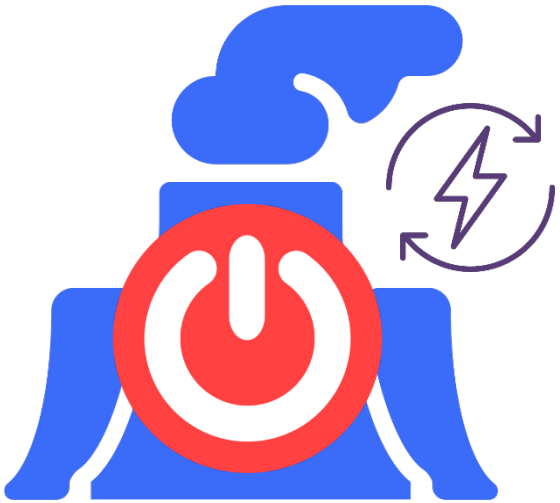
Inés Llopart Babot, Steffen Happel, Alex Tarancón, Alex Blanco
23-10-2025

Development of novel assays for DTM radionuclides in materials produced during nuclear decommissioning activities

TRISKEM
Expertise in Separation Chemistry

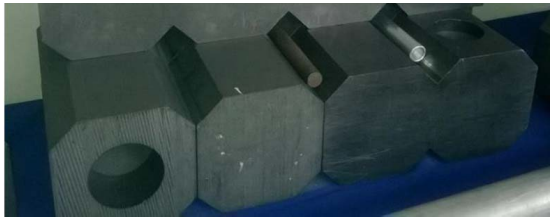
Radiological waste characterization



Which type of waste?

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

Stefan Nijst, 2014, Master Thesis



Radiological waste characterization

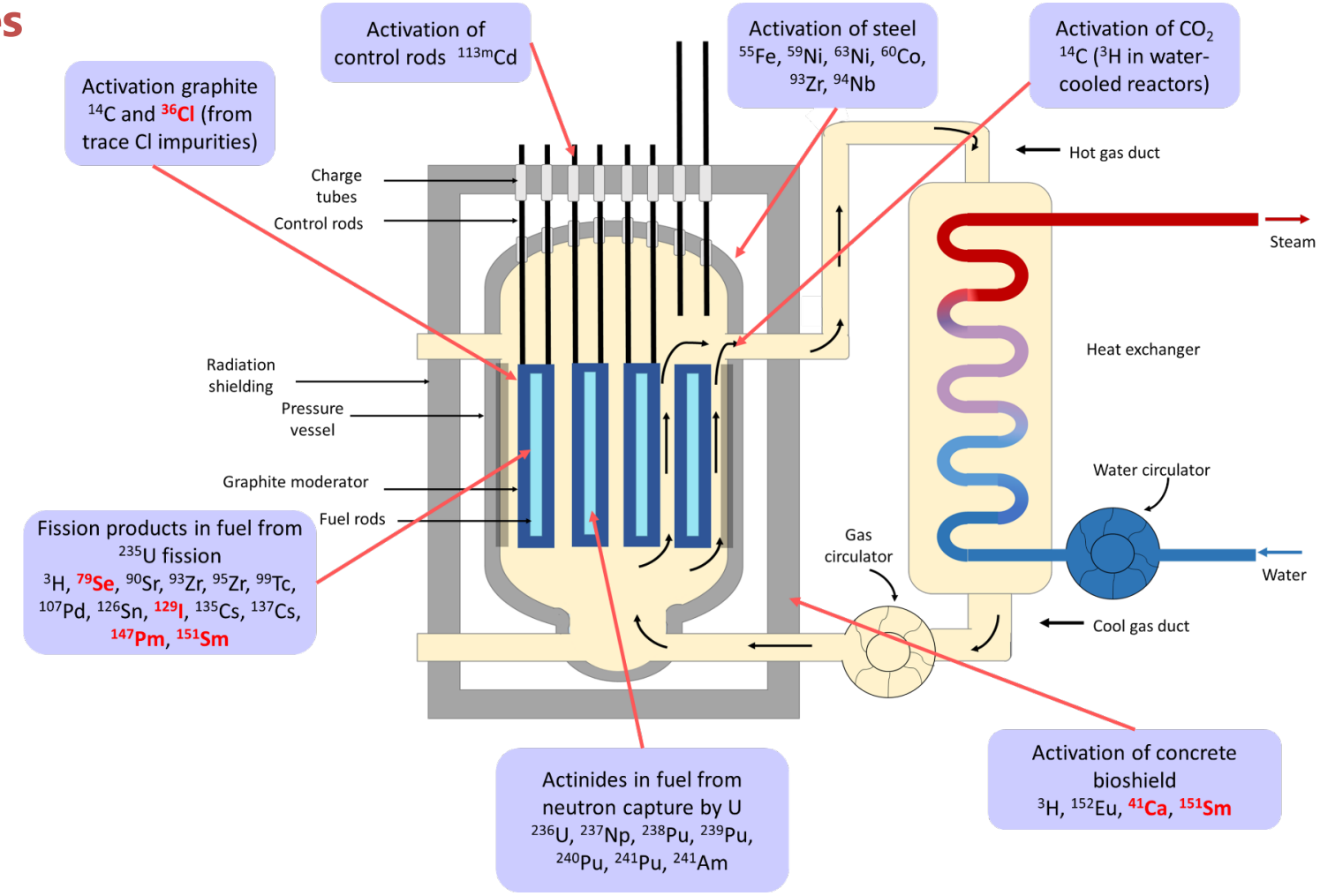
Which radionuclides can be expected?

Energy emission

α ,β, γ

Half-life

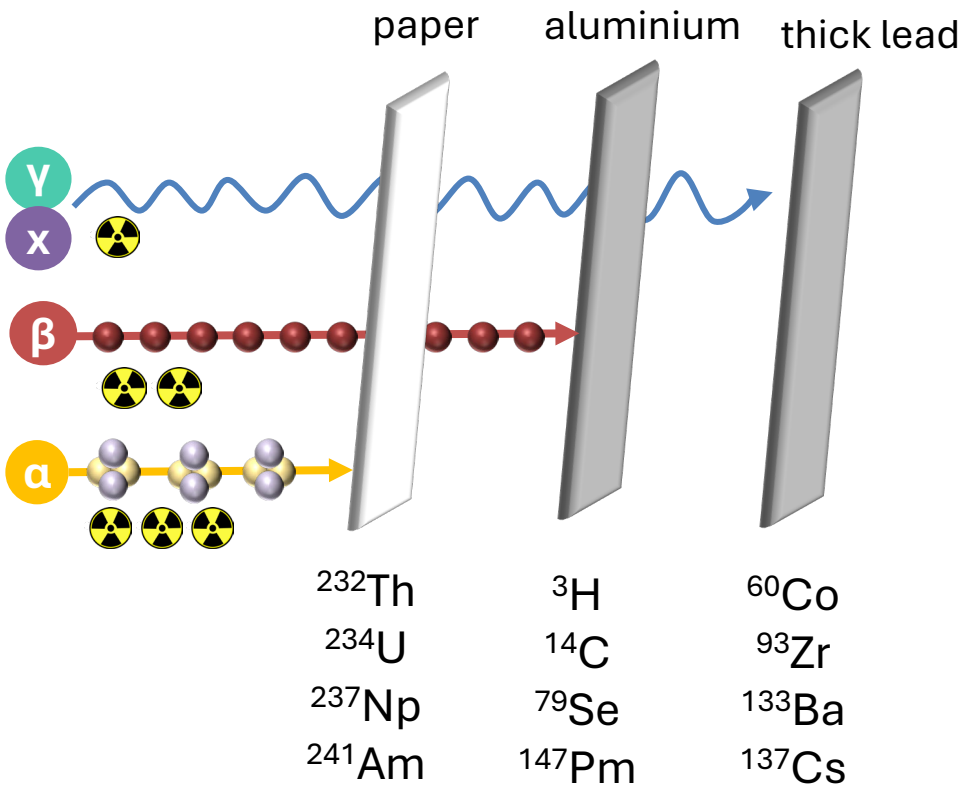
Short or long lived



Based on (Warwick et al., 2022)

Radiological waste characterization

Which radionuclides can be expected?



How can these radionuclides be quantified?

Non-destructive assay

"easy to measure" radionuclides — **ETM**

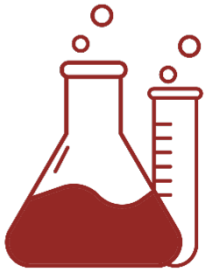
Destructive assay

"difficult to measure" radionuclides — **DTM**

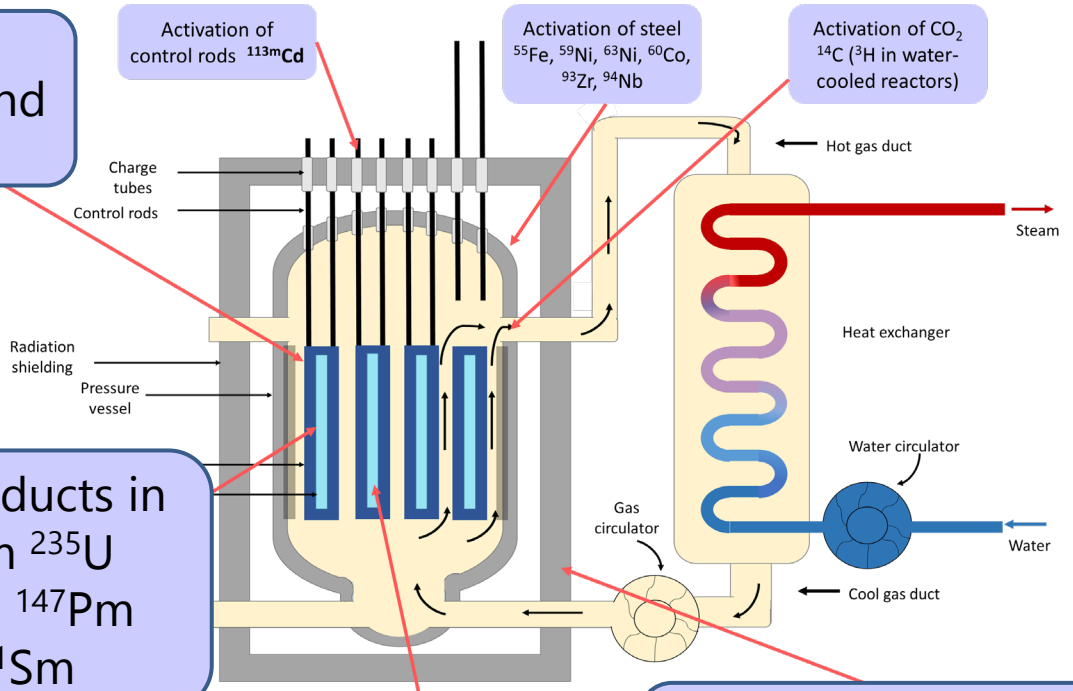
Selection of DTM radionuclides

MISSING

^{36}Cl and ^{129}I | **^{147}Pm and ^{151}Sm** | **^{79}Se** | **^{41}Ca**



Activation graphite ^{14}C and **^{36}Cl**



Fission products in fuel from ^{235}U **^{79}Se, ^{129}I,** ^{147}Pm and ^{151}Sm

Actinides in fuel from neutron capture by U ^{236}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu, ^{241}Am

Activation of concrete ^{3}H, **^{41}Ca**, ^{151}Sm, ^{55}Fe, ^{152}Eu

Selected radionuclides → beta decay (β^-)

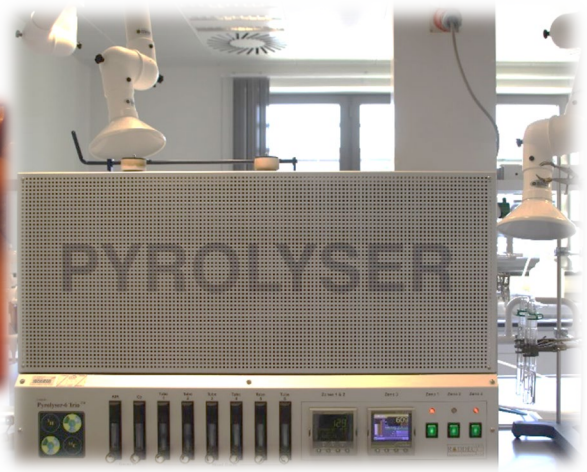
Determination of DTM radionuclides

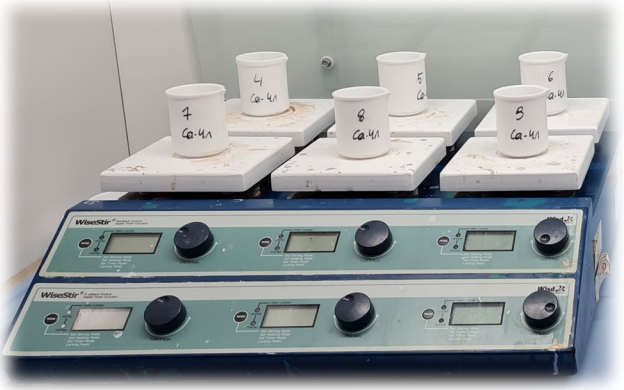
Sample treatment → Chemical separation → Measurement

Homogenization

Complete sample dissolution

Sample representativeness





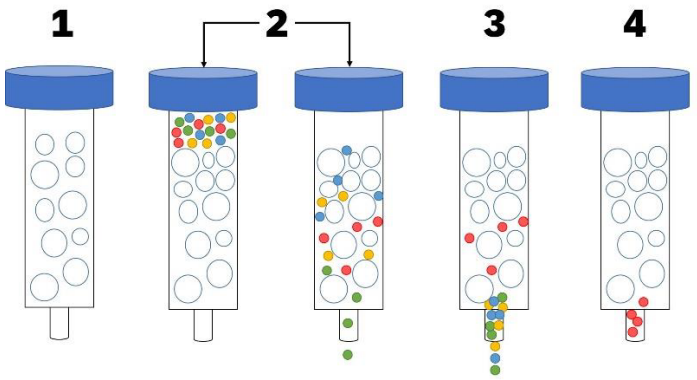
Determination of DTM radionuclides

Sample treatment → **Chemical separation** → Measurement

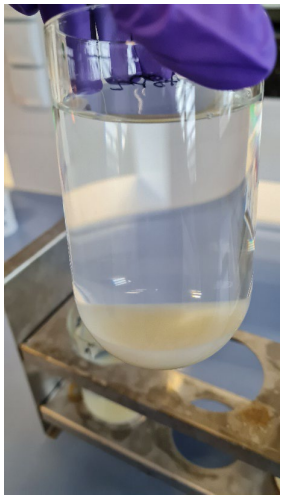
Pre-concentration

Interference removal

Time needed for the separation procedure



1 Conditioning
2 Sample loading
3 Washing / rinsing
4 Elution
Target radionuclide
Interferences



Determination of DTM radionuclides

Sample treatment → Chemical separation → **Measurement**

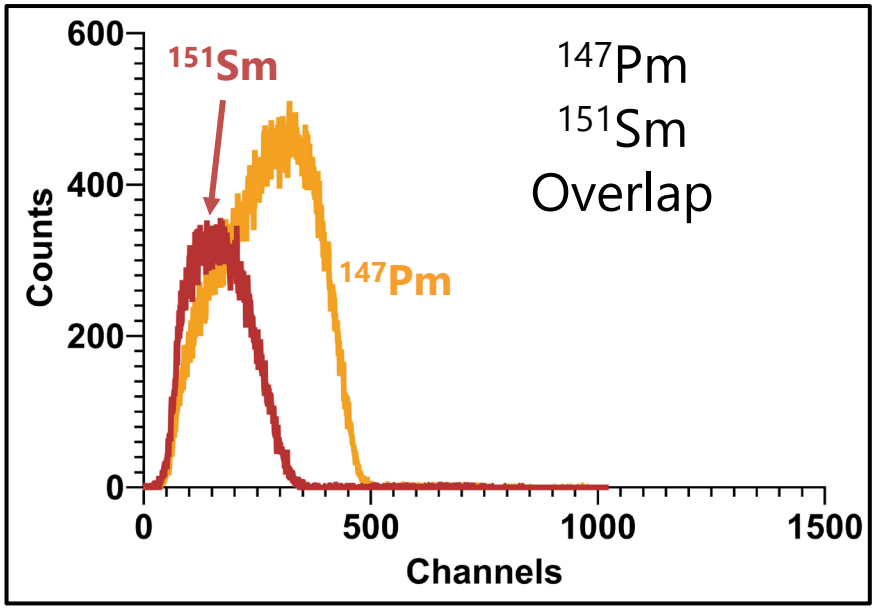
Detection limit

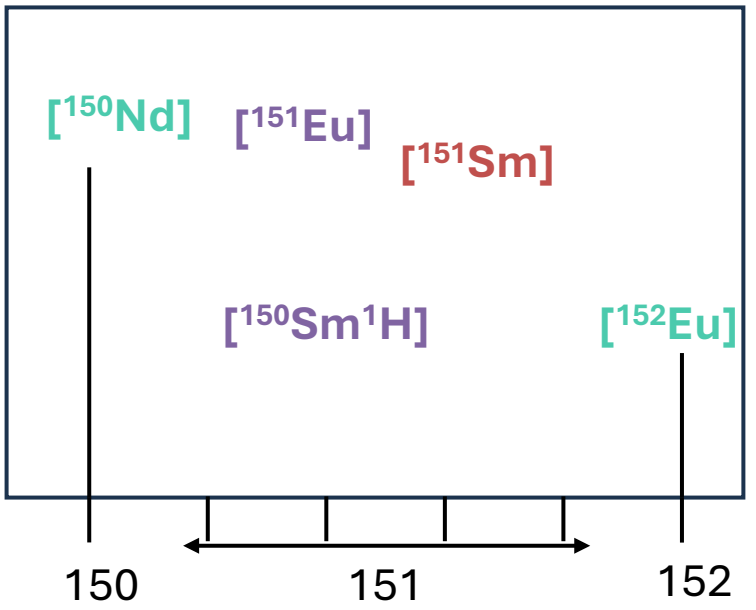
Effect of interferences

Time needed for measurement

Key issues to tackle

Interferences influencing the quantification of the activity





Radiometric (spectral) **Mass spectrometric (isobaric)**

Key issues to tackle

Interferences influencing the quantification of the activity

Lack of reference material

No ^{36}**Cl**/^{41}**Ca** reference material (concrete/graphite)

No ^{79}**Se** certified standard (validation)

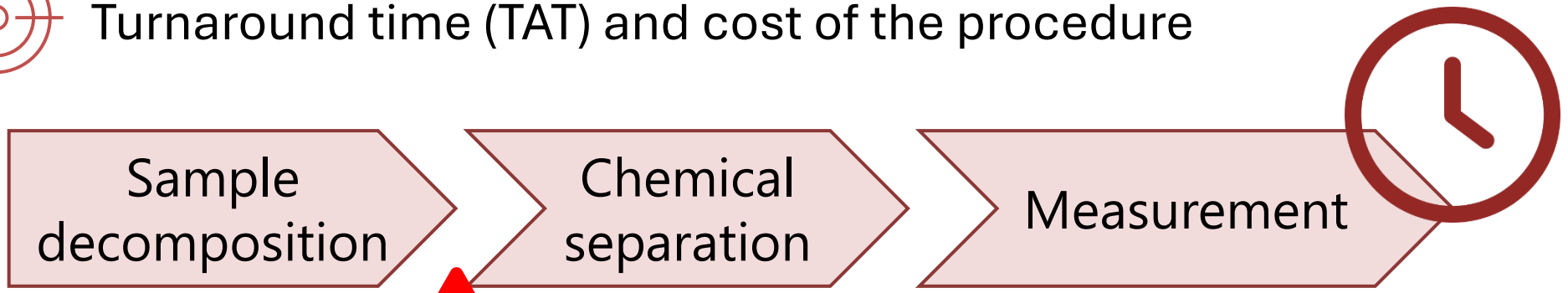
No ^{147}**Pm** stable isotope (chemical recovery)

Key issues to tackle

Interferences influencing the quantification of the activity

Lack of reference material

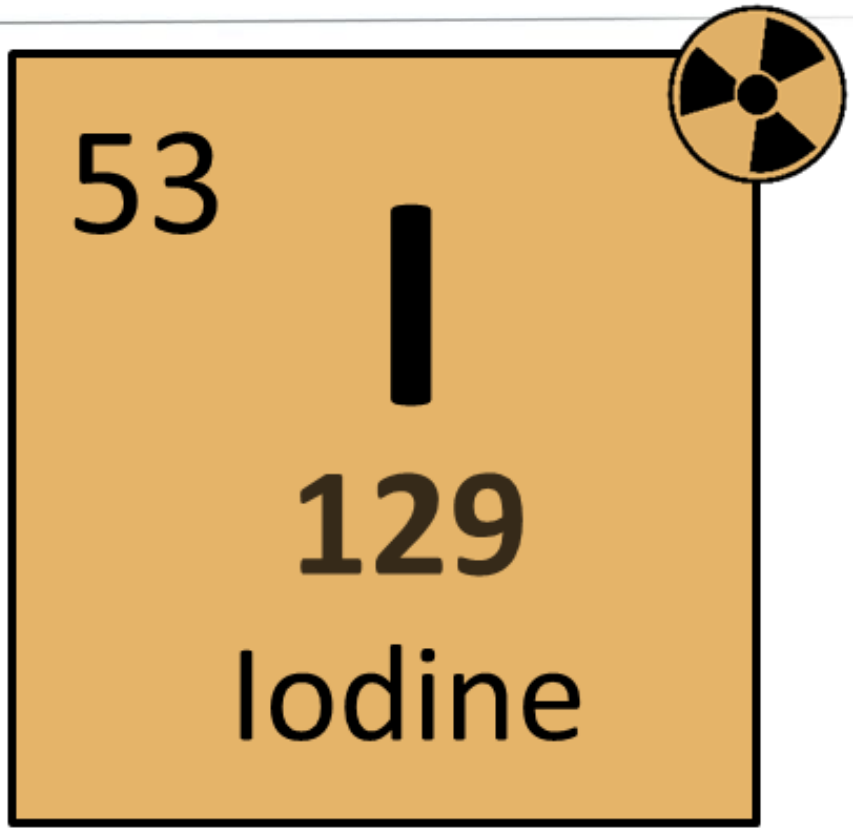
Turnaround time (TAT) and cost of the procedure



Lanthanides/halogens very similar properties

Different oxidation states of Se

Matrix interferences



$T_{1/2}$ = 3,02 ▪ 10^5 year

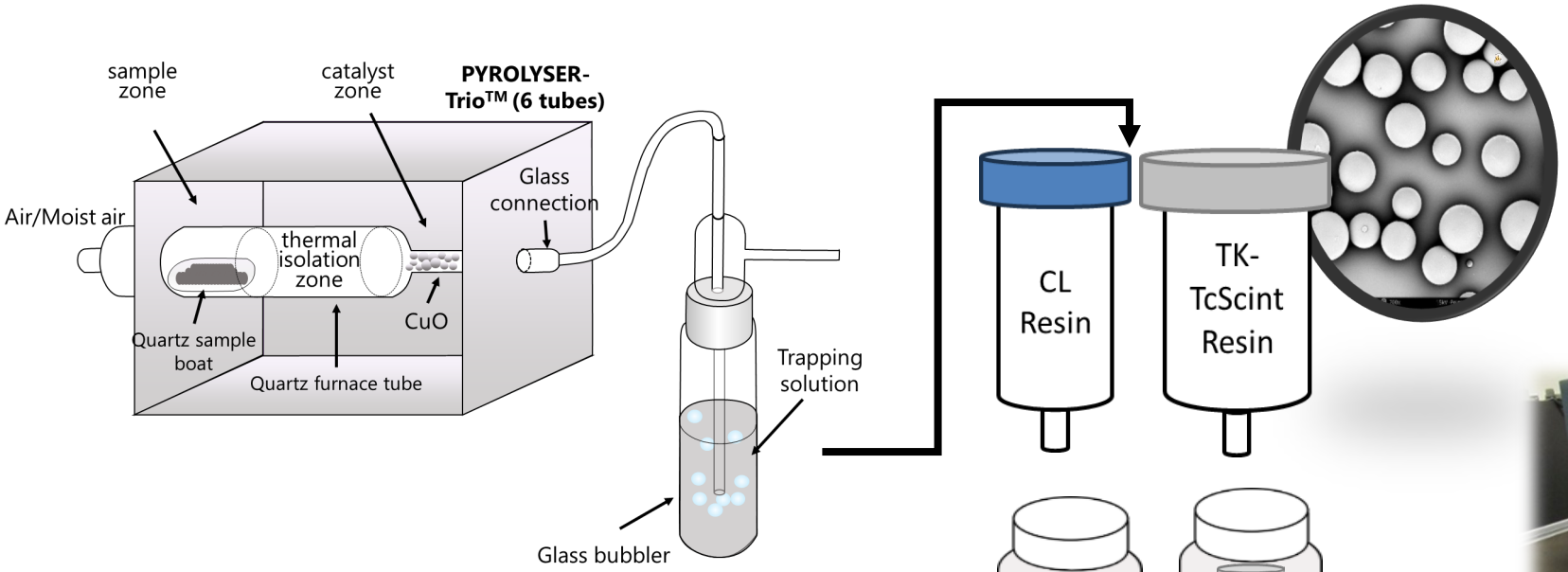
β-emitter E_{max} 709.6 keV

$T_{1/2}$ = 1,57 ▪ 10^7 year

β-emitter E_{max} 154 keV

^{36}Cl and ^{129}I determination

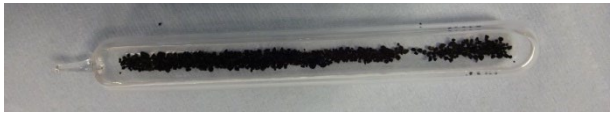
17 Cl	53 I
36	129
Chlorine	Iodine



Based on Warwick et al. 2010

Concrete

Graphite

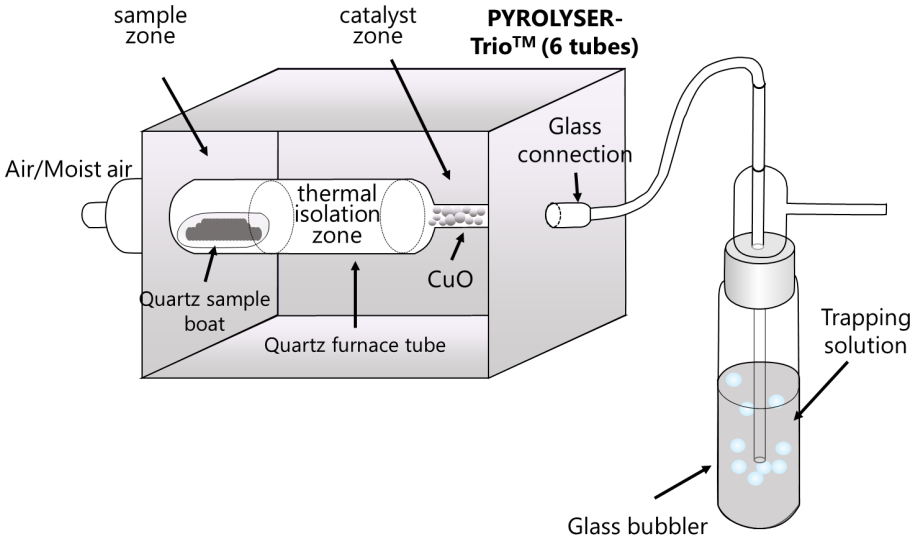


LSC Wallac Quantulus 1220™

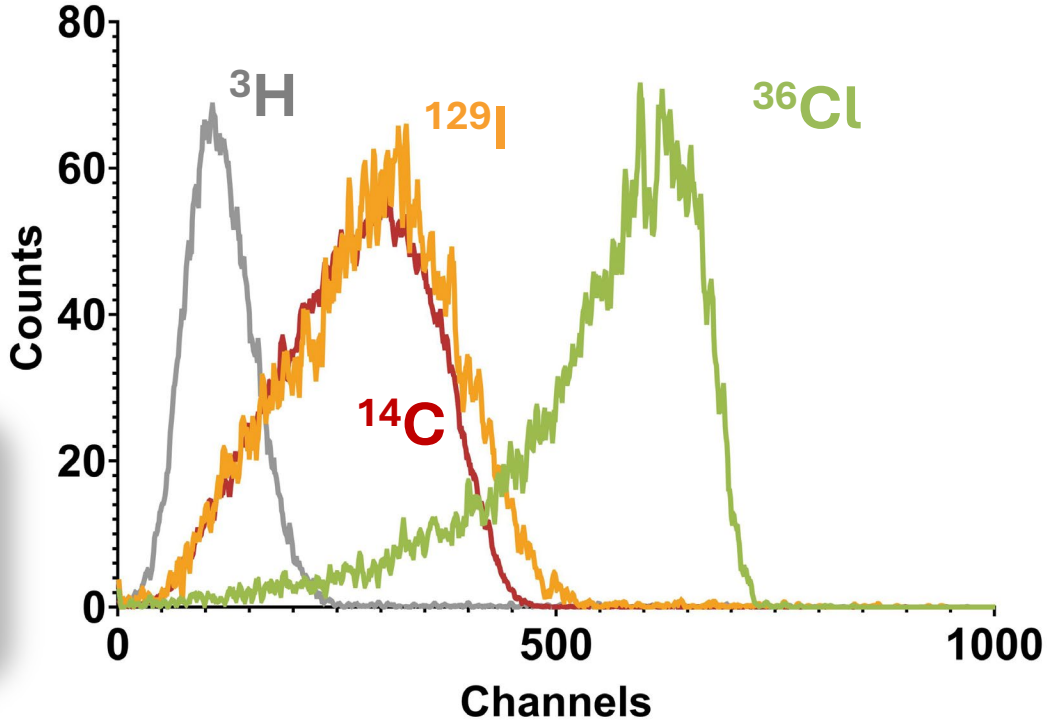
^{36}Cl and ^{129}I determination

17 **Cl** 36 Chlorine

53 **I** 129 Iodine



Interferences collected

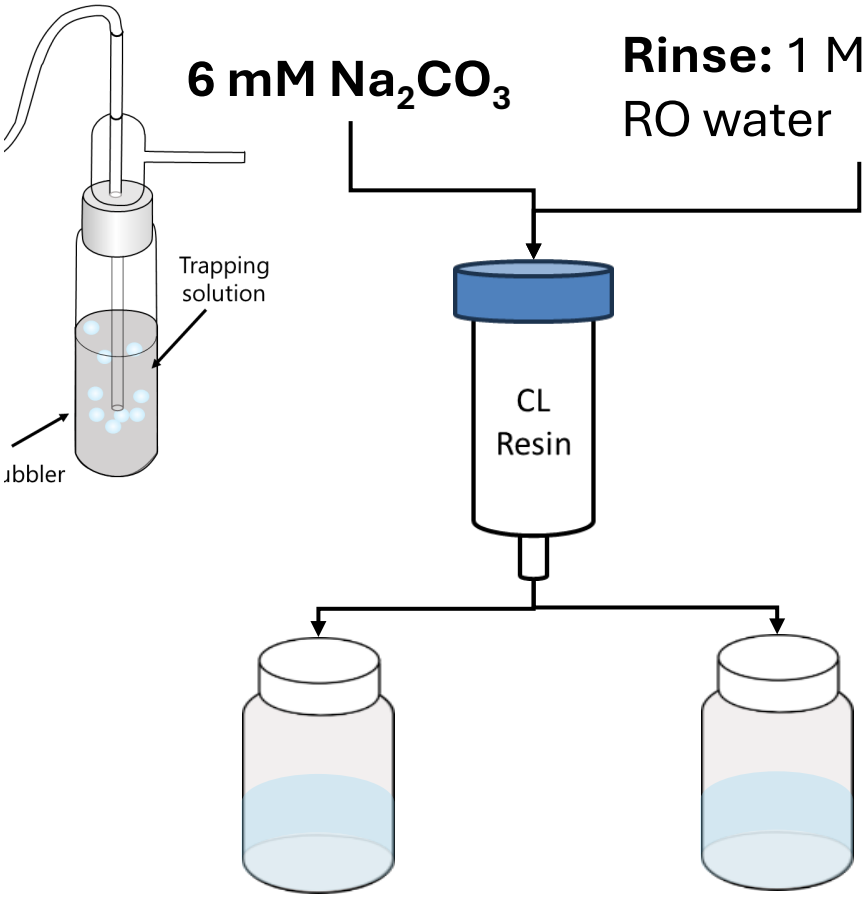


Need for chemical separation before LSC measurement

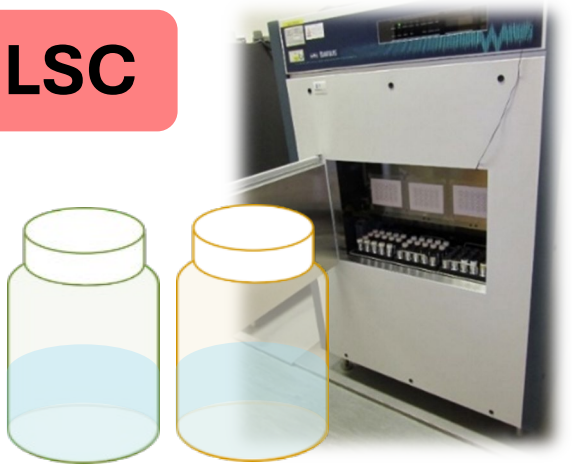
^{36}Cl and ^{129}I determination

17 **Cl** 36 Chlorine

53 **I** 129 Iodine



LSC



- Pure fractions
- 70-90% chemical recoveries

Cl elution:
5 mL 0,1 M NH_4SCN

I elution:
5 mL 0,35 M Na_2S

LOD

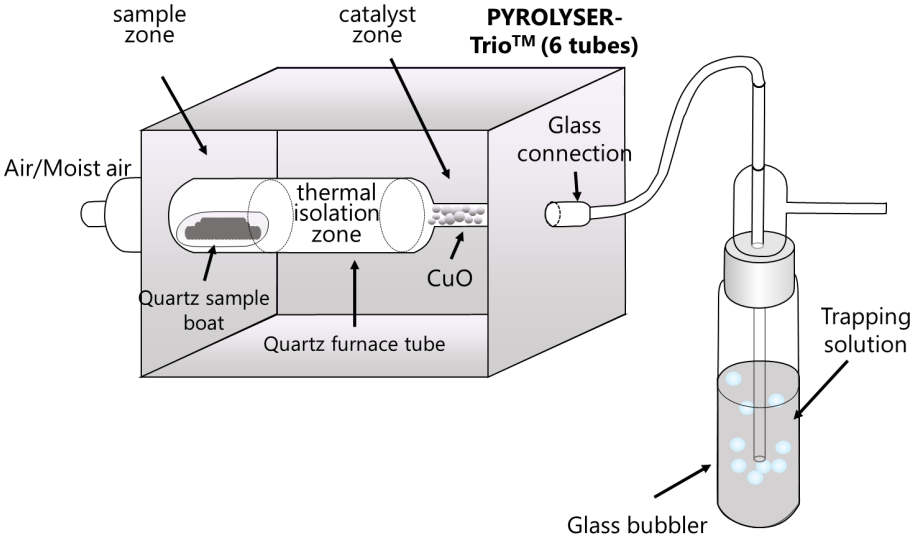
^{36}Cl

^{129}I

25 mBq/g

^{36}Cl and ^{129}I determination

17 Cl	53 I
36	129
Chlorine	Iodine



^{36}Cl memory effect

^{36}Cl detected on procedural blank samples

Moist air	Bubblers	Oxidant (if needed)
Quartz wool/beads	Quartz tubes	Sample boat

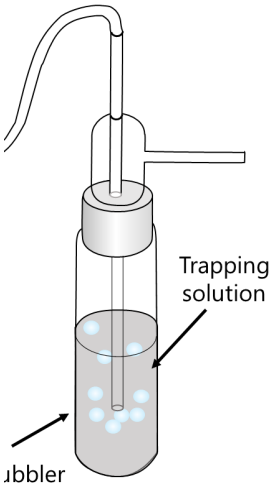
Can be removed

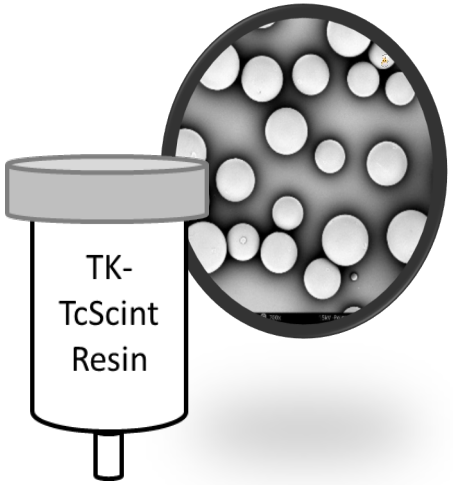
Major contributor

^{36}Cl and ^{129}I determination

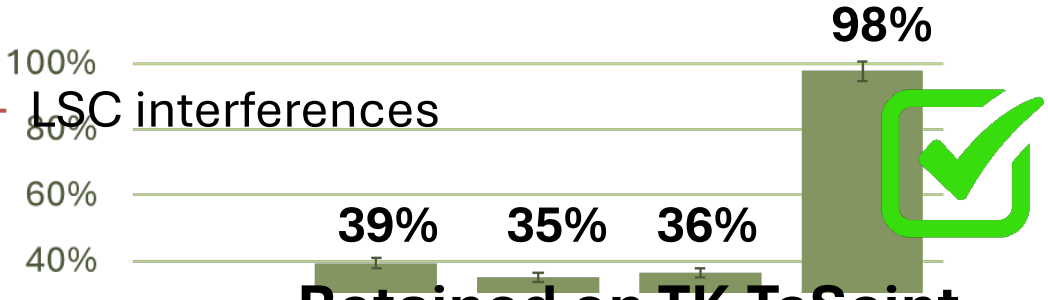
17 **Cl** 36 Chlorine

53 **I** 129 Iodine

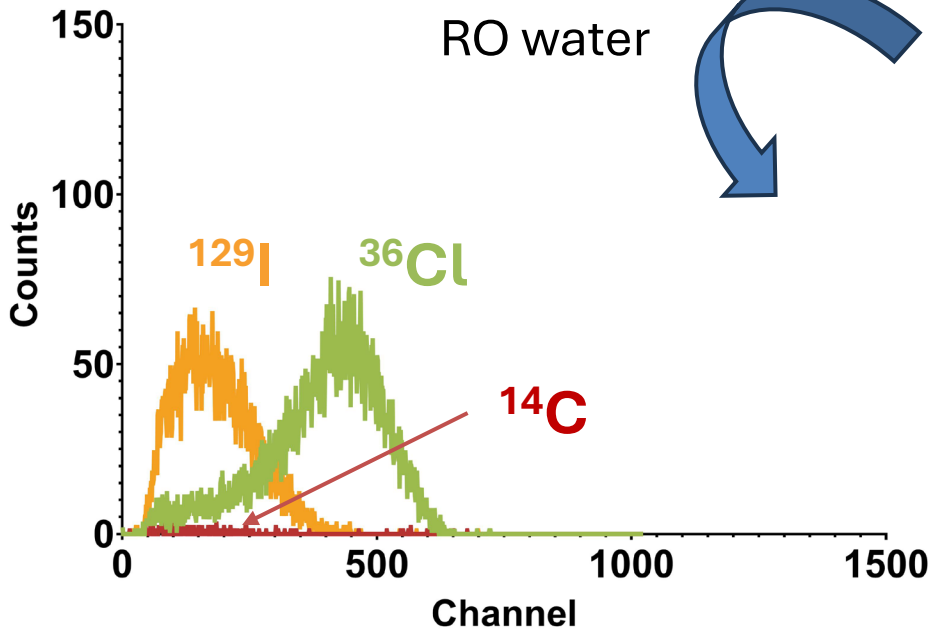




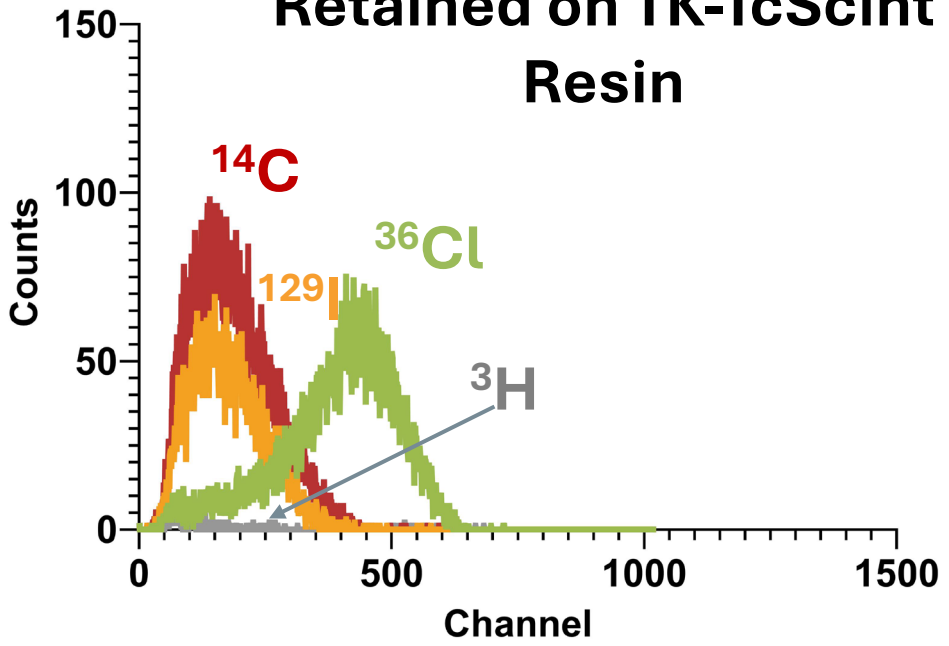
Trapping solution compatible with Cl/I retention on resin



RO water



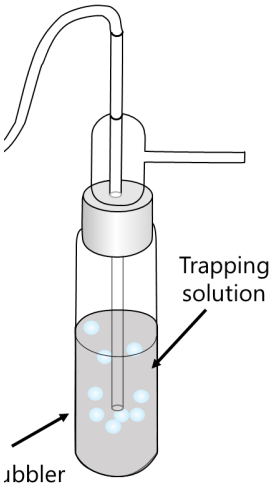
Retained on TK-TcScint Resin

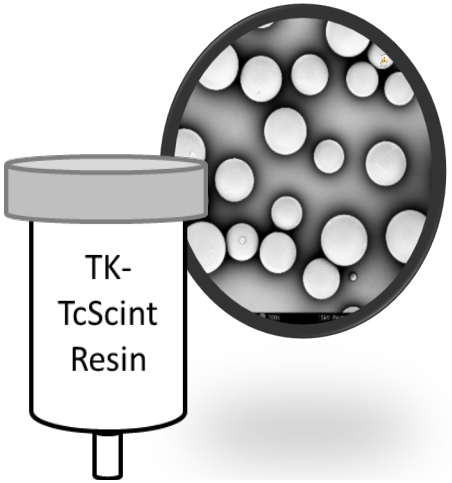


^{36}Cl and ^{129}I determination

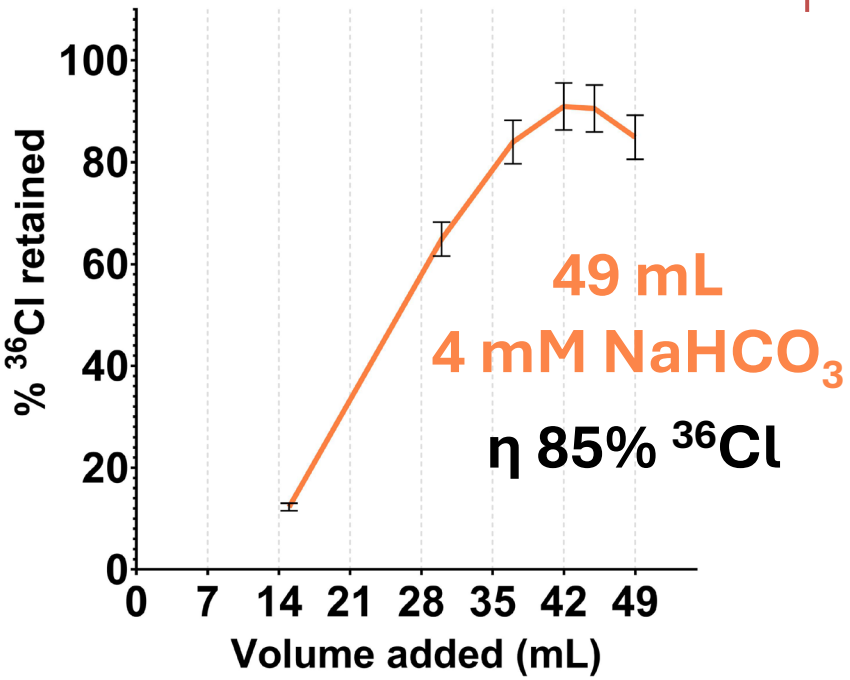
17 **Cl** 36 Chlorine

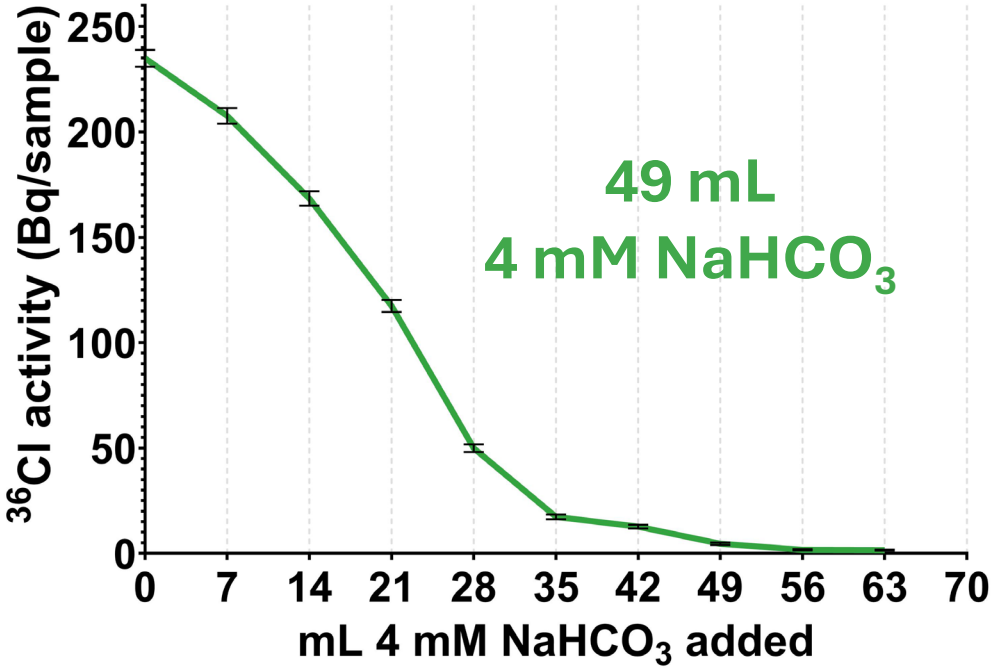
53 **I** 129 Iodine





- Trapping solution compatible with Cl/I retention on resin
- LSC interferences
- Cleaning PS Resin (separate wastes)

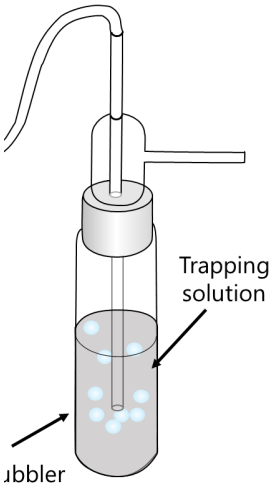


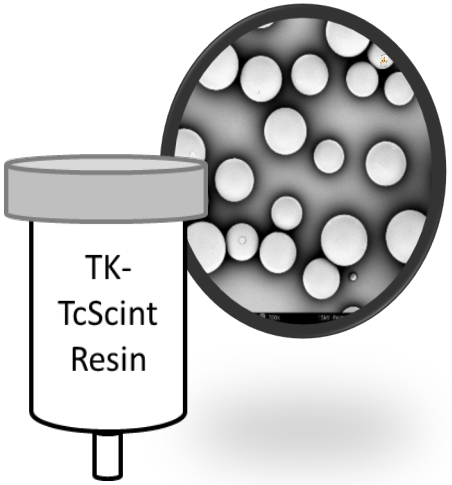


^{36}Cl and ^{129}I determination

17 **Cl** 36 Chlorine

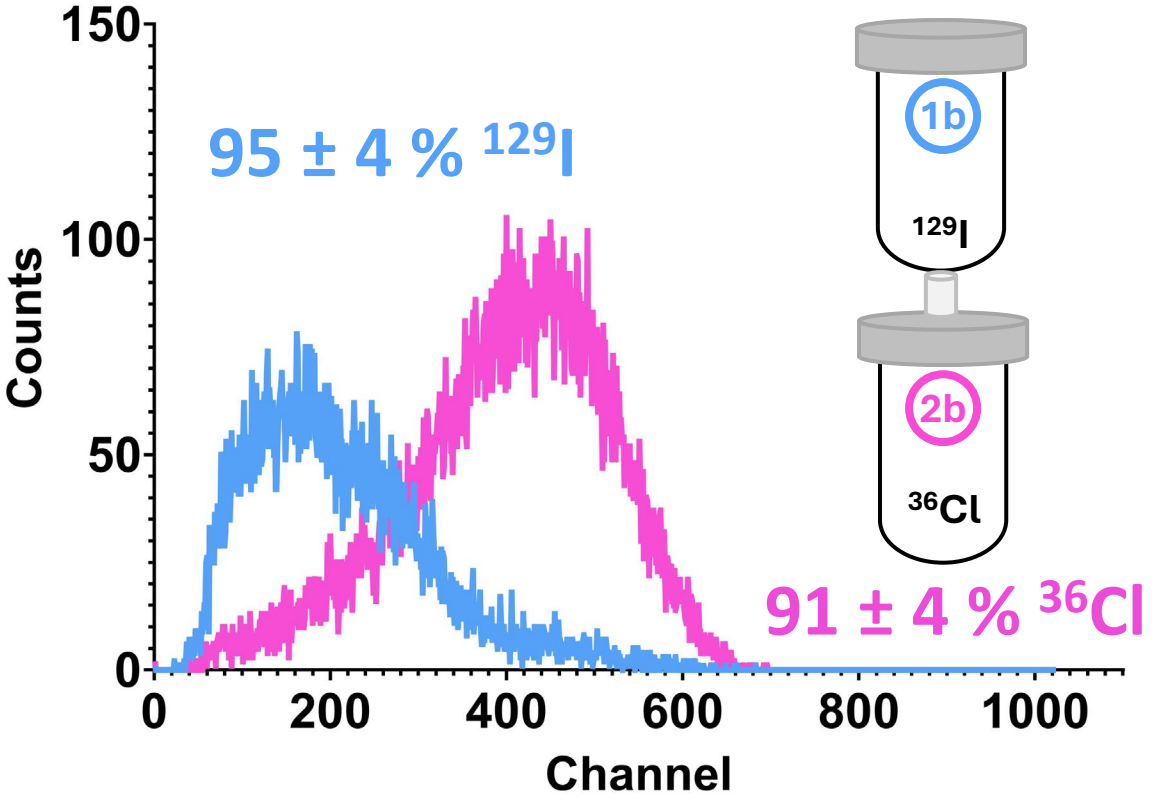
53 **I** 129 Iodine





Sequential separation

Rinse:
49 mL 4 mM $NaHCO_3$

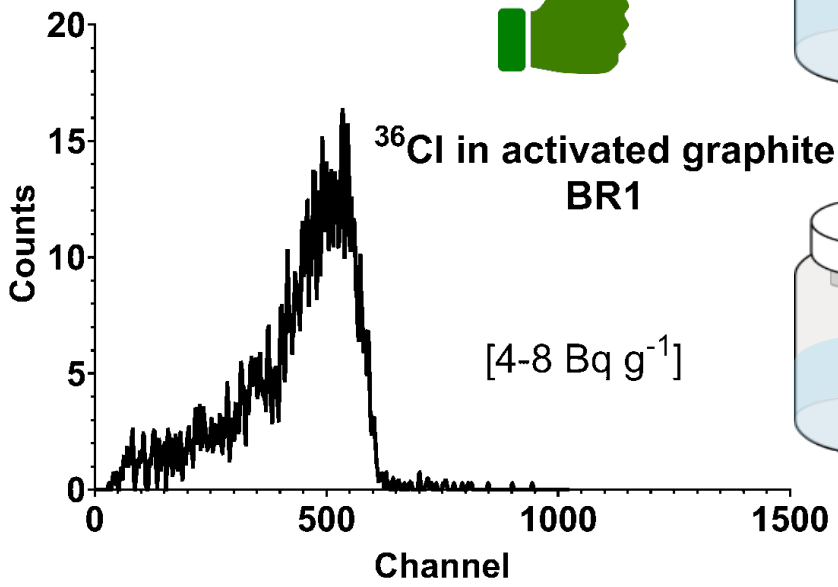


^{36}Cl and ^{129}I determination

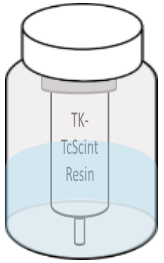
17 **Cl** 36 Chlorine

53 **I** 129 Iodine

Application



CL Resin



TK-Tc Scint Resin

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

Compared with calculated values through activation codes

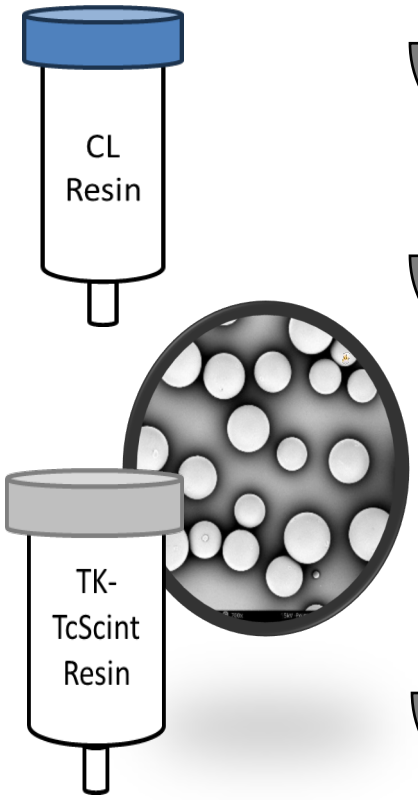
^{36}Cl and ^{129}I determination

17 Cl 36 Chlorine

53 I 129 Iodine

Application

All DL < clearance level



+ LS cocktail

LSC

ICP-MS/MS

NPL National Physical Laboratory

No mixed waste

+ LS cocktail

LSC

No mixed waste
Fewer chemicals used

^{36}Cl and ^{129}I determination

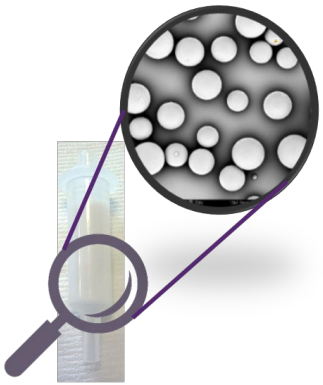
17 **Cl** 36 Chlorine

53 **I** 129 Iodine

Summary

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

Detection limit below clearance level (^{36}Cl)



NEW

New analytical method

Mixed waste

Turnaround time

- **Cleaning** and new glassware materials
- Choice of analytical techniques and resins for ^{36}Cl determination

$T_{1/2}$ = 3,56 ▪ 10^5 year

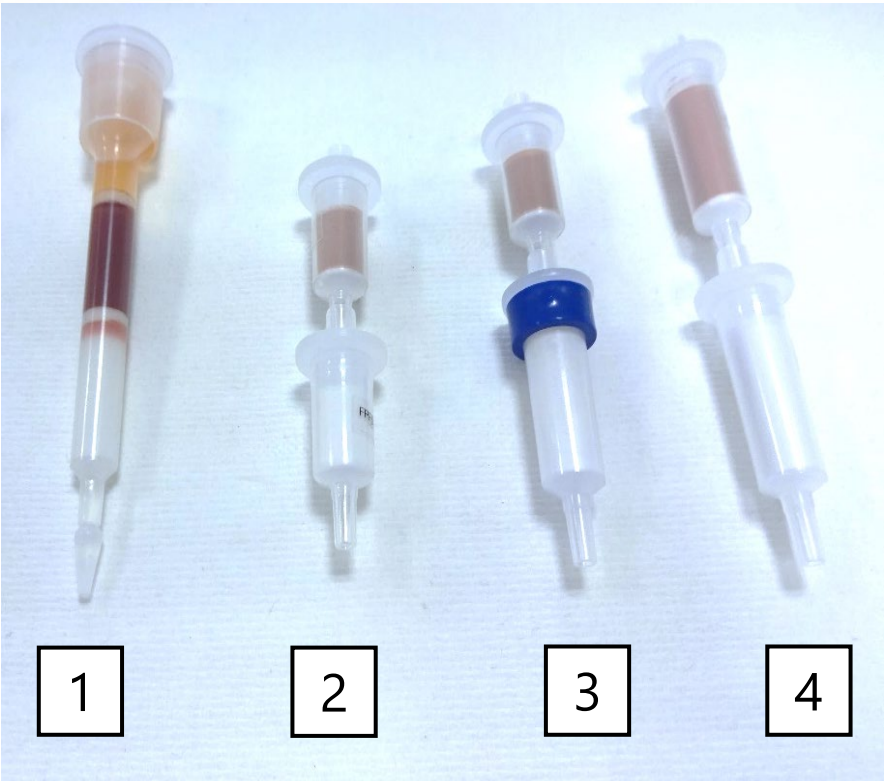
β-emitter E_{max} 151 keV

New approach for Se chemical separation

34 Se 79 Selenium

New SE Resin

TRISKEM



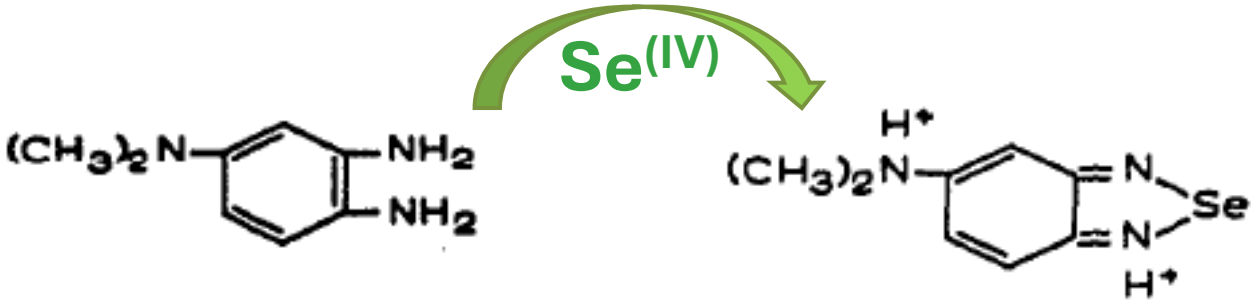
SE Resin

Se retention

Prefilter Resin

↓

extractant bleeding



Acid media (H^+)

Influence Se oxidation state

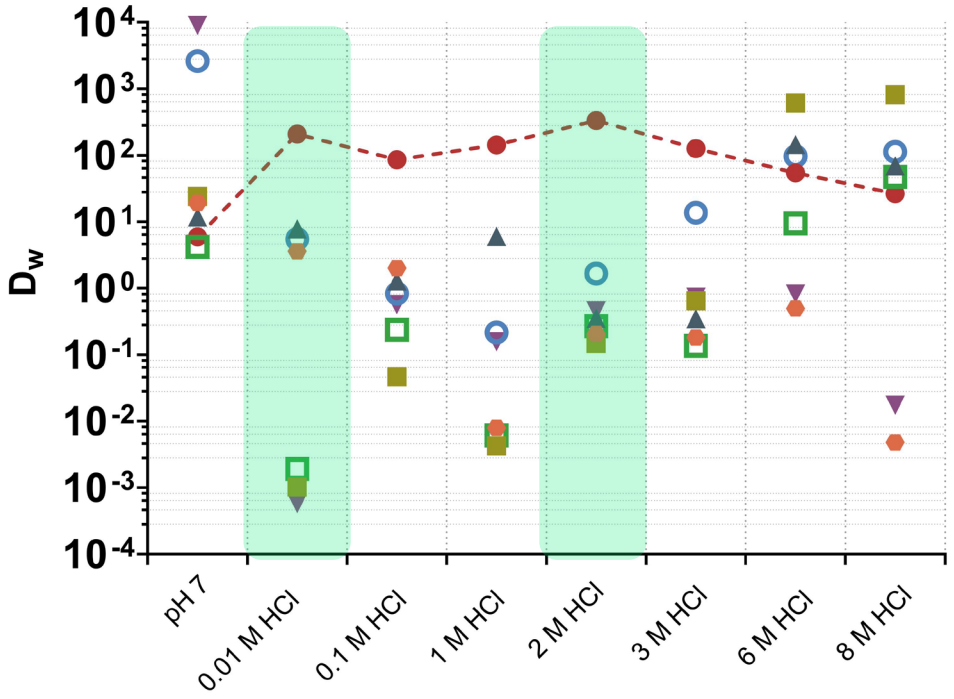
New approach for Se chemical separation

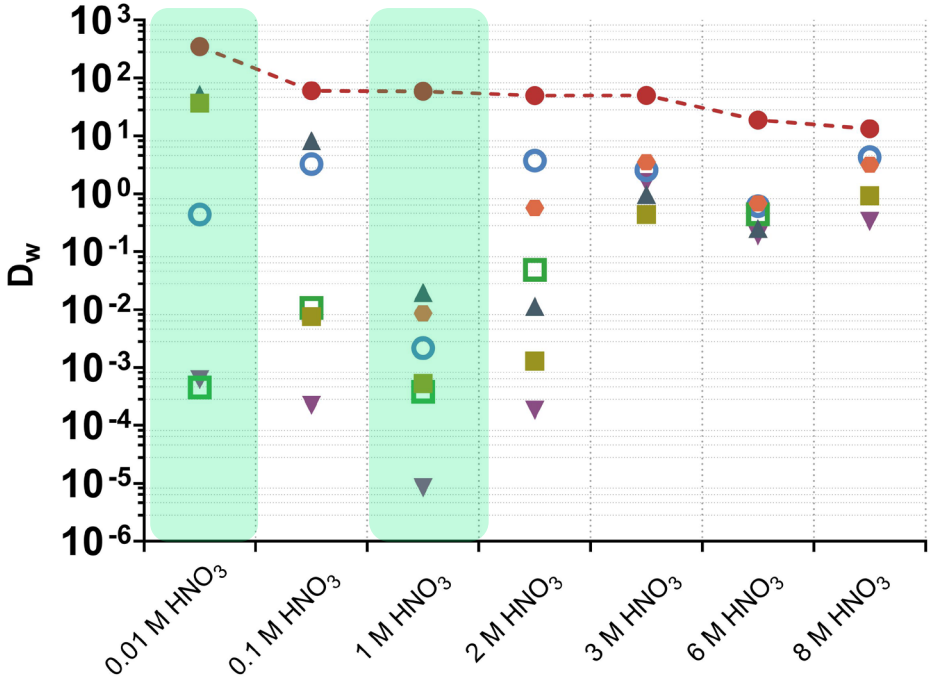
Batch experiments

As Sb Se In
Ga Ge Te

34 Se 79 Selenium

reported by Dirks et al. 2016

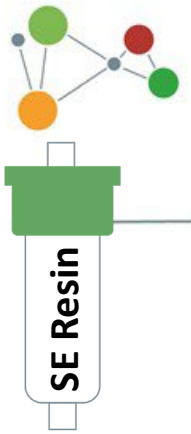


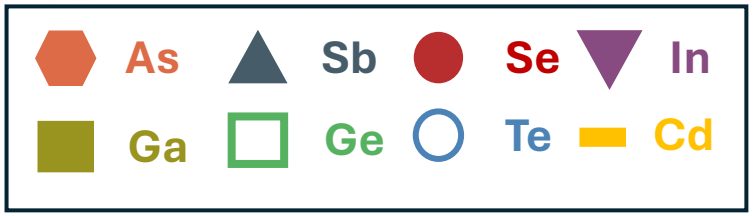


HCl

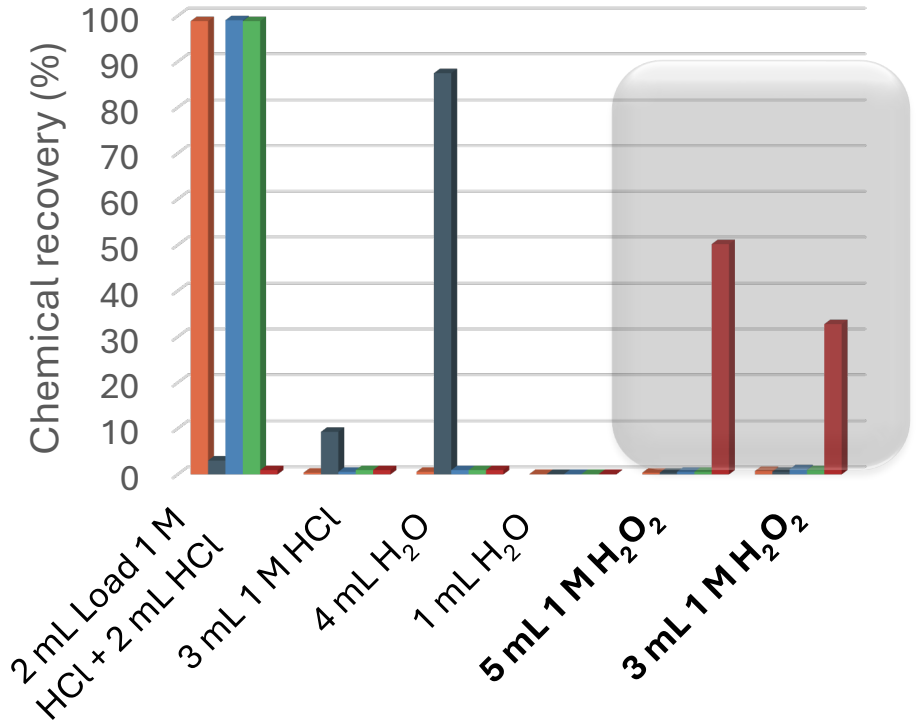
HNO_3

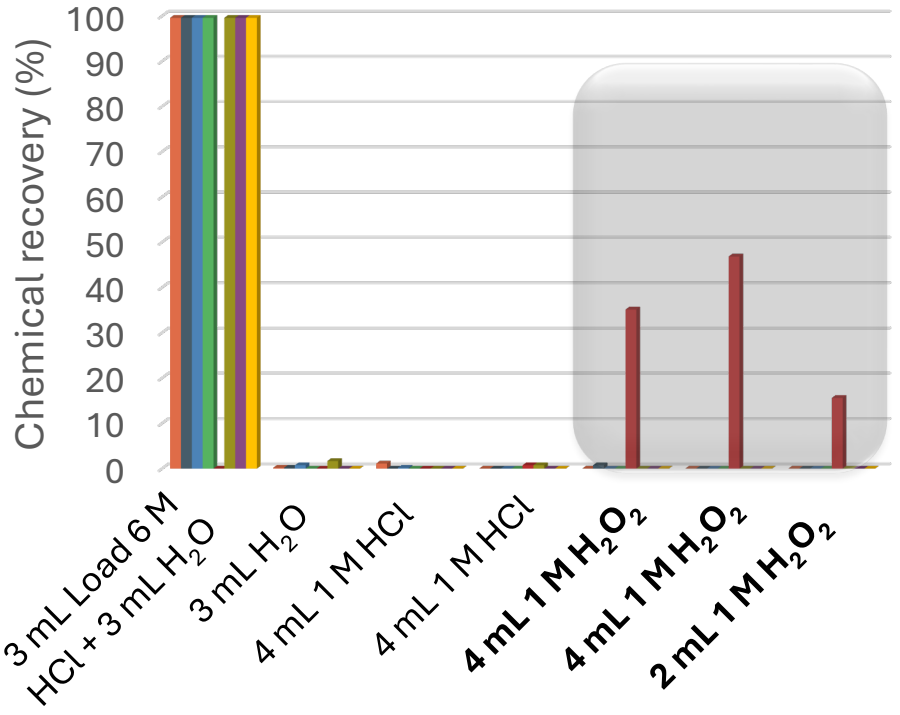
New approach for Se chemical separation





reported by Dirks et al. 2016





350 mg Se selective Resin **Load 1 M HCl**

300 mg Se selective Resin **Load 6 M HCl**

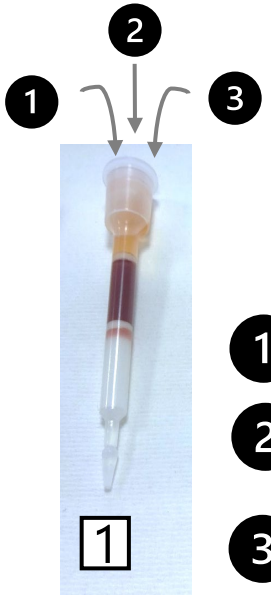
New approach for Se chemical separation

^{34}Se
79
Selenium

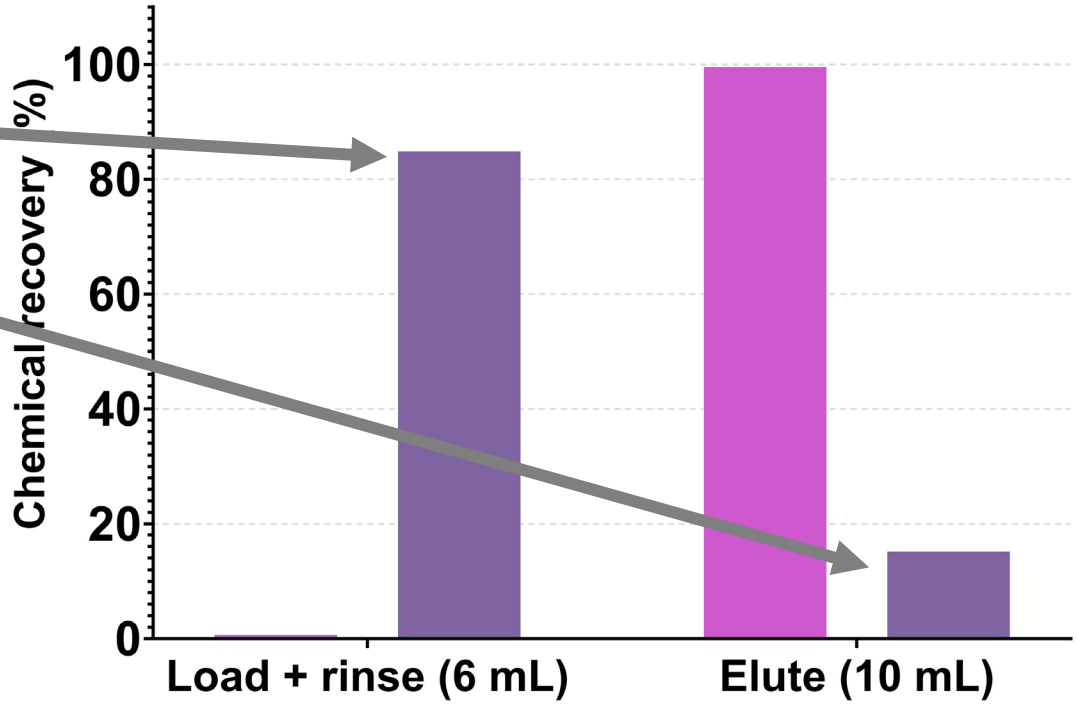
$Se^{(IV)}$ standard (2% HNO_3)

$Se^{(VI)}$ standard (in H_2O)

- 85% $Se^{(VI)}$
- 15% $Se^{(IV)}$



1. 7 mL 2.5 M HCl
2. 10 mL 2.5 M HCl
3. 2x10 mL 1 M NaOH



Different behavior of $Se^{(IV)}$ and $Se^{(VI)}$
❖ $Se^{(IV)}$ fully retained

New approach for Se chemical separation

34 Se 79 Selenium

Influence of pH on Se retention

Bosca & Mot, 2021 ➔ relevance of pH on p*iazselenol* formation (**pH~1.3**)

1. 1 mL 2.5 M HCl
2. 5 mL 2.5 M HCl
3. 2x10 mL 1 M NaOH

$Se^{(IV)}$ **standard**

$Se^{(VI)}$ **standard**

Clear **differences** between Se^{+4} and Se^{+6} retention

Se **reduction cycle** still needed

New approach for Se chemical separation

^{34}Se
79
Selenium

Se reduction using HCl

Ragnar Bye and Waiter Lund, 1988 ➔ relevance of HCl concentration, temperature and time on Se reduction

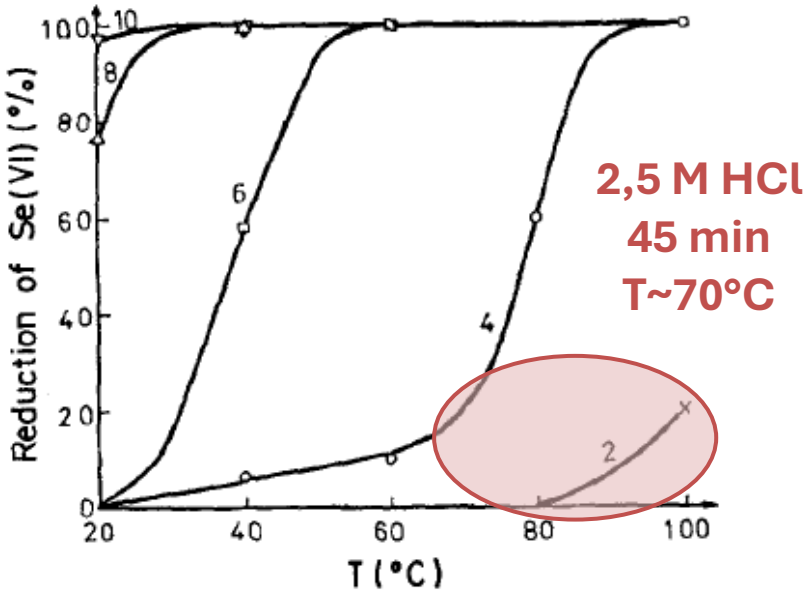


Fig. 2. Reduction of 1.6 µg Se(VI) with 10 ml HCl of various concentrations (mol/l) after 30 min in dependence on temperature

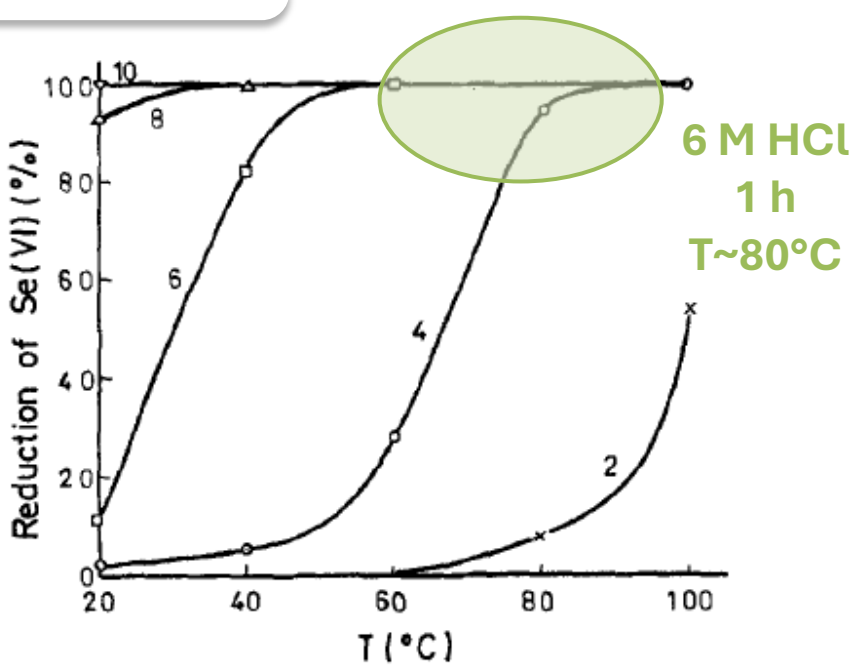
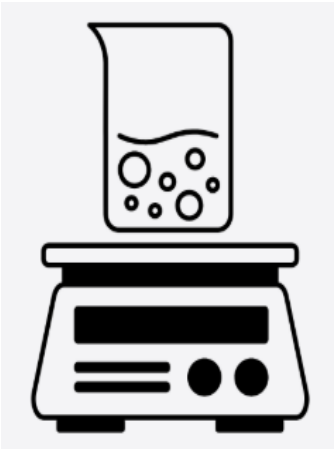


Fig. 4. Reduction of 1.6 µg Se(VI) with 10 ml HCl of various concentrations (mol/l) after 2 h in dependence on temperature

New approach for Se chemical separation

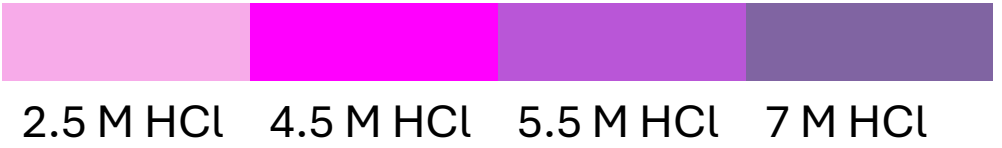
34 Se 79 Selenium

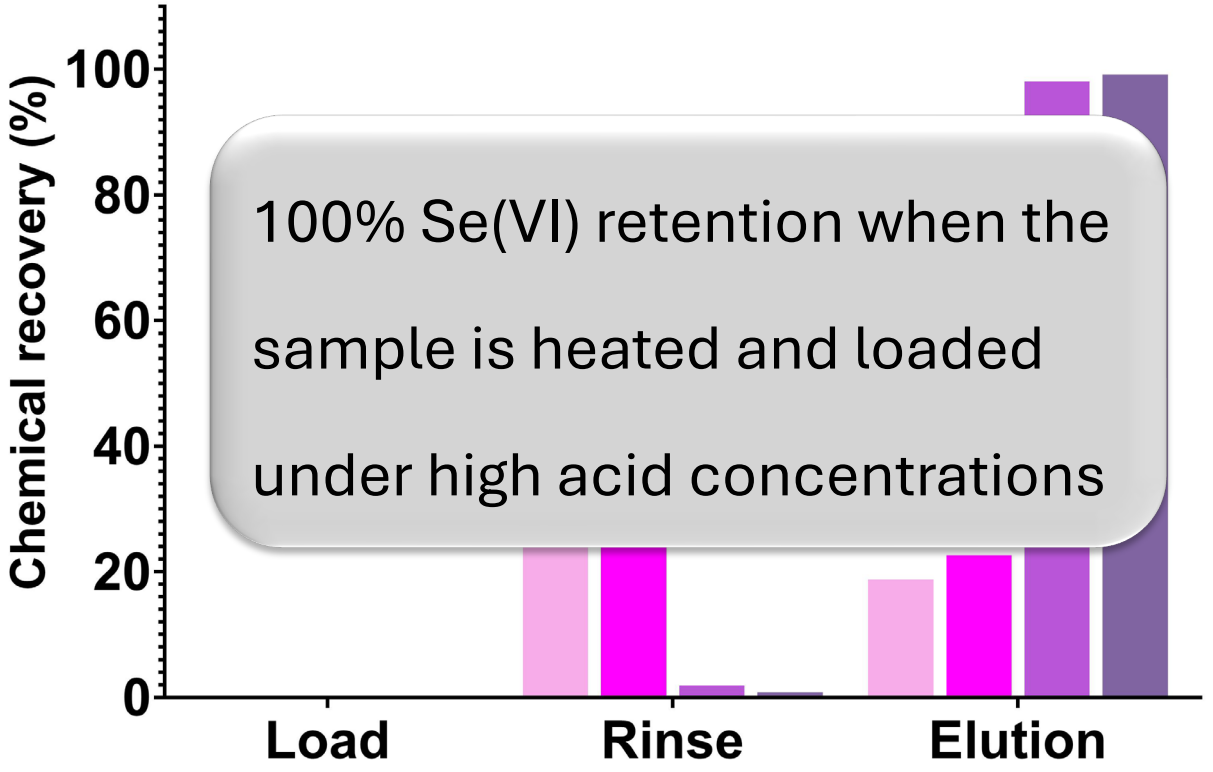
Se reduction using HCl



T=80°C
60 min

1. Load
2. 5 mL 2.5 M HCl
3. 2x10 mL 1 M NaOH





100% Se(VI) retention when the sample is heated and loaded under high acid concentrations

New approach for Se chemical separation

34 Se 79 Selenium

Interference removal

T=80°C
60 min

$Se^{(VI)}$
Fe
Ni
Co

Step	Fraction
Load	1 mL
Rinse	5 mL 2,5 M HCl
Elution	5 mL 1 M NaOH
Elution	5 mL 1 M NaOH

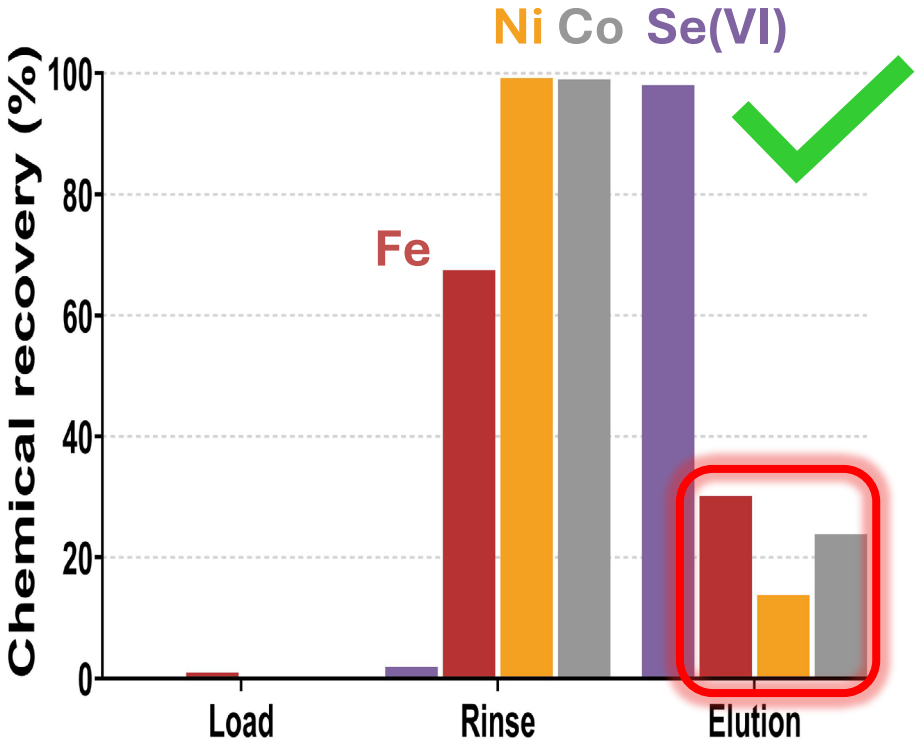
→ 5.5 M HCl
7 M HCl

New approach for Se chemical separation

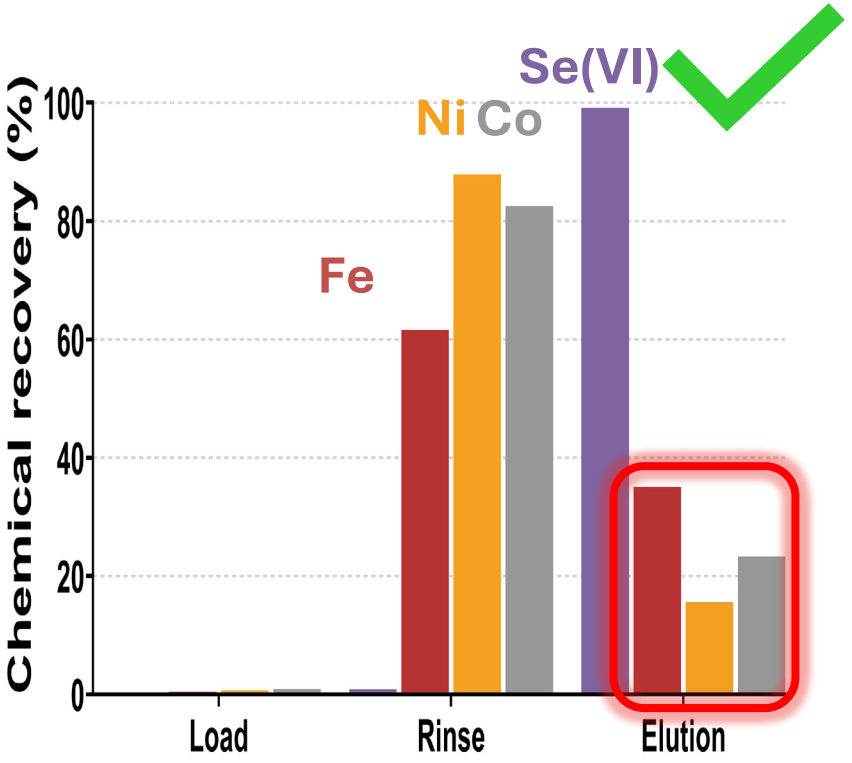
34 Se 79 Selenium

Interference removal

Load : 5.5 M HCl



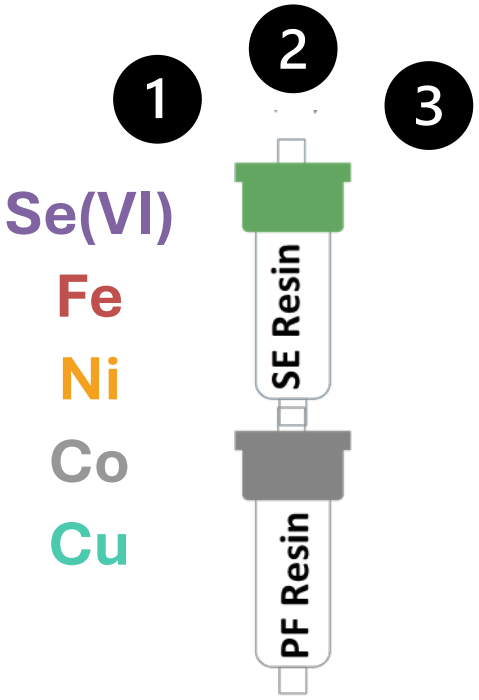
Load : 7 M HCl

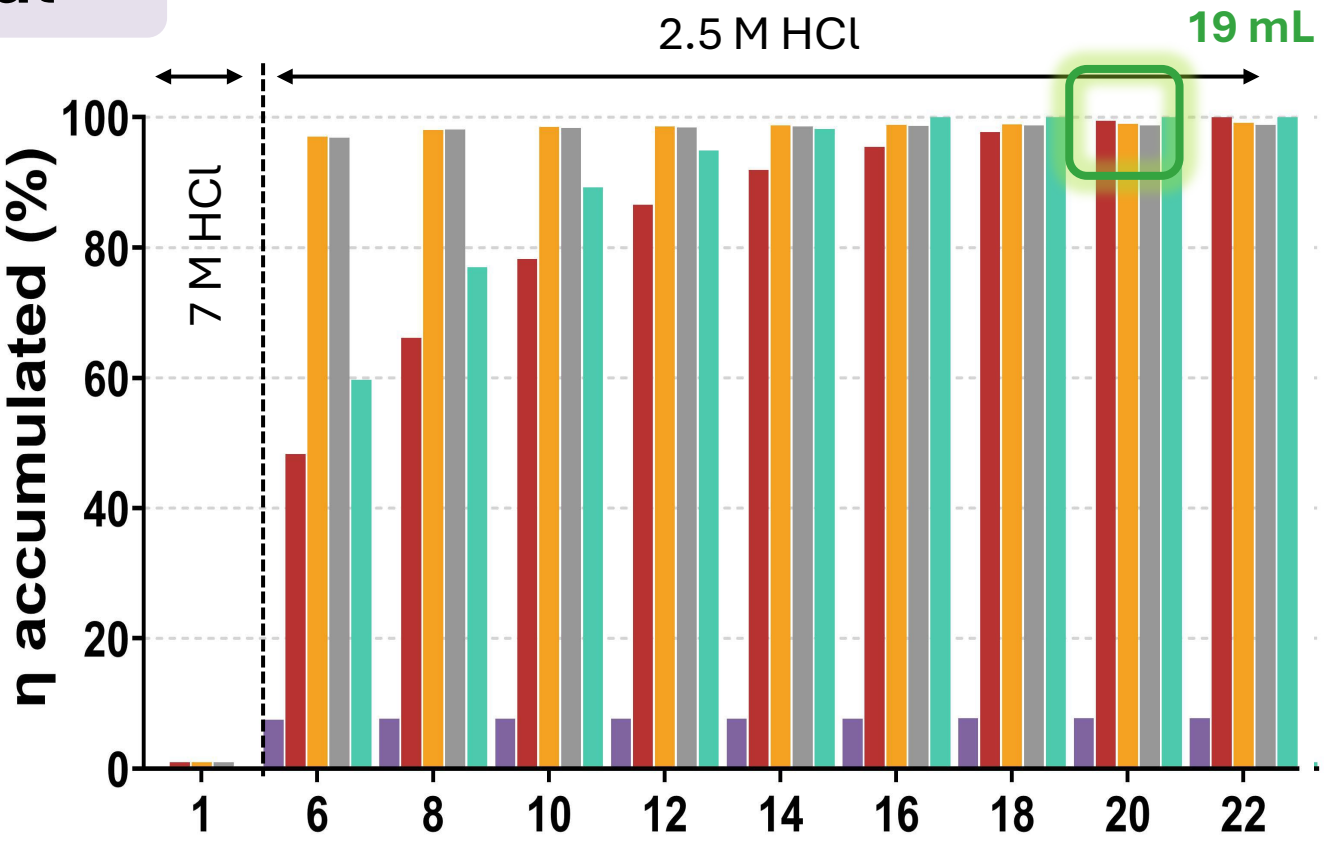


Se(VI) fully reduced when using ↑ [HCl] ➔ Full Se retention

New approach for Se chemical separation

Interference removal





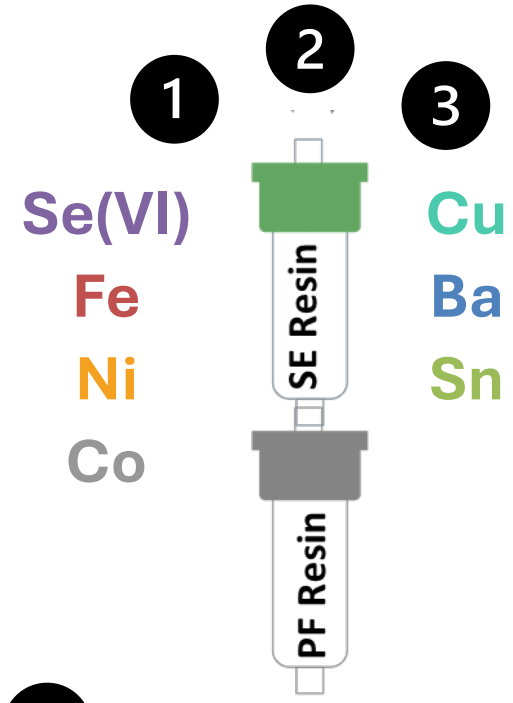
1. Condition: 2.5 M HCl
2. Load: 7 M HCl
3. Rinse: 2.5 M HCl

<10 % Se lost and interferences removed

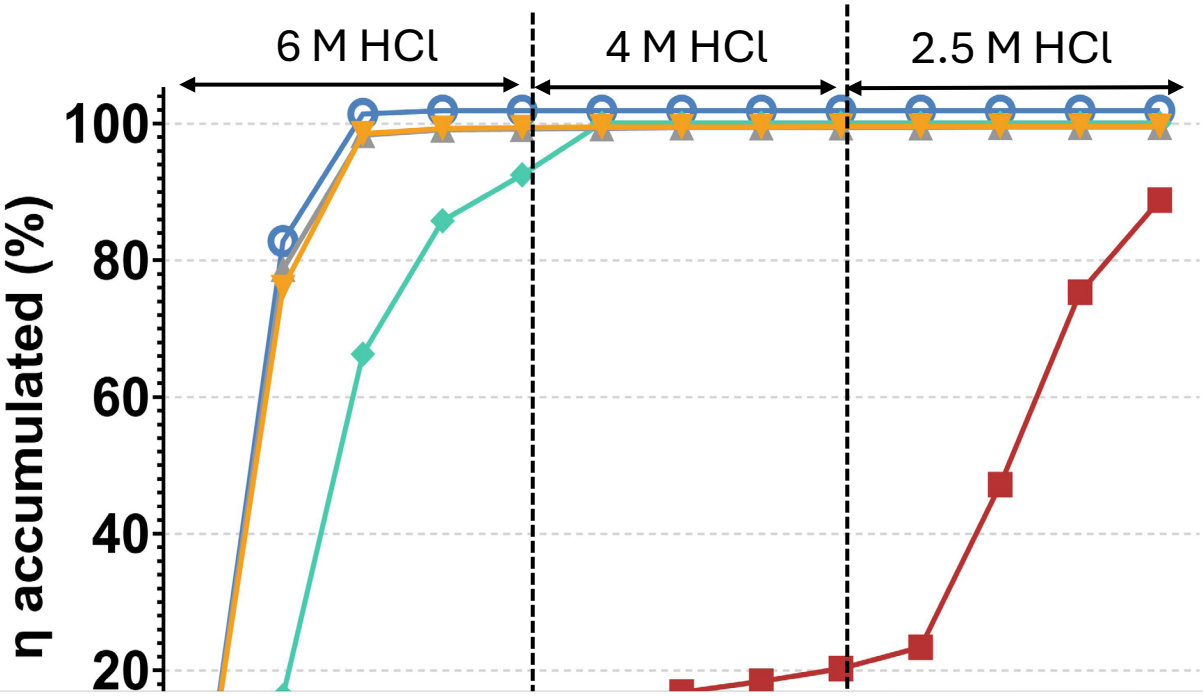
New approach for Se chemical separation

34 Se 79 Selenium

Interference removal



1. Condition: 6 M HCl
2. Load: 6 M HCl
3. Rinse: 2.5 M HCl



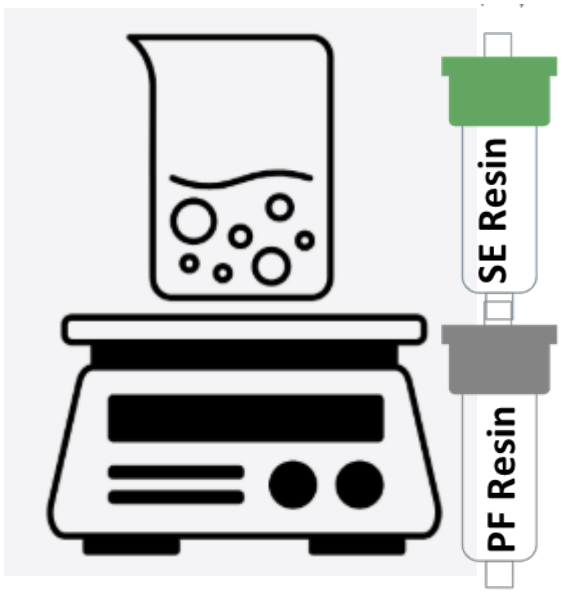
No Se lost and almost all interferences removed (Fe still present)

New approach for Se chemical separation

34 Se 79 Selenium

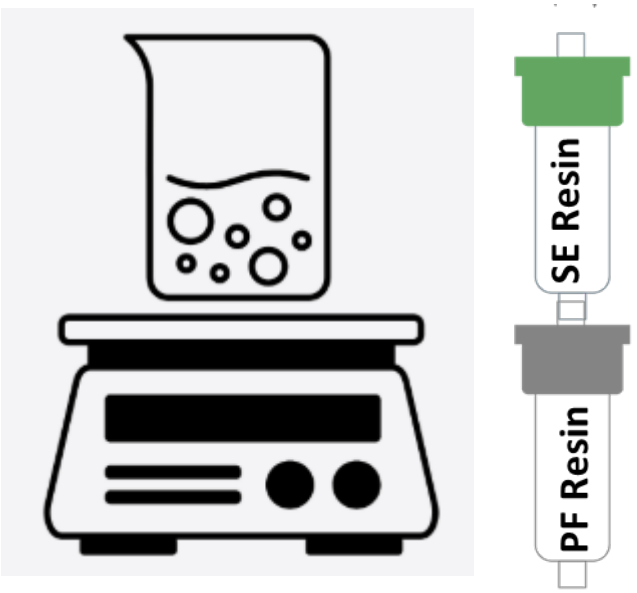
Final chemical separation procedure

Se(IV) Fe Ni
Co Sn



T=80°C
60 min

Se(VI) Fe Ni
Co Sn



T=80°C
60 min

1 Load

6 M HCl

2 Rinse

8 mL 6 M HCl

8 mL 2.5 M HCl

3 Elution

2 * 5 mL 1 M NaOH

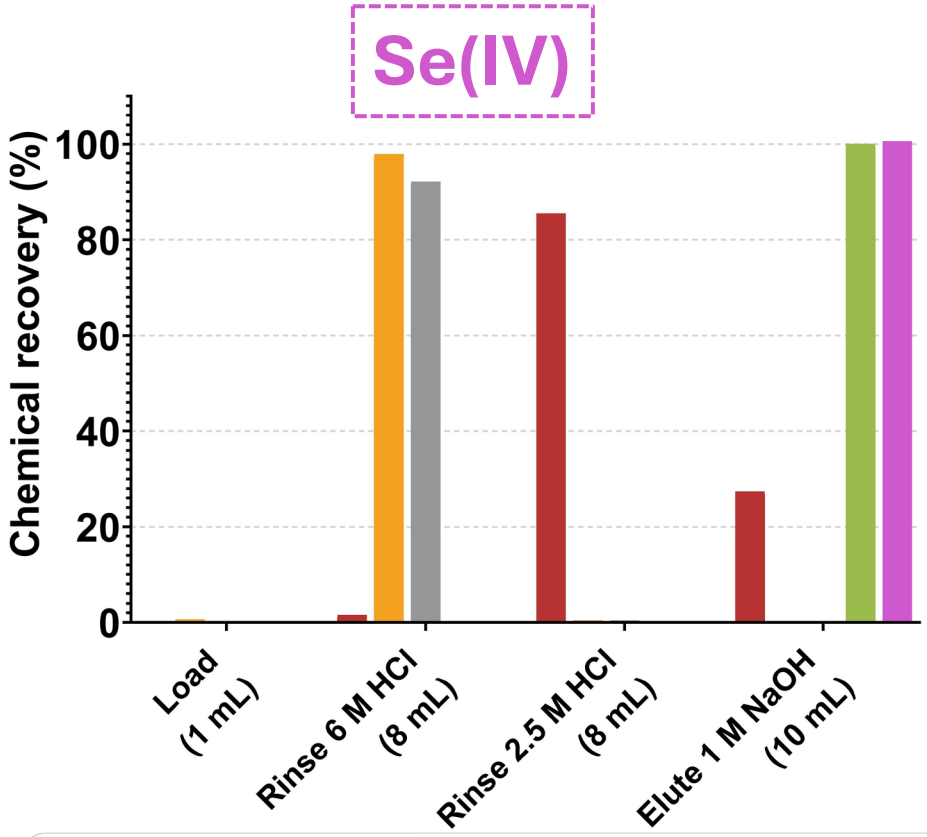
New approach for Se chemical separation

34 Se 79 Selenium

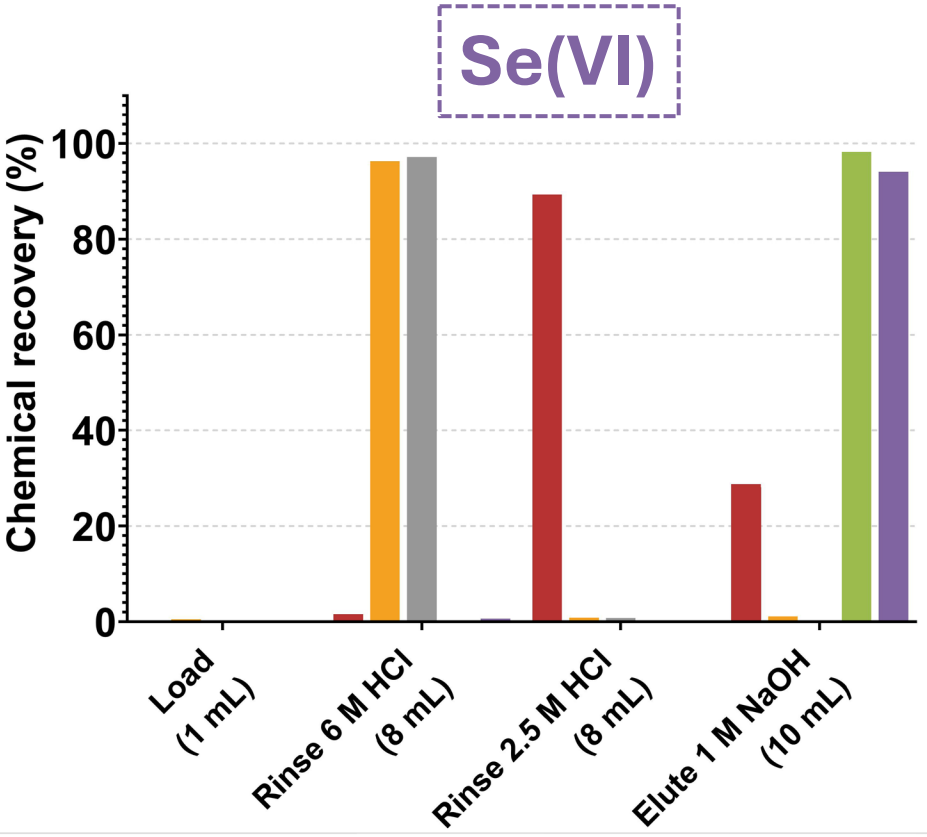
Final chemical separation procedure

Fe Ni Co Sn

Se(IV)



Se(VI)



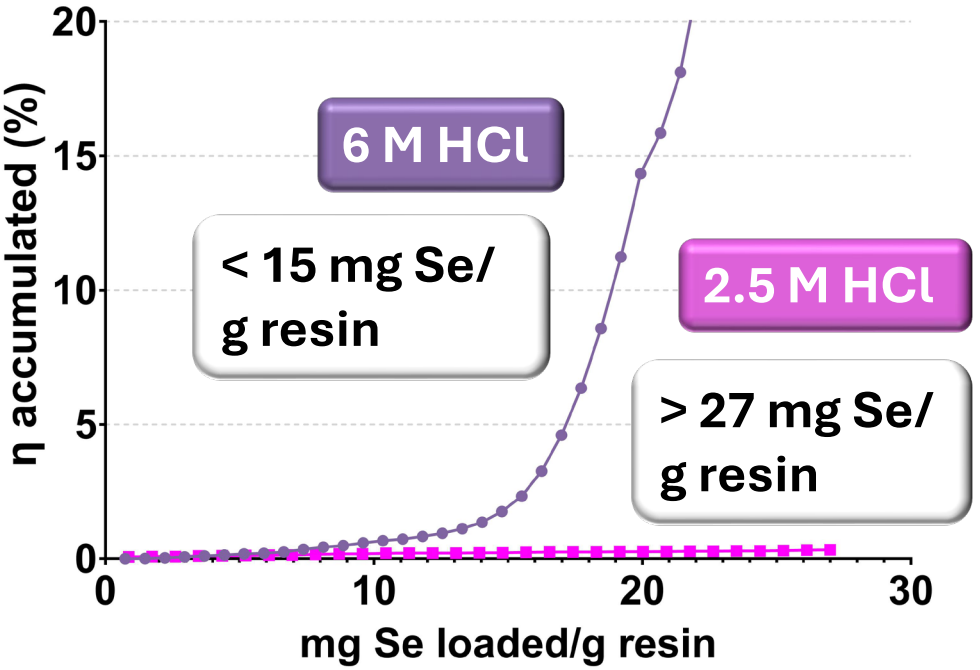
Complete Se retention (presence of Sn and few Fe)

New approach for Se chemical separation

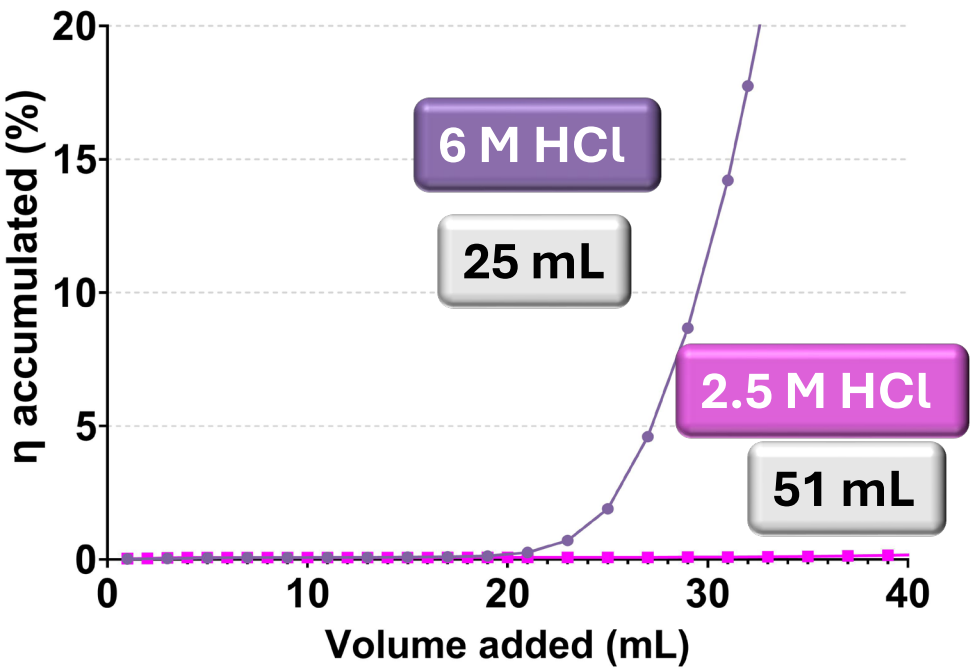
34 Se 79 Selenium

Resin capacity and breakthrough volume

Resin capacity



Breakthrough volume



New approach for Se chemical separation

^{34}Se
79
Selenium

Summary

Fixation of Se oxidation state — Redox conditions

Interference removal studies — ^{99}Tc, ^{147}Pm, ^{93}Zr, ^{63}Ni, ^{55}Fe

Application of the procedure

↑ Chemical recovery

↓ LOD

Se-75 diagnostic

NUCLEAR MEDICINE

^{40}**Ca**

41

Calcium

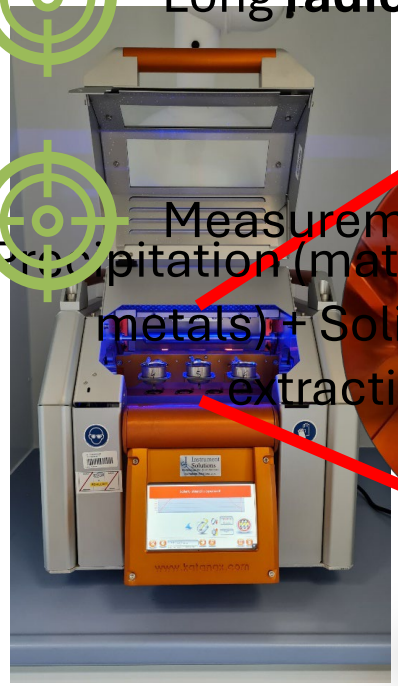
$T_{1/2} = 1 \blacksquare 10^5$ year

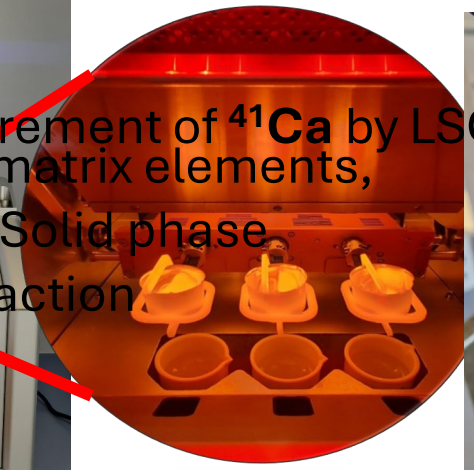
EC 421,6 keV

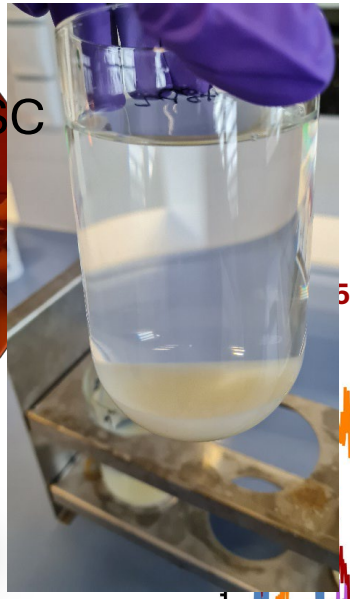
^{41}Ca determination in concrete

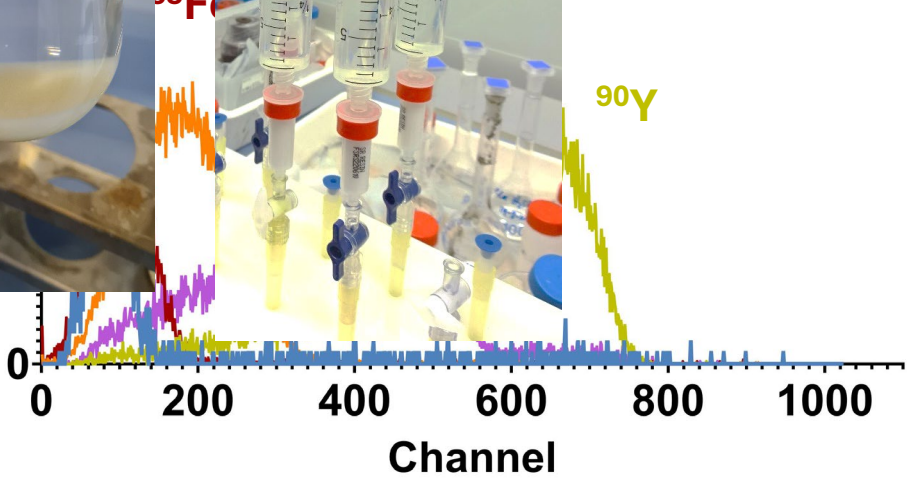
^{40}Ca
41
Calcium

- Complex procedures for **matrix dissolution**
- **Lithium borate fusion**
- Long **radiochemical separation** procedures
- Measurement of **^{41}Ca** by LSC
- Precipitation (matrix elements, metals) + Solid phase extraction





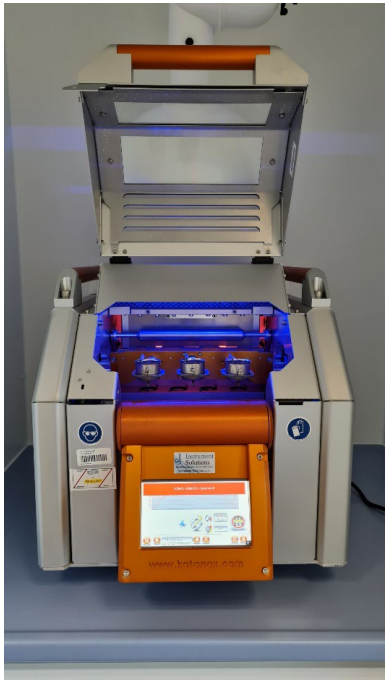




^{41}Ca determination in concrete

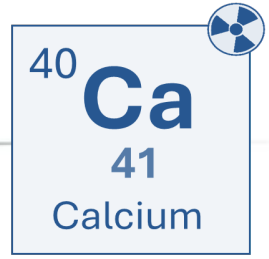
^{40}Ca
41
Calcium

Fusion



Unsieved concrete	Sieved concrete
✓ 0,1 g	✓ 0,5 g
✓ 0,2 g	
✓ 0,3 g	✓ 0,7 g
✗ 0,4 g	
✗ 0,5 g	✓ 0,9 g
	✗ 1 g

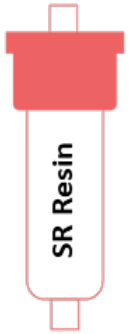
^{41}Ca determination in concrete



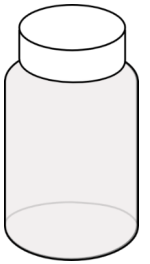
Chemical separation

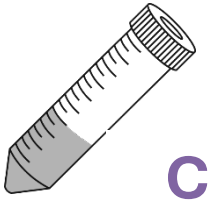
- polyethylene glycol (PEG) — ↑ pH 8 (NH_4OH) **$Fe(OH)_3$ PRECIPITATION** — Oxalic acid ↑ pH 5 (NH_4OH) **PRECIPITATION**

1 M HNO_3



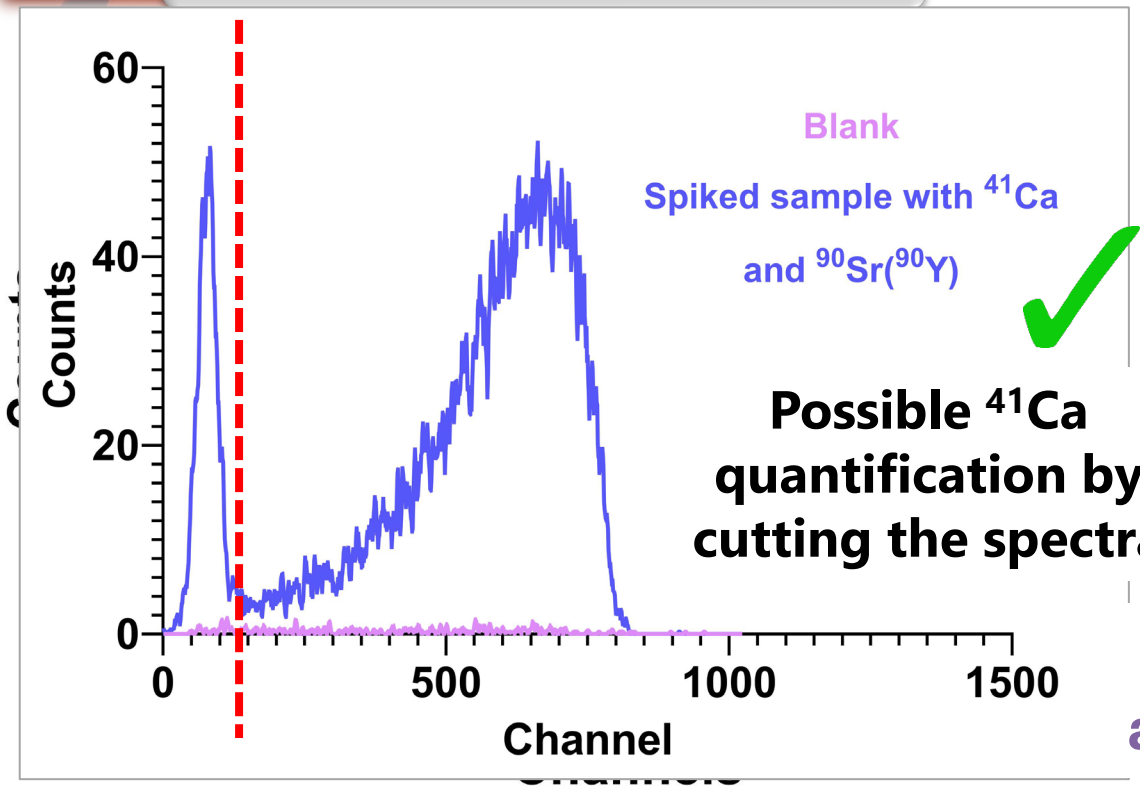
Evaporate to ½ volume





Ca η

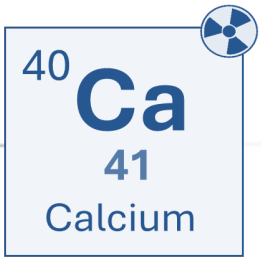
Single LSC spectra



Possible ^{41}Ca quantification by cutting the spectra

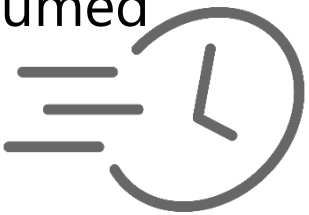
^{41}Ca activity

^{41}Ca determination in concrete

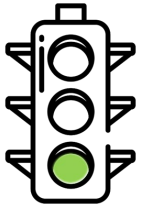


Summary

Shorter procedure (~2 working days) and fewer chemicals consumed

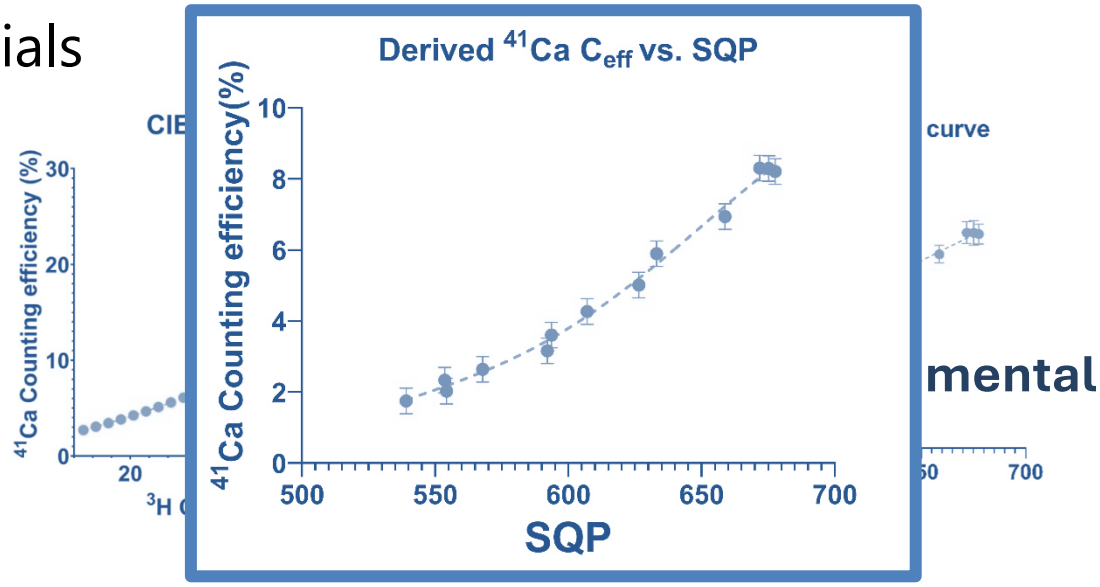


Detection limit below clearance level (^{41}Ca)

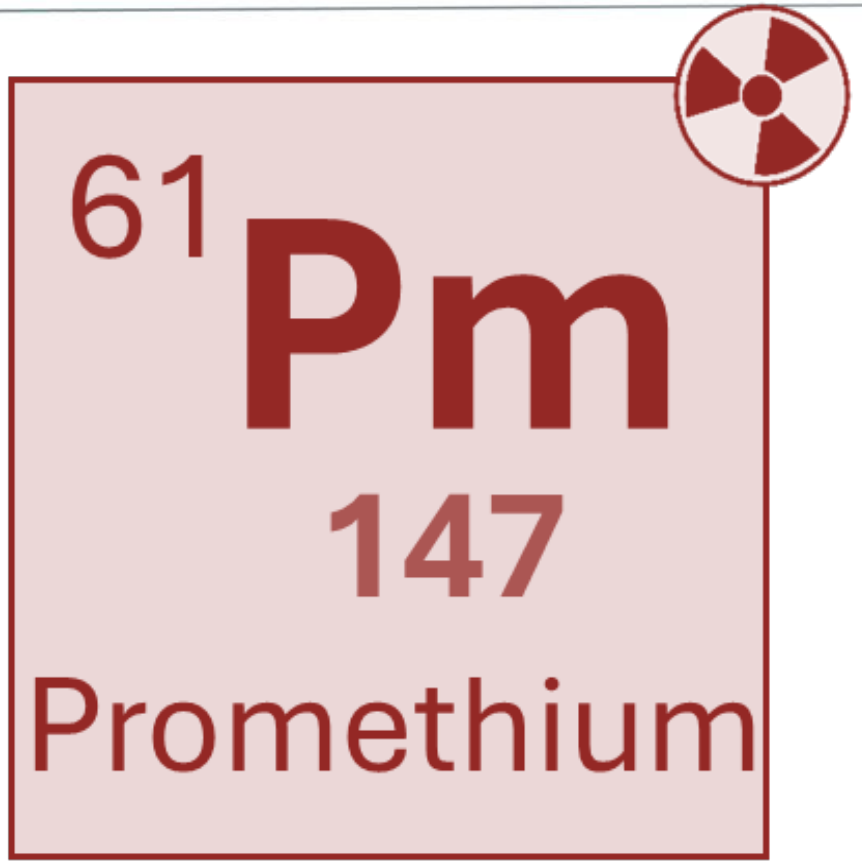


Limited reference solutions/materials

CIEMAT/NIST



^{41}Ca C_{eff}=8,2±0,4%



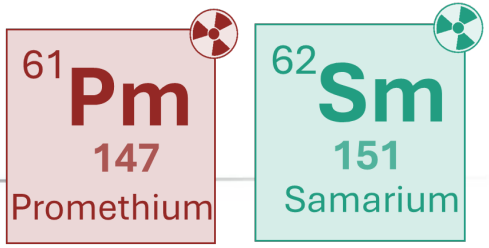
$T_{1/2}$ = 2.6 year

β-emitter E_{max} 224.1 keV

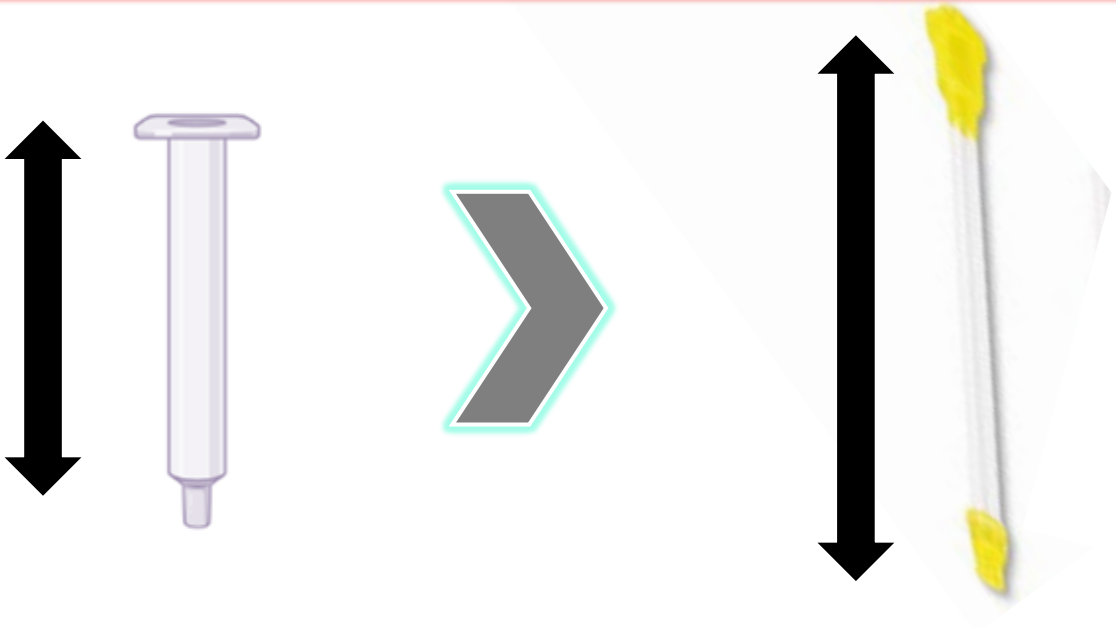
$T_{1/2}$ = 94,7 year

β-emitter E_{max} 76.4 keV

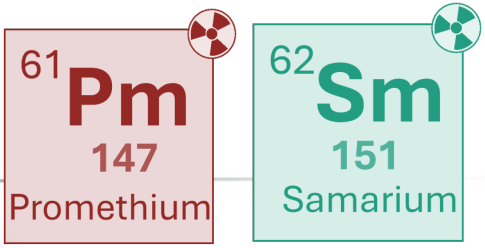
^{147}Pm and ^{151}Sm chemical separation



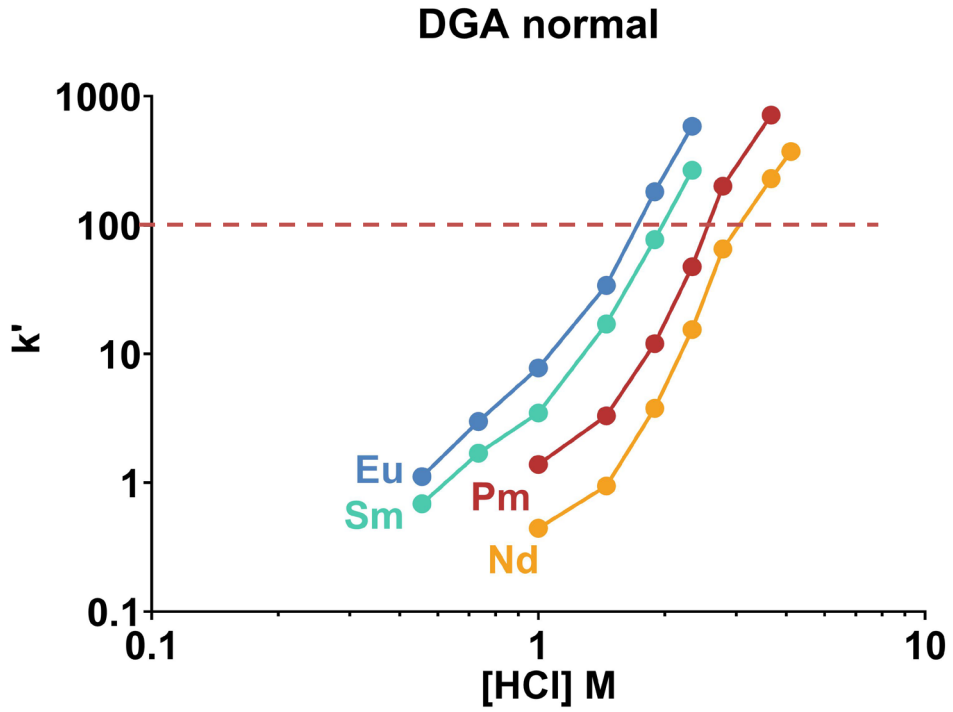
- **Complete radiochemical separation ^{147}Pm/^{151}Sm**
  - **Nd as ^{147}Pm carrier**
  - **Eu as interference**

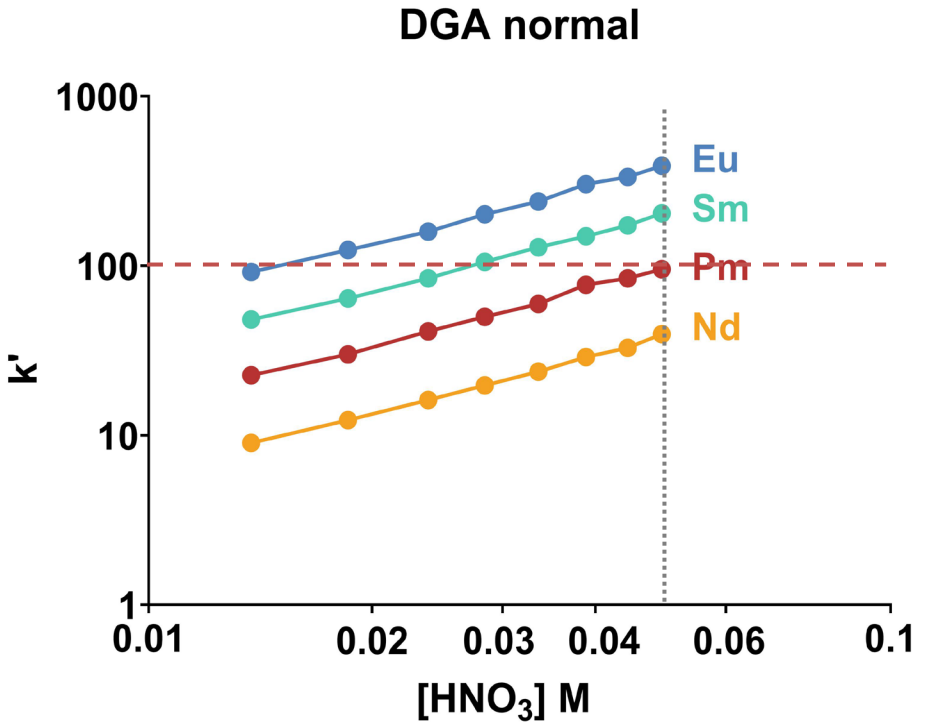


^{147}Pm and ^{151}Sm chemical separation

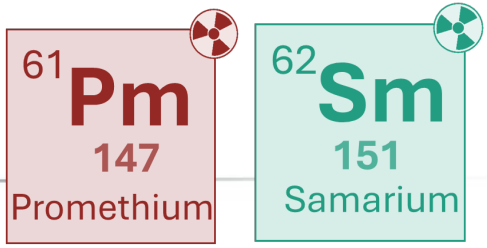


- High [acid] better Sm/Pm retention
- Low [acid] no retention

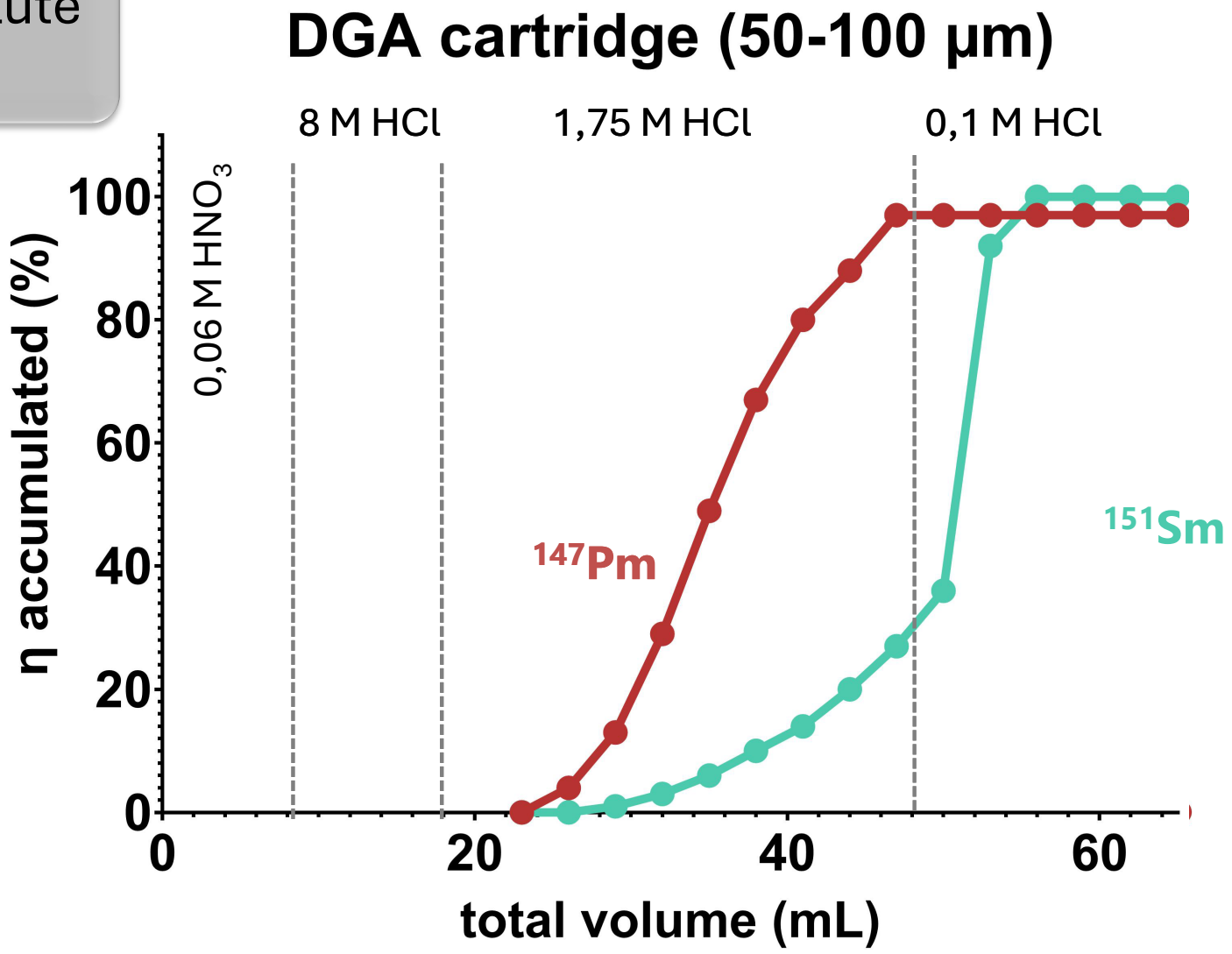




^{147}Pm and ^{151}Sm chemical separation



27% Sm co-elute with Pm

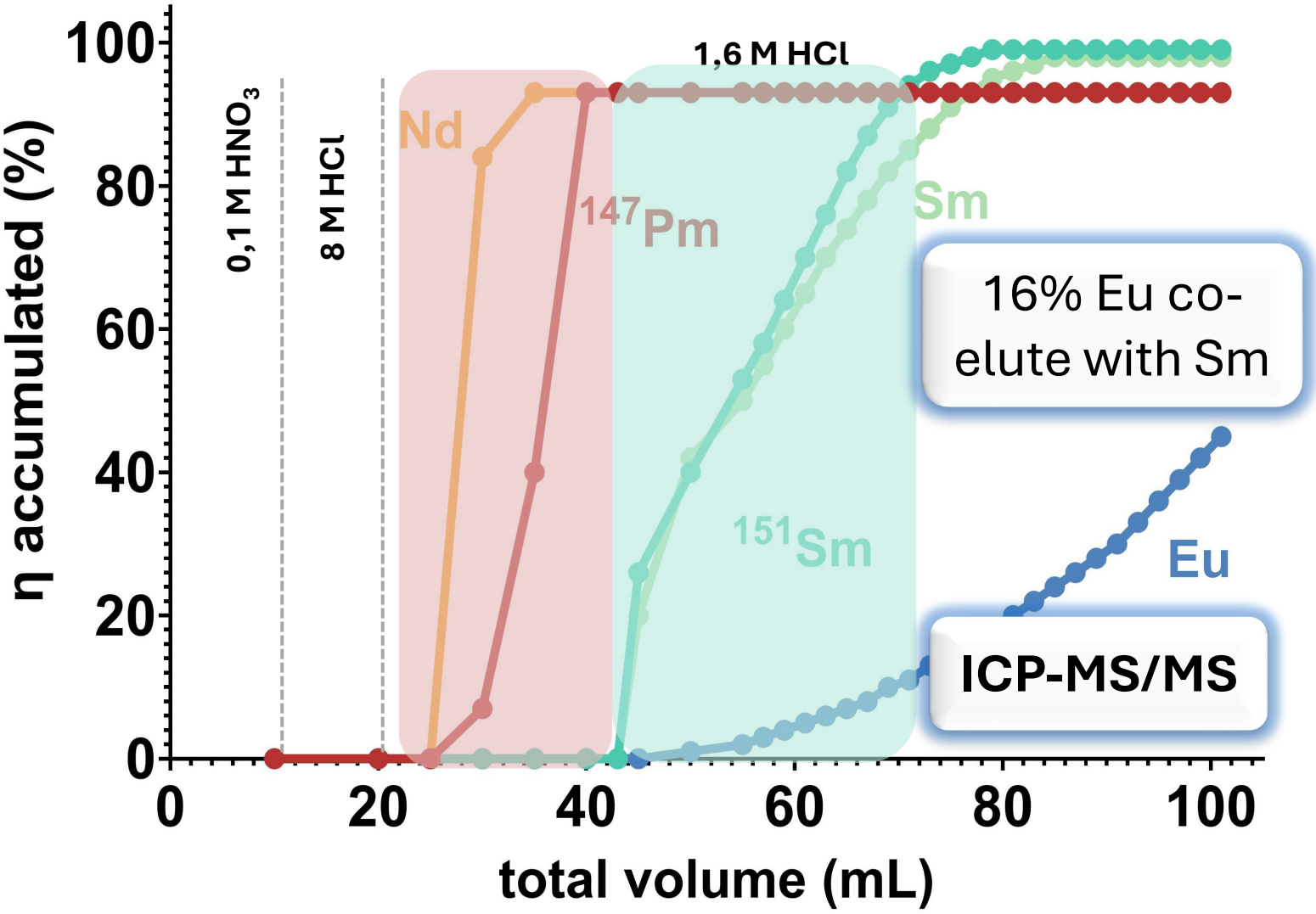


^{147}Pm and ^{151}Sm chemical separation

^{61}Pm 147 Promethium

^{62}Sm 151 Samarium

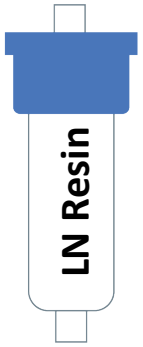
Larger column (higher resolution)

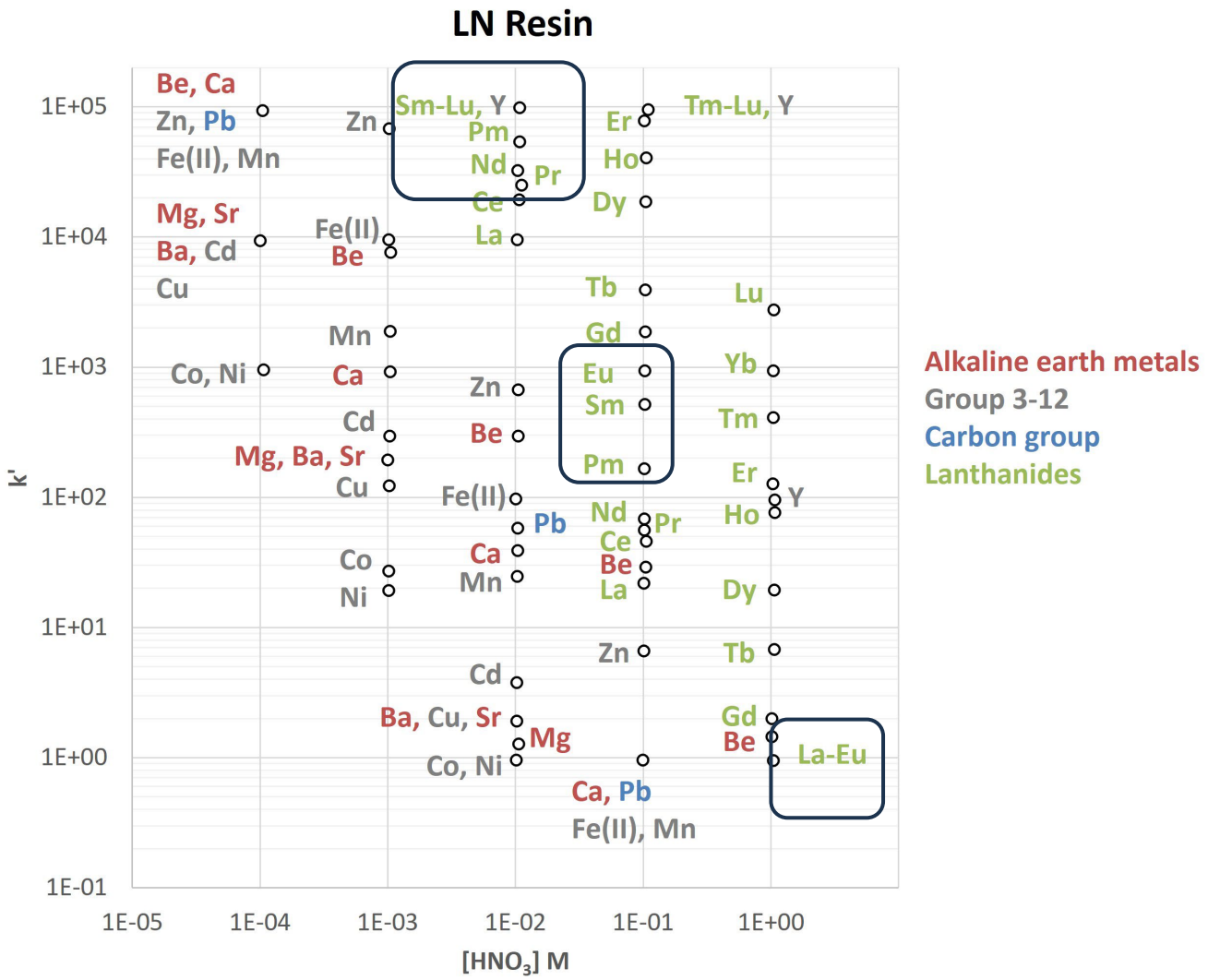


^{147}Pm and ^{151}Sm chemical separation

61 Pm 147 Promethium

62 Sm 151 Samarium



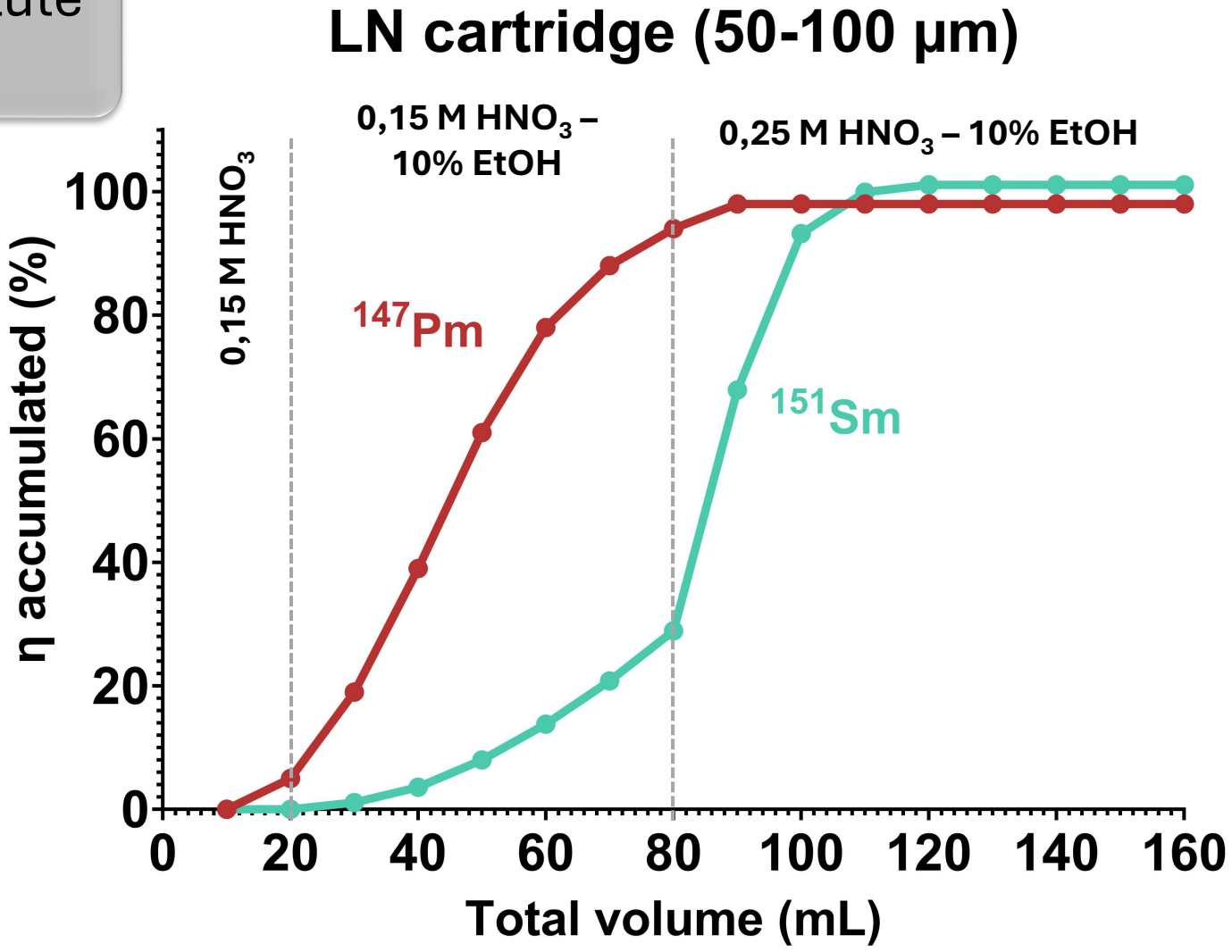


^{147}Pm and ^{151}Sm chemical separation

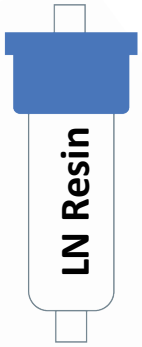
61 Pm 147 Promethium

62 Sm 151 Samarium

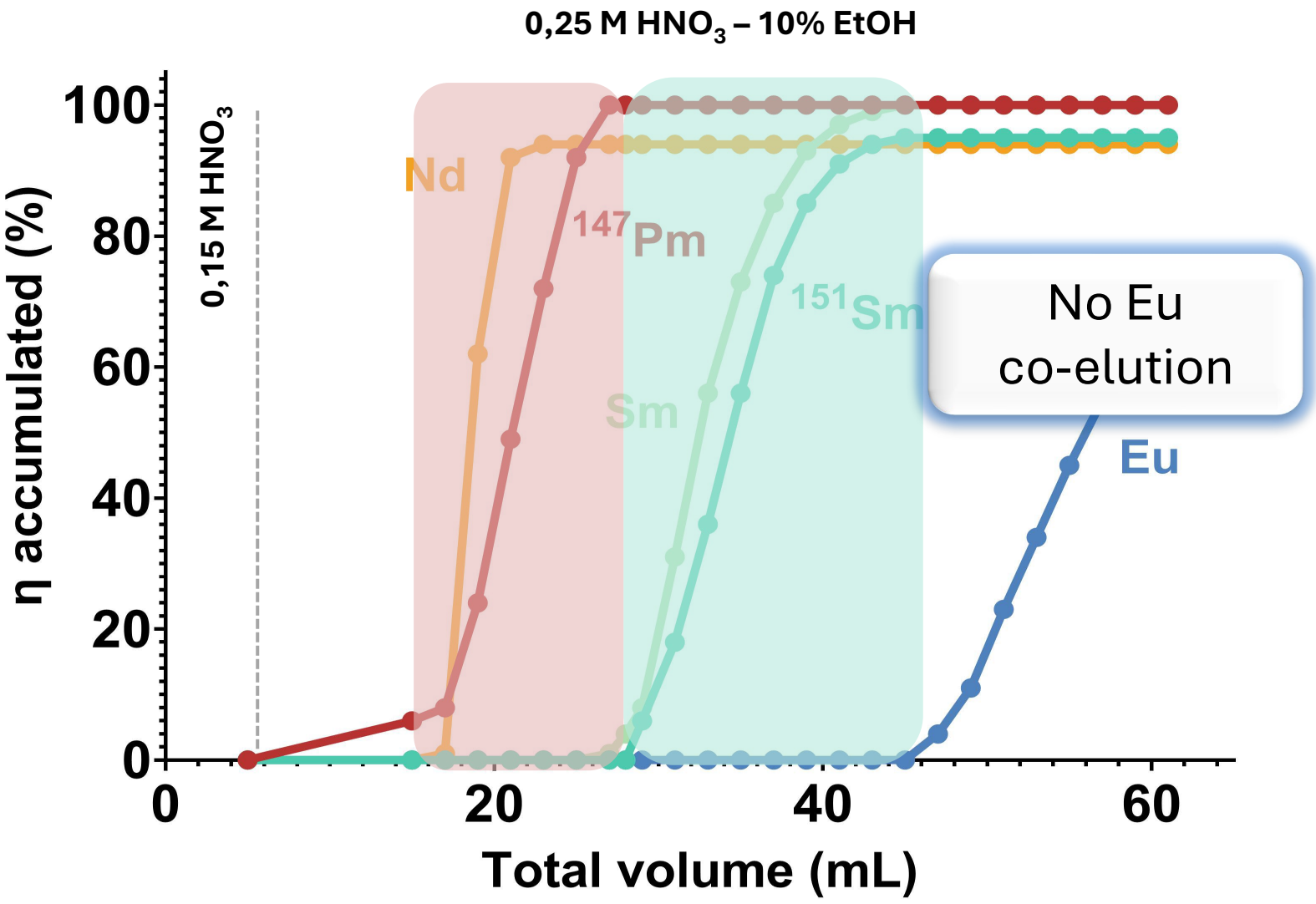
30% Sm co-elute with Pm



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



Larger column (higher resolution)



61 Pm 147 Promethium

62 Sm 151 Samarium

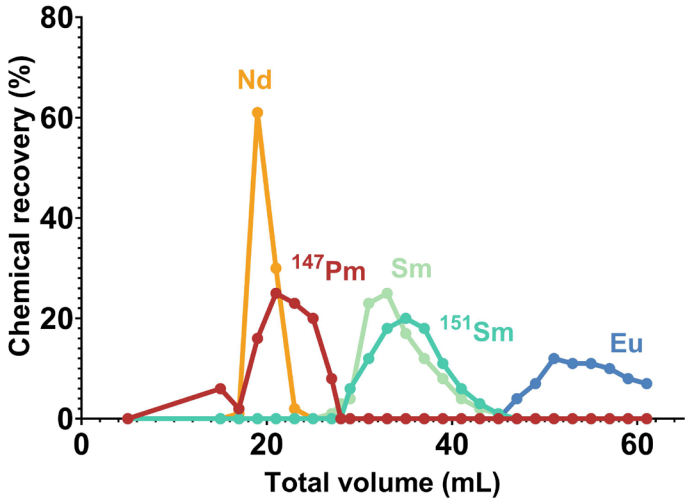
^{147}Pm and ^{151}Sm chemical separation

61 Pm 147 Promethium

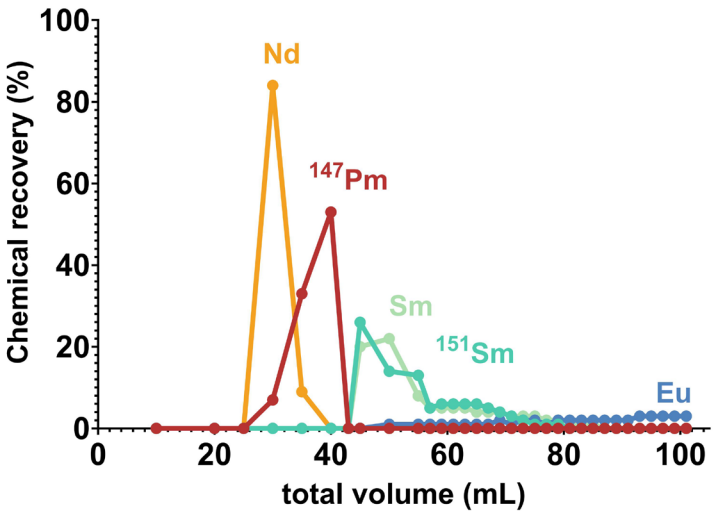
62 Sm 151 Samarium

Summary

LN Resin



DGA Resin



No Eu co-elution

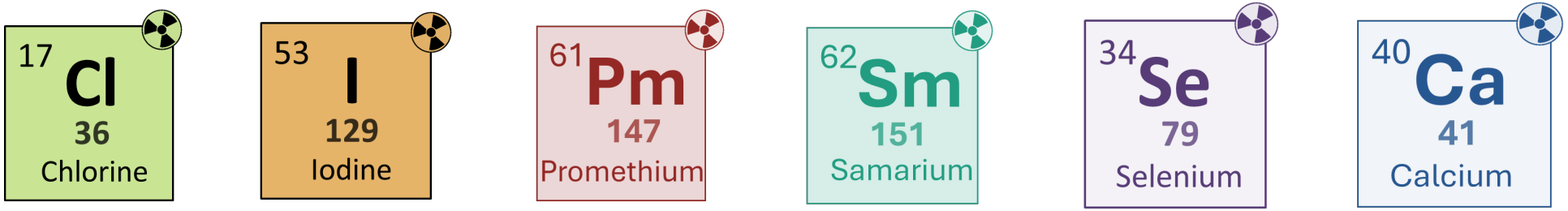
NEW

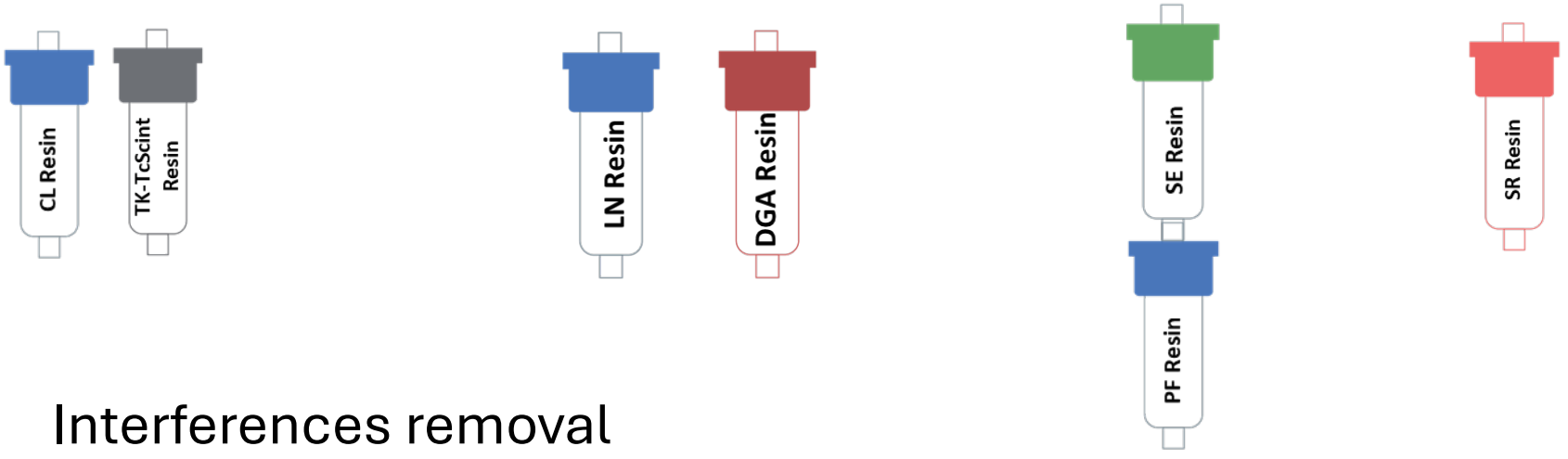
New approach

No need to use alcohol

Fewer solution volume for elution

Take home message





- Interferences removal
- Elution medium for further measurement
- Method application

Thank you for your attention!
Questions?

TRISKEM
Expertise in Separation Chemistry