Determination of ^{36}Cl in decommissioning samples using a Pyrolyser furnace and extraction chromatographic separations

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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

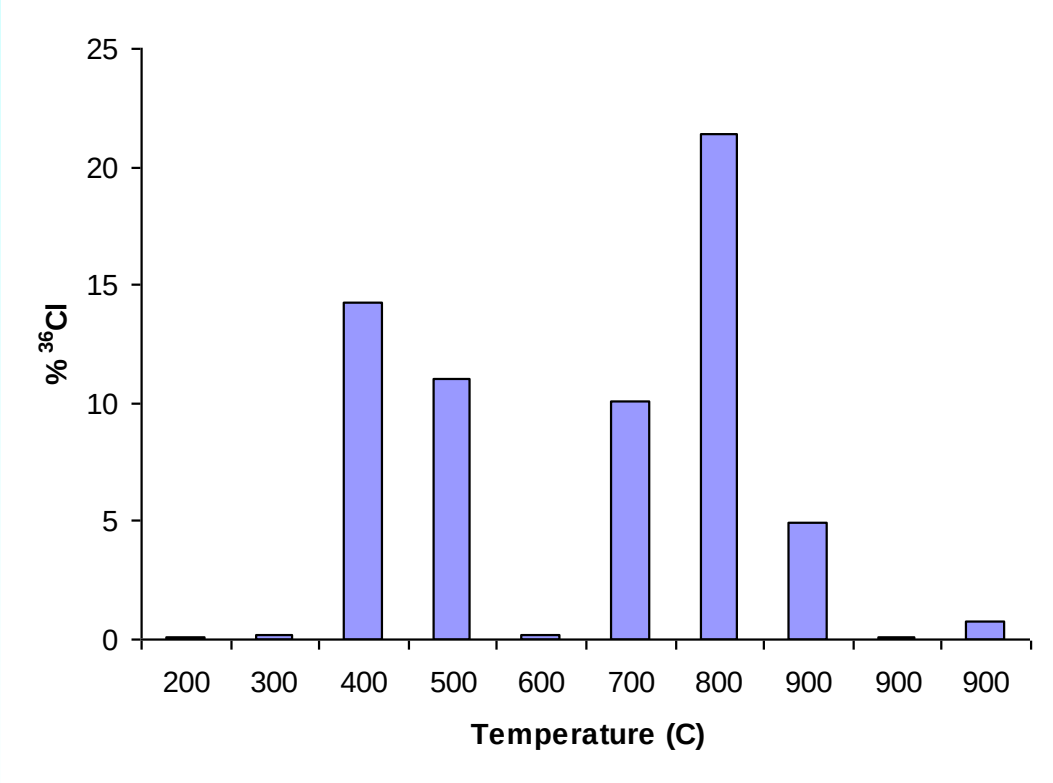
Current approaches

- Alkaline digestion followed by chemical separation.
- Acid digestion and volatilisation of ^{36}Cl.
- Thermal decomposition of the sample (with or without modifiers) and liberation of Cl species as HCl or Cl_2.
- Final measurement of ^{36}Cl by liquid scintillation counting (high counting efficiency).
- Potential interferences from ^{3}H, ^{14}C, ^{35}S, ^{129}I.

Proposed separation

- Thermal decomposition of the sample and desorption of Cl species.
- Samples heated to 900°C in a tube furnace using a controlled heating cycle (10°C/min to 900°C and held for 60 minutes – total time 2 hrs).
- Moist air used to flush system. Sample moistened with 1ml water.
- Combustion products trapped in an alkaline trap. Bubbler connected to furnace tube using ground glass joints.
- ^{36}Cl isolated from other radionuclides using Triskem ‘Cl resin’ conditioned with $AgNO_3$
- Total volume of eluent mixed with scintillation cocktail for liquid scintillation analysis.

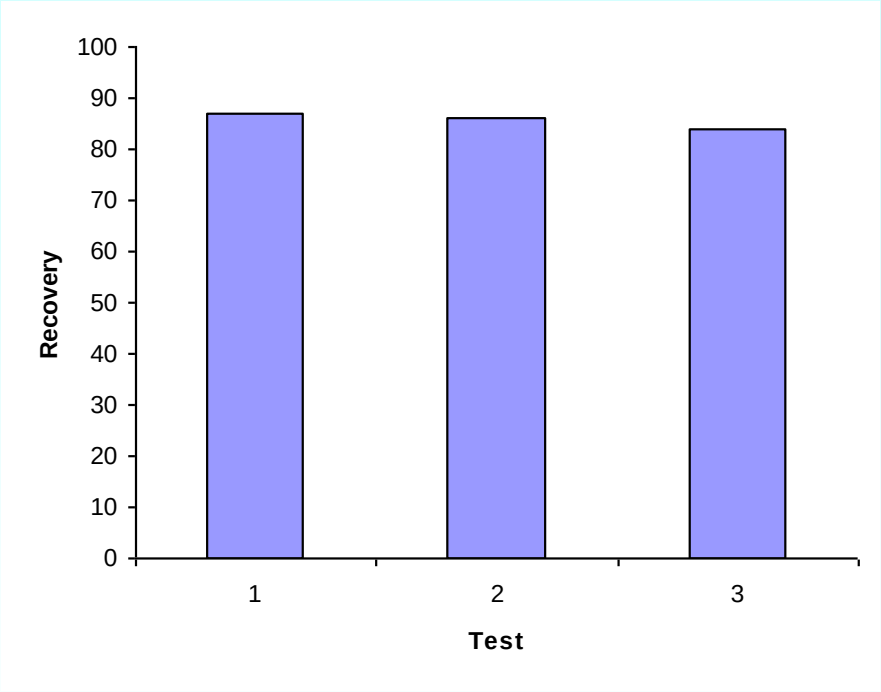
Thermal desorption of ^{36}Cl



Chlorine-36 standard as NaCl

Bubbler (20ml 6mM Na_2CO_3) changed at 100°C intervals

Recovery of standards

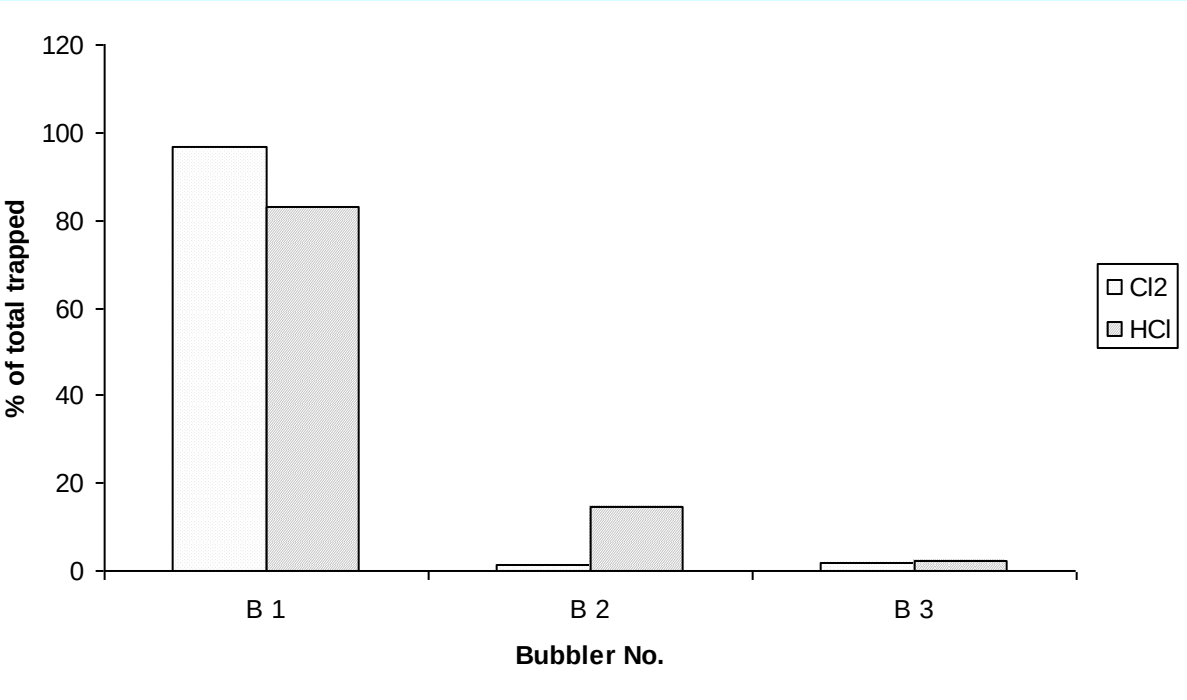


Results for replicate standard analyses

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

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

Trapping of Cl species



- ^{36}Cl liberated as either Cl_2 or HCl.
- Trapped in 20ml 6 mM Na_2CO_3 (bubblers 1+2) or 1M NaOH (bubbler 3)
- Air flow rate 200 ml/min

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

- quantative uptake of both isotopes by silver loaded Cl-resin
- ^{36}Cl is eluted quantatively 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

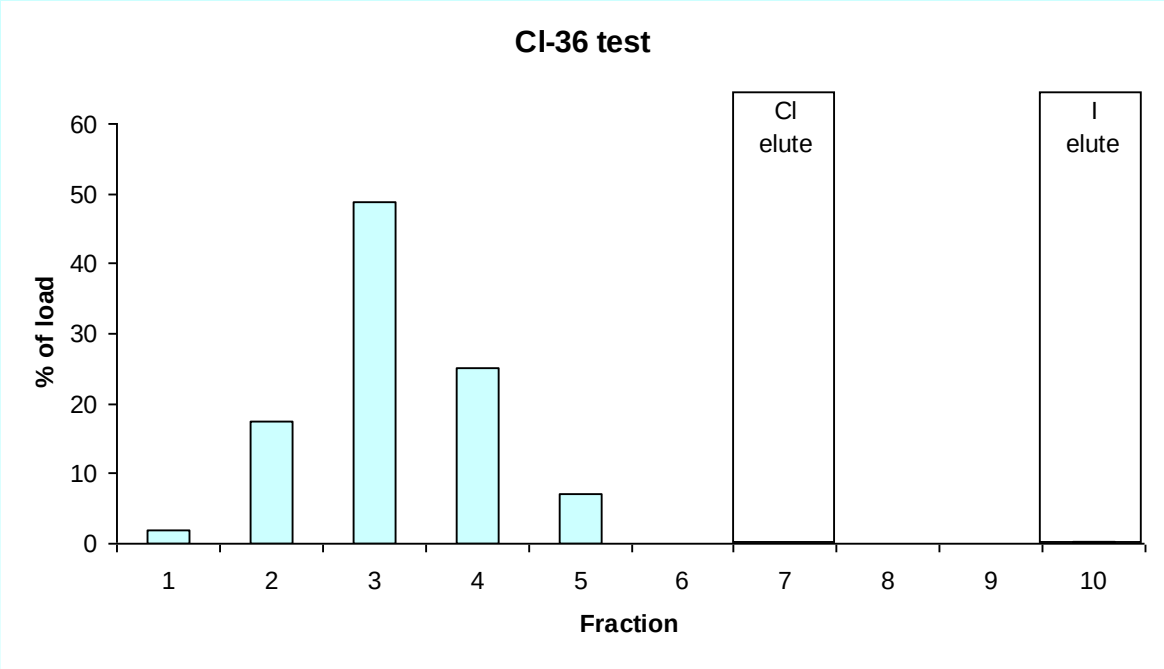
Chloride loading capacity

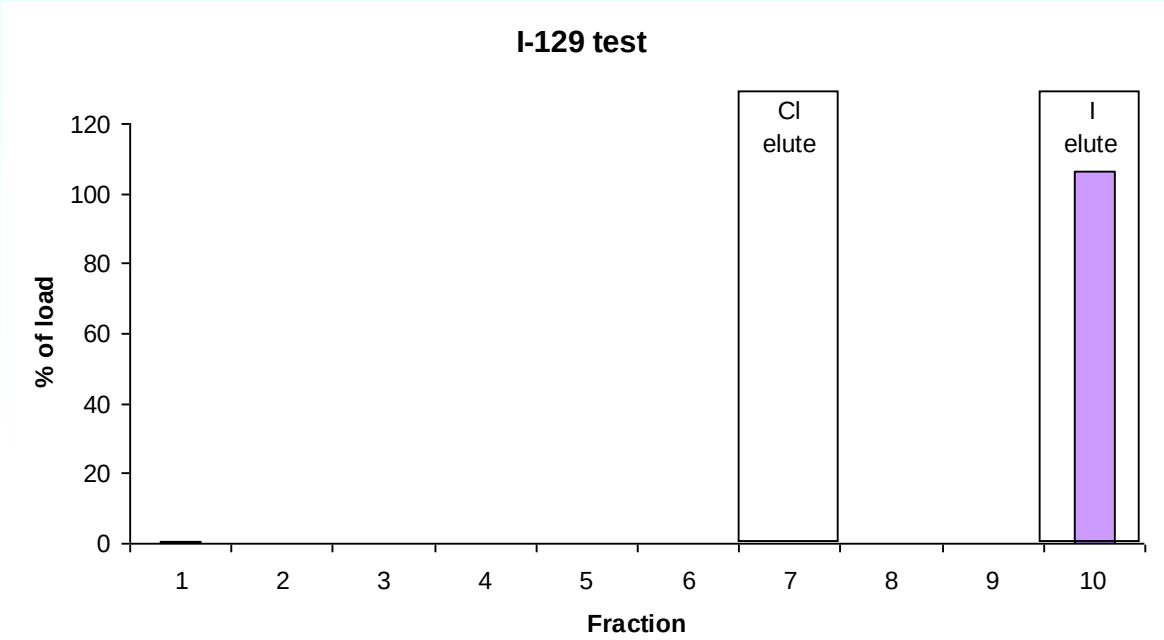
Analyte	Theoretical value	Experimental value
I-	14.9mg	16.3±1.6mg
Cl-	4.2mg	4.3 ±0.2mg

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

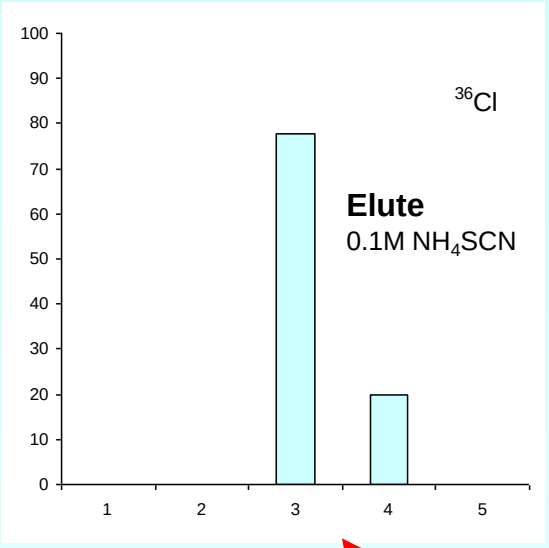
Data from Alexander Zulauf,
Philipps Universitat, Marburg

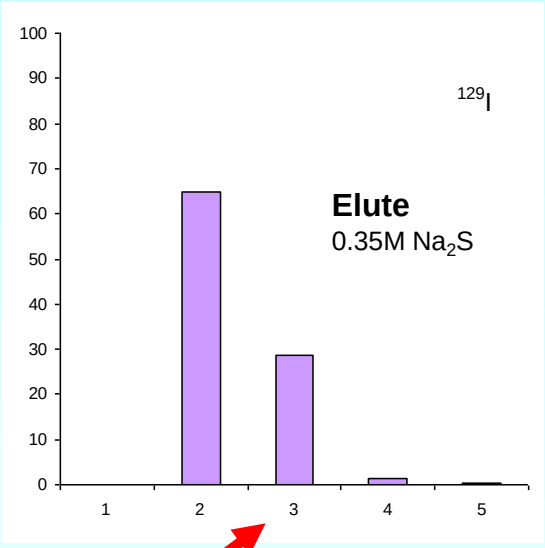
Separation of ^{36}Cl and ^{129}I from 1M NaOH

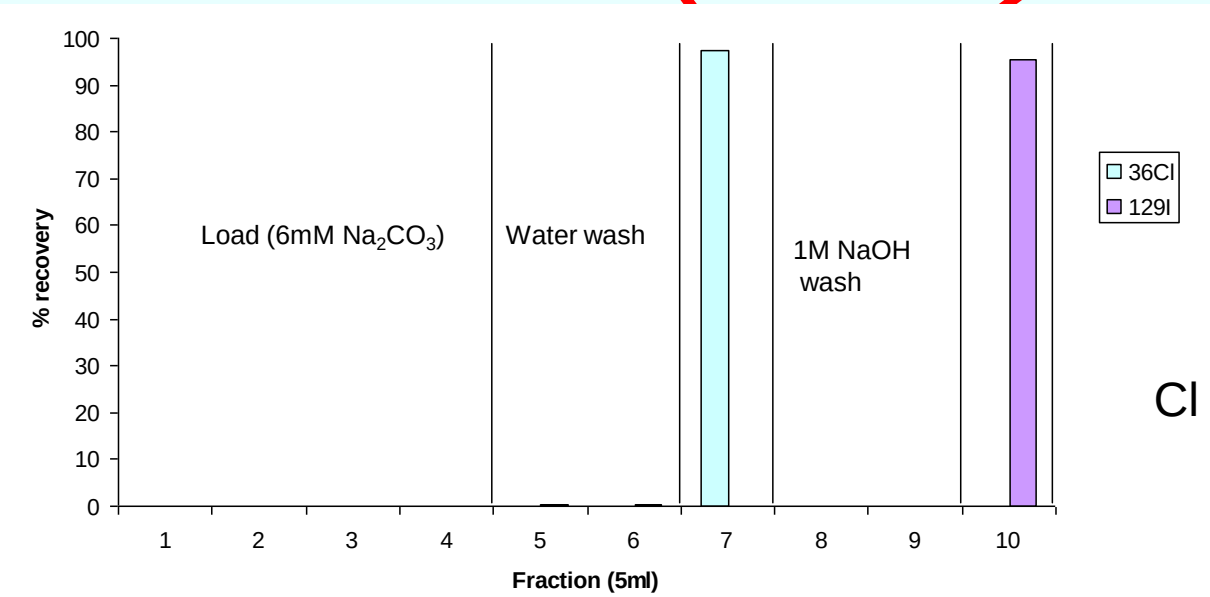




Separation from 6 mM Na_2CO_3

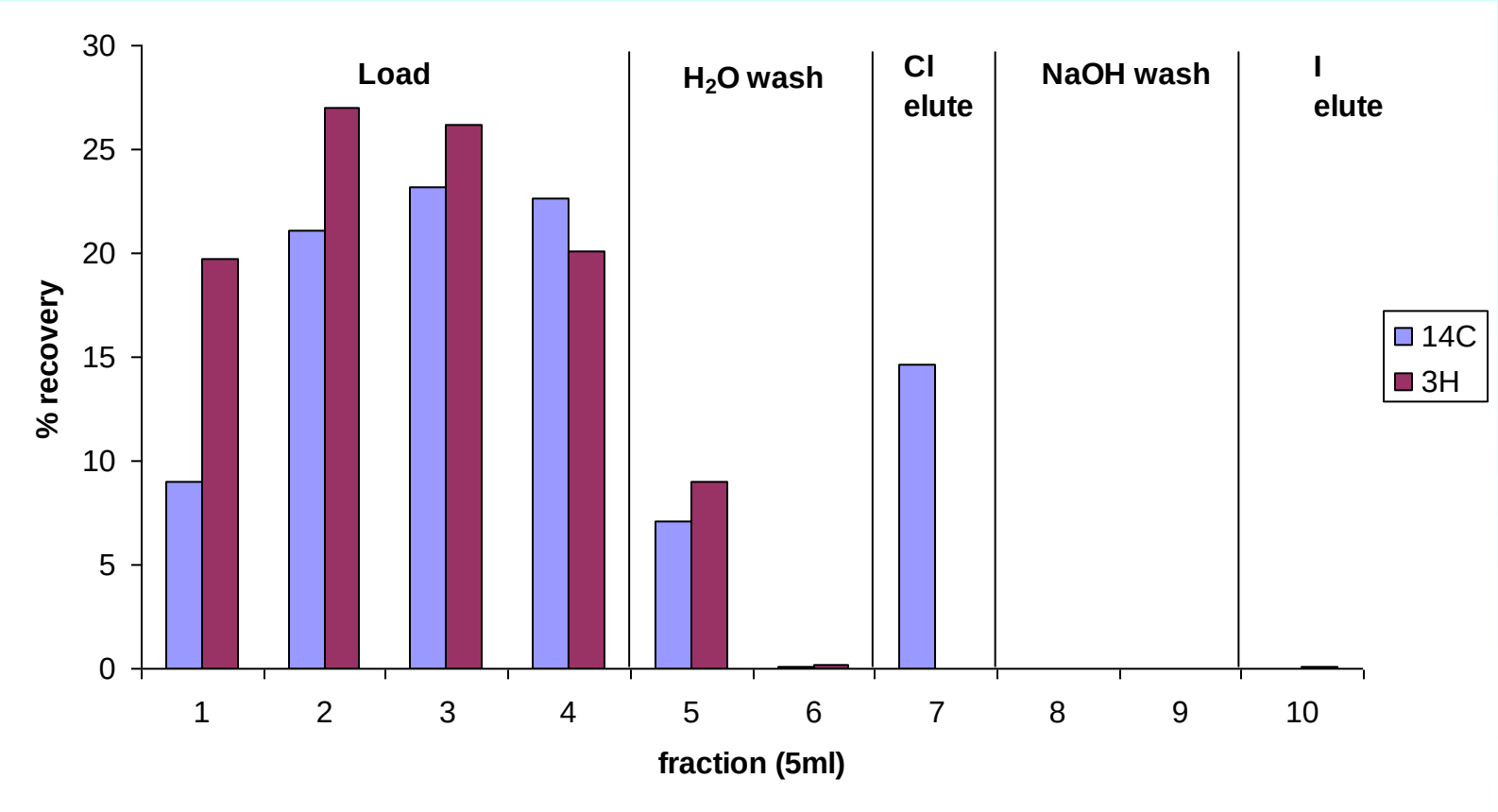




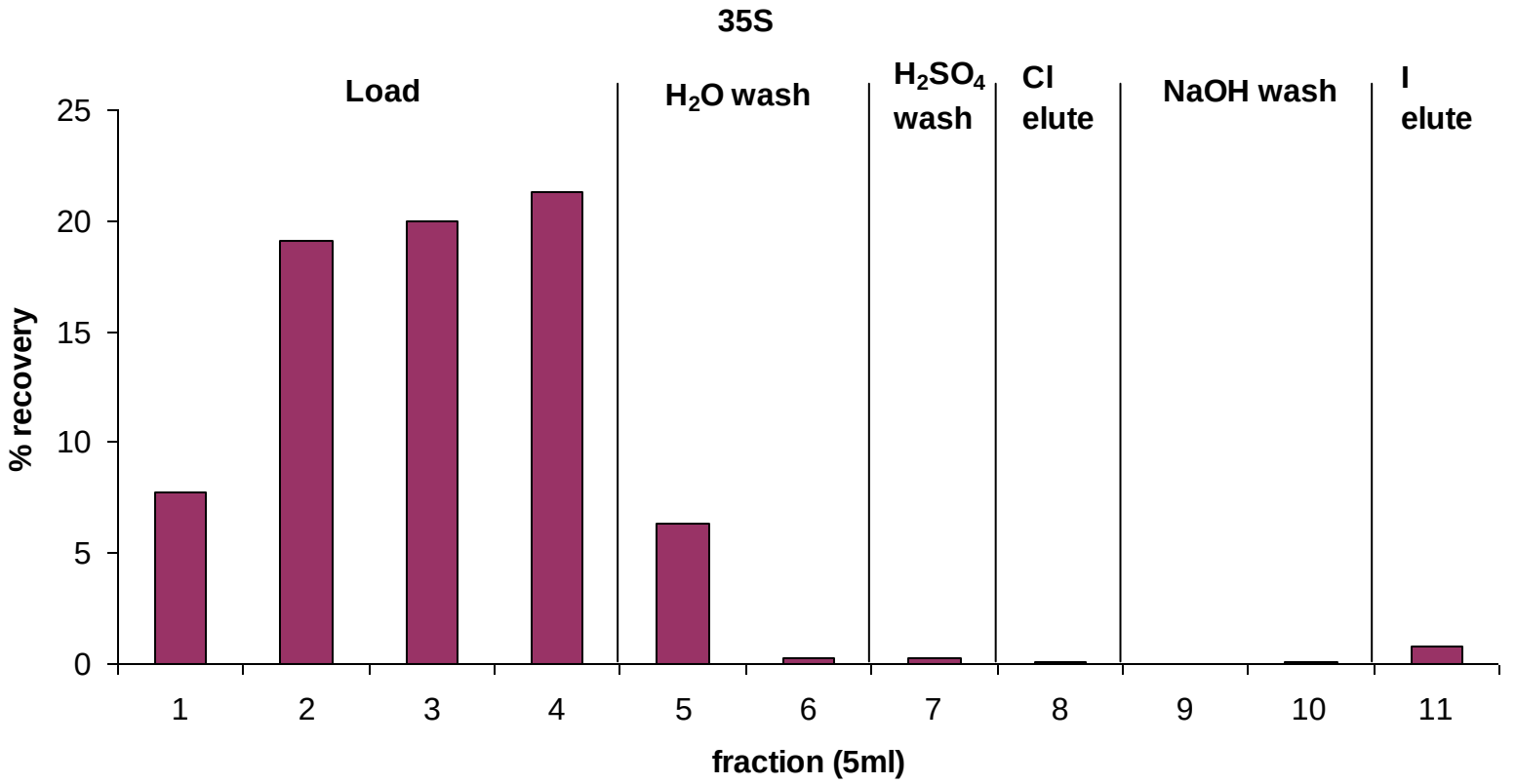


Cl recovery 98%

Decontamination factors (I)



Decontamination factors (II)



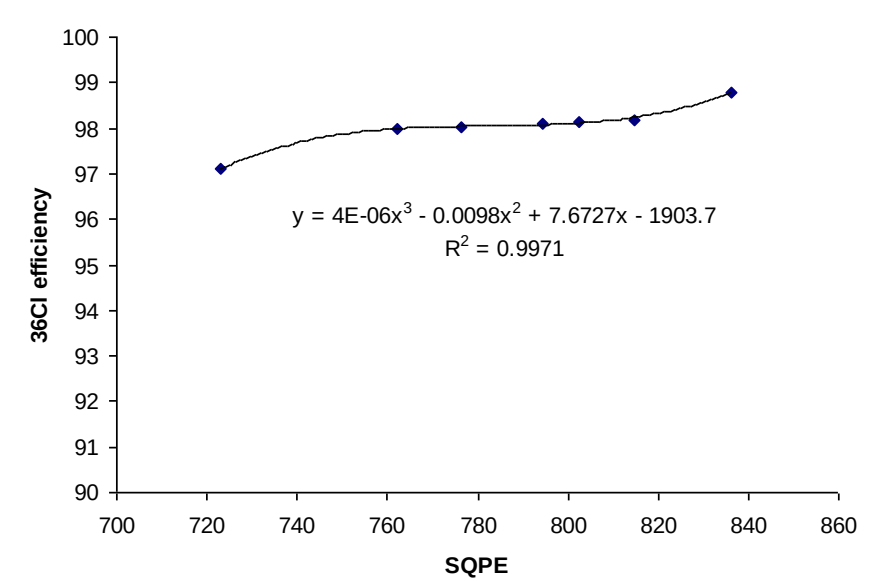
Additional 0.1M H_2SO_4 wash stage added to remove ^{14}C

Decontamination factors

	^{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	

Liquid scintillation analysis

- 5ml 0.1M NH_4SCN eluent mixed with 15ml Proflow P cocktail.
- Some cocktails contain additives which will reduce any residual Ag compounds co-eluted to elemental Ag resulting in a black solution unsuitable for liquid scintillation counting.
- Proflow P (Meridian) mixes well with the NH_4SCN eluent without reducing residual Ag^+.



Limit of detection

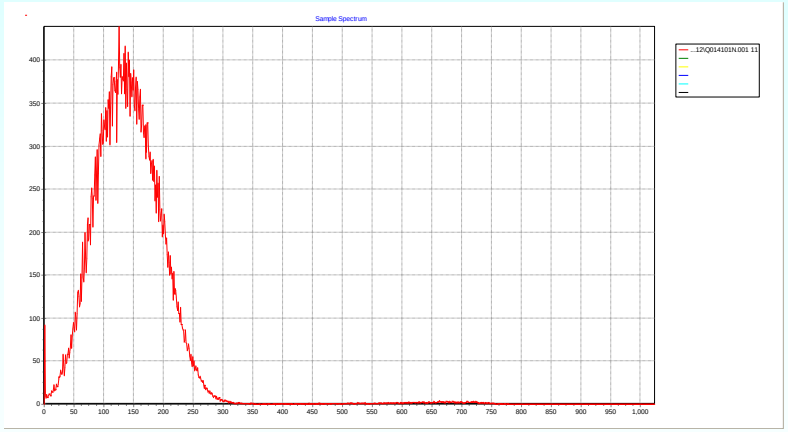
Sample mass (g)	1.0 g
Recovery %	86 %
Background CPM	11 cpm
Efficiency %	98 %
Count time (mins)	180 mins
LOD (Currie)	**0.02 Bq/g**

Spiked ion exchange resin

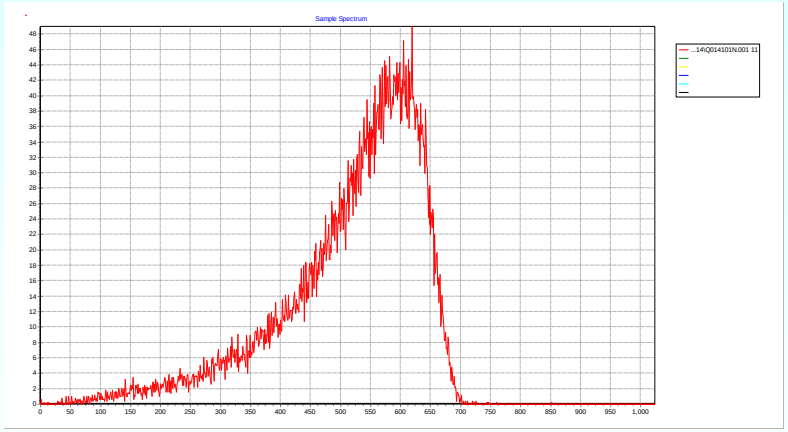
Sample type	Expected value	Measured value
Ion exchange resin	4.1 kBq	4.3 ± 0.1 kBq

Analysis of decommissioning samples

- Method tested using desiccant from a reactor site.



LSC spectra for bubbler solution (dominantly ^{3}H)



LSC spectra for purified bubbler solution (^{36}Cl)

Benefits over existing approaches

- Rapid procedure with analysis requiring 1 day for 6 samples.
- The total bubbler volume is used in the final measurement increasing sensitivity.
- Applicable to decommissioning samples containing other volatile radionuclides.
- Potential for sequential separation and quantification of other volatile radionuclides.

Summary

- Initial studies indicate that ^{36}Cl is effectively liberated from solid matrices using thermal desorption.
- Other volatile radionuclides co-trapped with ^{36}Cl can be efficiently separated using Cl-resin. The resin will also isolate ^{129}I.
- The combination of combustion and isolation of Cl using Cl-columns provides a rapid approach for the separation and purification of ^{36}Cl 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.


DISCOVERY