



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

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

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Radioecology and Tracer Studies  
DTU Nutech

06-09-2013

# Properties of Pu, Np, U and Tc



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

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



**Nuclear weapons testing**



**Nuclear power plants**

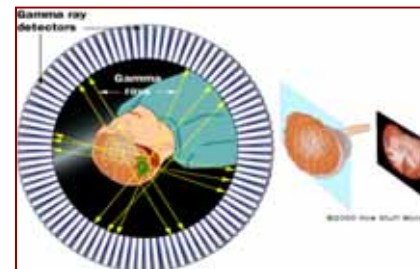
Pu isotopes,  
 $^{237}\text{Np}$ ,  $^{99}\text{Tc}$ ,  
 $^{236}\text{U}$



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

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

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

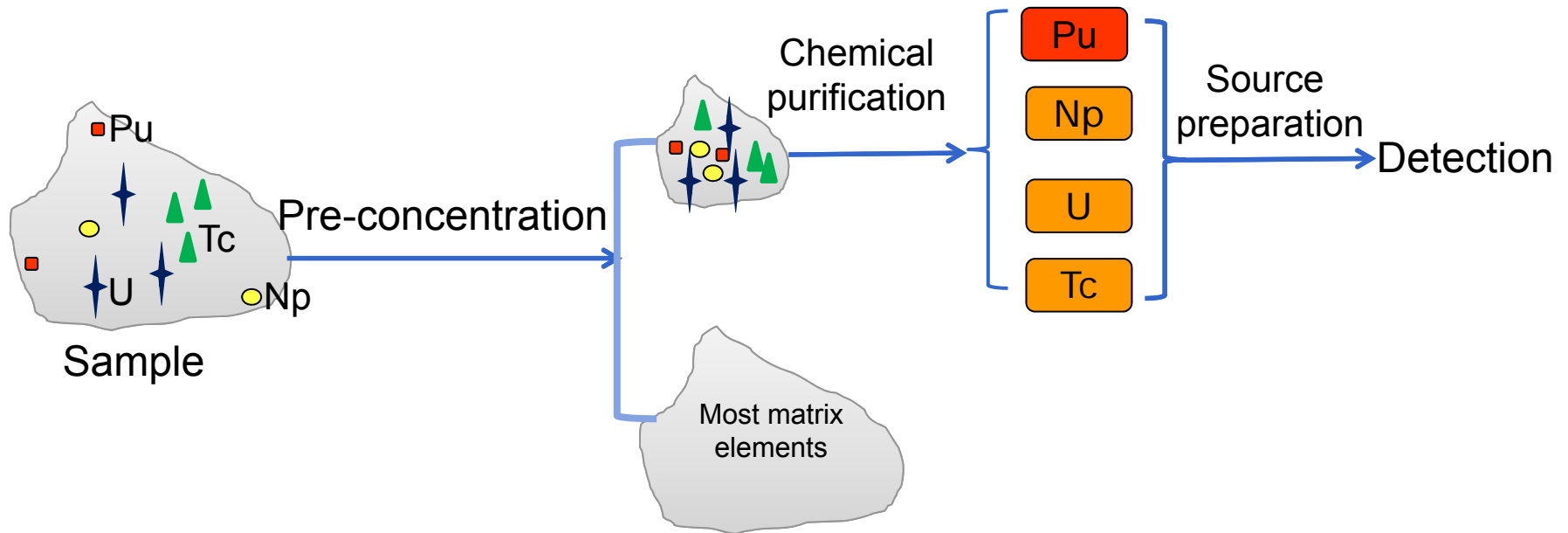
## Significances of Pu, Np, U and Tc determination



- 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...)

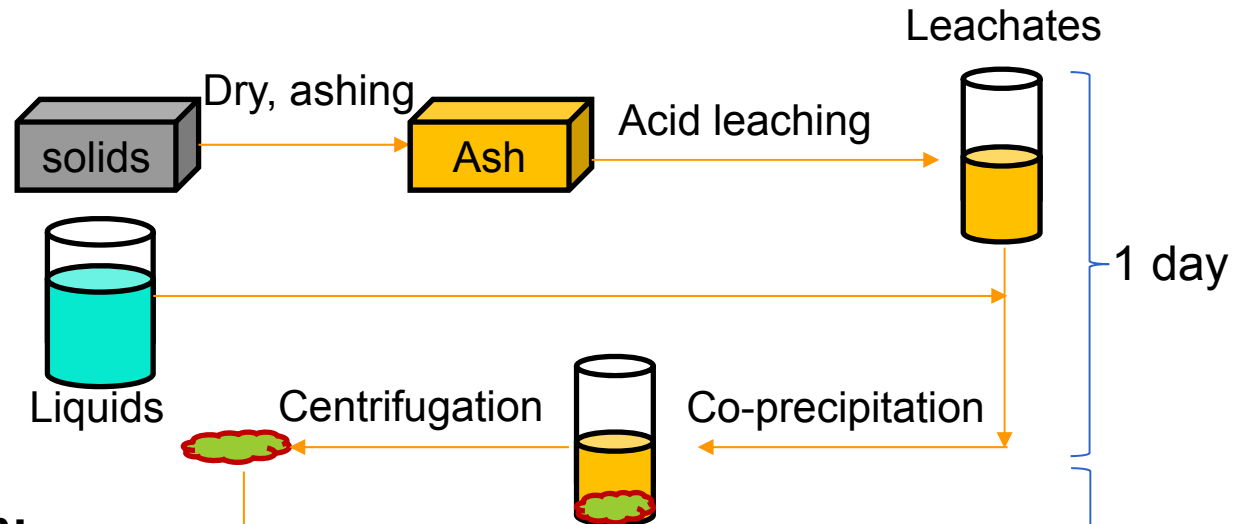




# Traditional analytical methods for Pu and Np

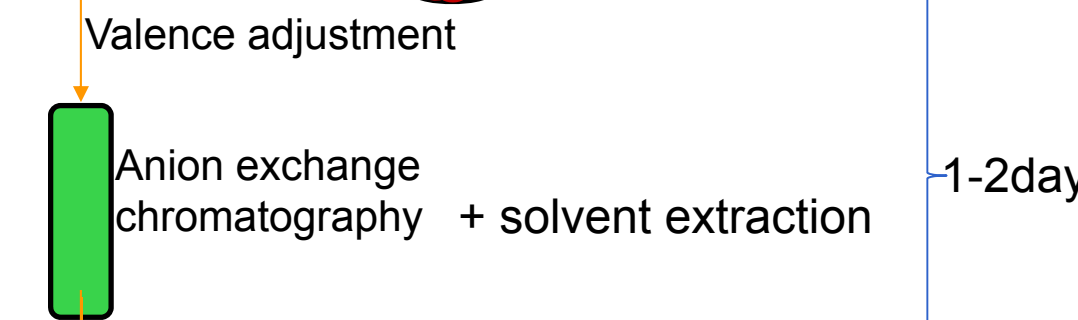
## Pre-concentration:

- 8-16 batchwise
- Fairly straightforward



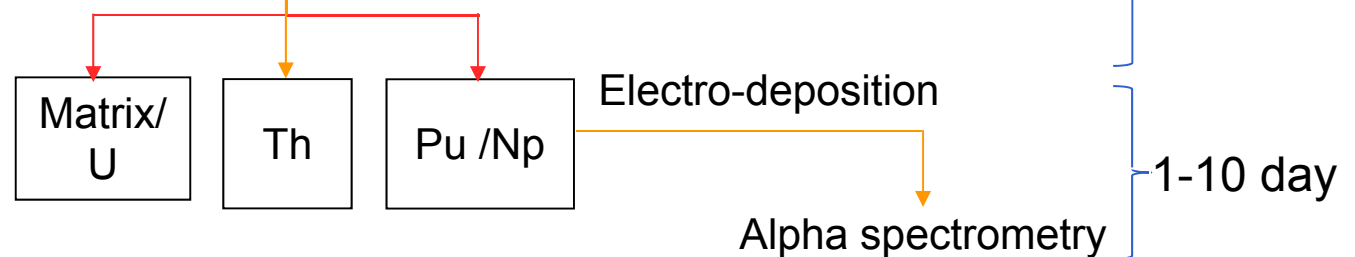
## Chemical purification:

- 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

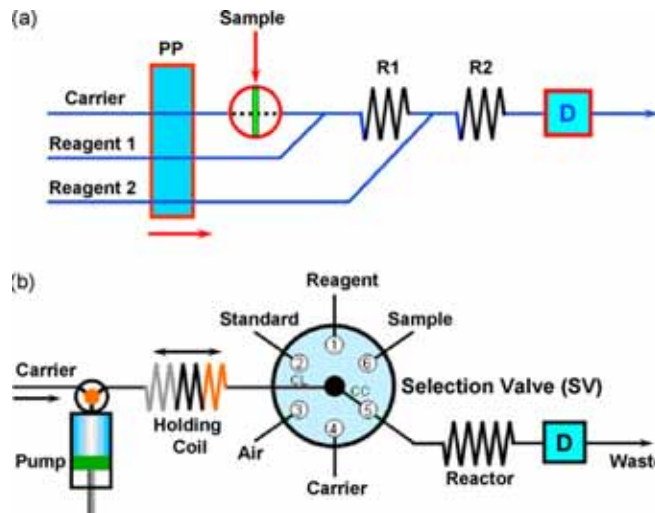
- Protocol simplification and optimization
- Automation

ii. Detection

- Mass spectrometry (ICP-MS, AMS)

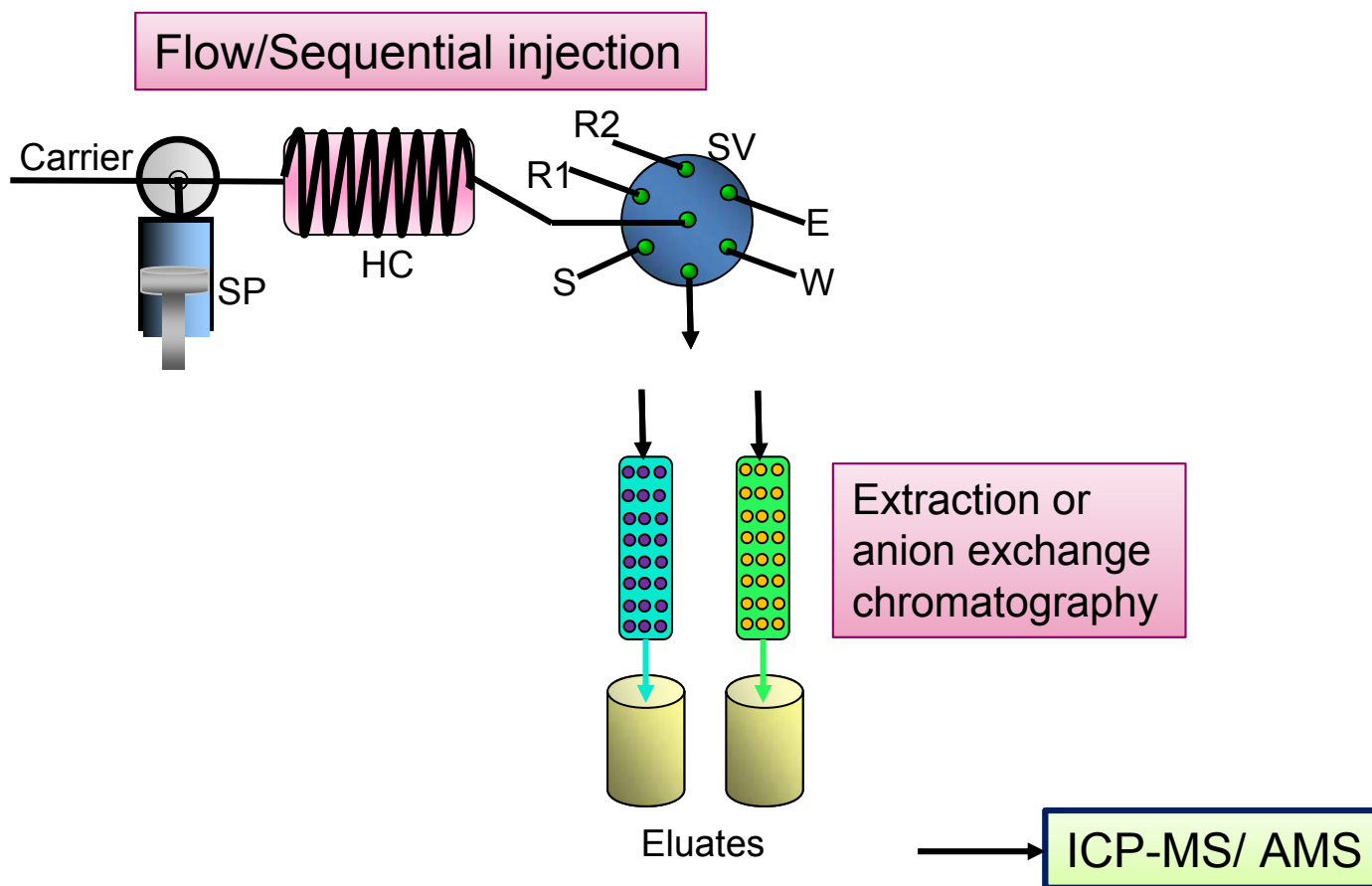
# Automation techniques

- 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:

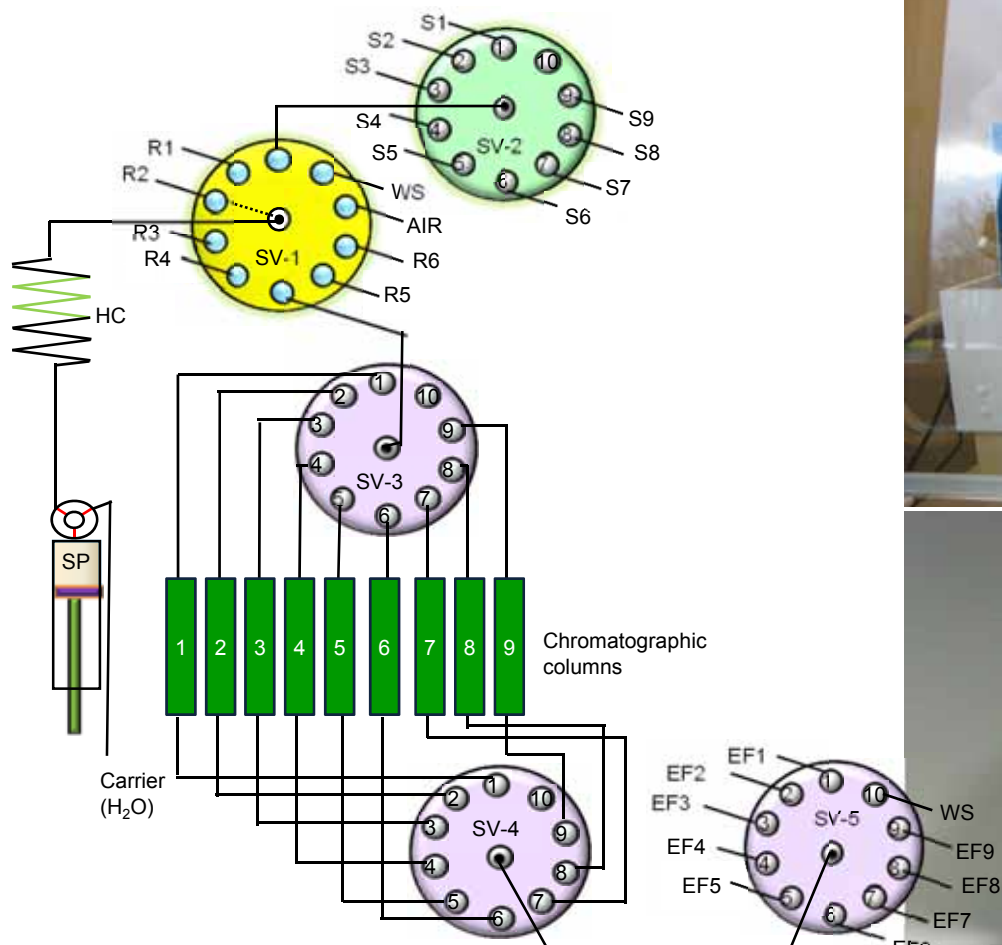
- Resin type (TEVA, AG1, AG MP-1M)
- Column size (1-20 mL)
- Washing solution (1-8 M HNO<sub>3</sub>)
- Elution solution (NH<sub>2</sub>OHHCl-HCl, 0.1-1.0 M HCl)
- Flow rate (1-5 mL/min)

## **Performance evaluation :**

Chemical yields; <sup>237</sup>Np/<sup>242</sup>Pu 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 Chimica Acta. 2011, 685, 111-119.

# Selected results for soil analysis



Method	Analyte	Resin	Chemical yield of $^{242}\text{Pu}$ , $Y_{\text{Pu}}$ (%)	Chemical yield of $^{237}\text{Np}$ , $Y_{\text{Np}}$ (%)	Ration of $Y_{\text{Np}}/Y_{\text{Pu}}$	$^{239}\text{Pu}$ measured (Bq/kg) *	$^{240}\text{Pu}$ measured (Bg/kg)**	Decontamination factor ***		
								$^{238}\text{U}$	$^{232}\text{Th}$	$^{208}\text{Pb}$
Extraction chromatography <sup>1,2)</sup>	Pu	TEVA (2mL, 0.7 × 5 cm)	97.7 ± 3.4	-	-	0.14 ± 0.01	0.09 ± 0.01	7.5 × 10 <sup>4</sup>	2.5 × 10 <sup>4</sup>	1.3 × 10 <sup>5</sup>
	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 <sup>4</sup>	7.0 × 10 <sup>3</sup>	1.0 × 10 <sup>4</sup>
Anion chromatography <sup>3,4)</sup>	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 <sup>3</sup>	2.4 × 10 <sup>4</sup>	2.7 × 10 <sup>4</sup>
		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 <sup>3</sup>	1.7 × 10 <sup>4</sup>	1.0 × 10 <sup>3</sup>
	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 <sup>3</sup>	2.5 × 10 <sup>5</sup>	1.0 × 10 <sup>3</sup>

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

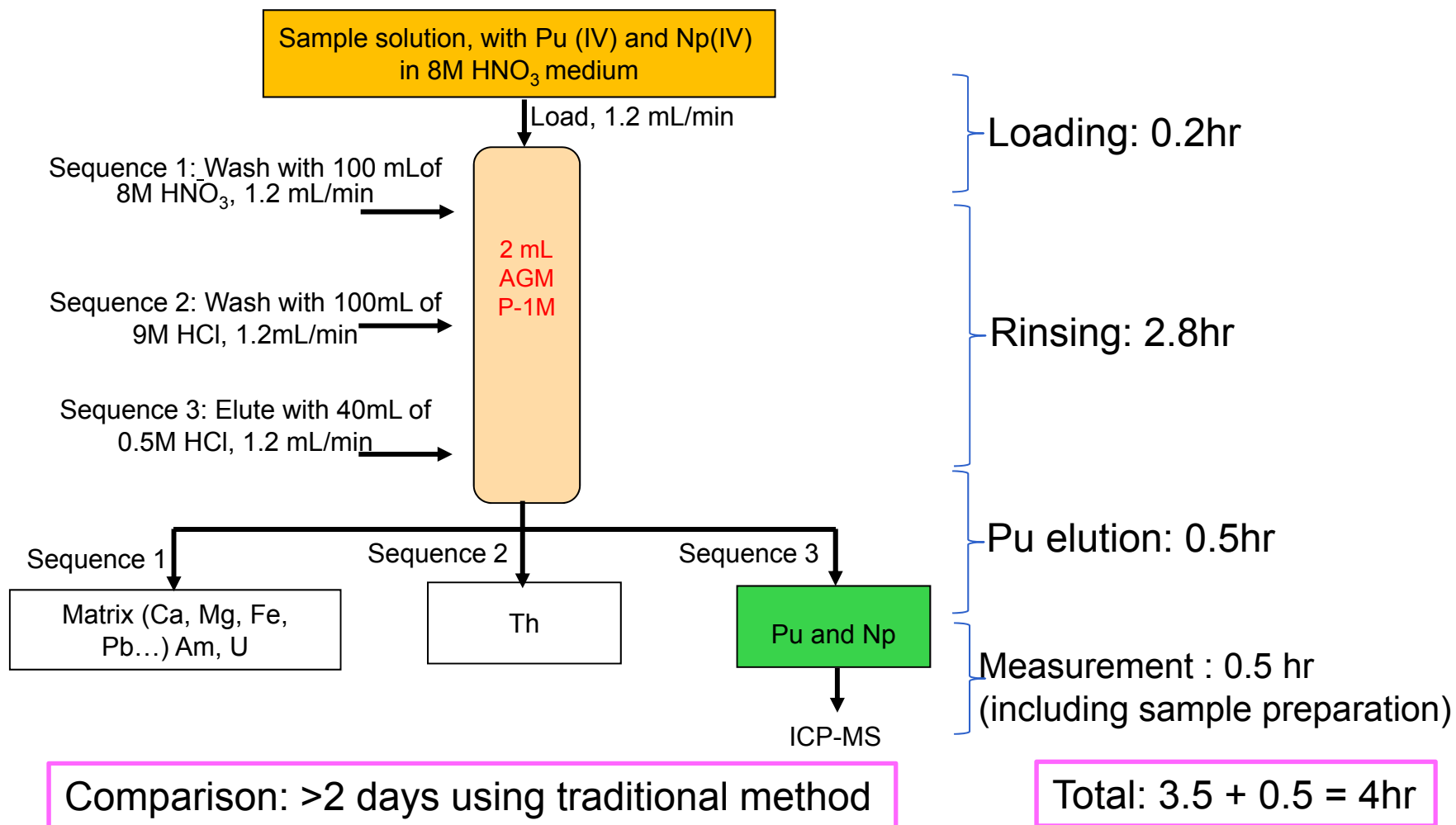
1) Qiao, J. X., Hou, X. L., Roos, P., Miró, M. Analytical Chemistry. 2009, 81, 8185-8192.

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 $^{238}\text{U}$ )	☹ Medium ( $1-10 \times 10^3$ for $^{238}\text{U}$ )
Accuracy	☺ High (RSD $\leq 5\%$ )	☹ Medium (RSD $\leq 10\%$ )
Consumption of chemicals	☺ Low (e.g. 10 mL of conc. $\text{HNO}_3$ /sample)	☹ High (e.g. 80 mL of conc. $\text{HNO}_3$ /sample)
<b>Recommendation</b>	<b>Pu determination using TEVA resin</b>	<b>Pu &amp;Np simultaneous determination using AG MP-1M resin</b>

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:

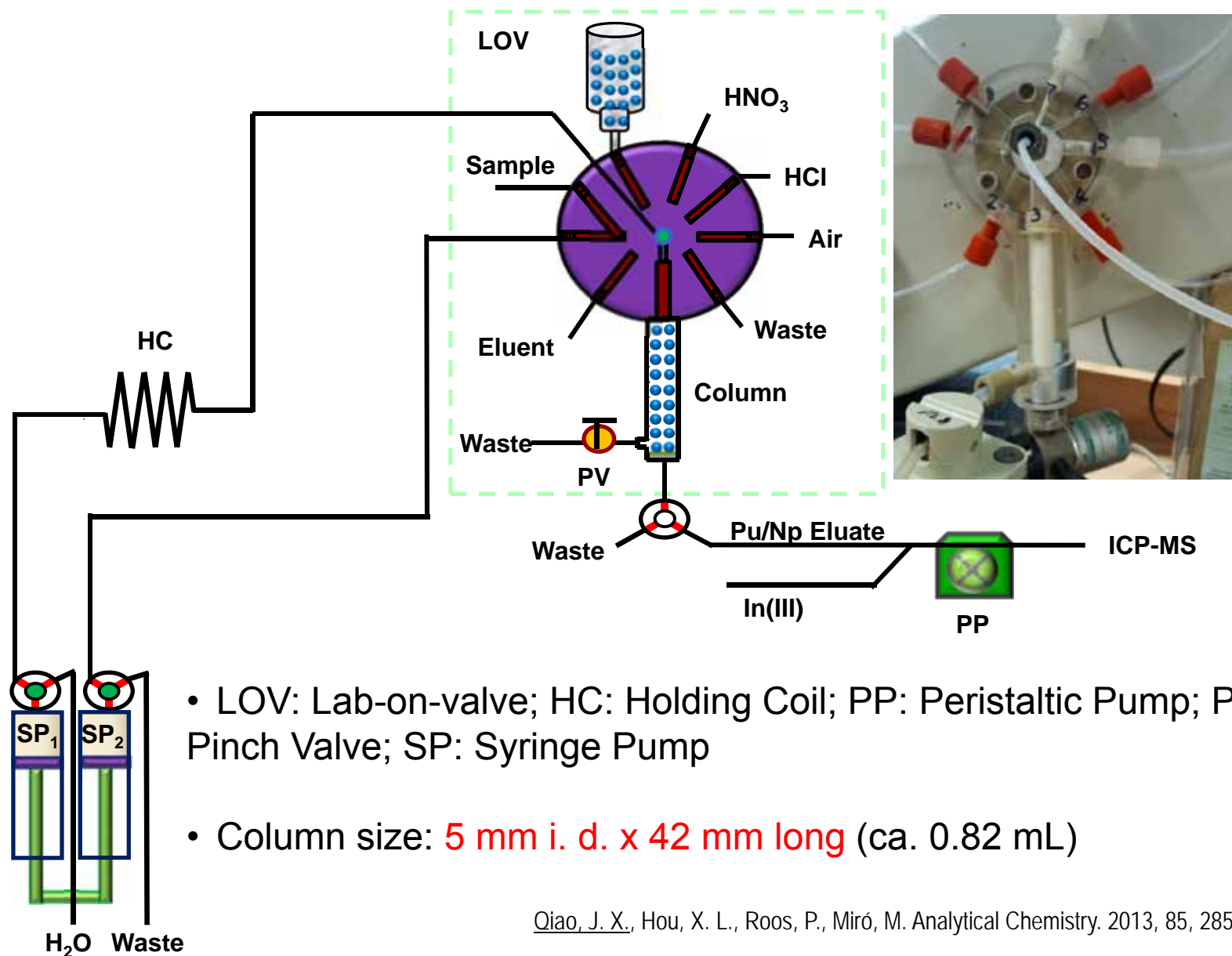
- Co-precipitation techniques ( $\text{Ca}_3(\text{PO}_4)_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{MnO}_2$ , etc.)
- Decomposition of organic matter (acid digestion/dry ashing)
- Washing solution (0.2-1 M  $\text{HNO}_3$ )
- Elution solution (0.025-0.5 M  $\text{HCl}$ )

## **Performance evaluation :**

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

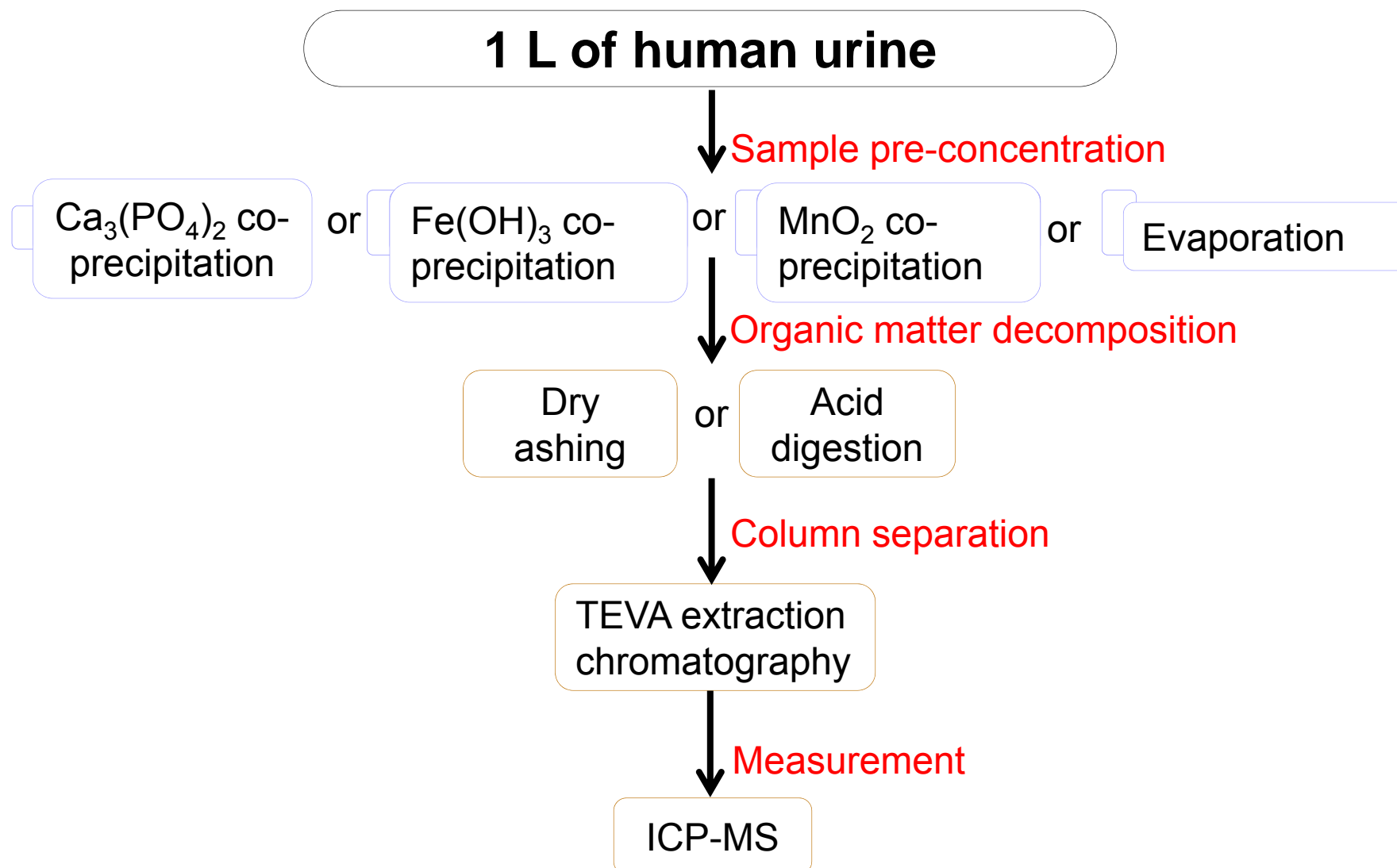
Method reability; Sample throughput

# 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		
					$^{242}\text{Pu}$ , %	$^{237}\text{Np}$ , %	$^{237}\text{Np}/^{242}\text{Pu}$
1	$\text{Ca}_3(\text{PO}_4)_2$ co-precipitation	Dry ash	Ascorbic acid / conc. $\text{HNO}_3$	13 hr	$84.7 \pm 5.7$	$80.9 \pm 10.7$	0.95
		Acid digestion		8 hr	$46.8 \pm 4.1$	$8.3 \pm 5.4$	0.18
2	$\text{Fe}(\text{OH})_2/\text{Fe}(\text{OH})_3$ co-precipitation	Dry ash	$\text{Fe}/\text{K}_2\text{S}_2\text{O}_5 / \text{conc.}\text{HNO}_3$	6 d	$84.3 \pm 15.6$	$73.3 \pm 33.0$	0.87
		Acid digestion		5.5 d	$80.3 \pm 9.9$	$77.9 \pm 10.9$	0.97
		Acid digestion		6 hr	$51.3 \pm 0.2$	$57.5 \pm 8.8$	1.12
3	<b><math>\text{MnO}_2</math> co-precipitation</b>	<b>Acid digestion</b>	<b><math>\text{Fe}/\text{K}_2\text{S}_2\text{O}_5 / \text{conc.}\text{HNO}_3</math></b>	<b>6 hr</b>	<b><math>88.4 \pm 8.0</math></b>	<b><math>91.4 \pm 10.0</math></b>	<b>1.03</b>
4	$\text{Ca}(\text{OH})_2/\text{Fe}(\text{OH})_2 / \text{Fe}(\text{OH})_3$ co-precipitation	Acid digestion	Ascorbic acid / conc. $\text{HNO}_3$	6 hr	$87.3 \pm 6.6$	$51.2 \pm 1.6$	0.59
5	Evaporation	Dry ash + acid leaching	$\text{Fe}/\text{K}_2\text{S}_2\text{O}_5 / \text{conc.}\text{HNO}_3$	1.5 d	$75.5 \pm 2.6$	$81.1 \pm 3.6$	1.07

# Methods Development-Pu, Np and U



## Environmental Sample:

- 10 L of seawater

## Parameters optimized:

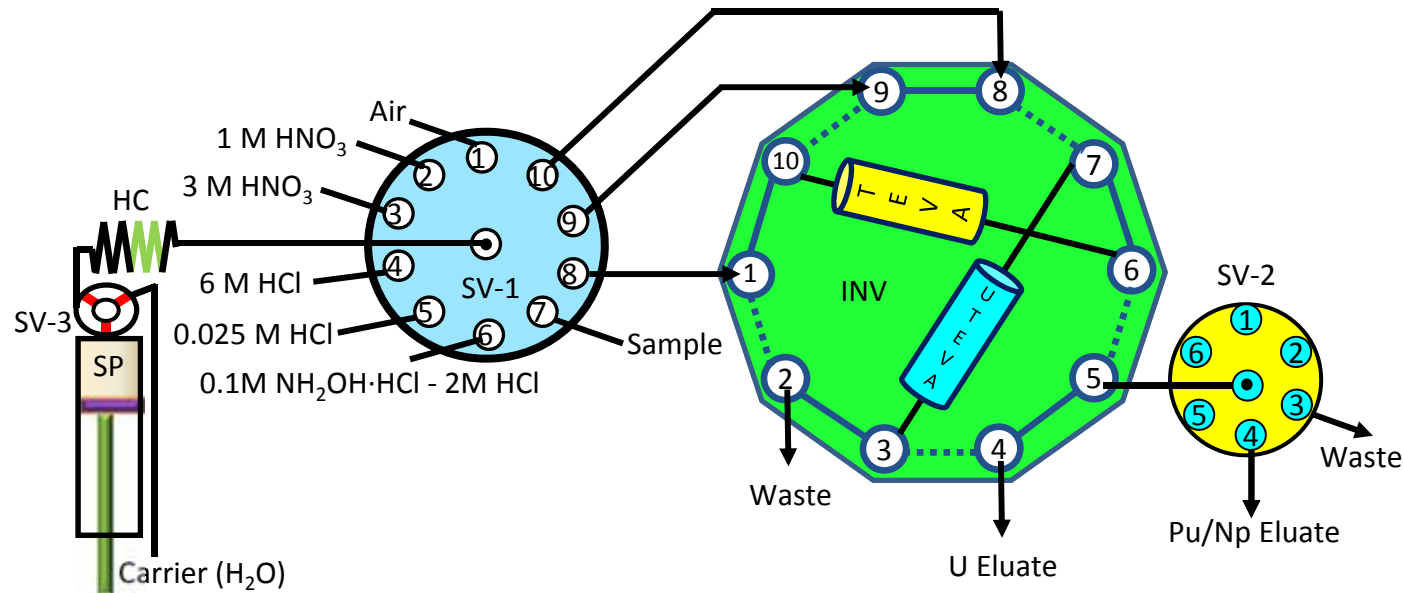
- Resin type (TEVA, UTEVA)
- Washing solution (1-4 M HNO<sub>3</sub>)
- Decomposition of organic matter

## **Performance evaluation :**

Chemical yields; <sup>237</sup>Np/<sup>242</sup>Pu chemical yield ratio;

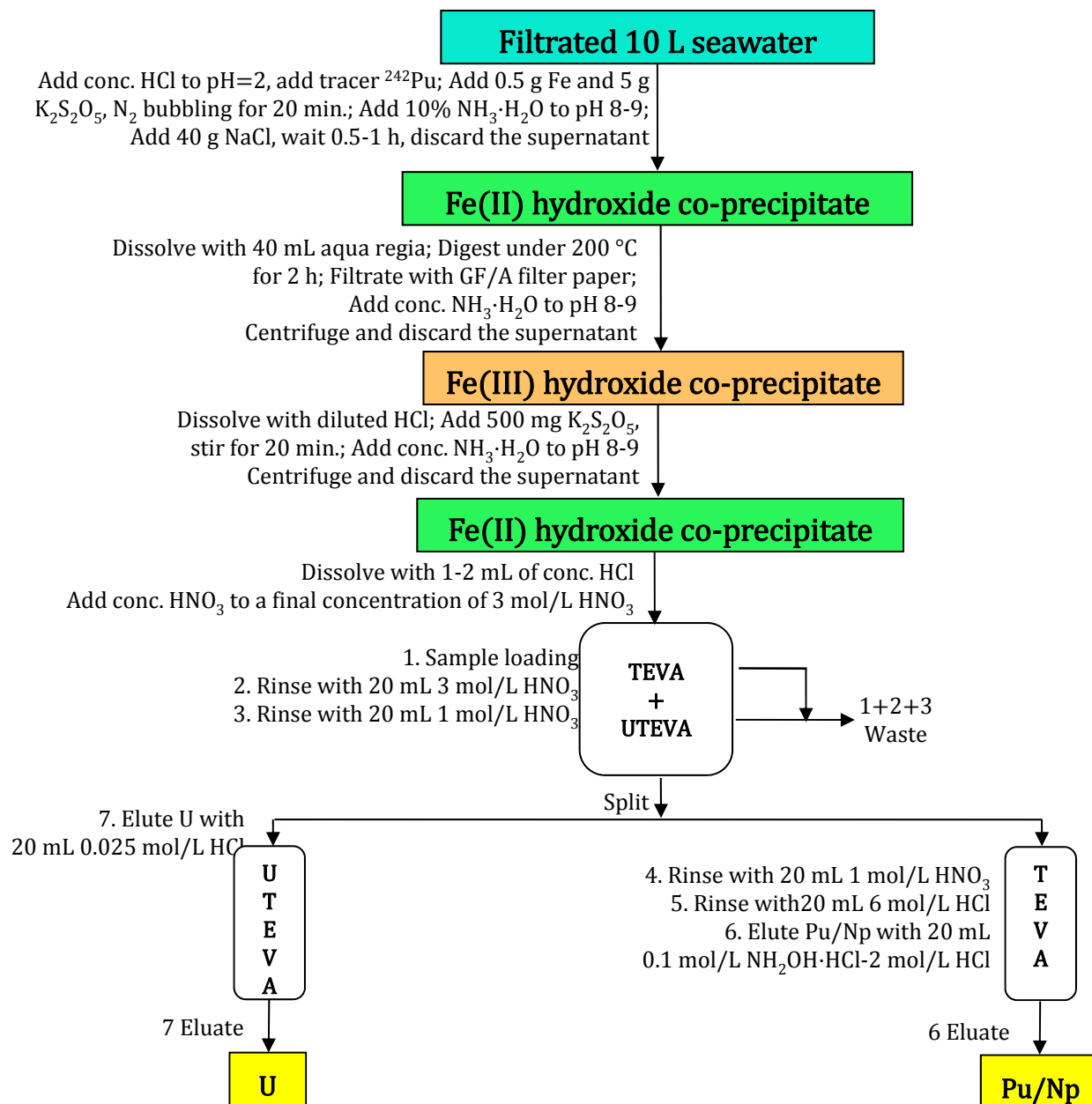
Method reability; Sample throughput

# 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
	<sup>242</sup> Pu	<sup>237</sup> Np	<sup>237</sup> Np/ <sup>242</sup> Pu ratio	<sup>238</sup> U	
8	73.6 ± 9.8	73.9 ± 5.6	1.01 ± 0.21	97.6 ± 20.6	(5.3 ± 0.5) × 10 <sup>4</sup>

## Method application with the use of AMS measurement

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

# Methods Development-Pu, Np, U and Tc



## Environmental Sample:

- 200 L of seawater

## Parameters optimized:

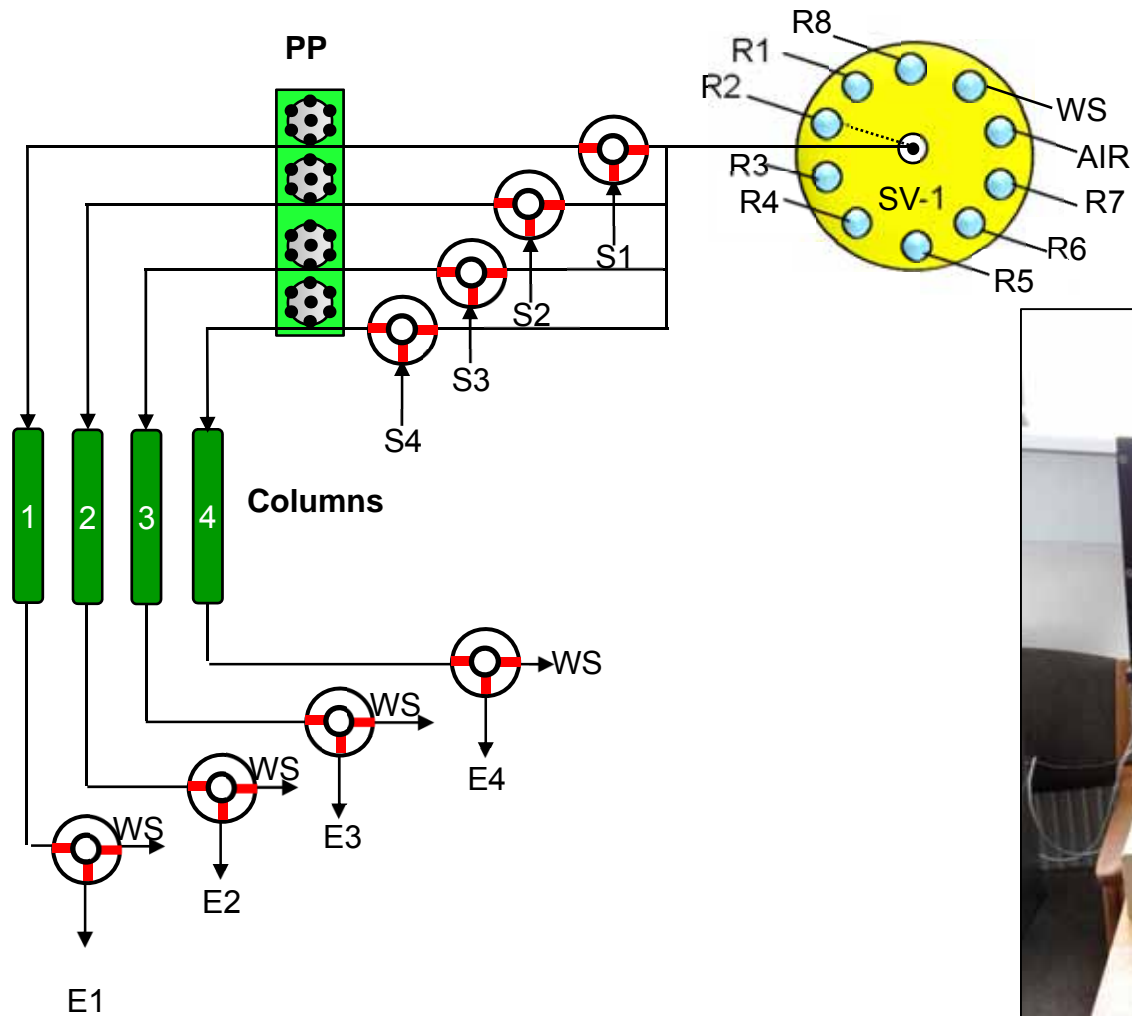
- Resin type (TEVA, UTEVA, AG MP-1M)
- Selection of Redox reagents
- Decontamination of interferences

## **Performance evaluation :**

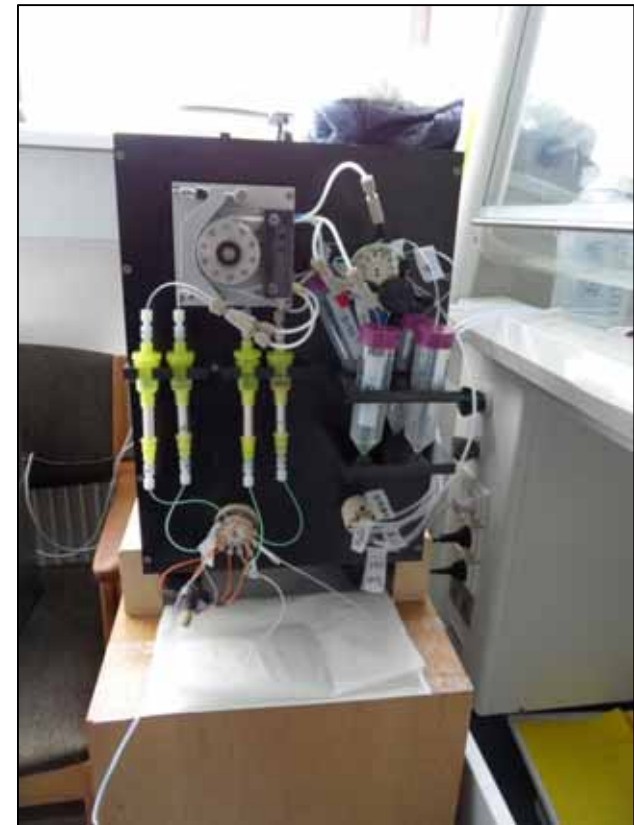
Chemical yields;  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yield ratio;

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"><li>•Environmental solids: 2-5 h/sample</li><li>•Large volume seawater: 1-2 days/sample</li><li>•Biological samples: 6 h/sample</li></ul>
2. Automation of the analytical procedure	<ul style="list-style-type: none"><li>•Sample pre-concentration: batchwise</li><li>•Chemical purification: automated<ol style="list-style-type: none"><li>1. Auto-unit no.1: sequentially 9 samples</li><li>2. Auto-unit no.2: automated column packing</li><li>3. Auto-unit no.3: automated dual connection</li><li>4. Auto-unit no.4: simultaneously handle 4 samples</li></ol></li><li>•Measurement: automated</li></ul>

# 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  $^{236}\text{U}$
- Multi-radionuclide determination (Pu/Np,U, Th, Am) in environmental samples

# Thank you!

Jixin Qiao

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