

Extraction chromatographic studies of Rf homologs with TEVA resin

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1. Introduction

It is of great interest to determine the chemical properties of the transactinide elements ($Z > 103$). These studies can help to assess the influence of relativistic effects on the chemical properties of the heaviest elements. The influence of relativistic effects is expected to result in deviation of periodic group trends [1]. In order to assess deviation of chemical behavior of the heaviest elements their chemical behavior should be compared to that of their lighter homologs that reside in the same periodic group. However, developing chemical systems suitable for study of the heaviest elements presents several challenges which stem from the short half-lives and low production rates of transactinide elements (TAns). The short-half lives of the TAns require the chemical system to be fast. Cross sections of nanobarns and smaller result in TAns being produced one atom-at-a-time. Since there is only a single atom present at a given time the atom can only interact with its surroundings and not with atoms of the same element. This makes development of chemical systems in which the single atom undergoes many exchange steps necessary [2]. Column chromatographic systems lend themselves well to this need and have successively been used for the study of the lightest TAns [3].

1.2 TEVA resin

The TEtraVAlent, TEVA, resin is commercially available from Eichrom Technologies, inc. with trialkyl methylammonium chloride sorbed to an inert polymeric substrate, where the alkyl chain lengths are C8 and C10 [4]. The TEVA resin, shown in Fig.1, is similar to an anionic exchange resin; however instead of the extractant molecule being chemisorbed to an inert support it is physisorbed to the inert support. Batch studies were conducted using 0.1 M to concentrated HCl, HNO₃, and H₂SO₄. Based upon

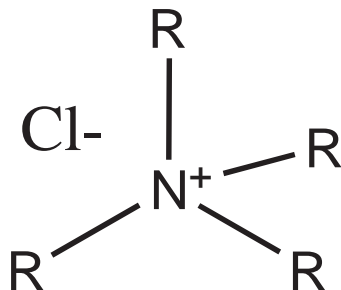


FIG. 1. The structure of the trialkyl methylammonium extractant on the TEVA resin.

the results of the batch study dynamic column studies were conducted.

1.3. HCl System

Hulet *et al.* previously showed that Rf in 12 M HCl behaves similarly to Hf on trioctylmethylammonium chloride (Aliquat 336) sorbed onto an inert support [5]. However, the chemical behavior of Rf has never been compared to that of Zr in HCl media on an Aliquat 336 resin. It was shown by Cerrai and Ghersini that a Whatman No. 1 CRL/1 type filter paper impregnated with Aliquat 336 showed separation of Zr and Hf at 1-4 and 8-10 M HCl in a thin-layer-chromatography-type experiment [6].

1.4 HNO₃ System

Lister and McDonald found an anionic specie(s) of Zr to exist in solutions above 4 M HNO₃ [7]. Faris and Buchanan found that Hf slightly adsorbs to Dowex 1x10, indicating the presences of an anionic species, while Zr exhibited a definite adsorption to the resin [8]. Recently Haba *et. al.* investigated the behavior of Zr, Hf and Rf on the anion exchange resin MCI GEL CA08Y and found that in nitric solutions ranging from 1.1 to 13.1 M Zr and Hf have lower adsorption to the anion exchange resin, indicating that Zr and Hf have a lower tendency to form anionic species compared to neutral or cationic species [9]. Haba and co-workers also found that Rf exhibited a similar chemical behavior to that of Zr and Hf, while Pu and Th formed $[M(NO_3)_6]^{2-}$ species, where M is Pu or Th [9]. This indicates that the anion exchange resin MCI GEL CA08Y could be used to remove actinides in a catcher block type experiment. For a discussion on catcher block experiments please see Ref. [10].

1.5 H₂SO₄ System

Ryabchikov and co-workers determined that the stability of inorganic complexes with Zr and Hf decrease in the order of $F^- > SO_4^{2-} \gg Cl^- > NO_3^-$ [11]. This indicates that SO_4^{2-} should bind Group 4 elements stronger than chloro or nitrate systems, which have been extensively studied for Rf. The sulfate systems of Rf should be of interest when assessing the chemical behavior of Rf compared to its homologs, Zr and Hf. Because the sulfate ion binds Group 4 elements so tightly it could provide insight into any relativistic effects that maybe affecting the chemical properties of Rf.

Recently, Li and co-workers investigated the ion-exchange behavior of Zr and Hf in 0.018-0.99 M H₂SO₄ for application to Rf chemistry. It was found that over this concentration range Zr and Hf adsorbed to both cation and anion exchange resins. In batch studies Zr and Hf behaved similarly on anion exchange resin and had a separation factor, $SF_{Zr/Hf}$, of 3 to 4. The dominant species that adsorbed to the anion exchange resin was $M(SO_4)_3^{2-}$, where M is Zr or Hf [12].

2. Experimental

2.1 Materials

The TEVA resin was purchased from Eichrom Technologies Inc. The concentrated HCl, HNO₃ and H₂SO₄ used for solution preparation were purchased from VWR. All chemicals were used without further purification. The actual concentrations of acid solutions were determined via titration with standardized 0.4895 M NaOH using a Class A buret and phenolphthalein indicator.

2.2 Radionuclide Solutions

⁹⁵Zr ($t_{1/2} = 64$ d) was obtained from Eckert and Ziegler Isotope Products in the oxalate form in 0.5 M oxalic acid (1 mCi). The ⁹⁵Zr oxalate was converted to the chloride form and purified upon receipt. The conversion from oxalate to chloride was done by precipitating Zr in the hydroxide form using concentrated ammonium hydroxide and lanthanum carrier. The precipitation was followed by dissolution in concentrated hydrochloric acid. The dissolved product was then passed over a Dowex 1 x 8 anion exchange column. The column was flushed with concentrated HCl to remove any impurities from the Zr. The Zr was then stripped from the anion exchange column using 2 M HCl. The resulting solution was diluted in 2 M HCl to a volume that resulted in an approximately 3 cps/mL ⁹⁵Zr solution.

The ¹⁷⁵Hf ($t_{1/2} = 70$ d) was produced from proton bombardment of lutetium foil, ^{nat}Lu(p,x)¹⁷⁵Hf, at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL). The ^{nat}Lu foil contained approximately 0.1 mCi ¹⁷⁵Hf. Upon receipt the foil underwent dissolution in aqua regia (1:1). The resulting solution was then loaded onto a Dowex 1 x 8 anion exchange column conditioned with concentrated HCl. The column was then rinsed with copious amounts of concentrated HCl to remove all impurities. The Hf was then eluted with 4 M HCl. The purified ¹⁷⁵Hf fraction was diluted in 2 M HCl and had an activity concentration of approximately 5 cps/mL.

2.3 Batch Studies

All tracer solutions were stored in 2 M HCl acid. An appropriate amount (3 to 5 cps) of each radionuclide to be studied was transferred to a clean, dry 12 x 55 mm plastic sample tube. This was then counted using a Perkin-Elmer Wizard² 2480 automatic NaI gamma counter for 30 minutes to establish the initial activity of each radionuclide of interest in the sample. The samples were then evaporated to dryness in a water bath with a jet of compressed air flowing over each sample, and reconstituted in 1 mL of the solution to be studied. 10-20 mg of the desired resin was quantitatively weighed into the 12 x 55 mm plastic sample tube containing the radionuclides. Samples were then placed on a shaker for one hour. The liquid sample was then extracted from the sample tube using a syringe equipped with a needle. The liquid sample was then passed through a syringe tip filter set-up and into a clean, dry 12 x 55 mm plastic sample tube. The sample was then counted using the same gamma counter as above for 1 hour to determine the quantity of activity taken up by the resin.

The activity on the resin is taken as the difference between final and initial activity in solution. The weight distribution, D_w , of the element of interest can be obtained using Equation 1. In Equation 1 A_0 is the initial activity of the solution; A_s is the activity on the solid phase; W is the mass of the resin in

grams and V is the volume of solution in milliliters. Once D_w is calculated k' , free column volume to peak maximum, can be found using Equation 2, where F is the resin factor. The resin factor, F, is available from Eichrom.

$$D_w = \left(\frac{A_p - A_s}{W} \right) + \left(\frac{A_s}{V} \right) \quad (1)$$

$$k' = D_w \times F \quad (2)$$

2.4 Column Studies

Column extraction of mixed radionuclides was performed with pre-packed 2 mL columns containing the TEVA resin. An appropriate volume of each stock solution was transferred to a clean, labeled 12 x 15 mm sample tube, and used as-is. The sample was evaporated to dryness in a water bath with a jet of compressed air flowing over each sample, reconstituted in 1 mL of the desired acid solution. The sample was then counted for 30 minutes on the same automatic gamma counter to determine the initial activity of each radionuclide present.

During the column extraction studies a vacuum box set-up was used, available from Eichrom International, Inc. The vacuum box set-up consisted of a 24-hole polycarbonate vacuum box equipped with a pressure regulator was used to accelerate the elution process. A pressure between 8 and 15 in Hg was maintained. The column was conditioned with the appropriate solution and then the 1 mL solution containing the radionuclides of interest was then loaded on the column. The elution profile of each radionuclide was then determined in 0.5 mL increments. The samples were then brought up to a volume of 1 mL to maintain counting geometry. The samples were then counted on the same Wizard² automatic gamma counter for 30 minutes to determine the quantity of radionuclides in each fraction.

3. Results and Discussion

3.1 HCl Solutions

3.1.1 Batch Studies

Preliminary results are discussed in the remainder of this report. The extraction behavior of Zr and Hf from 0.1 to 11.5 M HCl with the commercially available extraction chromatographic resin TEVA was studied. The results from this batch study are shown in Fig. 2.

It is apparent from Fig. 2 that both Zr and Hf have virtually no affinity for the TEVA resin below approximately 6 M HCl. This is expected, as it is well documented that Group 4 metals do not form an anionic complex below 6 M HCl, however above 6 M HCl the MCl_6^{2-} complex is formed, where M is Zr

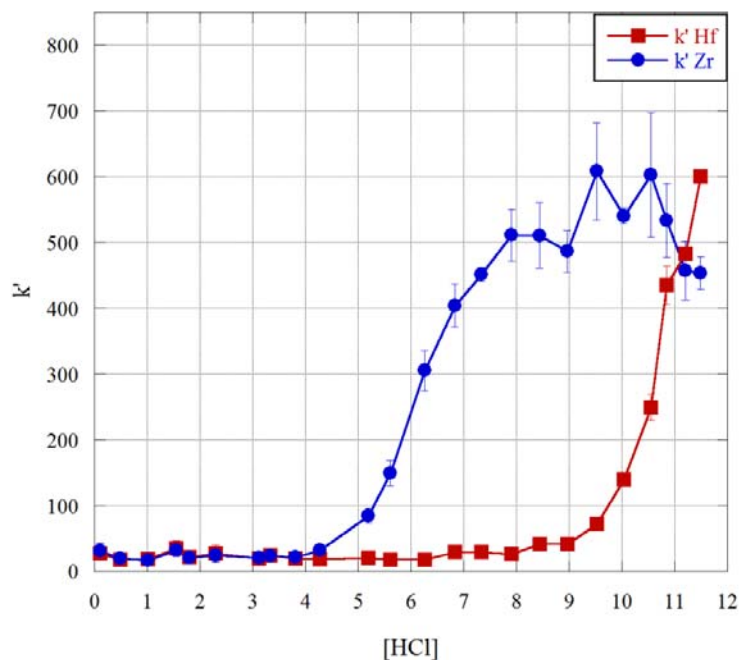


FIG. 2. The separation behavior of Zr and Hf on Eichrom's TEVA resin. The error bars are population standard deviations.

or Hf [13,14]. Zr has a much stronger affinity for the TEVA resin than does Hf, until 11 M HCl is reached. Above 11 M HCl the affinity trends appears to invert and Hf has a stronger affinity for the TEVA resin than Zr. This is most likely due to the presence of a large number of chloride anions, which causes increased formation of the HfCl_6^{2-} species. The largest separation of Zr from Hf occurs between 6 and 8.5 M HCl, as indicated by the separation factors for Zr and Hf ($\text{SF}_{\text{Zr/Hf}}$) listed in Table I. Based upon these results 6.256, 6.839, 7.332 and 7.900 M HCl were chosen for further investigation in a dynamic column study. It was believed that these concentrations would allow Hf to be eluted from the TEVA column while leaving Zr adsorbed to the column from a load solution of concentrated HCl (11.49 M).

Table 1. TEVA separation factor for Zr and Hf as a function of HCl concentration obtained in batch studies.

[HCl]	$\text{SF}_{\text{Zr/Hf}}$
0.1036	1.13±0.13
0.4886	1.13±0.11
1.005	0.95±0.09
1.549	0.93±0.04
1.792	1.00±0.13
2.297	0.90±0.04
3.118	1.03±0.01
3.335	0.99±0.04
3.811	1.13±0.23
4.273	1.77±0.27
5.189	3.96±0.50
5.600	8.24±0.40
6.256	17.0±4.8
6.830	14.0±1.11
7.332	15.5±2.87
7.900	19.2±3.26
8.432	12.1±1.35
8.956	11.7±1.74
9.516	8.39±0.93
10.00	3.85±0.16
10.45	2.41±0.33
10.84	1.22±0.05
11.20	0.94±0.06
11.49	0.75±0.03

3.1.2 Dynamic Column Studies

The column was loaded and then eluted with 6 aliquots of 0.5 mL of 6.256, 6.839, 7.332 or 7.900 M HCl. Based on the batch results it was believed that this would elute the Hf off the column while leaving Zr adsorbed to the column. Zr was then eluted with 6 aliquots of 0.5 mL of 3 M HCl. The elution curves of each Hf elution condition are shown in Fig. 3.

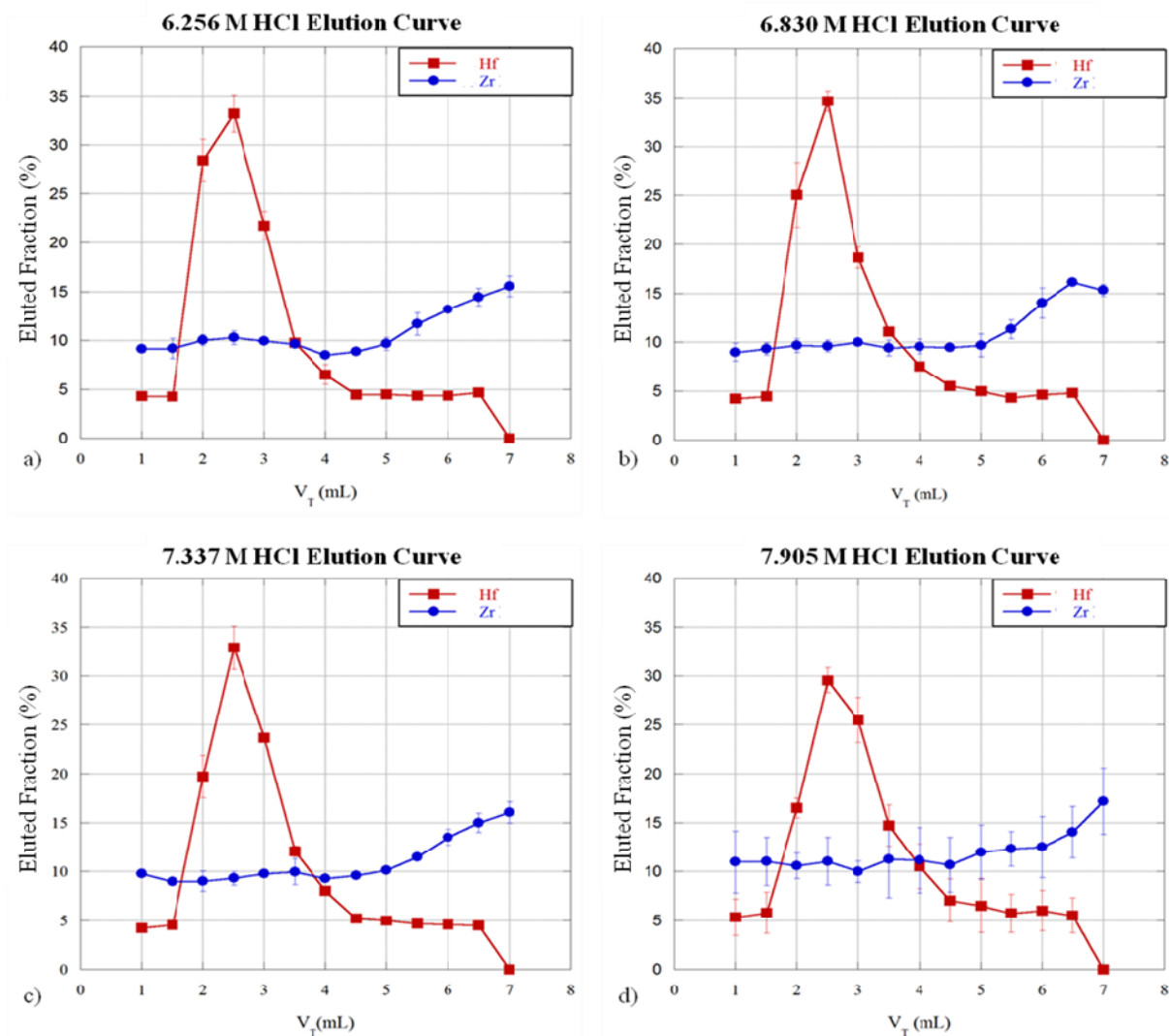


FIG. 3. The HCl elution profiles for Zr and Hf on Eichrom's TEVA resin, where V_T is the total solution volume passed through the column. All columns were loaded using a concentrated HCl solution. a) The elution profile using an eluent of 6.256 M HCl to elute Hf. b) The elution profile using an eluent of 6.830 M HCl to elute Hf. c) The elution profile using an eluent of 7.337 M HCl to elute Hf. d) The elution profile using an eluent of 7.905 M HCl to elute Hf. Zr was eluted from all columns using 3 M HCl.

In Fig. 3 the first data point at 1 mL indicates the load fraction and is not included in the eluted percentages below. In panel a there is separation of Hf and Zr. $104 \pm 3\%$ of Hf is eluted with the 3 mL of 6.256 M HCl, while $57.7 \pm 1.5\%$ of Zr is eluted with the Hf. This indicates a $SF_{Hf/Zr}$ of 1.80 ± 0.04 . In

panel b there is also separation of Hf and Zr. $101 \pm 4\%$ of Hf is eluted with 3 mL of 6.830 M HCl, while $57.6 \pm 1.5\%$ of Zr is eluted with the Hf. This indicates a $SF_{Hf/Zr}$ of 1.76 ± 0.04 . In panel c there is again separation of Hf and Zr. $101 \pm 3\%$ of Hf is eluted with 3 mL of 7.337 M HCl, while $57.4 \pm 1.6\%$ of Zr is eluted with the Hf. This indicates a $SF_{Hf/Zr}$ of 1.79 ± 0.05 . In panel d there, yet again, appears to be separation of Hf and Zr. $103 \pm 5\%$ of Hf is eluted with 3 mL of 7.905 M HCl, while $65.0 \pm 6.4\%$ of Zr is eluted with the Hf. This indicates a $SF_{Hf/Zr}$ of 1.58 ± 0.11 .

Based on these results if an experiment were to be done with Rf it would be recommended that the radioactivity be loaded onto the column from concentrated HCl, followed by an elution of Hf with 6.256, 6.830 or 7.337 M HCl; Zr could then be eluted from the column using 3 M HCl. Under these conditions the experiment would have to be conducted many times in order to minimize the effects of statistical fluctuations on the separation of Rf from its homologs.

3.1.3. Conclusions

The extraction chromatographic behavior of Zr and Hf in HCl has been investigated using the commercially available TEVA resin. Batch studies using carrier free ^{95}Zr and ^{175}Hf indicated Zr and Hf were best separated between 6 and 8.5 M HCl with separation factors of Zr from Hf ($SF_{Zr/Hf}$) exceeding 10. This result was then used during dynamic column studies to preferentially elute Hf and determine the optimal conditions for separating Hf from Zr. It was determined that a maximum separation factor of Hf from Zr ($SF_{Hf/Zr}$) was 1.89 at 6.3 M HCl, in dynamic column studies.

Based on these results it is recommended that the radioactivity be loaded on to the column from concentrated HCl, followed by an elution of Hf with 6.256, 6.830 or 7.337 M HCl, Zr could then be eluted from the column using 3 M HCl. Following this recommended separation procedure there would need to be many experiments to ensure proper chemical characterization of Rf, with respect to Zr and Hf, and not draw a conclusion based upon statistical fluctuation.

3.2 HNO₃ System

3.2.1 Batch Studies

The extraction behavior of Zr and Hf from 0.1 to 15.9 M HNO₃ with the commercially available extraction chromatographic resin TEVA was studied. The results from this batch study are shown in Fig. 4.

It is apparent from Fig. 4 that Zr and Hf have identical behavior on the TEVA resin, within error bars. Horwitz and co-workers report a k' for Th that is greater than 10^2 and k' for Pu that is greater than 10^4 [14]. Here, it is shown that the highest k' value for Zr and Hf is < 50 at 7.367 M HNO₃. Upon comparison of the k' values reported here for Zr and Hf and those reported for Th and Pu by Horwitz and co-workers it appears that the TEVA resin would work well for removal of actinides in a catcher block type experiment by sorbing the actinide elements and allowing Zr and Hf to pass through the resin. However, based on Fig.4 the TEVA resin is not a good candidate for intra-Group 4 separations and thus not a good candidate for chemically characterizing Rf with respect to its homologs, Zr and Hf.

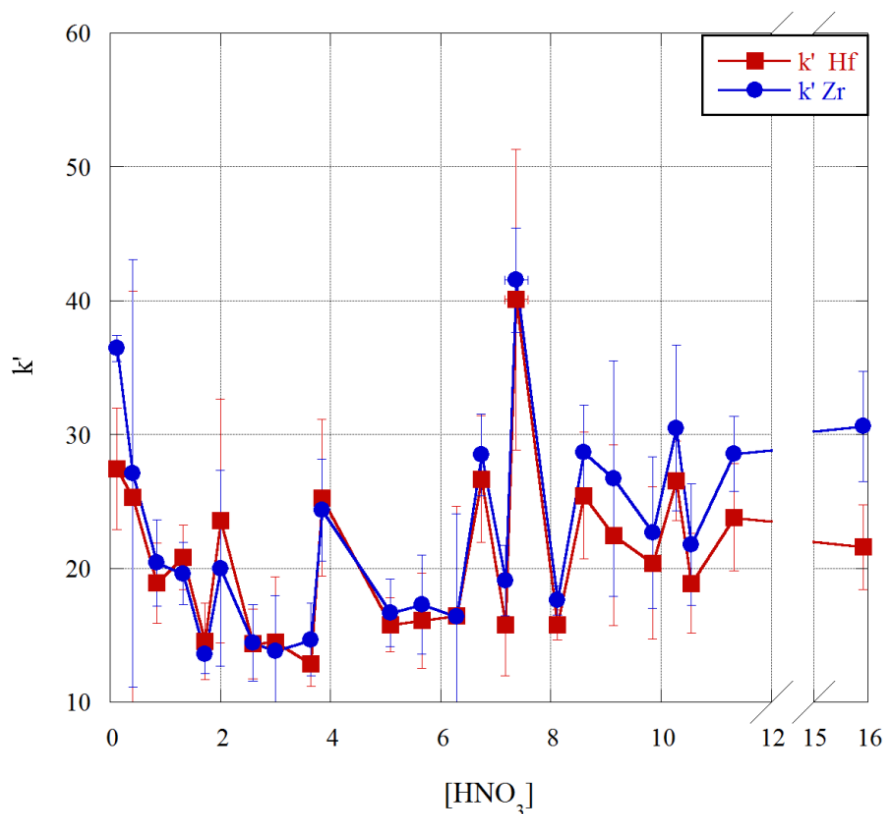


FIG. 4. The separation behavior of Zr and Hf in a nitric matrix on Eichrom’s TEVA resin. The error bars are population standard deviations.

Similar k' values are found in this study as in the study by Haba and co-workers [9], implying a similar speciation of Zr and Hf. It appears from these results that Zr and Hf have a lower tendency to form anionic species in nitric matrices and a higher tendency to form neutral or cationic species.

The separation factors for Zr from Hf ($SF_{Zr/Hf}$) at their respective acid concentrations are shown in Table II. It is apparent from the $SF_{Zr/Hf}$ values reported in Table II that there is virtually no separation of Zr from Hf. Even though little separation was found dynamic column studies were conducted to ensure that the static batch system is representative of the dynamic column system.

Table II. TEVA separation factor for Zr and Hf as a function of HNO₃ concentration obtained in batch studies

[HNO ₃]	SF _{Zr/Hf}
0.1199	1.35±0.21
0.4120	1.08±0.04
0.8452	1.08±0.04
1.324	0.94±0.02
1.712	0.95±0.13
1.995	0.85±0.11
2.589	1.01±0.11
2.992	0.96±0.03
3.642	1.13±0.13
3.840	0.98±0.08
5.083	1.05±0.05
5.653	1.08±0.10
6.285	1.00±0.08
6.734	1.08±0.10
7.173	1.23±0.14
7.367	1.06±0.20
8.119	1.12±0.02
8.530	1.14±0.10
9.134	1.18±0.05
9.843	1.12±0.07
10.28	1.14±0.15
10.55	1.15±0.06
11.33	1.21±0.09
15.91	1.42±0.09

3.2.2 Dynamic Column Studies

Each resin was pre-treated with 3 mL of concentrated HNO₃ prior to loading the column with 1 mL of solution containing Zr and Hf. The column was then loaded with the radionuclides of interest. The load solution containing Zr and Hf was in concentrated HNO₃; this was chosen to ensure if an anionic complex could form there would be enough nitrate ion present to bind Zr and/or Hf. The column was the eluted with 6 aliquots of 0.5 mL of 7.173, 8.119 or 11.325 M HNO₃. From the results of the batch studies it was expected that under all of these elution conditions both Zr and Hf would co-elute. However, to ensure all Zr and Hf were eluted off of the column 6 aliquots of 0.5 mL of 3 M HNO₃ were then taken after the initial elution solution of high molarity nitric acid. 3 M HNO₃ was chosen based on the batch studies; Zr and Hf had little affinity for the TEVA resin under these conditions. The elution curves for Zr and Hf under various HNO₃ elution conditions can be seen in Fig. 5.

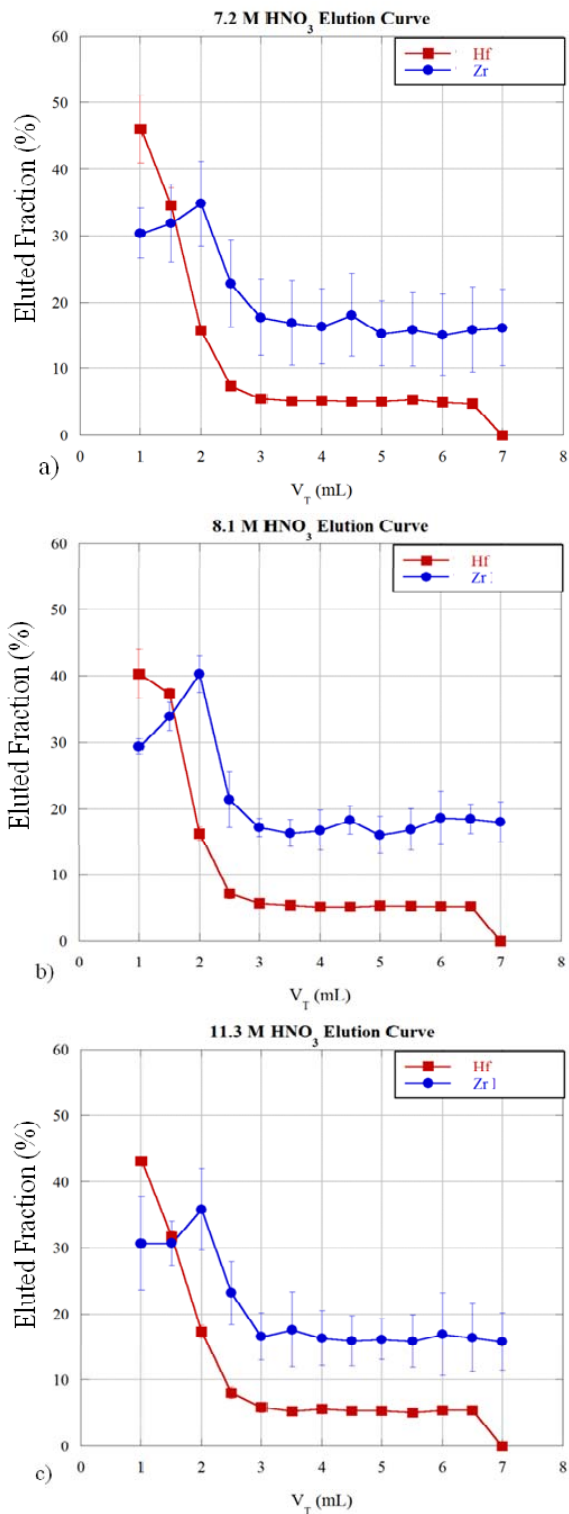


FIG. 5. The elution profiles for Zr and Hf on Eichrom's TEVA resin. All samples were loaded using a concentrated HNO₃ solution. a) The elution profile using an eluent of 7.173 M HNO₃. b) The elution profile using an eluent of 8.119 M HNO₃. c) The elution profile using an eluent of 11.325 M HNO₃. All errors are reported as population standard deviations.

In Fig. 5 the first data point at 1 mL indicates the load fraction. Despite the indications in the batch study that Zr and Hf behaved identically in a nitric matrix on the TEVA resin, Fig. 5 shows that Zr consistently elutes later than Hf. This indicates that Zr has a slightly higher affinity for the TEVA resin, in a nitric matrix, than does Hf. However, there is still little separation between the two elements. Under the 7.173 M HNO₃ elution conditions 140.±15% of the Zr is eluted with the 3 mL elution fraction and 73.4±2.7% of the Hf is eluted, Fig. 5a. Under the 8.119 M HNO₃ elution conditions 146±7% of the Zr is eluted with the 3 mL elution fraction and 76.9±1.7% of the Hf is eluted, Fig. 5b. Under the 11.325 M HNO₃ elution conditions 152±12% of the Zr is eluted with the 3 mL elution fraction and 73.7±9.1% of the Hf is eluted, Fig. 5c.

If the total elution fraction is summed over the entire elution curve a number >100% results. In order to explain this deviation the following is proposed: For Zr, the background levels in the counting windows of the automated gamma counter are approximately 0.3 cps and for Hf the background is approximately 0.2 cps. Generally, this small of a background would not be a problem however, being that the solution concentrations used in these studies are so low the 0.3 and 0.2 cps background becomes approximately 10% and 4% of the signal for Zr and Hf, respectively. Increasing the counting time of the sample to decrease the background is not a feasible option due to the number of samples processed. Increasing the quantity of activity in solution is also not an option, as this could lead to polynuclear formation, which is in turn not representative of atom-at-a-time chemistry [15,16,17].

Despite this rather large error it can still be seen that TEVA does not separate Zr and Hf in a nitric matrix that is suitable for chemically characterizing Rf with respect to its homologs. It is still possible to use the TEVA resin in a catcher block setup to purify the element of interest from tetravalent actinides.

3.2.3 Conclusions

The extraction chromatographic behavior of Zr and Hf in HNO₃ has been investigated using the commercially available TEVA resin. Batch studies using carrier-free ⁹⁵Zr and ¹⁷⁵Hf indicated that Zr and Hf behave identically in a nitric matrix and cannot be separated using the TEVA resin. Despite this dynamic column studies were carried out to ensure that static batch studies were representative of dynamic column studies.

In the dynamic column study it was found that Zr has a slightly higher affinity for TEVA than does Hf. However, there is not enough separation between Zr and Hf to render it useful for the chemical characterization of Rf with respect to its lighter homologs, Zr and Hf.

Both the batch and dynamic column studies indicates that Zr and Hf have a tendency to form an cationic or neutral species even in high nitric acid concentrations, an observation that has been noted by Haba and co-workers [9].

Despite not being useful for the chemical characterization of Rf with respect to Zr and Hf it is possible that TEVA could be used to separate out tetra- and hexavalent actinides from Group 4 elements in a catcher-block-type chemistry experiment.

3.3.1 H₂SO₄ System

3.3.1 Batch Studies

The extraction behavior of Zr and Hf from 0.1 to 15.9 M H_2SO_4 with the commercially available extraction chromatographic resin TEVA was studied. The results from this batch study are shown in Fig. 6.

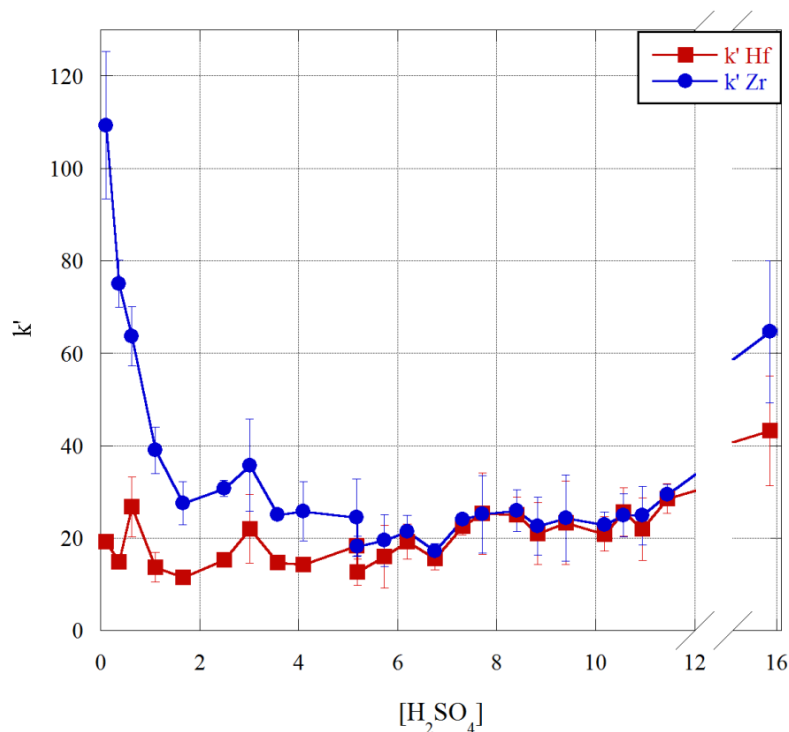


FIG. 6. The separation behavior of Zr and Hf in a sulfuric matrix on Eichrom's TEVA resin. The error bars are population standard deviations.

It can be seen from Fig. 6 that above 3 M H_2SO_4 Zr and Hf have nearly identical behavior to one another. The 3 – 15.9 M concentration regime is inadequate to chemical characterize Rf with respect to Zr and Hf. The behavior of Zr and Hf below 3 M is much more interesting for the chemical characterization of Rf. At 0.1069, 0.3696 and 0.6315 M H_2SO_4 Zr has a much higher affinity for the TEVA resin than Hf and shows promise for the separation of Zr and Hf and in turn investigation of relativistic effects in Rf.

The separation factors for Zr from Hf ($\text{SF}_{\text{Zr/Hf}}$) at their respective acid concentrations are shown in Table III. It is apparent from the $\text{SF}_{\text{Zr/Hf}}$ values reported in Table I that there is some separation of Zr from Hf at the lowest $[\text{H}_2\text{SO}_4]$. Based on the results of the batch study a load solution of concentrated (15.86 M) H_2SO_4 was chosen due to Zr and Hf both having similar and high adsorption to the TEVA resin from this solution. Elutions solutions of 0.1069, 0.3696, 0.6315 and 1.101 M H_2SO_4 were chosen to elute Hf from the column while leaving Zr on the column. Finally, an elution solution of 6.5 M H_2SO_4 was chosen to elute Zr and any remaining Hf from the column.

Table III. TEVA separation factor for Zr and Hf as a function of H₂SO₄ concentration obtained in batch studies.

[H ₂ SO ₄]	SF _{Zr/Hf}
0.1069	5.71±0.83
0.3696	5.10±0.56
0.6315	2.45±0.45
1.101	2.89±0.32
1.656	2.41±0.46
2.488	2.02±0.15
3.007	1.67±0.34
3.575	1.72±0.15
4.093	1.79±0.31
5.167	1.34±0.11
5.186	1.47±0.16
5.733	1.26±0.25
6.192	1.12±0.04
6.753	1.11±0.10
7.309	1.07±0.08
7.714	1.00±0.02
8.408	1.03±0.09
8.831	1.09±0.11
9.397	1.05±0.10
10.18	1.11±0.13
10.56	0.98±0.16
10.94	1.15±0.18
11.45	1.04±0.11
15.86	1.51±0.17

3.3.2 Dynamic Column Studies

Each resin was pre-treated with 3 mL of concentrated H₂SO₄ prior to loading the column with 1 mL of solution containing Zr and Hf. The column was then loaded with the radionuclides of interest. The load solution containing Zr and Hf was in concentrated H₂SO₄; this was chosen to ensure if an anionic complex could form there would be enough sulfate ion present to bind Zr and/or Hf. The column was eluted with 6 aliquots of 0.5 mL of 0.1069, 0.3696, 0.6315 or 1.101 M H₂SO₄. From the results of the batch studies it was expected that below 1 M H₂SO₄ Hf would elute leaving Zr on the column. To ensure all Zr and Hf were eluted off of the column 6 aliquots of 0.5 mL of 6.5 M H₂SO₄ were also eluted. This was chosen based on the batch studies; Zr and Hf had little affinity for the TEVA resin under these conditions. The elution curves for Zr and Hf under various H₂SO₄ elution conditions can be seen in Fig. 7.

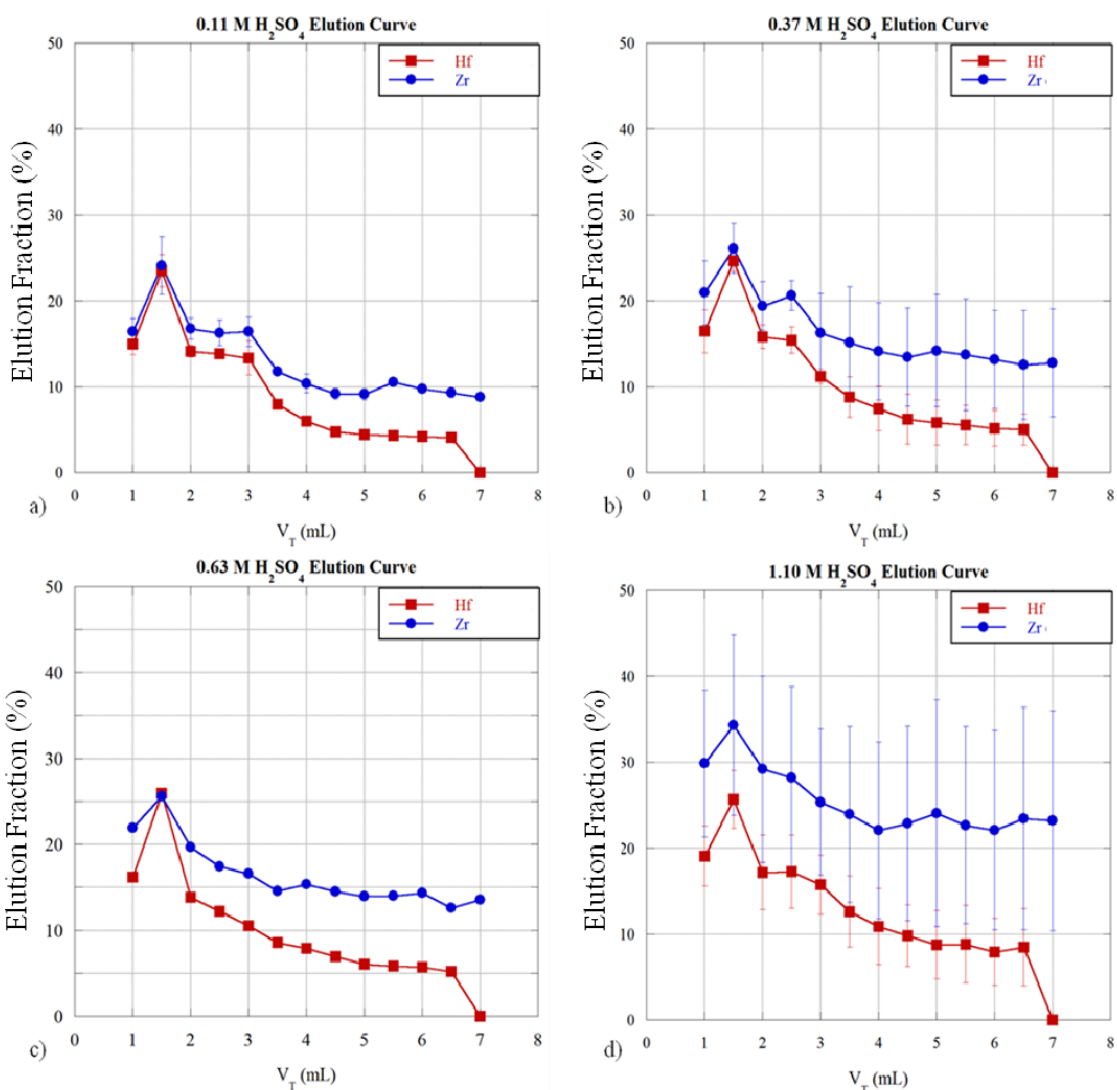


FIG. 7. The elution profiles for Zr and Hf on Eichrom's TEVA resin. All samples were loaded using a concentrated H_2SO_4 solution. a) The elution profile using an eluent of 0.1068 M H_2SO_4 followed by 6.5 M H_2SO_4 . b) The elution profile using an eluent of 0.3696 M H_2SO_4 followed by 6.5 M H_2SO_4 . c) The elution profile using an eluent of 0.6315 M H_2SO_4 followed by 6.5 M H_2SO_4 . d) The elution profile using an eluent of 1.101 M H_2SO_4 followed by 6.5 M H_2SO_4 . All errors are reported as population standard deviations.

In Fig. 7 the first data point at 1 mL indicates the load fraction. In the batch studies the $SF_{Zr/Hf}$ for 0.1036 and 0.3696 M H_2SO_4 were found to be > 5 , however it can be seen from Fig 7 a and b there is little separation of Zr and Hf on the dynamic column. Under the 0.1068 M H_2SO_4 elution conditions $95.7 \pm 4.3\%$ of the Zr eluted with the 3 mL elution fraction and $78.8 \pm 2.6\%$ of the Hf eluted, Fig. 37a. Under the 0.3696 M H_2SO_4 elution conditions $112 \pm 11\%$ of the Zr eluted with the 3 mL elution fraction and $83.4 \pm 4.3\%$ of the Hf eluted, Fig. 37b. Under the 0.6315 M H_2SO_4 elution conditions $109 \pm 15\%$ of the Zr eluted with the 3 mL elution fraction and $79.0 \pm 7.8\%$ of the Hf eluted, Fig 7c. Under the 1.101 M H_2SO_4 elution conditions $163 \pm 25\%$ of the Zr eluted with the 3 mL elution fraction and $98.9 \pm 9.9\%$ of the

Hf eluted, Fig 7d. Despite this rather large error it can still be seen that TEVA does not separate Zr and Hf in a sulfuric matrix that is suitable for chemically characterizing Rf with respect to its homologs.

3.3.3. Conclusions

The extraction chromatographic behavior of Zr and Hf in H₂SO₄ has been investigated using the commercially available TEVA resin. Batch studies using carrier free ⁹⁵Zr and ¹⁷⁵Hf indicated that Zr and Hf in a low molarity sulfuric matrix could be separated adequately for use in chemically characterizing Rf using the TEVA resin. This also indicates that Zr has a higher tendency to form an anionic species in a sulfuric matrix, than does Hf. Based on the batch study results dynamic column studies were carried out.

In the dynamic column study it was found that Zr has a slightly higher affinity for TEVA than does Hf. However, there was not enough separation between Zr and Hf to render it useful for the chemical characterization of Rf with respect to its lighter homologs, Zr and Hf.

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