Analysis of Pu isotopes and Np-237 in seawater by AMS

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Key elements of RML work

- Production and distribution of Reference Materials for radionuclides
  Preparation for accreditation: ISO Guide 17034 and ISO 17025
- Organisation of proficiency tests and inter-laboratory comparisons
  Plan for accreditation: ISO 17043
- Provision of quality assurance services to MSs and to international programs
- Providing experimental and scientific expertise and analytical capacities during aftermath of nuclear accidents
- Technical cooperation
- ALMERA network
- Laboratory and field work
- Research, training and communication

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IAEA Collaborating Centre

for

Accelerator-Based Analytical Techniques
for the Study of Radionuclides in Marine Samples

2016–2020

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^{237}Np

- $T_{1/2}=2.144\times10^{6}$ years.
- alpha emitter.
- produced by double neutron capture of ^{235}U in nuclear reactors.

$$^{235}\mathrm{U} \xrightarrow{(n,\gamma)} {}^{236}\mathrm{U} \xrightarrow{(n,\gamma)} {}^{237}\mathrm{U} \xrightarrow{(\beta)} {}^{237}\mathrm{Np}$$

- by fast neutron irradiation of ^{238}U in nuclear bomb testing and reactors.

$$^{238}\mathrm{U} \xrightarrow{(n,2n)} {}^{237}\mathrm{Pu} \xrightarrow{(\beta)} {}^{237}\mathrm{Np}$$

- by alpha decay of its parent ^{241}Am and grandparent ^{241}Pu.
- oceanographic tracer due to its conservative nature in seawater.

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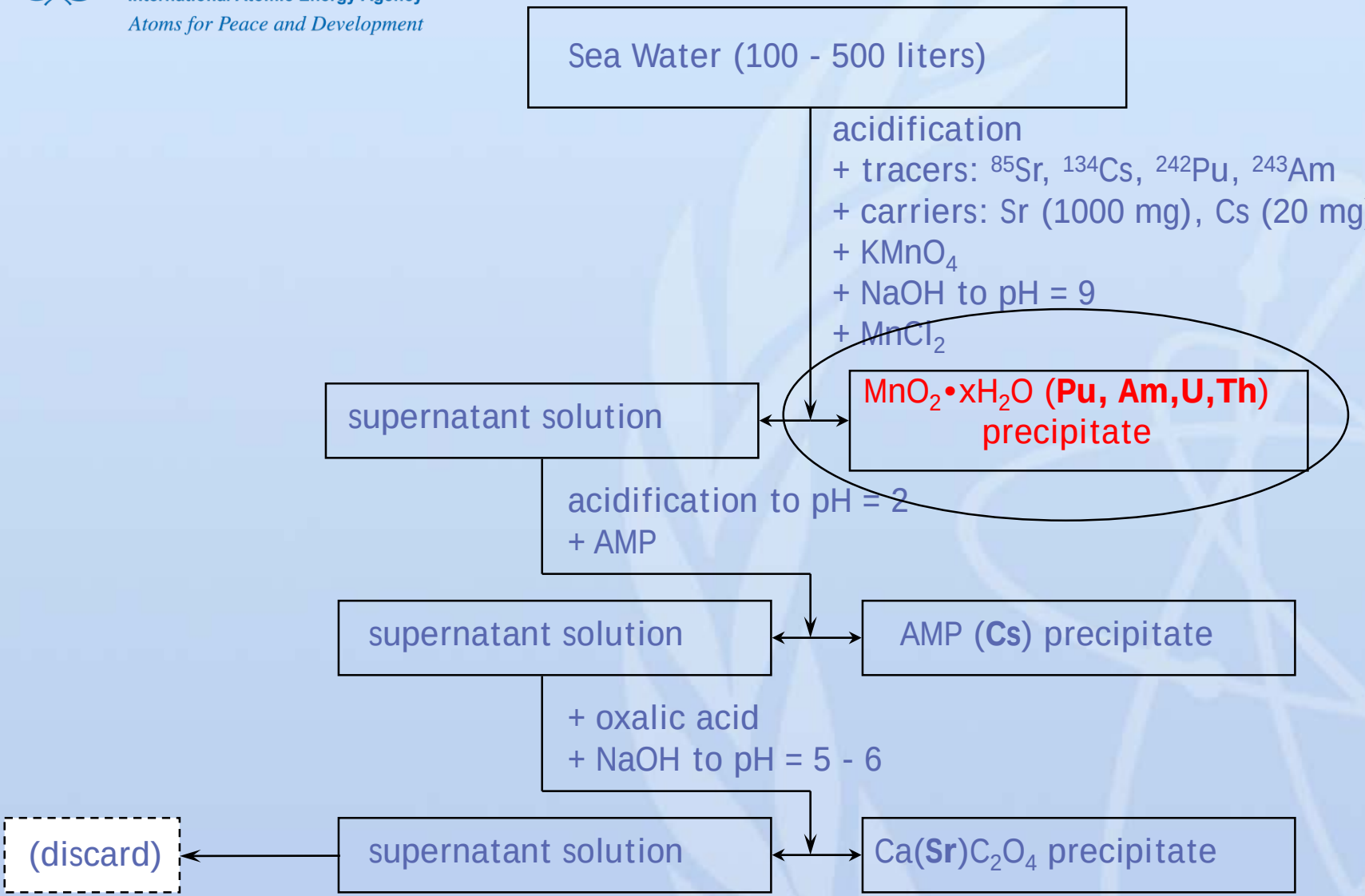
Sequential extraction procedure



➡ Allow the analysis of all anthropogenic elements in one sample.

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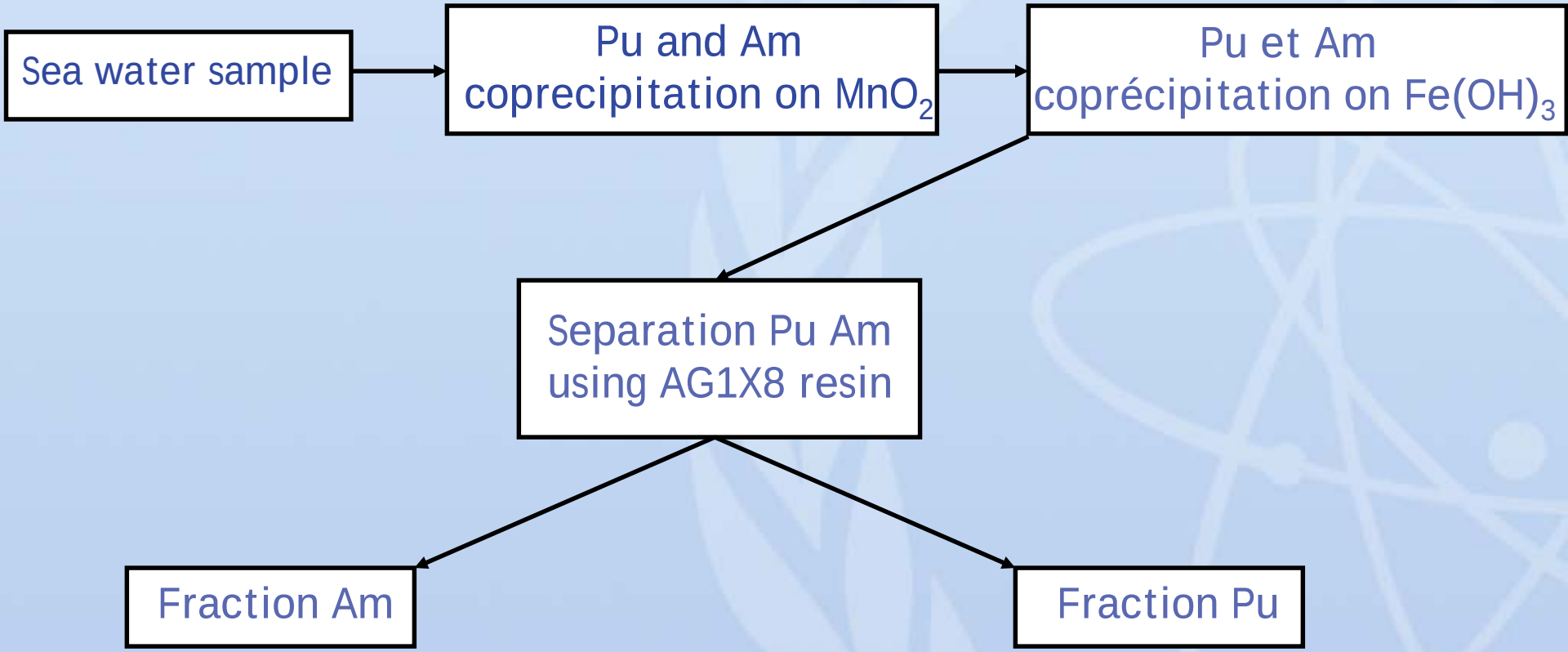
« Classical » method for Plutonium and Americium analysis



Pu and Am separation

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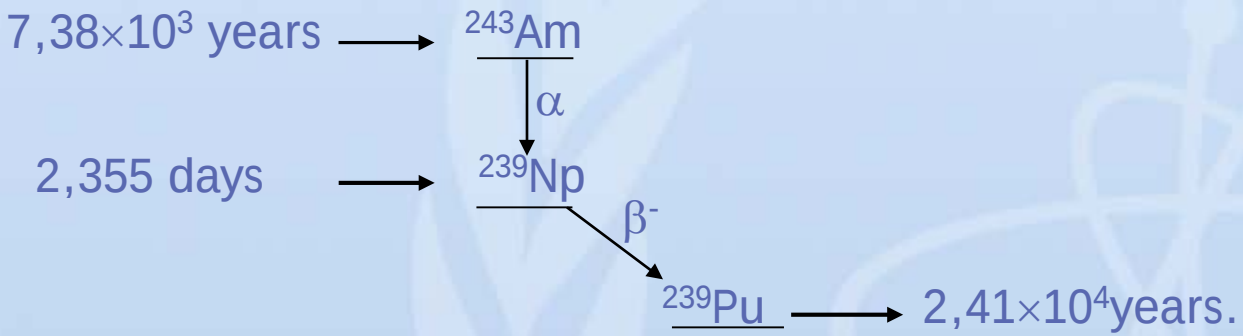
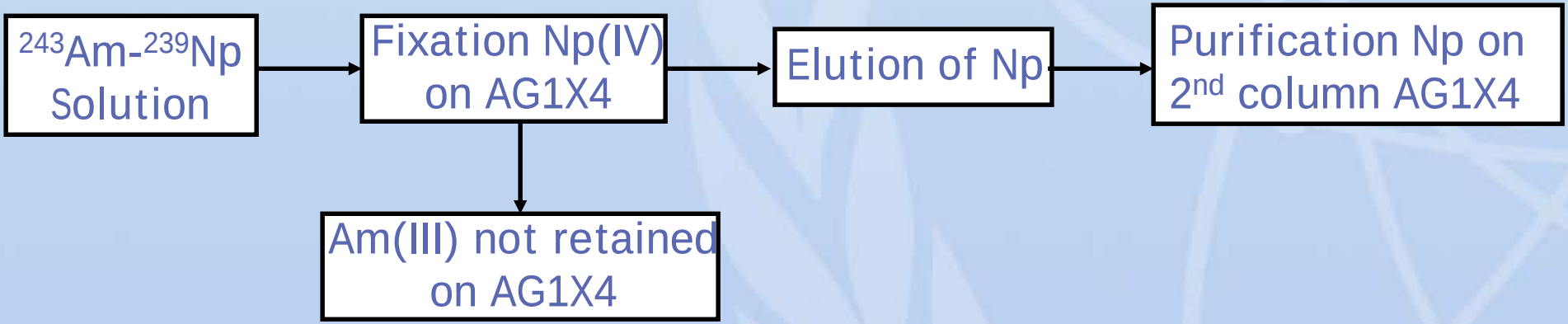
Neptunium tracer preparation

- No other Np isotope than ^{237}Np available.
- Use of ^{239}Np after radiochemical separation:





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Development of the new method for Plutonium, Americium and Neptunium determination

From the « classical » method, Analyze Neptunium as the same time as Plutonium and Americium.

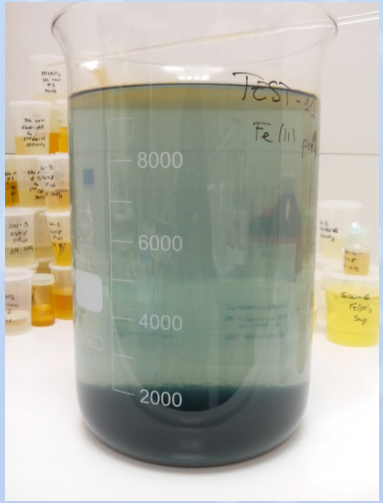
⇨ Different tests have been done.

Used isotope: ^{239}Np.

Coprecipitation tests

Different precipitates have been done with ^{239}Np tracer to test efficiency to coprecipitate Neptunium.

precipitates	Recovery ^{239}Np (%)
MnO_2	98
$Fe(OH)_2$	100
NdF_3	79
$Fe(OH)_3$	100
CaC_2O_4	5
$Fe(OH)_3$ after MnO_2	12
MnO_2 after MnO_2	90
$Fe(OH)_2$ after MnO_2	100



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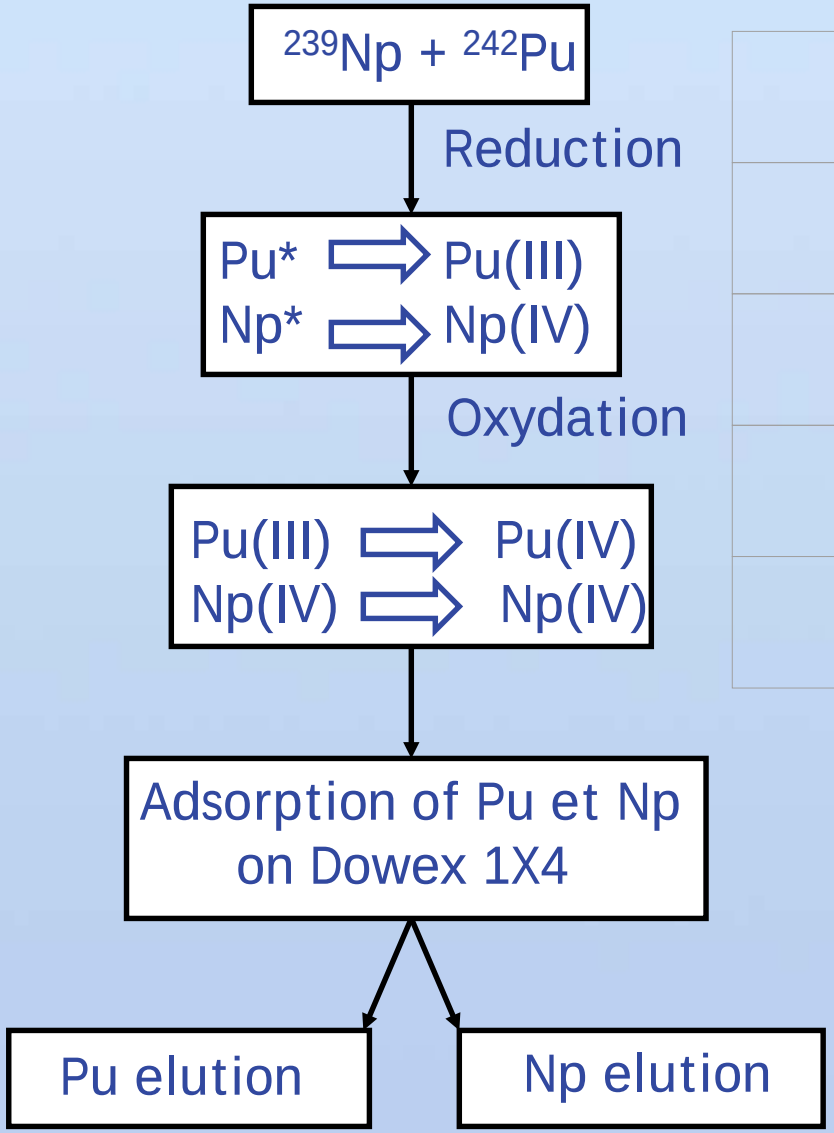
Adsorption tests of Np on anionic resin Dowex 1x4.



Fraction	**Activity(Bq)**	**Recovery(%)**
HNO_3 8M	7±3	2±1
HCl 10M	45±3	13±1
Pu Fraction	77±6	22±2
Np Fraction	147±12	42±3

^{239}Np activity in the different fractions of Dowex 1X4

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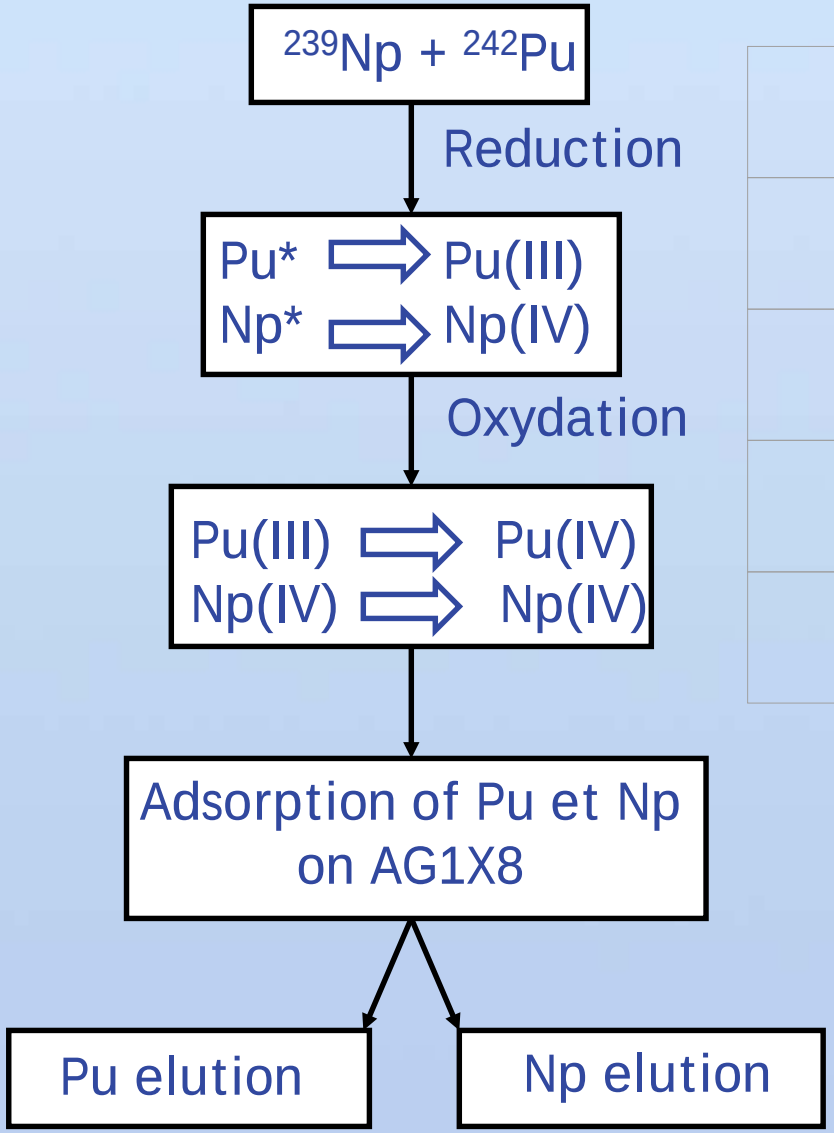
Adsorption tests of Np on anionic resin Biorad AG1X8.



Fraction	**Activity(Bq)**	**Recovery(%)**
HNO_3 8M	0	0
HCl 10M	1,0±0,2	1,0±0,5
Fraction Pu	0	0
Fraction Np	150±5	100±3

^{239}Np activity in the different fractions of AG1X8

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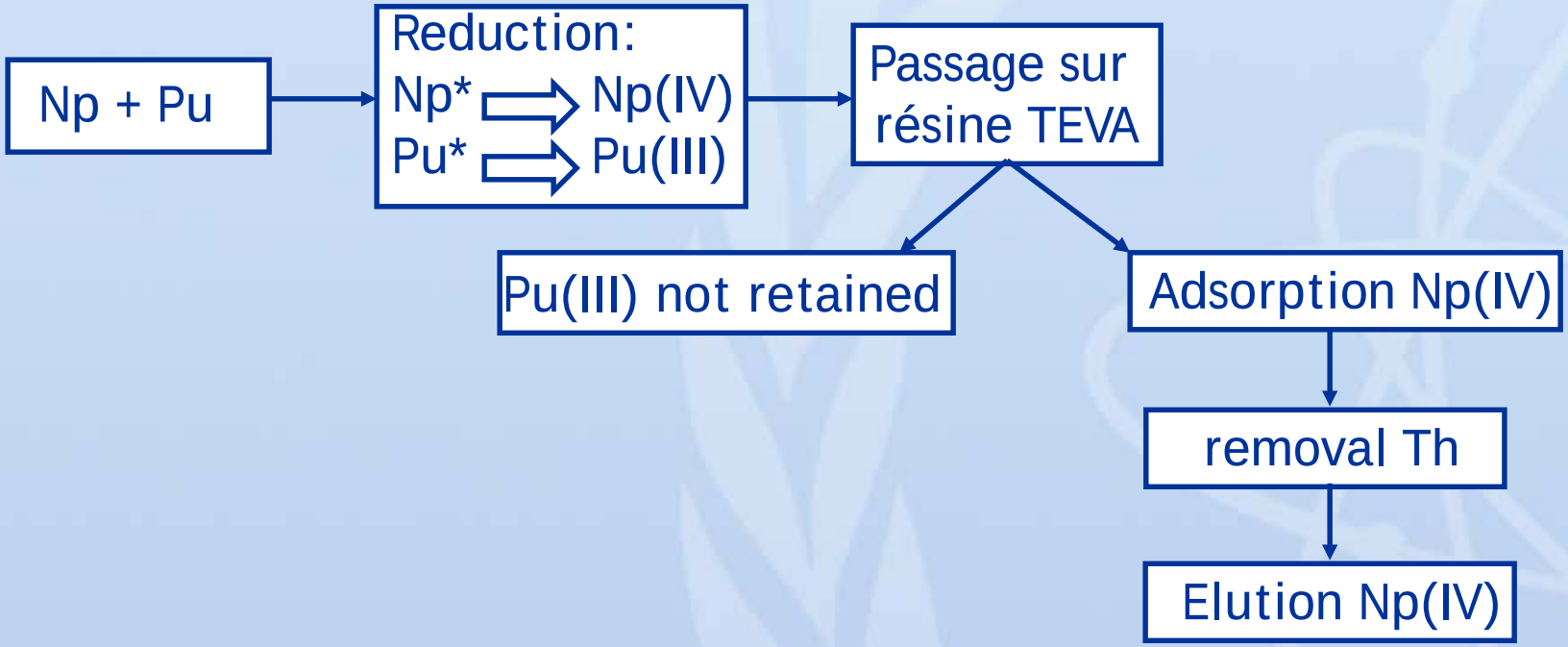
Purification tests of Neptunium: removal of Plutonium traces.

Use of TEVA® resin : liquid extractant adsorbed on a polymeric support.



⇒ Plutonium contribution in Neptunium fraction is of background level.

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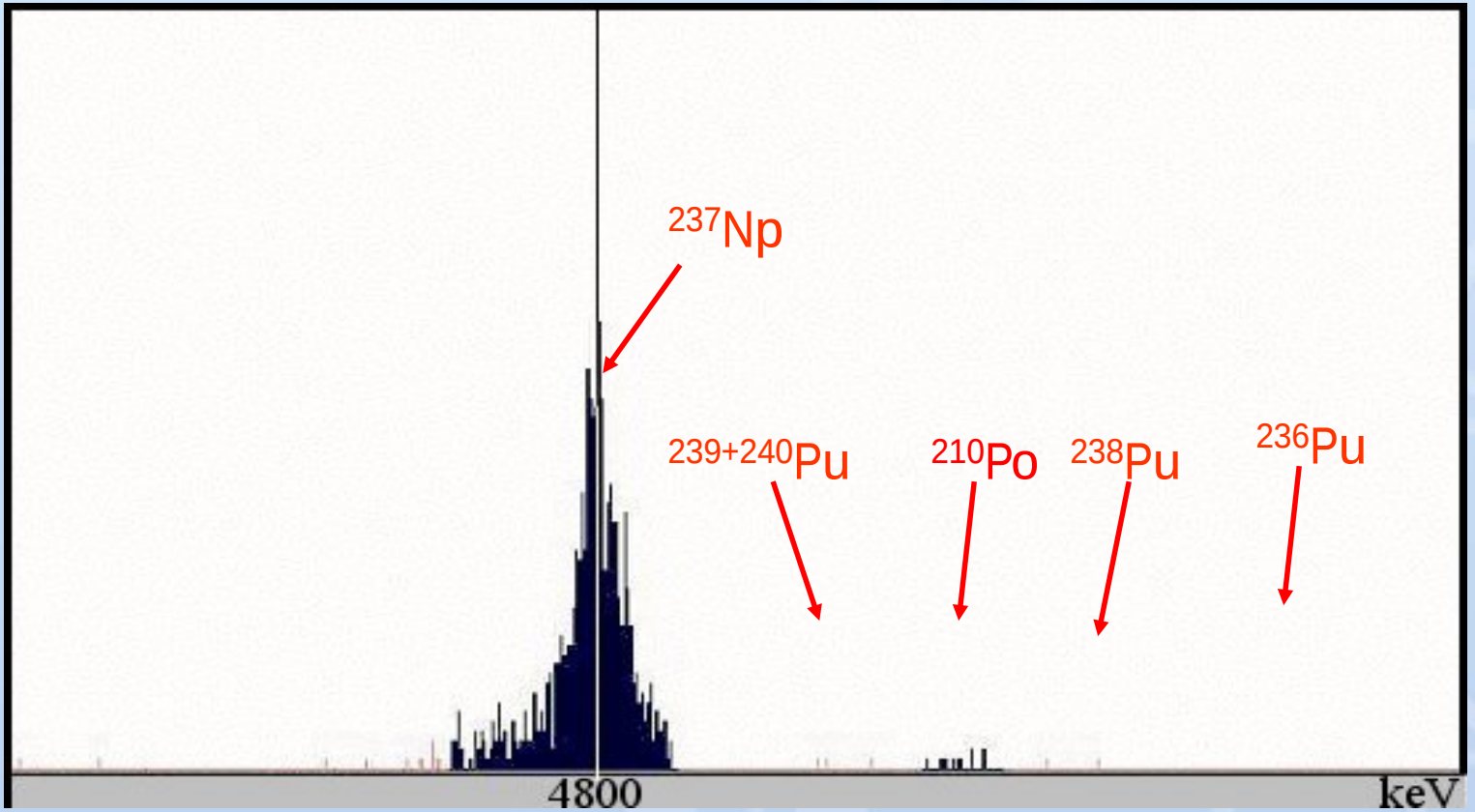
Alpha Spectrum of Neptunium in IAEA-381.



[^{237}Np]: 8,9 mBq/l certified value
[$^{239+240}$Pu]:13,5 mBq/l certified value
[^{238}Pu]: 3,2 mBq/l certified value

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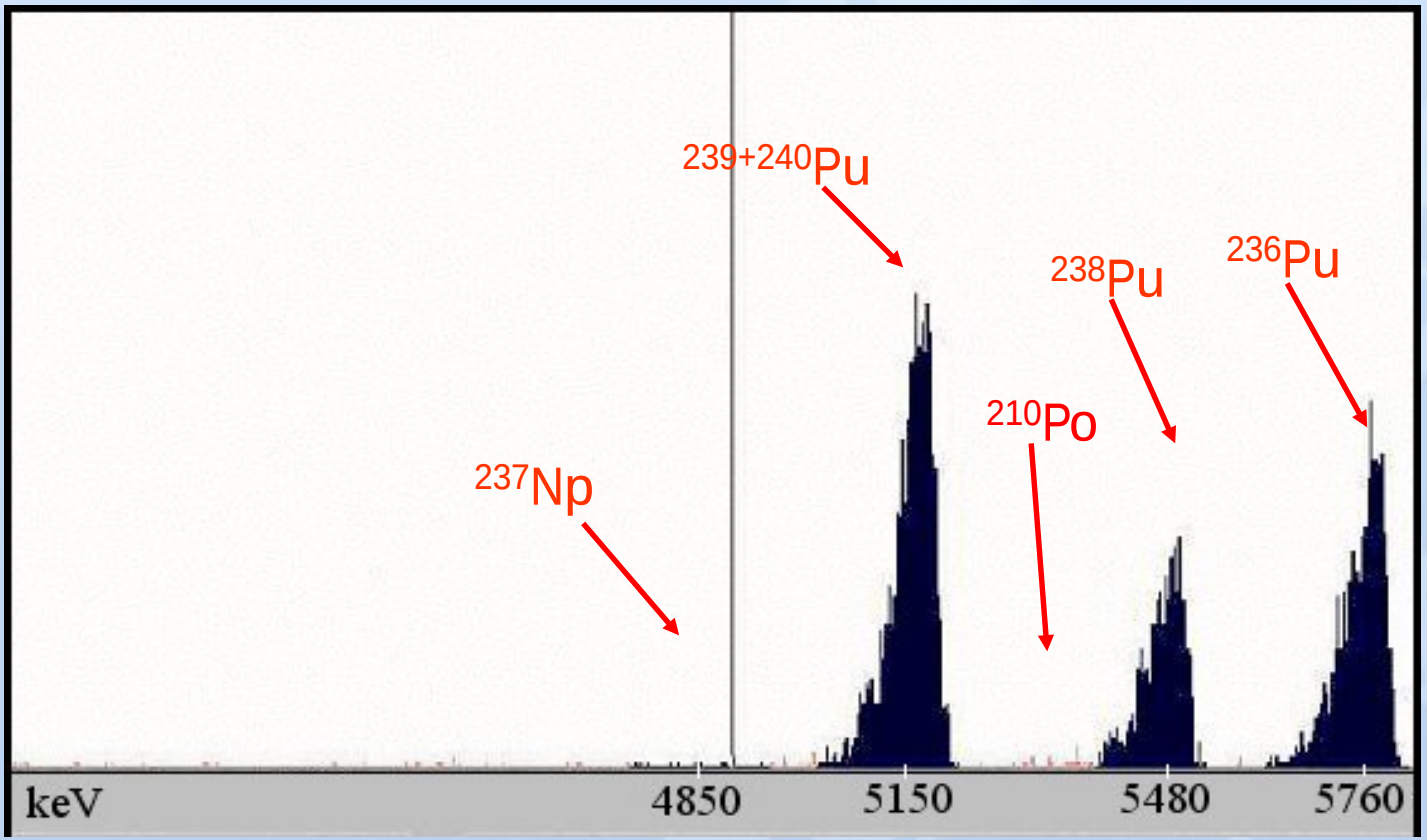
Alpha Spectrum of Plutonium in IAEA-381.



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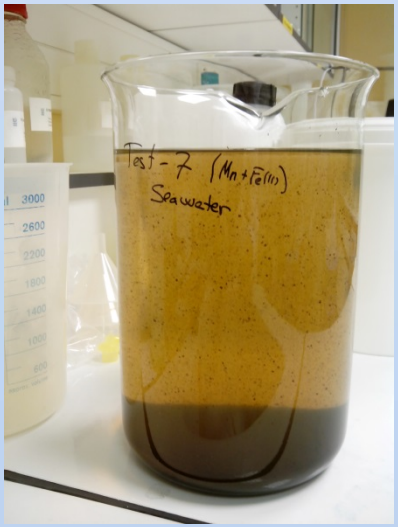
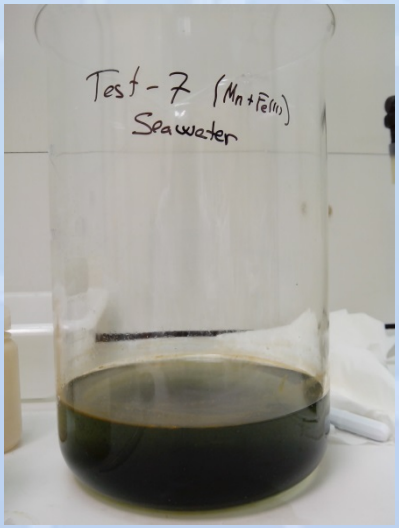
Separation method of Pu and Np for AMS analysis

Sea water sample

Pu and Np coprecipitation on MnO_2

Pu et Np coprécipitation on $Fe(OH)_2$





Separation Pu Np using AG1X8 resin

Fraction Pu

Fraction Np

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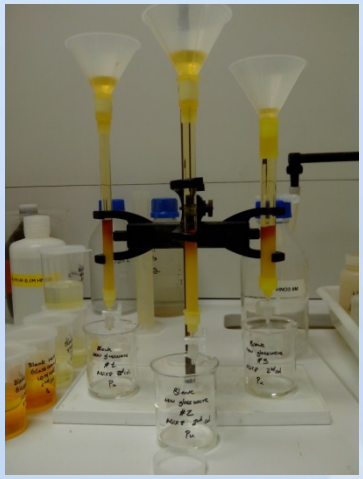
Purification of Pu and Np fractions for AMS analysis.

Fraction Pu



Removal of U, Th
Purification of Pu on AG1X8 resin

Alpha measurement

Cathode preparation for AMS measurement

Fraction Np

Removal of U
2 Coprécipitations of Np with NdF_3

Removal of Pu and Th
TEVA® column

Cathode preparation for AMS measurement

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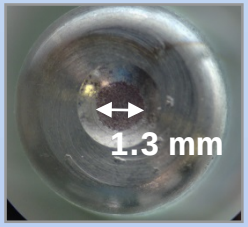
Cathodes preparation for AMS measurement

Np Fraction:

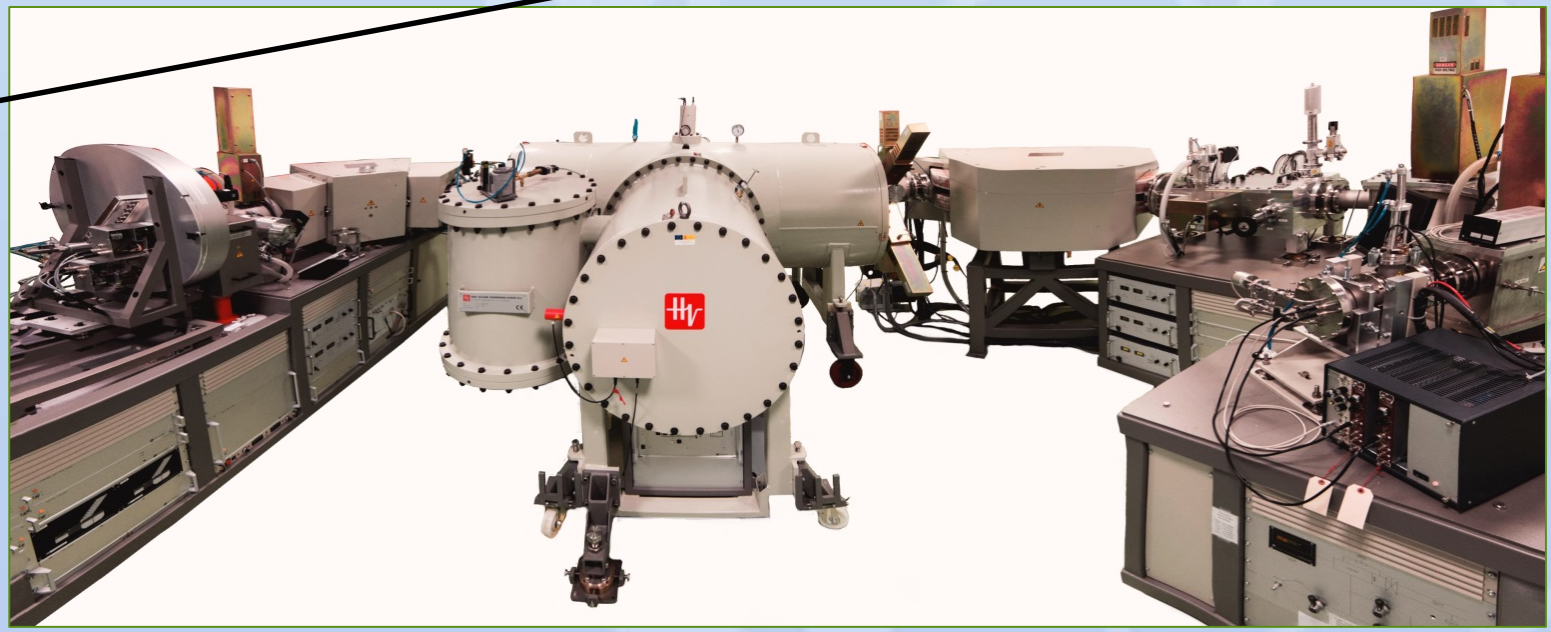
- 1mg Fe3+, 2pg U-233
- $Fe(OH)_3$ Precipitation
- ashing at 650°C
- Mix with 3mg Nb
- Pressed in 1 aluminum cathode

Pu Fraction:

- 1mg Fe^{3+},
- $Fe(OH)_3$ Precipitation
- ashing at 650°C
- Mix with 3mg Nb
- Pressed in 1 aluminum cathode



$XO_2+Fe_2O_3+Nb$



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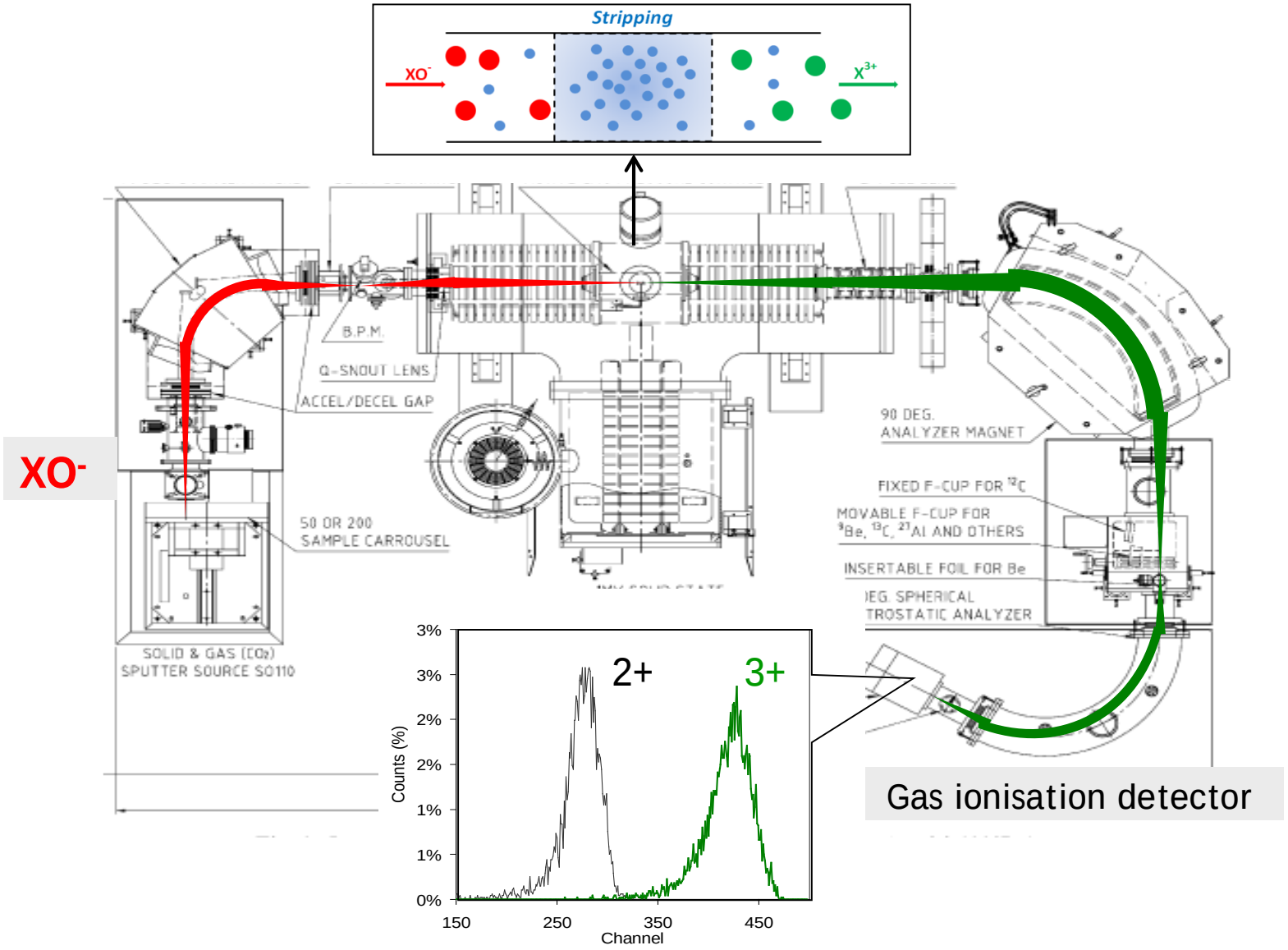
Accelerator Mass Spectrometry (AMS)



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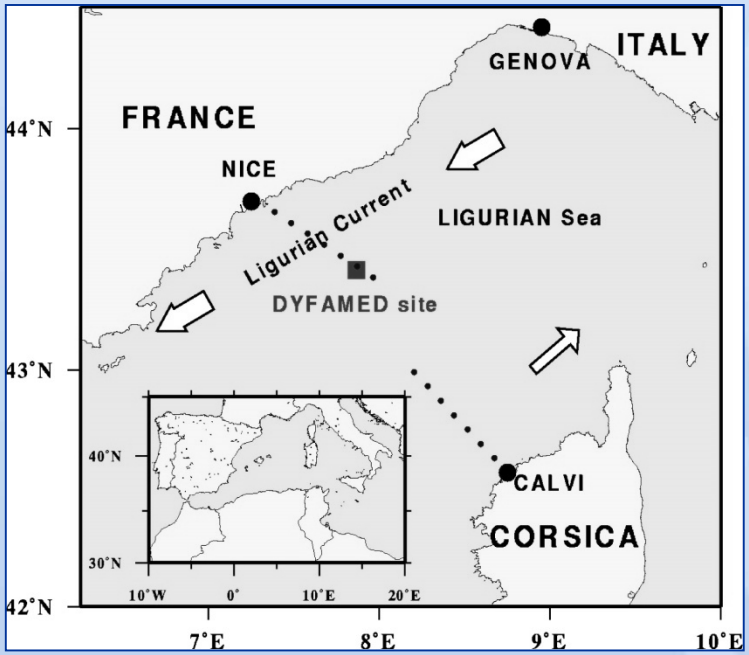
Application of the new method to DYFAMED samples



DYFAMED: Dynamique des Flux Atmosphériques en Méditerranée

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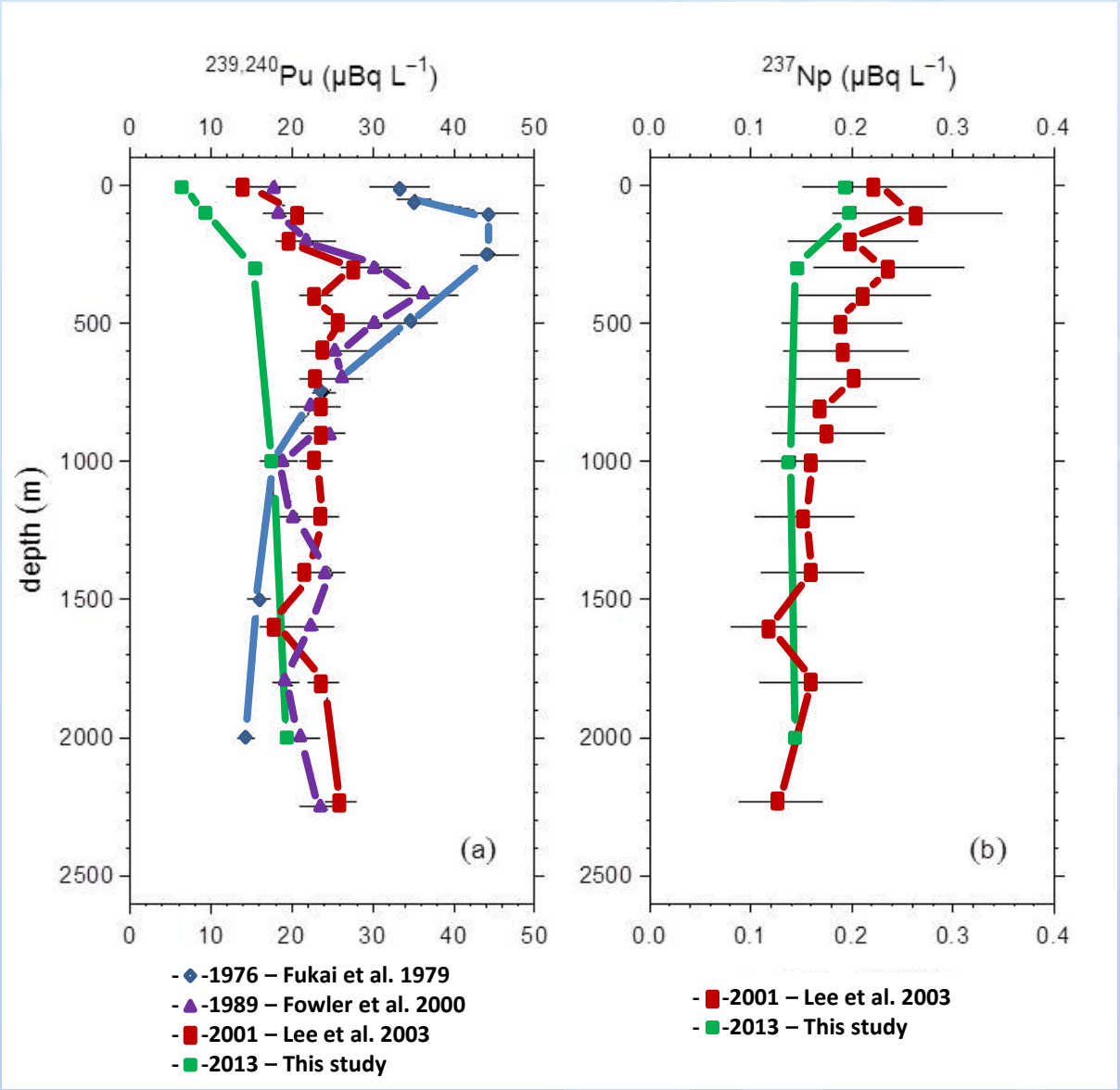
Results



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Reference material

IAEA 381	$^{239+240}$Pu	^{238}Pu	Rec(%)	^{237}Np	Rdt(%)
	mBq.l^{-1}	mBq.l^{-1}		mBq.l^{-1}	
J-18	16,1 ± 0,9	3,59 ± 0,26	65	7,2 ± 0,7	56
J-19	14,8 ± 0,4	3,43 ± 0,15	83	7,7 ± 0,6	104
J-20	14,6 ± 0,4	3,29 ± 0,15	76	8,7 ± 1,0	88
J-21	15,2 ± 0,4	3,37 ± 0,15	83	8,8 ± 1,1	94
J-22	14,7 ± 0,7	3,68 ± 0,41	95	8,3 ± 1,9	75
J-23	14,3 ± 0,7	3,89 ± 0,45	82	7,9 ± 1,8	75

[^{237}Np]: 8,9 mBq/l certified value
[$^{239+240}$Pu]:13,5 mBq/l certified value
[^{238}Pu]: 3,2 mBq/l certified value

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Blanks

Np Fraction

	^{237}Np (at)	Unc.
Blk-ng-1-Np	1.58E+08	1.70%
Blk-ng-2-Np	1.15E+08	6.00%
Blk-ng-3-Np	1.38E+08	3.00%
Blk-ng-4-Np	6.28E+07	2.50%
Blk-ng-5-Np	1.10E+08	1.90%
Blk-ng-6-Np	1.88E+08	2.10%

Pu Fraction

	^{239}Pu (at)	Uncer.
Blk-ng-1-Pu	8.11E+07	2.50%
Blk-ng-2-Pu	7.55E+07	2.50%
Blk-ng-3-Pu	7.66E+07	2.10%
Blk-ng-4-Pu	7.41E+07	1.90%
Blk-ng-5-Pu	7.82E+07	1.80%
Blk-ng-6-Np	7.08E+07	2.80%

Traces of ^{239}Pu and ^{237}Np in the blanks:

- ^{239}Pu daughter of ^{239}Np
- ^{237}Np daughter of ^{241}Am coming from ^{243}Am solution.

Optimization of the method for AMS

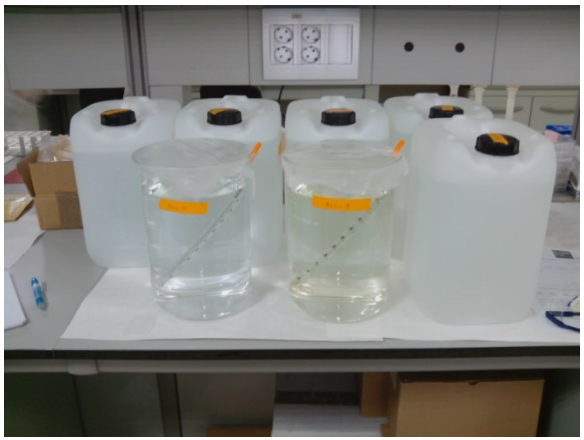
- **Volumes:**

Alpha spectrometry/ICP-MS Measurements

→ ~100 L

AMS measurements

→ ~10 L



- **Simplification of the method:** Some steps can be avoided for AMS measurements because purification of the different fractions is not so critical than with other techniques.
- ^{242}Pu tracer for Pu isotopes and ^{237}Np determination.
- include ^{236}U determination in the process.

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^{236}U

- $T_{1/2} = 2.34 \times 10^7$ years.
- alpha emitter.
- produced by neutron capture of ^{235}U in nuclear reactors.

- by alpha decay of its parent ^{240}Pu, ^{236}U $\xrightarrow{(n,\gamma)}$ ^{236}Pa and ^{236}Np.
- oceanographic tracer due to its conservative nature in seawater.

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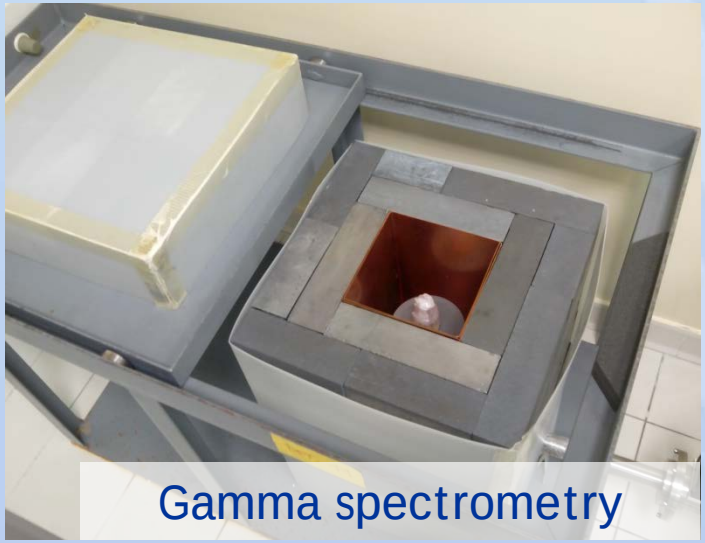
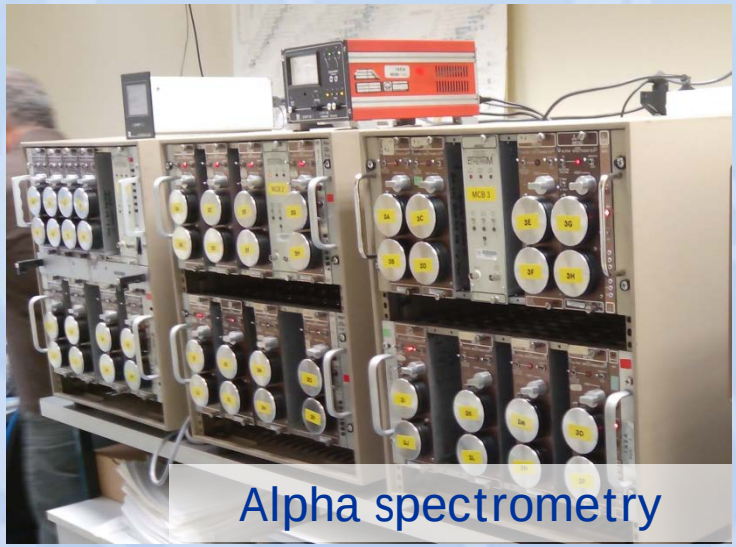
Two methods were tested: Method-1 and Method-2

Determination of the radiochemical yield

Element	**Neptunium**	**Uranium**	**Plutonium**
Tracers	^{239}Np	^{232}U	^{242}Pu
Technique	Gamma spectrometry	Alpha spectrometry	Alpha spectrometry


Gamma spectrometry


Alpha spectrometry

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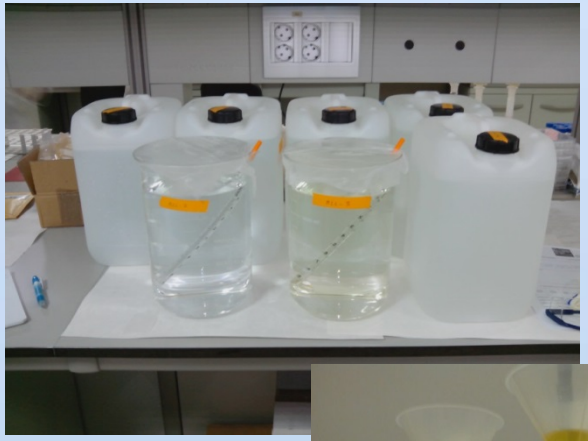
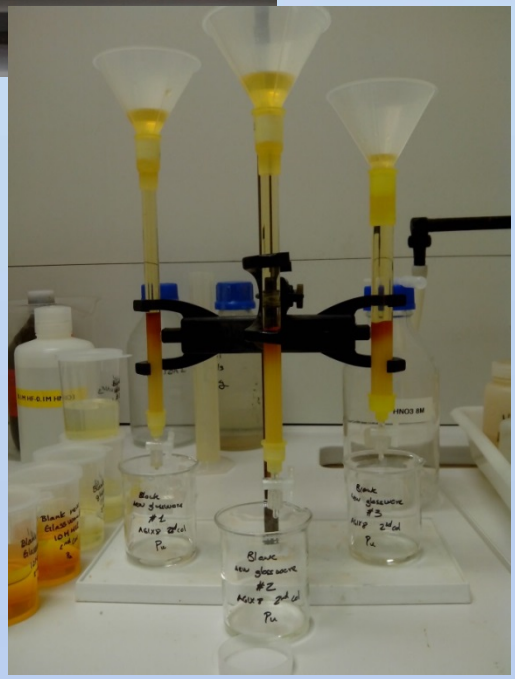
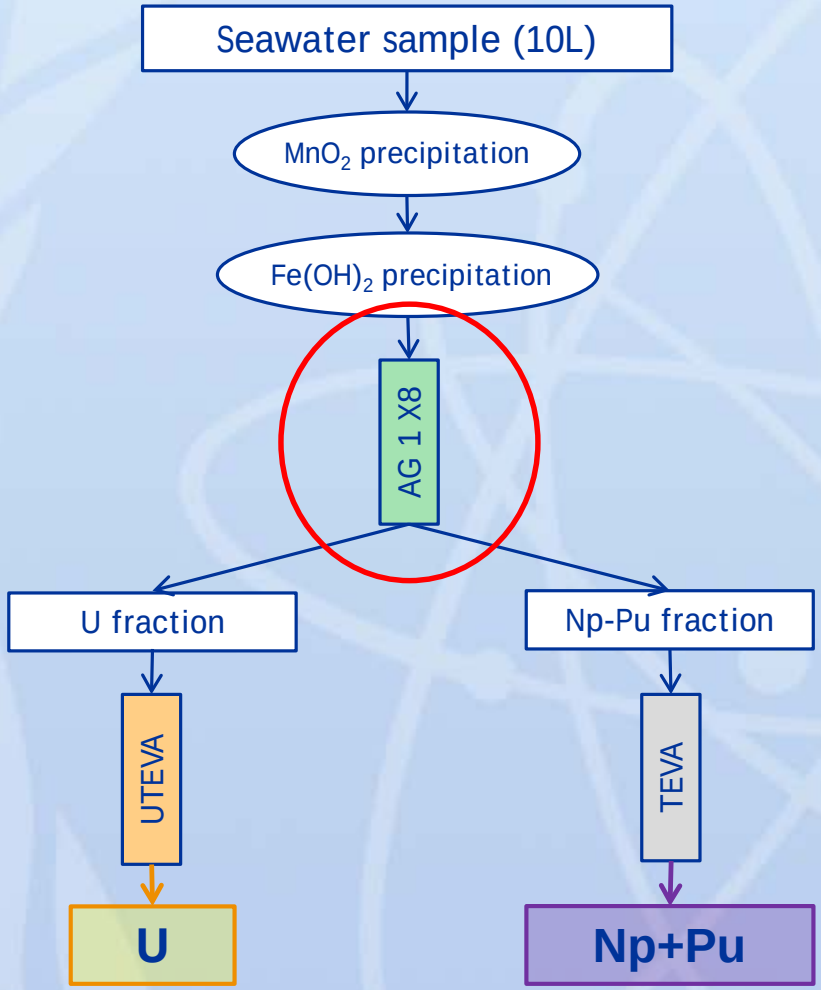
Method-1

- Test 1 performed using method previously presented.







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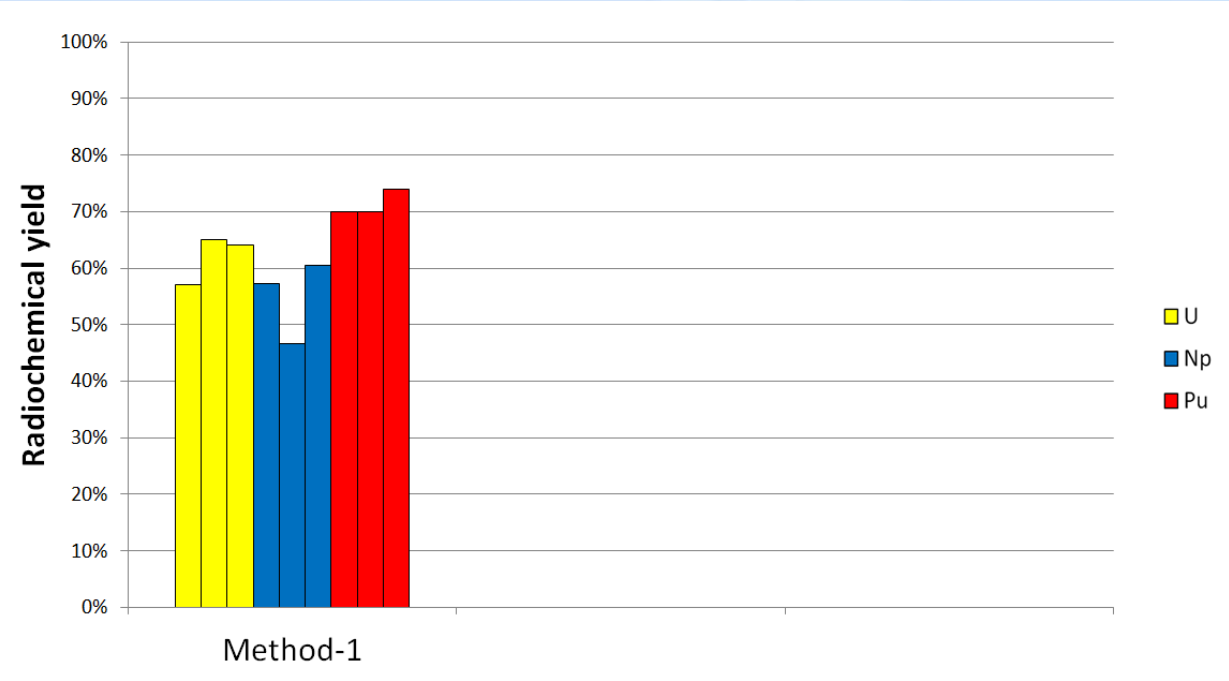
Results



- Main uranium losses due to double coprecipitation step
- Main Np-Pu losses due to oxidation state adjustment

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Test 2: influence of pH on coprecipitation.

Sample	pH		Coprecipitation yield (%)			
(10 L seawater)			U	Np (1st ppt)	Np (2nd ppt)	Np (final)
A	8 - 8.5		77 ± 11	69.2 ± 2.1	16.2 ± 0.6	85.5 ±2.2
B	8 - 8.5		25.2 ± 3.8	68.9 ± 2.7	11.0 ± 0.7	79.9 ±2.8
C	8 - 8.5		72 ± 11	67.0 ± 2.0	12.5 ± 0.6	79.5 ±2.1
		Avg.	58	68.4	13.2	81.6
		SD	29	1.2	2.7	3.3
D	9 - 9.5		82.5 ± 8.7			96.2 ± 2.2
E	9 - 9.5		112 ± 12			88.2 ±2.1
F	9 - 9.5		96 ± 10			93.9 ± 4.0
		Avg.	96.8			92.8
		SD	15			4.1

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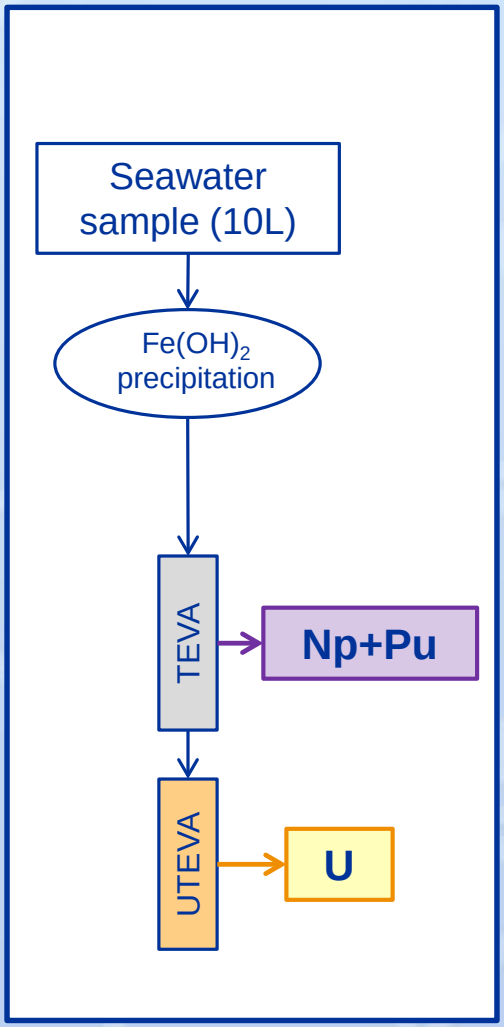
Method-2

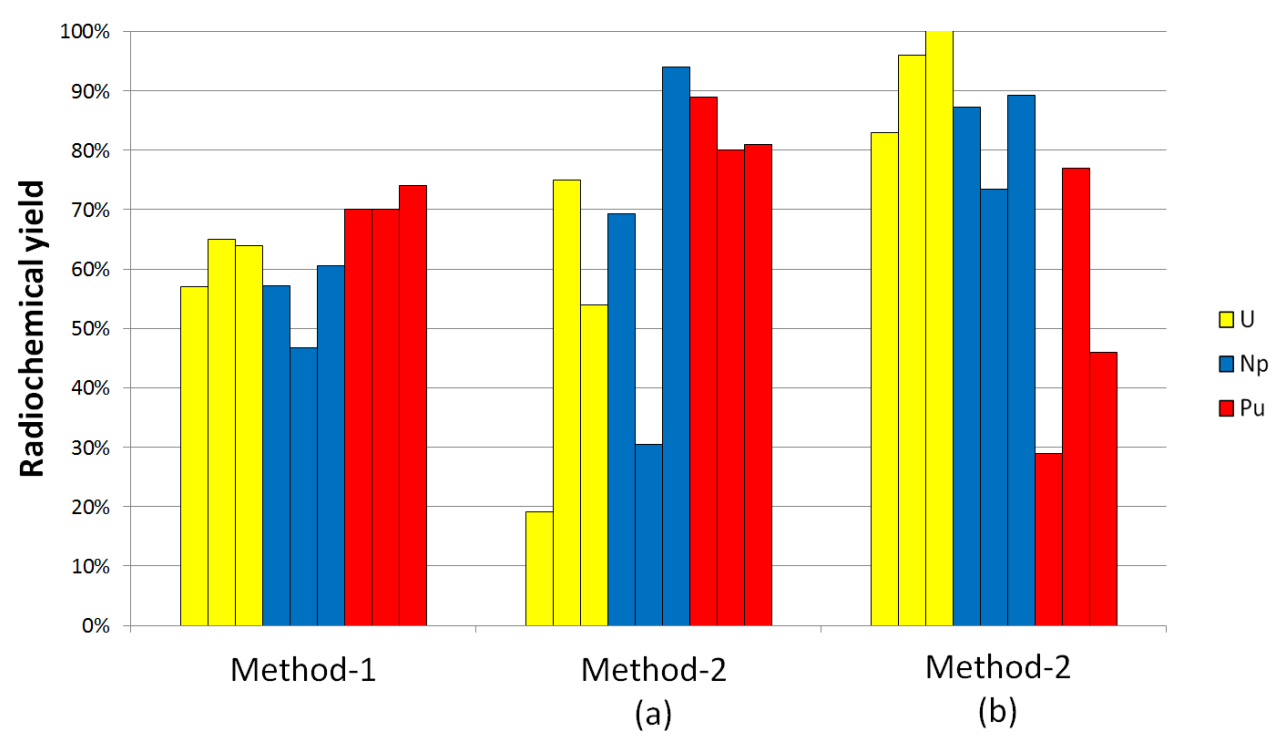
2 tests based on CNA's method for U-Pu.

Test a: $Fe(OH)_2$ dissolved in10mL of 1M HNO_3.
Addition of 0.5 mL Hydrazine (drop test*).
Addition of 10mL of conc. HNO_3.
(final concentration ~ 8M HNO_3).

Test b: $Fe(OH)_2$ dissolved in15mL of 1M HNO_3 (drop test*).
Addition of 200mg of Mohr's salt.
Addition of 2.5mL of conc. HNO_3.
(final concentration ~ 3M HNO_3).



*** Droptest**:
- Fe(III) in presence of NH_4SCN 5M shows a red blood color whereas Fe(II) is colorless
- Fe(II) in presence of 2,2'bipyridine shows a bright pink color and Fe(III) light yellow



Test a: Too much concentrated HNO_3 added: some Np was oxidised to Np(V)
Test b:Not enough concentrated HNO_3 added: some Pu was kept as Pu(III).

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AMS method

Seawater sample (10L) → $Fe(OH)_2$ precipitation → Oxydation state adjustement → TEVA → Np+Pu

TEVA → UTEVA → U

Separation of TEVA UTEVA

U → UTEVA → U elution → Cathode preparation

Np+Pu → TEVA → 1 → Th removal

TEVA → 2 → Prefilter → Np+Pu elution → Cathode preparation

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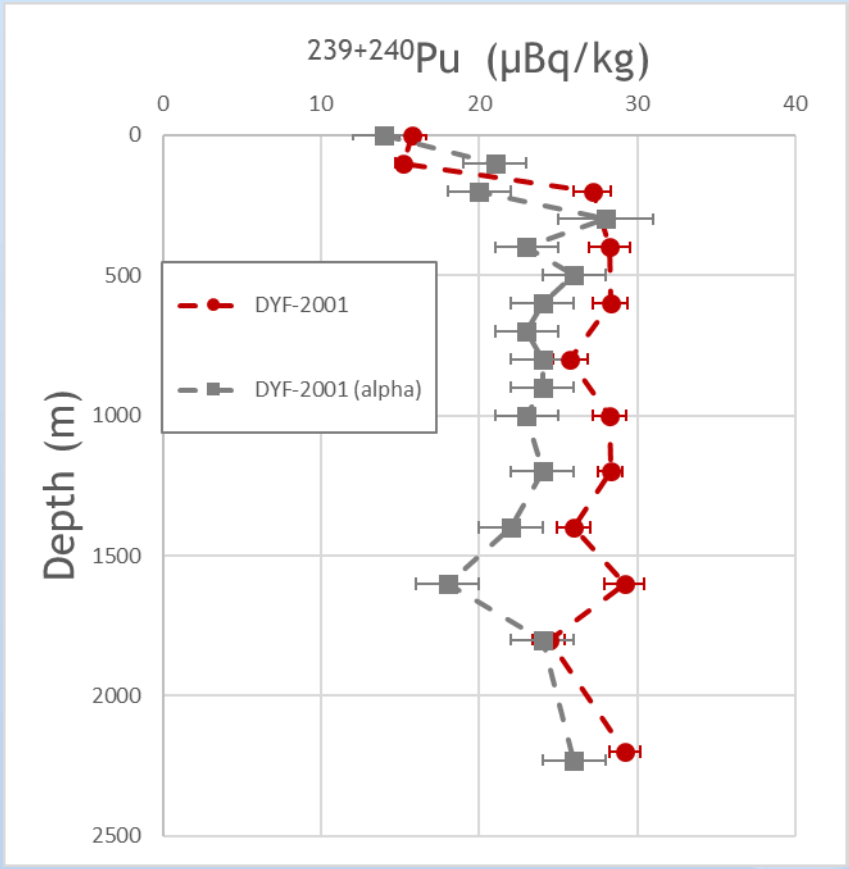
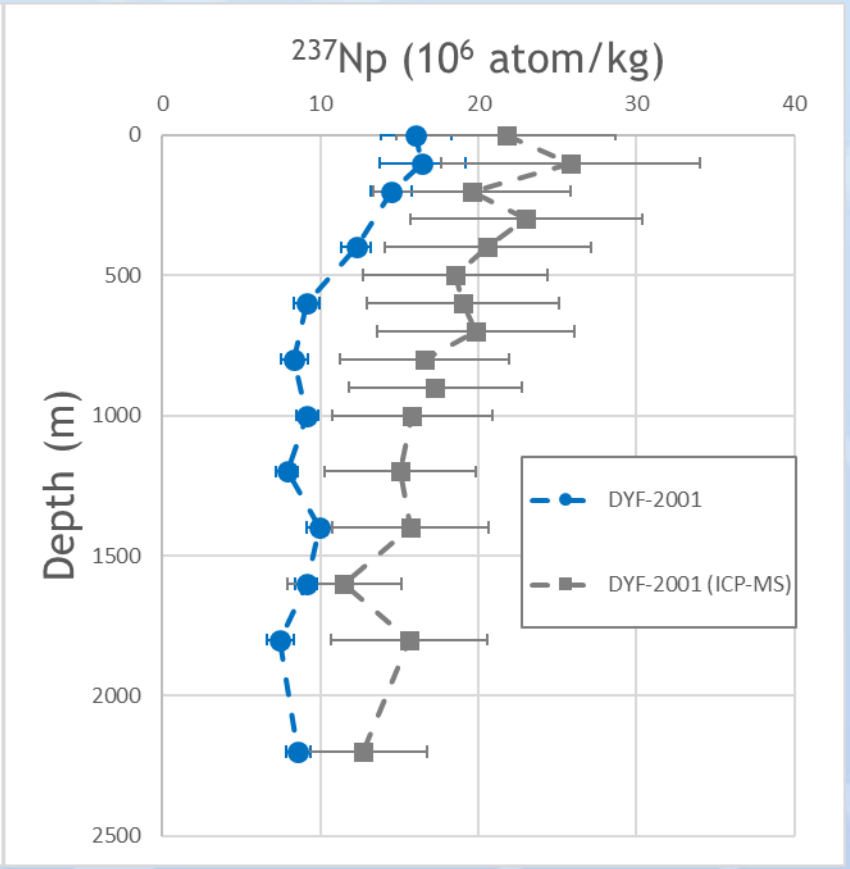
DYFAMED results





Analysis of 2.5 liters of DYFAMED samples collected in 2001 using the AMS method.

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Reference material

1) IAEA-443: Irish sea water.

Sample		Radiochemical yield (%)		^{237}Np (mBq kg^{-1})	
		Np	Pu	Measured value	Expected value
IAEA-443-a		67.7 ± 2.5	65 ± 10	9.6 ± 1.2	
IAEA-443-b		68.8 ± 2.6	74 ± 10	9.5 ± 1.1	
IAEA-443-c		71.3 ± 2.2	75 ± 11	9.1 ± 1.2	
	Avg.	69.3	71.4	9.39	8.7 ± 0.5
	SD	1.8	5.8	0.22	

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2) IAEA-418: Mediterranean sea

Sample		Concentration (10^6 at kg^{-1})				$^{236}U/^{238}U$ (10^{-9})	$^{240}Pu/^{239}Pu$	$^{237}Np/^{236}U$
		^{236}U	^{237}Np	^{239}Pu	^{240}Pu			
IAEA-418-1		25.9 ± 2.5	16.0 ± 3.2	10.33 ± 0.86	2.05 ± 0.22	3.24 ± 0.31	0.200 ± 0.027	0.62 ± 0.14
IAEA-418-2		27.4 ± 2.0	-	10.6 ± 1.2	1.71 ± 0.21	3.46 ± 0.24	0.162 ± 0.026	-
IAEA-418-3		27.3 ± 3.0	21.0 ± 3.3	10.7 ± 1.0	1.70 ± 0.18	3.43 ± 0.37	0.160 ± 0.022	0.77 ± 0.15
	Avg.	26.86	18.5	10.54	1.82	3.38	0.174	0.69
	SD	0.85	3.6	0.19	0.2	0.12	0.022	0.11

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Blanks

Total concentrations in blank samples			
	^{236}U (10^5 atoms)	^{237}Np (10^5 atoms)	^{239}Pu (10^5 atoms)
Blk-IAEA-1	16.3 ± 2.8	3.95 ± 0.79	0.81 ± 0.23
Blk-IAEA-2	7.9 ± 2.3	1.60 ± 0.56	0.40 ± 0.20
Blk-IAEA-3	13.5 ± 3.5	3.7 ± 1.1	ND
Blk-IAEA-4	17.1 ± 4.0	1.70 ± 0.78	ND
Blk-IAEA-5	7.0 ± 1.9	4.1 ± 1.1	ND
Blk-IAEA-6	7.4 ± 1.7	0.34 ± 0.38	ND

- Decrease of ^{237}Np contamination by a factor of 1000.
- Decrease of ^{239}Pu contamination by a factor of 100.
- Contamination of ^{236}U too high ➡ analysis of reagents: $K_2S_2O_5$, $FeSO_4$ and Mohr's salt.

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Check of reagents for ^{236}U contamination

Sample	Reagents	$FeSO_4$ (g)	$K_2S_2O_5$ (g)	Mohr's Salt (g)	^{236}U(at)	un.	^{236}U
							(at/g $FeSO_4$)
FeSO4-CNA-1-U	CNA	0.8584	0	0	1.13E+06	3.70%	1.32E+06
FeSO4-CNA-2-U	CNA	0.8685	0	0	1.06E+06	3.50%	1.22E+06
FeSO4-IAEA-1-U	IAEA	1.3011	0	0	1.57E+04	9.30%	1.21E+04
FeSO4-IAEA-2-U	IAEA	1.2856	0	0	7.59E+03	10.60%	5.91E+03
K2S2O5-CNA-1-U	CNA	0.8488	2.561	0	9.87E+05	3.70%	1.16E+06
K2S2O5-CNA-2-U	CNA	0.8862	2.5082	0	1.06E+06	3.40%	1.20E+06
K2S2O5-IAEA-1-U	IAEA	1.2854	2.6178	0	6.70E+04	8.20%	5.21E+04
K2S2O5-IAEA-2-U	IAEA	1.3439	2.539	0	1.01E+05	7.40%	7.50E+04
Mohr-CNA-1-U	CNA	0	0	0.2254	-	-	-
Mohr-CNA-2-U	CNA	0	0	0.2232	-	-	-
Mohr-IAEA-1-U	IAEA	0	0	0.2132	1.93E+04	12.40%	-
Mohr-IAEA-2-U	IAEA	0	0	0.2088	-	-	-
Blk-NB-a-U	CNA	0.85	2.5	0.2	1.04E+06	4.30%	1.22E+06
Blk-NB-b-U	CNA	0.85	2.5	0.2	1.00E+06	3.60%	1.18E+06
Blk-ST-U	CNA	-	-	-	1.21E+05	8.40%	-

Thank you for your attention!