

Supporting Information

**Automated method for concurrent determination of thorium
(^{230}Th , ^{232}Th) and uranium (^{234}U , ^{235}U , ^{238}U) isotopes in
water matrices with ICP-MS/MS**

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Table S.1 Optimized ICP-MS/MS parameter for Th and U measurement

Parameter	Settings	Unit
Plasma power	1560	W
Nebulizer gas flow rate	1.15	L/min
Auxiliary gas flow rate	1.2	L/min
Cooling gas flow rate	15	L/min
Extraction lens 1 voltage	-11.2	V
Extraction lens 2 voltage	-150.0	V
Octupole deflection voltage	-2.0	V
Octupole RF	170	V
He Gas flow rate	10	L/min
Energy discrimination	-10.3	V

Table S.2 Program of Clean Column R1

1	Load1		To Column
2	Load2		To Probe
3	SV1 Dispense		Syringe to loop
4	Start Loop	1	Number Loops
5	M1	8	Waste
6	M1	8	Release BP
7	Move Into(rrvv)	R1	rrvv
8	SV1 Dispense		To loop
9	M1	7	air
10	M1	7	
11	Delay	4	seconds
12	Fill S1	1900-20000	μl-μl/min
13	Wait Syringe Complete	S1	
14	Delay	10	seconds
15	M1	1	Reagent 1
16	M1	1	
17	Delay	5	seconds
18	Fill S1	10000-10000	μl-μl/min
19	Wait Syringe Complete	S1	Syringe Number
20	Delay	30	sec
21	M1	9	To Column
22	M1	9	
23	Delay	10	seconds
24	Dispense S1	12000-10000	μl-μl/min
25	Wait Syringe Complete	S1	Syringe Number
26	Delay	60	seconds for back pressure
27	M1	8	waste
28	M1	8	Empty syringes

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29	Delay	5	seconds
30	Dispense S1	12000-20000	μl-μl/min
31	Wait Syringe Complete	S1	Syringe Number
32	Delay	2	seconds
33	SV1 Fill		Vac out to Loop
34	Delay	1	seconds
35	Vacuum1 On		Rinse loop
36	Delay	4	seconds
37	Vacuum1 Off		
38	Delay	2	seconds
39	End Loop		

Table S.3 Program of Condition Column R2

1	Inject1		Bypass Column
2	Load2		To Probe
3	M1	8	Waste
4	M1	8	Release BP
5	SV1 Dispense		Syringe to loop
6	M1	7	Air
7	M1	7	
8	Delay	1	seconds
9	Fill S1	3000-20000	Pull Air
10	Wait Syringe Complete	S1	Syringe Number
11	Delay	4	seconds
12	M1	2	Reagent 2
13	M1	2	
14	Fill S1	500-10000	
15	Wait Syringe Complete	S1	Syringe Number
16	Move Into(rrvv)	R1	
17	Delay	4	seconds
18	M1	9	to probe
19	M1	9	
20	Dispense S1	2500-10000	Wash tubing
21	Wait Syringe Complete	S1	Syringe Number
22	Move Into(rrvv)	R2	
23	Dispense S1	1000-20000	
24	Move Up		
25	Wait Syringe Complete	1	Syringe Number
26	Delay	4	Back pressure seconds
27	M1	8	Waste
28	M1	8	Release BP
29	Delay	1	seconds
30	Dispense S1	12000-20000	Empty syringes

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31	Wait Syringe Complete	S1	Syringe Number
32	Delay	1	seconds
33	SV1 Fill		Vac out to loop
34	Delay	1	seconds
35	Vacuum1 On		Rinse loop
36	Delay	2	seconds
37	Vacuum1 Off		
38	Delay	2	seconds
39	Load1		To Column
40	Start Loop	1	Number Loops
41	M1	8	Waste
42	M1	8	Release BP
43	Move Into(rrvv)	R1	rrvv
44	SV1 Dispense		To loop
45	M1	7	air
46	M1	7	
47	Delay	4	seconds
48	Fill S1	1900-20000	$\mu\text{l}-\mu\text{l}/\text{min}$
49	Wait Syringe Complete	S1	
50	Delay	10	seconds
51	M1	2	Reagent 2
52	M1	2	
53	Delay	5	seconds
54	Fill S1	10000-10000	$\mu\text{l}-\mu\text{l}/\text{min}$
55	Wait Syringe Complete	S1	Syringe Number
56	Delay	30	sec
57	M1	9	To Column
58	M1	9	
59	Delay	10	seconds
60	Dispense S1	12000-2000	$\mu\text{l}-\mu\text{l}/\text{min}$
61	Wait Syringe Complete	S1	Syringe Number
62	Delay	60	seconds for back pressure
63	M1	8	waste
64	M1	8	Empty syringes
65	Delay	1	seconds
66	Dispense S1	12000-20000	$\mu\text{l}-\mu\text{l}/\text{min}$
67	Wait Syringe Complete	S1	Syringe Number
68	Delay	2	seconds
69	SV1 Fill		Vac out to Loop
70	Delay	1	seconds
71	Vacuum1 On		Rinse loop
72	Delay	4	seconds
73	Vacuum1 Off		

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74	Delay	2	seconds
75	End Loop		
76			

Table S.4 Program of DA-FC

1	Load1		To Column
2	Load2		To Probe
3	M1	8	Waste
4	Move Into(rrvv)	Waste	Equilibrate
5	Delay	4	seconds
6	SV1 Dispense		Syringe to Loop
7	M1	7	air
8	M1	7	Purge with air
9	Delay	1	seconds
10	Fill S1	12000-20000	μl-μl/min
11	Wait Syringe Complete	S1	Syringe Number
12	Delay	5	seconds
13	M1	9	Forward to column
14	Delay	2	
15	Dispense S1	12000-20000	μl-μl/min
16	Wait Syringe Complete	S1	Syringe Number
17	Delay	10	BP delay seconds
18	M1	8	Waste
19	M1	8	Equilibrate
20	Delay	2	seconds
21	Dispense S1	12000-20000	μl-μl/min
22	Wait Syringe Complete	S1	Syringe Number
23	SV1 Fill		Vac Out to Loop
24	Delay	1	seconds
25	Vacuum1 On		Rinse Loop
26	Delay	3	seconds
27	Vacuum1 Off		
28	Delay	2	seconds
29			

Table S.5 Program of Sample Load

1	Start Loop	1	Number Loops
2	Inject1		Bypass Column
3	Load2		To Probe
4	M1	8	Waste
5	M1	8	
6	Delay	1	seconds
7	Move Into(rrvv)	R1	rrvv

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8	SV1 Fill		Syringe to DI Water
9	Delay	1	seconds
10	Fill S1	4000-10000	μl-μl/min
11	Wait Syringe Complete	S1	Syringe Number
12	Delay	5	seconds
13	SV1 Dispense		Syringe to Loop
14	M1	7	air
15	M1	7	
16	Delay	1	seconds
17	Fill S1	200-10000	μl-μl/min
18	Wait Syringe Complete	S1	Syringe Number
19	Delay	2	seconds
20	M1	2	Reagent 2
21	M1	2	
22	Delay	1	seconds
23	Fill S1	4000-10000	μl-μl/min
24	Wait Syringe Complete	S1	Syringe Number
25	Delay	5	seconds
26	M1	9	bypass column
27	M1	9	To Probe
28	Dispense S1	12000-20000	μl-μl/min
29	Wait Syringe Complete	S1	Syringe Number
30	Delay	10	seconds
31	Move Into(rrvv)	R2	rrvv
32	Delay	2	seconds
33	Probe Up		
34	Delay	2	seconds
35	Fill S1	1400-5000	μl-μl/min
36	Wait Syringe Complete	S1	Syringe Number
37	Move Into(rrvv)	Sample destination	rrvv
38	Delay	4	seconds
39	Fill S1	9000-4000	μl-μl/min
40	Wait Syringe Complete	S1	Syringe Number
41	Delay	90	seconds
42	Probe Up		
43	Delay	2	seconds
44	Fill S1	1600-5000	μl-μl/min
45	Wait Syringe Complete	S1	Syringe Number
46	Move Into(rrvv)	Waste	rrvv
47	Delay	10	seconds
48	M1	9	
49	M1	9	
50	Load1		To Column

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51	Load2		To Probe
52	Delay	5	seconds
53	Dispense S1	12000-5000	μl-μl/min
54	Wait Syringe Complete	S1	Syringe Number
55	Delay	60	seconds
56	M1	8	
57	M1	8	
58	Dispense S1	12000-10000	μl-μl/min
59	Wait Syringe Complete	S1	Syringe Number
60	Delay	5	seconds
61	SV1 Fill		Vac To Loop
62	Delay	1	seconds
63	Vacuum1 On		Rinse Loop
64	Delay	3	seconds
65	Vacuum1 Off		
66	Delay	2	seconds
67	End Loop		
68			

Table S.6 Program of Wash Matrix R2

1	Load1		To Column
2	Load2		To Probe
3	SV1 Dispense		Syringe to loop
4	Start Loop	1	Number Loops
5	M1	8	Waste
6	M1	8	Release BP
7	Move Into(rrvv)	R1	rrvv
8	SV1 Dispense		To loop
9	M1	7	air
10	M1	7	
11	Delay	2	seconds
12	Fill S1	2000-10000	μl-μl/min
13	Wait Syringe Complete	S1	
14	Delay	5	seconds
15	M1	2	Reagent 2
16	M1	2	
17	Delay	2	seconds
18	Fill S1	10000-10000	μl-μl/min
19	Wait Syringe Complete	S1	Syringe Number
20	Delay	10	sec
21	M1	9	To Column
22	M1	9	
23	Delay	4	seconds

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24	Dispense S1	12000-10000	μl-μl/min
25	Wait Syringe Complete	S1	Syringe Number
26	Delay	30	seconds for back pressure
27	M1	8	waste
28	M1	8	Empty syringes
29	Delay	2	seconds
30	Dispense S1	12000-20000	μl-μl/min
31	Wait Syringe Complete	S1	Syringe Number
32	Delay	2	seconds
33	SV1 Fill		Vac out to Loop
34	Delay	1	seconds
35	Vacuum1 On		Rinse loop
36	Delay	3	seconds
37	Vacuum1 Off		
38	Delay	2	seconds
39	End Loop		
40			

Table S.7 Program of Wash Matrix R5

1	Load1		To Column
2	Load2		To Probe
3	SV1 Dispense		Syringe to loop
4	Start Loop	1	Number Loops
5	M1	8	Waste
6	M1	8	Release BP
7	Move Into(rrvv)	R1	rrvv
8	SV1 Dispense		To loop
9	M1	7	air
10	M1	7	
11	Delay	2	seconds
12	Fill S1	2000-10000	μl-μl/min
13	Wait Syringe Complete	S1	
14	Delay	5	seconds
15	M1	5	Reagent 5
16	M1	5	
17	Delay	2	seconds
18	Fill S1	10000-10000	μl-μl/min
19	Wait Syringe Complete	S1	Syringe Number
20	Delay	10	sec
21	M1	9	To Column
22	M1	9	
23	Delay	4	seconds
24	Dispense S1	12000-10000	μl-μl/min

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25	Wait Syringe Complete	S1	Syringe Number
26	Delay	30	seconds for back pressure
27	M1	8	waste
28	M1	8	Empty syringes
29	Delay	2	seconds
30	Dispense S1	12000-20000	μl-μl/min
31	Wait Syringe Complete	S1	Syringe Number
32	Delay	2	seconds
33	SV1 Fill		Vac out to Loop
34	Delay	1	seconds
35	Vacuum1 On		Rinse loop
36	Delay	3	seconds
37	Vacuum1 Off		
38	Delay	2	seconds
39	End Loop		
40			

Table S.8 Program of Elute Dispense R4

1	Inject1		Bypass Column
2	Load2		To Probe
3	M1	8	Waste
4	M1	8	Release BP
5	SV1 Dispense		Syringe to loop
6	M1	7	Air
7	M1	7	
8	Delay	1	seconds
9	Fill S1	3000-20000	Pull Air
10	Wait Syringe Complete	S1	Syringe Number
11	Delay	4	seconds
12	M1	4	Pull R4
13	M1	4	
14	Fill S1	3000-10000	
15	Wait Syringe Complete	S1	Syringe Number
16	Move Into(rrvv)	R1	
17	Delay	4	seconds
18	M1	9	to probe
19	M1	9	
20	Dispense S1	5000-10000	Wash tubing
21	Wait Syringe Complete	S1	Syringe Number
22	Move Into(rrvv)	R2	
23	Dispense S1	1000-20000	
24	Move Up		
25	Wait Syringe Complete	1	Syringe Number

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26	Delay	4	Back pressure seconds
27	M1	8	Waste
28	M1	8	Release BP
29	Delay	1	seconds
30	Dispense S1	12000-20000	Empty syringes
31	Wait Syringe Complete	S1	Syringe Number
32	Delay	4	seconds
33	SV1 Fill		Vac out to loop
34	Delay	1	seconds
35	Vacuum1 On		Rinse loop
36	Delay	4	seconds
37	Vacuum1 Off		
38	Delay	2	seconds
39	Load1		To Column
40	Start Loop	1	Number Loops
41	M1	8	Waste
42	M1	8	Release BP
43	Move Into(rrvv)	Waste	rrvv
44	SV1 Dispense		To loop
45	M1	7	air
46	M1	7	
47	Delay	4	seconds
48	Fill S1	2000-10000	μl-μl/min
49	Wait Syringe Complete	S1	
50	Delay	5	seconds
51	M1	4	Reagent 4
52	M1	4	
53	Delay	2	seconds
54	Fill S1	1000-10000	μl-μl/min
55	Wait Syringe Complete	S1	Sryinge Number
56	Delay	30	sec
57	M1	9	To Column
58	M1	9	
59	Delay	5	seconds
60	Dispense S1	12000-10000	μl-μl/min
61	Wait Syringe Complete	S1	Syringe Number
62	Delay	60	seconds for back pressure
63	M1	8	waste
64	M1	8	Empty syringes
65	Delay	1	seconds
66	Dispense S1	12000-20000	μl-μl/min
67	Wait Syringe Complete	S1	Syringe Number
68	Delay	4	seconds

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69	SV1 Fill		Vac out to Loop
70	Delay	1	seconds
71	Vacuum1 On		Rinse loop
72	Delay	3	seconds
73	Vacuum1 Off		
74	Delay	2	seconds
75	End Loop		
76			

Table S.9 Program of Elute R4

1	Inject1		Bypass Column
2	Load2		To Probe
3	M1	8	Waste
4	M1	8	Release BP
5	SV1 Dispense		Syringe to loop
6	M1	7	Air
7	M1	7	
8	Delay	1	seconds
9	Fill S1	3000-20000	Pull Air
10	Wait Syringe Complete	S1	Syringe Number
11	Delay	4	seconds
12	M1	4	Pull R4
13	M1	4	
14	Fill S1	3000-10000	
15	Wait Syringe Complete	S1	Syringe Number
16	Move Into(rrvv)	R1	
17	Delay	4	seconds
18	M1	9	to probe
19	M1	9	
20	Dispense S1	5000-10000	Wash tubing
21	Wait Syringe Complete	S1	Syringe Number
22	Move Into(rrvv)	R2	
23	Dispense S1	1000-20000	
24	Move Up		
25	Wait Syringe Complete	1	Syringe Number
26	Delay	4	Back pressure seconds
27	M1	8	Waste
28	M1	8	Release BP
29	Delay	1	seconds
30	Dispense S1	12000-20000	Empty syringes
31	Wait Syringe Complete	S1	Syringe Number
32	Delay	4	seconds
33	SV1 Fill		Vac out to loop

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34	Delay	1	seconds
35	Vacuum1 On		Rinse loop
36	Delay	4	seconds
37	Vacuum1 Off		
38	Delay	2	seconds
39	Load1		To Column
40	Start Loop	1	Number Loops
41	M1	8	Waste
42	M1	8	Release BP
43	Move Into(rrvv)	Destination 1	rrvv
44	SV1 Dispense		To loop
45	M1	7	air
46	M1	7	
47	Delay	4	seconds
48	Fill S1	2000-10000	µl-µl/min
49	Wait Syringe Complete	S1	
50	Delay	5	seconds
51	M1	4	Reagent 4
52	M1	4	
53	Delay	2	seconds
54	Fill S1	2000-10000	µl-µl/min
55	Wait Syringe Complete	S1	Syringe Number
56	Delay	30	sec
57	M1	9	To Column
58	M1	9	
59	Delay	5	seconds
60	Dispense S1	12000-10000	µl-µl/min
61	Wait Syringe Complete	S1	Syringe Number
62	Delay	60	seconds for back pressure
63	M1	8	waste
64	M1	8	Empty syringes
65	Delay	1	seconds
66	Dispense S1	12000-20000	µl-µl/min
67	Wait Syringe Complete	S1	Syringe Number
68	Delay	4	seconds
69	SV1 Fill		Vac out to Loop
70	Delay	1	seconds
71	Vacuum1 On		Rinse loop
72	Delay	2	seconds
73	Vacuum1 Off		
74	Delay	2	seconds
75	End Loop		
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Table S.10 Program of Clean Column R3

1	Load1		To Column
2	Load2		To Probe
3	SV1 Dispense		Syringe to loop
4	Start Loop	1	Number Loops
5	M1	8	Waste
6	M1	8	Release BP
7	Move Into(rrvv)	R1	rrvv
8	SV1 Dispense		To loop
9	M1	7	air
10	M1	7	
11	Delay	2	seconds
12	Fill S1	1900-20000	μl-μl/min
13	Wait Syringe Complete	S1	
14	Delay	10	seconds
15	M1	3	Reagent 3
16	M1	3	
17	Delay	5	seconds
18	Fill S1	10000-10000	μl-μl/min
19	Wait Syringe Complete	S1	Syringe Number
20	Delay	10	sec
21	M1	9	To Column
22	M1	9	
23	Delay	5	seconds
24	Dispense S1	12000-10000	μl-μl/min
25	Wait Syringe Complete	S1	Syringe Number
26	Delay	30	seconds for back pressure
27	M1	8	waste
28	M1	8	Empty syringes
29	Delay	1	seconds
30	Dispense S1	12000-20000	μl-μl/min
31	Wait Syringe Complete	S1	Syringe Number
32	Delay	2	seconds
33	SV1 Fill		Vac out to Loop
34	Delay	1	seconds
35	Vacuum1 On		Rinse loop
36	Delay	4	seconds
37	Vacuum1 Off		
38	Delay	2	seconds
39	End Loop		
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Table S.11 Program of Clean Column R4

1	Load1		To Column
2	Load2		To Probe
3	SV1 Dispense		Syringe to loop
4	Start Loop	1	Number Loops
5	M1	8	Waste
6	M1	8	Release BP
7	Move Into(rrvv)	R1	rrvv
8	SV1 Dispense		To loop
9	M1	7	air
10	M1	7	
11	Delay	2	seconds
12	Fill S1	1900-20000	μl-μl/min
13	Wait Syringe Complete	S1	
14	Delay	2	seconds
15	M1	4	Reagent 4
16	M1	4	
17	Delay	2	seconds
18	Fill S1	10000-10000	μl-μl/min
19	Wait Syringe Complete	S1	Syringe Number
20	Delay	10	sec
21	M1	9	To Column
22	M1	9	
23	Delay	5	seconds
24	Dispense S1	12000-10000	μl-μl/min
25	Wait Syringe Complete	S1	Syringe Number
26	Delay	30	seconds for back pressure
27	M1	8	waste
28	M1	8	Empty syringes
29	Delay	1	seconds
30	Dispense S1	12000-20000	μl-μl/min
31	Wait Syringe Complete	S1	Syringe Number
32	Delay	2	seconds
33	SV1 Fill		Vac out to Loop
34	Delay	1	seconds
35	Vacuum1 On		Rinse loop
36	Delay	4	seconds
37	Vacuum1 Off		
38	Delay	2	seconds
39	End Loop		
40			

Table S.12 Possible spectral interferences of minor Th and U isotopes

Target radionuclide	Possible interferences
^{230}Th	$^{198}\text{Hg}^{16}\text{O}_2^+$, $^{229}\text{ThH}^+$, tailing from ^{229}Th
^{234}U	$^{198}\text{Hg}^{35}\text{Cl}^+$, $^{198}\text{Hg}^{18}\text{O}_2^+$, $^{202}\text{Hg}^{16}\text{O}_2^+$, $^{233}\text{UH}^+$, $^{232}\text{ThH}_2^+$, tailing from ^{233}U
^{235}U	$^{199}\text{Hg}^{18}\text{O}_2^+$

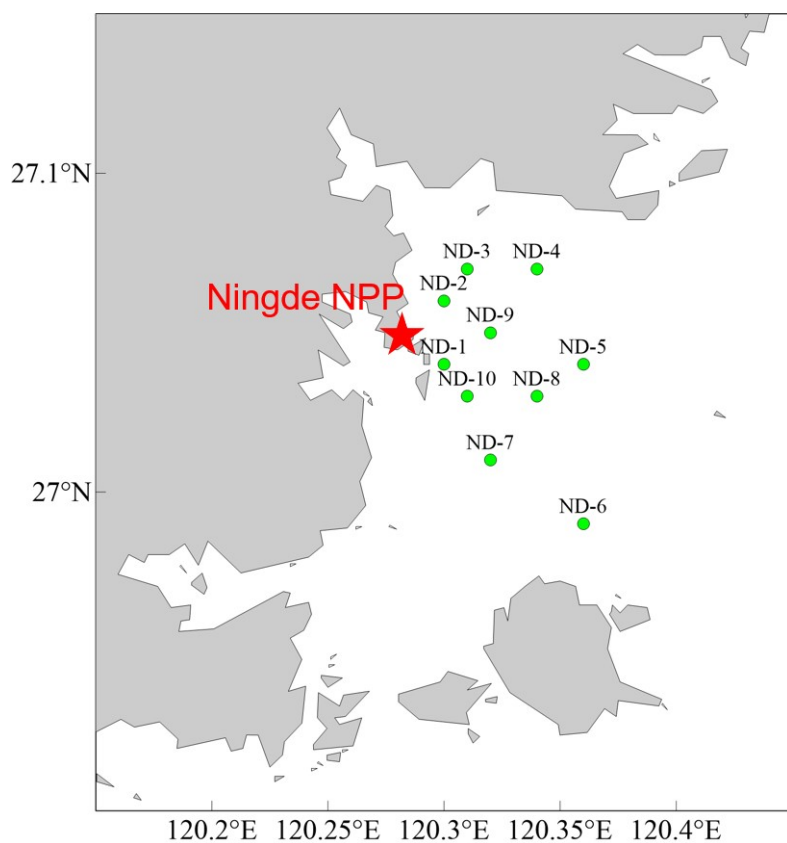


Fig. S.1 Locations of seawater samples around Ningde NPP

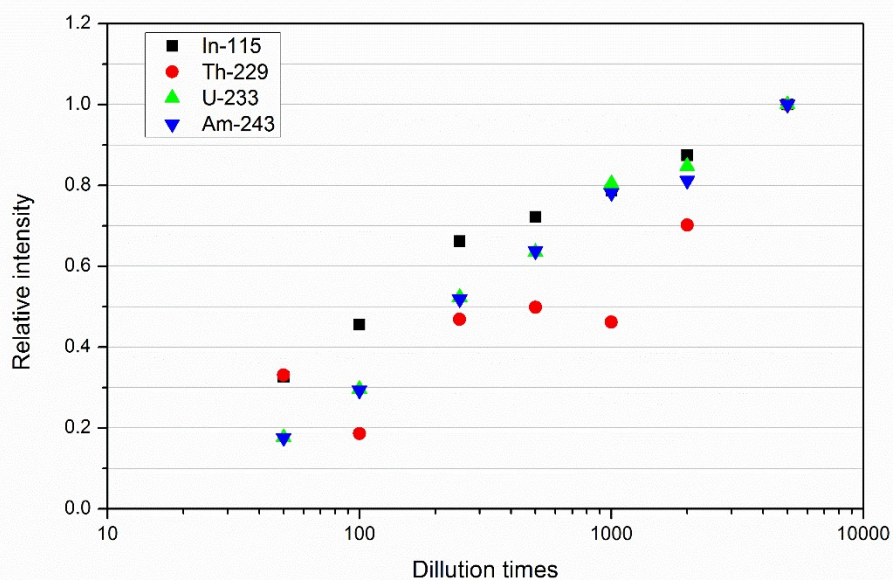


Fig. S.2 Influence of dilution factor on the ICP-MS/MS sensitivity

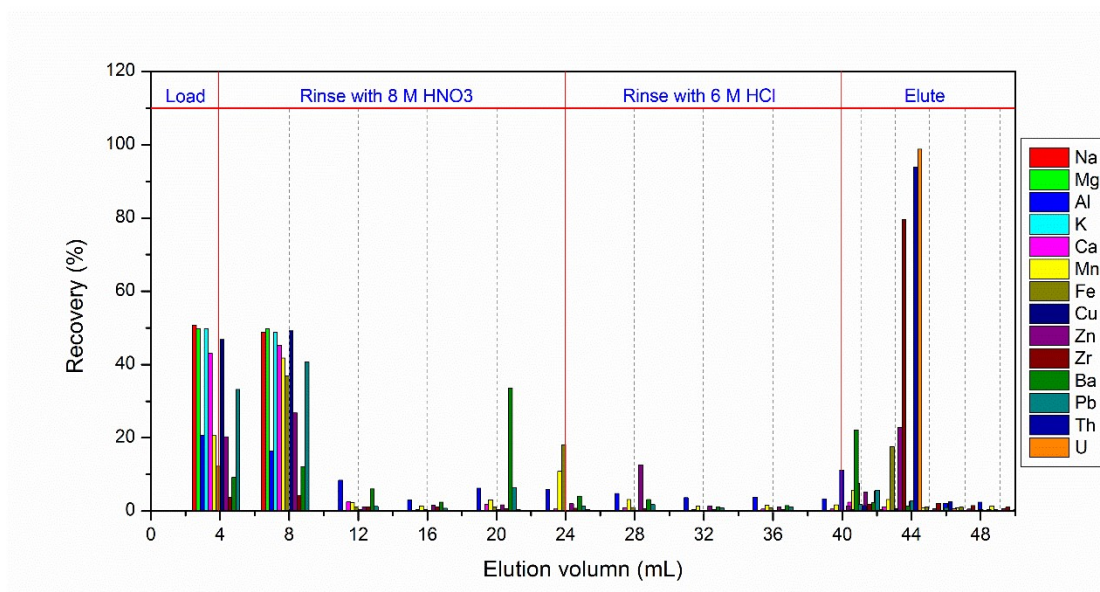


Fig. S.3 Elution profiles of primary matrix elements and Th and U

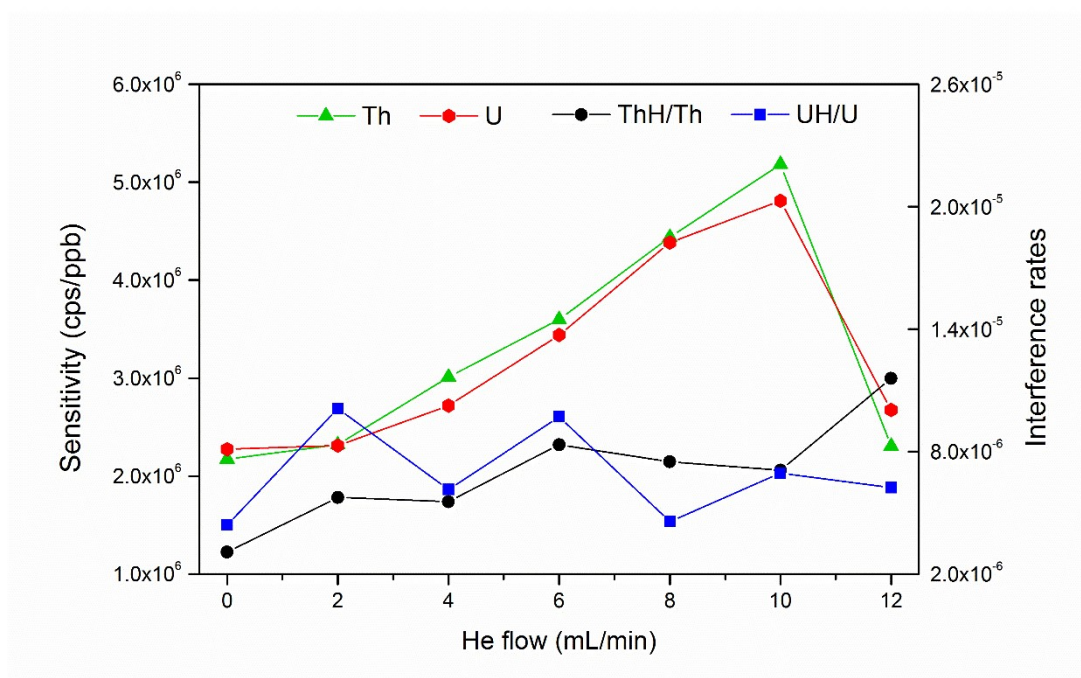


Fig. S.4 Instrumental sensitivity and interferences variation with He flow

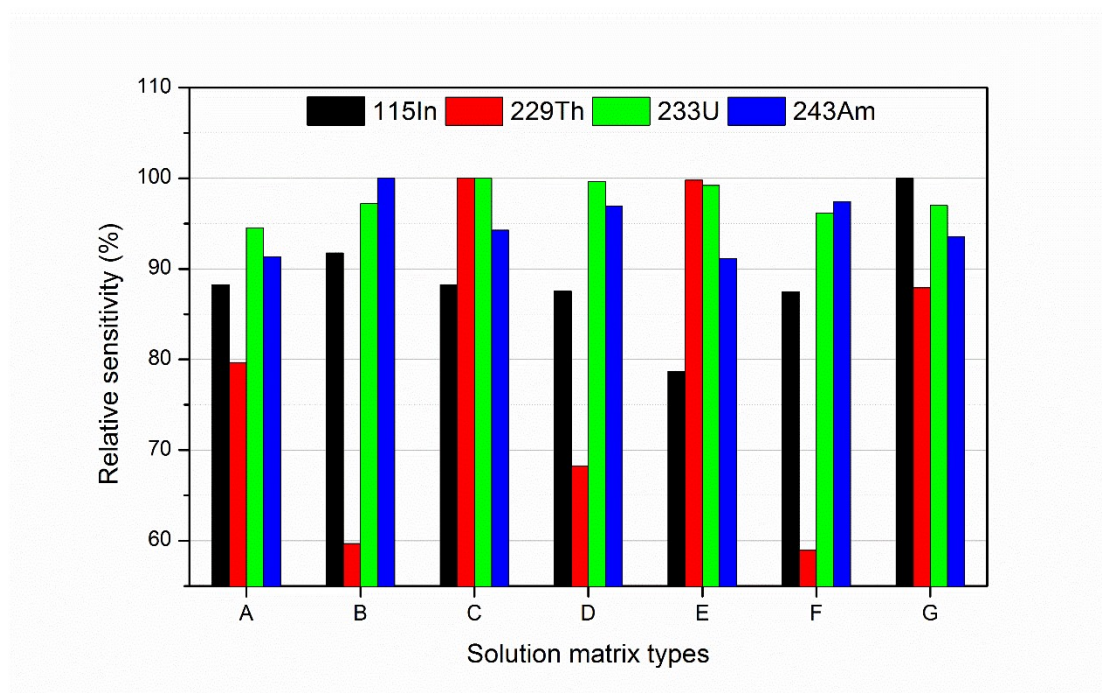


Fig. S.5 Influence of solution matrix on the instrumental sensitivity (A: 2% HNO₃; B: 0.01 M HNO₃; C: 0.01 M HNO₃-0.01 M HF; D: 0.1 M HNO₃; E: 0.1 M HNO₃-0.02 M HF; F: 0.1 M HCl; G: 0.5 M HCl)

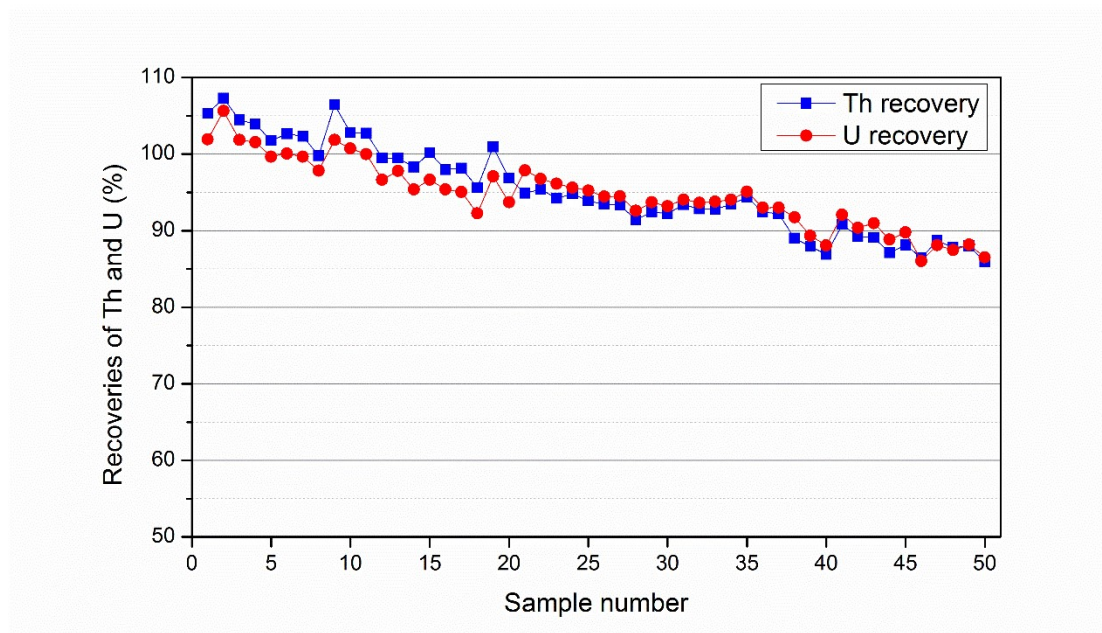


Fig. S. 6 Recoveries of Th and U in the repeated runs