

AN ABSTRACT OF THE THESIS OF

Corrie D. Black for the degree of Master of Science in Radiation Health Physics presented on May 19, 2011.

Title: The Investigation of Dipicolinic Acid Diamide Derivatives for the Separation of Actinides and Lanthanides using Solid Phase Extraction Chromatography

Abstract approved:

Alena Paulenova

An alternative extractant for the TRUEX/UNEX process was investigated in solid phase extraction chromatography. The para and ortho isomers of diamides derivatives of dipicolinic acid (N,N'-diethyl-N,N'-ditolyl-dipicolinamide, EtTDPA) have been found in the past to effectively separate actinides from lanthanides in solvent extraction and were successfully impregnated on two uncoated, inert macroporous polymeric support resin types. The ortho resins consistently yielded higher extractions while the para resin consistently yielded higher Am/Eu separations. These findings were consistent with past solvent extraction experiments and suggest the versatility of these extractants in a variety of applications. The use of complexing agents were also considered both in the eluent and on the resin and found to change the extraction properties of the resin enough to warrant further investigation.

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The Investigation of Dipicolinic Acid Diamide Derivatives for the Separation of
Actinides and Lanthanides using Solid Phase Extraction Chromatography

by

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Corrie D. Black, Author

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I would like to dedicate this work in my Dad's honor,
whose love for science and learning has inspired me.

Chapter 1: Introduction

Hydrometallurgy is the most mature industrial technology applied in spent nuclear fuel processing. This technology is based on partitioning or solvent extraction (SE) method, sometimes also called liquid-liquid extraction, where the separation of the species is achieved through their distribution between two immiscible solutions: aqueous solution, produced by dissolving the used fuel (mostly in nitric acid) and organic solution, containing an extractant dissolved in a suitable diluent. Extractant is an organic compound that forms a complex with the metal of interest, and since this complex is better soluble in the organic phase, the metal is removed from the aqueous to organic phase.

Extraction is already established as the most suitable method for light water reactor waste processing. During the 70-year history of development of separation methods for used nuclear fuel, a variety of extraction methods have been developed. They are based on different molecules of organic extractants and different conditions of distribution experiments, and their extraction performance has been studied in different diluents and various sizes of separatory funnels in laboratories, or on an industrial scale with different agitating setups such as mixer-settlers, centrifugal contactors, pulse columns or spray columns. The development toward separations of desired radionuclides from used nuclear fuel was followed by the development of separation methods of heavy and toxic metals, synthesis of new extractants and special diluents.

Alternative partitioning techniques involve immobilizing the liquid organic extraction phase onto a solid phase, for example, by impregnating a suitable support material (macroporous resin, porous membranes or hollow fibers) with the extraction organic compound. These methods involve two immiscible liquid phases, and have analogical selectivity toward desired metals and analogical dependence on the pH or acid concentration conditions as it was observed in a bulk solvent extraction setup. These new extraction materials offer a great opportunity for automation and minimization of the process and designing new or modernized separation technologies. Especially, the rapid and small scale separation methods have a potential application in a variety of sectors, including the medical radionuclides generators, the on-site environmental monitoring, nuclear forensics, development of radiochemical sensors, and fast laboratory methods for separation of radionuclides from the sample matrix prior to radiodetection.

In this thesis work, the opportunity to utilize the extraction properties of the diamides of dipicolinic acids in SPE for the separation of the trivalent minor actinides from the lanthanides was studied. Diamides of dipicolinic acids have been previously synthesized and investigated in our laboratory, and they proved themselves to be powerful extractants for this group of elements. The goal of this project was to investigate the application of the ortho isomer of N,N'-diethyl-N,N'-ditolyl-dipicolinamide [Et(o)TDPA] on a chromatographic resin and to determine the optimal conditions needed to provide an enhanced separation of americium (representing

trivalent actinides) from europium (representing trivalent lanthanides). The trivalent actinides and lanthanides are chemically very similar; it is what makes this research on separating these nuclides so challenging.

This thesis has five parts. In the beginning, an overview of spent nuclear fuel and reprocessing will be presented, followed by a more detailed description of solvent extraction and chromatography extraction in the background section. The literature review will encompass current chromatography techniques and the latest research in the diamides used for radionuclide separations, as well as the application of other diamides of dipicolinic acid that has been used in chromatography. A description of the impregnation of two different polymeric resins with the diamides of dipicolinic acid commonly employed in extraction chromatography are included in the Experimental section. Batch experiments with these resins were conducted to examine multiple variables such as nitric acid concentration and contact time to determine the optimal conditions needed for chromatography.

The last part of the thesis reports the results from the batch experiments to demonstrate the effectiveness of each condition tested. These data are discussed in comparison with the actual column chromatography trials conducted for this project. With the aim to enhance the separation of americium and europium, different conditions of elution were applied. It was concluded that the effectiveness of extraction chromatography with a resin loaded with N,N'-diethyl-N,N'-ditolyl-

dipicolinamides is comparable with the liquid extraction with these extractants as well as with other extraction chromatography resins.

Chapter 2: Background

It is estimated that the energy requirements to sustain mankind's lifestyle are going to nearly double by 2050². The great potential that nuclear energy holds in supplying the world's growing energy requirements has been established. This has been confirmed by recent advancements and expansion in nuclear reactor facilities worldwide. Irradiated nuclear fuel is a byproduct of the nuclear power industry, and is usually simply called "nuclear waste." This name is actually incorrect since it contains radioisotopes that are all rare chemical elements which instead of being disposed of should be separated from the used fuel and individually used in various applications such as in medicine (e.g., Sr-90), technological (e.g., Tc) applications or as reactor fuel (for example, Pu in mixed oxide fuel) to produce more energy.

Separating these radionuclides enhances the efficiency of nuclear power both by utilizing byproducts produced during fission and by addressing the hazardous waste issue. The safe handling and disposal of used fuel and irradiated reactor materials results in additional challenges associated with nuclear energy production, while also hindering the public's favor of this alternative energy source. Therefore, highly efficient and cost effective measures must be taken to reduce and contain the radiotoxicity of spent nuclear fuel and maximize energy production from the finite fuel reserves.

Commercial nuclear power first became available in 1957 in the United States. It grew through the 1970's into the 103 pressurized water and boiling water

reactors in operation today on 65 different sites³. The composition of irradiated fuel varies with reactor type but in general a 1,000 MW Pressurized Water Reactor (PWR) will produce 3.76E3 Ci/year of radioactive waste¹. In 2001 it was estimated that the United States has generated 45,000 MTHM (metric tons of heavy metal) of spent nuclear fuel in addition to the 380,000 m³ of HLW left over from the Manhattan Project³.

2.1 Nuclear Waste

Depending on the type, activity level and lifespan of the radionuclide constituents, radioactive waste has been classified into different categories, from VLLW waste (very low level) to high-level waste (HLW) with intervening low-level (LLW) and intermediate-level waste (ILW). It is said to be long-lived when its lifespan exceeds 30 years, as opposed to short-lived if the reverse applies.² Ninety percent of used nuclear fuel consists of short-lived radionuclides and is of minimal risk. This “low-level waste” (LLW) is often disposed of in near-surface facilities where it is monitored until nearly all of its activity reaches natural background levels. The other 10% of radioactive waste is considered “high-level waste” (HLW) as it is highly radioactive, capable of causing ill health effects to an exposed population. For example, after ten years, a spent fuel assembly is capable of giving a 10,000 rem/hour dose to someone directly exposed.⁴ Another concern with HLW is that many of its constituents are soluble in water; therefore if they were to end up in

ground water or some other natural water source, they may easily reach the food supply. Though the source may be diluted, it could cause radiation doses to the general public. In the United States, these radionuclides are left in the fuel elements containing the other 90% of LLW with the used fuel retained in secure interim storage sites. No permanent disposal method has been established in the USA. However, most countries consider some type of geological repository as the primary option.⁵ Geological repositories can store radioactive material adequately, but require extensive effort to ensure containment in addition to stringent security requirements. Therefore, it is of interest to condense the HLW into smaller amounts (volumes) to improve the efficiency of nuclear waste repositories.⁶

The most obvious way to reduce the volume of the spent nuclear fuel is to sort the radionuclides into respective groups based on their radiotoxicity. Most approaches group the spent fuel constituents in three categories: residual fuel, HLW, and LLW. The residual fuel is uranium and plutonium that can be recovered and reused in new fuel (known as mixed oxide fuel). Low-level waste consists mostly of short-lived gamma and beta-emitting fission products (FP) and thus presents a low-to-medium-level nuisance that becomes negligible after 300 years (10 half-lives) and long-lived low-level waste that are both the long-lived fission products with a specific activity level less than or equal to 3,700 Bq/g after 300 years and the alpha-emitters at 370 Bq/g or less at the end of the monitoring period (300 years).¹ LLW originates from nuclear facilities (gloves, filters, resins, etc), research laboratories and medical

and industrial users of radionuclides. It is predicted that by 2020 its volume will reach about 90% of the total radioactive waste volume.¹

The radionuclides of most concern in HLW originate in spent-fuel and include the transuranic elements as they are the alpha emitters and long-lived fission products (Tc-99, I-129, Cs-135, Zr-93, etc.) and also the short lived fission products (~30 y) Cs-137 and Sr-90 as they can be present in higher concentrations and are much more radioactive than the long-lived radionuclides. Hence, used nuclear fuel is anything but waste. Separation of the radionuclides that contribute to the high activity of HLW by their partitioning based on their individual characteristics and potential use reduces the amount and radiotoxicity of HLW. Additionally, reprocessing also recovers significant energy value from the used fuel by manufacturing and using mixed oxide fuel. For example, it is estimated if the uranium and plutonium stored currently in spent fuel around the United States was converted into new fuel, it could run all the U.S. reactors at 100 GWe for almost 30 years without any new uranium⁷. Hence, reprocessing is necessary if nuclear energy sustainability is to be achieved.

In view of the future energy needs and the potential solution nuclear power holds, the United States formed the Global Nuclear Energy Partnership (GNEP) in 2006. The International Atomic Energy Agency (IAEA), European Union, and Russia contributed input and the program sought to unite multiple nations in a program that encouraged nuclear growth while discouraging the proliferation of nuclear

weapons. This program today has grown into the International Framework for Nuclear Energy Cooperation, for which the USA's effort is currently called the Fuel Cycle Research and Development program (FCR&D). There are currently 25 participating countries. The initiative seeks to reverse the tone set in 1977 that associated the chemical reprocessing of irradiated nuclear fuel with proliferation. This tone was set in the United States when President Carter banned nuclear fuel reprocessing in fear of nuclear proliferation. The perspective of the FCR&D is that reprocessing actually promotes global security by reducing the HLW that is left in storage. Current goals of FCR&D include improving reprocessing technologies to be used to separate transuranic elements, excluding the isolation of plutonium, and developing advanced fast burner reactors capable of converting the transuranic elements into energy and less radiotoxic elements.

Various national and international research groups (FCR&D, EUROPART, ect) around the world (USA, France, Germany, UK, Japan, Russia, South Korea) are actively seeking improved radiochemical separation technologies that would aid in the development of programs that would not only minimize the HLW volume, but could eliminate it.⁸ This approach, known as "P&T" (Partitioning and Transmutation program)⁹ involves using separation techniques to isolate the HLW (the "Partitioning step") and then placing it in a fast neutron reactor to transmute the long-lived radionuclides into stable or shorter-lived elements (the "Transmutation" step). The minor actinides must be partitioned or separated from the lanthanides and fission

products before transmutation because they are present at much lower concentrations. Additionally, the lanthanides and fission products, if left with the HLW, will act as neutron poisons, preventing the fission or neutron capture of the minor actinides¹⁰ in the recycled batch of nuclear fuel. Therefore, advanced separation methods are needed to process these nuclides into respective groups.

2.2 Radionuclide Separation Methods

The original radiochemical separation method utilized during the Manhattan Project was a precipitation method using bismuth phosphate as a carrier that isolated Pu. This process was operated on a large scale in Oak Ridge and Hanford in the 1940's, but has significant disadvantages. Hence, the research was focused on development of a separation technology capable of also recovering uranium. Partitioning methods, based on distribution equilibrium of species between two immiscible liquids, aqueous and organic phase, have been extensively investigated since then. One of the first successful extraction methods invented in the early 1950's is the PUREX process, and it is today the most used separation process worldwide.

PUREX stands for **P**lутonium **U**ranium **R**ecovery by **E**xtraction. As the name implies, PUREX separates uranium and plutonium from a nitric acid solution using tributyl phosphate (TBP) in a N-alkane diluent¹. This extraction process separates tetra- and hexavalent actinides (Pu, U) leaving the trivalent actinides (Am, Cm) and fission

products (Cs, Sr, etc) in the aqueous phase (raffinate). Technetium and iodine are also coextracted during this process. The reprocessing technology based on PUREX has long been used as part of the commercial Mixed Oxide (MOX) fuel business. For example, in France and the UK, the PUREX process has been adopted as a commercial reprocessing procedure to supply MOX fuels to domestic and foreign nuclear reactors that are able to use MOX fuel as part of the reactor core.

Another option for nuclear waste processing is the pyrochemical method, which uses electrochemical techniques instead of chemical equilibrium of distribution of metal between aqueous and organic solutions. The separation of actinides is based on their high temperature redox reactions in non-aqueous media (chloride or fluoride salt melts). These methods use the differences in the volatilities or stabilities of complexes of actinides and fission products. This research started in the Oak Ridge National Laboratory about 50 years ago, and recently obtained a significant research interest with the progress and development of the high neutron flux reactor design.

In an effort to avoid nuclear proliferation by preventing the isolation of plutonium, advanced processing methods are being developed by several countries (France, UK, Russia, Japan, USA, South Korea, etc.). A modified PUREX process, also known as UREX¹¹, was developed at Argonne National Laboratory, and it also utilizes TBP diluted with n-dodecane for the extraction of actinides from fission products; however, by using acetohydroxamic acid to strip plutonium together with partially

extracted neptunium from the organic phase, only uranium and technetium are actually separated from the other fission products and transuranic elements in this innovative technology.

Also an extraction series, known as “UREX+”, it was proposed to achieve a maximal recovery of metals from the irradiated fuel dissolved in nitric acid¹². This series consists of several extractions combined in an order to provide stepwise isolation of cesium and strontium, actinides, and the fission products¹³. It starts with UREX (**U**ranium **E**xtraction, isolating U, Tc, and I), followed by FPEX (**F**ission **P**roduct **E**xtraction, isolating Cs and Sr), and then TRUEX (**T**ransuranic **E**xtraction, isolating Am and Cm). TRUEX uses CMPO to separate the lanthanides and actinides from the fission products. TALSPEAK was developed to separate the lanthanides from the actinides and it uses di(2-ethylhexyl)phosphoric acid (HDEHP). All these extraction steps utilize organophosphorous extractants: TBP in UREX, CMPO in TRUEX, and HDEHP in TALSPEAK. These compounds leave salts as undesirable residual waste in the extraction phases. Hence, development went into extraction compounds that could replace the organophosphorous compounds in spent fuel reprocessing. As they should consist only of carbon, hydrogen, oxygen, and nitrogen (approach known as the “CHON principle”), thereby are easily incinerated, producing less secondary waste¹⁴. One process, based on compounds following the CHON principle is DIAMEX, which uses malonamides to extract the lanthanides and actinides¹⁵.

2.2.1 Separation by the Solvent Extraction

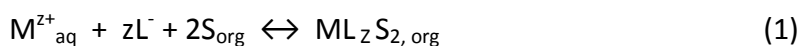
Since the late 1940's, nearly all radionuclide separation techniques that have been used are based on partitioning between two immiscible liquids (water/organics) or solid/liquid phases. Typically, the aqueous phase contains the dissolved species of interest while an organic phase contains the extractant molecule (organic solvent) dispersed in a more or less inert diluent. In the case of spent nuclear fuel processing, the irradiated fuel is typically dissolved in the aqueous solution of nitric acid.

Extractants are the organic molecules interacting with metals by forming the coordination metal-organic complexes. Extractants can be less selective (less specific) toward the targeted metal or class of metals, like, for example, tributylphosphate which extracts almost all known metals (under varying conditions) or very selective, for example crowns (dicyclohexano-18-crown-6 for Sr).

After the two phases are contacted, the metal-extractant complexes are formed on their interface. The extractant molecules are hydrophobic, therefore, their metal complexes are also much more soluble in the organic phase. Because of different solubility, the complexed metals are partitioned from aqueous phase to organic phase. When the maximal concentration of metal in organic phase is achieved, the system is in equilibrium and two phases can be split. Solvent extraction can be optimized by varying the conditions in both the aqueous and organic phases. Additionally, the liquid-liquid extraction is a straightforward technique for

investigation of fundamental characteristics and mechanism of partitioning equilibrium and kinetics of the separation process.

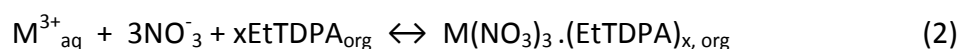
Most of extraction mechanisms can be qualified as solvation, chelation or an ion exchange¹⁰. The complexing mechanism is based on the type of functional groups and structure of the extractant molecule. During ion exchange, the ionic associates are formed, for example, tetralkylammonium salts with technetium (Aliquat). While the 2-thenoyltrifluoroacetone (TTA) or di-2-ethylhexylphosphoric acid (D2EHPA) are typical chelators, TBP or CMPO are typical neutral solvent extractants. They interact with metals by the solvent extraction mechanism, forming neutral solvent adducts (“solvates”) which are removed from aqueous phase (interface) to organic phase because of their better solubility in organic diluent. As the extracted molecule must be neutral, the change of metal cation is compensated with anion from the aqueous phase. In general, it can be described by this reaction:



where z is the charge of metal cation, L is a monovalent ligand (for example, nitrate or chloride) and S is the extracting solvent, diluted by an inert diluent (alkane, benzene, etc.). Typically, two molecules of solvent (TBP or CMPO) are coordinated around the central metal cation, forming a neutral solvate complex.

Diamides of dipicolinic acid, such as EtTDPA investigated in this project, are also neutral solvate extractants; however, unlikely to TBP or CMPO, they form their

metal solvates with 1-2 molecules of EtTDPA. While the divalent uranyl forms the solvate with just one molecule of EtTDPA, tetravalent Pu needs 2 molecules of EtTDPA, and trivalent Am forms both the mono- and di-solvate adducts with EtTDPA. This extraction mechanism can be represented by the following reaction:



where M^{3+} represents a trivalent metal being extracted, and $x \approx 1.5$ is the average number of EtTDPA in the solvate molecule.

When the extraction equilibrium is established, it can be quantified by the “distribution ratio”, which is the ratio of the analytical (total) concentrations of metal in the organic phase and in the aqueous phase, as it is expressed by Equation 2:

$$D = \frac{[M(NO_3)_3 \cdot (EtTDPA)]_{x,org}}{[M^{3+}]_{aq}} \quad (3)$$

D is a measure of the efficiency of extraction; it is bound with the extracted fraction of metal (Y, extraction yield) and volumes of the organic (V_{org}) and aqueous (V_{Aq}) phase by Equation 4:

$$Y = \frac{D \cdot \frac{V_{org}}{V_{aq}}}{1 + D \cdot \frac{V_{org}}{V_{aq}}} \quad (4)$$

Once the distribution equilibrium is established, the two phases are split, and the complexed and uncomplexed fractions of metal are physically separated from each other. The ratio of the distribution ratios for two metals defines their separation factor (SF) under the same given conditions (extractant, diluent, acid concentration, temperature, contacting time, etc):

$$SF_{Am/Eu} = \frac{D_{(Am)}}{D_{(Eu)}} \quad (5)$$

This is a measure of the efficiency with which the metals may be separated from each other. The separation can be enhanced through repeated solvent extraction steps. The distribution coefficient is highly dependent on variables such as the acidity of the aqueous phase, the aqueous and organic solvents used, the type and concentration of the extractant ligand, the temperature, and the contact time. Research toward selective and efficient separation processes is focused on optimization of these process parameters and synthesis of new more efficient and selective extractants.

2.2.2 Other Applications of Partitioning Methods

Partitioning separation methods can be modified by immobilizing the liquid organic extraction phase. There are a few resins where functional groups are covalently bound to a chain of a polymer; for example, a chelating resin based on phthalic acid-resorcinol-formaldehyde (PFR)¹⁶. Much more frequently, a suitable porous polymer material is impregnated with the extraction organic phase. The impregnated materials have the same extraction selectivity and very similar

dependence on the pH or acid concentration conditions as the bulk solvent extraction methods. Porous membranes or hollow fibers impregnated with a desired extraction organic compound lead to utilization of the membrane techniques for the industrial waste-water processes with maximal recycling of the recovered uni- and polyvalent metals and water. Hybrid processes, designed by combining the solid-support method with classical methods, are applied for purifying of chemical substances on a large scale.

While the impregnated hollow fibers are mostly used in flow-through separation membrane modules¹⁷, the macroporous resins saturated with almost any organic extraction compound are utilized in the newly designed or innovated methods like selective sorption (solid phase extraction, SPE), ion exchange and extraction chromatography (EC). Separations with extraction resins are elegant and clean methods that also offer a great opportunity for minimization of separation steps and development of rapid methods for the on-site radioenvironmental monitoring, nuclear forensics, and generators of medical radionuclides where the waste-volume-minimized separation and preconcentration techniques are necessary. When automated and coupled with liquid scintillation counting (LSC) or spectroscopic methods, they meet the requirements for continuous monitoring systems, ensuring the promptness and accuracy of the industrial process control. This approach is also very important for development of radiochemical sensors, and fast analytical

methods for separation of radionuclides from the sample matrix and preparation of liquid scintillation counting (LSC) samples or targets for alpha spectroscopy.

Radiochemical analysis with selective extractive resins, being procedurally simplified, produce less secondary low level waste (gloves, pipettes, vials, ect.) and require lower amounts of reagents thus potentially making it more economical. Additionally, reducing the manipulation with a liquid organic phase (practically an open radioactive source) minimizes the opportunity of accidental spills and personal exposures.

2.2.2a Extraction Resins

Like the solvent extraction, the separations with extraction resins involve two immiscible liquid phases,¹⁸ with the organic phase held as a “stationary phase”, either dispersed in macroporous solid support phase or coating a solid particles. The aqueous phase is the “mobile phase” that moves around and through the stationary phase” (see Figure 1).

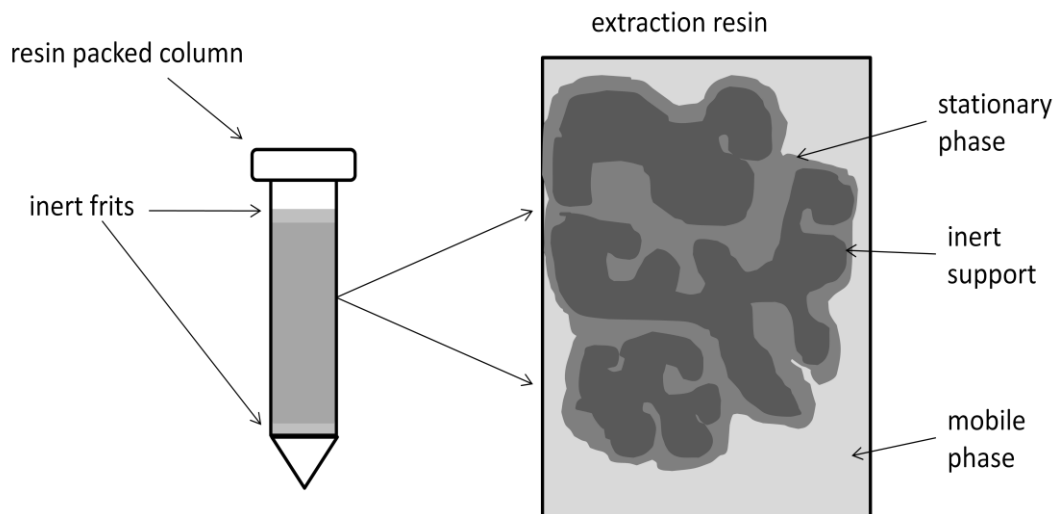


Figure 1: The extraction resin packed between two frits in a small column (“resin bed”, left) and the stationary phase impregnated onto an inert support (right)

Preparation of an extraction-functionalized solid material by impregnation of an organic extraction phase requires a carefully selected combination of the support resin and extraction organic phase. Silanized silica gel has been used in the past for the inert support but in the last twenty years macroporous polymer beads have become popular.¹⁹ This is primarily due to their high surface area which allows more sites for metal binding. The polymethacrylate (PMA) and polystyrene-divinylbenzene (PS-DVB) resins are common macroporous beads utilized in extraction chromatography. Typical size of resin beads are of 50-150 μm in diameter, with a 4-9 nm pore size, 0.6-1.1 cm^3/g pore volume, and a specific area of 150-900 m^2/g .¹⁸⁻²⁰ These characteristics provide a strong, rigid structure, and minimal solvent swelling of the resin when impregnated with the organic extractant or during application of

the resin with aqueous solutions of different acid concentrations. The extractant is held to the support through the weak, attractive forces, as opposed to covalent bonds. The attractive forces are usually between alkyl chains and/or aromatic rings on the ligand and the support.

The batch experiment involves contacting a known mass of impregnated resin with a known volume of an aqueous phase, spiked with a studied radiotracer or other metal. The phases are thoroughly agitated until the solute distribution equilibrium is achieved. The final concentration of the analyzed metal in the supernatant (aqueous phase) is determined utilizing the best possible method that fits the nature of studied metal or radionuclide. Both the radiodetection or chemical analytical methods are applicable.

The difference between the initial and final concentrations of the analyte in aqueous phase represents the amount of the analyte sorbed by the stationary phase (resin). K_D can then be determined with Equation 6:

$$K_D = \frac{C_{solid}}{C_{aqueous}} = \frac{A_0 - A}{A} \times \frac{V}{m_R} \quad (6)$$

where A_0 is the initial and A the final (equilibrium) activity of the radiotracer in the aqueous solution contacted with the resin, V is the volume of aqueous phase (mL) and m_R is the mass of the resin (g); hence, K_D has a unit of mL/g.

The extraction performance of an extraction resin is similar to the solvent extraction with the same extractant molecule and follows the same acid type and concentration dependence. Therefore, batch tests are useful for predicting the efficiency of a chromatography separation and selecting the mobile phases that should be utilized in extraction chromatography.

Many successful solvent extractants have been utilized as a stationary extraction phase for different metals; a short selection is listed in Table 1. Selective extraction resins can be used in radionuclide separation alone or in combination with other resin in a tandem column set up.

Table 1: Selection of extractants successfully utilized in commercial resins ¹⁰

EXTRACTANT	Metal [Ref.]
CMPO (Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide)	Actinides [35]
TBP (Tributylphosphate)	U, Pu, Np [36]
HDEHP (Di(2-ethyl)phosphoric acid)	Actinides [37]
Quaternary amine(s)	Np, Am, Tc [38-41]
TODGA (N,N,N', N'- tetraoctyl-3-oxapentane-1,5-diamide)	Th, U [42]
Crown ethers (dicyclohexano-18 crown-6)	Sr [43]

The large pores of resin, coated with the stationary phase, accommodate the organic complex formed with the desired metal that is then held in the resin until a suitable effluent solution is applied for elution of the metal, now separated from the other metals or from the sample matrix in general. Obviously, like in solvent extraction, the metal can be separated alone (for example, Sr with crown) or in a group (for example, actinides versus lanthanides). The loading and elution procedures, selection of effluent solutions, their order and concentration are developed mostly in batch experiments which are then converted into a column separation setup. These separations are applied prior to the bench-top radiodetection methods, especially when dry targets should be prepared for alpha-spectroscopy. However, column separations can be applied in online analyzes when utilized as prepacked cartridges with autosamplers. For example, microextraction by packed sorbent (MEPS) is a miniaturized solid phase extraction technique for the purification and concentration water sample of different origin (or plasma), and other samples prior to analysis by techniques such as high performance liquid chromatography. Cartridges with prepacked reverse phase (hydrophobized silica with C-8 or C-18 hydrocarbon chain) resins are routinely installed with an autosampler before injection into HPLC columns.

Extraction chromatography is capable of receiving samples through a collection line, while passing the species of interest along into a flow-through detector. These systems are small and portable, just ideal for the automation of the

microanalytical procedures that require a rapid separation method. The flow injection analyzers, flow-through LSC counters and phoswich detectors are the best candidates for such applications.

2.2.2b Extraction Chromatography

Extraction chromatography (EC) is known for combining the selectivity of solvent extraction with the eases of column chromatography^{10,19}. The method is often favored because of its simplicity in operation, fast recovery of separated species, and conservation of reagents.

The extraction chromatography column, where the separation takes place, is composed of extraction resin packed between two frits inside a glass column or plastic tube.^{10,19,20} The selective extraction of species from the loading solution is achieved by their binding with the molecule of organic extractant in the stationary phase as it is shown in Figure 1. The aqueous phase is the “mobile phase” that moves in a single direction around and through the stationary phase. There are always at least two aqueous mobile phases: one is the loading solution (sample matrix, soil digest, etc.) which passes through the column first, leaving species bound to stationary phase in the column. The second mobile phase is the effluent, whose role is to elute (remove) the desired species from the resin. Elution is a separation step analogical to stripping of species from the loaded organic phase in the solvent extraction. For example, in UREX, both uranium and plutonium are extracted to TBP,

and then Pu is stripped with a fresh aqueous phase (acetohydroxamic acid solution) while uranium is not. Analogically, the column is loaded with a mixture of metals, found in analyzed sample, and while some of them pass through the column unbound, the desired metal (or a group of metals) is bound to the resin in column. Hence, the selection of a correct resin is very important, and it is why the research into new resins is of great interest.

In the second step, a fresh mobile phase (aqueous effluent) is applied for selective stripping of metals bound to resin in the first step. Sometimes, it depends on the chemistry of the sample matrix; a short rinsing of the column (i.e. “scrubbing” in solvent extraction terminology) must be applied to prepare the column for the elution step. Chemical mechanism of elution is also similar to stripping – the appropriate mobile phase is selected accordingly to the distribution ratio data, collected either from the batch experiment with this resin, or from the solvent extraction experiments with this specific extractant in the stationary phase.

The aqueous solution that provides the smallest distribution ratio for the desired pair of extractant and metal is the correct effluent to apply. For example, if the distribution ratio (measured either in SE or SPE setup) increases with the nitric acid concentration, then the metal should be loaded in a higher concentration and eluted with a solution with a low concentration of acid.

In most cases, metals are removed from the loading solution as a group of metals with similar extractability with the stationary phase; therefore, their

separation can be achieved only with selective stripping when the effluent contains complexing ligand. Applying this principle to the example above, when both Pu and U are loaded to a TBP resin means: while they both will be eluted with a low concentration of nitric acid, an effluent based on acetohydroxamic acid should strip only Pu, leaving U in the column.

A chromatogram (elution profile) is a plot of the concentration of the analyte (activity of a desired radionuclide in our case) as a function of either the elution volume or elution time. If a constant flow rate is adjusted, both ways of plotting are identical. The elution of the analyte is indicated by the growth of the concentration peak (band) in the chromatogram. An example of a chromatogram is displayed in Figure 2. The volume units in the chromatogram can be expressed either in mL or in units of the free column volume (FCV), also called a column “void volume” (V_0), “hold-up volume” or “mobile phase volume” (V_m). All these names mean the same – it is the total volume of the mobile phase within the active part of the column at one time. It is the fraction of the resin bed volume that is filled by a mobile phase liquid (or air if the column has not been used yet), between and inside the resin beads.

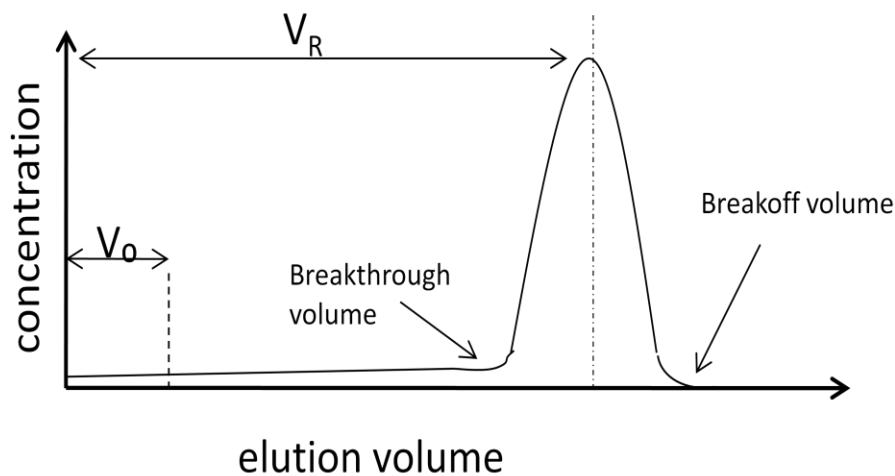


Figure 2: Typical chromatograph and components of elution profile: void volume (V_0), retention volume (V_R), and the breakthrough and break-off volumes

The “breakthrough volume” is the volume of mobile phase that passes through the column before the analyte elution starts. The “retention volume” (V_R) is the volume of mobile phase corresponding to the maximal concentration of the analyte (top of the peak in the chromatogram). The “break-off” volume is the volume that has passed through the column to completely elute the analyte from the column. The peak between the breakthrough and break-off volumes makes up the elution band for a particular solute (analyte). Ideally, this peak should be narrow and without tailing to avoid cross contamination with adjacent solutes being eluted as the next. The factors that affect the width of this peak include the chemical environment (extractant and effluent), loading with extractant, stability of resin (i.e., leaking of

extractant form resin), bead size, porosity and pore diameter, temperature, and the velocity of the mobile phase.¹⁰

The selectivity of a column method towards one analyte (A) versus another analyte (B) is expressed by the term “separation factor” (SF). Analogically to solvent extraction, where the separation factor is the ratio of distribution coefficients (D) for two analytes (A, B) under the same conditions (Equation 7a), the separation factor for two analytes in extraction chromatography (EC) is defined as the ratio of their retention factors, k' , or retention volumes (Equation 7b):

$$SF_{SE} = \frac{D(A)}{D(B)} \quad (a) \qquad SF_{EC} = \frac{k(A)}{k(B)} = \frac{V_{R,A}}{V_{R,B}} \quad (b) \quad (7)$$

The k' value is defined as the number of free column volumes necessary to reach the retention volume V_R ; hence, for the same column this value becomes a ratio of the retention volumes. Obviously, one can expect the same separation factors measured in the solvent extraction and extraction chromatography setup, because the retention factors and distribution ratios are related through the ratio of the stationary (V_S) and mobile phase (V_m) volumes in the resin bed. The mass of the resin bed m_R and the weight distribution ratio K_D can be used to determine the retention factor k' :¹⁰

$$k' = K_D \times \frac{m_R}{V_m} \quad (a) \qquad \text{or} \qquad k' = D \times \frac{V_S}{V_m} \quad (b) \quad (8)$$

Logically, both the equations 8a and 8b are analogs of each other; however, the attempts to compare the relative extractabilities of metals in the liquid-liquid and chromatographic systems must take into account the differences in the extractant concentrations in these two systems.

Chapter 3: Literature Review

Various diamide compounds have been considered for the replacement of CMPO in the TRUEX and UNEX (SE) processes. These compounds are consistent with the “CHON principle” and have proven to effectively complex americium. Various types have included malonic diamides, tetra alkyl diglycolamides, and diamides of dipicolinic acid (DPA or sometimes also PDA) ²¹. However, no significant extractability of americium with the tetra alkyl-diamides was found. ^{22,23} One of the most effective diamides found thus far have been the dialkyldiaryl diamides of dipicolinic acid as illustrated in Figure 3 ^{24,25}.

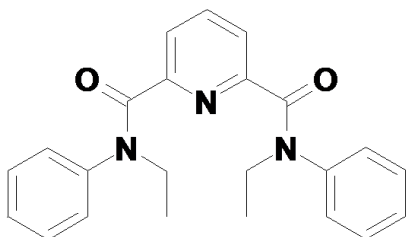


Figure 3: Chemical structure of a dialkyldiaryl-diamide derivative of dipicolinic acid

Of these compounds, the N,N'-diethyl-N,N'-ditolyl-diamide of dipicolinic acid (EtTDPA) shows much better extraction yields for americium than europium. ²¹ These results suggest that this compound could potentially replace CMPO in the UNEX process by separating americium from europium. They also suggest that these extractants may be useful in chromatography extraction when developing a rapid separation method for the trivalent minor actinides and trivalent lanthanides.

3.1 Soft-Hard Acid-Base Theory

The separation of the transuranium elements from the lanthanides is challenging because the physical and chemical properties are very similar between the two groups. This greatly limits the methods that may be used for separation. A slight difference between the groups lies in the fact that lanthanides have electrons filling the 4f orbital, while actinides have electrons filling the 5f orbital. The expanded electron shell in the actinides provides a degree of covalency and polarizability that has been used to extract the actinides from the lanthanides with the actinides being slightly “softer” electron acceptors.

The term “soft donor/acceptor” comes from the hard-soft acid base theory. It establishes a qualitative system for classifying elements and molecules as either “hard” or “soft.” Elements with large ionization energies are considered hard and therefore have a large gap between the highest occupied electron orbital and the lowest unoccupied electron orbital. Soft elements have a small gap between frontier electron orbitals and therefore require smaller amounts of energy to be ionized. Generally, the f-block elements including lanthanides and actinides are considered hard acids. However, in comparison, the lanthanides are considered “harder” and actinides are considered “softer.”

The elements within the hard-soft classifications follow trends in electronegativity, polarizability, size, and charge. These trends support binding

between hard/soft acids and bases as hard acids bind to hard bases and soft acids bind to soft bases. In general, hard acids have low electronegativity, small size, high charge, and a slightly polarizable electron cloud which binds well with hard bases that contain very high electronegativity, small size, and a similar stiff electron cloud. Soft acids and bases pose intermediate electronegativities, large size, low charge, and a polarizable electron cloud prone more towards covalent bonding. Therefore, in relation to lanthanides, actinides tend to be soft acceptors and in comparison to oxygen, nitrogen tends to be a soft donor. This phenomenon is the basis for the N-containing amides used in these extraction experiments, which should favor the trivalent Am over the trivalent lanthanides.

3.2 Soft Donor Ligands

Actinides and lanthanides are classified as Lewis acids. Therefore, they accept electron pairs, binding well with Lewis bases. The extractants proving to provide the most extractability towards americium have been classified as “soft Lewis bases.” This is because of the pyridine nitrogen and the two amide groups (Figure 3) are thought to attract the “softer” actinide elements over the “harder” lanthanide elements^{14,21,26}. Additionally, the tridentate binding socket on the extractant is ideal for complexing trivalent metals, making it ideal for the trivalent actinides.

3.2.1 EtDPA Isomers

Previous experiments done with EtTDPA have found that the three structural isomers of EtTDPA (ortho, meta, and para) have varying extraction efficiencies^{27, 28}. The structural differences are based on the position of the methyl group attached to the tolyl ring. The structures of these three isomers are shown in Figure 4.

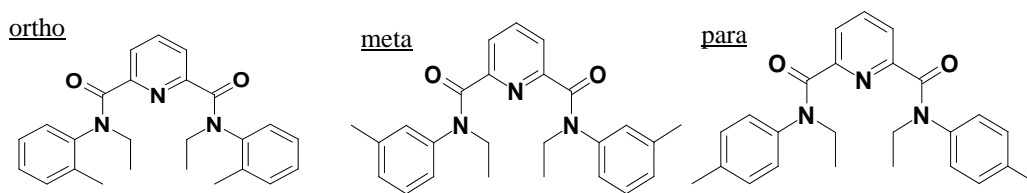


Figure 4: The structures of the three EtTDPA isomers: Et(ortho)TDPA, Et(meta)TDPA, and Et(para)TDPA

Solvent extraction experiments with these three isomers in a trifluoromethylphenyl sulfone (FS-13) diluent found extraction trends of ortho > meta > para and separation trends of meta > ortho > para. With 3 M HNO₃, distribution ratios were found to be 22, 18, and 13 for the ortho, meta, and para extractants. Separation factors were found to be 3.6, 3.3, and 3.0 for the meta, ortho, and para extractants. These extractants were found to show reasonable thermal and radiolytic stability. Thermal degradation was found at 180°C, 200°C, and 220°C for the meta, ortho, and para isomers respectively²⁹. Mass spectra of these compounds found that the ortho isomer shows the most hydrolysis stability, while consistently yielding higher degrees of extraction in harsh environments testing their radiolysis and hydrolysis stability³⁰.

3.2.2 Diamides in Solid Phase Extraction

Et(p)TDPA has been applied to a solid phase extraction system where the support was in the form of a fibrous polyacrylonitrile disc rather than polymer beads placed in a column³¹. The diamide was impregnated onto the woven fiber disc using a wet method (1.2 g/g) and used in batch extraction experiments for separation of Am and Eu. This research group³¹ has found that the contact time did not greatly affect the degree of recovery of any of the radionuclides. In 4 M HNO₃, 83% of Am was retained on the disc. There was substantial evidence that this method could be useful for separation of Am from Eu, as the distribution ratio K_D values of 67 and 1 were obtained, yielding a SF of 67.

Watanabe et al.³² impregnated PS-DVB (XAD 4) resin with four different DPA compounds using the dry method. They were concerned about the extractant leaking off the resin during separation; therefore, they chose diamides with longer alkyl chain lengths (butyl, octyl, decyl, and dodecyl) and sought to determine their effects on resin stability. It was found that indeed higher nitric acid concentrations caused the extractant to leak more and their data suggested that the longer alkyl chain lengths supported the retention of the extractant on the resin. At 3M HNO₃ they found the K_D to be 4.8 for Am and 0.4 for Eu. At the same pH, they also obtain the following SF: 5.3 (Bu-PDA), 6.9 (Octyl-DPA), 8.1 (Decyl-DPA), and 3.1 (Dodecyl-DPA).

Cowan and Shaw³³⁻³⁴ successfully applied both the dipicolinic acid³³ and the 4-chlorodipicolinic acid³⁴ as a stationary phase on the polystyrene-divinylbenzene

support resin to the high efficiency isocratic separation of transition and heavy metal ions. Their results illustrated the increased loading and selectivity of this chlorinated chelating molecule in comparison with unsubstituted dipicolinic acid, exemplified by the separation of 7 metals in fewer than 8 min.

3.3 Project Goals

With all the effort put towards the reprocessing of nuclear waste on large scale, there will be also a need for the development of the “process control” methods, i.e., further separation methods capable of pre-concentrating and isolating radionuclides of interest so the large scale separation lines may be routinely analyzed and supervised.⁴⁶⁻⁴⁸ The development of a monitoring process methods for nuclear waste processing facilities requires a system that can both identify and quantify alpha and beta emitting radionuclides that is highly accurate, reliable, and capable of giving onsite, immediate results.⁴⁶ Therefore, it is of interest to design rapid and effective separation techniques that can easily be automated and converted into a relatively small monitoring device that can be held near the shielded large scale radiochemical reprocessing line where it will serve for a routine and immediate process monitoring. Ideally, this system would be capable of receiving separated waste samples from a processing line, then simultaneously separate and pre-concentrate both the alpha and beta emitting nuclides individually so they may be continuously or periodically injected into an online flow-through detector. The pre-concentration of the

monitored nuclides using solid phase extraction resins promotes the sensitivity of the radiodetection because it removes other interfering nuclides or species present in the matrix while also increasing the signal.

The goal of this project was to prepare a resin functionalized with diamides of dipicolinic acid and investigate its behavior in the batch and extraction chromatography separation experiments. Since the para isomer has been already used in a filter solid-phase extraction filters,³¹ we utilized the ortho-isomer of the ethyltolyl diamide dipicolinate Et(o)TDPA as a stationary phase in the support resin; however, we also have prepared resins with the para-isomer of EtTDPA, for comparison of their extraction behavior and evaluation of the role of the position of the methyl group on the tolyl ring. To achieve a better, more stable impregnation of the diamides into support, two types of support resin were utilized: aromatic (polystyrene divinylbenzene; PS-DVB) and non-aromatic (polymethacrylate; PMA).

Batch experiments were conducted under a variety of the concentration and agitation time conditions. Considering the solvent extraction data obtained previously by our group,²⁷⁻²⁹ the concentration of nitric acid in aqueous solutions varied from 0.5 to 5 M, the resin and analyzed solutions were contacted from 0-24 hours, and the temperature in the laboratory of 22°C was relatively constant. These parameters helped to design the column experiment and optimize the separation of Am from Eu in extraction chromatography with the diamide-dipicolinate resins.

Chapter 4: *Experimental Design*

4.1 Reagents and Supplies

The synthesis and purification of the EtTDPA isomers was performed by J. Lapka, a member of our research group^{14,27,29}. Other chemicals used in the project, such as nitric acid, methanol, sodium acetate, and trisodium citrate, were of reagent grade purity [J.T. Baker].

The concentrations of the nitric acid and citrate solutions were justified by potentiometric titration using an automated titrator (DL58 by Mettler Toledo).

4.2. Resin Impregnation

The macroporous support resins utilized for impregnation with diamides were polymethacrylate [PMA] resin with the bead size of 100-150 μm (Prefilter Resin by Eichrom, IL) and the polystyrene divinylbenzene [PS-DVB] with the 75-150 μm size beads (Stratospheres of Aldrich Chemical Company).

A dry method⁴⁴ was utilized to impregnate EtTDPA onto the two resins. Methanol was used to first dissolve a predetermined amount of EtTDPA, and then a known amount of resin was added to the solution. The solution was left in an open beaker and gently swirled for several minutes ensuring thorough mixing. It was then left overnight to evaporate the methanol. The dryness of the impregnated resin was checked by weighing the resin continuously until its weight did not change (over

several days). The resins were stored in sealed glass vials until they were utilized in either a batch or column experiment. The optimum amount of EtDPA was experimentally determined by preparing resins with various ratios of EtDPA: inert resin and then comparing their K_D values measured in batch experiments.

4.3 Resin Characterization

The volume of the extraction resin in the column is just a fraction of the resin bed volume (Figure 1), and can be calculated (Equation 9) from the mass of resin placed into the column, divided by the density of the extraction resin (ρ_R):

$$V_R = \frac{m_R}{\rho_R} \quad (9)$$

With this aim, the density of the impregnated resin (ρ_R) should be determined pycnometrically first. This was done by weighing an empty 5 mL pycnometer (m_p), then with resin (m_{p+R}), and finally, filled up with deionized water (m_{p+R+H_2O}). The density of water (tabulated for the measured ambient temperature) and the difference in mass with and without water were then used to calculate the density of the impregnated resin (ρ_R):

$$\rho_R = \frac{m_R}{V_R} = \frac{m_{p+R} - m_p}{\frac{1}{\rho_{H_2O}} \times (m_{p+R+H_2O} - m_{p+R})} \quad (10)$$

4.4. Batch Experiments

Each batch experiment used 50 mg of resin and 1 mL of aqueous phase. Nitric acid concentrations ranging from 0.5-5 M was used as the aqueous phase. Am-241 and Eu-154 radiotracers were individually added to spike the aqueous phase prior to agitation with the resin. An additional vial was prepared with no resin so that the original activity in the aqueous phase could be accurately counted and used as a reference for determining the amount adsorbed onto the stationary phase. The vials were vortexed for five minutes and then shaken on a platform rocker for a desired time. The contact time varied from 5 minutes up to 24 hours to investigate the kinetics of solid phase extraction. In the end of agitation, the aqueous aliquots were taken and counted along with the reference (initial) activity sample. The measured activities were used in Equation 4 to determine the weight distribution ratio (K_D). The resin properties (shown in Table 2) were experimentally determined and used along with the measured K_D values to evaluate the retention factor k' (Equations 6-8). All experiments were done at room temperature ($\sim 22^\circ\text{C}$).

4.5. Column Experiments

4.5.1 Resin Packing

The impregnated resins were packed into plastic 2-mL columns supplied by Eichrom. These columns had an inner diameter of 0.8 cm and contained frits that

were placed on either end of the resin bed. Column chromatography experiments were prepared by slurry packing the impregnated resins into plastic columns. This was done by adding 0.5M HNO_3 to 0.2 g of resin and pouring the mixture into the column while gently swirling and tapping the column so that the resin packed evenly and air bubbles came out. Additional nitric acid was used to wash residual resin off the side of the column. Gravitational or gentle syringe pressure was used to push the nitric acid through the resin. Once drained, a frit was placed on the top of the resin and used to gently compress the resin into a further packed state. Before adding a radiotracer spike, the resin was conditioned with one milliliter of more concentrated nitric acid (actual concentration determined through batch experiments).

4.5.2 Void Volume Determination

The void volume of the column (also called a “hold up” volume) was estimated with an experiment that used tritiated water as a spike (250 μL) in a column (200 mg of para-EtTDPA/PMA resin) conditioned with regular deionized water. It was assumed that the tritiated water had zero or insignificant retention on the resin. Therefore the breakthrough volume of tritium was assumed to be the column void volume. Once the radiotracer was added to the column, regular deionized water was used as an eluent. 50 μL elution fractions were collected in a separate LSC vial each. 5 mL of a special tritium liquid scintillation cocktail (Parkard-

Monophase S) was added and counted using the TriCarb 3180 LSC counted (Perkin Elmer).

4.5.3. Extraction Chromatography

After the conditioning solvent fully eluted, the Am or Eu spike was added, followed by an additional half milliliter of the same nitric acid used to condition. Most column experiments done considered Am and Eu individually to simplify counting. After loading, approximately one void volume of an effluent was added repeatedly to the column and collected in separate sample vials. The activity of each elution sample was then counted. Their count rates were compared to a reference spiked solution (of equal value to the initial activity added in each column) to determine a fraction of metal eluted. Elution curves were created by plotting the fraction eluted versus the number of void volumes of eluent passed through the column. The fraction of the analyte (activity of either Eu or Am) retained on the column is calculated as the count rate of the reference spike sample (CR_{spike}) minus the count rate of the sample, divided by the count rate of the spike. Therefore the fraction eluted is just one minus the fraction retained on the column as shown in equation 11.

$$\text{Fraction Retained} = \frac{CR_{\text{loaded}} - CR_{\text{eluted}}}{CR_{\text{loaded}}} \quad (11)$$

$$\text{Fraction Eluted} = 1 - \frac{CR_{\text{loaded}} - CR_{\text{eluted}}}{CR_{\text{loaded}}} \quad (12)$$

4.6 Radiodetection

Both the batch and column effluent samples were collected and counted in the 2-mL screw cap tubes supplied by Axygen Scientific. Tritium was counted with the Parkard-Monophase S scintillation cocktail using a TriCarb 3180 (Perkin Elmer) liquid scintillation counter.

Am and Eu were quantified using a Packard Cobra II auto gamma counter. The counting windows were centered on 59 KeV (for Am-241) and 123 KeV (for Eu-154). In each case the analyzed samples were compared to a reference or initial spike activity therefore there was no necessity to include the detection efficiency values into calculations.

4.7 Experimental Uncertainty

The accuracy of all the data collected was limited by both the systematic and random errors. Careful and consistent lab practices were used to minimize random error. A quantitative estimation of the error was performed to correct for systematic errors and is included in Appendix 1. The systematic errors result from uncertainties of the tabulated constants or other the same, systematically used parameters affecting the accuracy of the obtained results, such as the calibration of pipettes or balances. For each contributing uncertainty, error propagation calculations were done for each individual data point. Example uncertainty calculations are shown below:

Count Rate Uncertainty: $\sigma_{count\ rate} = \frac{\sqrt{count\ rate}}{count\ time}$ (13)

K_D Uncertainty: $\sigma_{K_D} = K_D \sqrt{\frac{\sigma_{CRsample}^2}{CR_{Sample}} + \frac{\sigma_{spike-sample}^{*2}}{CR_{Spike} - CR_{Sample}} + \frac{\sigma_v^2}{V} + \frac{\sigma_w^2}{W}}$ (14)

Fraction Eluted (f.e.) Uncertainty:

$$\sigma_{f.e.} = f.e. \sqrt{\frac{\sigma_{spike-sample}^{*2}}{CR_{Spike} - CR_{Sample}} + \frac{\sigma_{CRspike}^2}{CR_{Spike}^2}} \quad (15)$$

*Uncertainty associated with the count rate difference between the spike and the sample:

$$\sigma_{spike-sample} = \sqrt{\sigma_{CRspike}^2 + \sigma_{CRsample}^2} \quad (16)$$

Chapter 5: *Discussion of Results*

5.1 Preparation and Characterization of Resin

The para isomer of Et(p)TDPA and the polymethacrylate resin PMA were selected for this experiment. The resins impregnated with 5 different amounts of extractant were dried and then used in the batch experiment with the radiotracer Am-241 to determine the best loading ratio (mass of extractant to mass of resin, g/g). These results are displayed in Figure 5, showing the americium distribution ratio as a function of acidity in the aqueous solution for 5 resin loading ratios. Analogically to the solvent extraction with these diamides, the extractability of americium increases with increasing concentration of nitric acid. As to be expected, when no extractant was added to the support resin, no extraction occurred. The values of distribution ratio first increase with the extractant: resin loading ratio; however, the increased nitric acid concentration causes an instability of the loaded resin. When the resin with the 4:1 ratio is contacted with 3M and more concentrated nitric acid, its extraction performance stops to rise and stays at about a constant number ($K_D=60$ mL/g). Similarly, the growth of extractability with the 3:1 loaded resin breaks at 4M HNO_3 . The resin with 2.5:1 ratio provides similar extraction yields as the resin 3:1 loading ratio; within experimental error, the same values of K_D were measured for these two resins. Based on this result, the impregnation of all the resins used in the following experiments was based on the DPA: support=3:1 loading ratio.

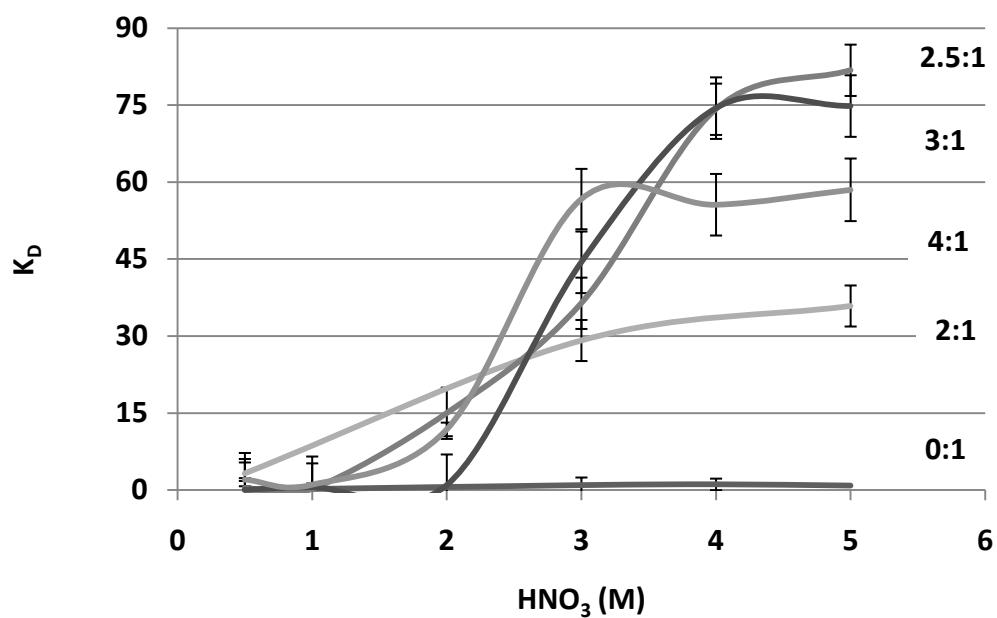


Figure 5: Resin impregnation capacity EtDPA (g) : resin (g)

The densities of each extractant and the extractant impregnated resins were experimentally determined (Equation 10). These results, as well as the extractant loading and bed density are reported in Table 2. These values were used to determine k' and D values based on batch experiment data.

Table 2: Impregnated resin properties experimentally found and used to determine k' and D

Resin support:	PMA		PS-DVB	
Extractant	para	ortho	para	ortho
extractant density (g/mL)	0.75	0.75	0.75	0.75
resin density (g/mL)	0.75	0.73	1.28	1.97
bed density volume	0.45	0.45	0.35	0.35
extractant loading (w/w)	3.00	3.00	3.00	3.00
V_s (mL)	0.27	0.27	0.27	0.27
V_m (mL)	0.17	0.17	0.30	0.30
V_s/V_m	1.55	1.54	0.89	0.89
D conversion factor (m_R/V_s)	4.29	4.29	2.48	2.48
k' conversion factor (V_s/V_m)	6.63	6.61	2.22	2.22
$D = K_D \times m_R / V_s$				
$k' = D \times V_s / V_m$				

5.2 Batch Experiments

5.2.1 Kinetics

Batch experiments were first conducted on the polymethacrylate (PMA) resin impregnated with the ortho isomer [Et(o)TDPA/PMA]. Kinetic trials were conducted for the solid phase extraction of both the Am and Eu radionuclides in five concentrations of nitric acid and 5 agitation times. The results are displayed in Figures 6-7.

These experiments established a baseline for further experiments, while indicating the length of time required to reach extraction equilibrium providing information about the stability of the impregnated resin at various $[\text{HNO}_3]$. For both Am and Eu, extraction increased with both contact time and nitric acid concentration as shown in Figure 6. Kinetic trials were also conducted on the Et(p)TDPA/PMA resin. The results were semi-consistent with the results for Et(o)TDPA/PMA in that extraction efficiency increased with contact time, although it appeared to level off somewhere between one and six hours as shown in Figure 7. While the equilibrium for the resin with the para-EtTDPA was established moderately fast, for the ortho-EtTDPA resin it still had not been established after 24 hours. Additionally, when the agitation time with the Et(o)TDPA/PMA resin was extended for a much longer time (24 hours), the Eu extraction even exceeded the Am extraction in the high nitric acid solution (5 M). It is yet unclear why; but one of possible reasons for increased metal

extraction is the presence of the products of acidic hydrolysis of the diamide in high nitric acid concentration.

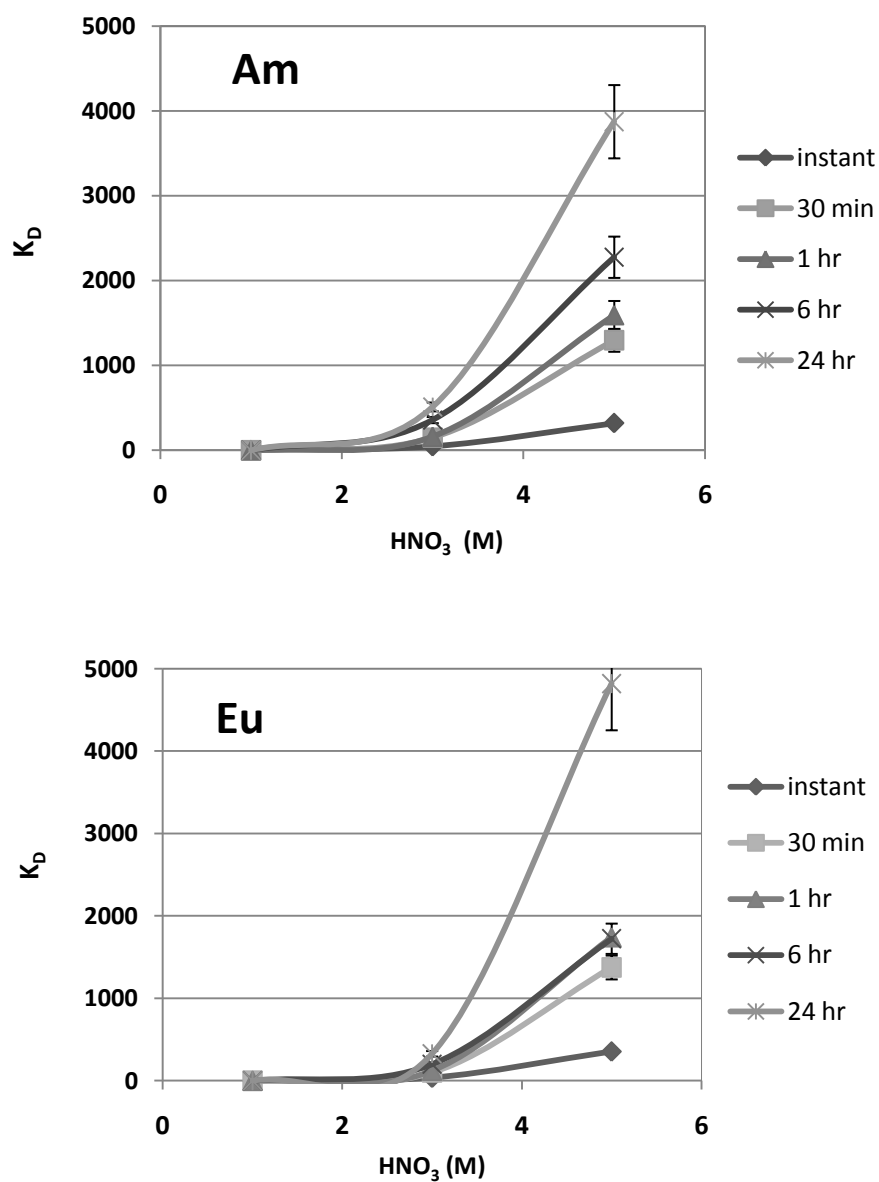


Figure 6: Comparison of Kinetics for Am (top) and Eu (bottom) at various $[\text{HNO}_3]$ with (o)EtDPA/PMA in batch experiment

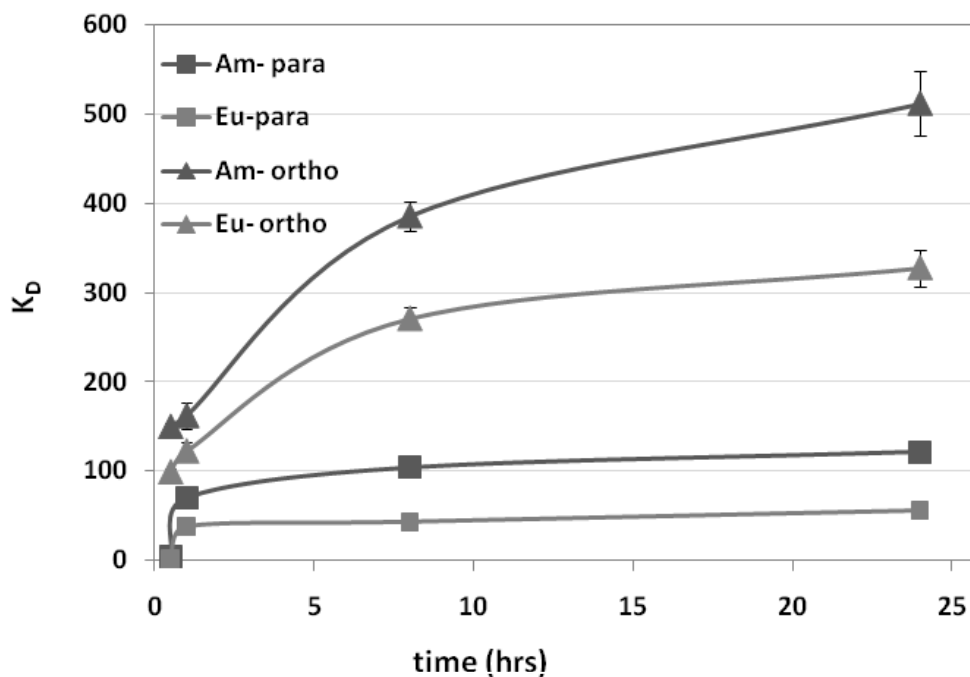


Figure 7: Comparison of kinetics for (o) and (p) EtDPA/PMA in 3 M HNO₃ batch experiment

Table 3 The Am/Eu separation factors for the PMA resin impregnated with ortho and para isomers of EtDPA and 3 M HNO₃

Time [hrs]	SF (Am/Eu)			
	0.5	1	8	24
(p) EtDPA/PMA	2.7 ± 0.2	1.8 ± 0.2	2.4 ± 0.2	2.2 ± 0.2
(o) EtDPA/PMA	1.5 ± 0.2	1.3 ± 0.2	1.4 ± 0.2	1.6 ± 0.2

Even though extraction with the para-EtDPA is lower than with the ortho-EtDPA resin, it consistently prefers Am over Eu, and the equilibrium is established

faster. Table 3 summarizes the separation factors (Am/Eu) for both the para and ortho-EtTDPA resin on PMA-support in 3M HNO₃ batch experiments.

5.2.2 Resin Binding Capacity

The binding capacity of the EtTDPA impregnated polymethacrylate-resin was determined by conducting a batch experiment where the amount of Am added was varied. At lower concentrations, approximately 94% of Am was retained on the Et(p)TDPA/PMA impregnated resin in 3 M HNO₃ aqueous phase. The maximum capacity was found to be ~12,000 cpm/50mg as shown in Figure 8. Since the detection efficiency of the gamma-counter used is known to be 34%, 12,000 cpm is equivalent to 35,294 decays per minute (dpm). Therefore the resin capacity for Am is approximately 1.33 Bq per gram of resin.

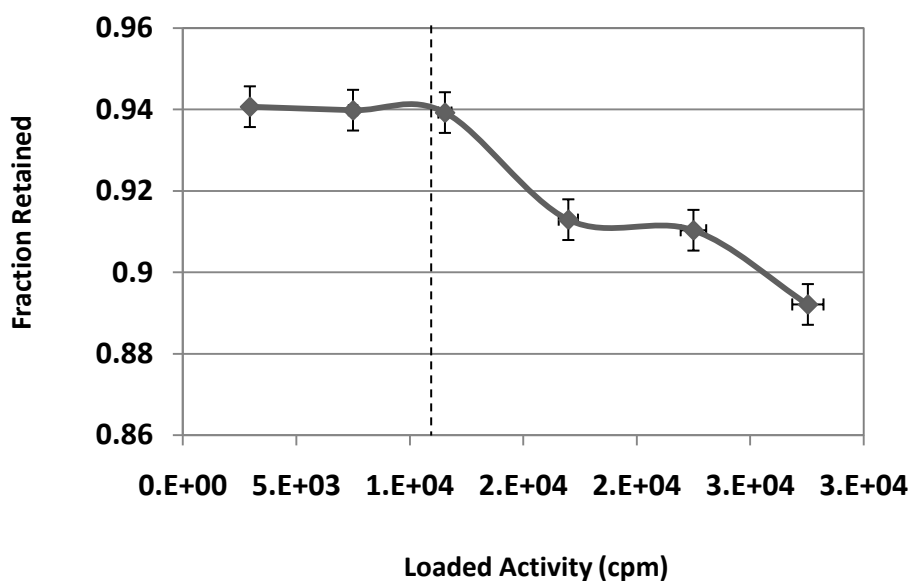


Figure 8: Batch experiment showing resin capacity on the Et(p)TDPA/PMA resin in 3 M HNO₃

5.2.3 Resin Comparison

Both the ortho and para isomers of EtTDPA were impregnated into two types of resin: with an aromatic ring in the polymeric structure (polystyrene divinylbenzene) and without an aromatic ring (polymethacrylate). The reasoning behind this was that the benzene groups that are π -electron donors should hold the diamide to the resin through π - π interactions, and the resin will be more stable against the extractant leaking.

Figure 9 compares the extraction results with the DPA-impregnated PMA and PS-DVB support resins under different conditions of nitric acid concentration after 6 hours contact time. Each resin type showed a preference for Am especially in the moderate nitric acid concentrations.

Generally, extraction increased with nitric acid concentration; appreciable values of distribution ratio were measured starting at 3 M HNO_3 , when both the Et(o)TDPA-loaded resins extract with much higher yields than the Et(p)TDPA-loaded resins. However, at the nitric acid concentration larger than 3 M, the distribution ratio values with the Et(o)TDPA/PS-DVB resin go through a significant maximum at 4 M HNO_3 , while with Et(o)TDPA/PMA they still go up to 10-fold larger numbers. This suggests that the Et(o)TDPA/PS-DVB is the least stable resin in 5 M nitric acid concentrations for prolonged periods of time. More likely, the polystyrene divinylbenzene is more vulnerable in strong acid solutions than the methacrylate,

as the yields with EtTDPA on PMA go up. Results of the batch tests in 3 M HNO_3 are highlighted in Figure 10 and indicate this order of the extraction performance: $\text{Et(o)TDPA/PMA} > \text{Et(o)TDPA/PS-DVB} > \text{Et(p)TDPA/PMA} > \text{Et(p)TDPA/PS-DVB}$.

From the other side, despite the para-isomer of EtTDPA resins showing lower extraction yields, these resins exhibit much higher separation factors than the ortho-isomer. The SF trends found were: $\text{Et(p)TDPA/PMA} > \text{Et(p)TDPA/PS-DVB} > \text{Et(o)TDPA/PMA} > \text{Et(o)TDPA/PS-DVB}$.

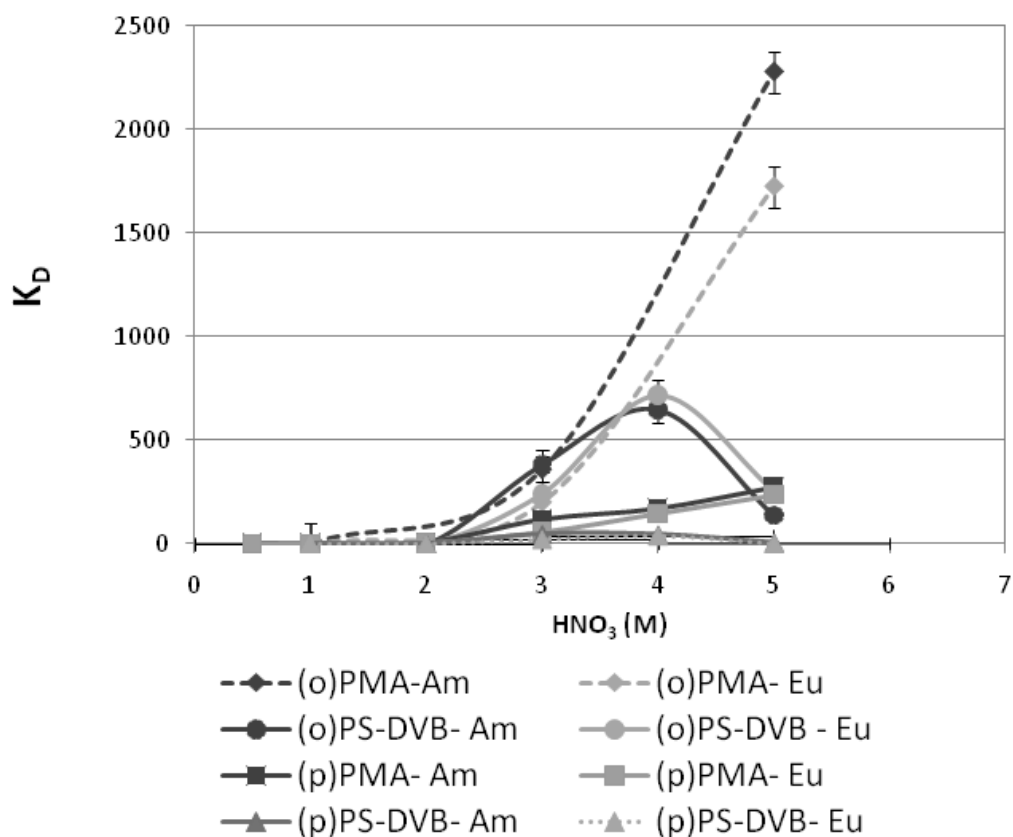


Figure 9: Batch test with the DPA-impregnated PMA and PS-DVB support resins in different nitric acid concentrations

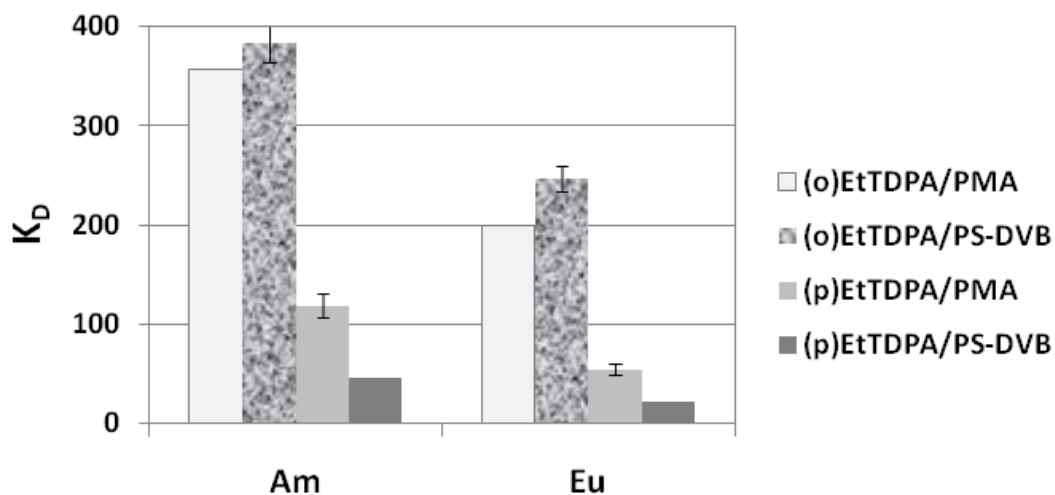


Figure 10: Comparison of two support resins, loaded with both the ortho and para EtTDPA in 3 M HNO_3

Using the experimental K_D values and the resin specific characteristics values from Table 2, both the distribution ratio D and retention factor k' were calculated. The D values for 3 M HNO_3 are listed in Table 4.

Table 4: Distribution ratios for Am and Eu in 3 M HNO_3 for the four resin types and their corresponding SF (Am/Eu)

Stationary phase	D(Am)	D(Eu)	SF(Am/Eu)
(ortho)EtTDPA/PMA	1529	857	1.8
(para)EtTDPA/PMA	509	234	2.2
(ortho)EtTDPA/PS-DVB	950	606	1.5
(para)EtTDPA/PS-DVB	114	54	2.1

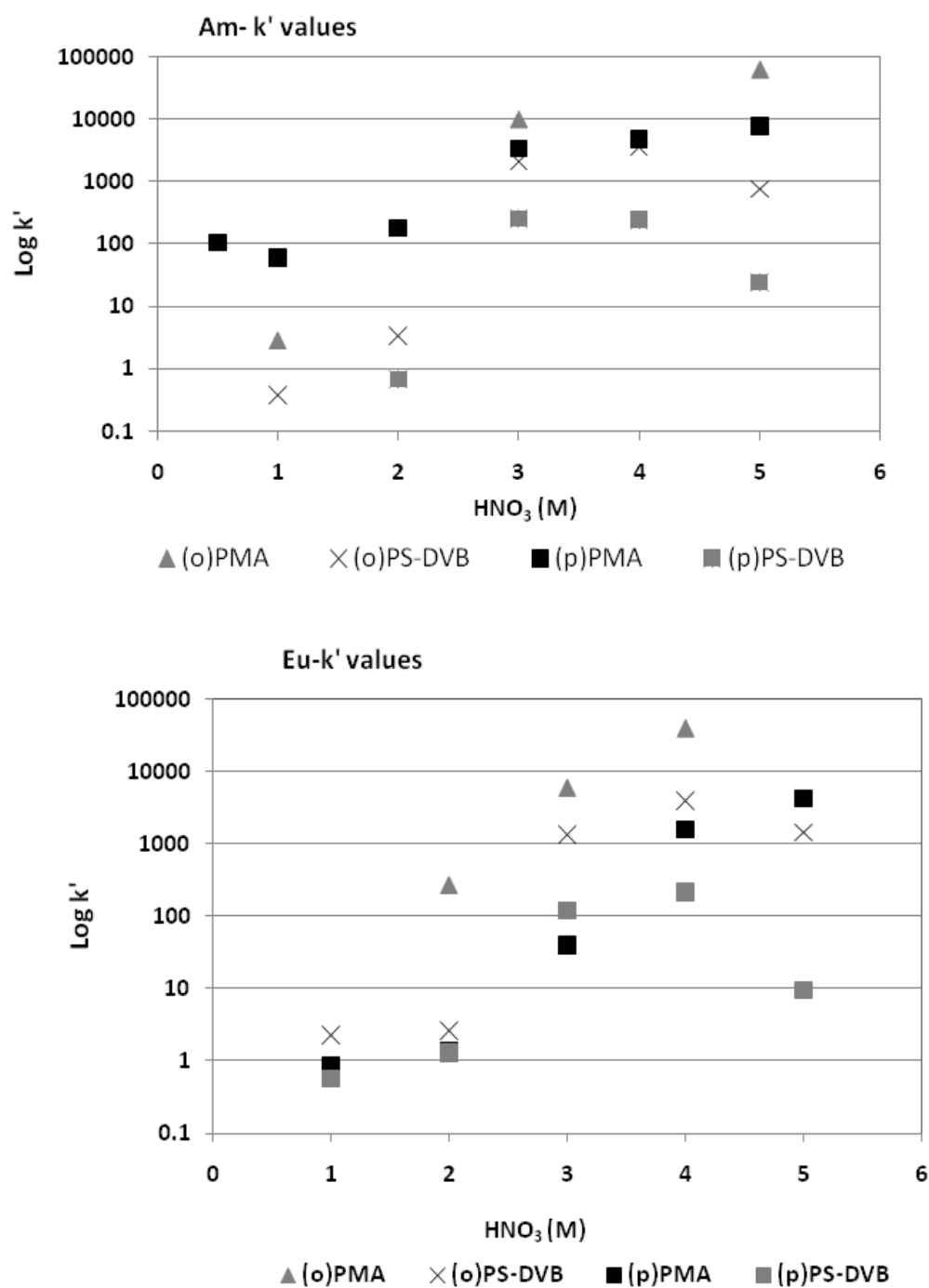


Figure 11: The k' values for Am (top) and Eu (bottom) with different resin type and HNO₃ concentration

The calculated parameters provide supplementary information to the measured K_D values by predicting the resin column retention behavior. Amongst the different resin types, the k' values plotted in Figure 11 suggest that in general, the Et(o)TDPA/PMA resin should yield the highest retention volumes (V_R) for both Am and Eu, and with the Et(p)TDPA/PMA resin the largest difference between k' values and better separation of Am and Eu can be expected.

5.3 Column Experiments

5.3.1 Determination of the Column Void Volume

The columns were packed as described in Chapter 4. For quantification of the elution profiles, the bed volume and free column volume (=void volume=mobile phase volume) have to be determined. Tritiated water was used for this purpose, assuming no significant interaction of water with the resin material; therefore, the breakthrough volume of tritium can be assumed to be equal to the void volume of the particular column being used. The tritium elution curve collected from the LSC counting data is shown in Figure 12.

The void volume determined from this plot was to be near 200-250 μL for a 0.9 mL resin bed volume prepared from 200 mg of Et(p)TDPA/PMA resin. All column experiments (and respective elution curves) evaluations were based on the assumed 250 μL void volume (using 200 mg of resin) despite the slight variations with each resin type and reproducibility of the manual column packing.

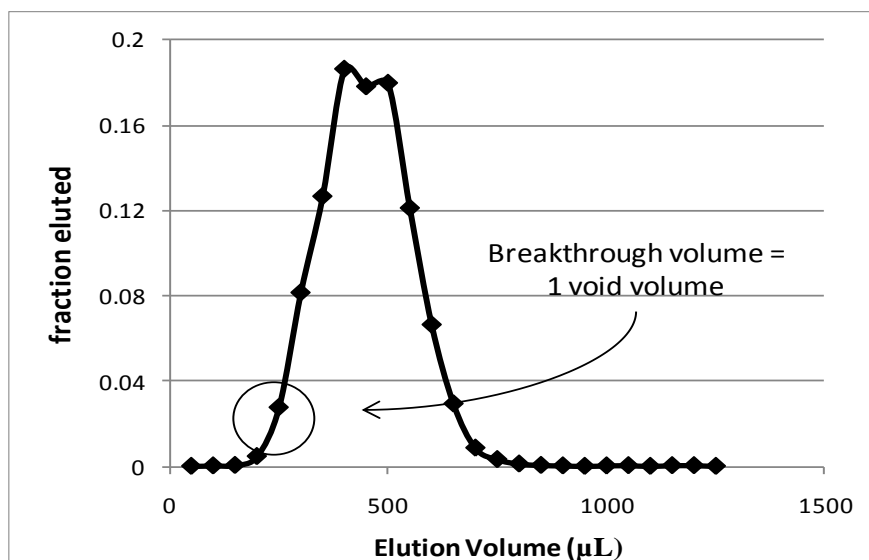


Figure 12: Tritium elution curve indicating the column void volume

5.3.2 Basic Column Tests

Column tests were done with each resin type. The selected conditioning and elution solutions were based on the batch test experimental results. 3 M nitric acid was selected as the optimum conditioner as this concentration enhanced extraction without damaging the resin. Dilute nitric acid (0.5 M) was selected as the effluent. The Am/Eu separation factors were consistent with the batch experiments where the Et(p)TDPA/PMA resin yielded the highest and the Et(o)TDPA resin yielded the lowest separation factor as shown in Figure 13.

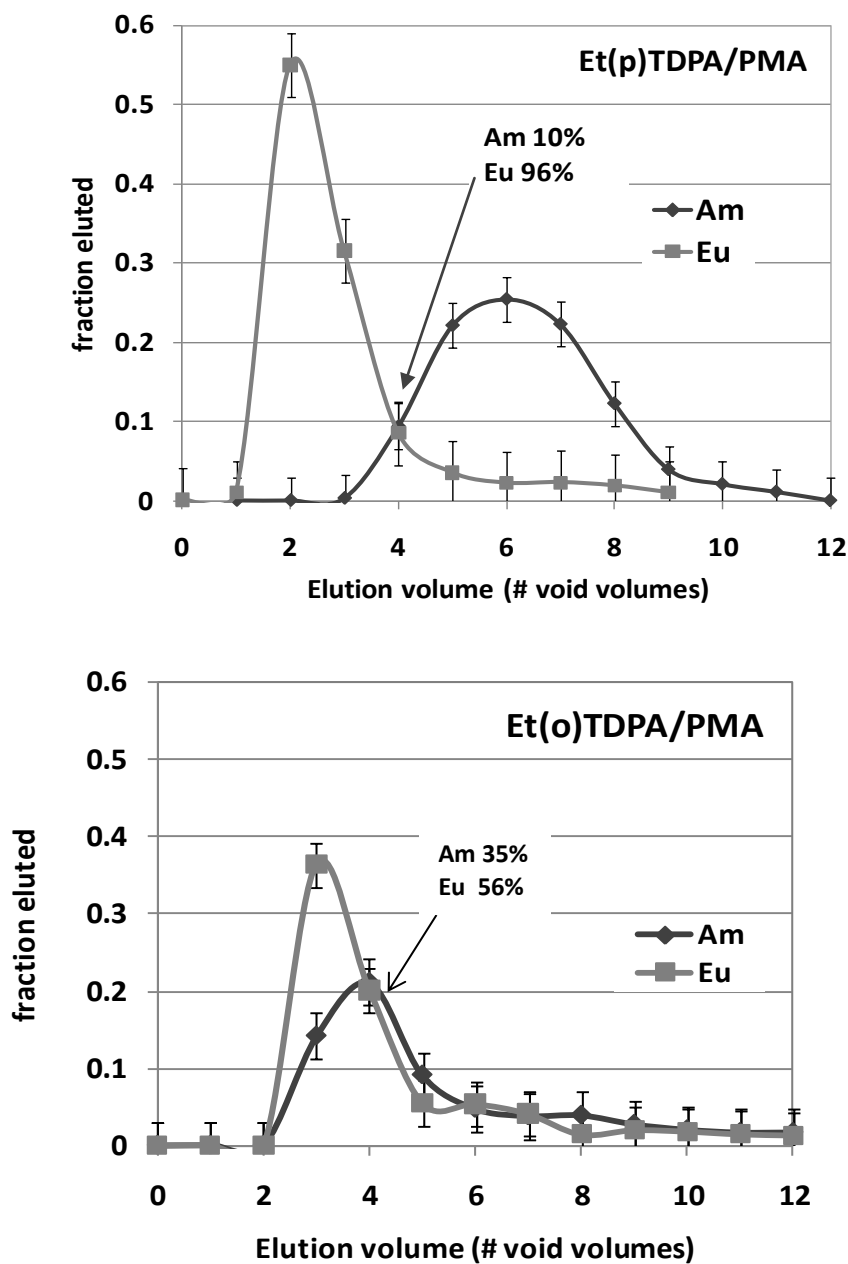


Figure 13: Elution curves for Et(p)TDPA/PMA (top) and Et(o)TDPA/PMA (bottom)

After four void volumes, the Et(p)TDPA/PMA column (Fig. 13, top) eluted only 10% fraction of the Am spike and 96% fraction of the Eu spike, yielding a Eu/Am

separation factor of 9.6. The ortho-isomer, Et(o)TDPA/PMA, yielded only a 1.6 separation factor with 35% of Am being eluted and 56% of Eu being eluted after four void volumes (Fig. 13, bottom). Similarly to batch experiments, the columns packed with resins loaded with ortho-isomers, did not separate Am and Eu well, because they retained both radionuclides. For example, after 12 void volumes, the both Am and Eu were fully eluted from the resins loaded with para-isomer, while the Et(o)TDPA resin still retained some fraction of both metals.

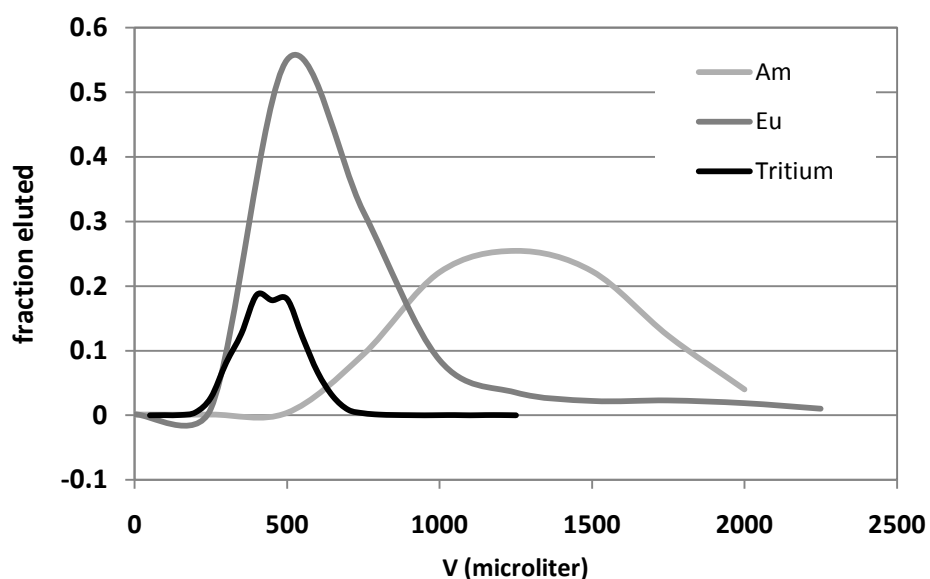


Figure 14: Comparison of the breakthrough volumes for H-3, Eu and Am on the (p)EtTDPA/PMA resin (Loading: 3 M HNO_3 , elution: 0.5 M HNO_3)

Figure 14 shows comparison of three elution curves, collected with the Et(p)TDPA/PMA resin. The elution curves collected for both the Am and Eu with the 0.5 M HNO_3 effluent are inlayed on the elution curve for H-3 eluted with deionized water. The Eu-peak is much higher and larger than the tritium peak, which

corresponds to the higher activity of Eu-152/154 loaded onto column. However, their elution starts at the same effluent volume, so the breakthrough volumes for Eu and H-3 are identical, confirming that Eu can be considered to be minimally complexed by the resin and retained on the column. However, the fact that the Eu peak is wider than the tritium peak indicates that Eu is slightly withheld by the resin.

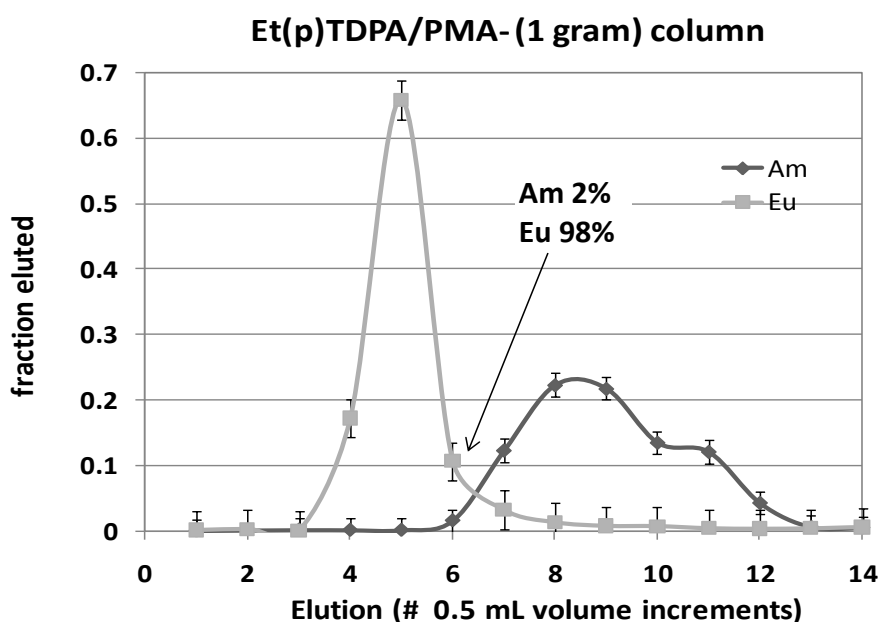


Figure 15: Column test with 1 gram of (p)EtTDPA/PMA resin
Conditioning/loading: 3 M HNO₃; effluent: 0.5 M HNO₃, added by 0.5 mL portions

Although the shift of the Am peak to the right indicates much better retention of Am than Eu, the separation is not ideal. For a better separation, Am should be retained better so that its peak is even farther to the right. Using the same column cartridge (i.e., the same diameter) and resin, Et(p)TDPA/PMA, a larger (longer) column was prepared with 1 gram of resin (versus 0.2 grams used in all other column

tests). Figure 15 shows the elution curve with 0.5 mL of 0.5 M HNO_3 . With a 5-fold increased number of functional groups in the resin bed, the separation improved a little. After adding six 0.5 mL portions of the effluent, 98% of the Eu-spike was found being eluted with only a 2% spillover of Am (5-fold less than in 0.2 g resin). This yielded a separation factor of 47. Note the elution volume represented in this elution curve (Figure 15) is given in number of the 0.5 mL portions of added effluent (or collected eluate).

5.3.3 Optimization of Separation with Complexing Ligands

The goal was to increase the resolution between the Am and Eu peaks by either eluting Eu faster or retaining Am longer. Improvement of separation factors was attempted by the use of oxygen-donor ligands in the effluent to preferentially strip Eu and shorten its elution time. Two complexing ligands (acetate and citrate) are known to bind with rare earth metals; hence, they were tested in an attempt to further increase the Am/Eu separation factors. Elution experiments were performed with two these ligands for comparison to an elution with the initially used effluents containing only the nitric acid of different concentrations. The ligands were applied as the 0.2 M solutions of their sodium salt added to the same nitric acid concentration as used in the reference column.

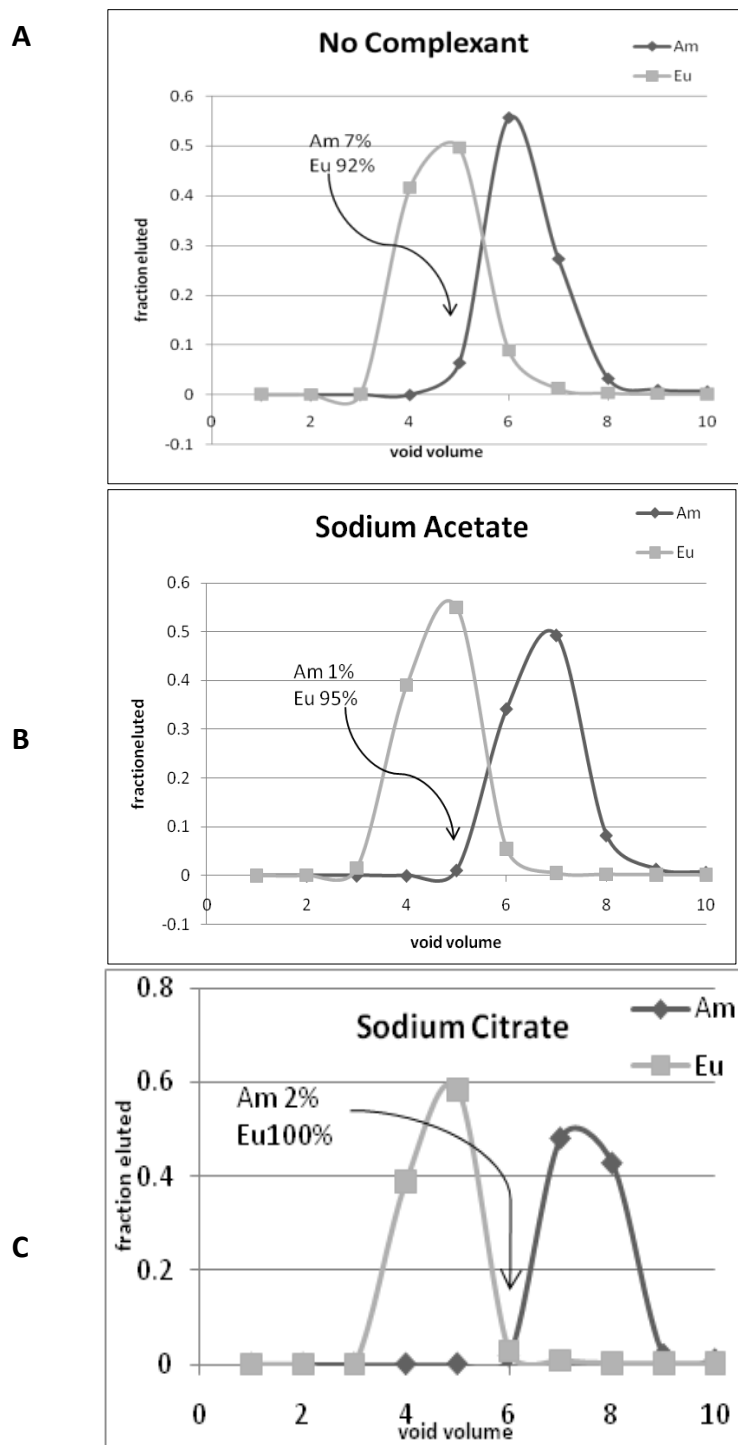


Figure 16: Complexant elution curves while eluting with 0.5 M HNO_3 (A), 0.2 M sodium acetate in 0.5 M HNO_3 (B), and 0.2 M trisodium citrate in 0.5 M HNO_3 (C)

When no ligand was added to the effluent, 92% of Eu was eluted in five void volumes, while only 7% of Am was eluted ($SF \sim 13$). At the same elution volume, the acetate effluent released 1% of Am and 95% of Eu ($SF \sim 95$). After six void volumes, the citrate effluent eluted only 2% of Am and 100% of Eu (50% separation). This provides the best chromatography resolution of the Am and Eu peaks. The elution curves are shown in Figure 16.

5.3.4 Optimization of Separation with a Second Extractant

The degree of separation was further investigated through the addition of a second extractant impregnated with DPA onto the resin. The additional ligand considered was tributyl phosphate (TBP). TBP is the well known extractant used in the PUREX/UREX process. It was combined with DPA and then impregnated onto the polymethacrylate resin. Batch experiments were done using resin made with TBP and the ortho isomer in ratios of 2:1, 1:1, 1:2 respectively.

The interaction of TBP+DPA was analyzed using Fourier transform infrared spectroscopy (FTIR). An FTIR spectrum of TBP, DPA, and the combination of the two in different concentrations is shown in Figure 17. Using results from these experiments, further batch and column experiments were done with both the ortho and para isomer individually combined with TBP. Column tests were conducted using both nitric acid effluents and citric acid effluents.

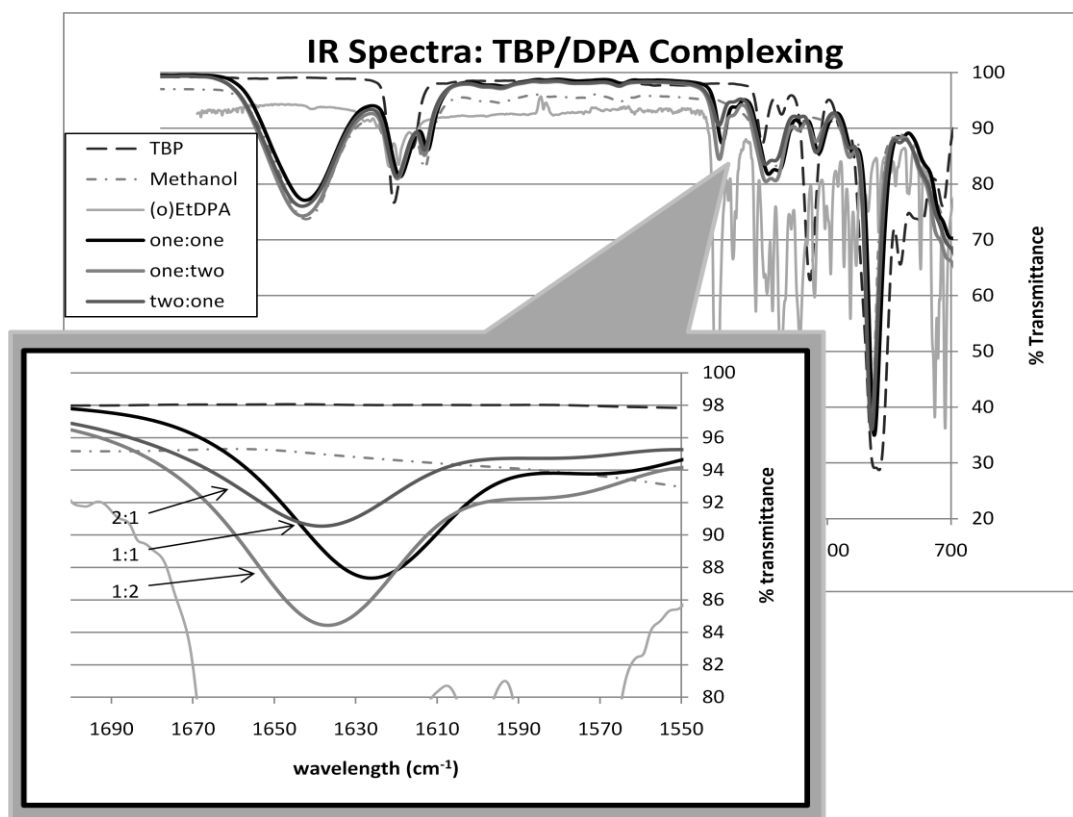


Figure 17: IR spectrum of TBP/Et(o)TDPA at different TBP:DPA ratios (2:1, 1:1, 1:2)

Most of the TBP-DPA spectrum is consistent with pure TBP, pure Et(o)TDPA, or the methanol that they were dissolved in. The different ratios of TBP: Et(o)TDPA affected the shapes and intensities of the bands. For example, around the carbonyl stretch ($\sim 1650 \text{ cm}^{-1}$) of DPA, the intensity of the TBP/Et(o)TDPA bands were in the ratio order $1:2 > 1:1 > 2:1$, accordingly to the decreasing concentration of Et(o)TDPA in the mixture. Batch experiments with PMA resin loaded with these three different TBP: Et(o)TDPA ratio mixtures showed similar trends in extraction. The 1:2 resin

yielded the highest extraction and the 2:1 yielded the lowest extraction, while the separation factors were in the opposite order. Both the extractability and separation factors for the TBP-Et(o)TDPA-PMA resin in 3 M HNO_3 are shown in Table 5.

Even though the extraction was higher with pure Et(o)TDPA than with the combined TBP-EtTDPA, separation was better with the combined extractants. Therefore, further experiments were done with PMA-resin loaded with 1.5:1 TBP: Et(o)TDPA mixture using both the para and ortho EtTDPA. Thirty minute batch experiments with solutions of varying nitric acid concentrations (0.5-5 M) showed that the para-TBP resin only minimally extracted both Am and Eu at each nitric acid concentration tested. As shown in Figure 18, the Et(o)TDPA-resin yielded a much higher extraction yields that increased as the nitric acid concentration increased.

Further batch tests were performed using the Et(o)TDPA-resin at different nitric acid concentrations while increasing the contact time to six hours. The six hour contact time yielded higher separation factors than the same resin used in 30 minute batch tests and pure Et(o)TDPA resin in six hour batch tests. Separation factors of 4, 6, 1.2, 2.6, and 2.6 for 1, 2, 3, 4, and 5 M HNO_3 respectively were found for the TBP-Et(o)TDPA-PMA resin. Despite higher separation power, the addition of TBP to the resin appeared to reduce extraction efficiency. This is shown in Figure 19, where the six hour batch test results are shown for both the pure Et(o)TDPA-PMA resin and the TBP-Et(o)TDPA-PMA resin.

Table 5: Distribution Ratios and Separation Factors for the TBP-Et(o)TDPA-PMA resin with 3 M HNO_3 after 30 minute batch test

TBP : Et(o)TDPA	1:2	1:1	2:1
$K_D(\text{Am})$	150 ± 2	47 ± 2	18 ± 2
$K_D(\text{Eu})$	126 ± 2	28 ± 2	9 ± 1
SF(Am/Eu)	1.2	1.7	2 ± 0.5

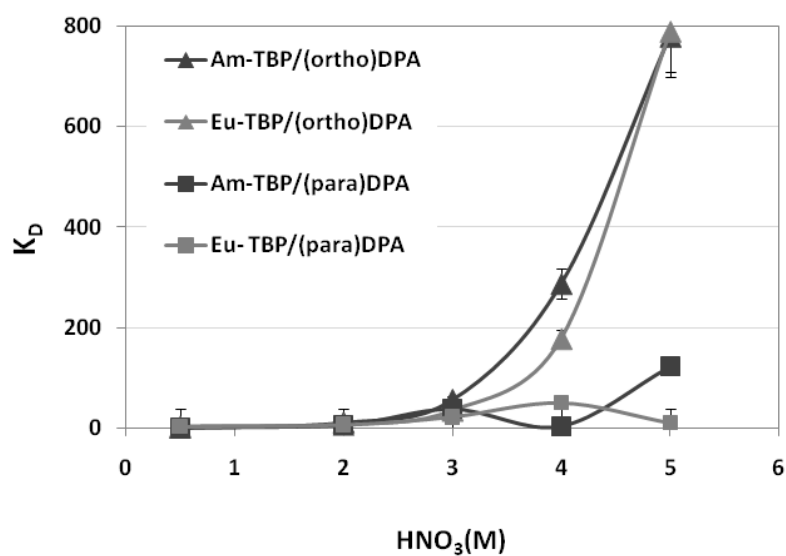


Figure18: TBP/EtTDPA isomer variation: thirty minute batch tests with the para and ortho isomers combined with TBP (PMA resin) at different acidities

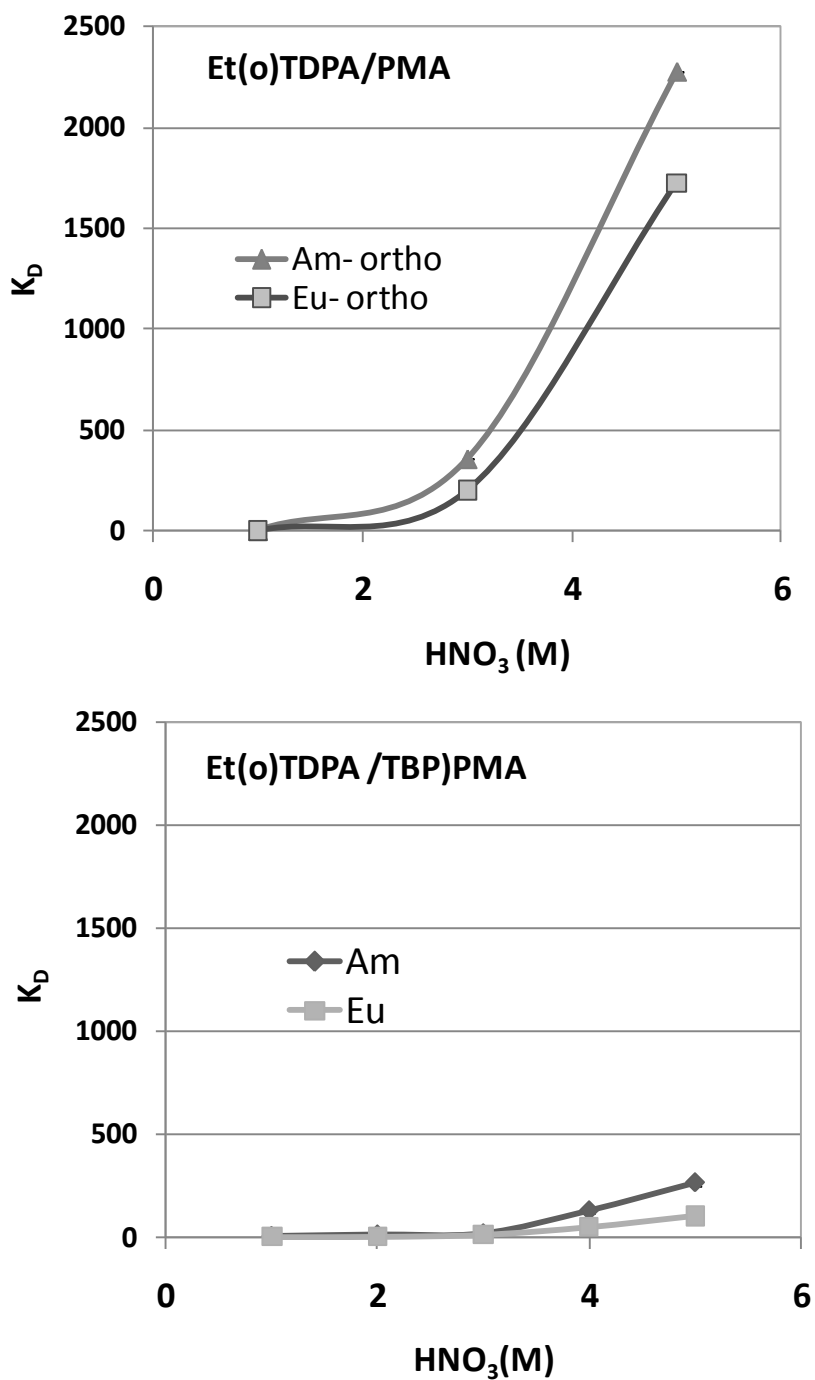


Figure 19: Comparison of the pure Et(o)TDPA-PMA (above) and the TBP- Et(o)TDPA-PMA (below) resins: partitioning of Am and Eu in batch experiment with various nitric acid concentrations and contact time

There are a number of factors that may be listed as causing the decrease in extraction efficiency when TBP is added; such as TBP reducing the polarity of the resin (needed to retain extractant impregnation), the formation of TBP adducts with nitrate anions that are then missing in extraction with diamides which are also neutral solvate extractants, or the formation of EtTDPA-TBP adducts and thereby blocked metal binding site. The difference in extraction between the two isomers when combined with TBP support the later reason and suggests the position of the methyl group on the tolyl ring of the DPA molecule is affecting this complexation.

Chapter 6: *Conclusions*

The ortho and para diamide derivatives of N,N'-diethyl-N,N'-ditolyl-dipicolinamide were successfully impregnated on two different polymeric inert support resins. All four extractant-resin combinations proved to extract both Am and Eu with a greater preference for Am. The extraction efficiency and separation factor of each resin type varied. The Et(p)TDPA/PMA resin yielded the highest separation factor for these two metal cations, while the Et(o)TDPA/PMA resin provided the highest extraction yields for both Am and Eu. During the kinetic batch trials, the Et(o)TDPA/PS-DVB resin exhibited a sensitivity to concentrated nitric acid over a prolonged period of time most likely due to leakage. The kinetic batch trials also confirmed that in general, extraction of both Am and Eu increased with contact time. Six hours was found as an optimum contact time that supported separation of the two metals. In addition to contact time, the acid concentration of the aqueous or mobile phase appeared to greatly affect extraction. More concentrated nitric acid sustained extraction of both metals while the lower nitric acid decreased extraction yields. This finding was used in column experiments where 3 M HNO₃ was used to load the metals onto the resin and 0.5 M HNO₃ was used to elute the metals.

Column experiment results supported the batch test findings where the Et(p)TDPA/PMA resin yielded the highest separation of Am from Eu with 96% of Eu being eluted after four void volumes while 90% of Am was retained. These findings

were enhanced in a column trial where the amount of resin used was increased from 0.2 gram to 1 gram, yielding 98% of Eu being eluted and 98% of Am being retained. Despite their high extraction efficiencies, the resins loaded with Et(o)TDPA did not support separation as both metals were more tightly bound to the column.

Addition of a synergistic extractant and/or another eluting ligand into the system was considered with the goal of enhancing the separation. The addition of metal complexing ligands to the effluent (acetate and citrate) were found to promote separation through their complexation with Eu. Citrate (0.2 M in 0.5 M HNO₃) was the most successful with 100% of Eu being eluted, while 98% of Am was retained.

Tributyl-phosphate was combined with DPA and believed to complex before being impregnated onto an inert support. Batch tests found that lower TBP: EtTDPA ratios resulted with higher extraction yields; however, higher ratios of TBP:EtTDPA yielded better separations. This suggested that the addition of TBP prohibits metal complexation but adds further selectivity for Am over Eu.

The extraction trends observed for the Et(o)TDPA-TBP resin were similar to the resin loaded with pure Et(o)TDPA in that the extraction increased as nitric acid concentration increased despite being much lower in value. The extractability of metals with the Et(p)TDPA/TBP/PMA resin however did not increase over increasing nitric acid concentration but consistently remained moderately low. The difference between the two ortho and para isomers of EtTDPA, when combined with TBP, suggests that the position of the methyl group on the tolyl ring of DPA is affecting the

complexation with TBP. The findings from these experiments suggest the Et(p)TDPA/PMA resin shows the highest potential when eluted with a dilute nitric acid or with the addition of a complexing ligand to the effluent. The addition of a complexing ligand in the effluent proved to enhance separation with both complexing ligands tested. Future work should examine more ligands and their concentrations in the eluent.

The addition of a synergistic extractant on the resin, such as TBP, appeared to enhance the separation power of the ortho isomer in extraction chromatography. It is of interest to further investigate addition of another extractant to Et(o)TDPA instead of TBP and as well as consider another diamide molecule that may be applied to this system. These variables may help improve the separation factors of extraction chromatography based on the DPA extraction system.

Additional consideration should be focused on the stability of the solid extraction resins. Variables affecting the stability of the resin include quantification of the extractant leakage, regeneration of resins, and their resistance to radiolysis and acidic hydrolysis. With the successful investigation and optimization of these variables the satisfactory values of separation factors for the Am/Eu couple can be achieved, and the new extraction chromatography resins for the use in automated, miniaturized radiochemical separations can be developed.

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APPENDIX

BATCH TESTS

Et(para) TDPA-PMA										
Am	1516.00	12.98								
[HNO ₃]	CR cpm	±ΔCR cpm	K _D	ΔK _D	ΔCR (init - fin)	±ΔCR cpm	Volume mL	±ΔV mL	Weight mg	±ΔW mg
0.5	1280.2	11.93	1.4	0.2	235.80	17.63	1.00	0.10	50.00	0.10
1	1370.6	12.34	0.00	0.00	145.40	17.91	1.00	0.10	50.00	0.10
2	1152.4	11.32	3.8	0.4	363.60	17.22	1.00	0.10	50.00	0.10
3	218.8	4.93	105	11	1297.20	13.88	1.00	0.10	50.00	0.10
4	158.8	4.20	153	16	1357.20	13.64	1.00	0.10	50.00	0.10
5	103.0	3.38	246	26	1413.00	13.41	1.00	0.10	50.00	0.10
Eu	1087.6	10.99								
0.5	1108.6	11.10	0.38	0.28	21.00	15.62	1.00	0.10	50.00	0.10
1	1142.6	11.27	0.96	0.29	55.00	15.74	1.00	0.10	50.00	0.10
2	1017.0	10.63	1.39	0.33	70.60	15.29	1.00	0.10	50.00	0.10
3	292.0	5.70	54.49	5.62	795.60	12.38	1.00	0.10	50.00	0.10
4	130.6	3.81	146.55	15.37	957.00	11.63	1.00	0.10	50.00	0.10
5	84.6	3.07	237.12	25.37	1003.00	11.41	1.00	0.10	50.00	0.10

Et(ortho)TDPA-PMA										
Am	CR cpm	±ΔCR cpm	K _D	ΔK _D	ΔCR (init - fin)	±ΔCR cpm	Volume mL	±ΔV mL	Weight mg	±ΔW mg
[HNO₃]	8954.40	31.54								
1	8911.00	31.47	0.1	0.10	43.40	44.55	1.00	0.10	50.00	0.10
3	475.60	7.27	356	36.10	8478.80	32.37	1.00	0.10	50.00	0.10
5	78.00	2.94	2276	243.45	8876.40	31.68	1.00	0.10	50.00	0.10
Eu										
[HNO₃]	7114.20	28.12								
1	7112.00	28.11	0.01	0.11	2.20	39.76	1.00	0.10	50.00	0.10
3	647.40	8.48	199	20.17	6466.80	29.37	1.00	0.10	50.00	0.10
5	81.60	3.01	1724	183.89	7032.60	28.28	1.00	0.10	50.00	0.10

Et(para)TDPA-PS-DVB										
[HNO ₃]	CR cpm	±ΔCR cpm	K _D	ΔK _D	ΔCR (init - fin)	±ΔCR cpm	Volume mL	±ΔV mL	Weight mg	±ΔW mg
Am	5243.2	24.14								
1	5251.8	24.16	0.03	0.13	8.6	34.2	1.00	0.10	50.00	0.10
2	5211.4	24.06	0.12	0.13	31.8	34.1	1.00	0.10	50.00	0.10
3	1590.4	13.29	45.94	4.62	3653	27.6	1.00	0.10	50.00	0.10
4	1627.8	13.45	44.42	4.47	3615	27.6	1.00	0.10	50.00	0.10
5	4305.2	21.87	4.36	0.46	938	32.6	1.00	0.10	50.00	0.10
Eu										0.10
	4236.6	21.70								0.10
1	4215.0	21.64	0.10	0.15	21.6	30.6	1.00	0.10	50.00	0.10
2	4187.2	21.57	0.24	0.15	49.4	30.6	1.00	0.10	50.00	0.10
3	2036.0	15.04	21.62	2.18	2201	26.4	1.00	0.10	50.00	0.10
4	1437.4	12.64	38.95	3.93	2799	25.1	1.00	0.10	50.00	0.10
5	3903.6	20.83	1.71	0.23	333	30.0	1.00	0.10	50.00	0.10

Et(ortho)TDPA-PS-DVB										
[HNO ₃]	CR cpm	±ΔCR cpm	K _D	ΔK _D	ΔCR (init - fin)	±ΔCR cpm	Volume mL	±ΔV mL	Weight mg	±ΔW mg
Am	7503.8	28.9								
1	7478.2	28.8	0.07	0.11	25.6	40.8	1.00	0.10	50.00	0.10
2	7283.4	28.5	0.61	0.13	220.4	40.5	1.00	0.10	50.00	0.10
3	372.8	6.4	382.6	38.86	7131.0	29.6	1.00	0.10	50.00	0.10
4	225	5.00	647	66.34	7278.8	29.3	1.00	0.10	50.00	0.10
5	951.2	10.	137.8	13.88	6552.6	30.7	1.00	0.10	50.00	0.10
Eu										
	6488.6	26.8								
1	6356.6	26.6	0.4	0.1	132.0	37.8	1.00	0.10	50.00	0.10
2	6337.8	26.5	0.5	0.1	150.8	37.8	1.00	0.10	50.00	0.10
3	491.8	7.4	244	24.7	5996.8	27.9	1.00	0.10	50.00	0.10
4	176	4.44	717	74	6312.6	27.2	1.00	0.10	50.00	0.10
5	467.6	7.21	257	26	6021.0	27.8	1.00	0.10	50.00	0.10

(TBP/(o)DPA)PMA										
TBP:DPA	CR cpm	±ΔCR cpm	K _D	ΔK _D	ΔCR (init - fin)	±ΔCR cpm	Volume mL	±ΔV mL	Weight mg	±ΔW mg
Am	2645.1	17.14								
1M HNO₃										
1:2	2845.7	17.78	0	∞			1.00	0.10	50.00	0.10
1:1	2721.7	17.39	0	∞			1.00	0.10	50.00	0.10
2:1	2706.7	17.34	0	∞			1.00	0.10	50.00	0.10
3M HNO₃										
1:2	310.7	5.88	150	15	2334.4	18.12	1.00	0.10	50.00	0.10
1:1	789.4	9.37	47.0	4.76	1855.7	19.53	1.00	0.10	50.00	0.10
2:1	1385.4	12.41	18.2	1.85	1259.7	21.16	1.00	0.10	50.00	0.10
1:2										
1:2	52.1	2.41	995	109.9	2593.0	17.31	1.00	0.10	50.00	0.10
1:1	71.4	2.82	721	77.7	2573.7	17.37	1.00	0.10	50.00	0.10
2:1	132.4	3.84	379.6	39.6	2512.7	17.57	1.00	0.10	50.00	0.10
Eu	3372.1	19.36								
1M HNO₃										
1:1	3444.4	19.56	0	∞			1.00	0.10	50.00	0.10
2:1	3503.7	19.73	0	∞			1.00	0.10	50.00	0.10
3M HNO₃										
1:2	462.4	7.17	125.9	12.8	2909.7	20.64	1.00	0.10	50.00	0.10
1:1	1402.4	12.48	28.1	2.8	1969.7	23.03	1.00	0.10	50.00	0.10
2:1	2324.1	16.07	9.0	0.93	1048.00	25.16	1.00	0.10	50.00	0.10
5M HNO₃										
1:2										
1:1	82.1	3.02	801.5	85.6	3290.0	19.59	1.00	0.10	50.00	0.10
2:1	186.7	4.55	341.2	35.2	3185.4	19.89	1.00	0.10	50.00	0.10

(TBP/(p)TBP)PMA- 30 minute contact time										
Am	CR cpm	±ΔCR cpm	K _D	ΔK _D	ΔCR (init - fin)	±ΔCR cpm	Volume mL	±ΔV mL	Weight mg	±ΔW mg
[HNO3]	4157									
0.5	4149	21	0.04	0.10	8	21	1.00	0.10	50.00	0.10
2	3219	19	5.8	0.60	938	19	1.00	0.10	50.00	0.10
3	1440	13	37.8	3.79	2717	13	1.00	0.10	50.00	0.10
4	3603	20	3.08	0.33	554	20	1.00	0.10	50.00	0.10
5	583	8	123	12.37	3574	8	1.00	0.10	50.00	0.10
Eu										
[HNO3]	3584									
1	3572	20	0.067	0.16	12.0	28.20	1.00	0.10	50.00	0.10
2	3366	20	1.29	0.21	218	27.79	1.00	0.10	50.00	0.10
3	2310	16	11.02	1.13	1274	25.59	1.00	0.10	50.00	0.10
4	1065	11	47.3	4.78	2519	22.73	1.00	0.10	50.00	0.10
5	594	8	100.7	10.2	2990	21.55	1.00	0.10	50.00	0.10

TBP-Et(o)TDPA-PMA - 6 hr contact time										
	CR cpm	±ΔCR cpm	K _D	ΔK _D	ΔCR (init - fin)	±ΔCR cpm	Volume mL	±ΔV mL	Weight mg	±ΔW mg
Am [HNO ₃]	4232	22								
1	41769	22	0.3	0.15	56.0	31	1.00	0.10	50.00	0.10
2	3057	18	7.7	0.8	1174	28	1.00	0.10	50.00	0.10
3	2545	17	13.3	1.4	1686	27	1.00	0.10	50.00	0.10
4	584	87	125	13	3647	23.	1.00	0.10	50.00	0.10
5	301	6	261	27	3930	22	1.00	0.10	50.00	0.10
Eu [HNO ₃]	3584	20								
1	3572	20	0.067	0.16	12.0	28.20	1.00	0.10	50.00	0.10
2	3366	20	1.29	0.21	218	27.79	1.00	0.10	50.00	0.10
3	2310	16	11.02	1.13	1274	25.59	1.00	0.10	50.00	0.10
4	1065	11	47.3	4.77	2519	22.73	1.00	0.10	50.00	0.10
5	594	8	100.7	10.19	2990	21.55	1.00	0.10	50.00	0.10

(TBP/(o)TBP)PMA- 30 minute contact time										
[HNO ₃]	CR cpm	±ΔCR cpm	K _D	ΔK _D	ΔCR (init - fin)	±ΔCR cpm	Volume mL	±ΔV mL	Weight mg	±ΔW mg
Am	4157	21								
0.5	3999	21	0.8	0.17	158	30	1.00	0.10	50.00	0.10
2	2628	17	11.6	1.18	1529	28	1.00	0.10	50.00	0.10
3	1083	11	57	5.72	3074	24	1.00	0.10	50.00	0.10
4	270	8	287	29.38	3887	22	1.00	0.10	50.00	0.10
5	104	3	780	82.20	4053	22	1.00	0.10	50.00	0.10
Eu	6709									
0.5	5635	25	3.8	0.4	1074	25	1.00	0.10	50.00	0.10
2	4884	23	7.5	0.8	1825	23	1.00	0.10	50.00	0.10
3	2429	16	35.2	3.5	4280	16	1.00	0.10	50.00	0.10
4	678	9	178	17.9	6031	8.7	1.00	0.10	50.00	0.10
5	166	4	789	82	6543	4.3	1.00	0.10	50.00	0.10

COLUMN TESTS

0.200 g of the Et(p)TDPA/PMA ; Loading/conditioning: 3M HNO ₃ Elution: 0.5M HNO ₃						
	cpm	count error	fraction eluted	spike*sample	error	elution error
Am	24468	31.28				
1	23.8	0.98	0.001	582343	31.3	1.24E-06
2	22.2	0.94	0.001	543194	31.3	1.16E-06
3	88	1.88	0.004	2153202	31.3	4.60E-06
4	2298.2	9.59	0.094	56232817	32.7	1.20E-04
5	5412	14.71	0.221	132421898	34.6	2.83E-04
6	6223	15.78	0.254	152265609	35.0	3.25E-04
7	5453.6	14.77	0.223	133439776	34.6	2.85E-04
8	3007	10.97	0.123	73575877	33.2	1.57E-04
9	974	6.24	0.040	23832027	31.9	5.09E-05
10	522.4	4.57	0.021	12782188	31.6	2.73E-05
11	282.4	3.36	0.012	6909820	31.5	1.48E-05
12	15.2	0.78	0.001	371917	31.3	7.96E-07
Eu	cpm	count error	fraction eluted	spike*sample	error	elution error
	12941	22.75				
0	15.8	0.79	0.001	204468	31.3	1.57E-06
1	127	2.25	0.010	1643507	31.4	1.25E-05
2	7116.2	16.87	0.550	92090744	35.5	7.03E-04
3	4081.2	12.78	0.315	52814809	33.8	4.03E-04
4	1104.6	6.65	0.085	14294629	32.0	1.09E-04
5	454.2	4.26	0.035	5877802	31.6	4.49E-05
6	285.4	3.38	0.022	3693361	31.5	2.82E-05
7	295.4	3.44	0.023	3822771	31.5	2.92E-05
8	241.2	3.11	0.019	3121369	31.4	2.38E-05
9	130	2.28	0.010	1682330	31.4	1.28E-05
1.0 g of the Et(p)TDPA/PMA ; Loading/conditioning: 3M HNO ₃ Elution: 0.5M HNO ₃						
Am	cpm	count error	fraction eluted	spike*sample	error	elution error
mL added	63658	50.46				
0.5	47.4	1.38	0.001	3017408	31.3	9.52E-07
1.5	116.4	2.16	0.002	7409838	31.4	2.34E-06
2	106.4	2.06	0.002	6773254	31.4	2.14E-06

2.5	106.4	2.06	0.002	6773254	31.4	2.14E-06
3	1033.4	6.43	0.016	65784591	31.9	2.08E-05
3.5	7844.4	17.71	0.123	499361953	36.0	1.58E-04
4	14225.4	23.85	0.223	905566203	39.3	2.86E-04
4.5	13872	23.56	0.218	883069325	39.2	2.79E-04
5	8609.4	18.56	0.135	548060629	36.4	1.73E-04
5.5	7716.4	17.57	0.121	491213678	35.9	1.55E-04
6	2734.4	10.46	0.043	174067529	33.0	5.49E-05
6.5	392	3.96	0.006	24954093	31.5	7.87E-06
7	334	3.66	0.005	21261906	31.5	6.71E-06
7.5	170	2.61	0.003	10821928	31.4	3.41E-06
8	124.4	2.23	0.002	7919105	31.4	2.50E-06
8.5	90.4	1.90	0.001	5754719	31.3	1.82E-06
9	68.4	1.65	0.001	4354235	31.3	1.37E-06
9.5	50.4	1.42	0.001	3208383	31.3	1.01E-06
10	35.4	1.19	0.001	2253507	31.3	7.11E-07
10.5	47.7	1.38	0.001	3036506	31.3	9.58E-07
11	40.4	1.27	0.001	2571799	31.3	8.11E-07
11.5	50.4	1.42	0.001	3208383	31.3	1.01E-06
12	33.4	1.16	0.001	2126191	31.3	6.71E-07

Eu	cpm	count error	fraction eluted	spike*sample	error	elution error
mL added	48879	44.22				
0.5	90.8	1.91	0.002	4438231	31.3	2.38E-06
1	171.2	2.62	0.004	8368119	31.4	4.48E-06
1.5	72.2	1.70	0.001	3529078	31.3	1.89E-06
2	8449.2	18.38	0.173	412990137	36.3	2.21E-04
2.5	32167.2	35.87	0.658	1572307002	47.6	8.41E-04
3	5224.8	14.46	0.107	255384044	34.5	1.37E-04
3.5	1611	8.03	0.033	78744391	32.3	4.21E-05
4	667.6	5.17	0.014	32631754	31.7	1.75E-05
4.5	400.8	4.00	0.008	19590783	31.5	1.05E-05
5	379.2	3.89	0.008	18534993	31.5	9.92E-06
5.5	222.4	2.98	0.005	10870734	31.4	5.82E-06
6	182.4	2.70	0.004	8915566	31.4	4.77E-06
6.5	213.6	2.92	0.004	10440597	31.4	5.59E-06
7	296.6	3.44	0.006	14497571	31.5	7.76E-06
7.5	202.8	2.85	0.004	9912702	31.4	5.30E-06
8	121.8	2.21	0.002	5953487	31.4	3.19E-06

8.5	52.2	1.44	0.001	2551494	31.3	1.37E-06
9	21.6	0.93	0.000	1055791	31.3	5.65E-07
9.5	23.8	0.98	0.000	1163325	31.3	6.23E-07
10	28.6	1.07	0.001	1397945	31.3	7.48E-07
10.5	49	1.40	0.001	2395081	31.3	1.28E-06
11	33.8	1.16	0.001	1652117	31.3	8.84E-07
11.5	25.6	1.01	0.001	1251308	31.3	6.70E-07

Et(o)TDPA/PMA ; Loading/conditioning: 3M HNO₃ Elution: 0.5M HNO₃						
	cpm	count error	fraction eluted	spike*sample	error	elution error
Am	33213.4	91.12				
0	4.9	1.11	0.0001	162746	91.1	4.13E-07
1	1.4	0.59	0.0000	46499	91.1	1.42E-07
2	4712.4	34.32	0.1419	156514826	97.4	3.89E-04
3	7022.4	41.90	0.2114	233237780	100.3	5.80E-04
4	3030.9	27.53	0.0913	100666494	95.2	2.50E-04
5	1580.4	19.88	0.0476	52490457	93.3	1.31E-04
6	1264.9	17.78	0.0381	42011630	92.8	1.04E-04
7	1296.9	18.01	0.0390	43074458	92.9	1.07E-04
8	906.4	15.05	0.0273	30104626	92.4	7.49E-05
9	673.4	12.97	0.0203	22365904	92.0	5.56E-05
10	553.4	11.76	0.0167	18380296	91.9	4.57E-05
11	556.9	11.80	0.0168	18496542	91.9	4.60E-05
Eu						
	37159.9	96.38				
	32.4	2.85	0.0009	1203981	96.4	2.26E-06
0	21.4	2.31	0.0006	795222	96.4	1.50E-06
1	13525.9	58.15	0.3640	502621091	112.6	9.44E-04
2	7481.4	43.25	0.2013	278008076	105.6	5.22E-04
3	2048.9	22.63	0.0551	76136919	99.0	1.43E-04
4	1999.9	22.36	0.0538	74316084	98.9	1.40E-04
5	1527.9	19.54	0.0411	56776611	98.3	1.07E-04
6	537.4	11.59	0.0145	19969730	97.1	3.75E-05
7	750.9	13.70	0.0202	27903369	97.4	5.24E-05
8	684.4	13.08	0.0184	25432236	97.3	4.78E-05
9	553.4	11.76	0.0149	20564289	97.1	3.86E-05
10	499.9	11.18	0.0135	18576234	97.0	3.49E-05
Et(o)TDPA/PS/DVB ; Loading/conditioning: 3M HNO₃ Elution: 0.5M HNO₃						
Am	cpm	count error	fraction eluted	spike*sample	error	elution error

0	32967.4	36.31				
1	4635.9	34.04	0.1406	152833570	49.8	1.55E-04
2	648.9	12.74	0.0197	21392546	38.5	2.17E-05
3	2823.9	26.57	0.0857	93096641	45.0	9.44E-05
4	1955.9	22.11	0.0593	64480938	42.5	6.54E-05
5	1797.9	21.20	0.0545	59272088	42.0	6.01E-05
6	1480.4	19.24	0.0449	48804939	41.1	4.95E-05
7	1483.4	19.26	0.0450	48903841	41.1	4.96E-05
8	1541.4	19.63	0.0468	50815950	41.3	5.15E-05
9	1364.4	18.47	0.0414	44980721	40.7	4.56E-05
10	1226.9	17.51	0.0372	40447703	40.3	4.10E-05
11	1133.4	16.83	0.0344	37365251	40.0	3.79E-05
12	1007.9	15.87	0.0306	33227842	39.6	3.37E-05
Eu						
	36965.9	96.13				
0	2527.9	25.14	0.0684	93446099	99.4	1.78E-04
1	2003.4	22.38	0.0542	74057484	98.7	1.41E-04
2	3528.9	29.70	0.0955	130448965	100.6	2.48E-04
3	2565.4	25.32	0.0694	94832320	99.4	1.80E-04
4	2363.4	24.31	0.0639	87365208	99.2	1.66E-04
5	2629.9	25.64	0.0711	97216620	99.5	1.85E-04
6	2332.4	24.15	0.0631	86219265	99.1	1.64E-04
7	2184.9	23.37	0.0591	80766795	98.9	1.54E-04
8	1891.9	21.75	0.0512	69935786	98.6	1.33E-04
9	1726.9	20.78	0.0467	63836413	98.4	1.21E-04
10	1458.9	19.10	0.0395	53929552	98.0	1.03E-04
11	1364.9	18.47	0.0369	50454757	97.9	9.60E-05

Tritium Elution						
microliter addition	cpm	count error	fraction eluted	spike*sample	error	elution error
H-3	9123	47.76				
50	0	0.00	0	0	47.76	0
100	2	0.71	0.00022	18246	47.76	1.28E-06
150	4	1.00	0.00044	36492	47.77	2.37E-06
200	42	3.24	0.00460	383166	47.87	2.41E-05
250	251	7.92	0.02751	2289873	48.41	0.000144
300	742	13.62	0.08133	6769266	49.66	0.000426
350	1154	16.99	0.12649	10527942	50.69	0.000662
400	1699	20.61	0.18623	15499977	52.01	0.000975
450	1624	20.15	0.17801	14815752	51.83	0.000932
500	1639	20.24	0.17966	14952597	51.87	0.00094
550	1104	16.61	0.12101	10071792	50.56	0.000633
600	605	12.30	0.06632	5519415	49.32	0.000347
650	267	8.17	0.02927	2435841	48.45	0.000153
700	78	4.42	0.00855	711594	47.96	4.48E-05
750	29	2.69	0.00318	264567	47.83	1.67E-05
800	10	1.58	0.00110	91230	47.78	5.77E-06
850	4	1.00	0.00044	36492	47.77	2.37E-06
900	2	0.71	0.00022	18246	47.76	1.28E-06
950	0	0.00	0	0	47.76	0
1000	2	0.71	0.0002	18246	47.76	1.28E-06
1050	3	0.87	0.0003	27369	47.77	1.81E-06
1100	0	0.00	0	0	47.76	0
1150	3	0.87	0.0003	27369	47.77	1.81E-06
1200	3	0.87	0.0003	27369	47.77	1.81E-06
1250	0	0.00	0	0	47.76	0

Et (p)TDPA/PMA: Condition/load: 3M HNO ₃ ; Elution: 0.5M HNO ₃ +0.2M complexant							
	cpm	Count error	Fraction eluted	Spike*sample	Error	Elution error	
Am	39574	99.5					
No Complexant							
1	6.1	1.23	0.0002	241401	99.47	3.93E-07	
2	2.7	0.82	0.0001	106850	99.47	1.83E-07	
3	11.7	1.71	0.0003	463015	99.48	7.46E-07	
4	17.4	2.09	0.0004	688586	99.49	1.11E-06	
5	2561.1	25.30	0.0647	101352715	102.63	1.63E-04	
6	22019.1	74.19	0.5564	871381661	124.09	1.40E-03	
7	10805.1	51.97	0.2730	427599947	112.23	6.86E-04	
8	1310.7	18.10	0.0331	51869511	101.10	8.32E-05	
9	409.4	10.12	0.0103	16201555	99.98	2.60E-05	
10	290.1	8.52	0.0073	11480388	99.83	1.84E-05	
11	163.7	6.40	0.0041	6478247	99.67	1.04E-05	
12	130.1	5.70	0.0033	5148564	99.63	8.26E-06	
13	101.7	5.04	0.0026	4024666	99.59	6.46E-06	
14	94.1	4.85	0.0024	3723904	99.58	5.98E-06	
15	66.4	4.07	0.0017	2627707	99.55	4.22E-06	
Sodium Acetate							
1	11.7	1.71	0.0003	463015	99.48	7.46E-07	
2	5.7	1.19	0.0001	225571	99.47	3.68E-07	
3	13.1	1.81	0.0003	518418	99.48	8.34E-07	
4	6.4	1.26	0.0002	253273	99.47	4.11E-07	
5	445.1	10.55	0.0112	17614343	100.02	2.83E-05	
6	13512.4	58.12	0.3414	534738366	115.20	8.58E-04	
7	19472.7	69.77	0.4921	770610683	121.50	1.24E-03	
8	3271.4	28.60	0.0827	129462056	103.50	2.08E-04	
9	532.4	11.54	0.0135	21069144	100.13	3.38E-05	
10	270.4	8.22	0.0068	10700783	99.81	1.72E-05	
11	178.7	6.68	0.0045	7071856	99.69	1.13E-05	
12	146.1	6.04	0.0037	5781747	99.65	9.28E-06	
13	86.1	4.64	0.0022	3407313	99.57	5.47E-06	
14	61.4	3.92	0.0016	2429837	99.54	3.90E-06	
15	61.7	3.93	0.0016	2441710	99.54	3.92E-06	
Sodium Citrate							
1	4.7	1.08	0.0001	185997	99.47	3.05E-07	
2	6.7	1.29	0.0002	265145	99.47	4.30E-07	
3	7.7	1.39	0.0002	304719	99.48	4.93E-07	

4	3.4	0.92	0.0001	134551	99.47	2.25E-07
5	19.4	2.20	0.0005	767734	99.49	1.23E-06
6	709.1	13.31	0.0179	28061852	100.35	4.50E-05
7	19076.4	69.06	0.4820	754927546	121.09	1.21E-03
8	16982.7	65.16	0.4291	672071672	118.91	1.08E-03
9	775.7	13.93	0.0196	30697474	100.44	4.93E-05
10	346.4	9.31	0.0088	13708399	99.90	2.20E-05
11	260.1	8.06	0.0066	10293171	99.79	1.65E-05
12	168.7	6.49	0.0043	6676117	99.68	1.07E-05
13	145.7	6.04	0.0037	5765917	99.65	9.25E-06
14	94.4	4.86	0.0024	3735776	99.58	6.00E-06
15	92.4	4.81	0.0023	3656628	99.58	5.87E-06
Eu 30562 87.41						
No Complexant						
1	34.1	2.92	0.0011	1042164	87.46	3.19E-06
2	20.7	2.27	0.0007	632633	87.44	1.94E-06
3	37.4	3.06	0.0012	1143019	87.46	3.50E-06
4	12705.4	56.36	0.4157	388302435	104.00	1.19E-03
5	15168.1	61.58	0.4963	463567472	106.92	1.42E-03
6	2721.4	26.08	0.0890	83171427	91.22	2.55E-04
7	381.7	9.77	0.0125	11665515	87.95	3.57E-05
8	110.7	5.26	0.0036	3383213	87.57	1.04E-05
9	60.1	3.88	0.0020	1836776	87.50	5.63E-06
10	52.1	3.61	0.0017	1592280	87.48	4.88E-06
11	43.7	3.31	0.0014	1335559	87.47	4.09E-06
12	31.7	2.82	0.0010	968815	87.46	2.97E-06
13	63.1	3.97	0.0021	1928462	87.50	5.91E-06
14	8.4	1.45	0.0003	256721	87.42	7.92E-07
15	27.7	2.63	0.0009	846567	87.45	2.59E-06
Sodium Acetate						
1	3.7	0.96	0.0001	113079	87.42	3.59E-07
2	19.1	2.19	0.0006	583734	87.44	1.79E-06
3	468.4	10.82	0.0153	14315241	88.08	4.38E-05
4	11938.7	54.63	0.3906	364870549	103.08	1.12E-03
5	16796.4	64.80	0.5496	513331577	108.81	1.57E-03
6	1668.7	20.42	0.0546	50998809	89.76	1.56E-04
7	162.1	6.37	0.0053	4954100	87.64	1.52E-05
8	78.1	4.42	0.0026	2386892	87.52	7.31E-06
9	63.7	3.99	0.0021	1946799	87.50	5.96E-06
10	42.7	3.27	0.0014	1304997	87.47	4.00E-06

11	42.1	3.24	0.0014	1286660	87.47	3.94E-06
12	42.7	3.27	0.0014	1304997	87.47	4.00E-06
13	34.7	2.95	0.0011	1060501	87.46	3.25E-06
14	28.1	2.65	0.0009	858792	87.45	2.63E-06
15	22.7	2.38	0.0007	693757	87.44	2.13E-06
Sodium Citrate						
1	5.7	1.19	0.0002	174203	87.42	4.78E-07
2	15.4	1.96	0.0005	470655	87.43	1.27E-06
3	32.7	2.86	0.0011	999377	87.46	2.69E-06
4	11889.4	54.52	0.3890	363363843	103.02	9.78E-04
5	17853.7	66.81	0.5842	545644779	110.02	1.47E-03
6	885.1	14.88	0.0290	27050426	88.67	7.28E-05
7	271.7	8.24	0.0089	8303695	87.80	2.23E-05
8	79.1	4.45	0.0026	2417454	87.52	6.51E-06
9	69.4	4.17	0.0023	2121003	87.51	5.71E-06
10	53.1	3.64	0.0017	1622842	87.49	4.37E-06
11	45.7	3.38	0.0015	1396683	87.48	3.76E-06
12	28.4	2.66	0.0009	867961	87.45	2.34E-06
13	25.4	2.52	0.0008	776275	87.45	2.09E-06
14	28.7	2.68	0.0009	877129	87.45	2.36E-06
15	18.4	2.14	0.0006	562341	87.44	1.52E-06

Et(p)TDPA/PMA Loading/conditioning: 3M HNO ₃ Elution: Citrate with various pH						
	cpm	count error	fraction eluted	spike*sample	error	elution error
Am	33332.9	91.29				
pH 2.4						
1	197.4	7.02	0.0059	6579914	91.6	0
2	810.9	14.24	0.0243	27029649	92.4	6.66E-05
3	1824.4	21.36	0.0547	60812543	93.8	0.00015
4	11857.9	54.45	0.3557	395258195	106.3	0.000974
5	2997.4	27.37	0.0899	99912034	95.3	0.000246
6	1932.9	21.98	0.0580	64429162	93.9	0.000159
7	549.4	11.72	0.0165	18313095	92.0	4.51E-05
8	356.4	9.44	0.0107	11879846	91.8	2.93E-05
9	397.9	9.97	0.0119	13263161	91.8	3.27E-05
10	257.9	8.03	0.0077	8596555	91.6	2.12E-05
11	271.9	8.24	0.0082	9063216	91.7	2.23E-05
12	163.9	6.40	0.0049	5463262	91.5	1.35E-05
pH 3.4	33332.9	91.29				
1	3490.9	29.54	0.1047	116361821	95.9	0.000287
2	4601.4	33.92	0.1380	153378006	97.4	0.000378
3	5435.9	36.86	0.1631	181194311	98.4	0.000447
4	4623.9	34.00	0.1387	154127996	97.4	0.00038
5	3021.4	27.48	0.0906	100712024	95.3	0.000248
6	2838.4	26.64	0.0852	94612103	95.1	0.000233
7	1034.4	16.08	0.0310	34479552	92.7	8.5E-05
8	779.4	13.96	0.0234	25979662	92.3	6.4E-05
9	562.4	11.86	0.0169	18746423	92.1	4.62E-05
10	325.4	9.02	0.0098	10846526	91.7	2.67E-05
11	22.4	2.37	0.0007	746657	91.3	1.84E-06
12	203.9	7.14	0.0061	6796578	91.6	1.68E-05
pH 4.4	31853.9	89.23				
1	29.4	2.71	0.0009	975489	91.1	2.43E-06

2	229.4	7.57	0.0069	7611469	91.4	1.9E-05
3	3096.9	27.82	0.0933	102754832	95.2	0.000256
4	3656.9	30.24	0.1102	121335576	96.0	0.000303
5	3392.9	29.12	0.1023	112576083	95.6	0.000281
6	3961.9	31.47	0.1194	131455446	96.4	0.000328
7	4815.9	34.70	0.1451	159791080	97.5	0.000398
8	2215.4	23.53	0.0668	73506750	94.1	0.000183
9	1485.9	19.27	0.0448	49302013	93.1	0.000123
10	1943.4	22.04	0.0586	64481818	93.7	0.000161
11	735.4	13.56	0.0222	24400498	92.1	6.08E-05
12	540.9	11.63	0.0163	17947008	91.8	4.47E-05
Eu						
pH 2.4	37261.4	96.52				
1	4265.4	32.66	0.1151	158934776	101.9	0.000298
2	13623.9	58.36	0.3677	507645587	112.8	0.000952
3	12028.4	54.84	0.3246	448195024	111.0	0.000841
4	1643.4	20.27	0.0444	61235385	98.6	0.000115
5	1146.4	16.93	0.0309	42716469	98.0	8.01E-05
6	1050.9	16.21	0.0284	39158005	97.9	7.35E-05
7	368.4	9.60	0.0099	13727100	97.0	2.58E-05
8	156.9	6.26	0.0042	5846314	96.7	1.1E-05
9	99.4	4.98	0.0027	3703783	96.6	6.95E-06
10	66.9	4.09	0.0018	2492788	96.6	4.68E-06
11	52.9	3.64	0.0014	1971128	96.6	3.7E-06
12	48.9	3.50	0.0013	1822082	96.6	3.42E-06
pH 3.4	37054.4	96.25				
1	10893.4	52.19	0.2924	363108613	109.7	0.000757
2	11316.9	53.19	0.3037	377225096	110.2	0.000787
3	6575.4	40.54	0.1765	219177151	104.7	0.000457
4	1705.9	20.65	0.0458	56862594	98.7	0.000119
5	1345.4	18.34	0.0361	44846084	98.2	9.35E-05

6	680.9	13.05	0.0183	22696372	97.4	4.73E-05
7	252.4	7.94	0.0068	8413224	96.8	1.75E-05
8	124.9	5.59	0.0034	4163279	96.7	8.68E-06
9	82.4	4.54	0.0022	2746631	96.6	5.73E-06
10	48.9	3.50	0.0013	1629979	96.6	3.4E-06
11	40.9	3.20	0.0011	1363316	96.6	2.84E-06
12	28.9	2.69	0.0008	963321	96.6	2.01E-06
pH 4.4	34891.9	93.40				
1	9313.9	48.25	0.2671	324784076	103.1	0.000715
2	11335.4	53.23	0.3251	395275600	105.5	0.00087
3	7796.4	44.15	0.2236	271867485	101.2	0.000599
4	1476.9	19.22	0.0424	51500832	93.1	0.000113
5	649.9	12.75	0.0186	22662598	92.0	4.99E-05
6	287.4	8.48	0.0082	10021897	91.5	2.21E-05
7	202.9	7.12	0.0058	7075306	91.4	1.56E-05
8	145.4	6.03	0.0042	5070229	91.3	1.12E-05
9	144.9	6.02	0.0042	5052793	91.3	1.11E-05
10	124.9	5.59	0.0036	4355375	91.2	9.59E-06
11	47.4	3.44	0.0014	1652881	91.1	3.64E-06
12	42.4	3.26	0.0012	1478526	91.1	3.26E-06

Et(o)TDPA/PMA; Loading/conditioning: 3M HNO ₃ Elution: Citrate trials with various pH						
	cpm	count error	fraction eluted	spike*sample	error	elution error
Am	33266	91.20				
pH 2.4						
1	5.4	1.16	0.0002	179639	91.20	4.53E-07
2	0.9	0.47	0.0000	29940	91.20	1.11E-07
3	7990.9	44.70	0.2402	265828476	101.56	6.59E-04
4	6365.9	39.89	0.1914	211770576	99.54	5.25E-04
5	3250.4	28.51	0.0977	108129107	95.55	2.68E-04
6	2186.4	23.38	0.0657	72733657	94.14	1.80E-04
7	1453.4	19.06	0.0437	48349386	93.17	1.20E-04
8	970.4	15.58	0.0292	32281715	92.52	8.00E-05
9	831.4	14.42	0.0250	27657685	92.33	6.85E-05
10	739.9	13.60	0.0222	24613809	92.20	6.10E-05
11	557.9	11.81	0.0168	18559325	91.96	4.60E-05
12	528.4	11.49	0.0159	17577966	91.92	4.35E-05
pH 3.4	33476	91.48				
1	28.9	2.69	0.0009	967468	91.52	2.36E-06
2	43.4	3.29	0.0013	1452876	91.54	3.54E-06
3	8710.4	46.66	0.2602	291592835	102.70	7.11E-04
4	4598.9	33.91	0.1374	153954616	97.56	3.75E-04
5	3338.4	28.89	0.0997	111757614	95.94	2.73E-04
6	1472.4	19.19	0.0440	49290651	93.47	1.20E-04
7	1202.4	17.34	0.0359	40252023	93.11	9.82E-05
8	892.4	14.94	0.0267	29874339	92.69	7.28E-05
9	520.4	11.41	0.0155	17421119	92.19	4.25E-05
10	702.9	13.26	0.0210	23530562	92.44	5.74E-05
11	511.4	11.31	0.0153	17119831	92.18	4.17E-05
12	346.4	9.31	0.0103	11596225	91.95	2.83E-05
pH 4.4	31854	89.24				
1	666.4	12.91	0.0209	21227439	90.17	5.86E-05
2	2134.9	23.10	0.0670	68004891	92.18	1.88E-04
3	5995.4	38.71	0.1882	190976872	97.27	5.27E-04
4	8301.9	45.56	0.2606	264447892	100.19	7.30E-04
5	5926.9	38.49	0.1861	188794880	97.19	5.21E-04
6	2647.9	25.73	0.0831	84345942	92.87	2.33E-04
7	1199.9	17.32	0.0377	38221495	90.90	1.06E-04
8	700.9	13.24	0.0220	22326399	90.21	6.16E-05
9	289.4	8.51	0.0091	9218519	89.64	2.55E-05
10	236.9	7.70	0.0074	7546189	89.57	2.08E-05
11	204.9	7.16	0.0064	6526864	89.52	1.80E-05
12	138.9	5.89	0.0044	4424507	89.43	1.22E-05
Eu						

pH 2.4	37128	96.34				
1	45.9	3.39	0.0012	1704171	96.40	3.21E-06
2	51.4	3.58	0.0014	1908374	96.41	3.59E-06
3	11134	52.76	0.2999	413396890	109.84	7.78E-04
4	5250.4	36.23	0.1414	194936326	102.93	3.67E-04
5	2411.4	24.55	0.0649	89530218	99.42	1.69E-04
6	1839.4	21.44	0.0495	68293059	98.70	1.29E-04
7	1246.9	17.66	0.0336	46294779	97.95	8.71E-05
8	869.9	14.75	0.0234	32297560	97.47	6.08E-05
9	922.4	15.19	0.0248	34246775	97.53	6.45E-05
10	741.9	13.62	0.0200	27545189	97.30	5.19E-05
11	637.4	12.62	0.0172	23665323	97.17	4.45E-05
12	539.9	11.62	0.0145	20045353	97.04	3.77E-05
pH 3.4	37128	96.34				
	0	0.00	0.0000	0	96.34	0.00E+00
1	26.4	2.57	0.0007	980177	96.38	1.85E-06
2	171.4	6.55	0.0046	6363722	96.57	1.20E-05
3	15397	62.04	0.4147	571654564	114.59	1.08E-03
4	5116.9	35.77	0.1378	189979752	102.77	3.58E-04
5	1907.4	21.84	0.0514	70817756	98.79	1.33E-04
6	1259.9	17.75	0.0339	46777441	97.96	8.81E-05
7	791.4	14.07	0.0213	29383020	97.36	5.53E-05
8	584.4	12.09	0.0157	21697545	97.10	4.08E-05
9	733.4	13.54	0.0198	27229602	97.29	5.13E-05
10	448.9	10.59	0.0121	16666714	96.92	3.14E-05
11	453.9	10.65	0.0122	16852354	96.93	3.17E-05
12	555.4	11.78	0.0150	20620836	97.06	3.88E-05
pH 4.4	34892	93.40				
1	190.9	6.91	0.0055	6660864	93.65	1.46E-05
2	1544.9	19.65	0.0443	53904496	95.44	1.19E-04
3	5957.9	38.59	0.1708	207882451	101.06	4.57E-04
4	5135.9	35.83	0.1472	179201309	100.03	3.94E-04
5	3734.9	30.56	0.1070	130317757	98.27	2.87E-04
6	1322.4	18.18	0.0379	46141049	95.15	1.01E-04
7	2203.4	23.47	0.0631	76880812	96.30	1.69E-04
8	852.9	14.60	0.0244	29759302	94.53	6.54E-05
9	1511.4	19.44	0.0433	52735618	95.40	1.16E-04
10	796.4	14.11	0.0228	27787909	94.46	6.11E-05
11	1045.9	16.17	0.0300	36493438	94.79	8.02E-05
12	1056.4	16.25	0.0303	36859803	94.80	8.10E-05