

Reduced uncertainty in radioxenon fission fractions to improve quantification of waste tank plutonium inventories— final report

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Abstract

Radioactive xenon isotopes (^{133}Xe and ^{135}Xe) generated by the spontaneous fission of ^{240}Pu are useful in identifying buried transuranic waste. The generation rate of these xenon isotopes depends on the amount of ^{240}Pu present and the cumulative fission yield (fission fraction) for each isotope. Published measurements of the cumulative yields for masses 133 and 135 were not consistent with one another. The uncertainties obtained from the variation in the literature are on the order of 13% and 10% for masses 133 and 135, respectively. The cumulative fission yields of ^{133}Xe and ^{135}Xe from ^{240}Pu spontaneous fission are measured through repeated gas sampling with the goal of reducing the uncertainty in these quantities below 5%. Twenty-four gas samples were collected and analyzed for ^{133}Xe , and 29 samples were collected and analyzed for ^{135}Xe . The final cumulative fission yields are $(6.6 \pm 0.2)\%$ for ^{133}Xe and $(5.8 \pm 0.2)\%$ for ^{135}Xe . The uncertainties represent 3% of the final quantities. This achieves the goal of reducing the uncertainty in the measured fission yields below 5% of the total.

Summary

Radioactive xenon isotopes (^{133}Xe and ^{135}Xe) generated by the spontaneous fission of ^{240}Pu are useful in identifying buried transuranic waste. The generation rate of these xenon isotopes depends on the amount of ^{240}Pu present and the cumulative fission yield (fission fraction) for each isotope. While fission yields have been measured and critically evaluated for neutron-induced fission of ^{239}Pu , there is significantly less knowledge regarding the yields from spontaneous fission of ^{240}Pu . Published measurements of the cumulative yields for ^{133}I and ^{135}I (which undergo beta decay to form ^{133}Xe and ^{135}Xe , respectively) are in poor agreement with one another. This leads to large uncertainties (on the order of 10-13%) in the necessary xenon cumulative yields.

This project aims to measure the cumulative fission yields of ^{133}Xe and ^{135}Xe from ^{240}Pu spontaneous fission with the goal of reducing the uncertainty in these quantities below 5%. This is accomplished by sampling the headspace gases from cylinders containing well-characterized plutonium nitrate solutions. The gases within the cylinder are allowed to come to secular and thermodynamic equilibrium, and then the headspace is flushed into a receptacle. Gamma spectrometry is used to quantify the radioxenon collected from the headspace. Reducing the uncertainty in the final values requires repeated sampling, and 24 samples are used to calculate the ^{133}Xe fission yield, and 29 samples are used for ^{135}Xe .

The uncertainty in the measured fission yields depends on several factors. Each individual measurement results in an estimated spontaneous fission yield with approximately 11% uncertainty. The uncertainties arise from xenon quantification and the amount of plutonium present in the cylinder. Systematic effects from other sources of xenon (spontaneous fission of ^{238}Pu and ^{242}Pu , neutron-induced fission of ^{239}Pu), and sampling/collection efficiency are accounted for in the analysis. Uncertainty from the systematic corrections is included in the final analysis. The uncertainty for each individual headspace gas sample is quantified by Monte Carlo analysis. The final cumulative fission yields are $(6.6 \pm 0.2)\%$ for ^{133}Xe and $(5.8 \pm 0.2)\%$ for ^{135}Xe where the reported uncertainties are the standard errors of the mean and account for the effect of collecting multiple measurements. The uncertainties represent 3% of the final quantities. This achieves the goal of reducing the uncertainty in the measured fission yields below 5% of the total.

This report explains the motivation for using the gas sampling technique, the quantification of plutonium in the cylinders, estimation of neutron-induced fission effects, the apparatus design (including engineering steps taken to maximize reproducibility of the measurements), and the gamma spectrometry analysis. Control experiments to establish the sampling efficiency are discussed and analyzed. The measured headspace activities are reported and used to calculate the cumulative fission yield of each isotope for each measurement. Finally, the calculated cumulative fission yields and associated uncertainties are discussed. The ^{133}Xe yield agrees with the literature, but the ^{135}Xe yield is anomalously low. Explanations for this result are explored with the likeliest being a small holdup of xenon in the solution phase that alters the partitioning of the short-lived ^{135}Xe while having minimal effect on the longer-lived ^{133}Xe partitioning.

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Acronyms and Abbreviations

AEA	Alpha Energy Analysis
a.u.	atomic unit (for mass)
CAD	Computer-Aided Design
COTS	Commercial Off-the-Shelf
CRM	Certified Reference Material
GEA	Gamma Energy Analysis
HPGe	High-purity Germanium
IF	Neutron-Induced Fission
LabSOCS	Laboratory Sourceless Calibration Software
LCS	Logging and Control Server
MFC	Mass Flow Controller
MQA	Minimum Quantifiable Amount
MTE	Modified Total Evaporation
NaI(Tl)	Thallium-doped sodium iodide (detector)
NBL	New Brunswick Laboratory
NGMS	Noble Gas Mass Spectrometry
NNSA	National Nuclear Security Administration
PNNL	Pacific Northwest National Laboratory
RGA	Residual Gas Analyzer
ROI	Region of interest
RMT	Radiological Materials Tracking (system)
RPL	Radiochemical Processing Laboratory
SF	Spontaneous Fission
SUL	Shallow Underground Laboratory
TE	Total Evaporation
TIMS	Thermal Ionization Mass Spectrometry
UV-Vis	Ultra-violet visible (spectrometry)

Contents

Abstract.....	ii
Summary.....	iii
Acknowledgments.....	iv
Acronyms and Abbreviations	v
Contents.....	vi
1.0 Introduction	1
1.1 Background/Relevance	1
1.2 Solubility Model	2
1.2.1 Model Derivation.....	2
1.3 Uncertainty	4
1.3.1 Experimental apparatus and sampling efficiency	4
1.3.2 Plutonium quantification and spontaneous fission rate.....	4
1.3.3 Xenon quantification	5
2.0 Experimental Design	6
2.1 Pu materials	6
2.1.1 Characterization of Pu materials.....	6
2.1.2 Conflicting sources of fission	11
2.2 Apparatus design	13
2.2.1 Design Considerations and Implementation of Experimental Design.....	13
2.3 Sampling protocols for control sample	21
2.4 Detection	21
3.0 Results	24
3.1 Raw activities for reliable samples	25
3.2 Control samples	26
3.2.1 Correction factor required for samples	26
3.2.2 Evaluation of the Sampling Efficiency.....	27
3.3 Fission fraction calculated for individual samples.....	30
3.4 Cumulative fission fraction estimate and uncertainty	32
3.4.1 Assessment of potential systematic sources of error	33
4.0 Conclusions.....	35
5.0 References.....	36
Appendix A – P&ID	A.1
Appendix B – Pu composition by confirmatory methods.....	B.1

Figures

Figure 1: MCNP simulation geometry	12
Figure 2: WENDI-2 neutron detector and ratemeter	13
Figure 3. Fully integrated automated sampling system configured for xenon extraction, showing inlet and outlet manifolds, nine sample and three control cylinders housed within a thermally regulated aluminum block, orbital shaker ($\frac{3}{4}$ -inch orbit at 30 RPM), and supporting subsystems including vacuum and line-clearing pumps.....	14
Figure 4. Precision-machined aluminum cylinder block with bored wells for nine sample and three control cylinders, designed to provide uniform heat distribution and maintain a stable thermal environment (37 °C) via embedded cartridge heaters.	15
Figure 5. Installed cylinder block with integrated process tubing, thermocouples, and manifold connections, illustrating system-level routing for controlled flow distribution, temperature monitoring, and volumetrically consistent sample handling.	15
Figure 6. Stainless steel sample cylinder (60 mL total capacity) with quick-disconnect interface, designed for secure integration with the solenoid assembly, reduced analyte adhesion via electrocoating, and efficient transfer of dissolved xenon samples. Aqueous samples and controls are nominally 30 mL.	16
Figure 7. Sample cylinder integrated with solenoid valve assembly, illustrating automated flow control, fail-safe isolation (normally closed configuration), and regulated interaction with nitrogen carrier gas during injection and extraction.....	16
Figure 8. Example of RGA extraction showing plateau of Kr (blue trace) after 240 mL volume collected.....	19
Figure 9. (Left) Schematic representation of the sample cylinder and solenoid assembly, identifying key components, snorkel tube geometry, and the controlled flow path through the system. (Right) Flow diagram illustrating nitrogen carrier gas injection through dual manifolds, snorkel-assisted headspace purge (~98% removal efficiency), and the controlled extraction pathway to downstream manifolds for xenon recovery.	20
Figure 10: Sample cylinder configured for measurement on the shielded HPGe detector	21
Figure 11: Statistical counting uncertainty as a function of count time.	22
Figure 12: Measured ^{133}Xe and ^{135}Xe activities by date.....	26
Figure 13: Pressure profiles for the control experiments (control 1: top left, control 2: top right, control 3: bottom left, control 4: bottom right).	28
Figure 14: Sample histogram from Monte Carlo analysis of the sample collected on 01/30/2025.	31
Figure 15. Process and Instrumentation Diagram of headspace gas sampling apparatus.....	A.1

Tables

Table 1: Half-lives, SF branching ratios, SF half-lives, and specific fission rates for ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{242}Pu	1
Table 2: Cumulative fission yields for ^{133}I and ^{135}I from ^{240}Pu SF.....	2
Table 3: Information provided by different analytical methods.....	7
Table 4: Dilution parameters for UV-Vis measurement preparation	8
Table 5: Plutonium concentration results	9
Table 6: Detector configuration for Pu isotopic TE measurements for RMT 48 and RMT 12962.	9
Table 7: Detector configuration for Pu isotopic TE measurements for RMT 125001.....	9
Table 8: Detector configuration and measurement routine for MTE measurements.	10
Table 9: TIMS Pu isotopic analysis results	11
Table 10: Primary sample analysis results (Pu masses per cylinder).....	11
Table 11: Induced-fission MCNP simulation results. Note that these consider only neutrons generated within the samples.....	13
Table 12: Typical values and associated uncertainties for calculating the activity of xenon isotopes in the headspace gas samples. All uncertainties are given at the 1σ level.	23
Table 13: ^{133}Xe and ^{135}Xe activities for each measurement.....	25
Table 14: Data and calculated values of ϵ for ^{132}Xe and ^{129}Xe from the control experiments.....	29
Table 15: Parameter distributions for Monte Carlo simulations	30
Table 16: ^{133}Xe and ^{135}Xe cumulative fission yields for each measurement	32
Table 17: Mean cumulative fission yields and uncertainties for ^{133}Xe and ^{135}Xe	33
Table 18: Combined AEA/GEA/LSC Pu isotopic analysis results.....	B.1

1.0 Introduction

Fission events create a spectrum of daughter nuclei with probability distributions that depend on multiple factors. For a given nucleus undergoing fission, the probability distribution will vary with the nature of the fission process (neutron-induced or spontaneous) and, if appropriate, the energy of the incident neutron. (Lestone, 2011) While products of neutron-induced fission (IF) for important nuclei (e.g., ^{235}U , ^{239}Pu) have been studied extensively, the results of spontaneous fission (SF) have seen less investigation and are much harder to measure. Measuring radioxenon as generated by SF has been demonstrated for underground sources containing ^{238}U (Hayes et al., 2013) or ^{240}Pu (Dresel and Waichler, 2004) The latter work would have benefited from published data on xenon production from ^{240}Pu – a lack of published data led them to assume that the SF yields were equivalent to the thermal neutron fission yields from ^{239}Pu . This report details measurements of the cumulative fission yields for xenon isotopes generated by the SF of ^{240}Pu using repeated gas samples collected above plutonium nitrate solutions.

1.1 Background/Relevance

The distribution of nuclei produced in fission (characterized by the mass and atomic numbers) can be described using various definitions. Independent fission yields are the fraction of fission events that directly produce a specific daughter nucleus. Cumulative fission yields are often reported for a given mass number and combine all the independent yields for nuclei with same mass. Like the latter definition, the cumulative fission yield for a specific isotope is fraction of fission events that lead directly or indirectly (by subsequent decay chains) to its production. In this report, the terms “fission fraction” and “fission yield” are used interchangeably.

Table 1: Half-lives, SF branching ratios, SF half-lives, and specific fission rates for ^{238}Pu , ^{239}Pu , ^{240}Pu , and ^{242}Pu .

Isotope	Half-life (y)	SF Branching Ratio	SF Half Life (y)	Specific SF Rate (fis. g ⁻¹ s ⁻¹)
^{238}Pu	87.7 ^(b)	$1.9 \times 10^{-7}\%$ ^(b)	$(4.745 \pm 0.083) \times 10^{10}$ ^(a)	1171 ± 20
^{239}Pu	24109 ^(b)	$3.0 \times 10^{-10}\%$ ^(b)	8.0×10^{15} ^(b)	0.007 ^(c)
^{240}Pu	6562 ^(b)	$5.796 \times 10^{-6}\%$ ^(b)	$(1.1608 \pm 0.0091) \times 10^{11}$ ^(a)	474.7 ± 3.7
^{242}Pu	375000 ^(b)	$5.5 \times 10^{-4}\%$ ^(b)	$(6.766 \pm 0.0037) \times 10^{10}$ ^(a)	807.7 ± 4.4
^a (Croft and Favalli, 2021)				
^b (NuDat, 2026)				
^c Calculated from the spontaneous fission half-life and atomic mass of ^{239}Pu				

Of specific interest is the production of xenon isotopes from SF of ^{240}Pu . This plutonium isotope is the result of ^{239}Pu capturing a neutron, thus it builds up during nuclear power generation. ^{240}Pu has a much higher SF rate than ^{239}Pu making it the main source of fission events even when it is present as a fraction of the ^{239}Pu content. Other isotopes (e.g., ^{238}Pu and ^{242}Pu) have high SF rates, but they tend to represent an even smaller fraction of the Pu content than ^{240}Pu . The SF half-lives and specific SF rates (fissions per gram per second) for the plutonium isotopes are provided in Table 1.

Table 2: Cumulative fission yields for ^{133}I and ^{135}I from ^{240}Pu SF.

Reference	Yield ^{133}I	Yield ^{135}I
Laidler and Brown, 1962	$8.19 \pm 0.12 \%$	$6.39 \pm 0.67 \%$
Bushuev <i>et al.</i> , 2007	----	$8.12 \pm 0.15 \%$
Toraskar and Melkonian, 1971	7.3%	7.25%
Demattè <i>et al.</i> , 1997	6.0%	7.8%

Cumulative iodine yields (^{133}I and ^{135}I) have been reported in the literature (Table 2). Of note, the measurements span a large range (6.0% to 8.19% for mass ^{133}I , 6.39% to 8.12% for ^{135}I). While the uncertainty for any one experiment may be relatively low, the disagreement between measurements makes the general uncertainty in these quantities quite high. Comparison between iodine and xenon cumulative fission yields is reasonable because the independent yield of the xenon isotopes is expected to be on the order of 0.01-0.55%. (Laidler and Brown, 1962)

This study presents measurements of the ^{133}Xe and ^{135}Xe cumulative fission yields from ^{240}Pu SF using a gas sampling method. Solutions of plutonium nitrate are allowed to come to secular and thermodynamic equilibrium with a closed headspace. Subsequently, the headspace gas is sampled and the radioxenon is quantified. Using more than twenty headspace measurements, the cumulative fission yield of each isotope is calculated. The uncertainty for each experiment is assessed using Monte Carlo techniques, and the standard error of the mean is reported.

1.2 Solubility Model

The experimental apparatus was designed to facilitate mass transfer of volatile species (i.e., xenon) from the solution into the headspace (Apparatus design). This allows thermodynamic equilibrium to govern the vapor/liquid partitioning of the xenon while secular equilibrium controls the amount of each xenon isotope in the cylinder. These assumptions guided the four-week separation between samples from a given cylinder.

1.2.1 Model Derivation

The solubility model assumes that the ^{133}Xe and ^{135}Xe both have time to come to secular equilibrium within the solution cylinder, and that each isotope is in vapor-liquid equilibrium described by Henry's Law (Equation 1).

$$H_s^{cc} = \frac{c_i^{aq}}{c_i^{vap}}$$

Equation 1

The authoritative compilation of Henry's Law constants (Sander 2023) defines ten different ways to express this parameter. This analysis uses the dimensionless solubility constant (H_s^{cc}) where the concentrations (c_i^{aq} and c_i^{vap}) are expressed in equivalent units (e.g., moles/L or Bq/cm³). The Henry's Law constant is isotope independent, though it must be used to partition each isotope separately.

The mass (activity) balance for isotope i at secular equilibrium in the cylinder (solution and headspace combined) is given by Equation 2 where G_i is the generation rate of isotope i , a_i^{vap} is the activity in the vapor phase, and a_i^{aq} is the activity in the aqueous phase.

$$G_i = a_i^{vap} + a_i^{aq} = N_i^{vap} \lambda_i + N_i^{aq} \lambda_i$$

Equation 2

Generation includes both SF and IF as expressed in Equation 3 where N_{238Pu} , N_{240Pu} , and N_{242Pu} are the number of atoms of ^{238}Pu , ^{240}Pu , and ^{242}Pu in the solution, respectively. The SF decay constants (λ_{238Pu}^{sf} , λ_{240Pu}^{sf} , and λ_{242Pu}^{sf}) are taken from the literature (Croft and Favalli 2021). The cumulative SF yields for each xenon isotope i (χ_i^{sf}) should depend on the Pu isotope; however, a single value (taken to be χ_i^{sf} of ^{240}Pu) is used since the contributions of ^{238}Pu and ^{242}Pu are too small to isolate in this study (see Spontaneous fission isotopes)

$$G_i = (N_{238Pu} \lambda_{238Pu}^{sf} + N_{240Pu} \lambda_{240Pu}^{sf} + N_{242Pu} \lambda_{242Pu}^{sf}) \chi_i^{sf} + R_{239Pu}^{IF} \chi_i^{IF}$$

Equation 3

Equation 4 combines Equation 2 and Equation 3 and replaces the number of atoms in each phase with the concentration (c_i^{vap} and c_i^{aq} , in atoms/cm³) multiplied by the corresponding phase volumes (V^{vap} and V^s).

$$(N_{238Pu} \lambda_{238Pu}^{sf} + N_{240Pu} \lambda_{240Pu}^{sf} + N_{242Pu} \lambda_{242Pu}^{sf}) \chi_i^{sf} + R_{239Pu}^{IF} \chi_i^{IF} = V^{vap} c_i^{vap} \lambda_i + V^s c_i^{aq} \lambda_i$$

Equation 4

Applying Henry's Law (Equation 1) gives rise to Equation 5 where c_i^{aq} is replaced with $H_s^{cc} c_i^{vap}$ to remove the unmeasurable concentration of dissolved xenon.

$$(N_{238Pu} \lambda_{238Pu}^{sf} + N_{240Pu} \lambda_{240Pu}^{sf} + N_{242Pu} \lambda_{242Pu}^{sf}) \chi_i^{sf} + R_{239Pu}^{IF} \chi_i^{IF} = V^{vap} c_i^{vap} \lambda_i + V^s H_s^{cc} c_i^{vap} \lambda_i$$

Equation 5

The headspace activity is $a_i^{vap} = V^{vap} c_i^{vap} \lambda_i$, which gives rise to Equation 6(a) (simplified in Equation 6(b)).

$$(N_{238Pu} \lambda_{238Pu}^{sf} + N_{240Pu} \lambda_{240Pu}^{sf} + N_{242Pu} \lambda_{242Pu}^{sf}) \chi_i^{sf} + R_{239Pu}^{IF} \chi_i^{IF} = a_i^{vap} + \frac{V^s}{V^{vap}} H_s^{cc} a_i^{vap} \quad (a)$$

$$(N_{238Pu} \lambda_{238Pu}^{sf} + N_{240Pu} \lambda_{240Pu}^{sf} + N_{242Pu} \lambda_{242Pu}^{sf}) \chi_i^{sf} + R_{239Pu}^{IF} \chi_i^{IF} = a_i^{vap} \left(1 + \left(\frac{V^s}{V^{vap}} \right) H_s^{cc} \right) \quad (b)$$

Equation 6

Solving for the cumulative SF yield leads to Equation 7.

$$\chi_i^{sf} = \frac{a_i^{vap} \left(1 + \left(\frac{V^s}{V^{vap}} \right) H_s^{cc} \right) - R_{239Pu}^{IF} \chi_i^{IF}}{(N_{238Pu} \lambda_{238Pu}^{sf} + N_{240Pu} \lambda_{240Pu}^{sf} + N_{242Pu} \lambda_{242Pu}^{sf})}$$

Equation 7

Finally, the sampling efficiency (ϵ) must be introduced to account for the fraction of the vapor phase activity captured during sampling (which is the measured quantity a_i^{meas}). Thus, the final expression for χ_i^{sf} is given in Equation 8.

$$\chi_i^{sf} = \frac{\frac{a_i^{meas}}{\epsilon} \left(1 + \left(\frac{V^S}{V^{vap}} \right) H_s^{cc} \right) - R_{239Pu}^{IF} \chi_i^{IF}}{(N_{238Pu} \lambda_{238Pu}^{sf} + N_{240Pu} \lambda_{240Pu}^{sf} + N_{242Pu} \lambda_{242Pu}^{sf})}$$

Equation 8

The values and uncertainties associated with each of these parameters will be discussed in subsequent sections.

1.3 Uncertainty

The contributions to the uncertainty budget are summarized in this section. The overall uncertainty includes contributions from the following categories: experimental apparatus and sampling efficiency, plutonium quantification and SF rate uncertainty, xenon quantification by gamma spectrometry. Each category is briefly described below along with relative contributions to the overall uncertainty. The experimental uncertainty is presented along with results below (Results).

1.3.1 Experimental apparatus and sampling efficiency

The sampling efficiency is affected by several aspects of the experimental apparatus design, each of which are physical phenomena that could contribute to Xe loss: adsorption of Xe to the walls and outlet HEPA filter, incomplete flushing of the headspace during sample collection, dead space within the apparatus, and potential leaks in the apparatus. These are systematic losses, the aggregate of which can be determined experimentally via control experiments where the headspace of a cylinder is filled with xenon gas and then sampled to determine the fraction recovered. The sampling efficiency is expected to be the greatest source of uncertainty related to the apparatus design. The experimental design was adapted to minimize the contribution from each of these sources of uncertainty, as described in greater detail below (Design Considerations and Implementation of Experimental Design). The sampling efficiency was experimentally measured at approximately $(100 \pm 13)\%$ (Evaluation of the Sampling Efficiency).

1.3.2 Plutonium quantification and spontaneous fission rate

This uncertainty contribution is comprised of the uncertainty in the amount of Pu in each cylinder, the isotopic composition of the Pu in each cylinder, the rate of IF of ^{239}Pu from both neutrons within the sample and neutrons in the external environment, and the SF constant for ^{240}Pu . The rate of IF is estimated at 2-5% of total fissions and therefore represents a negligible contribution to the measured radioxenon. The MCNP model used to calculate the estimated IF is discussed in further detail below (see Induced fission—neutron monitor and MCNP modeling). The ^{240}Pu per cylinder ranges from 50-60 mg, with 2-3.5% uncertainty (see Plutonium Quantification Results).

1.3.3 Xenon quantification

The xenon isotopes of interest (^{133}Xe and ^{135}Xe) are quantified via gamma spectrometry using a high-purity germanium (HPGe) detector. There are three main types of uncertainty associated with this method of analysis. First, there is a statistical uncertainty associated with counting discrete events. Second, there is uncertainty in the measurement efficiency. Third, there are uncertainties driven by nuclear data.

The governing equation for determining the activities from the collected spectra shows where each of these factors enter the analysis. The activity (a_i) for a given isotope measured using a specific gamma emission peak (γ) is given by Equation 9.

$$a_i = \frac{R_\gamma}{\varepsilon_\gamma \cdot BR_{i,\gamma} \cdot e^{-\lambda_i t_d} \cdot \frac{(1 - e^{-\lambda_i t_{real}})}{\lambda_i \cdot t_{real}}}$$

Equation 9

The count rate (R_γ) is measured for the γ peak chosen for each isotope. This is converted to activity by dividing by the detector efficiency for this peak (ε_γ), the branching ratio ($BR_{i,\gamma}$) for production of the specific γ from decay of the related isotope, the decay time between sample collection and the start of counting (t_d), the count time (t_{real}), and the decay constant of the relevant isotope (λ_i).

The measured activities of ^{133}Xe and ^{135}Xe are nominally 1 Bq with uncertainties of ~2.5% and 4.2% respectively. Due to the different half-lives of the two radioxenon isotopes, the optimal count time varies. The optimum count time for ^{133}Xe , with a half-life of 5.2 days, is 72 hours, after which diminishing improvement is observed. Meanwhile, ^{135}Xe with a 9.12-hour half-life must be counted more quickly before the nuclide decays. Optimum uncertainty for ^{135}Xe is obtained with a 24-hour count.

2.0 Experimental Design

The experimental design, including apparatus and choice of materials, aimed to minimize the sources of uncertainty discussed previously (Uncertainty). Specifically, the Pu materials were carefully chosen and quantified to minimize confounding influences from ^{238}Pu and ^{242}Pu SF. Models were constructed to estimate the systematic influence of IF of ^{239}Pu , and a neutron detector was used to monitor the external neutron background throughout the experiments. Finally, the experimental apparatus was designed with the goal of eliminating as many systematic uncertainties as possible.

2.1 Pu materials

Three sources of ^{240}Pu were needed to supply sufficient material for measurement of SF products from ^{240}Pu . These materials were sourced from in-house supply. They underwent characterization to verify major Pu isotopes and quantify minor isotopes that had not been previously analyzed.

2.1.1 Characterization of Pu materials

The characterization of the ingoing materials is key to reducing the uncertainty in the quantity of ^{240}Pu present in each sample, as well as avoiding confounding factors that would negatively impact data quality. This section discusses methods used for material characterization. Three parent sources of plutonium were prepared and characterized. They will henceforth be referenced by their PNNL Radiological Material Tracking (RMT) numbers: RMT 48, RMT 12962, and RMT 125001.

In general, larger quantities of daughters, e.g., ^{241}Am , were observed in RMT 48 and RMT 12962, while minimal quantities were observed in RMT 125001 which had recently undergone ion exchange separations, although the difference was insufficient to impact contributions from IF.

2.1.1.1 Material characterization overview

Quantification of the ingoing ^{240}Pu was important as an input parameter in the calculation of the SF yields. Additionally, quantification of the minor isotopes ^{238}Pu and ^{242}Pu is particularly important as these isotopes also have significant SF decay rates that may contribute excess fission products that increase uncertainty in the measured values. Likewise, knowledge of ^{239}Pu , ^{241}Am , and ^{241}Pu are used to estimate IF rates caused by the sample-generated and environmental neutron fields.

The characterized Pu sources were selected for low ^{238}Pu and low ^{242}Pu content relative to ^{240}Pu . Two of the sources, RMT 48 and RMT 125001, were already available in nitric acid solution, 5 M and 0.35 M respectively. The third Pu source, RMT 12962, was a solid containing 3.126 g of Pu, which was dissolved in a glove box with 20 mL concentrated nitric acid plus 60 μL concentrated HF, for a final HF concentration of 0.015 M.

Each Pu source was quantified to determine both total Pu concentration and isotopic composition using a range of techniques that provide complementary information about the sample. These techniques include ultraviolet-visible spectrometry (UV-Vis), gamma energy analysis (GEA), alpha energy analysis (AEA), liquid scintillation counting (LSC), and thermal

ionization mass spectrometry (TIMS). The information provided by each method is summarized in Table 3.

Table 3: Information provided by different analytical methods

Analysis method	Concentration (direct)	Concentration (indirect)	Isotopic info (caveats)
UV-Vis	Y	--	--
GEA	--	Y	Y (major isotopes)
AEA	--	Y	Y (except ^{241}Pu , cannot resolve ^{239}Pu & ^{240}Pu)
LSC	--	--	^{241}Pu only
TIMS	--	Y	Y ($^{241}\text{Pu}/^{241}\text{Am}$ and $^{238}\text{Pu}/^{238}\text{U}$ isobars)

The values for ^{240}Pu quantity used in the fission yield analysis were based upon UV-Vis for total plutonium concentration and TIMS for isotopic analysis. TIMS suffers from isobaric interferences from isotopes with similar masses, however these influence the experimental outcome minimally. The interferences are $^{241}\text{Pu}/^{241}\text{Am}$ and $^{238}\text{Pu}/^{238}\text{U}$. There is a non-negligible quantity of ^{241}Am due to the short half-life (14.4 yrs) of its parent ^{241}Pu , however these two isotopes have a negligible influence on the fission yield analysis. While ^{238}U is produced by the decay of ^{242}Pu in the source material, the long half-life of ^{242}Pu (3.75×10^5 yrs) means that the $^{238}\text{U}/^{238}\text{Pu}$ fraction in the sample is negligible. As such, this remainder of this section will focus exclusively on the interpretation of the UV/Vis and TIMS measurements. A summary of results from complementary measurements is provided in Appendix B.

2.1.1.2 UV-Vis measurements

The plutonium samples were gravimetrically (RMT 48 and RMT 12962) or volumetrically (RMT 125001) diluted to a concentration in the range of 2.4-7.2 mg/mL in 3 M nitric acid. The molar absorptivity of Pu(III) in various concentrations of nitric acid has been previously studied (Sinkov et al. 2020), including preparation of a calibration curve by dissolution of a high-purity pure metal Pu source. The solution for analysis was adjusted to 0.25 M ascorbic acid to fully reduce the Pu to Pu(III). The measured molar absorptivity of the sample at 414.32 and 647.28 nm is then compared against the previously prepared calibration curve to determine the concentration of the solution.

Most of the uncertainty associated with the UV-Vis measurements is associated with the dilution process. The mass of the stock and diluent as well as the stock density was measured and is given in Table 4. To measure the density of the stock for RMT 48 and 12961, a separate 2-ml ($\pm 2\%$) aliquot was taken and weighed. A balance was not available in the glovebox while RMT 125001 was being processed, therefore volumetric precision and accuracy of the pipettes used for processing were subsequently characterized by a set of five gravimetric measurements of deionized water and these volumes were used in dilution factor calculations. Note that this assumes that the pipette performance is not density dependent. A constant density of 0.9982 g/mL was used for the diluent (deionized water). The stock and diluent volumes are also listed in Table 2.

Table 4: Dilution parameters for UV-Vis measurement preparation

Sample	Stock Mass (g)	Diluent Mass (g)	Density of Stock (g/mL)	Stock Volume (mL)	Diluent Volume (mL)
RMT 48	0.0591 ± 0.0001	0.8656 ± 0.0001	1.23 ± 0.02	0.048 ± 0.001	0.8672 ± 0.0001
RMT 12961	0.0442 ± 0.0001	2.9927 ± 0.0001	1.48 ± 0.03	0.0299 ± 0.0006	2.9981 ± 0.0001
RMT 125001	N/A	N/A	N/A	0.200 ± 0.001	2.305 ± 0.008

A volumetric dilution factor was determined for each aliquot based upon the gravimetric measurements in Table 4. These were converted to volumes using the diluent and stock densities seen in Table 4. Thus, the plutonium concentration was determined by the following equation:

$$[Pu] = [Pu]_{UV-VIS}^{AQ} \cdot F_{VD} = [Pu]_{UV-VIS}^{AQ} \cdot \left(\frac{V_D + V_S}{V_S} \right)$$

Equation 10

where,

$[Pu]$ = concentration of Pu in the stock sample (mg/mL),

$[Pu]_{UV-VIS}^{AQ}$ = concentration of Pu measured in the aliquot via UV-Vis (mg/mL),

F_{VD} = volumetric dilution factor, and

$V = M/\rho$ = volume (mL) determined by mass (g) and density (g/mL).

Note that the subscripts D and S represent the diluent and stock, respectively. The uncertainty (denoted by σ) in the plutonium concentration is calculated by Equation 11 through Equation 13:

$$\sigma_{[Pu]} = [Pu] \cdot \sqrt{\left(\frac{\sigma_{[Pu]_{UV-VIS}^{AQ}}}{[Pu]_{UV-VIS}^{AQ}} \right)^2 + \left(\frac{\sigma_{F_{VD}}}{F_{VD}} \right)^2},$$

Equation 11

$$\sigma_{F_{VD}} = \sqrt{\left(\frac{\sigma_{V_D}}{V_S} \right)^2 + \left(\frac{\sigma_{V_S} \cdot V_D}{V_S^2} \right)^2}$$

Equation 12

and

$$\sigma_V = V \cdot \sqrt{\left(\frac{\sigma_M}{M} \right)^2 + \left(\frac{\sigma_\rho}{\rho} \right)^2}$$

Equation 13

The concentration measured in the diluted aliquots and calculated concentrations in the plutonium stock solutions are presented in Table 5. Note that TIMS concentration results are included for comparison, though there are no TIMS concentration results for RMT 125001 as there were issues with the dilution process. See next section for full discussion of TIMS analysis.

Table 5: Plutonium concentration results

Sample	$[Pu]_{UV/Vis}^{AQ}$ (mg/mL)	UV/Vis [Pu] (mg/mL)	TIMS [Pu] (mg/mL)
RMT 48	1.81 ± 0.04	35 ± 1	34.7 ± 0.6
RMT 12961	1.40 ± 0.03	142 ± 4	143 ± 3
RMT 125001	3.56 ± 0.07	44.6 ± 0.9	N/A

2.1.1.3 TIMS measurements

The samples from RMT 48 and RMT 12962 were analyzed for Pu isotopic composition using a Thermo Scientific Triton *Plus* multi collector thermal ionization mass spectrometer (TIMS), located in RPL/320-421. Two complimentary methods were used to assess the plutonium isotopics: the total evaporation (TE) and the modified total evaporation (MTE) methods. Both TE and MTE produce high quality results for major isotope ratios, while the MTE method is used for minor isotope ratios to correct for tailing effects from the major isotopes (Demattè, L., et al., 1997). This instrument has 10 faraday cups, allowing for simultaneous measurement of ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{242}Pu , and ^{244}Pu isotopes. Samples and standards were analyzed using a double rhenium filament assembly with the TE method using the detector configuration listed in Table 4. A $^{239}\text{Pu} + ^{240}\text{Pu} + ^{242}\text{Pu}$ signal of 10 V was targeted for each analysis. The TE method was assessed for instrumental mass fractionation by measuring the $^{242}\text{Pu}/^{239}\text{Pu}$ ratio of the New Brunswick Laboratory (NBL) Pu C128 standard. Approximately 70 ng of Pu were consumed per TE analysis.

Table 6: Detector configuration for Pu isotopic TE measurements for RMT 48 and RMT 12962.

Mass	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{244}Pu
Faraday detector	L2	L1	C	H1	H2	H3
Amplifier (TE)	10^{12}	10^{11}	10^{11}	10^{12}	10^{11}	10^{12}

The TE method for RMT 125001 was identical to RMT 48 and RMT12962, with minor modifications. The TE analysis of the standards for calibration (NBL Pu C128) consumed approximately 70 ng of material, however the TIMS samples for 125001 contained only ~5 ng of Pu and did not achieve the targeted Pu signal. The detector configuration is given in Table 7.

Table 7: Detector configuration for Pu isotopic TE measurements for RMT 125001

Mass	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{244}Pu
Faraday detector	L2	L1	C	H1	H2	H3
Amplifier (TE)	10^{12}	10^{11}	10^{11}	10^{12}	10^{11}	10^{11}

RMT 48 and RMT 12962 were also analyzed for Pu isotopic composition by modified total evaporation (MTE) using the detector configuration listed in Table 8. A $^{239}\text{Pu} + ^{240}\text{Pu}$ signal of ~5 V was targeted for each analysis. The $^{240}\text{Pu}/^{239}\text{Pu}$ ratio of the samples determined by TE were

used to correct the other Pu isotopic ratios of the samples measured by MTE for mass fractionation. Approximately 360 ng of Pu were consumed per MTE analysis.

Table 8: Detector configuration and measurement routine for MTE measurements.

Line	L2	L1	C	H1	H2	H3	Idle Time	Integration Time
Amplifier (MTE)	10 ¹²	10 ¹¹	10 ¹¹	10 ¹²	10 ¹²	10 ¹²		
1	²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	²⁴⁴ Pu	12 s	16.777 s
2	237.7 a.u.	238.7 a.u.	239.7 a.u.	240.7 a.u.	241.7 a.u.	243.7 a.u.	5 s	8.389 s
3	238.4 a.u.	239.4 a.u.	240.4 a.u.	241.4 a.u.	242.4 a.u.	244.4 a.u.	5 s	8.389 s
4	²³⁸ Pu	²³⁹ Pu	²⁴⁰ Pu	²⁴¹ Pu	²⁴² Pu	²⁴⁴ Pu	3 s	1.049 s

The output of the TIMS analysis was the atomic ratio of each isotope to ²³⁹Pu. These values were converted to atom fractions as follows:

$$f_A^N = \frac{R_{239}^N}{\sum_{i=238}^{i=242} R_{239}^i}$$

Equation 14

where,

f_A^N = the atom fraction of the Nth isotope of Pu, and

R_{239}^N = the atomic ratio of the Nth isotope of Pu to ²³⁹Pu.

The uncertainty of the atom fraction is given by Equation 15 through Equation 17:

$$\sigma_{f_A^N} = \sqrt{\sum_{i=238}^{i=242} \sigma_{R_{239}^i}^2 \cdot \left(\frac{\delta f_A^N}{\delta R_{239}^i} \right)^2}$$

Equation 15

where

$$\frac{\delta f_A^N}{\delta R_{239}^i} = \frac{-R_{239}^i}{\left(\sum_{k=238}^{k=242} R_{239}^k \right)^2} \text{ if } i \neq N$$

Equation 16

$$\frac{\delta f_A^N}{\delta R_{239}^i} = \frac{\sum_{k=238}^{k=242} R_{239}^k - R_{239}^N}{\left(\sum_{k=238}^{k=242} R_{239}^k \right)^2} \text{ if } i = N$$

Equation 17

The results of the TIMS isotopic analysis are presented in Table 9. Results of other analysis methods (AEA, GEA, LSC) were used to corroborate the results of UV/Vis and TIMS analysis and are shown in Appendix B. The results for major isotopes were in good agreement across

analysis methods. While some variability was observed for minor isotopes, the major isotopes agree across all analytical methods able to distinguish ^{239}Pu and ^{240}Pu .

Table 9: TIMS Pu isotopic analysis results

Isotope	Atom Fraction (%)		
	RMT 48	RMT 12962	RMT 125001
^{238}Pu	0.0655 ± 0.0008	0.00944 ± 0.00004	0.018 ± 0.002
^{239}Pu	89.389 ± 0.005	93.83 ± 0.04	93.819 ± 0.005
^{240}Pu	10.046 ± 0.005	5.87 ± 0.03	6.043 ± 0.004
^{241}Pu	0.1804 ± 0.0004	0.26 ± 0.05	0.072 ± 0.002
^{242}Pu	0.3198 ± 0.0003	0.1804 ± 0.0004	0.03141 ± 0.00005

2.1.1.4 Plutonium Quantification Results

The UV-Vis measurements (Table 5) and TIMS measurements (Table 9) were combined to describe the overall composition of the ingoing Pu materials. The composition of the ingoing Pu materials, including total Pu mass, ^{240}Pu mass, and the content of high SF isotopes ^{238}Pu and ^{242}Pu were determined and are reported in Table 10.

Table 10: Primary sample analysis results (Pu masses per cylinder)

Sample	Total Pu Mass (mg)	^{240}Pu Mass per cylinder (mg)	$^{240}\text{Pu}/^{238}\text{Pu}$ Ratio	$^{240}\text{Pu}/^{242}\text{Pu}$ Ratio	^{240}Pu SF Fraction (%)
RMT 125001	990 ± 20	59.8 ± 0.1	330 ± 30	127 ± 7	97.9 ± 0.8
RMT 12962	890 ± 30	52.5 ± 0.2	622 ± 3	186.8 ± 0.3	98.7 ± 0.8
RMT 48	207 ± 6	20.8 ± 0.6	153 ± 2	31.41 ± 0.03	92.9 ± 0.7

Only materials RMT 125001 and RMT 12962 were used to generate the reported results. The quantity of ^{240}Pu in RMT 48 was too small to produce a reliably measurable quantity of radioxenon. As such, the slightly elevated SF contribution for RMT 48 need not be considered in interpreting results.

2.1.2 Conflicting sources of fission

Any additional contributions to fission will produce an excess of radioxenon isotopes that are then collected with the headspace gas samples. This section considers sources of radioxenon fission products that are not derived from SF of ^{240}Pu .

2.1.2.1 Spontaneous fission isotopes

Among Pu isotopes, ^{240}Pu , ^{238}Pu , and ^{242}Pu are known for their high cross-sections for SF. Analysis of the ingoing Pu material by TIMS for characterization of Pu isotopics is discussed above (Section 2.1.1.3). The AEA analysis provides an additional screen for non-Pu isotopes with high cross-sections for SF: ^{252}Cf and ^{244}Cm . No peaks were detected in regions associated with these isotopes so they can reasonably be excluded from consideration when interpreting the data.

2.1.2.2 Induced fission—neutron monitor and MCNP modeling

While this experiment focused on measuring the fission yield of radioxenon isotopes from ^{240}Pu , the samples used were primarily composed of ^{239}Pu and ^{241}Pu , which both have large IF cross

sections. To assess potential interferences from radioxenon arising from IF, a set of Monte Carlo N-Particle (MCNP) Version 6.2 (Werner et al. 2018) simulations were produced.

The first of these simulations considered neutrons generated within the samples from SF and (α, n) reactions on oxygen and fluorine in the solution. The neutron emissions from each of the three samples were calculated using the SOURCES4C code (Shores et al. 2002). The primary source of sample-induced neutrons were $O(\alpha, n)$ reactions comprising ~65-70% of the neutron production depending on the sample. Spontaneous fission generated most of the remainder, with $F(\alpha, n)$ contributing less than 2%. The neutron energy spectra for the three sample types were virtually identical, differing only in total neutron output. The geometry in the MCNP simulation consisted of the nine stainless steel sample vials embedded in the aluminum block, as shown in Figure 1. The output of the simulation was the ratio of the IF to SF rate in each sample vial assuming no external source of neutrons. The ratios ranged from 0.1% to 0.3% with dependence upon sample isotopics and position (i.e. samples near the edge had lower IF rates). Table 11 contains the results of this simulation along with the SF rate for each sample.

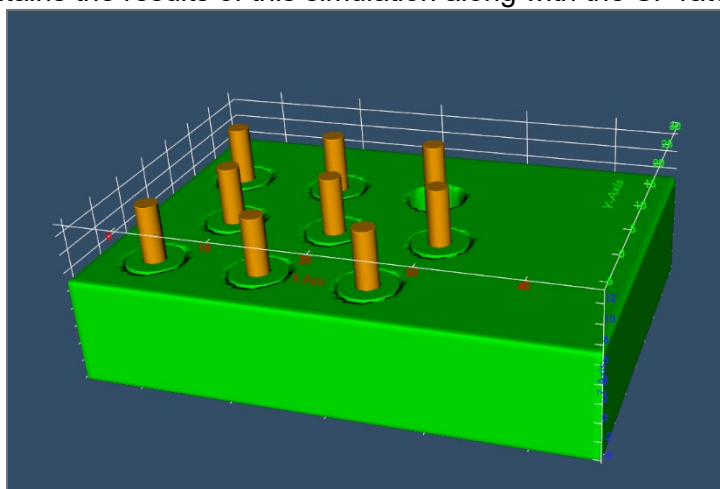


Figure 1: MCNP simulation geometry

The other two simulations address the issue of neutrons from an external source. There are standard background neutrons that are associated with cosmic radiation, however this experiment took place in the PNNL Radiochemical Processing Laboratory, where neutron backgrounds may be significantly higher due to a variety of potential sources. To track the neutron count rate a Ludlum Model 42-38 WENDI-2 (Wide Energy Neutron Detection Instrument) neutron detector along with a ratemeter with a 0-10V output (Figure 2) was installed next to the experimental apparatus. Neutron count rates were continuously logged throughout the entire experiment. A pair of simulations were developed to associate the measured neutron count rate with an IF rate. One simulation used the geometry shown in Figure 1, but with an external source of ^{252}Cf SF spectrum neutrons. The other was a validated model of the WENDI-2 detectors taken from Garcia-Fernandez et al. (2018) with the same source of ^{252}Cf SF spectrum neutrons. The combined output of these simulations was the ratio of the IF rate to the SF rate in each sample per count per second measured by the WENDI-2 detector. The neutron detector count rate was generally between 2-4 cps, with occasional short periods where the ratemeter would saturate (>10 cps). Based upon these values, it is expected that the xenon produced in the samples is 2-5% higher than it would be from SF alone (Table 11).

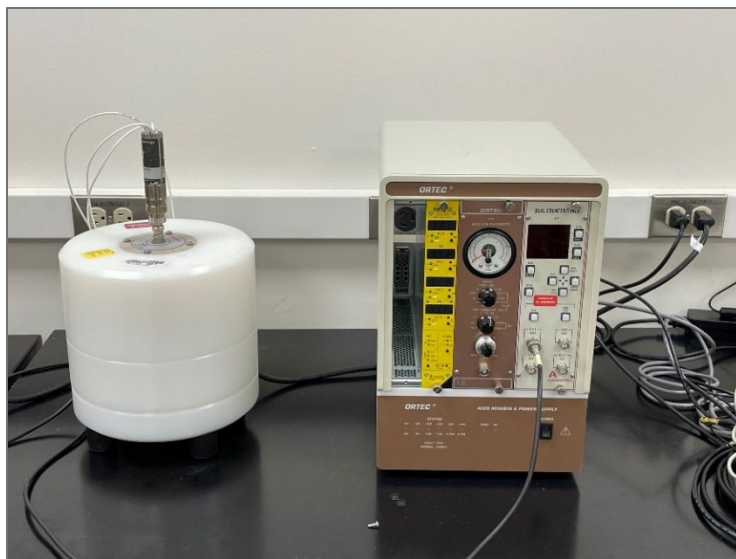


Figure 2: WENDI-2 neutron detector and ratemeter

Table 11: Induced-fission MCNP simulation results. Note that these consider only neutrons generated within the samples.

Sample RMT	Number of Samples	SF Rate (s^{-1})	Sample IF Ratio (IF/SF)	External IF Ratio (IF/SF/cps)
12962	3	29.91	0.28-0.31%	1.4-1.5%
48	1	17.46	0.12%	0.7%
125001	5	29.79	0.24-0.26%	0.9-1.4%

2.2 Apparatus design

The design of the apparatus has the potential to significantly impact safety and data quality. This section describes the goals of the design process as well as the features of the implemented design. The P&ID for the system is given in Appendix A.

2.2.1 Design Considerations and Implementation of Experimental Design

2.2.1.1 Design: Purpose & Considerations

The primary objective of this project was to develop an automatic sampling unit capable of delivering consistent test conditions across multiple samples with integrated safety features to prevent spread of contamination during the experiment. This system aims to optimize yield accuracy by significantly reducing measurement uncertainties and enhancing the efficient extraction of xenon from waste tanks. Achieving these objectives required integrating features such as automated control mechanisms, the ability to handle multiple test cylinders, precise temperature regulation, strict adherence to volumetric constraints, and automated flow control and totalization processes. Additionally, the design incorporates sample agitation to encourage release of xenon into the headspace above each sample, thereby minimizing xenon holdup in solution.

The physical design, shown in Figure 3, includes nine sample collection cylinders and three control cylinders, all arranged within a solid aluminum heated cylinder block that maintains a stable thermal environment. A robust orbital shaker, with a three-quarter-inch orbital rotation at 30 revolutions per minute, ensures uniform agitation across all 12 cylinders. The integration of 14 thermocouple probes and four pressure transducers, coupled with detailed volumetric regulation of piping and manifolds, provides comprehensive oversight and control over the entire system. The system is monitored and operated by a Linux-based logging and control server (LCS) (page 17).

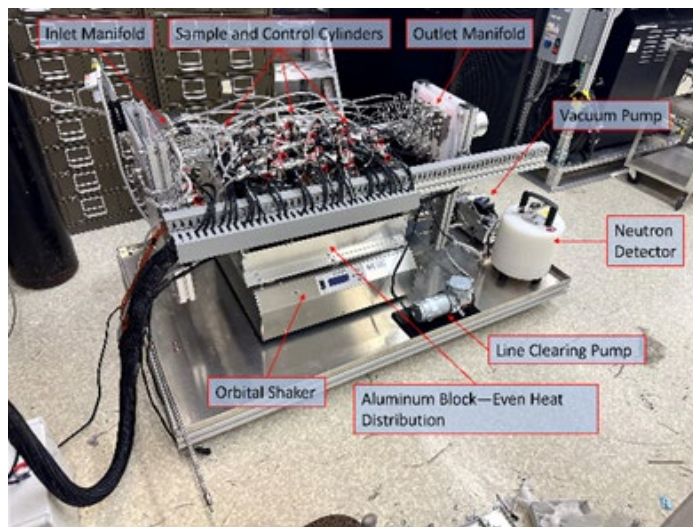


Figure 3. Fully integrated automated sampling system configured for xenon extraction, showing inlet and outlet manifolds, nine sample and three control cylinders housed within a thermally regulated aluminum block, orbital shaker ($\frac{3}{4}$ -inch orbit at 30 RPM), and supporting subsystems including vacuum and line-clearing pumps.

2.2.1.2 Design and Engineering

Temperature Control

The aluminum block (Figure 4) provides a stable thermal environment for the samples. The temperature is regulated to 37°C by four 48-watt cartridge heaters, with the internal temperature continuously monitored and logged by 14 strategically positioned thermocouple probes for reliable temperature readout across the aluminum block (Figure 5). The temperature of 37°C was selected to be slightly above room temperature to mitigate the effects of variable temperature in the building. The effects of evaporation at this temperature in a closed vessel were calculated to result in a loss of 0.1% of the liquid volume, which is considered negligible.



Figure 4. Precision-machined aluminum cylinder block with bored wells for nine sample and three control cylinders, designed to provide uniform heat distribution and maintain a stable thermal environment (37 °C) via embedded cartridge heaters.



Figure 5. Installed cylinder block with integrated process tubing, thermocouples, and manifold connections, illustrating system-level routing for controlled flow distribution, temperature monitoring, and volumetrically consistent sample handling.

Cylinder Assembly

Engineering the sample cylinder assembly was a pivotal aspect of this project. Each cylinder is designed to hold 30 mL of solution with 30 mL headspace, and the cylinder connects seamlessly to the solenoid assembly using a double-ended quick disconnect system. Internal components have been electrocoated with Siltride 1000 (SilcoTek) to lessen analyte adhesion, thereby enhancing the efficiency of sample transfers. Figure 6 shows the cylinder.



Figure 6. Stainless steel sample cylinder (60 mL total capacity) with quick-disconnect interface, designed for secure integration with the solenoid assembly, reduced analyte adhesion via electrocoating, and efficient transfer of dissolved xenon samples. Aqueous samples and controls are nominally 30 mL.

Each cylinder is topped with a solenoid valve that is actuated from the LCS (Figure 7). The solenoid valves are designed to withstand hazardous (e.g., corrosive) environments and allow for automation of sample collections. The solenoids revert to a closed position when no power is applied to avoid dispersion of headspace gases when not actively sampling.



Figure 7. Sample cylinder integrated with solenoid valve assembly, illustrating automated flow control, fail-safe isolation (normally closed configuration), and regulated interaction with nitrogen carrier gas during injection and extraction.

Electrical system

The electrical control design was made and built from modules that are well understood due to their previous use on other projects. Some cost savings were realized by repurposing used and excess modules from past projects. The assembly was focused on a design customized and

tailored for this need, but utilized Commercial Off-the-Shelf (COTS) items for ease of future maintenance.

In order to satisfy PNNL electrical Authority Having Jurisdiction while maintaining serviceability, the control system was constructed in a way where high voltage was segregated from the low voltage. This allows non-electrical-trained personnel more access to open and troubleshoot operational issues in the low voltage electrical control box.

For safety of operation, a manual enable circuit was implemented such that there is no way for software or a remote user to enable the power for opening the valves. While software or a remote user can disable and lock the valves, an operator must locally enable operation of the valves.

Logging and control software

The LCS provides high-level monitoring and control for the equipment. It serves two primary functions: automate the sampling procedures and save the system state to file regularly. It also enables remote monitoring so that staff can check the system status without having to travel to the system site. The code—written in C++ for use with a Linux operating system—uses software developed at PNNL over a period of more than 20 years. Roughly 90% of the code was used unaltered for standard operations (e.g., opening/closing valves, setting flow controllers). The remaining ~10% was customized for just this system (e.g., the sequence and timing for sample extraction). This server automates various controls, including those for solenoids, mass flow controllers, heaters, over-temperature protection, and vacuum pumps. Interlocks are embedded to ensure the correct operation of the apparatus while significantly reducing the potential for human error.

Safety

The design of the assembly maintained a consistent focus on safety. All components, including solenoids, are engineered to be suitable for hazardous environments. Solenoids remain closed when unpowered to isolate the plutonium sample solution from users, and outlets pass through HEPA filters, enabling sample collection in non-radiological conditions. Despite the system's considerable weight exceeding 750 pounds, low-friction, lockable casters allow it to be maneuvered by a single individual. Additionally, bundled protected wiring reduces wear on components due to the orbital motion of the shaker, while well-organized electrical cabinets minimize the risk of electrical shock during maintenance. The entire system underwent commissioning and inspection by various subject matter experts prior to introducing radioactive materials.

Updates and Required Changes

The design process was iterative, undergoing revisions along the way to adapt to performance observations and new information. Some situations requiring adaptation are summarized here:

- The apparatus needed to fit within a walk-in fume hood measuring 3 feet by 5 feet by 30 inches, accommodating the entire assembly, including the drip tray, beneath a table.
- The diameter of the gas lines was reduced from 1/4-inch lines to 1/8-inch lines, driven by volumetric constraints essential for maintaining the desired xenon flow.
- Output lines were configured into a helical pattern to maintain consistent length and internal volume, with each line precisely three feet long.

- Attaching the entire system to the shaker table alleviated line strain and eliminated component fatigue, enhancing quiet, reliable, and low-wear operation throughout the system's lifespan.

2.2.1.3 Testing and Verification

Before deployment, each component was subjected to rigorous testing for leaks and operational readiness, with leak tests conducted during fabrication, initial testing, and post-deployment. Pressure testing followed an identical protocol. Comprehensive inspections were performed by PNNL subject matter experts encompassing pressure, radiological, and electrical expertise. To bolster operational readiness, numerous verification samples were captured using a residual gas analyzer (RGA), with multiple test extractions performed at the fabrication site and post-deployment, using a krypton standard as an analog for xenon due to their chemical similarities.

The leak testing of the gas sampling apparatus had two phases. The cylinder and solenoid assembly was pressurized with nitrogen and submerged in water to find gross leaks. Additionally, all connections were tested with Snoop leak detection fluid while the system was pressurized with nitrogen. After all physical leak checks and repairs were made, full system high pressure and vacuums holds were done. All the lines were sufficiently leak tight before system operation validation was done with Krypton gas.

The system was validated for leak tightness and operation using Krypton gas and an RGA. The normal sample collection container was replaced with a sample collector with a 1/16 in Swagelok fitting on the back for direct connection to the RGA. With this setup, we were able to see the sample transfer to the collection cylinder in real time. All the cylinders were filled with 30ml of water to allow for the proper amount of headspace in each cylinder. The 3 control cylinders were loaded with Kr gas using the injection operation on the LCS which consisted of ten minutes of Kr gas pulled through the system using the purge pump and then 10 minutes of nitrogen gas purge of the sample lines using the installed bypass. After loading the test cylinders, a normal extraction operation was used to test each cylinder.

Before loading the Pu samples, the nine sample cylinders were also injected with Kr gas using a manual operation similar to the control cylinders. The main vacuum pump was used to pull the Kr through the selected sample cylinder for 10 minutes, manually opening solenoids and MFC's. The main sample cylinders do not possess bypasses to allow for nitrogen purge, so the line was evacuated with a vacuum pump for 10 minutes instead.

The RGA data showed a gradual increase in amount of Kr gas to a plateau corresponding with end of the sample extraction (Figure 8). The rise of Kr on the RGA data was much higher than nitrogen carrier gas indicating a full sample extraction of the headspace. A full atomic mass unit sweep was done after each sample extraction to look for ingress of atmospheric gases.

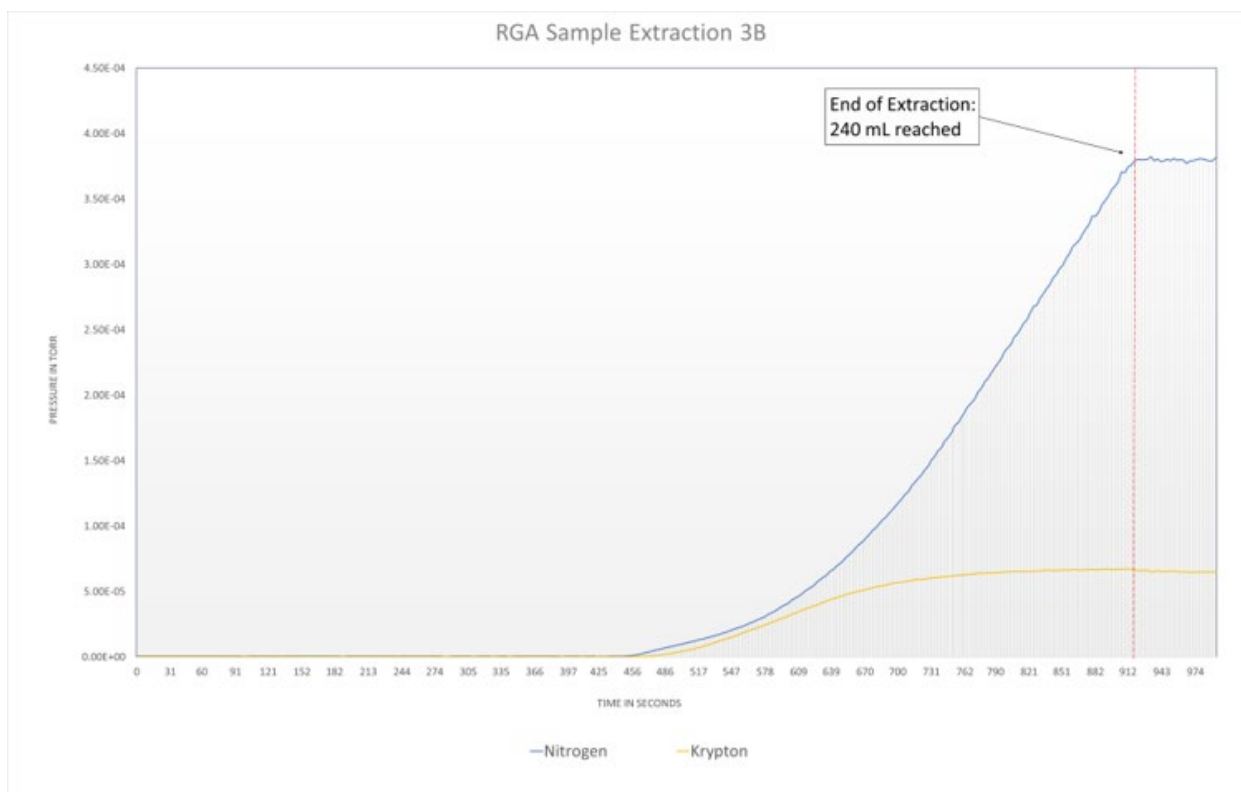


Figure 8. Example of RGA extraction showing plateau of Kr (blue trace) after 240 mL volume collected.

2.2.1.4 Sample Extraction

Sample extraction is initiated through the LCS, which precisely opens and closes solenoid valves, modulates flow rates via mass flow controllers and vacuum, and provides uniform sample extraction across all cylinders. The nitrogen carrier gas is introduced across all cylinders through dual manifolds. Nitrogen flow is regulated by a nitrogen injection solenoid valve and a mass flow controller. The LCS manages flow rate control and logs the cumulative gas throughput during the process.

Figure 9 provides a schematic representation of cylinder with solenoid (left) and the flow path of nitrogen through the sample headspace (right). Upon entering through the input solenoid valve (red), nitrogen gas passes through the snorkel tube (blue), effectively clearing the gas accumulated in the headspace (yellow) of the cylinder. Flow modeling demonstrated a 98% removal of headspace accumulation with the use of the snorkel tube.

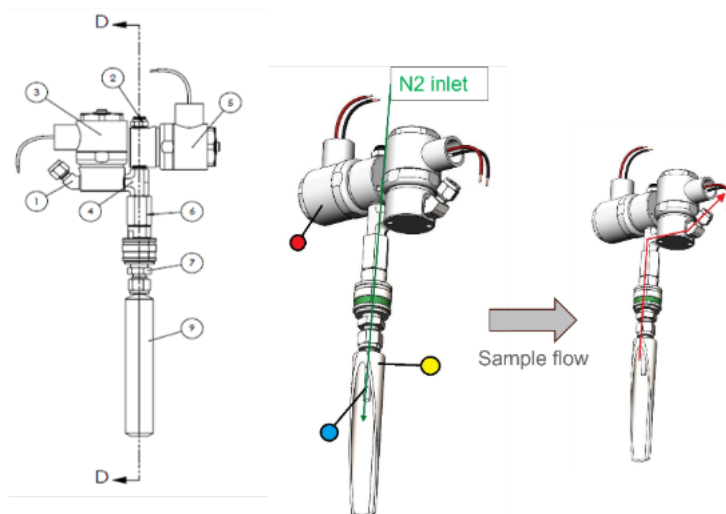


Figure 9. (Left) Schematic representation of the sample cylinder and solenoid assembly, identifying key components, snorkel tube geometry, and the controlled flow path through the system. (Right) Flow diagram illustrating nitrogen carrier gas injection through dual manifolds, snorkel-assisted headspace purge (~98% removal efficiency), and the controlled extraction pathway to downstream manifolds for xenon recovery.

The sample holder is connected to the system by a dual-end quick shut-off that automatically seals when disconnected to prevent loss of sample. Each sample holder has a capacity of 250 mL. Manual valve operations further curtail sample loss by isolating unused portions of the manifold. Closure of unused outlet manifolds effectively mitigates volume and sample loss while reducing the risk of withdrawing from the incorrect bank of sample cylinders.

The operation sequence for a normal sample extraction starts with evacuation of the back end of the system, comprising the sample holder and all the lines downstream of the mass flow controllers. A pump pulls a vacuum for 5 minutes then the LCS holds for 5 minutes to test for leaks before sample collection begins. If the vacuum hold is successful (i.e., no pressure increase is observed), the solenoids open, nitrogen carrier gas begins to flow, and the mass flow controller (MFC) slowly ramps up to 30mL/min to minimize sample turbulence. The totalizer on the MFC resets before every system operation; the sample extraction is complete when 240 mL of gas moves through the sample MFC. After passing through mass flow controllers, samples pass through HEPA filters and are drawn into the sample collection cylinder (aka “pancake”) by residual vacuum. The HEPA filters provide compliance with radiological controls, permitting the free flow of xenon isotopes while capturing particulate contaminants, e.g., Pu, ensuring safe, efficient operation, and sample extraction.

Totalizer data for both the carrier gas and sample MFC’s is compared after the operation and any errors are recorded in the system health files by the LCS. The final pressure of the sample container is recorded and then the sample is disconnected from the system and transferred to a HPGE detector for counting. The LCS additionally records parameters such as pressure, time, and flow for each sample.

A series of headspace gas samples were extracted over the course of the project, with results presented and discussed in Section 3.0.

2.3 Sampling protocols for control sample

Incorporated within the system are three control cylinders filled with nitric acid, which undergo xenon standard injection to serve as experimental controls. Internally, these cylinders contain the same solution matrix as the plutonium samples. The xenon injection process initiates with the cylinder being charged with a known quantity xenon standard, which is then pulled through the cylinder until headspace is fully occupied by the xenon standard. Post-charging, solenoids seal the system, and lines are purged with nitrogen to remove any residual xenon. The extraction procedure mirrors that of the other nine cylinders, executed automatically via the LCS.

2.4 Detection

Headspace gas samples were collected in an aluminum cylinder with a 4.45-cm inner diameter, a 4.03-cm depth, and a 0.32-cm wall thickness on its side and bottom. The sample cylinder was then transferred to the counting laboratory where it was placed directly on the face of a Ortec GEM coaxial high-purity germanium (HPGe) detector enclosed in a thick lead shield (Figure 10). The samples were typically measured for three days minimum with some samples measured for approximately a week. The process of transferring the sample to the count lab and beginning the measurement usually took less than an hour. Cumulative spectra were saved every four hours, since the optimal count time is different for the two xenon isotopes detected in the samples. Statistical uncertainty is optimized for ^{135}Xe after approximately 24 hours, while ^{133}Xe continues to improve but only minimally after 3 days of counting (Figure 11). Each of three empty sampling cylinders were measured for 2-days count time prior to the beginning of the set of sampling experiments and showed no indication of background peaks that would interfere with radioxenon measurements. One of the three sampling cylinders was shipped to Eckert & Zeigler Analytics for conversion into a NIST-traceable gas simulant mixed gamma standard ([link](#)) that was used to efficiency calibrate the detector system.



Figure 10: Sample cylinder configured for measurement on the shielded HPGe detector

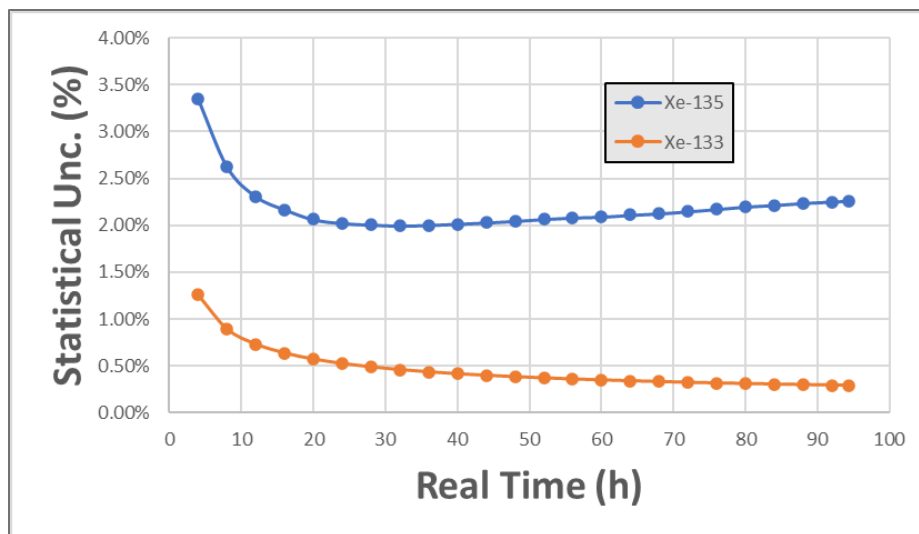


Figure 11: Statistical counting uncertainty as a function of count time.

The activity of xenon in the headspace gas sample is determined by the following equation:

$$A = \frac{C}{t_{live} \cdot \varepsilon_{\gamma} \cdot BR_{\gamma} \cdot e^{-\lambda_A t_d} \cdot \frac{(1 - e^{-\lambda_A t_{real}})}{\lambda_A \cdot t_{real}}}$$

Equation 18

where,

A = the measured xenon activity in the sample (Bq),

C = the measured counts in the photopeak,

t_{live} = the measurement live time (s),

ε_{γ} = the detection efficiency for the photopeak of interest (counts/gamma),

BR_{γ} = the branching ratio of the gamma of interest (gammas/decay),

$e^{-\lambda_A t_d}$ = a correction factor for decay between sampling and measurement, and

$\frac{(1 - e^{-\lambda_A t_{real}})}{\lambda_A \cdot t_{real}}$ = a correction factor for decay during measurement.

Typical values and their associated uncertainties can be found in Table 12. Count rates and uncertainties are determined using PeakEasy gamma spectral analysis software (Rooney et al. 2024). These varied significantly between samples and are one of the major drivers of measurement uncertainty. The gas simulant mixed gamma standard contains several isotopes which bound the energies of interest of the xenon isotopes (81 and 250 keV for ^{133}Xe and ^{135}Xe , respectively). The gamma output of these lines was certified to better than 2.1% at the 1σ level. The standard was counted in the measurement geometry until the statistical uncertainty was negligible. The spectra were analyzed using Mirion GENIE spectroscopy software, which interpolated between the data points and determined the efficiency and uncertainty at the energies of interest. Branching ratios and half-lives for decay correction are taken from the National Nuclear Data Center (Khazov et al. 2011, Singh et al. 2008).

Table 12: Typical values and associated uncertainties for calculating the activity of xenon isotopes in the headspace gas samples. All uncertainties are given at the 1σ level.

	¹³³ Xe		¹³⁵ Xe	
	Value	Rel. Unc (%)	Value	Rel. Unc (%)
Count Rate (cps)	1.3e-3 – 2.3e-2	1 - 11	1.7e-3 – 2.7e-2	2 - 22
Efficiency (counts/y)	5.06e-2	1.9	5.80e-2	1.5
Branching Ratio (γ/decay)	0.373	1.0	0.90	3.3
Decay Correction	0.6-0.7	0.01	0.3 – 0.4	0.2
Measured Activity (Bq)	0.1 - 1.84	2 - 11	0.08 – 1.60	4 - 22

The spectra were also analyzed for metastable isotopes of xenon that occur as fission products: ^{131m}Xe and ^{133m}Xe. The minimum detectable activity (MDA) was calculated for each of these isotopes based upon Equation 18 with the number of counts in the photopeak replaced by the Currie detection limit (Currie 1968) given by Equation 19:

$$L_D = 2.71 + 4.65 \cdot \sqrt{C_{BKGD}}$$

Equation 19

where,

C_{BKGD} = the number of counts in the background in the photopeak region-of-interest (ROI).

3.0 Results

Headspace gas samples were collected between October 2024 and March 2026. The experiment had nine cylinders holding plutonium nitrate solution. Each cylinder's headspace was sampled twice. After the initial set of headspace samples had been collected, the measured activities were reviewed according to the following criteria:

1. (reproducible) Were the measured activities from a cylinder consistent?
2. (credible) Did the measured xenon activities agree with the amounts expected based on the broad range of published cumulative SF yields?

The cumulative SF yields from ^{240}Pu for mass 133 and mass 135 range from 6-8.19% and 6.39-8.12%, respectively. (Ladler and Brown, 1962; Bushuev et al., 2007; Toraskar and Melkonian, 1971; Demattè et al. 1997). Cylinders with initial activity measurements below 1 Bq for both ^{133}Xe and ^{135}Xe were rejected on the grounds of credibility since these would have cumulative yields of 4% or less. These measurements likely suffered from sampling issues such as headspace leaks or gas flow. The initial hypothesis for the low activity measurements involved issues with the plutonium solution (e.g., precipitation or crud formation) in the cylinder. This was disproven upon visual inspection when the cylinders were emptied after the sampling campaign.

From the initial analysis, three of the nine cylinders gave reasonable headspace activity measurements. One cylinder was disregarded because it contained significantly less plutonium than the others and the resulting xenon activities were too small for reliable measurement. Five cylinders (including all three from one manifold) had issues with reproducibility and credibility.

Three additional considerations were used to reject measurements from the reliable cylinders.

3. Was an issue reported during sample collection (e.g., valves not properly configured)?
4. Was the interval between samples too short to allow ^{133}Xe to reach secular equilibrium?
5. Was there evidence of sample contamination from other sampling activities?

The short interval arises for a sequence of measurements taken at one-week intervals from the same cylinder using ^{135}Xe as a fiducial to establish reproducibility of the system. This sampling cadence allowed for ^{135}Xe (but not ^{133}Xe) to reach secular equilibrium. Thus, the ^{135}Xe activity measurements for each of these samples is reliable while the ^{133}Xe must be rejected. The contamination issue arose for samples collected shortly after attempts to inject control samples spiked with ^{133}Xe to measure the sampling efficiency. These samples showed no increase in ^{135}Xe compared to other measurements, but the elevated ^{133}Xe was explained by the contamination from the tracer gas.

After applying these criteria to evaluate the data, there were 24 acceptable ^{133}Xe measurements and 29 acceptable ^{135}Xe measurements.

3.1 Raw activities for reliable samples

The individual measurement results are presented in Table 13. A graphical representation of these measurements as a function of the measurement date is given in Figure 12. The reproducibility of the measurements was excellent outside of a few measurements that are still included based on the criteria discussed previously.

Table 13: ^{133}Xe and ^{135}Xe activities for each measurement.

Measurement Date	Pu Material (RMT)	^{133}Xe activity (Bq) ^e	^{135}Xe activity (Bq) ^e
10/31/2024	125001	1.24 ± 0.03	1.16 ± 0.05
11/14/2024	125001	1.81 ± 0.04	1.69 ± 0.07
12/05/2024	12962	1.63 ± 0.04	1.46 ± 0.06
01/30/2025	125001	1.75 ± 0.04	1.51 ± 0.06
02/06/2025	125001	---- ^a	1.58 ± 0.07
02/20/2025	125001	---- ^a	1.52 ± 0.06
02/27/2025	125001	---- ^a	1.52 ± 0.06
03/13/2025	125001	1.84 ± 0.04	1.60 ± 0.06
04/17/2025	125001	1.80 ± 0.04	1.58 ± 0.07
04/24/2025	12962	1.80 ± 0.04	1.50 ± 0.06
06/12/2025	125001	1.11 ± 0.03	0.94 ± 0.04^b
06/19/2025	125001	1.41 ± 0.04	1.20 ± 0.05
06/26/2025	12962	1.40 ± 0.03	1.21 ± 0.05
07/02/2025	125001	1.74 ± 0.04	1.58 ± 0.07
07/17/2025	125001	2.30 ± 0.06	1.57 ± 0.07
07/24/2025	12962	---- ^c	1.65 ± 0.07
07/30/2025	125001	---- ^c	1.46 ± 0.06
08/14/2025	125001	1.81 ± 0.04	1.52 ± 0.06
08/21/2025	12962	1.95 ± 0.05	1.58 ± 0.07
08/28/2025	125001	1.86 ± 0.04	1.58 ± 0.07
09/18/2025	125001	1.74 ± 0.04	1.37 ± 0.06
09/25/2025	12962	1.88 ± 0.05	1.68 ± 0.12^d
10/01/2025	125001	1.89 ± 0.04	1.57 ± 0.07
11/13/2025	125001	1.84 ± 0.04	1.57 ± 0.07
11/19/2025	12962	1.90 ± 0.05	1.65 ± 0.07
12/04/2025	125001	1.86 ± 0.04	1.65 ± 0.07
02/19/2026	12962	1.74 ± 0.04	1.41 ± 0.06
02/26/2026	125001	1.84 ± 0.04	1.67 ± 0.07
03/12/2026	125001	1.73 ± 0.04	1.55 ± 0.07
^a Insufficient time for ^{133}Xe equilibration – samples collected to verify ^{135}Xe reproducibility			
^b Measurement retained because sample ^{133}Xe activity is within expected range based on literature values			
^c Samples contaminated by memory effects from attempted ^{133}Xe control experiments			
^d Counting started one day after sample collection, so poor statistics on ^{135}Xe measurement			
^e The uncertainties reported here are strictly related to the activity measurement			

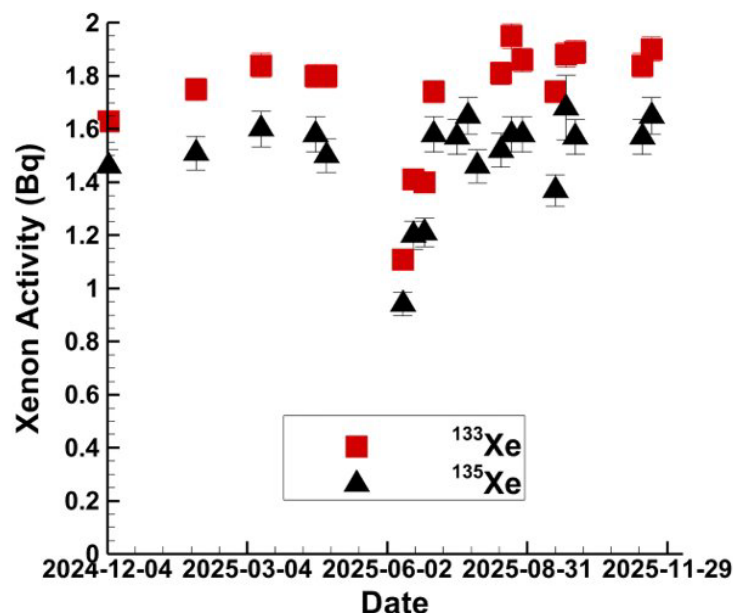


Figure 12: Measured ¹³³Xe and ¹³⁵Xe activities by date.

3.2 Control samples

Control experiments were performed to establish the sampling efficiency (ϵ) of the apparatus. This quantity is the fraction of xenon in the headspace that winds up being collected in the sample cylinder and measured in the analysis. The control experiment methodology is described in Section 2.3. In short, gas with a known xenon concentration is injected into the headspace of a cylinder containing a nitric acid solution that mirrors the solutions in the experimental cylinders but does not contain plutonium or other fissile materials. The injected gas is then extracted from the headspace using the same sampling procedure as the routine headspace sampling. The injected gas had a nominal composition of 15:85 Xe:N₂ (as measured in mole percent).

Four control experiments were performed, and three of these were accepted. The first measurement had an abnormally high injection pressure, so the experiment was modified slightly to first purge the lines to the control cylinder with N₂ prior to injecting the sample. This resulted in three experiments with consistent injection and extraction pressures.

3.2.1 Correction factor required for samples

Calculating ϵ requires determining the ratio of xenon extracted to the xenon injected.

$$\epsilon = \frac{n_{Xe}^{extracted}}{n_{Xe}^{injected}}$$

Equation 20

In this equation, $n_{Xe}^{extracted}$ is the number of moles of Xe in the collected sample and $n_{Xe}^{injected}$ is the number of moles in the headspace after injection. The ideal gas law can be used to change this expression into measurable quantities.

$$\epsilon = \frac{x_{Xe}^{extracted} p^{extracted} V^{sample} / (RT^{extracted})}{x_{Xe}^{injected} p^{injected} V^{headspace} / (RT^{injected})}$$

Equation 21

This expression depends on the mole fraction (x_{Xe}) of xenon in the injected gas and the extracted sample, the pressure of the injected gas in the headspace ($p^{injected}$), the pressure of the extracted sample ($p^{extracted}$), the headspace volume ($V^{headspace}$), the sample cylinder volume (V^{sample}), the gas constant (R), and the temperature of the injected ($T^{injected}$) and extracted ($T^{extracted}$) gases. The gas sat in the cylinder for a short time (a few minutes) before extraction, and the extraction used room temperature N_2 to flush the headspace. Therefore, it is reasonable to assume that the temperatures of both the injected and extracted gases cancel from the expression. In simplified form, ϵ is evaluated from the measured pressures, measured mole fractions, and known volumes.

$$\epsilon = \frac{x_{Xe}^{extracted} p^{extracted} V^{sample}}{x_{Xe}^{injected} p^{injected} V^{headspace}}$$

Equation 22

3.2.2 Evaluation of the Sampling Efficiency

When evaluating the sampling efficiency, data came from multiple sources. The volumes were known from design and assembly of the apparatus ($V^{headspace} = 30\text{cm}^3$ and $V^{sample} = 240\text{cm}^3$). The composition of the injected gas and extracted samples were measured using the RGA. Pressures were measured with transducers in the apparatus (these were logged in the state-of-health files). The P&ID for the apparatus (Appendix A) shows where the pressure transducers were located (specifically, the transducers located before cylinder 4a and before the pancake/sample cylinder). The pressure profiles during sample injection and extraction are shown in Figure 13.

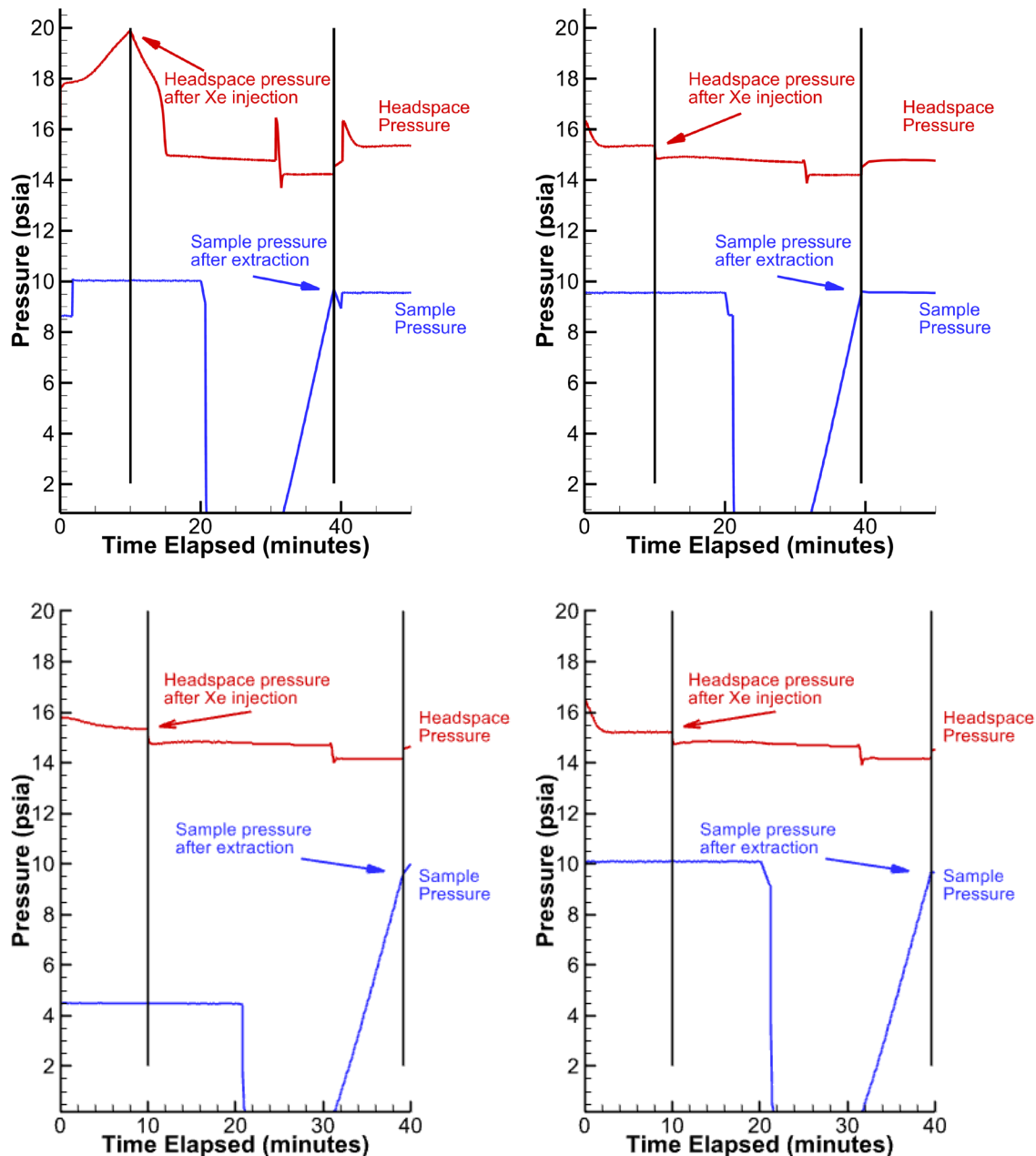


Figure 13: Pressure profiles for the control experiments (control 1: top left, control 2: top right, control 3: bottom left, control 4: bottom right).

The RGA analysis proves less tractable than originally anticipated. Analysis of the RGA histograms (partial pressure vs. mass number) was used to quantify the different isotopic compositions. The N_2 (mass 28) signal was sufficiently strong and spilled over into the adjacent mass numbers (mass 27 and 29). A significant signal was also obtained for N^+ (mass 14) indicating that some of the N_2 dissociated upon ionization. The xenon peaks were obtained over the range of mass 128 through mass 136. The absence of significant signals at mass 133 and mass 135 (corresponding to radioactive xenon isotopes) is consistent with stable xenon that sat for months or years. Surprisingly, there are visible peaks for mass 64 to mass 68. These correspond to doubly ionized xenon atoms (since the reported mass is really the mass divided

by the charge). However, these were discarded in favor of using specific xenon isotopes in the analysis.

$$x_i^{eff} = \frac{P_i}{\left(P_{28} + P_{27} + P_{29} + \frac{1}{2}P_{14} + P_{32} + \frac{1}{2}P_{16} + P_{18} + P_{17}\right)}$$

Equation 23

The values of j in P_j are the mass numbers (e.g., P_{28} is the partial pressure of mass 28) while the subscript i references the xenon isotope of interest (i.e., 129 or 132). The factors of $\frac{1}{2}$ for mass 14 (N^+) and mass 16 (O^+) arise because they are single atom partial pressures which contribute to the overall signal for N_2 and O_2 , respectively.

The calculated values of ϵ are presented in Table 14 along with the interpreted RGA data, pressures, and volumes necessary for the calculation.

 Table 14: Data and calculated values of ϵ for ^{132}Xe and ^{129}Xe from the control experiments

	Experiment			
	Control 1	Control 2	Control 3	Control 4
$V^{headspace} (\text{cm}^3)$	30	30	30	30
$V^{sample} (\text{cm}^3)$	240	240	240	240
$P^{inject} (\text{psia})$	19.9	15.3	15.3	15.1
$P^{extracted} (\text{psia})$	9.7	9.6	9.6	9.7
injected x_{132}^{eff}	0.027	0.027	0.027	0.027
extracted x_{132}^{eff}	0.0040	0.0055	0.0056	0.0063
ϵ_{132}	0.58	1.0	1.0	1.2
injected x_{129}^{eff}	0.029	0.029	0.029	0.029
extracted x_{129}^{eff}	0.0041	0.0057	0.0057	0.0066
ϵ_{129}	0.55	0.98	0.98	1.2

The results from control experiment 1 were rejected because the injected pressure was significantly higher than observed in the other control experiments (see Figure 13). This may be attributed to the fact that nothing was done to precondition the apparatus after a long laboratory closure prior to the control experiments. The efficiencies were 0.98-1.0 for control experiments 2 and 3 and 1.2 for control experiment 4. From these results, the best way to proceed appears to be setting the mean efficiency ($\bar{\epsilon}$) to 1.0 reflecting the maximum value it can physically take. The calculated standard deviation based on this mean value is 0.13.

3.3 Fission fraction calculated for individual samples

Calculating the fission fraction (cumulative fission yield) requires evaluating Equation 8 for each acceptable activity measurement. The uncertainty for each calculated fission fraction is determined using Monte Carlo simulation over the possible values of the parameters. Each parameter in Equation 8 is assigned a distribution (either uniform or normal) with the appropriate breadth (uniform) or standard deviation (normal). The Monte Carlo simulation then generates 10,000 sets of input parameters for each experiment, and the resulting distribution is used to evaluate the sample standard deviation. The sample standard deviations are then used to estimate the standard error of the mean (i.e., the uncertainty around the average fission fraction). The sample standard deviation is taken to be the average of the standard deviations calculated for each experiment. These values tend to cluster around a similar value with smaller values arising from the consistency of the activity measurements.

The parameter distributions for the Monte Carlo simulations are presented in Table 15. Minimum and maximum values for normal distribution are chosen based on physical bounds (e.g., keeping a value positive when required) or as 6 standard deviations from the mean. Where possible, the minimum and maximum values were (approximately) symmetric around the mean. Most of these have been discussed in the preceding sections; however, a few will require explanation.

Table 15: Parameter distributions for Monte Carlo simulations

Parameter	Distribution Type	Mean	Std. Dev.	Minimum	Maximum
$V^S(\text{cm}^3)$	Uniform	----	----	29	31
$V^{vap}(\text{cm}^3)$	Uniform	----	----	29	31
$m_{\text{Pu}_{\text{tot}}}(\text{mg})$	Normal	990 ^a 890 ^b	20 ^a 30 ^b	0	2000
$m_{240\text{Pu}}(\text{mg})$	Normal	59.8 ^a 52.5 ^b	0.1 ^a 0.2 ^b	0	120
$m_{240\text{Pu}}/m_{238\text{Pu}}$	Normal	330 ^a 622 ^b	30 ^a 3 ^b	170 ^a 604 ^b	510 ^a 640 ^b
$m_{240\text{Pu}}/m_{242\text{Pu}}$	Normal	127 ^a 186.8 ^b	7 ^a 0.3 ^b	85 ^a 185 ^b	169 ^a 188.6 ^b
ϵ	Normal	1.0	0.13	0.22	1.78
H_s^{cc}	Uniform	----	----	0.07856	0.08553
Internal IF/SF Ratio	Normal	0.003 ^a 0.0025 ^b	0.00015 ^a 0.000125 ^b	0 ^a 0 ^b	0.006 ^a 0.006 ^b
External IF/SF/cps Ratio	Normal	0.015 ^a 0.012 ^b	0.00015 ^a 0.000125 ^b	0 ^a 0 ^b	0.03 ^a 0.03 ^b
Neutron Rate (cps)	Normal	3.0	0.5	0	10
$\chi_{133\text{Xe}}^{IF}$	Normal	0.0701	0.0004	0.06	0.08
$\chi_{135\text{Xe}}^{IF}$	Normal	0.0763	0.0005	0.065	0.085
a. For plutonium cylinders containing material from RMT125001 (see Section 2.1.1.4)					
b. For plutonium cylinders containing material from RMT12962 (see Section 2.1.1.4)					

The $m_{240\text{Pu}}$ parameter controls the mass of ^{240}Pu . This is combined with the $m_{240\text{Pu}}/m_{238\text{Pu}}$ and $m_{240\text{Pu}}/m_{242\text{Pu}}$ to obtain the ^{238}Pu and ^{242}Pu masses. These are combined with SF decay constants (Croft and Favalli, 2021) to calculate the total SF rate. The internal fission rate is calculated as a fraction of the SF rate. The internal IF rate is directly applied while the external IF rate requires also calculating count rate of the neutron detector. Finally, the IF yields ($\chi_{133\text{Xe}}^{IF}$ and $\chi_{135\text{Xe}}^{IF}$) are obtained for ^{239}Pu from the JENDL library (Tsubikihara et al., 2021). These

values agree well with the ENDF/B-VII.1 database (Chadwick and Kawano, 2011; England and Rider, 1992) though there is disagreement with the JEFF-3.3 database (Schmidt, 2024). As the JENDL and ENDF/B-VII.1 show agreement despite relying on different underlying data sources, the mass 133 yield of 0.0701 ± 0.0004 and mass 135 yield of 0.0763 ± 0.0005 are accepted for this work.

An example histogram from the Monte Carlo analysis of the ^{133}Xe measurements obtained using the above parameters is shown in Figure 14. This analyzes the 01/30/2025 measurement in Table 13. The resulting cumulative ^{133}Xe fission yield is 0.063 ± 0.009 . The distribution is not quite normal; the skew arises from the requirement that several quantities be positive.

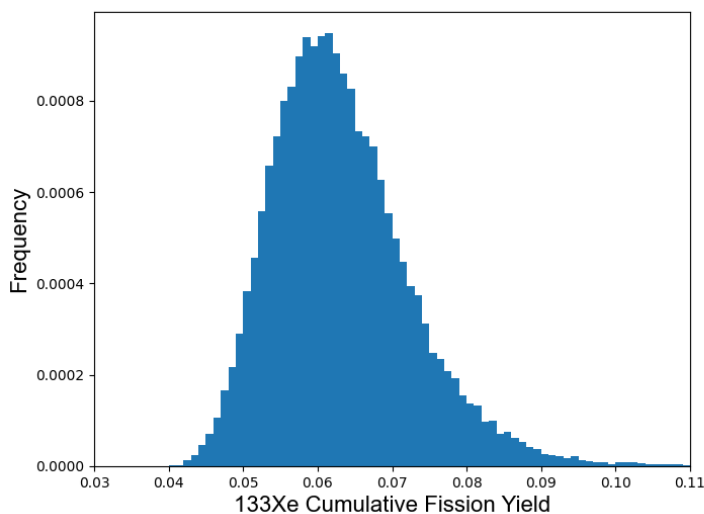


Figure 14: Sample histogram from Monte Carlo analysis of the sample collected on 01/30/2025.

The results for each individual measurement are presented in Table 16. These are calculated using the results in Table 13 and the model parameters in Table 15.

Table 16: ^{133}Xe and ^{135}Xe cumulative fission yields for each measurement

Measurement Date	Pu Material (RMT)	$\chi_{133\text{Xe}}^{sf}$	$\chi_{135\text{Xe}}^{sf}$
10/31/2024	125001	0.044 ± 0.007	0.040 ± 0.006
11/14/2024	125001	0.065 ± 0.010	0.061 ± 0.009
12/05/2024	12962	0.068 ± 0.010	0.061 ± 0.009
01/30/2025	125001	0.063 ± 0.010	0.054 ± 0.008
02/06/2025	125001	---- ^a	0.054 ± 0.009
02/20/2025	125001	---- ^a	0.054 ± 0.008
02/27/2025	125001	---- ^a	0.054 ± 0.008
03/13/2025	125001	0.066 ± 0.010	0.057 ± 0.009
04/17/2025	125001	0.065 ± 0.010	0.056 ± 0.009
04/24/2025	12962	0.076 ± 0.011	0.062 ± 0.009
06/12/2025	125001	0.039 ± 0.006	0.032 ± 0.005
06/19/2025	125001	0.050 ± 0.007	0.042 ± 0.007
06/26/2025	12962	0.058 ± 0.008	0.050 ± 0.008
07/02/2025	125001	0.063 ± 0.009	0.056 ± 0.009
07/17/2025	125001	0.084 ± 0.012	0.056 ± 0.009
07/24/2025	12962	---- ^b	0.069 ± 0.010
07/30/2025	125001	---- ^b	0.052 ± 0.008
08/14/2025	125001	0.065 ± 0.010	0.054 ± 0.008
08/21/2025	12962	0.082 ± 0.012	0.066 ± 0.010
08/28/2025	125001	0.067 ± 0.010	0.056 ± 0.009
09/18/2025	125001	0.063 ± 0.009	0.048 ± 0.007
09/25/2025	12962	0.079 ± 0.011	0.070 ± 0.011
10/01/2025	125001	0.068 ± 0.010	0.056 ± 0.009
11/13/2025	125001	0.066 ± 0.010	0.056 ± 0.009
11/19/2025	12962	0.080 ± 0.012	0.069 ± 0.010
12/04/2025	125001	0.067 ± 0.010	0.059 ± 0.009
02/19/2026	12962	0.073 ± 0.011	0.058 ± 0.009
02/26/2026	125001	0.066 ± 0.010	0.060 ± 0.009
03/12/2026	125001	0.062 ± 0.009	0.055 ± 0.008
^a Insufficient time for ^{133}Xe equilibration – samples collected to verify ^{135}Xe reproducibility			
^b Samples contaminated by memory effects from attempted ^{133}Xe control experiments			

3.4 Cumulative fission fraction estimate and uncertainty

The Monte Carlo results for each experiment presented in the previous section may now be combined to estimate the mean cumulative fission yields and the standard error (uncertainty) of these mean values. The standard error of the mean is calculated using Equation 24 where σ_{meas} is the average standard deviation of a single measurement obtained from the Monte Carlo analysis and $N_{measurements}$ is the number of accepted measurements for the given xenon isotope. σ_{meas} is accepted as the population standard deviation instead of using the standard deviation of the cumulative fission yield values because it is a better estimate of the actual uncertainty in each measurement.

$$stderr = \frac{\sigma_{meas}}{\sqrt{N_{measurements}}}$$

Equation 24

The final calculated results are shown in Table 17. The average standard deviation of a single measurement (σ_{meas}) is 0.011 for ^{133}Xe and 0.009 for ^{135}Xe .

Table 17: Mean cumulative fission yields and uncertainties for ^{133}Xe and ^{135}Xe

$\chi_{133\text{Xe}}^{sf}$	$\chi_{133\text{Xe}}^{sf}$ Uncertainty (%)	$\chi_{133\text{Xe}}^{sf}$	$\chi_{135\text{Xe}}^{sf}$ Uncertainty (%)
0.066 ± 0.002	3%	0.058 ± 0.002	3%

This study determined values of 0.066 ± 0.002 and 0.058 ± 0.002 for the ^{133}Xe and ^{135}Xe SF cumulative yields, respectively. Previous measurements of the cumulative yields from ^{240}Pu SF suggested values of 0.06-0.0819 for mass 133 and 0.0639-0.0812 for mass 135. (Laidler and Brown, 1962; Bushuev et al., 2007; Toraskar and Melkonian, 1971; Demattè et al. 1997) While this study focused on the ^{133}Xe and ^{135}Xe yields, these should be a close approximation of the cumulative mass 133 and mass 135 yields as the independent yields for Xe, Cs, and Ba tend to be quite small. The value for ^{133}Xe is within the range of previous measurements while the ^{135}Xe value is below the published range. The repeated measurements presented here relied on a statistical approach to obtain an estimate of these quantities.

3.4.1 Assessment of potential systematic sources of error

The major question related to these results is how to explain the ^{135}Xe results. There are a few reasons that this quantity may be systematically lower than expected. Earlier analysis of the sampling efficiency (Section 3.2) indicated that there wasn't a systematic issue that would lower the measured xenon activities. Therefore, other explanations are required. In the existing literature, the mass 135 yield is usually higher than the mass 133 yield. (Bushuev et al. 2007; Toraskar and Melkonian, 1971; Demattè et al. 1997) The only exception was the data from Laidler and Brown (1962). Likewise, cumulative yields for ^{239}Pu IF are higher for mass 135 than mass 133. (Tsubukihara et al, 2021)

The most likely explanation for the ^{135}Xe yield being lower than the ^{133}Xe yield and range of reported values is that mass transfer in the system is not as rapid as originally thought. If an average of two hours passed from the time a xenon atom was generated until it reached the headspace, then 14% of the ^{135}Xe would decay in transit while only 1.1% of the ^{133}Xe would be lost in the same manner. A quick accounting for transport losses suggests that approximately two hours holdup is sufficient to make the two cumulative fission yields equal and to bring the ^{135}Xe into the experimental range while having a statistically insignificant impact on the ^{133}Xe yield. In these experiments, the solution was heated and swirled to encourage mass transport. However, the solution may simply have been too deep to eliminate the effects of mass transport.

A second source of error arises from the attempt to separate the contribution of IF from SF. The MCNP simulations discussed previously (Induced fission—neutron monitor and MCNP modeling) attempted to quantify the amount of IF arising from internal and external sources. Without knowing the energy spectrum of the neutrons incident on the system and while keeping the MCNP model relatively simple, the contribution was potentially too large. However, removing IF from the model only raises the final fission yields by around 0.003. This is insufficient to explain the apparently low SF yield of ^{135}Xe .

Despite the low value for the ^{135}Xe yield, the ^{133}Xe yield looks reasonable. Additionally, the technique showed that reproducible measurements were achievable once the behavior of the

apparatus was understood and characterized. In the end, uncertainties of 3% were achieved for the measured fission yields. This matches the project's goal of reducing the uncertainty on these measurements below 5%. Therefore, a value of 0.066 ± 0.002 for the cumulative fission yield of ^{133}Xe appears reasonable.

4.0 Conclusions

The project aimed to measure the ^{133}Xe and ^{135}Xe cumulative fission yields (fission fractions) from ^{240}Pu SF with uncertainty of less than 5%. The final values are $(6.6 \pm 0.2)\%$ for ^{133}Xe and $(5.8 \pm 0.2)\%$ for ^{135}Xe . The final uncertainties are 3% of the measured value for ^{133}Xe and ^{135}Xe . Thus, the measurement goal of less than 5% uncertainty was achieved.

The uncertainty analysis included systematic corrections for the sampling efficiency and for confounding IF and SF events. The final uncertainty included the uncertainty in these systematic contributions plus the uncertainties arising from radioxenon quantification, sample composition, and thermodynamic parameters. The average uncertainty for an individual measurement was 14.6% for ^{133}Xe and 15.3% for ^{135}Xe . The standard error of the mean for each cumulative fission yield was tempered by the number of measurements used.

The final cumulative fission yield for ^{133}Xe agrees with corresponding ^{133}I yield measurements in the literature, and it provides a value with a reasonable uncertainty. However, the cumulative fission yield for ^{135}Xe is significantly lower $(5.8 \pm 0.2)\%$ than any of the previous literature reports $(6.39\text{--}8.12)\%$. This disagreement likely results from a small, but nonzero, transport time for xenon in the solution. Due to the short half-life of ^{135}Xe (9.14 hours), holdup of approximately 2 hours in solution would significantly impact its partitioning between the liquid and vapor phases while having a negligible impact on the ^{133}Xe partitioning. Therefore, the cumulative fission yield of ^{135}Xe should be used with caution.

The technique of headspace sampling appears to offer advantages when investigating volatile isotopes with significant fission yields and sufficiently long half-lives. While the headspace samples were only able to provide quantitative ^{133}Xe and ^{135}Xe yields, this technique could be adjusted to measure the $^{131\text{m}}\text{Xe}$ cumulative yield or to isolate other species of interest. With thoughtful engineering and repeated measurements, it is possible to measure cumulative fission yields with a reasonable uncertainty.

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Appendix A – P&ID

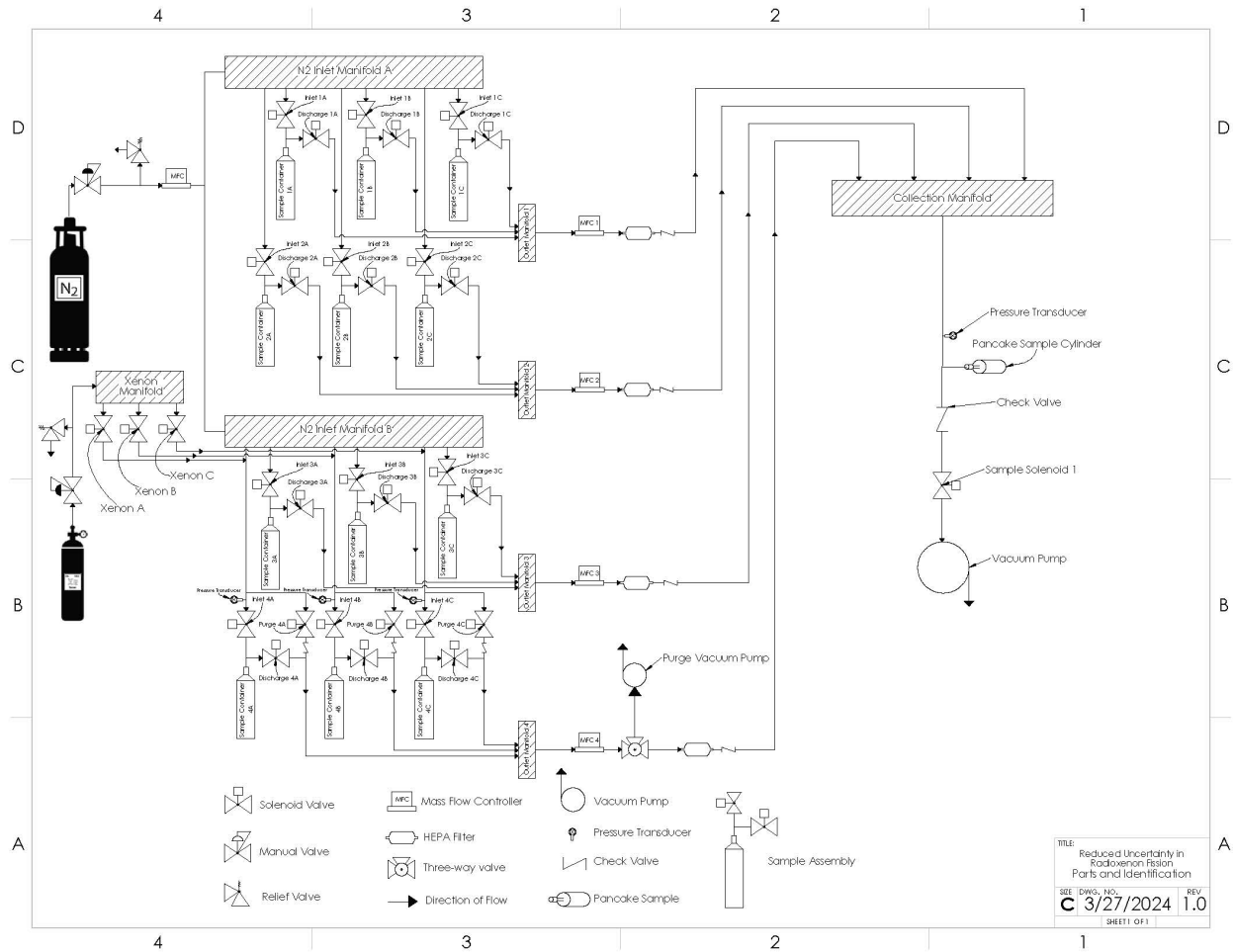


Figure 15. Process and Instrumentation Diagram of headspace gas sampling apparatus

Appendix B – Pu composition by confirmatory methods

Table 18: Combined AEA/GEA/LSC Pu isotopic analysis results

Isotope	Atom Fraction (%)		
	RMT 48	RMT 12962	RMT 125001
²³⁸ Pu	0.152 ± 0.004	0.056 ± 0.002	0.0280 ± 0.0008
²³⁹ Pu	90 ± 2	94 ± 3	94 ± 3
²⁴⁰ Pu	10.1 ± 0.3	5.9 ± 0.2	6.0 ± 0.2
²⁴¹ Pu	0.011 ± 0.001	0.0044 ± 0.0004	0.072 ± 0.003
²⁴² Pu	0.147 ± 0.008	0.173 ± 0.009	0.26 ± 0.02

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