A Novel Sequential Injection Method for Rapid and Simultaneous Determination of ^{236}U, ^{237}Np and Plutonium isotopes in Seawater

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This Supporting Information describes the details of experimental operations including sample pre-treatment and chromatographic separations. It also contents one Figure and two Tables.

EXPERIMENTAL

Sample pre-treatment

To optimize the iron hydroxide co-precipitation condition, 200 mL of seawater sample spiked with known amounts of ^{242}Pu (ca. 10 mBq) and ^{237}Np (ca. 1 mBq) was used and 0.2-2 mL of conc. HCl was added to acidify the seawater to 0.9-1.9. 0.03-0.2 mL of 0.1 g/mL Fe (in the form of $FeCl_3$) was added to a Fe concentration of 15-100 mg/L. Unless otherwise stated, the sample was stirred for 20 minutes with nitrogen bubbling after addition of 600 mg of $K_2S_2O_5$. 6 mol/L NaOH was added to adjust the pH to 10-11 and the supernatant was discarded after centrifuging the sample at 4000 rpm for 10 minutes. The residue was dissolved with 2 mol/L HCl and 110 mg of $K_2S_2O_5$ was added. Conc. $NH_3 \cdot H_2O$ was added to adjust the pH to 8-9 and the sample was centrifuged. After discarding the supernatant, the residue was dissolved with 2 mol/L HCl to 10 mL.

To further optimize the pre-concentration procedure for 10 L filtrated seawater, 10 mL of conc. HCl was added to adjust pH to 2. Known amounts of ^{237}Np and ^{242}Pu were spiked. 2-5 mL of 0.1 g/mL Fe solution (corresponding to 20-100 mg/L Fe in 10 L seawater) and 2-20 g of $K_2S_2O_5$ were added. The sample was stirred by N_2 bubbling for 20 minutes, then a two-step co-precipitation or one-step co-precipitation combing acid digestion was applied depending on the experimental conditions (see Table 1). In the two-step co-precipitation, 6 mol/L NaOH was added to adjust the pH to 10-11. The sample was kept still overnight, and then the supernatant was discarded. Conc. HCl was added to dissolve the residue and conc. $NH_3 \cdot H_2O$ was added to adjust pH to 8-9. The sample slurry was centrifuged at 4000 rpm for 5 minutes and the

supernatant was poured away. The residue was dissolved with conc. HNO_3 and the sample was finally constituted to 3 mol/L HNO_3 for the automated chromatographic separation.

In the one-step co-precipitation, 10% $NH_3 \cdot H_2O$ was slowly added to adjust the pH to 8-9 and 40 g of NaCl was then added with vigorously N_2 bubbling. The sample was kept still for 0.5-1 h, and then the supernatant was discarded. The sample slurry was centrifuged at 4000 rpm for 5 minutes and the supernatant was discarded. Afterwards, acid digestion was performed to decompose the organic substances/colloids contained in the precipitate. In detail, the residue was dissolved with 40 ml of *aqua regia* and boiled on a hotplate at 200 ºC for 2 h. After cool down, the sample was filtrated with a GA/F filter paper, the filter paper and the beaker were washed with 30 mL of 0.2 mol/L HCl and combined into the filtrate. Conc. $NH_3 \cdot H_2O$ was then added to adjust the pH to 8-9 and the sample was centrifuged at 4000 rpm for 10 minute. The residue was dissolved with 3 mL of conc. HCl and the solution was diluted to ca. 200 mL with water. 500 mg of $K_2S_2O_5$ was added and sample was stirred for 20 minutes. 10% $NH_3 \cdot H_2O$ was added to pH 8-9 and the sample was centrifuged at 4000 rpm for 10 minutes. After discarding the supernatant, the residue was firstly dissolved in 1-2 mL of conc. HCl and then with conc. HNO_3. The sample was finally adjusted to 3 mol/L HNO_3 for the automated chromatographic separation.

Chromatographic separation

Investigation on separation behaviour of radionuclides on UTEVA column

An artificial solution in HCl or HNO_3 media spiked with ca. 0.5 mBq of ^{237}Np, 5 mBq of ^{242}Pu, 62 µBq (5 ng) of ^{238}U, 20 µBq (5 ng) of ^{232}Th and 30 mg of Fe was prepared. A freshly packed 1-mL (0.5 cm i.d. × 5 cm length) UTEVA column was used during the investigation, which was preconditioned with acidic solution identical to the sample loading media prior to the column separation.

Condition A: 200 mg of ascorbic acid was added to a 5-mL artificial solution in 6 mol/L HCl. The sample was loaded onto the UTEVA column. The column was rinsed with 10 mL of 0.1 mol/L NH_2OH·HCl-6 mol/L HCl and uranium was finally eluted with 10 mL of 0.025 mol/L HCl.

Condition B: 200 mg of ascorbic acid and 100 mg of $NaNO_2$ were sequentially added to a 5-mL artificial solution in 2 mol/L HNO_3. The sample was loaded onto the UTEVA column, which was then rinsed with 10 mL of 2 mol/L HNO_3 and 10 mL of 6 mol/L HCl. Plutonium and neptunium were eluted with 10 mL of 0.1 mol/L NH_2OH·HCl-2 mol/L HCl. Uranium was finally eluted with 10 mL of 0.025 mol/L HCl.

Condition C: 200 mg of ascorbic acid and 100 mg of $NaNO_2$ were sequentially added to 5-mL of artificial solution in 3 mol/L HNO_3. The sample was loaded onto the UTEVA column. The column was rinsed with 10 mL of 3 mol/L HNO_3 and 10 mL of 6 mol/L HCl. Plutonium and neptunium were eluted with 10 mL of 0.1 mol/L NH_2OH·HCl-2 mol/L HCl. Uranium was finally eluted with 10 mL of 0.025 mol/L HCl.

Condition D: 200 mg of ascorbic acid and 100 mg of $NaNO_2$ were sequentially added to a 5-mL of artificial solution in 2 mol/L HNO_3. 0.2 g of $Al(NO_3)_3$ was added to the sample which was then loaded onto the UTEVA column. The column was sequentially rinsed with 20 mL of 2 mol/L HNO_3, 20 mL of 6 mol/L HCl and 20 mL of 6 mol/L HCl-0.05 mol/L $H_2C_2O_4$. Uranium was eluted with 20 mL of 0.025 mol/L HCl.

All effluents, washes and eluates from the column separation were collected in 5-10 ml fractions, evaporated to dryness, and finally re-constituted in 5 mL of 0.5 mol/L HNO_3 for quantification of ^{237}Np, ^{242}Pu, ^{232}Th and ^{238}U with ICP-MS.

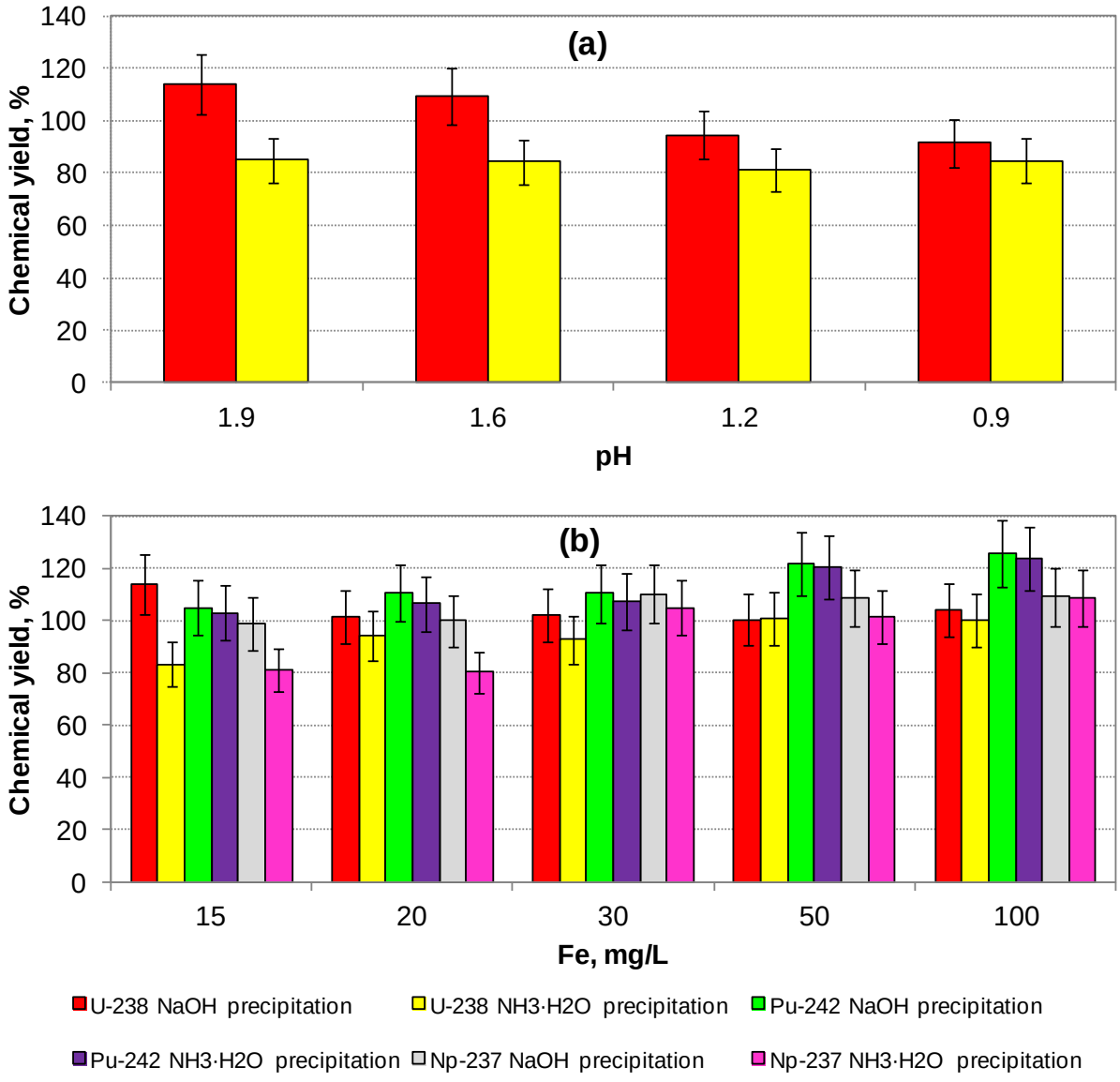
Investigation on separation performance of TEVA-UTEVA column

To investigate the effect of nitric acid concentration on the separation behaviour of stacked TEVA-UTEVA, 100 mL of 0.2 mol/L HCl was spiked with ca. 20 mBq of ^{242}Pu, 1.0 Bq (80 µg) of ^{238}U and 800 mg of Fe. 500 mg of $K_2S_2O_5$ was added and the sample was stirred for 20 minutes. 6 mol/L NaOH was added to adjust the pH to 9-10 and the sample was centrifuged at 4000 rpm for 10 minutes. The supernatant was discarded and the precipitate was dissolved with conc. HNO_3 to a final concentration of 4 mol/L HNO_3, and 200 mg of $NaNO_2$ was added. The sample (ca. 20 mL) was evenly divided into four sub-samples by weight, three of which were diluted with de-ionized water to 1, 2 and 3 mol/L HNO_3, respectively. Each sub-sample was loaded manually onto a stacked TEVA-UTEVA column (both were 1 mL volume), which was then rinsed with 100 mL of HNO_3 of identical concentration to the sample loading solution. After splitting the stacked TEVA-UTEVA column, plutonium was eluted from TEVA with 50 mL of 0.1 mol/L $NH_2OH{\cdot}HCl$-2 mol/L HCl, while uranium was eluted from UTEVA with 50 mL of 0.025 mol/L HCl. Effluents, washes and eluates were collected in 5-10 mL fractions, evaporated to dryness, and finally reconstituted in 5 mL of 0.5 mol/L HNO_3 for quantification of ^{237}Np and ^{242}Pu with ICP-MS.

FIGURE CAPTIONS

Figure S-1. Effect of pH (a) and iron concentration (b) in seawater on the co-precipitation efficiency of uranium, neptunium and plutonium (> 100% chemical yields for U, Pu and Np might be consequences of artifact of matrix effects in the ICP-MS measurement)

Figure S-1.


(a)
Chemical yield, %
140
120
100
80
60
40
20
0
1.9
1.6
1.2
0.9
pH
(b)
Chemical yield, %
140
120
100
80
60
40
20
0
15
20
30
50
100
Fe, mg/L
U-238 NaOH precipitation
U-238 NH3·H2O precipitation
Pu-242 NaOH precipitation
Pu-242 NH3·H2O precipitation
Np-237 NaOH precipitation
Np-237 NH3·H2O precipitation

TABLES

Table S-1. Sorption and elution behaviour of thorium, uranium, neptunium and plutonium on UTEVA resin*

Experimental condition	Sample loading medium	Valence adjustment reagents	Loading, washing and eluting solution	Chemical yield, %			
				^{232}Th	^{237}Np	^{238}U	^{242}Pu
A	6 mol/L HCl	200 mg of ascorbic acid	5 mL of sample loading solution in 6 mol/L HCl	34.5	43.1	0.4	93.2
			10 mL of 0.1 mol/L NH_2OH·HCl-6 mol/L HCl	64.7	2.2	0.2	6.8
			10 mL of 0.025 mol/L HCl	0.8	54.7	99.4	0.0
B	2 mol/L HNO_3	200 mg of ascorbic acid + 100 mg of $NaNO_2$	5 mL of sample loading solution in 2 mol/L HNO_3	0.5	42.9	0.0	3.9
			10 mL of 2 mol/L HNO_3	3.3	7.5	0.0	0.2
			10 mL of 6 mol/L HCl	90.9	0.0	0.2	0.0
			10 mL of 0.1 mol/L NH_2OH·HCl-6 mol/L HCl	5.2	0.0	0.1	2.1
			10 mL of 0.025 mol/L HCl	0.1	49.6	99.6	93.8
C	3 mol/L HNO_3	200 mg of ascorbic acid + 100 mg of $NaNO_2$	5 mL of sample loading solution in 3 mol/L HNO_3	0.5	3.4	0.0	2.3
			10 mL of 3 mol/L HNO_3	5.8	3.9	0.2	0.1
			10 mL of 6 mol/L HCl	89.9	2.8	0.8	0.0
			10 mL of 0.2 mol/L NH_2OH·HCl-6 mol/L HCl	0.3	86.2	97.0	97.7
			10 mL of 0.025 mol/L HCl	3.5	3.4	1.9	0.0
D	2 mol/L HNO_3	200 mg of ascorbic acid + 100 mg of $NaNO_2$ #	5 mL of sample loading solution in 2 mol/L HNO_3	7.9	60.5	0.0	4.3
			0-10 mL of 2 mol/L HNO_3	5.2	26.9	0.0	5.6
			10-20 mL of 2 mol/L HNO_3	6.0	2.7	0.0	1.1
			0-10 mL of 6 mol/L HCl	50.4	0.2	0.0	0.1
			10-20 mL of 6 mol/L HCl	4.9	11.5	0.1	8.8
			0-10 mL of 0.05 mol/L $H_2C_2O_4$-6 mol/L HCl	13.1	0.0	0.2	6.8
			10-20 mL of 0.05 mol/L $H_2C_2O_4$-6 mol/L HCl	6.4	0.1	1.1	16.5
			0-10 mL of 0.025 mol/L HCl	1.9	0.1	95.0	55.2
			10-20 mL of 0.025 mol/L HCl	0.1	0.1	1.2	0.0
			Ashed UTEVA	4.1	0.0	2.4	1.5

*The uncertainties of all values are < 10%.

Before sample loading, 0.2 g of $Al(NO_3)_3$ was added to increase $[NO_3^-]$ without changing $[H^+]$.

Table S-2. The programmable operations and positions of valves in the SI analyzer for chromatographic separation of uranium, neptunium and plutonium with TEVA and UTEVA

Step no.	Operation of syringe pump	Flow rate, mL/min	Valve Position		
			INV[&]	SV-1[#]	SV-2[#]
I	1) aspirate 25 mL of deionised water*	12.0	1	1	1
	2) dispense 25 mL of deionised water	6.0	1	8	1
	3) aspirate 1 mL air	6.0	1	1	1
	4) aspirate 15 mL of 3 mol/L HNO_3	12.0	1	3	1
	5) dispense 5mL of 3 mol/L HNO_3	6.0	1	7	1
	6) dispense 5 mL of 3 mol/L HNO_3	6.0	1	9	4
	7) dispense 5 mL of 3 mol/L HNO_3	6.0	1	8	4
II	8) aspirate 20 mL of 3 mol/L HNO_3	12.0	1	3	4
	9) dispense 20 mL of 3 mol/L HNO_3 to TEVA-UTEVA	3.0	2	8	4
III	10) aspirate the sample solution (ca. 20 mL)	3.6	2	7	4
	11) dispense the sample solution (ca. 20 mL) onto connected TEVA-UTEVA	1.2	2	8	4
IV	12) aspirate 20 mL of 3 mol/L	12.0	2	3	4
	13) dispense 20 mL of 3 mol/L to connected TEVA-UTEVA	1.2	2	8	4
V	14) aspirate 20 mL of 1 mol/L	12.0	2	2	4
	15) dispense 20 mL of 1 mol/L to connected TEVA-UTEVA	1.2	2	8	4
	Repeat step 12-13 for three times				
VI	16) aspirate 20 mL of 1 mol/L HNO_3	12.0	2	2	4
	17) dispense 20 mL of 1 mol/L HNO_3 to TEVA	2.4	1	9	3
	18) aspirate 20 mL of 6 mol/L HCl	12.0	1	4	3
	19) dispense 20 mL of 6 mol/L HCl to TEVA	2.4	1	9	3
VII	20) aspirate 20 mL of 0.1 mol/L $NH_2OH{\cdot}HCl$ -2 mol/L HCl	12.0	1	6	3
	21) dispense 20 mL of 0.1 mol/L $NH_2OH{\cdot}HCl$ -2 mol/L HCl to TEVA	1.2	1	9	4
	22) aspirate 20 mL of 0.025 mol/L HCl	12.0	1	5	4
	23) dispense 20 mL of 0.025 mol/L HCl	1.2	1	10	4

*Only for operation, the solenoid valve (SV-3) located at the head of the syringe pump is assigned to 'in' position; for all the other operations, SV-3 is always at 'out' position. & position 1: port 1 and 2, port 3 and 4, port 5 and 6, port 7 and 8, and port 9 and 10, are connected respectively; position 1: port 1 and 10, port 2 and 3, port 4 and 5, port 6 and 7, and port 8 and 9 are connected, respectively. #position no. *x* means that, the central port of the selection valve is connected with the ambient port no. *x*.