

AN ABSTRACT OF THE THESIS OF

M. Alex Brown for the degree of Master of Science in Radiation Health Physics presented on March 15, 2010.

Title: Influence of Temperature on the Extraction of Pu(IV) by Tri-*n*-butyl Phosphate from Acidic Nitrate Solutions.

Abstract approved:

Alena Paulenova

The goal of Advanced Fuel Cycle Initiative program is to efficiently separate and recover actinides in attempts to reprocess irradiated nuclear fuel and reduce the necessary storage volume. In order to facilitate large-scale industrial applications of liquid-liquid separation processes, knowledge of the thermodynamic constants associated with the distribution of metal ions between immiscible media is necessary.

The influence of temperature on the extraction of Pu(IV) into 30 vol.% tri-*n*-butyl phosphate in *n*-dodecane from acidic nitrate solutions has been investigated at temperatures ranging from $T = (294 \text{ to } 313) \text{ K}$. Temperature was found to decrease the distribution of Pu(IV). Three species of plutonium were considered present in the aqueous solution: Pu^{4+} , $\text{Pu}(\text{NO}_3)^{3+}$ and $\text{Pu}(\text{NO}_3)_2^{2+}$. The enthalpy and entropy of the extraction, calculated using Van't Hoff plots, are $-60.4 \pm 3.3 \text{ kJ}\cdot\text{mol}^{-1}$ and $-120 \pm 10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively.

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Influence of Temperature on the Extraction of Pu(IV) by Tri-*n*-butyl Phosphate
from Acidic Nitrate Solutions

by
M. Alex Brown

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

M. Alex Brown, Author

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LIST OF ACRONYMS

AFCI – Advanced Fuel Cycle Initiative
AHA – Acetohydroxamic Acid
Aq – Aqueous phase
BG – Background
CPM – Counts Per Minute
CCD-PEG – Chlorinated Cobalt Dicarbollide Polyethylene Glycol
CR – Count Rate
DOE – Department of Energy
FP – Fission Products
GNEP – Global Nuclear Energy Partnership
HDEHP – Di(2-ethylhexyl) phosphoric acid
HTTA – Thenoyl Trifluoroacetone
Ln - Lanthanides
LSC – Liquid Scintillation Counting
LWR – Light Water Reactor
MOX – Mixed Oxide Fuel
NRC – Nuclear Regulatory Commission
Or – Organic phase
PMT – Photomultiplier Tube
PUREX – Plutonium Uranium Recovery by Extraction
SIT – Specific Ion Interaction Theory
TALSPEAK – Trivalent Actinide Lanthanide Separation by Phosphorous
Extractant from Aqueous Komplexes
TBP – Tri-*n*-butyl Phosphate
TM – Transition Metals
TRU – TransUranic Elements
TRUEX – Transuranic Extraction
UNF – Used Nuclear Fuel
UREX – Uranium Recovery by Extraction
U.S. – United States

1 INTRODUCTION

Currently, energy is the forefront of major political issues in the United States and other countries. The search for a carbon free yet sufficient energy source continues worldwide. Because of the outstanding demand for electricity, the necessity of a large base-load and its ability to generate clean electricity, nuclear power remains as one of the top candidates to replace fossil fuel power technologies. The major concern regarding the expansion of nuclear power, however, is the accumulating irradiated nuclear fuel (INF). The U.S. and 16 other international agencies have recently adopted policies that propose the safe expansion of nuclear power and handling of high-level waste. GNEP (Global Nuclear Energy Partnership) was created in 2006 and promoted the wide-scale use of safe and secure nuclear power and also addressed issues regarding proliferation and nuclear waste disposal. AFCI (Advance Fuel Cycle Initiative) more specifically addresses the advancement and transition to a closed nuclear fuel cycle in the U.S. The goals of AFCI are to effectively reduce the volume and toxicity of high-level radioactive waste and enable the recovery of valuable material from the used fuel.

The U.S. produces thousands of metric tons of INF each year. As of 2010, on-site storage is the protocol for handling INF in the U.S. Because reprocessing was deferred in the 1970s, the U.S. has now accumulated the largest amount of heavy metal tonnes of INF of any country.¹

The concept of INF reprocessing involves the separation of uranium and plutonium from other actinides and fission products. Once processed for fuel fabrication, the uranium and plutonium can be recycled back into reactors to provide additional energy for electricity production. Reprocessing can also significantly reduce the volume of the waste since uranium and plutonium constitute nearly 96% of the used fuel.

An ideal reprocessing scheme accurately separates uranium, plutonium, minor actinides, lanthanides and transition metals in a safe, proliferation resistant and economically favorable manner. The separation of these elements relies on the various chemical properties of actinides and fission products. A thorough understanding of the solution chemistry of metals is necessary.

The title of this investigation is *Influence of Temperature on the Extraction of Pu(IV) by Tri-n-butyl Phosphate from Acidic Nitrate Media*. The work presented here is a summary of the research conducted during 2007 – 2009. The content of this work is very relevant to the already existing process commonly known as PUREX (Plutonium Uranium Recovery by Extraction). The technical background, relevant literature and all experimental data and analysis are organized as follows:

Chapter 2: This chapter discusses irradiated fuel, the history of reprocessing, its fundamentals and the challenges facing reprocessing today. We also discuss the importance of plutonium, the literature relevant to this work and the goals of this project.

Chapter 3: This chapter focuses on fundamental principles of solvent extraction, solution equilibria and chemical thermodynamics. We also investigate the history and properties of the organic extractant tri-*n*-butyl phosphate (TBP) and the fundamental solution chemistry of plutonium.

Chapter 4: This chapter discusses the methods and analytical instrumentation used in these experiments including absorption spectroscopy and liquid scintillation.

Chapter 5: In this chapter, results are presented and discussed. We first investigate, in detail, the mechanisms and side reactions that take place when plutonium is extracted into TBP from acidic nitrate solutions. Then the experimental data is analyzed and rearranged to produce Van't Hoff plots. From these plots we can calculate thermodynamic constants with an appropriate error margin.

2 BACKGROUND & PROJECT SUMMARY

2.1 Irradiated Fuel and Reprocessing Chemistry

Each year, the U.S. produces approximately 40,000 ft³ of INF between 104 operating reactors.² At the end of 2006, there was more than 55,000 metric tons of heavy metal irradiated commercial fuel.³ This highly toxic and radiologically hazardous material is stored on-site in reactor containment buildings in boron-based metal grids to prevent further neutron activation or fission. U.S. utility companies still maintain responsibility for the used fuel produced by commercial reactors. Numerous disposal methods have been suggested. These options include the Antarctic, outer space, deep seabed, and deep geologic disposal. Of these, only the latter has been thoroughly investigated and even constructed. Long-term storage in geological depositories places the used fuel in metal canisters hundreds of meters underground in excavated tunnels. These tunnels are then backfilled with the excavated rock. Concerns regarding long-term geological disposal are mainly directed at the possibility of constituents of the used fuel leaking into the environment. In 1987, Yucca Mountain in Nevada was designated as the first U.S. repository. The site was constructed but failed to gain public and political support and never became operational.

The U.S. does not reprocess its commercial INF unlike the majority of countries that utilize nuclear power. Some reprocessing takes place in the U.S. but it is primarily defense related.⁴ France, United Kingdom, Japan and Russia

reprocess their commercial used fuel and in many ways lead the research in radiochemistry and reprocessing technologies. Ironically, the U.S. invented the concepts and technologies of reprocessing during the Second World War era. But before reprocessing could be implemented into the commercial nuclear industry, political force came about in 1977 when the government halted reprocessing in light of plutonium and proliferation concerns.⁴

Nuclear proliferation and reprocessing became a major political issue in the mid-1970s. In 1974, India announced a successful nuclear explosion. This event, although claimed to have peaceful incentives, made a clear statement to the U.S. and the rest of the world that special nuclear material was more easily obtainable than once thought. In 1976, President Gerald Ford announced that reprocessing was not necessary for a successful nuclear fuel cycle and in 1977, President Jimmy Carter prompted investigations that would study the extent of nuclear power and weapons proliferation. Although these studies conflicted with each other in many cases, the result was that a once-through fuel cycle was the most proliferation resistant. Reprocessing became an issue again in 1981 when the Reagan administration lifted the ban and ordered the DOE to conduct another study on the feasibility of commercial reprocessing. No immediate outcomes came from these investigations and several years later, the Clinton administration shut down reprocessing research and development in the 1990s.⁵

Low-enriched uranium (constituting 3-5% ²³⁵U) fuel that has been irradiated for three years consists of approximately 94% ²³⁸U, 1.2% ²³⁵U, 0.8% Pu

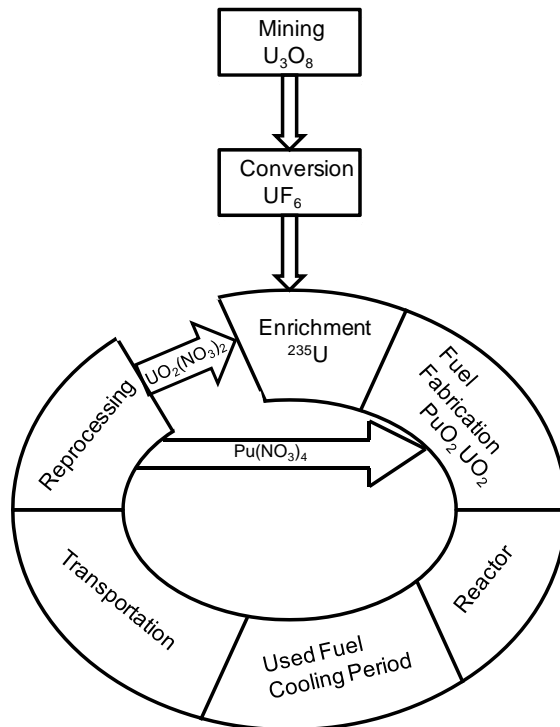


Figure 1: A closed nuclear fuel cycle. The uranium extracted from reprocessing can be cycled back into the enrichment plant and the plutonium is sent for fuel fabrication for production of the metal oxide compound. Each stage produces an amount of low-level waste except reprocessing which involves the storage of high-level waste. The excess depleted uranium from enrichment and reprocessing can either be stored or used in the production of mixed-oxide fuel.

and the remainder consists of fission products (Cs, Sr etc.), transuranic elements (Np, Am, Cm etc.) and ^{236}U .⁴ The plutonium isotopes span $^{238-242}\text{Pu}$ with the majority being ^{239}Pu . Therefore, approximately 96% of INF is still valuable after the first cycle. A closed fuel cycle approach is based on the chemical separation of uranium and plutonium from INF. Based on a once-through fuel cycle and the established mining facilities, there is enough uranium to power the world's 439 reactors (370 GWe) for approximately 80 years.⁶ Reprocessing of uranium and plutonium would extend this time.

In a typical reprocessing scheme, the used fuel is chopped and dissolved in hot concentrated nitric acid which also releases gaseous fission products (^{137}Xe , ^{131}I , ^3H etc.) first, then uranium and plutonium are separated by solvent extraction.

The process results in uranyl-nitrate compounds which are converted to UF_6 in order to separate ^{235}U and ^{238}U by centrifugation and eventually made into uranium dioxide; the plutonium-nitrate solution is sent for fuel fabrication and converted to plutonium dioxide. The left over fission products and transuranics can either be stored (making up some 4% of the original amount) or partitioned and transmuted into shorter lived isotopes. A mixture of plutonium and uranium dioxides can be used for fuel as a mixed-oxide fuel (MOX).

It should be noted, however, that the Nuclear Regulatory Commission (NRC) has not licensed MOX for light water reactors (LWR) and thus introducing plutonium as a LWR fuel in the U.S. is not operational as of 2000.⁴

2.1 Plutonium and Reprocessing

Plutonium occupies an exclusive place in chemistry, nuclear energy and political relations. It has favorable fissile properties that allow for the extraction of large amounts of energy; the fission cross section of ^{239}Pu is more than 30% higher than that of ^{235}U . Within several years of its synthesis in 1940, the primary use of plutonium was for nuclear weapons. For many years following, plutonium has sparked political debates, nuclear war and provided countries with energy for electricity. In 2005, approximately 2000 metric tons of plutonium existed in forms of INF and nuclear weapons.⁷

Plutonium also exhibits a unique solution chemistry seldom seen by other elements. It is one of the few metals that can disproportionate and coexist as

multiple oxidation states in solution. Autoradiolysis and radiolysis of various mineral acids from the high specific alpha activity of certain isotopes can also result in undesirable oxidation-reduction reactions. Hydrolysis and complexation with multiple aqueous ligands are also prevalent chemical reactions when considering plutonium in aqueous solution. This elaborate and often complicated behavior makes plutonium a difficult element to predict in aspects such as environmental and chemical modeling.

The separation of plutonium from fission products and uranium is feasible through established separation procedures such as ion exchange, electrolysis and solvent extraction. Solvent extraction is the most mature and world-wide used process to recover uranium and plutonium from dissolved INF. This process is commonly referred to as PUREX and is the preferred technology for countries that utilize a closed fuel cycle.

PUREX uses the organic extractant TBP at a concentration of $1.1M$ and is typically diluted in a heavy hydrocarbon such as *n*-dodecane. This mixture is able to extract tetra- and hexavalent actinides from nitric acid solutions. Uranium, plutonium, technetium are extracted and the remaining fission products and trivalent actinides are left in the aqueous stream. The plutonium is then stripped (back-extracted) from the organic phase and into a fresh aqueous phase by increasing the temperature, lowering the acid concentration and introducing a reducing agent such as ferrous sulfamate. This process is also able to remove trace amounts of Np from the organic phase. The uranium/technetium mixture remains

unaffected; these two elements can be separated by ion exchange. The use of ferrous sulfamate, however, adds undesirable inorganic salts to the high-level aqueous waste. In the recent decade, significant progress in the separation of uranium from plutonium and neptunium has been achieved by the addition of the salt-free reagent acetohydroxamic acid (AHA). This process, although not yet commercially available, has come to be known as UREX (Uranium Recovery by EXtraction) and is a subset of the larger process UREX+ which is currently being developed by Argonne National Laboratory.

2.2 Literature Review and Project Goals

The following report addresses thermodynamics of plutonium extraction under PUREX conditions. The primary focus is on the effects of elevated temperatures on plutonium extraction by TBP from acidic nitrate solutions. Trends in extraction data as a function of temperature can be used to calculate thermodynamic constants such as enthalpy, entropy and Gibbs free energy. It is important to understand the dynamics of plutonium behavior at elevated temperatures for several reasons. Primarily, INF is considered high-level waste and the transuranic elements and fission products produce heat as a result of radiation and radiolysis. Additionally, metal extractions can be suppressed at elevated temperatures. In the interest of modeling these types of processes, it is critical to have thermodynamic constants under the appropriate conditions. The enthalpy and entropy constants derived for the distribution reaction of metal

Table 1: A comparison of selected literature on the distribution ratios of Pu into TBP from ~1M HNO₃ at various temperatures.

Ref. [8]		Ref. [9]		Ref. [10]		this work	
T/K	D _{Pu(IV)}	T/K	D _{Pu(IV)}	T/K	D _{Pu(IV)}	T/K	D _{Pu(IV)}
293	1.4	293	2.8	283	2.3	294	1.4
303	1.3	303	3.0	298	2.8	303	0.6
323	1.2	313	3.2	333	3.7	313	0.3

neutral complexes give important information about hydration and organic phase solvation; however, very few investigations have been dedicated to this problem

At present, the data reported⁸⁻¹⁰ concerning the effect of temperature on extraction of plutonium under PUREX conditions has been contradictory. Table 1 compares selected distribution data:- Rozen *et al.*⁸ found that increasing temperature decreases the distribution of Pu(IV) while Kolarik⁹ and Ramanujan *et al.*¹⁰ argue the opposite trend at acid concentrations below 6M. Danesi *et al.*¹¹ studied the effect of temperature on the extraction of plutonium nitrates into long chain amines and found the distribution to decrease with temperature. Also, the extraction of Pu(VI) from nitric acid into TBP was found to decrease with temperature according to Sajun *et al.*¹²

The previously mentioned studies⁸⁻¹⁰ that were conducted on the distribution of Pu(IV) into TBP from acidic nitrate solutions conflict with results of this project and with one another. The discrepancies cannot be justified exactly but one can make the argument that radiation detection technology was not as mature and efficient as it is today. It can also be said that computational methods for calculating activity coefficients of species have become more advanced since the mid 20th century. One study⁸ neglected to mention mixing times between the

two phases and another eluded to Am impurities during the radioassay.¹⁰ Kolarik mentioned the difficulty in calculating activity coefficients under the appropriate conditions.⁹ Rozen *et al.*⁸ completely neglected any hydrolysis and disproportionation of Pu(IV) at low acid concentrations. With advances in analytical instrumentation techniques over the past two decades, the chemistry of actinides in acidic solution is better understood. It is now known that elevated temperatures enhance hydrolysis and disproportionation and can greatly affect the calculation of extraction constants at lower acid concentrations.¹³

We attempted to develop a comprehensive database of experimental values related to the distribution of plutonium. The partitioning of Pu(IV) in the extraction system consisting of TBP, nitric acid and lithium nitrate was investigated with regards to variations in temperature and nitrate concentrations. Thermodynamic and stability constants for plutonium extraction from acidic nitrate solutions by TBP are discussed and calculated in the present work.

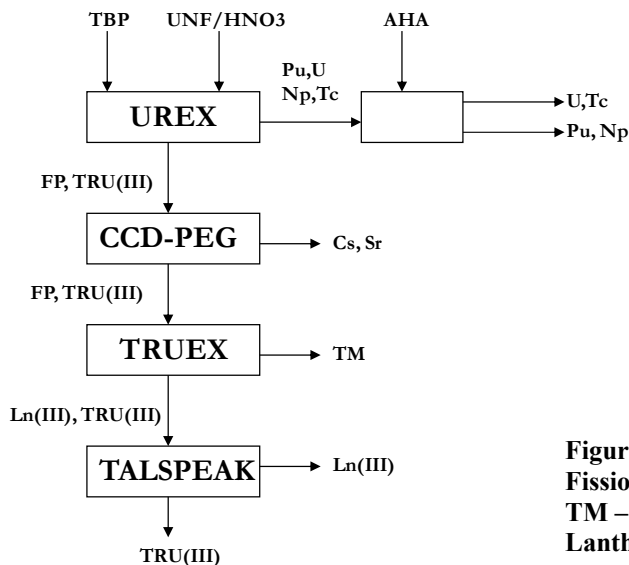


Figure 2: The UREX+ process. FP – Fission Products; TRU – Transuranic; TM – Transitional Metals; Ln(III) - Lanthanides

3 FUNDAMENTALS OF SOLVENT EXTRACTION & SOLUTION CHEMISTRY

Understanding the basic theory and applications of these topics is crucial towards deriving and calculating thermodynamic parameters associated with the solution speciation and extraction of plutonium at elevated temperatures.

3.1 Solvent Extraction

Solvent extraction plays an important role in many aspects of the chemical industry including pharmaceuticals, environmental waste, biomedicine and the nuclear industry. Although evidence of using immiscible media to isolate compounds dates back to the B.C. era,¹⁴ an overwhelming interest in solvent extraction came about during the U.S. Manhattan Project in order to reprocess INF.

Solvent extraction refers to the distribution of a solute between two immiscible liquids that are contacted with each other. In most cases presented here, the solute refers to a charged metal cation. The immiscible liquids in solvent extraction are typically a water based aqueous phase (referred to as Aq) and an organic solvent (Or). The differences in density govern which phase is on the top or bottom of the system. In general, although not the case with chlorinated hydrocarbons, the organic phase has a lower density and resides as the top layer.

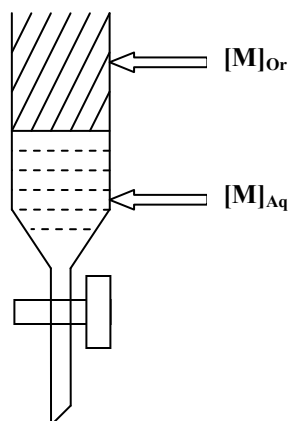


Figure 3: A schematic of a soluble metal M distributed between an organic solvent (top) and an aqueous phase (bottom). Brackets indicate concentrations.

The term *distribution ratio* quantifies the distribution of the solute between the two phases. It is defined as the ratio of the summations of organic to aqueous solute concentrations and is usually measured at equilibrium. In the case of a soluble metal M the distribution is defined as:

$$D_M = \frac{\sum [M]_{Or}}{\sum [M]_{Aq}} \quad (1)$$

The term *partition coefficient* is the ratio (Or/Aq) of the summations of concentrations of a desired species of study such as $M(IV)$. The percentage of M extracted from the aqueous phase into the organic phase is given by:

$$\%Extracted = \frac{D_M}{(1 + D_M)} 100\% \quad (2)$$

Equation (1) quantifies the distribution of a soluble metal between two phases. This term, however, is dependent on a substantial amount of variables such as organic and aqueous phase concentrations, metal concentration, temperature, mass transfer, mixing time and can even depend on the isotope of an element with regards to radiolysis and radiation decay type. All variables in solvent extraction

must be considered when designing a model that will successfully predict the distribution of an element. Therefore, fundamental concepts of chemical thermodynamics and solution equilibria for each element of concern are essential.

3.2 Tri-*n*-butyl Phosphate

TBP is an organic, phosphorous-based extracting agent with the molecular formula $(C_4H_9O)_3PO$. It's primary purpose is to separate groups of metals by solvent extraction but it has gained notable popularity in many applications of the chemical industry.¹⁵

The extracting power of TBP derives from the phosphoryl group. The oxygen atom that is bonded with phosphorous coordinates with metals and forms solvate adducts. These types of extractants are commonly known as neutral extractants because they remain uncharged as they bond to metals. It is therefore most effective in the presence of nitrates and other inorganic acids that are able to provide negatively charged anions to form complexes with metals. These anions and their concentration also regulate the selectivity and magnitude of extraction.

TBP is almost always used in conjunction with an inert diluent, usually a heavy hydrocarbon such as *n*-dodecane. The purpose of the diluent is to add desirable physical properties such as a lower density and viscosity. In addition, the diluent suppresses the extraction power of TBP. A 30% vol. mixture of TBP in *n*-dodecane is highly selective towards tetra- and hexavalent cations over fission products and trivalent actinides. Its unique selectivity for tetra- and hexavalent

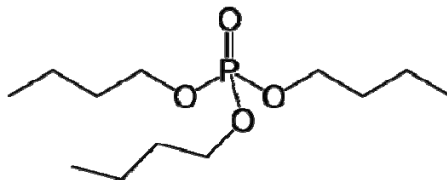


Figure 4: The chemical structure of TBP.

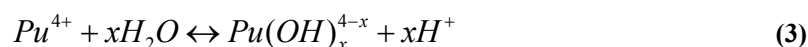
cations makes it a valuable asset in nuclear reprocessing as it has the capability to separate uranium and plutonium from fission products. This development was first discovered during the Manhattan Project and was utilized at Hanford for nuclear waste recovery.

The decision to make TBP the primary solvent in the nuclear industry came as a result of numerous advantages over other solvents such as MIBK (methylisobutylketone), HDEHP (di(2-ethylhexyl) phosphoric acid) and HTTA (thenoyl trifluoroacetone). TBP has sufficient extracting powers even in the absence of salting-out agents, good physical properties when diluted with a hydrocarbon and reasonable stability under reprocessing conditions with regards to high acidity.

TBP does, however, suffer from defects as a reprocessing solvent. While it is able to remove actinides from most of the fission products, complete decontamination is impossible. The result is often a loaded solvent with traces of zirconium, ruthenium, niobium and technetium. TBP also undergoes radiological degradation which can alter its chemical composition and result in a loss of actinide extraction because of the different extractability and solubility of plutonium complexes with products of radiolysis.

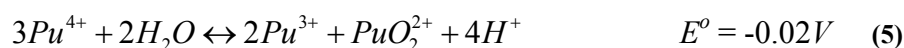
3.3 Hydrolysis and Disproportionation of Pu(IV)

Plutonium, particularly in its tetravalent state, is the most susceptible to hydrolysis in relation to the actinides Th, U and Np¹⁶. The hydrolysis reaction for plutonium can be written as:



$$K_H = \frac{[Pu(OH)_x^{4-x}][H^+]^x}{[Pu^{4+}]} \quad (4)$$

Hydrolysis of plutonium is important to consider because the hydrolyzed species is not readily extracted by TBP. The mechanism of hydrolysis has been studied under acidic and non-acidic conditions and has been described as very rapid, irreversible and enhanced at elevated temperatures.¹⁷ Although recent studies have shown quantities of extracted hydrolyzed species,¹⁸ the present work assumes the hydrolyzed species extraction to be negligible under the chosen conditions. At low acidic conditions the chemistry of plutonium becomes more complicated because Pu^{4+} can also disproportionate to form trivalent and hexavalent oxidation states.



These various oxidation states are known to co-exist in solutions. The Nernst equation verifies that Pu^{4+} is unstable with respect to disproportionation at $pH > 0$ under standard conditions,

$$E = E^o + 2(59.4mV)pH - \frac{RT}{\nu F} \ln \frac{[PuO_2^{2+}][Pu^{3+}]^2}{[Pu^{4+}]^3} \quad (6)$$

where R is the gas constant, F is Faraday's constant and ν the number of electrons exchanged during the reaction.

Costanzo *et al.*¹⁷ reported significant concentrations of Pu(III), Pu(IV), Pu(VI) as well as hydrolyzed species at concentrations below 0.6M HNO₃. Elevated temperatures were found to have a considerable effect on the disproportionation of Pu(IV) and polymerization from 25°C to 50°C. Therefore, in the present work, acid concentrations in the range of 2M – 5M were selected.

3.4 Metal-Ligand Complexation in Aqueous Solution

For a metal ion, M , and a ligand, L , mixture in a solution of constant ionic strength, the equilibrium is given by:



The equilibrium complexation constant, neglecting activity coefficients, is:

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \quad (8)$$

The stability constants are then defined as:

$$\beta_n = \frac{[ML_n]}{[M][L]^n} \quad (9)$$

and it can be shown that:

$$\beta_n = K_1 K_2 K_3 \dots K_n \quad (10)$$

3.4.1 Nitrate Complexation with Pu(IV)

Spectroscopic studies show evidence of various tetravalent plutonium-nitrate complexes in aqueous solutions. Veirs *et al.*¹⁹ identified mono-, di- and tetranitrate complexes of Pu(IV) at nitric acid concentrations less than 6M. At higher concentrations, hexanitrate complexes can exist. Incorporating formation constants, the total plutonium concentration in the aqueous phase is:

$$[Pu(IV)]_{aq} = [Pu^{4+}(H_2O)_n] + [Pu(OH)_x^{4-x}] + [Pu(NO_3)^{3+}] + [Pu(NO_3)_2^{2+}] + [Pu(NO_3)_4] + [Pu(NO_3)_6^{2-}] \quad (11)$$

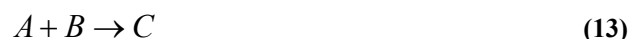
which can be rewritten as:

$$[Pu(IV)]_{aq} = [Pu^{4+}(H_2O)_n] \left(1 + \frac{K_H}{\{H^+\}} + \beta_1 \{NO_3^-\} + \beta_2 \{NO_3^-\}^2 + \beta_4 \{NO_3^-\}^4 + \beta_6 \{NO_3^-\}^6 \right) \quad (12)$$

where K_H represents the hydrolysis constant, β_x the formation constant of the plutonium-nitrate complexes (the subscript symbol is the number of nitrates in the plutonium complex) and n ($n=7-12$) the number of aqua ligands bound to the plutonium cation. Taking into account the hydrolysis constant for Pu(IV) studied by Metivier *et al.*²⁰, the hydrolyzed species of Pu(IV) can be considered negligible at acid concentrations $\geq 2M$. It should also be noted that Metivier *et al.* reported multiple hydrolyzed species of plutonium. The formation constants β_4 and β_6 are not well understood and have seldom been studied. Despite the slight presence of tetra- and hexanitrate complexes reported for the acid range of 2M – 5M, this work assumes their formation to be negligible and the aqueous speciation consists of mono-, dinitrate complexes and Pu^{4+} .

3.5 Activity Coefficients

For a given reaction of species, the equilibrium constant is typically calculated as the ratio of product to reactant concentrations. However, this ratio does not take into account the decrease in attraction between cations and anions as the ionic atmosphere increases. For example, if we consider the equilibrium:



where the equilibrium constant is:

$$K = \frac{[C]}{[A][B]} \quad (14)$$

and if we add an inert salt X that does not partake in reaction (13), the equilibrium constant may change according to:

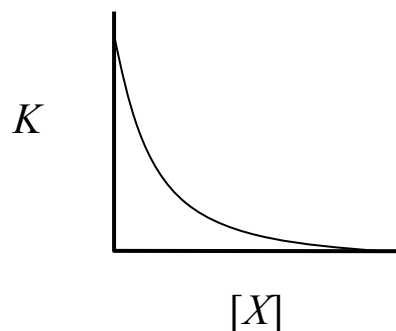


Figure 5: An example of the change in equilibrium constant (K) as an inert electrolyte (X) is added to the reaction mixture.

This type of behavior was seen in the case of $\text{Fe}(\text{SCN})^{2+}$ as KNO_3 was added to the mixture.²¹

To correct for non-ideality, we introduce the term γ as activity coefficients.

Activity coefficients are a function of ionic strength μ :

$$\mu = \frac{1}{2} \sum_i c_i z_i^2 \quad (15)$$

where c and z are the concentration and effective charge of each ion, respectively. The earliest and simplest model used to calculate activity coefficients of ions in solution is the Debye-Hückel equation:

$$\log \gamma_j = \frac{-A_j |z_+ z_-| \sqrt{\mu}}{1 + B\alpha \sqrt{\mu}} \quad (16)$$

where A and B are constants depending on the solution medium and α is the ionic radius. This equation has expanded since it was published in 1923 by adding empirically determined coefficients. The specific interaction theory equation (SIT) introduces a new term, ε , to the Debye-Hückel equation.

$$\log \gamma_j = \frac{-A_j |z_+ z_-| \sqrt{\mu}}{1 + 1.5\sqrt{\mu}} + \varepsilon_j m \quad (17)$$

This term models ion interactions and is tabulated for most metals in solution; m is the molality of the ion in question.

Introducing activity coefficients, equation (14) can be rewritten as:

$$K = \frac{[C]^c}{[A]^a [B]^b} \frac{\gamma_C^c}{\gamma_A^a \gamma_B^b} = \frac{a_C^c}{a_A^a a_B^b} \quad (18)$$

The product of the concentration and activity coefficient of a species is more commonly referred to as the activity (a) or sometimes is labeled with braces (the activity of nitrate can also be $\{\text{NO}_3^-\}$). Some notable trends in activity coefficients as a function of concentration $[X]$, charge (z) and radius (α) are:

$$\begin{aligned} \gamma &\rightarrow 1 & [X] &\rightarrow 0 \\ \gamma &\rightarrow 0 & z &\rightarrow \infty \\ \gamma &\rightarrow 0 & \alpha &\rightarrow 0 \end{aligned} \quad (19)$$

3.6 Van't Hoff Equation

Considering the system:



and ignoring activity coefficients, the equilibrium equation can be written as:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (21)$$

Using the equation for Gibbs energy

$$\Delta G^\circ = -RT \ln K(T) \quad (22)$$

and:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (23)$$

a Van't Hoff plot of the natural logarithm of $K(T)$ versus the inverse temperature will yield a slope proportional to the enthalpy and an intercept proportional to the entropy.

$$\ln K(T) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (24)$$

Using equation (23), the Gibbs energy for a reaction at a specific temperature can be calculated. The parameters ΔH° , ΔG° and ΔS° give some insight on the dynamics of a reaction. When $\Delta H^\circ > 0$, the reaction is endothermic and K increases with increasing temperature. When $\Delta H^\circ < 0$, the reaction is exothermic and is less spontaneous with temperature. The term ΔG° is the *standard* Gibbs energy at specific conditions. When $\Delta G^\circ < 0$ ($K > 1$), the equilibrium lies towards the right which favors the products C and D . Conversely, when $\Delta G^\circ > 0$ ($K < 1$), the species A and B are favored. It should be noted that ΔG° does not govern the

spontaneity of a reaction; this term is reserved for ΔG . ΔS° is the term for entropy and describes disorder or randomness; $\Delta S^\circ \geq 0$ for all systems.

4 EXPERIMENTAL APPROACH & METHODS

4.1 UV-visible Absorption Spectrometry of Plutonium

Absorption spectroscopy measures the absorption of electromagnetic radiation by a molecule at a characteristic frequency that corresponds to energy transformation between vibrational or electronic energy levels. Each chemical species has its own specific spectrum profile, characterized by a distinguished shape. Changes in a species' concentration result in a proportional decrease or increase of the absorption spectrum height at the characteristic wavelength.

The absorbance at a specific wavelength, A_λ , is based on the transmission of light through the sample. For an initial beam intensity of P_0 and a final intensity P , the absorbance is calculated as:

$$A_\lambda = -\log\left(\frac{P}{P_0}\right) \quad (25)$$

The concentration of a species in solution can be calculated using the Beer-Lambert law at a specific wavelength λ :

$$A_\lambda = \varepsilon_\lambda l C \quad (26)$$

where ε is the molar extinction coefficient, l the pathlength of the cuvette and C the concentration of the absorbing species in solution.

Different oxidation states of metals form species with different vibrational or electronic energy levels; each oxidation state has its own specific absorption

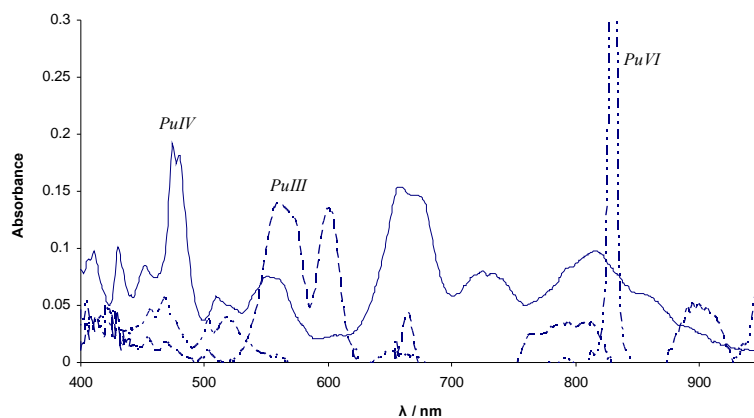


Figure 6: Visible Spectrum of Pu(III) , Pu(IV) and Pu(VI) in 4M HClO₄ at 25°C.

spectrum. Oxidation states of plutonium (Pu(III), Pu(IV) and Pu(VI)) in acidic solution have characteristic peaks within the visible and ultraviolet regions of the spectrum (400 – 900 nm). All three oxidation state spectra are shown in Figure 6.

Pu(VI) is often seen when evaporating acidic solutions of plutonium to dryness and re-dissolving the crystals; Pu(IV) is oxidized to Pu(VI) which has a strong absorption peak at 830 nm. A small excess of 3% H₂O₂ typically reduces Pu(VI) to Pu(III) which is characterized by the two peaks at 560 nm and 600 nm. To oxidize Pu(III) to Pu(IV), NaNO₂ crystals can be added until the Pu(IV) peak at 470 nm is dominant and Pu(III) and Pu(VI) peaks are no longer present. Absorption spectroscopy was namely used to determine what oxidation state of plutonium was present in stock solutions.

4.2 Radiotracer Stock Solution

²³⁹Pu was obtained from Argonne National Laboratory as a chloride. The ²⁴¹Am

impurity was removed by anion exchange chromatography (Dowex 1X-4). The americium was washed from the column with 7M HNO₃ and Pu(IV) was eluted with 0.36M HCl. The Pu(IV) chloride solution was evaporated and dissolved in 4M acid and adjusted to tetravalent oxidation state using H₂O₂ and solid NaNO₂. Purity of the tetravalent oxidation state was confirmed to be approximately 99% by the characteristic absorption peak at 475nm. The presence of nitrite ions and 4M acidity was able to stabilize the tetravalent oxidation state over the course of the experiments.

4.3 Pre-equilibration of Organic Phase

TBP (98%, Alfa Aesar) was dissolved in *n*-dodecane (+99%, Alfa Aesar) to 30 vol.%. Prior to extraction, the TBP solutions needed to be pre-equilibrated since it was found that nitric acid is extracted into TBP.²² A volume ratio of 1:2 organic to aqueous solutions at room temperature (294 ± 1 K) with nitric acid and lithium nitrate solutions of the desired nitrate concentrations was rigorously agitated for one minute. The organic layer was contacted with a fresh portion of the same nitrate aqueous solution and the procedure was repeated. The resulting organic solution was used for plutonium extraction.

4.4 Extraction of Pu(IV)

Equal volumes of pre-equilibrated TBP and fresh nitrate solutions were spiked with 20 μ L of Pu(IV) stock, heated to the desired temperature, rigorously

agitated in extraction vials for one minute and heated again. This procedure was repeated six times for each extraction. During agitation, extraction vials were insulated to maintain the temperature of the system at ± 1 K (the efficiency was previously determined by using samples absent of Pu). The samples were then centrifuged and separated. Aliquots from both the organic and aqueous phases were taken for analysis. The remaining organic phase was then subject to a back extraction with fresh portions of nitrate solution and the extraction process was repeated. The phases were then separated.

For determination of equilibrium analytical concentrations of plutonium, liquid scintillation counting was selected because of its high detection efficiency for solutions containing radioisotopes. A 200 μ L aliquot from each phase was mixed with 5mL of scintillation cocktail (Ultima Gold) and counted for ten minutes by LSC (TriCarb 3180 – Perkin Elmer). The same concentration of background samples containing either TBP or HNO₃ with no Pu was prepared and mixed with 5mL of the scintillation cocktail to measure background activity. There was no quenching discrepancy between nitrate and TBP media and thus the detection efficiency was the same for each phase. The distribution ratios were calculated as the ratio of organic to aqueous activity concentration:

$$D = \frac{\left(\frac{CR_o - BG_o}{V_o} \right)}{\left(\frac{CR_A - BG_A}{V_A} \right)} \quad (27)$$

4.5 Liquid Scintillation Counting

Liquid scintillation counting (LSC) is based on the fluorescence of excited organic molecules caused by collisions of charged particles from radionuclides. When a radionuclide decays by alpha or beta emission, the kinetic energy of that charged particle excites the solvent molecule which in turn excites the scintillator to an elevated singlet state. From this energy level, the scintillator molecule fluoresces down to a ground state. The light output, when converted through a photo-multiplier tube (PMT), should be proportional to the integral energy deposited by the radionuclide and thus can be used to determine the unknown concentration of the nuclide.

LSC offers many advantages over other nuclear detection methods because of its high counting efficiency and uniform geometry. It is one of the most appropriate detection methods when attempting to determine the concentration of a radionuclide in solution. Self-absorption of charged particles is essentially non-existent as well as backscattering of beta particles. Detection efficiency is on the order of 99% for measuring alpha particles in the MeV energy range.²³ This efficiency can be increased even further by introducing two PMT on opposite sides of the sample. In this case, only coincidental pulses are counted which prevents interference from background noise (since noise typically affects only one PMT).

Some issues must be addressed when using LSC. The most common problem is encountered with the scintillation cocktail since most radionuclide solutions are water-based. The cocktail used in LSC during its early development

was originally a toluene-organic based solvent. However, modern scintillation cocktails are designed to accommodate both aqueous and organic solutions. They can contain emulsifiers and solubilizers which can produce samples that are pseudo-homogenous. More recent LSC technologies promote safer, biodegradable and more efficient scintillation cocktails.²⁴

The TriCarb 3180 (Perkin Elmer) used in these experiments is an automated LSC counter with background subtraction capabilities. The detector window range was set at 200-2000 keV as another means to reducing background from external gamma emissions and chemiluminescence. To prevent external light output from the scintillation vials, all samples were left in the dark for 20 min. prior to counting.

4.6 Evaluation of Data Uncertainties

The values reported in Appendices I-III are an average value between a forward and reverse extraction under the specified extraction system conditions. The combined uncertainty in the distribution ratio, D , can be calculated as

$$\sigma_D = D \sqrt{\left(\frac{\sigma_{Or}}{[Pu]_{Or}}\right)^2 + \left(\frac{\sigma_{Aa}}{[Pu]_{Aa}}\right)^2} \quad (28)$$

where σ represents the absolute uncertainty in the concentration of plutonium (cpm/ μ L) in either the organic or aqueous phase. Since the distribution ratios were calculated by counting a sample from each phase, we can perform a simplified calculation of combined uncertainties that incorporates uncertainties from

pipetting samples and radiation detection. The uncertainties in the concentrations of nitrates in extraction media can be omitted since these concentrations (2-5M) are several orders of magnitude larger than the concentration of Pu and calculation of their uncertainties often lead to unreasonably low values.

As an example of a simplified calculation, if we know the uncertainty of the calibrated pipette (1%) and assuming a 5% error in LSC, we can calculate an error for a sample that has a D value of 2 (2000cpm – Or, 1000cpm – Aq) and no detectable BG. For 200 μ L samples of each phase, we can define the uncertainty in that phase as

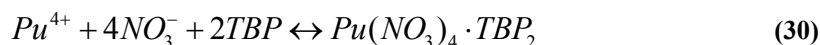
$$\sigma_x = [Pu]_x \sqrt{\left(\frac{\sigma_{CR}}{CR_x}\right)^2 + \left(\frac{\sigma_V}{Volume_x}\right)^2} \quad (29)$$

where x can be either Aq or Or. The resulting uncertainty in each phase can be put back into equation (28). The final D value including uncertainty is then 2.0 ± 0.1 . Since propagation of uncertainties in these types of calculations can be laborious and they cannot predict accidental or experimenter mistakes, distribution ratios are here reported as average values with standard deviations of replicate experiments.

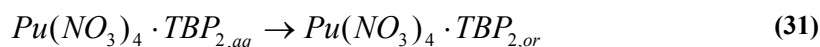
5 RESULTS & DISCUSSION

5.1 *Extraction Mechanism*

The complexation of Pu(IV) by nitric acid and TBP has been extensively studied and reviewed in multiple publications^{1,2,3,25} and is generally accepted as the formation of the neutral solvate adduct complex of Pu⁴⁺ with four nitrate anions:



The mechanism by which Pu(IV) is extracted into TBP was assumed to be similar to that of hexavalent uranium described by Rydberg *et al.*²⁶ The plutonium in aqueous solutions is complexed with neutral aqua ligands. The nitrate ions then fill the four valence shells as bidentate ligands and two TBP molecules form the adduct complex Pu(NO₃)₄·TBP₂. Therefore, the rate determining step is the transfer of the plutonium complex from the aqueous phase into the organic phase.



The speciation of plutonium in both the aqueous and organic phases is very important; all possible aqueous equilibria must be considered in order to distinguish between species in the aqueous solution. Factors to consider are hydrolysis, disproportionation and nitrate complexation.

5.2 *Extraction of Nitric Acid*

TBP is a neutral extractant. In addition to metals, it is able to extract other components from aqueous solution. Chaiko and Vandegrift²² studied the

thermodynamics of the distribution of nitric acid into 1.095M TBP in kerosene. The speciation of nitric acid in TBP was found as $\text{HNO}_3 \cdot \text{TBP}$, $\text{HNO}_3 \cdot \text{TBP}_2$ and $(\text{HNO}_3)_2 \cdot \text{TBP}$. The majority of the extracted nitric acid existed as $\text{HNO}_3 \cdot \text{TBP}$ and the dinitric acid complex did not exist below acid concentrations of 6M. The TBP_f concentration (TBP unbound to nitric acid) decreased with increasing nitric acid. Adamskii *et al.*²⁷ also studied the speciation of extracted nitric acid by 0.736M TBP in kerosene with similar results and calculated the concentration of TBP_f in the presence of plutonium and uranium. The authors²⁷ extended the research into the effect of temperature and concluded that temperature had a negligible effect on the distribution and speciation of nitric acid.

5.3 Extraction Equilibria

The equilibrium constant at specific temperatures, $K_{ex}(T)$, for the complexation of Pu(IV) by TBP is:

$$K_{ex}(T) = \frac{[\text{Pu}(\text{NO}_3)_4 \cdot \text{TBP}_2][\text{H}_2\text{O}]^n}{[\text{Pu}^{4+}(\text{H}_2\text{O})_n][\text{NO}_3^-]^4[\text{TBP}_f]^2} \frac{\gamma_{\text{Pu}(\text{NO}_3)_4 \cdot \text{TBP}_2} \gamma_{\text{H}_2\text{O}}^n}{\gamma_{\text{Pu}^{4+}(\text{H}_2\text{O})_n} \gamma_{\text{NO}_3^-}^4 \gamma_{\text{TBP}_f}^2} \quad (32)$$

The distribution coefficient of Pu(IV) is defined as the concentration ratio of Pu(IV) in the organic and aqueous phases, or

$$D_{\text{Pu(IV)}} = \frac{[\text{Pu(IV)}]_{or}}{[\text{Pu(IV)}]_{aq}} \quad (33)$$

Substituting (12) into equation (32), the equilibrium constant, $K_{ex}(T)$, can be defined as:

$$K_{ex}(T) = \frac{D_{Pu(IV)}[H_2O]^n}{[NO_3^-]^4[TBP_f]^2} (1 + \beta_1 \{NO_3^-\} + \beta_2 \{NO_3^-\}^2) \frac{\gamma_{Pu(NO_3)_4 \cdot TBP_2} \gamma_{H_2O}^n}{\gamma_{Pu^{4+}(H_2O)_n} \gamma_{NO_3^-}^4 \gamma_{TBP_f}^2} \quad (34)$$

where γ represents the activity coefficients of each species and T is the absolute temperature in Kelvin of the extraction reaction. Betas represent the stability constants for plutonium-nitrate complexes and braces indicate activities of the species. The activity coefficients of plutonium in the organic phase and TBP_f are assumed to be one. The activity coefficients of Pu^{4+} were estimated using SIT and the approach of chemical analogs and similar behavior of tetravalent thorium and plutonium. The SIT interaction parameter, $\Delta\epsilon$, was chosen to be 0.31 as reported by Neck *et al.*²⁸ for thorium solutions. The influence of temperature on the stability constants β_1 and β_2 should be considered. Numerous studies have been conducted on the plutonium-nitrate system but to our knowledge, none have investigated the effects of temperature on the nitrate complexation with Pu(IV).^{29 - 37} This work assumes β_1 and β_2 to be dependent on ionic strength but independent of temperature as well as the concentration of water and the dehydration energy of Pu(IV). Equation (34) can then be written as:

$$K_{ex}(T) = \frac{D_{Pu(IV)}}{[NO_3^-]^4[TBP_f]^2} (1 + \beta_1 \{NO_3^-\} + \beta_2 \{NO_3^-\}^2) \frac{1}{\gamma_{Pu^{4+}} \gamma_{NO_3^-}^4} \quad (35)$$

Experimental data show that the distribution of Pu(IV) is a complex process. Figure 7 plots the distribution as a function of agitation time at various nitric acid concentrations. D_{Pu} decreases with agitation time at 1M HNO₃ and below whereas 7M is able to maintain consistent values. At low acid

concentrations, longer contact times result in the production of inextractable species such as Pu(III) and hydrolyzed plutonium. These reactions are shown in Eqs. (3) and (5). It was measured that 6 min. extraction time was sufficient to achieve equilibrium at acid concentrations $\geq 2M$. Values of D_{Pu} as a function of nitric acid concentration are shown in Figure 8. As the concentration of nitric acid increases, the distribution of Pu(IV) increases until a maximum is reached at approximately $7M$ HNO_3 . Beyond $7M$, the distribution of Pu(IV) begins to decrease as the majority of the TBP is complexed with nitric acid. Table 2 specifically lists the forward and back extraction values at nitrate concentrations between $2M - 5M$ for each temperature. From the distribution data, the equilibrium constants at each temperature can be calculated using equation (35). Bromley's method³⁸ was used to calculate the activities of nitrates in solution; the variations in activities with temperature were found using SIT approach. The concentration of TBP_f , β_1 and β_2 as a function of nitrate concentration were calculated and reported in the recent work¹⁴ and were employed in calculation of the equilibrium constant at a given temperature.

In order to verify the number of nitrate ligands and the valence state of plutonium when it is extracted by TBP, we can use slope analysis of the distribution data. The logarithm of equation (35) gives:

$$\log K_{ex} = \log [D_{Pu(IV)}(1 + \beta_1 \{NO_3^-\} + \beta_2 \{NO_3^-\}^2)] - 4 \log \{NO_3^-\} - 2 \log \{TBP_f\} \quad (36)$$

When TBP_f is unity, a plot of $\log [D_{Pu(IV)}(1 + \beta_1 \{NO_3^-\} + \beta_2 \{NO_3^-\}^2)]$ versus $\log \{NO_3^-\}$

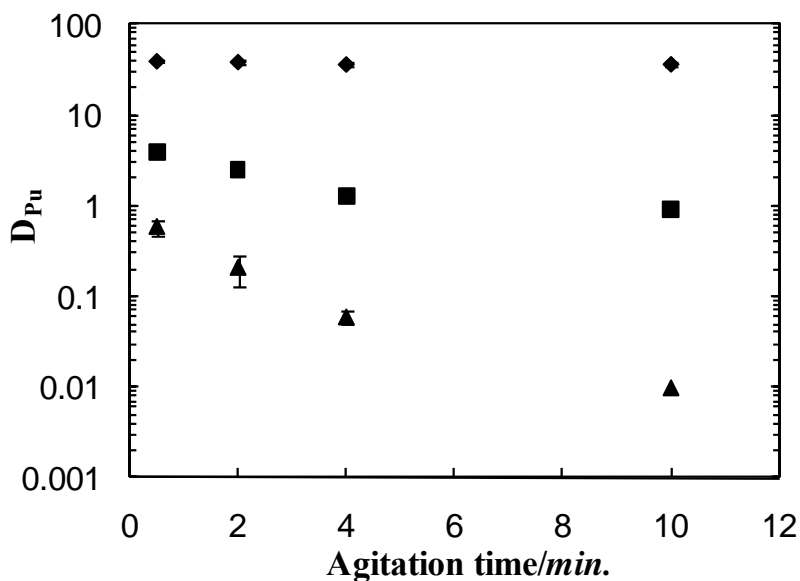
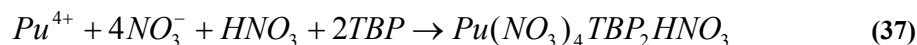


Figure 7: The effect of agitation on the distribution of plutonium at 294 K: (◆) 7M HNO₃; (■) 1M HNO₃; (▲) 0.1M HNO₃.

should yield a line of slope 4. Figure 9 shows this relationship. At lower nitrate concentrations, lines of slope 4 were well observed. This indicates that plutonium was tetravalent and complexed with four nitrate ligands before solvating with two TBP molecules, coinciding with the equilibrium in equation(30). At about 2M nitrate, the data began to deviate to a slope larger than 4. There are several possible explanations for this trend. The most likely scenario is the equilibrium that was predicted by Tkac *et al.*²⁵:



In this equation, an additional nitric acid molecule is extracted into the organic phase. A total of five nitrate ligands is bound to plutonium and thus the slope of

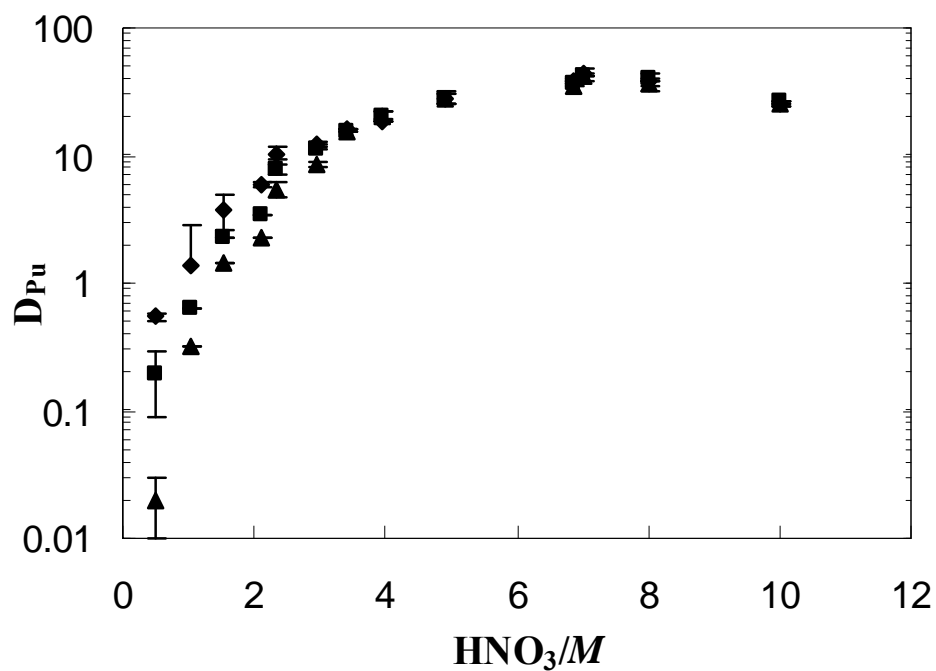


Figure 8: The distribution of plutonium at various temperatures for a system containing nitric acid: T = (♦) 294 K; (■) 303 K; (▲) 313 K.

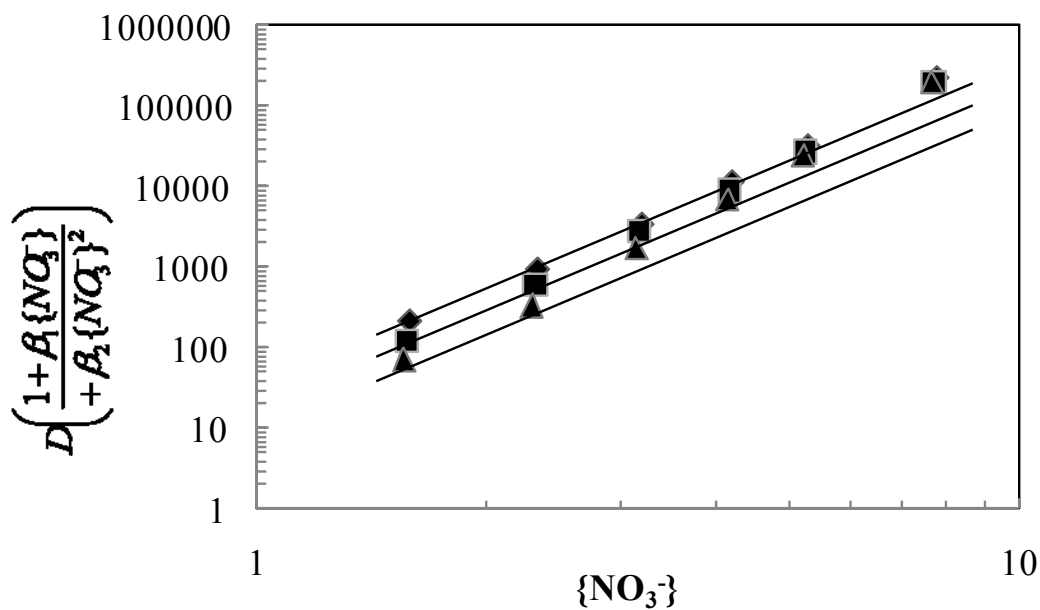


Figure 9: A logarithmic plot used to analyze the valence state and number of nitrate ligands of plutonium when extracted by TBP. T = (♦) 294 K; (■) 303 K; (▲) 313 K. Lines are of slope 4.

Table 2: The distribution of Pu(IV) for nitrate concentrations between 2M – 5M. (D_{Pu}^I) forward extractions; (D_{Pu}^{II}) back extractions.

HNO ₃ /M	LiNO ₃ /M	total NO ₃ /M	T/K=294			T/K=303			T/K=313		
			D_{Pu}^I	D_{Pu}^{II}	D_{Pu}^{Avg}	D_{Pu}^I	D_{Pu}^{II}	D_{Pu}^{Avg}	D_{Pu}^I	D_{Pu}^{II}	D_{Pu}^{Avg}
2.0	-	2.0	6.1	5.7	5.9 ± 0.3	3.7	3.7	3.7 ± 0.0	2.4	2.2	2.3 ± 0.2
2.4	-	2.4	11.3	9.6	10.5 ± 1.2	8.5	7.3	7.9 ± 0.8	6.6	4.3	5.4 ± 1.7
2.9	-	2.9	12.1	12.5	12.3 ± 0.3	11.2	11.5	11.4 ± 0.2	8.3	8.8	8.5 ± 0.4
3.4	-	3.4	16.2	16.0	16.1 ± 0.1	15.9	15.5	15.7 ± 0.3	14.7	16.5	15.6 ± 1.3
3.9	-	3.9	19.1	18.6	18.9 ± 0.3	18.9	21.3	20.1 ± 1.7	18.7	21.3	20.0 ± 1.8
4.9	-	4.9	26.3	30.5	28.4 ± 3.0	26.1	29.5	27.8 ± 2.4	25.1	31.3	28.2 ± 4.4
2.0	0.5	2.5	12.3	9.4	10.9 ± 2.0	8.0	6.1	7.1 ± 1.4	5.3	2.6	4.0 ± 1.9
2.0	1.0	3.0	18.4	16.0	17.2 ± 1.7	15.1	13.1	14.1 ± 1.4	9.6	8.1	8.9 ± 1.0
2.0	1.5	3.5	27.8	26.2	27.0 ± 1.1	22.8	19.1	20.9 ± 2.7	17.9	15.9	16.9 ± 1.5
2.0	2.0	4.0	38.2	39.0	38.6 ± 0.6	34.5	32.0	33.3 ± 1.7	28.8	32.1	30.4 ± 2.4
2.0	3.0	5.0	68.5	89.8	79.2 ± 15.1	59.5	84.1	71.8 ± 17.4	57.0	88.9	72.9 ± 22.5

the log-log plot in Figure 9 would be 5. Another possibility for the deviation in Figure 9 is the effect of temperature on the hydrolysis of plutonium and its extraction. Tkac *et al.*¹⁸ found quantities of hydrolyzed plutonium in TBP. This recent find would most likely alter the stoichiometric equilibrium in equation (27). Table 3 lists the activities of Pu^{4+} , nitrate, TBP_f concentrations and the calculated equilibrium constants at different temperatures. It can be seen that the extraction equilibrium constants changed with nitrate concentration. This behavior was also reported by Rozen *et al.*¹ The gradient was likely associated with some error in the activity coefficient assumptions, such as assuming the organic solution activities of TBP_f and $\text{Pu}(\text{NO}_3)_4 \cdot \text{TBP}_2$ to be set equal to one. As it was mentioned before, no sufficient literature exists on the values of plutonium-nitrate stability constants at different temperatures; therefore, all β were assumed independent of temperature. The behavior of $\ln K_{ex}(T)$ with nitrate concentration, however, is linear and can be extrapolated to $[\text{NO}_3^-] = 0M$ where the activity coefficient is equal to one. Using computer software, linear trends can be fit to give the extrapolated equilibrium constants for each temperature. The extrapolated $\ln K_{ex}^0(T)$ values are listed in Table 3. Plotting the natural logarithm of $K_{ex}^0(T)$ versus inverse temperature, as in Figure 10, reveals a line ($R^2 = 0.99$) with a slope and intercept of 6.99 and -13.6, respectively. These parameters yield $\Delta H^\circ = -58.1 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S^\circ = -113 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ which suggest an exothermic reaction that should, according to equation (23), favor the reactants with increasing temperature.

Table 3: Parameters used to calculated equilibrium constants and Gibbs free energies for various nitric acid concentrations.

HNO ₃ /M	TBP _l /M	$\gamma_{\text{Pu}^{4+}}$	{NO ₃ }*	ln K _{ex} (T)					
				T/K=294		T/K=303		T/K=313	
2.0	0.45	0.0010	1.75	12.0	11.4	11.0			
2.3	0.35	0.0012	2.06	12.7	12.4	12.0		ln K _{ex} ⁰ (T)	
2.9	0.24	0.0016	2.86	12.8	12.7	12.4	10.1	9.4	8.7
3.4	0.18	0.0020	3.59	13.2	13.2	13.2			
3.9	0.13	0.0024	4.54	13.7	13.7	13.7			
4.9	0.07	0.0033	6.68	14.9	13.6	14.9	-24.8	-23.8	-22.6

*{NO₃} indicates nitrate activity

Table 4: Parameters used to calculated equilibrium constants and Gibbs free energies for various nitrate concentrations.

NO ₃ /M	TBP _l /M	$\gamma_{\text{Pu}^{4+}}$						{NO ₃ }*					
		T/K=294		T/K=303		T/K=313		T/K=294		T/K=303		T/K=313	
2.0	0.45	0.0009	0.0008	0.0006	1.62	1.62	1.63						
2.5	0.36	0.0011	0.0010	0.0007	2.32	2.30	2.27						
3.0	0.29	0.0013	0.0012	0.0009	3.18	3.15	3.11	10.4	9.5	8.7			
3.5	0.24	0.0017	0.0015	0.0011	4.17	4.14	4.10						
4.0	0.19	0.0020	0.0018	0.0014	5.25	5.21	5.16						
5.0	0.13	0.0031	0.0027	0.0022	7.74	7.69	7.63	-25.2	-24.0	-22.7			

*{NO₃} indicates nitrate activity

This trend is in agreement with the decreasing distribution values at higher temperatures. The values calculated for $\Delta G^{\circ}(T)$ are listed in Table 3. Rozen *et al.*¹ reported an enthalpy of $-25.1 \text{ kJ}\cdot\text{mol}^{-1}$ without an entropy value for a similar system containing 20 vol.% TBP in kerosene. Salting-out agents can vastly increase the distribution of plutonium. The addition of an inextractable nitrate salt, in this case lithium nitrate, lowers the concentration of nitric acid while keeping the total nitrate concentration high. This also increases the concentration of TBP_f . Systems containing 2M HNO_3 and 1M – 3M LiNO_3 were used to analyze the distribution of Pu(IV). Table 4 lists values of $D_{\text{Pu(IV)}}$ for systems containing lithium nitrate. The equilibrium constants at each nitrate concentration and concentration, as in Figure 11, produces three isothermal trends that can be extrapolated to $[\text{NO}_3^-] = 0\text{M}$ ($R^2 = 0.99$ for all temperatures). The Van't Hoff plot for this system is shown in Figure 10 ($R^2 = 0.99$). The enthalpy and entropy temperature were calculated using equation (24) and are listed in Table 4. Plotting the natural logarithm of the equilibrium constants as a function of nitrate were calculated to be $-62.8 \text{ kJ}\cdot\text{mol}^{-1}$ and $-128 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively. It should be reinstated that the distribution ratios at a constant nitrate concentration are much higher for systems with added nitrate than those with nitric acid only on account of the increased nitrate and TBP_f concentrations. The thermodynamic characteristics, however, should be similar. Therefore, an average enthalpy and entropy can be calculated from the two systems: $\Delta H = -60.4 \pm 3.3 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta S = -120 \pm 10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

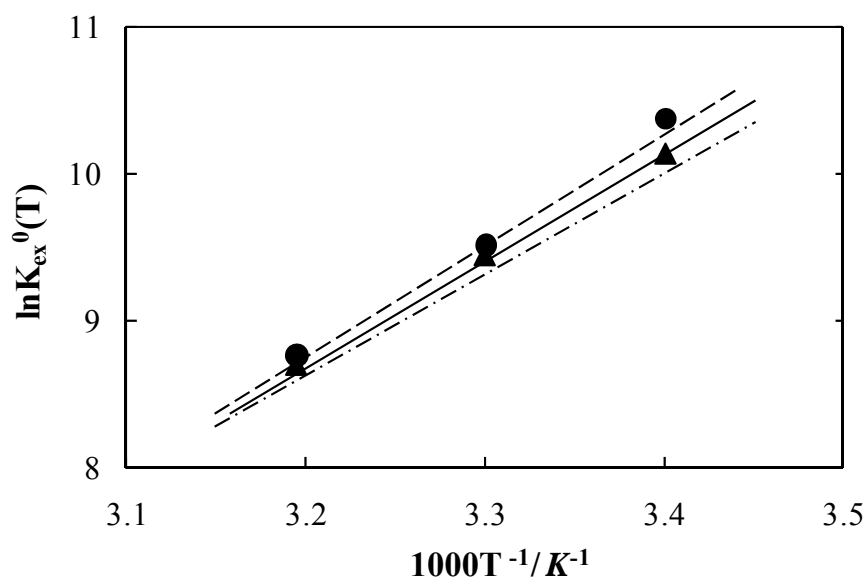


Figure 10: Van't Hoff plots for systems containing (▲) nitric acid: slope = 6.99, y-intercept = -13.6; (●) 2M HNO₃ + LiNO₃: slope = 7.56, y-intercept = -15.4; (dashed) average linear regression.

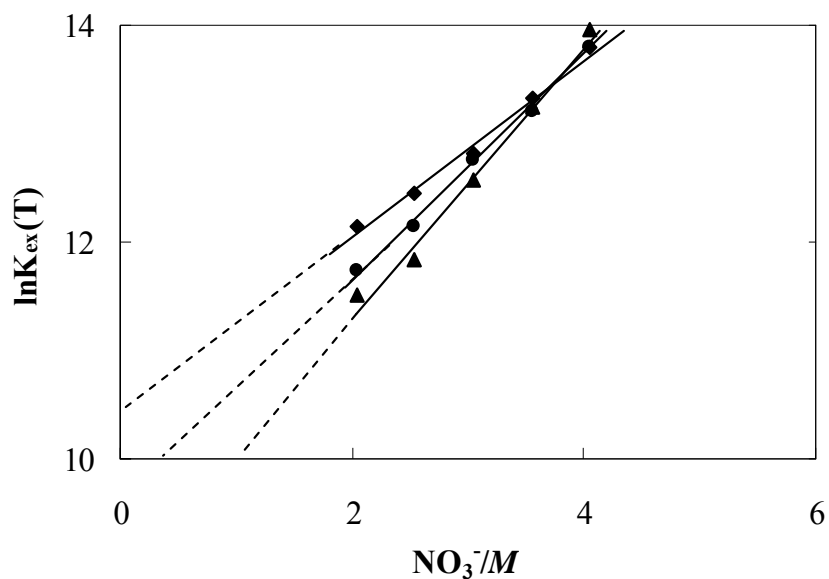


Figure 11: The equilibrium constants at various temperatures calculated by equation (32) for a system containing 2M HNO₃ and LiNO₃. Values for $\ln K_{ex}^0(T)$ were found at the extrapolated point $[NO_3^-] = 0M$. T = (♦) 294 K; (●) 303 K; (▲) 313 K.

6 CONCLUSION

This work investigated some thermodynamic properties of the extraction of plutonium by TBP from acidic nitrate solutions. Solvent extraction of actinides with TBP was first utilized during the Manhattan Project to separate uranium and plutonium from INF. This led to the production of thousands of nuclear warheads between the U.S. and Russia. However, the same process used to build warheads can also be used to recycle uranium and plutonium back into reactors as MOX fuel. While the majority of nuclear-friendly countries decided to pursue this route, the U.S. failed to come to a political agreement on nuclear reprocessing and has operated on a once-through fuel cycle since the 1970s. The issue of long-term fuel storage in the U.S. is also un-resolved as of 2010.

The most important aspect of plutonium extraction is understanding its solution equilibria. Plutonium has rare chemical properties that distinguish it from other elements; but because of its unique properties, we are able to separate it from other actinides with reasonably good efficiency. Three oxidation states of plutonium can be present in acidic solutions of less than 1M (Pu(III), Pu(IV) Pu(VI)). These oxidation states have very different TBP extraction properties. The hydrolysis, polymerization and complexation with inorganic ligands must also be considered since these factors can enhance or diminish distribution values.

The influence of temperature on the extraction of Pu(IV) by 30 vol.% TBP in *n*-dodecane from acidic nitrate solutions has been investigated at temperatures ranging from $T = (294 \text{ to } 313) \text{ K}$. When evaluating the extraction behavior of

Pu(IV) at elevated temperatures, the intricate behavior of plutonium in aqueous solutions must be considered. Although the concentrations of nitrate and TBP_f have an overwhelming influence on the extraction of Pu(IV), it is evident that the distribution decreases with temperature. The largest changes in D_{Pu} values were seen at nitric acid concentrations $< 2M$ due, in part, to the enhanced hydrolysis and disproportionation. Therefore, only the extraction data for the nitrate concentration range of $2M - 5M$ were considered. The three species of plutonium present in the aqueous solution (Pu^{4+} , $Pu(NO)^{3+}$ and $Pu(NO)_2^{2+}$) were used for the estimation of thermodynamic characteristics. The enthalpy and entropy of Pu(IV) extraction into TBP from acidic nitrate solutions were calculated to be -60.4 ± 3.3 $\text{kJ}\cdot\text{mol}^{-1}$ and -120 ± 10 $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The decrease in the distribution of Pu(IV) with temperature can be explained by the increase of $\Delta G(T)$.

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Appendix I – Distribution data for figure 7

0.1M HNO₃

°C	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
30 seconds	5267.86	2731.86	5241.36	2705.21	7946.57	0.52
	4870	3282.43	4843.5	3255.78	8099.28	0.67
2 min.	6340	1690	6313.5	1663.35	7976.85	0.26
	6904.71	1091.14	6878.21	1064.49	7942.7	0.15
4 min.	7395.57	540.71	7369.07	514.06	7883.13	0.07
	7571.43	457.29	7544.93	430.64	7975.57	0.06
10 min.	7726.29	108.14	7699.79	81.49	7781.28	0.01
	7793	115.29	7766.5	88.64	7855.14	0.01

1M HNO₃

°C	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
30 seconds	1552.86	5969.14	1526.36	5942.49	7468.85	3.89
	1452.71	5780	1426.21	5753.35	7179.56	4.03
2 min.	2177.14	5380.43	2150.64	5353.78	7504.42	2.49
	2135.57	5330.86	2109.07	5304.21	7413.28	2.51
4 min.	3544.86	4487.57	3518.36	4460.92	7979.28	1.27
	3623.43	4676.14	3596.93	4649.49	8246.42	1.29
10 min.	4285.86	4094	4259.36	4067.35	8326.71	0.95
	4436.57	3929.43	4410.07	3902.78	8312.85	0.88

7M HNO₃

°C	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
30 seconds	123.29	3937.29	96.79	3910.64	4007.43	40.40
	124.57	3895.29	98.07	3868.64	3966.71	39.45
2 min.	129.43	3886.86	102.93	3860.21	3963.14	37.50
	122	3914.29	95.5	3887.64	3983.14	40.71

4 min.	135.71	3895.29	109.21	3868.64	3977.85	35.42
	130.14	3971	103.64	3944.35	4047.99	38.06
10 min.	125.43	3845.14	98.93	3818.49	3917.42	38.60
	134.57	3839.71	108.07	3813.06	3921.13	35.28

Appendix II – Distribution data for figure 8.

Final H+		1.1416					
°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	25.6	2727.1	5.44E+03	27015	54126	81141	2.00
21	25.6	2199.7	1751.8	21741	17262	39003	0.79
30	23.4	4311	2802.15	42876	27787.5	70663.5	0.65
30	22.2	4099	2582.37	40768	25601.7	66369.7	0.63
40	23.8	6.18E+03	1.96E+03	61566	19392	80958	0.31
40	24.3	9.76E+02	3.21E+02	9512	2962	12474	0.31

Final H+		1.64704					
°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	25.6	1485.6	6.78E+03	14600	67542	82142	4.63
21	25.6	1471.4	4339.9	14458	43143	57601	2.98
30	23.6	2319	5565.6	22954	55420	78374	2.41
30	23.7	2111	4644.2	20873	46205	67078	2.21
40	23.8	3.40E+03	4.93E+03	33717	49023	82740	1.45
40	24.3	1.84E+03	1.66E+03	18131	16357	34488	0.90

Final H+		2.053					
°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	23.6	2994.6	1.82E+04	14855	90667	105522	6.10
21	23.7	1137	6413.4	11133	63897	75030	5.74
30	23.6	2300.9	8525.8	22773	85022	107795	3.73
30	23.7	1779.4	5421.1	17557	53974	71531	3.07
40	26.7	3.13E+03	7.47E+03	31074	74480	105554	2.40
40	26.7	1.96E+03	4.20E+03	19290	41772	61062	2.17

Final H+ 2.42272

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	22.4	681.5	7.47E+03	6591	74451	81042	11.30
21	22.2	689	6438.7	6668	64165	70833	9.62
30	22.4	893.5	7397.4	8711	73750	82461	8.47
30	22.2	840.2	6017.9	8180	59957	68137	7.33
40	23.8	1.12E+03	7.31E+03	10984	72898	83882	6.64
40	24.3	1.25E+03	5.22E+03	12214	51933	64147	4.25

Final H+ 2.87674

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	23.6	1615.1	1.93E+04	7957.5	96271.5	104229	12.10
21	23.7	685.1	8.32E+03	6614	82957	89571	12.54
30	23.6	895	9781.8	8714	97582	106296	11.20
30	23.7	756.8	8485.6	7331	84619	91950	11.54
40	26.7	1.09E+03	8.84E+03	10640	88096	98736	8.28
40	26.7	8.89E+02	7.62E+03	8626	75902	84528	8.80

Final H+ 3.44416

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	22.4	493.3	7.63E+03	4709	76090	80799	16.16
21	22.2	451.9	6.89E+03	4297	68689	72986	15.99
30	22.4	509.4	7757.5	4870	77351	82221	15.88
30	22.2	472.9	7007.6	4507	69854	74361	15.50
40	23.8	5.52E+02	7.80E+03	5281	77810	83091	14.73
40	24.3	4.58E+02	7.18E+03	4333	71508	75841	16.50

Final H+ 3.95392

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	22.4	423.7	7.69E+03	4013	76690	80703	19.11
21	22.2	402.6	7.11E+03	3804	70879	74683	18.63
30	22.4	429	7701.6	4066	76792	80858	18.89
30	22.2	360.8	7225.2	3386	72030	75416	21.27
40	23.8	4.46E+02	7.94E+03	4224	79118	83342	18.73
40	24.3	3.68E+02	7.35E+03	3436	73269	76705	21.32

Final H+ 4.7641

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	23.6	408	1.01E+04	3844	101052	104896	26.29

21	23.7	341.6	9.72E+03	3179	96971	100150	30.50
30	23.6	450	11152.6	4264	111290	115554	26.10
30	23.7	376.8	10550.1	3531	105264	108795	29.81
40	26.7	4.33E+02	1.02E+04	4067	101928	105995	25.06
40	26.7	3.43E+02	9.92E+03	3163	98914	102077	31.27

Final H+ 6.62074

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	23.6	312.5	1.02E+04	2889	102253	105142	35.39
21	23.7	252.1	9.88E+03	2284	98522	100806	43.14
30	23.6	334.6	10343.9	3110	103203	106313	33.18
30	23.7	260.7	9797.9	2370	97742	100112	41.24
40	26.7	3.59E+02	1.04E+04	3319	103585	106904	31.21
40	26.7	2.79E+02	1.02E+04	2518	101598	104116	40.35

Appendix III – Distribution data for Table 4.

[NO3-] 2.0408

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	24.9	987.9	7.15E+03	9630	71221	80851	7.40
21	24.9	1086.8	5433.2	10619	54083	64702	5.09
30	22.6	1434.8	6864.7	14122	68421	82543	4.84
30	22.6	1733	4205.9	17104	41833	58937	2.45
40	24.2	2.55E+03	5.59E+03	25276	55642	80918	2.20
40	24.2	5.77E+02	4.86E+03	5529	48335	53864	8.74

[NO3-] 2.5422069

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	24.9	638.5	7.57E+03	6136	75435	81571	12.29
21	24.9	708.4	6459.8	6835	64349	71184	9.41
30	22.6	927.2	7264.1	9046	72415	81461	8.01
30	22.6	952.6	5689.2	9300	56666	65966	6.09
40	24.2	1.34E+03	6.99E+03	13151	69698	82849	5.30
40	24.2	1.97E+03	5.12E+03	19504	50952	70456	2.61

[NO3-] 3.04137

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	24.9	440.2	7.67E+03	4153	76430	80583	18.40
21	24.9	449.4	6815.2	4245	67903	72148	16.00
30	22.6	525.1	7608.8	5025	75862	80887	15.10

30	22.6	543.7	6823.6	5211	68010	73221	13.05
40	24.2	8.08E+02	7.53E+03	7835	75048	82883	9.58
40	24.2	8.09E+02	6.41E+03	7844	63872	71716	8.14

[NO3-] 3.5510167

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	24.9	307.9	7.89E+03	2830	78682	81512	27.80
21	24.9	305.3	7377.9	2804	73530	76334	26.22
30	22.6	367.3	7889.5	3447	78669	82116	22.82
30	22.6	398.4	7182.5	3758	71599	75357	19.05
40	24.2	4.59E+02	7.82E+03	4346	77918	82264	17.93
40	24.2	4.75E+02	7.17E+03	4512	71498	76010	15.85

[NO3-] 4.0439822

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	24.9	232.9	7.96E+03	2080	79386	81466	38.17
21	24.9	219.6	7617.8	1947	75929	77876	39.00
30	22.6	249.4	7840.8	2268	78182	80450	34.47
30	22.6	258.8	7588.2	2362	75656	78018	32.03
40	24.2	3.03E+02	8.04E+03	2786	80119	82905	28.76
40	24.2	2.65E+02	7.75E+03	2405	77264	79669	32.13

[NO3-] 5.0444188

°C	BG	CPM AQ	CPM ORG	CMP AQ NET	CPM ORG NET	Σ	D
21	24.9	141.6	8.02E+03	1167	79980	81147	68.53
21	24.9	112.6	7904.1	877	78792	79669	89.84
30	22.6	157.2	8030.8	1346	80082	81428	59.50
30	22.6	115.9	7864.1	933	78415	79348	84.05
40	24.2	1.70E+02	8.32E+03	1454	82941	84395	57.04
40	24.2	1.18E+02	8.32E+03	934	82986	83920	88.85