PNNL-28695

Pacific Northwest
NATIONAL LABORATORY

Synthesis of Plutonium Oxide Specimens for a Statistically Designed Nuclear Forensics Study

May 2019

GJ Lumetta
JC Carter
RA Clark
JF Corbey
MK Edwards
FD Heller
BK McNamara
DE Meier
CM Parker
KL Pellegrini
BM Rapko
IJ Schwerdt
SI Sinkov
LE Sweet
JM Tingey

U.S. DEPARTMENT OF
ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights**. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from
the Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062
www.osti.gov
ph: (865) 576-8401
fox: (865) 576-5728
email: reports@osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
or (703) 605-6000
email: info@ntis.gov
Online ordering: http://www.ntis.gov

PNNL-28695

Synthesis of Plutonium Oxide Specimens for a Statistically Designed Nuclear Forensics Study

GJ Lumetta	CM Parker
JC Carter	KL Pellegrini
RA Clark	BM Rapko
JF Corbey	IJ Schwerdt
MK Edwards	SI Sinkov
FD Heller	LE Sweet
BK McNamara	JM Tingey
DE Meier	

May 2019

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Abstract

This report describes the synthesis of plutonium oxide (PuO_2) samples at a bench-scale (10 g Pu) to support nuclear forensics research. The key unit operations that were performed included dissolving the PuO_2 feed material, purifying the Pu by ion exchange, precipitating as plutonium (III) oxalate, and reconverting to PuO_2 by calcination of the oxalate compound. Seventy-six PuO_2 synthetic runs were performed in execution of a statistically designed test matrix. The process parameters varied in these synthesis runs included temperature (30 or 50 °C), the Pu concentration in the feed solution (10, 30, or 50 g Pu/L), the HNO_3 concentration in the feed solution (1, 2, or 3 M), the direction of reagent addition (direct or reverse strike), the source of oxalic acid (solid or solution), and the reagent addition rate (as fast as possible, 20, or 40 minutes). This report describes the synthesis of the 76 PuO_2 specimens. The characterization of these specimens will be described in separate reports.

Summary

Pacific Northwest National Laboratory (PNNL) has established a bench-scale (10 g Pu per batch) capability to synthesize plutonium oxide (PuO_2) to support nuclear forensics research. The key unit operations in the PuO_2 synthesis system are as follows. The feed plutonium material is received at the Radiochemical Processing Laboratory (RPL) in oxide form. The as-received oxide is dissolved in nitric acid media with fluoride added to accelerate the dissolution. The resulting solution is subjected to anion exchange to remove impurities from the plutonium stream, and then the plutonium is precipitated as plutonium (III) oxalate. Finally, the Pu (III) oxalate is converted back to PuO_2 by heating (calcining). In order to make this capability a useful tool for nuclear forensics research, the system was designed to be flexible, allowing variations in the different process parameters (e.g., temperature, manner of reagent addition, or type of precipitating agent used in the precipitation step).

This report describes the 76 PuO_2 synthetic runs that were done in the bench-scale system during the execution of a statistically designed test matrix, based on the Pu (III) oxalate process. The process parameters varied in these test runs included temperature (30 or 50 °C), the Pu concentration in the feed solution (10, 30, or 50 g Pu/L), the HNO_3 concentration in the feed solution (1, 2, or 3 M), the direction of reagent addition (direct or reverse strike), the source of $H_2C_2O_4$ (solid or solution), and the reagent addition rate (as fast as possible, 20, or 40 minutes). This report describes the synthesis of the 76 PuO_2 specimens. The characterization of these specimens will be described in separate reports.

Acknowledgments

The authors thank the National Technical Nuclear Forensics Center within the Countering Weapons of Mass Destruction (CWMD), formerly the Domestic Nuclear Detection Office (DNDO), of the Department of Homeland Security for funding this work, and in particular, Sandra Gogol and Margaret Goldberg. The authors also thank the members of the Plutonium Expert Panel for all of their helpful advice. The panel includes Leonard Gray, Alice Murray, Major Thompson, Donald Thorp, and Ted Venetz. The assistance of Jamin Trevino of PNNL's Shielded Facilities Operation Group is gratefully acknowledged. Finally, the authors wish to thank Bill Ulicny and Jeff Morrison for their efforts.

Acronyms and Abbreviations

BET	Brunauer-Emmett-Teller
BV	Bed volume
°C	degree(s) Celsius
cm	centimeter(s)
g	gram(s)
h	hour(s)
H_2O_2	hydrogen peroxide
HDPE	high-density polyethylene
HNO_3	nitric acid
in.	inch(es)
L	liter(s)
mL	milliliter(s)
mol	mole(s)
PFA	perfluoroalkoxy
PNNL	Pacific Northwest National Laboratory
PTFE	polytetrafluoroethylene (Teflon®)
Pu	plutonium
PuO_2	plutonium dioxide
PXRD	powder X-ray diffraction
RPL	Radiochemical Processing Laboratory
SEM	scanning electron microscopy
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
XRD	X-ray diffraction

Contents

Figures

Tables

1.0 Introduction

Under the auspices of the National Technical Nuclear Forensics Center of the Department of Homeland Security's Countering Weapons of Mass Destruction (CWMD) Office, Pacific Northwest National Laboratory (PNNL) has established a bench-scale capability to synthesize plutonium oxide (PuO_2) to support nuclear forensics research.[1] In this context, "bench-scale" is defined as nominally 11.3 g PuO_2 (10.0 g Pu) per batch produced. Originally, the bench-scale PuO_2 system was split between two gloveboxes in two different rooms in the Radiochemical Processing Laboratory (RPL). Early in calendar year 2017, the capability was consolidated into a single glovebox, greatly increasing the efficiency of the operation.

The key unit operations in the PuO_2 synthesis system were as follows. The feed plutonium material was received at the RPL in oxide form.[a] The as-received oxide was dissolved in HNO_3 media with HF added to accelerate the dissolution. The resulting solution was subjected to anion exchange to remove impurities from the plutonium stream, and then the plutonium was precipitated as plutonium (III) oxalate. Finally, the Pu (III) oxalate was converted back to PuO_2 by heating (calcining) to 650 °C. In order to make this capability a useful tool to support nuclear forensics research, the system was designed to be flexible, allowing variations in the different process parameters (e.g., temperature, manner of reagent addition, or type of precipitating agent used in the precipitation step).

This report describes the 76 PuO_2 synthetic runs that were done using the bench-scale system in the execution of a statistically designed experiment, based on the Pu (III) oxalate process. The variable parameters explored in the statistically designed test matrix include:

1. temperature (30 or 50 °C)
2. Pu concentration in the feed solution (10, 30, or 50 g Pu/L)
3. HNO_3 concentration in the feed solution (1, 2, or 3 M)
4. direction of reagent addition (direct or reverse strike)
5. source of $H_2C_2O_4$ (solid or 0.9 M solution)
6. reagent addition rate (as fast as possible, 20, or 40 minutes); with the digestion duration adjusted accordingly to total 40 minutes.

This report describes the synthesis of the 76 PuO_2 specimens *via* the Pu (III) oxalate route. The characterization of these specimens will be described in separate reports.

---

[a] Later in the project, PuO_2 produced in earlier runs were redissolved and re-run through the anion exchange purification to produce Pu nitrate solutions for additional tests.

2.0 Synthesis of Plutonium Oxide

This section describes the experimental steps taken to prepare the 76 PuO_2 samples required by the statistically designed test matrix.

2.1 Dissolution of the Starting Plutonium Oxide Material

The general approach to dissolving the starting PuO_2 stock material involved mixing the PuO_2 with 500 mL of concentrated (16 mol/L) HNO_3, heating to 110 °C, and adding HF in increments to promote dissolution. These steps were repeated as necessary to completely dissolve the PuO_2 material. The specific details for each batch dissolved are described below.

2.1.1 First Batch of SRNL Plutonium Oxide (Test Instruction NTNFC-TI-D003)

The PuO_2 (118.1 g, 104.2 g Pu) was transferred from the AF-1-7 container received from Savannah River National Laboratory (SRNL) to the 1-L polytetrafluoroethylene (PTFE; Teflon®) dissolution vessel. Concentrated HNO_3 (500 mL of 16 mol/L) was added. While stirring with a PTFE-coated magnetic stir bar, the mixture was heated at 110 °C for approximately five hours. After cooling overnight, the solution was inspected and little dissolution had occurred. Aqueous hydrofluoric acid (HF) (10 mol/L; 0.1 mL; 0.001 mol) was added and the mixture was stirred and heated at 110 °C. After three hours, an additional 0.1-mL aliquot (0.001 mol) of 10 mol/L HF was added, and the mixture was heated for another five hours. After cooling overnight, considerable solids remained. The heating and stirring process was continued for ~7.5 hours, with four 0.2-mL aliquots of 10 mol/L HF being added through the course of the day. The mixture was allowed to cool, and the remaining undissolved solid was allowed to settle. Approximately 450 mL of dark green solution was decanted.

To dissolve the remaining PuO_2, another 500 mL of 16 mol/L HNO_3 was added. The mixture was heated and stirred in the manner describe above, with one 0.2-mL aliquot, and two 0.4-mL aliquots of 10 mol/L HF being added over a 6.75 hour time period. At this point, there was no visual indication of solids. The two portions of dissolve Pu solution were vacuum filtered through Whatman™ 42 ashless filter paper (part number 1442-090), and were combined.

2.1.2 Second Batch of SRNL Plutonium Oxide (Test Instruction NTNFC-TI-D004)

The PuO_2 (195.7 g, 172.6 g Pu) was transferred from the M016129 container received from SRNL to the 1-L PTFE dissolution vessel. Concentrated HNO_3 (~600 mL of 16 mol/L) was added. While stirring with a PTFE-coated magnetic stir bar, the mixture was heated at 110 °C. During this first dissolution strike, three 0.2-mL aliquots of 10 mol/L HF were added. After cooling and settling overnight, the solution was decanted from the solids and vacuum filtered through an Advantec 0.5-µm PTFE membrane (part number H050A090C). The dissolution vessel, containing the undissolved portion of PuO_2, was charged with 500 mL of 16 mol/L HNO_3 plus 0.4 mL 10 mol/L HF. After heating at 110 °C and stirring for approximately 5.5 hour, the mixture was allowed to cool and settle. The solution was decanted and vacuum filtered through an Advantec 0.5-µm PTFE membrane; it was then combined with the solution obtained from the first dissolution strike. A third dissolution strike was performed in a similar manner. The combined solution was used as feed to the anion exchange (test instruction NTNFC-TI-IX006).

Two additional dissolution strikes were performed to complete the dissolution of the remaining PuO_2 solids. The first used 500 mL of 16 mol/L HNO_3 plus 0.4 mL 10 mol/L HF, and the second used 500 mL of 16 mol/L HNO_3 plus 0.4 mL 10 mol/L HF. In both cases, the mixtures were stirred and heated at 110 °C for several hours, then filtered as indicated in the preceding paragraph, and combined.

2.1.3 First Batch of Recycled Plutonium Oxide (Test Instruction NTNFC-TI-D005)

Portions of the PuO_2 materials prepared in runs 1, 2, 3, 4, 5, 7, 8, and 9 were combined and re-dissolved for use in additional precipitation/calcination runs. Also combined into this mixture was a portion of the PuO_2 from one of the preliminary runs done with in-house PNNL Pu material (from run PNNL4). A total of 49.7 g PuO_2 was dissolved. This material was transferred into the 1-L PTFE dissolution vessel. Concentrated HNO_3 (500 mL of 16 mol/L) was added along with 0.2 mL of 10 mol/L HF. While stirring with a PTFE-coated magnetic stir bar, the mixture was heated at 110 °C for two hours, resulting in complete dissolution of the PuO_2. The solution was decanted and vacuum filtered through an Advantec 0.5-µm PTFE membrane.

Separately, the diluted Pu fraction from NTNFC-TI-IX005 (see below) was combined with recycled solutions generated during sample preparation activities. This was also combined with a small amount of previously purified Pu solution that did not contain enough Pu to perform a precipitation/calcination run (i.e., < 10 g Pu). This combined solution was concentrated by distilling off the excess liquid. The concentrated solution was combined with the solution generated from dissolving the recycled PuO_2, yielding 858 mL of solution with a Pu concentration of 77.1 g Pu/L (66.2 g Pu).

2.1.4 Third Batch of SRNL Plutonium Oxide (Test Instruction NTNFC-TI-D006)

The PuO_2 (171.2 g, 151.0 g Pu) was transferred from the M016152 container received from SRNL to the 1-L PTFE dissolution vessel. Concentrated HNO_3 (500 mL of 16 mol/L) and 10 mol/L HF (0.5 mL) were added. While stirring with a PTFE-coated magnetic stir bar, the mixture was heated at 110 °C. After heating for 6.6 hours, the mixture was allowed to cool overnight. The PuO_2 had not dissolved completely, so an additional 0.3 mL of 10 mol/L HF was added. The mixture was again stirred and heated at 110 °C for 2.3 h. After cooling to ambient temperature under static (unstirred) conditions, the solution was decanted from the dissolution vessel and filtered (Advantec 0.5-µm PTFE membrane). Undissolved PuO_2 remained at the bottom of the dissolution vessel. The dissolution vessel was charged with 700 mL of 16 mol/L HNO_3 plus 0.6 mL 10 mol/L HF. After heating at 110 °C and stirring for approximately 3.2 hours, the mixture was allowed to cool and settle. The solution was decanted and vacuum filtered through an Advantec 0.5-µm PTFE membrane; it was then combined with the solution obtained from the first dissolution strike. A third dissolution strike was performed in a similar manner (800 mL of 16 mol/L HNO_3 and 0.8 mL 10 mol/L HF, added in four 0.2-mL aliquots). The filtered solutions from the first three dissolution strikes were combined, yielding 2.14 L of solution with a density of 1.40 g/mL.

A fourth dissolution strike was required to completely dissolve the material. For the fourth dissolution strike, 800 mL of 16 mol/L HNO_3 and 0.6 mL 10 mol/L HF were added and the mixture was heated at 110 °C for seven hours. This resulted in complete dissolution of the remaining PuO_2 solid. The solution from the fourth dissolution strike had a total volume of 0.96 L and a density of 1.37 g/mL.

2.1.5 Fourth Batch of SRNL Plutonium Oxide (Test Instruction NTNFC-TI-D007)

The PuO_2 (173.6 g, 153.1g Pu) was transferred from the XBS8490A container received from SRNL to the 1-L PTFE dissolution vessel. Concentrated HNO_3 (500 mL of 15 mol/L) and 10 mol/L HF (0.5 mL) were added. Additional concentrated HNO_3 was used to rinse residual PuO_2 from the XBS8490A container into the dissolver. While stirring with a PTFE-coated magnetic stir bar, the mixture was heated at 110 °C for approximately 50 minutes. The mixture was allowed to cool until the following morning, when heat was applied for an additional six hours. After cooling for approximately 45 minutes, no solids were observed floating in the solution. Approximately 400 mL of solution was decanted and vacuum filtered through an Advantec 0.5-µm PTFE membrane. Decanting ceased when solids became visible in the solution, leaving upwards of 200 mL of solution in the dissolver. Approximately 460 mL of concentrated HNO_3 and 0.5mL of 10 mol/L HF were added into the dissolver. The mixture was heated at 110 °C for approximately four hours and left to cool overnight. After cooling, most of the solution was decanted onto a second Advantec 0.5-µm PTFE membrane for vacuum filtration. The combined two filtrates yielded approximately 1.2 L of solution. It was noticed at this point that the magnetic stirrer was not operating properly, so it was replaced. Approximately 500 mL of concentrated HNO_3 and 0.3 mL of 10 mol/L HF were added into the dissolver. Additional concentrated HNO_3 was used to rinse visible solids from the funnel and the second filter back into the dissolver. The mixture in the dissolver was stirred and heated to 110 °C for approximately 18 hours.

At this point, fine particulate was observed in the previously filtered solution. Attempts were made to refilter his solution (~1.2 L) through the 0.5-µm PTFE membrane, but the membrane continually clogged. The filter medium was switched to a 1-µm PTFE membrane and the solution was successfully filtered. During this, and subsequent filtration steps, the filter membranes were replaced as needed to maintain reasonable filtrate flow rates. The solution from the dissolver (third dissolution strike) was decanted, filtered, and combined with the filtered solution from the first two dissolution strikes (total volume of filtered solution was ~1.8L).

Approximately 250 mL of concentrated HNO_3, 500 mL of 10.7 mol/L HNO_3, and 0.3 mL of 10 mol/L HF were added into the dissolver, and the stirring/heating process was continued for approximately four hours. After cooling overnight, 60–70mL of a nitric acid solution that had been used to recover plutonium from previous testing was added to the fifth filter to be combined with the former strikes. Solution from cooled evaporator was decanted onto the Advantec 1-µm PTFE membrane for vacuum filtration until the 2-L filter flask appeared full (approx. 230 mL decanted). This combined filtered solution was transferred into a 2-L PTFE bottle labeled *D007 Pu Solution* (referred to as *D007-1*), containing a total of 3044.6 g (approx. 2.1 L) from dissolution strikes 1 through 4. While D007-1 was filtering, upwards of 520mL of solution remained in the dissolver. HF (0.3mL of 10 mol/L) was added to the dissolver and the mixture was stirred and heated for approximately three hours. The remaining solution was decanted onto the Advantec PTFE membrane for vacuum filtration. The filtered solution was then transferred into a graduated 2-L Teflon bottle labeled *D007-2*, containing a total of 836 g (approx. 0.55 L) of solution. After rinsing the filtration apparatus with concentrated HNO_3 into the dissolver (unknown amount, estimated 200 mL), 0.3mL of 10 mol/L HF was added and the solution was left stirring at room temperature overnight. The next morning, approximately 450 mL of 12 mol/L HNO_3, 250mL of 5.8 mol/L HNO_3, and 0.3 mL of 10 mol/L HF were added into the dissolver (approx. 0.9 L total volume). The mixture was stirred and heated for approximately five hours, and allowed to cool over the weekend. The next working day, the cooled solution was decanted and filtered. Solids were still visible on the bottom of the dissolver. The filtered solution was then transferred into a graduated 2-L Teflon bottle labeled *D007-3*, containing a total of 764.6 g (approx. 0.6 L) of solution. The combined D007 solutions 1–3 summed to 4645.2g (3.25 L) of solution. Approximately 500 mL of concentrated HNO_3 and 0.3 mL of 10 mol/L HF were added into the dissolver with the remaining material (approx. 800 mL total volume). The solution was heated at 110 °C until the end of the work day, and left to cool overnight. The following morning, the solution had visible suspended solids. Heating was continued for approximately five hours. Approximately 0.8 L of the remaining solution with undissolved solids was transferred to a 2-L Teflon bottle. Concentrated HNO_3 used to rinse the dissolver was combined with the unfiltered solution, resulting in approximately 0.9 L of carry over solution for D008 (see Section 2.1.6).

2.1.6 Dissolution of Plutonium Oxide from Laboratory Scale Run 1 (Test Instruction NTNFC-TI-D008)

The PuO_2 (110.9 g, 97.8g Pu) was transferred from the LS1 PuOx poly bottle to the 1-L PTFE dissolution vessel. Approximately 225 mL of concentrated HNO_3 (15 mol/L) was used to rinse residual PuO_2 from the LS1 PuOx poly bottle into the dissolver. Some of the PuO_2 appeared to be embedded in the side of the poly bottle and could not be easily rinsed out. Based on the dry mass of the bottle and the bottle tare mass, this amounted to 1.2 g of PuO_2 (1.1 g Pu). Approximately 500 mL of unfiltered solution left over from D007 and 0.5 mL of 10 M HF were added into the dissolver. The dissolver was heated for approximately 20 minutes (maximum temperature: 40°C) before leaving for the evening. Heating continued the next morning up to 110 °C while stirring for approximately 2.5 hours. The undissolved solids were allowed to settle and the solution was decanted and vacuum filtered through an Advantec 1-µm PTFE membrane until solids were visible. A total of 775.1 g (approximately 550 mL) of solution was filtered and added to a 5-L carboy labeled Ion Exchange Feed Vessel #1, leaving approximately 175 mL leftover in the dissolver. Note that a pre-graduated 2-L Teflon bottle was used to estimate filtrate volume. This filtrate was combined with 1159.9 g (approximately 900 mL) of Ion Exchange Feed Solution #2 left over from IX012, totaling approximately 1.45 L of solution stored in Ion Exchange Feed Vessel #1. The remaining unfiltered solution left over from D007 (approximately 400 mL) was added to the dissolver, along with approximately 600 mL concentrated HNO_3 and 0.5mL of 10 M HF. The approximately 1.175L solution (near maximum dissolver volume) was heated to 110 °C while stirring for approximately two hours before cooling overnight.

The following day, the unfiltered solution appeared cloudy. 0.375 mL of 10 M HF was added into the dissolver, and the solution was heated to 110 °C while stirring for approximately two hours. The solution was decanted and vacuum filtered through an Advantec 1-µm PTFE membrane until solids were visible, resulting in 838.1g (approximately 600 mL) of filtered solution. This second filtrate was added to Ion Exchange Feed Vessel #1, leaving approximately 575 mL of solution remaining in the dissolver. Approximately 500 mL concentrated HNO_3 and 0.4mL of concentrated (29.3 mol/L) HF was added to the dissolver (approximately 1075 mL total volume), and was left stirring at ambient temperature overnight. The mixture was heated to 110 °C the following day for approximately eight hours. The entire dissolved solution was transferred to a 2-L Teflon bottle for storage until filtering on a later date. The approximately 1.1-L unfiltered solution appeared to be the darkest green of the three fractions. The dissolver and stir bar was rinsed with approximately 100 mL concentrated HNO_3, which was added to the remaining unfiltered solution. This solution was filtered over two days. The filtered solution and approximately 1.25 L of dilute IX012 Pu Fractions and 40 mL of Pu samples returned from analytical efforts were added to Ion Exchange Feed Vessel #1. This resulted in a total of 6050.8 g of filtered solution in the Ion Exchange Feed Vessel #1. The density was determined to 1.320 g/mL, which was used to calculate a total solution volume of 4.583 L. The Pu concentration in the resulting solution was 27.7 g Pu/L, with $[HNO_3] = 9.37 \pm 0.13$ mol/L. The used filters were collected and estimated to contain a net 2.7 g of wet material (< 2g Pu).

2.1.7 Second Batch of Recycled Plutonium Oxide (Test Instruction NTNFC-TI-D009)

Plutonium oxide materials from completed experiments were collected together for dissolution, purification, and reuse in additional statistical design runs. This material was collected from previously prepared PuO_2 samples that were no longer needed for analysis, completed BET samples, and materials produced by ashing of filter papers and other Pu-containing residues from the project. The estimated total mass of Pu in the combined recycled materials was 72.2 g. The PuO_2 was placed in the PTFE dissolution vessel and 500 mL of 15.8 M HNO_3 was added along with 0.5 mL of 10 M HF. Before proceeding with heating of the vessel, alpha contamination was discovered in the circulating cooling bath used to chill the condenser on the dissolution vessel. As a result of this, the dissolver slurry was transferred to a PTFE bottle and moved to the laboratory scale plutonium oxide system. The bench-scale dissolver vessel was also transferred and hooked up to the laboratory scale system. After a delay of approximately 2 weeks, the material was transferred back into the dissolver and the dissolution process was commenced. Over a period of two days, the mixture was held at 110 °C for at least 6 hours. After allowing the mixture to cool and the undissolved solids to settle overnight, the solution was decanted into a PTFE bottle.

Another charge of 500 mL 15.8 M HNO_3 and 0.5 mL 10 M HF was added and the mixture heated and stirred at 110 °C for at least 5 h. An additional ~ 0.5 mL of 10 M HF was added and heating was resumed the following day (~ 3 h at 110 °C). This resulted in near complete dissolution of the material with very little solid remaining (that remaining was saved for subsequent dissolution). The dissolved Pu solution was transferred from the laboratory scale system back to the bench scale system, where it was filtered in preparation for the anion exchange purification. A total of 1.83 L of clarified Pu nitrate solution was obtained (labeled as *D009 Pu Solution*).

2.2 Purification by Anion Exchange

The general procedure for purifying the Pu nitrate solution was as follows. Aluminum nitrate solution (1.6 mol/L) was added to the impure Pu nitrate solution to complex the fluoride ion added during the PuO_2 dissolution process. The amount of $Al(NO_3)_3$ added was sufficient to achieve an Al:F mole ratio of 2. Nitric acid solution was added to adjust the HNO_3 concentration to 7 mol/L. The concentration of the HNO_3 solution used for this adjustment depended upon the initial HNO_3 concentration in the impure Pu nitrate solution, but the HNO_3 concentration for the solution added was ≥ 0.5 mol/L to avoid formation of Pu (IV) polymer. In three nearly equal increments, 30% H_2O_2 (1 mL/g Pu) was added with stirring to fully adjust the Pu oxidation state to +4.

For the bench-scale system, Reillex HPQ anion exchange resin was packed into a quartz column (10 cm inner diameter × ~25 cm bed height). Before initially loading the resin into the column, it was converted to the nitrate form by treatment with $NaNO_3$. Once packed, 2 L (approximately 1 bed volume (BV)) of 7 mol/L HNO_3 was passed through the column to ensure the Pu solution would remain at 7 mol/L HNO_3 during loading. The anion exchange column was operated in a down-flow mode only, with solutions being fed to the top of the column using a peristaltic pump. The flowrate through the column was approximately 50 mL/min, although the column was successfully operated at flows as high as 70 mL/min or as low as 25 mL/min.

After conditioning the column with 7 mol/L HNO_3, the adjusted feed solution was passed through the column. The Pu was retained by the column in the form of the green $[Pu(NO_3)_6]^{2-}$ complex (Figure 1, left). The column loading step was continued until a) the entire feed solution was transferred to the column, or b) the Pu front was approximately 75% down the length of the column. Typically, 50 g of Pu could easily be processed in a given anion exchange run. Following loading of the Pu on the column, the column was scrubbed with approximately 6 L (~3 BV) of 7 mol/L HNO_3. This scrubbing washed the impurities (e.g., ^{241}Am) away from the Pu, which remained on the column as $[Pu(NO_3)_6]^{2-}$.

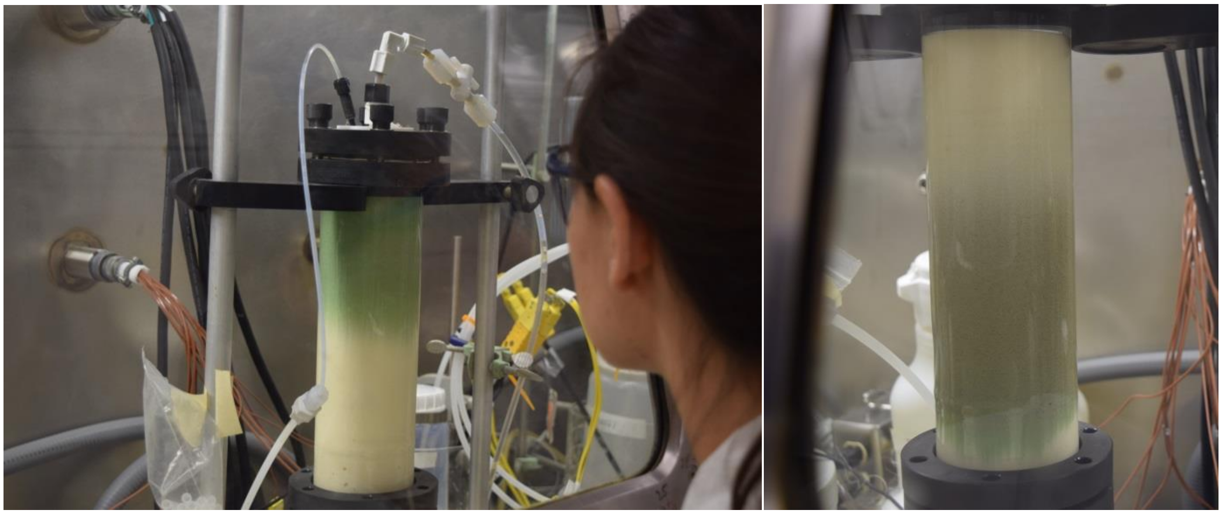

Figure 1. Left: Loading of $[\mathrm{Pu}\ (\mathrm{NO}_3)_6]^{2-}$ onto Reillex HPQ Anion Exchange Resin at 7 mol/L HNO_3; Right: Elution of Pu with 0.35 mol/L HNO_3

After the column scrubbing step, the Pu was eluted from the column with 0.35 mol/L HNO_3. Under this dilute HNO_3 condition, the Pu is converted to cationic forms, which have no affinity for the anion exchange resin, and thus the Pu is eluted from the column (Figure 1, right). The manner in which the Pu eluent was collected evolved as more experience was gained in running the anion exchange process. Originally, the Pu eluent was collected as a single fraction, beginning with the first sign of brown coloration in the solution exiting the bottom of the column, and ending when the solution exiting the column appeared colorless. This resulted in solutions that were too dilute to be used directly for some of the Pu (III) oxalate/calcination runs, especially those requiring 50 g Pu/L. In these cases, the solution had to be concentrated by evaporation. The evaporation in turn resulted in HNO_3 concentrations too high to achieve the target HNO_3 concentrations for some of the Pu (III) oxalate/calcination runs, especially those requiring 1 mol/L HNO_3. So yet another step was required—denitration by treatment with formic acid. The denitration step proved to be difficult to control. In one case, the reaction was vigorous enough to cause some of the Pu solution to foam out of the reaction vessel. This material had to be recovered and run through the anion exchange again. In another case, the denitration step went smoothly, but it was subsequently discovered that the Teflon coating on the thermocouple had delaminated, exposing the solution to the metallic components of the thermocouple. Furthermore, an organic film was observed floating on the top of the solution, and a green solid had precipitated. In this case, the concentrated Pu solution was filtered through a 1.0-µm PTFE membrane, which removed the solids and also appeared to remove the organic film. However, because the purity of this solution had been compromised, it again had to be purified by anion exchange.

Because of the challenges associated with the formic acid denitration step, changes were made to the manner in which the Pu eluent was collected. In the first evolution of this approach, the first ~100 mL of eluent exiting the column (after the first appearance of the brown coloration of the eluent solution) was collected. Then, the main portion of the eluent solution was collected separately. When the coloration of the Pu solution exiting the column began to fade again, the remainder was collected and combined with the first ~100 mL eluted from the column (the combined solution was referred to as the dilute fraction). Although this was an improvement, evaporation and denitration was still found to be necessary. In an alternative approach, the first ~100 mL of eluent exiting the column was collected, then the remaining eluent solution was collected in ~200-mL fractions. In this way, fractions with Pu concentrations in excess of 50 g/L and relatively low HNO_3 concentrations were obtained. Fractions with similar concentrations were combined for use in the Pu (III) oxalate/calcination runs. Fractions that were too dilute to be used in the Pu (III) oxalate/calcination runs were added into the feeds for subsequent anion exchange runs. Using this approach, the need to evaporate and denitrate the solutions was eliminated.

Table 1 summarizes the various anion exchange runs that were performed. Table 2 summarizes the Pu source materials used in each ion exchange run. Anion exchange runs IX003 and IX004 used the original approach in which the purified Pu nitrate was collected in a single fraction. Runs IX005, IX006, and IX007 collected the purified Pu nitrate in two fractions (a main fraction and a dilute fraction). All subsequent anion exchange runs collected the purified Pu nitrate in multiple fractions, and combined those of similar Pu concentration. Exceptions to this were NTNFC-TI-IX010 and NTNFC-TI-IX011. In the case of NTNFC-TI-IX010, a main fraction and dilute fraction were collected. These were later combined to form a single fraction. In the case of NTNFC-TI-IX011, the amount of Pu being processed exceeded the capacity of the column, so two loading/scrubbing/elution cycles were performed. For each cycle, the Pu was collected as main and dilute fractions. The main fractions from each elution cycle were combined together, as were the dilute fractions. The solutions from NTNFC-TI-IX010 and NTNFC-TI-IX011 were transferred to the Laboratory Scale Unit for use in the first 200-g scale run.

The last two anion exchange runs that were performed to provided purified Pu nitrate for the statistical design campaign were performed in the Laboratory Scale Plutonium Oxide system.[2] Using the laboratory scale system allowed acceleration of the PuO_2 preparations by (a) providing larger batches of stock purified Pu nitrate and (b) freeing up the glovebox with the bench scale system so that it could be dedicated to performing oxalate precipitations and calcinations. For these larger-scale anion exchange purification runs, the feed adjustment was very similar to that described above. That is, $Al(NO_3)_3$ was added to achieve an Al:F mole ratio of 2. Nitric acid was added as required to adjust the HNO_3 concentration to 7 mol/L. Hydrogen peroxide (30%) was added in three nearly equal increments with stirring to fully adjust the Pu oxidation state to +4. The solution was mixed by sparging with nitrogen during these ion exchange feed adjustment steps.

The anion exchange column was operated in an up-flow mode during the column conditioning and loading steps. The column was conditioned with one BV of 7 M HNO_3 before introducing the adjusted feed solution to the bottom of the column. The entire Pu feed material was pumped into the column to load the column. Once all the Pu was loaded, the column was scrubbed with 3 BVs of 7 M HNO, again in the up-flow direction. The Pu was eluted from the column with 0.35 M HNO_3 in the down-flow direction. The progress of the Pu elution was followed by in-line spectrophotometry. The Pu was collected into relatively concentrated fractions (> 50 g Pu/L) and dilute fractions.

Table 1 Summary of Pu Nitrate Stock Solutions Prepared by Anion Exchange

Test Instruction	Solution ID	Pu Concentration, g/L	HNO_3 Concentration, mol/L
NTNFC-TI-IX004	IX004 Concentrated Pu(a)	113	0.80
NTNFC-TI-IX005	IX005 Purified Pu	28.8	1.19
NTNFC-TI-IX006	IX006 Purified Pu(b)	36.0	0.99
NTNFC-TI-IX007	IX007 Purified Pu	48.6	1.28
NTNFC-TI-IX008	IX008 Combo A	76.1	0.60
	IX008 Combo B	63.8	1.02
	IX008 Combo C	41.3	1.35
NTNFC-TI-IX009	IX009 Fraction A	22.1	1.12
	IX009 Fraction B	55.1	0.51
	IX009 Fraction C	70.9	0.42
NTNFC-TI-IX010	IX010 Purified Pu	36.2	0.81
NTNFC-TI-IX011	IX011 Purified Pu	63.9	0.53
NTNFC-TI-IX012	IX012 Fraction 1A	9.42	3.62
	IX012 Fraction 2A	56.2	0.59
	IX012 Fraction 3A	81.9	(c)
	IX012 Fraction 4A	63.3	0.84
	IX012 Fraction 5A	20.4	0.89
	IX012 Fraction 6A	1.88	0.35(d)
	IX012 Fraction 7A	0.36	0.35(d)
	IX012 Fraction 8A	0.16	0.35(d)
	IX012 Fraction 1B	6.30	4.32
	IX012 Fraction 2B	41.3	0.40
	IX012 Fraction 3B	79.0	0.39
	IX012 Fraction 4B	69.2	0.39
	IX012 Fraction 5B	39.4	0.45
	IX012 Fraction 6B	9.59	0.37
	IX012 Fraction 7B	1.26	0.35(d)
	IX012 Fraction 8B	0.37	0.35(d)
NTNFC-TI-IX013	IX013 Fraction 1A	0.33	6.69
	IX013 Fraction 2A	24.8	2.53
	IX013 Fraction 3A	76.9	0.41
	IX013 Fraction 4A	77.7	0.35(d)
	IX013 Fraction 5A	49.2	0.35(d)
	IX013 Fraction 6A	11.4	0.35(d)
	IX013 Fraction 7A	1.07	0.35(d)
	IX013 Fraction 8A	0.28	0.35(d)
	IX013 Fraction 1B	0.44	5.98
	IX013 Fraction 2B	14.7	2.20
	IX013 Fraction 3B	57.5	0.48
	IX013 Fraction 4B	74.5	(e)
	IX013 Fraction 5B	54.6	0.35(d)
	IX013 Fraction 6B	14.3	0.35(d)
	IX013 Fraction 7B	1.44	0.35(d)
	IX013 Fraction 8B	0.36	0.35(d)
NTNFC-TI-IX014	IX014 Fraction 1	12.3	3.9(f)
	IX014 Fraction 2	41.4	1.66
	IX014 Fraction 3	71.8	0.54
	IX014 Fraction 4	78.6	0.34
	IX014 Fraction 5	74.6	0.38
	IX014 Fraction 6	59.8	0.42
	IX014 Fraction 7	40.0	0.35(d)
	IX014 Fraction 8	11.1	0.35(d)
	IX014 Fraction 9	2.41	0.35(d)

Test Instruction	Solution ID	Pu Concentration, g/L	HNO_3 Concentration, mol/L
NTNFC-TI-IX015[g]	IX015 20190206-1	67.3	1.0
	IX015 20190206-1	67.3	1.0
	IX015 Conc 2	60.9	0.54
NTNFC-TI-IX016[g]	IX016 Conc 1	89.2	0.69

[a] The purified Pu nitrate solutions from NTNFC-TI-IX003 and NTNFC-TI-IX004 were combined and concentrated by evaporation, followed by denitration with HCOOH.

[b] The IX006 Purified Pu solution was not used for any PuO_2 preparations. During evaporation and denitration of this solution, the purity of the solution was compromised (see section on deviations from the plan). This material was re-processed through anion exchange in NTNFC-TI-IX009.

[c] This value could not be reliably measured.

[d] In these cases, the HNO_3 concentration was too low to accurately measure; 0.35 mol/L is assumed since this was the concentration of the eluant solution.

[e] A value of 2.21 M HNO_3 was determined in a single measurement for this fraction, but this clearly was not likely to be correct given the fact that HNO_3 concentration in the fractions immediately before and after this fraction were well below this value.

[f] Based on titration of only one aliquot.

[g] These ion exchange runs were performed in the Laboratory Scale Pu Oxide system.

Table 2 Plutonium Source Materials for the Statistical Design PuO_2 Preparations

Pu Source	Dissolution TI	Ion Exchange TI
AF-1-7	NTNFC-TI-D003	NTNFC-TI-IX004
AF-1-7	NTNFC-TI-D003	NTNFC-TI-IX005
M016129	NTNFC-TI-D004	NTNFC-TI-IX007
M016129	NTNFC-TI-D004	NTNFC-TI-IX008
M016129	NTNFC-TI-D004	NTNFC-TI-IX009
XBS8490A	NTNFC-TI-D007	NTNFC-TI-IX012
XBS8490A and recycle from Lab Scale Run 1	NTNFC-TI-D007 and NTNFC-TI-D008	NTNFC-TI-IX013
Recycled material from previous runs	NTNFC-TI-D007 and dilute fractions from NTNFC-TI-IX013	NTNFC-TI-IX014
Recycled material from previous runs	NTNFC-TI-D008	NTNFC-TI-IX015
Recycled material from previous runs	NTNFC-TI-D009	NTNFC-TI-IX016

2.3 Plutonium (III) Oxalate Precipitation

Figure 2
Plutonium(III) Feed Solution for Run 1

A portion of purified Pu nitrate solution, containing 10 g Pu, was adjusted with 10 mol/L HNO_3 and deionized water as needed to yield the desired Pu and HNO_3 concentrations in the feed solution. This adjustment was done in such a way that the Pu solution was never exposed to only deionized water. Rather, the quantities of 10 mol/L HNO_3 and deionized water were first combined, then the resulting HNO_3 solution was mixed with the Pu nitrate solution. This avoided the possibility of Pu (IV) polymer formation. A solution of $N_2H_4{\cdot}HNO_3$ (1.8 mol/mol Pu) was added to serve as a nitrite scavenger to stabilize the Pu (III) solution. After mixing for ~30 seconds, solid ascorbic acid was added (1.5 g/g Pu; 2 mol/mol Pu) and the solution was mixed. This resulted in the formation of a deep blue Pu (III) nitrate solution (Figure 2).

For preparation done in the direct strike mode, the feed was placed in a 2-L high-density polyethylene (HDPE) wide mouthed bottle, which served as the precipitation vessel. The vessel was equipped with a modified lid that allowed for the insertion of an overhead mixer and solution addition line. The latter consisted of a plastic tube that discharged approximately 2.5 cm above the mixing impeller. The precipitation vessel was placed in a water bath and the temperature was allowed to equilibrate (either at 30 or 50 °C). If the oxalic acid was to be added as a 0.9 mol/L solution, this was placed in a separate water bath and also brought to the desired temperature. Once the temperature had equilibrated, the oxalic acid solution was pumped into the precipitation vessel through the addition tube. The pump was set to deliver the solution over a period of 20 or 40 minutes. If the addition rate was for 20 minutes, an additional 20 minutes of digestion time was allowed after the oxalic acid was added. For those cases where the oxalic acid was to be added as fast as possible, or as a solid, the stirring motor was temporarily stopped and the vessel opened. The oxalic acid solution, or the oxalic acid solid, was added as fast as possible, then the vessel was closed again and stirred for a total digestion time of 40 minutes.

For the reverse strike mode, the oxalic acid solution was placed in the precipitation vessel and brought to temperature. The Pu (III) solution was heated in a separate water bath to reach the equilibrium temperature. The pump was set to deliver the Pu (III) solution into the precipitation vessel over a period of 20 or 40 minutes. If the addition rate was for 20 minutes, an additional 20 minutes of digestion time was allowed after the Pu (III) solution transfer. Figure 3 presents an example case of the configuration for a reverse strike experiment.

In all cases, the amount of oxalic acid used was such that an excess of 0.2 mol/L oxalic acid would be present after complete precipitation of the Pu.

Figure 3 Experimental Set Up for a Reverse Strike Experiment (Run 16 Shown)

After the designated mixing/digestion time, the mixer was stopped and the $Pu_2(C_2O_4)_3 \cdot 10H_2O$ solid was allowed to settle (Figure 4, left). The supernatant liquid was decanted from the solids and vacuum filtered through Whatman™ 42 ashless filter paper (part number 1442-090). The Pu (III) oxalate solid was washed three successive times with 150-mL portions of 0.5 mol/L HNO_3 plus 0.2 mol/L $H_2C_2O_4$. Following each wash, the solid was allowed to settle and the supernatant liquid was filtered to collect any suspended Pu (III) oxalate solid. Three additional washes were performed in a similar manner with 150-mL portions of 0.2 mol/L $H_2C_2O_4$. During the final washing step, the solids were kept suspended in the 0.2 mol/L $H_2C_2O_4$ solution and the slurry was passed through the filter to collect the product $Pu_2(C_2O_4)_3 \cdot 10H_2O$. The solid was allowed to air dry (Figure 4, right).

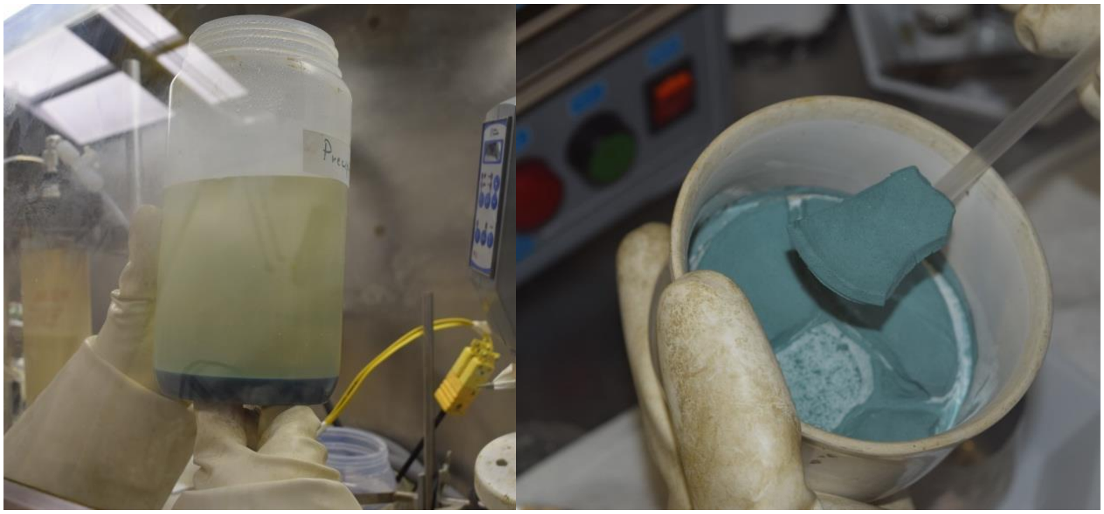

Figure 4 Left: Settled Pu (III) Oxalate Solid; Right: Dried Pu (III) Oxalate Solid

2.4 Calcination of Plutonium (III) Oxalate

The $Pu_2(C_2O_4)_3 \cdot 10H_2O$ was transferred into a platinum crucible and was spread as thin as reasonably possible. The crucible was placed in a muffle furnace and mostly covered with a platinum lid (i.e., the lid was cracked to allow air flow into the crucible). While purging with dry air, the furnace was heated to

650 °C. The heating profile used is shown in Table 3 (see Section 4.2 on deviations from the plan). The Pu (III) oxalate was first heated to 30 °C at a rate of 1 °C/min and was held at that temperature for 10 minutes. It was then heated to 150 °C at a rate of 1.5 °C/min and held at 150 °C for one hour. After this, the temperature was increased to 650 °C/min at a rate of 5 °C/min and held at this temperature for two hours. After completion of the calcination step, the PuO_2 was allowed to cool under a stream of dry air, and then was collected and weighed.

Table 3 Planned Heating Profile for Calcination of Pu (III) Oxalate to PuO_2

Step #	Target T, °C	Ramp rate, °C/min	Hold time, min
1	30	1	10
2	150	1.5	60
3	650	5	120

3.0 The Plutonium Oxide Statistical Design Runs

The first batch of plutonium oxide (AF-1-7) from the Savannah River Site (SRS) was received at PNNL on September 1, 2016. Eight 10-g scale processing runs were successfully performed using this material. One run was compromised because of a pump failure during the course of the experiment, which resulted in a delay between the time the Pu was adjusted to the +3 oxidation state and the time the oxalate precipitation was performed. Evidence for re-oxidation to Pu +4 was observed (color change from blue to brown) during the precipitation step for that run. This run was successfully repeated after replacing the pump. A second batch of PuO_2 stock material (M016129) was received from SRS in February 2017. This material was successfully dissolved and purified through a series of anion exchange runs. Plutonium (III) oxalate precipitation and calcination runs began with this material on April 5, 2017. A third batch or PuO_2 (XBS8490A) was dissolved in November 2017 for use in the statistical design study. These were the primary sources of Pu used in this work. Later in the project, excess PuO_2 samples prepared earlier in the project were redissolved and recycled; in some cases these materials were supplemented with Pu taken from existing stocks at PNNL (see Table 2).

Table 4 summarizes the 76 experimental conditions used in the PuO_2 preparations, and Table 5 indicates the purified Pu nitrate stock solutions used for each run. Yields of PuO_2, based on the initial 10 g of Pu used for each run, were variable, ranging from 64% to essentially quantitative. In some cases, additional precipitation of $Pu_2(C_2O_4)_3 \cdot 10H_2O$ was observed in the filtrate after collection of the product. Inefficient filtration of the Pu (III) oxalate solid is another possible explanation for low yields for some of the runs. Any solids observed in the oxalate filtrate solutions were collected by filtration and thermally decomposed to PuO_2 for recycle into subsequent runs.

Table 4 Experimental Conditions used for the 10-g Pu Processing Runs

Run Order #	Oxalate Source(a)	Reagent Addition Time, min	Digestion Time, min	Nitric Acid Conc., mol/L	Strike Direction(b)	Temp., °C	Pu Conc., g/L	Yield, %(c)
1	solution	0	40	3	reverse	50	10	71
2	solid	0	40	1	direct	30	10	95
3	solution	0	40	2	direct	50	50	95
4	solution	0	40	1	reverse	50	50	95
5	solution	20	20	2	reverse	50	30	94
6	solid	0	40	2	direct	30	50	99
7	solid	0	40	2	direct	50	10	92
8	solution	40	0	3	reverse	50	10	112(d)
9	solution	20	20	3	reverse	30	10	87
10	solid	0	40	3	direct	50	30	84
11	solution	20	20	2	direct	30	30	97
12	solid	0	40	1	direct	50	50	96
13	solution	20	20	1	direct	50	10	99
14	solution	40	0	1	reverse	30	50	98
15	solid	0	40	3	direct	30	50	94
16	solution	40	0	1	reverse	50	10	98
17	solution	0	40	3	direct	30	10	86
18	solution	0	40	1	direct	30	50	97
19	solid	0	40	1	direct	30	50	101
20	solid	0	40	2	direct	50	30	96
21	solution	0	40	1	reverse	30	10	99
22	solid	0	40	2	direct	50	30	94
23	solution	0	40	3	direct	30	50	97
24	solution	40	0	1	direct	50	30	100
25	solid	0	40	1	direct	30	10	95
26	solid	0	40	1	direct	50	30	98
27	solution	40	0	3	direct	30	10	87
28	solution	40	0	3	direct	30	30	91
29	solution	0	40	2	reverse	30	30	97
30	solution	20	20	1	reverse	30	50	88
31	solution	20	20	2	direct	30	30	93
32	solution	40	0	3	reverse	50	50	92
33	solution	40	0	2	direct	50	50	98
34	solid	0	40	1	direct	30	30	95
35	solution	20	20	2	reverse	50	30	95
36	solid	0	40	3	direct	30	10	80
37	solution	20	20	2	direct	30	50	97
38	solution	20	20	1	reverse	30	10	94
39	solution	0	40	3	direct	50	30	92
40	solid	0	40	1	direct	50	10	64(e)
41	solution	40	0	3	direct	50	30	80
42	solution	40	0	1	direct	50	30	100
43	solution	20	20	2	reverse	50	30	97
44	solid	0	40	1	direct	50	10	99
45	solid	0	40	3	direct	30	30	94(e)
46	solution	40	0	1	reverse	50	50	87
47	solution	20	20	3	reverse	30	50	92
48	solid	0	40	2	direct	50	50	96
49	solution	40	0	3	reverse	50	10	84
50	solid	0	40	2	direct	30	10	94
51	solution	0	40	2	direct	50	10	97
52	solution	40	0	3	reverse	30	10	92
53	solution	40	0	1	direct	50	10	93
54	solid	0	40	2	direct	30	50	98
55	solution	20	20	1	direct	50	50	99
56	solution	20	20	2	direct	30	30	98
57	solution	0	40	1	reverse	30	50	94

58	solution	0	40	1	reverse	30	10	96
59	solution	0	40	1	direct	30	10	93
60	solution	40	0	1	reverse	30	10	94
61	solution	0	40	3	reverse	50	50	95
62	solution	40	0	1	direct	30	10	98
63	solid	0	40	1	direct	50	50	96
64	solid	0	40	3	direct	30	50	89
65	solution	20	20	2	reverse	50	30	96
66	solution	40	0	3	reverse	30	50	96
67	solid	0	40	2	direct	30	30	94
68	solution	20	20	2	direct	30	30	98
69	solid	0	40	3	direct	50	50	86
70	solid	0	40	3	direct	50	10	64(e)
71	solid	0	40	2	direct	30	30	95
72	solution	20	20	3	direct	50	50	82
73	solution	20	20	2	direct	30	30	95
74	solution	20	20	3	direct	50	10	85
75	solution	40	0	2	reverse	30	30	94
76	solution	0	40	3	reverse	40	10	94

(a) solution = 0.9 mol $H_2C_2O_4$/L; solid = $H_2C_2O_4 \cdot 2H_2O$

(b) direct strike = oxalic acid added into the Pu solution; reverse strike = Pu solution added into oxalic acid solution

(c) All yields are calculated based on the target Pu concentrations in the feed solution to the oxalate precipitation step.

(d) The calculated yield for Run 8 was greater than 100%, suggesting that the starting amount of Pu was actually slightly higher than the target 10 g.

(e) Significant post-filtration precipitation of Pu (III) oxalate was observed during this run.

Table 5 Plutonium Solutions used in the Statistical Design PuO_2 Preparations

Run Order #	Stock Solution ID
1	IX004 Concentrated Pu
2	IX004 Concentrated Pu
3	IX004 Concentrated Pu
4	IX004 Concentrated Pu
5	IX004 Concentrated Pu
6	IX008 Combo B
7	IX005 Purified Pu
8	IX005 Purified Pu
9	IX004 Concentrated Pu
10	IX007 Purified Pu
11	IX007 Purified Pu
12	IX008 Combo A
13	IX008 Combo C
14	IX008 Combo A (94 mL) plus IX008 Combo B (65 mL)
15	IX008 Combo A
16	IX009 Fraction A (428 mL) plus IX008 Combo C (12 mL)
17	IX007 Purified Pu
18	IX009 Fraction C
19	IX008 Combo C (19 mL) plus IX009 Fraction C (130 mL)
20	IX007 Purified Pu
21	IX007 Purified Pu
22	IX008 Combo C (58 mL) plus IX009 Fraction B (137 mL)
23	IX013 Fraction 4A (129 mL)
24	IX009 Fraction B
25	IX013 Fraction 2A (177 mL) IX013 Fraction 5A (49 mL) IX013 Fraction 6A (252 mL) IX013 Fraction 7A (255 mL) IX013 Fraction 8A (211 mL)
26	IX013 Fraction 4A (119 mL) X013 Fraction 2B (12 mL) IX013 Fraction 5B (8 mL) IX013 Fraction 6B (10 mL)
27	IX012 Fraction 4A (177 mL)
28	IX012 Fraction 3A (122 mL)
29	IX012 Fraction 3A (122 mL)
30	IX012 Fraction 3B (126 mL)
31	IX012 Fraction 3B (126 mL)
32	IX012 Fraction 3A (20 mL) IX012 Fraction 4A (103 mL) IX012 Fraction 4B (26 mL)
33	IX012 Fraction 4B (144 mL)
34	IX012 Fraction 2A (178 mL)
35	IX012 Fraction 2A (84 mL) IX012 Fraction 5B (133 mL)
36	IX012 Fraction 1A (127 mL) IX012 Fraction 5A (263 mL) IX012 Fraction 1B (108 mL)

	IX012 Fraction 2B (7 mL) IX012 Fraction 6B (245 mL)
37	IX014 Fraction 3 (139 mL)
38	IX012 Fraction 4B (78 mL) IX012 Fraction 5B (112 mL) IX013 Fraction 4B (4 mL)
39	IX012 Fraction 2B (228 mL) IX013 Fraction 4B (7.5 mL)
40	IX014 Fraction 1 (134 mL) IX014 Fraction 2 (140 mL) IX014 Fraction 8 (189 mL) IX014 Fraction 9 (185 mL)
41	IX014 Fraction 2 (39.5 mL) IX014 Fraction 6 (4.8 mL) IX014 Fraction 7 (202 mL)
42	IX015 Conc 2 (164 mL)
43	IX015 Conc 2 (164 mL)
44	IX015 Conc 2 (164 mL)
45	IX015 Conc 2 (164 mL)
46	IX014 Fraction 4 (127 mL)
47	IX014 Fraction 5 (134 mL)
48	IX014 Fraction 3 (44.0 mL) IX014 Fraction 4 (42.0 mL) IX014 Fraction 5 (47.5 mL)
49	IX015 Conc 2 (164 mL)
50	IX015 Conc 2 (164 mL)
51	IX015 Conc 2 (164 mL)
52	IX015 20190206-1 (149 mL)
53	IX015 20190206-1 (149 mL)
54	IX014 Fraction 6 (167 mL)
55	IX015 20190206-1 (20 mL) IX015 Conc 2 (142 mL)
56	IX015 20190206-1 (149 mL)
57	IX016 Conc. 1 (112 mL)
58	IX015 20190206-1 (149 mL)
59	IX015 20190206-1 (149 mL)
60	IX015 20190206-1 (149 mL)
61	IX015 20190206-2 (149 mL)
62	IX015 20190206-1 (45 mL) IX015 20190206-2 (104 mL)
63	IX016 Conc. 1 (112 mL)
64	IX015 20190206-2 (149 mL)
65	IX015 20190206-2 (149 mL)
66	IX015 20190206-2 (149 mL)
67	IX015 20190206-2 (149 mL)
68	IX015 20190206-2 (149 mL)
69	IX016 Conc. 1 (112 mL)
70	IX016 Conc. 1 (112 mL)
71	IX016 Conc. 1 (112 mL)
72	IX016 Conc. 1 (112 mL)
73	IX016 Conc. 1 (112 mL)
74	IX016 Conc. 1 (112 mL)
75	IX016 Conc. 1 (112 mL)
76	IX016 Conc. 1 (112 mL)

During the initial runs performed, the Pu concentration in the feed solution to the oxalate precipitation step was not directly measured. In these cases, the Pu concentrations were calculated from the measured Pu concentrations in the stock solutions used. Runs included in this category were 1–5 and 7–11. The Pu concentration in the run 17 feed was also not directly measured because the sample of the feed solution taken was inadvertently recycled before the spectrophotometric analysis was performed. In other runs, a sample of the oxalate precipitation feed solution was taken for Pu analyses by spectrophotometry. Early on, this sample was taken after reduction to Pu^{3+}; that is, after the addition of ascorbic acid. Runs sampled in this manner included runs 6, 12–16, and 18–21. The results of these spectrophotometric determinations of Pu were complicated by a) baseline distortion in the spectra caused by the intense yellow coloration of the oxidation products of ascorbic acid, and b) precipitation of Pu from solution over time (which is believed to be from the formation of Pu (III) oxalate, with the oxalate formed from degradation of ascorbic acid). These complications, especially the slow precipitation of Pu with time, led to Pu concentrations that were typically biased low. This low bias was also evidenced by the fact that if the determined values were used to calculate the PuO_2 yield in the process, the yields were 10 to 20% high. Further complications regarding the Pu concentrations in runs 6, 12, 13, and 14 are discussed in Section 4.3. For runs 22 and above, the oxalate precipitation feed solution was sampled immediately before addition of ascorbic acid. This led to more reliable determination of the Pu concentration by spectrophotometry. Table 6 presents the Pu concentrations in the oxalate precipitation feed solutions.

Table 6 also presents the HNO_3 concentrations in the oxalate precipitation feed solutions as determined by potentiometric titration with standardized NaOH. For the first ~20 runs, the measured HNO_3 concentrations were generally higher than expected. One possible explanation for this is that, for most of these runs, the contribution of the HNO_3 produced through oxidation of ascorbic acid by Pu^{4+} was not taken into account during the feed adjustment step. For each run with 10 g of Pu, 0.04 moles of HNO_3 was produced through this mechanism. There is also a contribution from the HNO_3-neutralized hydrazine during titration with NaOH. This amounts to another 0.05 moles of HNO_3.

Table 6 Comparison of Target Pu and HNO_3 Concentrations to the Measured Values

Run Order Number	Target Pu Conc., g/L	Measure Pu Conc., g/L	Target HNO_3 Conc., M	Measured HNO_3 Conc., M
1	10	Not measured	3	3.49 ± 0.07
2	10	Not measured	1	0.73 ± 0.05
3	50	Not measured	2	2.78 ± 0.04
4	50	Not measured	1	1.84 ± 0.06
5	30	Not measured	2	3.91 ± 0.50
6	50	55.9(a)	2	2.54 ± 0.20
7	10	Not measured	2	2.95 ± 0.21
8	10	Not measured	3	4.03 ± 0.38
9	10	Not measured	3	3.63 ± 0.26
10	30	Not measured	3	3.24 ± 0.15
11	30	Not measured	2	3.32 ± 0.03
12	50	56.5(a)	1	1.89 ± 0.20
13	10	11.3(a)	1	1.51 ± 0.06
14	50	57.0(a)	1	1.66 ± 0.05
15	50	49.0	3	3.76 ± 0.05
16	10	8.40(b)	1	0.93 ± 0.03
17	10	Not measured	3	3.74 ± 0.15
18	50	42.1(b)	1	1.67± 0.07
19	50	48.3	1	1.43± 0.05
20	30	23.6(b)	2	2.57 ± 0.12
21	10	8.8(b)	1	2.64 ± 0.39
22	30	31.3	2	2.15 ± 0.10
23	50	49.9	3	3.0(c)
24	30	30.8	1	1.21 ± 0.13
25	10	10.2	1	1.05 ± 0.03
26	30	30.2	1	1.2(c)
27	10	10.3	3	3.03 ± 0.10
28	50	50.4	3	2.91 ± 0.01
29	30	30.6	2	1.91 ± 0.07
30	50	49.9	1	0.84 ± 0.03
31	30	30.4	2	1.95 ± 0.02
32	50	51.0	3	2.81 ± 0.12
33	50	51.4	2	1.96 ± 0.10
34	30	29.5	1	1.05 ± 0.05
35	30	32.1	2	1.99 ± 0.01
36	10	11.0	3	2.96 ± 0.01
37	50	50.5	1	0.93 ± 0.01
38	10	10.8	1	0.93 ± 0.01
39	30	32.1	3	3.27 ± 0.10
40	10	10.4	3	3.3(c)
41	30	27.7	3	3.2(c)
42	30	30.8	1	1.3(c)
43	30	31.0	2	1.87 ± 0.03
44	10	10.2	1	0.91 ± 0.01
45	30	32.2	3	2.94 ± 0.10
46	50	51.4	1	0.99 ± 0.03
47	50	50.4	3	2.75 ± 0.05
48	50	51.3	2	1.46 ± 0.05
49	10	10.6	3	2.97 ± 0.08
50	10	10.4	2	2.07 ± 0.04
51	10	10.5	2	2.01 ± 0.02

Run Order Number	Target Pu Conc., g/L	Measure Pu Conc., g/L	Target HNO_3 Conc., M	Measured HNO_3 Conc., M
52	10	10.4	3	2.95 ± 0.01
53	10	10.2	2	2.15 ± 0.03
54	50	51.0	1	1.04 ± 0.01
55	50	51.2	1	0.99 ± 0.03
56	30	30.6	2	1.86 ± 0.03
57	50	49.5	1	0.96(c)
58	10	10.2	1	1.00 ± 0.01
59	10	10.2	1	1.03 ± 0.03
60	10	10.2	1	1.08 ± 0.04
61	50	50.7	3	2.85 ± 0.01
62	10	10.2	1	1.05 ± 0.10
63	50	49.3	1	0.99(c)
64	50	51.7	3	2.94 ± 0.10
65	30	30.8	2	1.97 ± 0.06
66	50	51.2	3	3.11 ± 0.23
67	30	30.3	2	2.00 ± 0.02
68	30	30.8	2	2.03 ± 0.03
69	50	49.5	3	2.9(c)
70	10	10.4	3	3.01 ± 0.06
71	30	29.7	2	1.91(c)
72	50	49.6	3	2.88 ± 0.12
73	30	29.7	2	1.90 ± 0.04
74	10	10.4	3	2.98 ± 0.02
75	30	30.5	2	1.97 ± 0.12
76	10	10.0	1	0.92 ± 0.02

(a) See discussion in Deviations from the Plan section.

(b) The Pu concentrations measured in the feed solution for runs 16, 18, 20, and 21 are believed to be erroneously low. See text for a detailed discussion.

(c) Only single aliquot titrated, so standard deviation not reported.

Table 7 presents an evaluation of these contributions to the measured HNO_3 concentrations. Although this improves the agreement between expected and measured HNO_3 concentrations, it does not fully explain the discrepancies. The discrepancies are likely attributed to experimental error. Because the titrations were performed in open-faced fume hoods, it was necessary to take relatively small aliquots (0.1-mL) of the adjusted feed solution for titration. Evaporation of these samples prior to titrimetric analysis are a likely source of the high bias to the measured HNO_3 concentrations. Also, sub-aliquots of 20 to 30 µL were used for the titrimetric analysis, introducing the possibility of pipetting error. To mitigate these sources of error, a protocol was established in which the sample vials were centrifuged (to move any condensation on the walls of the vial into the bulk sample at the bottom), and the entire 0.1 mL was diluted into 1.0 mL of deionized water. The latter allowed larger sub-aliquots to be taken for titration, reducing the pipetting error.

Table 7 Evaluation of Ascorbic Acid Oxidation and Hydrazinium Nitrate to the Measured HNO_3 Concentrations

Run Order Number	Target Pu Conc., g/L	Target HNO_3 Conc., M	Adjusted Target HNO_3 Conc., M	Measured HNO_3 Conc., M	Measured Agrees with Adjusted Target?
1	10	3	3.09	3.49 ± 0.07	No
2	10	1	1.09	0.73 ± 0.05	No
3	50	2	2.45	2.78 ± 0.04	No
4	50	1	1.45	1.84 ± 0.06	No
5	30	2	2.27	3.91 ± 0.50	No
6	50	2	2.45	2.54 ± 0.20	Yes
7	10	2	2.09	2.95 ± 0.21	No
8	10	3	3.09	4.03 ± 0.38	No
9	10	3	3.09	3.63 ± 0.26	No
10	30	3	3.27	3.24 ± 0.15	Yes
11	30	2	2.27	3.32 ± 0.03	No
12	50	1	1.45	1.89 ± 0.20	No
13	10	1	1.09	1.51 ± 0.06	No
14	50	1	1.24(b)	1.66 ± 0.05	No
15	50	3	3.45	3.76 ± 0.05	No
16	10	1	1.09(b)	0.93 ± 0.03	No
17	10	3	3.09	3.74 ± 0.15	No
18	50	1	1.24(b)	1.67± 0.07	No
19	50	1	1.24(b)	1.43± 0.05	No
20	30	2	2.27	2.57 ± 0.12	No
21	10	1	1.09	2.64 ± 0.39	No
22	30	2	2.14(b)	2.15 ± 0.10	Yes
23	50	3	3.0	3.0	(c)
24	30	1	1.14(b)	1.21 ± 0.13	Yes
25	10	1	1.09	1.05 ± 0.03	No
26	30	1	1.00(b)	1.2	(c)

(a) Target HNO_3 concentration adjusted for the 0.04 mole H^+ generated from oxidation of ascorbic acid, and 0.05 moles of H^+ contributed by $N_2H_5NO_3$.

(b) In these cases, the oxidation of ascorbic acid and contribution of $N_2H_5NO_3$ was accounted for during the feed adjustment step.

(c) Only a single titrimetric measurement was made of the acid concentration; the value is within reasonable agreement with the target given the uncertainty associated with a single measurement.

4.0 Deviations from the Plan

This section discusses aspects of the work that varied from the original experimental plan.

4.1 Runs Performed Out of Sequence

A number of the runs were done out of sequence from the statistical design run order. There were two reasons for this. First, prior to implementation of the above described adjustments to the ion exchange fraction collection method, some of the runs with 50 g Pu/L required evaporation and denitration of the purified Pu nitrate solution from the ion exchange step. Because of the challenges associated with the evaporation/denitration (see Section 2.2), it was decided that the need for this step could be minimized by grouping two or three of these 50 g/L runs together. Thus, some of these runs were skipped over until the higher purified Pu stock solution was available. Second, some runs were skipped over due to the failure of the metering pump used to transfer the reagent solutions into the precipitation vessel. In order to keep moving forward on the testing, it was decided to proceed with runs that did not require the pump, while the pump issue was resolved. A different type of pump (a peristaltic pump) was chosen to replace the metering pumps that proved unreliable.

4.2 Inconsistent Heating Profiles

Following the first few runs performed, it was discovered that, in some cases, the heating profiles used in the calcination step were not consistent with the planned heating profiles. Table 3 summarizes the heating profile intended to be used during calcination of the Pu (III) oxalate to PuO_2. For six of the early runs performed, the heating profile indicated in Table 3 was not achieved. In all cases, the ramp from 150 to 650 °C and the subsequent two hour hold, was properly executed. However, the first two steps varied somewhat. In the cases of runs 1, 2, 3, and 9, the temperature was held at 30 °C for one hour instead of 10 minutes. The temperature was then raised to 100 °C at a rate of 1 °C/min, and then to 650 °C at a rate of 5 °C/min. In these cases, there was no hold at 150 °C. In the cases of runs 4 and 5, the steps in Table 3 were performed, except that, again, there was no 60-minute hold at 150 °C.

Upon discovery of these inconsistencies, a step was introduced into the test instructions to verify that the heating program was properly inputted into the calcination furnace. All runs, other than those mentioned in the preceding paragraph, were performed using the heating profile indicated in Table 3.

4.3 Higher than Expected Plutonium Concentrations

A series of runs was performed in May 2017, for which the initially determined yields of PuO_2 were 10–12% higher than expected (runs 6, 12, 13, and 14). The stock solutions used for these runs all came from ion exchange run NTNFC-TI-IX008. The Pu concentrations of the stock solutions were determined by spectrophotometry using a technique in which all the Pu in the sample is reduced to Pu (III) and the spectrum is determined from the intensity of the absorbance at ~600 nm. Because the yields were high by almost an identical amount for each of these four runs, it was suspected that the original determination of the Pu was biased low. Originally, a value of 41.3 $L \cdot mol^{-1} \cdot cm^{-1}$ was used for the Pu(III) extinction coefficient at 600 nm, which was taken from the literature.[3] Subsequently, a value of 36.6 $L \cdot mol^{-1} \cdot cm^{-1}$ was applied to the spectrophotometric data. The latter value for the extinction coefficient was determined at PNNL using a solution produced by dissolving a known quantity of a Pu metal standard, and it is consistent with other reports.[4] With this adjustment, much more reasonable values for the PuO_2 yields were obtained (Table 8). However, the implication was that the Pu concentrations in the Pu (III) feed solutions were somewhat higher than the targeted values.

Table 8 Summary of Runs with Apparently High Pu Concentrations

Run #	Target Pu Concentration, g/L	Estimated Pu Concentration, g/L[a]	Measured Pu Concentration, g/L[b]	PuO_2 Yield, %
6	50	55.9	50.2	99
12	50	56.5	54.0	96
13	10	11.3	10.0	99
14	50	57.0	50.2	98

[a] Determined based on spectrophotometric analysis of the Pu stock solution.

[b] Determined by spectrophotometric analysis of the adjusted Pu (III) feed solution.

Column 3 of Table 8 lists the Pu concentrations in the adjusted Pu(III) solutions from runs 6, 12, 13, and 14 based on the spectrophotometrically-determined Pu concentrations in the stock solutions used (using the ε_{600} value of 36.6 $L \cdot mol^{-1} \cdot cm^{-1}$). As expected based on initially determined high PuO_2 yields, the Pu concentrations were all ~11% higher than the target values for these four runs. A complicating feature to this story is the results of the spectrophotometric determination of the Pu concentration in the adjusted Pu (III) feeds (also presented in Table 8, Column 4). With the exception of run 12, these results indicated good agreement with the targeted Pu concentrations. However, the spectrophotometric analyses of these solutions were complicated by the presence of a yellow-colored species formed from the oxidation of ascorbic acid. Although baseline corrections to the spectra were made for this species, it did introduce additional uncertainty in the measurement. Based on this, along with the observed high yields of PuO_2, the values listed in column 3 of Table 8 are viewed as the more reliable values for the Pu concentration during these four Pu (III) oxalate runs.

4.4 Free Oxalic Acid Concentration Off Target

Upon reviewing the test instruction for Run 24, an error was discovered in the calculation to determine the amount of 0.9 M $H_2C_2O_4$ required to yield a 0.2 M excess in the final reaction mixture. Recalculation based on the actual amount of 0.9 M $H_2C_2O_4$ added indicated that the oxalic acid excess was actually 0.14 M, rather than 0.2 M.

5.0 Summary

Seventy-six PuO_2 specimens were successfully prepared as part of the statistical design study for developing Pu processing signatures. The PuO_2 specimens were prepared from purified Pu nitrate solutions. The Pu (III) oxalate route was used in all cases. The yield of PuO_2 ranged from 64% to essentially quantitative. A number of deviations from the original plan occurred, especially in the early days of the project. These deviations are documented in this report. Various analyzes of these samples are planned, the results of which will be reported separately, when they are available.

6.0 References

1. Lumetta, G. J.; Buck, E. C.; Carter, J. C.; Casella, A. J.; Clark, R. A.; Corbey, J. F.; Edwards, M. K.; McNamara, B. K.; Meier, D. E.; Parker, C. M.; Pellegrini, K. L.; Rapko, B. M.; Sinkov, S. I.; Sweet, L. E.; Tingey, J. M. *Bench-Scale System for Preparing Plutonium Oxide Samples: Description and Initial Hot Run*; PNNL-25549; Pacific Northwest National Laboratory: Richland, Washington, 2016.

2. Lumetta, G. J.; Meier, D. E.; Tingey, J. M.; Casella, A. J.; Delegard, C. H.; Edwards, M. K.; Orton, R. D.; Rapko, B. M.; Smart, J. E. *Design of the Laboratory-Scale Plutonium Oxide Processing Unit in the Radiochemical Procesing Laboratory*; PNNL-24205; Pacific Northwest National Laboratory: Richland, Washington, 2015.

3. Kim, S.-Y.; Asakura, T.; Morita, Y. Electrochemical and spectroscopic studies of Pu(IV) and Pu(III) in nitric acid solutions. J. Radioanal. Nucl. Chem. **2013,** *295,* 937-942.

4. Hagan, P. G.; Miner, F. J. *Spectrophotometric Determination of Plutonium III, IV, and VI in Nitric Acid Solutions*; RFP-1391; The Dow Chemical Company Rocky Flats Division: Golden, Colorado, 1969.

Pacific Northwest
NATIONAL LABORATORY

www.pnnl.gov

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

U.S. DEPARTMENT OF
ENERGY