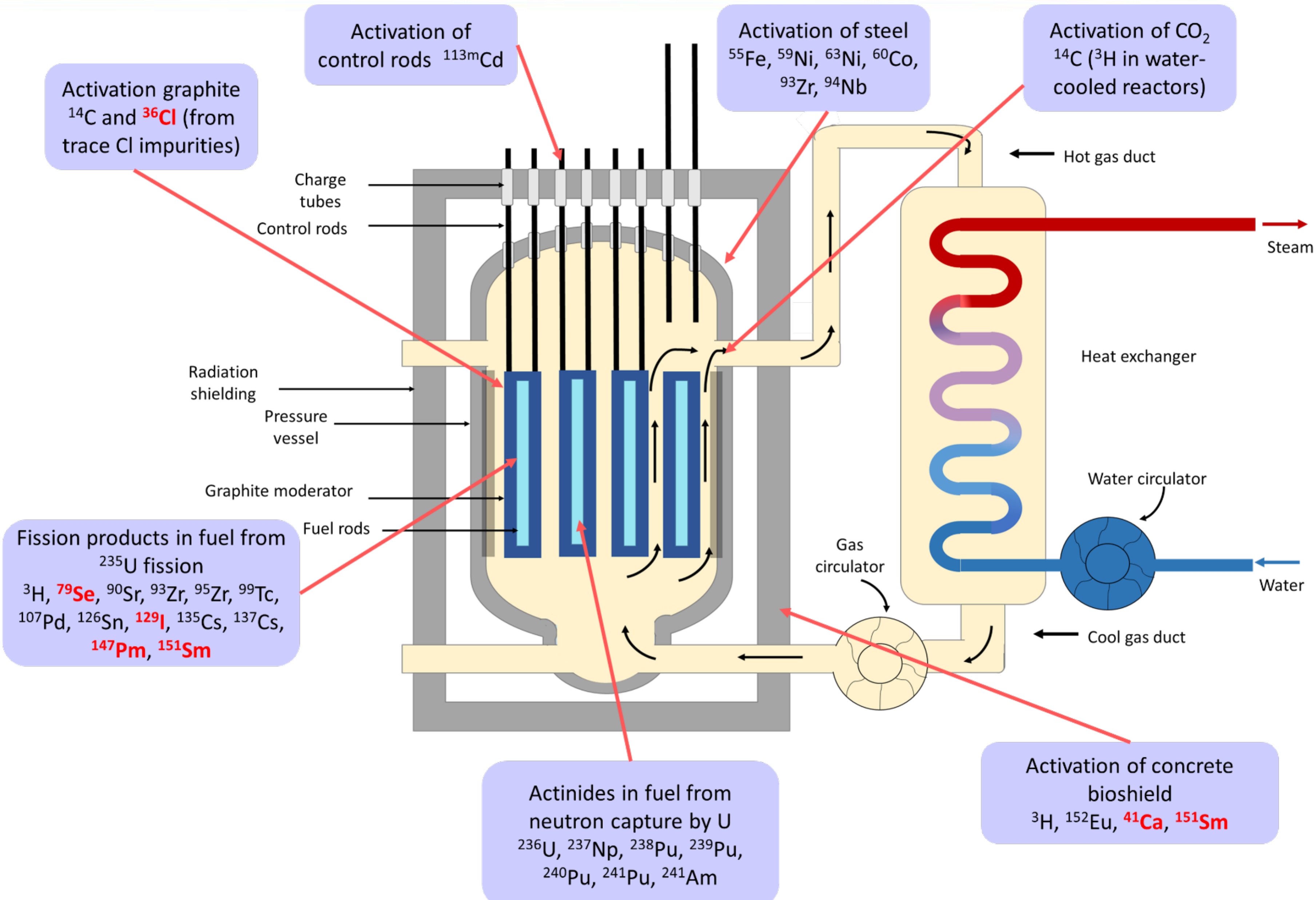
Inés Llopart Babot
20-10-2025

Optimization of the determination procedures to quantify DTM radionuclides in decommissioning samples

TRISKEM
Expertise in Separation Chemistry

Waste characterization



Waste characterization

Exempt

Natural origin

Bq/g	Radionuclide
10	^{40}K
1	Others

Artificial origin

Bq/g	Radionuclide
0,01	^{129}I
0,1	^{60}Co
1	^{14}C, ^{36}Cl, ^{75}Se, ^{90}Sr
100	^{3}H
1000	^{55}Fe, ^{90}Y, ^{147}Pm, ^{151}Sm

IAEA SAFETY STANDARDS SERIES

Application of the Concepts of Exclusion, Exemption and Clearance

Waste characterization

Exempt

Very short lived

Very low level

stored for decay

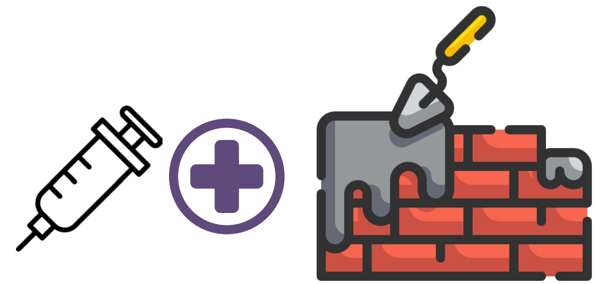
No need high containment

^{192}Ir
^{99m}Tc

NORM
Trace activation/fission products

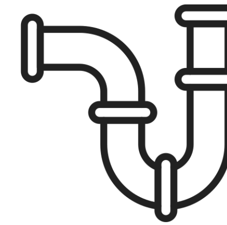
$T_{1/2}$

Acceptance criteria



IAEA No. GSG-1

Waste characterization



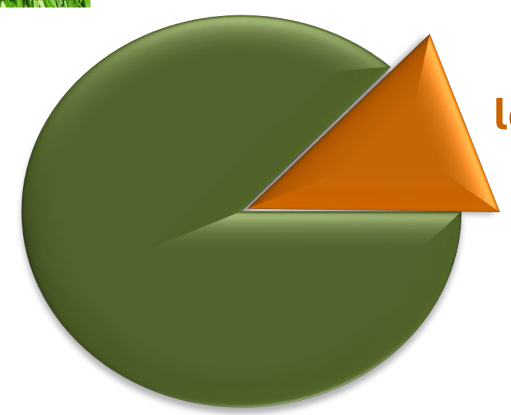
Exempt

Very short lived

Very low level

Low level

Short-lived beta/ gamma emitters



long-lived nuclides at low levels

robust containment and isolation

IAEA No. GSG-1

Waste characterization

Exempt

Very short lived

Very low level

Low level

Intermediate level

long-lived radionuclides

greater degree of containment

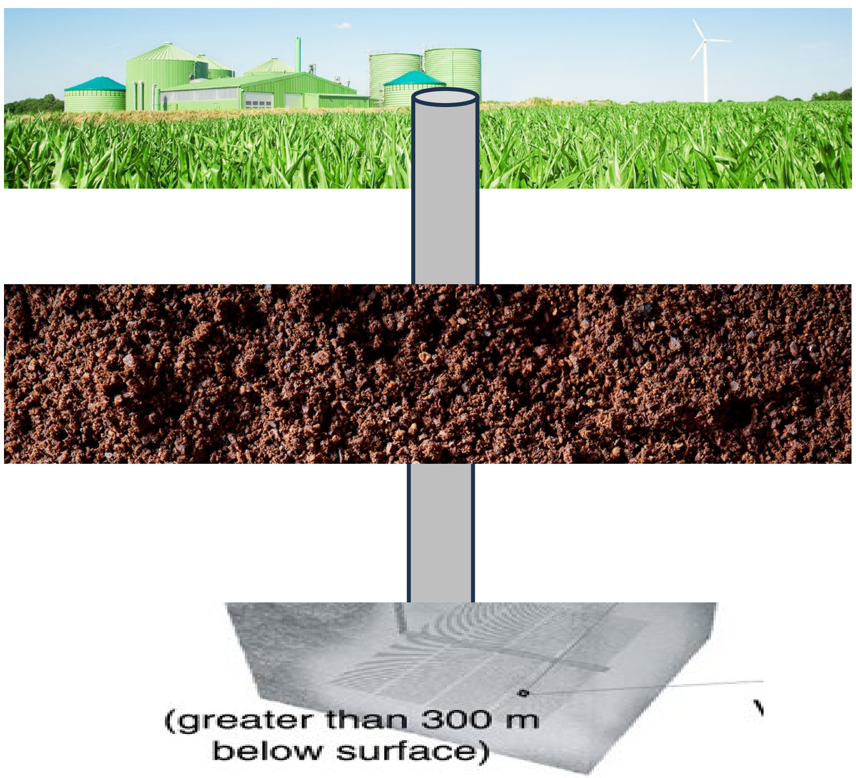
IAEA No. GSG-1

Waste characterization

Exempt

Very short lived

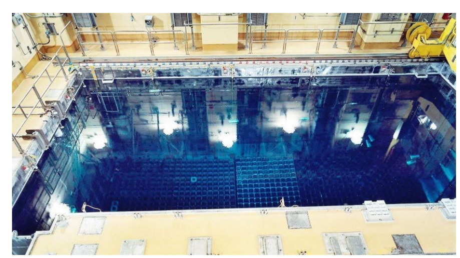
Very low level



Low level

Intermediate level

High level



Generates heat

10^4 -10^6 TBq/m^3

reprocessing of spent fuel

IAEA No. GSG-1

Methodology of sorting out the wastes

END SOLUTIONS

- Release
  - Unconditional
  - Conditional
- Radioactive waste
  - Surface disposal
  - Geological disposal

⇩

DOSE IMPACT STUDY

Separate studies/scenarios for every end solution

⇩

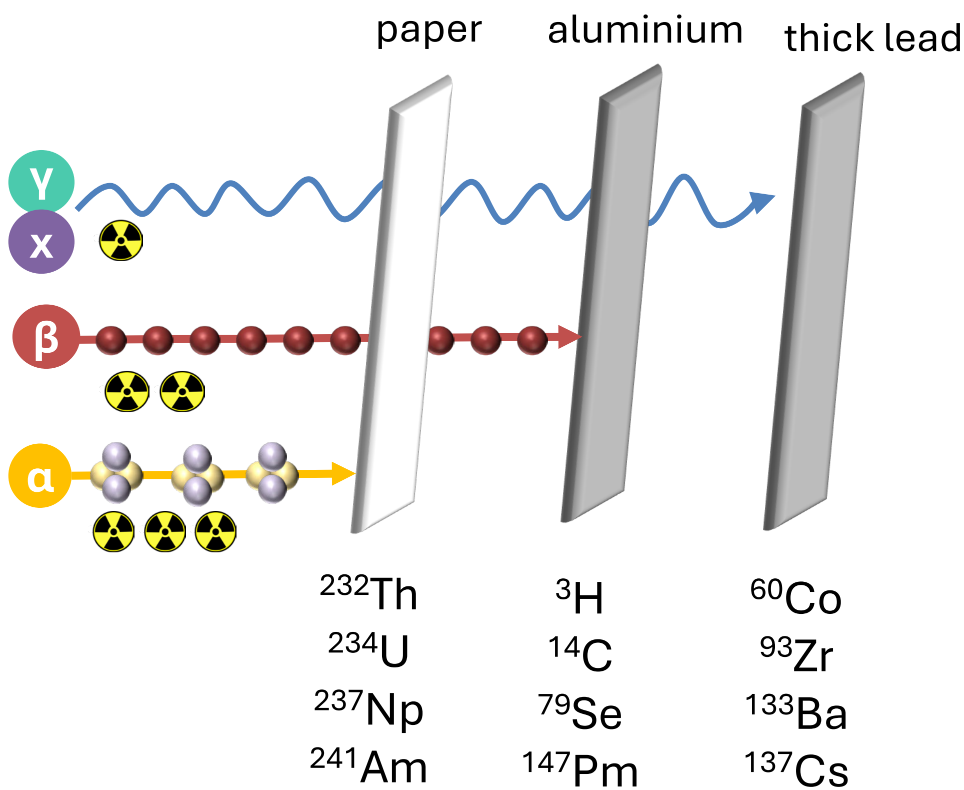
LIST OF REQUIREMENTS

Maximum activity (concentration) for each single radionuclide

All the materials have to be nuclide specific characterized due to the legislation requirements

Radiological waste characterization

Which radionuclides can be expected?



How can these radionuclides be quantified?

Non-destructive assay

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

Destructive assay

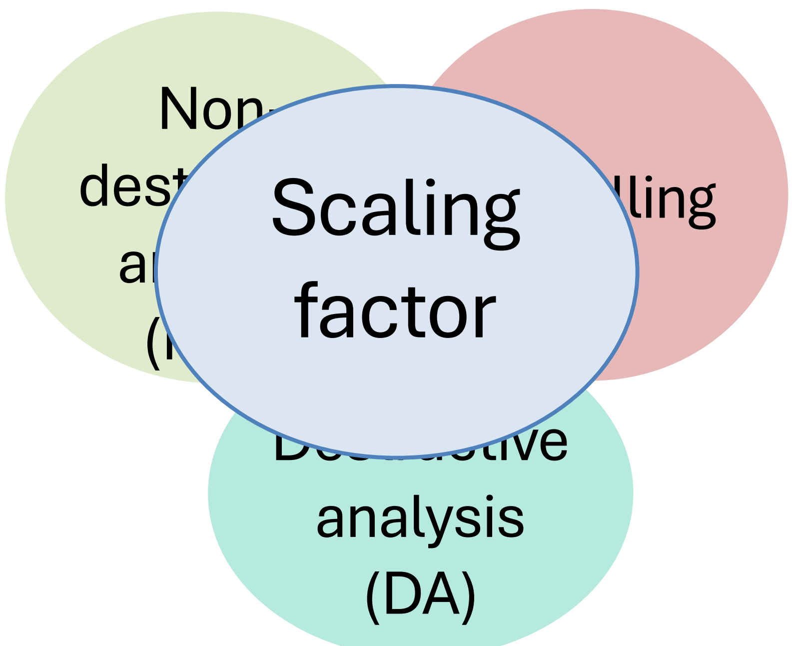
"difficult to measure" radionuclides — **DTM**

Difficult-to-measure 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

How is the activity of DTM radionuclides estimated?



Activity **ETM** radionuclides

γ-ray emitters

Mathematical correlation

REQUIRED

Activity **DTM** radionuclides

α and β particle emitters

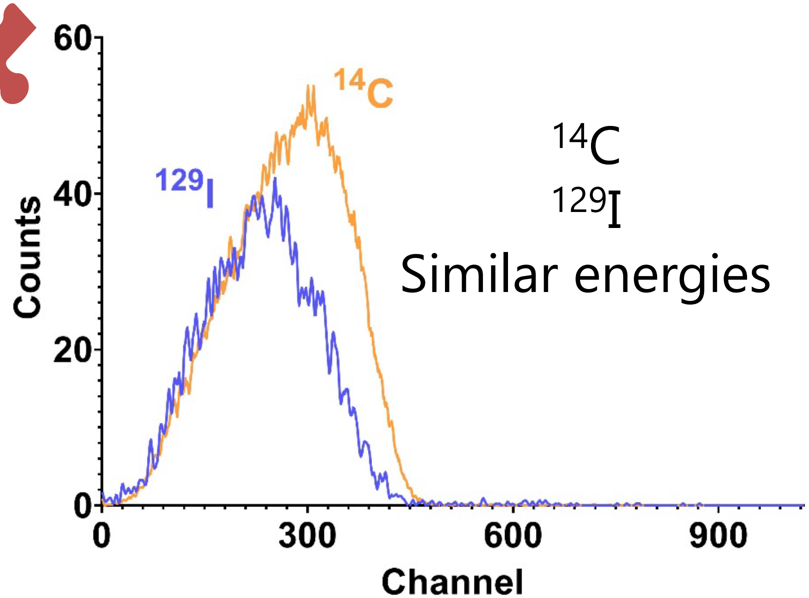
Validation using **experimental data**

General challenges

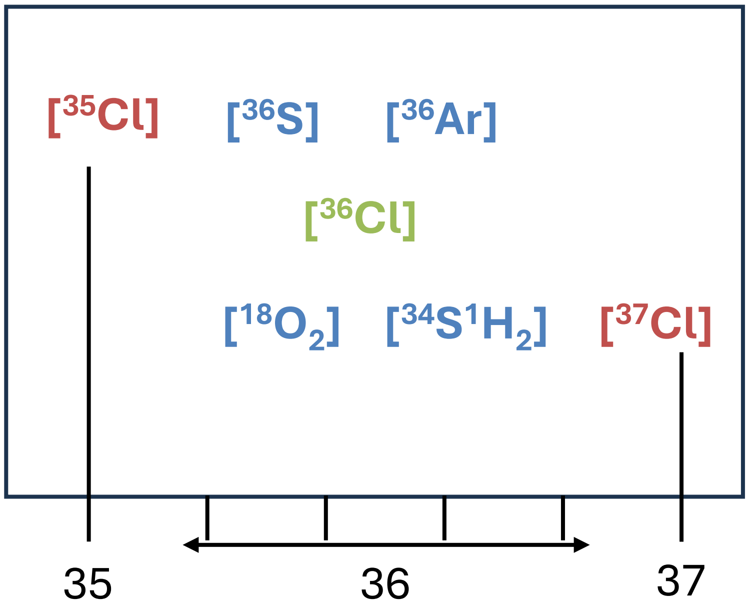
Develop and validate reliable analytical methods for the accurate determination of specific DTM radionuclides

Challenges

Interferences influencing the quantification of the activity



^{14}C
^{129}I
Similar energies



Radiometric (spectral)

Mass spectrometric (isobaric)

General challenges

Develop and validate reliable analytical methods for the accurate determination of specific DTM radionuclides

Challenges

Low detection limit **(DL)** required

Clearance level
^{36}**Cl –** 1 Bq g^{-1}

DL > clearance level

Procedure not applicable

General challenges

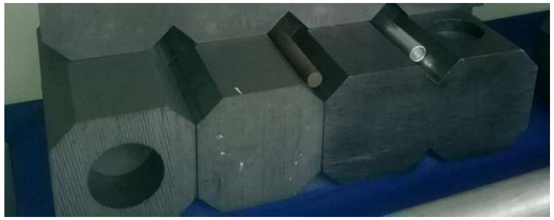
Develop and validate reliable analytical methods for the accurate determination of specific DTM radionuclides

Challenges

Variety of matrices

Sample preparation and homogenization

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



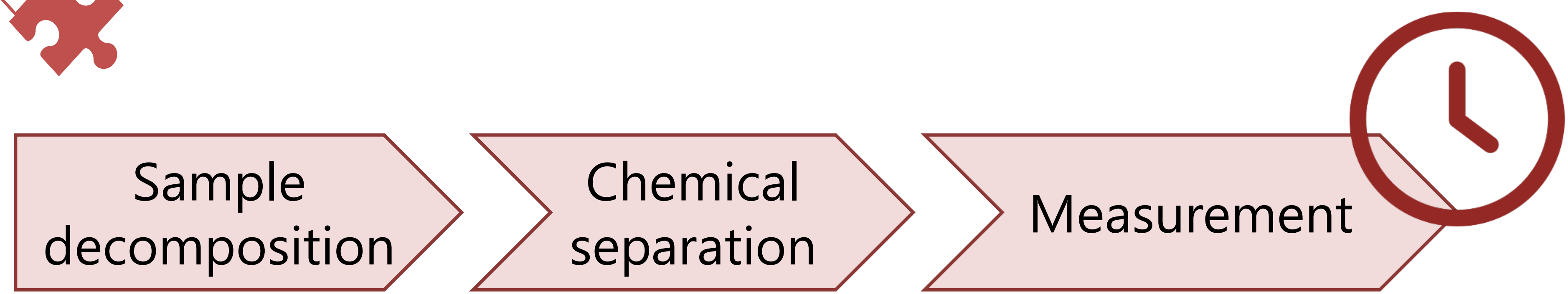
Stefan Nijst, 2014, Master Thesis

General challenges

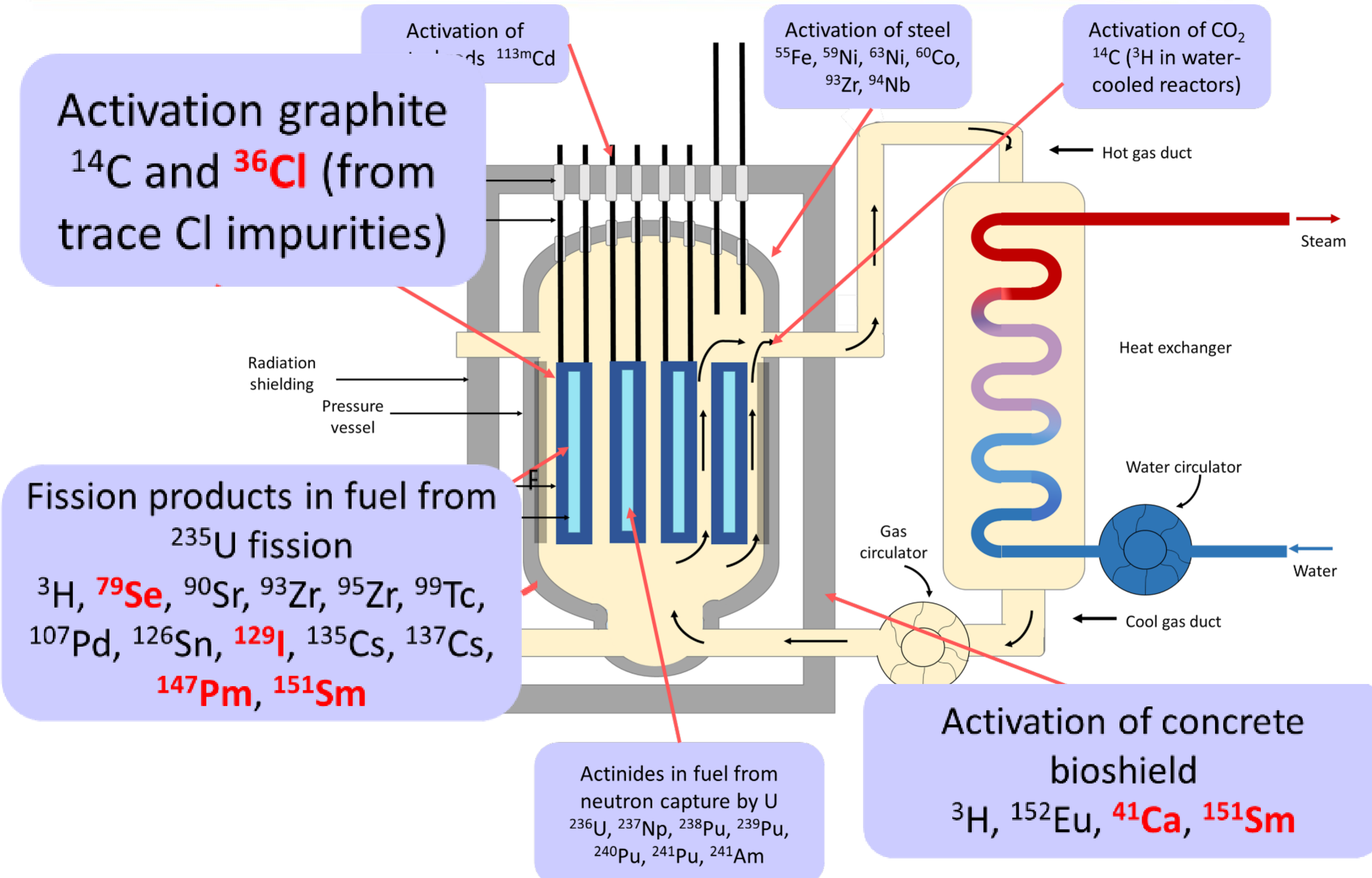
Develop and validate reliable analytical methods for the accurate determination of specific DTM radionuclides

Challenges

Turnaround time (TAT) and cost of the procedure



Selection of DTM Radionuclides



^{36}Cl and ^{129}I in decommissioning samples

Significant in terms of *half-life* and *environmental mobility for* **final waste disposal**

^{36}Cl

- Neutron activation of naturally occurring ^{35}Cl
- $\mathbf{T_{1/2}} = 3{,}02 \cdot 10^5$ year
- **β-emitter** E_{max} 709.6 keV
- Present in nuclear graphite, concrete, ion exchange resins and auxiliary circuits

Clearance level < 1 Bq/g

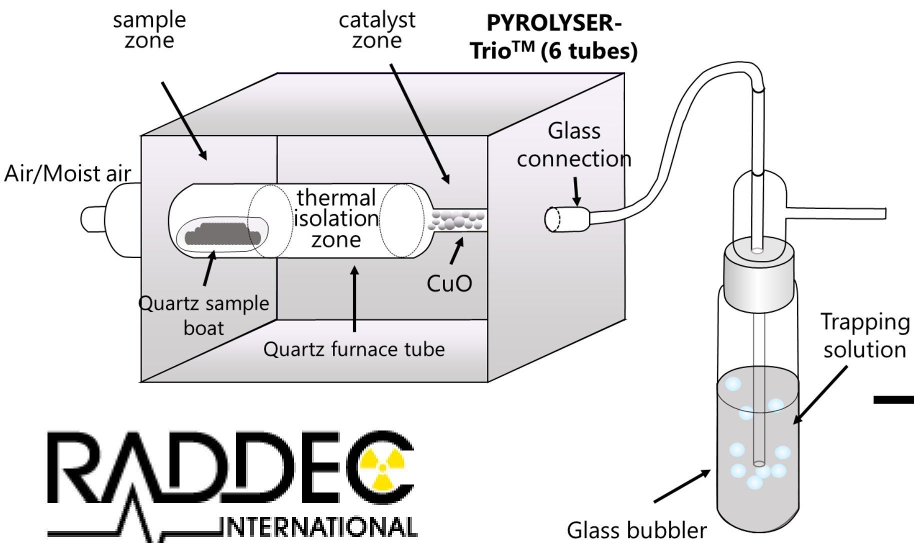
^{129}I

- Fission product of ^{235}U and neutron activation of Te
- $\mathbf{T_{1/2}} = 1{,}57 \cdot 10^7$ year
- **β-emitter** E_{max} 154 keV
- Present in activated carbon filters, ion exchange resins and spent nuclear fuel and soils

Clearance level < 0,01 Bq/g

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

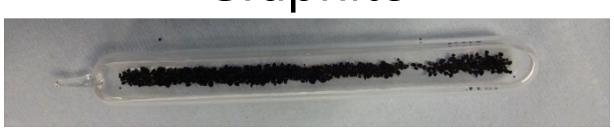
Pyrolisis (volatile elements)



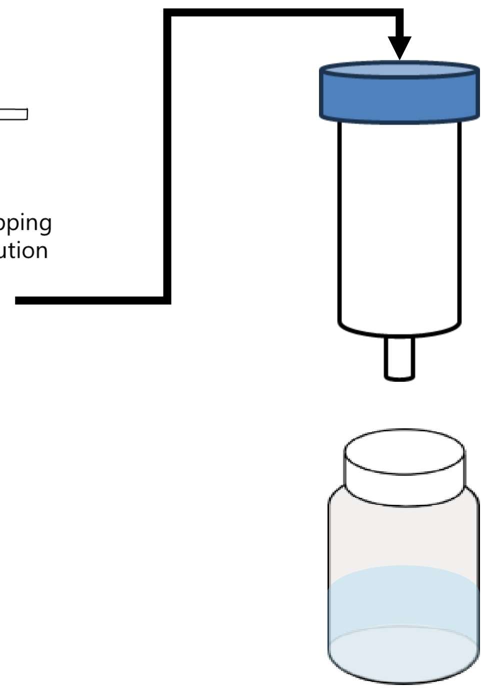
Based on Warwick et al. 2010

Concrete

Graphite



Chemical separation



LSC

Wallac Quantulus 1220™

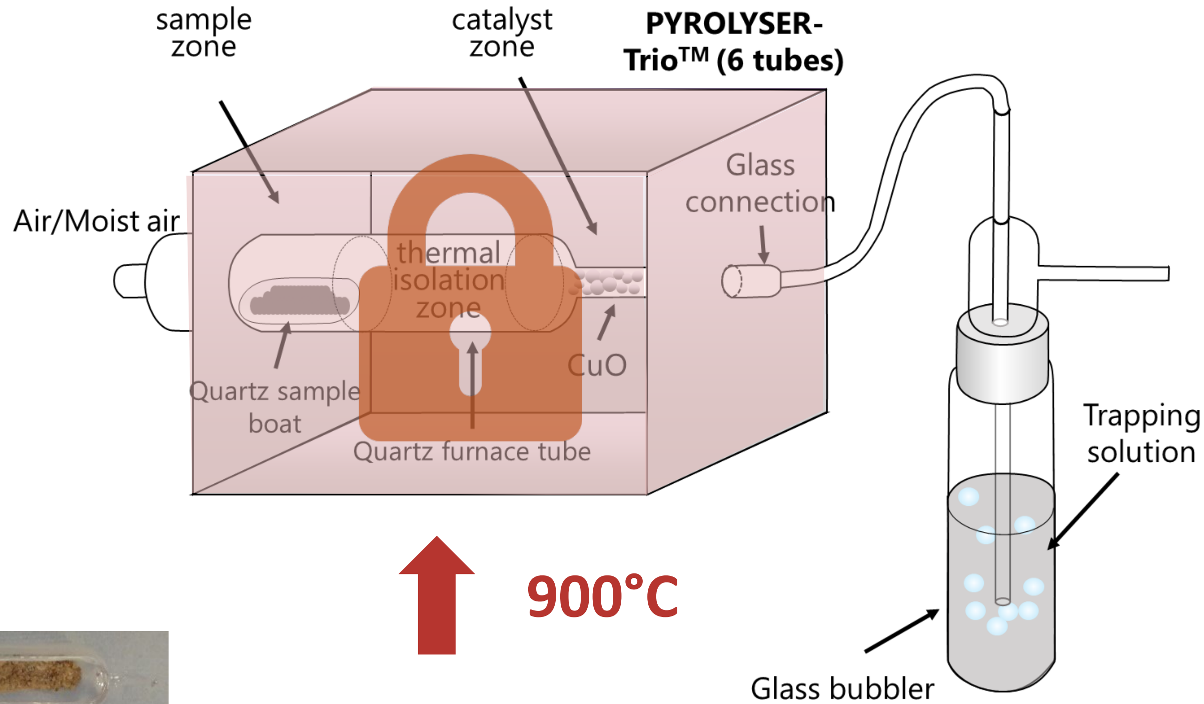
ICP-MS

η chemical recovery

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

Pyrolisis (volatile elements)

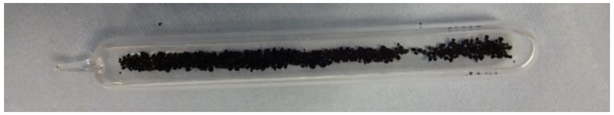
Based on Warwick et al. 2010



RADDEC INTERNATIONAL

Concrete

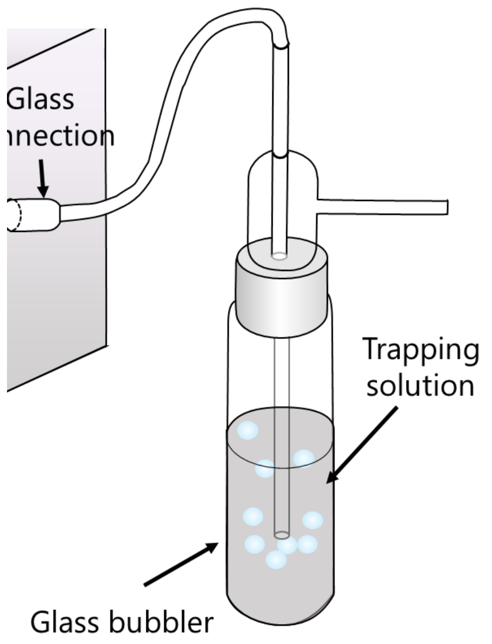
Graphite



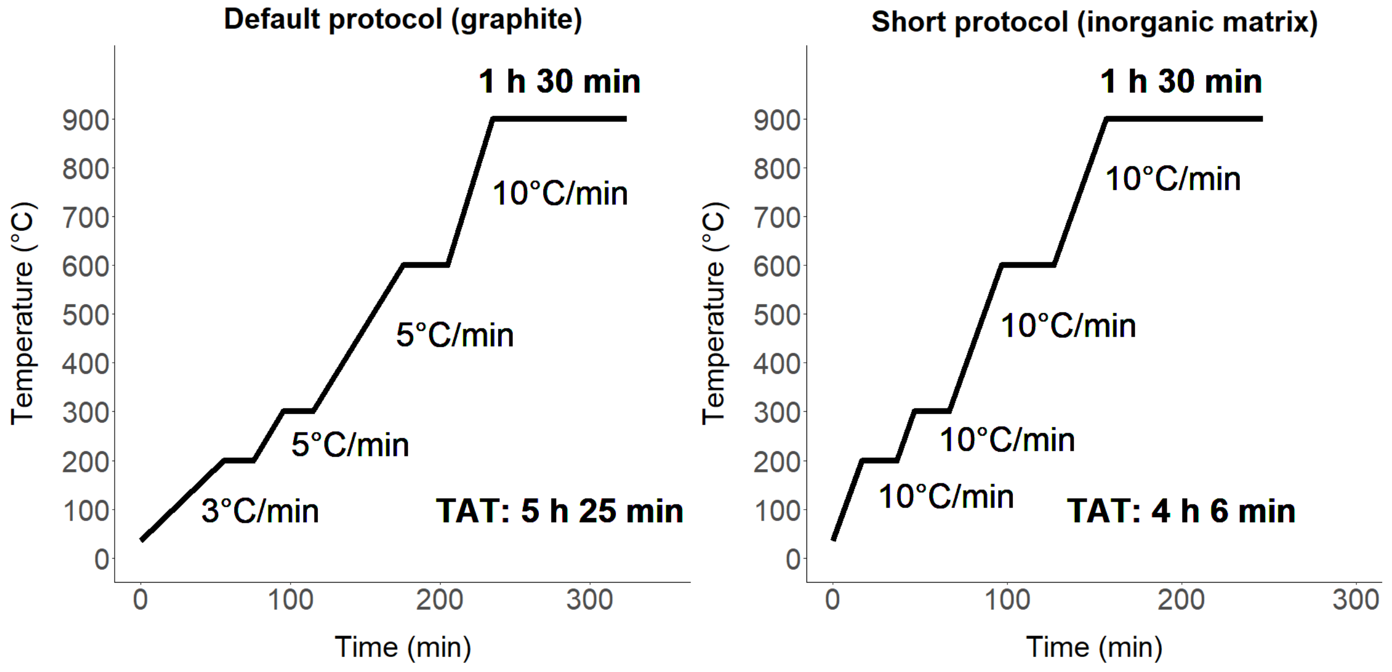
Reaction of trapping solution with Cl/I released

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

Pyrolisis (volatile elements)

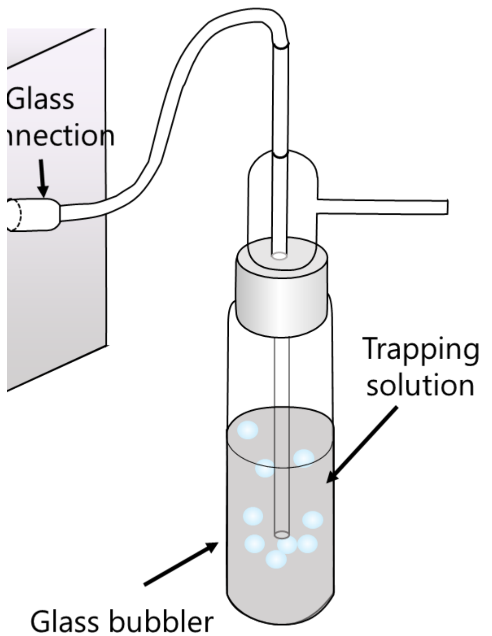


Suitable ramping temperature protocol

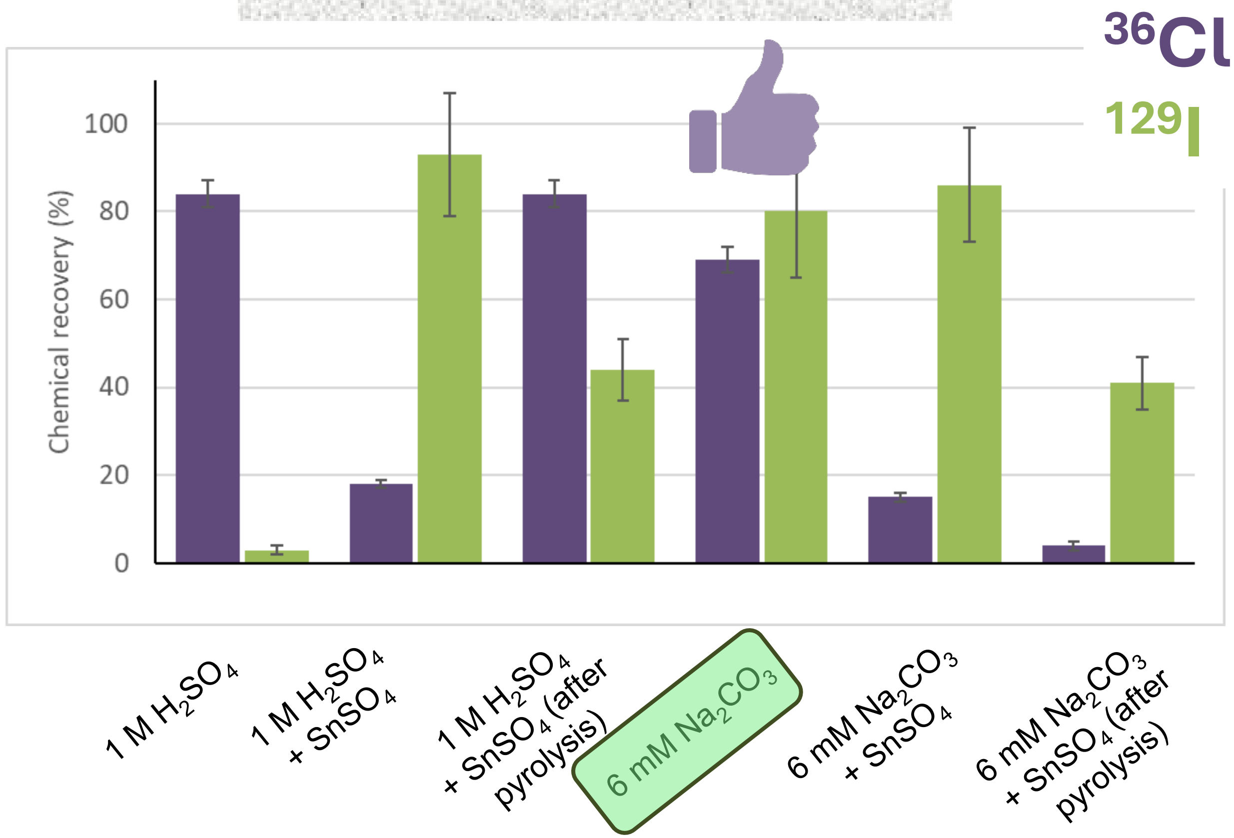


^{36}Cl and ^{129}I determination

Pyrolisis (volatile elements)

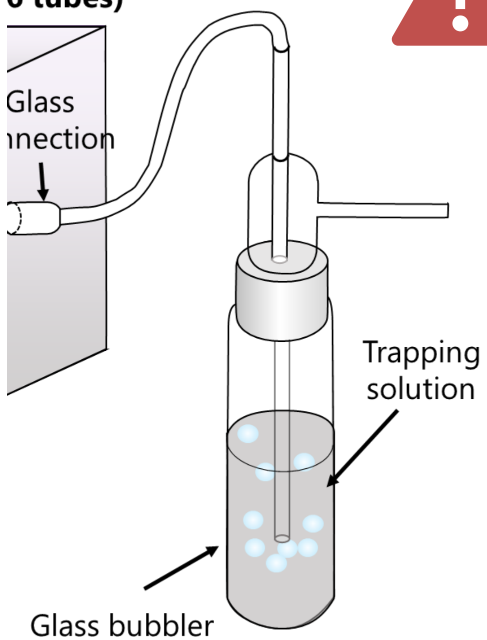


Suitable loading medium



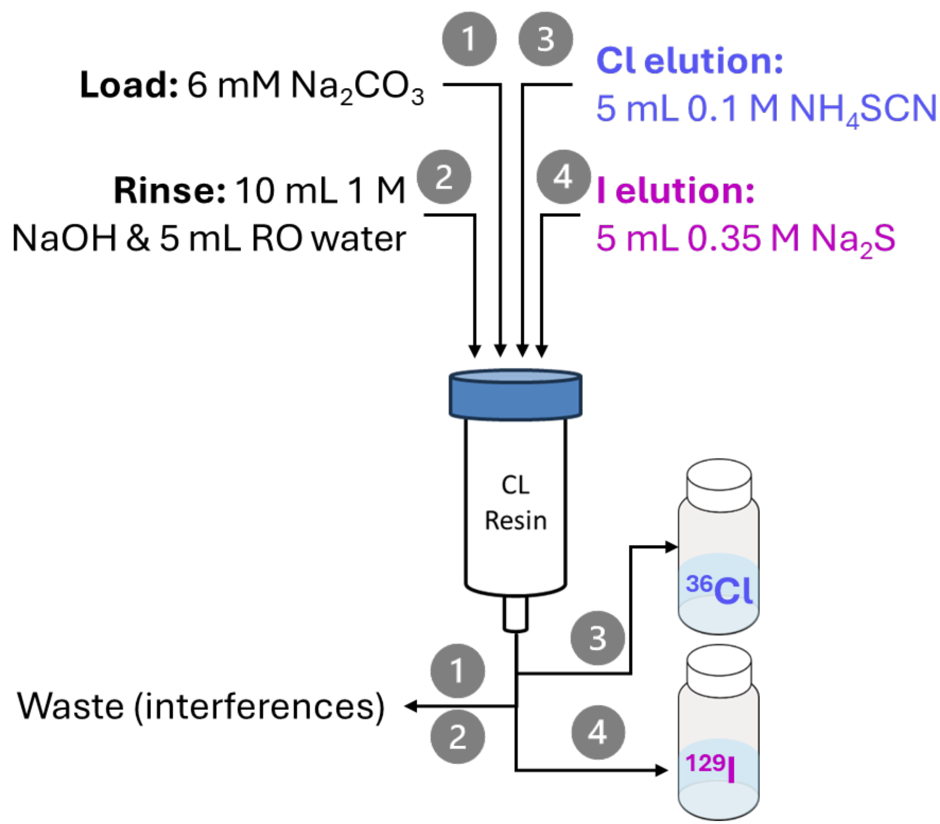
^{36}Cl and ^{129}I determination

Chemical separation and LSC measurement



6 mM Na_2CO_3

Volatile elements collected

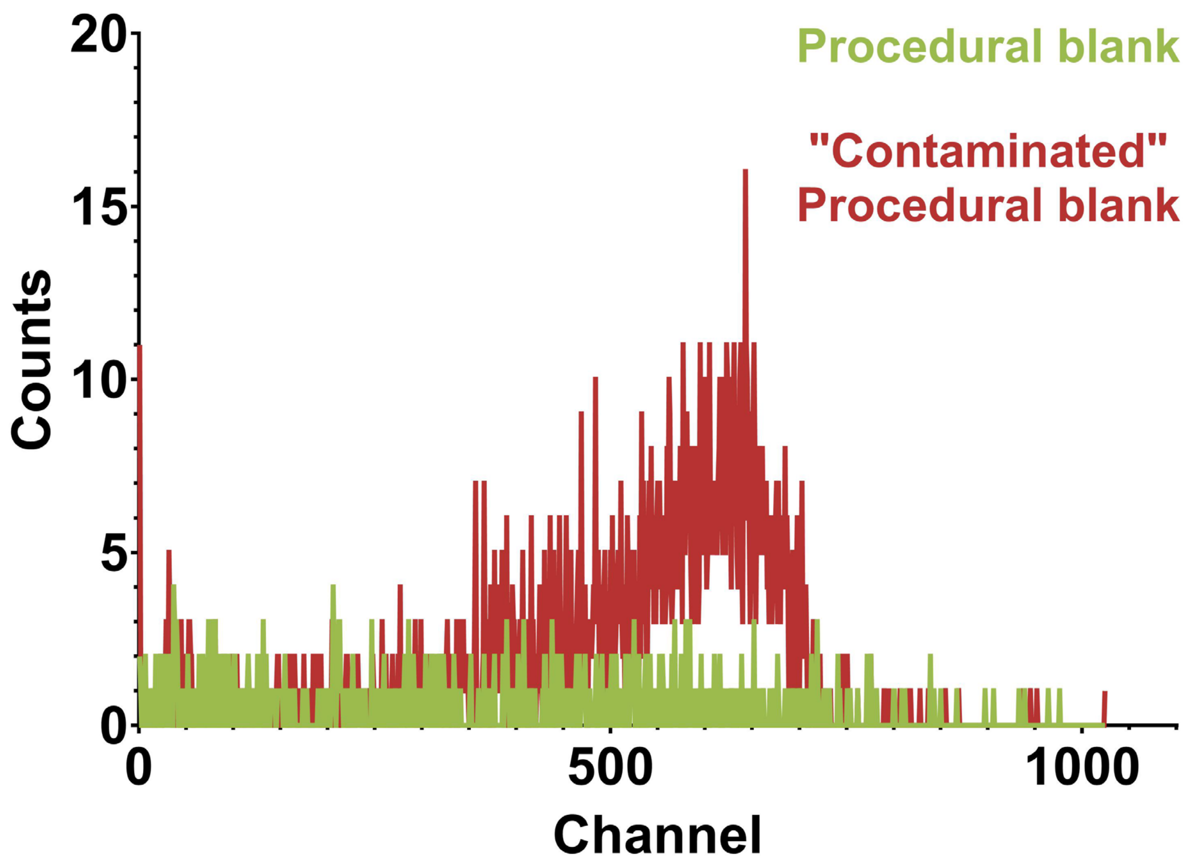


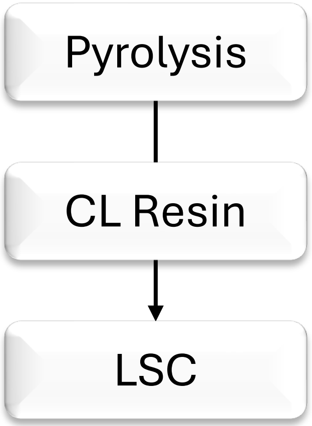
Blanks "contaminated" with ^{36}Cl

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

^{36}Cl memory effect

^{36}Cl detected on procedural blank samples

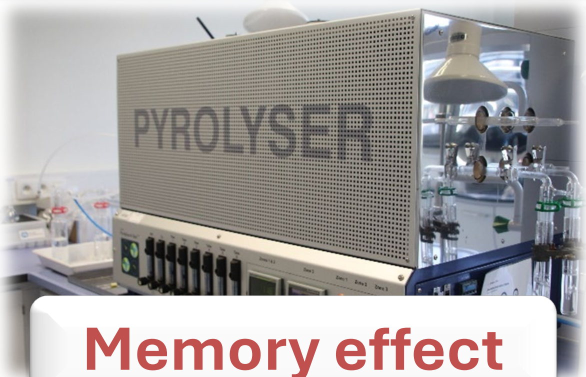




^{36}Cl and ^{129}I determination

^{36}Cl memory effect

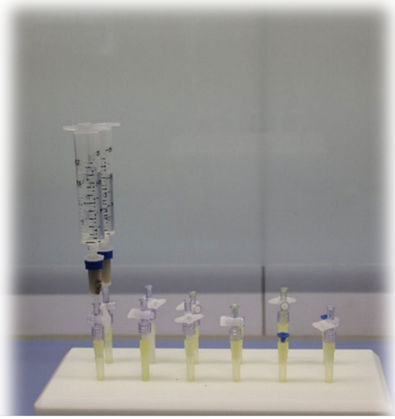
1. Sample combustion



Memory effect

Pyrolyser

2. Separation



Cross-contamination

CL Resin

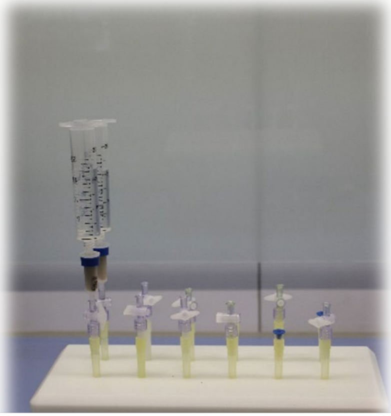
3. Measurement

Liquid Scintillation Counting (LSC)

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

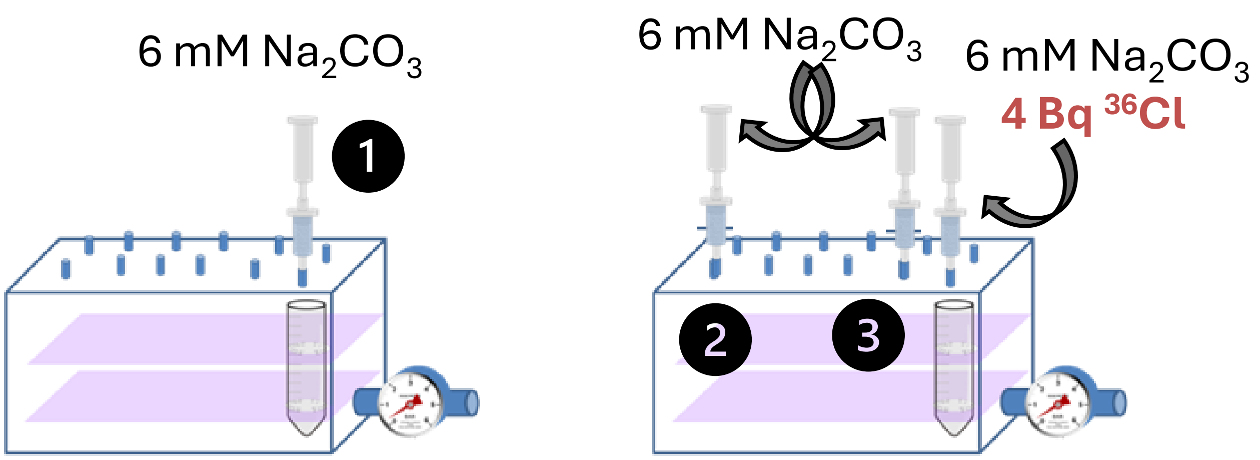
^{36}Cl memory effect

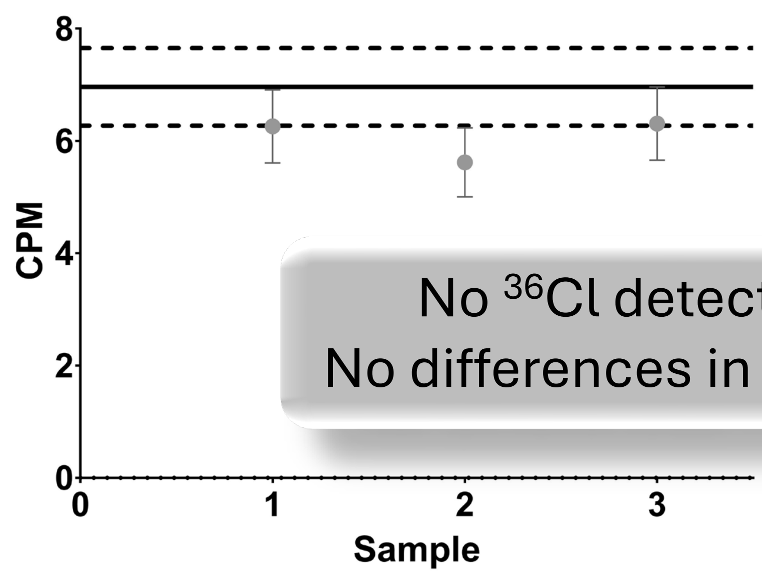
2. Separation



Cross-contamination

CL Resin



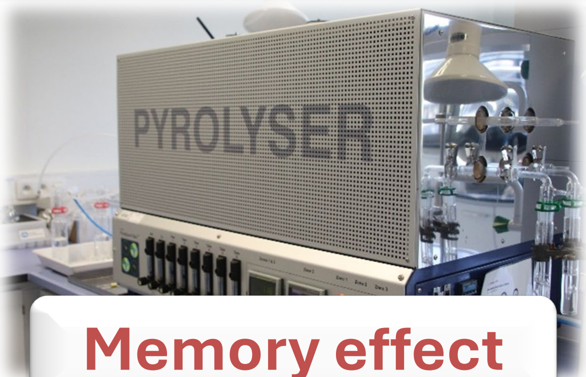


No ^{36}Cl detected
No differences in blanks

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

^{36}Cl memory effect

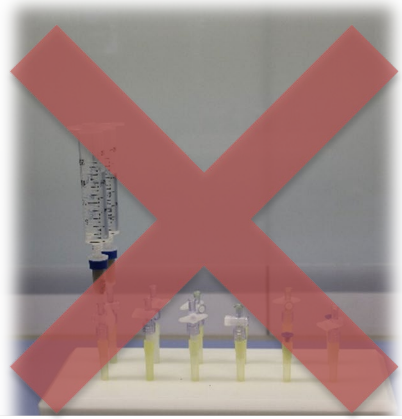
1. Sample combustion



Memory effect

Pyrolyser

2. Separation



Cross-contamination

CL Resin

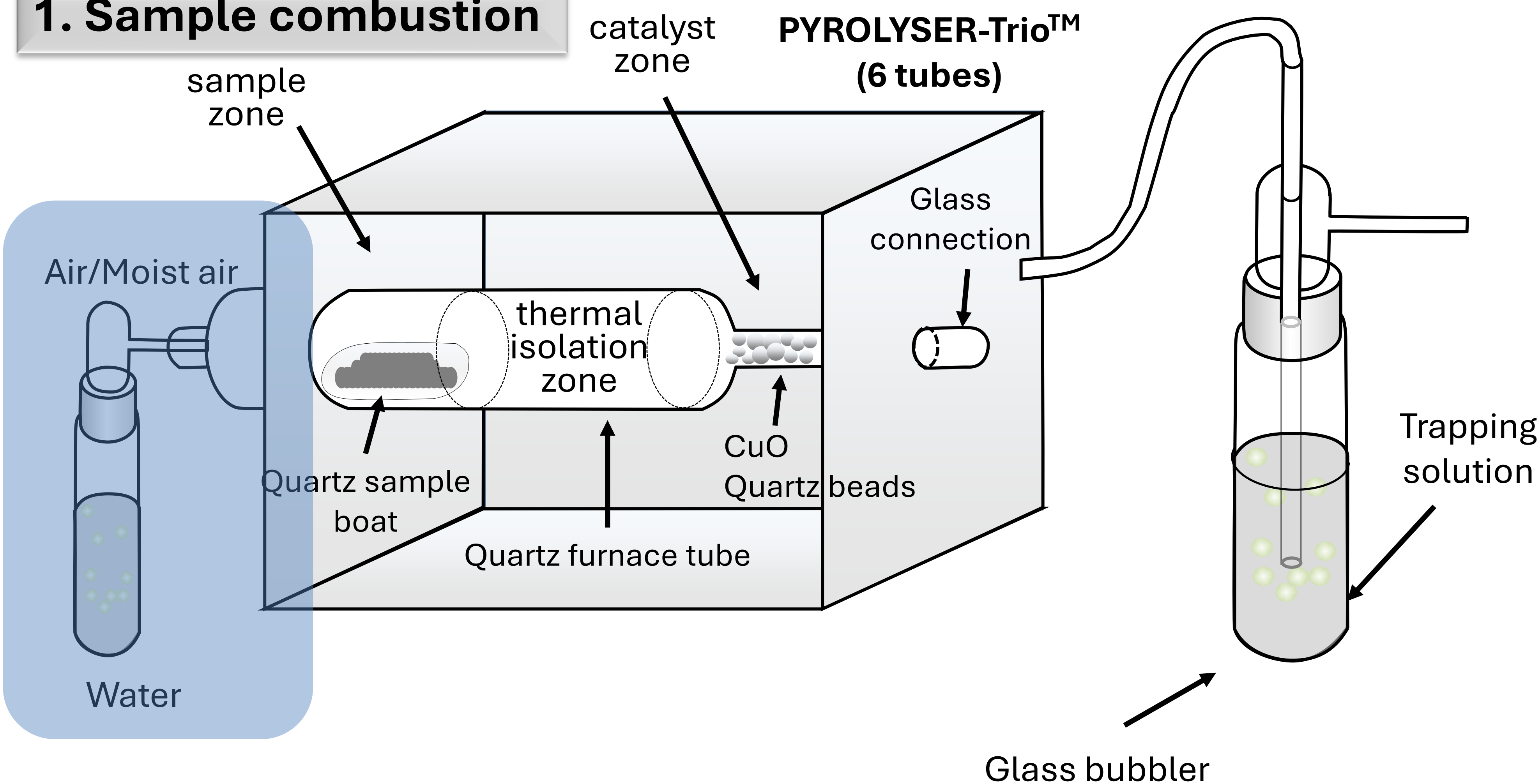
3. Measurement

Liquid Scintillation Counting (LSC)

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

^{36}Cl memory effect

1. Sample combustion



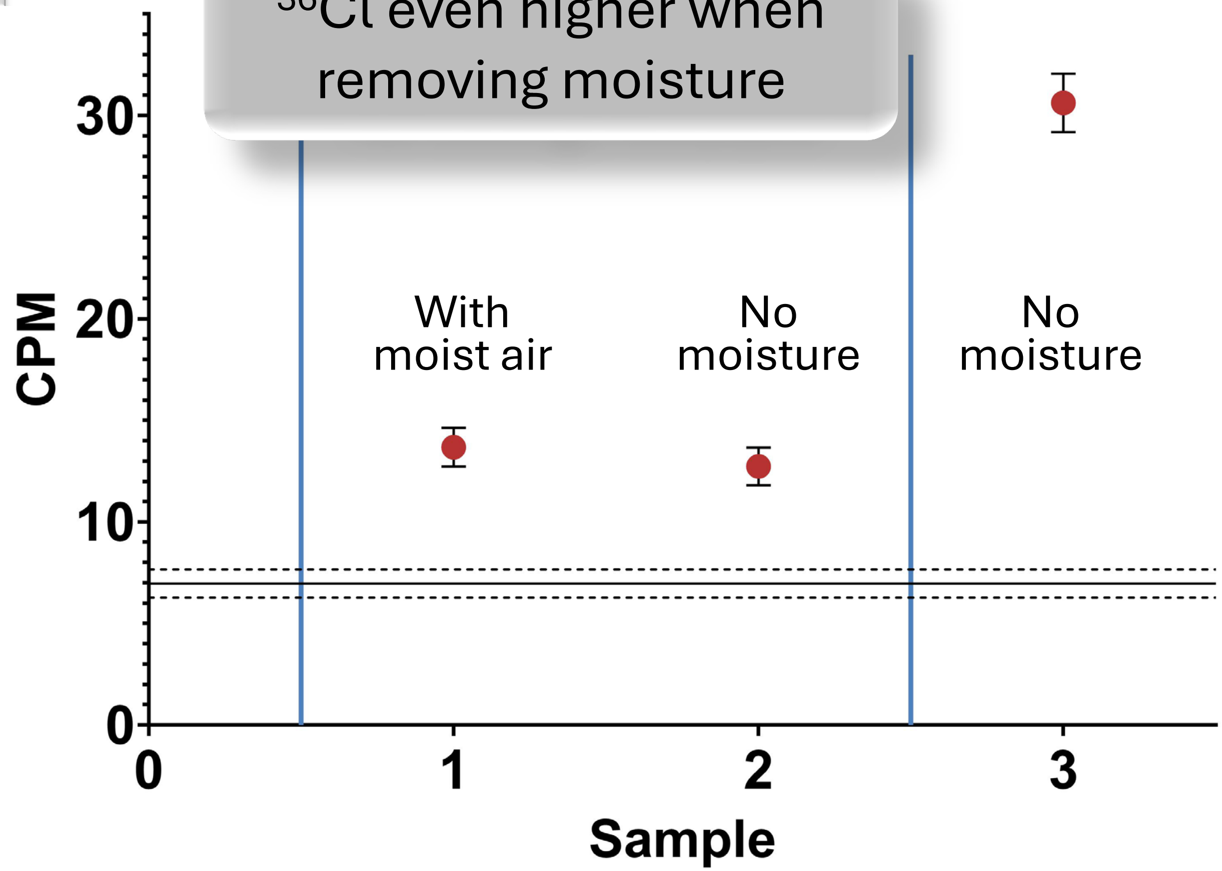
^{36}Cl and ^{129}I determination

^{36}Cl memory effect

1. Sample combustion

1. Spiked 4 Bq ^{36}Cl
2. BLANK
3. BLANK
4. Spiked 4 Bq ^{36}Cl
5. BLANK

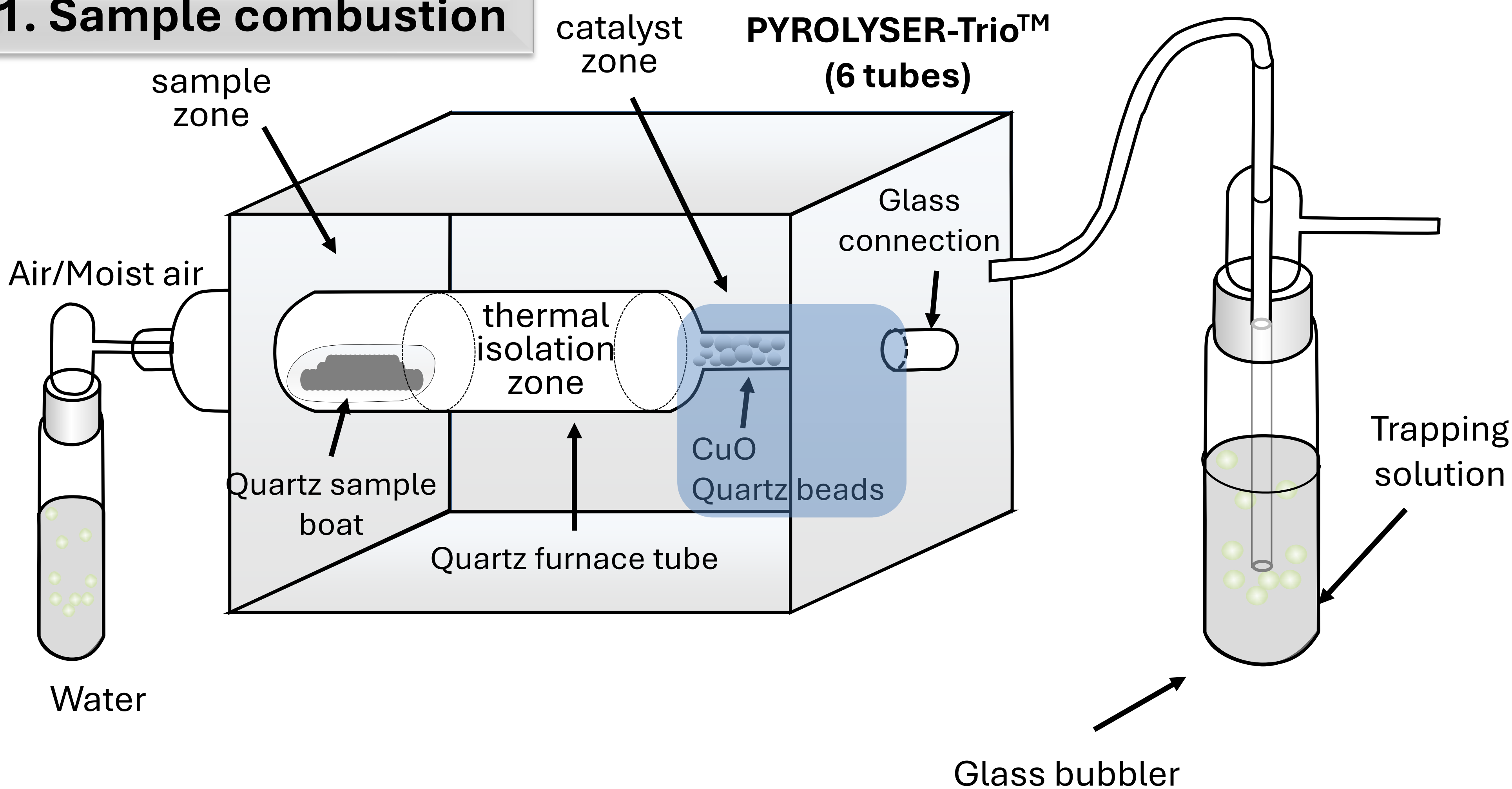
^{36}Cl even higher when removing moisture



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

^{36}Cl memory effect

1. Sample combustion



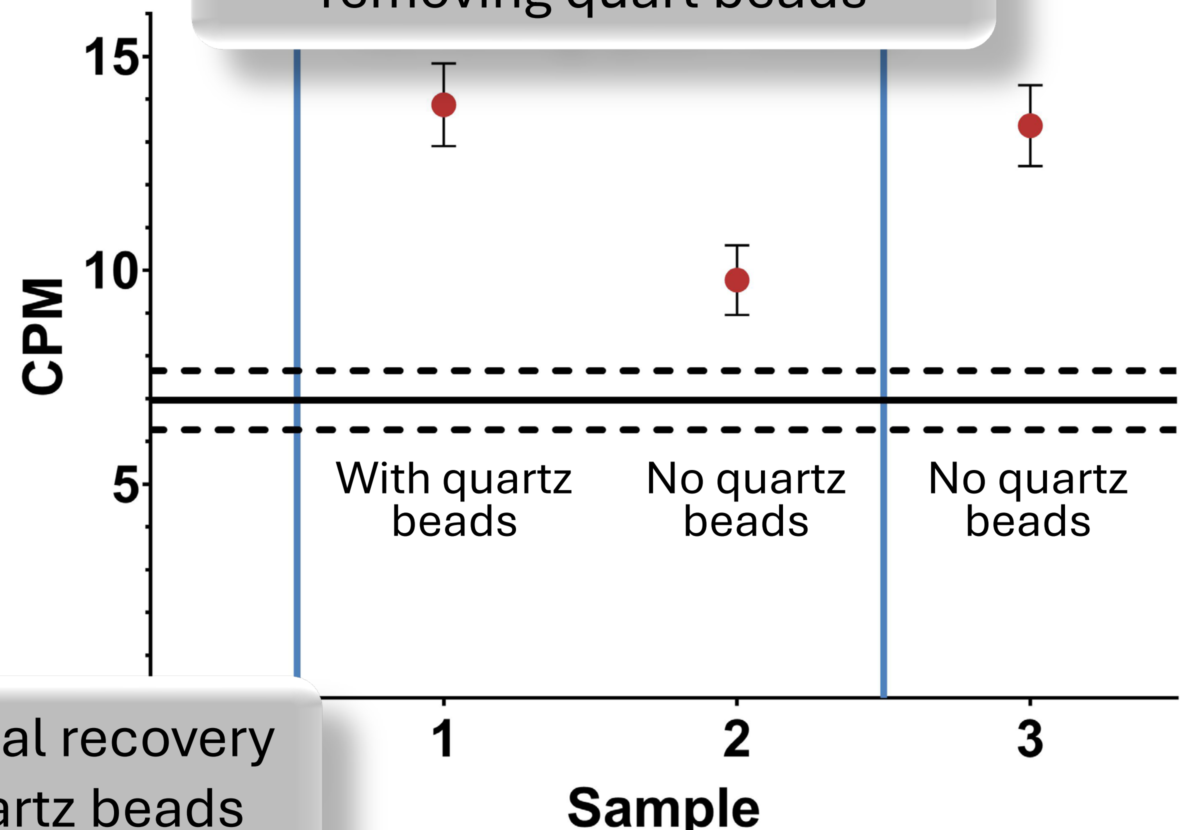
^{36}Cl and ^{129}I determination

^{36}Cl memory effect

1. Sample combustion

1. Spiked 4 Bq ^{36}Cl
2. BLANK
3. BLANK
4. Spiked 4 Bq ^{36}Cl
5. BLANK

^{36}Cl decreased when removing quart beads



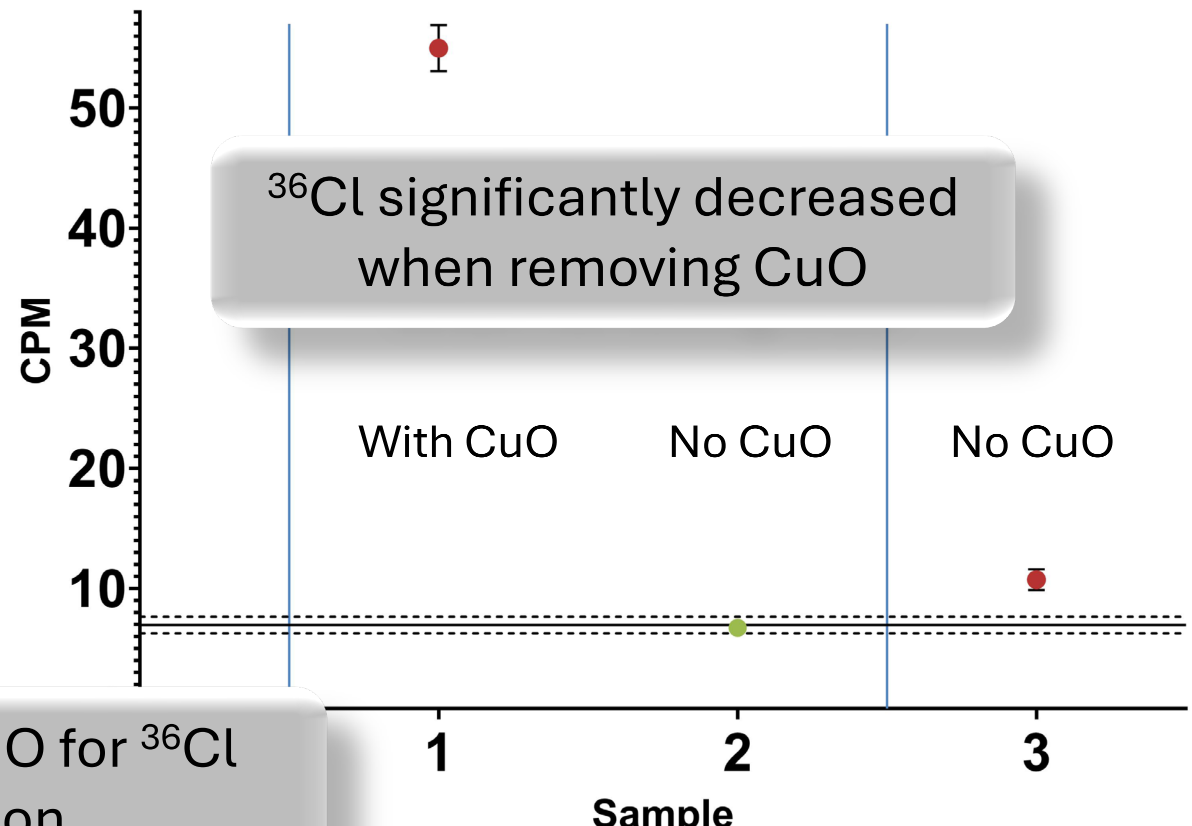
✓ No effect on chemical recovery when removing quartz beads

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

^{36}Cl memory effect

1. Sample combustion

1. Spiked 4 Bq ^{36}Cl
2. BLANK
3. BLANK
4. Spiked 4 Bq ^{36}Cl
5. BLANK



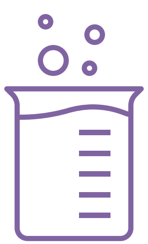
No need to use CuO for ^{36}Cl determination

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

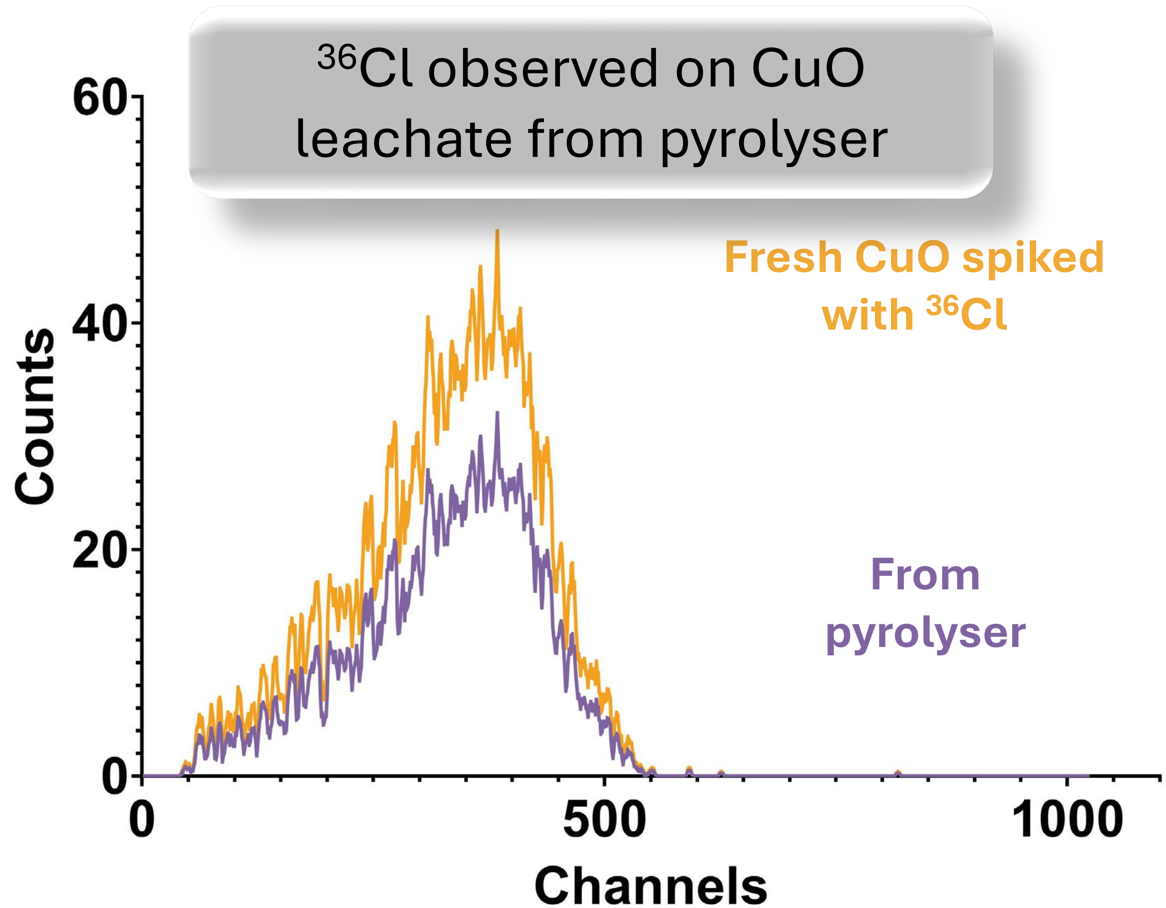
^{36}Cl memory effect

1. Sample combustion

From pyrolyser



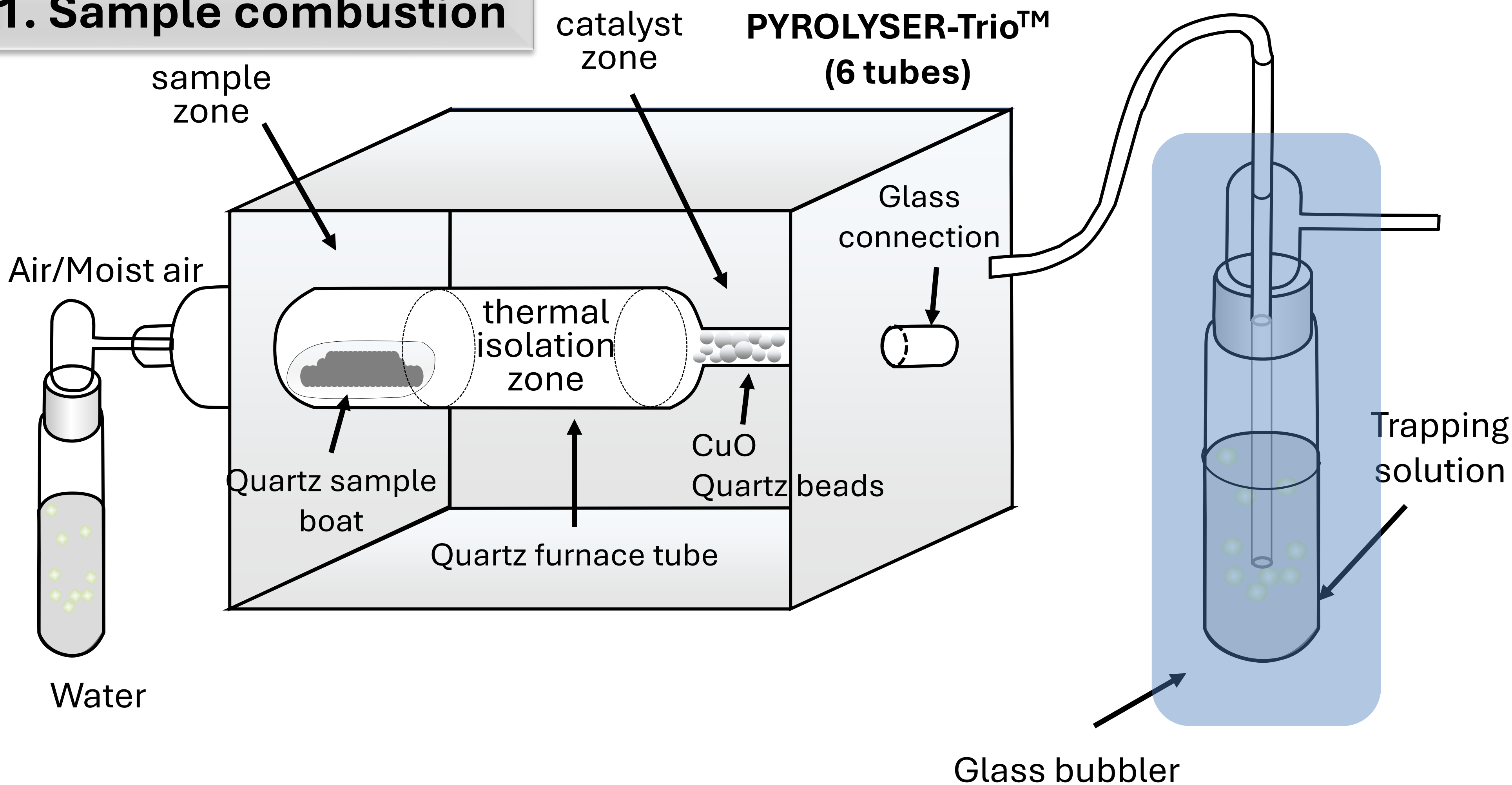
Fresh CuO spiked with ^{36}Cl



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

^{36}Cl memory effect

1. Sample combustion

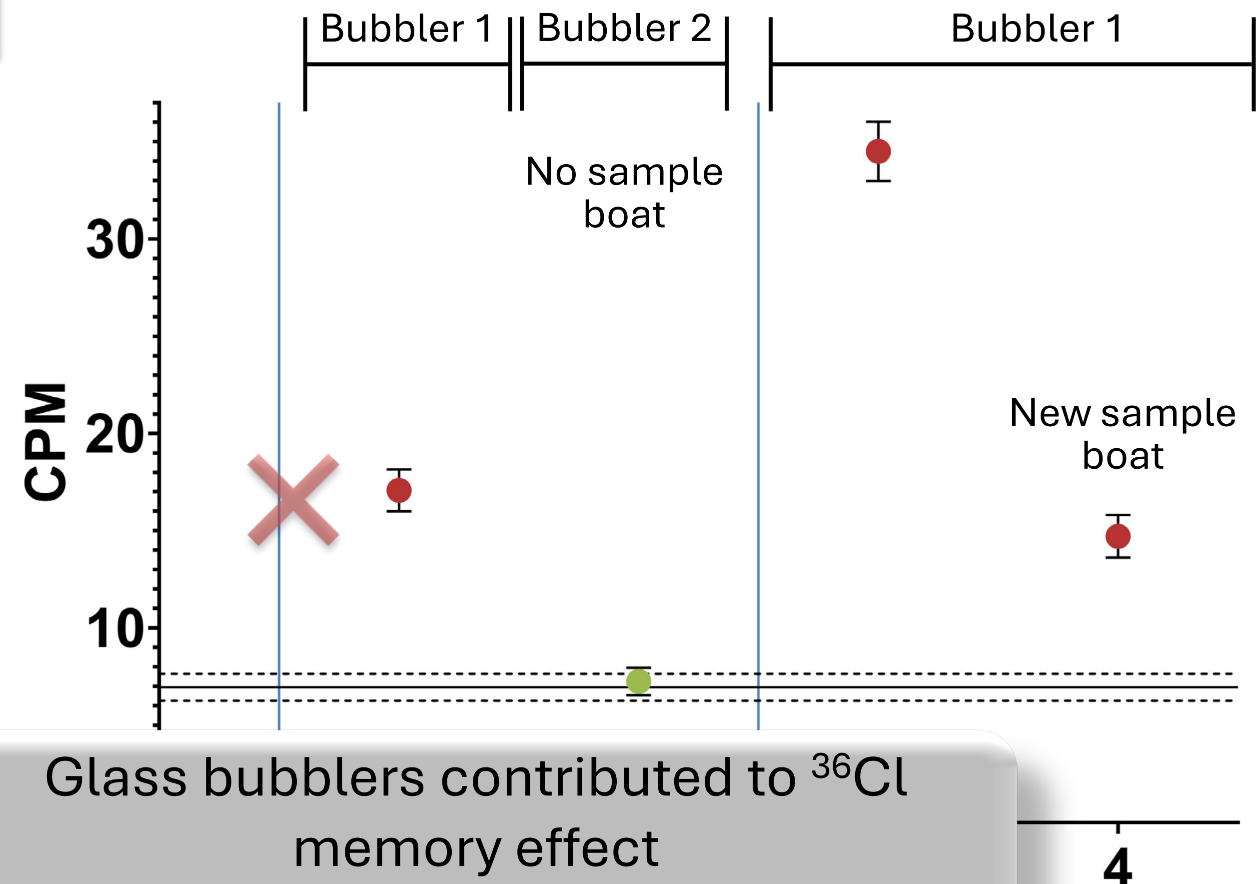


^{36}Cl and ^{129}I determination

^{36}Cl memory effect

1. Sample combustion

1. Spiked 4 Bq ^{36}Cl
2. BLANK, bubbler 1
3. BLANK, bubbler 2, no sample boat
4. Spiked 4 Bq ^{36}Cl
5. BLANK , bubbler 1
6. BLANK , bubbler 1, new sample boat

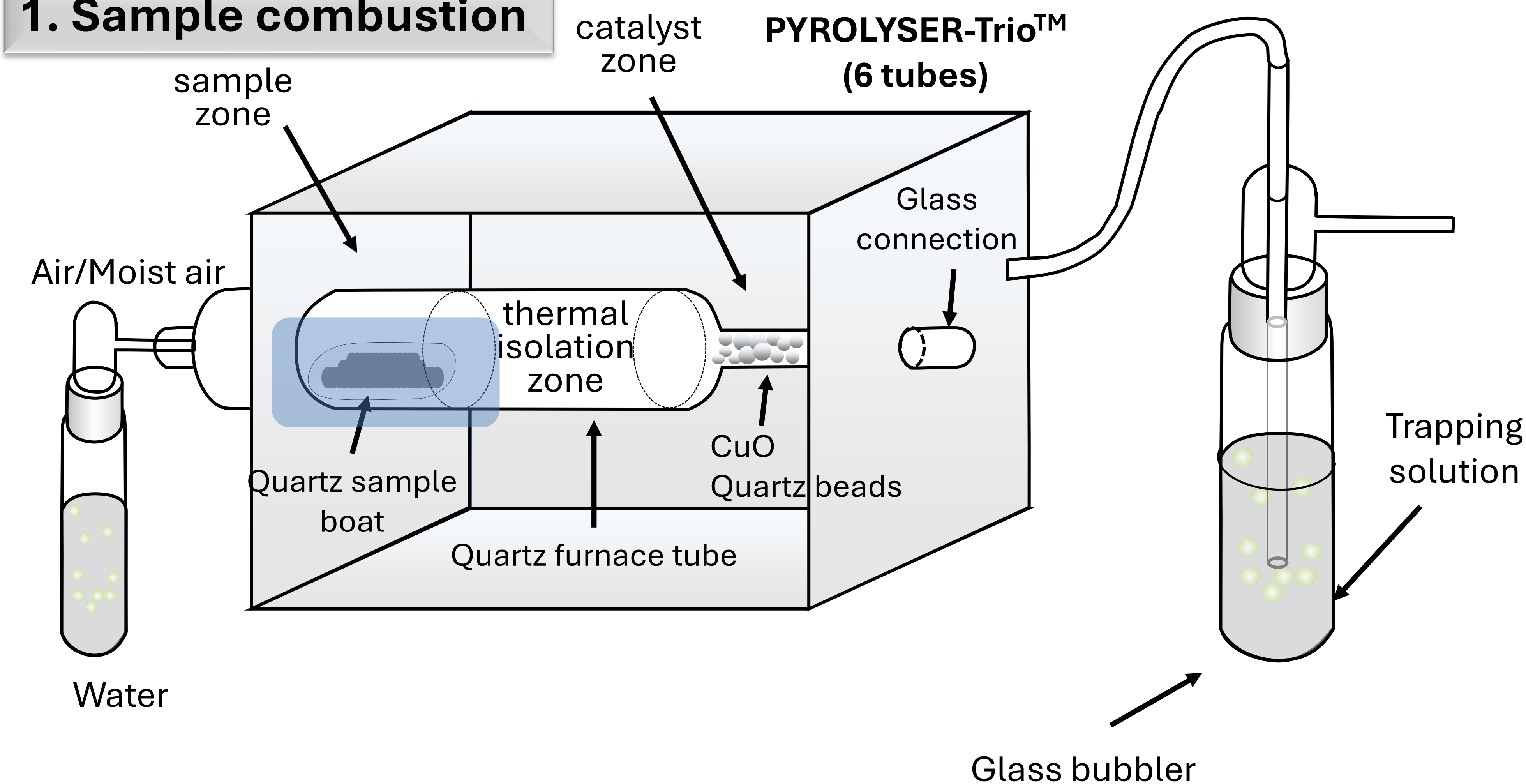


Glass bubblers contributed to ^{36}Cl memory effect
Not the only contributors

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

^{36}Cl memory effect

1. Sample combustion

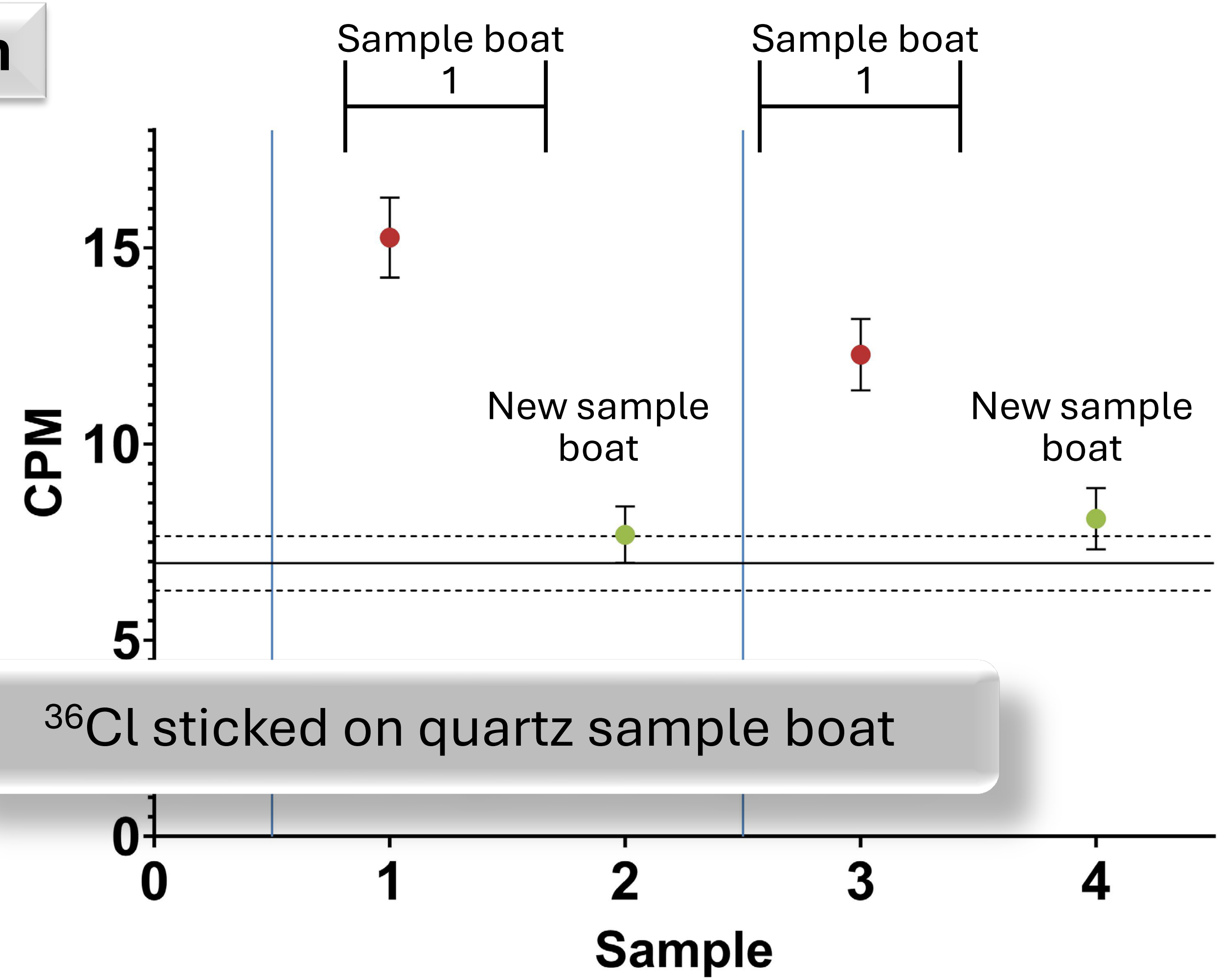


^{36}Cl and ^{129}I determination

^{36}Cl memory effect

1. Sample combustion

1. Spiked 4 Bq ^{36}Cl
2. BLANK
3. BLANK, new sample boat
4. Spiked 4 Bq ^{36}Cl
5. BLANK
6. BLANK, new sample boat

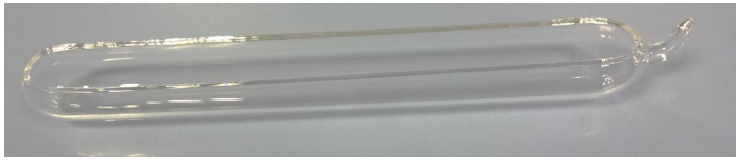


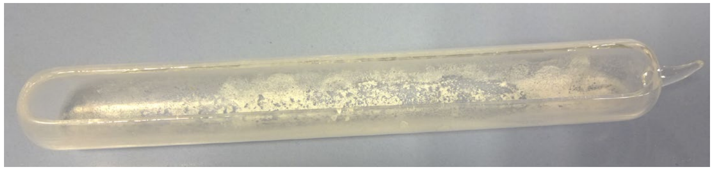
^{36}Cl sticked on quartz sample boat

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

^{36}Cl memory effect

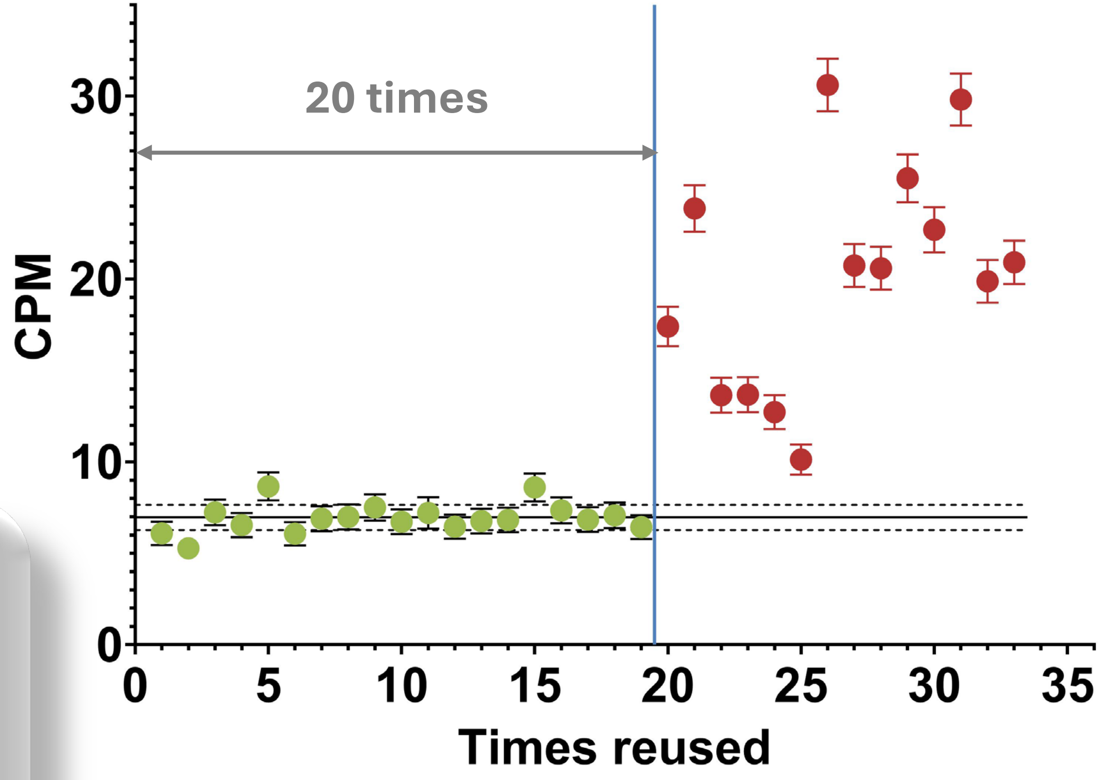
1. Sample combustion





Ageing effect observed on quartz sample boats

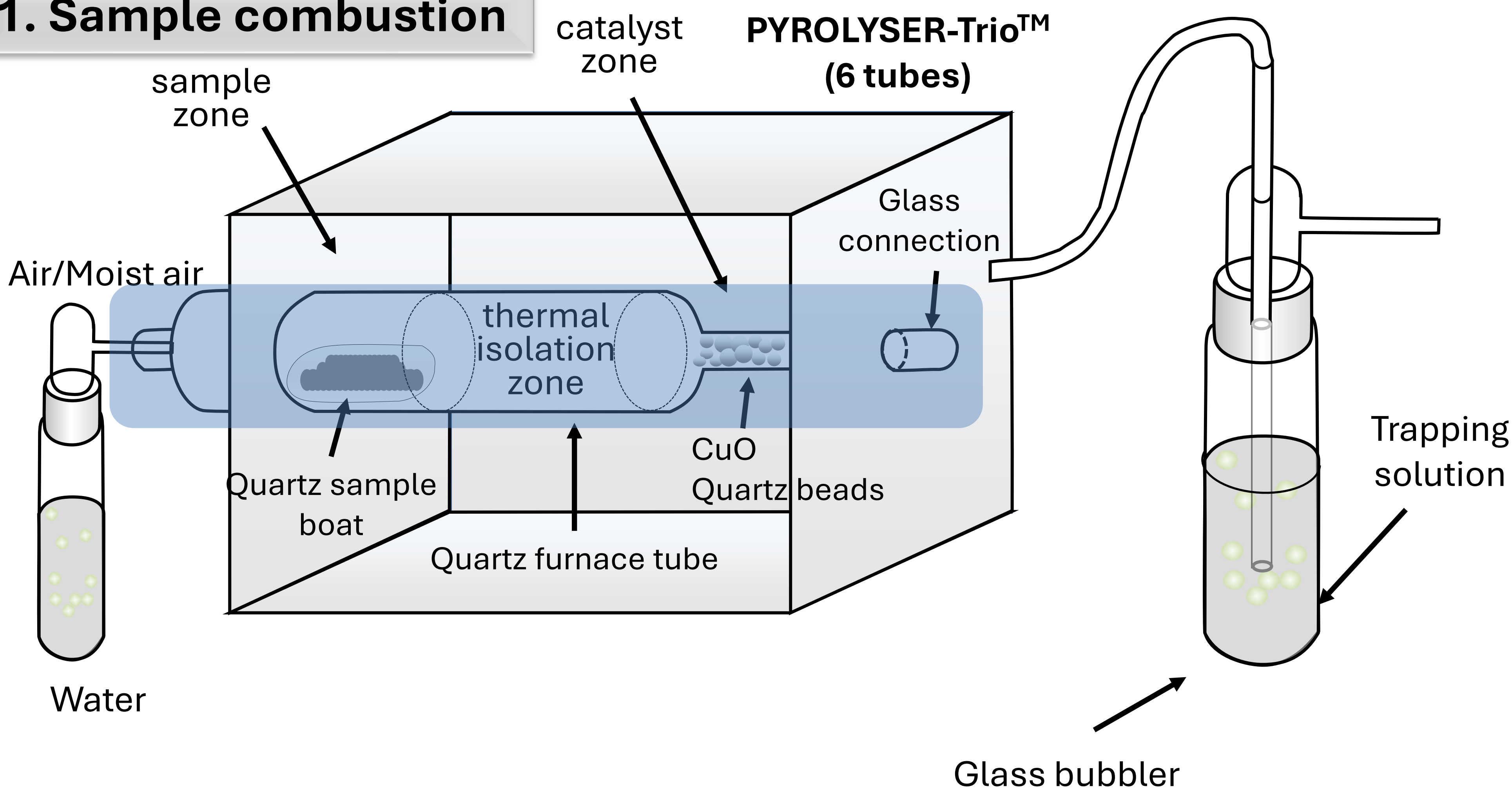
^{36}Cl measured after **20 times** reusing the materials



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

^{36}Cl memory effect

1. Sample combustion

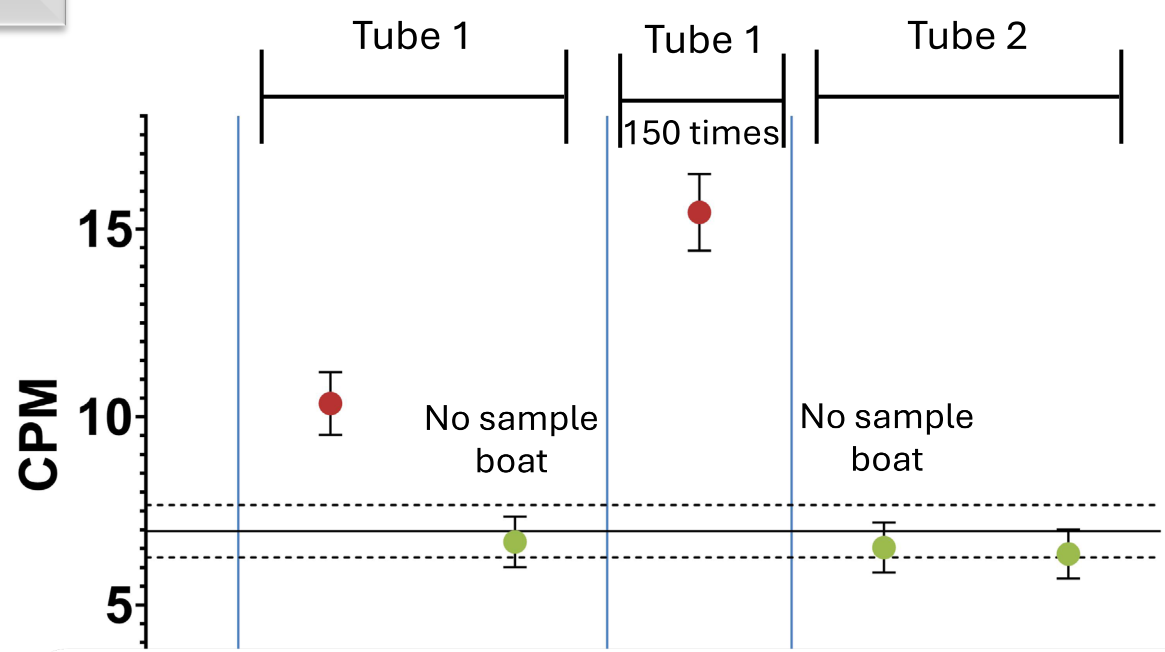


^{36}Cl and ^{129}I determination

^{36}Cl memory effect

1. Sample combustion

1. Spiked 4 Bq ^{36}Cl
2. BLANK
3. BLANK, no sample boat
4. Spiked 4 Bq ^{36}Cl
5. BLANK, reused tube 150 times
6. Spiked 4 Bq ^{36}Cl
7. BLANK, no sample boat
8. BLANK



Ageing effect observed on quartz tubes

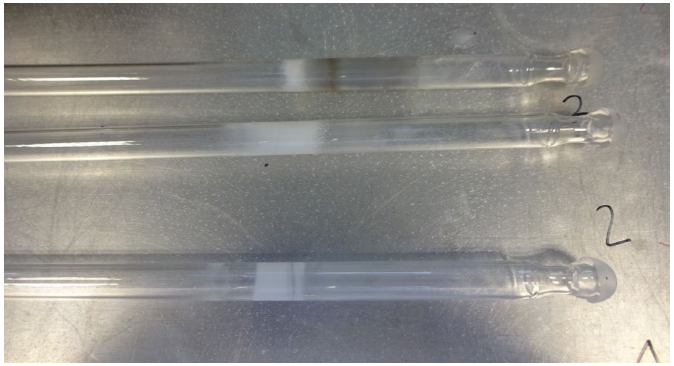
^{36}Cl measured after **150 times** reusing the materials

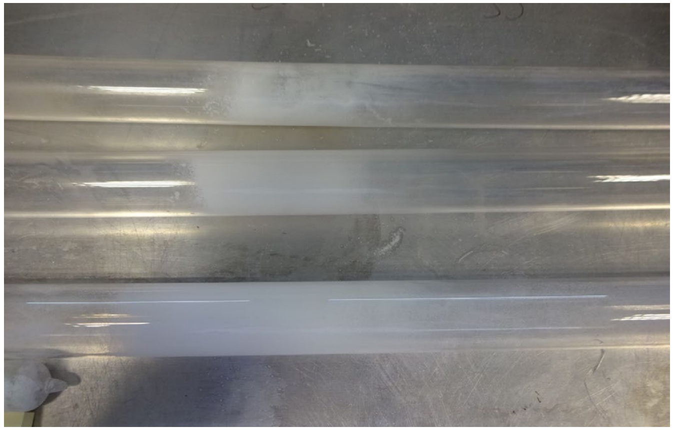
^{36}Cl and ^{129}I determination

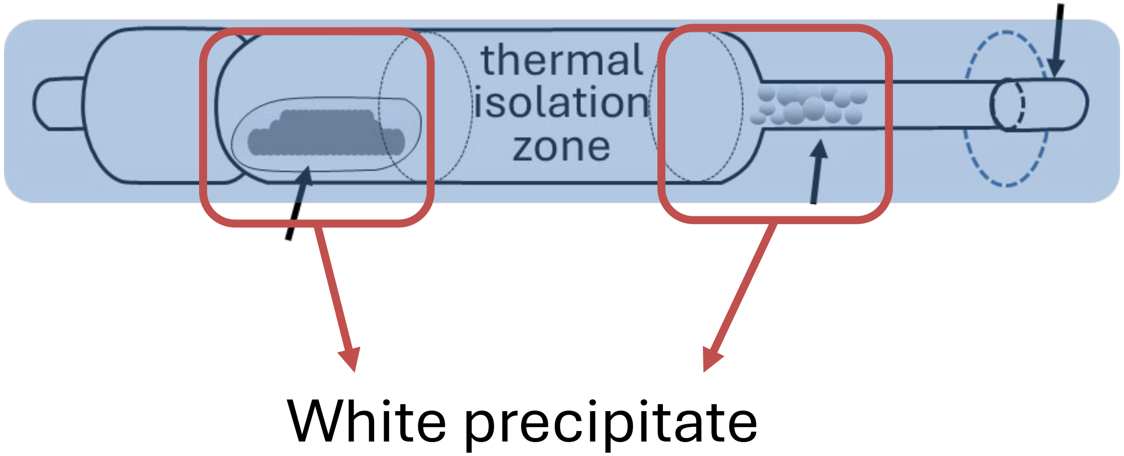
^{36}Cl memory effect

1. Sample combustion

Used for 163 experiments with ^{36}Cl-containing samples



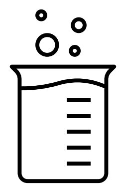




^{36}Cl and ^{129}I determination

^{36}Cl memory effect

1. Sample combustion

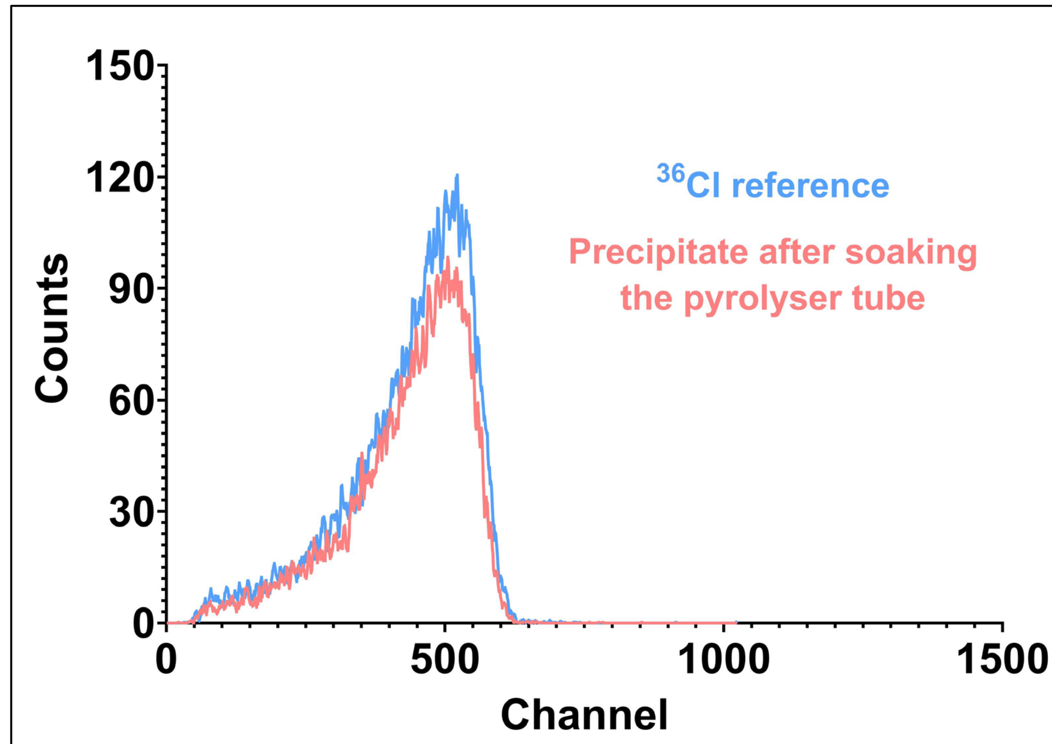


Addition $AgNO_3$

AgCl(s)

7 mL NH_3

LSC measurement



^{36}Cl presence on tubes reused for more than 163 experiments

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

^{36}Cl memory effect

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

Can be removed

Major contributor

adsorption or interaction of chlorine on the different surfaces comprising the pyrolysis system

✗ ^{36}Cl memory effect **removal**

✓ ^{36}Cl memory effect **corrected**

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

Determination using Plastic scintillators

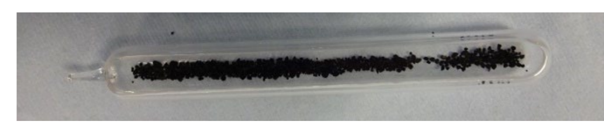
Plastic Scintillation ⟷ Liquid Scintillation

≠

Solid state of plastic scintillators

Separation and detection processes integrated

↑ Chemical recovery



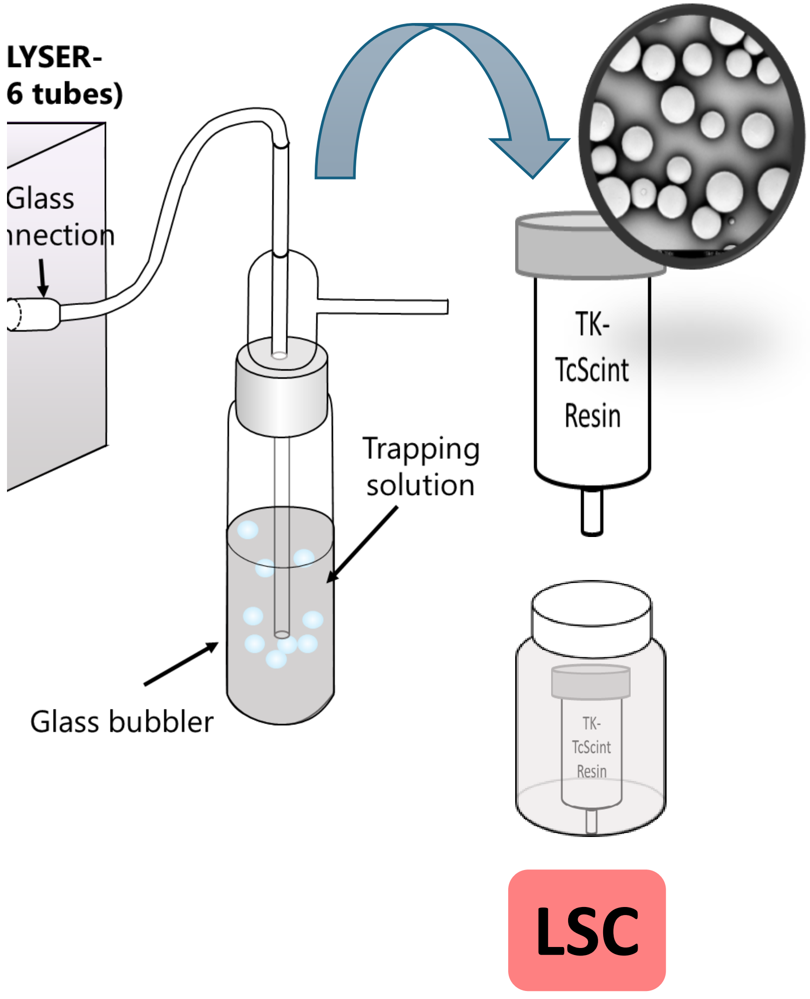
Graphite

↑ Removal of interferences (^{129}I, ^{14}C and ^{3}H)

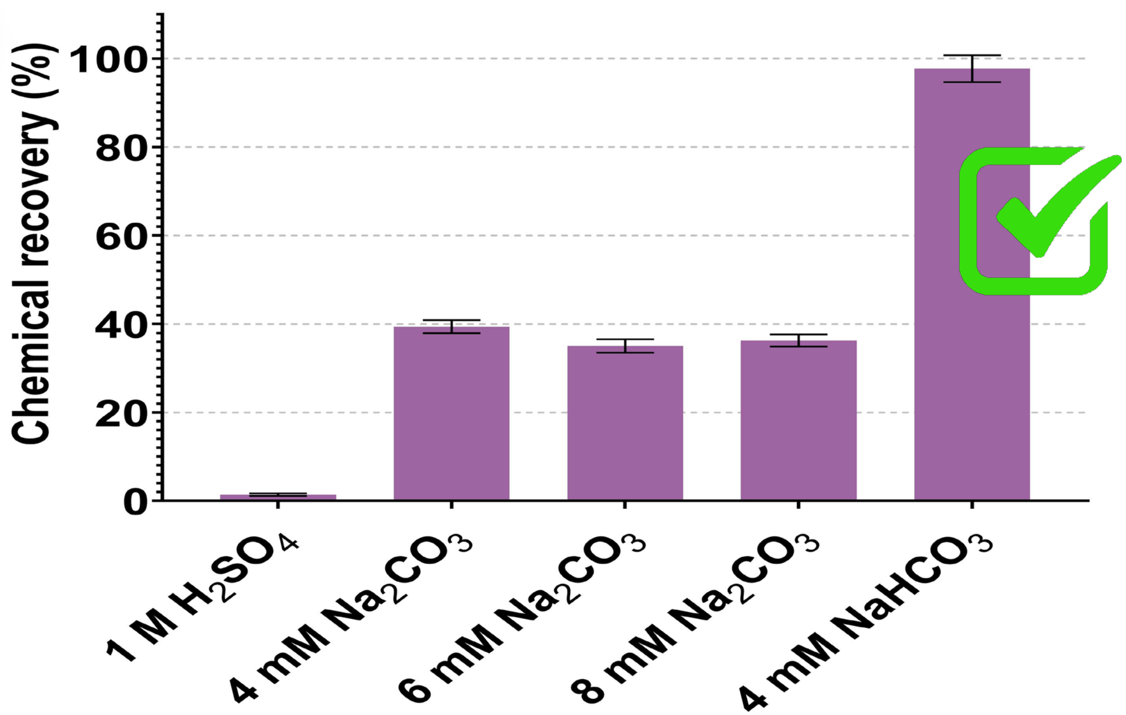
↓ turnaround time

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

Determination using Plastic scintillators

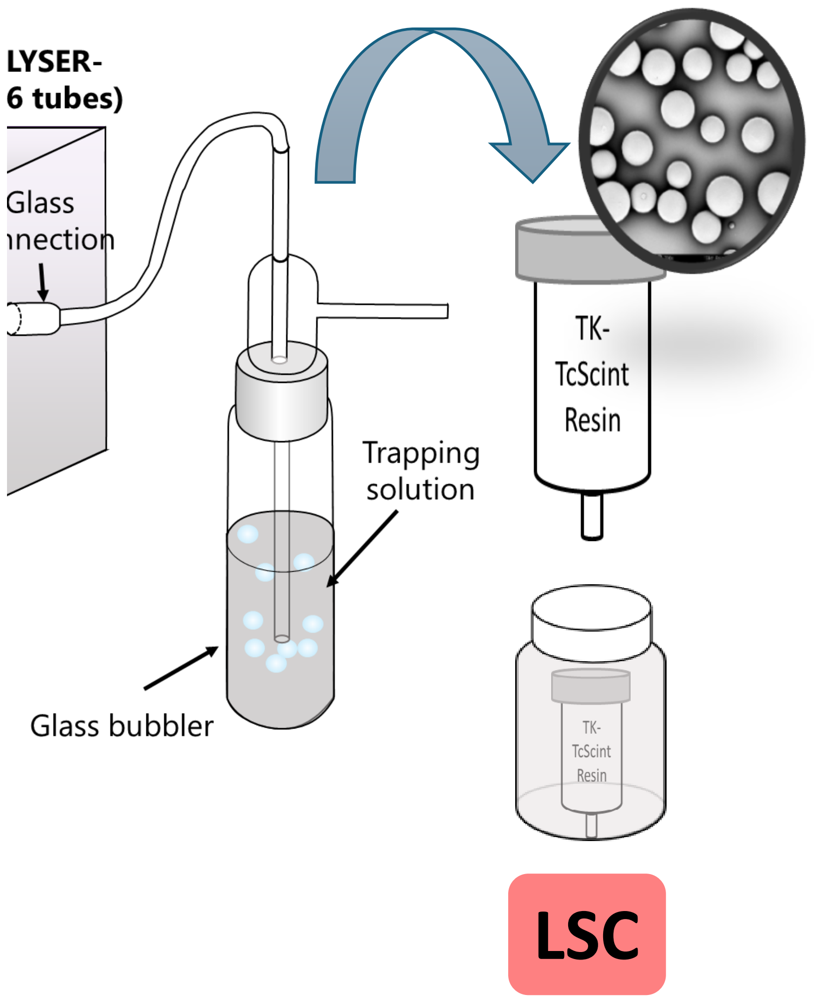


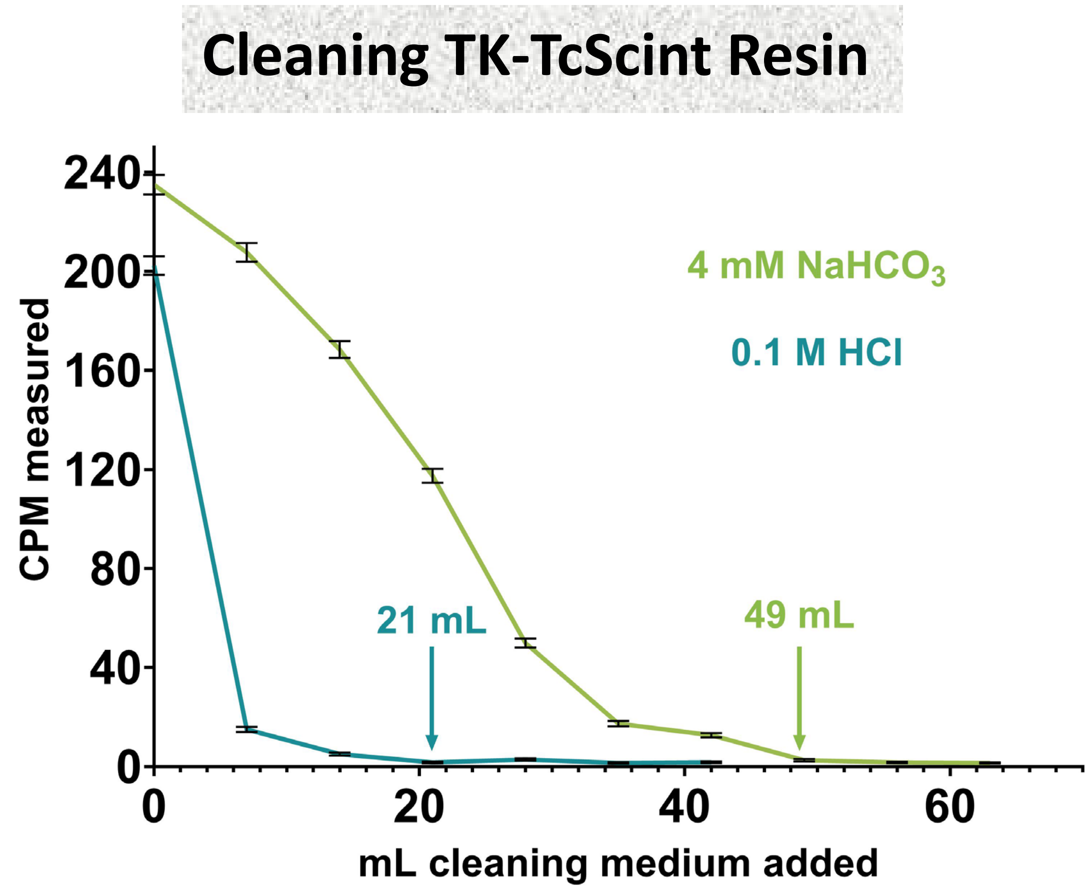
Suitable trapping media to retain ^{36}Cl on TK-TcScint Resin



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

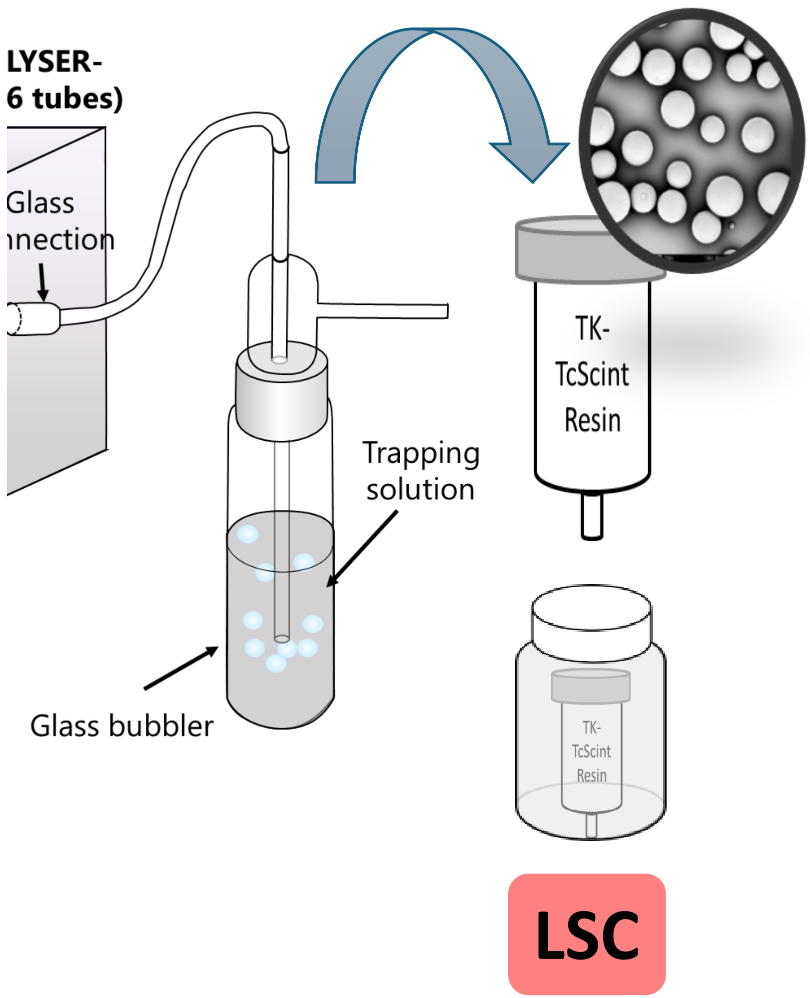
Determination using Plastic scintillators





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

Determination using Plastic scintillators

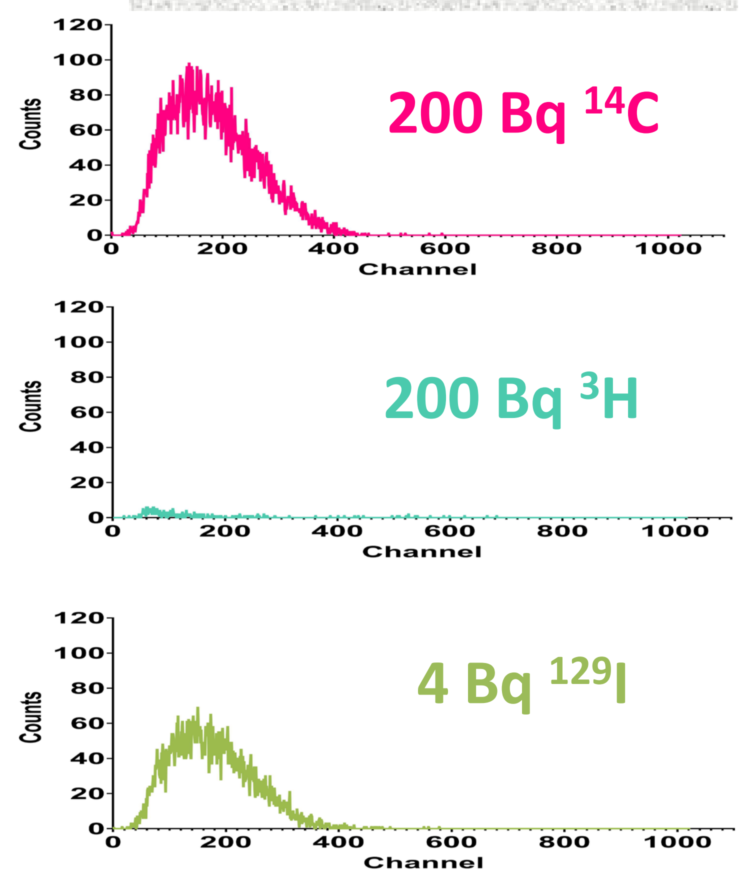


~2% retained

No retention

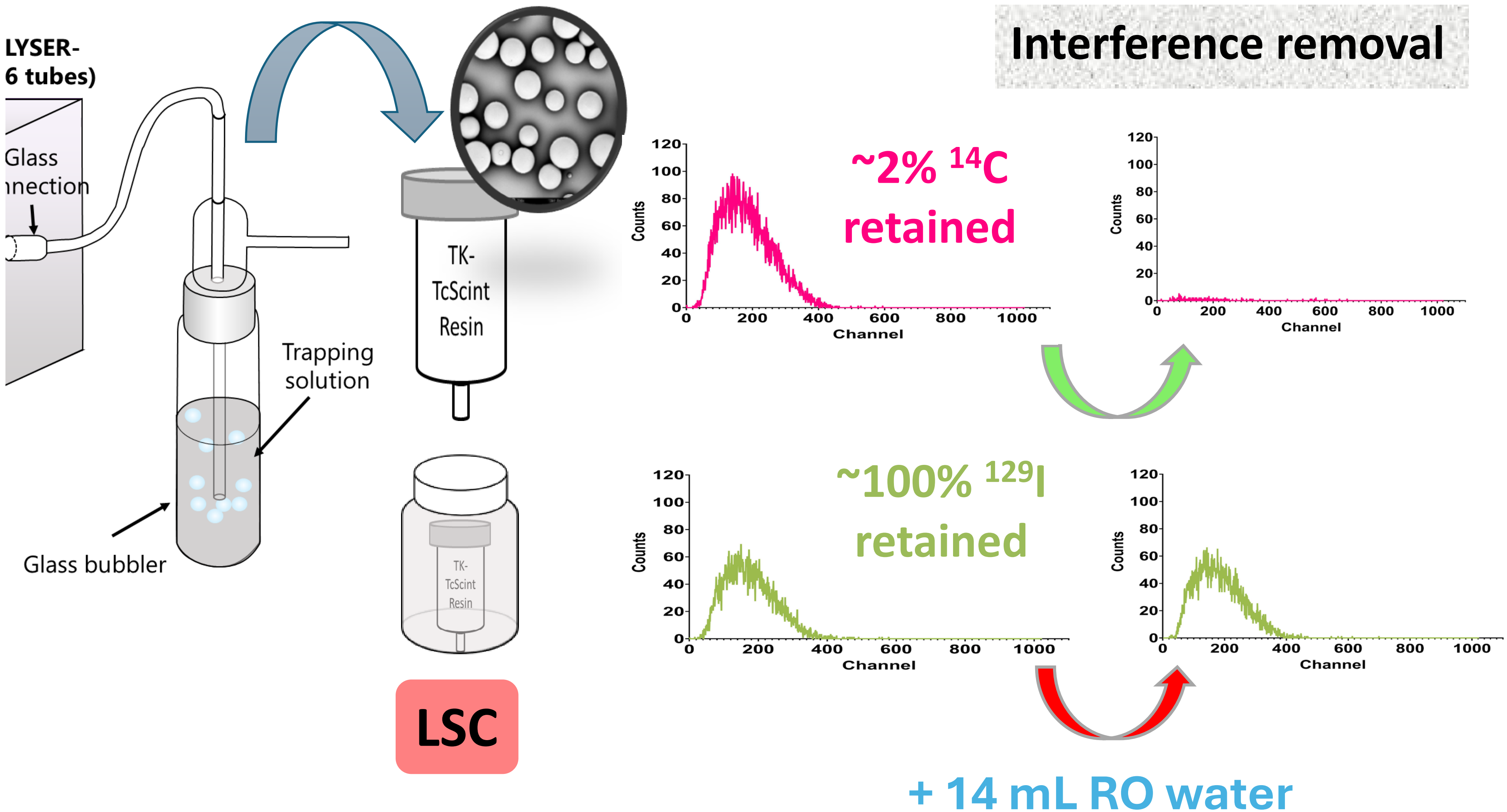
~100% retained

Interference removal



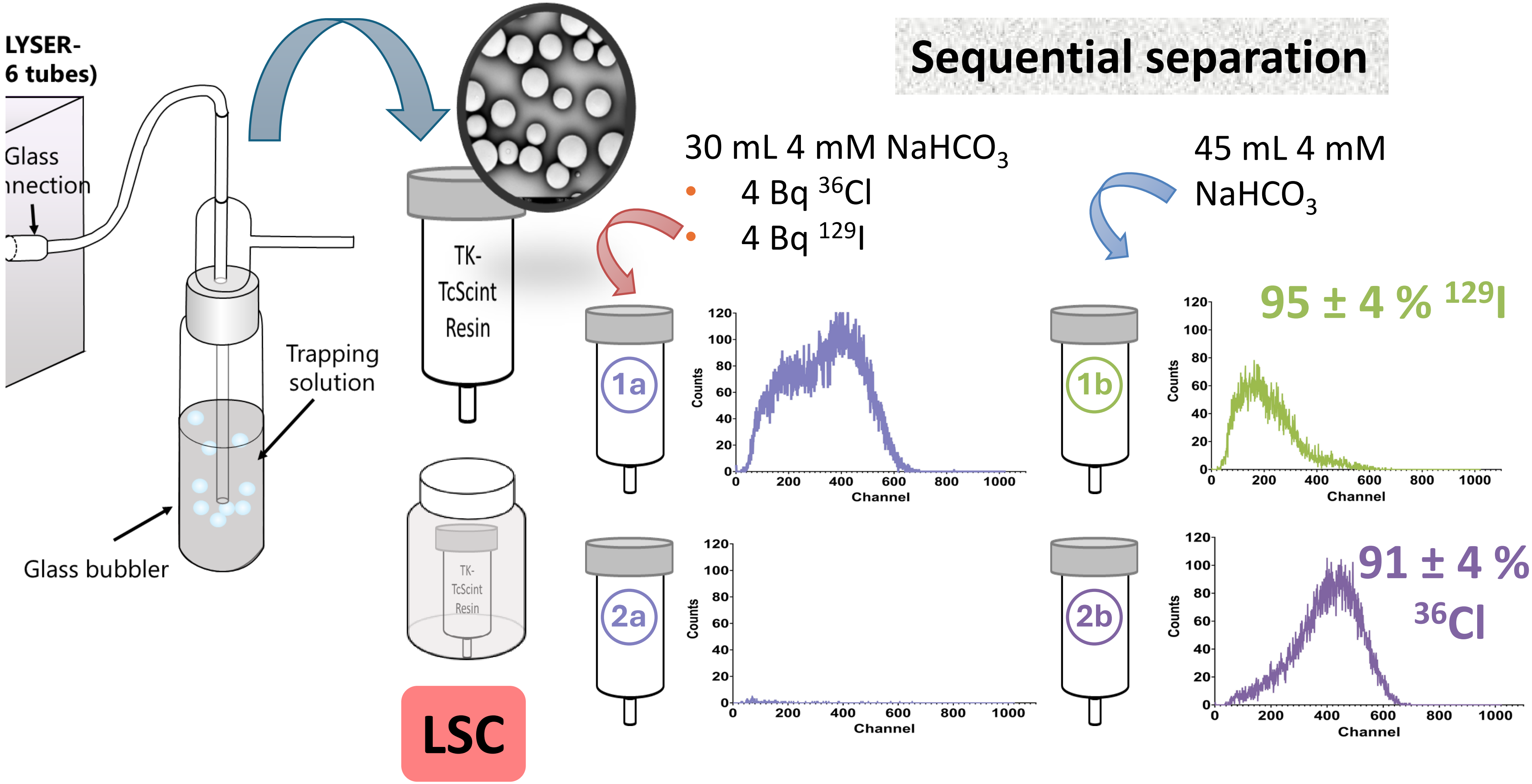
^{36}Cl and ^{129}I determination

Determination using Plastic scintillators



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

Determination using Plastic scintillators



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

Application

Measurements by ICP-MS (stable Cl and I)

Element	White sand (%)	Concrete (%)	Graphite (%)
Chlorine	76 ± 9	66 ± 7	64 ± 6
Iodine	82 ± 11	59 ± 9	33 ± 5

LOD

Parameter	^{36}Cl		^{129}I	
Count rate blank	3,8 CPM	Clearance level by Belgian legislation	3,5 CPM	Clearance level by Belgian legislation
Counting time	100 min		100 min	
Mass of the sample	1 g		1 g	
Chemical recovery	64%		65%	
Counting efficiency	98%		92%	
LOD ($\alpha=\beta=0.05$)	25 mBq g^{-1}	<1000 Bq g^{-1}	25 mBq g^{-1}	>10 Bq g^{-1}

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

Application

Concrete from BR3

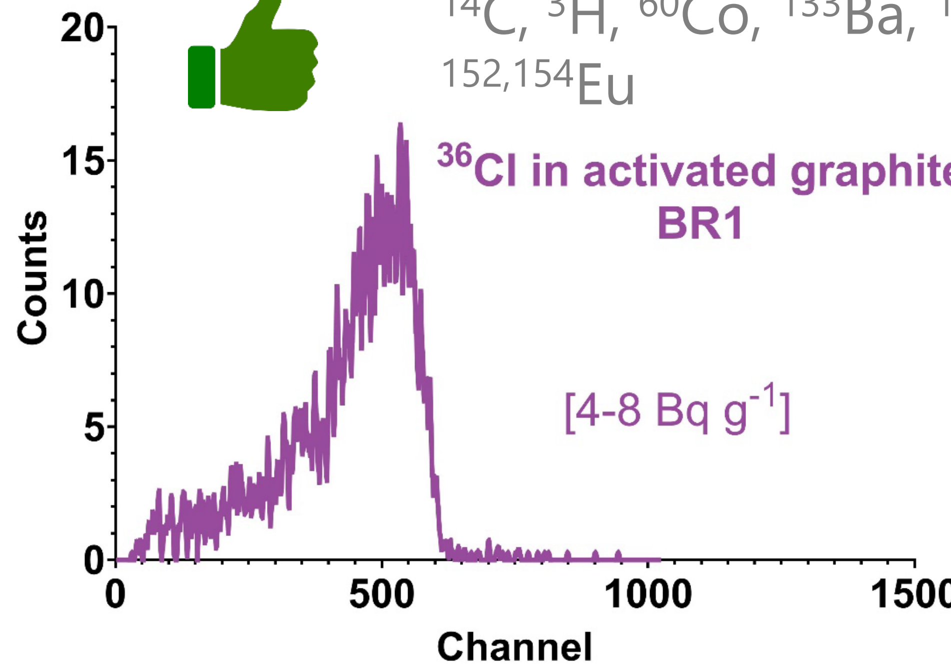
Scaling factor <3 mBq g^{-1}

^{36}Cl quantified <25 mBq g^{-1}

^{14}C, ^{3}H, ^{60}Co, ^{133}Ba, ^{137}Cs, ^{152}Eu

Graphite from BR1

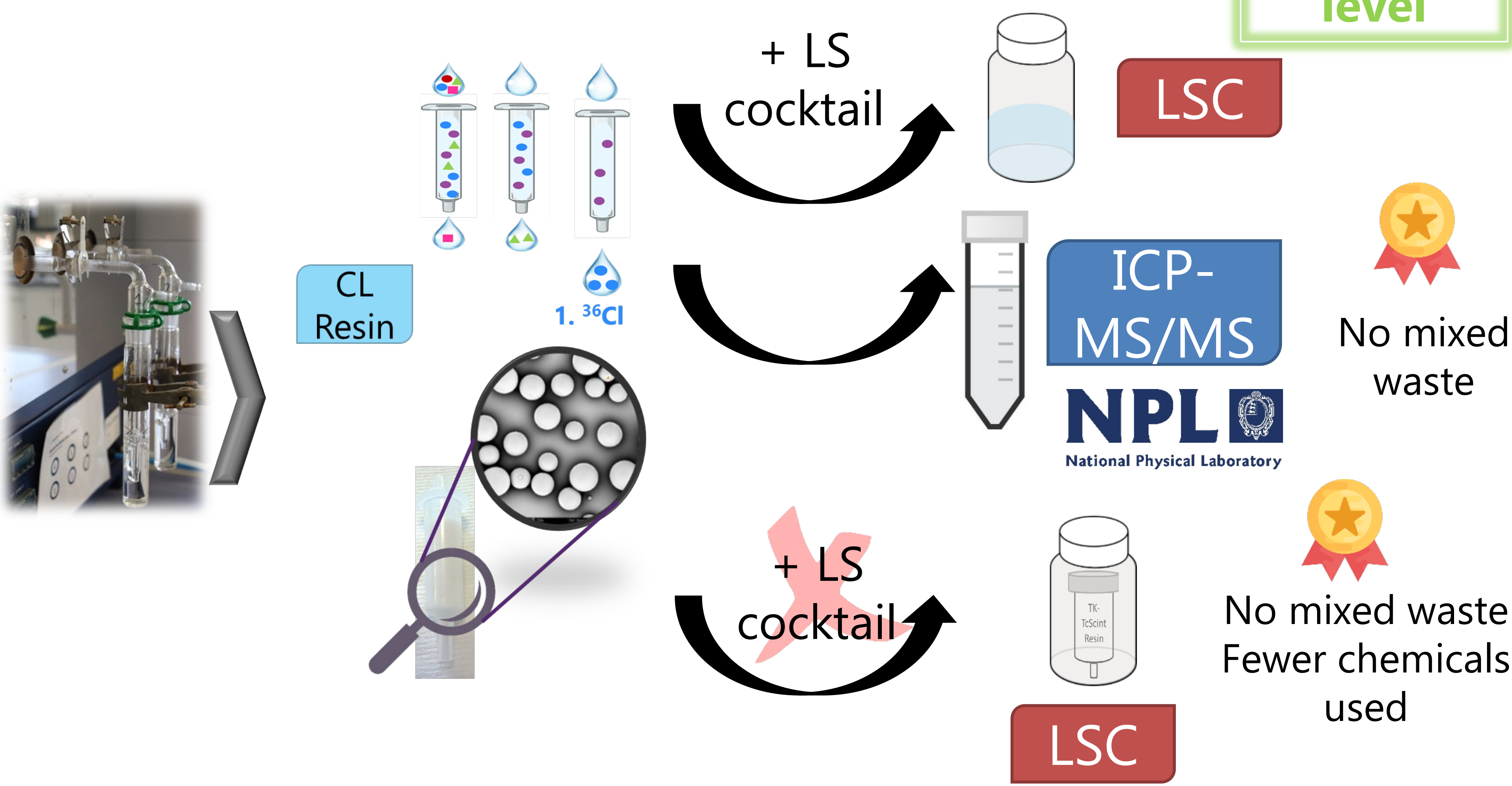
^{14}C, ^{3}H, ^{60}Co, ^{133}Ba, ^{134}Cs, ^{152,154}Eu



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

Comparison of different methods/techniques

All DL < clearance level



^{41}Ca in concrete samples

Significant in terms of *half-life* and *environmental mobility for* **final waste disposal**

^{41}Ca

- Neutron activation of naturally occurring ^{40}Ca
- **$T_{1/2}$** = 3,02 ▪ 10^5 year
- **Electron capture** E < 3,6 keV
- Present in concrete structures (bioshield and containment)

Clearance level < 100 Bq/g

^{41}Ca in bioshield concrete samples

Physical barrier that protects against neutron and gamma-ray emissions from the nuclear reactor

Denser concrete compared to normal concrete

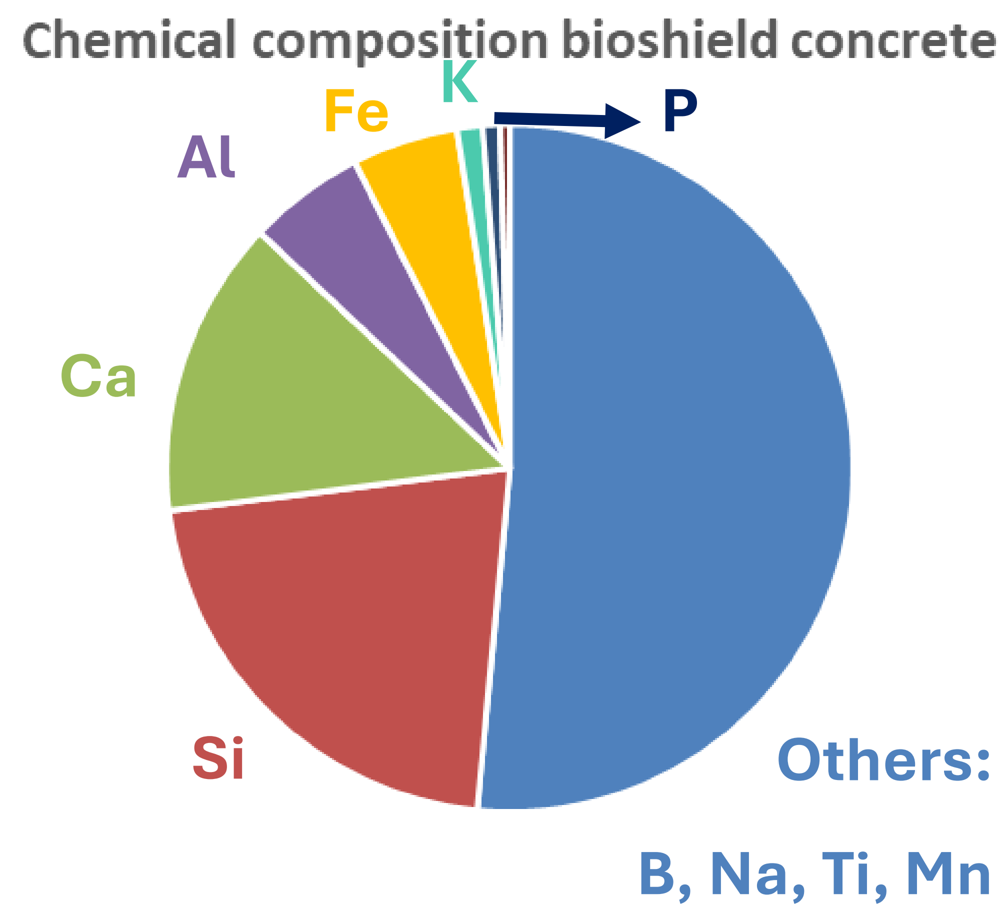
Contains higher amount of shielding materials: boron, barite

Calcium predominant component

(8 – 35%)

Silica

Barium

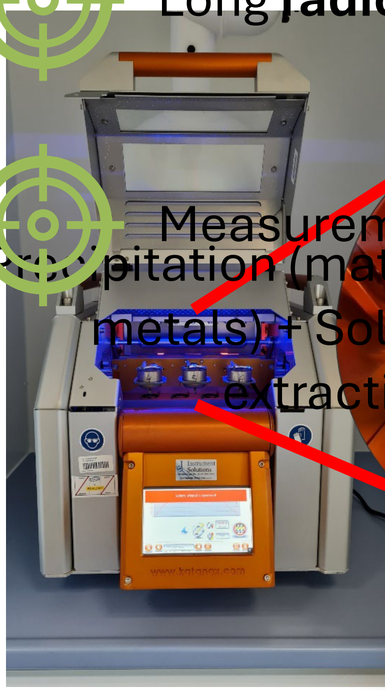


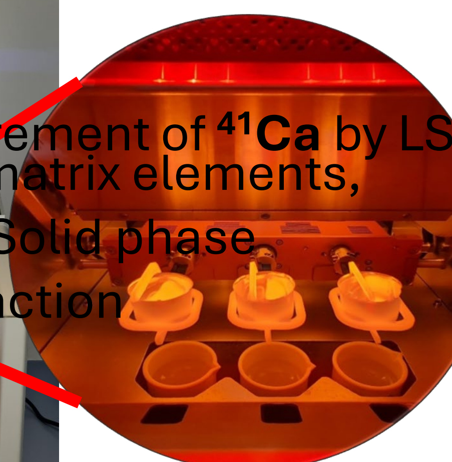
Evans, J.C et al. 1984. Long-lived activation products in reactor materials. Nureg/Cr-3474 1–185.

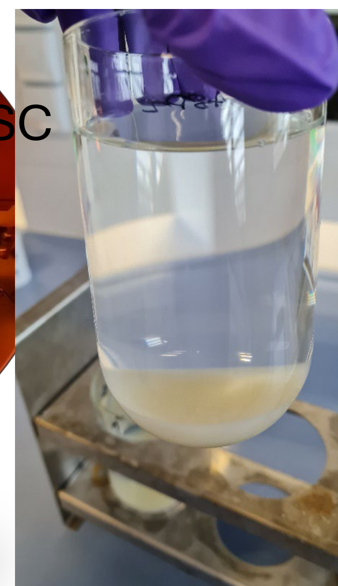
^{41}Ca determination in concrete

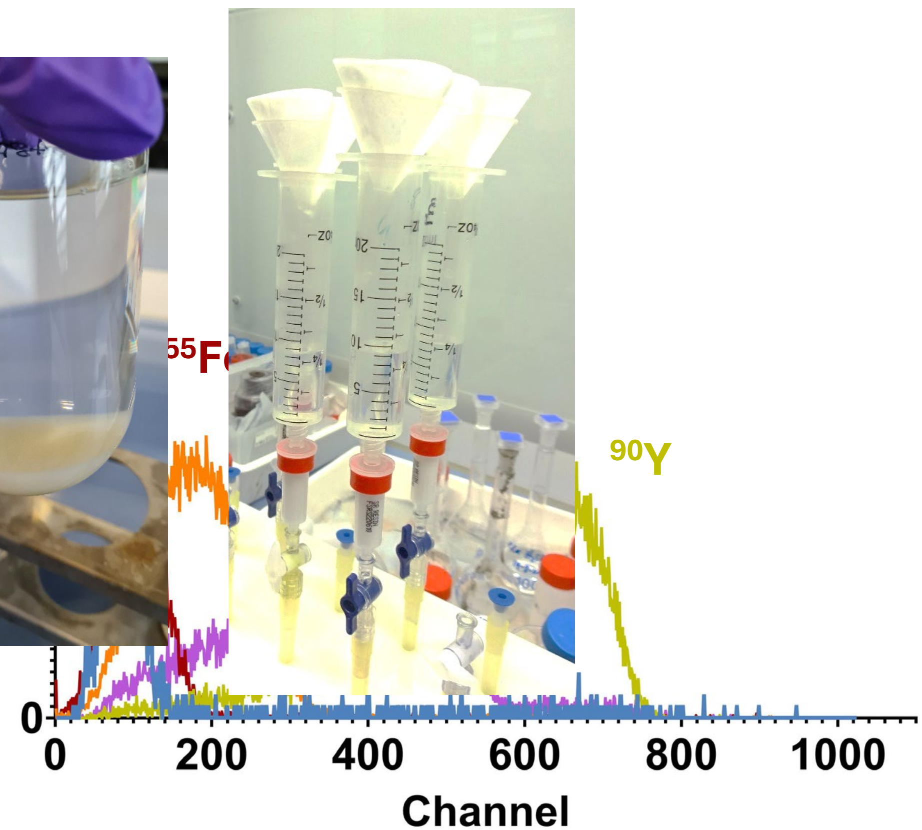
- Complex procedures for **matrix dissolution**
- **Lithium borate fusion**
- Long **radiochemical separation** procedures
- Measurement of ^{41}**Ca** by LSC

Precipitation (matrix elements, metals) + Solid phase extraction





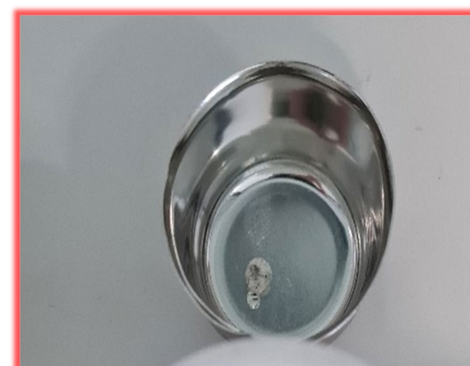




^{41}Ca determination in concrete

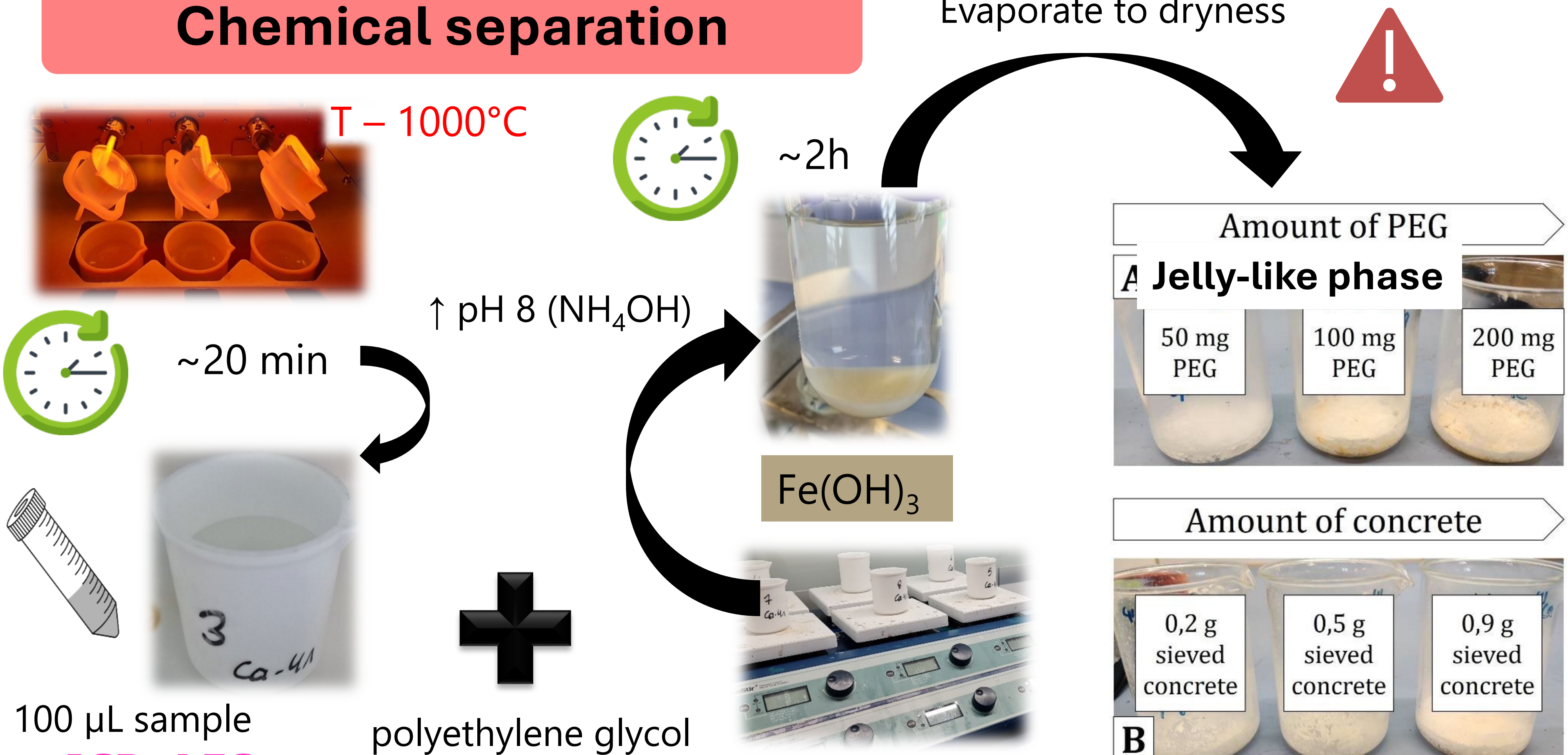
Fusion

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



^{41}Ca determination in concrete

Chemical separation



100 μL sample for **ICP-AES**

polyethylene glycol (PEG) **PRECIPITATION**

overnight

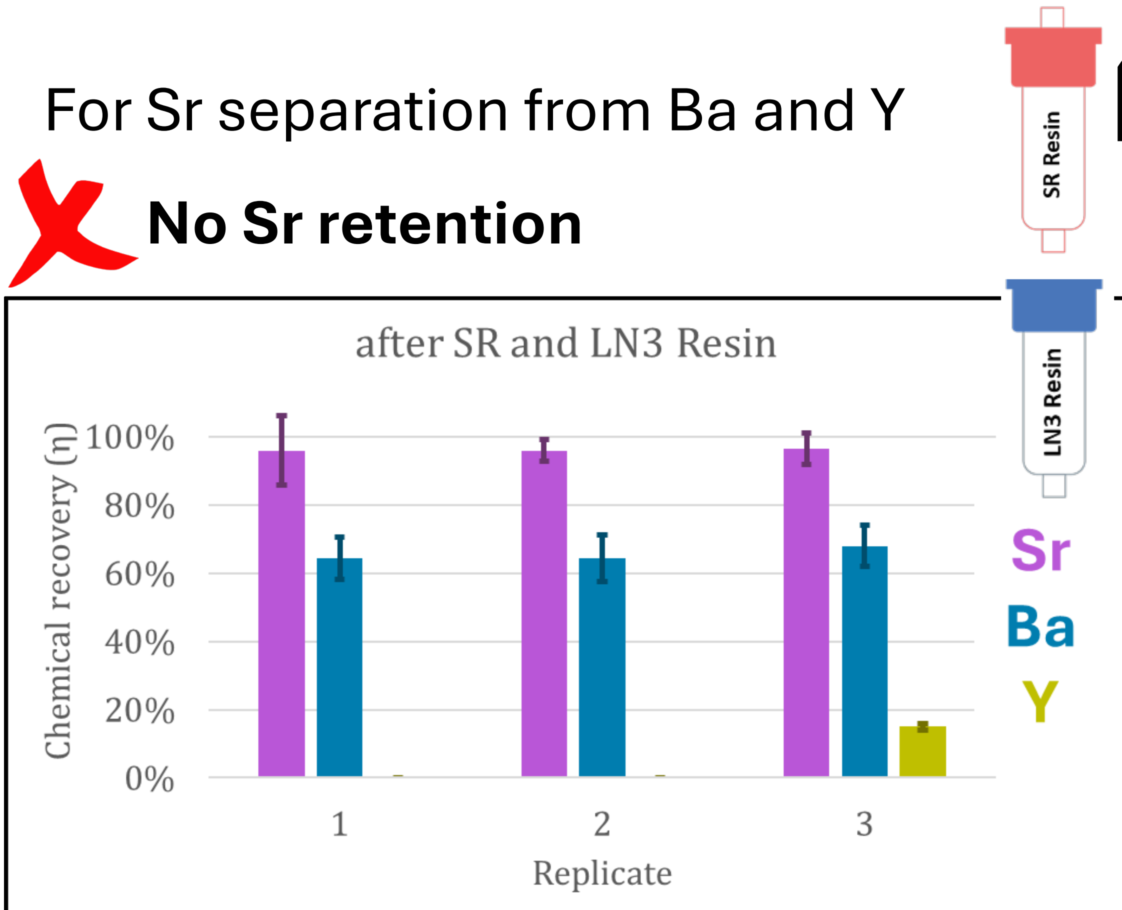
Based on Russell et al., 2021

^{41}Ca determination in concrete

Chemical separation

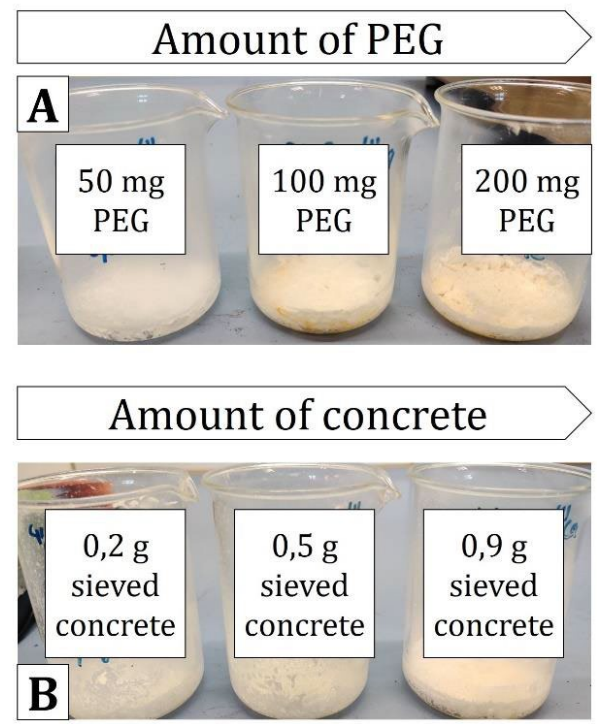
For Sr separation from Ba and Y

No Sr retention



Y retention

Evaporate to dryness



^{41}Ca determination in concrete

Chemical separation

T – 1000°C

~2h

~20 min

↑ pH 8 (NH_4OH)

100 µL sample for **ICP-AES**

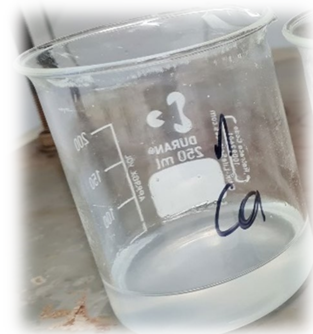
polyethylene glycol (PEG) **PRECIPITATION**

$Fe(OH)_3$

overnight

~1h

Oxalic acid
↑ pH 5 (NH_4OH)
PRECIPITATION

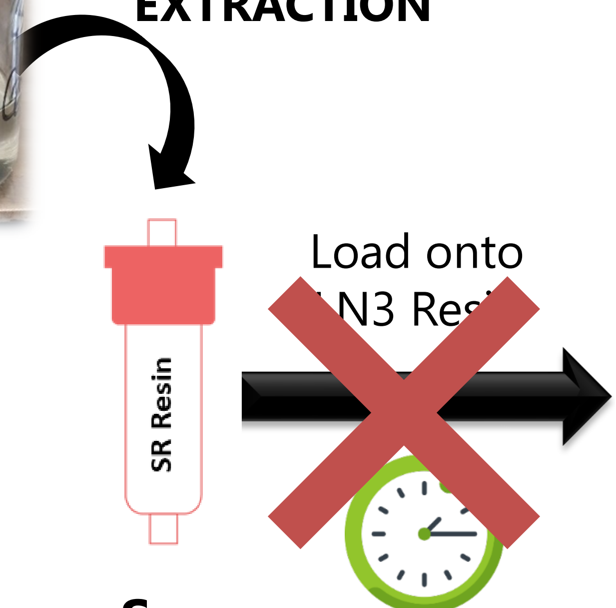


Dissolve precipitate in 1 M HNO_3

^{41}Ca determination in concrete

Chemical separation

Loading in SR Resin
SOLID PHASE EXTRACTION

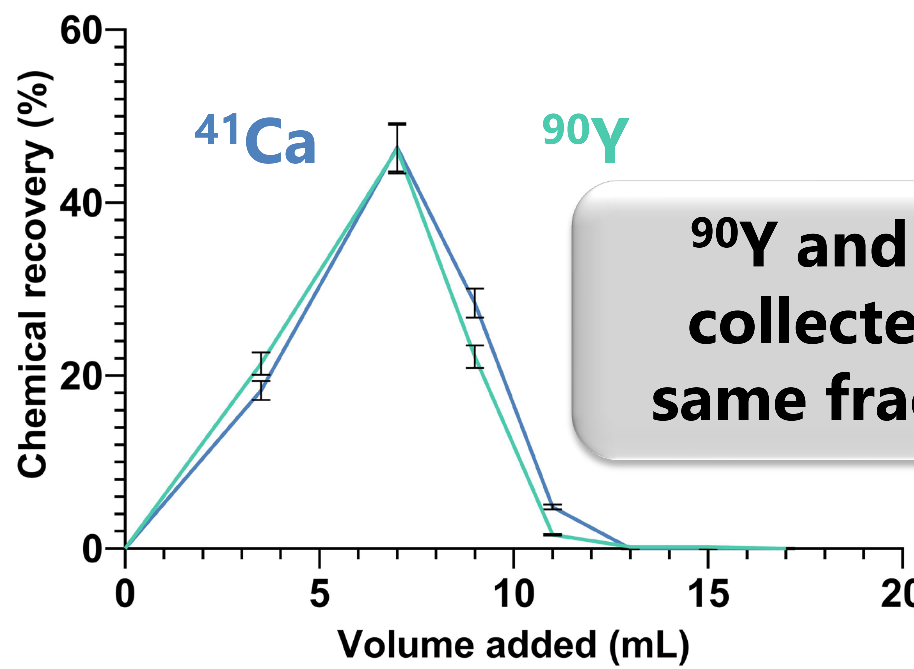


~30 min

Sr removal

~10 min

Possible ^{41}Ca quantification when ^{90}Y is present?



^{90}Y and ^{41}Ca collected on same fractions

^{41}Ca determination in concrete

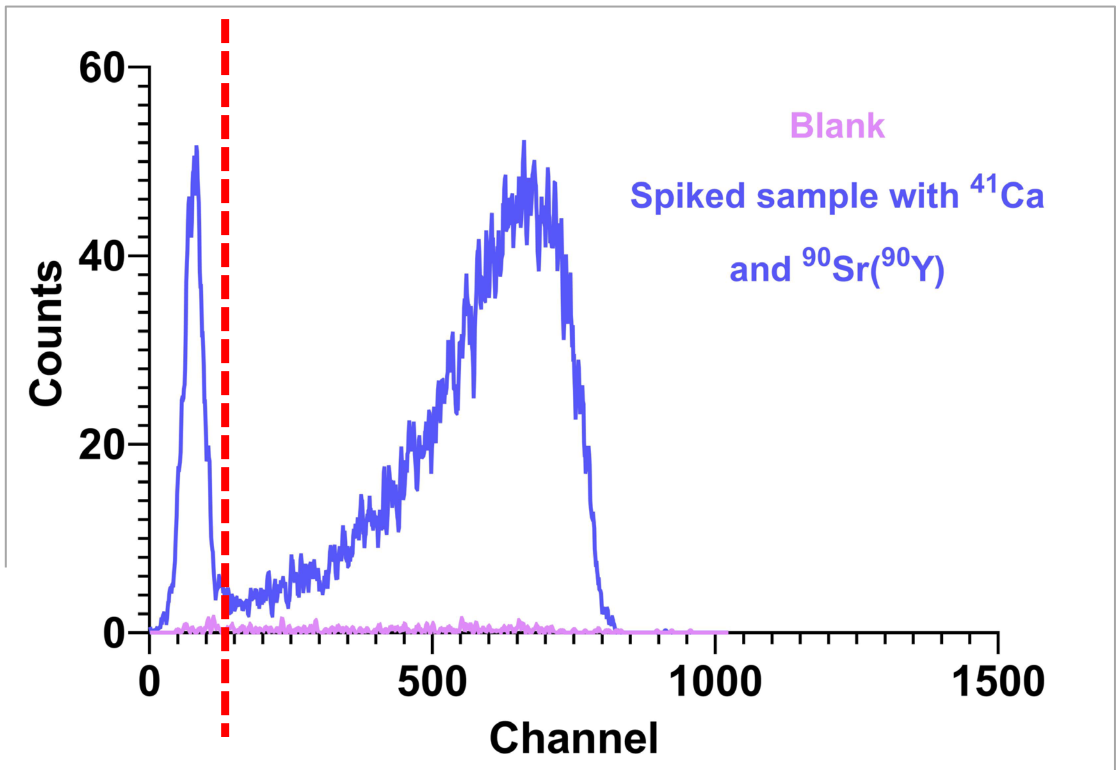
Chemical separation

Loading in SR Resin
SOLID PHASE EXTRACTION

~30 min

Possible ^{41}Ca quantification by cutting the spectra

Single LSC spectra



^{41}Ca determination in concrete

Chemical separation

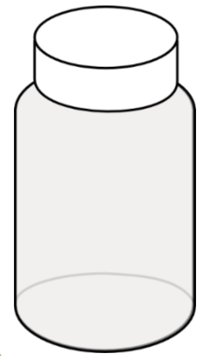
Loading in SR Resin
SOLID PHASE EXTRACTION

~30 min

Evaporate to ½ volume

~1 h 30 min

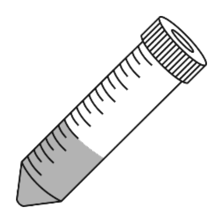
½ sample for **LSC**



60 min

~80% ^{41}Ca chemical recovery

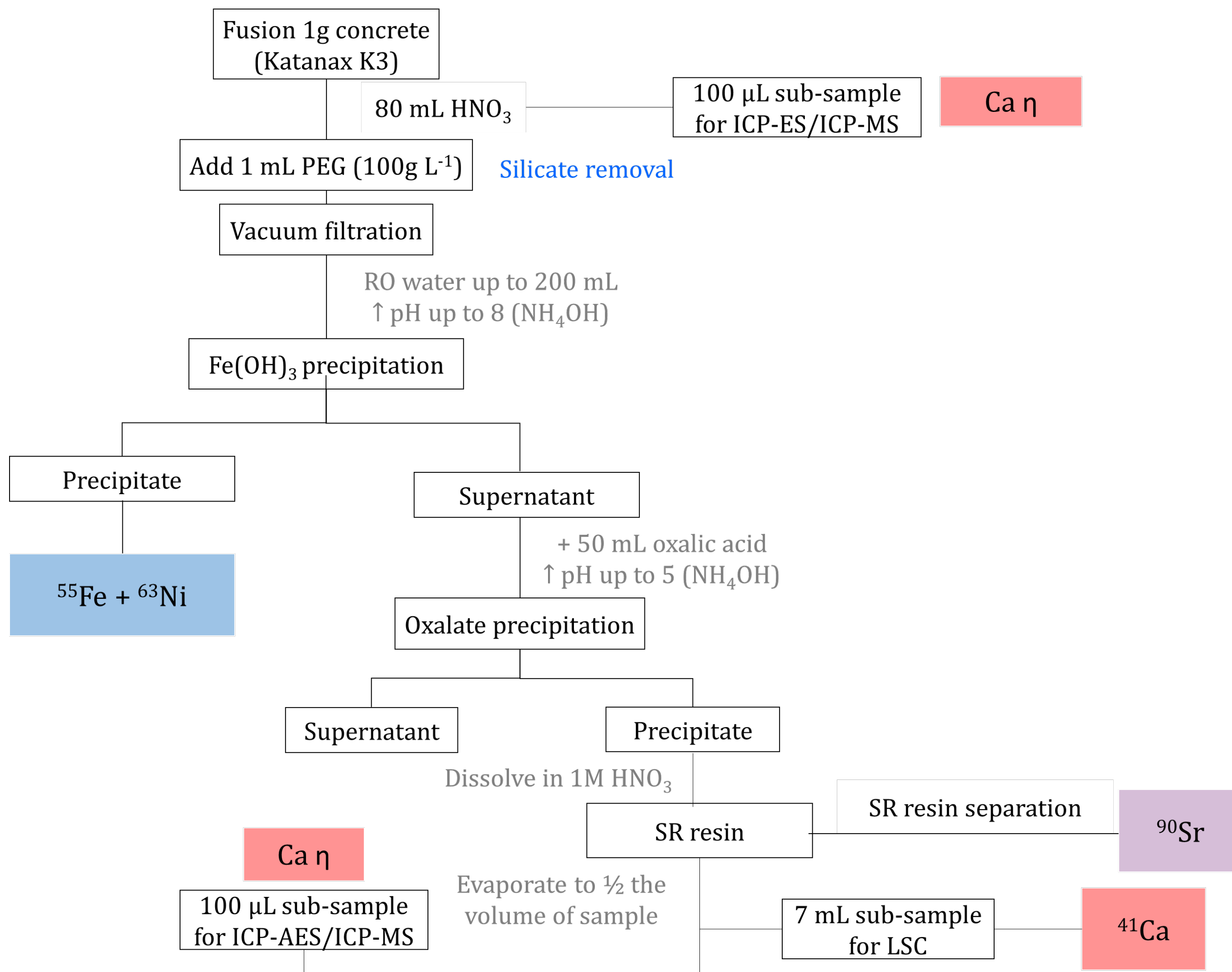
100 µL sample for **ICP-AES**



~64% calcium chemical recovery

^{41}Ca determination in concrete

Application



^{41}Ca determination in concrete

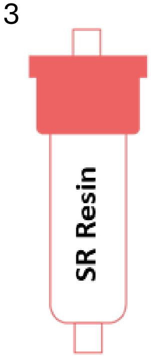
Application

polyethylene glycol (PEG) **PRECIPITATION**

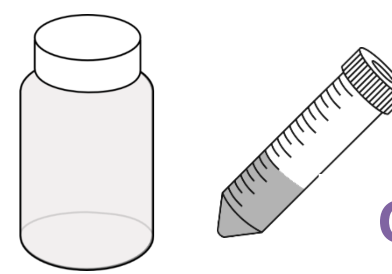
↑ pH 8 (NH_4OH) **$Fe(OH)_3$ PRECIPITATION**

Oxalic acid ↑ pH 5 (NH_4OH) **PRECIPITATION**

1 M HNO_3



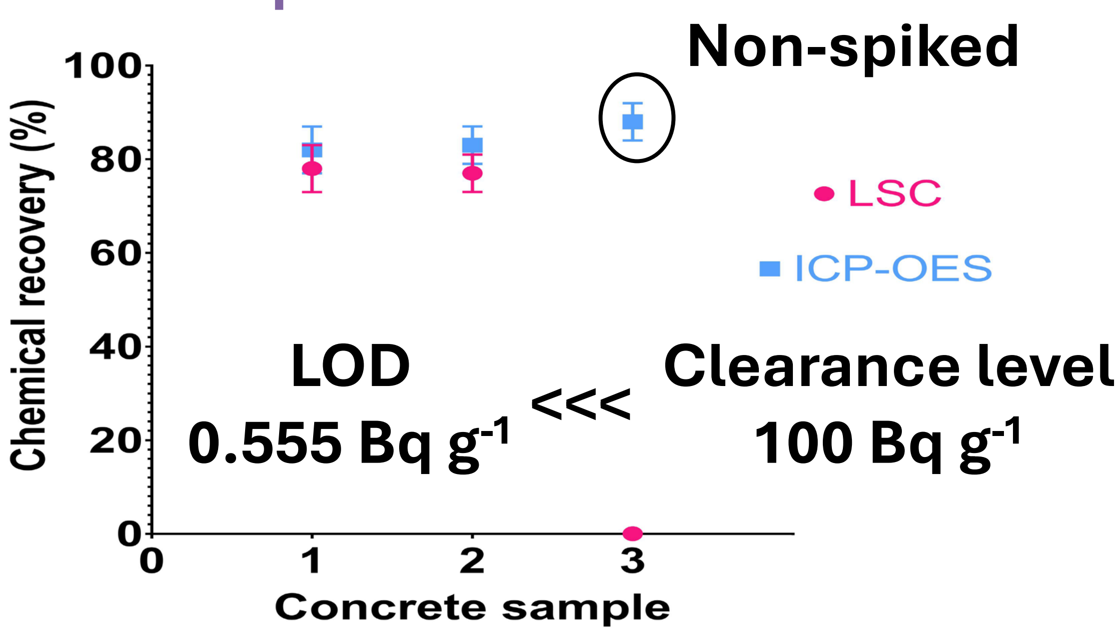
Evaporate to ½ volume



^{41}Ca activity

Ca η

Ca η



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

Difficult to **chemically separate** both lanthanides and quantify "pure" fractions

^{147}Pm

- Fission product from ^{235}U bombardment with thermal neutrons
- **$T_{1/2}$** = 2,6 year
- **Beta emitter** E < 224 keV
- Present in waste solutions

Clearance level < 1000 Bq/g

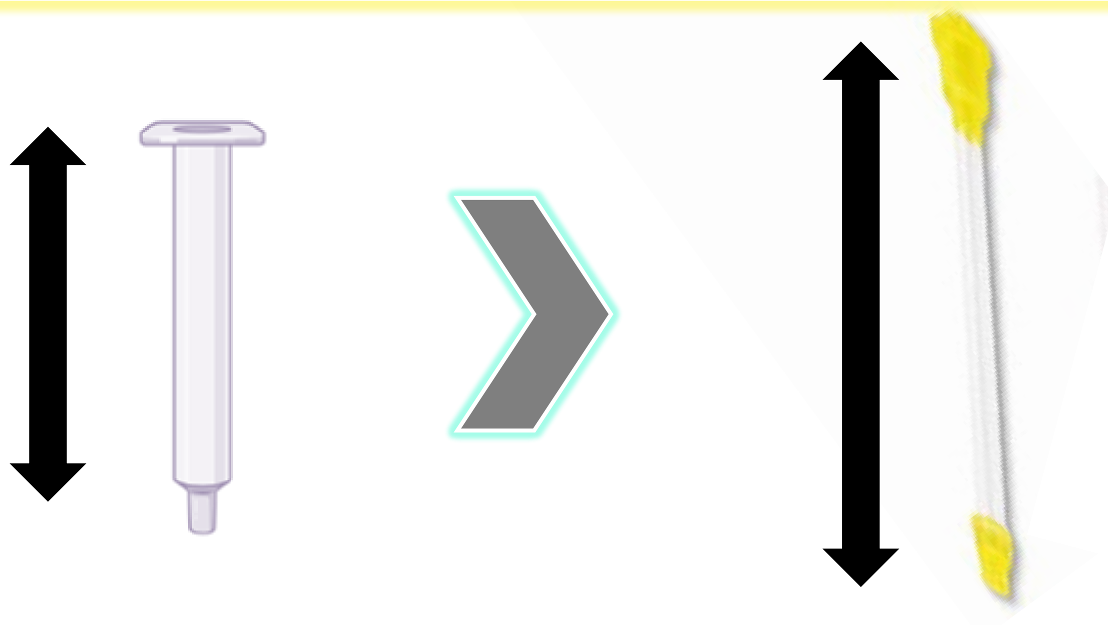
^{151}Sm

- Fission product (low yield) or activation of ^{150}Sm
- **$T_{1/2}$** = 94,7 year
- **Beta emitter** E < 74,4 keV
- Present in concrete structures and waste solutions

Clearance level < 1000 Bq/g

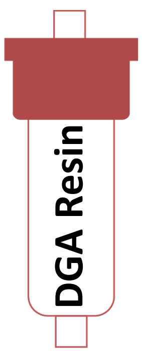
^{147}Pm and ^{151}Sm chemical separation

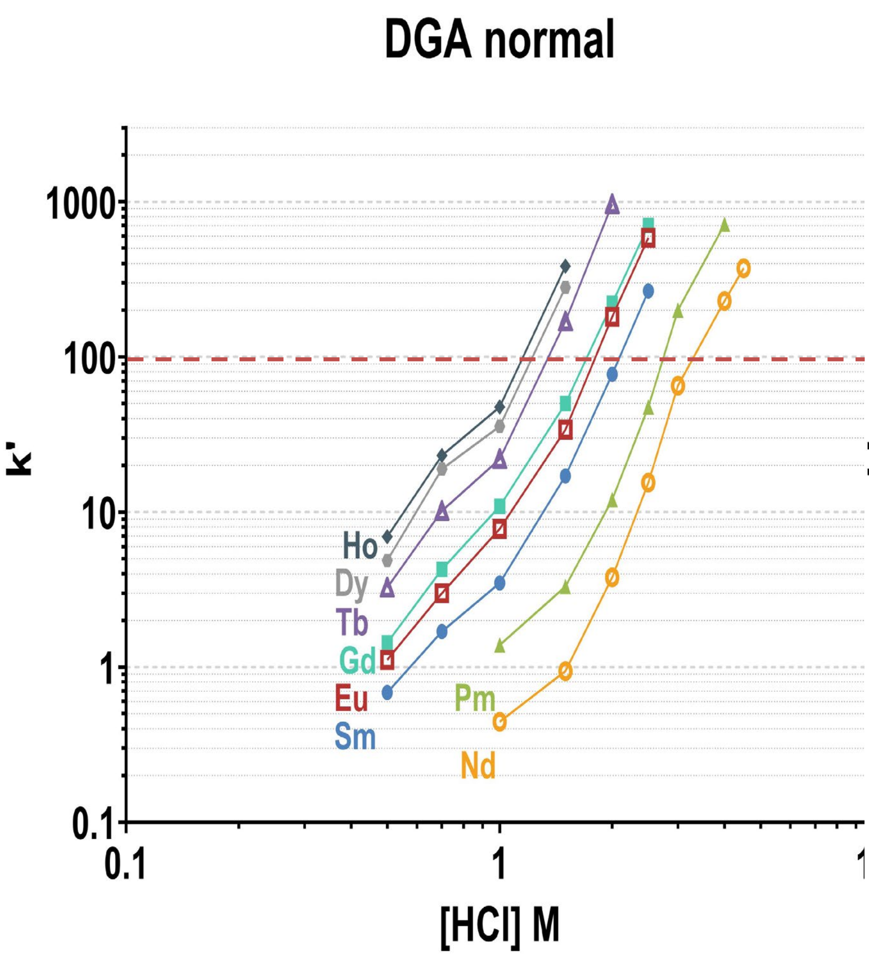
- **Complete radiochemical separation $^{147}Pm/^{151}Sm$**
- **Nd as ^{147}Pm carrier**
- **Eu as interference**

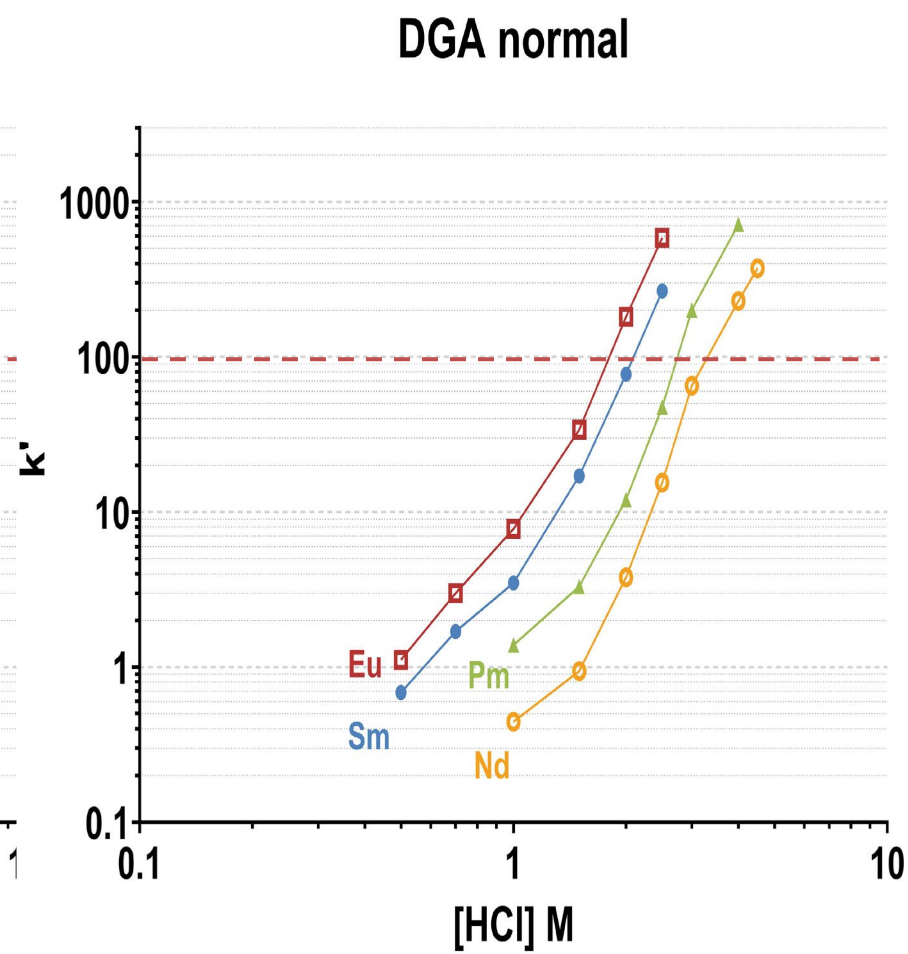


^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction





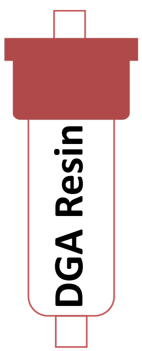


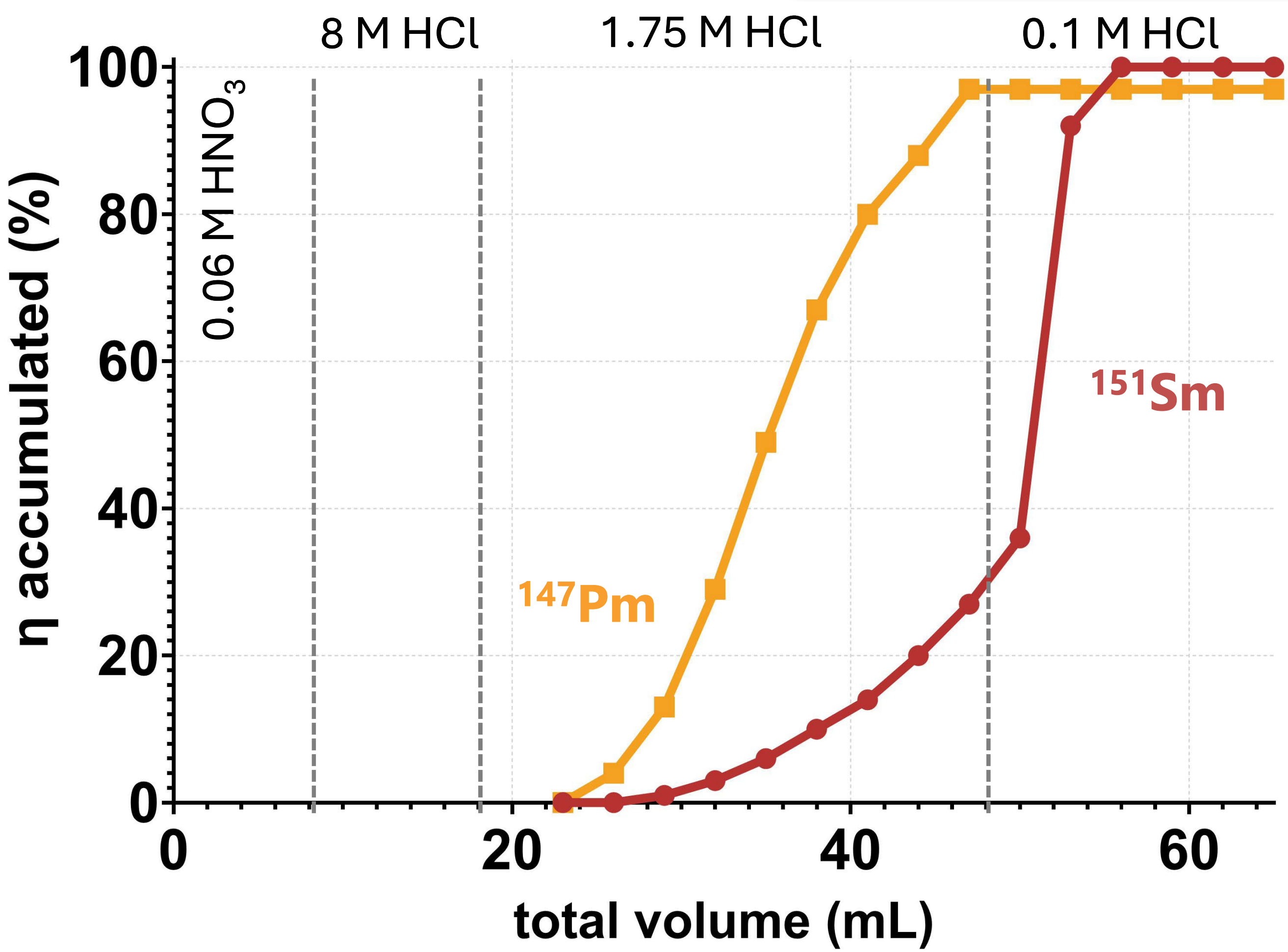
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction

DGA cartridge
50-100 µm

27% Sm co-elute with Pm



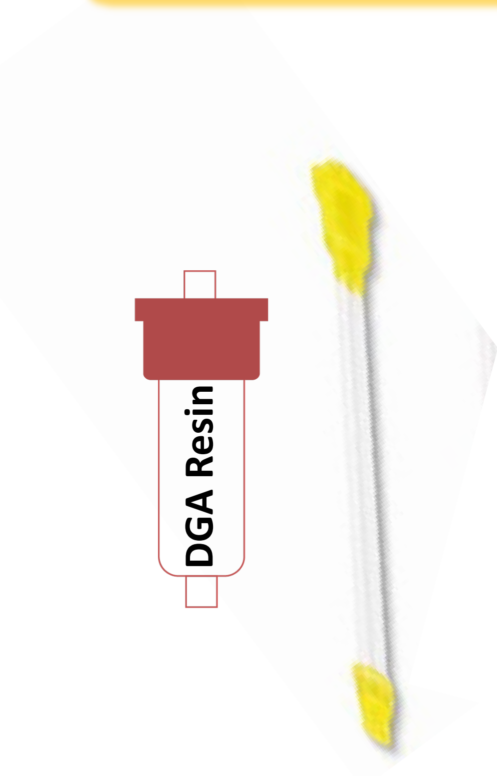


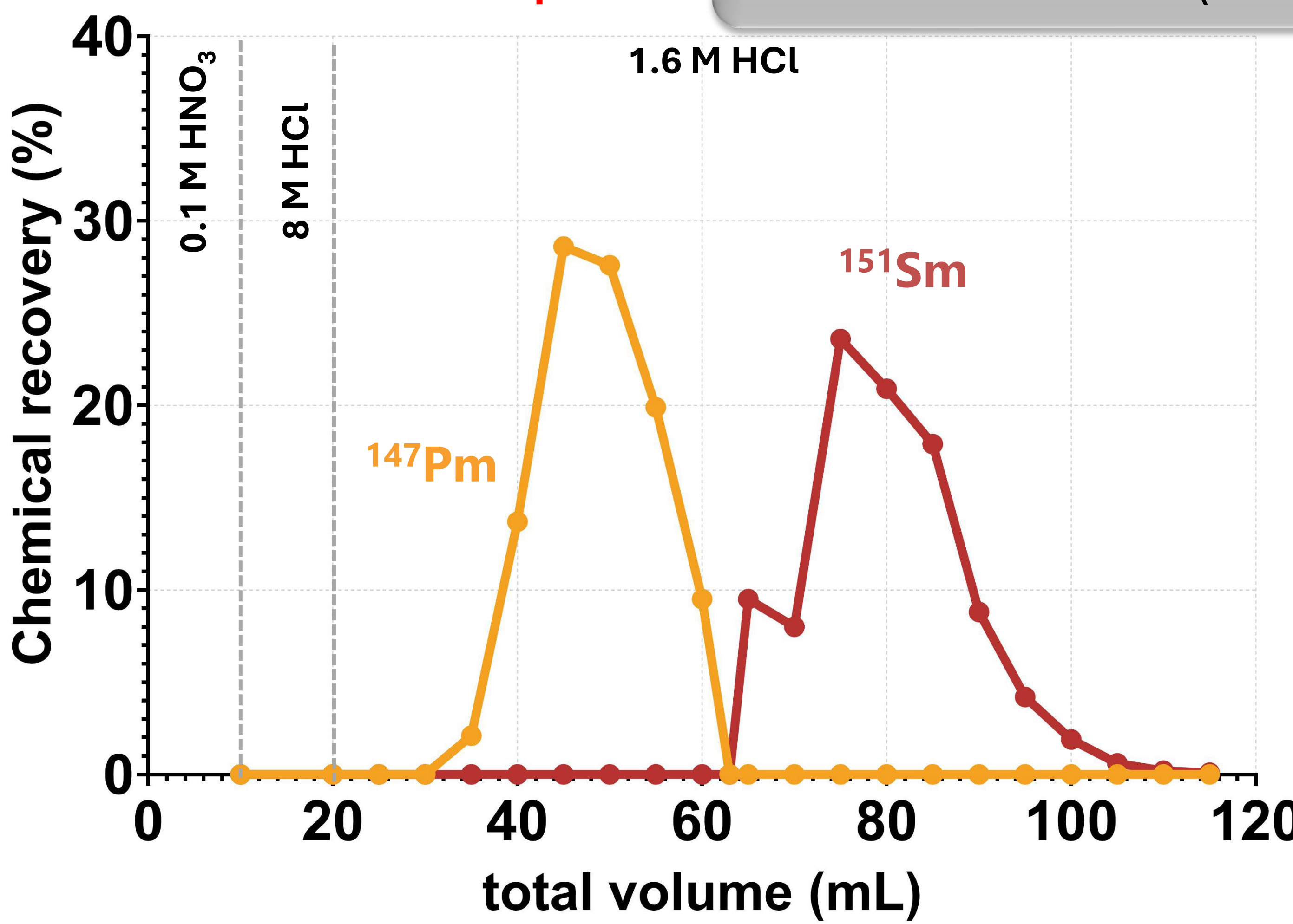
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction

DGA column
100-150 µm

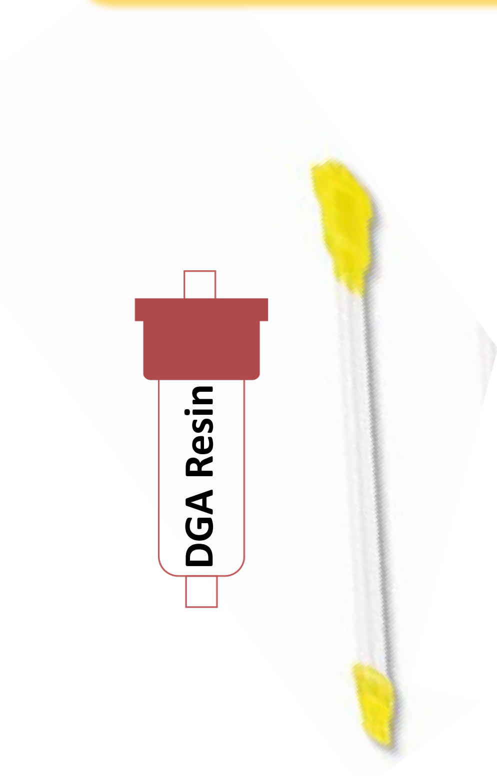
40 mL 1.6 M HCl (^{147}Pm)
40 mL 1.6 M HCl (^{151}Sm)





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

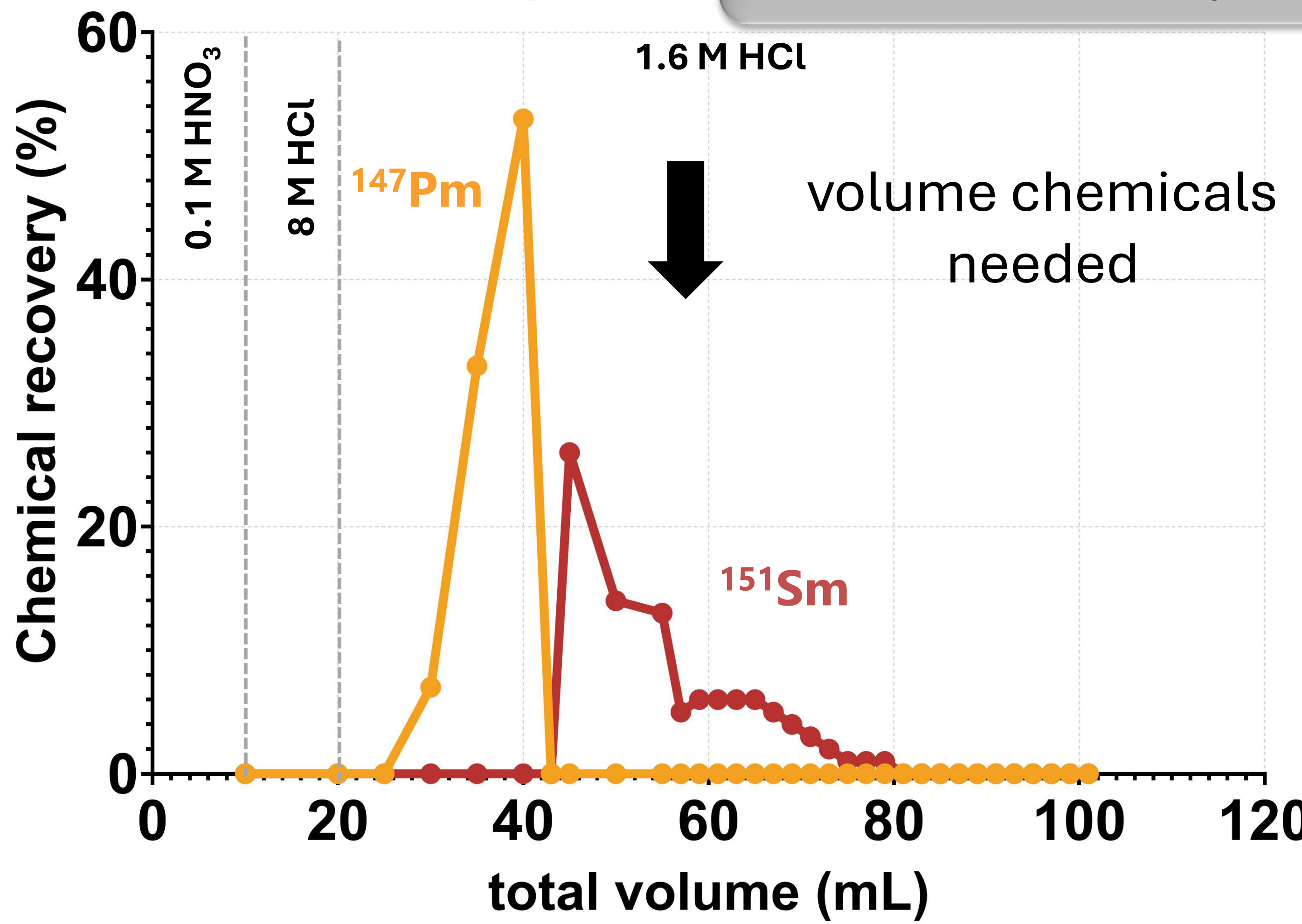
Solid phase extraction



DGA column

50-100 µm

20 mL 1.6 M HCl (^{147}Pm)
35 mL 1.6 M HCl (^{151}Sm)

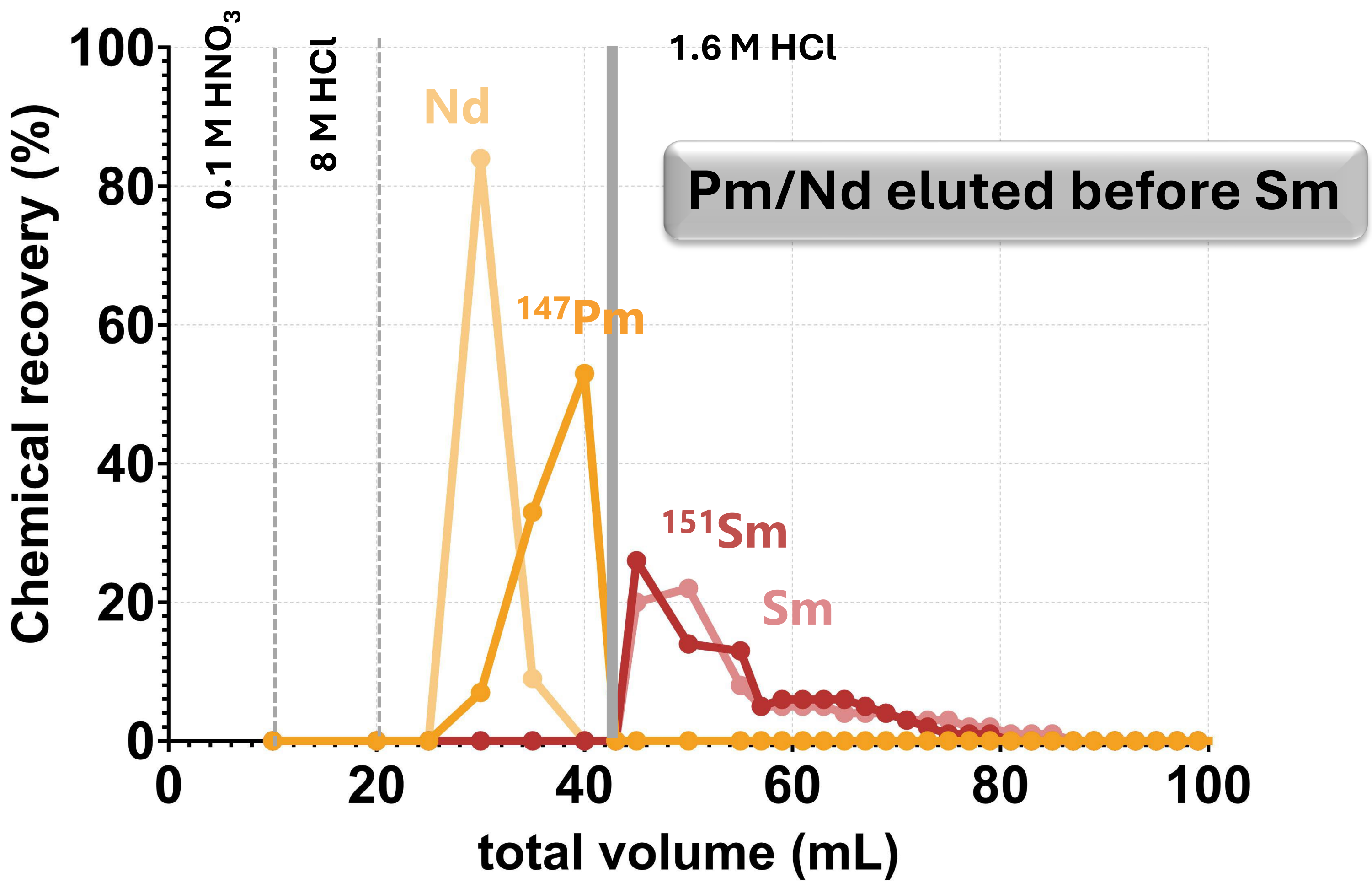


^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction

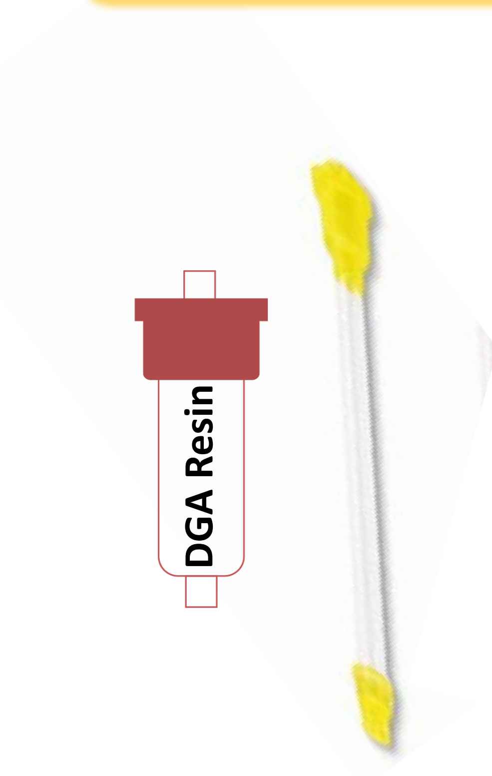
DGA Resin, Normal

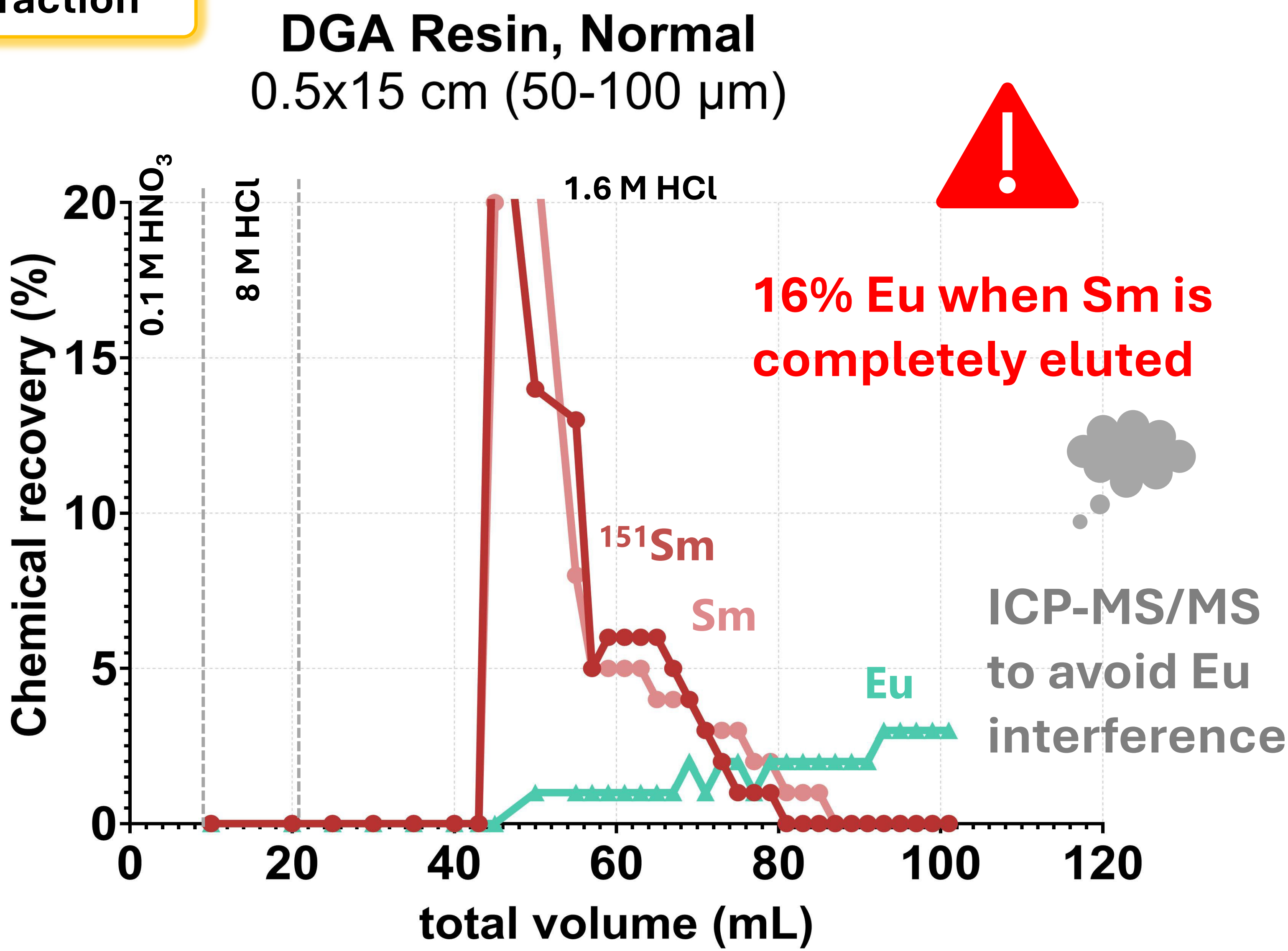
0.5x15 cm (50-100 µm)



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

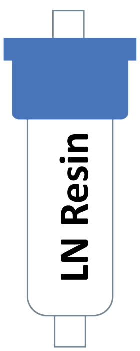
Solid phase extraction

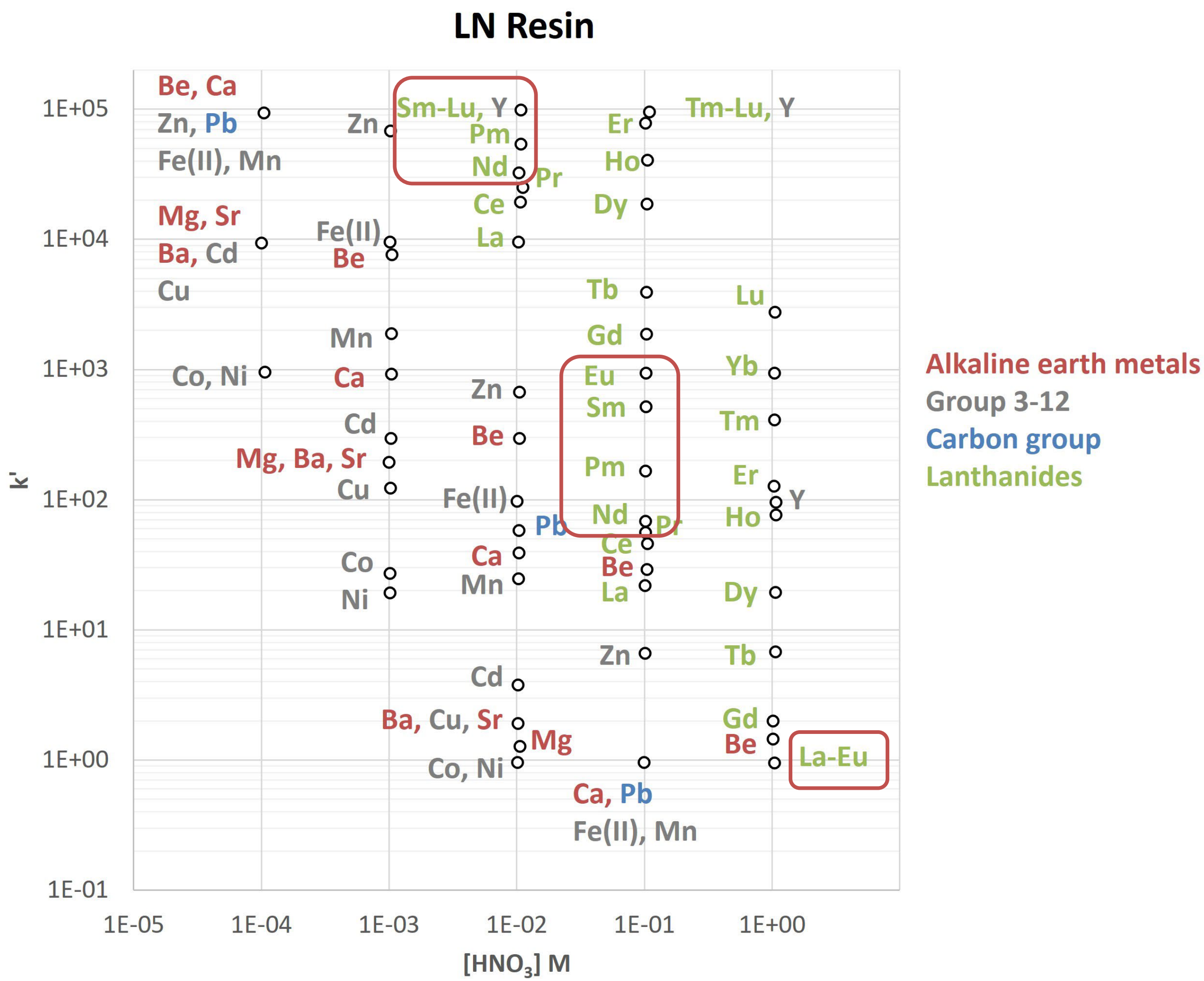




^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction



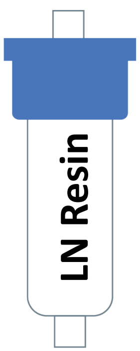


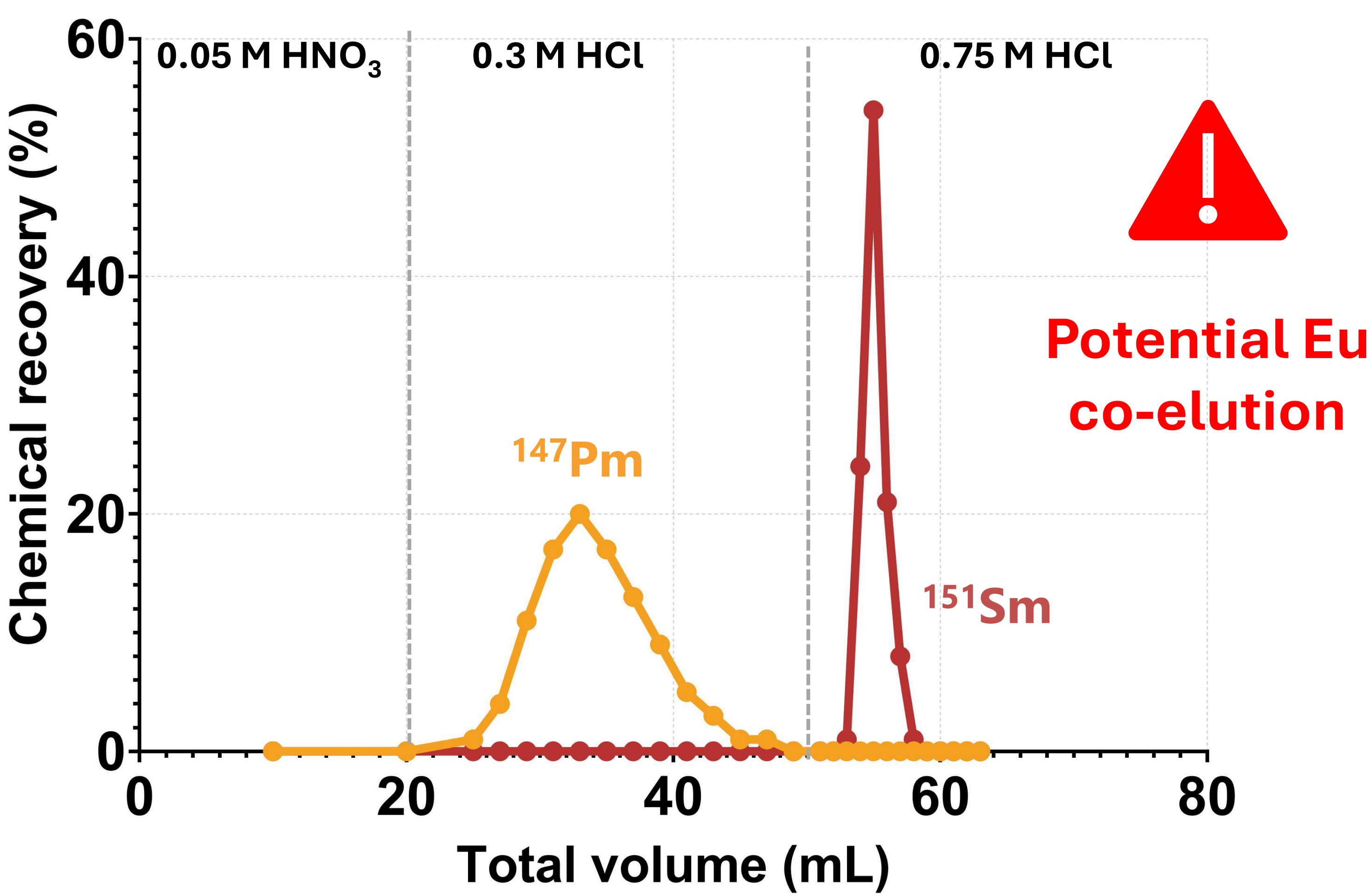
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction

LN cartridge
50-100 µm

No co-elution



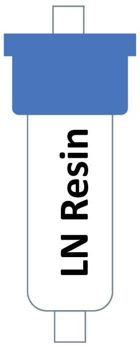


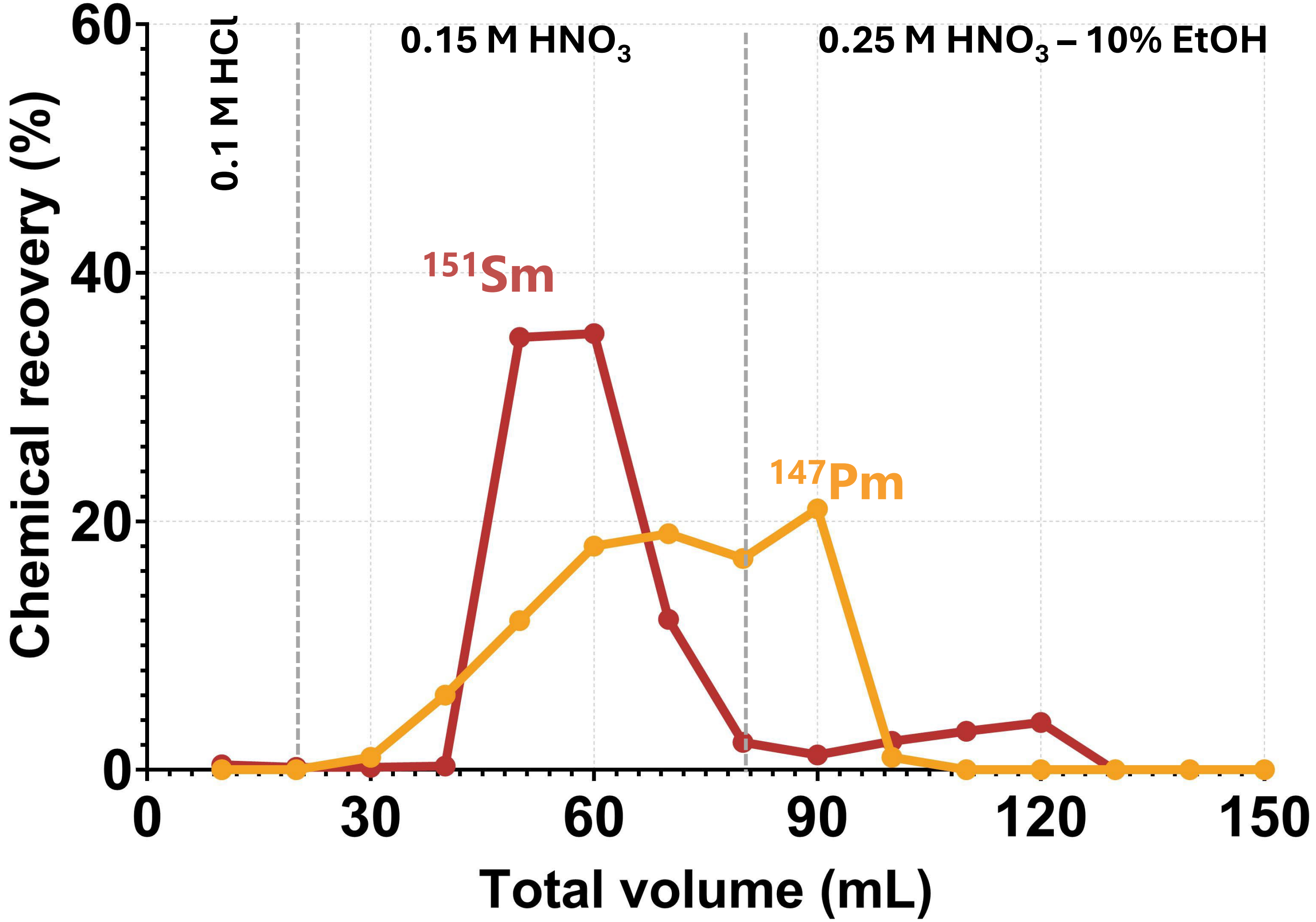
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction

LN cartridge
50-100 µm

Sm co-elute with Pm



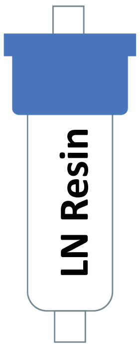


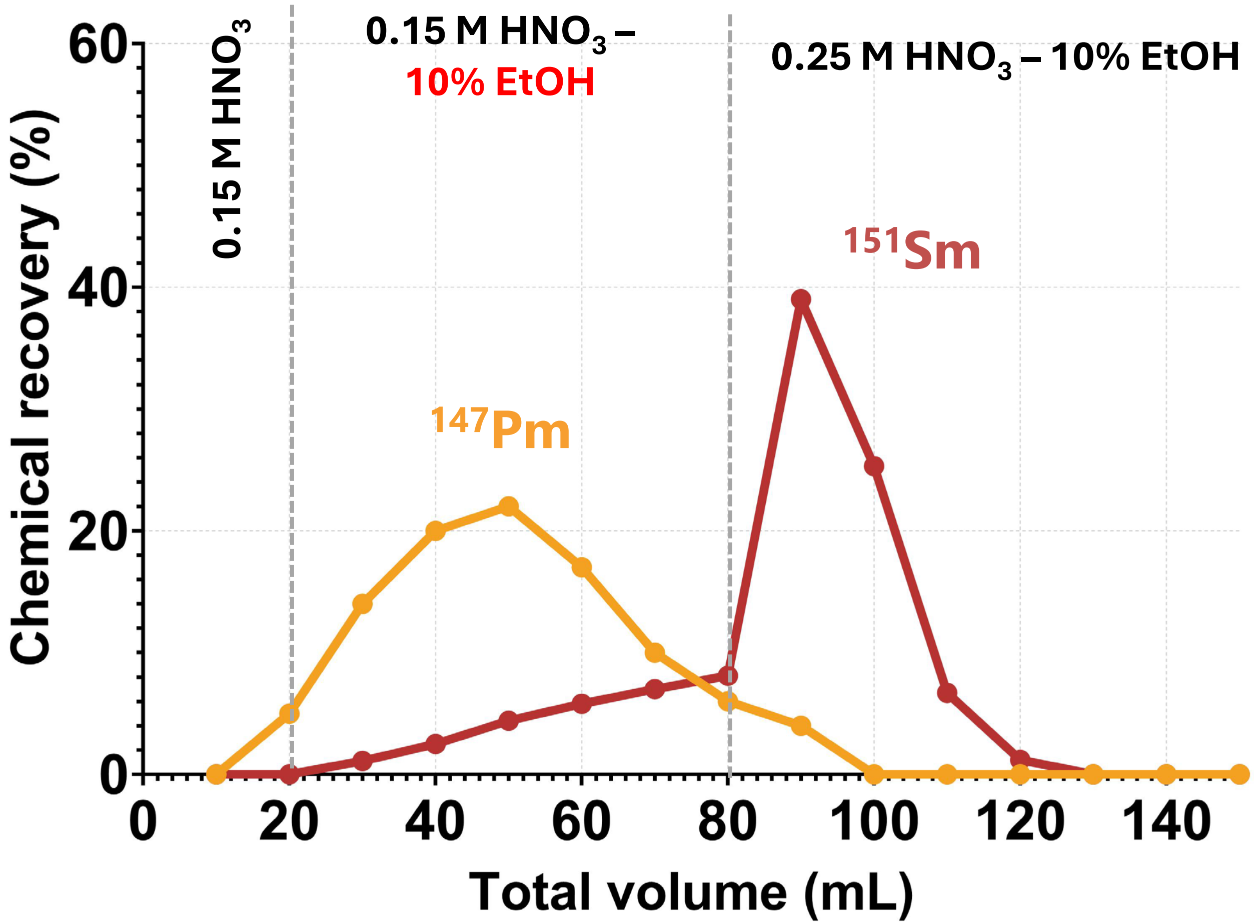
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction

LN cartridge
50-100 µm

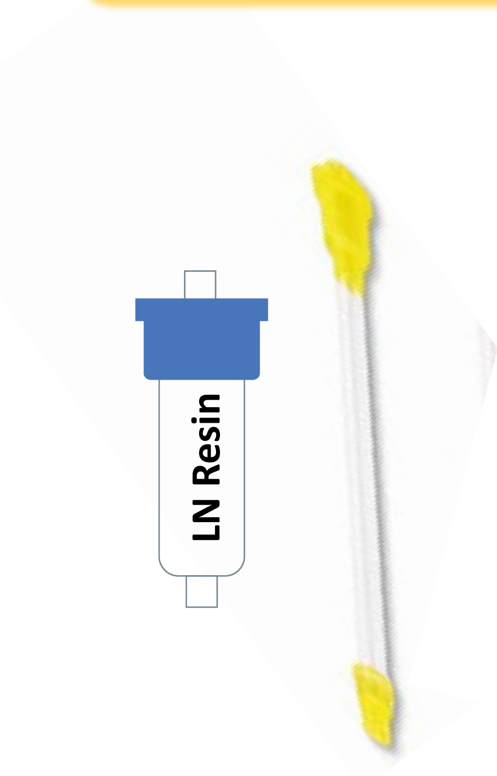
30% Sm co-elute with Pm





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

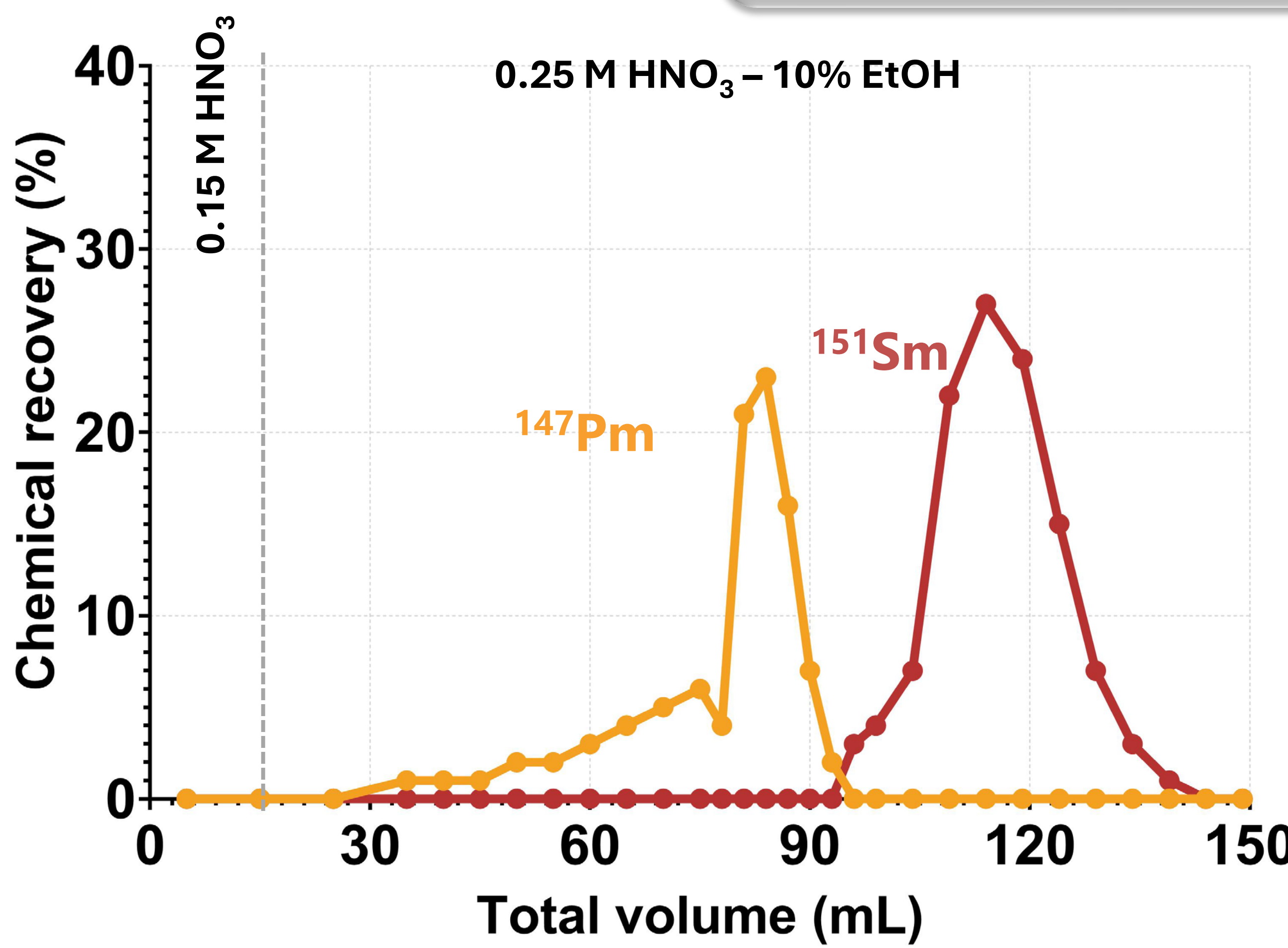
Solid phase extraction



LN column

100-150 µm

0.25 M HNO_3-10% EtOH
68 mL (^{147}Pm)
46 mL (^{151}Sm)

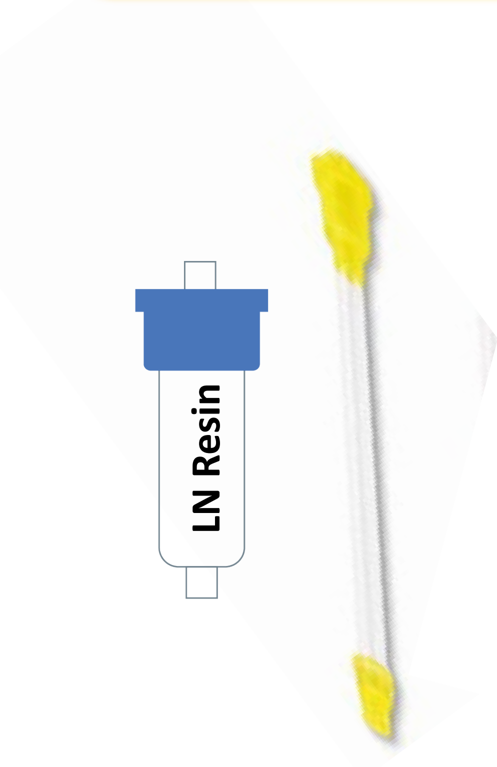


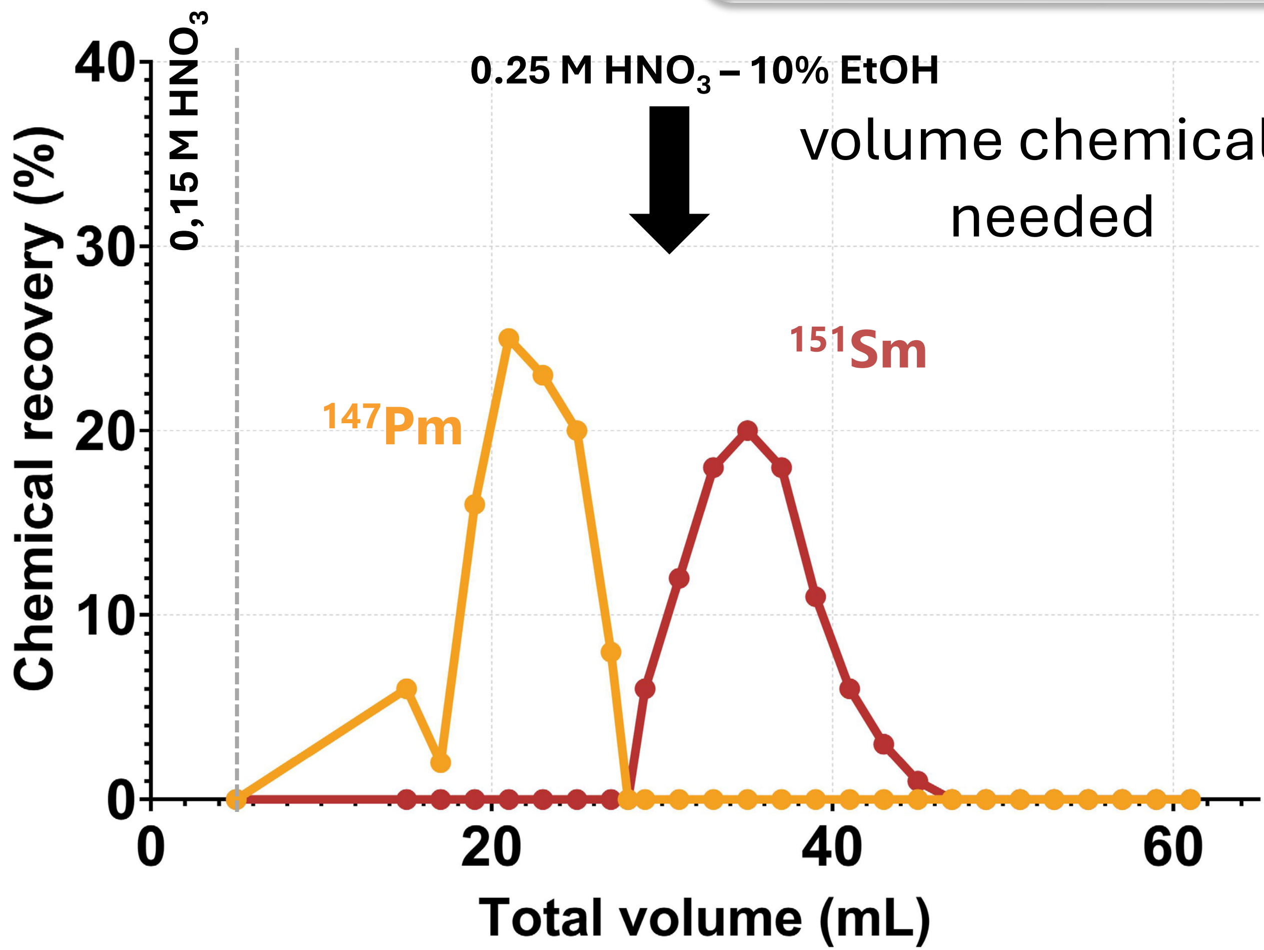
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction

LN column
50-100 µm

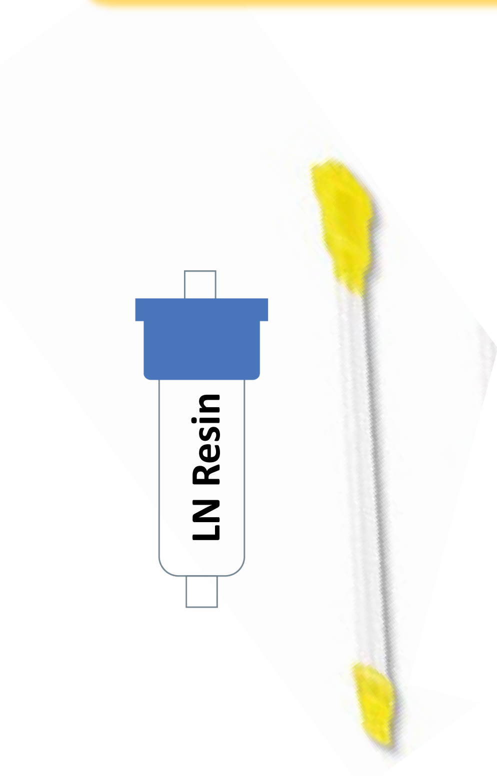
0.25 M HNO_3-10% EtOH
12 mL (^{147}Pm)
16 mL (^{151}Sm)





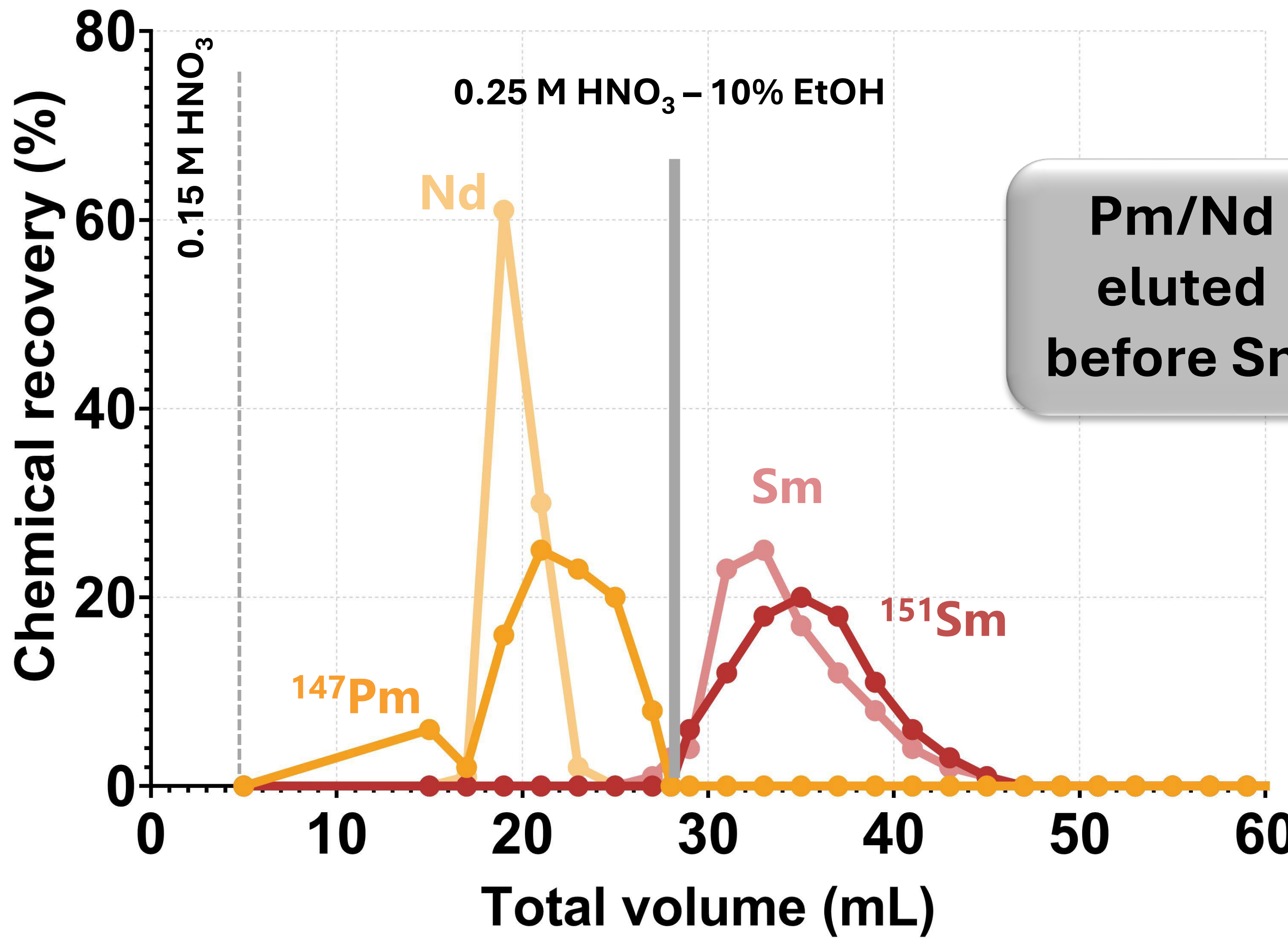
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction



LN Resin

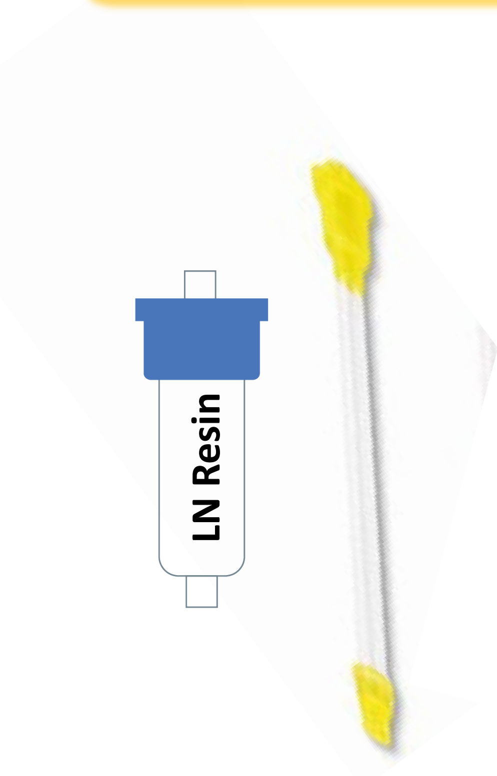
0.5x15 cm (50-100 µm)



Pm/Nd eluted before Sm

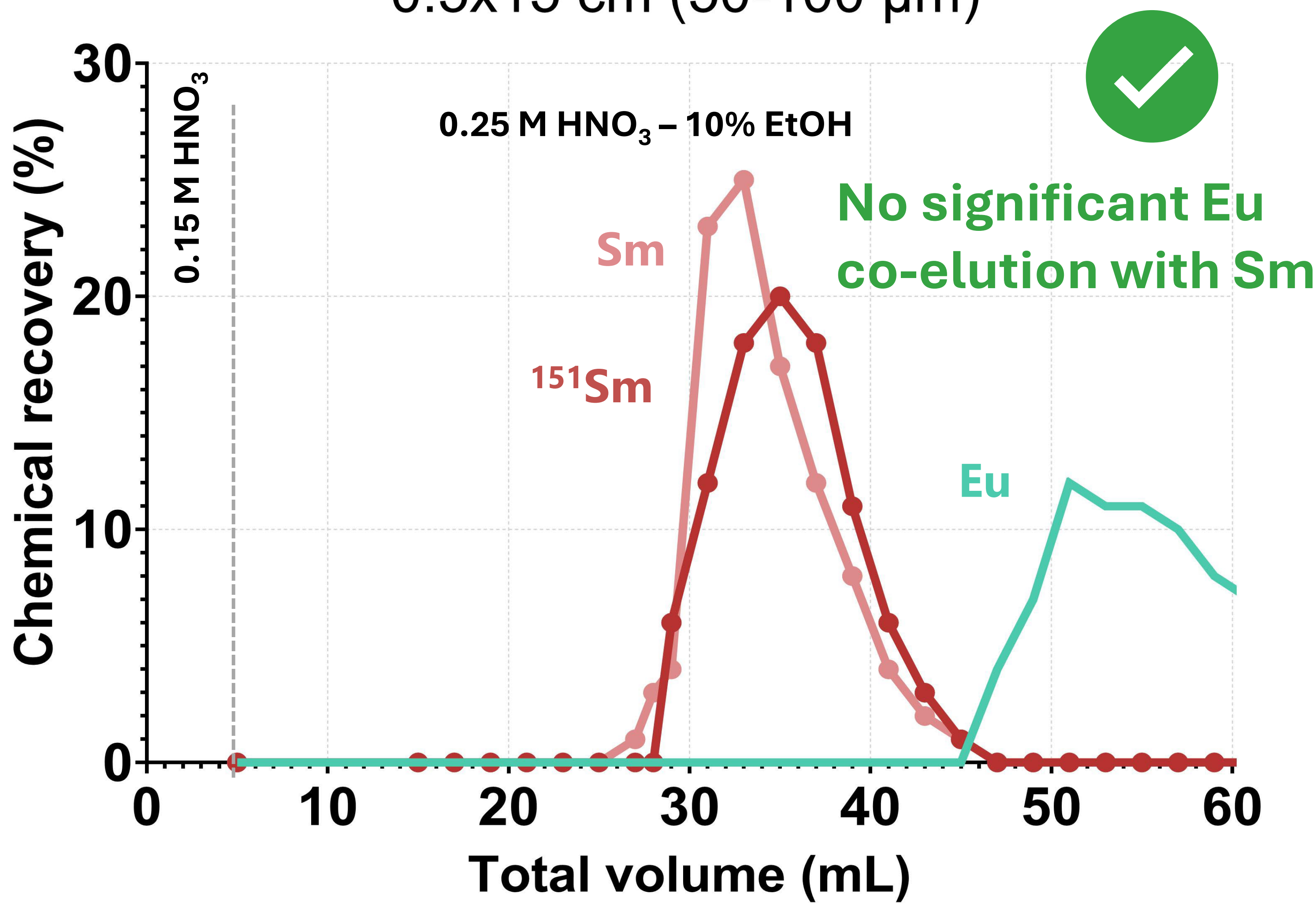
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction



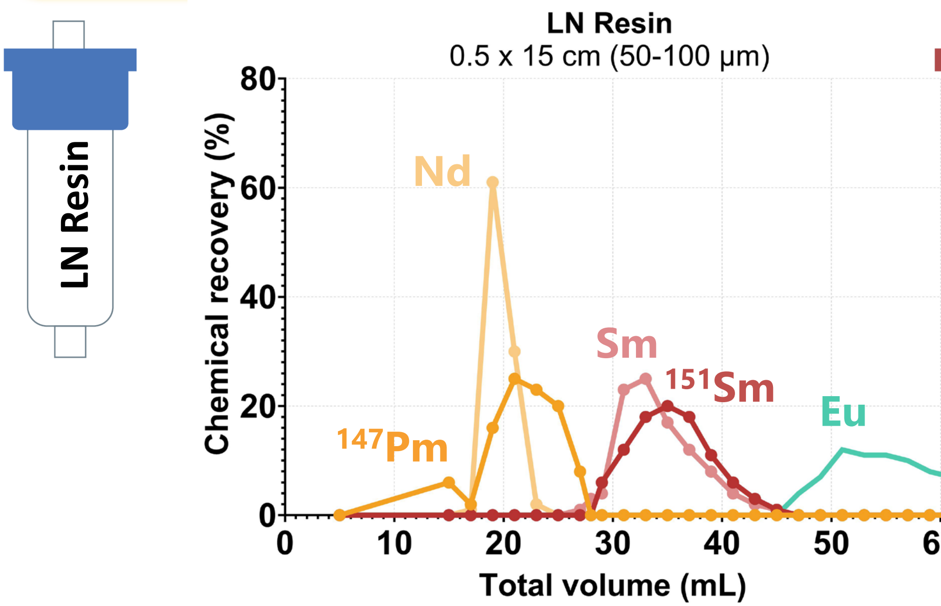
LN Resin

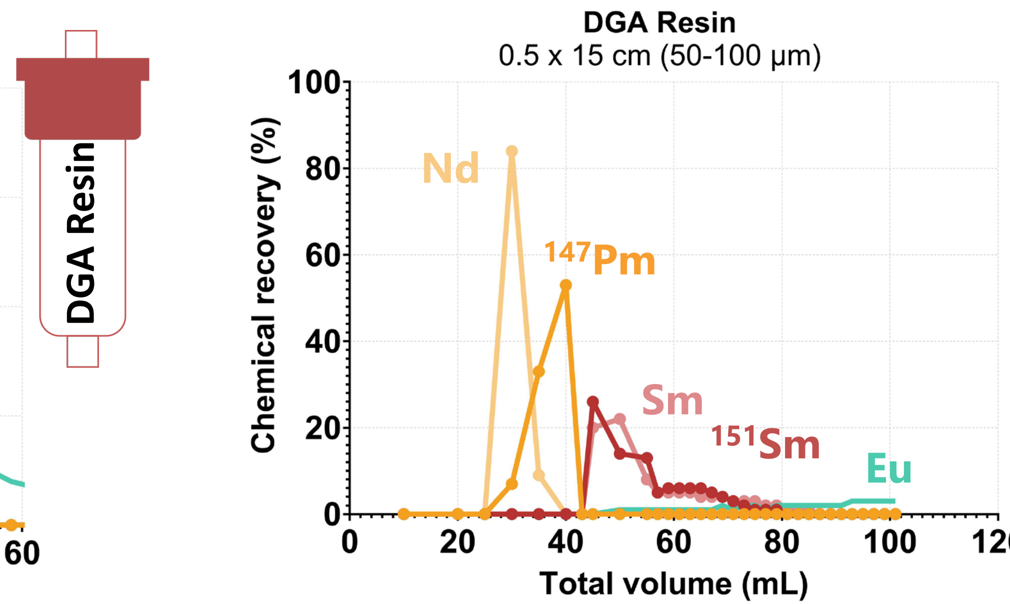
0.5x15 cm (50-100 µm)



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

Solid phase extraction





No Eu co-elution

NEW

New approach

Fewer solution volume for elution

No need to use alcohol

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

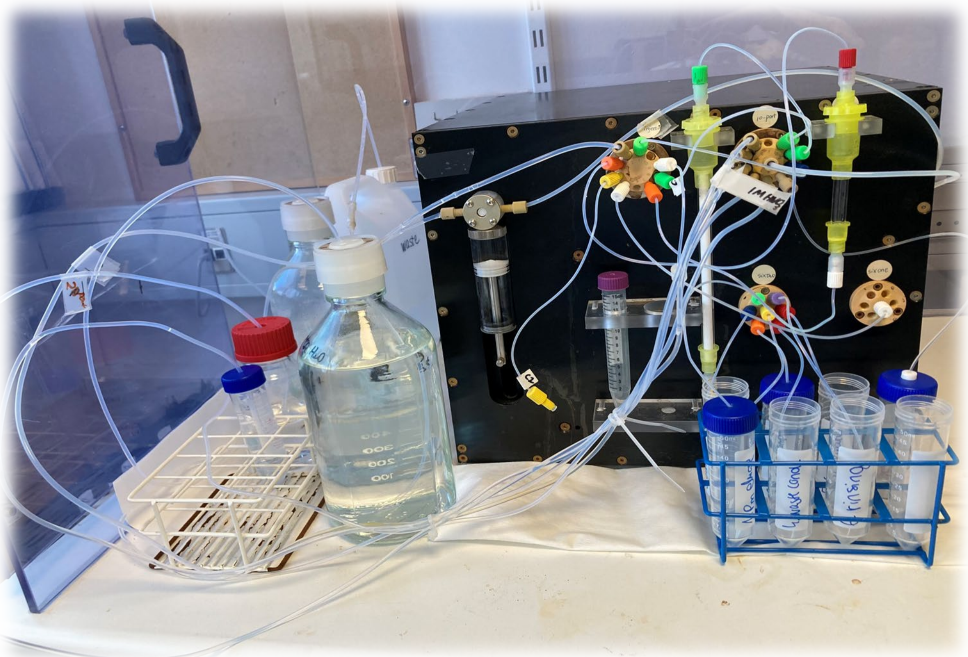
Solid phase extraction-automated system

AUTOMATED SEPARATION SYSTEM

In-house prepared in DTU

Challenges:

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



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

Solid phase extraction-automated system

Volume accumulated reservoir (death volume)

➔ reduce flow rate

Death volume ⟷ *Resin wet*

↓

Dilution of solutions loaded

↓

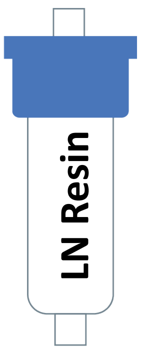
Delay on the elution of the lanthanides

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

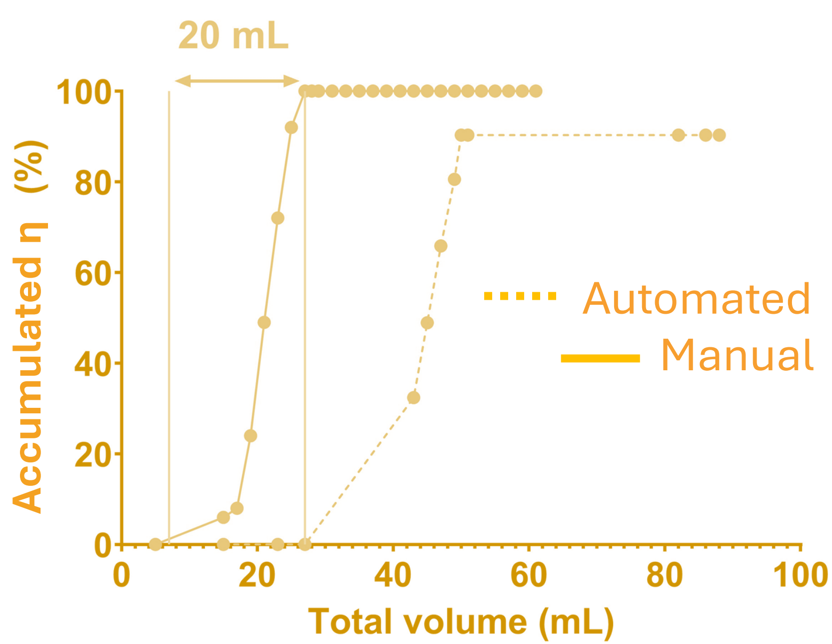
^{147}Pm and ^{151}Sm chemical separation

Solid phase extraction-automated system

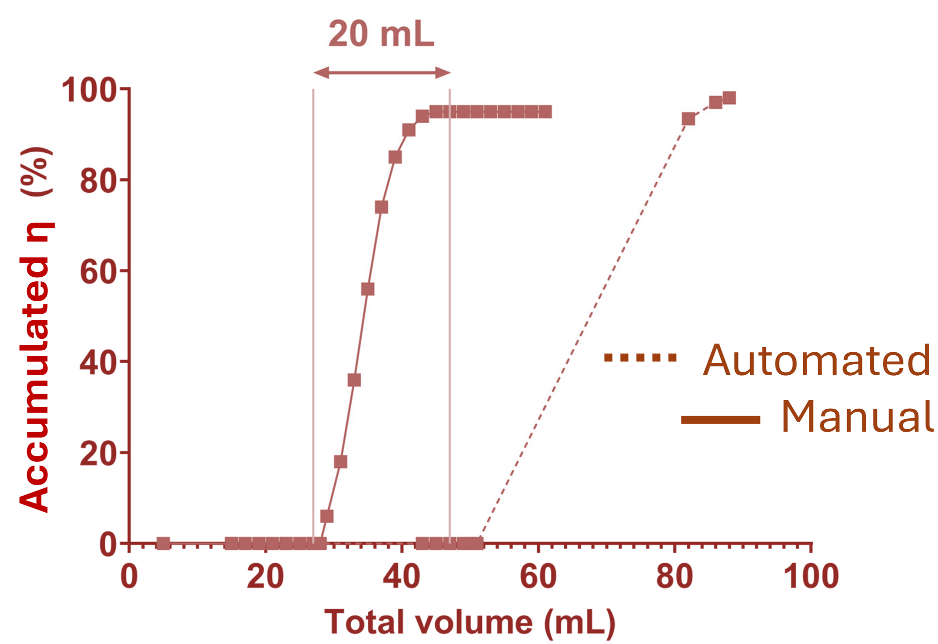
2 h 35 min



^{147}Pm elution



^{151}Sm elution



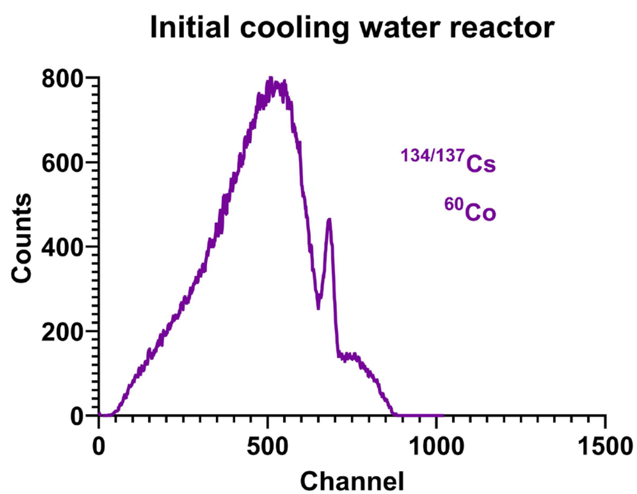
- Delay on ^{147}Pm and ^{151}Sm elution
- Additional 20 mL 0.25 M HNO_3 /10% EtOH needed

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

Solid phase extraction-automated system

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

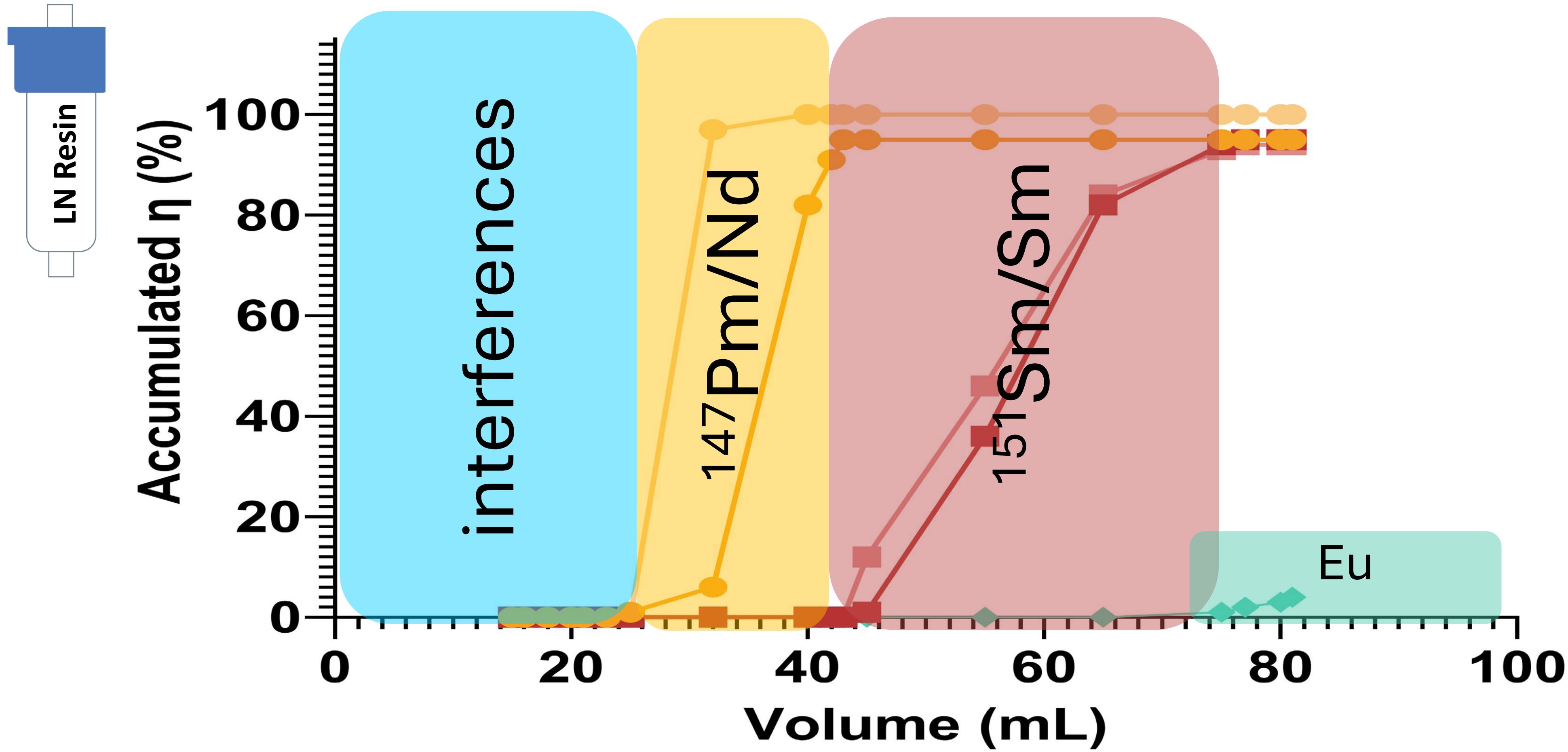
Expected: ^{54}Mn, ^{60}Co, ^{134}Cs and ^{137}Cs

Measured by gamma and LSC

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

Solid phase extraction-automated system

Application in reactor cooling water from a Boiling Water Reactor



Main conclusions

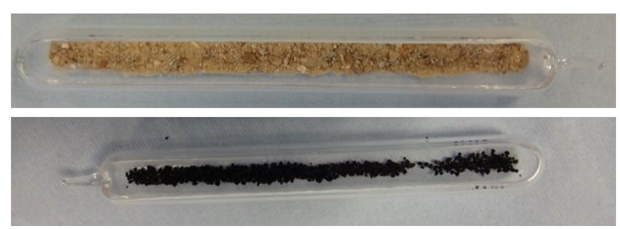
Develop and validate reliable analytical methods for the accurate determination of specific DTM radionuclides

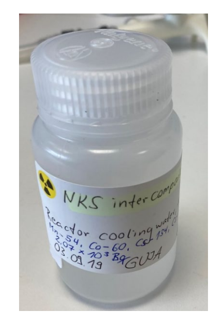
Challenges

Interferences

Low detection limit **(DL)** ≪ Clearance level

Variety of matrices





Turnaround time (TAT) Results in about 24-48 h

Thank you for your attention!!

Questions?

TRISKEM
Expertise in Separation Chemistry