

AN ABSTRACT OF THE THESIS OF

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Title: The Effects of Radiolysis and Hydrolysis on the Stability of Extraction Systems for Minor Actinides

Abstract approved:

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Industrial reprocessing of irradiated nuclear fuel (INF) is one of the most complex procedures performed on a large scale; the process is intricate due to the mix of radionuclides present in INF. As a global trend for nuclear power and reprocessing continues, research is geared toward optimizing the extraction of targeted radionuclides from the assortment of byproducts with the aim to decrease the radioactivity of the stored waste and recycle the targeted radionuclides in mixed oxide fuel. Currently, simultaneous separation of radionuclides in one extraction cycle is the leading approach to processing spent nuclear fuel. The process implements a universal extraction mixture for one-step extraction of all targeted radionuclides, followed with selective stripping of individual metals with aqueous solutions.

“Group Extraction of Actinides and Fission Products”, one of the top approaches in this effort, is based on a modification of the Universal Extraction (UNEX) solvent. The process is currently performed using an extraction mixture

composed of the organic complexant octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide (CMPO), the cation exchanger, chlorinated cobalt dicarbollide (CCD), and polyethyleneglycol (PEG) in the diluent phenyltrifluoromethyl sulfonate (FS-13). The solution extracts both fission products and actinides. However, this composition was initially developed for low level waste, and it is of limited use when it comes to processing solutions containing large amounts of actinides and lanthanides, such as in INF.

The current process is restricted by the limited solubility of CMPO and its complexes with metals. In order to more effectively process acidic aqueous solutions containing large amounts of actinides and lanthanides, modifications must be made to the current composition of the mixed solvent. Previously, it has been shown that diamides of dipicolinic acid have increased capacity to extract actinide and lanthanide metals, when compared to CMPO. Furthermore, these diamides exhibit synergistic behavior with CCD to extract cesium, strontium, and trivalent metals.

This study investigated the possibility of replacing CMPO with diamides of 2,6-pyridinedicarboxylic acid (dipicolinic acid) with N,N' diethyl N, N' ditolyl dipicolinamide (EtTDPA). Stability of selected diamides was tested in a simulation of the harsh environment of dissolved nuclear fuel in order to determine their viability for use in reprocessing. Acidic hydrolysis and radiolysis conditions are always present in such systems. EtTDPA, in solution with CCD and FS-13, were exposed to nitric acid and irradiation by gamma photons (Co-60). The stability of EtTDPA was determined through analysis of distribution ratios for Am-241 and Eu-252 and Eu-254 extracted from acidic aqueous solutions. Mass spectrometry was also employed

to determine if any structural changes occurred in the chemicals as a result of hydrolysis or radiolysis. Results showed that Et(o)TDPA was the most stable isomer across radiolysis, and also withstood hydrolysis.

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The Effects of Radiolysis and Hydrolysis on the Stability of Extraction Systems for
Minor Actinides

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Emily C. Wade

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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.

Emily C. Wade, Author

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TABLE OF CONTENTS

	<u>Page</u>
1 Introduction.....	1
2 Background.....	3
2.1 Current State of Solvent Extraction Processing	7
2.2 Extraction Chemistry	12
2.3 Radiolysis and Hydrolysis	15
2.4 Project Goals	18
3 Materials and Methods	20
3.1 Chemicals	20
3.2 Sample Preparation	23
3.2.1 Radiolysis.....	23
3.2.2 Hydrolysis	24
3.3 Extraction Procedure.....	24
3.3.1 Calculations	25
3.4 Mass Spectrometry.....	25
4 Results and Discussion	27
4.1 Extraction Studies	27
4.1.1 Distribution Ratios.....	28
4.1.2 Separation Factors.....	36
4.2 Analysis of Molecular Damage	37
4.3 Error Analysis	43
5 Conclusion and Future Work	46

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Appendices.....	48
Appendix A – Radiolysis Data	49
Appendix B – Hydrolysis Data.....	53
Appendix C – Mass Spectrometry	54
Bibliography	57

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2.1 Molecular structure of Et(o)TDPA	14
2.2 EtTDPA bond cleavage	18
2.3 Dipicolinic acid chemical structure	18
2.4 N-ethyl toluidine chemical structure.....	18
3.1 Molecular structure of species in the extractant solution.....	22
4.1 Americium distribution ratios from extraction with acid-unsaturated extractant as a function of absorbed dose.....	33
4.2 Americium distribution ratios from extraction with acid-saturated extractant as a function of absorbed dose.....	33
4.3 Europium distribution ratios from extraction with acid-unsaturated extractant as a function of absorbed dose.....	34
4.4 Europium distribution ratios from extraction with acid-saturated extractant as a function of absorbed dose.....	34
4.5 Effects of hydrolysis on distribution ratios for Am and Eu with Et(o)TDPA at 50 °C over time.....	35
4.6 Comparison of distribution ratios from extractions with hydrolysis and acid-saturated radiolysis samples over time.....	35
4.7 Chromatogram (positive mode) overlay of radiolysis samples	41
4.8 Chromatogram (negative mode) overlay of radiolysis samples	41
4.9 Mass spectrum in positive mode (Et(o)TDPA)	42
4.10 Mass Spectrum in negative mode (CCD)	42

LIST OF TABLES

<u>Table</u>	<u>Page</u>
2.1 Characteristics of nuclear and fossil-fuelled power plants	3
4.1 Separation factors for Am/Eu with diamide extractant EtTDPA.....	36

LIST OF APPENDIX FIGURES

<u>Figure</u>	<u>Page</u>
C.1 Mass spectra across doses (positive mode)	55
C.2 Mass spectra across doses (negative mode)	56

LIST OF APPENDIX TABLES

<u>Figure</u>	<u>Page</u>
A.1 Americium extraction with unsaturated extractant	49
A.2 Americium extraction with saturated extractant	50
A.3 Europium extraction with unsaturated extractant	51
A.4 Europium extraction with saturated extractant	52
B.1 Americium extraction with Et(o)TDPA extractant exposed to hydrolytic conditions	53
B.2 Europium extraction with Et(o)TDPA extractant exposed to hydrolytic conditions	53
C.1 Mass Spectrometry Settings	54

The Effects of Radiolysis and Hydrolysis on the Stability of Extraction Systems for Minor Actinides

Chapter 1 Introduction

Reprocessing used nuclear fuel can greatly reduce waste volume and toxicity and allow for better utilization of natural uranium resources, but is currently not practiced in the United States. With the volume of nuclear waste growing and repository space dwindling, reprocessing may be the best option to manage used nuclear fuel. If reprocessing becomes implemented in the United States, uranium mining can also be cut back significantly for years to come because uranium, which comprises 95% of used fuel, can be salvaged. The science behind reprocessing, specifically radiochemistry, is a crucial area of research and can lead to technological advances in reprocessing techniques.

This study is part of the larger effort to develop the solvent extraction process for simultaneous extraction of actinides and fission products. The current Universal Extraction (UNEX) solvent is based on the use of the extraction mixture composed of the organic complexant octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphine oxide (CMPO), chlorinated cobalt dicarbollide (CCD), and polyethyleneglycol (PEG) in the diluent phenyltrifluoromethyl sulfonate (FS-13). This mixture provides simultaneous extraction of all major radionuclides (cesium, strontium, actinides and lanthanides) from solutions up to 2 M nitric acid and 4-M total nitrate concentration. However, this composition (0.08 M-HCCD and 0.007-0.02 M-PEG-400, with 0.02 M CMPO) was initially developed for low level waste, and it is of limited use when it comes to processing solutions containing large amounts of actinides and lanthanides such as irradiated nuclear fuel (INF).

The main objective of this study is to characterize the radiolytic and hydrolytic stability of the ortho, meta, and para isomers of N,N'-diethyl N, N'-ditolyl dipicolinamide (EtTDPA), a diamide of dipicolinic acid, and determine its viability to replace CMPO in the UNEX solvent, and extend its application for higher concentrations of radionuclides typical for solutions of irradiated fuel. Unlike CMPO, EtTDPA and its complexes are more soluble in polar diluents. Thus, the diamide can be used to process acidic solutions containing large amounts of actinides and fission products.

The specific goal of this project is to quantify the stability of the extractant when it is exposed to both radiation and strong acid concentrations, typical of extraction process conditions. To study radiolytic stability, samples of the diamide were irradiated in a Co-60 irradiator for various doses: 20 kGy, 40 kGy, 60 kGy, and 80 kGy. Each sample was then used to extract both Am-241 and Eu-152/154 from nitric acid solution. The distribution ratios for each nuclide were calculated after measuring their activity in the aqueous and organic phases. To study hydrolytic stability, samples of the diamide were saturated with nitric acid and exposed to various temperatures for varying amounts of time. Americium and europium distribution ratios were also calculated for these samples.

Separation factors were determined from distribution ratios to assess the ability of the extractant to separate the actinide from the lanthanide. Mass spectrometry was performed on the radiolysis samples to observe any significant chemical changes that may have occurred in the solution as a result of irradiation.

Chapter 2 Background

Nuclear power has environmental, economic, and security benefits over fossil-fuelled power. When used in energy production, fossil fuels such as coal, oil, and natural gas emit massive amounts of carbon dioxide, which leads to global warming, as well as sulfur dioxide, and nitrogen oxides, which cause acid rain and smog. Nuclear power plants do not emit these hazardous pollutants into the environment. Table 2.1 displays the comparison of nuclear fuel and fossil fuels in terms of amount of fuel required to produce 7 TWh of electricity, and corresponding amounts of carbon dioxide and ash produced as byproducts. Nuclear power emits no carbon dioxide into the environment and very small amounts of ash compared to fossil-fuelled power. From an environmental standpoint, nuclear power exceeds fossil-fuelled power as a clean form of energy production (NEA 2007).

Table 2.1 Characteristics of nuclear and fossil fuel-fuelled power plants
(quantities for the generation of 7 TWh of electricity) (NEA 2007)

Fuel type	Quality of fuel (tonnes)	C02 released (tonnes)	Ash Produced (tonnes)
Hard coal	3 500 000	7 200 000	280 000
Oil	1 700 000	5 000 000	35 000
Natural gas	1 600 000	4 000 000	small
Uranium in PWR		0	very small
Ore	50 000		
U ₃ O ₈	200		
Enriched U	30		

In the long-term, nuclear power is a strategic economic investment. The cost of nuclear fuel comprises less than 20% of the total cost of reactors currently in operation, compared to 40-80% fuel costs for thermal power plants. Over time, the cost of nuclear

power would be less than that of fossil-fuelled power. The cost of the nuclear reactor itself would be absorbed by the comparatively lower cost of nuclear fuel (NEA 2007).

Though the elements used in nuclear fuel are non-renewable resources, nuclear power plants have promise for longer operation than the also non-renewable fossil fuels. Based on current global energy consumption, it is predicted that oil reserves can only support 40 more years of energy production, natural gas reserves may last for only 65 more years, and coal reserves can last over 150 years. It is projected that uranium reserves for nuclear power are sufficient to meet the world's energy demands for 85 years, with the once-through open fuel cycle method. However, nuclear fuel is unique to other types of fuel because used fuel from first use in a nuclear plant can be reprocessed and subsequently recycled (closed cycle). The implementation of the recycle of nuclear fuel has the potential to increase the lifetime of nuclear power from 85 years to more than 4000 years. Overall, nuclear power is a better option than fossil-fuelled power, from environmental, economic, and longevity perspectives (NEA 2007).

If nuclear power becomes a predominant means of electricity generation in the world, reprocessing of used fuel is an extremely important option to consider. The main goals of recycling fuel are to reduce waste volume and increase the sustainability of nuclear power. Reprocessing would salvage usable fissile and fertile materials, and provide significant amounts of energy, as well as reduce the volume and toxicity of waste that requires long-term storage (NEA 2007).

Currently, half of the world's used nuclear fuel is not reprocessed, and half is reprocessed to recycle mixed oxide (MOX) fuel elements. The storage of irradiated nuclear

fuel in deep geological repositories is the chief option for its isolation. Without actinide separations, radioactivity levels in a repository will remain above natural background for up to several million years. The future of nuclear power depends on the achievement of long term supervision of repositories to reliably predict the lifetime of engineered or natural barriers, used to sequester the waste, which must be durable for at least 10,000 years. Public acceptance of such repositories is also vital (Nash 2006).

Used nuclear fuel contains a wide variety of chemical elements, and many of them are radionuclides, with different half-lives ranging from very short to the very long. The long-lived radionuclides, with half-lives greater than 30 years, lead to long-term radiological toxicity of INF. These elements include the residual uranium, plutonium, minor actinides (such as Np, Am, Cm), fission products (such as Cs, Sr) and activation products (such as Co-60) (Boullis 2005-2006).

Analysis of the residual radiotoxicity of the used nuclear fuel a few centuries after disposal shows that this is predominantly due to the quantities of plutonium present, then secondarily attributed to minor actinides. Fission products also contribute to radiotoxicity of irradiated fuel, but to a lesser extent. A strategy for the reduction of the long-term radiotoxicity of the waste is reprocessing of used fuel. The primary concern is extracting the uranium and plutonium, which is feasible by means of the PUREX process, and subsequently recycling it in MOX fuel. Once the uranium and plutonium is extracted, minor actinides, which comprise about a thousandth of the total mass of used fuel, are the main source of residual toxicity, or radioactivity. Removal of actinides will immensely reduce the time it will take for the waste to decay to low radiation levels. The goal to

extract minor actinides, in order to further reduce radiotoxicity of the long-term waste, drives the development of enhanced separation strategies. Hence, radiochemistry, combined with separation science, is a vital area of research for development of viable methods for sustainable energy generation (Boullis 2005-2006).

Industrial reprocessing of used nuclear fuel is one of the most complex chemical processes done on a large scale. The conglomeration of elements and byproducts in used nuclear fuel complicates separations and extractions. Radiation decomposition, criticality risks, and proper radiation safety measures further increase the difficulty of reprocessing (Choppin 2001).

The first actinide separations date back to the late 1800s, shortly after the discovery of radioactivity by Antoine Henri Becquerel in 1896. Scientists realized that adding carbonate to uranium and thorium solutions led to formation of precipitates which contained radioactivity, while the parent radionuclide remained in solution. This separation technique became known as precipitation/coprecipitation. It remained the leading method of actinide separations up to the mid-1900s (Nash 2006).

In the early 1940s, chemists working on the Manhattan Project in the race to complete the first atomic bomb used the bismuth phosphate process for separations; this process implemented precipitation techniques to isolate plutonium from uranium and fission products, with Bi^{3+} as a carrier for the precipitate. However, the precipitation technique is not feasible for industrial applications, where fuel elements need to be isolated to very high levels of purity. In the late 1940s, the bismuth phosphate process was replaced by solvent extraction, also known as liquid-liquid extraction, for large scale reprocessing

(Choppin 2001). Industrial scale reprocessing has been practiced for 60 years, and has led to significant development of the theory and methods behind performing separations, as well as challenges related to disposal and environmental remediation at reprocessing sites (Nash 2006). A brief summary of current extraction technologies is provided the next subchapter.

2.1 Current State of Solvent Extraction Processing

In order to reprocess used nuclear fuel through solvent extractions, the used fuel is first dissolved in nitric acid (HNO_3). The resulting acidic and highly radioactive solution is contacted with an immiscible organic extractant solution and agitated so as to attain contact between the aqueous and organic phases (Lahr 2007). The liquids should be mutually immiscible, non-reactive, and the phase interface should be distinct to avoid carryover (Lahr 2007). The targeted elements are transported from the aqueous phase to the organic phase by the extracting chemicals. The mechanism of extraction can include formation of chelation complexes, such as EtTDPA or alkylphosphoric acids, ion association complexes, such as CCD, or neutral solvates, such as CMPO or TBP.

The development of successful processes for separations of elements from INF depends on the use of reagents that can withstand an acidic radioactive environment. Hydrolysis and radiolysis of ligands, diluents and solvents can produce negative effects on distribution ratios and separation factors of metals and can also affect the physical properties of solvents (Pikaev 1988; Mincher 2009).

Predominant methods of processing used nuclear fuel in the United States include PUREX and TRUEX. The DIAMEX process is implemented in France, and the UNEX process is conducted in Russia. All of these processes involve solvent extraction. A requirement for all types of liquid-liquid extraction techniques used in reprocessing is that the radiolytic and hydrolytic byproducts of the extractant and diluent must not impede the processes; factors to be considered are extraction capacity and the ability to recycle the chemicals afterwards (Mowafy 2003).

Although no longer practiced in the United States, the Plutonium Uranium Refining by Extraction (PUREX) process has been a leading method of processing used nuclear fuel for decades. The process involves dissolving the used fuel in nitric acid, and then adding the extractant in organic solution. Tributyl phosphate (TBP) is the extractant used. Typically, 30% TBP is in kerosene or n-dodecane, both odorless hydrocarbon solvents (NEA 1997). TBP is moderately prone to degradation by radiolysis and hydrolysis. When TBP is broken down, dibutyl and monobutyl phosphoric acids are formed, which can cause difficulties during the process of stripping actinides (Cuillerdier 1991; Nash 1993b; Spjuth 2000; Mathur 2001). The PUREX procedure to reprocess used fuel is geared toward extraction of elements that can be used in MOX fuel. The process can either partition uranium separately or concurrently with neptunium and plutonium, depending on valence states of metals, which can be fixed during pre-treatment. After extraction, the metal-loaded organic solvent is stripped to collect the uranium and/or neptunium and plutonium. The extractant can be recycled for further contacts with

freshly dissolved nuclear fuel (Mincher 2010). After six decades, the PUREX process is still the principal system of processing INF.

Transuranic Extraction (TRUEX) is a process geared toward the separation of elements with atomic number greater than 92, or any element that lies beyond uranium on the periodic table, from aqueous nitrate or chloride waste solutions (NEA 1997). The metal-extracting solvent used in the TRUEX extractant solution is octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). CMPO is used in conjunction with TBP and some diluent, which is typically a paraffinic hydrocarbon having 12 carbon atoms. Specifically, the TRUEX extractant mixture consists of approximately 0.2 M CMPO and 1 M TBP (NEA 1997).

Compared to TBP, CMPO does not break down as readily when exposed to radiation. However, CMPO still can break down into acids which interfere with actinide stripping (Nash 1993a; Nash 1993b). Moreover, both TBP and CMPO cannot be disposed of by burning, and create more waste. A rule of thumb known as the “CHON” principal is that only compounds containing carbon (C), hydrogen (H), oxygen (O) and nitrogen (N) are incinerable. A drawback to both TBP and CMPO is that both contain phosphorus, rendering them noncombustible. This factor leads to an increase in volume of secondary waste, which counteracts one of the main goals of reprocessing. The French invented a process known as Diamide Extraction (DIAMEX) to combat this problem (NEA 1997).

Like TRUEX, the DIAMEX process is targeted towards extraction of transuranics. However, unlike the previously mentioned procedures, the chemical extractants used in DIAMEX do not contain phosphorus. Thus, the extraction solvent is entirely incinerable.

DIAMEX implements amides in lieu of phosphorus-containing chemicals. Monoamides can extract tetravalent actinides and lanthanides through coordination with the oxygen atom in the amide group, and diamides can be used to extract trivalent actinides and lanthanides because they have two oxygen atoms (Shimada 2004).

A common diamide used in DIAMEX is dimethyldibutyltetradecylmalonamide (DMDBTDMA). The use of diamides is advantageous because they are not readily soluble in the aqueous nitric acid solutions, and they are able to withstand radiation and heat. However, the malonamide is unable to extract elusive trivalent americium atoms well, so further research must be done to identify a more versatile amide (NEA 1997).

A common disadvantage of PUREX, TRUEX, and DIAMEX is that multiple organic phases must be used to complete the separations. While one solvent extraction can pull the targeted nuclides to the organic phase, fresh organic solvent must be added in order to separate the extracted elements from each other. This is costly because there is increased the amount of waste to be stored and the amount of chemicals that are required for the procedure. Furthermore, TBP is susceptible to thermal and radiation degradation, and does not have the properties necessary to be a reusable extractant.

In an effort to create a solvent extractant that can be reused, scientists in Russia invented the Universal Extraction (UNEX) process. UNEX is a simultaneous extraction procedure, targeted toward cesium, strontium, actinides, and lanthanides (Romanovskiy 2006). The UNEX extractant consists of 0.08 M of chlorninated cobalt dicarbollide (CCD) in acid form, up to 0.02 M polyethylene glycol (PEG), and 0.02 M of a carbamoylmethyl phosphine oxide (CMPO) derivative in the inert polar diluent

phenyltrifluoromethyl sulfone (FS-13) (Romanovskiy 2006). CMPO and CCD are both relatively stable against degradation effects.

CCD is a widely implemented extractant of cesium. Synergistic effects can occur when some chemical extractants are used in combination with CCD, which can greatly increase the extraction yield and other properties of the reaction. In the UNEX process, cesium and strontium, along with actinides and lanthanides, can be simultaneously extracted from the acidic solution with high distribution ratios (Romanovskiy 2006). The high extraction yield is attributable to the synergistic nature of CCD with CMPO.

UNEX was initially implemented for extractions only in radioactive waste containing low concentrations of radionuclides. The main goal of the procedure was to reduce the amount of waste requiring long-term storage and disposal. The UNEX process could not be used to treat dissolved nuclear fuel because used fuel is too concentrated with actinides, lanthanides and fission products. The reason for this limited utility is that CMPO and CMPO-metal complexes have low solubility in the organic solution. CMPO has a maximum solubility of 0.02 M in FS-13 (Romanovskiy 2006).

Inspired by DIAMEX, specifically the use of diamides as extractants, researchers have sought to replace CMPO in the UNEX process, although not because of their adherence to the CHON rule. Substituting diamides for CMPO in the UNEX process will allow for the processing of waste with high concentrations of radionuclides because diamides have higher solubility in FS-13 than CMPO. Also, diamides are relatively inexpensive to produce, and like CMPO, will act synergistically with CCD.

Used alone, diamides form neutral solvates with the targeted metal through a chelating mechanism. When the diamides and CCD are used together, their unified extraction ability is greater than the sum of each on their own. Thus, CCD and diamides are synergistic extractants, and their combined use has the potential to renovate extraction procedures used for reprocessing used nuclear fuel and improve the nuclear industry immensely. Several diamides have been proposed as replacements for CMPO, although their radiation and thermal stability still must be tested to ensure they are feasible for UNEX.

2.2 Extraction Chemistry

Extraction chemistry must be thoroughly examined in order to design an optimal diamide to replace the poorly soluble CMPO in the UNEX process. Polarizability of a molecule is a useful property to manipulate when strategizing a chemical extraction. Polarizability is closely related to electronegativity; specifically, the property is linked to the size of the atom or ion, and how easy its electron cloud can be distorted (Carey 2000). Polarizability can be qualitatively defined as either soft or hard. When atoms have similar electronegativities, the larger atoms tend to be softer than smaller atoms. Soft species usually act as bases and are more chemically reactive because they can more readily donate their electrons. Interactions between hard species are typically governed by electrostatic attraction. “Soft-soft” interactions tend to be dominated by mutual polarization (Pearson; Ho 1977; Jenson 1980). Greater hardness trends with greater electronegativity.

Specifically, metal cations will become harder as their oxidation number increases (Carey 2000).

Actinides are electropositive and in solution they typically have oxidation states from 2 to 6. An actinide cation is a hard Lewis acid, meaning it is prone to accept an electron pair from a donor species, preferably a hard Lewis base site on the ligand to which it binds. Actinide-ligand complexes are usually formed through ionic bonding, and their thermodynamic bond strengths are governed by both electrostatic attraction and steric strain. Generally, the bond strengths of actinide complexes increase in the order $AnO_2^+ < An^{3+} \leq AnO_2^{2+} < An^{4+}$. Trivalent americium is an actinide of particular interest because it eludes extraction by commonly used chemicals. Studying americium's lanthanide counterpart, or "homolog", europium, is also important. Americium and europium have analogous electron configurations in their ground and ionized states (Choppin 2006).

In general, favorable reactions occur between species of like polarities. Hard species are more reactive with other hard species, and likewise, soft with soft. Trivalent actinide and lanthanide cations with similar ionic radii will bind equally well to hard donor ligands, which contain either oxygen or fluorine. The hard actinide or lanthanide species will still bind with a soft ligand, although not as strongly. Soft donor ligands contain either nitrogen, sulfur, or a halide other than fluorine. In general, trivalent actinide cations tend to form more thermodynamically stable complexes with soft donor ligands than do trivalent lanthanides cations (Choppin 2006).

An actinide-ligand complex with a soft donor ligand will be best formed in organic solvent because water is a strong donor and will steal the actinide from the soft ligand

(Choppin 2006). Complexation of actinides with soft donor ligands requires either high concentrations of the ligand, multiple bonding sites on the ligand, or a supplementary hard donor site on the ligand. Particularly, diamides of dipicolinic acid contain soft donor ligands, an aromatic nitrogen site, and supplementary hard-donor carbonyl groups on either side. A diamide of dipicolinic acid, known as N, N' dimethyl N, N' ditolyl dipicolinamide is shown in the image below. Specifically depicted is the ortho isomer, Et(o)TDPA.

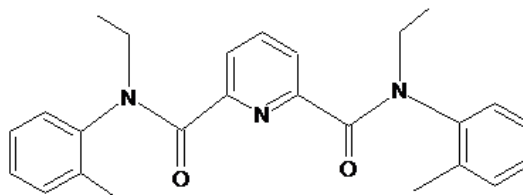
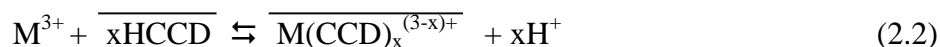
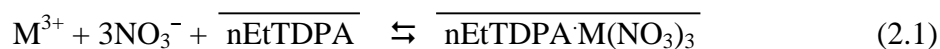
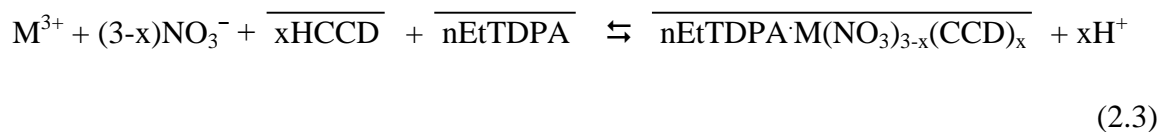


Figure 2.1 Molecular structure of Et(o)TDPA

These diamides are tridentate ligands and act as neutral chelating extractants (Cuillerdier 1991) as they have three separate sites to bind a single metal cation. CCD forms ion-association complexes. Both chemical reactions are displayed in equations 2.1 and 2.2 below:



These two equations can be combined to represent the chemical reaction that would occur with both extractants in solution, shown in equation 2.3:



At lower acid concentrations, extraction by CCD is the predominant mechanism, and the complex $[M \cdot nEtTDPA](CCD)_3$ is formed. At higher acidities, extraction by EtTDPA dominates; the possible complexes formed are $[M \cdot nEtTDPA](CCD)_3$, $[M(NO_3) \cdot nEtTDPA](CCD)_2$, $[M(NO_3)_2 \cdot nEtTDPA](CCD)$, and $[M(NO_3)_3 \cdot nEtTDPA]$, depending on the pH of the solution (Rais 1999).

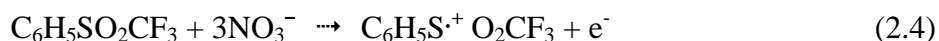
2.3 Radiolysis & Hydrolysis

Radiolysis is the decomposition or dissociation of a substance or molecule as a result of radiation. Exposure to radiation can cause cleavage of one or more chemical bonds. It is important to study a radionuclide-extractant's ability to withstand radiation because if it is used in dissolved nuclear fuel, it will be bombarded with all kinds of decay products and needs to be able to maintain its extraction properties. Radiolytic production of transient reactive radical species, such as $\bullet OH$ and $\bullet NO_3$, from irradiated solutions and their reactions with molecules in solution are known to be important sources of radiation damage (Lapka 2010; Mincher 2010).

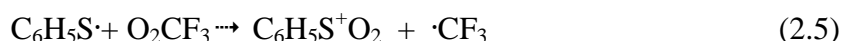
Hydrolysis occurs when a water molecule dissociates and either the proton or the hydroxide ion attacks a chemical bond in another species and cleaves it. Hydrolysis can occur in neutral solution, or be an acid or base catalyzed reaction. It is essential to study the hydrolytic effects on an extractant used in dissolved nuclear fuel, because the fuel is dissolved in nitric acid which will lead to acid-catalyzed hydrolysis.

In the UNEX process, several chemicals may undergo radiolytic degradation. The diluent used, FS-13, is the inert solvent in which the metal extractants are dissolved. Given

that the diluent comprises more than 99% of the extractant solution, radiolysis products of FS-13 may have a significant effect on the stability of the diamides. It is possible that unstable radiolysis products of FS-13 will cleave the diamide molecules, causing changes in their structure and extraction ability. Direct products of the radiolysis of FS-13 may include free electrons and the sulfone radical cation, as shown in equation 2.4 (Mincher 2007):



The unstable radical cation produced will then decay into a sulfur-centered cation and the trifluoromethane radical, shown in equation 2.5 (Mincher 2007):

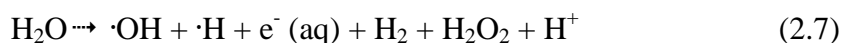


Next, two fluoromethane radicals would combine to produce hexafluoroethane (CF_3CF_3) (KRI 1999).

There is likely also some water present in solution, which may lead to hydrolytic effects. The trace amounts of water present may hydrolyze the sulfur-centered cation (produced from the radiolysis of FS-13) to produce a benzenesulfonic acid, as shown in equation 2.6 (KRI 1999).



The radiolytic products of water are shown in equation 2.7 (Buxton 1988):



If dissolved O_2 is also present, the solvated electron and the hydrogen radical will be scavenged by the O_2 molecule, shown in the following equations 2.8 and 2.9 (Spinks 1991):



As a result, the hydroxyl radical ($\cdot OH$) is the predominant reactive species produced from radiolysis and will act as an oxidizing agent.

Due to the acidic environment created by dissolving nuclear fuel, the radiolysis of nitric acid is also important to extraction chemistry. The radiolysis of nitric acid will produce the hydrogen radical and the nitrogen trioxide radical (Mincher 2007). This may lead to increased degradation because there will be more free radicals available to cleave chemical bonds. It is expected that molecules in the sample solutions will be fragmented by radiolysis and hydrolysis.

Hydrolysis and radiolysis of the diamide molecule is of particular interest. Previous studies have shown that the most likely point of cleavage of an amide is at the carbonyl-nitrogen bond; this is because the C-N bond is relatively weak (Carey 2000). Referring to bond dissociation to uncharged radical fragments, the energy required to break the C-N bond is only 66 kcal/mol, compared to the cleavage of the C-C bond which needs 81 kcal/mol, and the carbonyl bond which requires 173 kcal/mol (Janz 1967). Figure 2.2 displays an image of Et(m)TDPA with the likely points of cleavage highlighted in red.

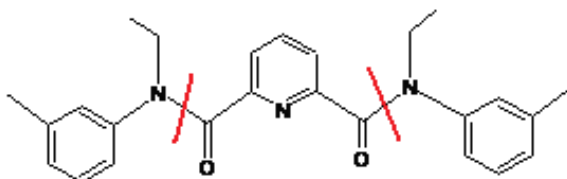


Figure 2.2 EtTDPA bond cleavage

The diamide molecule may be ionized or broken down into radicals. The molecule would then stabilize to its dipicolinic acid derivative, shown in Figure 2.3:

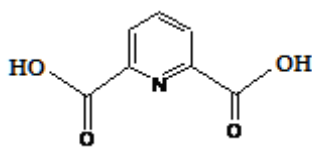


Figure 2.3 Dipicolinic acid chemical structure

The other fragment produced would be an amide molecule, specifically the corresponding isomer of N-ethyl toluidine, displayed in Figure 2.4:

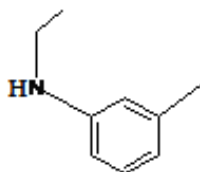


Figure 2.4 N-ethyl toluidine chemical structure

2.4 Project Goals

This study attempted to investigate a suitable replacement for CMPO with a more soluble organic complexant, which will also act synergistically with CCD. Due to these desired features, diamides of dipicolinic acid were selected for this study. In order to evaluate the effectiveness of EtTDPA for industrial reprocessing purposes, radiolytic and

hydrolytic resistance of the proposed extractant was examined by exposure of the samples to gamma radiation or hot nitric acid; then their extraction performance was tested.

Distribution ratios of trivalent americium and europium were determined to quantify the effect of irradiation or hydrolysis on the separation factors and extraction yields. Selected samples were analyzed using high performance liquid chromatography coupled with mass spectrometry (HPLC-MS), with the aim to determine changes in the molecular structures of the investigated diamides. The changes observed in the experiment are quantified and discussed in the present work.

Chapter 3 Materials and Methods

This chapter details the experiments performed in order to evaluate the radiolytic and hydrolytic stability of the extractant. Included are the chemical synthesis procedures, information on where chemicals were obtained, structural information, sample preparation procedures, and experimental procedures.

3.1 Chemicals

The ortho, meta, and para EtTDPA isomers were synthesized through the reaction of thionyl chloride with dipicolinic acid, which formed acyl chlorides. Next, the acyl chlorides were mixed with either ortho, meta, or para isomers of N-ethyltoluidine to produce the respective EtTDPA isomeric solution (Nikitskaya 1958). The chemicals used were obtained from TCI Co. LTD and were analytical grade; they were not additionally purified for the synthesis of EtTDPA.

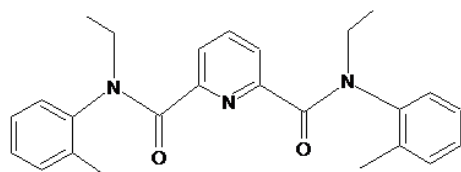
The polar solvent trifluoromethyl-phenyl sulfone (FS-13) used in this study was obtained from Marshallton Research Laboratories Inc., located in King, NC, USA. No modifications were made to the polar solvent; it was used as received. The cesium salt of chloro-protected cobalt bis(dicarbollide), $\text{Cs}[(8,9,1\text{-Cl}_3\text{-C}_2\text{-B}_9\text{-H}_8)_2\text{-3-Co}]_2$ (CsCCD) was obtained from Katchem, located in Rez, Czech Republic, and used as received.

The stock solution of hexavalent chlorinated cobalt dicarbollide acid (HCCD) was synthesized by first dissolving the cesium salt CsCCD in FS-13. Next, the solution was agitated with a significant stoichiometric excess of perchloric acid, converting the salt into the acid form, HCCD. The solution was washed with dilute nitric acid (HNO_3) in order to

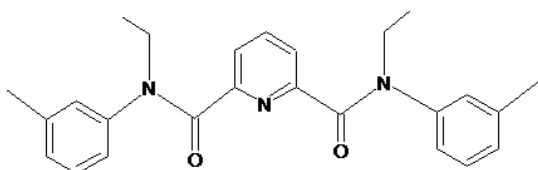
remove any residual perchlorate. The resulting stock solution was titrated using a potentiometric titrator with standard base to determine the concentration of HCCD. The ratio of $\text{H}^+:\text{CCD}^-$ was 1:1 in the organic phase, due to the cation exchange with the excess acid. In solution, the HCCD is dissociated into its ionic components, and it is assumed to behave as a strong acid (Vanura 1982).

Finally, in order to create the extractant used in this study, the EtTDPA was combined with the HCCD in FS-13 at the desired concentrations of each. The stock solution of EtTDPA was diluted to 0.01 M in FS-13. The stock solution of HCCD was diluted with FS-13 to 0.02 M.

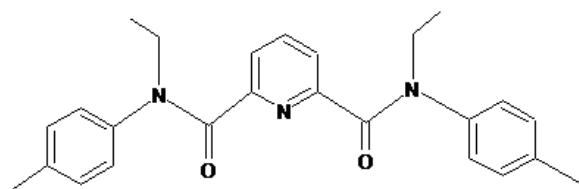
Figure 3.1 displays the structures of the chemicals used in the extraction solutions. Figures 3.1a-c show the three isomeric structures of EtTDPA. Figure 3.1c presents the structure of the CCD^- anion and Figure 3.1d shows the structure of the solvent FS-13.



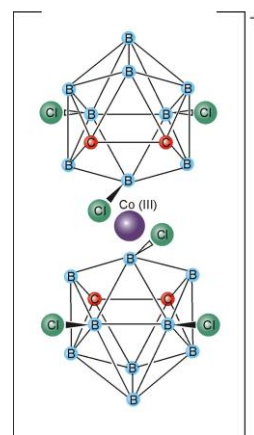
a) N,N'-diethyl- N,N' di(ortho)tolyl-diamide of dipicolinic acid
(Et(o)TDPA)



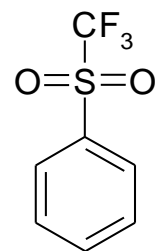
b) N,N'-diethyl- N,N' di(meta)tolyl-diamide of dipicolinic acid
(Et(m)TDPA)



c) N,N'-diethyl- N,N' di(para)tolyl-diamide of dipicolinic acid
(Et(p)TDPA)
(molecular weight: 401 amu)



c) Chlorinated Cobalt Dicarborllide
(CCD⁻)
(Molecular weight: 530 amu)



d) Trifluoro methyl phenyl sulfone
(FS-13)
(Molecular weight: 210 amu)

Figure 3.1 Molecular structures of species in the extractant solution

3.2 Sample Preparation

The samples used to study the stability of the extractant were prepared in 7-mL glass vials. A micropipette was used to transfer 2 mL of the extractant into each vial. Unsaturated samples of the extractant were used directly from this preparation. Nitric acid-saturated samples were prepared by first adding an equal volume of 3 M nitric acid to the sample vials, and then agitating them for 4 minutes. The samples were then centrifuged for one minute to achieve aqueous-organic phase separation. The acidic aqueous phase was siphoned out of the vial.

3.2.1 Radiolysis

Prior to irradiation, for each EtTDPA isomer, two sample sets were created: unsaturated and acid-saturated. The purpose of analyzing both unsaturated and saturated solutions was to allow for observation of hydrolysis effects and radiolysis effects, both together and separately. Irradiation was carried out in a GAMMACELL 220 cobalt-60 irradiation unit, which consists of a ring-shaped source. The cobalt-60 annular source is housed behind lead shielding and within a cylindrical holder.

For each radiolysis sample set, four radiation doses were obtained: 20 kGy, 40 kGy, 60 kGy, and 80 kGy. All samples were stored in a refrigerator (approximately 34 °C) until extraction and spectroscopy experiments were carried out in order to avoid any chemical processes that may lead to degradation of the extractant.

3.2.2 Hydrolysis

Solutions containing Et(o)TDPA, along with the other components of the extractant, were saturated with nitric acid prior to heating. The temperature was held constant in a thermostat, and samples were removed at various exposure times: 24 h, 48 h, 72 h, and 96 h. Once prepared, all samples were refrigerated until experimental use for consistency.

3.3 Extraction Procedure

The extraction experiments were carried out in 2-mL plastic sample vials. A micropipette was used to transfer 500 uL of each extractant sample into a corresponding vial. Next, 500 uL of 3 M nitric acid was added to all extraction vials. The vials were agitated for 4 minutes and then centrifuged. The aqueous phase was removed from each sample. This was done in order to pre-equilibrate the samples because the chemicals studied are also known to extract nitric acid.

Subsequently, 490 mL of 3 M nitric acid was added to each extraction vial. Then, 10 uL of aqueous source (either Am-241 or Eu-152/154) was added to each vial and the samples were again agitated for four minutes, then centrifuged to achieve phase separation. For each sample, equal amounts of each phase (200 uL - 250 uL) were removed and transferred to glass liquid scintillation counting (LSC) vials. For each extraction sample, two LSC vials were prepared: one for the aqueous phase sample, and one for the organic phase. Each vial was counted in a sodium iodide well detector for five minutes.

3.3.1 Calculations

Distribution ratios were determined using equation 3.1. Parameters included in the equation are count rate (CR) measured from the organic (org) or aqueous (aq) sample, and volume (V) of the solution that was counted in the detector. Extraction yield (Y) can also be determined, along with separation factors (SF); calculations for each are shown in equations 3.2 and 3.3, respectively.

$$D = \frac{(CR_{org})/V_{org}}{CR_{aq}/V_{aq}} \quad (3.1)$$

$$Y = \frac{D}{D+1} \quad (3.2)$$

$$SF = \frac{D_{Am}}{D_{Eu}} \quad (3.3)$$

The distribution ratios quantify the success of the extraction experiments. A higher the distribution ratio indicates a better extraction, and that more of the targeted metal was removed from the initial aqueous solution. From the distribution ratios, the extraction yield can be calculated, which represents the fraction of the metal removed from aqueous solution. The separation factors, which were also subsequently calculated using distribution ratios, are of significance because the ultimate goal of any separation is to isolate radionuclides in solution.

3.4 Mass Spectrometry

Liquid chromatography, followed by mass spectrometry (LC-MS), was performed on radiolysis samples to analyze the structure. LC-MS was performed with an Applied

Biosystems MDS Sciex 3200 Q Trap LC (Shimatzu Prominance)-MS/MS system. The gradient for the LC-system applied a 10% - 90% acetonitrile in water solution for the positive mode analysis to get separation of compounds during elution over approximately 50 minutes. The elution gradient for the negative mode analysis used a solution containing 10% - 90% acetonitrile in formic acid. A C-18 column was used for all elutions. Additional settings used in the LC-MS process are displayed in Table C.1 of Appendix C.

Mass spectrometry was performed on acid-unsaturated radiolysis sample solutions of Et(o)TDPA with CCD and FS-13. Hydrolysis samples and the acid-saturated radiolysis samples were unable to be analyzed because nitric acid is damaging to the mass spectrometry equipment used.

Chapter 4 Results and Discussion

This chapter of the thesis reports and analyzes the extraction and mass spectrometry data acquired for three studied molecular derivatives of diamides of dipicolinic acid: Et(o)TDPA, Et(m)TDPA, and Et(p)TDPA. These chemicals are being investigated with regards to their radiolytic and hydrolytic stability in the extraction processes designed for separation of americium from europium and other lanthanides.

4.1 Extraction Studies

In order to establish the effects of radiolysis on the stability and viability of the extractants in real separation systems, the data on distribution ratios obtained from extraction experiments with both nitric acid-saturated and acid-unsaturated extractants are plotted as a function of gamma dose. Data from hydrolysis experiments are also presented in this section; only the ortho isomer was chosen for examination of hydrolytic effects. The distribution ratios for americium and europium were used to calculate separation factors for the actinide and lanthanide, in order to assess the ability of the extractant molecule to target and isolate the desired radionuclides in the real extraction process. Overall, the purpose of analyzing the distribution ratio data is to determine the effects of isomeric structure, irradiation dose, and acidic conditions on the extraction capabilities of diamides of dipicolinic acid. In order to be useful in large-scale reprocessing undertakings, the chemical extractant must be able to withstand conditions, both hydrolytic and radiolytic, within the dissolved nuclear fuel.

4.1.1 Distribution Ratios

Figure 4.1 displays the dependence of distribution ratio as a function of absorbed gamma dose for the extraction of americium-241 with the irradiated acid-unsaturated extractants. Results show a significant disparity between the distribution ratios from extractions performed with the ortho isomer of the diamide of dipicolinic acid compared with the meta and para isomers. Et(o)TDPA is clearly the most effective extractant for americium, and all distribution ratios are above 10, indicating that more than 90% of the metal was extracted (see equation 3.2).

Furthermore, distribution ratio significantly increases from 0 dose to 20 kGy, and Et(o)TDPA fares well even when given doses as high as 80 kGy. This indicates that the extractant is not only stable under radiolytic conditions, but that irradiation improves its extractability. This phenomena has been observed in other studies, and is an established effect (McKay 1984). This enhancement in distribution ratio by absorbed radiation dose may be attributed to the formation of radiolytic byproducts that contribute to the extraction process. Compared to the non-irradiated solution, the irradiated extractant does a better job of removing americium from the aqueous phase and transferring it to the organic phase.

The extractions done with Et(m)TDPA and Et(p)TDPA never reach a distribution ratio of 10. Irradiated samples containing meta and para isomers of EtTDPA have a declining trend in extraction capacity with increased absorbed dose. Their extraction potential is much lower than Et(o)TDPA.

Figure 4.2 displays data from americium extractions with the acid-saturated solutions. These data also indicate that the Et(o)TDPA solution is a significantly better

extractant for americium, even when acid-saturated (exposed to hydrolytic interactions). Again, radiation effects are shown as the acid-saturated Et(o)DTPA is the most effective extractant for Am-241 when given a 20 kGy gamma dose, even compared to the Et(o)TDPA solution that was not irradiated. This finding parallels results from similar studies, as well as from the unsaturated data set previously discussed from this study. This agreement suggests that, to a degree, radiolytic conditions are favorable in terms of the diamide's ability to extract trivalent metals.

Distribution ratios for the Et(o)TDPA solution decline in an approximately exponential manner after the 40 kGy dose, however they remain above 10, indicating a high extraction yield for all samples. Unlike the Figure 4.1, Figure 4.2 shows that the Et(o)TDPA solution does not have enhanced extractability at doses higher than 40 kGy. This may indicate that the combination of a hydrolytic environment at doses of 60 kGy and higher causes degradation of the extraction capacity of Et(o)TDPA, as well as the solutions containing Et(m)TDPA and Et(p)TDPA. The data displayed in Figure 4.2 indicate that the Et(o)TDPA solution can withstand both radiolysis and acid effects to a reasonable degree, and these findings are in agreement with the results from extraction experiments displayed in Figure 4.1. The americium extraction data show that the Et(o)TDPA extractant solution is stable to, and even enhanced by radiolysis.

Figure 4.3 displays data from europium extractions with the unsaturated extractants. Similar to findings from the americium study, Figure 4.3 shows that the extractant proves to have enhanced extractability when delivered a 20 kGy absorbed dose. Consistent with the americium study is the significant increase in the europium distribution ratio using

Et(o)TDPA when the extractant received doses of 20 kGy and higher. Again, a possible explanation is that irradiation results in structural or chemical modification of the extractant in a way that makes it more conducive to extraction of the trivalent metal.

Also similar to the findings from the americium-241 study, Et(o)TDPA is the best extractant for europium. The data verifies that the ortho isomer extracts europium significantly better than meta and para isomers. Et(o)TDPA is stable over increasing dose increments. The radiolytic stability of Et(o)TDPA is apparent, and verified by the plateau shape in the distribution ratio plot at doses of 20 kGy and above.

Figure 4.4 displays the europium distribution ratios with the acid-saturated extractant as a function of gamma dose. It is clear that that acid-saturated Et(o)TDPA solutions do not fare as well as the unsaturated extractant in terms of extraction capability for europium when exposed to radiation and acid effects. There is no increase in distribution ratio with increased absorbed dose, as was with the americium extraction data, and the unsaturated europium extraction data. Perhaps the combination of radiolytic and hydrolytic degradation causes chemicals to break down to a state that is destructive to the extraction of the trivalent lanthanide cation.

All extraction experiments indicated that Et(o)TDPA solutions were the best extractants compared to the other isomers. It is uncertain as to why the Et(o)TDPA is the best extractant, but this finding could be due to sterics of the extraction reaction. The constituent positions of the methyl group on the tolyl rings of the diamide may have significant effects on the ability of the diamides to latch onto the targeted metal. The ortho

isomeric structure allows for the most “room” for the metal to attach to the donor sites on the molecule.

Figure 4.5 displays data from hydrolysis experiments on the extraction capability of Et(o)TDPA. The data collected only demonstrate the effects of hydrolysis, isolating the acid effects. The Et(o)TDPA solution extracted americium better than it did europium overall. The experiment showed that the Et(o)TDPA solution has hydrolytic stability over longer periods of time for the extraction of americium, and the distribution ratios even increase significantly with time. This distribution ratio augmentation with hydrolysis of the chemicals may be due to formation of chemicals that aid in extractions.

Hydrolytic enhancement of extractions was not observed from europium experiments. There was a measureable decrease in the extraction capability of the system under purely hydrolytic conditions for europium extraction, though the extractant maintained decent effectiveness. The increase in distribution ratio for americium experiments but not europium extractions may be due to hydrolysis of the chemicals and the subsequent formation of an amide (see Figure 2.4). Because the amide contains a soft donor site (N), it may preferentially extract trivalent americium over trivalent europium due to thermodynamics.

Americium extractions by Et(o)TDPA are enhanced by hydrolytic environments, and to a degree by radiolytic conditions as well. Europium extractions with unsaturated solutions were enhanced with radiation, although not with hydrolysis in conjunction with radiation, nor with hydrolysis alone. Overall, Et(o)TDPA retains its extraction ability and

appears that Et(o)TDPA has good stability when exposed to radiolytic and hydrolytic environments.

Figure 4.6 displays the comparison between americium distribution ratios for saturated radiolysis and hydrolysis samples for Et(o)TDPA extractants over time. The time for the radiolysis samples was measured from the time the samples were in the irradiator. It took approximately 48 hours to achieve a 20 kGy dose increment. The hydrolysis and radiolysis sample sets coincide very well, and both maintain distribution ratios above 10, meaning that upwards of 99% of the americium is extracted (from equation 3.2). It appears that the Et(o)TDPA extractant mixture can withstand both irradiation and heat. The acid saturated radiolysis sample set yields similar distribution ratios as the hydrolysis samples. This finding indicates that radiolytic effects are minimal on the Et(o)TDPA solution, which is a desirable characteristic of the extractant.

Overall, Et(o)TDPA is a better extractant for americium than it is for europium, which enhances the separation factors for actinides and lanthanides. The difference in extraction efficiency was expected. The diamide is a tridentate neutral chelator, because EtTDPA has two hard donor sites (oxygen) and one soft donor site (aromatic nitrogen). Due to the fact that generally, trivalent actinide cations form more thermodynamically stable complexes with soft donor ligands than do trivalent lanthanides cations, it is reasonable that americium extractions yielded higher distribution ratios than did europium extractions. The findings that the Et(o)TDPA is best when it comes to extracting americium is consistent with previous findings in other studies (Lapka 2010).

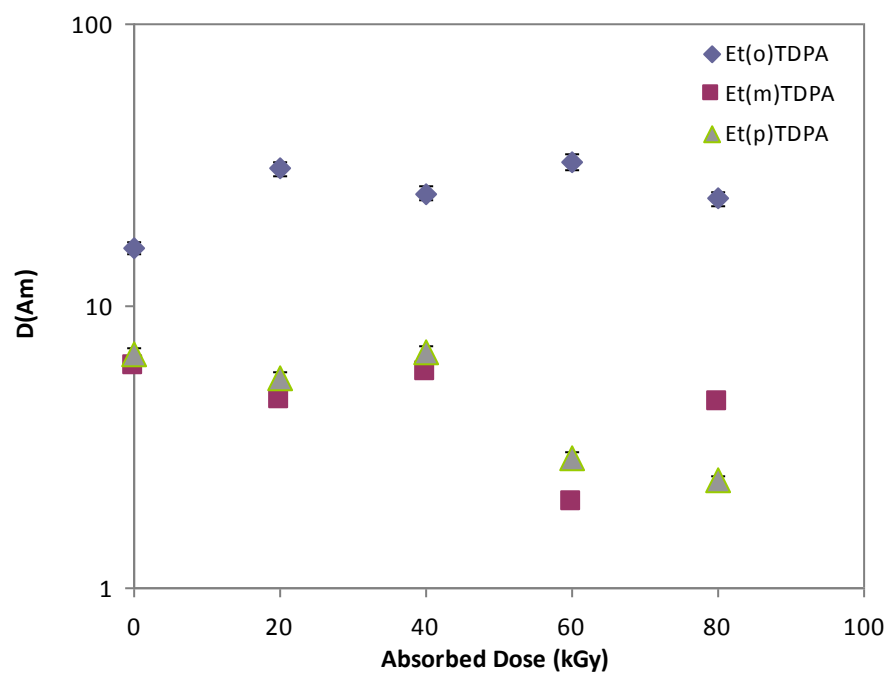


Figure 4.1 Americium distribution ratios from extraction with acid-unsaturated extractant as a function of absorbed dose

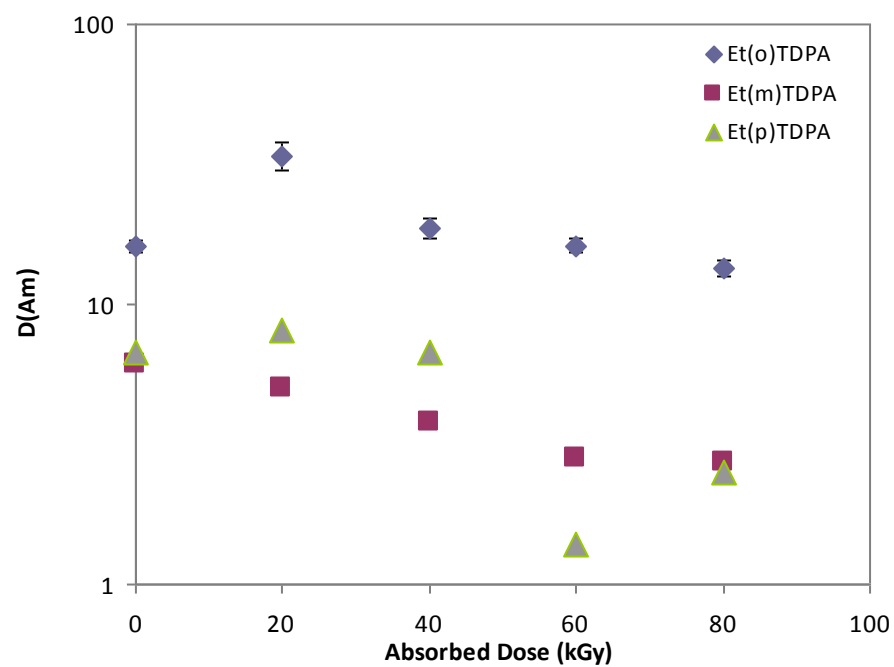


Figure 4.2 Americium distribution ratios from extraction with acid-saturated extractant as a function of absorbed dose

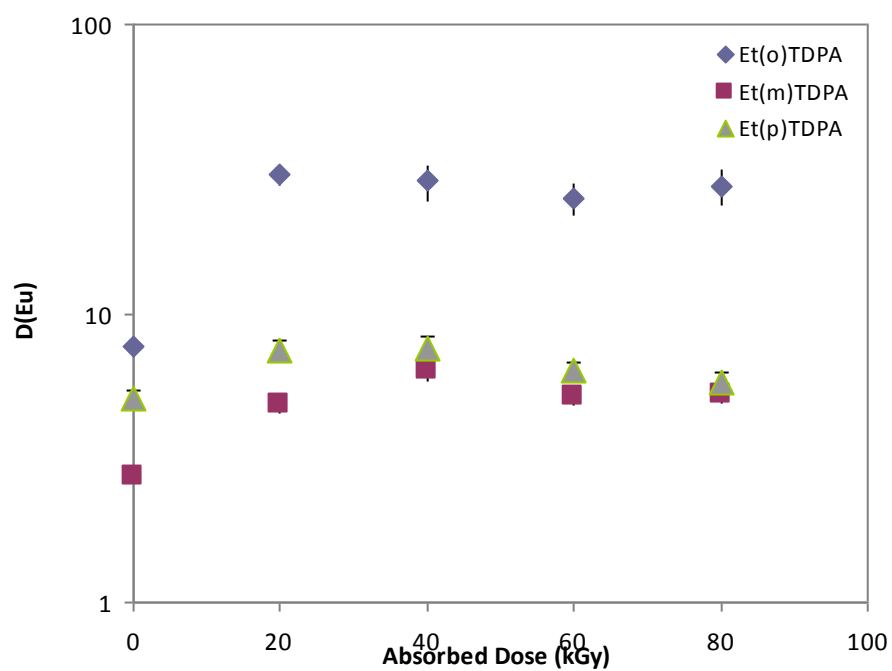


Figure 4.3 Europium distribution ratios from extraction with acid-unsaturated extractant as a function of absorbed dose

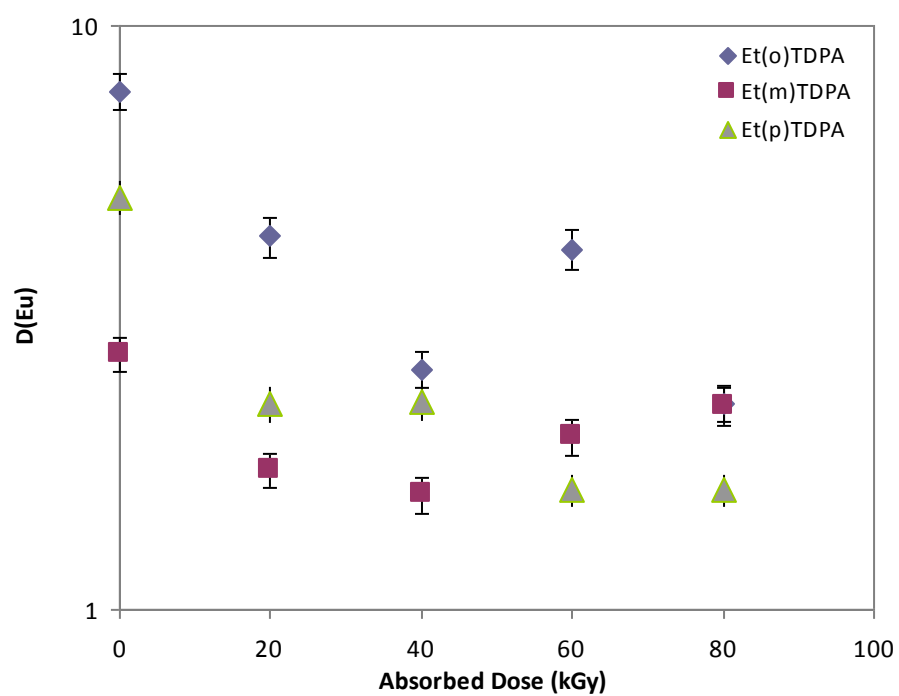


Figure 4.4 Europium distribution ratios from extraction with acid-saturated extractant as a function of absorbed dose

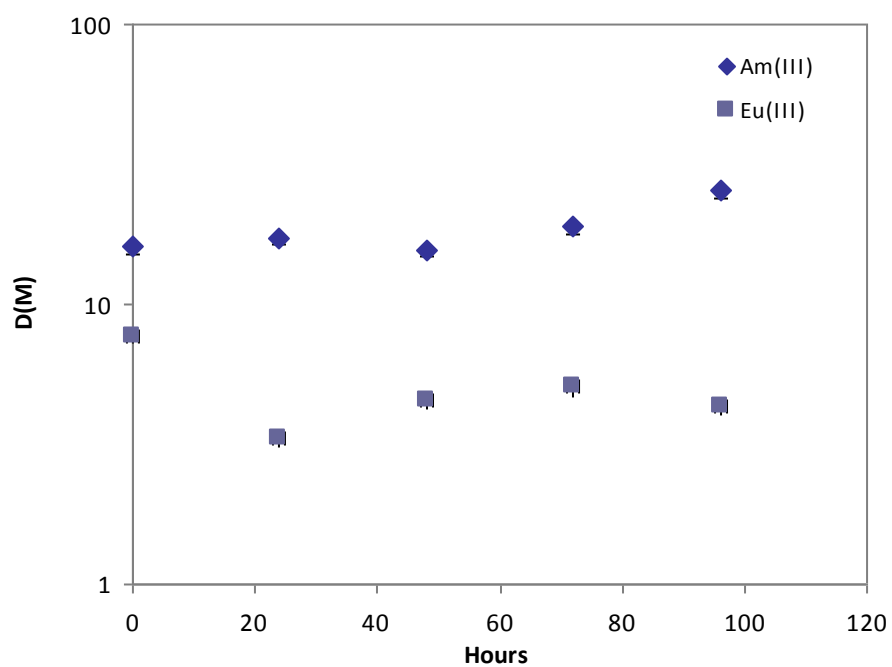


Figure 4.5 Effects of hydrolysis on distribution ratios of Am and Eu with Et(o)TDPA at 50 °C over time

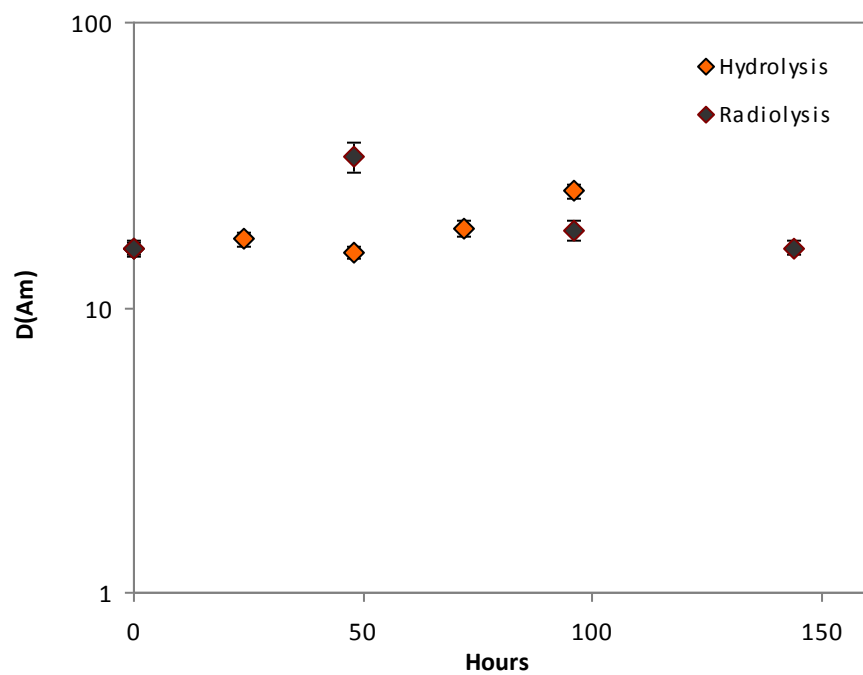


Figure 4.6 Comparison of distribution ratios from extractions with hydrolysis and acid-saturated radiolysis samples over heating and irradiation time

4.1.2 Separation Factors

As previously mentioned, Et(o)TDPA is a better extractant for americium than for europium. This feature allows for separation of the two radionuclides. The ability to separate the species is an important function of the extractant, as isolation of radionuclides is of great value. Trivalent europium is notoriously difficult to isolate, relative to other lanthanides; this is due to its ionic radius (Cotton 2006). The Am/Eu separation factors calculated for all radiolysis and hydrolysis experiments are summarized in Table 4.1.

Table 4.1 Separation factors for Am/Eu with diamidic extractant EtTDPA

a) Irradiated, acid-unsaturated extractant			
Dose [kGy]	Et(o)TDPA	Et(m)TDPA	Et(p)TDPA
0	2.1 ± 0.2	2.2 ± 0.2	1.3 ± 0.1
20	1.0 ± 0.1	1.0 ± 0.1	0.8 ± 0.1
40	0.9 ± 0.1	0.9 ± 0.1	0.9 ± 0.1
60	1.3 ± 0.2	0.4 ± 0.0	0.5 ± 0.0
80	0.9 ± 0.1	0.9 ± 0.1	0.4 ± 0.0
b) Irradiated, acid-saturated extractant			
Dose [kGy]	Et(o)TDPA	Et(m)TDPA	Et(p)TDPA
0	2.1 ± 0.2	2.2 ± 0.2	1.3 ± 0.1
20	7.8 ± 1.1	2.9 ± 0.2	3.6 ± 0.3
40	7.2 ± 0.8	2.4 ± 0.2	3.0 ± 0.3
60	4.0 ± 0.4	1.4 ± 0.1	0.9 ± 0.1
80	6.0 ± 0.6	1.2 ± 0.1	1.6 ± 0.1
c) Hydrolyzed extractant			
Dose [kGy]	Et(o)TDPA	Et(m)TDPA	Et(p)TDPA
0	2.1 ± 0.2		
20	5.2 ± 0.5		
40	3.4 ± 0.3		
60	3.8 ± 0.4		
80	5.9 ± 0.6		

Unsaturated solutions do not produce good separation of the two metals. In general, there is a decline in separation factor with increased dose. The acid- saturated extractants produce much better separations of the americium from europium than do the acid-

unsaturated solutions. This finding is apparent for both the irradiated sample series, as well as for the hydrolysis sample series. This could be due to formation of the amide constituent of the EtTDPA molecule upon degradation with both radiolysis and hydrolysis, or hydrolysis alone. As previously mentioned, an amide contains a soft donor ligand. The soft donor ligand will preferentially bind with trivalent americium over trivalent europium, thus enhancing the separation factors with increased formation of the amide. On the whole, the data obtained from extraction experiments with solutions exposed to both forms of degradation, radiolysis and hydrolysis, yielded the best separations. Solutions exposed only to hydrolytic conditions also showed decent separation properties.

4.2 Analysis of Molecular Damage

This investigation attempted to identify changes in chemical properties, such as structural reorganization or breakage of the extractant molecules. Analyses of the irradiated Et(o)TDPA solutions were performed over each of the 20 kGy increments of absorbed dose. The chromatograms and mass spectra collected as described in chapter 3.4 were compared to extraction data to ensure data sets are in support of each other.

Mass spectrometry is a very sensitive technique used to both qualitatively and quantitatively determine the masses of atoms, molecules, or their fragments present in the analyzed sample. The species in the analyzed sample are separated on a liquid chromatographic column and then automatically injected into the nebulizer capillary of the mass spectroscope, and ionized. The ions are accelerated and separated in the applied electric field according to their mass-to-charge (m/z) ratio of each species. The spectrum

is plotted with respect to relative abundance vs. m/z . The integral of each peak in the spectrum is proportional to the abundance of a corresponding species (Harris 2007).

During the mass spectrometry analysis, the neutral diamide will be converted to a protonated cation once it is condensed and enmeshed with the positively charged analyte. Since CCD^- is an anion, formed upon dissociation of HCCD in the polar organic diluents, it can be observed in the negative mode spectrum. For this reason, both the positive and negative mode spectra were collected.

Mass spectrometry is a useful tool for analysis of organic molecules; hence, if the Co-60 gamma rays (1.17 and 1.33 MeV) cleave chemical bonds in the diamide or CCD^- and fragment their molecules, these changes should be apparent in the mass spectra.

However, the technique does have drawbacks as well, due to the fact that radiolysis of the solution has not been studied in detail, and fragments produced are not definitively known. The resulting spectra contain an assortment of peaks that must be interpreted with scrutiny, as potentially, there may be many possible ions present. Also, other aerosol ions can be produced from the complexation of a neutral or charged molecule with an adduct. Common adducts include protons, ammonium ions, sodium ions, and potassium ions. Furthermore, the analyte may be chemically altered by radical species produced during electrospray.

Figure 4.7 displays an overlay of the positive chromatogram of the irradiated solutions containing Et(o)TDPA in the extractant solution. This positive chromatogram corresponds to the diamide in solution, and indicated that the diamide component of the sample solution was eluted from the liquid chromatography column at a time of 10.11

minutes. The chromatogram shows that there is not a significant change in the chemical composition of the diamide across the different gamma doses.

Figure 4.8 presents an overlay of the negative chromatogram of the non-irradiated solutions containing the ortho diamides of dipicolinic acid extractant solution. This negative chromatogram corresponds to the negative ion CCD^- in the solution, and shows that the anion was eluted from the liquid chromatography column at 17.46 minutes. There is also no significant change in the chromatogram across gamma doses. These findings support the data from the extraction experiments. The distribution ratios from the americium and europium extractions with Et(o)TDPA un-saturated solutions resemble a plateau, also indicative of the stability of the diamides with respect to radiolytic conditions.

Further investigation was done by analyzing the mass spectra of the two components apparent in the chromatography peaks in positive and negative mode. Mass spectra for the diamide and CCD^- are shown in Figures 4.9 and 4.10, respectively. Figure 4.9 displays the electrospray ionization mass spectra in positive mode for 20 kGy dose of the ortho solution at the corresponding 10.11 minute elution time. Alone, the diamide has a mass 401 amu and has neutral charge. Through processing in mass spectrometry, different adducts will attach to the diamide to produce a positively charged molecule that can be analyzed. The peak that occurs at a mass-to-charge ratio of 402 corresponds to the diamide of dipicolinic acid with a proton adduct. The peak that occurs at a mass-to-charge ratio of 424 corresponds to the diamide with a sodium cation adduct. All spectra are similar and show no considerable change across doses, therefore only one spectrum is included in this section. The positive mode mass spectra collected for the other sample doses are included

in Figure 1 of appendix C. A possible indicator of radiolytic stability of the diamides is that no change in the mass spectra is apparent across doses, and no byproducts of irradiation can be identified. However, this may in fact be a sign of reformation of the diamide from its constituents, after fragmentation from radiolysis.

A similar trend is shown in Figure 4.10 with displays the electrospray ionization mass spectrum in negative mode corresponding to the 17.46 minute elution time of CCD^- . Alone, CCD^- has a mass of 530 amu. The characteristic isotopic pattern of CCD^- is clearly displayed in this figure. CCD^- is loaded with B and Cl, which have various isotopes. The differences in their masses account for this isotopic pattern. Since CCD^- is already an anion an adduct is not required to analyze the molecule. As with the positive mass spectral analysis, there is no noteworthy change in the intensity of the spectra across the irradiated samples shown in the negative mass spectra across doses, so only the spectrum for the 20 kGy sample is included in this section. The observation of no change in the mass spectra of CCD^- across doses is expected, as CCD^- is known to be very stable (Rais 2004). The negative mode mass spectra collected for the other sample doses are included in Figure 2 of Appendix C.

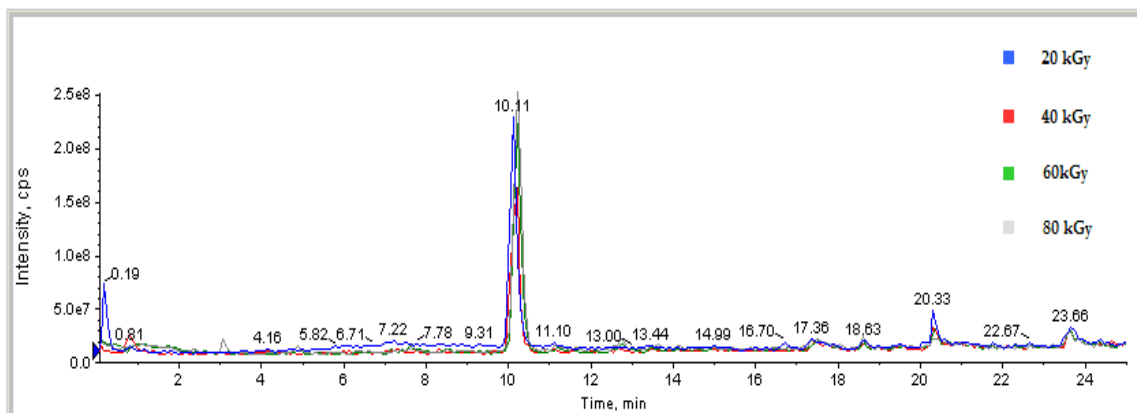


Figure 4.7 Chromatogram (positive mode) overlay of radiolysis samples

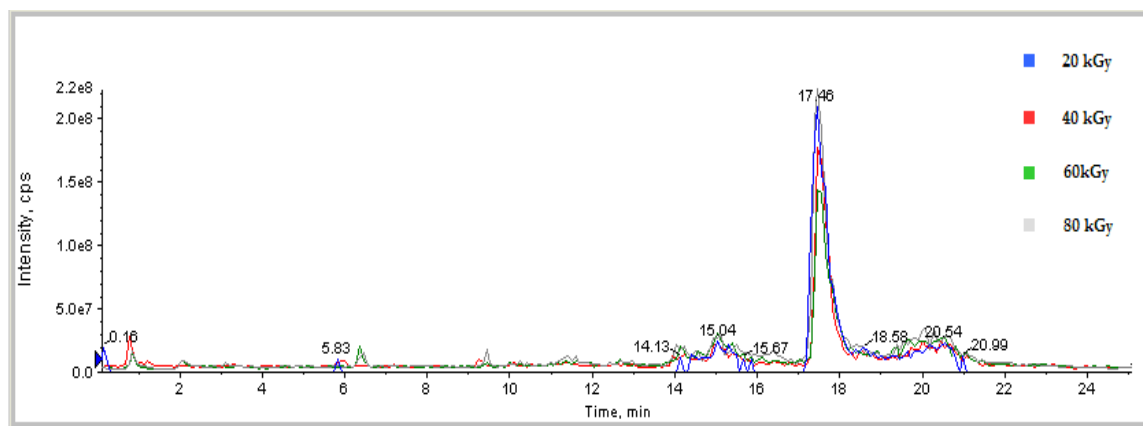


Figure 4.8 Chromatogram (negative mode) overlay of radiolysis samples

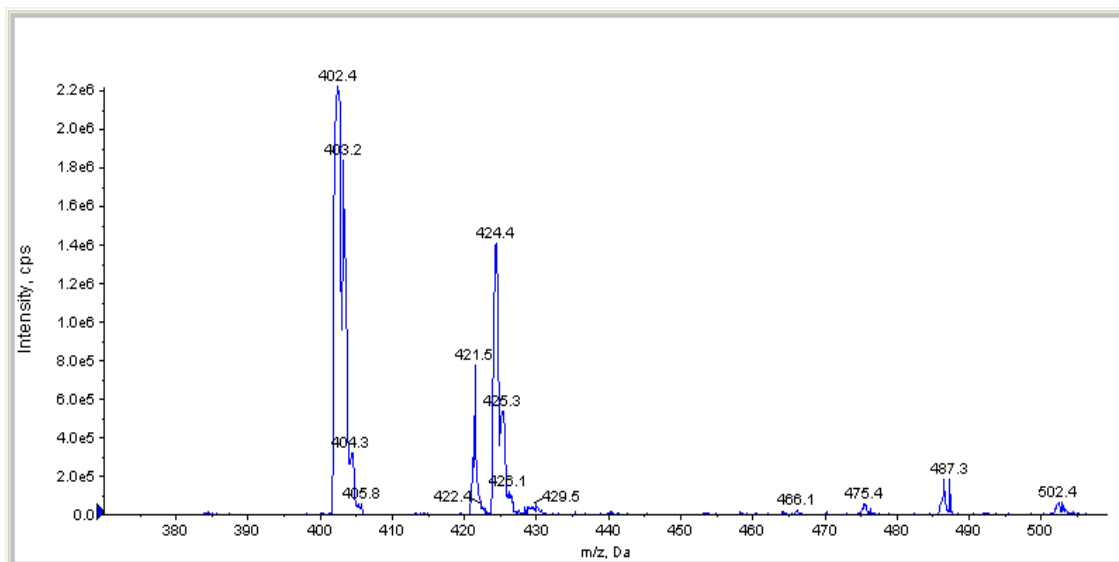


Figure 4.9 Mass spectrum in positive mode (Et(o)TDPA)

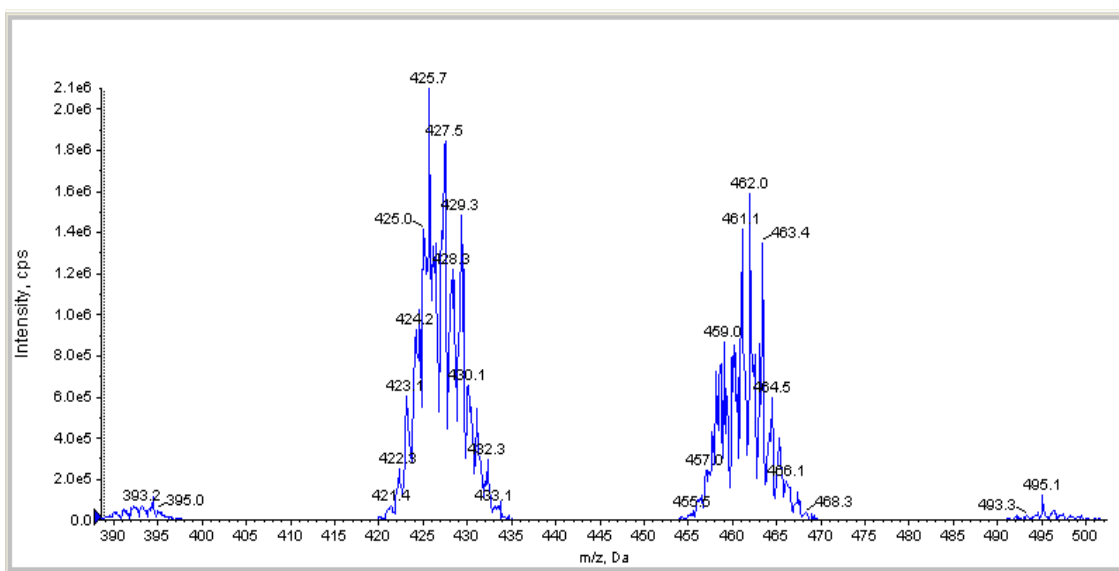


Figure 4.10 Mass Spectrum in negative mode (CCD)

The data from mass spectrometry is in agreement with the data from the extraction experiments. The Et(o)TDPA extraction solutions show a plateau with relation to extraction efficiency with respect to dose, indicative of stability; the resistance of Et(o)TDPA is supported by spectral analysis. Complementary studies performed by J. Lapka have analyzed the mass spectra of the meta and para isomers of the diamides, without CCD (Lapka 2010). The data from that experiment show a correlation with considerable changes in distribution ratios of extractions of americium and europium with significant changes in the mass spectra across gamma doses for Et(m)TDPA and Et(p)TDPA solutions (Lapka 2010). Due to the stability of the ortho configuration of the diamide, the mass spectra and liquid chromatography analysis of the samples do not differ significantly across doses.

4.3 Error Analysis

Error can arise from both random and systematic sources. Random error includes error in measurement, which in this case is due to volume uncertainty when pipetting solutions and detection uncertainty. Systematic error includes error in equipment calibration. In the case of the project presented in this work, systematic error is insignificant compared with sources of random error.

Uncertainty in the distribution ratios and separation factors were calculated in order to evaluate the accuracy of the data. The uncertainty in distribution ratio (σ_D) was calculated with equation 4.1:

$$\sigma_D = D \sqrt{\left(\frac{\sigma_{Or}}{[M]_{Or}}\right)^2 + \left(\frac{\sigma_{Aq}}{[M]_{Aq}}\right)^2} \quad (4.1)$$

The parameters in equation 4.1 include distribution ratio (D), absolute uncertainty (σ_x) in the metal concentration in each phase in counts per minute per unit volume (cpm/mL) (where x represent either organic (Or) or aqueous (Aq) phases), and measured metal concentration $[M]_x$ in cpm/mL for each phase. Absolute uncertainty in metal concentration was calculated using equation 4.2,

$$\sigma_x = [M]_x \sqrt{\left(\frac{\sigma_{CR}}{CR_x}\right)^2 + \left(\frac{\sigma_V}{V_x}\right)^2} \quad (4.2)$$

where x represents either Or or Aq, and σ_{CR} is the counting error (cpm) which is equal to the square root of the measured counts divided by the count time. Other parameters include count rate (CR) of the given phase (cpm), error in volume measurements (mL), represented by σ_V , and the volume in mL of either phase counted (V) in the detector. The upper limit of relative uncertainty in the volume transferred through the calibrated pipette is 3%. Thus 0.03 was the value used for relative error in volume, denoted by $\frac{\sigma_V}{V_x}$.

Uncertainty values for distribution ratios are given along with extraction date in Tables A.1-A.4 in Appendix A, and Tables B.1 and B.2 in Appendix B. Also of importance was the error in separation factors. Again, separation factor is just a ratio of distribution ratios, specifically the distribution ratio of the actinide metal for a given extraction experiment divided by the distribution ratio of the lanthanide metal. In order to determine

the uncertainty in separation factors, the standard deviation for both of the distribution ratios needs to be incorporated into the calculation, as shown in equation 4.3:

$$\sigma_{SF} = SF \sqrt{\left(\frac{\sigma_{D_{Am}}}{D_{Am}}\right)^2 + \left(\frac{\sigma_{D_{Eu}}}{D_{Eu}}\right)^2} \quad (4.3)$$

Uncertainty in separation factors are shown in Table 4.1. Uncertainty analysis is valuable to discern the accuracy and precision of data.

Chapter 5 Conclusion and Future Work

This study shed light on the possibility of using diamides of dipicolinic acid as a substitute for CMPO in the Group Extraction process. Important stability features of the chemicals used in the proposed extractant were analyzed through extraction procedures, as well as spectral analysis. It is concluded that the ortho isomer of the diamides of dipicolinic acid is the most effective extractant, as well as the most consistent across all derogative exposures.

Future work must be conducted to further understand the diamides of dipicolinic acid before they are used in industrial processes. The ortho isomer was the only structure studied using both hydrolysis and mass spectrometry. An important area of future research would be into the molecular changes that occur within the para and meta isomeric samples to determine a correlation between changes in distribution ratios from extractions and changes in chemical composition across doses. It is important to determine a correlation between changes in distribution ratios over radiation doses, and molecular structure of the extractant. The mass spectrometry data from the ortho samples analyzed does not give enough information into the relation between distribution ratios and molecules present in the extractant solutions. The consistent extraction efficiency of the ortho isomer, and lack of changes observed through spectral analysis, possibly indicates that the molecules present in the extractant solution have inherent structural stability.

Furthermore, with respect to the ortho extractant samples, another mass spectrometry analysis must be performed. It is important that all samples, including a non-

irradiated sample, are analyzed with the same dilution factors, and with the same chromatography column.

Research into the improvement of reprocessing techniques for used nuclear fuel is vital to find solutions to reduce the amount of irradiated nuclear fuel, and to work towards closing the nuclear fuel cycle. Reprocessing will cut down on the volume of used fuel to be stored, the decay heat, and radiotoxicity of the irradiated fuel. This study has shown that Et(o)TDPA appears to be a suitable replacement for CMPO in the simultaneous extraction solvent due to its resistance to degradation due to radiolysis and hydrolysis.

Appendices

Appendix A- Radiolysis Data

Table A.1. Americium extraction with unsaturated extractant

Isomer	Sample	CR[CPM]	$D_{Am} \pm \sigma_D$	Dose [kGy]
Ortho	O0 org	3154.2	16.1 ± 0.9	0
	O0 aq	195.8		
	O1 org	3160.0	30.6 ± 1.9	20
	O1 aq	103.2		
	O2 org	3135.2	25.1 ± 1.5	40
	O2 aq	124.8		
	O3 org	3154.4	32.4 ± 2.0	60
	O3 aq	97.4		
	O4 org	3239.8	24.1 ± 1.4	80
	O4 aq	134.2		
Meta	M0 org	2931.2	6.1 ± 0.3	0
	M0 aq	477.8		
	M1 org	2912.4	4.7 ± 0.2	20
	M1 aq	624.0		
	M2 org	3055.6	5.9 ± 0.3	40
	M2 aq	521.8		
	M3 org	1986.8	2.0 ± 0.1	60
	M3 aq	991.4		
	M4 org	2518.2	4.6 ± 0.2	80
	M4 aq	551.8		
Para	P0 org	2979.4	6.7 ± 0.3	0
	P0 aq	443.2		
	P1 org	3062.6	5.6 ± 0.3	20
	P1 aq	547.3		
	P2 org	3087.6	6.9 ± 0.3	40
	P2 aq	449.6		
	P3 org	2247.8	2.9 ± 0.1	60
	P3 aq	779.4		
	P4 org	2347.6	2.4 ± 0.1	80
	P4 aq	979.8		

Table A.2. Americium extraction with saturated extractant

Isomer	Sample	CR[CPM]	$D_{Am} \pm \sigma_D$	Dose [kGy]
Ortho	O0 org	3154.2	16.1 ± 0.9	0
	O0 aq	195.8		
	O1' org	4749.5	33.8 ± 3.9	20
	O1' aq	140.5		
	O2' org	4350.5	18.7 ± 1.5	40
	O2' aq	232.5		
	O3' org	4112.5	16.2 ± 0.9	60
	O3' aq	253.5		
	O4' org	4288.5	13.5 ± 1.0	80
	O4' aq	318.5		
Meta	M0 org	2931.2	6.1 ± 0.3	0
	M0 aq	477.8		
	M1' org	3060.1	5.0 ± 0.2	20
	M1' aq	615.6		
	M2' org	3553.5	3.8 ± 0.2	40
	M2' aq	936.5		
	M3' org	1726.8	2.8 ± 0.1	60
	M3' aq	609.8		
	M4' org	2233.6	2.7 ± 0.1	80
	M4' aq	818.0		
Para	P0 org	2979.4	6.7 ± 0.3	0
	P0 aq	443.2		
	P1' org	3253.0	8.1 ± 0.4	20
	P1' aq	400.2		
	P2' org	3018.4	6.7 ± 0.3	40
	P2' aq	448.3		
	P3' org	1959.6	1.4 ± 0.1	60
	P3' aq	1405.8		
	P4' org	2473.8	2.5 ± 0.1	80
	P4' aq	984.2		

Table A.3 Europium extraction with unsaturated extractant

Isomer	Sample	CR[CPM]	$D_{Eu} \pm \sigma_D$	Dose [kGy]
Ortho	O0 org	323.9	7.7 ± 0.5	0
	O0 aq	41.9		
	O1' org	294.4	30.2 ± 2.7	20
	O1' aq	2.8		
	O2' org	280.8	28.7 ± 4.3	40
	O2' aq	9.8		
	O3' org	307.0	25.2 ± 3.5	60
	O3' aq	12.2		
	O4' org	275.0	27.5 ± 4.1	80
	O4' aq	10.0		
Meta	M0 org	256.9	2.7 ± 0.2	0
	M0 aq	93.9		
	M1' org	256.4	4.9 ± 0.4	20
	M1' aq	52.8		
	M2' org	263.0	6.4 ± 0.5	40
	M2' aq	41.4		
	M3' org	247.4	5.2 ± 0.4	60
	M3' aq	48.0		
	M4' org	235.6	5.3 ± 0.4	80
	M4' aq	44.8		
Para	P0 org	296.9	5.1 ± 0.3	0
	P0 aq	58.4		
	P1' org	251.4	7.4 ± 0.7	20
	P1' aq	33.8		
	P2' org	187.8	7.5 ± 0.8	40
	P2' aq	25.0		
	P3' org	325.6	6.3 ± 0.5	60
	P3' aq	51.6		
	P4' org	263.4	5.7 ± 0.5	80
	P4' aq	46.0		

Table A.4 Europium extraction with saturated extractant

Isomer	Sample	CR[CPM]	$D_{Eu} \pm \sigma_D$	Dose [kGy]
Ortho	O0 org	323.9	7.7 ± 0.5	0
	O0 aq	41.9		
	O1 org	225.6	4.4 ± 0.4	20
	O1 aq	51.8		
	O2 org	199.8	2.6 ± 0.2	40
	O2 aq	77.4		
	O3 org	233.0	4.1 ± 0.3	60
	O3 aq	56.2		
	O4 org	202.8	2.3 ± 0.2	80
	O4 aq	90.0		
Meta	M0 org	256.9	2.7 ± 0.2	0
	M0 aq	93.9		
	M1 org	188.0	1.7 ± 0.1	20
	M1 aq	108.2		
	M2 org	169.2	1.6 ± 0.1	40
	M2 aq	107.4		
	M3 org	185.2	2.0 ± 0.1	60
	M3 aq	93.6		
	M4 org	188.8	2.2 ± 0.2	80
	M4 aq	84.6		
Para	P0 org	296.9	5.1 ± 0.3	0
	P0 aq	58.40		
	P1 org	191.0	2.2 ± 0.2	20
	P1 aq	85.0		
	P2 org	193.0	2.3 ± 0.2	40
	P2 aq	85.2		
	P3 org	173.0	1.6 ± 0.1	60
	P3 aq	107.8		
	P4 org	176.0	1.6 ± 0.1	80
	P4 aq	110.0		

Appendix B – Hydrolysis Data

Table B.1 Americium extraction with Et(o)TDPA extractant exposed to hydrolytic conditions

Sample	CR [CPM]	$D_{Am} \pm \sigma_D$	Dose [kGy]
O0 org	151.8	16.1 ± 1.1	0
O0 aq	132.0		
O1' org	3073.4	17.3 ± 0.9	20
O1' aq	177.4		
O2' org	3144.6	15.6 ± 0.8	40
O2' aq	201.0		
O3' org	2897.4	19.0 ± 1.2	60
O3' aq	152.8		
O4' org	2860.8	25.5 ± 1.5	80
O4' aq	112.0		

Table B.2 Europium extraction with Et(o)TDPA extractant exposed to hydrolytic conditions

Sample	CR [CPM]	$D_{Eu} \pm \sigma_D$	Dose [kGy]
O0 org	323.9	7.7 ± 0.5	0
O0 aq	41.9		
O1' org	221.2	3.3 ± 0.2	20
O1' aq	67.0		
O2' org	240.8	4.6 ± 0.4	40
O2' aq	52.6		
O3' org	239.0	5.1 ± 0.4	60
O3' aq	47.2		
O4' org	241.2	4.3 ± 0.3	80
O4' aq	55.6		

Appendix C- Mass Spectroscopic Data

Table C.1 Mass Spectrometry Settings

Software Version Injection	Analyst 1.5.1		
Volume used	1.00 µl		
Mass Spectrometer	3200 Q TRAP		
Config Table Version	01		
Firmware Version	M401402 B4T0301 M3L1417 B3T0300		
Component Name	Linear Ion Trap Quadrupole LC/MS/MS Mass		
Component ID	Spectrometer		
Manufacturer	3200 Q TRAP		
Model	AB Sciex Instruments		
	1031491 - A		
Serial Number	AF16040805		
Source/Ion Path Electronics	On		
Source Type	Turbo Spray		
Source Temperature (at set point)	450.0 C		
Time from start	60.4000 min		
Total Flow 1:	0.0000 mL/min		
B Conc 1:	0.0 %		
B Curve 1:	0		
Total Flow 2:	0.2000 mL/min		
B Conc 2:	20.0 %		
B Curve 2:	0		
Pressure Range (Pump A/B):	0 - 4000 psi		
Pressure Range (Pump C/D):	0 - 4000 psi		
Scan Type:	Q1 MS (Q1)	Scan Type:	Q1 MS (Q1)
Polarity:	Positive	Polarity:	Negative
Scan Mode:	Profile	Scan Mode:	Profile
Ion Source:	Turbo Spray	Ion Source:	Turbo Spray
Resolution Q1:	Unit	Resolution Q1:	Unit
Intensity Thres.:	0.00 cps	Intensity Thres.:	0.00 cps
Settling Time:	700.0000 msec	Settling Time:	700.0000 msec
MR Pause:	5.0070 msec	MR Pause:	5.0070 msec
MCA:	No	MCA:	No
Center/Width:	No	Center/Width:	No
Step Size:	0.10 Da	Step Size:	0.10 Da
Detector Parameters (Positive):		Detector Parameters (Negative):	
CEM	2600.0	CEM	2300.0

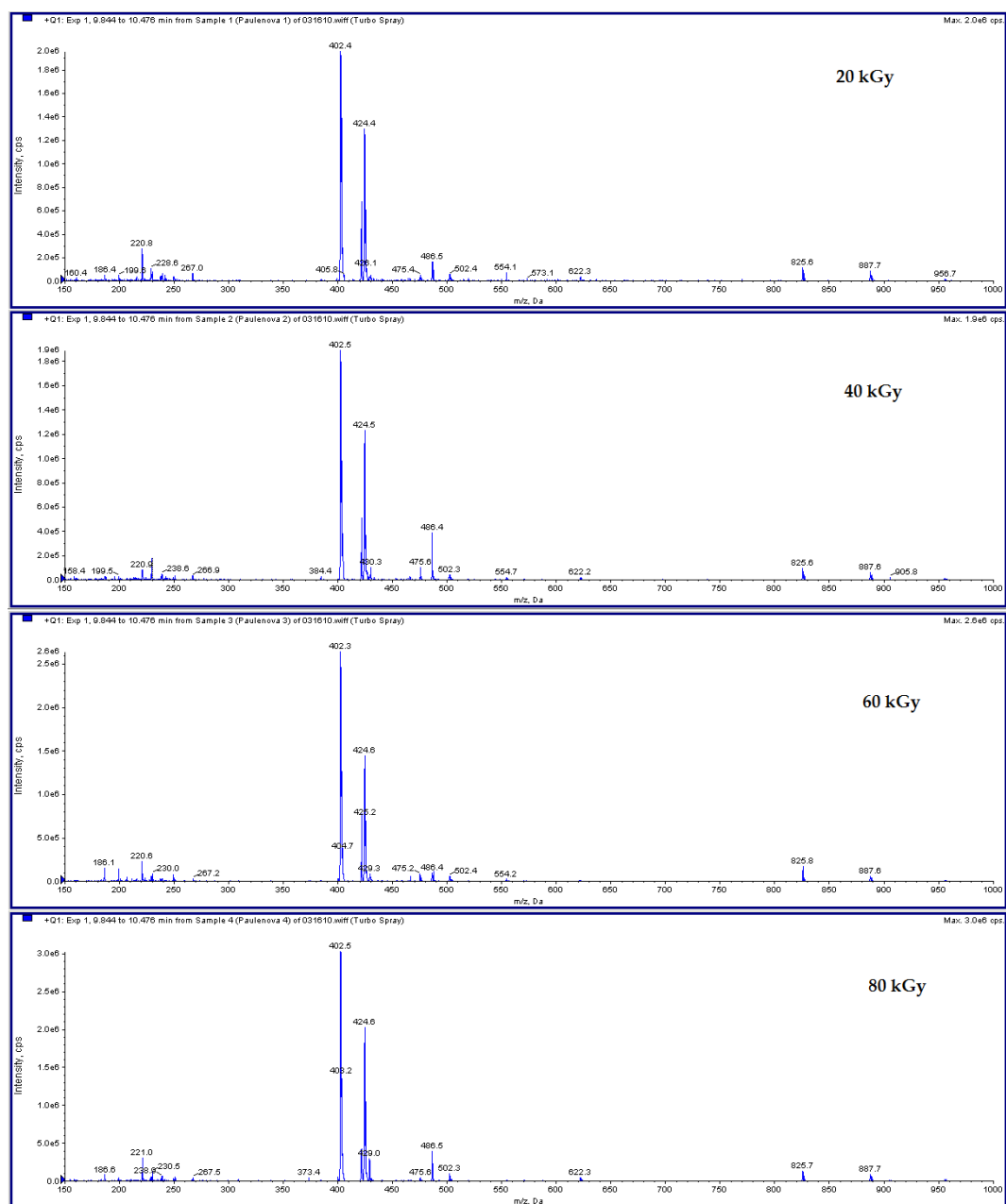


Figure C.1 Positive Ion Mass Spectra Comparison

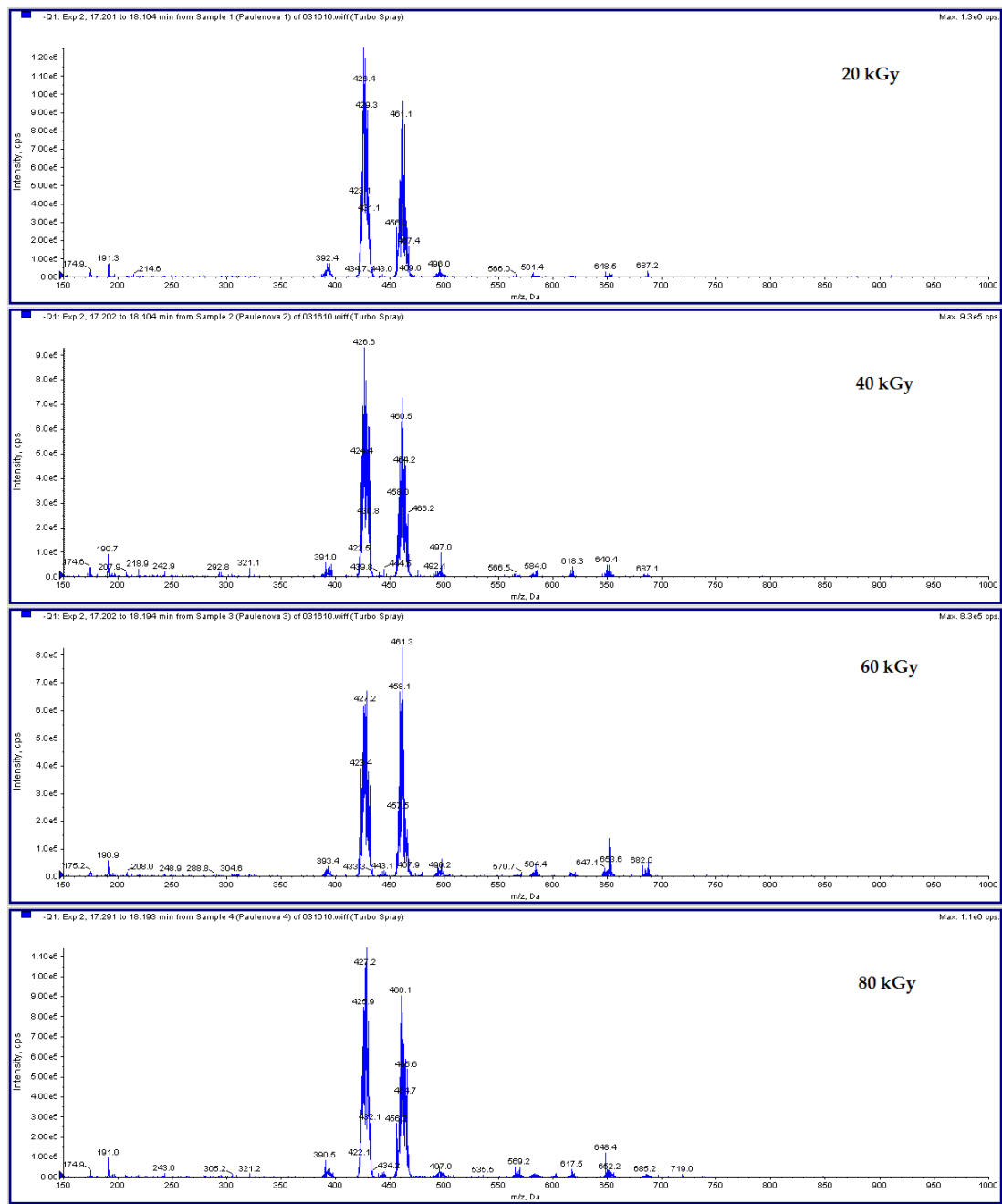


Figure C.2 Negative Ion Mass Spectra Comparison

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