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Extraction chromatographic studies of rutherfordium and dubnium homologs

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EXTRACTION CHROMATOGROPHIC STUDIES OF RUTHERFORDIUM AND DUBNIUM HOMOLOGS

By

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ABSTRACT

Extraction Chromatographic Studies of Rutherfordium and Dubnium Homologs

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Studying the chemistry of transactinide elements does not only allow for these elements to be properly placed in the Periodic Table, but it also permits for the extrapolation of the electronic structure based upon the position of the element in the Periodic Table. In addition it enable for the assessment of the role that relativistic effects play in the chemical behavior of the heaviest elements. An improved understanding of the role of relativistic effects in chemistry of the heaviest elements allows for a better understanding of the fundamentals principles that govern the Periodic Table. In order to investigate the chemistry of the transactinides, chemical studies on the homologs and pseudo-homologs of the element must first be performed.

Chemical studies of the homologs and pseudo-homologs can be completed in a number of ways. Gas-phase chemistry, solvent extraction and ion-exchange chromatography have all been used to study a number of transactinide elements as well as their respective homologs and pseudo-homologs. No matter the method of study, a given system must fulfill the following requirements to be considered suitable; fast kinetics, high separation factors, large number of exchange steps, highly selective and samples easily prepared for alpha spectroscopy. The system must allow for rapid separation due to the short half-

lives of transactinide elements (on the order of a few seconds up to a minute). A large number of exchange steps are necessary due to the fact there is only one atom present at a given time. In order for one atom to be statistically representative of a macroscopic amount the atom must undergo many interactions with the two phases of the separation system. The system should also be highly selective to ensure that background contamination is removed and separation of the transactinide from its homologs and pseudo-homologs is achieved. Finally, the samples generated from the separation must be easily and rapidly prepared for alpha spectroscopy so that the decay of the short lived transactinide element can be directly detected.

The aim of this research is to develop two separation schemes for elements 104 and 105 that fulfill all of these requirements. For element 105 the proposed extractant molecule is a tetra diglycoloamide in a mixed acid matrix. In the case of element 104 crown ether based ligands of interest. The proposed separation schemes for element 104 and 105 are based on both commercially available and in-house synthesized resins.

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CHAPTER 1

INTRODUCTION

1.1 Historical Perspective

The goal of studying transactinide elements is to further understand the fundamental principles that govern the periodic table. Prior to the 1940's, elements up to uranium, with the atomic number 92 (Z=92) were known. The discovery of the neutron by James Chadwick in 1932 paved the way for experiments involving neutrons and the discovery of transuranic elements.[1] Enrico Fermi and Emilio Segré were believed to be the first to produce transuranic elements in 1934 through the neutron bombardment of uranium, which was followed by a β^- decay.[2] In 1939 Otto Hahn and Fritz Straβmann concluded that the reaction products in neutron bombardment of uranium were isotopes of known elements and proposed that the uranium nucleus had split into two parts.[3, 4] Later that same year, Lise Meitner and Otto Robert Frisch provided the theoretical interpretation for these results and coined the process of a nuclei splitting into two parts "fission".[5] With the discovery of fission, the quest for transuranic elements begun. In 1939 Edwin McMillan and co-workers discovered element 93, known today as neptunium, in the fission fragments of a neutron bombardment of (Uranium-238) ^{238}U followed by a β^- decay to ^{239}Np.[6] A second transuranic element, plutonium, was discovered a year later through the deuteron bombardment of ^{238}U followed by two successive β^- decays to ^{238}Pu (plutonium-238) by Glenn T. Seaborg and co-workers.[7] Curium-242 and Americium-242, ^{242}Cm and ^{242}Am respectively, were discovered in the early 1940's, as well.[8] In 1945 Seaborg put forth the actinide concept, which proposed that transuranic elements belonged to a series, within the periodic table, similar to the elements of the lanthanide series.[8] Based on this concept, the elements thorium (Th) through element 103 would have similar chemical behavior to one another and this behavior could be predicted. This concept lead to the discovery of four new transuranic elements from 1949 to 1952, berkelium (Bk) and californium(Cf) through bombardment of actinide targets with deuterons; fermium (Fm) and einsteinium (Es) in the debris from "MIKE", a thermonuclear test.[9-11] Between 1955 and 1961 the actinide series was completed with the addition of elements 101-103, Mendelevium (Md), Nobelium (Nb) and Lawrencium (Lr), respectively, with Md being the first element to be produced one atom-at-a-time.[12, 13] A step-wise approach, element by element, can be used to produce elements up to Fm through neutron capture in high-flux reactors followed by successive β^- decays.[14] Elements beyond Fm incur problems of low production rates, short half-lives and large probabilities for spontaneous fission. The production rate of Fm and elements beyond are such that appreciable quantities for targets cannot be produced and thus the step-wise approach with neutrons and deutrons up the periodic table ceases.

The instability of elements beyond Fm can be explained by a combination of the liquid drop and nuclear shell models. The stability of nuclei is governed by the total binding energy and size of the nuclei in question, which is proportional to the mass number of the nuclei. These characteristics lead to the assumption that the nucleus exhibits a liquid drop like behavior.[15] The liquid drop model of the nucleus states that a nucleon interacts with its nearest neighbor through nuclear forces and that there are no interactions over long distances. Also, the volume of the nucleus is equal to the volume of the nucleons present in the nucleus and at some finite volume the nucleus will no longer be able to contain the nucleons. The semi-empirical mass formula, shown in

Equation 1 is a result of the liquid drop model of the nucleus.[15] In Equation 1, the first term is the volume term which considers how the energy of the nucleus is directly proportional to the number of nucleons present; the second term of the equation is the asymmetric term, which accounts for variation in the neutron to proton ratio; the third term is the Coulombic term which accounts for Coulombic repulsion between protons; the fourth term considers the Strong Nuclear Force. The Strong Nuclear Force is analogous to surface tension in the liquid drop model, at the outer most point of the nucleus; the final term is the pairing term and allows for consideration of the odd-even effect on stability. For odd proton-odd neutron (odd-odd) nuclei this term is negative, for odd A nuclei the term is zero, and for even proton-even neutron this term is positive. As the binding energy (E_B) of the nucleus is increased more energy is needed to separate the nucleus and thus the nucleus is more stable. Based on this as Z increases the asymmetric term and Coulombic term increase and therefore destabilize the nucleus. As the nucleus becomes increasingly destabilized, the nucleus will tend to fission and production rates and half-lives of these elements will become increasingly small. However, the liquid drop model predicts that the periodic table ends around element 100, this is not the case as elements through 118 have been produced. At this point, the liquid drop model becomes inadequate to explain the phenomenon of transfermium elements. In order to fully explain the existence of elements beyond Z=100 an additional model is needed.

$$E_B(MeV) = a_v A - \frac{a_a (N-Z)^2}{A} - a_c \frac{Z^2}{A^{1/3}} - a_s A^{2/3} \pm \delta(A,Z)$$

Equation 1

The nuclear shell model helps to further explain the existence of elements beyond einsteinium. In the nuclear shell model protons and neutrons occupy nuclear shells, which are analogous to electronic orbitals in an atom. The nuclear closed shells are spherical shells and referred to as "magic numbers" and occur at proton and neutron numbers of 2, 8, 20, 28, 50, and 82. At these magic numbers the nuclei have a higher binding energy and are more stable. If a nuclei has both a magic number of protons and neutrons, then the nuclei is said to be doubly magic. For protons 114, 164 and 182 are predicted to be magic numbers as well, for neutrons these predictions occur at 126, 184 and 196.[16] William Myers and Wladyslaw Swiatecki predicted an island of stability, where the nuclei would have increased stability due to the existence of a spherical nuclear shell. These nuclei on the island of stability should be separated from the peninsular of known nuclei by a sea of instability.[17] The notion of the island of stability prompted experimental attempts to land on the island however until recently experiments have failed to reach the island. To date, only the shore of the island of stability has been reached and the inland of the island has yet to be explored.[18-21] Historically, step-wise expansion of the periodic table has proven more fruitful.

The current periodic table is shown in Figure 1.1. Element 104, Rutherfordium (Rf) begins a new transition metal series, called the transactinides. The credit for discovery of the first two transactinide elements, Rf and dubnium, Db are shared by the groups at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia and the group at the Berkeley Heavy Ion Linear Accelerator (HILAC) in Berkeley, California.[22]

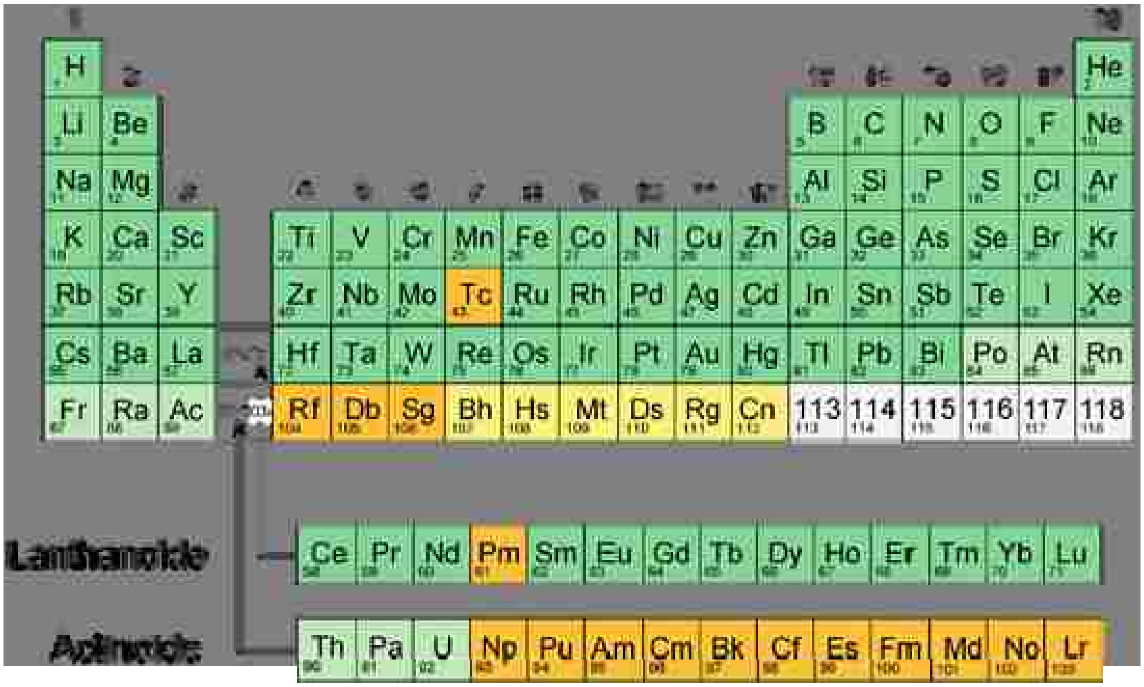

Figure 1.1. The current Periodic Table of Elements.[23]

Rf was produced via the reaction $^{244}Pu + ^{22}Ne \rightarrow ^{260}Rf + 4n$ in Dubna, Russia by G.N. Flerov and co-workers and via the $^{249}Cf + ^{12}C \rightarrow ^{257}Rf + 4n$ reaction in Berkeley, USA by A. Ghiorso et. al.[24, 25] Dubnium was produced via the $^{243}Am + ^{22}Ne \rightarrow ^{260}Db$ (^{261}Db) $+5n(4n)$ reaction by the Dubna group and via the $^{249}Cf + ^{15}N \rightarrow ^{260}Db + 4n$ by the Berkeley group.[26, 27] In addition to Rf and Db, elements 106 to 112 have been recognized by the International Union of Pure and Applied Chemistry (IUPAC) and element 106 to 111 have officially been named, Seaborgium, Bohrium, Hassium, Meitnerium, Darmstadtium, Roentgenium and Copernicium, respectively.[28-34] In addition, claims for the discovery of element 113 have been brought forth by a Japanese group and by a joint American-Russian collaboration. Claims for the discovery of elements 114 to 118, have also been brought forward by a joint American-Russian collaboration and are awaiting conformation.[18-21, 35]

1.2 Heavy Element Production

Any transuranic element is man-made and does not exist in nature, with the exception of Pu. Traces of ^{244}Pu and ^{239}Pu have been found in meteorites and in natural U ores, respectively.[36-45] Element neptunium through curium can be produce in reactors while elements berkelium through fermium need to be produced in high-flux reactors. These elements are formed through neutron capture reactions followed by successive β^- decays. However, transfermium elements cannot be produced in a high-flux reactors because there is a lack of β^- decay, short α decay and large probability for spontaneous fission, which prevent higher elements from being reached.[14] Elements above fermium are only accessible through the use of nuclear reactions involving heavy-ions ($Z > 2$). In heavy-ion fusion reactions a heavy-element target is bombarded with accelerator produced heavy-ions. For elements produced an atom-at a-time ($Z > 100$) a thin target, 0.8 mg/cm^2, is necessary to allow for the fused nuclei to recoil out of the target and be collected. Thicker targets can be used, for the production of larger quantities of these elements, however this requires a half-life long enough to allow for the dissolution of the target required to make the element accessible for chemical studies. The target is typically bombarded with a beam intensity of approximately 3×10^{12} ions per second. This beam and target combination result in a production rate of a few atoms per minute (Rf and Db production) to an atom every week or lower (upper transactinide elements).[1, 14, 16] There are two primary methods for achieving heavy-ion fusion: cold and hot fusion. In a successful fusion reaction, of either type, the projectile and target nuclei fuse together then evaporate neutrons to de-excite the compound nucleus to form the element of interest. The probability of a successful fusion reaction depends upon overcoming the Coulomb barrier between the positively charged projectile and target nuclei.[16] Production of an unstable compound nucleus, transfer reactions (transfer of some number nucleons, below A, from the projectile to the target nucleus) or no reaction between the projectile and target occur if the Coulomb barrier is not overcome.

A nuclear reaction resulting in nuclear excitation energies of 10-15 MeV is commonly called a "cold fusion" reaction. Such excitation energies occur when a spherical target nuclei, such as ^{208}Pb or ^{209}Bi, is bombarded with a medium-heavy projectile, in the range from Ca to Zn. These cold fusion reactions tend to cause evaporation of 1 to 2 neutrons, leaving behind a neutron deficient isotope. The neutron deficiency tends to result in isotopes with shorter half-lives than their neutron heavy counter parts.[16] Isotopes with longer half-lives can be achieved through hot fusion reactions. A nuclear reaction resulting in nuclear excitation energies of 40-50 MeV is considered a "hot fusion" reaction. These excitation energies occur when an actinide target is bombarded with a lighter heavy ion beam, such as O, Ne and Mg. Hot fusion reactions tend to cause evaporation of 4 to 5 neutrons from the compound nucleus. The neutron evaporation causes the nucleus to de-excite. The increased excitation energy leads to a higher fission probability.[16] Recently, a projectile of ^{48}Ca and an actinide target have been used in successful attempts to produce longer lived nuclides of elements above 112.[18-20] The use of ^{48}Ca as a projectile resulted in a comparably much higher reaction cross section of approximately a picobarn (approximately one atom per week) for all reactions in this regime. It is thought that ^{48}Ca provides additional stabilization to the compound nucleus due to its doubly magic nature. The doubly magic nature gives two advantages: 1) The ^{48}Ca has cold-fusion like properties and will steer the compound nucleus away from fission; 2) The hot fusion like asymmetry between the target and projectile create an easier fusion pathway.[16]

1.3 Relativistic Effects

The goal of studying transactinide elements (TAn) is to further understand the fundamental principles that govern the periodic table. The current arrangement of the periodic table allows for the extrapolation of chemical behavior of an element based on the group to which it belongs. The correct position of a TAn can be assessed by investigating its chemical behavior and comparing it to that of the homologs and pseudo-homologs of a TAn. Homologs of a TAn are the elements in the same group of the periodic table as the TAn. Pseudo-homologs of a TAn are elements possessing the same main oxidation state and similar ionic radius to the TAn. For example, the homologs of Rf, are titanium, zirconium and hafnium (Ti, Zr and Hf); the pseudo-homologs of Rf are thorium, Th, and Pu. Understanding the chemical behavior of a TAn compared to its homologs and pseudo-homologs also allows for the assessment of the role relativistic effects play in determining its electronic structure and therefore its chemical behavior.

Relativistic effects occur when the velocity of the s-orbital electrons closest to the nucleus approaches the speed of light. The velocity of these electrons can approach the speed of light because they have no orbital momentum. Electrons will approach relativistic velocities when there is a strong enough Coulombic attraction between the electrons and the nucleus. The attraction force increases as Z increases and there is sufficient attraction beginning at $Z = 79$. The increase in electron velocity causes two effects, first there is an increase in electron mass, m, for inner electronic orbitals, which causes a decrease in the Bohr radius, a_B, (Equation 2). .[46, 47] Therefore a contraction of outer s and p orbitals is also seen. The contraction of these orbitals results in an energy destabilization of the outer most shell, in the case of transactinides this would be the 5f and 6d orbitals. This destabilization of the outer most orbitals causes a stabilization of valence s and p orbitals. The valance s and p orbitals become stabilized due to decreased screening of effective nuclear charge. The outer most d shell and all f shells can also experience a radial expansion due to the fact that these orbitals are being screened from the effective nuclear charge.[16, 46, 48, 49] Another relativistic effect is the "spin-orbit splitting" for p, d and f orbitals into j = 1± ½ states.[16] Where j is the total angular momentum vector and l is angular quantum number. All of these effects have the same order of magnitude and increase roughly according to Z^2. [16] This feature is what makes studying the heavy elements so interesting because the chemical properties of transactinide elements should strongly be affected by these effects. For this work the terms heavy elements and transactinide elements will be used interchangeably. They are defined as elements with an atomic number greater than 103, Z > 103.

$$a_B = \frac{\hbar^2}{mc^2}$$

Equation 2

1.4 Transactinide Chemistry

1.4.1 Atom-at-a-Time Chemistry

The nature of transactinide element production makes chemical studies of these elements difficult. TAn elements are produced on an atom-at-a-time basis due to their low production cross sections. Highly sensitive detection systems are necessary to record the nuclear decay of the separated products so that the identified decay scheme can be unanimously attributed to a single TAn element. Requirements for positive identification are genetic correlation through successive α decay signatures or direct detection of an α decay energy of a known element.[50] In some cases the decay series will end in a spontaneously fissioning isotope. In this case the alpha decay energies of the preceding nuclides as well as the total kinetic energies of the fission fragments can be employed for identification. Based on the low production rates and short half-lives, rapid, selective, and efficient chemical separations are necessary. Currently, chemical studies can be carried out with nuclides with half-lives on the order of a few seconds and have been carried out on elements 104-108, 112 and 114. Many of these studies have been conducted in the gas phase due to the ability of gas phase experiments to access short lived products. The reason gas phase experiments can access short-lived products, compared to liquid phase experiments, is due to the lack of need to remove solvent prior to detection.

Due to the atom-at-a-time nature of TAn production the question is raised as to the validity of results obtained on a sub-microscopic level compared to the macroscopic world. This must be considered from both a thermodynamic and kinetic viewpoint. From a thermodynamic viewpoint, in the macroscopic world chemical equilibrium is represented according to the law of mass action, shown in Equation 3, for the chemical reaction aA +bB ↔cC + dD. In Equation 3, *a* represents the activities of the given species and *K* is the equilibrium constant. If a metal ion is a constituent of both A and C, and the reaction is in equilibrium then the metal ions of A and C exchange at a constant rate, however if only a single atom of a metal is present, it cannot exist in both A and C simultaneously. If this is the case, then the equilibrium constant cannot be defined, as the activity of A or C is zero. Guillaumont and co-workers have derived a law of mass action that is valid for atom-at-a-time chemistry by substituting the activities and concentrations with the probabilities of finding the species in a given phase. For example, in an extraction chromatography experiment for a TAn the activities and concentrations would be substituted by the probability of finding the atom in the mobile or stationary phase, providing the measurement is made many times.[50-52]

$$K = \frac{a^c(C)a^d(D)}{a^a(A)a^b(B)}$$

Equation 3

A kinetic view point of atom-at-a-time chemistry also needs to be examined, due to the short half-lives of TAn elements. For the reaction, MA + B↔MB + A there is both a forward and backward rate. The forward rate is the speed at which MA reacts with B to form products MB and A, the reverse rate is true for the opposite reaction of the forward rate. The rate at which the reaction proceeds will be dependent upon the activation energy barrier height. If this barrier is large the reaction will proceed slowly and equilibrium will be slowly established. In order to have an applicable chemical system for the study of transactinide chemistry, equilibrium must be established quickly, due to the short half-lives of TAn elements. It has been shown that if the activation energy is less than 60 kJ, equilibrium will be established in a short period of time, compared to the mean half-life of the TAn element.[53]

The chemical experiments can be performed in static or dynamic fashion. In a static fashion, the distribution coefficient of a single atom between two phases is determined by repeating the same experiment hundreds of times. An example of a static experiment is early liquid-liquid extraction experiments, where hundreds of chemical experiments were done to determine if the atom resided in the aqueous or organic phase, as determined by alpha counting. In a single dynamic experiment there are successive static experiments done. An example of a dynamic experiment would be passing a single solution though a column containing a chromatographic resin, where the atoms in the solution undergo hundreds of sorption-desorption exchange steps while traveling through the column. These two methods can be continuous or discontinuous. In a continuous process the experiment is on-going and never stops. SISAK (Short-lived Isotopes Studied by the AKUFVE technique) is a continuous, static liquid-liquid separation apparatus.[54] In a discontinuous set-up, common in extraction chromatographic experiments, the experiment stops at some point, generally for maintenance to the chemistry apparatus. ARCA (Automated Rapid Chemistry Apparatus) is a discontinuous, dynamic extraction chromatography apparatus.[55, 56]

In order for a transactinide chemistry experiment to be performed the chemical system must be systematically studied with the homologs and pseudo-homologs of the desired TAn element, to determine the optimum experimental conditions. This can be done through batch, dynamic, and on-line experiments. Batch experiments are an initial study to probe a large variety of conditions and determine the best candidates. Dynamic studies are performed after batch studies to investigate the effect of chromatographic transport along the column or flow conditions in a liquid extraction system. These studies are aimed at determining the optimal conditions for the experiment and testing resin viability. Finally, on-line studies are accelerator based experiments performed with short-lived isotopes of the homolog elements to assess the performance of a given experimental set-up before it is actually used with transactinides. On-line experiments also provide invaluable information regarding the kinetics of the system and the chemical species present after the nuclear reaction and subsequent transport.

The chemical system employed must also be highly selective for the desired element. This is necessary because during production of a TAn many reaction products other than the desired element are created by transfer of nucleons between the projectile and target. The production rates for such transfer products are typically several orders of magnitude greater than that of the elements of interest. These reaction products can interfere with the positive identification of the transactinide element of interest. Magnetic pre-separators, like the TransActinide Separator and Chemistry Apparatus (TASCA)) at Gesellschaft für Schwerionenforschung (GSI) and the Berkeley Gas-filled Separator (BGS) at Lawrence Berkeley National Laboratory (LBNL) can be used as an alternative to chemical separations to aid in the reduction of unwanted reaction products.

1.4.2 Extraction Chromatography

Chromatography is the process by which two components of a system are separated, based on their affinity for a solid or mobile phase. Extraction is the act of removing something from its surroundings. Based on this, extraction chromatography is the process of removing a component of a system from its surrounds based on its affinity for the mobile or solid phases. In extraction chromatography the selectivity of liquid-liquid separations is combined with the multitude of interaction steps of a column chromatographic set-up. Figure 1.2 depicts a schematic example of the structure of an extraction chromatographic resin.[57] The stationary phase is the extractant of interest, which is physisorbed to the inert support. An example of a stationary phase is the di-tetracyclohexano-18-crown-6 extractant being physic-sorbed onto the inert support Amberchrom in the case of Eichrom's Pb resin. These two components make up the composition of the resin. The mobile phase flows along the surface of the resin and contains the elements to be separated and/or the eluents to remove the elements bound to the stationary phase. If a component of the solution has more affinity or attraction to the stationary phase, then the component will remain sorbed to that phase longer, thus retarding its progress through the column. If a component of the solution is repelled by the stationary phase or has a higher affinity for the mobile phase, then the component will travel through the column quickly.

Determination of uptake or how well a component is retained by the resin is done through the calculation of weight distribution ratios, D_W, and column capacity factors, k'. The relation of D_w to k' is shown in Equations 4-7[58, 59] In Equation 4, A_0 and A_S are the aqueous phase metal concentration before and after equilibration, w is the weight of resin in grams and V is the volume of aqueous phase in mL. In Equation 5, D_V is the volume distribution ratio, d_{extr} is the density of the extractant, and 0.4 is the extractant loading in grams of extractant per gram of resin, which is resin dependent. D_V is calculated so that the weight distribution ratios can be converted to column capacity factor. Equation 6 is used to convert the volume distribution ratio to the column capacity factor, where V_S and V_m are the volumes of extractant and mobile phases, respectively. This is true for slurry packed columns and the values are available from Eichrom Technologies, Inc. These values can be determined for in house synthesized resins providing the weight loading of the resin is well known. Equations 5 and 6 can be combined to obtain Equation 7.[58, 59] Extraction chromatography lends itself extremely well to transactinide chemical experiments for two reasons. First, the extractant and mobile phase can be widely varied, opening up many systems for the study of transactinide elements.[60] Second, and most importantly, extraction chromatography is fast, selective, dynamic, sensitive to speciation, automatable and efficient.

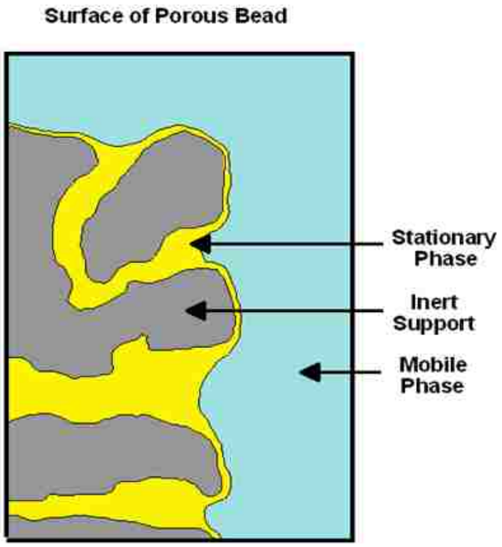

Figure 1.2. Depiction of the operation of extraction chromatography column.

$$D_W = \left(\frac{A_0 - A_S}{W}\right)\left(\frac{A_S}{V}\right)$$

Equation 4

$$D_V = D_W \frac{d_{extr}}{0.4}$$

Equation 5

$$k^{'} = D_V \left(\frac{V_S}{V_m}\right)$$

Equation 6

$$k^{'} = D_W \frac{d_{extr} V_S}{0.4 V_m}$$

Equation 7

1.5 Chromatography Literature Review

1.5.1 Introduction

In a chromatographic chemical on-line study of transactinide elements and/or their homologs and pseudo-homologs, carrier-free radionuclides are produced in a nuclear reaction. These products are then transported, e.g. by a gas-jet, to the chemistry apparatus where they are dissolved in the mobile phase and then column chromatography is performed. The goal of such experiments is to determine the weight distribution for a given element and thus determine the affinity of each element for the resin. By determining the affinity an element has for a given resin the chemical properties of the element can be assessed. These experiments tend to be performed in a dynamic, discontinuous method.

1.5.2 Group IV Liquid Phase Chemistry

The hydrolysis of Group IV elements in dilute acidic acids causes difficulty in assessing the speciation and behavior of mononuclear species. It is necessary to study mononuclear species because transactinides are present one atom at a time and therefore cannot form polynuclear species. It has been shown that both tetravalent Zr and Hf form polynuclear species in metal concentrations of 10^{-4} M and greater in 2M acidic solutions.[61] The formation of polynuclear species causes the adsorption behavior on a cationic resin to change and even block resin sites. Zr and Hf behave similarly in HCl and HNO_3 acid solutions except below 3M.[62, 63] Polynuclear species form below 5 M HCl and as acid concentration decreases the degree of polynuclear formation increases.[64, 65]

Initial chemical studies of Rf were aimed at confirmation of the Group IV placement in the periodic table. Two of the first liquid phase chemistry experiments were performed by Silva and Hulet et.al. In 1970 R.J. Silva and co-workers performed the first Rf, chemistry using cation exchange chromatography and α-hydroxyisobutyric acid (α-HiB). In this work, ^{261}Rf was produced at the Berkeley Heavy Ion Linear Accelerator (HILAC), the recoil products from the target were stopped in helium gas and transported via gas-jet (this method of transportation is common and will be omitted from further experimental descriptions), then deposited on a surface of Pt foil coated with ammonium chloride. The recoil products were then rinsed from the ammonium chloride surface with

50 μL of 0.1M ammonium α-HiB and transferred to the top of a 80°C Dowex 50x12 cation exchange column. Fractions of ammonium α-HiB were collected and evaporated to dryness and placed over an α detector. The first fraction consisted of two drops and contained little to no activity. The second fraction consisted of 4 drops and contained activity attributed to Rf. The experiments showed that Rf behaved similarly to Zr and Hf but very different compared to di- and tri-valent ions, confirming that Rf is indeed a Group IV member.[66] In 1980 E.K. Hulet and co-workers performed an extraction chromatographic experiment using Aliquot 336 (trioctylmetyl ammonium chloride) resin due to the faster kinetics the resin provided. Anionic chloro complexes are strongly adsorbed to Aliquot 336 and Group IV elements form these complexes above 6M HCl. Based on this, the recoil transfer products were dissolved in 12M HCl and later stripped from the column using 6M HCl, α samples were prepared and it was determined that Rf exhibited Group IV like behavior.[67]

Rajan, Pfrepper, Trubert, Stub, Kronenberg, Toyoshima and Ishii et.al. have all studied Fluoride complexation of Group IV elements. Rajan and co-workers determined that Amberlite IRA 400 and Dowex 2 effectively separated small amounts of Hf from large amount of Zr based on the formation of a hexafluoro complex formation.[68, 69] Pfrepper et.al. determined, using a multicolumn system (2 cationic exchange columns with an anionic exchange column sandwiched in between the cation columns) that Rf exhibited Hf like behavior in on-line studies.[70] Trubert and co-workers showed that Group IV elements are best separated at low concentration of hydrochloric acid and at 0.02M HF on Bio-Rad AG-MP1 resin. Neutral or cationic species are most likely extracted.[71] Strub and co-workers determined that on a Dowex 1x8 anion exchange column Group IV elements could be eluted off the column with 5 M HNO_3/0.001M HF from a 0.1M HNO_3/0.1M HF load solution. It was also found that Rf is eluted from the column at an HF concentration an order of magnitude higher than that of its homologs, Zr and Hf in a mixed nitric acid and hydrofluoric acid system. The concentration of HF needed to elute Rf was still lower than that needed to elute Th off the column in the same system.[72] Toyoshima and Ishii found similar trends as Strub, but determined that Rf forms a hexafluoro di-anionic complex, and that the formation of the fluorocomplex for Rf is much weaker than that of its lighter homologs.[73, 74] Kronenberg and co-workers, using a similar chemical set-up to Pfrepper, determined that in a mixed nitric acid and hydrofluoric acid system the presence of nitric acid severely decreases the adsorption of Rf to the anionic exchange column. The decrease in adsorption of Rf to the column causes Rf to elute rapidly off the column. This rapid elution initially seemed to indicate Rf does not form a anionic chloro complex, however, it is reasonable to state that Rf does form an anionic chloro complex similar to its lighter homologs, if the suppression of Rf adsorption due to the presence of nitric acid is considered.[75]

Chloride systems, both pure and mixed, of Group IV elements have been investigated by Huffman, Street and Kraus et.al. Huffman and co-workers have assessed Group IV behavior on an anion exchange column and on an Amberlite IRA 400 column. It was found that on an anion exchange column in a mixture of hydrochloric and hydrofluoric acids Group IV elements can be separated due to the formation of anionic chloro complexes.[76] It was also determined that on the Amberlite IRA 400 column Hf and Zr can be separated, most likely due to the formation of anionic chloro-fluoro complex.[77] On a Dowex 50 column it was found that Hf and Zr can be separated using 6M HCl to elute the elements off the column.[78] Dowex 1 can be used to separate Zr and HF when 1M HCl/0.5M HF is used to elute the elements, Hf elutes first.[79]

The behavior of Group IV elements in pure sulfuric acid has been investigated by Szeglowski and co-workers.[80] A multi-column system was used for these experiments. The system consisted of two Dowex 50x8 cation columns with a Dowex 1x8 anion exchange column sandwiched between the two cation exchange columns. It was determined that this multi-column system is viable for Rf chemical studies because Group IV elements adsorb to the cation column in dilute sulfuric acid solutions.[80]

1.5.3 Group V Liquid Phase Chemistry

Although Pa is not a Group V element, it is considered a pseudo-homolog of dubnium and will be discussed in this section. The hydrolysis of Group V elements in dilute acids makes it difficult to assess the speciation and behavior of mononuclear products. It has been predicted that the hydrolysis will decrease in the order Nb > Ta > Db >> Pa. As the ionic radius increases, hydrolysis will also increase and make extraction more difficult.[81] In the absence of strong complexing agents Pa will form hydrolyzed species that consist of oxo and mixed hydroxo complexes. The strength of complexing agents decrease as $F^- > OH^- > SO_4^{2-} > Cl^- > Br^- > I^- > NO_3^- > ClO_4^-$. In hydrofluoric media Pa is not hydrolyzed and forms septa and octofluoro complexes.[82] In a sulfuric acid matrix Pa tends to form anionic and cationic oxysulfide complexes.[82] In a hydrochloric acid media Pa tends to form oxychloro complexes when at high concentrations, where as Ta tends to form a hexachloro anionic complex and Nb has equal tendency to form an oxypentachloro and a hexachloro, as well as hydoxychloro anionic complex.[82, 83] At low hydrochloric acid concentrations Ta tends to form cationic species.[71, 82-85] As acid concentration decreases Nb and Ta begin to form polynuclear species, even at metal concentration of 10^{-3}M.[84-86] In high nitric acid concentration matrices Ta tends to form cationic species.[85] In mixed acid media the speciation of Pa is currently unknown.[82] Currently, there is very little information about the speciation of Group V elements and Pa in mixed acid-fluoride matrices in the literature. In a pure hydrochloric or nitric acid matrix, Group V elements tend to adsorb on surfaces. This is a concern, especially at very low concentration, because it causes a large percent of the nuclides to be lost due to sorption.[87-89] The addition of hydrofluoric acid to a pure acid matrix greatly decrease loss due to sorption. HF is therefore a needed and much utilized matrix component when very low concentrations of Group V elements are being studied, as is the case in atom-at-a-time chemistry. The addition of F^- to the matrix likely causes an oxygen atom to be displaced by a fluorine atom. This results in a break of a O--HO hydrogen bond between the metal complex and the glass surface.[90]

In addition to placing this element in the Periodic Table, chemical studies of Db have been mainly aimed at determining which homolog or pseudo-homolog it behaves most similar to. The first liquid chromatography experiment with Db was performed with ARCA II using a triisooctylamine (TiOA) column. It was shown that the majority of the Db eluted in the Nb/Pa fraction, which consisted of 4 M HCl/ 0.02 M HF. Under these conditions Db showed non-tantalum like behavior.[91] In the same study it was attempted to demonstrate whether Db behaves more Pa or Nb like and it was found that upon elution Db came out in the two fractions nearly equally. In 1992, Kratz et.al. studied the behavior of Db on an Aminex A6 column, using α-HiB, to elute Group IV elements on ARCA II. Db eluted from the column with the other Group IV elements, confirming the placement of Db in Group V.[92, 93] Later that same year, Gober and co-workers studied the Db behavior on diisobuytylcarbinol (DIBC) resin using ARCA II and mixed HCl/HF systems for elutions. It was found that the system only extracted 40 % and was not sensitive enough to characterize Db.[94] In 1993, Zimmermann et.al. revisited the TIOA column using ARCA II. Zimmermann and co-workers found that using a HCl/HF matrix Pa and Nb could be separated to determine Db likeness to the homolog and pseudo-homolog. It was found that Db eluted near its pseudo-homolog, Pa.[95] Paulus et.al. investigated both the fluoride and chloride resins of Aliquot 336. On the chloride resin Db behaved more line Nb than Ta and on the fluoride resin Db eluted from the column with Group V elements and not with Pa, suggesting that Nb and Ta both from $HM(OH)F_6^-$ or MF_6^-, where M is Nb or Ta, below 3M HF. Between 3 to 10M HF it is suggested that Nb continues to form $HNb(OH)F_6^-$ or NbF_6^-, while Ta tends to form the $HTaF_7^-$.[96] In 2004 Nagame and co-workers showed that Db behaves Pa like on a quaternary amine resin in a mixed nitric and hydrofluoric acid system.[97] Wilk et.al showed in reverse phase chromatography that methyl isobutyl ketone (MIBK) separated Group V elements from Zr and Pa.[98] Finally, in 2009 Tsuskada and co-workers studied the behavior of Group V elements and Pa on an anion exchange column (MCI GEL CA08Y) and it was found that as the concentration of HF was increased, retention on the column decreased and that Db is more Pa like. A summary of the experiments are shown below in Table 1.1.

Table 1.1 A summary of chemical experiments with Db and/or its homologs.

Author	Elution 1	Elution 2, 3	Elution Order
Kratz (TiOA)	4M HCl/0.02M HF	6M HNO_3/0.015M HF	Nb≈Pa>Ta
Kratz (TiOA)	10M HCl/0.025M HF	10M HCl/0.015M HF	Pa>Nb
Gober (DIBC)	6M HCl/0.0002M HF	0.5M HCl	Nb>Pa
Schädel (Aminex A6)	0.025M α-HiB*	0.05M α-HiB	Ta>Nb≈Pa
Zimmermann (TiOA)	0.5M HCl/0.01M HF	4M HCl/0.02M HF	Pa>Nb
Paulus (Aliquot 336/Cl-)	10M HCl	6M HNO_3/0.015HF	Ta>Nb≈Pa
Paulus (Aliquot 336/F-)	4M HF	6M HNO_3/0.015M HF	Pa>Nb≈Ta
Nagame (quaternary amine)	14M HF	6M HNO_3/0.015M	Pa>Nb≈Ta
Wilk (Kel-F/MIBK)	6MHCl/6MHF	1.5M HCl/0.5MHF, H_2O	Pa>Nb>Ta
Tsuskada(MCI GEL CA08Y)	13.9M HF	6M HNO_3/0.015M	Db≈Pa>Ta≈Nb

1.6 Research Goals

The goal of this research is to perform systematic studies on different extraction chromatographic resins that can be applied to the chemical characterization of elements 104 and 105, Rf and Db, respectively. DGA and the crown ether based Strontium and Lead resins are extraction chromatographic resins that are commercially available from Eichrom Technologies, Inc. The diglycoloamide and crown ether extractant molecules on these resins of interest are shown in Figure 1.3.[99, 100] In order for these resins to be effective in assessing the role of relativistic effects in the chemical behavior of Rf and Db, they must exhibit a difference in extraction behavior between the lighter homologs and pseudo-homologs. Two types of chemistry set-ups can be envisioned for the use of Eichrom's DGA resin, either as a separation step for nuclides embedded in a catcher block based experiments or for chemistry experiments performed behind a gas-filled physical pre-separator. In the case of Eichrom's Strontium and Lead resins the chemistry must be done behind a gas-filled pre-separator, for reasons to be discussed later.

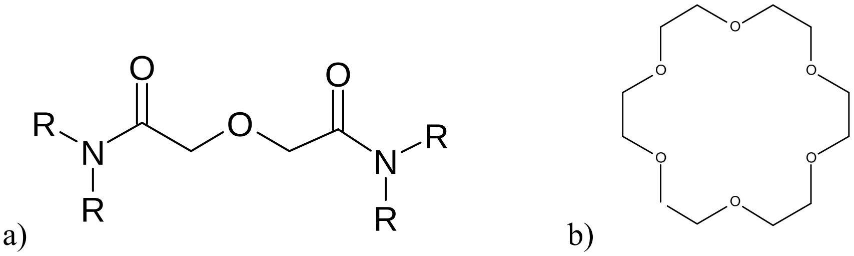

Figure 1.3. The extractant molecules of interest. a) The tetradiglycolamide extractant in Eichrom's DGA resin where the R groups represent the straight or branched C8 chains. b) The basic, non-functionalized crown ether extractant.

In a catcher block experimental setup a metal block or foil is placed behind the target during the irradiation and nuclei recoiling from the target position will implant themselves in the block. The copper block is subsequently dismounted and sputter cleaned. It is then shaved with a micro-lathe. The 7 – 10 μm copper shavings are then subjected to chemical separation[101] An example of copper block chemistry being employed was in the chemical investigation of a 28 h ^{268}Db isotope from the decay of element 115.[102] Following irradiation and shaving the copper is dissolved in aqua regia. Lanthanum carrier is added to the aqua regia to precipitate tri-, tetra- and penta- valent cations when ammonium hydroxide is added. The precipitate is then washed and converted to the nitrate form. This solution is then added onto a cation exchange column, the eluent is deposited and dried on a polypropylene film and then counted on solid state detectors.[102] Catcher block based chemistry can be used if the isotope of interest has a long half life (hours or greater) and if the extraction chromatographic system is selective for the element of interest because additional separations can be done to isolate the element. In the case of isotopes with shorter half-lives, if the extraction chromatographic selection is not selective enough for the element of interest, then the chemistry must be performed behind a magnetic pre-separator to reduce the presence of unwanted recoil products. This is the case in crown ether based extraction systems.

Crown ethers are very selective for intragroup metal separations but do not exhibit efficient separations when a larger variety of metals are present.[103] This property of crown ethers is what renders them useless for catcher block based setups or experiments without pre-separation, however with the physical pre-separation of unwanted reaction products provided by a gas-filled separator, crown ethers can be used to assess the role of relativistic effects in chemical behavior of transactinide elements. It has recently been shown, in on-line liquid-liquid extraction experiments, that dibenzo-18-crown-6, dicyclohexano-18-crown-6 and dicyclohexano-24-crown-8 all extract Zr and Hf and that these elements exhibit subtle differences in extraction behavior.[104]

As part of this research optimum extraction conditions will be determined for both the DGA and crown ether systems. This will be done by varying type, concentration and combinations of acids in batch experiments. Once optimum conditions for batch extraction have been determined, column experiments will follow. The goal of the column experiments will be to further refine the extraction conditions and to test the viability of the resin for reuse.

CHAPTER 2

EXPERIMENTAL METHODS AND INSTRUMENTATION

2.1 Off-Line Studies

2.1.1 Method Selection

A highly selective, reproducible, efficient and rapid method is necessary for chemical investigations of TAn elements. Extraction chromatography lends itself extremely well to all of these requirements. The Automated Rapid Chemistry Apparatus (ARCA), Automated Ion exchange separation apparatus coupled with the Detection system for Alpha spectroscopy (AIDA) and Multi-Column Technique (MCT) are three ion exchange chromatography automated system that have been used to probe the chemical behavior of TAn elements. The ARCA and AIDA systems are essentially miniaturized, computer controlled High-Performance Liquid Chromatography (HPLC) instruments.[55, 56, 105] The MCT system is a three column system, in which an anion exchange column is sandwiched between two cation exchange columns. The first cation exchange column removes actinide transfer products, the anion exchange column retains the TAn of interest, and the final column retains the actinide decay products of the TAn. Recently, sequential extraction chromatography (SEC) or extraction chromatography has been investigated for use with TAn elements. On a SEC resin an inert support is coated with an organic extractant. The advantage of SEC based resins is that it combines the selectivity of liquid-liquid extraction methods with the ease of operation and the larger number of exchange steps of ion-exchange chromatography methods.

Eichrom Technologies Inc. has developed a series of SEC based resins. Three of these resins are the DGA, Pb and Sr Spec resins. The DGA resin is based on tetraalkyldiglycolamide extractant molecules, shown in Figure 2.1, where the tetraalkyl refers to the R groups and the diglycoloamide refers to the remainder of the extractant molecule.[99] There are two types of DGA resin, normal (TODGA) and branched. The R group in the normal DGA resin is a straight chain octyl group, where as the R group for the branched DGA resin is an ethylhexyl branched octyl group. The DGA resin has been studied as a potential extraction chromatography system to investigate the chemical behavior of dubnium. DGA is attractive for dubnium chemistry because it has been demonstrated that it is highly selective for tri-, tetra- and hexavalent metal ions in both nitric and hydrochloric acid matrices, while maintaining fast exchange kinetics and resin stability.[58] The Pb and Sr Spec resins are crown ether based resins, shown in Figure 2.2. These resins are an attractive option for the chemical characterization of Rf because it has previously been shown that crown ethers of similar structure allow for intragroup separations.[104] Two additional crown ether resins, made in house using the method developed by Horwitz et. al[106, 107] were also investigated for direct comparison to the liquid-liquid extraction system investigated by Sudowe et. al.[104] The structures of the crown ethers on the resins made in house are shown in Figure 2.3 and Figure 2.4.

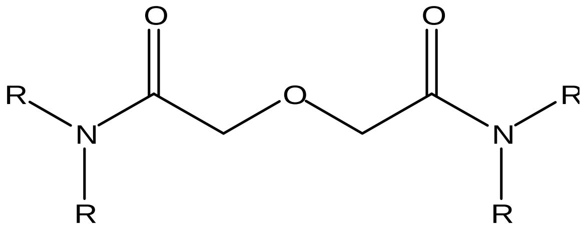

Figure 2.1. The tetradiglycolamide molecule sorbed to Eichrom's DGA resin.

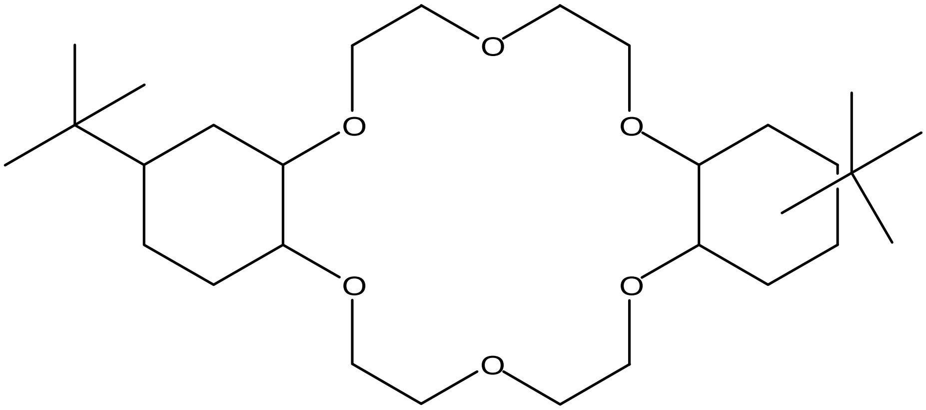

Figure 2.2. The crown ether extractant molecule on Eichrom’s Sr and Pb resins.

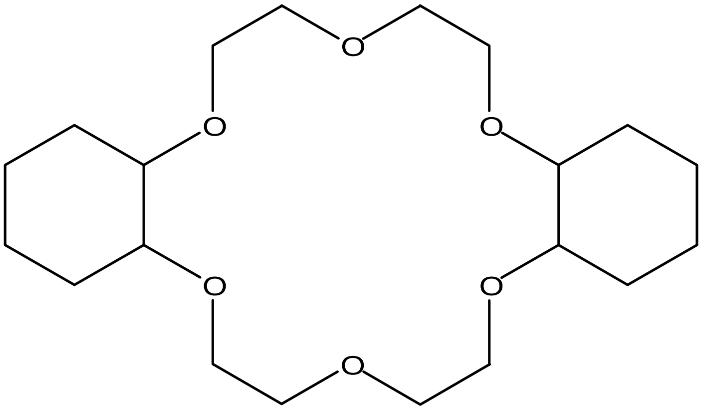

Figure 2.3. The structure of dicyclohexano-18-crown-6.

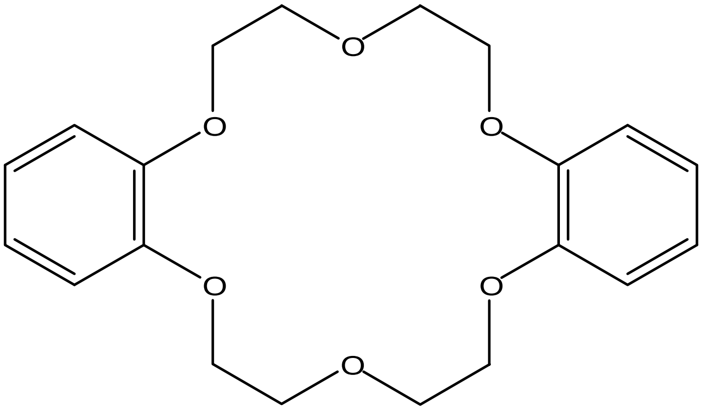

Figure 2.4. The structure of dibenzo-18-crown-6.

2.1.2 Reagents and Materials

2.1.2.1 Chemicals

During batch studies 50-100μm resin bead size, of the appropriate Eichrom unpacked or free resin, commercially available from Eichrom Technologies, Inc., was used. Pre-packed 2mL columns containing 50-100μm bead size, of the appropriate Eichrom resin, commercially available from Eichrom Technologies, Inc., were used in column separation studies. In the case of the resins made in house, either free resin or a 2mL hand packed vacuum was used for batch and column studies, respectively. Hydrochloric, nitric and hydrofluoric acid solutions were prepared from reagent grade acids and de-ionized water. Acids were obtained from Aristar Plus, J.T. Baker and Spectrum, respectively. The source of the de-ionized water was an 18MΩ·cm Millipore or Milli Q system (Millipore, Billerica, MA). Ammonium bioxalate solution is prepared using ammonium oxalate and oxalic acid (p.a. grade, Malinckrodt, MO,).

2.1.2.2 Radionuclide Stock Solutions

2.1.2.2.1 ^{95}Zr and ^{95}Nb Solutions

Two different suppliers of carrier-free ^{95}Zr were used for these studies. One source, obtained from Lawrence Livermore National Laboratory (courtesy of Roger A. Henderson), consisted of ^{95}Zr produced as fission products from the thermal-neutron induced fission of ^{235}U and was prepared in 2M HNO_3/0.2M HF with an approximate activity concentration of 4cps. The ^{95}Nb is the daughter product of the ^{95}Zr and had an approximate activity concentration of 16cps.

In addition three stock solutions of ^{95}Zr were obtained from Eckert and Ziegler Isotope Products (Cat #6095, Source #1290-65, 05/01/2008; Cat #6095, Source #1292-

68, 07/01/2008; Cat #7095; Source #1443-9, 05/15/2010; Eckert & Ziegler Isotope Products) and consisted of ^{95}Zr in the oxalate4 form in 0.5M oxalic acid (1mCi). The ^{95}Zr oxalate was converted to the chloride form and purified upon receipt. In order to convert the ^{95}Zr oxalate to the chloride form 1mL of 10mg/mL lanthanum carrier (in the form of lanthanum nitrate) was added to 1mL of the ^{95}Zr oxalate solution followed by 5 drops of concentrated ammonium hydroxide to cause precipitation of ^{95}Zr in the form of the hydroxide. The precipitate was then centrifuged for 15 minutes; the supernatant was removed and counted using gamma spectroscopy for two hours. The precipitate was rinsed with 2mL of de-ionized water and then centrifuged for ten minutes. The supernatant was removed and counted using gamma spectroscopy for two hours. The precipitate rinse, centrifugation and supernatant procedures were repeated. Afterwards the precipitate was then dried and counted for one hour using gamma spectroscopy. The precipitate was then dissolved in 3mL of concentrated hydrochloric acid and the resulting solution was further purified using ion exchange. A 5mm internal diameter by 7cm high slurry packed column of Dowex 1 X 8 resin bead size 100-200 mesh was prepared. The column was washed with 10 to 15mL of de-ionized water until a neutral pH was achieved, as indicated by pH paper. The column was then conditioned with four, one-milliliter aliquots of concentrated hydrochloric acid. Afterwards the ^{95}Zr chloride solution was loaded onto the column. The load fraction was collected and counted for 10 minutes using gamma spectroscopy. The column was then washed with three free column volumes of concentrated hydrochloric acid. The rinse fraction was also collected and counted for 10 minutes using gamma spectroscopy. The ^{95}Zr was then eluted with three aliquots of 2mL of 2.0M hydrochloric acid. The resulting solution was then diluted to provide a solution with an activity of 5cps ^{95}Zr solution.

2.1.2.2.2 ^{175}Hf, ^{182}Ta, ^{233}Pa Solutions

The ^{175}Hf was produced by proton bombardment of a lutetium foil using the ^{175}Lu(p,n)^{175}Hf reactions, at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL) with a beam energy of 12MeV and an intensity of 3.7 particle-microampers on the target for 233 minutes . The final ^{175}Hf solution, following a cooling down period, dissolution and separation was prepared in 2M HNO_3/0.2M HF and had an activity concentration of approximately 10cps. The ^{182}Ta stock solution (Cat # 1364-93-3, 08/07/2009, Eckert & Ziegler Isotope Products) was prepared in 4M HNO_3/0.2M HF and had an activity concentration of approximately 2cps. The ^{233}Pa is the daughter product of ^{237}Np therefore a Np stock solutions (source #7600, 08/22/1958, LLNL) was obtained form LLNL. The solution was prepared in 3M HCl and had activity concentrations of approximately 0.2cps. The ^{243}Am stock solution (Source# 9900, 1986, LLNL) used as obtained from LLNL was prepared in 3M HCl with an activity concentration of 0.04cps.

2.1.3 High Purity Germanium Gamma Spectroscopy

High-Purity Germanium (HPGe) detectors are often used in gamma spectroscopy when high resolution of peaks is necessary. Germanium detectors provide a resolution that is 30 times, at full width at half maximum (FWHM) greater than NaI detectors, and Ge can provide more detail about energy level structure of a nuclei. Both Ge and NaI detectors operate however on the same basic interaction principles.[108]

Upon entering the detector the gamma ray collides with electrons and energy transfer occurs. There are three means of energy transfer: 1) photoelectric effect, 2) the Compton effect, 3) pair production. The process for energy transfer depends upon the absorption cross section for Ge and the energy of the incident gamma ray.[108]

In the photoelectric process all energy is transferred from the gamma ray to the electron upon collision. This electron then creates a vacancy, or hole, from where it was knocked out, this is referred to as an electron-hole pair. The electron-hole pair then migrates to the charge collection site where it is detected (this is true for all mechanisms of energy transfer). The detected pulse is proportional to the original energy of the gamma ray. This detected pulse creates the photopeak in the spectrum.[108]

In the Compton process some energy is transferred from the gamma ray to the electron during the collision. The amount of energy transferred depends upon the angle of collision. At an angle of 180º degrees the gamma ray transfers the maximum amount of energy to the electron, creating the appearance of the Compton edge in the spectrum. As the angle of collision increases (from 0 to 180º) the amount of energy transferred increases. This increase in energy transfer creates the Compton continuum feature of the spectrum. [108]

Pair production is the finally possibility for an the energy transfer mechanism. When the gamma ray enters the detector an electron-positron pair is created. In order for the creation of the electron-positron pair to occur, the incident gamma ray must have an energy of at least 1.02 MeV because the electron and positron each have a mass corresponding to an energy of 0.511 MeV. Once the electron-positron pair is created' three events can occur: 1) double escape, 2) single escape, 3) no escape. When the positron annihilates in the detector two gamma rays are produced. If neither of the gamma rays escapes the detector the signal will be detected at the total energy peak. If one of the gamma rays escapes then there will be a peak 0.511MeV below the total energy peak. Finally if both of the gamma rays, created by the positron annihilation, escape then there will be a peak at 1.02 MeV lower than the total energy peak.[108]

2.1.3.1 Activity Measurements

Two different high purity germanium (HPGe) detectors were used depending on where experiments were conducted, either at Lawrence Livermore National Laboratory (LLNL) in California or at University of Nevada – Las Vegas (UNLV). Activity measurements performed at LLNL were made on a 175% HPGe spectroscopy instrument (LLNL# 34-940461A, Ortec, Oak Ridge, TN). Data files were recorded with an Ortec multichannel analyzer (DSPEC) and analyzed using Maestro version 5.35.01 (Ortec). Activity measurements performed at UNLV were made on two 60% HPGe gamma detectors (Detector Model GC6020, Serial#799709 and #2921277, Canberra). Specta were recorded with a Canberra DSA 1000 multichannel analyzer and analyzed using Canberra Genie 2000 software. The HPGe detector at UNLV was calibrated using ^{60}Co and ^{137}Cs sealed point sources. The point sources were counted such that greater than 10,000 counts were seen in each peak of interest. The detector was then further calibrated using a 1mL ^{152,154}Eu in a 15mL centrifuge tube; this is the same counting geometry as was used for the batch and column studies. Gamma energies with the highest relative yield and no spectral interference were chosen for the determination of activity of each radionuclide. The 724.2keV (44.17%) and 765.8keV (100%) gamma energies were chosen for ^{95}Zr and ^{95}Nb, respectively. The 343.4keV (84%) gamma energy was chosen for ^{175}Hf. The 1121.3keV (34.9%) gamma energy was chosen for ^{182}Ta. The 311.9keV (38.5%) gamma energy was chosen for ^{233}Pa. The 74.7keV (67.2%) gamma energy was chosen for ^{243}Am. All gamma energies and relative yield were taken from the Lawrence Berkeley Isotopes Project webpage developed by Firestone and Ekström.[109] Similar counting geometry was maintained for all samples by using the same volume and same vial type for each sample, 1mL and 15mL polypropylene centrifuge tube, respectively. This minimized systematic counting error.

2.1.4 Extraction Chromatography

2.1.4.1 Batch Method

In order to investigate a wide variety of conditions, a batch method was initially used, once optimal conditions were determined column elution studies followed the batch studies. An appropriate amount (1 to 10cps/mL) of each radionuclide to be studied was transferred to a clean, dry 15mL polypropylene centrifuge tube. The sample was then counted using gamma spectroscopy 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 1mL of the solution to be studied. Approximately 10-20mg of the desired resin was quantitatively weighed into the 15mL polypropylene centrifuge tube containing the radionuclide solutions. Samples were then briefly placed on a vortex mixer (VWR part no.14005-824) before being put on a shaker (set to 1200rpm) for one hour. The sample was then extracted from the 15mL centrifuge tube using a 3mL syringe with a blunt tip needle affixed to the bore. The needle was removed and a 0.45µm polypropylene filter (Whatman part no. 6786-2504 was placed on the bore of the syringe. The solution was then forced through the filter into a clean, dry 15mL polypropylene centrifuge tube. The sample was counted using gamma spectroscopy for 30-60 minutes to determine the quantity of activity taken up by the resin (see section 1.4.2 for a discussion of the calculation made).

2.1.4.2 Column Method

Column chromatography on mixed radionuclide solutions was performed with pre-packed 2mL columns containing the appropriate resin for the resins available through Eichrom (Part No. DN-R50-S, PB-B20-S, SR-B25-S Lots No. DNSR7A, DNSR8A, PBS04155, PBSR10A, SRS05148, SRSR6D, SRSR8G, Eichrom Technologies, Inc. Darien, IL) For the resins produced in-house a hand packed 2mL Eichrom vacuum cartridge was used. An appropriate volume of each stock solutions was transferred to a clean, labeled 15mL centrifuge tube, used as is (VWR International, West Chester, PA). The sample was evaporated to dryness in a water bath and reconstituted in 1mL of the desired acid solution. The sample was then counted for 30 minutes on the HPGe detector to determine the initial activity of each radionuclide present. Group V elements are known to adsorb to surfaces, in order to track this phenomenon the empty centrifuge tube that contained the radionuclide solutions was counted at the end of each experiment.

During the column extraction studies one of two vacuum box set-ups was used. One vacuum box set-up consisted of a 24-hole polycarbonate vacuum box (Part No. Ac-24-BOX, Eichrom Technologies Inc., Darien, IL) equipped with a pressure regulator was used to accelerate the elution process. The Eichrom vacuum box is equipped with a vacuum gauge that indicates the amount of vacuum being applied to the inside of the box. A pressure between 25 and 30inHg was maintained. The 2mL pre-packed Eichrom columns were affixed to a disposable inner tip that is nested in another tip (Part no. AC-1000-IT and AC-1000-IT, Eichrom Technologies, Inc., Darien, IL) that is placed in the lid of the vacuum box. This design minimizes cross contamination. The pre-packed Eichrom column was then affixed with a reservoir (25mL Luer-lock syringe, B-D, NJ). The second vacuum box set-up used was made in house and held five pre-packed columns. The pressure of this vacuum box was regulated using a digital vacuum regulator (DVR-200, JKem Scientific), the pressure was maintained between 200-400torr. The column was pretreated with 5mL of the acid solution (the same concentration as the load solution) prior to loading. The 1mL solution containing the radionuclides of interest was loaded on the column and the various radionuclides were then sequentially eluted. Following elution, each fraction was evaporated to dryness in a water bath, with a jet of compressed air flowing over the sample, and reconstituted in 1mLof acid solution. This was done in order to maintain counting geometry. The samples were then counted on a HPGe detector for 30 minutes.

2.1.4.4 Resin Bleeding Investigation

Once the optimal load solution was determined, a study to determine if and when the extractant comes off or bleeds off of the inert support was performed. Approximately 1g of resin was placed, in the absence of radioactivity, in 100mL of solution identical in composition to that of the load solution. The samples were stirred for the first 30 days. At appropriate time intervals 1mL samples of the solution were withdrawn using a syringe with a needle affixed to the bore, filtered through 0.45μm polypropylene into a clean 15mL polypropylene centrifuge tube. The samples were then prepared for analysis using electro-spray mass-spectrometry (ES-MS). The samples to be analyzed using ES-

MS underwent a 1:10 dilution with de-ionized water. This was necessary as to not saturate the detector.

2.1.4.4.1 Electrospray-Mass Spectrometry

A MSQ plus mass spectrometer equipped with Chromeleon software available from Dionex was used to analyze the samples from the bleeding study. This technique was chosen due to the soft ionization of macromolecules. Soft ionization offers the advantage of leaving a macromolecule nearly fully intact where as hard ionization causes a large amount of fragmentation. A large amount of fragmentation causes difficulty in determining the chemical structure of the original molecule. The samples are aerosolized into the ionization chamber. During aerosolization the molecules in the sample, in this case the extractant that has bleed off the resin, under goes the loss of a single proton, leaving the extractant molecule or complex negatively charged. The negatively charged extractant molecule is then attracted to the positively biased focusing cones. These cones also serve the purpose of focusing the sample into a collimated beam. After passing through the cones the sample enters the quadrapole region of the mass spectrometer. The quadrapoles are set such that the voltage on the oppositely charged rods produces a magnetic field that will allow the desired mass-to-charge ratio to pass straight through the quadrapoles and impinge on the detector (generally a dynode), while the undesired mass-to-charge ratios have a curved trajectory that results in those mass-to-charge ratios not impinging upon the detector. In the studies presented here the samples were analyzed for the naked extractant molecule, acidic complex, acidic adduct, hydronium complex, protonated and de-protonated extractant molecule.

2.1.5 Synthesis of Resins

In order to synthesize resins in house, first the ratio of moles of extractant to dry inert support was determined via a molarity calculation. Once these values were determined the appropriate amount of inert support (commercially available) was placed into a beaker. The known mass of extractant (commercially available) was then diluted with the calculated volume of solvent. Once a homogenous solution was obtained the required amount of dry inert support was placed into a round bottom flask. The dry inert support was then slurried in approximately 100-200mL of methanol or dichloromethane to wet the resin, in order to ensure the extractant would adsorb to the inert support. The extractant/solvent solution was quantitatively transferred to the round bottom flask containing the dry inert support slurry. The round bottom flask was placed on a rotary evaporator until the resin appeared dry. The round bottom flask was then placed in a 40°C oven overnight to ensure complete drying of the resin. The dried resin was then transferred to a plastic screw top container and wrapped in parafilm for long term storage and further characterization.

CHAPTER 3

EXTRACTIONS WITH EICHROM'S DGA RESIN

3.1 Off-line Studies

3.1.1 Batch Extractions

3.1.1.1 Results and Discussion

In the presence of nitric acid Group V elements have a high adsorption to surfaces.[87-89] In order to counteract this hydrofluoric acid is added to the sample matrix because it is well known that the addition of hydrofluoric acid (HF) greatly decreases the loss of Group V elements due to sorption. Therefore a mixed nitric acid (HNO_3) and HF matrix was chosen to investigate the extraction of Group V elements with Eichrom's DGA resin. Initially, a range of 0.001 to 8M for nitric acid was chosen. Three HF concentrations were examined over this nitric acid range, 0.002, 0.02 and 0.1M, respectively. Figure 3.1 shows the uptake of both ^{95}Zr and ^{95}Nb in 0.002M HF and various HNO_3 concentrations. For all HNO_3 concentrations Nb is extracted less than Zr at 0.002M HF. DGA is a neutral extractant. In nitric acid it is know that Zr forms polynuclear species below 5M and as acid concentration decrease there is increased polynuclear formation.[64, 65] The likely explanation for the lower uptake of Zr on DGA below 3M HNO_3 is the formation of cationic species that are not extracted due to DGA being a neutral extractant. The largest uptake of Zr on DGA occurs from 3 to 6M HNO_3. Zr is likely forming a neutral species, which allows for Zr to be extracted by DGA. Above 6M the uptake of Zr on DGA seems to level off or even drop. A drop in uptake can be explained by Zr forming a dianionic species similar the species Zr forms in pure hydrochloric acid (HCl), $[ZrCl_6]^{2-}$. Above 3M HNO_3 Hf and Zr have similar trends.[62, 63] If this holds true for all mixed nitric hydrofluoric acid system investigated then it can be expected that Hf will be taken up on DGA and eluted under the same conditions as Zr. There is very little literature on the speciation of Group V elements in mixed acid media, so it is very difficult to speculate as to the speciation of Nb in the system. For example, Nb is known to form anionic halide complexes and mixed oxo-halide and hydroxy-halide species in a pure hydrochloric or pure hydrofluoric acid matrix.[110] As the complexity of the matrix increases the larger the diversity in possible species formed becomes. If Nb forms species in a pure nitric acid system similar to the species formed in a pure HCl or HF system, then in a mixed HNO_3/HF system there could be fluoro, mixed fluoro-nitrato or oxy-fluoro-nitrato species formed in addition to the formation of anionic halide, oxo-halide and hydroxy-halide species.

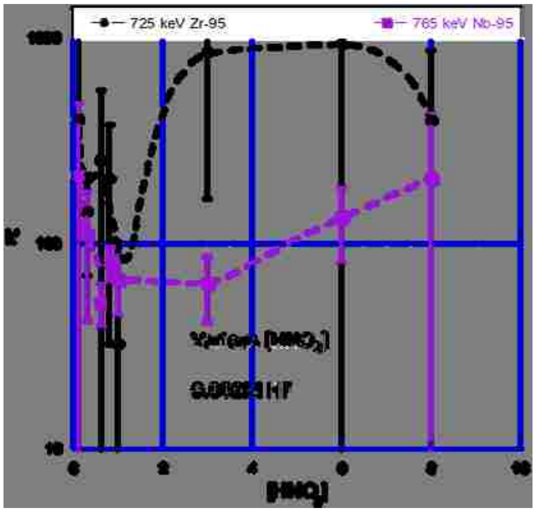

Figure 3.1. The uptake of Zr and Nb on DGA resin from various [HNO_3]/0.002M HF. The error bars are representative of population standard deviation. The values of each data point are given in Appendix A Table 6.1

The uptake of ^{95}Zr onto DGA from various HNO$_3$ at 0.02 and 0.1M HF is shown Figure 3.2. It is clear from this figure that the uptake of ^{95}Zr is affected by the amount of HF present, likely due to the formation of anionic species. When the k' values from Figure 3.1 and Figure 3.2 are compared it can be determined that the largest uptake for Zr lies between 3-6M HNO$_3$ and at 0.02 or 0.002M HF, likely due to the formation of a neutral species.

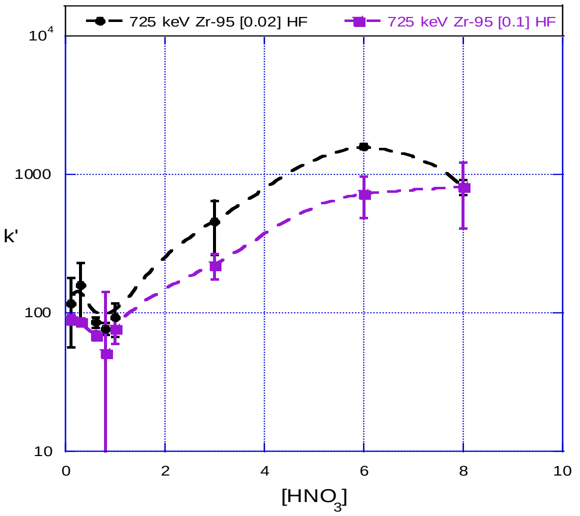

Figure 3.2. The uptake of ^{95}Zr is affected by the concentration of HF present. ^{95}Zr has a higher uptake at lower HF concentrations. The error bars are representative of population standard deviation. The values of each data point are given in Appendix A Table 6.2 and Table 6.3.

The uptake of ^{95}Nb onto DGA from various HNO$_3$ at 0.02 and 0.1M HF can be seen in Figure 3.3. From this figure it can be seen that the uptake of ^{95}Nb is not affected by the amount of HF present. When the k' values from Figure 3.1, Figure 3.2 and Figure 3.3 are compared it can be determined that Nb has less affinity for DGA than Zr. This is promising for the separation of Group IV and V elements.

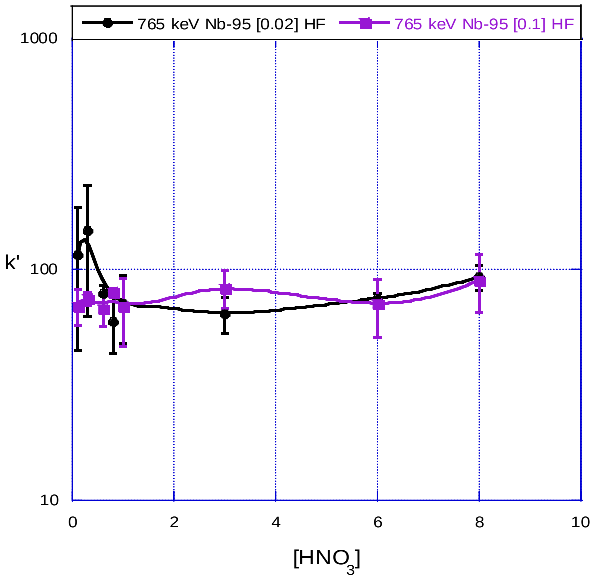

Figure 3.3. The uptake of ^{95}Nb onto the DGA resin is relatively unaffected by the concentration of HF. The error bars are representative of population standard deviation. The value of each data point is given in Appendix A Table 6.2 and Table 6.3.

Batch studies using ^{95}Zr, ^{95}Nb, ^{175}Hf, ^{182}Ta, and ^{233}Pa over various HNO_3 concentrations at concentrations of HF ranging from 0.001 to 1.0M were conducted by Henderson et. al .[111] The results of these batch studies are shown in Figure 3.4, Figure 3.5, Figure 3.6, Figure 3.7, Figure 3.8, and Figure 3.9. In the case of Zr and Ta the stock solutions are not carrier free. The curvature of the data may be due to the presences of non-carrier free material. The presence of carrier in the material would block resin sites not allowing for the radionuclides to occupy those sites. Since only radioanalysis was performed on the solutions the non-active carrier material would go undetected and thus not be accounted for in the adsorption curves. The behavior of Np is not discussed because no attempt to control its oxidation state was made. Americium was not used in the batch study because its behavior on DGA is well known.[111] It can be seen from Figure 3.4 that at 0.001M HF ^{182}Ta is retained at low nitric acid concentration, while ^{95}Zr,

^{95}Nb, ^{175}Hf and ^{233}Pa have increasing retention on DGA up to 6M HNO_3. Comparing Figure 3.4 and Figure 3.5 reveal similar behavior of the nuclides in 0.001 and 0.02M HF. A similar behavior was also noted in the comparison of Figure 3.1 and Figure 3.2. Upon comparison of Figure 3.5 and Figure 3.6 it can be seen that Zr is less retained when there is increased presence of HF, these results were also seen when comparing Figure 3.1 and Figure 3.2. When Figure 3.4, Figure 3.5 and Figure 3.6 are compared it is noticed that Zr and Hf behave similarly and that they have an increased retention on the DGA resin between 1 and 6M HNO_3. This indicates that a load solution in this range would result in Zr and Hf adsorbing to the column and that the elements can later be stripped using a lower concentration of HNO_3.

Comparison of Figure 3.3, Figure 3.4, Figure 3.5, Figure 3.6, Figure 3.7, Figure 3.8 and Figure 3.9 indicates that Nb has little retention on DGA. This means that Nb should elute from the column in the early fractions. Figure 3.6, Figure 3.7, Figure 3.8 and Figure 3.9 show that as [HF] and [HNO_3] are increased Ta has a reduced retention on DGA, this indicates that Ta can be loaded onto the column from low concentration of HF and HNO_3 and then stripped off the resin in high HF and HNO_3 concentrations. Comparing the behavior of Nb and Ta in the batch studies indicates that these two Group V elements can be separated on DGA using a low nitric and hydrofluoric acid concentration load solution. Nb should elute early from this load solution while Ta is retained on the column. Ta can be stripped from DGA, following the elution of Nb by passing high concentration of HNO_3 and HF through the column.

Figure 3.3, Figure 3.4, Figure 3.5, Figure 3.6, Figure 3.7, Figure 3.8 and Figure 3.9 indicate that Pa has very little retention on DGA at HF concentrations greater than

0.001M. At 0.001M HF Pa has little affinity for DGA from 0.1 to 2M HNO_3. Based on these batch results Pa and Ta can be separated on DGA using a low nitric and hydrofluoric acid concentration load solution.

Based on the results presented in Figure 3.3, Figure 3.4, Figure 3.5, Figure 3.6, Figure 3.7, Figure 3.8 and Figure 3.9 the conditions presented in Table 3.1 were chosen for further investigation in column experiments. A load solution of 4M HNO_3/0.001M HF was chosen because under these conditions Ta, Pa Zr, and Hf should be retained on DGA and Nb should pass through the column thus quickly separating Nb from the Group IV and other Group V elements. Upon elution of Nb, if additional 4M HNO_3/0.001M HF is passed through the column Pa should elute, while Ta, Zr, and Hf remain on the column thus separating Pa from Group IV and Ta. Zr and Hf both have high retention on DGA under 4M HNO_3/0.001M HF. Both Zr and Hf should be eluted from DGA using 0.04M HNO_3/0.02M HF while Ta remains retained on the DGA resin, this allows for decontamination of the sample from Group IV elements. After elution of Zr and Hf, Ta can then be eluted from the column using 8M HNO_3/1M HF.

Based on Figure 3.10 Am should be retained on the DGA column under the conditions proposed in Table 3.1. It has also been shown that Am can be stripped from DGA using either ammonium bioxalate or 0.1M HCl.[111]

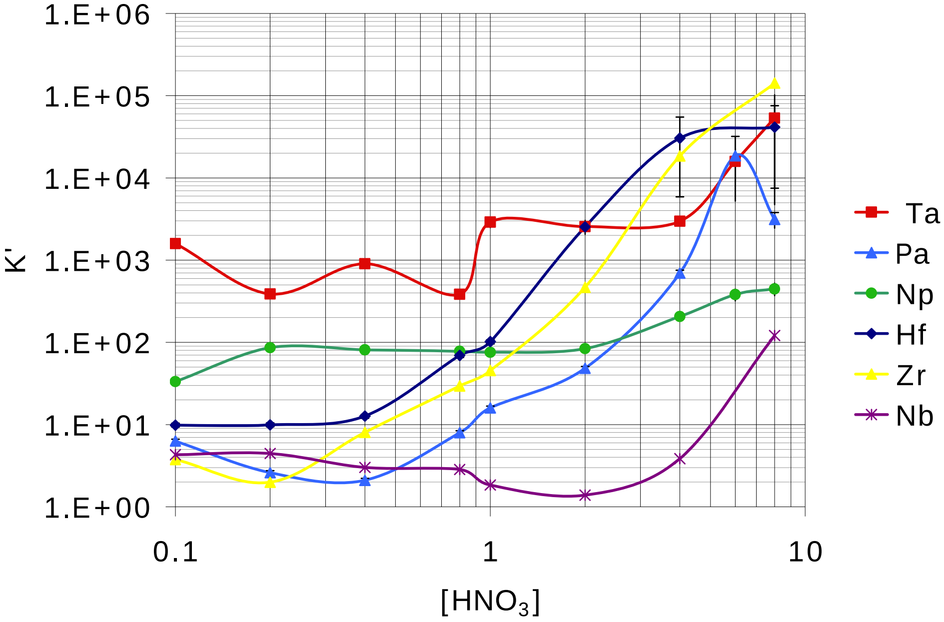

Figure 3.4. Uptake of Pa, Nb, Ta, Np, Hf, and Zr on DGA-normal resin, 50-100μm particle size versus [HNO$_3$] at [HF] = 0.001 M, 22(2)°, 1 hour equilibration.

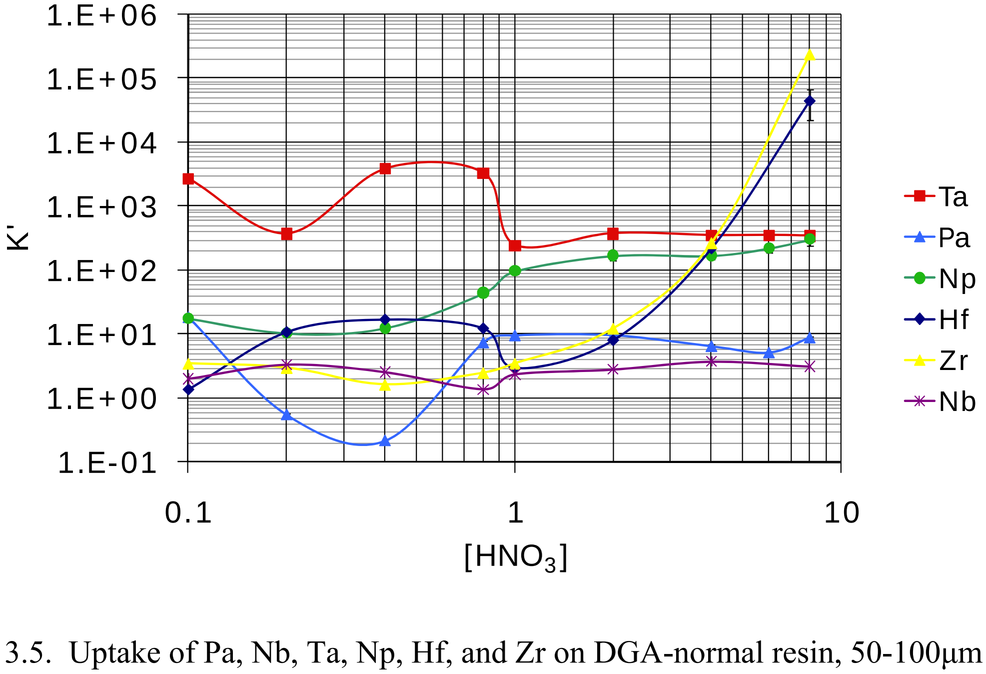

Figure 3.5. Uptake of Pa, Nb, Ta, Np, Hf, and Zr on DGA-normal resin, 50-100μm particle size versus [HNO$_3$] at [HF] = 0.02 M, 22(2)°, 1 hour equilibration.

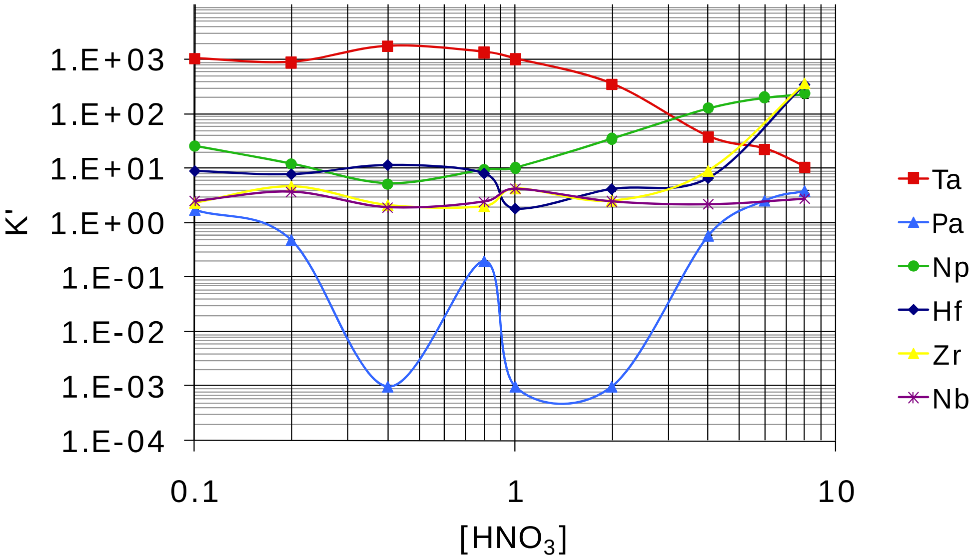

Figure 3.6. Uptake of Pa, Nb, Ta, Np, Hf, and Zr on DGA-normal resin, 50-100um particle size versus [HNO$_3$] at a constant [HF] = 0.1 M, 22(2)°, 1 hour equilibration.

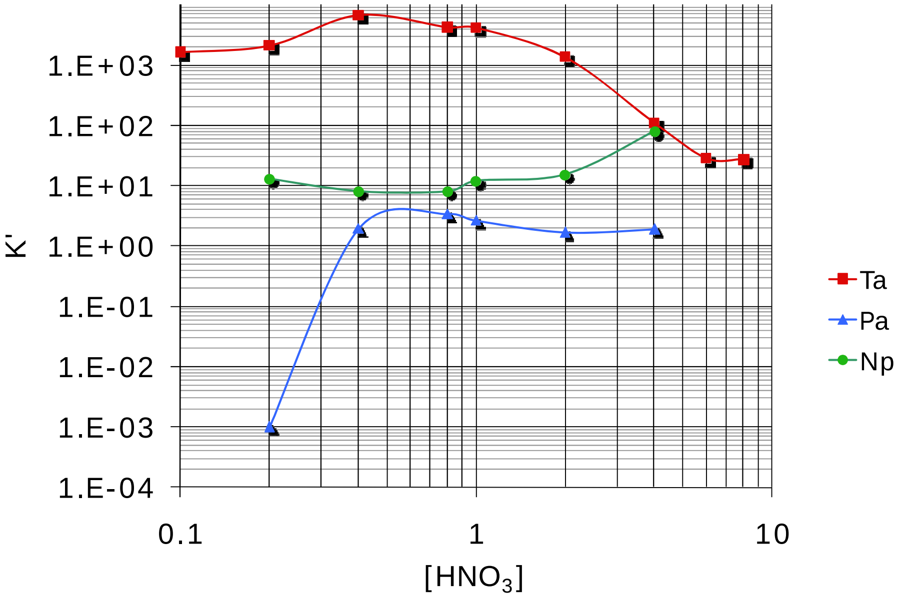

Figure 3.7. Uptake of Pa, Nb, Ta, Np, Hf, and Zr on DGA-normal resin, 50-100um particle size versus [HNO$_3$] at a constant [HF] = 0.2 M, 22(2)°, 1 hour equilibration.

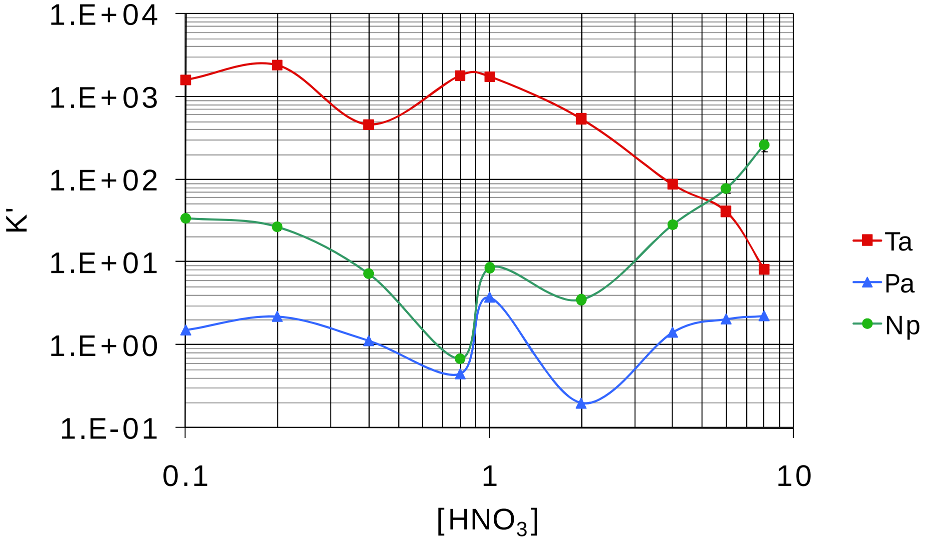

Figure 3.8. Uptake of Pa, Nb, Ta, Np, Hf, and Zr on DGA-normal resin, 50-100 um particle size versus [HNO_3] at a constant [HF] = 0.5 M, 22(2)°, 1 hour equilibration.

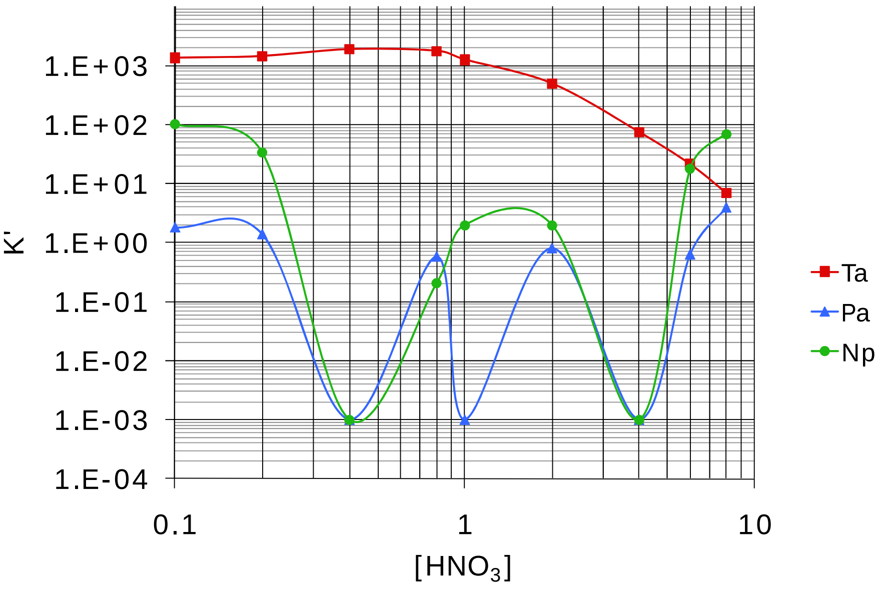

Figure 3.9. Uptake of Pa, Nb, Ta, Np, Hf, and Zr on DGA-normal resin, 50-100 um particle size versus [HNO_3] at a constant [HF] = 1.0 M, 22(2)°, 1 hour equilibration.

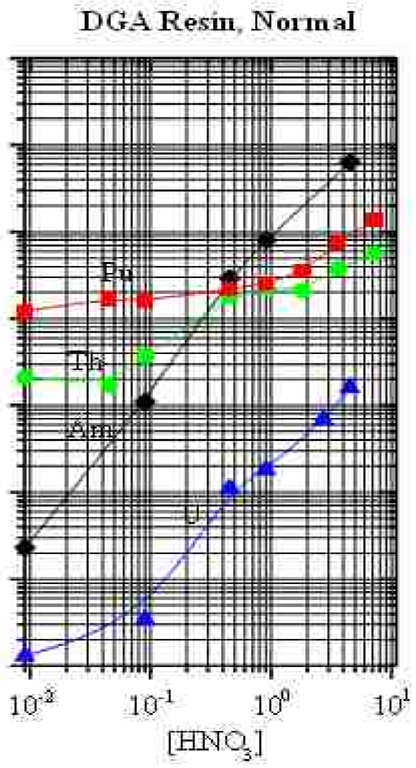

Figure 3.10. Uptake of Am on DGA-normal resin, 50-100μm particle size versus $[HNO_3]$, 22(1)ºC, 1 hour equilibration time.[99]

Table 3.1. Elution conditions chosen for column studies based on the results of the batch studies. Using a 2 mL pre-packed DGA column. The nuclide that is expected to elute is shown in parentheses.

Fraction	Elution Conditions	Proposed Species
Load	1mL 4M HNO_3/0.001M HF	Neutral nitrato/fluoro species with the exception of Nb and Pa, which form anionic species
Fraction 1 (Nb)	2mL 4M HNO_3/0.001M HF	Anionic nitrato/fluoro
Fraction 2 (Pa)	5mL 4M HNO_3/0.001M HF	Anionic nitrato/fluoro
Fraction 3 (Zr, Hf)	2x5mL 0.4M HNO_3/0.02M HF	Cationic nitrato/fluoro
Fraction 4 (Ta)	3x5mL 8M HNO_3/1M HF	Anionic nitrato/fluoro
Fraction 5 (Am)	2x5ml 0.1M HCl or 15 mL 0.1M ammonium bioxalate	Anionic oxalate or cationic species

Over the course of this study it was noticed that Ta inconsistently loaded on to the column, due to adsorption on the surface of the centrifuge tube. In order to correct this situation, batch studies were carried out in both various nitric/hydrofluoric acid and in hydrochloric/hydrofluoric acid matrices. If inconsistent loading is present then it is impossible to determine how much of a radionuclide was retained on the column. Figure 3.11and Figure 3.12 show the percent of Ta that remained adsorbed to the original tube after the radionuclide solution was loaded onto the column (% Ta lost). The nitric acid concentration was held constant at 4M, while the concentration of the hydrofluoric acid was varied from 0 to 1M. It was found that Ta was inconsistently removed from the tube on to the column and a large percentage of the Ta remained in the load tube. Based on this result it was determined that a mixed nitric/hydrofluoric acid media provided insufficient loading conditions and a mixed hydrochloric/hydrofluoric acid media was investigated. It was found that Ta consistently loaded on to the column from 6M HCl/various HF. The optimum condition for consistently transferring Ta from the load tube to the column was from a 6M HCl/8M HF matrix. A possible explanation for this behavior is that at higher acid concentrations the Ta has less tendency to form hydrolysis complexes and thus there is less likelihood for a hydrogen bond to form between the Ta complex and the polypropylene. This is the purpose of the first reconstitution step prior to loading the column. However, this step introduces a sufficient amount of fluoride ion to cause precipitation. To remedy the precipitation of the radionuclides, the samples were then reconstituted in concentrated nitric acid. This is the purpose of the second reconstitution step prior to column loading. The third evaporation and reconstitution step is to get the radionuclides into the desired load solution.

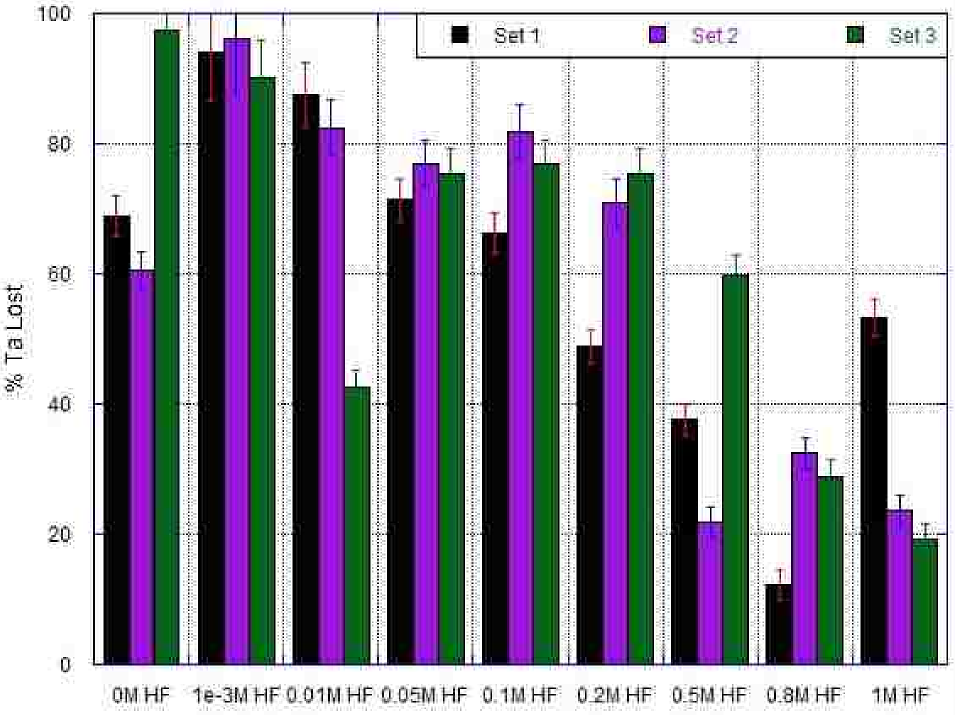

Figure 3.11. The sorption of Ta across 4M HNO3 and various [HF]. The variation across the three sets per concentration indicates inconsistencies in behavior. Error bars represent counting errors. The value of each data point is given in Appendix A Table 6.4.

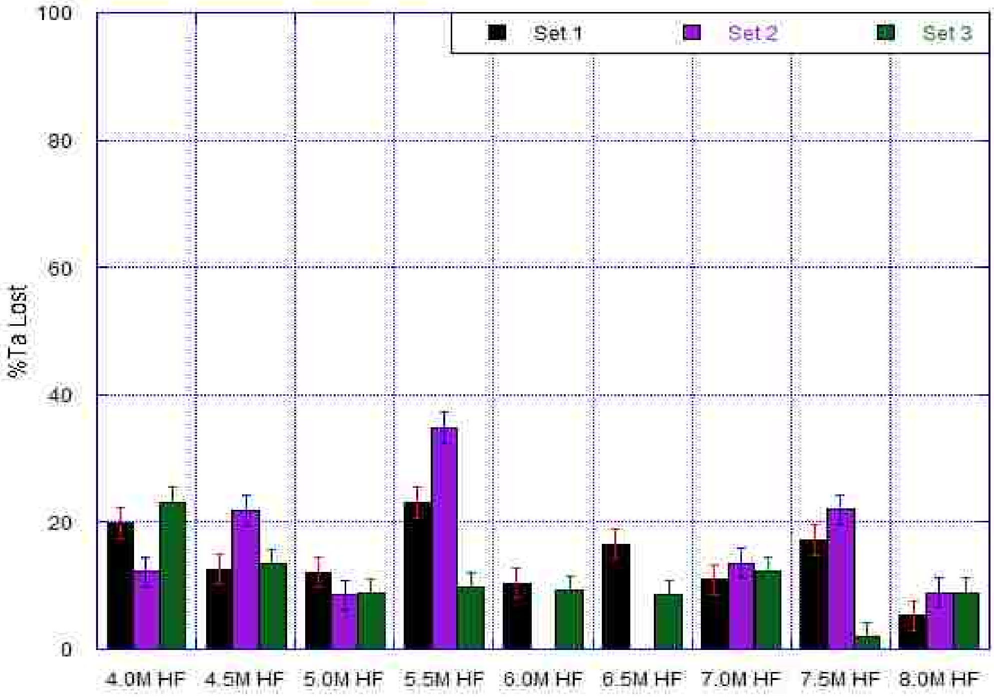

Figure 3.12. The sorption of Ta across 6M HCl and various [HF]. The variation across the 3 sets per concentration indicates that Ta loads much more consistently in this system. Error bars represent counting errors. The value for each data point is given in Appendix A Table 6.5.

3.1.1.2 Conclusions

Batch studies indicated that there was significant and inconsistent Ta adsorption onto the polypropylene tube from various [HNO_3] and [HF] matrices, however in a mixed [HCl]/[HF] matrix Ta adsorbed far less and more consistently to the polypropylene tube. From this it was determined that the samples should undergo a reconstitution and evaporation in 2mLof 6M HCl/8M HF prior to the samples being processed. Following this the samples need to be reconstituted and evaporated in 2mL of concentrated HNO_3 to dissolve the fluoride precipitates. It was also determined that a solution of 1mL of 6M HNO_3/0.1M HF causes Ta to be quantitatively removed from the centrifuge tube, while ensuring Zr, Hf, Nb, Pa and Am would sorb to the DGA resin. The results from the batch study showed promise for separation of Zr, Hf, Nb, Ta, Pa and Am. In order for these elements to adsorb to the DGA resin a neutral complex must be formed, once this neutral complex no longer exists the elements will desorb from the resin. An elution scheme for dynamic column studies was also proposed and is shown in Table 3.1 along with proposed species.

3.1.2 Column Extractions

3.1.2.1 Results and Discussion

The same stock solutions, as used in the batch studies, containing ^{95}Zr, ^{95}Nb, ^{175}Hf, ^{182}Ta, ^{233}Pa and ^{243}Am were evaporated to dryness in a water bath, reconstituted with 2mL of 6M HCl/8M HF and evaporated again to dryness in a water bath. The residue was reconstituted with 2mL of concentrated nitric acid, evaporated to dryness in a water bath, and followed by a reconstitution in the desired load solution. The purpose of these steps was discussed in section 3.1.1.1.

The DGA resin was pretreated with 5mL of 4M HNO_3/0.001M HF prior to column loading. The 1mL solution containing the radionuclides of interest was then loaded on the column. The various radionuclides were then sequentially eluted based on the scheme shown in Table 3.1. The elution solutions were chosen based on batch and column study results.[111]

Column extraction studies were performed to determine if ^{95}Zr, ^{95}Nb, ^{175}Hf, ^{182}Ta, ^{233}Pa, and ^{243}Am could be dynamically separated. The data presented in Figure 3.13 and Figure 3.14 was obtained using a load matrix of 6M HCl/0.1M HF. Figure 3.13 shows that Zr elutes off the column in both the Pa and first Ta fractions (strip 2 and 3). Nb elutes off the column with Pa in the load and strip 1. Hf elutes off the column in the first two strips and the first Ta strip. Ta elutes off the column in the first two fractions of the third strip and Am elutes with the first ammonium bioxalate strip. These results indicate that Group IV (Zr, Hf) and V (Nb. Ta) elements are not sufficiently separated. It is advantageous to separate Group IV and V elements to ensure that chemistry is performed on Db and not on Rf. To achieve the goal of separating Group IV and V elements, the second strip was increased from 2mL to 10mL. These results are presented in Figure 3.14. Increasing the second strip volume caused Zr to elute in two fractions separate from Group V elements. Hf, however eluted with Nb and Pa. It has previously been shown that Zr has a high affinity for DGA resin at high concentrations of nitric acid.[111] Hf should behave chemically similar to Zr, based on this the load matrix was changed from 6M HCl/0.1M HF to 10M HNO_3/0.1M HF. When the load matrix was changed to nitric acid/hydrofluoric acid it was necessary to confirm that Ta was not remaining in the load tube. Figure 3.15 shows that all radionuclides were efficiently removed from the load tube to the column upon the load matrix being changed. The elution behavior of the radionuclides from DGA with a load matrix of 10M HNO_3/0.1M HF is shown in Figure 3.16. Figure 3.16 clearly shows that Group IV and V elements are separated. Nb and Pa elute from the column in the first strip, Zr and Hf elute during the second strip, Ta elutes during the third step, and Am elutes during the fourth and final strip of the DGA column. It has been previously shown that Am has a high affinity for DGA.[111] It would be ideal if all Am could be eluted from the resin so that the resin can be re-used. To accomplish this, an elution solution of 0.1M HCl was investigated and the results are shown in Figure 3.17. Figure 3.17 demonstrates that 0.1M HCl is effective in stripping all Am from the DGA column. Separation of Nb and Pa would greatly help in assessing their chemical similarity to dubnium, however, the data presented in Figure 3.13, Figure 3.14, Figure 3.15, Figure 3.16 and Figure 3.17shows that separation of these two elements is not possible under current conditions. The possible reason for the elution order is that Nb and Pa elute first due to their tendency to form of anionic complexes and not neutral species. Zr and Hf elute due to the formation of either cationic or polynuclear species. Ta elutes due to the formation of anionic species and finally Am is eluted with bioxalate which forms an anionic oxalate complex with Am. It is possible that the difference from batch and dynamic column studies can be explained by a mass loading effect, which causes blockage of resin sites. Blockage of resins sites would explain why the elements are not eluting in smaller fraction volumes. For example, Ta should elute in one fraction but elutes small quantities throughout the column study. When Am is eluted with 0.1M HCl a cationic chloride species is formed. Another possible explanation for the separation not being as large as possible is due to, the presence of not enough theoretical plates for separation. The pre-packed columns available from Eichrom are approximately 3cm in height. One way to increase the number of theoretical plates without changing the quantity of resin being used is to increase the column height and decrease the inner diameter of the column. Doing this would increase the number of theoretical plates in the column and allow the elements to interact with the resin longer, which may allow for enhanced separation.

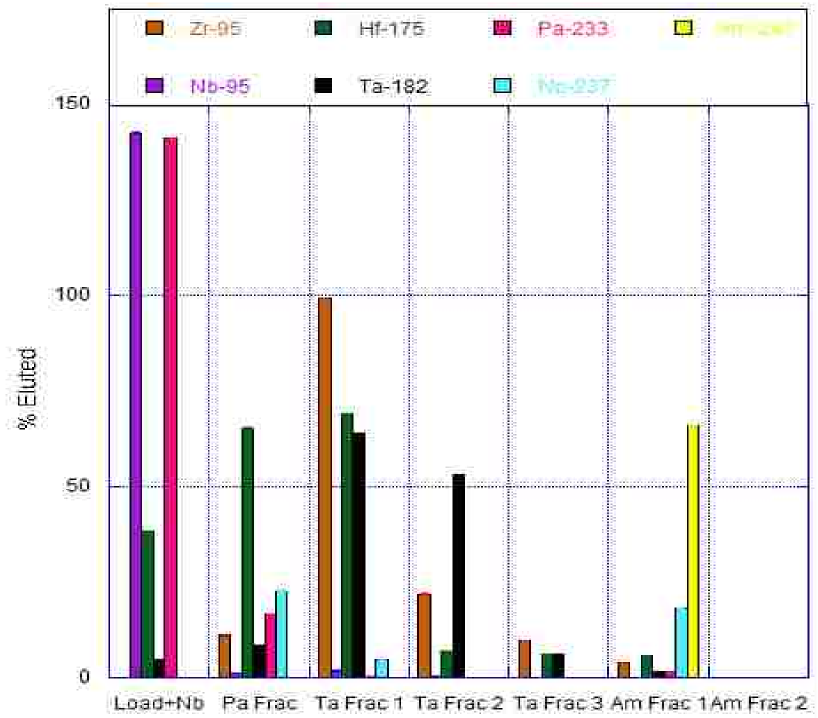

Figure 3.13. Elution behavior of various radionuclides on DGA. The load and Nb fraction correspond to 3mL of 4M HNO_3/0.001M HF, the Pa fraction corresponds to 10ml of 0.4M HNO_3/0.02M HF, the Ta fractions corresponds to 5mL each of 8M HNO_3/1M HF, and the Am fractions correspond to a 10mL followed by 5mL of 0.1 ammonium bioxalate strip. Error bars represent counting error and contained within the data point. The values for each data point are given in Appendix A Table 6.6 and Table 6.7.

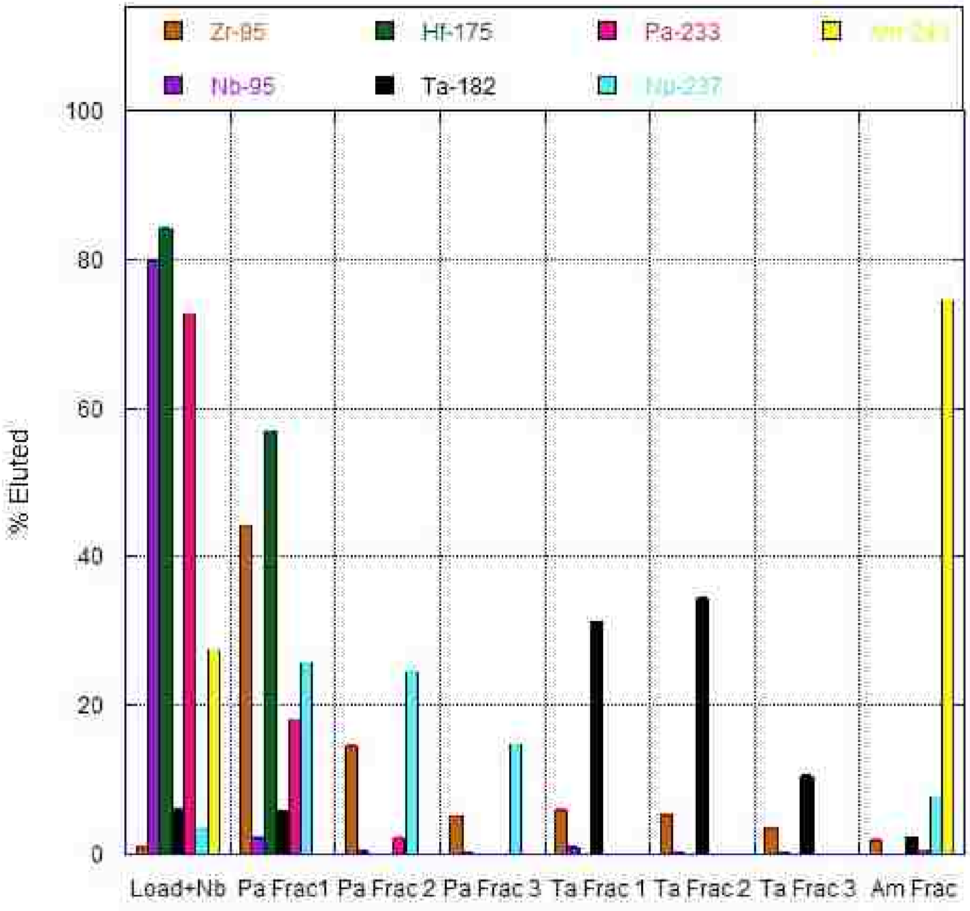

Figure 3.14. Elution behavior of various radionuclides on DGA, when the second strip is increased from a 2 mL to a 10 mL volume. The load and Nb fraction correspond 3mL of 4M HNO_3/0.001M HF, the first two Pa fractions corresponds 3mL each of 0.4M HNO_3/0.02M HF and the third Pa fraction is 4mL of 4M HNO_3/0.02M HF. Each Ta fractions corresponds to 5mL of 8M HNO_3/1M HF, and the Am fractions correspond to an ammonium bioxalate 15mL of 0.1M ammonium bioxalate. Error bars represent counting errors and contained within the data point. The values for each data point are given in Appendix A Table 6.8 andTable 6.9.

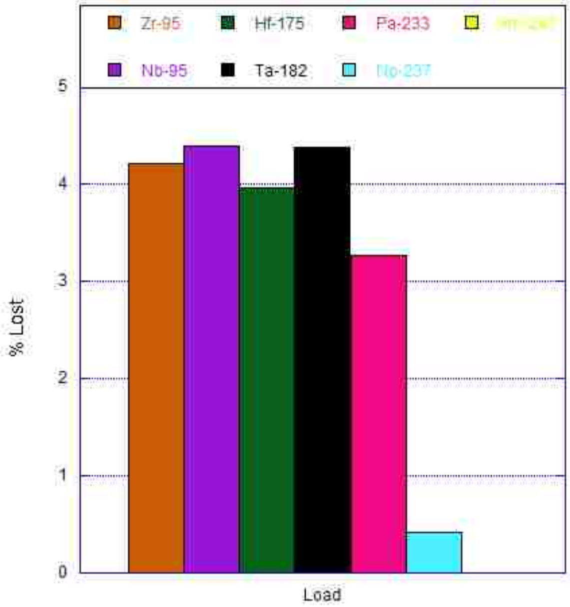

Figure 3.15. Less than five percent of each radionuclide remained in the load tube. Error bars represent counting errors and are contained within the data point. The values for each data point are given in Appendix A Table 6.10.

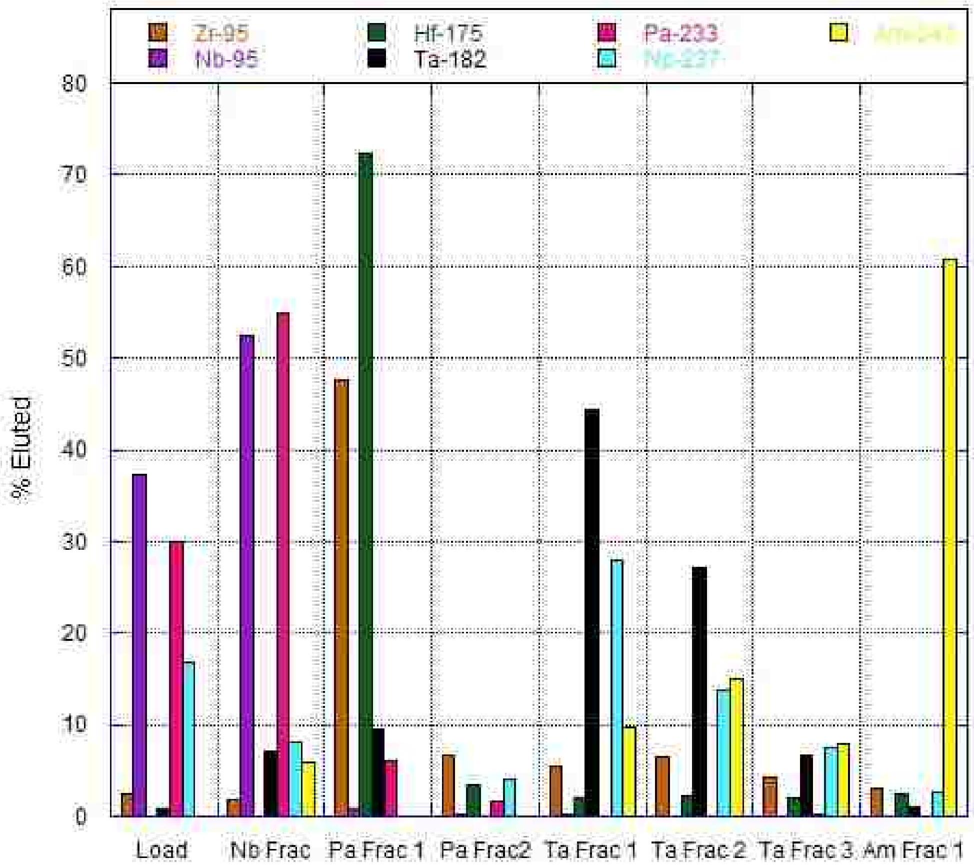

Figure 3.16. Elution behavior of various radionuclides on DGA where the load solution is 1mL of 10M HNO3/0.1M HF. The Nb fraction corresponds to 2mL of 4M HNO_3/0.001M HF. The two Pa fractions correspond to 5mL each of 0.4M HNO_3/0.02M HF. The Ta fractions correspond to 5mL each of 8M HNO_3/1M HF, and the Am fractions correspond to a 15mL 0.1M ammonium bioxalate strip in Table 3.1. Error bars represent counting error and contained within the data point. The values corresponding to each data point are given in Appendix A Table 6.11 and Table 6.12.

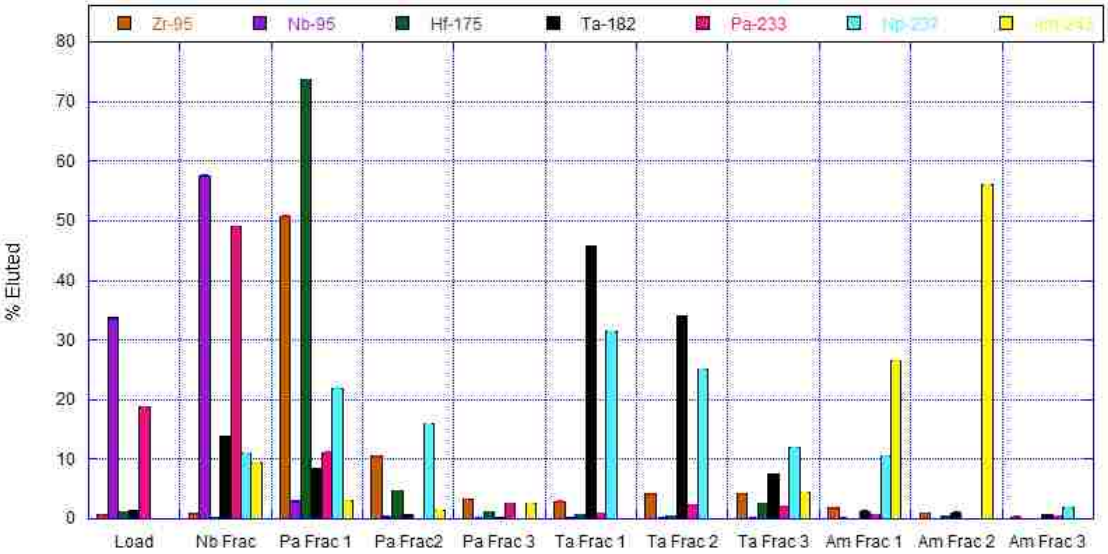

Figure 3.17. Elution behavior of various radionuclides on DGA where the load solution is 1mL of10M HNO3/0.1M HF. The Nb fraction correspond to 2mL of 4M HNO_3/0.001M HF. Each Pa fraction corresponds to 5mL of 0.4M HNO_3/0.02M HF. The Ta fractions corresponds to 5mL of 8M HNO_3/1M HF. The first two Am fractions correspond to two 5mL 0.1M HCl strips, and the final Am fraction corresponds to a 5mL ammonium bioxalate strip in Table 3.1. Error bars represent counting errors and are contained within the data point. The values of each data point are given in Appendix A Table 6.13 and Table 6.14.

3.1.2.2 Conclusions

An effective separation method for the homologs and pseudo-homologs of Rf and Db has been developed based on Eichrom Technologies Inc.'s DGA resin. It has been determined that for batch and column studies the presence of higher acid concentration (most likely due to HF) is necessary in order to have consistent loading of Ta onto the column. It has also been shown that Nb and Pa have similar elution curves and are inseparable under current conditions. Eichrom's DGA resin provides a viable chemical system for the study of the chemical behavior of Db, if the conditions presented in Table 3.1 are used.

3.1.3 Resin Bleeding

Due to the nature of atom-at-at-time chemistry experiments it would be extremely useful if new DGA columns were not required for every chemical separation. It would be ideal to re-use columns or resin instead. It has been shown that DGA is an extremely robust and stable system and has minimal bleed off of the extractant.[111] It was determined that over the course of 77 days the DGA extractant molecule did not detectably bleed from the resin in solutions of 2M HNO_3, 10M HNO_3 of 10M HNO_3/1M HF in the form of the naked extractant, mononitrato complex, nitric acid adduct, protonated or deprotanated species, as determined using Electrospray-mass spectrometry. The detection limit for the naked DGA extractant molecule was determined to be between 5 and 0.5 parts per billion.

3.1.4 Future Work

The proposed separation scheme should be tested with on-line produced short-lived isotopes to ensure the off-line studies presented here are truly reflective of on-line chemistry experiments. Examples of short-lived on-line produced isotopes that could be used in an on-line study are ^{85}Zr, ^{169}Hf, ^{90}Nb, ^{178m}Ta and an online produced upper actinide. ^{85}Zr can be produced by bombarding ^{nat}Ge with 84MeV ^{18}O.[104] ^{169}Hf can be produced by bombarding ^{124}Sn with a 228MeV ^{50}Ti.[104] ^{90}Nb can be produced through the bombardment of ^{nat}Zr with protons.[112] ^{178m}Ta can be produced by bombarding ^{nat}Nb with protons.[112] If the on-line chemistry experiments corroborate the results of the off-line studies and show separation of Zr, Hf, Nb, Ta and an upper actinide then the system should be used to chemically characterize short-lived ($t_{1/2}$ ~30s) Db isotopes. In this experiment physical pre-separation of the transfer products should be used due to the short half-life. Also, the short-lived Db should be compared to just its homologs, Nb and Ta, and pseudo-homolog, Pa. Provided the proposed separation scheme is successful in chemically characterizing short-lived Db, then isotopes the system should be used to attempt separation of on-line produced Zr, Hf, Nb and Ta from Db. If this experiment is successful the system could be used to chemically characterize long-live Db isotopes ($t_{1/2}$ ~28h). In this experiment use of a catcher block instead of a physic pre-separator would be necessary. Chemically characterizing both short- and long-lived Db isotopes with one system will provide insight as to any difference in their chemical nature as well as the role that kinetics play on the separation.

CHAPTER 4

EXTRACTIONS WITH CROWN ETHER BASED RESINS

4.1 Off-line Studies

4.1.1 Solvent Effects

4.1.1.1 Batch Extractions

4.1.1.1.1 Results and Discussion

It has previously been shown that dicyclohexano-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) extract Zr and Hf in the presences of sufficiently high concentrations of HCl.[104] The extracted species is most likely in the form of an ion-association complex between two crown ether-hydronium complexes and a Group IV metal-chloro complex. In order for the necessary metal-chloro complex to form, the concentration of HCl must be high enough to allow formation of the di-anionic hexachloro-metal complex of the form $[MCl_6]^{2-}$, where M is Zr or Hf.[104] A depiction of the ion-association complex is shown in Figure 4.1.

The effect of three solvents on the ability of the resin to separate Zr and Hf in a HCl matrix has been investigated. The chemical structure of the three solvents, 1-octanol, 1-dodecanol and dichloromethane are shown in Figure 4.2. 1-Octanol was chosen as it is the same solvent used in the preparation of the commercially available crown ether based Sr resin from Eichrom .[100] 1-Dodecanol was chosen to investigate the effects of alkyl chain length on the separation of Zr and Hf. Finally, dichloromethane was chosen for the vast difference in chemical structure and properties from those of octanol and dodecanol as well as the high solubility of the crown ether in this solvent.

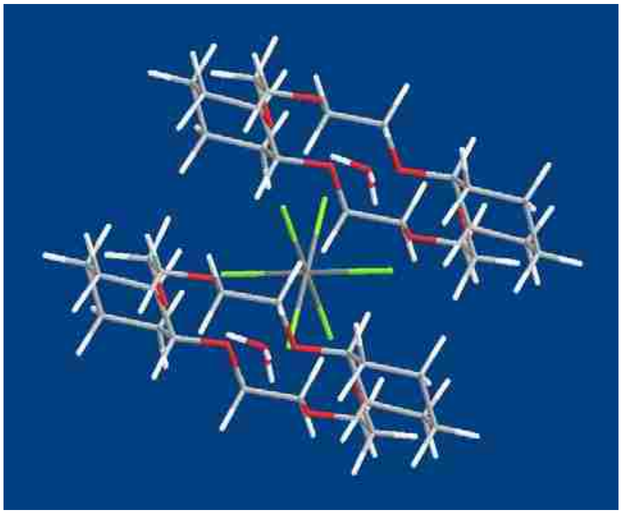

Figure 4.1. Two crown ether molecules with hydronium ions extracted into the crown ether cavities are shown extracting a $[MCl_6]^{2-}$ complex to form a neutral.

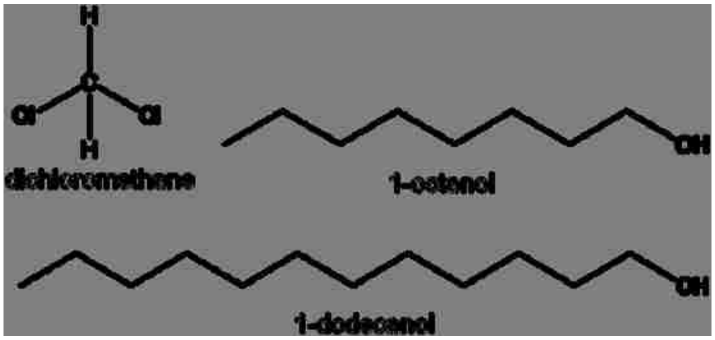

Figure 4.2. The chemical structure of the dichloromethane, 1-octanol and 1-dodecanol.

Table 4.1. Selected chemical properties of dichloromethane, octanol and dodecanol.

Properties	Dichloromethane	1-Octanol	1-Dodecanol
Molecular Weight (amu)	84.93	130.23	158.29
Vapor Pressure 25°C (mm Hg)	400	0.07	0.0085
Melting Point (°C)	-97	-17	7
Boiling Point (°C)	39.8	194.5	231
Specific Gravity 25°C	1.318	0.827	0.83

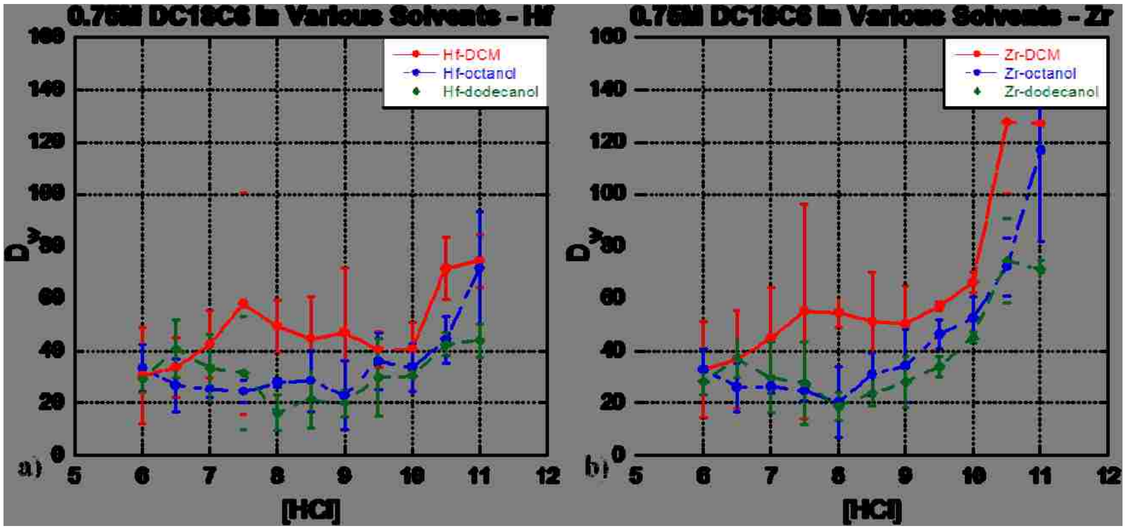

Figure 4.3. A direct comparison of the performance of each resin during batch studies for each element of interest. a) The uptake of Hf on each of the resins at various [HCl]. b) The uptake of Zr on each of the resins at various [HCl]. The values for each data point can be found in Appendix B in Table 7.2 and Table 7.3.

Some selected chemical properties of the three solvents are shown in Table 4.1.[113-115] The results from the batch studies for the resins synthesized with 0.75M DC18C6 and the three different solvents are shown in Figure 4.3. For both the behavior of Zr and Hf on the resins there appears to be little change in uptake on the resin until a concentration of 10M HCl is reached and within error bars the resins behave very similar. This is of interest as the results of Sudowe et. al. indicate an increase of extraction of the $[MCl_6]^{2-}$ into the crown ether from the aqueous HCl phase beginning at 7M HCl and the extraction leveling off at 9.5M HCl. It has been reported that while solvent extraction and extraction chromatographic methods are not quantitatively the same they still follow similar qualitative trends.[59] Based on this observation by Horwitz and co-workers one would expect similar trends in the work presented here, however this is not the case. One possible explanation for this observation is that the crown ether molecules are not close enough in proximity to one another to form the necessary sandwich structure, shown in

Figure 4.1, to extract Zr and Hf. The lack of formation of the sandwich complex maybe be due to an insufficient concentration of crown ether or it may be due binding constraints of the crown ether to the inert support that do not allow the crown ether molecules to associate closely enough with one another. It should also be noted that the resins synthesized with 1-octanol and 1-dodecanol show a nearly identical behvaior for both Zr and Hf for all concentrations of HCl used, with the exception of the highest concentration, 11M. This indicates that the alkyl chain length has little impact on the extraction behavior of Zr and Hf at these concentrations. However, at 11M HCl the octanol resin behaves more closely to the resin synthesized with dichloromethane. A possible explanation for the difference in behavior occurring at 11M HCl is there is an increase in the presence of the $[MCl_6]^{2-}$ species, and the presence of the additional four methylene groups of the dodecanol have been blocking the cavity of the crown ether all along but this is not evident until there is a greater quantity of species to uptake. It is also evident from Figure 4.3 that the resin synthesized with dichloromethane has a greater affinity for both Zr and Hf compared to the resins synthesized with 1-ocatanol and 1-dodecanol. This may be attributed to the high vapor pressure of dichloromethane. The dichloromethane evaporates off of the slurried extractant and inert support while the resin is being synthesized. This leaves just the crown ether present on the inert support with no solvent taking up void space on the support. This is not true for 1-octanol and 1-dodecanol as their vapor pressures are too low to evaporate off during the synthesis of the resin. An important observation from the comparison of Figure 4.3 a) and b) is that Hf has a much lower uptake on all three resins compared to that of Zr. This indicates that Hf and Zr can be separated from one another and the systems therefore show promise for the chemical characterization of Rf. The separation factors (A_{Zr}/A_{Hf}) for all concentrations of HCl and all DC18C6 resins are shown below in Table 4.2. Based on Table 4.2 the best separation of Zr and Hf can be achieved between 10 and 11M HCl. It can also be seen from Figure 4.3 that both Zr and Hf have very little retention on the resin below acid concentrations below 10M therefore the resin will not extract Zr and Hf below this concentration.

Table 4.2. The separation factor for each resin at various HCl concentrations.

[HCl]	Dichloromethane	1-Octanol	1-Dodecanol
6.0	1.08 ± 0.13	0.99 ± 0.07	0.98 ± 0.03
6.5	1.03 ± 0.21	0.99 ± 0.03	0.95 ± 0.10
7.0	1.01 ± 0.11	1.03 ± 0.09	0.92 ± 0.13
7.5	0.96 ± 0.06	1.01 ± 0.03	0.96 ± 0.24
8.0	1.08 ± 0.08	0.76 ± 0.43	1.23 ± 0.45
8.5	1.09 ± 0.10	1.10 ± 0.20	1.22 ± 0.42
9.0	1.10 ± 0.15	1.38 ± 0.23	1.28 ± 0.09
9.5	1.25 ± 0.14	1.18 ± 0.11	1.20 ± 0.29
10.0	1.46 ± 0.10	1.31 ± 0.20	1.35 ± 0.01
10.5	1.28 ± 0.07	1.24 ± 0.03	1.39 ± 0.11
11.0	1.30 ± 0.07	1.24 ± 0.03	1.34 ± 0.15

4.1.1.1.2 Conclusions

Based on the batch study results presented in Figure 4.3 the solvent used during synthesis of the resin has little effect on the separation behavior of Zr and Hf. All three resins show potential for applications to Rf chemistry. The highest potential for separation on a dynamic column would result from a load solution of concentrated HCl and elution of Hf in 10 to 11M HCl, as this is where the highest separation factors for Zr and Hf have been measured. However, the results of Sudowe and co-workers showed tht in solvent extraction experiments the best separation of Zr and Hf occured between 7 and

8M HCl. Based on the results of the batch studies presented in Figure 4.3 and Table 4.2 of section 4.1.1.1.1 and the results of Sudowe et. al. the elution behavior of Hf at 7, 8, 10 and 11M HCl should be investigated, while Zr elution off the column should be investigated at 3M HCl. A solution of 3M HCl for the elution of Zr was selected for two reasons. First, it is well known that the $[MCl_6]^{2-}$ species does not form below 6M HCl therefore there will be no extraction of Zr onto the crown ether resin. Second, below 3M HCl hydrolysis of Zr can occur, which may interfere with recovery of Zr during the separation. A possible explanation for the difference between the data shown here and the solvent extraction experiments performed by Sudowe et. al. is that in solvent extraction systems the crown ether can move freely and can easily form the ion association complex with the metal. On the other hand in a resin based system the crown ether is bound to an inert support and its movement is severely restrained.

4.1.1.2 Column Extractions

4.1.1.2.1 Results and Discussion

Samples containing ^{95}Zr and ^{175}Hf were evaporated to dryness and reconstituted in 1mL of reagent grade concentrated HCl. This prepared the samples to undergo separation by dynamic column studies. The three resins investigated in section 4.1.1.1 via batch studies were also investigated using dynamic column studies, according to the recommendations described in section 4.1.1.1.2.

Each resin was pre-treated with 5mL of concentrated HCl prior to loading the column with the 1mL solution containing the radionuclides of interest. The 1mL solution containing the radionuclides of interest was then loaded on the column. The various radionuclides were then eluted from the 0.75M DC18C6 synthesized with dichloromethane, 1-octanol or 1-dodecanol column using 6 aliquots of 0.5mL (0.88, 0.79 and 0.80, respectively) for both Zr and Hf. Based on the results of the batch study it was believed that Hf would elute of the column first, followed by Zr on all the resins. The results for Hf elutions at concentrations of 7, 8, 10 and 11M HCl for the resins synthesized with dichloromethane, 1-octanol and 1-dodecanol are shown in Figure 4.4, Figure 4.5 and Figure 4.6, respectively. Figure 4.4 a-d shows there is very little separation of Zr and Hf under any of the conditions investigated. However as one proceeds from a to d the Zr peaks begin to slightly shift towards higher elution volumes. Although there is not a significant enough shift to conclude that Zr and Hf are ever completely separated on the resin synthesized with dichloromethane. For the resin synthesized with dichloromethane at Hf elution conditions of 7M HCl 85±27% Hf and 83±20% of Zr elutes in the first 4mL. Under the conditions where 8M HCl is used to elute Hf 85±11% of Hf and 82±6% of Zr elutes in the first 4mL. When 10M HCl is used to elute Hf 71±19 of the Hf and 37±21% of the Zr elutes in the first 4mL. Finally, when 11M HCl is used to elute Hf 68±6% of the Hf and 65±6% of the Zr elutes in the first 4mL. This same conclusion can be drawn for the resins synthesized with 1-octanol and 1-dodecanol based on Figure 4.5 and Figure 4.6. In the case of the resin synthesized with 1-octanol at Hf elution conditions of 7M HCl 86±21% Hf and 84±13% elute in the first 4mL. Under the conditions where 8M HCl is used to elute Hf 81±27% of Hf and 80±42% of Zr elutes in the first 4mL. When 10M HCl is used to elute Hf 83±7% of the Hf and 78±5% of the Zr elutes in the first 4mL. Finally, when 11M HCl is used to elute Hf 87±9% of the Hf and 84±12% of the Zr elutes in the first 4mL. For the resin synthesized with 1-dodecanol at Hf elution conditions of 7M HCl 79±10.% Hf elutes in the first 4mL and 84±7% of Zr elutes. Under the conditions where 8M HCl is used to elute Hf 78±11% of Hf and 85±7% of Zr elutes in the first 4mL. When 10M HCl is used to elute Hf 77±5 of the Hf and 27±3% of the Zr elutes in the first 4mL. Finally, when 11M HCl is used to elute Hf 45±4% of the Hf and 10.±3% of the Zr elutes in the first 4mL. If Zr and Hf cannot be separated from one another, as the case with the 0.75M DC18C6 resin synthesized with dichloromethane, 1-octanol and 1-dodecanol, then no assessment of the behavior of Rf with respect to Zr and Hf can be obtained.

The elution profiles, shown in Figure 4.4, Figure 4.5 and Figure 4.6 under the same conditions for each resin, synthesized with various solvents, can be compared. If this is done for the 7M HCl elution profile, then Zr and Hf have very similar elution profiles, with the highest % elution, approximately 40%, at 2mL (free column volume = 0.88). When the elution profiles at 8M HCl are compared, the Hf elution peaks 0.5mL before Zr. Hf and Zr peak at 2mL and 2.5mL, respectively for the resin synthesized with dichloromethane. This is slightly different from the resins synthesized with 1-octanol and 1-dodecanol, which each exhibit identical elution profiles for both Zr and Hf peaking at 1.5mL and 2mL (free column volume of 0.79 and 0.80), respectively. The difference in behavior of the resin synthesized with dichloromethane can be explained by experimental error. However, within experimental error all three resins elute approximately the same quantity of Zr and Hf. A comparison of the elution profiles under 10M HCl conditions shows that while Zr and Hf initially have similar elution profiles, some Zr is being bound more tightly on the resin causing elution to occur at higher volumes, however this effect is not strong enough to fully separate Zr from Hf.

The same conclusion that can be drawn for the 10M HCl elution profiles can also be extracted from the 11M HCl elution profiles.

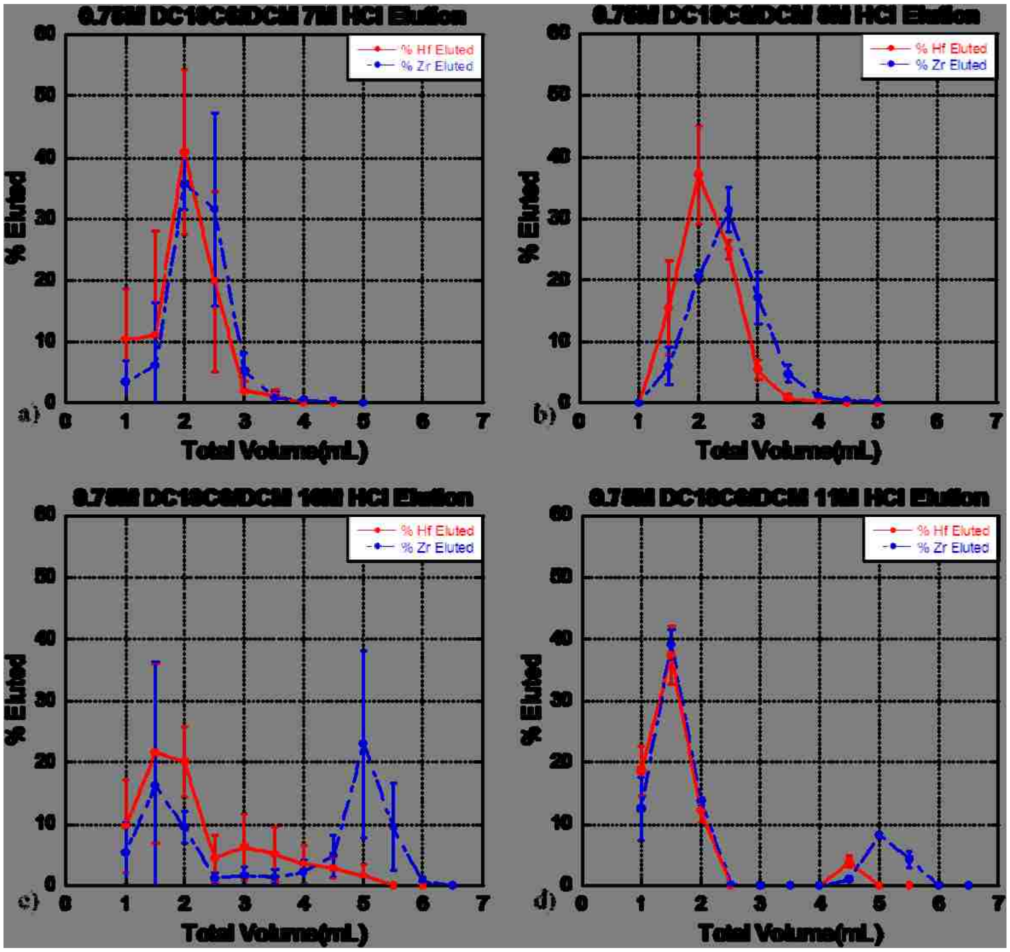

Figure 4.4. The elution profiles for the 0.75M DC18C6 resin prepared with dichloromethane. a) The elution profile for Hf and Zr using 7 and 3M HCl, respectively. b) The elution profile for Hf and Zr using 8 and 3M HCl, respectively. c) The elution profile for Hf and Zr using 10 and 3M HCl, respectively. d) The elution profile for Hf and Zr using 11 and 3M HCl, respectively. The values corresponding to each data point can be found in Appendix B Table 7.4, Table 7.5, Table 7.6and Table 7.7.

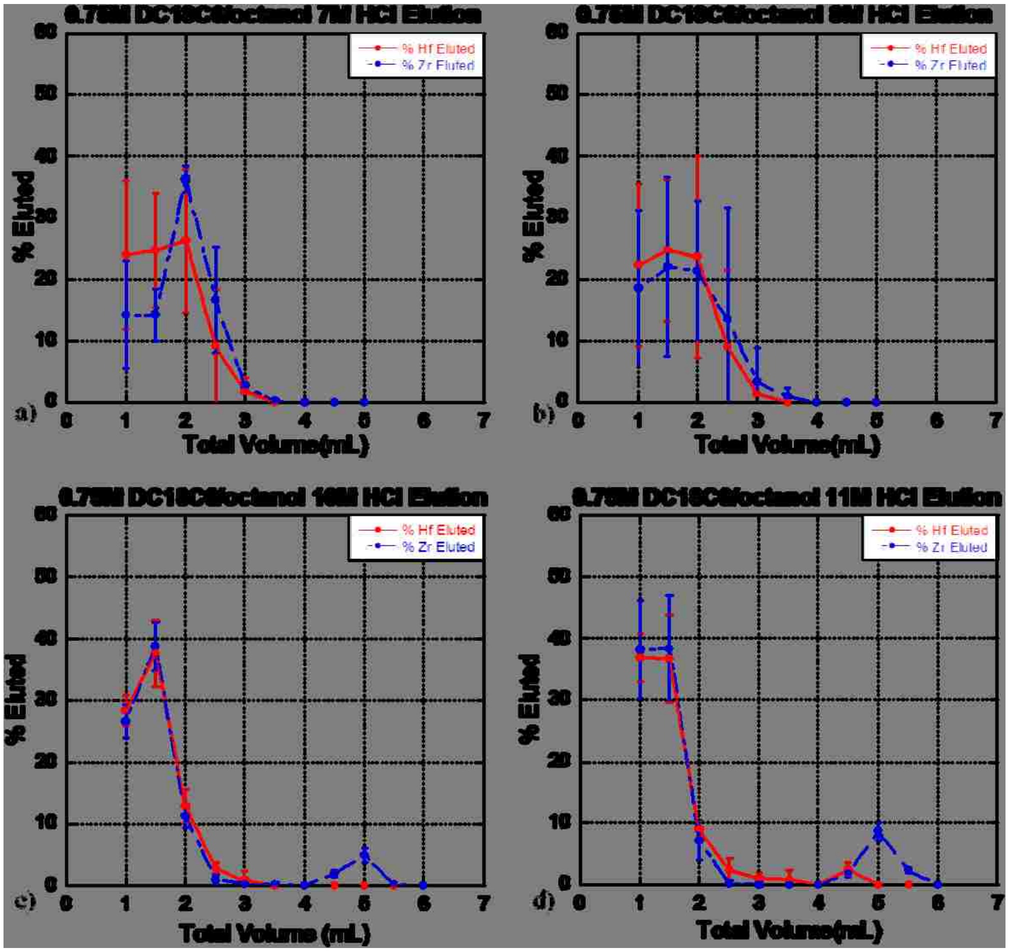

Figure 4.5. The elution profiles for the 0.75M DC18C6 resin prepared with 1-octanol. a) The elution profile for Hf and Zr using 7 and 3M HCl, respectively. b) The elution profile for Hf and Zr using 8 and 3M HCl, respectively. c) The elution profile for Hf and Zr using 10 and 3M HCl, respectively. d) The elution profile for Hf and Zr using 11 and 3M HCl, respectively. The values corresponding to each data point can be found in Appendix B Table 7.8, Table 7.9, Table 7.10 and Table 7.11.

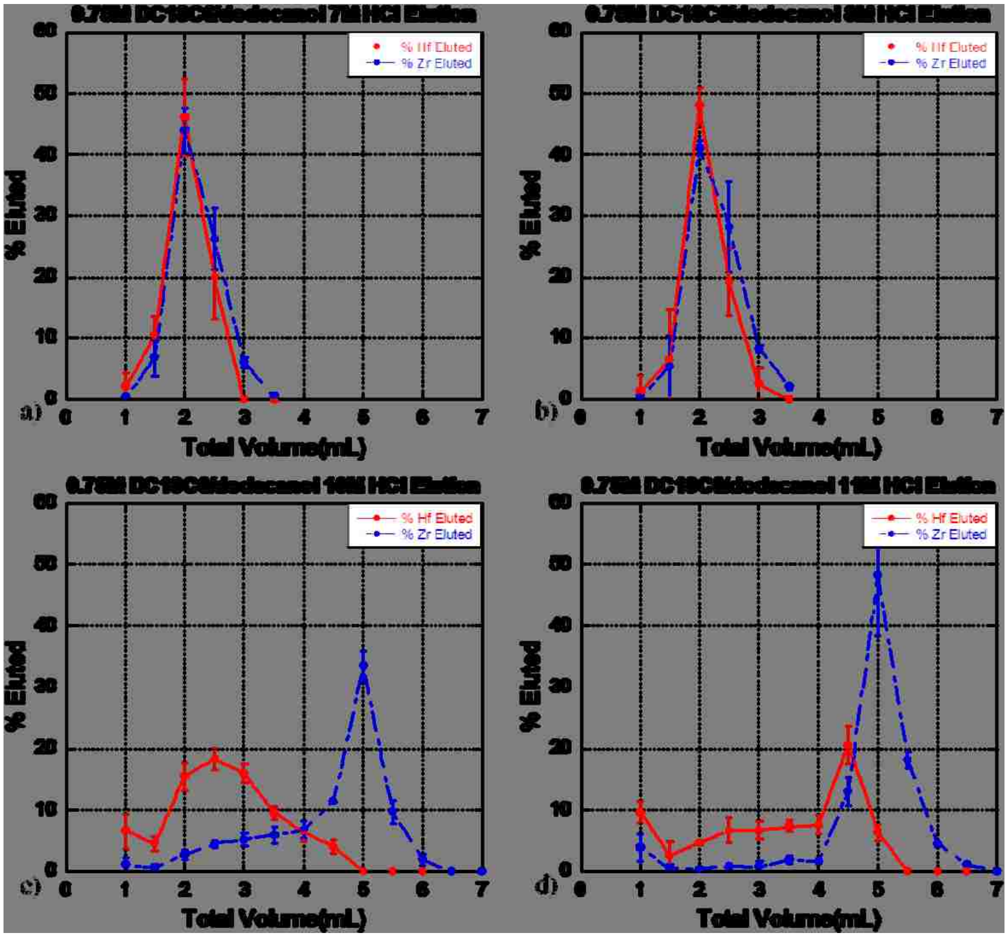

Figure 4.6. The elution profiles for the 0.75M DC18C6 resin prepared with 1-dodecanol. a) The elution profile for Hf and Zr using 7 and 3M HCl, respectively. b) The elution profile for Hf and Zr using 8 and 3M HCl, respectively. c) The elution profile for Hf and Zr using 10 and 3M HCl, respectively. d) The elution profile for Hf and Zr using 11 and 3M HCl, respectively. The values corresponding to each data point can be found in Appendix B Table 7.12, Table 7.13, Table 7.14 and Table 7.15.

4.1.1.2.2 Conclusions

Three resins containing 0.75M dicyclohexano-18-crown-6 synthesized with dichloromethane, 1-octanol and 1-dodecanol have been investigated to determine the influence the solvent has on the separation of Zr and Hf. It was expected, from batch studies that Hf would elute from the columns first, followed by Zr. The elution profiles for Hf were investigated at 7, 8, 10 and 11M HCl, while Zr was eluted from the column with 3M HCl. It was determined that none of the resin showed sufficient separation of Zr and Hf to be used to assess the chemical behavior of Rf compared to its lighter homologs.

4.1.2 Functional Group Effects

4.1.2.1 Batch Extractions

4.1.2.1.1 Results and Discussion

The results from the solvent effects study, discussed in section 4.1.1 showed that the solvent used in the synthesis of the resin has almost no effect on the separation of Zr and Hf. Based on this several functional groups off of the crown ether were investigated. The resins investigated for this study were a commercially available resin and two in-house resins synthesized with dichloromethane. The commercially available resin was Eichrom's Pb resin, which contains 0.75M di-t-butylcyclohexano-18-crown-6 coated with isodecanol. The in-house resins contained either 0.75M dicyclohexano-18-crown-6 (DC18C6) or 0.75M dibenzo-18-crown-6 (DB18C6). The differences in functional groups of the three resins investigated are shown in Figure 4.7. The results from the batch studies for all three resins are shown in Figure 4.8.

It is apparent from comparison of the three panels that Zr exhibits more uptake on all the resins. It is also apparent that, within error bars, Zr and Hf behave very similar on all the resins. On all three resins the uptake of Zr and Hf does not begin to exhibit differences in behavior until an acid concentration greater than 9M HCl are reached. This is of interest as the results of Sudowe et. al. indicate an increase of extraction of the $[MCl_6]^{2-}$ into the crown ether from the aqueous HCl phase beginning at 7M HCl and the extraction leveling off at 9.5M HCl. It has been reported that while solvent extraction and extraction chromatographic methods are not quantitatively the same they follow similar qualitative trends.[59] Based on this observation by Horwitz and co-workers, one would expect similar trends in the work presented here, however this is not the case. One possible explanation for this observation is that the crown ether molecules are not in close enough proximity to one another to form the necessary sandwich structure, shown in Figure 4.1, to extract Zr and Hf. The separation factors at each concentration for each acid are shown in Table 4.3. Based on these observations all three resins will be investigated under dynamic column conditions. In the case of Eichrom's Pb resin Hf elution conditions of 7, 8, 9 and 10M HCl will be investigated. In the case of the in-house synthesized resins Hf elution conditions of 7, 8, 10 and 11M HCl will be investigated. Zr elution conditions of 3M HCl will be used for all three resins.

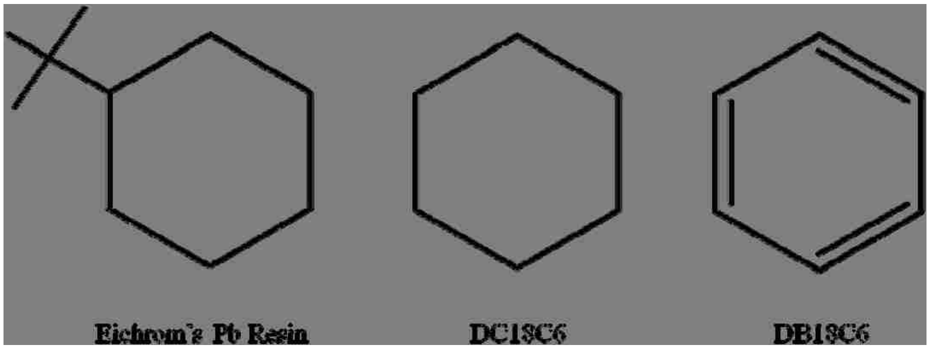

Figure 4.7. The functional groups attached to the 18-crown-6 ring.

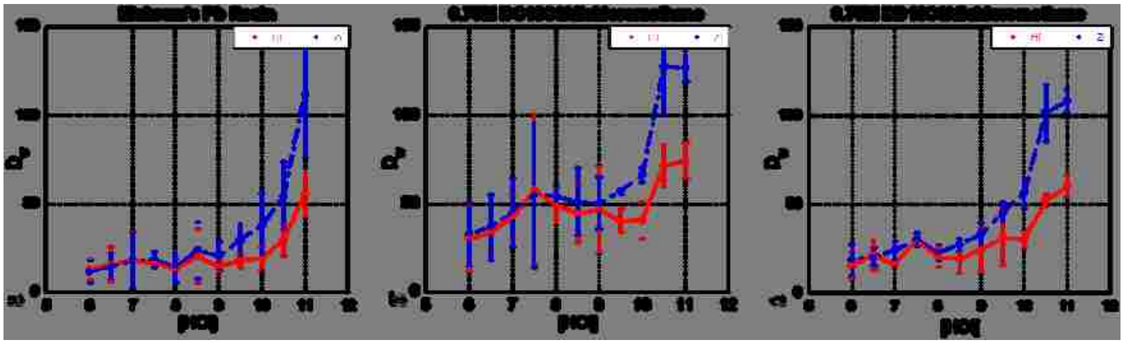

Figure 4.8. A side by side comparison of the results from the batch studies aimed at investigating the effect of functional groups on the separation of Zr and Hf. a) The separation behavior of Zr and Hf on Eichrom's Pb resin. b) The separation behavior of Zr and Hf on an in-house synthesized resin containing DC18C6. c) The separation behavior of Zr and Hf on an in-house synthesized resin containing DB18C6. The values for each data point can be found in Appendix B Table 7.16, Table 7.17 and Table 7.18.

Table 4.3. Separation factors for Zr and Hf under each acid condition for all three resins.

[HCl]	Eichrom's Pb Resin	DC18C6	DB18C6
6.0	0.89± 0.19	1.08 ± 0.13	1.02 ± 0.19
6.5	1.04± 0.21	1.03 ± 0.21	0.87 ± 0.16
7.0	0.98± 0.17	1.01 ± 0.11	0.88 ± 0.04
7.5	1.07± 0.23	0.96 ± 0.06	1.07 ± 0.14
8.0	1.02± 0.07	1.08 ± 0.08	1.05 ± 0.08
8.5	1.43± 0.61	1.09 ± 0.10	1.01 ± 0.14
9.0	1.26 ± 0.26	1.10 ± 0.15	1.06 ± 0.12
9.5	1.41± 0.13	1.25 ± 0.14	1.12 ± 0.07
10.0	1.45± 0.27	1.46 ± 0.10	1.26 ± 0.30
10.5	1.37± 0.04	1.28 ± 0.07	1.26 ± 0.11
11.0	1.40± 0.09	1.30 ± 0.07	1.18 ± 0.09

4.1.2.1.2 Conclusions

Three resins containing 0.75M di-t-butylcyclohexano-18crown-6, 0.75M dicyclohexano-18-crown-6 and 0.75M dibenzo-18-crown-6 have been investigated to determine the influence the functional group has on the separation of Zr and Hf and all three resins show promise for application to Rf chemistry. Based on the batch study results presented in Figure 4.8 and Table 4.3 the best potential for separation on a dynamic column would be shown by a load solution of 11M or concentrated HCl and elution of Hf in 10 to 11M HCl, as this is where the highest separation factors of Zr and Hf occur. However, the results of Sudowe and co-workers showed the best separation of Zr and Hf to occur between 7 and 8M HCl. Based on the results of the batch studies presented in Figure 4.8 and Table 4.3 of section 4.1.2.1.1 and the results of Sudowe et. al. the elution behavior of Hf at 7, 8, 9 and 10M HCl from a load solution of 11M HCl should be investigated for Eichrom's Pb resin and elution behavior of Hf at 7, 8, 10 and 11M HCl from a load solution of concentrated HCl should be investigated for the in-house synthesized resins. Zr elution off the columns should be investigated at 3M HCl. 3M HCl is chosen for two reasons. First, it is well known that the $[MCl_6]^{2-}$ species does not form below 6M HCl therefore there will be no extraction of Zr onto the crown ether resin. Second, below 3M HCl hydrolysis of Zr can occur, which may interfere with recovery of Zr during the separation.

4.1.2.2 Column Extractions

4.1.2.2.1 Results and Discussion

Samples containing ^{95}Zr and ^{175}Hf were evaporated to dryness and reconstituted in 1mL of reagent grade concentrated HCl. This prepared the samples to undergo separation by dynamic column studies. The three resins investigated in section 4.1.2.1 via batch studies were also investigated using dynamic column studies, according to the recommendations described in section 4.1.1.2.2.

Each resin was pre-treated with 5mL of concentrated HCl prior to loading the column with the 1mL solution containing the radionuclides of interest. The 1mL solution containing the radionuclides of interest was then loaded on the column. The various radionuclides were then eluted from the 0.75M crown ether of the form 18-crown-6 functionalized with di-t-butylcyclohexano-, dicyclohexano- or dibeno- groups column using 6 aliquots of 0.5mL (0.55, 0.88, 0.85 respectively) for both Hf and Zr. Based on the results of the batch study it was believed that Hf would elute of the column first, followed by Zr on all the resins. The results for Hf elutions at concentrations of 7, 8, 9 and 10M HCl for Eichrom's Pb resin are shown in Figure 4.9. Figure 4.9 a-d shows there is very little separation of Zr and Hf under any of the conditions investigated. However as one proceeds from a to d the Zr peaks does begin to slightly shift towards higher elution volumes but there is not a significant enough shift to conclude that Zr and Hf can ever be completely separated on Eichrom's Pb resin. For Eichrom's Pb resin at Hf elution conditions of 7M HCl 91±11% Hf and 89±47% of Zr elutes in the first 4mL . Under the conditions where 8M HCl is used to elute Hf 87±12% of Hf and 80±43% of Zr elutes in the first 4mL. When 9M HCl is used to elute Hf 82±9 of the Hf and 33±6% of the Zr elutes in the first 4mL. Finally, when 10M HCl is used to elute Hf 69±7% of the Hf and 31±7% of the Zr elutes in the first 4mL. This same conclusion can be drawn for the resins functionalized with dicyclohexano- and dibenzo- groups based on Figure 4.10 and Figure 4.11. For the DC18C6 resin synthesized with dichlormethane at Hf elution conditions of 7M HCl 86±27% Hf elutes in the first 4mL and 84±20.% of Zr elutes. Under the conditions where 8M HCl is used to elute Hf 88±11% of Hf and 82±7% of Zr elutes in the first 4mL. When 10M HCl is used to elute Hf 71±19 of the Hf and 37±21% of the Zr elutes in the first 4mL. Finally, when 11M HCl is used to elute Hf 68±6% of the Hf and 65±6% of the Zr elutes in the first 4mL. For the DB18C6 resin at Hf elution conditions of 7M HCl 77±21% Hf elutes in the first 4mL and 81±29% of Zr elutes. Under the conditions where 8M HCl is used to elute Hf 74±27% of Hf and 81±20% of Zr elutes in the first 4mL. When 10M HCl is used to elute Hf 74±4 of the Hf and 70±5% of the Zr elutes in the first 4mL. Finally, when 11M HCl is used to elute Hf 75±5% of the Hf and 64±5% of the Zr elutes in the first 4mL. If Zr and Hf cannot be separated from one another, as the case with the 0.75M DC18C6 resin functionalized with di-t-butylcyclohexano-, dicyclohexano- or dibenzo- groups then no assessment of the behavior of Rf with respect to Zr and Hf can be made.

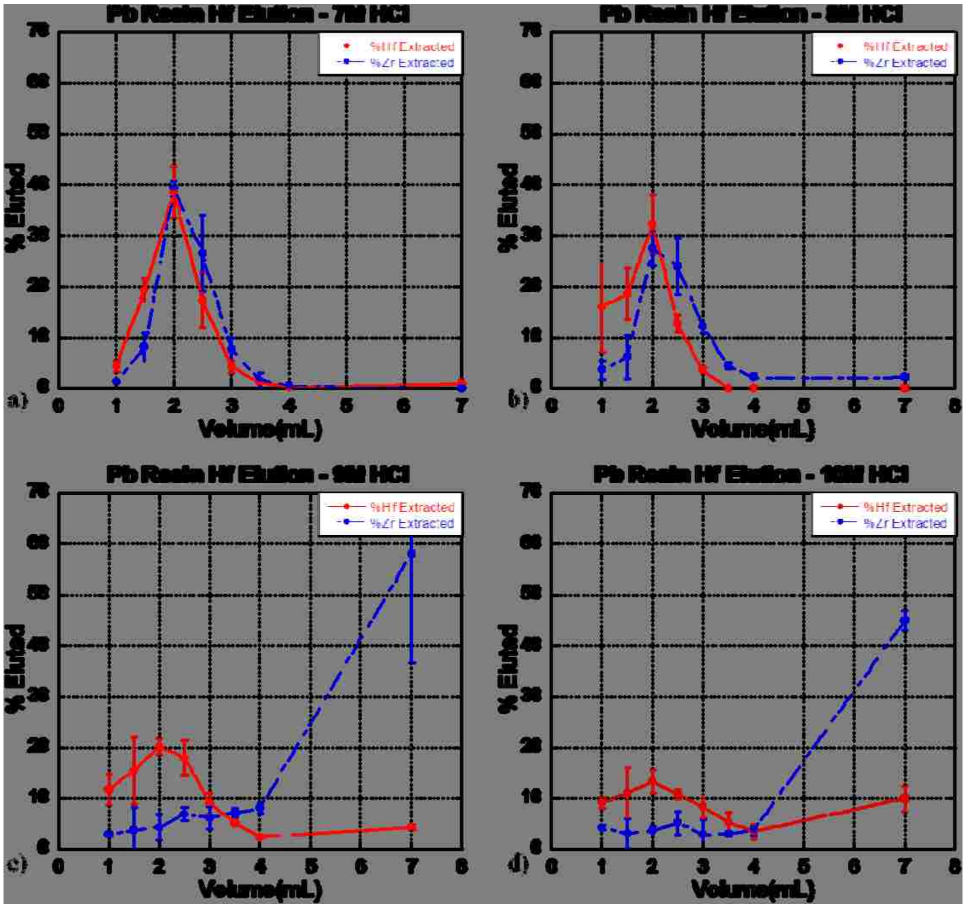

Figure 4.9. The elution profiles for Eichrom's Pb resin. a) The elution profile for Hf and Zr using 7 and 3M HCl, respectively. b) The elution profile for Hf and Zr using 8 and 3M HCl, respectively. c) The elution profile for Hf and Zr using 9 and 3M HCl, respectively. d) The elution profile for Hf and Zr using 10 and 3M HCl, respectively. The values corresponding to each data point can be found in Appendix B Table 7.19, Table 7.20, Table 7.21 and Table 7.22.

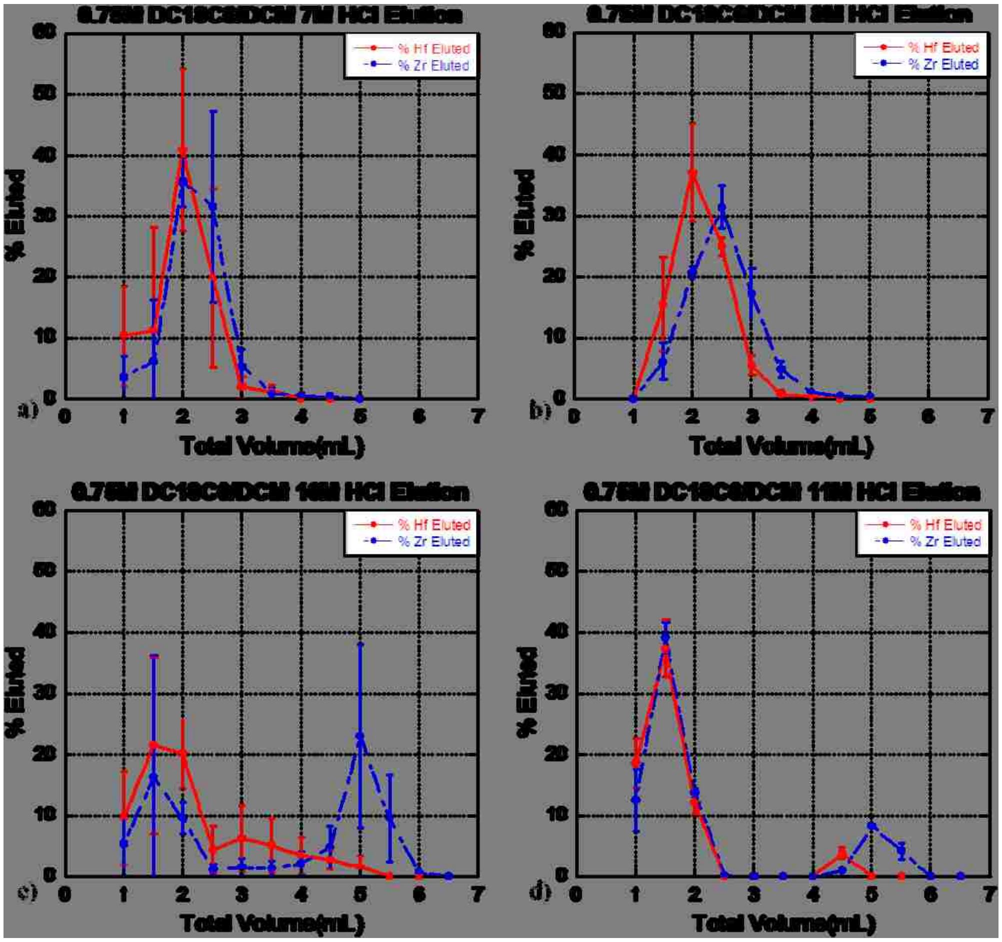

Figure 4.10. The elution profiles for the in-house DC18C6 resin. a) The elution profile for Hf and Zr using 7 and 3M HCl, respectively. b) The elution profile for Hf and Zr using 8 and 3M HCl, respectively. c) The elution profile for Hf and Zr using 10 and 3M HCl, respectively. d) The elution profile for Hf and Zr using 11 and 3M HCl, respectively. The values corresponding to each data point can be found in Appendix B Table 7.4, Table 7.5, Table 7.6 and Table 7.7.

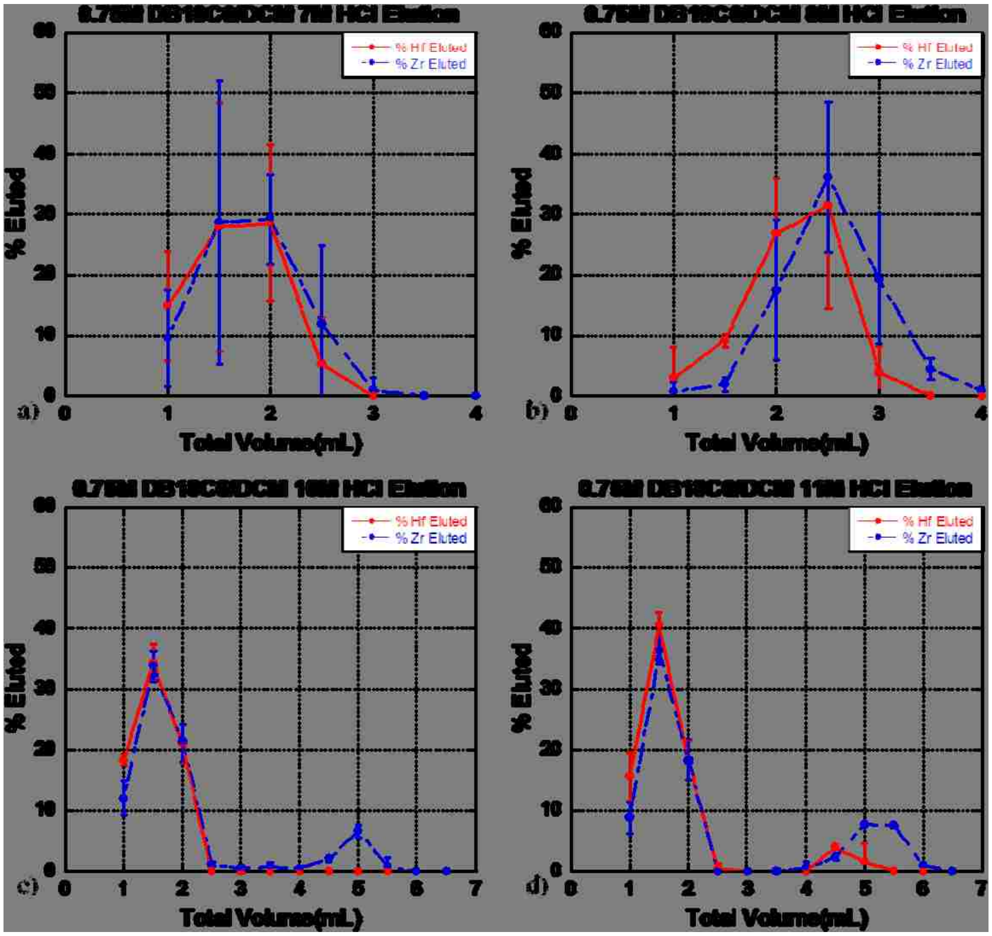

Figure 4.11. The elution profiles for the in-house DB18C6 resin. a) The elution profile for Hf and Zr using 7 and 3M HCl, respectively. b) The elution profile for Hf and Zr using 8 and 3M HCl, respectively. c) The elution profile for Hf and Zr using 10 and 3M HCl, respectively. d) The elution profile for Hf and Zr using 11 and 3M HCl, respectively. The values corresponding to each data point can be found in Appendix B Table 7.23, Table 7.24, Table 7.25 and Table 7.26

The elution profiles, shown in Figure 4.9, Figure 4.10 and Figure 4.11, under the same conditions for each resin, synthesized with various solvents, can be compared directly. If this is done for the 7M HCl elution profile, then Zr and Hf are shown to have very similar elution profiles, they both have the highest % elution, approximately 35%, at 2mL. When the elution profiles under the 8M HCl conditions are compared, Hf and Zr exhibit similar elution profiles and quantities. Hf and Zr peak at 2 to 2.5mL. The slight difference in elution profile and quantity can be best explained by experimental error. A comparison of the elution profiles under 10M HCl conditions shows that while Zr and Hf initially have similar elution profiles, some Zr is being bound more tightly on the resin and eluting at higher volumes, however is effect is not dominate enough to fully separate Zr from Hf. This separation is more enhanced for Eichrom's Pb resin; however there is still not sufficient separation of Zr and Hf for transactinide applications. The same conclusion that is drawn for the 10M HCl elution profiles can also be applied to the 11M HCl elution profiles.

4.1.2.2.2 Conclusions

Three resins containing 0.75M di-t-butylcyclohexano-18crown-6, 0.75M dicyclohexano-18-crown-6 and 0.75M dibenzo-18-crown-6 have been investigated to determine the influence the functional group has on the separation of Zr and Hf and none of the resin show promise for application to Rf chemistry. It was expected, from batch studies that Hf would elute from the columns first. The elution profiles for Hf were investigated at 7, 8, 9 and 10M HCl for Eichrom's Pb resin and at 7, 8, 10 and 11M HCl for the in-house resin, while Zr was eluted from the column with 3M HCl. It was determined that none of the resin showed sufficient separation of Zr and Hf to be used to assess the chemical behavior of Rf compared to its lighter homologs.

4.1.3 Concentration Effect Studies

4.1.3.1 Batch Extractions

4.1.3.1.1 Results and Discussion

It has previously been shown (section 4.1.1) that the solvent used in the resin synthesis has no effect on the chemical separation of Zr and Hf. It was also shown (section 4.1.2) that the functional group on the 18-crown-6 has no effect on the chemical separation of Zr and Hf. Based on these results the effect of concentration of the crown ether extraction was investigated using two commercially available resins from Eichrom, the Pb and Sr resin. The specifications of each resin are shown in Table 4.4.

Table 4.4. The specification of Eichrom's Pb and Sr resins.

Specification	Pb Resin	Sr Resin
[Crown Ether]	0.75	1.0
Solvent	Isodecanol	1-Octanol

The effect of increased d-t-butylcyclohexano-18-crown-6 was investigated over a range of concentrations of HCl from 6 to 11M. The results of these batch studies are shown in Figure 4.12. It can be seen from Figure 4.12 that both Zr and Hf have a higher uptake on Eichrom's Sr resin compared to the Pb resin. This indicates that as concentration of the extractant increases there is an increased potential for Hf and Zr separation. The separation factors for each resin at the various HCl concentrations can be found in Table 4.4. Based on the separation factors the columns would be best loaded in 11M HCl, Hf eluted by 10M HCl followed by elution of Zr in 3M HCl.

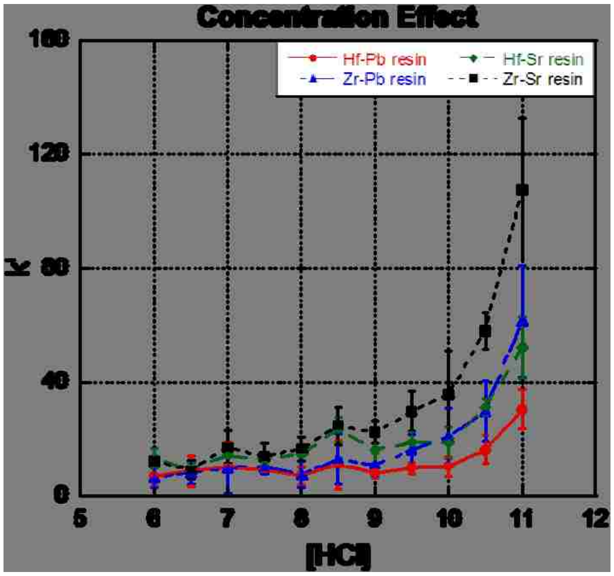

Figure 4.12. Uptake of Zr and Hf in batch studies for commercially available resins. The values of each data point can be found in Appendix B Table 7.27 and Table 7.28.

Table 4.5. The separation factors at various HCl concentrations for Eichrom's Pb and Sr resins.

[HCl]	Eichrom's Pb Resin	Eichrom's Sr Resin
6.0	0.89± 0.19	0.9 ± 0.09
6.5	1.04± 0.21	0.96 ± 0.13
7.0	0.98± 0.17	1.11 ± 0.10
7.5	1.07± 0.23	1.03 ± 0.19
8.0	1.02± 0.07	1.07 ± 0.14
8.5	1.43± 0.61	1.03 ± 0.05
9.0	1.26 ± 0.26	1.22 ± 0.10
9.5	1.41± 0.13	1.27 ± 0.07
10.0	1.45± 0.27	1.32 ± 0.08
10.5	1.37± 0.04	1.22 ± 0.03
11.0	1.40± 0.09	1.25 ± 0.03

4.1.3.1.2 Conclusions

Two resins containing 0.75M di-t-butylcyclohexano-18crown-6 at various concentrations have been investigated to determine the influence of extractant concentration on the separation of Zr and Hf. It appears that concentration has no effect on the separation of Zr and Hf, making both resins potentially useful for Rf chemistry. Based on the batch study results presented in Figure 4.11 and Table 4.4 the best potential for separation on a dynamic column would be shown by a combination of a load solution of 11M, followed by an elution of Hf in 10 M HCl, as this is where the highest separation factors of Zr and Hf occur. Zr elution off the columns should be investigated at 3M HCl. 3M HCl is chosen for two reasons. First, it is well known that the $[MCl_6]^{2-}$ species does not form below 6M HCl therefore there will be no extraction of Zr onto the crown ether resin. Second, below 3M HCl hydrolysis of Zr can occur, which may interfere with recovery of Zr during the separation.

4.1.3.2. Column Extractions

4.1.3.2.1 Results and Discussion

Samples containing ^{95}Zr and ^{175}Hf were evaporated to dryness and reconstituted in 1mL of reagent grade concentrated HCl. This prepared the samples to undergo separation by dynamic column studies. The two resins investigated in section 4.1.3.1 described in batch studies were also investigated using dynamic column studies, according to the recommendations described in section 4.1.3.1.2.

Each resin was pre-treated with 5mL of concentrated HCl prior to loading the column with the 1mL solution containing the radionuclides of interest. The 1mL solution containing the radionuclides of interest was then loaded on the column. The various radionuclides were eluted from the di-t-butylcyclohexano-18-crown-6 columns using 6 aliquots of 0.5mL for both Hf and Zr. Based on the results of the batch study it was believed that Hf would elute of the column first, followed by Zr on all the resins. The results for Hf elutions at 10M HCl for Eichrom’s Pb and Sr resins are shown in Figure

4.13. Figure 4.13 shows that Eichrom's Pb and Sr show nearly identical elution behavior for both Zr and Hf, despite the results of batch study, which indicated the Sr resin had a higher retention of Zr and Hf. This is interesting as the results of Sudowe et. al. indicate an increase of extraction of the $[MCl_6]^{2-}$ into the crown ether as the concentration of the crown ether extractant is increased. It has been reported that while solvent extraction and extraction chromatographic methods are not quantitatively the same they follow similar qualitative trends.[59] Based on this observation by Horwitz and co-workers one would expect similar trends in the work presented here, however this is not the case. One possible explanation for this observation is that the crown ether molecules are not in close enough proximity to one another to form the necessary sandwich structure, shown in Figure 4.1, to extract Zr and Hf. In a solvent extraction system, as the one investigated by Sudowe et. al. the extractant molecule can freely move about in the organic phase, this allows for two crown ether molecules to come together to form the necessary sandwich complex around the dianionic hexachloro complex and allow for the extraction of the metal complex. In a resin based system, such as the one used here, the crown ether is physi-sorbed to the inert support and does not have the ability to move freely. The inability of the crown ether to move freely may cause difficulty in formation of the sandwich complex, if the concentration of the extractant is not high enough, and thus hinder extraction of the metal ion.

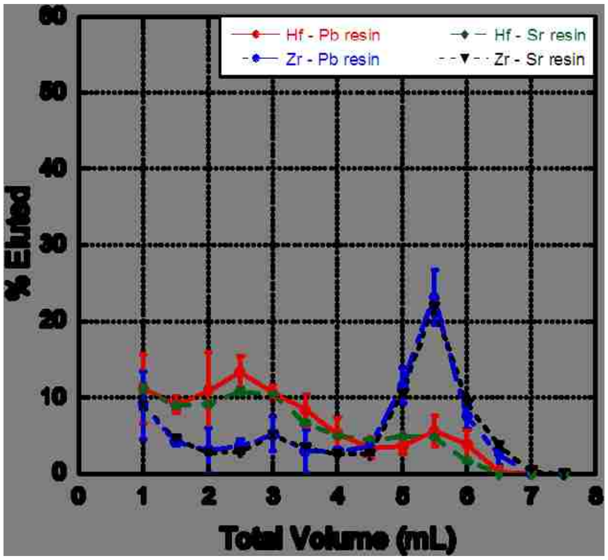

Figure 4.13. Elution profiles of Zr and Hf on Eichrom's Pb and Sr resins. The value of every data point can be found in Appendix B in Table 7.22 and Table 7.29.

4.1.3.2.2 Conclusions

Two resins containing 0.75M di-t-butylcyclohexano-18-crown-6 at different concentration have been investigated to determine the influence of the concentration of the crown ether extractant has on the separation of Zr and Hf. Neither resin showed adequate separation of Zr and Hf to be usefully in chemical investigations of Rf. It was expected, from batch studies that Zr and Hf would have higher retention on Eichrom's Sr resin and eluted at higher volumes. It was also expected that Hf would elute from the columns first, followed by Zr. The elution profiles for Hf were investigated at 10M HCl, while Zr was eluted from the column with 3M HCl. It was determined that neither of the resin showed sufficient separation of Zr and Hf to be used to assess the chemical behavior of Rf compared to its lighter homologs.

4.1.4 Future Work

Based on the results presented above, it is evident that the various prepared 18-crown-6 extractant molecules are ineffective at separating Zr and Hf under the current conditions. It is recommended that a resin of dicyclohexano-18-crown 6 is synthesized at much higher concentration and a batch study be conducted. A higher concentration of crown ether on the resin may have a better chance of having two crown ether molecules close enough in proximity to one another to form the necessary sandwich complex and cause enhanced extraction and separation of Zr and Hf. Once the batch study is conducted, a dynamic column study investigating the elution profile of Hf can be investigated at 7, 8, 10 and 11M HCl from a concentrated HCl load solution.

CHAPTER 5

CONCLUSIONS

Seven different chemical systems based on two different extractant molecules have been investigated to determine their suitability for use with the transactinide elements Rf and Db. The separation system aimed at the chemical characterization of Db utilized Eichrom's DGA resin. The active extractant molecule on the DGA resin is N,N, N',N'-tetra-n-dioctylglycolamide. It was determined that the DGA resin can be utilized for the separation of Group IV, V and actinide elements. A more detailed conclusion of these results can be found in section 5.1.

Six of the systems investigated utilized crown ether based extractants and were aimed at the chemical characterization of Rf. The crown ether based resins were all based off of an 18-crown-6 structure with various solvents, functional groups and concentrations. The solvent investigation yielded the conclusion that the solvent used to synthesize the resin has little impact on the separation behavior of Zr and Hf. The functional group study showed that the functionalization of the crown also has little impact on the separation of Zr and Hf. Finally, concentration of the crown ether was investigated and it was determined that while the uptake behavior of Zr and Hf appear to be concentration dependent in batch studies, this is not the case in dynamic column studies. Overall, it was concluded that none of the investigated crown ether based resins exhibited sufficient separation of Zr and Hf to be deployable in the chemical characterization of Rf. A more detailed conclusion of these results can be found in section 5.2.

5.1 DGA System

Based on the batch studies using Eichrom's DGA resin it was determined that the samples needed to undergo a reconstitution and evaporation step in 2mLof 6M HCl/8M HF. Following this the samples needed to be reconstituted and evaporated in 2mL of concentrated HNO_3 to dissolve the fluoride precipitates. The samples were then loaded on to the column from a 1mL of 10M HNO_3/0.1M HF solution to ensure that Ta did not sorb to the centrifuge tube and was quantitatively loaded onto the column, while ensuring the other radionuclides present in the system would sorb to the DGA column. A elution scheme for column studies was developed, as shown in Table 5.1. Once this elution scheme had been developed, dynamic column studies were conducted to determine if Group IV, Group V and actinide elements could be separated. It has been determined in batch and column studies of homologs and pseudo-homologs that the presence of HCl is necessary in order to have consistent loading of Ta onto the column. It has also been shown that Nb and Pa have similar elution curves and are inseparable under current conditions. Eichrom's DGA resin presents a viable chemical system for the study of the chemical behavior of dubnium, if conditions presented in Table 5.1 are followed. It was also determined that the DGA extractant molecule does not bleed from the resin over the course of 77 days the DGA extractant molecule did not detectably bleed from the resin in solutions of 2M HNO_3, 10M HNO_3 of 10M HNO_3/1M HF in the form of the naked extractant, mononitrato complex, nitric acid adduct, protonated or deprotanated species, as determined using Electrospray-mass spectrometry.

Based on the stability of the resin, batch and dynamic column studies on-line homolog studies should be conducted. If the on-line experiments continue to show promise for the separation of Zr, Hf, Nb, Ta, Pa and Am short- and long-lived Db experiments should be conducted to determine which homolog or pseudo-homolog Db is chemically similar too.

Table 5.1. Elution conditions chosen for column studies based on the results of the batch studies. Using a 2 mL pre-packed DGA column. The nuclide that is expected to elute is shown in parentheses.

Fraction	Elution Conditions
Fraction 1 (Nb)	2mL 4M HNO_3/0.001M HF
Fraction 2 (Pa)	5mL 4M HNO_3/0.001M HF
Fraction 3 (Zr, Hf)	2x5mL 0.4M HNO_3/0.02M HF
Fraction 4 (Ta)	3x5mL 8M HNO_3/1M HF
Fraction 5 (Am)	2x5ml 0.1M HCl or 15 mL 0.1M ammonium bioxalate

5.2 Crown Ether Based Systems

5.2.1 Solvent Effect Studies

Resins containing 0.75M dicyclohexano-18-crown-6 synthesized with dichloromethane, 1-octanol or 1-dodecanol were investigated to determine the effect the solvent had on separations of Zr and Hf. Batch study results indicated there was little difference in uptake of Zr and Hf on the resins synthesized with different solvents. There was an indication that the best potential for separation on a dynamic column would be from a load solution of concentrated HCl followed by elution of Hf in acidconcentrations between 10 and 11M HCl, as this was where the highest separation factors of Zr and Hf were found. However, the results of Sudowe and co-workers showed the best separation of Zr and Hf to occur between 7 and 8M HCl. Based on the results of the batch studies and the results of Sudowe et. al. the elution behavior of Hf at 7, 8, 10 and 11M HCl was investigated, while Zr elution off the column was investigated at 3M HCl.

It was expected, from batch studies that Hf would elute from the columns first, followed by Zr. The elution profiles for Hf were investigated at 7, 8, 10 and 11M HCl, while Zr was eluted from the column with 3M HCl. It was determined that none of the resin showed sufficient separation of Zr and Hf to be used to assess the chemical behavior of Rf compared to its lighter homologs.

5.2.2 Functional Group Effect Studies

Three resins containing 0.75M di-t-butylcyclohexano-18crown-6, 0.75M dicyclohexano-18-crown-6 and 0.75M dibenzo-18-crown-6 have been investigated to determine the influence the functional group has on the separation of Zr and Hf. Based on the batch study results the best potential for separation on a dynamic column should be obtained by a load solution of 11M or concentrated HCl and elution of Hf in 10 to 11M HCl, as this is where the highest separation factors of Zr and Hf occurred. However, the results of Sudowe and co-workers showed the best separation of Zr and Hf to occur between 7 and 8M HCl. Based on the results of the batch studies and the results of Sudowe et. al. the elution behavior of Hf at 7, 8, 9 and 10M HCl from a load solution of 11M HCl was investigated for Eichrom's Pb resin and elution behavior of Hf at 7, 8, 10 and 11M HCl from a load solution of concentrated HCl was investigated for the in-house synthesized resins. Zr elution off the columns was investigated at 3M HCl.

It was expected, from batch studies that Hf would elute from the columns first, followed by Zr. The elution profiles for Hf were investigated at 7, 8, 9 and 10M HCl for Eichrom's Pb resin and at 7, 8, 10 and 11M HCl for the in-house resin, while Zr was eluted from the column with 3M HCl. It was determined that none of the resin showed sufficient separation of Zr and Hf to be used to assess the chemical behavior of Rf compared to its lighter homologs.

5.2.3 Concentration Effect Studies

Two resins containing di-t-butylcyclohexano-18crown-6 at concentrations of 0.75 and 1.0M have been investigated to determine the influence of extractant concentration on the separation of Zr and Hf. Based on the batch study results a combination of a load solution of 11M and elution of Hf in 10 M HCl should show the best potential for separation on a dynamic column was from, as this is where the highest separation factors of Zr and Hf were measured. Zr elution off the columns was investigated at 3M HCl.

It was expected, from batch studies that Zr and Hf would have higher retention on Eichrom's Sr resin and eluted at higher volumes. It was also expected that Hf would elute from the columns first, followed by Zr. The elution profiles for Hf were investigated at 10M HCl, while Zr was eluted from the column with 3M HCl. It was determined that neither of the resin showed sufficient separation of Zr and Hf to be used to assess the chemical behavior of Rf compared to its lighter homologs.

APPENDIX A

DGA DATA

Table 6.1 The values of each data point at various [HNO_3]/0.002M HF that correspond to Figure 3.1.

[HNO_3]	Average k' Zr	stdev	Average k' Nb	stdev
0.1	403.74	591.47	215.77	268.73
0.3	142.25	72.12	111.12	69.32
0.6	255.46	297.94	51.70	12.61
0.8	206.63	174.09	80.78	15.79
1	32.61	69.34	66.32	21.40
3	857.35	693.31	63.63	22.38
6	939.90	1237.18	133.56	53.01
8	399.20	465.74	208.38	219.88

Table 6.2. The values of each data point at various [HNO_3]/0.02M HF that correspond to Figure 3.2 and Figure 3.3.

[HNO_3]	Average k' Zr	stdev	Average k' Nb	stdev
0.1	117.02	61.12	114.59	70.12
0.3	157.87	71.39	146.04	84.02
0.6	85.40	7.42	78.16	6.08
0.8	76.57	7.64	59.41	16.42
1	92.09	25.29	70.64	22.80
3	454.44	194.10	64.32	11.60
6	1583.20	55.44	74.74	3.92
8	808.36	98.81	92.28	11.57

Table 6.3. The values of each data point at various [HNO_3]/0.1M HF that correspond to Figure 3.2 and Figure 3.3.

[HNO_3]	Average k' Zr	stdev	Average k' Nb	stdev
0.1	97.40	-	79.25	-
0.3	80.18	-	71.30	-
0.6	67.00	-	53.18	-
0.8	83.92	-	62.53	-
1	87.09	-	76.05	-
3	249.78	-	89.35	-
6	733.69	-	66.70	-
8	442.00	-	62.01	-

Table 6.4. The values of each data point at 4M HNO_3/various HF that corresponds to Figure 3.11.

[HF]	% Ta Lost	stdev
0	75.58	19.43
0.001	93.46	3.01
0.01	70.84	24.65
0.05	74.60	2.89
0.1	75.00	7.94
0.2	65.00	14.20
0.5	39.77	19.13
0.5	24.59	10.81
1	32.08	18.50

Table 6.5. The values of each data point at 6M HCl/various HF that corresponds to Figure 3.12.

[HF]	% Ta Lost	stdev
4.0	75.58	18.37
4.5	93.46	15.95
5.0	70.84	9.86
5.5	74.60	22.50
6.0	75.00	9.84
6.5	65.00	12.55
7.0	39.77	12.30
7.5	24.59	13.75
8.0	32.08	7.66

Table 6.6. The values of each data point at 6M HCl/various HF that corresponds to Figure 3.13

Fraction	% Zr Eluted	%Nb Eluted	%Hf Eluted	%Ta Eluted	% Pa Eluted	% Np Eluted	% Am Eluted
Load +Nb	0.00	142.41	38.53	4.66	141.06	0.00	0.00
Pa	11.11	1.12	65.30	8.69	16.77	22.68	0.00
Ta – 1	99.30	1.83	68.98	63.81	0.34	4.81	0.00
Ta – 2	21.93	0.21	7.14	53.27	0.00	0.00	0.00
Ta – 3	9.68	0.03	6.06	6.32	0.00	0.00	0.00
Am – 1	3.82	0.00	5.99	1.44	1.71	18.18	65.98
Am – 2	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 6.7. The error in the values of each data point at 6M HCl/various HF that corresponds to Figure 3.13.

Fraction	% Zr Error	%Nb Error	%Hf Error	%Ta Error	% Pa Error	%Np Error	% Am Error
Load +Nb	0.05	0.14	0.05	0.03	0.07	0.04	0.02
Pa	0.05	0.09	0.05	0.03	0.05	0.05	0.02
Ta – 1	0.07	0.09	0.05	0.04	0.05	0.05	0.02
Ta – 2	0.06	0.09	0.05	0.04	0.05	0.04	0.02
Ta – 3	0.05	0.09	0.05	0.03	0.05	0.04	0.02
Am – 1	0.05	0.09	0.05	0.03	0.05	0.04	0.03
Am – 2	0.05	0.09	0.05	0.03	0.05	0.04	0.02

Table 6.8. The values of each data point at 6M HCl/various HF that corresponds to Figure 3.14.

Fraction	% Zr Eluted	%Nb Eluted	%Hf Eluted	%Ta Eluted	% Pa Eluted	% Np Eluted	% Am Eluted
Load +Nb	0.94	79.76	84.12	6.05	72.52	3.44	27.37
Pa – 1	44.15	2.19	56.89	5.74	18.06	25.56	0.00
Pa – 2	14.61	0.38	0.00	0.00	2.16	24.51	0.00
Pa – 3	5.10	0.09	0.00	0.00	0.00	14.80	0.00
Ta – 1	5.98	0.85	0.00	31.25	0.00	0.00	0.00
Ta – 2	5.25	0.24	0.00	34.40	0.00	0.00	0.00
Ta – 3	3.49	0.16	0.00	10.55	0.00	0.00	0.00
Am – 1	1.90	0.00	0.00	2.38	0.51	7.62	74.30

Table 6.9. The error in the values of each data point at 6M HCl/various HF that corresponds to Figure 3.14.

Fraction	% Zr Error	%Nb Error	%Hf Error	%Ta Error	% Pa Error	%Np Error	% Am Error
Load +Nb	0.06	0.15	0.04	0.04	0.11	0.04	0.04
Pa – 1	0.07	0.11	0.05	0.04	0.10	0.04	0.03
Pa – 2	0.06	0.11	0.04	0.04	0.10	0.04	0.03
Pa – 3	0.06	0.11	0.04	0.04	0.09	0.03	0.03
Ta – 1	0.06	0.11	0.04	0.04	0.09	0.03	0.03
Ta – 2	0.06	0.11	0.04	0.05	0.09	0.03	0.03
Ta – 3	0.06	0.11	0.04	0.04	0.09	0.03	0.03
Am – 1	0.06	0.11	0.04	0.04	0.10	0.03	0.03

Table 6.10. The % lost values of each data point at correspond to Figure 3.15

Fraction	% Zr	%Nb	%Hf	%Ta	% Pa	%Np	% Am
Load Tube	4.21	4.40	3.96	4.38	3.27	0.42	0.00
Error	0.06	0.11	0.05	0.04	0.04	0.05	0.02

Table 6.11. The values of each data point that correspond to Figure 3.16.

Fraction	% Zr Eluted	%Nb Eluted	%Hf Eluted	%Ta Eluted	% Pa Eluted	% Np Eluted	% Am Eluted
Load	2.54	37.22	0.00	0.86	30.02	16.88	0.00
Nb	1.77	52.39	0.00	7.13	54.84	8.02	5.88
Pa – 1	47.65	0.91	72.41	9.54	6.17	0.00	0.00
Pa – 2	6.68	0.15	3.52	0.03	1.69	4.01	0.00
Ta – 1	5.57	0.24	2.08	44.40	0.00	28.06	9.80
Ta – 2	6.41	0.03	2.33	27.12	0.00	13.71	15.03
Ta – 3	4.23	0.06	2.13	6.70	0.24	7.59	7.84
Am – 1	3.01	0.02	2.43	1.01	0.00	2.74	60.78

Table 6.12. The error in the values of each data point that correspond to Figure 3.16.

Fraction	% Zr Error	%Nb Error	%Hf Error	%Ta Error	% Pa Error	%Np Error	% Am Error
Load	0.06	0.12	0.05	0.04	0.04	0.05	0.02
Nb	0.06	0.13	0.05	0.04	0.05	0.05	0.02
Pa – 1	0.07	0.10	0.05	0.04	0.04	0.05	0.02
Pa – 2	0.06	0.10	0.05	0.04	0.04	0.05	0.02
Ta – 1	0.06	0.10	0.05	0.04	0.04	0.05	0.02
Ta – 2	0.06	0.10	0.05	0.04	0.04	0.05	0.02
Ta – 3	0.06	0.10	0.05	0.04	0.04	0.05	0.02
Am – 1	0.06	0.10	0.05	0.04	0.04	0.05	0.02

Table 6.13. The values of each data point that correspond to Figure 3.17.

Fraction	% Zr Eluted	%Nb Eluted	%Hf Eluted	%Ta Eluted	% Pa Eluted	% Np Eluted	% Am Eluted
Load	0.66	33.72	1.19	1.34	18.81	0.00	0.00
Nb	0.87	57.62	0.21	13.76	48.99	10.96	9.50
Pa – 1	50.78	3.02	73.64	8.52	11.16	21.92	3.00
Pa – 2	10.51	0.32	4.75	0.73	0.00	15.98	1.50
Pa – 3	3.32	0.07	1.09	0.27	2.55	0.00	2.50
Ta – 1	2.92	0.18	0.67	45.67	0.85	31.51	0.00
Ta – 2	4.18	0.04	0.47	34.04	2.44	25.11	0.00
Ta – 3	4.27	0.11	2.64	7.44	2.02	11.87	4.50
Am – 1	1.79	0.07	0.05	1.29	0.64	10.50	26.50
Am – 2	0.99	0.01	0.47	1.07	0.00	0.00	56.00
Am – 3	0.35	0.00	0.00	0.70	0.43	1.83	0.00

Table 6.14. The error in the values of each data point that correspond to Figure 3.17.

Fraction	% Zr Error	%Nb Error	%Hf Error	%Ta Error	% Pa Error	%Np Error	% Am Error
Load	0.06	0.12	0.05	0.04	0.04	0.05	0.02
Nb	0.06	0.12	0.05	0.04	0.05	0.05	0.02
Pa – 1	0.07	0.10	0.05	0.04	0.04	0.05	0.02
Pa – 2	0.06	0.10	0.04	0.04	0.04	0.05	0.02
Pa – 3	0.06	0.10	0.04	0.04	0.04	0.05	0.02
Ta – 1	0.06	0.10	0.04	0.04	0.04	0.05	0.02
Ta – 2	0.06	0.10	0.04	0.04	0.04	0.05	0.02
Ta – 3	0.06	0.10	0.04	0.04	0.04	0.05	0.02
Am – 1	0.06	0.10	0.04	0.04	0.04	0.05	0.02
Am – 2	0.06	0.10	0.04	0.04	0.04	0.05	0.02
Am – 3	0.06	0.10	0.04	0.04	0.04	0.05	0.02

APPENDIX B

CROWN ETHER DATA

Table 7.1 The values of each data point that correspond to Figure 4.3 and the resin synthesized with dichloromethane.

[HCl]	Average D_w Hf	stdev	Average D_w Zr	stdev
6	30.49	18.48	32.90	18.48
6.5	33.78	11.59	36.85	18.72
7	42.54	12.98	44.84	19.41
7.5	58.13	42.38	55.26	41.11
8	49.30	10.04	54.52	5.49
8.5	44.65	16.27	51.07	19.19
9	47.00	24.66	50.30	14.90
9.5	40.46	6.70	57.18	1.53
10	40.67	10.29	66.30	3.88
10.5	71.62	11.83	127.61	27.21
11	74.47	10.22	127.08	7.78

Table 7.2. The values of each data point that correspond to Figure 4.3 and the resin synthesized with 1-octanol.

[HCl]	Average D_w Hf	stdev	Average D_w Zr	stdev
6	33.39	9.12	32.83	8.22
6.5	27.00	9.98	26.21	9.11
7	25.47	3.21	26.50	2.66
7.5	24.56	4.37	24.80	3.51
8	27.81	1.57	20.48	13.37
8.5	28.61	11.48	31.05	8.04
9	22.98	13.19	34.29	13.83
9.5	36.10	10.71	46.49	5.44
10	33.59	9.22	52.46	8.28
10.5	44.33	8.85	72.20	10.93
11	71.78	21.54	116.77	34.89

Table 7.3. The values of each data point that correspond to Figure 4.3 and the resin synthesized with 1-dodecanol.

[HCl]	Average D_w Hf	stdev	Average D_w Zr	stdev
6	29.26	5.32	28.31	5.01
6.5	40.71	11.13	36.95	7.36
7	33.34	12.95	29.71	13.42
7.5	31.60	21.65	27.59	15.66
8	16.43	6.85	18.74	5.25
8.5	21.47	10.88	23.68	4.91
9	19.94	5.06	28.20	9.83
9.5	29.85	14.79	34.00	3.83
10	30.47	1.75	45.15	2.09
10.5	42.50	4.33	74.50	16.21
11	43.94	6.36	71.29	3.51

Table 7.4 The values of each data point that correspond to Figure 4.4 panel a) and the resin synthesized with dichloromethane.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	10.36	8.17	3.59	3.46
Hf – 1	11.18	16.91	6.29	10.04
Hf – 2	40.95	13.33	35.63	4.00
Hf – 3	19.86	14.60	31.52	15.70
Hf – 4	1.94	1.75	5.31	2.93
Hf – 5	1.21	1.07	0.96	0.85
Hf – 6	0.00	0.00	0.45	0.48
Zr – 1	0.00	0.00	0.32	0.55
Zr – 2	0.00	0.00	0.00	0.00
Zr – 3	-	-	-	-
Zr – 4	-	-	-	-
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.5. The values of each data point that correspond to Figure 4.4 panel b) and the resin synthesized with dichloromethane.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	15.55	7.72	6.15	3.03
Hf – 1	37.03	7.93	20.73	0.94
Hf – 2	25.02	1.45	31.42	3.53
Hf – 3	5.52	1.61	17.21	4.28
Hf – 4	0.72	0.72	4.85	1.34
Hf – 5	0.33	0.58	1.08	0.20
Hf – 6	0.00	0.00	0.50	0.09
Zr – 1	0.00	0.00	0.26	0.45
Zr – 2	0.00	0.00	0.11	0.20
Zr – 3	-	-	-	-
Zr – 4	-	-	-	-
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.6. The values of each data point that correspond to Figure 4.4 panel c) and the resin synthesized with dichloromethane.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	9.69	7.52	5.30	5.12
Hf – 1	21.50	14.47	16.26	19.96
Hf – 2	20.17	5.63	9.60	2.59
Hf – 3	4.45	3.87	1.12	0.97
Hf – 4	6.26	5.43	1.58	1.42
Hf – 5	5.13	4.46	1.38	1.22
Hf – 6	3.50	3.05	2.23	1.93
Zr – 1	2.80	1.68	4.83	3.46
Zr – 2	1.62	1.73	22.99	15.09
Zr – 3	0.00	0.00	9.59	7.07
Zr – 4	0.00	0.00	0.66	0.65
Zr – 5	0.00	0.00	0.00	0.00
Zr – 6	-	-	-	-

Table 7.7. The values of each data point that correspond to Figure 4.4 panel d) and the resin synthesized with dichloromethane.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	18.67	4.01	12.48	5.07
Hf – 1	37.38	4.74	39.09	2.51
Hf – 2	12.18	1.80	13.70	0.61
Hf – 3	0.00	0.00	0.14	0.25
Hf – 4	0.00	0.00	0.00	0.00
Hf – 5	0.00	0.00	0.00	0.00
Hf – 6	0.00	0.00	0.00	0.00
Zr – 1	3.86	0.93	0.99	0.23
Zr – 2	0.00	0.00	8.26	0.31
Zr – 3	0.00	0.00	4.22	1.34
Zr – 4	0.00	0.00	0.00	0.00
Zr – 5	0.00	0.00	0.00	0.00
Zr – 6	-	-	-	-

Table 7.8. The values of each data point that correspond to Figure 4.5 panel a) and the resin synthesized with 1-octanol.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	23.95	12.15	14.19	8.79
Hf – 1	24.68	9.31	14.30	4.18
Hf – 2	26.25	11.65	36.27	2.15
Hf – 3	9.22	9.12	16.74	8.50
Hf – 4	1.70	2.34	2.70	0.54
Hf – 5	0.00	0.00	0.18	0.31
Hf – 6	0.00	0.00	0.00	0.00
Zr – 1	0.00	0.00	0.00	0.00
Zr – 2	0.00	0.00	0.00	0.00
Zr – 3	-	-	-	-
Zr – 4	-	-	-	-
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.9. The values of each data point that correspond to Figure 4.5 panel b) and the resin synthesized with 1-octanol.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	0.00	0.00	0.00	0.00
Hf – 1	22.35	13.22	18.62	22.35
Hf – 2	24.67	11.56	22.07	24.67
Hf – 3	23.60	16.40	21.38	23.60
Hf – 4	9.07	12.37	13.55	9.07
Hf – 5	1.34	2.33	3.24	1.34
Hf – 6	0.00	0.00	0.87	0.00
Zr – 1	0.00	0.00	0.00	0.00
Zr – 2	0.00	0.00	0.00	0.00
Zr – 3	-	-	-	-
Zr – 4	-	-	-	-
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.10. The values of each data point that correspond to Figure 4.5 panel c) and the resin synthesized with 1-octanol.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	28.36	2.52	26.65	2.67
Hf – 1	37.66	5.53	38.85	4.04
Hf – 2	12.96	2.80	11.29	1.87
Hf – 3	2.92	0.87	1.00	0.87
Hf – 4	0.86	1.49	0.36	0.62
Hf – 5	0.00	0.00	0.23	0.39
Hf – 6	0.00	0.00	0.00	0.00
Zr – 1	0.00	0.00	1.95	0.52
Zr – 2	0.00	0.00	5.00	1.15
Zr – 3	0.00	0.00	0.21	0.37
Zr – 4	0.00	0.00	0.00	0.00
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.11. The values of each data point that correspond to Figure 4.5 panel d) and the resin synthesized with 1-octanol.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	36.98	3.96	38.21	7.98
Hf – 1	36.76	7.12	38.38	8.67
Hf – 2	8.94	1.21	7.12	3.15
Hf – 3	2.27	1.99	0.21	0.37
Hf – 4	1.00	0.96	0.00	0.00
Hf – 5	0.83	1.44	0.00	0.00
Hf – 6	0.00	0.00	0.00	0.00
Zr – 1	2.52	1.09	1.96	0.59
Zr – 2	0.00	0.00	8.62	1.50
Zr – 3	0.00	0.00	2.27	0.38
Zr – 4	0.00	0.00	0.00	0.00
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.12. The values of each data point that correspond to Figure 4.6 panel a) and the resin synthesized with 1-dodecanol.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	2.22	2.18	0.33	0.58
Hf – 1	10.36	3.24	6.78	2.94
Hf – 2	46.10	6.30	43.92	3.66
Hf – 3	19.92	6.70	26.22	5.07
Hf – 4	0.00	0.00	6.09	0.76
Hf – 5	0.00	0.00	0.41	0.72
Hf – 6	-	-	-	-
Zr – 1	-	-	-	-
Zr – 2	-	-	-	-
Zr – 3	-	-	-	-
Zr – 4	-	-	-	-
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.13. The values of each data point that correspond to Figure 4.6 panel b) and the resin synthesized with 1-dodecanol.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	1.45	2.51	0.42	0.73
Hf – 1	6.48	8.34	5.42	4.91
Hf – 2	48.09	2.88	41.11	1.20
Hf – 3	19.26	5.44	28.16	7.36
Hf – 4	2.59	2.55	8.24	0.51
Hf – 5	0.00	0.00	2.12	0.41
Hf – 6	-	-	-	-
Zr – 1	-	-	-	-
Zr – 2	-	-	-	-
Zr – 3	-	-	-	-
Zr – 4	-	-	-	-
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.14. The values of each data point that correspond to Figure 4.6 panel c) and the resin synthesized with 1-dodecanol.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	6.51	2.86	1.16	1.02
Hf – 1	4.50	1.15	0.63	0.55
Hf – 2	15.46	2.23	2.69	0.79
Hf – 3	18.29	1.82	4.41	0.57
Hf – 4	15.97	1.58	5.15	0.99
Hf – 5	9.61	1.04	5.89	1.46
Hf – 6	6.49	1.73	6.83	1.37
Zr – 1	3.99	1.13	11.45	0.13
Zr – 2	0.00	0.00	33.55	2.36
Zr – 3	0.00	0.00	9.75	1.91
Zr – 4	0.00	0.00	1.90	0.80
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.15. The values of each data point that correspond to Figure 4.6 panel d) and the resin synthesized with 1-dodecanol.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	9.70	1.73	3.85	2.20
Hf – 1	2.58	2.26	0.58	0.54
Hf – 2	4.64	0.32	0.37	0.34
Hf – 3	6.69	2.08	0.85	0.45
Hf – 4	6.76	1.48	0.83	0.80
Hf – 5	7.43	0.90	1.88	0.57
Hf – 6	7.62	1.56	1.64	0.17
Zr – 1	20.62	3.13	13.01	2.26
Zr – 2	6.37	1.33	48.30	9.88
Zr – 3	0.00	0.00	18.17	1.41
Zr – 4	0.00	0.00	4.45	0.46
Zr – 5	0.00	0.00	1.18	0.33
Zr – 6	0.00	0.00	0.00	0.00

Table 7.16. The values of each data point that corresponds to Figure 4.8 panel a).

[HCl]	Average D_w Hf	stdev	Average D_w Zr	stdev
6	12.87	5.90	11.83	6.39
6.5	15.94	9.68	15.00	7.36
7	18.25	16.13	18.02	15.94
7.5	16.91	2.13	18.35	4.19
8	13.09	5.79	14.17	8.68
8.5	20.30	15.33	23.81	16.03
9	14.64	3.03	20.38	8.05
9.5	17.93	4.09	29.54	9.78
10	19.10	6.29	37.83	18.42
10.5	29.67	8.91	54.34	19.24
11	55.44	12.56	111.72	35.46

Table 7.17. The values of each data point that correspond to Figure 4.8 panel b).

[HCl]	Average D_w Hf	stdev	Average D_w Zr	stdev
6	30.49	18.48	32.90	18.48
6.5	33.78	11.59	36.85	18.72
7	42.54	12.98	44.84	19.41
7.5	58.13	42.38	55.26	41.11
8	49.30	10.04	54.52	5.49
8.5	44.65	16.27	51.07	19.19
9	47.00	24.66	50.30	14.90
9.5	40.46	6.70	57.18	1.53
10	40.67	10.29	66.30	3.88
10.5	71.62	11.83	127.61	27.21
11	74.47	10.22	127.08	7.78

Table 7.18. The values of each data point that correspond to Figure 4.8 panel c).

[HCl]	Average D_w Hf	stdev	Average D_w Zr	stdev
6	36.29	18.25	33.76	12.34
6.5	28.66	7.74	23.87	7.76
7	36.09	26.49	29.11	19.46
7.5	23.10	6.40	24.65	4.04
8	37.31	6.92	40.21	8.88
8.5	38.93	18.97	37.10	10.10
9	38.66	6.00	41.56	1.08
9.5	47.35	3.05	56.78	2.07
10	78.43	68.97	91.58	74.88
10.5	56.75	19.02	89.64	29.02
11	78.78	16.09	111.11	11.61

Table 7.19. The values of each data point for Eichrom's Pb resin that corresponds to Figure 4.9 panel a).

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	5.86	6.93	4.23	5.86
Hf – 1	4.36	1.10	1.24	4.36
Hf – 2	19.36	2.30	8.09	19.36
Hf – 3	38.50	4.96	39.26	38.50
Hf – 4	17.32	5.45	26.54	17.32
Hf – 5	4.20	1.24	7.62	4.20
Hf – 6	1.02	0.96	1.58	1.02
Total Zr	0.21	0.36	0.31	0.21

Table 7.20. The values of each data point for Eichrom's Pb resin that corresponds to Figure 4.9 panel b).

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	4.07	3.47	2.59	4.07
Hf – 1	15.93	8.85	3.61	15.93
Hf – 2	18.61	4.99	6.21	18.61
Hf – 3	32.22	5.84	27.44	32.22
Hf – 4	12.65	1.68	23.93	12.65
Hf – 5	3.51	0.49	12.05	3.51
Hf – 6	0.00	0.00	4.37	0.00
Total Zr	0.00	0.00	2.19	0.00

Table 7.21. The values of each data point for Eichrom's Pb resin that corresponds to Figure 4.9 panel c).

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	2.82	2.63	1.95	1.07
Hf – 1	11.69	3.07	2.88	0.25
Hf – 2	15.40	6.70	3.67	4.44
Hf – 3	20.11	1.45	4.21	2.60
Hf – 4	17.92	3.43	6.85	1.27
Hf – 5	8.86	2.13	6.16	2.17
Hf – 6	5.10	0.39	7.06	0.88
Total Zr	2.37	0.39	8.11	1.02

Table 7.22. The values of each data point for Eichrom's Pb resin that corresponds to Figure 4.9 panel d).

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	11.20	4.55	8.92	4.43
Hf – 1	9.10	1.06	4.18	0.43
Hf – 2	11.01	4.93	3.07	2.91
Hf – 3	13.24	2.20	3.62	0.83
Hf – 4	10.72	0.92	5.19	2.26
Hf – 5	8.30	2.23	2.94	2.83
Hf – 6	5.27	2.05	2.99	0.44
Total Zr	3.43	1.36	3.59	0.96

Table 7.23. The values of each data point for the in-house synthesized resin with DB18C6 that correspond to Figure 4.11 panel a)

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	14.90	9.07	9.57	8.03
Hf-1	27.89	20.47	28.72	23.40
Hf-2	28.64	12.91	29.27	7.38
Hf-3	5.30	7.44	11.88	13.00
Hf-4	0.00	0.00	1.09	1.88
Hf-5	0.00	0.00	0.00	0.00
Hf-6	0.00	0.00	0.08	0.13
Zr-1	-	-	-	-
Zr-2	-	-	-	-
Zr-3	-	-	-	-
Zr-4	-	-	-	-
Zr-5	-	-	-	-
Zr-6	-	-	-	-

Table 7.24. The values of each data point for the in-house synthesized resin with DB18C6 that correspond to Figure 4.11 panel b).

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	2.96	5.13	0.83	1.44
Hf – 1	9.14	1.13	1.93	1.03
Hf – 2	26.83	9.09	17.56	11.58
Hf – 3	31.42	17.08	36.13	12.42
Hf – 4	3.75	4.49	19.32	10.71
Hf – 5	0.00	0.00	4.51	1.72
Hf – 6	0.00	0.00	0.94	0.63
Zr – 1	0.00	0.00	0.23	0.39
Zr – 2	-	-	-	-
Zr – 3	-	-	-	-
Zr – 4	-	-	-	-
Zr – 5	-	-	-	-
Zr – 6	-	-	-	-

Table 7.25. The values of each data point for the in-house synthesized resin with DB18C6 that correspond to Figure 4.11 panel c).

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	18.39	0.90	12.06	2.86
Hf – 1	34.42	3.06	33.79	2.50
Hf – 2	21.04	3.29	21.27	3.09
Hf – 3	0.00	0.00	1.21	0.42
Hf – 4	0.00	0.00	0.47	0.61
Hf – 5	0.00	0.00	0.77	0.69
Hf – 6	0.00	0.00	0.53	0.46
Zr – 1	0.00	0.00	2.08	0.47
Zr – 2	0.00	0.00	6.64	0.95
Zr – 3	0.00	0.00	0.82	1.42
Zr – 4	0.00	0.00	0.00	0.00
Zr – 5	0.00	0.00	0.00	0.00
Zr – 6	-	-	-	-

Table 7.26. The values of each data point for the in-house synthesized resin with DB18C6 that correspond to Figure 4.11 panel d).

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	15.61	3.92	8.89	2.70
Hf – 1	40.66	1.90	36.46	2.34
Hf – 2	18.28	3.21	18.30	3.24
Hf – 3	0.50	0.86	0.09	0.16
Hf – 4	0.00	0.00	0.00	0.00
Hf – 5	0.00	0.00	0.00	0.00
Hf – 6	0.00	0.00	0.59	1.02
Zr – 1	3.97	0.00	2.33	0.50
Zr – 2	1.65	2.86	7.76	0.08
Zr – 3	0.00	0.00	7.58	0.16
Zr – 4	0.00	0.00	0.99	0.50
Zr – 5	0.00	0.00	0.00	0.00
Zr – 6	-	-	-	-

Table 7.27. The values of each data point for Eichrom's Pb resin that correspond to Figure 4.12.

[HCl]	Average k' Hf	stdev	Average k' Zr	stdev
6	7.08	3.24	6.51	3.52
6.5	8.77	5.33	8.25	4.05
7	10.04	8.87	9.91	8.76
7.5	9.30	1.17	10.09	2.30
8	7.20	3.18	7.79	4.77
8.5	11.17	8.43	13.10	8.81
9	8.05	1.67	11.21	4.43
9.5	9.86	2.25	16.25	5.38
10	10.50	3.46	20.81	10.13
10.5	16.32	4.90	29.89	10.58
11	30.49	6.91	61.44	19.50

Table 7.28. The values of each data point for Eichrom's Sr resin that correspond to Figure 4.12.

[HCl]	Average k' Hf	stdev	Average k' Zr	stdev
6	13.28	3.60	12.49	1.55
6.5	9.80	2.28	9.41	3.28
7	14.45	2.69	17.31	5.80
7.5	13.15	1.96	13.94	4.48
8	14.90	2.34	16.67	4.07
8.5	23.31	4.50	24.67	6.77
9	16.25	5.06	22.46	4.07
9.5	18.82	3.62	29.71	7.08
10	18.75	5.50	35.68	15.33
10.5	31.17	3.05	58.02	6.62
11	52.15	10.64	107.58	25.00

Table 7.29. The values of each data point for Eichrom's Sr and Pb resin, respectively, that corresponds to Figure 4.13.

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	11.20	4.55	8.92	4.43
Hf – 1	8.94	1.31	4.43	0.54
Hf – 2	9.16	3.70	2.77	2.01
Hf – 3	10.86	1.15	2.90	0.62
Hf – 4	10.50	1.16	5.01	2.28
Hf – 5	6.53	0.84	3.27	0.97
Hf – 6	4.96	1.28	2.67	0.76
Zr – 1	4.41	2.35	2.57	1.06
Zr – 2	11.40	2.04	45.68	1.58
Zr – 3	11.20	4.55	8.92	4.43
Zr – 4	8.94	1.31	4.43	0.54
Zr – 5	9.16	3.70	2.77	2.01
Zr – 6	10.86	1.15	2.90	0.62

Fraction	% Hf Eluted	stdev	% Zr Eluted	stdev
Load	9.10	1.06	4.18	0.43
Hf – 1	11.01	4.93	3.07	2.91
Hf – 2	13.24	2.20	3.62	0.83
Hf – 3	10.72	0.92	5.19	2.26
Hf – 4	8.30	2.23	2.94	2.83
Hf – 5	5.27	2.05	2.99	0.44
Hf – 6	3.43	1.36	3.59	0.96
Zr – 1	5.60	2.05	11.60	2.35
Zr – 2	3.86	1.84	23.18	3.57
Zr – 3	0.33	0.58	7.50	1.68
Zr – 4	0.10	0.17	2.52	1.36
Zr – 5	0	0	0	0
Zr – 6	0	0	0	0

Table 7.30. The actual concentrations of the acids used.

Nominal [HCl]	Actual [HCl]	stdev
6	6.29	0.151
6.5	6.53	0.340
7	7.06	0.122
7.5	7.42	0.081
8	7.73	0.236
8.5	8.42	0.472
9	8.81	0.750
9.5	9.24	0.693
10	9.11	0.650
10.5	10.20	0.766
11	10.95	0.761

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    ii. **M.E. Bennett**, W.A. Alexander, J. W. Lu, D. Troya, J.R. Morris. Collisions of Polar and Nonpolar Gases with Hydrogen Bonding and Hydrocarbon Self-Assembled Monolayers. Journal of Physical Chemistry C (2008), 112(44), 17272-17280.

iii. M.M.Hoffmann, **M.E. Bennett**, J.D. Fox, D.P. Wyman. Water partitioning in "dry" poly(ethylene oxide) alcohol (CmEn) nonionic surfactant-a proton NMR study. Journal of Colloid and Interface Science (2005), 287(2), 712-716.

2) Manuscripts in preparation

i. Yu. Ts. Oganessian', F. Sh. Abdullin, P. D. Bailey, D. E. Benker, **M. E. Bennett**, S. N. Dmitriev, J. G. Ezold, J. H. Hamilton, R. A. Henderson, M. G. Itkis, Yu. V. Lobanov, A. N. Mezentsev, K. J. Moody, S. L. Nelson, A. N. Polyakov, C. E. Porter, A. V. Ramayya, F. D. Riley, J. B. Roberto, M. A. Ryabinin, K. P. Rykaczewski, R. N. Sagaidak, D. A. Shaughnessy, I. V. Shirokovsky[1], M. A. Stoyer[5], V. G. Subbotin[1], R. Sudowe[3], A. M. Sukhov, Yu. S. Tsyganov, V. K. Utyonkov, A. A. Voinov, G. K. Vostokin, and P. A. Wilk. Identification of a New Element with Z = 117. Phys. Rev. C. In preparation.

ii. R.A. Henderson, J.M. Gostic, K.J. Moody, D.A. Shaughnessy, **M.E. Bennett**, R. Sudowe. A New Chemical Separation Scheme for Db using Eichrom's DGA Resin. In preparation.

3) Published conference abstracts

i. **M.E. Bennett**; R.A. Henderson; D.A. Shaughnessy; R. Sudowe. Extraction chromatographic studies of Rf and Db homologs. Book of Abstracts, Asian-Pacific Symposium On RadioChemistry(APSORC) '09, Napa, CA, November 29 – December 4, 2009

ii. **M.E. Bennett**; R.A. Henderson; D.A. Shaughnessy; R. Sudowe. Extraction chromatographic studies of Rf and Db homologs. Book of Abstracts, The 7th Workshop on the Chemistry of the Heaviest Elements, Mainz, Germany, October 11-13, 2009.

iii. R.A Henderson; K.J. Moody, D.A. Shaughnessy, J.M Gostic, **M.E Bennett**; R. Sudowe. Automated Chemistry Efforts at LLNL using Eichrom's DGA resin. Book of Abstracts, The 7th Workshop on the Chemistry of the Heaviest Elements, Mainz, Germany, October 11-13, 2009.

iv. **M.E. Bennett**; R.A. Henderson; D.A. Shaughnessy; R. Sudowe. Extraction chromatographic studies of Rf and Db homologs. Abstracts of Papers, 237th ACS National Meeting, Salt Lake City, UT, United States, March 22-26, 2009 (2009), NUCL-041.

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