Supplementary Information

Extraction Chromatographic Methods in the Sample Preparation Sequence for Thermal Ionization Mass Spectrometric Analysis of Plutonium Isotopes

Jay W. Grate, Matthew J. O'Hara, Anne F. Farawila, Matt Douglas, Morgan M. Haney, Steven L. Petersen, Tapas C. Maiti, and Christopher L. Aardahl*

EXPERIMENTAL SECTIONS

Radiotracer materials and separations. Solutions of 7.5 M or 7.2 M nitric acid were spiked with actinides. Sulfamic acid, ferrous ammonium sulfate, and sodium nitrite or hydrogen peroxide were then added according to the procedure below. All chemicals were reagent grade or better. TEVA-resin separations were carried out as described in **Table SI-1,** while DGA –resin separations were carried out as in **Table SI-2**. Flow rates were 1 mL/min for all solutions on TEVA-resin and DGA-resin. Anion exchange separations at 2 mL and 0.1 mL column bed volumes were carried out by the procedures in **Table SI-3**. Steps and reagents are the same for both column sizes except for a water rinse that was added to the 0.1 mL column procedure to improve plutonium recovery. For the 2 mL anion exchange columns, flow rates were 3 mL/min for non critical steps (e.g. condition, wash, Th elution) and 1 mL/min for the more critical sample load and Pu/Np elution steps. For the 0.1 mL column, the flow rates were 500 μL/min for non critical steps (e.g. condition, wash, Th elution) and 250 μL/min for the more critical sample load and Pu/Np elution steps.

The ^{239}Pu, ^{230}Th, and ^{233}U were analyzed using a liquid scintillation analyzer (Perkin Elmer Tri-Carb 3100TR) with a 70-2000 channel window. Typically, 0.2mL of each fraction was dispensed to 15mL of liquid scintillation cocktail (Perkin Elmer Ultima

Gold AB) and counted for 30 min to 1 hour. Background vials containing typically 0.2mL nitric acid at 7.5M in cocktail were also counted. The ^{241}Am, and ^{237}Np were analyzed using a gamma counter (Perkin Elmer Wizard 1470). Counts were recorded using a fixed window (3-75 channels for Am and 3-150 channels for Np). Typically 1 mL of each fraction was dispensed into a test tube and counted for 30 min to 1 hour. Background test tubes containing typically nitric acid at 7.5M were also counted. For each instrument, background counts were averaged and the value was subtracted from the raw counts resulting in "net counts" reporting data. In addition, an aliquot of the loading solution was counted and used as reference to determine the actinide recovery in each fraction. The percent recovery threshold for each collected fraction for both the liquid scintillation and gamma counting was 0.5%". *Caution: radioactive isotopes represent radiological hazards.*

Table SI-1. Method for Pu/Np isolation on TEVA-resin

Step	**Reagent/Sample**	**Volume (typical), mL[c]**	**Actinide Eluted**	**Notes**
1. Column condition	7.5 M HNO_3[a]	10		
2. Sample load	Sample in 7.5 M HNO_3[b]	8	Am, U	d
3. Column Wash	7.5 M HNO_3[a]	15	Am, U	d
4. Pu Oxidation	6M HCl + 0.2M $NaNO_2$	5		
5. Th elute	9M HCl	7.5	Th	
6. Pu/Np elute	0.2M HCl	10	Pu/Np	

a Solution contains 0.1M H_2NSO_3H and 0.02M $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$

b Direct spike: same as (1) above with the addition of 0.2M $NaNO_2$ just before the load

c Flow rates through TEVA columns were 1 mL/min

d Warning: Np may partially elute if Np(IV) reduction is incomplete.

Table SI-2. Method for Pu/Np isolation on DGA-resin.

Step	Reagent/Sample	Volume (typical),[c] mL	Actinide Eluted	Notes
1. Column condition	7.5 M HNO_3[a]	5		
2. Sample load	Sample in 7.5 M HNO_3[b]	8		d
3. Column Wash	7.5 M HNO_3[a]	10		d
4. U elute	0.35M HNO_3[a]	15	U	
5. Pu Oxidation	1M HCl + 0.2M $NaNO_2$	5		
6. Am elute	1M HCl	15	Am	
8. Pu / Np / Th elute	0.5M HNO_3 + 0.03M $C_2O_4H_2$	20	Pu / Np / Th	e

a Solution contains 0.1M NH_2SO_3H, 0.02M $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and 0.01M $NaNO_2$

b Simple sample matrix for spike same as (1) above

c Flow rates through TEVA columns were 1 mL/min

d Warning: Np may partially elute if Np(IV) reduction is incomplete.

e Th may prematurely elute, depending on sample matrix and DGA column geometry

Table SI-3. Methods for the anion exchange column separations

Step	Reagent/ Sample	2 mL AnIX		0.1 mL AnIX		Actinide Eluted
		Volume, mL	Flow rate, mL/min	Volume, µL	Flow rate, µL/min	
1. Column condition	7.2 M HNO_3[a]	5	3	500	500	
2. Sample load	Sample in 7.2 M HNO_3[b]	6	1	500	250	Am
3. Column Wash	7.2 M HNO_3[a]	32[c]	3	1200	500	U
4. Th elute	9 M HCl	12	3	600	500	Th
5. Pu/Np elute	1.2 M HCl	15	1	300	250	Pu/Np
5. Pu/Np elute	water	0	_	500	250	Pu/Np

a. Solution contains 0.01 M H_2O_2

b. Solution contains 0.1M H_2NSO_3H, 0.02M $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ and 0.01 M H_2O_2. The later was added just before the column load

c. The first 4mL of wash is added to the sample fraction to complete Am elution

RESULTS AND DISCUSSION

Radiotracer-level recoveries from the column-based separations.

Table SI-4. Calculated cumulative yields (%) in Pu/Np fraction for hypothetical sequences starting with TEVA-resin.

Separations\actinide	Am	U	Th	Np	Pu
TEVA-resin (1)	<0.5	1.5	<0.5	95	100
TEVA-resin – 2 mL AnIX (1 x 2a)	<0.5	<0.5	<0.5	78	87
TEVA-resin – 2 mL AnIX – 0.1 mL AnIX (1 x 2a x 2b)	<0.5	<0.5	<0.5	58	86
TEVA-resin – 2 mL AnIX – 0.1 mL AnIX (1 x 3)	<0.5	<0.5	<0.5	48	88

Table SI-5. Calculated cumulative yields (%) in Pu/Np fraction for hypothetical sequences starting with DGA-resin.

Separations\actinide	Am	U	Th	Np	Pu
DGA-resin (1)	<0.5	<0.5	90	78	91
DGA-resin – 2 mL AnIX (1 x 2a)	<0.5	<0.5	1.4	64	79
DGA-resin – 2 mL AnIX – 0.1 mL AnIX (1 x 2a x 2b)	<0.5	<0.5	<0.5	48	78
DGA-resin – 2 mL AnIX – 0.1 mL AnIX (1 x 3)	<0.5	<0.5	0.5	40	80