Characterisation of an extraction chromatographic resin for the separation and determination of Cl-36 and I-129

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(Part of PhD thesis A. Zulauf, Uni Marburg)

- Scope
- Batch experiments
  - Characterization of the Cl-resin
  - Preparation and characterization of a silver loaded resin
- Column experiments
  - Method development and optimization
  - Decontamination factors
- Precision of the method
- Spiked samples
- Summary and outlook

Scope

- Monitoring of nuclear facilities for long-lived radionuclides
  - operation
  - decommissioning
- Cl-36 and I-129 frequently determined by LSC
  - Requiring thorough and selective sample preparation for accurate results
- Existing methods often complicated and time-consuming
- Aim: development of a simple and quick method for preconcentration and separation of Cl-36 and I-129 from environmental and decommissioning samples for LSC
- Cl and I retained as chloride and iodide
  - Oxidation state adjustment might be necessary (e.g. Sn(II))

General procedures

General procedure batch experiments

Weight distribution ratios D_w and capacities

- Weigh approx. 50mg of the resin in an 2ml Eppendorf tube
- Add 300µl of the acid (e.g. 1M H_2SO_4)
- Close cap and shake for 30 minutes
- Add 1ml of the standard solution (e.g. 50Bq Cl-36 in 1M H_2SO_4)
- Close cap and shake for another 30 minutes
- Centrifuge for 15 minutes at 4000rpm
- Withdraw 0.5ml of the supernatant, analyze (LSC or ICP-MS)

All distribution factors and maximum uptake were determined in triplicate

Equations

Weight distribution ratio

$$D_W = \frac{(N_{A0} - N_A)}{N_A} \times \frac{V}{m_R}$$

N_{A0} = net count rate of standard solution
N_A = net count rate of sample
V = Volume in ml
m_R = mass of the resin in g

Maximum uptake under given conditions

$$K = \frac{(V_{A0} * c_{Ag,A0} - V_A * c_{Ag,A})}{m_R}$$

$C_{Ag,A0}$ = silver concentration in standard solution
$C_{Ag,A}$ = silver concentration in sample
m_R = mass of the resin in g
V_{A0}, V_A = sample volumina

Batch experiments

Characterisation of the Cl-resin – D_w values

Analyte	D_w
Ag	650000
Mn	<1
Fe	<1
Ni	<1
Co	<1
Cu	<1
Zn	25
Cd	<1
Ce	4
Pd	87000

Table1: D_w values of various elements in 1M H_2SO_4 on Cl resin

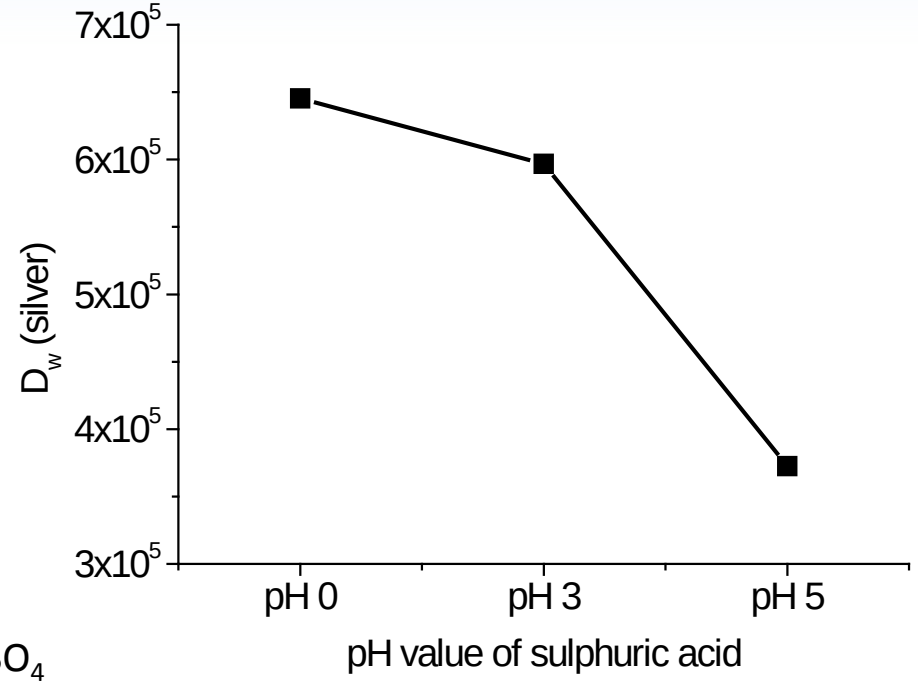


Figure1: D_w (Ag) vs. pH (H_2SO_4)

- Selective for Pd and Ag
- D_w(Ag) slightly decreases with increasing pH
  - ➢ remains >3E+5 at pH 5

Batch experiments

Characterisation of the Cl-resin – maximum silver uptake

- Maximum uptake depending on Ag^+ excess
- Column experiments: 16.5 – 19.8 mg Ag^+/g resin
- Silver uptake on column time depending
  - Equilibrium reached between 0.5 and 2.5 hours

Batch experiments

Preparation of the silver loaded resin

- 10 g Cl-resin weighed in a 250 mL PE flask
- 650 mg $AgNO_3$ dissolved in 100 mL 1M H_2SO_4
- $AgNO_3$- solution added to Cl-resin, flask capped and shaken for 2 hours at a medium speed
- Resin filtered and rinsed twice with 1M H_2SO_4
- Dried

Preparation of the silver loaded resin - capacities

- Determined via column experiments
- Results in mg per 2ml column

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

Table 2: Chloride and iodide capacities of silver loaded Cl-resin

➢ Good agreement between theoretical and experimental values

Batch experiments

Characterisation of the silver loaded resin – weight distribution ratios

Experimental conditions for retention and elution

Cl-36 und I-129 retention

- 1M H_2SO_4

Cl-36 Elution

- 0.01-0.2M KSCN

I-129 Elution

- 0.04 – 0.35M Na_2S

Batch experiments

Characterisation of the silver loaded resin - results

Isotope	D_w retention
Cl-36	1600
I-129	1980

Table 3: retention of ^{36}Cl and ^{129}I in 1M H_2SO_4

- Quantitative uptake of both isotopes by silver loaded Cl-resin in 1M H_2SO_4

	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

Table 4: D_w values for different KSCN concentrations

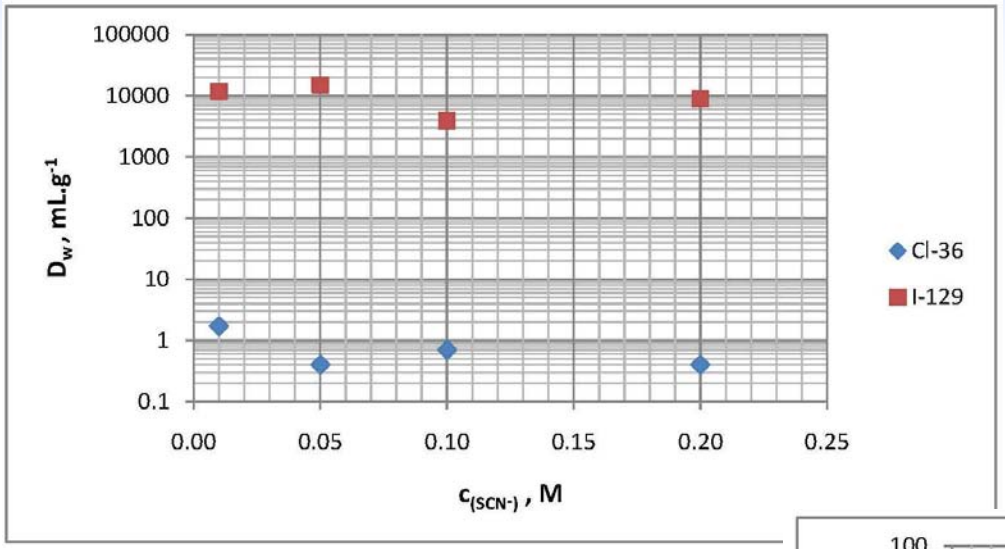
- ^{36}Cl eluted quantitatively eluted at all KSCN concentrations
- ^{129}I remains on the resin at any KSCN concentration

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

Table 5: D_w values for different Na_2S concentrations

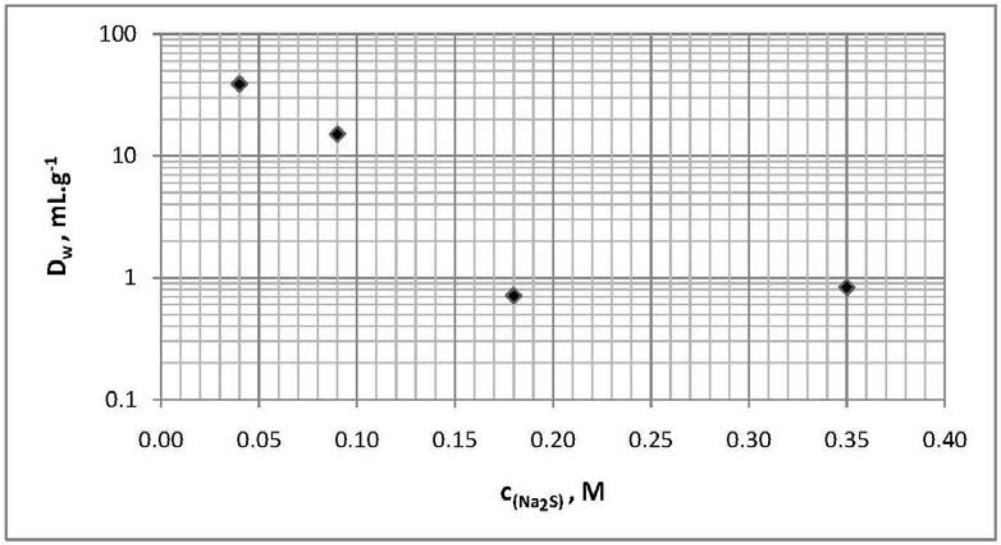
- ^{129}I eluted at elevated Na_2S concentrations

Batch experiments



D_w of Cl^- and I^- on Ag^+ loaded Cl resin at pH 7 and varying SCN^- concentrations

D_w of I^- on Ag^+ loaded Cl resin at pH 7 and varying Na_2S concentrations



Column experiments

- Accurately weigh approx. 0.65g of Cl-resin, add 10ml 1M H_2SO_4 and shake for 2h
- pack column, add 2ml of sulfuric $AgNO_3$ solution (corresponding to 13mg Ag^+)
- let resin rest for at least 2.5 hours

- load with 10ml 1M H_2SO_4 containig 50Bq ^{36}Cl
- load with 10ml 1M H_2SO_4 containig 50Bq ^{129}I

- elute several times with 5ml of 0.1M KSCN

- add 10ml ProSafe HC and count → ^{36}Cl fractions
- rinse with 10ml MilliQ
- elute with 5ml 0.35M Na_2S

- add 10ml ProSafe HC and count → ^{129}I fractions

Column experiments

Developement and optimization of the method

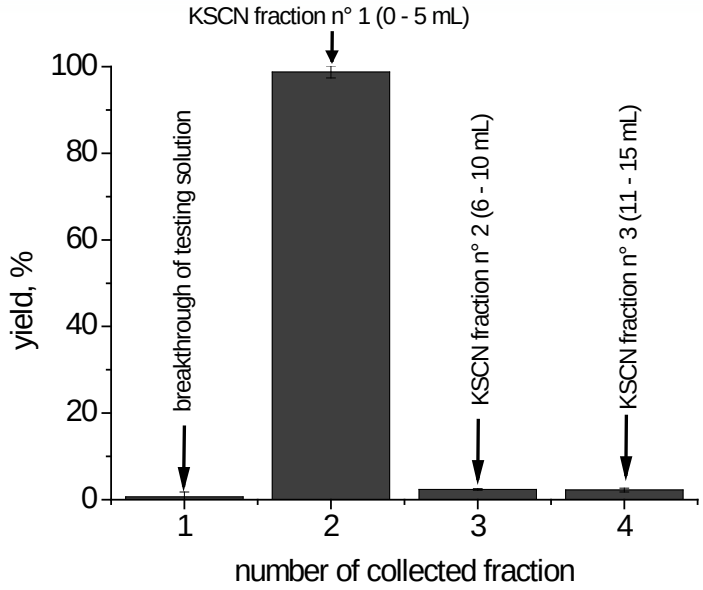


Figure 3: ^{36}Cl-elution with 0.1M KSCN (fractions 2-4)

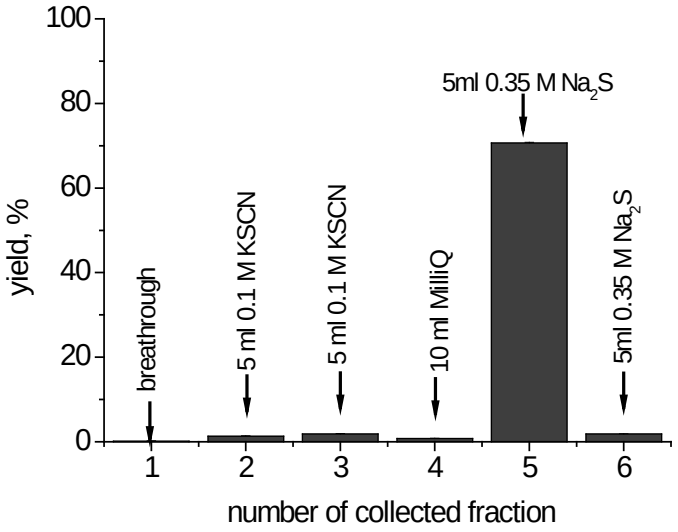


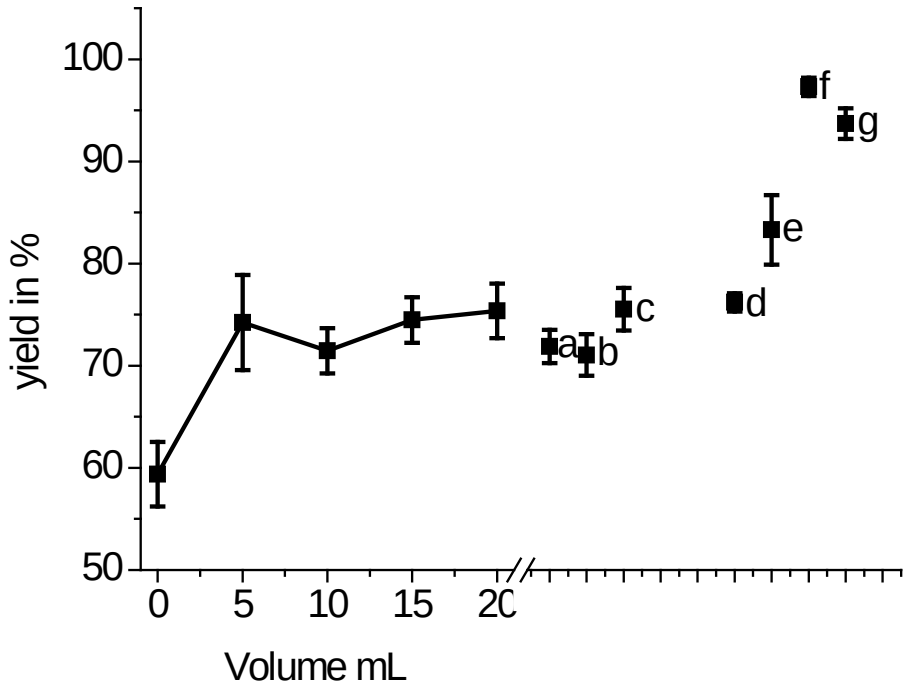
Figure 4: ^{129}I-elution

- ^{36}Cl eluted with 5ml of 0.1M KSCN
- As expected from batch experiments ^{129}I not effected by KSCN
- ^{129}I eluted with 5ml 0.35M Na_2S, elution not quantitative

Column experiments

Developement and optimization of the method

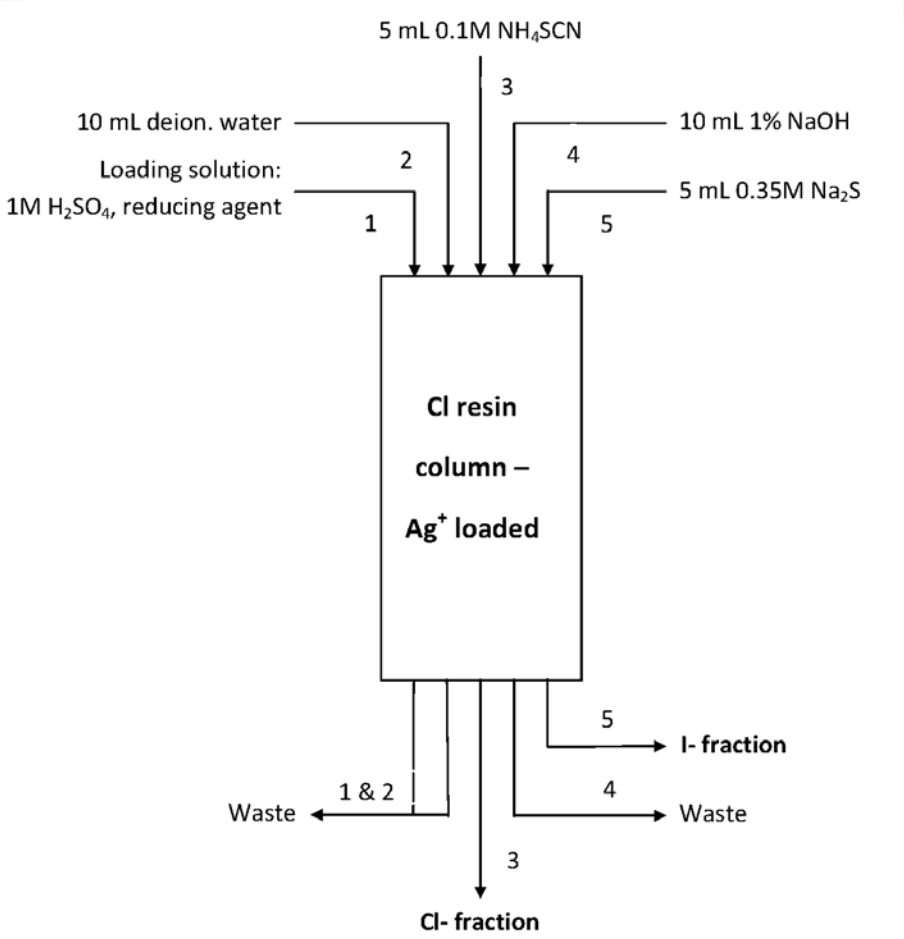
Optimization of ^{129}I recovery



- Best results achieved with NH_3 and NaOH:
  - NH_3 : 97.3±0.9%
  - NaOH: 93.7±1.4%
- NaOH preferred
  - Ag bleeding with NH_3
  - Interference in LSC

Figure 5: Influence of the rinsing step upfront to the I-129 elution with Na_2S:
Rinsing with various volumes of dest. water; 10ml 0.01M $NaHSO_3$ (a), 10ml 0.1M $NaHSO_3$ (b), 10ml 1M $NaHSO_3$ (c), 10ml 1M $NaNO_2$ (d) 10ml 30% H_2O_2 (e), 10ml 1%NH_3 (f) and 10ml 1% NaOH (g)

Column experiments



Scheme – Optimized method

- Load sample (1M H_2SO_4)
  - ➢ Addition of reducing agent if necessary
- Rinse with 10ml of MilliQ
- Elute ^{36}Cl with 5ml of 0.1M SCN^-
- Wash with 10ml of 1% NaOH
- Elute ^{129}I with 5ml of 0.35M Na_2S

Column experiments

Developement and optimization of the method

Cl / I separation optimized method

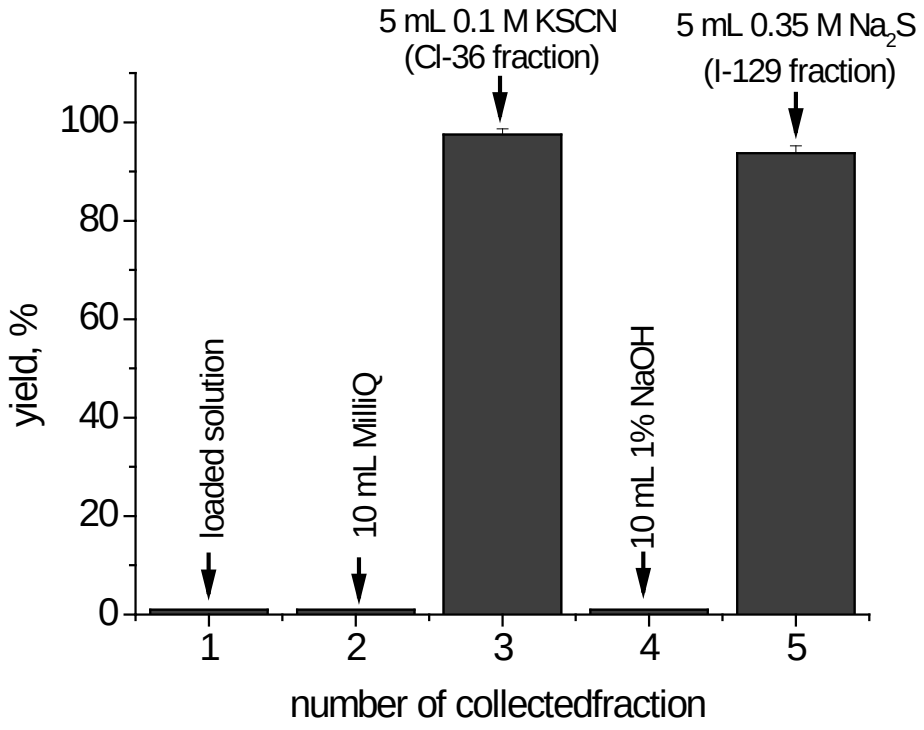


Figure 6: Combined Cl/I elution study with optimized method

Column experiments

Decontamination factors

- Good deconfactors in SCN^- and Na_2S fractions
- Clean I / CL separation

Analyte	Df in Cl fraction	Df in I fraction
Cr	>29	>430
Mn	>210	>370
Co	>170	>1500
Ni	>170	>320
Cu	>210	>190
Zn	>32	>11
Rb	>16	>2300
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

Validation

Results on Precision

- 300ml of water spiked with Cl-36 and I-129
- Sample was divided into 30 parts
- Volume of each part was 10ml
- Activity of each isotope was 5Bq per 10ml
- Samples were analyzed on three days, 10 samples per day

Analyte	$\overline{X_{ges}}$ %	σ_w	rel. σ_w %	σ_b	rel. σ_b %	σ_t	rel. σ_t %
Cl-36	96.98	2.39	2.5	0.20	0.2	2.40	2.5
I-129	91.66	5.20	5.7	7.62	8.3	9.22	10.1

Table 6: results on precision

n for $\overline{X_{ges}}$ = 30

n for σ_w and σ_b = 3

- Also determined: inter-person repeatability (N = 3): Cl^-: 5.1%, I^-: 5.7%

Validation

Spiked samples I - water

- 50ml tap water adjusted to 1M H_2SO_4
- Spiked with known activities of Cl-36 and I-129
- Addition of 17Bq of each Co-60, Sr-90 and Cs-137
- Three 10ml aliquots analyzed following optimized method
- LSC measurement of Cl- and I-fractions

Validation

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

Table 7: Comparison determined vs. reference activities, water, 3 replicates, bias and E_n, k=2

- Overall good agreement, slight negative bias for Cl-

Validation

Spiked samples II – soil, concrete, filter

- Soil, concrete and filter samples (250 mg each)
- Spiked with known activities of Cl-36 and I-129
- 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

Validation

Spiked samples II - 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

Table 8: Comparison determined vs. reference activities, soil, 3 replicates, bias and E_n, k=2

- Overall good agreement, negative bias for I-

Validation

Real sample II - concrete

		determined activities		reference activities			
	^{129}I	$A(^{129}I)$, Bq	$U_{A(129I)}$, Bq	$A(^{129}I)$, Bq	$U_{A(129I)}$, Bq	Bias, %	E_n
concrete	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

Table 9: Comparison determined vs. reference activities, concrete, 3 replicates, bias and E_n, k=2

- Overall good agreement, negative bias for I-

Validation

Real sample II - 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

Table 10: Comparison determined vs. reference activities, filter, 3 replicates, bias and E_n, k=2

- Overall good agreement, slight negative bias for I-

Validation

Real samples III – Effluents (Subatech)

- 4 spiked effluent samples
  - Cl 0: Blank samples
  - 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, 12 – 125 keV, 60 min)

Validation

Real samples III – Effluents

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

Table 11: Comparison determined vs. reference activities, effluents, bias and zeta,

- Very good agreement
- Repeatability Cl1/Cl2: 3.7% (N = 2, k = 1)
- Clean Cl/I separation

On-going work

- Combined use of Raddec Pyrolyser and resin
  - Co-operation with Raddec (UK) → presentation P. Warwick at 11th ERA
- Analysis of real samples and comparison with other methods
  - Co-operation with Subatec (France)
- ‘Beta testing‘ by different labs
  - If you are interested in participating please contact me!

Summary and outlook

- A method for the preconcentration, separation and determination of ^{36}Cl and ^{129}I is presented
  - Applies to chlorid and iodid
  - Reduction with Sn(II) if necessary
- Cl-resin selective for PG metals (Hg, Ag and Au)
  - Method robust against potential interferences
- Analysis of simulated real samples showed overall good agreement
- Use of internal standard preferable