

CL Resin

Main Applications

- Separation of chloride and iodide

Packing

Order N°.	Form	Particle size
CL-B25-A, CL-B50-A, CL-B100-A, CL-B200-A	25g, 50g, 100g and 200g bottles CL Resin	100-150 µm
CL-C20-A, CL-C50-A	Boxes of 20, 50 and 200 CL Resin columns	100-150 µm
CL-B25-S, CL-B50-S, CL-B100-S, CL-B200-S	25g, 50g, 100g and 200g bottles CL Resin	50-100 µm
CL-B25-L, CL-B50-L, CL-B100-L, CL-B200-L	25g, 50g, 100g and 200g bottles CL Resin	150-300 µm

Physical and chemical properties

Density : 0,37 g/ml

Capacity : 6,5 mg Cl⁻/g CL Resin (loaded with 20 mg Ag⁺)
25 mg I⁻/g CL Resin (loaded with 20 mg Ag⁺)

Conditions of utilization

Recommended T of utilization : /

Flow rate : A grade: 0.6 – 0.8 mL/min

Storage : Dry and dark, T<30°C

For additional information see enclosed literature study

Methods

Reference	Description	Matrix	Analytes	Support
TKI-CL01	Cl-36 / I-129 separation	Environmental and decommissioning samples	Cl-36, I-129	Bulk, columns

CL RESIN

The CL Resin is used for the separation of chloride and iodide and is based on an extraction system that is selective for platinum group metals, gold and silver. The selectivity for halides is introduced by loading the resin with silver.

Table 1 shows D_W values of selected cations on the CL Resin, for practical reasons sulphuric acid was chosen as extraction medium. It can be seen that the CL Resin has high selectivity for Pd and Ag, whereas the D_W values of the other elements tested are low. Ag further shows high D_W values over a wide pH range (from 1M H_2SO_4 to dilute sulphuric acid (pH 5)). It will thus be extracted or remain fixed over a wide range of pH values.

Table 1: D_W values CL Resin of selected cations in sulphuric acid (data taken from (1)).

Analyte	Extraction condition	$D_W, mL.g^{-1}$
Ag	1M H_2SO_4	650000
Ag	Sulfuric acid, pH 3	600000
Ag	Sulfuric acid, pH 5	350000
Cd	1M H_2SO_4	<1
Ce	1M H_2SO_4	4
Co	1M H_2SO_4	<1
Cu	1M H_2SO_4	<1
Fe	1M H_2SO_4	<1
Mn	1M H_2SO_4	<1
Ni	1M H_2SO_4	<1
Pd	1M H_2SO_4	87000
Zn	1M H_2SO_4	25

The loading of the resin with silver cations allows good selectivity for anions, especially halides, forming sparingly or insoluble Ag complexes. D_W values for chloride and iodide on the silver loaded CL Resin in 1M H_2SO_4 were determined to be 1600 and 1980 respectively. Both are thus well retained under those conditions. The CL Resin used for the D_W experiments was loaded with 20 mg Ag^+ per g of CL Resin prior to the extraction experiments

which corresponds to a typical working capacity. The capacities for chloride and iodide of the silver loaded resin under these conditions are: 16.3 +/- 1.6 mg iodide per 2 mL column (approx. 25 mg iodide per g resin) and 4.3 +/- 0.2 mg chloride per 2 mL column (approx. 6.5 mg chloride per g resin). Higher capacities for halides can be obtained by increasing the silver load of the CL Resin.

In order to evaluate best suited conditions for the separation of chloride and iodide D_W values of chloride and iodide were determined on silver loaded CL Resin in varying SCN^- and S^{2-} concentrations: Fig. 1 and 2 show the obtained results.

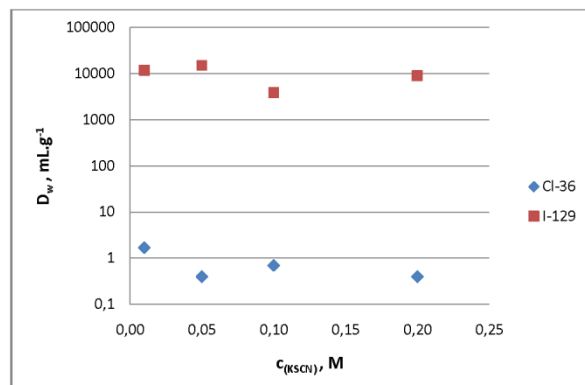


Figure 1: D_W of Cl and I on Ag^+ loaded CL Resin at pH 7 and varying SCN^- concentrations (1).

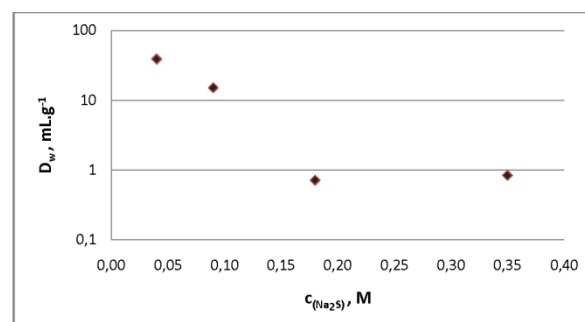


Figure 2: D_W of I on Ag^+ loaded CL Resin at pH 7 and varying Na_2S concentrations (1).

Chloride can be easily eluted from the resin using SCN^- solutions whereas iodide remains fixed. Iodide can then be eluted from the resin using a high concentration solution of S^{2-} . Based on this information, a method for the separation of chloride and iodide was developed and optimized by Zulauf et al. [1]; fig. 3 schematically shows this method. In order to assure that both chlorine and iodine are present as chloride and iodide, the sample might be loaded from a sulphuric acid solution containing 0.1M $SnSO_4$ as reducing agent. This is especially important in case of chlorine since e.g. chlorate is not fixed on the

resin, whereas iodate is extracted, as could be expected from silver salt solubility data.

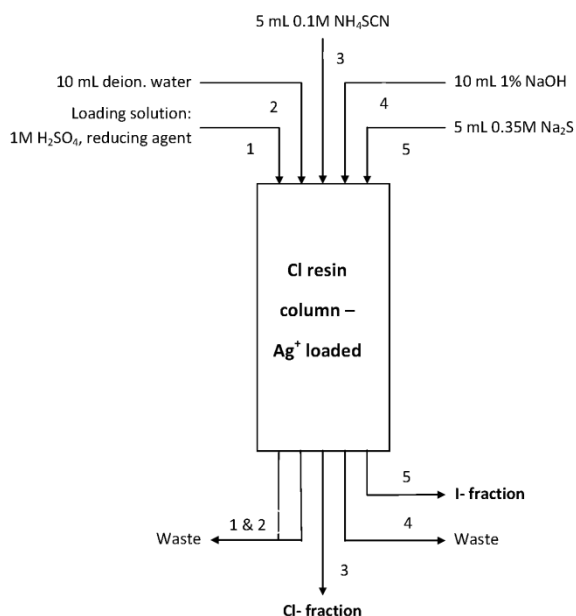


Figure 3: Scheme of optimized Cl⁻ / I⁻ separation method (1).

The sample is preferably loaded onto the silver loaded CL Resin from 1M H₂SO₄ (slightly acidic or even neutral conditions are also acceptable). During a first rinse (deionised water) matrix elements and potential interferents are removed from the column. Chloride is then eluted in a small volume of NH₄SCN or NaSCN.

During method optimization it was shown that rinsing the column with a dilute alkaline solution before iodide elution lead to a strong increase of the iodide yield. Therefore, the CL Resin column is accordingly rinsed with 1% NaOH before iodide is finally eluted in a small volume of a Na₂S solution (Remark: all work with the Na₂S solutions should be performed under a fume hood, including the addition of the liquid scintillation cocktail.).

The small elution volumes used for elution allow for direct measurement of the obtained fractions by LSC (Remark: some LSC cocktails reduce traces of Ag⁺ co-eluted from the column resulting in 'blackened' LSC samples; it is thus advisable to test your cocktail before use. ProSafe HC was found to be a suitable cocktail).

Fig. 4 shows the result of an elution study performed using a solution containing Cl-36 and I-129 as chloride and iodide respectively. Both Cl-36 and I-129 are quantitatively recovered in a small volume of the respective eluting agent, the separation of both is very clean.

LITERATURE STUDY

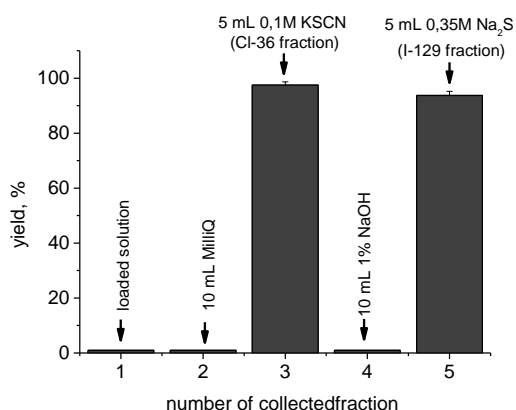


Figure 4: Elution profile of combined ³⁶Cl and ¹²⁹I with optimized method, 2 mL CL Resin column (Ag⁺ loaded).

In order to obtain additional information on the purity of the chloride and iodide fractions decontamination factors (D_f) were determined by applying the optimized method to several multi-element solutions and solutions of radioactive standards, table 2 summarizes the results.

Table 2: Decontamination factors D_f of various elements in chloride and iodide fractions.

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

Overall the method shows very good selectivity for chloride and iodide.

Mean chemical yields of the separation were found to be 97.0 % ± 2.5% (k=1, N=30) for chloride and 91.7% % ± 10.1% (k=1, N=30) for iodide [1]. These yields were then applied to the analysis of spiked tap water samples (defined Cl-36 and I-129 activities plus approx. 17 Bq each of Co-60, Sr-90 and Cs-137). Table 3 compares obtained and spiked activities, both agree very

well. Even though results obtained applying fixed separation yields were found to be very satisfying it is advisable to perform a yield determination (e.g. *via* ion chromatography) if possible.

Table 3: Comparison determined vs. added activities, spiked tap water samples, 3 replicates, bias and E_n , $k=2$.

I-129	determined activities		added activities		Bias /%	E_n
	A(I-129) / Bq	$U_{A(I-129)}$ / Bq	A(I-129) / Bq	$U_{A(I-129)}$ / Bq		
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	determined activities		added activities		Bias /%	E_n
	A(Cl-36) / Bq	$U_{A(Cl-36)}$ / Bq	A(Cl-36) / Bq	$U_{A(Cl-36)}$ / Bq		
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

A similar experiment was performed at the SUBATECH laboratory in France [2]. Four effluent samples were spiked (Samples CI1 and CI2 with identical amounts of Cl-36 and no I-129; sample CI3 with Cl-36 and I-129 at an activity ratio of 1:1 and sample CI4 with Cl-36 and I-129 at an activity ratio of 1:10) and analysed for Cl-36 activity. Table 4 summarizes the obtained results [2]. Obtained and reference activities agree very well. Even at high I-129 excess no positive bias is introduced into the Cl-36 results, further stating the clean chloride/iodide separation. The standard deviation of the results obtained for samples CI1 and CI2 is 3.7% ($N = 2$, $k = 1$) thus confirming the good repeatability of the separation.

Table 4: Comparison determined vs. reference activities, spiked effluent samples, bias and zeta values.

Sample	Cl-36 Theoretical activity		I-129 Theoretical activity		Perkin Elmer TriCarb 3190TRSL				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
	CI0	Blank	-	Blank	-	236.3	5.22	< LOD	-	-
CI1	1.873E+04	6.556E+02	0	-	239.8	1774.8	1.809E+04	1.191E+03	-3.44	0.47
CI2	1.873E+04	6.556E+02	0	-	243.9	1871.4	1.905E+04	1.255E+03	1.72	0.23
CI3	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
CI4	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

In addition to aqueous samples Zulauf et al. [3] also tested the separation method on spiked soil, concrete and membrane filter samples.

In a first step mean chloride and iodide leaching yields were determined for the three matrices. Samples (approx. 250 mg) of each material were spiked with Cl-36, I-129 respectively, dried and then leached with 1M NaOH for 4h at 70°. The Cl-36 or I-129 activity of the leaching solutions was then determined via

LITERATURE STUDY

liquid scintillation counting. Leaching yields obtained were generally > 90%.

Fresh sets of spiked samples were then prepared by spiking the respective matrix with defined amounts of Cl-36 and I-129, followed by a drying step. The dried samples were then leached and separated as described before. Analyses were performed in triplicate, mean leaching and separation yields were assumed for activity calculation. Tables 5a-c summarize the obtained results.

Table 5a: Comparison determined vs. reference activities, soil, 3 replicates, bias and E_n , $k=2$.

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

soil	³⁶ Cl	determined activities		reference activities		Bias, %	E_n
		A(³⁶ Cl), Bq	$U_{A(36Cl)}$, Bq	A(³⁶ Cl), Bq	$U_{A(36Cl)}$, Bq		
	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 5b: Comparison determined vs. reference activities, concrete, 3 replicates, bias and E_n , $k=2$.

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

concrete	³⁶ Cl	determined activities		reference activities		Bias, %	E_n
		A(³⁶ Cl), Bq	$U_{A(36Cl)}$, Bq	A(³⁶ Cl), Bq	$U_{A(36Cl)}$, Bq		
	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 5c: Comparison determined vs. reference activities, filter, 3 replicates, bias and E_n , $k=2$.

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

filter	³⁶ Cl	determined activities		reference activities		Bias, %	E_n
		A(³⁶ Cl), Bq	$U_{A(36Cl)}$, Bq	A(³⁶ Cl), Bq	$U_{A(36Cl)}$, Bq		
	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

Overall determined and reference activities agree very well, however especially for concrete and soil samples I-129 results show a slight

LITERATURE STUDY

negative bias, determining the chemical yield of the separation is thus advisable and will lead to further improvement of the accuracy of the method.

Warwick et al. [4] developed a method for the analysis of decommissioning samples (e.g. spent resin) based on another sample preparation type. Their method is based on the thermal decomposition of the sample to be analysed using a 'Pyrolyser' furnace. Volatilized chlorine species are transported by a stream of moistened air into a bubbler containing a 6 mM Na₂CO₃ solution where they are retained. Mean recovery of this sample treatment step was found to be 86%.

The bubbler solution is then directly loaded onto silver loaded CL Resin. The authors found that, since the sample is not loaded from a highly acidic sample solution, an additional rinsing step is necessary ('modified wash') in order to improve C-14 decontamination. Fig. 5 shows the developed and optimized method.

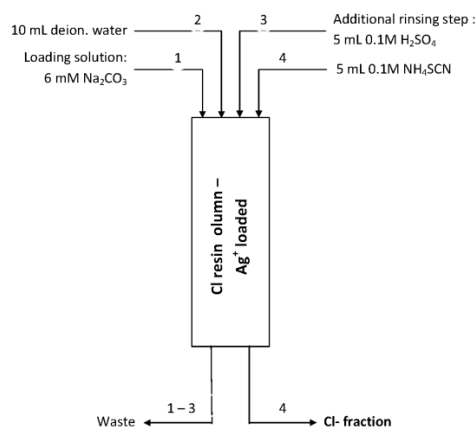


Figure 5: Scheme of Cl / I separation method optimized for use with RADDEC's Pyrolyser (4).

Table 6 shows the decontamination factors for the Cl fraction obtained by the authors ("modified wash" is referring to results obtained using the method including the additional rinse with dilute sulphuric acid). Decontamination factors obtained are high; the additional wash significantly improved C-14 decontamination of the Cl fraction.

The overall yield of the method (pyrolyser step plus column separation) was found to be close to 86% which allowed obtaining a detection limit of 20 mBq.g⁻¹ for a sample mass of 1g, a liquid scintillation counting efficiency of 98% and 180 min counting time.

Table 6 : Decontamination factors of Pyrolyser / CL Resin based method [4].

	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	

The method was further tested on a spent resin sample. A very good agreement between the specific activity determined through the pyrolyser / CL Resin method (4.3±0.1 kBq) and the expected value (4.1 kBq) was found [4].

Bibliography

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- (4) P E Warwick, A Zulauf, S Happel, I W Croudace: Determination of ³⁶Cl in decommissioning samples using a Pyrolyser furnace and extraction chromatographic separations. Presentation at the 11th ERA Symposium, 16/09/2010, Chester (UK); available online: http://www.triskem-international.com/iso_album/11_era_chester_warwick_determination_of_36cl_in_decommissioning_samples_using_a_pyrolyser.pdf.