Characterization of Group V Dubnium Homologs on DGA Extraction Chromatography Resin from Nitric and Hydrofluoric Acid Matrices

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Characterization of Group V Dubnium Homologs on DGA Extraction Chromatography Resin from Nitric and Hydrofluoric Acid Matrices and Initial Investigation of Element 114 Homolog Ge

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1. Introduction

Studies of the chemical properties of superheavy elements (SHE) pose interesting challenges due to their short half-lives and low production rates. Chemical systems must have extremely fast kinetics, fast enough kinetics to be able to examine the chemical properties of interest before the SHE decays to another nuclide. To achieve chemistry on such time scales, the chemical system must also be easily automated. Most importantly however, a chemical system must be developed which provides suitable separation and kinetics before an on-line study of a SHE can be performed.

Relativistic effects make studying the chemical properties of SHEs interesting due to the impact these effects could have on the SHEs chemical properties. Relativistic effects arise when the velocity of the s orbital electrons approach the speed of light. As this velocity increases, the Bohr radius of the inner electron orbitals decreases and there is an increase in the particles mass [1, 2]. This contraction results in a destabilization of the energy of the outer d and f electron orbitals (5f and 6d in the case of SHE), which can cause these to expand due to their increased shielding from the nuclear charge [2-5]. Another relativistic effect is the spin-orbit splitting for p, d, and f orbitals into j = 1±1/2 states [4]. This can lead most interestingly to a possible increased stability of element 114, which due to large spin-orbit splitting of the 7p orbital and the relativistically stabilized $7p_{1/2}$ and 7s orbital gives rise to a closed shell ground state of $7s^2 7p_{1/2}^2$ [6].

The homologs of element 105, dubnium (Db), Ta and Nb and the pseudo-homolog Pa, are well known to hydrolyze and form both neutral and non-neutral monoatomic and polyatomic species that may cause issues with extraction from a given chemical system [7,8]. Early ion-exchange and solvent-extraction studies show mixed results for the behavior of Db. Some studies show Db behaving most similar to Ta [8-10], while others show it behaving somewhere between Nb and Pa [11, 12]. Much more recent studies have examined the properties of Db from HNO_3/HF matrices, and suggest Db forms complexes similar to those of Pa [13, 14, 15].

Very little experimental work into the behavior of element 114 has been performed. Thermochromatography experiments of three atoms of element 114 indicate that the element 114 is at least as volatile as Hg, At, and element 112. Lead was shown to deposit on gold at temperatures about 1000 $^{\circ}$C higher than the atoms of element 114. Results indicate a substantially increased stability of element 114 [16]. No liquid phase studies of element 114 or its homologs (Pb, Sn, Ge) or pseudo-homologs (Hg, Cd) have been performed. Theoretical predictions indicate that element 114 is should have a much more stable +2 oxidation state and neutral state than Pb, which would result in element 114 being less reactive and less metallic than Pb [6]. The relativistic effects on the $7p_{1/2}$ electrons are predicted to cause a diagonal relationship to be introduced into the periodic table. Therefore, 114^{2+} is expected to behave as if it were somewhere between Hg^{2+}, Cd^{2+}, and Pb^{2+}[17,18].

In this work two commercially available extraction chromatography resins are evaluated, one for the separation of Db homologs and pseudo-homologs from each other as well as from potential interfering elements such as Group IV Rf homologs and actinides, and the other for separation of element 114 homologs. One resin, Eichrom's DGA resin, contains a N,N,N',N'-tetra-n-octyldiglycolamide extractant, which separates analytes based on both size

and charge characteristics of the solvated metal species [19], coated on an inert support. The DGA resin was examined for Db chemical systems, and shows a high degree of selectivity for tri-, tetra-, and hexavalent metal ions in multiple acid matrices with fast kinetics [20-22]. The other resin, Eichrom's Pb resin, contains a di-t-butylcyclohexano 18-crown-6 extractant with isodecanol solvent, which separates analytes based on steric interactions between the cavity of the crown ether and electrostatic interactions between the oxygen's of the ether and cations in the mobile phase [23]. This particular resin has been shown to have an extremely high uptake affinity for Pb, a direct homolog of element 114, and is thus a good initial extractant to examine for a potential element 114 chemical system [24]. Figure 1.1 shows the respective extractant molecules from the DGA and Pb resins [25, 26].
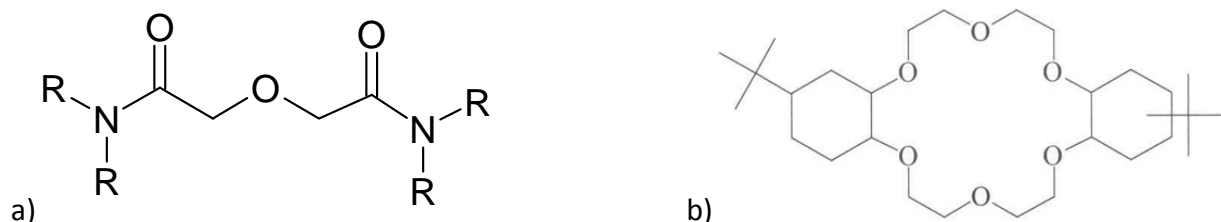

a)   b)

Figure 1.1 a) The tetradiglycolamide extractant in Eichrom's DGA resin where the R groups represent the straight or branched C8 chains. b) The crown either extractant in Eichrom's Lead resin.

Batch uptake experiments were conducted to examine the uptake behavior of Ta on the DGA resin. Batch uptake experiments were also conducted to examine the uptake behavior of Ge on the Pb resin. Column experiments were designed based on batch uptake experiments of Ta, Am, Pa, Np, Zr, and Nb to establish a sequential extraction of Group IV/V homologs as well as Am for potential use as a Db chemical system.

2. Experimental

2.1 Reagents and Materials

Eichrom's DGA normal resin or Pb resin was used for batch and column experiments (Eichrom Technologies). All acids were prepared from reagent grade acids and de-ionized water (18 MΩcm). Tracers of ^{182}Ta ($t_{1/2}$ = 114.43 d), ^{237}Np ($t_{1/2}$ = 2.144 x 10^6 y), ^{233}Pa ($t_{1/2}$ = 26.967 d), ^{95}Zr ($t_{1/2}$ = 64.02 d), ^{95}Nb ($t_{1/2}$ = 34.975 d), ^{243}Am ($t_{1/2}$ = 7.37 x 10^3 y), and ^{68}Ge ($t_{1/2}$ = 270.8 d) were prepared to have activity concentrations of 8 to 17 cps per 100 μL of solution with ^{68}Ge having a ^{68}Ga activity concentration of 1 to 2 cps per 100 μL of solution.

2.2 Activity Measurements

All measurements were taken with a high purity germanium (HPGe) gamma spectrometer with a Canberra multi-channel analyzer. Spectra were analyzed with Genie2000 spectroscopy software (Canberra Industries, Inc.) The spectral lines with the least interference and highest yield were used for identification of the radionuclides. The gamma energy chosen for ^{182}Ta was 67.7497 keV (41.2 %); for ^{233}Pa the 311.9 keV (38.5 %) line was chosen; for ^{237}Np the 86.5 keV (12.4 %) line was chosen; for ^{95}Zr the 724.199 keV (44.17 %) line was chosen; for ^{95}Nb the 765.794 keV (100 %) line was chosen; for ^{243}Am the 74.7 keV (67.2 %) line was chosen; and for ^{68}Ge the 1077.35 keV (3.0 %) ^{68}Ga line was chosen (^{68}ga reaches secular equilibrium with ^{68}Ge in about 15 hours).

2.3 Batch Experiments

The uptake of Ta on DGA resin in HNO$_3$ and HF as well as Ge on Pb resin in HNO$_3$ was determined by batch experiments. To a 15 mL polypropylene centrifuge tube 10 to 20 mg of either DGA or Pb resin was added. To each centrifuge tube 1 mL of 0.1 M – 8.0 M HNO$_3$ and 0.001 M - 0.1 M HF for the Ta on DGA study or 0.1 M – 10.0 M HNO$_3$ for the Ge on Pb resin study was added. The samples were allowed to shake for 10 minutes to allow wetting of the resin. A 100 μL spike of activity, ^{182}Ta in 4.0 M HNO$_3$ and 2.0 M HF or ^{68}Ge in 4.0 M HNO$_3$, was added to each centrifuge tube. The samples were allowed to mix for one hour (two hours in the case of ^{68}Ge) to allow equilibration while each sample was counted on an HPGe gamma spectrometer for 10 minutes. After equilibration each sample was filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter for removal of the resin from solution. The filtered supernate liquid was counted for 10 minutes on the same HPGe gamma spectrometer. For the ^{68}Ge samples 24 hours was allowed to pass to allow the ^{68}Ga daughter (used for detection) to grow to secular equilibrium.

2.4 Column Experiments

Column extraction studies of mixed and single radionuclides were performed using pre-packed 2 mL columns containing dry DGA resin. Aliquots of each desired tracer were mixed in a 15 mL polypropylene centrifuge tube and evaporated to dryness in a warm water bath, then

reconstituted in 1 mL of the desired column load solution. All evaporations were done multiple times without fully taking the solution to dryness to prevent nitric acid from etching the activity into the centrifuge tube. Prior to loading the column, tracer activity was determined by counting the 1 mL load solution on an HPGe gamma spectrometer for 30 minutes. For the extraction experiments a 24-hole polycarbonate vacuum box (Eichrom, Darien, IL, USA) with a pressure regulator was used to accelerate the elutions and maintain a flow rate of approximately 1 mL per minute. Prior to loading, the columns were conditioned with 5 mL of the load solutions acid matrix. Sequential elutions were performed with various acid matrices and volumes based on batch experiments. Columns with ^{243}Am were stripped using a final elution of 0.1 M ammonium bioxalate [27-29]. Each fraction was collected in a 15 mL centrifuge tube (evaporated and reconstituted in 1 mL of the same acid matrix if lager than 1 mL elution fraction) and counted on an HPGe gamma spectrometer. Table 2.1 summarizes the first column experiment.

Table 2.1. Column 1 summary, ^{182}Ta, ^{95}Nb, ^{95}Zr, ^{243}Am, ^{233}Pa, and ^{237}Np tracers used in load solution.

Fraction	Fraction Matrix	Fraction Volume (mL)
Load Fraction/Solution (^{182}Ta, ^{95}Nb, ^{95}Zr, ^{243}Am, ^{233}Pa, and ^{237}Np tracers)	8.0 M HNO$_3$ / 0.001 M HF	1
Rinse Fractions (four)	8.0 M HNO$_3$ / 0.001 M HF	1 each
First Elution (ten)	0.1 M HNO$_3$ / 0.001 M HF	1 each
Am strip (five)	0.1 M Ammonium bioxalate	1 each
Am strip (one)	0.1 M Ammonium bioxalate	5

Table 2.2 summarizes the second column experiment.

Table 2.2. Column 2 summary, ^{182}Ta and ^{243}Am tracers used in load solution.

Fraction	Fraction Matrix	Fraction Volume (mL)
Load Fraction/Solution (^{182}Ta, and ^{243}Am tracers)	8.0 M HNO$_3$ / 0.001 M HF	1
Rinse Fractions (four)	8.0 M HNO$_3$ / 0.001 M HF	1 each
First Elution (ten)	0.1 M HNO$_3$ / 0.001 M HF	1 each
Am strip (five)	0.1 M Ammonium bioxalate	1 each
Am strip (one)	0.1 M Ammonium bioxalate	5

Table 2.3 summarizes the third column experiment.

Table 2.3. Column 3 summary, ^{182}Ta tracer used in load solution load solution prepared by evaporation of tracer in Teflon beaker verses centrifuge tube.

Fraction	Fraction Matrix	Fraction Volume (mL)
Load Fraction/Solution (^{182}Ta tracers)	8.0 M HNO$_3$ / 0.001 M HF	1
Rinse Fractions (two)	8.0 M HNO$_3$ / 0.001 M HF	5 each

Table 2.4 summarizes the fourth column experiment.

Table 2.4. Column 4 summary, ^{182}Ta tracer used in load solution and column top frit removed.

Fraction	Fraction Matrix	Fraction Volume (mL)
Load Fraction/Solution (^{182}Ta tracers)	8.0 M HNO$_3$ / 0.001 M HF	1
Rinse Fractions (two)	8.0 M HNO$_3$ / 0.001 M HF	5 each

Table 2.5 summarizes the fifth column experiment.

Table 2.5. Column 5 summary, ^{182}Ta tracer used in load solution and column top frit present.

Fraction	Fraction Matrix	Fraction Volume (mL)
Load Fraction/Solution (^{182}Ta tracers)	8.0 M HNO$_3$ / 0.001 M HF	1
Rinse Fractions (two)	8.0 M HNO$_3$ / 0.001 M HF	5 each

Table 2.6 summarizes the sixth column experiment.

Table 2.6. Column 6 summary, ^{182}Ta and ^{243}Am tracers used in load solution prepared by adjusting stock tracer solution with concentrated HNO$_3$ without evaporation.

Fraction	Fraction Matrix	Fraction Volume (mL)
Load Fraction/Solution (^{182}Ta and ^{243}Am tracers)	8.071 M HNO$_3$ / 0.135 M HF	1
Rinse Fractions (four)	8.071 M HNO$_3$ / 0.135 M HF	1 each
Am strip (two)	0.1 M Ammonium bioxalate	5

Table 2.7 summarizes the seventh column experiment.

Table 2.7. Column 7 summary, ^{182}Ta, ^{95}Nb, ^{95}Zr, ^{243}Am, ^{233}Pa, and ^{237}Np tracers used in load solution.

Fraction	Fraction Matrix	Fraction Volume (mL)
Load Fraction/Solution (^{182}Ta, ^{95}Nb, ^{95}Zr, ^{243}Am, ^{233}Pa, and ^{237}Np tracers)	8.0 M HNO$_3$ / 0.1 M HF	1
Rinse Fractions (fifteen)	8.0 M HNO$_3$ / 0.1 M HF	1 each
First Elution (fifteen)	0.1 M HNO$_3$ / 0.1 M HF	1 each
Am strip (seven)	0.1 M Ammonium bioxalate	1 each
Am strip (one)	0.1 M Ammonium bioxalate	5

3. Results and Discussion

3.1 Batch Experiments

All batch results are presented in terms of the column capacity factor (k'), or number of free column volumes to reach peak maximum for a given elution. This value can be inferred from the batch extraction distribution ratio. The weigh distribution ratio, D_w, is defined as the amount of metal ion taken up by a given mass of resin, and is given by:

$$D_w = \left(\frac{A_o - A_s}{A_s}\right)\left(\frac{mL}{g}\right) \qquad \text{(Eqn. 1)}$$

Where A_o and A_s are the initial and final activities in cps of the metal ion in a solution of given volume, mL, and g is the mass of resin. A unitless volume distribution ratio can be calculated from the following equation:

$$D_v = \frac{(D_w)(d_{extr})}{0.4} \qquad \text{(Eqn. 2)}$$

Where D_w is the weight distribution ratio from Equation 1, d_{extr} is the density of the resin, and 0.4 is the weight loading of the resin (40 % for both DGA and Pb resins). The capacity factor (k') can be calculated by Equation 3:

$$k' = (D_v)\left(\frac{V_s}{V_m}\right) \qquad \text{(Eqn. 3)}$$

Where V_s and V_m are the volumes of the stationary (extractant) and mobile phases, which are constants derived from the slurry packed characteristics of the resin. From Equation 2 and 3, k' can be calculated by:

$$k' = (D_w)(F); \qquad F = \left(\frac{d_{extr}}{0.4}\right)\left(\frac{V_s}{V_m}\right) \qquad \text{(Eqn. 4)}$$

Where F is 0.57 and 0.55 for Eichrom's DGA and Pb resin respectively.

The uptake of Ta on the DGA resin as a function of HNO_3 at constant HF concentrations is shown in Figure 3.1.
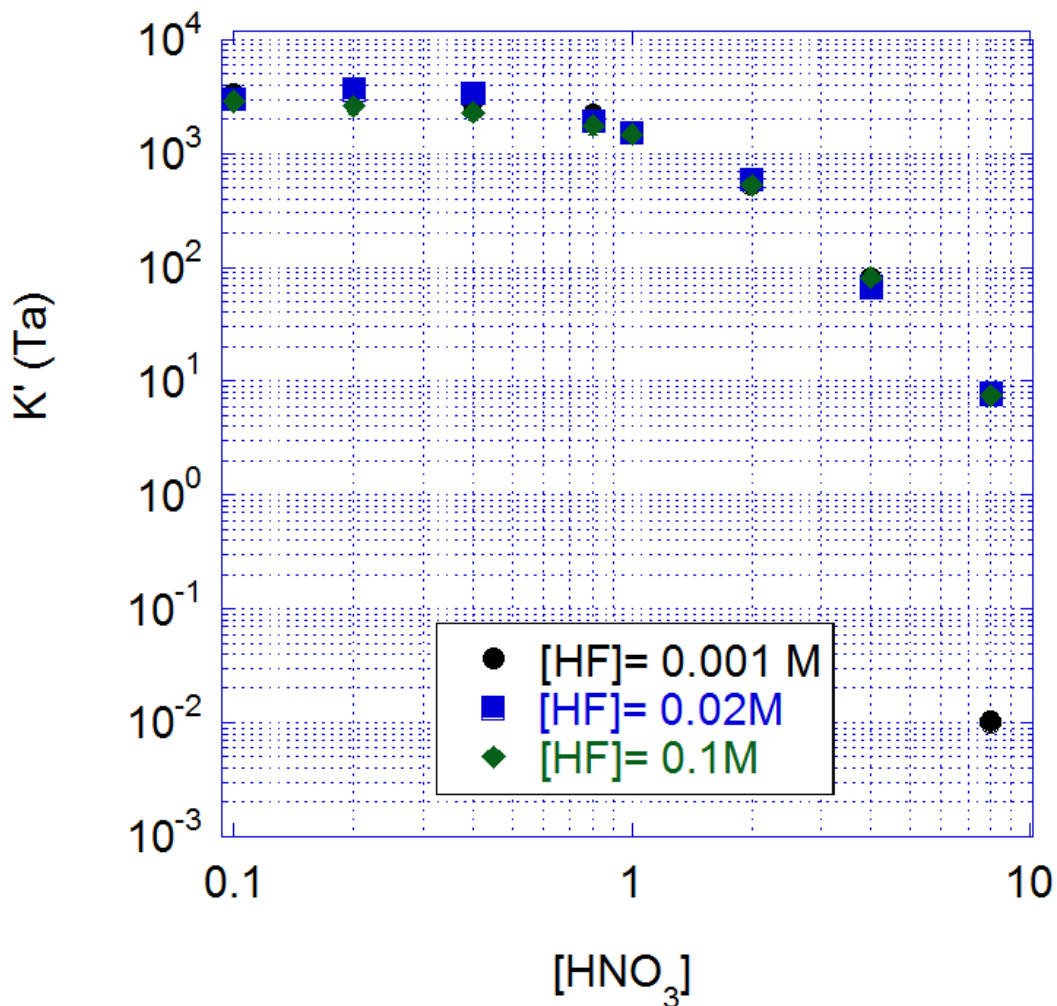
Figure 3.1. Uptake (k') of [182]Ta (carrier added) on DGA-normal resin, 50-100 μm particle size, vs. [HNO$_3$] at constant [HF] = 0.001, 0.02, and 0.1 M, one hour equilibration.

Under the conditions examined, the concentration of HF has no effect on the extraction of Ta by DGA resin, only the concentration of HNO$_3$ has an effect. At lower HNO$_3$ concentrations uptake of Ta is the highest as seen in Figure 1.

The uptake of Ge on the Pb resin as a function of HNO$_3$ concentration is shown in Figure 3.2.
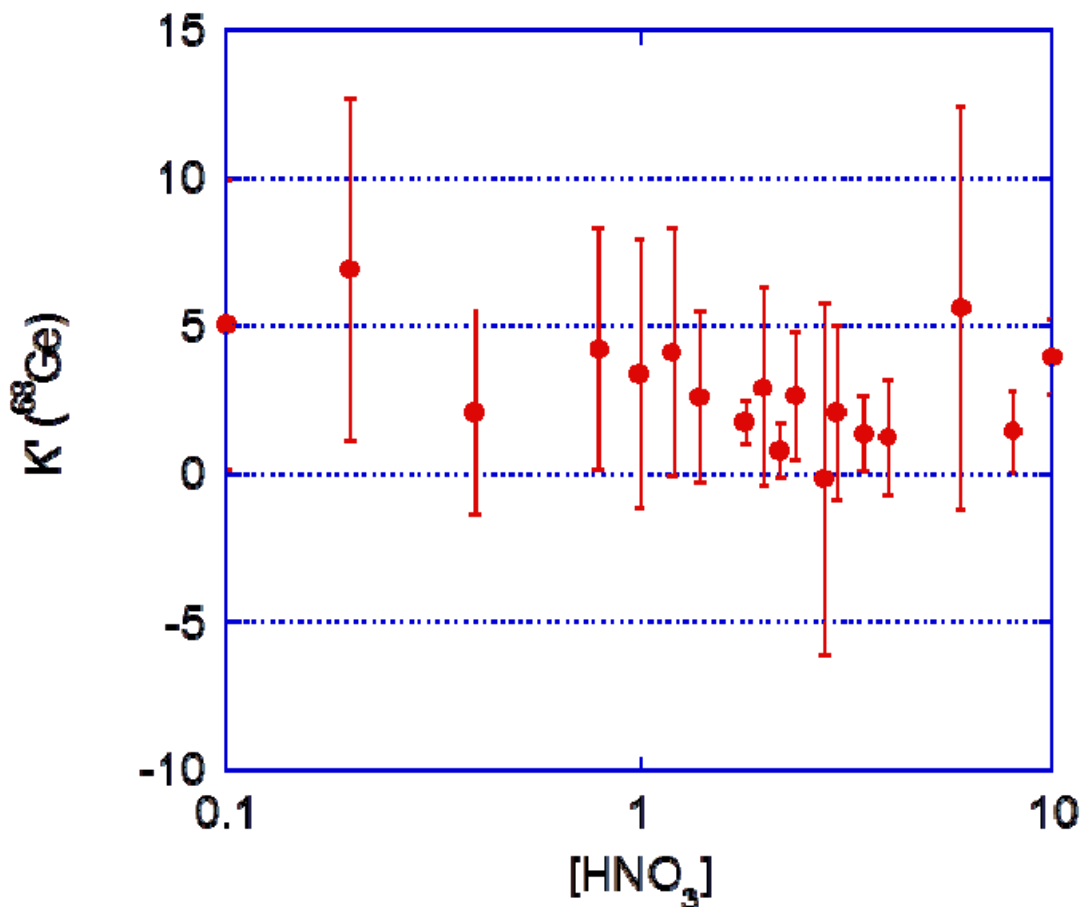
Figure 3.2. Uptake (k') of ^{68}Ge on Pb resin, 50-100 μm particle size, vs. [HNO$_3$], two hour equilibration.

Under the conditions examined, there is no uptake of Ge on the Pb resin. Eichrom's Pb resin shows extremely high uptake of Pb between 0.1 and 10 M HNO$_3$ [24]. Due to the fact the crown ether extractant is size selective and that Ge has an ionic radius much smaller than lead the lack of uptake of Ge on the Pb resin is expected.

3.2 Column Experiments

3.2a Column 1

From batch uptake experiments of ^{182}Ta, ^{95}Nb, ^{95}Zr, ^{243}Am, ^{233}Pa, and ^{237}Np on the DGA-normal resin, the column procedure in Table 2.1 was performed to attempt separation of Group IV/V homologs and Am. Figure 3.3 shows the results of the column procedure performed with the elution profile in Table 2.1.
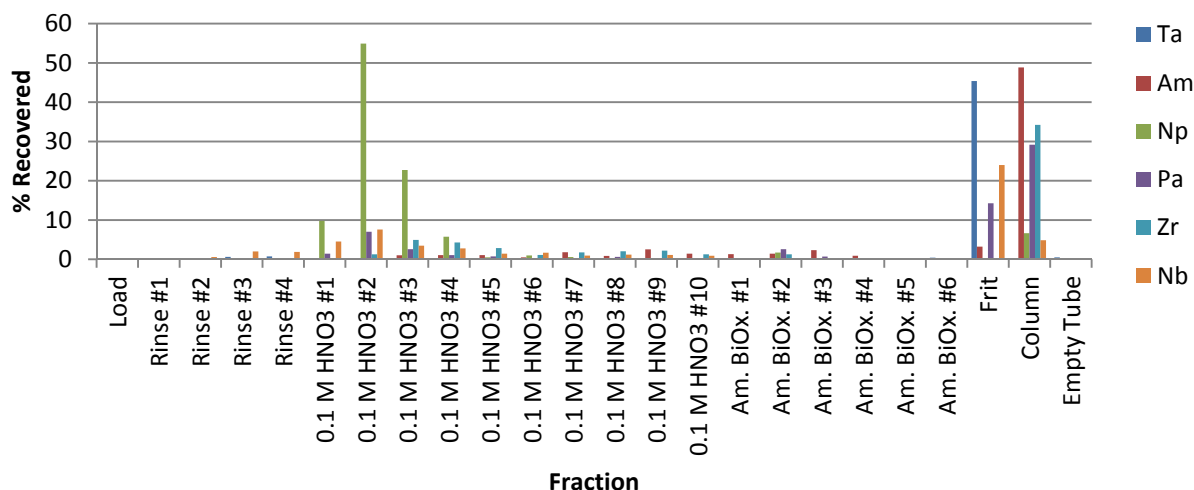
Figure 3.3. Sequential extraction of Group IV and V homologs from DGA resin using HNO$_3$/HF acid matricies from Table 2.1.

As can be seen from Figure 3.3 nearly all of the activity remained stuck to the top column frit or the column, when the load solution and rinses should have eluted Ta and other Group V elements according to the batch uptake experiments. Zirconium and Np, which should have eluted with the 0.1 M HNO$_3$ fractions, also remained on the top frit or column. This phenomenon could be explained by presence of some species formed by portions of the polypropylene centrifuge tube being removed during evaporation of the load solution, an interaction between the radionuclides and the top frit of the pre-packed column, or the HF concentration being too low.

3.2b Column 2

To assess the loss of activity to the top frit of the pre-packed column in the first procedure, the same procedure was repeated with only ^{182}Ta and ^{243}Am (Table 2). Figure 3.4 shows the results of the column procedure performed with the elution profile in Table 2.2.
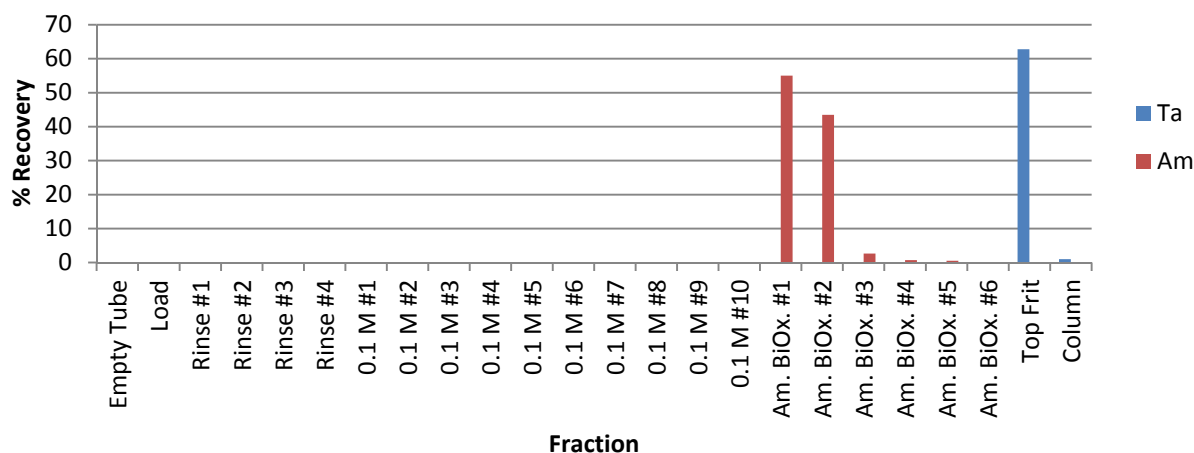
Figure 3.4. Sequential extraction of Ta from Am.

As can be seen in Figure 3.4, the Ta, which should have eluted in the rinse fractions, remained stuck to the top frit of the column like in the first column procedure. As mentioned above possible reasons for this occurrence are the presence of some species formed by portions of the polypropylene centrifuge tube being removed during evaporation of the load solution, an interaction between the radionuclides and the top frit of the pre-packed column, or the HF concentration being too low.

3.2c Column 3

To determine if the evaporation in the polypropylene centrifuge tube was causing some species to be formed that allows Ta to stick to the top frit of the column, the column procedure was performed with just Ta; however, the Ta was evaporated in a Teflon beaker. Figure 3.5 shows the results of the column procedure performed with the elution profile in Table 2.3.
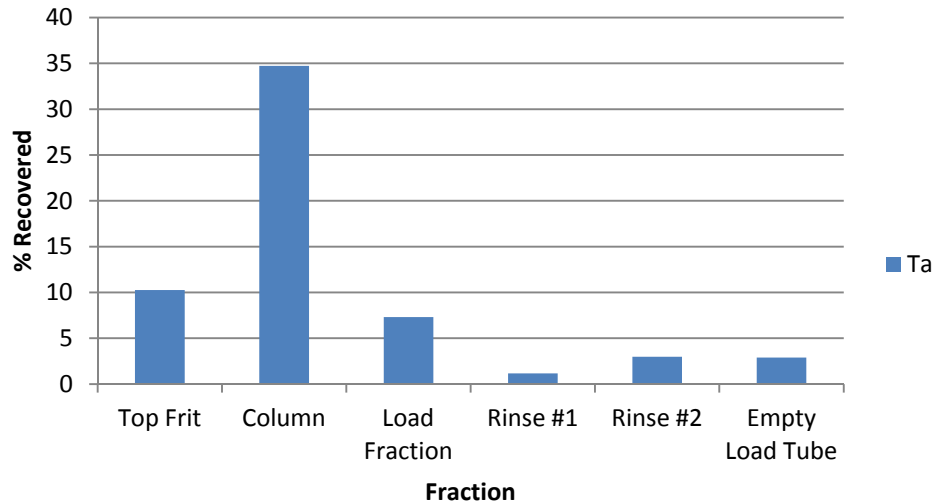

Figure 3.5. Elution of Ta from DGA pre-packed column using procedure from Table 2.3, with evaporation of load solution performed in a Teflon Beaker.

Changing the evaporation method had little effect on the elution of Ta from the DGA pre-packed column. There was still a significant amount of Ta, retained on the top frit and within the column, which did not elute with the appropriate fraction. Therefore, evaporating the load solution in a polypropylene centrifuge tube was not causing the loss of activity to the top frit of the column.

3.2d Column 4 and 5

To assess if the top frit itself was causing the Ta to interact and stick, the column procedures in Table 2.4 and 2.5 were performed with the only difference being the presence or absence of the pre-packed column's top frit. Figure 3.6 shows the results of the column procedure performed with the elution profile in Table 2.4, top frit removed.
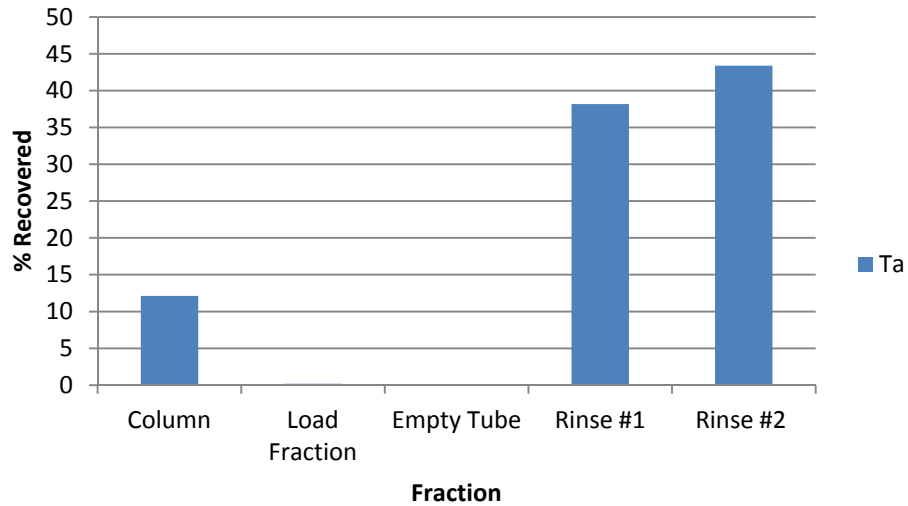

Figure 3.6. Elution of Ta from DGA pre-packed column using procedure from Table 2.4, with column top frit removed.

Figure 3.7 shows the results of the column procedure performed with the elution profile in Table 2.5, same procedure as shown in Figure 3.6/Table 2.4 but with the top frit of the column present.
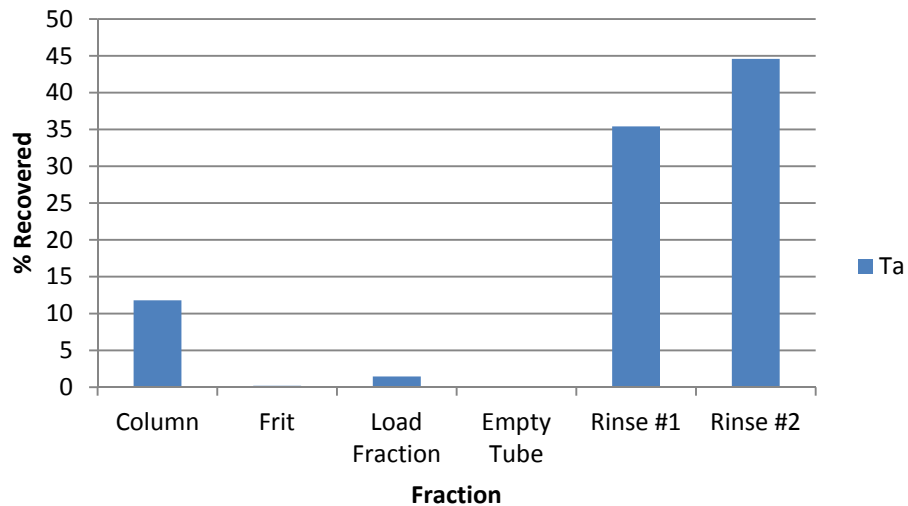

Figure 3.7. Elution of Ta from DGA pre-packed column using procedure from Table 2.5, with column top frit present.

Both the procedure with the top frit and without the top frit were nearly identical, the majority of the Ta eluted in the rinse fractions as expected from the batch uptake experiments. However, there was still a significant amount of activity remaining on the column.

3.2e Column 6

To assess whether the concentration of HF plays a roll on the Ta sticking to the column or top frit of the column, the procedure from Table 2.6 was performed with a much higher HF concentration once again with the presence of Am. Figure 3.8 shows the results of the column procedure performed with the elution profile in Table 2.6.
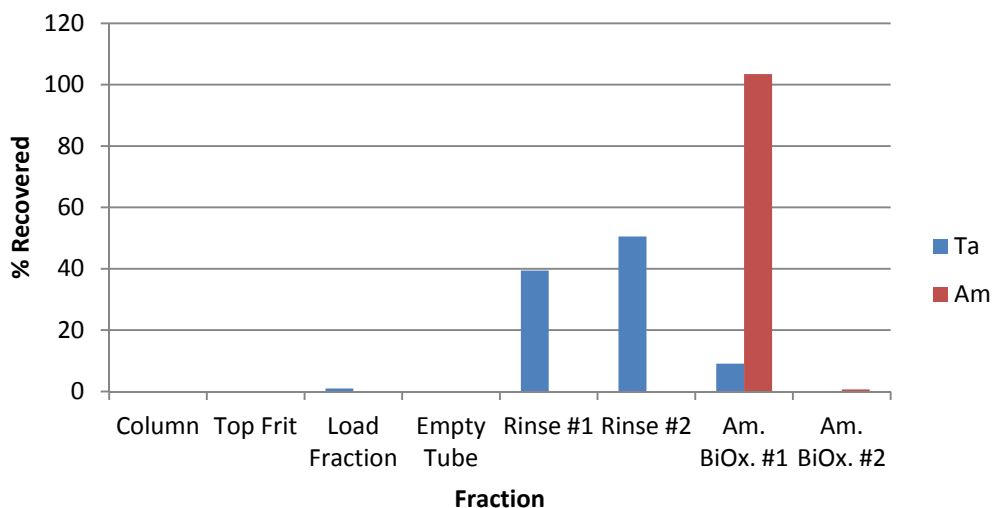

Figure 3.8. Elution of Ta and Am from DGA pre-packed column using procedure from Table 2.6, with a higher [HF] = 0.135 M.

Increasing the HF concentration from 0.001 M to 0.135 M, as seen in Figure 8, allowed for elution of Ta in the proper fraction as well as showed no Ta remaining on the column or on the top frit. Therefore, the initial separation procedure from Table 2.1 was modified for a final column.

3.2f Column 7

A final column designed to separate Group IV/V homologs and Am, was performed using the elution profile from Table 2.7, the exact same elution matricies as the first column (Table 2.1) but with 0.1 M HF verses 0.001 M HF. Figure 3.9 shows the results of the column procedure performed with the elution profile in Table 2.7.
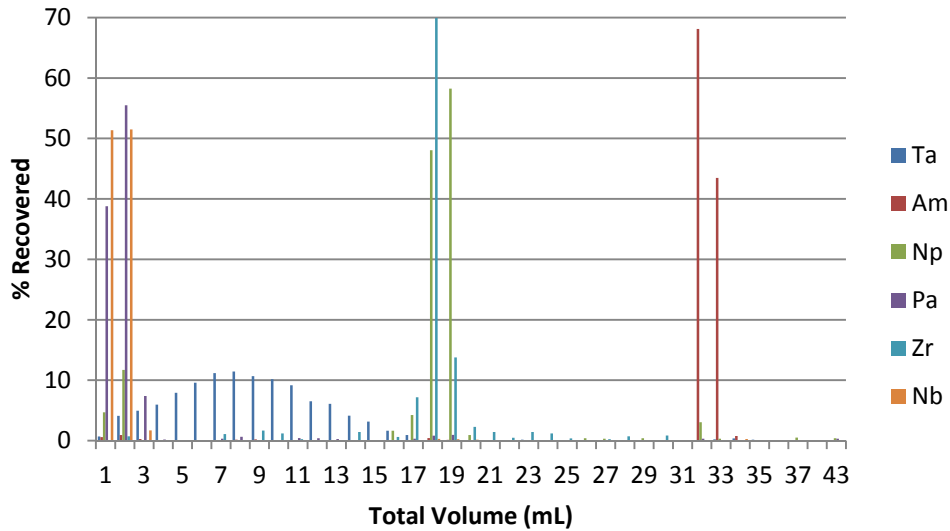
Figure 3.9.   Sequential extraction of Group IV and V homologs from DGA resin using HNO$_3$/HF acid matricies from Table 2.7.

Figure 3.10 shows the same results; however, the total percent eluted after a given volume is plotted against total volume, versus the percent recovered at a given volume as shown in Figure 3.9.
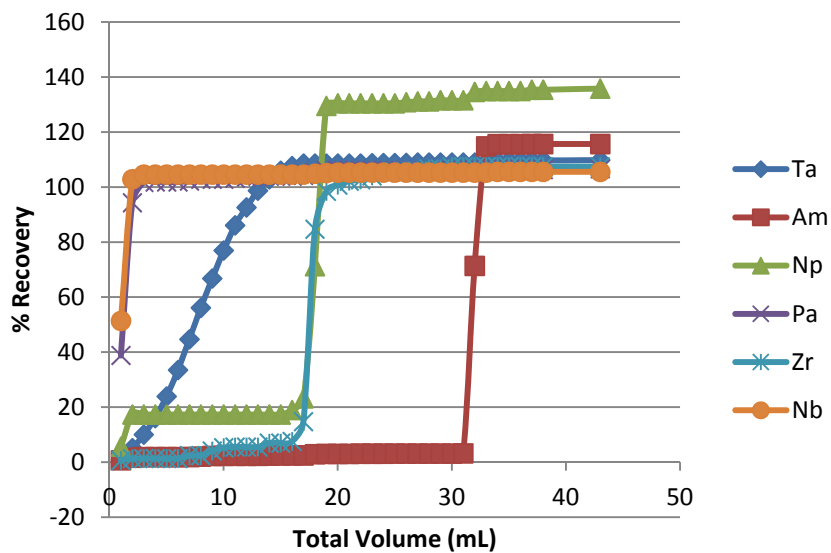

Figure 3.10.   Sequential extraction of Group IV and V homologs from DGA resin using HNO$_3$/HF acid matricies from Table 2.7. Lines are present only as a visual guide.

From Figure 3.10 it is shown that a separation of the Group IV from V homologs and Am is possible with Eichrom's DGA resin. Possible reasons for greater than 100 % recoveries are due to extra counts on each individual fraction from increased continuums due to high sample count rates.

4. Conclusions

A sequential extraction scheme was established for separation of Group IV and V homologs from each other and from Am, using Eichrom's DGA resin. It was established that a higher HF concentration is needed to avoid losses of activity during column procedures due to sticking to the column frit or various areas within the column (not representative of an interaction with the extractant molecule). Germanium was shown to have no uptake on Eichrom's Pb resin, which is expected due to the much smaller ionic radius when compared with that of Pb (an element with high uptake on the resin).

5. Future Work

Eichrom's Pb resin will be investigated further for potential development of a chemical system for the investigation element 114 and 115. Batch uptake experiments will be performed from HCl, HNO_3, H_2SO_4, and mixed H_2SO_4/HI matrices with both the homologs and pseudo-homologs of elements 114 and 115 (Pb, Sn, Ge, Hg, Cd for element 114 and Bi, Sb, As, Tl, In for element 115). If suitable uptakes are observed for separations, column experiments will be performed to assess the potential separation schemes. Assuming a working separation scheme for the homologs and pseudo-homologs of element 114 or 115 can be established, kinetic studies will be performed to assess the validity of the system for on-line SHE experiments. If no separation scheme can be established, new ligands will be investigated.

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