CL Resin based methods for the separation and determination of Cl-36 and I-129 in environmental and decommissioning samples

Outline

- Scope
- Resin characterization
- Method optimization
- Spiked samples
- Summary

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Scope

- Interest: monitoring of nuclear facilities for long-lived radionuclides
- Cl-36 (and I-129) frequently determined by LSC
  - Cl-36 (3.01 E+04 y, $E_{\beta max}$= 708.6 keV),
  - I-129 (1.61 E+07 y, $E_{\beta max}$= 151.2 keV)
  - Existing separation methods often complicated and time-consuming
- Aim:
  - Development and characterization of a suited resin
  - Development of a simple and quick method for separation of Cl-36 and I-129 from environmental and decommissioning samples
- Cl and I retained as chloride and iodide
  - Oxidation state adjustment might be necessary (e.g. Sn(II))

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Resin characterization – CL resin

- Determination of D_w values
  - For practical reasons in sulfuric acid (Sn(II))

Analyte	D_w
Mn	<1
Fe	<1
Ni	<1
Co	<1
Cu	<1
Zn	25
Cd	<1
Ce	4
Pd	87000

D_w values, selected elements, 1M H_2SO_4 ,CL resin

- D_w (Ag):
  - 1M H_2SO_4: 6,5E+05
  - H_2SO_4 (pH 3): 6,0E+05
  - H_2SO_4 (pH 5): 3,5E+05
- Ag uptake:
  - 17 – 20 mg Ag^+ per 2 mL column
  - extraction equilibrium reached < 30 min

- Selective for Pd and Ag (plus other PGE, Au, Hg)
- D_w(Ag) very high over wide pH range

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Resin characterization – Ag^+ loaded CL resin

- Maximum chloride and iodide uptake evaluated via column experiments (2 mL column loaded with 13 mg Ag^+)
  - I: 16.3±1.6mg; Cl: 4.3 ±0.2mg
  - Can be increased by using higher Ag^+ amounts and longer resin / Ag^+ contact times
- D_w values of chloride and iodide
  - Extraction conditions: 1M H_2SO_4
  - Elution conditions:
    - Chloride: 0.01 – 0.2M SCN^-
    - Iodide: 0.01 – 0.2M SCN^-; 0.04 – 0.35M Na_2S
- Batch experiments

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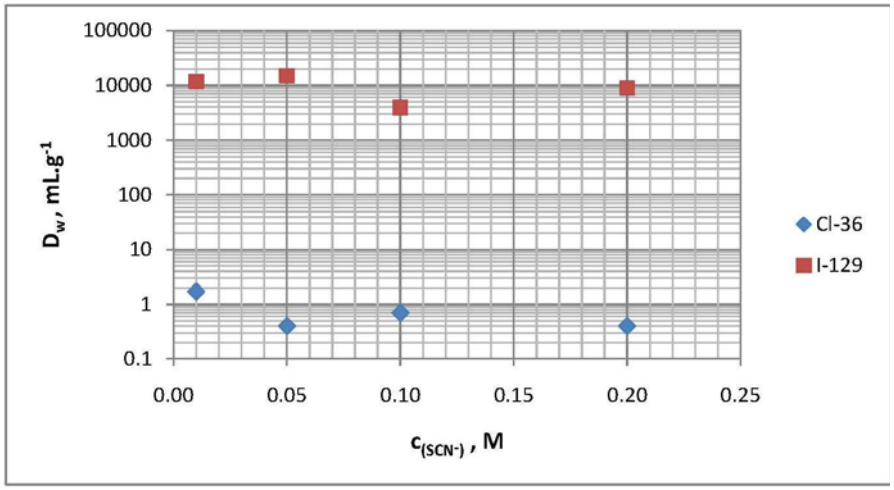
Resin characterization – Ag^+ loaded CL resin

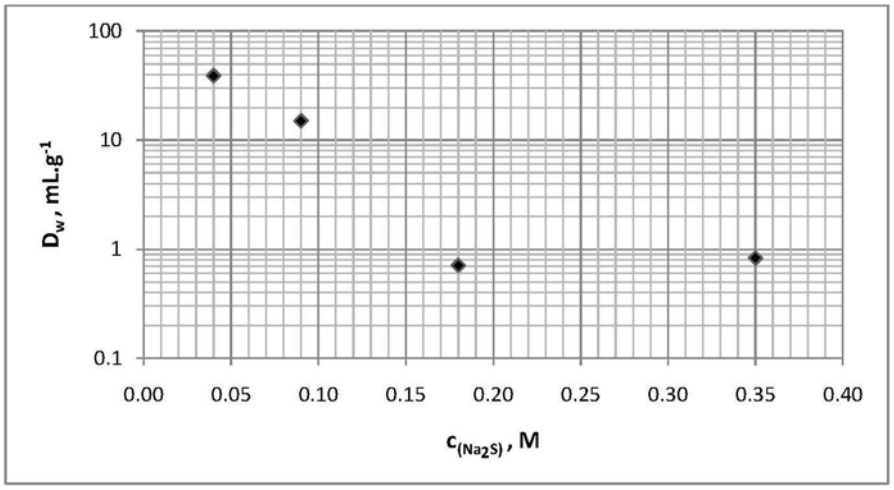
Isotope	D_w retention
Cl-36	1600
I-129	1980

Retention of chloride (^{36}Cl) and iodide (^{129}I) in 1M H_2SO_4

- High uptake of chloride and iodide onto Ag^+ loaded CL-resin in 1M H_2SO_4
- Remark: iodate also retained, chlorate not



D_w of chloride (^{36}Cl) and iodide (^{129}I) on Ag loaded CL resin at pH 7 and varying SCN^- concentrations



D_w of iodide (^{129}I) on Ag loaded CL resin at pH 7 and varying Na_2S concentrations

- Chloride: very low D_w at all tested SCN^- concentrations
- Iodide: high D_w at all tested SCN^- concentrations,
  low D_w at elevated Na_2S concentrations

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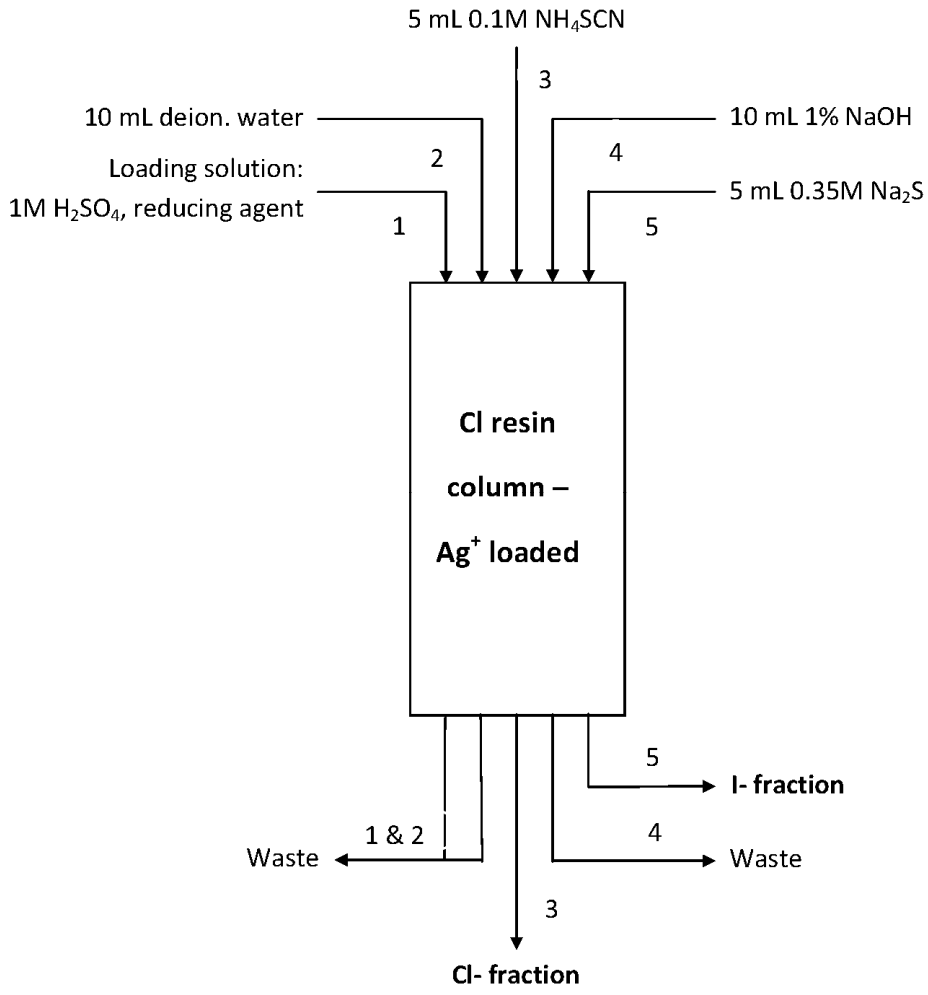
Scheme – Optimized method



- Load sample in 1M H_2SO_4
  - ➢ Less acidic, neutral or slightly alkaline also possible
  - ➢ Addition of reducing agent if necessary (e.g. Sn(II))
- Rinse with 10ml of deion. water
- Elute chloride with 5ml of 0.1M SCN^-
- Rinse with 10ml of 1% NaOH
  - ➢ Increases iodide yield
- Elute iodide with 5ml of 0.35M Na_2S

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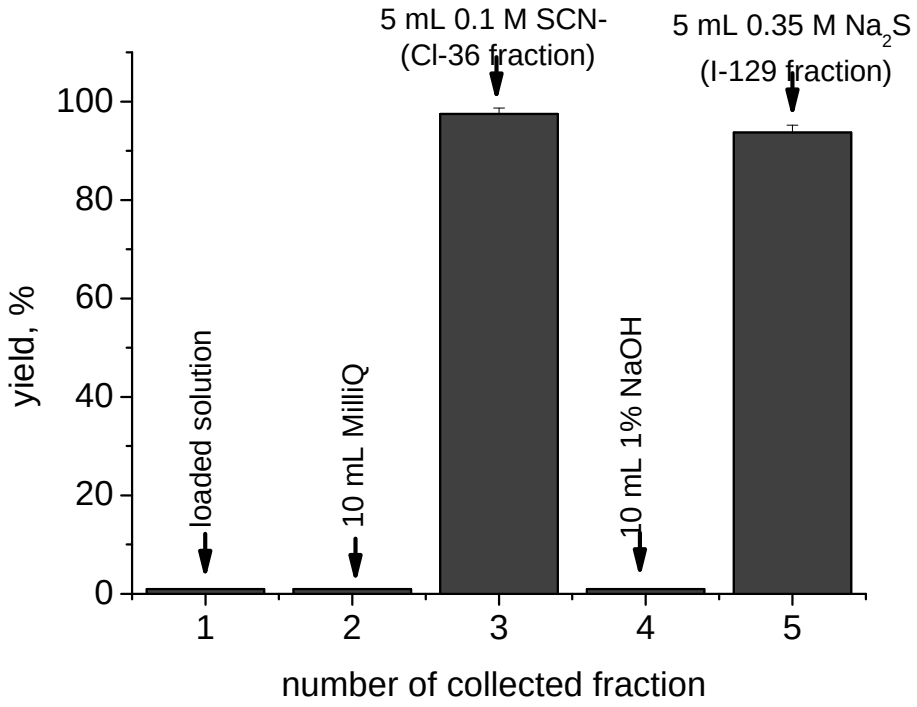
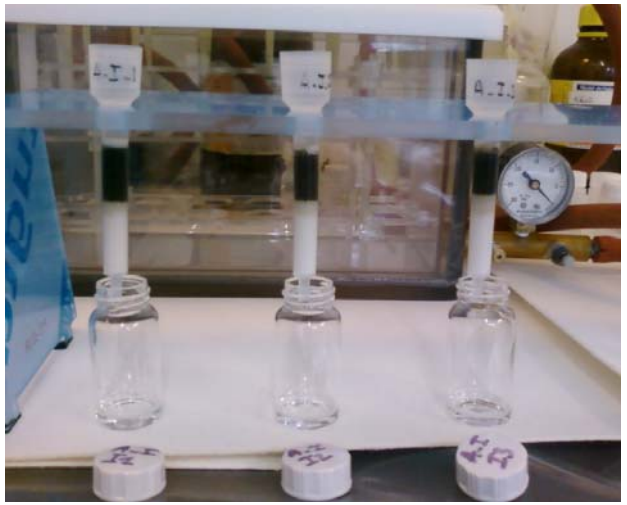
Elution study

- Method applied to ^{36}Cl and ^{129}I containing solution



Combined Cl/I elution study, optimized method



I^- elution from CL Resin

- Clean ^{36}Cl / ^{129}I separation
- Fractions can be directly measured by LSC

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Decontamination factors (D_f)

Analyte	D_f in Cl fraction	D_f in I fraction
Mn	>210	>370
Co	>170	>1500
Ni	>170	>320
Cu	>210	>190
Sr	>180	>17000
Cd	>6900	>7700
Cs	>200	>6200
Ba	>1000	>600
Pb	>300	>720
U	>1900	>200
Cs-137	>150	>150
Co-60	>320	>320
Sr/Y-90	>180	>160
Cl-36	NA	>160
I-129	>420	NA

Method applied to

- Multi-element solutions
  - ICP-MS

- Cs-137, Co-60, Sr-90, Cl-36 or I-129 containing solutions
  - LSC

- Good decontamination factors in SCN^- and Na_2S fractions

- Clean I^- / Cl^- separation

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Spiked samples I - water

- 50ml tap water adjusted to 1M H_2SO_4
- Spiked with known activities of Cl-36, I-129 respectively
- Each 0.5 mg NaCl and NaI
- Addition of 17Bq of each Co-60, Sr-90 and Cs-137
- Three 10ml aliquots analyzed following optimized method
- Chemical yields obtained in previously performed reproducibility test applied
    - Determination of chemical yield for each separation via e.g. ion chromatography preferable
- LSC measurement of chloride and iodide fractions

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Spiked samples I - water

	determined activities		added activities			
I-129	A(I-129) / Bq	$U_{A(I-129)}$ / Bq	A(I-129) / Bq	$U_{A(I-129)}$ / Bq	Bias / %	E_n
Repl. 1	8,24	1,98	8,22	1,31	0,3%	0,01
Repl. 2	8,17	1,97	8,22	1,31	-0,5%	0,02
Repl. 3	7,86	1,89	8,22	1,31	-4,4%	0,16
Cl-36	A(Cl-36) / Bq	$U_{A(Cl-36)}$ / Bq	A(Cl-36) / Bq	$U_{A(Cl-36)}$ / Bq	Bias / %	E_n
Repl. 1	8,97	1,05	9,44	0,94	-5,1%	0,34
Repl. 2	9,11	1,06	9,44	0,94	-3,5%	0,23
Repl. 3	9,12	1,06	9,44	0,94	-3,5%	0,23

Comparison determined vs. reference activities, water, 3 replicates, bias and E_n, k=2

- Overall good agreement, slight negative bias for Cl-36

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Spiked samples II – effluents (Subatech)

- 4 spiked effluent samples
  - Cl 0: Blank sample
  - Cl 1 and Cl2: No I-129, identical Cl-36 activities
  - Cl 3: Cl-36 / I-129 activity ratio 1:1
  - Cl 4: Cl-36 / I-129 activity ratio 1:10
- Preparation loading solutions:
  - 2.5 mL Standard solution (Cl1 – Cl4)
  - 0.5 mL 0.1M NaCl and 0.5 mL 0.1M NaI
  - 6.5 mL 1M H_2SO_4
- Cl fraction collected, 5 mL 0.1M NaSCN added
- 10 mL Cocktail
- LSC (TriCarb 3170TR/SL, 12 – 250 keV, 60min)

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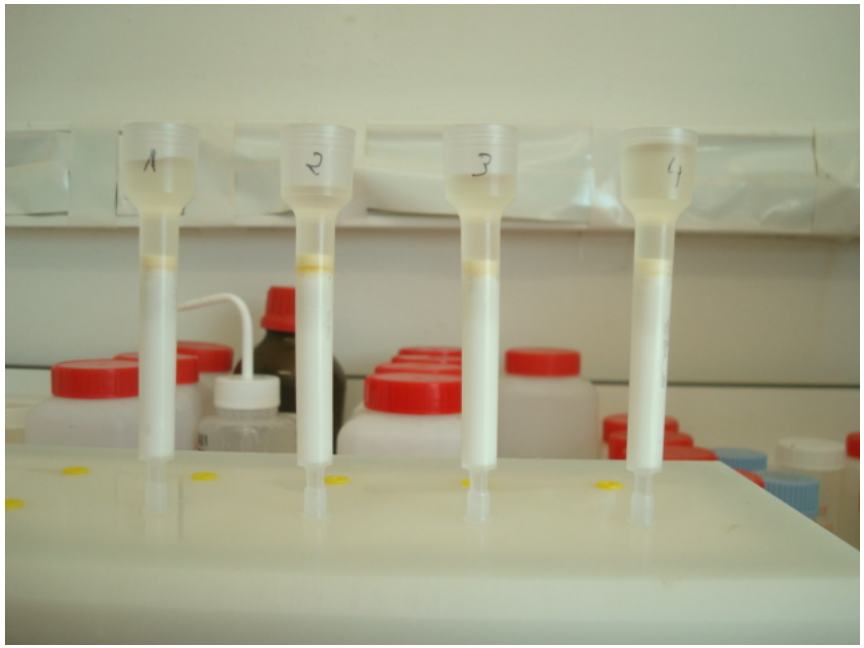
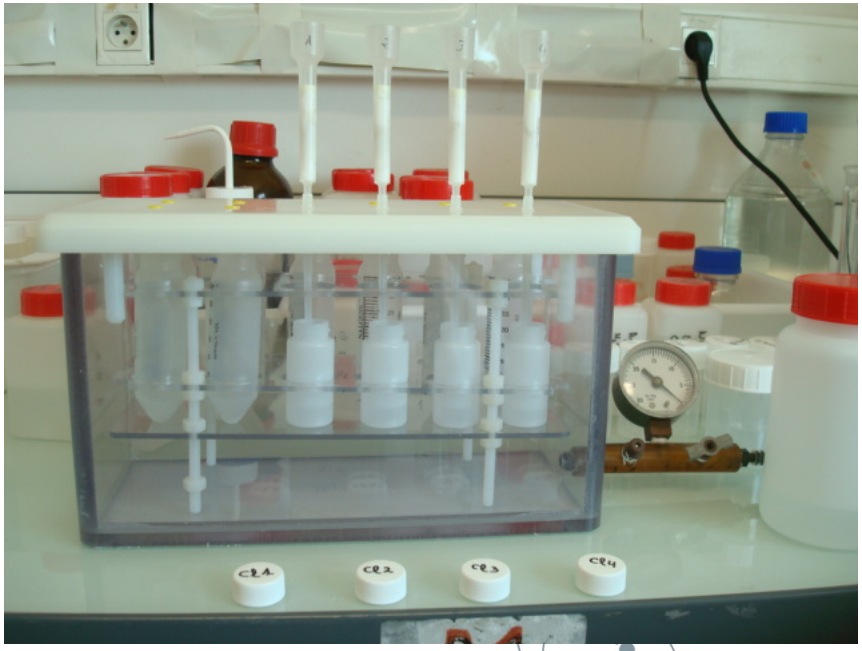
Spiked samples II – effluents (Subatech)



Column loading



Chloride elution

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Spiked samples II – effluents (Subatech)

Sample	Cl-36 Theoretical activity		I-129 Theoretical activity		Perkin Elmer TriCarb 3190TR/SL				Comparison of Cl-36 activity	
	A ($Bq.L^{-1}$)	U_A ($Bq.L^{-1}$)	A ($Bq.L^{-1}$)	U_A ($Bq.L^{-1}$)	tSIE	cpm	A ($Bq.L^{-1}$)	U_A ($Bq.L^{-1}$)	Deviation (%)	Zeta test
Cl0	Blank	-	Blank	-	236.3	5.22	< LOD	-	-	-
Cl1	1.873E+04	6.556E+02	0	-	239.8	1774.8	1.809E+04	1.191E+03	-3.44	0.47
Cl2	1.873E+04	6.556E+02	0	-	243.9	1871.4	1.905E+04	1.255E+03	1.72	0.23
Cl3	1.873E+04	6.556E+02	1.889E+04	5.100E+02	252.0	1865.3	1.806E+04	1.189E+03	-3.57	0.49
Cl4	1.873E+03	6.556E+01	1.897E+04	5.121E+02	254.2	189.85	1.792E+03	1.226E+02	-4.35	0.59

Comparison determined vs. reference activities, effluents, bias and zeta test values

- Very good agreement between theoretical and obtained activity
- Repeatability Cl1/Cl2: 3.7% (N = 2, k = 1)
- Increased I-129 activity not introducing positive bias into Cl-36 results
  - ➢ Clean chloride / iodide separation

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Spiked solid samples

- Filter, soil and concrete samples (each 250 mg)
- Spiked with known activities of Cl-36, I-129 respectively
- Extracted with 1M NaOH at 70°C for 4h
- Centrifugation, residue rinsed with 2 mL water
- Supernatants combined, adjusted to 1M H_2SO_4 and filled up to 50 mL
- Analysis of three 10 mL aliquots
- Average extraction and separation yields used for result calculation
    - Determined upfront for given extraction conditions and matrix

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Spiked samples III – filter

		determined activities		reference activities			
filter	^{129}I	$A(^{129}I)$, Bq	$U_{A(129I)}$, Bq	$A(^{129}I)$, Bq	$U_{A(129I)}$, Bq	Bias , %	E_n
	Repl. 1	7.89	2.82	8.22	1.31	-4.04	0.11
	Repl. 2	8.28	2.96	8.22	1.31	0.78	0.02
	Repl. 3	7.58	2.71	8.22	1.31	-7.79	0.21
	^{36}Cl	$A(^{36}Cl)$, Bq	$U_{A(36Cl)}$, Bq	$A(^{36}Cl)$, Bq	$U_{A(36Cl)}$, Bq	Bias , %	E_n
	Repl. 1	9.58	1.47	9.44	0.94	1.46	0.08
	Repl. 2	9.20	1.41	9.44	0.94	-2.52	0.14
	Repl. 3	9.70	1.48	9.44	0.94	2.71	0.15

Comparison determined vs. reference activities, filter, 3 replicates, bias and E_n, k=2

- Overall good agreement, slight negative bias for iodide

Spiked samples IV - soil

		determined activities		reference activities			
soil	^{129}I	$A(^{129}I)$, Bq	$U_{A(129I)}$, Bq	$A(^{129}I)$, Bq	$U_{A(129I)}$, Bq	Bias , %	E_n
	Repl. 1	7.65	1.59	8.22	1.31	-6.94	0.28
	Repl. 2	7.60	1.58	8.22	1.31	-7.49	0.30
	Repl. 3	7.47	1.56	8.22	1.31	-9.09	0.37
	^{36}Cl	$A(^{36}Cl)$, Bq	$U_{A(36Cl)}$, Bq	$A(^{36}Cl)$, Bq	$U_{A(36Cl)}$, Bq	Bias , %	E_n
	Repl. 1	9.39	1.76	9.44	0.94	-0.55	0.03
	Repl. 2	9.59	1.79	9.44	0.94	1.60	0.07
	Repl. 3	9.55	1.79	9.44	0.94	1.20	0.06

Comparison determined vs. reference activities, soil, 3 replicates, bias and E_n, k=2

- Overall good agreement, slight negative bias for iodide

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Spiked samples V - concrete

		determined activities		reference activities			
concrete	^{129}I	$A(^{129}I)$, Bq	$U_{A(129I)}$, Bq	$A(^{129}I)$, Bq	$U_{A(129I)}$, Bq	Bias , %	E_n
	Repl. 1	7.71	1.96	8.22	1.31	-6.22	0.22
	Repl. 2	7.74	1.97	8.22	1.31	-5.83	0.20
	Repl. 3	7.61	1.94	8.22	1.31	-7.36	0.26
	^{36}Cl	$A(^{36}Cl)$, Bq	$U_{A(36Cl)}$, Bq	$A(^{36}Cl)$, Bq	$U_{A(36Cl)}$, Bq	Bias , %	E_n
	Repl. 1	9.40	1.56	9.44	0.94	-0.47	0.02
	Repl. 2	9.32	1.54	9.44	0.94	-1.30	0.07
	Repl. 3	9.35	1.55	9.44	0.94	-0.91	0.05

Comparison determined vs. reference activities, soil, 3 replicates, bias and E_n, k=2

- Overall good agreement, slight negative bias for iodide

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Pyrolyser method

- Allows for analysis of larger samples (several g)
- Thermal decomposition of the samples and desorption of Cl Species in Pyrolyser furnace at 900°C (ca. 2h)
- System flushed with humidified air; samples also humidified (1ml water)
- Decomposition products trapped in bubbler containing alkaline solution
  - 6 mM Na_2CO_3 used (yield > 80%)
  - Alternative: 1M NaOH (quantitative sorption)

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Pyrolyser method

- Bubbler connected directly with furnace via glass connector
  - Avoid losses due to condensation in tubing
- ^{36}Cl separated via Ag^{+} loaded Cl resin
  - Separation similar to standard method, but bubbler solution loaded directly onto column
  - When loading column directly from 6 mM Na_2CO_3 additional rinsing with 0.1M H_2SO_4 necessary for improved C-14 decontamination (« modified wash »)
- Similar method currently tested for iodide

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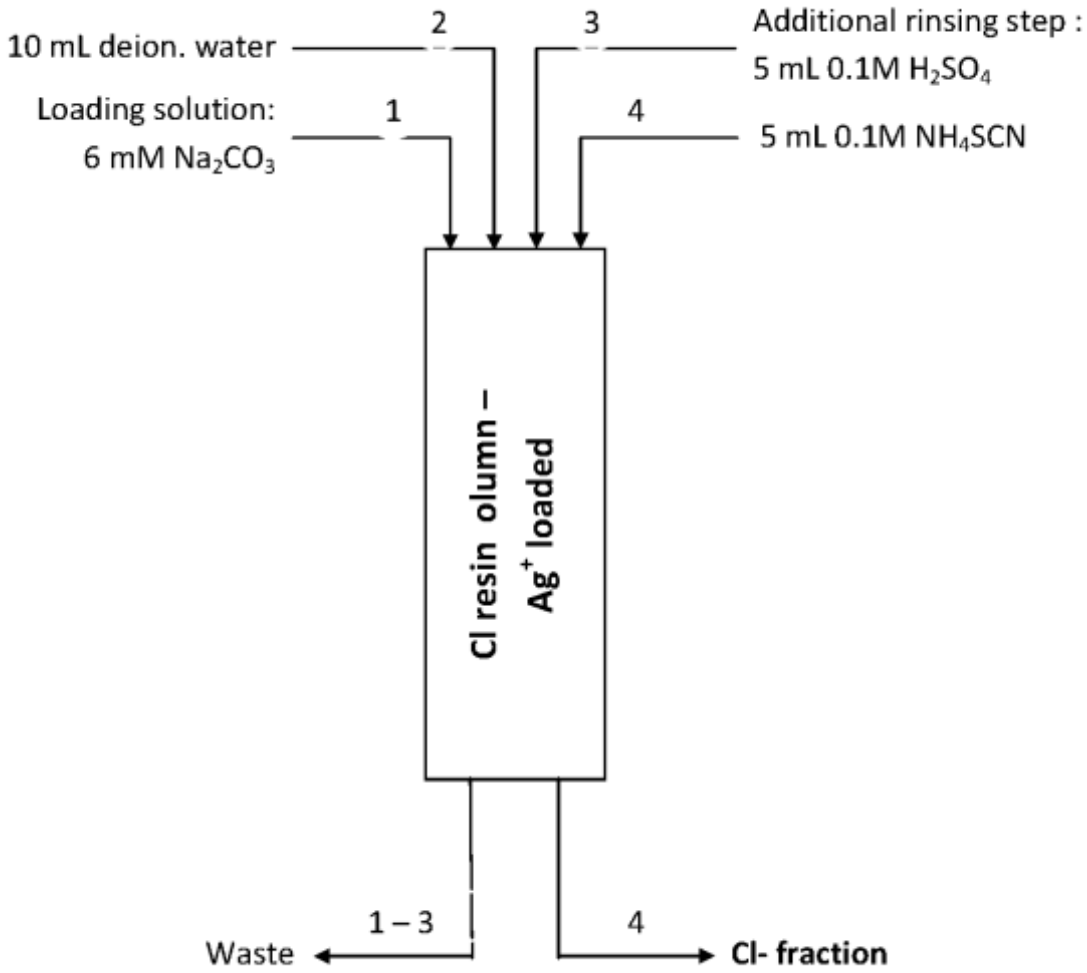
Pyrolyser method

(GAU, 6 mM Na_2CO_3 load)



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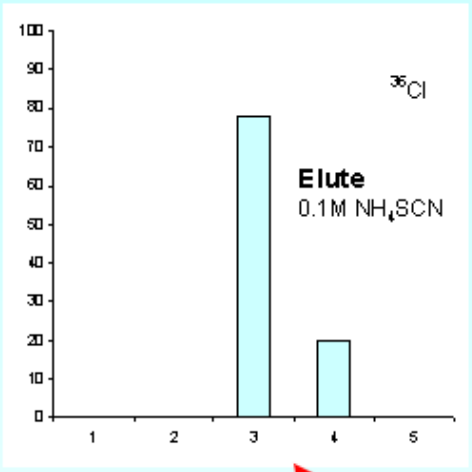
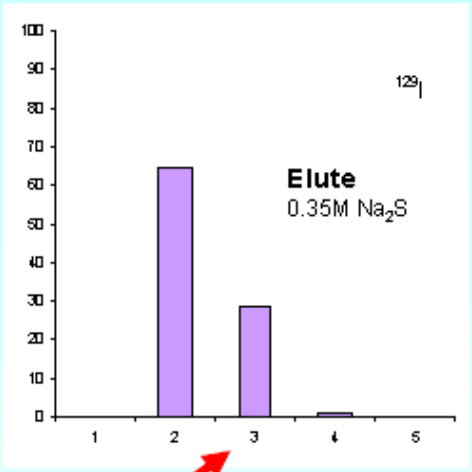
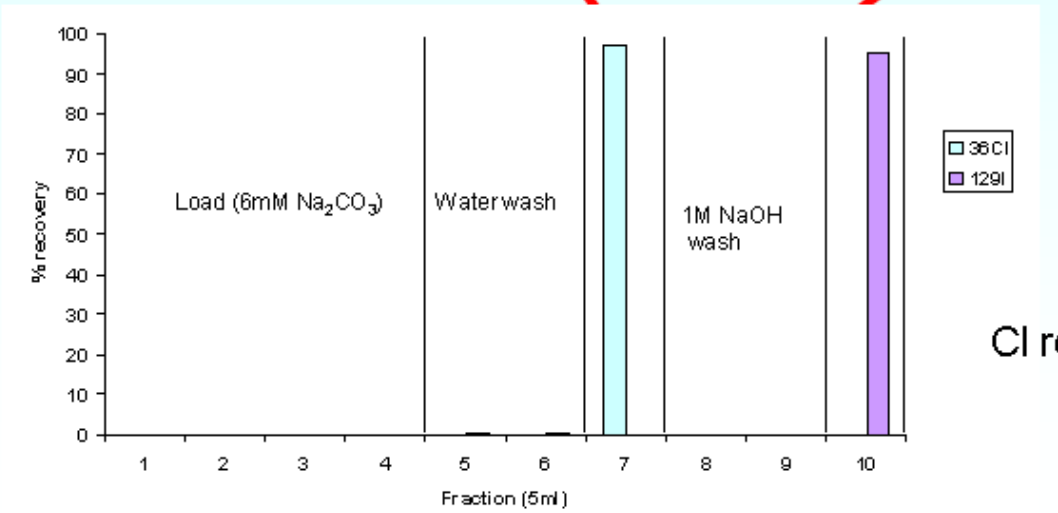
Pyrolyser method

(GAU, 6 mM Na_2CO_3 load)

Separation from 6 mM Na_2CO_3







Cl recovery 98%

Pyrolyser method

- Decontamination factors D_f:

	^{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	

- High D_f
- Clean Cl-36 / I-129 separation
- Cl-36 separation yield > 95%

- Analysis of spent resin

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

- Good agreement

All Data from P. Warwick, GAU Radioanalytical, Southampton (UK)

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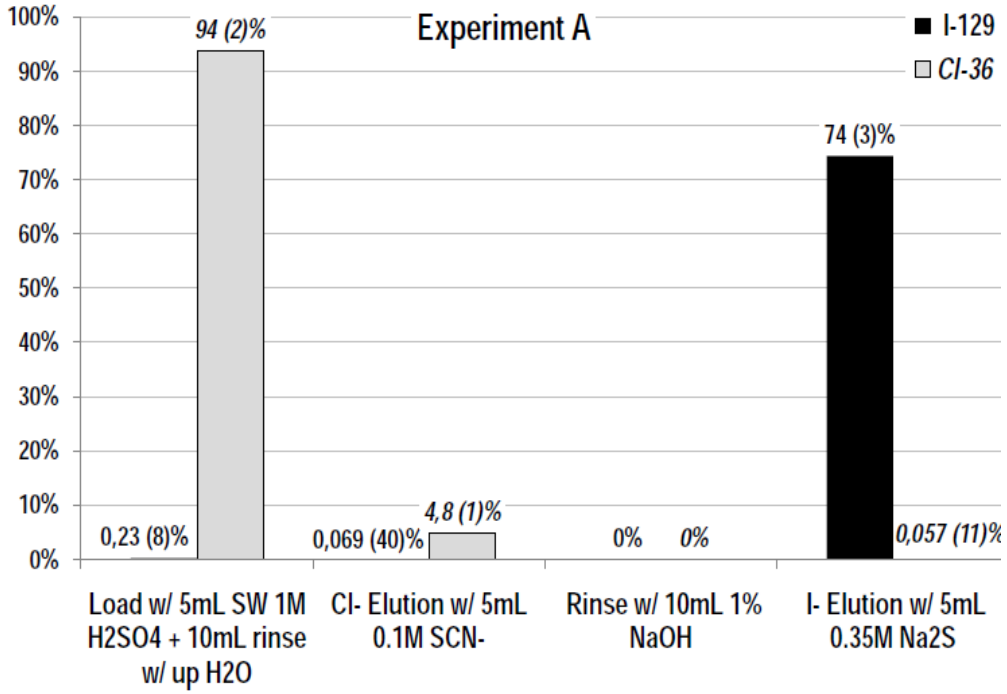
I-129 in sea water

- 10 ml sea water spiked with Cl-36, I-129 respectively
- Separation following standard method



Elution study spiked sea water

- No I-129 breakthrough during load and rinse
- Iodide elution needs to be optimized (yields ~75%)

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Removal of radio-iodide from radioactive process effluents

- Cooperation with IRE (Belgium)
- Mo-99 production by irradiation of U targets
- Process effluents contain elevated activities of radio-iodine
- Removal of radio-iodine before storage
- Process effluents acidic and oxidizing
  - Radio-iodine presentn several oxidation states and species

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Removal of radio-iodide from radioactive process effluents

- Iodine removal via alumina column plus « Mixed Bed » column
- « Mixed Bed » column
  - XAD-4 resin for I_2
  - Ag loaded CL Resin for iodide and remaining iodate
- Optimized Mixture: 4g XAD-4 / 3g CL resin (L grade)
- Flow rates up to 160 $mL.min^{-1}$
- Radio-iodine retention: 89% - 98%
- Retention of up to 2000 GBq per 7g column

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Summary

- CL-resin selective for PG metals (and Hg, Ag and Au)
  - Method robust against potential interferences
- Selectivity for chloride and iodide introduced by loading with Ag^+
- Methods for preconcentration, separation and determination of ^{36}Cl and ^{129}I developed
  - Applies to chloride and iodide
  - Reduction with Sn(II) if necessary
- Analysis of spiked real samples showed overall good agreement
  - aqueous samples, leached and thermally decomposed solid samples
- Determination of chemical yield preferable
- Use for iodine removal
- Potential use for iodine concentration
  - e.g. NucMed waste

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