Virtual Conference on Applied Radiation Metrology (vCARM) 2021

Determination of ^{36}Cl and ^{129}I in nuclear solid decommissioning samples

Our challenges: ^{36}Cl memory effect and how to deal with it?

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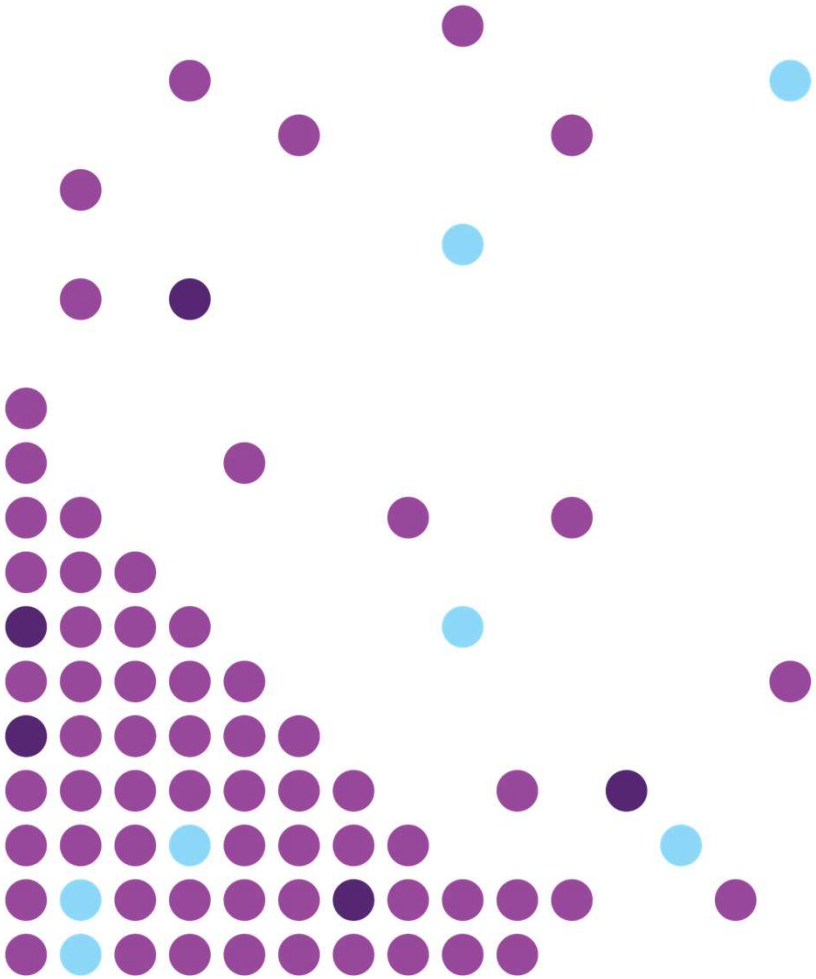

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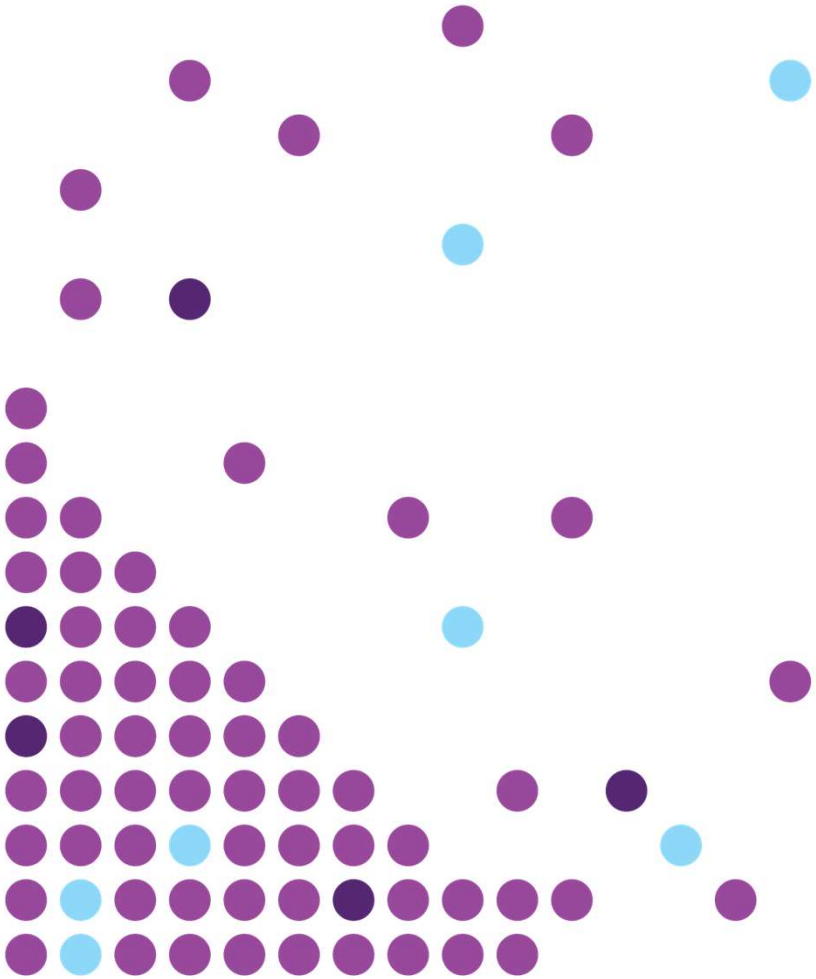
1. Framework
2. Aim of the study
3. Experimental set-up
4. How to deal with ^{36}Cl memory effect?
5. Application of the method
6. Detection limit (DL)
7. Conclusions and further work



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Decommissioning phase of a nuclear facility

RELEASE

Unconditional

Conditional

RADIOACTIVE WASTE

Near Surface Disposal

Deep Geological Disposal

Radiological risk of wastes

Dose impact study — In order to meet — Specifications

Materials nuclide specific characterized

Radiological waste characterization

Measurement of the waste

Non-destructive analysis — Easy-to-measure (ETM) — Mainly γ-ray emitters

Destructive analysis — Difficult-to-measure (DTM) — Mainly α/β particle emitters

Current approach

Scaling factors

Activity γ-emitter ⇕ Activity DTM

Calculation codes

Validated via real analysis

Uncertainty inventory of DTM radionuclides

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

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

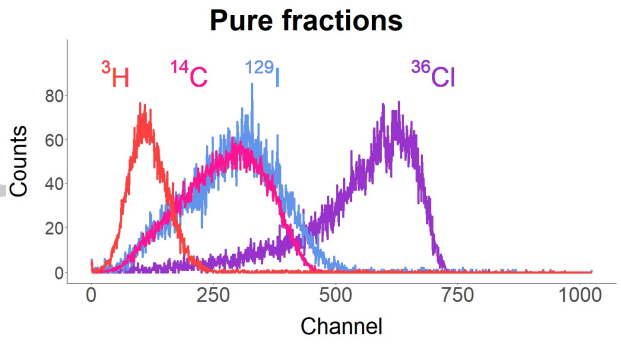
^{36}Cl

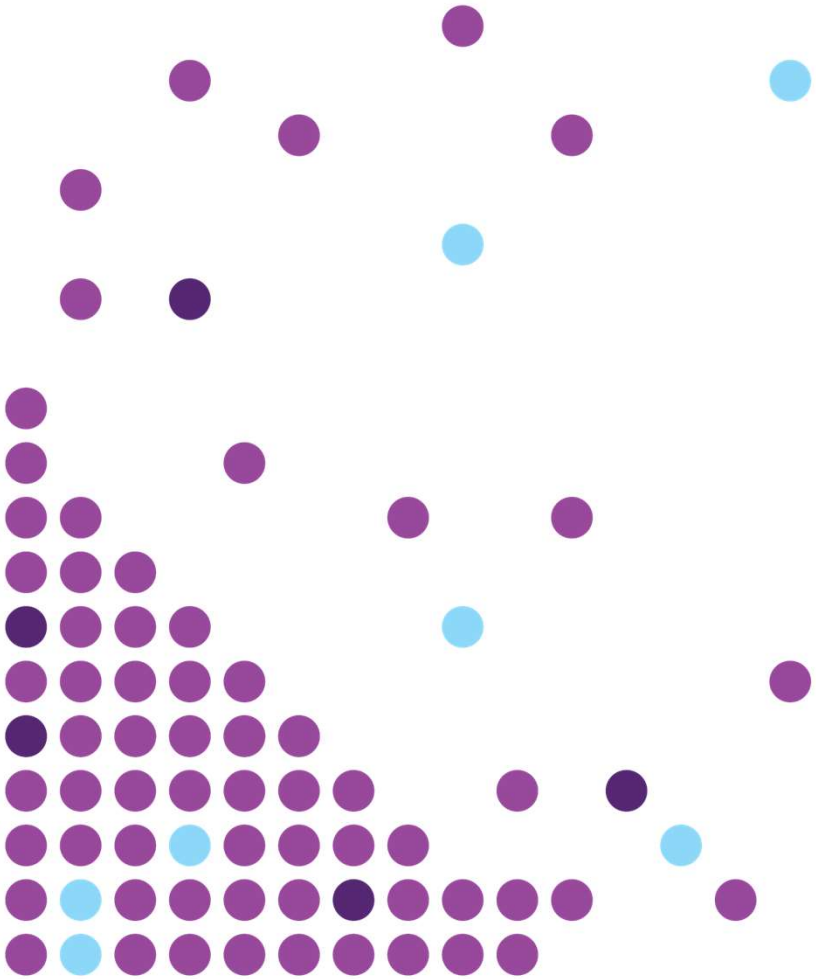
- ❑ Neutron activation natural ^{35}Cl
- ❑ $T_{1/2}$= $3.02 \cdot 10^5$ year
- ❑ E_{max}= 709.6 keV
- ❑ In construction materials (as trace element) and in the primary circuit coolant

^{129}I

- ❑ Fission product ^{235}U
- ❑ $T_{1/2}$= $1.57 \cdot 10^7$ year
- ❑ E_{max}= 154 keV
- ❑ In spent nuclear fuel and in the primary cooling circuit of a nuclear reactor

β emitters





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General and specific aims

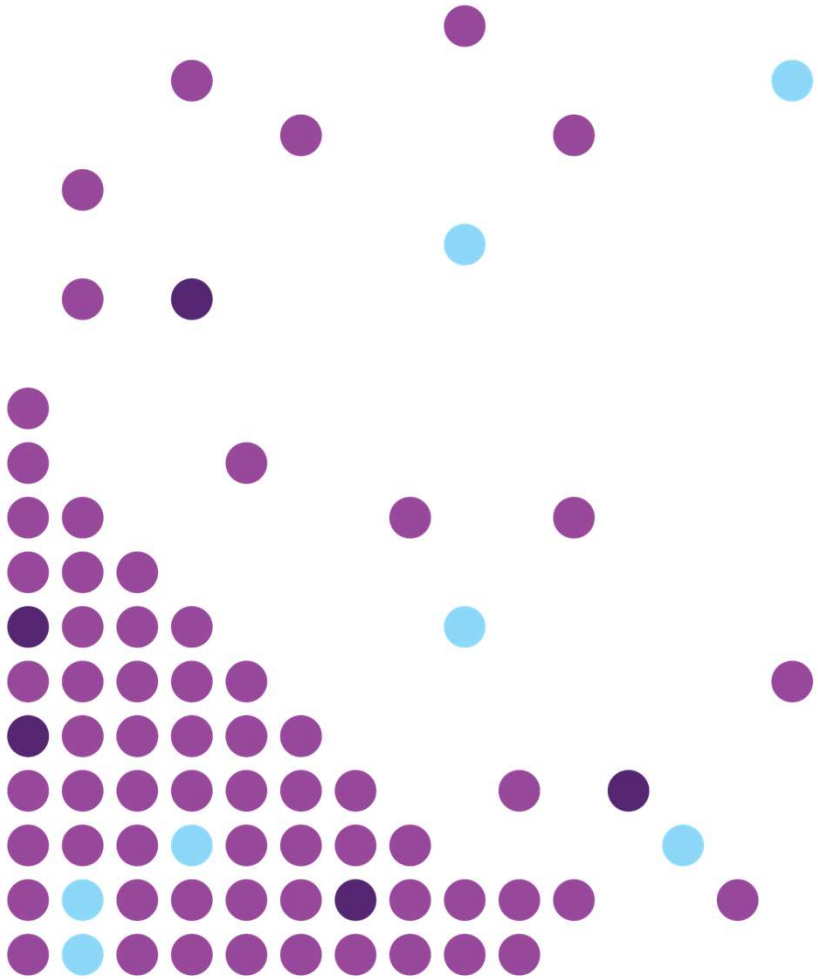
- To optimize the quantification of ^{36}Cl and ^{129}I in solid samples coming from decommissioning scenarios

CURRENT ISSUES

- ↑ uncertainty on the inventory of DTM
- ↑ DL
- Turn around time (TAT) ↑
- Chemicals needed ↑

APPLICATION FOR

- Improving radiological characterization
- Reaching low DL to comply with exemption and clearance principles
- Including of the procedure in routine analysis



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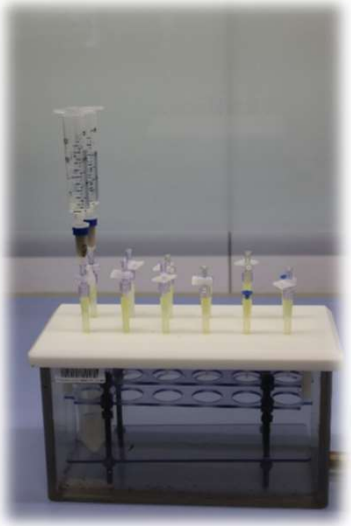
Step by step

1. Sample combustion

Pyrolyser

2. Separation



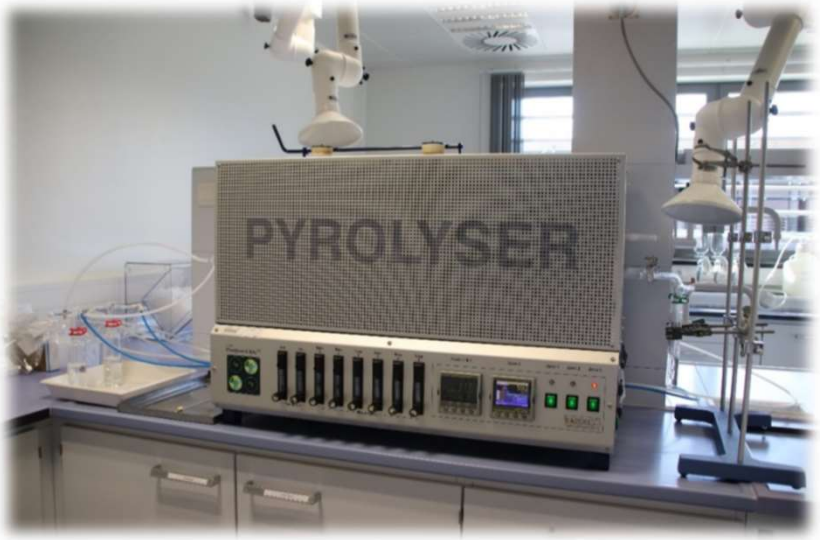
Cl-resin

3. Measurement

Liquid Scintillation Counting (LSC)

1. Combustion

- Pyrolyser from RADDEC is used (procedure adapted from *Warwick et al. 2010*)



Temperature protocols depending on the matrix

Maximum temperature: 900°C — Fully Cl release

Flow rate: 200 mL/min — Carry gases

No catalyst/quart beads — Flow rate regulation

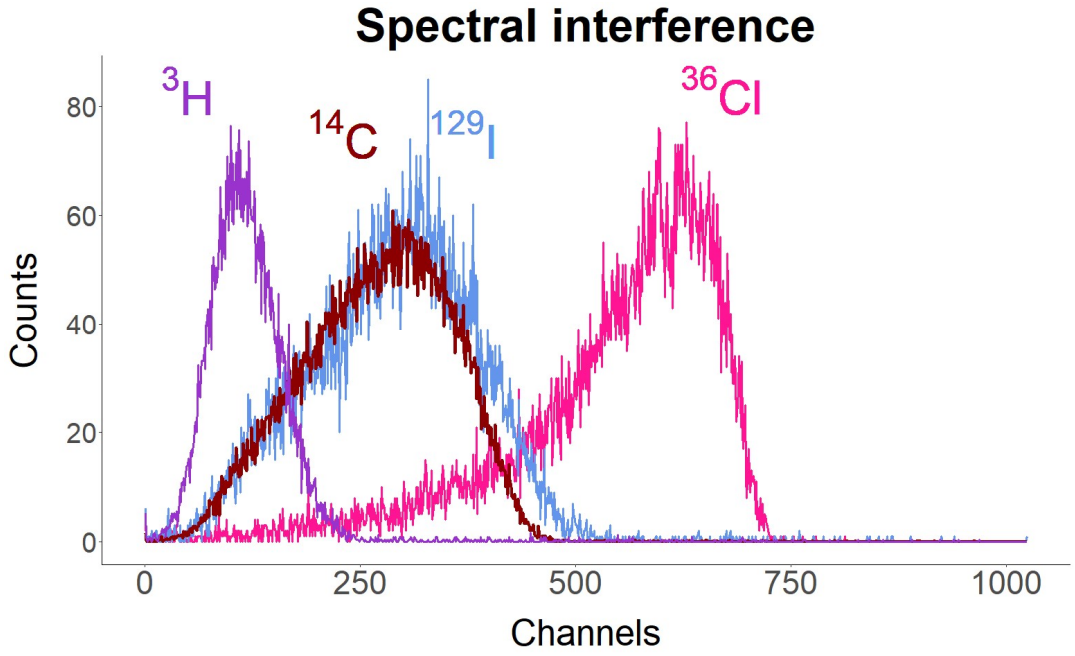
Glass connections and quartz tubes and sample boats — Avoid plastic surfaces

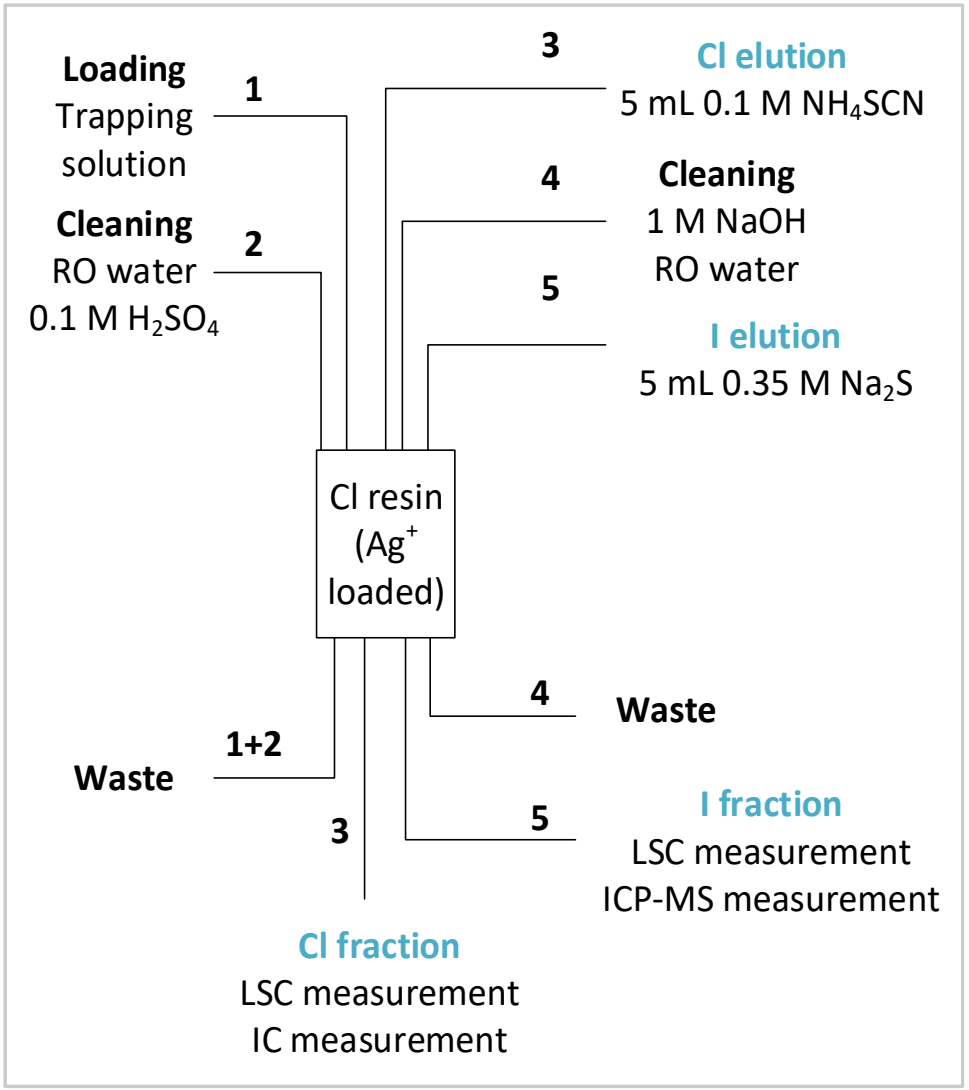
Cl and I carriers → η quantification

Running blank samples after active samples

2. Radiochemical separation

- Based on Zulauf et al. 2010
- **Cl-resin** cartridges + vacuum box are used





3. Sample measurement

Massic activity

Liquid Scintillation Counting (LSC)

- Wallac Quantulus 1220™ **low-level** LS counter

4.9 mL elution medium + 15 mL Optiphase Hisafe III

$$A\left(\frac{Bq}{g}\right) = \frac{CPS_{measured}}{C_{eff} * \eta * m_{sample}}$$

Chemical recovery quantification (η)

Ion chromatography (IC) — Stable Cl

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) — Stable I

0,1 mL subsample from elution medium

Calibration with Quench Curves

Optimization of the procedure

COMBUSTION

- Temperature protocol
- Holding time at maximum temperature
- Amount of the sample
- **Memory effect**

SEPARATION

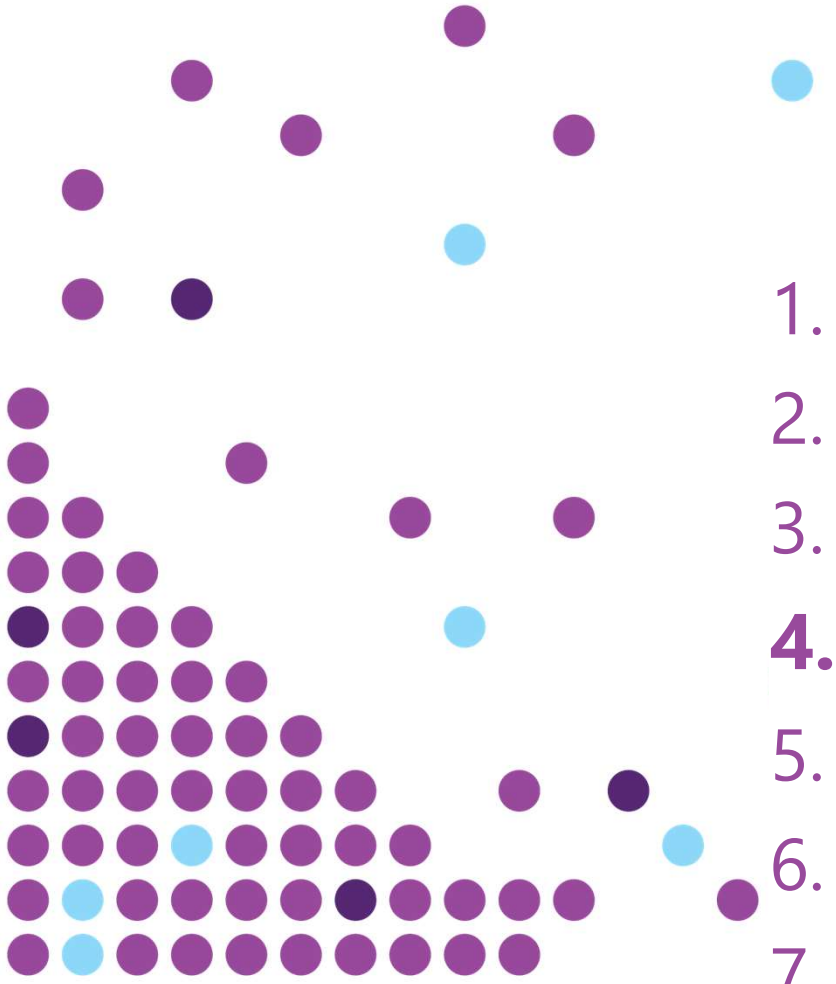
- Compatibility with different media
- **Cleaning steps**

MEASUREMENT

- Counting efficiency calibration
- Homogeneity and stability

^{36}Cl contamination in the blanks

^{129}I no contamination in the blanks



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Cross-contamination / memory effect?

- Cross contamination on the vacuum box
  - Blanks + spiked samples
  - Blanks in a different vacuum box
- Memory effect

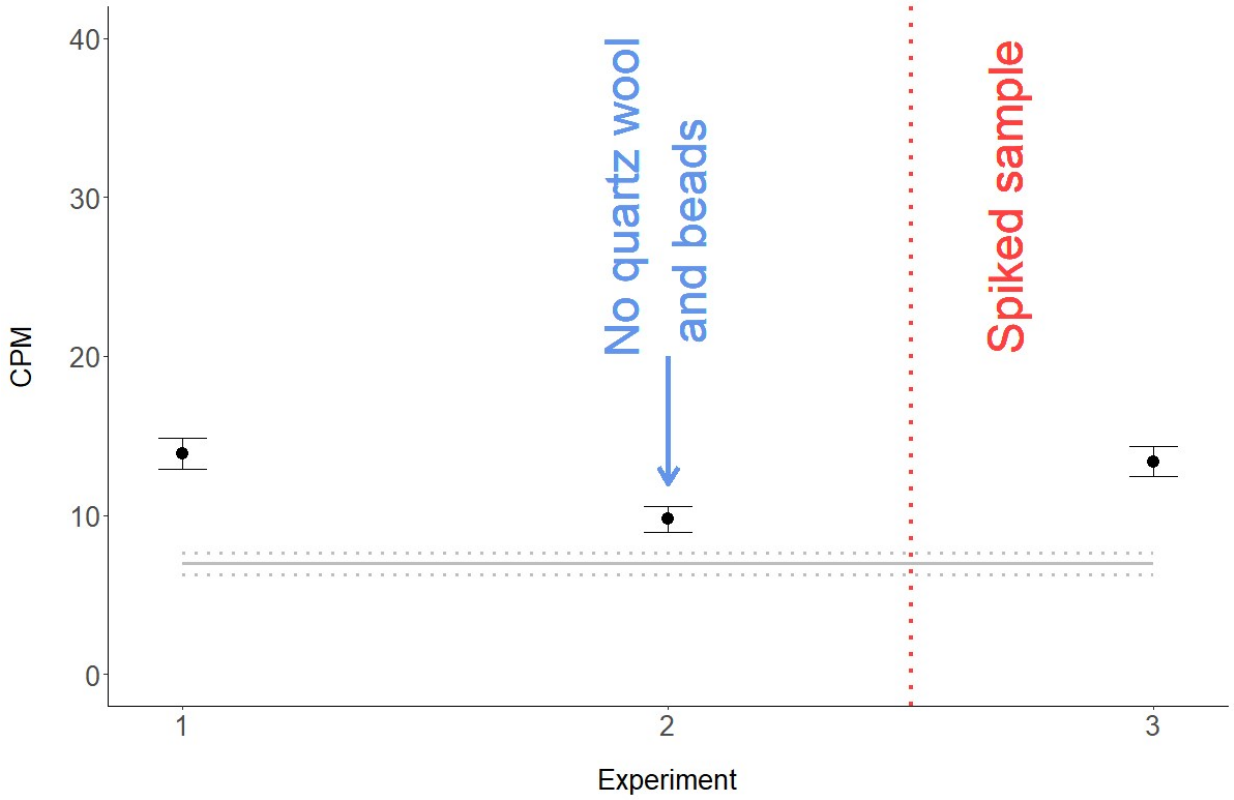
No cross-contamination

Spiked sample with ^{36}Cl → Blank sample

1. Quartz wool/beads
2. Moist air
3. Bubblers
4. Sample boats

^{36}Cl Memory effect

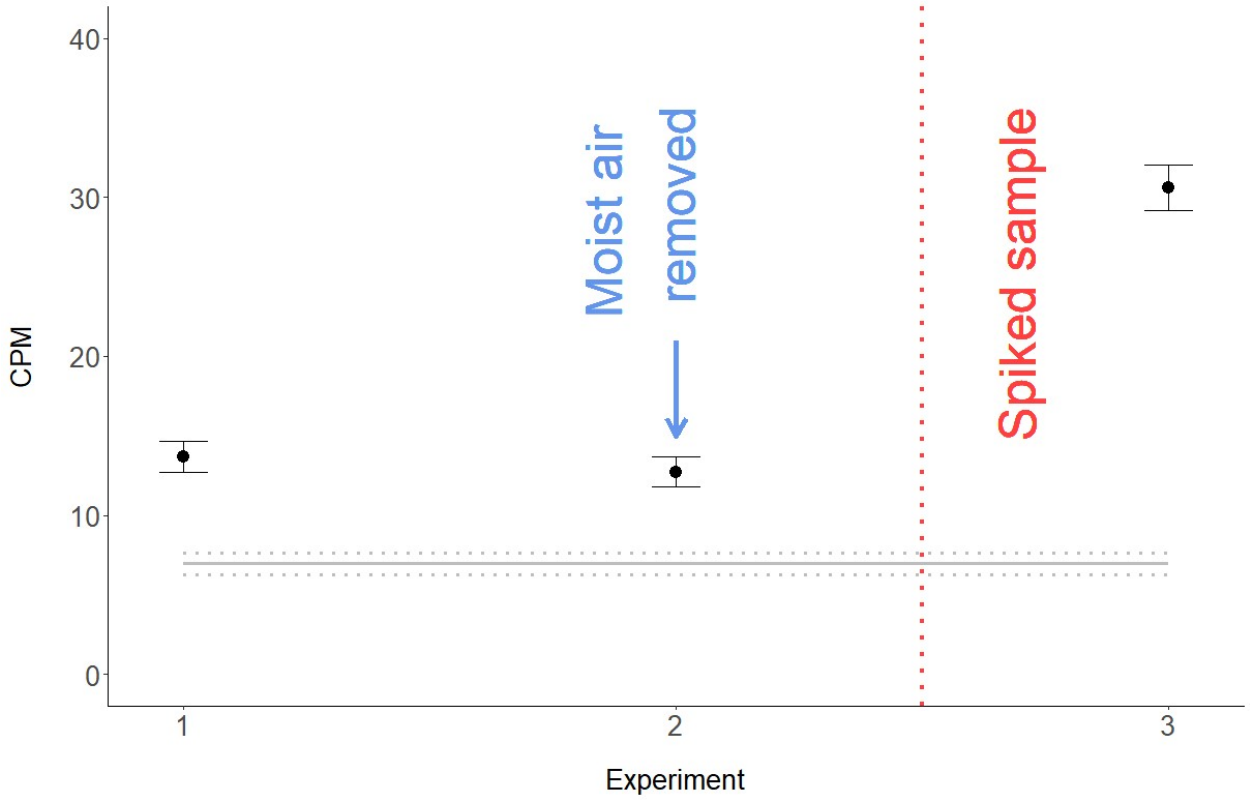
Quartz wool / beads?



- ↓ CPM when removing quartz wool and quartz beads
- Not possible to remove completely the effect
- Chemical recoveries not significantly affected

CPM: counts per minute

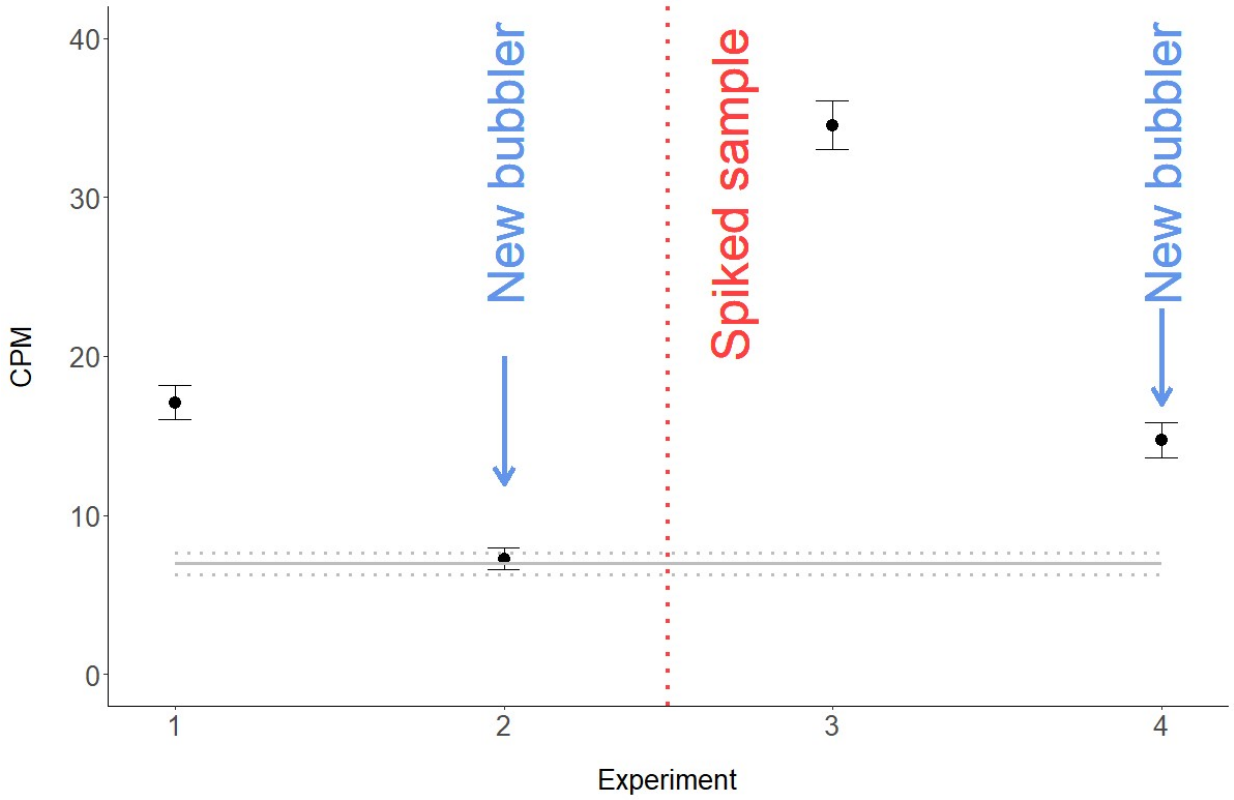
Moist air?



- No differences in CPM while removing the moist air
- Moist air was not affecting ^{36}Cl memory effect
- No significant differences on the chemical recovery

CPM: counts per minute

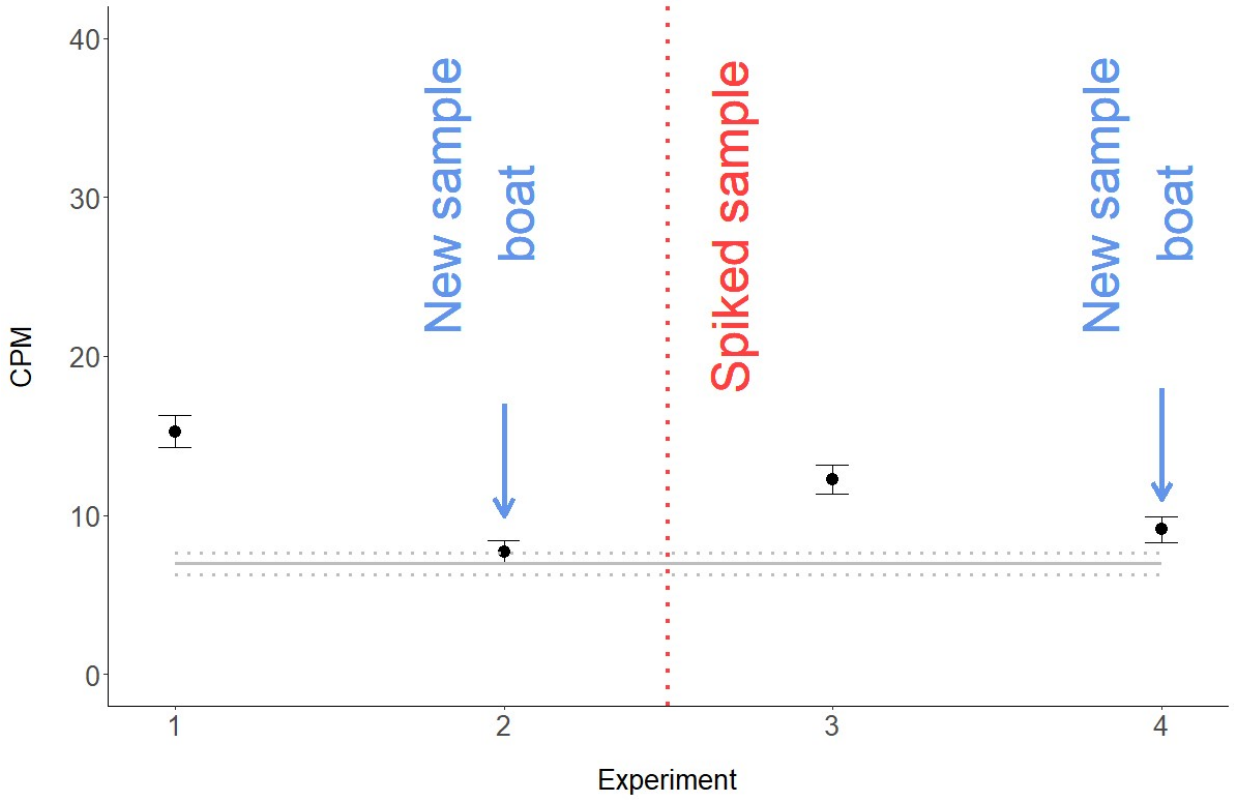
Bubblers?



- ↓ CPM when changing the bubbler
- Not possible to remove completely the effect

CPM: counts per minute

Sample boat?

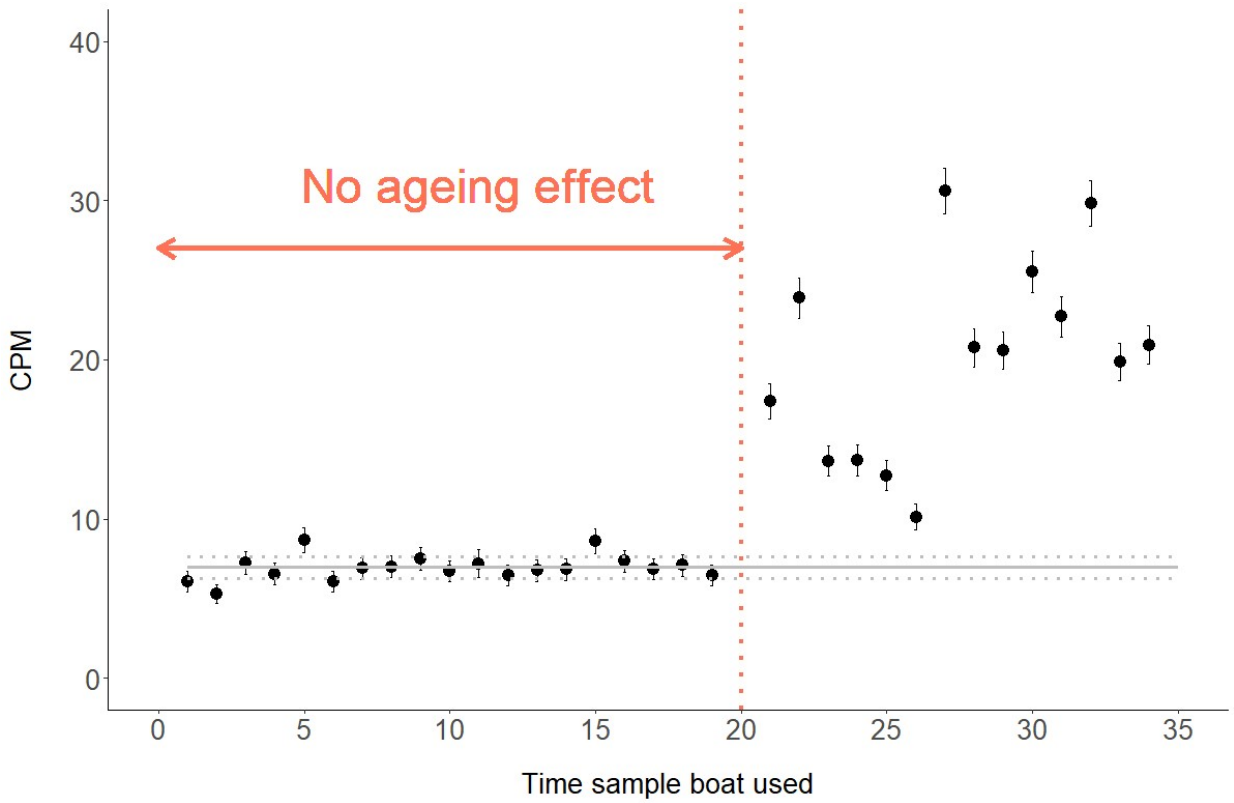


- ↓ CPM when changing the sample boat
- Not possible to remove completely the effect

CPM: counts per minute

Ageing of the sample boats

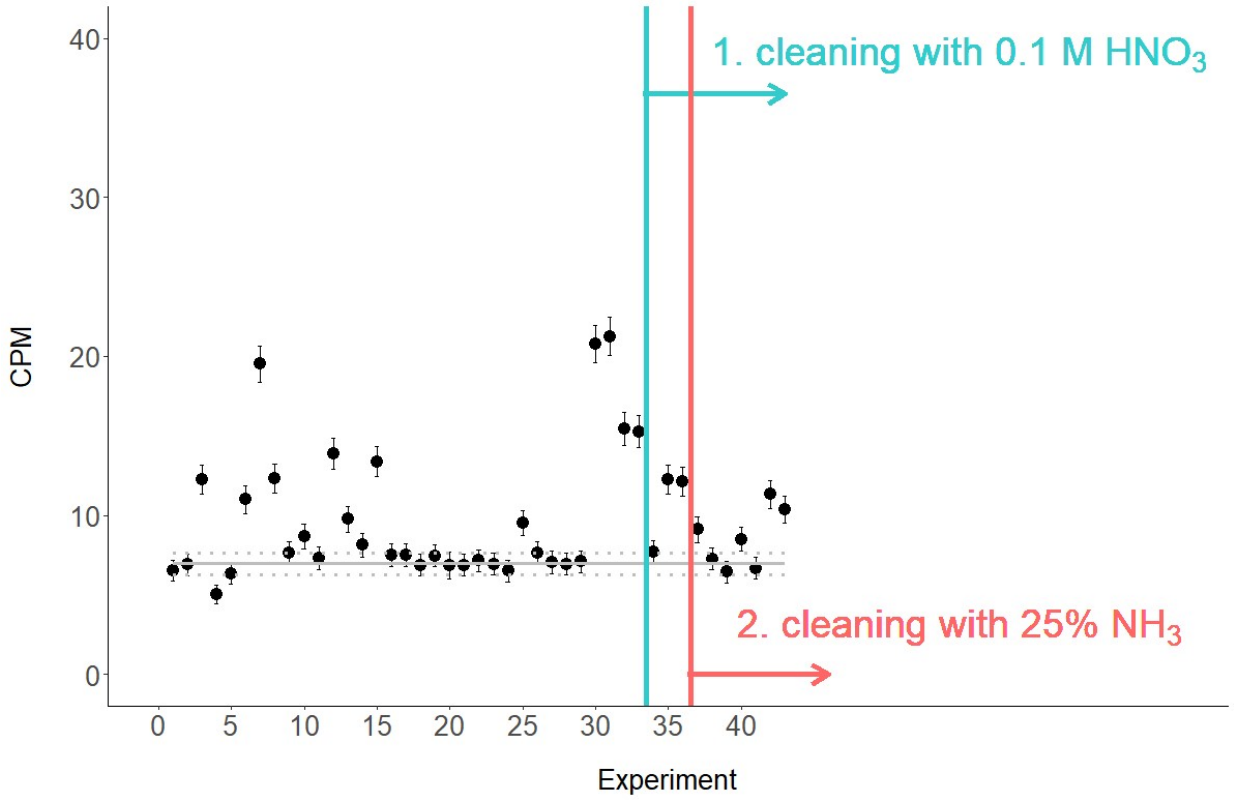
(Peng and Redfern 2013)



- Variations of quartz structure while ↑ temperature ↑ CPM while reusing the sample boat
- Memory effect ↑ when > 20 times used
- Chemical recovery affected for the reuse

CPM: counts per minute

^{36}Cl memory effect



- Extra cleaning steps cannot avoid the memory effect
- Reasonable background level between 8-13 CPM

Average

6.96±0.69 CPM

CPM: counts per minute

Catalyst used in other set-ups

- In some cases catalyst is needed (depending on the matrix and radionuclides) for **different reactions** of the target elements *(Prabir Basu 3rd edition 2018)*

Reduction

Ni

(Pearce and Hill 1986)

Oxidation

CuO

(Herod et al. 2014)
(Hou 2005)

Pt-alumina

*(*Croudace et al. 2017*)*

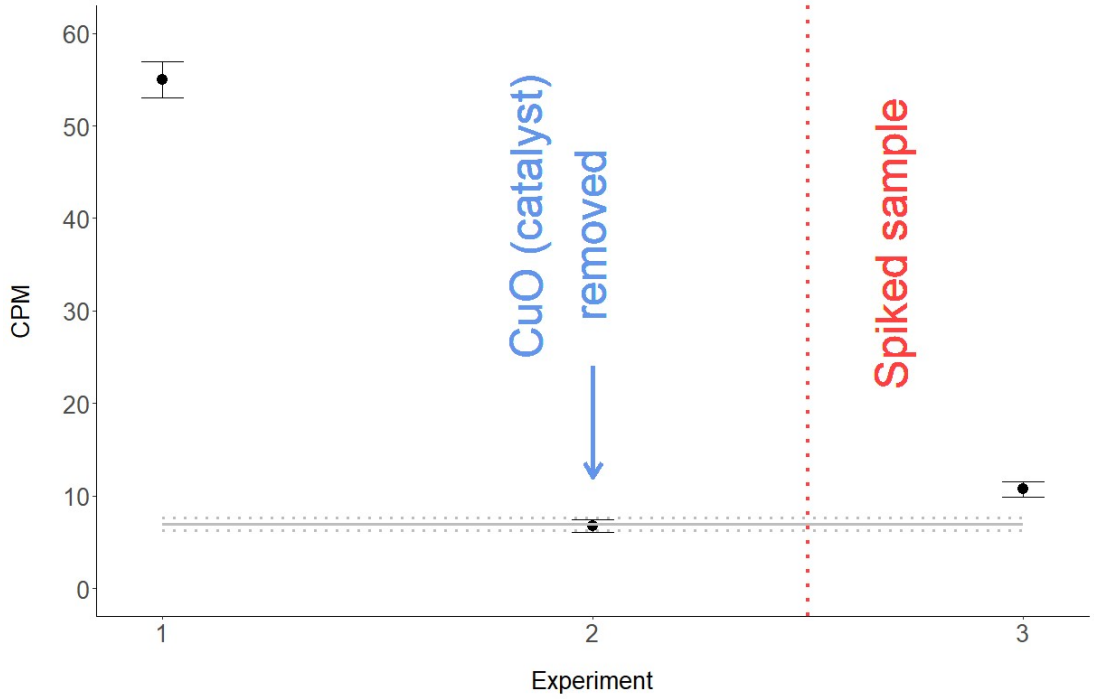
Acceleration breakage bond

Fe_2O_3

(Du et al. 2020)

- In some cases catalyst **cannot** be removed → included in the pyrolyser set-up
  - Horizontal Split tube furnaces up to 1100 °C *(ENTECH 1918)*

Catalyst?

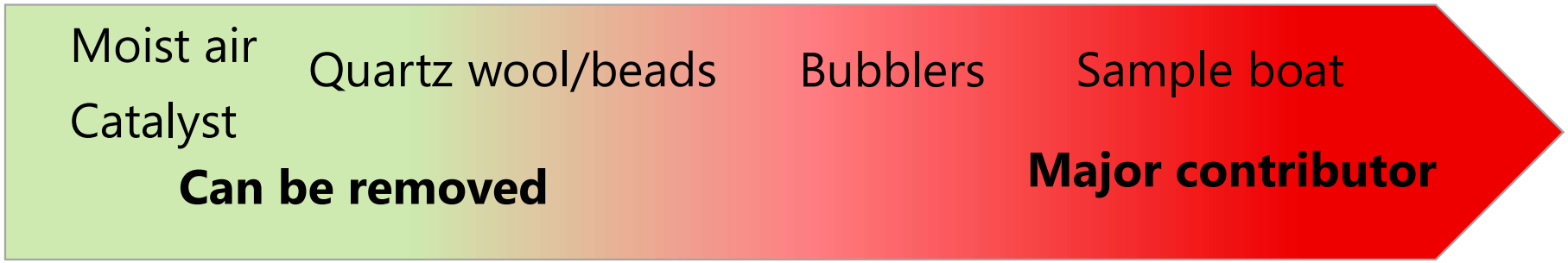


- ↓ CPM when removing the catalyst (CuO)
- Not possible to remove completely the effect

Long-term Cl memory effect was considered for AMS measurements *(Pavetich et al. 2013)*

CPM: counts per minute

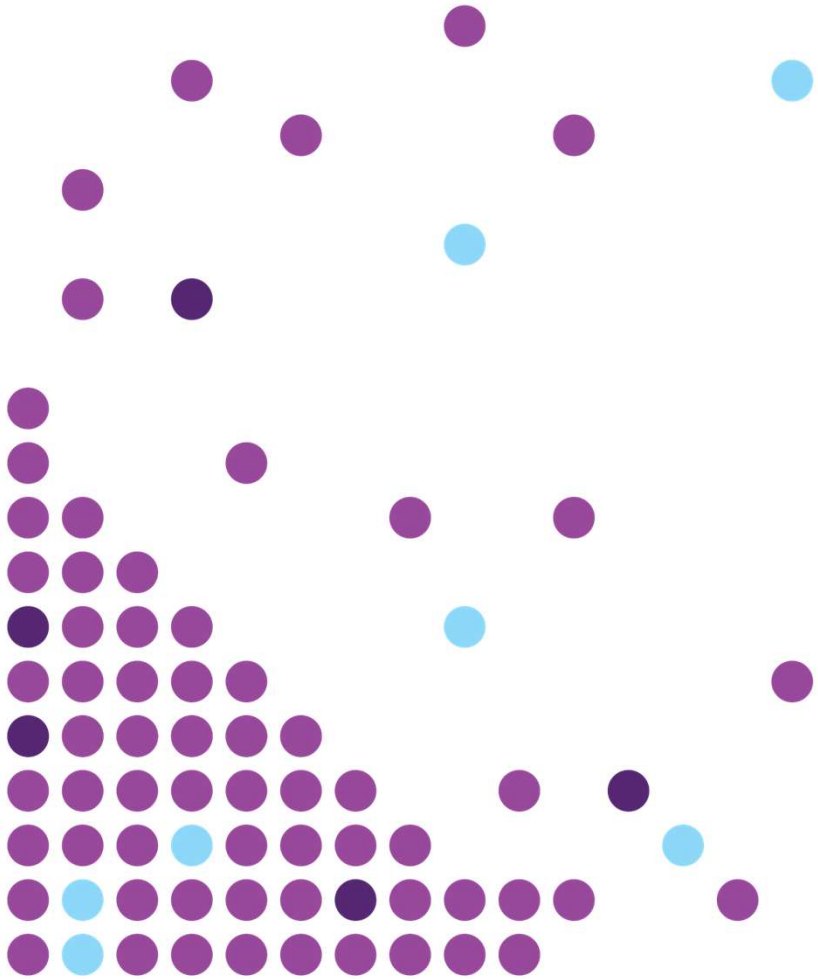
Approach



^{36}Cl memory effect ~ **Random** effect

^{36}Cl memory effect **removal**

^{36}Cl memory effect **corrected**



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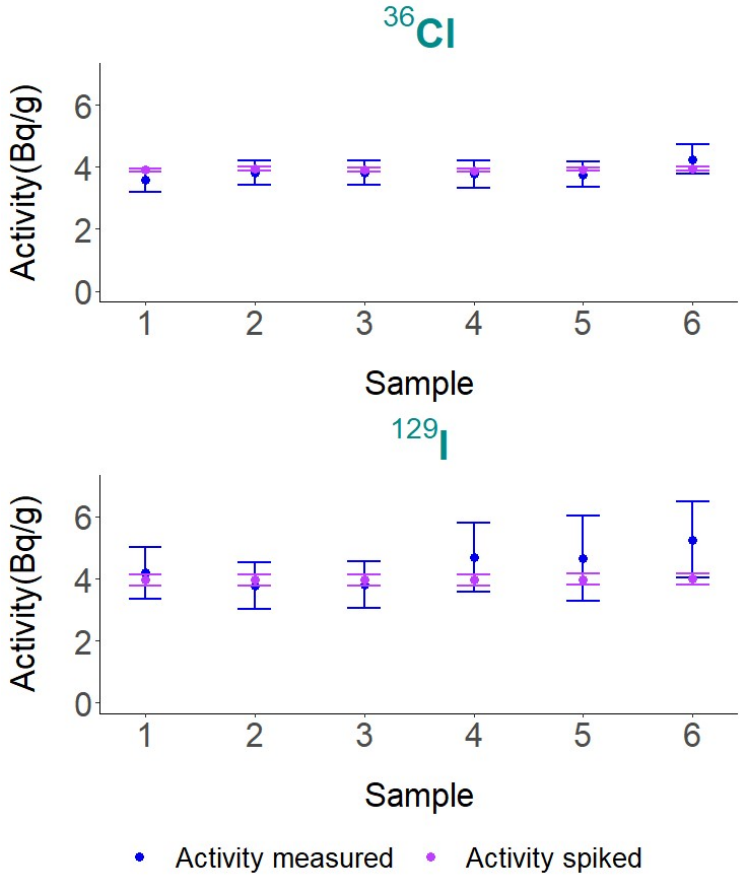
Application using blank concrete and graphite

CONCRETE



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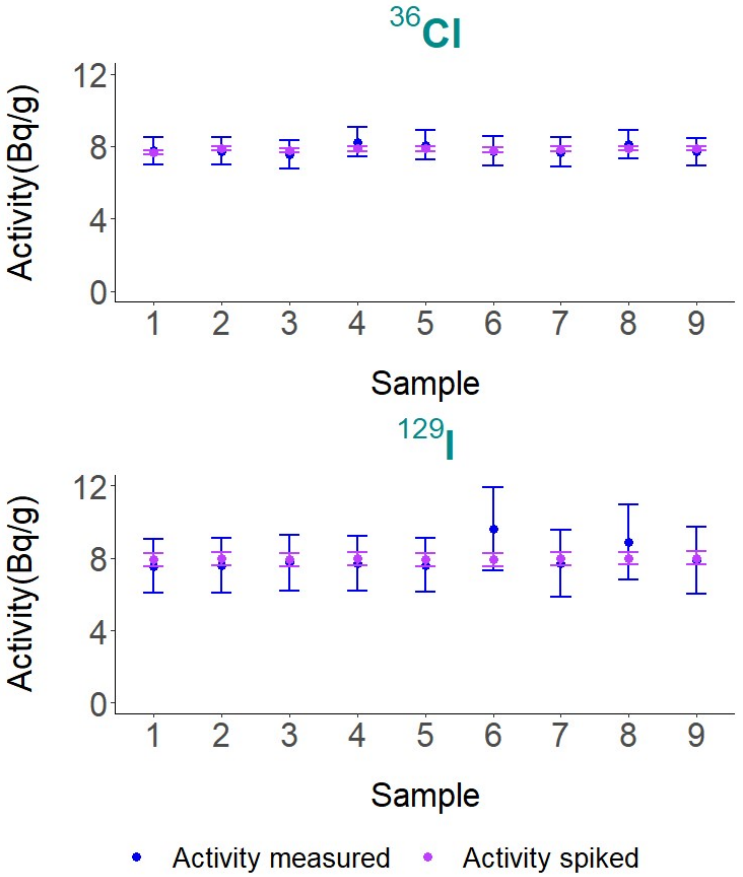

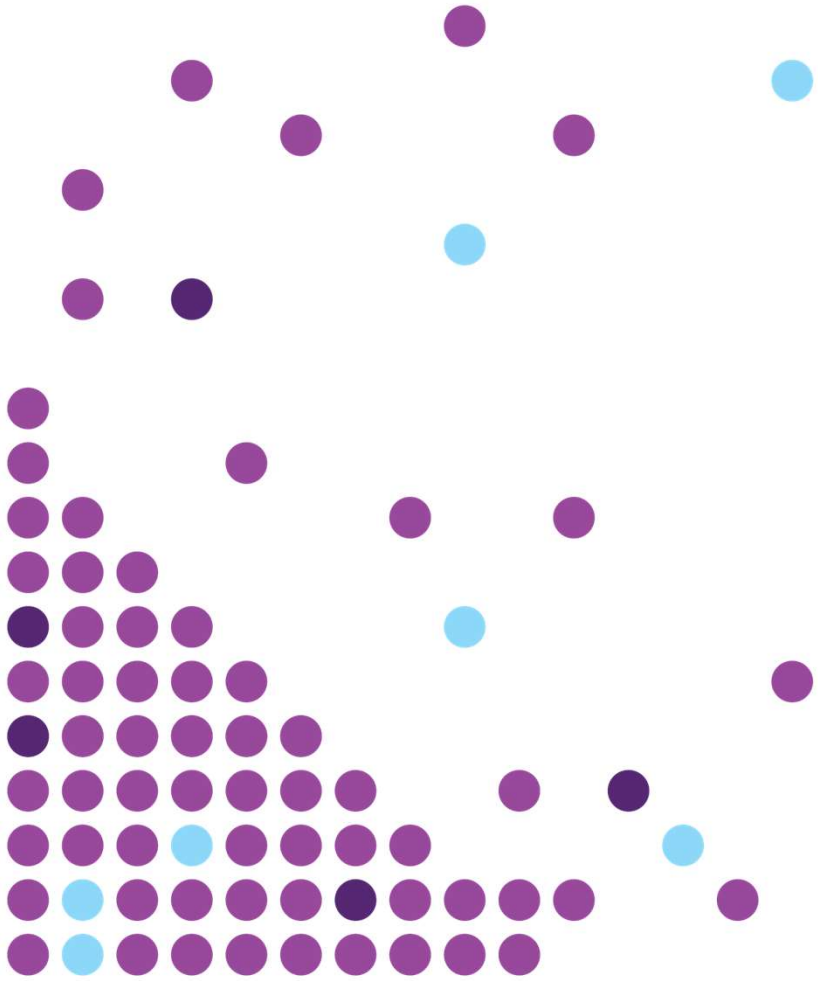

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Calculation of the detection limit (DL)

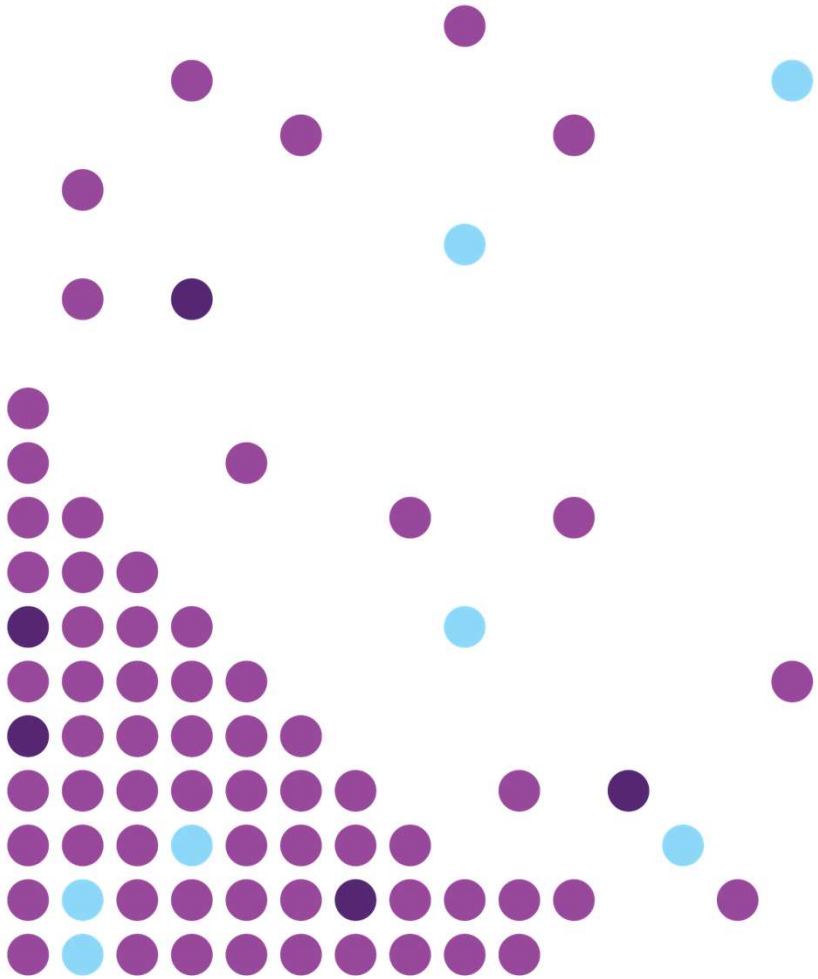
- Evaluated based on measurements of several blanks (non-spiked solid samples)
- Calculated according to ISO 11929

Considering ^{36}Cl memory effect

Parameters (mean values)	^{36}Cl	^{129}I
DL	25 mBq/g	25 mBq/g
Activity concentration values for exemption	1000 mBq/g	10 mBq/g

(Current Basic Safety Standard Directive (96/29/Euratom))

^{36}Cl
45 mBq/g



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Conclusions

- ✓ Optimized procedure can be applied to the analyses of **real samples**
- ✓ Optimized procedure can reach the **required limits** by the legislation for ^{36}Cl
- ✓ Catalyst is not needed in this set-up reducing the issues with ^{36}Cl memory effect
- ⚠ **Blanks are required** after running an active sample (memory effect evaluation)

Further work

- Investigation of the application to Plastic Scintillating Microspheres (PSm) for ^{36}Cl determination
- Improvement of iodine quantification in order to reach the limits required by the legislation of ^{129}I free release

Interlaboratory comparisons and availability of reference materials for these radionuclides **are needed**

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THANK YOU VERY MUCH FOR YOUR ATTENTION!

For further questions do not hesitate to contact me by email

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