Measurement of ^{36}Cl and ^{129}I in decommissioning wastes

Phil Warwick, Dave Reading & Ian Croudace

University of Southampton

GAU Radioanalytical Laboratories

UNIVERSITY OF Southampton

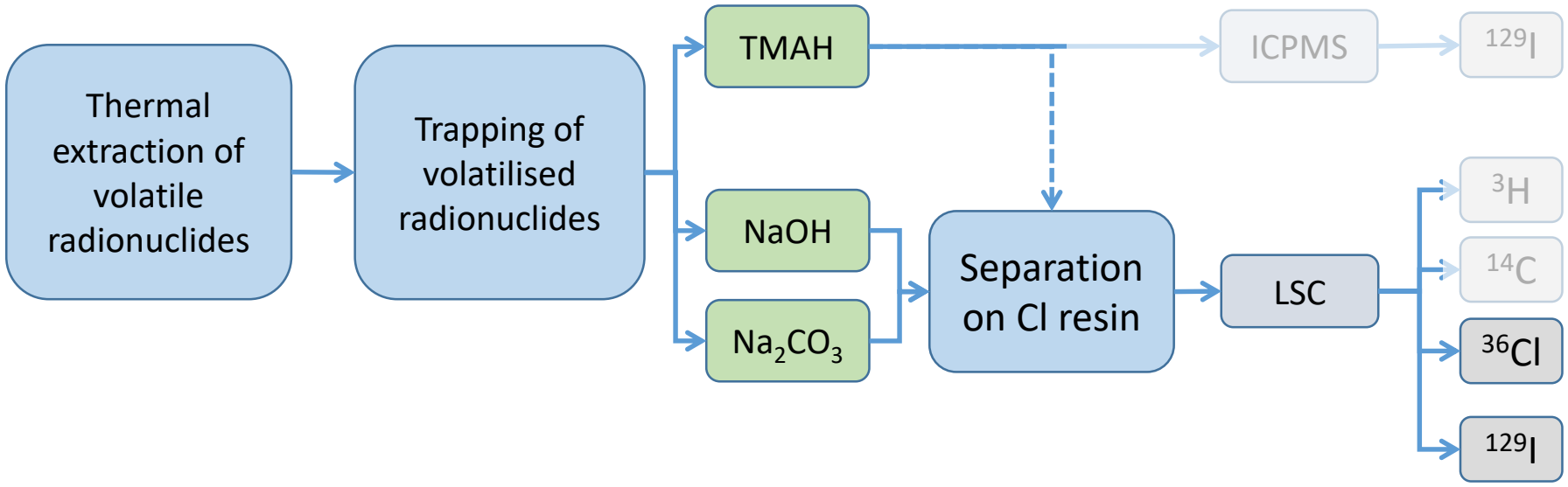
Origin of ^{36}Cl

- ^{36}Cl is predominantly produced via neutron activation of naturally occurring ^{35}Cl .
- ^{36}Cl is a long lived (3.02×10^5 y) beta emitting radionuclide (E_{max} = 709.6 keV).
- ^{36}Cl is present in nuclear graphite, concretes, ion exchange resins & desiccants.
- Characterisation of ^{36}Cl in nuclear wastes is important due to its mobility in the geosphere and high soil – plant transfer factor

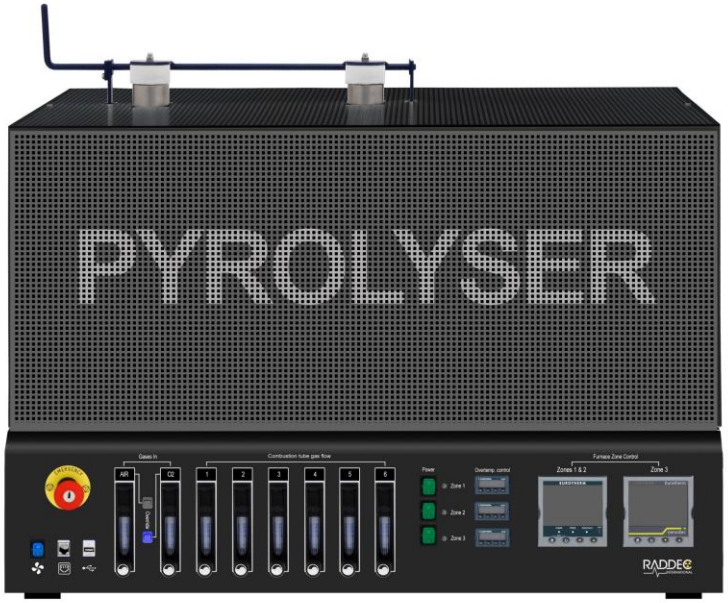
Origin of ^{129}I

- ^{129}I is a fission product and is also produced via neutron activation of Te isotopes.
- ^{129}I is a long lived (1.57×10^7 y) beta emitting radionuclide (E_{max} = 154 keV).
- ^{129}I is present in activated carbon filters, ion exchange resins & fuel pond sludges.
- Characterisation of ^{129}I in nuclear wastes again due to its mobility and its long half life.

Proposed analytical scheme



Thermal desorption of halogens



^{129}I separation for AMS and LSC

No catalyst
Zone filled with quartz beads

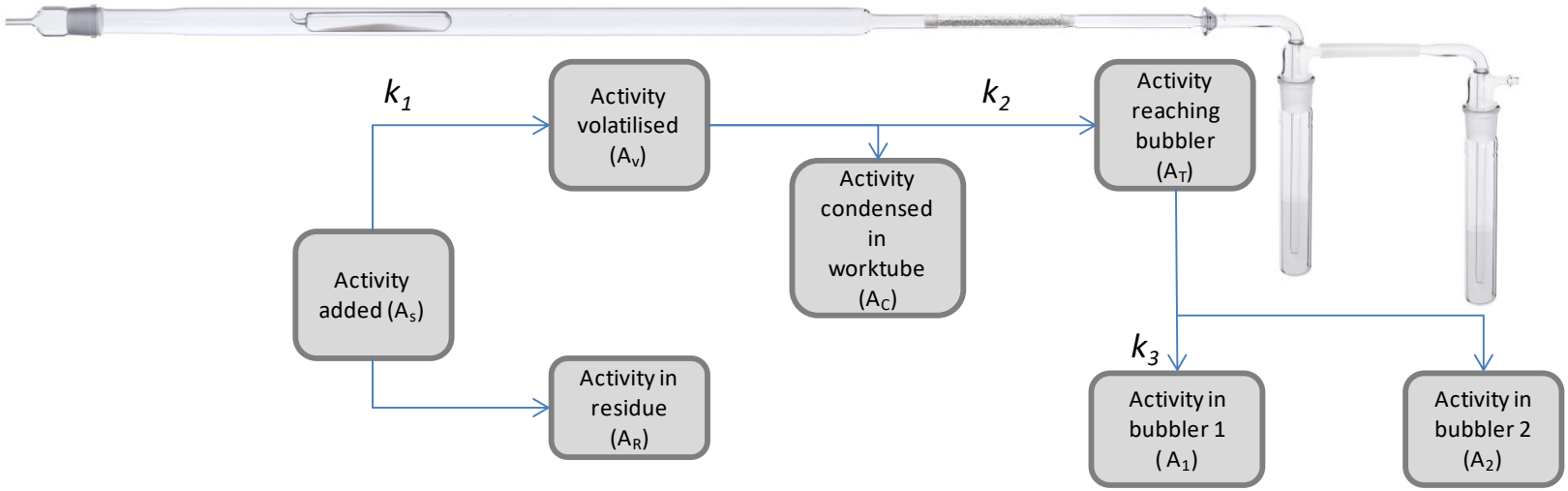
Ground glass joint connections (halogens adsorb to silicone tubing)

Trapping solution is 6mmol Na_2CO_3 for LSC and 0.2M NaOH for AMS*

Xi'an AMS facility, China

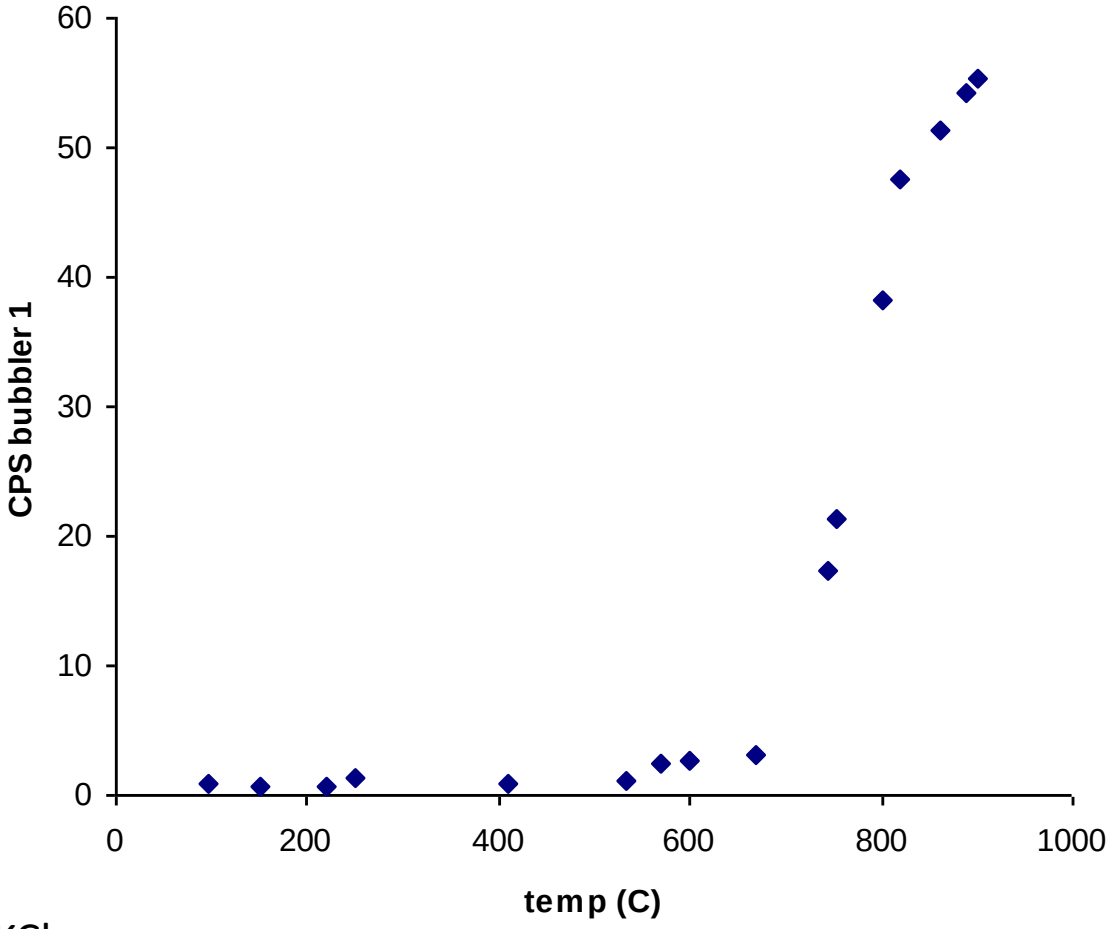
*Hou, X., Wang, Y., 2016. Determination of ultra-low level 129I in vegetation using pyrolysis for iodine separation and accelerator mass spectrometry measurement. J. Anal. At. Spectrom. doi:10.1039/C6JA00029K

Recovery of halogens



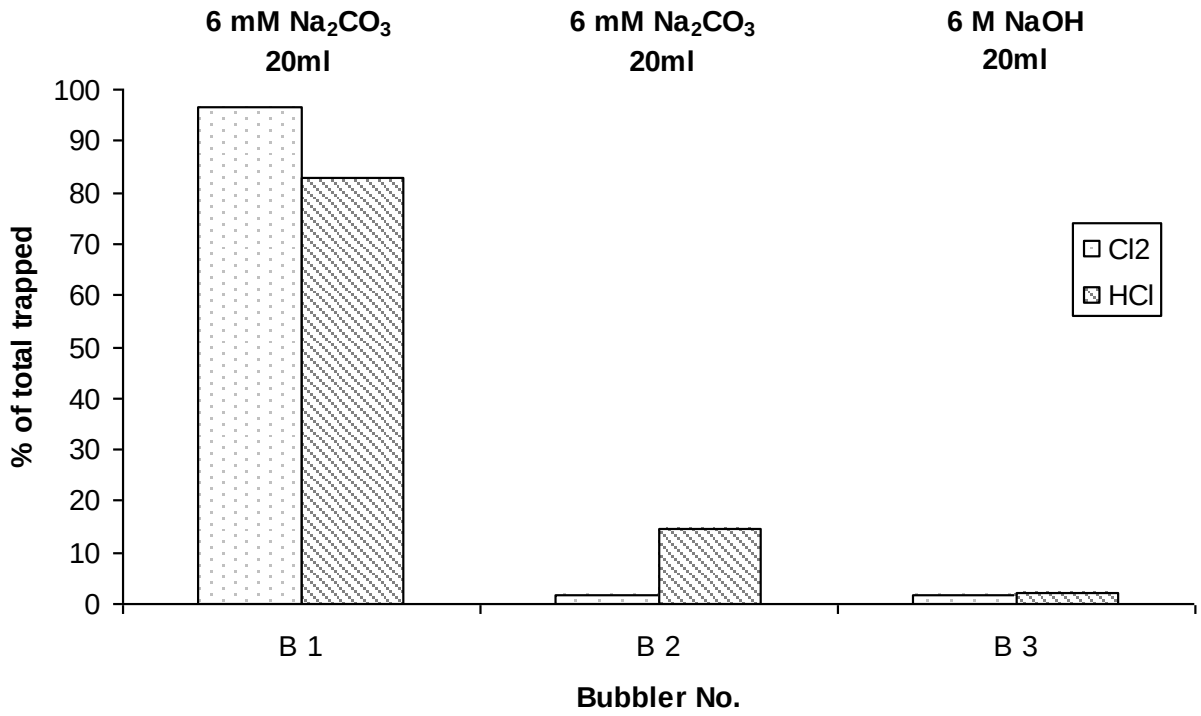
k_1 = Volatilisation factor
k_2 = Transfer factor
k_3 = Trapping factor
Overall recovery = k_1 x k_2 x k_3

Thermal desorption of ^{36}Cl



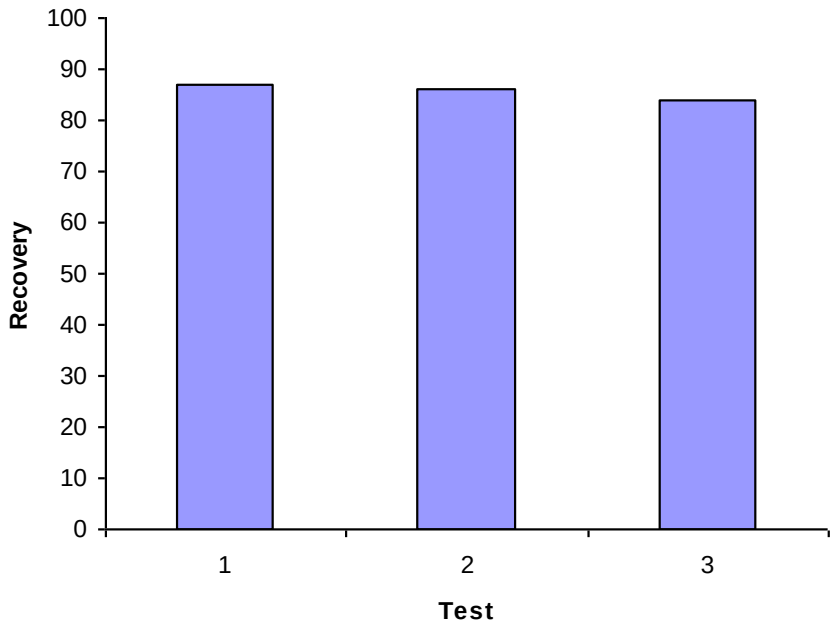
From irradiated KCl

Trapping of ^{36}Cl



Theoretical capacity for 20ml 6mM Na_2CO_3 is 8.5 mg Cl

Recovery of ^{36}Cl from standards

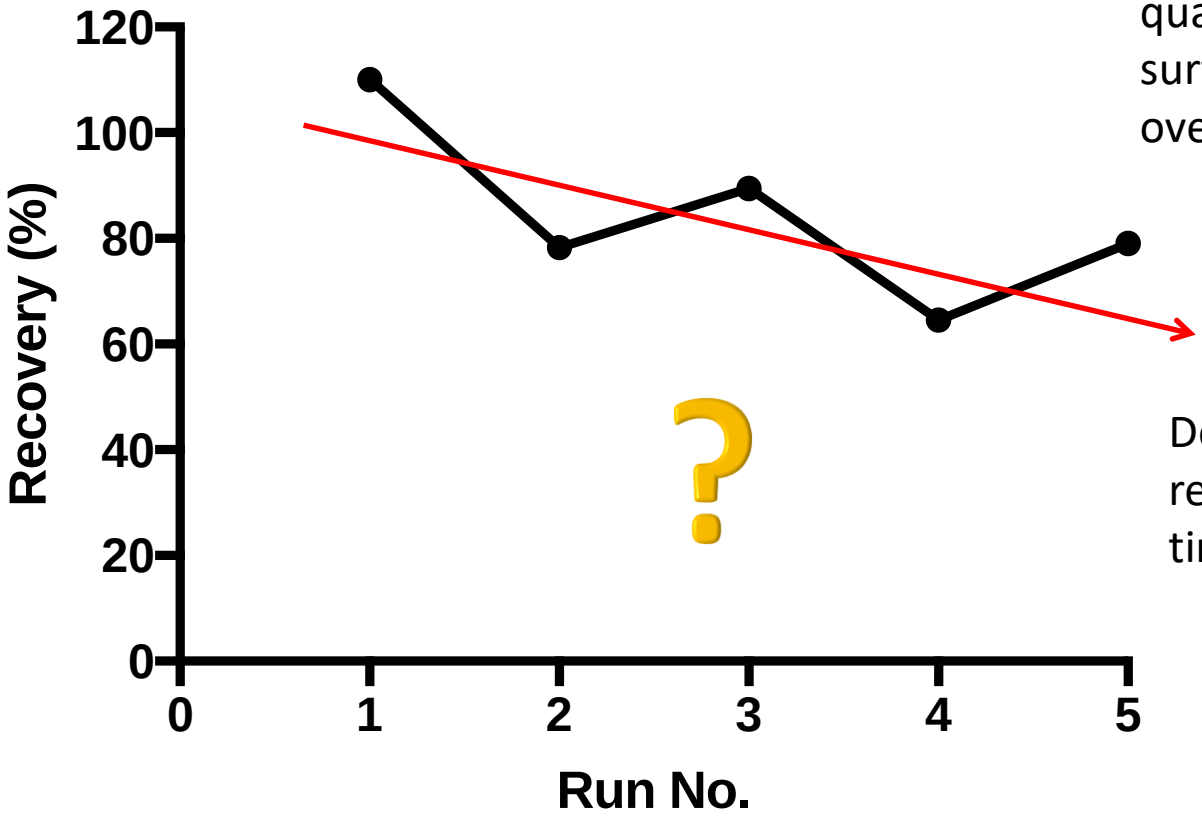


Results for replicate standard analyses

Mean recovery = 86%
(all in 1st Na_2CO_3 bubbler)

Blanks run between samples
Carry over between samples < 0.1%
Residual activity in sample boat ~ 0.3%

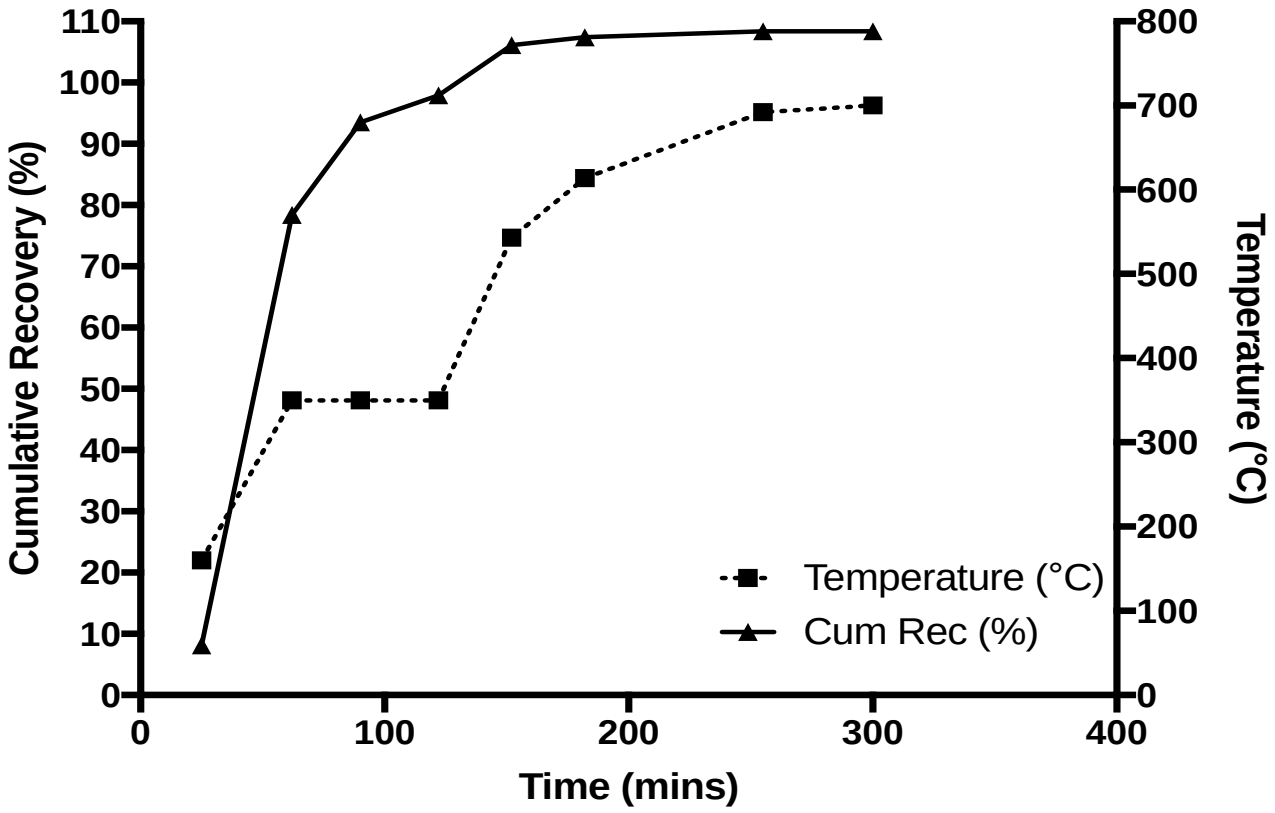
Recovery of ^{36}Cl over time



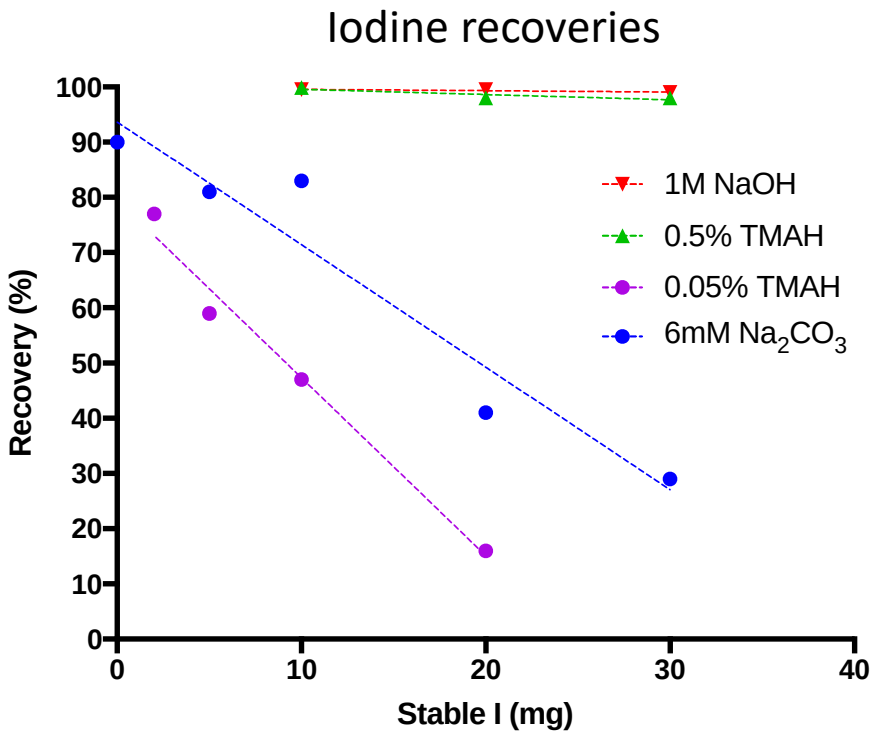
Interaction of Cl with quartz glass – glass surface deterioration over time?

Decrease in recovery over time

Thermal desorption profiles – ^{129}I



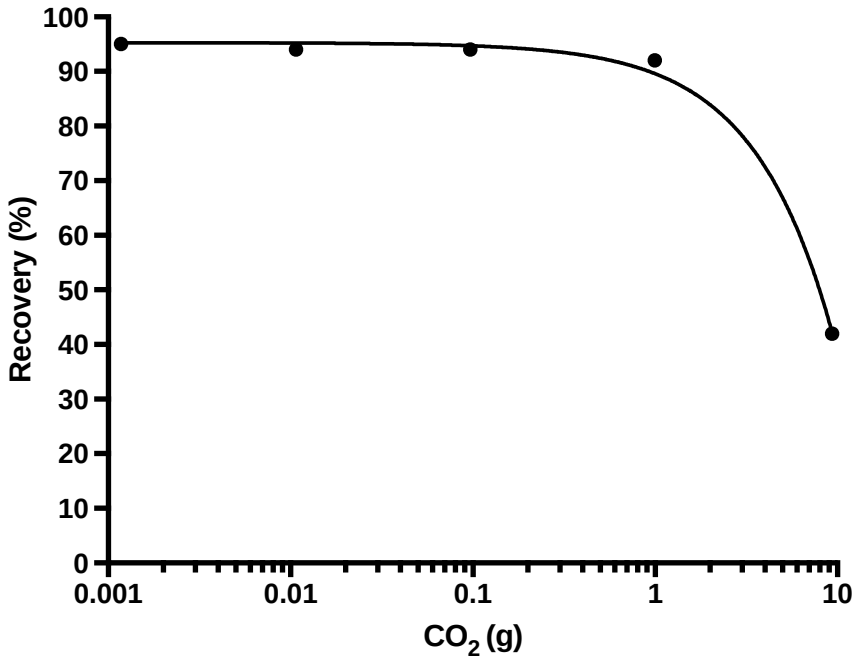
Effect of stable I mass



Trapping agent	Cl (mg)	I (mg)
0.05% TMAH	2	7
0.5% TMAH	20	70
6mM Na_2CO_3	9	30
1M NaOH	710	2540

Theoretical trapping capacities for a 20ml bubbler.

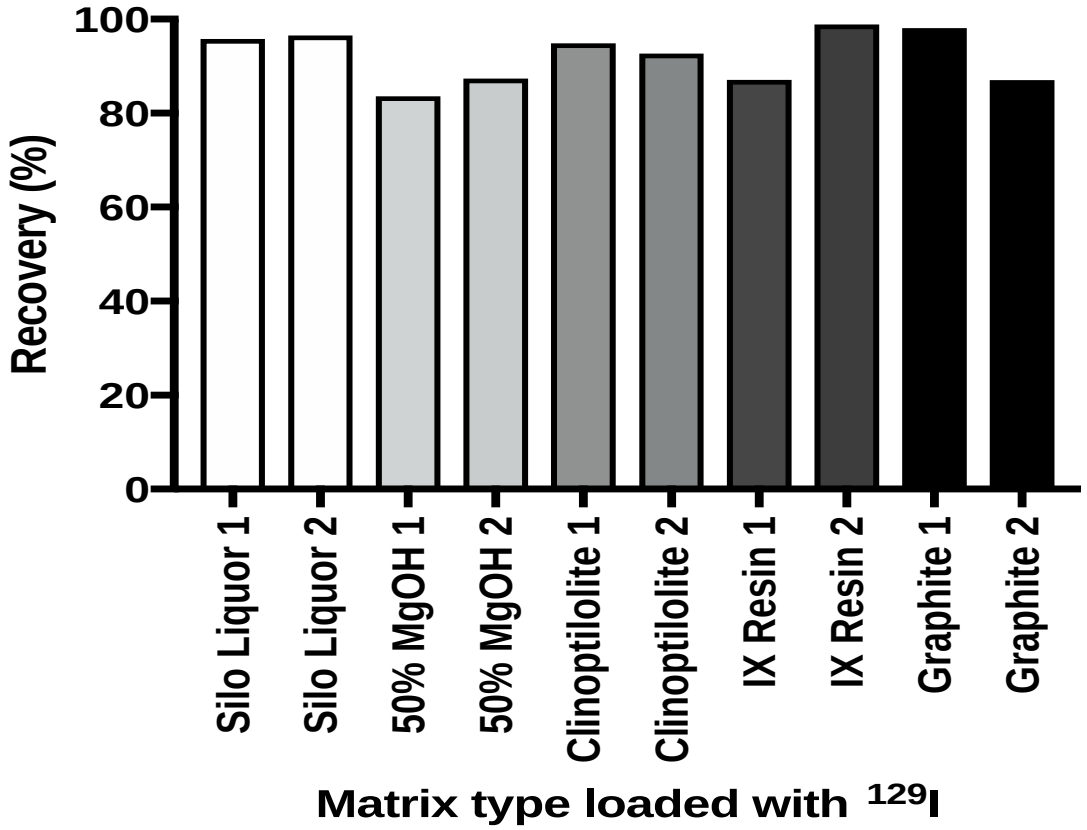
Effect of CO_2



A 20ml bubbler containing 0.5% TMAH can tolerate up to 1 g CO_2

20mg I
0.5% TMAH

Recovery of ^{129}I from various matrices



Slightly lower recoveries observed for Mg(OH)2. Iodine retained in the sample boat even when combusted at 950°C

Chemical separation of Cl and I

Characterisation of the Cl resin

Retention of ^{36}Cl and ^{129}I in 1M H_2SO_4

Isotope	D_w retention
Cl-36	1600
I-129	1980

D_w values for different KSCN concentrations

	Cl-36	I-129
KSCN conc.	D_w elution	D_w elution
0.01M	1.7	12000
0.05M	0.4	15000
0.1M	0.7	4000
0.2M	0.4	9000

D_w values for different Na_2S concentrations

Na_2S conc	Mean D_w
0.04M	40
0.09M	15
0.18M	0.7
0.35M	0.8

- quantitative uptake of both nuclides by silver loaded Cl-resin
- ^{36}Cl is eluted quantitatively at any KSCN concentration
- ^{129}I remains on the resin at any KSCN concentration
- ^{129}I is eluted at elevated Na_2S concentrations

Data from Alexander Zulauf,
Philipps Universitat, Marburg

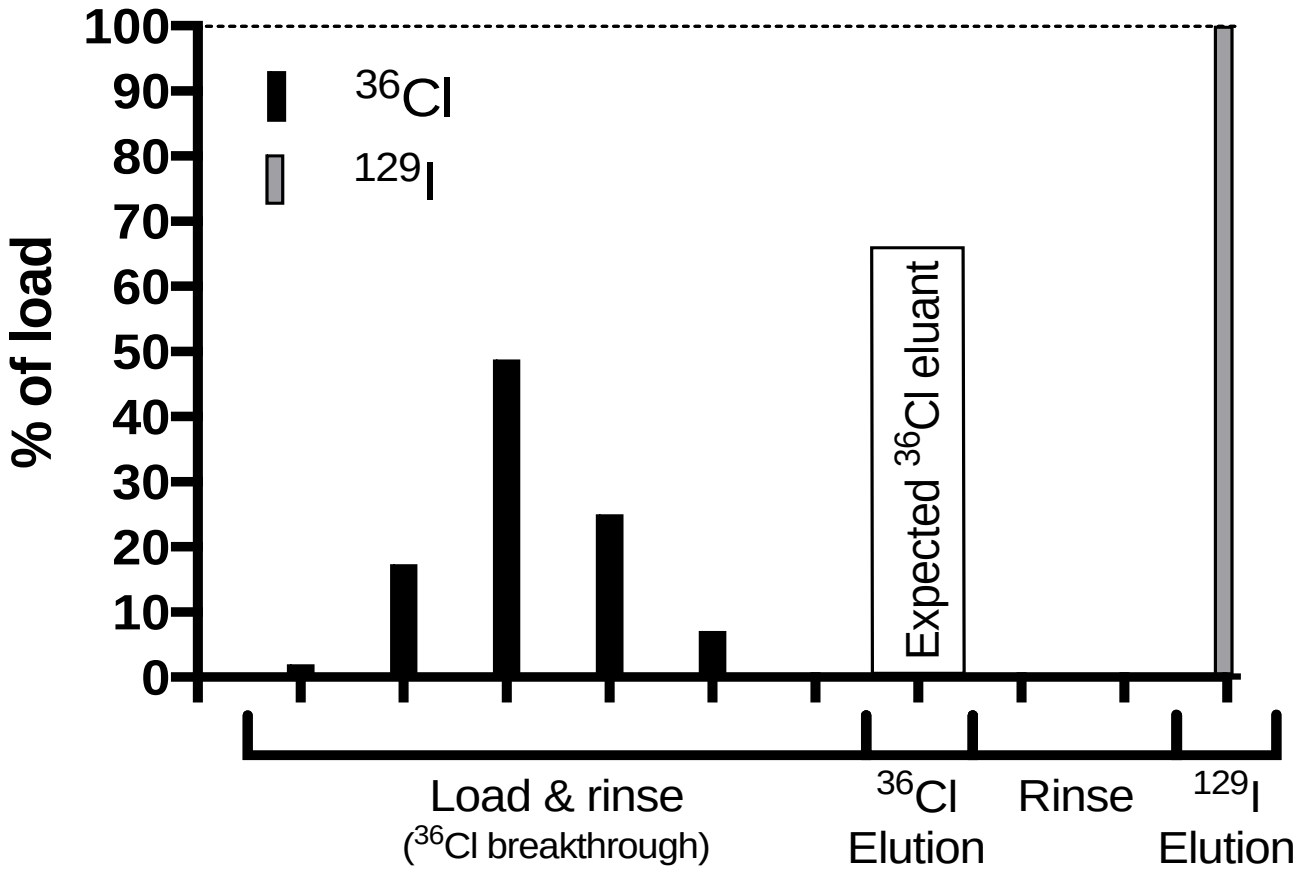
Loading capacity

Analyte	Theoretical value	Experimental value
I-	14.9mg	16.3±1.6mg
Cl-	4.2mg	4.3 ±0.2mg

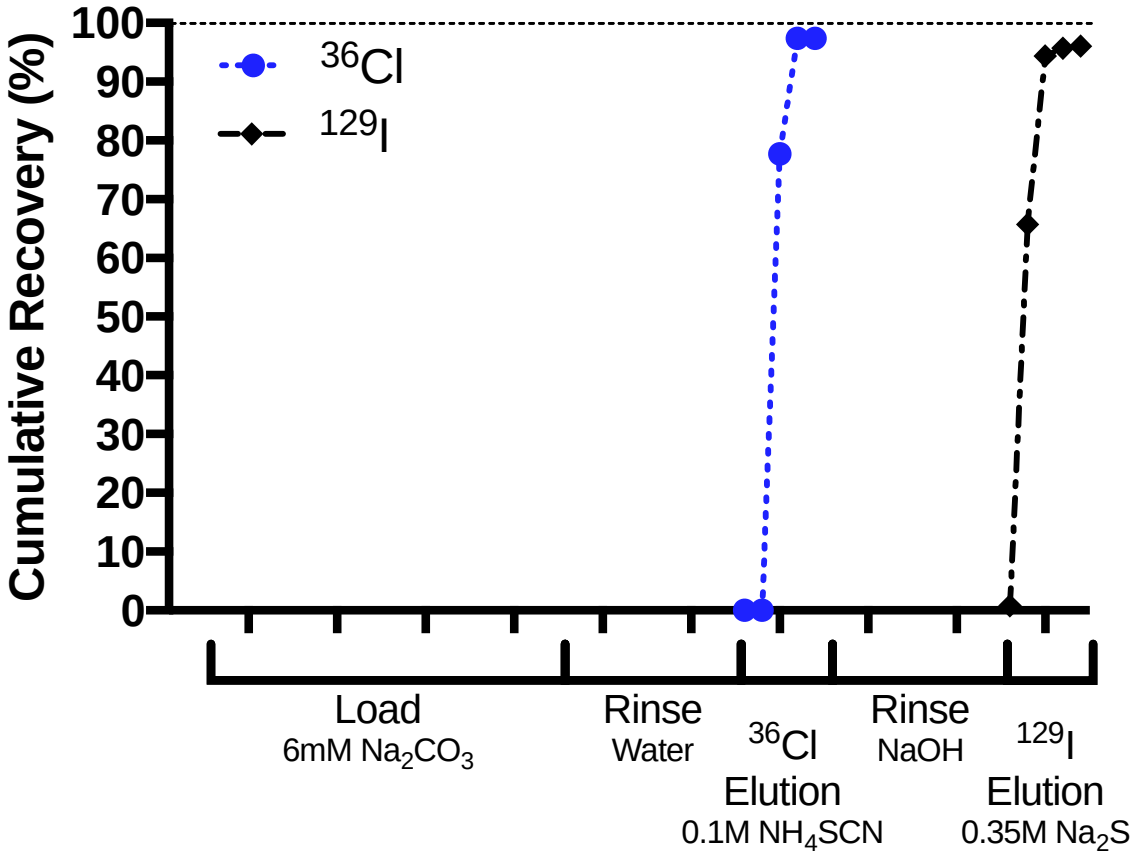
Loadings are dependent on the quantity of Ag initially loaded onto the resin.
Above values are based on 13mg Ag loading

Data from Alexander Zulauf,
Philipps Universitat, Marburg

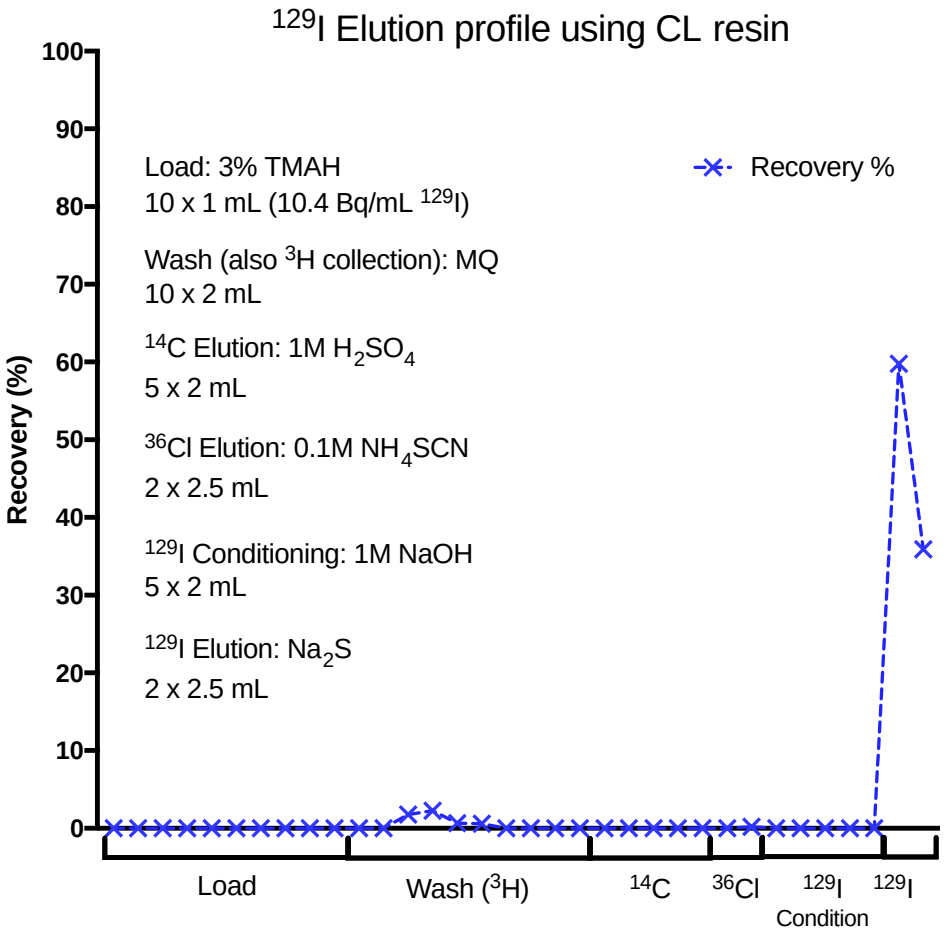
Separation of ^{36}Cl & ^{129}I from 1M NaOH



Separation of ^{36}Cl & ^{129}I from 6mM Na_2CO_3



Separation of ^{129}I from TMAH



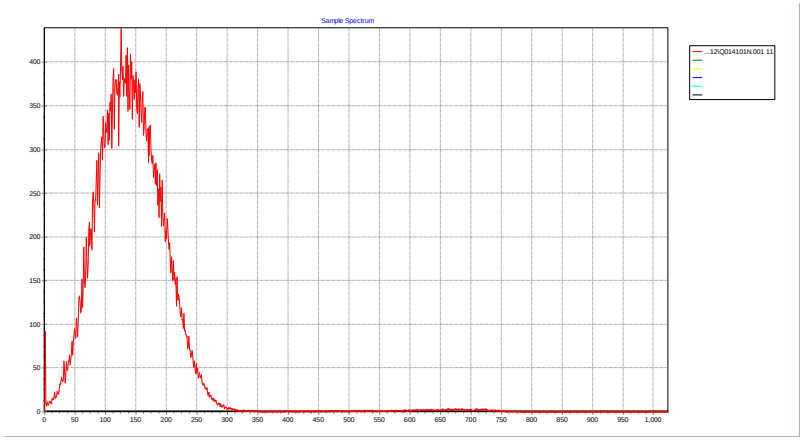
Separation of interferents

	^{36}Cl fraction	^{129}I fraction
^{3}HTO	> 500	> 2000
$^{14}CO_3$	7	5000
^{14}C modified wash	700	
^{35}S modified wash	1500	1000
^{36}Cl		> 2000
^{129}I	1300	

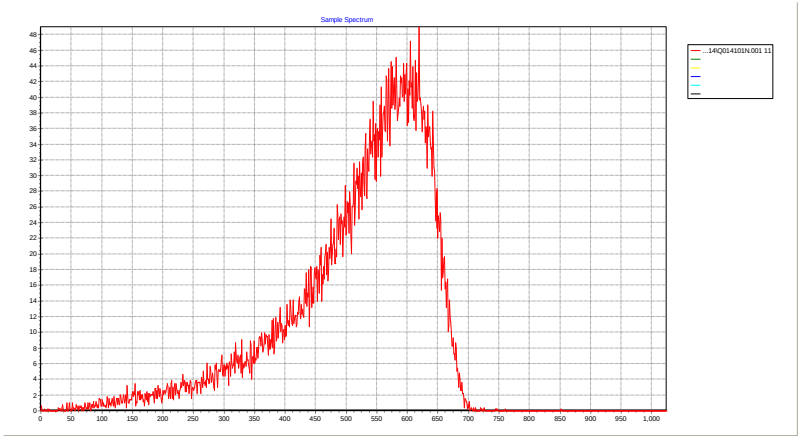
Decontamination factors

Loading in Na_2CO_3
Modified wash – 1M H_2SO_4 wash prior to Cl elution

Purification of ^{36}Cl from desiccant



Bubbler solution before separation



Purified Cl fraction

Summary

- Initial studies indicate that ^{36}Cl and ^{129}I are liberated from solid matrices using thermal desorption although further work is required to optimise ^{36}Cl recoveries.

- Other volatile radionuclides co-trapped with ^{36}Cl / ^{129}I can be efficiently separated using Cl-resin.

- The combination of combustion and isolation of Cl and I using Cl-columns provides a rapid approach for the separation and purification of ^{36}Cl and ^{129}I from solid matrices avoiding the need for time-consuming digestion procedures.

- The Cl and I fractions arising from the separation are readily miscible with commercially available liquid scintillation cocktails.

- Further studies are required to validate the technique and confirm that ^{36}Cl can be quantitatively extracted from the range of materials routinely analysed for ^{36}Cl.

- Parallel studies of ^{129}I measurement by ICP-QQQ are also being undertaken.

Any questions?

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