

A forensic investigation of the PUREX process to determine Pu separation conditions

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A forensic investigation of the PUREX process is underway to measure the distribution coefficients (D-values) and decontamination factors (DFs) of various fission products throughout the process, and to determine how these values may change under varying conditions. The goal is to learn more about how a sample of unknown Pu was separated by measuring the distribution of the trace fission products remaining in the separated Pu. Several PUREX extractions have been performed to determine the impact of temperature, acidity, and U saturation on the D-values of various fission product elements. All extractions are performed in a contained glovebox, and all extraction yields are assayed via gamma spectrometry. U saturation describes the ratio of U atoms in the aqueous phase to extractant molecules in the organic phase, multiplied by two. This is because a single U atom will chelate with two extractant molecules. Extractions performed at high U saturations have fewer free extractant molecules; therefore, the extraction yield of all metals in solution decreases. Table I shows how the D-values of some fission products change between extractions with low U saturation (0.5%) and high U saturation (50%). These saturations were used because they represent potential U saturation in various streams of a PUREX plant.

Table I. Fission product distribution coefficients (D-values) at two different U saturations.

Radionuclide	0.5% U Saturation		50% U Saturation	
	D-value	Extraction Yield	D-value	Extraction Yield
²⁴¹ Am	$(3.0 \pm 0.2) \times 10^{-2}$	$(8.1 \pm 0.5)\%$	$(8 \pm 1) \times 10^{-3}$	$(1.6 \pm 0.2)\%$
¹⁴⁴ Ce	$(2.1 \pm 0.2) \times 10^{-2}$	$(6.0 \pm 0.5)\%$	$(3.64 \pm 0.03) \times 10^{-3}$	$(0.830 \pm 0.007)\%$
¹⁵⁵ Eu	$(5.0 \pm 0.4) \times 10^{-2}$	$(13 \pm 1)\%$	$(1.30 \pm 0.07) \times 10^{-2}$	$(2.9 \pm 0.2)\%$
¹⁵⁴ Eu	$(4.9 \pm 0.3) \times 10^{-2}$	$(12.9 \pm 0.6)\%$	$(1.2 \pm 0.1) \times 10^{-2}$	$(2.7 \pm 0.3)\%$
¹⁰⁶ Ru	$(5.9 \pm 0.5) \times 10^{-2}$	$(15 \pm 1)\%$	$(1.7 \pm 0.1) \times 10^{-2}$	$(3.8 \pm 0.2)\%$
¹³⁷ Cs	$(3.77 \pm 0.08) \times 10^{-5}$	$(0.0113 \pm 0.0003)\%$	$(1.19 \pm 0.03) \times 10^{-5}$	$(0.0027 \pm 0.0001)\%$

In the general PUREX process, Pu and U are partitioned from each other by reducing Pu(IV) to Pu(III) to strip it from the organic phase (30% tri-*n*-butyl phosphate in *n*-dodecane), while U remains in the organic phase. Prior to this partition, all extractions performed will have D-values similar to the 50% U saturation columns in Table 1. After the partition, all further Pu purification extractions are performed at low U concentrations, similar to the 0.5% U saturation columns. Therefore, the difference in D-values between these extractions may be used to determine whether a sample of Pu(NO₃)₄ received further PUREX separations after the Pu-U partition step. Table II shows how the extracted inter-elemental

fission product ratios change between the two different extraction conditions. The biggest difference between the two extraction conditions can be seen in the Ce inter-elemental ratios.

Table II. Inter-elemental ratios of fission product distribution coefficients (D-values) compared at two different U saturations at 3 M HNO₃. Difference is calculated as (50% – 0.5%)/50%.

Inter-elemental Ratio	0.5% U Saturation	50% U Saturation	Difference
²⁴¹ Am/ ¹⁴⁴ Ce	1.4 ± 0.1	2.1 ± 0.3	35%
²⁴¹ Am/ ¹⁵⁴ Eu	0.59 ± 0.06	0.60 ± 0.09	1%
²⁴¹ Am/ ¹⁰⁶ Ru	0.50 ± 0.06	0.45 ± 0.07	-10%
²⁴¹ Am/ ¹³⁷ Cs	780 ± 60	650 ± 90	-21%
¹⁴⁴ Ce/ ¹⁵⁴ Eu	0.43 ± 0.05	0.28 ± 0.02	-52%
¹⁴⁴ Ce/ ¹⁰⁶ Ru	0.36 ± 0.04	0.21 ± 0.01	-69%
¹⁴⁴ Ce/ ¹³⁷ Cs	570 ± 50	305 ± 9	-86%
¹⁵⁴ Eu/ ¹⁰⁶ Ru	0.8 ± 0.1	0.76 ± 0.07	-11%
¹⁵⁴ Eu/ ¹³⁷ Cs	1330 ± 120	1080 ± 70	-22%
¹⁰⁶ Ru/ ¹³⁷ Cs	1570 ± 140	1400 ± 100	-10%

Fig. 1(a) plots two Ce inter-elemental activity ratios against each other at multiple HNO₃ concentrations to show how distinct the differences between the two extraction conditions can be. Using this preliminary data, it may be possible to distinguish if a sample of Pu(NO₃)₄ experienced PUREX extractions after the partition of U or not. Fig. 1(b) plots the ¹⁵⁴Eu/¹⁰⁶Ru activity ratio against nitric acid

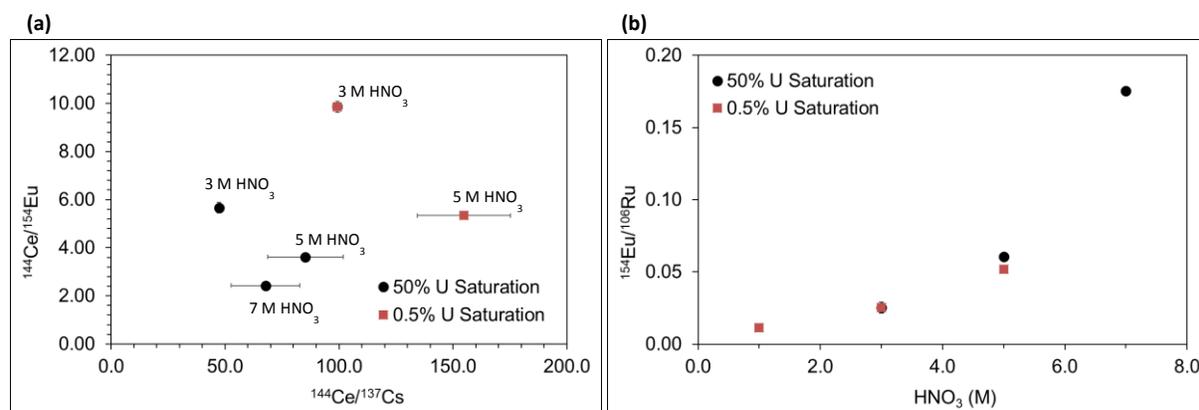


FIG. 1. Examples of how the activity ratio of fission product elements may be used to determine the separation conditions of Pu(NO₃)₄. Fig (a) on the left shows separation between PUREX extractions performed at two different U saturations over varying HNO₃ concentrations. Fig (b) on the right shows the possible U saturation independence of one fission product activity ratio.

concentration for the two different U saturations. Preliminary data suggests that the ¹⁵⁴Eu/¹⁰⁶Ru activity ratio may be independent of U saturation. This is useful information that would allow the determination of the HNO₃ concentration used in a PUREX separation regardless of the U saturation of the system.

Further effort is underway to complete the remaining extractions at 1, 3, 5, and 7 M HNO₃ at both 50% and 0.5% U saturation to investigate these effects in more detail.