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PREPARATION AND CHARACTERIZATION OF EXTRACTION CHROMATOGRAPHY RESINS USING N-DONOR EXTRACTANTS FOR TRIVALENT ACTINIDE AND LANTHANIDE SEPARATIONS

by

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A dissertation submitted in partial fulfillment of
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Doctor of Philosophy in Radiochemistry
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May 2011

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May 2011

ABSTRACT

Preparation and Characterization of Extraction Chromatography Resins Using N-Donor Extractants for Trivalent Actinide and Lanthanide Separations

by

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Assistant Professor of Health Physics and Radiochemistry
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Actinide and lanthanide elements exist in the geosphere and biosphere due to both natural abundances and anthropogenic activities. The investigation of the presence and transport of actinides through the environment is of great scientific interest. In order to prepare environmental samples for precise measurements, the individual actinides must be separated from the chemically similar lanthanides, and from neighboring actinides. Existing extraction chromatography resins are either poorly suited for this separation, have bleeding problems, are not reusable, or fail the CHON principle. In an effort to resolve these issues, malonamides and N-donor extractants from the BTP and BTBP classes of solvent extraction ligands were coated onto solid resin supports and characterized. The extraction behavior of the resins was determined in test batches to optimize the parameters of the resins. Nitric and hydrochloric acids were used to characterize the resins in batch studies for extraction of Pu-239, Am-241, Cm-244, and natural Eu. The resins were studied on columns with Am-241, and bleeding was also determined. This dissertation shows that the isobutyl-BTP resin which was created had the best performance, with minimal bleeding and maximal extraction. The C5-BTBP and CyMe4-BTBP resins were less favorable. Future work should focus on the kinetics of the BTBP resins, or on expanding the extraction knowledge of the isobutyl-BTP resin.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATIONS

CHAPTER 1

INTRODUCTION

Significance and Goals

Actinide elements exist as ions and compounds in the geosphere due to both natural abundances and a number of anthropogenic activities. Some of the actinides such as uranium-238 have been present since the formation of the earth, while some such as uranium-234 are still present due to their occurrence in the natural decay chains of primordial actinides.[1] Some of the human activities which resulted in the release of actinides into the environment include testing of nuclear weapons, re-entry of and dispersal from nuclear powered satellites, reactor accidents, and releases from nuclear wastes such as used reactor fuel and defense wastes.[2] These actinides can be transported from the geosphere to the biosphere, mainly through aqueous processes.[2] Because of popular concern regarding the presence of radioactive materials, and the dose which can result from bioaccumulation, it is necessary to monitor these radionuclides in soil, water, and air, as well as in biological systems.[3] To accomplish measurement of the actinides, they must be separated from one another because of overlapping alpha energies in alpha-spectroscopy, and because of complications with similar but unresolved masses in mass-spectroscopy. Separated samples also provide cleaner spectra in gamma-spectroscopy, improving the quality of data that can be gathered. These separations can be strongly affected by the presence of elements such as iron, aluminum, and lanthanides which are able to form complexes with the ligands used to effect the extractions and compete for binding sites, especially when the concentration of matrix elements are orders of magnitude larger than the concentration of actinides.[4]

Column chemistry lends itself to separations of trace elements because of the high number of exchange steps occurring along the column. Historically, ion-exchange resins have been used, but these are relatively nonspecific in their binding and separation abilities, relying on the charge density and size of complexes formed in acidic or basic solutions or the use of counter-ligands like α-hydroxyisobutyric acid to effect the separation.[5] Anion exchange resins have been particularly popular, making use of the negative nitrate and chloride complexes formed with the actinides. Extraction chromatography resins more specific to the actinides have also been commercialized, utilizing ligands developed for solvent extraction. The ligands used have come from processes which were focused on the extraction of pentavalent neptunium (NpO_2^+) and tetravalent plutonium (Pu^{+4}) like octyl(phenyl)-N,N'-diisobutyl-carbamoyl-methyl-phosphine oxide (CMPO)[4], or that have shown high extraction of trivalent americium (Am^{+3}) like N,N,N',N'-tetra-n-octyldiglycolamide. However, many of these ligands have weak extraction or poor selectivity for americium(III) in the presence of other actinides and interfering matrix elements.[6] Many of them also include elements other than carbon, hydrogen, oxygen and nitrogen, causing them to leave behind hazardous wastes upon incineration; the desire to avoid the production of these wastes is called the CHON Rule.[7] In addition, some of these resins degrade over time and are not usable for sequential elution of actinides.[4]

Significance

By preparing extraction chromatography resins from extractants designed for trivalent actinide separations which also follow the CHON rule, the resulting resins should be able to preferentially extract trivalent actinides such as americium and curium, and will be completely incinerable. The resins created from such extractants could improve on the elution and separation characteristics of other column materials. Advances in the separations of americium and curium are needed in order to satisfy analytical capabilities to succeed in detecting or investigating undeclared nuclear activities.[8] By generating data on the performance of these ligands when adsorbed to solid supports, it will be possible to determine whether the novel resins should be studied further. Comparisons can also be made between this research and data available in literature on the performance of the ligands in solvent extraction and extraction chromatography to determine if these ligands behave the same way on solid supports as they do in liquid solvents.

Research Goals

The purpose of this work was to prepare, characterize, and compare extraction chromatography resins based on extractants which can selectively extract trivalent actinides, can easily be eluted, and which follow the CHON Rule. The goal was for these novel resins to have enhanced extraction capacity and selectivity for trivalent actinides. The ligands which were investigated for use on extraction chromatography resins were 2-(2-hexyloy-ethyl)-N,N'-dimethyl-N,N'-dioctyl-malonamide (DMDOHEMA), dimethyl-dibutyl-tetradecyl-1,3-malonamide (DMDBTDMA), 2,6-di(5,6-diisobutyl-1,2,4-triazin-3-yl)pyridine (isobutyl-BTP), 6,6'-bis-(5,6-dipentyl[1,2,4]triazin-3-yl)-[2,2']bipyridinyl (C5-BTBP), and 6,6'-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-2,2'-bipyridine (CyMe$_4$-BTBP) with structures shown in Figure 1. Americium, curium, plutonium and europium were used as elements of interest in experiments with both free resin and resin in columns. Changes in extraction behavior dependent on acidity, ionic media, support materials, and ligand structure were investigated.

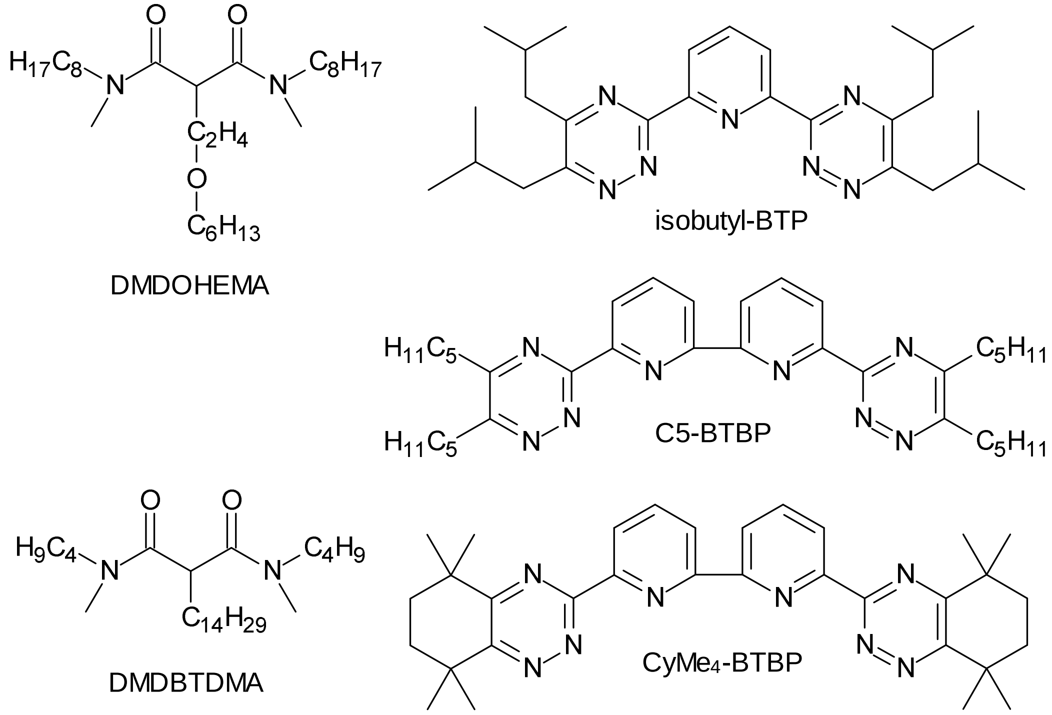
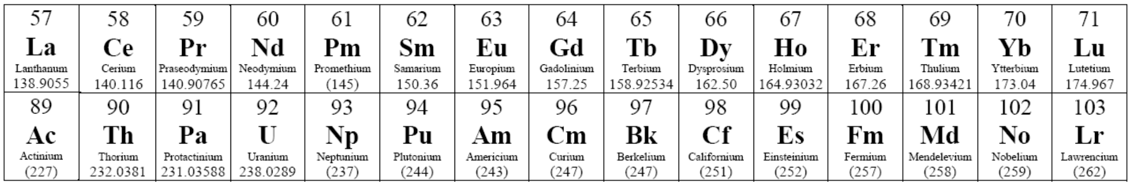


Figure 1 Structures of extractants used in this work.

Background

For the reasons introduced earlier, analyses of material containing actinides or lanthanides must generally take place after the elements are separated. In addition, since most of the analyses are performed to monitor the movement of actinides in the environment or to detect undeclared nuclear activities, it is important to understand how much of the material is naturally occurring compared to man-made. Uranium is the highest Z element generally found in nature, with neptunium and plutonium being found in trace amounts.[9] Thus, the absence of natural americium and curium raise no concerns in analyses, but natural abundances of the lanthanides do need to be considered depending on the purpose of the separation because of their similar chemistry with the actinides.[10] While these pre-analysis separations are performed currently, they are not as easy as separating elements such as sodium/cesium based on size or strontium/yttrium based on charge. The trivalent actinides and lanthanides have similar sizes and charge densities, and separations must be used which can exploit small differences in these properties and in bonding. In order to highlight some of the ways these small differences might be exploited, the chemistry of the actinides and lanthanides will be discussed below, in addition to discussing the sources of actinides and lanthanides in the environment.



57 **La** Lanthanum 138.9055	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
89 **Ac** Actinium (227)	90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Figure 2 Lanthanide and actinide elements

Actinides

Sources and sinks in the geosphere and biosphere

The actinide elements are comprised of nuclides with atomic numbers ranging from 89-103, as in Figure 2. The group takes its name from the first member of the series, actinium. Addition of f-electrons formally begins with the 2nd member and ends with the 15th, for a total of 14 f-electrons.[11] In reality, some of these electrons add to d-orbitals such as with Th or No, due to shifting energies of the orbitals as electrons are added. The early actinide elements display greater covalency in their bonding than the lanthanides,[12] but beyond plutonium their covalency decreases due to shifting of the orbital energy levels.[13] The actinides beyond uranium are formed by neutron capture in nuclear fuels up to curium, while elements through fermium are reachable with higher neutron fluxes in specially designed reactors or under rapid neutron capture conditions such as those present in thermo-nuclear weapon explosions and supernova. The elements beyond fermium are produced by man in accelerators.[11]

Many thorium and uranium isotopes are primordial, and were incorporated into the Earth's inventory at the time of planetary accretion. These major actinides decay into minor primordial actinides such as actinium and protactinium. Thorium-232 decays by emitting an alpha particle to form radium-228, which can then decay by beta emission into actinium-228, which can again emit a beta particle to form thorium-228.[14] Uranium-238 has a similar decay pattern which passes through thorium-234, then protactinium-234 before reaching uranium-234. Ultra-trace levels of some other nuclides can also be found in the environment due to neutron capture (e.g. uranium-236, neptunium-237, plutonium-239), but these are present at concentrations of picomoles per mole U and lower.[3] These naturally occurring actinides can be transported in the environment by dissolution in groundwater, and can move along the surface of the geosphere and through soils or fractured bedrocks. Wave action and weather phenomena can cause the presence of actinides in aerosols. Anthropogenic activities such as mining can also cause release of both major and minor primordial actinides to the accessible environment by enhancing the surface area and exposure to natural erosive forces.[3]

Anthropogenic actinides include protactinium-233, uranium-233, uranium-236, neptunium-237, plutonium-238, plutonium-239, plutonium-240, plutonium-241, plutonium-242, americium-241, americium-243, curium-242, curium-243, and curium-244. Several of these emit alpha particles of similar energy, such as americium-241 at 5.486 MeV and plutonium-238 at 5.499 MeV.[14] As observed with plutonium-239 and plutonium-240 with decays of 5.156 and 5.168, a difference of more than 0.012 MeV is required to resolve the resulting peaks by alpha spectroscopy, otherwise extensive chemical separations are required. About 2000 tons of plutonium have been produced around the world for defense purposes, creating a large amount of waste which contains both fission products and activated actinides.[13] Release of anthropogenic nuclides could occur for a variety of reasons related to their uses, and public concern has created a mandate for environmental monitoring.[15,16]

The actinide nuclides above result from neutron capture on natural uranium or thorium, or manmade plutonium. The most prevalent way of producing and releasing these nuclides simultaneously was also one of the earliest pathways for release – the detonation of nuclear weapons both for military and testing purposes. Atmospheric testing released a large number of these nuclides in particulate form, which generally settled out over time, but were found to persist in regions of the atmosphere depending on particle size.[17] When testing was moved underground, these nuclides were still introduced to the geosphere, but were “sealed” within cavities. They can however become mobile as these cavities fracture over time and allow groundwater to flow through them.[18] When nuclear reactions are used as the heat source for propulsion or the production of electricity, the same reactions are able to occur as in nuclear weapons, but at a slower and controlled rate, and with slightly varied fission product yields due to lower neutron energies. Because of the lower neutron flux and different fuels used, variations will exist in the amounts of actinide elements produced, but they will still be present along with the other products of fission. Naval vessels, in particular submarines, have used nuclear propulsion for over 50 years and release of radionuclides can occur after these vessels sink and corrode or from deliberately sunk cores.[19] Releases have also occurred from reactors on land such as the second unit at Three Mile Island[20] and the fourth unit at Chernobyl.[21] Radioisotope thermoelectric generators on satellites have also added to the global inventory when some satellites powered by them have failed and burned up upon reentry to the atmosphere.[17] After fuel is used in a nuclear reactor, it needs to be stored and cooled before it can be recycled or disposed of in a repository. Releases of material could occur before or after disposal. In all of these scenarios, separations are required to analyze environmental samples for release of radionuclides.

Plutonium has been widely studied due to the historically high interest in how the element moves through the environment and how it might impact living organisms. Plutonium is also particularly toxic compared to other actinides due to the chemical similarities between iron(III) and plutonium(IV), allowing for plutonium uptake by transferrin and ferritin causing a long biological half-life and wide distribution through the body.[23] In terms of uptake in humans, the main routes of entry are via inhalation, ingestion, and through injection.[23] The majority of the plutonium in the general environment consists of fallout from weapons testing which has settled out and remains within the top 5 cm of soil.[24] Re-suspension due to wind or forest fires followed by inhalation of the plutonium is a thousand times more important than ingestion when considering the body burden.[25] This is due to the fact that the inhaled plutonium stays with the tissue in the lungs, whereas ingested plutonium tends to pass through the GI tract before absorption can occur. If the plutonium is chelated by bacterial or plant siderophores, plutonium can cross cell membranes with relative ease, and could then be concentrated through the food-chain.[23] Injection is only considered to be a route of entry among nuclear workers. Among marine organisms, factors such as particulate ingestion, food ingestion, biological chelation, physiologic incorporation and ion exchange on tissues and membranes may all affect uptake of the actinides. Seaweed especially accumulates plutonium, and concentration factors of 10^5 have been observed, while bottom fish, sea urchins, and starfish all exhibit concentration factors of 0.5, 12, and 600 respectively.[26] It has been calculated that humans have always had a base load of ~2 attomoles (10^{-18}) of plutonium mostly in the skeleton and liver, however this has been increased by 5 orders of magnitude since 1945. Measurements from 1970-1980 showed that the contribution of weapon testing to the body load ranges from 30 to 200 mBq of plutonium-239&240.[27] Plutonium isotopes are a major concern because of their biological and physical half-lifes.

Chemical properties and resulting separation challenges

To separate actinides, an understanding of their unique chemistry is required. The actinide elements have electrons populating the 5f orbitals whereas the lanthanide elements have electrons populating the 4f orbitals. Among the early actinides, promotion of electrons from 5f → 6d orbitals occurs more readily than the corresponding 4f → 5d promotion in the lanthanides.[11] This leads to a number of accessible oxidation states in the earlier actinides, such that it is possible to find plutonium in four different oxidation states in natural waters (3^+ thru 6^+). The tetravalent states tend to be less soluble and mobile, except perhaps when colloids form. In mildly oxidizing waters a trend is observed where the preferred oxidation state begins at +3 with actinium and peaks at +6 with uranium, before returning to +3 with americium. The common oxidation state in aqueous solutions is then constant at +3 except for the drop to +2 for nobelium. The oxidation states found in nature as well as other known states are shown in Figure 3.[22] In addition to the 5f → 6d electron promotions, the 5f orbitals have greater extension with respect to 7s and 7p than do 4f orbitals relative to 6s and 6p.[11] This leads to a greater contribution of 5f electrons to bonding and a higher degree of covalency in actinide bonds than in lanthanide bonds. This greater extension of the f-orbitals in the actinides makes the f-electrons more polarizable, such that while actinides are still hard acids, they are softer acids than lanthanides which are smaller and less polarizable due to the contraction of the 4f orbitals.[28]

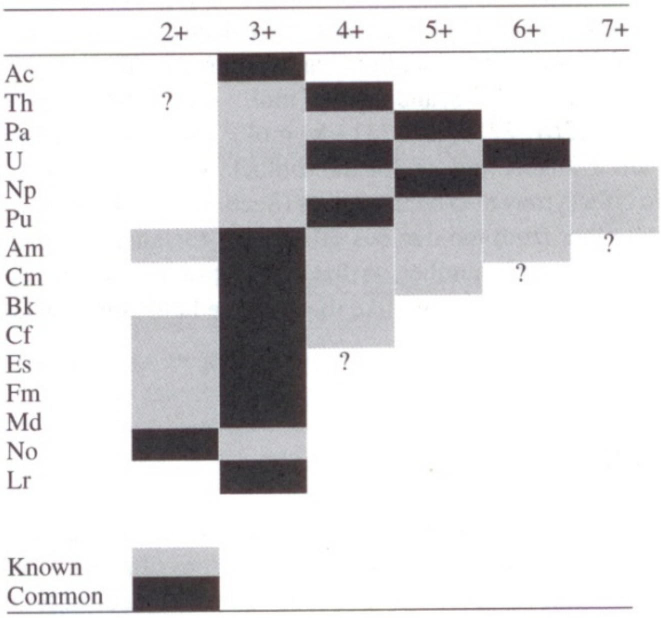


Figure 3 Oxidation states of the actinides [22]

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Many existing methods for the separation of the actinides rely on controlling the oxidation states in order to promote sorption or solvation, and then selectively changing the oxidation state of a single element to promote its stripping. In the Plutonium-Uranium Redox EXtraction process (PUREX), hexavalent uranium (UO_2^{+2}) and tetravalent plutonium (Pu^{+4}) in acidic solution can complex with nitrates to form $Pu(NO_3)_4$ and $UO_2(NO_3)_2$ which then interact with tributyl phosphate in the organic phase to effect the phase transfer. Hydrazine mixed with hydroxylamine, or a solution of U^{+4} can then be contacted with the organic phase to reduce the tetravalent plutonium to the trivalent state to back-extract it into the aqueous phase. The uranium can then be stripped from the organic phase using lower acid/nitrate concentration. A similar process is used with ion-exchange resins to separate plutonium from uranium.

Using multiple oxidation states to effect separations is possible for actinides through americium, though americium requires much stronger oxidants than plutonium. However, oxidation states higher than III are troublesome to reach in curium, and non-existent in einsteinium or fermium, preventing the widespread application of this technique for elements beyond americium. In addition, though it is possible to oxidize americium to separate it from other elements, the penta- or hexa-valent americium readily oxidizes organic ligands and solvent molecules in solvent extraction.[29] Instead of using different oxidation states to separate the higher actinides, recent work has focused on exploiting the difference in acid characteristics of the actinides by using softer bases as extraction ligands.[30] This more recent work will be further explored in a later discussion of ligands used in both solvent extraction and extraction chromatography.

As shown in Figure 4, the measured ionic radii of trivalent actinides range from 94 to 112 pm and the differences between neighboring nuclei are very slight.[31, fair use] For example, americium and curium have trivalent radii of 98 and 97 pm respectively. In addition, the lanthanides have overlapping ionic radii with the actinides, for instance americium and neodymium overlap as do curium and promethium. These differences can be used to separate elements within a group, but separations based on size alone are not possible when both lanthanides and actinides are present.

It is also possible to use kinetic differences in binding between the metal and ligand to preferentially extract actinides or lanthanides as in the Trivalent Actinide Lanthanide Separation by Phosphorus-reagent Extraction from Aqueous Komplexes [sic] process (TALSPEAK),[32] which will also be further discussed in a later section on ligands used in both solvent extraction and extraction chromatography.

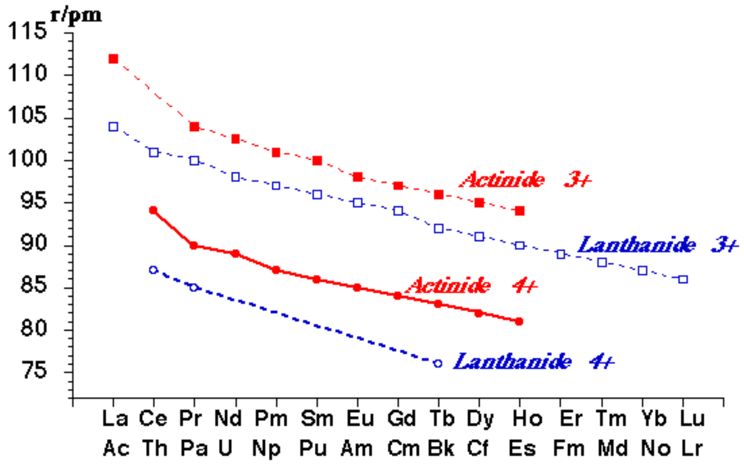

Figure 4 Ionic Radii of actinides and lanthanides [31]

Lanthanides

The lanthanide elements are comprised of nuclides with atomic numbers ranging from 57-71 as shown in Figure 2. The group takes its name from the first member of the series, lanthanum. Addition of f electrons formally begins with the 2nd member and ends with the 15th, for a total of 14-f electrons. As opposed to the actinides, a higher energy barrier decreases the promotion of electrons from 4f to 5d orbitals, limiting the available oxidation states. The lanthanides are much less covalent in their bonding than actinides because the 4f electrons are not as extended compared to the 6s and 6p orbitals.[11] The smaller nuclear charge also means that relativistic effects which influence the actinides are not as evident among the lanthanides.[11] The lanthanides all exist in nature with the lowest abundance being that of promethium with a global crustal inventory of only a few hundred grams,[33] while cerium has an abundance of 60 ppm which is comparable to that of copper.[34] Thus, stable lanthanides must be expected to be present in any environmental samples to be analyzed for actinides.

While neutron activation of the uranium in nuclear fuel is responsible for the generation of the transuranic elements, the radio-lanthanides are primarily formed as fission products. Nuclides such as promethium-147, samarium-151, and europium-155 all have half-lives of a few years and their fission yields from uranium-235 are 2.25%, 0.419%, and 0.03% respectively.[14] Relative to the fission yield from uranium-235 for other high-mass products, these yields are low compared to the maximum of 7.87% for mass 134.[14] These radio-lanthanides will be present in used nuclear fuel at much higher concentrations than the transuranic elements, but most of them will decay during the fuel cooling process. Only the nuclides with half-lives on the order of years or longer will still be present during waste disposal, which includes meta-stable states like holmium-166m with a half life of 1200 years. Release to the environment of any of these fission products could occur during refueling or from corrosion in the cooling ponds in addition to being released due to nuclear accidents, and signatures from these radio-lanthanides could be used to detect undeclared nuclear activities.

Another source for some of the lanthanides is natural decay. As detection becomes more advanced, longer half-lives are measureable. Several lanthanides have been found to have naturally occurring radioactive isotopes including lanthanum-138, samarium-147&148, gadolinium-152, lutetium-176, and more recently europium-151.[14,33] However, these represent a very small portion of the lanthanide inventory. The promethium-147 from alpha decay of europium-151 comprises less than 5% of the global inventory of a few hundred grams of promethium.[33] Regardless of their source, all of the lanthanides are easily incorporated into geological materials, evidence for this coming from the 54 known lanthanide minerals.[35]

Separation Techniques

Elemental separations have been important since before recorded history for the discovery, isolation, and use of elements such as copper, gold, and mercury. More recently, elemental separations have been the focus of research in elemental discovery,[36] treatment of nuclear wastes,[32] and analytical chemistry on environmental and biological samples.[37] Ion-exchange, solvent extraction, and extraction chromatography are all useful techniques in elemental separations, and will be briefly described. A few of the extractants which have been used in solvent extraction and/or extraction chromatography will also be discussed.

Ion Exchange

"Ion exchange occurs in inanimate soils, sands, and rocks, and in living organisms."[38] In ion exchange, insoluble solid materials exchange with stoichiometrically equivalent amounts of ions. Cation exchangers often carry sodium or protons, while anion exchangers often carry chloride. Helfferich uses the analogy of a charged sponge with counter ions in its pores to describe ion exchangers.[38] Mineral ion exchangers are generally cation exchangers, composed of crystalline alumino-silicates such as analcite ($Na[Si_2AlO_6]_2 \cdot H_2O$) or montmorillonite ($Al_2[Si_4O_{10}(OH)_2] \cdot nH_2O$). Zeolites such as analcite have a fixed three-dimensional structure, whereas montmorillonite is an example of a layered structure which can swell.[38] There are also synthetic inorganic ion exchangers, usually synthesized hydrothermally from solutions containing silica, alumina, and alkali metals which have zeolite structures. Ion exchange resins are "irregular, macromolecular, three-dimensional network[s] of hydrocarbon chains."[38] Cation exchange resins can carry the negative sulfate, carbonic, phosphate, or arsenate groups on their backbones, while anion exchangers carry primary, secondary, tertiary, or quaternary amines or tertiary sulfur. While the polymeric backbones of the ion exchange resins are hydrophobic, the charged groups introduce some hydophilicity, and can swell in solution like a true sponge.

Ion exchange materials are characterized mainly by their charge exchange capacity. The capacity is simply the number of ionogenic groups per specified amount of ion exchange material, which can me expressed as mEq per gram of resin. This is a measured quantity, and when determined by different methods a variety of capacities can be calculated, all dependent on the experimental conditions, such as whether protons or sodium ions are exchanged. When used in columns, ion exchange materials are characterized by initial breakthrough of ions from the resin, and also by the height of the equivalent theoretical plates (HETP, H). As shown in Equation 1, L is the length of the column bed, V_{max} is the volume of eluate to peak maximum, and the width of the elution peak at 1/e times the maximum peak concentration is W.

Equation 1

$$H=\frac{L*W^2}{8*V_{max}^2}$$

Solvent Extraction

A common feature of all solvent extraction processes is the use of two immiscible phases between which a species can partition. In many cases other reactions can occur in either phase, which can help drive the transfer of material between phases. One of the two phases is usually aqueous, which can contain acids or other salts. Chelating agents or adduct-forming agents can also be present in the system. For the extracted complex of a cation to be highly partitioned to the organic phase it must be neutral. This neutral complex can either be formed in the aqueous phase before extraction by association with anions as in Equation 2, or it can be formed at the interface of the organic phase by chelation with organic acids. The malonamide, BTP, and BTBP molecules which were used as part of this research extract neutral complexes from the aqueous phase into the organic phase, while other extractants such as 2,6-bis-(benzoxazolyl)-4-dodecyloxylpyridine require synergists such as 2-bromodecanoic acid to effect complex formation and extraction. Each of the chelation and complex formation steps are equilibrium reactions and Le'Châtelier's Principle can be applied in terms of molecular concentrations, ionic strength, and temperature.[39] Experimentally, solvent extraction can be carried out in test tubes, centrifuge tubes, or microscale vessels. Industrially, solvent extraction can be carried out in large contactors, mixer-settlers, or pulse columns with plumbing and pumps between extraction stages.

Equation 2

$$M^{+3}(aq) + 3\,NO_3^-\,(aq) \leftrightarrow M(NO_3)_3(aq)$$

$$M(NO_3)_3(aq) \leftrightarrow M(NO_3)_3(org)$$

The distribution ratio is the main measure of extraction, and is calculated by dividing the total concentration of the extracted metal in the organic phase by the total concentration in the aqueous phase as in Equation 3. This ratio does not differentiate between free metal or complexed metal in either phase, and thus when using radioactive metals such as the actinides, the specific activity (activity per mass, or activity per volume) can be substituted for the concentration.

Equation 3

$$D_M = \frac{[M]_{org}}{[M]_{aq}} = \frac{S(M)_{org}}{S(M)_{aq}}$$

Some of the disadvantages of solvent extraction as a technique for elemental separation include the use of flammable solvents, the large volumes of waste created, and the fact that mixing in a single vessel is only equivalent to one exchange step of the material. In order to achieve multiple exchange steps, multiple extraction stages are required. However, the main advantages of solvent extraction are its ease of application to industrial processes, and its much higher selectivity than ion exchange, evidenced by its deployment in both uranium purification and nuclear waste reprocessing.

Extraction Chromatography

Extraction chromatography has not always been the term used to refer to selective partitioning of element(s) from an aqueous solution onto a ligand coated solid support. The term does not appear in literature until Hulet proposed its use in 1964 to simplify references to what at the time was called reversed-phase partition chromatography.[40] The term reversed-phase partition chromatography first appears in the literature in 1951 when Partridge and Chilton reported a procedure for coating chloroform or benzene onto glass for use in separating mixtures of o-nitraniline and p-nitraniline or o-nitrophenol and p-nitrophenol.[41] Initially the technique was used for separations of organic molecules and biochemical molecules. Siekierski and Kotlinska first applied this technique to lanthanide separations in 1959.[42] Shortly following this in 1960, Hamlin and Roberts in the U.K. were the first to apply the technique to the separation of actinide(s) using a stationary phase of tri-butyl phosphate coated onto a proprietary "Kel-F" moulding powder for the separation of uranium from contaminants, and also for the separation of plutonium from uranium.[43] Each of these pioneering researchers were inspired by the ligands which had been investigated for use in solvent extraction at the time, and used them for new applications. Since the 1960s a number of researchers have expanded the field of extraction chromatography using a variety of solid supports and novel extractants.[6,44-47]

While solvent extraction uses two immiscible liquids, extraction chromatography replaces one of the two liquids with a solid phase. This solid phase consists of a support which could be a polymeric resin, treated or untreated diatomaceous earth, or an inorganic matrix. The solid phase can be coated to create binding sites or to modify the surface properties. Phase transfer equilibria are still important, as are complexation reactions in the accompanying mobile phase and on the surface of the solid. The extracted complex does not necessarily displace other molecules or ions from the solid surface, but some of the extraction chromatography resins do extract charged complexes.

Since the 1960s many researchers have made key contributions to the field of extraction chromatography, notably Dr. Horwitz from Argonne National Laboratory who has contributed to the commercialization of a number of extraction chromatography resins along with his collaborators. These resins are marketed by Eichrom Technologies, Inc. and many of their resins have used ligands first developed for solvent extraction processes. Using their work as inspiration, it should be possible to create new resin materials which make use of more specific ligands from more recent work in solvent extraction.

Ligands used in Solvent Extraction and/or Extraction Chromatography

Several ligands, including some of those shown in Figure 1 and Figure 5, have been used in solvent extraction (SX) and/or extraction chromatography (EXC). These ligands will be briefly discussed as they pertain to both solvent extraction and extraction chromatography.

TBP

Tributyl phosphate (TBP) has been used in both the PUREX process and the suite of Uranium Redox EXtraction processes (UREX). In the PUREX process, a 30% solution of TBP in a diluent such as kerosene, n-dodecane, or hydrogenated polypropylene tetramer (HPT) is used as the organic phase.[31] This phase is brought into contact with ~4 M HNO_3 which has been diluted from the concentrated nitric acid previously used to dissolve the metals of interest. In the first step of the process, uranium(VI) and plutonium(IV) are co-extracted into the organic phase. The organic phase is then contacted with fresh nitric acid solution and the plutonium is reduced from IV to III by uranium(IV), or hydrazine mixed with hydroxylamine to effect the phase transfer. The remaining uranium is back-extracted from the organic phase by contacting it with dilute nitric acid. In this process, the lanthanides remain mostly with the raffinate, and do not transfer to a large extent to the organic phase; other fission products also remain in the raffinate.

In addition to the much lower nitric acid concentration used for the extraction step (0.1 M) in the UREX process, no pure plutonium stream is separated. This is due to the presence of acetohydroxamic acid (AHA) which complexes with and helps decrease extraction of tetravalent plutonium.[32] The AHA also reduces plutonium to the trivalent state, which is not extracted by TBP. Technetium in the form of pertechnetate ions will be coextracted with uranium in UREX, whereas they generally remain with the raffinate in PUREX because of the higher concentration of nitrate competing for uranium complexation. In both UREX and PUREX, TBP is the ligand which stabilizes the neutral nitrato complexes $Pu(NO_3)_4 \cdot 2TBP$ and $UO_2(NO_3)_2 \cdot 2TBP$ in the organic phase.

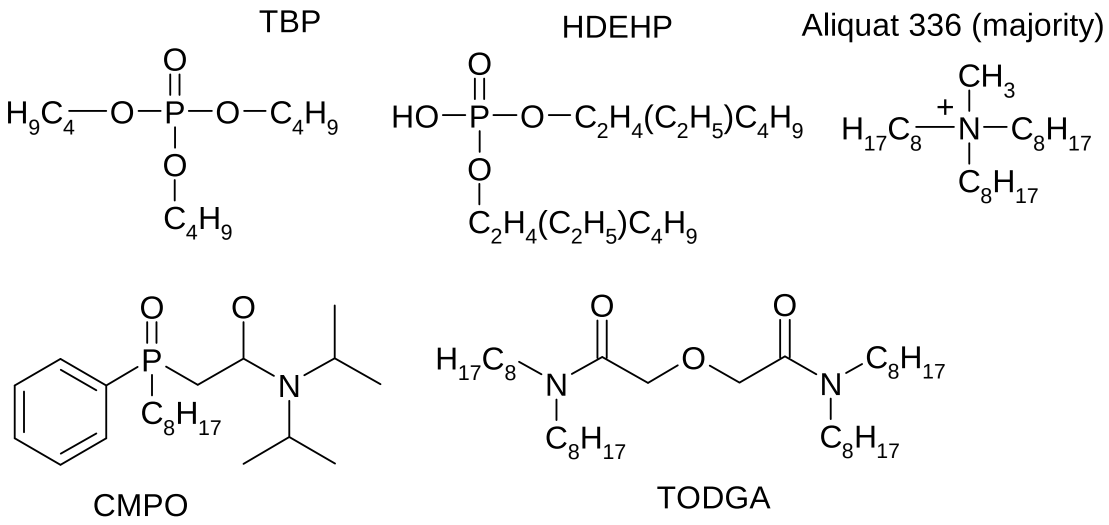

Figure 5 Structures of some ligands in SX and EXC

Hamlin and Roberts at the U.K Atomic Energy Authority prepared columns with TBP and Kel-F support as the extractant for their investigation of uranium purification.[43] Impurities in the uranium solution were washed out with ~5.5 M HNO_3 and the uranium was stripped with deionized water. The TBP column was effective for separating uranium from many metals including chromium, copper, aluminum, iron, tungsten, as well as some of its daughter products. Hamlin and Roberts also used this column material with HCl solutions to separate reduced plutonium from uranium.

Fuks, Lis, and Fidelis used silicone treated kielsguhr (diatomaceous earth) with TBP in hexane for a “dry” impregnation technique, where the hexane was slowly evaporated. The coated resin was then used in columns with hexavalent uranium, neptunium, and plutonium (UO_2^{+2}, NpO_2^{+2}, PuO_2^{+2}) to determine the peak positions so that extraction coefficients could be calculated.[48]

Resin with TBP and Amberlite XAD-4 has also been prepared by Aardaneh and colleagues for use in the separation of yttrium from strontium targets in the presence of aluminum.[49] The resin was prepared by contacting TBP in distilled water with the dried resin, in a "wet" impregnation technique. If only the TBP resin was used for elutions, TBP and its degradation products would contaminate the final yttrium product, so a second column of uncoated XAD-4 resin was used to catch the TBP and its hydrolysis products. The TBP extraction chromatography resin was applied to two successful separations of yttrium from strontium. TBP on XAD-4 has also been investigated by Kimura[50] and Serrano[51], on XAD-7 by Yamaura[52], and on silica by Naik.[53]

Resins with a mixture of N,N,N',N'-tetra-n-octyldiglycolamide (TODGA) and TBP have also been prepared, by Modolo and colleagues. A dry technique with hexane was used to coat the Amberchrom CG71 C with TODGA/TBP and the resins were used to separate actinides and lanthanides from bulk fission products.[54]

In addition to leaving behind hazardous waste upon incineration, TBP coated resins have significant problems with loss (bleeding) of the extractant off the resin, and with hydrolysis of the TBP itself, resulting in organic contamination of the elution products as reported by Aardaneh.[49] This problem alone may be responsible for preventing any commercial offering of this type of resin.

CMPO

Octyl(phenyl)-N,N-diisobutylcarbamoy1methylphosphine oxide (CMPO), shown in Figure 5, has been used in both solvent extraction and commercial resins. CMPO is used in the TRans-Uranic EXtraction process (TRUEX). TRUEX was designed as a process which would use the aqueous waste stream from PUREX, such that after adding oxalic acid the remaining transuranic elements (Np, Am, Cm, etc) could be extracted.[31] The organic phase is the same as that used in PUREX, with added CMPO. The CMPO acts as a ligand which can extract actinides and lanthanides selectively over other fission products. The actinides and lanthanides can be back extracted by contacting the loaded organic phase with an aqueous mixture of oxalic and nitric acids. In the process the TBP inhibits the formation of third phases, and acts synergistically with the CMPO during extraction.

The Horwitz group used the ligands from the TRUEX process to prepare both TRU® and RE® resins which have different concentrations of the CMPO to optimize their extraction properties for the transuranic and rare-earth elements, respectively.[4] However, their resins do contain TBP as a synergist, which is known to bleed.[49]

Yamaura and Matsuda also used a CMPO/TBP mixture to coat XAD-7 resin for use in separating americium, europium, and cerium from uranium and from plutonium.[55] They found the coated resin to be effective for the actinide separations, but not for separating americium from europium and from cerium.

Suresh and colleagues used XAD-7 and XAD-4 supports with neat CMPO for their resin preparation. They found that the resins had higher and faster extraction of uranium than americium, while the backbone of XAD-7 performed better than the backbone of XAD-4.[56]

Zhang and colleagues have used CMPO on silica based supports as part of their research on reprocessing systems. A "dry" impregnation technique was used along with a silica based resin. They found relatively constant bleeding of CMPO from the support, ~48 ppm CMPO was in the effluent at 298 K and ~37 ppm CMPO was in the effluent at 323 K.[57] They investigated only lanthanides and other typical fission products in their 2006 paper.

HDEHP

Di(2-ethylhexyl) phosphoric acid (HDEHP) is used in the TALSPEAK process. In this solvent extraction process, the aqueous phase contains lactic acid to buffer the solution between 2.5 and 3, and diethylenetriaminepentaacetic acid (DTPA) as a complexant.[31] In this solution, both lanthanides and actinides will associate with the DTPA, but the lanthanides will be extracted by HDEHP at a faster rate than the actinides. This separation therefore relies on the kinetics of extraction to effect the intergroup separation. The extraction properties are very dependent on pH and the DTPA concentration. Research has also shown the process could be reversed, such that the actinides and lanthanides start in the organic phase with HDEHP, and are extracted into the lactic acid and DTPA aqueous phase.

The Horwitz group has also used HDEHP from the TALSPEAK process along with CELITE (treated diatomaceous earth) to perform separations of americium, curium, berkelium, and californium.[58] In their study they used the resin in columns to determine the distribution ratios of the elements studied, and to determine separation factors of the neighbors. Based on their results, they were able to separate curium from californium, and berkelium from californium. Horwitz and Bloomquist would later apply their HDEHP/CELITE resin to the separation of elements from irradiated uranium targets in the search for super-heavy elements.[45] The resin using HDEHP on CELITE eventually became the Lanthanide resin from Eichrom, with similar phosphonic acids being used for their LN2 and LN3 resins.

Bednarczyk and Fidelis used silicone treated kielsguhr as a solid support for a coating of HDEHP in 1,3,5-trimethylbenzene. An *in-situ* technique was used, where the hydrophobic kielsguhr was dry packed into a column, and the HDEHP/1,3,5-trimethylbenzene solution was added to the column. After columns were prepared, solutions of hexavalent uranium, neptunium, and plutonium were eluted from the columns with varying concentrations of hydrochloric acid and perchloric acid in order to determine the first and second stability constants of the chloride complexes.[59] The first order stability constants were reported with 5-10% relative standard deviations, and the second order stability constants were reported with 10-20% relative standard deviation. Based on the general lack of change in the stability constants the authors determined that the chloride formed outer sphere complexes with hexavalent uranium, neptunium, and plutonium.

Wei and colleagues coated HDEHP onto both XAD-7 and silica based resins to investigate kinetic differences and distribution ratios with trivalent americium, gadolinium, europium, cerium, and neodymium. Neodymium sorption peaked after a shorter contact time with the silica based resin than with the XAD-7 support. The silica based resin was used for the distribution experiments, where gadolinium and europium were observed to extract more strongly than americium or cerium.[60]

McAlister and Horwitz used HDEHP and some other branched phosphoric acids coated onto Amberchrom CG71ms to determine distribution ratios and capacity factors for americium, as well as distribution ratios for a wide variety of multivalent metals. Based on the ratios they determined, they were able to propose separation methods for aluminum-gallium, strontium-yttrium, and actinium-lanthanum-[cerium, praseodymium, neodymium].[61]

Aliquat 336

The mixture of trioctyl-methylammonium chloride and tridecyl-methylammonium chloride is commonly called Aliquat 336, with the majority of the mixture being from the C_8 molecule, and the mixture having an average molecular weight of 442. Aliquat 336 has not been applied to any reprocessing flow sheets yet, but it has been researched for the extraction of certain lanthanides as secondary products from the manufacture of phosphoric acid out of apatite ores.[62] Aliquat 336 has been investigated for use in actinide separations. Moore used Aliquat 336 which had been converted from the chloride to the thiocyanide form dissolved in xylene to study the extraction of tracer levels of americium and europium, as well as other lanthanides and curium, berkelium, and californium.[63] Khopkar and Mathur used Aliquat 336 in solvent extraction to determine the stability constants of californium(III) with chloride, nitrate, thiocyanate, and sulfate, curium(III) with chloride, nitrate, and sulfate, and americium(III) with sulfate.[64] Landgren and Liljenzin also used Aliquat 336 with actinides, dissolved in 1,3-diisopropyl benzene and contacted with a nitrate system to study the extraction behavior of thorium, uranium, neptunium, plutonium, americium, curium, and also technetium.[65] These are by no means the only studies on solvent extraction with Aliquat 336, but they are representative of some of the applications.

The first extraction chromatography resin prepared by Horwitz was done in collaboration with Orlandini and Bloomquist in 1966, and used Aliquat 336.[44] Silanes were used to treat diatomaceous earth to render it hydrophobic, and Aliquat-336 was used as the coating. The resin was prepared because other literature had shown that Aliquat-336 had promising separation factors for curium and americium, and was then tested in a column using extraction chromatography techniques. Aliquat-336 has since been applied to a polymethacrylate resin and investigated before being commercialized as TEVA® resin.[66]

Malonamides

Malonamides have been tested in France for use in the DIAMide EXtraction process known as DIAMEX. The malonamides (aka diamides) are dissolved in HPT and used to extract trivalent actinides and lanthanides from nitric acid solutions.[31] The goals of this process are similar to that of TRUEX, but the malonamide ligands which have been tested follow the CHON rule which is emphasized in research and process chemistry in Europe. Two malonamides have been designed and optimized for extraction and solubility for testing in pilot runs, N,N'-dimethyl-N,N'-dibutyltetradecylmalonamide (DMDBTDMA), which has the advantage of lower solubility in the aqueous phase,[67] and N,N'-dimethyl-N,N'-dioctylhexylethoxymalonamide (DMDOHEMA) which has shown improved extraction of americium.[68] Cuillerdier has published on the subject[69,70], and the DIAMEX process has been a subject of interest with the French

Commissariat a l’Energie Atomique (CEA) and also within the European Commission.[7]

Mohopatra and colleagues have coated DMDBTDMA onto a variety of solid supports including Chromosorb W, Chromosorb 102, Amberlite XAD-4 and Amberlite XAD-7. They used a dry coating procedure with acetone as the volatile solvent, and compared results from the dry coating procedure to results from a wet coating procedure which used a mixture of methanol and water. Distribution ratios for uranium(VI), plutonium (IV), americium(III), europium(III), cesium(I), and strontium(II) were determined from nitric acid solutions.[46] The resin was also used in columns to test separations from a simulated waste solution.

Van Hecke and Modolo have used DMDOHEMA on Amberchrom CG-71 C to investigate the use of such material for batch removal of actinides from low level liquid wastes. The resin was prepared using the dry method with hexane as the volatile solvent, and showed fast sorption for americium and europium from simulated low level waste.[47]

Malonamides which are lacking the alkyl chain off the α-carbon in the structure have been tethered to chloromethylated resins by Ansari and colleagues. These are made with N,N’-dimethyl-N,N’-dibutyl malonamide (DMDBMA) in dimethyl formamide with chloromethylated polystyrene-divinyl benzene polymer and sodium hydride in a water free vessel. The resulting polymer was washed free from reactants with water and methanol, and was initially studied with uranium and thorium.[71] Later studies included americium(III), plutonium(III), plutonium(IV), thorium(IV), and uranium(IV) as well as interfering elements iron, aluminum, strontium, cesium, and vanadium. The resin was used in columns to separate americium, plutonium, and uranium.[72]

Isobutyl-BTP

The 2,6-di(5,6-diisobutyl-1,2,4-triazin-3-yl)pyridine (isobutyl-BTP) molecule shown in Figure 1 has been studied for use in solvent extraction. It has been investigated for actinide separations because tridentate ligands exhibit higher extraction and separation efficiency than bidentate ligands, and because the nitrogen donating extractants are more stable than sulfur donating extractants.[73] Good separation factors were observed for americium and europium with the ligand in HPT, and the isobutyl derivative was found to be stable in solution whereas butyl, ethyl, and methyl substituted extractants decomposed in the organic phase.[73] The structure of these extractants with trivalent lanthanides has been studied, and new complexes have been reported.[74] These complexes contained three of the tridentate ligands forming 9-coordinate complexes with the smaller lanthanides (Sm-Lu). The formation of this three ligand complex is proposed as the explanation for the enhanced separation factors with these ligands.

A similar molecule, 2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine or nPr-BTP has been investigated as well. In many studies, the coordination of 3 ligands to 1 metal has been confirmed.[75,76,77] Extractions with nPr-BTP were relatively fast,[78] but were slower and had lower distributions than with the iso-propyl-BTP.[79]

Some resins have been prepared with the isobutyl-BTP, but they have been silica based supports. Those that have been investigated have shown high extraction of americium, and high separation factors for americium-gadolinium.[80] Extractions with the isobutyl-BTP have been performed up to 4 M $NaNO_3$ with 0.1 M HNO_3. The isobutyl-BTP based resin is very stable at 0.1 M HNO_3, and is more stable than n-butyl-BTP below 6 M HNO_3.[80] Another group has investigated the same resin material with the lanthanides and increasing nitric acid concentration. Competing ligands such as formic, citric, and diethylenetriaminepentaacetic acid were also used in distribution experiments. Despite the authors' stated conclusions, the data in their paper indicate that cerium was the only lanthanide separated from the others, and a poor separation exists between other lanthanides when a column was used.[81]

The higher stability of the isobutyl-BTP compared to other BTP extractants, and the stability of its tridentate complexes made it a promising candidate for sorption to polymethacrylate based resins for use in radioanalytical separations.

C5-BTBP

The 6,6'-bis-(5,6,-dipentyl-[1,2,4]triazin-3-yl)-[2,2']bipyridinyl (C5-BTBP) molecule shown in Figure 1, has been studied for use in solvent extraction because BTP molecules in prior research were difficult to strip of metals, and it was intended to be more resistant to hydrolysis and radiolysis.[82] It was synthesized in the UK at the University of Reading, and has been investigated for actinide separations because it is a polycyclic nitrogen donating ligand similar to other ligands with good extraction properties.[83] Good separation factors were observed for americium and europium with the ligand in tert-butylbenzene, but extraction and separation factor both decrease in longer chain alcohol solvents.[84] The C5-BTBP extractant has also been studied in a cyclohexanone diluent for europium, americium, curium, and californium distribution.[85] The distribution constant of berkelium has also been determined for some nitrate concentrations with C5-BTBP in cyclohexanone at both fixed and varying ionic strength.[86] Good separation factors were observed for americium and europium with the ligand in short chain alcohols, tetrachloroethane, or nitrobenzene. The structure of these extractants with trivalent lanthanides has been studied, and new complexes have been reported.[87] These complexes generally contained 1 tetradentate ligand with the metal and nitrates forming 10-coordinate complexes with some being 9-coordinate (Yb, Lu). While C5-BTBP exhibited many favorable properties, the relatively slow kinetics of extraction were troublesome in solvent extraction.[88]

At the time this research was begun, no publications with C5-BTBP on solid supports were known. Since the research has been completed, a single publication focused on C5-BTBP on polyacrylonitrile has been found which evidently yielded unfavorable results.[89] The work was also presented at a conference, and another group used a similar molecule C4-BTBP on their own silica-polymer background.[90]

Since it was reported that C5-BTBP had more favorable results for stripping of metals relative to isobutyl-BTP, it was a promising candidate for sorption to polymethacrylate based resins for use in radioanalytical separations.

CyMe$_4$-BTBP

The 6,6'-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-2,2'-bipyridine (CyMe$_4$-BTBP) molecule shown in Figure 1 has been studied for use in solvent extraction. It has been investigated for actinide separations because BTP molecules in prior research were difficult to strip of metals, and it was intended to be more resistant to hydrolysis and radiolysis.[82] Good separation factors were observed for americium and europium with the ligand in mixtures of TPH with *n*-octanol, and the kinetics of extraction were improved by the addition of DMDOHEMA as a phase transfer catalyst.[91] Other work with this extractant in solvent extraction systems has been promising.[92, 93, 94]

No resins have been prepared previously using CyMe$_4$-BTBP. The more favorable results for stripping of metals from CyMe$_4$-BTBP relative to isobutyl-BTP, and its greater stability when compared to C5-BTBP made it a promising candidate for sorption to polymethacrylate based resins for use in radioanalytical separations.

CHAPTER 2

INSTRUMENTATION AND METHODS

Synthesis

Resins which required washing were washed with de-ionized water as described in the product literature, and then dried overnight at 105 °C [95,96]. The dry resin was weighed on a Mettler Toledo New Classic MF balance, and then slurried in the appropriate solvent using glass round bottom flasks with ground glass 24/40 necks. A suitable amount of extractant based on the resin mass was weighed out on the same balance and dissolved in the same solvent in a 50 mL glass beaker before being added to the slurry. Amberchrom CG-71 M resin, an acrylic ester polymer with a mean diameter of 75 μm, was obtained from Rohm and Hass. Amberlite XAD 4 resin which is an aromatic polymer with a harmonic mean diameter of 49-69 µm, and Amberlite XAD 7HP resin which is an aliphatic acrylic polymer with a harmonic mean diameter of 56-71 µm, were both obtained from Sigma Aldrich. The N,N'-dimethyl-N,N'-dibutyltetradecylmalonamide DMDBTDMA, and N,N'-dimethyl-N,N'-dioctylhexyl-ethoxymalonamide DMDOHEMA, were obtained from Dr. Clément Hill of CEA-Marcoule. The 2,6-bis(5,6-diisobutyl-1,2,4-triazine-3-yl)pyridine isobutyl-BTP extractant which had a reported purity over 95% was obtained from Prof. Yuezhou Wei of Shanghai University. The 6,6'-bis(5,6-dipentyl-[1,2,4]-triazin-3-yl)-2,2'-bipyridine C5-BTBP and 6,6'-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-2,2'-bipyridine CyMe$_4$-BTBP extractants were obtained from Emma Aneheim and Prof. Christian Ekberg of Chalmers University of Technology. Methanol, acetone, and hexane were reagent grade and obtained from Sigma-Aldrich.

After being slurried, Dow Corning High Vacuum Silicone Grease was applied to the necks of round bottom flasks and the flasks were attached to a Heidolph Laborota 4011 Digital Rotary-Evaporator, and rotated at 120 rpm. The flask was lowered into a water bath maintained at 25 °C, and was kept closed at atmospheric pressure overnight to allow for even mixing of the slurry. After rotating overnight, the water bath temperature was raised to 30 °C for the isobutyl-BTP resin, and to 35 °C for the BTBP resins. A Heidolph Rotovac Valve Control was used to reduce the pressure which was regulated by a solenoid controlled by a Heidolph Vac Control Automatic. The pressure was typically reduced to 250 torr for methanol, 300 torr for hexane, and 300 torr for acetone to allow for evaporation of the solvent over a period of not less than two hours so the coating process would approach a reversible process, allowing for a more homogeneous product. A WKL 230 LAUDA cooling pump was used to circulate water through the condenser of the rotovap. After evaporation, the round bottom flask with the coated resin was placed inside a larger beaker and dried overnight at 45 °C in a VWR Oven Model 1320. After cooling, resin was transferred to translucent high density polyethylene sample containers, and the mass recovered was measured on the same balance used to weight the uncoated resin and dry extractants.

Physical Characterization

When large batches of the resins were produced, densities of the coated resins were determined by placing a known mass of dry coated resin, typically between 0.25 and 0.4 g, into dry 25 mL glass volumetric flasks. De-ionized water at room temperature was added and the flasks were capped and vortexed using a VWR MiniVortexer MW1 at no less than 2500 rpm for several minutes to ensure complete wetting of the resin. Using the temperature and mass of water along with water density tables, the volume of the resin was calculated using the displacement method. These wet, known masses of resin were then added to general purpose glass columns from Kontes with precision bores which were previously plugged with glass wool and acid washed sand. Columns were checked for air bubbles, and were resettled when necessary. Only gravity flow was used for settling the columns. By measuring the height of the resin bed, the volume of the resin bed could be calculated using the equation for the volume of a cylinder. The resin density, resin mass, weight loading, and bed volume were then used to calculate the volume of the mobile phase per bed volume, and the volume of the extractant phase per bed volume.

Pre-weighed samples of the dry coated and uncoated resin were sent to Atlantic Microlab in Norcross, Georgia for CHN Elemental Analysis, who reported the mass percent of C, H, and N present in each sample. Using the percent nitrogen of uncoated and coated resins, the weight loading of extractant, which was the only source of nitrogen in the coated resins, could be calculated.

Infrared Spectroscopy Theory

In analyzing the resin material before and after coating with the extractant molecules, Infrared (IR) Spectroscopy can be useful for detecting the presence or absence of functional groups on the surface of the resin material. Infrared light is lower in energy than visible light, and has longer wavelengths. Because the energies are lower, electrons are not excited or ionized in this analytical technique, but molecules are vibrationally excited. Molecules can vibrate in a number of ways, including scissoring, wagging, asymmetric and symmetric stretches. Because of the effective masses of different functional groups and their different bond strengths, they will have different vibrational behavior. The energy it takes to move the molecule from one vibrational mode to another is equal to the energy of the infra-red light that can be absorbed by said molecule. Thus, functional groups will have different absorbance peaks, and slight changes to the R groups can shift the vibrational energy. Hooke's Law given as Equation 4 can be used to model molecular stretches because they are analogous to the behavior of springs. In Hooke's law, k is the spring constant which is related to the strength of the spring, or the strength of the bond in the case of these molecules, and x is the distance of stretching from the equilibrium position of the spring. The mass (m) is included when one solves for the cyclic frequency of a spring based system; Equation 5 is solved for when one end of the spring is fixed and a weight is attached, as in the case of a large molecule with a single atom or small functional group attached.

Equation 4

$$U=\frac{1}{2}kx^2$$

Equation 5

$$v=\frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

The instrument is calibrated by using a blank matrix which for attenuated total reflectance (ATR) was the absence of anything on the diamond surface with which the IR light interacts, and non-absorbed wavelengths are reflected back. The intensity of the light reflecting “off” the blank is taken as I_0 while the intensity of light which reflects off the actual sample is I. An assumption is made in that by adding the sample you are not significantly changing the amount of blank material in the beam path. The ratio of I to I_o is known as the transmittance, which is a common way of displaying data taken using IR. It is possible to convert this to absorbance by taking the opposite of the logarithm of Transmittance. These are shown in Equation 6 and Equation 7.

Equation 6

$$T \equiv \frac{I}{I_0}$$

Equation 7

$$A \equiv -\log_{10} T = \log_{10} \frac{I_0}{I}$$

Infrared Spectroscopy Methods

Portions of the dry coated and uncoated resin were examined on a Shimadzu IR-Prestige 21 with a triple-bounce diamond ATR from PIKE Technologies in the wavenumber region from 750 cm^{-1} to 4000 cm^{-1}. The IR was run in %T mode, with Happ-Genzel Apodization, 32 scans per run, 4 cm^{-1} resolution, and auto gain and aperture. The ATR was used with no sample for the background scans, and sample sizes were used which evenly covered the diamond surface.

Surface Area Theory

The surface area of a material can be determined using BET Theory. In this theory, the atmospheric pressure p_0, sample pressure p, total volume v, and a constant c dependent on the gas utilized are used to plot adsorption isotherms using Equation 8.

Equation 8

$$\frac{p}{v(p_o - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{p}{p_o}$$

The NOVA-1000 Surface Area Analyzer used to measure surface area relies on precise pressure transducers to measure pressure. Empty sample tubes with matched filler rods inserted are calibrated on the instrument for their empty volume. Once a known mass of sample is placed at the bottom of the sample tube, the sample is heated under vacuum to remove adsorbed water. After this sample preparation is complete, sample volume can be determined using the pressure and the known volume of the sample tube. The sample is then cooled using liquid nitrogen, which brings the temperature below the condensation point of the analysis gas, which is a requirement for determining adsorption isotherms and applying BET Theory. The pressure will then be measured at multiple points after allowing the analysis gas to bleed into the sample and begin forming the monolayer. Modern instrumentation allows for the selection of different analysis gasses, which have stored constants. The NOVA-1000 used also conducts a least squares fit on the data, and reports the fitting values as well as the calculated surface area. Dividing the measured surface area by the sample mass allows for the calculation of the specific surface area, reported in square meters per gram.

Surface Area Analysis

Empty 9 mm bulbless short glass sample cells with matched glass filler rods were calibrated on a NOVA-1000 Surface Area Analyzer using the instructions provided with the instrument. Uncoated and coated resins were weighed before and after analysis, and were dried overnight under vacuum surrounded by heating mantles at 100 °C. Surface areas were determined by multipoint analysis using Ultra High Purity nitrogen gas supplied by Praxair.

Batch Extractions

The extraction experiments were performed by pre-equilibrating 10.0-20.0 mg of coated resin weighed on a Mettler Toledo XP 205 DeltaRange balance with 4.950 mL of aqueous hydrochloric or nitric acid with concentrations ranging from 0.1 M to 4 M. Resin and solution were contacted for 10-15 minutes in 15 mL polypropylene centrifuge tubes from VWR; afterwards a 50 µL spike of the appropriate nuclide or element was added. Eppendorf pipettors were used for solvent and spike measurement and transfers. All de-ionized water (DI) used had a nominal resistance of 18.2 MΩ and was supplied by a Pall Cascada IX-Water system. The concentrated hydrochloric and nitric acids used were both reagent grade, from JT Baker and VWR respectively. Europium with natural isotopics was obtained as NIST Standard Reference Material 3117a in 10% nitric acid. Radionuclides were obtained from Isotope Products Laboratories, and diluted to 2000 Bq/mL or 1000 Bq/mL working solutions. The americium-241 and curium-244 were supplied as trivalent nitrates, while the plutonium-239 was supplied as a tetravalent chloride. Three samples and one control were used at each acid concentration for each nuclide for each resin, except for some screening studies on the isobutyl-BTP resin.

Weight Distribution Ratios were determined from the europium(III) concentrations and the radionuclide activities using Equation 9 based on the resin mass (m), solution volume (V_s), the original activity or stable concentration (A_o) determined from a control, and activity or stable concentration remaining in the sample solution (A_s). These ratios were converted when possible using Equation 10 to the number of free column volumes to peak maximum, *k'* (i.e. the resin capacity factor), which takes into account the density of the extractant and mass percent of the extractant on the resin, as well as the volume of the mobile and extractant phases per mL of bed volume (V_m, V_s) determined after packing of the resin in columns. This factor was determined using the methods previously described by Horwitz.[97,98]

Equation 9

$$D_w = \frac{A_o - A_s}{A_s} * \frac{V_s}{m}$$

Equation 10

$$k' = D_w * \frac{\rho_{extr} * V_s}{mass_{\%extr} * V_m}$$

Liquid Scintillation Counting Theory

The actinide isotopes used to characterize the resin materials were all alpha emitters, therefore making the contact solutions from batch extractions well suited to analysis on a Liquid Scintillation Counter. The solutions to be analyzed were transferred to plastic vials which were translucent and which contained a cocktail designed for LSC. The cocktail consisted of a solvent which aided in energy transfer and which was responsible for dissolving the sample and the other components, a fluor molecule which emitted light when excited, a wave-shifter which absorbed light emitted by the fluor and shifted it to lower energies (longer wavelengths) which were less likely to reabsorbed by other fluor molecules or the cocktail, and which were also more ideal for the detectors outside of the vial.

When one of the actinides being analyzed decayed in the cocktail, the alpha particle passed through solvent for several micrometers and deposited all of its energy in a localized region through ionizations. Many of those ionized molecules recombined because they are so close together, but some of these ionizations of solvent molecules allowed energy to be transferred to fluor molecules, which then emitted light, which was then absorbed and reemitted by a wave shifter before exiting the vial. The fluor molecules can also be excited directly by ionizations, but with lower probability. Because a single alpha particle deposits so much energy, each decay and interaction produced a large number of photons from the fluor molecules which were emitted in random directions such that the light exits the vial isotropically. By using mirrors to reflect the photons towards two photomultiplier tubes (PMT) on each side of the vial, the counting efficiency was maximized. When the photons struck the photocathode of a photo-multiplier tube, electrons were ejected and drawn to the stepped anodes which are called dynodes. These dynodes also released electrons when they were struck by arriving electrons. As the electrons passed from the photo-cathode to each successive dynode they were accelerated, and multiplied. The large number of electrons which reached the final anode of the PMT created a current pulse which then passed through other electronics. Since the light emitted by a true decay event in the sample is emitted isotropically, both PMTs registered true signals from the sample at the same time. A coincidence circuit was used to reject noise from data by only passing the signals through when they arrived at the same time. Decay events which released more energy will cause the formation of more light, which in turn resulted in greater current pulses. A multichannel analyzer and other electronics along with software were used to plot a spectrum using the number of detected events over a range of energies. Regions were set to focus on the peaks of interest and to exclude noise from the concentration measurement.

Care was taken in analysis of samples to ensure that the sample stayed as consistent as possible from batch to batch, because variations in acid concentration, or oxidant and reductant concentrations could have caused spectral shifts or even degradation of the LSC cocktail. The spectral shift was determined by using an external source of radiation of barium-133 to excite the cocktail and measure the response to a standard spectrum of Compton electrons. This shift is reported using the Transformed Spectral Index of the External Standard/Automatic Efficiency Control (tSIE/AEC).

Liquid Scintillation Counting Methods

After mixing the resin using a MaxQMini 4450 Incubator at room temperature overnight at 120 rpm for a total of 12 to 18 hours with the spiked solution, the samples were centrifuged and 1.000 mL aliquots were transferred to 20 mL polyethylene LSC vials supplied by VWR and mixed with 10 mL of Ultima Gold scintillation cocktail supplied by Perkin Elmer for counting on a Packard TriCarb 2900TR Liquid Scintillation

Analyzer for 60 minutes with a 2s% terminator of 2.0%. Windows were set from 0-75, 75-1000, and 0-2000 channels with the peaks falling in the 75-1000 window. The static controller was turned on, 18 ns was allowed for coincidence and there was a 75 ns delay before burst. The tSIE/AEC values for samples were used to ensure measurements were within the calibrated range of quenching. A Packard 2700 TR/AB was used as an alternate counting instrument with matched settings to the 2900TR. All samples and controls for a resin and acid batch were run on the same instrument to limit systematic errors.

ICP-AES Theory

Metals in solution are introduced into the instrument through an Inductively Coupled Plasma, which caused ionization of the sample. The ionized atoms in the sample emitted light as they recombined with electrons. The optics in the instrument gathered this emitted light and reflected/focused it onto a charge-coupled device for detection. Between the torch and the detector, the light passed through a polychromator to separate the light in 2 dimensions based on wavelength. Since each element has discrete electronic levels, the light emitted when excited electrons de-excite depends on the energy difference between these levels. The specific energies of light emitted by a particular element have in many cases been well characterized, and the wavelengths and intensities of light detected can be used to identify and quantify elements in samples. ICP-AES was used when analyzing europium samples which ranged from micro-molar to milli-molar concentrations.

ICP-AES Methods

Europium(III) concentrations were determined using a Thermo iCap 6000 series inductively coupled plasma - atomic emission spectrometer at a wavelength of 381.967 nm to avoid interferences. Ultra High Purity argon from Praxair was used as the coolant gas, auxiliary gas, and nebulizer gas, while UHP nitrogen from Praxair was used as the purge gas. Three repeats were used on each sample or standard, with a 45 second sample flush and 45 second rinse time between samples. The pump was run at 50 rpm with 5 seconds for stabilization while an interval of 15 seconds was allowed for both axial and radial integration. The torch was run at 1150 W (RF), with 0.5 L/min auxiliary gas flow, 0.51 L/min nebulizer gas flow, and 12 L/min coolant gas flow. Europium standards were prepared from the NIST SRM 3117a reference material at concentrations of 126.9, 42.3, 12.69, 4.23, 1.269, 0.423, 0.1269, and 0.0423 ppm, and were run with a blank prior to analysis of samples as a linearity and instrument calibration check. The instrument had a linear response over the concentration range of the standard dilutions. Samples were prepared for ICP-AES by taking 1.000 mL aliquots from the contact solutions and diluting to 10 mL with DI in 15 mL polypropylene centrifuge tubes from VWR.

Column Elutions

The same Kontes general purpose glass columns used to determine properties of the resins were used for column experiments. These columns had a precision bore 4 mm inner diameter, with a 15 mL reservoir for a total height of 200 mm. Glass wool and acid washed sand were used to create a uniform base onto which wet resin was added. Columns were inspected during the filling for air bubbles, and were resettled if any were present. After filling the columns using DI and resin, the free column volume (FCV) was determined by litmus paper and an appropriate concentration of nitric acid. The FCV was typically 100 µL for a 2 cm bed height (250 µL bed volume), or 200 µL for a 4 cm bed height (500 µL bed volume). After the resin was settled, additional nitric acid was passed through the column to condition the resin. A solution of ~24 Bq of americium(III) in 1 or 2 M nitric acid was used to load activity onto columns, and the eluent was collected for counting. More nitric acid of the appropriate concentration was passed through as a rinse and collected for counting, followed by fixed volume fractions of the appropriate elution solution. Aliquots of 100 µL were sampled from the load, rinse, and each fraction and combined with 10 mL of LSC cocktail in 20 mL vials for counting using liquid scintillation as described above in the section on batch extractions.

Stability Experiments

Solutions from the extraction experiments with BTBP resins were allowed to sit in contact with resin for 4-6 months. The contact time for isobutyl-BTP resins was 6-8 months. If hydrolysis of the extractants occurred during the contact times, the products could have been detected by analyzing the contact solutions. Likewise, if protonation of the extractants occurred, changing the solubility of the ligands in aqueous solutions, evidence of this bleeding could have been found in the aqueous phases.

UV-Vis Spectroscopy Theory

Ultraviolet-Visible Spectroscopy is similar in some ways to IR, but the light used has higher energy and shorter wavelengths which do cause excitation of electrons instead of just vibrational excitation as in IR spectroscopy. Another similarity is that the intensity of the light passing through a blank or background sample is taken as I_0 while the intensity of light which passes through the actual sample is I. An assumption is made in that by adding the sample, the amount of blank material in the beam path is not significantly changed. The ratio of I to I_o is known as the transmittance, which is a common way of displaying data taken using IR. It is possible by taking the opposite of the logarithm of transmittance to convert this to absorbance, which is the preferred unit for UV-Vis spectroscopy. These equations were shown earlier as Equation 6 and Equation 7. When certain assumptions hold true, which they do for the samples analyzed in this work, the Beer-Lambert Law states that the absorbance (A) is equal to the product of the molar absorptivity (ε), path length (l), and concentration (c) as shown in Equation 11.

Equation 11

$$A = \varepsilon * l * c$$

The electrons excited by UV-Vis are generally π electrons, and their excitation to π^* anti-bonding orbitals are allowed transitions, such that these $\pi \rightarrow \pi^*$ transitions exhibit molar absorptivities on the order of 10^4 or higher. While other transitions such as those of non-bonding lone pair or n electrons to π^* anti-bonding orbitals are possible, they are forbidden transitions and exhibit molar absorptivities on the order of 10^2 or less. Extended or conjugated π bonds can increase the absorptivity which results in a hyperchromic shift, and the conjugation will also shift the $\pi \rightarrow \pi^*$ transitions to longer wavelengths which result in bathochromic shifts. Since the BTP and BTBP molecules in this study have conjugated π systems in their cores, they are uniquely suited for concentration analysis by UV-Vis.

UV-Vis Methods

The contact solutions were stored in cabinets within secondary containment, and were periodically checked for leaks. Standards of the isobutyl-BTP, C5-BTBP, and $CyMe_4$-BTBP were examined on a Cary6000i using a double beam method with 0.1 s averaging time, 0.1 nm intervals, and a scan rate of 60 nm/min from 200 to 800 nm. Optical quartz cuvettes with a reduced volume of 700 µL were used with the standard solutions in the front beam with matched background solutions in the second reference beam. The standards as well as the contact solutions along with fractions from the column experiments were examined using a Cary50 UV-Vis with an attached Cary 50 MPR micro-plate reader, using the same settings as the Cary6000i, but with a scan rate of 600 nm/min over 1 nm intervals. Corning Costar 96-well flat-bottom UV micro-plates were used which had well volumes of 370 µL and were filled with 174 µL of solution resulting in a geometrically calculated solution path length of 0.5 cm.

ESI-MS Theory

The ElectroSpray Ionization Mass Spectrometer was used to determine whether molecules of interest were present in the contact solutions. The solvated samples were forced through a thin tube, at the end of which a large electric potential was applied, causing charged droplets to form as the solution exited the tube. These charged droplets passed through a nitrogen drying gas, causing solvent to evaporate while the higher mass solute remained charged and passed through skimmer cones into the mass-spectrometer. The lack of a plasma in the sample introduction process prevented excessive fragmentation of larger molecules, which increased the efficiency for measurement of the unfragmented molecule. The intensity of detected molecules was displayed versus the mass to charge ratio, which for singly charged ions is equal to the mass of the ion. These spectra were used to determine if bleeding of extractant from the resin in batch or column experiments was occurring.

ESI-MS Methods

Fractions from the column experiments and some of the batch contact solutions were analyzed by a MSQ™ Plus Electro-spray Ionization Mass Spectrometer (ESI-MS) with a 3 kV needle potential and 30 V cone potential for BTP, and a 4 kV needle potential and 50 V cone potential for BTBP samples. The 1176 V potential on the detector, 350 °C probe temperature, and 200 µL/min sample flow were constant for all samples. The drying gas was nitrogen which was supplied by a Dionex Nitrogen Generator. Settings were chosen based on prior work in literature on isobutyl-BTP [76,99], and C5-BTBP and CyMe$_4$-BTBP complexes.[100] The mass ranges for scans varied, but were wide enough to allow the main molecular peak and any large fragments to be visible. In addition, the range for the BTBP molecules generally allowed for several L_2M^{++} peaks to be observed, where M was a 3d transition metal. Methanol was run as a background for all samples since it was the only solvent for the BTBP standards, and it was the majority of the solvent in the BTP standard. Water was the other solvent in the BTP standard and was already a component of the 50/50 acetonitrile/water elution solution. Injections were 100 µL to ensure complete filling of the 10 µL sample loop. After manually starting collection on the Xcalibur software package, the manual injection port was turned to select the sample loop, and data collection was allowed to continue for

2 minutes, or as long as necessary for molecular peaks to reach background levels. When data collection was stopped, the injection port was turned to the load position and the next sample was injected. All standards and samples were run at least twice.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION

DMDBTDMA

The malonamide DMDBTDMA was coated onto Amberchrom CG-71 using either hexane, acetone, or methanol to dissolve the ligand. The resin prepared with hexane used 0.5055 g Amberchrom mixed with 0.1014 g of DMDBTDMA for a theoretical weight loading of 16.7%. The resin prepared with acetone consisted of 0.5269 g Amberchrom mixed with 0.1025 g DMDBTDMA for a theoretical weight loading of 16.3%. The resin prepared with methanol consisted of 0.5173g Amberchrom mixed with 0.1038 g DMDBTDMA for a theoretical weight loading of 16.7%. The effect of the solvent used was investigated by screening each resin for americium(III) extraction in single replicate batch experiments. The weight distribution ratio is used to display the results since the *k'* conversion factors were not determined for these initial resins due to the limited amounts of material available. Results for the initial screening of the resins are shown in Figure 6, and the open points represent data for DMDBTDMA resins. Several points are not displayed, because the activity remaining in solution was equivalent to the control signifying there was no extraction. The values calculated for D_w using Equation 9 are generally less than 10, however the resin prepared in methanol approached a D_w of 10 at 4 M nitric acid. Because the results were lower than expected based on a similar malonamide coated on the same resin with a larger particle size,[47] the resins were analyzed again using four replicates. Despite the greater number of samples the results obtained as shown in Figure 7 were no more favorable. While several points have D_w ~20, just as many sample sets showed no extraction. Because these results were unfavorable for the DMDBTDMA resin, especially when compared with the results for the isobutyl-BTP resin discussed later, it was determined that no further investigation would be made of the DMDTBDMA resin, and no more batches of this resin were prepared.

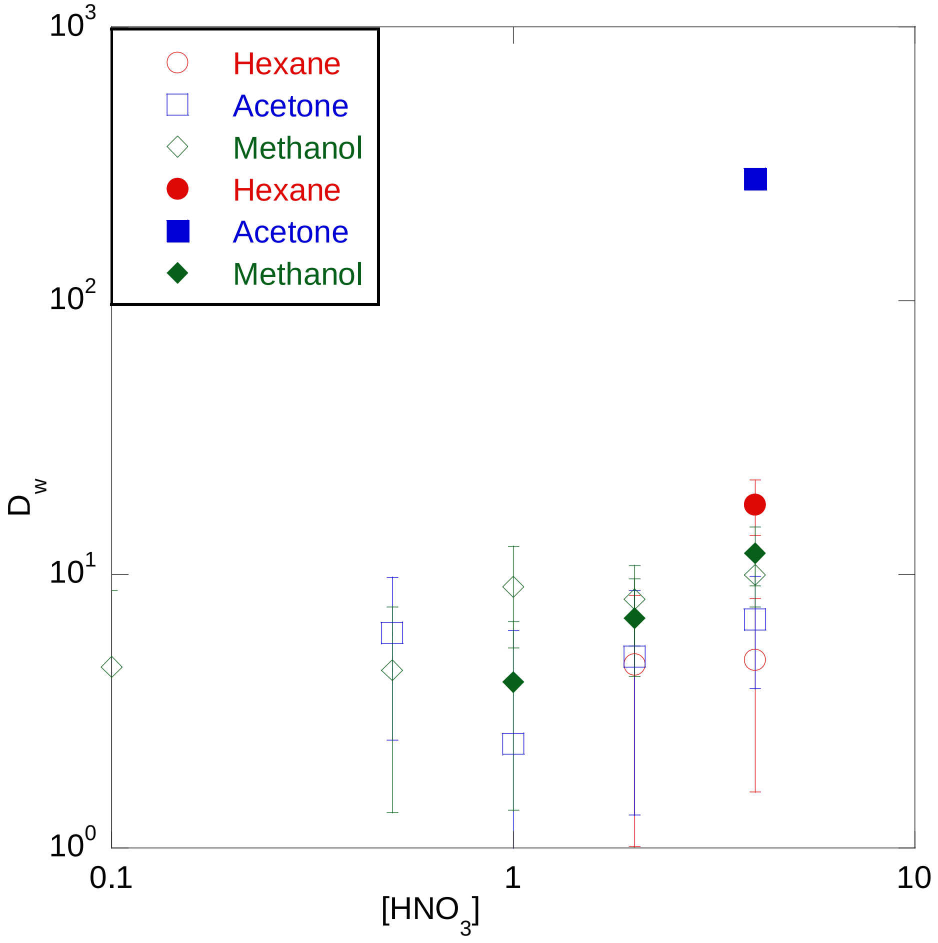

Figure 6 Extraction of Am(III) by single replicates of malonamides.

Open for DMDBTDMA and Closed for DMDOHEMA. Negative values are omitted. See Table 10 in the Appendix for data.

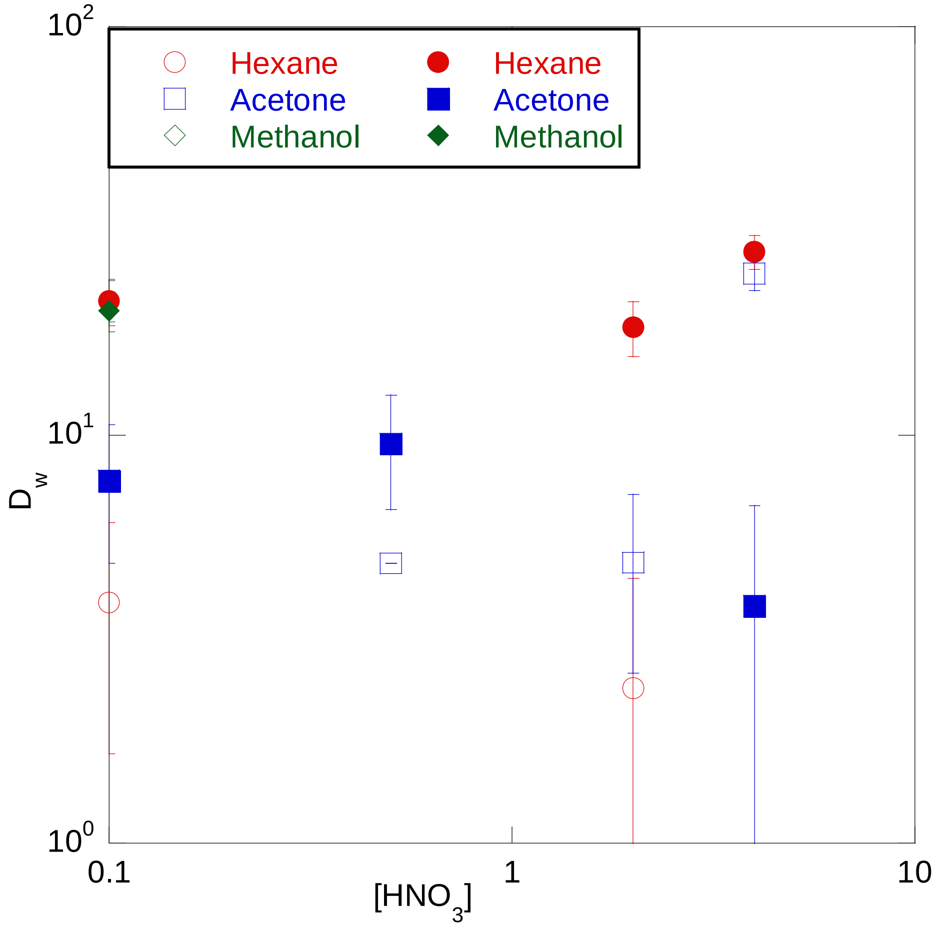

Figure 7 Extraction Data for Am(III) on Malonamide Resins with multiple replicates. Open for DMDBTDMA and Closed for DMDOHEMA. Negative values are omitted. See Table 11, Table 12, and Table 13 in the Appendix for data.

DMDOHEMA

The malonamide DMDOHEMA was coated onto Amberchrom CG-71 using either hexane, acetone, or methanol to dissolve the ligand. The resin prepared with hexane used 0.5280 g Amberchrom mixed with 0.1075 g of DMDBTDMA for a theoretical weight loading of 16.9%. The resin prepared with acetone consisted of 0.5546 g Amberchrom mixed with 0.1035 g DMDBTDMA for a theoretical weight loading of

15.7%. The resin prepared with methanol consisted of 0.6335g Amberchrom mixed with 0.1115 g DMDBTDMA for a theoretical weight loading of 15.0%. The effect of the solvent used was investigated by screening each resin for americium(III) extraction in single replicate batch experiments. The weight distribution ratio is used to display the results since the *k'* conversion factors were not determined for these initial resins due to the limited amounts of material available. Results for the initial screening of the resins are shown in Figure 6, and the closed points represent data for DMDOHEMA resins. Several points are not displayed, because the activity remaining in solution was equivalent to the control signifying there was no extraction. The values calculated for D_w using Equation 9 are generally less than 10, however the resin prepared in acetone exhibited a D_w of over 100 at 4 M nitric acid, with no extraction at any other acid concentration. Because the results were lower than expected based on the same malonamide coated on the same resin with a larger particle size,[47] the resins were analyzed again using four replicates. Despite the greater number of samples the results obtained as shown in Figure 7 were no more favorable. While several points have D_w ~20, just as many sample sets showed no extraction. Because these results were unfavorable for the DMDOHEMA resin, especially when compared with the results for the isobutyl-BTP resin discussed later, it was determined that no further investigation would be made of the DMDOHEMA resin, and no more batches of this resin were prepared.

Isobutyl-BTP

Three batches of isobutyl-BTP resin were prepared using either hexane, acetone, or methanol to dissolve the BTP ligand. The resin prepared with hexane used 0.5020 g Amberchrom mixed with 0.0458 g of BTP for a theoretical weight loading of 8.36%. The resin prepared with acetone consisted of 0.5581 g Amberchrom mixed with 0.0490 g BTP for a theoretical weight loading of 8.07%. The resin prepared with methanol consisted of 0.6178g Amberchrom mixed with 0.0538 g BTP for a theoretical weight loading of 8.01%. The effect of the solvent used was investigated by screening each resin for americium(III) extraction in single replicate batch experiments. The weight distribution ratio is used to display the results since the *k'* conversion factors were not determined for these initial resins due to the limited amounts of material available. As shown in Figure 8, there were differences in the resin performance related to the solvent. These differences may arise from the varied solubility of the BTP; those solvents in which BTP was more soluble retained more of the ligand during the evaporation of the solvent, preventing a small amount of BTP from binding to the resin, effectively lowering the weight loading. For successive batches of the isobutyl-BTP resin, hexane was used to dissolve the BTP ligand.

Higher and lower weight loadings of the isobutyl-BTP onto resin were investigated using hexane to dissolve the extractant. The amounts used to prepare the resins were 0.5648 g of Amberchrom with 0.0245 g BTP, and 0.2470 g Amberchrom with 0.0494 g BTP which would result in theoretical weight loadings of 4.16% and 16.7% respectively. Extraction was determined in triplicate for americium(III) on these two resins and the resin prepared from hexane earlier with weight loadings of 4.16%, 8.36%, and 16.7%. Weight distribution ratios are again used in displaying the results since many of the physical properties were not determined for these initial batches of resin due to limited amounts of material.

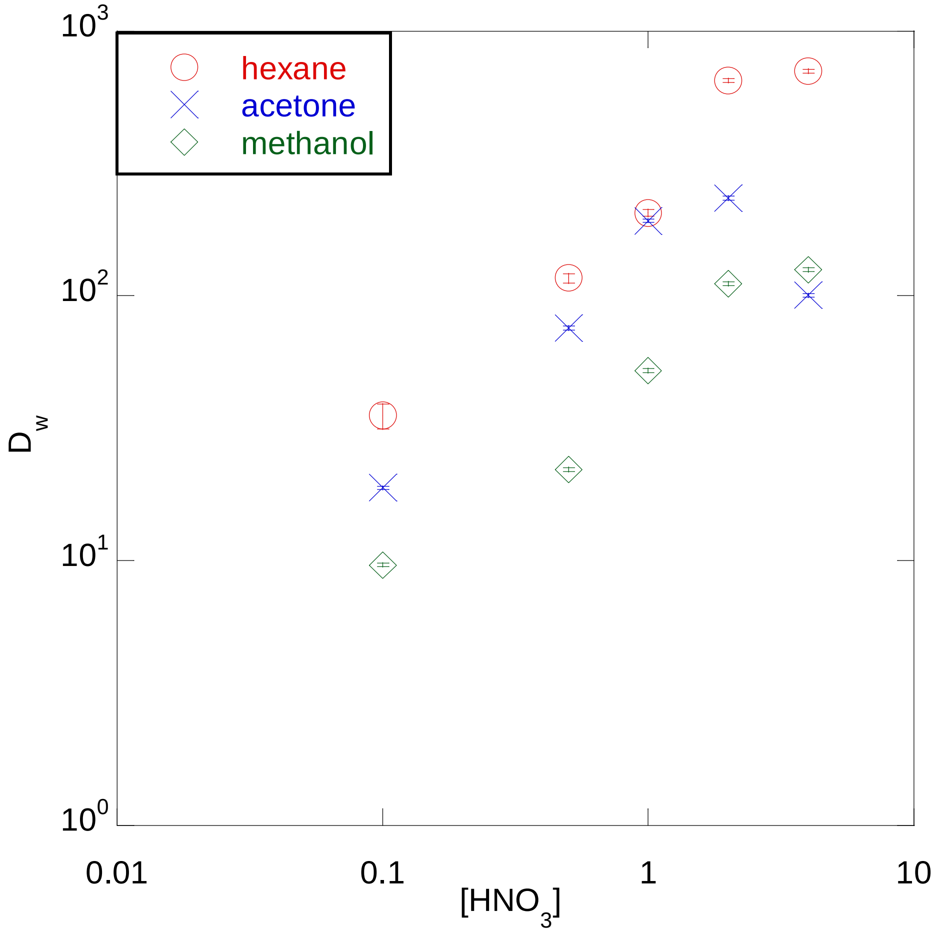

Figure 8 Extraction of Am(III) by isobutyl-BTP resin as a function of the solvent used in preparation and the initial nitric acid concentration.

See Table 14 in the Appendix for data.

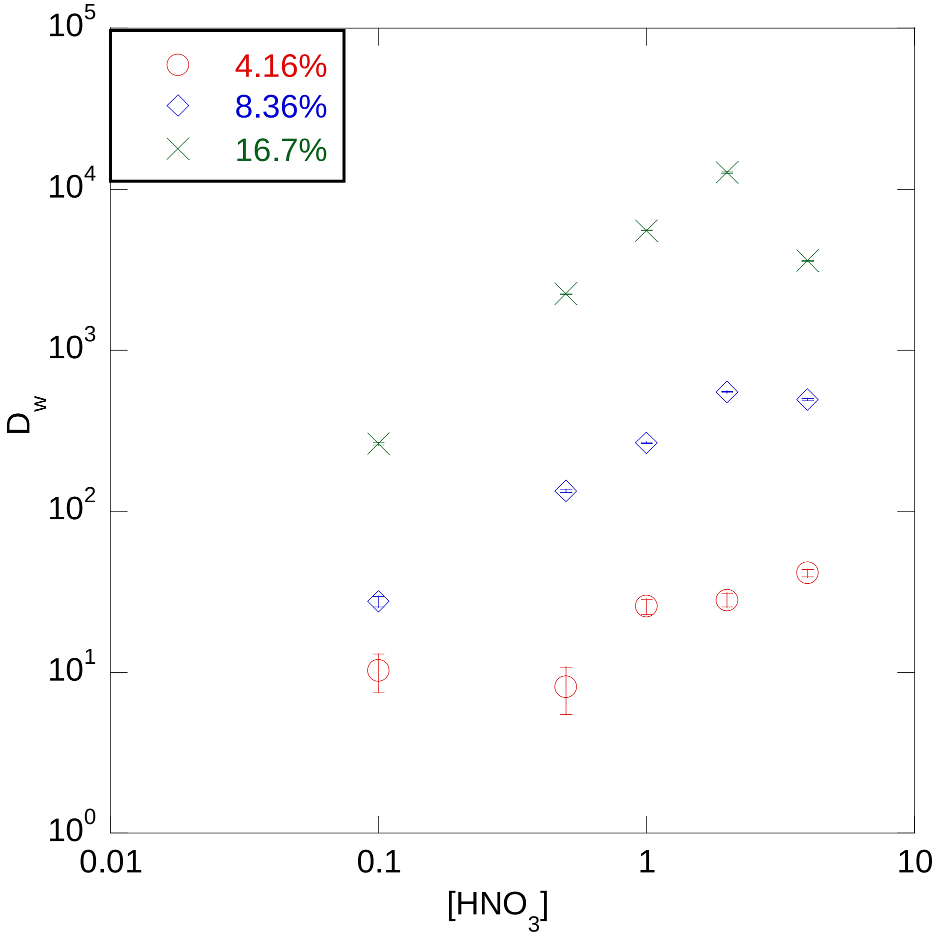

Figure 9 Extraction of Am(III) by isobutyl-BTP resin as a function of weight percent of extractant and the initial nitric acid concentration.

See Table 15 in the Appendix for data.

Based on the extraction data from different solvents and different weight loadings, hexane was used to prepare a larger batch of the 16.7% isobutyl-BTP resin for further characterization. Elemental analysis was performed on this resin, and the results for the uncoated resin were 62.5% C, and 7.60% H with no N detected. The coated resin had 62.6% C, 7.73 % H, and 3.28 % N, which allowed the weight loading of isobutyl-BTP to be calculated as 15.4%, close to the theoretical 16.7%. Physical properties were also determined for the coated resin based on the density of the ligand as 1.055 g/cm^3 from calculations using Advanced Chemistry Development Software V8.19 (1994-2010 ACD/Labs).[101] The resin density was 1.257 g/cm^3, the bed density was 0.244 g/cm^3, while the V_s was 0.0356 mL/mL bed and the V_m was 0.808 mL/mL bed. Based on these parameters and Equation 10, the weight distributions could be converted to *k'* by multiplying by 0.302. This factor was used in further characterization of the resin since all other experiments made use of this single batch of isobutyl-BTP resin with 15.4% weight loading of isobutyl-BTP.

In comparing the properties which contribute to the *k'* conversion factor with published literature values for some other extraction chromatography resins, the volume of the mobile phase relative to the bed volume (V_m) is comparable, especially when compared to those resins which make use of the Amberchrom CG-71 support. However, the value for the volume of the extracting phase relative to the bed volume (V_s) seems rather low. The value of 0.0356 for V_s obtained in this work is not comparable to the values of 0.17 or 0.146 for Eichrom's DGA and Sr-Spec resins respectively.[97,102] This discrepancy in otherwise similar systems is likely due to a combination of factors including the lower weight loading of 15.4% for the isobutyl-BTP resin compared to 40% for both DGA and Sr-Spec, the higher density of 1.055 g/cm^3 for the isobutyl-BTP ligand compared to 0.88 g/cm^3 and 0.912g/cm^3 for TODGA and the di-tertbutyl-18-crown-6 solution in 1-octanol respectively, the fact that the isobutyl-BTP is a solid at room temperature while TODGA is a liquid and the crown is dissolved in octanol, and the lower bed density from gravity flow of 0.244 g/cm^3 for isobutyl-BTP compared to pressurized flow resulting in 0.38 g/cm^3 and 0.33 g/cm^3 for DGA and Sr-Spec respectively.[97,102] Despite these differences above and the lower *k'* conversion factor, the isobutyl-BTP resin still achieved an extraction of americium(III) close to that of the DGA resin.[102]

The surfaces of the uncoated and coated resin were examined by ATR-IR. Excluding the large difference in carbon dioxide (~2400 cm^{-1}) associated with each sample shown in Figure 10, the only significant differences are near 1000 cm^{-1}, suggesting that the majority of the BTP has penetrated the pores of the resin.

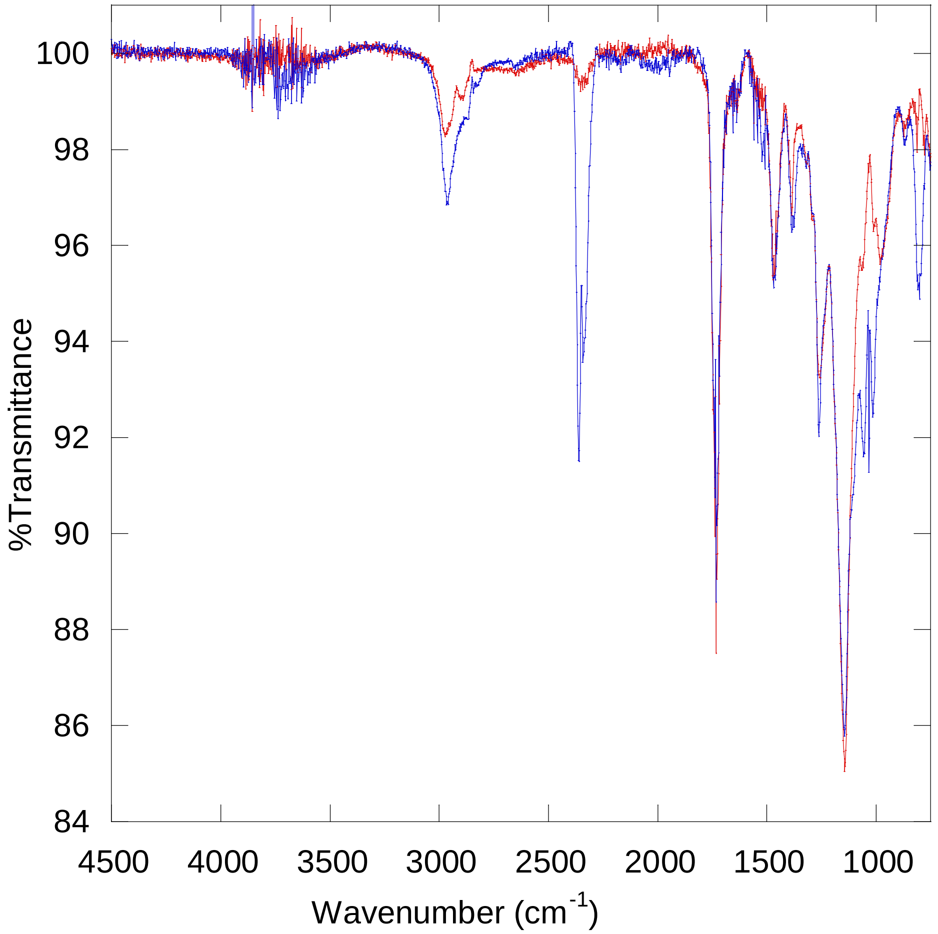

Figure 10 ATR-FT-IR Transmittance of coated (blue) and uncoated (red) isobutyl-BTP resin.

C5-BTBP

The extractant C5-BTBP was coated onto three different solid supports. Amberchrom CG-71, Amberlite XAD-4 and Amberlite XAD-7HP were used. The C5-BTBP had very poor solubility in hexane which had been chosen as the solvent for the isobutyl-BTP resin. Attempts were made to coat using pure methanol and mixtures of methanol and hexane. The pure methanol coated the resin with C5-BTBP while leaving the least excess of unbound extractant behind with the resin, which was a problem when using the methanol/hexane mixtures. Because of these observations, all three resins were prepared using pure methanol to dissolve the extractant. The amount of uncoated resin used was 378 mg, 369 mg, and 630 mg, with 61 mg, 37 mg, and 69 mg of extractant resulting in theoretical weight loadings of 13.9%, 9.11% and 9.86% for the CG-71, XAD-4, and XAD-7HP resins respectively. Physical properties of the uncoated resins are summarized in Table 1. The coated and uncoated resins were analyzed, and the data from elemental analysis is reported in Table 2 along with the elemental mass percents of C5-BTBP for comparison. Based on the elemental analysis, resin weight loadings were calculated and are displayed together with the measured surface areas of the coated resins in Table 3. The elemental analysis, weight loading, and surface area data for the coated Amberchrom resin listed is for the final batch of resin which had a theoretical weight loading of 9.90% and was prepared on this solid support for the reasons discussed below.

Each of the coated resins was tested for extraction with americium(III) in triplicate. The weight distribution ratio is used to display the results since the *k'* conversion factors were not determined for these initial resins due to the limited amounts of material available. As shown in Figure 11, there were differences in extraction behavior based on the resin used as the solid support. Since some unbound extractant was observed with the CG-71 resin during extraction and column experiments, the theoretical weight loading of 13.9% is probably high. The aromatic XAD-4 resin extracted americium(III) much more poorly than either XAD-7HP or the CG-71. This large difference in extraction is thought to be related to the binding mechanism between the extractant and the resin. Since the XAD-4 consists of an aromatic polymer, the polymer interacts more with the aromatic core of the C5-BTBP than with its aliphatic side chains. Because the N-donors involved in actinide extraction are co-located with the aromatic core, the C5-BTBP is prevented from assuming favorable confirmations for extraction of actinides from solution. The final batch of C5-BTBP on Amberchrom CG-71 was prepared using 0.675 g of extractant with 6.145 g of uncoated resin, yielding a theoretical weight loading of 9.90%. While the XAD-7 and CG-71 coated resins had actual weight loadings approximately 1% lower than theoretical due to the inability of all extractant to bind to the resin, the almost exact agreement between the theoretical and actual weight loadings of the XAD-4 resin agree with the explanation of binding and lowered extraction by the XAD-4 resin.

Table 1 Physical Properties of Uncoated Resins.

Resin	Matrix	Mean Diameter	Surface Area Lit.	Surface Area Meas.	Pore Size
Amberchrom CG-71	acrylic ester	75 µm	500 m^2/g	580 m^2/g	250 Å
Amberlite XAD-4	aromatic	490-690 µm	750 m^2/g	850 m^2/g	140 Å
Amberlite XAD-7 HP	aliphatic acrylic	560-710 µm	380 m^2/g	430 m^2/g	370 Å

Table 2 Elemental Analysis Results of Uncoated and C5-BTBP Coated Resins

Element	Amberchrom CG-71		Amberlite XAD-4		Amberlite XAD-7HP		C5-BTBP
	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Theor.
C	62.36%	63.55%	90.93%	89.66%	62.47%	62.50%	72.69%
H	8.00%	8.06%	7.90%	8.14%	7.86%	8.00%	8.48%
N	0.00%	1.67%	0.15%	1.86%	0.00%	1.50%	18.83%

Table 3 Physical Properties of C5-BTBP Coated Resins.

Coated Resins	Amberchrom CG71	Amberlite XAD4	Amberlite XAD7HP
Weight Loading	8.87%	9.15%	7.96%
Surface Area	411 m^2/g	642 m^2/g	317 m^2/g

The batches with CG-71 and XAD-7HP resulted in similar amounts of americium(III) extracted, however the trends were different as the XAD-7HP exhibited peak extraction at a lower nitric acid concentration than the CG-71. For this reason, as well as the more desirable physical properties of the CG-71 resin for column preparation, subsequent observations were made only with the C5-BTBP coated onto Amberchrom CG-71. While the data for surface area was included in this section with the other physical properties of the resins, these analyses were not done until after most other work with the final batch of resin had taken place, and will be discussed in a later section.

Physical properties were also determined for the coated resin based on the density of the ligand as 1.061 g/cm^3 from calculations using Advanced Chemistry Development Software V9.02 (1994-2010 ACD/Labs).[101] The resin density was 1.273 g/cm^3, the bed density was 0.273 g/cm^3, while the V_s was 0.0228 mL/mL bed and the V_m was 0.789 mL/mL bed. Based on these parameters and Equation 10, the weight distribution ratios found for the C5-BTBP resin could be converted to *k'* by multiplying by 0.346. This factor was used in further characterization of the resin since all other experiments made use of this single batch of C5-BTBP resin with 8.87% weight loading. While this factor and other column characteristics are very different from literature values on other resins, the solid properties of the extractant being the main reason for this difference from liquid or solvated extractants that was already discussed earlier in this work.

As was the case with the isobutyl-BTP resin, the IR spectra of coated and uncoated resin shown in Figure 12 do not have any noticeable difference. This is most likely due to the extractant penetrating the pores of the resin, becoming inaccessible to spectroscopic analysis at the surface. While this was also a reason why the first resin did not show much difference, the difference at 1000 cm^{-1} that was observed previously may have been due to the higher weight loading of the isobutyl-BTP resin at 15.4% compared to 8.87% for this C5-BTBP resin, or it could have been a unique stretch.

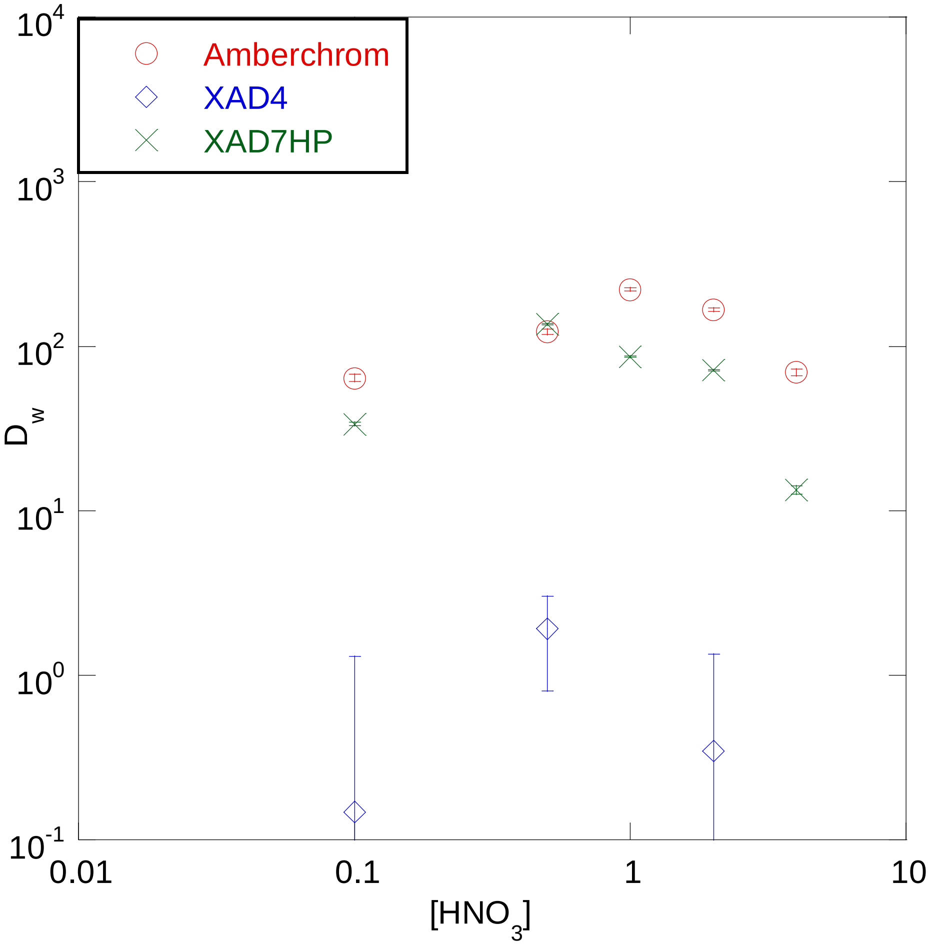

Figure 11 Extraction of Am(III) by C5-BTBP on a variety of solid supports. Negative values are omitted. See Table 16 in the Appendix for data.

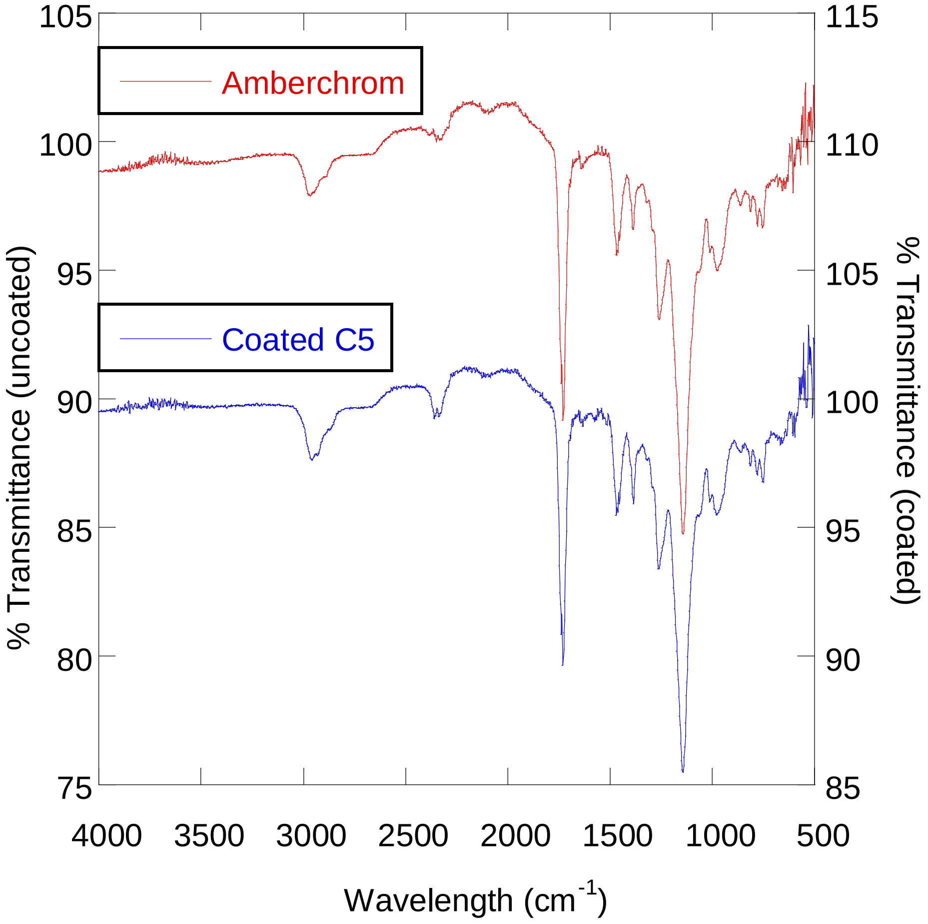

Figure 12 IR of Amberchrom CG-71 with and without C5-BTBP coating.

CyMe$_4$-BTBP

The extractant CyMe$_4$-BTBP was coated onto three different solid supports; Amberchrom CG-71, Amberlite XAD-4 and Amberlite XAD-7HP were used. Since pure methanol provided the best results for coating C5-BTBP onto resin, it was again used to coat CyMe$_4$-BTBP onto the backbones. The uncoated resin masses used were 555 mg, 591 mg, and 630 mg, with 59 mg, 67 mg, and 70 mg of extractant resulting in theoretical weight loadings of 9.61%, 10.18%, and 10.00% on CG-71, XAD-4, and XAD-7HP respectively. At the time of their preparation, no unbound extractant was observed in any of the resin batches. Physical properties of the uncoated resins were previously summarized in Table 1. The coated and uncoated resins were analyzed, and the data from elemental analysis is reported in Table 4 along with the elemental mass percents of CyMe$_4$-BTBP for comparison. Based on the elemental analysis resin weight loadings were calculated and are displayed with the measured surface areas of the coated resins in Table 5. It should be noted that the elemental analysis, weight loading, and surface area data for the coated Amberchrom resin listed is for the final batch of resin which was prepared on this solid support for the reasons discussed below.

Table 4 Elemental Analysis Results of Uncoated and CyMe$_4$-BTBP Coated Resins

Element	Amberchrom CG-71		Amberlite XAD-4		Amberlite XAD-7HP		CyMe$_4$-BTBP
	Uncoated	Coated	Uncoated	Coated	Uncoated	Coated	Theor.
C	62.36%	63.94%	90.93%	89.79%	62.47%	62.88%	71.88%
H	8.00%	8.04%	7.90%	8.08%	7.86%	7.99%	7.16%
N	0.00%	2.10%	0.15%	1.85%	0.00%	1.43%	20.96%

Table 5 Physical Properties of CyMe$_4$-BTBP Coated Resins.

Coated Resins	Amberchrom CG-71	Amberlite XAD-4	Amberlite XAD-7HP
Weight Loading	9.98%	8.15%	6.82%
Surface Area	571 m^2/g	533 m^2/g	346 m^2/g

Each of the coated resins was tested for extraction with americium(III) in triplicate. The weight distribution ratio is used to display the results since the *k'* conversion factors were not determined for these initial resins due to the limited amounts of material available. As shown in Figure 13, there were differences in extraction behavior based on the resin used as the solid support. The aromatic XAD-4 resin extracted americium(III) an order of magnitude less than either XAD-7HP or the CG-71. This large difference in extraction is similar again to the difference observed with the C5-BTBP extractant on XAD-4, and lends further credence to the earlier explanation of decreased extraction relative to the other resins.

The batches with CG-71 and XAD-7HP resulted in similar amounts of americium(III) extracted; peak D_w values were however larger by ~1000 for XAD7HP resin compared to CG-71. On the other hand, both resins showed decreased extraction for acid concentrations above 2 M. Based on the trend observed from 0.1 to 1 M acid, it appears that extraction is already falling off by 2 M. Because the other two extractants investigated were coated onto the CG-71 backbone, and also because of the more desirable physical properties of the CG-71 resin for column preparation, subsequent observations were made only with the $CyMe_4$-BTBP coated onto Amberchrom CG-71. The final batch of resin was prepared using 0.830 g of extractant with 7.470 g of resin for a theoretical weight loading of 10.0%. This is extremely close to the 9.98% determined by elemental analysis because while no unbound resin was observed after the resin was prepared, some was observed when other studies with the resin were carried out. Because the other batches of resin for all extractants typically displayed weight loadings lower than the theoretical values, it is likely that the actual weight loading of the resin used is less than 9.98%.

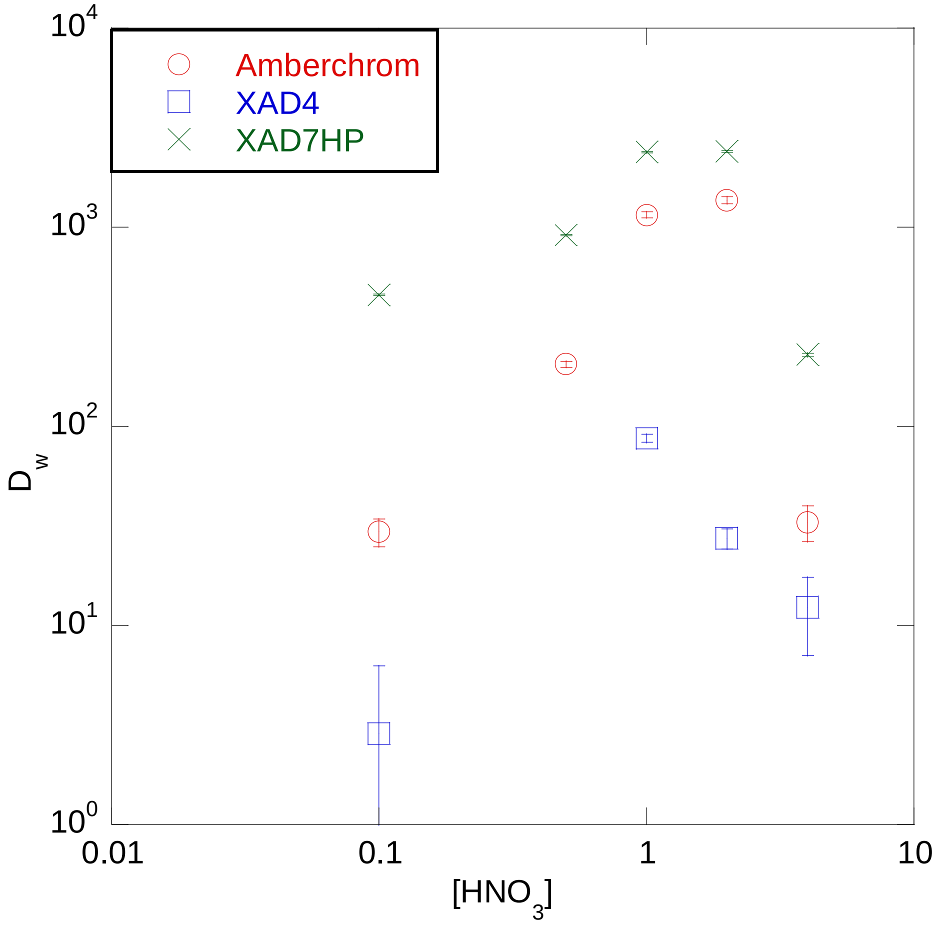

Figure 13 Extraction of Am(III) by CyMe$_4$-BTBP on a variety of solid supports. Negative values are omitted. See Table 17 in the Appendix for data.

Physical properties were also determined for the coated resin based on the density of the ligand as 1.117 g/cm^3 from calculations using Advanced Chemistry Development Software V9.02 (1994-2010 ACD/Labs).[101] The resin density was 1.145 g/cm^3, the bed density was 0.285 g/cm^3, while the V_s was 0.0255 mL/mL bed and the V_m was 0.750 mL/mL bed. During the determination of resin density and column parameters it became clear that a small amount of unbound extractant was present in the final batch of the CyMe$_4$-BTBP resin, and this unbound extractant could have influenced all of the measurements on the resin. Based on the measured parameters and Equation 10, the weight distribution ratios found for the CyMe$_4$-BTBP resin could be converted to *k'* by multiplying by 0.381. This factor was used in further characterization of the resin since all other experiments made use of this single batch of CyMe$_4$-BTBP resin with 9.98% weight loading. While this factor and other column characteristics are very different from literature values on other resins, they are very similar to the other resins discussed in this work, and the solid properties of the extractant being the main reason for this difference from liquid or dissolved extractants was discussed earlier in this work.

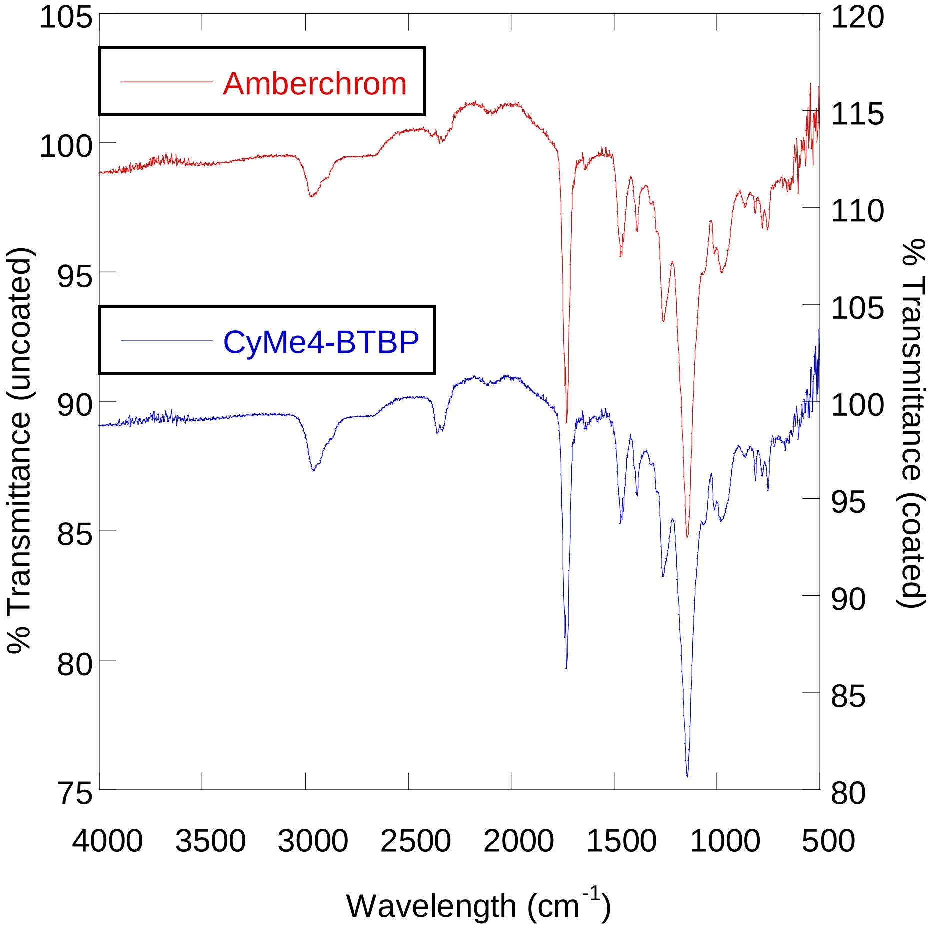

Figure 14 IR of Amberchrom CG-71 with and without CyMe$_4$-BTBP coating.

As was the case with the isobutyl-BTP resin, the IR spectra of coated and uncoated resin shown in Figure 14 do not have any noticeable difference. This is most likely due to the extractant penetrating the pores of the resin, becoming inaccessible to spectroscopic analysis at the surface.

Surface Area and Extraction

The surface area of each resin was measured three times, and averaged to determine the values reported in Table 1, Table 3, and Table 5. It should be noted that the coating procedure decreased the surface area of all resins. The surface are of the resins coated with C5-BTBP ranged from 71-76% of the uncoated surface area. The surface areas of the $CyMe_4$-BTBP resins varied from 63-99% of the uncoated surface area. The 1% change in surface area observed for the $CyMe_4$-BTBP on CG-71 could have been a result of the presence of unbound extractant, or it could have been a result of the higher weight loading. Despite the lower surface area and the lower weight loading of the $CyMe_4$-BTBP XAD-7HP resin (346 m^2/g, 6.82%) compared to the $CyMe_4$-BTBP CG-71 resin (571 m^2/g, 9.98%), more americium(III) was extracted by the former. This greater extraction could be due to the larger pore sizes of the resin, or it could be due to a greater abundance of paired BTBP’s on the surface of the resin. It has been previously reported that americium(III) forms bis-complexes with $CyMe_4$-BTBP.[103] For the C5-BTBP on CG-71 and XAD-7HP there is a smaller difference in the surface areas of the coated resins when compared to each other, so the density of ligand on the surfaces would be more similar, and this could be responsible for the more closely related extraction behavior with americium(III). Other than these observations, there are no other clear relationships between the surface area and the extraction behavior that would indicate a large influence of one over the other.

After the extractants isobutyl-BTP, C5-BTBP, and CyMe$_4$-BTBP were screened in the manner described above for americium(III) extraction, all three ligands were coated onto Amberchrom CG-71 for further characterization. The results from these more intensive batch extractions as well as column studies and stability studies are discussed in the following Chapters 4, 5 and 6.

CHAPTER 4

BATCH STUDY RESULTS

Isobutyl-BTP

The isobutyl-BTP ligand was used in this research because of prior work discussed earlier showing its effectiveness for actinide-lanthanide separations. To characterize the performance of this ligand as a coating for extraction chromatography the interaction of some trivalent actinides and europium with the prepared resin was investigated. Shown in Figure 15 are the results for the extraction of americium(III), curium(III), europium(III), and plutonium(IV) in nitric acid. Plutonium(IV) was included because of its importance in forensic and other analytical separations, and since much of the prior work on isobutyl-BTP in solvent extraction has excluded plutonium due to the focus on the conditions present in the Selective Actinide Extraction (SANEX) process. Since the plutonium stock solution used consisted of a dissolved tetravalent chloride and no special steps were taken to control the oxidation state, the plutonium was considered to be in the tetravalent state, which predominates in acidic solutions at the concentrations used in these experiments.[104]

Matrix effects were further explored by testing the extraction of americium(III), curium(III), europium(III), and plutonium(IV) in hydrochloric acid. These results are displayed in Figure 16, and show that all extraction is diminished by two to three magnitudes in the presence of hydrochloric acid relative to the extraction in nitric acid, due to the weaker binding of chloride with actinides. In many of the extraction samples in hydrochloric acid there was no detectable difference in the metal concentration between the sample and the control, so no D_w or *k'* could be calculated and those points are not displayed.

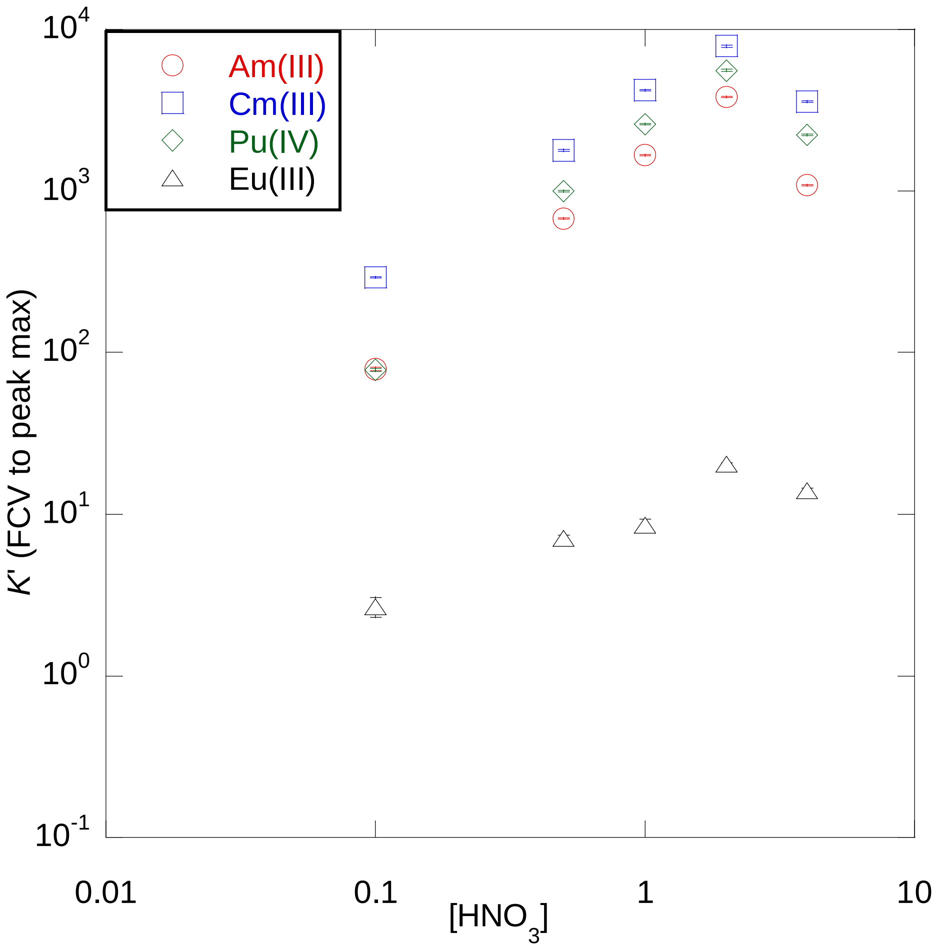

Figure 15 Extraction of Am(III), Cm(III), Eu(III), and Pu(IV) by isobutyl-BTP resin as a function of initial nitric acid concentration.

See Table 18 in the Appendix for data.

Based on the observed trends in extraction of americium(III), curium(III), europium(III), and plutonium(IV) from both nitric and hydrochloric acids, the effectiveness of the isobutyl-BTP ligand for actinide-lanthanide separations was confirmed, and it is proposed that this resin could be used for such separations on analytical samples. The separation factors of ~190 for americium(III) over europium(III) are greater with the isobutyl-BTP resin than ~100 with 1.9 M $(H,NH_4)NO_3$ contacted with isobutyl-BTP in a TPH diluent as measured by Kolarik.[73] Other separation factors of interest are shown in Table 6. There are no errors given for the americium(III) separation from nitric to hydrochloric acid due to the rather significant errors associated with the k' values under 1. Based on the decreased extraction performance at 4 M HNO_3, 2 M acid was used for loading activity in the column studies.

Table 6 Separation Factors Using Isobutyl-BTP Resin.

Elements used to calculate separation factors with (acid)	Am / Eu (HNO_3)	Am / Cm (HNO_3)	Am / Pu (HNO_3)	Am (HNO_3) / Am (HCl)
2 M	187.1±5.2	0.49±0.01	0.69±0.02	4440.3
1 M	195.2±4.2	0.40±0.01	0.64±0.01	2601.2

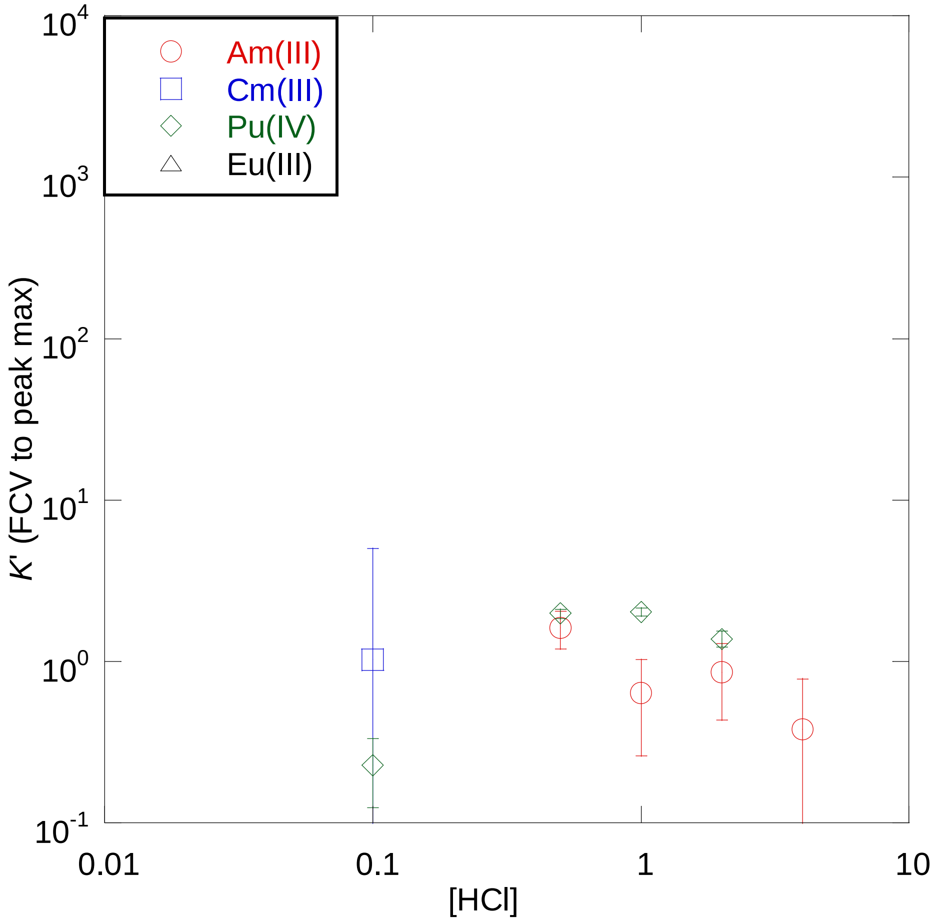

Figure 16 Extraction of Am(III), Cm(III), Eu(III), and Pu(IV) by isobutyl-BTP resin as a function of initial hydrochloric acid concentration.

Negative values are omitted. See Table 19 in the Appendix for data.

C5-BTBP

The C5-BTBP ligand was used in this research because of prior work showing its effectiveness for actinide-lanthanide separations. Select trivalent actinides and europium were used to characterize the performance of this ligand as a coating for extraction chromatography. Shown in Figure 17 are the results for extraction of americium(III), curium(III), europium(III), and plutonium(IV) in nitric acid.

The extraction of americium(III), curium(III), europium(III), and plutonium(IV) in hydrochloric acid was also observed to study matrix effects. These results are displayed in Figure 18, and show that all extraction is diminished by an order of magnitude in the presence of hydrochloric acid relative to the extraction in nitric acid, again due to the weaker association of chloride with actinides. In many of the extraction samples in hydrochloric acid there was no detectable difference in the metal concentration between the sample and the control, so no D_w or *k'* could be calculated and those points are not displayed. There was no detectable extraction of plutonium(IV) at any concentration of HCl. Likewise, there was no detectable extraction of europium(III) at some of the nitric acid concentrations.

The extraction of americium(III) drops from a *k'* of ~77 at 1 M HNO_3 to ~58 at 2 M HNO_3, to ~24 by 4 M HNO_3. The extraction of plutonium(IV) and curium(III) also decreases in 4 M HNO_3. This decrease in extraction could have been due to bleeding of the extractant, or protonation of the ligand on the resin, and will be further discussed when stability of the resin is addressed.

Based on the observed trends in the extraction of americium(III), curium(III), europium(III), and plutonium(IV) from both nitric and hydrochloric acids, the effectiveness of the C5-BTBP ligand for actinide-lanthanide separations at equilibrium was confirmed. Separation factors are displayed in Table 7, and where a k' was unavailable due to a lack of observed extraction, the average of the nearest neighbors was used to calculate the separation factor. Compared to literature values on C5-BTBP in solvent extraction, the separation factor for americium(III)/europium(III) at 1 M HNO_3 of ~40 is lower than the values reported by Foreman of 180 and Nilsson of 150 for 0.015 M C5-BTBP in octanol-kerosene and 0.005 M C5-BTBP in cyclohexanone respectively.[84,88] However, the separation factor for americium(III)/curium(III) at 1 M HNO_3 of 2.7±0.1 is greater than the 1.8 reported by Nilsson for 0.005 M C5-BTBP in cyclohexanone.[84] Based on the more favorable separation factors as well as decreased extraction at higher acidities, 1 M HNO_3 was used for loading activity in the column studies.

Table 7 Separation Factors Using C5-BTBP Resin.

Elements used to calculate separation factors with (acid)	Am / Eu (HNO_3)	Am / Cm (HNO_3)	Am / Pu (HNO_3)	Am (HNO_3) / Am (HCl)
2 M	29.7±3.4	1.8±0.1	0.41±0.01	26.3±15.2
1 M	41.1±5.8	2.7±0.1	1.17±0.03	30.7±16.2

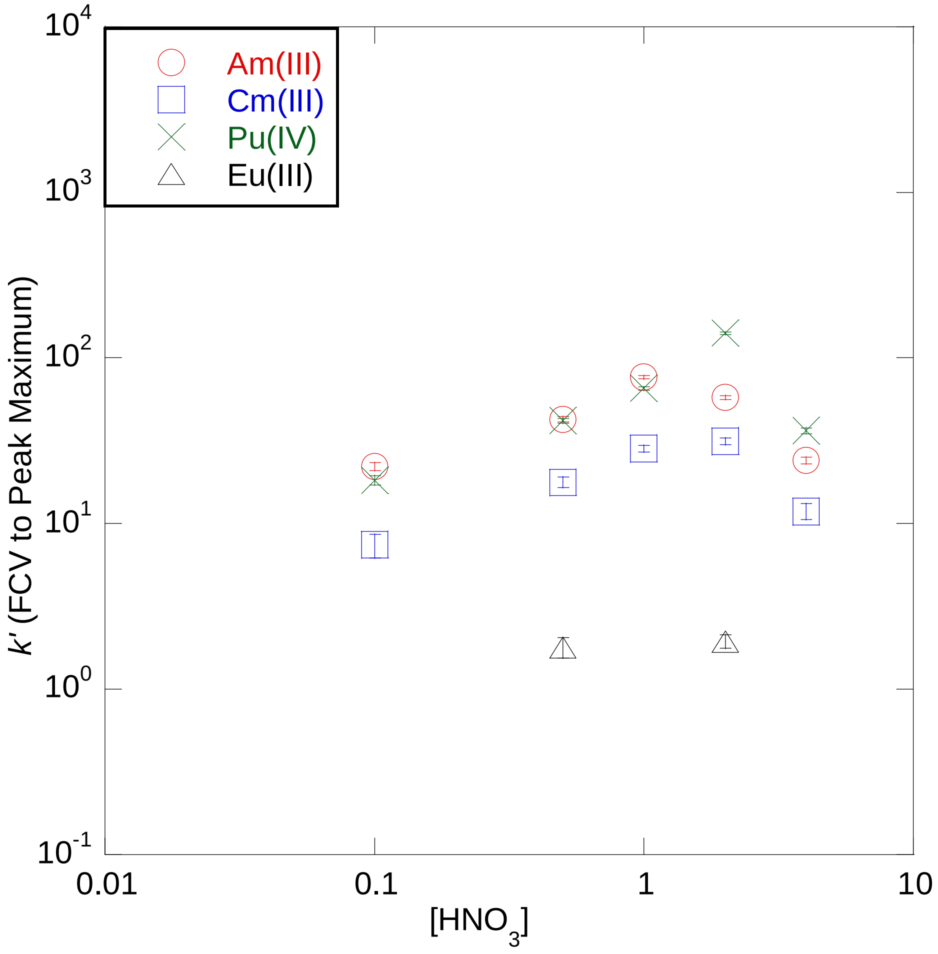

Figure 17 Extraction of Am(III), Cm(III), Pu(IV), and Eu(III) by C5-BTBP resin as a function of initial nitric acid concentration.

Negative values are omitted. See Table 20 in the Appendix for data.

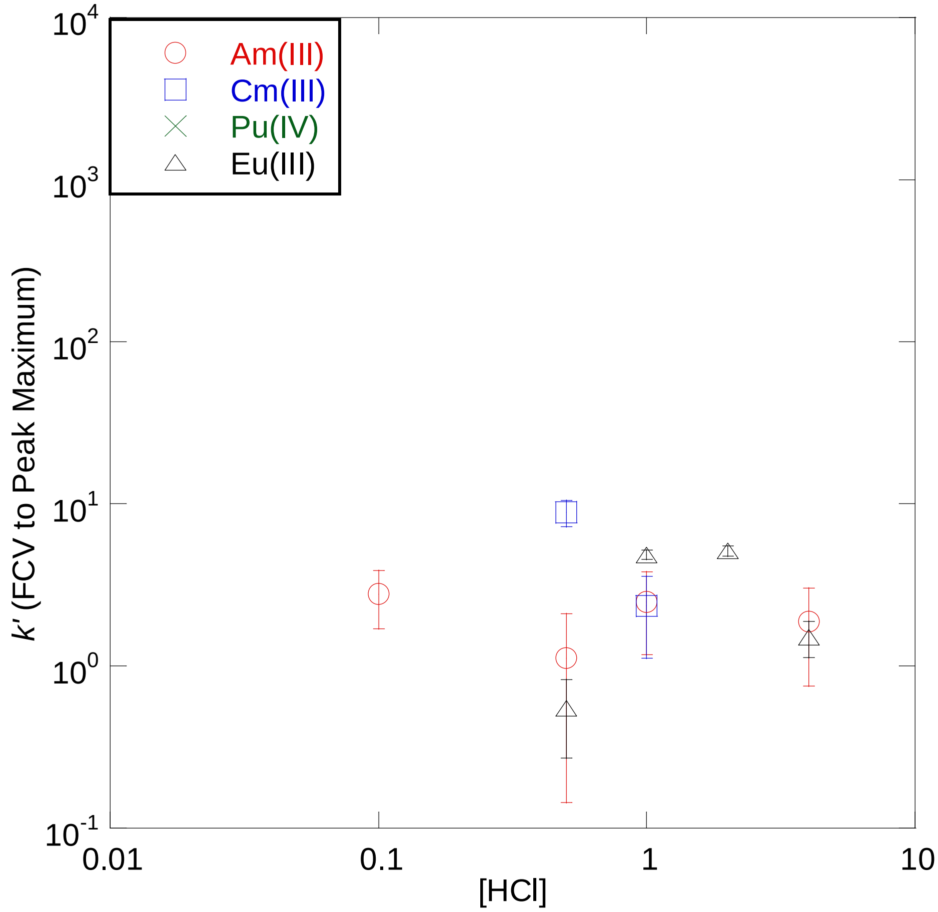

Figure 18 Extraction of Am(III), Cm(III), Pu(IV), and Eu(III) by C5-BTBP resin as a function of initial hydrochloric acid concentration.

Negative values are omitted. See Table 21 in the Appendix for data.

CyMe$_4$-BTBP

The CyMe$_4$-BTBP ligand was used in this research because of prior work discussed earlier showing its effectiveness for actinide-lanthanide separations. Select trivalent actinides and europium were used to characterize the performance of this ligand as a coating for extraction chromatography. Shown in Figure 19 are the results for the extraction of americium(III), curium(III), europium(III), and plutonium(IV) from nitric acid. The extraction of all three actinides is decreased at 4 M HNO_3. This decrease in extraction could be due to bleeding of the extractant, or protonation of the ligand on the resin, and will be further discussed when stability of the resin is addressed. The dip in americium(III) extraction at 0.5 M shown in Figure 19 might be due to excess extractant which was present as unbound crystals in some of the resin samples. This in-homogeneity of the resin was not observed until batch experiments were begun, and was again observed when the density and column parameters were determined, but this defect in the resin preparation methods did not appear to have affected any of the other extraction batches.

The extraction of americium(III), curium(III), europium(III), and plutonium(IV) in hydrochloric acid was also investigated to study matrix effects. These results are displayed in Figure 20, and show that because of the weaker association of chloride ions with actinides, extraction is diminished by two orders of magnitude in the presence of hydrochloric acid relative to the extraction in nitric acid. In many of the extraction samples in hydrochloric acid there was no detectable difference in the metal concentration between the sample and the control, so no D_w or *k'* could be calculated and those points are not displayed. Extraction of Eu(III) was only detected at 2 M HCl.

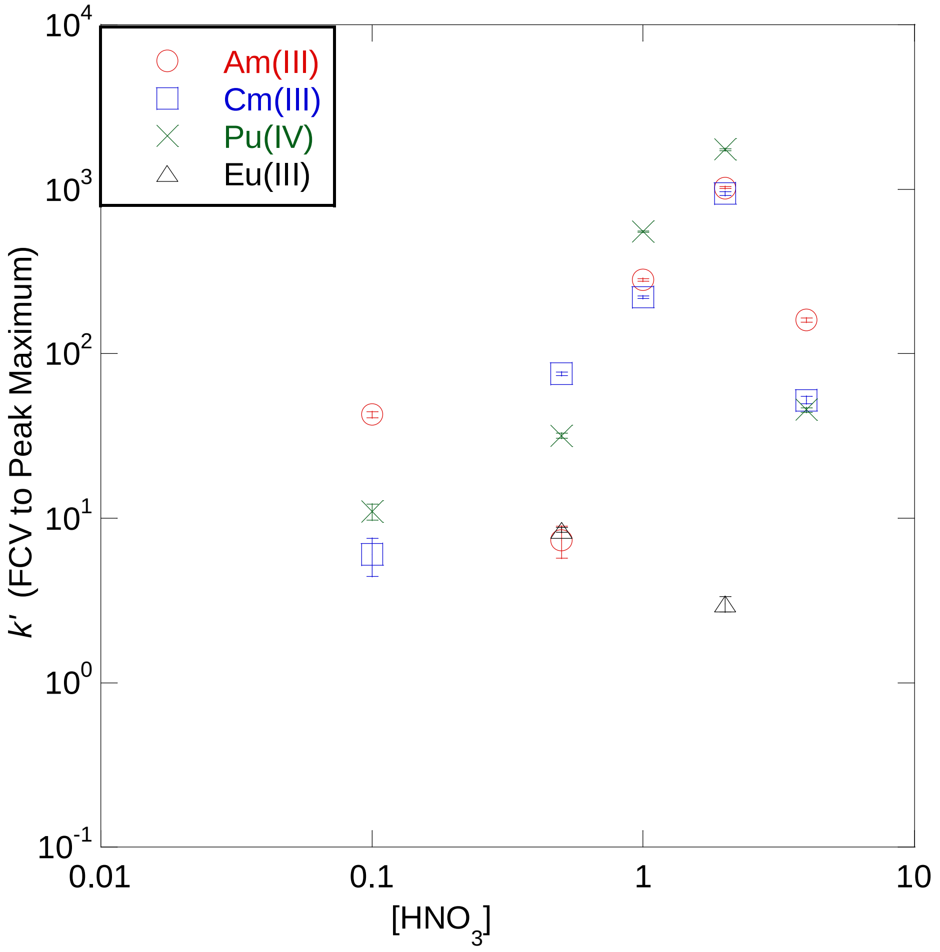

Figure 19 Extraction of Am(III), Cm(III), Pu(IV), Eu(III) by CyMe$_4$-BTBP resin as a function of initial nitric acid concentration.

Negative values are omitted. See Table 22 in the Appendix for data.

Table 8 Separation Factors Using CyMe4-BTBP Resin.

Elements used to calculate separation factors with (acid)	Am / Eu (HNO_3)	Am / Cm (HNO_3)	Am / Pu (HNO_3)	Am (HNO_3) / Am (HCl)
2 M	339±57	1.08±0.03	0.583±0.013	681
1 M	49±2	1.27±0.04	0.509±0.010	175

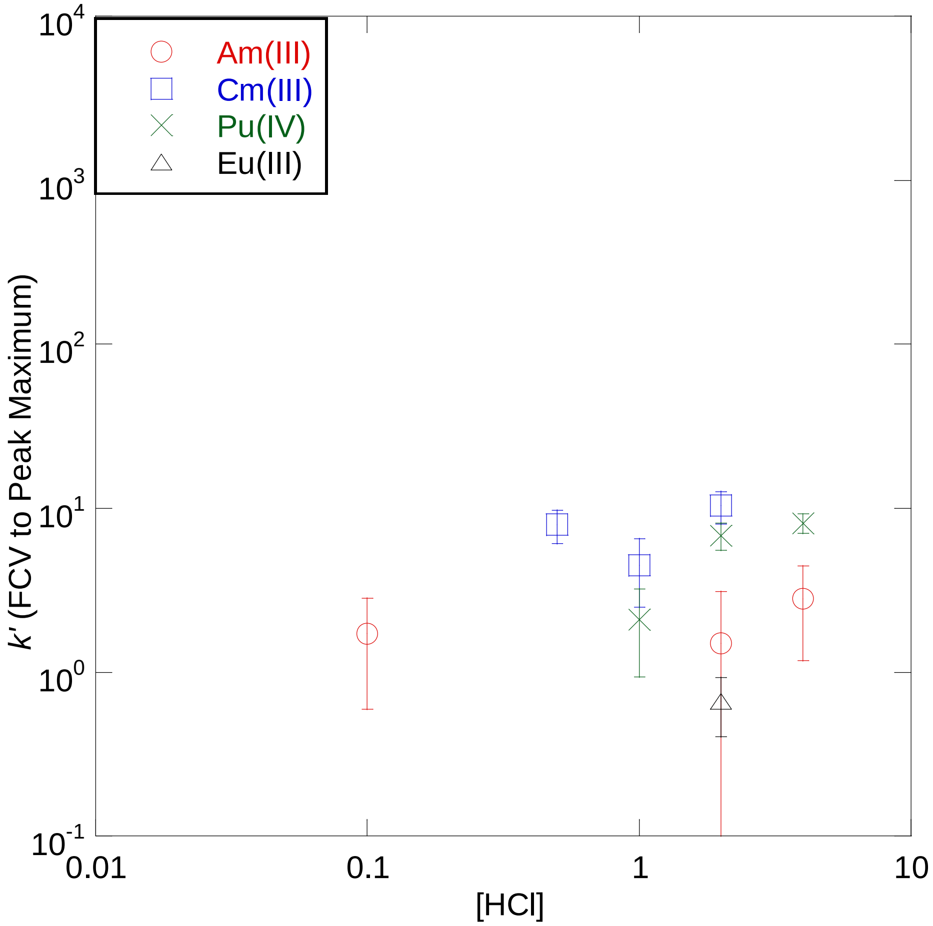

Figure 20 Extraction of Am(III), Cm(III), Pu(IV), Eu(III) by CyMe$_4$-BTBP resin as a function of initial hydrochloric acid concentration.

Negative values are omitted. See Table 23 in the Appendix for data.

Based on the observed trends in the extraction of americium(III), curium(III), europium(III), and plutonium(IV) from both nitric and hydrochloric acids, the effectiveness of the $CyMe_4$-BTBP ligand for actinide-lanthanide separations at equilibrium was confirmed. Separation factors are displayed in Table 8, and where a k' was unavailable due to a lack of observed extraction, the average of the nearest neighbors was used to calculate the separation factor. There are no errors given for the americium(III) separation from nitric to hydrochloric acid due to the rather significant errors associated with the k' values under 1. Compared to literature values on $CyMe_4$-BTBP in solvent extraction, the separation factor for americium(III)/europium(III) at 1 M HNO_3 of ~50 is lower than the value reported by Geist of approximately 100 for 0.001 M $CyMe_4$-BTBP + 0.25 M DMODOHEMA in octanol but is at least of the same magnitude.[91] The separation factor for americium(III)/curium(III) at 1 M HNO_3 is also comparable to the values estimated from figures in the Geist work.[91] Based on the slightly decreased extraction at 2 M HNO_3, and prior work with a C5-BTBP resin, 1 M HNO_3 was used for loading activity in the column studies.

CHAPTER 5

COLUMN STUDY RESULTS

The behavior of many extraction chromatography resins can change when investigations move from the equilibrium conditions in batch experiments, as described in Chapter 4, to the dynamic conditions which are present during column separations as discussed in this chapter. Since extraction chromatography resins are primarily applied to separations using columns, insight into the usability of the resin can be gained from the following results.

Isobutyl-BTP

The isobutyl-BTP extractant was coated onto Amberchrom CG-71 for the reasons discussed earlier in Chapter 3CHAPTER 3, and using the methods described earlier in Chapter 2. When the resin was characterized for extraction of americium(III) in hydrochloric acid relative to nitric acid, lower extraction was observed in HCl so hydrochloric acid at 0.1 M was included in testing for the stripping of loaded columns. Ethylenediaminetetraacetic acid (EDTA) a known complexation agent was included at 0.1 M as well as 0.1 M nitric acid and de-ionized water. Each column used to characterize the isobutyl-BTP resin had a Free Column Volume (FCV) of 200 µL except for the column used with 0.1 M HCl which had a FCV of 225 µL. As seen in Figure 21, water alone or 0.1 M nitric acid are poor stripping agents for americium(III) from isobutyl-BTP. Another run performed on a shorter and wider column with the same FCV displayed a very broad elution peak for the americium(III) seen in Figure 22. This confirms that 0.1 M nitric acid is a poor stripping agent. However, as seen in Figure 23, both 0.1 M EDTA and 0.1 M HCl proved to be effective stripping agents. Complete elution with HCl does occur more quickly than with EDTA, but EDTA elutes with a sharper peak than HCl. These differences could be due to the alkaline nature of the EDTA solution due to its preparation from the molecular form and NaOH instead of from the more desirable disodium salt.

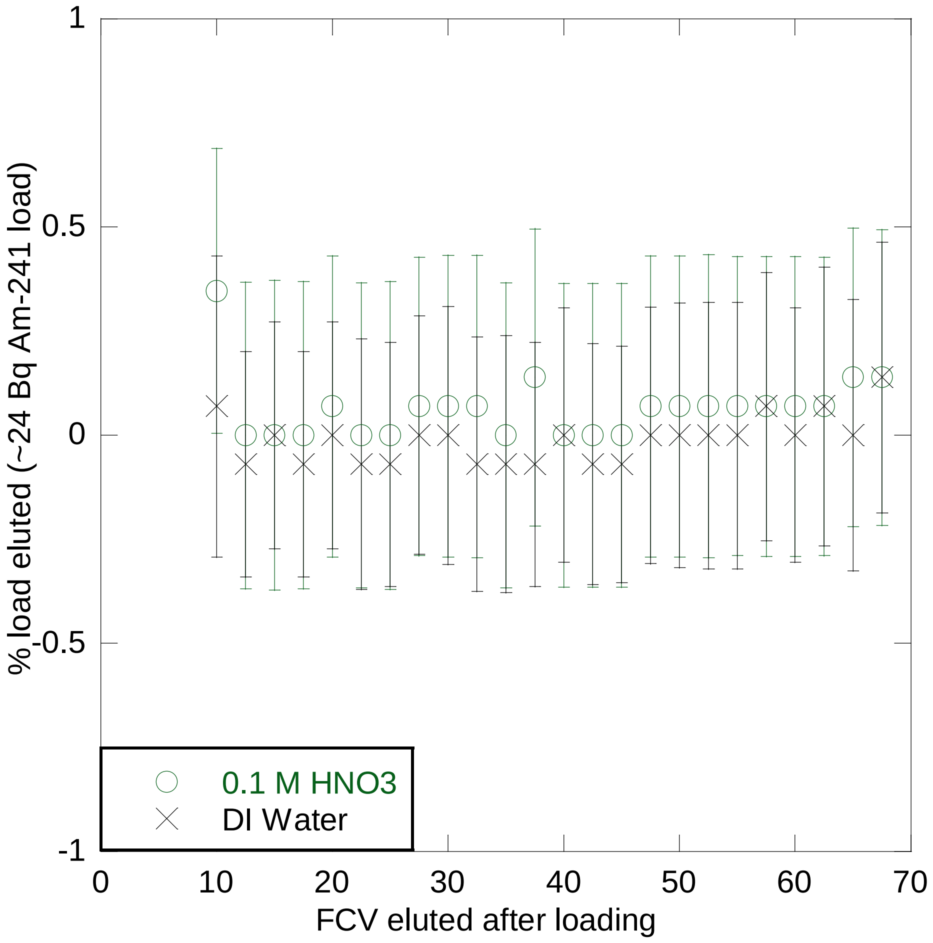

Figure 21 Elution of Am(III) from isobutyl-BTP resin.

In addition to loading and elution with americium(III), the isobutyl-BTP was used in a column to test for the europium(III) capacity. This was expected to be low since the resin exhibited low extraction of europium(III) in both nitric and hydrochloric acid solutions as shown in Figure 15, and Figure 16. While the resin has a theoretical capacity of 16.9 mg Eu/g resin, the actual capacity was found to be only 450 µg Eu/g resin based on the breakthrough curve shown in Figure 24.

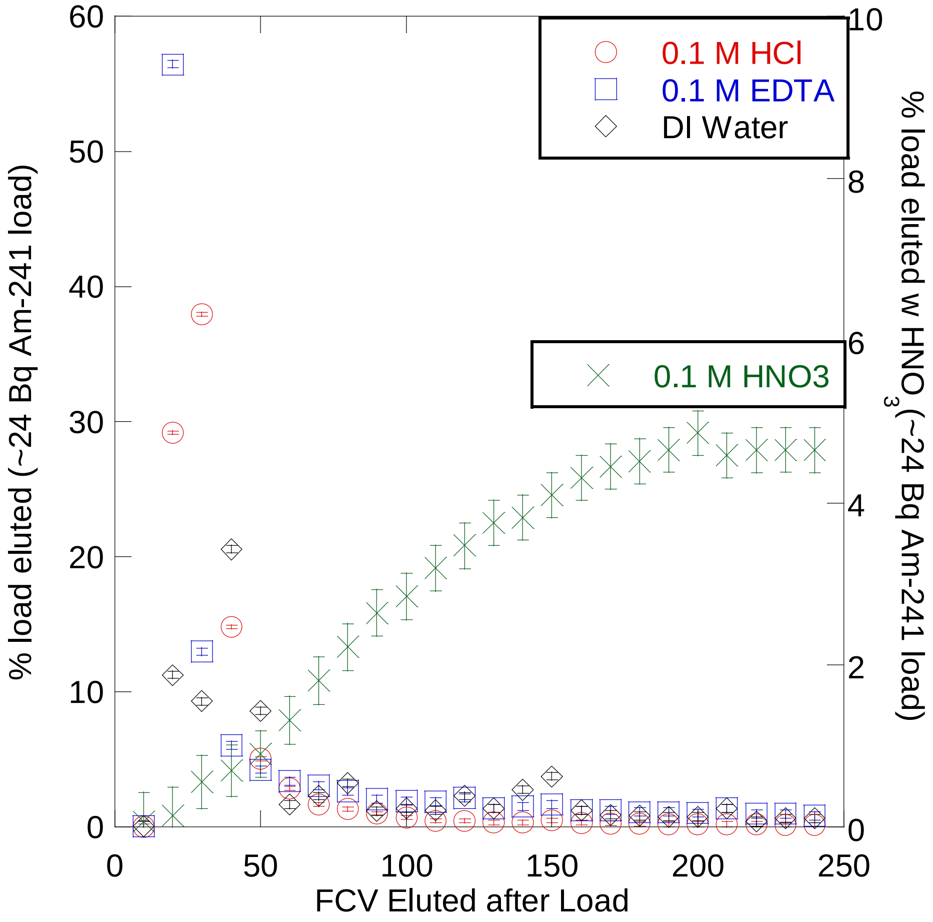

Figure 22 Elution of Am(III) from isobutyl-BTP with alternate column geometry.

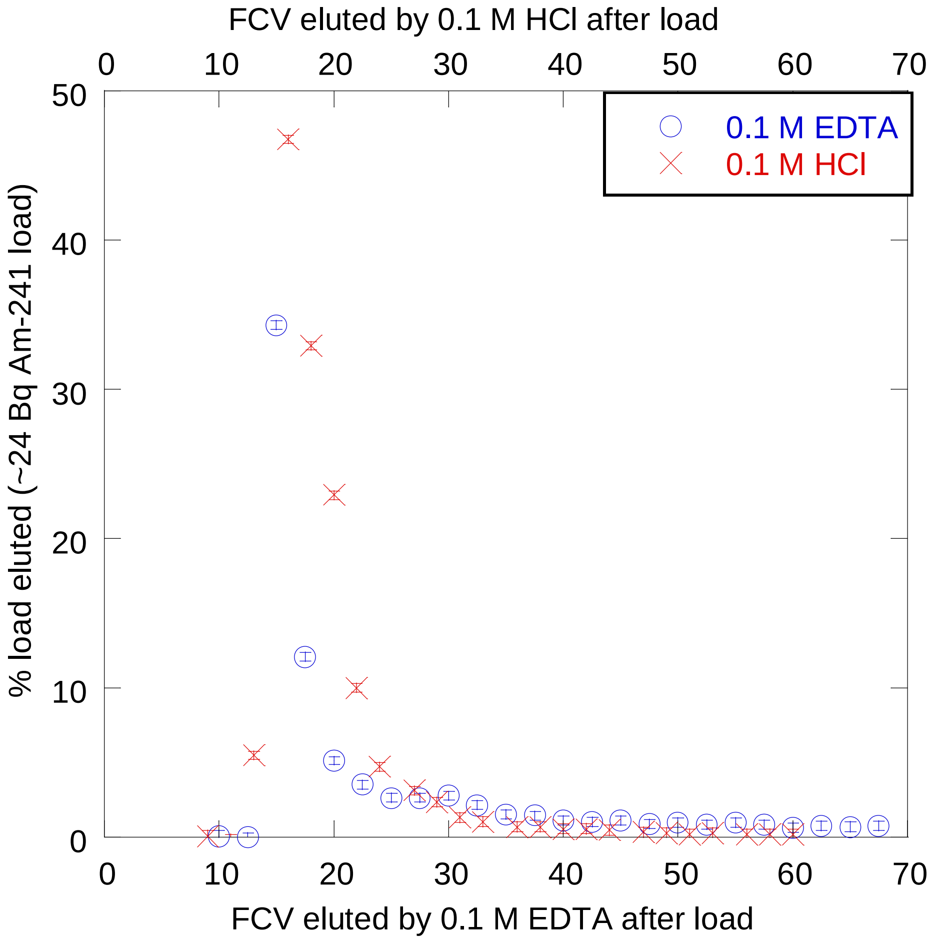

Figure 23 Elution of Am(III) from isobutyl-BTP resin.

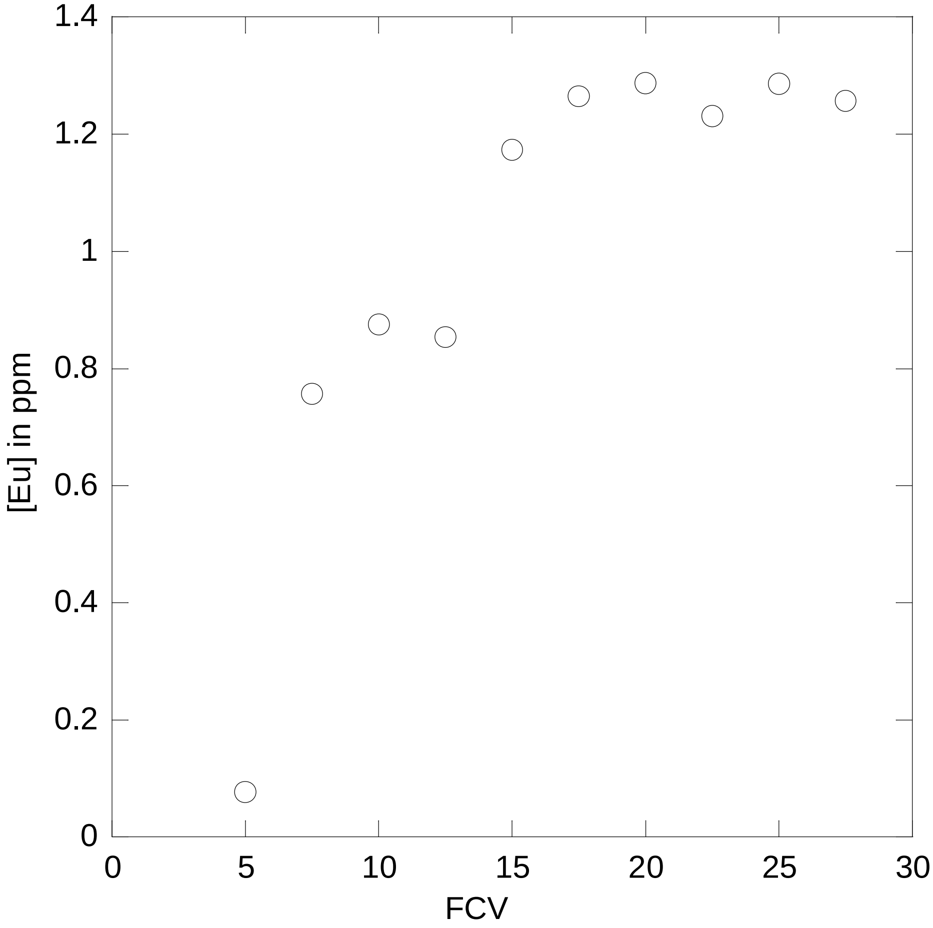

Figure 24 Breakthrough of Eu(III) from a column of isobutyl-BTP resin.

C5-BTBP

The C5-BTBP extractant was coated onto Amberchrom CG-71 for the reasons discussed earlier in Chapter 3, and using the methods described earlier in Chapter 2. When the resin was characterized for the extraction of americium(III) in hydrochloric acid relative to nitric acid, lower extraction was observed in HCl so hydrochloric acid at 0.1 M was included in testing for the stripping of loaded columns. EDTA a known complexing agent was included at 0.1 M, as well as 0.1 M nitric acid and de-ionized water. Each column used had a FCV of 100 µL. As seen in Figure 25, EDTA was the best stripping agent, followed by HCl, HNO_3, then DI water. However, despite the use of Am-241 at a concentration less than 1 millionth that of the theoretical column capacity calculated based on two ligands per complex, significant breakthrough in the load (10 FCV) and rinse (30 FCV) fractions was observed. This breakthrough could be due to slower kinetics, despite the use of gravity flow for elution, which would be confirmed by the reports of slow kinetics in solvent extraction experiments.[88]

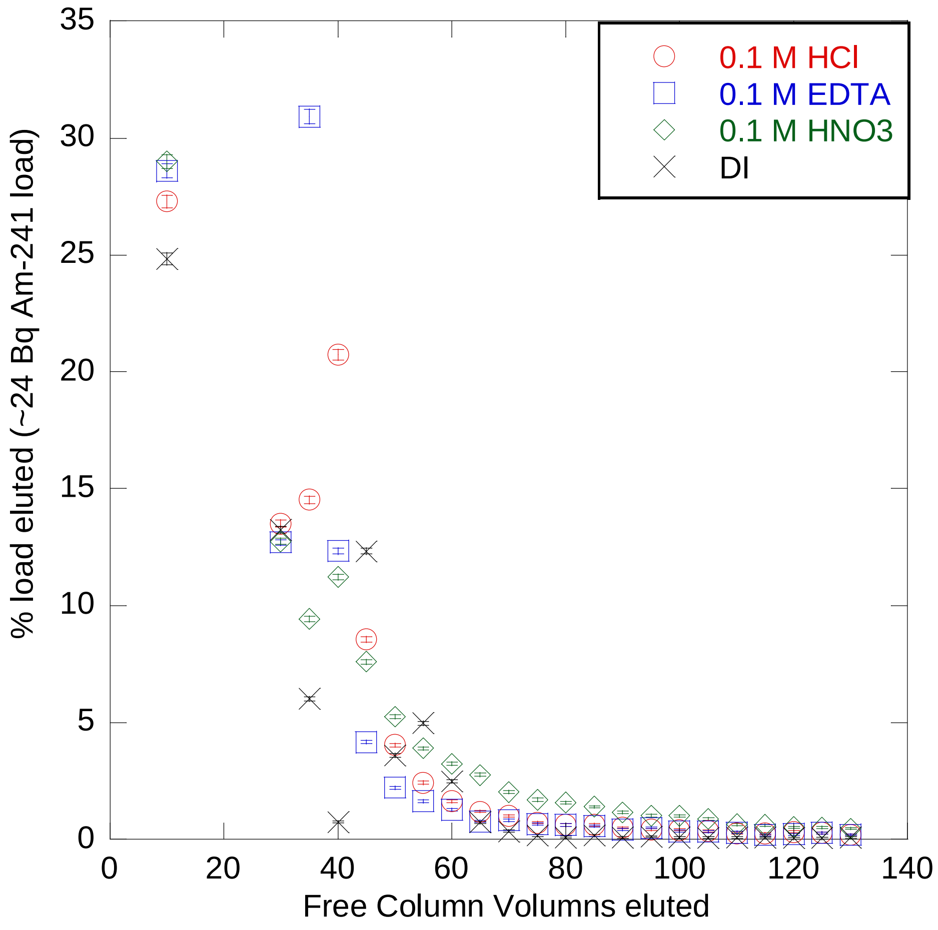

Figure 25 Load, Rinse, and Strip fractions of Am(III) from C5-BTBP resin.

CyMe$_4$-BTBP

The CyMe$_4$-BTBP extractant was coated onto Amberchrom CG-71 for the reasons discussed earlier in Chapter 3, and using the methods described earlier in Chapter 2. When the resin was characterized for the extraction of americium(III) in hydrochloric acid relative to nitric acid, lower extraction was observed in HCl so hydrochloric acid at 0.1 M was included in testing for the stripping of loaded columns. EDTA a known complexing agent was included at 0.1 M, as well as 0.1 M nitric acid and de-ionized water. Each column used had a FCV of 100 µL. Similar to the C5-BTBP, EDTA was the best stripping agent, followed by HCl, HNO_3, than DI water as seen in Figure 26. However, despite the use of Am-241 at a concentration less than 1 millionth that of the theoretical column capacity calculated based on two ligands per complex, significant breakthrough in the load (10 FCV) and rinse (30 FCV) fractions was observed. This breakthrough could be due to slower kinetics, despite the use of gravity flow for elution, which has also been observed in solvent extraction experiments.[91]

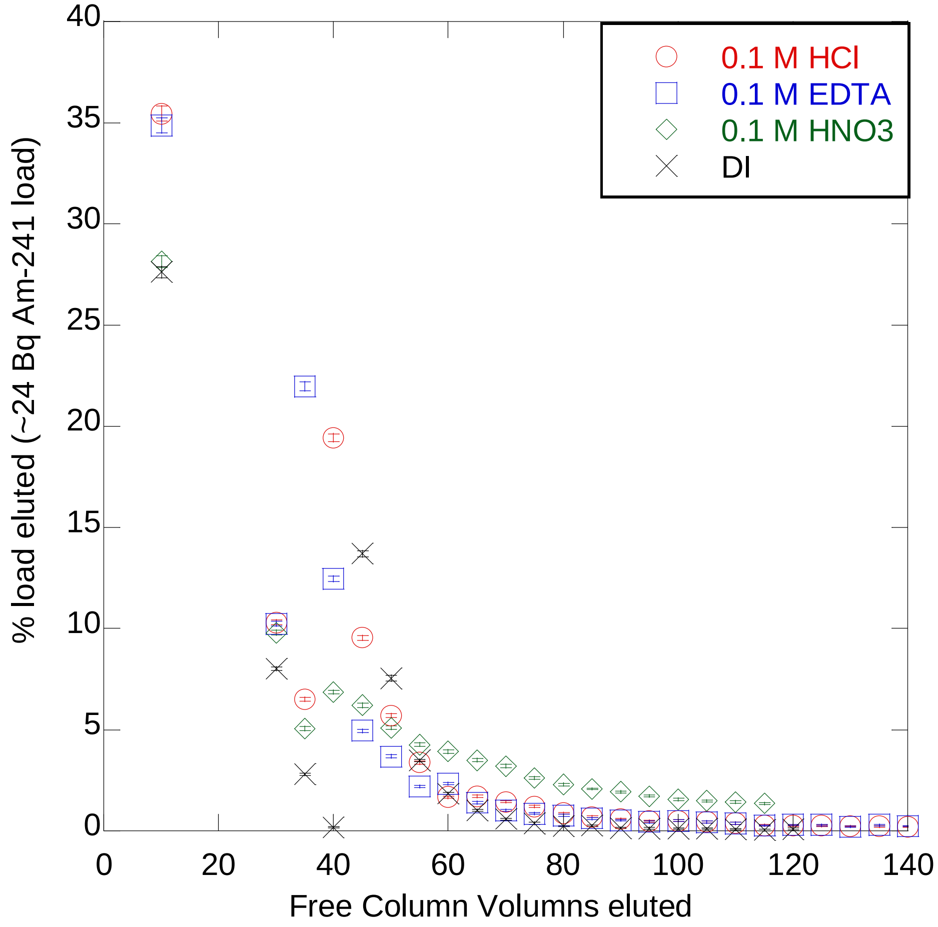

Figure 26 Load, Rinse, and Strip fractions of Am(III) from $CyMe_4$-BTBP resin.

CHAPTER 6

STABILITY STUDY RESULTS

Isobutyl-BTP

While it has been reported by Kolarik that the isobutyl-BTP was stable in contact with aqueous solutions of 0.90 M HN03 + 1.0 M NH_4NO_3, some degradation of the resin was visible in the 2 and 4 M acids from this work.[73] In Figure 9 and Figure 15 a clear drop in extraction can be seen at 4 M nitric acid compared to 2 M. This effect was investigated further by analyzing contact solutions for the presence of BTP.

In Figure 27, the absorbance of isobutyl-BTP within a portion of the UV region (240-360 nm) can be seen, the lower three traces are for isobutyl-BTP at a concentration of 180 nM, while the three traces at higher absorbances are for a concentration of 36.0 µM. The three traces at each concentration are for 0.1 M, 0.5 M, and 2 M HCl. Traces for intermediate BTP and HCl concentrations are omitted for clarity. At the lower concentration of 180 nM BTP where no significant absorbance peaks are visible the background increases as HCl increases, while the absorbance peaks near 265 nm and 320 nm are both enhanced at the higher BTP concentration. Despite the incomplete overlap of spectra at the wavelengths 280 nm and 305 nm, they were treated as isosbestic points. From this assumption the molar absorptivity at 305 nm was calculated to be 25,600 $M^{-1}cm^{-1}$ and 38,600 $M^{-1}cm^{-1}$ at 280 nm from the 36.0 µM absorbance curve. These molar absorptivities are of the magnitude associated with $\pi\rightarrow\pi^*$ transitions. Placing isobutyl-BTP into nitric acid was inconclusive due to the interactions of protonated BTP with nitrate ions preventing accurate determination of absorbance by background subtraction. The lowest detectable standard concentration of isobutyl-BTP in HCl was 180 nM. The spectra obtained with isobutyl-BTP agree reasonably well with other spectra obtained for n-propyl-BTP.[105] A further limitation with these spectroscopy experiments was the limited transmission below 240 nm of the 96-well microplates used.

Fluorescence was also investigated for use in characterizing samples. The emission spectrum from excitation at 327 nm can be seen in Figure 28. The emission peaks at 594, 618, and 694 nm are most intense for excitation photons ranging from 320 to 340 nm, but are apparent at longer excitation wavelengths as well. Quenching occurred at higher acidities, and the limitations of instrumentation did not allow for the probing of lower excitation wavelengths such as 265 nm. Radioactive samples could not be run at high throughput on fluorescence but they could be on UV.

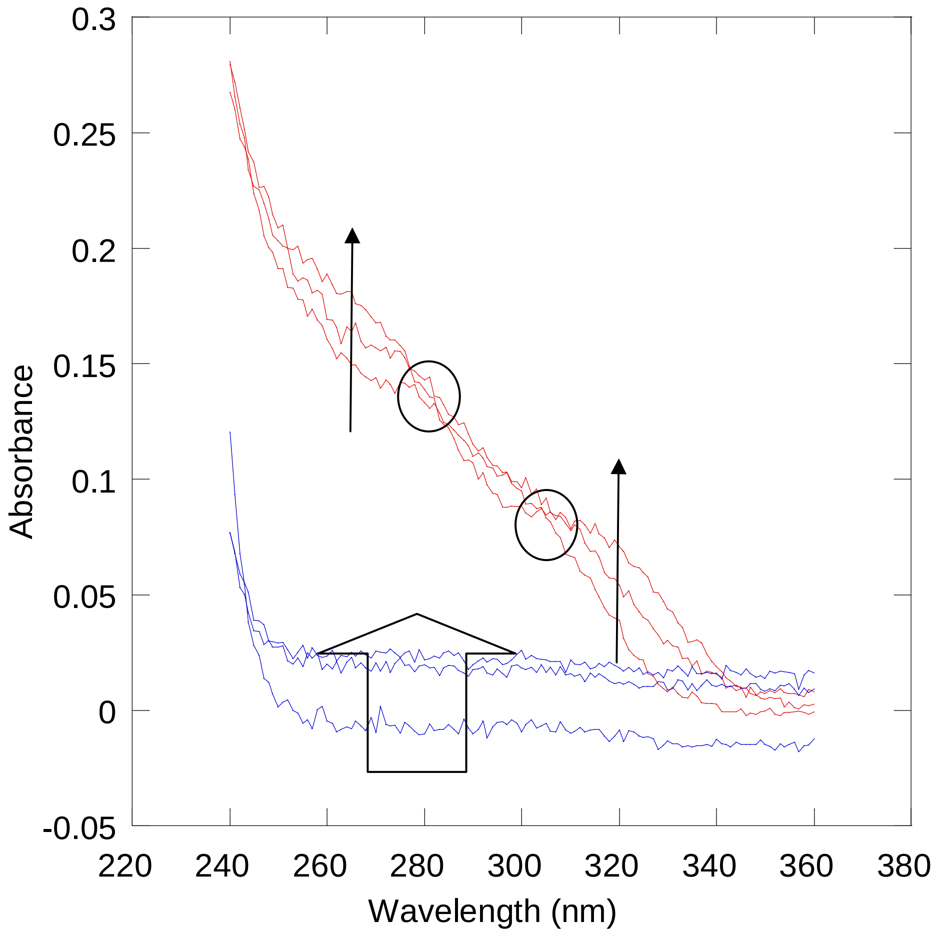

Figure 27 Absorbance in the UV region by isobutyl-BTP at 180 nm (blue) and 36.0 µM (red) with increasing HCl.

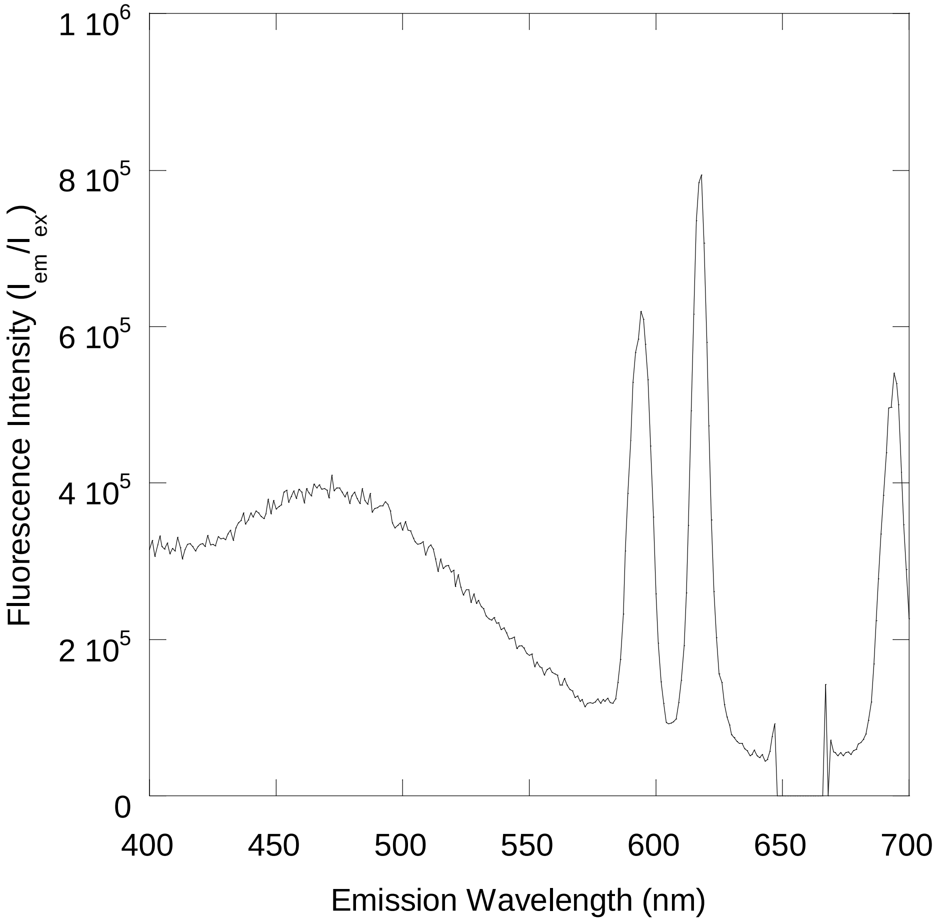

Figure 28 Fluorescence of isobutyl-BTP at an excitation wavelength of 327 nm. Data at ~660 nm was excised due to scattering of the excitation photons.

With the knowledge of UV absorbance peaks for BTP in HCl, solutions from the extraction experiments in HCl were analyzed for BTP. Results for the solutions from the europium(III) extraction in HCl are given in Figure 29, with the average absorbance from three samples at the same acidity shown. Results for americium(III), curium(III) and plutonium(IV) were all similar to those shown for europium(III). It should be noted from comparison of this figure with Figure 27 that the change in hydrochloric acid present cannot alone explain the increase in absorbance by the solutions. Not only must isobutyl-

BTP be present in the solutions from these resin extractions, but the amount present must be dependent on the concentration of HCl in the contacting solution. The maximum concentration of isobutyl-BTP was found in the 4 M HCl solution. From the molar absorptivities of isobutyl-BTP the concentration was calculated as 34 µM and 32 µM based on the wavelengths 280 and 305 nm respectively. Using the average of 33 µM, there were 132 nmol of isobutyl-BTP dissolved in the 4 mL of solution remaining in contact with the resin. This represents less than 0.004% of the 3.85 mmol which were coated onto the resin which was in contact with the solution. Thus, while bleeding does occur from the isobutyl-BTP resin at the relatively high concentration of 4 M HCl, it does not account for the lowered extraction of the resin observed in Figure 9 and Figure 15. During these investigations it became apparent that it was also important to determine whether the bleeding observed was due to hydrolysis of the BTP or protonation, and whether either or both were also responsible for the lower extraction at higher acidities.

When fractions from the 0.1 M HCl elution were analyzed by UV absorption, there was no detectable BTP, and the interfering peak from nitrate was present in the first three fractions. To investigate whether any of the BTP was bleeding from the resin during the elution, and to determine if any BTP present was hydrolyzed, ESI-MS was used on these same samples. The background and isobutyl-BTP standard mass traces from ESI-MS are shown in Figure 30 and Figure 31. The molecular peak near 462.3 amu is likely the result of a gain of H^+ by the isobutyl-BTP molecule which has a mass of 461.3 amu. Mass peaks which would correspond to the loss of methyl, propyl, isobutyl, or triazinediisobutyl groups are not evident in the spectrum. If such peaks are present due to fragmentation of the sample in the instrument, they are indistinguishable from background. Other peaks appearing in the background and standard spectra can be explained by the formation of various solvent cluster ions. The mass trace for the initial fraction from the 0.1 M HCl elution is shown in Figure 32. Mass traces for the first through fourth fractions are shown in Figure 33 in more detail near the molecular peak for isobutyl-BTP. It is clear from the electrospray-mass spec data that isobutyl-BTP was present in the early fractions coming off the column in the 0.1 M HCl eluent, and likely for the other eluents as well. The concentration is at a maximum in the first fraction, which decreases for subsequent fractions until by the fourth fraction, there is no detectable isobutyl-BTP by ESI-MS. Since the BTP in the fourth fraction was also below the detection limit of 180 nM on the UV, this means that by the fourth fraction less than 0.00004% of the isobutyl-BTP is bleeding in each fraction.

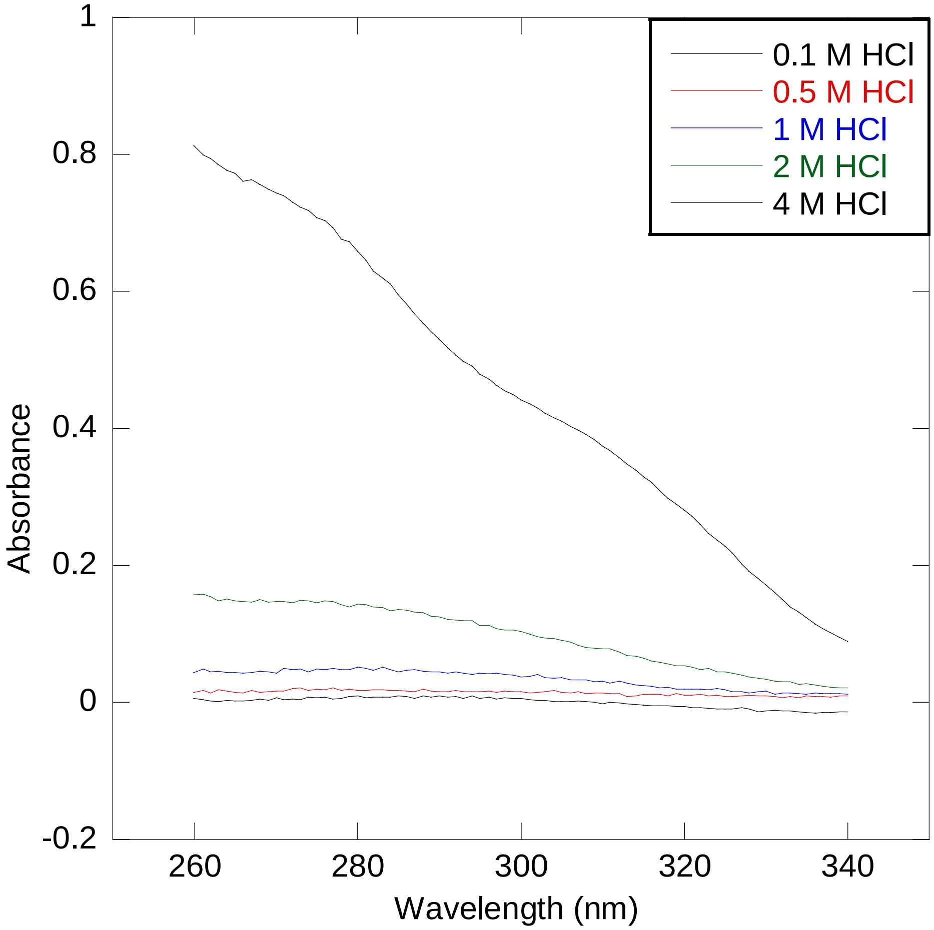

Figure 29 Average absorbance from 260 to 340 nm of isobutyl-BTP in HCl solutions from Eu(III) extractions.

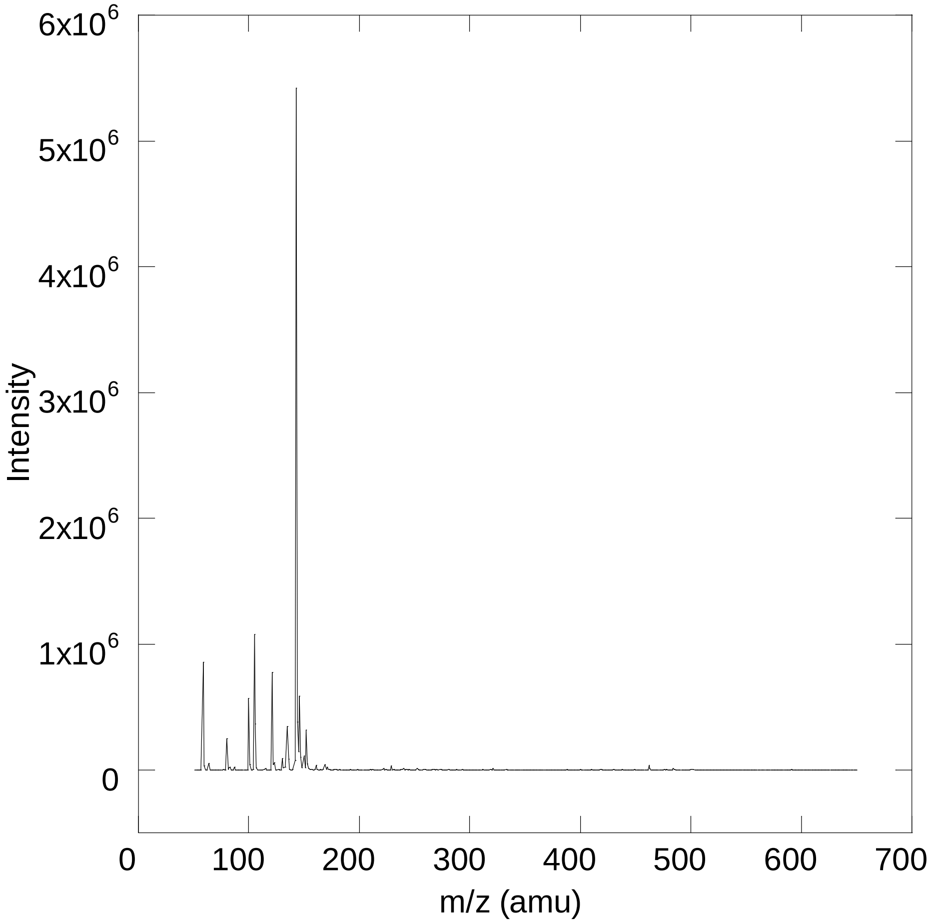

Figure 30 Background mass trace from 50-650 amu with a methanol rinse solution in 50:50 water:acetonitrile on the MSQ Plus ESI-MS.

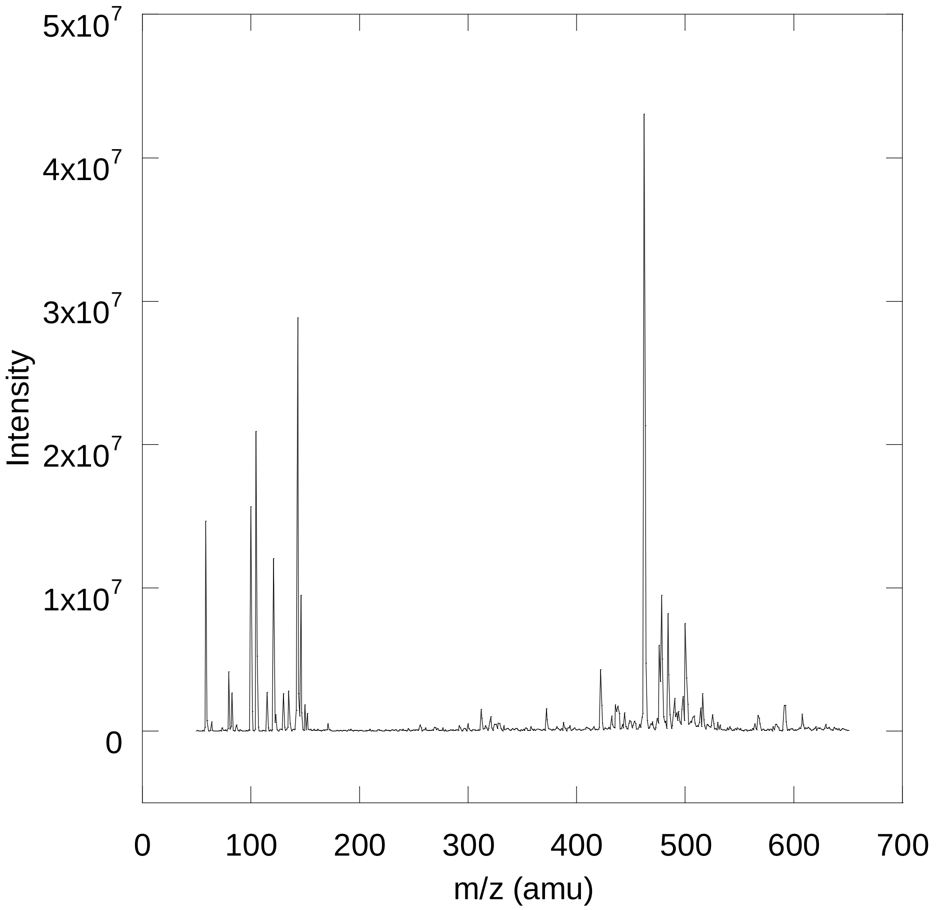

Figure 31 Mass trace from 50-650 amu of isobutyl-BTP dissolved in methanol eluted with 50:50 water:acetonitrile.

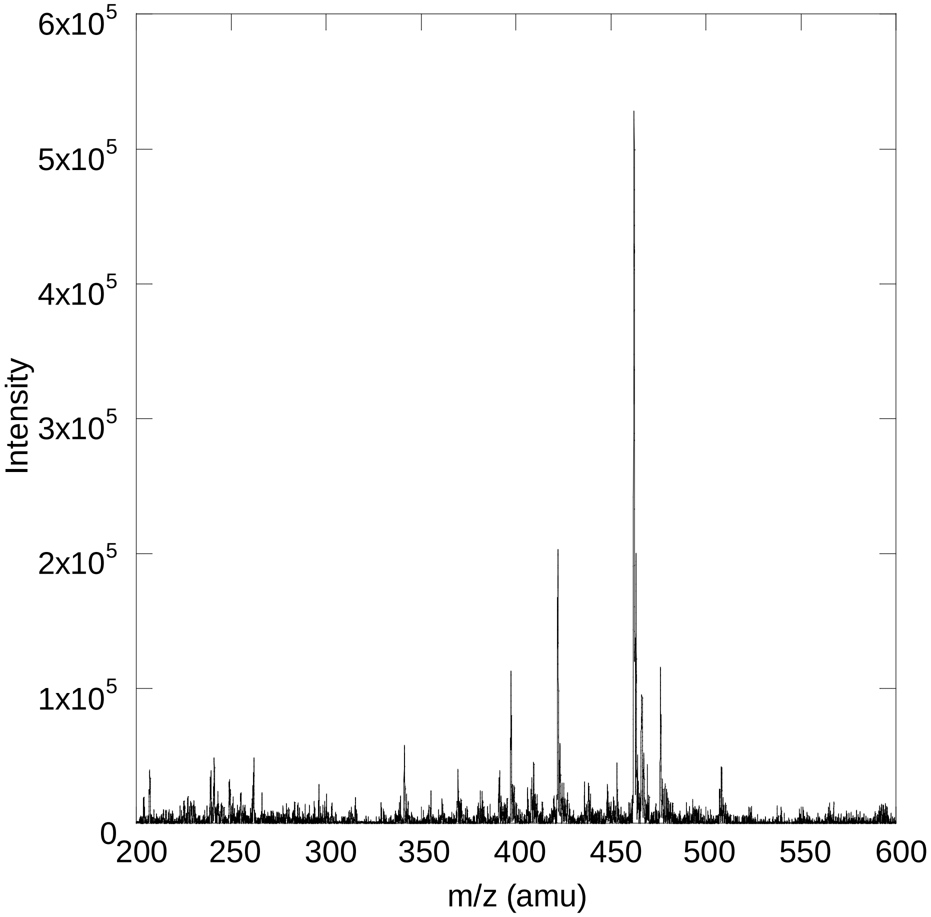

Figure 32 0.1 M HCl column elution with Am(III), Fraction 1 Mass Trace ESI-MS

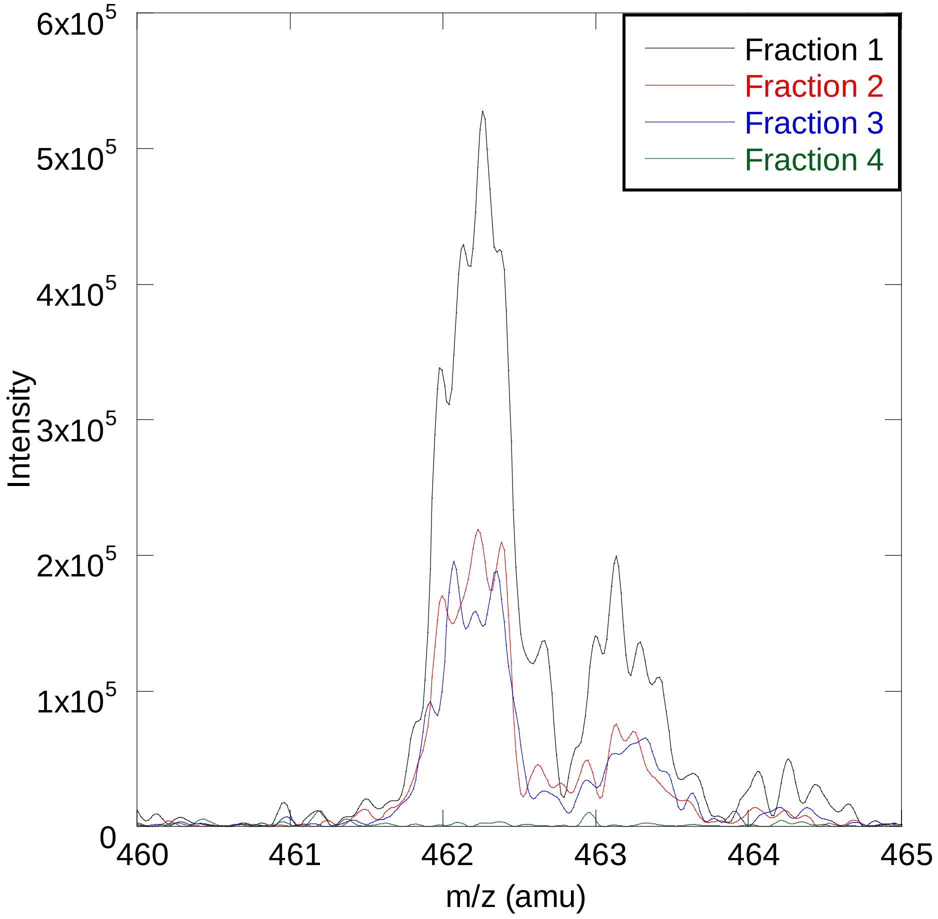

Figure 33 0.1 M HCl column elution with Am(III), Fractions 1-4, isobutyl-BTP molecular and M+1 peaks.

Because of the lack of evidence from ESI-MS for hydrolysis, it is proposed that the isobutyl-BTP ligand is not hydrolyzed on the resin support but is instead protonated at higher acidities. The decreased extraction performance in 4 M acid is evidence of this mechanism, as is data from UV and fluorescence. The protonation effect has been observed as enhanced UV absorption and quenched fluorescence in standard solutions of the isobutyl-BTP. The effect can also be observed by eye as resin in contact with higher acidities has a deeper, orangeish-yellow color compared to the creamy yellow in more dilute solutions. The protonated form of isobutyl-BTP has a higher solubility in aqueous solutions than the neutral form, but the low bleeding is evidence of the strong binding between the ligand and the resin support.

C5-BTBP

It has previously been reported that molecules such as C5-BTBP, which contain benzylic hydrogens are easily oxidized in acidic and nitrogen oxoacid environments.[82] In Figure 11 and Figure 17 extraction decreases by half at 4 M nitric acid compared to 2 M, and there even seems to be decreased extraction at 2 M compared to 1 M. This effect was investigated further by analyzing solutions for the presence of C5-BTBP.

In Figure 34, the absorbance of C5-BTBP within a portion of the UV region (240-400 nm) can be seen as can the dependence on the percent of methanol in the solution. Unlike isobutyl-BTP, C5-BTBP does not display any clear dependence on HCl concentration from 0.1 M to 4 M. Because a 50/50 methanol-aqueous matrix nearly doubled the absorbance of C5-BTBP, this was chosen as the matrix for further analysis. The absorption spectrum of 161.1 μM C5-BTBP is shown in Figure 35, from which molar absorptivities at 280 nm and 330 nm can be calculated as 22,300 $cm^{-1}M^{-1}$ and 14,800 $cm^{-1}M^{-1}$ respectively, which are of the magnitude associated with $\pi \rightarrow \pi^*$ transitions. This spectrum also agrees well with that of C5-BTBP in cyclohexanone reported by Nilsson.[84] Placing C5-BTBP into nitric acid was inconclusive due to the interactions of protonated BTBP with nitrate ions preventing accurate determination of absorbance. For the standard concentrations used, the lowest concentration of C5-BTBP in HCl with distinguishable peaks was 4 μM. A further limitation with these spectroscopy experiments was the limited transmission below 240 nm of the 96-well microplates used.

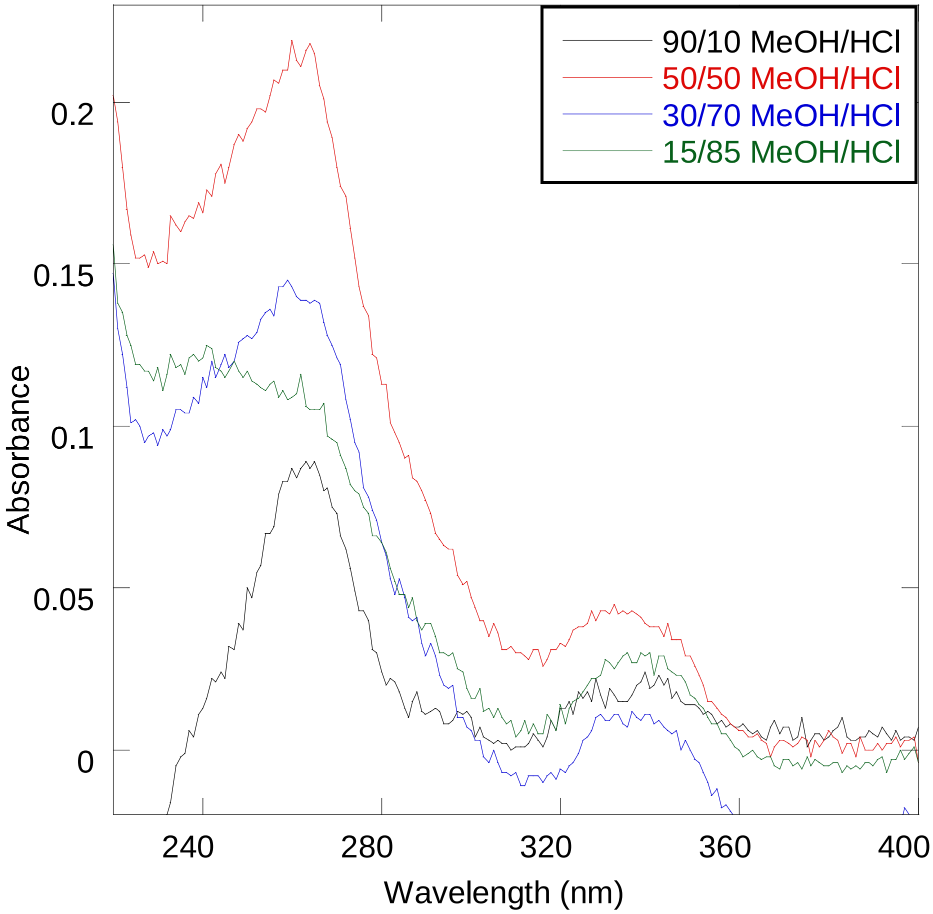

Figure 34 UV Absorbance of a constant concentration of C5-BTBP in varied Methanol / 4 M HCl solutions

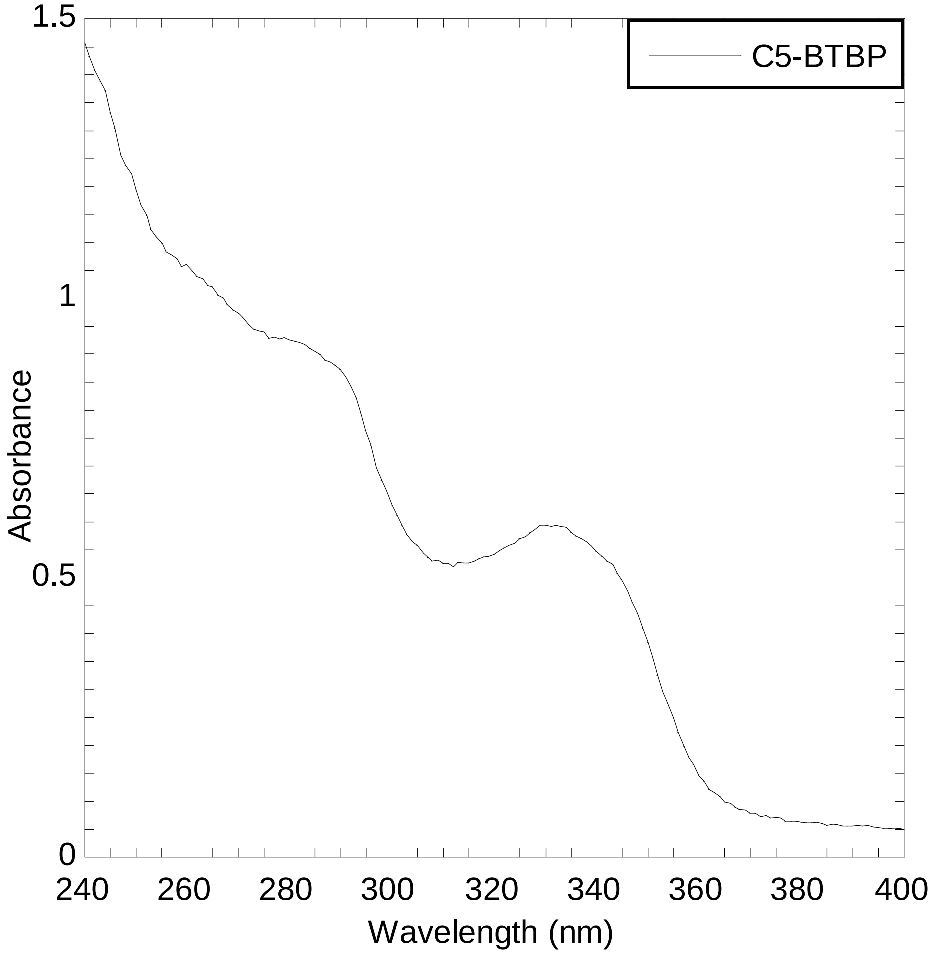

Figure 35 UV Absorbance of 161.1 μM C5-BTBP in 50:50 water and methanol

Solutions from batch experiments in HCl and fractions from columns were analyzed for the presence of C5-BTBP in 50% methanol, and no bleeding was observed. Some peaks were present as seen in Figure 36, and their absorbances were acid dependent, but their shifts were hypsochromic which would not be expected with the transitions observed in the standard solutions. The peak heights did not correlate to the amounts of resin as with isobutyl-BTP bleeding, and the shapes of the peaks are also dissimilar to the standard peaks. The lack of detectable C5-BTBP from any of the batch solutions was promising. Likewise, no C5-BTBP was detected in the column fractions, and so the column fractions and samples from the batches were run on ESI-MS to determine if lower concentrations were present, or if hydrolysis products could be observed.

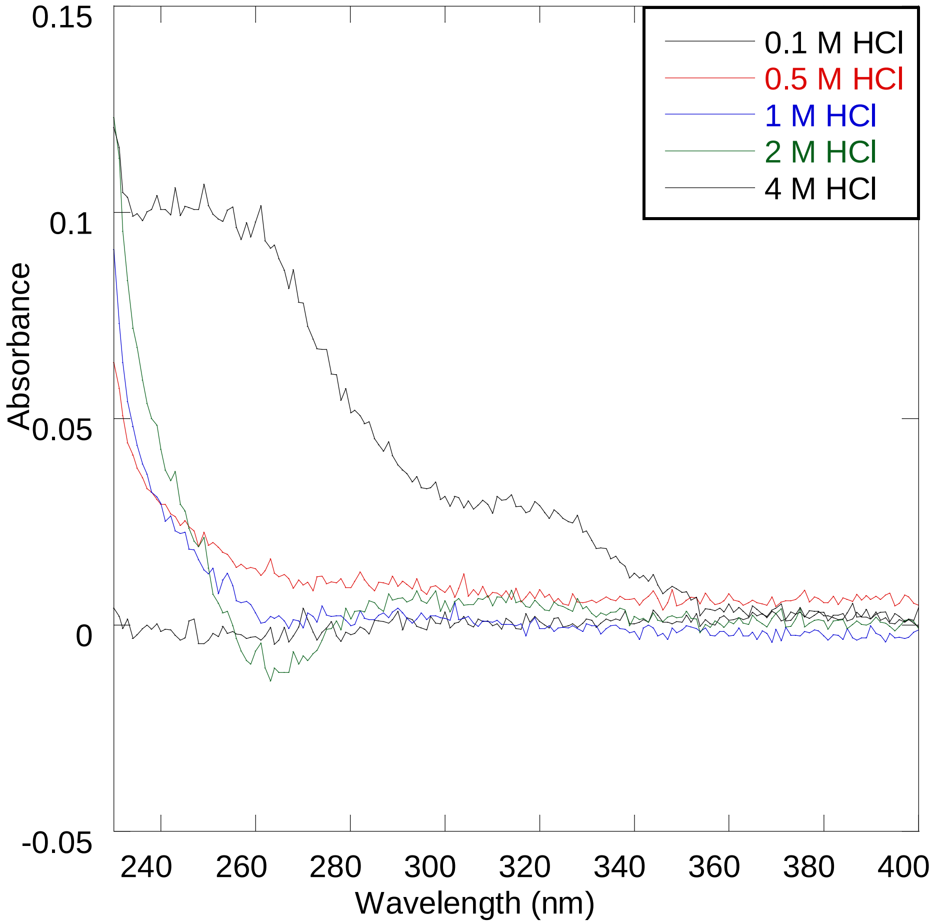

Figure 36 Average Absorbance of C5-BTBP resin contact solutions from HCl

Figure 37 displays a background mass spectrum from an injection of methanol with peaks characteristic of solvent clusters. In the same figure, the spectrum of a standard C5-BTBP solution in methanol can be seen. The peaks present are displayed and identified in Figure 38, based on the prior work by Retegan, et al.[100] Intensities of these complexes differ from those reported earlier, but could be due to the different instrument and analysis conditions used in this work as indicated in the Instrumentation and Methods Chapter. There is a peak at 374.39 m/z which could correspond to the loss of a triazine with both C5 chains from the end of the extractant, but no other peaks indicative of fragments are present and there are many peaks near 374 amu in the methanol background spectrum. No other fragments were observed in this work. Integrated intensities for the peaks at 595.11 and 596.18 m/z are displayed in Figure 39, and in this micromolar region the instrument response is linear to the C5-BTBP concentration. At higher concentrations of 20.1 µM and 161 µM the response becomes non-linear, but concentrations above 4 µM could be detected instead with UV absorbance barring the presence of interfering species.

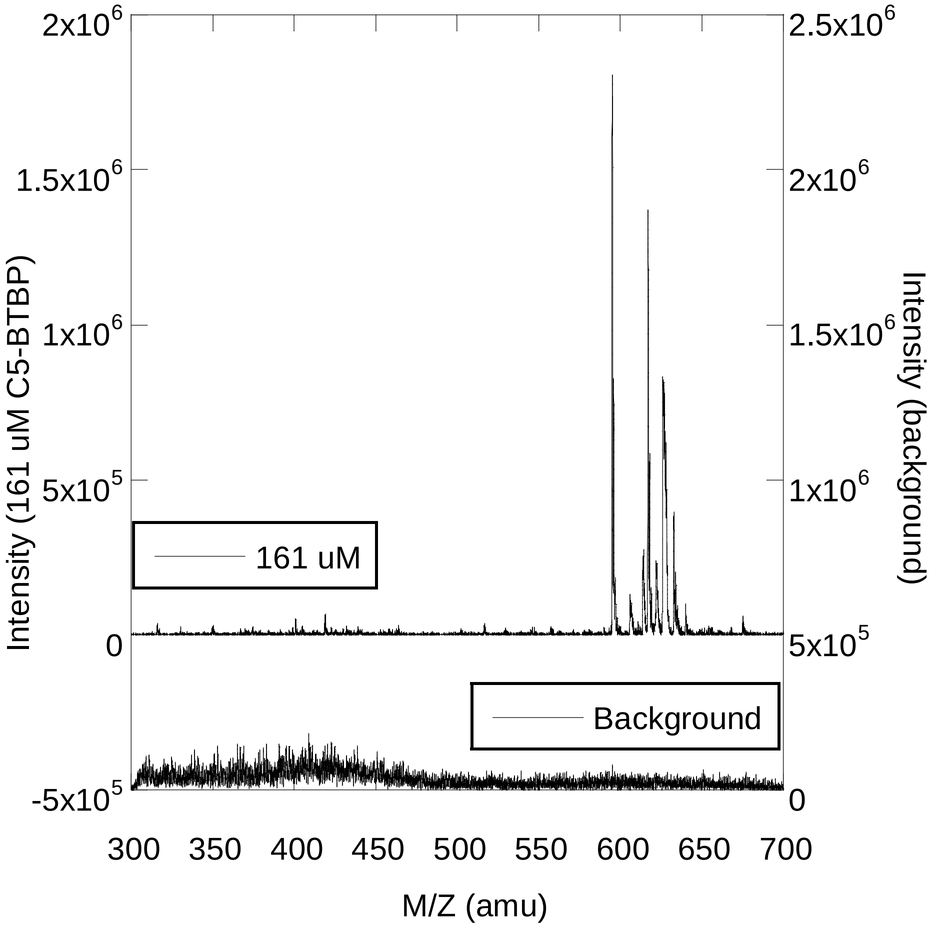

Figure 37 Electrospray Mass Spectrum of a methanol solution (background) and a standard solution of C5-BTBP

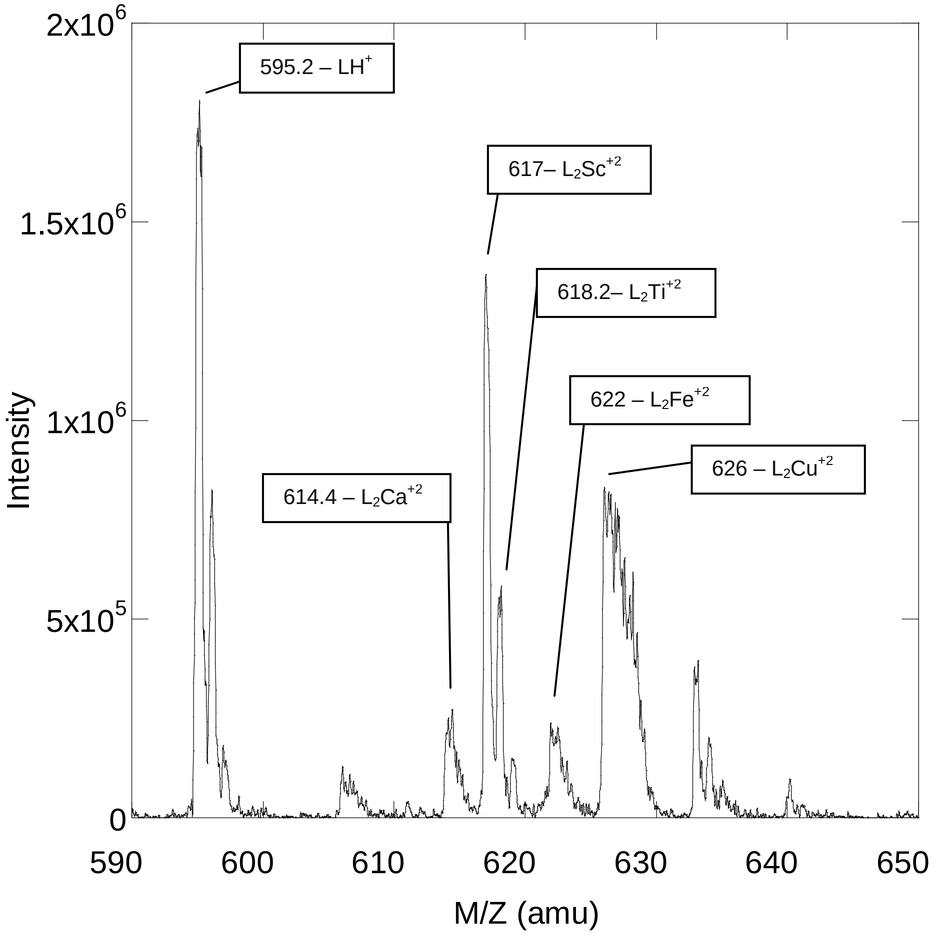

Figure 38 Electrospray Mass Spectrum of C5-BTBP and natural complexes

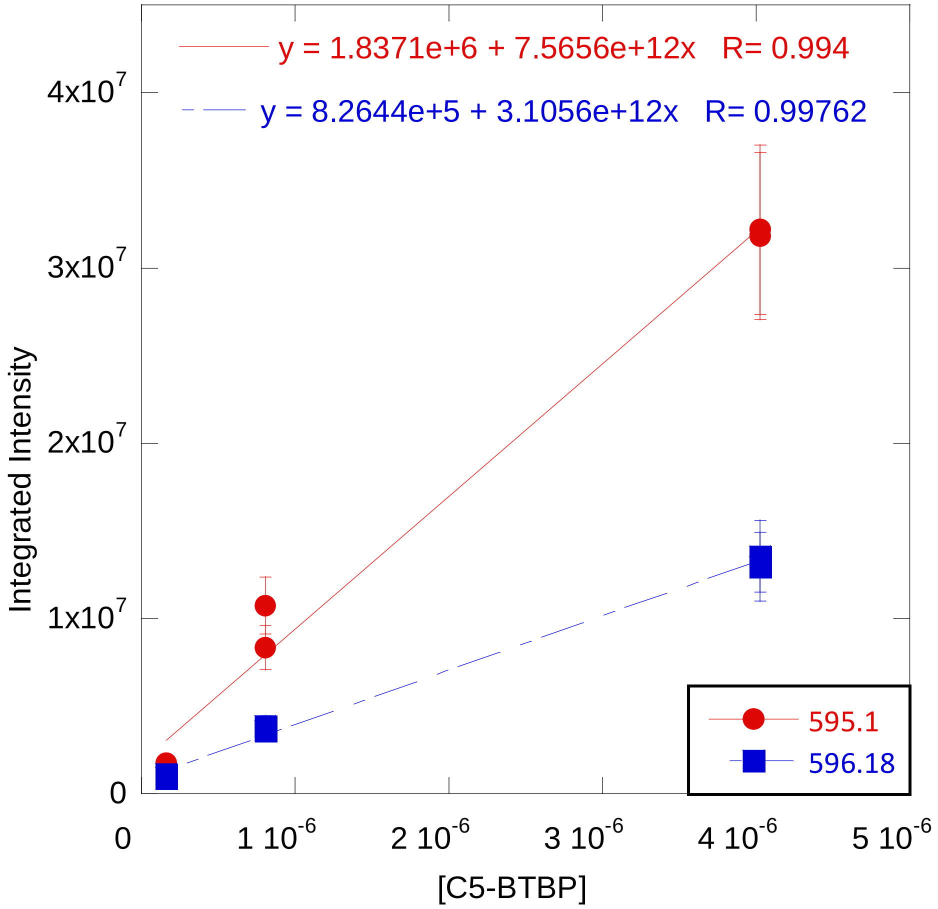

Figure 39 Linearity of ESI-MS for µM concentrations of C5-BTBP

No C5-BTBP peaks were present in fractions from the column run with 0.1 M HCl, or in the batch samples tested. This is not unreasonable, since no C5-BTBP was detected by UV absorbance below 4 M acid, and the columns were loaded with 1 M nitric acid in which bleeding was not expected. Data from ESI-MS is shown in Figure 40 for the first fractions off the column loaded with americium(III) and eluted with 0.1 M HCl. This lack of bleeding also agrees with the lack of C5-BTBP in the aqueous phase from solvent extraction reported by Nilsson.[84] From the data gathered on stability, it is proposed that the C5-BTBP ligand behaves similarly to isobutyl-BTP in that it is not hydrolyzed on the resin support but is instead protonated at higher acidities. The decreased extraction performance in 4 M and even 2 M acid is evidence of this mechanism, as is data from UV and ESI-MS. The effect of protonation can be observed by eye as resin in contact with higher acidities has a deeper yellow color compared to the creamy yellow in more dilute solutions. The protonated form of C5-BTBP has no detectable solubility in aqueous solutions in this work, and the non-existent bleeding is evidence of both the low aqueous solubility and the strong binding between the ligand and the resin support.

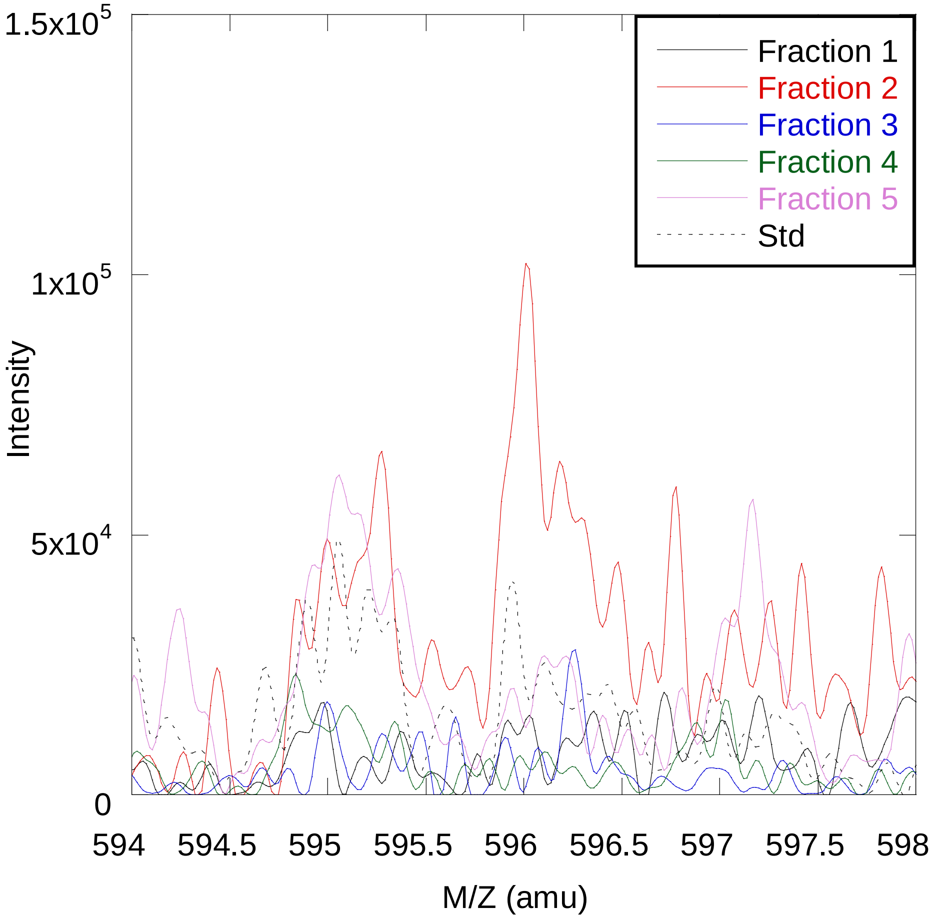

Figure 40 ESI-MS of Fractions 1-5 from the C5-BTBP Column loaded with Am(III) and eluted with 0.1 M HCl. The background trace is included.

CyMe$_4$-BTBP

It has previously been reported that molecules such as CyMe$_4$-BTBP, which do not contain benzylic hydrogens are less easily oxidized in acidic and nitrogen oxoacid environments than other BTBP ligands.[82] In Figure 13 and Figure 19 a drop in extraction by a factor of four can be seen at 4 M nitric acid compared to 2 M, and there even seems to be decreased extraction at 2 M compared to 1 M. This effect was investigated further by analyzing solutions for the presence of CyMe$_4$-BTBP.

Based on previous measurements of UV absorbance for C5-BTBP in a variety of solutions, standard concentrations of CyMe$_4$-BTBP were measured over a range of 0.1 M to 4 M HCl in 50% methanol solutions. Some of the results from these measurements are shown in Figure 41 for a portion of the UV region (240-400 nm). CyMe$_4$-BTBP displays a clear dependence on HCl concentration from 0.1 M to 4 M with peaks at 280 nm and 330 nm enhanced as [HCl] increases. The absorbance spectra for both concentrations approach isosbestic behavior near 292.5 nm. The average absorbance of all solutions at this wavelength for 251.1 µM CyMe$_4$-BTBP was 1.092 and so the molar absoptivity was calculated as 17,400 $M^{-1}cm^{-1}$ at this wavelength. As with the earlier work on C5-BTBP, this value is of the magnitude associated with $\pi\rightarrow\pi^*$ transitions. For the standard concentrations used, the lowest concentration of CyMe$_4$-BTBP in HCl with distinguishable peaks was 6.3 µM. A further limitation with these spectroscopy experiments was the limited transmission below 240 nm of the 96-well microplates used.

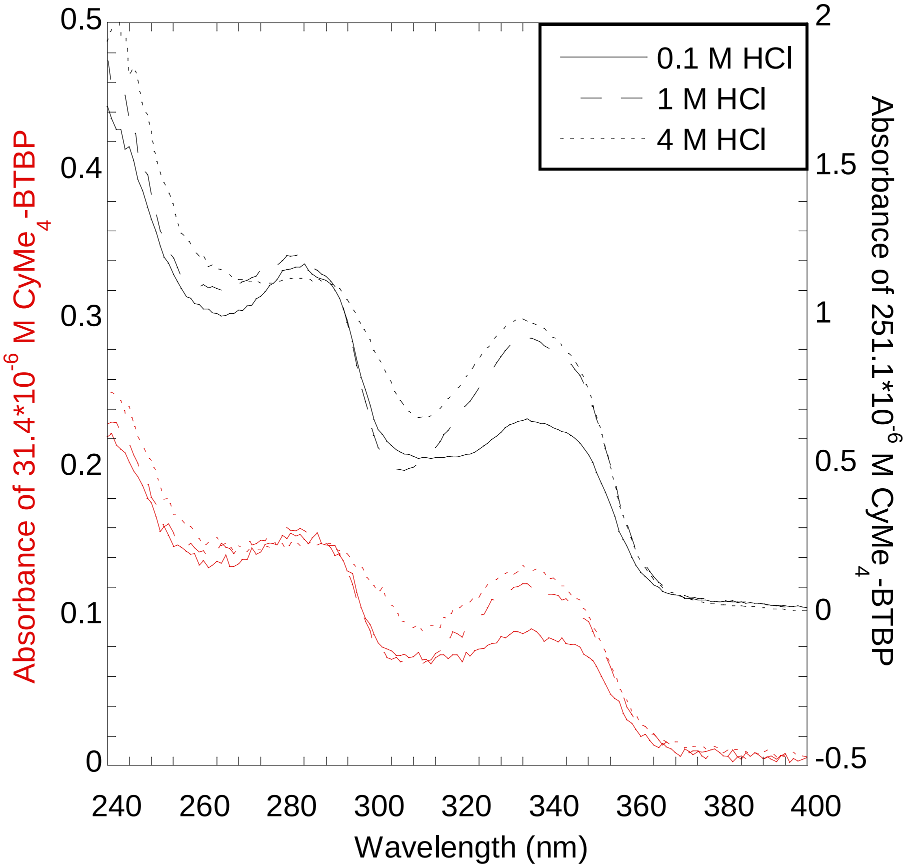

Figure 41 UV Absorbance of CyMe$_4$-BTBP at two concentrations in varied [HCl] and 50% methanol

Solutions from batch experiments in HCl and fractions from columns were analyzed for the presence of CyMe$_4$-BTBP. There was detectable CyMe4-BTBP from resin in 1 M and higher concentrations of HCl. The concentration present in the 4 M HCl batches with europium(III) was determined to be 300 µM, which is rather high when compared to the non-detectable bleeding from C5-BTBP resin, and the ~30 µM bleeding from isobutyl-BTP resin. The CyMe4-BTBP present in 4 M HCl solutions with americium(III), curium(III), and plutonium(III) were all less than 300 µM, but were still the same magnitude. Because of interference from nitrate species, no CyMe$_4$-BTBP was detectable in the column fractions by UV-Vis, and so these samples were run on ESI-MS to determine concentrations and to attempt observation of hydrolysis products.

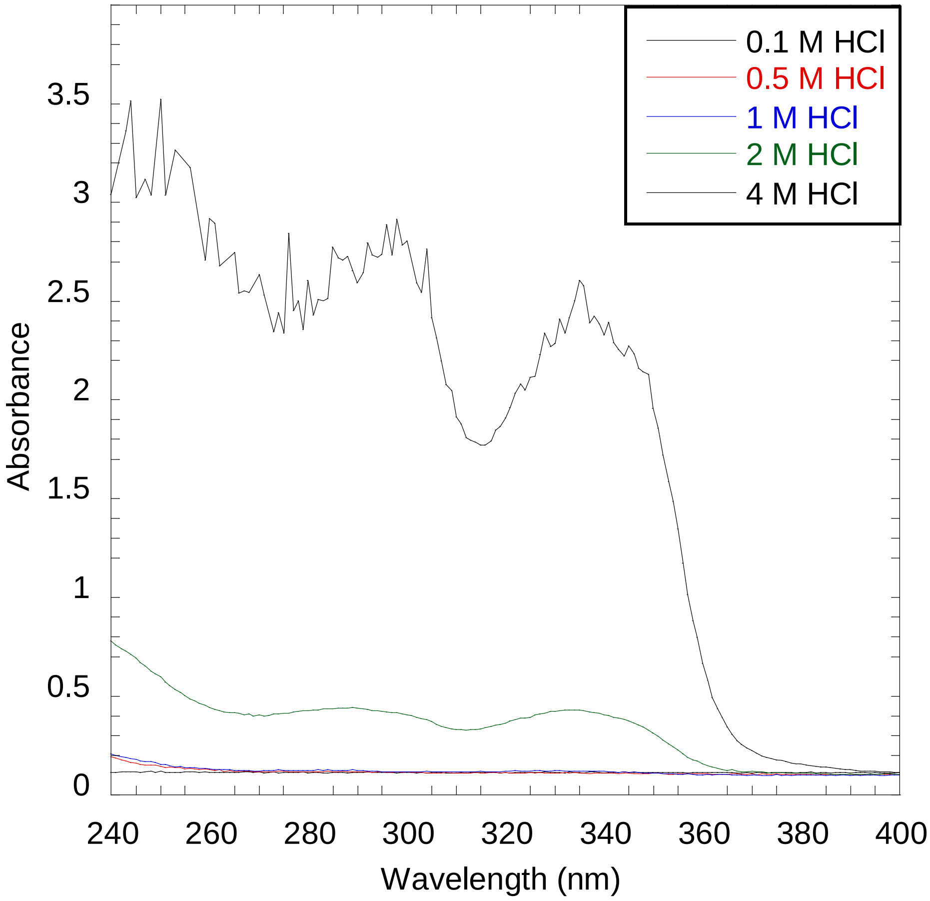

Figure 42 UV Absorbance of CyMe$_4$-BTBP resin contact solutions from Eu(III) batches in varied HCl

Figure 43 displays a background mass spectrum from an injection of methanol with peaks characteristic of solvent clusters. In the same figure, the spectrum of a standard CyMe$_4$-BTBP solution in methanol can be seen. The peaks present are displayed and identified in Figure 44, based on the prior work by Retegan, et al.[100]

Intensities of these complexes differ from those reported earlier, but could be due to the different instrument and analysis conditions used in this work as indicated in Chapter 2. The spectrum in the region where large fragments of CyMe4-BTBP would be expected is shown in Figure 45, but the peaks present can be explained by solvent clusters as their intensities are close to the peaks observed in the background. Integrated intensities for the peaks at 535.2 and 536.2 m/z are displayed in Figure 46, and in this micromolar region the instrument response is linear to the $CyMe_4$-BTBP concentration. At higher concentrations of 31.4 µM and 251.1 µM the response becomes non-linear, but concentrations above 6.3 µM could be detected instead with UV absorbance barring the presence of interfering species.

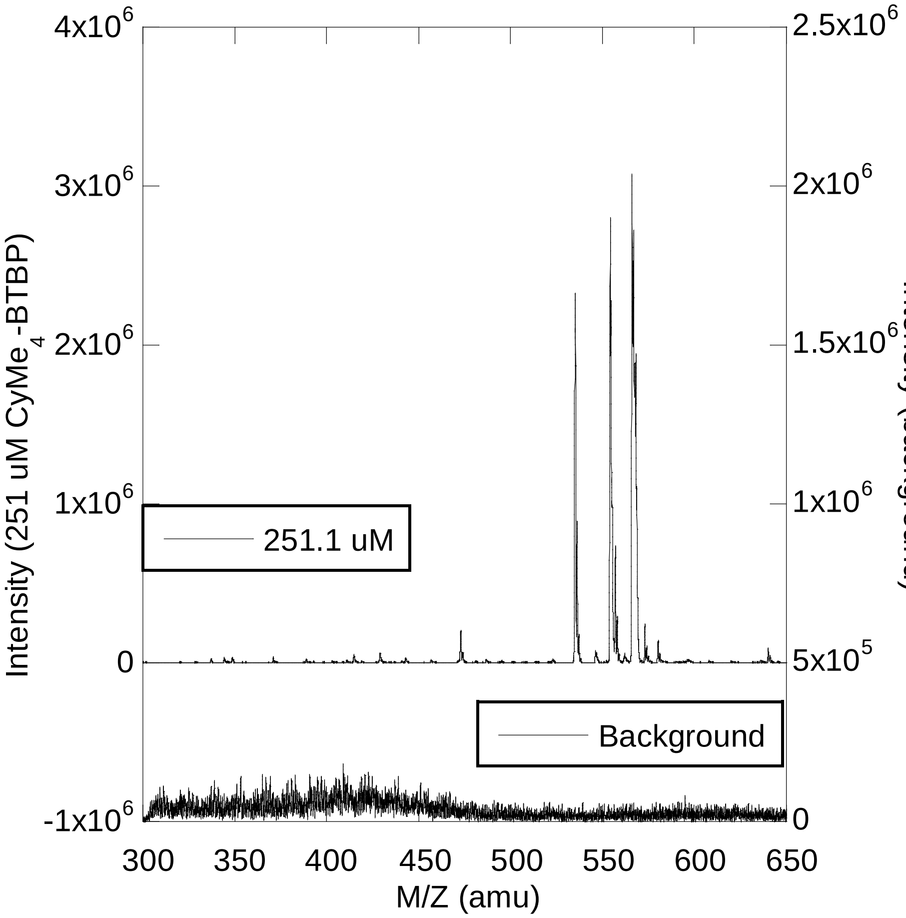

Figure 43 Electrospray Mass Spectrum of a methanol solution (background) and a standard solution of CyMe$_4$-BTBP

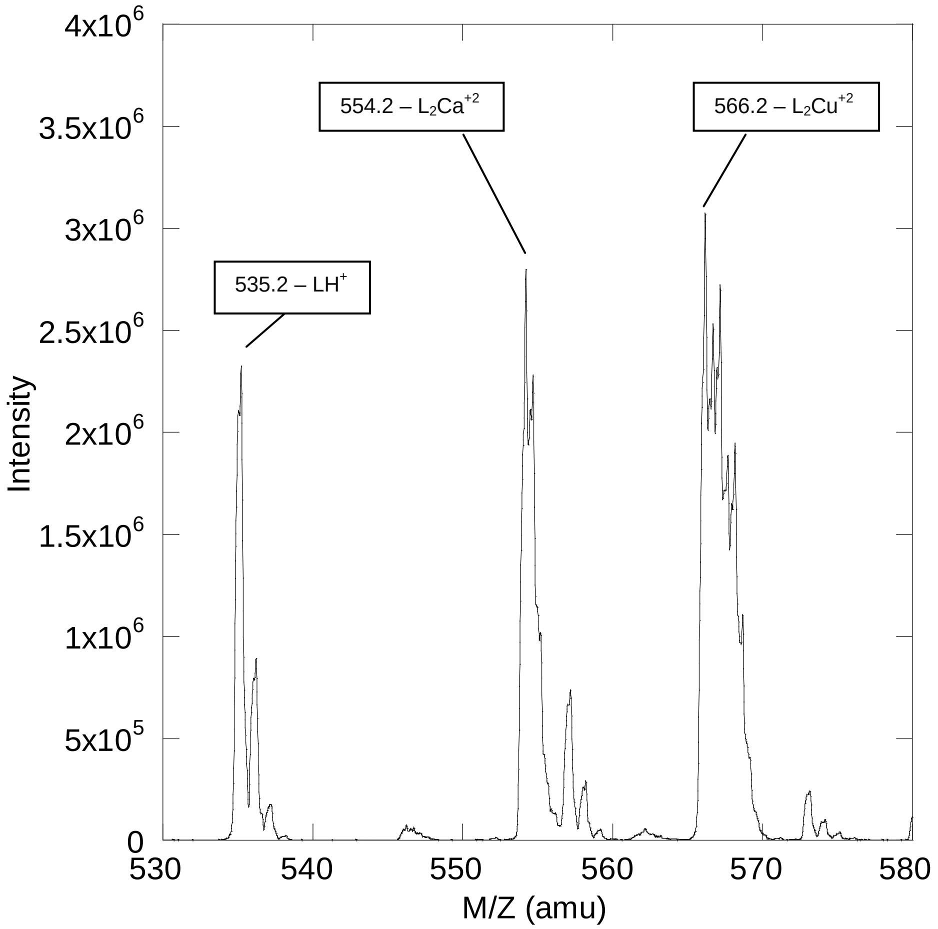

Figure 44 Electrospray Mass Spectrum of CyMe$_4$-BTBP and natural complexes

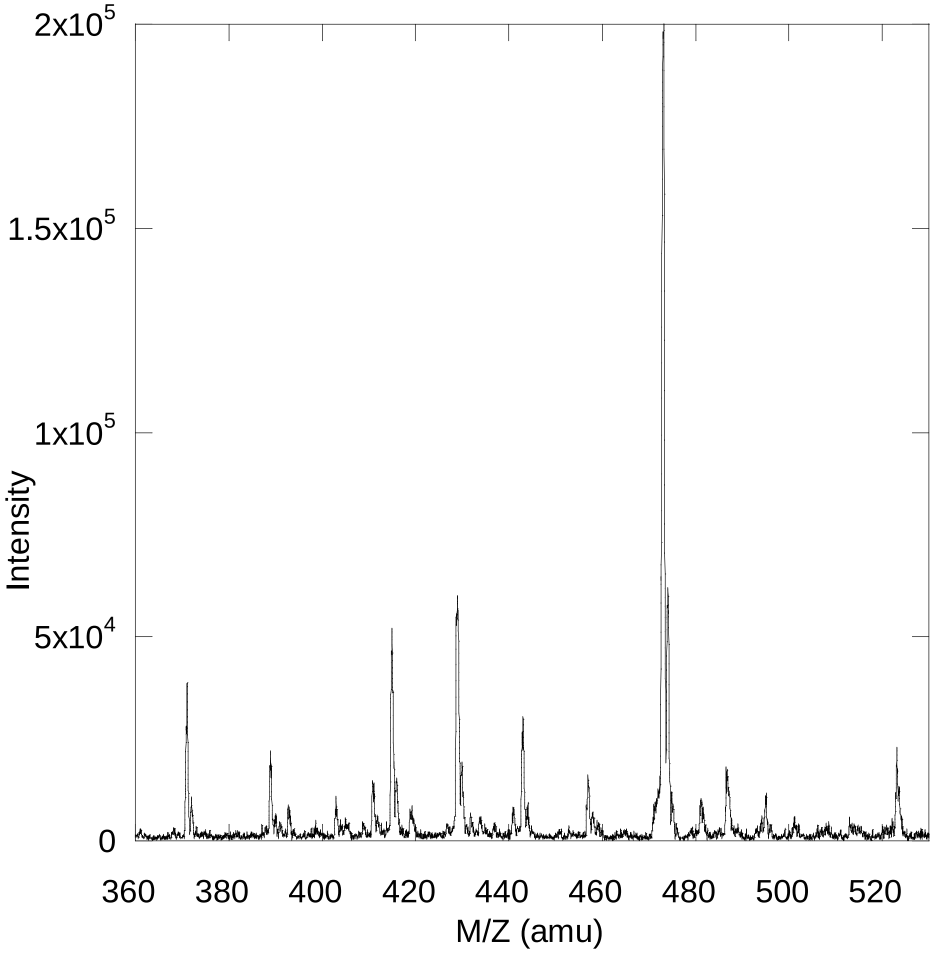

Figure 45 Electrospray Mass Spectrum of CyMe$_4$-BTBP fragments

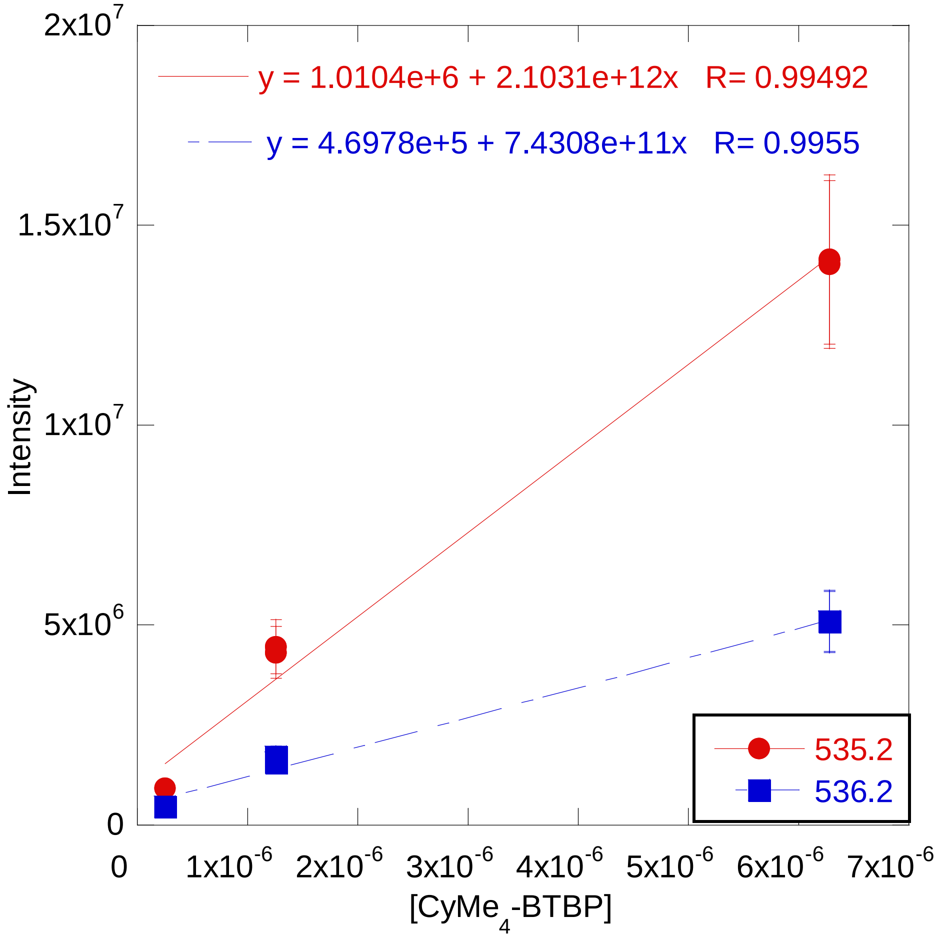

Figure 46 Linearity of ESI-MS for micromolar concentrations of CyMe$_4$-BTBP

No CyMe$_4$-BTBP peaks were present in fractions from the column run with 0.1 M HCl, or in the batch samples tested. The only peak present that could be related is at 566.2 amu, which would correspond to a complex with Fe according to work by Retegan.[100] Since this peak was not present in the standards, and since no main peak or complex peaks for Ca or Cu as in the standard are present, this peak will not be considered as indicative of the presence of the extractant.

From the data gathered on stability, it is proposed that the CyMe$_4$-BTBP ligand behaves similarly to isobutyl-BTP and C5-BTBP in that it is not hydrolyzed on the resin support but is instead protonated at higher acidities. The decreased extraction performance in 4 M and even 2 M acid is evidence of this mechanism, as is data from UV and ESI-MS. The effect of protonation can be observed by eye as resin in contact with higher acidities has a deeper yellow color compared to the creamy yellow in more dilute solutions. The protonated form of CyMe$_4$-BTBP has higher solubility in aqueous solutions than the neutral form, as indicated by the UV absorbance data. As discussed above, during some of the extraction work and in some of the columns, small crystals of the extractant were observed which were not bound to any resin. The presence of this excess extractant did not appear to influence any of the extraction data other than a single set. However, the extractant crystals could be preferentially protonated and solvated in the range of acid used and could therefore be responsible for the significantly elevated levels of extractant in solutions from the batch experiments. At this time bleeding cannot be ruled out, but based on the stability of C5-BTBP resin and the greater stability of CyMe$_4$-BTBP in other reports, there is confidence that the resin itself is stable and that the CyMe$_4$-BTBP detected in UV-Vis was the result of easily solvated extractant crystals.

CHAPTER 7

CONCLUSIONS

Isobutyl-BTP

Isobutyl-BTP has been investigated for use as a coating on extraction chromatography resins for the separation of trivalent actinides from trivalent lanthanides. The resin prepared in this work demonstrated elevated extraction of trivalent actinides over the trivalent lanthanides, resulting in promising separation factors for analytical applications, such as the separation factor of ~190 for americium(III) over europium(III). Tetravalent plutonium is also extracted, and behaves similarly to americium(III) and curium(III). The resin is stable and extracts well up to 2 M nitric acid, with a decreased performance in extraction at 4 M nitric acid but with minimal bleeding of extractant. The excellent stability of this resin and its extraction properties warrant further investigation for application to analytical separations.

The detectable bleeding and loss of extractant in the column and batch studies is practically a non-issue. If the bleeding remained constant for the life of the column, the column could be used 25,000 times before even 1% of extractant had bled off. If the desired application of this resin required even lower bleeding, it might be possible to further stabilize this resin by grafting or chemically anchoring the extractant to the resin as has been done with a malonamide and chloromethylated resin.[71,72] It might also be possible to incorporate the extractant into the structure of the resin by including it in the polymerization mixture, effectively encapsulating the extractant and preventing its release.[106-109] Despite the drawbacks of slower kinetics, lower extraction, and greater susceptibility to hydrolysis of nPr-BTP, future work could include the preparation and characterization of this resin in order to compare the behavior of isobutyl-BTP with nPr-BTP both in solvent extraction and on solid supports. Comparisons of their kinetics and their stability with respect to bleeding would also be valuable to the scientific community.

Overall, the isobutyl-BTP resin was very successful, and no issues were observed that would prevent its further use “as-is” for separations work. Several of the excellent properties of this resin are summarized in Table 9. Future work should involve characterization of this resin with other metals which are known to interfere with trivalent actinide extractions. Attempts should also be made to maximize the ligand loading.

C5-BTBP

C5-BTBP has been coated onto resin and the resulting product has been characterized for use in extraction chromatography to separate trivalent actinides from trivalent lanthanides. The resin prepared in this work demonstrated acceptable extraction of trivalent actinides over trivalent lanthanides, with the separation factor of 2.7 for americium(III) from curium(III) at 1 M HNO_3 being the most promising outcome. Tetravalent plutonium is also extracted, and behaves more like americium(III) than curium(III). The resin is extremely stable up to 4 M HCl or HNO_3, but does exhibit decreased extraction beginning at 2 M acid. In addition to the americium(III)/curium(III) separation factor the lack of detectable bleeding is extremely favorable.

The slow kinetics of this resin when used in columns are the major obstacle to its use in extraction chromatography. It might be possible to include a malonamide such as DMDOHEMA in the preparation of the coated resin, as has been done with CyMe4-

BTBP in solvent extraction, to make the extraction by C5-BTBP more kinetically favorable.[91] It would also be worthwhile to explore whether C5-BTBP can be dissolved in other suitable solvents such as 1-octanol for coating of the resin. Experiments with C5-BTBP on a different backbone could also be useful, both with and without DMDOHEMA as a phase transfer agent, and with and without 1-octanol or other suitable solvents as coating agents. Backbones such as polyacrylonitriles could be considered for further exploration.

Despite the problems with kinetics, if time and the process setup allow for the mixing of resin with contact solutions for extended periods of time (12-24 hours) such that equilibrium can be reached, then the favorable separation factor for americium(III)/curium(III) could possibly be exploited.

$CyMe_4$-BTBP

$CyMe_4$-BTBP has been coated onto resin and the resulting product has been characterized for use in extraction chromatography to separate trivalent actinides from trivalent lanthanides. The resin prepared in this work demonstrated strong extraction of trivalent actinides over trivalent lanthanides, with the separation factors in 2 M HNO_3 being the most promising outcome, such as ~340 for americium(III) over europium(III). Tetravalent plutonium is extracted to a greater extent than either americium(III) or curium(III), which is not necessarily a drawback for analysis of analytical samples. The resin is extremely stable up to 4 M HCl or HNO_3, but does exhibit decreased extraction beginning at 2 M acid.

The presence of CyMe$_4$-BTBP in many of the contact solutions could be attributable to the presence of excess extractant crystals in the resin, and better preparation methods should be explored. In addition to the problems with preparation, the slow kinetics of this resin when used in columns preclude its use in extraction chromatography. It might be possible to include a malonamide such as DMDOHEMA in the preparation of the coated resin, as has been done with CyMe4-BTBP in solvent extraction, to make the extraction by CyMe$_4$-BTBP more kinetically favorable.[91] It would also be worthwhile to explor whether CyMe$_4$-BTBP can be dissolved in other suitable solvents such as 1-octanol for coating of the resin. Experiments with CyMe$_4$-BTBP on a different backbone could also be useful, both with and without DMDOHEMA as a phase transfer agent, and with and without 1-octanol or other suitable solvents as coating agents. Backbones such as polyacrylonitriles could be considered for further exploration. All of these options could help the kinetics of extraction, and they might also allow for a cleaner preparation method which will not leave behind unbound extractant which can interfere with the extraction.

Currently the CyMe$_4$-BTBP resin has too many problems, ranging from bleeding to kinetics, for it to be applied to separations.

Table 9 Summary of Resin Properties from Final Amberchrom CG-71 Batches

Extractant	Weight Loading	Kinetics	Bleeding	Highest $k'_{Am(III)}$	Highest $k'_{Pu(IV)}$	Best HNO_3 Am/Eu SF	Best HNO_3 Am/Cm SF	Best Am(III) Eluent	Largest Issue
isobutyl-BTP	15.4%	fast	minimal	3827.22	4034.45	195.2 (1M)	0.49 (2M)	0.1 M HCl	None
C5-BTBP	8.87%	slow	none	76.68	141.39	41.1 (1M)	2.7 (1M)	0.1 M EDTA	Kinetics
$CyMe_4$-BTBP	9.98%	slow	problematic	1020.48	1749.51	339 (2M)	1.27 (2M)	0.1 M EDTA	Preparation, Bleeding

APPENDIX

EXTRACTION DATA

Table 10 Extraction Data for Single Replicate Malonamide Resins

Prep Method	Ligand	[HNO_3]	D_w	σ_{Dw}
Hexane	DMDBTDMA	0.01	-1.16	-3.15
		0.1	-2.62	-2.78
		0.5	-1.88	-3.59
		1	-3.51	-3.73
		2	4.70	3.69
		4	4.88	3.28
	DMDOHEMA	0.01	4.09	3.35
		0.1	-5.06	-3.73
		0.5	-4.54	-3.48
		1	-6.44	-3.18
		2	-0.95	-3.63
		4	17.97	4.10
Acetone	DMDBTDMA	0.01	4.75	0.07
		0.1	-1.02	-0.02
		0.5	6.11	0.09
		1	2.40	0.04
		2	5.02	0.08
		4	6.84	0.10
	DMDOHEMA	0.01	15.54	0.24
		0.1	-2.53	-0.04
		0.5	-3.39	-0.05
		1	-5.18	-0.08
		2	-9.01	-0.14
		4	278.14	4.77
Methanol	DMDBTDMA	0.01	-3.76	-0.06
		0.1	4.60	0.07
		0.5	4.47	0.07
		1	9.00	0.14
		2	8.12	0.12
		4	9.98	0.15
	DMDOHEMA	0.01	2.34	0.04
		0.1	-2.66	-0.04
		0.5	-5.28	-0.08
		1	4.04	0.06
		2	6.93	0.11
		4	11.98	0.18

Table 11 Extraction Data for Malonamide Resins Prepared Using Hexane

Ligand	[HNO_3]	Avg. D_w	σ_{avg}
DMDBTDMA	0.1	3.89	2.23
	0.5	-1.92	2.18
	1	-1.34	2.16
	2	2.40	2.06
	4	-2.09	1.99
DMDOHEMA	0.1	-5.97	2.12
	0.5	4.85	4.23
	1	-0.40	2.27
	2	4.88	2.27
	4	24.88	2.25

Table 12 Extraction Data for Malonamide Resins Prepared Using Acetone

Ligand	[HNO_3]	Avg. D_w	σ_{avg}
DMDBTDMA	0.1	21.43	2.46
	0.5	-4.30	2.81
	1	-8.60	2.39
	2	-3.16	2.12
	4	-37.12	2.70
DMDOHEMA	0.1	21.33	2.78
	0.5	-3.64	2.31
	1	-14.79	2.57
	2	18.43	2.81
	4	28.17	2.72

Table 13 Extraction Data for Malonamide Resins Prepared Using Methanol

Ligand	[HNO_3]	Avg. D_w	σ_{avg}
DMDBTDMA	0.1	7.74	2.89
	0.5	9.54	2.98
	1	-3.67	2.87
	2	-11.87	2.81
	4	3.82	2.91
DMDOHEMA	0.1	20.20	2.29
	0.5	-4.72	2.59
	1	-4.07	2.70
	2	-3.99	2.74
	4	-0.63	2.98

Table 14 Extraction data for initial isobutyl-BTP batches

Prep Method	[HNO_3]	D_w	σ_{Dw}
methanol	0.01	12.23	0.19
	0.1	9.64	0.15
	0.5	22.08	0.34
	1	52.22	0.82
	2	111.21	1.80
	4	125.78	2.06
acetone	0.01	31.29	0.48
	0.1	18.84	0.29
	0.5	75.84	1.20
	1	192.58	3.18
	2	233.47	4.06
	4	100.48	1.59
hexane	0.01	16.40	3.04
	0.1	35.28	3.74
	0.5	116.84	4.71
	1	206.11	6.07
	2	650.22	11.50
	4	706.06	12.47

Table 15 Extraction data for varied weight loading isobutyl-BTP resins

Resin Weight %	[HNO_3]	Avg. D_w	σ_{avg}
8.36%	0.1	27.52	2.04
	0.5	133.42	2.65
	1	266.82	3.16
	2	550.46	4.72
	4	492.92	4.61
4.16%	0.1	10.23	2.72
	0.5	8.14	2.67
	1	25.70	2.78
	2	28.23	2.70
	4	41.33	2.31
16.7%	0.1	262.55	3.15
	0.5	2239.49	15.27
	1	5539.62	34.07
	2	12672.9	121.24
	4	3598.60	26.00

Table 16 Extraction Data for C5-BTBP on Various Solid Supports

Resin	$[HNO_3]$	Avg. D_w	σ_{avg}
Amberchrom CG-71	0.1	35.80	3.87
	0.5	46.47	4.40
	1	84.71	4.22
	2	176.04	5.59
	4	80.74	6.03
Amberlite XAD-4	0.1	0.15	1.15
	0.5	1.92	1.12
	1	-5.51	1.01
	2	0.35	1.00
	4	-9.27	0.93
Amberlite XAD-7HP	0.1	33.65	0.84
	0.5	135.61	1.27
	1	86.40	1.06
	2	71.54	0.98
	4	13.41	0.80

Table 17 Extraction Data for $CyMe_4$-BTBP on Various Solid Supports

Resin	$[HNO_3]$	Avg. D_w	σ_{avg}
Amberchrom CG-71	0.1	29.59	4.75
	0.5	205.74	7.28
	1	1156.29	38.18
	2	1367.92	49.02
	4	33.13	6.73
Amberlite XAD-4	0.1	2.88	3.41
	0.5	-21.83	3.28
	1	86.92	4.03
	2	27.42	3.23
	4	12.32	5.22
Amberlite XAD-7HP	0.1	456.95	4.15
	0.5	911.17	7.58
	1	2392.42	20.71
	2	2398.69	19.35
	4	229.42	4.51

Table 18 Extraction data for isobutyl-BTP resin with Am(III), Cm(III), Pu(IV), and Eu(III) in Nitric Acid.

Element	[HNO_3]	Avg. D_w	σ_{avg}	k'	$\sigma_{k'}$
Americium-241 (III)	0.1	262.54	6.53	79.29	1.97
	0.5	2244.26	23.69	677.77	7.157
	1	5539.62	82.43	1672.96	24.90
	2	12672.90	224.96	3827.22	67.94
	4	3598.60	40.76	1086.78	12.31
Curium-244 (III)	0.1	966.38	10.40	291.85	3.14
	0.5	5935.62	62.95	1792.56	19.01
	1	13986.26	197.13	4223.85	59.53
	2	26078.83	482.03	7875.81	145.57
	4	11868.88	161.74	3584.40	48.84
Plutonium-239 (IV)	0.1	257.69	5.03	77.82	1.52
	0.5	3095.35	31.75	934.79	9.59
	1	7148.50	83.88	2158.85	25.33
	2	13359.09	183.96	4034.45	55.56
	4	6266.68	71.64	1892.54	21.63
Europium (III)	0.1	8.91	1.27	2.69	0.38
	0.5	23.62	1.14	7.13	0.34
	1	153.73	2.34	46.43	0.71
	2	67.79	1.46	20.474	0.44
	4	46.18	1.89	13.95	0.57

Table 19 Extraction data for isobutyl-BTP resin with Am(III), Cm(III), Pu(IV), and Eu(III) in Hydrochloric Acid.

Element	[HNO_3]	Avg. D_w	σ_{avg}	k'	$\sigma_{k'}$
Americium-241 (III)	0.1	-5.99	3.77	-1.81	1.14
	0.5	5.38	2.83	1.62	0.85
	1	2.57	2.80	0.78	0.84
	2	-9.53	2.39	-2.88	0.72
	4	1.26	2.65	0.38	0.80
Curium-244 (III)	0.1	5.26	6.35	1.59	1.92
	0.5	-3.35	5.31	-1.01	1.60
	1	-25.66	4.82	-7.75	1.46
	2	-9.61	8.26	-2.90	2.50
	4	-36.15	5.31	-10.92	1.60
Plutonium-239 (IV)	0.1	0.76	3.38	0.23	1.02
	0.5	6.63	3.49	2.00	1.06
	1	6.78	3.21	2.05	0.97
	2	2.47	3.34	0.75	1.01
	4	-3.49	3.57	-1.05	1.08
Europium (III)	0.1	-2.87	0.94	-0.87	0.28
	0.5	-8.89	1.25	-2.68	0.38
	1	-5.45	0.71	-1.65	0.21
	2	-4.00	0.95	-1.21	0.29
	4	-9.17	0.99	-2.77	0.30

Table 20 Extraction data for C5-BTBP resin with Am(III), Cm(III), Pu(IV), and Eu(III) in Nitric Acid.

Element	[HNO_3]	Avg. D_w	σ_{avg}	k'	$\sigma_{k'}$
Americium-241 (III)	0.1	64.10	3.37	22.18	1.16
	0.5	123.02	4.31	42.57	1.49
	1	221.63	4.79	76.68	1.66
	2	166.81	4.35	57.72	1.51
	4	69.70	3.29	24.12	1.14
Curium-244 (III)	0.1	21.47	3.55	7.43	1.23
	0.5	51.38	4.01	17.78	1.39
	1	82.10	3.94	28.41	1.36
	2	91.05	4.16	31.50	1.44
	4	34.28	3.71	11.86	1.28
Plutonium-239 (IV)	0.1	52.91	3.43	18.31	1.19
	0.5	120.52	4.08	41.70	1.41
	1	188.99	3.85	65.39	1.33
	2	408.64	6.25	141.39	2.16
	4	104.81	3.90	36.26	1.35
Europium (III)	0.1	-2.75	1.24	-0.95	0.43
	0.5	5.17	0.72	1.79	0.25
	1	-6.93	0.61	-2.40	0.21
	2	5.61	0.53	1.94	0.18
	4	-0.70	0.81	-0.24	0.28

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Table 21 Extraction data for C5-BTBP resin with Am(III), Cm(III), Pu(IV), and Eu(III) in Hydrochloric Acid.

Element	[HNO_3]	Avg. D_w	σ_{avg}	k'	$\sigma_{k'}$
Americium-241 (III)	0.1	8.05	3.14	2.79	1.09
	0.5	3.24	2.83	1.12	0.98
	1	7.21	3.83	2.50	1.32
	2	-2.69	3.68	-0.93	1.27
	4	5.46	3.29	1.89	1.14
Curium-244 (III)	0.1	-10.33	3.39	-3.58	1.17
	0.5	25.60	4.70	8.86	1.63
	1	6.78	3.56	2.35	1.23
	2	-8.38	3.06	-2.90	1.06
	4	-38.17	-6.04	-13.21	-2.09
Plutonium-239 (IV)	0.1	-8.73	3.63	-3.02	1.25
	0.5	-17.02	3.64	-5.89	1.26
	1	-8.33	4.80	-2.88	1.66
	2	-4.18	5.54	-1.44	1.92
	4	-1.55	5.87	-0.53	2.03
Europium (III)	0.1	-2.32	1.37	-0.80	0.47
	0.5	1.59	0.80	0.55	0.28
	1	14.04	0.94	4.86	0.33
	2	14.90	1.15	5.16	0.40
	4	4.36	1.09	1.51	0.38

Table 22 Extraction data for CyMe$_4$-BTBP resin with Am(III), Cm(III), Pu(IV), and Eu(III) in Nitric Acid.

Element	[HNO$_3$]	Avg. D$_w$	σ_{avg}	k'	$\sigma_{k'}$
Americium-241 (III)	0.1	112.04	4.90	42.69	1.87
	0.5	19.29	4.27	7.35	1.63
	1	738.18	12.87	281.25	4.91
	2	2678.41	43.28	1020.48	16.49
	4	421.96	12.73	160.77	4.85
Curium-244 (III)	0.1	15.76	4.10	6.00	1.56
	0.5	198.11	5.55	75.48	2.11
	1	579.35	12.78	220.73	4.87
	2	2483.95	65.50	946.38	24.96
	4	137.34	7.09	52.33	2.70
Plutonium-239 (IV)	0.1	28.79	3.16	10.97	1.21
	0.5	82.96	3.08	31.61	1.17
	1	1450.56	15.94	552.67	6.07
	2	4591.89	69.80	1749.51	26.59
	4	119.55	3.72	45.55	1.42
Europium (III)	0.1	-2.93	0.95	-1.12	0.36
	0.5	22.26	0.78	8.48	0.30
	1	-0.51	0.57	-0.19	0.22
	2	7.90	0.86	3.01	0.33
	4	-2.03	0.57	-0.77	0.22

Table 23 Extraction data for CyMe$_4$-BTBP resin with Am(III), Cm(III), Pu(IV), and Eu(III) in Hydrochloric Acid.

Element	[HNO$_3$]	Avg. D$_w$	σ_{avg}	k'	$\sigma_{k'}$
Americium-241 (III)	0.1	4.50	2.93	1.71	1.12
	0.5	-4.28	3.19	-1.63	1.22
	1	-9.11	3.87	-3.47	1.47
	2	3.93	4.18	1.50	1.59
	4	7.36	4.26	2.80	1.62
Curium-244 (III)	0.1	-16.22	-7.46	-6.18	-2.84
	0.5	20.81	4.84	7.93	1.84
	1	11.76	5.26	4.48	2.00
	2	27.17	6.05	10.35	2.30
	4	-24.46	5.08	-9.32	1.94
Plutonium-239 (IV)	0.1	-5.60	3.11	-2.13	1.18
	0.5	-4.72	2.84	-1.80	1.08
	1	5.45	2.99	2.08	1.14
	2	17.87	3.38	6.81	1.29
	4	21.25	2.84	8.10	1.08
Europium (III)	0.1	7.45	0.65	2.84	0.25
	0.5	-5.48	0.57	-2.09	0.22
	1	-8.31	0.73	-3.17	0.28
	2	1.74	0.68	0.66	0.26
	4	-6.21	0.98	-2.36	0.38

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