THESIS

EFFECTS OF MAJOR INORGANIC CONSTITUENTS OF ASPHALT ON THE RAPID DETERMINATION OF PLUTONIUM

Submitted by

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ABSTRACT

EFFECTS OF MAJOR INORGANIC CONSTITUENTS OF ASPHALT ON RAPID DETERMINATION OF PLUTONIUM

In case of a nuclear incident, standard radioanalytical techniques must be available to analyze radionuclides in unusual matrices. Radiochemical analysis of samples in standard matrices of soil, water, and air are very well established; however, much less research has been conducted on the effect of unusual matrices such as steel, concrete, glass, and asphalt. In the event of a detonation of an improvised nuclear device (IND) in an urban environment, the standard separation techniques used for plutonium separations from asphalt samples originating from roadways and roofing shingles must rigorously be tested to provide useful insight on the characteristics of the special nuclear material. Batch studies were used to determine the changes in uptake of plutonium on extraction chromatography resins in the presence of trace metal components found in asphalt including aluminum, iron, and manganese at possible ranges found in asphalt samples. In these studies, selected cations with a +3-oxidation state had some interesting effects on the uptake of plutonium on the extraction chromatography resins. Aluminum increased the sorption of plutonium only on DGA and TRU resins especially at rising concentrations. Iron very unexpectedly increased the sorption of plutonium on all resins particularly at high concentrations. Additionally, metals found in the +3 oxidation state were shown to interfere with the recovery of plutonium from column studies conducted due to the synergistic effects. From this data, the contaminates found in asphalt with a +3-oxidation state may either compete with plutonium or give rise to a “salting out” effect that increases the sorption on the extraction chromatography

resins and will need to be considered during the development of a rapid separation technique for plutonium from asphalt samples.

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CHAPTER 1: INTRODUCTION

1.1 Background

The rise of terror attacks in the last few decades has led to increased concern regarding the use of improvised nuclear devices (IND).[1] Although INDs are more difficult to construct than a radiological dispersion device (RDD), the devastation that such a device could cause in an urban environment would be catastrophic.[2,3] Beyond the initial blast from an IND, the resulting of fallout could spread deposits across a vast area as well as generate mass public panic and have devastating economic impacts.[4,5]

As defined in a 2008 report by the Department of Homeland Security, an IND is an "illicit nuclear weapon bought, stolen, or otherwise originating from a nuclear state, or a weapon fabricated by a terrorist group" which has a nuclear yield capable of "[producing] extreme heat, powerful shockwaves, and prompt radiation that would be acutely lethal for a significant distance".[3] An additional complication can arise with a misfiring of an IND which does not result in a nuclear yield.[6] In this case, the weapon mimics an RDD with the radiological material released being fissile. Regardless of the success in producing a nuclear yield, the need to accurately identify the isotopic signatures of the weapon in a timely fashion is of vital importance to emergency management and law-enforcement investigations following such an incident.[1,3,7,8]

If a terrorist group managed to acquire a weapon capable of producing a nuclear yield, the likelihood of targeting a large city is significantly greater than the likelihood of targeting a less

populated area. Ultimately, this would cause the greatest devastation and economic impact possible. Although many standard methods exist to separate radionuclides from standard matrices, such as air, soil and water, special considerations must be taken when sampling urban samples as elemental constituents of various samples can affect the recovery of radionuclides of interest.[5,9] Samples from an urban environment present particular challenges because they often contain asphalt among many other building materials due to its uses to construct roadways and roof shingles.[9]

1.1.1 Plutonium

Since the 1940s, the idea of using fissile material in weapons to cause mass destruction has been a main concern of many countries and will continue to be a point of concern for decades to come.[10] From the race to build the first nuclear weapons during World War II to the nuclear arms race during the Cold War to Russia's recent invasion of Ukraine in 2020, followed by the most recent rejection of the Nuclear Test Ban Treaty by Russian authorities; nuclear weapons have been integral in shaping the modern world as we know it today and will continue to do so for many years to come.[11,12]

The foundational requirement of an IND is the fissile core. For any material to be fissionable, it must have a high atomic number (high Z-value) and it must have a low neutron to proton (n-p) ratio. Additionally, for material to be considered fissile as opposed to fissionable, it must be able to fractionate after absorbing a thermal neutron.[13] Due to the specific needs of a fissionable device such that each fission must also produce enough neutrons to generate a sustained chain reaction, only a few radionuclides could be used to construct an IND which are typically

classified as special nuclear material. The main nuclides that could be used to create an IND include ^{233}U, ^{235}U, and ^{239}Pu.[14]

Plutonium was first discovered and isolated as ^{238}Pu through the bombardment of uranium targets with 16 MeV deuterons.[15] Another method of producing plutonium was discovered through the bombardment of ^{238}U with neutrons.[16] In a reactor, ^{239}Pu is generated through the process of neutron capture of ^{238}U. Neutron capture of ^{238}U results in the formation of ^{239}U which beta decays to ^{239}Np. Following the formation of ^{239}Np, the product beta decays again to ^{239}Pu.[17]

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{239}_{92}\mathrm{U} \xrightarrow{\beta^-} {}^{239}_{93}\mathrm{Np} \xrightarrow{\beta^-} {}^{239}_{94}\mathrm{Pu}$$

Although a uranium-based weapon is easier to construct using a gun type mechanism, the need to enrich uranium to above ninety percent ^{235}U makes it more challenging for terrorist organizations to generate the requisite material to build this type of weapon.[16] Plutonium on the other hand presents different challenges due to the nature of the material requiring an implosion type mechanism to start fission which requires more sophisticated electronics and coordination of explosives. One of the greater concerns with plutonium-based weapons is the need (or lack thereof) to process the material to remove less fissile isotopes of plutonium before making the core of the weapon.[6,18] In some cases, reactor grade plutonium (plutonium harvested from spent fuel) containing up to 20% ^{240}Pu can be used to create a fissionable weapon.[6] This is rather concerning considering the risk of proliferation of nuclear technology from civilian programs and considering the quantities of plutonium and special nuclear materials currently declared to the International Atomic Energy Agency (IAEA).[19–21]

Additional information about the nature of an IND can also be gleaned based on a clean separation of the core material from daughter products from decay processes, activation products created as a result of neutron capture as well as other components found within the device. In particular, the ingrowth of ^{241}Am and other daughter products can also be used as a chronometer in plutonium-based weapons to determine the time at which the plutonium was last chemically separated.[22] Americium-241 is a decay product of ^{241}Pu, which is produced in a reactor through neutron capture of ^{239}Pu to produce ^{240}Pu followed by a secondary neutron capture leading to ^{241}Pu which subsequently beta decays to ^{241}Am.[17] The decay scheme for ^{241}Am is shown below:

$$^{239}\mathrm{Pu}(\mathrm{n},\gamma)^{240}\mathrm{Pu}(\mathrm{n},\gamma)^{241}\mathrm{Pu} \xrightarrow{-\beta^-} {}^{241}\mathrm{Am}$$

Furthermore, the ratios of daughter-products (^{241}Pu: ^{241}Am: ^{237}Np for example) can be used to determine if attempts were made to hide the actual age of the weapon by tampering with the anticipated ratios. Additional information about the weapon can be determined based on the isotopic composition of the core itself. If ^{239}Pu is left within a reactor, it continues to capture neutrons producing a variety of other isotopes including ^{240}Pu, ^{241}Pu, and ^{242}Pu. The amount of ^{240}Pu is a good indicator of the length of time plutonium has spent within a reactor and the intended use of the special nuclear material. Lower ratios of ^{240}Pu to ^{239}Pu are more indicative of plutonium produced to create weapons due to minimized time spent exposed to neutron fluence.[16] Nuclear forensics investigations can be aided by rapid, accurate separations of plutonium from other actinides, radionuclides, and various urban matrices.

Plutonium has unique chemical properties for an actinide element which must be accounted for in separation procedures. Five oxidation states of plutonium can be prepared and stabilized in solution under select conditions including Pu(III), Pu(IV), Pu(V), Pu(VI), and Pu(VII). In

addition to the multitude of oxidation states of plutonium, the small separation of energies between each state creates additional complications in plutonium chemistry. In more acidic conditions, the lower oxidation state of plutonium such as Pu(III) and Pu(IV) are more stable whereas higher oxidation states are more stable in alkaline conditions including Pu(VI) and Pu(VII). The most abundant oxidation states of plutonium include tetravalent plutonium followed by the trivalent and hexavalent states.[23]

One of the most intriguing aspects of plutonium chemistry is the reduction-oxidation (redox) relationship between plutonium ions in solution particularly between the four most common oxidation states of plutonium (III, IV, V, and VI). Since these states are comparable in magnitude and very close to 1 V, a unique situation arises in which multiple different oxidation states of plutonium can coexist within a solution. Using electrochemical potentials and redox reactions, the oxidation state of plutonium can be predicted and advantageously prepared for separation chemistry. Additionally, the selection of reversible or irreversible redox couples should be considered for plutonium chemistry.[23] For column studies discussed later, the reversible redox couple, Pu(III)/Pu(IV), was utilized in a separation scheme in which tetravalent plutonium was selectively adsorbed to TRU resin and titanium trichloride was used to reduce plutonium to a trivalent state to strip plutonium from the column.

The hydrolytic behavior of plutonium in solution is an additional consideration which needs to be accounted for. Hydrolysis leads to the formation of precipitates or different ionic species which can stick to glassware or not behave as chemically expected. The following equation demonstrates a general mechanism of plutonium hydrolysis.

$$Pu^{x+} + nH_2O \leftrightarrow Pu(OH)_n^{(x-n)+} + nH^+$$

Additionally, the tetravalent form of plutonium forms colloidal polymers in solution following hydrolysis. These colloids interfere with normal chemical reactions. To counteract the issues associated with hydrolysis and colloid formation, plutonium separations should be carried out in acidic solutions.[23]

1.1.2 Asphalt

Current urban debris matrices are modeled after the rubble created by the destruction of the World Trade Tower on September 11, 2001. Analysis of the rubble revealed the contents to be largely a mixture of concrete, glass, paper, gypsum wallboard, and other construction materials.[9] Asphalt presents a unique set of challenges for uniformity of sampling. Asphalt cement in the sense of roadway construction material is a mixture of course and fine aggregates and bituminous materials.[24] Similar to concrete materials, the aggregate material used for asphalt concrete may be locally sourced from various quarries and may have some variability in the quantities of metals present particularly depending on slag content.[5,24] Additionally, weathering of roadways has a great impact on the metal constituents found in asphalt.[25] Table 1 shows the total metal and semimetal content in a set of asphalt samples which demonstrates the variability in metals based on the traffic levels and weathering of the roadways.

Table 1. Absolute metal and metalloid concentrations in asphalt[25]

		Low traffic			High traffic		
		Fresh	Weathered	Norm. change	Fresh	Weathered	Norm. change
Na	g/kg	2.2 ± 0.4	4.5 ± 0.3	+ 20%	2.3 ± 0.4	0.7 ± 0.4	− 88%
Mg	g/kg	1.45 ± 0.12	2.8 ± 0.2	+ 12%	2.1 ± 1.0	2.3 ± 0.4	− 54%
Al	g/kg	7.2 ± 1.2	12.6 ± 0.5	0%	8.1 ± 1.4	20.1 ± 1.8	0%
K	g/kg	4.8 ± 1.3	5.9 ± 0.3	− 30%	4.8 ± 1.0	6.2 ± 0.7	− 48%
S	g/kg	0.86 ± 0.15	1.64 ± 0.04	+ 9%	0.69 ± 0.14	2.8 ± 0.4	+ 65%
Ca	g/kg	8 ± 3	12.83 ± 0.16	− 11%	7 ± 4	9.7 ± 1.1	− 44%
Fe	g/kg	9 ± 3	40 ± 10	+ 144%	8 ± 5	22 ± 4	+ 7%
Li	mg/kg	< 0.9	< 0.7	–	< 0.9	< 3	–
P	mg/kg	390 ± 150	440 ± 40	− 35%	200 ± 60	550 ± 70	+ 10%
V	mg/kg	16.0 ± 1.0	32.3 ± 2.0	+ 16%	15 ± 4	43 ± 6	+ 15%
Cr	mg/kg	14.3 ± 1.0	20.66 ± 0.16	− 17%	8.5 ± 1.3	18.0 ± 1.6	− 15%
Mn	mg/kg	200 ± 100	700 ± 200	+ 105%	100 ± 50	600 ± 100	+ 131%
Co	mg/kg	1.22 ± 0.06	4.2 ± 0.4	+ 100%	1.2 ± 0.4	3.0 ± 0.3	− 1%
Ni	mg/kg	7.7 ± 0.2	17 ± 2	+ 28%	9 ± 2	19 ± 3	− 14%
Cu	mg/kg	< 2	< 2	+ 16%	< 2	< 4	− 7%
Zn	mg/kg	10.7 ± 0.3	22 ± 2	+ 46%	13 ± 2	31 ± 4	− 32%
Sr	mg/kg	32 ± 6	82 ± 6	+ 108%	37 ± 10	63 ± 6	− 33%
As	mg/kg	2.44 ± 0.17	8.8 ± 0.8	+ 25%	2.4 ± 0.6	4.0 ± 0.2	− 6%
Mo	mg/kg	0.96 ± 0.14	2.09 ± 0.16	− 35%	0.9 ± 0.3	2.2 ± 0.3	+ 10%
Se	mg/kg	< 2	< 2	–	< 2	< 3	–
Cd	mg/kg	< 0.06	< 0.2	–	< 0.08	0.25 ± 0.06	–
Ba	mg/kg	160 ± 40	390 ± 30	+ 41%	160 ± 50	260 ± 40	− 35%
Ce	mg/kg	16 ± 2	17.6 ± 1.6	− 36%	12 ± 3	15.6 ± 1.4	− 49%
Pb	mg/kg	4.8 ± 1.3	6.9 ± 0.2	− 17%	4.0 ± 0.9	6.3 ± 0.9	− 36%
Th	mg/kg	2.3 ± 0.7	2.6 ± 0.2	− 36%	1.8 ± 1.0	3.3 ± 1.2	− 28%
U	mg/kg	0.37 ± 0.04	0.88 ± 0.02	+ 38%	0.27 ± 0.12	0.70 ± 0.02	+ 2%

Values represent averages ± standard deviation (n = 3). Norm. change: change between weathered and fresh samples based on Al-normalized values. For normalized data see Table S2

The most notable metals found in significant quantities in asphalt samples include sodium, magnesium, aluminum, potassium, calcium, iron, and manganese. Of the metals listed, prior data are available on the influence of sodium, magnesium, potassium, and calcium on extraction chromatography resins; however, iron, aluminum, and manganese give cause for further investigation due to their presence in significant quantities as well as interferents in a tripositive

state for iron and aluminum as well as the seven different oxidation states available to manganese.[26,27]

Furthermore, the use of organic material from the crude oil process for the creation of the bituminous material which helps bind the matrix together and create a waterproof coating creates additional challenges. The bituminous materials used in asphalt known as asphaltenes originate from the crude oil process and consist of large hydrophobic molecules approximately twenty or more carbons in length.[28] Figure 1 shows a model of asphaltenes found in bituminous materials which demonstrates the complexity of the organic materials used to waterproof roadways.[28] Due to the size and complexity of the structures shown below, extra considerations must be taken to dissolve samples into solution prior to analysis. Additionally, organic materials can complex with metals in solution leading to further interferences in a separation process.

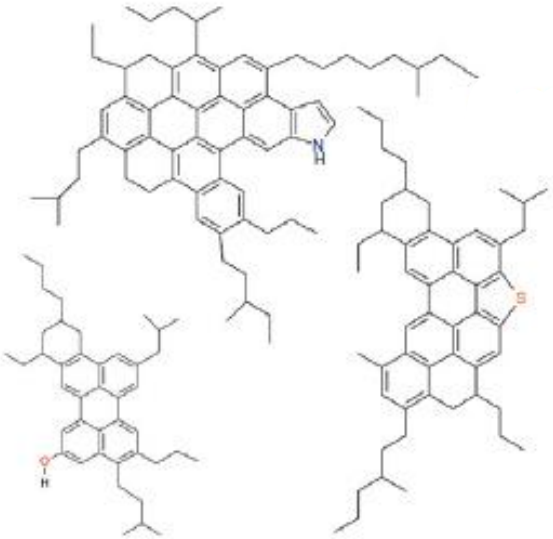


Figure 1. Model of Asphaltene in Bituminous Materials[28]

1.2 Extraction Chromatography

Extraction Chromatography is a widely used radioanalytical separation technique which combines the principles and selectivity of solvent extraction with the convenience of a chromatographic resin. This technique is useful for separating radionuclides from a wide variety of sample matrices rapidly and accurately.[29]

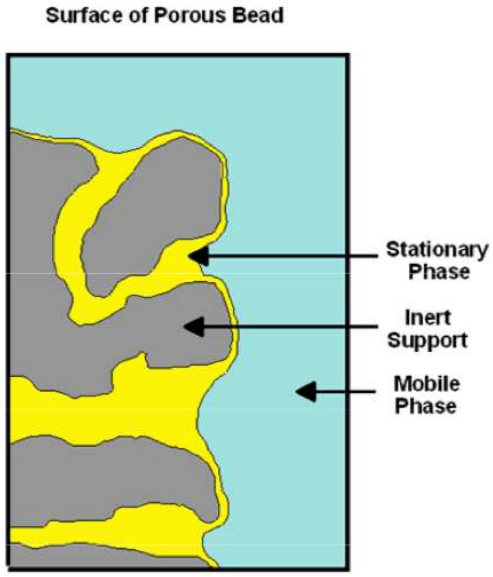


Figure 2. Diagram of Extraction Chromatography Resins[30]

An extraction chromatography system is composed of three parts. The stationary phase, the mobile phase, and the inert support all function together to create a working system. The inert support is typically made of porous silica or polymeric beads ranging from 50 to 150 µm in diameter. The inert support does not interfere with any reactions taking place between the stationary and mobile phases; however, the pore size can affect the rate of the reaction by restricting diffusion and movement.[31] The stationary phase is composed of organic liquid extractants and is contained within the pores of the bead.[32] When an aqueous solution—the

mobile phase—is in contact with the resin, two environments are available for the radionuclide of interest to sort itself into.[33] By changing the acid matrix, concentration, or addition of other analytes to the mobile phase, the possibility of changing the favorability for the radionuclide to exist in the stationary phase or the mobile phase becomes a very useful tool to selectively separate multiple radionuclides sequentially.[29]

1.3 Weight Distribution Ratios and Column Capacity Factors

The distribution ratio is a useful tool in solvent extraction used to determine the amount of solute extracted into the organic phase by comparing the relative concentration of analyte in the aqueous phase to the total amount of analyte added to the solution. In extraction chromatography, a similar quantity is described using the distribution ratio.[33,34] Since the stationary phase is contained within the resin beads, the distribution ratio cannot be used as it is in a different physical state. The weight distribution ratio, D_w, is calculated by accounting for the activity of analyte adsorbed to the resin per gram of resin, m_r, and comparing it to the activity in solution, A_s, per volume of solution, V_s. The following equation can be used to calculate the weight distribution ratio.[35] In this equation, the amount of analyte adsorbed to the resin is shown as the difference between initial activity, A_0, add to the batch experiment and the activity of the solution after contacting the resin, A_s.

$$D_w = \frac{A_0 - A_s}{A_s} \cdot \frac{V_s}{m_r}$$

The column capacity factor, k', can then be calculated from the weight distribution ratio by a specified factor for each given resin.[34,35] The column capacity factor denotes the number of free column values required to reach the peak elution for the given analyte. Table 2 describes the conversion factors between the weight distribution ratio and the column capacity factors.

Table 2. Conversion factors associated with extraction chromatography resins produced by Eichrom Technologies, LLC

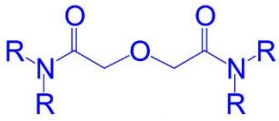
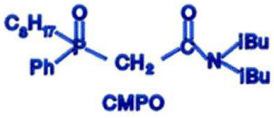
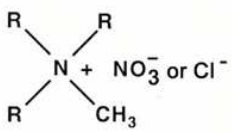
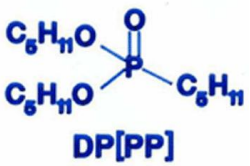
Resin	Extractant System	Conversion from D_w to k'
DGA	N, N, N', N' tetraoctyldiglycolamide (TODGA)	1.75
TRU	Octylphenyl-N—N-di-isobutyl carbamoylphoshine oxide (CMPO)	1.80
TEVA	Aliquat® 336	1.90
UTEVA	Diamyl amylphophonate (DAAP)	1.67

The column capacity factor, k', is used as a measure of retention of an analyte on the extraction chromatography resins studied. The k' values were used to demonstrate trends in the retention of analytes for the acid dependency curves, interferent batch studies, and stable element batch studies discussed in later sections.

1.4 Eichrom Resins

Eichrom Technologies, LLC, was founded in 1990 to provide commercialized products for radiochemistry, nuclear medicine, and geochemistry.[30] The extraction chromatography and ion exchange resins that they provide have been widely accepted throughout the broader radiochemistry community and have proven to have a broad range of separation applications. In this work, four Eichrom extraction chromatography resins were studied in regard to their ability to adsorb plutonium and their potential to separate plutonium from other radionuclides. The four resins include DGA, TRU, TEVA, and UTEVA which are summarized in Table 3. All resins used contain beads ranging from 50 – 150 µm in diameter.

Table 3. Stuctures of Extactant Molecules of Resins

DGA	TRU	TEVA	UTEVA
			
N, N, N', N' tetraoctyldiglycolamide (TODGA)	octylphenyl-N-N-di-isobutyl carbamoylphoshine oxide (CMPO)	trialkyl, methylammonium nitrate or chloride (Aliquat-336).	diamyl amylphophonate (DAAP)

Acid dependency curves demonstrate the retention of analytes on resins depending on acid type and concentration. Such curves can and should be utilized to generate a separation scheme which can selectively load a radionuclide, allow for rinsing of undesired radionuclides from the system, and strip the radionuclide of interest very selectively. Acid dependency curves are shown in later figures for several ions on the resins studied in nitric acid systems and hydrochloric acid systems. The figures shown below were also used to inform the decision to evaluate the influence of metals found in asphalt at the selected acid concentrations. *Horwitz, et. al.* observed an increase in column capacity factor, k', for DGA resin at lower acid concentrations so all batch studies for DGA were conducted at 1 M acid concentration. Similarly, TRU, TEVA, and UTEVA show

greater k' values at higher concentration so these batch studies and column studies were conducted at 3 M acid concentrations.

1.4.1 DGA

DGA resin is available as normal DGA and branched DGA. Normal DGA resin was used for batch distribution studies, and the extractant is composed of N, N,N'N'-tetra-n-octyldiglycolamide in the stationary phase.[36] Figure 3 shows the structure of normal DGA resin. In the figure, the R functional groups represent 1-octyldiglycolamide. Acid dependency studies have been conducted on a variety of actinides in nitric acid and hydrochloric acid systems and are shown in Figure 4.

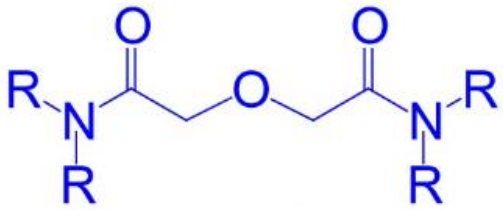


Figure 3. Molecular structure of extractant of DGA Resin: N, N, N', N' tetraoctyldiglycolamide (TODGA). R-functional groups are hydrocarbon chains.[36]

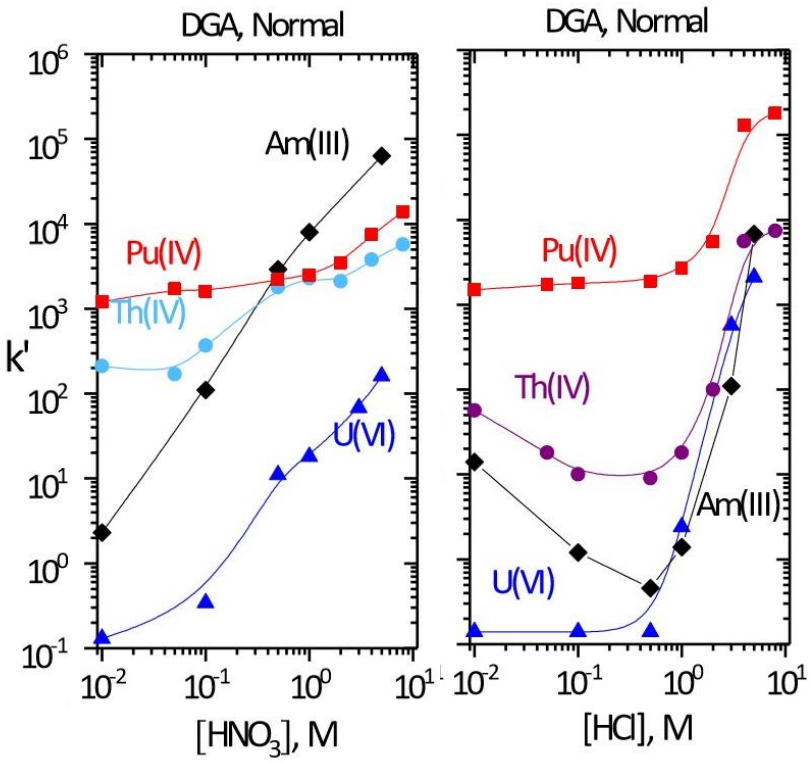


Figure 4. Acid dependancy curves for the uptake of actinides in on DGA resin at 23-25°C.[36]

DGA has a strong affinity for elements that exist in a tripositive state such as Am(III) or trivalent rare earth metals. The mechanism shown below is responsible for this behavior:

$$M^{+3} + 3DGA + 3X^{-} \leftrightarrow M(DGA)_3X_3$$

Where M is a tripositive analyte of interest and X is a nitrate or chloride counterion. Due to this interaction, DGA is largely applied to separate americium from a variety of samples. Since the extractant used for DGA is neutral, every tripositive analyte requires three counter ions in addition. Another mechanism has been described for the interaction of tetravalent metal with normal DGA as shown below:

$$M^{+4} + 4DGA + 4X^{-} \leftrightarrow M(DGA)_4X_4$$

Similar to trivalent metals, the tetravalent metals require four nitrates or chlorides, however, they only require two organic extractant molecules to form a complex.[36]

1.4.2 TRU

The extractant used in Transuranic (TRU) resin is octylphenyl-N,N-di-isobutyl carbamoylphophine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP) and is shown in Figure 5.[37] Acid dependency studies for several analyte have been conducted in nitric acid and hydrochloric acid with TRU resin and are depicted in Figure 6.

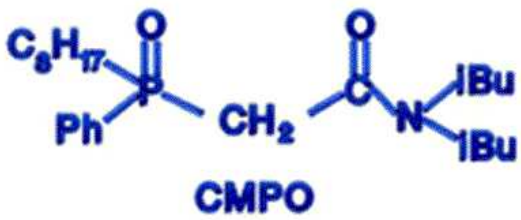


Figure 5. Molecular stucture of extractant of TRU resin: octylphenyl-N-N-di-isobutyl carbanoylphosphine oxide (CMPO)[37]

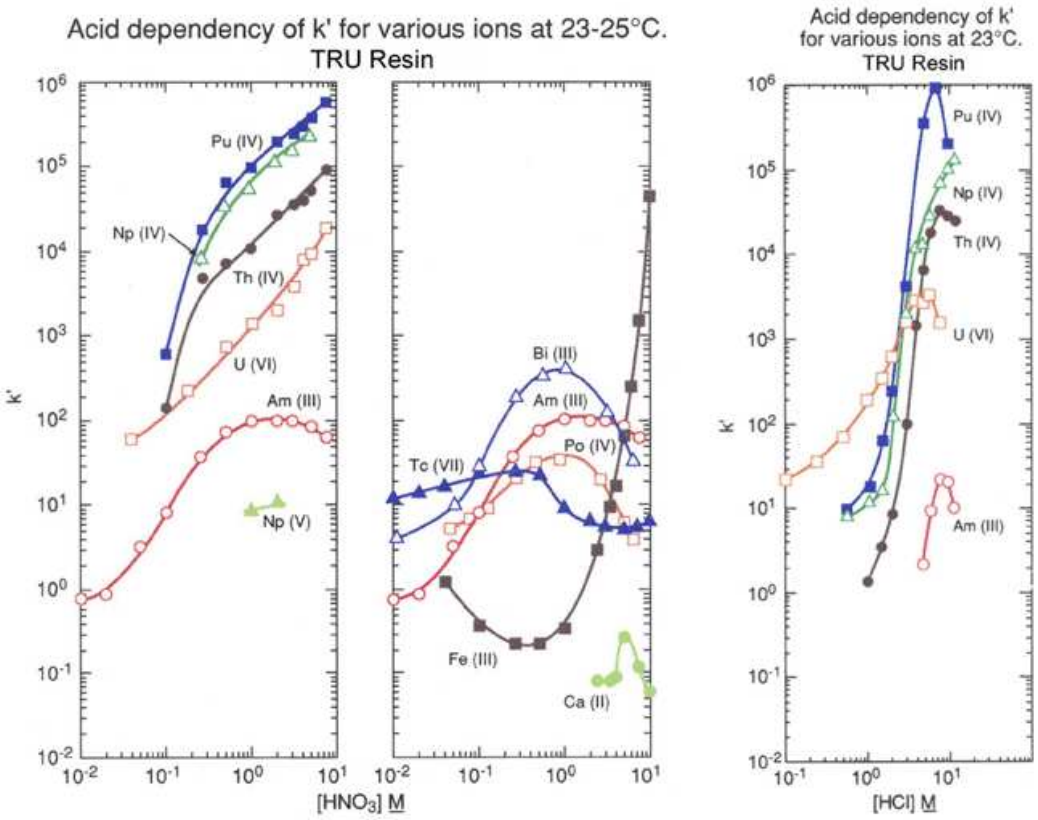


Figure 6. Acid dependency curve for the uptake of select ions on TRU resin.[37]

TRU resin is a very dynamic resin and is useful for separating actinides. When TRU resin interacts with trivalent metals, it uses the following mechanism by complexing two extractant molecules with three nitrates or chlorides for one metal ion.[37]

$$M^{+3} + 3X^{-} + 2TRU \leftrightarrow MX_3TRU_2$$

TRU resin also has an affinity for tetravalent metals and uranium (VI). The mechanism for complexing with metals in the aforementioned oxidation state is shown below.[37]

$$M^{+4} + 4X^{-} + 2TRU \leftrightarrow MX_4TRU_2$$

1.4.3 TEVA

Aliquat-336, which is trialkyl,methylammonium nitrate or chloride ,composes the extractant used in Tetravalent Actinide (TEVA) resin.[38] Figure 7 represents a depiction of Aliquat-336. Figure 8 shows a set of acid dependency curves for TEVA resin for a variety of radionuclides in nitric acid and hydrochloric acid systems.

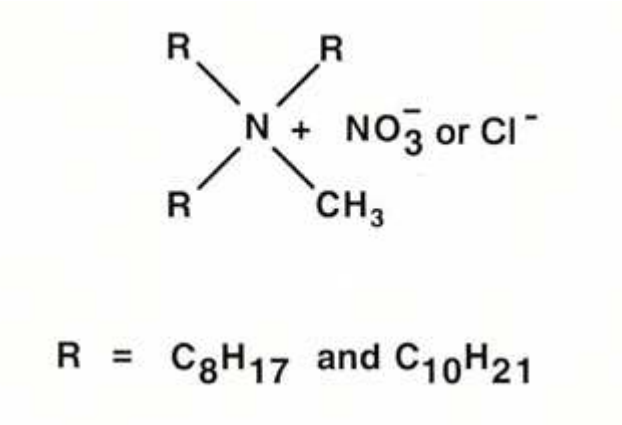


Figure 7. Molecular structure of extractant of TEVA resin: trialkyl, methylammonium nitrate or chloride (Aliquat-336). The R groups consist of hydrocarbon chains eight or ten carbons in length.[38]

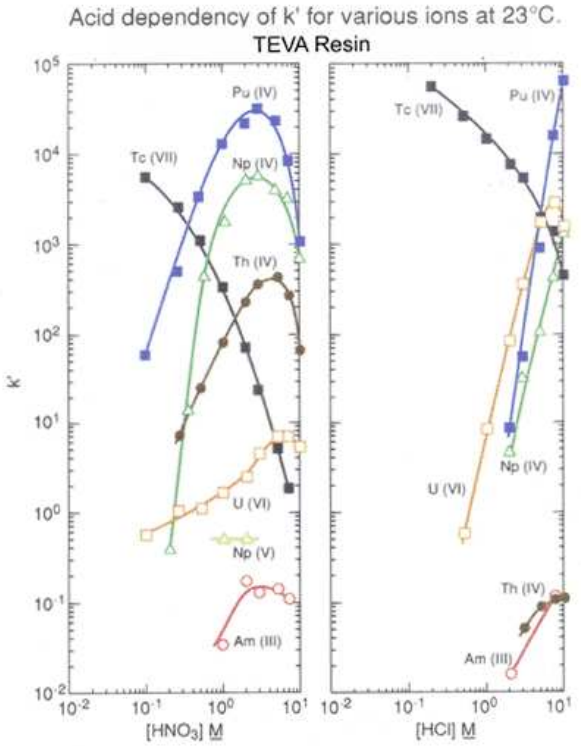


Figure 8. Acid dependancy curves for the uptake of various ions on TEVA resin.[38]

TEVA resin is an excellent resin when applied to separations of tetravalent metals. The extractant used for TEVA resin complexes with these metals with six nitrates or chlorides and two organic extractant molecules for every metal ion as shown in the mechanism below.

$$M^{+4} + 4X^- + 2TEVA \cdot 2X^- \leftrightarrow E_2^+ \cdot MX_6^{-2}$$

Figure 8 shows good retention of Pu (IV) above 1M acid concentrations for both nitric and hydrochloric acid whereas retention of Am (III) is low meaning the separation factor between the two analytes is very good.[38]

1.4.4 UTEVA

The extractant used in Uranium and Tetravalent Actinide (UTEVA) resin is composed of diamyl, amylphosphonate (DAAP) and is shown in Figure 9.[39] Acid dependency curves for a variety of ions on UTEVA resin are shown in Figure 10 both in nitric acid and hydrochloric acid systems.

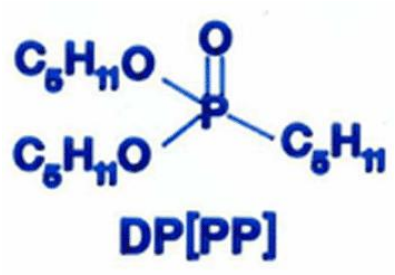


Figure 9. Molecular structure of extractant of UTEVA resin: diamyl, amylphosphonate (DAAP).[39]

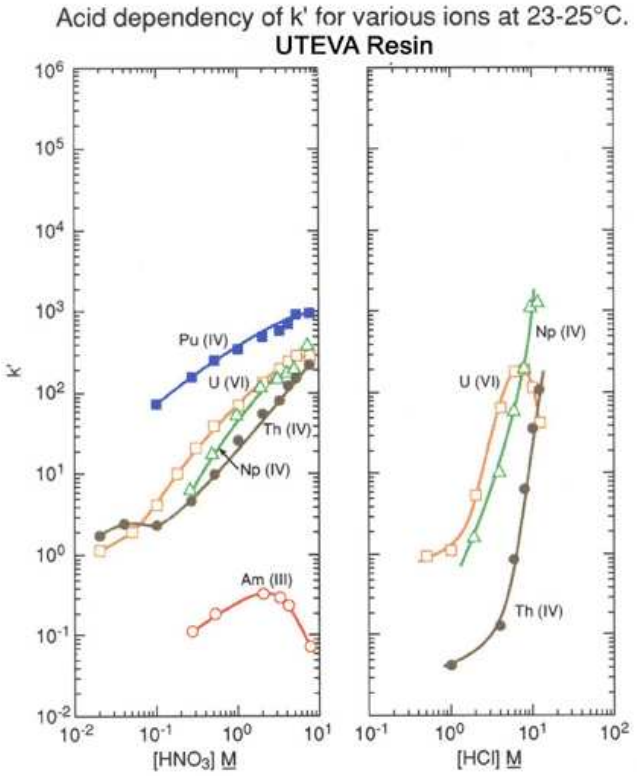


Figure 10. Acid dependency curve for the uptake of actinides on UTEVA resin.[39]

Similar to TEVA resin, UTEVA is useful for separating tetravalent actinides. The mechanism shown below demonstrates the method by which the extractant complexes with tetravalent metals.[39]

$$M^{+4} + 4X^{-} + 2UTEVA \leftrightarrow MX_4TEVA_2$$

The extractant remains a neutral complex and requires two extractant molecules and four nitrate or chloride ions for one tetravalent metal ion to form a complex. In addition, UTEVA resin complexes with uranium (VI) as shown in the mechanism below.[39]

$$MO_2{}^{+2} + 2X^{-} + 2UTEVA \leftrightarrow MO_2X_2UTEVA_2$$

1.5 Batch Distribution Studies

Prior to conducting dynamic chromatography experiments, batch distribution studies can provide insight into the uptake and retention of specific elements on a given resin. Batch distribution studies are utilized to characterize the uptake of radionuclides on a resin of interest under specified conditions. Functionally, batch distribution studies are used to quantify the activity of a radionuclide sorbed to a resin after a radionuclide has been in contact with the resin of interest. The activity sorbed to the resin is then compared to the initial activity which can be utilized to calculate the weight distribution ratio and thereby the column capacity factor for a radionuclide at the specified condition. By completing multiple batch studies at differing but sequentially related conditions, a trend can be established for the column capacity factor when subjected to changes in the conditions studied. For example, acid dependency curves demonstrate the relationship between acid concentration and the column capacity factor for a given analyte.

Trends in retention of analytes on a specific resin can be used to generate a chromatographic separation scheme based on retention at varying acid type and concentration. Additionally, batch distribution studies can be utilized to determine trends in the uptake of an analyte on a resin in the presence of contaminants found in the sample.

1.6 Column Chromatography Studies

Column chromatography studies test the functionality of a separation protocol by generating elution profiles. Column studies functionally have three phases including loading the radionuclide onto the column, rinsing other nuclides off the column, and eluting the radionuclide of interest from the column. This scheme allows for specific separations of radionuclides during desired times. Fractions collected during each step of a column study are measured and their activities are compared to the activity of the sample added to the column initially. The recovery of the radionuclide in each fraction is then used to generate an elution profile to identify if the radionuclide elutes at the desired time or if it breaks though during other phases of the procedure.

As a follow up to batch distribution studies, column studies can be used to test the function of the resin in a real scenario as well as ensuring that the trends determined during batch studies translate accordingly. The introduction of individual components of an unusual matrix within a column study is useful to identify the components needing treatment within or prior to running a separation protocol.

1.7 Liquid Scintillation Counting

Alpha-emitting radionuclides such as plutonium can be detected and quantified with gross alpha counting, liquid scintillation counting, and alpha spectroscopy.[40] Liquid scintillation counting (LSC) is the preferred method of quantifying low activity levels of plutonium in solution in the following experiments because the efficiency of measuring alpha-emitting radionuclides is exceptional at about 99.9% efficient and the samples studied should not have other alpha emitting radionuclides in solution. The efficiency of LSC measurements is associated with the nature of completely solvating radionuclides within the detector, which is unique compared to other methods of detection. Samples are prepared by adding an aliquot to a known amount of liquid scintillation cocktail which contains the detector molecules within solution.

The liquid scintillation cocktail contains the most important component, the organic scintillator molecules, and two additional supporting components, the solvent and waveshifter molecules. The organic scintillator molecules function by de-exciting electrons from an excited state to the ground state by fluorescing. The organic scintillator molecules are typically dissolved in an organic solvent such as xylene or toluene.[40] Additional secondary organic molecules may be present in liquid scintillation cocktail to function as a waveshifter which adjust the wavelength of light emitted by organic scintillator molecules to a more favorable wavelength for detection by photomultiplier tubes.

Following radioactive decay, energy from an alpha particle is deposited within the solvent of the liquid scintillation cocktail which transfers energy to the scintillator molecules. The scintillator molecules produce a photon following excitation. The waveshifter can absorb the photon emitted

by the scintillator and emit another photon at a longer wavelength which can be detected by a photomultiplier tube (PMT).[41] The PMT converts the photon output to an electrical output by knocking electrons off a series of dynodes which end in an anode. The electrical pulses measured are counted within the software and are converted to a count rate in counts per minute (CPM).[42] Figure 11 shows a schematic of liquid scintillation counting.

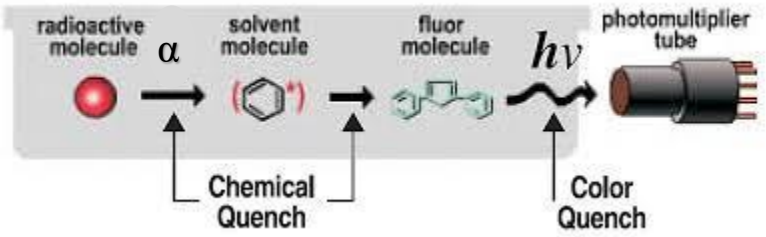


Figure 11. Schematic of liquid scintillation counting process.[41]

Quenching is an important factor to consider in liquid scintillation counting. Whether created chemically or optically, quenching is an effect which causes a loss of counts within the sample measured.[41] Chemical quenching stops light from reaching the PMT by preventing excitation of the primary scintillating molecule. This effect is seen more with beta counting especially at low energies due to absorption of energy without re-emission of energy deposited within the solvent. Similarly, optical or color quenching prevents some amount of light from reaching the PMT by absorbing photons within the coloring of the sample.[41] Color quenching is a significant concern for samples containing large amounts of iron due to its characteristic yellow orange color and will be discussed further with respect to asphalt samples. Within the liquid scintillation detector, a set of standard solutions with known activities are used to calibrate the detector prior to use. The standards used help to determine the efficiency of the system as well as internally calculate the Special Index of the Transformed External Standard Spectrum (tSIE). The tSIE provides an

estimate of the quench within the system on a scale of 0 (most quenched) to 1,000 (unquenched).[41]

1.8 ICP-OES Measurements

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) measures atomic emission spectra to analyze elements of interest. Elements can be identified and quantified based on characteristic light emissions depending on the electronic configurations of their atomic orbitals. Characteristic photons are emitted when electrons in higher energy level orbitals drop to lower energy levels.[43]

A plasma torch is used to ionize samples so the spectra of samples can be measured. The plasma torch is started using inert argon gas exposed to a high radio frequency field. A discharge spark starts ionization of the gas, and an electromagnetic field accelerates electrons to generate plasma. Samples are aerosolized with a stream of argon carrier gas and introduced to the plasma torch for ionization using a nebulizer loaded by a peristaltic pump. Mirrors and optical components directly emitted photons from analytes of interest though the instrument until they reach a monochromator. The monochromator separates light based on wavelength prior to detection of the photons using a charged coupled device (CCD) which is a type of solid-state detector divided into pixels which allows for a broad range of detectable wavelengths.[43,44]

1.9 Objective of Research

A couple of methods have been described to separate plutonium from asphalt and building materials; however, the methods described are limited based on the samples tested. Since asphalt

presents a great variety of metals present based on sampling location, age, and weathering, further testing of extraction chromatography resins is necessary to ensure the rigor of the protocol as well as places where the process can be optimized for more rapid analysis of samples. The objective of this research is to investigate the influence of the major inorganic constituents present in asphalt on the radioanalytical determination of plutonium using the following extraction chromatography resins: DGA, TRU, TEVA, and UTEVA. Since prior studies had been conducted with respect to sodium, calcium, magnesium, and potassium, this study is aimed at investigating the effects of other metals found in significant quantities with differing oxidation states on the uptake of plutonium on the resins. The effects of iron, aluminum, and manganese were characterized as their impacts on the separation of plutonium from nonstandard matrices.

CHAPTER 2: LITERATURE BACKGROUND

2.1 Literature Background

Some studies have investigated the effects of select elemental constituents of ocean water and bone ash on the uptake of ^{239}Pu and ^{241}Am on extraction chromatography systems. The data collected in these studies are pertinent to studies of the interferent in asphalt due to the shared interferents of sodium and calcium in ocean water as well as calcium, potassium, and magnesium in bone ash. These studies do not investigate the influence of other major analytes found in asphalt such as iron, aluminum, and manganese.

Other studies have investigated the development of separation schemes for actinides and plutonium from asphalt matrices; however, there are no data on the durability of these separation schemes when subjected to large quantities of interferents in solution.

2.2 Daum et al. 2018

The effect of two of the main constituents which contribute to the salinity of ocean water on the adsorption of ^{239}Pu and ^{241}Am on six extraction chromatography resins was investigated in this work.[45,46] Sodium and calcium were studied separately then in combination in artificial ocean water. Results for the uptake of ^{239}Pu on DGA, TRU, TEVA, UTEVA, Actinide, and Diphonix resins in the presence of increasing amounts of sodium in nitric acid and hydrochloric acids system are shown in Figures 12 and 13. Similarly, the uptake of ^{239}Pu on the six extraction chromatography resins in the presence of increasing amounts of calcium in nitric acid and hydrochloric acid systems are shown in Figures 14 and 15.

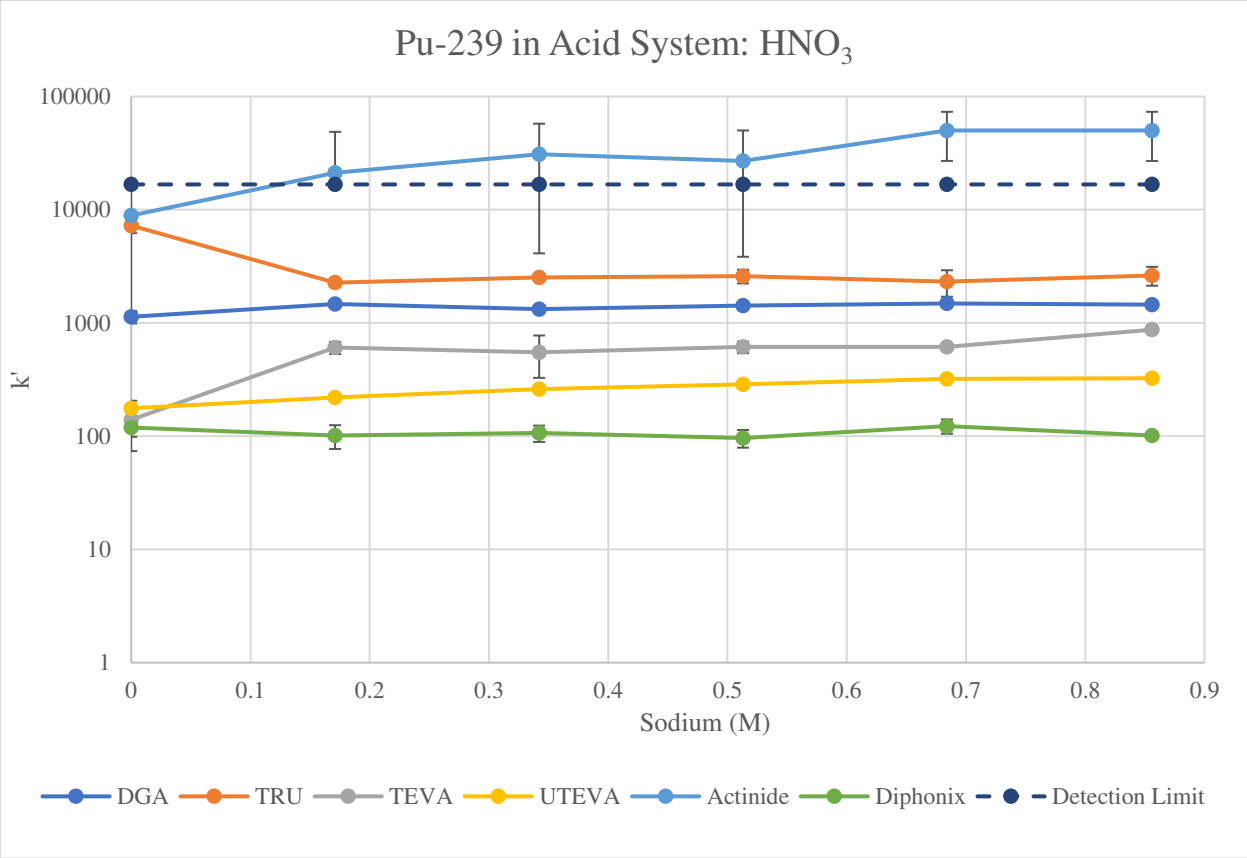


Figure 12. Retention factor for the adsorption of plutonium-239 from nitric acid on six extraction chromatography resins in the presence of varying concentrations of sodium salt solution.[45,46]

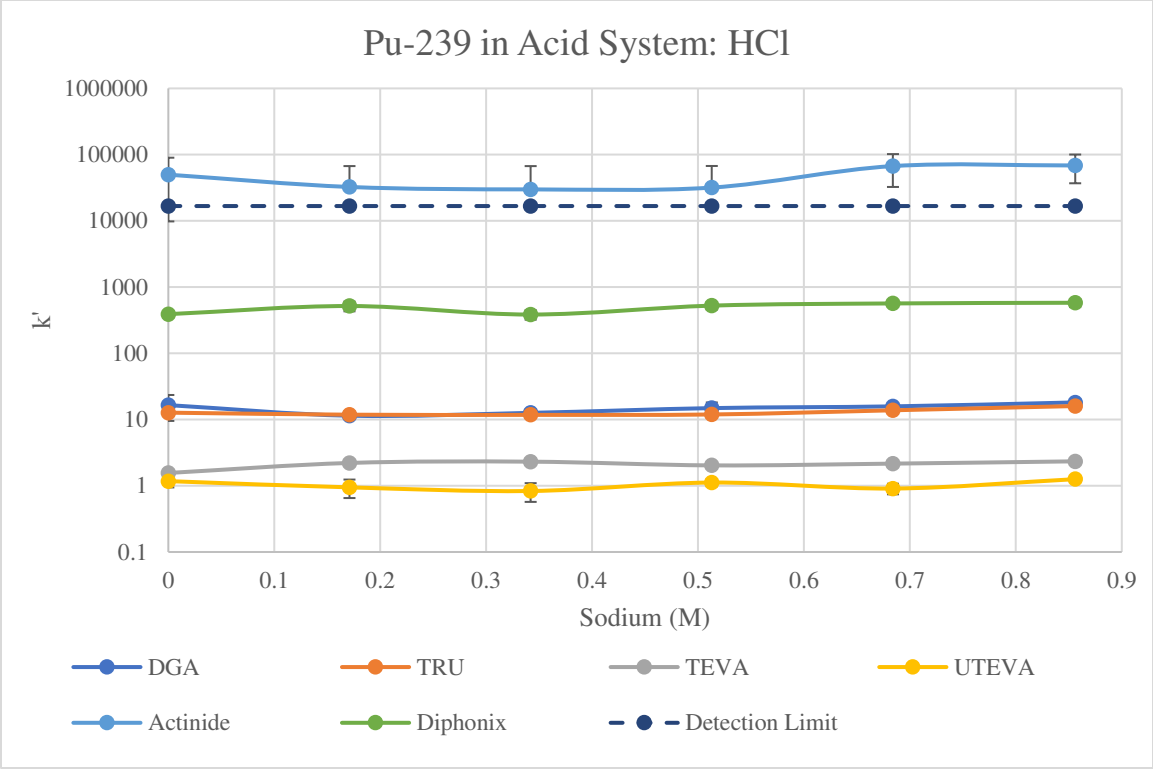


Figure 13. Retention factor for the adsorption of plutonium-239 from hydrochloric acid on six extraction chromatography resins in the presence of varying concentrations of sodium salt solution.[45,46]

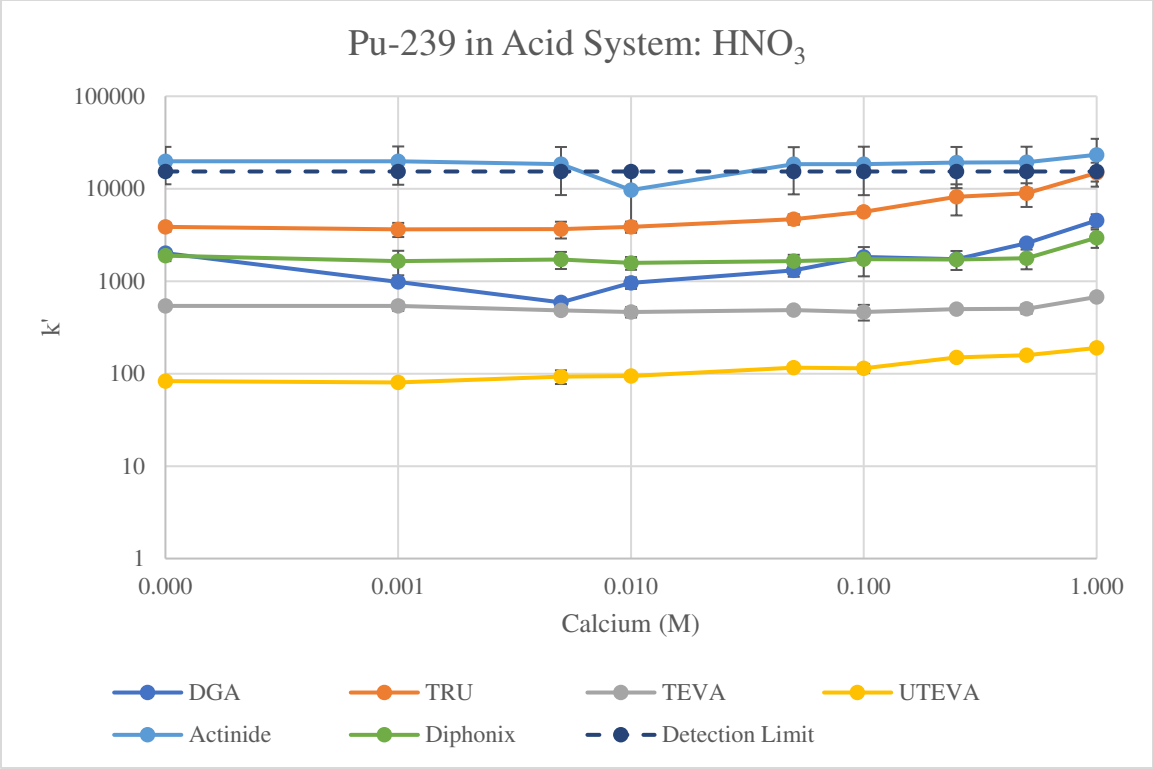


Figure 14. Retention factor for the adsorption of plutonium-239 from nitric acid on six extraction chromatography resins in the presence of varying concentrations of calcium nitrate solution.[45]

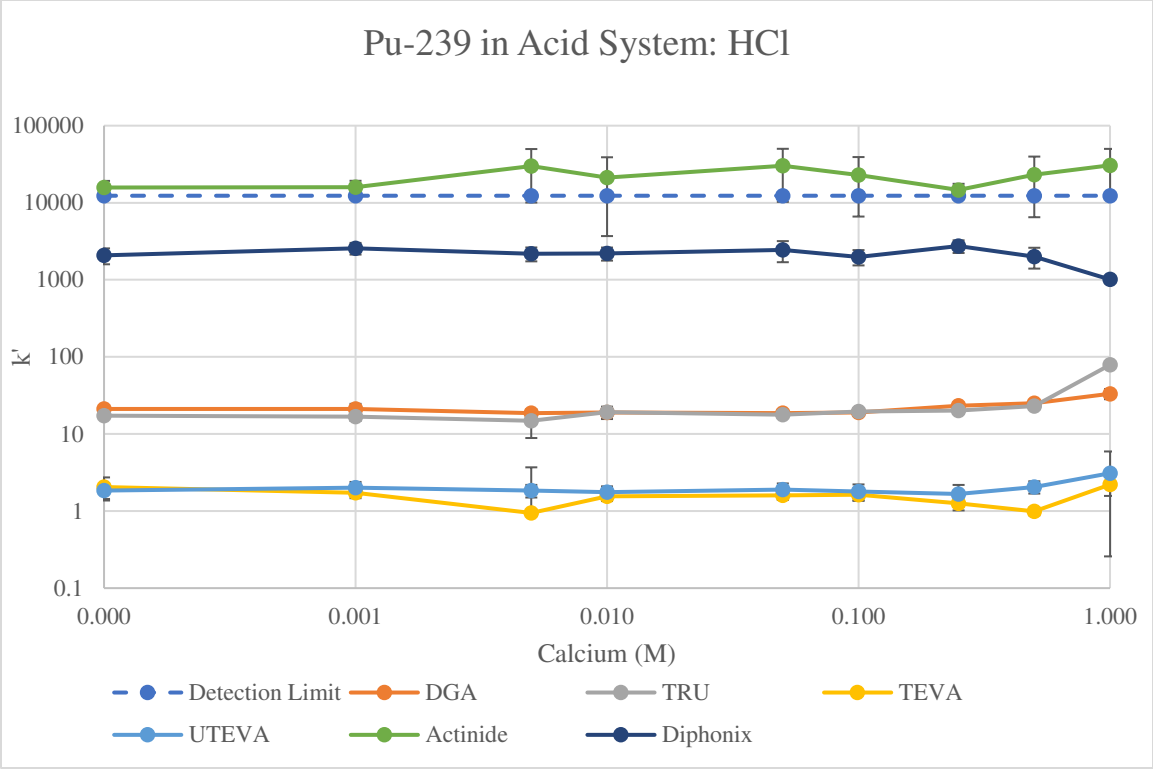


Figure 15. Retention factor for the adsorption of plutonium-239 from hydrochloric acid on six extraction chromatography resins in the presence of varying concentrations of calcium chloride solution.[45]

This study demonstrated that the components of ocean water did not significantly impact the retention of ^{239}Pu on the six extraction chromatography resins studies. Retention of ^{241}Am was unaffected by sodium within the system but was affected by low concentrations of calcium on DGA resin. The uptake of ^{241}Am was unaffected on other resins in the presence of calcium. Batch studies with artificial ocean water showed the same trends of uptake of ^{241}Am on the extraction chromatography resin as studies conducted with calcium.

2.3 Ngygen et al.

The impact of the major constituents of bone including calcium, magnesium, and potassium on the uptake of ^{239}Pu and ^{241}Am on four extraction chromatography resins was investigated in this

work.[47] The resin studied included DGA, TRU, TEVA, and UTEVA. Results for the uptake of ^{239}Pu in nitric acid and hydrochloric acid systems in the presence of potassium are shown in Figures 16 and 17. Results for the uptake of ^{239}Pu in nitric acid and hydrochloric acid systems in the presence of magnesium are shown in Figures 18 and 19.

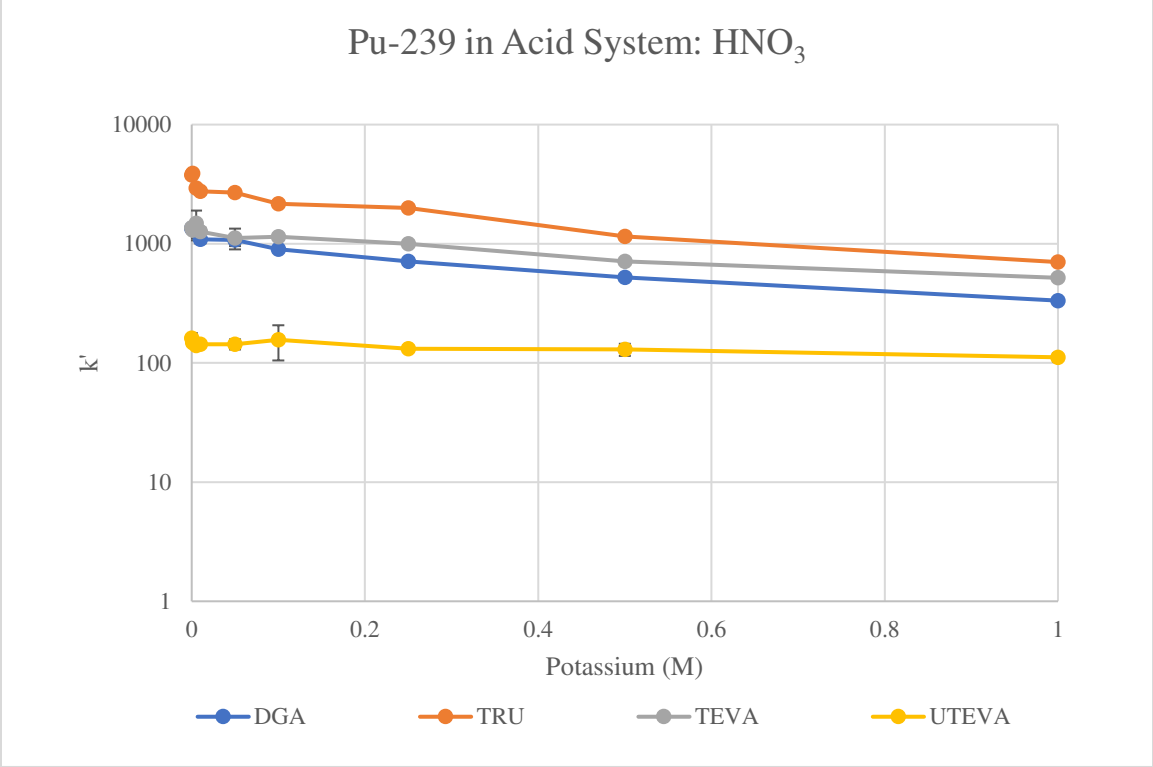


Figure 16. Retention factor for the adsorption of plutonium-239 from nitric acid on four extraction chromatography resins in the presence of varying concentrations of potassium nitrate solution.[47]

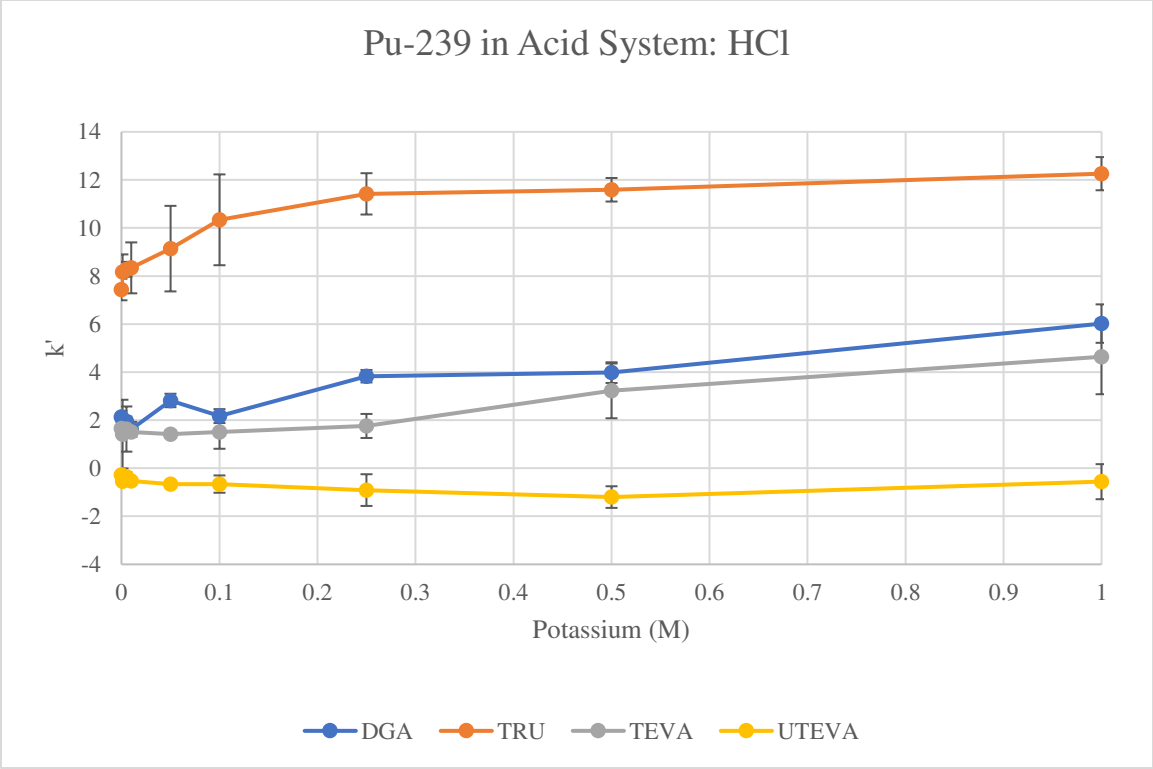


Figure 17. Retention factor for the adsorption of plutonium-239 from hydrochloric acid on four extraction chromatography resins in the presence of varying concentrations of potassium chloride solution.[47]

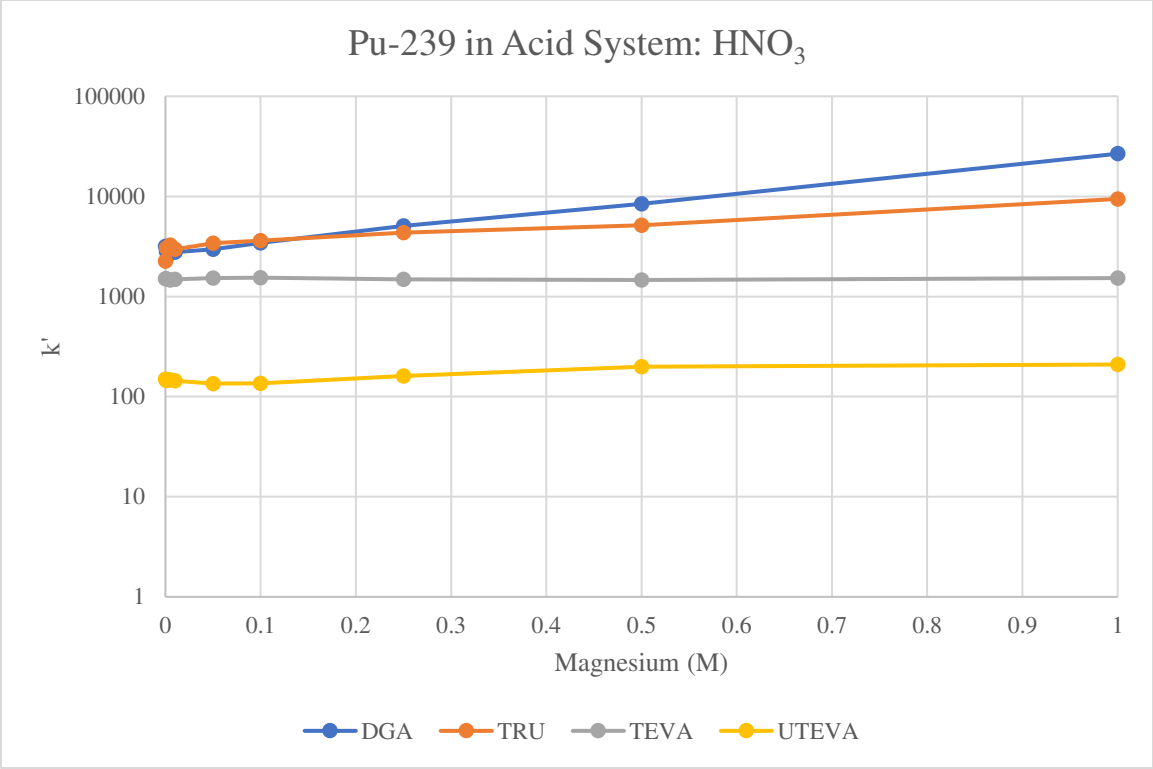


Figure 18. Retention factor for the adsorption of plutonium-239 from nitric acid on four extraction chromatography resins in the presence of varying concentrations of magnesium nitrate solution.[47]

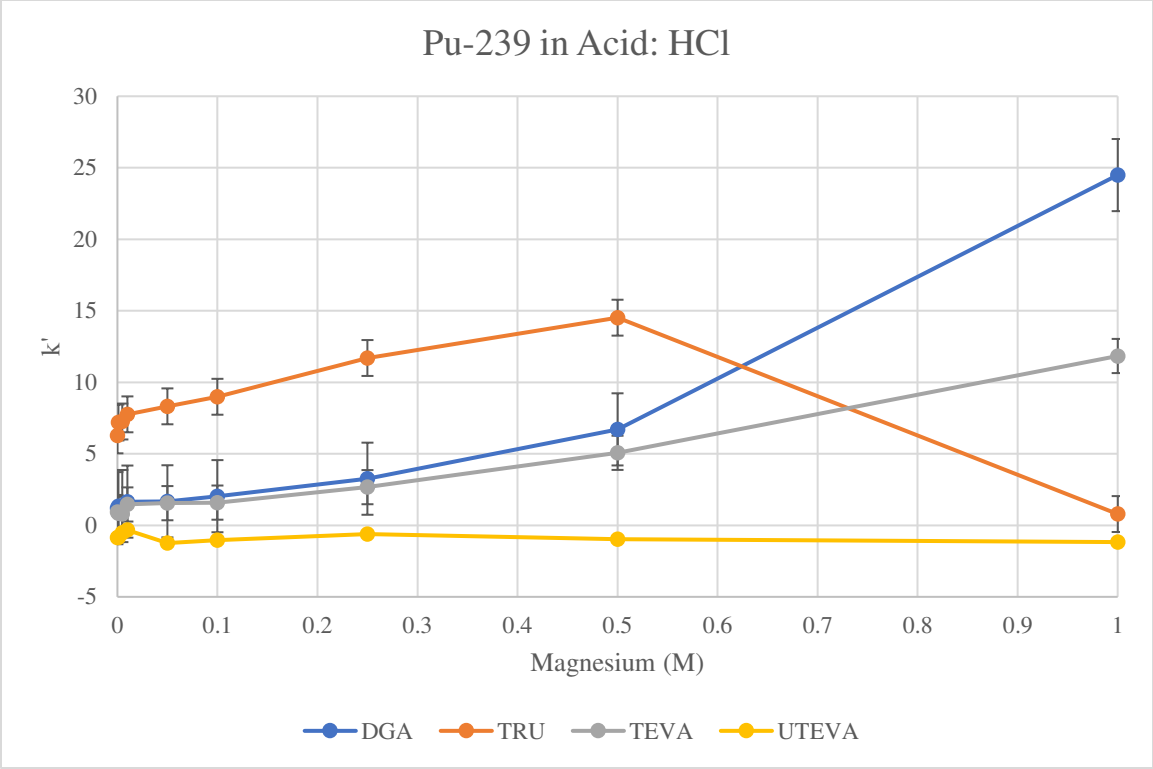


Figure 19. Retention factor for the adsorption of plutonium-239 from hydrochloric acid on four extraction chromatography resins in the presence of varying concentrations of magnesium chloride solution.[47]

The results from this study are summarized in Table 4. Some minor fluctuations were observed in the retention of ^{239}Pu in the presence of some ions studied.[47] Most notably, some slight decreases were seen with the introduction of potassium on DGA, TRU, and TEVA in nitric acid systems. Other minor fluctuations occurred showing slight increases in the k' trend in the presence of all three ions for DGA and TEVA in hydrochloric acid systems. Additionally, this study showed effects on the retention of ^{241}Am on DGA in the presence of calcium, potassium, and magnesium both synergistically in hydrochloric acid systems and inhibitory in nitric acid system. The uptake of ^{241}Am was not significantly impacted by the presence of these ions on other extraction chromatography resins. Ultimately, the trends shown here should not gravely

impact the use of extraction chromatography resins to rapidly separate plutonium and americium from bone samples.

Table 4. Summary of effects on elemental constituents of bone on the uptake of plutonium-239 and americium-241 on four extraction chromatography resins

	Hydrochloric Acid		Nitric Acid		
	Pu-239	**Am-241**	**Pu-239**	**Am-241**	
DGA	Slight increase of k' from 0-0.2 M, then tapers off.	Slight increase of k' from 0.25-1 M	Slight decrease of k' up to 0.5 M, then increase of k'	Rapid decrease of k' from 0-0.1 M, then tapers off	**Ca**
	Slight increase of k' from 0.25-1 M	Slight increase of k' from 0.25-1M	Slight decrease of k' from 0-1 M	Rapid decrease of k' from 0-1 M	**K**
	Slight increase of k' from 0-1 M	Slight increase of k' from 0-0.25 M then larger increase after 0.25	Slight increase of k' from 0-1 M	Rapid increase of k' from 0-1 M	**Mg**
TRU	No effect	No effect	No effect	No effect	**Ca**
	No effect	No effect	Slight decrease of k' from 0-1 M	No effect	**K**
	No effect	Small or no uptake	Slight increase of k' from 0-1 M	No effect	**Mg**
TEVA	Slight increase of k' from 0-0.5 M, then tapers off	No uptake	No effect	No uptake	**Ca**
	Slight increase of k' from 0.25-1 M	No uptake	Slight decrease of k' from 0-1 M	No uptake	**K**
	Slight increase of k' from 0-1 M	No effect	No effect	No uptake	**Mg**
UTEVA	No uptake	Slight decrease of k' from 0-1 M	No effect	No uptake	**Ca**
	No uptake	No effect	No effect	No uptake	**K**
	No uptake	No uptake	No effect	Minor fluctuation of k'	**Mg**

2.4 Maxwell et al.

This study provides a rapid method for determining actinides in asphalt samples using stacked TRU and DGA columns.[48] The method provides a quick digestion scheme using a rapid furnace step and sodium hydroxide fusion prior to the separation scheme for plutonium, uranium, americium, and curium which can be employed for emergency response. Asphalt samples were spiked with MAPEP 24 standard soil and analyzed with alpha spectroscopy. For the plutonium analysis, ^{242}Pu was used as a tracer. Tracer recoveries for this method were measured at 91.3 ± 6.2% which is indicative of effective sample preparation and measurement.[48] In this method, plutonium is separated using TRU resin.

2.5 EPA method

The Environmental Protection Agency (EPA) also provides a separation scheme for ^{238}Pu and $^{239/240}$Pu in building materials, such as concrete or brick, using TEVA resin.[49] When used in conjunction with the rapid sodium hydroxide fusion of asphalt matrices provided by the EPA, a complete method is available to separate plutonium from asphalt matrices with acceptable recoveries even at low concentrations.[49,50] The methods described can also be combined with other rapid radiochemical methods described by the EPA. The reported method is capable of meeting the required uncertainty limits as well as the required minimum detectable concentrations set forth by the EPA.[49]

CHAPTER 3: METHODS AND MATERIALS

3.1 Batch Distribution Studies

Specific metal ion contributions on the adsorption of plutonium on DGA, TRU, TEVA, and UTEVA resins were determined with batch distribution studies. Variations in the stable metal ion concentrations were designed to mimic the possible concentration of analytes found in asphalt which could be dissolved into solution. The results obtained from these studies were converted into column capacity values, k' -values, by measuring the activity of ^{239}Pu in solution initially and after contacting with each resin. The k' values were graphed as a function of concentration of analytes on a logarithmic scale to visualize trends.

Since many separation schemes commonly used varying concentrations of nitric acid and hydrochloric acid to strategically adsorb actinides to extraction chromatography resins or strip them at varying points, both mineral acid systems were studied. Additional nitrates or chloride ions are present in the working solutions do not need to be altered following addition to each sample since working solutions were generated to match the concentration of each mineral acid concentration during batch experiments. This is important because ^{239}Pu need to be stored in acidic conditions to prevent hydrolysis and subsequent colloid formation.

3.2 Solution Preparation Procedures

Salt solutions and stock ^{239}Pu solutions were prepared ahead of time. The salt solutions were prepared at concentrations which could be expected following a complete dissolution of asphalt noting that each salt solution was prepared taking into account the volume of ^{239}Pu tracer

solution to be added, such that the final concentration of the analyte of interest in the mobile phase was at the desired concentration (0, 0.001, 0.005, 0.01, 0.05, 0.1, 0.25, 0.5, and 1 M).

The ^{239}Pu working solutions were prepared with nitric acid or hydrochloric acid at 1 M and 3 M concentrations from a stock solution with an activity of 1000 Bq/mL. Each solution was brought to dryness then brought up in concentrated mineral acid three times to convert the counter ion in solution to the desired acid system. The final solution was brought up in the desired acid. A 50 µL aliquot of the final solution was brought to dryness on a stainless steel planchet and counted on the Ludlum 3030 to determine the activity of plutonium in solution given the count rate, volume of solution, and efficiency of the detector. The final solution was then diluted to achieve an activity of ~1000 Bq/mL. An aliquot was also analyzed via liquid scintillation counting to confirm the activity of solutions prior to use in batch study experiments.

3.3 Batch Study Procedure

3.3.1 Resin Preparation

Prior literature review was conducted to determine the optimal conditions to conduct batch studies based on acid dependency and kinetics experiments for each extraction chromatography resin. Labeled polypropylene microcentrifuge tubes were filled with 50 ± 0.05 mg of resin (DGA, TRU, TEVA, or UTEVA). Each set of samples was prepared with four replicates.

3.3.2 Preconditioning the Resin

A preconditioning step was then carried out to ensure the plutonium solution could optimally interact with the pores of the resin beads. During this step, the acid type and concentration of the

mobile phase were determined for each given experiment. For studies using DGA resin, either 1 M nitric acid or 1 M hydrochloric acid was used to precondition the resin. Experiments conducted that used TRU, TEVA, or UTEVA were preconditioned with 3 M nitric acid or 3 M hydrochloric acid. Each tube containing measured amounts of resin received 0.45 mL of the appropriate mineral acid for samples destined to be spiked with ^{239}Pu. For stable element studies, 0.5 mL of dilute acid was added to each sample during preconditioning. Each batch was agitated by securing a set of samples on their side to a Thermo Scientific Labquake shaker and allowed to shake at a fixed speed for one hour.

3.3.3. Spiking the Resins

Following preconditioning, 1 mL of the requisite salt solution at each concentration was added to the microcentrifuge tubes. Additionally, approximately 50 Bq of ^{239}Pu was added to each tube by adding a 50 µL aliquot of ~1000 Bq/mL ^{239}Pu solution in the appropriate acid solution to each tube. The analytes of interest and plutonium in solution were allowed to contact the resin for one hour during another shaking process using the Thermo Scientific Labquake shaker table. This process allows for ions in solutions to reach an equilibrium between the mobile phase and stationary phase. Figure 20 shows an example of the spiked samples.

Figure 20. Resin spiked with plutonium-239 in a gradient of iron chloride solutions ranging from 0 – 1 M concentrations.

3.3.4. Filtration

Following the shaking process to allow the reaction to reach a state of equilibrium, each sample was filtered to separate the resin from the supernatant. The supernatant was collected into new labeled microcentrifuge tubes to be counted via liquid scintillation counting. Each sample was filtered using a 3 mL Luer-Lok syringe with an attached 0.45 µm PTFE syringe filter.

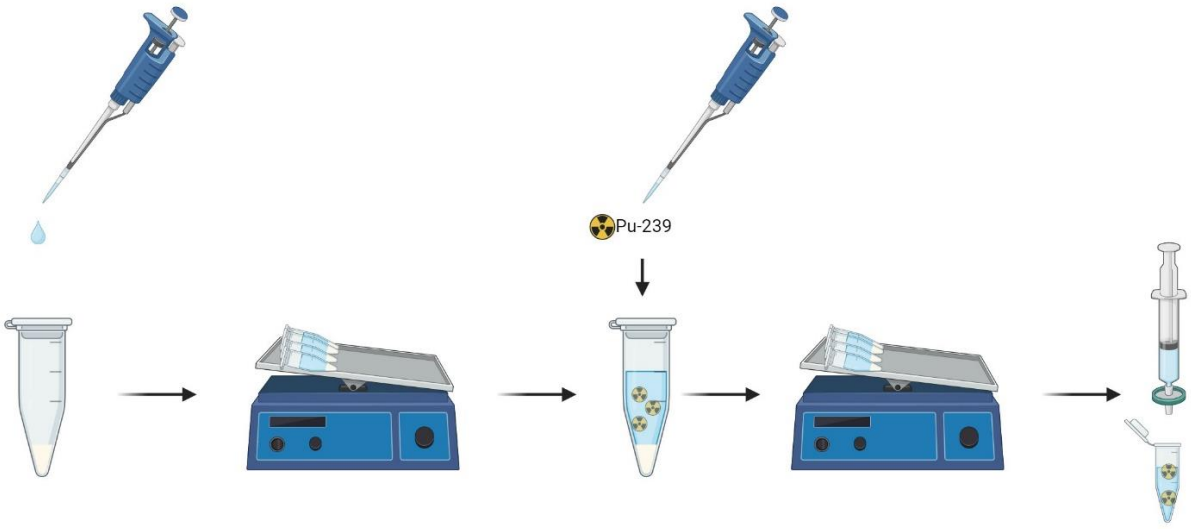


Figure 21. Overall schmatic of the batch distribution procedure.[51]

3.4. Column Chromatography Studies

Following batch distribution studies, the metal ion contributions on the sorption of plutonium was applied in practice using TRU columns. In these studies, 2 mL vacuum-flow cartridges which were packaged in a factory were used to maintain the uniformity of bed packing and reduce error in the column procedure. The TRU cartridges were fitted to a vacuum box produced by Eichrom Technologies for column studies. Studies were conducted in 3 M nitric acid for the load condition to match the determined column capacity factor, k', for the batch studies conducted. Metal ion concentrations were studied at 1 M for the stable analyte to mimic the worst-case scenario possible following complete dissolution of asphalt. Data collected from these samples were converted to percent recovery for each fraction. The recoveries were graphed on a bar chart to visualize the elution profile. The method for column separation studies is based on the procedure developed by *Maxwell et al* for TRU columns.[48]

3.4.1. Load Solution Preparation

Acid-salt solutions were prepared ahead of time to ensure complete solvation of metal ions in solution. These solutions were prepared with a calculated amount of salt diluted in 3 M HNO_3 to an appropriate volume to achieve a load solution consisting of 3 M HNO_3 – 1 M salt. A 15 mL sample of the 3 M HNO_3 – 1 M salt solution was added to a 50 mL centrifuge tube The 15 mL sample was spiked with 667 µL of 3000 Bq/mL ^{239}Pu solution in 1M HNO_3. The solution was capped and mixed thoroughly.

3.4.2. Preconditioning Column

Each cartridge was used straight out of the box. Each column was set up with a snug-fitting white inner tip as well as the barrel of Luer-Lok 10 mL syringe. The column was then placed in a yellow outer tip in the vacuum box procured from Eichrom Technologies as shown in Figure 22.

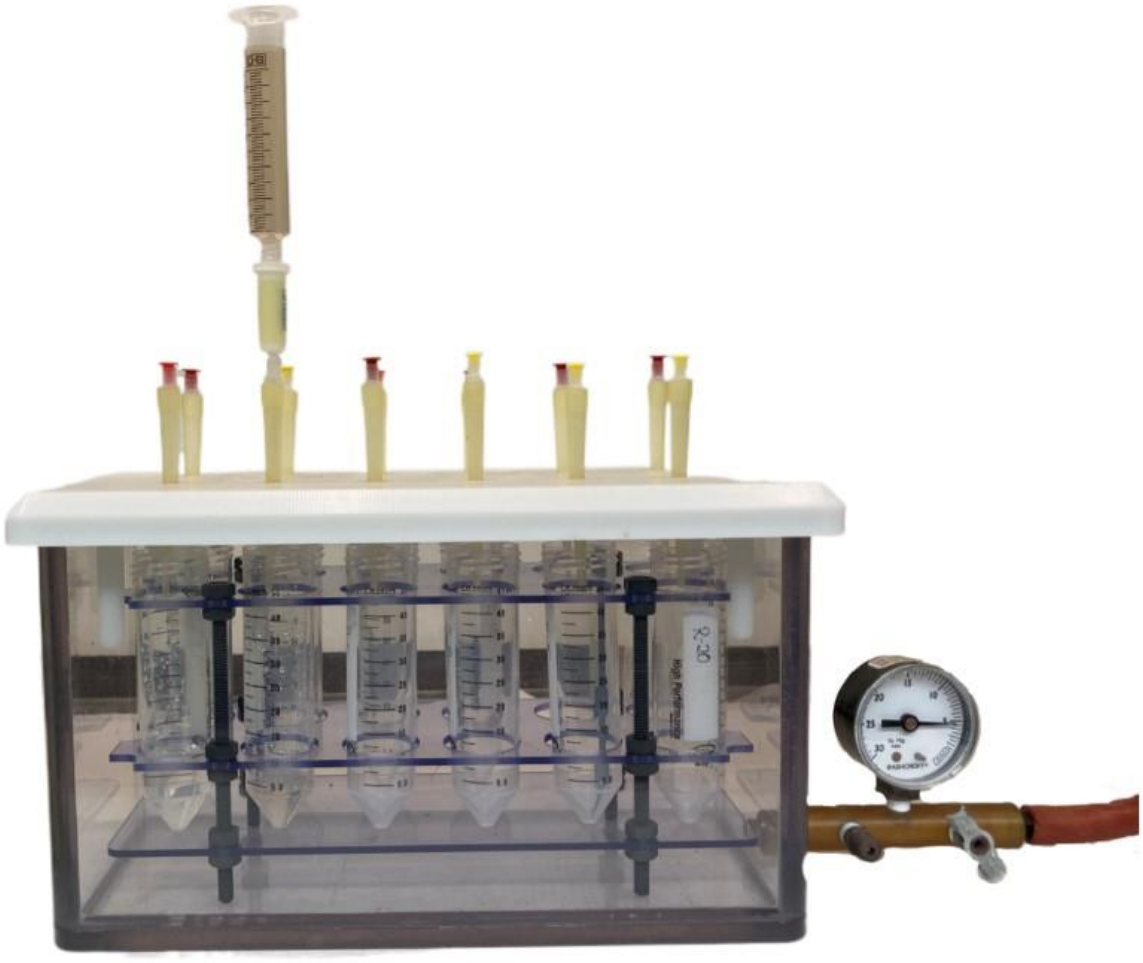


Figure 22. Column set up with vacuum box

A 5 mL aliquot of 3 M HNO_3 was added to the barrel of the syringe. Vacuum was applied to start the flow of liquid through the column. The flow rate was adjusted to ~1 mL min^{-1} (approximately 5 in. Hg vacuum pressure) which was maintained throughout the procedure. The column was pulled to dryness for this fraction and each following fraction.

3.4.3. Load Phase

The spiked load solution was transferred to the barrel of the syringe using a disposable transfer pipette.

3.4.4. Rinse Phase

A 5 mL aliquot of 10 M HNO_3 was added to the emptied 50 mL centrifuge tube which contained the spiked load solution. The tube was capped and swirled well to ensure complete transfer of plutonium to the column. The 5 mL aliquot was then transferred to the column followed by an additional 5 mL aliquot of 10 M HNO_3. The column was then rinsed with 15 mL of 4 M HCl. In the original procedure outlined by *Maxwell et al.* 10 M HNO_3 was used to elute Po^{+4} from the column and 4 M HCl was used to elute ^{241}Am from the column.

3.4.5. Elution of Plutonium

Plutonium was eluted off the column with 15 mL of 3 M HCl-0.02 M $TiCl_3$.

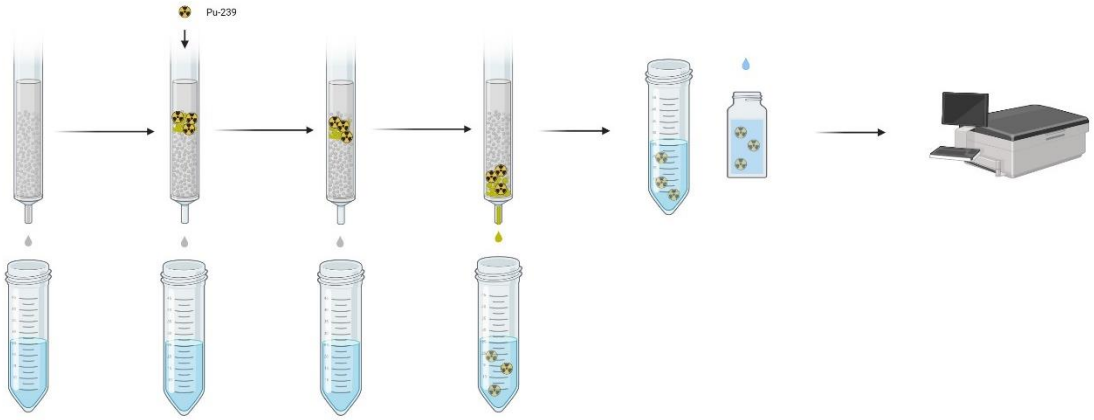


Figure 23. Schematic of column procedure.[51]

3.5. Liquid Scintillation Counting Procedure

Samples were counted in 20 mL plastic scintillation vials and measured using either a Perkin Elmer Model Tri-Carb 5110TR or a Tri-Carb 2800TR liquid scintillation counter for alpha counting. Each set of samples was counted along with a blank sample and spiked sample. The blank samples were prepared with 1 mL of nitric acid or hydrochloric acid to match the given experiment and 15 mL of Ultima Gold Liquid Scintillation Cocktail. Blank samples were used to background correct the count rates observed in the samples and standards measured. The ^{239}Pu spike samples were prepared with 50 µL of plutonium working solution to match the plutonium working solutions used earlier in the experiment with 15 mL of Liquid Scintillation Cocktail. Spike samples were used to compare the initial activity of plutonium added to each sample to calculate the weight distribution values and column capacity values. Samples for counting were prepared using 1 mL aliquots of the supernatant collected after filtration for batch studies or 5 mL fractions from column studies added along with 15 mL of Liquid Scintillation Cocktail. The activity of each sample was measured during a 60-minute count time per vial. The count mode was set to discriminate alpha and beta regions with the alpha region set from 0 to 1000 keV and

the beta region set from 0 to 2000 keV. Microsoft Excel was used to subtract the blank sample measurements from the spike and sample measurements to account for background. The count rates were used to calculate the k' values for ^{239}Pu for each replicate using Microsoft Excel. The average of the four replicates at each concentration was calculated and plotted using the standard deviation of the replicates to represent uncertainty. Additional statistical analyses were conducted using R studio to evaluate outliers as needed.

3.6. ICP-OES Measurement Procedure for Stable Element

Stable element studies were measured using a Thermo Jerrel-Ash iCAP 61E inductively coupled plasma optical emission spectrometer (ICP-OES) with an attached AS300 autosampler. A set of calibration standards for iron and aluminum was generated within the sensitive range of the instrument prior to the measured samples to ensure appropriate working response of the ICP-OES. The iron standards ranged from 0.1000 ppm to 50.0000 ppm (0.10, 0.50, 1.00, 5.00, 10.00, 25.00, 50.00 ppm). The aluminum standards ranged from 0.5000 ppm to 50.0000 ppm (0.50, 1.00, 5.00, 10.00, 25.00, 50.00 ppm). Samples were prepared from salt solutions used in batch studies with plutonium to investigate the sorption of stable trivalent ions on the extraction chromatography resins at 0.001 M, 0.01 M, 0.1 M, and 1 M. Precontact solutions were prepared in labeled microcentrifuge tubes with 1 mL of salt solution and 0.5 mL of matching concentration of nitric or hydrochloric acid to mimic the concentration of salt in the given batch experiments. A 0.1 mL aliquot of the pre-contact solution was then diluted to 10.0 mL with a 2 % trace metal grade nitric acid solution (ICP-OES blank solution). A 0.1 mL aliquot of the filtrate from the stable element batch study procedure was diluted to 10.0 mL of ICP-OES blank solution. Concentrations of iron and aluminum analytes in solution before and after contact with

the resins was used to calculate k' values and establish trends with increases in analyte concentration.

3.7. Materials

A list of materials used for all experiments can be found in appendix II.

CHAPTER 4: RESULTS

4.1 Batch Distribution Studies

Iron, aluminum, and manganese were identified as metal ions of interest found in significant quantities in asphalt samples which could potentially cause interference effects with a separation scheme. The effect on the absorption of plutonium was studied in the presence of each interferent at nine concentrations: 0, 0.001, 0.005, 0.01, 0.05, 0.1, 0.25, 0.5, and 1 M. This range was chosen to mimic the possible concentration of ions which could be present in solution following complete dissolution of asphalt samples. Additionally, both nitric acid and hydrochloric acid systems were studied due to the use of both types of acid within separation protocols for plutonium. Each concentration of the given analytes was replicated in batches of four. The data points shown on the following figures are averaged values of the k' calculated for four replicates performed. Error bars shown are based on the standard deviation for the set of replicates in each data point. Some error bars shown may be smaller than the size of the data point.

4.1.1 Batch Distribution Studies Data

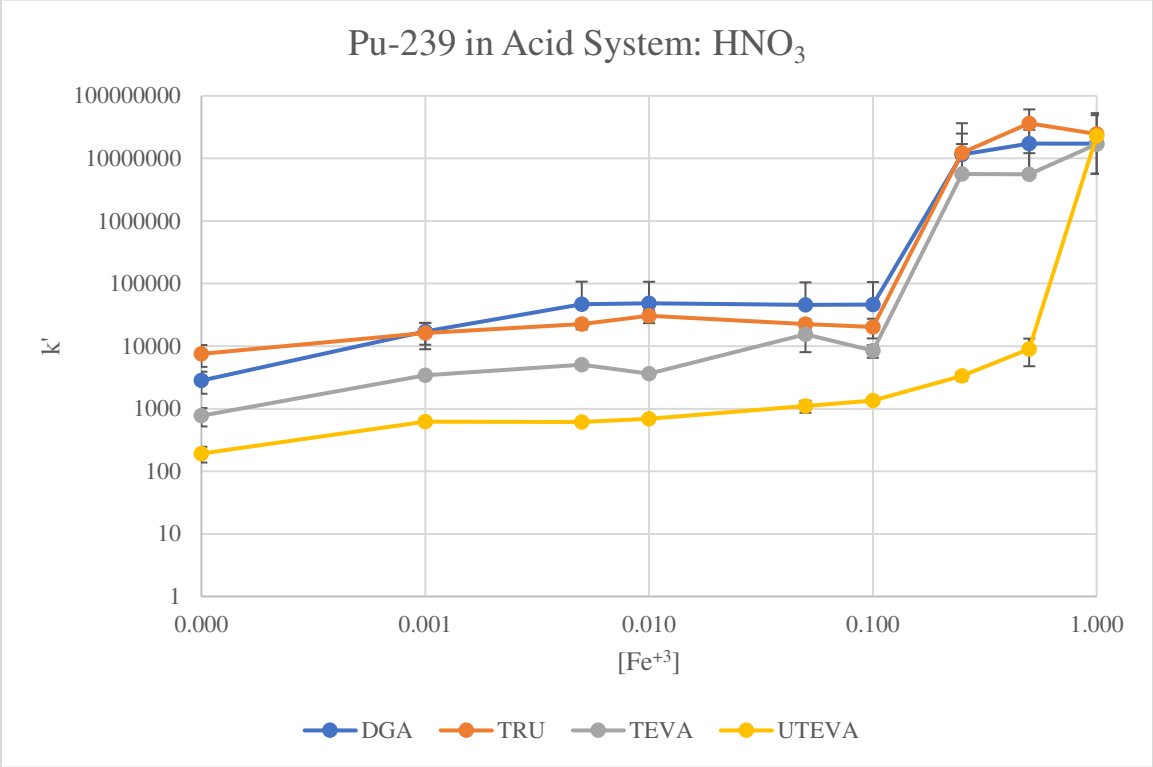


Figure 24. Retention factors for the adsorption of plutonium-239 from nitric acid on four extraction chromatography resins in the presence of varying concentrations of iron (III) nitrate solution.

To observe the effects of iron on the uptake of ^{239}Pu on the extraction chromatography resins, iron nitrate was dissolved in 1 M nitric acid for DGA and in 3 M nitric acid for TRU, TEVA, and UTEVA to make salt solutions for batch distribution studies. Figure 24 shows a synergistic effect of iron on with plutonium uptake on all resin at concentrations above 0.1 M.

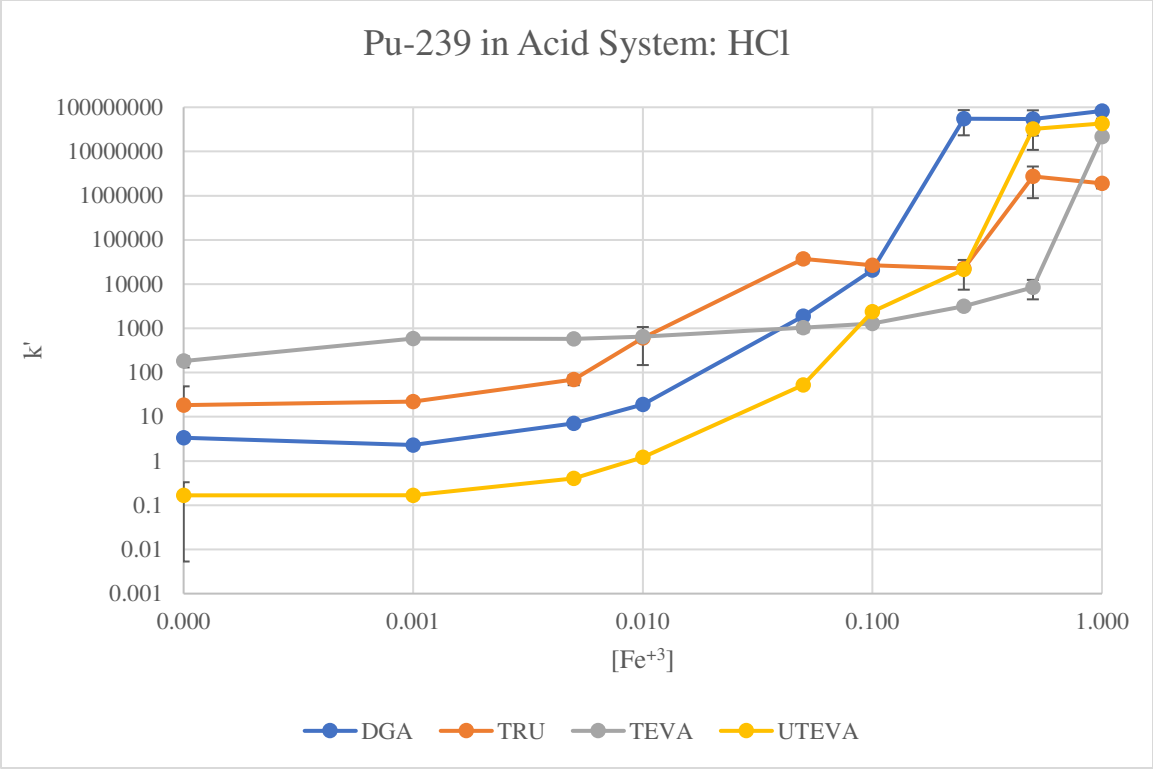


Figure 25. Retention factors for the adsorption of plutonium-239 from hydrochloric acid on four extraction chromatography resins in the presence of varying concentrations of iron (III) chloride solution.

Iron chloride was dissolved in 1 M hydrochloric acid for DGA studies and in 3 M hydrochloric acid for TRU, TEVA, and UTEVA studies to observe trends within this study. Significant synergistic effects were observed in all resins with the increase of iron chloride in solution. DGA, TRU and UTEVA demonstrated significant increases in the sorption of ^{239}Pu at concentrations above 0.1 M as shown in Figure 25. TEVA was less affected by the iron content not showing synergistic effects until an iron concentration of 0.25 M was reached.

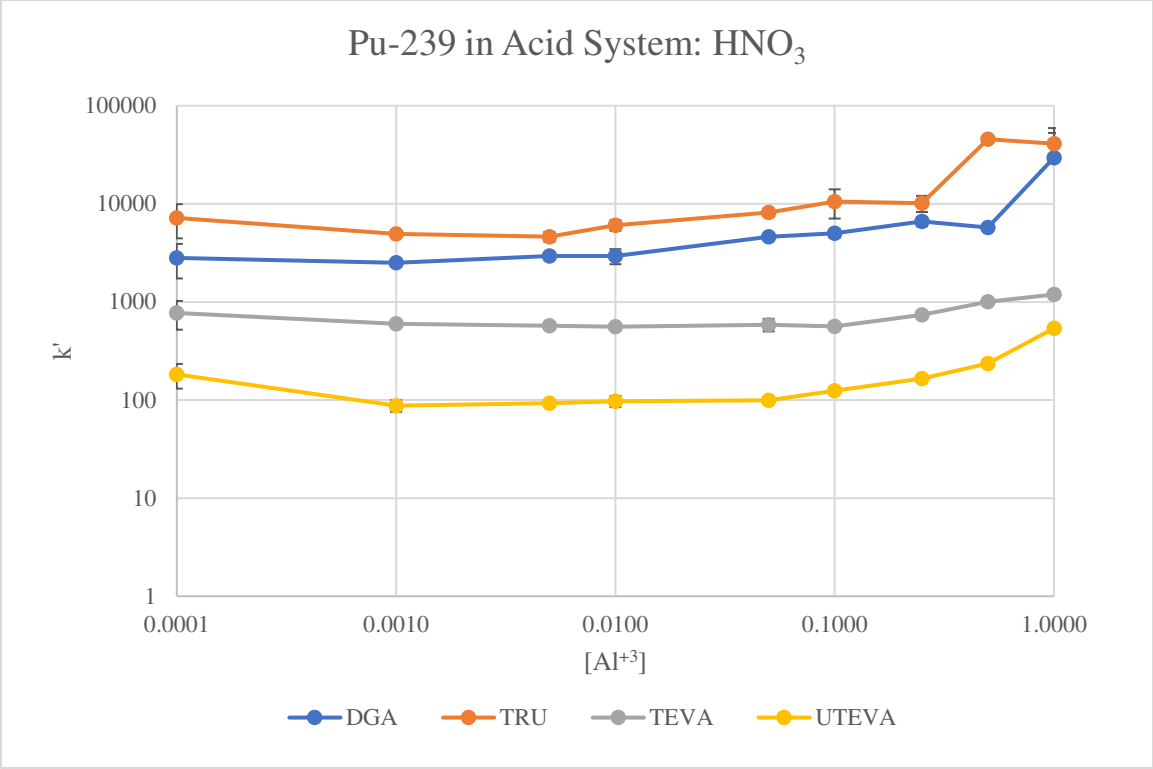


Figure 26. Retention factors for the adsorption of plutonium-239 from nitric acid on four extraction chromatography resins in the presence of varying concentrations of aluminum (III) nitrate solution.

Figure 26 shows the trends observed in the uptake of ^{239}Pu with increasing amount of aluminum on the four extraction chromatography resins. Aluminum nitrate was dissolved in 1 M nitric acid for the study conducted on DGA. Aluminum nitrate was dissolved in 3 M nitric acid for the studies conducted on TRU, TEVA, and UTEVA. Aluminum showed minimal effects on the uptake of plutonium using extraction chromatography resins in a nitric acid system. Some synergistic effects were seen with DGA and TRU resins at concentrations above 0.5 M. TEVA and UTEVA were unaffected by aluminum added to the system at any concentration studied.

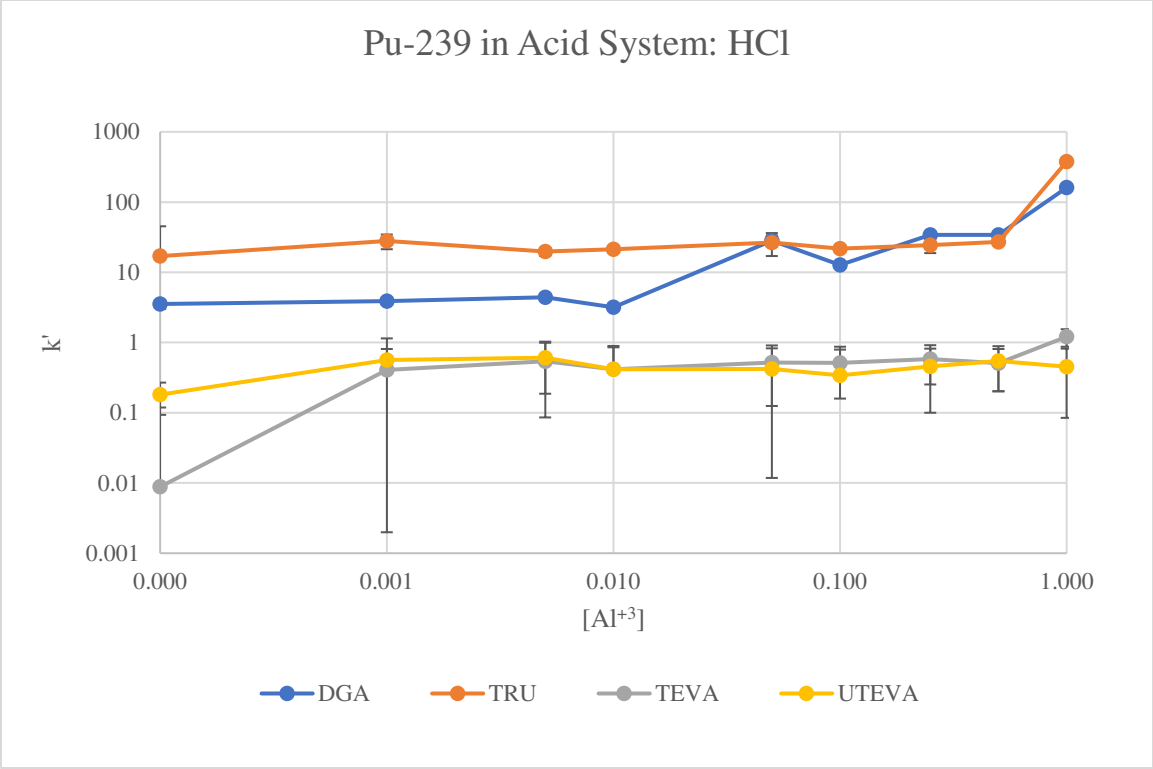


Figure 27. Retention factors for the adsorption of plutonium-239 from hydrochloric acid on four extraction chromatography resins in the presence of varying concentrations of aluminum (III) chloride solution.

Trends for the uptake of ^{239}Pu on the extraction in the presence of increasing aluminum concentrations in a hydrochloric acid system were plotted on Figure 27. Aluminum chloride was dissolved in 1 M hydrochloric acid for the DGA studies and in 3 M hydrochloric acid for TRU, TEVA, and UTEVA studies. Some minor or limited synergistic effects were seen with the introduction of aluminum on the uptake of ^{239}Pu at concentrations above 0.01 M for DGA and at 0.5 M for TRU in a hydrochloric acid system. TEVA and UTEVA were unaffected by the introduction of aluminum at any concentration.

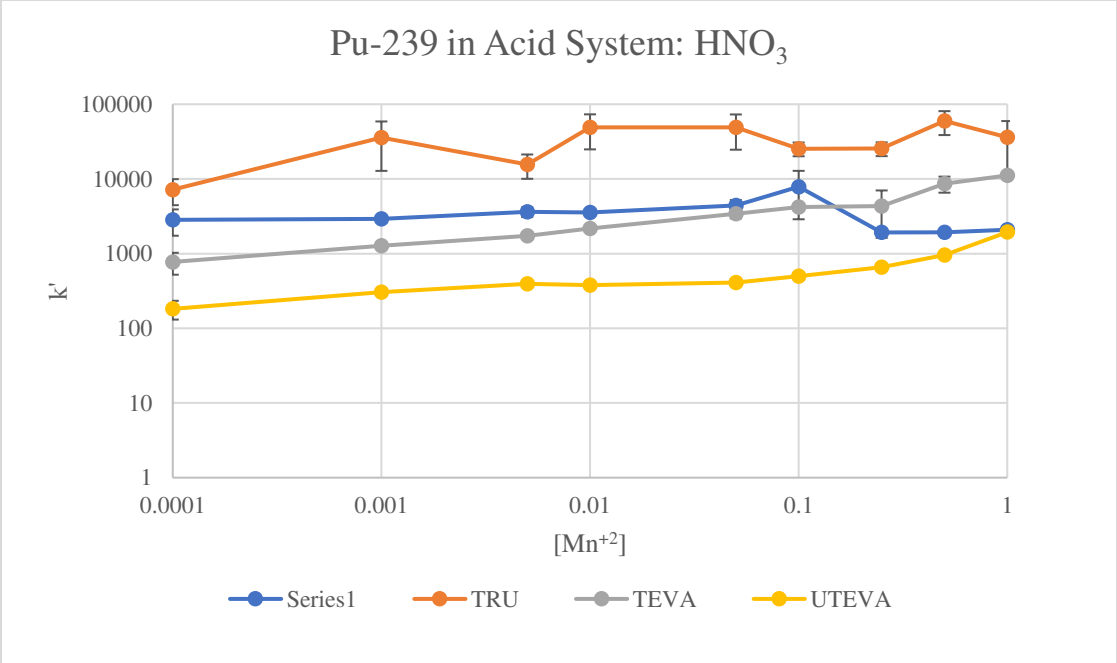


Figure 28. Retention factors for the adsorption of plutonium-239 from nitric acid on four extraction chromatography resins in the presence of varying concentrations of manganese (II) nitrate solution.

Manganese nitrate was dissolved in 1 M nitric acid for DGA studies and in 3 M nitric acid for TRU, TEVA, and UTEVA to observe trends in the uptake of ^{239}Pu with increasing amounts of manganese in nitric acid. All the resins were found to have slight increases in the k' values as the concentration of manganese increased. TRU experienced the greatest effects even at low concentrations of manganese as well as fluctuations in the k' value measured at varying concentrations. DGA, TEVA, and UTEVA demonstrate consistent mild synergistic effects with increasing concentrations of manganese in solution as shown in Figure 28.

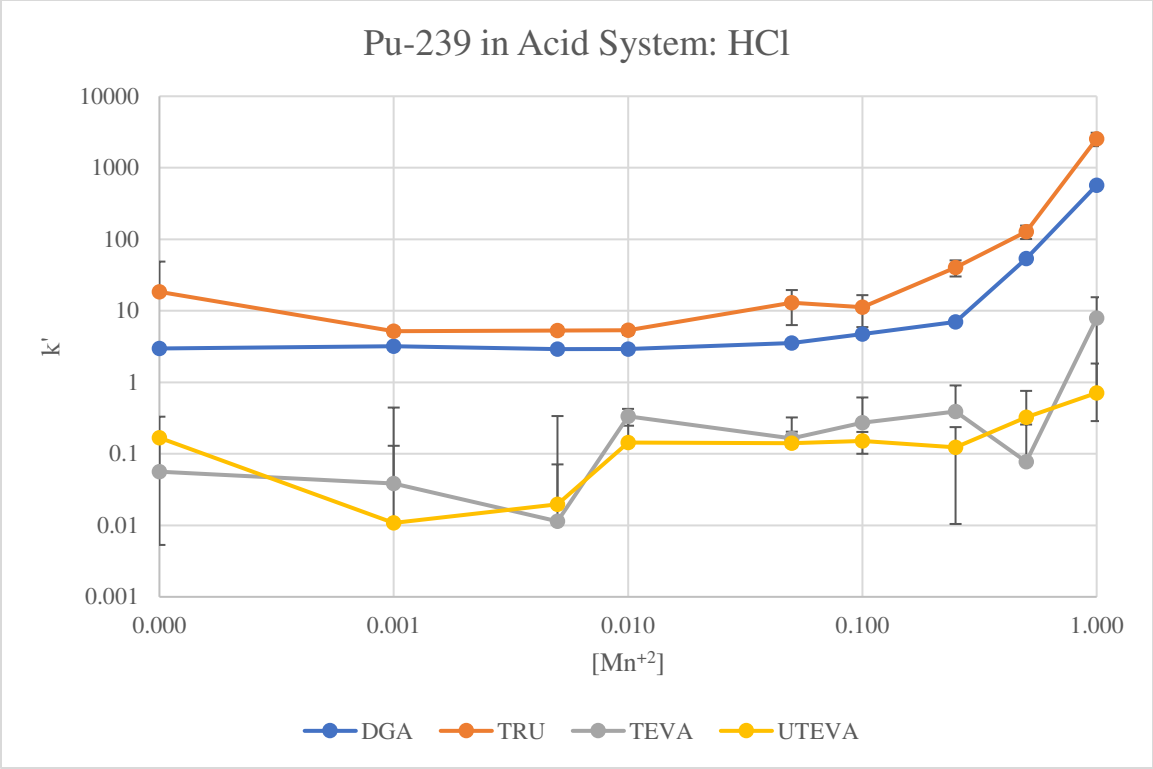


Figure 29. Retention factors for the adsorption of plutonium-239 from nitric acid on four extraction chromatography resins in the presence of varying concentrations of manganese (II) chloride solution.

Trends in the uptake of ^{239}Pu in the presence of manganese in a hydrochloric acid system were studied and are shown in Figure 29. Manganese chloride was dissolved in 1 M hydrochloric acid for DGA studies and in 3 M hydrochloric acid for TRU, TEVA, and UTEVA studies. In hydrochloric acid, manganese showed some synergistic effects from 0.25 M to 1 M concentrations with DGA and TRU resins. On the other hand, TEVA and UTEVA were not affected by the introduction of manganese at any concentration.

4.1.2 Stable Element Batch Distribution Studies

As a follow up to the batch distribution studies with iron, which showed significant synergistic effects, stable element studies were conducted to investigate the adsorption of iron and aluminum

(both of which are trivalent metals) on the four extraction chromatography resins. During batch distribution studies, iron was noted to sorb to the resins, especially TRU and TEVA, giving a distinct yellow hue to the resin post contact as shown in Figure 30. Similarly, during the filtration step the flow rate was greatly reduced and the syringe filters were noted to turn yellow or orange. Since the pores of the syringe filters are 0.45 μm, free iron ions should pass though the filter meaning iron was sorbing to the resin to some degree as shown in Figure 31. Stable element batch distribution studies were conducted with iron (III) nitrate, iron (III) chloride, aluminum (III) nitrate, and aluminum (III) chloride on all four extraction chromatography resins. Due to a shortage of time, only one replicate was performed at each concentration, but each sample was measured twice via ICP-OES. The average of the two measurements was used to calculate k' and is shown in the following figures. Calibration curves for aluminum and iron for the ICP-OES instrument are shown in Figures 32 and 33.

Figure 30. Visualization of iron (III) adsorbed to TEVA resin.

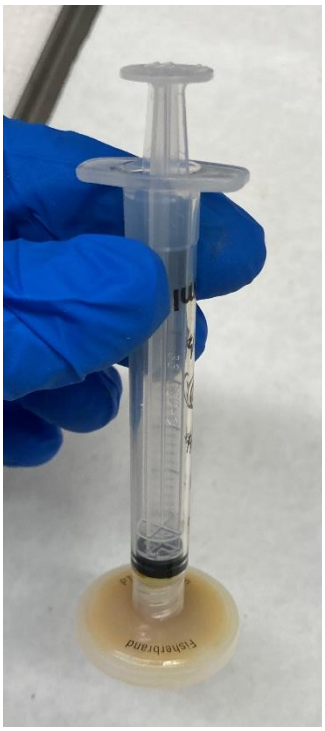


Figure 31. Visualization of iron (III) sorbed to the extraction chromatography resin caught in the syringe filter.

Calibration standards were created and measured for iron ranging from 0.1000 ppm to 50.0000 ppm. Standards were also created and measured for aluminum ranging from 0.5000 ppm to 50.000 ppm. The calibration standards were measured and plotted on Figure 32 and 33 for aluminum and iron, respectively.

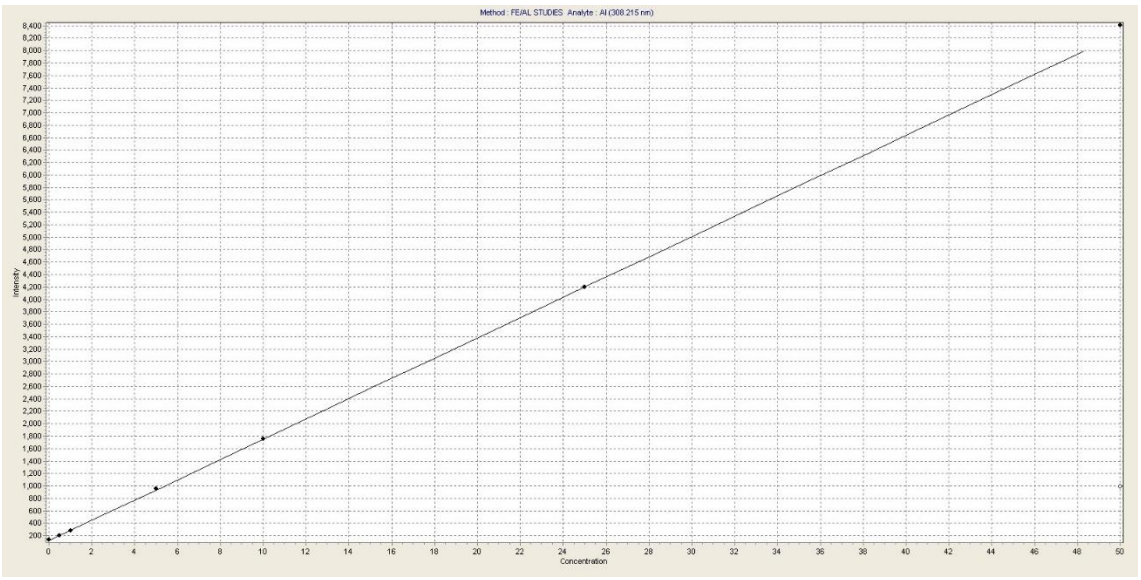


Figure 32: Calibration Curve for Aluminum

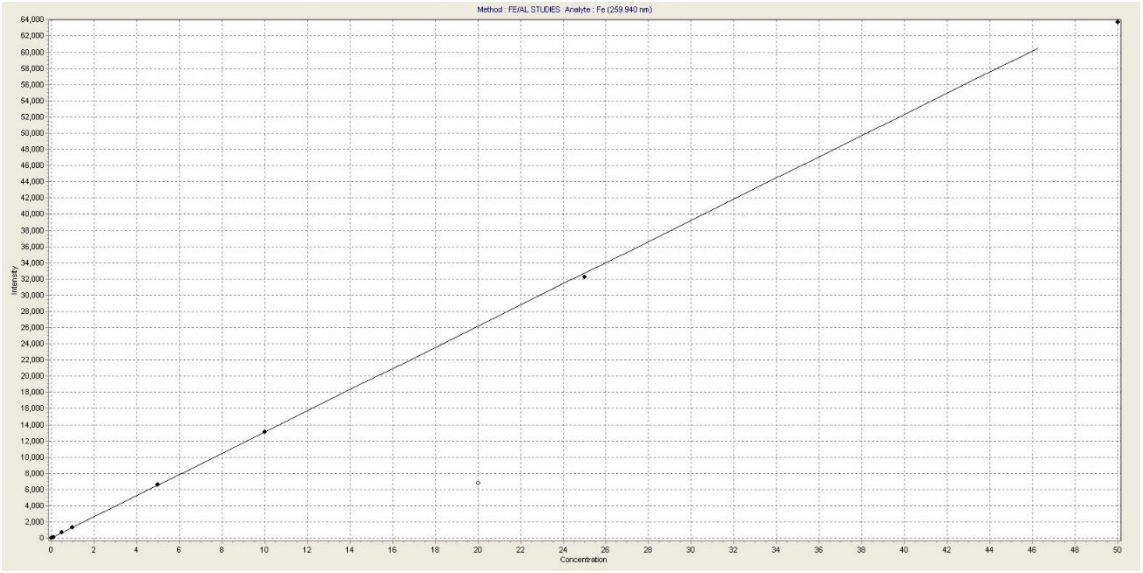


Figure 33: Calibration Curve for Iron

The calibration curves relates the intensity of light emitted from the ionized sample in the plasma torch to the concentration of analyte in solution. Within the sensitive region of the instrument,

the trend is linear in nature. The calibration curve which relates intensity to concentration of aluminum is listed below.

$$[Al^{+3}] = (6.14 \times 10^{-3}) \times Intensity - 7.48 \times 10^{-1}$$

The calibration curve which relates intensity to concentration of iron is listed below.

$$[Fe^{+3}] = (7.645 \times 10^{-4}) \times Intensity + 6.08 \times 10^{-5}$$

The calibration curves were used to convert the raw intensities to concentration values. These values were subsequently used to calculate k' values which are plotted in Figures 34, 35, 36, and 37.

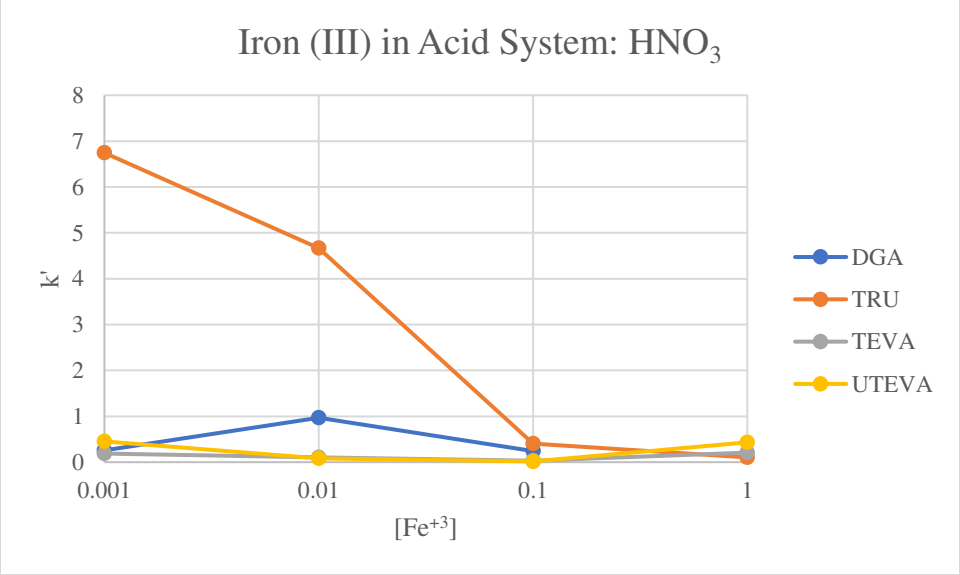


Figure 34. Retention factor for the uptake iron (III) from nitric acid as it relates to varying concentrations of iron (III) nitrate.

The uptake of iron on the four extraction chromatography resins with respect to increasing iron concentration was investigated and plotted on Figure 34. Iron nitrate was dissolved in 1 M nitric acid for the DGA studies and in 3 M nitric acid for the TRU, TEVA, and UTEVA studies. At low

concentrations, TRU takes up iron in addition to plutonium. As the iron concentration increases, the resin is quickly overwhelmed, so the k' decreases even though iron is taken up by TRU. DGA, TEVA, and UTEVA on the other hand showed limited uptake of iron.

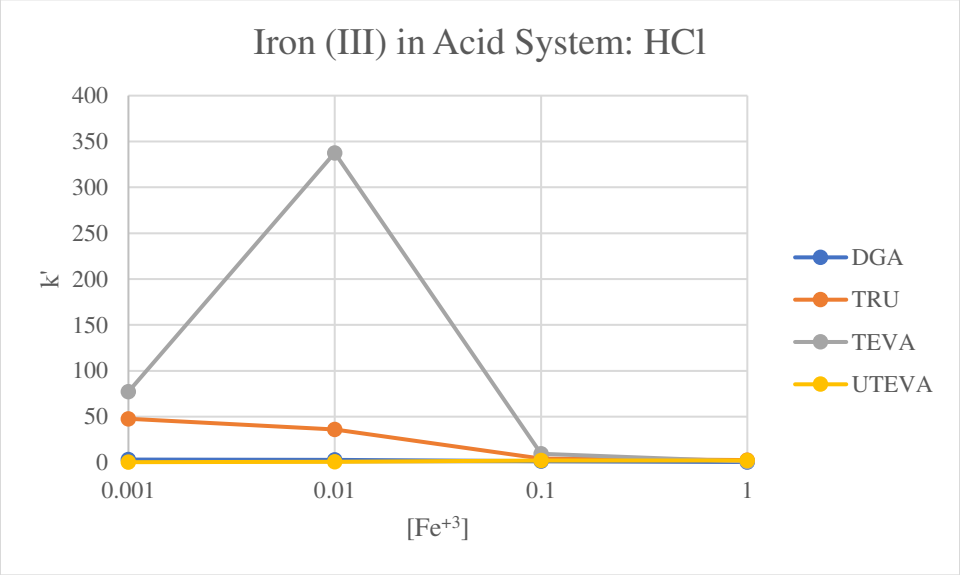


Figure 35. Retention factor for the uptake iron (III) from hydrochloric acid as it relates to varying concentrations of iron (III) chloride.

To quantify the uptake of iron on the extraction chromatography resins in a hydrochloric acid system as it pertains to the batch contact studies conducted earlier, iron (III) chloride was dissolved in 1 M hydrochloric acid for DGA studies and in 3 M hydrochloric acid for TRU, TEVA, and UTEVA studies. Both TRU and TEVA showed uptake of iron at lower concentrations; however, as the concentration of iron increased, the resin quickly reached capacity of extractant molecules able to complex with iron as shown in Figure 35. DGA and UTEVA showed low uptake of iron at these concentrations.

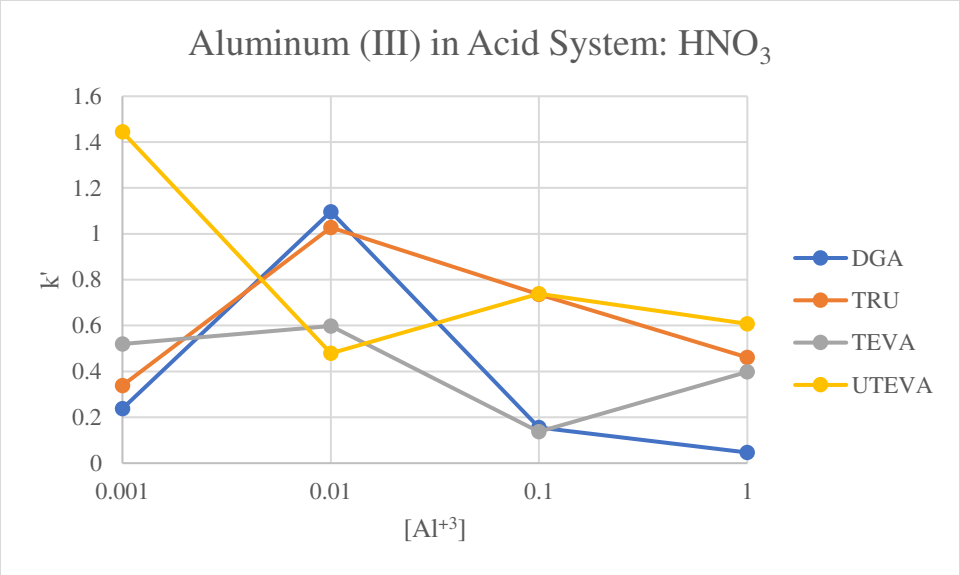


Figure 36. Retention factor for the uptake aluminum (III) from nitric acid as it relates to varying concentrations of aluminum (III) nitrate.

Similar to the stable element studies conducted with iron, batch studies were conducted to investigate the uptake of aluminum on the extraction chromatography resins. For the studies conducted in nitric acid, aluminum (III) nitrate was dissolved in 1 M nitric acid for DGA studies and 3 M nitric acid for TRU, TEVA, and UTEVA studies. Aluminum showed essentially no uptake on any resin at any concentration as shown in Figure 36. This study indicates that the charge density of the atomic nucleus plays a significant role in the sorption on the extraction chromatography resins in nitric acid and generation of a "salting out" effect observed in earlier batch studies.

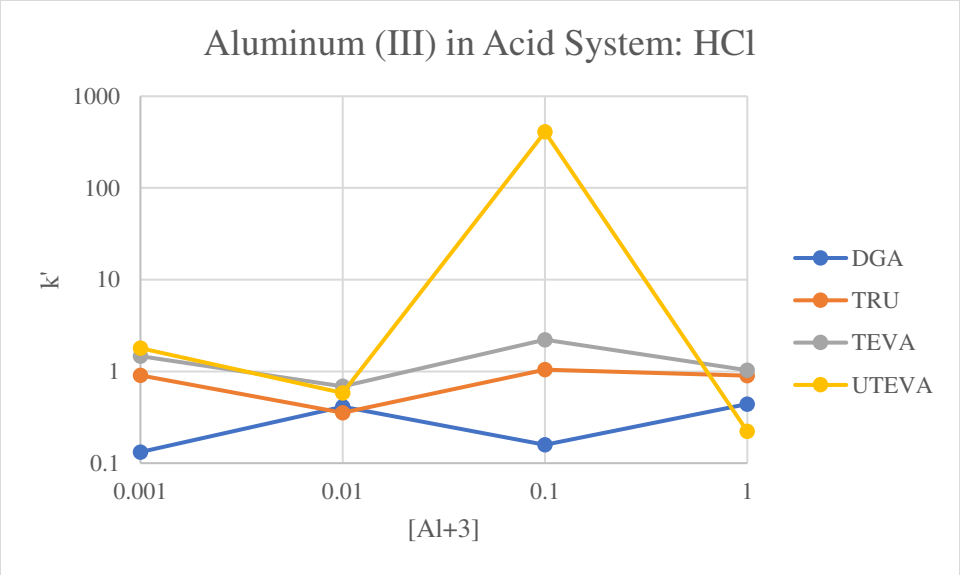


Figure 37. Retention factor for the uptake aluminum (III) from nitric acid as it relates to varying concentrations of aluminum (III) chloride

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The uptake of aluminum on the extraction chromatography resins was also studied in a hydrochloric acid system to follow trends shown in batch studies with ^{239}Pu. For these studies, aluminum chloride was dissolved in 1 M hydrochloric acid for DGA studies and in 3 M hydrochloric acid for TRU, TEVA, and UTEVA studies. Similar to the nitric acid study with aluminum, no significant uptake of aluminum (III) was observed as shown in Figure 37. The increase in the sorption of aluminum at 0.1 M concentration in UTEVA is likely erroneous due to experimenter error. This study also indicates that charge density likely has more influence on the uptake of analytes on the extraction chromatography resins in a hydrochloric acid system compared to oxidation state alone.

4.3 Column Chromatography Studies

In addition to batch distribution studies, column chromatography studies were conducted to investigate the interference effects of iron, aluminum, and manganese in a functional test of the

extraction chromatography resins in a realistic separations scheme for ^{239}Pu. The method used was adapted from the rapid method for separating actinides described by *Maxwell et. al* which uses TRU resin to separate plutonium from other actinides.[48] This method includes steps to rinse Po^{+4} and Am^{+3} from the column during the rinse phase with 10 M nitric acid and 4 M hydrochloric acid, respectively. All load solutions were standardized to 3 M nitric acid to match with the batch study data previously obtained. Load solutions with interfering elements were studied at "worst-case scenario" for analytes in solution where batch study data demonstrated the most effects which was shown around 1 M concentrations for most salts. Recoveries in each fraction and total recoveries for studies conducted without interfering elements, with iron, with aluminum, with manganese, and with a synthetic asphalt mixture are shown in Figure 37. Each column was replicated three times. Each data point shown in Figure 38 is based on the average percent recovery of plutonium for each fraction. Error bars shown are based on the standard deviation of recovery for each fraction between the three columns.

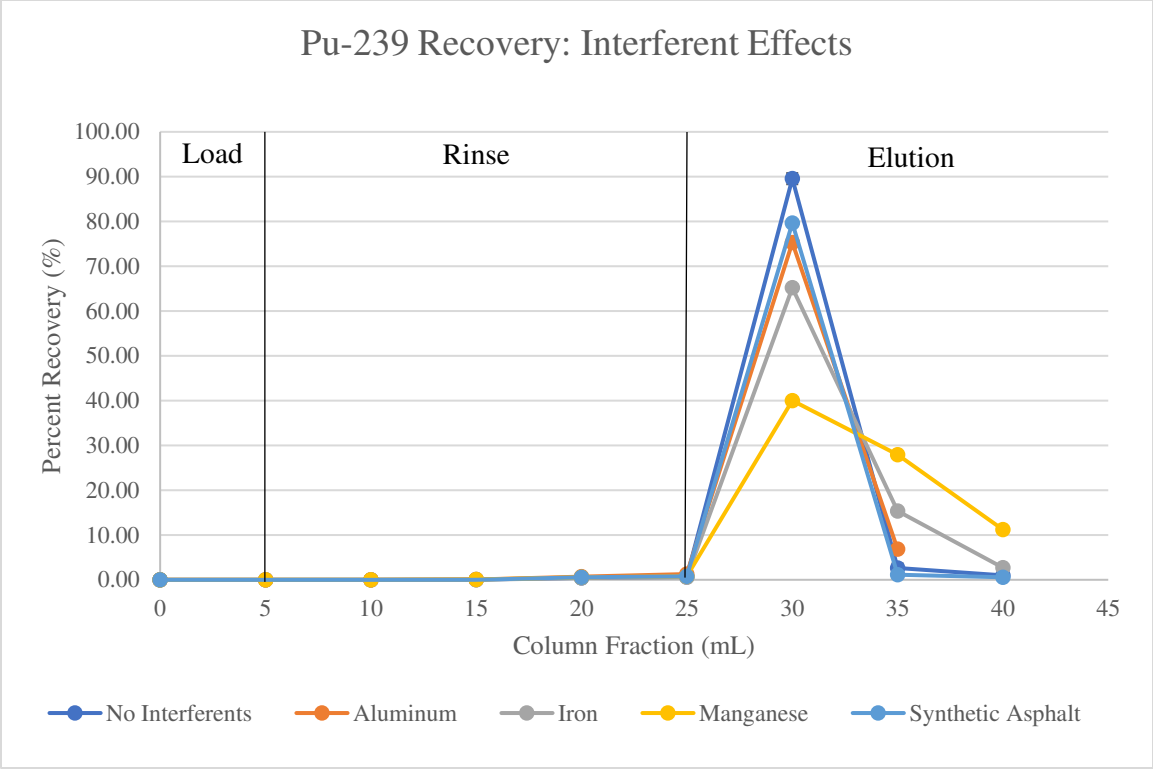

Figure 38. Recovery of plutonium-239 from TRU column fractions

Table 5 shows the percent recovery of plutonium for each column study as it relates to Figure 38. The recoveries shown below were based on the average percent recovery for the three replicates in each column study. The standard deviation listed is based on the standard deviation calculated for the three replicates in each study.

Table 5. Percent Recovery for Column Studies

Interferent	Percent Recovery (%)	Standard Deviation (%)
No Interferent	94.25	0.44
Aluminum	86.07	1.60
Iron	84.21	0.85
Manganese	80.55	2.40
Synthetic Asphalt	82.64	8.82

Without any interferents in the system, the method demonstrated a viable strategy to separate ^{239}Pu with good recovery and limited breakthrough. Recovery of ^{239}Pu without interfering analyte averaged at 94.25% with 93.18% eluted during the stripping phase and 1.07% breakthrough in the rinse phase. This set of data was used as the baseline to evaluate the effect of added analytes in solution.

The effect of adding aluminum to the system in the load was tested by dissolving aluminum nitrate in 3 M nitric acid to make the load solution. With the introduction of aluminum to the system, recovery of ^{239}Pu was reduced to 86.07% with 84.01% recovered during the elution phase and 2.06% breakthrough in the rinse phase. Despite the significant reduction in the recovery of plutonium, the average recovery was still good. The reduction in the recovery is likely to be associated with the increased sorption of plutonium as observed in the batch study data, suggesting a synergistic effect with aluminum at higher concentrations both in nitric acid and hydrochloric acid.

Iron nitrate was dissolved in 3 M nitric acid to make a 3 M nitric acid – 1 M iron (III) nitrate solution to load on the column to observe the effect of iron on the recovery of ^{239}Pu using this separation scheme. The introduction of iron in the system resulted in a total recovery of plutonium at 84.21% with 83.24% recovered in the elution phase and 0.97% recovered in the rinse phase. The synergistic effects observed in the batch studies earlier likely contributed to less breakthrough in the rinse phase; however, this effect also contributed to increased sorption on the column resulting in lower recoveries in the elution phase. Despite the interferences shown here, recoveries were still reasonably good and acceptable at over 80% recovery.

Additional columns were conducted on the influence of manganese on the recovery of plutonium on this separation scheme. Manganese nitrate was dissolved in 3 M nitric acid to make a 3 M nitric acid – 1 M manganese nitrate load solution. The addition of manganese showed an additional decrease in the recovery of ^{239}Pu to 80.55% where 79.16% of the plutonium recovery occurred during the elution phase and 1.39% broke though in the rinse phase. Similar to aluminum and iron, the increased retention of plutonium in the presence of manganese in nitric acid and in hydrochloric acid likely contributed to the decrease in recovery of plutonium from the columns. Despite a decrease in recovery of plutonium by 14%, the total recovery is still acceptable at over 80%.

Since asphalt samples do not come with single analytes at a time, a study was conducted to investigate the effect that the presence of multiple interfering elements has on the recovery of plutonium using this protocol on TRU resin. A synthetic asphalt solution was created by dissolving iron nitrate, aluminum nitrate, and manganese nitrate in 3 M nitric acid to observe

effects on the recovery of ^{239}Pu in the presence of all three ions. Since the greatest "salting out" effect was demonstrated with large amounts of iron and manganese based on batch distribution studies and preliminary column studies, the synthetic asphalt solution was modeled after the trace metal values reported by *von Gunten et al* with the greatest amounts of iron and manganese.[25] The concentrations of iron, aluminum, and manganese for low traffic weathered asphalt cement are shown in Table 6.

Table 6. Literature values for concentration of metals of interest in low traffic weathered asphalt cement used for synthetic asphalt solution.[25]

Literature Values of Metals for Low Traffic Weathered Asphalt Cement	
Fe	40 g/kg
Al	12.6 g/kg
Mn	700 mg/kg

The synthetic asphalt solution was composed of 3 M nitric acid - 0.717 M iron nitrate - 0.468 M aluminum nitrate - 0.013 M manganese nitrate in solution. Using the synthetic asphalt solution, the total recovery was on average 82.64 % which 81.35% was from the elution phase of the column and 1.29% recovered as break through during the rinsing phase. Due to significant amounts of analytes present in the synthetic asphalt solution which have synergistic effects with ^{239}Pu, there was a 14% decrease in the percent recovery of ^{239}Pu from the TRU column which is still sorbed to the column using the *Maxwell et al* separation procedure.[48] Additionally, the introduction of multiple analytes in the column system contributed to greater variance in the recovery of plutonium with standard deviations at 8.82% compared to standard deviations less than 2.5% for all other studies.

CHAPTER 5: DISCUSSION

5.1 Batch Distribution Studies

Data collected from the batch distribution studies provided valuable insight into the effects of major metal constituents on the uptake of ^{239}Pu on DGA, TRU, TEVA, and UTEVA resins developed by Eichrom Technologies. The major analytes of interest found in asphalt cement include sodium, magnesium, aluminum, potassium, calcium, iron, and manganese. By combining prior reported data from *Daum et al.* and *Nguyen et al.* along with data collected here on the influences of aluminum, iron, and manganese, trends can be summarized regarding uptake of ^{239}Pu in the presence of each analyte and can be described rather comprehensively and used to predict analytes with the greatest effect on column separations.[45,47,52] Results from the two prior studies and results collected here are summarized in Table 7.

Table 7. Summary of trends in the column capacity factor, k', for the uptake of plutonium-239 in the presences of major metals found in asphalt.

	Analyte	^{239}Pu Uptake in Nitric Acid	^{239}Pu Uptake in Hydrochloric Acid
DGA	Na^{+}	No effect	No effect
	Ca^{+2}	No effect	No effect
	K^{+}	Slight increase of k' from 0-1 M	Slight increase of k' from 0.25-1 M
	Mg^{+2}	Slight increase of k' from 0-1 M	Slight increase of k' from 0-1 M
	Al^{+3}	Some increase of k' at 1 M	Moderate increase of k' from 0.05-1 M
	Fe^{+3}	Significant increase in k' from 0.25-1 M	Significant increase of k' from 0.05-1 M
	Mn^{+2}	Fluctuations in k' from 0.1-1 M	Moderate increase of k' from 0.1-1M
TRU	Na^{+}	Slight decrease of k' from 0-0.001M	No effect
	Ca^{+2}	No effect	No effect
	K^{+}	Slight decrease of k' from 0-1 M	No effect
	Mg^{+2}	Slight increase of k' from 0-1 M	No effect
	Al^{+3}	Moderate increase of k' from 0.5-1 M	Moderate increase of k' from 0.5-1 M
	Fe^{+3}	Significant increase of k' from 0.25-1 M	Significant increase of k' from 0.05-1 M
	Mn^{+2}	Significant increase and fluctuations in k' from 0-1M	Moderate increase of k' from 0.1-1M
TEVA	Na^{+}	Slight increase of k' from 0-0.001 M	No uptake
	Ca^{+2}	No effect	No uptake
	K^{+}	Slight decrease of k'	Slight increase of k' from 0.25-1 M
	Mg^{+2}	No effect	Slight increase of k' from 0-1 M
	Al^{+3}	No effect	No uptake
	Fe^{+3}	Significant of k' from 0.25-1 M	Significant increase of k' from 0.25-1 M
	Mn^{+2}	Slight increase in k' from 0-1 M	No uptake
UTEVA	Na^{+}	No effect	No uptake
	Ca^{+2}	No effect	No uptake
	K^{+}	No effect	No uptake
	Mg^{+2}	No effect	No uptake
	Al^{+3}	No effect	No uptake
	Fe^{+3}	Significant increase of k' from 0.25-1 M	Significant increase of k' from 0.05-1 M
	Mn^{+2}	Slight increase in k' from 0-1 M	No uptake

5.1.1 Prior Data Discussion

From data acquired from prior studies, most of the analytes studied should not greatly affect a separation scheme using these extraction chromatography resins. The most interesting effect was demonstrated with varying amounts of potassium which, as noted, decreased the k' value with increasing concentration of potassium in nitric acid This effect could potentially translate to seeing some breakthrough of plutonium in the load fraction of a column study, but further studies would need to be conducted to confirm this hypothesized result. No other analytes including sodium, magnesium, or calcium would be expected to impact the recovery of plutonium should future investigations in the form of column chromatography studies be conducted.

5.1.2 New Data Discussion

From the data collected from batch studies conducted and presented here, aluminum, iron, and manganese demonstrate some effects ranging from minimal influences on the uptake of plutonium on extraction chromatography resin to a rather dramatic impact.

Aluminum showed minimal effects on the resins. Some increases were seen in the sorption of plutonium mostly with DGA and TRU at higher concentrations of aluminum. This effect most likely is based on the increase of counter ions available in solution. Both DGA and TRU show rapid increases in the k' values with increasing acid concentration in nitric acid and hydrochloric acid as shown in graphs provided by Eichrom Technologies.[36] TEVA and UTEVA show less dramatic increases in the sorption of plutonium with increases in acid concentration which matches well with the data collected in these studies. Aluminum nitrate is an excellent salt which is commonly used in separations, especially since it effectively increases the nitrate load in

solution since it provides three nitrates for every aluminum ion in solution. This is exemplified by the use of aluminum nitrate in the methods described by the EPA and *Maxwell et al.*[48,49] Additionally, stable batch studies demonstrated essentially no uptake of aluminum on any of the extraction chromatography resins which is optimal for minimal interference on sorption of actinides on the resins. Aluminum is also used to complex with phosphates to minimize their interference in a separation scheme[35]. Aluminum's lack of interference on the uptake of plutonium combined with its ability to significantly increase the counter ion load is useful and potentially supportive of separations of plutonium using extraction chromatography resins.

Iron had the greatest impact on the uptake of plutonium on all four extraction chromatography resin (DGA, TRU, TEVA, and UTEVA) compared to any other analyte studied previously or within this study. Blanks at each concentration were created and measured along with samples to correct for color quenching to increase confidence in the results obtained in these studies. In nitric acid, significant "salting out" occurs with iron above 0.1 M concentrations. Salting out is defined as a decrease in solubility of a substance with increasing salt concentration.[53] When the concentration of charged ions in solution increases, the water molecules in solution congregate around soluble ions which takes a significant toll on the enthalpy of the aqueous phase (mobile phase in extraction chromatography) which drives less soluble analytes such as plutonium in this case to interact with the organic phase of a system.[53,54] In hydrochloric acid, the trend was even more dramatic, where synergistic effects could be shown above 0.001 M concentrations with DGA, TRU, and UTEVA; noting that synergistic effects were not observed with TEVA until 0.1 M concentrations were reached. Similar to aluminum, it is important to note that each atom of iron introduced to the system comes with three nitrates or chlorides. By comparing the trends

and changes in magnitude of k' values observed with trends seen with the aluminum batch studies since both interferents have a trivalent state, conclusions can be drawn regarding interactions between iron ions and plutonium with the organic extractants used in extraction chromatography resins.

Stable batch studies were conducted after noting the iron in solution was adsorbing to the resins and sticking to the filter even when the filter pore size was large enough to allow free iron ions to pass through but not large enough to allow the resins to pass through. ICP-OES studies confirmed the resins have an affinity to take up iron from solution particularly with TRU and TEVA as shown here and with DGA at higher acid concentrations.[36] These studies also demonstrated the quantity of iron in solution could simultaneously adsorb to the resin while also causing plutonium to salt out of the mobile phase of all the extraction chromatography resins. Quantities of iron in asphalt samples can reach up to 0.71 M and should be considered within a separation scheme for plutonium. Since k' values for iron were so high, the major concern would be a reduced recovery, or an increased reagent volume required for stripping from the column.

Though manganese is a smaller constituent of asphalt, it is not insignificant where samples can reach up to 0.1 M concentrations.[25] Manganese also adds additional complexity due to the multiplicity of oxidation states available which include the following: 7, 6, 5, 4, 3, 2, 1, -1, -2, or -3.[26,27] Due to its ability to complete electrochemical processes so easily, the oxidation state at which manganese exists in these acidic system is not as predicable. Despite these qualities, the major effects of added manganese were some increases and fluctuations in k' values with increasing amounts of manganese. In nitric acid, TRU was the most greatly affected by the

addition of manganese with considerable fluctuations and increases in deviations in the uptake of plutonium. An error occurred with the measurement of DGA samples above 0.1 M as they were not initially recorded and recounted later. Due to this fact, these results are suspected to track with an increase in k' similar to the trend shown with TEVA and UTEVA. In hydrochloric acid only DGA and TRU showed increases in k' above 0.1 M concentrations which may affect the ability to strip plutonium from a column at exceedingly high concentrations on manganese. When considering the observed synergistic effects of manganese and iron, the correlation between atomic radius, oxidation state, and salting out within the resin could be cause for further investigation. These data suggest that manganese should not significantly impact the separation of plutonium from unusual matrices.

From the batch study data collected, most of the major inorganic constituents should not gravely impact a separation scheme for plutonium. Additionally, the decreases in the recovery of plutonium in column studies could likely be associated with the salting out trends shown with these analytes as well as the synergistic effects observed with iron on the adsorption of plutonium on these resins.

5.2 Column Chromatography Studies

Column studies were conducted to investigate the individual elemental and combined constituent impacts on a separation protocol for plutonium from asphalt described by *Maxwell et al* using TRU resin.[48] Data collected here provided valuable insight into the ruggedness of a rapid separation technique for plutonium as well as steps which could be optimized within the protocol. Of the major constituents found in asphalt, the impacts of aluminum, iron, and

manganese were studied individually and simultaneously on the separation of plutonium using TRU pre-packed columns made available commercially by Eichrom Technologies.
As expected, aluminum affected the recovery of plutonium the least. The increase in the k' value in both nitric and hydrochloric acid may have contributed to the decrease in recovery, but not significantly enough to be of concern or to be considered a poor recovery at 86% of the plutonium load recovered from the column.

As predicted, the increase in the k' value with the added iron in solution reduced the recovery of plutonium by 10%. However, the effect of salting out on TRU resin did not impact the recovery of plutonium as severely as initially anticipated since the recovery was still reasonably good at 84% on average. During this set of experiments, the iron could be visualized as a yellow hue which colored the entire column after the loading phase. The color remained relatively constant until the elution phase of the procedure. At the end of the procedure, much of the yellow hue had been stripped from the column, but a significant yellow coloring was still present on the bottom third of the column. This set of experiments suggested that steps to remove iron could improve the recovery of plutonium but are not necessary to achieve a reasonable recovery and during source preparation.

The reduction in recovery of plutonium in the presence of manganese was not predicted based on the batch study data collected earlier. This result may be accurate but is suspected to be not representative of the true result. It was noted that the 4 M HCl – 0.02 M $TiCl_3$ solution became more translucent the longer it sat on the shelf, as well as progressively less effective at stripping plutonium from the column. The titanium chloride experimentally appears to be sensitive to the

presence of other elements in aqueous solution, especially if they have a lower reduction potential than plutonium. A fresh stripping solution was made following this set of experiments which drastically improved the recovery of plutonium and matched more closely with the elution profile generated with the initial tests of this column procedure. Despite the less effective stripping solution used, the recovery of plutonium was still relatively good at 80.55% on average. Repeating this set of experiments would likely result in higher recoveries of plutonium.

Since real asphalt samples contain multiple analytes, a study was conducted to ascertain if any effects on the recovery of plutonium would present themselves when multiple analytes were present in solution. The first rendition of synthetic asphalt solution was created with aluminum, iron, and manganese only to match with data collected in the batch experiments and column studies conducted earlier. The synthetic asphalt solution was selected to be modeled after the worst-case scenario from literature values which had the highest iron and manganese content. The recovery of ^{239}Pu from this load solution was still good at an average of 82.64% recovery. The most notable effect of adding multiple analytes to the solution was an increase in the variance for the recovery of plutonium. Additional studies could provide insight into the cause of the variance observed. Potentially, the addition of multiple analytes along with plutonium create opportunities for complexes to occur based on local concentrations of ions in solution within the resin which led to less consistent results; however, steps were taken to ensure mixing of samples occurred as needed to prevent nonhomogeneous solutions from introducing errors. An unusual effect was observed during the elution phase of these columns. Similar to the iron columns, a significant amount of iron was visibly retained on the column during the loading phase and remained there for the duration of the rinsing phase. During the elution phase, a blue band was

formed which traveled down the column but never reached the bottom entirely leaving some of the yellow band still on the column as shown in Figure 38. Further studies could be conducted to better understand the mechanisms of the interactions occurring here. Currently, the blue hue is hypothesized to be manganese adsorbed to the resin. When the stripping solution contacts the resin, manganese likely undergoes redox reactions with the titanium chloride in solution to reach a different oxidation state which creates the blue hue seen here.

Figure 39: Visualization of chemical interaction on TRU column in the elution phase with synthetic asphalt solution as the loading parameter.

Initial assessments demonstrate the protocol described by *Maxwell et al.* has good potential to separate plutonium efficiently and effectively using TRU resin even in the presence of substantial amounts of various asphalt matrix constituents.[48] Large quantities of iron may need to be considered and treated prior to using extraction chromatography resins to separate plutonium to improve the recovery of plutonium. Alternatively, adding hydrofluoric acid to the stripping solution may need to be considered to maximize recovery of plutonium in samples containing substantial amounts of iron without pretreating for iron content. Iron content may need additional considerations if DGA is following a TRU column in sequence for separations of americium and during source preparation.

CHAPTER 6: CALCULATIONS & UNCERTAINY ANALYSIS

6.1 Mean Calculations

The mean was used for all sets of data to represent the central value for all data sets measured. The equation used to calculate the experimental mean, $\bar{x}$, of any given data set is shown below.

$$\bar{x} = \frac{1}{N} \cdot \sum_{n=1}^{N} x_i$$

In the equation shown above, x_i is an independently measured quantity out of *N* data points.[40]

6.2 Standard Deviation Calculations

The standard deviations used to report uncertainty as depicted with error bars in plots reported is based on deviation from the sample mean. The equation shown below was used to calculate standard deviations, σ, within data sets.

$$\sigma = \sqrt{\frac{1}{N-1} \cdot \sum_{n=1}^{N} (x_i - \bar{x})^2}$$

As noted above, x_i and *N* are the same values defined above.

Similarly, the standard deviation for an individual sample is defined in the equation below.

$$\sigma = \sqrt{x}$$

In this equation, x is defined as the number of counts measured in an individual sample. The liquid scintillation counting procedure was designed to measure each sample long enough to count 40,000 counts, meaning the standard deviation of counts measured should allow for 0.5% uncertainty in the counting statistic.

6.3 Recovery Yield Calculations

For column studies, data is reported in recovery of plutonium. Spiked samples were measured to provide a reference to which fractions were compared. The following equation was used to calculate recoveries for column fractions.

$$Recovery\ (\%) = \frac{A_f}{A_i} \cdot 100$$

6.4 Total Uncertainty Analysis

In certain instances, samples measured were recorded with fewer counts than sample blanks. To determine if samples were within detection limits as needed, a total uncertainty analysis was performed using the following equation to sum uncertainties throughout the batch study experiments.

$$\sigma_T = \sqrt{\sum_{n=1}^{N} \left(\frac{\partial f}{\partial \bar{x}_i}\right)^2 \cdot \sigma_i}$$

6.5 Analyses for Outliers

Analyses were completed for data sets to evaluate measurements for outliers as needed. A t-test was used to determine if select points were skewing data. The equation below was used to calculate test statistics and compared to a rejection region determined using R.

$$t_{test} = \frac{\bar{y} - \mu_0}{(s/\sqrt{n})}$$

Additionally, Z-scores were used to determine if data points were outliers. If a data point had a Z-score greater than 3 (greater than three standard deviations from the mean of the data set), the data point was considered an outlier and was not used in mean and standard deviation

calculations displayed on figures. The following equation was used to calculate Z-scores as needed.

$$Z = \frac{Y - \mu}{\sigma}$$

CHAPTER 7: CONCLUSION

7.1 Overview

Batch studies were conducted using extraction chromatography resins produced by Eichrom Technologies to characterize the influence of major inorganic constituents present in asphalt on the uptake of plutonium on DGA, TRU, TEVA, and UTEVA. Select stable analytes were also studied for their uptake on the resins to further investigate their interactions with extractants as they relate to interactions with plutonium and extractant molecules. Column studies were conducted using TRU resin to relate data collected in batch studies on realistic separation applications from asphalt samples.

7.2 Batch Studies

Prior studies provided data demonstrating the trends in k' values on the uptake of plutonium on DGA, TRU, TEVA, and UTEVA in the presence of sodium, calcium, potassium, and magnesium. These studies indicated that no remarkable effects were observed on the uptake of plutonium in the presence of sodium, calcium, or magnesium. Some inhibitory effects were seen in the k' trend of ^{239}Pu with increasing potassium concentration.

The studies conducted in this work provided insight into trends in the k' values for plutonium on the four extraction chromatography resins in the presence of iron, aluminum, and manganese. Iron (III) showed significant synergistic effects on the sorption of ^{239}Pu on all resins. Stable studies with iron indicated significant sorption particularly on TRU and TEVA leading to conclusions of salting out the resins at high concentrations of iron in solution. Aluminum showed

some synergist effects on the uptake of plutonium above 0.1 M concentration on DGA and TRU only. Stable studies with aluminum showed no uptake of aluminum on any of the resins indicating the increases in the k' trends observed with DGA and TRU may be more likely related to increases in nitrate and chloride concentrations since each added aluminum (III) ion comes with three additional counterions. Due to this observed trend, the presence of aluminum is likely supportive of separations of plutonium. Manganese showed synergistic effects with all resins in nitric acid with additional fluctuations in the k' trend with TRU only. Manganese also showed synergistic effects on the uptake of plutonium on DGA and TRU only in hydrochloric acid. The fluctuations observed in the k' values in the presence of manganese may have implications in the variance of some of the column studies.

7.3 Column Studies

Column studies were conducted to investigate the application of k' trends observed in batch distribution studies to realistic separations of plutonium from samples containing substantial amounts of nonstandard analytes in solution sourced from asphalt. The effects of aluminum, iron, and manganese were studied separately and in combination on a separation protocol developed by *Maxwell et al* using TRU resin.[48] The synergistic effects observed with all three analytes led to decreases in the recovery of plutonium from the column in all cases. Individual interferant studies were conducted at concentrations where k' values were most affected (1 M concentrations in all cases), whereas interferents were studied in combination based on a model of literature value concentrations of analytes found in asphalt. Without any interferants, recovery of ^{239}Pu using this procedure averaged around 94.25%. The introduction of aluminum decreased the recovery of plutonium to 86.07%. The addition of iron to the system reduced the recovery of

plutonium to 84.21%. The addition of manganese decreased the recovery of plutonium to 80.55%. The synthesized asphalt solution had a recovery of 82.64% and the greatest standard deviation of any other set of columns at 8.82%. The recovery of plutonium from the columns loaded with synthesized asphalt solution was driven mostly by the iron content with some additional effects with manganese in solution. The combination of manganese and iron generated an increased variability in recovery of plutonium from the TRU column.

7.4 Future Work

Continuation of this work should investigate the effects of the organic components of asphalt on extraction chromatography resins as well as digestion techniques to destroy asphaltenes in bituminous material. Studies could also be conducted on additional interferants found in asphalt including sulfates and phosphates as well as other metals not previously studied. Similarly, acid leeching studies could be conducted on standard reference material or sampled asphalt to characterize and quantify metal contents dissolved into solution. Further studies could be conducted to extend the interference studies to additional alpha emitting radionuclides as well as important fission products. Further studies could be conducted on separations of radionuclides from complicated matrices such as synthesized urban melt glass with additions of steel, asphalt, concrete, and other building materials.

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APPENDIX I: CHEMICALS

Nitric Acid, ACS Grade

CAS: 7697-37-2

Nitric Acid, Trace Metal Grade

CAS: 7697-37-2

Hydrochloric Acid, ACS Grade

CAS: 7647-01-0

Iron (III) Nitrate

CAS: 7782-61-8

Aluminum (III) Nitrate

CAS: 7784-27-2

Manganese (II) Nitrate

CAS: 20694-39-7

Iron (III) Chloride

CAS: 10025-77-1

Aluminum (III) Chloride

CAS: 7784-13-6

Manganese (II) Chloride

CAS: 13446-34-9

Titanium Chloride

CAS: 7705-07-9

^{239}Pu, Isotope Product

APPENDIX II: MATERIALS AND REAGENTS

^{239}Pu in 1 mol L^{-1} nitric acid, 1000 Bq mL^{-1}

^{239}Pu in 3 mol L^{-1} nitric acid, 1000 Bq mL^{-1}

^{239}Pu in 1 mol L^{-1} hydrochloric acid, 1000 Bq mL^{-1}

^{239}Pu in 3 mol L^{-1} hydrochloric acid, 1000 Bq mL^{-1}

^{239}Pu in 1 mol L^{-1} nitric acid, 3000 Bq mL^{-1}

^{239}Pu in 3 mol L^{-1} nitric acid

DGA resin, loose, Eichrom Technologies

TRU resin, loose, Eichrom Technologies

TEVA resin, loose, Eichrom Technologies

UTEVA resin, loose, Eichrom Technologies

TRU resin, pre-packed column, Eichrom Technologies

Nitric Acid, 1 mol L^{-1}

Nitric Acid, 3 mol L^{-1}

Nitric Acid, 10 mol L^{-1}

Hydrochloric acid, 1 mol L^{-1}

Hydrochloric acid, 3 mol L^{-1}

Hydrochloric acid, 4 mol L^{-1}

Hydrochloric acid – Titanium Chloride, 3 mol L^{-1} – 0.02 mol L^{-1}

Thermo Scientific Labquake Shaker (fixed speed)

Thermo Scientific Fisher and Life Science PTFE membrane Syringe Filters, 0.45 μm pore size

Eichrom Vacuum Box

Vacuubrand Vacuum Pump

APPENDIX III

Table 8: Raw data for Figure 12[45]

Ionic Species: Sodium	^{239}Pu in Acid System: Nitric Acid		
Limit of Detection	Concentration [M]	k' value	
	0	16724.03	
	0.171	16724.03	
	0.342	16724.03	
	0.513	16724.03	
	0.684	16724.03	
	0.856	16724.03	
DGA	Concentration [M]	k' value	Standard Deviation
	0	1133.363	143.572
	0.171	1469.416	65.169
	0.342	1322.154	90.313
	0.513	1420.304	51.06
	0.684	1485.722	55.82
	0.856	1451.557	37.657
TRU	Concentration [M]	k' value	Standard Deviation
	0	7256.304	1049.578
	0.171	2271.237	196.819
	0.342	2519.135	156.783
	0.513	2593.709	359.353
	0.684	2312.806	607.339
	0.856	2632.283	498.879
TEVA	Concentration [M]	k' value	Standard Deviation
	0	139.732	65.944
	0.171	606.276	74.389
	0.342	551.1	223.762
	0.513	613.048	71.577
	0.684	615.919	16.2469
	0.856	871.749	70.22
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	176.307	2.913
	0.171	219.273	7.329
	0.342	259.775	15.975
	0.513	286.409	15.903
	0.684	321.301	13.195

	0.856	324.859	8.668
Actinide	Concentration [M]	k' value	Standard Deviation
	0	8894.022	7622.817
	0.171	21269.12	27492.133
	0.342	30841.35	26721.898
	0.513	26984.38	23141.842
	0.684	50126.22	23141.842
	0.856	50126.22	23141.842
Diphonix	Concentration [M]	k' value	Standard Deviation
	0	119.36	20.615
	0.171	101.064	23.969
	0.342	106.495	17.46
	0.513	96.261	17.119
	0.684	122.764	17.69
	0.856	101.192	5.651

Table 9. Raw data for Figure 13[45]

Ionic Species: Sodium	^{239}Pu in Acid System: Hydrochloric Acid		
Limit of Detection	Concentration [M]	k' value	
	0	16724.03	
	0.171	16724.03	
	0.342	16724.03	
	0.513	16724.03	
	0.684	16724.03	
	0.856	16724.03	
DGA	Concentration [M]	k' value	Standard Deviation
	0	16.504	6.979
	0.171	11.421	0.871
	0.342	12.611	0.651
	0.513	14.875	3.221
	0.684	15.797	1.962
	0.856	18.132	1.968
TRU	Concentration [M]	k' value	Standard Deviation
	0	12.701	0.698
	0.171	11.838	0.478
	0.342	11.759	0.358

	0.513	11.925	0.161
	0.684	13.789	0.498
	0.856	15.979	1.286
TEVA	Concentration [M]	k' value	Standard Deviation
	0	1.56	0.063
	0.171	2.21	0.073
	0.342	2.311	0.027
	0.513	2.031	0.166
	0.684	2.158	0.249
	0.856	2.339	0.14
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	1.175	0.232
	0.171	0.946	0.294
	0.342	0.833	0.262
	0.513	1.118	0.139
	0.684	0.908	0.165
	0.856	1.258	0.089
Actinide	Concentration [M]	k' value	Standard Deviation
	0	49798.5	39993.605
	0.171	32480.7	34635.478
	0.342	29850.6	37231.127
	0.513	31794	35602.839
	0.684	67116.2	34635.478
	0.856	68599.9	31668.158
Diphonix	Concentration [M]	k' value	Standard Deviation
	0	389.902	38.979
	0.171	517.382	87.096
	0.342	384.915	63.161
	0.513	524.515	67.273
	0.684	566.265	43.388
	0.856	579.294	81.162

Table 10. Raw Data for Figure 14[45]

Ionic Species: Calcium	^{239}Pu in Acid System: Nitric Acid		
DGA	Concentration [M]	k' value	Standard Deviation

	0	2010.101	173.482
	0.001	981.284	65.646
	0.005	589.498	20.369
	0.01	962.047	136.922
	0.05	1308.85	191.794
	0.1	1824.54	90.947
	0.25	1732.887	103.383
	0.5	2574.563	104.424
	1	4543.599	747.322
TRU	Concentration [M]	k' value	Standard Deviation
	0	3858.565	423.921
	0.001	3635.101	632.668
	0.005	3645.493	750.114
	0.01	3881.571	522.643
	0.05	4687.785	594.59
	0.1	5611.105	452.563
	0.25	8149.925	3009.687
	0.5	8903.208	2553.454
	1	14821.75	4292.756
TEVA	Concentration [M]	k' value	Standard Deviation
	0	539.01	8.909
	0.001	538.33	60.239
	0.005	481.837	39.788
	0.01	463.805	58.817
	0.05	488.277	19.604
	0.1	464.589	89.564
	0.25	499.194	17.279
	0.5	503.156	57.301
	1	674.849	49.362
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	83.144	4.785
	0.001	80.267	3.869
	0.005	92.869	15.651
	0.01	94.554	6.153
	0.05	116.282	3.791
	0.1	114.617	12.453
	0.25	149.84	10.966
	0.5	158.317	4.174

	1	189.565	3.976
Actinide	Concentration [M]	k' value	Standard Deviation
	0	19754.35	8590.671
	0.001	19849.41	8805.1
	0.005	18396.35	9857.015
	0.01	9677.868	6307.286
	0.05	18410.86	9725.977
	0.1	18498.07	9979.291
	0.25	19213.25	9072.906
	0.5	19269.26	9188.347
	1	23300.29	11354.298
Diphonix	Concentration [M]	k' value	Standard Deviation
	0	1882.579	235.892
	0.001	1644.559	486.796
	0.005	1713.429	359.358
	0.01	1577.087	248.759
	0.05	1647.174	280.892
	0.1	1733.706	605.603
	0.25	1720.954	400.026
	0.5	1770.278	425.882
	1	2953.379	661.663

Table 11: Raw Data for Figure 15[45]

Ionic Species: Calcium	^{239}Pu in Acid System: Hydrochloric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	21.097	2.51
	0.001	21.176	3.429
	0.005	18.641	0.472
	0.01	18.958	1.126
	0.05	18.695	1.011
	0.1	19.051	0.612
	0.25	23.146	0.288
	0.5	25.136	2.069
	1	33.251	4.976
TRU	Concentration [M]	k' value	Standard Deviation
	0	17.326	0.947
	0.001	16.714	1.888

	0.005	14.838	5.976
	0.01	19.12	3.495
	0.05	17.754	1.194
	0.1	19.473	1.363
	0.25	20.166	0.5
	0.5	22.933	1.018
	1	78.797	3.104
TEVA	Concentration [M]	k' value	Standard Deviation
	0	2.052	0.681
	0.001	1.732	0.263
	0.005	0.945	2.747
	0.01	1.557	0.209
	0.05	1.604	0.21
	0.1	1.634	0.274
	0.25	1.26	0.241
	0.5	0.993	0.113
	1	2.203	0.631
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	1.8393	0.407
	0.001	2.017	0.37
	0.005	1.842	0.343
	0.01	1.762	0.328
	0.05	1.89	0.391
	0.1	1.794	0.421
	0.25	1.666	0.517
	0.5	2.059	0.373
	1	3.095	2.837
Actinide	Concentration [M]	k' value	Standard Deviation
	0	15809.56	3397.774
	0.001	15846.32	3417.531
	0.005	29912.85	19844.486
	0.01	21301.2	17606.933
	0.05	30188.47	19922.429
	0.1	22885.8	16263.558
	0.25	14656.34	2954.335
	0.5	23109.66	16618.701
	1	30603	19412.195

	Concentration [M]	k' value	Standard Deviation
Diphonix	0	2075.496	484.342
	0.001	2569.277	442.967
	0.005	2183.071	446.725
	0.01	2199.35	423.315
	0.05	2435.703	743.579
	0.1	1984.274	446.036
	0.25	2742.582	513.629
	0.5	2001.78	604.017
	1	1009.77	109.871

Table 12. Raw Data for Figure 16[47]

Ionic Species: Potassium	^{239}Pu in Acid System: Nitric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	1347.91	97.85
	0.001	1324.1	36.66
	0.005	1303.33	194.39
	0.01	1087.99	81.62
	0.05	1076.65	120.82
	0.1	898.1	24.02
	0.25	712.87	34.34
	0.5	523.11	13.41
	1	333.3	5.3
TRU	Concentration [M]	k' value	Standard Deviation
	0	3767.73	493.8
	0.001	3885.37	314
	0.005	2926.02	301.41
	0.01	2750.38	153.92
	0.05	2684.13	211.63
	0.1	2169.38	51.78
	0.25	2003.2	91.31
	0.5	1149.68	31.05
	1	701.91	24.03
TEVA	Concentration [M]	k' value	Standard Deviation
	0	1362.7	57.26
	0.001	1306.55	49.65
	0.005	1483.07	415.7
	0.01	1261.64	107.11

	0.05	1118.31	221.58
	0.1	1147.53	11.56
	0.25	999.99	29.73
	0.5	710.45	23.63
	1	517.84	20.03
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	161.43	16.9
	0.001	147.83	13.21
	0.005	139.9	2.42
	0.01	143	4.26
	0.05	143.68	13.97
	0.1	156.01	51.08
	0.25	131.3	4.69
	0.5	129.67	15.08
	1	111.51	8.79

Table 13: Raw Data for Figure 17[47]

Ionic Species: Potassium	^{239}Pu in Acid System: Hydrochloric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	2.13	0.26
	0.001	2.03	0.16
	0.005	1.95	0.2
	0.01	1.62	0.31
	0.05	2.82	0.28
	0.1	2.17	0.29
	0.25	3.83	0.26
	0.5	3.98	0.43
	1	6.02	0.8
TRU	Concentration [M]	k' value	Standard Deviation
	0	7.44	0.45
	0.001	8.17	0.73
	0.005	8.28	0.31
	0.01	8.34	1.06
	0.05	9.14	1.78
	0.1	10.34	1.89
	0.25	11.42	0.86
	0.5	11.59	0.49
	1	12.26	0.69

TEVA	Concentration [M]	k' value	Standard Deviation
	0	1.66	0.25
	0.001	1.42	1.43
	0.005	1.63	0.94
	0.01	1.51	0.15
	0.05	1.42	0.15
	0.1	1.51	0.7
	0.25	1.76	0.5
	0.5	3.22	1.14
	1	4.64	1.56
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	-0.27	0.11
	0.001	-0.54	0.12
	0.005	-0.35	0.18
	0.01	-0.53	0.06
	0.05	-0.66	0.1
	0.1	-0.66	0.36
	0.25	-0.91	0.66
	0.5	-1.2	0.45
	1	-0.56	0.73

Table 14: Raw Data for Figure 18[47]

Ionic Species: Magnesium	^{239}Pu in Acid System: Nitric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	3166.39	184.02
	0.001	2803.96	292.63
	0.005	2694.3	441.8
	0.01	2770.31	429.34
	0.05	2960.21	119.92
	0.1	3424.27	89.14
	0.25	5077.9	499.68
	0.5	8448.1	1023.26
	1	26664.48	10120.27
TRU	Concentration [M]	k' value	Standard Deviation
	0	2253.42	661.7
	0.001	3056.88	248.15
	0.005	3257.92	526.94

	0.01	2966.82	293.31
	0.05	3408.87	426.26
	0.1	3623.75	250.34
	0.25	4329.69	461.15
	0.5	5155.08	817.82
	1	9428.25	1944.31
TEVA	Concentration [M]	k' value	Standard Deviation
	0	1508.8	40.88
	0.001	1506.59	102.02
	0.005	1464.62	71.93
	0.01	1481.88	108.52
	0.05	1526.94	42.92
	0.1	1541.78	101.46
	0.25	1482.6	33.9
	0.5	1461.35	117.12
	1	1528.74	70.29
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	149.12	6.8
	0.001	145.22	8.59
	0.005	146.71	9.46
	0.01	144.33	3.16
	0.05	135.01	8.55
	0.1	136	4.15
	0.25	160.17	1.42
	0.5	199.46	9.96
	1	209.27	18.62

Table 15: Raw Data for Figure 19[47]

Ionic Species: Magnesium	^{239}Pu in Acid System: Hydrochloric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	1.2	0.24
	0.001	1.34	0.2
	0.005	1.35	0.37
	0.01	1.66	0.1
	0.05	1.68	0.33
	0.1	2.04	0.25
	0.25	3.26	0.22

	0.5	6.71	0.67
	1	24.49	0.79
TRU	Concentration [M]	k' value	Standard Deviation
	0	6.29	1.06
	0.001	7.19	0.41
	0.005	7.26	0.66
	0.01	7.76	0.33
	0.05	8.32	0.87
	0.1	8.99	0.58
	0.25	11.7	0.35
	0.5	14.52	0.9
	1	0.79	2.72
TEVA	Concentration [M]	k' value	Standard Deviation
	0	0.93	0.53
	0.001	0.84	0.2
	0.005	0.8	0.11
	0.01	1.46	0.42
	0.05	1.55	0.15
	0.1	1.59	0.48
	0.25	2.67	1.01
	0.5	5.07	0.81
	1	11.84	2.18
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	-0.86	0.23
	0.001	-0.83	0.53
	0.005	-0.53	0.28
	0.01	-0.33	0.03
	0.05	-1.24	0.3
	0.1	-1.04	0.63
	0.25	-0.62	0.36
	0.5	-0.97	0.19
	1	-1.17	0.47

Table 16: Raw Data for Figure 24

Ionic Species: Iron	^{239}Pu in Acid System: Nitric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	2819.99	1084.69
	0.001	17092.75	6535.56
	0.005	46803.28	60616.68
	0.01	48672.02	58291.77
	0.05	45577.03	59018.74
	0.1	46242.93	59650.91
	0.25	11586234.06	13351970.95
	0.5	17205973.86	11463243.21
	0	17231047.50	11472319.57
TRU	Concentration [M]	k' value	Standard Deviation
	0	7530.71	2867.58
	0.001	16176.77	7253.19
	0.005	22497.62	3989.45
	0.01	30461.22	7134.69
	0.05	22417.50	4178.46
	0.1	20361.30	7067.81
	0.25	12199506.25	24316993.41
	0.5	36428909.99	24302377.28
	0	24562476.01	28387385.69
TEVA	Concentration [M]	k' value	Standard Deviation
	0	773.04	251.74
	0.001	3440.72	284.62
	0.005	5041.64	672.57
	0.01	3635.12	21.18
	0.05	15494.87	7480.04
	0.1	8443.99	1928.91
	0.25	5647184.43	11332151.80
	0.5	5568471.75	11163263.01
	0	16869993.54	11232145.45
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	192.06	54.07
	0.001	620.56	64.85
	0.005	610.93	17.98
	0.01	687.75	51.48
	0.05	1101.65	238.91

	0.1	1355.74	147.11
	0.25	3337.98	525.58
	0.5	8980.41	4202.90
	0	22791254.74	26317311.37

Table 17: Raw Data for Figure 25

Ionic Species: Iron	^{239}Pu in Acid System: Hydrochloric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	3.33	0.26
	0.001	2.30	0.18
	0.005	7.15	0.14
	0.01	19.06	0.47
	0.05	1882.03	55.08
	0.1	20957.79	952.12
	0.25	54791872.53	31571395.85
	0.5	54146738.88	31262111.59
	1	82761479.35	27551210.79
TRU	Concentration [M]	k' value	Standard Deviation
	0	18.35	30.41
	0.001	22.05	2.41
	0.005	69.47	17.67
	0.01	610.00	462.18
	0.05	37287.92	7698.99
	0.1	26821.15	3707.25
	0.25	22657.86	2882.42
	0.5	2729426.54	1848748.57
	1	1891992.19	429078.57
TEVA	Concentration [M]	k' value	Standard Deviation
	0	181.95	51.22
	0.001	587.89	61.43
	0.005	578.78	17.04
	0.01	651.55	48.77
	0.05	1043.67	226.34
	0.1	1284.38	139.36
	0.25	3162.30	497.92
	0.5	8507.76	3981.69
	1	21591715.02	24932189.72

	Concentration [M]	k' value	Standard Deviation
UTEVA	0	0.17	0.16
	0.001	0.17	0.02
	0.005	0.41	0.02
	0.01	1.21	0.02
	0.05	52.64	2.69
	0.1	2371.06	235.80
	0.25	21387.15	13893.37
	0.5	32528892.43	21658378.82
	1	43146746.69	214311.91

Table 18: Raw Data for Figure 26

Ionic Species: Aluminum	^{239}Pu in Acid System: Nitric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	2819.99	1084.69
	0.001	2506.71	153.35
	0.005	2930.90	172.53
	0.01	2937.54	512.39
	0.05	4613.21	276.55
	0.1	5010.66	522.75
	0.25	6618.54	710.91
	0.5	5736.95	425.76
	1	29573.25	29617.66
TRU	Concentration [M]	k' value	Standard Deviation
	0	7186.45	2736.49
	0.001	4942.01	284.86
	0.005	4629.76	533.38
	0.01	6067.38	745.71
	0.05	8186.74	749.18
	0.1	10565.99	3492.36
	0.25	10155.26	1904.92
	0.5	45591.98	344.66
	1	41027.89	11814.19
TEVA	Concentration [M]	k' value	Standard Deviation
	0	773.04	251.74
	0.001	599.33	23.88
	0.005	571.70	6.54

	0.01	559.53	27.92
	0.05	586.62	85.60
	0.1	561.27	15.22
	0.25	736.62	16.37
	0.5	1006.62	82.93
	1	1190.71	114.18
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	181.95	51.22
	0.001	87.67	11.86
	0.005	92.82	3.95
	0.01	97.28	12.47
	0.05	99.56	5.80
	0.1	124.62	7.07
	0.25	165.97	6.09
	0.5	236.07	18.92
	1	538.37	37.44

Table 19: Raw Data for Figure 27

Ionic Species: Aluminum	^{239}Pu in Acid System: Hydrochloric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	3.54	0.52
	0.001	3.91	0.29
	0.005	4.40	0.22
	0.01	3.18	0.20
	0.05	28.40	5.25
	0.1	12.71	1.14
	0.25	34.05	0.93
	0.5	34.18	0.77
	1	160.54	1.33
TRU	Concentration [M]	k' value	Standard Deviation
	0	17.03	28.21
	0.001	27.92	6.60
	0.005	19.69	2.59
	0.01	21.32	1.93
	0.05	26.64	9.59
	0.1	21.86	1.99
	0.25	24.46	5.67
	0.5	27.24	1.69

	1	378.06	12.21
TEVA	Concentration [M]	k' value	Standard Deviation
	0	0.01	0.11
	0.001	0.41	0.40
	0.005	0.54	0.45
	0.01	0.42	0.44
	0.05	0.52	0.39
	0.1	0.52	0.36
	0.25	0.58	0.33
	0.5	0.51	0.30
	1	1.21	0.34
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	0.18	0.09
	0.001	0.56	0.58
	0.005	0.61	0.42
	0.01	0.42	0.48
	0.05	0.42	0.41
	0.1	0.34	0.45
	0.25	0.46	0.36
	0.5	0.54	0.34
	1	0.45	0.37

Table 20: Raw Data for Figure 28

Ionic Species: Manganese	^{239}Pu in Acid System: Nitric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	2819.99	1084.69
	0.001	2918.25	186.87
	0.005	3620.13	536.04
	0.01	3559.16	5.40
	0.05	4426.72	781.48
	0.1	7853.42	4971.58
	0.25	1919.67	9.29
	0.5	1933.14	99.43
	1	2090.07	166.00
TRU	Concentration [M]	k' value	Standard Deviation
	0	7186.45	2736.49
	0.001	35793.09	22986.29

	0.005	15631.17	5606.99
	0.01	49019.39	24171.79
	0.05	48777.19	24164.57
	0.1	25408.80	5302.85
	0.25	25513.78	5326.26
	0.5	59737.11	21083.67
	1	35924.82	23560.25
TEVA	Concentration [M]	k' value	Standard Deviation
	0	773.04	251.74
	0.001	1272.99	88.69
	0.005	1720.90	53.44
	0.01	2167.86	90.44
	0.05	3409.21	446.73
	0.1	4213.53	241.27
	0.25	4314.58	2690.29
	0.5	8631.47	2091.91
	1	11128.96	1232.72
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	181.95	51.22
	0.001	304.42	16.50
	0.005	392.08	8.90
	0.01	378.59	13.41
	0.05	409.83	39.12
	0.1	498.63	24.10
	0.25	658.60	33.96
	0.5	956.99	56.42
	1	1936.87	169.45

Table 21: Raw Data for Figure 29

Ionic Species: Manganese	^{239}Pu in Acid System: Hydrochloric Acid		
DGA	Concentration [M]	k' value	Standard Deviation
	0	2.96	0.07
	0.001	3.19	0.13
	0.005	2.93	0.12
	0.01	2.92	0.05
	0.05	3.55	0.06
	0.1	4.72	0.16
	0.25	7.00	0.14

	0.5	53.74	1.84
	1	571.72	15.19
TRU	Concentration [M]	k' value	Standard Deviation
	0	18.35	30.41
	0.001	5.19	0.66
	0.005	5.29	0.64
	0.01	5.35	0.72
	0.05	12.91	6.60
	0.1	11.24	5.32
	0.25	40.46	10.28
	0.5	128.11	27.25
	1	2548.38	542.32
TEVA	Concentration [M]	k' value	Standard Deviation
	0	0.06	0.11
	0.001	0.04	0.41
	0.005	0.01	0.33
	0.01	0.34	0.09
	0.05	0.16	0.04
	0.1	0.27	0.34
	0.25	0.39	0.51
	0.5	0.08	0.18
	1	7.89	7.60
UTEVA	Concentration [M]	k' value	Standard Deviation
	0	0.17	0.16
	0.001	0.01	0.12
	0.005	0.02	0.05
	0.01	0.14	0.16
	0.05	0.14	0.18
	0.1	0.15	0.05
	0.25	0.12	0.11
	0.5	0.32	0.44
	1	0.71	1.12

Table 22. Raw Data for Figure 34

Ionic Species: Iron	Acid System: Nitric Acid	
DGA	Concentration [M]	k' value
	0.001	0.259776

	0.01	0.968376
	0.1	0.241729
	1	56660.49
TRU	Concentration [M]	k' value
	0.001	6.745147
	0.01	4.669077
	0.1	0.405586
	1	0.104454
TEVA	Concentration [M]	k' value
	0.001	0.190018
	0.01	0.102178
	0.1	0.032291
	1	0.208559
UTEVA	Concentration [M]	k' value
	0.001	0.452659
	0.01	0.086646
	0.1	0.016541
	1	0.435331

Table 23. Raw Data for Figure 35

Ionic Species: Iron	Acid System: Hydrochloric Acid	
DGA	Concentration [M]	k' value
	0.001	3.260346
	0.01	2.749303
	0.1	1.587968
	1	0.576876
TRU	Concentration [M]	k' value
	0.001	47.72032
	0.01	36.06408
	0.1	4.285279
	1	2.688965
TEVA	Concentration [M]	k' value
	0.001	77.24896
	0.01	337.6381

	0.1	9.40746
	1	1.126897
UTEVA	Concentration [M]	k' value
	0.001	0.402493
	0.01	0.710077
	0.1	2.137984
	1	2.287352

Table 24. Raw Data for Figure 36

Ionic Species: Aluminum	Acid System: Nitric Acid	
DGA	Concentration [M]	k' value
	0.001	0.237905
	0.01	1.096612
	0.1	0.154996
	1	0.046508
TRU	Concentration [M]	k' value
	0.001	0.338627
	0.01	1.027988
	0.1	0.735544
	1	0.461483
TEVA	Concentration [M]	k' value
	0.001	0.520323
	0.01	0.598226
	0.1	0.137039
	1	0.398757
UTEVA	Concentration [M]	k' value
	0.001	1.444687
	0.01	0.479121
	0.1	0.738775
	1	0.606948

Table 25. Raw Data for Figure 37

Ionic Species: Aluminum	Acid System: Hydrochloric Acid	
DGA	Concentration [M]	k' value

	0.001	0.132181
	0.01	0.410887
	0.1	0.158428
	1	0.441289
TRU	Concentration [M]	k' value
	0.001	0.905666
	0.01	0.354534
	0.1	1.045358
	1	0.899519
TEVA	Concentration [M]	k' value
	0.001	1.467342
	0.01	0.687341
	0.1	2.218689
	1	1.033046
UTEVA	Concentration [M]	k' value
	0.001	1.795589
	0.01	0.584558
	0.1	407.8989
	1	0.22232

Table 26. Raw Data for ^{239}Pu Recovery from Standard Columns (Figure 39)

Ionic Species: Blank	^{239}Pu Recovery from TRU column fractions	
Fraction (mL)	Percent Recovery Avg	SD (% recovery)
Load	0.00	0.00
R-5	0.00	0.00
R-10	0.00	0.00
R-15	0.04	0.03
R-20	0.40	0.12
R-25	0.62	0.01
E-5	89.55	0.85
E-10	2.63	0.65
E-15	0.99	0.16
Avg Total Recovery	94.25	
SD (Total Recovery)	0.44	

Table 27. Raw Data for ^{239}Pu recovery from Aluminum Columns (Figure 39)

Ionic Species: Aluminum	^{239}Pu Recovery from column fractions	
Fraction (mL)	Percent Recovery Avg	SD (% recovery)
Load	0.00	0.00
R-5	0.00	0.00
R-10	0.00	0.00
R-15	0.05	0.01
R-20	0.74	0.12
R-25	1.28	0.37
E-5	75.28	1.24
E-10	6.84	1.02
E-15	1.89	0.23
Avg Total Recovery	86.07	
SD (Total Recovery)	1.60	

Table 28. Raw Data for ^{239}Pu recovery from Iron Columns (Figure 39)

Ionic Species: Iron	^{239}Pu Recovery from TRU column fractions	
Fraction (mL)	Percent Recovery Avg	SD (% recovery)
Load	0.00	0.00
R-5	0.00	0.00
R-10	0.00	0.00
R-15	0.00	0.00
R-20	0.38	0.07
R-25	0.59	0.12
E-5	65.18	3.12
E-10	15.36	2.09
E-15	2.69	1.25
Avg Total Recovery	84.21	
SD (Total Recovery)	0.85	

Table 29. Raw Data for ^{239}Pu recovery from Manganese Columns (Figure 39)

Ionic Species: Manganese	^{239}Pu Recovery from column fractions	
Fraction (mL)	Percent Recovery Avg	SD (% recovery)
Load	0.01	0.00

R-5	0.00	0.00
R-10	0.00	0.00
R-15	0.03	0.01
R-20	0.59	0.04
R-25	0.75	0.06
E-5	40.01	3.92
E-10	27.95	0.77
E-15	11.20	0.95
Avg Total Recovery	80.55	
SD (Total Recovery)	2.40	

Table 30. Raw Data for ^{239}Pu recovery from Synthesized Asphalt Columns (Figure 39)

Ionic Species: Synthesized Asphalt	^{239}Pu Recovery from TRU column fractions	
Sample	Percent Recovery Avg	SD (% recovery)
Load	0.00	0.00
R-5	0.00	0.00
R-10	0.00	0.00
R-15	0.00	0.00
R-20	0.56	0.08
R-25	0.74	0.03
E-5	79.64	9.53
E-10	1.14	0.39
E-15	0.57	0.38
Avg Total Recovery	82.64	
SD (Total Recovery)	8.82	

CURRICULUM VITAE

Raissa Chunko

3116 Laporte Ave, Fort Collins, CO 80521 | (970) 817-1330| Raissa.Chunko@colostate.edu

Education

Currently enrolled in Master of Science—Radiological health sciences—Health physics specializaion 3.948 GPA
colorado state university, anticipated graduation May 2024

Bachelor of Science – Neuroscience, Minor – Mathemetics 3.640 GPA
Colorado State university, December 2020

Concentrated on cellular and molecular neuroscience with a major focus on biochemistry, organic chemistry, immunology, and functional neuroanatomy. Demonstrated expert mathematical analysis and modeling with a minor in mathematics. COVID-19 research and thesis.

Dean's Honor List| Member of National Society of Collegiate Scholars | Leader of Neuroscience Student Organization and College Council (2018 – 2020) | Commencement Speaker

Research

Currently conducting batch studies and column studies to characterize the effects of metal ions found in asphalt on the uptake of plutonium on extraction chromatography resins as well as behaviors of plutonium in a separation scheme in the presence of select metal ions.

Conducted a pH optimization study for electrodepositing americium to improve the production of americium targets for neutron capture studies under the guidance of Evelyn Bond, Ph.D.

Conducted volume correction studies and batch studies of resins for an americium/curium separation study under the guidance of Samantha Labb, Ph. D.

Conducted additional gamma spectroscopy analyses on additional samples.

Undergraduate thesis written on the potential post-sequelae syndrome of SARS-COV-2 using literary sources. Defended research to CSU Panel of immunologists earning endorsement for publication in the CSU Undergraduate Research Journal.

Leadership

President for the CSU Health Physics Society Student Chapter 2023-Current
Vice President for the CSU Health Physics Society Student Chapter 2022-2023
Vice President for CSU Neuroscience Student Organization (NSO) 2019 -2020
Member of CSU College of Veterinary Medicine & Biomedical Sciences College Council 2017 – 2020

Skills

Separation interference research in progress
Laboratory operation of survey meters, Geiger-mueller counters, gas-flow proportional counters, sodium-iodide detectors, high purity germanium detectors, alpha spectroscopy, liquid scintillation counters
Radiochemistry techniques including batch studies and column studies
Laboratory maintenance including laboratory surveys, filling HPGe detectors with liquid nitrogen, and inventory management
Analytical chemistry techniques including volume correction studies, titrations, density studies, and pipette calibrations
Assisted in the design and completion of experiments
Computer skills including excel, MS word, Genie 2000, and R

Work History

Graduate Research Assistant 2023 - Current
Los Alamos National Laboratory

Graduate Research Assistant 2022 - Current
Colorado State University

Professional Groom 2021 – 2022
Stave Mill Farm

Dressage Instructor, Professional Groom 2014 – 2023
Raissa Chunko Dressage (Self Employed)

Mathematics & Science Tutor 2016 – 2020

Presentations

"The Effects of Asphalt Debris on Radiochemical Analysis of Plutonium" at Mountain and Plains Education Research Center Research Day, April 4, 2023

"The Effect of Asphalt on Radiochemical Analysis of Plutonium" at the Central Rocky Mountain Chapter of the Health Physic Society Technical Meeting on April 21, 2023

"The Influence of Trace Metals in Asphalt on Plutonium Uptake on Extraction Chromatography Resins" at the Radiobioassay & Radiochemical Measurements Conference on October 31, 2023

"Effects of trace metals found in asphalt on plutonium uptake on extraction chromatography resins" at the College of Veterinary Medicine and Biomedical Sciences Research Day on January 27, 2024

"Effects of Trace Metals found in Asphalt on Plutonium Uptake on Extraction Chromatography Resins" at the Environmental and Radiological Health Sciences Poster Session on February 6, 2024

"Effects of Major Inorganic Constituents of Asphalt on the Rapid Determination of Plutonium" at Thesis Defense on February 23, 2024

"Effects of Major Inorganic Constituents of Asphalt on the Rapid Determination of Plutonium" at Tsukuba University on March 18, 2024

"Effects of Trace Metals found in Asphalt on Plutonium Uptake on Extraction Chromatography Resins" at the Mountain and Plains Education Research Cener on April 4, 2024

"Major Inorganic Constituents of Asphalt Influences on the Rapid Determination of Plutonium" at the Central Rocky Mountain Chapter of the Health Physic Society Technical Meeting on April 25, 2024

Publications

Newsletter articles for the Health Physics Society, Spring 2023

Volunteer and Community Service

CSU Health Physics Student Chapter – President	2023 - Current
CSU Health Physics Student Chapter – Vice President	2022 - 2023
CSU Neuroscience Student Organization - Vice President	2018 - 2020
College of Veterinary Medicine and Biomedical Sciences Student Council	2017 - 2020
Brain Awareness Week Volunteer	2018 - 2019
Neuroscience Student Organization Tutor	2019
Northern Colorado Dressage Association – Volunteer	2007 - Current
Rocky Mountain Dressage Society Volunteer	2007 - Current
USDF Region 5 Junior/Young Rider Show Elf/Fundraising	2015 – 2020
Salvation Army – Trombonist in Brass Quartet	2018 - 2019
Hearts and Horses Therapeutic Riding Center Volunteer	2014 - 2016