RadWorkshop 2024
9-13th September

SCK CEN

VUB VRIJE UNIVERSITEIT BRUSSEL

DTU

PhD project funded by:

ENGIE

Novel assays for '**difficult-to-measure**' radionuclides in materials produced during nuclear **decommissioning** activities

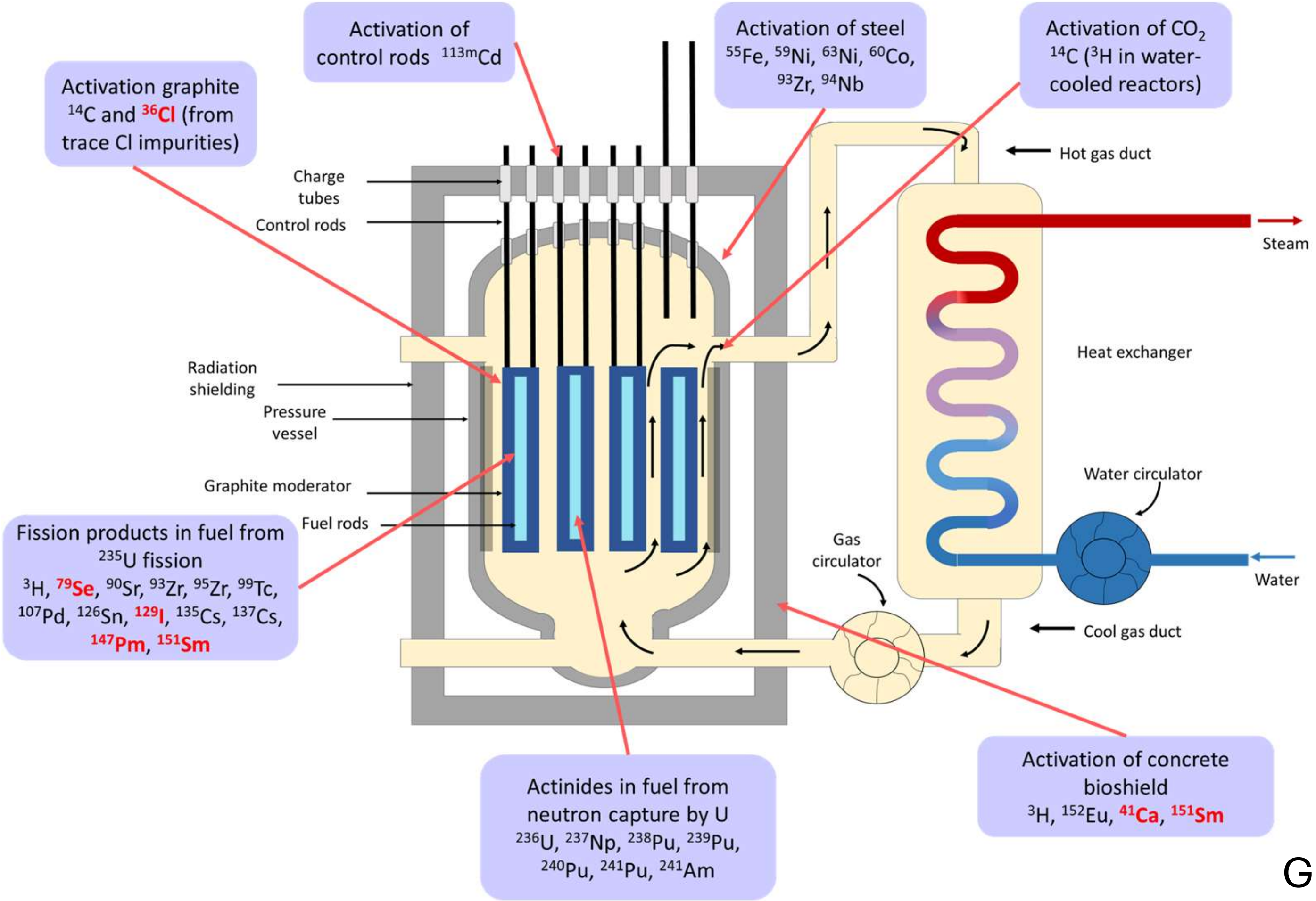
Inés Llopart Babot

09-09-2024

Vasile, M., Dobney, A., Boden, S., Leermakers, M., Qiao, J.
Bruggeman, M., Warwick, P., Tarancón, A., Bagan, H., de Souza, V., Russell, B., Kolgomorova, S., Adriaensen, L., Lutter, G., Rades, E., Happel, S.

TRISKEM
Expertise in Separation Chemistry

Radiological waste characterization



Based on (Warwick et al., 2022)

Which type of waste?

Reactor coolant water

Concrete

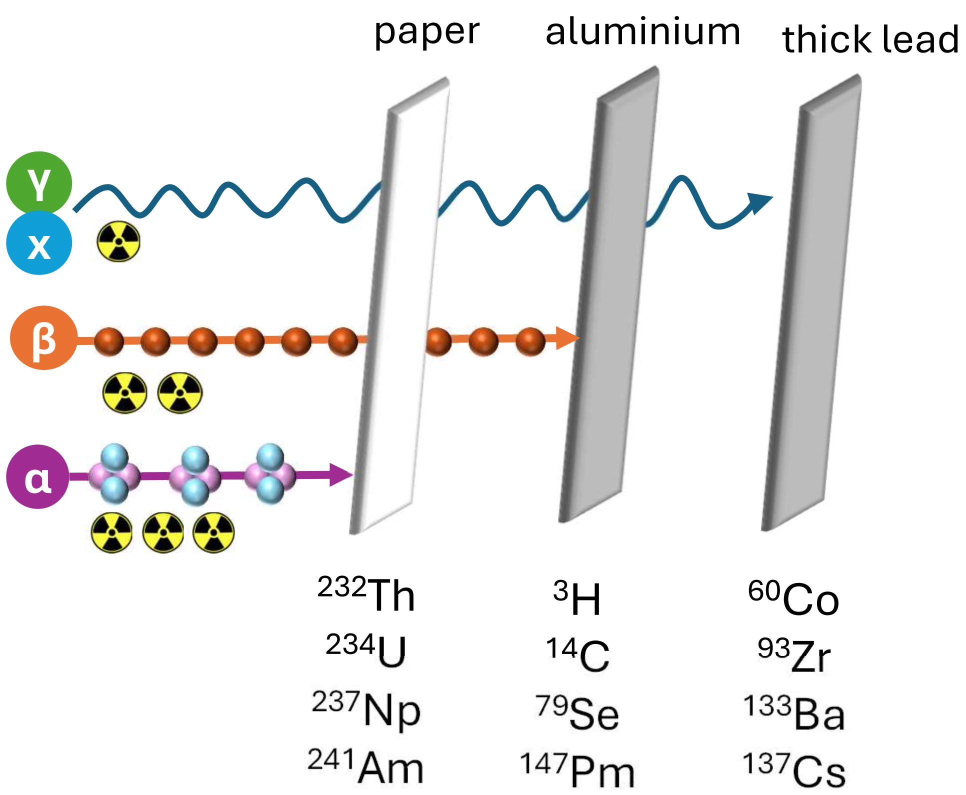
Graphite

Leaching solution

Spent nuclear fuel

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**

DTM radionuclides

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

ISO standard 24390:2023

Scaling factor method

Activity **ETM** radionuclides

Activity **DTM** radionuclides

REQUIRED

Validation using **experimental data**

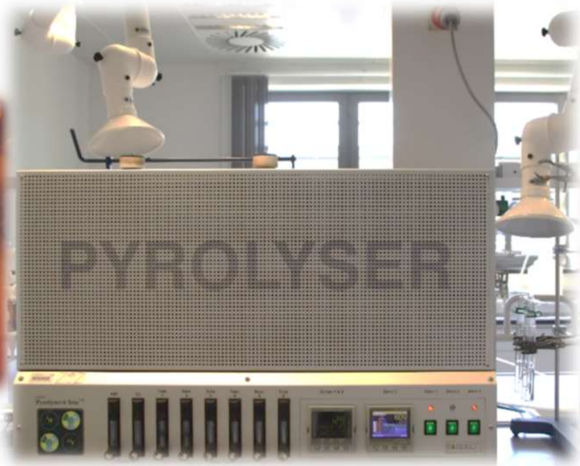
Analytical methods required

Sample treatment → Chemical separation → Measurement

Homogenization

Complete sample dissolution

Sample representativeness



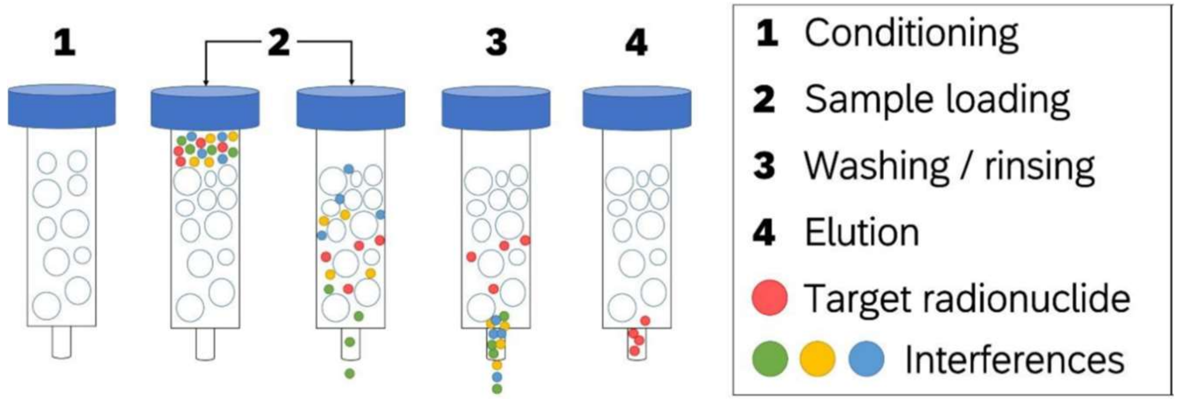
Analytical methods required

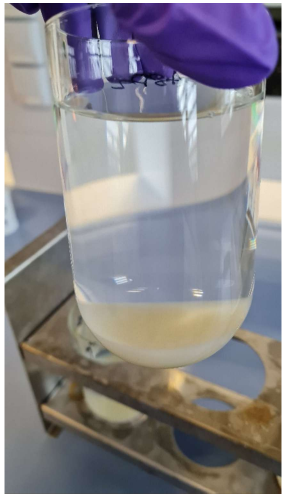
Sample treatment → **Chemical separation** → Measurement

Pre-concentration

Interference removal

Time needed for the separation procedure





Analytical methods required

Sample treatment → Chemical separation → **Measurement**

Detection limit

Effect of interferences

Time needed for measurement

Scope of the project

63 radionuclides required to be determined for **category A waste disposal** site

^{3}H	^{58}Co	^{93}Mo	^{110m}Ag	^{135}Cs	^{155}Eu	^{234}U	^{240}Pu	^{242}Cm
^{10}Be	^{60}Co	^{93}Zr	^{125}I	^{137}Cs	^{226}Ra	^{235}U	^{241}Pu	^{243}Cm
^{14}C	^{59}Ni	^{94}Nb	**^{129}I**	^{144}Ce	^{229}Th	^{236}U	^{242}Pu	^{244}Cm
^{35}S	^{63}Ni	^{99}Tc	^{131}I	**^{147}Pm**	^{230}Th	^{238}U	^{244}Pu	^{245}Cm
^{36}Cl	**^{79}Se**	^{106}Ru	^{125}Sb	**^{151}Sm**	^{232}Th	^{237}Np	^{241}Am	^{246}Cm
^{41}Ca	^{85}Kr	^{107}Pd	^{126}Sn	^{152}Eu	^{231}Pa	^{238}Pu	^{242m}Am	^{247}Cm
^{54}Mn	^{90}Sr	^{108m}Ag	^{134}Cs	^{154}Eu	^{233}U	^{239}Pu	^{243}Am	^{248}Cm

(de Bock, 2019)

Optimization and development of **novel assays** for the **determination** of the target radionuclides

- Solid sample preparation
- Use of extraction chromatography
- Measurement by LSC

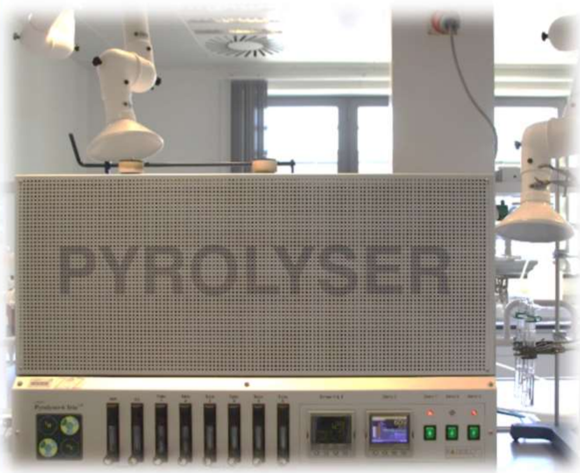
Analytical methods

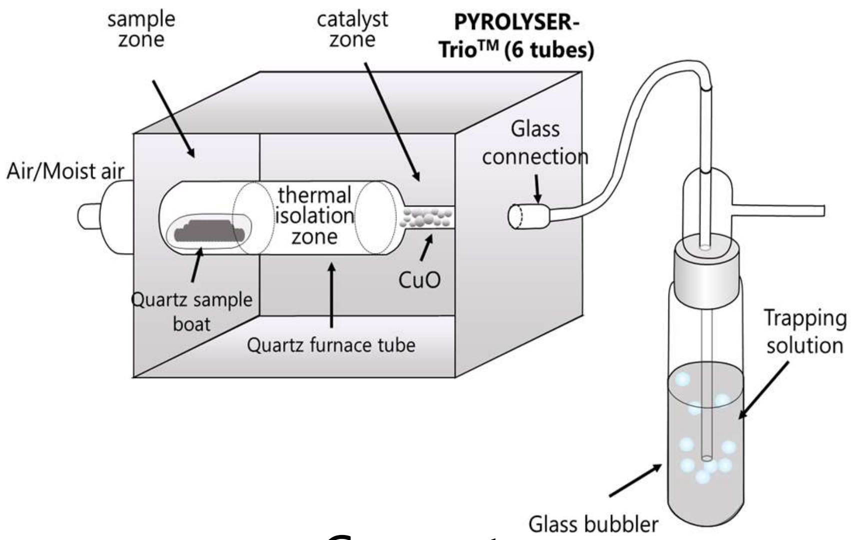
^{36}Cl and ^{129}I determination

Sample treatment

Chemical separation

Measurement





Concrete

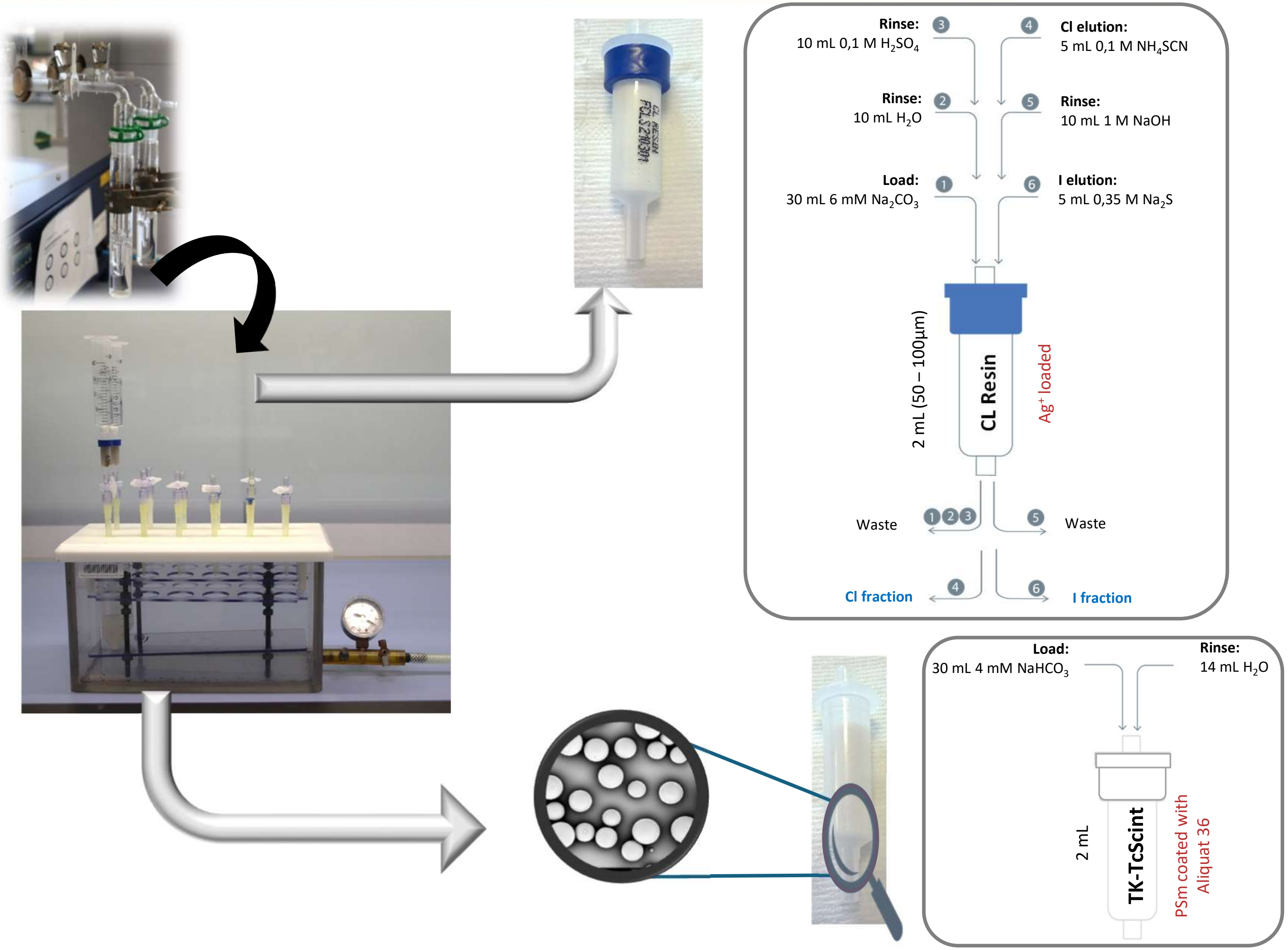
Graphite

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

Sample treatment

Chemical separation

Measurement



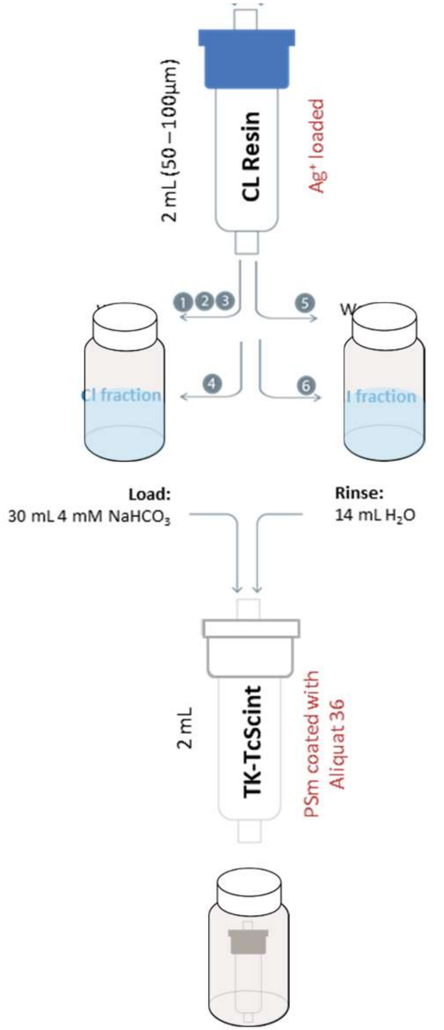
Analytical methods

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

Sample treatment

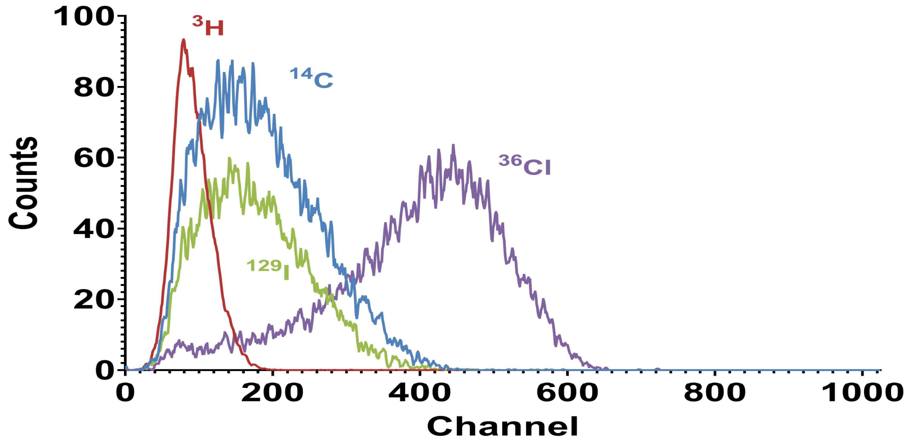
Chemical separation

Measurement



➕ LS cocktail

Liquid Scintillation Counting

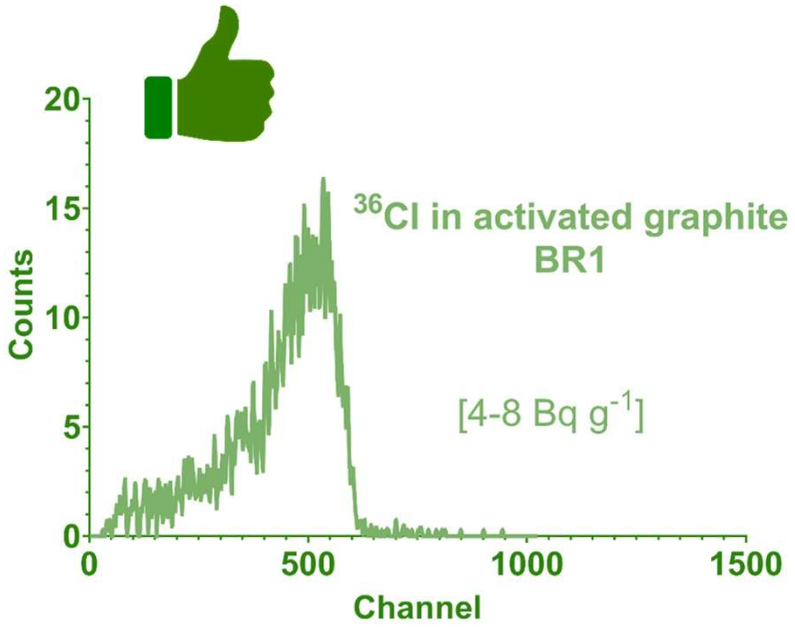


Analytical methods

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

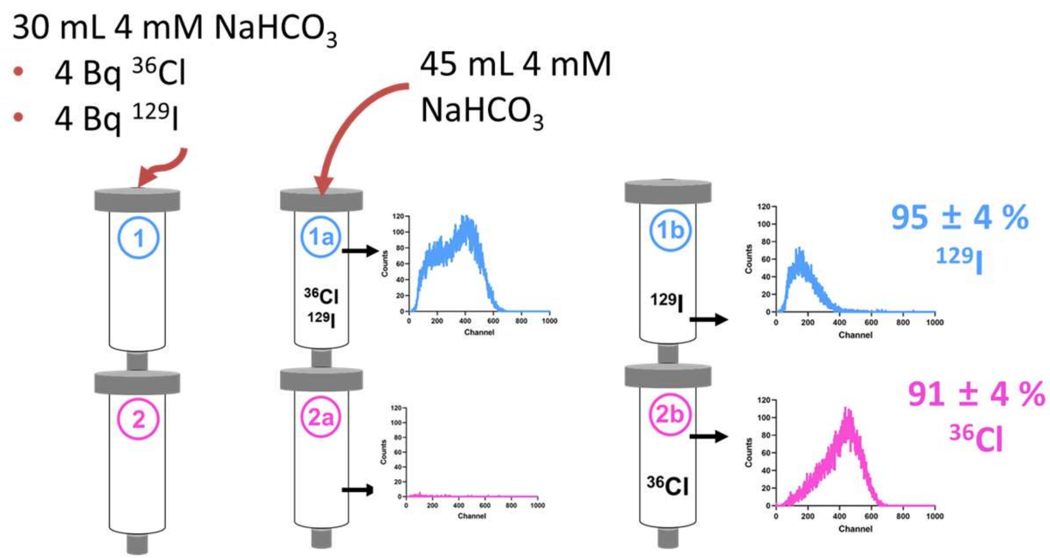
Sample treatment | Chemical separation | Measurement | **Application**

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



CL Resin **TK-TcScint Resin**

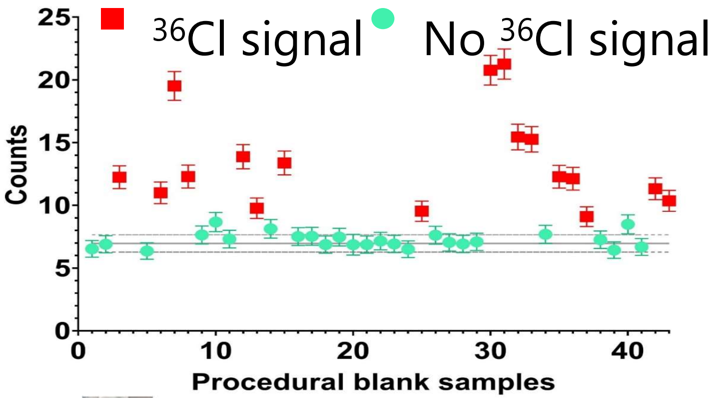
Sequential separation procedure with
2 TK-TcScint Resins

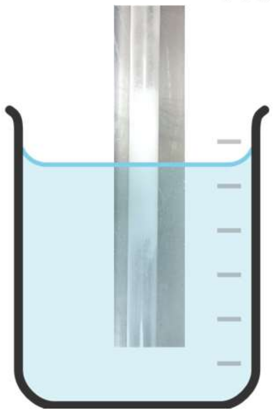


Analytical methods

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

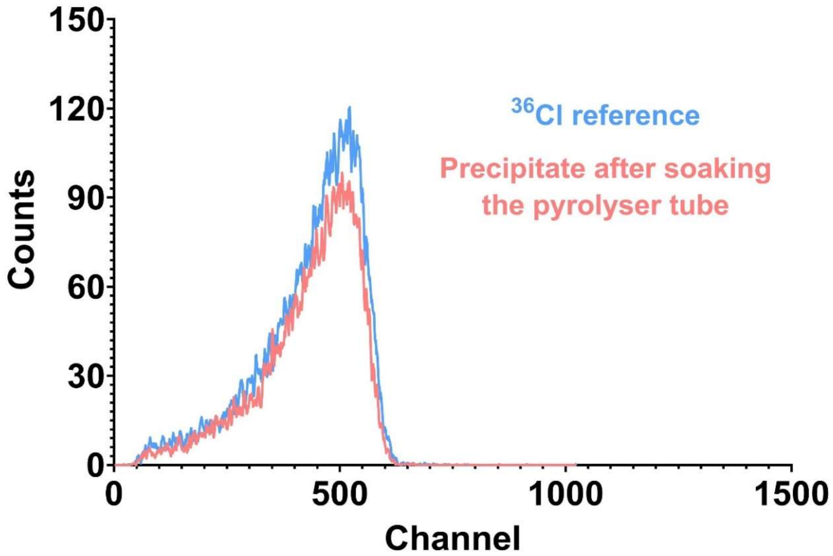
^{36}Cl memory effect





$AgNO_3$

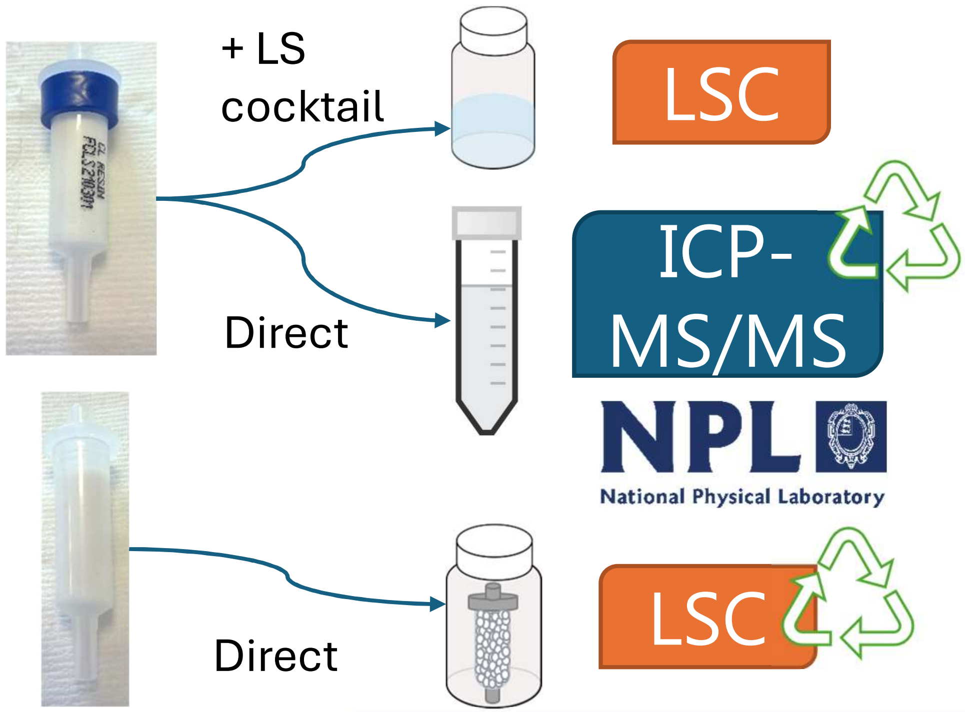
White precipitate AgCl



Analytical methods

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

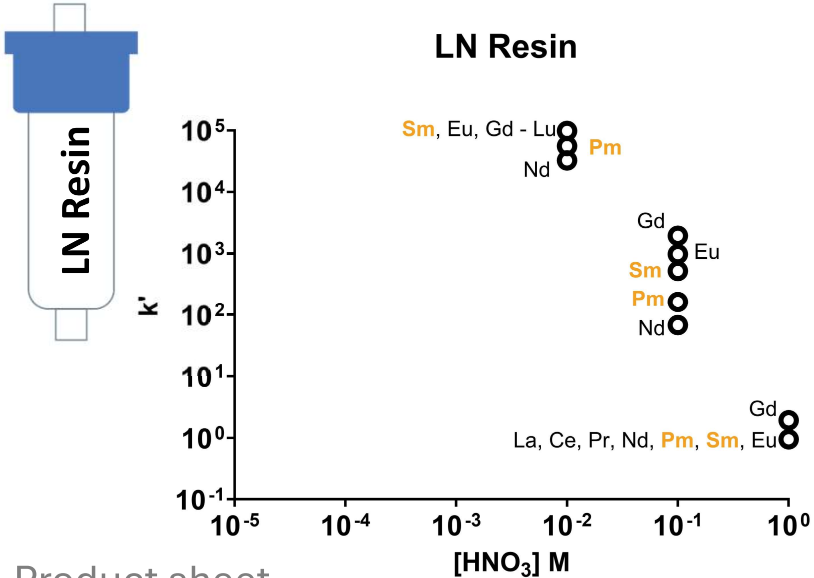
Comparison of ^{36}Cl measurement with different techniques



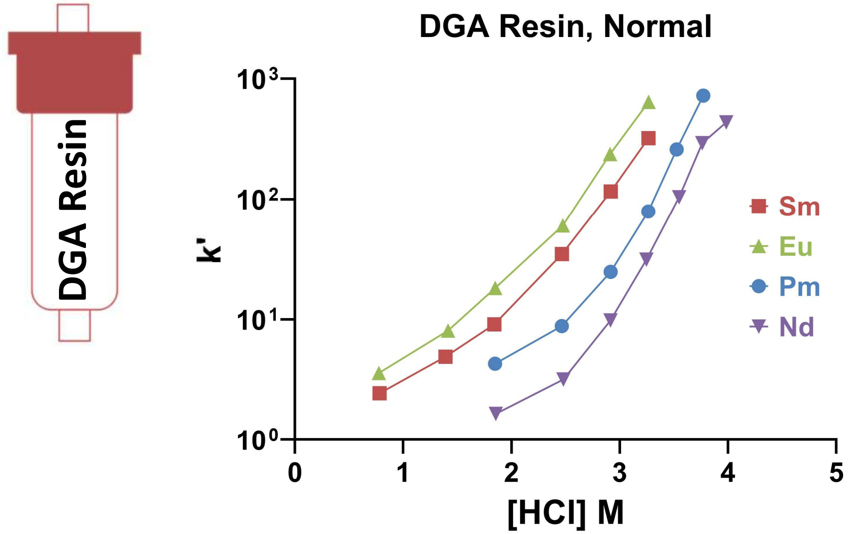
DL < clearance level

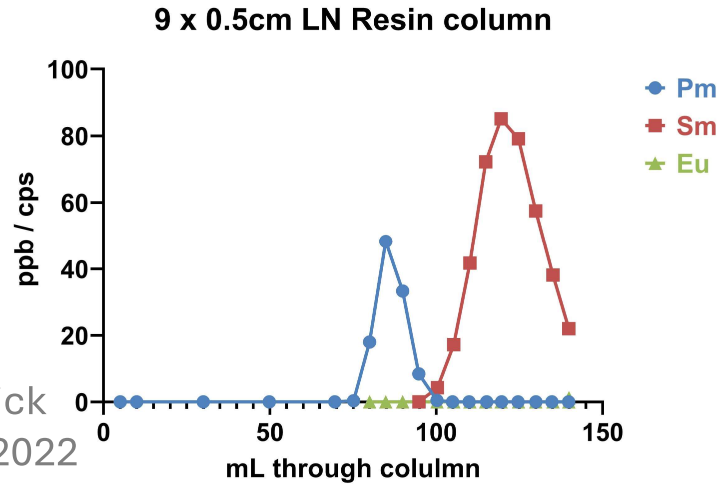
Analytical methods

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

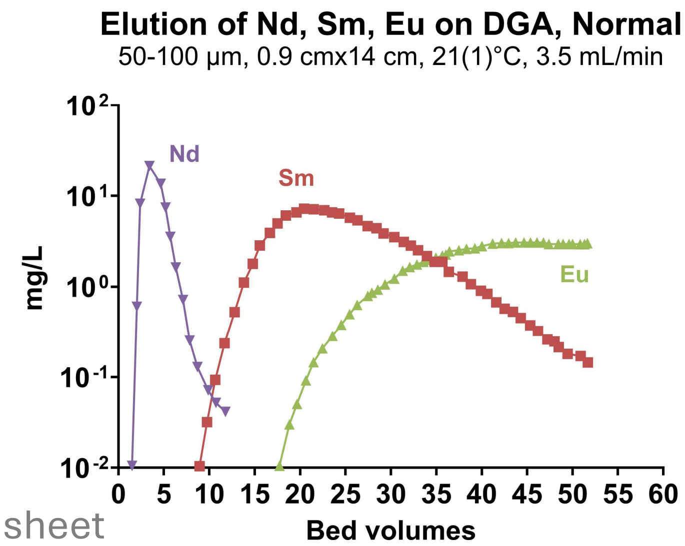


Product sheet





Warwick et al. 2022



Product sheet

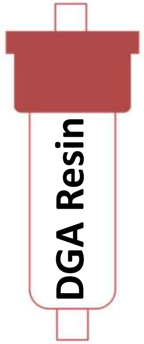
Analytical methods

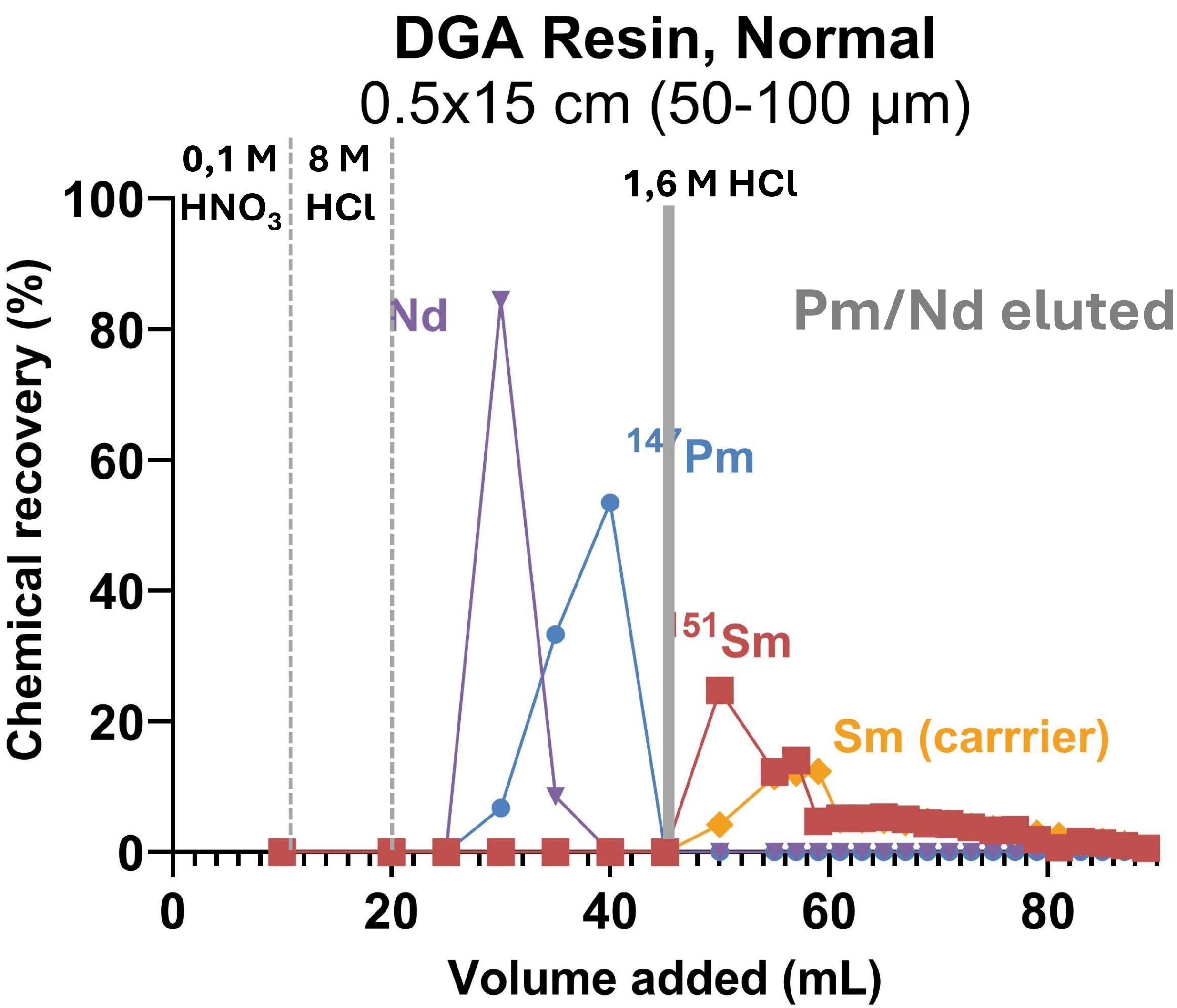
^{147}Pm and ^{151}Sm separation

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

Analytical methods

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

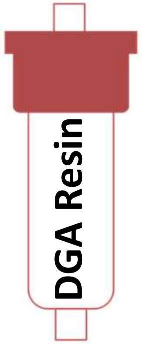


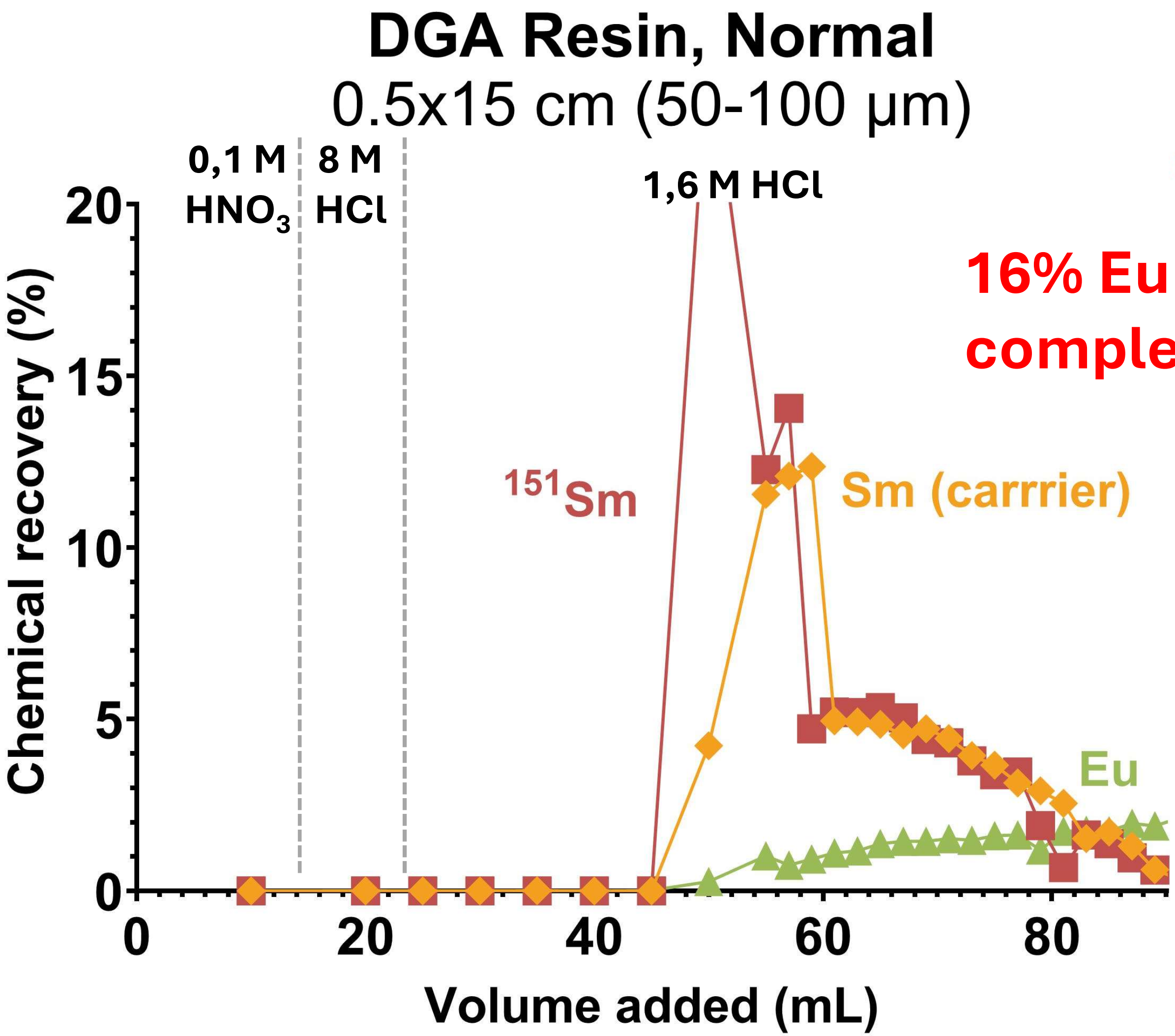


Pm/Nd eluted before Sm

Analytical methods

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



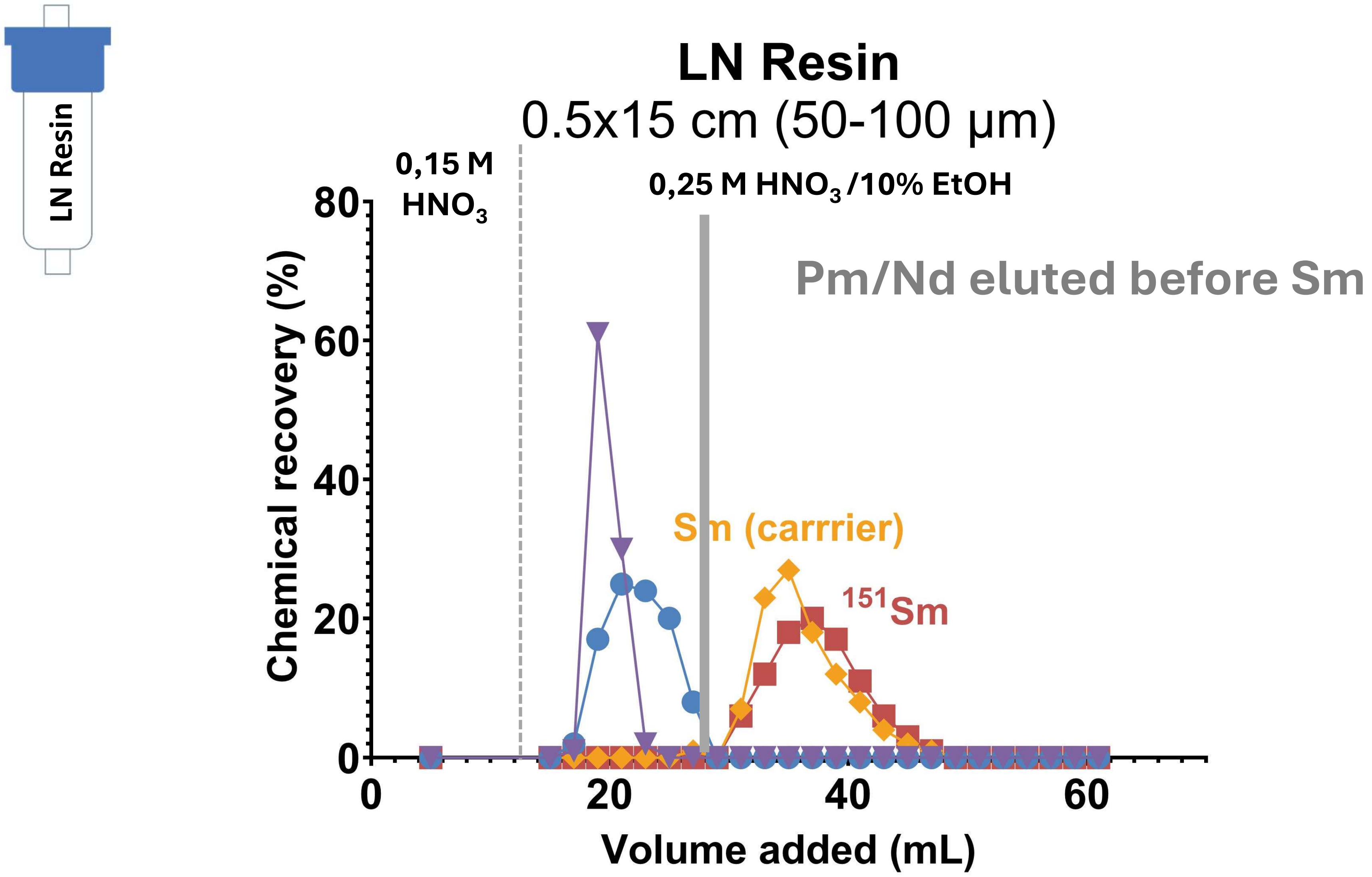


16% Eu when Sm is completely eluted

ICP-MS/MS to avoid Eu interference

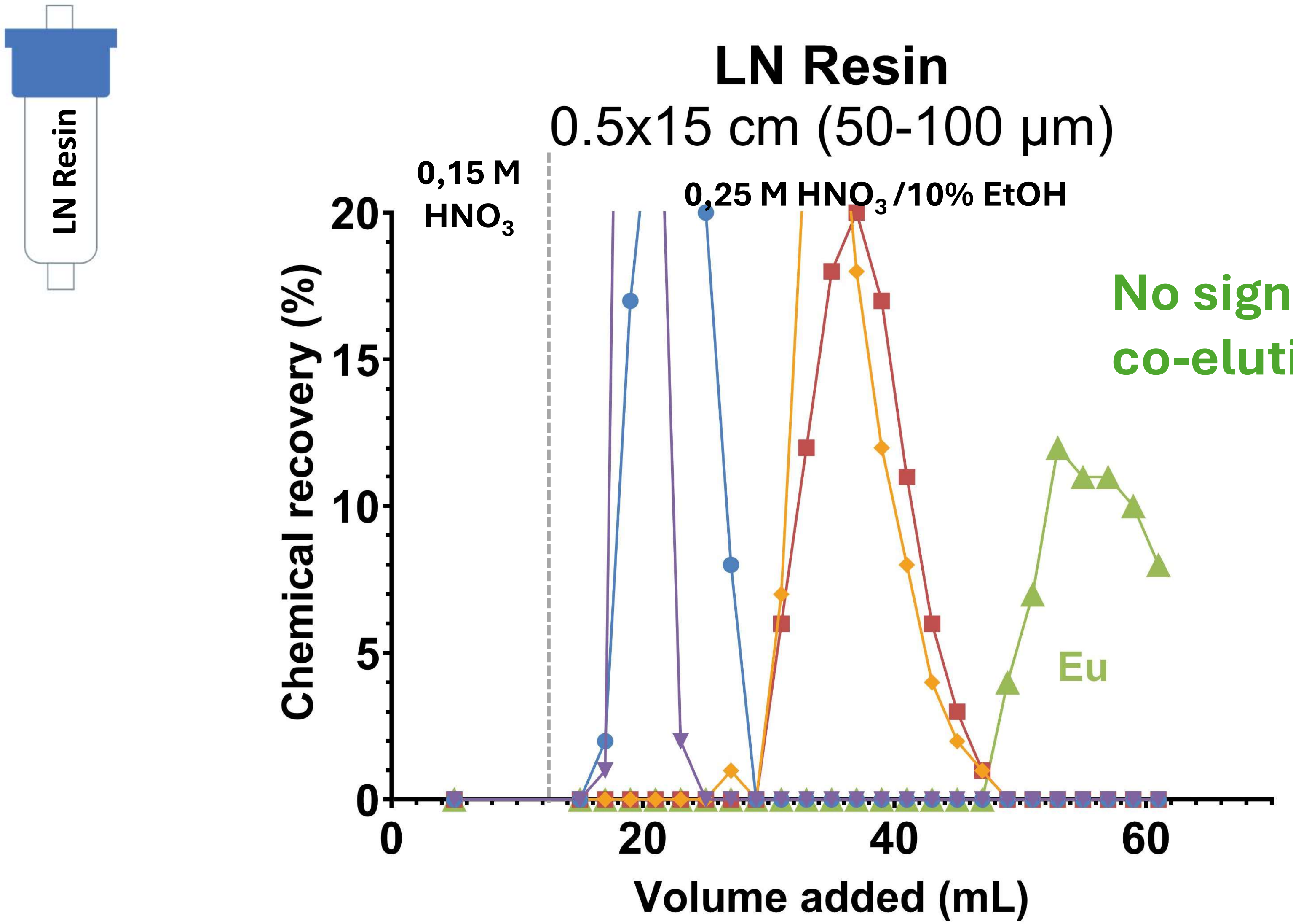
Analytical methods

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



Analytical methods

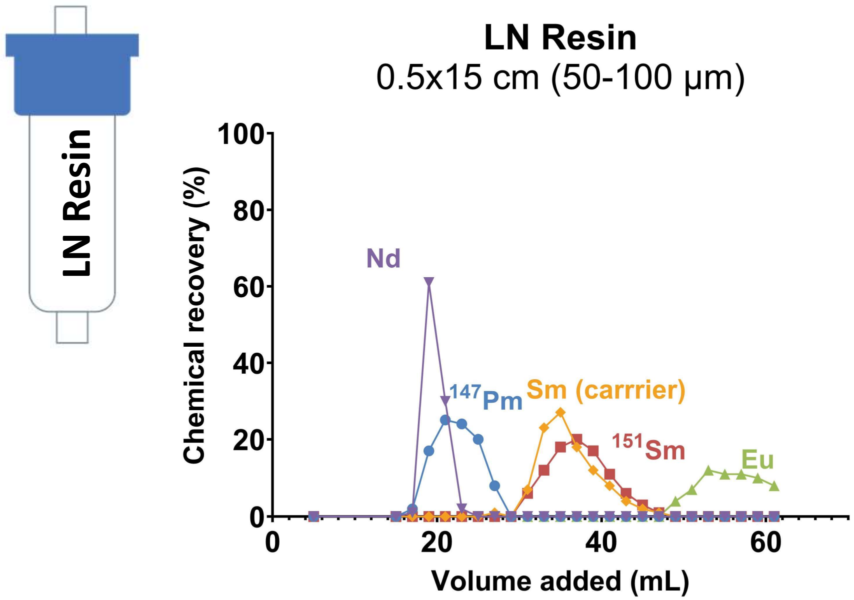
^{147}Pm and ^{151}Sm separation

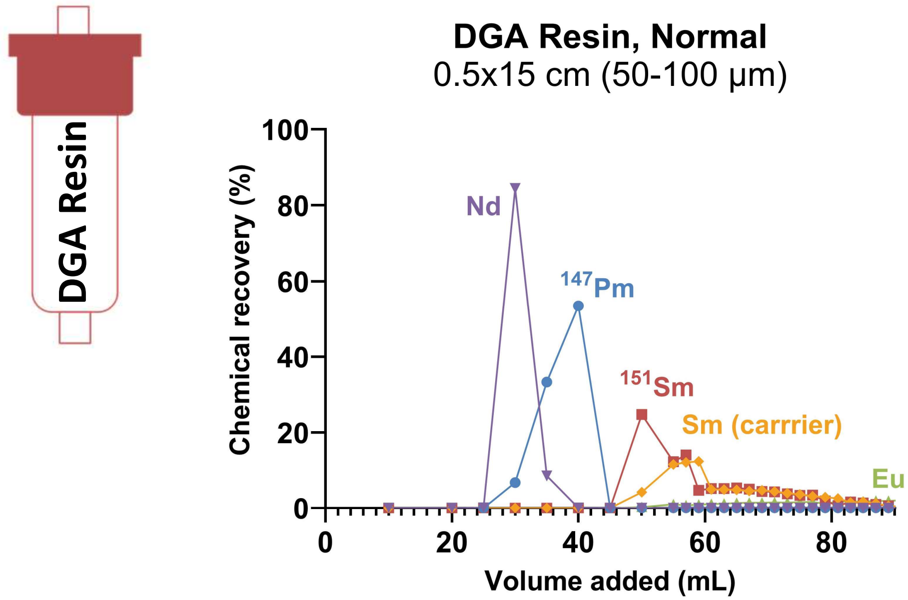


No significant Eu co-elution with Sm

Analytical methods

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





No Eu co-elution

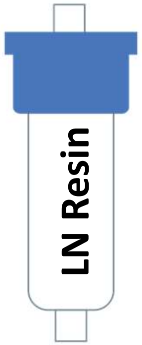
NEW

New approach

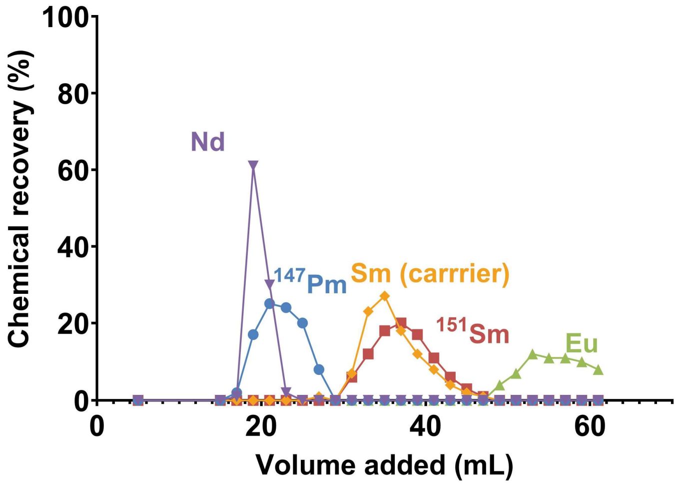
Fewer solution volume for elution

No need to use alcohol

Analytical methods
^{147}Pm and ^{151}Sm separation

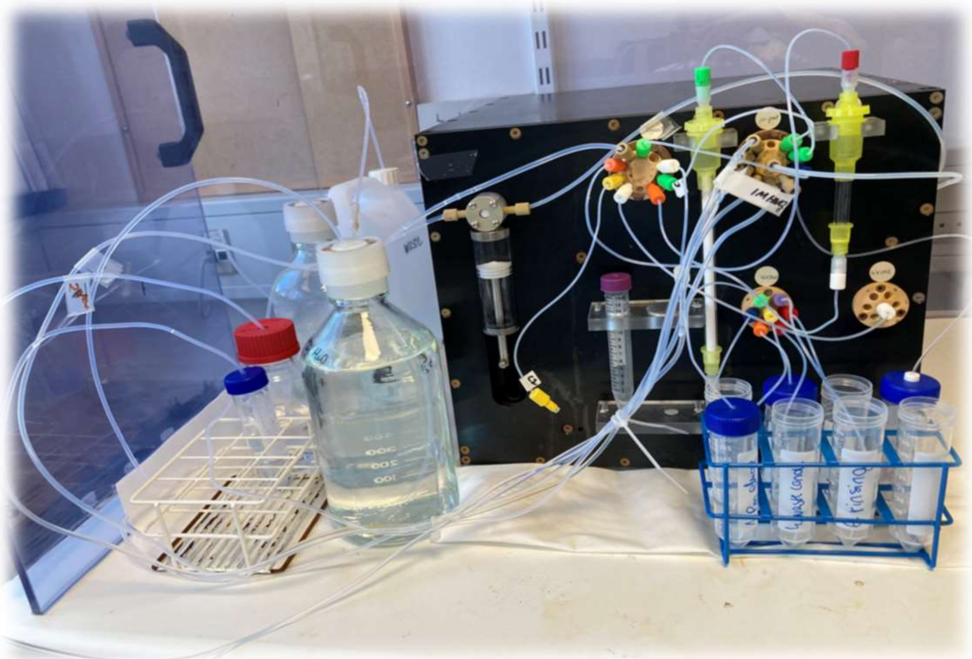


LN Resin
0.5x15 cm (50-100 µm)



AUTOMATED SEPARATION SYSTEM

In-house prepared in DTU

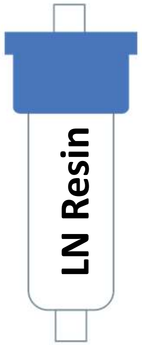


Challenges:

- Column size (thinner and larger) – backpressure
- Volume repeatability
- Turnaround time

Analytical methods

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



Volume accumulated reservoir (*death volume*)

➔ reduce flow rate

Death volume ⟷ *Resin wet*

↓

Dilution of solutions loaded

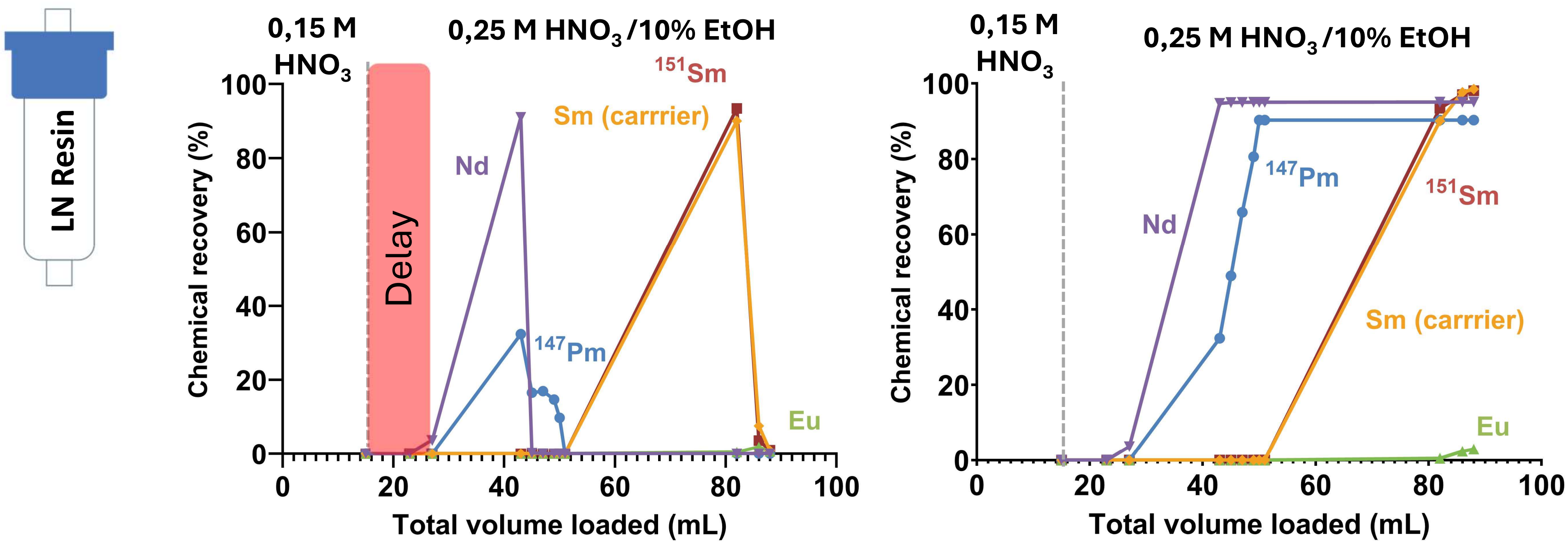
↓

Delay on the elution of the lanthanides

New elution profiles for ^{147}Pm and ^{151}Sm radiochemical separation

Analytical methods

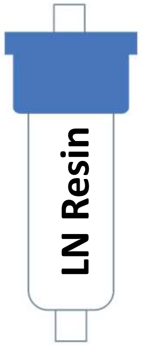
^{147}Pm and ^{151}Sm separation

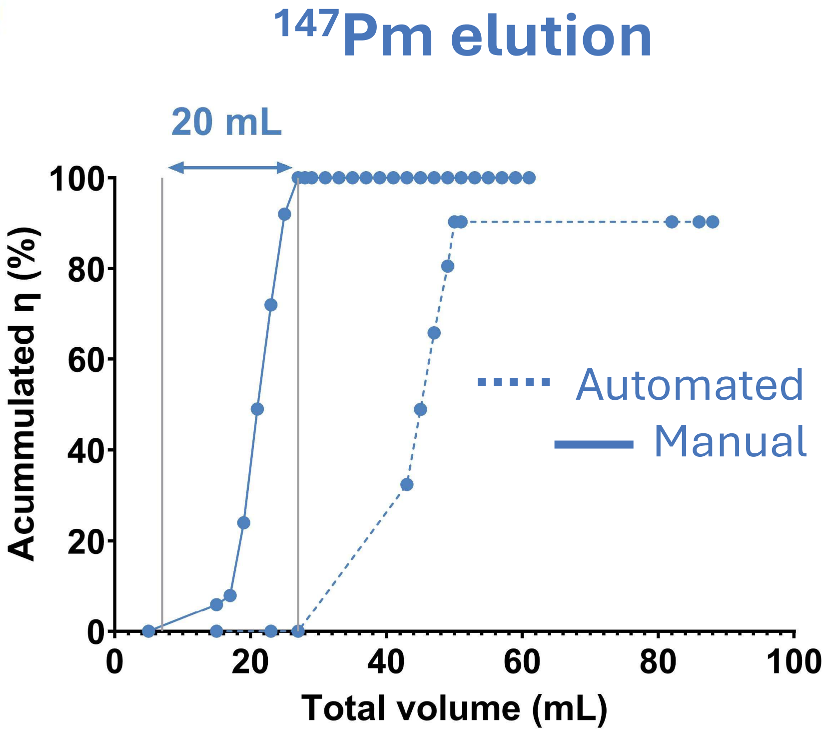


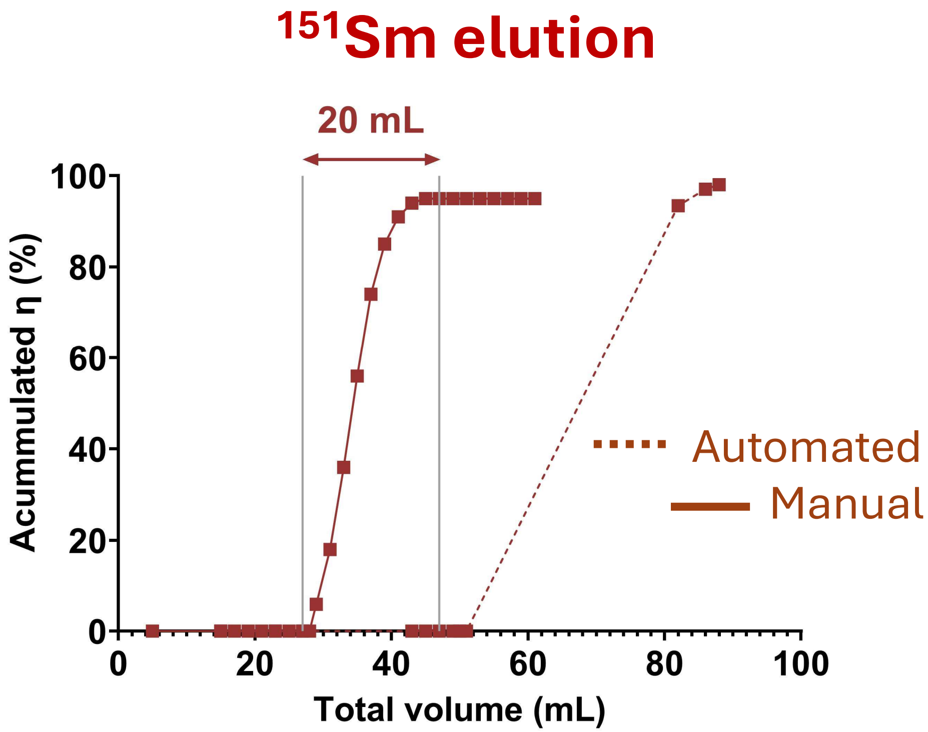
- Complete ^{147}Pm and ^{151}Sm radiochemical separation
- Reproducible results
- Total turnaround time: **2 h 35 min**
  - 86 mL loaded + 7 mL conditioning → 0,6 mL/min

Analytical methods

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

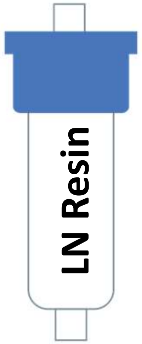






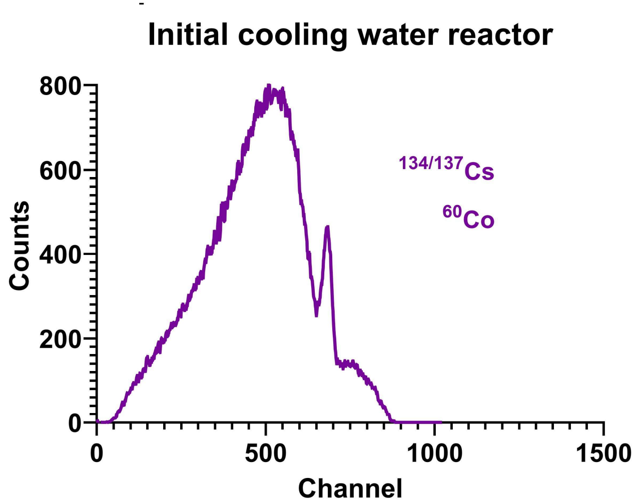
- Delay on ^{147}Pm and ^{151}Sm elution
- Additional 20 mL 0,25 M HNO_3 /10% EtOH needed

Analytical methods
^{147}Pm and ^{151}Sm separation



Application in reactor cooling water from a Boiling Water Reactor

Previously used in Nordic inter-laboratory comparison



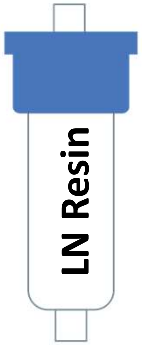
+ 13 Bq ^{147}Pm
+13 Bq ^{151}Sm
+ 0,5 mg Nd
+ 0,5 mg Sm

Expected: ^{54}Mn, ^{60}Co, ^{134}Cs and ^{137}Cs

Measured by gamma and LSC

Analytical methods

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



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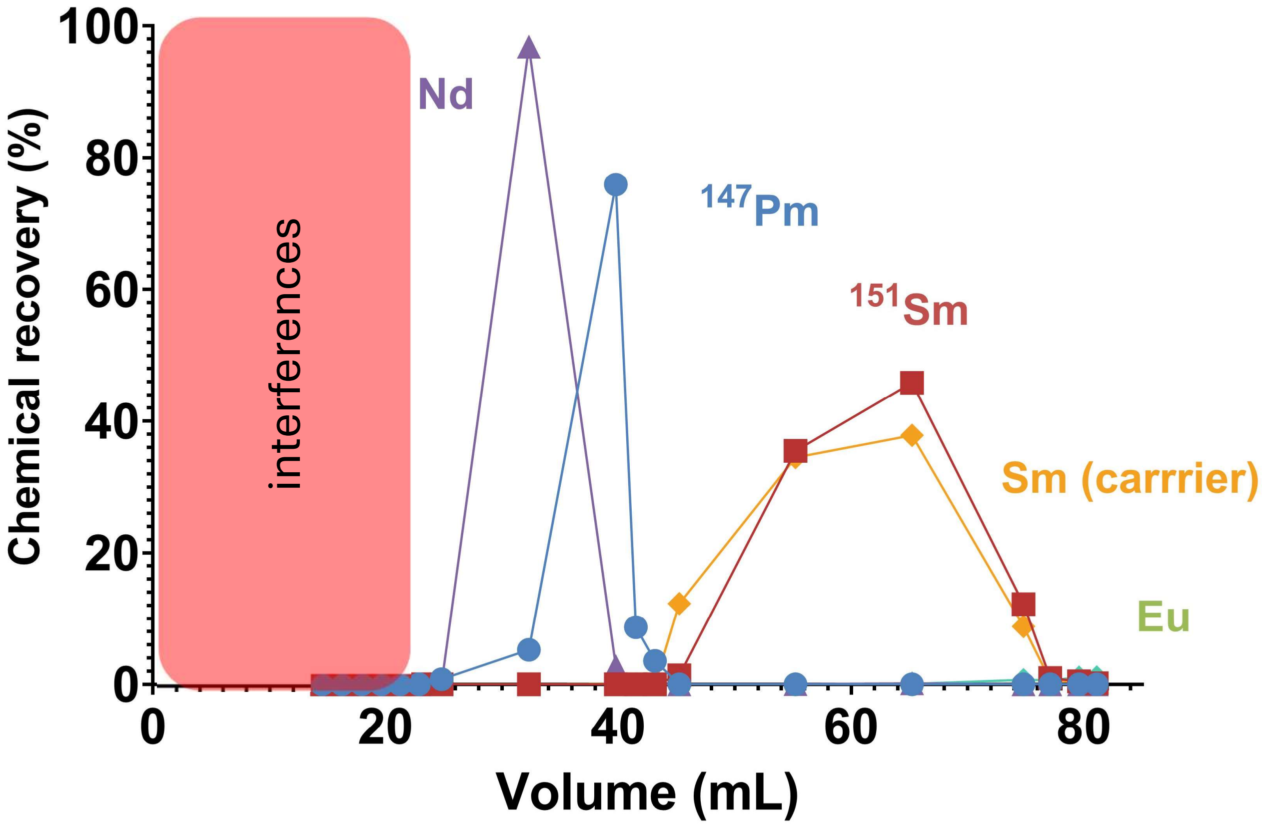
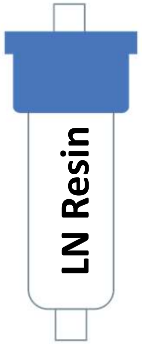


Analytical methods

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



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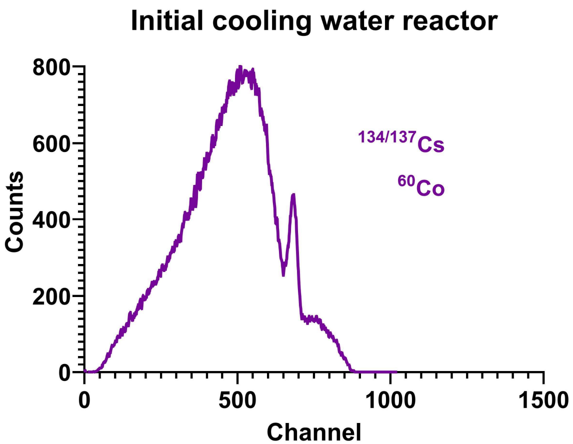
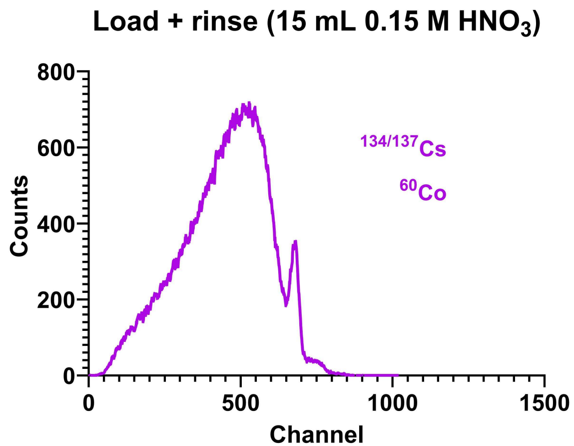
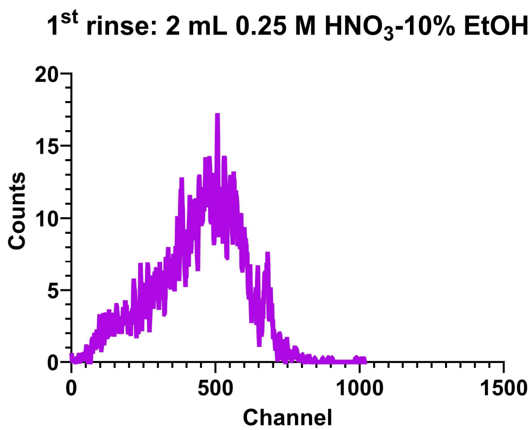
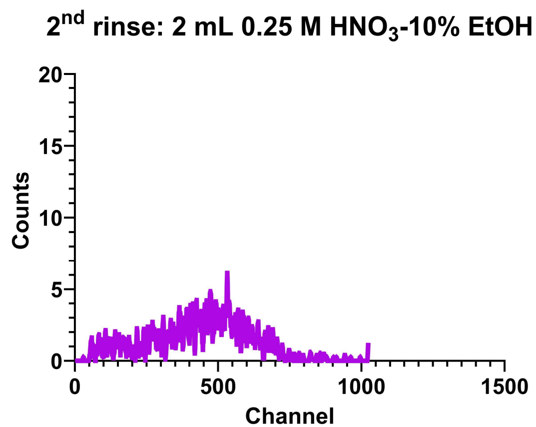




Expected: ^{54}Mn, ^{60}Co, ^{134}Cs and ^{137}Cs

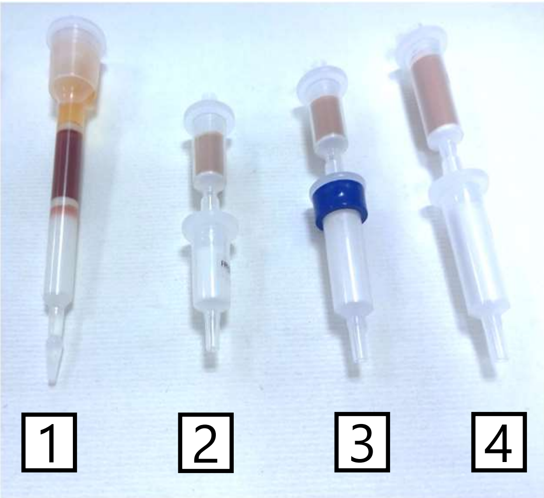
Measured by gamma and LSC





Analytical methods

On the determination of ^{79}Se



New SE Resin TRISKEM

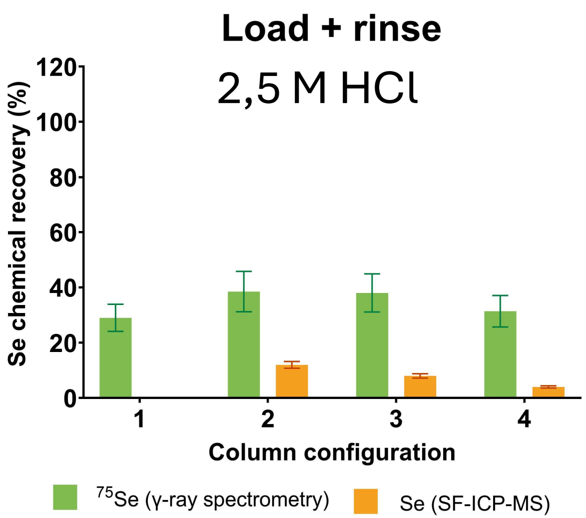
SE Resin	Se retention
Prefilter Resin	↓ extractant bleeding

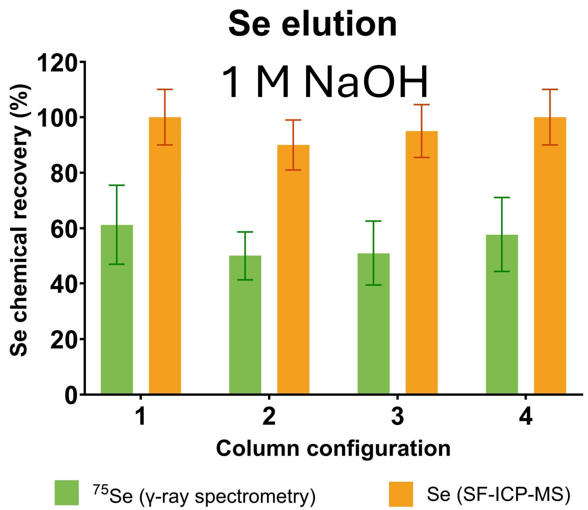
6 Bq ^{75}Se

Measured by gamma-ray spectrometry

1 mg stable Se

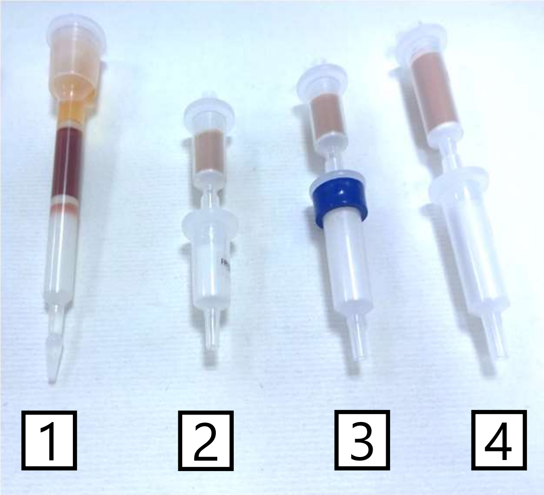
Measured by SF-ICP-MS





Analytical methods

On the determination of ^{79}Se



New SE Resin

TRISKEM

SE Resin Se retention

Prefilter Resin ↓ extractant bleeding

6 Bq ^{75}Se

Measured by gamma-ray spectrometry

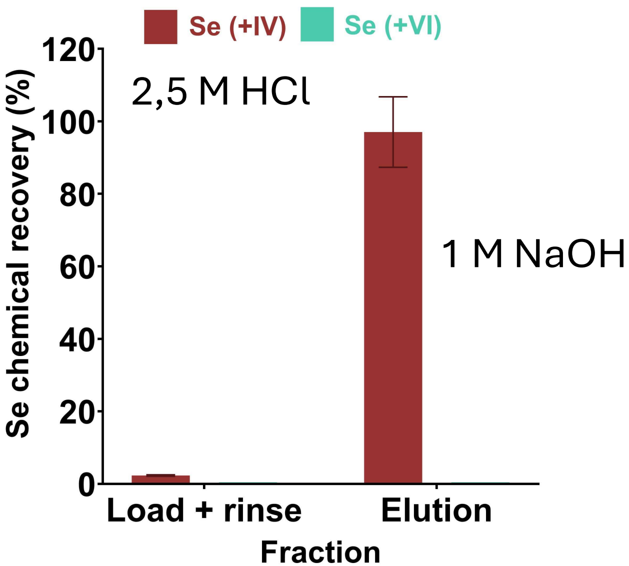
1 mg stable Se

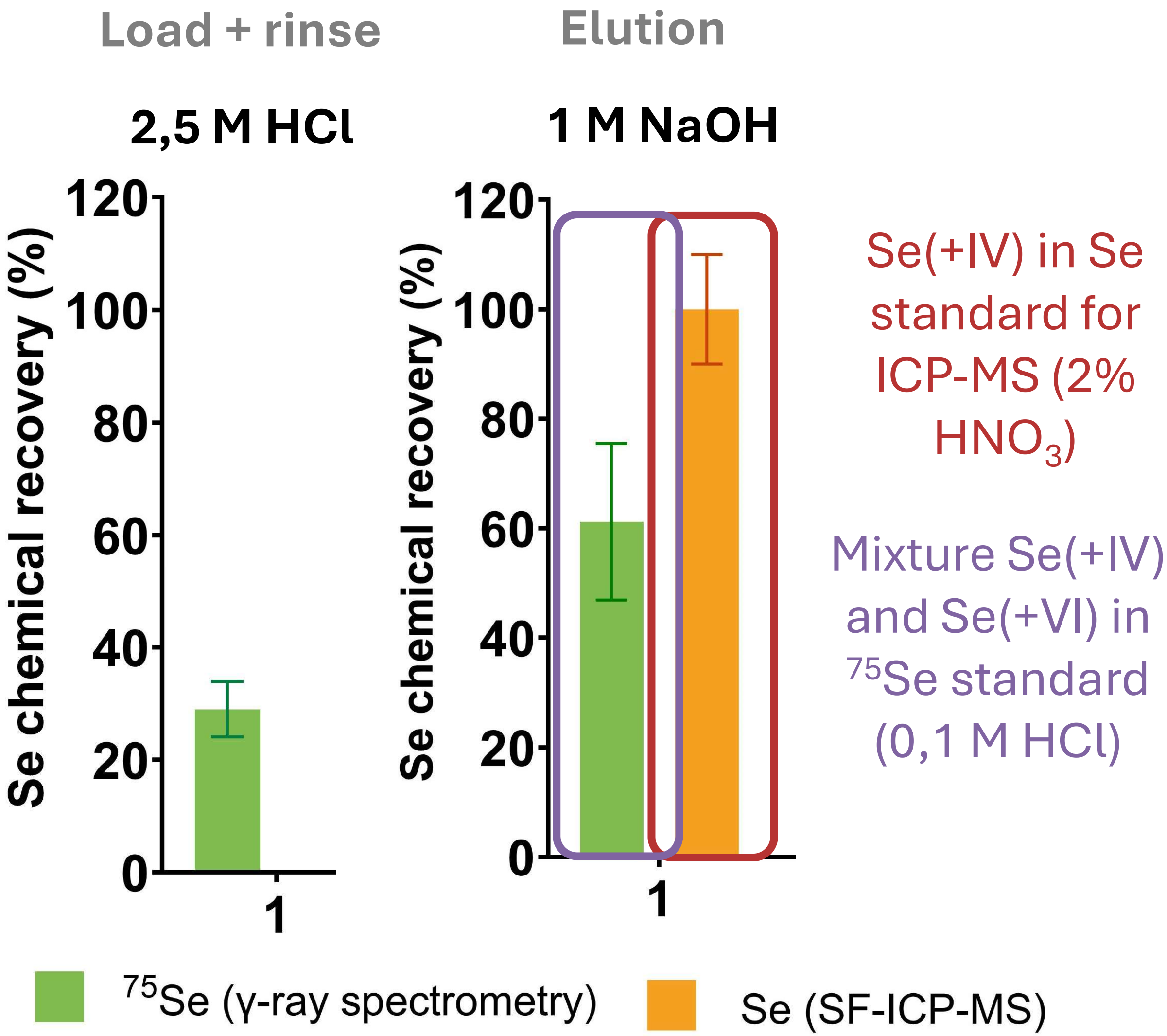
Measured by SF-ICP-MS

Disagreement between gamma-ray spectrometry and ICP-MS

Analytical methods

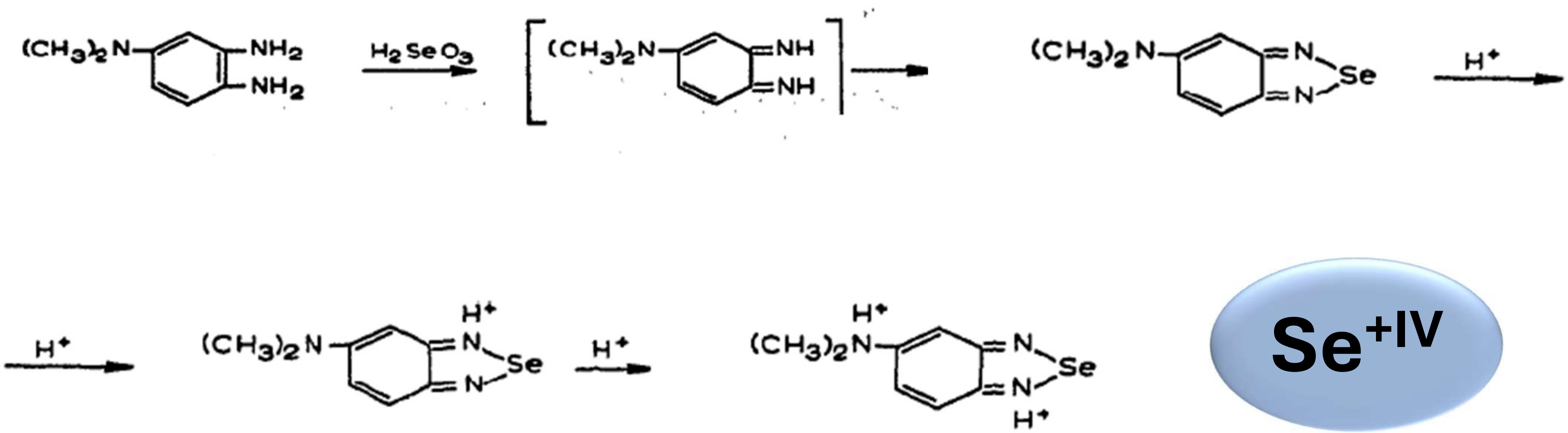
On the determination of ^{79}Se





Analytical methods
On the determination of ^{79}Se

Principle of piazselenol formation



Se^{+IV}

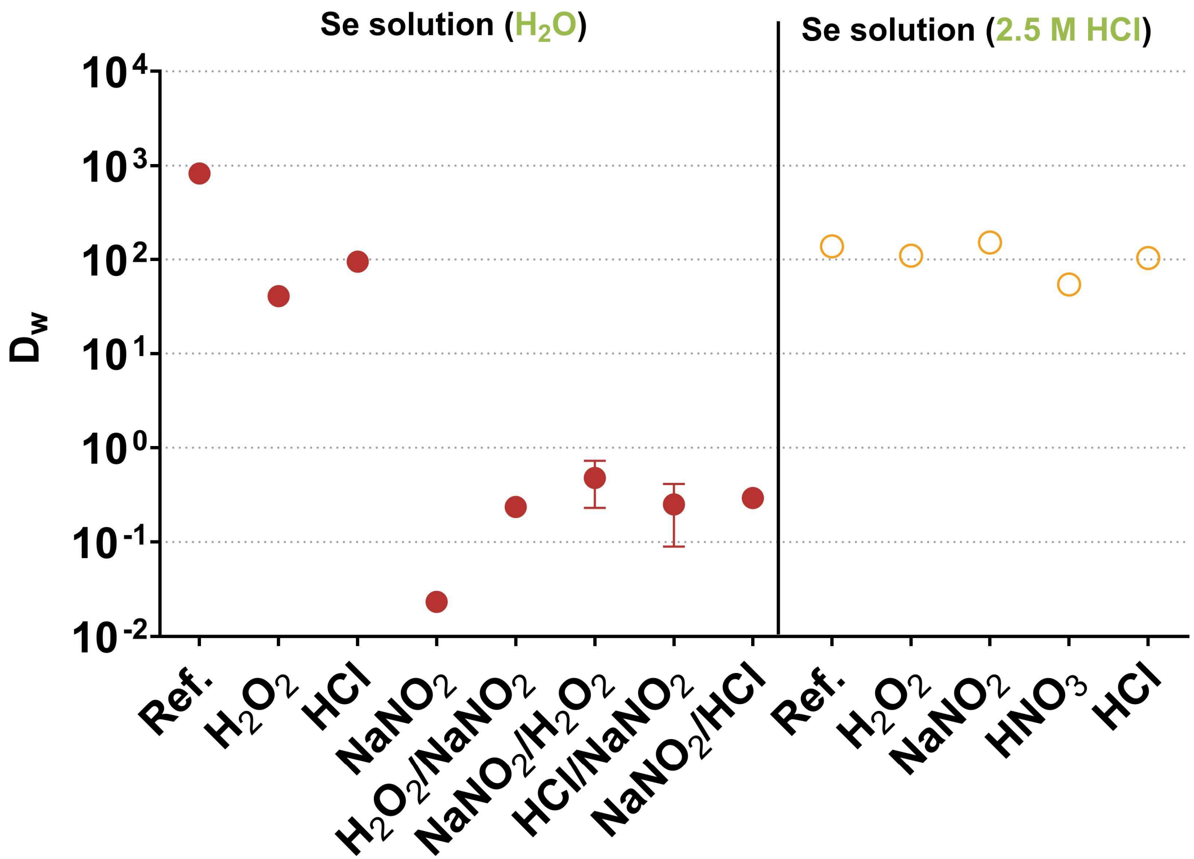
Anal. Chim. Acta, 27 (1962) 288–294

Oxidation state fixation needed

Analytical methods
On the determination of ^{79}Se

Different initial solutions treated with oxidant and reducing agents

Batch experiment → 50 mg SE Resin

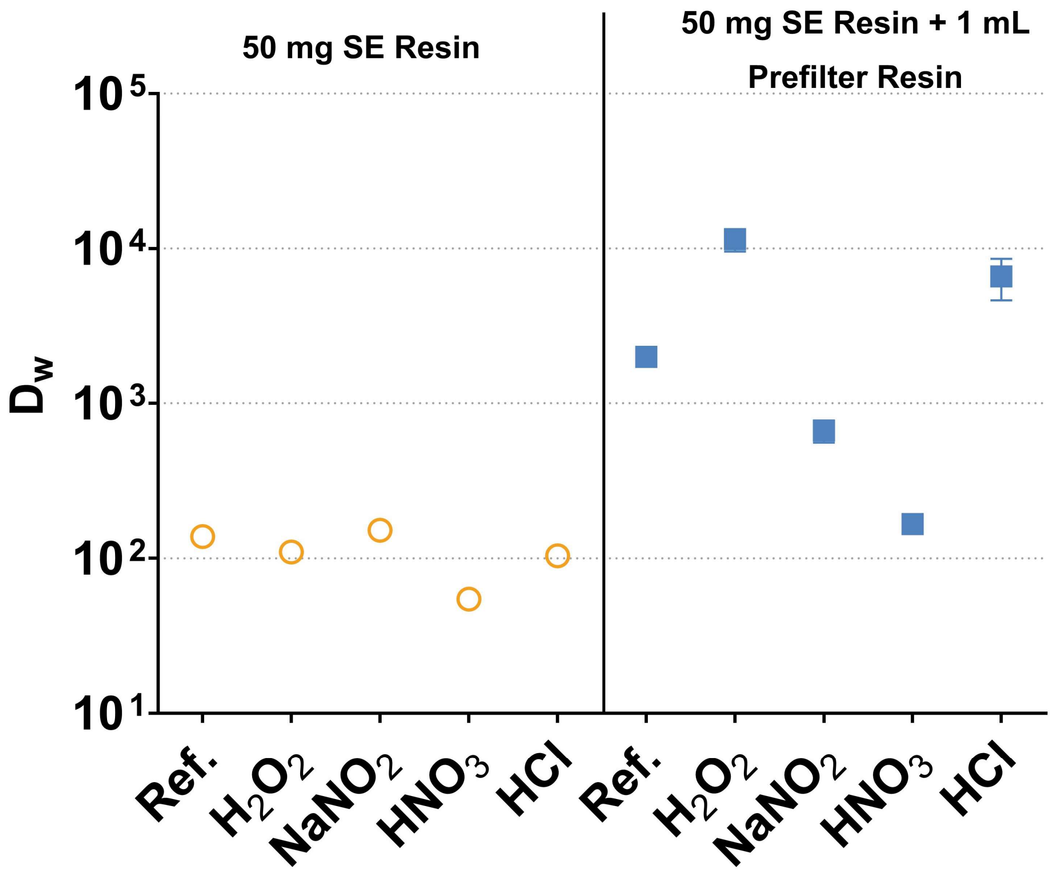


- ↑ **Dw** loading sample in H_2O
- ↓ **Dw** loading samples **oxidized** when initial solution was in H_2O
- **~Dw** loading samples in different conditions when initial solution was in 2,5 M HCl

Analytical methods

On the determination of ^{79}Se

Initial solution (2,5 M HCl) treated with different chemicals

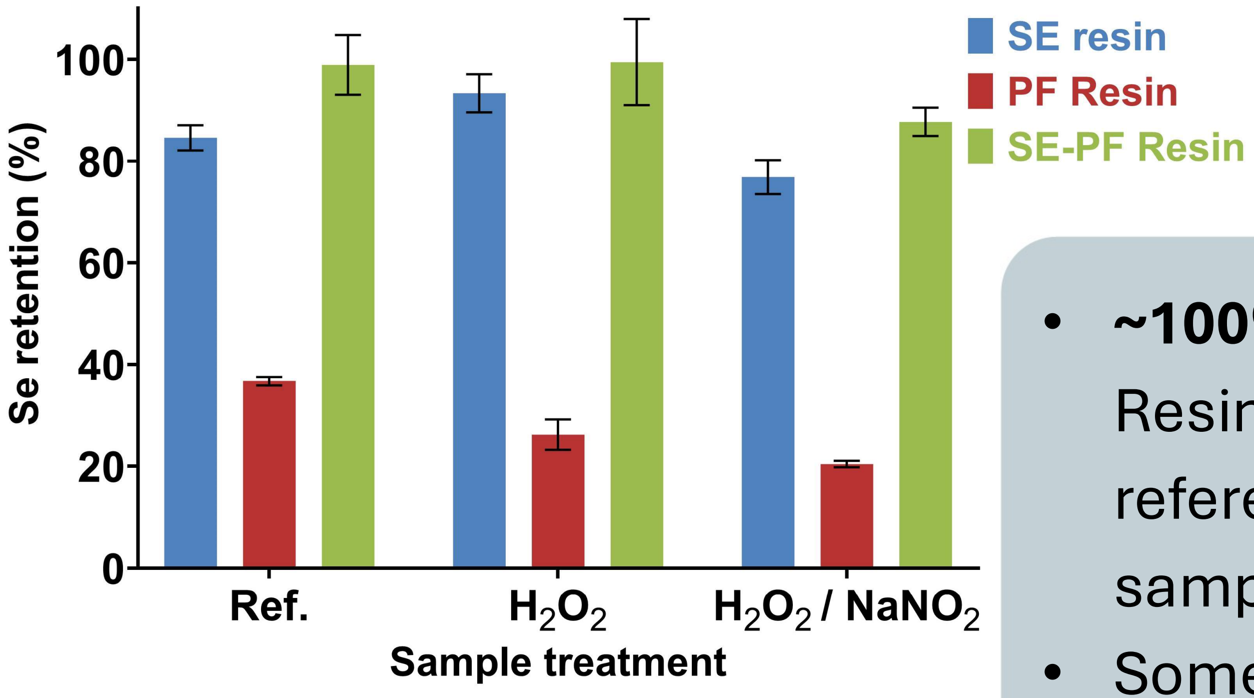


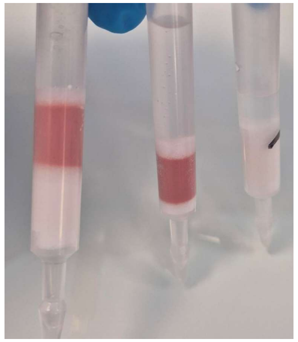
- ↑↑ **Dw** loading sample with PF Resin
- More differences on Dw values when passing through the solution on a PF Resin

Analytical methods

On the determination of ^{79}Se

Initial solution (2,5 M HCl) treated with different chemicals and loaded in **3 different resins**



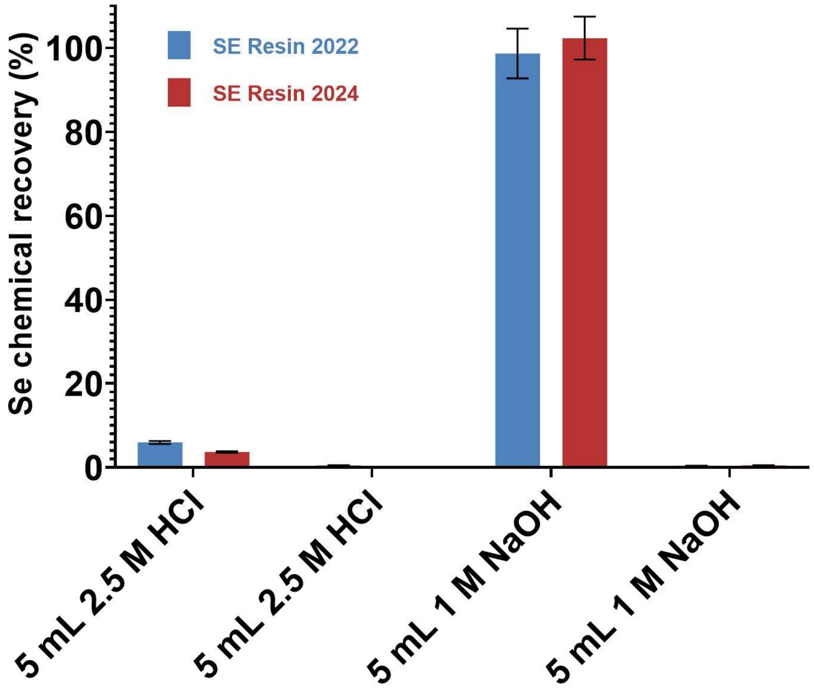


- **~100%** retention in SE-PF Resin when loading the reference (2,5 M HCl) and sample treated with H_2O_2
- Some **retention of Se** on PF Resin

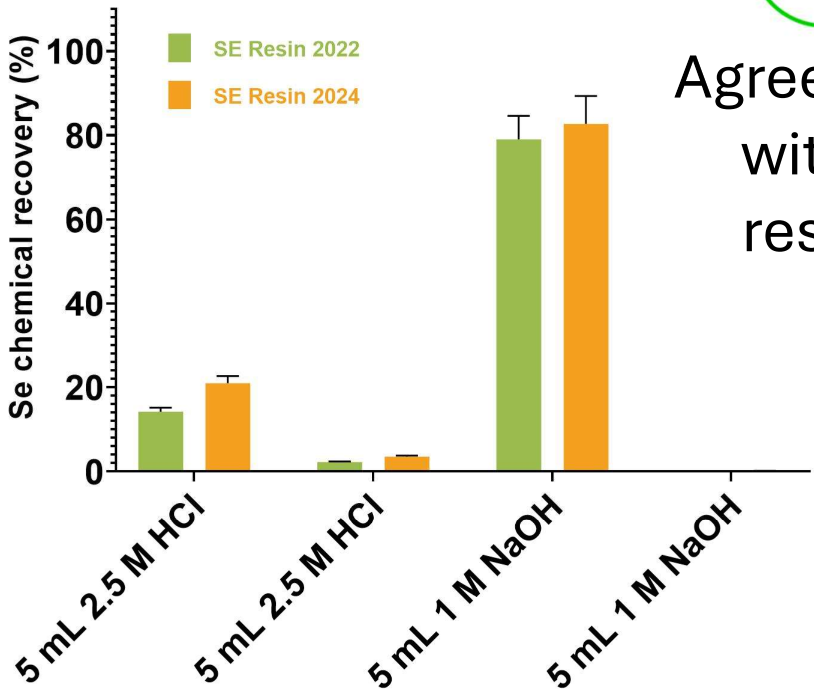
Analytical methods
On the determination of ^{79}Se

Stability of SE Resin over time

No treatment



with H_2O_2



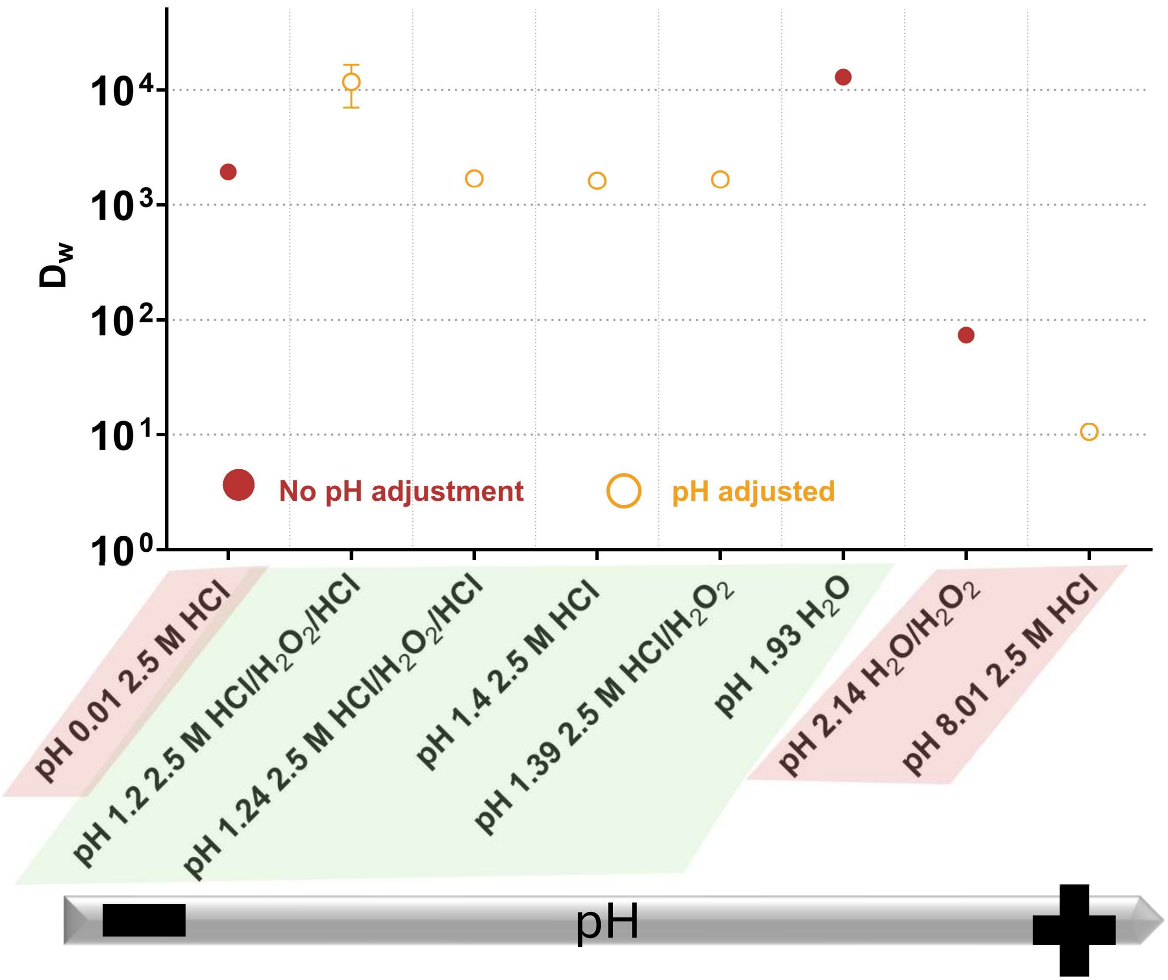
Agreement within resins

- Promising results on Se retention (even in oxidant media)

Analytical methods

On the determination of ^{79}Se

pH effect on Se retention



- Bosca & Mot, 2021 → relevance of pH on *piazselenol* formation (**pH~1,3**)
- **Dw ≥ 10^3** when pH~1,3 (no dependence on sample pretreatment)

Analytical methods

On the determination of ^{79}Se

Batch experiments + elution profiles with specific Se oxidation state standards

Se(+IV) Se(+VI)

- pH
- Acid concentration
- Volume

Possibility to apply PS Resins on Se radiochemical separation and measurement

Investigation of interferences and development of a method for Se determination in different samples

Overview

NEW

New analytical methods required

Selection of resins, equipment and measurement techniques based on availability and needs

RM

Reference materials needed to validate the different methods

Thank you for your attention!!

Questions?

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