

Automation and Methodology Development for Environmental and Biological Determination of Pu, Np, U and Tc

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Properties of Pu, Np, U and Tc



Nuclide	Isotope	Main origination	Half-life	Main production	Principal decay mode
Pu	^{238}Pu	Anthropogenic	87.7 y	NA and β decay of ^{235}U and ^{238}U	α
	^{239}Pu		2.4×10^4 y	Bombardment of ^{238}U	α
	^{240}Pu		6.6×10^3 y	^{239}Pu (n, γ) ^{240}Pu	α
	^{241}Pu		14.4 y	^{240}Pu (n, γ) ^{241}Pu	β^-
Np	^{237}Np	Anthropogenic	2.4×10^6 y	NA and β decay of ^{235}U and ^{238}U	α
U	^{234}U	Natural	2.4×10^6 y		α
	^{235}U	Natural	2.5×10^5 y		α
	^{236}U	Anthropogenic	2.3×10^7 y	^{235}U neutron activation (NA)	α
	^{238}U	Natural	4.5×10^9 y		α
Tc	^{99}Tc	Anthropogenic	2.1×10^5 y	^{235}U , ^{239}Pu fission product	β^-

Sources of Pu, Np, U and Tc in the environment



Nuclear weapons testing



Nuclear power plants

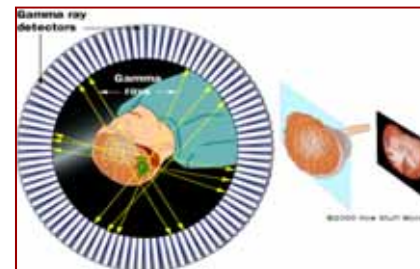
Pu isotopes,
 ^{237}Np , ^{99}Tc ,
 ^{236}U



Nuclear reprocessing plants



Nuclear accidents



Nuclear medicine

Sources of Pu, Np, U and Tc in the environment



Sources of Pu and Np in the environment

Source term	^{238}Pu , Bq	^{239}Pu , Bq	^{240}Pu , Bq	^{241}Pu , Bq	^{237}Np , Bq	$^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio
Nuclear weapons testing	3.3×10^{14}	7.4×10^{15}	5.2×10^{15}	1.7×10^{17}	3.9×10^{13}	~0.19
Burn up of SNAP-9A	6.3×10^{14}	-	-	-	-	-
Thule, Greenland, 1968	-	1×10^{13}		-	-	-
Palomares, Spain	-	5.5×10^{10}		-	-	-
Chernobyl, 1986	3.0×10^{13}	2.6×10^{13}	3.7×10^{13}	5.5×10^{15}	-	~0.39
Sellafield reprocessing plant	1.2×10^{14}	6.1×10^{14}		2.2×10^{16}	-	-
La Hague reprocessing plant	2.7×10^{12}	3.4×10^{12}		1.2×10^{14}	-	-

Sources of Pu, Np, U and Tc in the environment

Sources of ^{99}Tc and ^{236}U in the environment	
Source term	^{99}Tc released, Bq
Sellafield nuclear reprocessing plant	1.72×10^{15}
La Hague nuclear reprocessing plant	1.54×10^{14}
Global weapons fallout (1940s-1970s)	1.40×10^{14}
Nuclear accident in Chernobyl	7.5×10^{11}
Estimated nuclear accident in Fukushima	$>2.5 \times 10^{11}$
Estimated medical application (^{99}Mo - $^{99\text{m}}\text{Tc}$ generator)	$<2 \times 10^{10}$
Estimated nuclear power plants	$<1 \times 10^{10}$
Source term	^{236}U released, Bq
Natural	8.4×10^{10}
Anthropogenic	2.4×10^{15}

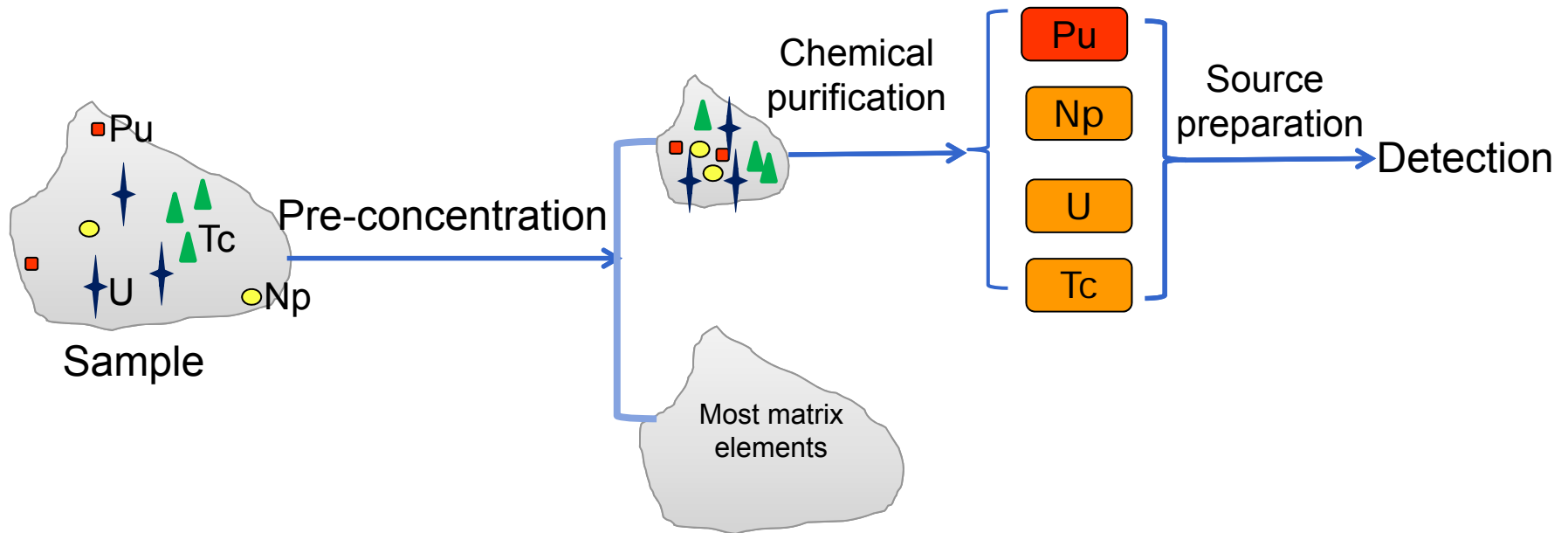
Significances of Pu, Np, U and Tc determination



- 1) Environmental risk assessment and monitoring
- 2) Nuclear emergency preparedness
- 3) Routine occupational health monitoring
- 4) Nuclear Forensics
- 5) Nuclear decommissioning and waste disposal
- 6) Radioecology and tracer studies

Distribution characters of Pu, Np, U and Tc in environmental and biological samples

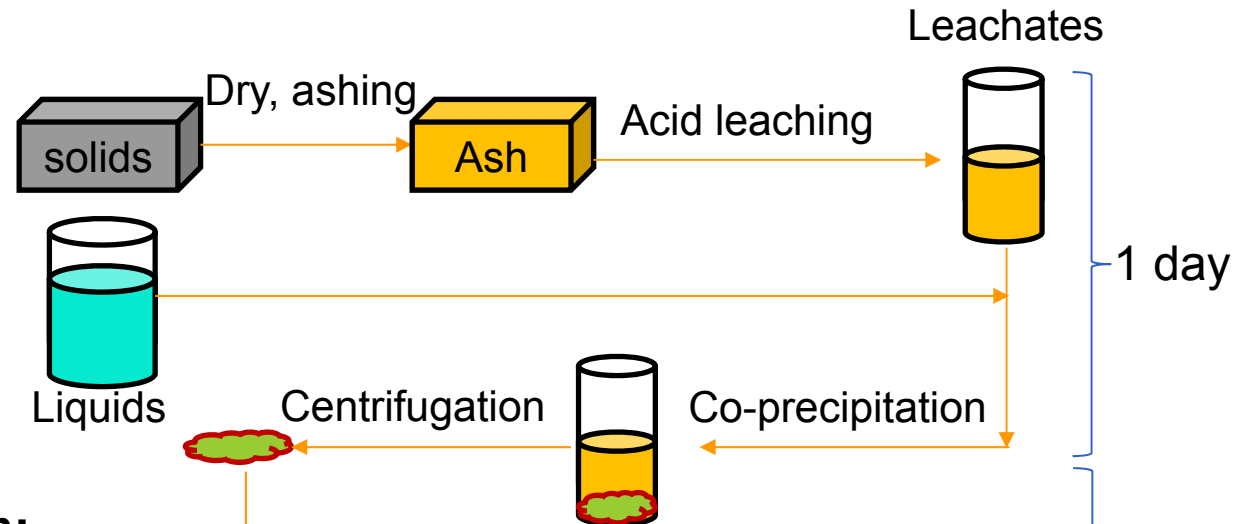
- 1) Levels are very **low** and **vary** with location or sample type
- 2) Often coexist with **matrix elements** (Ca, Mg, Al, V, Ru, Mo...) and **other interfering radionuclides** (Th, Am, Cm...)



Traditional analytical methods for Pu and Np

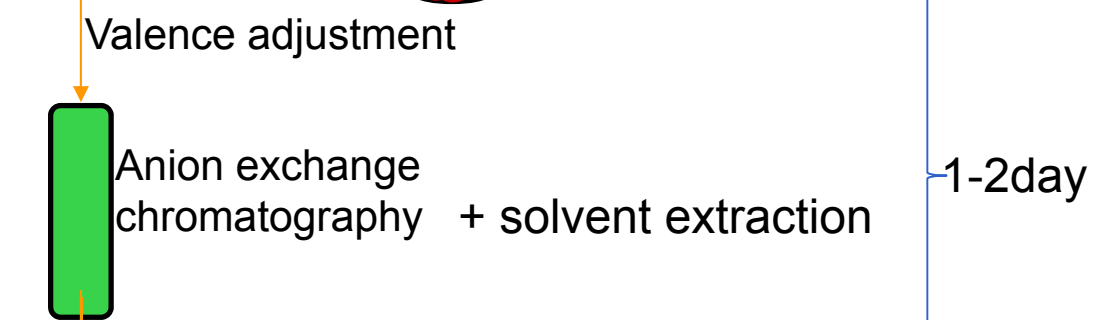
Pre-concentration:

- 8-16 batchwise
- Fairly straightforward



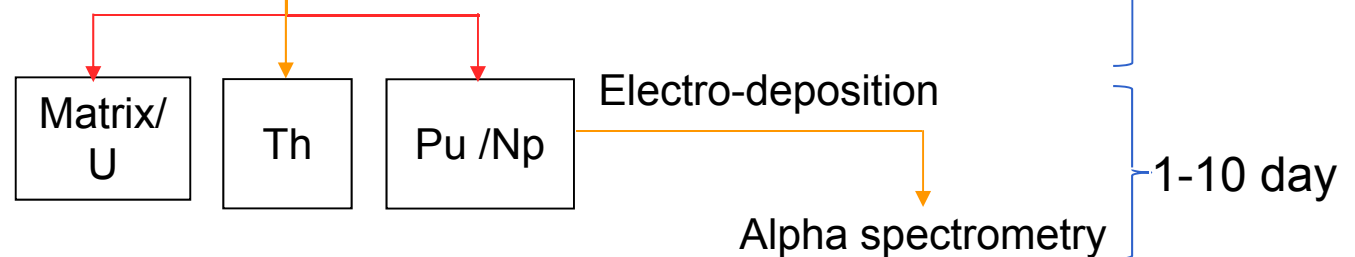
Chemical purification:

- Lengthy
- High labor intensity
- High consumption of resin
- Organic waste



Detection:

- Long counting time
- High detection limit



Our objectives

1. Rapid determination of Pu, Np, U and Tc
2. Automation of the analytical procedure

Specific focuses:

i. Chemical purification

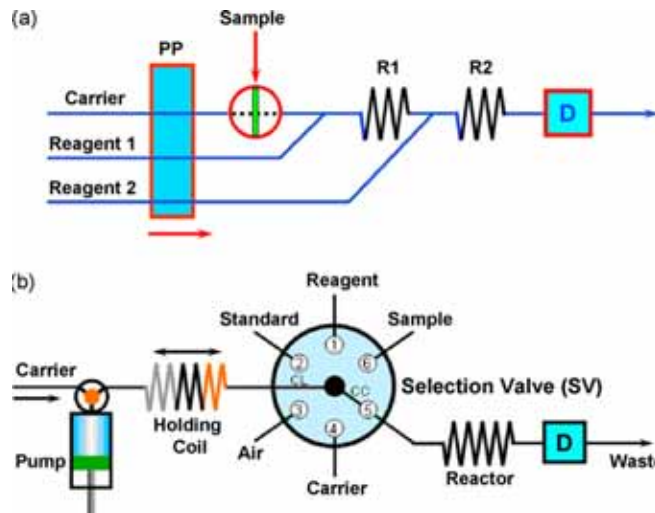
- Protocol simplification and optimization
- Automation

ii. Detection

- Mass spectrometry (ICP-MS, AMS)

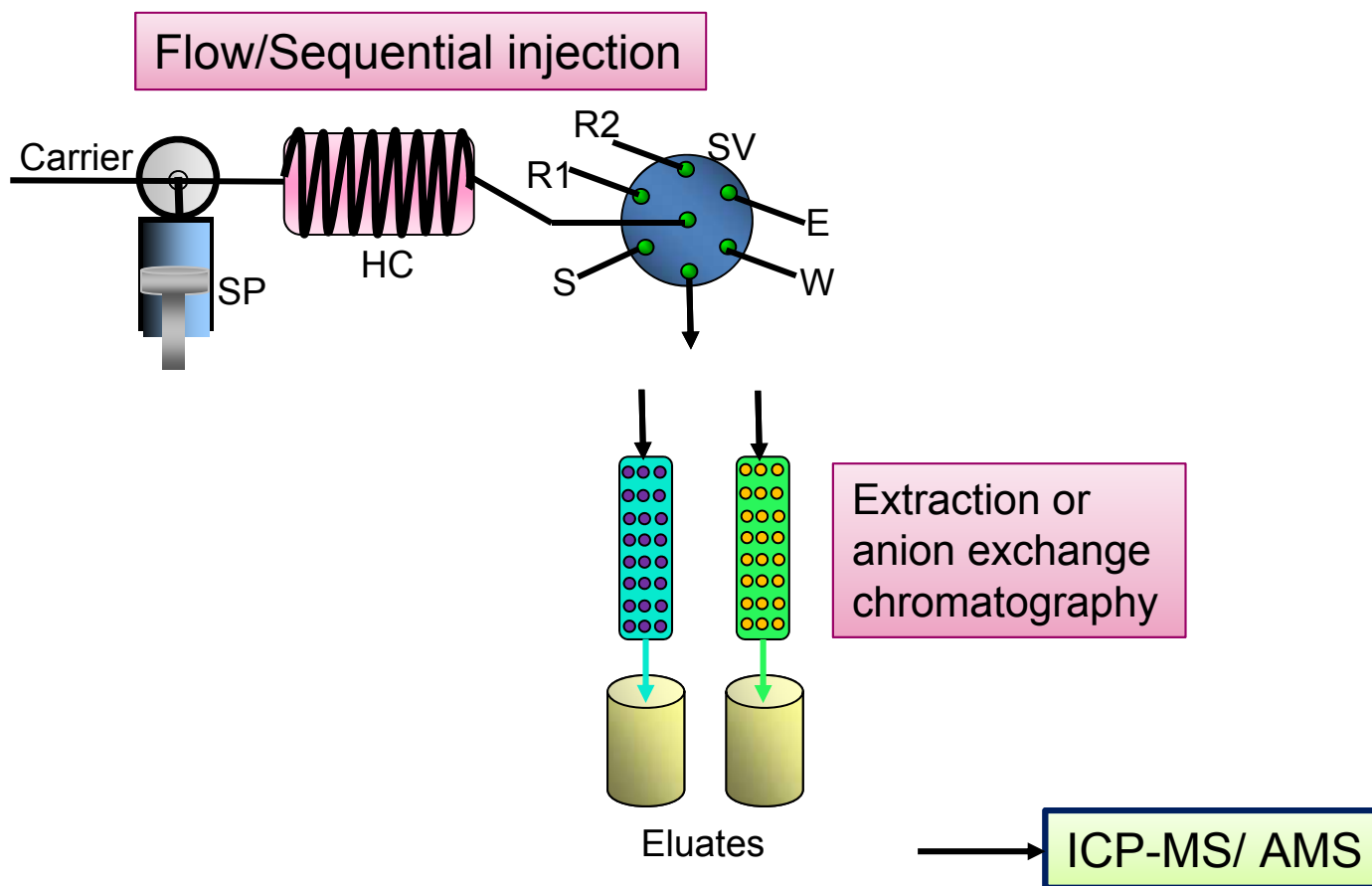
Automation techniques

- Vacuum box
- HPLC
- Flow injection/Sequential injection



Qiao, J. X., Hou, X. L., Miró, M., Roos, P. Analytica Chimica Acta. 2009, 652, 66-84.

Final strategies



Methods Development-Pu and Np



Environmental Samples:

- 0.5-200 g of soil, sediment or seaweed
- 50-200 L of seawater

Parameters optimized:

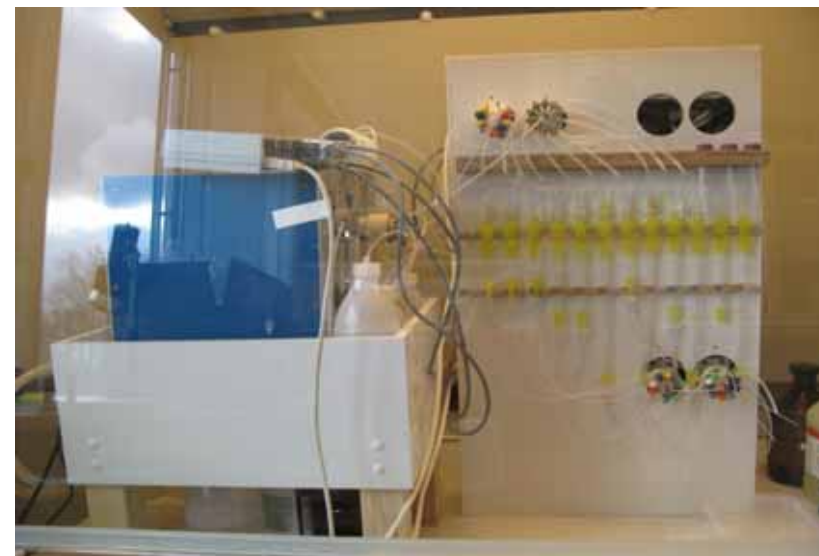
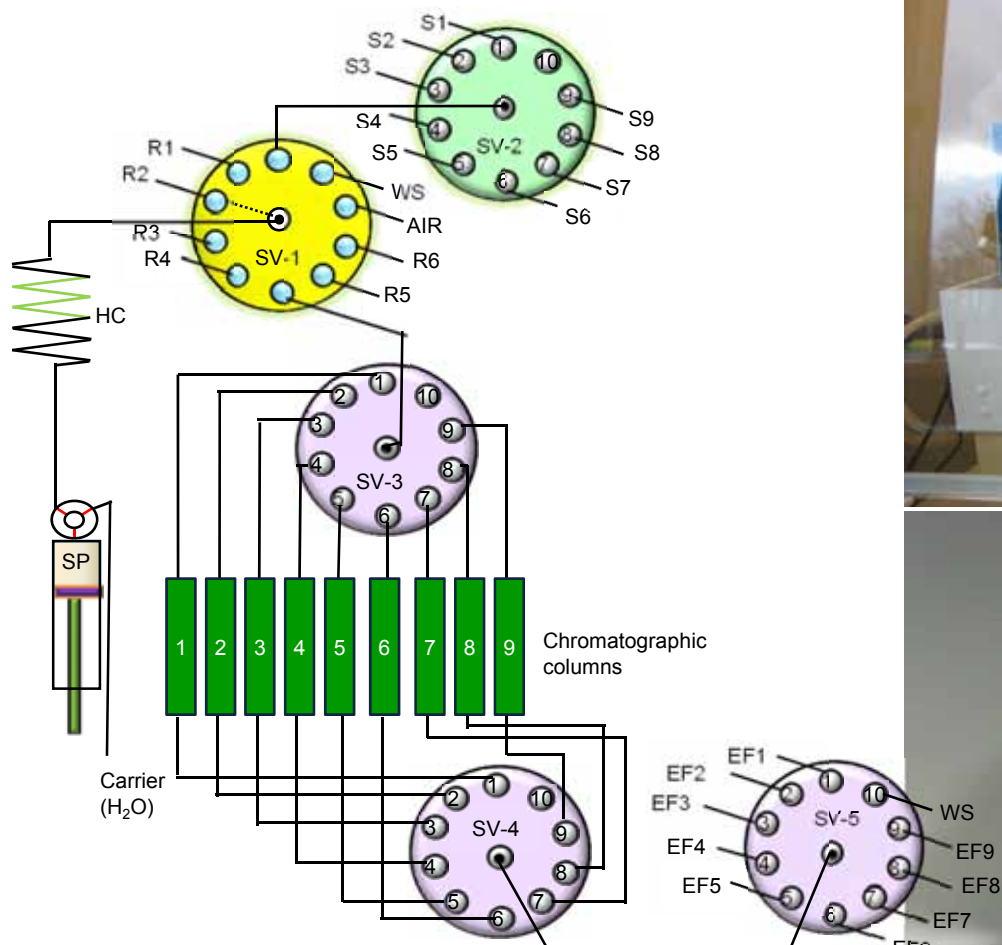
- Resin type (TEVA, AG1, AG MP-1M)
- Column size (1-20 mL)
- Washing solution (1-8 M HNO₃)
- Elution solution (NH₂OHHCl-HCl, 0.1-1.0 M HCl)
- Flow rate (1-5 mL/min)

Performance evaluation :

Chemical yields; ²³⁷Np/²⁴²Pu chemical yield;

Decontamination of U; Method reability; Sample throughput

Auto-uint no.1---Sequential injection



Automatically handle 9 samples!
Work overnight !

Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytica Chimic Acta. 2011, 685, 111-119.

Selected results for soil analysis



Method	Analyte	Resin	Chemical yield of ^{242}Pu , Y_{Pu} (%)	Chemical yield of ^{237}Np , Y_{Np} (%)	Ration of $Y_{\text{Np}}/Y_{\text{Pu}}$	^{239}Pu measured (Bq/kg) *	^{240}Pu measured (Bq/kg)**	Decontamination factor ***		
								^{238}U	^{232}Th	^{208}Pb
Extraction chromatography ^{1,2)}	Pu	TEVA (2mL, 0.7 × 5 cm)	97.7 ± 3.4	-	-	0.14 ± 0.01	0.09 ± 0.01	7.5 × 10 ⁴	2.5 × 10 ⁴	1.3 × 10 ⁵
	Np & Pu	TEVA (2mL, 0.7 × 5 cm)	88.1 ± 3.4	85.7 ± 3.9	0.97	0.14 ± 0.01	0.09 ± 0.01	1.0 × 10 ⁴	7.0 × 10 ³	1.0 × 10 ⁴
Anion chromatography ^{3,4)}	Pu (&Np)	AG 1-X4 (50-100mesh), (2mL, 0.5 × 10cm)	103.0 ± 5.2	84.8 ± 5.3	0.75	0.14 ± 0.02	0.09 ± 0.01	3.9 × 10 ³	2.4 × 10 ⁴	2.7 × 10 ⁴
		AG 1-X4 (100-200mesh), (2mL, 0.5 × 10cm)	91.6 ± 4.6	75.8 ± 4.6	0.77	0.14 ± 0.01	0.10 ± 0.01	6.9 × 10 ³	1.7 × 10 ⁴	1.0 × 10 ³
	Np & Pu	AG MP-1M (100-200mesh), (2mL, 0.5 × 10cm)	86.5 ± 4.3	85.3 ± 4.3	0.99	0.14 ± 0.02	0.10 ± 0.01	3.9 × 10 ³	2.5 × 10 ⁵	1.0 × 10 ³

10 g of soil was used in each analysis. *The reference value is 0.140 ± 0.008 Bq/kg. **The reference value is 0.098 ± 0.006 Bq/kg. *** The relative standard deviations were in all instances better than 10%.

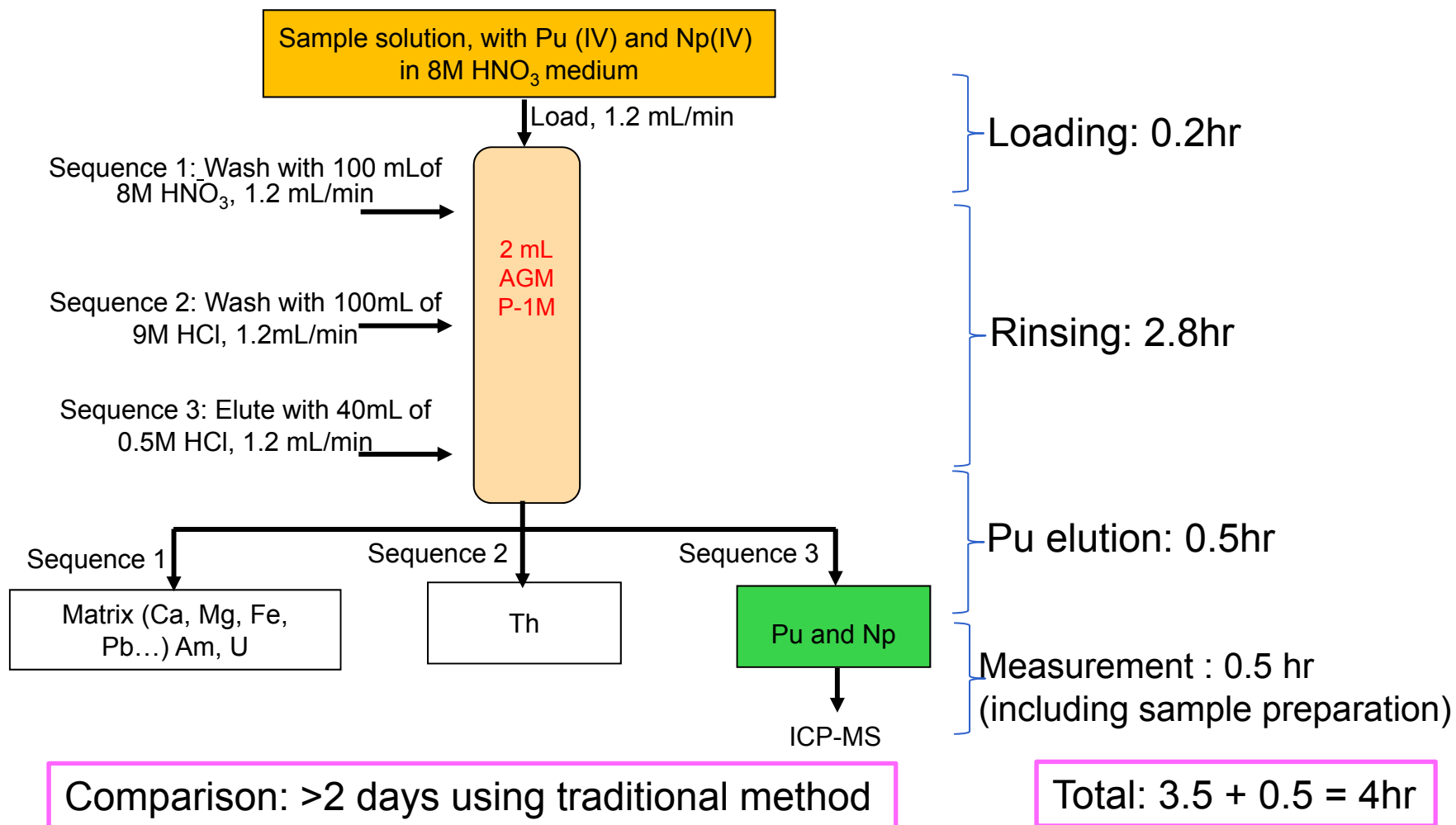
1) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2009, 81, 8185-8192.

2) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Journal of Analytical Atomic Spectrometry. 2010, 25, 1769-1779.

3) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytica Chimica Acta. 2009, 652, 66-84.

4) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Talanta. 2011, 84, 494-500.

Optimized chemical purification for Pu and Pu simultaneous determination



Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2011, 83, 374-381.

Performance comparison

Item	Extraction chromatography	Anion exchange chromatography
Price of resin	☹ High (e.g. 5600 €/500 g)	☺ Relatively Low (e.g. 330-1000 €/500 g)
Chemical yields	80-100% (Pu), ☹ 40-80% (Np&Pu)	☺ 80-100% (Pu), 70-90% (Np&Pu, AG MP-1M resin)
Separation time	☺ 1.5 hr/sample	☹ 2.5-3.5 hr/sample
Decontamination	☺ High ($1-10 \times 10^4$ for ^{238}U)	☹ Medium ($1-10 \times 10^3$ for ^{238}U)
Accuracy	☺ High (RSD $\leq 5\%$)	☹ Medium (RSD $\leq 10\%$)
Consumption of chemicals	☺ Low (e.g. 10 mL of conc. HNO_3 /sample)	☹ High (e.g. 80 mL of conc. HNO_3 /sample)
Recommendation	Pu determination using TEVA resin	Pu &Np simultaneous determination using AG MP-1M resin

Qiao, J. X. Risø-PhD-75 (EN), ISBN 978-87-550-3889-9, March 2011, Roskilde, Denmark.

Methods Development-Pu and Np



Biological samples:

- 1-5 L urine

Parameters optimized:

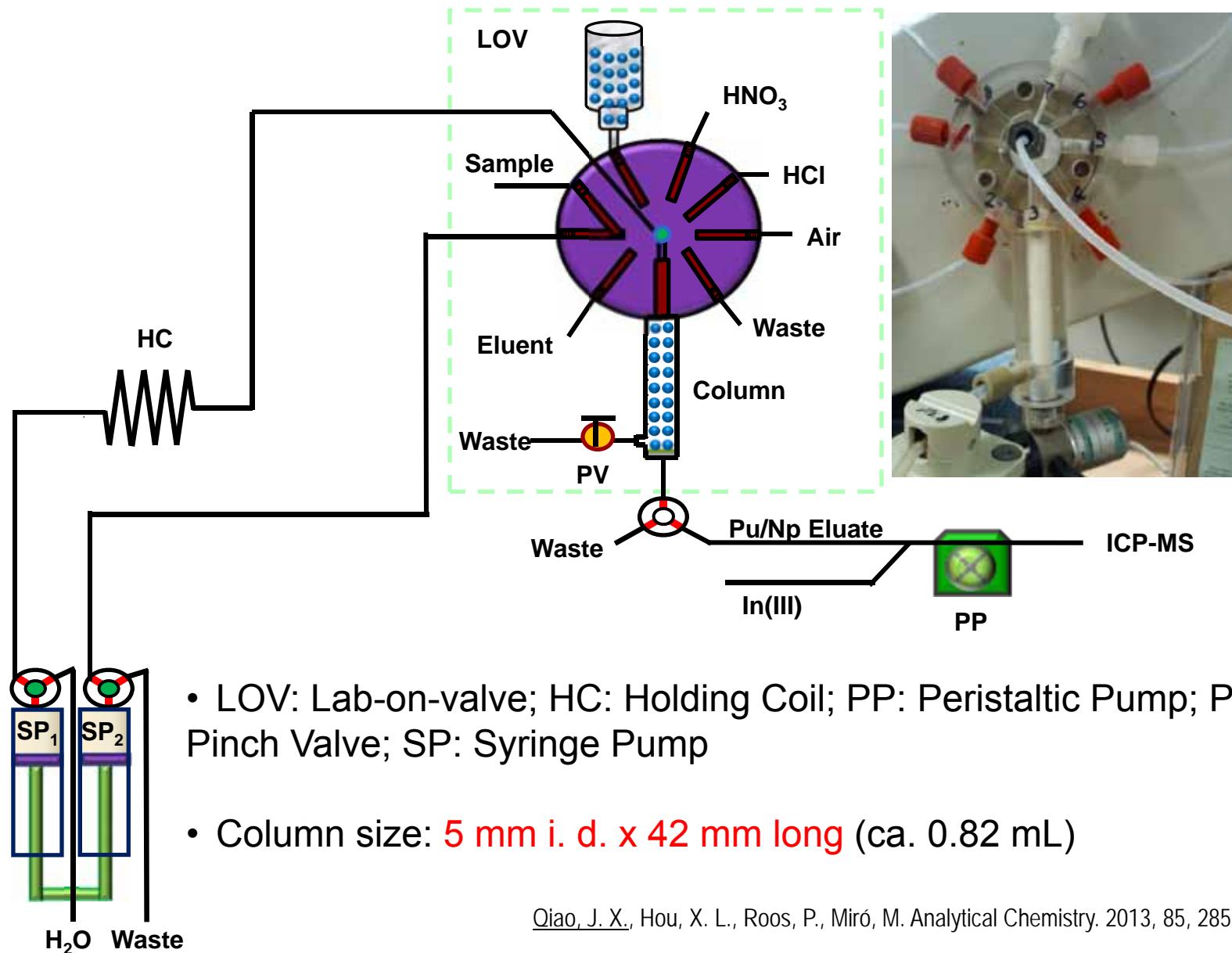
- Co-precipitation techniques ($\text{Ca}_3(\text{PO}_4)_3$, $\text{Fe}(\text{OH})_3$, MnO_2 , etc.)
- Decomposition of organic matter (acid digestion/dry ashing)
- Washing solution (0.2-1 M HNO_3)
- Elution solution (0.025-0.5 M HCl)

Performance evaluation :

Chemical yields; $^{237}\text{Np}/^{242}\text{Pu}$ chemical yield ratio;

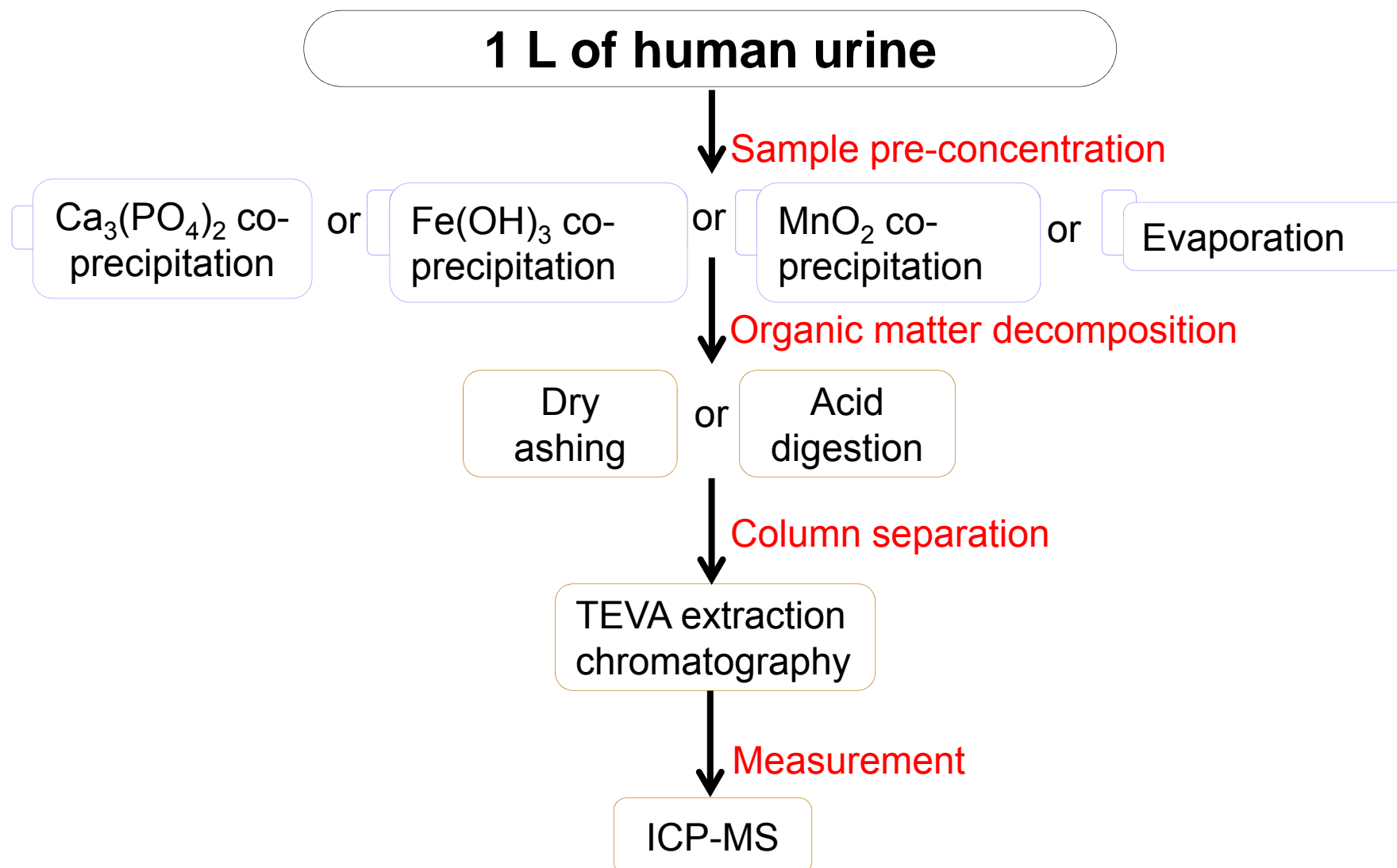
Method reability; Sample throughput

Auto-unit no.2---LOV bead injection



Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2013, 85, 2853-2859.

Analytical procedure for urine analysis



Selected results for urine analysis



Group no.	Pre-concentration method	Organic matter decomposition	Valence adjustment reagents	Operation time	Chemical yield		
					²⁴² Pu, %	²³⁷ Np, %	²³⁷ Np/ ²⁴² Pu
1	Ca ₃ (PO ₄) ₂ co-precipitation	Dry ash	Ascorbic acid / conc.HNO ₃	13 hr	84.7 ± 5.7	80.9 ± 10.7	0.95
		Acid digestion		8 hr	46.8 ± 4.1	8.3 ± 5.4	0.18
2	Fe(OH) ₂ /Fe(OH) ₃ co-precipitation	Dry ash	Fe/K ₂ S ₂ O ₅ / conc.HNO ₃	6 d	84.3 ± 15.6	73.3 ± 33.0	0.87
		Acid digestion		5.5 d	80.3 ± 9.9	77.9 ± 10.9	0.97
		Acid digestion		6 hr	51.3 ± 0.2	57.5 ± 8.8	1.12
3	MnO₂ co-precipitation	Acid digestion	Fe/K₂S₂O₅ / conc.HNO₃	6 hr	88.4 ± 8.0	91.4 ± 10.0	1.03
4	Ca(OH) ₂ /Fe(OH) ₂ /Fe(OH) ₃ co-precipitation	Acid digestion	Ascorbic acid / conc.HNO ₃	6 hr	87.3 ± 6.6	51.2 ± 1.6	0.59
5	Evaporation	Dry ash + acid leaching	Fe/K ₂ S ₂ O ₅ / conc.HNO ₃	1.5 d	75.5 ± 2.6	81.1 ± 3.6	1.07

Methods Development-Pu, Np and U



Environmental Sample:

- 10 L of seawater

Parameters optimized:

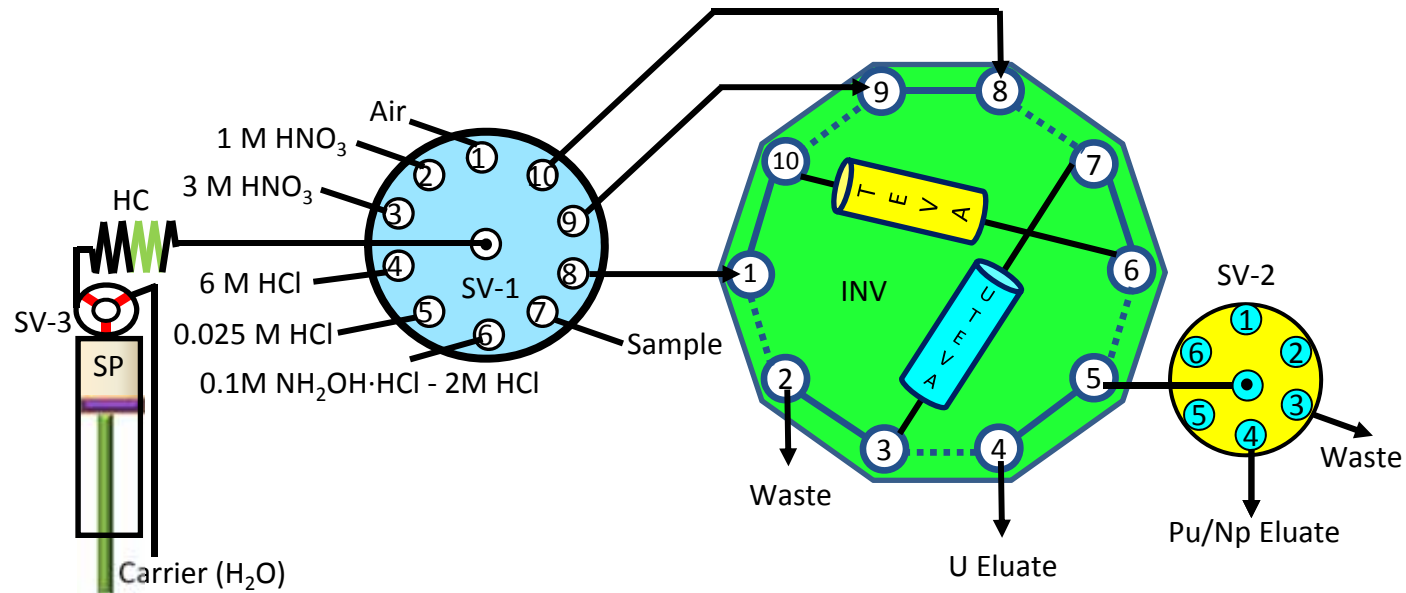
- Resin type (TEVA, UTEVA)
- Washing solution (1-4 M HNO₃)
- Decomposition of organic matter

Performance evaluation :

Chemical yields; ²³⁷Np/²⁴²Pu chemical yield ratio;

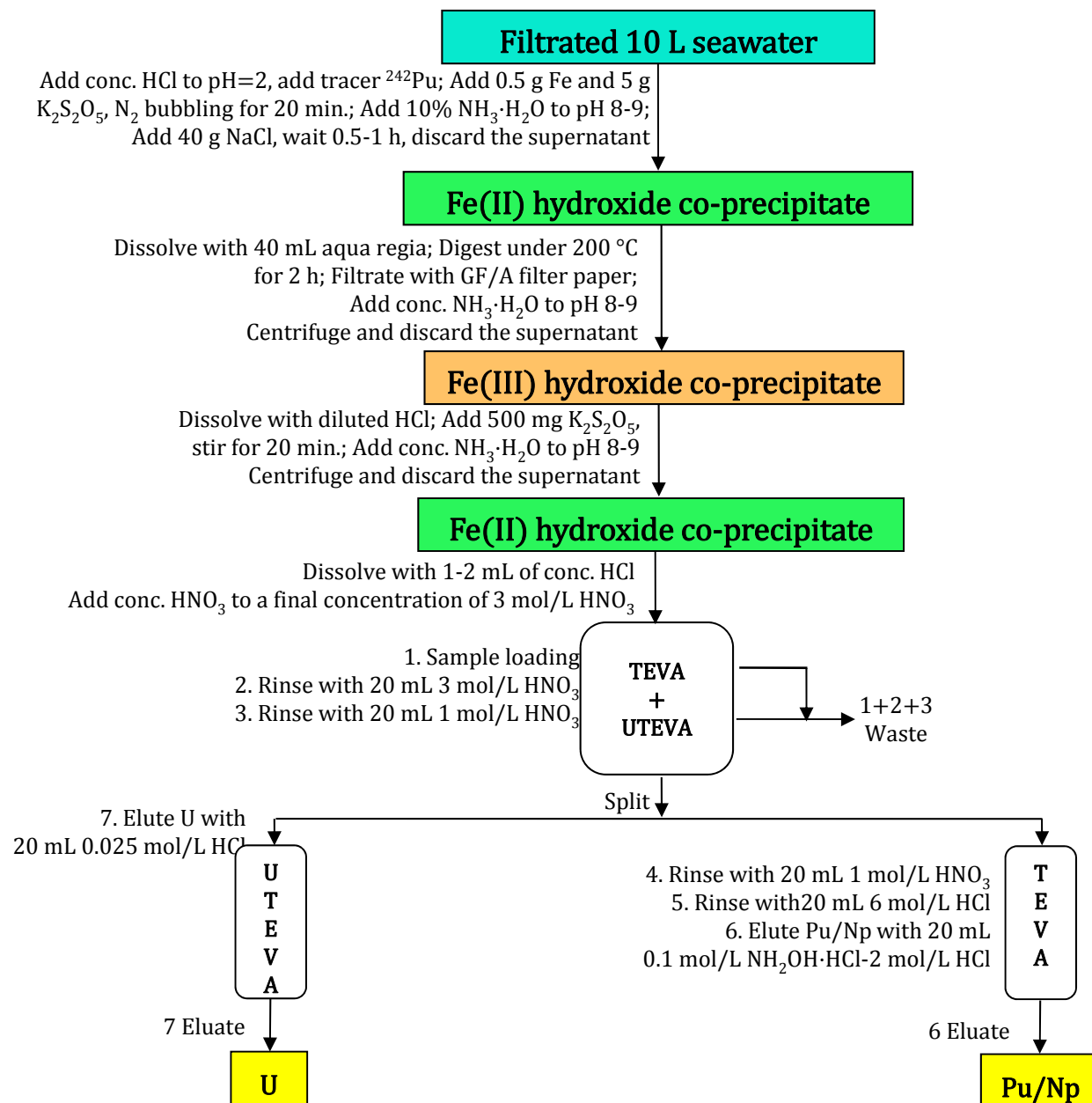
Method reability; Sample throughput

Auto-unit no.3---Dual-column sequential injection



Flexible control the connection of two columns!

Qiao, J. X., Hou, X. L., Steier, P., Golser, R. Analytical Chemistry. 2013, submitted.



Selected results for Pu/Np/U seawater analysis

Typical analytical performance

Analytical time, h	Chemical yield, %				DU
	²⁴² Pu	²³⁷ Np	²³⁷ Np/ ²⁴² Pu ratio	²³⁸ U	
8	73.6 ± 9.8	73.9 ± 5.6	1.01 ± 0.21	97.6 ± 20.6	(5.3 ± 0.5) × 10 ⁴

Method application with the use of AMS measurement

Sample ID	²³⁶ U/ ²³⁸ U, × 10 ⁻⁸	²³⁸ U, µg/L	²³⁶ U atom/L,	Measured value, mBq/L		Expected value, mBq/L	
				²³⁷ Np	²³⁹ Pu	²³⁷ Np	²³⁹ Pu
North Atlantic-1	8.88 ± 1.33	2.76 ± 0.41	(6.21 ± 0.93) × 10 ⁸	<0.001	<0.005	-	-
North Atlantic-2	2.03 ± 0.30	2.17 ± 0.33	(1.11 ± 0.17) × 10 ⁸	0.18	1.02	0.20	1.12
Roskilde Fjord-1	1.40 ± 0.21	1.65 ± 0.28	(6.88 ± 1.03) × 10 ⁷	<0.001	0.03	-	-
Roskilde Fjord-2	1.65 ± 0.25	1.65 ± 0.28	(5.85 ± 0.88) × 10 ⁷	0.16	1.18	0.15	1.12

Methods Development-Pu, Np, U and Tc



Environmental Sample:

- 200 L of seawater

Parameters optimized:

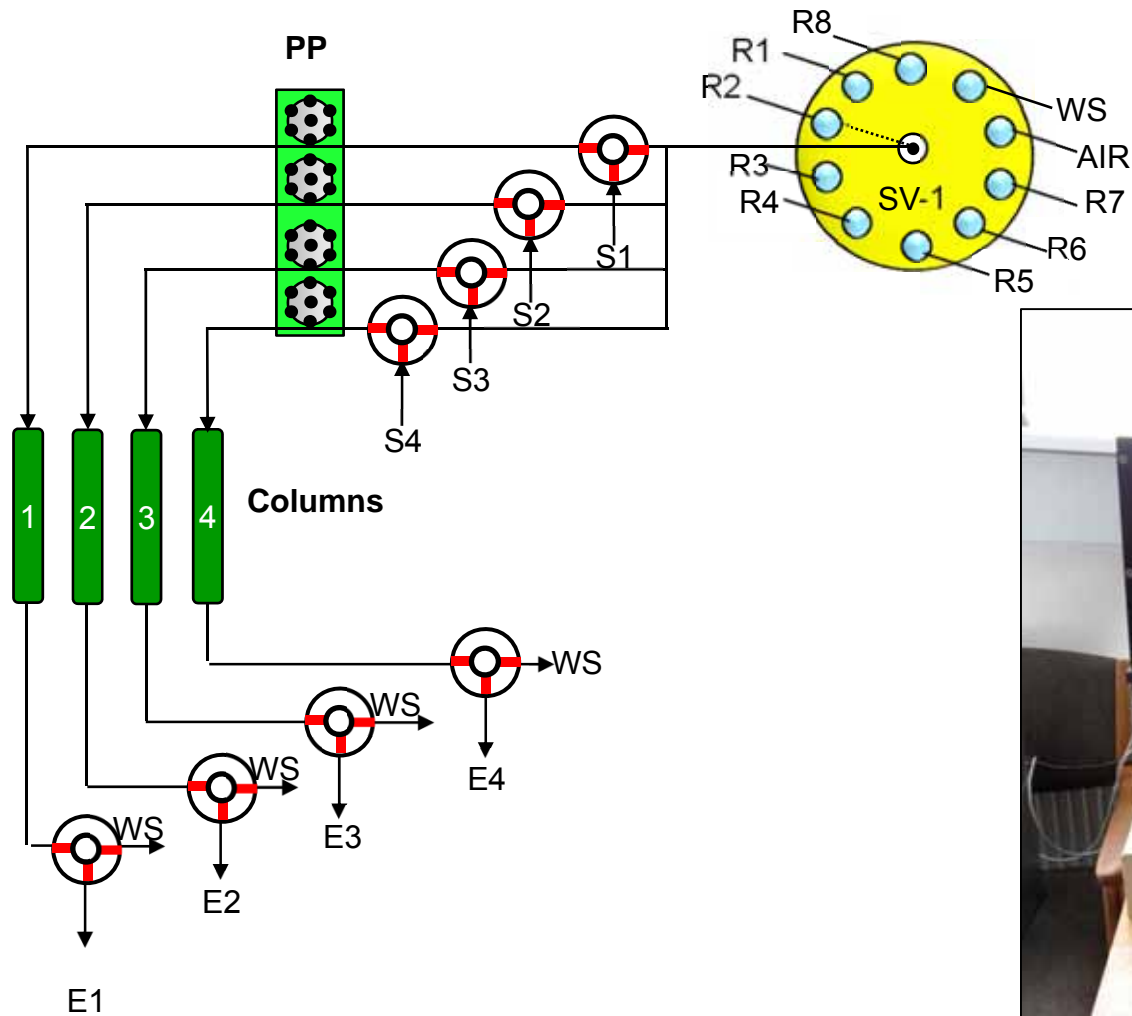
- Resin type (TEVA, UTEVA, AG MP-1M)
- Selection of Redox reagents
- Decontamination of interferences

Performance evaluation :

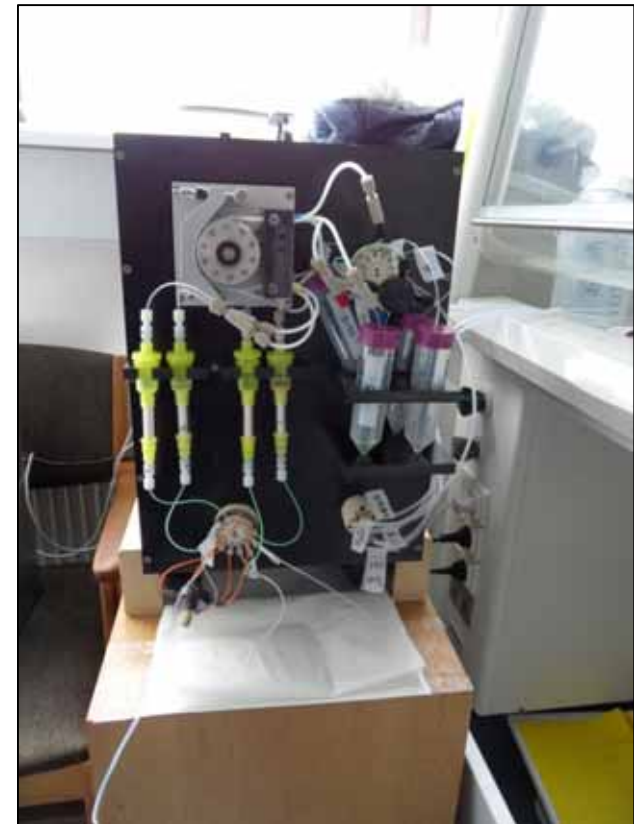
Chemical yields; $^{237}\text{Np}/^{242}\text{Pu}$ chemical yield ratio;

Method reability; Sample throughput

Auto-uint no.4---Flow injection



Simultaneously handle 4 samples!



Summary



Objectives	Achievement
1. Rapid determination of Pu, Np, U and Tc	<ul style="list-style-type: none">•Environmental solids: 2-5 h/sample•Large volume seawater: 1-2 days/sample•Biological samples: 6 h/sample
2. Automation of the analytical procedure	<ul style="list-style-type: none">•Sample pre-concentration: batchwise•Chemical purification: automated<ol style="list-style-type: none">1. Auto-unit no.1: sequentially 9 samples2. Auto-unit no.2: automated column packing3. Auto-unit no.3: automated dual connection4. Auto-unit no.4: simultaneously handle 4 samples•Measurement: automated

Conclusions and perspectives



Innovation of the previous work:

- Automatic
- Rapid and simple
- No need of Np isotopic tracer
- Low consumption of resins
- High sample throughput
- Low labor intensity

On-going projects:

- Tracer application studies of Pu and ^{236}U
- Multi-radionuclide determination (Pu/Np,U, Th, Am) in environmental samples

Thank you!

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