affected by the calcium matrix introduced into the system, with the resulting k' values decreasing by three orders of magnitude over the range of calcium concentrations examined, as shown in Fig. 1. The affinity of DGA

Fig. 1 Retention factors for the adsorption of ^{241}Am from nitric acid on six extraction chromatographic resins (in the presence of varying concentrations of a calcium salt solution). Error bars are shown for all data measurements and most are smaller than the individual markers
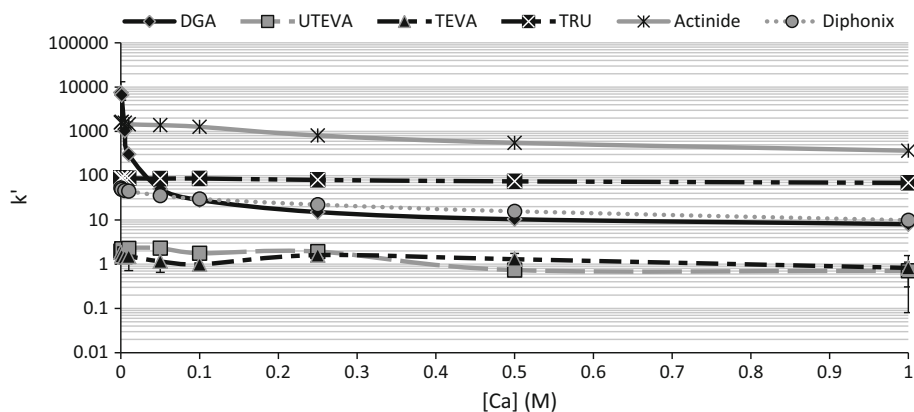
resin for ^{241}Am was reduced immediately when calcium was introduced into the system and followed an exponential decrease in retention factor value over the concentration range. This trend indicates that there is severe competition between the divalent calcium (ionic radii: 100 pm) and the trivalent americium (ionic radii: 98 pm) for the extraction sites on DGA resin [4]. The batch study to examine the calcium interference on americium adsorption on DGA resin was repeated, but instead of a 1 M nitric acid system, the concentration of nitric acid was increased to 3 M to examine if the increase in nitrates would increase the retention of americium over calcium on the resin. A comparison of the retention factor of ^{241}Am from 1 M and 3 M nitric acid on DGA resin examined in the presence of varying amounts of calcium is shown in Fig. 2. The results indicate that increasing the nitric acid concentration of the system resulted in a larger retention of ^{241}Am(III) compared to Ca(II). However, the retention of ^{241}Am on DGA resin from 3 M HNO$_3$ was still significantly affected by the calcium matrix introduced into the system with k' values decreasing by two orders of magnitude over the calcium concentration examined. The concentration of nitric acid was only increased to 3 M to match the acid concentration of the other resins examined in this work, as well as to match common acid

concentrations used within radioanalytical separation schemes. However, as previously mentioned in the introduction, DGA resin has an affinity for Ca(II) above 0.5 M HNO$_3$, with k' values reaching a max at $\sim$ 200 at 2 M HNO$_3$. Additionally, the k' value of Am(III) on DGA resin increases with increasing acid concentration [39]. Therefore, if the acid concentration was increased to > 6 M HNO$_3$, the calcium matrix introduced into the system would be expected not to significantly interfere with the retention of ^{241}Am on DGA resin. However, the increased acid concentration would require more volume of acid to be added initially to certain samples, when considering some radioanalytical separation techniques require initial acidification.

The retention factors for plutonium on the six extraction chromatographic resins from nitric acid determined in the presence of varying amounts of calcium are shown in Fig. 3. The retention of ^{239}Pu on the six extraction chromatographic resins was not significantly affected by the calcium matrix constituent at any concentration. However, in the case of DGA and TRU resin, there was a slight increase in the retention of ^{239}Pu, when calcium was introduced into the system. This slight increase could be attributed to (1) a synergistic effect due to the presence of calcium in solution or more likely (2) the increased nitrate

Fig. 2 Retention factors for the adsorption of ^{241}Am from 1 M and 3 M nitric acid on DGA resin (in the presence of varying concentrations of a calcium salt solution). Error bars are shown for all data measurements and most are smaller than the individual markers
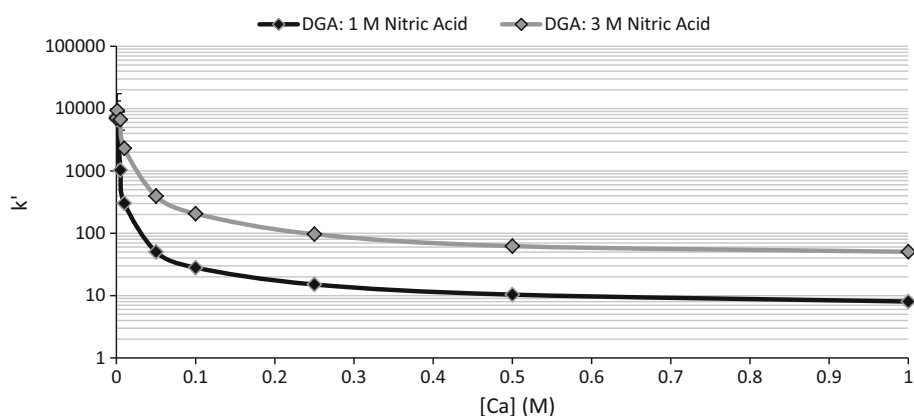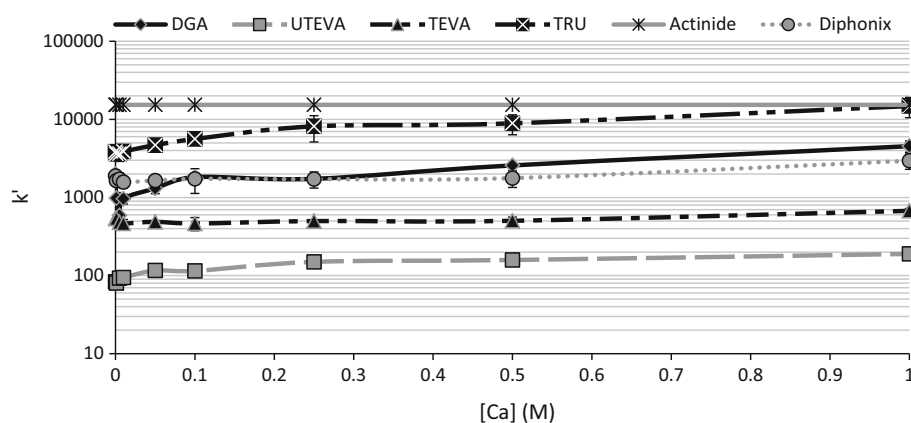
Fig. 3 Retention factors for the adsorption of ^{239}Pu from nitric acid on six extraction chromatographic resins (in the presence of varying concentrations of a calcium salt solution). Error bars are shown for all data measurements and most are smaller than the individual markers.

All data measurements that were determined above the detection limit of the Tri-Carb 5110TR instrument were reported as the detection limit

concentration from the $Ca(NO_3)_2$ salt introduced into the system. Literature has shown that the retention of Pu(IV) on both DGA and TRU resin increases with increased acid/nitrate concentration [34, 39]. All six of the resins had a strong affinity for ^{239}Pu with k' values > 100 for all resins examined. These trends indicate that these resins have a stronger affinity for the tetravalent ^{239}Pu and that calcium is not strongly competing against plutonium for the extraction sites on the resins. Actinide resin had the greatest affinity for ^{239}Pu with k' values around 10^4, which was near the detection limit of the LSC instrument. The affinity of the different extraction chromatographic resins for ^{239}Pu followed the trend: Actinide > TRU > Diphonix = DGA > TEVA > UTEVA resin.

Hydrochloric acid system

The retention factors for americium on the six extraction chromatographic resins from hydrochloric acid determined in the presence of varying amounts of calcium are shown in Fig. 4. The retention of ^{241}Am on the six extraction chromatographic resins was not significantly affected by the calcium matrix constituent at any concentration. A significant change in retention would have been indicated by retention factors that differed by orders of magnitude. However, even though there was no significant change in retention, the results indicated that the retention factor for ^{241}Am on both Actinide or Diphonix resin decreased with an increase in calcium concentration, much like the results seen for the nitric acid system. This slight decrease was attributed to the increased chloride concentration from the $CaCl_2$ salt introduced into the system. Literature has shown that the retention of Am(III) on Actinide resin decreases with increased acid/chloride concentration [44]. Actinide resin had the greatest affinity for ^{241}Am with k' values

around 10^3, which was right below the detection limit of the LSC instrument. The affinity of the different extraction chromatographic resins for ^{241}Am followed the trend: Actinide > Diphonix > DGA = TRU = UTEVA = TEVA resin. Retention factors that were less than one indicated that the radioisotope was not significantly retained by the resin. Any variances for retention factors less than one were attributed to experimental error. Resins that had k' values that were less than one were still examined in order establish a consistent set of data with the same methodology as well as to examine any synergistic effects that Ca might have on the adsorption of Am on these resins.

As previously mentioned in the introduction, both Diphonix and Actinide resin were examined for Ca interference on Am(III) adsorption [42, 44]. The k' values determined in this work matched the weight distribution (Diphonix resin) and retention factor (Actinide resin) trends presented in the literature. The work described here was conducted at 3 M HCl, while the literature was performed at 0.4, 1, and 5 M HCl (Diphonix resin) as well as 1, 2, and 4 M HCl (Actinide resin). The adsorption of Am(III) on either Diphonix or Actinide resin was not hindered at any acid concentration by the increasing amounts of calcium over the same range of salt concentration examined. However, even though there was no significant change, the results showed that the k' values decreased with an increase in salt concentration. Retention factor values of Am(III) on Actinide resin in this work (3 M HCl) matched k' values that were located between values determined in the literature for 2 M and 4 M HCl.

The retention factors for plutonium on the six extraction chromatographic resins from hydrochloric acid determined in the presence of varying amounts of calcium are shown in Fig. 5. The retention of ^{239}Pu on the six extraction chromatographic resins was not significantly affected by the

Fig. 4 Retention factors for the adsorption of ^{241}Am from hydrochloric acid on six extraction chromatographic resins (in the presence of varying concentrations of a calcium salt solution). Error bars are shown for all data measurements and most are smaller than the individual markers
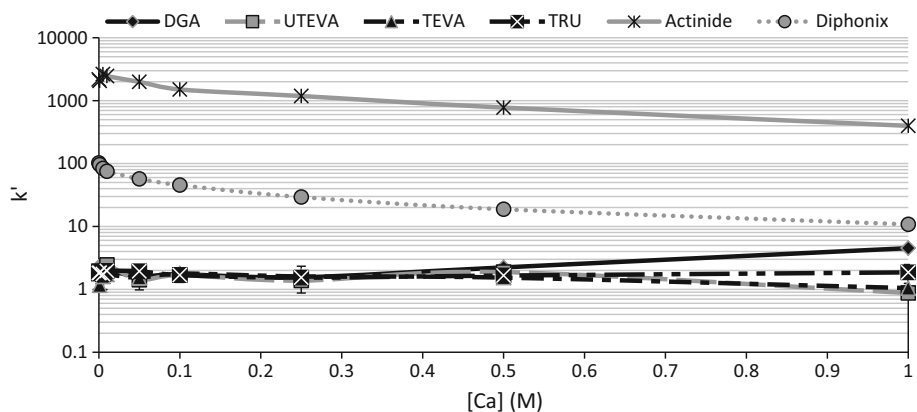
calcium matrix constituent at any concentration. As previously mentioned, a significant change in retention would have been indicated by retention factors that differed by orders of magnitude. Actinide resin not only had the greatest affinity for ^{241}Am, but also had the greatest affinity for ^{239}Pu with k' values around 10^4, which was near the detection limit of the LSC instrument. The affinity of the different extraction chromatographic resins for ^{239}Pu followed the trend: Actinide > Diphonix > DGA = TRU > UTEVA > TEVA resin. Retention factors that were less than one indicated that the radioisotope was not significantly retained by the resin. TEVA and UTEVA resin showed little affinity for the tetravalent Pu with k' values around 1. Any variances for retention factors less than one were attributed to experimental error. However, it was worth noting that the k' values reported for TEVA resin in this work were an order of magnitude less than what was reported in the literature [37]. This difference could be attributed to (1) a different batch of resin being used or (2) that the acid concentration used within this work was at the beginning of the acid range examined in the literature and/

or that the final acid concentration reported was not accurate between methods/results. TEVA resin as well as the other resins that had k' values that were less than one were still examined in order establish a consistent set of data with the same methodology as well as to examine any synergistic effects that Ca might have on the adsorption of Pu on these resins.

Calcium adsorption studies

The significant effect of calcium on the retention of americium on DGA resin called for an investigation regarding the capacity of the six extraction chromatographic resins for uptake of calcium from both nitric acid and hydrochloric acid. The capacity of a resin is the amount of metal ion that can be adsorbed onto an amount of resin. The capacity of the resins for calcium was determined by contacting the resin with a concentrated calcium solution and measuring the amount of calcium in a given volume of solution before and after contact with the resin.
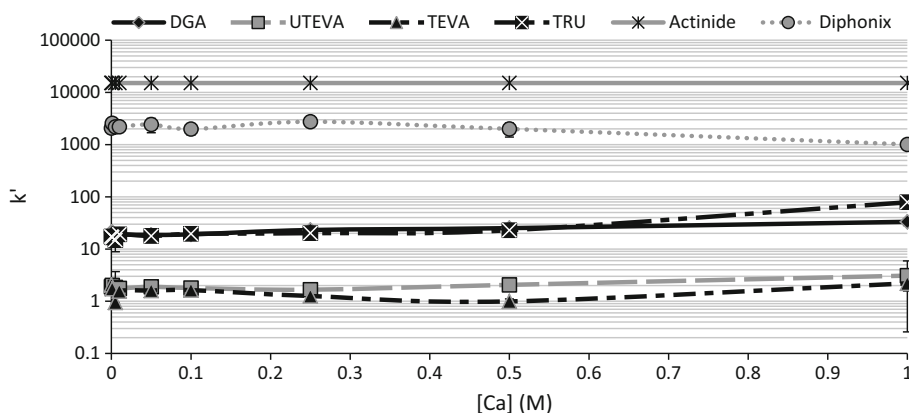
Fig. 5 Retention factors for the adsorption of ^{239}Pu from hydrochloric acid on six extraction chromatographic resins (in the presence of varying concentrations of a calcium salt solution). Error bars are shown for all data measurements and most are smaller than the

individual markers. All data measurements that were determined above the detection limit of the Tri-Carb 5110TR instrument were reported as the detection limit

The only resin that showed an uptake of calcium was DGA resin in contact with nitric acid, which was not surprising, since this is the same system that exhibited a significant interference of americium adsorption. The capacity of DGA resin for calcium was found to be 4.53 ± 0.08 mg Ca g^{-1} DGA resin. Therefore, radioanalytical separation methods that utilize DGA resin within their separation scheme must either remove or dilute the calcium present prior to the sample solution being loaded onto a DGA column in nitric acid in order for the calcium not to interfere with the uptake of radionuclides.

Conclusions

The results of the batch study experiments showed that there was no significant calcium interference on either americium or plutonium adsorption on the majority of the extraction chromatographic resins studied from either a nitric acid or hydrochloric acid system. The only exception was americium adsorption on DGA resin from nitric acid. The retention of ^{241}Am decreased by over two orders of magnitude when calcium was introduced into the system.

In general, the retention of ^{241}Am or ^{239}Pu was stronger from nitric acid than compared to the retention from hydrochloric acid. For a given resin (except DGA resin), the retention factors for ^{241}Am or ^{239}Pu did not significantly differ with an increase in calcium ions. These results indicated that there is little/no completion from the divalent calcium for the extraction sites on the six extraction chromatographic resins. It is important to note that even though there was no significant change in retention, the results also indicated that the retention factor for ^{241}Am on either Actinide or Diphonix resin from either nitric or hydrochloric acid decreased with an increase in calcium concentration.

The significant effect of calcium on the retention of ^{241}Am on DGA resin has to be considered when evaluating the suitability of this resin for radiochemical separations in the presence of larger amount of calcium. DGA resin has been used in several standard methods due to the fact that the resin has a high selectivity/retention for americium. Any developed method that utilized DGA resin would have to either remove the calcium completely or lower its concentration prior to the sample solution being loaded onto a column in nitric acid.

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