

# **Irradiated UAmO<sub>2</sub> transmutation discs analyses: from dissolution to accurate isotopic analyses**

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## **Experimental**

### **Reagents**

Nitric acid ( $w = 67-70\%$ , J.T. Baker) was of Ultrex II reagent grade. Hydrofluoric acid ( $w = 40\%$ , Merck) was of Suprapur grade. Deionised water was provided by a MilliQ system (resistivity:  $18.2\text{ M}\Omega\text{ cm}$ , Millipore, Milford).

A  $2\text{ mol L}^{-1}\text{ HNO}_3$  solution containing  $2\times 10^{-3}\text{ mol L}^{-1}$  ascorbic acid and  $2\times 10^{-3}\text{ mol L}^{-1}$  hydroxylammonium nitrate (hereafter referred to as UTEVA/Pu elution solution) was freshly prepared before use by diluting high purity nitric acid with deionized water and by weighing ascorbic acid (Sigma Aldrich, pharmaceutical secondary standard) and hydroxylammonium hydrochloride, (Sigma Aldrich, purity  $> 99.999\%$  for trace metal analysis).

A solution containing  $7\times 10^{-3}\text{ mol L}^{-1}$  ammonium oxalate (hereafter this solution is referred to as UTEVA/U elution solution) was prepared by dissolving ammonium oxalate monohydrate (Aldrich Chemistry, purity  $\geq 99.99\%$  for trace analysis) in deionized water.

( $0.3\text{ mol L}^{-1}/0.05\text{ mol L}^{-1}$ )  $\text{HNO}_3/\text{HF}$  mixture was prepared by diluting high purity nitric acid and hydrofluoric acid (Merck, Suprapur) in deionized water. Hereafter this solution is referred to as TEVA/Pu elution solution.

HPLC eluents was prepared by dissolution of 2-Hydroxy-MethylButyric Acid (HMB, Sigma-Aldrich, Purity  $> 98\%$ ) in deionised water and adjusted to the desired pH with  $28\%$  ammonia (Sigma Aldrich, purity  $\geq 99.99\%$ ). Two solutions were prepared:  $[\text{HMB}] = 0.1\text{ mol L}^{-1} / \text{pH} = 3.6$  and  $[\text{HMB}] = 0.2\text{ mol L}^{-1} / \text{pH} = 4.5$ . The pH was determined by a Metrohm 713 pHmeter. The HPLC eluents were filtered on a Millipore filter with  $0.22\text{ }\mu\text{m}$  pore diameter.

## Reference Materials

The U spike solution was the IRMM 054 certified reference material (CRM) provided by the Joint Research Centre of the European Commission (EC-JRC). This CRM contains high amounts of  $^{235}\text{U}$  isotope and is certified for the  $^{235}\text{U}$  isotope amount content and the isotope ratios.

The Pu spike solution was the IRMM 049d CRM provided by EC-JRC. This CRM contains high amounts of  $^{242}\text{Pu}$  isotope and is certified for the  $^{242}\text{Pu}$  isotope amount content and the isotope ratios.

The Am spike solution was the STAM CRM provided by the Analytical Methods Committee (CETAMA) of the CEA. It contains high amounts of  $^{243}\text{Am}$  isotope and is certified for the  $^{243}\text{Am}$  isotope amount content and the isotope ratios.

The Nd spike solution was prepared by dissolving a  $^{150}\text{Nd}$  enriched (95%) non-radioactive neodymium oxide powder provided by Eurisotop in  $3 \text{ mol L}^{-1} \text{ HNO}_3$ . Once the dissolution was achieved, the solution was diluted to obtain a Nd mass fraction of about  $10 \mu\text{g g}^{-1}$  (this solution is hereafter referred to as  $^{150}\text{Nd}$  spike solution). The  $^{150}\text{Nd}$  spike is not certified for isotope ratios or mass fraction.

The 3135a CRM (natural Nd), provided by the National Institute of Standards and Technology (NIST) was used to determine the  $^{150}\text{Nd}$  spike mass fraction by reverse isotope dilution. The 3135a CRM is certified for the mass fraction (and not for isotope ratios).

Analytical method validation for  $^{234}\text{U}/^{238}\text{U}$  and  $^{236}\text{U}/^{238}\text{U}$  isotope ratios determination was performed on the IRMM 187 CRM provided by EC-JRC. This solution is certified for the  $^{234}\text{U}/^{238}\text{U}$  (0.00038700(16),  $k = 2$ ) and  $^{236}\text{U}/^{238}\text{U}$  (0.000071965(39),  $k = 2$ ) isotope ratios.

## Separation experimental set-up

### TEVA resin separation

The TEVA resin (Triskem, 100–150  $\mu\text{m}$  particle size in 2 mL prepackaged columns) was used to separate U, Pu and trivalent elements (Am, Cm and Nd). This separation is compared of several steps (Figure S1). First,  $\text{HNO}_3$  was added to each sample to reach an amount fraction of  $8 \text{ mol L}^{-1}$  in the solution. Before entering the glove box, the TEVA resin-filled column is first conditioned with  $8 \text{ mol L}^{-1}$   $\text{HNO}_3$ . After entering the glove box, the sample is deposited on top of the column. The resin extracted U and Pu and did not retain the trivalent elements. This fraction is retrieved in a PFA vial.  $4.5 \text{ mL}$  of  $8 \text{ mol L}^{-1}$   $\text{HNO}_3$  was fed to the column to elute the remaining trivalent elements. The trivalent elements fraction was retrieved in the same PFA vial. The trivalent element traces were washed with  $4.5 \text{ mL}$  of  $8 \text{ mol L}^{-1}$   $\text{HNO}_3$ . This fraction was not retrieved. Next, U was eluted with  $4.5 \text{ mL}$  of  $3 \text{ mol L}^{-1}$   $\text{HNO}_3$  and retrieved if needed. U was washed with  $13.5 \text{ mL}$  of  $3 \text{ mol L}^{-1}$   $\text{HNO}_3$ , which were retrieved. Lastly, Pu was eluted with the TEVA/Pu solution:  $4.5 \text{ mL}$  are poured and retrieved.

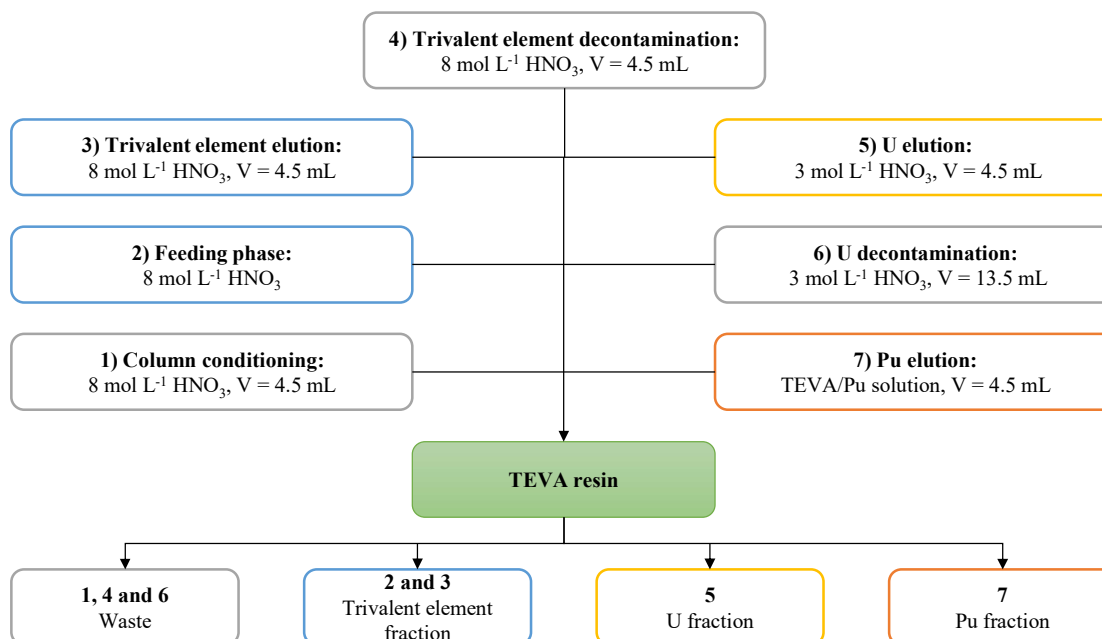


Fig. S1: Separation scheme used for the TEVA resin

### UTEVA resin separation

The UTEVA resin (Triskem, 100–150  $\mu\text{m}$  particle size in 2 mL prepackaged columns) was used to obtain purified fractions of U and Pu (see Figure S2). Before entering the glove box, the UTEVA resin was conditioned with 4.5 mL of  $(6 \text{ mol L}^{-1}/0.1 \text{ mol L}^{-1}) \text{HNO}_3/\text{H}_2\text{O}_2$  mixture. After entering the glove box, the sample, previously conditioned in  $(6 \text{ mol L}^{-1}/0.1 \text{ mol L}^{-1}) \text{HNO}_3/\text{H}_2\text{O}_2$  mixture, was fed to the column. Trivalent elements, not retained by the resin, was washed by 9 mL of  $(6 \text{ mol L}^{-1}/0.1 \text{ mol L}^{-1}) \text{HNO}_3/\text{H}_2\text{O}_2$  mixture, and not retrieved. Pu was eluted by 4.5 mL of UTEVA/Pu elution solution, and this elution fraction, containing purified Pu, was retrieved in a PFA vial. The remaining Pu was washed by several successive depositions of 4.5 mL UTEVA/Pu elution solution: six successive depositions of 4.5 mL were performed when the separation was dedicated to isotopic ratio analyses and three successive depositions of 4.5 mL were performed when the separation was dedicated for double isotope dilution measurements. Lastly, U was eluted by 4.5 mL UTEVA/U elution solution.

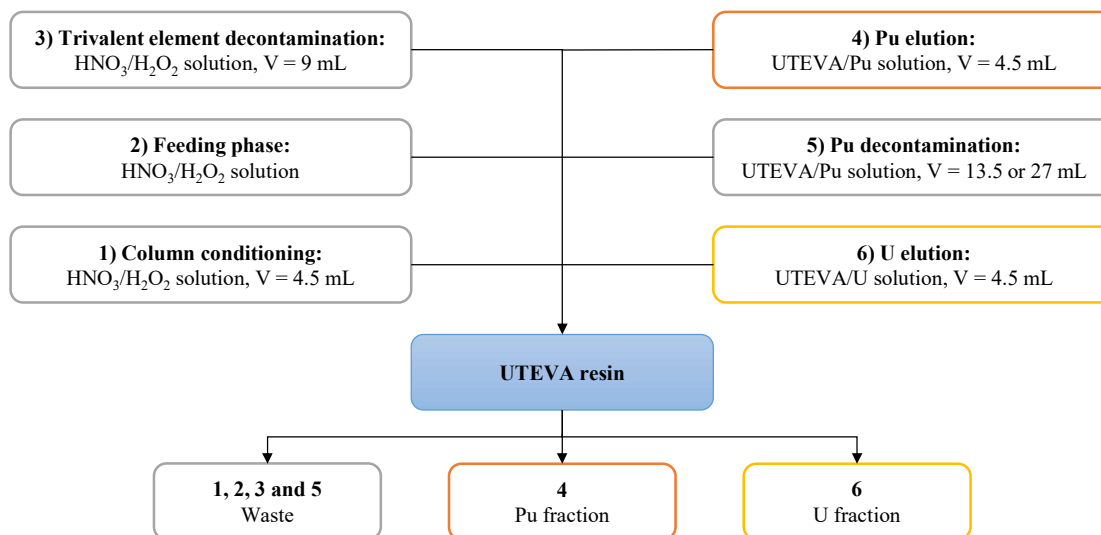


Fig. S2: Separation scheme used for the UTEVA resin

### *HPLC separation*

The HPLC system is composed of an Agilent 1200 series quaternary pump, isocratic pump, and vacuum degasser, a six-way manually operated rotary Rheodyne valve (model 7125) with 20  $\mu\text{L}$  sample loop and the appropriate injection syringe, the Phenomenex LUNA SCX column (particle size = 5  $\mu\text{m}$ , pore sizes = 100  $\text{\AA}$ , internal diameter = 4.6 mm and column length = 250 mm), a 10 mm Z-flow cell connected to UV/Vis Agilent Cary 60 spectrophotometer by optical fibers (SEDI ATI SR600). PEEK tubing with internal diameter of 0.25 mm was used. The Rheodyne valve, the syringe, the LUNA SCX column and the Z-flow cell are located inside the glove box. The Agilent 1200 series system, the eluents and the UV/Vis spectrophotometer are located outside the glove box. The separation was performed with a flow rate fixed at 1  $\text{mL min}^{-1}$  for the quaternary pump (HMB solutions) and at 0.5  $\text{mL min}^{-1}$  for the isocratic pump (0.5  $\text{mol L}^{-1}$   $\text{HNO}_3$  solution). The HMB eluent was introduced in gradient mode: the gradient started at  $t = 0$  min with 100 % [HMB] = 0.1  $\text{mol L}^{-1}$  / pH = 3.6 and finished at  $t = 30$  min with 50 % [HMB] = 0.1  $\text{mol L}^{-1}$  / pH = 3.6 and 50 % [HMB] = 0.2  $\text{mol L}^{-1}$  / pH = 4.5.

**Nd isotope ratio of the NIST 3135a CRM and the  $^{150}\text{Nd}$  spike**

	$^{142}\text{Nd}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{145}\text{Nd}/^{144}\text{Nd}$	$^{146}\text{Nd}/^{144}\text{Nd}$	$^{148}\text{Nd}/^{144}\text{Nd}$	$^{150}\text{Nd}/^{144}\text{Nd}$
Results	1.1400	0.51204	0.34868	0.7230	0.24234	0.23757
RSD	0.02%	0.01%	0.01%	0.02%	0.03%	0.05%
$U(k = 2)$	0.0018	0.00067	0.00044	0.0012	0.00057	0.00075
$U(\%, k = 2)$	0.15%	0.13%	0.13%	0.15%	0.23%	0.31%

Table S1: Nd isotope ratio for the NIST 3135a CRM using the TE method

	$^{142}\text{Nd}/^{150}\text{Nd}$	$^{143}\text{Nd}/^{150}\text{Nd}$	$^{144}\text{Nd}/^{150}\text{Nd}$	$^{145}\text{Nd}/^{150}\text{Nd}$	$^{146}\text{Nd}/^{150}\text{Nd}$	$^{148}\text{Nd}/^{150}\text{Nd}$
Résultats	0.01105	0.005613	0.012664	0.004780	0.011461	0.009906
RSD	0.64%	0.31%	0.28%	0.26%	0.20%	0.08%
$U(k = 2)$	0.00014	0.000036	0.000072	0.000026	0.000052	0.000034
$U(\%, k = 2)$	1.3%	0.63%	0.57%	0.53%	0.46%	0.34%

Table S2: Nd isotope ratio for the  $^{150}\text{Nd}$  spike using the TE method