Compendium of Phase-I Mini-SHINE Experiments

Nuclear Engineering Division

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by

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CONTENTS

ABSTRACT.....	1
1 INTRODUCTION	2
2 EXPERIMENTAL DESCRIPTION.....	5
2.1 Linac	5
2.1.1 Beam-Line Configuration	6
2.1.2 Beam Position Monitoring and Tuning.....	6
2.2 Photo-neutron Target	7
2.2.1 Target Design.....	8
2.2.2 Cooling Systems Design.....	9
2.3 The Target-Solution Vessel	12
2.3.1 Solution Vessel Design	13
2.3.2 Solution Handling.....	14
2.3.3 Storage “Dump” Tank.....	17
2.4 Irradiations	19
2.4.1 Irradiation #1 (02/23/2015).....	19
2.4.2 Irradiation #2 (03/04/2015).....	21
2.4.3 Irradiation #3. (04/13/2015).....	21
2.4.4 Irradiation #4 (04/24/2015).....	23
2.4.5 Irradiation #5 (05/19/2015).....	24
2.4.6 Irradiation #6 (09/27/2015).....	27
2.4.7 Irradiation #7 (10/03/2015).....	28
2.4.8 Irradiation #8 (10/14/2015).....	29
2.5.10 Irradiation #9 (10/25/2015).....	31
2.5 Concluding Remarks.....	32
3 ANALYSIS OF RADIOLYSIS GASES	34
3.1 Experimental Set-up.....	35
3.2 Analytical Data	38
3.2.1 Phase-1 Experiment: Uranium Sulfate Irradiation (2/23/15).....	39
3.2.2 Phase-1 Experiment: Uranium Sulfate Irradiation (3/4/15).....	41
3.2.3 Phase-1 Experiment: Uranium Sulfate Irradiation (4/13/15).....	44
3.2.4 Phase-1 Experiment: Uranium Sulfate Irradiation (4/24/15).....	46
3.2.5 Phase-1 Experiment: Uranium Sulfate Irradiation (5/19/15).....	48
3.2.6 Phase-1 Experiment: Uranium Sulfate Irradiation (9/27/15).....	50
3.2.7 Phase-1 Experiment: Uranium Sulfate Irradiation (10/14/15).....	52
3.3.8 Phase-1 Experiment: Uranium Sulfate Irradiation (10/25/15).....	53
3.2.9 Phase-1 Experiment: Uranium Sulfate Irradiation (12/02/15).....	56
3.3 Summary	57

CONTENTS (Cont.)

4	TARGET-SOLUTION MONITORING AND PROCESSING	59
4.1	Introduction.....	59
4.2	Experimental.....	60
4.2.1	Target-Solution Monitoring Glovebox	60
4.2.2	Molybdenum Recovery Glovebox.....	61
4.2.3	LabVIEW System	61
4.2.4	Gamma Counting.....	64
4.3	Results.....	65
4.3.1	Mini-SHINE Irradiation #1	65
4.3.2	Mini-SHINE Irradiation #2.....	71
4.3.3	Mini-SHINE Irradiation #3.....	76
4.3.4	Mini-SHINE Irradiation #4.....	81
4.3.5	Mini-SHINE Irradiation #5.....	86
4.3.6	Mini-SHINE Irradiation #6.....	89
4.3.7	Discussion on Mo-Recovery Column Results	96
4.3.8	Mini-SHINE irradiation #1- No Processing	96
4.3.9	Mini-SHINE Irradiation #2: No Processing	98
4.3.10	Mini-SHINE Irradiation #3: No Processing	98
5	CONCENTRATION AND PURIFICATION OF THE MO PRODUCT	101
5.1	Experimental Design Features of Bigfoot Hot Cell.....	101
5.2	Concentration Column Design and Operation.....	105
5.3	LEU Modified Cintichem Process	107
5.4	Experimental.....	109
5.4.1	Chemicals.....	109
5.4.2	LEU Modified Cintichem Process	111
5.4.3	Gamma Counting.....	116
5.5	Results and Discussion	118
5.5.1	Mini-SHINE #1.....	118
5.5.2	Mini-SHINE #2.....	121
5.5.3	Mini-SHINE #3.....	124
5.5.4	Mini-SHINE #4.....	127
5.5.5	Mini-SHINE #5.....	131
5.5.6	Mini-SHINE #6.....	134
5.6	Summary	137
	REFERENCES	139

CONTENTS (Cont.)

APPENDIX A: THERMAL HYDRAULIC ANALYSIS OF THE TANTALUM TARGET ASSEMBLY	A-1
A.1 Introduction.....	A-1
A.2 Overall Hydraulic Analysis.....	A-2
A.3 Thermal Hydraulic Analysis of the Target	A-5
A.4 Conclusion	A-7
APPENDIX B: SUMMARY OF FEA RESULTS FOR THE STAINLESS STEEL PROCESS VESSEL FOR 99MO ISOTOPE PRODUCTION	B-1
B.1 Geometry, Material, and Loads	B-1
B.2 Failure Criteria	B-1
B.3 Method of Reinforcing Vessel	B-1
B.4 Results.....	B-1
APPENDIX C: THERMAL HYDRAULIC ANALYSIS OF THE REACTION VESSEL.....	C-1
C.1 Introduction.....	C-1
C.2 Thermal Hydraulic Analysis Description – Reaction Vessel	C-3
C.3 Results and Conclusions - Reaction Vessel	C-4
C.4 Thermal Hydraulic Analysis Description – Return Heat Exchanger.....	C-6
APPENDIX D: CONCENTRATION COLUMN PROCEDURE.....	D-1
APPENDIX E: LEU MODIFIED CINTICHEM PROCESS	E-1

FIGURES

1.1	Flow Diagram of the Mini-SHINE Experiment	3
2.1	Beam Energy versus Pulse Current for Fully Upgraded Linac. Measurements were taken at 20 kW RF power per modulator. The maximum average beam power, 25kW, is achieved at 30-MeV beam energy, 240-Hz pulse rate, and 5.5- μ s pulse width.....	5
2.2	Beamline Configuration for Mini-SHINE Phase 1 Irradiations	6
2.3	End of the Beamline Leading to the Ta Photo-neutron Target. The long collimator electrically isolated from the rest of beamline allowed reliable positioning of the beam on the target. Later, an OTR detection system was incorporated to provide even better reproducibility.	7

FIGURES (Cont.)

2.4	Photonuclear Cross Sections for Ta. Peak for the neutron production corresponds to 16 MeV photon energy.....	8
2.5	Tantalum Target Drawings.....	9
2.6	Temperature Distribution in Ta Target Heated with 10-kW Electron Beam	10
2.7	P/I Diagram of the Cooling System.....	11
2.8	Cut-away View of the Shielded Box with Target Solution Vessel and Tantalum Target.....	12
2.9	Shielded Box for Containment and the Target-Solution Vessel	13
2.10a	Target-Solution Vessel Assembly: Vessel	15
2.10b	Target-Solution Vessel Assembly: Top Flange.....	16
2.11	ANSYS CFX Temperature Contour Results at Mid-plane	17
2.12	Shielded Storage “Dump” Tank for Uranyl Sulfate Solution	18
2.13	Beam Power History for Irradiation #1. First 30 min is not shown on the graph. Fast Current Transformer signal refers to beam current monitor located before first 10° magnet and FTC#1 to the signal before second 10° magnet. Good agreement between two FTC signals indicates efficient beam transfer up to second 10° bending magnet. For this irradiation ~10% of the beam was lost on collimator, which explains difference in beam powers from this figure and Table 2.2.	20
2.14	Beam Power History for First Part of Irradiation #5. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet.....	25
2.15.	Beam Power History for the Second Part of Irradiation #5. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet.	27
2.16	Beam Power History for Irradiation #7. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet.	29
2.17	Beam Power History for Irradiation #8. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet.....	30

FIGURES (Cont.)

2.18	Beam Power History for First Part of Irradiation #8. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet. Beam interruption in the middle of irradiation corresponds to shut down for replacement of the relay in the interlock chain. Beam-off time was cut out from the figure to make figure more compact.	32
3.1	Diagram of the Solution Vessel and Analytical and Gas Collection System.....	35
3.2	Mini-SHINE Gas-Analysis Cabinet	36
3.3	Diagram of the Gas Collection System	37
3.4	Photograph of the Gas Collection System. When in use the cabinet door is closed.....	38
3.5	Hydrogen, Oxygen, and Beam Power Plotted as a Function of Time (2/23/15).....	40
3.6	Hydrogen Measured Plotted as a Function of Time (2/23/15)	41
3.7	Hydrogen Measured as a Function of Beam Energy (2/23/15).....	41
3.8	Hydrogen and Oxygen Concentrations and Beam Power as a Function of Time (3/4/15)	42
3.9	Hydrogen Plotted as a Function of Time (3/4/15).....	43
3.10	Hydrogen Measured as a Function of Beam Energy (3/4/15).....	43
3.11	Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (4/13/15, Part 1).....	44
3.12	Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (4/13/15, Part 2).....	45
3.13	Hydrogen Plotted as a Function of Time (4/13/15, Part 1)	45
3.14	Hydrogen as a Function Beam Energy (4/13/15, Part 1).....	46
3.15	Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (4/24/15, Part 1).....	47
3.16	Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (4/24/15, Part 2).....	47
3.17	Hydrogen as a Function of Time (4/24/15, Part 1).....	48

FIGURES (Cont.)

3.18	Hydrogen as a Function of Beam Energy (4/24/15).....	48
3.19	Hydrogen Content, Oxygen Content, and Beam Power as a Function of Time (5/19/15)	49
3.20	Hydrogen as a Function of Time (5/19/15)	49
3.21	Hydrogen as a Function of Beam Energy (5/19/15).....	50
3.22	Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (9/27/15)	50
3.23	Hydrogen as a Function of Time (9/27/15)	51
3.24	Hydrogen as a Function of Beam Energy (9/27/15).....	51
3.25	Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (10/14/15)	52
3.26	Hydrogen Production as a Function of Time (10/14/15).....	53
3.27	Hydrogen as a Function of Beam Energy (10/14/15).....	53
3.28	Hydrogen and Oxygen Concentrations and Beam Power as a Function of Time (10/25/15, Part 1).....	54
3.29	Hydrogen and Oxygen Concentrations and Beam Power as a Function of Time (10/25/15, Part 2).....	54
3.30	Hydrogen Production as a Function of Time (10/25/15, Part 1)	55
3.31	Hydrogen as a Function of Beam Energy (10/25/15, Part 1)	55
3.32	Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (12/2/15)	56
3.33	Hydrogen Production as a Function of Time (12/2/15).....	56
3.34	Hydrogen as a Function of Beam Energy (12/2/15).....	57
4.1	Photos of Target-Solution Monitoring Glovebox. The turbidity cell, conductivity cell, and pH electrode can be seen in A. Photo B shows a close-up of the target- solution monitoring glovebox.....	60
4.2	Photos of the Mo-Recovery Glovebox and the Remote-Controlled Equipment Installed	62

FIGURES (Cont.)

4.3.	Screen Capture of the Data Acquisition and Remote Control Program Written in the LabVIEW Environment.....	63
5.1	Bigfoot Hot Cell, Where Final Purification of ^{99}Mo is Performed	101
5.2	Transfer Cask Previously Used to Transfer ^{99}Mo Product from Recovery Column to Bigfoot.....	102
5.3	White Glovebox Previously Used to Connect the Transfer Cask to Interior of Bigfoot.....	103
5.4	Image of Interior of Bigfoot and Mini-SHINE Concentration Column, Column Control Board, Acidification Vessel, pH Probe, Reagent Vial, and Valves for Exterior Solution Line	104
5.5	Image of Quick-connect System: Gas Compressed Gas Connection Exhaust Valve Connecting to Gas Collection System, and Water In/Out	105
5.6	Schematic Diagram of ^{99}Mo Concentration Column	106
5.7	Alpha-benzoin Oxime	107
5.8	Scheme of LMC Process for Purification of ^{99}Mo from Fission Products.....	108
5.9	Drawing of Two-Sided Bottle, Plastic Coated	112
5.10	Drawing of One-Sided Bottle, Plastic Coated.....	113
5.11	Drawing of Fritted Bottle for Filtration of Mo-ABO Precipitate	113
5.12	Drawing of Short Fritted Column Used for Charcoal Vent during Dissolution of Mo-ABO Precipitate.....	114
5.13	Drawing of Long Fritted Column Used for Combination Column	114
5.14	Iodine Filtration in LMC Process	115
5.15	Filtration of Mo-ABO Precipitate in LMC Process	116
5.16	Photograph of White Precipitate That Formed after Acidification of Product from Concentration Column Just Before Start of LMC.....	119
5.17	Stripping of Mo from Sachtopore Sorbent with 1 M and 0.1 M NaOH.....	125
5.18	Photograph of Black Precipitate That Formed after Precipitation of Mo with ABO.....	131

FIGURES (Cont.)

A.1	Ta Target Design	A-1
A.2	Hydraulic “Fathom” Model	A-2
A.3a	“Fathom” Output	A-3
A.3b	“Fathom” Output	A-3
A.3c	“Fathom” Output	A-4
A.3d	“Fathom” Output	A-4
A.3e	“Fathom” Output	A-5
A.4	“ANSYS CFX” Meshed Model of Target and Surrounding Flow Channel	A-6
A.5	“ANSYS CFX” Temperature Results	A-6
A.6	“ANSYS CFX” Vector Flow Field in Coolant Channel Result	A-7
B.1	Plot of Stress for Entire Vessel. Overall, stress is well below the allowable. The maximum value shown in the legend occurs at a displacement constraint and can be safely disregarded. The actual high stress regions occur where the rods connect to the top and bottom of the vessel.	B-2
B.2	Plot of Stress for the Added Plates at the Top of the Vessel. This plot is intended to illustrate the location shown in the next figure.	B-3
B.3	A Closer Look at the Plates That Reinforce the Rod Connection Points at the Top of the Vessel. The maximum membrane plus bending stress is 18.8 ksi, which is well below the allowable of 25 ksi.	B-3
B.4	Plot of Stress for the Added Plates at the Bottom of the Vessel. This plot is intended to illustrate the location shown in the next figure.	B-4
B.5	A Closer Look at the Plates That Reinforce the Rod Connection Points at the Bottom of the Vessel. The maximum membrane plus bending stress is 20.9 ksi, which can be seen more clearly in the next figure that looks from underneath.	B-4
B.6	A View of the Rod Connections at the Bottom of the Vessel, Viewed from Underneath. The maximum stress in the reinforcement plates is 20.9 ksi, which is below the allowable stress of 25 ksi.	B-5
C.1	Design of the Reaction Vessel Assembly	C-1
C.2	Design of the Reaction Vessel Inner Sub-assembly	C-2

FIGURES (Cont.)

C.3	Design of the Blind Closure Flange with Heat Exchangers	C-2
C.4	ANSYS CFX Meshed Geometry Model of the Reaction Vessel Assembly	C-4
C.5	ANSYS CFX Temperature Contour Results at Mid-plane	C-5
C.6	ANSYS CFX Vector Velocity Field at Mid-plane.....	C-5
D.1	Flowchart.....	D-3

TABLES

1.1	Mini-SHINE Irradiations Performed with a LEU Solution as Uranyl Sulfate	4
2.1	Summary of Beam Parameters of Mini-SHINE Irradiations	19
2.2	The Time Table of Irradiation #1. Beam energy was 35.0 ± 0.5 MeV.	20
2.3.	The Time Table of Irradiation #2. Beam energy was 35.0 ± 0.5 MeV.	21
2.4	The Time Table of Irradiation #3. Beam energy was 35.0 ± 0.5 MeV.	22
2.5.	The Time Table of Irradiation #4. Beam energy was 37.0 ± 0.8 MeV.	23
2.6	The Time Table of Irradiation #5. Beam energy was 35.0 ± 1.0 MeV.	24
2.7.	The Time Table of Irradiation #5. Beam energy was 35.0 ± 0.8 MeV.	26
2.8.	The Time Table of Irradiation #6. Beam energy was $E = 34.0 \pm 0.5$ MeV.....	28
2.9.	The Time Table of Irradiation #7. Beam energy was $E = 34.5 \pm 0.4$ MeV.....	28
2.10	The Time Table of Irradiation #8. Beam energy was $E = 35.2 \pm 0.7$ MeV.....	30
2.11	The Time Table of Irradiation #9. Beam energy was $E = 35.0 \pm 0.7$ MeV.....	31
3.1	Summary Data of Hydrogen Production	58
4.1	List of Nuclides, Their Half-life, Gamma Peak Used for Analysis, and Branching Ratio at the Corresponding Energy Analyzed	64
4.2	Mini-SHINE Irradiations Performed with a LEU Solution as Uranyl Sulfate	65

TABLES (Cont.)

4.3	Activities of Isotopes in the Various Samples Collected with Their 1 σ Values for Irradiation #1.....	67
4.4	Gamma Counting Results for the Feed Solution and Strip Samples with Their 1-Sigma Values for Irradiation #1	69
4.5	Activities of Isotopes and 1-Sigma Values for the Feed, Column Effluent, and Acid Wash Samples for Irradiation #2	72
4.6	Activities and 1-Sigma Values for the Isotopes Found in the Feed and Strip Samples for Irradiation #2	74
4.7	Activities of Isotopes and 1-Sigma Values for the Feed, Column Effluent, and Acid Wash Samples for Irradiation #3	77
4.8	Gamma Counting Results and 1-Sigma Values for the Feed Solution and Strip Samples for Irradiation #3	79
4.9	Isotope Activities and 1-Sigma Values for the Feed, Column Effluent, and Acid Wash Samples for Irradiation #4	82
4.10	Gamma Counting Results for the Feed Solution and Strip Samples along with 1-Sigma Values Shown under Activity Values for Irradiation #4.....	84
4.11	Gamma Counting Results and 1-Sigma Values for the Feed Solution and Strip Samples for Irradiation #5	87
4.12	Activities of Isotopes and Corresponding 1-Sigma Values for the Feed, Column Effluent, and Acid Wash Samples for Irradiation #6	90
4.13	Gamma Counting Results and 1-Sigma Values for the Feed Solution, NaOH Wash, and Strip Samples for Irradiation #6	93
4.14	Gamma Counting Results for the Irradiation on 05/21/15	97
4.15	Gamma Counting Results for the Irradiation on 09/27/15	99
4.16	Gamma Counting Results for the Irradiation on 10/03/15	100
5.1	List of Nuclides, Their Peak Energies, and Half-Lives.....	117
5.2	Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #1	118
5.3	Activities Detected in Concentration Column Fractions and Calculated at EOB in Run #1	119

TABLES (Cont.)

5.4	Distribution of Mo and I in Various Fractions of Concentration Column in Run #1	120
5.5	Activities Detected in LMC Fractions Calculated at EOB in Run #1	120
5.6	Distribution of Mo, Ru, I, and Sb in Various Fractions of LMC in Run #1	121
5.7	Radionuclidic Purity in ⁹⁹ Mo Product Solution from LMC Process Calculated at 36 hr after EOB in Run #1	121
5.8	Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #2	121
5.9	Activities Detected in Concentration Column Fractions Calculated at EOB in Run #2	122
5.10	Distribution of Mo, Ru, I, and Sb in Various Fractions of Concentration Column in Run #2	122
5.11	Activities Detected in LMC Fractions Calculated at EOB in Run #2	123
5.12	Distribution of Mo, Ru, I, and Sb in Various Fractions of LMC in Run #2	123
5.13	Radionuclidic Purity in ⁹⁹ Mo Product Solution from the LMC Process Calculated at 36 hr after EOB in Run #2	124
5.14	Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #3	124
5.15	Activities Detected in Concentration Column Fractions and Calculated at EOB in Run #3	125
5.16	Distribution of Mo, Ru, I, Rh, Sn, and Sb in Various Fractions of Concentration Column in Run #3	126
5.17	Activities Detected in LMC Fractions and Calculated at EOB in Run #3	126
5.18	Distribution of Mo, Ru, I, Zr, Rh, and Sn in Various Fractions of LMC in Run #3 ...	127
5.19	Radionuclidic Purity in ⁹⁹ Mo Product Solution from the LMC Process Calculated at 36 hr after EOB in Run #3	127
5.20	Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #4	128
5.21	Activities Detected in Concentration Column Fractions and Calculated at EOB in Run #4	128

TABLES (Cont.)

5.22	Distribution of Zr, Mo, Ru, I, Rh, and Sb in Various Fractions of Concentration Column in Run #4	129
5.23	Activities Detected in LMC Fractions and Calculated at EOB in Run #4	129
5.24	Distribution of Mo, Ru, I, and Sb in Various Fractions of LMC in Run #4	130
5.25	Radionuclidic Purity in ⁹⁹ Mo Product Solution from the LMC Process Calculated at 36 hr after EOB in Run #4.....	131
5.26	Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #5	131
5.27	Activities Detected in Concentration Column Fractions and Calculated at EOB in Run #5	132
5.28	Distribution of Mo, Ru, I, Rh, Sn, and Sb in Various Fractions of Concentration Column in Run #5	133
5.29	Activities Detected in LMC Fractions and Calculated at EOB in Run #5	133
5.30	Distribution of Zr, Nb, Mo, Ru, I, and Sb in Various Fractions of LMC in Run #5...	133
5.31	Radionuclidic Purity in ⁹⁹ Mo Product Solution from the LMC Process Calculated at 36 hr after EOB in Run #5.....	134
5.32	Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #6	134
5.33	Activities Detected in Concentration Column Fractions Calculated at EOB in Run #6	135
5.34	Distribution of Zr, Mo, Ru, I, La, and Sb in Various Fractions of Concentration Column in Run #6	136
5.35	Activities Detected in LMC Fractions and Calculated at EOB in Run #6	136
5.36	Distribution of Mo, Ru, I, Zr, and Sn in Various Fractions of LMC in Run #6.....	137
5.37	Radionuclidic Purity in ⁹⁹ Mo Product Solution from LMC Process Calculated at 36 hr after EOB in Run #6.....	137
5.38	Distribution of I-131 and Ru-103 in Key Fractions of CC and LMC Process and Total Mo-99 Yield for Both Processes in All Mini-SHINE Runs.....	138

COMPENDIUM OF PHASE-I MINI-SHINE EXPERIMENTS

ABSTRACT

Argonne National Laboratory is assisting SHINE Medical Technologies in their efforts to develop the technology to become a domestic Mo-99 producer using low-enriched uranium (LEU). Mini-SHINE experiments are being performed with the high-current electron linear accelerator (linac) at Argonne. The target solution is a 90-150 g-U/L LEU uranyl sulfate at pH 1. In Phase 1, the convertor was tantalum with a maximum beam power on the convertor of 10 kW, and the target solution was limited to 5 L. This configuration generated a peak fission power density of 0.05 W/mL. Nine experiments were performed between February and October 2015. Results are reported and discussed for each experiment regarding the off-gas analysis system, the sampling and Mo-recovery operation, and the Mo-product concentration and purification system. In Phase 2, the convertor will be depleted uranium; beam power will increase to 20 kW; and the solution volume will be 18 L. This configuration will generate a fission power density of up to 1 W/mL.

1 INTRODUCTION

Under the National Nuclear Security Administration's Material Management and Minimization (M³) Program [HOWELL-2015], Argonne National Laboratory is assisting SHINE Medical Technologies in their efforts to develop the technology to become a domestic Mo-99 producer using low enriched uranium (LEU). Molybdenum-99 is of interest because it is the parent isotope of technetium-99m, which is the most widely used isotope in diagnostic nuclear medicine procedures.

The major development effort at Argonne to assist in SHINE technology development is the mini-SHINE experiment. The mini-SHINE experimental setup includes an electron linac and electron/X-ray/neutron convertor, a shielded cell that houses the target-solution vessel, a gas collection and analysis system, glove boxes containing a target-solution-sampling and Mo-recovery systems, and a separate hot cell used for the Mo-product concentration and purification process. Samples are collected following irradiation and during the initial Mo-recovery process, and all secondary purification steps are performed in a separate hot cell. Samples collected during all processing steps are retrieved and gamma counted to determine Mo-recovery yields, fission-product partitioning, and product purity. Figure 1.1 is a high-level schematic of the experiment.

SHINE's technology produces Mo-99 by neutron-induced fission of LEU in a sub-critical aqueous solution. SHINE will produce primary neutrons by the collision of a beam of deuterium (D) ions with a tritium (T) gas target; these high-energy neutrons will induce fission in the U-235 in solution [PITAS-2014]. Fission-produced Mo-99 can be extracted from the aqueous solution and purified. Argonne's mini-SHINE was developed to (1) provide insight into radiolytic gas generation and an understanding of the solution chemistry under operating conditions, (2) develop the Mo-recovery and purification system, and (3) provide samples of Mo-99 produced by the proposed SHINE technology to technetium-generator manufacturers for testing.

Mini-SHINE experiments are being performed using the high-current electron linear accelerator (linac) at Argonne. This linac can provide electron-beam energies of up to 50 MeV and deposited power on a target of up to 30 kW. Mini-SHINE experiments use an electron/x-ray/neutron convertor to produce neutrons that will produce fission in the target solution. The target solution is a 90-150 g-U/L LEU uranyl sulfate at pH 1. In Phase 1, the convertor was tantalum with a maximum beam power on the convertor of 10 kW, and the target solution was limited to 5 L. This configuration generated a peak fission power density of 0.05 W/mL. In Phase 2, for which experimental equipment is currently being installed, the convertor will be depleted uranium; beam power will increase to 20 kW; and the solution volume will be 18 L. This configuration will generate a fission power density of up to 1 W/mL. Several interim reports have been published on mini-SHINE development [CHEMERISOV-2011,-2012, YOUKER-2013, -2015, ROTSCH-2014, KALENKY-2014].

FIGURE 1.1 Flow Diagram of the Mini-SHINE Experiment

In Phase 1, approximately 5 liters of pH 1 uranyl sulfate solution was irradiated in nine runs at the linac. Irradiation varied from 2 hours to ~40 hours (total time of beam on target). Full processing was completed for six of the nine uranyl sulfate irradiations. Full processing includes:

- Passing the irradiated uranyl sulfate solution through a titania Mo-recovery column, washing the column with sulfuric acid and then water, and stripping the Mo from this column in base solution.
- Acidifying the Mo-product with nitric acid and passing it through a second titania column¹ (concentration column), followed by nitric-acid and water washes, and stripping the Mo from the column using an alkaline solution.

¹ In one irradiation, the concentration column was an anion-exchange column, which eliminated the two acidification steps but provided poor Mo yield.

- After acidification with nitric acid, purifying the product using the LEU-Modified Cintichem process.

Irradiations with processing were completed for four runs with 93.7 g-U/L and two runs with 149 g-U/L solution. Particulars of each irradiation are shown in Table 1.1.

This report is divided into sections that (1) describe the linac, the convertor, the target solution vessel and containment, and the conditions for each irradiation, (2) present and discuss results obtained in the off-gas analysis system, (3) describe the operation and discuss results from the sampling and Mo-recovery operation, and (4) present and discuss results from the Mo-product concentration and purification system. Each section will describe conditions and results of the individual mini-SHINE experiments. The last section will provide an overview of the results with discussion and conclusions.

TABLE 1.1 Mini-SHINE Irradiations Performed with a LEU Solution as Uranyl Sulfate

Irradiation Number	Date of Irradiation	Uranium Concentration	
		(g-U/L)	Processing
1	2/23/2015	93.7	Yes
2	3/4/2015	93.7	Yes
3	4/20/2015	93.7	Yes
4	4/26/2015	93.7	Yes
5	5/21/2015	93.7	No
6	9/27/2015	149	No
7	10/3/2015	149	No
8	10/14/2015	149	Yes
9	10/26/2015	149	Yes

2 EXPERIMENTAL DESCRIPTION

2.1 LINAC

The Argonne linac was originally installed in 1969 and commissioned in 1971 with a maximum beam energy limited to 22 MeV. In 2012, the linac was upgraded in two stages. First, the average power of the RF system was increased from 10 kW per modulator (20 kW total RF power) to 25 kW per modulator (50 kW total RF power). This upgrade increased the maximum average beam power to 25 kW. In the second part of the upgrade, new accelerator structures from MEVEX Corporation (Canada) were installed, and the maximum beam energy (unloaded) was increased to 55 MeV. The beam energy as a function of pulse current for the upgraded linac at nominal operation parameters (20 kW peak RF power per klystron) is shown on Figure 2.1.

FIGURE 2.1 Beam Energy versus Pulse Current for Fully Upgraded Linac. Measurements were taken at 20 kW RF power per modulator. The maximum average beam power, 25kW, is achieved at 30-MeV beam energy, 240-Hz pulse rate, and 5.5- μ s pulse width.

2.1.1 Beam-Line Configuration

In this experiment, the accelerated electron beam is delivered to a photo-neutron target through a beam line that consists of several beam elements. The shielded enclosure housing the mini-SHINE experiment is located on the -10° line. To direct the beam to the target, it is first deflected by 10° right, then 10° left, creating an offset from the zero-degree beamline. This beamline has two pairs of quadrupole magnets (focusing elements) and a pair of correction dipole magnets. Drawings of the beamline are shown in Figure 2.2.

FIGURE 2.2 Beamline Configuration for Mini-SHINE Phase 1 Irradiations

2.1.2 Beam Position Monitoring and Tuning

Before each irradiation, the beam energy was tuned to 35 MeV, then the electron beam was transported to the target, and transport was optimized to achieve minimum loss. To achieve reliable positioning of the beam on the target, we used a long collimator, shown in Figure 2.3. The collimator was electrically isolated from the target and beam line via a dielectric break, so that current (beam losses) can be continuously monitored. Optimal positioning of the beam on the target was achieved when beam losses in the collimator were minimal. Typical beam loss on the collimator during irradiations was 5–7%. There is still a possibility of slight beam misalignment (indicated in Figure 2.3 by blue color beam trajectory). To eliminate this possibility in later experiments, we incorporated optical transition radiation (OTR) detection to verify proper beam alignment.

FIGURE 2.3 End of the Beamline Leading to the Ta Photo-neutron Target. The long collimator electrically isolated from the rest of beamline allowed reliable positioning of the beam on the target. Later, an OTR detection system was incorporated to provide even better reproducibility.

2.2 PHOTO-NEUTRON TARGET

When a high-energy incident electron beam strikes a high-Z material, the beam creates a cascade shower of lower energy electrons and bremsstrahlung photons (braking radiation). Neutrons are produced primarily by interactions of bremsstrahlung photons with target nuclei. There are two main mechanisms through which photons can be absorbed by a nucleus: giant dipole resonance (GDR) and quasi-deuteron absorption (relevant for photon energies below 150 MeV). The GDR is a collective vibrational resonance of the entire nucleus induced by an incoming photon. GDR dominates the photonuclear processes when the wavelength of the photon is comparable to the size of the nucleus, which typically occurs in the range of 12–16 MeV. Above the GDR region, photons are mostly absorbed via the quasi-deuteron absorption. In this process, photons interact with the dipole moment of a correlated neutron–proton pair inside the nucleus. Photonuclear cross sections for the Ta target from evaluated Nuclear Data File database (ENDF/B-VII, <http://www.nndc.bnl.gov/endl/b7.1>) are shown in Figure 2.4. Neutron yields for photo-neutron targets were discussed in detail previously [MAKARASHVILI-2012]. We calculated that, for our linac, the most efficient beam energy for neutron generation is 35 MeV.

FIGURE 2.4 Photonuclear Cross Sections for Ta. Peak for the neutron production corresponds to 16 MeV photon energy.

2.2.1 Target Design

While tantalum has a very high melting point (3020°C), the stainless steel target housing had to be cooled to maintain a vacuum in the beamline. We utilized water cooling for the target and target housing. One of the challenges for this small target is to be able to dissipate heat generated in the target without water boiling at the tantalum surface. The target assembly is shown in Figure 2.5. The coolant water at 20°C enters the assembly through the port drilled in the side of the modified 4.5-in. CF vacuum flange. The flow is diverted 90° into half of the annular space between the inner and outer tubes; it exits on the other side. The two flow channels are separated by two parallel bars that run the length of the annular space. The coolant flow passes over the Ta target's outer surface. The flow is directed to the back of the target and then is redirected back through the other half of the annular space and out through the return port in the flange. The cone configuration of the Ta is intended to distribute the beam energy over the length of the target.

FIGURE 2.5 Tantalum Target Drawings

Figure 2.6 shows the calculated temperature distribution within the Ta target. The commercial computer code ANSYS CFX was used to model the target cooling. The heat generation within the target was assumed uniform with a total power of 10 kW. While this assumption is not consistent with the actual heat distribution, the limiting factor for the cooling is heat transfer between the target material and the cooling water, which is independent of the temperature distribution in the target. An insulated boundary was assumed at the vacuum end (beam line) of the target. The forced convection coefficients between the coolant and the wetted target surfaces are inherently calculated by the CFX Code based on the calculated flow values. The resulting target temperatures are shown in Figure 2.6. The maximum temperature of 300°C is expected to be at the centerline of the target and is an acceptable operating temperature for the Ta. Also, the maximum wetted surface temperature of the target was calculated to be 77°C, which is below the boiling point of the water. More detailed information on Ta target design and associated calculations is given in Appendix A.

2.2.2 Cooling Systems Design

Initial irradiations were performed with an existing cooling system. The maximum flow rate provided by this system was 9 gpm ($5.7 \times 10^{-4} \text{ m}^3/\text{s}$), which is lower than the 10 gpm ($6.3 \times 10^{-4} \text{ m}^3/\text{s}$) used in calculations. Later, we designed and assembled a cooling system capable of high flow rates suitable for cooling of the target in Phase-2 mini-SHINE experiments.

FIGURE 2.6 Temperature Distribution in Ta Target Heated with 10-kW Electron Beam

The P/I diagram of this cooling system is shown in Figure 2.7. Constructed of 304-grade stainless steel, this system is capable of providing 43 gpm ($2.7 \times 10^{-3} \text{ m}^3/\text{s}$) cooling water flow at 40 psi ($2.8 \times 10^5 \text{ Pa}$) pressure. An existing 23 kW chiller is used for the primary-side cooling system. This cooling system is located inside an enclosure. All valves, the pump, the heat exchanger, the filters, and connections are inside to prevent leaks of potentially contaminated water. Welded coolant lines connect the target to the cooling system.

The cooling system is instrumented with pressure transducers, thermocouples, and a flow meter. It utilizes a mixed-bed deionized water cartridge to maintain high water purity and a strainer to remove any particles that could affect flow through the target. The water level in the cooling system is maintained by a make-up tank, which is equipped with a water-level measuring system that will shut down the pump if the water level drops by 0.1 m. This feature limits the maximum amount of water that can be lost due to leaking.

FIGURE 2.7 P/I Diagram of the Cooling System

2.3 THE TARGET-SOLUTION VESSEL

The mini-SHINE experiment creates a significant radiation field around the target during irradiation and for a long time after fissioning has stopped. To prevent excessive activation of the target room during irradiation and to allow access to the target room shortly after irradiation, the target vessel has been located in a lead-shielded containment cell. The electron beam enters the left side of the shielded box and strikes the convertor. The neutrons and x-rays from the convertor cause fission in the aqueous solution. Figure 2.8 is a representation of the experimental assembly inside the shielded cell and shows the cooling/reflector region surrounding the target solution, penetrations for temperature probes and neutron detectors in the solution, and the condensers at the top of the target-solution tank. The only valve inside the shielded cell is a manual one to dump the solution into a container in a shielded well in the case of equipment failure.

Figure 2.9 is a photograph of the containment box and the target-solution vessel. The containment box is constructed from lead sheets with carbon steel structural beam. Shielding of the containment box is 4-in. thick lead on all sides except the front, where the lead shielding is 8-in. thick. The leaded glass is 12-in. thick (density of 5.2 g/cm^3). Internal and external surfaces of the shielded box are covered by aluminum sheets. Aluminum was chosen because of the low activation and short half-life of the radioisotopes produced during irradiation.

FIGURE 2.8 Cut-away View of the Shielded Box with Target Solution Vessel and Tantalum Target

FIGURE 2.9 Shielded Box for Containment (left) and the Target-Solution Vessel (right)

2.3.1 Solution Vessel Design

The target solution vessel was designed per the ASME Boiler & Pressure Vessel Code, Section VIII Division 2. For 304L stainless steel, Table 5a of the code lists 16.7 ksi (115.1 MPa) as the maximum stress when only membrane stress is present, and 25 ksi (172.4 MPa) as the maximum stress for when membrane stress and bending combine. We used six rods to tie the top and bottom of the vessel together (Figure 2.10). This greatly increases the rigidity of the vessel without affecting its overall size. This also keeps the total mass of the vessel low. The rods are 1/4-in. OD tubes with a 1/32-in. wall thickness. To ensure that the rods have sufficiently strong connections to the walls of the vessel, small plates (1/8-in. thick) are added near the points of attachment. Without the added rods, high bending stresses occurred at the edges of the conical top and bottom of the vessel. Adding the rods eliminates this problem, but the connection areas require additional thickness. After strengthening the connections, the highest stress at the top of the vessel is 18.8 ksi (130 MPa), and the highest stress in the bottom of the vessel is 20.9 ksi (144.1 MPa). Both values are below the allowable stress of 25 ksi (172.4 MPa). More detailed results of the stress analysis are presented in Appendix B.

The uranyl sulfate solution in the target-solution vessel is heated due to internal heat generation caused by radiation from the Ta target and fissioning of uranium in solution. The target-solution vessel assembly is shown in Figure 2.10. The coolant water at near ambient temperature enters the reflector volume through a 1-in. tube that extends to the bottom of the vessel. The flow then circulates around in the outer vessel and discharges through a 1-in. tube at the top of the vessel. The inner vessel that contains the uranyl sulfate solution is immersed in the coolant flow in the outer vessel. The solution in the inner vessel is isolated from the reflector coolant flow, and heat transfer is by convection and conduction through the wall of the inner vessel. There is a top flange that mates to the flange at the top of the inner vessel. There are small

instrumentation penetrations as well as a small hydrogen re-combiner with heat exchangers that are mounted on this flange. The top flange is shown in the Figure 2.10a and b. The return heat exchanger on the top flange is analyzed in the attached report (Appendix C) following the target-solution vessel analysis. The inner vessel is essentially a closed vessel with a relief valve. The inner vessel fluid has no forced convection, and heat transfer from the uranium solution to the inner vessel wall is completely by natural convection (i.e., fluid motion is driven by temperature differences within the fluid). Also, convective heat transfer from the outside of the inner vessel to the coolant flow in the outer vessel is mostly by natural convection due to the low flow velocities in the outer vessel. A thermal hydraulic analysis was first performed to assure that the process fluid remains below its boiling point at atmospheric pressure.

Heat generating profiles for the solution volume were input to the ANSYS CFX model. An insulated boundary was assumed at the outer surface of the outer vessel. Also, the top surface of the process fluid was assumed to be insulated. The properties of the coolant in the outer vessel were based on water at ambient conditions. Also, for this case, the process fluid was assumed to have water properties at 1 atm pressure. All stainless steel walls were considered to have negligible heat capacity and thermal resistance. The forced and natural convection coefficients at the inner vessel wall surfaces are calculated by the CFX code based on the calculated flow field and fluid temperatures.

First results showed essentially no stable steady-state solution to this model. This condition is due to buoyancy within the fluid and the associated temperature differences. Therefore, a transient run was performed over a significant period until the average temperature and the maximum temperature within the process fluid became relatively constant ($t=100$ s starting from the unstable steady-state solution). A temperature contour plot at this time is shown in Figure 2.11. The plot indicates that the maximum process fluid temperature is 144°F (62.2°C). Also, the calculated mass average temperature of the fluid is 111°F (43.9°C). These results verify that the process fluid is significantly below the boiling point of the assumed water.

2.3.2 Solution Handling

During irradiation, the uranyl sulfate solution was continuously sampled (circulated) in the solution-monitoring glovebox. The solution was drawn from the 1/4-in. line located at the bottom of the inner vessel, pumped through sample-collection loops, and returned to the vessel through a penetration in the top flange. After completion of the irradiation, the solution was transferred to the dump tank via the emergency dump valve (gravity feed) to achieve better mixing of the solution, and then it was moved back to irradiation vessel. After the solution was returned to the irradiation vessel, it was pumped through the Mo-recovery column. The uranyl sulfate solution, minus the molybdenum and other solution components adsorbed on the column, was returned to the dump tank for storage and reuse in consecutive irradiations.

FIGURE 2.10a Target-Solution Vessel Assembly: Vessel

FIGURE 2.10b Target-Solution Vessel Assembly: Top Flange

FIGURE 2.11 ANSYS CFX Temperature Contour Results at Mid-plane

2.3.3 Storage “Dump” Tank

Between irradiations, the uranyl sulfate solution was stored in the dump tank. Drawings of the dump tank are shown in Figure 2.12. The dump tank has an inner and outer container. Both containers of this tank are manufactured from 304L stainless steel. The internal vessel has a 30-L internal volume to accommodate 20 L solution volume planned for phase-2 experiments. The inner tank is connected to the target-solution vessel, process glovebox, and gas collection system using 1/4-in. stainless steel tubing. The primary container is positioned on top of the load cells to measure the solution mass in the dump tank. The primary solution vessel is enclosed inside the secondary containment vessel. The volume of the containment vessel is large enough to accommodate 20 L of solution if it escapes from the primary containment. The secondary containment vessel is connected to the bottom of the shielded cell via a Z-shaped enclosure to maintain continuous double encapsulation of the uranyl sulfate solution. Tubing for liquid and gas transfers from the dump tanks is double-valved to allow removal and replacement of the dump tank without release of the radioactive gases or liquid. Primary and the secondary volumes of the dump tank are located inside 6-in. lead shielded cask to reduce dose to personnel and allow fast access to the irradiation room after irradiation. A lead thickness of 6 in. was chosen based on a dose rate of less than 1 mR/h at 30 cm from the surface of the shielded cask for freshly irradiated solution.

FIGURE 2.12 Shielded Storage “Dump” Tank for Uranyl Sulfate Solution

2.4 IRRADIATIONS

In the phase-1 mini-SHINE experiment, we conducted multiple irradiations varying in time of irradiation and power on the target. Typical parameters for irradiation were beam energy of 35 MeV and maximum beam power on the target of 10 kW. These parameters were picked during the design phase and correspond to high efficiency for accelerator operation and photo-neutron production and maximum power that can be safely dissipated in the Ta target. Table 2.1 summarizes the irradiation conditions for the phase-1 experiments. Specifics for each of the nine irradiations follow.

TABLE 2.1 Summary of Beam Parameters of Mini-SHINE Irradiations

Start Date	Beam Energy (MeV)	Maximum Repetition Rate (Hz)	Maximum Average Current (μ A)	Maximum Average Power (kW)	Irradiation Time at Full Power (hr)
2/23/2015	35.2	100	203.0	7.15	2
3/04/2015	35.0	100	218.0	7.6	7.33
4/13/2015	35.0	130	269.5	9.4	23.22
4/24/2015	37.0	130	267.0	9.8	6.41
5/19/2015	35.0	120	280.0	9.8	12.1
9/27/2015	34.0	90	211.0	7.5	1
10/03/2015	34.5	60	165	5.7	2.23
10/14/2015	35.2	110	279.0	9.8	4
10/25/2015	35.0	110	280.0	9.9	16.65

2.4.1 Irradiation #1 (02/23/2015)

The first irradiation of the uranyl sulfate solution in the mini-SHINE experiment was conducted on February 23, 2015. The time for irradiation was limited to a maximum 2 hr at high power. This run duration was chosen for two reasons. One-tenth of full-production scale allows good estimation of activity produced at full irradiation, and two hours would be enough to establish thermal equilibrium in the mini-SHINE solution as well as steady-state gas generation rates. This irradiation provided us with fission-product production rates, which were compared with expectation from our MCNPX calculations. This irradiation went as planned.

Irradiation started with ~140 W of beam power on the target. Over 45 min, power was increased to 7.15 kW, where it stayed for two hours. Table 2.2 (first column) shows the time steps when the beam power was changed; the second column gives the pulse repetition rate, the third column, beam current lost on collimator; the fourth column, average beam current on the Ta target, and the fifth column, average beam power on the target calculated by multiplying average current on the target by beam energy.

TABLE 2.2 The Time Table of Irradiation #1.
Beam energy was 35.0 ± 0.5 MeV.

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
13:30	2	0.4	4.1	0.14
13:45	5	0.9	10.4	0.37
13:55	15	2.6	31.4	1.1
14:00	30	5.5	62.5	2.2
14:08	60	12	124	4.4
14:16	100	24	203	7.15
16:16	Stop

FIGURE 2.13 Beam Power History for Irradiation #1. First 30 min is not shown on the graph. Fast Current Transformer (FCT#0) signal refers to beam current monitor located before first 10° magnet and FCT#1 to the signal before second 10° magnet. Good agreement between two FCT signals indicates efficient beam transfer up to second 10° bending magnet. For this irradiation $\sim 10\%$ of the beam was lost on collimator, which explains difference in beam powers from this figure and Table 2.2.

2.4.2 Irradiation #2 (03/04/2015)

This irradiation was planned to last up to 10 hours at full power. Electron beam energy for this irradiation was set to 35 ± 0.5 MeV. This irradiation provided a second Mo-99 production rate measurement as well as approached the total time required to irradiate the solution to produce 2 Ci of Mo-99. Original MCNPX calculations predicted production of Mo-99 at the 14 hour mark at 10 kW beam power. The irradiation was interrupted two times. First, radiation levels in the Spectroscopy Room, where the gas analysis cabinet is located, reached 5 mR/hr and tripped the linac interlock system. We thus installed additional shielding around the enclosure and continued irradiation. Subsequently, the computer-based acquisition system that monitored temperatures of the solution and target cooling water failed, so the run was terminated at this point. Total irradiation time at full power (7.5 kW) for this experiment was 7.5 hr. Table 2.3 shows the data and events for irradiation #2.

TABLE 2.3. The Time Table of Irradiation #2.
Beam energy was 35.0 ± 0.5 MeV.

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
13:35	2			
14:15	5	0.85	10.7	0.4
14:20	15	2.6	31.9	1.0
14:25	30	5.3	63.7	2.2
14:30	60	10	128	4.5
14:40	100	16	214	7.5
14:45	100	14	216	7.5
17:20	Stop (Spectr. Room rad. Interlock trip)			
17:22	100	12	218	7.6
22:02	Stop (Temp. control system failure)			

2.4.3 Irradiation #3 (04/13/2015)

After the problems with the reflector cooling system were fixed, we prepared for a second 32-hr irradiation to produce 2 Ci of Mo-99. After just five hours at full beam power on the target, we lost high voltage to the injector. We had to stop irradiation and wait for the radiation field inside the accelerator room to decrease to a reasonable level before starting repairs. Table 2.4 summarizes the data and events in irradiation #3.

Due to breakdown of a high-voltage injector cable and several interlock trips, we were able to achieve only 24 hr of full power beam on the target. The amount of Mo-99 produced in this run was much lower than expected, but we still were trying to ship >1 Ci of Mo-99, so we prepared for the next irradiation.

TABLE 2.4 The Time Table of Irradiation #3.
Beam energy was 35.0 ± 0.5 MeV.

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
13:00	5	0.3	10.7	0.38
13:15	15	1.1	31.9	1.1
13:25	30	2.3	63.7	2.2
13:35	60	6.0	126	4.4
13:45	100	14.0	206	7.2
14:00	130	17.0	269	9.4
19:05	Stop (Injector HV cable is broken)			

This run was continued on the next day after
replacing of injector HV cable (04/14/2016).

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
16:20	2	0.25	4.15	0.14
17:35	5	0.6	10.4	0.37
17:45	15	1.7	31.3	1.1
17:57	30	3.3	62.7	2.2
18:10	60	7.7	124.3	4.3
18:16	60	6.6	125.4	4.4
18:20	100	13	207	7.2
18:30	130	16.5	269.5	9.4
04/15/2015				
03:33	Stop (Arc in Injector, vacuum trip)			
03:52	2			0.14
03:55	30			2.2
04:07	60			4.3
04:13	100			7.2
04:22	130			9.4
06:50	70			5.1
06:53	100			7.2
06:56	130			9.4
18:45	Stop (Waveguide SF6 interlock trip)			
20:25	2			0.14
20:47	5	0.55		0.37
20:53	15	1.7		1.1
21:02	30	2.9		2.2
21:10	60	6.5		4.4
21:20	100	12		7.2
21:30	130	17		9.4
24:00	Stop			

2.4.4 Irradiation #4 (04/24/2015)

This irradiation was planned for 40 hr to produce >1 Ci of Mo-99. Unfortunately, we encountered multiple problems during this irradiation. Temperature and flow of the coolant for the target was fluctuating as well as the power supply current of the Helmholtz coils. We had to stop the irradiation to assess the reasons for the fluctuations. Because of these stops, this irradiation run lasted over three days, and full beam power on the target was only for ~20 hr. Table 2.5 summarizes the data and events during irradiation #4.

TABLE 2.5. The Time Table of Irradiation #4.
Beam energy was 37.0 ± 0.8 MeV.

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
20:25	2	0.4	4.0	0.15
20:45	5	0.9	10.1	0.37
20:55	15	2.7	30.3	1.1
21:05	30	5.3	60.7	2.2
21:15	60	11	121	4.5
21:27	90	15	183	6.4
21:37	Stop (Arc in 2 nd Acc. Structure)			
21:42	90	15	183	6.4
21:50	130	19	267	9.8
04-25-2015				
01:50	Stop (Injector current spiked)			
02:15	130	19	268	9.8
04:14	Stop (Arc in Accelerator)			
04:40	130	19	268	9.8
14:40	Stop (Refill the target cooling water tank)			
14:50	2	0.38	4.0	0.15
15:00	5	0.7	10.3	0.38
15:20	15	2.3	30.7	1.1
15:40	30	4.5	61.5	2.2
16:00	60	9.5	122.5	4.5
16:30	90	14	184	6.8
17:12	60	9.0	123	4.5
17:18	Stop (HH power supply is tripped)			
04-26-2015				
11:05	5	0.7	10.3	0.38
11:15	15	2.3	30.7	1.1
11:25	30	4.8	61.2	2.2
11:35	60	8.0	124	4.5
11:50	90	12.0	186	6.8
12:20	Stop (Vacuum trip in 1st Acc. Structure)			
12:30	90			6.8
21:55	Stop			

2.4.5 Irradiation #5 (05/19/2015)

We planned to produce >1 Ci of Mo-99 in this irradiation. At the beginning of irradiation, the temperature of the uranyl sulfate solution started to climb and reached 75°C; the irradiation was thus stopped. After a cool-down period, the irradiation room was accessed, and the reflector cooling-water pump was restarted. Table 2.6 shows the data and events associated with irradiation #5. Figure 2.14 represents the beam power in two position of the beamline (before first and second 10° magnets) over time.

TABLE 2.6 The Time Table of Irradiation #5.
Beam energy was 35.0 ± 1.0 MeV.

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
12:20	2	0.3	4.7	0.16
12:25	5	0.7	11.8	0.39
13:00	15	1.5	36	1.26
13:10	30	2.6	72.4	2.5
13:30	60	7.0	143	5.0
13:45	90	12	213	7.5
13:55	Stop (Arc in the gun and structure)			
14:05	15			
14:10	30	2.9	72.1	2.5
14:15	60	6.0	144	5.0
14:20	90	12.0	213	7.5
14:30	120	15.0	285	10.0
14:42	Stop (Arc in 2 nd Acc. Structure)			
14:53	120	15.0	285	10.0
16:25	Stop (Solution temperature raised up to 75°C)

FIGURE 2.14 Beam Power History for First Part of Irradiation #5. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet.

Irradiation was resumed the next day (05/20/2015). Due to problems with the power supply in the Helmholtz coils, we had to stop after ~12 hr at full power. After this run, the Helmholtz power supply was replaced. Table 2.7 shows the data and events during the continuation of irradiation #5.

**TABLE 2.7. The Time Table of Irradiation #5
(continuation). Beam energy was 35.0 ± 0.8 MeV.**

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
11:55	2	0.3	4.7	0.16
12:25	5	0.7	11.8	0.41
12:35	15	2.1	35.4	1.2
12:50	30	4.5	70.5	2.4
13:18	60	7.8	142.2	5.0
13:35	90	10.0	215	7.5
13:55	120	15.0	285	10.0
20:32	Stop (Vacuum trip)			
20:43	15			
20:48	30			
20:53	60			
20:58	90			
21:02	120	13	277	9.7
21:55	120	15.0	285	10.0
23:10	120	13.0	277	9.7
05-21-2015				
00:40	Stop (vacuum spiked)			
00:43	15			
00:46	30			
00:49	60			
00:52	90			
00:55	120	14.0	280	9.8
01:05	5			
01:07	15			
01:08	30			
01:10	60			
01:12	90			
01:15	120	14.0	280	9.8
01:20	90	9.0	211	7.4
01:30	100	10.0	237	8.3
02:20	60			
02:27	90	9.0	211	7.4
03:00	Stop (HH power supply failure)

FIGURE 2.15. Beam Power History for the Second Part of Irradiation #5. FCT#0 signal refers to beam current monitor located before first 10° magnet, and FCT#1 to the signal before second 10° magnet.

2.4.6 Irradiation #6 (09/27/2015)

The low yield of Mo-99 in the prior irradiation triggered measurement of the uranium concentration in the target solution; it was found to be 93.7 g-U/L. Additional uranyl sulfate was added to the solution to increase the concentration to 149 g-U/L. Because the solution concentration was changed, we had to experimentally measure the Mo-99 yield.

We planned to start with a two-hour irradiation, but were not able to accomplish this run because of a vacuum failure on the beam line. The dielectric break before the last collimator failed and was replaced, and a follow-up irradiation was planned for 10/03/2016. Table 2.8 summarizes the data and events during irradiation #6

TABLE 2.8 The Time Table of Irradiation #6.
Beam energy was $E = 34.0 \pm 0.5$ MeV.

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
14:17	15	4.0	41	1.4
14:30	30	10.0	80	2.8
14:40	60	22.3	157.7	5.5
15:00	90	59	211	7.4
15:41	100	64	236	8.2
15:47	Stop (Acc. Current dropped down)			

2.4.7 Irradiation #7 (10/03/2015)

This irradiation was planned for 2 hr. We had some instability in the injector beam current during this run, and the maximum beam power on the target was ~6 kW. Table 2.9 and Figure 2.16 summarize the data and events during this irradiation.

TABLE 2.9 The Time Table of Irradiation #7.
Beam energy was $E = 34.5 \pm 0.4$ MeV.

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
09:25	2	0.8	5.4	0.21
10:45	5			0.5
12:00	15	3.4	41.2	1.4
12:38	30	6.8	83.2	2.9
13:20	60	15.5	161.5	5.6
13:40	15			1.4
14:07	30	5.0	80.0	2.8
14:12	60	9.3	160.7	5.6
15:00	2			
15:03	60	10.0	165.0	5.7
15:39	30			
15:45	60			5.7
15:53	30			2.8
16:20	60			5.7
16:28	30			2.8
17:00	60			5.7
17:14	30			2.8
17:33	Stop

FIGURE 2.16 Beam Power History for Irradiation #7. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet.

2.4.8 Irradiation #8 (10/14/2015)

This irradiation was planned for 4 hr at full power on the target. It was used to verify Mo-99 production rates and to perform the entire Mo-99 recovery and purification process in preparation for a production run with a GE HealthCare shipment. This irradiation went without problems.

Table 2.10 shows data and events during this irradiation. Figure 2.17 shows beam power on the target over time. Only one arc in the accelerator structure occurred during power ramp-up. The power drops shown on the figure are artifacts of the measurements. Three times during irradiation, synchronization between the accelerator and data collection computer was lost, resulting in zero beam power. The power shown in the figure is higher than the real power on the target because those measurements are based on the beam current going into the second 10° magnet. Before the beam strikes the Ta target, 7–10% of the current is lost on the collimator.

TABLE 2.10 The Time Table of Irradiation #8.
Beam energy was $E = 35.2 \pm 0.7$ MeV.

Time	Rep. Rate (Hz)	Coll. Current (μ A)	Avg. Current (μ A)	Avg. Power (kW)
11:20	2	1.5	4.1	0.14
11:25	5	1	13	0.45
12:35	5	0.8	13.2	0.46
12:40	15	3.5	38.5	1.4
12:45	15	2.8	39.2	1.4
12:52	30	5.8	78.2	2.8
13:13	Stop (Arc in accelerator structure)			
13:15	2			
13:16	15	2.4	39.6	1.4
13:20	30	4.4	79.6	2.8
13:37	45	14.0	112	3.9
14:00	45	12.0	114	4.0
14:10	60	16	152	5.6
14:20	80	23.0	201	7.1
14:30	110	33.0	275	9.7
14:38	110	29.0	279	9.8
18:30	Stop

FIGURE 2.17 Beam Power History for Irradiation #8. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet.

2.5.10 Irradiation #9 (10/25/2015)

This irradiation was planned as a production run for shipment of Mo-99 sample to GE HealthCare. Based on the previous two irradiations, we would produce ~2 Ci of Mo-99 in 20 hours. After 7.5 hours of irradiation at full power, the experimental interlock inside the irradiation room opened. We had to wait ten hours before we could access the target room to assess the problem. We found that a semiconductor relay has failed due to radiation damage. This relay was replaced with an electromechanical one, and the irradiation continued for an additional nine hours. We then had to stop the irradiation to allow time for processing and shipment. Table 2.11 and Figure 2.18 present data and events for irradiation #9.

TABLE 2.11 The Time Table of Irradiation #9.
Beam energy was $E = 35.0 \pm 0.7$ MeV.

Time	Rep. Rate (Hz)	Coll. Current (μA)	Avg. Current (μA)	Avg. Power (kW)
10:50	2	0.56	5.0	0.18
11:05	5	0.6	13.4	0.47
11:38	15	2.56	39.35	1.4
11:55	30	7.0	77.0	2.7
12:12	45	11.0	115	4.0
12:30	60	13.0	155	5.4
12:48	80	18.0	206	7.2
13:17	110	24.0	284	10.0
16:49	Stop (Arc in 1 st Acc. Structure)			
16:52	110			10.0
20:50	Stop (Interlock trip in Cell-1)			
10-26-2015				
09:12	2			
09:15	5	0.4	13.6	0.47
09:20	15	2.7	39.3	1.4
09:25	30	7.0	77	2.7
09:30	45	10.0	116	4.0
09:37	60	15.0	153	5.4
09:46	90	20.0	232	8.2
09:55	110	30.0	278	10.0
19:00	Stop

FIGURE 2.18 Beam Power History for First Part of Irradiation #8. FTC#0 signal refers to beam current monitor located before first 10° magnet, and FTC#1 to the signal before second 10° magnet. Beam interruption in the middle of irradiation corresponds to shut down for replacement of the relay in the interlock chain. Beam-off time was cut out from the figure to make figure more compact.

2.5 CONCLUDING REMARKS

The irradiation experiments described above revealed many opportunities for improvement of the experimental setup for the irradiation of a uranyl-sulfate target solution. All those lessons learned will be incorporated into the phase-2 mini-SHINE experiments.

Multiple irradiations in the mini-SHINE phase 1 experiments allowed us to improve the reliability of the accelerator. We have learned that, with increased radiation fields, most of the electronic components are prone to failure. For phase-2 mini-SHINE experiments, most of the equipment with sensitive electronic components is being relocated outside of the irradiation room. New Helmholtz coil power supplies were installed in an adjacent room. Also, a thermo-stabilized supply for cooling water is provided from outside of the radiation room.

Handling a high-power beam presents separate challenge for beam-line transport. For phase 2, we are adding water cooling to the beamline components that can be contacted by the beam. We are also eliminating dielectric breaks from the beamline.

The OTR detection of the beam position on the target proved to be extremely useful for reliable positioning of the beam on the target. For phase-2 mini-SHINE experiments, OTR signal detection will be the primary means of tuning the beam position and shape on the target.

3 ANALYSIS OF RADIOLYSIS GASES

Radiolysis of water in the target solution is due to both its irradiation by x-rays and by fissioning of the U-235 and U-238. The overall reaction in the radiolysis of water is $2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}_2$. The initial stage of the process begins with the formation of a solvated electron, and the ionized and excited forms of the water molecule [$\text{H}_2\text{O}^\bullet$, H_2O^+ , $e^-(\text{aq})$] created by the incident radiation. Radical fragments are then generated: H^+ , $\text{H}^\bullet$, $\text{OH}^\bullet$, and OH^- . Next, fragments combine to form molecular species (H_2 , H_2O_2) or the water recombines. This is a simplification of a complicated process that is well described by Spinks and Woods [SPINKS-1990]. Many radical reactions occur, and the generated species are able to escape the track in which they are generated to diffuse into solution. Solute concentration affects the reaction pathways significantly. Pure water produces a minimal amount of hydrogen product. When a solute is added to water, hydrogen generation increases significantly. The production of hydrogen in the uranium sulfate solution increases with respect to pure water.

The cover gas in the mini-SHINE experiment is helium. The requirement to add air in the initial phase of the experiment comes from the fact that hydrogen is liberated into the headspace faster than oxygen in the initial stages of radiolysis. According to Allen et al., “Water can decompose directly to molecular hydrogen as well as forming free radicals that may react with solutes. In the absence of a sufficiently high concentration of solutes, the hydrogen reacts with radicals and is converted back to water; but almost any solute capable of oxidation or reduction will destroy the radicals and allow the molecular hydrogen to appear”[ALLEN-1950]. Hydrogen peroxide (H_2O_2) is produced from the reaction of radicals and ions. Molecular oxygen is produced from the decomposition of H_2O_2 . Oxygen also has a greater solubility in the solution than hydrogen. This all has the effect of delaying the occurrence of oxygen in the headspace gases.

A steady-state hydrogen concentration is reached in the solution vessel after the oxygen additions. Oxygen fluctuates as the headspace of the vessel is purged with helium while hydrogen remains mostly constant. The steady-state hydrogen concentration appears to be dependent on the rate of recombination from the catalyst and the linac beam power. If the rate of production went up due to higher power, the steady-state hydrogen concentration would be higher as long as the flow through the catalyst were constant. Since the beam power for Mo-99 production will be as high as possible, the hydrogen concentration in the vessel should be determined by the rate of hydrogen/oxygen recombination, i.e., the flow rate through the catalyst.

As reported in Section 2, nine experiments were performed from February through October of 2015 at the Argonne linac. A 5200 mL solution of uranyl sulfate at 93.7 g-U/L and later at 149 g-U/L was irradiated to produce Mo-99. The accelerator’s 35 MeV electron beam was used to produce a neutron flux by striking a tantalum target that is positioned inside of a dry well at the center of the uranium solution. The Mo-99 product was produced by the fission of LEU. During the irradiations, neutrons, high-energy gamma rays, and x-rays caused radiolysis of water. Radiolysis produces a host of radicals and ions in the solution, which ultimately forms the molecular products hydrogen, hydrogen peroxide, and oxygen. This section will describe the gas analysis and collection system and the results of gas analysis during the experiments.

3.1 EXPERIMENTAL SET-UP

The target solution resides inside the solution vessel as shown in Figure 3.1. The headspace gas of the vessel is recirculated through a catalyst by an explosion-proof pump (Air Dimensions Inc. Model R221-FV-RA1-AHK). The catalyst is composed of platinum/palladium on alumina/cordierite and has a honeycomb configuration that allows the gas to flow down the length of the bed. This catalyst is commonly used to reduce emissions in diesel engine exhaust. It is being used here as a reactor to re-combine the hydrogen and oxygen produced from the radiolysis of water. This is done to reduce the concentration of hydrogen in the headspace of the vessel to well below the lower flammable limit of 4%. The catalyst is heated to 115°C to facilitate the removal of water generated in the catalyst bed during the recombination hydrogen and oxygen. This operating temperature also prevents condensation of water vapor on the catalyst surface caused by humidity in the headspace gas. It was found during earlier experiments that if the humidity is too high, the condensation inhibits the active sites of the catalyst; thus, it fails to recombine the gases. This caused a fast buildup of hydrogen in the vessel and the experiment was halted for safety concerns. A condenser located before the recirculating pump also serves to drop the humidity of the headspace gas prior to entering the catalyst.

FIGURE 3.1 Diagram of the Solution Vessel and Analytical and Gas Collection System

The analytical instrument is connected to the headspace by stainless steel tubing. A diaphragm pump (KNF Model 810) is used to transport the gas from the headspace of the solution vessel to the analytical system. The gas is pulled from the headspace, analyzed, then

returned to the vessel. Headspace gases were analyzed with a Pfeiffer Prisma Plus QMG 220 Residual Gas Analyzer (RGA), which is equipped with a quadrupole mass filter and a secondary electron multiplier (SEM) detector. Two RGAs and associated equipment are housed inside a closed cabinet (Figure 3.2), which is outside the linac target room.

FIGURE 3.2 Mini-SHINE Gas-Analysis Cabinet

The vessel/analytical systems are not a completely closed system. The headspace of the vessel is connected to a Gas Collection System through a single ¼-in. stainless steel tube. The Gas Collection System (Figures 3.3 and 3.4) maintains the solution vessel at sub-atmospheric pressure, which is a safety requirement of the experiment. It is kept sub-atmospheric to prevent the release of fission gasses Xe-135, Kr-85, and volatile radioisotopes of iodine. It also provides an outlet for excess gases to prevent over-pressurization of the vessel. Waste gases from the analytical system are exhausted to this system. Gases are stored using two chambers and a high-pressure cylinder. Chamber #1 is connected to the vessel and analytical systems. It contains a pressure transducer (OMEGA Engineering Model MMA030V10H3C0T3A6CE) and a diaphragm pump (GAST Manufacturing Corporation Model D0AP704AAEMD). The inlet of the pump is open to the chamber volume. The outlet of the pump is connected to Chamber #2. The pump inside Chamber #1 is actuated when the pressure reaches 970 mbar. This evacuates Chamber #1 and fills chamber #2. Chamber #2 contains a pressure transducer (OMEGA Engineering, INC. Model MMG5.0KV10P2C0T3A6CE) and a scuba pump (NARDI Compressor Atlantic 100). The pump inlet is open to the chamber volume. The outlet is connected to high-pressure cylinders. When the pressure inside Chamber #2 reaches 4 psig, the scuba pump actuates and fills the high-pressure cylinder.

FIGURE 3.3 Diagram of the Gas Collection System

Part of the safety basis for these experiments is to keep the concentration of hydrogen to less than 2%. When necessary, using a calibrated mass flow controller (OMEGA Engineering, INC. model FMA5502-ST), we added air to the vessel headspace to control the concentration of hydrogen.

The total volume of gas in the system was determined in several ways. First, CAD diagrams of the system were used to calculate volumes of solution vessel, condensers, and various parts that required close tolerances, and volumes could be easily calculated. Second, using Boyle's Law the pressure and volume relationships were used to determine the volume of some parts of the system. Third, the length of tubing was measured, and the volume was determined from its specified inner diameter. The total gas volume of the system includes the solution vessel headspace, condensers, catalyst bed, and interconnecting tubes in the system. The total gas volume was determined to be 8.3 L when the solution vessel is filled with 5300 mL of solution. This does not include the Gas Collection System, which is treated as a separate part of the overall system. Although there may be exchange of headspace gas between the Vessel/Analytical Systems and the Gas Collection System, we assumed it to be minimal, and calculations are based only on the volume of the Vessel/Analytical System.

FIGURE 3.4 Photograph of the Gas Collection System. When in use the cabinet door is closed.

The total moles of gas present in the system depends on the volume, which is assumed to be constant. The system pressure is kept at $970 \text{ mbar} \pm 10 \text{ mbar}$, so it is taken to be constant for calculation purposes. The temperature of the gas is variable throughout the system, so the total moles occupying the system is the sum of the gas components. The reflector-water temperature that surrounds the vessel represents the temperature of approximately 52.3% of the total gas volume of the system. The other large volume is the condensers, which are at 9°C . This represents 35.6% of the system volume. The remaining 12.1% consists of valves and lines that are at room temperature (25°C).

3.2 ANALYTICAL DATA

The RGA was calibrated with standards prepared from a primary standard procured from a vendor and had been certified to an accuracy of $\pm 5\%$. The instrument was calibrated at the pressure inside the analytical system. The calibration was verified with a check standard and was acceptable (within $\pm 10\%$ of the true value). With RGA, hydrogen has a detection limit of 50 ppm, and oxygen has a detection limit of 30 ppm.

The analytical data presented are indicative of what is occurring in the solution vessel. The large volume, especially of the analytical condenser, causes a time delay between the actual solution vessel concentration and the analytical data. The first indication of what occurs in the vessel takes approximately one minute. The data reported as rates of hydrogen generation per minute should be well within the time of what occurs inside the vessel. These data were taken before oxygen was introduced to control the hydrogen concentration. It is also when beam power is kept constant. This usually occurred during the linac tune-up. The data regarding hydrogen production with respect to energy input were taken from the same time frame as the generation rate.

There are experimental set-up factors that may affect these data. Residual oxygen and air leakage into the system will affect these data. Since we have a catalyst recombining hydrogen and oxygen, residual oxygen will tend to skew hydrogen-measured production rates lower than actual. The leak rate of air into the system was small (approximately 1 ppm/min). Another factor that would affect the data is the rate at which beam power was adjusted. Data were selected from the times that the beam was held at constant power, but every experiment was slightly different in the way the beam was tuned. As experiments progressed, linac operation became more efficient, and beam tuning time became shorter. Because of the analytical delay, data extracted too near a power increase would be more representative of the previous power level. Experiments will be performed on a smaller scale, which will provide a clearer picture with regard to energy input and hydrogen generation. These experiments should also provide meaningful data with regard to oxygen generation.

3.2.1 Phase-1 Experiment: Uranium Sulfate Irradiation (2/23/15)

The target solution was purged with helium several times to remove atmosphere from the vessel and solution. The system was purged for 1.5 hours. The residual oxygen remained in the headspace at 70 ppm prior to experiment start. During this irradiation, beam power was increased slowly. Initially the power was 0.3 kW for 9 min, then was increased to 1.0 kW and held for 8 min. Subsequently, power was increased to 2.0 kW and held for 7 min, then increased to 4.0 kW and held for 8 min. Finally, power was increased to 7.6 kW and held for 120 min. The reflector water temperature was at 80°C during irradiation. Condenser temperatures were set to 9°C.

Figure 3.5 shows the percent hydrogen and oxygen in the system as a function of time plotted with beam power for this irradiation. Air was added during the irradiation to control the concentration of hydrogen present in the vessel headspace. This is done as part of the safety basis since hydrogen concentration cannot exceed 2%. The total volume of air added was 102 mL, corresponding to 875 μmol of oxygen.

FIGURE 3.5 Hydrogen, Oxygen, and Beam Power Plotted as a Function of Time (2/23/15)

As seen in Figure 3.5, oxygen stayed very low even as air was added to the system, indicating an initial excess hydrogen production. It catalytically combined with excess hydrogen and stayed at about $<0.02\%$ throughout the irradiation. The first indication of excess hydrogen occurred at 18 min into the run at 2 kW power, with a sharp rise beginning at 4 kW. Hydrogen can be seen rising as beam power is increased in Figure 3.5. Air was added starting at 75 min. It was added in several doses, as indicated by the dips and rises in hydrogen between 75 and 115 min. Solution processing began at 152 min. When processing occurs a valve at the bottom of the solution vessel is opened, and the solution flows by gravity into the Dump Tank. Gas analysis monitoring continued during this process. During this time a steady decrease in hydrogen occurs. This is probably due to release of oxygen that is dissolved in solution from the mixing that occurs during the dump. Air is also introduced from the solution processing part of the system.

Figure 3.6 shows the excess hydrogen production prior to air addition. The graph is the short segment of time during which hydrogen is showing a sharp rise in concentration. When plotted linearly, a rate of excess hydrogen of $36 \mu\text{mol H}_2/\text{min}$ was determined from the slope of the line. With the catalyst continuously recombining hydrogen and oxygen, this is seen as the “excess” hydrogen production rate because the amount of oxygen reaching the headspace of the vessel is unknown. We do know there is a delay in the rise of oxygen.

FIGURE 3.6 Hydrogen Measured Plotted as a Function of Time (2/23/15)

Figure 3.7 is a graph of the same portion of the irradiation as shown in Figure 3.6, but it relates hydrogen production to beam energy. The graph is from the portion of the irradiation where power is at a constant 7.6 kW, and hydrogen is on the increase. When plotted linearly, the slope of the line determines the hydrogen production with respect to energy and is found to be $4.8 \mu\text{mol H}_2/\text{kW-min}$.

FIGURE 3.7 Hydrogen Measured as a Function of Beam Energy (2/23/15)

3.2.2 Phase-1 Experiment: Uranium Sulfate Irradiation (3/4/15)

Before this irradiation, the target solution was purged with helium several times to remove atmosphere from the vessel and solution. The system was purged for 1 hour. The residual oxygen remained in the headspace at 200 ppm prior to the start.

During this irradiation, beam power was increased more rapidly than in the prior experiment. Initially, the power was 1.0 kW for 8 min, increased to 2.2 kW and held for 4 min, increased to 4.4 kW and held for 8 min, and increased to 9.0 kW and held for 5 min. Power was then reduced to 7.5 kW and held for 439 min. The reflector water temperature was 80°C during irradiation. Condenser temperatures were set to 9°C. Room temperature was 25°C.

This was a 7.5 hour irradiation, and power was increased rapidly. Figure 3.8 shows the concentration of hydrogen and oxygen measured over time. Residual oxygen concentration decreased to undetectable levels as the power increased due to the production of hydrogen and its subsequent recombination with oxygen in the catalyst. The first indication of hydrogen production occurred at 12 min into the run at 2 kW power. Headspace hydrogen was in excess of oxygen during the initial stage of the experiment. The first addition of air occurred at 50 min to control the concentration of hydrogen. Since it was unknown how much oxygen would be needed, we added nine short additions between 50 and 220 min. A total of 4578 μmol of oxygen was added. After the final addition of air, hydrogen concentration remained almost constant throughout the rest of the irradiation. This result is indicative of a steady state between the radiolysis reactions that produce hydrogen and oxygen, as shown in Figure 3.8 between 230 and 469 min. The steady-state level of hydrogen in the headspace was 400 ppm.

FIGURE 3.8 Hydrogen and Oxygen Concentrations and Beam Power as a Function of Time (3/4/15)

During solution processing, the oxygen level rose. This effect can be attributed to several factors: residual oxygen in the dump tank is entering the vessel, the solution is de-gassing dissolved oxygen from the solution as it is agitated during the dump, and the residual hydrogen peroxide generated from radiolysis is decomposing.

Figure 3.9 shows the excess-hydrogen production rate, prior to air addition, to be $60 \mu\text{mol H}_2/\text{min}$. Beam power was increased more rapidly as compared to the experiment on 2/23/15. The beam was at 9 kW for at least 5 min before it was reduced to 7.5 kW. This short bump in power is the most likely reason the rate of hydrogen production was faster in the initial stages of the irradiation than the previous experiment. The graph is from the portion of the irradiation where power is at a constant 7.6 kW and hydrogen is increasing.

FIGURE 3.9 Hydrogen Plotted as a Function of Time (3/4/15)

Figure 3.10 is a graph of the same portion of the irradiation as shown in Figure 3.9. It shows the rise in hydrogen prior to the addition of air as related to the beam energy. The graph is from the portion of the irradiation where power is at a constant 7.6 kW and hydrogen is increasing. When plotted linearly, the slope of the line determines the hydrogen production with respect to beam energy and is found to be $8.0 \mu\text{mol H}_2/\text{kW-min}$.

FIGURE 3.10 Hydrogen Measured as a Function of Beam Energy (3/4/15)

3.2.3 Phase-1 Experiment: Uranium Sulfate Irradiation (4/13/15)

Prior to this irradiation, the target solution was purged with helium several times to remove atmosphere from the vessel and solution. The system was purged for 1.5 hours. The residual oxygen content remaining in the headspace was 140 ppm. The reflector water temperature was at 80°C during irradiation. The condenser temperature was set to 9°C. The experiment was performed in two parts because we encountered a problem with the linac. These problems occurred over the next few experiments due to equipment failure. As the experiment progressed over the months, improvements increased the stability and positioning of the beam on the target.

Figure 3.11 shows Part 1 of this experiment. The beam was tuned over the first 60 min and held at 9.4 kW for the duration. Air was added at 60 min and totaled 4070 μmol of oxygen. Hydrogen reached a steady-state concentration of about 0.04% beginning at 100 min.

Figure 3.12 shows Part 2 of this experiment. The beam was tuned over the first 110 min and held at 9.4 kW for the duration. Air was added for 30 min and totaled 2035 μmol of oxygen. Hydrogen reached a steady concentration of about 600 ppm.

FIGURE 3.11 Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (4/13/15, Part 1)

FIGURE 3.12 Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (4/13/15, Part 2)

Figure 3.13 shows hydrogen measured as a function of time. The plot shows a production rate of $114 \mu\text{mol H}_2/\text{min}$. Only Part 1 of the experiment is shown here because oxygen concentration was high during the tune-up in Part 2. This oxygen increase may reduce the validity of the hydrogen generation rates due to its recombining with oxygen at the catalyst.

Figure 3.14 shows hydrogen plotted as a function of beam energy during beam tune-up at a power of 7.2 kW and before the addition of air. Oxygen concentration was low at this time. The rate of generation was $13 \mu\text{mol H}_2/\text{kW-min}$.

FIGURE 3.13 Hydrogen Plotted as a Function of Time (4/13/15, Part 1)

FIGURE 3.14 Hydrogen as a Function Beam Energy (4/13/15, Part 1)

3.2.4 Phase-1 Experiment: Uranium Sulfate Irradiation (4/24/15)

Before this irradiation, the target solution was purged with helium several times to remove atmosphere from the vessel and solution. The system was purged for 1.5 hours. The residual oxygen content remaining in the headspace was 400 ppm. The reflector water temperature was 80°C during irradiation. The condenser temperature was set to 9°C.

Because more problems were encountered with the linac, the experiment was performed in two parts. Figures 3.15 and 3.16 show hydrogen, oxygen, and beam power during both parts of the experiment. In Part 1, the beam tune-up occurred over 90 min. Air addition was required at 6.4 kW to control the hydrogen concentration. Maximum power was 9.8 kW during the run. After the first air addition, hydrogen concentration stayed relatively constant between 0.04% and 0.06% throughout the entire experiment, as shown in Figure 3.15. Simultaneous dips in hydrogen with a corresponding rise in oxygen occurred when the beam was shut down due to instability. This effect reflects the halt in hydrogen production and de-gassing of oxygen from the solution. Part 1 was terminated after 745 min.

As evident in Figure 3.16 (Part 2), the maximum power was 6.8 kW, and there was difficulty focusing the beam on the target. Later, we found that the accelerator had a faulty power supply. The addition of air was required when the beam power reached approximately 6 kW. Only one air addition was required. The system was purged with helium occasionally to reduce the radiation field generated by fission product gasses in the analytical system.

FIGURE 3.15 Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (4/24/15, Part 1)

FIGURE 3.16 Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (4/24/15, Part 2)

Figure 3.17 shows hydrogen measured as a function of time. Only Part 1 is given in this section because oxygen levels in Part 2 were very high at the beginning of the experiment. Since the oxygen concentration was high, the measured hydrogen generation rate may not be accurately represented. This measurement problem is due to the recombining of H_2 and O_2 , which would make the generation rate of hydrogen appear lower. It shows a rate of $62 \mu\text{mol } H_2/\text{min}$.

Figure 3.18 shows hydrogen plotted as a function of beam energy before the addition of air during beam tune-up at a power of 4.5 kW. Oxygen concentration was low at this time. The rate of generation was $14 \mu\text{mol } H_2/\text{kW-min}$.

FIGURE 3.17 Hydrogen as a Function of Time (4/24/15, Part 1)

FIGURE 3.18 Hydrogen as a Function of Beam Energy (4/24/15)

3.2.5 Phase-1 Experiment: Uranium Sulfate Irradiation (5/19/15)

Before this irradiation, the target solution was purged with helium several times to remove atmosphere from the vessel and solution. The system was purged for 1.5 hours. Residual oxygen content remaining in the headspace was 400 ppm. The reflector water temperature was 80°C during irradiation. The condenser temperature was set to 9°C.

During this experiment, a problem occurred with the reflector water cooling system. There was also instability in the beam. Several attempts were required to bring the beam to full power only to lose it due to the instability. Provided below in Figure 3.19 are the hydrogen content, oxygen content, and beam power plotted over time. Between 400 and 1500 min, the cooling system problem was corrected, and the beam was restored. Since there was no hydrogen to recombine with, oxygen rose to about 1.4 % due to the initial air addition. At approximately

1500 min, the beam was restored. Air was added to control the hydrogen concentration. The hydrogen concentration remained constant between 0.09% and 0.12% for the duration of the experiment.

Figure 3.20 shows the rise in hydrogen before the introduction of oxygen. As mentioned before, since the initial oxygen concentration was high, the measured hydrogen generation rate may be lower than it actually is. The generation rate was measured as $120 \mu\text{mol H}_2/\text{min}$.

FIGURE 3.19 Hydrogen Content, Oxygen Content, and Beam Power as a Function of Time (5/19/15)

FIGURE 3.20 Hydrogen as a Function of Time (5/19/15)

Figure 3.21 shows the rise in hydrogen prior to oxygen introduction as a function of beam energy. As mentioned before, the measured hydrogen generation rate may be lower than it actually is. The rate of hydrogen generation with respect to energy was measured to be $24 \mu\text{mol H}_2/\text{kW}\cdot\text{min}$.

FIGURE 3.21 Hydrogen as a Function of Beam Energy (5/19/15)

3.2.6 Phase-1 Experiment: Uranium Sulfate Irradiation (9/27/15)

This experiment was a test for the accelerator. A camera was installed in the beam line to focus the beam more accurately on the target. Fresh concentrated uranyl sulfate was added to the target solution to bring its concentration to 149 g-U/L. A new gas mix was installed to reduce the concentration of hydrogen. The O₂/N₂ mix was 39.98% O₂ and 0.994% N₂ in helium.

Figure 3.22 shows the plot of hydrogen content, oxygen content, and beam power for this test. As mentioned before, the measured hydrogen generation rate may appear to be lower than it is.

FIGURE 3.22 Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (9/27/15)

Figure 3.23 shows the rise in hydrogen before the introduction of oxygen. Since the oxygen concentration was high, the hydrogen generation rate data may not be accurate due to the recombining of H_2 and O_2 , which would make the generation rate of hydrogen appear to be lower. The generation rate was measured to be $193 \mu\text{mol } H_2/\text{min}$.

FIGURE 3.23 Hydrogen as a Function of Time (9/27/15)

Figure 3.24 shows the rise in hydrogen prior to oxygen introduction as a function of beam energy. The rate of generation with respect to energy was $30 \mu\text{mol } H_2/\text{kW-min}$, though this value may be low for the reason given above.

FIGURE 3.24 Hydrogen as a Function of Beam Energy (9/27/15)

3.2.7 Phase-1 Experiment: Uranium Sulfate Irradiation (10/14/15)

The gas system was purged with helium prior to the experiment. Residual oxygen was low, but a small amount of air was added (400 ppm) when the valve in the solution processing part of the system had to be opened. Figure 3.25 shows hydrogen content, oxygen content, and beam power plotted with time for the experiment. The tune-up phase was slow to ensure good beam stability and positioning. During the tune-up, we were required to add air to reduce hydrogen concentration in the recycle gas. This started while the beam power was at 2.8 kW and occurred over 83 min. A total of 4360 μmol of oxygen was added. The O_2/N_2 -mix flow was stopped at the 180 min mark, which is shown at the dip in oxygen concentration. Hydrogen at this time leveled off at approximately 0.15% for the rest of the experiment.

FIGURE 3.25 Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (10/14/15)

Figure 3.26 shows the rise in hydrogen prior to the addition of air, where the sharp rise occurs during tune-up. Beam power was at 2.8 kW at this time. The rate of production is 115 $\mu\text{mol H}_2/\text{min}$.

FIGURE 3.26 Hydrogen Production as a Function of Time (10/14/15)

Figure 3.27 shows hydrogen as a function of beam energy. This is the same part of the experiment described above. Beam power is at 2.8 kW at this time. The data indicate a production rate of 40 $\mu\text{mol H}_2/\text{kW-min}$.

FIGURE 3.27 Hydrogen as a Function of Beam Energy (10/14/15)

3.3.8 Phase-1 Experiment: Uranium Sulfate Irradiation (10/25/15)

This experiment took place in two parts, displayed in Figures 3.28 and 3.29. This was due to the failure of a relay, which caused an accelerator interlock to trip. Before it could be replaced, radiation fields in the accelerator cell needed to diminish to a safe level. The vessel could not be purged prior to this experiment, so hydrogen data regarding production rates will be lower than actual.

As shown in Figure 3.28 {Part 1 of the experiment}, the initial oxygen level was 0.31%. The O₂/N₂ mix was added to control the hydrogen concentration. A total of 4690 μ mol oxygen was added. After the oxygen addition, the hydrogen concentration settled at 0.17%. During the purge to reduce radiation field in the analytical system, hydrogen rose to 0.20%. This part of the experiment was terminated when an interlock tripped at 586 min. Figure 3.29 shows a continuation of the experiment after the interlock relay was replaced. After the oxygen was added, the steady-state hydrogen concentration stayed between 0.20% and 0.23%.

FIGURE 3.28 Hydrogen and Oxygen Concentrations and Beam Power as a Function of Time (10/25/15, Part 1)

FIGURE 3.29 Hydrogen and Oxygen Concentrations and Beam Power as a Function of Time (10/25/15, Part 2)

Figure 3.30 shows the rise in hydrogen before the introduction of oxygen. Since the oxygen concentration was high, the data for hydrogen generation rate data may not be accurate due to the recombining of H_2 and O_2 , which would make the generation rate of hydrogen appear lower. It is given here for comparison (180 $\mu\text{mol } H_2/\text{min}$ at 4 kW beam power) and may not be indicative of the actual occurrence. Data for Part 2 are not displayed. Oxygen introduction occurred during this part of the experiment.

FIGURE 3.30 Hydrogen Production as a Function of Time (10/25/15, Part 1)

Figure 3.31 shows the rise in hydrogen prior to oxygen introduction as a function of beam energy. The rate of generation with respect to energy is 45 $\mu\text{mol } H_2/\text{kW-min}$; however, this value may be low for the reason given above

FIGURE 3.31 Hydrogen as a Function of Beam Energy (10/25/15, Part 1)

3.2.9 Phase-1 Experiment: Uranium Sulfate Irradiation (12/02/15)

This was a short experiment at low beam power. Figure 3.32 shows the hydrogen and oxygen concentration as well as beam power during the experiment. There was a long tune-up period at the beginning and there was about 150 ppm oxygen present. The oxygen fell to undetectable levels at about 45 min, indicating the formation of hydrogen. The sharp rise in hydrogen started at about 60 min, followed by the introduction of oxygen at 84 min.

FIGURE 3.32 Hydrogen and Oxygen Concentration and Beam Power as a Function of Time (12/2/15)

Figure 3.33 is a plot of hydrogen during its rise after about 60 min and before oxygen introduction. It shows a rate of 180 $\mu\text{mol H}_2/\text{min}$ at 3 kW beam power, which is reasonably consistency with previous experiments.

FIGURE 3.33 Hydrogen Production as a Function of Time (12/2/15)

Figure 3.34 shows the rise in hydrogen prior to oxygen introduction as a function of energy deposited into solution. The rate of generation with respect to energy was $180 \mu\text{mol H}_2/\text{kW}\cdot\text{min}$.

FIGURE 3.34 Hydrogen as a Function of Beam Energy (12/2/15)

3.3 SUMMARY

Table 3.1 contains a summary of the data represented by all the graphical results presented in the previous sections. Included is the date of the experiment, uranium concentration, maximum beam power, beam power during determinations, hydrogen generation rate, and hydrogen generation with respect to beam energy.

The hydrogen generation rate and hydrogen generation energy data were taken from the short period of time, usually during beam tune-up, when hydrogen was sharply rising and oxygen was at its lowest concentration. Since this is occurring during tune-up, the accelerator is not yet at maximum power. Also provided is the beam power at which these determinations were made. The hydrogen production as a function of time was taken from the graphical data. It is the slope of the line from the graphs of hydrogen as a function of time and reflects the hydrogen generation rate before oxygen is introduced into the vessel.

TABLE 3.1 Summary Data of Hydrogen Production

DATE	U-Conc	Maximum beam Power	Beam Power for Determinations	H ₂ Production as a Function of Time	H ₂ Production as a Function of Beam Energy	Steady State Hydrogen Concentration
			(KW)	μmol/min	(μmol/KW*min)	%
2/23/15	93.7	7.6	7.6	36	4.8	0.04
3/4/15	93.7	7.5	7.5	60	8.0	Not Determined
4/13/15	93.7	9.4	7.2	114	13	0.04
4/24/15	93.7	9.8	4.5	62	14	0.05
5/19/15	93.7	10	5.0	120	24	0.12
9/27/15	149	8.0	5.5	193	30	Not Determined
10/14/15	149	10	2.8	115	40	0.15
10/25/15	149	10	4.0	180	45	0.17
12/2/15	149	3.0	3.0	124	41	Not Determined

4 TARGET-SOLUTION MONITORING AND PROCESSING

4.1 INTRODUCTION

As reported in earlier sections, 5 L of uranyl sulfate solution was irradiated at the linac nine separate times as part of the mini-SHINE experiments. Each irradiation was performed by impinging the linac electron beam on a water-cooled tantalum target, which is located in a dry well of the target vessel holding the ~5 L of target solution. Irradiation times varied from 2 hours to ~40 hours total beam time on target. Full processing was completed for 6 of the 9 irradiations. Full processing included:

- Passing the irradiated uranyl sulfate solution through a titania Mo-recovery column, washing the column with sulfuric acid and then water, and stripping the Mo from this column using an alkaline solution;
- Acidifying the Mo-product with nitric acid and passing it through a second titania column (concentration column), followed by nitric-acid and water washes, and stripping the Mo from the column using an alkaline solution; and
- After acidification with nitric acid, purifying the product using the LEU-Modified Cintichem process.

Four irradiations with processing were completed with a solution containing 93.7 g-U/L, and the final two irradiations with processing were completed with a solution containing 149 g-U/L.

Results from the Mo-recovery column are qualitative rather than quantitative due to the fact that isotope activities in the feed solution were mostly low due to poor mixing and/or cross contamination between samples during the retrieval process. Some of the end-of-processing samples and NaOH wash and/or strip samples were also likely contaminated. However, partitioning results show that Mo-99, Zr-95, and I-131 adsorb on titania with the greatest affinity. Most fission products show better than 50% activity in the column effluent (little adsorption on titania). Results from the concentration column feed and final Mo-product show that Ru-103, I-131, I-133, Sb-127, Sn-125, and Rh-105 are the biggest contaminants that co-strip with the Mo product. Purity specifications were met for all of the irradiations except the third irradiation, where the concentration of NaOH used to strip the Mo from the first titania column was increased from 0.1 to 1 M, which most likely changed the chemical form of Ru, making it more difficult to remove.

The separation system and LabView software are discussed in detail below. All processing steps can be performed remotely immediately after irradiation except sample retrieval, which was done manually 12–24 hours post-irradiation.

4.2 EXPERIMENTAL

4.2.1 Target-Solution Monitoring Glovebox

In an effort to collect the maximum amount of data, we installed a target-solution monitoring loop in the target-solution monitoring glovebox. The monitoring loop included a pH meter, conductivity probe, and turbidity meter. However, bubble formation during irradiation prevented these instruments from giving reliable results. Figure 4.1 shows the target-solution monitoring glovebox, which also included a sample ladder that allowed collection of up to 7 samples during and after irradiation. After the first irradiation with processing, we felt that proper mixing was needed to obtain a more accurate measurement of Mo-99 activity in the feed solution. After each irradiation, the solution was transferred to the dump tank from the target vessel to mix the solution and then returned back to the target vessel. Samples were collected before the column was loaded. Unfortunately, each loop in the sample ladder shared a single length of tubing, so most of the samples were cross-contaminated, preventing determination of an accurate value for Mo-99 and other fission products in the feed solution for the initial recovery column.

FIGURE 4.1 Photos of Target-Solution Monitoring Glovebox. The turbidity cell (Kemtrak), conductivity cell (Fisher Scientific), and pH electrode (Hanna Instruments) can be seen in A. Photo B shows a close-up of the target-solution monitoring glovebox.

4.2.2 Molybdenum Recovery Glovebox

During target solution monitoring, a pump drew solution from the target vessel in the mini-hot cell. The solution first entered the Mo recovery glovebox (Figure 4.2) at one of the inlet solenoid valves on the left-hand side. The target solution was then drawn to the target-solution monitoring glovebox. The solution passed through the turbidity cell, then the conductivity cell, then the pH electrode cell, then finally through a sampling ladder consisting of eight pairs of solenoid valves. The solution was then drawn back to the Mo recovery glovebox and then passed through the pump. After the pump, the solution exits the Mo recovery glovebox at one of the outlet solenoid valves on the right-hand side as it returned to the target vessel.

At the end of irradiation, the target solution was passed into the dump tank and returned to the target vessel for sample collection and processing (the mixing step took place for all irradiations except the first). The column was pre-equilibrated with pH 1 sulfuric acid at 80°C, and all subsequent steps were also done at 80°C. Approximately 5 L of irradiated uranyl sulfate solution was loaded onto the column in the up-flow direction. Four to six samples of the column effluent were collected. The flow rate for equilibration, loading, and acid and water washes was 40 mL/min. The column was washed with 300 mL of pH 1 sulfuric acid in the up-flow direction, and samples were collected. The remaining acid wash was collected in an effluent bottle. The column was then washed with 300 mL of water in the up-flow direction, and the entire water wash was collected in an effluent bottle. The column was washed with 1 M NaOH (100 mL) at 20 mL/min in the down-flow direction to change the pH of the column. Samples were taken during this step for some of the mini-SHINE irradiations, but the wash was sent directly to a separate processing cell (BigFoot). The Mo-99 was stripped using 0.1 M NaOH at 20 mL/min in the down-flow direction. Samples were taken of the strip solution. The remaining strip solution was sent directly to Bigfoot and mixed with the 1 M NaOH prior to being acidified and passed through the concentration column. The Mo recovery column was then washed with 300 mL of water in the down-flow direction at 40 mL/min. This final water wash was collected in an effluent bottle.

4.2.3 LabVIEW System

LabVIEW was used to remotely control all of the solenoid valves and record process parameters.

The system can be operated either in automated or manual mode. In manual mode, a user has full control of all the liquid solenoid valves. During automated mode, the user simply presses the NEXT STEP button, seen on the right side of Figure 4.3. With each press of the button, the solenoid valves relevant to the current step in the process are opened, and unnecessary valves are closed. The 24 VDC solenoid valves are controlled by quad-format solid-state relays from Measurement Computing Corp. The program captures the temperatures of the upper and lower pre-heaters and the column. In addition, the program records the values of the load cells serving the dump tank and the pressure gauges in the gas collection system. All parameters recorded are time-stamped. To facilitate documentation of an experimental run, several comment boxes are available for users to enter time-stamped comments.

FIGURE 4.2 Photos of the Mo-Recovery Glovebox (A) and the Remote-Controlled Equipment Installed (B and C)

FIGURE 4.3. Screen Capture of the Data Acquisition and Remote Control Program Written in the LabVIEW Environment

4.2.4 Gamma Counting

All samples generated in the target solution and Mo recovery gloveboxes were gamma counted with a HPGe detector (Ortec), and spectra were analyzed with GammaVision software (Ortec). The detector was calibrated for efficiency using an Eckert&Ziegler multinuclide standard. Due to the complex spectra of multiple radionuclides present in most of the samples, only certain radionuclides could be clearly identified (Table 4.1). To better detect Mo-99 activity in the column effluent and acid wash, we assumed that transient equilibrium occurred during gamma counting of all samples, so the half-life of Mo-99 (65.9 h) was used as the half-life for Tc-99m. Due to its short half-life, I-132 was tracked with the half-life of its parent, Te-132. Niobium-97 was also tracked via its parent, Zr-97.

TABLE 4.1 List of Nuclides, Their Half-life, Gamma Peak Used for Analysis, and Branching Ratio at the Corresponding Energy Analyzed

Radionuclide	Half-life	Gamma Peak Analyzed (keV)	Branching Ratio at Energy Analyzed
Te-132	78.2 h	49.82	14.40%
I-132	78.2 h	522.68	16.09%
Nd-147	11.0 d	91.1	27.90%
Mo-99	65.9 h	181.07	6.00%
Tc-99m	65.9 h	140.5	87.20%
U-237	6.75 d	208.01	21.90%
Y-93	10.25 d	266.91	6.80%
Np-239	56.5 h	277.6	14.10%
Ce-143	33 h	293.27	42.80%
Rh-105	35.4 h	318.9	19.20%
Pm-151	28.4 h	340.06	22.40%
Ba-140	12.7 d	423.7	3.15%
Ru-103	39.25 d	497.08	91%
I-133	20.8 h	529.87	87%
Sr-91	9.5 h	555.56	61.50%
I-131	8.04 d	636.97	7.30%
Nb-97	16.9 h	657.92	98.20%
Cs-137	30 y	661.66	85.10%
Sb-127	92.4 h	685.5	35.70%
Zr-97	16.9 h	743.36	98%
Zr-95	64 d	756.73	54.50%
Nb-95	34.97 d	765.81	99.80%
Te-131m	30 h	793.77	13.80%
Cs-136	13.2 d	818.51	99.70%
Sn-125	9.6 d	1088.9	4.20%
Eu-156	15.2 d	1230.69	8.80%
I-135	6.57 h	1260.41	28.90%
La-140	40.27 h	1596.21	95.40%

4.3 RESULTS

Table 4.2 shows the nine different irradiations that were performed from February through October 2015. Molybdenum-99 separation, recovery, and purification processes were completed for six of the nine irradiations. In this section, gamma counting results for samples from all Mo-recovery processing steps are shown for the six irradiations performed with full processing. Also in this section, gamma-counting results for isotopes produced in the target solution will be discussed separately for the three irradiations performed without processing.

**TABLE 4.2 Mini-SHINE Irradiations
Performed with a LEU Solution as Uranyl
Sulfate**

Date of Irradiation	Uranium Concentration (g-U/L)	Processing
#1 - 2/23/2015	93.7	Yes
#2 - 3/4/2015	93.7	Yes
#3 - 4/20/2015	93.7	Yes
#4 - 4/26/2015	93.7	Yes
#5 - 10/14/2015	149	Yes
#6 - 10/26/2015	149	Yes
#1 - 5/21/2015	93.7	No
#2 - 9/27/2015	149	No
#3 - 10/3/2015	149	No

4.3.1 Mini-SHINE Irradiation #1

The first mini-SHINE irradiation with LEU uranyl sulfate solution was performed on 02/23/15. The concentration of uranium in the target solution was 93.7 g-U/L, and the total irradiation time was 2 hours. All gamma counting results were decay corrected to end of bombardment (EOB), which was 4:17 pm on 02/23/15. The final sample collected at the end of irradiation was used to determine the amount of activity in the feed for the first titania column; however, insufficient mixing of the target solution prior to sample collection and/or cross contamination of the samples resulted in a 20% underestimation of the activities in the feed. The activity in the strip solution from the first titania column (feed for concentration column after acidification) showed 80.7 mCi Mo-99, and the feed solution for the first titania column showed 63 mCi Mo-99, which is based on a feed solution volume of 5270 mL. Hence, these data must be considered qualitative.

Table 4.3 shows the activities for the feed, column-effluent (CE) samples, and acid-wash (AW) samples. The CE samples were collected every 20 min as the feed solution passed through the column, and the two AW samples were collected at 3.75-min intervals as acid passed through the column. The 1-sigma values associated with the gamma counting results for the CE and

AW samples are given under the activity values. Based on the data in the table, Zr-95 has a high affinity for titania. Some Te-132, Ru-103, and I-131 (higher errors) also adsorb on titania. The main isotopes that were found in the column effluent and/or acid wash are U-237, Np-239, Ba/La-140, Ce-143, Rh-105, Sr-91, Pm-151, and Y-93. Isotopes that were reported as less than values [minimal detectable activity (MDA)] or had high 1-sigma values associated with them include Eu-156, Cs-137, Mo-99, Sn-125, and Sb-127.

Table 4.4 shows the activities in the feed sample and strip samples (collected every 9 min). For the first irradiation, no individual samples were taken of the 1 M NaOH wash. The 1-sigma values for the gamma counting for the feed and strip samples are given under the activity values. Radionuclides that are present in the strip solutions (low 1-sigma values) include Mo-99, Tc-99m, I-132, I-131, I-133, Ba/La-140 (in the first strip fraction), Sb-127, Ru-103 (about 7% in first strip fraction), Rh-105, and possibly some Sr-91, but the 1-sigma values are high. Radionuclides that are not present in the strip solution due to MDA values reported as less than values and/or high 1-sigma values associated with the activities reported include Zr/Nb-95, U-237, Eu-156, Cs-137, Np-239, Cs-136, Nd-47, Te-132, Sr-92, and Sn-125.

TABLE 4.3 Activities of Isotopes in the Various Samples Collected with Their 1 σ Values for Irradiation #1^a

Radionuclide	Feed ($\mu\text{Ci/g}$) 1 σ (%)	CE#1 ($\mu\text{Ci/g}$) 1 σ (%)	CE#2 ($\mu\text{Ci/g}$) 1 σ (%)	CE#3 ($\mu\text{Ci/g}$) 1 σ (%)	CE#4 ($\mu\text{Ci/g}$) 1 σ (%)	CE#5 ($\mu\text{Ci/g}$) 1 σ (%)	CE#6 ($\mu\text{Ci/g}$) 1 σ (%)	AW#1 ($\mu\text{Ci/g}$) 1 σ (%)	AW#2 ($\mu\text{Ci/g}$) 1 σ (%)
Zr-95	0.51 1.97	<0.0032	0.005 79.7	0.0048 24.7	0.005 64.7	<0.0043	0.008 55.0	0.003 83.7	0.001 67.9
Nb-95 ^b									
U-237	2.06 3.09	1.00 4.62	2.11 4.00	2.00 3.52	1.81 4.13	2.11 3.91	2.09 4.11	1.06 5.20	0.18 11.7
Eu-156	0.01 54.4	0.04 42.9	0.080 33.6	0.022 47.3	0.073 38.5	0.060 58.4	<0.009 49.1	0.030 49.1	0.009 57.4
Cs-137	0.004 41.8	<0.0038	<0.0054	0.011 10.2	<0.0051	<0.0049	0.006 97.2	0.025 20.8	0.0050 12.7
Np-239	20.2 3.12	10.8 3.76	20.4 3.6	19.9 3.61	19.2 3.75	20.6 3.57	22.2 3.66	11.2 3.98	1.62 6.0
Mo-99	9.93 2.02	0.2 81.9	1.02 34.1	0.37 39.7	0.25 88.3	0.59 48.0	0.45 44.7	0.85 33.6	0.07 92.6
Ru-103	0.41 1.93	0.018 4.13	0.2 4.4	0.19 2.42	0.24 3.57	0.32 2.93	0.41 3.21	0.37 3.41	0.23 1.95
I-132 ^c	7.27 3.16	3.85 3.76	4.06 4.10	4.39 3.26	5.03 3.79	5.62 3.57	6.50 3.60	8.35 3.53	6.62 3.2
Te-131m	2.10 5.39	1.3 15.9	1.8 12.7	2.53 23.1	1.74 13.7	2.05 13.7	1.73 17.6	3.24 10.2	3.76 12.9
I-131	0.65 4.02	0.16 30.8	0.21 33.7	0.14 31.7	0.20 48.7	0.30 9.0	0.39 19.1	0.32 19.4	0.30 5.36
I-133	11.9 1.92	1.90 7.54	<0.11	<0.86	3.54 4.47	4.28 4.52	0.42 31.7	3.67 5.76	4.58 12.2
Cs-136	0.006 22.2	<0.0043	0.02 39.7	<0.0029	<0.0062	<0.0062	<0.0075	<0.0058	0.0024 34.1
Ba-140	2.00 4.16	0.66 18.9	1.74 12.3	1.43 6.91	2.11 10.4	2.73 11.4	2.84 11.1	1.82 16.8	0.31 20.8
La-140 ^b									
Ce-143	22.4 1.77	11.1 2.44	22.0 2.48	21.7 2.75	20.1 2.45	22.1 2.38	22.8 2.5	11.4 2.67	2.23 9.18
Zr-97	38.8 3.17	<0.068	0.47 29.5	6.29 45.5	0.44 42.0	0.31 36.9	0.41 44.9	0.25 47.6	2.74 57.7

TABLE 4.3 (Cont.)

Radionuclide	Feed ($\mu\text{Ci/g}$) 1 σ (%)	CE#1 ($\mu\text{Ci/g}$) 1 σ (%)	CE#2 ($\mu\text{Ci/g}$) 1 σ (%)	CE#3 ($\mu\text{Ci/g}$) 1 σ (%)	CE#4 ($\mu\text{Ci/g}$) 1 σ (%)	CE#5 ($\mu\text{Ci/g}$) 1 σ (%)	CE#6 ($\mu\text{Ci/g}$) 1 σ (%)	AW#1 ($\mu\text{Ci/g}$) 1 σ (%)	AW#2 ($\mu\text{Ci/g}$) 1 σ (%)
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	10.3 3.38	<0.0085	0.02 67.3	<0.0089	<0.011	0.031 44.0	0.030 58.0	0.040 41.9	0.016 46
Te-132	8.22 4.46	5.01 4.73	5.55 5.33	5.82 3.99	6.97 5.18	6.97 3.70	7.97 4.45	10.8 3.95	8.37 3.33
Nb-97 ^c	41.5 3.18	<0.073	0.16 63.4	4.57 38.9	0.32 28.5	<0.089	0.2 53	0.17 67.7	3.48 36
Rh-105	3.99 3.09	1.72 6.79	2.63 6.13	4.85 6.2	2.79 5.87	3.91 4.77	4.02 5.24	3.34 5.85	2.04 8.86
Sn-125	<0.01	0.07 69.6	<0.34	0.03 88.9	<0.02	0.064 75.9	<0.0518	0.2 59.4	0.037 57.9
Sb-127	0.13 4.23	0.079 24.9	0.05 25.7	0.065 19.4	0.03 88.8	0.086 21.1	0.17 21.9	0.13 20.0	0.020 39.3
Sr-91 ^d	66.3 2.1	31.9 12.2	66.8 9.16	>12 Half-lives	70.8 6.50	72.8 8.38	87.2 9.36	44.5 10.7	>12 Half-lives
Nd-147	2.04 3.32	0.59 6.21	1.64 4.6	1.16 4.04	1.13 5.16	1.73 4.40	1.76 4.56	0.47 12.5	0.066 9.57
Pm-151	1.45 4.35	0.55 35.8	1.65 12.2	1.22 53.4	1.65 12.3	1.71 9.36	2.34 13.8	0.55 63.4	0.96 46.2
Y-93	0.75 4.21	0.46 21.5	0.71 18.1	0.33 9.49	0.55 14.9	0.49 16.2	1.07 15.7	0.34 27.4	0.045 41.9
I-135 ^d	24.7 29.0	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives

^a Less than values are shown for peaks that were not seen, and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.

^d ">12 half-lives" means more than 12 half-lives have passed during gamma counting.

TABLE 4.4 Gamma Counting Results for the Feed Solution and Strip Samples with Their 1-Sigma Values for Irradiation #1^a

Radionuclide	Feed (μCi/g) 1 σ (%)	Strip#1 (μCi/g) 1 σ (%)	Strip#2 (μCi/g) 1 σ (%)	Strip#3 (μCi/g) 1 σ (%)	Strip#4 (μCi/g) 1 σ (%)	Strip#5 (μCi/g) 1 σ (%)	Strip#6 (μCi/g) 1 σ (%)	Strip#7 (μCi/g) 1 σ (%)
Zr-95	0.51 1.97	0.016 29.7	0.025 28.6	0.002 67.6	0.0062 39.3	<0.0011	0.0054 44.1	0.004 49.3
Nb-95 ^b								
U-237	2.06 3.09	<0.042	0.07 67	0.06 46.4	61.8 60	0.04 52.6	0.05 86.7	<0.012
Eu-156	0.01 54.4	0.050 43.9	0.03 79.4	<0.0041	<0.0044	<0.0055	<0.0047	0.01 65.8
Cs-137	0.004 41.8	0.003 96.3	0.0082 34.6	0.0051 31.5	0.0072 24.2	0.046 27.8	0.0066 20.9	0.0029 30
Np-239	20.2 3.12	0.41 47.5	<0.12	0.1 77.5	0.36 32.4	0.23 34.3	0.2 62	0.11 42.3
Mo-99	9.93 2.02	13.5 4.25	9.28 6.88	3.87 5.44	3.56 8.66	2.52 10.4	1.75 12.1	1.26 10.5
Ru-103	0.41 1.93	0.26 4.72	0.27 3.06	0.037 13.6	0.039 11.8	0.033 13.9	0.033 13.5	0.026 9.01
I-132 ^c	7.27 3.16	0.46 15.3	0.1 66.2	<0.021	<0.0096	0.03 58.8	<0.0078	0.02 53.9
Te-131m	2.10 5.39	0.29 40.2	<0.03	0.2 50.4	0.08 61.6	0.21 31.3	<0.02	0.2 24.2
I-131	0.65 4.02	9.20 2.79	11.4 2.35	4.63 2.73	4.75 2.72	2 4.23	1.06 5.93	0.61 6.1
I-133	11.9 1.92	209 1.86	262 1.86	102 1.87	104 1.87	42.3 1.94	22 2.19	13.7 2.04
Cs-136	0.006 22.2	<0.00074	<0.0018	<0.00058	<0.00052	<0.0007	<0.00043	<0.00058
Ba-140	2.00 4.16	2.28 27.8	2.63 14.2	0.96 18.8	1.09 20	0.56 22.4	0.3 50.5	0.4 50.9
La-140 ^b								
Ce-143	22.4 1.77	<0.059	0.2 57.2	0.07 63.5	0.2 56.7	0.21 31.1	<0.05	<0.0075
Zr-97	38.8 3.17	0.64 27.1	0.83 18.9	0.1 61.1	0.18 48.1	0.1 60	<0.086	0.07 64.9

TABLE 4.4 (Cont.)

Radionuclide	Feed (μCi/g) 1 σ (%)	Strip#1 (μCi/g) 1 σ (%)	Strip#2 (μCi/g) 1 σ (%)	Strip#3 (μCi/g) 1 σ (%)	Strip#4 (μCi/g) 1 σ (%)	Strip#5 (μCi/g) 1 σ (%)	Strip#6 (μCi/g) 1 σ (%)	Strip#7 (μCi/g) 1 σ (%)
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	10.3	14.3	9.66	3.63	3.67	2.14	1.58	1.41
	3.38	3.61	3.62	3.66	3.71	3.78	3.98	3.71
Te-132	8.22	0.40	<0.18	<0.045	0.09	<0.052	0.06	<0.012
	4.46	55.3			90.3		83	
Nb-97 ^c	41.5	0.40	0.18	<0.045	0.088	0.05	0.062	0.01
	3.18	13.0	16.1		29.9	70.2	33.3	58.3
Rh-105	3.99	1.93	2.6	0.24	0.22	0.3	0.2	0.1
	3.09	16.7	14.2	43.8	49.5	36.3	68.7	50
Sn-125	<0.01	0.04	0.41	0.1	0.5	0.084	<0.03	<0.0078
		86.6	21.5	54.9	55.9	27.7		
Sb-127	0.13	0.33	0.11	0.27	0.31	0.3	0.28	0.28
	4.23	6.4	21.6	7.37	6.36	5.59	8.3	4.93
Sr-91	66.3	13.5	12.9	0.9	7.63	5.75	4.9	2.08
	2.1	35.3	34	86.5	34.8	34.4	43.7	31.1
Nd-147	2.04	<0.029	<0.028	0.3	<0.017	<0.015	<0.017	<0.008
	3.32			74.1				
Pm-151	1.45	<0.21	1.1	0.44	0.49	<0.092	0.32	<0.044
	4.35		40.4	40.4	46.8		44.8	
Y-93	0.75	0.54	0.2	0.2	0.1	0.1	0.2	<0.028
	4.21	32.2	94.8	39.1	60.5	71.3	51.2	
I-135 ^d	24.7	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
	29.0							

^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes who activity at time of counting is indicative of mother's behavior.

^d ">12 half-lives" means more than 12 half-lives have passed during gamma counting.

4.3.2 Mini-SHINE Irradiation #2

The second mini-SHINE irradiation with LEU uranyl sulfate solution was performed on 03/04/15. The concentration of uranium in the target solution was 93.7 g-U/L, and the total irradiation time was 7 hr, 15 min. All gamma counting results are decay corrected to EOB, which was 10:03 pm on 03/04/15. At the end of irradiation, the solution was passed into the dump tank via an emergency valve, which took about 12 min. The solution was then passed back into the target vessel, which took about 2.5 hr at 40 mL/min. Once all of the solution was in the target vessel, it was passed through the target-solution monitoring loop for about 1 hr. Seven samples were collected every 9 min, and the activities in the feed were much closer to the activities that were actually produced. The fifth sample collected was used to determine the activities in the feed solution for the first titania column; the feed was found to contain 331 mCi Mo-99 (total feed solution volume was 5240 mL). This was comparable to the Mo-99 activity in the feed for the concentration column of 326 mCi. Samples collected after this irradiation showed that sufficient mixing had occurred without cross contamination among samples during the retrieval process.

Table 4.5 shows the activities for the feed, column-effluent samples, and acid-wash samples along with their corresponding 1-sigma values shown under the activity values. Each column-effluent sample was collected after 20 min of feed solution having passed through the column (no CE#2 sample was present in the sampling loop during the retrieval process), and each acid-wash sample was collected after 3.75 min of acid having passed through the column. Based on the data shown below, Zr-95 has the highest affinity for titania, which is consistent with irradiation #1 results. It appears that most of the Cs-137 stays on the column, but the 1-sigma values are in the 20% range. Some other isotopes that appear to adsorb on the column are I-131 (15-20% 1-sigma values), Ba-140, Ce-143, Ru-103, Rh-105, Sb-127 (30-40% 1-sigma values), Sr-91, Nd-147, Pm-51, and Y-93. The principal isotopes that were found mainly in the column effluent and/or acid wash include U-237, Np-239, Te-132, and I-132. Isotopes with MDA activities reported as less than values or high 1-sigma values associated with them include Eu-156, Cs-136, Mo-99, and Sn-125.

Table 4.6 shows the activities in the feed solution and strip samples (collected every 9 min) along with the corresponding 1-sigma values given under the activity values. For this second irradiation, no individual samples were taken of the 1 M NaOH wash. Radionuclides that were present in the strip solutions (low 1-sigma values) include Mo-99, Tc-99m, I-131, and Ru-103 (8-10% found in strip fraction relative to feed concentration). Some isotopes that were present in some of the strip samples include Ba-140 (3-5% of feed activity in two strip samples), Ce-143, Rh-105 (10% in one strip sample), Te-132 (~3% in one strip sample), and Y-93 (~1.5% in most strip samples). Radionuclides that are not present in the strip solution due to MDA values reported as less than values and/or high 1-sigma values associated with the activities reported include Zr/Nb-95, U-237, Eu-156, Cs-137, Np-239, Cs-136, Nd-47, Pm-151, Sr-92, and Sn-125.

TABLE 4.5 Activities of Isotopes and 1-Sigma Values for the Feed, Column Effluent, and Acid Wash Samples for Irradiation #2^a

Radionuclide	Feed (μCi/g) 1σ (%)	CE#1 (μCi/g) 1σ (%)	CE#3 (μCi/g) 1σ (%)	CE#4 (μCi/g) 1σ (%)	CE#5 (μCi/g) 1σ (%)	CE#6 (μCi/g) 1σ (%)	AW#1 (μCi/g) 1σ (%)	AW#2 (μCi/g) 1σ (%)
Zr-95	2.58 1.97	0.01 76.7	<0.0052	0.02 66.8	0.01 76.1	0.03 71.5	<0.015	0.02 53.3
Nb-95 ^b								
U-237	8.83 3.10	3.12 4.07	5.13 3.62	7.41 3.72	7.030 3.720	6.76 4.59	4.84 4.73	0.41 21.1
Eu-156	0.07 41.1	0.1 52.4	0.09 53.1	0 51	<0.22 59	0.3 59	0.1 76.9	0.1 56.9
Cs-137	0.16 7.84	0.032 20.5	<0.0061	0.042 25.4	0.056 18.1	0.044 45.7	0.055 28.2	0.033 24.4
Np-239	100 3.12	36.8 3.65	58.6 3.48	85.3 3.52	83.3 3.51	74.7 3.87	55 4.02	12.1 6.17
Mo-99	52.7 2.00	<0.16	1.61 20.9	<0.73	<0.63	3 51.2	4 49.6	2 55.5
Ru-103	2.3 1.94	0.94 2.82	1.12 2.21	1.14 2.67	1.16 2.43	1.23 4.22	1.22 3.72	0.98 3.79
I-132 ^c	35.3 3.14	19.1 3.48	21.6 3.22	22.2 3.25	25.7 3.51	27.6 4.26	38 3.74	41.9 3.45
Te-131m	8.78 4.41	6.88 8.95	8.14 7.71	5.2 33.6	8.67 10.6	9.14 16.2	12 12.6	13 16.5
I-131	3.74 6.14	0.41 24.9	0.89 9.95	0.74 20.3	0.78 17.6	0.98 29.9	1.41 16.3	1 16.1
I-133	69.2 1.9	<0.3	0.56 49.3	0.6 88.8	0.9 53.7	<0.97	1.16 66	7.66 18.3
Cs-136	<0.0058	<0.01	<0.011	<0.02	<0.019	<0.038	<0.027	<0.012
Ba-140	13.5 2.78	4.16 12.1	5.85 6.89	8.74 5.12	9.1 6.13	9.54 12	8.58 13.5	3.83 22.1
La-140 ^b								
Ce-143	108 1.76	38.0 2.49	60.4 2.38	88.2 2.4	85.6 2.5	76.5 3.1	56.2 2.77	11.7 6.51
Zr-97	185 3.17	2.2 29.9	1.63 28	2.61 31.6	0.9 64.8	1 73.2	4.8 29.1	<1.47

TABLE 4.5 (Cont.)

Radionuclide	Feed (μCi/g) 1σ (%)	CE#1 (μCi/g) 1σ (%)	CE#3 (μCi/g) 1σ (%)	CE#4 (μCi/g) 1σ (%)	CE#5 (μCi/g) 1σ (%)	CE#6 (μCi/g) 1σ (%)	AW#1 (μCi/g) 1σ (%)	AW#2 (μCi/g) 1σ (%)
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	55.6	0.03	0.067	0.1	0.12	<0.067	<0.053	0.08
	3.38	79.4	38.6	46.3	36.8			58.2
Te-132	41.4	23.7	28.3	28.4	32.8	34.4	44.4	54.4
	3.18	3.63	3.47	3.96	3.65	4.39	3.74	3.37
Nb-97 ^c	205	0.4	<0.27	<0.48	1.66	1.61	2	4.89
	3.18	87.4			26.3	70.4	47.4	36.5
Rh-105	19.5	7.92	11.7	16.3	15.8	15.5	12.5	6.96
	3.04	5.22	4.15	4.53	4.51	7.1	7.4	13.4
Sn-125	<0.058	0.2	<0.064	<0.13	<0.13	<0.27	<0.11	0.2
		63.2						95.3
Sb-127	0.94	0.16	0.13	0.18	0.32	0.59	0.17	0.22
	3.55	33.4	43.7	44.6	19.9	29.7	36.4	36.9
Sr-91 ^d	308	148	317	341	273	365	281	>12 Half-lives
	1.93	15.4	13.9	11	19.1	20.4	21.1	
Nd-147	4.57	3.54	3.66	5.34	5.33	4.84	3.23	0.75
	3.43	4.22	4.16	4.3	4.25	7.34	5.64	9.54
Pm-151	7.05	3.08	3.68	6.33	5.77	6.48	2.67	2.72
	3.74	17.8	10.3	10.1	10.6	18.8	35.5	4.01
Y-93	9.66	0.68	1.00	1.32	1.36	1.72	1.6	<0.21
	3.36	20.4	12.8	16.5	15.4	24.4	20.8	
I-135 ^d	153	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
	2.51							

^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.

^d "> 12 half-lives" means more than 12 half-lives have passed during gamma counting.

TABLE 4.6 Activities and 1-Sigma Values for the Isotopes Found in the Feed and Strip Samples for Irradiation #2^a

Radionuclide	Feed (μCi/g) 1σ (%)	Strip#1 (μCi/g) 1σ (%)	Strip#2 (μCi/g) 1σ (%)	Strip#3 (μCi/g) 1σ (%)	Strip#4 (μCi/g) 1σ (%)	Strip#5 (μCi/g) 1σ (%)	Strip#6 (μCi/g) 1σ (%)	Strip#7 (μCi/g) 1σ (%)
Zr-95	2.58 1.97	0.061 15.5	0.018 34.9	0.021 31.4	0.024 31.5	0.011 45.7	<0.0018	<0.0029
Nb-95 ^b								
U-237	8.83 3.1	<0.12	0.22 31.8	0.09 62.9	0.2 83.2	0.08 56.7	0.3 55.6	<0.042
Eu-156	0.07 41.1	0.04 58.4	0.060 39.5	0.050 43.2	<0.025	0.044 41.8	0.05 82.5	<0.013
Cs-137	0.16 7.84	0.008 66.1	0.012 27.2	0.0084 33.7	0.012 38.1	0.010 19.9	0.016 29.7	0.012 34.5
Np-239	100 3.12	0.8 62.5	1.50 23.2	1.04 36.2	<0.39	0.42 48.1	0.9 56.0	0.5 51.4
Mo-99	52.7 2	75.2 2.80	8.45 7.92	16.7 4.47	45.9 3.37	9.82 8.12	31.8 4.38	9.85 14.4
Ru-103	2.3 1.94	2.88 2.10	0.85 2.30	0.54 2.68	1.15 2.18	0.38 2.89	0.60 4.97	0.41 4.69
I-132 ^c	35.3 3.14	0.51 36.2	6.99 3.88	0.20 47.9	<0.047	0.07 54.4	0.2 55.3	0.25 41.9
Te-131m	8.78 4.41	1.23 41.3	2.95 18.4	0.98 36.5	<0.3	0.5 52.1	1.25 42.5	1.24 33.4
I-131	3.74 6.14	62.2 2.00	7.50 2.41	18.8 2.20	76.4 1.93	5.11 3.16	45.8 2.06	3.91 5.82
I-133	69.2 1.9	1385 1.86	163 1.96	416 1.89	1710 1.85	112 2.03	1020 1.88	73.4 2.99
Cs-136	<0.0058	<0.0015	0.003 59.0	0.0080 37.8	<0.0016	<0.0018	<0.0012	0.0093 31.7
Ba-140	13.5 2.78	2.68 14.4	0.83 24.7	0.5 56.1	4.08 16.5	0.72 26.2	1.52 43.6	0.89 35.1
La-140 ^b								
Ce-143	108 1.76	<0.35	2.06 20.2	0.3 88.0	1.25 49.2	<0.13	2 55.6	1.21 28.7
Zr-97	185 3.17	<2.99	1 73.3	<1.42	<2.42	<0.95	<2.63	0.7 98.1

TABLE 4.6 (Cont.)

Radionuclide	Feed (μCi/g) 1σ (%)	Strip#1 (μCi/g) 1σ (%)	Strip#2 (μCi/g) 1σ (%)	Strip#3 (μCi/g) 1σ (%)	Strip#4 (μCi/g) 1σ (%)	Strip#5 (μCi/g) 1σ (%)	Strip#6 (μCi/g) 1σ (%)	Strip#7 (μCi/g) 1σ (%)
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	55.6	76.5	8.16	17.0	48.2	8.22	30.1	7.22
	3.38	3.59	3.81	3.66	3.61	3.74	3.63	3.96
Te-132	41.4	1	8.40	<0.18	<0.34	0.24	0.7	<0.13
	3.18	55.0	4.93			48.3	51.1	
Nb-97 ^c	205	3.14	1.55	1	2.21	1.14	1	<0.61
	3.18	27.5	32.4	55.7	39.9	30.6	52.4	
Rh-105	19.5	12.5	2.78	2.07	4.75	1.28	4.29	1
	3.04	14.5	19.5	35.6	27.3	33.9	31.6	86.5
Sn-125	<0.058	0.31	0.30	0.27	0.33	0.32	0.2	<0.049
		40.9	26.9	32.7	34.6	21.7	54.3	
Sb-127	0.94	1.95	0.31	1.13	1.52	1.09	1.32	1.29
	3.55	4.68	12.2	4.92	4.17	4.75	6.63	6.4
Sr-91 ^d	308	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
	1.93							
Nd-147	4.57	<0.078	<0.032	<0.04	<0.077	<0.026	<0.069	<0.033
	3.43							
Pm-151	7.05	<0.82	<0.36	3	<1.00	0.92	2	2
	3.74			51.7		45.1	56.3	57.2
Y-93	9.66	0.84	0.2	0.31	0.6	0.2	0.76	<0.16
	3.36	41.3	57.4	42.5	95.4	58.0	35.6	
I-135 ^d	153	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
	2.51							

^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.

^d "> 12 half-lives" means more than 12 half-lives have passed during gamma counting.

4.3.3 Mini-SHINE Irradiation #3

The third mini-SHINE irradiation with LEU uranyl sulfate solution was performed over the course of 3 days due to problems with a linac cable and power supply. The concentration of uranium in the target solution was 93.7 g-U/L, and irradiation time was close to 40 hr, with about 31.5 hr at full power. The end of irradiation occurred at midnight on 04/16/15. The first sample collected after mixing was used to determine the activities in the feed solution for the first titania column, which showed 760 mCi Mo-99 (total feed volume was 5185 mL). This is significantly less than what was found in the concentration column feed (900 mCi). Samples collected after this irradiation showed that insufficient mixing and/or cross contamination between samples had occurred during the retrieval process because the Mo-99 activity in the feed sample was ~140 mCi less than what was sent to BigFoot for further processing.

Table 4.7 shows the activities for the feed, column effluent samples, and acid wash samples. Each column effluent sample was collected after 20 min of feed solution having passed through the column (no CE#1 sample was in the loop during retrieval process), and only one acid wash sample was in the loop during the retrieval process (collected 3.75 min after acid having passed through the column). Also included in Table 4.7 are the 1-sigma values associated with the gamma counting results for each isotope, which are given under the activity values. Based on the data shown below, Zr-95 has the highest affinity for titania, which is consistent with irradiation #1 and #2 results. Nearly all of the U-237, Np-239, Ce-143, Nd-147, and Pm-151 are found in the column effluent samples and acid wash, but it is known that the activities in the feed are at least 15% low. Some isotopes are present in the column effluent and acid wash with increasing concentrations that peak at a percentage (concentration in stream relative to concentration in the feed). They include I-131 (22%), Ru-103 (74%), I-132 (77%), Ba-140 (82%), Te-132 (82%), Sb-127 (60%), and Y-93 (80%). Note that Rh-105 shows little adsorption, and about 50% of the Sn-125 is found in the effluent and acid wash.

Table 4.8 shows the activities in the feed solution, 1 M NaOH wash (collected every 2.5 min), and strip samples (collected every 9 min). Table 4.8 also shows the 1-sigma values for the gamma counting results under the activity values. There is most likely cross contamination from the acid wash with the first 1 M NaOH wash because certain nuclides are present in this wash with relatively low 1-sigma values that are not expected to be found in the NaOH wash. They include Zr-95, U-237, Np-239, and Ce-143. Note that Mo-99 activity is the highest in the first strip sample, but it is also present in the 1 M NaOH wash fractions. Other nuclides present in the strip fractions include Ru-103, I-132, I-131, Sb-127, and Ba-140.

TABLE 4.7 Activities of Isotopes and 1-Sigma Values for the Feed, Column Effluent, and Acid Wash Samples for Irradiation #3^a

Radionuclide	Feed (μCi/g) 1σ (%)	CE#2 (μCi/g) 1σ (%)	CE#3 (μCi/g) 1σ (%)	CE#4 (μCi/g) 1σ (%)	CE#5 (μCi/g) 1σ (%)	CE#6 (μCi/g) 1σ (%)	AW#1 (μCi/g) 1σ (%)
Zr-95	7.76 9.95	0.02 59.2	0.01 87.6	0.02 60.2	0.03 83.8	0.03 71.4	0.075 30.6
Nb-95 ^b							
U-237	26.0 3.07	24.3 3.12	25.7 3.08	27.9 3.1	27.7 3.27	24.8 3.15	26.5 3.55
Eu-156	0.18 30.6	0.55 34	0.25 36.2	0.22 49.3	0.3 66.3	0.31 36.5	0.3 75.3
Cs-137	0.083 9.46	0.067 18.9	0.072 11.6	0.072 18.1	0.12 20.9	0.17 10.1	0.096 23.6
Np-239	220 3.13	213 3.16	227 3.14	246 3.16	248 3.33	220 3.22	239 3.54
Mo-99	123 2.14	3.62 35.1	2.22 24.1	4.65 38.4	10.9 33.2	<0.79	3 61.3
Ru-103	6.92 1.87	3.99 2.03	4.23 1.91	4.53 1.95	4.6 2.57	4.76 2.07	5.14 2.16
I-132 ^c	82.8 3.15	39.8 3.28	49.6 3.19	55.3 3.27	59.8 3.63	59.6 3.31	64.1 3.48
Te-131m	20.1 4.98	9.82 25.4	12.1 9.56	15.1 13.9	33.3 16.1	14.3 10.7	20.5 17
I-131	9.82 2.27	1.3 21.1	1 22.7	1.57 13.9	2.19 22.4	1.13 38.6	1.76 34.7
I-133	183 1.94	<1.29	2 41.8	3.16 48.8	<3.13	5.49 35.6	8.79 30.3
Cs-136	<0.012	0.054 29.4	0.073 12.5	0.076 31.6	0.12 23.1	0.15 20.9	0.16 30.2
Ba-140	34.1 2.63	14.5 3.76	15.6 3.99	18.7 5.07	19.4 7.97	22.8 5.38	27.8 3.93
La-140 ^b							
Ce-143	200 1.78	193 1.84	206 1.79	225 1.85	226 2.08	202 1.89	220 2.5
Zr-97	332 3.20	5.41 43.8	2.97 42.9	3 95.4	15.1 43.4	5 55.9	9.71 29

TABLE 4.7 (Cont.)

Radionuclide	Feed (μCi/g) 1σ (%)	CE#2 (μCi/g) 1σ (%)	CE#3 (μCi/g) 1σ (%)	CE#4 (μCi/g) 1σ (%)	CE#5 (μCi/g) 1σ (%)	CE#6 (μCi/g) 1σ (%)	AW#1 (μCi/g) 1σ (%)
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	121 3.38	<0.056	<0.033	<0.057	<0.12	<0.068	0.35 36.6
Te-132	96.1 4.45	47.7 4.7	58.4 4.66	64.6 4.64	68.3 4.86	66.8 4.76	78.5 4.2
Nb-97 ^c	235 3.2	3.13 46.1	2.46 40.6	2 89	8.86 47.2	3 77.4	<3.27
Rh-105	45.7 3.12	40.7 3.58	46 3.21	49.7 3.52	53.7 4.54	47.2 3.9	51.9 4.76
Sn-125	0.98 13.8	0.57 43.5	0.65 23.9	<0.15	3 76.9	<0.11	<0.19
Sb-127	2.46 3.9	0.83 12.4	0.73 7.93	0.93 11.2	1.44 15.4	1 15.9	1.46 19.9
Sr-91 ^d	759 14.1	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Nd-147	15.7 3.32	14.1 3.41	15 3.34	16.3 3.39	22.2 3.49	14.7 3.46	18 4.07
Pm-151	10.6 7.3	12.9 9.13	13.3 8.45	16.3 11.5	15.7 16.7	17.6 15.7	14.7 20.9
Y-93	4.34 4.65	2.41 11.3	2.95 6.43	3.45 8.47	4.32 13.2	2.21 16.1	3.48 14.4
I-135 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives

^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.

^d "> 12 half-lives" means more than 12 half-lives have passed during gamma counting.

TABLE 4.8 Gamma Counting Results and 1-Sigma Values for the Feed Solution and Strip Samples for Mini-SHINE Irradiation #3^a

Radionuclide	Feed (μCi/g) 1 σ (%)	NaOH Wash#1 (μCi/g) 1 σ (%)	NaOH Wash#2 (μCi/g) 1 σ (%)	Strip#1 (μCi/g) 1 σ (%)	Strip#2 (μCi/g) 1 σ (%)	Strip#3 (μCi/g) 1 σ (%)	Strip#4 (μCi/g) 1 σ (%)	Strip#5 (μCi/g) 1 σ (%)
Zr-95	7.76	0.031	0.029	0.54	0.93	0.88	0.67	0.65
Nb-95 ^b	9.95	31.5	13	3.2	2.98	2.65	2.46	2.32
U-237	26.0	6.63	0.3	<0.0065	0.25	0.27	0.11	0.14
Eu-156	3.07	3.72	10.1		41.6	42.9	48.7	37.2
	0.18	0.1	0.035	0.05	0.0069	0.002	0.029	0.005
	30.6	91.9	42.2	53.5	29.6	92	48.3	79.6
Cs-137	0.083	0.039	0.0069	<0.005	<0.0076	0.009	<0.0036	<0.0029
	9.46	23.8	43.1			65.7		
Np-239	220	55.3	4.29	1.69	1.37	0.91	0.1	0.1
	3.13	3.57	6.25	29.8	30.7	37.6	61.9	84
Mo-99	123	9.39	14.2	74.3	54.2	23.1	16.1	11.4
	2.14	12.6	3.25	2.52	3.24	3.83	4.38	3.91
Ru-103	6.92	1.93	0.4	6.12	6.21	5.3	4.66	3.47
	1.87	2.37	3.22	1.89	1.91	1.92	1.9	1.89
I-132 ^c	82.8	13.7	4.31	0.86	1.15	0.62	0.3	0.33
	3.15	3.75	3.53	14.6	19	20	53.3	21.7
Te-131m	20.1	4.72	0.4	0.3	0.42	0.7	0.2	0.33
	4.98	14.9	51.9	61.8	48	46.5	54.5	41.6
I-131	9.82	3.33	15.2	51.3	35.1	16	13	8.97
	2.27	6.77	2.07	1.93	2.2	2.46	2.14	2.17
I-133	183	51.4	180	625	421	184	149	105
	1.94	2.32	1.88	1.85	1.93	1.97	1.88	1.9
Cs-136	<0.012	<0.018	<0.0043	<0.0019	<0.0016	<0.0014	<0.00044	<0.00064
Ba-140	34.1	7.49	1.51	3.63	3.05	0.5	<0.15	0.34
	2.63	10.6	15.1	14.7	20.7	66.6		45.2
La-140 ^b								
Ce-143	200	50.8	3.3	1.89	0.97	<0.22	0.45	0.27
	1.78	2.56	4.24	21.8	38		28.9	35.2
Zr-97	332	2.11	1.03	15.9	28.4	26.5	19.9	20.1
	3.20	25.3	30.3	6.12	4.92	4.24	3.91	3.59

TABLE 4.8 (Cont.)

Radionuclide	Feed ($\mu\text{Ci/g}$) 1 σ (%)	NaOH Wash#1 ($\mu\text{Ci/g}$) 1 σ (%)	NaOH Wash#2 ($\mu\text{Ci/g}$) 1 σ (%)	Strip#1 ($\mu\text{Ci/g}$) 1 σ (%)	Strip#2 ($\mu\text{Ci/g}$) 1 σ (%)	Strip#3 ($\mu\text{Ci/g}$) 1 σ (%)	Strip#4 ($\mu\text{Ci/g}$) 1 σ (%)	Strip#5 ($\mu\text{Ci/g}$) 1 σ (%)
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	121 3.38	6.65 3.67	22.1 3.59	78.1 3.59	55.4 3.39	23.7 3.41	17.7 3.6	11.8 3.6
Te-132	96.1 4.45	18.8 4.57	1.23 15.2	<0.23	0.6 50.6	0.3 68.4	0.46 36.4	0.21 45.3
Nb-97 ^c	235 3.2	1.23 41.1	1.1 18.9	15.3 4.25	27.2 4.05	24.4 3.89	19.1 3.59	19.7 3.44
Rh-105	45.7 3.12	11.6 5.07	<0.21	1.87 46.1	3.49 23.8	2.47 29.8	1.98 25	1.07 23.7
Sn-125	0.98 13.8	0.1 75.2	0.2 50.3	0.58 13.4	1.14 14.6	0.41 26.9	0.33 23.2	0.24 21.8
Sb-127	2.46 3.9	0.54 12.2	0.2 11.4	2.96 3.49	5.66 3.51	2.17 4.64	3.79 3.31	4.06 3.26
Sr-91	759 14.1	202 17.6	13.5 44.6	<22.19	42.1 43.8	222 18.5	27.6 38.2	160 11.8
Nd-147	15.7 3.32	4.44 4.35	0.22 16.1	<0.072	<0.069	<0.041	<0.025	<0.018
Pm-151	10.6 7.3	3.46 18.3	0.69 38.6	<0.59	2 54.7	<0.48	0.9 36.3	0.58 32.9
Y-93	4.34 4.65	0.98 20	0.27 34.4	0.47 46.9	0.4 66.8	<0.17	0.2 59.5	0.24 38.7
I-135 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives

^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.

^d ">12 half-lives" means more than 12 half-lives have passed during gamma counting.

4.3.4 Mini-SHINE Irradiation #4

The fourth mini-SHINE irradiation with LEU uranyl sulfate solution was performed over the course of 3 days due to problems with the cooling water system for the Ta target. The concentration of uranium in the target solution was 93.7 g-U/L, and the solution was irradiated for 10 hr at 9.8 kW and 10 hr at 6.8 kW with 24 hr of decay between the irradiations. End of irradiation occurred at 10 pm on 04/26/15. The second sample collected after mixing was used to determine the activities in the feed solution for the first titania column, which showed 380 mCi Mo-99 based on a feed volume of 5070 mL. This is within range of the Mo-99 activity found in the concentration column feed (340 mCi).

Table 4.9 shows the activities for the feed, column effluent samples, and acid wash samples along with the corresponding 1-sigma values. Each column effluent sample was collected after 30 min of feed solution having passed through the column, and four acid wash samples were collected after 3.75 min of loading. The acid wash was increased from the previous irradiation to help aid in the removal of Ru, which was present in the final product at a concentration above the purity specifications. Based on the data shown below, Zr-95 has the highest affinity for titania, which is consistent with irradiations #1 to #3. It is difficult to decipher what is happening with Cs-137 because the activity in the feed is low, and the 1-sigma results are high. The concentrations of U-237 in the column effluent samples and acid wash samples are lower than expected based on the concentration of U-237 in the feed. More Np-239 was expected in the column effluent based on results from irradiations #1 to #3. Note that Ru-103 is comparable in concentration to the feed from the first few column effluent samples, but it begins to decrease in the CE#4 and AW#1 samples. About 50% I-132 and 25% I-131 are found in the effluent. Nearly all the Pm-151, Nd-147, and Y-93 are present in the column effluent samples. Also, Ba-140 and Rh-105 still remain adsorbed on the initial column to a certain extent. In addition, Ce-143 is mostly in the effluent, but some most adsorb on the column because not enough activity is found in the strip samples to obtain a complete mass balance.

Table 4.10 shows the activities and 1-sigma values in the feed solution, 1 M NaOH wash (collected every 2.5 min), and strip samples (collected every 9 min) along with 1-sigma values shown under activity values. The gamma counting results for NaOH wash #2 and strip #1 had high dead times (17 and 16%) due to high Mo-99 activity. As a result, the activities for U-237, Np-239, Ru-103, Ba-140, Pm-151, Nd-147, Sn-125, Rh-105, and Y-93 in the second NaOH wash and strip #1 have high 1-sigma values and are an overestimation of the true activity due to the higher dead times. The main isotopes that are present in the Mo-product solution include I-132, I-131, Ru-103, very little Ba-140, Sn-125, and Sb-127.

TABLE 4.9 Isotope Activities and 1-Sigma Values for the Feed, Column Effluent, and Acid Wash Samples for Irradiation #4^a

Radionuclide	Feed (μCi/g) 1 σ (%)	CE#1(μCi/g) 1 σ (%)	CE#2 (μCi/g) 1 σ (%)	CE#3 (μCi/g) 1 σ (%)	CE#4 (μCi/g) 1 σ (%)	AW#1 (μCi/g) 1 σ (%)	AW#2 (μCi/g) 1 σ (%)	AW#3 (μCi/g) 1 σ (%)	AW#4 (μCi/g) 1 σ (%)
Zr-95	3.84	0.074	<0.014	0.08	0.04	0.06	0.083	0.083	0.02
Nb-95 ^b	1.93	39.5		52.4	92	65.8	41.1	45.6	65.6
U-237	37.9	14.1	25.7	39.2	19.9	19.5	3.3	2.15	0.44
Eu-156	3.43	3.62	3.44	3.42	3.34	4.35	11.8	17.1	36.4
	0.21	0.5	1.16	0.61	0.8	0.5	0.79	<0.033	0.09
	23.9	50.3	27.6	44.4	62.6	50.3	28		52.7
Cs-137	0.11	0.092	<0.042	0.06	0.16	0.17	0.085	0.04	0.027
	4.58	30.9		63.9	27.4	23.8	29.5	64.1	49.6
Np-239	120	46.2	87.3	102	103	61.2	20.4	7.65	4.3
	3.48	3.71	3.58	3.44	3.45	3.85	5.93	8.46	13.5
Mo-99	63	4	<1.80	<1.48	3	<1.08	<0.96	<1.1	2
	2.51	50.8			87.6				60.2
Ru-103	7.33	2.86	5.24	6.46	6.2	4.92	2.77	1.58	1.26
	1.87	3.65	2.73	2.3	2.34	2.27	2.95	10.1	3.74
I-132 ^c	45	22.7	30	33.6	35.2	58.1	49.8	29.4	22.2
	3.16	4.05	3.84	3.8	3.83	3.6	4	3.8	3.64
Te-131m	15.6	5.49	8.92	7.88	8.22	12.9	11.2	5.43	4.9
	13.1	17.1	15	13.2	16.6	11.9	9.34	8.92	16
I-131	4	1.89	1.94	2.03	<0.45	1	1.36	1.47	0.79
	4.08	30.8	33.6	37.4		78.8	46.7	39.9	32
I-133	<2.8	0.4	5.89	1.35	1.06	10.2	4.08	1.97	2.43
		76.5	7.97	31.6	45.3	8.45	13.7	25	18.2
Cs-136	0.089	0.12	0.0075	0.08	<0.07	0.083	<0.021	<0.017	0.028
	14.5	21.8	46.4	50.4		37.9			26.8
Ba-140	28.4	9.86	17.4	17.7	18.8	15.3	3.72	2.64	1.47
	2.39	16.3	13.2	13.6	12.3	14.6	37.4	42.5	46.5
La-140 ^b									
Ce-143	97.8	39.4	74.1	86.9	86.4	42.3	6.07	1.52	1.26
	2.51	2.37	2.14	1.95	2.23	2.63	6.19	15.8	23.9
Zr-97	126	0.6	0.87	1.31	1.63	1.24	<0.25	0.72	1.34
	5.91	60.8	33.3	33.3	27.3	40.2		42	31.8

TABLE 4.9 (Cont.)

Radionuclide	Feed (μCi/g) 1 σ (%)	CE#1(μCi/g) 1 σ (%)	CE#2 (μCi/g) 1 σ (%)	CE#3 (μCi/g) 1 σ (%)	CE#4 (μCi/g) 1 σ (%)	AW#1 (μCi/g) 1 σ (%)	AW#2 (μCi/g) 1 σ (%)	AW#3 (μCi/g) 1 σ (%)	AW#4 (μCi/g) 1 σ (%)
Sr-92 ^d	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives
Tc-99m ^c	62.2 3.59	0.35 28.5	0.44 31.6	0.34 30	0.64 21.1	0.3 50	0.1 72.3	0.2 55.5	0.15 48.1
Te-132	62.9 3.29	27.2 5.7	34.4 7.44	40.6 5.3	43.2 5.59	66.7 4.82	55.8 4.76	32.4 5.41	24.2 5.14
Nb-97 ^c	116 5.58	<0.18	<0.37	<0.32	1.31 27.1	1.17 30.4	0.88 30.1	0.5 52.1	<0.3
Rh-105	53.1 3.76	8.62 6.57	16.6 5.44	19.8 4.57	19.1 5.01	9.93 10.2	3.85 20.5	2.79 24.9	2.06 25
Sn-125	0.77 16	<0.32	0.6 73.2	1 63.6	0.4 78.2	<0.21	<0.2	1.61 2.2	<0.071 0.05
Sb-127	1.79 3.64	<0.077	0.94 17.1	0.8 17.6	0.88 26.1	0.49 38.3	0.29 44.4	0.13 39.8	0.05 67.3
Sr-91 ^d	>12Half-lives	66.8 6.03	126 7.5	>12Half-lives	>12Half-lives	78.8 9.13	16.4 19.6	8.68 30.3	55.4 36
Nd-147	18 3.88	5.6 5.58	10.2 6.22	13.4 4.05	13.1 4.31	6.04 6.09	0.61 32.3	<0.13	<0.1
Pm-151	10.5 15.7	2 66	7.56 14	5.51 18.1	5.82 18.4	5.08 27.1	0.4 91.1	1 59.4	0.7 66.7
Y-93	4.64 4.26	7.23 20.5	7.28 15	8.56 13.9	8.07 15.4	4.02 18.9	<0.48	<0.42	<0.31
I-135 ^d	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives

^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.

^d "12 half-lives" means more than 12 half-lives have passed during gamma counting.

TABLE 4.10 Gamma Counting Results for the Feed Solution and Strip Samples along with 1-Sigma Values Shown under Activity Values for Irradiation #4^a

Radionuclide	Feed (μCi/g) 1σ (%)	NaOH Wash#1 (μCi/g) 1σ (%)	NaOH Wash#2 (μCi/g) 1σ (%)	Strip#1 (μCi/g) 1σ (%)	Strip#2 (μCi/g) 1σ (%)	Strip#3 (μCi/g) 1σ (%)	Strip#4 (μCi/g) 1σ (%)
Zr-95	3.84 1.93	0.051 15.6	0.33 30.4	<0.066	0.068 24.8	0.017 31.4	0.016 26.5
Nb-95 ^b							
U-237	37.9 3.43	0.1 59.3	1 94.3	3.31 29.1	0 95.9	<0.12	<0.054
Eu-156	0.21 23.9	0.065 41.2	<0.091	0.3 60.8	0.15 32.8	<0.016	0.02 64.6
Cs-137	0.11 4.58	0.005 73.8	<0.064	0.07 76	0.008 87.4	<0.007	0.0054 45.6
Np-239	120 3.48	0.61 40.6	7.01 26.3	4.38 39.6	<0.24	<0.22	0.1 89.7
Mo-99	63 2.51	2.95 20	2933 2.7	2205 2.68	112 2.6	25.9 10.5	2.78 7.65
Ru-103	7.33 1.87	1.53 2.13	1.68 12.4	0.96 14.1	0.81 3.47	0.48 3.38	0.28 2.93
I-132 ^c	45 3.16	1.32 8.42	1 73.7	3 50.3	<0.085	0.2 85	0.11 47.5
Te-131m	15.6 13.1	0.55 31.7	5.08 30.9	<1.14	0.6 49.7	1.14 27.9	0.16 46.8
I-131	4 4.08	15.5 2.16	195 2.16	154 2.12	23.1 2.58	6.25 4.54	3.01 4.19
I-133	<2.8	168 1.86	2132 1.9	1733 1.9	240 1.94	63 2.1	30.6 2.01
Cs-136	0.089 14.5	<0.0009	0.14 23.3	<0.015	<0.0021	<0.0028	<0.00085
Ba-140	28.4 2.39	2.31 14.6	19 40.3	20.3 22.5	2.42 27.4	0.99 36.7	0.37 42.5
La-140 ^b							
Ce-143	97.8 2.51	0.3 44.1	4 66.8	<1.1	<0.18	0.4 53.1	0.1 62.2
Zr-97	126 5.91	0.24 39.3	<6.98	5 93.8	<0.72	<0.36	0.3 52.2

TABLE 4.10 (Cont.)

Radionuclide	Feed (μCi/g) 1σ (%)	NaOH Wash#1 (μCi/g) 1σ (%)	NaOH Wash#2 (μCi/g) 1σ (%)	Strip#1 (μCi/g) 1σ (%)	Strip#2 (μCi/g) 1σ (%)	Strip#3 (μCi/g) 1σ (%)	Strip#4 (μCi/g) 1σ (%)
Sr-92 ^d	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives
Tc-99m ^c	62.2 3.59	3.28 3.96	2985 4.41	2230 4.41	115 3.39	21.6 3.5	7.6 3.74
Te-132	62.9 3.29	1.41 12	<2.36	<1.39	1.05 47.5	<0.26	0.2 64.5
Nb-97 ^c	116 5.58	0.17 49.7	<1.57	<1.48	0.3 78.1	<0.14	<0.075
Rh-105	53.1 3.76	0.55 37.2	30 23.7	3 74.9	<0.37	<0.33	<0.13
Sn-125	0.77 16	<0.021	7.87 20.9	3.74 25.8	0.1 78.1	0.41 42.7	0.22 23.5
Sb-127	1.79 3.64	0.045 29.2	1.33 23.4	2.34 18.1	1.31 6.18	1.76 5.37	1.45 3.93
Sr-91 ^d	>12Half-lives	16.7 23	97.9 36.7	<13.6	<6.79	23.2 36.7	4 51.9
Nd-147	18 3.88	<0.039	9.74 13.3	<0.69	<0.13	<0.12	<0.039
Pm-151	10.5 15.7	0.3 80.6	14 29.3	17 37.6	1 53.2	2.33 29.2	<0.068
Y-93	4.64 4.26	0.71 22.1	9.35 33.6	6.15 42.5	2.53 32.4	1.06 31.4	<0.073
I-135 ^d	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives	>12Half-lives

^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.

^d ">12 Half-lives" means more than 12 half-lives have passed during gamma counting.

4.3.5 Mini-SHINE Irradiation #5

The fifth mini-SHINE irradiation with LEU uranyl sulfate solution and processing was performed on 10/14/15. The concentration of uranium in the target solution was 149 g-U/L, and the solution was irradiated for 4 hr at 10 kW power on the target. Total irradiation time was slightly over 7 hr. End of irradiation occurred at 6:30 pm on 10/14/15. The third sample collected after mixing was used to determine the activities in the feed solution for the first titania column, which showed 390 mCi Mo-99 based on a feed volume of 5330 mL. This is less than what was found in the concentration column feed (460 mCi). Samples collected after this irradiation showed that insufficient mixing and/or cross contamination between samples had occurred during the retrieval process because the Mo-99 activity in the feed sample was ~70 mCi less than what was sent to Bigfoot for further processing.

A solenoid valve failed due to an electrical connection in the glovebox during processing for the fifth irradiation. As a result, no samples were collected of the column effluent and acid wash. Table 4.11 shows the activities in the feed solution, 1 M NaOH wash (collected every 2.5 min), and strip samples (collected every 9 min) along with the corresponding 1-sigma values shown under the activity values. There is most likely cross-contamination of the acid wash with the 1 M NaOH Wash #1 sample due to the high activities of some isotopes that are not expected in the NaOH wash. The data show that qualitatively Ru-103, I-131, Rh-105, and Sb-127 are present in the Mo-product solution.

TABLE 4.11 Gamma Counting Results and 1-Sigma Values for the Feed Solution and Strip Samples for Irradiation #5^a

Radionuclide	Feed (μCi/g) 1σ (%)	NaOH Wash#1 (μCi/g) 1σ (%)	NaOH Wash#2 (μCi/g) 1σ (%)	Strip#1 (μCi/g) 1σ (%)	Strip#2 (μCi/g) 1σ (%)	Strip#3 (μCi/g) 1σ (%)	Strip#4 (μCi/g) 1σ (%)
Zr-95	4.78	0.11	0.015	0.013	0.019	0.0095	0.0061
Nb-95 ^b	2.17	2.29	6.48	9.01	15.2	14.6	15.6
U-237	5.44	0.34	<0.048	0.073	<0.2	<0.091	<0.065
Eu-156	4.45	7.35		29.9			
	<0.36	<0.025	<0.025	<0.017	<0.056	<0.014	<0.013
Cs-137	0.21	0.0045	<0.002	<0.0014	<0.0053	<0.0016	<0.0015
	11.3	12.7					
Np-239	131	5.16	<0.45	<0.71	<1.32	<0.62	<0.66
	3.56	4.9					
Mo-99	60.9	66.6	91.9	104	317	66.6	19.2
	3.52	2.61	2.56	2.56	2.7	2.67	3.21
Ru-103	3.94	0.28	0.073	0.16	0.28	0.16	0.11
	2.13	2	2.48	2.09	2.36	2.08	2.1
I-132 ^c	34.4	1.49	<0.14	<0.16	<0.48	<0.15	<.096
	3.54	5.16					
Te-131m	13	<2.3	<3.36	<2.6	<3.4	<2.98	<2.69
	11.6						
I-131	2.8	1.79	5.62	53	92.5	50.1	20.8
	10.3	2.33	2.12	1.97	1.88	1.97	1.99
I-133	46.8	<11.5	123	1020	>12 Half-lives		
	2.97		5.75	2.14			
Cs-136	0.12	0.0057	<0.0025	<0.0016	<0.0046	<0.001	<0.0015
	24.7						
Ba-140	15.6	0.37	<0.15	<0.16	<0.37	<0.13	<0.12
	4.97	9.39					
La-140 ^b							
Ce-143	132	6.8	<1.31	<1.99	<7.5	<1.81	<1.12
	2.48	7.64					
Zr-97 ^d	190	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
	3.42						

TABLE 4.11 (Cont.)

Radionuclide	Feed (μCi/g) 1σ (%)	NaOH Wash#1 (μCi/g) 1σ (%)	NaOH Wash#2 (μCi/g) 1σ (%)	Strip#1 (μCi/g) 1σ (%)	Strip#2 (μCi/g) 1σ (%)	Strip#3 (μCi/g) 1σ (%)	Strip#4 (μCi/g) 1σ (%)
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	56.3 3.59	67.9 3.3	95.9 3.3	85 3.3	321 3.15	69.9 3.31	19.9 3.32
Te-132	42 3.5	1.98 5.98	<0.24	<0.32	1 29.7	<0.28	<0.2
Nb-97 ^d	198 3.34	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Rh-105	26.2 4.76	3.72 12.8	<1.7	14 12.6	30.7 18.6	14 13.5	5.59 16.5
Sn-125	<0.87	<0.04	<0.053	0.14 20.7	0.3 22.8	0.15 17.9	0.11 21.4
Sb-127	1.29 11.2	0.1 8.38	0.093 13.8	0.9 3.89	>12 Half-lives	1.753 3.48	
Sr-91 ^d	753 15.2	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Nd-147	7.36 4.44	0.61 4.31	0.29 5.55	<0.038	0.9 5.6	<0.03	<0.022
Pm-151	7.66 15.3	<4.12	<4.61	<8.9	<23.8	<8.28	<7.34
Y-93	18.86 24.9	0.073 28.3	<0.066	<0.15	<0.31	<0.17	
I-135 ^d	<12 Half-lives	<12 Half-lives	<12 Half-lives	<12 Half-lives	<12 Half-lives	<12 Half-lives	<12 Half-lives

^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.

^d ">12 half-lives" means more than 12 half-lives have passed during gamma counting.

4.3.6 Mini-SHINE Irradiation #6

The sixth mini-SHINE irradiation with LEU uranyl sulfate solution and processing was performed on 10/26/15. Total time for beam on the target was 20 hr, with 17 hr at full power (~10 kW). The end of irradiation occurred at 7:00 pm on 10/26/15. Based on the activity in the feed for the concentration column, 1.42 Ci of Mo-99 was produced at EOB. After irradiation, the Mo-99 was separated and purified. Approximately 1.1 Ci was shipped to GE Healthcare (UK) on Tuesday, October 27th. The second sample collected after mixing post-irradiation was used to quantify the activity in the feed solution for the initial recovery column. Results indicate that poor mixing and/or cross-contamination had occurred because the activity in the feed sample was 980 mCi Mo-99 based on a feed volume of 5330 mL, which is 440 mCi less than what was found in the feed for the concentration column (~31% lower activity than what was produced based on concentration column feed results).

Table 4.12 shows the activities for the feed, column effluent samples, and acid wash samples along with 1-sigma values (shown under activity values in the table). Each column effluent sample was collected after 30 min of feed solution passing through the column, and only one acid wash was collected after 3.75 min of loading. Based on the data shown below, Zr-95 has the highest affinity for titania, which is consistent with all previous irradiations. Other isotopes that qualitatively show some adsorption on titania include Ru-103, I-132, I-131, Cs-136, Cs-137, Te-132, Sb-127, and Y-93. Radionuclides that show almost no adsorption on titania include U-237, Np-239, Ba-140, Nd-147, Pm-151, Ce-143, and Rh-105.

Table 4.13 shows the activities and 1-sigma values (given under activity values in the table) in the feed solution, 1 M NaOH wash (collected every 2.5 min), and strip samples (collected every 9 min). There is most likely cross-contamination in the first NaOH wash because isotopes that are not expected in this stream are present according to gamma counting results. These isotopes include U-237, Np-239, Ce-143, and Ba-140. Isotopes that are clearly present in the Mo-product solution include Ru-103, I-131, I-132, Rh-105, Sn-125, and Sb-127.

TABLE 4.12 Activities of Isotopes and Corresponding 1-Sigma Values for the Feed, Column Effluent, and Acid Wash Samples for Irradiation #6^a

Radionuclide	Feed (μCi/g) 1σ (%)	CE#1 (μCi/g) 1σ (%)	CE#2 (μCi/g) 1σ (%)	CE#3 (μCi/g) 1σ (%)	CE#4 (μCi/g) 1σ (%)	AW#1 (μCi/g) 1σ (%)
Zr-95	7.9	0.028	<0.058	<0.071	<0.070	<0.065
	2.69	22.3				
Nb-95 ^b						
U-237	14.3	8.96	17.3	20.3	20.1	12.3
	5.99	5.27	3.59	3.59	3.57	3.82
Eu-156	<1.16	<0.15	<0.52	<0.6	<0.55	<0.45
Cs-137	0.9	0.082	0.19	0.18	0.16	0.16
	19.1	6.76	7.23	9.21		9.62
Np-239	344	188	398	429	432	286
	3.57	3.88	3.17	3.25	3.23	3.32
Mo-99	153	<2.94	<6.82	<7.42	<4.72	<6.84
	4.12					
Ru-103	9.34	3.12	7.31	8.2	8.45	9.3
	2.33	1.92	1.94	1.95	1.95	1.94
I-132 ^c	104	22.5	64.5	83.6	88.4	148
	3.63	3.29	3.5	3.5	3.42	3.27
Te-131m	24.2	14.9	<24.1	<32.3	55.8	<31.9
	10.5	26.1			24.6	
I-131	10.3	1.31	2.4	2.69	3.06	4.6
	12.9	8.69	12.2	14.4	12	8.14
I-133	138	<34.7	<83.7	<99.3	<98.7	<93.6
	2.28					
Cs-136	0.79	<0.049	0.14	0.17	0.27	0.19
	13.7		18.9	18	17.2	21.5
Ba-140	41.9	9.12	35.2	41.5	46.7	36.2
	12.8	5	3.61	3.89	2.57	3.57
La-140 ^b						

TABLE 4.12 (Cont.)

Radionuclide	Feed (μCi/g) 1σ (%)	CE#1 (μCi/g) 1σ (%)	CE#2 (μCi/g) 1σ (%)	CE#3 (μCi/g) 1σ (%)	CE#4 (μCi/g) 1σ (%)	AW#1 (μCi/g) 1σ (%)
Ce-143	311 2.42	169 2.97	373 2.32	378 2.13	393 2.4	260 2.84
Zr-97 ^d	337 3.28	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	147 3.6	0.56 12.6	<0.42	<0.5	<0.49	<0.47
Te-132	116 3.73	27.6 5.39	72.2 3.71	90.5 3.68	93.9 3.59	155 3.46
Nb-97 ^{c,d}	372 3.22	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Rh-105	55.5 4.68	65.1 4.59	153 4.47	163 4.83	170 4.66	136 5.29
Sn-125	<3.08	<0.49	1.44 28.9	<1.04	<1.62	<1.51
Sb-127	2.64 11.8	0.81 9.74	1.75 11.1	1.8 11.7	1.9 13.5	1.45 13.9
Sr-91 ^d	597 4.17	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Nd-147	22.6 5.37	11.8 3.62	28.3 3.52	25.8 3.6	25.7 3.59	18.2 3.56
Pm-151	15.9 11.5	24.6 16.5	47.3 22.5	69.1 24.8	<44.3	<40.1
Y-93	13 17.8	1.45 10.6	3.32 10.8	5.17 9.1	5.46 8.39	3.8 11.2
I-135 ^d	<385	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives

Footnotes continued on next page.

TABLE 4.12 (Cont.)

- ^a Less than values are shown for peaks that were not seen and the minimum detection limit was calculated.
- ^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.
- ^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.
- ^d "12 half-lives" means more than 12 half-lives have passed during gamma counting.

TABLE 4.13 Gamma Counting Results and 1-Sigma Values for the Feed Solution, NaOH Wash, and Strip Samples for Irradiation #6^a

Radionuclide	Feed (μCi/g) 1 σ (%)	NaOH Wash#1 (μCi/g) 1 σ (%)	NaOH Wash#2 (μCi/g) 1 σ (%)	Strip#1 (μCi/g) 1 σ (%)	Strip#2 (μCi/g) 1 σ (%)	Strip#3 (μCi/g) 1 σ (%)	Strip#4 (μCi/g) 1 σ (%)	Strip#5 (μCi/g) 1 σ (%)
Zr-95	7.9	0.026	0.011	0.022	0.03	0.014	0.0012	0.013
Nb-95 ^b	2.69	17.5	19.8	24	20.6	20.5	17.6	20.1
U-237	14.3	1.63	0.36	<0.45	<0.49	<0.3	<0.22	<0.14
Eu-156	5.99	7.48	21.4	<0.079	<0.07	<0.038	<0.044	<0.037
Eu-156	<1.16	<0.11	<0.038	<0.079	<0.07	<0.038	<0.044	<0.037
Cs-137	0.9	0.02	<0.0057	<0.013	<0.011	<0.006	<0.0044	<0.0035
Cs-137	19.1	17						
Np-239	344	25.8	3.97	<3.41	<2.31	<1.88	<1.67	<1.03
Np-239	3.57	4.83	12.8					
Mo-99	153	5.09	63.3	216	160	74.7	35.4	16.5
Mo-99	4.12	19.4	3.05	2.89	3.09	3.14	3.72	6.42
Ru-103	9.34	1.64	0.46	1.21	2.75	2.28	1.61	1.11
Ru-103	2.33	1.98	2.3	2.09	1.94	1.89	1.9	1.95
I-132 ^c	104	30.7	3.96	<0.7	<0.6	<0.36	<0.25	<0.22
I-132 ^c	3.63	3.32	4.82					
Te-131m	24.2	7.94	3.44	<7.96	<6.74	<3.66	<3.63	<2.44
Te-131m	10.5	29.3	28					
I-131	10.3	2.85	32.7	131	184	122	54	22.7
I-131	12.9	5.34	2.01	1.9	1.88		2	2.04
I-133	138	<23.2	553	2098	2982	1955	866	377
I-133	2.28		2.3	2.2	2.06		2.18	2.75
Cs-136	0.79	<0.029	<0.011	<0.015	<0.0037	<0.002	<0.0062	<0.0071
Cs-136	13.7							
Ba-140	41.9	4.18	0.77	<1.03	<0.89	<0.48	<0.36	<0.19
Ba-140	12.8	8.04	15.4					
La-140 ^b								

TABLE 4.13 (Cont.)

Radionuclide	Feed (μCi/g) 1 σ (%)	NaOH Wash#1 (μCi/g) 1 σ (%)	NaOH Wash#2 (μCi/g) 1 σ (%)	Strip#1 (μCi/g) 1 σ (%)	Strip#2 (μCi/g) 1 σ (%)	Strip#3 (μCi/g) 1 σ (%)	Strip#4 (μCi/g) 1 σ (%)	Strip#5 (μCi/g) 1 σ (%)
Ce-143	311 2.42	22.7 5.86	4.15 26.9	<2.94	<8.05	<5.37	<3.37	<2.77
Zr-97 ^d	337 3.28	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Sr-92 ^d	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Tc-99m ^c	147 3.6	5.08 3.48	66.9 3.31	217 3.16	164 3.16	76 3.31	36.5 3.32	19.1 3.34
Te-132	116 3.73	33.7 5.19	4.07 7.96	<1.51	<1.13	<0.68	<0.66	<0.49
Nb-97 ^{c,d}	372 3.22	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Rh-105	55.5 4.68	13 12.4	5.69 30	29 21.9	31.7 23.7	25.6 15.7	<5.9	6.43 23.6
Sn-125	<3.08	0.36 27.6	<0.14	0.51 19.2	0.76 19.3	0.55 14.1	0.43 19.3	0.35 19.6
Sb-127	2.64 11.8	<0.13	1.08 5.52	3.6 4.21	8.52 3.45	8.6 3.31	6.93 20.1	5.48 3.34
Sr-91 ^d	597 4.17	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives
Nd-147	22.6 5.37	1.61 4.4	<0.072	<0.23	<0.23	<0.1	<0.072	<0.058
Pm-151	15.9 11.5	<12.2	<7.29	<28.9	<29.9	<14.9	<12	<9.32
Y-93	13 17.8	0.42 25.3	<0.33	<0.75	<0.93	<0.36	<0.32	<0.2
I-135 ^d	<385	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives	>12 Half-lives

Footnotes continued on next page.

TABLE 4.13 (Cont.)

- ^a Less than values are shown for peaks that were not seen, and the minimum detection limit was calculated.
- ^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.
- ^c Daughter isotopes whose activity at time of counting is indicative of mother's behavior.
- ^d "12 half-lives" means more than 12 half-lives have passed during gamma counting.

4.3.7 Discussion on Mo-Recovery Column Results

From all mini-SHINE irradiations, Zr-95 adsorbs on titania with high affinity. However, it can be seen in the concentration column feed for irradiations #4 and #6. These irradiations were performed 6 days (#4) and 12 days (#6) after a previous irradiation. Despite the fact that a small amount of Zr-95 was observed in the concentration column feed (Rf1 and RW fractions), it was not detected in the final product. The contaminants consistently found in the concentration column feeds for all irradiations include Ru-103, I-133, and I-131. For irradiations #2-#6, Sb-127 was also observed in the concentration column feed. Also, Sn-125 was found in the concentration column feed for irradiations #3, #5, and #6, and Rh-105 was found in the concentration column feed for irradiations #3, #4, #5, and #6. The sixth irradiation had the most contaminants in the concentration column, which included the previously discussed isotopes plus Cs-136, Y-93, and I-135. The largest activities were produced in the sixth irradiation.

For all of the mini-SHINE irradiations, Zr-95 and I-131 had less than 50% activity in the column effluent sample when compared to the feed (again most of the feed numbers were low and most samples were cross-contaminated); however, it is obvious that Zr-95, the I isotopes, and Mo-99 adsorb on the column with the highest affinity. Also, Zr-97 followed the behavior of Zr-95, but it could only be seen in irradiations #3 and #4. Furthermore, the following isotopes showed less than 50% activity in the column effluent:

- Y-93 for irradiations #1, #2, and #6
- Ba-140 and Eu-156 for irradiation #2
- Cs-137 for irradiations #2, #5, and #6 I-132, Rh-105, and Sb-127 for irradiation #4
- Cs-136 for irradiations #5 and #6

In addition, Te-132 and I-133 showed more than 50% activity on the column for irradiation #2. By contrast, U-237, Np-239, Ru-103, I-132, Nd-147, Ba-140, Ce-143, Te-132, Rh-105, and Sb-127 do not adsorb on the Mo-recovery column to an extent greater than 50% for the majority of the mini-SHINE irradiations.

4.3.8 Mini-SHINE irradiation #1- No Processing

A 12-hr irradiation was performed from 5/20/2015 to 5/21/2015. The target solution concentration was 93.7 g-U/L, and EOB was 3:00 am on May 21st. The solution was not processed due to loss of a pressure transducer used to monitor flow and a thermocouple malfunction on the column, which caused a vapor lock on the solenoid valves and prevented flow of solution through the column. Table 4.14 shows the gamma counting results, where about 200 mCi Mo-99 was produced at EOB based on a total volume of 5400 mL.

TABLE 4.14 Gamma Counting Results for the Irradiation on 05/21/15

Nuclide	Peak Info	Activity at Time of Counting (μCi)	Activity at EOB (μCi)	EOB Activity ($\mu\text{Ci/g}$)	EOB Total Activity (mCi)	1 Sigma (%)
Zr-95		0.591	0.63	1.70	11.0	1.98
Nb-95 ^a						
U-237		1.39	2.45	6.64	42.9	3.48
Eu-156	MDA ^b	0.035	0.045	0.12	0.78	
Cs-137	MDA	0.003	0.003	0.007	0.044	
Np-239		4.19	21.0	57.0	368	3.48
Mo-99		2.87	11.4	31.0	200	2.82
Ru-103		0.84	0.92	2.50	16.2	1.90
I-132 ^c		1.50	4.82	13.09	84.6	3.30
Te-131		0.1	2.09	5.66	36.6	11.03
I-131		0.41	0.65	1.77	11.5	4.36
I-133		0.16	13.0	35.2	227	2.29
Cs-136	MDA	0.002	0.002	0.006	0.039	
Ba-140		2.14	2.9	7.81	50.5	3.92
La-140 ^a						
Ce-143		1.41	22.2	60.3	390	2.40
Zr-97		0.14	32.9	89.2	577	3.33
Sr-92	>12 Half-lives ^d		>12 Half-lives	>12 Half-lives	>12 Half-lives	
Tc-99m ^c		2.77	11.0	29.9	194	3.59
Te-132		3.19	10.2	27.8	180	3.32
Nb-97 ^c		0.16	34.8	94.4	611	3.26
Rh-105		0.40	5.30	14.4	93.1	4.00
Sn-125	MDA	0.049	0.073	0.20	1.29	
Sb-127		0.089	0.24	0.65	4.18	6.67
SR-91	>12 Half-lives	0.014	>12 Half-lives	>12 Half-lives	>12 Half-lives	14.6
Nd-147		1.1	1.55	4.22	27.3	4.06
Pm-151		0.066	1.65	4.47	28.9	13.0
Y-93		0.31	0.45	1.22	7.89	8.30
I-135	>12 Half-lives		>12 Half-lives	>12 Half-lives	>12 Half-lives	

^a Less than values are shown for peaks that were not seen, and the minimum detection limit was calculated.

^b Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^c Daughter isotopes who activity at time of counting is indicative of mother's behavior.

^d "12 half-lives" means more than 12 half-lives have passed during gamma counting.

4.3.9 Mini-SHINE Irradiation #2: No Processing

A 12-hr irradiation was performed on 09/27/15. The target solution concentration was 149 g-U/L, and EOB was 3:30 pm on September 27th. The solution was not processed due to a vacuum problem with the linac. The target solution was only irradiated for 1.5 hr before the irradiation ended. Table 4.15 shows the gamma counting results where only about 60 mCi Mo-99 was produced at EOB based on a total volume of 5430 mL.

4.3.10 Mini-SHINE Irradiation #3: No Processing

A 2 Ci Mo-99 production run was attempted on 10/3/15. The target solution concentration was 149 g-U/L, and EOB was 5:30 pm on October 3rd. The solution was not processed because there was something wrong with the linac RF. The maximum stable repetition rate that we were able to operate with was 30 Hz, which is not enough for a Mo-99 shipment. Table 4.16 shows the gamma counting results for the irradiation that took place on 10/03/15, where about 200 mCi Mo-99 was produced based on a total volume of 5250 mL.

TABLE 4.15 Gamma Counting Results for the Irradiation on 09/27/15

Nuclide	Peak Info	Activity at Time of Counting (μCi)	Activity at EOB (μCi)	EOB Activity ($\mu\text{Ci/g}$)	EOB Total Activity (mCi)	1 Sigma
Zr-95		0.56	0.57	1.03	6.72	2.10
Nb-95 ^a						
U-237		0.34	0.38	0.69	4.51	7.02
Eu-156	MDA ^b	0.06	0.059	0.11	0.70	
Cs-137		0.06	0.061	0.11	0.72	17.9
Np-239		7.22	9.84	17.9	117	3.18
Mo-99		4.13	5.38	9.81	63.9	3.72
Ru-103		0.38	0.39	0.71	4.61	2.31
I-132 ^c		2.50	3.13	5.70	37.2	3.36
Te-131		0.44	0.79	1.43	9.33	7.44
I-131		0.59	0.65	1.18	7.67	7.74
I-133		5.69	13.2	24.0	157	1.89
Cs-136	MDA	0.01	0.01	0.01	0.10	
Ba-140		1.42	1.50	2.73	17.8	9.84
La-140 ^a						
Ce-143		6.08	10.3	18.8	123	1.88
Zr-97		6.56	18.6	33.8	221	3.10
Sr-92		0.14	90.7	165	1077	4.16
Tc-99m ^c		3.78	4.92	8.97	58.5	3.16
Te-132		2.83	3.54	6.45	42.0	3.74
Nb-97 ^c		7.39	20.8	37.9	247	3.12
Rh-105		1.05	1.72	3.14	20.5	3.84
Sn-125	MDA	0.05	0.05	0.10	0.65	
Sb-127		0.06	0.07	0.12	0.81	13.3
SR-91		5.30	32.6	59.3	387	1.89
Nd-147		0.41	0.43	0.79	5.15	6.17
Pm-151		0.33	0.60	1.10	7.18	6.74
Y-93		5.80	6.23	11.3	74.0	3.36
I-135		2.68	38.4	69.9	456	2.07

^a Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^b MDA indicates that the activities provided are all less than values.

^c Daughter isotope who activity at time of counting is indicative of mother's behavior.

TABLE 4.16 Gamma Counting Results for the Irradiation on 10/03/15

Nuclide	Peak Info	Activity at Time of Counting (μCi)	Activity at EOB (μCi)	EOB Activity ($\mu\text{Ci/g}$)	EOB Total Activity (mCi)	1 Sigma
Zr-95		2.04	2.11	2.74	17.3	2.12
Nb-95 ^a						
U-237		1.58	2.14	2.78	17.5	4.24
Eu-156	MDA ^b	<0.12	<0.14	<0.18	<1.14	
Cs-137		0.05	0.05	0.07	0.45	21.7
Np-239		19.4	46.4	60.3	380	3.49
Mo-99		11.5	24.4	31.7	199	2.88
Ru-103		1.40	1.47	1.92	12.1	1.99
I-132 ^c		6.76	12.7	16.5	104	3.21
Te-131		0.70	3.62	4.71	29.7	7.06
I-131		2.85	3.68	4.78	30.1	3.37
I-133		6.06	64.8	84.2	530	1.89
Cs-136	MDA	<0.02	<0.03	<0.04	<0.23	
Ba-140		6.26	7.35	9.55	60.2	5.50
La-140 ^a						
Ce-143		10.1	44.9	58.3	368	2.38
Zr-97		3.83	71.9	93.4	589	3.23
Sr-92 ^d	>12 Half-lives					
Tc-99m ^c		11.2	23.7	30.8	194	3.59
Te-132		8.80	16.5	21.5	135	3.35
Nb-97 ^c		4.25	78.5	102	643	3.18
Rh-105		2.00	8.05	10.5	65.9	3.92
Sn-125	MDA	<0.11	<0.14	<0.18	<1.11	
Sb-127		0.24	0.42	0.54	3.42	6.30
SR-91		0.72	119	155	978	3.23
Nd-147		2.90	3.50	4.55	28.6	4.04
Pm-151		0.46	2.63	3.42	21.5	7.37
Y-93		1.46	1.78	2.31	14.6	7.94
I-135		0.09	161	209	1320	17.0

^a Daughter isotope whose activity at EOB could not be accurately calculated from counting data.

^b MDA indicates that the activities provided are all less than values.

^c Daughter isotope who activity at time of counting is indicative of mother's behavior.

^d ">12 Half-lives" means more than 12 half-lives have passed during gamma counting.

5 CONCENTRATION AND PURIFICATION OF THE MO PRODUCT

The strip solution from the Mo-recovery column was transferred from the target solution to a shielded cell in an adjacent room to be concentrated, acidified, and fed into the LEU-Modified Cintichem process.

5.1 EXPERIMENTAL DESIGN FEATURES OF BIGFOOT HOT CELL

The Mo-99 produced by subcritical fission of an aqueous solution of uranyl sulfate was recovered from the irradiated solution on a titania column, washed with acid and then water, and eluted with base. The basic strip, containing the desired ^{99}Mo , was transferred directly to a hot cell (Bigfoot) for final purification (Figure 5.1). Initial experiments eluted ^{99}Mo into a transfer cask, which was later moved to the adjoining room and connected to Bigfoot via a small glove box (Figures 5.2 and 5.3, respectively). A transfer line (mentioned earlier) was put in place to allow for immediate processing of the product and for lowering of the dose to researchers. The line for Phase I is a single length (no breaks) of 1/8-in. diameter 304 stainless steel tubing and spans ~90 in.. A second line, for Phase II, was installed during the installment of the Phase I line, which is 1/4-in. diameter 304 SS tubing in 6-in. lengths welded end to end, ~90 in. long. Both lines are held inside of secondary containment for safety purposes. Prior to sealing the secondary containment, the lines were vacuum and liquid tested. Minimal solution holdup was observed. Several liquid monitors were installed in the secondary containment for leak detection. Both lines were swage-lock connected to valves within Bigfoot.

FIGURE 5.1 Bigfoot Hot Cell, Where Final Purification of ^{99}Mo is Performed

**FIGURE 5.2 Transfer Cask
Previously Used to Transfer ^{99}Mo
Product from Recovery Column to
Bigfoot**

The interior of Bigfoot was designed to accommodate various different aspects of the project and allow for adaptation to the research being performed. An image of the interior of Bigfoot is shown in Figure 5.4; various features are pointed out in the image. A quick-connect system was installed that enables three vacuum connections for simultaneous use, water in and out, and the option for compressed gas (Figure 5.5). These features rest on scaffolding that was welded to the back wall of the hot cell. This was purposefully done to increase floor space and thus work space. The scaffold supports the quick connect system, vacuum line, vacuum traps, gas scrubbers, pumps, pH probes, solution vessels, columns, the concentration column valve board, valves for the ^{99}Mo transfer lines, and electrical. It also serves as a barrier to protect and manage various tubing. Electric controls for heaters, stirrers, balances, pH probe readout, lights, etc., were placed on the exterior of the hot cell. Consideration was given to the placement (interior or exterior of the cell) for systems that require routine replacement or recharging. Every item that requires replacement or recharging (columns, solutions, etc.) may require entry of personnel into the hot cell. For example, the solutions spent during column operation are recharged during hot cell entries. This task can easily be removed, to minimize exposure of workers, by placement of the solution containers on the exterior of the hot cell. Solution lines would require safety controls such as secondary containment and redundant check valves

(ensuring single direction flow of solutions). If placement of items from within the hot cell to the exterior is not reasonable (i.e., the column), quick connects or simple “manipulator friendly” connections should be employed. In designing experiments requiring hot cells, consideration should be made to minimize personnel entries.

Other considerations to the experiments to be performed within the hot cell should also be made when designing hot cells. This is not a trivial task as the purpose of hot cells will change over time. However, some general design requirements, from the view of performing work within the hot cell, should include: manipulators that reach and perform tasks near the ceiling of the hot cell, guillotine doors for antechamber access, large outward swing access doors, floor ports for trash disposal or sample entry, multiple upper ports for equipment data cables and plumbing, and maximum floor space by mounting equipment to walls.

FIGURE 5.3 White Glovebox Previously Used to Connect the Transfer Cask to Interior of Bigfoot

FIGURE 5.4 Image of Interior of Bigfoot and Mini-SHINE Concentration Column (A), Column Control Board (B), Acidification Vessel (C), pH Probe (D), Reagent Vial (E), and Valves for Exterior Solution Line (F)

FIGURE 5.5 Image of Quick-Connect System: Gas Compressed Gas Connection (A) Exhaust Valve Connecting to Gas Collection System (B), and Water In/Out (hidden behind the board)

5.2 CONCENTRATION COLUMN DESIGN AND OPERATION

The Mo product from the recovery column in NaOH solution was received within Bigfoot in a pre-weighed 1 L vessel. The solution was mixed and then sampled prior to purification. Sampling the solution provides an accurate account of the product strip from the recovery column, which allows for determinations of experiment and equipment performance. On average, ~950 g of solution was transferred from the recovery glovebox to Bigfoot. This volume is too large to operate the LEU Modified Cintichem (LMC) process (maximum volume, 100 mL). Therefore, the solution was concentrated using a second column. A schematic diagram depicts the system used during concentration column operation (Figure 5.6). The column separation system consists of an FMI pump (positive displacement pump); Swagelok 3, 4, and 5-way switching valves; and Hamilton 3-port flow valves with a T-plug to direct process streams. All of the valves were mounted on a board (valve board), and the board was mounted on the scaffold previously mentioned. Reagent bottles were mounted to the scaffold and connected to the valve board using high density polyethylene (HDPE) tubing (1/8 in.). Stainless-steel tubing (1/8 in.) was used to connect the valves to each other and the pre-heater, and HDPE or

polyetheretherketone (PEEK) tubing was used to connect the column, reagent, and collection bottles. A stainless-steel line was used for the connection to the transfer cask (not used in later experiments). An FMI pump allows for forward and reverse flow. The concentration column system is equipped with a solution preheater, and the column is also wrapped with a heating tape.

FIGURE 5.6 Schematic Diagram of ^{99}Mo Concentration Column

After the ^{99}Mo solution was sampled, it was passed from the 1-L receiving vessel into the acidification vessel. Here the solution's pH was adjusted with 8 M HNO_3 to $\text{pH} = 2$ (monitored with a calibrated pH probe). The system was purged of air by passing water through the lines. The dead volume of the system was significant, 15 mL; hence, column pre-equilibration, wash, and strip volumes were increased to ensure that an appropriate volume reaches the column and is collected. The pre-equilibration, loading, and washing steps were carried out at 80°C . An Omnifit BenchMark column packed with S40 Sachtopore sorbent (ZirChrom Separations, Inc Anoka, MN) (1×1 cm, 0.8 mL bed volume) was pre-equilibrated with 36 mL of 0.01 M HNO_3 and subsequently loaded with 0.9 L of acidified Mo solution at 16 mL/min in the up-flow direction. Subsequently, the column was washed with 20 mL of 0.01 M HNO_3 and 20 mL of water solution at 16 mL/min in the up-flow direction at 80°C . During the product-stripping step, the initial 10 mL of strip solution was loaded, and eluent was collected in the water wash collection flask (to remove the water present in the system dead volume). Subsequently, Mo was

stripped with 25 mL of 1 M NaOH in the down-flow direction at 4 mL/min and 70°C. As the last step, lines were rinsed with 16 mL of water and collected as waste. Each process stream was collected in pre-marked and pre-weighed bottles. Samples of the eluent, acid wash, water wash, waste, and final product were collected for analysis. A complete detailed procedure is available in Appendix D.

5.3 LEU MODIFIED CINTICHEM (LMC) PROCESS

The Cintichem process is a small-scale (starting solution is ~50 mL) method for purification of fission molybdenum using specifically designed glassware designed for remote operation in hot cell. The original process was developed in 1974 [HIROFUMI-1974] for separation of useful isotopes like ^{99}Mo from mixed fission products produced by irradiation of 93% ^{235}U highly enriched uranium (UO_2) at the Cintichem facility in New York. The research facility was later sold to Hoffman-LaRoche and became Cintichem Inc. From 1980–1989 Cintichem Inc. was the only U.S. producer of ^{99}Mo , with weekly production of ~2000 6-day Ci/week ($1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$). The Cintichem process was later modified (LMC process) by Argonne to accommodate production of ^{99}Mo by LEU foil target, and sulfuric acid was replaced by nitric acid [WU-1995, -1996; ALILUDIN-1995; LEONARD-1996; BAKEL-2008].

Several full-scale demonstrations of the LMC process were performed at the BATAN (Indonesian Badan Tenaga Atom Nasional) facility in Indonesia in 1998–2010 by processing irradiated LEU-foil targets [MUTALIB-1998]. Recently, many papers have been published regarding the LMC process [MUSHTAQ-2009, BAKEL-2008, MCDONALD-2000, MUTALIB-1999, HWANG-2002, DIAS-2011, TKAC-2014, LIEM-2015], indicating continuous interest in this small-scale purification process. The key reagent of the process, α -benzoin oxime (ABO, Figure 5.7), allows selective precipitation of Mo from acidic conditions (~1 M HNO_3), where molybdenum is present as molybdenyl cation (MoO_2^{2+}) according to following reaction:

FIGURE 5.7 Alpha-benzoin Oxime (ABO)

Although the process was developed for purification of Mo from other fission products produced by irradiation of UO_2 or U foil targets, its application is not limited to these Mo-99 production pathways. However, in order to process Mo-99 produced in the SHINE system, Argonne needed to further modify the LMC process. After producing Mo-99 in the SHINE system (or any other uranium solution-based target or fuel), molybdenum can be separated from uranium by loading the uranium solution in moderate acid ($\text{pH} \sim 1$) containing fission products on a titania-based column. While uranium and some other fission products pass through, Mo is retained on the column and then recovered using 0.1 M NaOH, which needs to be converted to ~ 1 M HNO_3 in order to further purify Mo from other fission products using ABO.

The LMC process consists of several purification steps designed to purify Mo from other fission products (Figure 5.8).

FIGURE 5.8 Scheme of LMC Process for Purification of ^{99}Mo from Fission Products (Ag/C = silver-coated activated charcoal column; HZO = hydrated zirconium oxide)

The starting solution contains fission products, including Mo in ~ 1 M HNO_3 . Most attention is given to removal of radioactive iodine. During the dissolution of uranium foil or UO_2 in nitric acid, most of the iodine is present as I_2 and is collected in an iodine trap, although other iodine species such as I^- , IO_3^- , and IO_4^- may form during fissioning. In an accelerator-driven process using uranium-salt solution fuel, although the same iodine species can be expected, their distribution is expected to be different from solid U targets due to redox reactions in the solution occurring during irradiation. The sorption of iodine on titania sorbent is limited (I_2 adsorbs, but

the anionic species do not), and a fraction of the iodine will be in the eluent. For a full scale process where the feed into Mo recovery column is ~250 L, the strip solution needs to be concentrated by using another titania-based column. Before LMC, this solution needs to be further concentrated by evaporation and converted to ~1 M HNO₃.

After processing of 5 L of solution on Mo recovery column, the strip solution volume is usually about 1 L, and after the concentration column, it is reduced to ~25 mL. Since the volume is small, evaporation is not performed, and solution is then acidified with 10 M HNO₃ to make ~1.2 M HNO₃ solution (0.25 mL of 10 M HNO₃ is added per 1 mL of Mo product in 1 M NaOH).

After converting solution to ~1 M HNO₃, iodide is precipitated as AgI by adding NaI and AgNO₃ (Figure 5.8). The remaining silver is precipitated by adding HCl. Precipitation of iodide ion by the addition of silver nitrate is considered quantitative; the solubility of AgI is 8.3×10^{-17} M [SKOOG-1963]. Since I₂ does not co-precipitate with silver ion, it can be removed by reaction with silver metal to form the insoluble AgI. The solubility of silver iodate is also limited, but is significantly larger (3.1×10^{-8} M) than that of AgI. It is likely that AgIO₄ is even more soluble than AgIO₃. Vandegrift et al. [1997] have shown that radioactive iodine present as periodate can be removed by co-precipitation with AgI and AgCl if sufficient time is allowed for isotopic exchange.

The next step in the LCM process is addition of Mo carrier, and Ru and Rh hold back carriers to prevent their co-precipitation with Mo. To keep Mo in the hexavalent oxidation state, potassium permanganate is added. After addition of ABO, a white flocculate precipitate is formed and is collected on a fritted column with glass beads. The Mo-ABO precipitate is then washed multiple times with 0.1 M HNO₃. The Mo-ABO precipitate is then dissolved in NaOH/H₂O₂ solution upon heating. The glass beads in the filter provide better washing of the precipitate and better dissolution. The solution containing Mo and re-dissolved ABO is passed through a silver-coated charcoal column (Ag/C). The Mo passes through, while organic residuals are retained on charcoal resin. If I₂ is present, it reacts with silver metal on the Ag/C column to form insoluble AgI. Before the solution is loaded on the combination column that consist of activated charcoal, HZO (which acts as a cation exchanger), and Ag/C, precipitation of trace iodine is repeated by adding NaI and AgNO₃. The AgI precipitate is collected on the combination column, Mo passes through the column, and a final wash of the column with 0.2 M NaOH removes the Mo held up in the dead volume of the column.

5.4 EXPERIMENTAL

5.4.1 Chemicals

All chemical reagents used in this work were of analytical-reagent-grade purity and were used without further purification. All aqueous solutions were prepared with deionized water having a resistivity ≥ 18 M Ω •cm.

Silver-coated Charcoal Sorbent

Twenty grams of activated charcoal (50-100mesh) was mixed with water to form a slurry-like mixture, and 15 mL of 10% AgNO_3 in 0.1 M HNO_3 was added and mixed for 5 min. Then, 4 mL of freshly prepared 5% Na_2SO_3 was added and mixed. Next, 40 mL of 0.1 M NaOH was added while mixing and heated at 80-90°C for 30 min. After cooling, resin was washed several times with water until wash solution was clear.

HZO Sorbent

Hydrated zirconia (HZO) was prepared by dissolving ZrOCl_2 in water and precipitating HZO by adding enough NH_4OH to make a solution with $\text{pH} \geq 8$. The slurry was covered and mixed for 20 min, and the pH was checked again and adjusted with NH_4OH if needed. The precipitate was allowed to settle overnight, then centrifuged and washed with water until the pH of the supernatant reached $\text{pH} = 5-7$. After the final water wash, the precipitate was filtered under vacuum and slowly dried at $\sim 40^\circ\text{C}$ for ~ 3 days. After drying, the precipitate was slurried in water, and very fine particles were decanted with the water. After decanting, the material was allowed to air dry overnight and then sieved into 100-200 mesh. The HZO was washed again with water and 0.2 M NaOH and stored under 0.2 M NaOH .

Alpha-benzoin oxime (2% in 0.4 M NaOH)

0.4 g of ABO was combined with 20 mL of 0.4 M NaOH and heated while stirring until fully dissolved. The solution was allowed to cool and was used the same day.

Mo Carrier Solution (10 mg Mo/mL)

375 mg of MoO_3 was dissolved in 15 mL of 1 M NaOH , neutralized with 5 mL of 4 M HNO_3 , and diluted to 25 mL with 0.1 M NaOH .

Rh carrier solution (8 mg Rh/mL)

500 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was transferred into volumetric flask containing 15 mL of water, then 1 mL of 70% HNO_3 was added, and solution was diluted to 25 mL with water. The solution was mixed until RhCl_3 was completely dissolved.

Ru Carrier Solution (5 mg Ru/mL)

250 mg of K_3RuCl_6 was added into volumetric flask containing 11 mL of 70% HNO_3 and mixed. Solution was carefully diluted with water to 50 mL.

Fission Product Carrier Solution

10 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was transferred into flask containing 50 mL of water, acidified with 1 mL of 70% HNO_3 , and mixed until fully dissolved.

11 mL of 70% HNO₃ was added into a beaker containing 5 mL of water. Then, 10 mg of K₃RuCl₆ was added and mixed until fully dissolved.

500 mg of MoO₃ was dissolved in 20 mL of 1 M NaOH and acidified with 2 mL of 4 M HNO₃. Also, Rh, Ru, and Mo solutions were combined in a volumetric flask and diluted to 200 mL with water.

Ethyl acetate Pre-equilibrated

0.33 mL of 0.1 M NaOH was combined with 3.33 mL of 10% H₂SO₄ and mixed. Then, 167 µL of Fe₂(SO₄)₃ (10 mg Fe/mL) in 1% H₂SO₄ was added and mixed, followed by 0.33 mL of 50% NH₄SCN in water and mixed again. Then, 0.83 mL of 10% SnCl₂ in 10% HCl was added and mixed. The solution was combined with 20 mL of ethyl acetate and mixed for 1 min using a vortex. Phases were separated by centrifugation, and ethyl acetate was used the same day.

Thiocyanate Extraction of Mo

100 µL of fission product carrier solution was added into 10 mL of 10% H₂SO₄ and mixed. Then, 0.5 mL of Fe₂(SO₄)₃ (10 mg Fe/mL) in 1% H₂SO₄ was added, followed by addition of 0.1 mL Mo-99 product solution obtained after the LMC process, 1 mL of 50% NH₄SCN in water, and 2.5 mL of 10% SnCl₂ in 10% HCl. The solution was mixed after every addition. Aqueous solution was then combined with 12 mL of ethyl acetate (pre-equilibrated) and mixed for 2 min using a vortex. Aqueous phase was separated and combined with 5 mL of fresh ethyl acetate (pre-equilibrated) and mixed for another 2 min using a vortex. Aqueous phase was separated and used to determine the activity of fission products by gamma counting.

Iodine Extraction Using Chloroform

One drop of KI in water (10 mg I/mL) was added into 10 mL of water followed by addition of 0.1 mL of Mo-99 product solution obtained after the LMC process. Then, one drop of 70% HNO₃ was added, and solution was combined with 5 mL of CHCl₃. Then, two drops of 35% HCl and 4 drops of 20% NaNO₂ in water were added and mixed for 1 min using a vortex. Phases were allowed to separate, and organic phase (bottom phase) was transferred into a new vial. After addition of two drops of 20% NaNO₂ in water into the aqueous phase, the solution was combined with 5 mL of CHCl₃ and mixed for 1 min using a vortex. Phases were allowed to separate, and organic phases were combined and used to determine the activity of I-131 by gamma counting.

5.4.2 LEU Modified Cintichem Process

The LMC was performed according to working instructions for processing the mini-SHINE solution (see Appendix E). Figures 5.9–5.13 show drawings of the glassware used in the LMC. Double-sided needles were used for solution transfer and were constructed by combining two needles with male-to-male luer-lock connectors. In addition, 18Ga needles were used for solution transfer, 16Ga needles for transfer of precipitate suspensions (iodine precipitate,

Mo-ABO precipitate), and ^{21}Ga needles for vacuum lines. Figures 5.14 and 5.15 show some of the processing steps performed in the Bigfoot hot cell. Figure 5.14 shows the apparatus for filtration of initial iodine precipitation. The RF1 bottle on the top contains feed into LMC after the concentration-column step. After addition of iodine carrier, iodide is precipitated as AgI and filtered using 40 mm/ $0.3\ \mu\text{m}$ polypropylene filter (Zenpure) under vacuum (vacuum line connected into RF2 bottle on the bottom).

Figure 5.15 is a photograph of the apparatus for precipitation and filtration of Mo-ABO. The RF2 bottle on top contains the Mo precipitate after addition of ABO. The slurry is transferred into the fritted bottle, while the solution containing the majority of other fission products passes through the filter into the RFW bottle. The fritted bottle contains glass beads that allow better mixing during washing steps of Mo-ABO precipitate and during the dissolution of Mo-ABO precipitate. For these experiments the fritted bottle was modified from the original design (Figure 5.11) by the Argonne glass blower by extending the height of the bottle to allow a better grip with remote manipulators.

FIGURE 5.9 Drawing of Two-sided Bottle, Plastic Coated

FIGURE 5.10 Drawing of One-sided Bottle, Plastic Coated

FIGURE 5.11 Drawing of Fritted Bottle for Filtration of Mo-ABO Precipitate

FIGURE 5.12 Drawing of Short Fritted Column Used for Charcoal Vent during Dissolution of Mo-ABO Precipitate

FIGURE 5.13 Drawing of Long Fritted Column Used for Combination Column

FIGURE 5.14 Iodine Filtration in LMC Process

FIGURE 5.15 Filtration of Mo-ABO Precipitate in LMC Process

5.4.3 Gamma Counting

Gamma counting of samples was performed with a HPGe detector (Ortec), and spectra were analyzed using GammaVision software (Ortec). The detector was calibrated for efficiency with a Eckert & Ziegler multinuclide standard. Due to the complex spectra from multiple radionuclides present in most of the samples, only some radionuclides were able to be clearly identified and are listed in Table 5.1. Due to presence of high Mo-99 and I-131, I-133, and I-135 activities, even a few milligram aliquots had a significant dead time; therefore, the signals of some radionuclides with lower abundance (low branch peak) (such as Sn-125) were hard to identify in some samples. The activity of La-140 is not reported because, when Ba-140 is present, it decays to La-140, and gamma counting results for samples at different times and decayed to EOB would not provide the same activity for La-140 due to the presence of its parent. However, I-131 could be easily identified in all samples of the concentration column or LMC since Te-131m (parent of I-131) or Te-132 (parent of I-132) was removed in the Mo recovery column. The same is true for I-133 and I-135. Also, Y-93 could be identified in some samples

since its parents (Sr-93, Y-93m, Rb-93, Kr-93, and Br-93) all have short half-lives (minutes to few seconds), and its activity is not affected by parents when counted one day or more after EOB. No U-237 or Np-239 was identified in any of the CC feed, since they were removed on Mo recovery column.

TABLE 5.1 List of Nuclides, Their Peak Energies, and Half-Lives

Nuclide	Energy (keV)	Half-life	Branch
Te-132	49.82	78.2 h	14.4%
Nd-147	91.1	11.0 d	27.9%
Sm-156	165.73	9.4 h	61.7%
Mo-99	181.07	65.9 h	6.0%
U-237	208.01	6.75 d	21.9%
Y-93	266.91	10.25 d	6.80%
Np-239	277.6	56.5 h	14.1%
Ce-143	293.27	33 h	42.8%
Rh-105	318.9	35.4 h	19.2%
Pm-151	340.06	28.4 h	22.4%
Ba-140	423.7	12.7 d	3.15%
Ru-103	497.08	39.25 d	91%
I-133	529.87	20.8 h	87%
Sr-91	555.56	9.5 h	61.5%
I-131	636.97	8.04 d	7.30%
Nb-97	657.92	72.1 m	98.2%
Cs-137	661.66	30 y	85.1%
Sb-127	685.5	92.4 h	35.7%
Zr-97	743.36	16.9 h	98%
Zr-95	756.73	64 d	54.5%
Nb-95	765.81	34.97 d	99.8%
Te-131m	793.77	30 h	13.8%
Cs-136	818.51	13.2 d	99.7%
Sn-125	1088.9	9.6 d	4.20%
Eu-156	1230.69	15.2 d	8.80%
I-135	1260.41	6.57 h	28.9%
La-140	1596.21	40.27h	95.4%

To measure impurities (except radioiodine isotopes) in the LCM Mo product, the Mo was extracted from the product solution using the procedure described in Section 5.4.1. To measure radioiodine impurities, the procedure also described in Section 5.4.1 was used. With the exception of the impurities in the final LCM product, the activities of radioisotopes for all gamma counting were calculated back to EOB. The final-product activities were calculated for 36 hr following EOB.

5.5 RESULTS AND DISCUSSION

5.5.1 Mini-SHINE #1

Irradiation and processing times for irradiation #1 in the Bigfoot hot cell are listed in Table 5.2.

TABLE 5.2 Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #1 (EOB on 02/23/15 at 4:17 pm)

Operation	Start	End
Solution transfer	02/23/15 6:53 pm	02/23/15 7:45 pm
Concentration column	02/23/15 8:01 pm	02/23/15 11:11 pm
LEU Modified Cintichem	02/24/15 1:30 am	02/24/15 5:00 am

The molybdenum-strip solution obtained from the Mo-recovery column in 0.1 M NaOH was transferred into Bigfoot and acidified by HNO₃ and then loaded onto the concentration column. The strip from the concentration column, containing Mo-99 and other fission products, was acidified before processing with LMC to ~1 M HNO₃. We observed that upon addition of nitric acid, the colorless solution turned into a cloudy white, indicating formation of some insoluble species (Figure 5.16). (We later learned that the precipitate was silica gel, from silicon leaching out of the titania sorbent; in the future, the titania sorbent will be pre-treated to remove the silicon before use.) The LMC was performed as shown in Figure 5.8.

Activities detected in the concentration column (CC) fractions for mini-SHINE #1 and the relative distribution for Mo and I are listed in Tables 5.3 and 5.4, respectively. The majority of iodine partitioned into the CC eluent, and only a small fraction was fed to the LMC. The waste stream contains solution that was combined after water washing of the lines after feeding the column and stripping the product from the column.

FIGURE 5.16 Photograph of White Precipitate That Formed after Acidification of Product from Concentration Column Just before Start of LMC

TABLE 5.3 Activities Detected in Concentration Column Fractions and Calculated at EOB in Run #1

Radionuclide	Feed, mCi (1 σ , %)	Eluent, mCi (1 σ , %)	HNO ₃ Wash, mCi (1 σ , %)	H ₂ O Wash, mCi (1 σ , %)	Waste, mCi (1 σ , %)	Mo-99 Product, mCi (1 σ , %)
Mo-99	8.1E+01 (4.2)	<1.E+00	8.E-02 (54.5)	1.E-01 (32.2)	2.7E-01 (5.2)	7.72E+01 (2.0)
Ru-103	1E-01 (57.3)	2.0E-01 (29)	<1.79E- 03	2.6E-03 (37.0)	1.8E-03 (19.8)	4.0E-02 (16)
I-131	8.2E+00 (7.4)	1.1E+01 (7.2)	1.4E-01 (11)	4.8E-02 (21.7)	4E-03 (72.2)	3E-01 (24.1)
I-133	2.03E+02 (2.0)	2.15E+02 (2.0)	2.45E+00 (2.1)	3.77E-01 (3.2)	6.23E-02 (4.4)	2.00E+00 (2.3)

TABLE 5.4 Distribution of Mo and I in Various Fractions of Concentration Column (percent of that measured in CC feed) in Run #1

Radionuclide	Eluent	HNO ₃ Wash	H ₂ O Wash	Waste	Product	Balance
Mo-99	1.3%	0.1%	0.15%	0.3%	95.7%	97.6%
I-131	131%	1.8%	1.8%	0.0%	3.7%	138.3%
I-133	105.9%	1.2%	0.2%	0.0%	1.0%	108.3%

Tables 5.5 and 5.6 show the distribution of activities in the LMC fractions. It should be noted that the activity of Mo-99 in the RF-1 bottle (LMC feed, Table 5.5) is slightly lower compared to the CC product (Table 5.3) because a small aliquot was taken for gamma counting. However, data indicate that some iodine is being removed during the acidification step before LMC; this is most likely due to the formation of I₂, which is volatile and could be released upon heating of the solution by HNO₃ addition.

The recovery of Mo in the LMC process was ~94.2% (Table 5.6), which is comparable to yields obtained in previous experiments, and only about 0.1% of Mo-99 was found in the raw fission waste (RFW) bottle after the ABO precipitation step. Table 5.7 shows the data for radionuclidic purity in the LMC product solution. No iodine was detected in the LMC product, and the Mo-99 product solution met the specifications for the presence of Ru-103 and I-131. The data for the total alpha activity were determined by alpha spectroscopy.

TABLE 5.5 Activities Detected in LMC Fractions Calculated at EOB in Run #1

Radionuclide	RF-1, mCi (1σ, %)	RFW, mCi (1σ, %)	LMC Product, mCi (1σ, %)
Mo-99	6.82E+01 (2.0)	7.9E-02 (15)	6.43E+01 (2.0)
Ru-103	1.79E-02 (6.6)	9.76E-03 (3.5)	8.1E-04 (12)
I-131	5.1E-02(23.8)	9.7E-02 (4.8)	2.4E-03 (79.8)
I-133	6.30E-01 (2.7)	2.05E-01 (2.1)	2E-01 (51.2)
Zr-97	5.E-02 (44.9)	8.58E-02 (3.6)	>12 Half-lives
Rh-105	8.7 E-02 (10.4)	4.3 E-02 (6.2)	2E-02 (88.3)
Sb-127	2.00E-01 (3.6)	2.15E-01 (3.3)	2E-03 (64.7)

TABLE 5.6 Distribution of Mo, Ru, I, and Sb in Various Fractions of LMC in Run #1

Radionuclide	RFW	LMC Product
Mo-99	0.1%	94.2%
Ru-103	54.5%	4.5%
I-133	32.6%	31.1%
Rh-105	49.4%	22.2%
Sb-127	107%	0.8%

TABLE 5.7 Radionuclidic Purity in ⁹⁹Mo Product Solution from LMC Process Calculated at 36 hr after EOB in Run #1

Ratio	Determined Value 36 hr After EOB	Product Specification	Within Specification
¹³¹ I/ ⁹⁹ Mo	4.8E-05	$\leq 5 \times 10^{-5}$	YES
¹⁰³ Ru/ ⁹⁹ Mo	1.8E-05	$\leq 5 \times 10^{-5}$	YES
$\Sigma\alpha$ / ⁹⁹ Mo	2.5×10^{-12}	$\leq 1 \times 10^{-9}$	YES

$\Sigma\alpha$ = total alpha activity

5.5.2 Mini-SHINE #2

Irradiation and processing times for irradiation #2 in the Bigfoot hot cell are listed in Table 5.8.

TABLE 5.8 Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #2 (EOB on 03/04/15 at 10:03 pm)

Operation	Start	End
Solution transfer	03/05/15 4:44 am	03/05/15 5:30 am
Concentration column	03/05/15 5:45 am	03/05/15 9:05 am
LEU Modified Cintichem	03/05/15 9:45 am	03/05/15 12:30 pm

Activities detected in concentration column fractions and the radionuclide distribution are shown in Tables 5.9 and 5.10, respectively. As was found in the previous run, a white precipitate appeared after acidification of the concentration column product.

TABLE 5.9 Activities Detected in Concentration Column Fractions Calculated at EOB in Run #2

Radionuclide	Feed, mCi (1 σ , %)	Eluent, mCi (1 σ , %)	HNO ₃ Wash, mCi (1 σ , %)	H ₂ O Wash, mCi (1 σ , %)	Waste, mCi (1 σ , %)	Mo-99 Product, mCi (1 σ , %)
Mo-99	3.26E+02 (3.0)	1E-0 (40.0)	3E-02 (35.4)	1.2E-01 (7.0)	1.49E+00 (2.0)	3.29E+02 (2.0)
Ru-103	1.07E+00 (2.5)	8.62E-01 (2.0)	2.57E-02 (2.0)	1.24E-02 (2.1)	1.61E-02 (2.0)	1.90E-01 (3.6)
I-131	3.55E+01 (2.0)	3.09E+01 (2.0)	5.79E-01 (2.1)	2.50E-01 (2.0)	1.18E-01 (2.0)	2.51E+00 (1.9)
I-133	7.27E+02 (2.0)	6.70E+02 (2.0)	1.25E+01 (2.0)	5.42E+00 (2.0)	2.42E+00 (2.0)	5.68E+01 (2.2)
Sn-125	2.1E-01 (53.0)	5E-02 (23)	2E-03 (74.4)	<7E-04	4.03E-03 (11)	6.67E-02 (9)
Sb-127	1.01E+00 (8.5)	2E-02 (32)	4E-04 (59.3)	<2E-04	1.03E-01 (3.0)	7.67E-01 (5.5)

TABLE 5.10 Distribution of Mo, Ru, I, and Sb in Various Fractions of Concentration Column in Run #2

Radionuclide	Eluent	HNO ₃ Wash	H ₂ O Wash	Waste	Product	Balance
Mo-99	0.2%	0.0%	0.0%	0.5%	100.9%	101.6%
Ru-103	80.6%	2.4%	1.2%	1.5%	17.8%	103.4%
I-131	87.0%	1.6%	0.7%	0.3%	7.1%	96.8%
I-133	92.2%	1.7%	0.7%	0.3%	7.8%	102.8%
Sb-127	1.7%	0.0%	0.0%	10.2%	75.9%	87.8%

About 90% of iodine was found in the eluent, a small fraction (0-2%) was also present in washes and waste, and 7-8% was found in the CC product and was fed into the LMC.

Approximately 10% of Sb-127 was found in the waste stream, but the majority of antimony was present in the product. It is also worth noting that ~80% of Ru-103 was present in the eluent, and very similar behavior can be expected for the Mo recovery column, since both are TiO₂-based columns. This could cause an accumulation of Ru in uranium solution over time and potentially complicate its separation if not removed in the target-solution cleanup.

Tables 5.11 and 5.12 show the activities and percent distribution of radionuclides in the LMC fractions, respectively. As in the first run, the data indicate that some iodine is being removed during the acidification step before the LMC, since the activities in LMC feed are significantly lower compared to the CC product (after adjusting for activity taken for sampling). Also, activities of Ru-103 and Sb-127 are lower compared to the CC product (Table 5.9), which could be due to some co-precipitation with “white” precipitate. To reduce processing time and obtain more concentrated Mo-99 product, the LMC was performed without use of the Ag/C column. This column is used mostly for removal of iodine, but significant amounts of iodine are being removed on both titania columns before the LMC process. About 4% of I-131 and 14% of Ru-103 activities fed into the CC were found in the LMC feed (RF1 fraction). Most of the Ru from the LMC feed is found in the waste (RFW), and the remaining fraction is likely removed by HZO on the combination column.

**TABLE 5.11 Activities Detected in LMC Fractions
Calculated at EOB in Run #2**

Radionuclide	RF-1, mCi (1 σ , %)	RFW, mCi (1 σ , %)	LMC Product, mCi (1 σ , %)
Mo-99	3.15E+02 (3.0)	2.74E-01 (6.0)	3.00E+02 (2.3)
Ru-103	1.49E-01 (8.0)	6.70E-02 (2.0)	2.94E-03 (3.0)
I-131	1.54E+00 (3.0)	2.83E-01 (2.0)	1.34E-03 (6.0)
I-133	3.18E+01 (2.0)	6.10E+00 (2.0)	3.73E-02 (9.0)
Sn-125	2E-01 (36)	8.1E-02 (7.0)	2E-03 (39)
Sb-127	6.7E-01 (9.0)	6.27E-01 (3.0)	8.0E-04 (18)

**TABLE 5.12 Distribution of
Mo, Ru, I, and Sb in Various
Fractions of LMC in Run #2**

Radionuclide	RFW	LMC Product
Mo-99	0.1%	95.2%
Ru-103	45.0%	2.0%
I-131	18.4%	0.1%
I-133	19.2%	0.1%
Sn-125	33.4%	0.9%
Sb-127	93.7%	0.1%

The recovery of Mo in the LMC process was ~95.2%, and only about 0.1% of Mo-99 was found in the RFW bottle after the ABO precipitation step. Table 5.13 shows the data for radionuclidic purity in the LMC product solution. The radionuclidic purity of the product

solution met the specifications for the presence of Ru-103 and I-131. Removal of the Ag/C column did not have any negative impact on purity or recovery of Mo, but shortened the processing time (~3 hr compared to ~3.5 hr), and reduced the volume of final product by 15–20%. All further experiments were performed without the Ag/C column.

TABLE 5.13 Radionuclidic Purity in ⁹⁹Mo Product Solution from the LMC Process Calculated at 36 hr after EOB in Run #2

Ratio	Determined Value 36 hr after EOB	Product Specification	Within Specification
¹³¹ I/ ⁹⁹ Mo	9.9E-06	≤ 5×10 ⁻⁵	YES
¹⁰³ Ru/ ⁹⁹ Mo	1.4E-05	≤ 5×10 ⁻⁵	YES
Σα/ ⁹⁹ Mo	6.5E-13	≤ 1×10 ⁻⁹	YES

Σα = total alpha activity

5.5.3 Mini-SHINE #3

Irradiation and processing times for irradiation #3 in the Bigfoot hot cell are listed in Table 5.14.

TABLE 5.14 Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #3 (EOB on 04/16/15 at 12:00 am)

Operation	Start	End
Solution transfer	04/16/15 5:56 am	04/16/15 6:47 am
Concentration column	04/16/15 7:00 am	04/16/15 9:50 am
LEU Modified Cintichem	04/16/15 10:45 am	04/16/15 2:30 pm

Since 1 M NaOH shows better Mo stripping performance than 0.1 M NaOH from the Mo recovery column (Figure 5.17), it was tested in this experiment.

Activities detected in concentration column fractions and the distributions of the radionuclides are shown in Tables 5.15 and 5.16, respectively. The distribution of iodine in the eluent differs significantly from the previous runs. Only ~60% of I was found in the eluent compared to ~80-90% in the previous run. This difference suggests different speciation of iodine as indicated by the total iodine balance pointing to sorption of iodine on titania column, and

slightly lower partitioning of iodine into the CC product. However, the total fraction of I-131 activity fed into the LMC was similar to that of the previous run (~3.1%).

FIGURE 5.17 Stripping of Mo from Sachtopore Sorbent with 1 M and 0.1 M NaOH

TABLE 5.15 Activities Detected in Concentration Column Fractions and Calculated at EOB in Run #3

Radionuclide	Feed, mCi (1 σ , %)	Eluent, mCi (1 σ , %)	HNO ₃ Wash, mCi (1 σ , %)	H ₂ O Wash, mCi (1 σ , %)	Waste, mCi (1 σ , %)	Mo-99 Product, mCi (1 σ , %)
Mo-99	8.96E+02 (1.6)	4E+00 (25.0)	3E-02 (44.7)	1.18E+00 (2.6)	1.55E+00 (2.5)	9.64E+02 (2.7)
Ru-103	8.11E+00 (5.5)	7.08E+00 (0.3)	1.46E-01 (1.9)	5.18E-02 (1.9)	4.59E-02 (1.9)	7.67E-01 (3.3)
I-131	1.53E+02 (2.8)	9.39E+01 (0.4)	1.46E+00 (1.9)	6.68E-01 (2.0)	2.32E-01 (2.9)	7.96E+00 (4.0)
I-133	1.76E+03 (0.2)	1.15E+03 (0.2)	1.76E+01 (1.8)	7.99E+00 (1.9)	2.53E+00 (1.9)	9.63E+01 (2.5)
Rh-105	1.38E+01 (28)	6.34E+00 (14)	1.32E-01 (13)	4.27E-02 (19)	<6E-03	<7E-01
Sn-125	6E+00 (31)	4E-01 (21)	<9E-04	10E-03 (23)	1.7E-02 (11)	1.1E+00 (11)
Sb-127	2.2E+00 (16)	3 E-02 (60)	1E-03 (28)	3.7E-03 (13)	3.28E-01 (3.2)	4.03E+00 (4.9)

TABLE 5.16 Distribution of Mo, Ru, I, Rh, Sn, and Sb in Various Fractions of Concentration Column in Run #3

Radionuclide	Eluent	HNO ₃ Wash	H ₂ O Wash	Waste	Product	Balance
Mo-99	0.4%	0.1%	0.1%	0.2%	107.6%	108.4%
Ru-103	87.3%	0.6%	1.8%	0.6%	9.5%	99.8%
I-131	61.4%	0.4%	1.0%	0.2%	5.2%	68.1%
I-133	65.3%	0.5%	1.0%	0.1%	5.5%	72.4%
Rh-105	45.9%	0.3%	1.0%	0.0%	5.0%	52.2%
Sn-125	6.6%	0.2%	0.2%	0.3%	18.7%	25.9%
Sb-127	1.4%	0.2%	0.2%	14.5%	179%	195.3%

Tables 5.17 and 5.18 show the activities and percent distributions of the radionuclides in the LMC fractions, respectively. As in previous runs, the data indicate that some iodine is being removed during the acidification step before the LMC. Also activities of Ru-103 and Sb-127 are lower compared to those for the CC product, which could be due to some co-precipitation with “white” precipitate that forms after acidification of the CC product solution.

TABLE 5.17 Activities Detected in LMC Fractions and Calculated at EOB in Run #3

Radionuclide	RF-1, mCi (1 σ , %)	RFW, mCi (1 σ , %)	LMC Product, mCi (1 σ , %)
Mo-99	8.59E+02 (2.0)	1.33E+00 (3.0)	7.54E+02 (2.3)
Ru-103	7.1E-01 (8.6)	2.04E-01 (1.9)	2.75E-02 (1.9)
I-131	4.8E+00 (12.9)	7.15E-01 (2.2)	3.5E-03 (8.9)
I-133	4.09E+01 (2.1)	7.72E+00 (1.9)	1.41E-02 (3.7)
Zr-97	8.43E+00 (5.6)	1.89E+00 (3.4)	3.06E-03 (46.6)
Rh-105	3E-01 (91)	1.2E-01 (18)	2.4E-03 (28)
Sn-125	2.3E+00 (17)	3.02E-01 (3.6)	<2E-04
Sb-127	7.74E-01 (6.3)	1.23E+00 (3.1)	7.67E-03 (3.8)

TABLE 5.18 Distribution of Mo, Ru, I, Zr, Rh, and Sn in Various Fractions of LMC in Run #3

Radionuclide	RFW	LMC Product
Mo-99	0.15%	87.7%
Ru-103	28.7%	3.9%
I-131	15.0%	0.07%
I-133	18.9%	0.03%
Zr-97	22.4%	0.04%
Rh-105	37.8%	0.8%
Sn-125	13.2%	0.01%

TABLE 5.19 Radionuclidic Purity in ⁹⁹Mo Product Solution from the LMC Process Calculated at 36 hr after EOB in Run #3

Ratio	Determined Value 36 hr After EOB	Product Specification	Within Specification
¹³¹ I/ ⁹⁹ Mo	6.0E-06	$\leq 5 \times 10^{-5}$	YES
¹⁰³ Ru/ ⁹⁹ Mo	5.1E-05	$\leq 5 \times 10^{-5}$	NO

The recovery of Mo in the LMC process was ~87.7%. Significantly less Ru-103 was found in the RFW fraction compared to the first two runs (28.7% versus 54.5% in mini-SHINE #1 and 45% in mini-SHINE #2). About 9% of the initial Ru-103 activity from the CC feed was introduced into LMC, which is less compared to the mini-SHINE #2 run (13.9%). Slightly elevated activity of Ru-103 in the LMC product could perhaps be attributed to different speciation of Ru in the eluent from the Mo recovery column due to different NaOH concentration (1M NaOH in this run vs. 0.1M NaOH in previous runs). The radionuclidic purity of the product solution (Table 5.19) met the specifications for the presence of I-131; however, the activity of Ru-103 at 36 hr after EOB was slightly above the specification limit. Total alpha activity in the sample was not determined.

5.5.4 Mini-SHINE #4

Irradiation and processing times for irradiation #4 in the Bigfoot hot cell are listed in Table 5.20.

TABLE 5.20 Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #4 (EOB on 04/26/15 at 10:00 pm)

Operation	Start	End
Solution transfer	04/27/15 10:30AM	04/27/15 1:15AM
Concentration column	04/27/15 12:00PM	04/27/15 2:18PM
LEU Modified Cintichem	04/28/15 9:20AM	04/28/15 1:00PM

Since the 1 M NaOH used for stripping Mo from the Mo-recovery column in mini-SHINE #3 could have caused a slightly elevated activity of Ru-103 in the final Mo-99 product, 0.1 M NaOH was used to strip Mo from the recovery column for the remaining runs. Activities detected in the CC fractions and the distributions of radionuclides are shown in Tables 5.21 and 5.22, respectively. Although the total balance for activities reported in Table 21 exceeds 100% (see Table 5.22), it can be concluded that the majority of I and Ru activities is present in the CC eluent, and most of the Sb-127 partitioned in the Mo product is as observed for mini-SHINE #2.

TABLE 5.21 Activities Detected in Concentration Column Fractions and Calculated at EOB in Run #4

Radionuclide	Feed, mCi (1 σ , %)	Eluent, mCi (1 σ , %)	HNO ₃ Wash, mCi (1 σ , %)	H ₂ O Wash, mCi (1 σ , %)	Waste, mCi (1 σ , %)	Mo-99 Product, mCi (1 σ , %)
Zr-95	3.7E-02 (11.4)	<2E-02	6E-04 (40.9)	<3E-04	3E-04 (48.7)	1.9E-02 (19)
Mo-99	3.37E+02 (2.3)	<2E+00	<1E-02	2.13E-01 (3.5)	7.50E-01 (3.4)	3.51E+02 (2.7)
Ru-103	5.21E-01 (2.0)	4.36E-01 (3.0)	1.13E-02 (3.1)	1.6E-03 (9.6)	5.38E-03 (4.8)	1.21E-01 (5.6)
I-131	3.27E+01 (1.9)	5.44E+01 (1.9)	6.25E-01 (2.3)	1.30E-01 (2.4)	1.09E-01 (6.3)	1.1E+00 (9.8)
I-133	3.55E+02 (1.8)	5.89E+02 (1.8)	6.79E+00 (1.8)	1.12E+00 (1.9)	7.44E-01 (2.0)	1.52E+01 (2.8)
Rh-105	1.70E+00 (28)	<5E-01	2.E-02 (25)	<2E-03	<2E-03	<7E-04
Sb-127	9.01E-01 (3.4)	2E-01 (41.9)	1E-03 (48.2)	1.7E-03 (12)	2.17E-01 (3.3)	1.45E+00 (3.6)

TABLE 5.22 Distribution of Zr, Mo, Ru, I, Rh, and Sb in Various Fractions of Concentration Column in Run #4

Radionuclide	Eluent	HNO ₃ Wash	H ₂ O Wash	Waste	Product	Balance
Zr-95	60%	1.7%	0.8%	0.7%	51.5%	114.7%
Mo-99	0.5%	0.1%	0.06%	0.2%	104.2%	105.1%
Ru-103	83.7%	0.3%	2.2%	1.0%	23.2%	110.4%
I-131	166.4%	0.4%	1.9%	0.3%	3.5%	172.5%
I-133	165.9%	0.3%	1.9%	0.2%	4.3%	172.6%
Rh-105	30.1%	1.4%	0.1%	0.1%	0.04%	31.7%
Sb-127	27.1%	0.1%	0.2%	24.1%	160.9%	212.4%

Tables 5.23 and 5.24 show the distribution of activities and radionuclides in the LMC fractions, respectively. Approximately 3.3% of I-131 and 22.2% of Ru-103 from the CC feed solution were present in the LMC feed. Contrary to previous runs, there is no indication of removal of I, Ru, or Sb after acidification of the CC product solution, and all activities correspond to Mo-99 activity (~95.5% of activity enters the LMC process due to sampling of the CC product and RF1 solution after acidification).

TABLE 5.23 Activities Detected in LMC Fractions and Calculated at EOB in Run #4

Radionuclide	RF-1, mCi (1 σ , %)	RFW, mCi (1 σ , %)	LMC Product, mCi (1 σ , %)
Zr-95	1.8E-02 (19)	2E-02 (43.3)	<3E-05
Mo-99	3.35E+02 (2.7)	1.18E+02 (2.4)	1.59E+02 (2.0)
Ru-103	1.16E-01 (5.6)	6E-02 (22)	8.3E-04 (5.5)
I-131	1.1E+00 (9.8)	2E-01 (47.2)	1E-03 (46)
I-133	1.46E+01 (2.8)	7E-01 (17)	5.0E-03 (8.8)
Sn-125	4E-01 (9.9)	4.3E-01 (17.1)	<2E-04
Sb-127	1.4E+00 (3.6)	6.7E-01 (6.2)	2.5E-03 (5.5)

TABLE 5.24 Distribution of Mo, Ru, I, and Sb in Various Fractions of LMC in Run #4

Radionuclide	RFW	LMC Product
Mo-99	35.2%	47.5%
Ru-103	53.3%	0.7%
I-131	18.1	0.1%
I-133	4.7%	0.03%
Sb-127	48.2%	0.2%

Due to a slightly elevated concentration of Ru in the LMC product in mini-SHINE #3, several modifications were made in the LMC for mini-SHINE #4. Approximately 10 mL of KMnO_4 was added after addition of the Mo carrier, while usually much less KMnO_4 is used (<1–2 mL). After addition of Ru and Rh carriers, 30 min was allowed, during which shaking of the mixture was performed every ~5 min (in normal operation, ABO is added after briefly mixing the Ru and Rh carriers). When ABO was added into the solution, a dark-colored precipitate containing Mo-ABO “stuck” to the bottle, and extensive washing of the RF2 bottle with 0.1 M HNO_3 was not effective in removing the Mo-ABO precipitate. Therefore, 0.4M $\text{NaOH}/1\% \text{H}_2\text{O}_2$ solution was added into the RF2 bottle in order to potentially lower the Mo losses by dissolving the Mo-ABO precipitate. Solution was then collected and used for the dissolution of Mo-ABO precipitate collected on a fritted bottle with glass beads. After heating and partial dissolution of the Mo-ABO precipitate in the fritted bottle, a warm solution was used to wash the RF2 bottle again. This action was also repeated with 0.2 M $\text{NaOH}/1\% \text{H}_2\text{O}_2$ solution, but a significant amount of precipitate was still present in both the RF2 bottle and the fritted bottle. This result is most likely due to partial decomposition of ABO by the large excess of KMnO_4 solution that was added. Figure 5.18 shows the fritted bottle containing the black precipitate after dissolution and washing with 0.2 M NaOH . The significant portion of the Mo-99 found in the RFW fraction (35.2%, Table 5.24) was due to either insufficient complexation between Mo and ABO, or decomposition of the Mo-ABO complex before its dissolution.

Although the radionuclidic purity of the product solution (Table 5.25) met the specifications for the presence of I-131 and Ru-103, very poor Mo-99 yield was observed (47.5%, Table 5.24) due to high permanganate concentration introduced into the LMC process to potentially eliminate Ru contamination. We highly recommend that when potassium permanganate is titrated in before the addition of ABO, the solution is checked for the first sighting of a deep pink, which should not fade for several seconds, to avoid addition of excess permanganate. Total alpha activity in the sample was not determined.

FIGURE 5.18 Photograph of Black Precipitate That Formed after Precipitation of Mo with ABO

TABLE 5.25 Radionuclidic Purity in ^{99}Mo Product Solution from the LMC Process Calculated at 36 hr after EOB in Run #4

Ratio	Determined Value 36 hr After EOB	Product Specification	Within Specification
$^{131}\text{I}/^{99}\text{Mo}$	1.19EE-05	$\leq 5 \times 10^{-5}$	YES
$^{103}\text{Ru}/^{99}\text{Mo}$	7.38E-06	$\leq 5 \times 10^{-5}$	YES

5.5.5 Mini-SHINE #5

Irradiation and processing times for irradiation #5 in Bigfoot are listed in Table 5.26.

TABLE 5.26 Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #5 (EOB on 10/14/15 at 6:30 pm)

Operation	Start	End
Solution transfer	10/15/15 1:00 pm	10/15/15 1:45 pm
Concentration column	10/15/15 2:35 pm	10/15/15 4:20 pm
LEU Modified Cintichem	10/16/15 8:40 am	10/16/15 11:45 am

Activities detected in concentration-column fractions and the distributions of radionuclides are shown in Tables 5.27 and 5.28, respectively. As shown in Table 5.28, 65.5% of Ru-103 and ~80% of I-131(133) partitioned into the eluent, and 77% Sb-127 was found in the CC product and was fed into the LMC. Tables 5.29 and 5.30 show the distribution of activities and radionuclides in the LMC fractions, respectively. Similar to run #4, and contrary to runs #2 and #3, there is no indication of removal of I, Ru, or Sb after acidification of the CC product solution, and all activities correspond to Mo-99 activity (~95.5% of activity enters LMC due to sampling of the CC product and RF1 solution after acidification). However, only ~1.5% of I-131 from the CC feed was found in the LMC feed. As seen in mini-SHINE #4, ~23% of Ru found in the CC feed partitioned into the LMC. Surprisingly, only ~70% of Mo-99 was recovered in the LMC. Only 0.5% Mo-99 was found in the RFW, indicating good complexation of Mo with ABO. Moreover, the Mo-ABO precipitate was effectively washed out from the RF2 bottle. A possible explanation for the low yield of Mo-99 could be inadequate dissolution of Mo-ABO precipitate or some sorption of Mo on the HZO column. Both the fritted bottle that holds the Mo-ABO precipitate and the combination column were disposed and were not available for gamma counting. Another explanation could be that the Mo-99 product solution after the LMC was not properly mixed before sampling, and the fraction with lower Mo-99 activity was sampled for gamma counting. Except for I-131, the activity of which is unknown due to a delay in gamma counting the sample, the LMC product met the specification for radionuclidic purity (Table 5.31).

TABLE 5.27 Activities Detected in Concentration Column Fractions and Calculated at EOB in Run #5

Radionuclide	Feed, mCi (1 σ , %)	Eluent, mCi (1 σ , %)	HNO ₃ Wash, mCi (1 σ , %)	H ₂ O Wash, mCi (1 σ , %)	Waste, mCi (1 σ , %)	Mo-99 Product, mCi (1 σ , %)
Zr-95	<6E-02	2.2E-02 (17)	<2E-04	<2E-04	<5E-04	2.8E-02 (20.5)
Nb-95	<2E-02	7E-03 (25.1)	<9E-05	<2E-05	<4E-04	4.3E-02 (9.4)
Mo-99	4.63E+02 (2.8)	1.92E+01 (3.8)	1.6E-01 (6.6)	5.10E-01 (2.7)	3.78E+00 (2.5)	4.31E+02 (2.7)
Ru-103	3.11E-01 (13.7)	2.03E-01 (2.7)	2.66E-03 (3.7)	6.62E-04 (2.8)	1.02E-02 (3.4)	7.46E-02 (11.8)
I-131	6.70E+01 (2.3)	5.31E+01 (1.9)	4.43E-01 (2.0)	1.23E-01 (1.9)	1.29E-01 (3.9)	1.0E+00 (12.2)
I-133	1.22E+03 (1.9)	9.93E+02 (1.9)	8.10E+00 (1.9)	2.30E+00 (1.9)	2.14E+00 (5.1)	2.44E+01 (4.6)
Rh-105	5.73E+00 (29)	7.82E+00 (15)	5.70E-02 (20)	2.06E-02 (13)	<8.25E-02	<8.64E-01
Sn-125	9E-01 (28)	<7E-02	<4E-03	<3E-04	9.7E-02 (8.4)	<1E-01
Sb-127	1.0E+00 (13.3)	<2E-02	<5E-04	4.8E-04 (13.6)	5.68E-01 (3.3)	7.7E-01 (7.1)

TABLE 5.28 Distribution of Mo, Ru, I, Rh, Sn, and Sb in Various Fractions of Concentration Column in Run #5

Radionuclide	Eluent	HNO ₃ Wash	H ₂ O Wash	Waste	Product	Balance
Mo-99	4.1%	0.0%	0.1%	0.8%	93.0%	98.1%
Ru-103	65.5%	0.9%	0.2%	3.3%	24.0%	93.8%
I-131	79.4%	0.7%	0.2%	0.2%	1.5%	81.9%
I-133	81.2%	0.7%	0.2%	0.2%	2.0%	84.2%
Rh-105	136.5%	1.0%	0.4%	1.4	15.1	154.4%
Sn-125	7.4%	0.4%	0.03%	9.4%	20.2	37.4%
Sb-127	2.3%	0.05%	0.05%	56.6%	77.0%	136%

TABLE 5.29 Activities Detected in LMC Fractions and Calculated at EOB in Run #5

Radionuclide	RF-1, mCi (1 σ , %)	RFW, mCi (1 σ , %)	LMC Product, mCi (1 σ , %)
Zr-95	2.7E-02 (21)	1.4E-03 (16)	2E-04 (25)
Nb-95	4.2E-02 (9.4)	1.3E-03 (7.6)	<1E-04
Mo-99	4.20E+02 (2.7)	2.24E+00 (2.6)	2.93E+02 (2.5)
Ru-103	7.3E-02 (12)	1.30E-02 (2.5)	5.41E-03 (3.1)
I-131	9.9E-01 (12.2)	8.50E-02 (4.8)	<2E-02
I-133	2.38E+01 (4.4)	1.04E+00 (3.5)	<1E-01
Sn-125	1.84E-01 (16)	1.54E-01 (4.2)	<4E-03
Sb-127	7.53E-01 (7.1)	6.24E-01 (3.2)	<1E-03

TABLE 5.30 Distribution of Zr, Nb, Mo, Ru, I, and Sb in Various Fractions of LMC in Run #5

Radionuclide	RFW	LMC Product
Zr-95	5.2%	0.8%
Nb-95	3.1%	0.0%
Mo-99	0.5%	69.8%
Ru-103	17.9%	7.4%
I-131	8.6%	1.9
I-133	4.4%	N/A
Sb-127	82.8%	0.4%

TABLE 5.31 Radionuclidic Purity in ⁹⁹Mo Product Solution from the LMC Process Calculated at 36 hr after EOB in Run #5^a

Ratio	Determined Value 36 hr After EOB	Product Specification	Within Specification
¹³¹ I/ ⁹⁹ Mo	<5.7E-05 ^b	≤ 5×10 ⁻⁵	UNKNOWN
¹⁰³ Ru/ ⁹⁹ Mo	2.63E-05	≤ 5×10 ⁻⁵	YES
Σα/ ⁹⁹ Mo	1.1E-12	≤ 1×10 ⁻⁹	YES

^a Less than value based on MDA value reported and decayed 36 hr after EOB.

^b Determined ¹³¹-I activity was below detection limit; MDA value was used here.

Σα = total alpha activity

5.5.6 Mini-SHINE #6

Irradiation and processing times for irradiation #6 in Bigfoot are listed in Table 5.32.

TABLE 5.32 Irradiation and Processing Times for Operations in Bigfoot for Mini-SHINE #6 (EOB on 10/26/15 at 7:00 pm)

Operation	Start	End
Solution transfer	10/26/15 1:15 am	10/26/15 2:01 am
Concentration column	10/26/15 2:50 am	10/26/15 4:41 am
LEU Modified Cintichem	10/26/15 5:00 am	10/26/15 8:15 am

Activities detected in concentration-column fractions and the distributions of radionuclides are shown in Tables 5.33 and 5.34, respectively. Due to a longer irradiation time, processing right after irradiation, and prompt gamma counting of the CC feed (~40 hr after EOB), more radionuclides were identified in the initial feed. Together with Ru, I, and Rh, a significant amount of Y-93 (89.7%) was found in the CC eluent, although the presence of I was lower (50-60%) compared to previous runs (80-90%). Surprisingly, Sn-125 was not removed in the CC column and partitioned into the CC product. The white precipitate that typically forms after acidification of the CC product solution was collected using a 40 mm/0.3 μm PP filter (Zenpure). In addition, 54.5% of Ru and 25.1% of Rh-105 from the CC product were collected on the filter. Also, about 10% of I-131(I-133) and 1.3% of Mo-99 were found on the filter.

Tables 5.35 and 5.36 show the distribution of activities and radionuclides in the LMC fractions, respectively. Only 6.3% of Ru-103 present in the CC feed was found in the LMC feed, while an unusually high (10.5%) percentage of iodine was present in the LMC feed. The significant amount of iodine in the RFW fraction (45%) could point to the presence of I₂ or iodate, since removal of iodide in the silver precipitation step is considered to be quantitative. The majority of Ru and Sb present in the LMC feed was found in the RFW fraction, and only 2.2% of Ru was found in the LMC product. In addition, 96.7% of Mo-99 was recovered in the LMC, and the product met the radionuclidic purity specifications (Table 5.37). Also, 55.5g of final product solution containing 1.06 Ci of Mo-99 was then loaded into a cask and shipped to GE Healthcare for further analyses.

According to a GE press release [2015], the Mo-99 was separately loaded onto a DRYTEC™ Tc-99m Generator, and the Tc-99m product was tested using GE Healthcare Tc-99m-based products: Myoview™ (kit for the preparation of Tc99m-Tetrofosmin for injection) and Ceretec™ (kit for the preparation of Tc99m Exametazime for injection). Quality control testing performed on the reconstituted kits indicated feasibility for Tc-99m radiopharmaceuticals prepared using Mo-99 product solution provided by Argonne.

TABLE 5.33 Activities Detected in Concentration Column Fractions Calculated at EOB in Run #6

Radionuclide	Feed, mCi (1σ, %)	Eluent, mCi (1σ, %)	HNO ₃ Wash, mCi (1σ, %)	H ₂ O Wash, mCi (1σ, %)	Waste, mCi (1σ, %)	Mo-99 Product, mCi (1σ, %)	Filter, mCi (1σ, %)
Zr-95	7.70E-02 (27)	<3E-02	<1E-03	<3E-04	<4E-04	<5E-02	<4E-04
Nb-95	<5E-02	3E-02 (25)	1.8E-03 (16)	<3E-04	<3E-04	<3E-02	<2E-04
Mo-99	1.42E+03 (2.7)	2.64E+00 (21)	1.77E-01 (13)	1.46E+00 (2.6)	2.80E+00 (2.7)	1.47E+03 (2.3)	1.95E+01 (2.3)
Ru-103	3.18E+00 (2.2)	2.76E+00 (1.9)	3.10E-02 (2.4)	5.20E-03 (3.4)	3.06E-02 (2.0)	3.2E-01 (9.3)	1.75E-01 (1.9)
I-131	1.92E+02 (1.9)	1.03E+02 (1.9)	5.34E+00 (1.9)	1.44E+00 (2.0)	8.00E-01 (1.9)	2.81E+01 (2.8)	2.84E+00 (2.0)
I-133	3.27E+03 (1.9)	1.77E+03 (1.9)	9.25E+01 (1.9)	2.46E+01 (1.9)	1.33E+01 (1.9)	4.65E+02 (1.9)	4.60E+01 (2.0)
Cs-136	9.9E-02 (13)	<2E-02	<8E-04	<3E-04	1.1E-03 (7.6)	3.E-02 (26)	<3E-04
Rh-105	7E+00 (21)	4.4E+00 (13)	1.5E-01 (15)	2.4E-02 (20)	<2E-02	1.9E+00 (28)	5E-01 (24)
Sn-125	9.19E-01 (28)	<3.50E-01	3.32E-02 (19)	1.23E-02 (19)	5.73E-02 (4.3)	9.88E-01 (26)	8.19E-03 (25)
Sb-127	5.43E+00 (3.6)	8E-02 (30)	<3E-03	<1E-03	3.89E-01 (3.1)	3.10E+00 (4.0)	<4E-03

TABLE 5.33 (Cont.)

Radionuclide	Feed, mCi (1 σ , %)	Eluent, mCi (1 σ , %)	HNO ₃ Wash, mCi (1 σ , %)	H ₂ O Wash, mCi (1 σ , %)	Waste, mCi (1 σ , %)	Mo-99 Product, mCi (1 σ , %)	Filter, mCi (1 σ , %)
Sr-91	<6E+01	1.8E+01 (16)	5.8E-01 (17)	2.0E-01 (20)	2.7E-01 (25)	<1E+01	>12 Half-lives
Y-93	3.8E+00 (18)	3.44E+00 (8.3)	1.5E-01 (7.8)	4.5E-02 (9.1)	2.2E-02 (15)	<1E+00	<1E-02
I-135	4.91E+03 (2.7)	2.96E+03 (2.3)	1.57E+02 (2.4)	4.05E+01 (2.3)	2.32E+01 (4.6)	7.69E+02 (5.8)	>12 Half-lives

TABLE 5.34 Distribution of Zr, Mo, Ru, I, La, and Sb in Various Fractions of Concentration Column in Run #6

Radionuclide	Eluent	HNO ₃ Wash	H ₂ O Wash	Waste	Product	Filter	Balance
Mo-99	0.19%	0.01%	0.10%	0.20%	103.2%	1.33% ^a	103.6%
Ru-103	86.8%	1.0%	0.2%	1.0%	10.1%	54.3% ^a	99.0%
I-131	53.5%	2.8%	0.8%	0.4%	14.6%	10.1% ^a	72.1%
I-133	54.0%	2.8%	0.8%	0.4%	14.2%	9.9% ^a	72.2%
I-135	60.3%	3.2%	0.8%	0.5%	15.7%	N/A	80.5%
Cs-136	0.0%	0.0%	0.0%	1.1%	30.8%	0.83%	31.9%
Rh-105	61.0%	2.0%	0.3%	0.0%	25.9%	25.1% ^a	89.3%
Sn-125	0.0%	3.6%	1.3%	6.2%	107%	0.83% ^a	118.6%
Sb-127	1.6%	0.0%	0.0%	7.2%	57.1%	0.1%	65.8%
Y-93	89.7%	3.9%	1.2%	0.6%	0.0%	1.1%	95.3%

^a Percent of activity present in CC product solution.

TABLE 5.35 Activities Detected in LMC Fractions and Calculated at EOB in Run #6

Radionuclide	RF-1, mCi (1 σ , %)	RFW, mCi (1 σ , %)	LMC Product, mCi (1 σ , %)
Zr-95	<5E-02	3.8E-03 (8.8)	4.02E-03 (4.0%)
Nb-95	8.8E-02 (11)	1.2E-03 (16)	8.64E-03 (2.2%)
Mo-99	1.32E+03 (2.3)	3.06E+00 (3.6)	1.27E+03 (2.3)
Ru-103	2.0E-01 (14.5)	1.58E-01 (1.9)	4.40E-03 (3.1)
I-131	2.01E+01 (3.0)	9.02E+00 (1.9)	5E-03 (26)
I-133	3.37E+02 (1.9)	1.46E+02 (1.9)	5.53E-02 (2.9)
Sn-125	8.9E-01 (19)	5.88E-01 (3.7)	<3E-03
Sb-127	2.89E+00 (4.9)	3.29E+00 (3.2)	<6E-04

TABLE 5.36 Distribution of Mo, Ru, I, Zr, and Sn in Various Fractions of LMC in Run #6

Radionuclide	RFW	LMC Product
Zr-95	7.8%	8.3%
Nb-95	1.4%	9.8%
Mo-99	0.2%	96.7%
Ru-103	79.2%	2.2%
I-131	44.9%	0.03%
I-133	43.4%	0.02%
Sn-125	66.1%	<0.34%

TABLE 5.37 Radionuclidic Purity in ⁹⁹Mo Product Solution from LMC Process Calculated at 36 hr after EOB in Run #6

Ratio	Determined Value 36 hr after EOB	Product Specification	Within Specification
¹³¹ I/ ⁹⁹ Mo	5.3E-06	$\leq 5 \times 10^{-5}$	YES
¹⁰³ Ru/ ⁹⁹ Mo	4.9E-06	$\leq 5 \times 10^{-5}$	YES
$\Sigma\alpha$ / ⁹⁹ Mo	6.5E-12	$\leq 1 \times 10^{-9}$	YES

$\Sigma\alpha$ = total alpha activity

5.6 SUMMARY

Whether the ¹⁰³Ru and ¹³¹I met radionuclide purity specifications for the Mo-99 product after the LMC process is summarized in Table 5.38. In run #3, the activity of ¹⁰³Ru was slightly above the specifications (¹⁰³Ru/⁹⁹Mo = 5.1×10^{-5} vs. 5.0×10^{-5}), and in run #5, the activity of ¹³¹I was below the detection limit; as a result, the MDA value that was used to calculate the ¹³¹I/⁹⁹Mo ratio was too high to prove that it met the specifications for ¹³¹I.

TABLE 5.38 Distribution of I-131 and Ru-103 in Key Fractions of CC and LMC Process and Total Mo-99 Yield for Both Processes in All Mini-SHINE Runs

Run	CC Eluent		CC Product		LMC RFW		Meet Specifications?			Total Yield
	I-131	Ru-103	I-131	Ru-103	I-131	Ru-103	I-131	Ru-103	Alpha	Mo-99
#1	130.7%		1%		32.6% ^a	54.5%	YES	YES	YES	79.7%
#2	87.0%	80.6%	7.1%	17.8%	18.4%	45.0%	YES	YES	YES	92.0%
#3	61.4%	87.3%	5.2%	9.5%	15.0%	28.7%	YES	NO	ND ^b	84.1%
#4	166.4%	83.7%	3.5%	23.2%		53.3%	YES	YES	ND	47.2%
#5	79.4%	65.5%	1.5%	24.0%	8.6%	17.9%	?#	YES	YES	63.3%
#6	53.5%	86.8%	14.6%	10.1%	44.9%	79.2%	YES	YES	YES	89.5%

^a Determined that ¹³¹I activity was below detection limit; MDA value was used.

^b ND – not determined.

Modifications made to the LMC process by removing Ag/C have not affected the purity of the product, but in general, they have shortened the total processing time and decreased the volume of the product by 15-20%. It was observed that the majority of I-131 and Ru-103 in the CC partitioned into the eluent of the concentration column. Fluctuation of the I-131 fraction found in the RFW fraction of the LMC may indicate some differences in speciation of iodine from run to run. When a higher amount of KMnO₄ was added before the ABO precipitation of Mo, it negatively affected the recovery of Mo-99. The Mo-99 product from run #6 was shipped to GE Healthcare, and Tc-99m eluted from DRYTEC™ Tc-99m Generator was successfully tested with two GE Healthcare Tc-99m-based products: Myoview™ and Ceretec™.

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APPENDIX A: **THERMAL HYDRAULIC ANALYSIS OF THE TANTALUM TARGET ASSEMBLY**

J.L. Bailey, Nuclear Engineering Division, 1/17/12

A.1 INTRODUCTION

Forced cooling of the Ta Target is required due to internal heat generation from the electron beam impinging on the target. The target assembly is shown in Figure A.1. The coolant water at near ambient temperature enters the assembly through the port drilled in the side of the MDC vacuum flange. The flow is diverted into half of the annular space between the inner and outer tubes. The flow is separated by two parallel bars that run the length of the annular space. The coolant flow then passes over the Ta target's outer surface. The flow is then directed to the back of the target and then is redirected back through the other half of the annular space and out through the return port in the flange. The electron beam passes through the inner tube and impinges on the Ta target at the coned surface. The cone configuration is intended to distribute the beam energy over the length of the target. The inner tube is at UHV conditions. The outside of the outer tube is immersed partially in the uranium solution, partially in the surrounding cooling water and partially in ambient air. A hydraulic analysis was first performed to determine the overall pressure drop through the assembly at design flow conditions. A second thermal hydraulic analysis was performed for the target and surrounding water flow at the target to determine the surface temperature of the target and temperature rise of the coolant water.

FIGURE A.1 Ta Target Design

A.2 OVERALL HYDRAULIC ANALYSIS

A hydraulic analysis was performed considering the coolant flow from the inlet connection on the MDC flange to the outlet connection at the flange. The commercial computer code “FATHOM” was used to model the flow. A diagram showing the flow path is shown in Figure A.2. Resistance coefficients at all the turns were approximated by right angle mitered elbows. Friction resistance along the annular path was calculated using a hydraulic diameter equivalent. The design flow rate was assumed to be 10 GPM water at near ambient conditions. The overall pressure drop from inlet to outlet connections was determined to be 27.3 psi. The detailed input and results are shown in Figure A.3.

FIGURE A.2 Hydraulic “Fathom” Model

AFT Fathom 7.0 Output
ANL

(1 of 5)

1/16/2012

AFT Fathom Model

=====

== BEGINNING OF INPUT DATA ==

=====

General

Title: AFT Fathom Model

Input File: C:\Users\bailey\Documents\CSE Projects\Acc211\Ta Target\TAFLOW_3.ftb

Number Of Pipes= 7

Number Of Junctions= 8

Pressure/Head Tolerance= 0.0001 relative change

Flow Rate Tolerance= 0.0001 relative change

Temperature Tolerance= 0.0001 relative change

Flow Relaxation= (Automatic)

Pressure Relaxation= (Automatic)

Heat Transfer with Energy Balance

Fluid Database: AFT Standard

Fluid: Water at 1 atm

Max Fluid Temperature Data= 212 deg. F

Min Fluid Temperature Data= 32 deg. F

Default Temperature= 100 deg. F

Default Density= 62.00014 lbm/ft3

Default Viscosity= 1.6356 lbm/hr-ft

Default Vapor Pressure= 0.95524 psia

Viscosity Model= Newtonian

Atmospheric Pressure= 1 atm

Gravitational Acceleration= 1 g

Turbulent Flow Above Reynolds Number= 4000

Laminar Flow Below Reynolds Number= 2300

Pipe Input Table

Pipe	Name	Pipe Defined	Length	Length Units	Hydraulic Diameter	Hydraulic Diam. Units	Friction Data Set	Roughness	Roughness Units	Losses (K)	Junctions (Up,Down)	Geometry	Material
1	Pipe	Yes	1.62	inches	0.41	inches	Unspecified	0.00006	inches	0	2, 1	Cylindrical Pipe	Unspecified
2	Pipe	Yes	8.39	inches	0.15265	inches	Unspecified	0.00006	inches	0	1, 7	Noncylindrical Pipe	Unspecified
3	Pipe	Yes	0.5	inches	0.15265	inches	Unspecified	0.00006	inches	0	3, 9	Noncylindrical Pipe	Unspecified
4	Pipe	Yes	8.39	inches	0.15265	inches	Unspecified	0.00006	inches	0	8, 5	Noncylindrical Pipe	Unspecified
5	Pipe	Yes	1.62	inches	0.41	inches	Unspecified	0.00006	inches	0	5, 6	Cylindrical Pipe	Unspecified
6	Pipe	Yes	2.36	inches	0.15265	inches	Unspecified	0.00006	inches	0	7, 3	Noncylindrical Pipe	Unspecified

FIGURE A.3a “Fathom” Output

AFT Fathom 7.0 Output
ANL
(2 of 5)
1/16/2012

AFT Fathom Model

Pipe	Name	Pipe Defined	Length	Length Units	Hydraulic Diameter	Hydraulic Diam. Units	Friction Data Set	Roughness	Roughness Units	Losses (K)	Junctions (Up,Down)	Geometry	Material
7	Pipe	Yes	2.36	inches	0.15265	inches	Unspecified	0.00006	inches	0	9, 8	Noncylindrical Pipe	Unspecified

Pipe	Special Condition
1	None
2	None
3	None
4	None
5	None
6	None
7	None

Pipe Fittings & Losses

Assigned Flow Table

Assigned Flow	Name	Object Defined	Inlet Elevation	Elevation Units	Special Condition	Type	Flow	Flow Units	Loss Factor
2	Assigned Flow	Yes	0	feet	None	Inflow	10	gal/min	0

Bend Table

Bend	Name	Object Defined	Inlet Elevation	Elevation Units	Type	Angle (Degrees)	Loss Factor
1	Bend	Yes	0	feet	Custom	90	1.188
3	Bend	Yes	0	feet	Custom	90	1.188
5	Bend	Yes	0	feet	Custom	90	1.188
9	Bend	Yes	0	feet	Custom	90	1.188

Branch Table

Branch	Name	Object Defined	Inlet Elevation	Elevation Units	Special Condition	(Pipe #1) K In. K Out	(Pipe #2) K In. K Out
7	Branch	Yes	0	feet	None	(P2) 0, 0	(P6) 0, 0
8	Branch	Yes	0	feet	None	(P4) 0, 0	(P7) 0, 0

FIGURE A.3b “Fathom” Output

AFT Fathom 7.0 Output
ANL

(3 of 5)

1/16/2012

AFT Fathom Model

Reservoir Table

Reservoir	Name	Object Defined	Liquid Elev.	Liquid Elev. Units	Surface Pressure	Surface Pressure Units	Balance Energy	Balance Concentration	(Pipe #1) K In	(Pipe #1) K Out	(Pipe #1) Depth	Pipe Depth Units
6	Reservoir	Yes	0	feet	1	atm	No	No	(P5) 0.0	(P5) 0.0	(P5) 0	feet

=====

== BEGINNING OF OUTPUT DATA ==

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General

Title: AFT Fathom Model

Analysis run on: 1/16/2012 4:13:50 PM

Application version: AFT Fathom Version 7.0 (2008.04.30)

Input File: C:\Users\bailey\Documents\ICSE Projects\Acc211\Ta Target\TAFLOW_3.fth

Execution Time= 0.03 seconds

Total Number Of Head/Pressure Iterations= 0

Total Number Of Flow Iterations= 2

Total Number Of Temperature Iterations= 2

Number Of Pipes= 7

Number Of Junctions= 8

Matrix Method= Gaussian Elimination

Pressure/Head Tolerance= 0.0001 relative change

Flow Rate Tolerance= 0.0001 relative change

Temperature Tolerance= 0.0001 relative change

Flow Relaxation= (Automatic)

Pressure Relaxation= (Automatic)

Heat Transfer with Energy Balance

Fluid Database: AFT Standard

Fluid: Water at 1 atm

Max Fluid Temperature Data= 212 deg. F

Min Fluid Temperature Data= 32 deg. F

Default Temperature= 100 deg. F

Default Density= 62.00014 lbm/ft3

Default Viscosity= 1.6356 lbm/hr-ft

Default Vapor Pressure= 0.95524 psia

Viscosity Model= Newtonian

Atmospheric Pressure= 1 atm

Gravitational Acceleration= 1 g

Turbulent Flow Above Reynolds Number= 4000

FIGURE A.3c “Fathom” Output

AFT Fathom 7.0 Output
ANL

(4 of 5)

1/16/2012

AFT Fathom Model

Laminar Flow Below Reynolds Number= 2300

Total Inflow= 1.388 lbm/sec
Total Outflow= 1.388 lbm/sec
Total Energy Inflow= 55.82 Btu/s
Total Energy Outflow= 55.82 Btu/s
Maximum Pressure is 41.95 psia at Junction 2 Inlet
Minimum Pressure is 11.03 psia at Junction 5 Outlet
Maximum Static Temperature is 100.0 deg. F at Junction 6 Inlet
Minimum Static Temperature is 72.00 deg. F at Junction 1 Inlet

Reservoir Summary

Jct	Name	Type	Liq. Height (feet)	Liq. Elevation (feet)	Surface Pressure (psia)	Liquid Volume (feet3)	Liquid Mass (lbm)	Net Vol. Flow (gal/min)	Net Mass Flow (lbm/sec)
6	Reservoir	Infinite	N/A	0	14.70	N/A	N/A	10.00	1.388

Pipe Output Table

Pipe	Name	Vol. Flow Rate (gal/min)	Velocity (feet/sec)	dP Stag. Total (psid)	dP Static Total (psid)	P Static In (psia)	P Static Out (psia)	P Stag. In (psia)	P Stag. Out (psia)	Int. Conv. Coef. (Btu/hr-ft2-R)	T Inlet (deg. F)	dT (deg. F)	T Outlet (deg. F)	Heat Transfer Area (feet2)	Heat Rate (kW)
1	Pipe	10.00	24.30	0.3056	0.3056	41.95	41.64	45.92	45.61	0	72.00	0	72.00	0.01449	0
2	Pipe	10.00	23.25	4.9356	4.9356	37.26	32.32	40.89	35.96	0	72.00	0	72.00	0.21068	0
3	Pipe	10.00	23.25	0.2941	0.2941	26.62	26.33	30.25	29.96	0	72.00	0	72.00	0.01256	0
4	Pipe	10.00	23.25	4.9356	4.9356	20.62	15.68	24.25	19.32	0	72.00	0	72.00	0.21068	0
5	Pipe	10.00	24.30	0.3056	0.3056	11.03	10.73	15.00	14.70	0	72.00	0	72.00	0.01449	0
6	Pipe	10.00	23.25	1.3883	1.3883	32.32	30.94	35.96	34.57	0	72.00	0	72.00	0.05926	0
7	Pipe	10.00	23.25	1.3883	1.3883	22.01	20.62	25.64	24.25	0	72.00	0	72.00	0.05926	0

Pipe	Flow Area (inches2)
1	0.1320
2	0.1380
3	0.1380
4	0.1380
5	0.1320
6	0.1380
7	0.1380

FIGURE A.3d “Fathom” Output

AFT Fathom 7.0 Output
ANL

(5 of 5)

1/16/2012

AFT Fathom Model

All Junction Table

Jct	Name	P Static In (psia)	P Static Out (psia)	P Stag. In (psia)	P Stag. Out (psia)	Vol. Flow Rate Thru Jct (gal/min)	Mass Flow Rate Thru Jct (lbm/sec)	Loss Factor (K)
1	Bend	41.64	37.26	45.61	40.89	10.00	1.388	1.188
2	Assigned Flow	41.95	41.95	45.92	45.92	10.00	1.388	0.000
3	Bend	30.94	26.62	34.57	30.25	10.00	1.388	1.188
5	Bend	15.68	11.03	19.32	15.00	10.00	1.388	1.188
6	Reservoir	14.70	14.70	14.70	14.70	10.00	1.388	0.000
7	Branch	32.32	32.32	35.96	35.96	10.00	1.388	0.000
8	Branch	20.62	20.62	24.25	24.25	10.00	1.388	0.000
9	Bend	26.33	22.01	29.96	25.64	10.00	1.388	1.188

FIGURE A.3e “Fathom” Output

A.3 THERMAL HYDRAULIC ANALYSIS OF THE TARGET

A thermal hydraulic analysis was performed using the flow conditions above to determine the temperature distribution within the Ta target. The commercial computer code “ANSYS CFX” was used to model the target and the flowing coolant around the target. The model geometry is shown in Figure A.4. The heat generation within the target was assumed uniform with a total power of 10 kW. An insulated boundary was assumed at the vacuum end (beam line) of the target. The forced convection coefficients between the coolant and the wetted target surfaces are inherently calculated by the CFX Code based on the calculated flow field. The resulting target temperatures are shown in Figure A.5. The maximum temperature of 574°F is shown to be at the centerline of the target which is an acceptable operating temperature for the Ta. Also, the maximum wetted surface temperature of the target is shown to be 171°F which is below the boiling point of the water coolant. Figure A.6 shows the coolant vector flow in the coolant channels which indicate that here is reasonably uniform flow at the target surface and that cavitation is not present.

FIGURE A.4 “ANSYS CFX” Meshed Model of Target and Surrounding Flow Channel

FIGURE A.5 “ANSYS CFX” Temperature Results

FIGURE A.6 “ANSYS CFX” Vector Flow Field in Coolant Channel Result

A.4 CONCLUSION

Flow velocities and resulting pressure drop across the target are within reasonable design parameters. The target temperatures under these flow conditions are within the material’s allowable. The temperature at the target’s wetted surface is below the boiling point of the water coolant which eliminates concerns about channel “burn out” or flow imbalance. Based on this thermal hydraulic analysis the target as shown in Figure A.1 should operate satisfactorily.

APPENDIX B: SUMMARY OF FEA RESULTS FOR THE STAINLESS STEEL PROCESS VESSEL FOR 99MO ISOTOPE PRODUCTION

Philip Strons – Nuclear Engineering Division-EO
Completed for Chemical Sciences and Engineering Division of ANL

B.1 GEOMETRY, MATERIAL, AND LOADS

A surface model of the vessel was created in Inventor 2012 using dimensions taken from the initial set of fabrication drawings. This geometry was then imported into ANSYS Workbench R13. All wall thicknesses were assumed to be 1/16 in., and the material was assumed to be 304L stainless steel with an elasticity of 28×10^6 psi. Assuming a density for water of 1000 kg/m^3 , hydrostatic pressure was applied to the outer shell. Using the same density value, the weight of the water (~300 lb) was applied as a uniform force to the bottom of the vessel. An internal pressure of 3.5 psi was applied to all surfaces that bound the volume between the inner and outer portions of the vessel.

B.2 FAILURE CRITERIA

The maximum allowable stress was determined by referencing the ASME Boiler & Pressure Vessel Code, Section VIII Division 2. For 304L stainless steel, Table 5a of the code lists 16.7 ksi as the maximum stress when only membrane stress is present, and 25 ksi as the maximum stress for when membrane stress and bending combine.

B.3 METHOD OF REINFORCING VESSEL

Following the results of the analysis of the Aluminum Process Vessel, the same, general approach was applied to reinforcing the stainless steel vessel: use six rods to tie the top and bottom of the vessel together. This solution greatly increases rigidity of the vessel without affecting its overall size. This also keeps the total mass of the vessel low. In this vessel, the rods are 1/4-in. OD tubes with a 1/32-in. wall thickness. To ensure that the rods have sufficiently strong connections to the walls of the vessel, small plates (1/8-in. thick) are added near the points of attachment.

B.4 RESULTS

Since shell elements are used, the type of stress in an element can be determined during post-processing. Any areas of high stress, shown in the following figures, have both membrane and bending stress present. Therefore, the maximum allowable stress is 25 ksi for all figures presented here. Without the added rods, high bending stresses occurred at the edges of the

conical top and bottom of the vessel. Adding the rods eliminates this problem, but the connection areas require additional thickness. After strengthening the connections, the highest stress at the top of the vessel is 18.8 ksi, and the highest stress in the bottom of the vessel is 20.9 ksi. Both values are below the allowable stress of 25 ksi.

FIGURE B.1 Plot of Stress for Entire Vessel. Overall, stress is well below the allowable. The maximum value shown in the legend occurs at a displacement constraint and can be safely disregarded. The actual high stress regions occur where the rods connect to the top and bottom of the vessel.

FIGURE B.2 Plot of Stress for the Added Plates at the Top of the Vessel. This plot is intended to illustrate the location shown in the next figure.

FIGURE B.3 A Closer Look at the Plates That Reinforce the Rod Connection Points at the Top of the Vessel. The maximum membrane plus bending stress is 18.8 ksi, which is well below the allowable of 25 ksi.

FIGURE B.4 Plot of Stress for the Added Plates at the Bottom of the Vessel. This plot is intended to illustrate the location shown in the next figure.

FIGURE B.5 A Closer Look at the Plates That Reinforce the Rod Connection Points at the Bottom of the Vessel. The maximum membrane plus bending stress is 20.9 ksi, which can be seen more clearly in the next figure that looks from underneath.

FIGURE B.6 A View of the Rod Connections at the Bottom of the Vessel, Viewed from Underneath. The maximum stress in the reinforcement plates is 20.9 ksi, which is below the allowable stress of 25 ksi.

APPENDIX C: THERMAL HYDRAULIC ANALYSIS OF THE REACTION VESSEL

J.L. Bailey, Nuclear Engineering Division 2/8/12

C.1 INTRODUCTION

Cooling of the process fluid in the Reaction Vessel is required due to internal heat generation caused by radiation from the Ta Target. The Reaction Vessel Assembly is shown in Figure C.1. The coolant water at near ambient temperature enters the outer vessel through the 1 in. tube that extends to the bottom of the vessel. The flow then circulates around in the outer vessel and discharges through the 1 in. tube at the top of the vessel. The inner vessel that contains the process fluid is immersed in the coolant flow in the outer vessel.

FIGURE C.1 Design of the Reaction Vessel Assembly

Figure C.2 shows the inner vessel sub-assembly. The inner vessel process fluid is isolated from the out vessel coolant flow and heat transfer is by convection and conduction through the wall of the inner vessel. There is a Blind Closure Flange that mates to the flange at the top of the inner vessel. There are small instrumentation penetrations as well as a small hydrogen re-combiner with heat exchangers mounted on this flange. The Blind Closure Flange is shown in the Figure C.3.

The Return Heat Exchanger on the Blind Flange is analyzed in this report following the Reaction Vessel analysis. The inner vessel is essentially a closed vessel with a relief valve. The inner vessel fluid has no forced convection and heat transfer from the uranium solution to the inner vessel wall is completely by natural convection. (i.e., fluid motion is driven temperature differences within the fluid). Also, convective heat transfer from the outside of the inner vessel to the coolant flow in the outer vessel is mostly by natural convection due to the low flow velocities in the outer vessel. A thermal hydraulic analysis was first performed to determine the average and maximum temperature of the process fluid under operating conditions. The significant design criterion for satisfactory operation is to assure that the process fluid remains below its boiling point at atmospheric pressure.

C.2 THERMAL HYDRAULIC ANALYSIS DESCRIPTION – REACTION VESSEL

A thermal hydraulic analysis was performed considering the anticipated normal flow rate into the outer vessel of about 0.5 GPM at 72°F. A calculation in the attachment indicates that at the expected total heat generation of 400 W in the uranium solution the temperature difference between the inlet and outlet flows of the outer vessel is about 5°F. The commercial computer code “ANSYS CFX” was used to model the Reaction Vessel thermal hydraulic characteristics. The model geometry is shown in Figure C.4. The heat generation within the process fluid is divided into two sources, and hence, there are two superimposed heat generation profiles. The first is a “one over radius squared” correlation with a total heat generation of 100 W. This is distributed over the entire process fluid region with the ordinate ($r=0$) located at the center of the Ta Target. This profile is a result of the neutron radiation emanating from the target. The second heat generation profile is cone shaped around the target tube and expands at a 10 degree angle from where the tube enters the inner vessel to the opposite wall of the inner vessel. The total heat generated in this region is 300 W. This second heat generation source is due to gamma radiation from the electron beam. The volumetric heat generation density that corresponds to these profiles is calculated in the attachment. These profiles were input in to the ANSYS CFX model. An insulated boundary was assumed at the outer surface of the outer vessel. Also, the top surface of the process fluid was assumed to be insulated. The properties of the coolant in the outer vessel were based on water at ambient conditions. Also, for this case, the process fluid was assumed to have water properties at 1 atm pressure. All stainless steel walls were considered to have negligible heat capacity and thermal resistance. The forced and natural convection coefficients at the inner vessel wall surfaces were inherently calculated by the CFX Code based on the calculated flow field and fluid temperatures.

FIGURE C.4 ANSYS CFX Meshed Geometry Model of the Reaction Vessel Assembly

C.3 RESULTS AND CONCLUSIONS - REACTION VESSEL

First results showed that essentially there is not a stable steady state (SS) solution to this model. This condition is due to buoyancy within the fluid and the associated temperature differences. Therefore, a transient run was performed over a significant period of time until the average temperature and the maximum temperature within the process fluid became relatively constant ($t=100$ s starting from the unstable SS solution). A temperature contour plot at this time is shown in Figure C.5. The plot indicates that the maximum process fluid temperature is 144°F . Also, the calculated mass average temperature of the fluid is found to be 111°F . These results verify that the process fluid is significantly below the boiling point of the assumed water and, therefore, the significant design criterion is met. Figure C.6 shows a typical plot of coolant and process fluid vector flow fields. The plot indicates that the forced flow through the outer vessel is very low with negligible pressure drop. The maximum fluid velocity of 0.2 ft/s occurs at the 1-in. diameter tube inlet and outlet. A typical natural convection flow in the inner vessel is also shown. It is concluded that these results confirm that the thermal hydraulic design is within reasonable design parameters and is practical.

FIGURE C.5 ANSYS CFX Temperature Contour Results at Mid-plane

FIGURE C.6 ANSYS CFX Vector Velocity Field at Mid-plane

C.4 THERMAL HYDRAULIC ANALYSIS DESCRIPTION – RETURN HEAT EXCHANGER

Thermal hydraulic calculations were performed for the heat exchanger shown in Figure C.3. The purpose of this exchanger is to cool the return helium and water vapor that is flowing from the hydrogen/ oxygen recombiner back to the Reaction Vessel. The helium/vapor gas flows through the 1/4-in. tubing spiral, and cooling water is circulated through the outer container. The cooling water temperature is assumed constant because of its large heat capacity compared to the helium capacity. Note that there is also a small heat exchanger in the line from the Reaction Vessel to the recombiner. This small exchanger essentially has no load requirements and is there to scavenge any vapor that may accidentally flow to the recombiner. No analysis is performed on this small exchanger.

Calculation assumptions follow:

Given

$$T_{\text{ingas}} := 250^{\circ}\text{C} \quad \text{Temperature of gas leaving recombiner}$$

$$T_{\text{outgas}} := 80^{\circ}\text{C} \quad \text{Required temperature of gas returning to Reaction Vessel}$$

$$T_{\text{avewater}} := 15^{\circ}\text{C} \quad \text{Temperature of cooling water to exchanger shell}$$

$$T_{\text{avegas}} := \frac{T_{\text{ingas}} + T_{\text{outgas}}}{2} = 165^{\circ}\text{C}$$

$$q_{\text{required}} := 40\text{W} \quad \text{Heat of reaction estimate is 20 W with a safety factor of 2 = 40 W}$$

$$\text{OD}_{\text{tube}} := .25\text{in}$$

$$t_{\text{wall}} := .035\text{in}$$

$$\text{ID}_{\text{tube}} := \text{OD}_{\text{tube}} - 2 \cdot t_{\text{wall}} = 0.18\text{in}$$

$$L_{\text{tube}} := 12\text{in} \quad \text{Assumed length of 1/4" OD tube}$$

He properties at average temperature of 165 C

$$\rho_{\text{he}} := .007 \frac{\text{lb}}{\text{ft}^3}$$

$$C_{p_{\text{he}}} := 1.24 \frac{\text{Btu}}{\text{lb} \cdot \Delta^{\circ}\text{F}}$$

$$\nu_{\text{he}} := 2.33 \cdot 10^{-3} \frac{\text{ft}^2}{\text{s}}$$

$$k_{\text{he}} := .1 \frac{\text{Btu}}{\text{hr} \cdot \text{ft} \cdot \Delta^{\circ}\text{F}}$$

$$\text{Pr}_{\text{he}} := .69$$

Based on the above assumptions and helium properties the flow conditions in the tube are:

$$F_{\text{avegas}} := \frac{q_{\text{required}}}{\rho_{\text{he}} \cdot C_{p_{\text{he}}} \cdot (T_{\text{ingas}} - T_{\text{outgas}})}$$

$$F_{\text{avegas}} = 24.252 \cdot \frac{\text{L}}{\text{min}}$$

$$A_{\text{xtube}} := \frac{\pi \cdot ID_{\text{tube}}^2}{4} = 0.025 \cdot \text{in}^2$$

$$v_{\text{aveair}} := \frac{F_{\text{avegas}}}{A_{\text{xtube}}} = 80.774 \cdot \frac{\text{ft}}{\text{s}} \quad \text{Gas velocity through 1/4" OD tube}$$

$$Re_{\text{air}} := \frac{v_{\text{aveair}} \cdot ID_{\text{tube}}}{\nu_{\text{he}}} = 520.004 \quad \text{Laminar flow in tube}$$

The heat exchange parameters from the helium to the cooling water are given by:

$$Nu_{\text{he}} := 1.86 \cdot \left(Re_{\text{air}} \cdot Pr_{\text{he}} \cdot \frac{ID_{\text{tube}}}{L_{\text{tube}}} \right)^{.33} = 3.241 \quad \text{Nusselt Number for fully developed laminar flow in duct.}$$

$$h_{\text{he}} := \frac{Nu_{\text{he}} \cdot k_{\text{he}}}{ID_{\text{tube}}} = 21.609 \cdot \frac{\text{Btu}}{\text{hr} \cdot \text{ft}^2 \cdot \Delta^\circ\text{F}} \quad \text{Convective heat transfer coefficient for gas flow in tube. Condensation heat transfer is assumed negligible.}$$

$$A_{\text{surtube}} := \pi \cdot ID_{\text{tube}} \cdot L_{\text{tube}} = 6.786 \cdot \text{in}^2 \quad \text{Convective heat transfer area in tube}$$

$$q_{\text{conv}} := A_{\text{surtube}} \cdot h_{\text{he}} \cdot (T_{\text{avegas}} - T_{\text{avewater}}) = 80.577 \text{ W} \quad \text{Heat transfer due to convection in tube}$$

Summary

The heat carried by the gas flow considering a temperature differential of 250C to 80C and a flow of 24.2 l/min is 40 W (assumed air at average temperature). The total convective heat transfer from the gas to the 12" x 1/4" OD tube wall is 81 W under the same flow conditions. The target heat removal rate based on heat of reaction and a safety factor of 2 is 40 W, therefore the 12" long 1/4" tube is adequate.

Note:

The log mean temp difference typically used for heat exchanger sizing is probably more appropriate for this problem, but is less intuitive. The lmt calculation below shows a heat exchange capacity a bit lower than the linear average used above.

$$\Delta T_a := T_{\text{ingas}} - T_{\text{avewater}} = 423 \cdot \Delta^\circ\text{F}$$

$$\Delta T_b := T_{\text{outgas}} - T_{\text{avewater}} = 117 \cdot \Delta^\circ\text{F}$$

$$\Delta T_{\text{lmtd}} := \frac{\Delta T_a - \Delta T_b}{\ln \left(\frac{\Delta T_a}{\Delta T_b} \right)} = 238.096 \cdot \Delta^\circ\text{F}$$

$$q_{\text{lmtd}} := A_{\text{surtube}} \cdot h_{\text{he}} \cdot \Delta T_{\text{lmtd}} = 71.056 \text{ W}$$

Attachment

Cooling Water Flow Outer Vessel

$$q_{\text{gen}} := 400 \text{ W}$$

$$\rho_w := 62.3 \frac{\text{lb}}{\text{ft}^3}$$

$$C_{p_w} := 1 \frac{\text{Btu}}{\text{lbm} \cdot \Delta^\circ\text{F}}$$

$$\Delta T_{\text{io}} := 5 \Delta^\circ\text{F}$$

$$\dot{m} := \frac{q_{\text{gen}}}{\rho_w \cdot C_{p_w} \cdot \Delta T_{\text{io}}} = 0.546 \text{ gpm}$$

$$D_{\text{tube}} := 1 \text{ in}$$

$$A_{\text{tube}} := \pi \cdot \frac{D_{\text{tube}}^2}{4} = 5.454 \times 10^{-3} \text{ ft}^2$$

$$v_w := \frac{\dot{m}}{A_{\text{tube}}} = 0.223 \frac{\text{ft}}{\text{s}}$$

Internal Volumetric Heat Generation Determination

$$q_{3p}(C_q, r_s) := \frac{C_q}{r_s^2}$$

Assume that the volumetric heat generation " q_{3p} " is proportional to $1/r^2$, where C_q is the constant of proportionality and is to be solved for given the total heat generated within the sphere

$$A_s(r_s) := 4 \cdot \pi \cdot r_s^2$$

Integrating the surface area of the sphere times the volumetric heat generation over " r ", yields the total heat generated in the sphere assuming a 1-D problem.

$$q_{\text{Tr.s}}(r_o, r_i, C_q) := \int_{r_i}^{r_o} A_s(r_s) \cdot q_{3p}(C_q, r_s) dr_s$$

$$q_{\text{Tr.s}}(r_o, r_i, C_q) \rightarrow -4 \cdot \pi \cdot C_q (r_i - r_o)$$

Given

$$r_o := 3.625 \text{ in}$$

$$r_i := .66 \text{ in}$$

$$q_T := .5 \text{ kW}$$

Solving for C_q given the inner and outer radii of the sphere and the total heat generation, q_T , within the sphere

APPENDIX D:
CONCENTRATION COLUMN PROCEDURE

Name: _____

Date: _____

Mo-99 concentration column process procedure

Checks

- Solutions in syringes (4): 0.01 M nitric acid - 60 mL; water - 60 mL; 1 M NaOH - 60 mL; 10 M NaOH – 10 mL
- 2 waste septa vials (60 mL)
- 2 collection septa vials (60 mL) (HNO₃ wash, water wash)
- RF1 bottle – from Cintichem
- Eluent bottle (1 L)
- Nitric acid syringes with luer lock and stopcock, 8 M HNO₃, 30 mL
- NaOH syringe with luer lock and stopcock, 1 M NaOH, 30 mL
- 6 septa vials (20 mL) (Mo-99 product, HNO₃ wash, water wash, feed init., eluent, waste #2)
- 6 – 1 mL syringes with needles (2 - 8" needle, 5 - 5" needles)
- Syringe rack septa bottle (20 mL)
- pH 2 calibration standard and water bottle for pH probe calibration

Solution transfer (PERFORM THIS TASK PRIOR TO SOLUTION TRANSFER)

- Beam Parameters:
 - Energy: _____
 - Power: _____
 - Start time of irradiation: _____
 - EOB time: _____
- High Pressure Gas Cylinder from gas collection system pressure reading: _____
- Open bottom valve to gas collection and connect needle to 1L intermediate vessel
- Place balance near center of bigfoot and put 1L intermediate vessel on balance
 - Record Mass: _____ g (obtained with all lines connected)
- Open Solution Transfer Valve
 - Located above valve board in the two valve set, above the three valve set (see image on side of bigfoot)

Solution Transfer Should be in Progress

- Start time of solution transfer from Recovery Glove box: _____
- HP should obtain dose of room and lines
 - Average Dose of room at door: _____
 - Average Dose of lines at 30 cm: _____
 - Average Dose of lines on contact with bricks: _____
- End time of solution transfer from Recovery Glove box: _____
 - Record Mass of 1L intermediate vessel: _____ g (obtained with all lines connected)

Pre-procedure (can be performed any time prior to transfer of solution into round bottom/acidification vessel)

- Calibrate pH probe
- **Pre-weigh all bottles**
- Waste bottle #1: _____ g
- Waste bottle #2: _____ g
- Water wash bottle: _____ g
- Nitric acid wash bottle: _____ g
- Eluent (1 L) bottle: _____ g
- RF1 bottle: _____ g
- Intermediate 1 L bottle: _____ g (obtain mass with all lines connected)

FIGURE D.1 Flowchart (1 L receiving vessel is also known as the “intermediate 1 L bottle”)

Step 1. Close Solution Transfer Valve

- Close valve to solution transfer line

Step 2. Sample and then Transfer Solution to Acidification Vessel

- Pick up 1 L vessel and swirl in order to mix solution
- Sample with 3 mL syringe affixed with long needles “Feed Init.”
 - Pre-weigh the empty sampling vial
 - Weigh sampling vial after filled with sample
- Transfer solution to acidification vessel
- Input valve: Feed
- Pump control valves
 - Upper: bypass
 - Lower: column
- Column control valves
 - Right: N/A
 - Upper: N/A
 - Lower: N/A
 - Left: N/A
- Pump to Reverse: use screw driver to reverse pump direction
- Pump on: 95%, visual – until the 1 L vessel is empty and the lines have pushed air into the round bottom flask/acidification vessel (bubbles will be observable)

Step 2. Adjust the pH of the feed and sample

- Pre-weigh HNO₃ syringe: _____ g
- Time of acidification: _____
- Turn on stirrer with control panel on left of bigfoot
- Note initial pH: _____
- Adjust feed to pH 2 using 8 M HNO₃, volume: ~120 mL for 950 mL of Feed solution
 - First 90 mL can be added relatively quickly.
WARNING: addition of strong acid to base is exothermic and potentially violent, add acid with caution

Note final pH: _____

Mass of 8 M HNO₃ syringe after acidification: _____ g

Mass of added (if needed) 10 M NaOH _____

- Sample with 3 mL syringe affixed with long needles “Feed final.”
 - Pre-weigh the empty sampling vial
 - Weigh sampling vial after filled with sample

Step 3-4. Bleed lines with (1) water

Turn on heaters – Solution heater and column heater set to 80° C, press RESET

Step 3.

- Input valve: water
- Pump control valves
 - Upper: column
 - Lower: column
- Column control valves
 - Right: upflow
 - Upper: upflow
 - Lower: upflow
 - Left: upflow
- Output valve: Waste
- Gas collection line connected to waste bottle #1
- *VERIFY FLOW RATE, suggested pump percentage = 64%*
- Pump on: 16 mL/min, _____%, 45 sec, 12 mL

Step 4.

- Input valve: water
- Pump control valves
 - Upper: column
 - Lower: column
- Column control valves
 - Right: downflow
 - Upper: downflow
 - Lower: downflow
 - Left: downflow
- Output valve: Waste
- Gas collection line connected to waste bottle #1
- Pump on: 16 mL/min, _____%, 45 sec, 12 mL

Step 5. Pre-equilibrate column

- Input valve: 0.01 M HNO₃
- Column control valves
 - Right: upflow
 - Upper: upflow
 - Lower: upflow
 - Left: upflow
- Pump control valves
 - Upper: column
 - Lower: column
- Output valve: waste
- Gas collection line connected to waste bottle #1
- Pump on: 16 mL/min, _____%, 2 min 18 sec, 36 mL

Step 6. Bleed line with feed

- Input valve: Feed
- Pump control valves
 - Upper: bypass
 - Lower: column
- Column control valves
 - Right: upflow
 - Upper: upflow
 - Lower: upflow
 - Left: upflow
- Pump on: 16 mL/min, _____%, visual – until air pushed out of feed line

Step 7. Load feed and check the flow rate

- Stirring off
- Input valve: Feed
- Column control valves
 - Right: upflow
 - Upper: upflow
 - Lower: upflow
 - Left: upflow
- Pump control valves
 - Upper: column
 - Lower: column
- Output valve: Eluent
- Gas collection line connected to 1 L eluent bottle
- Pump on: 16 mL/min, _____%, 60 min, 954 mL
- Be prepared to tilt vessel in order to use all solution near end of load
 - Turn off pump when bubbles noticed in line leaving vessel towards the column

Step 8. Acid wash

- Input valve: 0.01 M HNO₃
- Column control valves
 - Right: upflow
 - Upper: upflow
 - Lower: upflow
 - Left: upflow
- Pump control valves
 - Upper: column
 - Lower: column
- Output valve: HNO₃ wash
- Gas collection line connected to HNO₃ wash bottle
- Pump on: 16 mL/min, _____%, 1 min 30 sec, 20 mL

Step 9. Water wash

- Lower column heater and solution heater to 70° C
- Input valve: water
- Column control valves
 - Right: upflow
 - Upper: upflow
 - Lower: upflow
 - Left: upflow
- Pump control valves
 - Upper: column
 - Lower: column
- Output valve: water wash
- Gas collection line connected to water wash bottle
- Pump on: 16 mL/min, _____%, 1 min 15 sec , 20 mL

Step 10. Product strip - dead volume to water wash (this is actually 1 M NaOH, the label inside of bigfoot was not changed)

- Input valve: NH₄OH
- Column control valves
 - Right: downflow
 - Upper: downflow
 - Lower: downflow
 - Left: downflow
- Pump control valves
 - Upper: column
 - Lower: column
- Output valve: water wash
- Gas collection line connected to water wash bottle
- *VERIFY FLOW RATE, suggested pump percentage = 16%*
- Pump on: Pump on: 4 mL/min, _____%, 2 min 30 sec, 10 mL

Step 11. Product strip (this is actually 1 M NaOH, the label inside of bigfoot was not changed)

- Input valve: NH_4OH
- Column control valves
 - Right: downflow
 - Upper: downflow
 - Lower: downflow
 - Left: downflow
- Pump control valves
 - Upper: column
 - Lower: column
- Output valve: Mo-99 product
 - Attach line to RF1 bottle
- Gas collection line connected to RF1 bottle
- Pump on: 4 mL/min, _____%, 6 min 15 sec, 25 mL **ENSURE THAT 25 ML WAS COLLECTED**

End Time: _____

Step 12. Rinse lines with water

- Input valve: water
- Column control valves
 - Right: downflow
 - Upper: downflow
 - Lower: downflow
 - Left: downflow
- Pump control valves
 - Upper: column
 - Lower: column
- Output valve: waste 2
- Switch needled line to Waste 2 bottle
- Gas collection line connected to waste bottle #2
- Pump on: 16 mL/min, _____%, 1 min, 16 mL

Turn off heaters

Replace pH probe in storage holder

High Pressure Gas Cylinder from gas collection system pressure reading: _____

Post procedure

- Weigh bottles with solutions

	Mass of Empty Vessel	Mass of Vessel with Solution	Mass of Solution
Intermediate bottle			
Eluent (1L)			
Water wash			
Acid Wash			
Waste Bottle #2			
RF1 bottle			

MIX/SHAKE BOTTLES BEFORE SAMPLING

Collect samples for counting

Sample	Mass of Vial Empty	Mass of Vial with Solution	Mass of Sample
Feed Initial			
Eluent (1L)			
Acid Wash			
Water Wash			
Waste #2			
RF1 Bottle			

NOTES:

Dead volume: 15.0 mL

Laptop username: labuser Password: Bigfoot#cc

T-tare, P-print

Dominique 773-818-5305

Dave 847-445-6071

APPENDIX E:
LEU MODIFIED CINTICHEM PROCESS

**Procedure for Processing SHINE Solution without Ag/C Column:
Demonstration Using Revised Cintichem Procedure**

Solution List

	Solution	Purpose	Solution Volume, Syringe Volume
	NaI carrier 4.0 mL at 1mg/mL	AgI ppt	4.0, 5.0
	10% AgNO ₃ in 0.1 M HNO ₃	AgI ppt	0.5, 1.0
	1 M HCl	Aid in ppt. of NaI/Cl	1.0, 1.0
	4M HNO ₃	Rinse the filter	11, 25
	Mo carrier (10mg/mL)	Mo carrier	0.5, 1.0
	2.5% KMnO ₄	Mo oxidation	10, 10
	Rh carrier (8mg/mL)	Rh carrier	1.5, 2.0
	Ru carrier (5mg/mL)	Ru carrier	2.0, 2.0
	Fresh 2% alpha-benzoin-oxime in 0.4M NaOH	Mo ppt	20, 25
	0.1M HNO ₃	Rinse	20, 25
	0.1M HNO ₃	Rinse-second	20, 25
	0.1M HNO ₃	Rinse-third	20, 25
	0.1M HNO ₃	Rinse	10, 10
	0.1M HNO ₃	Rinse-second	10, 10
	0.1M HNO ₃	Rinse-third	10, 10
	0.1M HNO ₃	Rinse-fourth	10, 10
	0.1M HNO ₃	Rinse-fifth	10, 10
	0.4M NaOH with ~1% H ₂ O ₂	Dissolve ppt	10, 10
	0.2M NaOH with ~1% H ₂ O ₂ .	Dissolve ppt	10, 10
	0.2M NaOH.	Fritted column rinse	10, 10
	1 mg/mL NaI	AgI ppt	4.0, 5.0
	10% AgNO ₃ in 0.1M HNO ₃	AgI ppt	0.5, 1.0
	0.2M NaOH	Ag/C/HZO/AC column rinse	10, 10

Starting solution is ~25-200mL of ~1M HNO₃

Time	Process Step	Operator
	1. Weigh RF-1 bottle, RFW bottle and 1-B bottle and record mass below: RF-1(Mo-99 product from CC): _____ RFW (empty): _____ 1-B (empty): _____ RFW sample vial: _____ 1-B sample vial: _____	
_____	2. If NO evaporation is performed, and TiO ₂ column is used, take the product solution from the concentration column (Mo in 1M NaOH) and determine the volume by weight. Move to RF-1 bottle. Add 0.25mL of 10M HNO ₃ per 1mL of product (1M NaOH) to make ~1.2M HNO ₃ solution, e.g. 2.5mL of 10M HNO ₃ per 10mL of product solution. <i>Using a one-mL syringe, remove ~0.1-mL sample from the “RF-1” bottle for sampling</i> Record mass, RF-1: _____	
_____	3. Add 4.0 mg of NaI carrier (4.0 mL at 1 mg/mL) into the “Raw Fission No. 1” bottle containing Mo solution in ~1M HNO ₃ (~50mL)	_____
_____	4. Add 0.5 mL of 10% AgNO₃ in 0.1M HNO₃ , shake. A <i>white precipitate should form</i> . Wait ~2 minutes.	_____
_____	5. Add 1 mL of 1.0 M HCl . <i>Additional Precipitate should form</i> . Wait ~2 minutes.	_____
_____	6. <i>Pass the solution through 0.3µm and 0.2µm filter assembly into another bottle marked “Raw Fission 2. Rinse the filter assembly with 11 mL of 4M HNO₃. (Add rinse to the bottle)</i>	_____
_____	7. Add 0.5 mL of Mo carrier (10 mg/mL).	_____
_____	8. Add 2.5% KMnO ₄ solution slowly to the raw fission liquor until a deep pink color holds for ~30 seconds. This may require up to 25 mL of solution.	_____
_____	9. Add 1.5 mL of Rh carrier (8 mg/mL) to the raw fission liquor, and shake.	_____
_____	10. Add 2.0 mL of Ru carrier (5 mg/mL) and shake	_____

Time	Process Step	Operator
_____	11. Add 20 mL of fresh 2% alpha-benzoin-oxime in 0.4M NaOH to the raw fission liquor, shake well.	_____
_____	12. Wait about one (1) minute. A white, flocculent precipitate should form.	_____
_____	13. Filter the precipitate through a 51-mm fritted-glass column. Make sure all liquid is drained from the column into the “Raw Fission Waste” bottle	_____
_____	14. Rinse the Raw Fission No. 2 bottle with 20 mL of 0.1M HNO₃ Pass this wash through the column into the “Raw Fission Waste” bottle.	_____
_____	15. Wash the “Raw Fission No. 2” slurry feed bottle <u>twice more</u> with 20 mL of 0.1M HNO₃ each time. Drain the washes through the fritted-glass column into the “Raw Fission Waste” bottle.	_____
_____	16. Inspect the “Raw Fission 2” solution bottle for remnants of the precipitate before discarding it. If any of the alpha-benzoin-oxime precipitate remains in the bottle, the wash should be repeated until the bottle is clean.	_____
_____	17. Wash the precipitate in the column <u>five times</u> with 10 mL of 0.1M HNO₃ , shaking the column well after each wash is injected. Drain these washes into the “Raw Fission Waste” bottle.	_____
_____	18. The acid wash should appear clear. If there is evidence of the precipitate, the acid waste should be passed through the fritted glass column.	_____
_____	19. Remove the fritted column from the filtering assembly. Vent the Raw Fission Waste” bottle through a charcoal filter and store it. Record mass of RFW bottle with solution: _____ <i>Using a 5-10-mL syringe, remove ~5-mL sample from the “Raw Fission Waste” bottle for sampling</i> Record mass of RFW vial with sample: _____	_____
_____	20. Put a new base (“1-A bottle”) in the filtering assembly.	_____

Time	Process Step	Operator
_____	21. To dissolve the precipitate, inject 10 mL of 0.4M NaOH with ~1% H ₂ O ₂ into the column, vent through a charcoal filter.	_____
_____	22. Heat the column that contains the solution with forced hot air until the solution begins to boil.	_____
_____	23. Remove the column from the heat, wait about five (5) minutes, then drain the dissolved precipitate into the “1-A” bottle.	_____
_____	24. Repeat the dissolution and heating with 10 mL of 0.2M NaOH with ~1% H₂O₂ .	_____
_____	25. Remove the column from the heat, wait about five (5) minutes, then drain the dissolved precipitate into the “1-A” bottle.	_____
_____	26. Rinse fritted column with 10 mL of 0.2M NaOH into the 1-A bottle.	_____
_____	27. Add 4.0 mg of NaI carrier (4.0 mL of 1 mg/mL NaI) to the 1-A bottle.	_____
_____	28. Add 0.5 mL of 10% AgNO₃ in 0.1M HNO₃ solution to the 1-A bottle. Shake well, and wait ~5 minutes.	_____
_____	29. The slurry in bottle 1-A is fed to the AgC/ZrO/AC combination column. Use a new top (the AgC/ZRO/AC column) and base (the 1-B bottle). Gravity will allow a flow rate of 1 -3 mL/minute.	_____
_____	30. Wash the column with 10 mL of 0.2M NaOH solution. The combined solution is product 1-B. Record mass, 1-B with Mo-99 product: _____ Total mass of Mo-99 product (subtract the mass of bottle):_____	_____
_____	31. <i>Using a one-mL syringe, remove ~0.5-mL sample from the “1-B” bottle and introduce it through the septum into the QC-5 sample vial.</i> Record mass of 1-B vial with Mo-99 product: _____	_____

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