^{36}Cl determination in graphite samples using plastic scintillator materials

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Exploring a better tomorrow

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PhD student

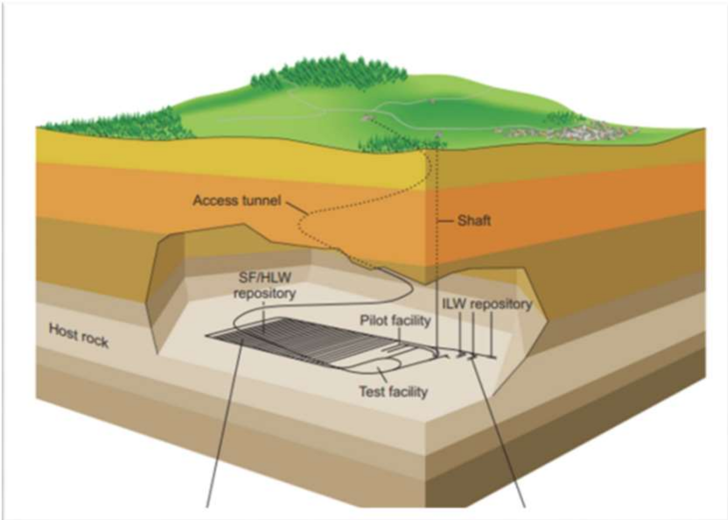
Introduction

Decommissioning of nuclear facilities

ONDRAF/NIRAS

Sorting out

Waste characterization



2018 SE Ignalina Nuclear Power Plant

CRITICAL RADIONUCLIDES

Graphite (reactor)

^{3}H, ^{14}C, ^{55}Fe, ^{63,59}Ni, ^{60}Co, ^{152}Eu, ^{36}Cl

Concrete

^{41}Ca, ^{60}Co, ^{55}Fe, ^{63,59}Ni, ^{133}Ba, ^{152}Eu

Stainless steel

^{55}Fe, ^{63,59}Ni, ^{36}Cl, ^{93}Zr, ^{93}Mo, ^{94}Nb, ^{60}Co, ^{152}Eu, transuranics

Hou, X. 2013. Determination of pure beta emitters using LSC for characterization of waste from nuclear decommissioning. LSC 2013

^{36}Cl in decommissioning samples

CRITICAL RADIONUCLIDES

Graphite (reactor)

^{3}H, ^{14}C, ^{55}Fe, ^{63,59}Ni, ^{60}Co, ^{152}Eu, ^{36}Cl

Concrete

^{41}Ca, ^{60}Co, ^{55}Fe, $^{63, 59}$Ni, ^{133}Ba, ^{152}Eu

Stainless steel

^{55}Fe, ^{63,59}Ni, ^{36}Cl, ^{93}Zr, ^{93}Mo, ^{94}Nb, ^{60}Co, ^{152}Eu, transuranics

- Activation product
- Long-lived radionuclide ($T_{1/2}$= 3.01 E+05 years)
- Beta-particle emitter (E_{max}=709.6 keV)
- High mobility in the environment
- Present in graphite samples (4 - 44 Bq g^{-1})

Based on Von Lensa W, Vulpius D, Steinmetz HJ et al (2013) Treatment and disposal of irradiated graphite and other carbonaceous waste. Mol 6:66

How ^{36}Cl is currently determined?

Sample decomposition

- Acid digestion
- Alkali fusion
- Pyrolysis

Radiochemical separation

- Silver chloride precipitation
- Cation exchange resins
- Solid phase extraction using Cl resin

Measurement technique

- Liquid scintillation counting
- ICP-MS/MS
- AMS (lesser extend)

^{36}Cl determination

Why ^{36}Cl determination is still a topic of interest?

- Lack of solid reference material
- Large amount of waste
- High cost/technical demands
- Long turnaround time (TAT) of radiochemical separation procedures

Plastic scintillator materials (PS)

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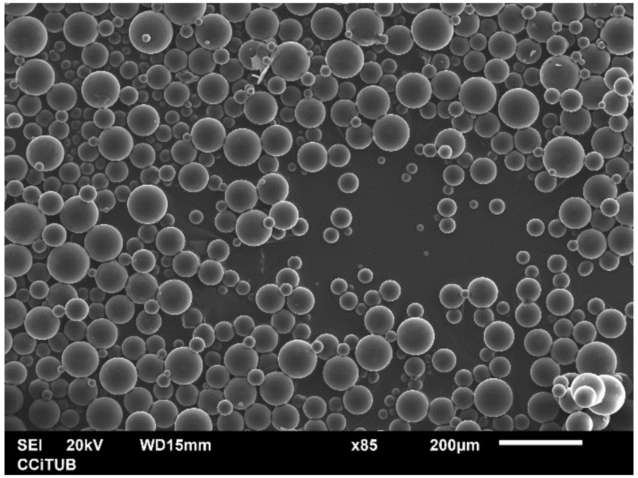
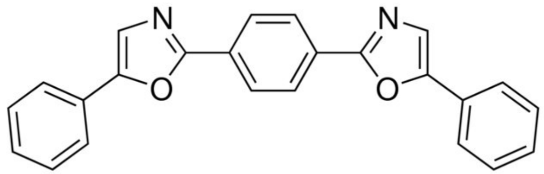
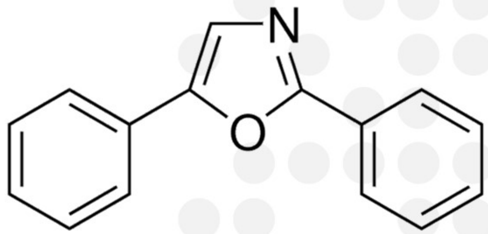


- Polymeric solvent
- Primary and secondary scintillators



POPOP



PPO

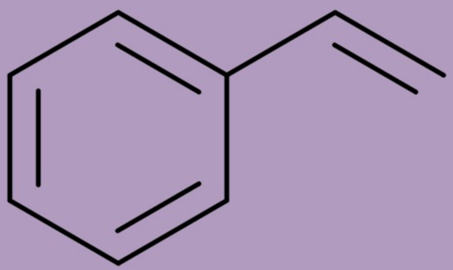
Composition PS ≈ Composition LS cocktail

Tarancón A, Bagán H, García JF (2017) Plastic scintillators and related analytical procedures for radionuclide analysis. J Radioanal Nucl Chem 314:555–572

Plastic scintillator materials (PS)

PS microspheres (PSm)

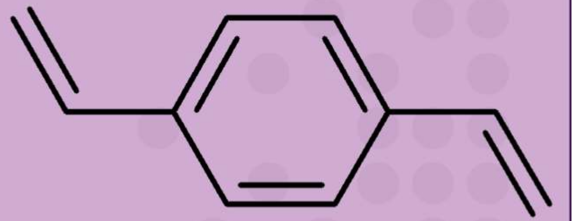
Solvent: linear chain



Styrene

Cross-linked PS microspheres (CPSm)

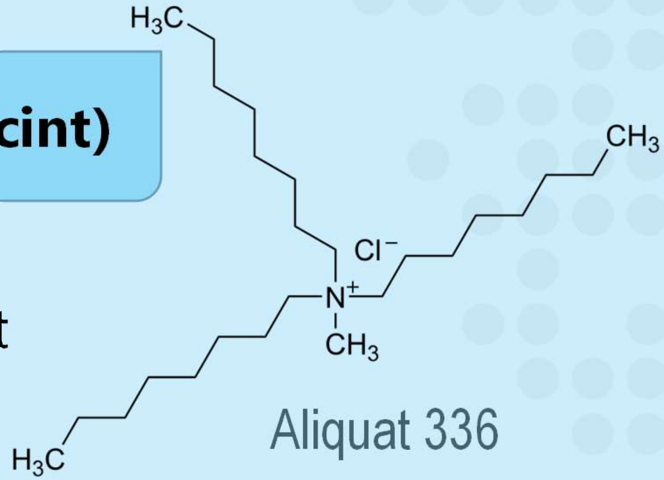
Solvent: cross linker (↑ stability against aggressive media)



Divinylbenzene

PS resin (TK-TcScint)

PSm coated with a selective extractant

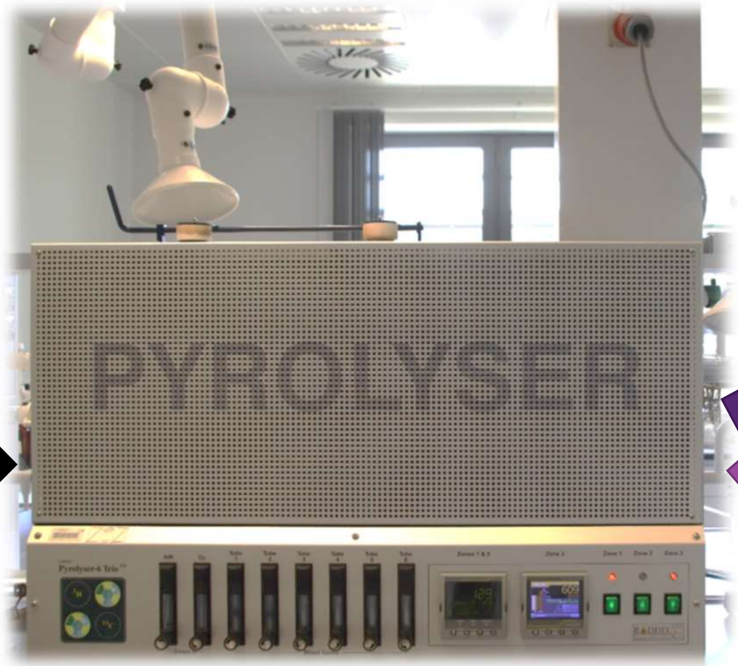


Aliquat 336

Methods

Sample combustion: Pyrolysis

0,5 g graphite sample



Cl_2

?

HCl

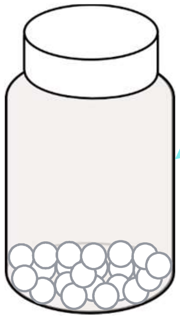
Pyrolyser-Trio™
(Raddec International Ltd.)

Based on Llopart Babot, I. et al. **2022a**. On the determination of 36 Cl and 129 I in solid materials from nuclear decommissioning activities. J. Radioanal. Nucl. Chem.

Sample combustion: Pyrolysis

1st set-up

Cl_2 ?



Trapping solution

Based on Llopart Babot et al. **2023**. Investigation of a new approach for ^{36}Cl determination in solid samples using plastic scintillators. Appl. Radiat. Isot. 193

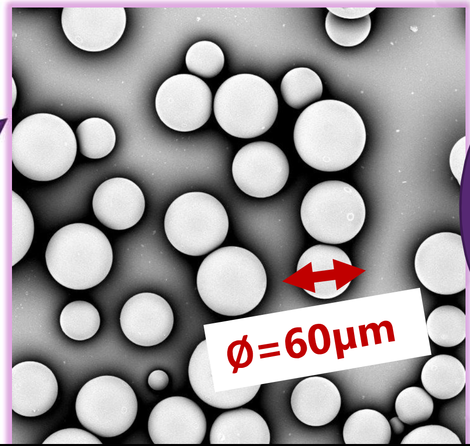
Sample treatment after combustion

1st set-up

30 mL
6 mM Na_2CO_3

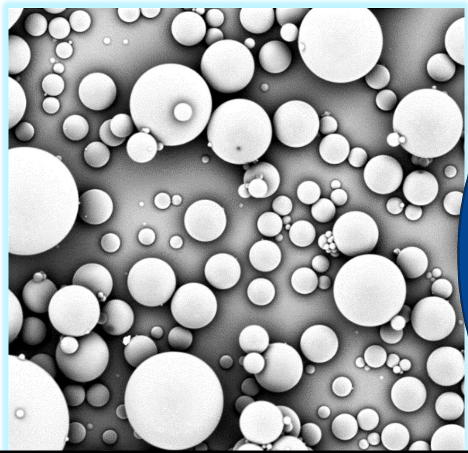
Collection of ^{36}Cl not retained by the PS material

Direct measurement



SEM image PSm 100µm

Plastic scintillator microspheres (PSm)



SEM image CPSm 100µm

Cross-linked plastic scintillator microspheres (CPSm)

ISC: Restricted

Sample combustion: Pyrolysis

2nd set-up

Trapping solution

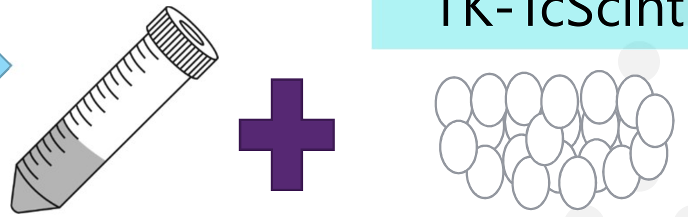
?

HCl

Sample treatment after combustion

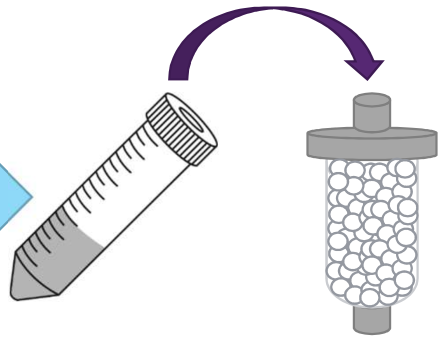
2nd set-up

1st approach



PSm / CPSm/ TK-TcScint

2nd approach

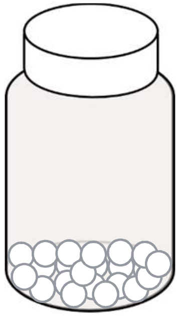


TK-TcScint

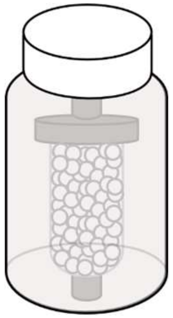
Based on Llopart Babot et al. **2023**. Investigation of a new approach for ^{36}Cl determination in solid samples using plastic scintillators. Appl. Radiat. Isot. 193

Sample measurement

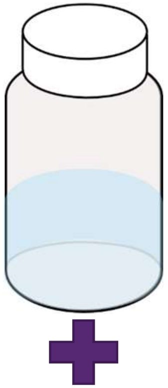
Vials containing



PSm/CPSm



TK-TcScint cartridge



LS cocktail

Collected liquid fractions

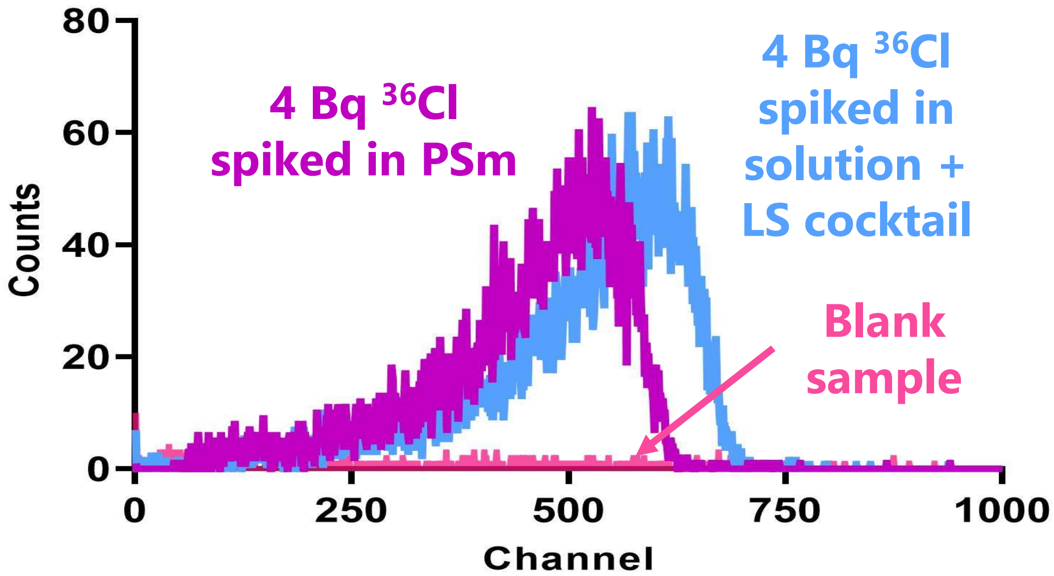
Liquid scintillation counting (LSC)

Wallac Quantulus 1220™

Results

1st set-up: pyrolyser connected to an LS vial containing PS

^{36}Cl LS spectra



Background check

Mass PSm	Counting time	Counting rate (CPM)	SQP[E]
1 g	60 min	1,4 ± 0,2	676± 9
3 g	60 min	1,8 ± 0,2	688 ± 4
1 g	120 min	1,4 ± 0,1	678 ± 4
3 g	120 min	1,7 ± 0,1	686 ± 7

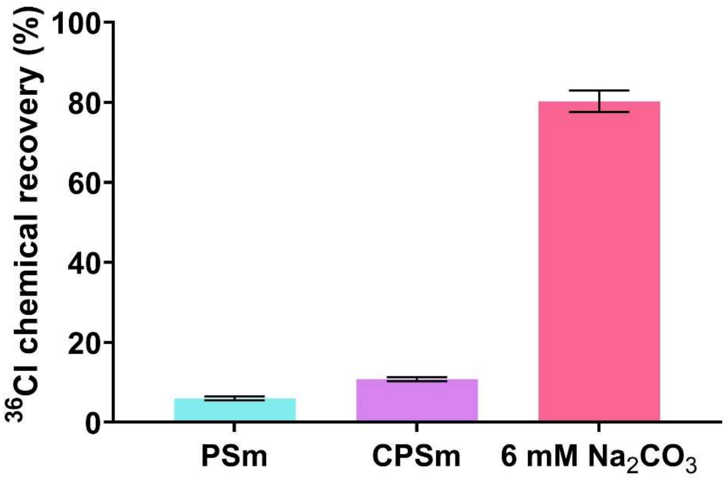
1 g PSm and 120 min counting time

Lowest background level

Low DL

1st set-up: pyrolyser connected to an LS vial containing PS

Different trapping media



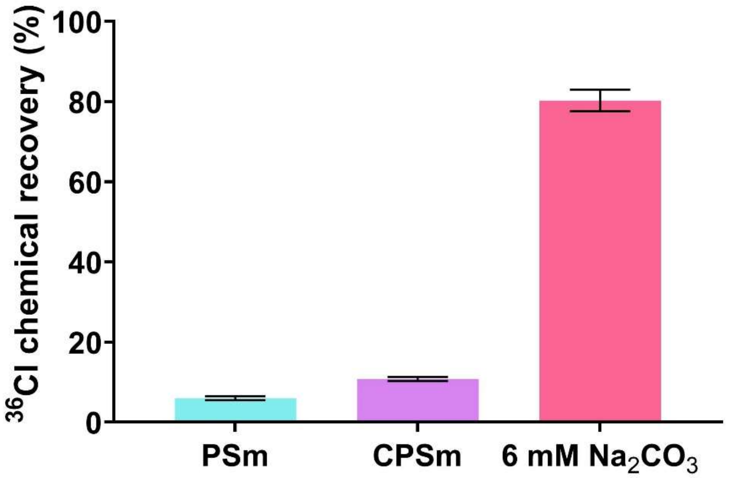
PSm 6.0 ± 0.5 %

CPSm 10.8 ± 0.5 %

30 mL 6 Mm Na_2CO_3 80.3 ± 2.7 %

1^{st} set-up: pyrolyser connected to an LS vial containing PS

Different trapping media



Based on Mitev. K 2016. Measurement of 222Rn by absorption in plastic scintillators and alpha/beta pulse shape discrimination. Appl. Radiat. Isot. 110, 236–243.

Low η when using PSm/CPSm as trapping medium

About 50-70 % ^{36}Cl measured in the second bubbler

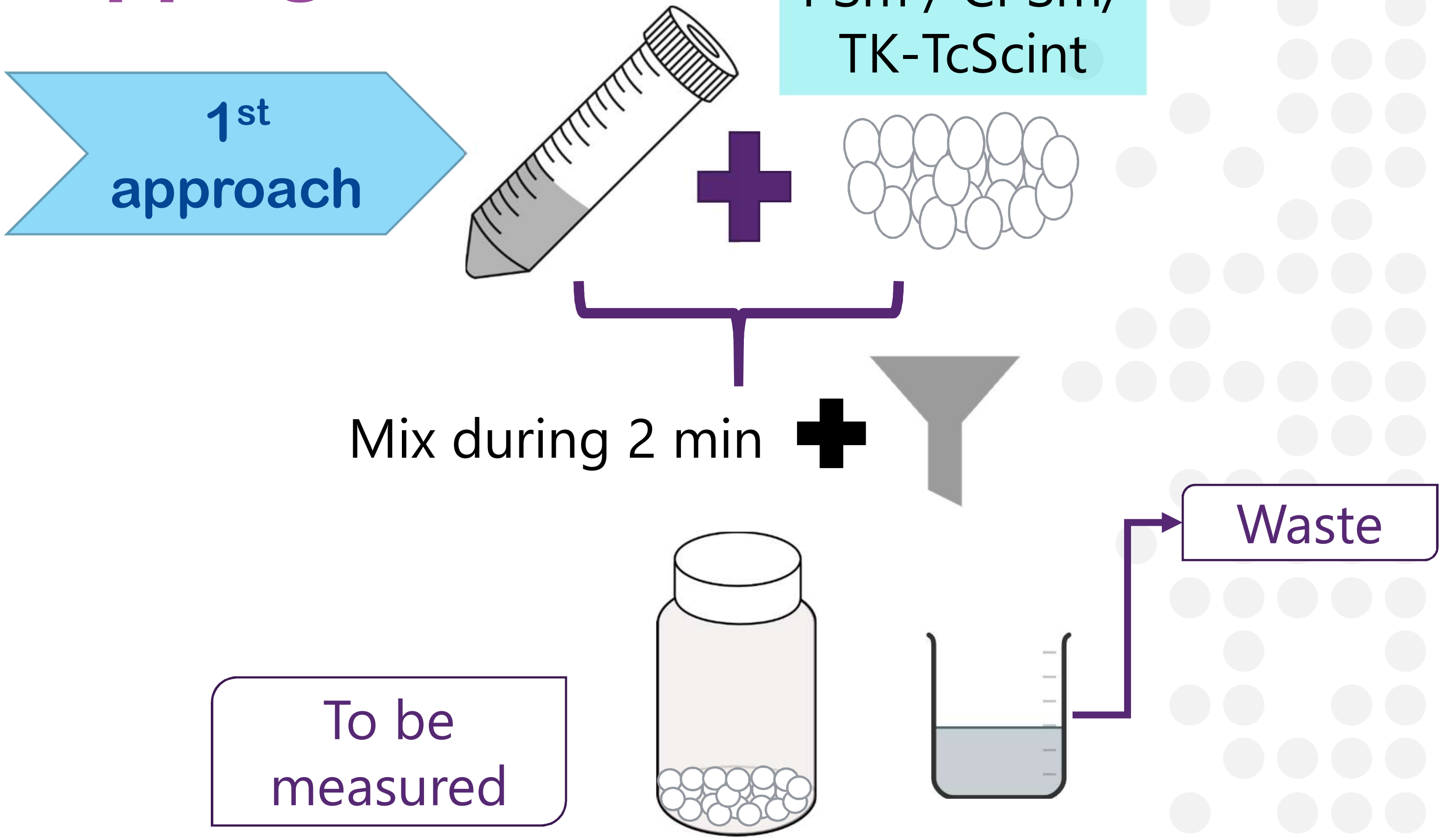
^{36}Cl memory effect during pyrolysis

Llopart Babot, I. et al. **2022b**. Investigating the ^{36}Cl memory effect in pyrolysis of solid samples from nuclear decommissioning activities. J. Radioanal. Nucl. Chem.

Only a small amount of Cl is released as Cl_2

Gas adsorption in PS materials

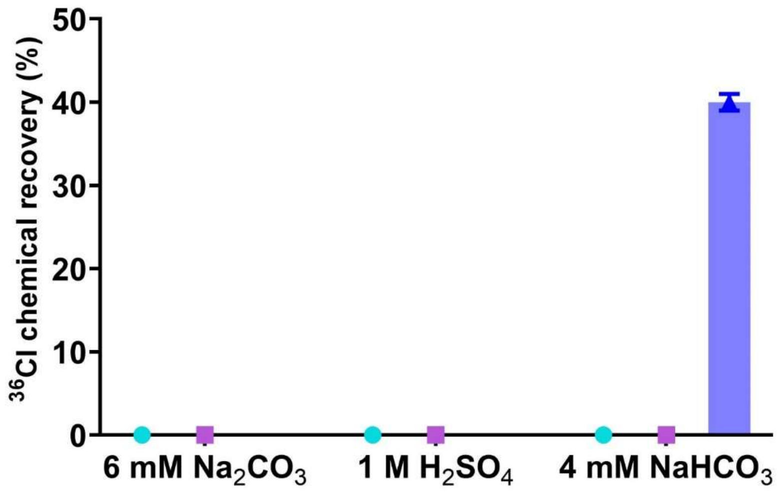
2nd set-up: pyrolyser connected to a bubbler containing a trapping solution



2nd set-up: pyrolyser connected to a bubbler containing a trapping solution

1st approach

^{36}Cl retention in different PS materials



^{36}Cl η

Mixing 6 mM Na_2CO_3 **with**
- **PSm**
- **CPSm**

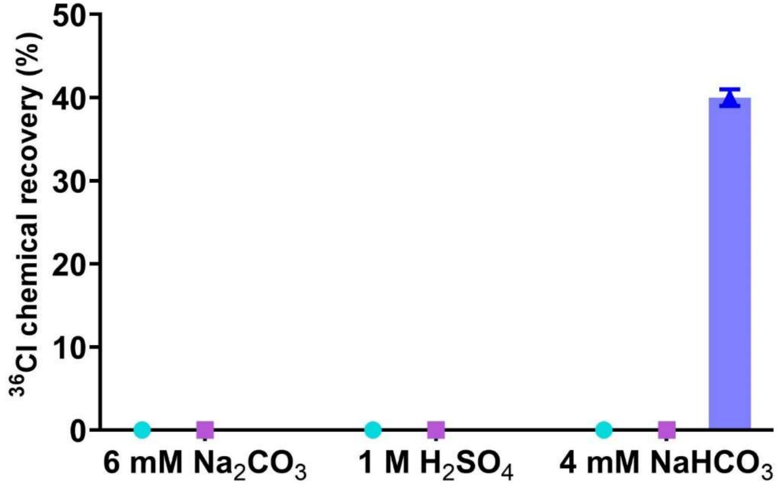
Mixing 1 M H_2SO_4 **with**
- **PSm**
- **CPSm**

Mixing 4 mM $NaHCO_3$ **with**
- **PSm**
- **CPSm**
- **TK-TcScint** 40 ± 1 %

2^{nd} set-up: pyrolyser connected to a bubbler containing a trapping solution

1^{st} approach

^{36}Cl retention in different PS materials



PS materials without extractant ➔ no Cl retention

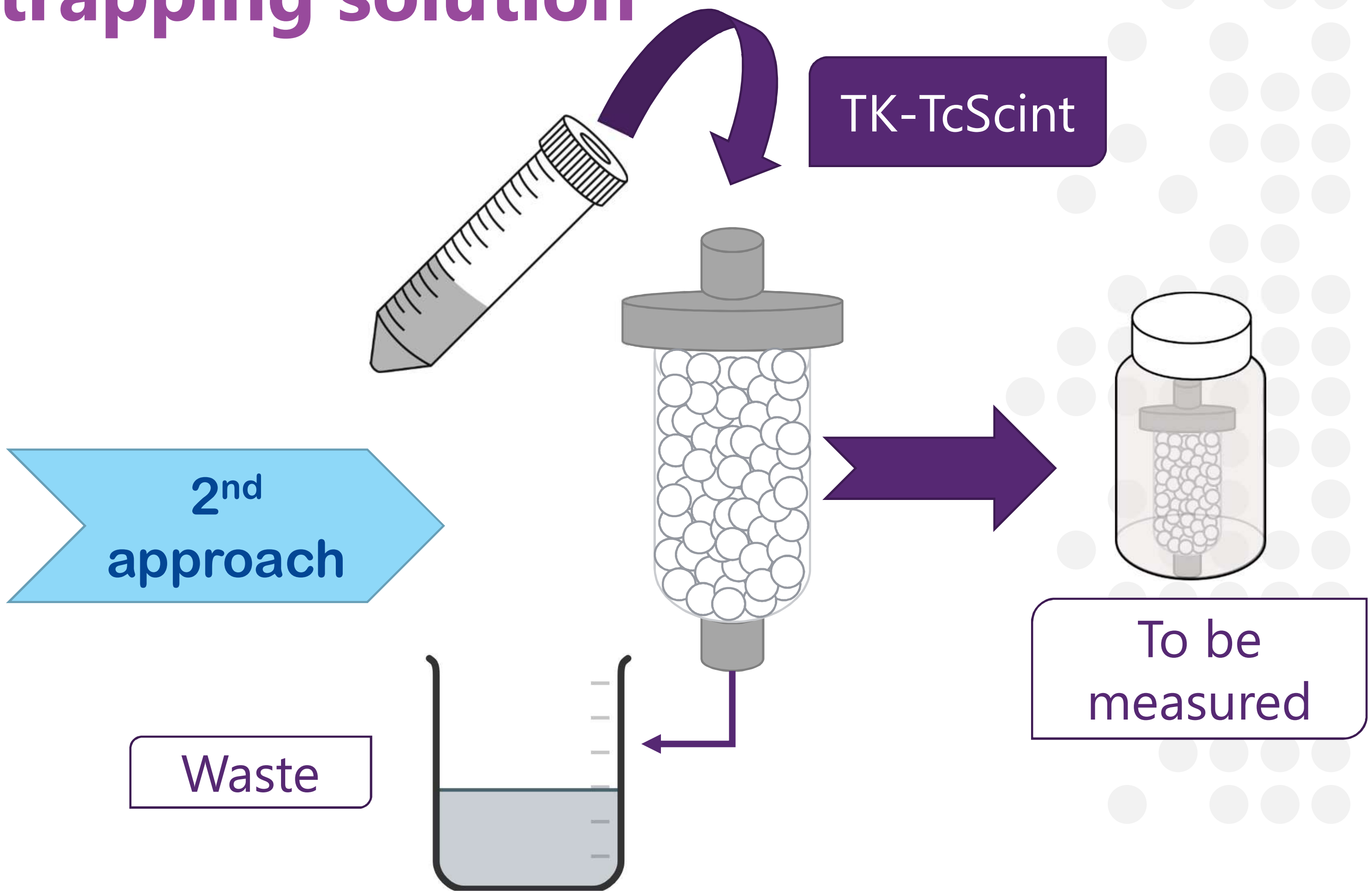
Confirmation that **Cl^- form** is not interacting with PS materials without extractant

40% ^{36}Cl analysed in PS resin

Short interaction time ?

TK-TcScint resin best performing material

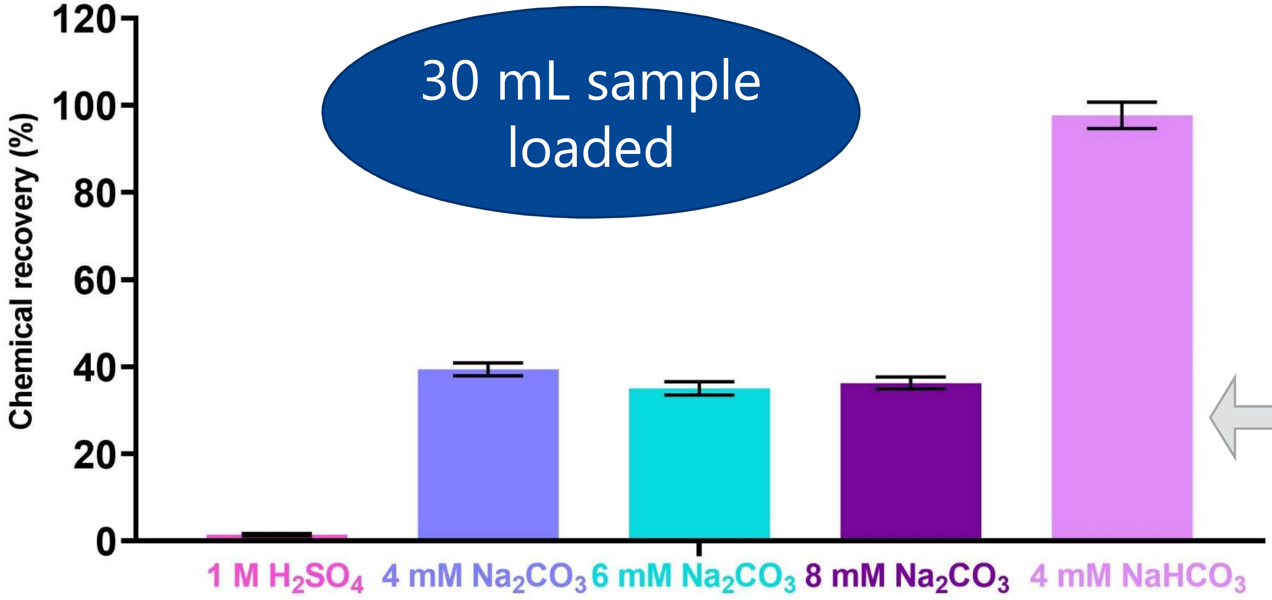
2nd set-up: pyrolyser connected to a bubbler containing a trapping solution



2nd set-up: pyrolyser connected to a bubbler containing a trapping solution

2nd approach

Compatibility of TK-TcScint with different loading media



Aliquat 336 works between acid pH and slight alkaline

Lower η when loading with Na_2CO_3

4 mM $NaHCO_3$ most promising loading solution

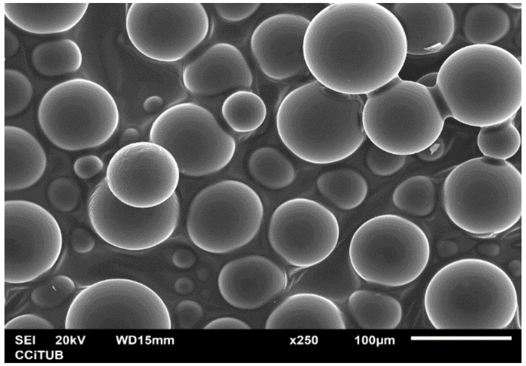
2^{nd} set-up: pyrolyser connected to a bubbler containing a trapping solution

2^{nd} approach

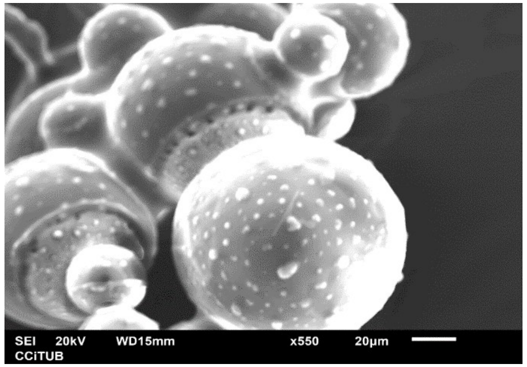
Different loading media

SEM images to confirm loading solution effects

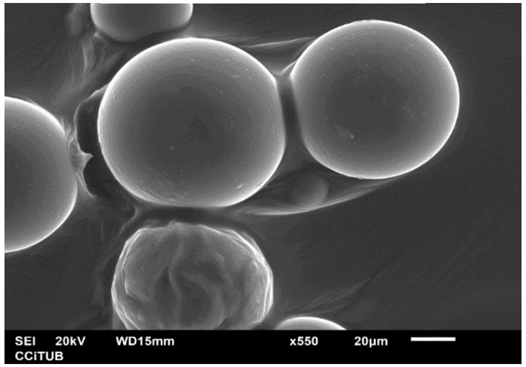
Blank



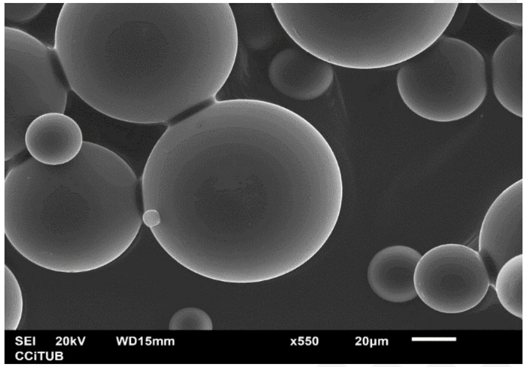
1 M H_2SO_4



6 mM Na_2CO_3



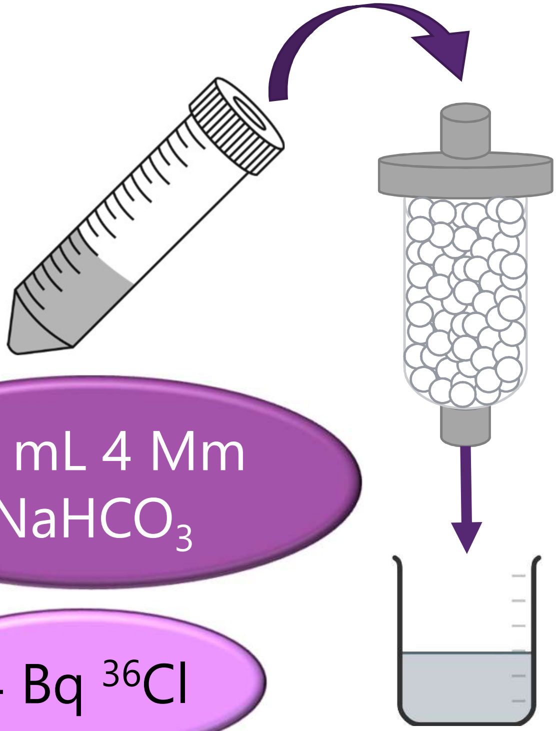
4 mM $NaHCO_3$



2nd set-up: pyrolyser connected to a bubbler containing a trapping solution

2nd approach

Cleaning of TK-TcScint resin



30 mL 4 Mm $NaHCO_3$

4 Bq ^{36}Cl

Addition 7 mL cleaning media

Measure TK-TcScint cartridge

^{36}Cl activity decrease

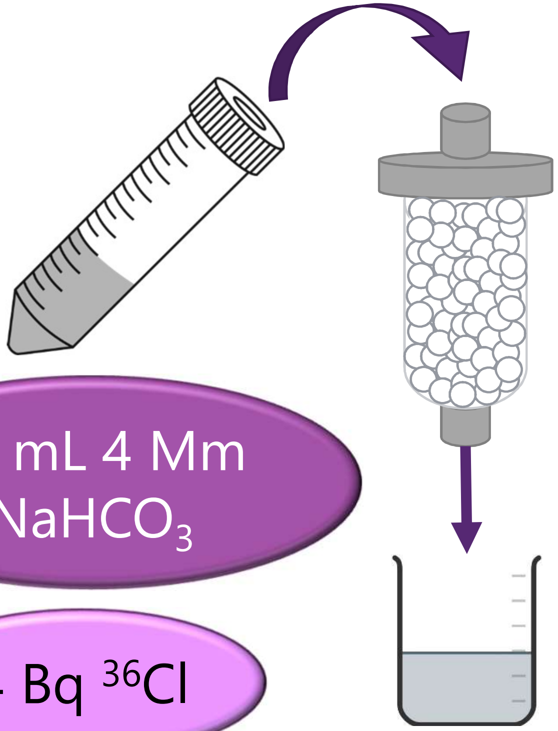
Measure collected waste

^{36}Cl removed from the cartridge

2^{nd} set-up: pyrolyser connected to a bubbler containing a trapping solution

2^{nd} approach

Cleaning of TK-TcScint resin

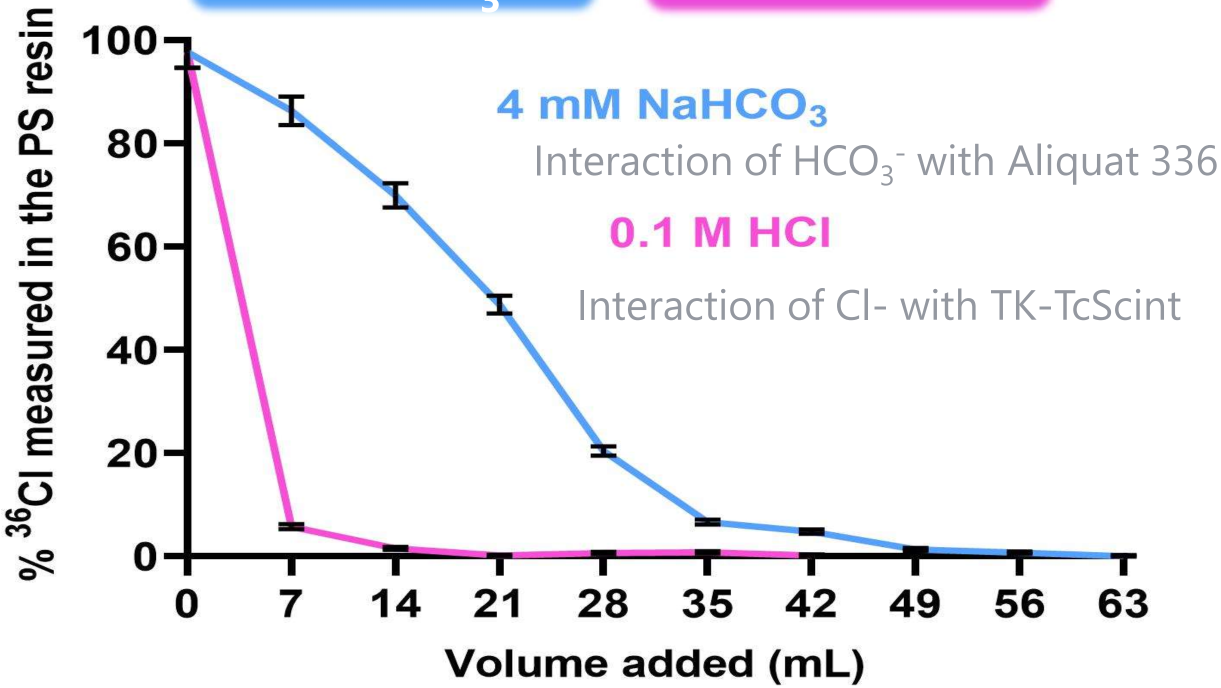


30 mL 4 Mm $NaHCO_3$

4 Bq ^{36}Cl

49 mL 4 mM $NaHCO_3$

14 mL 0,1 M HCl



2nd set-up: pyrolyser connected to a bubbler containing a trapping solution

2nd approach

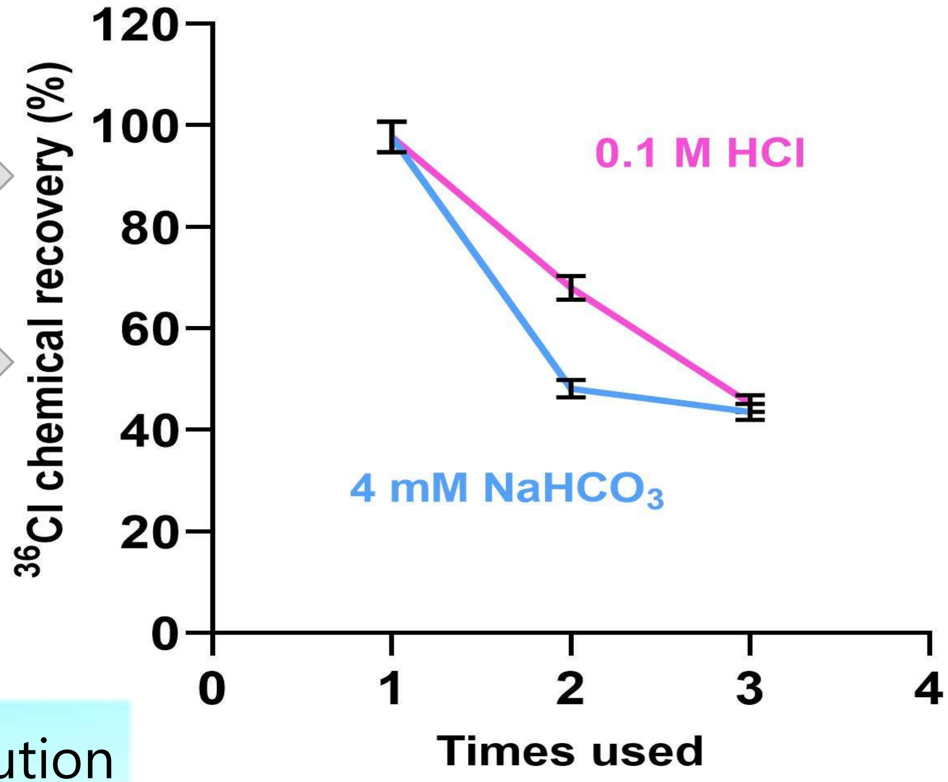
Reuse of the TK-TcScint resin

^{36}Cl chemical recovery ↓ after reusing the resin

2nd reuse → ~50% ^{36}Cl η

Reaction of Aliquat 336 and anions (Cl^- and HCO_3^-) becomes irreversible (crystals)

n° sites available ↓ when adding solution



2nd set-up: pyrolyser connected to a bubbler containing a trapping solution

2nd approach

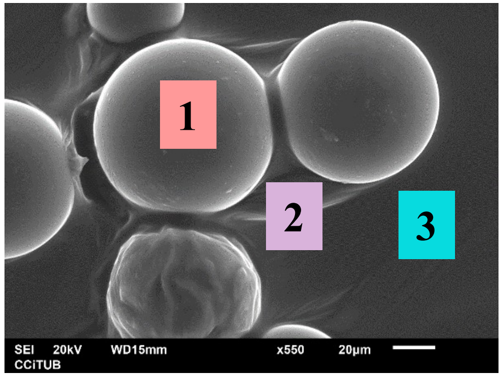
Saturation of the resin

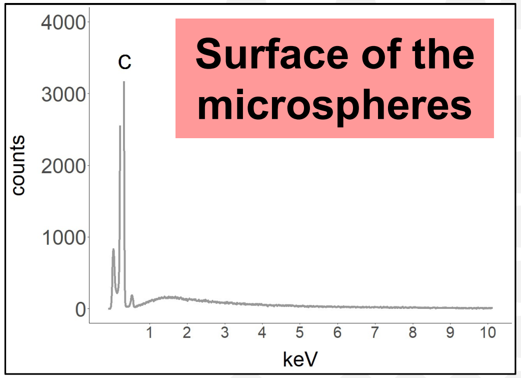
30 mL 4 mM $NaHCO_3$ loaded

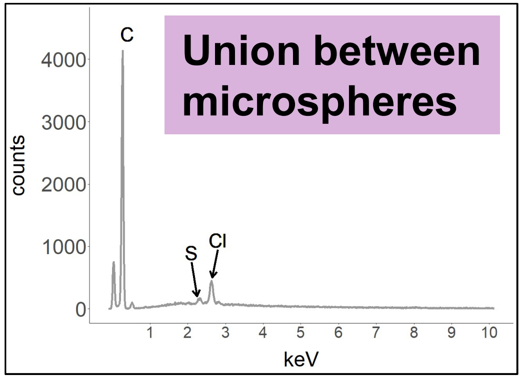
Activity spiked ^{36}Cl (Bq)	Stable chlorine added (mg)	^{36}Cl η (%)
4	0	98 ± 3
4	1	98 ± 3
12	1	100 ± 3

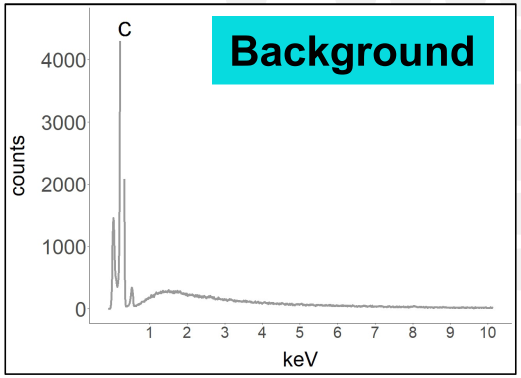
η not affected by the amount of stable Cl or ^{36}Cl activity spiked

Where is Cl in the TK-TcScint resin?









2nd set-up: pyrolyser connected to a bubbler containing a trapping solution

2nd approach

Possible interferences

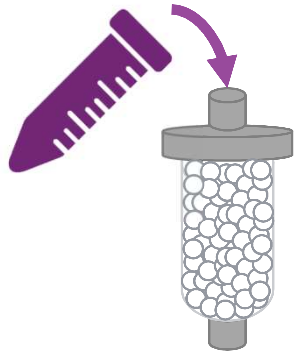
spiked with

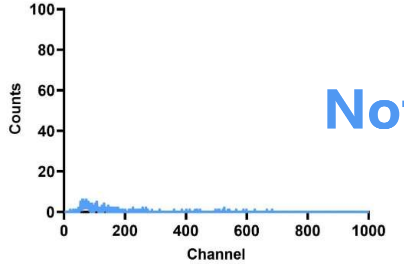
30 mL 4 mM $NaHCO_3$

^{3}H
200 Bq

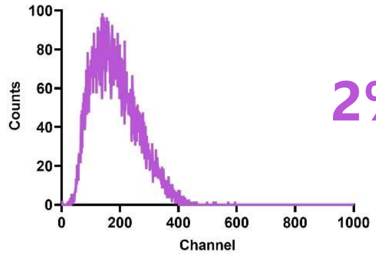
^{14}C
200 Bq

^{129}I
4 Bq

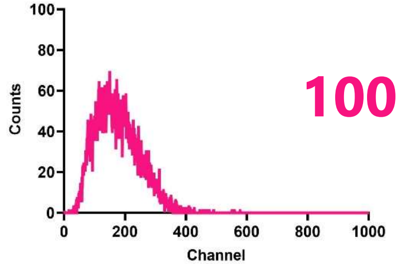




Not retained



2% retained



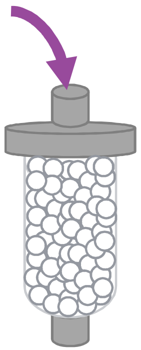
100% retained

2nd set-up: pyrolyser connected to a bubbler containing a trapping solution

2nd approach

Interference removal

14 mL RO water

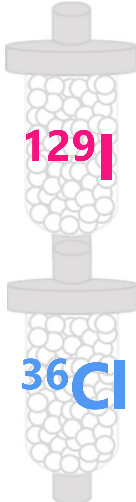


^{14}C

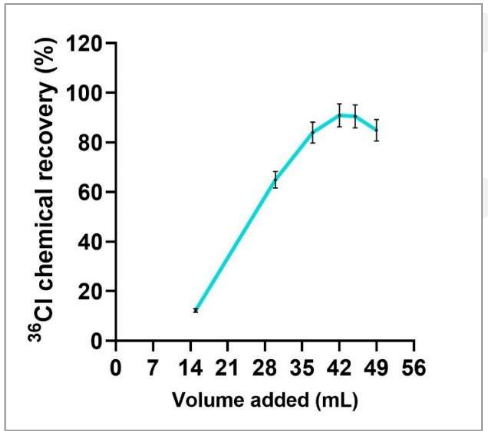
^{129}I

- 6 mM Na_2CO_3
- 0,35 M Na_2S
  Iodine elution Cl-resin
- 1 % TMAH
  Stabilize iodine as iodide
- 1 mM KI
  Anionic exchange $^{129}I^-$ and I^-

2nd TK-TcScint resin needed



Breakthrough volume



45 mL 4 mM $NaHCO_3$

91 ± 4 % ^{36}Cl

2nd set-up: pyrolyser connected to a bubbler containing a trapping solution

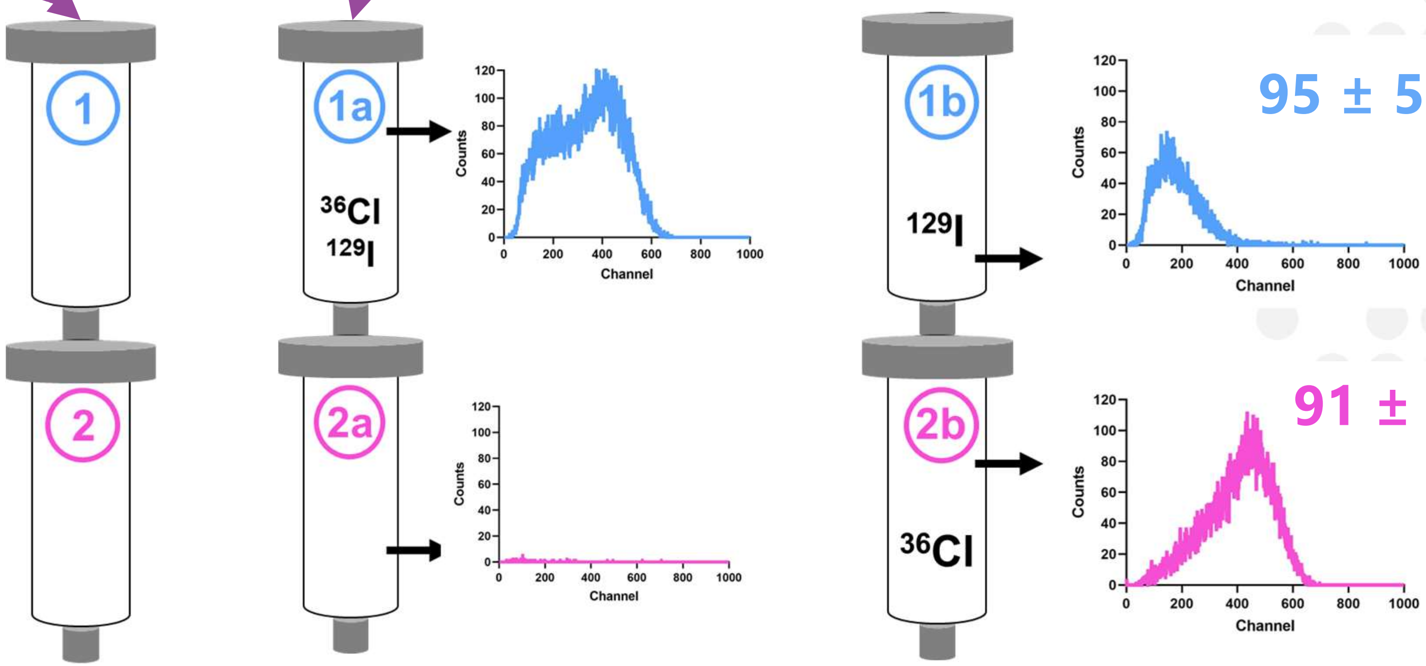
2nd approach

Interference removal

45 mL 4 mM $NaHCO_3$

30 mL 4 mM $NaHCO_3$

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



95 ± 5 % ^{129}I

91 ± 4 % ^{36}Cl

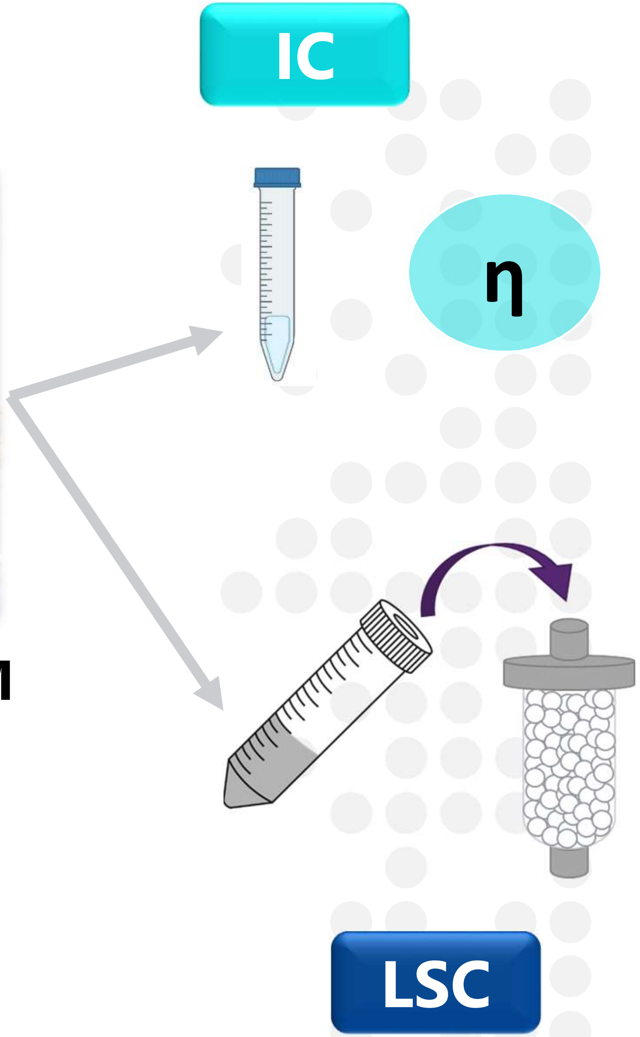
Method application

^{36}Cl spiked graphite samples

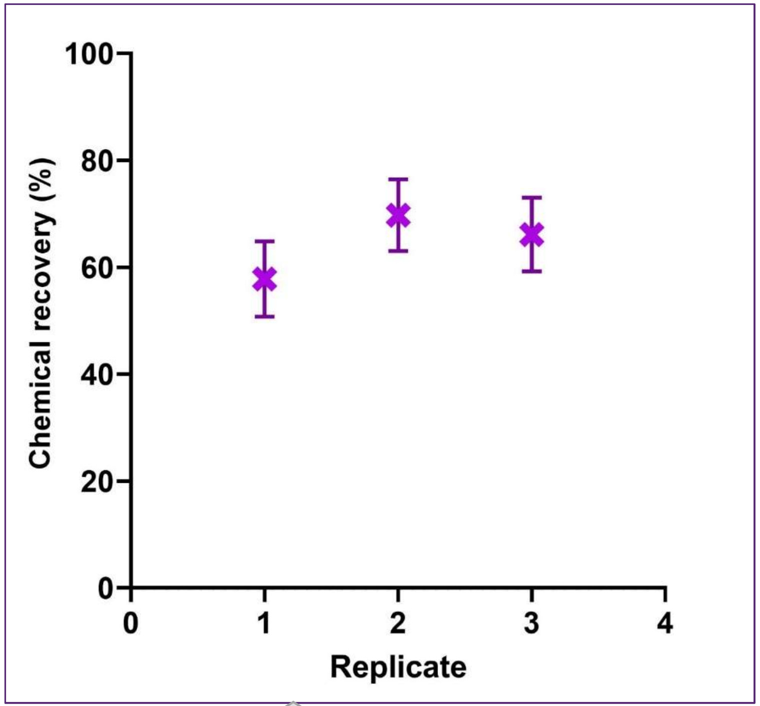
0,5 g blank graphite
- 4 Bq ^{36}Cl
- 1 mg stable Cl

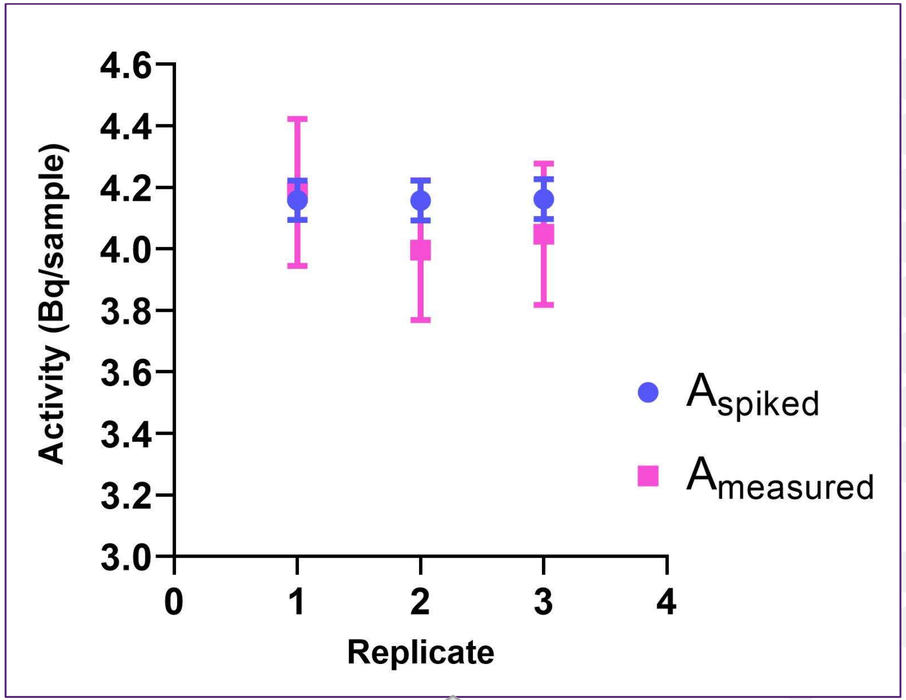
Combustion

30 mL 4 mM $NaHCO_3$



^{36}Cl spiked graphite samples





^{36}Cl η ➔ **65 ± 6%**
Reproducible chemical recoveries

Activity measured agreed within the measurement uncertainty k=2

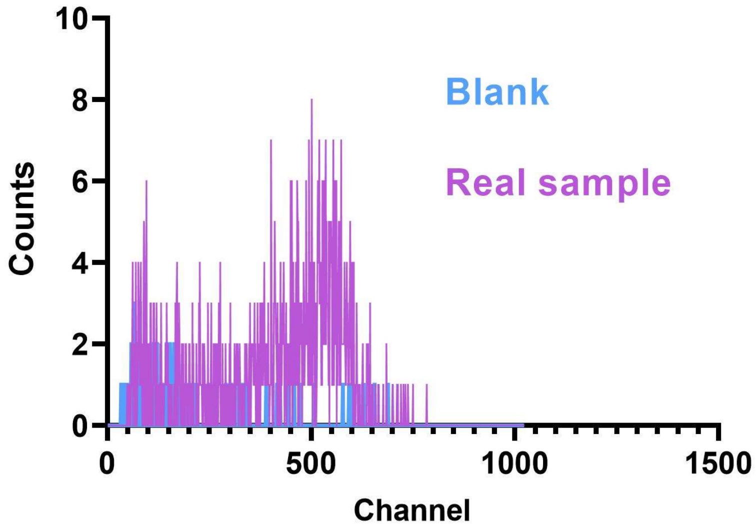
Activated graphite samples from BR1

0,1 g activated graphite

Which radionuclides can affect ^{36}Cl determination?

^{3}H

^{14}C



Activated graphite samples from BR1

0,1 g activated graphite

Which radionuclides can affect ^{36}Cl determination?

^{3}H

^{14}C

	Replicate 1	Replicate 2
Chlorine chemical recovery (%)	74.0 ± 7.9	74.8 ± 6.8
^{36}Cl massic activity (Bq g^{-1})	3.8 ± 0.9	3.8 ± 0.8

Computed values: between 4.1 and 8.3 Bq g^{-1}

Based on Von Lensa W, Vulpius D, Steinmetz HJ et al (2013) Treatment and disposal of irradiated graphite and other carbonaceous waste. Mol 6:66

Analytical parameters

Turnaround time (TAT): 7 h

Less than one working day

Detection limit: 20 mBq g^{-1}

Lower than clearance levels

Less chemicals involved

ISO14001 CERTIFIED VINÇOTTE

Conclusions

Outcome and overview

Development of a method for ^{36}**Cl determination** using different **PS materials**

Application of the method for ^{36}**Cl determination** in actual activated graphite samples from Belgian Reactor 1

TK-TcScint most suitable PS materials

Comparable DL with the method previously reported

1. Mixed wastes are avoided (no LS cocktail needed)
2. Fewer chemicals required
3. Shorter TAT
4. Gamma and beta interferences not affecting ^{36}Cl quantification

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