

Rapid Concentration and Isotopic Measurements of Ultra-trace ^{235}U Fission Products with Comparison to an ORIGEN Isotope Depletion Model

Benjamin D. Roach^{A,1}, Emilie K. Fenske^{A,B}, David C. Glasgow^A, John D. Partridge^A, Tamara J. Keever^A, and Joseph M. Giaquinto^A

^A*Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN, 37830, USA.*

^B*Institute for Nuclear Security, University of Tennessee, 1640 Cumberland Avenue, Knoxville, TN, 37996, USA.*

¹ Corresponding author: roachbd@ornl.gov

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ABSTRACT

This article presents the application of an automated online separation–direct analysis method, RAPID (Rapid Analysis of Post-Irradiation Debris), to measure both radioactive and stable fission isotopes from an irradiated highly-enriched uranium target. Developed for the measurement of the concentration and isotopic composition of over 40 elements down to the femtogram level, the RAPID method possesses the sensitivity, stability, and precision required to achieve accurate, low-level analyses of elements of non-natural origin. The isotopic compositions and concentrations of key fission elements cesium, strontium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, and samarium have been measured repeatedly over a six-week period. The validity of these measurements was confirmed using ORIGEN (Oak Ridge Isotope GENERation), an isotope depletion and decay modeling software, to within 1–3%.

Keywords: rapid, ICPMS, ion chromatography, fission products, isotopic analysis, ORIGEN.

INTRODUCTION

The precise and timely analysis of trace levels of fission isotopes in irradiated materials is key to a number of research and development areas in the nuclear field, specifically for modeling and simulation validation, nuclear forensics, and isotope production [1,2]. The analysis of the short-lived, long-lived, and stable fission isotopes resulting from a nuclear event is critical in the forensic attribution process that will follow [3]. The improvement of modeling capabilities also occurs through the verification of fission products formed during reactor operation [4–8] and material irradiation [9,10]. ^{235}U thermal fission products, being very well characterized, vary from stable isotopes to numerous short- and long-lived isotopes [11,12], thus, both radiometric and mass-based analyses are traditionally utilized for full characterization. To adequately and efficiently characterize the short-lived isotopes at the same time as the longer-lived and stable isotopes, an inclusive, rapid analytical method is desired.

Due to the limited sample size, the analytical tools traditionally employed for fission product analysis are radio-analytical techniques, such as non-destructive gamma-ray spectroscopy [13–15], and neutron activation analysis [16]. Unfortunately, in such samples, spectral interferences and the need for background discrimination increase dramatically the closer to the time of irradiation the analysis occurs. Either a cooling-period must be observed, to allow for shorter lived isotopes to decay, or the results will be subject to increased uncertainties and detection limits [17,18]. ^{135}Cs , ^{90}Sr , and ^{147}Pm are prime examples of important fission-generated analytes that suffer from both signal suppression and significant interferences using traditional radiochemical techniques and currently cannot be directly detected without significant, and lengthy, chemical separations [19].

High-pressure ion chromatography (HPIC) allows for the time of the chemical separations to be reduced and, when combined with an inductively-coupled plasma mass spectrometer (ICP-MS), can separate fission elements of interest from isobaric and polyatomic interferences, resulting in the quantification of both stable and radioactive isotopes in nuclear materials simultaneously [20–23]. This combination of HPIC and ICP-MS allows direct analyses of trace-level quantities of fission elements from various matrices, such as environmental samples, nuclear waste, and uranium ore. In 1991 Almon et al. [24] pioneered the analysis of fission products and actinides in nuclear waste using HPIC directly coupled to ICP-MS (HPIC-ICP-MS). Similar methods were, in turn, developed to analyze numerous metals in samples such as “urban road dust” and atmospheric

particles [25], environmental samples [26,27], uranium materials [20], and spent nuclear fuel [28–32]. More recently, work has been done to isolate and determine the concentrations of elements such as Np [33], Mg [34], Sr [35,36], Cs [37], and various lanthanides and actinides [38–44] from subsequent interferences and sample matrices.

An HPIC-ICP-MS method, developed at Oak Ridge National Laboratory (ORNL), has been shown to complete a full isotopic analysis of over 40 elements, post-dissolution, in less than one hour per sample. RAPID (Rapid Analysis of Post-Irradiation Debris), as it was named, was qualified as an analytical method for the analysis of nuclear materials, and the stability and sensitivity of the method together with its robustness to a silicon-based soil matrix have been reported [45–47]. Preliminary work separating fission products from a uranium matrix after a significant decay period confirmed that it was possible to measure a number of non-natural isotope ratios to within 1–2% of that predicted by decay modeling software developed at ORNL, the Oak Ridge Isotope Generation (ORIGEN) code [48].

With the goal to achieve measurements of non-natural isotopic signatures at concentrations ranging from those in spent fuels to those likely present in post-detonation material [49,50], this study presents the analysis of a highly-enriched uranium (HEU) target irradiated to yield $\sim 10^{14}$ fissions. With the initial analysis occurring less than 200 h post-irradiation and requiring less than one hour per sample, multiple analyses over a six-week period enabled the measurement of shifting isotopic compositions of nine key fission elements, namely, Ce, Sr, Y, La, Ce, Pr, Nd, Pm, and Sm. The isotopic concentrations were subsequently determined via both RAPID and ICP-MS using NIST-traceable natural standards, and high-purity germanium (HPGe) gamma detectors were utilized to confirm the determined concentrations of several short-lived fission isotopes. The determined isotopic abundances and concentrations are presented in terms of precision and accuracy when compared to those predicted by the ORIGEN modeling software.

MATERIAL AND METHODS

Software and Data Processing

The SCALE code system [51], used internationally in support of spent nuclear fuel transportation and storage applications, includes an isotope depletion and decay analysis module known as ORIGEN [52]. The ORIGEN module was used to predict the changing isotopic masses of fission products in an irradiated HEU target over a six-week period. The model accurately reproduces the flux spectrum in the specific pneumatic tube used for irradiation in ORNL's neutron activation analysis (NAA) laboratory, enabling accurate prediction of total fissions in the target based on the mass of fissile material loaded. All measured isotopic data reported references the integrated isotopic peak areas in a transient signal as determined by the Thermo Fisher Scientific Qtegra software, using an m/z trace and a pre-determined elution time. Peak fitting and smoothing in the Qtegra software were applied post-acquisition, statistically reducing the observed uncertainties and enabling peak area comparisons between isotope peaks from the same element, yielding isotopic ratios in atom percent. The chromatographic peak fitting and smoothing settings applied to determine peak area, found within the "Peak Detection" settings of the Qtegra software, are as detailed previously [45–47]. Additionally, fission product impact depths into the ampoule walls during irradiation were obtained with a software package focused on the stopping power and range into matter (SRIM), which calculates the range of variously-energized ions into targets using a quantum mechanical model of ion-atom collisions [53].

Instrumentation

A Dionex ICS-5000+ HPIC system coupled to a Thermo Scientific iCAPQ quadrupole ICP-MS was used for this work. Chromatographic separation was performed using a metal-free HPIC pump, a 50 μL injection loop, an IonPac CS5A column complete with an IonPac CG5A guard column, and a thermal compartment set at 35°C for consistent elution times. The analytical column was connected to the nebulizer of the ICP-MS instrument using PEEK tubing via a mixing tee-piece. Nitric acid (HNO_3 , Optima, 1.25 M, ~5%) was pumped into the mixing tee-piece at 0.1 mL/min to acidify the eluent, post-column, prior to nebulization to aid in ionization and to increase signal stability. The iCAP Q was fitted with a cyclonic quartz spray chamber, a nickel sampler cone, and a nickel skimmer cone with a high matrix insert (3.5 mm). The setup is housed within a radiological fume hood, in a contamination enabling the analyses of highly-radioactive samples. Table 1 in the ESI summarizes the experimental and operating conditions of the HPIC-ICP-MS system.

Reagents and standards

Eluents for HPIC, samples, and standards were prepared with trace-metals basis grade chemicals and ultra-pure water (18.2 M Ω cm) from a Millipore Milli-Q™ water purification system. Chemicals for eluents include: diglycolic acid (DGA, $\text{C}_4\text{H}_6\text{O}_5$, >98% purity, recrystallized, Acros Organics, NJ, USA), 2,6-pyridinedicarboxylic acid (PDCA, $\text{C}_7\text{H}_5\text{NO}_4$, 99.999% metals basis, Fluka, Sigma-Aldrich Co.), glacial acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, 99.99% trace metals basis, Sigma-Aldrich Co., MO, USA), and oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$, 99.999% trace metals basis, recrystallized, Sigma-Aldrich Co., MO, USA). These were buffered with ammonium hydroxide (NH_4OH , 0-22% as NH_3 , trace metal grade, Fisher Scientific, NJ, USA), to a final pH of 4.8.

The HEU target was prepared using the certified reference standard U930-D (93.2% ^{235}U , New Brunswick Laboratory, IL, USA). Working standard solutions were prepared for HPIC-ICP-MS analyses in 5% nitric acid (HNO_3) by diluting the stock standard solutions in ultra-pure water: IV-ICPMS-71A (10 mg L^{-1}), IV-ICPMS-71B (10 mg L^{-1}), and IV-ICPMS-71D (10 mg L^{-1}) (Inorganic Ventures, VA, USA).

Material irradiation and sample preparation

The HEU target was prepared by evaporating portions of U930-D into a high-purity quartz ampoule (ESI Figure 1), resulting in a target containing ~80 μg ^{235}U . After flame-sealing under partial vacuum, the ampoule was counted on HPGe detectors to verify the fissile mass prior to irradiation. Following the guidance of the Los Alamos National Laboratory Passive Non-Destructive Assay (PANDA) manual [54], the 185.7 keV gamma-ray was analyzed in background-subtracted spectra. An ORIGEN calculation resulted in an irradiation time required to reach 10^{14} fissions, ensuring enough fission material is produced but minimizing the required cooling period post-irradiation. The target was irradiated at the Nuclear Analytical Chemical and Isotopics Laboratory (NACIL) Neutron Activation Analysis (NAA) laboratory, located within the High Flux Isotope Reactor (HFIR) facility. The thermal and epithermal flux populations were measured using dilute manganese and gold flux monitors, respectively. The thermal flux was 4.17×10^{14} and the epithermal measured 1.12×10^{13} , with both having units of neutrons $\text{cm}^{-2} \text{s}^{-1}$. For modeling

purposes, the total flux over the broader neutron spectrum was calculated to be 6.57×10^{14} n cm⁻² s⁻¹. The target was sealed in a graphite rabbit and irradiated for one hour. Post-irradiation and a 24 h cooling period, the dose rate of the unopened rabbit was measured. After a further cooling period, the irradiated target was shipped from the HFIR facility to another NACIL laboratory building for chemical processing and analysis. The received target was leached, while sealed, in 4M HNO₃, and tare weights in a Savillex vessel were determined. The target was opened by submersion in 4M HNO₃ (Optima) in a pre-leached, malleable polytetrafluoroethylene (PTFE) vessel under controlled crushing with a pre-cleaned mini-vice (ESI Figure 2). The opened target was then quantitatively transferred back into the pre-tared leaching vessel for sealed heat leaching. The vessel was heat-leached at ~80°C for 4 h in HNO₃ (3 mL, 4M, Optima), allowed to cool, and the final weight was taken to determine solution weight and volume. Post-leaching, the uranium content was determined with isotope dilution mass spectrometry (IDMS) using a certified ²³⁸U standard (IV-ICPMS-71A, Inorganic Ventures).

HPIC Elution scheme

The HPIC elution scheme employed in this study is a four-eluent, gradient-elution profile employing: deionized water; 6 mM PDCA (with 90 mM acetic acid, buffered to pH 4.8 with NH₄OH); 150 mM oxalic acid (buffered to pH 4.8 with NH₄OH); and 100 mM DGA (buffered to pH 4.8 with NH₄OH) as described earlier [48] see also reagents and standards section. A two-minute washing period of 100% oxalic acid, followed by a five-minute washing period of 100% PDCA was incorporated to ensure any contaminants built up from the eluents were removed in preparation for the following sample. The resulting separation scheme, together with the approximate elution times of the elements of interest, is graphically represented in Figure 1, and the complete profile can be found in the supplementary information (ESI Figure 3 and Table 2).

Figure 1. The gradient elution profile, with the corresponding elution times illustrated, for the elemental isolation of the fission elements of interest (cesium, strontium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, and yttrium). Barium and zirconium are also pictured as these are two of the key elements that have isobaric interferences for cesium, yttrium, and strontium.

RESULTS AND DISCUSSION

The irradiated ²³⁵U target leachate was analyzed for fission product isotopic content 178 hours post-irradiation, focusing on the lanthanide elements (Figure 2), as well as cesium (Figure 3), strontium, and yttrium (Figure 4). A 50 μL sample of a 2× dilution of the leachate, the equivalent of 20 fg–10 pg of each isotope, was injected with the HPIC system and eluted directly into the iCAP Q ICP-MS at 1 mL/min using the elution protocol shown above. The transient *m/z* signals, directly monitored by ICP-MS, show elemental separation by peak elution time, resolving isobaric and polyatomic mass interferences. The resulting peaks with the same elution time, after smoothing and peak fitting, are integrated, and their areas are directly related to their atomic percent abundance in the sample. For the majority of the analytes natural contamination was not observed in the sample to any measurable degree, the strontium and yttrium isotopes were the exception. The *m/z* traces for these analytes required background subtraction of a matrix blank, resulting in much noisier baselines than observed for the other analytes. This was confirmed to be

due to the presence of trace levels of natural strontium and zirconium in the eluents (10-50pg mL), which had an impact on the m/z traces 88 and 90.

Figure 2. The transient ICP-MS signals for m/z 139–154, encompassing the lanthanide elements, from 1200–1800 s elution time (left) for a 50 μ L injection of the irradiated target leachate 178 h post-irradiation. The central figure depicts the same transient signals separated by m/z , clarifying which isotopes have isobaric interferences. By limiting the elution time to encompass a single element, in this case, neodymium at 1460–1520 s, then rotating the figure to remove the “Time” axis, the atomic percent abundances of the neodymium isotopes can be observed (right).

Figure 3. The transient ICP-MS signals for m/z 133, 135, and 137, the neutron-induced fission masses for cesium, for a 50 μ L injection of the irradiated target leachate 178 h post-irradiation (left). The central figure depicts the same transient signals separated by m/z , showing a clear separation between cesium isotopes and those of both natural and fission-induced barium isobars ^{135}Ba and ^{137}Ba . By limiting the elution time to encompass a single element, in this case, cesium at 75–190 s, then rotating the figure to remove the “Time” axis, the atomic percent abundances of the neutron-induced fission isotopes of cesium can be observed (right).

Figure 4. The transient ICP-MS signals for m/z 88–91, the neutron-induced fission masses for strontium and yttrium, for a 50 μ L injection of the irradiated target leachate 178 h post-irradiation (left). The central figure depicts the same transient signals separated by m/z , showing a clear separation between the isobars $^{89}\text{Sr}/^{89}\text{Y}$, $^{90}\text{Sr}/^{90}\text{Zr}$, and $^{91}\text{Y}/^{91}\text{Zr}$. Separation from the solvent front, and from natural zirconium contamination, is important for accurate isotopic analyses. By limiting the elution time to encompass a single element, in this case, yttrium at 1940–2000 s, then rotating the figure to remove the “Time” axis, the atomic percent abundances of the neutron-induced fission isotopes of yttrium can be observed.

Mass Bias Correction

Two independent lots of a mixed-element standard of natural isotopic abundance were analyzed before and after each sample to determine and quantify the mass bias of the iCAP Q quadrupole mass analyzer for each element. The measured isotopic ratios for each element were compared with known values [55], and a quadrupolar bias towards the heavier isotopes was observed. For each analysis, the measured biases were plotted as a function of the percent deviation from a centroid isotope per AMU. A linear fit over the entire mass range for each element yielded equations that could be applied to elements of both natural and non-natural isotopic abundance. The primary mixed-element standard was used to determine the mass bias, and the secondary standard was used as a control to ensure the bias applied to the analyzed samples was accurate. For the lanthanide elements, it was determined that there was $\sim 1.5\%$ bias per AMU from a centroid isotope. An example of this correction can be found in the supplementary information (ESI Figure 4). For non-naturally occurring isotopes, ^{147}Nd for example, a linear plot for the naturally-occurring isotopes was calculated and the bias for ^{147}Nd could then be interpolated. For elements with only a single naturally-occurring isotope (i.e. La, Pr, and Y), the calculated mass bias for a neighboring element was applied. For promethium, an element with no naturally-occurring isotopes, the mass bias calculated for the mass difference of the naturally-occurring ^{147}Sm and ^{149}Sm isotopes was employed.

Precision and Bias of Isotopic Analysis

The irradiated leachate was analyzed on three occasions over the course of six weeks. For each analysis, three replicates were analyzed over a 2.5 h period and, post mass bias correction, the average atomic percent abundances for each element were calculated. The precision of the measurement, shown in Table 1 as a 2σ standard deviation of the replicates, was heavily dependent on the quantity of each element analyzed, the number of neutron-induced fission isotopes monitored for each element, and the atomic percent abundance of each isotope. The levels of isotopes analyzed ranged from ~ 20 fg (e.g. ^{135}Sm) to ~ 10 pg (e.g. ^{145}Nd) with the majority of the highly-abundant isotopes showing a 1–3% precision and a 1–2% accuracy when compared with the ORIGEN predictions at each time post-irradiation.

Table 1. The measured average atomic percent (at. %) abundances together with the ORIGEN-predicted atomic percentage for each isotope at $t = 178$ h, 504 h, and 1018 h post-irradiation. The precision of the measurement is a 2σ standard deviation of the replicates.

Time Post Irradiation (h)	178		504		1018	
	RAPID (meas. at. %) (2σ , n=3)	ORIGEN (calc. at. %)	RAPID (meas. at. %) (2σ , n=3)	ORIGEN (calc. at. %)	RAPID (meas. at. %) (2σ , n=3)	ORIGEN (calc. at. %)
Sr-88	26.5(3)	26.2	27.5(10)	27.7	29.3(9)	29.8
Sr-89	31.1(2)	31.4	27.7(7)	27.5	21.5(3)	22.1
Sr-90	42(2)	42.4	45(1)	44.8	49.1(6)	48.1
Y-89	7.7(8)	7.9	20.5(7)	21.0	37.3(6)	37.1
Y-91	92.3(8)	92.1	79.5(7)	79.0	62.7(6)	62.9
Cs-133	14.8(2)	22.7	14.5(3)	33.4	15.2(6)	35.0
Cs-135	35.5(6)	38.7	34.6(14)	33.4	35(1)	32.6
Cs-137	49.7(8)	38.6	50.9(15)	33.2	49.7(8)	32.4
La-139	91.5(3)	91.6	95.68(5)	95.6	98.5(3)	98.6
La-140	8.4(3)	8.4	4.32(5)	4.4	1.5(3)	1.4
Ce-140	8.4(2)	8.2	20.1(17)	21.2	31.2(4)	29.4
Ce-141	26.2(5)	27.6	20.8(7)	19.8	12.6(4)	12.7
Ce-142	34(2)	32.2	31.6(4)	31.1	30.2(4)	31.3
Ce-143	0.76(4)	0.8	0.07(3)	0.0	0(0)	0.0
Ce-144	30.3(4)	29.8	27(1)	27.8	26.0(6)	26.6
Pr-141	15.4(4)	15.9	48(1)	48.9	82.3(6)	82.0
Pr-143	84.6(4)	84.1	52(1)	51.1	17.7(6)	18.0
Nd-143	10.9(3)	11.8	26.3(5)	27.0	33.7(4)	34.4
Nd-144	0.92(14)	0.8	2.5(2)	2.0	3.5(2)	3.6
Nd-145	32.6(4)	32.2	28.4(13)	28.4	26.4(5)	25.9
Nd-146	25(1)	24.6	21.5(3)	21.6	19.8(3)	19.8
Nd-147	11.3(2)	11.5	4.15(11)	4.2	1.0(1)	1.0
Nd-148	13.6(5)	13.7	12.4(9)	12.1	11.3(2)	11.0
Nd-150	5.6(4)	5.4	4.8(6)	4.7	43(2)	4.3

Pm-147	88.7(5)	88.5	99.9(1)	99.9	100.0(1)	100.0
Pm-149	11.3(5)	11.5	0.08(1)	0.1	0(0)	0.0
Sm-147	0(0)	0.0	0.8(4)	0.8	2.7(1)	2.4
Sm-149	54.6(6)	56.0	57(2)	58.2	56(2)	57.3
Sm-151	23(1)	23.8	22(2)	22.6	22.2(5)	22.2
Sm-152	17(1)	15.3	15(1)	14.4	14(1)	14.1
Sm-153	0.62(7)	0.6	0.01(3)	0.0	0(0)	0.0
Sm-154	4.5(6)	4.3	5(1)	4.0	4.9(4)	3.9

It can be seen in Table 1 that the measured cesium isotopic compositions do not agree with the ORIGEN-predicted values. Initially, barium interferences were thought to be influencing the cesium isotopic measurements; however, as can be seen in Figure 2, clear separation of barium and cesium is observed. The unexpected cesium isotopic composition is likely due to the parent fission isotopes for the cesium isotopes being xenon. The low abundance of ^{133}Cs relative to the ^{135}Cs and ^{137}Cs indicates a potential breach in the ampoule prior to crushing and leaching for this analysis. Using the ORIGEN model, it was determined that the composition of the cesium was fixed at ~ 24 h post-irradiation, corresponding with the removal of the pellet from the decay station. This indicates a potential microfracture or pinhole leak that allowed the xenon fission gas to escape. With ^{133}Xe ($t_{1/2} = 5.25$ d) having a significantly longer half-life relative to the ^{135}Xe ($t_{1/2} = 9.14$ h) and ^{137}Xe ($t_{1/2} = 3.82$ m), the 24 h post-irradiation breach resulted in the loss of more ^{133}Xe and, in turn, lower levels of ^{133}Cs in the target leachate.

Table 2 shows another way to view the data: isotope ratios as a function of time. With two isotopes growing in and one decaying away during the experiment, the neodymium isotope ratios are a good example of how closely the RAPID method can match extremely low-level (~ 80 fg of ^{144}Nd was injected onto the column in the first analysis) isotope ratios with multiple potential isobaric interferences.

Table 2. The measured and ORIGEN-predicted atomic percent ratios for neodymium at $t=178$ h, 504 h, and 1018 h post-irradiation. The precision of the measurement is a 2σ standard deviation of the replicates.

Time Post Irradiation (h)	178		504		1018	
	RAPID (meas. at. %) (2σ , $n=3$)	ORIGEN (calc. at. %)	RAPID (meas. at. %) (2σ , $n=3$)	ORIGEN (calc. at. %)	RAPID (meas. at. %) (2σ , $n=3$)	ORIGEN (calc. at. %)
$^{143}\text{Nd}/^{146}\text{Nd}$ \uparrow	0.46(2)	0.48	1.23(3)	1.25	1.70(4)	1.74
$^{144}\text{Nd}/^{146}\text{Nd}$ \uparrow	0.038(4)	0.033	0.12(3)	0.093	0.18(3)	0.18
$^{145}\text{Nd}/^{146}\text{Nd}$ $-$	1.36(6)	1.31	1.322(8)	1.31	1.33(3)	1.31
$^{147}\text{Nd}/^{146}\text{Nd}$ \downarrow	0.47(2)	0.47	0.19(6)	0.19	0.051(6)	0.051
$^{148}\text{Nd}/^{146}\text{Nd}$ $-$	0.56(3)	0.56	0.58(4)	0.56	0.57(1)	0.56
$^{150}\text{Nd}/^{146}\text{Nd}$ $-$	0.24(2)	0.22	0.22(3)	0.22	0.22(1)	0.22

$\downarrow\uparrow-$ represent decaying, ingrowing, and static numerator respectively.

Two masses of particular interest were 143 and 147 as, over the six-week period of analysis, quantitative shifts in the $^{143}\text{Ce}/^{143}\text{Pr}/^{143}\text{Nd}$ and $^{147}\text{Nd}/^{147}\text{Pm}/^{147}\text{Sm}$ abundances were observed (see

Figure 5). These measurements were fitted with an exponential decay curve, and the half-lives of ^{147}Nd and ^{143}Pr were calculated as 10.6(3) d and 13.9(4) d respectively ($t_{1/2} \text{ } ^{147}\text{Nd} = 10.98 \text{ d}$, $t_{1/2} \text{ } ^{143}\text{Pr} = 13.57 \text{ d}$ [56]). This was only possible due to the baseline resolution of the neighboring isotopes. To correct for day-to-day systematic, bias-inducing, variations in an ICP-MS, normalization of the isotope signals was performed using a stable isotope standard within each run.

Figure 5. The transient ICP-MS signals for m/z 143 (left) and 147 (right) for a 50 μL injection of the irradiated target leachates at 178 h, 504 h, and 1018 h post-irradiation. The figure depicts the transient signals separated by time, showing a clear separation between the isobars $^{143}\text{Ce}/^{143}\text{Pr}/^{143}\text{Nd}$ and $^{147}\text{Nd}/^{147}\text{Pm}/^{147}\text{Sm}$. When a staggered plot of the transient signals is plotted by analysis time post-irradiation, the decay and ingrowth of the isobars can be observed.

Additional Leachate Analyses

IDMS of the target leachate using a NIST-traceable, certified, ^{238}U standard (IV-ICPMS-71A, Inorganic Ventures) yielded a uranium recovery of 98(3) percent, with the main source of uncertainty being the verified initial mass of the loaded uranium target. The target was then analyzed for fission content using the RAPID determined isotopic compositions for each of the fission elements and NIST-traceable multi-element standards. The elemental concentrations in the irradiated target leachate were determined using both the RAPID online analysis and offline ICP-MS analysis (utilizing a traditional linear regression external calibration for masses without pre-determined isobaric interferences). Both analyses agreed within 2–5% for all analytes, however, when compared to the ORIGEN-predicted values, the elemental recoveries were only ~55–60 percent. Figure 6 shows the offline (red square) and online (black circle) results determined for each isotope mass (isotopes of the same mass were summed) in the target and compared with that predicted by ORIGEN (blue dotted line). These data sets were overlaid on an offline ICP-MS mass spectrum scan, which further illustrates the utility of separation before analysis; without it, no differentiation can be made between isobars, and other interfering factors such as Xe, Kr, and doubly-charged ^{235}U (all noted in Figure 6). There were a number of analytes that can be measured offline but were either too low to detect via online analysis, or do not elute with the current HPIC separation protocol, namely molybdenum and technetium.

Figure 6. A plot displaying the offline (red square) and online (black circle) analysis for each isotope mass (isotopes of the same mass were summed) in the target, compared with that predicted by ORIGEN (blue dotted line). The right y-axis is for the mass spectrum scan (gray lines) and the left y-axis is for the measured and predicted concentration data.

Lastly, gamma spectra of the irradiated pellet leachate were acquired using an HPGe detector. A number of fission isotopes were observed (see supplementary information), six of which were measured using both methods at 178 h with very good agreement. Table 3 shows the total amount of each of the fission isotopes in the irradiated pellet measured through both gamma analysis and RAPID. The recoveries of these isotopes in particular, when compared to gamma analysis, demonstrates the efficiency of the separation scheme, as all of these species have at least one isobaric interference when analyzed by mass.

Table 3.

The concentrations of six short-lived isotopes determined using both gamma spectroscopy and the RAPID protocol.

Analyte	Half-Life (d)	Gamma (ng total)	RAPID (ng total)	mass _{gamma} /mass _{RAPID} (%)
¹⁴⁰ La	1.68	0.107	0.108	99%
¹⁴¹ Ce	32.51	1.072	1.028	104%
¹⁴³ Ce	1.38	0.024	0.023	105%
¹⁴⁴ Ce	284.91	1.330	1.250	106%
¹⁴⁷ Nd	10.98	0.338	0.345	98%
¹⁴⁹ Pm	2.21	0.021	0.022	99%

It was hoped that the previous application of IDMS to RAPID for the acquisition of low-uncertainty measurements of lanthanide elements in a complex matrix [47] could be repeated here. However, it would only be warranted if full recovery of the sample was achieved. To understand this issue of low recovery, the SRIM software [53] was used to calculate the range of these fission isotopes, with an assumed 200 MeV energy (per fission), into a silicon target. It was calculated that, upon fission, the fission isotopes embed themselves ~20–25 μm into the walls of the quartz ampoule, making complete recovery via leaching difficult. A second, more aggressive, 8-hour heated leach with nitric (2ml, 8M, Optima) and hydrochloric acid (1ml, 10M, Optima) yielded an additional 20% recovery, confirming that the primary leach was not aggressive enough and that the assumption of uranium recovery being equivalent to the fission product recoveries was incorrect. In order to completely recover the elemental concentrations of these fission products in future studies, a partial microwave-assisted digest of the ampoule will be required.

CONCLUSIONS AND FUTURE WORK

The work presented here shows both the sensitivity and precision of the RAPID method when applied to elements of non-natural isotopic abundances in a uranium matrix. After leaching of the irradiated HEU targets, the isotopic compositions of several key fission elements, namely cesium, strontium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, and samarium, were investigated. Fission isotopes with half-lives as short as 33 h were successfully measured by mass 178 h post-irradiation. The majority of the major isotopes of each element presented a 1–2% difference between measured and an ORIGEN model, even with some of the analyzed masses existing at the femtogram level. Elemental concentrations were also determined using both the RAPID method and an offline ICP-MS linear regression external calibration. The isotopic concentrations of a number of short-lived isotopes were further confirmed by gamma analysis. Although the uranium in the target leachate was confirmed within 1% of the loaded material, the energetic nature of fission products resulted in partial recovery of the fission elements. This knowledge will lead to a more intensive digestion of future irradiated samples. Further investigations include the application of IDMS for high-precision fission isotopic concentration measurements and the application of the method to an irradiated ²³⁹Pu-based material. Once the method has been established using well-characterized isotopes, we also plan on extending the application to lesser characterized and modeled isotopes, such as ²³⁷Np, which is of interest at ORNL, as it is the target isotope used for the production of ²³⁸Pu.

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