Novel assays for ‘**difficult-to-measure**’ radionuclides involved in **decommissioning** activities

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18-04-2024

Vasile, M., Dobney, A., Boden, S., Leermakers, M., Qiao, J.

sck cen

VUB VRIJE UNIVERSITEIT BRUSSEL

DTU

ENGIE

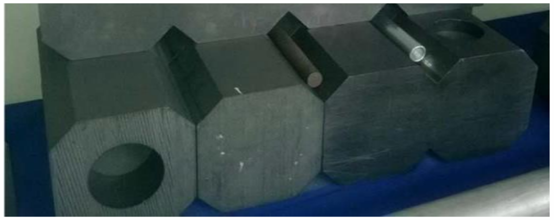
TRISKEM
Expertise in Separation Chemistry

Decommissioning phase

Which type of waste?

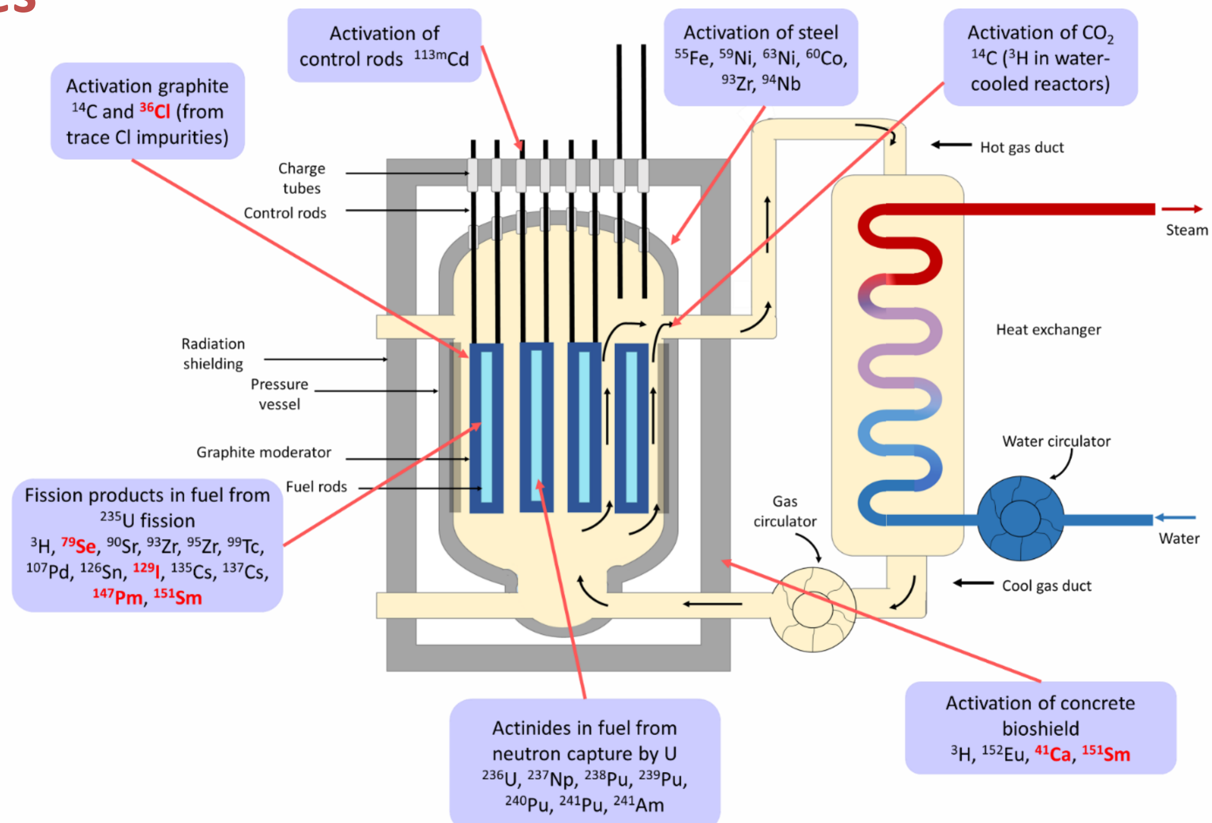
https://www.sckcen.be/nl/deco

Stefan Nijst, 2014, Master Thesis



Radiological waste characterization

Which radionuclides can be expected?



Based on (Warwick et al., 2022)

Radiological waste characterization

How can the activity be quantified?

ETM

Non-destructive assay — **"easy to measure"** radionuclides — γ-ray emitters

DTM

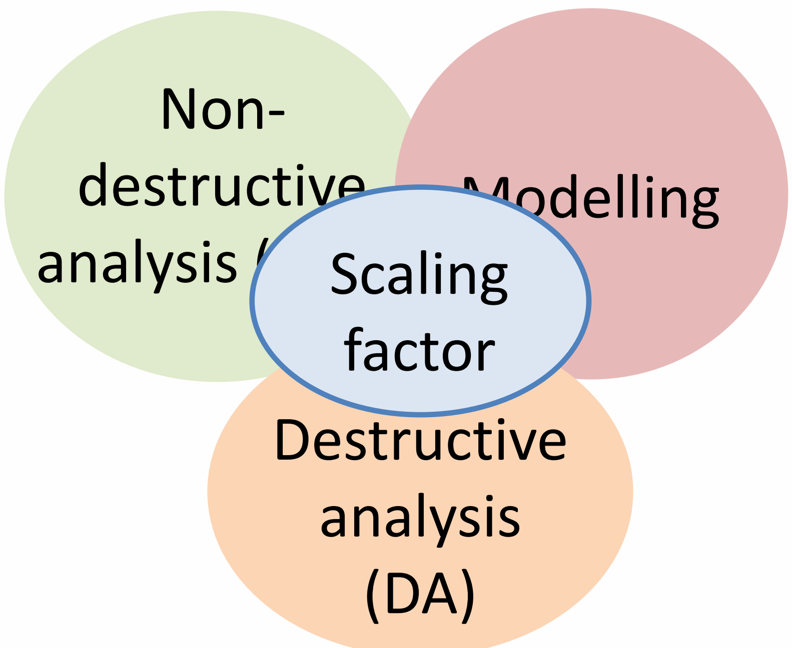
Destructive assay — **"difficult to measure"** radionuclides — α and β particle emitters

DTM radionuclides quantification

ISO standard 24390:2023

*"a radionuclide whose radioactivity is difficult to measure **directly from the outside** of the waste packages by non-destructive assay means"*

How is the activity of DTM radionuclides estimated?



Activity **ETM** radionuclides

γ-ray emitters

Activity **DTM** radionuclides

α and β particle emitters

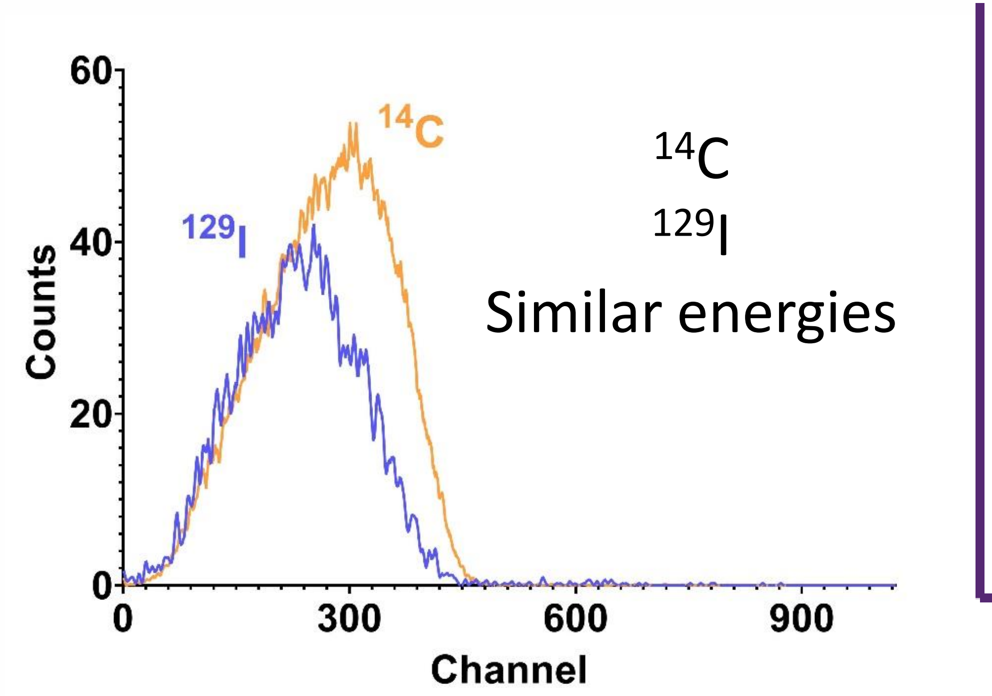
Mathematical correlation

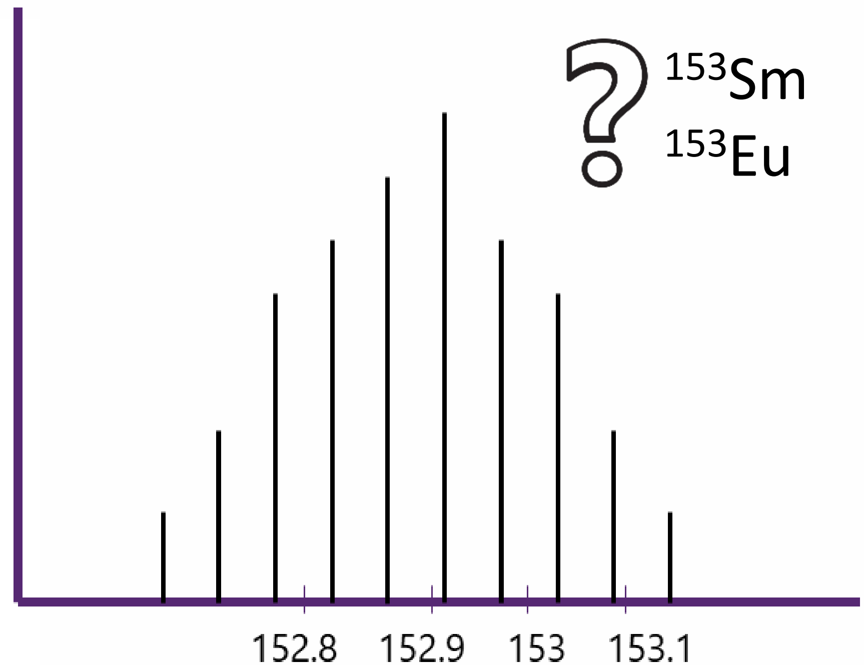
REQUIRED

Validation using **experimental data**

Lack of analytical methods suitable to determine DTM radionuclides

- Interferences influencing the quantification of the activity





Radiometric (spectral)

Mass spectrometric (isobaric)

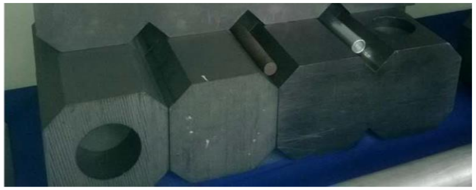
Lack of analytical methods suitable to determine DTM radionuclides

- Interferences influencing the quantification of the activity
- Low detection limit (DL) required

Clearance level ^{36}Cl – 1 Bq g^{-1} ❯ DL > clearance level ❯ **Procedure not applicable**

- Variety of matrices

https://www.sckcen.be/nl/deco



Stefan Nijst, 2014, Master Thesis

Sample preparation and homogenization

Selection of the target DTM radionuclides

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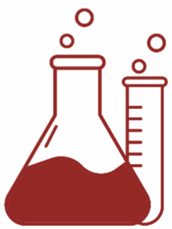
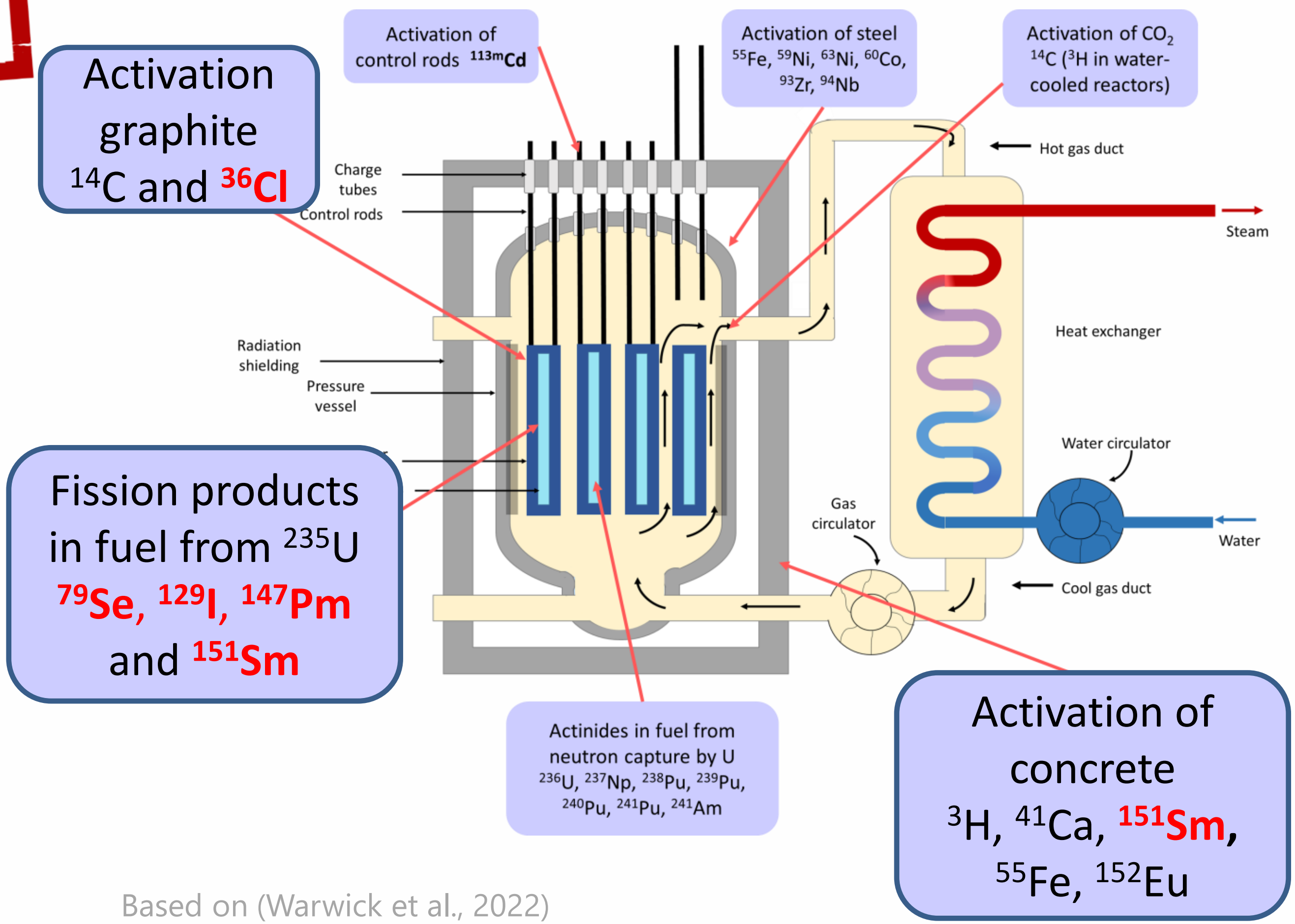
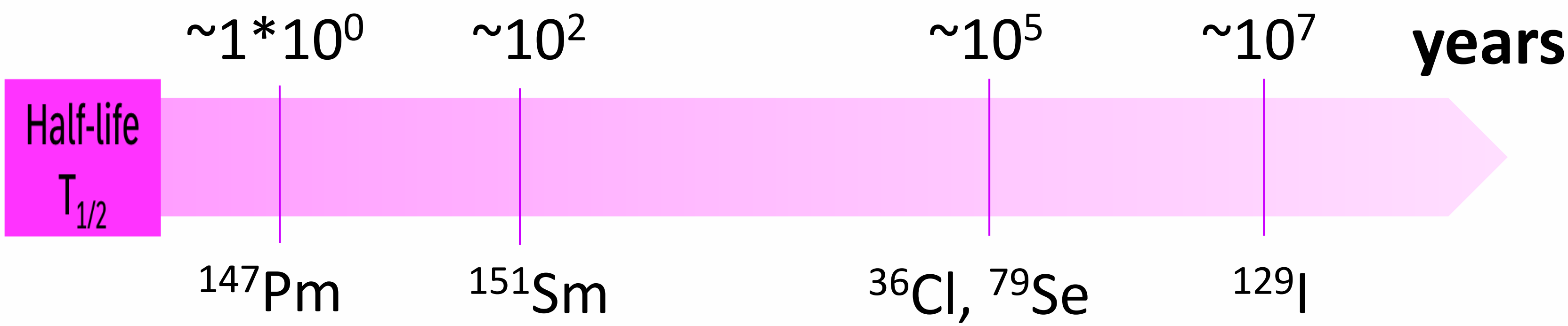
beta decay (β^-)

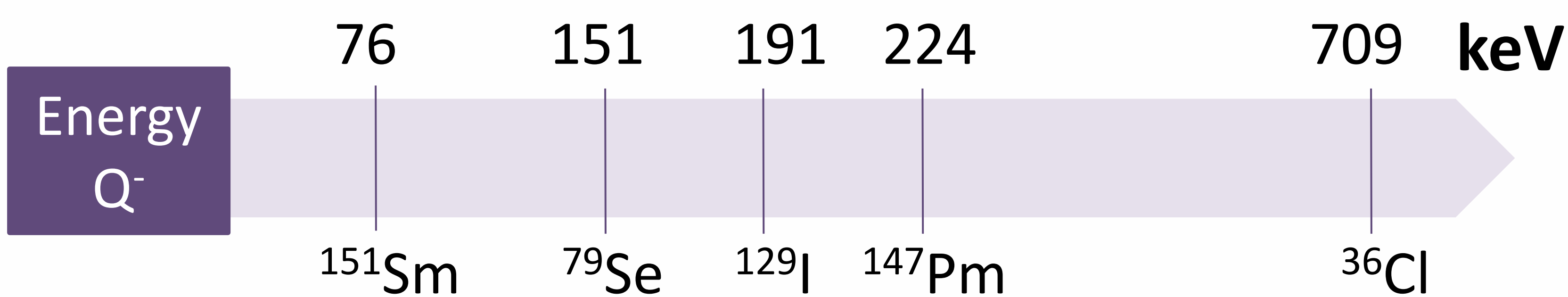




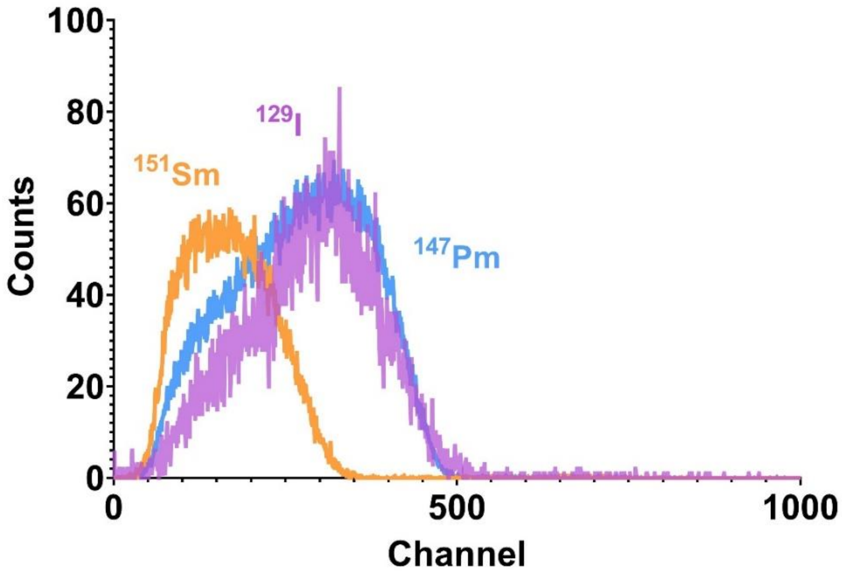
Based on (Warwick et al., 2022)

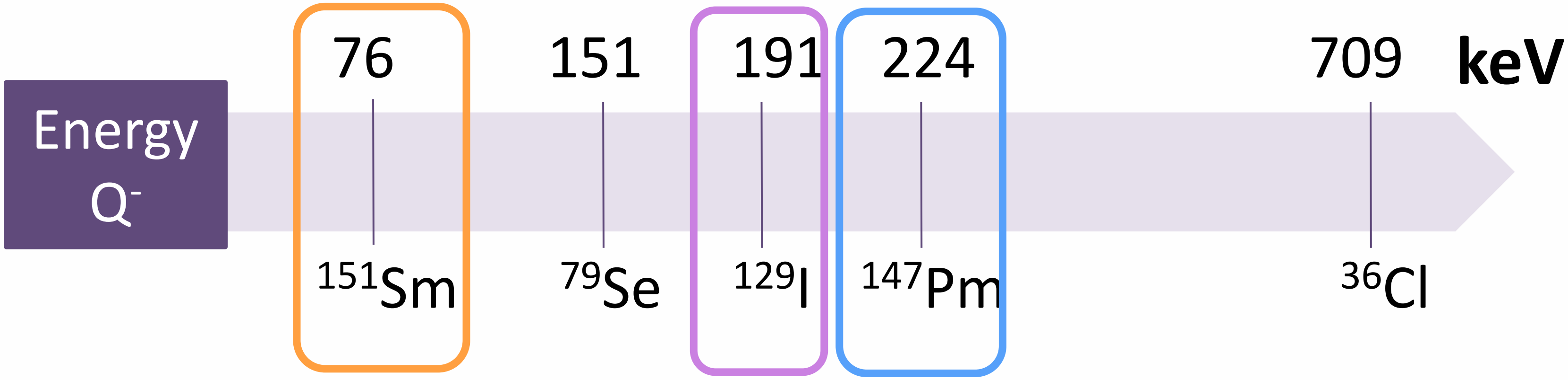
Properties of the target DTM radionuclides

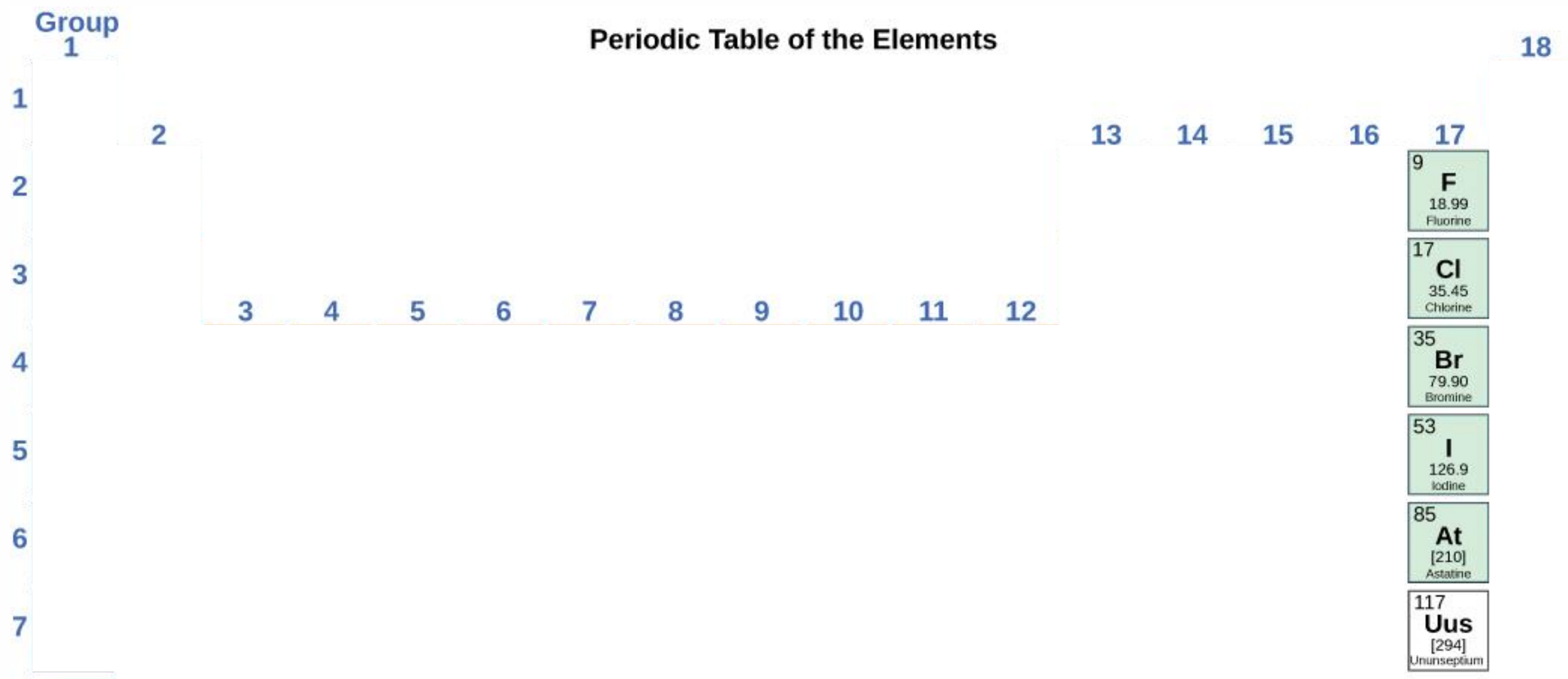


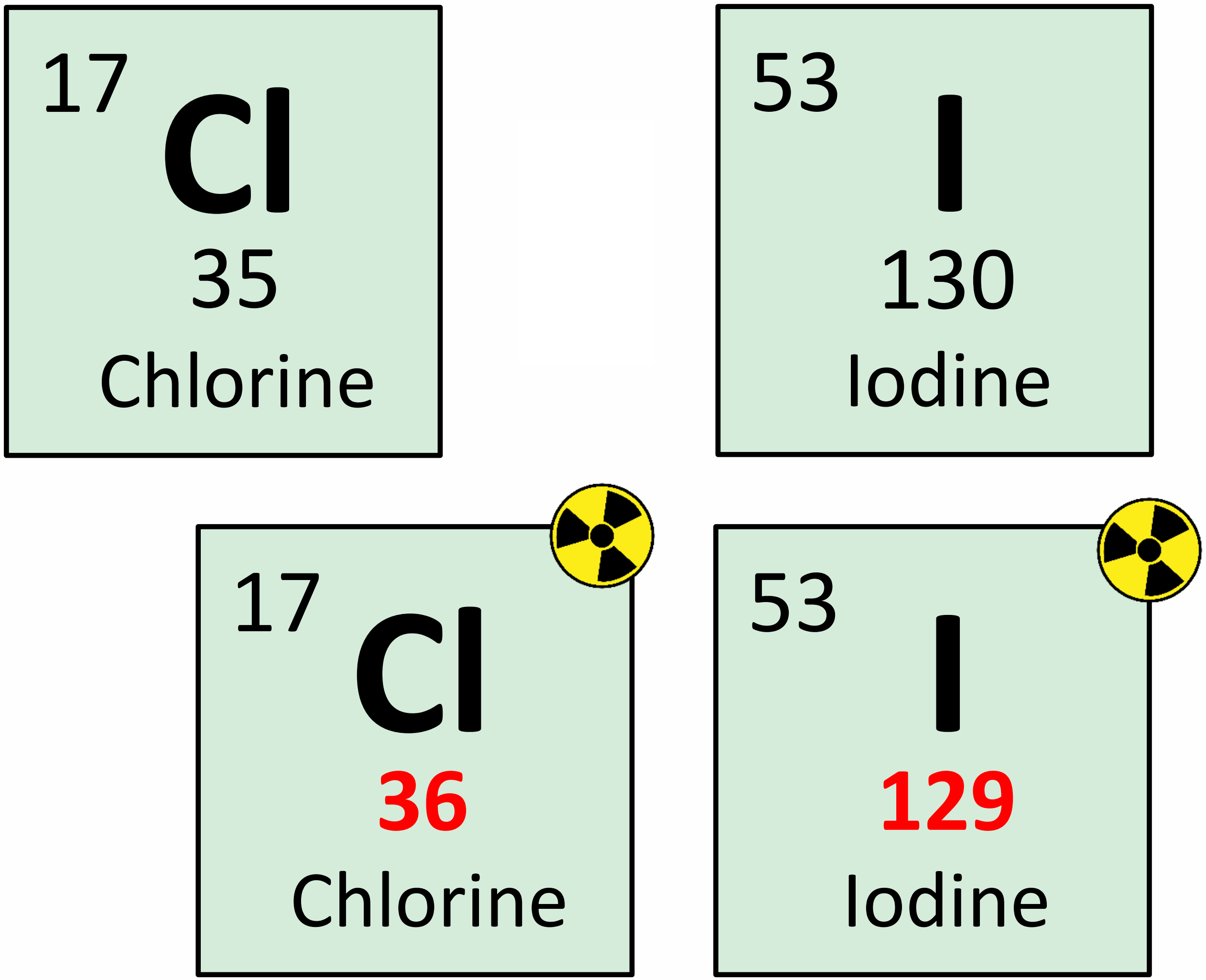


Properties of the target DTM radionuclides

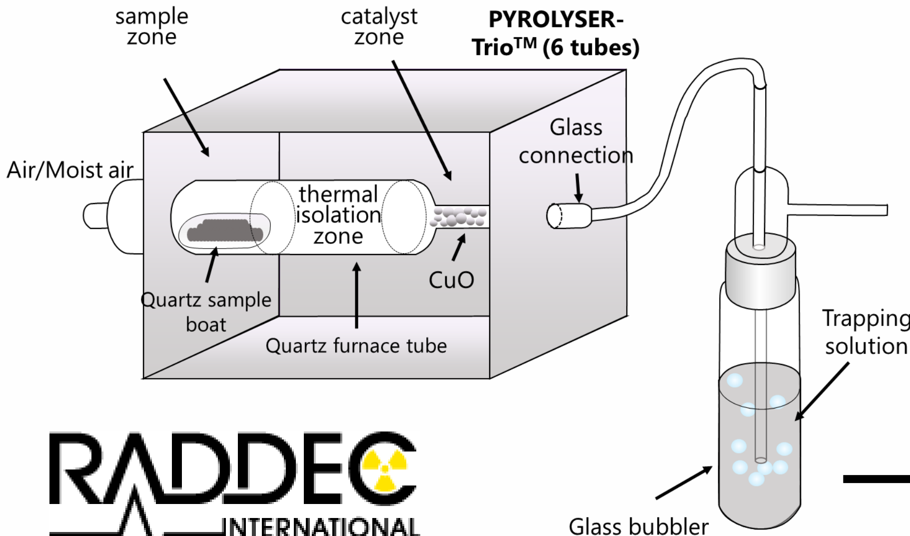





Periodic Table of the Elements
Group 1
2
3 4 5 6 7 8 9 10 11 12
13 14 15 16 17
18
1 2 3 4 5 6 7
9 F 18.99 Fluorine
17 Cl 35.45 Chlorine
35 Br 79.90 Bromine
53 I 126.9 Iodine
85 At [210] Astatine
117 Uus [294] Ununseptium

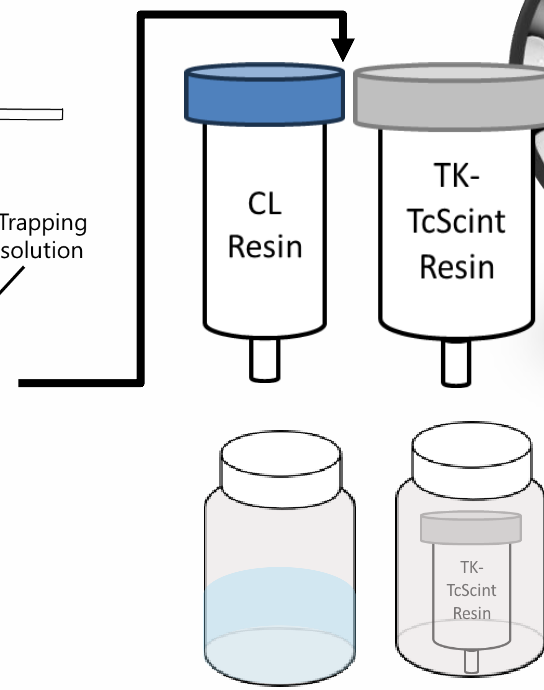

17
Cl
35
Chlorine
53
I
130
Iodine
17
Cl
36
Chlorine
53
I
129
Iodine

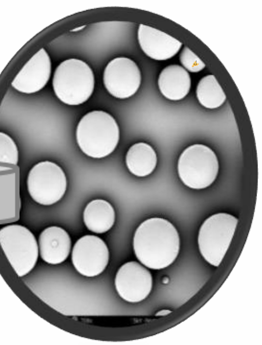
^{36}Cl and ^{129}I determination in solid samples



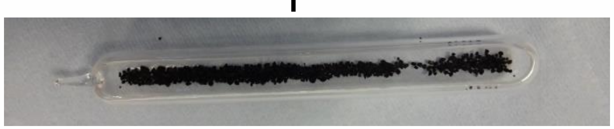
RADDEC INTERNATIONAL

Based on Warwick et al. 2010





Concrete

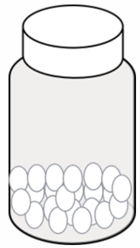


Graphite

LSC

Wallac Quantulus 1220TM

^{36}Cl and ^{129}I determination in solid samples



2nd bubbler with 6 mM Na_2CO_3 (collection of ^{36}Cl not retained by the microspheres)

Gas adsorption in PS materials

Based on Mitev, 2016

Few chlorine released as Cl_2

HCl collected in trapping solution

% ^{36}Cl collected 1st bubbler	% ^{36}Cl in trapping solution
80,3 ± 2,7	-
6,0 ± 0,5	50,1 ± 2,2
10,8 ± 0,5	60,3 ± 2,5

^{36}Cl and ^{129}I determination in solid samples

PS material	Trapping solution	^{36}Cl in PS material (%)	^{36}Cl in trapping solution (%)
PSm	4 mM $NaHCO_3$	Not detected	97 ± 5
CPSm	4 mM $NaHCO_3$	Not detected	94 ± 3
PS resin	4 mM $NaHCO_3$	40 ± 1	58 ± 2

Chlorine retention in TK-TcScint resin

Longer interaction time needed

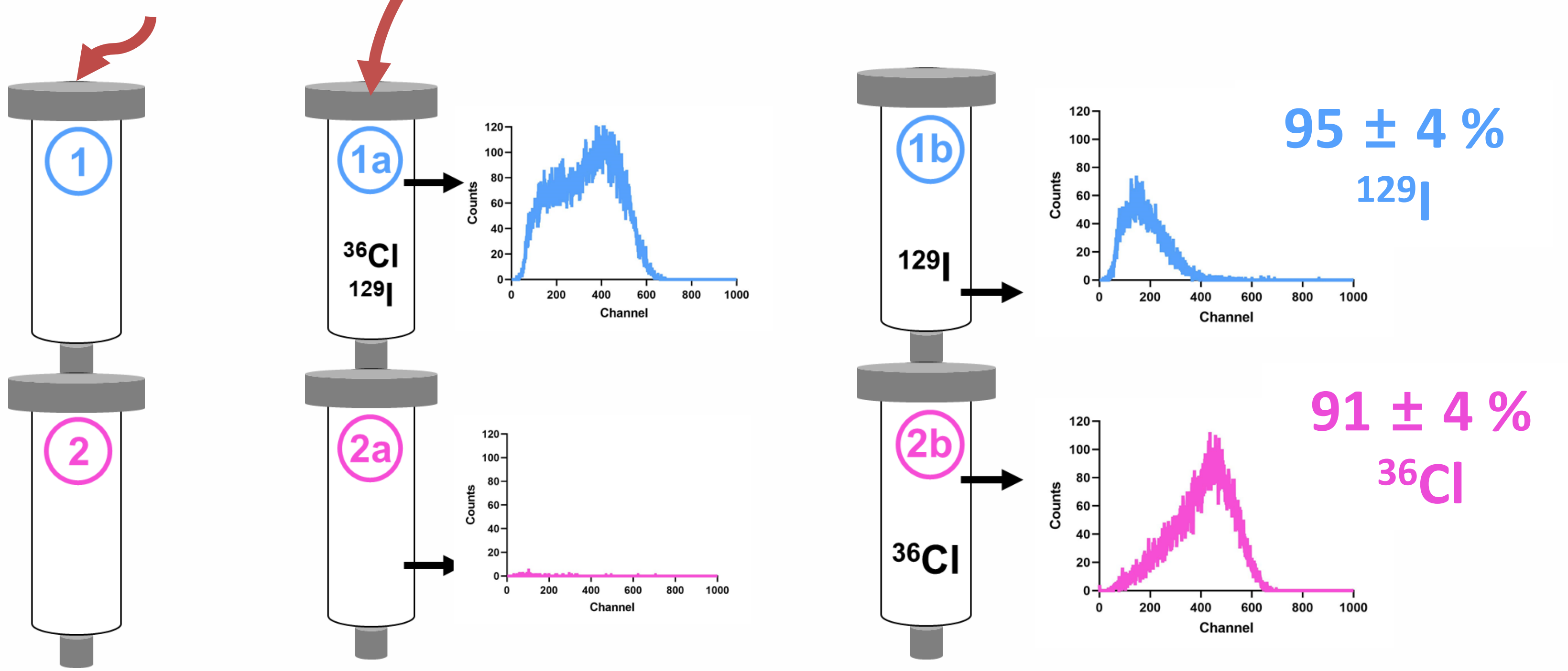
No chlorine in ionic (solution) form retained

^{36}Cl and ^{129}I determination in solid samples

30 mL 4 mM $NaHCO_3$

- 4 Bq ^{36}Cl
- 4 Bq ^{129}I

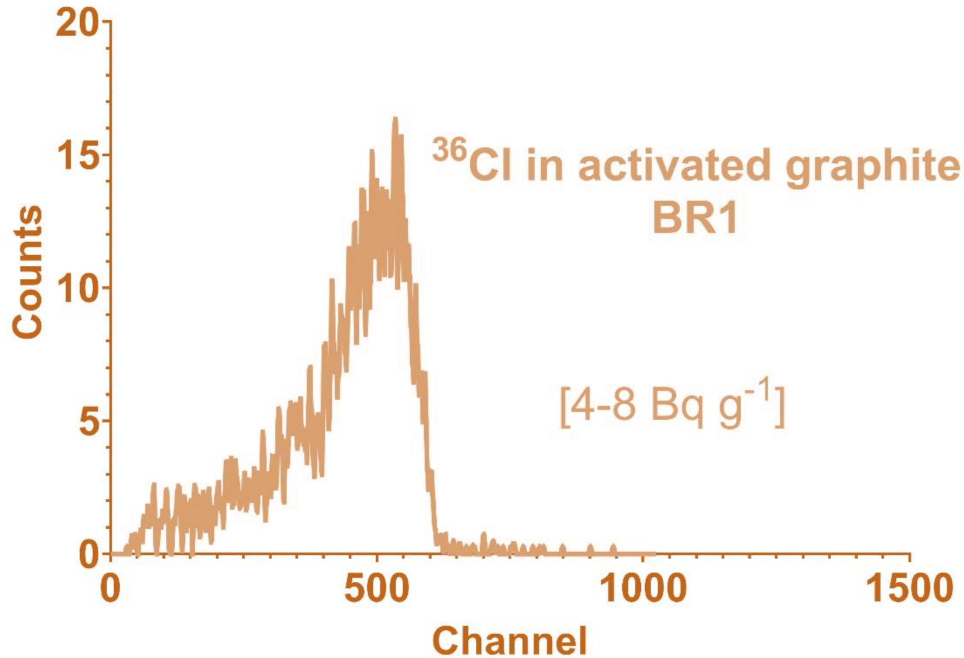
45 mL 4 mM $NaHCO_3$



^{36}Cl and ^{129}I determination in solid samples

Application in activated graphite

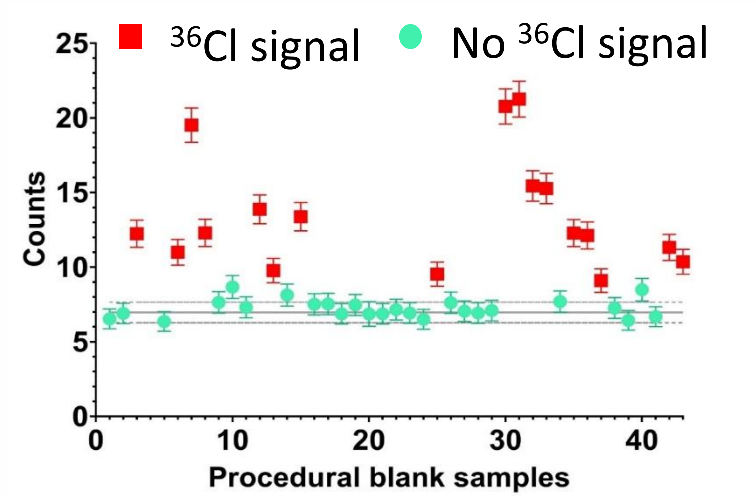
^{14}C, ^{3}H, ^{60}Co, ^{133}Ba, ^{134}Cs, ^{152,154}Eu

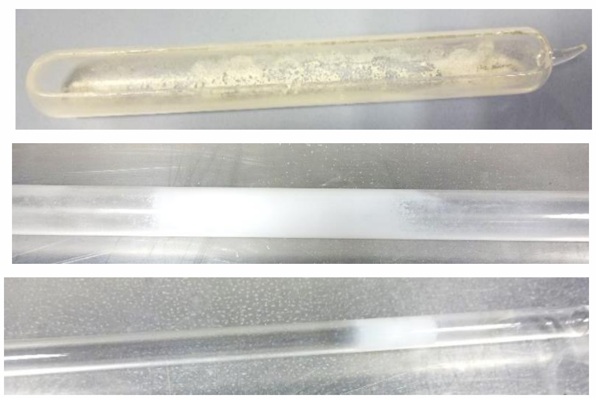


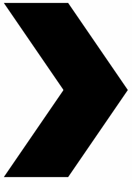
Compared with calculated values through activation codes

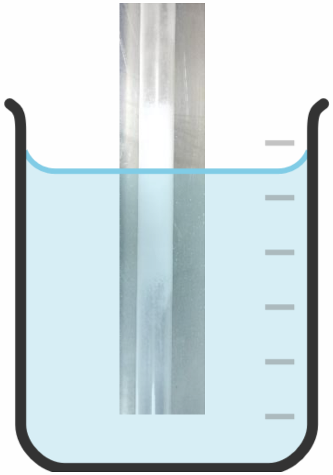
^{36}Cl and ^{129}I determination in solid samples

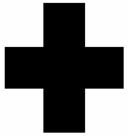
^{36}Cl memory effect







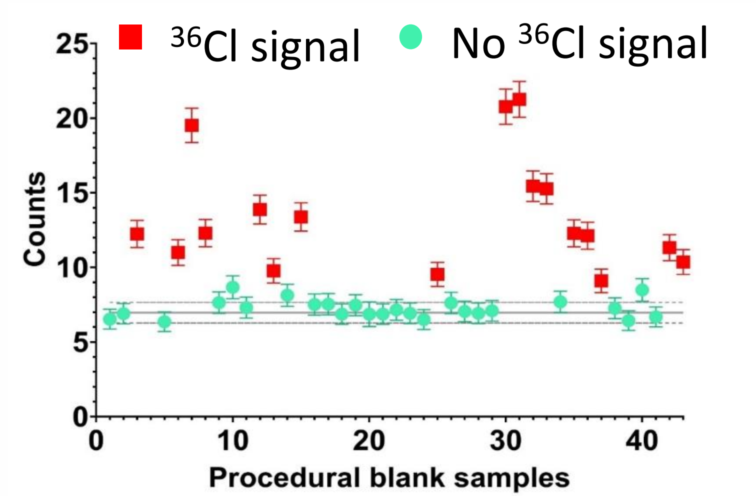


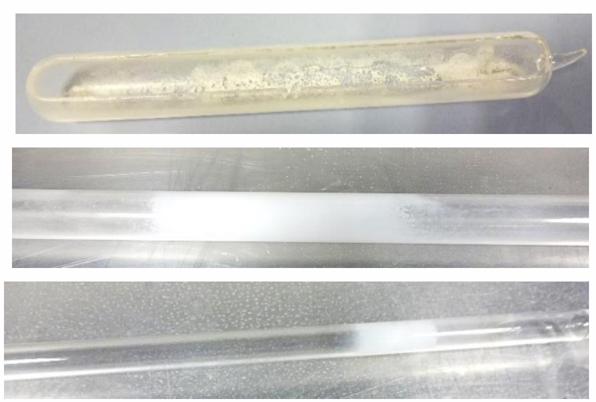


$AgNO_3$

^{36}Cl and ^{129}I determination in solid samples

^{36}Cl memory effect





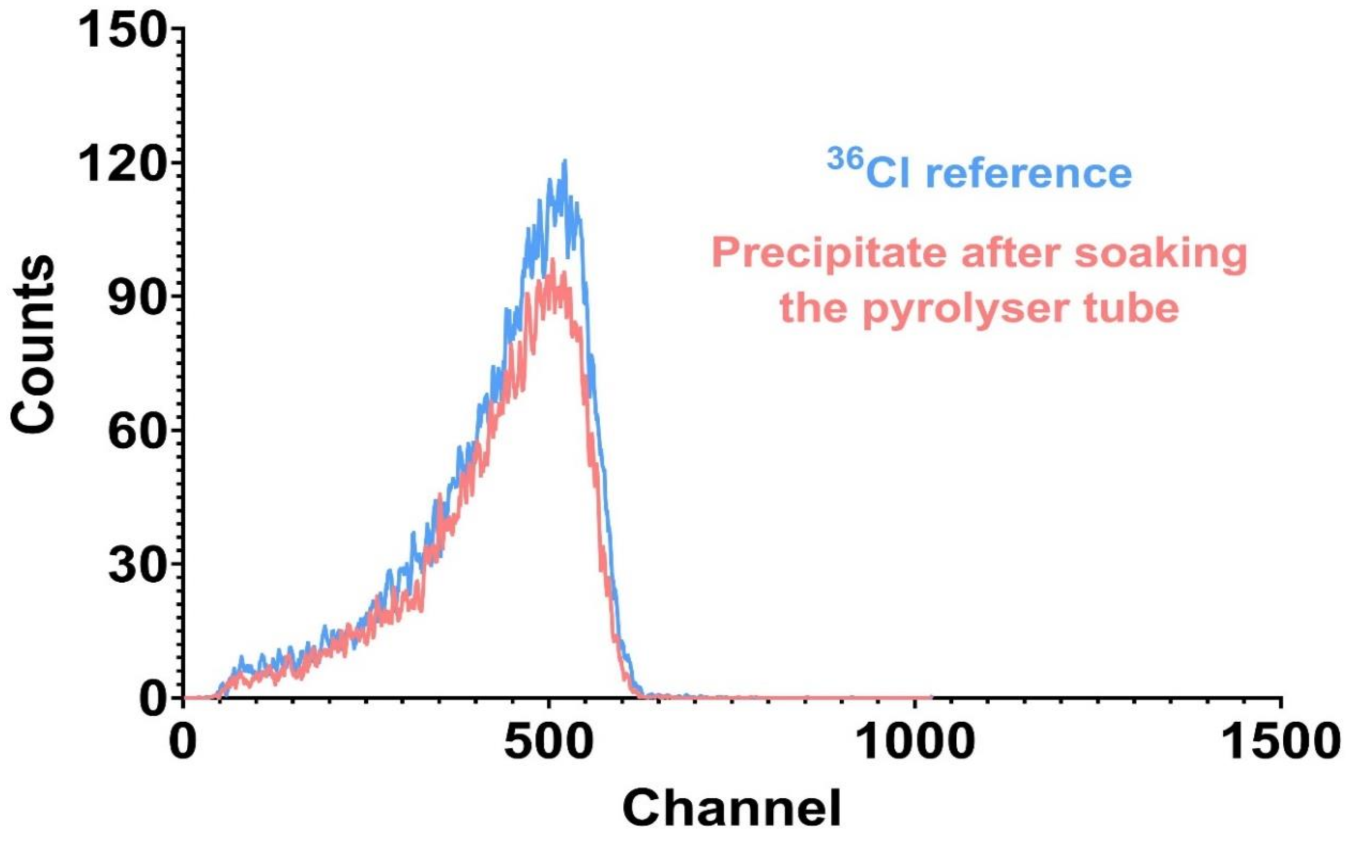
White precipitate

? AgCl

^{36}Cl and ^{129}I determination in solid samples

TRISKEM Expertise in Separation Chemistry

^{36}Cl memory effect



^{36}Cl and ^{129}I determination in solid samples

Moist air

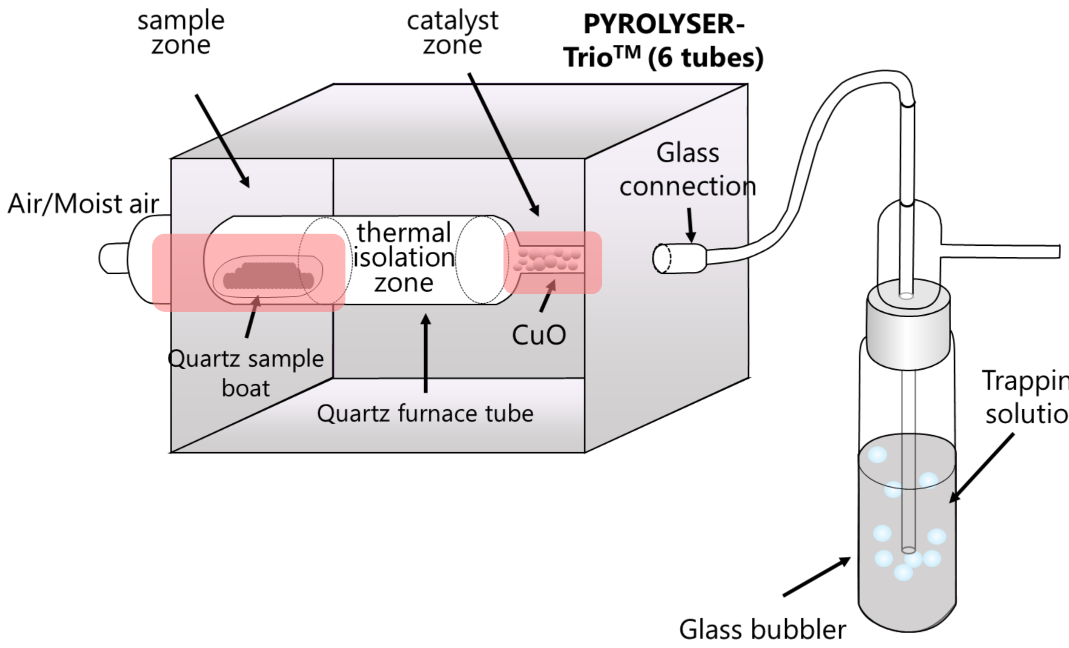
Bubblers

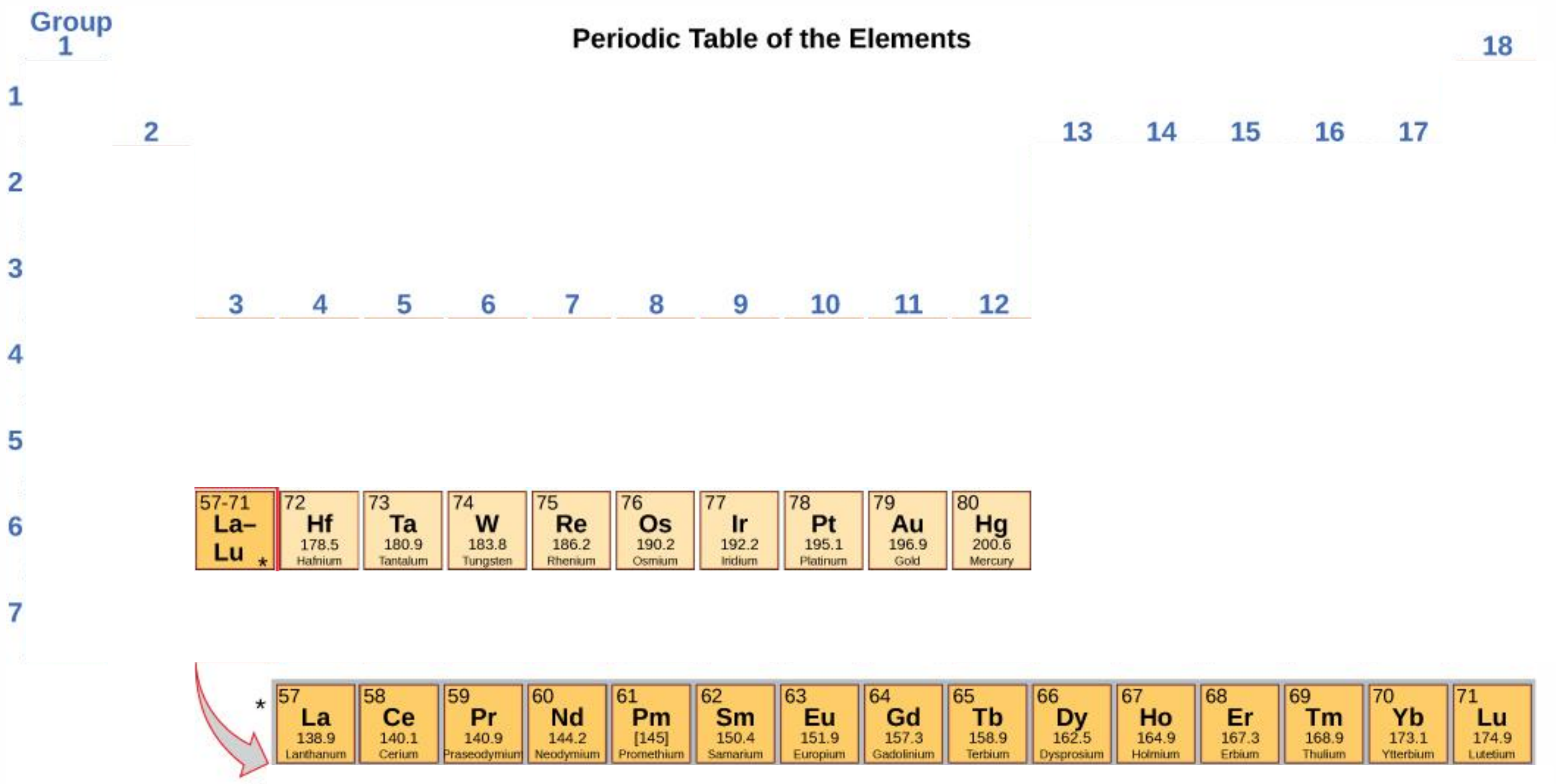
Oxidant (if needed)

Quartz wool/beads

Quartz tubes

Sample boat




Periodic Table of the Elements
Group 1
18
1
2
13 14 15 16 17
2
3
3 4 5 6 7 8 9 10 11 12
4
5
6
57-71 La– Lu *
72 Hf 178.5 Hafnium
73 Ta 180.9 Tantalum
74 W 183.8 Tungsten
75 Re 186.2 Rhenium
76 Os 190.2 Osmium
77 Ir 192.2 Iridium
78 Pt 195.1 Platinum
79 Au 196.9 Gold
80 Hg 200.6 Mercury
7
*
57 La 138.9 Lanthanum
58 Ce 140.1 Cerium
59 Pr 140.9 Praseodymium
60 Nd 144.2 Neodymium
61 Pm [145] Promethium
62 Sm 150.4 Samarium
63 Eu 151.9 Europium
64 Gd 157.3 Gadolinium
65 Tb 158.9 Terbium
66 Dy 162.5 Dysprosium
67 Ho 164.9 Holmium
68 Er 167.3 Erbium
69 Tm 168.9 Thulium
70 Yb 173.1 Ytterbium
71 Lu 174.9 Lutetium

61 **Pm** 145 Promethium

62 **Sm** 150 Samarium

61 **Pm** **147** Promethium

62 **Sm** **151** Samarium

^{147}Pm and ^{151}Sm radiochemical separation

TRISKEM
Expertise in Separation Chemistry

Complete separation of ^{147}Pm and ^{151}Sm from each other

Interference removal (similar lanthanides)

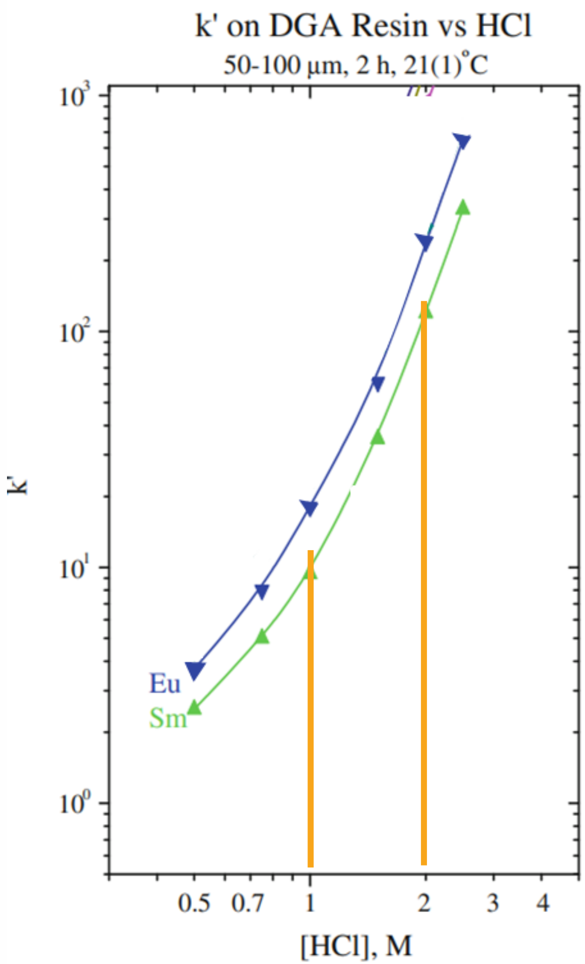
60 **Nd** 144 Neodymium	61 **Pm** 145 Promethium	62 **Sm** 150 Samarium	63 **Eu** 152 Europium

Carrier for ^{147}Pm chemical recovery quantification (no stable Pm)

60 **Nd** 144 Neodymium	61 **Pm** 145 Promethium

61 **Pm** **147** $T_{1/2}$ (β^-) 2.6 y	61 **Pm** **148** $T_{1/2}$ (β^-) 5.4 d

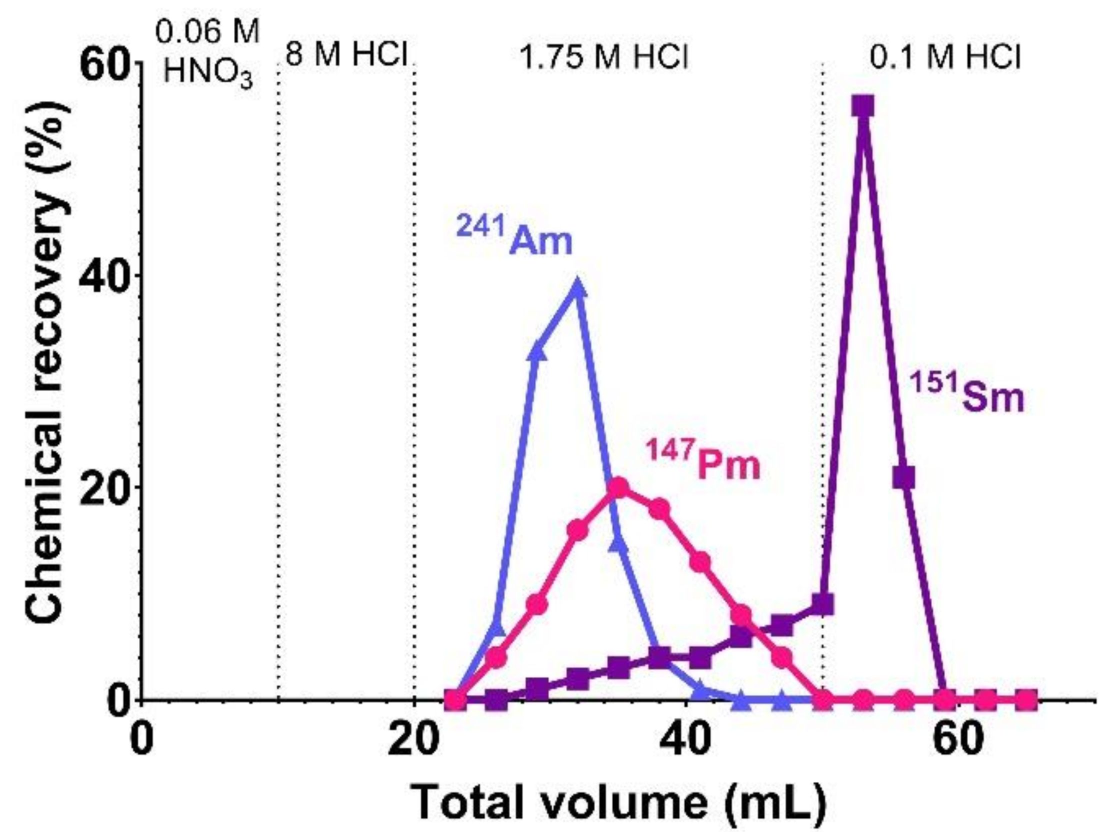
^{147}Pm and ^{151}Sm radiochemical separation



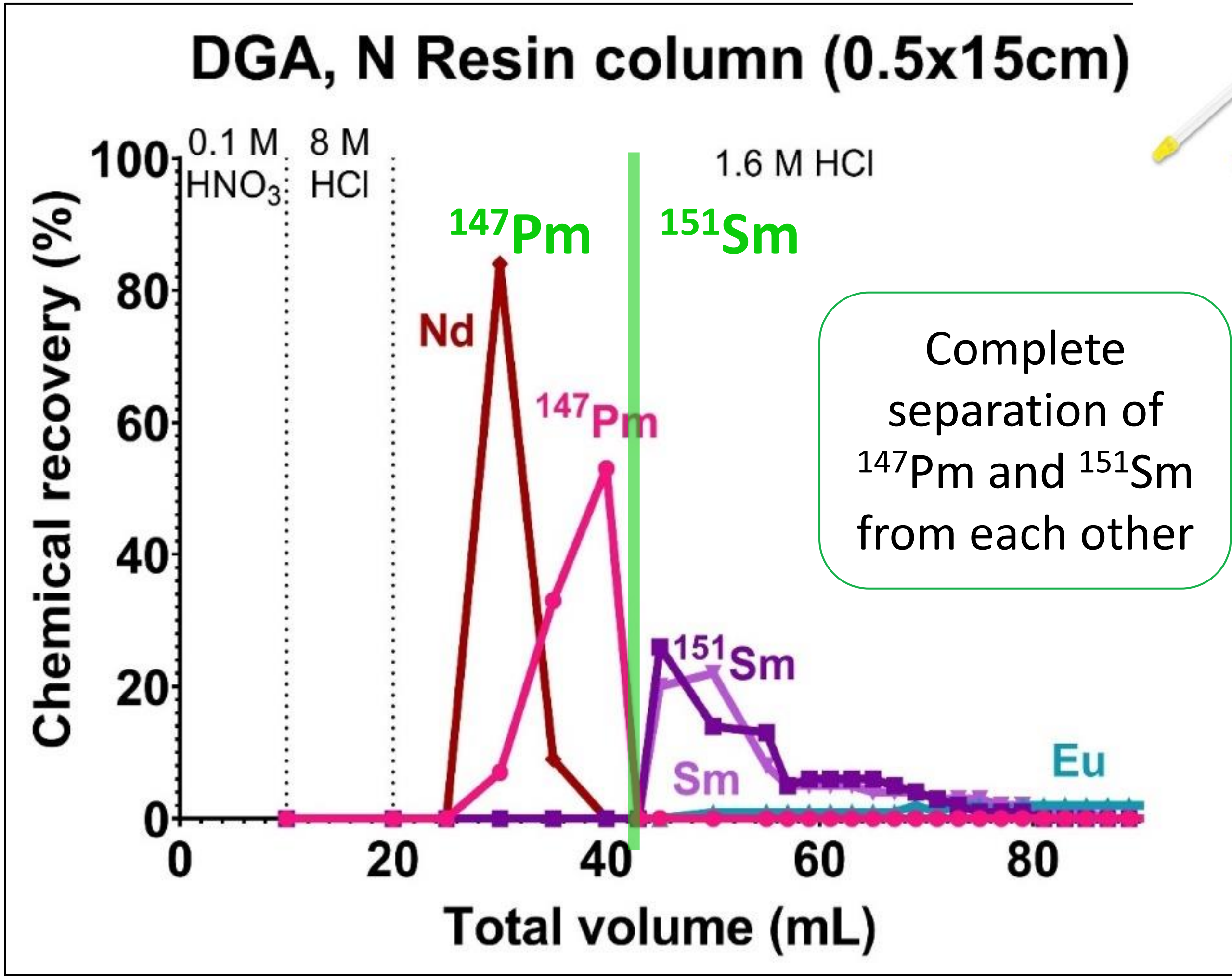
From Sherrod L. Maxwell et al. 2012

- Nd as a carrier for ^{147}Pm chemical recovery
- Eu as interference in ^{151}Sm fraction
- 1-2 M HCl higher retention of Sm compared to Pm/Nd
- ↑ column length → ↑ peak resolution

^{147}Pm and ^{151}Sm radiochemical separation

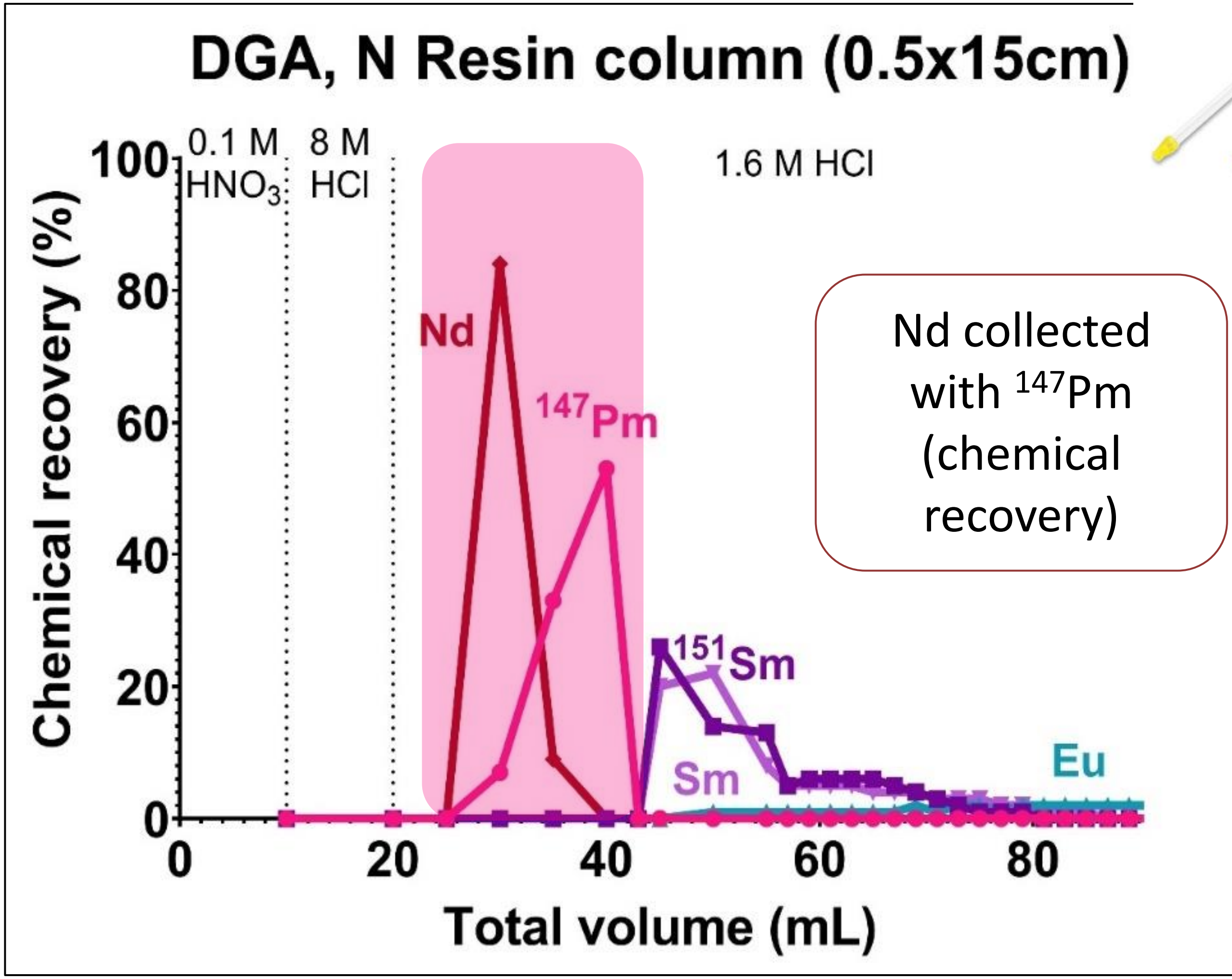


^{147}Pm and ^{151}Sm radiochemical separation



Complete separation of ^{147}Pm and ^{151}Sm from each other

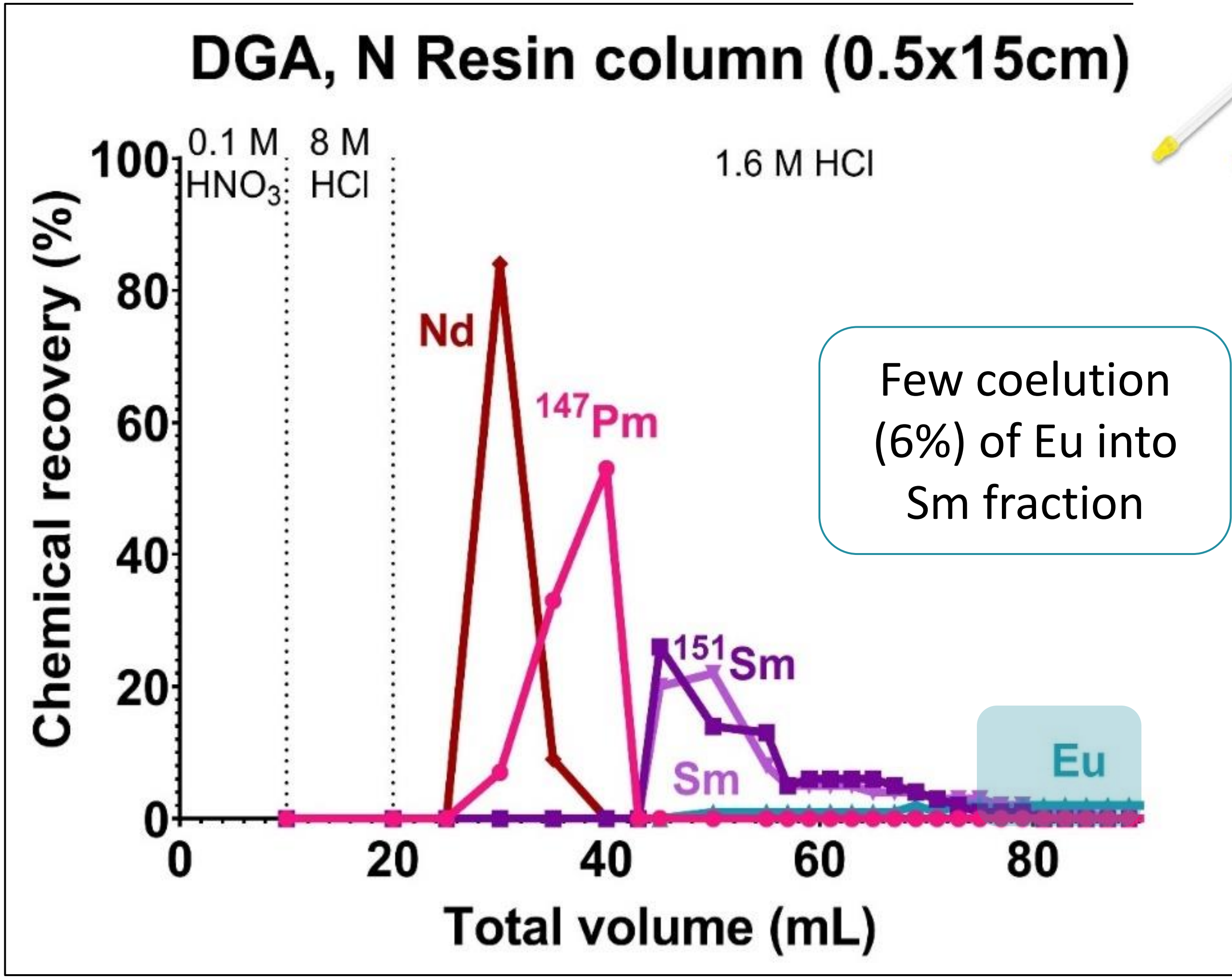
^{147}Pm and ^{151}Sm radiochemical separation



Nd collected with ^{147}Pm (chemical recovery)

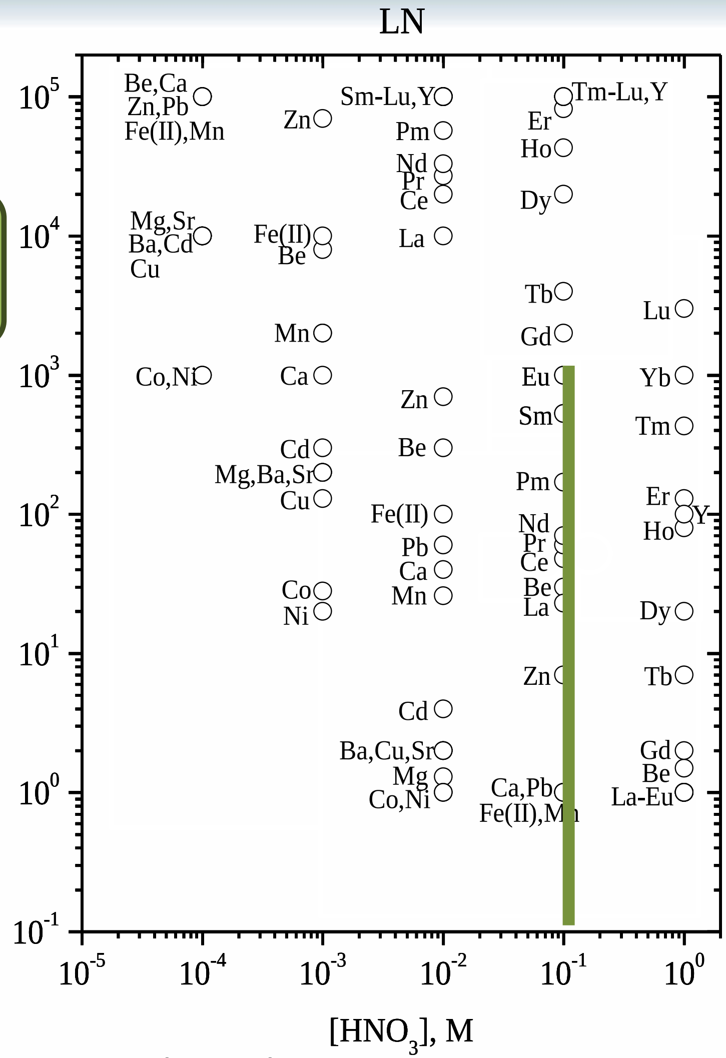
^{147}Pm and ^{151}Sm radiochemical separation

DGA,N resin



Few coelution (6%) of Eu into Sm fraction

^{147}Pm and ^{151}Sm radiochemical separation

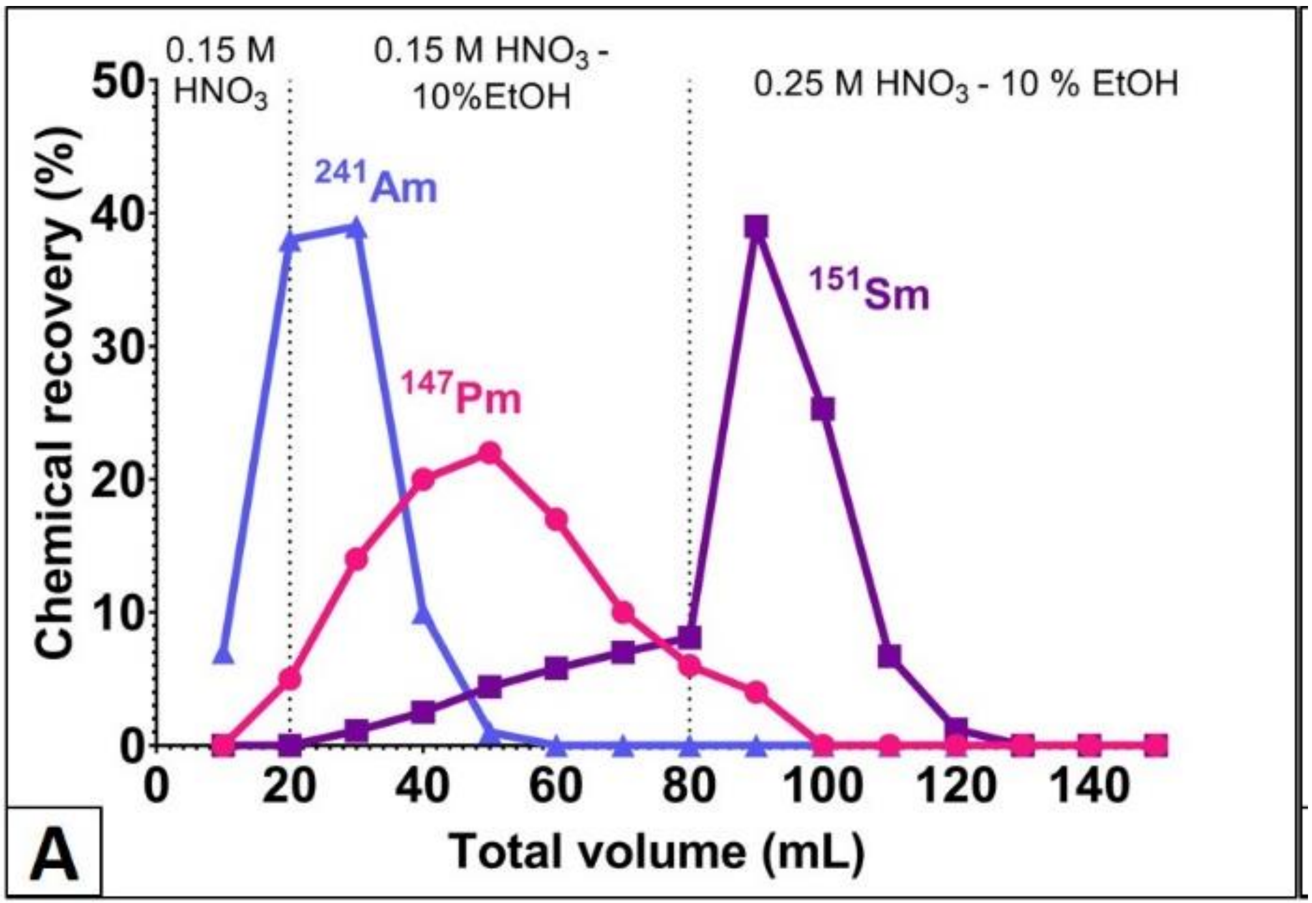


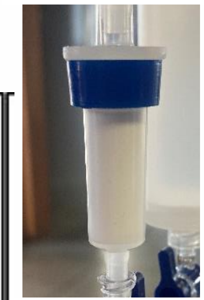
From LN / LN2 / LN3 resins product sheet, Triskem, 2020

- Nd as a carrier for ^{147}Pm chemical recovery
- Eu as interference in ^{151}Sm fraction
- 0,1 M HNO_3 higher retention of Sm compared to Pm/Nd
- ↑ column length → ↑ peak resolution

^{147}Pm and ^{151}Sm radiochemical separation

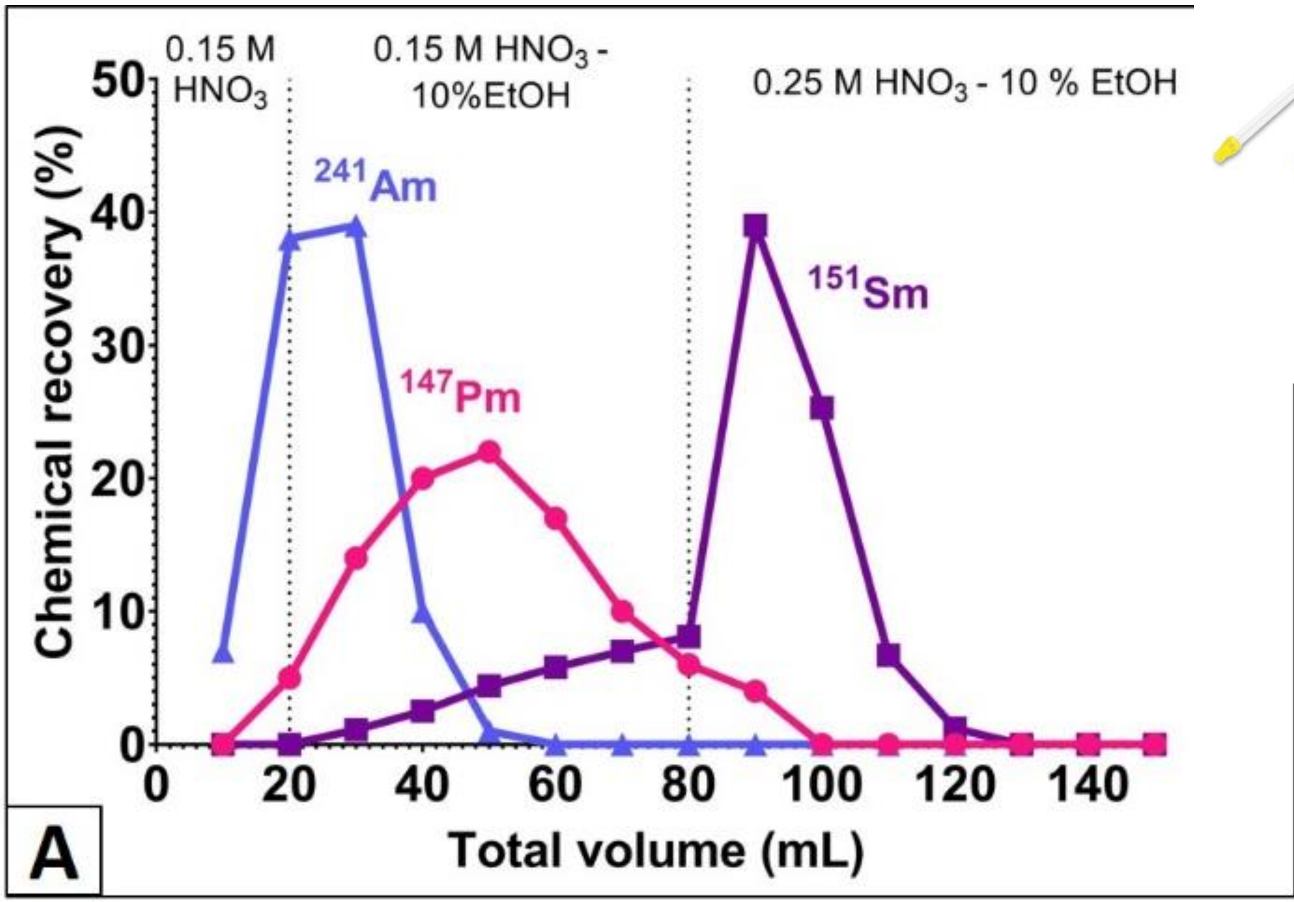
Procedure based on Warwick et al. 2022





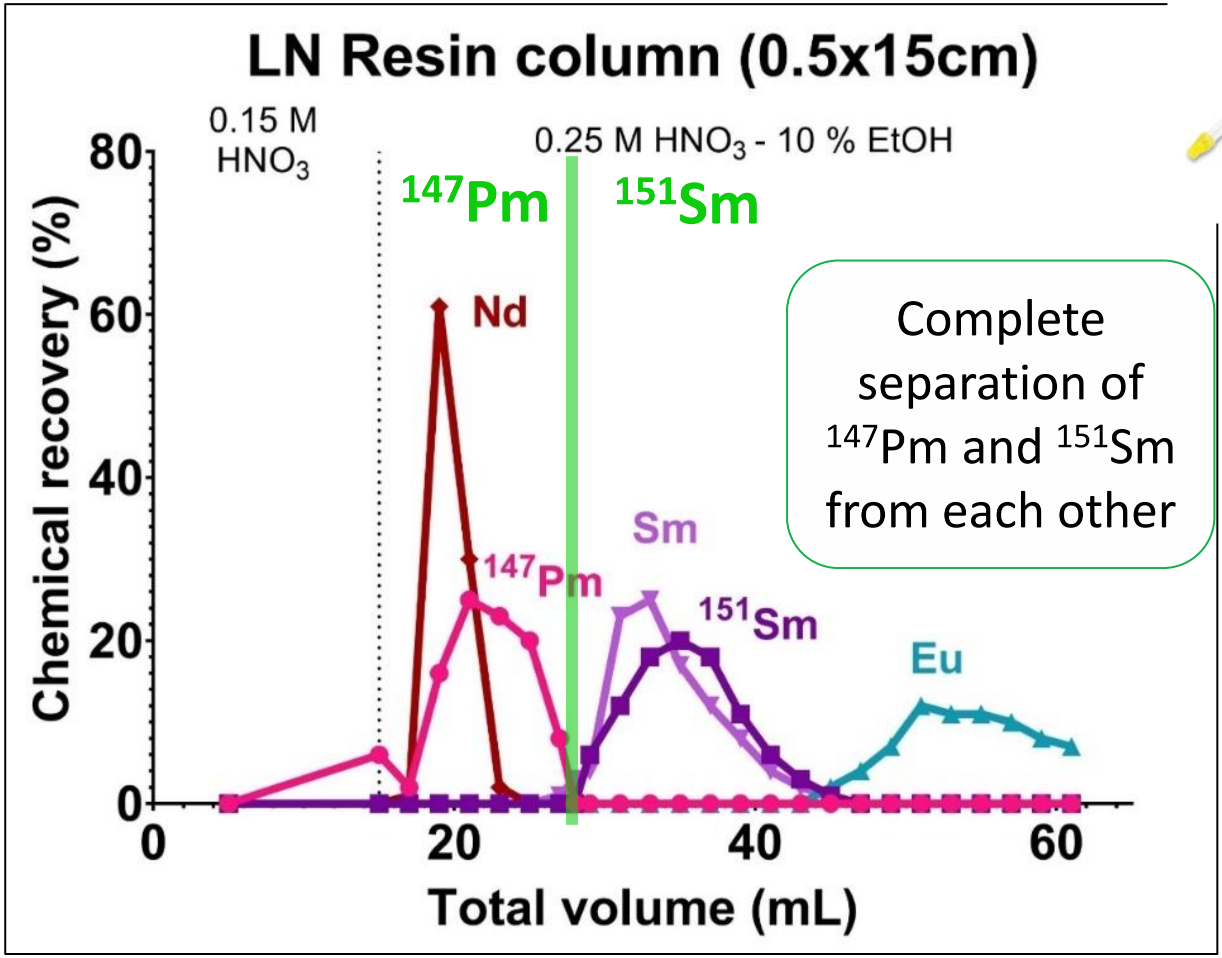
^{147}Pm and ^{151}Sm radiochemical separation

Procedure based on Warwick et al. 2022



^{147}Pm and ^{151}Sm radiochemical separation

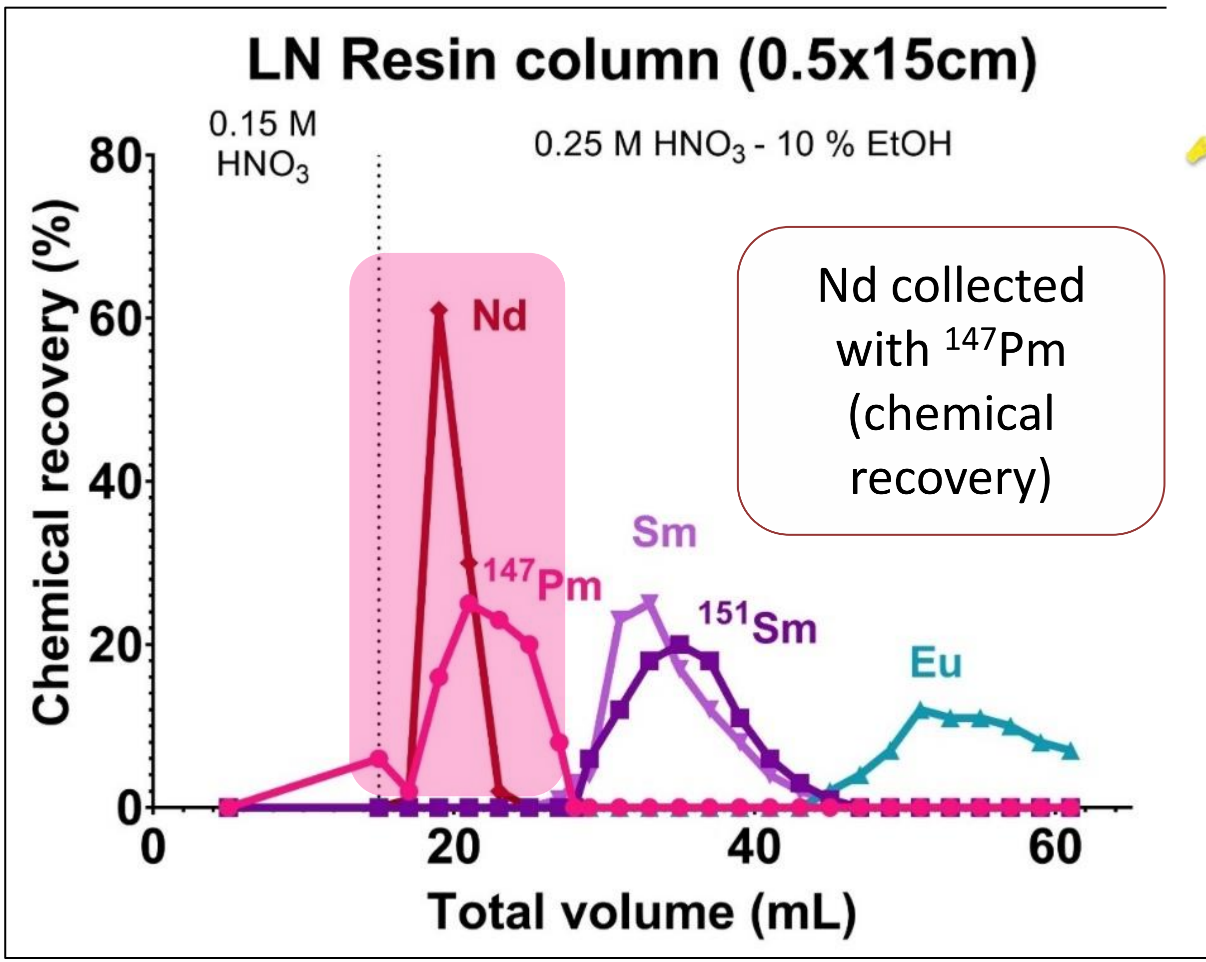
Procedure based on Warwick et al. 2022



Complete separation of ^{147}Pm and ^{151}Sm from each other

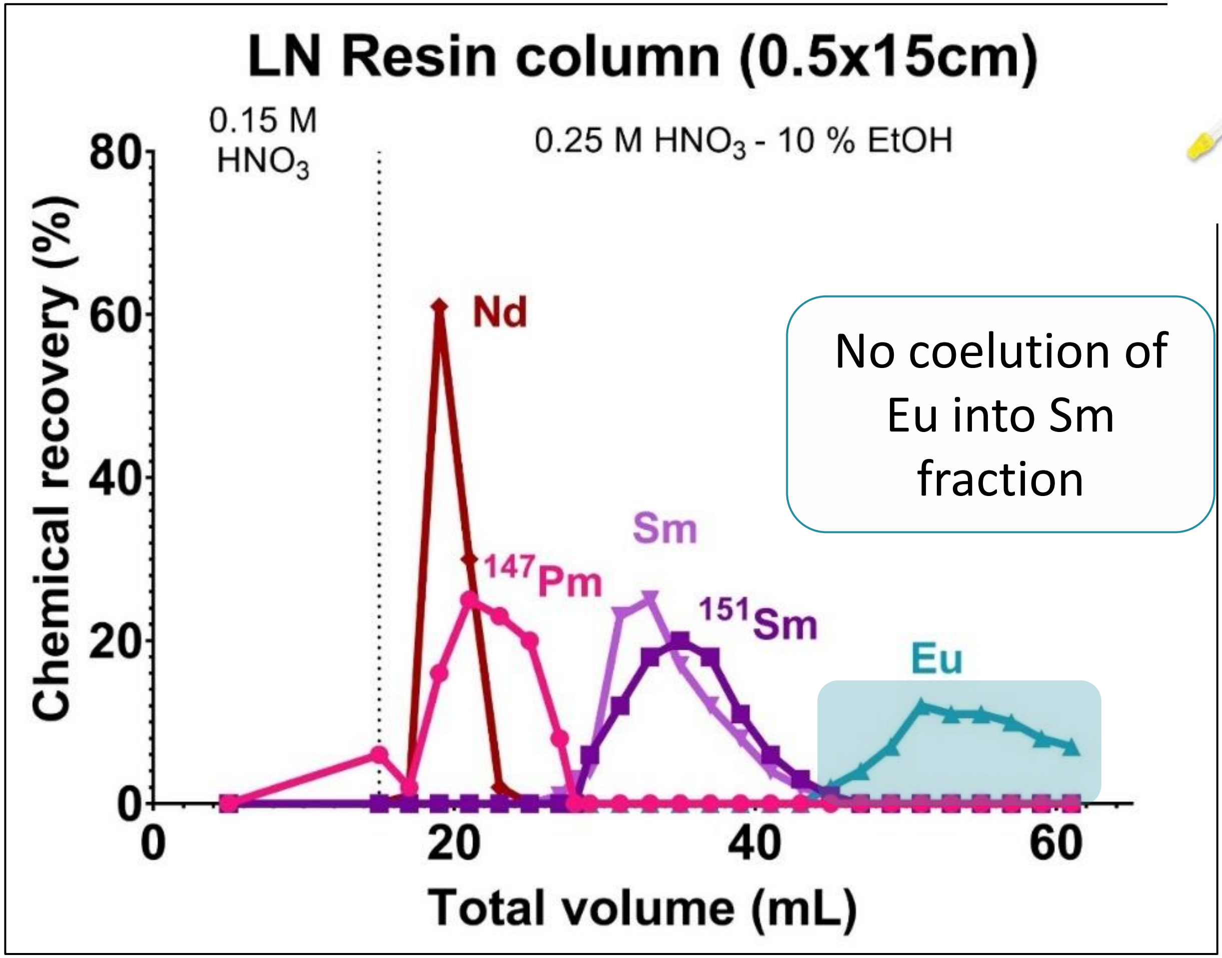
^{147}Pm and ^{151}Sm radiochemical separation

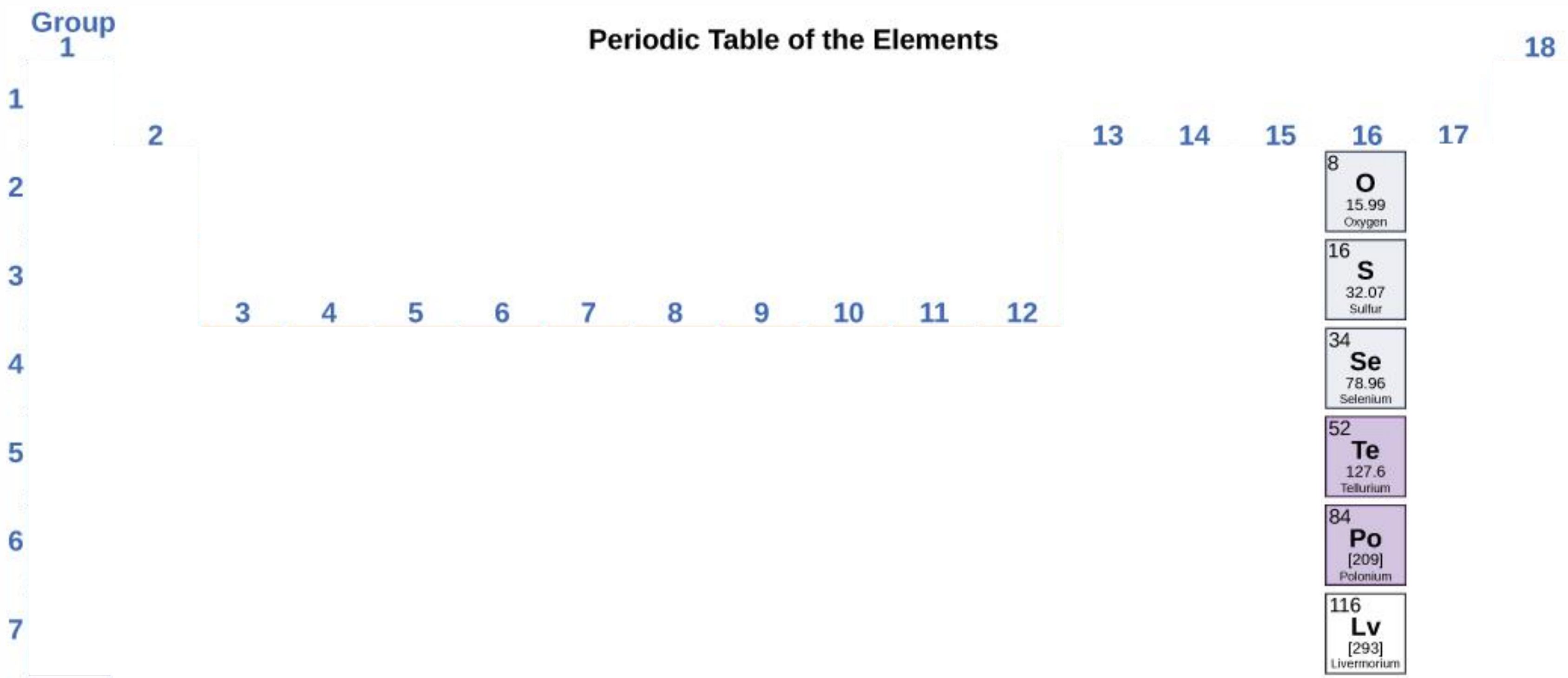
Procedure based on Warwick et al. 2022

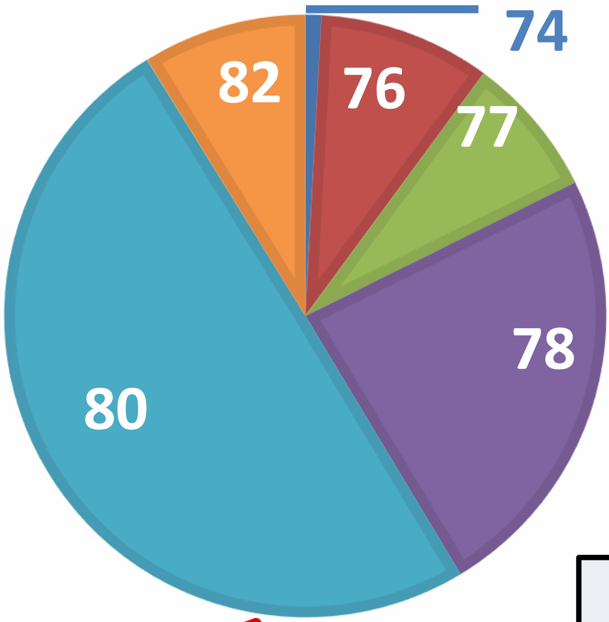


^{147}Pm and ^{151}Sm radiochemical separation

Procedure based on Warwick et al. 2022




Periodic Table of the Elements
Group
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
1
2
3
4
5
6
7
8
O
15.99
Oxygen
16
S
32.07
Sulfur
34
Se
78.96
Selenium
52
Te
127.6
Tellurium
84
Po
[209]
Polonium
116
Lv
[293]
Livermorium



WARNING

$Se^{(II-)}$
$Se^{(0)}$
$Se^{(IV)}$
$Se^{(VI)}$

34 Se 78 Selenium

34 Se **75** Selenium

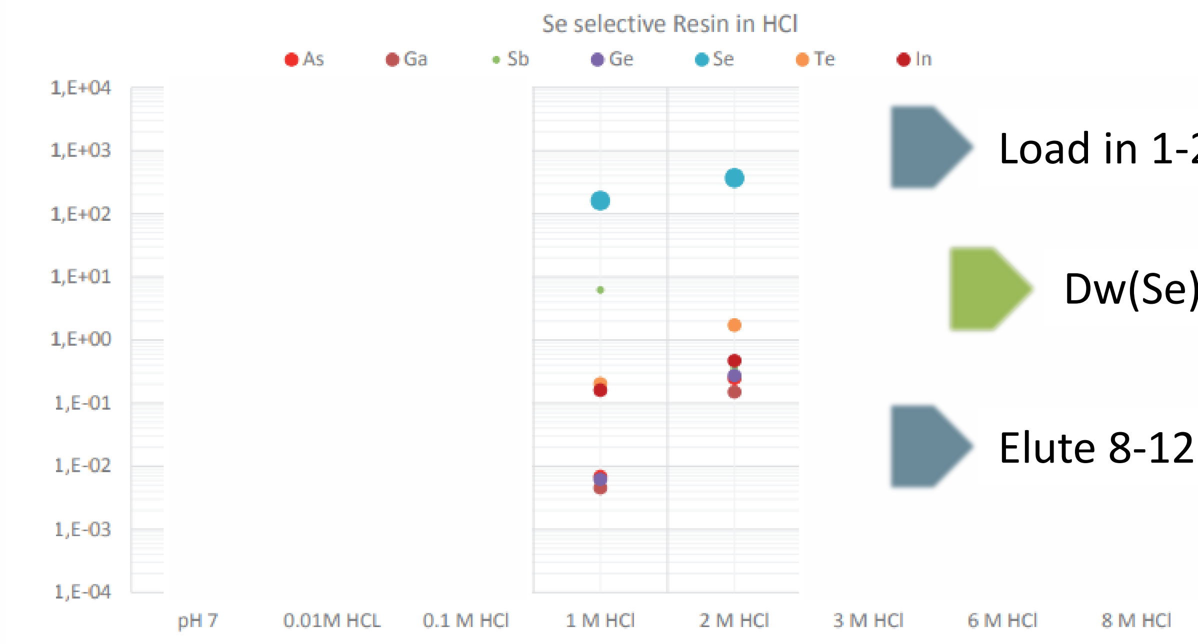
34 Se **79** Selenium

No reference material

Preliminary study for the determination of ^{79}Se → Radiochemical separation

SE Resin

Se selectivity → Amino compound in ionic liquid

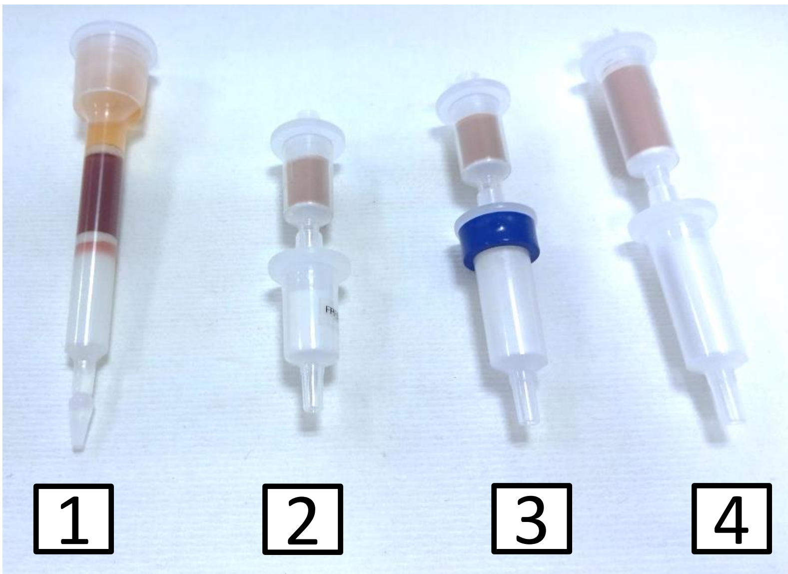


- Load in 1-2 M HCl
- Dw(Se) >> Dw(Sb, Ga, Te)
- Elute 8-12 mL H_2O_2

Taken from Dirks et al. 2016

Preliminary study for the determination of ^{79}Se → Radiochemical separation

SE Resin new prototype

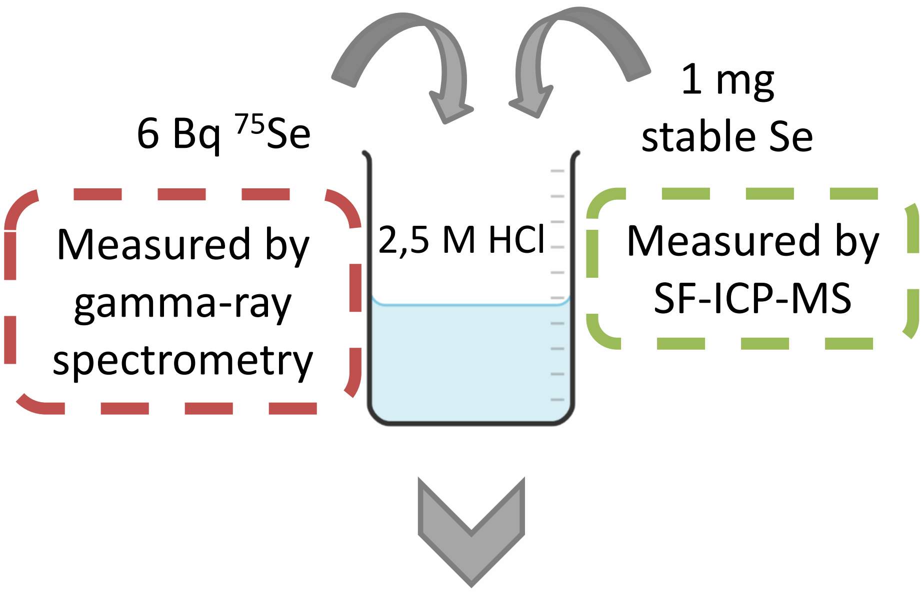


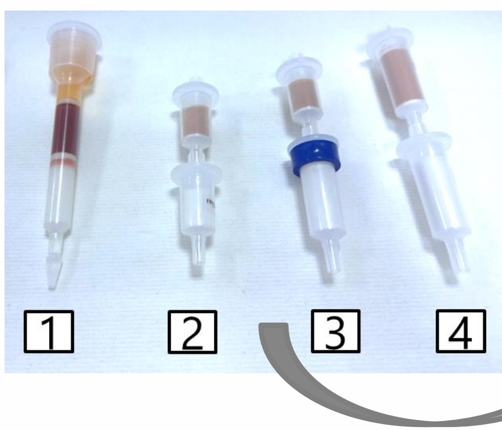
Vacuum box needed

SE Resin new prototype:

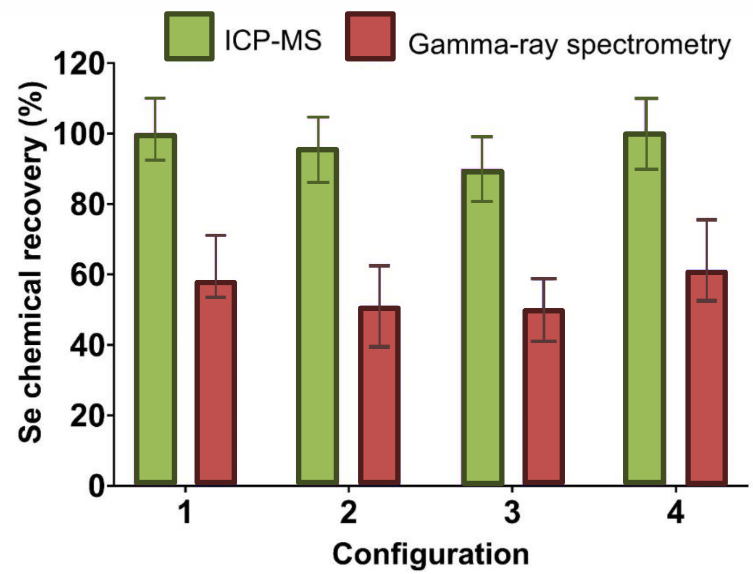
- 1-2 mL SE Resin
- 1-2 mL Prefilter Resin

Preliminary study for the determination of ^{79}Se → Radiochemical separation

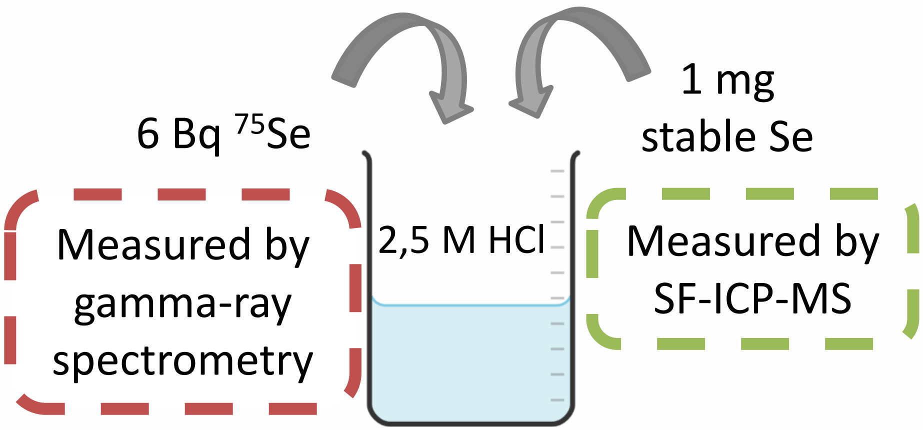




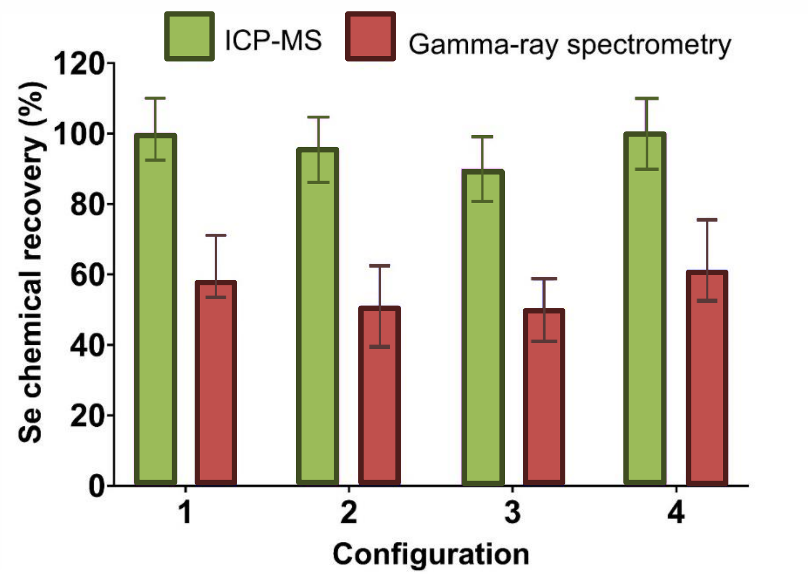
Elution 1 M NaOH



Preliminary study for the determination of ^{79}Se → Radiochemical separation



Disagreement between gamma-ray spectrometry and ICP-MS

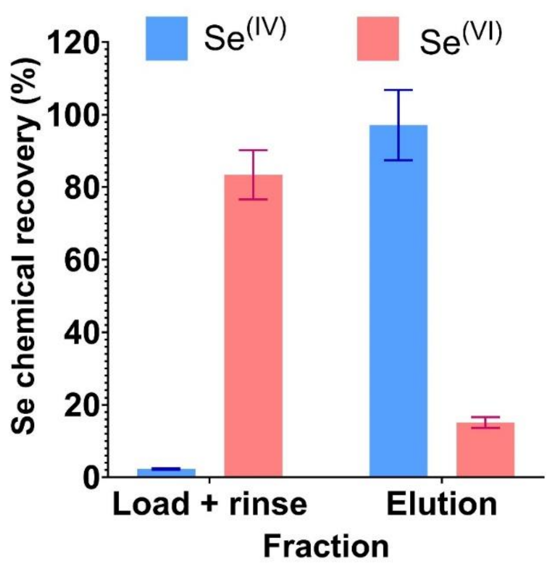


OXIDATION STATE OF SE

Preliminary study for the determination of ^{79}Se → Radiochemical separation

1 mg stable **Se(IV)**

Reduction – oxidation cycle needed



1 mg stable **Se(VI)**

Se(IV) highly retained

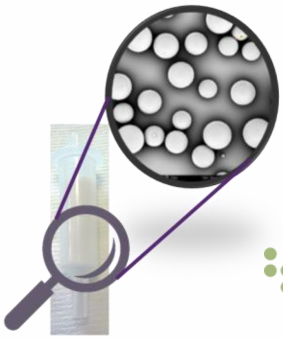
Se(VI) suitable for elution

Conclusions

17 Cl 36 Chlorine	53 I 129 Iodine

Shorter procedure (~1 working day) and fewer chemicals consumed

Detection limit below clearance level



NEW

New analytical method

Mixed waste

Turnaround time

- ❑ **Cleaning** and new glassware materials

Choice of resins for ^{36}Cl determination

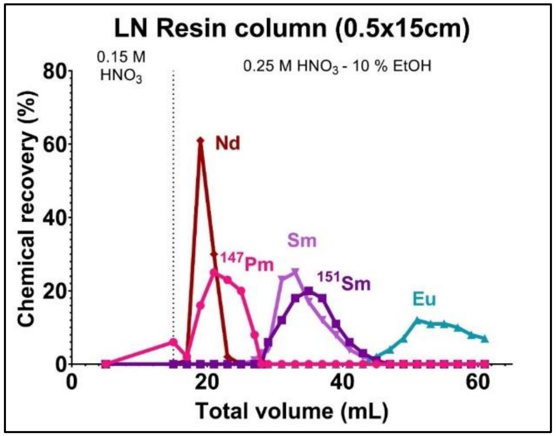
Conclusions

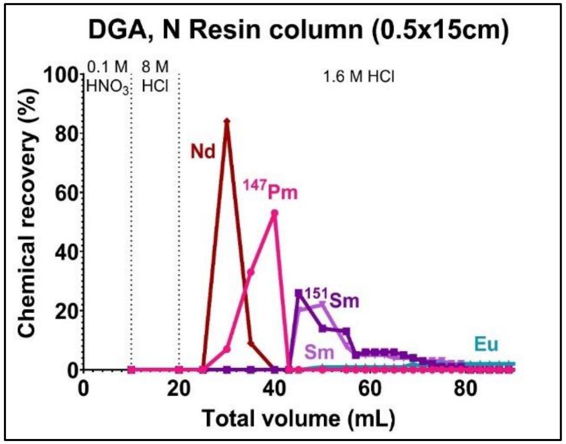
61 **Pm** 147 Promethium	62 **Sm** 151 Samarium

Complete radiochemical separation using **2** different **resins** (longer columns)

Nd used to quantify chemical recovery of ^{147}Pm

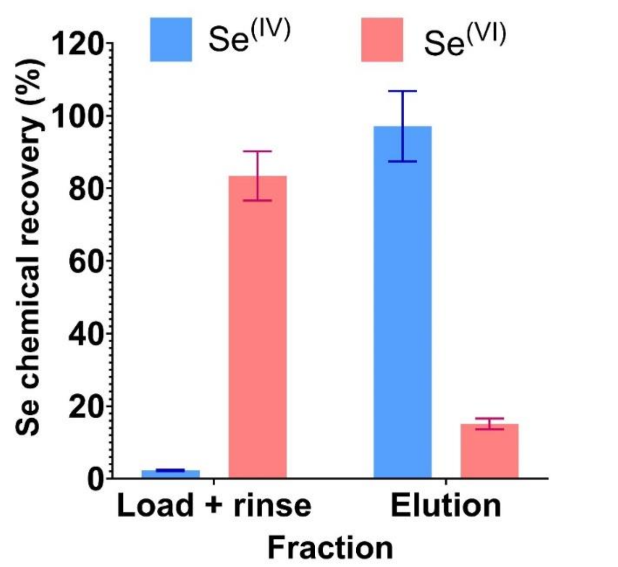
Eu does not strongly interfere in Sm fraction





Conclusions

34 **Se** 75 Selenium	34 **Se** 79 Selenium



Only **Se(IV)** suitable for retention on SE Resin

Elution on SE Resin suitable when **Se(VI)** is the oxidation state

Currently TRISKEM

Loading medium → Se(IV) in solution

Elution medium → removal of Se as Se(VI)

Compatible for LSC

Additional information

I. Llopart Babot, et al. On the determination of ^{36}Cl and ^{129}I in solid materials from nuclear decommissioning activities. *J. Radioanal. Nucl. Chem*. 331 (2022) 3313–3326. https://doi.org/10.1007/s10967-022-08327-92.

II. I. Llopart Babot, et al. Investigating the ^{36}Cl memory effect in pyrolysis of solid samples from nuclear decommissioning activities, *J. Radioanal. Nucl*. Chem. 331 (2022) 4239–4249. https://doi.org/10.1007/s10967-022-08492-x3.

III. I. Llopart Babot, et al. Investigation of a new approach for ^{36}Cl determination in solid samples using plastic scintillators, *Appl. Radiat. Isot.* 193 (2023). https://doi.org/10.1016/j.apradiso.2022.1106464.

IV. I. Llopart Babot, et al. A comparison of different approaches for the analysis of ^{36}Cl in graphite samples, *Appl. Radiat. Isot.* 202 (2023). https://doi.org/https://doi.org/10.1016/j.apradiso.2023.111046

Thank you for your attention!

TRISKEM
Expertise in Separation Chemistry