Simultaneous Determination of Multiple Actinide Elements in a Variety of Soils Utilizing a Standardized Sequential Extraction Protocol

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SIMULTANEOUS DETERMINATION OF MULTIPLE ACTINIDE ELEMENTS IN A VARIETY OF SOILS UTILIZING A STANDARDIZED SEQUENTIAL EXTRACTION PROTOCOL

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ABSTRACT

Simultaneous Determination of Multiple Actinide Elements in a Variety of Soils Utilizing a Standardized Sequential Extraction Protocol

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To obtain a better understanding of the mobility of actinide element contaminants in the environment, the association of the contaminants with specific host phases of soils and sediments must be investigated. This investigation is most commonly conducted using sequential extraction techniques that employ the selective dissolution of soil phases with increasingly aggressive chemical treatment. Though several sequential extraction studies exist in literature, conclusions cannot be made by direct comparison of data due to the lack of uniformity in the protocols used. This work aims to continue development of a standard sequential extraction protocol and expanding its capabilities to include the analysis of multiple actinide elements across a broad range of soil types.

A five-step sequential extraction procedure was used to analyze extraction behaviors of $^{232}$Th, $^{238}$U, $^{239,240}$Pu and $^{241}$Am from four standard reference materials chosen to represent a broad range of geochemical soil types. Radioanalytical separations were performed using an extraction chromatography based separation procedure prior to CeF$_3$ microprecipitation sample mounting and counting by alpha spectroscopy. Stable element analysis of aluminum, iron, manganese, and strontium was performed by inductively coupled plasma – mass spectrometry to monitor phase selectivity and model potential fission product mobility. An investigation of complete dissolution techniques for a potential sixth fraction was conducted for the application to soils with high concentrations of insoluble metals. Results
show variations in leaching behaviors potentially caused by the geochemical host phase of the soil, chemical form of the extracted elements, and environmental weathering conditions.
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CHAPTER 1 INTRODUCTION

Destructive chemical analysis of soil and sediment is quite common and includes several widely accepted methods of dissolution, fusion, leaching, etc. While these techniques offer valuable information on total metal concentrations, they lack in their ability to accurately predict mobility and bioavailability of contaminants in the environment. To obtain a better understanding of contaminant mobility, the association of contaminants with specific host phases of soils and sediments must be investigated. This investigation is most commonly conducted using a technique referred to as sequential extraction.

Sequential extraction is defined as the selective dissolution of soil phases with increasingly aggressive chemical treatment. A well-optimized sequential extraction procedure can furnish information about the origin, physicochemical and biological availability, mode of occurrence, mobilization and transport of trace metal and actinide contaminants [1]. Many variations of sequential extraction procedures exist, each trying to perfect a method that most completely dissolves the selected phase without attacking other host phases of the soil. Variations of factors such as soil geochemistry, extracted elements, and the number and definition of target phases make direct comparison of results impossible.

1.1 Motivation for Research

In 1995, the National Institute of Standards and Technology (NIST) held a speciation workshop to address a need to investigate the partitioning of radioactive elements in NIST natural matrix standards [2]. The main goal of the workshop was to develop a radioanalytical method for the measurement of radionuclide fractionation in soil. Since the environmental mobility of radioactive elements is dependent upon the physicochemical
form of the element, sequential extraction techniques were chosen as the primary basis for this investigation. Information obtained from sequential extraction results would provide regulatory authorities with information for long-term risk assessment based on the potential mobility and bioavailability of radiological contaminants.

At the workshop, a total of 12 modified sequential extraction procedures, accounting for variations in geochemical composition between samples, were presented. While sample-specific dependencies are of concern, it was decided that a carefully developed procedure could accommodate variations in results caused by dissimilarities in soil composition. Potential problems with previous sequential extraction procedures were discussed, including target phase non-selectivity and readsoption of the analyte during the reaction period. A presentation by Sue Clark mentioned that two different sequential extraction methods applied to the same soil had significant variations in the amount of available contaminants per host phase, thus making a strong argument for the development of a standard approach and rigorous examination of experimental parameters.

The results of the workshop led to the recommendation of the development of a simple, standard sequential extraction protocol, that would be optimized for reagent to sample ratio, reagent concentration, reaction time, and reaction temperature; all factors that can greatly influence metal partitioning. Several considerations were made for modifications of previous procedures:

1. A water soluble fraction was eliminated and the step replaced with an overnight soaking period in favor of a more compact procedural design,

2. The organic matter extraction was placed towards the beginning of the procedure to account for the fact that most soils and sediments are coated with an organic layer, which may inhibit extraction in other fractions,
3. The organic fraction reagent was changed from nitric acid (HNO₃)/hydrogen peroxide (H₂O₂) (Tessier) to sodium hypochlorite (NaOCl) because of its relatively higher effectiveness observed in experimental data, and

4. Separation of aqueous and solid phases was recommended by high speed centrifugation followed by filtration with a 0.1 μm filter to minimize loss of solid sample during removal of the leachate.

The recommended experiments mentioned above were carried out in a joint project by researchers at NIST and Florida State University. An ocean sediment standard reference material (NIST SRM 4350B) was used for initial procedure development. Results from the study were published by Schultz et al. in 1998 [3] and generally agreed to within one standard deviation for replicate measurements. Use of NaOCl for extraction of contaminants within the organic phase is not recommended for carbonate bearing samples due to the non-selective dissolution of the carbonate phase.

In 2009, Outola et al. published a follow-up to the work done by Schultz et al. that involved the optimization of the sequential extraction procedure for a fresh-water lake standard reference material (NIST SRM 4354) [4]. A full factorial design was used to optimize three settings each of three variables for maximum extraction of $^{238}\text{U}$ and $^{239,240}\text{Pu}$. The results of the study are presented in more detail in Chapter 2.

While the previous research has provided valuable information and gotten much closer to a standardized sequential extraction protocol, several problems still need to be addressed. Issues such as method repeatability between laboratories, applicability to a broad range of soil types, maximum extraction of multiple actinide elements, and complete dissolution of soils for total activity determination must be considered.
1.1.1 Interlaboratory Comparison of Standard Sequential Extraction Protocols

Despite the number of sequential extraction experiments that have been conducted over the years, there still have been many cited examples of disagreements of extraction values between laboratories. A 1999 study by Rauret et al. saw interlaboratory relative standard deviations higher than 20\% for extraction of certain elements using a three-step sequential extraction procedure due to inconsistent moisture content measurement of soils before extraction [5]. A study by Ph. Quevauviller in 1998 found only six out of eighteen total extraction steps had coefficients of variation of less than 20\% with some values as high as 80\%, which were attributed to very low metal concentrations in the soils [6]. Straying from technical requirements of the standardized procedure can also attribute to error. Quevauviller reported a laboratory with systematically low recoveries due to the use of a reciprocating shaker instead of the recommended end-over-end shaker.

It is clear from the literature that in order to create a standardized sequential extraction protocol, there must be good agreement of results within interlaboratory studies. Strict adherence to techniques is required and larger sample sizes must be analyzed. This research investigated the repeatability of the previously optimized NIST sequential extraction protocol [4] by performing five replicates of the procedure at the UNLV radiochemistry laboratories.

1.1.2 Standardization of a Sequential Extraction Procedure for Actinide Elements

Much of the sequential extraction literature focuses on examination of the extraction of trace metals from soils, but does not include information on actinide element extraction. In the studies that do focus on actinide extraction, variations in elements, sequential extraction procedures, and sediments are seen. A standardized sequential extraction procedure could
optimally be used to investigate the simultaneous extraction of multiple actinide elements in a wide variety of soils and sediments.

Table 1. Comparison of literature extraction results for actinide specific sequential extraction studies.

<table>
<thead>
<tr>
<th>Method</th>
<th>Thorium</th>
<th>Uranium</th>
<th>Plutonium</th>
<th>Americium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bunzl et al. [7] Grassland soil 4 step</td>
<td>x</td>
<td>x</td>
<td>Organic Oxides</td>
<td>Organic Oxides</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Residual Residual</td>
<td>Residual Residual</td>
</tr>
<tr>
<td>Lee et al. [8] BOMARC soil 6 step</td>
<td>x</td>
<td></td>
<td>Residual Reducible</td>
<td>Acid-soluble Reducible</td>
</tr>
<tr>
<td>Aubert et al. [9] Mountain soil 7 step procedure</td>
<td>Organic</td>
<td>Organic</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Lucey et al. [10] Estuary sediment 5 step</td>
<td>x</td>
<td>x</td>
<td>Acid-soluble</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Exchangeable</td>
<td></td>
</tr>
<tr>
<td>McDonald et al. [12] Irish Sea sediment McLaren and Crawford 5 step</td>
<td>x</td>
<td>x</td>
<td>Organic Residual</td>
<td>Organic Carbonate</td>
</tr>
<tr>
<td>Schultz et al. [3] Ocean sediment 6 step</td>
<td>x</td>
<td></td>
<td>Residual Carbonate</td>
<td>Organic Fe/Mn oxides Residual</td>
</tr>
<tr>
<td>Outola et al. [4] Lake sediment 5 step</td>
<td>x</td>
<td></td>
<td>Carbonate Organic</td>
<td>x</td>
</tr>
</tbody>
</table>

Further investigation into the literature shows little to no agreement between extraction results from a number of procedures tested on a variety of soil samples. This is shown in Table 1, which lists variations in actinide-specific extraction schemes. The Method column lists the reference, type of soil, and number of steps used in the sequential extraction procedure. The four actinide-labeled columns list the target phase with, in which
each element is most highly associated. Fields with an "x" represent elements that were not investigated.

The summary of research in Table 1 is proof that the environmental radiochemistry community would benefit from a standardized sequential extraction procedure for actinide analysis. Such a procedure should be applicable to a large range of actinides and across a broad range of soil types.

**Simultaneous Analysis of Multiple Actinides**

Some studies within the literature seem to focus on extraction of anthropogenic radionuclides to assess contaminant mobility within environments that are typically contaminated [7] [10] [12]. Other studies focus on naturally occurring radioisotopes to examine distribution and origin [9]. While both types of studies are able to obtain important information about associations of radionuclide contaminants with geochemical host phases, there is usually no direct comparison between anthropogenic and naturally occurring nuclides. A standard sequential extraction protocol would allow the simultaneous analysis of multiple actinides in a variety of soil types. This research will investigate the coupling of an extraction chromatography based separation scheme with the NIST sequential extraction procedure to more quickly and efficiently separate multiple actinide elements.

**Application of Standardized Procedure to Multiple Soils**

A large variety of soil and sediment samples have been analyzed for actinide extraction by sequential extraction procedures, as evidenced in Table 1. Researchers typically modify an already existing sequential extraction procedure to best extract the radionuclides of interest based on the geochemical host phases represented by the soil they are analyzing. This leads to a large amount of literature on sequential extraction of actinides from various soils and sediments, with no means of comparison between the studies. Use of a standard
procedure, on the other hand, should provide information on extractability regardless of soil type. Quevauviller et al. suggest the need to apply a standardized sequential extraction procedure to a wide variety of soil and sediment samples in order to pursue efforts to further validate these methods [6]. This research investigated the application of the sequential extraction procedure by Outola et al. that has been recommended as a standard protocol, to several soil and sediment standard reference materials. Stable elements will also be analyzed to assess phase selectivity and to assist in comparison of results from a single sequential extraction method applied to different soils.

**Complete Dissolution**

Many reports mention incomplete dissolution of actinides following a sequential extraction procedure [3] [8] [11]. The amount of radionuclides remaining in the undissolved fraction will vary based on soil type and radionuclide speciation. While it is important to understand radionuclide behavior based on geochemical host phase, it is also necessary to quantify the total concentration of actinides of interest within the soil. Analysis of undissolved fractions will give better insight into actinides that may be present in forms such as high-fired oxides or other complex refractory matrices. This research examined both microwave digestion and fusion procedures for complete dissolution following sequential extraction.

**Correlation between Radionuclide Source Term and Sequential Leaching Behaviors**

Radionuclide contaminant mobility depends on a variety of factors including the original chemical form of the element. While sequential extraction studies have proven invaluable for predicting contaminant mobility, they often lack in the relation of leaching behaviors to the original physicochemical form of the extracted elements. Such correlations would yield important information for both radioecology (contaminant mobility) and
nuclear forensics (material origin) and would be complementary to data already present in
the literature. This research investigated the correlation between actinide leaching
behaviors in the five fractions of the sequential extraction procedure with original source
term information of the actinides in the four reference materials used in this work.
Conclusions on radionuclide mobility based on source information are drawn relating to the
suspected original physicochemical form of the actinides examined in this work.

1.2 Project Goals

The goal of this research was to investigate the standardization of a sequential
extraction protocol for maximum dissolution of multiple actinide elements. Figure 1
presents a flow chart representing the work conducted for this dissertation, along with the
section number where each experiment is presented.

An existing sequential extraction procedure, previously optimized by Outola et al. [4],
was repeated with five replicates of each of each reference material to determine method
repeatability across different laboratories. Stable trace metals were measured to evaluate
phase selectivity and to model important groups of environmental contaminants such as
fission products and heavy metals. In order to achieve quicker, more efficient separation of
multiple radionuclides, an extraction chromatography based separation procedure was
tested to be employed following sequential leaching. This research also investigated the
total dissolution methods of microwave digestion and alkali metal hydroxide fusion to be
applied at the end of the sequential extraction procedure. The addition of the total
dissolution method allows for a more thorough approach to the investigation of difficult
sample matrices, such as high-fired oxides, urban matrices, and other materials significant
to nuclear forensics.
1.3 Dissertation Overview

Chapter 1 provides a general overview of the dissertation, including motivation for the project and research goals. Chapter 2 covers background information on the methods and instrumentation used in this project, as well as an extensive literature review. Chapter 3 provides information on analytical details of all wet chemistry and instrumental techniques used throughout the research. The main body of this work is contained in Chapters 4, 5, and
6. Each chapter includes experimental details, results, and recommendations for future work. Conclusions are presented in Chapter 8. Supplemental (raw) data supporting all tables and figures presented in the body of this work is shown in the Appendix.
CHAPTER 2  BACKGROUND

This chapter will provide a discourse on the radionuclides, methods, and instrumentation used in this research. The radionuclides investigated in this work – uranium, thorium, americium and plutonium – and their sources within the environment will be discussed in detail. Background information and theories behind chemical analysis methods utilized will be presented along with a review of the literature relating to the methods. In addition, the basic operating principles of the instrumentation used will be discussed.

2.1 Actinides in the Environment

Both naturally occurring and man-made radionuclides exist in the environment in a variety of forms. Typically, uranium and thorium exist as natural elements found in ore deposits created during the formation of the earth. Other elements such as plutonium and americium, can be found within the environment due to fallout from nuclear weapons testing, nuclear accidents such as Chernobyl and Fukushima, and release into the environment from sources such as the Hanford waste tanks and Sellafield waste streams. Actinide contaminants in the environment are a source of concern due to their potential mobility and bioavailability. This section presents a discussion of each radionuclide analyzed in this research, sources within the environment and potential modes of transport.

2.1.1 Thorium

Important Isotopes of Thorium

Thorium-232 is the most abundant isotope of natural thorium at 100% and is the parent of the (4n) decay chain, which also includes $^{228}\text{Th}$. The (4n + 2) decay chain, proginated by $^{238}\text{U}$, produces $^{230}\text{Th}$ and small amounts of $^{234}\text{Th}$. Nearly undetectable concentrations of
$^{231}$Th and $^{227}$Th are produced by the $(4n + 3)$ decay chain starting with $^{235}$U [13]. A table with relevant thorium isotopes, half-lives, decay energies and intensities is presented below.

Table 2. Thorium isotopes relevant to this work along with half-lives, alpha energies and intensities of the strongest transitions [13].

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (years)</th>
<th>Decay Energy (MeV)</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{228}$Th</td>
<td>1.9116</td>
<td>5.423</td>
<td>72.7</td>
</tr>
<tr>
<td>$^{229}$Th*</td>
<td>7340</td>
<td>4.845</td>
<td>56</td>
</tr>
<tr>
<td>$^{230}$Th</td>
<td>75380</td>
<td>4.687</td>
<td>76.3</td>
</tr>
<tr>
<td>$^{232}$Th</td>
<td>1.405E10</td>
<td>4.016</td>
<td>77</td>
</tr>
</tbody>
</table>

*$^{229}$Th is used as a tracer in these studies.

Environmental Occurrence and Mobility

Most thorium isotopes exist naturally in the environment at an average concentration of 6 ppm in rock, soil and water [14]. Primary anthropogenic sources of thorium include uranium and thorium mining, milling and processing, phosphate rock processing, fertilizer production, and emissions from coal-fired utilities [15]. The geochemistry of thorium is relatively straightforward with the tetravalent state being the only oxidation state of thorium known in nature [16].

In soils, the presence of thorium is strongly correlated with the presence of iron, aluminum and manganese, which are likely co-precipitated or adsorbed onto particles of insoluble oxides. Thorium also has a tendency to form mixed insoluble compounds with alkaline earth metals such as magnesium and calcium [17]. It is often relatively immobile within the environment due to its high sorption tendency, with anticipated removal only in extremely acidic environments [18]. Though thorium is most commonly known to be associated with residual fractions, it is also known to associate with natural organic matter,
which indicates thorium migration as anionic complexes with organic matter or as negatively charged particles [16].

2.1.2 Uranium

Important Isotopes of Uranium

Uranium-238 is the most abundant natural isotope of uranium with a natural abundance of 99.2742%. It is also the progeny of the (4n + 2) decay chain, which also contains naturally-occurring and 0.0054% abundant $^{234}\text{U}$. The parent of a third decay chain (4n + 3), $^{235}\text{U}$, is the third natural isotope of uranium with an abundance of 0.7204% [19]. A table with relevant uranium isotopes, half-lives, decay energies and intensities is presented below.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (years)</th>
<th>Decay Energy (MeV)</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{232}\text{U}^*$</td>
<td>68.9</td>
<td>5.320</td>
<td>68.6</td>
</tr>
<tr>
<td>$^{233}\text{U}$</td>
<td>245500</td>
<td>4.777</td>
<td>72</td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>703800000</td>
<td>4.397</td>
<td>57</td>
</tr>
<tr>
<td>$^{236}\text{U}$</td>
<td>23415000</td>
<td>4.494</td>
<td>74</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>4.468E9</td>
<td>4.196</td>
<td>77</td>
</tr>
</tbody>
</table>

*$^{232}\text{U}$ is used as a tracer for this research.

Environmental Occurrence and Mobility

Uranium is present naturally in the earth’s crust in over 200 minerals, the bulk of which are U(VI) minerals and U(IV) oxides, phosphates and silicates. It has a reported concentration range in soil of 0.3 – 11.7 mg kg$^{-1}$ [20]. Correlations have been made between the soil concentrations of uranium and the oxides of iron and aluminum [17]. Tetravalent
uranium in the environment is very insoluble and has a similar behavior to thorium, but can be easily oxidized into more mobile hexavalent uranium [21].

It is well known that uranium is associated with the organic matter present in soil, partially by cationic exchange mechanisms. Research by Martinez-Aguirre and Garcia-Leon implies the main process of uranium incorporation from river water into sediment is by coprecipitation with amorphous ferromanganese oxyhydroxides [22]. In a 2005 study by Blanco et al., uranium was seen bound mainly to organic matter (46%) and in the residual phase (38.8%), but also was associated with the carbonate fraction of soil by 10% [23].

2.1.3 Plutonium

Important Isotopes of Plutonium

Plutonium is mainly an anthropogenic radionuclide originating from nuclear weapons testing, nuclear fuel reprocessing, and nuclear accidents including Chernobyl. Two isotopes of plutonium, $^{239}\text{Pu}$ and $^{244}\text{Pu}$, are considered natural in origin. Small amounts of $^{239}\text{Pu}$ are produced in nature by nuclear processes in uranium ore. Minute quantities of $^{244}\text{Pu}$ are from remnants of stellar nucleosynthesis [24]. Common isotopes include $^{238}\text{Pu}$, $^{239}$, $^{240}\text{Pu}$ and $^{241}\text{Pu}$. Plutonium-242 and $^{236}\text{Pu}$ are typically used as radiotracers. Plutonium-239 is produced in nuclear reactors and nuclear weapons by neutron capture of $^{238}\text{U}$ followed by beta decays of short-lived $^{239}\text{U}$ and $^{239}\text{Np}$. Heavier isotopes of plutonium are created by successive neutron capture starting with $^{239}\text{Pu}$. Plutonium-238 is created by neutron capture on $^{235}\text{U}$ and subsequent beta decay of $^{237}\text{Np}$. It can also be created in an n,2n reaction on $^{238}\text{U}$ during the explosion of a nuclear weapon. An additional source of $^{238}\text{Pu}$ in the environment is the burn-up of satellites using radioisotope thermoelectric generators.
Table 4. Plutonium isotopes relevant to this work along with half-lives, alpha energies and intensities of the strongest transitions [24].

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (years)</th>
<th>Decay Energy (MeV)</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>87.7</td>
<td>5.499</td>
<td>70.9</td>
</tr>
<tr>
<td>$^{239}\text{Pu}$</td>
<td>24110</td>
<td>5.157</td>
<td>70.77</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>6561</td>
<td>5.168</td>
<td>72.8</td>
</tr>
<tr>
<td>$^{242}\text{Pu}^*$</td>
<td>375000</td>
<td>4.902</td>
<td>76.49</td>
</tr>
</tbody>
</table>

*$^{242}\text{Pu}$ is used as a tracer for this research.

Environmental Occurrence and Mobility

Plutonium has a very complex chemistry in nature. Due to the small energy differences between its oxidation states, it can exist in several oxidation states in one solution. Therefore careful adjustment and stabilization of valence states must be considered for plutonium experiments. In aquatic environments, plutonium tends to preside in the $+5$ oxidation state. In soils and sediments, plutonium is predominantly in the $+3$ and $+4$ oxidation state [25]. It is assumed that high affinity for mineral surfaces and low solubility limits environmental mobility of plutonium [25].

Though plutonium will readily sorb to various mineral and become immobilized, there are often other factors at play within complex natural environments. Subsurface migration of plutonium can also occur via colloids (real, pseudo or bio), dissolved organic ligand complexes, or oxidized species with minimal retardation [25]. It is suggested that colloids and solids present in solution compete for free plutonium in water, leading to both plutonium colloid-associated species and immobile species retained on solids. The relatively large surface area of the colloids leads to competition with solids, affecting the fate and transport of plutonium [26]. Sequential extraction studies have suggested plutonium is mainly associated with fractions containing high amounts of fulvic/humic acid [27], and residual fractions typically dissolved by strong nitric acid [28].
2.1.4 Americium

Important Isotopes of Americium

Americium is anthropogenic in nature. Americium-241 is found in the environment as a result of nuclear weapons testing and releases from nuclear reactors, nuclear waste storage facilities and nuclear accidents. Occurrence in the environment is from both direct deposition and from ingrowth of $^{241}\text{Pu}$ decay. Americium-241 resulting from ingrowth of $^{241}\text{Pu}$ is mainly seen from nuclear weapons testing, while other nuclear releases such as that of the Chernobyl accident contain americium both from ingrowth and direct deposition [29]. Americium has a high radiotoxicity so investigation of its mobility is important for risk assessment. A table with relevant americium isotopes, half-lives, decay energies and intensities is presented below.

Table 5. Americium isotopes relevant to this work along with half-lives, alpha energies and intensities of the strongest transitions [30].

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-life (years)</th>
<th>Decay Energy (MeV)</th>
<th>Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{241}\text{Am}$</td>
<td>432.7</td>
<td>5.486</td>
<td>84</td>
</tr>
<tr>
<td>$^{243}\text{Am}^*$</td>
<td>7380</td>
<td>5.277</td>
<td>88</td>
</tr>
</tbody>
</table>

$^{243}\text{Am}$ is used as a tracer for this research.

Environmental Occurrence and Mobility

Americium typically appears in nature in the trivalent oxidation state and tends to behave chemically similar to trivalent lanthanides and rare earth elements. It is predominantly associated with carbonates and residual fractions. Carbonate binds americium in solution and carbonate minerals can be expected to provide excellent surfaces for sorption [15]. Americium has also been seen following behavior similar to plutonium. A sequential extraction study on plutonium and americium migration in soils shows
americium associated primarily with immobile forms corresponding to oxidizable components such as organic matter [31].

2.2 Sequential Extraction

Sequential extraction techniques are commonly used to predict mobility and bioavailability of both stable and radioactive metal contaminants in the environment. This section discusses the history of sequential extraction, methods specific determination of radionuclide mobility, and definitions of target phases relevant to this work.

2.2.1 Background

Several sequential extraction procedures have been developed over the years to assess geochemical information, trace element contaminant mobility, and radioisotope behavior in the environment. The analysis of metal fractionation in soils has been of interest since the late seventeenth century when studies focused on improvement of soils for agricultural needs [2]. Focus shifted in the late 20th century to analysis of stable metal contaminant mobility in environmental systems [1]. Since then, sequential extraction procedures have been widely used to attempt to understand radionuclide contaminant mobility and bioavailability within soil and sediment samples. A discussion of sequential extraction procedures aimed at metal contaminant fractionation is presented in the next section, with a more focused discussion on radionuclide specific fractionation studies in the section following.

2.2.2 History

Sequential extraction methods used to determine metal fractionation for estimation of contaminant mobility and bioavailability became popular in the late 20th century. Several
procedures that were developed to examine stable element mobility are commonly used today for investigation of radionuclide contaminant mobility. The most popular procedures include the Tessier method [1], the BCR method [32] and the Miller method [33], all discussed in greater detail below.

**Tessier Method, 1979 [1]**

The Tessier method, published in 1979, describes a sequential extraction procedure with five fractions: exchangeable, carbonate bound, iron and manganese oxide bound, organic matter bound and residual [1]. This method evaluated for the trace metals cadmium, cobalt, copper, nickel, lead, zinc, iron and manganese. Sediment samples analyzed in this procedure were collected from Saint-Marcel and Pierrville in Quebec, Canada and were dried, pulverized and homogenized before analysis. Sample sizes of 1 gram (g) were used and treated with reagent volumes of 8 to 20 milliliters (mL). Analysis of trace metals was conducted using atomic absorption spectroscopy.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Target Phase</th>
<th>Extracting Reagent</th>
<th>Reaction Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Exchangeable</td>
<td>1 M MgCl₂ or 1 M NaOAc</td>
<td>Room temp, 1 hour</td>
</tr>
<tr>
<td>II</td>
<td>Carbonate Bound</td>
<td>1 M NaOAc, pH adjusted to 5 with HOAc</td>
<td>Room temp, to completion</td>
</tr>
<tr>
<td>III</td>
<td>Fe/Mn Oxide Bound</td>
<td>0.3 M Na₂SO₄ + 0.175 M Na-citrate + 0.025 M H-citrate + 0.04 M NH₂OH·HCl in 25% (v/v) HOAc</td>
<td>96 °C to completion</td>
</tr>
<tr>
<td>IV</td>
<td>Organic Matter Bound</td>
<td>0.02 M HNO₃, 30% H₂O₂</td>
<td>85 °C, 2 hours</td>
</tr>
<tr>
<td>V</td>
<td>Residual</td>
<td>HF-HClO₄</td>
<td>Evaporate to dryness</td>
</tr>
</tbody>
</table>

Table 6. Target phases and reaction conditions for Tessier procedure [1].
Each fraction was analyzed to assess for phase selectivity. The low levels of silicon, aluminum, and sulfur leached from fraction one imply that magnesium chloride (MgCl₂) does not affect silicates, sulfides, or organic matter. The completeness of dissolution in the carbonate fraction was evidenced by the disappearance of the dolomite x-ray diffraction peak. In fraction three, low levels of Si and Al imply only slight attachment of major silicate components. Oxidation is excessive, yet incomplete in fraction four, with sulfide minerals also being extracted to a large extent. Results in fractions three and four show reagents have a scavenging action for trace metals far out of proportion to their own concentration. Trace metal concentrations found in fraction five are higher than those observed in any other fraction.

A number of observations were made that should be considered when applying the Tessier sequential extraction procedure. The time required for carbonate dissolution depends on a number of factors including particle size, percentage and type of carbonate present in the sample. Even though oxidation of all organic matter forms may not be complete using hydrogen peroxide in an acidic medium, more efficient methods often suffer from lack of phase specificity in that they can partially attack silicate lattices. The use of higher sediment to solution ratios could improve detection limits when analyzing leachates. Precision and accuracy of the procedure is limited by the inherent heterogeneity of the sample.

Miller Method, 1986[33]

Miller et al. developed a method in 1986 that examined the effect of sequence in extraction of trace metals from soils [33]. Three topsoils were used to examine the effect of extractants and extraction sequence on the results of metal fractionation. Reagent selection was based on literature, citing reagents that were selective based on chemical forms of trace
metals in soils. An eight-step extraction scheme was created based on a 0.5 g sample size and 20 mL solution volume (25 mL for the final fraction). A ninth fraction targeting the residual phase was added at the end of the procedure consisting of 1 mL of aqua regia and 10 mL of hydrofluoric acid (HF) at 110 °C for 2 hours in a Parr digestion bomb. All reactions in the procedure were carried out at room temperature, shaken end-over-end, and washed between extractions with 0.025 M Ca(NO₃)₂ to remove occluded solutions.

Table 7. Target phases and reaction conditions for the Miller sequential extraction procedure [33].

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Target Phase</th>
<th>Extracting Reagent</th>
<th>Reaction Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Soluble</td>
<td>H₂O</td>
<td>16 h</td>
</tr>
<tr>
<td>II</td>
<td>Exchangeable</td>
<td>0.5 M Ca(NO₃)₂</td>
<td>16 h</td>
</tr>
<tr>
<td>III</td>
<td>Pb-displaceable</td>
<td>0.5 M Pb(NO₃)₂ + 0.1 M Ca(NO₃)₂</td>
<td>16 h</td>
</tr>
<tr>
<td>IV</td>
<td>Acid soluble</td>
<td>0.44 M CH₃COOH + 0.1 M Ca(NO₃)₂</td>
<td>8 h</td>
</tr>
<tr>
<td>V</td>
<td>Mn-oxide occluded</td>
<td>0.01 M NH₂OH-HCl + 0.01 M HNO₃</td>
<td>30 min</td>
</tr>
<tr>
<td>VI</td>
<td>Organically bound</td>
<td>0.1 M K₂P₂O₇</td>
<td>24 h</td>
</tr>
<tr>
<td>VII</td>
<td>Amorphous Fe-oxide</td>
<td>0.175 M (NH₄)₂C₂O₄ + 0.1 M H₂C₂O₄</td>
<td>4 h in darkness</td>
</tr>
<tr>
<td>VIII</td>
<td>Crystalline Fe-oxide</td>
<td>Oxalate reagent</td>
<td>85 °C, under UV irradiation, 3 h</td>
</tr>
</tbody>
</table>

Several conclusions were drawn from this work relating to phase specificity and extraction sequence. Soluble and exchangeable phases have been extensively used in sequential extraction procedures, thus were not evaluated in this work. The lead extraction step likely only displaces metal ions that are covalently bound to oxidic or organic functional groups, while the CH₃COOH is expected to solubilize more metals since it is capable of dissolving some poorly crystalline hydroxyl and carbonate metal phases. The sequence of the Pb-displaceable and acid soluble phases, therefore, was recommended in
the order shown in Table 7 due to the relative weakness and higher specificity of the lead extractant. The weak reducing agent hydroxylamine hydrochloride is very effective in dissolving manganese oxides, while the stronger reagents including pyrophosphate (K₄P₂O₇) have been known to partially dissolve Mn-oxides. For this reason, the Mn-oxide occluded fraction was placed before the organic matter and Fe-oxide occluded phases. Iron oxide extraction was left for last since neither K₄P₂O₇ nor hydroxylamine hydrochloride (NH₂OH·HCl) had a significant effect on the iron bearing minerals. Amorphous Fe-oxides were solubilized in the absence of light using acidic ammonium oxalate while metals held within the silicate mineral structures were dissolved using an HF-based method such as Bernas (1968). The inclusion of the residual (crystalline Fe-oxide) extraction is important, as a substantial portion of trace metals are often found in this form.

**BCR Method, 1992 [32]**

The proposal of the European Community Bureau of Reference for a sequential extraction procedure was developed to minimize errors in the analysis and treatment of samples and to identify the most appropriate procedure for application to reference materials [32]. The goals of this collaborative project were to perform an interlaboratory trial analysis of soil and sediment extractions by single and sequential extraction for the elements cadmium, chromium, copper, nickel, lead and zinc, and to provide soil and sediment reference materials with certified extractable content values. Four laboratories tested three different sequential extraction themes with seven sediments and one soil sample. Sequential extraction schemes included a modified Tessier procedure by Forstner [34], the short method of Salomons and Forstner [35], and a procedure by Meguellati [36]. Results of the intercomparison study showed fractional contents by the different procedures were in good enough agreement for the sediments to be sufficiently well characterized for decision making on the use of the sediments. Serious failures in detail,
however, led to the conclusion that, while promising results were shown, improvements must be made if the procedure will be used to certify reference materials. A recommendation for all future studies to be conducted using a single, well specified procedure was made. Ure et al. then conducted a trial run of a simple three-step extraction procedure adapted from Salomons and Forstner, outlined in Table 8.

Table 8. Target phases, reaction conditions for BCR sequential extraction procedure [32].

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Target Phase</th>
<th>Extracting Reagent</th>
<th>Reaction Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Acid reducible</td>
<td>20 mL 0.11 M HAc</td>
<td>5 h</td>
</tr>
<tr>
<td>II</td>
<td>Organic</td>
<td>20 mL 0.1 M NH₂OH·HCl</td>
<td>16 h, pH 2</td>
</tr>
<tr>
<td>III</td>
<td>Residual silicate</td>
<td>10 mL 8.8 M H₂O₂</td>
<td>twice</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 mL 1 M NH₄Ac</td>
<td>Overnight, pH 5</td>
</tr>
</tbody>
</table>

The simplified three-step procedure had much poorer recoveries than single extraction techniques cited in the paper. The principal cause of the poor results was concluded to be the very low metal concentrations of the sediments used for the experiments. Conclusions stated that certification of sediment contents using this procedure must include more sensitive analytical techniques or even a more highly contaminated sediment.

2.2.3 Sequential Extraction Procedures for Radionuclide Leaching

Since the development of sequential extraction procedures for stable element analysis, many procedures have been developed, mainly as modifications of the above-mentioned procedures, to attempt to predict radionuclide contaminant mobility in the environment. The three procedures discussed below are those most relevant to this research.
Clark et al., 1996 [37]

A 1996 study by Clark et al. compared two sequential extraction techniques to estimate geochemical controls on mobility of fission product, actinide, and heavy metal contaminants [37]. The research examined a modified Tessier procedure and a modified Miller procedure to determine contaminant mobility in soils samples collected in two locations from a shallow, unlined seepage pond. A soil to solution ratio of 1:40 was used for each method. The tables below show the parameters used in each method. Extractants from each method were analyzed by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) in a scanning mode. Samples were spiked with known quantities of internal standards and, in most cases, diluted prior to analysis.

Results showed that, by following dissolution of both contaminants and matrix elements, inconsistent results from the two techniques could be resolved. It was discovered that the Tessier method did not effectively extract iron oxides in one step and the operational definition of the organic matter did not adequately represent the phase removed for the soil studied. Both modified procedures yielded similar results for most metals in the soil matrix, however, inconsistencies in uranium and lead extraction were seen between the two methods. It was recommended that a sequential extraction approach should provide evidence for the estimation of refractory concentrations of uranium and other toxic metals.
Table 9. Sequential extraction parameters for the modified Tessier procedure examined in Clark et al. [37].

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Target Phase</th>
<th>Extracting Reagent</th>
<th>pH</th>
<th>Extracting Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Exchangeable</td>
<td>1 M NH₄Ac</td>
<td>7.0</td>
<td>Shake 16 h Rinse with ultrapure H₂O</td>
</tr>
<tr>
<td>II</td>
<td>Carbonate</td>
<td>1 M acetic acid</td>
<td>5.0</td>
<td>Shake 16 h Rinse with ultrapure H₂O</td>
</tr>
<tr>
<td>III</td>
<td>Fe/Mn oxides</td>
<td>0.4 M NH₂OH·HCl inlet 25% acetic acid</td>
<td>1.0</td>
<td>Shake 6 h @ 80 °C Rinse with ultrapure H₂O</td>
</tr>
<tr>
<td>IV</td>
<td>Organically bound</td>
<td>30% H₂O₂ NH₄Ac in 20% HNO₃</td>
<td>2.0</td>
<td>Digest in H₂O₂ @ 80 °C Shake in acetate 16 h, rinse w/H₂O</td>
</tr>
<tr>
<td>V</td>
<td>Residual</td>
<td>1:10 mixture aqua regia/HF</td>
<td>0</td>
<td>Digest in acid bomb @ 105 °C for 3 h</td>
</tr>
</tbody>
</table>

Table 10. Sequential extraction parameters for the modified Miller procedure examined in Clark et al. [37].

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Target Phase</th>
<th>Extracting Reagent</th>
<th>pH</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Water soluble</td>
<td>Ultrapure water</td>
<td>5.5</td>
<td>Shake 16 h rinse with ultrapure H₂O</td>
</tr>
<tr>
<td>II</td>
<td>Exchangeable</td>
<td>0.5 M Ca(NO₃)₂</td>
<td>5.5</td>
<td>Shake 16 h rinse with 0.01 M Ca(NO₃)₂</td>
</tr>
<tr>
<td>III</td>
<td>Acid soluble</td>
<td>0.44 M acetic acid 0.5 M Ca(NO₃)₂</td>
<td>2.5</td>
<td>Shake 8 h rinse with 0.01 M Ca(NO₃)₂</td>
</tr>
<tr>
<td>IV</td>
<td>Mn oxide bound</td>
<td>0.01 M NH₂OH·HCl</td>
<td>1.1</td>
<td>Shake 5 h rinse with 0.01 M Ca(NO₃)₂</td>
</tr>
<tr>
<td>V</td>
<td>Organically bound</td>
<td>0.1 M Na₄P₂O₇</td>
<td>10</td>
<td>Shake 24 h rinse with 0.01 M Ca(NO₃)₂</td>
</tr>
<tr>
<td>VI</td>
<td>Amorphous oxides</td>
<td>0.18 M (NH₄)₂C₂O₂ 0.1 M H₂C₂O₄</td>
<td>3.5</td>
<td>Shake 4 h in dark rinse with 0.01 M Ca(NO₃)₂</td>
</tr>
<tr>
<td>VII</td>
<td>Crystalline oxides</td>
<td>0.15 M sodium citrate, 0.05 M citric acid 0.75 g sodium dithionite</td>
<td>5.5</td>
<td>Shake 0.5 h @ 50 °C rinse with 0.01 M Ca(NO₃)₂</td>
</tr>
<tr>
<td>VIII</td>
<td>Residual</td>
<td>1:10 mixture aqua regia/HF</td>
<td>0</td>
<td>Digested in acid bomb 105 °C for 3 h</td>
</tr>
</tbody>
</table>
Schultz et al., 1998 [3]

A 1998 study by Schultz et al. evaluated a method based on the Tessier method using IAEA 135 sediment standard as the extractable material [3]. The procedure outlines six operationally-defined fractions and concentrates on identifying the fractionation of radioactive elements. Experiments were carried out using 1-2 g sediment aliquots in a 15:1 reagent to sample ratio to avoid artifacts associated with incomplete dissolution. The table below shows the parameters used in this procedure. Extractants from each method were analyzed by alpha spectroscopy (Americium, Plutonium and Uranium) and by ICP-MS (stable elements). Method selectivity was monitored by the recovery of stable elements (aluminum, calcium, iron, manganese, and titanium). Aluminum and titanium were good indicators of highly insoluble mineral phases while stable manganese can be found in both the carbonate phase as well as in oxide form. Calcium was used to monitor the dissolution of carbonate phases, while iron represented a relatively insoluble oxidized form.

Table 11. Sequential extraction parameters for the modified Tessier procedure examined in Schultz et al. [3].

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Target Phase</th>
<th>Extracting Reagent</th>
<th>pH</th>
<th>Extracting Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Water soluble/Exchangeable</td>
<td>H$_2$O/0.4 M MgCl$_2$</td>
<td>5</td>
<td>Room temp, 1 h</td>
</tr>
<tr>
<td>II</td>
<td>Organic matter</td>
<td>5-6% NaOCl</td>
<td>7.5</td>
<td>96 °C, 0.5 h x2</td>
</tr>
<tr>
<td>III</td>
<td>Carbonates</td>
<td>1.0 M NaAc in 25% HAc</td>
<td>4</td>
<td>Room temp, 2 h x2</td>
</tr>
<tr>
<td>IV</td>
<td>Oxides (Fe/Mn)</td>
<td>0.04 M NH$_2$OH·HCl</td>
<td>2</td>
<td>Room temp, 5 h</td>
</tr>
<tr>
<td>V</td>
<td>Residue</td>
<td>NaOH fusion or HNO$_3$/HCl/HF/HClO$_4$</td>
<td>0</td>
<td>550 °C, 8h</td>
</tr>
</tbody>
</table>

The procedure included several modifications to the Tessier method as proposed at the 1995 NIST speciation workshop. An overnight soak period was added to allow for swelling of clay minerals. The organic fraction was placed earlier in the extraction process due to
sediments often being coated by a layer of organic matter. A NaOH fusion was added to the end of the procedure to completely dissolve the residue fraction. The paper also investigated possible re-adsorption of metal-ions onto the target fraction by adding a double-spiking technique.

Results showed good agreement of extraction profiles for $^{241}\text{Am}$, $^{239,240}\text{Pu}$, and $^{238}\text{U}$ in duplicate runs, most agreeing to within one standard deviation interval based on counting statistics. Wide variations between replicates were corrected with the inclusion of a 0.1 μm filtration step. The use of NaOCl to extract metals associated with organic material is not recommended for carbonate-bearing soils due to the non-selective dissolution of the carbonate phase.

**Outola et al., 2009**

A 2009 study by Outola et al. built on the 1998 Schultz procedure to optimize extraction of $^{238}\text{U}$ and $^{239,240}\text{Pu}$ from lake and ocean sediments based on extraction time, reagent concentration and reaction temperature [4]. A soil to solution ratio of 1:15 was used for the procedure, with a soil mass of 12 g used for each sample. Extractants from each fraction were analyzed by alpha spectroscopy (uranium and plutonium) and Inductively Coupled Plasma-Optical Emission Spectroscopy (stable elements).

Table 12. Optimized sequential extraction parameters for the modified Tessier procedure examined in Outola et al. [4].

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Target Phase</th>
<th>Extracting Reagent</th>
<th>Extracting Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Exchangeable</td>
<td>0.1 M MgCl$_2$</td>
<td>25°C, 1 h</td>
</tr>
<tr>
<td>II</td>
<td>Carbonates</td>
<td>1 M NH$_4$Ac in 25% (v/v)HAc</td>
<td>50°C, 2 h</td>
</tr>
<tr>
<td>III</td>
<td>Oxides (Fe/Mn)</td>
<td>0.1 M NH$_2$OH·HCl in 25% (v/v) HAc</td>
<td>70°C, 6 h</td>
</tr>
<tr>
<td>IV</td>
<td>Organic Matter</td>
<td>H$_2$O$_2$ in 0.02 M HNO$_3$ (pH 2)</td>
<td>70°C, 3 h</td>
</tr>
<tr>
<td>V</td>
<td>Residue</td>
<td>4 M HNO$_3$</td>
<td>90°C, 4 h</td>
</tr>
</tbody>
</table>
The optimized procedure shown in Table 12 reflects parameters that showed maximum extraction of uranium and plutonium from target phases with minimal extraction of non-target phases. A comparison was drawn between the results from this work and previous sequential extractions performed on ocean sediment by Schultz et al. The final optimized procedure represents a compromise between maximum extractability of the uranium and plutonium from two sediments so that the optimized procedure can be applied to a wider range of soil samples. The sequential extraction procedure provides as a robust technique as long as the extraction settings are selected properly.

2.2.4 Target Phase Definitions

The geochemical host phases evaluated in this research are operationally defined as exchangeable, carbonate bound, iron and manganese oxide bound, organic matter bound and residually bound. Each of these host phases will be discussed in detail along with common reagents used to attack each phase. Information will be presented on types of metal interactions, reagents used to release metals and common elements associated with each phase.

**Fraction I – Exchangeable**

The first fraction to be attacked for extraction is the exchangeable fraction in which metals are most weakly bound and therefore most easily released into solution. The metals associated with this phase are held by electrostatic interaction on the exchange sites of negatively charged complexes [38]. These metals can be released by ion-exchange processes and neutral salts [39]. Alkali and alkaline earth metals as exchangeable cations are replaced by neutral salts with a different cation (Ca²⁺ replacing Mg²⁺ or K⁺ replacing Na⁺) [38]. The most common reagent is MgCl₂, which combines the strong ion-exchange capacity of Mg²⁺ with the weak complexing ability of Cl⁻. MgCl₂ does not attack silicates, metal
sulfides or organic matter [40]. Carbonates have been shown to be slightly dissolved in this fraction, but this can be avoided by a shorter extraction time [1]. Calcium and manganese are common elements extracted from this fraction. Aside from MgCl₂, other reagents commonly used for the extraction of the exchangeable phase are acetate salts, nitrate salts and calcium salts [41].

Fraction II – Carbonate/Acid Soluble

The carbonate bound phase has also been referred to as the acid soluble phase and is most susceptible to changes in pH. Metals in the carbonate phase are thought to be associated with the soil matrix by co-precipitation with carbonate minerals and as specifically sorbed to some sites of iron and manganese oxides, clays and organic matter [40]. Metal release occurs through dissolution with a reagent having a pH close to 5 [41]. A buffered acetic acid-sodium acetate system is typically used to dissolve the metals in the carbonate phase. Common elements associated with the carbonate phase are zinc and uranium [4]. Aside from the acetic acid-sodium acetate system, other extracting reagents include 25% acetic acid and 1 N acetic acid [38] [41].

Fraction III – Iron and Manganese Oxide

Iron and manganese oxides are perhaps the best scavengers of metals, having much greater adsorption capacities than aluminum and silicon oxides [38]. These oxides are thermodynamically unstable under anoxic conditions (low Eh) [1]. Reagents containing both a reducing agent and a ligand to retain released ions are most useful for this fraction [40]. The most common reagent used for extracting metals from this fraction is hydroxylamine, but oxalic acid and dithionite are also commonly used. Some elements associated with the iron and manganese oxide phase are zinc and iron [4].
**Fraction IV – Organic/Oxidizable**

The organic matter fraction includes metals that are incorporated on living organisms and organic coatings on inorganic particles. Organic content is mainly humic acid and other products such as proteins, peptides, amino acids and carbohydrates [40]. This organic matter can be degraded and released from the solid matrix under oxidizing conditions [1]. Common elements associated with the organic phase are cobalt, aluminum, nickel and plutonium [4]. Three reagents are commonly reported in literature for extracting metals bound to organic matter, hydrogen peroxide ($\text{H}_2\text{O}_2$), sodium hypochlorite (NaOCl) and alkali pyrophosphate (Na$_4$P$_2$O$_7$ or K$_4$P$_2$O$_7$). Hydrogen peroxide may be the most commonly used reagent, but it is often criticized for not totally destroying organic matter and for partially dissolving sulfides [1] [38]. Sodium hypochlorite was found to destroy the organic matter of soils with less dissolution of iron and manganese oxides [42]. Rose (1975) determined that sodium hypochlorite treatment will also attack sulfides present in the sample [43]. Alkali pyrophosphates contain anions that can remove stabilizing metals such as calcium, iron and aluminum, causing the effective extraction of metals from humic materials [44]. Extraction with pyrophosphates does not attack sulfides, but its action on poorly crystallized species of iron oxides is not well understood.

**Fraction V – Residual**

The residual fraction contains metals associated within the crystalline structure of primary and secondary minerals. Digestion with strong acids such as hydrofluoric, perchloric, hydrochloric and nitric is commonly performed to release metal ions from this phase [41]. Fusion with alkali fluxes such as sodium carbonate, lithium metaborate and lithium tetraborate has also been used [38]. Common elements associated with this phase are aluminum and silicon.
2.3 Extraction Chromatography

Extraction chromatography allows for the separation of radionuclides from a wide range of sample matrices [45]. It combines the performance and simplicity of column chromatography with the versatility and selectivity of solvent extraction. The extraction chromatography system consists of three major components, the inert support, the stationary phase and the mobile phase, depicted in Figure 2.

The inert support usually consists of a 50 to 150 µm diameter silica or organic polymer. The stationary phase consists of liquid extractants bound to the resin. The mobile phase typically consists of an aqueous solution, usually mineral acids such as hydrochloric or nitric acid, which can selectively elute metal ions from the column based on varying acid concentrations.

Figure 2. Schematic of extraction chromatographic resin [45].
The free column volumes to peak maximum, \( k' \), is an important value in extraction chromatography that can be used to assess metal retention properties of the column. The relationship between the distribution ratio (D), used in solvent extraction, and \( k' \) is expressed as:

**Equation 1. Calculation of \( k' \) based on distribution ratio.**

\[
k' = D \cdot \frac{v_s}{v_m}
\]

Where \( v_s \) is the volume of the stationary phase and \( v_m \) is the volume of the mobile phase.

For extraction chromatography, however, it is much easier to calculate D and \( k' \) from the measured value of the weight distribution ratio, \( D_w \). The distribution ratio is calculated by:

**Equation 2. Calculation of \( D_w \) based on known and sorbed activity.**

\[
D_w = \frac{A_o - A_s}{A_s} \cdot \frac{mg}{L}
\]

Where \( A_o - A_s \) is the activity sorbed on a known weight of resin (g) and \( A_s \) is the activity in a known volume of solution (mL).

### 2.3.1 TEVA

Eichrom’s TEVA resin is most commonly used for separation of tetravalent actinides and for the separation of americium from lanthanides [46]. The active component is an aliphatic quaternary amine, triakyl, methylammonium nitrate or chloride (see Figure 3), which gives it properties similar to strong base anion exchange resins. The functional groups are in a liquid form, giving greater flexibility to coordinate around target anions.
Figure 3. TEVA Aliquat 336, triakyl, methylammonium nitrate (or chloride)

\[
\begin{align*}
R & = C_{8}H_{17} \text{ and } C_{10}H_{21} \\
\end{align*}
\]

As evident from Figure 4, plutonium and thorium in the tetravalent states show maximum uptake between 2 and 4 M nitric acid concentrations while trivalent americium and hexavalent uranium are not well retained in that range.

Figure 4. Acid dependency of k' for various ions on TEVA [46].
Figure 5. Separation of light lanthanides from Am using TEVA.

Eichrom Technologies TRU resin employs an extractant system of octylphenyl-N-N-diisobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP), shown in Figure 6 [47]. The CMPO/TBP extractant complexes actinides and extracts them out of aqueous solution. The uptake of actinide elements by nitric acid solutions is shown in Figure 7.
Figure 6. TRU – octylphenyl-N, N-di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP) [47].

![Chemical Structure of CMPO](image)

Figure 7. Acid dependency of k' for various ions on TRU resin in nitric and hydrochloric acid [47].

![Acid dependency of k' for various ions on TRU resin](image)
Tetravalent actinides show high retention on the TRU columns in nitric acid concentrations greater than 2 M, where hexavalent uranium is about an order of magnitude less in k’ value. In hydrochloric acid, americium has a very low affinity and is therefore stripped from the resin.

2.3.3 DGA

Eichrom Technologies DGA normal resin contains an extractant system consisting of N,N,N’,N’-tetra-octyldiglycolamide, shown in Figure 8 [48].

Figure 8. DGA – N,N,N’,N’-tetra-octyldiglycolamide [48].

DGA resins allows for the selective extraction of Am(III) without breakthrough due to weak retention. The resin shows a high affinity for americium under some conditions, but the americium is easily eluted under other conditions. In fact, DGA has a much higher retention factor for americium than TRU resin does, as shown by Figure 9 [48]. Americium that has been retained on DGA following loading in nitric acid can then be eluted using low concentration hydrochloric acid as shown in the elution curves in Figure 10.
Figure 9. $k'$ for Th(IV), U(VI), Am(III) and Pu(IV) on TRU and DGA normal resin.

![Graph showing $k'$ for Th(IV), U(VI), Am(III) and Pu(IV) on TRU and DGA normal resin.]

Figure 10. $k'$ for Th(IV), U(VI), Am(III), and Pu(IV) on DGA normal resin vs HCl.

![Graph showing $k'$ for Th(IV), U(VI), Am(III), and Pu(IV) on DGA normal resin vs HCl.]
2.4 Total Dissolution

Complete dissolution of soil samples yields important information about the total amounts of contaminant concentrations or radionuclides present in the sample. Once a sample is dissolved, it can be subject to additional chemical separations to prepare it for alpha spectroscopy or stable element analysis by ICP-MS or Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Three major categories of total dissolution exist in the literature: acid digestion, microwave digestion and fusion. This work will focus on microwave digestion and fusion, as they offer quick and complete dissolution without the safety concerns of acid digestion.

2.4.1 Microwave Digestion

Microwave digestion methods involve dissolving a sample using strong acids in an open or closed vessel microwave system. A variety of samples can be dissolved using this technique, including rocks, soil, vegetation, foods, metals etc. The controlled temperature and pressure of the microwave system works to speed up the digestion process for quick and complete sample dissolution. The goal is to rapidly break down the sample and convert it into a soluble form ready for elemental analysis by ICP-MS, ICP-AES or Atomic Absorption spectroscopy (AA).

Closed Vessel Microwave Digestion

Closed vessel microwave digestion systems offer dissolution of highly insoluble matrices that require high reaction pressures and temperatures for complete sample destruction. Systems consist of a microwave unit with a carousel on which closed reaction vessels can be placed. Vessels typically are made of TFM or quartz and come in a wide range of sizes. The figure below shows the Milestone Ethos EZ closed vessel microwave digestion unit that is used in this work.
Some advantages of closed vessel microwave digestion include complete dissolution and quick reaction times, on the order of 20-40 minutes. Sample size, however, is limited by the volume of the vessel and the pressure it can withstand. Reaction temperatures in closed vessel systems can reach 260 – 300 °C [50]. A rotating turntable is often used to ensure equal distribution of microwave radiation across the samples. Increased temperature in a closed system also leads to increased pressure, causing concern for safety. Fortunately, most common vessels used in closed vessel systems have safety features such as burst disks and reaction sensors help prevent the buildup of pressure.

**Procedures**

Many microwave digestion procedures exist in literature, each attempting to maximize dissolution based on sample matrix. This discussion will focus only on closed vessel microwave digestion procedures, as that was the type of system used for this research. Most procedures use one or a combination of mineral acids such as HNO₃, HCl and HF for digestion and target a large number of elements for dissolution. EPA method 3052 was designed for microwave digestion of sediments, sludges, soils and oils. It was intended to
mimic dissolution using conventional heating with nitric acid, but allows the addition of hydrochloric acid for more difficult matrices [51]. Other methods were designed to digest more difficult matrices such as carbonate rock. A procedure developed by Kemp and Brown uses the addition of acetic acid to carbonate samples before microwave assisted digestion in order to evolve CO₂ gas before the sample is placed in the closed vessel [52]. Details on the microwave digestion procedures used in this research are presented in chapter 6.

2.4.2 Fusion

Fusion techniques are typically used when complete dissolution of a difficult matrix is required. Digestion is achieved by heating a small amount of sample with a salt (flux) to a temperature above the melting point of the salt. Heating is usually done using a muffle furnace or a gas burner. The resulting salt melt is swirled and fusion continues until a clear melt is obtained. The fused material is then dissolved in either warm water or dilute acid once the temperature drops back to room temperature. Table 13 shows some common fusion procedures, including the NaOH fusion method used in this work and presented in Chapter 6.

Alkali-Metal Hydroxide Fusion

The fusion method used in this research is a sodium hydroxide fusion performed in a zirconium crucible. Alkali-metal hydroxide fusion is typically used for the dissolution of silicates, oxides, phosphates, fluorides, and soils for actinide analysis [55]. The fusions are generally rapid and result in a melt that is easily dissolved in water. Due to the lower fusion temperatures (~600 °C), platinum crucibles are not needed, making the procedure more cost effective. Losses due to volatility are also reduced due to the lower temperature. Most fusion procedures take less than 20 minutes to form a salt melt. Specific details of the fusion procedure are discussed in chapter 6.
Table 13. Common fusion procedures along with salt (flux), fusion temperature, and crucible type [53] [54].

<table>
<thead>
<tr>
<th>Flux</th>
<th>Temperature (°C)</th>
<th>Crucible Type</th>
<th>Sample Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂S₂O₇ or K₂S₂O₇</td>
<td>Up to red heat</td>
<td>Pt, quartz, porcelain</td>
<td>Insoluble oxides and oxide containing samples</td>
</tr>
<tr>
<td>NaOH or KOH</td>
<td>450-600</td>
<td>Ni, Ag, glassy carbon</td>
<td>Silicates, oxides, phosphates and fluorides</td>
</tr>
<tr>
<td>Na₂CO₃ or K₂CO₃</td>
<td>900-1,000</td>
<td>Ni, Pt for short periods</td>
<td>Silicates and silica-containing samples, refractory oxides, quartz, insoluble phosphates and sulfates</td>
</tr>
<tr>
<td>Na₂O₂</td>
<td>600</td>
<td>Ni; Ag, Au, Zr; Pt (&lt;500 °C)</td>
<td>Sulfides, acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; Pt alloys</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td></td>
<td>Pt</td>
<td>Sand, aluminum silicates, titanite, natural aluminum oxide</td>
</tr>
<tr>
<td>Na₂B₄O₇</td>
<td>1,000-1,200</td>
<td>Pt</td>
<td>Al₂O₃; ZrO₂ and zirconium ores, minerals of rare earths, Ti, Nb, Ta</td>
</tr>
<tr>
<td>Li₂B₂O₇ or LiBO₂</td>
<td>1,000-1,100</td>
<td>Pt, graphite</td>
<td>Anything except metals and sulfides. Tetraborate for basic oxides and metaborate for acidic oxides</td>
</tr>
<tr>
<td>NH₄HF₂, NaF, KF or KHF₂</td>
<td>900</td>
<td>Pt</td>
<td>Removal of silicon, destruction of silicates and rare earth minerals</td>
</tr>
</tbody>
</table>

2.5 Alpha Spectroscopy

Alpha spectroscopy is one of the most common methods for identifying and quantifying actinides. It is a simple, low-cost method with relatively high instrument stability. The most commonly used detector in modern day alpha spectrometry systems is a passivated ion implanted silicon (PIPS) detector, which will be discussed in more detail below.

There are many considerations that must be taken into account when analyzing samples by alpha spectroscopy. Count times for environmental samples are often long, on the order of several weeks, due to the typically low activity concentration of the samples. Extensive chemical purification and isotope separation is required for alpha spectroscopy samples to
avoid attenuation and overlapping peaks. Though the resolution of modern-day detectors is very low (on the order of 10 keV), it is not low enough to resolve the peaks of $^{239}$Pu (5.156 MeV) and $^{240}$Pu (5.168 MeV). If isotope-specific concentrations are needed, another analysis technique method, such as mass spectrometry, must be used.

2.5.1 Alpha Spectrometry System

Alpha systems have the ability to collect, store and create a spectrum of the energies of the particles emitted from an alpha source. Isotopes can be identified by the corresponding energy or energies of the emitted alpha particle(s), since alpha decay results in a monoenergetic line spectrum that allows assignment of lines to individual transitions. Quantification of isotopes is achieved by sorting each individual alpha particle reaching the detector into “bins” within the multi-channel analyzer (MCA). Information from the MCA is used by the Genie 2000 software to generate a spectrum.

Count rates are determined by summing the counts under a given peak and dividing by the count time. This value is then converted into an activity measured in disintegrations per second using the previously determined efficiency of the detector.

The figure below shows a schematic of a typical alpha spectroscopy system. A vacuum pump is connected to the system to evacuate the sample chamber to eliminate attenuation of alpha particles in air while travelling to the detector. The sample chamber contains the detector and a sample holder that can be placed at varying distances from the detector. A bias is applied to the detector so the charge created by the free electrons will be collected causing an electrical pulse. The signal is then amplified and sent to the multi-channel analyzer. The MCA sorts signals based on energies into “bins.” The software then creates a spectrum based on the information provided by the MCA.
2.5.2 PIPS Detectors

Passivated Implanted Planar Silicon (PIPS) detectors are commonly used for alpha spectrometry when high sensitivity and resolution are required. They offer lower noise, higher stability, better resolution and efficiency than older technologies such as surface barrier and diffused junction detectors. The detector is a silicon wafer with doped junction contacts that form a p-n junction. A reverse bias is applied to create a depletion region in which alpha particles are detected. Electron-hole pairs directly proportional to the energy of the incoming particle are formed within the depletion region. This creates a charge pulse which is sent through a preamplifier to produce a voltage pulse [56].

A uniformly thin entrance window and low leakage current can provide for detectors with high resolution. For a 450 mm² active area detector, alpha resolution of ≤ 17 keV is often achieved. A minimum depletion depth of 140 microns allows absorption of alpha particles up to 15 MeV and enhances sensitivity [57].
2.5.3 Resolution and Efficiency

The distance between the source and detector must be carefully considered because of the effect it may have on the spectrum. One can achieve greater counting efficiency and shorter count times by placing the source close to the detector. Greater potential for contamination will occur, however, the closer the source is to the detector. A source that is placed too close to the detector will also have degraded peak resolution due to the solid angle of the alpha particles reaching the detector. Variations in solid angle lead to disparities in energy loss in the dead layer of the detector. Figure 13 shows the effect on efficiency at various source-to-detector distances for a 25 mm source diameter.

Figure 13. Efficiency as a function of source-detector distance for a 25 mm diameter source [57].
2.6 ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique commonly used for the determination of elemental concentrations. It has a number of advantages over other techniques such as ICP-AES and AA, including better detection limits, minimum matrix interferences due to high temperature of plasma, superior detection to ICP-AES with same sample throughput and ability to obtain isotopic information.

The technique combines a high temperature inductively coupled plasma source with a mass spectrometer. Samples are aerosolized and sent through the plasma source where the gaseous atoms are ionized. The ions are then forwarded to the mass spectrometer and separated by their mass-to-charge ratio by either a magnetic or electric sector. Signals are then collected by a detector and passed on to the computer software for analysis.

Figure 14. ICP-MS schematic diagram
CHAPTER 3  ANALYTICAL

This chapter discusses the materials and methods used throughout this research. Soil and sediment reference materials and radioisotope tracers will be discussed in detail, yet will not include all information included in the cited certificates. The general methods for all wet chemistry procedures will also be discussed, with any changes to the procedures used in specific experiments noted in the chapter relating to that experiment. Details on instrumental techniques will also be discussed.

3.1 Materials

This section will discuss the materials used in this research. Reference materials from IAEA and NIST were used for procedure modification in order to gain a better understanding of changes seen in the sequential extraction procedure. Radioisotope tracers were used to monitor radioelement recoveries from all experiments including sequential extraction, extraction chromatography, and complete dissolution studies. Reagents used in this research will be presented in Chapters 4-6 with the specific experimental details.

3.1.1 Reference Materials

In order to obtain a better understanding of performance of the sequential extraction procedure, well-characterized reference materials must be used. Soil and sediment reference materials used in this research were chosen based on their radiochemical and geochemical properties. For example, moss-soil (IAEA 447) and lake sediment (NIST 4354) are both representative of soils with higher organic content. Moss-soil, however, due to the relatively undisturbed nature of its growth, carries a well-kept memory record of radioactive fallout [58]. The lake sediment reference material, on the other hand, was designed to be representative of a true environmental sample. Fangataufa lagoon sediment
(IAEA 384) and ocean sediment (NIST 4357) are both representative of materials with higher carbonate concentration. Nuclear weapons testing was carried out in the French Polynesian Lagoon where IAEA 384 was collected so the sediment is more representative of post-detonation debris [59]. The conditions under which NIST 4357 were subjected to makes it a good model for ocean sediment that is not affected by weapons testing. All reference materials are highly characterized for the elements analyzed in the following experiments. Details of the reference materials and their characterization can be found in the sections below.

NIST SRM 4354 – Lake Sediment

Standard reference material 4354, lake sediment, was collected from Perch Lake in the Chalk River Nuclear Laboratories’ waste management area in Canada [60]. Over 30 years prior to collection, the lake received low-levels of actinides, fission products, and activation products primarily from global fallout and streams fed by radwaste pits at the site. The lake sediment reference material contains radionuclide concentrations of approximately one order of magnitude higher than generally expected within the environment so relatively good precision may be obtained by the analyst. Radionuclides within the sediment are expected to have been weathered by natural processes for a sufficient period of time to become equilibrated within their environment. This reference material was chosen for this research based on its high organic content, good representation of typical lake sediment, as well as to repeat sequential extractions previously completed at NIST for verification purposes.

The fresh water lake sediment was collected using sludge pumps, dewatered by centrifugation, then freeze dried. Sediment was then pulverized by and air-jet mill constructed as a silicon carbide lined hollow disk with tangential high pressure air jets.
Homogenization took place using a 10 ft\(^3\) V-cone blender with a high speed intensifier bar over the span of one hour. An average particle diameter, by weight, of approximately 8 µm was obtained with greater than 99% by mass of particles between 2 and 20 µm in diameter. The density was measured to be 0.3 g cc\(^{-1}\).

Homogeneity of gamma emitting radionuclides was measured by analyzing eight 30 g bottles in a NaI well detector with count rates analyzed over an energy region of 0.05 to 1.8 MeV. Data from interlaboratory comparisons were used to assess the inhomogeneity of thorium and uranium isotopes and \(^{239+240}\)Pu. The radionuclide concentration values for \(^{210}\)Pb, \(^{226}\)Ra, \(^{230}\)Th, and \(^{234}\)U are listed as uncertified due to either significant discrepancies or lack of collaborative measurements. The reference date for decay correction is 14 February 1986 [60].

### Table 14. Certified activities for NIST SRM 4354, fresh water lake sediment.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Activity Concentration [Bq g(^{-1})]</th>
<th>Tolerance Limits [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{60})Co</td>
<td>3.20 \times 10^{-1}</td>
<td>13</td>
</tr>
<tr>
<td>(^{90})Sr</td>
<td>1.09</td>
<td>23</td>
</tr>
<tr>
<td>(^{137})Cs</td>
<td>5.92 \times 10^{-2}</td>
<td>7</td>
</tr>
<tr>
<td>(^{228})Th</td>
<td>2.86 \times 10^{-2}</td>
<td>13</td>
</tr>
<tr>
<td>(^{232})Th</td>
<td>2.68 \times 10^{-2}</td>
<td>10</td>
</tr>
<tr>
<td>(^{235})U</td>
<td>7.5 \times 10^{-4}</td>
<td>19</td>
</tr>
<tr>
<td>(^{238})U</td>
<td>1.74 \times 10^{-2}</td>
<td>8</td>
</tr>
<tr>
<td>(^{238})Pu</td>
<td>2.6 \times 10^{-4}</td>
<td>+14 -38</td>
</tr>
<tr>
<td>(^{239+240})Pu</td>
<td>4.00 \times 10^{-3}</td>
<td>+7 -18</td>
</tr>
<tr>
<td>(^{241})Am</td>
<td>1.1 \times 10^{-3}</td>
<td>+30 -81</td>
</tr>
</tbody>
</table>

### Table 15. Uncertified activities for NIST SRM 4354, fresh water lake sediment.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Activity Concentration [Bq g(^{-1})]</th>
<th>Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{210})Pb</td>
<td>1.2 \times 10^{-1}</td>
<td>NBS, ORNL</td>
</tr>
<tr>
<td>(^{226})Ra</td>
<td>3 \times 10^{-2}</td>
<td>EML</td>
</tr>
<tr>
<td>(^{230})Th</td>
<td>1.3 \times 10^{-2}</td>
<td>EML, NBS</td>
</tr>
<tr>
<td>(^{234})U</td>
<td>1.9 \times 10^{-2}</td>
<td>EML, NBS</td>
</tr>
</tbody>
</table>
NIST SRM 4357 – Ocean Sediment

Standard reference material 4357 from NIST consists of a blend of sediment collected from the Irish Sea off the coast of Sellafield, UK, and in the Chesapeake Bay, USA, in a respective weight ratio of 1:200 [61]. The ocean sediment reference material was developed for use in testing measurements of environmental radioactivity in matrices similar to ocean sediment. Over the course of 50 years from 1950-2000, there were several off-site releases of radionuclides into the environment surrounding the Sellafield nuclear reprocessing site. The Irish Sea sediment was blended with sediment from the Chesapeake Bay in order to reduce the plutonium concentration to approximately $10^{-2}$ Bq g$^{-1}$. This reference material was chosen for this research based on its good representation of typical ocean sediment, as well as to repeat sequential extractions previously completed at NIST for verification purposes.

The Sellafield sediment was collected, sieved to -200 mesh, dried and analyzed by the National Radiological Protection Board in the UK before being sent to NIST. Chesapeake Bay sediment was freeze dried and blended with the Sellafield sediment before being sterilized with 50 kGy from $^{60}$Co source. The combined sediment was then pulverized with a pancake-style air-jet mill which resulted in an average particle size of 6 μm with more than 99% of particles, by weight, less than 20 μm in diameter. Sample heterogeneity was measured using sample sizes ranging from 10 to 100 g for gamma emitting radionuclides. For $^{90}$Sr and transuranic nuclides, a sample size of 10 g was used for heterogeneity determination. All actinides and their daughters are approximately 87% removed from the sample with leaching procedures using nitric acid or aqua regia solutions. Testing was conducted by 20 different laboratories. Analytical methods included gamma spectroscopy, alpha and beta spectroscopy and thermal ionization mass spectrometry. The reference date for decay correction is 1 March 1997 [61].
Table 16. Certified massic activities with normal distribution of results for NIST SRM 4357, ocean sediment.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Mean ± 2s_m,* [mBq g⁻¹]</th>
<th>2.5 to 97.5% tolerance limit,** [mBq g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴⁰K</td>
<td>225 ± 5</td>
<td>190-259</td>
</tr>
<tr>
<td>²²⁶Ra</td>
<td>12.7 ± 0.4</td>
<td>10.3-15.0</td>
</tr>
<tr>
<td>²²⁸Ra</td>
<td>13.3 ± 0.8</td>
<td>9.2-17.4</td>
</tr>
<tr>
<td>²²⁸Th</td>
<td>12.1 ± 0.3</td>
<td>9.7-14.6</td>
</tr>
<tr>
<td>²³⁰Th</td>
<td>12.0 ± 0.5</td>
<td>9.6-14.4</td>
</tr>
<tr>
<td>²³²Th</td>
<td>13.0 ± 0.3</td>
<td>11.6-14.3</td>
</tr>
</tbody>
</table>

*Two standard deviations of the mean.
**Normal tolerance limit for 95% confidence and 95% coverage.

Table 17. Certified massic activities with non-normal distribution of results for NIST SRM 4357, ocean sediment.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Mean ± 2s_m,* [mBq g⁻¹]</th>
<th>2.5 to 97.5% tolerance limit,** [mBq g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁹⁰Sr</td>
<td>4.4 ± 0.3</td>
<td>2.1-8.4</td>
</tr>
<tr>
<td>¹³⁷Cs</td>
<td>12.7 ± 0.2</td>
<td>10.8-15.9</td>
</tr>
<tr>
<td>²³⁹Pu</td>
<td>2.32 ± 0.06</td>
<td>2.01-3.02</td>
</tr>
<tr>
<td>²³⁹⁺²⁴⁰Pu</td>
<td>10.4 ± 0.2</td>
<td>9.2-13.3</td>
</tr>
</tbody>
</table>

*Two standard deviations of the mean.
**Normal tolerance limit for 95% confidence and 95% coverage.

Table 18. Uncertified massic activities for NIST SRM 4357, ocean sediment.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Massic Activity [mBq g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹²⁹I</td>
<td>0.009</td>
</tr>
<tr>
<td>¹⁵⁵Eu</td>
<td>1.4</td>
</tr>
<tr>
<td>²¹⁰Po</td>
<td>14</td>
</tr>
<tr>
<td>²¹⁰Pb</td>
<td>24</td>
</tr>
<tr>
<td>²¹²Pb</td>
<td>14</td>
</tr>
<tr>
<td>²¹⁴Bi</td>
<td>14.5</td>
</tr>
<tr>
<td>²³⁴U</td>
<td>12</td>
</tr>
<tr>
<td>²³⁵U</td>
<td>0.6</td>
</tr>
<tr>
<td>²³⁷Np</td>
<td>0.007</td>
</tr>
<tr>
<td>²³⁸U</td>
<td>12</td>
</tr>
<tr>
<td>²⁴¹Am</td>
<td>10</td>
</tr>
</tbody>
</table>
Certified Reference Material 447, moss-soil, was collected from an abandoned red marble mine in Gerecse Mountain in northwestern Hungary in the summer of 2007 [58]. The 3-5 cm thick fresh soil layer was collected from the groovings in the large marble surfaces and mixed with the moss. Due to the relatively undisturbed growing conditions of the moss-soil, the soil accumulated radionuclide fallout and represents a memory record of the fallout.

The moss-soil was dried overnight at 80 °C then milled in a large volume ceramic drum mill. A maximum particle size distribution of 150 μm was obtained by sieving. The density of the material was determined from five test portions to be 1.03 ± 0.05 g cm⁻³. After bottling into 150 g bottles, the material was sterilized by a 25 kGy total dose of ⁶⁰Co gamma irradiation to inhibit microbial action and prolong shelf life. Homogeneity of the material was tested on 30 portions of material using gamma spectroscopy. The homogeneity of ²¹⁰Po, ²²⁶Ra, ²³⁴U, ²³⁸U, ²³⁸Pu, ²³⁹+²⁴⁰Pu, and ²⁴¹Am were determined by isotope dilution alpha spectrometry while ²¹⁰Pb and ⁹⁰Sr were determined by liquid scintillation counting following sample dissolution and separations.

Characterization of the moss-soil was performed by the IAEA Terrestrial Environment Laboratory and confirmed by the Radioanalytical Laboratory, Food and Safety Division in Hungary and the Laboratory of Radiological Measurements in Slovenia. A total of 30 bottles were analyzed by the three laboratories for characterization. Liquid scintillation counting was used to characterize ⁹⁰Sr, ²¹⁰Pb, and ²⁴¹Pu, alpha spectrometry was used to characterize ²¹⁰Po, ²²⁶Ra, ²³⁴U, ²³⁸U, ²³⁸Pu, ²³⁹+²⁴⁰Pu, and ²⁴¹Am and gamma spectroscopy was used to characterize gamma emitting radionuclides. Inductively coupled plasma mass spectrometry
was used for characterization of \(^{232}\text{Th}\) while \(^{228}\text{Ra}\) values were determined indirectly from \(^{228}\text{Ac}\) at secular equilibrium. The reference date for decay correction is 15 November 2009.

Table 19. Certified values for massic activities for IAEA CRM 447, moss-soil.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Certified Value [Bq kg(^{-1})]</th>
<th>Uncertainty* [Bq kg(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{137}\text{Cs})</td>
<td>425</td>
<td>10</td>
</tr>
<tr>
<td>(^{210}\text{Pb})</td>
<td>(0.42 \times 10^3)</td>
<td>(0.02 \times 10^3)</td>
</tr>
<tr>
<td>(^{210}\text{Po})</td>
<td>423</td>
<td>10</td>
</tr>
<tr>
<td>(^{212}\text{Pb})</td>
<td>37.0</td>
<td>1.5</td>
</tr>
<tr>
<td>(^{226}\text{Ra})</td>
<td>25.1</td>
<td>2.0</td>
</tr>
<tr>
<td>(^{228}\text{Ac})</td>
<td>37.0</td>
<td>2.0</td>
</tr>
<tr>
<td>(^{234}\text{U})</td>
<td>21.8</td>
<td>0.8</td>
</tr>
<tr>
<td>(^{238}\text{U})</td>
<td>22.2</td>
<td>0.8</td>
</tr>
<tr>
<td>(^{238}\text{Pu})</td>
<td>0.15</td>
<td>0.02</td>
</tr>
<tr>
<td>(^{239+240}\text{Pu})</td>
<td>5.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

*Uncertainty is expressed as a mixture model median based standard deviation \(S(MM\text{-median}), k-1\) [1]

Table 20. Information values for massic activities for IAEA CRM 447, moss-soil.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Information value [Bq kg(^{-1})]</th>
<th>Uncertainty* [Bq kg(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{40}\text{K})</td>
<td>(0.55 \times 10^3)</td>
<td>(0.02 \times 10^3)</td>
</tr>
<tr>
<td>(^{90}\text{Sr})</td>
<td>5.0</td>
<td>0.3</td>
</tr>
<tr>
<td>(^{232}\text{Th})</td>
<td>37.3</td>
<td>2.0</td>
</tr>
<tr>
<td>(^{241}\text{Am}^{**})</td>
<td>2.2</td>
<td>0.2</td>
</tr>
<tr>
<td>(^{241}\text{Pu})</td>
<td>8.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Uncertainty is expressed as a mixture model median based standard deviation \(S(MM\text{-median}), k-1\) [1]

** The value of \(^{241}\text{Am}\) should be corrected for un-growth from \(^{241}\text{Pu}\)
IAEA CRM 384 – Fangataufa Sediment

Certified Reference Material 384, Fangataufa lagoon sediment, was collected in Fangataufa Lagoon (French Polynesia) by the IAEA Marine Environment Laboratory in July 1996 [59]. The area which the sediment was collected from had been exposed to previous nuclear weapons testing.

The Fangataufa sediment was frozen for 2 hours at 40 °C, freeze-dried with a + 5 °C increase in temperature per hour, then secondarily dried over 24 hours under a pressure of 0.02 mbar at a constant temperature of 40 °C. The sediment was then ground and sieved at 250 μm prior to bottling under nitrogen gas into 100 g bottles. After bottling, the material was sterilized in accordance with ISO standards by a 25 kGy total dose in an irradiation facility. The material was characterized in an interlaboratory comparison with participation of 94 laboratories including the IAEA Marine Environment Laboratory in Monaco between 1998 and 1999. Most analysis was conducted by gamma spectroscopy with transuranic element analysis conducted by radiochemical separation and alpha or beta counting.

Homogeneity of the material was tested on 30 portions of material by measuring the activity of $^{40}$K, $^{60}$Co, $^{137}$Cs, $^{155}$Eu, $^{210}$Pb, $^{226}$Ra, $^{235}$U, $^{238}$Pu, $^{239+240}$Pu, and $^{241}$Am. Activity concentration of $^{210}$Po, $^{235}$U, $^{238}$U, $^{238}$Pu, $^{239+240}$Pu, and $^{241}$Am was measured by alpha spectrometry, prior to radiochemical purification. The reference date for decay correction is 1 August 1996.
Table 21. Certified values for massic activities for IAEA CRM 384, Fangataufa sediment.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Certified Value [Bq kg⁻¹]</th>
<th>95% Confidence Interval [Bq kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁴⁰K</td>
<td>6.8</td>
<td>6.5-7.1</td>
</tr>
<tr>
<td>⁶⁰Co</td>
<td>2.50</td>
<td>2.40-2.60</td>
</tr>
<tr>
<td>¹⁵⁵Eu</td>
<td>7.0</td>
<td>6.7-7.3</td>
</tr>
<tr>
<td>²³⁰Th</td>
<td>2.50</td>
<td>2.38-2.61</td>
</tr>
<tr>
<td>²³⁸U</td>
<td>35.5</td>
<td>33.4-36.8</td>
</tr>
<tr>
<td>²³⁸Pu</td>
<td>39.0</td>
<td>38.6-39.6</td>
</tr>
<tr>
<td>²³⁹-²⁴⁰Pu</td>
<td>107</td>
<td>103-110</td>
</tr>
<tr>
<td>²⁴¹Am*</td>
<td>7.1</td>
<td>6.7-7.4</td>
</tr>
</tbody>
</table>

*The values should be corrected for in-growth from ²⁴¹Pu.

Table 22. Information values for massic activities – IAEA CRM 384, Fangataufa sediment.

<table>
<thead>
<tr>
<th>Radionuclide</th>
<th>Information Value [Bq kg⁻¹]</th>
<th>95% Confidence Interval [Bq kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>⁹⁰Sr</td>
<td>1.7</td>
<td>1.5-1.9</td>
</tr>
<tr>
<td>¹³⁷Cs</td>
<td>0.30</td>
<td>0.24-0.50</td>
</tr>
<tr>
<td>²¹⁰Pb (²¹⁰Po)*</td>
<td>22</td>
<td>21-23</td>
</tr>
<tr>
<td>²²⁶Ra</td>
<td>2.4</td>
<td>2.0-2.9</td>
</tr>
<tr>
<td>²²⁸Ra</td>
<td>1.6</td>
<td>0.8-2.0</td>
</tr>
<tr>
<td>²³²Th</td>
<td>0.022</td>
<td>0.008-0.024</td>
</tr>
<tr>
<td>²³⁴U</td>
<td>40</td>
<td>35-43</td>
</tr>
<tr>
<td>²³⁵U</td>
<td>1.70</td>
<td>1.60-1.96</td>
</tr>
<tr>
<td>²³⁹Pu</td>
<td>98</td>
<td>85-105</td>
</tr>
<tr>
<td>²⁴⁰Pu</td>
<td>17.5</td>
<td>15.1-18.7</td>
</tr>
<tr>
<td>²⁴¹Pu</td>
<td>55</td>
<td>41-69</td>
</tr>
</tbody>
</table>

*²¹⁰Pb and ²¹⁰Po are considered to be in equilibrium.

3.1.2 Radioisotope Standards – Tracers and Calibration Sources

Radioisotope Tracers

Four radioisotope tracers were used in this research; ²²⁹Th, ²³²U, ²⁴²Pu, and ²⁴³Am. The tracers were used in all experiments to monitor recovery of natural and anthropogenic radionuclides leached from the soil reference materials. Tracers were also used to test the extraction chromatography based separation procedure used in this research. Selection of tracers was based on minimizing energy interferences with isotopes present in the soil reference materials. The americium and thorium tracers were previously diluted to activity
concentrations seen in the table below, while the uranium and plutonium tracers were diluted as a part of this research. Details of isotope dilution are discussed in the next section.

Table 23. Tracer information including activity concentration and chemical form.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Activity Conc. [Bq mL⁻¹]</th>
<th>Chemical Form</th>
<th>Half-life [years]</th>
<th>Reference Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>²²⁹Th</td>
<td>1.70</td>
<td>Th(NO₃)₄ in 0.1 M HNO₃</td>
<td>7340 ± 160</td>
<td>1 July 2006</td>
</tr>
<tr>
<td>²³²U</td>
<td>0.101</td>
<td>UO₂(NO₃)₂ in 2.0 M HNO₃</td>
<td>68.9</td>
<td>1 July 2002</td>
</tr>
<tr>
<td>²⁴²Pu</td>
<td>0.0707</td>
<td>3.2 M HNO₃</td>
<td>373,500</td>
<td>7 June 1994</td>
</tr>
<tr>
<td>²⁴³Am</td>
<td>1.76</td>
<td>AmCl₃ in 1 M HCl</td>
<td>2,690,000</td>
<td>1 August 2006</td>
</tr>
</tbody>
</table>

The thorium tracer used in this research is ²²⁹Th from Isotope Products Laboratories, source number 1198-23-9 [62]. The original mass of the solution was 5.00540 g in a 5 mL vial with a concentration of 1.998 μCi g⁻¹ or 73.93 kBq g⁻¹. Activity of the solution was determined using gamma ray spectroscopy at a peak energy of 193.5 keV with a branching ratio of 0.0441 gammas per decay. Of thorium isotopes present in the tracer, ²²⁹Th accounted for 99.938% of the activity of solution. Total uncertainty at the 99% confidence level is ± 3.2%. It should be noted that major sorption of thorium occurs onto walls of plastic containers even at a pH < 1, so the tracer should be stored in a glass container. The decay energy of ²²⁹Th (4.845 MeV) is close to that of ²³⁰Th (4.688 MeV), so the ²³⁰Th peak can be difficult to resolve in an alpha spectrum with and significant low-energy tailing of the ²²⁹Th peak.

The uranium tracer used in this research is ²³²U from NIST, source ID 4324B [63]. The original mass of the solution was 5.321 g in a 5 mL vial with a concentration of 0.001033 μCi
g$^{-1}$ or 38.22 Bq g$^{-1}$. Activity of the solution was determined using coincidence/anticoincidence counting. Uncertainty listed on the certificate is ± 0.80%. Due to the relatively low half-life of this tracer, it should be purified before use to separate the $^{228}$Th daughter from the $^{232}$U tracer.

The plutonium tracer used in this research is $^{242}$Pu from NIST, source ID 4334H [64]. The original mass of the solution was 5.5 g in a 5 mL vial with a concentration of 0.000711 μCi g$^{-1}$ or 26.31 Bq g$^{-1}$. Activity of the solution was determined using liquid scintillation counting of material from the master solution. Uncertainty listed on the certificate is ± 0.72%.

The americium tracer used in this research is $^{243}$Am from Isotope Products Laboratories, source number 1198-23-8 [65]. The original mass of the solution was 5.08496 g in a 5 mL vial with a concentration of 1.967 μCi g$^{-1}$ or 72764 Bq g$^{-1}$. Activity of the solution was determined using gamma ray spectroscopy at a peak energy of 74.7 keV with a branching ratio of 0.674 gammas per decay. Total uncertainty at the 99% confidence level is ± 3.0%.

**Isotope Dilution**

Standard solutions of $^{232}$U and $^{242}$Pu from NIST were diluted using the procedure for accurately diluting and dispensing radioactive solutions [66]. The neck of the glass ampoule containing the original tracer solution was filed and broken and the tracer solution was transferred to a polyethylene ampoule for weighing. Polyethylene ampoules were a 5 cc volume and obtained from Canus Plastics, Inc [67].

The tracer solution was then transferred into a dilution flask and diluted to 2 L. Weights were measured between each step with no taring of the scale. Ampoule masses in the table
below reflect the weight of the ampoule plus the beaker they were contained within. Diluted tracer activities were calculated gravimetrically using the weights shown in Table 24.

Figure 15. Polyethylene ampoule used for standard dilution.

Table 24. Weights of $^{232}\text{U}$ and $^{242}\text{Pu}$ tracer solutions throughout standard dilution procedure.

<table>
<thead>
<tr>
<th>Container</th>
<th>Mass for $^{232}\text{U}$ [g]</th>
<th>Mass for $^{242}\text{Pu}$ [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empty dilution flask</td>
<td>460.6</td>
<td>438.5</td>
</tr>
<tr>
<td>Full glass ampoule</td>
<td>40.2387</td>
<td>40.3460</td>
</tr>
<tr>
<td>Empty polyethylene ampoule</td>
<td>31.9384</td>
<td>32.4617</td>
</tr>
<tr>
<td>Full polyethylene ampoule</td>
<td>37.2395</td>
<td>37.9011</td>
</tr>
<tr>
<td>Empty glass ampoule</td>
<td>34.9311</td>
<td>34.9028</td>
</tr>
<tr>
<td>Empty polyethylene ampoule</td>
<td>31.9396</td>
<td>32.4707</td>
</tr>
<tr>
<td>Dilution flask + standard</td>
<td>465.7</td>
<td>444.0</td>
</tr>
</tbody>
</table>

Calibration Standards

Calibration standards were used for energy and efficiency calibrations of all alpha detectors used in this research. Two mixed sources from Eckert & Ziegler were used for energy calibrations [68]. A single energy source of $^{241}\text{Am}$ from Eckert & Ziegler was used for
efficiency calibrations [69]. All sources are a 24.1 mm diameter x 0.65 mm thick stainless steel disk that was prepared by electrodeposition of the alpha emitting nuclides onto the stainless steel disk. Total alpha activity for each source was determined using a ZnS scintillation detector.

Table 25. Alpha spectroscopy calibration source information.

<table>
<thead>
<tr>
<th>Source ID</th>
<th>Isotope</th>
<th>Activity [dpm]</th>
<th>Half-life [years]</th>
<th>Energy Range [keV]</th>
<th>Calibration Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>75338-602</td>
<td>$^{241}$Am</td>
<td>1.044E4</td>
<td>4.322 E2</td>
<td>N/A</td>
<td>26 July 2007</td>
</tr>
<tr>
<td>75337-602</td>
<td>$^{230}$Th</td>
<td>1.010E4</td>
<td>7.538 E4</td>
<td>4450-4730</td>
<td>24 July 2007</td>
</tr>
<tr>
<td>75337-602</td>
<td>$^{239}$Pu</td>
<td>1.006 E4</td>
<td>2.41 E4</td>
<td>4950-5240</td>
<td>24 July 2007</td>
</tr>
<tr>
<td>75337-602</td>
<td>$^{244}$Cm</td>
<td>1.011 E4</td>
<td>1.810 E1</td>
<td>5610-5850</td>
<td>24 July 2007</td>
</tr>
<tr>
<td>75336-602</td>
<td>$^{238}$U</td>
<td>99.0</td>
<td>4.468 E9</td>
<td>3900-4290</td>
<td>9 May 2007</td>
</tr>
<tr>
<td>75336-602</td>
<td>$^{234}$U</td>
<td>97.9</td>
<td>2.455 E5</td>
<td>4580-4860</td>
<td>9 May 2007</td>
</tr>
<tr>
<td>75336-602</td>
<td>$^{239}$Pu</td>
<td>87.8</td>
<td>2.41 E4</td>
<td>4950-5240</td>
<td>9 May 2007</td>
</tr>
<tr>
<td>75336-602</td>
<td>$^{241}$Am</td>
<td>97.5</td>
<td>4.322 E2</td>
<td>5275-5590</td>
<td>9 May 2007</td>
</tr>
</tbody>
</table>

3.2 Chemical Analysis

This section presents the wet chemistry techniques used in this research and their general methods. The figure below is a flow chart representing sample treatment from start to finish. The procedures for all wet chemistry can be found in the Appendix.

Any changes to these methods will be noted in individual chapters (4-6). All reagents listed are ACS grade unless stated otherwise. Several procedures are used from start to finish for every sample analyzed. Each procedure will be discussed in detail in the following sections.
3.2.1 Sequential Extraction

Standard reference materials discussed in section 3.1.1 were used for sequential extraction experiments. The general sequential extraction procedure, previously optimized by NIST, is presented below. Any modifications to the procedure for specific experiments
will be discussed in Chapters 4-6. The sequential extraction procedure is shown in the Appendix.

Table 26. Reagent concentrations, reaction times and temperatures for the sequential extraction procedure.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Target Phase</th>
<th>Reagent</th>
<th>Concentration (M)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Exchangeable</td>
<td>MgCl₂</td>
<td>1</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>Carbonates</td>
<td>NH₄Ac in 25% HAc</td>
<td>2</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>III</td>
<td>Fe/Mn Oxides</td>
<td>NH₂OH·HCl in 25% HAc</td>
<td>0.1</td>
<td>70</td>
<td>6</td>
</tr>
<tr>
<td>IV</td>
<td>Organic Material</td>
<td>30% H₂O₂ in 0.02 M HNO₃</td>
<td>30 wt %</td>
<td>70</td>
<td>3</td>
</tr>
<tr>
<td>V</td>
<td>Persistently Bound</td>
<td>HNO₃</td>
<td>16</td>
<td>90</td>
<td>4</td>
</tr>
</tbody>
</table>

Approximately 70 g of sediment was measured into a VWR Erlenmeyer flask and dried overnight in a VWR model 1320 thermostatically controlled oven according to reference material certificate guidelines. Sediment was then divided into five replicates of 12 g each and measured into Corning polypropylene 250 mL centrifuge bottles. Thirty-five milliliters of deionized water was added to each bottle containing sediment and left to sit overnight to expand clay minerals. All deionized water used in this research is purified using a Pall Cascada LS Deionized water system.

Following soil pretreatment, 180 mL of the first reagent, 1 M MgCl₂ (Mallinckrodt, Lot # H09N54), was added to the soil in the 250 mL centrifuge bottle. The bottles were then sealed with parafilm and placed in a Thermo Electron Corporation Precision water bath model 2870 set to the temperature and reaction time shown in Table 26. The shaker table was set to 200 rpm for every reaction.
Upon completion of the leaching process, bottles were removed and centrifuged at 3000 rpm for 30 minutes in a Beckman Coulter Allegra 6 Centrifuge. The leachate was poured into a 500 mL bottle following centrifugation. The sediment was rinsed twice with 25 mL of 1 M MgCl₂ and 25 mL of DI, respectively, before being centrifuged again after each rinsing at 3000 rpm for 10 minutes. The supernatant from each rinse was poured off into the same bottle as the leachate.

Figure 17. Precision water bath (left) and Allegra 6 centrifuge (right) used in sequential extraction experiments.

Each leachate was then filtered through a 0.45 μm, 47 mm diameter Pall filter (Lot # T71813) and acidified to a pH of approximately 1 with HNO₃, as recommended by Outola et al [4]. The filter with respective solid was added to the centrifuge bottle for the next fraction and the leachate was set aside for future alpha and stable element analysis. An aliquot of 50 mL volume was removed from each leachate, evaporated to dryness, reconstituted in 1% HNO₃ and saved for stable element analysis by ICP-MS/AES. Tracers including ²²⁹Th, ²³²U, ²⁴²Pu and ²⁴¹Am were added to the remaining leachate, which was then transferred to a VWR 600 mL glass beaker for evaporation prior to preconcentration.
Experimental steps from reagent addition to preconcentration preparation were repeated for fractions II, III, and V using ammonium acetate (BDH, Lot # 48221850) in acetic acid (BDH Aristar, Lot # 200917611), hydroxylamine hydrochloride (J.T. Baker, Lot # H34467) in acetic acid, and nitric acid (BDH, Lot # E09028), respectively. For fraction four, the sediment was slurried out of the bottle into a 600 mL beaker using 70 mL of 0.5 M HNO₃. A volume of 110 mL of 30% H₂O₂ (BDH, Lot # 49154926) was then added to the sample in the beaker dropwise on a VWR hot plate at approximately 200 °C until the reaction was complete. The sample was then transferred back into the centrifuge bottle for separation of leachate from the solid phase as mentioned above for all other fractions.

3.2.2 Preconcentration

A preconcentration step was performed to concentrate actinides in the sample for simpler analysis with less sample bulk. Two preconcentration steps are taken, a ferric hydroxide coprecipitation and a cerium fluoride microprecipitation. The ferric hydroxide co-precipitation reduces sample mass and destroys some common interferences that can affect alpha spectra. The cerium fluoride microprecipitation further reduces sample mass and leaves the sample in a matrix acceptable for loading onto extraction chromatography columns for separations.

Ferric Hydroxide Co-Precipitation

Each sample was reconstituted in 100 mL DI and 100 mL 1.0 M HCl following evaporation. Next, 0.5 mL of 20 mg Fe³⁺ mL⁻¹ iron carrier (ferric chloride, BDH, Lot # 84211) was added and the sample was heated to boiling. After the sample had boiled for 20 minutes, ammonium hydroxide (EMD, Lot # 48213) was added dropwise until turbidity persisted. An additional 10 mL of ammonium hydroxide was then added. The sample remained on the hot plate for 10 more minutes, then was removed to cool for 30 minutes.
before the supernatant and precipitate were separated. The precipitate was washed twice with 15 mL DI and centrifuged at 3000 rpm for 5 minutes with supernatant being removed between washes. The washed precipitate was then dissolved in 6.0 mL of 1.5 M HCl (J.T. Baker, Lot # E09028) and 7.5 mL of 0.01 M HCl.

**Cerium Fluoride Microprecipitation**

The cerium fluoride microprecipitation discussed in this section is part of the Maxwell procedure leading up to column separations [70]. The procedure was scaled down to minimize the volume of concentrate hydrofluoric acid used. Discussion of the scaling down will be presented in Chapter 4.

A volume of 0.2 mL of 0.00155 g mL\(^{-1}\) cerium carrier (99.5% cerium (III) nitrate hexahydrate, Alfa Aesar, Lot # I21P30) was added to the dissolved ferric hydroxide precipitate. Next, 1.1 mL of concentrated hydrofluoric acid was added and the sample was placed in an ice bath for 10 minutes to reduce solubility. The samples were then filtered onto 0.1 \(\mu\)m polypropylene Eichrom Resolve filters with the assistance of a Millipore filtration manifold (model # 1225) connected to a GAST model # DOL 122A-AA vacuum pump. The precipitate was washed off the filters into a 50 mL centrifuged tube using 10 mL of 3.0 M HNO\(_3\) – 0.25 M boric acid at approximately 50 °C. The sample was then reconstituted in 7.0 M HNO\(_3\) – 2.0 M Al(NO\(_3\))\(_3\) for column loading.

### 3.2.3 Separations

The separation procedure used for this research was designed for rapid separations of radionuclides from soil matrices [70]. The flow chart in the figure below shows the steps taken in the procedure, including from which extraction chromatographic resin each element elutes. The sections below discuss the specifics of the procedure.
Sample Matrix and Valence Adjustments

Each sample is loaded onto the stacked columns in a 7 M HNO₃ – 2 M Al(NO₃)₃ matrix. The nitric acid will aid in the elements of interest sticking to the columns while the aluminum nitrate acts as a salting out agent to increase the nitrate concentration without increasing the acidity. Valence adjustments are made to the sample prior to column loading to ensure all elements to be analyzed are in the correct oxidation state. Sulfamic acid works as a holding agent and a reducing agent to reduce plutonium to the trivalent state. Ascorbic acid is added to reduce iron and manganese contaminants that can be problematic for plutonium oxidation. Finally, sodium nitrite is added to oxidize plutonium to the tetravalent state so it will sorb to TEVA.
Column Preparation and Sample Loading

Eichrom extraction chromatographic resins are stacked onto an Eichrom 24 sample vacuum box connected to a vacuum pump. The cartridges are stacked with Pre-filter resin on top, followed by TEVA, TRU, then DGA. Approximately 10 mL of 3 M HNO₃ is run through the columns before sample loading to wet the resins. Once the samples are loaded, the load tubes are rinsed with 3 mL 6 M HNO₃ and the rinse is added to the columns. The cartridges are then separated and elutions are performed on each separately.

Separation of Thorium

Following column loading, 7 mL of 3 M HNO₃ was run through TEVA columns to remove any residual uranium. The eluent was saved for future addition to TRU. Next, 10 mL of 5 M HNO₃ followed by 10 mL of 3 M HNO₃ were added to TEVA to remove matrix components. Thorium was then eluted using 23 mL of 9 M HCl.

Figure 19. Eichrom vacuum box with stacked TEVA, TRU and DGA for column separation experiments.
**Separation of Plutonium**

Once thorium had been eluted from TEVA, 5 mL of 3 M HNO₃ was added to reduce the amount of residual extractant. Plutonium was then eluted using 20 mL of 0.1 M HCl – 0.05 M HF – 0.03 M TiCl₃. A volume of 0.5 mL of 30 wt. % H₂O₂ was added to oxidize the plutonium back to the tetravalent state prior to sample mounting.

**Separation of Uranium**

A volume of 5 mL 0.25 M HNO₃ was added to DGA to remove any residual uranium. This volume was added to the volume of residual uranium removed from TEVA discussed in the thorium separation section. The residual uranium was then added to TRU prior to uranium elution. Approximately 20 mL of 4 M HCl – 0.2 M HF was added to TRU to remove any residual thorium that may have passed through TEVA onto TRU. Three mL of 3 M HNO₃ was then added to TRU to reduce the amount of residual extractant before stripping uranium. A volume of 15 mL of 0.1 M ammonium bioxalate was then used to strip uranium from TRU. Uranium was then reduced to the tetravalent state using 0.5 mL 20 wt. % TiCl₃.

**Separation and Purification of Americium**

Americium was stripped from DGA using 10 mL of 0.25 M HCl. The eluant was then transferred to a 100 mL glass beaker. The sample tube was rinsed with 3 mL concentrated HNO₃ with the rinse then added to the beaker. A volume of 0.05 mL of 1.8 M sulfuric acid was added to the beaker and evaporated to dryness to enhance destruction of and extractant present in the solution. Once dry, 2 mL of 15.8 M HNO₃ and 2 mL of 30 wt. % H₂O₂ were added to the beaker and again evaporated to dryness. The sample was then redissolved in 5 mL of 4 M ammonium thiocyanate – 0.1 M formic acid to remove any rare earth elements which would interfere with alpha spectrometry peak resolution.
The americium sample was loaded onto a 2 mL TEVA cartridge, followed by 10 mL of 1.5 M ammonium thiocyanate – 0.1 M formic acid. Americium was then stripped from the column using 20 mL of 1 M HCl. The sample beaker was washed first with 5 mL warm 1 M HCl, then 15 mL 1 M HCl with both rinses being added to the column.

3.2.4 Sample Mounting

A cerium fluoride microprecipitation procedure was used to mount samples for counting by alpha spectroscopy [71]. A volume of 0.1 mL of 0.00155 g mL\(^{-1}\) cerium carrier in the form of cerium nitrate hexahydrate was added to each sample post column separations. For every uranium sample, 0.5 mL of 20 wt. % titanium trichloride was added to reduce uranium to the tetravalent state so a precipitate will form. A volume of 1.0 mL of 28 M hydrofluoric acid was then added to each sample and allowed to precipitate for 30 minutes.

Figure 20. Millipore filtration manifold used for alpha source preparation and other filtration procedures.
During precipitation, Eichrom Resolve filters are loaded onto the Millipore filtration manifold. A few mL of 80% ethanol is added to each filter to open the pores. The filter is then rinsed with DI. Following precipitation, the samples are poured into a sample well on the filtration manifold. Once each sample is filtered, the sample well is rinsed with DI, then a few mL of 80% ethanol is added to aid in filter drying. Filters are then carefully removed from the filtration manifold using Teflon tipped tweezers then dried under a heat lamp. Once dry, the filters are mounted onto stainless steel planchets using double sided tape. The samples are then placed in petri dishes and taped to prevent sample loss and cross-contamination.

![Eichrom Resolve filter mounted to a stainless steel planchet for counting.](image)

**3.3 Instrumental Analysis**

Alpha spectroscopy was used for analysis of all samples in which thorium, uranium, plutonium and americium were being analyzed. The specifics of the instruments and counting procedures are discussed in section 3.3.1. Stable element analysis was performed using a combination of ICP-MS and ICP-AES. Elements with a concentration of less than 100
ppm were analyzed by ICP-MS since single digit percent recoveries of those elements from any fraction of sequential extraction would leave only 1 ppm concentration of that element in the sample.

3.3.1 Alpha Spectrometry

**Instrument Specifics**

Alpha samples were counted on three alpha spectrometry systems using a total of 23 Passivated Implanted Planar Silicon (PIPS) detectors each with an active volume of 450 mm$^2$ and 10.2 keV resolution. Two systems were Canberra Alpha Analysts and the third was an Oxford Oasis. All three systems run Genie 2000 software for data acquisition and analysis.

**Energy Calibration**

Energy calibration was performed on all detectors using the calibration standards discussed in section 3.1.2. Standards were counted for a time long enough to obtain at least 10,000 counts under the peaks, then saved as calibration files. The calibration file corresponding to the detector in use was then loaded with each sample that was counted throughout this research.

**Efficiency Calibration**

An $^{241}$Am standard discussed in section 3.1.2 was used for efficiency calibrations on all detectors. The standard was counted three times on each detector until at least 10,000 counts were achieved under the peak. Average count rates were calculated in counts per second which were then used to calculate detector efficiency using the certificate value for activity and Equation 3. Calculated efficiencies for each detector are shown in Table 30 in the appendix.
Equation 3. Equation for the calculation of detector efficiency.

\[ Efficiency = \frac{cps}{dps} \]

**Counting Procedure**

Samples are loaded on the stainless steel (Canberra systems) or Teflon (Oxford system) planchet holders, which are then placed in the chamber at shelf level 4, approximately 15 mm from the detector. Shelf 4 is ideal because it is far enough away from the detector to obtain better energy resolution due to the solid angle and close enough to obtain acceptable detector efficiency. Chambers are evacuated to a pressure of 0.200049 torr. Count times are set for 168 hours (1 week) which allows at least 10,000 counts to be recorded under the peak for most samples. Samples that have not reached 10,000 counts in a one-week count time will be counted for up to five weeks. This results in a counting error of 1% or less. Count times for sequential extraction samples discussed in chapter 5 were based on obtaining 1% counting statistics on the tracer peaks.

3.3.2 Inductively Coupled Plasma – Mass Spectrometry

**Instrument Parameters**

A Perkin Elmer Elan DRC II ICP-MS was used for analysis of stable element extraction. A daily performance evaluation was performed after a 30 minute instrument warmup period. Oxide formation, monitored by analyzing cerium, and formation of doubly charged ions, monitored by barium, were measured before the start of each run and determined to be anywhere from 1.4 – 1.7%. All runs were performed in pulse mode except for iron, which was run separately in analog mode.
Counting Procedure

The five replicates of each sequential extraction leachate previously dissolved in 1% ultrapure nitric acid were analyzed by ICP-MS with five replicate runs for each sample. Samples were measured following a 30 second read delay with a 20 second rinse with DI water between each sample. Analysis of no more than five analytes was done at one time. Initial measurements were performed on undiluted samples and additional measurements were taken after appropriate dilutions. Dilution data is shown in Tables 45 and 46 in the appendix.

3.4 Data Analysis and Calculation of Error

3.4.1 Alpha Spectroscopy Data Analysis

Data was saved as a Genie 2000 .CNF file then converted to a Microsoft Excel .csv file using ProSpect software. Background was then subtracted from each individual file, each representing one sample. Peaks area was determined and entered into a separate spreadsheet specific to the experiment. Activity for each peak was determined by dividing the total counts by the live count time. Equation 1 was then used to convert activity to disintegrations per second. Calculation of recovery values for the method verification studies discussed in chapter four, where only tracers were analyzed, was done using equation 4.

Equation 4. Calculation of Tracer Recovery

\[
Recovery = \frac{dps}{\text{known activity of tracer (Bq)}}
\]

The calculation of $^{232}$Th, $^{238}$U, $^{238}$Pu (for IAEA 384 only), $^{239,240}$Pu, and $^{241}$Am recovery from the four reference materials discussed in chapter five was a bit lengthier. The tracer
recovery was first calculated as discussed for chapter four results. A correction factor was used to account for the amount of leachate removed for stable element analysis:

Equation 5. Correction factor for ICP-MS leachate removal

\[
Total \ Counts \ Recorded = \frac{Measured \ Counts}{Fraction \ of \ Leachate \ used \ for \ Alpha \ Analysis}
\]

Once the volume factor was calculated, dps was determined using equation 3. To account for procedural losses, dps was corrected using equation 6.

Equation 6. DPS Corrected

\[
Corrected \ dps = \frac{measured \ dps}{tracer \ recovery}
\]

Isotope recovery was then calculated by dividing the corrected dps by the activity expected from a 12 g sample based on values listed on the certificate for each reference material. Decay corrections were made, as necessary using equation 10.

Equation 7. Decay correction

\[
A = A_0 e^{-\lambda t}
\]

Where A = current activity

\[
A_0 = activity \ at \ the \ time \ of \ certification \ of \ reference \ material \ or \ tracer
\]

\[
\lambda = \frac{\ln 2}{T_1}
\]

\[
t = time \ since \ certification
\]
3.4.2 Inductively Coupled Plasma – Mass Spectrometry Data Analysis

Results from ICP-MS analysis were initially reported in parts per billion. Reagent grade nitric acid that was used in sequential leaching experiments was analyzed separately and subtracted from data in fractions four and five to eliminate stable element contributions from impurities in the acid. Data was then converted to milligrams. Measured masses were divided by a correction factor based on the fraction of total sequential extraction leachate analyzed by ICP-MS and converted to parts per million for direct comparison with reference values.

3.4.3 General Data Analysis

In general, results discussed in chapters four through six are presented as the mean of three to five replicate samples, calculated using equation 4.

Equation 8. Calculation of mean values

\[ \bar{x} = \frac{\sum_{i=1}^{N} x_i}{N} \]

where: \( \bar{x} = \) mean
\( N = \) number of samples.

Error bars shown on plots throughout the results chapters represent the standard deviation of replicates, as calculated by equation 5.


\[ \sigma = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}} \]

where: \( \sigma = \) standard deviation
Calculation of combined standard deviations for total recovery values were done by taking the quadrature sum, shown in equation 6.

Equation 10. Quadrature sum

\[
\sigma_u = \sqrt{\sigma_x^2 + \sigma_y^2}
\]

Suspected outliers were removed using a Q-test, shown in equation 11.

Equation 11. Q test for removal out outliers

\[
Q_n = \frac{|x_a - x_b|}{R}
\]

where: \(R\) = the range of all data points

\(x_a\) = the suspected outlier

\(x_b\) = the point closest to \(x_a\)

3.4.3 Sources of Error

As with any experiment, several sources of error exist that may affect the data. The main source of error seen in this research was counting error. While it is typically desirable to achieve 1% counting error or less, the nature of this work and the materials analyzed did not allow counting errors this low in the length of time available to count. Samples were generally counted long enough to achieve 1% counting error for the tracers used, unless there was severely low recovery in a sample, in which case it was counted for a maximum of three weeks. Counting error was calculated using equation 10 and is reported with all raw data alpha in the appendix.
Equation 12. Counting error

\[
\sigma = \sqrt{N}
\]

Another significant source of error comes from the calculation of recovery values based on uncertified values reported on reference material certificates. All of the stable element values were listed as information values and some of the radionuclide activity concentrations were uncertified. The amount of error listed on certificate values can have a large effect on the calculation of recovery values and will be discussed in the results for affected elements. Other sources of error are minimal and arise from pipetting, glassware, balances, extraction chromatography resins, etc.
CHAPTER 4  RADIOANALYTICAL METHOD VERIFICATION

Many techniques exist for radioanalytical separations including solvent extraction, ion exchange, extraction chromatography, etc. Extraction chromatography, as discussed in greater detail in chapters 2 and 3, offers a quick and efficient way for the simultaneous separation of multiple radionuclides, while creating less waste than other separation procedures. Past research by Outola et al. used an anion exchange separation procedure for the separation of plutonium and uranium from post-sequential extraction leachates [4]. This research examines the usefulness of an extraction chromatography procedure originally developed for the rapid determination of radionuclides in soil samples by Maxwell et al. for the separation of these nuclides from sequential extraction leachates [70].

This chapter discusses the steps taken to verify an extraction chromatography based separation procedure for the radiochemical separations of sequential extraction leachates. The Maxwell separation procedure was first verified by running single tracers through the partitioning process to assess for any breakthrough and to compare total yields with those presented in the Maxwell paper. An investigation of potential effects caused by sequential extraction reagents was then conducted. The details of each experiment are presented in the sections below.

4.1 Extraction Chromatography Method Verification

Research by Maxwell et al. led to the development of a rapid column extraction method for removal of actinides from soil matrices. The separation procedure, discussed in chapter 3, employs a fusion technique for soil dissolution, iron hydroxide precipitation for concentration of actinides, and a cerium fluoride microprecipitation for elimination of the soil matrix. Actinides are separated using stacked 2 mL Eichrom cartridges of TEVA, TRU, and DGA. Method performance was tested using 5 g aliquots of soil samples traced with
242Pu, 243Am and 232U. Laboratory control standards (LCS) were also analyzed and consisted of a 3 M HNO₃ blank spiked with 238Pu, 241Am and 235U [70].

The research discussed below involves investigation of the elution properties of a single tracer at a time to obtain a better understanding of radioelement behavior and potential losses through the whole separation procedure. Running single tracers through the procedure eliminates interferences from the soil matrix, sequential extraction reagents, and interferences from other tracers present in solution.

4.1.1 Experimental

The extraction chromatography procedure used for this study was presented in detail in chapter 3. Triplicate samples of a single tracer for each radionuclide (229Th, 232U, 242Pu and 243Am) were prepared by evaporating a known volume of the tracer at 80 °C in a 50 mL centrifuge tube then reconstituting the residue in a 7 M HNO₃ – 2 M Al(NO₃)₃ load solution. As samples were run through the separation procedure, eluents from each step were collected in 50 mL centrifuge tubes and saved for subsequent analysis by alpha spectroscopy. Americium and uranium samples were each tracked through the entire separation procedure while thorium and plutonium samples were followed up to the respective elution steps for separation of thorium and plutonium. Each eluent was prepared for alpha spectroscopy using the cerium fluoride microprecipitation procedure discussed in chapter 3.

4.1.2 Results and Discussion

Overall, tracers behaved as expected throughout the separation procedure. Recoveries for americium, thorium, and uranium were all near 100%, while plutonium had a yield of
83%. Recovery values for each tracer are shown in Figure 22. Error bars shown in Figure 22 and 22 represent the standard deviation of the sample sets.

Lower plutonium recovery could be the result of incomplete valence adjustments due to the complex nature of plutonium redox chemistry. Further investigations should be conducted by tracking plutonium in the steps beyond plutonium elution in the separation procedure to obtain a better understanding of plutonium losses.

Figure 22. Single isotope study results including elution steps for $^{229}$Th, $^{232}$U, $^{242}$Pu, and $^{243}$Am
Figure 23 shows the recovery for all fractions in which a tracer was not eluted. No breakthrough higher than 1% was seen for any isotope in any eluent except for uranium in the first 3 M HNO₃ wash of TEVA at 2.3 ± 0.1%. This is expected, however, as the 3 M HNO₃ wash was designed to remove any residual uranium from TEVA that may have been retained during sample loading onto the columns.

Figure 23. Elution behaviors of $^{239}$Th, $^{232}$U, $^{242}$Pu, and $^{243}$Am.
Figure 24 shows a comparison of the recoveries obtained for $^{232}$U, $^{242}$Pu and $^{243}$Am in this research and by Maxwell et al. Uranium and americium results match well, but the plutonium recovery in this work is significantly lower than the recovery reported in the literature. Maxwell et al. did not determine a recovery for thorium.

Figure 24. Comparison of recovery for $^{232}$U, $^{242}$Pu, and $^{243}$Am in this work and reported by Maxwell et al.

4.1.3 Conclusions and Recommendations for Future Work

The investigation of single isotope behavior throughout the separation procedure confirmed high recoveries for uranium, americium, and thorium, suggesting the method is
ideal for separations of the isotopes and activity concentrations relevant to this research. Future work should include a complete investigation of thorium and plutonium elution behavior by tracking each tracer separately through the entire separation procedure. If plutonium recoveries still do not total up to near 100%, a more complete investigation of pre-column valence adjustments of plutonium should be considered.

4.2 Pre-Column Preconcentration Scaling Experiments

The Maxwell separation procedure [70] includes a cerium fluoride precipitation step to ensure complete removal of the soil matrix. This preconcentration step involves the use of 22 mL concentrated HF per sample, which was not feasible in the UNLV facilities and could prove to be a safety issue at other laboratories. A scaled down version of the CeF$_3$ procedure was tested in triplicate for all tracers used in the following experiments.

4.2.1 Experimental

Three replicates were tested for a 1:20 scale down of the Maxwell pre-column CeF$_3$ procedure. Tracers of $^{229}$Th, $^{232}$U, $^{242}$Pu and $^{243}$Am were added to a 50 mL volume of deionized water and evaporated to dryness. Following reconstitution in 200 mL of 0.5 M HCl, the ferric hydroxide coprecipitation procedure, mentioned in detail in chapter 3, was applied to the triplicate samples to preconcentrate the actinides. A CeF$_3$ microprecipitation was performed using 0.2 mL of 0.155 g mL$^{-1}$ cerium carrier and 1.1 mL of concentrated hydrofluoric acid. Samples were then reconstituted in the column load solution after being dissolved in 5 mL of warm 3 M HNO$_3$ – 0.25 M boric acid to assist in fluoride destruction. Separations were subsequently performed on all samples before CeF$_3$ microprecipitation sample mounting for alpha spectrometric analysis.
4.2.2 Results and Discussion

Figure 25 shows the recoveries for the scaled down pre-column CeF₃ procedure. The recovery includes assessment of sample loss from the time of tracer addition, through both pre-column preconcentrations, column separations, CeF₃ sample mounting and sample counting by alpha spectroscopy. Recoveries near or above 80% were seen for all tracers, suggesting the scaling of the pre-column CeF₃ microprecipitation is acceptable to use for future work.

Figure 25. Recovery of $^{229}$Th, $^{232}$U, $^{242}$Pu, and $^{243}$Am after utilizing a scaled down CeF₃ pre-column procedure.

4.2.3 Conclusions and Recommendations for Future Work

Investigations of the scaling down of reagent volumes used in the CeF₃ soil matrix removal step in the Maxwell separation procedure showed consistently high method recoveries among the four tracers tested. This information will allow the use of the separation method with lower quantities of hydrofluoric acid, making the procedure more
safe and applicable to laboratories with limits on the use of hydrofluoric acid. All following experiments utilized the scaled down volumes of cerium carrier and hydrofluoric acid.

4.3 Removal of Supernatant Following Sample Preconcentration

Analysis of radioactive samples with environmental concentrations must be carefully conducted to avoid losses of low amounts of radioactivity. Due to this concern, previous studies involved removal of supernatant from the pre-column CeF₃ procedure by simply pouring it off. Initial results showed highly variable and severely low recovery values for several fractions. Poured-off supernatants were saved for analysis by alpha spectroscopy to investigate losses in decanting. In addition, a filtration method including a washing step of the filters was tested.

4.3.1 Experimental

Measurement of Supernatant

All experiments in this section were discussed previously in section 4.3. Supernatants that were poured off were saved for analysis by alpha spectroscopy. Samples were run through the separation procedure then mounted onto Eichrom Resolve filters using the cerium fluoride microprecipitation procedure presented in chapter 3.

Investigation of Filtration Method

Single tracers of ²³²U, ²⁴²Pu, and ²⁴³Am were run through the CeF₃ microprecipitation and then filtered through 0.1 micron pore size, 25 mm diameter Eichrom Resolve filters using a Millipore filtration manifold. The precipitate was then washed from the filters using 5 and 10 mL volumes of warm (~60 °C) 3 M HNO₃ – 0.25 M boric acid. The resulting wash solution was then prepared for assay using a CeF₃ microprecipitation and counted by alpha spectroscopy. Washed filters were saved for future analysis for cases of low wash recovery.
4.3.2 Results and Discussion

Measurement of Supernatant

Figure 26 shows combined recoveries of sample and supernatant. Severe losses of uranium due to decanting were seen in fractions 1 and 2 and americium in fraction 1. Significant losses were also seen for all tracers across the board. The variations in recovery loss from decanting were severe enough to warrant the investigation of alternate filtration methods for separation of precipitate from supernatant. Decanting by pouring off the supernatant is highly discouraged.

![Figure 26. Sample and supernatant recoveries of $^{232}$U, $^{242}$Pu, and $^{243}$Am tracers from Maxwell separations procedure.](image)

Investigation of Filtration Method

Tracer recovery results for 5 and 10 mL wash volumes are shown in the figure below. Uranium and plutonium recoveries were low enough with a 5 mL wash to warrant an additional 5 mL wash, which increased the recovery by an additional 10%. Recovery for all three tracers is above 90% following a 5 mL to 10 mL wash.
4.3.3 Conclusions and Recommendations for Future Work

Results from the above studies clearly show the need for filtration of samples following pre-column CeF₃ microprecipitation. Decanting should not be performed by pouring off the supernatant as the precipitate is not visible and is likely to be poured off in an unknown amount with the supernatant. Future work should involve the analysis of thorium removal from filters.

4.4 Investigation of Effects of Sequential Extraction Reagents on Separation Efficiency

It is well known that Eichrom extraction chromatographic resins can suffer from decreased separation efficiency due to matrix interferences from the elements present within the samples. Several studies have been conducted to examine single element interferences on a variety of Eichrom resins. Due to the multitude of elements and chemicals present in the reagents used in sequential extraction studies, it was considered important to examine the effects of these reagents on separation efficiency. This was done
by using each sequential extraction reagent as initial sample matrix, tracing it with $^{232}$U, $^{242}$Pu, and $^{243}$Am, and applying the complete separation procedure to it.

4.4.1 Experimental

Triplicate samples were prepared for each sequential extraction reagent consisting of 50 mL of reagent at concentrations shown in Table 26. Control samples were prepared using 50 mL of deionized water. All samples were traced with $^{232}$U, $^{242}$Pu, and $^{243}$Am. Samples were evaporated to dryness and reconstituted in 100 mL DI and 100 mL 1 M HCl prior to Fe(III)OH precipitation for preconcentration of actinides. Following preconcentration and subsequent reconstitution, samples were subject to the scaled-down CeF$_3$ microprecipitation discussed in section 4.2. Samples were then reconstituted in 5 mL of 3 M HNO$_3$ – 0.25 M boric acid, 6 mL of 7 M HNO$_3$, and 7.5 mL of 2 M Al(NO$_3$)$_3$ for column loading. Separations were then performed following the procedure outlined in chapter 3. Samples were prepared for alpha spectroscopy using a cerium fluoride microprecipitation.

4.4.2 Results and Discussion

Results showed some variation in recovery based on tracer and sequential extraction reagent examined, but overall recoveries were above 50%, with several recoveries in the 80% – 100% range. The recovery of each element is discussed in detail below. Recoveries of ~80% match the previous results from the scaling down of the pre-column CeF$_3$ microprecipitation. Recovery of uranium, shown in Figure 28, was above 80% for all fractions except the organic fraction.
Figure 28. Uranium recovery in five fractions of sequential extraction procedure using only extraction reagents.

The low recovery combined with the high error bars in the organic fraction suggests incomplete and inconsistent oxidation of uranium to U(VI) between replicates which could leave varying amounts of less soluble U(IV) in the sample, thus explaining low recoveries. Fraction four leaching consists of a H₂O₂ – HNO₃ oxidation performed on a hotplate, with the reaction endpoint being determined by the experimenter. This makes the reaction conditions far less defined than the rest of the fractions that have a definite reaction time and temperature controlled by the water bath. The extraction conditions for the organic fraction should be investigated more closely in an attempt to increase uranium extraction from the organic target phase.

Recovery of plutonium, shown in Fig. 26, was near or above 70% for all fractions except the exchangeable target phase.
Low recovery of plutonium from the exchangeable target phase could be caused by plutonium complexing with the magnesium in solution [72], thus increasing the solubility of plutonium, causing incomplete precipitation of plutonium prior to column separation. Recovery of plutonium was also low in the Fe/Mn oxide leaching step. This is possibly due to an incomplete reduction of plutonium. The rate of reduction of hydroxylamine can decrease significantly with slight variations in pH (Thompson 1980). A more thorough monitoring of pH throughout the Fe/Mn oxide reduction step may provide insight into the low plutonium recoveries seen in the fraction. Low plutonium recovery from the Fe/Mn oxide target phase has been observed, but not discussed, by others in literature [3] [73].

Recovery of americium, shown in Fig. 27, was above 70% for all fractions except the exchangeable and Fe/Mn oxide target phases.
Figure 30. Americium recovery in five fractions of sequential extraction procedure using only extraction reagents.

Low recovery of americium from the exchangeable and Fe/Mn oxide phases was seen. Though americium has a high recovery in the organic fraction, the higher error bars point to inconsistent leaching of americium from the organic fraction, as seen with uranium discussed previously.

4.4.3 Conclusions and Recommendations for Future Work

Results of the investigation of sequential extraction reagents on separation efficiency show promise. With the majority of recoveries above 75%, there are no major issues that would cause the Maxwell separation procedure to not be useful for these experiments. Since tracers are used in all sequential extraction experiments, a lower than 100% recovery from the extraction chromatography procedure will only result in slightly longer count times and
increased detection limits. Future work should investigate creating more defined extraction conditions for the organic target phase to reduce variation between samples and increase recovery, especially for uranium.

4.5 Chapter Conclusions

Element breakthrough, method repeatability, interferences of sequential extraction reagents on separation efficiency, and an optimal method for decanting were all investigated in this chapter. Results of all studies in the separation procedure method verification suggest the Maxwell procedure is fit to be coupled with the sequential extraction procedure for separation of radioisotopes from sequential extraction leachates for alpha analysis.

Future work should include investigation of plutonium and thorium breakthrough following the elution step for completeness and in attempt to find the missing 20% of plutonium. More defined extraction conditions for the organic target phase should be investigated to decrease extraction variability and potentially increase uranium extraction efficiency. A more thorough monitoring of pH throughout the Fe/Mn oxide reduction should be considered in attempt to provide insight into low plutonium and americium recoveries. All separations of precipitate from the pre-column CeF₃ precipitation should be done by filtration followed by a wash of the filter with at least 10 mL of warm 3 M HNO₃ – 0.25 M boric acid.
CHAPTER 5  VERIFICATION AND CAPABILITY EXPANSION OF A STANDARD SEQUENTIAL EXTRACTION PROTOCOL

Standardization of a sequential extraction protocol would allow for certification of reference materials for radionuclide association within geochemical host phases in reference soils, an important tool for researchers. A standard protocol would also allow direct comparison of radionuclide leaching behavior from various soils. Most sequential extraction studies found in literature make slight variations to existing protocols to assess leaching of various radionuclides from soils ranging from natural sediment to soil affected by uranium mining. Since the reaction conditions are not identical in each experiment, no direct comparison of radionuclide dissolution can be made.

The first step in standardizing a sequential extraction procedure was completed by Outola et al. with the optimization of reaction parameters. The next logical step is to attempt to replicate the procedure at other laboratories to ensure reproducibility with similar results for the same reference materials.

This chapter discusses the verification and expansion of capabilities of a standard sequential extraction protocol. Previous studies by Outola et al. [4] were repeated in this work in an attempt to confirm the optimized procedure by showing similar leaching behaviors at a different laboratory. Recovery of stable elements such as aluminum, iron, manganese, and strontium was measured in an attempt to better understand phase selectivity. Leaching behavior of americium and thorium was monitored for the potential expansion of the standard sequential extraction protocol to include ability for analysis of multiple radionuclides. The previously optimized procedure was then applied to two additional certified reference materials, IAEA 384 (Fangataufa sediment) and IAEA 447 (moss-soil), to determine differences in behavior across a broad range of soil types.
Experimental details, results, conclusions, and recommendations for future work are presented in the following sections.

5.1 Sequential Extraction Method Verification

Work by Outola et al. examined extraction of $^{238}$U and $^{239,240}$Pu from lake and ocean sediment reference material. The sequential extraction procedure, a modification of the Tessier procedure [1], was optimized for reaction time, reaction temperature, and reagent concentration. Reaction conditions are shown in the table below, with the optimum conditions listed in bold. Numbers in parentheses were not mentioned in testing conditions, but were chosen for optimized extraction conditions.

Table 27. Extraction conditions for sequential extraction procedure optimized by Outola et al. [4].

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Reagent</th>
<th>Temperature $^\circ C$</th>
<th>Concentration (M)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>MgCl$_2$</td>
<td>25/50/90</td>
<td>0.1/0.4/1.0</td>
<td>1/2/4</td>
</tr>
<tr>
<td>Carbonate</td>
<td>NH$_4$Ac in 25% HAc</td>
<td>25/50/90</td>
<td>0.5/1/2</td>
<td>1/4/16</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>NH$_2$OH-HCl in 25% HAc</td>
<td>25/50/90 (70)</td>
<td>0.01/0.04/0.1</td>
<td>1/4/16</td>
</tr>
<tr>
<td>Organic</td>
<td>30% H$_2$O$_2$ in 0.02 M HNO$_3$</td>
<td>50/70/90</td>
<td>-</td>
<td>1/3/6</td>
</tr>
<tr>
<td>Residual</td>
<td>HNO$_3$</td>
<td>25/50/90</td>
<td>4/8/16</td>
<td>1/4/16</td>
</tr>
</tbody>
</table>

The research in this section aimed to replicate extraction results seen by Outola et al. by repeating sequential extraction experiments at the optimized conditions, with five replicates for each fraction from NIST 4354 (lake sediment) and NIST 4357 (ocean sediment).
5.1.1 Experimental

Five replicates of lake sediment (NIST 4354) and five replicates of ocean sediment (NIST 4357) were passed through the optimized sequential extraction protocol, as discussed in detail in chapter 3. Measurements of soil mass were taken between each leaching step to assess for losses of soil due to dissolution or leachate filtration. Prior to addition of tracers, a fraction of each leachate (50 mL) was measured gravimetrically and set aside for analysis of stable metal concentrations by ICP-MS. Tracers of $^{229}$Th, $^{232}$U, $^{242}$Pu, and $^{243}$Am were added in activity concentrations matching certificate values for the reference materials.

Some reaction conditions were adjusted based on properties of the reference materials. Lake sediment samples were centrifuged at 5000 rpm after the first leaching step since 3000 rpm was not enough to separate the leachate from the solid material. Due to the high carbonate content of the ocean sediment reference material, carbon dioxide gas was allowed to evolve from the centrifuge bottle between addition of the extracting reagent and capping of the bottles for the leaching reaction. All other experimental conditions matched those discussed in chapter 3.

5.1.2 Results and Discussion

Leaching results of $^{238}$U and $^{239,240}$Pu from lake and ocean sediment reference materials are shown in Fig. 30. Uranium extracts more completely from lake sediment, likely due to its association with more soluble compounds such as carbonates and organic matter. Anoxic conditions in the lake environment could potentially lead to microbial oxidation of U(IV) to the more soluble U(VI), which then can form uranyl carbonate complexes, thus the high extraction of uranium from the carbonate target phase. Uranium is more evenly, yet less
completely, extracted from ocean sediment. It is likely that the majority of unleached uranium still remains in the highly insoluble U(IV) form. This should be verified by performing a complete dissolution on the previously leached ocean sediment.

Total plutonium recovery of over 90% was seen for both lake and ocean sediment. In lake sediment, plutonium leaching mostly occurred in the organic and residual target phases, suggesting plutonium exists in more insoluble forms. High recovery of plutonium from the leaching of the carbonate target phase suggests more soluble plutonium and that the extraction behavior correlates with soil geochemistry. A more detailed discussion about extraction results is presented below along with comparison of this data to literature values from Outola et al.

Figure 31. Uranium and plutonium extraction results for lake and ocean sediment
Uranium Extraction from Ocean and Lake Sediment

Extraction values for uranium from lake and ocean sediment are shown in Figure 32. Uranium extraction values from ocean sediment followed similar trends to results from the literature for both target phases and total extraction values. Differences not within error bars between this work and literature values are higher recovery from exchangeable fraction and lower recovery from Fe/Mn oxide fraction at UNLV. The differences are minimal (< 5%), however, so they may disappear with the addition of error bars on the Outola data. Total uranium extracted was measured to be 39% vs Outola's ~47%. Outola et al. only reported the average standard deviation of 2 to 13% for $^{238}$U and $^{239,240}$Pu in the five fractions.

Uranium extraction from lake sediment matched Outola data in all but the carbonate and organic fractions. Outola saw a higher amount of uranium extract from the carbonate phase, suggesting the association of uranium with carbonate complexes in the lake sediment. UNLV saw a higher amount of uranium leached from the organic fraction, as expected with a sample with high organic content.

There was no discussion of sediment pretreatment, other than wetting to expand clay minerals, within Outola's experimental discussion. It is possible that different sediment pretreatment methods (i.e. drying conditions) could lead to discrepancies in the data between the two laboratories, as suggested by literature [5]. Total leaching of uranium from lake sediment matched well between this work (96%) and Outola (100%).
Plutonium Extraction from Ocean and Lake Sediment

Extraction values for plutonium from lake and ocean sediment are shown in Fig. 31. UNLV plutonium extraction values from ocean sediment reference material showed much higher leaching from the carbonate target phase than seen by Outola (57.6 ± 4.4% vs. 22%). This could be due to the sample pretreatment, as discussed for uranium extraction from lake sediment. The organic content of the ocean sediment reference material is less than 2%, so high leaching from the organic fraction in Outola’s data suggests a possible problem with phase selectivity in the organic target phase. Extraction of plutonium from the Fe/Mn oxide, organic, and residual target phases matched the trend seen by Outola, though at lower values due to the high amount of plutonium extracted in the carbonate fraction at UNLV. Though differences were seen in leaching behaviors between fractions, the total plutonium recovery matched well between UNLV (97%) and Outola et al. (100%).
Plutonium extraction from lake sediment matched well with Outola results except for the organic and residual fractions. High error bars in this work point to incomplete leaching from some replicates in the organic target phase. Those replicates that were incompletely leached in the organic phases had higher recovery in the residual fraction, since there was more plutonium left to be leached. This points to a potential problem with the definition of reaction conditions for the organic target phase. The organic target phase is the only fraction where reaction conditions are not controlled by a water bath for a set amount of time. The oxidation reaction takes place in a beaker on a hot plate with instructions to leach until the reaction is complete, leaving more room for error and deviations between replicates than in the other four fractions. Reaction conditions should be better defined before standardizing a sequential extraction protocol. Total extraction results for $^{239,240}$Pu from lake sediment were 94% for UNLV and 98% for Outola.

Figure 33. Ocean sediment (left) and lake sediment (right) extraction results for plutonium vs Outola

![Graph showing extraction results for plutonium](image-url)
5.1.3 Conclusions and Recommendations for Future Work

Though total leaching recoveries matched for uranium and plutonium in both lake and ocean sediment between this work and Outola, some discrepancies were seen in regards to the fractions from which $^{238}$U and $^{239,240}$Pu were leached. Majority of uranium leaching from lake sediment is seen in the carbonate and organic fractions, while leaching from ocean sediment is from exchangeable, carbonate, and residual. Plutonium leaching from lake sediment is mainly from organic and residual while plutonium leaching from ocean sediment is primarily from carbonate and organic. Future work should focus on creating more defined reaction conditions for the reference material pretreatment and extraction from the organic target phase to make the procedure more user-friendly and ready for standardization. A complete dissolution should be performed on ocean sediment reference material to determine the amount of uranium remaining in the residual sediment.

5.2 Addition of Americium and Thorium Analysis Capabilities

Results from the previous section show that there is promise for a standard sequential extraction protocol following a few slight procedural adjustments. That said, a good standard procedure will allow the analysis of several actinide and stable elements from soils and sediments. This section discusses the addition of analysis capabilities for americium and thorium extraction from lake and ocean sediment.

There are few studies assessing americium leaching from soil and sediment via sequential extraction. Of the few studies in literature, americium leaching behavior is not similar, likely because of the use of different reaction conditions [7] [8] [11] [12]. Not only was americium seen extracted from different host phases, but some studies show correlation of americium and plutonium leaching while others do not. It is clear that the standardization of a sequential extraction protocol would benefit the research community.
Research on thorium association to geochemical host phases of soils and sediments is also scarce. Thorium extraction data is important because it can provide information on source contributions as well as provide great insight into mobility of certain actinide contaminants, mainly uranium. For example, if $^{230}\text{Th}:{^{238}\text{U}}$ ratios vary from $^{232}\text{Th}:{^{238}\text{U}}$ ratios, this suggests different sources of thorium, since $^{230}\text{Th}$ is present in the $^{238}\text{U}$ decay series and $^{232}\text{Th}$ is not [22].

5.2.1 Experimental

Experiments in this section were performed along with the experiments in section 5.1. Tracers of $^{229}\text{Th}$ and $^{243}\text{Am}$ were added to sequential extraction leachates after a volume was removed for stable element analysis by ICP-MS. All samples were prepared and analyzed in the same manner as plutonium and uranium samples discussed in section 5.1.

5.2.2 Results and Discussion

**Americium Extraction**

Figure 33 shows americium extraction behavior from lake and ocean sediment. Leaching of americium varied greatly depending on the reference material, with the majority of americium leaching from the residual target phase in lake sediment and the carbonate phase in ocean sediment. No americium was seen extracted from the organic fraction in lake sediment, a material with relatively high organic content, while the majority of americium is leached from the carbonate target phase in ocean sediment, a material with high carbonate content. A continuation of the discussion of americium leaching behavior will follow below, with leaching results for all four actinides taken into account.
Figure 34. Americium-241 leaching from lake and ocean sediment.

![Bar chart showing recovery of americium from different phases of sediment](chart.png)

Total americium extraction from ocean sediment was higher than 100%, despite several correction factors to account for background, decay correction, sample geometry, and contributions of $^{241}\text{Am}$ from impurities in the $^{243}\text{Am}$ and $^{242}\text{Pu}$ tracers. The high recovery is likely due to americium results being calculated based off uncertified values listed on the reference certificate. Americium concentration for ocean sediment was reported as 10 mBq g$^{-1}$, with a range of 7 – 18 mBq g$^{-1}$. If, for example, the actual concentration was 18 mBq g$^{-1}$ instead of the 10 mBq g$^{-1}$ used to calculate all recoveries in this work, the total americium extracted from ocean sediment would have been 72% instead of 128%. Future work should include a complete dissolution of ocean sediment and subsequent determination of americium activity concentration for comparison to sequentially leached results.
Thorium Extraction

Extraction results for thorium from lake and ocean sediment are shown in Fig. 34. Extraction of thorium from lake sediment is more evenly distributed with a 72% overall recovery. Thorium leached from ocean sediment mainly from the residual target phase, as expected due to the relatively insoluble nature of thorium. A total of 82% thorium was leached from ocean sediment. Additional conclusions about thorium leaching from lake and ocean sediment will be presented in the following sections discussing leaching results for all four actinides.

Figure 35. Thorium-232 recovery from lake and ocean sediment
Extraction of Multiple Actinide Elements from Ocean Sediment

Figure 36 shows the extraction behaviors of $^{232}$Th, $^{238}$U, $^{239,240}$Pu, and $^{241}$Am from ocean sediment. Figure 37 shows the same values as presented in Figure 36, but normalized to 100% total recovery to show the extraction from each target phase more clearly. The primordial radioisotopes $^{232}$Th and $^{238}$U behave similarly, both with less than 30% leaching from the first three target phases. Anthropogenic radioisotopes $^{239,240}$Pu and $^{241}$Am also behave in a similar manner to each other, with over 70% extraction from the first three target fractions. This leaching behavior is likely due to the chemical form and origin of the isotopes. Thorium and uranium would likely be more bound to the ocean sediment due to their natural incorporation within the mineral phases of the sediment. Plutonium and americium, however, were introduced into the ocean environment by human activities. Their original chemical forms may lead to formation of carbonate complexes with ocean sediment, thus making them less soluble and more mobile.

Figure 36. Extraction data for americium, uranium, thorium, and plutonium for Ocean Sediment (NIST 4357)
Figure 37. Extraction data for americium, uranium, thorium, and plutonium for ocean sediment normalized to 100%.

Extraction of Multiple Actinide Elements from Lake Sediment

Figure 38 shows the extraction behaviors of $^{232}$Th, $^{238}$U, $^{239,240}$Pu, and $^{241}$Am from lake sediment. Figure 39 shows the same values as presented in Figure 38, but normalized to 100% total recovery to show the extraction from each target phase more clearly. These results vary drastically from those presented in Fig. 35 for extraction from ocean sediment, suggesting a possible effect on leaching caused by geochemical content of the sediment samples. Recovery of primordial radioisotopes $^{232}$Th and $^{238}$U matches well, with the majority of leaching seen in the carbonate and organic target phases. The high total recovery of usually insoluble thorium suggests acidic conditions and relatively high amounts of dissolved organic carbon within the lake environment [74]. Total recovery of thorium and uranium from the first three target phases was 39% and 61%, respectively, suggesting a much higher mobility potential in lake sediment than in ocean sediment. Recovery of anthropogenic $^{239,240}$Pu is similar to recovery of $^{241}$Am, with a total extraction in the first three target phases of 15% and 34%, respectively. Americium and plutonium
isotopes are relatively less soluble in lake sediment than in ocean sediment, suggesting differences in speciation based on environmental conditions.

Figure 38. Extraction data for americium, uranium, thorium, and plutonium for Lake Sediment (NIST 4354)

![Bar chart showing recovery of americium, uranium, thorium, and plutonium in lake sediment.]

Figure 39. Extraction data for americium, uranium, thorium, and plutonium for lake sediment normalized to 100%.

![Bar chart showing total recovery of americium, uranium, thorium, and plutonium in lake sediment, normalized to 100%.]
5.2.3 Conclusions and Recommendations for Future Work

There are many variables affecting the extraction of actinide and stable elements from soils and sediments, including pH, sorption, redox potentials of surrounding waters and sediments, colloid formation, etc. Though it is difficult to determine exactly which variables affect speciation, this work shows that both chemical form of the elements of interest and geochemical content of the soil or sediment have an effect on mobility of contaminants in the environment. To obtain an even better understanding of leaching behaviors in different environments, future work should include the analysis of thorium and americium extraction from the IAEA reference materials of moss-soil and Fangataufa sediment.

5.3 Application of Procedure to Additional Soils

While work by Outola et al. tested a potential standard sequential extraction protocol on two very different sediments, development of the procedure could benefit from the analysis of even more soils and sediments. Published literature tends to focus on sequential extraction from both natural environments and those that have been affected in some way by anthropogenic radionuclides, whether it be local fallout, mining, or phosphate fertilizer production waste. Two additional reference materials were analyzed for plutonium extraction behavior using the optimized sequential extraction procedure. Moss-soil (IAEA 447) represents relatively undisturbed soil that carries a good record of global fallout, while Fangataufa sediment (IAEA 384) represents post-detonation debris material with high carbonate content.

5.3.1 Experimental

The optimized sequential extraction procedure was applied to five replicates of IAEA 447 and five replicates of IAEA 384, as presented in section 3.2. A 50 mL volume of leachate
from each leachate was saved for stable element analysis. A $^{242}$Pu tracer was added to each leachate to monitor plutonium recovery throughout the preconcentration, separation, and sample mounting procedures. As with NIST 4357, IAEA 384 samples were left uncapped after the addition of NH$_4$Ac in fraction two until CO$_2$ gasses evolved. The bottles were then capped and subjected to the reaction time and temperature shown in Table 12.

5.3.2 Results and Discussion

Plutonium extraction results for all four reference materials are shown in Fig. 39. Fangataufa sediment and ocean sediment reference materials show similar trends, suggesting that extraction behavior may be correlated to soil geochemistry. Though the Fangataufa sediment showed the highest plutonium leaching from the carbonate fraction, leaching from other fractions suggests incomplete phase selectivity. Since the sediment consists of nearly 100% CaCO$_3$, plutonium was expected to almost completely leach from the carbonate fraction. A better understanding of phase selectivity could potentially be obtained by stable element analysis of calcium by ICP-AES. Plutonium extraction from lake sediment and moss-soil also followed similar trends (to each other), with the majority of plutonium being leached from the organic and residual phases. This is expected due to the relatively high organic content of the reference materials. Higher extraction from the residual target phase suggests a good portion of plutonium is bound to highly insoluble minerals. This is further supported by the high recovery of aluminum and iron from lake sediment in the residual fraction, discussed in section 5.4. Reaction conditions in the first three target phases represent relatively weakly leaching processes that are more likely to be seen within the environment than conditions represented by the fourth and fifth fractions. Leaching of plutonium from the first three fractions from ocean sediment and Fangataufa sediment was approximately 70% versus approximately 30% combined
extraction from fractions one through three in lake sediment and moss-soil. This suggests plutonium will be more mobile and environmentally available from soils and sediments with properties similar to ocean sediment and Fangataufa sediment.

Figure 40. Plutonium extraction results for all four reference materials.
5.3.3 Conclusions and Recommendations for Future Work

Evaluation of plutonium extraction from four different reference materials provides a better understanding of leaching behavior relative to soil geochemistry. Leaching from the two reference materials higher in organic content, moss-soil and lake sediment, was similar, suggesting a correlation with soil content. Similar leaching behaviors were also seen within samples with higher carbonate content, Fangataufa sediment and ocean sediment. Future work should include stable element analysis of calcium by ICP-AES to model extraction from, most specifically, the carbonate target phase. Extraction of uranium, americium, and thorium from IAEA reference materials should also be considered for future work.

5.4 Evaluation of Phase Selectivity by Stable Element Analysis

In order to obtain a better understanding of reagent specificity for radionuclide extraction from the intended target geochemical host phase, stable element extraction was monitored. Manganese was measured to monitor extraction from the first three target phases due to the more soluble nature of the element. Iron extraction can be related to the Fe/Mn oxide target phase and the residual phase, due to its tendency to be present in insoluble minerals such as hematite and goethite, as well as highly insoluble oxide forms. Aluminum extraction should be seen mainly in the residual phase, representing highly insoluble alumino-silicate minerals. Strontium was measured to model fission product extraction behavior. Each element was measured by ICP-MS. While calcium is a good indicator for extraction from the carbonate phase, it was not able to be measured due to the lack of proper instrumentation and should be included in future work.
5.4.1 Experimental

As mentioned in section 5.1.1, 50 mL volumes of each sequential extraction leachate were measured gravimetrically and saved in 50 mL centrifuge tubes for stable element analysis. Samples were evaporated to dryness on a hotplate at 80 °C. Once dry, samples were reconstituted in 40 mL of 1-2% ultrapure HNO₃, and filtered using 13 mm, 0.45 μm PTFE membrane Pall Acrodisc syringe filters. All samples were measured on an Elan DRC II ICP-MS using the parameters presented in section 3.3.2. Data was analyzed as presented in section 3.4.2.

5.4.2 Results and Discussion

Stable element extraction data for lake and ocean sediment is shown in Fig. 40. Overall higher recovery of stable elements was seen in lake sediment samples. Lower extraction values were seen from ocean sediment samples, likely due to the elements being in a more insoluble state.

Figure 41. Stable element extraction from lake and ocean sediment.
Recovery of greater than 100% for manganese from lake sediment is likely due to the comparison of measured values to those listed on the reference certificate that were reported as semi-quantitative values with relative uncertainties of plus 50% and minus 33%. Extraction data for iron from the organic target phase in lake sediment is not shown due to a saturated signal on the ICP-MS. These values will be remeasured by ICP-AES in future work. A more detailed discussion about stable element extraction results is presented below along with comparison of this data to literature values from Outola et al.

Figure 42 shows a comparison of UNLV and Outola stable element extraction data from ocean sediment. In general, there is good agreement between data. Standard deviation among replicates in UNLV data was measured to be 1-9%, while Outola reported an average standard deviation of 2-6% for stable element analysis. Taking error into account, all UNLV and Outola data matched except for iron, which will be remeasured by ICP-AES.

Figure 42. Stable element data for Ocean Sediment (NIST 4357) UNLV and Literature
A higher extraction of manganese from the carbonate phase is likely due to the temperature setting. Schultz et al. [75] recommended low temperature settings for the carbonate fraction due to increased manganese extraction at higher temperatures. The recommendation by Outola for the standardized procedure, however, was the medium temperature setting due to more uranium being released at higher temperatures from the carbonate fraction, which is also the fraction uranium was most associated with in lake sediment samples. Higher extraction values of iron and plutonium from the carbonate phase are either due to the increased temperature or the longer reaction time in the carbonate phase at UNLV to account for evolution of CO$_2$ gas from the sample before capping the centrifuge bottles. Strontium was extracted from the exchangeable phase by a factor of nearly three times more at UNLV than seen in data by Outola. Since the exchangeable phase is defined as weakly binding, it is possible that differences in sample pretreatment prior to sequential extraction caused the difference in strontium extraction values. Stable element extraction data for lake sediment is shown in Figure 43. Good agreement between UNLV and Outola data is generally seen, and all results match within the reported error.

Figure 43. Stable element data for Lake Sediment (NIST 4354) UNLV and Literature
**Manganese Extraction**

The complete extraction of manganese from lake sediment suggests phase selectivity as expected. Since manganese is relatively soluble, it should extract almost completely, with the majority leached from the first three target phases, as shown by this data. Incomplete extraction of manganese from ocean sediment with a high percentage of leaching from the residual target phase suggests manganese is in a less soluble form within ocean environment conditions. A better understanding of manganese extraction from ocean sediment could be obtained by performing a complete dissolution of the previously leached sediment to determine the amount of remaining manganese, representing a highly insoluble form.

**Iron Extraction**

Iron was expected to be extracted from the Fe/Mn oxides and residual target phases, but the data shows otherwise. Leaching of iron from lake sediment was highest in the organic phase, although was not quantifiable due to saturation in the ICP-MS. Extraction data of iron from ocean sediment showed significant iron concentrations in the carbonate target phase. The values of iron extraction from the carbonate phase in ocean sediment were also significantly higher than reported by Outola et al. This likely points to a problem with phase selectivity within the carbonate target phase for ocean sediment, which could also explain the significantly higher plutonium extraction from the carbonate phase. Future analysis of calcium extraction data from ocean sediment should give a better understanding of potential phase selectivity issues for the carbonate target phase in ocean sediment studies.
Aluminum Extraction

Total recovery of aluminum from both lake and ocean sediment followed similar trends to manganese extraction. Though a higher total extraction was seen in lake sediment, the majority of aluminum leached from the organic and residual target phases, suggesting relative immobility and insolubility of aluminum. Less than 16% of aluminum was leached from ocean sediment, suggesting a high amount of insoluble aluminum is still left as undissolved. Aluminum extraction values point to good phase selectivity for the organic and residual target phases.

Strontium Extraction

Strontium extraction was measured in order to model potential fission product mobility. Though incomplete leaching was seen, the majority of strontium extraction was seen in the first three target phases. This suggests that strontium is relatively soluble in lake and ocean environments and potentially more mobile than aluminum and iron. A complete dissolution should be performed on previously leached lake and ocean sediment samples to determine if any strontium remains in an insoluble form.

5.4.3 Conclusions and Recommendations for Future Work

Stable element extraction from lake and ocean sediment was measured for manganese, iron, aluminum, and strontium by ICP-MS. Total extraction values were higher for lake sediment, which was verified by Outola's data. In general, data from this study matched the values reported by Outola. Future work should include the analysis of more elements by ICP-AES, namely calcium as an indicator of carbonate phase extraction. Iron should also be remeasured by ICP-AES to obtain missing information from the organic target phase in lake sediment.
5.5 Chapter Conclusions

Research presented in this chapter aimed to verify and expand the capabilities of a standard sequential extraction protocol, previously developed by researchers at NIST. Verification studies determined that sediment pretreatment and reaction conditions for the organic target phase must be more defined for a more repeatable standard protocol. Stable element extraction data helped obtain a better understanding of phase selectivity and pointed to differences in extraction behaviors from differing geochemical soil profiles. Data from stable element studies matched well to data reported from the studies by Outola et al. Americium and thorium extraction from lake and sediment was studied in order to expand the capabilities of the standard sequential extraction protocol. Extraction of plutonium from four different reference materials showed that geochemical content of soils has a measurable effect on mobility of radionuclides.

Future work should include a total dissolution of previously leached ocean sediment to determine uranium concentration left in the sediment following sequential leaching. Extraction behaviors of americium and thorium from Fangataufa sediment and moss-soil reference materials should be analyzed to provide a better understanding of speciation based on original chemical form and environmental conditions. Analysis of calcium extraction from lake and ocean sediment should be performed by ICP-AES, since ICP-MS analysis wasn’t feasible due to interferences. Iron samples should also be run on ICP-AES to determine whether ICP-MS interferences had an effect on extraction data reported in this study.
CHAPTER 6  INVESTIGATION OF A SIXTH FRACTION FOR TOTAL DISSOLUTION

Complete dissolution of soil samples is important for assessing total radionuclide concentration. When utilizing a sequential chemical extraction, total dissolution is also important for measuring highly insoluble radionuclide species, such as refractory material, that may have not previously been leached from the soil. Though complete dissolution will not provide information on contaminant mobility and bioavailability because such leaching conditions are unlikely to exist in nature, it is still important to assess for total metal concentrations of the soils being analyzed. The goal is to find a method capable of dissolving soil and sediment across a broad range of soil profiles, which is user-friendly and results in a total dissolution.

Several total dissolution procedures have been tested prior to application to a previously sequentially leached reference material. Two microwave digestion procedures and one fusion procedure were investigated in this research. Acid leaching was not examined due to the more complete dissolutions offered by microwave digestion and fusion procedures. Each procedure is discussed in detail in the sections below. An optimal method was chosen based on experiment length, radionuclide recovery, and safety. The chosen method was then applied to previously leached IAEA 384 sediment.

6.1 Microwave Digestion

Microwave digestion procedures are commonly used to completely dissolve a wide range of sample matrices including soil, vegetation, urban matrices, etc. The combination of acid digestion with the assistance of microwave radiation, increased temperature and pressure make it a powerful dissolution technique. Both open vessel and closed vessel
systems are available, but only closed vessel digestion was used in this research. A more in
depth discussion on the basics of microwave digestion was presented in chapter 2.

6.1.1 Experimental

Two different microwave digestion procedures were investigated as part of this
research, EPA Method 3052 [51] and a method for digestion of carbonate rock samples by
Kemp and Brown [52]. Five replicates of Fangataufa sediment (IAEA 384) were analyzed
due to the relatively high plutonium concentration in the sample. Sediment was dried
overnight at 50 °C, and then measured out in 0.25 g quantities into the microwave digestion
vessels. Recovery of plutonium isotopes $^{239,240}$Pu and $^{238}$Pu was considered for each method.
A Milestone Ethos EZ closed vessel microwave digestion system with SK-10 rotor and
reaction vessel (Figure 11) was used for both experiments. Details of each method are
presented in the section below.

**EPA Method 3052**

In a fume hood, 9 mL of concentrated HNO$_3$ and 3 mL of concentrated HF were added to
each vessel containing soil and one empty vessel to be used as a method blank. Vessels were
sealed according to instrument specifications, placed on the rotor and into the microwave.
Temperature and pressure probes were inserted into the vessel containing the blank to
monitor reaction parameters throughout the digestion. Temperature feedback control on
the microwave system is important to control any unfamiliar reactions that may occur
during sample leaching of samples with unknown composition. The microwave unit was set
at full power (630 W) to rise to 175 °C in 5.5 minutes and remain at that temperature for an
additional 4.5 minutes. Pressure should peak between 5 and 10 minutes, depending on
sample composition.
After cooling to room temperature, the vessels were vented in a fume hood due to toxic fumes produced during digestion. Samples were then quantitatively transferred to 50 mL centrifuge tubes and centrifuged at 3,000 rpm for 10 minutes. The supernatant was filtered through 0.1 μm Resolve filters and then evaporated to dryness on a hot plate at 80 °C. Dried samples were transferred to a 600 mL beaker using 100 mL of 1 M HCl and diluted to 200 mL with DI. An amount of 0.3535 Bq of $^{242}$Pu tracer was added to each sample to monitor $^{239,240}$Pu and $^{238}$Pu recovery. Tracer addition should have been performed before microwave digestion, and was added before the dissolution reaction for all experiments in the following sections. Iron hydroxide and cerium fluoride preconcentrations were performed on all samples, as discussed previously, before separations and sample mounting by CeF$_3$ precipitation for counting by alpha spectroscopy.

**Carbonate Specific Method**

A 20 mL volume of acetic acid was added to each digestion vessel containing 0.25 g of IAEA 384. An activity of 0.3535 Bq of $^{242}$Pu tracer was added to each sample to monitor $^{239,240}$Pu and $^{238}$Pu recovery. Samples were heated on a hot plate at 150 °C until the evolution of carbon dioxide gases had ceased. After the samples had been allowed to sufficiently cool, 1 mL of 42% hydrofluoric acid and 3 mL of concentrated HNO$_3$ were added to each vessel. Vessels were then sealed and placed on the rotor with a temperature and pressure sensor placed in the vessel containing the blank.

Two programs were run on the microwave system for sample digestion; 3 minutes at 630 W followed by 30 minutes at 570 W. Once the vessels returned to room temperature and were vented, 10 mL of 4% boric acid was added to each. The vessels were placed back in the microwave for an additional 10 minutes at 380 W. Following digestion, vessels were allowed to cool to room temperature before venting in a fume hood. The digested samples
were then transferred to 50 mL centrifuge tubes and evaporated to dryness at 80 °C. Dried samples were transferred to a 600 mL beaker using 100 mL of 1 M HCl and diluted to 200 mL with DI. Iron hydroxide and cerium fluoride preconcentrations were performed on all samples, as discussed previously, before separations and sample mounting by CeF₃ for counting by alpha spectroscopy.

6.1.2 Results and Discussion

EPA Method 3052

The microwave digestion using EPA Method 3052 resulted in a cloudy solution. Following a five minute centrifugation at 3000 rpm, a large white precipitate was present. Supernatants were filtered through previously weighed 0.1 μm polypropylene filters. The dried filters were reweighed and determined to have collected none of the precipitate, which remained in the original centrifuge tube. Precipitate mass was measured to be approximately nine times the starting mass of the sediment sample after drying in the centrifuge tube at 80 °C on a hot plate.

Figure 44. Dried precipitate resulting from EPA Method 3052 microwave digestion of IAEA 384.
Supernatant, which had been filtered into new 50 mL centrifuge tubes, was saved for later analysis by alpha spectroscopy, as discussed in the experimental section. The precipitate was suspected to be CaF$_2$, formed by the addition of hydrofluoric acid to the Fangataufa sediment, which has high carbonate content. Precipitates from two of the replicates were prepared for powder X-ray diffraction analysis to determine the content of the precipitate. The sample was measured on a Bruker D8 Advance powder XRD for 2 hours. The precipitate was determined to be 100% CaF$_2$ with fm3m crystal structure by fitting the data to a model using Rietveld analysis.

Figure 45. Powder XRD pattern for CaF$_2$ precipitate.

Alpha counting was performed on supernatant solutions after the preconcentration and separation procedures discussed in the experimental section were performed. Precipitate from replicates not used for powder XRD analysis were dissolved in 6 mL 1.5 M HCl and diluted to 7.5 mL 0.01 M HCl prior to preconcentration using the pre-column CeF$_3$ microprecipitation procedure discussed in chapter 4. Samples were run through the
Maxwell separation procedure, mounted onto Eichrom Resolve filters using a CeF$_3$ microprecipitation, and counted by alpha spectroscopy. Figure 46 shows the recovery of plutonium from both the supernatant and the precipitate, for the replicates analyzed. Replicate 1 had not been analyzed at the time of writing. Since calcium hydroxide precipitation is a typical method for preconcentration of actinides, it was fully expected to see most of the plutonium recovered from the precipitate samples.

Figure 46. Results for EPA Method 3052 microwave digestion of IAEA 384 solution and precipitate. Precipitate from replicates 2 and 3 was used for XRD analysis.

Carbonate Specific Method

The Kemp and Brown microwave digestion method for complete dissolution of carbonate rock samples resulted in a total dissolution of IAEA 384 with no visible precipitate. The dissolved sample was filtered through a pre-weighed 0.1 μm polypropylene filter. Lack of precipitate was confirmed by re-weighing the dried filters. Following preconcentration, separation, sample mounting and alpha spectroscopy, an average
recovery of 95.5 ± 0.2% of $^{242}$Pu tracer was obtained. Recovery for $^{239,240}$Pu was measured as 91.4 ± 10.5% and recovery of $^{238}$Pu was measured as 87.7 ± 9.1%.

6.1.3 Conclusions and Recommendations for Future Work

Two microwave digestion procedures were tested on Fangataufa sediment certified reference material, EPA Method 3052, and a method for carbonate rock samples by Kemp and Brown. The EPA method for soil dissolution resulted in a CaF$_2$ precipitate due to the high carbonate content of the reference material combined with the addition of fluoride from HF in the digestion procedure. The carbonate specific procedure performed well on the Fangataufa sediment, producing recoveries of close to 100%. Since this research aimed to find a total dissolution method applicable to all reference materials used in the study, the EPA soil method is not recommended due to its failure to completely dissolve a high carbonate content sample without the formation of a precipitate. Though the carbonate specific microwave digestion procedure worked well on Fangataufa sediment, it is recommended that future work investigate the dissolution of other soil reference materials using this method.

6.2 Fusion

Fusion dissolution techniques typically involve mixing a soil, sediment, concrete, or other sample with a salt flux and heating to temperatures which melt the flux-sample combination. Several methods exist, as discussed in chapter 2, that vary the flux material, crucible material, and fusion temperatures. A NaOH fusion procedure [76] for cement was chosen for this research due to the high carbonate content of the Fangataufa sediment and the relatively low cost of the zirconium crucibles.
6.2.1 Experimental

EPA Method 402-R-14-004 was chosen for this research due to the ability to effectively digest refractory radionuclides that may be present in samples with high carbonate content. Fangataufa sediment was dried overnight at 105 °C. Two replicates of 0.25 g each were measured into zirconium crucibles. The procedure was developed for 1 g samples, but this research investigated 0.25 g samples (procedure scaled 1:4) to maintain sample size consistency between fusion and microwave digestion procedures. An activity of 0.3535 Bq of $^{242}$Pu tracer was added to each sample and a procedure blank to monitor plutonium recovery. Samples were heated to dryness on a hot plate on medium heat and allowed to cool to room temperature once dry. A mass of 3.75 g NaOH was added to each crucible, the crucible was then covered with a lid and placed in a Vulcan box furnace (Model 3-550) at 600 °C for about 15 minutes. Crucibles were removed from the furnace using tongs and allowed to cool.

About 10 minutes after removing the crucibles from the furnace, 12.5 mL of DI water was added to each crucible and heated on a hot plate to loosen and dissolve solids. A volume of 1.56 mL of 20 mg mL$^{-1}$ iron carrier was added to a labelled 50 mL centrifuge tube. A volume of 0.806 mL of 1.55 mg mL$^{-1}$ cerium carrier was added to the same centrifuge tube. The fused samples were transferred to the tubes with carriers and the crucibles were rinsed with DI water and the rinse transferred to the centrifuge tubes. The samples were each diluted to 40 mL with DI water.

Three milliliters of 1.25 M Ca(NO$_3$)$_2$ and 5 mL 3.2 M (NH$_4$)$_2$HPO$_4$ were pipetted into each centrifuge tube, tubes were capped and the solution was mixed well. A volume of 0.625 mL of 20 wt. % TiCl$_3$ was then added to each tube and mixed immediately to reduce uranium from VI to IV to enhance chemical yields. Samples were placed in an ice bath for
approximately 10 minutes to reduce solubility, and then centrifuged at 3500 rpm for 6 minutes. The supernatant was poured off and discarded as waste. The precipitate was redissolved by adding 15 mL of 1.5 M HCl to the centrifuge tube. Each tube was then diluted to 42 mL with 0.01 M HCl. A cerium carrier was added in a volume of 0.161 mL and concentration of 0.155 mg mL\(^{-1}\) to aid in the reduction of matrix interferences, including silica, which can cause column flow problems. For uranium reduction, 0.375 mL of 20 wt. % TiCl\(_3\) was added to the samples. Addition of 5.5 mL concentrated hydrofluoric acid was performed on all samples to form a precipitate. Samples were capped, mixed, and set in an ice bath for 10 minutes. Following precipitation, samples were centrifuged for 10 minutes at 3000 rpm. The supernatant was filtered and the filter rinsed into the centrifuge tube using warm 3 M HNO\(_3\) – 0.25 M boric acid. Samples were then reconstituted in the 7 M HNO\(_3\) – 2 M Al(NO\(_3\))\(_3\) column load solution, run through the separation procedure, mounted onto Eichrom Resolve filters using CeF\(_3\) microprecipitation and counted by alpha spectroscopy.

It is important to note that samples should be ground to at least 50-100 mesh size prior to fusion, if possible. The fusion itself takes approximately 1 hour for a batch of 20 samples. Preconcentration steps to eliminate alkaline fusion matrix and collect radionuclides should take an additional hour. Sufficient cleaning of zirconium crucibles is important, and should be done between each fusion by washing with soap and water followed by warm nitric acid then water. Blanks should be measured to monitor cleanliness of crucibles.

6.2.2 Results and Discussion

The NaOH fusion procedure produced completely dissolved samples with high recoveries in a relatively short period of time. Plutonium recoveries from Fangataufa sediment were 90.3 ± 5.2% for \(^{239,240}\)Pu and 94.3 ± 7.6% for \(^{238}\)Pu.
6.2.3 Conclusions and Recommendations for Future Work

The NaOH fusion procedure tested in this work produced similar plutonium recoveries from IAEA 384 as the carbonate specific microwave digestion procedure. The fusion method, however, was much quicker (~1/2 day vs 2 days). This was mainly due to the preconcentration steps being built into the fusion procedure, eliminating the lengthy evaporation step prior to reconstitution for Fe(III)OH coprecipitation following microwave digestion. The NaOH fusion method, therefore, will be used for the complete dissolution of previously leached Fangataufa sediment, discussed in the next section. Future work should include applying the NaOH fusion procedure to NIST 4354 (lake sediment), NIST 4357 (ocean sediment), and IAEA 447 (moss-soil) to determine the applicability of the procedure across a broad range of soil profiles.

6.3 Application to Previously Leached IAEA 384

As discussed previously, it is important to perform a total dissolution on a soil or sediment sample even after sequential chemical leaching, to obtain a more complete understanding of radionuclide association with soil phases. Some radionuclides may be still bound to undissolved soil phases in highly insoluble forms such as high-fired oxides. This complete dissolution step will allow investigators to assess for incomplete leaching seen in five-step sequential extraction procedures, such as the ~40% uranium recovery from NIST 4357, as discussed in chapter 5. The NaOH fusion method was selected for application to previously leached Fangataufa sediment due to the high recoveries and quick dissolution time.
6.3.1 Experimental

Undissolved solids from all sequential extraction experiments had been saved for future analysis by total dissolution. After the final (4 M HNO₃) sequential extraction leachate had been poured off from the 250 mL centrifuge bottle, the leachate was filtered and the filter added to the centrifuge bottle still containing undissolved reference material. Of the five replicates of previously sequentially leached Fangataufa sediment, all had seen severe deterioration (loss of sample mass) during the time spent sitting in the dry centrifuge bottle. Replicate five had an immeasurable mass and replicates two and three had disintegrated filters that could interfere with the fusion process. The other two replicates were analyzed in this research.

Undissolved reference material from the two viable replicates was transferred to the zirconium crucibles using DI water to rinse the bottles. Samples were allowed to dry overnight in order to obtain a dry mass of the transferred sediment. Crucible mass was determined before and after addition of the dry reference material, once the crucible had cooled following evaporation of the DI water used to transfer the sediment from the centrifuge bottles. The NaOH fusion procedure discussed in section 6.2 was used to dissolve the previously leached Fangataufa sediment. Following dissolution, the samples were run through the Maxwell separation procedure, mounted onto Eichrom Resolve filters using a CeF₃ microprecipitation, and counted by alpha spectroscopy.

6.3.2 Results and Discussion

Masses of replicates one and four were measured to be 0.074 g and 0.046 g respectively, much lower than the 12 g left in the centrifuge bottle following sequential leaching one year prior. Results calculated based on measured masses, however, show extremely high
plutonium recoveries not expected from previous sequential extraction results. The results, therefore, were calculated based on a 12 g sample size that was initially contained within the centrifuge bottle, thus introducing some error into the calculations. It is assumed that sediment disintegration was caused by HNO$_3$ fumes left within the closed centrifuge bottle over the course of one year, yet all unleached plutonium remained within the bottles.

Recovery based on a 12 g IAEA 384 starting mass was determined to be $1.2 \pm 0.1\%$ for $^{239,240}\text{Pu}$ and $0.5 \pm 0.9\%$ for $^{238}\text{Pu}$. This brought the sum for both isotopes for all six fractions to $100\%$ within the error bars. Final leaching results for all six fractions from Fangataufa sediment for $^{239,240}\text{Pu}$ and $^{238}\text{Pu}$ are shown in Figure 47.

Figure 47. Leaching results for $^{239,240}\text{Pu}$ and $^{238}\text{Pu}$ from IAEA 384 based on the 6 step sequential extraction procedure.
6.3.3 Conclusions and Recommendations for Future Work

Application of the NaOH fusion to previously sequentially leached Fangataufa sediment showed some plutonium was still left in the undissolved soil following sequential extraction. The sequential extraction sequence should be repeated on Fangataufa sediment immediately followed by a fusion of the leached sediment to determine results under conditions where the residue has not disintegrated. The method has proven viable for experiments investigating soils with high carbonate content, such as Fangataufa sediment, but should be tested on a more broad range of soil profiles before being applied. If the NaOH fusion works on other soil matrices, it should be applied to previously leached reference materials for a more complete investigation of radionuclide association within the geochemical host phases of soil and sediment.

6.4 Chapter Conclusions

Three methods for total dissolution of soil and sediment reference materials were tested and compared in this research. EPA Method 3052 for soil dissolution was not useful for the Fangataufa sediment due to its high carbonate content, which caused a CaF$_2$ precipitate to form in the digested sample. For this reason, the method was not chosen to proceed since it will not be applicable to a broad range of soil profiles. An additional microwave digestion procedure and a NaOH fusion method, both specific for high-carbonate content materials, were then tested on Fangataufa sediment. Both procedures produced a completely dissolved sample with plutonium recoveries greater than 90%. The NaOH fusion was ultimately chosen as the method to proceed based on its relative simplicity and much shorter dissolution time. When applied to previously leached Fangataufa sediment, the NaOH fusion procedure leached the remaining plutonium from the sediment. Though the
NaOH fusion procedure worked well for Fangataufa sediment dissolution, future work should include dissolution of the other three reference materials analyzed in this research.
CHAPTER 7  CORRELATIONS BETWEEN SEQUENTIAL LEACHING BEHAVIORS, RADIONUCLIDE SPECIATION, AND SOIL GEOCHEMISTRY

The dispersion of radionuclides into the environment is influenced by a number of factors including the physicochemical form of the radionuclides upon release, local soil and water conditions, and soil geochemistry. The physicochemical characteristics of radionuclides can include oxidation state, morphology, size, charge, density, and degree of complexation [77]. This chapter will focus on the role of the physicochemical form of radionuclides as they were originally released into the environment and the correlations that can be drawn on its relation to the sequential leaching behaviors seen in this work. For each reference material that was sequentially leached, more detailed information on known or suggested source terms for the actinides analyzed in this work is provided in Section 7.2. Section 7.3 provides an interpretation of the sequential leaching results from this work as they relate to the source term information presented in Section 7.2. Conclusions will be presented in Section 7.4 along with thoughts on how to obtain missing information to strengthen this case in future work.

7.1 Introduction

An understanding of radionuclide speciation in various environments is important for the assessment of contaminant mobility and origin of material. Sequential extraction studies on soil and sediment samples from differing environments have proven invaluable to the field of radioecology. The studies allow a better understanding of the effects of chemical speciation and soil geochemistry on radionuclide leaching and the potential mobility of the contaminants within the environment. Studies on isotope ratios have provided important information relevant to both radioecology and nuclear forensics. Variations in $^{240}$Pu/$^{239}$Pu isotope ratios point to contributions of radionuclide contaminants from sources other than
global fallout in numerous studies [78] [79] [80]. Research is missing, however, on the direct correlation between radionuclide source term information and sequential leaching results for various soil types. Such studies would yield important information for both radioecology (contaminant mobility) and nuclear forensics (material origin) and would be complementary to data collected from previous sequential extraction and isotope ratio studies. The discussion presented in this chapter aims to draw conclusions on radionuclide mobility and source information based on the suspected original physicochemical form of the actinides examined in this work. Actinide leaching behaviors in the five fractions of the sequential extraction procedure are correlated with the source term information of the actinides in the four reference materials used in this work.

7.2 Reference Material Source Term Information

The four reference materials analyzed in this work were chosen to represent a variety of soil types in an attempt to determine differences in radionuclide leaching based on soil geochemistry. The information presented in this section aims to provide a better understanding of radionuclide source term information based on the histories of the sites where the references materials were collected from and reports on radionuclide speciation within the soils found in the literature.

7.2.1 NIST SRM 4354 – Freshwater Lake Sediment

Site History

Perch Lake is a small, anoxic lake located within the boundaries of Canada’s Chalk River Nuclear Site. Sediment for NIST 4354 was collected from the gyttja (mud formed by the partial decay of peat) layer of bottom sediment, consisting of about 8% solid material, of
which approximately 50% was organic material [81]. The location of the lake in relation to nuclear facilities is shown in Figure 48, along with the direction of surface water drainage into the lake.

Figure 48. Location of Perch Lake in relation to Chalk River Laboratories and waste disposal pits and basins [82].
Chalk River Laboratories opened in 1944 in Ontario, Canada, near the Village of Chalk River. Facilities at the site include research reactors, chemical extraction plants, and a waste disposal area consisting of a sand-filled rock basin with a single water outlet into Perch Lake [83]. The Perch Lake basin was used for waste management since the outlet from the lake could be monitored and the lake itself is situated within the restricted area of the site. Radioactive waste from processing plants, scrap from the repair the NRX reactor, radioactive waste water from the NRX reactor accident in 1952, and other waste has been deposited in the area of Perch Lake, primarily in sealed containers [83].

Sources of Radionuclide Contamination

Sources of contamination in Perch Lake exist from the flow of contaminants from the up-stream rock-sand basin and from the direct disposal of radioactive waste from Chalk River Laboratories [83]. Minimal information was found in the literature relating to specific species of radionuclides released from the nuclear facility. Estimates of waste volumes and radioactivity content from waste management activities can be found in Table 2.1 of the report on the ecological effects of Chalk River Laboratories [82]. Information on liquid effluent discharges can be found in Table 2.2 of the same report.

Speciation Information

Research by Robertson et al. [84] investigated the speciation of radionuclides within Perch Lake and the surrounding areas. The most common chemical form of radionuclides seen by Robertson was associated with organic material. Increased actinide mobility was seen in and/or near the disposal site due to the formation of anionic radionuclide complexes, likely caused by organic complexation with natural fulvic/humic substances. Though the groundwater in the chemical pit plumes was determined to be slightly acidic and oxidizing groundwater conditions change to contain very low dissolved oxygen.
concentrations and high concentrations of ferrous iron, indicative of less oxidizing conditions, as it flowed into the East Swamp area [84]. In addition to radionuclide complexation with organic matter originating from humic and fulvic acids from plant and animal residue decomposition, Robertson also saw evidence pointing to negatively charged radionuclide species complexing with anthropogenic organic chelating agents, such as ethylenediamine tetraacetic acid (EDTA), which was disposed of in the chemical pit. Other potentially mobile forms of radionuclide complexes in the Chalk River area may include inorganic complexes with common ligands such as sulfato-, chloro-, and hydroxo-species as well as inorganic colloidal materials with negatively charged surface sites.

7.2.2 NIST SRM 4357 – Ocean Sediment

Site History

The ocean sediment reference material from NIST was collected from the Irish Sea off the coast of Sellafield and down-blended with Chesapeake Bay sediment (1:200 mass ratio) to be more representative of environmental radioactivity samples. The Chesapeake Bay sediment used to down-blend represents radionuclide concentrations originating from global fallout of plutonium and americium as well as naturally occurring uranium and thorium. Irish Sea sediment has seen contributions from waste streams from the Sellafield nuclear site, containing actinides, activation and fission products.

The Sellafield nuclear site in the UK was constructed at the beginning of the UK nuclear program. The primary operations at the site included spent fuel reprocessing, nuclear waste management, and nuclear energy generation [85]. Two air-cooled reactors were used for uranium irradiation and subsequent plutonium production during World War II. The
irradiated fuel was stored in open water pond and then reprocessed. Two plutonium purification plants and a plutonium finishing plant also existed on the site [85].

**Sources of Radionuclide Contamination [85]**

Releases of radioactive effluents from the Sellafield site have taken place since the beginning of operations. Pipelines used to discharge the waste were designed based on results of previous dilution and movement experiments in 1947 and on the study of tidal and current movements in 1950-52. Two major sources of liquid effluent released into the Irish Sea were process liquors from reprocessing operations and fuel storage pond purge waters. Prior to 1970, fuel storage pond water was released without treatment, with the radioactivity of the effluent increasing with time due to the increased storage time and corrosion of the Magnox fuel stored in the ponds. The release of americium and plutonium increased in the 1970s due to a rise in reprocessing activity, but decreased after the introduction of a flocculation precipitation treatment facility. Figure 49 shows the activity per year of principal alpha emitters released into the Irish Sea from Sellafield.

Figure 49. Discharges of alpha emitters into the Irish Sea from Sellafield, 1952-92 [85].
Speciation Information

Though no specific information on the chemical form of released radionuclides was found in the literature, many studies did investigate the speciation of elements found in the released effluents. In general, actinides have been released in either hydrolyzed or particulate form, as reported by Perna et al. [86]. Actinides in these forms typically precipitate directly from the water column or are scavenged by suspended particulate matter. Perna et al. also reported that, prior to the startup of the effluent treatment plant, actinides were mainly associated with particulate matter in the waste stream, and hot particles were found within the sediments near the release area. Hamilton et al. reported “agglomerates of smaller particles, bonded by organic matter and coated with iron and manganese oxides” [87].

The discharge of $^{239,240}$Pu into the Irish Sea from Sellafield up to the end of 1992 represented 45% of the estimated inventory in the North Atlantic due to global fallout [88]. Nearly all of the released plutonium is the form of Pu(IV), which is highly insoluble [89]. Any other plutonium was dissolved as Pu(V) [90] [91] or associated with particulate matter suspended in the waters of the Irish Sea as Pu(IV) [89]. The latter fraction has been carried out to Irish Sea [86]. The two forms of plutonium represent a “dual mechanism for dispersion of plutonium” [89], which also effects $^{241}$Am distributions due to the decay of $^{241}$Pu. Mitchell et al. reported that americium discharge occurred completely in the form of Am(III), which is highly particle-reactive [89].

Experiments conducted by Pentreath et al. involving a 1:104 dilution of sea tank effluent samples into sea water showed solubilization of the particle-bound plutonium over the course of a year, along with a shift in plutonium oxidation state from the reduced to oxidized form. Plutonium from the fuel storage pond effluent, however, was far less
oxidized and a shift to a lower oxidation state was observed [92]. Hot particles, likely stemming from fuel, were also identified in the effluent [93]. The hot particles were fairly immobile in the marine disposal environment [94] [95]. Solubilization changes were also seen for $^{241}$Am, with more than 30% of both sea tank and pond effluent being solubilized over the course of 360 days [92].

7.2.3 IAEA CRM 447 – Moss-Soil

Site History

Moss used for IAEA CRM 447 was grown undisturbed in the groovings of large red marble stone surfaces in an abandoned mine in the north-west part of Hungary (Gerecse Mountain). Both moss and the soil it grew on were collected for the moss-soil reference material, due to the difficulty in separating the moss from the soil. The resulting reference material represents largely undisturbed soil and vegetation with high organic content. Due to the undisturbed nature of the moss growth and the isolation of the area from anthropogenic sources of radiation, the reference material is expected to carry a good record of radionuclide deposition from global fallout.

Sources of Radionuclide Contamination and Speciation Information

The main and potentially only source of radionuclide contamination seen in the moss-soil reference material is from global fallout. Most mosses don’t develop a real root system due to their derivation of nourishment from the atmosphere [96]. Radionuclides originating from fallout are therefore absorbed through the leaves of the moss. This leads to a close correlation between atmospheric deposition and concentrations found within the plant, since radionuclide uptake from the soil can essentially be ruled out [96]. The reference material consists of both the moss vegetation and the soil the moss grew in, however, which
could contain high-fired oxides of plutonium that have deposited into the soil from global fallout. This suggests two potentially different plutonium species could be present within the reference material; more soluble plutonium produced by the neutron flux during weapons testing and collected onto the moss, and highly insoluble plutonium in the form of high-fired oxides resulting from the high heat of explosions on the plutonium contained within the device. The latter species would be more likely deposited into the soils surrounding the moss and less mobile [97].

7.2.4 IAEA CRM 384 – Fangataufa Sediment

Site History

The Fangataufa sediment certified reference material was collected from sediment at the Fangataufa Atoll in French Polynesia, where French nuclear weapons testing was conducted from the 1970s through the 1990s. The French conducted two types of experiments at Fangataufa and the nearby Muruora Atolls, nuclear-weapons tests and nuclear-weapon safety trials. Nuclear weapons tests consisted of detonating nuclear devices releasing fission energy both underground and in the atmosphere above the atoll. Nuclear weapons safety trials were conducted on Muruora Atoll by subjecting nuclear devices to simulated accident conditions and destroying the nuclear weapon cores with conventional explosives. [98].

Sources of Radionuclide Contamination

The contamination at the Fangataufa Atoll originated from local and global fallout, as well as direct deposition from underground tests. Four atmospheric tests were conducted at the atoll, three of them from devices hanging at a considerable elevation from a balloon. The fourth test was conducted on a barge in the atoll with the detonation approximately three
meters above ground. Fallout from the three balloon tests was generally widely distributed as global fallout due to the height of the detonations, while the fallout from the barge test was locally deposited in the area of the atoll [99]. Localized high levels of plutonium, americium, and fission products were found in the sediments directly below ground zero of the barge test. Ten underground tests were also conducted; two in holes drilled in the rim and eight in the lagoon within shafts drilled vertically into the volcanic rock beneath the rim [99]. Figure 50 shows the locations and yields of the 10 underground tests conducted at Fangataufa Atoll.

Figure 50. Locations and yields of Fangataufa underground [99].
Speciation Information

Little is known about the original speciation of actinides in Fangataufa Atoll due to the path by which the plutonium was introduced into the surrounding environment. Any plutonium from the original payload of the weapons that survived the detonation would be converted into very insoluble high-fired oxides. Plutonium is however also formed during the explosion by a series of \((n,\gamma)\) reactions on \(^{238}\text{U}\) and subsequent decay of the products \((^{239}\text{U},^{240}\text{U},^{241}\text{U})\). About 2/3 of the total plutonium released is generated in this manner and would be in a similar chemical form to that seen in nuclear reprocessing waste. It would be representative of single atoms, and much more soluble [97]. Partitioning of plutonium as refractory material into the lava following underground tests was found to be about 98% [99]. Potential for leaching of refractory plutonium from the lava material over time has been shown and is represented in Figure 51.

Figure 51. Total and specific activity of radionuclides in lava beneath Fangataufa Atoll as a function of time [99].
This leaching would make the plutonium become more mobile, but this is expected to happen on a relatively long time scale.

7.3 Interpretation of Fractionation Results Based on Original Radionuclide Source Term

7.3.1 Thorium

Thorium in NIST lake and ocean sediment reference materials is expected to originate solely from primordial sources and therefore be present as relatively insoluble Th(IV). Since the original speciation of thorium is expected to be the same in lake and ocean sediment, variations in leaching behaviors between the two reference materials is expected to be due primarily to the differences in soil geochemistry. Low overall recovery of thorium from ocean sediment suggests the thorium is relatively insoluble due to the natural incorporation within the mineral phases of the sediment. Greater extraction from lake sediment, however, suggests acidic conditions and relatively high amounts of dissolved organic carbon within the lake environment [74]. In order to draw conclusions on any potential variations in fractionation of thorium by sequential extraction, further studies would need to be carried out that investigate thorium leaching from different materials, with a normalization of contributions from different soil compartments.

7.3.2 Uranium

Though it is likely that uranium is present in the waste streams from both the Sellafield and Chalk River sites, the speciation of uranium in the reference materials is likely to be the most heavily influenced by the presence of natural uranium in the sediment. This has been verified by the presence of secular equilibrium between $^{234}\text{U}$ and $^{238}\text{U}$ in each reference material. As with thorium, the speciation of uranium in lake and ocean sediment is expected
to be similar, therefore sequential leaching results are likely more strongly tied to soil geochemistry than original chemical speciation of uranium. Similarities in sequential leaching behavior between uranium and thorium further suggest that soil geochemistry and environmental conditions surrounding the sediment plays a primary role in their mobility. This is further supported by the relatively different fractionation patterns of anthropogenic $^{239,240}$Pu and $^{241}$Am in both lake and ocean sediment reference materials. Additional studies including sequential extraction of uranium from soils with known and ideally different beginning uranium species are needed in order to make any direct conclusions about the effect of speciation on uranium fractionation.

### 7.3.3 Americium

Americium fractionation varied significantly from that of uranium and thorium extraction from lake and ocean sediment. In general, americium appears to be completely leached from both lake and ocean sediment, however leaching behaviors vary drastically between the two sediments. Americium is more immobile in lake sediment with only $\sim$35% being dissolved in the first three fractions. In ocean sediment, americium is highly mobile, with over 90% leached from the first three fractions in sequential extraction. The speciation of americium in lake and ocean sediment is not expected to be significantly different, since they are both representative of sediments that have collected waste from nuclear facilities. The addition of americium fractionation analysis in Fangataufa sediment or moss-soil reference materials could add a new dimension to this work and perhaps allow conclusions to be drawn on the effect of speciation on fractionation.
7.3.4 Plutonium

Plutonium fractionation was examined for all four reference materials, allowing a more complete data set to draw conclusions on the relationship of chemical speciation and fractionation. The leaching behavior of plutonium from each reference material is shown in Figure 52. Analogous trends are seen between ocean sediment and Fangataufa sediment reference materials with similar geochemistry; however, slight differences in plutonium fractionation may point to a potential tie between chemical speciation and fractionation.

The original speciation of plutonium is expected to vary between reference materials since plutonium was introduced into the materials in different manners. Table 28 shows sources and suggested speciation information for plutonium in all four reference materials used in this work.

Figure 52. Plutonium fractionation in lake sediment, moss-soil, Fangataufa sediment, and ocean sediment reference materials, normalized to 100% extraction.
Table 28. Plutonium source and potential speciation information for all four reference materials used in this work.

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Source</th>
<th>Speciation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Sediment</td>
<td>Flow of contaminants from up-stream rock-sand basin into Perch Lake, direct disposal of radioactive waste from Chalk River Laboratories</td>
<td>Associated with organic material, anionic complexes, organic complexes with fulvic/humic acids, complexes with anthropogenic organic chelating agents</td>
</tr>
<tr>
<td>Ocean Sediment</td>
<td>Radioactive effluents from Sellafield site. Process liquors from reprocessing of spent nuclear fuel and fuel storage pond purge water</td>
<td>Hydrolyzed or particulate form, association of particulate matter in waste streams, agglomerates bonded by organic matter and coated with Fe/Mn oxides. Nearly all Pu(IV), some Pu(V) associated with suspended particulate matter</td>
</tr>
<tr>
<td>Moss-soil</td>
<td>Global fallout</td>
<td>Fallout plutonium accumulated onto the leaves of moss, high-fired oxides deposited into the soil originating from global fallout</td>
</tr>
<tr>
<td>Fangataufa Sediment</td>
<td>Global and local fallout, direct deposition from underground testing</td>
<td>Insoluble high-fired oxides of plutonium originating from plutonium within the devices exposed to high temperatures, More soluble forms of plutonium created by ((n,\gamma)) reactions after detonation</td>
</tr>
</tbody>
</table>

Fractionation of plutonium in ocean sediment and Fangataufa sediment matches well, which could suggest similar chemical speciation of plutonium in the two reference materials. Since the sediments were both collected from marine systems, however, environmental conditions in the Irish Sea and Fangataufa Atoll could also be affecting fractionation patterns. Further experiments investigating the chemical speciation of plutonium prior to sequential extraction studies will need to be conducted in order to better define the contribution of plutonium speciation on sequential leaching behaviors in Fangataufa and ocean sediment reference materials.

Though lake sediment and moss-soil reference materials are similar in that they contain a high fraction of organic matter, slight differences were seen in the fractionation of
plutonium from the two materials. Plutonium leaching from the exchangeable, carbonate, and organic fractions of each reference material matched within the error bars, yet a large difference was seen in plutonium extraction from the residual phase. It is likely that the plutonium species within the lake sediment are in a more insoluble form than plutonium species in moss soil. This is supported by research by Robertson et al. [81], which reported plutonium association with insoluble organic complexes of fulvic and humic acid. It is further supported by the fact that fallout plutonium deposited onto the leaves of moss represents a more soluble form of plutonium.

7.3.5 Strontium

Although strontium fractionation was only investigated from lake and ocean sediment reference materials, the results suggest contribution of two chemical forms of strontium. The speciation of strontium originating from the Sellafield and Chalk River nuclear sites are expected to be similar, which is represented by the similar fractionation and total leaching of strontium from both reference materials. Only 40% and 50% of the total strontium was leached from ocean and lake sediment, respectively, suggesting a relatively insoluble source of strontium. Of the strontium that did leach from the sediments, however, over 80% leached from the first three target phases, representing more soluble forms of strontium. This data suggests two or more original chemical forms of strontium. Natural strontium, which behaves similarly to calcium, would likely to be seen leached from the carbonate phase, while anthropogenic strontium originating from the nuclear facilities would be in a more insoluble form.
7.3.6 Conclusions

This section examined the correlation between the original chemical speciation of radionuclides and fractionation behaviors seen in sequential extraction studies. In order to obtain a more complete data set relating to differences in leaching behaviors based on various chemical forms of the elements analyzed, future work should focus on sequential extraction studies using moss-soil and Fangataufa sediment reference materials for the fractionation of thorium, uranium, and americium. Fractionation results pointed to multiple chemical forms of plutonium and strontium existing within a single reference material. Future work should include the sequential extraction of strontium from IAEA reference materials to determine any differences in fractionation within the materials compared to the NIST reference sediments. The addition of suggested future work should allow further correlations between radionuclide speciation and fractionation. The resulting information will add valuable for the field of radioecology and nuclear forensics.

7.4 Interpretation of Fractionation Results Based on Reference Material Composition

This section discusses the potential correlations between sequential extraction results and the soil geochemistry of the reference materials used in this work. Table 29 shows the most significant leaching results for each reference material along with the suggested reasoning. The information presented in the table is discussed in more detail in the following sections.
Table 29. Leaching results based on reference material.

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Element</th>
<th>Fraction</th>
<th>Reasoning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moss-Soil Pu</td>
<td>Organic</td>
<td></td>
<td>High organic material takes up soluble Pu</td>
</tr>
<tr>
<td></td>
<td>Residual</td>
<td></td>
<td>Contributions from insoluble Pu in soil</td>
</tr>
<tr>
<td>Fangataufa Pu</td>
<td>Carbonate</td>
<td></td>
<td>High carbonate complexes soluble Pu</td>
</tr>
<tr>
<td></td>
<td>Organic</td>
<td></td>
<td>Uptake of Pu by marine organisms</td>
</tr>
<tr>
<td>Lake Sediment Th</td>
<td>Organic</td>
<td></td>
<td>High organic matter takes up soluble Th</td>
</tr>
<tr>
<td></td>
<td>Carbonate</td>
<td></td>
<td>Soluble Th complexing with carbonates</td>
</tr>
<tr>
<td></td>
<td>U</td>
<td>Organic</td>
<td>High organic matter takes up soluble U</td>
</tr>
<tr>
<td></td>
<td>Carbonate</td>
<td></td>
<td>Soluble U complexing with carbonates</td>
</tr>
<tr>
<td>Pu</td>
<td>Organic</td>
<td></td>
<td>High organic matter takes up soluble Pu</td>
</tr>
<tr>
<td>Pu</td>
<td>Residual</td>
<td></td>
<td>Insoluble Pu introduced into lake</td>
</tr>
<tr>
<td>Am Fe/Mn Oxides</td>
<td></td>
<td></td>
<td>Lake is anoxic/reducing</td>
</tr>
<tr>
<td>Am</td>
<td>Residual</td>
<td></td>
<td>Insoluble Pu introduced into lake</td>
</tr>
<tr>
<td>Ocean Sediment Th</td>
<td>Residual</td>
<td></td>
<td>Th located in mineral grains</td>
</tr>
<tr>
<td>U</td>
<td>Residual</td>
<td></td>
<td>U located in mineral grains</td>
</tr>
<tr>
<td>U</td>
<td>Carbonate</td>
<td></td>
<td>Ocean expected to have carbonates</td>
</tr>
<tr>
<td>U</td>
<td>Exchangeable</td>
<td></td>
<td>Soluble U expected in ocean</td>
</tr>
<tr>
<td>Pu</td>
<td>Carbonate</td>
<td></td>
<td>High carbonate complexes soluble Pu</td>
</tr>
<tr>
<td>Pu</td>
<td>Organic</td>
<td></td>
<td>Uptake of Pu by marine organisms</td>
</tr>
<tr>
<td>Am Carbonate</td>
<td></td>
<td></td>
<td>High carbonate complexes soluble Am</td>
</tr>
<tr>
<td>Mn Residual</td>
<td></td>
<td></td>
<td>Stable Mn located in mineral grains</td>
</tr>
<tr>
<td>Mn Fe/Mn Oxides</td>
<td></td>
<td></td>
<td>Reducing conditions in ocean environment</td>
</tr>
<tr>
<td>Mn Carbonate</td>
<td></td>
<td></td>
<td>Ocean expected to have carbonates</td>
</tr>
<tr>
<td>Fe Residual</td>
<td></td>
<td></td>
<td>Stable Fe located in mineral grains</td>
</tr>
<tr>
<td>Fe Fe/Mn Oxides</td>
<td></td>
<td></td>
<td>Reducing conditions in ocean environment</td>
</tr>
<tr>
<td>Al Residual</td>
<td></td>
<td></td>
<td>Stable Al located in mineral grains</td>
</tr>
</tbody>
</table>

7.4.1 IAEA 447 – Moss-Soil

As stated in Chapter 5, moss-soil was only analyzed for the sequential leaching behavior of plutonium. High recovery of plutonium (26%) from the organic fraction is expected due to the high organic content of the reference material. This suggests a strong correlation between soil geochemistry and leaching behavior of plutonium. High recovery of plutonium (19%) from the residual fraction is likely due to the contribution of plutonium found in the soil that was collected and mixed with the moss. This suggests the plutonium in the moss-soil reference material exists in two slightly different chemical forms – plutonium
associated with the organic moss material, and less soluble plutonium, which is strongly bound to the minerals in soil. Both of these conclusions support the influence of soil geochemistry on potential mobility of plutonium.

7.4.2 IAEA 384 – Fangataufa Sediment

Similar to moss-soil, Fangataufa sediment was only analyzed for the sequential leaching behavior of plutonium. Plutonium leaching from the nearly 100% calcium carbonate-composed Fangataufa sediment is mainly seen from the carbonate phase (60%), suggesting the carbonate material had complexed with soluble forms of plutonium in the marine environment. This again suggests a strong correlation between soil geochemistry and sequential leaching behaviors. High amounts of plutonium were also leached from the organic fraction (25%). Plutonium associated with the organic fraction is less soluble than that found in the carbonate target phase, and likely exists as a different original chemical form. This could possibly be explained by the uptake of plutonium by marine plants and organisms, causing plutonium to be associated with organic matter found in ocean sediment [100].

7.4.3 NIST 4354 – Lake Sediment

Lake sediment reference material was analyzed for leaching behaviors of $^{232}$Th, $^{238}$U, $^{239,240}$Pu and $^{241}$Am. High recoveries of thorium, uranium, and plutonium from the organic target phase (28%, 33%, and 32%, respectively) suggest leaching behavior and subsequent mobility of radionuclides is strongly tied to the sediment geochemistry, due to the high organic content of the lake sediment. Significant amounts of uranium and thorium (48% and 38%, respectively) were seen leached from the carbonate target phase. This suggests
the complexation of soluble uranium and thorium with carbonate material expected to be present within the lake sediment. Plutonium and americium were leached in relatively high quantities from the residual phase (51% and 67%, respectively). This suggests that plutonium and americium were introduced into the lake environment in a more insoluble form. Eighteen percent of americium was leached from the Fe/Mn Oxide fraction likely due to the anoxic conditions of the lake environment. The conclusions drawn from the leaching behaviors of actinides from lake sediment reference material suggest a strong correlation to sediment characteristics and conditions within the lake environment, as well as the relative insolubility of the released plutonium and americium.

7.4.4 NIST 4357 – Ocean Sediment

Ocean sediment reference material was analyzed for leaching behaviors of $^{232}$Th, $^{238}$U, $^{239,240}$Pu and $^{241}$Am. The 20% of uranium leached from the exchangeable target phase is representative of soluble uranium expected to be found in an ocean environment. Significant leaching of uranium, plutonium, americium, and manganese (29%, 59%, 66%, 27%, respectively) from the carbonate fraction correlates well to the high carbonate content of marine sediment. Extraction of iron and manganese (15% and 21% respectively) from the Fe/Mn oxide target phase alludes to the reducing conditions of the ocean environment. Association of plutonium with the organic phase of ocean sediment (18%) is similar to that seen in Fangataufa sediment. The possibility of plutonium uptake by marine plants and organisms is a likely explanation for this behavior. The presence of thorium, uranium, and stable elements manganese, iron, and aluminum in the leachate of the residual fraction (77%, 27%, 37%, 39%, and 65%, respectively) suggests the elements are
incorporated within the mineral grains of the ocean sediment and therefore highly insoluble.

7.4.5 Conclusions

Results presented in this section suggest a strong correlation between sequential leaching behavior and soil geochemistry. This conclusion holds true across a broad range of soil types, proving the standardized sequential extraction technique utilized in this work is capable of estimating the mobility and bioavailability of radionuclides in a variety of environments. The standardized sequential extraction procedure can now be expanded in attempt to make sequential extraction a useful tool for nuclear forensic analysis. Future studies should focus on the determination of radionuclide isotope ratios within each geochemical host phase of soil in order to provide data complementary to this work and useful to the field of nuclear forensics.

7.5 Conclusions and Recommendations for Future Work

This chapter examined the correlation between the fractionation behaviors seen in sequential extraction studies and both chemical speciation of radionuclides and geochemical properties of the reference materials used in this work. Strong correlations were seen between radionuclide fractionation and the available geochemical host phases of the reference materials used in this work. Therefore, the standardized sequential extraction protocol presented in this work has been proven an important tool for assessing the mobility and bioavailability of radionuclides across a wide range of environments. The correlation of original radionuclide speciation to plutonium and strontium fractionation suggests the existence of multiple chemical forms of the two elements between different
and within the same reference materials. The ability to pinpoint different chemical forms of radionuclides within a soil sample is important for obtaining information on the origin of an unknown sample. This information would be extremely beneficial to the field of nuclear forensics since the existence of multiple chemical forms of a radionuclide suggests contributions of contamination from more than one source. Further research investigating the chemical speciation of radionuclides prior to sequential extraction studies are needed to confirm and expand this conclusion.

Other future work should include sequential extraction studies on moss-soil and Fangataufa sediment reference materials for the fractionation of thorium, uranium, and americium. Sequential extraction studies of strontium should be completed on IAEA reference materials for a more thorough study and to determine any differences in fractionation within the material compared to the NIST reference sediments.
CHAPTER 8  CONCLUSIONS

The research presented in this dissertation aimed to verify an existing standardized sequential extraction protocol while expanding capabilities to include simultaneous analysis of multiple actinide elements across a broad range soil types. A standardized protocol, when consistently used by future researchers, will allow direct comparison of leaching results from an even broader range of soil matrices than presented in this work. Information furnished by such results will lead to a better understanding of radionuclide mobility and bioavailability in different environments, which, in turn, will help with decision making in areas such as environmental remediation and nuclear forensics. The verification of an extraction chromatography based separation procedure, an expansion of capabilities of a sequential extraction procedure, and the addition of a sixth fraction for complete dissolution of soil matrices were all studied in this research. A detailed discussion of results from each study is presented in the following sections.

8.1 Extraction Chromatography Method Verification

An extraction chromatography procedure was investigated for applicability to post-sequential extraction leachates to facilitate the separation of samples containing multiple actinide elements. Investigation of single actinide elution behaviors for method verification proved the separation procedure to be reliable when applied at different laboratories. Plutonium elution, however, was not complete, warranting future investigations into pre-column valence adjustments. Scaling experiments to reduce the amount of hydrofluoric acid used in the pre-column matrix removal step resulted in a safer procedure that will be more applicable to a wider range of laboratory capabilities. Due to noted elemental interferences that can occur with extraction chromatography resin use, tracers and sequential extraction reagents were passed through the separation process to determine reagent effects on
recovery without the addition of the complicated soil matrix. Minimal breakthrough and recoveries of over 75% for most target phases suggest the separation scheme can be successfully used in tandem with the sequential extraction procedure. Losses seen due to decanting supernatant following pre-column Fe(III)OH led to the suggestion that decanting should always be performed by filtration to avoid losses. Filtration of samples using 0.1 μm Eichrom Resolve filters is sufficient, when the filters are washed with at least 10 mL of a 3 M HNO₃ – 0.25 M boric acid solution at 60 °C.

Results of all studies in the separation procedure method verification suggest the procedure by Maxwell et al. is suitable to be coupled with the sequential extraction procedure for separation of radioisotopes from sequential extraction leachates for alpha analysis. Future work should include investigation of thorium breakthrough following the elution step for completeness and a closer look at pre-column valence adjustments of plutonium in attempt to obtain a plutonium recovery closer to 100%.

8.2 Standardized Sequential Extraction Protocol Capability Expansion

Research presented in chapter five aimed to verify and expand the capabilities of the standard sequential extraction protocol that previously had been developed by researchers at NIST. Method verification of the NIST standardized sequential extraction protocol was conducted by analyzing five replicate samples of lake sediment and ocean sediment reference materials for extraction of $^{238}$U and $^{239,240}$Pu. Results were mostly in agreement between laboratories, with any discrepancies likely arising from inconsistent reaction parameters within the sequential extraction procedure. Sediment pretreatment and reaction conditions for the organic target phase must be more defined for a more repeatable standard protocol. Extraction of americium and thorium from lake and ocean sediment was investigated in attempt to expand the capabilities of the sequential extraction procedure.
Thorium extraction behaviors tended to follow those of uranium in both lake and ocean sediment, while americium extracted similarly to plutonium, confirming that the origin and perhaps the chemical form of the leached actinide has an effect on speciation and environmental mobility. Plutonium leaching from moss-soil and Fangataufa sediment reference materials showed varying leaching behaviors based upon differing geochemical content of soils. The information furnished from actinide leaching in chapter five can provide insight not only into conditions under which contaminants can become environmentally mobile, but also into the determination of origin of unknown samples and mode of occurrence of actinides based on extraction behaviors.

Iron, manganese, and aluminum extraction data provided a better understanding of phase selectivity and confirmed differences in extraction behaviors from various soil types suggested by the actinide extraction data. Extraction behavior of strontium suggests the common fission product is potentially mobile in both lake and ocean environments. Stable element data matched well to data reported from the studies by Outola et al., suggesting a well-developed standardized sequential extraction protocol.

A more complete understanding of the results presented in chapter five could be obtained by future studies on actinide and stable element extraction behaviors in all four reference materials studied in this work. A total dissolution of previously leached ocean sediment would allow the determination of the concentration of undissolved uranium remaining in the sediment following sequential leaching. Analysis of uranium, americium, and thorium extraction from Fangataufa sediment and moss-soil reference materials would provide a better understanding of speciation based on original chemical form and environmental conditions. Stable element analysis of calcium extraction from lake and ocean sediment by ICP-AES would provide missing information on phase selectivity,
especially for the carbonate fraction. Iron samples should also be run on ICP-AES to
determine whether ICP-MS interferences had an effect on extraction data reported in this
study.

8.3 Addition of a Sixth Fraction for Complete Dissolution

Chapter six presented an investigation of microwave digestion and fusion techniques for
complete dissolution of soil samples to account for any undissolved metals remaining in the
soil matrix following sequential leaching. Since a procedure applicable to a broad range of
soil types was desired, EPA method 3052 was eliminated due to CaF₂ precipitate formation
following dissolution of the high carbonate content Fangataufa sediment. A carbonate
specific microwave digestion method by Kemp and Brown provided acceptable results, with
plutonium recoveries higher than 90% from Fangataufa sediment. A NaOH fusion
dissolution, however, was ultimately chosen as the method to proceed based on its relative
simplicity and much shorter dissolution time. When applied to previously leached
Fangataufa sediment, the NaOH fusion procedure leached the remaining plutonium from
the sediment, allowing for a more complete understanding of plutonium fractionation in the
sediment. Though the NaOH fusion procedure worked well for Fangataufa sediment
dissolution, future work should include an investigation of the dissolution of the other three
reference materials analyzed in this research, before and after sequential leaching.

8.4 Correlations Between Sequential Leaching Behavior, Radionuclide Speciation, and Soil
Geochemistry

Chapter 7 examined the correlation between the fractionation behaviors seen in
sequential extraction studies and both chemical speciation of radionuclides and
geochemical properties of the reference materials used in this work. The correlations
between radionuclide fractionation and the available geochemical host phases of the reference materials suggest the standardized sequential extraction protocol presented in this work has been proven an important tool for assessing the mobility and bioavailability of radionuclides across a wide range of environments. The existence of multiple chemical forms of the plutonium and americium between different and within the same reference materials was seen with correlation of original radionuclide speciation to fractionation of the two elements. Since the existence of multiple chemical forms of a radionuclide suggests contributions of contamination from more than one source, the information presented in this work along with suggested future work would be extremely beneficial to the field of nuclear forensics.

8.5 Suggestions for Future Work

Future work, in addition to that mentioned previously, should include the investigation of the chemical form of radionuclides and soil geochemistry prior to sequential chemical leaching. Understanding of radionuclide speciation prior to fractionation studies would provide much better insight to the effect of chemical form on leaching behaviors. Sequential extraction analysis of actinides with different starting chemical forms should also be studied. If radionuclide fractionation results differ based on various pre-leaching chemical forms, the information furnished would be better able to predict origin of radionuclides within the soils. The analysis of radionuclide extraction from soils and sediments with quantified geochemical host phases should be studied to provide a better understanding of extraction behaviors based on the contribution of minerals and compounds from within the soil. For example, quantification of carbonates in a soil sample would allow normalization of leaching behavior based on the percentage of the soil associated with the carbonate phase.
Such quantification and normalization should allow a more direct comparison of extraction behaviors from soils and sediments with various geochemical host phases. Finally, sequential extraction studies of real world samples with similar geochemical profiles as those studied in this research would provide for interesting future work.
Figure 53. Sequential extraction flow chart. Previous work is shown in black while this work is shown in green. IEX = anion exchange, EXC = extraction chromatography.
Standardized Sequential Extraction Procedure

The procedure presented below represents the standardized sequential extraction protocol including stable element analysis preparation as well as preconcentration, separation, and sample mounting details for actinide analysis. Details are presented in the sections below.

1. Sequential Extraction

1.1 Introduction

The procedure presented in this section is based on a modification of the Tessier sequential extraction protocol. It was previously optimized by researchers at the National Institute of Standards and Technology (NIST) for maximum extraction of $^{238}\text{U}$ and $^{239,240}\text{Pu}$ from lake sediment and ocean sediment standard reference materials (NIST 4354 and NIST 4357, respectively). Reagent concentration, reaction time, and reaction temperature parameters were optimized by Outola et al. [4].

1.2 Reagents and Equipment

- 0.1 M MgCl$_2$, ACS grade, Mallinckrodt, Lot H09N54
- 1.0 M NH$_4$Ac in 25% (v/v) HAc, ACS grade, BDH, Lot 48221850
- 0.1 M NH$_2$OH·HCl in 25% (v/v) HAc, ACS grade, JT Baker, Lot H34467
- Acetic acid, ACS grade, BDH Aristar, Lot 200917611
- 30 wt. % H$_2$O$_2$, ACS grade, BDH, Lot 49154926
- 0.02 M HNO$_3$, ACS grade, BDH, Lot 2013082772
- 4 M HNO$_3$, ACS grade, BDH, Lot 2013082772
- Deionized water from Pall Cascada LS system
- Thermo Electron Corporation Precision water bath, Model 2870
- Mettler Toledo New Classic MF balance, Model MS 3035/03
- Beckman Coulter Allegra 6 centrifuge
- VWR Hot plate/stirrer, Cat # 11301-064
- Nalgene centrifuge bottles, 250 mL
- Nalgene bottles, 500 mL

1.3 Experimental

Table 29 represents the reagents and reaction conditions (time and temperature) used in the sequential extraction procedure in this work.
Table 30. Sequential extraction reaction conditions [4].

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Reagent</th>
<th>Concentration (M)</th>
<th>T (°C)</th>
<th>Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>MgCl₂</td>
<td>0.1</td>
<td>25</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>NH₄Ac in 25% (v/v) HAc</td>
<td>1.0</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>III</td>
<td>NH₂OH·HCl in 25% (v/v) HAc</td>
<td>0.1</td>
<td>70</td>
<td>6</td>
</tr>
<tr>
<td>IV</td>
<td>30 % H₂O₂ in 0.02 M HNO₃ pH 2</td>
<td></td>
<td>70</td>
<td>3</td>
</tr>
<tr>
<td>V</td>
<td>HNO₃</td>
<td>4</td>
<td>90</td>
<td>4</td>
</tr>
<tr>
<td>VI</td>
<td>NaOH Fusion</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.3.1 Dry sediment overnight at 60 °C in a thermostatically controlled oven

1.3.2 Weigh sediment into 250 mL centrifuge bottle

1.3.2.1 Weigh empty centrifuge bottle

1.3.2.2 Measure 12 g sediment into bottle, record the difference in weights

1.3.3 Add 35 mL deionized water to expand clay minerals, mix vigorously, allow to sit overnight

1.3.4 Add 180 mL 0.1 M MgCl₂ to centrifuge bottle containing sediment

1.3.5 Cap bottle and place in water bath set to the temperature and reaction time shown in the table above

1.3.6 Remove centrifuge bottle from water bath

1.3.7 Centrifuge bottle at 3000 rpm for 25 minutes

1.3.8 Decant supernatant into a clean 500 mL Nalgene bottle

1.3.9 Rinse residual sediment with 25 mL of the extracting reagent

1.3.10 Centrifuge at 3000 rpm for 10 minutes

1.3.11 Decant supernatant into 500 mL Nalgene bottle with previous supernatant

1.3.12 Rinse the residual sediment with 25 mL DI

1.3.13 Centrifuge at 3000 rpm for 10 minutes

1.3.14 Decant supernatants into 500 mL bottle containing previous supernatant

1.3.15 Filter supernatant through 0.45 μm filter (47 mm diameter) and transfer the filtrate back into the Nalgene bottle

1.3.16 Place the filter in the centrifuge bottle with the sediment to be rinsed before the next extraction
1.3.17 Acidify leachate to pH 1 with HNO₃ and save for stable element and actinide analysis

1.3.18 Repeat steps 1.3.4 – 1.3.17 for Fractions II, III, and V

1.3.19 For Fraction IV, slurry the sediment from the centrifuge bottle into a 600 mL beaker using 70 mL 0.02 M HNO₃

1.3.20 Place beaker on hot plate at 70 °C

1.3.21 Add 110 mL of H₂O₂ drop-wise, with occasional agitation, until reaction is complete. This should take approximately 3 hours. Monitor pH and keep close to 2.

1.3.22 Transfer sediment and solution back into centrifuge bottle and repeat steps 1.3.7 – 1.3.17

2. NaOH Fusion

2.1 Introduction

The procedure presented below is a scaled down (1:4) version of EPA Method 402-R-14-004. The method was scaled down for this work in order to match sample sizes to those used in microwave digestion studies. It is suggested that the original method be used for future work to allow larger (1.0 g) sample sizes for dissolution.

2.2 Reagents and Equipment

- Deionized water from Pall Cascada LS system
- 2 M Al(NO₃)₃, ACS grade, EMD, Lot 41079419
- 3.2 M (NH₄)₂HPO₄, 98%, Alfa Aesar, Lot K02R053
- 0.25 M H₃BO₃, ACS grade, EMD, Lot 47039716
- 1.25 M Ca(NO₃)₂·4H₂O, Sigma Aldrich
- 20 mg mL⁻¹ Fe(NO₃)₃·9H₂O, ACS grade, BDH, Lot 84211
- HCl, N.F., JT Baker, Lot E09028
- HF, ACS grade, BDH, Lot 2012122607
- 1.55 mg mL⁻¹ cerium carrier, cerium (III) nitrate hexahydrate, 99.5%, Alfa Aesar, Lot I21P30
- HNO₃, ACS grade, BDH, Lot 2013082772
- 2 M Na₂CO₃, GR, EM Scientific, Lot 38068846
- NaOH pellets, purified grate, Fisher, Lot 960753
- TiCl₃, 20 wt. % in 3 wt. % HCl, ACS grade, Alfa Aesar, Lot K030014
-³²³⁹Th tracer, Th(NO₃)₃ in 0.1 M HNO₃, Isotopes Products Laboratories, Source No. 1198-23-9
• $^{232}$U tracer, in 2.0 M HNO$_3$, NIST, Source No. 4324B
• $^{242}$Pu tracer, in 3.2 M HNO$_3$, NIST, Source No. 4334H
• $^{243}$Am tracer, AmCl$_3$ in 1 M HNO$_3$, Isotopes Produces Laboratories, Source No. 1198-23-8
• Mettler Toledo New Classic MF balance, Model MS 3035/03
• Beckman Coulter Allegra 6 centrifuge
• VWR Hot plate/stirrer, Cat # 11301-064
• VWR centrifuge tubes, 50 mL
• Zirconium crucibles, 50 mL with lids
• Vulcan box furnace (Model 3-550)
• Long handled tongs
• Tweezers

2.3 Experimental

2.3.1 Measure 0.25 g of reference material from the centrifuge bottle into the Zr crucible following the leaching of Fraction V

2.3.2 Add radioisotope tracers in an activity concentration matching the expected activity of the sample

2.3.3 Place crucibles on a hot plate and heat to medium heat, evaporate to dryness

2.3.4 Remove crucibles and allow cooling

2.3.5 Add 3.75 g NaOH to crucible

2.3.6 Place lids on crucible and place in muffle furnace at 600 °C for ~15 minutes

2.3.7 Remove crucibles carefully using tongs and transfer to hood

2.3.8 Add 12.5 mL DI to crucible and heat on hotplate to loosen/dissolve solids

2.3.9 Pipet 1.56 mL of iron carrier into a labeled 50 mL centrifuge tube

2.3.10 Add 0.806 mL of 1.55 mg mL$^{-1}$ cerium carrier to centrifuge tube

2.3.11 Transfer fused sample into the centrifuge tube, rinse crucibles well with DI and transfer rinse to tube

2.3.12 Dilute sample to 40 mL with DI

2.3.13 Pipet 3 mL 1.25 M Ca(NO$_3$)$_2$ and 5 mL 3.2 M (NH$_4$)$_2$HPO$_4$ into centrifuge tube, cap and mix well

2.3.14 Pipet 0.625 mL 20 wt. % TiCl$_3$ into each tube, cap and mix immediately
2.3.15 Cool centrifuge tubes in an ice bath for ~10 minutes
2.3.16 Centrifuge at 3500 rpm for 6 minutes
2.3.17 Pour off the supernatant and discard to waste
2.3.18 Add 15 mL 1.5 M HCl, cap and shake to dissolve solids as well as possible
2.3.19 Dilute to 42 mL with 0.01 M HCl
2.3.20 Pipet 0.161 mL of cerium carrier into centrifuge tube
2.3.21 For uranium samples, add 0.375 mL of 20 wt. % TiCl₃
2.3.22 Add 5.5 mL concentrated HF to centrifuge tube, cap, mix and set in an ice bath for ~10 minutes
2.3.23 Centrifuge at 3000 rpm for 10 minutes
2.3.24 Pour off supernatant through a 0.1 μm polypropylene filter
2.3.25 Rinse filter into centrifuge tube using warm 3 M HNO₃ – 0.25 M H₃BO₃
2.3.26 Proceed to Section 5.3 for separations

3. Removal of Aliquots for Stable Element Analysis

3.1 Introduction

This section provides details for removing aliquots from the sequential extraction leachate for samples requiring stable element analysis.

3.2 Reagents and Equipment

- Nitric acid, ultrapure, Baseline, Lot # 1207060
- VWR digital heat block, Cat. #12621-096
- Mettler Toledo New Classic MF balance, Model MS 3035/03
- 50 mL volumetric flask
- 50 mL centrifuge tube
- 13 mm, 0.45 μm PTFE membrane Pall Acrodisc syringe filters
- BD 5 mL syringe, Luer-loc tip, Ref. 309661

3.3 Experimental

3.3.1 Weigh 50 mL volumetric flask
3.3.2 Transfer 50 mL of sequential extraction reagent into 50 mL volumetric flask
3.3.3 Reweigh full flask
3.3.4 Transfer to labeled 50 mL centrifuge tube
3.3.5 Reweigh empty volumetric flask
3.3.6 Evaporate sample to dryness in centrifuge tube
3.3.7 Reconstitute in 40 mL 1% ultrapure nitric acid
3.3.8 Filter using 13 mm diameter, 0.45 μm PTFE membrane syringe filters
3.3.9 Save for analysis by ICP-MS or ICP-AES

4. **Tracer Addition and Preconcentration**

4.1 Introduction

This section describes the addition of tracers to sequential extraction leachates. Following tracer addition, the samples are evaporated to dryness and subject to two preconcentration steps; Fe(III)OH and CeF₃.

4.2 Reagents and Equipment

- $^{229}$Th tracer, Th(NO$_3$)$_3$ in 0.1 M HNO$_3$, Isotopes Products Laboratories, Source No. 1198-23-9
- $^{232}$U tracer, in 2.0 M HNO$_3$, NIST, Source No. 4324B
- $^{242}$Pu tracer, in 3.2 M HNO$_3$, NIST, Source No. 4334H
- $^{243}$Am tracer, AmCl$_3$ in 1 M HNO$_3$, Isotopes Produces Laboratories, Source No. 1198-23-8
- Deionized water from Pall Cascada LS system
- 20 mg mL$^{-1}$ Fe(NO$_3$)$_3$·9H$_2$O, ACS grade, BDH, Lot 84211
- 1.55 mg mL$^{-1}$ cerium carrier, cerium (III) nitrate hexahydrate, 99.5%, Alfa Aesar, Lot I21P30
- HCl, N.F., JT Baker, Lot E09028
- HNO$_3$, ACS grade, BDH, Lot 2013082772
- H$_3$BO$_3$, ACS grade, EMD, Lot 47039716
- NH$_4$OH, ACS grade, EMD, Lot 48213
- TiCl$_3$, 20 wt. % in 3 wt. % HCl, ACS grade, Alfa Aesar, Lot K030014
- HF, ACS grade, BDH, Lot 2012122607
- Beckman Coulter Allegra 6 centrifuge
- Eichrom 0.1 μm Resolve filters, 25 mm diameter, Lot RF061313
- Transfer pipettes
- VWR Hot plate/stirrer, Cat # 11301-064
• Watch glass
• 50 mL centrifuge tube

4.3 Experimental

4.3.1 Add tracer and record mass before and after tracer addition

4.3.2 Transfer solution to 600 mL beaker, rinse bottle with DI, add rinse to beaker

4.3.3 Evaporate to dryness on hotplate

4.3.4 For Fractions II and III, add 2 mL 30 wt. % H₂O₂ and 2 mL concentrated HNO₃ and evaporate to dryness

4.3.5 Reconstitute in 200 mL 0.5 M HCl

4.3.6 Add 0.5 mL iron carrier

4.3.7 Heat to boiling for 20 minutes

4.3.8 Add NH₄OH until turbidity persists, add ~10 mL more NH₄OH

4.3.9 Allow boiling for 10 more minutes

4.3.10 Remove from hotplate to cool for at least 30 minutes

4.3.11 Decant the supernatant by pipette

4.3.12 Transfer precipitate to 50 mL centrifuge tube, rinse with DI and add rinse to tube

4.3.13 Centrifuge at 3000 rpm for 5 minutes and discard supernatant

4.3.14 Rinse precipitate with 15 mL DI, centrifuge at 3000 rpm for 5 minutes, discard supernatant, repeat

4.3.15 Dissolve precipitate in 6 mL 1.5 M HCl

4.3.16 Add 0.2 mL cerium carrier

4.3.17 Add 1.1 mL concentrated HF

4.3.18 Cap, mix well, and set in ice bath for ~10 minutes

4.3.19 Filter precipitate using 0.1 μm Resolve filter

4.3.20 Wash filter into centrifuge tube with 10 mL 3 M HNO₃ – 0.25 M H₃BO₃ at ~60 °C
5. Separations

5.1 Introduction

The following separation procedure was taken from Maxwell et al. [70]. It provides separation and purification of uranium, thorium, plutonium, and americium from soil matrices. While the Maxwell procedure includes a soil dissolution step at the beginning, the work only uses the separation portion of the procedure.

5.2 Reagents and Equipment

- HNO₃ (0.25 M, 3 M, 5 M, 6 M, concentrated), ACS grade, BDH, Lot 2013082772
- HCl (0.25 M, 1 M, 4 M, 9 M), ACS grade, JT Baker, Lot E09028
- 1 M Al(NO₃)₃, ACS grade, EMD, Lot 41079419
- 1.5 M sulfamic acid, ACS grade, EMD, Lot TE17DZEMS
- 1.5 M ascorbic acid, made fresh, ≥ 99.0%, Sigma Aldrich, Lot SLBC7863V
- 3.5 M NaNO₂, made fresh, ACS grade, JT Baker, Lot J08622
- 0.1 M HCl – 0.05 M HF – 0.03 M TiCl₃
- 30 wt. % H₂O₂, ACS grade, BDH, Lot 49154926
- 4 M HCl – 0.2 M HF
- Ammonium oxalate monohydrate, ACS grade, EMD, Lot A971592 952
- Oxalic acid, ACS grade, JT Baker, Lot J08622
- 0.1 M ammonium bioxalate
- TiCl₃, 20 wt. % in 3 wt. % HCl, ACS grade, Alfa Aesar, Lot K030014
- 1.8 M H₂SO₄, ACS grade, Sigma Aldrich
- Ammonium thiocyanate, ACS grade, EMD, Lot A972313
- Formic acid, ACS grade, Sigma Aldrich, Lot 47796PH
- 4 M ammonium thiocyanate – 0.1 M formic acid
- 1.5 M ammonium thiocyanate – 0.1 M formic acid
- Eichrom Prefilter 2 mL resin cartridges, Lot PFLR13A
- Eichrom TEVA 2 mL resin cartridges, 50-100 μm, Lot TESR13F
- Eichrom TRU 2 mL resin cartridges, 50-100 μm, Lot TRSR8A
- Eichrom DGA 2 mL resin cartridges, 50-100 μm, Lot DNSR7A
- Eichrom 24-position Vacuum box
- Eichrom yellow outer tips, Lot 030106
- Eichrom white inner tips, Lot 022806
- BD 20 mL syringe, Luer-loc tip, Ref. 309661
- Vacuubrand GMBH CO KG MD1C vacuum pump
- VWR Hot plate/stirrer, Cat # 11301-064

5.3 Experimental

5.3.1 Precolumn Valence Adjustments
5.3.1.1 Reconstitute previous samples (2.3.26 and 4.3.20) in $x$ mL $7 \text{M HN}O_3 - x$ mL $2 \text{M Al(NO}_3)_3$

5.3.1.2 Add 0.5 mL 1.5 M sulfamic acid to centrifuge tube

5.3.1.3 Add 1.25 mL 1.5 M ascorbic acid to centrifuge tube, swirl to mix, wait 3 minutes

5.3.1.4 Add 1 mL 3.5 M NaNO$_2$ to centrifuge tube, swirl to mix

5.3.2 Column Preparation and Loading

5.3.2.1 Stack Eichrom resin cartridges on vacuum box in the order of (top to bottom) Pre-filter, TEVA, TRU, DGA

5.3.2.2 Place 50 mL centrifuge tube in vacuum box to collect eluent

5.3.2.3 Connect vacuum and check seal

5.2.3.4 Wet the resins by running $\sim 10$ mL of 3 M HNO$_3$ through the stacked columns

5.3.2.5 Load the sample onto stacked columns

5.3.2.6 Rinse load tube with 3 mL 6 M HNO$_3$, add rinse to column

5.3.2.7 Separate cartridges

5.3.3 TEVA Only

5.3.3.1 Replace 50 mL tube inside vacuum box with one labeled U for TRU

5.3.3.2 Adjust vacuum pressure to 5 in Hg

5.3.3.3 Add 7 mL 3 M HNO$_3$ to column

5.3.3.4 Remove U for TRU tube and add 3 mL concentrated HNO$_3$ to tube, save for later

5.3.3.5 Replace centrifuge tube in vacuum box with one labeled for waste

5.3.3.6 Add 10 mL 5 M HNO$_3$ to column

5.3.3.7 Add 10 mL 3 M HNO$_3$ to column

5.3.3.8 Remove tube, discard waste, replace with tube labeled for thorium

5.3.3.9 Add 23 mL 9 M HCl to column

5.3.3.10 Remove tube and replace with HNO$_3$ waste tube

5.3.3.11 Add 5 mL 3 M HNO$_3$ to the column
5.3.3.12 Remove tube and discard waste, replace tube with clean one labeled for plutonium

5.3.3.13 Add 20 mL 0.1 M HCl – 0.5 M HF – 0.03 M TiCl$_3$ to the column

5.3.3.14 Remove tube and add 0.5 mL 30 wt. % H$_2$O$_2$

5.3.4 *DGA Only*

5.3.4.1 Replace tube with U for TRU from earlier

5.3.4.2 Add 5 mL 0.25 M HNO$_3$ to column

5.3.4.3 Remove tube and add 4 mL conc. HNO$_3$ to centrifuge tube, save for later

5.3.5 *TRU Stacked on DGA*

5.3.5.1 Place HCl waste centrifuge tube in vacuum box

5.3.5.2 Add 15 mL 4 M HCl to the column

5.3.5.3 Discard waste and unstack columns

5.3.6 *TRU Only*

5.3.6.1 Place HNO$_3$ waste centrifuge tube in vacuum box

5.3.6.2 Add saved uranium for TRU solutions to column

5.3.6.3 Remove HNO$_3$ waste tube, discard waste replace with HCl waste tube

5.3.6.4 Add ~20 mL 4 M HCl – 0.2 M HF to the column

5.3.6.5 Remove HCl waste tube, discard waste, and replace with HNO$_3$ waste tube in vacuum box

5.3.6.6 Add 3 mL 3 M HNO$_3$ to the column

5.3.6.7 Remove tube, discard waste, and replace centrifuge tube with clean one labeled for uranium

5.3.6.8 Adjust vacuum pressure to 2-3 In. Hg

5.3.6.9 Add 15 mL 0.1 M ammonium bioxalate to the column
5.3.6.10 Remove tube and add 0.5 mL 20 wt % TiCl$_3$ to uranium centrifuge tube

5.3.7 **DGA Only**

5.3.7.1 Place clean centrifuge tube labeled DGA eluant (Am)

5.3.7.2 Add 10 mL 0.25 M HCl to the column

5.3.8 **Americium on Hot Plate**

5.3.8.1 Transfer DGA eluent to 100 mL glass beaker

5.3.8.2 Rinse centrifuge tube with 3 mL concentrated HNO$_3$ and add rinse to beaker

5.3.8.3 Add 0.05 mL 1.8 M sulfuric acid to beaker

5.3.8.4 Evaporate to dryness

5.3.8.5 Let cool and add 2 mL conc. HNO$_3$ and 2 mL 30 wt % H$_2$O$_2$, evaporate to dryness

5.3.8.6 Redissolve sample by adding 5 mL 4 M ammonium thiocyanate – 0.1 M formic acid

5.3.9 **TEVA Only**

5.3.9.1 Place new TEVA cartridge on vacuum box with a new reservoir

5.3.9.2 Place new waste centrifuge tube and adjust vacuum pressure to 7-10 In. Hg

5.3.9.3 Load solution from step 5.3.8.6 onto column

5.3.9.4 Add 10 mL 1.5 M ammonium thiocyanate – 0.1 M formic acid to column

5.3.9.5 Replace centrifuge tube with new clean one labeled for americium

5.3.9.6 Add 20 mL 1 M HCl to column

5.3.9.7 Warm 5 mL of 1 M HCl on the hot plate

5.3.9.8 Rinse load beaker with 5 mL warm 1 M HCl, add rinse to column

5.3.9.9 Rinse beaker with 15 mL 1 M HCl, add rinse to column
6. *CeF₃* sample mounting

6.1 Introduction

The procedure below is from Sill et al. [cite] for a cerium fluoride microprecipitation method to mount samples for counting by alpha spectroscopy.

6.2 Reagents and Equipment

- Deionized water from Pall Cascada LS system
- TiCl₃, 20 wt % in 3 wt% HCl, ACS grade, Alfa Aesar, Lot K030014
- 1.55 mg mL⁻¹ cerium carrier, cerium (III) nitrate hexahydrate, 99.5%, Alfa Aesar, Lot I21P30
- HF, ACS grade, BDH, Lot 2012122607
- Ethanol
- Millipore filtration manifold Model 1225
- GAST Model DOL-122A-AA vacuum pump
- Filters
- Teflon tweezers
- Stainless steel planchets
- Double sided tape
- Petri dish
- Heat lamp

6.3 Experimental

6.3.1 Add 0.1 mL 1.55 mg mL⁻¹ cerium carrier to sample from steps 5.3.3.9, 5.3.3.14, 5.3.6.10, 5.3.9.9

6.3.2 Add 1 mL concentrated HF, let sit for 30 minutes

6.3.3 Place filters on Millipore filtration manifold, wet with ethanol to open pores

6.3.4 Rinse sample reservoir with DI

6.3.5 Add sample to filtration manifold reservoir

6.3.6 Once sample has passed through, rinse reservoir with ~3 mL DI and ~3 mL 80% ethanol

6.3.7 Remove filter, dry under heat lamp

6.3.8 Attach filter to a stainless steel planchet using double sided tape

6.3.9 Place planchet in a labeled petri dish for storage prior to alpha spectroscopy
Table 31. Calculated detector efficiencies at the fourth shelf level, approximately 1 cm from detector window.

<table>
<thead>
<tr>
<th>Location</th>
<th>Detector</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEB 2119B</td>
<td>1A</td>
<td>0.0880</td>
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<tr>
<td></td>
<td>1B</td>
<td>0.0862</td>
</tr>
<tr>
<td></td>
<td>2B</td>
<td>0.1397</td>
</tr>
<tr>
<td></td>
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<td>0.0903</td>
</tr>
<tr>
<td></td>
<td>3B</td>
<td>0.0904</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>4B</td>
<td>0.0916</td>
</tr>
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<td></td>
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</tr>
<tr>
<td></td>
<td>5B</td>
<td>0.0923</td>
</tr>
<tr>
<td></td>
<td>6A</td>
<td>0.0921</td>
</tr>
<tr>
<td></td>
<td>6B</td>
<td>0.0876</td>
</tr>
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<td>BHS 105</td>
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<td>0.0878</td>
</tr>
<tr>
<td></td>
<td>1B</td>
<td>0.0865</td>
</tr>
<tr>
<td></td>
<td>2A</td>
<td>0.0854</td>
</tr>
<tr>
<td></td>
<td>2B</td>
<td>0.0891</td>
</tr>
<tr>
<td></td>
<td>3A</td>
<td>0.0860</td>
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<tr>
<td></td>
<td>3B</td>
<td>0.0867</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>4B</td>
<td>0.0842</td>
</tr>
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<td>BHS 117</td>
<td>3</td>
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</tr>
<tr>
<td></td>
<td>4</td>
<td>0.1069</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.1095</td>
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<tr>
<td></td>
<td>6</td>
<td>0.1064</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.1047</td>
</tr>
</tbody>
</table>

Table 32. Raw data for Figure 24: Total recovery (%) of $^{229}$Th, $^{242}$Pu, $^{243}$Am, and $^{232}$U in this work and reported recoveries for $^{242}$Pu, $^{243}$Am, and $^{232}$U by Maxwell et al.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>This work (%)</th>
<th>Maxwell (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{232}$U</td>
<td>97.7 ± 5.3</td>
<td>98.4 ± 4.4</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>83.1 ± 7.5</td>
<td>104 ± 5.3</td>
</tr>
<tr>
<td>$^{243}$Am</td>
<td>97.2 ± 8.6</td>
<td>105.2 ± 13</td>
</tr>
<tr>
<td>$^{229}$Th</td>
<td>95.4 ± 25.4</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Table 33. Raw data for Figures 22 and 23: Recovery of $^{229}$Th, $^{242}$Pu, $^{243}$Am, and $^{232}$U in each eluent of separation procedure. Only one replicate had been counted at time of writing for uranium recoveries listed without error.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Th-229</th>
<th>Pu-242</th>
<th>Am-243</th>
<th>U-232</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 M HNO$_3$</td>
<td>0.14 ± 0.08</td>
<td>0.32 ± 0.13</td>
<td>N/A</td>
<td>2.33 ± 0.06</td>
</tr>
<tr>
<td>5 M HNO$_3$</td>
<td>0.20 ± 0.11</td>
<td>0.46 ± 0.42</td>
<td>0.07 ± 0.69</td>
<td>0.17</td>
</tr>
<tr>
<td>3 M HNO$_3$</td>
<td>0.29 ± 0.34</td>
<td>0.72 ± 0.63</td>
<td>0.04 ± 0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>9 M HCl</td>
<td>94.79 ± 25.35</td>
<td>0.41 ± 0.46</td>
<td>0.02 ± 0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>3 M HNO$_3$</td>
<td>0.17 ± 0.05</td>
<td>0.05 ± 0.05</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>0.1 M HCl - 0.05 M HF - 0.03 M TiCl$_3$</td>
<td>80.67 ± 7.56</td>
<td>0.01 ± 0.14</td>
<td>0.31 ± 0.16</td>
<td></td>
</tr>
<tr>
<td>0.25 M HNO$_3$</td>
<td>0.03 ± 0.01</td>
<td>0.28 ± 0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 M HCl</td>
<td>0.03 ± 0.01</td>
<td>0.13 ± 0.08</td>
<td>0.28 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>U for TRU</td>
<td>0.12 ± 0.05</td>
<td>0.28 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 M HCl - 0.2 M HF</td>
<td>0.02 ± 0.01</td>
<td>0.14 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 M HNO$_3$</td>
<td>0.03 ± 0.00</td>
<td>0.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 M ammonium bixalate</td>
<td>not counted</td>
<td>not counted</td>
<td>93.47</td>
<td></td>
</tr>
<tr>
<td>0.25 M HCl</td>
<td>not counted</td>
<td>not counted</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 M HCl</td>
<td>97.7 ± 8.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 34. Raw data for Figure 25: Recovery values for $^{229}$Th, $^{242}$Pu, and $^{243}$Am for Maxwell scaling experiments.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{243}$Am</td>
<td>83.0 ± 3.5</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td>87.1 ± 5.5</td>
</tr>
<tr>
<td>$^{229}$Th</td>
<td>79.0 ± 13.9</td>
</tr>
<tr>
<td>$^{232}$U</td>
<td>77.6 ± 15.7</td>
</tr>
</tbody>
</table>
Table 35. Raw data for Figure 26: Sample and supernatant recoveries from removal of supernatant study.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Sample</th>
<th>Supernatant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>90.6</td>
<td>2.9</td>
</tr>
<tr>
<td>Exchangeable</td>
<td>12.1</td>
<td>75.5</td>
</tr>
<tr>
<td>Carbonate</td>
<td>25.6</td>
<td>70.7</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>72.0</td>
<td>5.9</td>
</tr>
<tr>
<td>Organic</td>
<td>57.9</td>
<td>23.4</td>
</tr>
<tr>
<td>Residual</td>
<td>64.6</td>
<td>14.0</td>
</tr>
</tbody>
</table>

Table 36. Raw data for Figure 27: Amount of tracer removed from filters with 5 mL and 10 mL washes of 3 M HNO₃ – 0.25 M boric acid at 60 °C.

<table>
<thead>
<tr>
<th>Tracer</th>
<th>5 mL wash</th>
<th>10 mL wash</th>
</tr>
</thead>
<tbody>
<tr>
<td>²³²U</td>
<td>77.1 ± 4.0</td>
<td>99.8 ± 7.9</td>
</tr>
<tr>
<td>²⁴²Pu</td>
<td>62.2 ± 0.3</td>
<td>94.6 ± 8.4</td>
</tr>
<tr>
<td>²⁴³Am</td>
<td>90.9 ± 5.5</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 37. Raw data for Figures 28 – 30: Measured recoveries (%) for ²³²U, ²⁴²Pu, and ²⁴³Am from reagent interference studies.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Uranium</th>
<th>Plutonium</th>
<th>Americium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>93.2 ± 7.6</td>
<td>82.7 ± 3.1</td>
<td>75.4 ± 2.1</td>
</tr>
<tr>
<td>Exchangeable</td>
<td>87.6 ± 6.5</td>
<td>54.9 ± 6.6</td>
<td>54.4 ± 2.8</td>
</tr>
<tr>
<td>Carbonate</td>
<td>86.3 ± 2.5</td>
<td>89.0 ± 3.8</td>
<td>64.5 ± 6.2</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>77.9 ± 6.3</td>
<td>66.9 ± 9.9</td>
<td>58.9 ± 2.4</td>
</tr>
<tr>
<td>Organic</td>
<td>62.0 ± 13.6</td>
<td>89.7 ± 3.2</td>
<td>85.2 ± 17.0</td>
</tr>
<tr>
<td>Residual</td>
<td>78.6 ± 15.3</td>
<td>87.5 ± 0.5</td>
<td>72.1 ± 6.6</td>
</tr>
</tbody>
</table>
Table 38. Raw data for Figures 31 – 33, 36, and 37: Extraction of uranium and plutonium from ocean sediment.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Sample Recovery</th>
<th>Count Error</th>
<th>Sample Recovery</th>
<th>Count Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>7.9 ± 0.5</td>
<td>5.7 ± 1.8</td>
<td>4.9 ± 0.9</td>
<td>7.9 ± 3.2</td>
</tr>
<tr>
<td>Carbonate</td>
<td>11.2</td>
<td>3.7</td>
<td>57.6 ± 4.4</td>
<td>2.1 ± 0.6</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>3.8 ± 0.1</td>
<td>13.8 ± 0.9</td>
<td>9.3 ± 1.8</td>
<td>6.6 ± 1.2</td>
</tr>
<tr>
<td>Organic</td>
<td>5.6 ± 1.2</td>
<td>8.3 ± 2.0</td>
<td>17.5 ± 2.6</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>Residual</td>
<td>10.5 ± 7.7</td>
<td>26.1 ± 13.4</td>
<td>7.9 ± 2.7</td>
<td>6.9 ± 1.4</td>
</tr>
</tbody>
</table>

Table 39. Raw data for Figures 31 – 33, 36, and 37: Extraction of uranium and plutonium from lake sediment.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Sample Recovery</th>
<th>Count Error</th>
<th>Sample Recovery</th>
<th>Count Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>3.2 ± 1.6</td>
<td>12.7 ± 8.6</td>
<td>2.4 ± 0.3</td>
<td>10.6 ± 4.2</td>
</tr>
<tr>
<td>Carbonate</td>
<td>45.9 ± 5.5</td>
<td>4.4 ± 0.2</td>
<td>9.2 ± 1.1</td>
<td>4.7 ± 0.5</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>11.1 ± 2.6</td>
<td>15.7 ± 3.7</td>
<td>4.2 ± 0.9</td>
<td>8.3 ± 0.6</td>
</tr>
<tr>
<td>Organic</td>
<td>31.7 ± 5.6</td>
<td>18.9 ± 5.0</td>
<td>30.5 ± 11.9</td>
<td>5.8 ± 1.9</td>
</tr>
<tr>
<td>Residual</td>
<td>3.9 ± 0.6</td>
<td>20.4 ± 7.3</td>
<td>47.7 ± 21.4</td>
<td>2.8 ± 0.6</td>
</tr>
</tbody>
</table>

Table 40. Raw data for Figures 34 – 37: Extraction of thorium and americium from ocean sediment.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Sample Recovery</th>
<th>Count Error</th>
<th>Sample Recovery</th>
<th>Count Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>Not Detected</td>
<td>Not Detected</td>
<td>24.8 ± 4.0</td>
<td>4.2 ± 1.4</td>
</tr>
<tr>
<td>Carbonate</td>
<td>11.5 ± 1.7</td>
<td>5.4 ± 2.5</td>
<td>84.9 ± 2.5</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>1.5 ± 0.5</td>
<td>9.8 ± 1.5</td>
<td>10.5 ± 2.2</td>
<td>9.2 ± 4.6</td>
</tr>
<tr>
<td>Organic</td>
<td>5.6 ± 1.5</td>
<td>5.4 ± 0.4</td>
<td>7.5 ± 1.1</td>
<td>7.3 ± 0.3</td>
</tr>
<tr>
<td>Residual</td>
<td>63.9 ± 4.8</td>
<td>1.6 ± 0.1</td>
<td>0.6 ± 0.2</td>
<td>17.4 ± 5.0</td>
</tr>
</tbody>
</table>
Table 41. Raw data for Figures 34 – 37: Extraction of thorium and americium from lake sediment.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>232\textsuperscript{Th} Sample Recovery</th>
<th>232\textsuperscript{Th} Count Error</th>
<th>241\textsuperscript{Am} Sample Recovery</th>
<th>241\textsuperscript{Am} Count Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>4.4 ± 2.3</td>
<td>6.6 ± 1.6</td>
<td>5.3 ± 3.7</td>
<td>16.1 ± 5.4</td>
</tr>
<tr>
<td>Carbonate</td>
<td>27.8 ± 2.2</td>
<td>2.3 ± 0.1</td>
<td>10.8 ± 11.4</td>
<td>11.6 ± 3.6</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>6.5 ± 2.1</td>
<td>5.1 ± 1.3</td>
<td>17.9 ± 9.9</td>
<td>11.4 ± 2.0</td>
</tr>
<tr>
<td>Organic</td>
<td>20.6 ± 7.7</td>
<td>14.3 ± 6.1</td>
<td>Not Detected</td>
<td>16.9 ± 3.4</td>
</tr>
<tr>
<td>Residual</td>
<td>13.3 ± 7.1</td>
<td>11.1 ± 8.3</td>
<td>68.7 ± 15.1</td>
<td>6.7 ± 0.7</td>
</tr>
</tbody>
</table>

Table 42. Raw data for Figure 40: \textsuperscript{239,240}Pu recovery from IAEA 447 (moss-soil)

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>\textsuperscript{239,240}Pu Recovery</th>
<th>Count Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>4.6 ± 2.7</td>
<td>10.7 ± 3.8</td>
</tr>
<tr>
<td>Carbonate</td>
<td>11.1</td>
<td>3.7</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>13.8 ± 10.3</td>
<td>7.1 ± 2.6</td>
</tr>
<tr>
<td>Organic</td>
<td>26.2 ± 6.2</td>
<td>3.6 ± 2.0</td>
</tr>
<tr>
<td>Residual</td>
<td>19.2</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 43. Raw data for Figure 40: \textsuperscript{238}Pu and \textsuperscript{239,240}Pu recovery from IAEA 384 (Fangataufa sediment)

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>\textsuperscript{238}Pu Recovery</th>
<th>Count Error</th>
<th>\textsuperscript{239,240}Pu Recovery</th>
<th>Count Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>5.5 ± 1.1</td>
<td>2.8 ± 0.5</td>
<td>2.5 ± 1.5</td>
<td>5.2 ± 1.9</td>
</tr>
<tr>
<td>Carbonate</td>
<td>57.3 ± 10.9</td>
<td>1.1 ± 0.2</td>
<td>60.0 ± 7.7</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>8.2 ± 1.2</td>
<td>2.4 ± 0.9</td>
<td>3.4 ± 0.6</td>
<td>4.7 ± 2.1</td>
</tr>
<tr>
<td>Organic</td>
<td>25.2 ± 7.1</td>
<td>1.8 ± 0.7</td>
<td>24.6 ± 7.4</td>
<td>1.6 ± 0.7</td>
</tr>
<tr>
<td>Residual</td>
<td>7.5 ± 3.3</td>
<td>2.0 ± 0.8</td>
<td>6.4 ± 3.7</td>
<td>3.0 ± 0.6</td>
</tr>
</tbody>
</table>
Table 44. Raw data for Figure 41: Stable element extraction from ocean sediment.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Mn Recovery</th>
<th>Fe Recovery</th>
<th>Al Recovery</th>
<th>Sr Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>8.9 ± 1.0</td>
<td>1.5 ± 0.3</td>
<td>0.1 ± 0.0</td>
<td>31.2 ± 3.2</td>
</tr>
<tr>
<td>Carbonate</td>
<td>17.6 ± 1.4</td>
<td>22.7 ± 0.4</td>
<td>2.1 ± 0.1</td>
<td>5.9 ± 1.3</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>9.5 ± 1.1</td>
<td>19.8 ± 1.9</td>
<td>3.0 ± 0.3</td>
<td>3.5 ± 0.6</td>
</tr>
<tr>
<td>Organic</td>
<td>4.7 ± 0.6</td>
<td>12.6 ± 0.9</td>
<td>1.7 ± 0.2</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Residual</td>
<td>23.6 ± 0.9</td>
<td>35.9 ± 3.1</td>
<td>12.7 ± 0.5</td>
<td>8.6 ± 0.5</td>
</tr>
</tbody>
</table>

Table 45. Raw data for Figure 41: Stable element extraction from lake sediment.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Mn Recovery</th>
<th>Fe Recovery</th>
<th>Al Recovery</th>
<th>Sr Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>72.9 ± 4.5</td>
<td>1.3 ± 0.6</td>
<td>2.8 ± 1.0</td>
<td>22.8 ± 7.2</td>
</tr>
<tr>
<td>Carbonate</td>
<td>35.2 ± 7.5</td>
<td>20.9 ± 3.4</td>
<td>10.1 ± 1.7</td>
<td>22.3 ± 3.0</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>8.1 ± 2.0</td>
<td>17.0 ± 2.0</td>
<td>8.8 ± 2.7</td>
<td>7.4 ± 1.0</td>
</tr>
<tr>
<td>Organic</td>
<td>4.5 ± 0.9</td>
<td>SATURATED</td>
<td>34.8 ± 2.8</td>
<td>4.9 ± 1.3</td>
</tr>
<tr>
<td>Residual</td>
<td>5.5 ± 0.4</td>
<td>17.4 ± 1.9</td>
<td>22.7 ± 3.3</td>
<td>5.2 ± 0.3</td>
</tr>
</tbody>
</table>

Table 46. ICP-MS dilution data for ocean sediment.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Mn Dilution</th>
<th>Fe Dilution</th>
<th>Al Dilution</th>
<th>Sr Dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>N/A</td>
<td>1:100</td>
<td>1:100</td>
<td>1:10</td>
</tr>
<tr>
<td>Carbonate</td>
<td>1:10</td>
<td>1:1000</td>
<td>1:100</td>
<td>1:10</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>1:10</td>
<td>1:1000</td>
<td>1:1000</td>
<td>None</td>
</tr>
<tr>
<td>Organic</td>
<td>1:10</td>
<td>1:1000</td>
<td>1:1000</td>
<td>None</td>
</tr>
<tr>
<td>Residual</td>
<td>1:100</td>
<td>1:2000</td>
<td>1:1000</td>
<td>1:10</td>
</tr>
</tbody>
</table>

Table 47. ICP-MS dilution data for lake sediment.

<table>
<thead>
<tr>
<th>Target Phase</th>
<th>Mn Dilution</th>
<th>Fe Dilution</th>
<th>Al Dilution</th>
<th>Sr Dilution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchangeable</td>
<td>1:100</td>
<td>1:1000</td>
<td>1:1000</td>
<td>1:10</td>
</tr>
<tr>
<td>Carbonate</td>
<td>1:100</td>
<td>1:2000</td>
<td>1:1000</td>
<td>1:10</td>
</tr>
<tr>
<td>Fe/Mn Oxides</td>
<td>1:100</td>
<td>1:2000</td>
<td>1:2000</td>
<td>1:10</td>
</tr>
<tr>
<td>Organic</td>
<td>1:100</td>
<td>1:2000</td>
<td>1:2000</td>
<td>1:10</td>
</tr>
<tr>
<td>Residual</td>
<td>1:100</td>
<td>1:2000</td>
<td>1:2000</td>
<td>1:10</td>
</tr>
</tbody>
</table>
Table 48. Raw data for Figure 46: Plutonium recovery from soil and CaF$_2$ precipitate using EPA method 3052 for microwave digestion of soils. Replicates 2 and 3 were used for XRD analysis and were therefore not available for alpha analysis.

<table>
<thead>
<tr>
<th>Replicate</th>
<th>$^{238}\text{Pu}$ Solution</th>
<th>$^{238}\text{Pu}$ Precipitate</th>
<th>$^{239,240}\text{Pu}$ Solution</th>
<th>$^{239,240}\text{Pu}$ Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.3</td>
<td>--</td>
<td>5.6</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>3.7</td>
<td>--</td>
<td>7.0</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
<td>3.6</td>
<td>95.6</td>
<td>7.1</td>
<td>90.5</td>
</tr>
<tr>
<td>5</td>
<td>3.1</td>
<td>98.7</td>
<td>18.0</td>
<td>86.3</td>
</tr>
</tbody>
</table>
REFERENCES


[51] EPA, Microwave assisted acid digestion of siliceous and organically based matrices, 1996.


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