Forensic investigations of two irradiated UO$_2$ fuels

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The detection and prevention of the proliferation of weapons-grade Pu is key to national nuclear security. Pu is produced as a byproduct of UO$_2$ irradiation in a nuclear reactor among other actinides and fission products (FPs). These FPs typically range between 70-170 amu and can be composed of more than 30 different elements. The exact distribution of these FPs within irradiated UO$_2$ depends upon the irradiation history of the fuel; some of the most important parameters are burnup, neutron spectrum, fuel enrichment, and cooling time (time since irradiation). Therefore, by measuring the FP distribution within unseparated irradiated nuclear fuel, modern forensics can attribute these parameters of the fuel's history to learn about the potential origin of unseparated fuel containing weapons-grade Pu. These techniques do not work, however, for separated (chemically purified) Pu. The process used to separate the Pu will decontaminate each FP differently, such that the FP distribution no longer correlates to the fuel's history.

A maximum likelihood technique to determine the most likely irradiation history of separated Pu has recently been developed, which utilizes various FP isotope ratios within the fuel[1]. The use of isotope ratios makes the process agnostic to chemical separation, and therefore applicable to separated or unseparated Pu. This technique has been shown to work for simulated fuel but remains to be tested against real fuel samples. Some of the nuclides necessary for these isotope ratios are stable and need to be measured by mass spectrometry. The most common type of mass spectrometry used in nuclear forensics is inductively coupled plasma mass spectrometry (ICP-MS); although it is a high sensitivity technique capable of detecting some FPs to the part-per-trillion (ppt) level, it is unable to resolve atomic isobars. This presents a challenge since some of the nuclides required for the maximum likelihood technique suffer from isobaric interference. For example, ^{150}Sm in the fuel experiences isobaric interference from ^{150}Nd, which is also present in the fuel. As a result, Sm and Nd must be separated prior to analysis by ICP-MS such that the ^{150}Sm/^{149}Sm isotope ratio may be measured for use with the maximum likelihood technique. The most commonly employed technique to separate lanthanides from each other is cation exchange chromatography utilizing α-hydroxyisobutyric acid (α-HIB) as an eluent.

Two different fuel samples have been separated to determine various Sm isotope ratios for use with the maximum likelihood technique. The first fuel sample was irradiated in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory, and the second in the University of Missouri Research Reactor (MURR). The HFIR fuel was 12.9 mg of ^{dep}UO$_2$ irradiated in a pseudo-fast spectrum of neutrons to a burnup of 4.4 ± 0.3 GWd/MTU[2], and the MURR fuel was three 16 mg pellets of ^{nat}UO$_2$ irradiated in a thermal spectrum to 0.97 ± 0.03 GWd/MTU[3]. The HFIR fuel was intended to resemble fuel originating from the blanket material of a fast breeder reactor (FBR), and the MURR fuel was

intended to resemble fuel originating from the core of a pressurized heavy-water reactor (PHWR). These reactor types are more commonly found in nations which are not under International Atomic Energy Agency (IAEA) safeguards. Therefore, fuel originating from these reactor types may be more susceptible to proliferation.

Chromatography was performed on the benchtop for each fuel sample using a 300 mm height by 3.1 mm inner diameter column. The stationary phase was a DOWEX 50W X4 200-400 mesh strong cation exchange resin prepared in the NH_4^+ form with a bed height of 200 mm. The fuel samples were loaded onto the column using a 1 M NH_4Cl solution at pH 3.00, then eluted through the column at 0.500 mL/min with 0.4 M α-HIB at pH 3.00. Fractions were collected for each free column volume, corresponding to 550 µL each, and assayed individually by ICP-MS after dilution to 5 mL with 1% HNO_3. The relevant mass bins were swept through the spectrometer 90 times total for each fraction, producing an average and standard deviation for each mass bin of each fraction. Calibration standards were prepared for Cs, Ce, Nd, Sm, Eu, Gd, and U with concentrations ranging between 0.01 to 1 ppb. Preliminary results for the chromatogram of the HFIR fuel is shown in Fig 1.
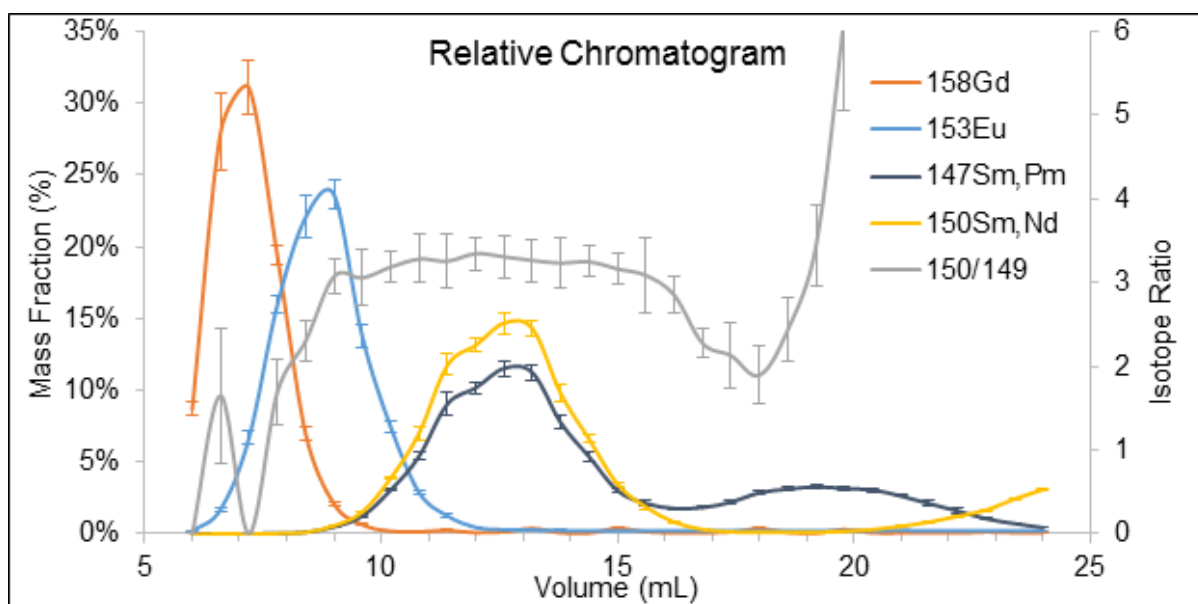

FIG. 1. Chromatogram of the HFIR fuel pellet performed at 0.4 M α-HIB and pH 3.00. The 150/149 (gray) ratio (read from the right-hand axis) is constant in the Sm elution peak.

The lanthanides are shown to elute in the expected order of decreasing atomic number. The 150 mass bin (yellow) shows a distinct elution profile for Sm at 13 mL, while Nd is shown to begin eluting at 21 mL. As Sm and Nd were successfully separated, the $^{150}Sm/^{149}Sm$ isotope ratio was determined using the fractions within the Sm elution peak. The mass bin ratio (gray) is shown to be constant in this region, indicating a constant $^{150}Sm/^{149}Sm$ isotope ratio. Twenty other Sm isotope ratios were determined in this way, as shown in Table I. The relevant $^{150}Sm/^{149}Sm$ and $^{152}Sm/^{149}Sm$ isotope ratios were measured successfully with low experimental error and are to be used with the maximum likelihood method to determine the most likely irradiation history of both fuel samples. These histories will then be compared

to the known history of the samples. The MURR fuel is still being investigated to measure the twenty other Sm isotope ratios.

A second approach to determine the irradiation history of separated Pu by investigating the Plutonium Uranium Redox Extraction (PUREX) process is underway. If the decontamination factor (DF) through the PUREX process were known for every FP element within irradiated fuel, it would be

Table I. Sm isotope ratios measured in the HFIR fuel after separation by cation exchange chromatography with 0.4 M α-HIB at pH 3.00.

Sm Ratio	Measured Value
147/148	$12.2 \pm 6.8\%$
147/150	$1.31 \pm 2.2\%$
147/151	$3.97 \pm 2.2\%$
147/152	$1.44 \pm 0.91\%$
147/154	$4.43 \pm 1.7\%$
148/152	$0.104 \pm 3.7\%$
148/151	$0.32 \pm 5.5\%$
148/152	$0.117 \pm 2.9\%$
148/154	$0.35 \pm 7.0\%$
149/147	$0.237 \pm 2.4\%$
149/148	$3.0 \pm 16\%$
149/151	$0.93 \pm 1.7\%$
149/154	$1.03 \pm 3.2\%$
150/149	$3.23 \pm 2.7\%$
150/151	$3.02 \pm 2.1\%$
150/152	$1.112 \pm 0.79\%$
150/154	$3.3 \pm 5.0\%$
151/152	$0.365 \pm 0.82\%$
151/154	$1.12 \pm 2.0\%$
152/149	$2.93 \pm 1.3\%$
152/154	$3.06 \pm 1.4\%$

possible to reconstruct the original FP distribution within separated Pu. If the original FP distribution were reconstructed, then traditional forensic techniques could be used to determine the burnup, cooling time, neutron spectrum, and enrichment of the fuel. Efforts in this investigation have focused on performing PUREX liquid-liquid extractions in the laboratory based on the industrial PUREX reprocessing scheme as developed at the Barnwell Nuclear Fuel Plant, an American reprocessing facility that was constructed but never operated commercially. Progress so far includes transcribing the industrial 10-stage counter-current flow process for the first PUREX extraction into a series of 15 batch extractions performed in the laboratory. These extractions were performed on the HFIR fuel feed with aqueous phase conditions of 3 M HNO_3 and 0.85 M $UO_2(NO_3)_2$ against an organic stream of n-dodecane containing 30% TBP by volume at 40°C. The phase ratio used for all 15 extractions was 2.3 mL of organic phase to 1 mL of aqueous phase. The DFs measured at the end of these 15 extractions are shown in Table II and represents the DFs of several FP elements through the first step of the PUREX process. Errors may be estimated on the order of 10%. The FP elements listed in this table are those which are readily assayed by

gamma or alpha spectrometry; other FP elements remain to be measured via mass spectrometry. Work will continue by performing the final 7 steps of the PUREX process and measuring the DFs of each FP element at each step. The measured DF at each step will then be multiplied across all steps to determine the overall DF of each FP element throughout the whole process.

Table II. Decontamination factors for the first step of the PUREX process.

Nuclide	Extraction (%)	Decontamination Factor
^{239}Pu	99	-
^{106}Ru	0.506	197.6
^{241}Am	0.67	150
^{144}Ce	0.212	470
^{125}Sb	0.028	3600
^{137}Cs	0.0018	55000
^{154,155}Eu	1.00	100

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