Separation and Determination of Cl-36 and I-129 using CL Resin

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Steffen Happel[1], Alexander Zulauf[2], Bandombele Marcel Mokili[3], Aude Bombard[1]

1/ TrisKem International, Rennes, France
2/ *NUKEM Technologies GmbH , Alzenau, Germany*
3/ Laboratoire SUBATECH (CNRS/IN2P3 / Ecole des Mines de Nantes / Université de Nantes), Nantes, France

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
  - Cl-36 (3.01 E+05 y, $E_{\beta max}$= 708.6 keV),
  - I-129 (1.61 E+07 y, $E_{\beta max}$= 151.2 keV)
  - Frequently measured by LSC
  - 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

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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 (1/2)

- 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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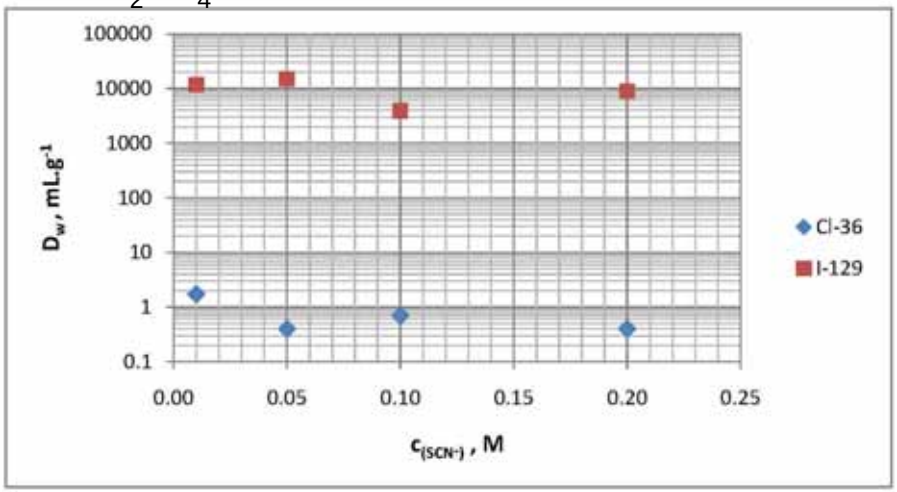
Resin characterization – Ag+ loaded CL Resin (2/2)

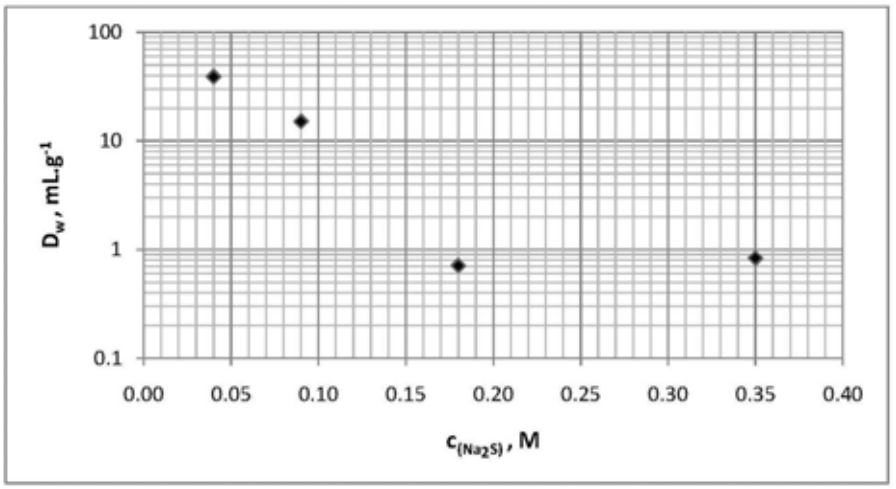
Isotope	D_w retention
Cl-36	1600
I-129	1980

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, but not chlorate



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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Chemistry used with CL Resin (1/3)

The CL Resin chemistry is based on the strength of Ag+ precipitation / complexation with anions within the solution and competition amongst these anions.

1/ Equilibrium at the sample loading step:

Sample solution at pH 0 to 7 (in H_2SO_4 or HNO_3) for the load

$$\mathbf{R\text{-}Ag^+ + Cl^- \rightarrow R\text{-}AgCl}\ \text{(precipitate)}$$

solubility product $Ks_{AgCl} = [Ag^+] \times [Cl^-] = 10^{-9,5}$

$$\mathbf{R\text{-}Ag^+ + I^- \rightarrow R\text{-}AgI}\ \text{(precipitate)}$$

solubility product $Ks_{AgI} = [Ag^+] \times [I^-] = 10^{-16,07}$

Reactions are moved towards the retention of Cl^- and I^-.

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Chemistry used with CL Resin (2/3)

2/ Equilibrium at the Cl^- elution step:

Use of SCN^- solution

$$Ks_{AgSCN} = [Ag^+] \times [SCN^-] = 10^{-11,7}$$

$$Ks_{AgCl} = [Ag^+] \times [Cl^-] = 10^{-9,5}$$

$$Ks_{AgI} = [Ag^+] \times [I^-] = 10^{-16,07}$$

$$\textbf{R-AgCl + } SCN^- \longrightarrow \textbf{R-AgSCN + } Cl^-$$

$$\textbf{R-AgCl + } SCN^- \longleftarrow \textbf{R-AgSCN + } I^-$$

$Ks_{AgSCN} = 10^{-11,7} < Ks_{AgCl} = 10^{-9,5} \Rightarrow$ AgSCN precipitate stronger than AgCl precipitate : Cl^- back in solution

$Ks_{AgI} = 10^{-16,07} < Ks_{AgSCN} = 10^{-11,7} \Rightarrow$ AgI precipitate stronger than AgSCN : **NO** elution of I^-

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Chemistry used with CL Resin (3/3)

3/ Equilibrium at the I^- elution step:

Use of S^{2-} solution

$$Ks_{Ag2S} = [Ag^+]^2 \times [S^{2-}] = 10^{-24,1}$$

$$Ks_{AgI} = [Ag^+] \times [I^-] = 10^{-16,07}$$

$$Ks_{Ag2S} < Ks_{AgI}$$

$$\mathbf{2\ R\text{-}AgI + S^{2-} \longrightarrow (R\text{-}Ag)_2S + 2\ I^-}$$

No Cl^- involved as all as been eluted with SCN^- solution.

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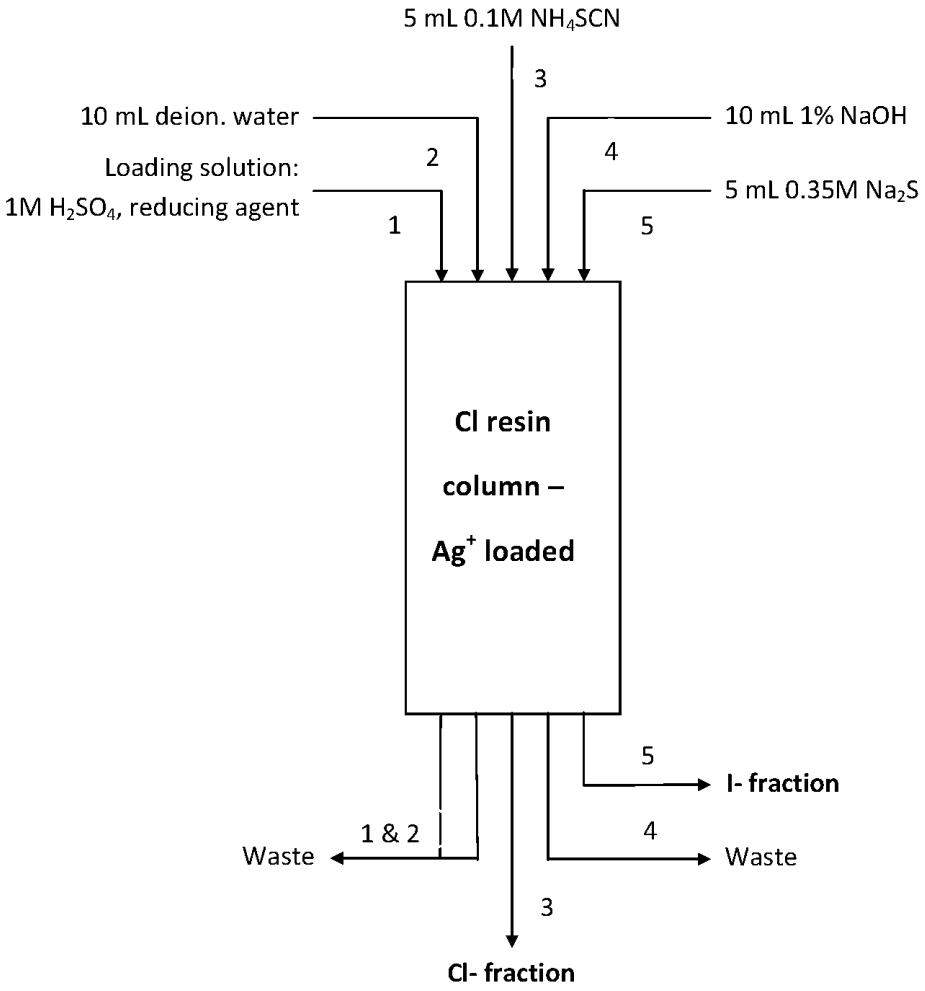
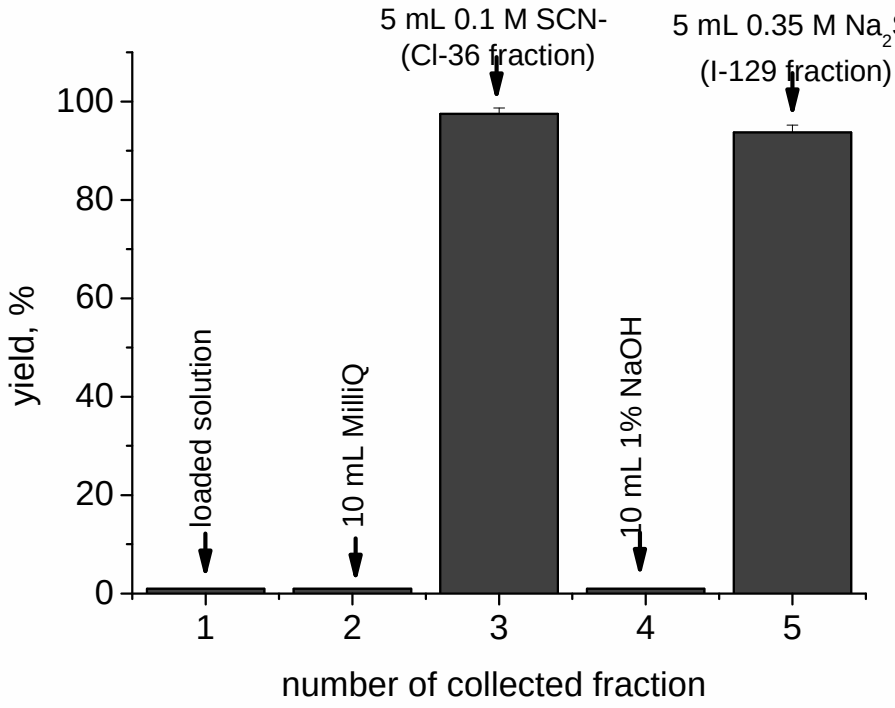
Scheme – Optimized method



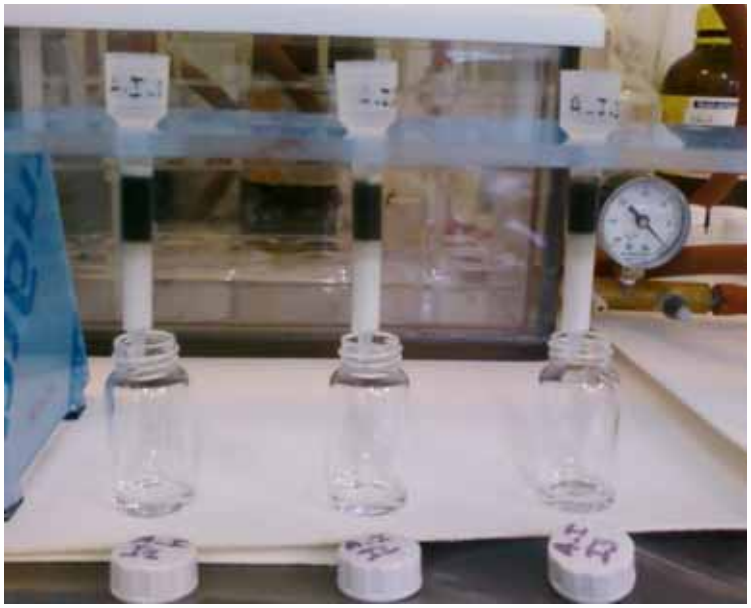
- Load sample in 1M H_2SO_4
  - ➢ Less acidic, neutral or slightly alkaline also possible
  - ➢ Addition of reducing agent if necessary (e.g. Sn(II))
- Rinse with 10ml of deion. water
- Elute chloride with 5ml of 0.1M SCN^-
- Rinse with 10ml of 1% NaOH
  - ➢ Increases iodide yield
- Elute iodide with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

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 (Df)

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 (1/2)

- 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
- 3 x 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 (2/2)

	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

Spiked samples II – effluents (Subatech) (1/3)

- **4 spiked effluent samples**
  - Cl 0: Blank sample
  - Cl 1 and Cl 2: 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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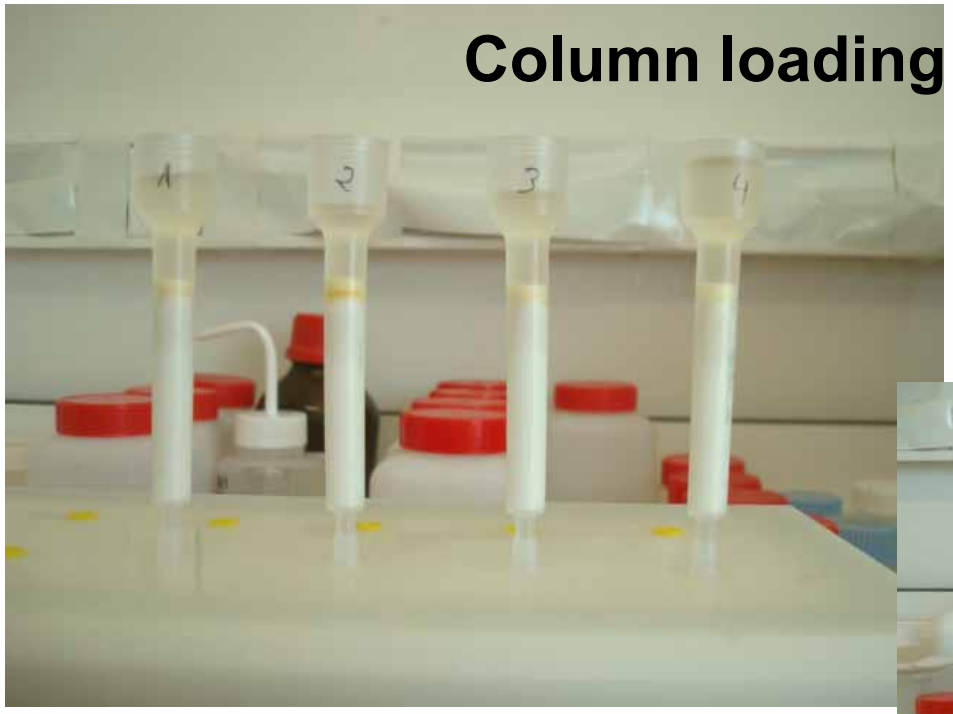
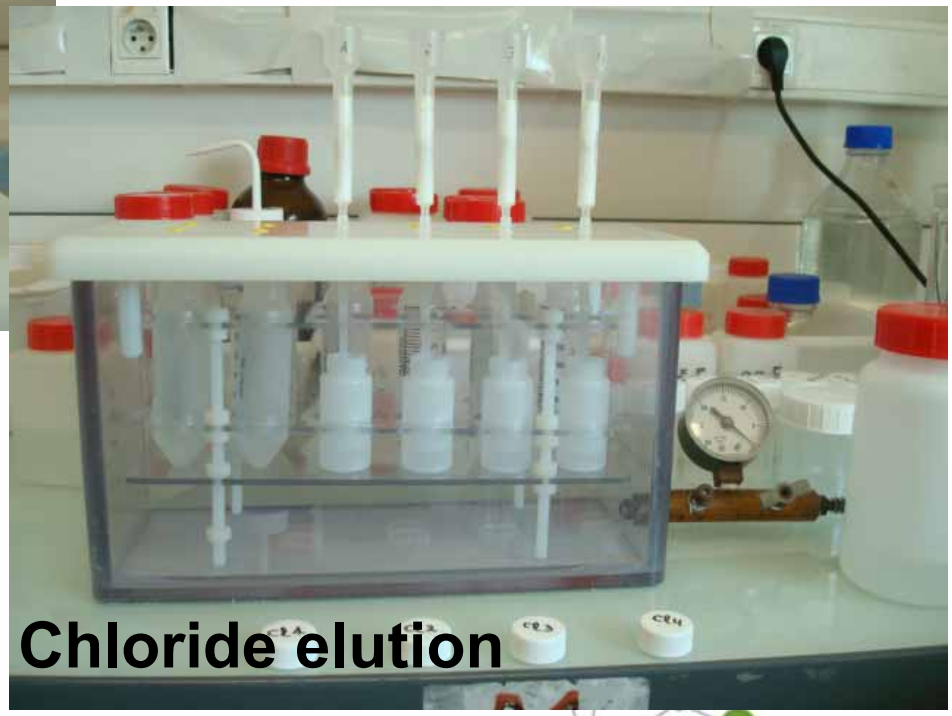
Spiked samples II – effluents (Subatech) (2/3)





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Spiked samples II – effluents (Subatech) (2/3)

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	1.87E+04	6.56E+02	0	-	239.8	1774.8	1.81E+04	1.19E+03	-3.44	0.47
Cl2	1.87E+04	6.56E+02	0	-	243.9	1871.4	1.91E+04	1.26E+03	1.72	0.23
Cl3	1.87E+04	6.56E+02	1.89E+04	5.10E+02	252.0	1865.3	1.81E+04	1.19E+03	-3.57	0.49
Cl4	1.87E+03	6.56E+01	1.90E+04	5.12E+02	254.2	189.85	1.79E+03	1.23E+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 Cl 1/Cl 2: 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 3 x 10 mL aliquots
- Average extraction and separation yields used for result calculation
    - Determined upfront for given extraction conditions and matrix

Spiked samples III – filter

	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	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
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	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

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Spiked samples IV - soil

	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	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
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	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		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	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
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	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 (1/5)

P E Warwick, A Zulauf, S Happel, I W Croudace: Determination of 36Cl in decommissioning samples using a Pyrolyser furnace and extraction chromatographic separations. Presented at the 11th ERA Symposium, September 2010, Chester (UK)

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

- 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)

http://www.triskem-international.com/iso_album/11_era_chester_warwick_determination_of_36cl_in_decommissioning_samples_using_a_pyrolyser.pdf

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Pyrolyser method (2/5)

- 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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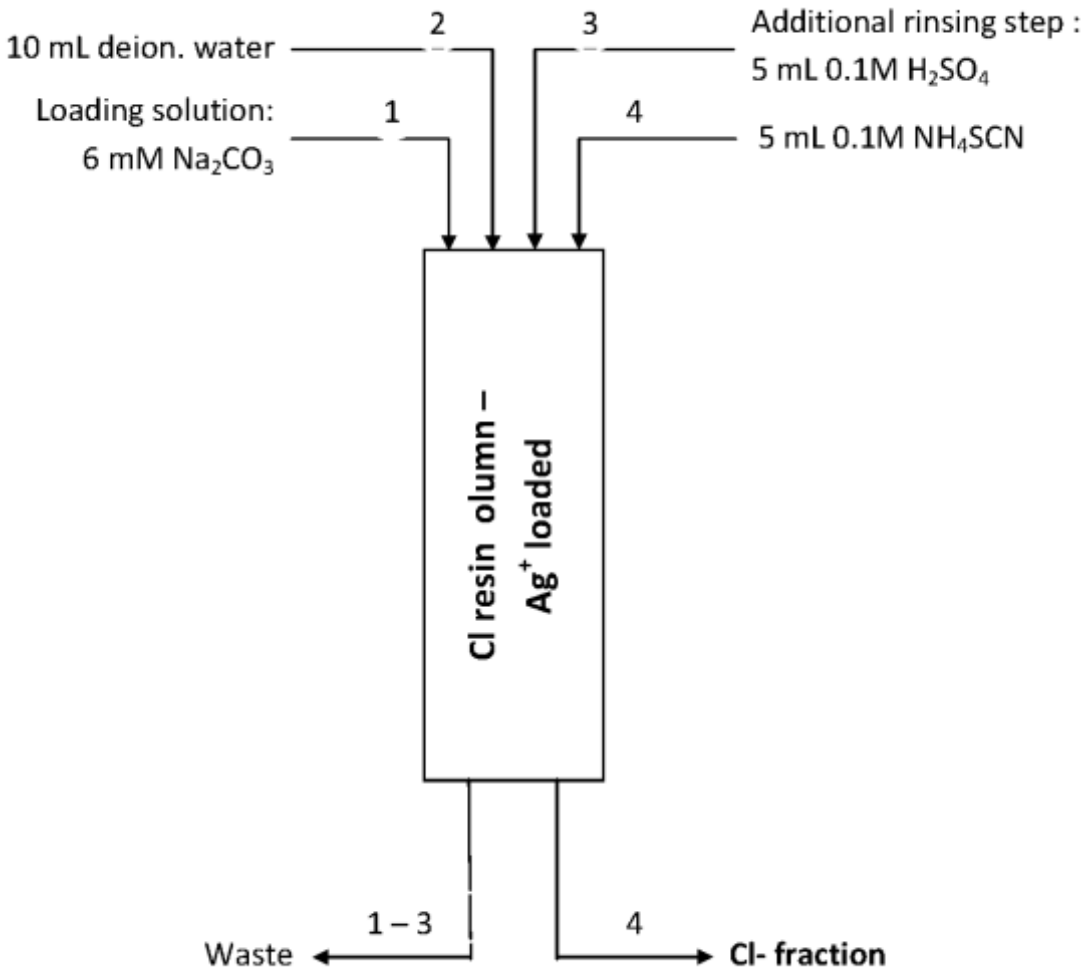
Pyrolyser method (3/5)

GAU: 6 mM Na_2CO_3 load



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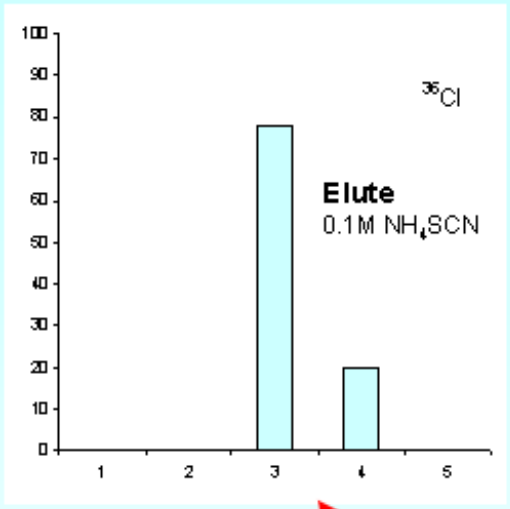
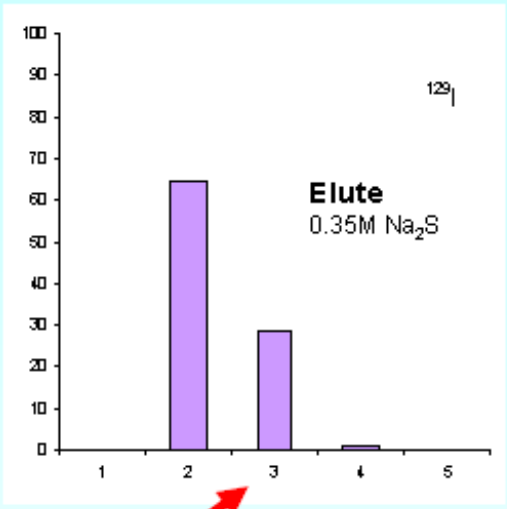
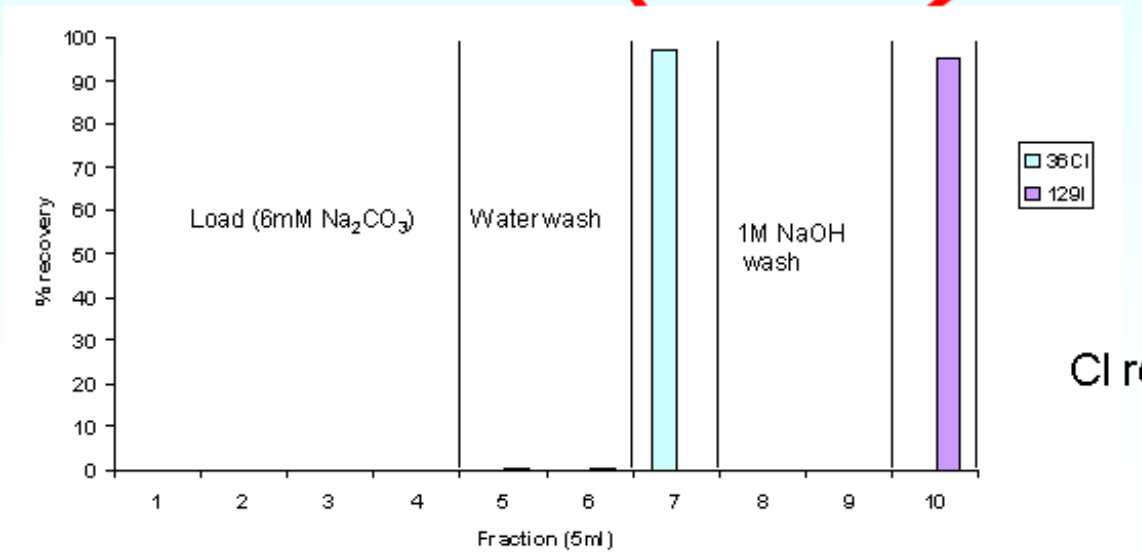
Pyrolyser method (4/5)

Separation from 6 mM Na_2CO_3







Cl recovery 98%

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Pyrolyser method (5/5)

- 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

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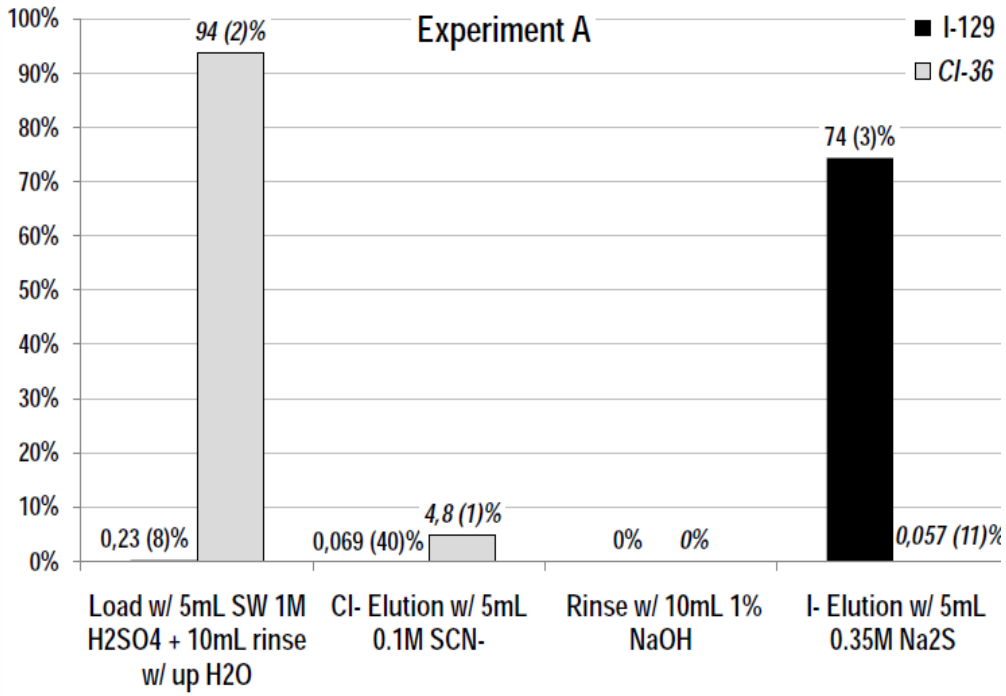
I-129 in sea water

- 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* (1/2)

**Decamp, C., Happel, S.. J Radioanal Nucl Chem, DOI10.1007/s10967-013-2503-1*

- Cooperation with IRE (Intitute for RadioElements, 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 present in several oxidation states and species

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Removal of radio-iodide from radioactive process effluents (2/2)

- 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 (1/2)

- 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 (especially regarding Cl species)

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Summary (2/2)

- 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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Thank you for your attention!

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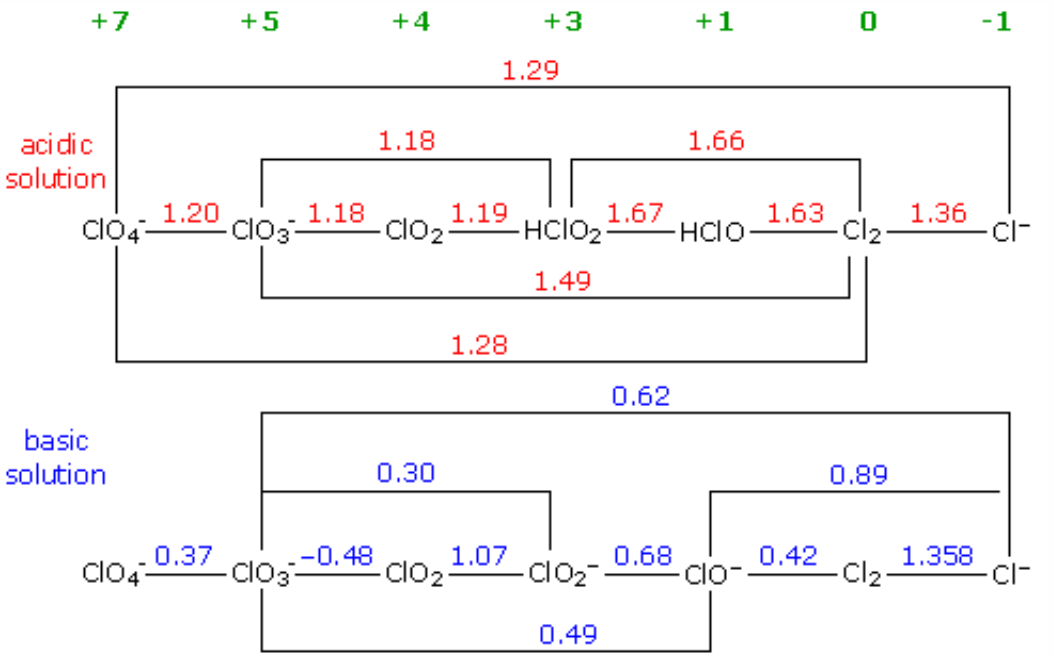
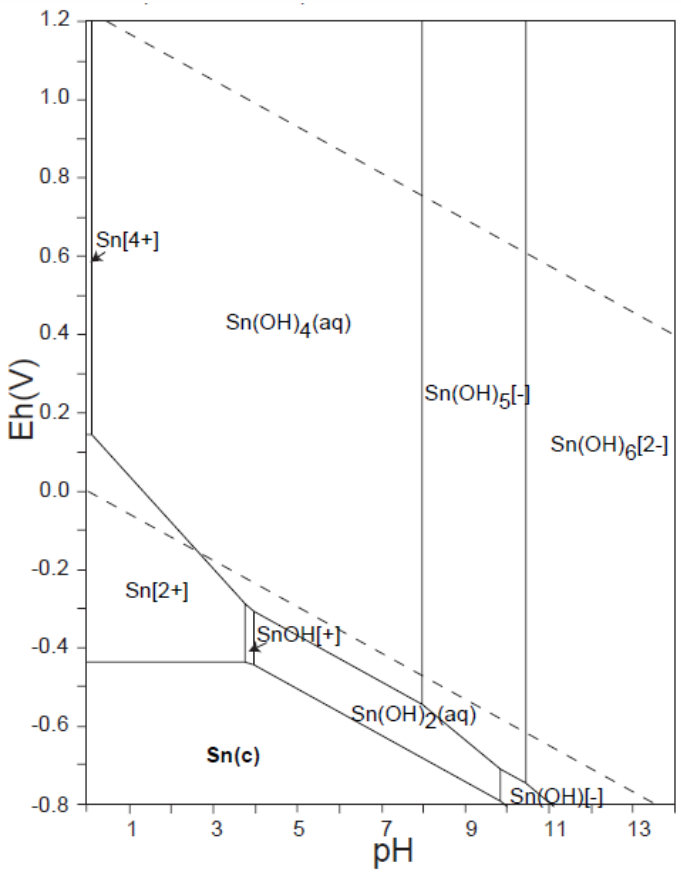
Use of a reducing agent to control Cl species





Sn^{4+}/Sn^{2+} = 0,14 V (E_H) in 1M H_2SO_4