

# Characterization of an extraction chromatographic resin for the separation and determination of $^{36}\text{Cl}$ and $^{129}\text{I}$

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**Abstract** The monitoring of long-lived radionuclides is of great importance in the context of the surveillance of nuclear facilities, during their operation as well as during their decommissioning. This is especially true for radionuclides of rather volatile elements, such as chlorine and iodine, the main interest being in  $^{36}\text{Cl}$  and  $^{129}\text{I}$ . Liquid Scintillation Counting (LSC) is a widely used measurement technique especially for the determination of  $^{36}\text{Cl}$  that requires a thorough and selective sample preparation in order to give accurate results. Sample preparation methods frequently employed such as volatilization and/or repeated precipitation steps can be rather elaborate and time consuming. Therefore, an attempt has been made to develop an ‘easy to use’ extraction chromatographic resin that allows extraction, and subsequent separation, of chloride and iodide from pretreated environmental and decommissioning samples for their determination via LSC. First results of the characterization of the resin including  $D_w$  values of  $\text{Cl}^-$ ,  $\text{I}^-$  and potential interferences, and of the method development are presented as well as the result of the analysis of a simulated real sample.

**Keywords**  $^{36}\text{Cl}$  ·  $^{129}\text{I}$  · LSC · Extraction chromatography · Resin · Decommissioning · Monitoring

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## Introduction

Beside numerous other radionuclides, the long-lived and rather volatile  $^{36}\text{Cl}$  (half-life  $3.01(3) \times 10^5$  years; 98.1%  $\beta^-$  decay to  $^{36}\text{Ar}$ ,  $E_{\beta,\text{max}}$ : 708.6 keV; 1.9% electron capture to  $^{36}\text{S}$  [1]) and  $^{129}\text{I}$  (half-life  $16.1(7) \times 10^6$  years; 100%  $\beta^-$  decay to  $^{129}\text{Xe}$ ,  $E_{\beta,\text{max}}$ : 190.8 keV [1]) are determined in various sample matrices within the context of the monitoring of nuclear installations, during operation and especially also during decommissioning.  $^{36}\text{Cl}$  is, in addition to natural production processes, produced in nuclear installation during the irradiation of nuclear fuel by neutron activation of  $^{35}\text{Cl}$  [2].  $^{129}\text{I}$  is a fission product that is, compared to  $^{131}\text{I}$  (half-life 8.0233(19) d [1]), produced with a rather low yield, but that has a very long half-life [3]. Both,  $^{36}\text{Cl}$  and  $^{129}\text{I}$  can be released as gaseous and/or liquid effluents and will be present in radioactive wastes originating from nuclear installations.

Numerous techniques for the determination of  $^{36}\text{Cl}$  and  $^{129}\text{I}$  are described in literature,  $^{36}\text{Cl}$  is frequently determined via AMS [4, 5] or LSC [2, 6, 7],  $^{129}\text{I}$  via NAA [8], AMS [9], ICP-MS [10, 11] or  $\beta$ -spectrometry [12]. LSC measurements have the advantage of availability for a large number of laboratories and are thus interesting especially for routine monitoring. In order to allow the determination of  $^{36}\text{Cl}$  and  $^{129}\text{I}$  via LSC, and to obtain accurate and precise results, the samples have to pass a number of sample preparation steps; among these steps are the chemical separation and purification of the nuclides and the subsequent preparation of counting samples suitable for LSC. Sample preparation methods frequently employed such as volatilization [2, 6, 12], precipitation and/or ion exchange steps [7] can be rather elaborate. Therefore, the attempt of developing an extraction chromatographic resin that allows extraction, and subsequent separation, of  $\text{Cl}^-$  and  $\text{I}^-$  from pretreated environmental and decommissioning samples

has been made. The suggested method only applies to chloride and iodide, any chlorine or iodine present in the sample in elemental form or as oxoanions will need to be reduced to chloride or iodide during sample preparation.

Results of the characterization of the resin are presented as well as some first results of the development and validation of methods based on this resin. The results of the analysis of a simulated real sample are presented.

## Experimental

### Reagents and apparatus

All reagents used were of analytical grade, 18 M $\Omega$  deionized water was used throughout all experiments. pH values were measured using a pH meter and adjusted when necessary using NaOH and H<sub>2</sub>SO<sub>4</sub>. The Cl resin samples prepared by TrisKem International were used as received without further purification. Ag<sup>+</sup> loaded Cl resin was prepared by contacting 10 g of the Cl resin with 100 mL of a 1 M H<sub>2</sub>SO<sub>4</sub> solution containing 650 mg of AgNO<sub>3</sub> in a 250 mL PE flask on a vortex shaker over a period of 2 h. The resin was then filtered, rinsed with 1 M H<sub>2</sub>SO<sub>4</sub> (until absence of Ag<sup>+</sup> in the filtrate) and dried.

2 mL PP columns with appropriate funnels (both TrisKem International) were employed for elution studies and separation tests, 2 mL Eppendorf centrifuge tubes for batch experiments. Element concentrations were determined by ICP-MS measurement using an ELAN 6000 (PerkinElmer), all samples were measured after appropriate dilution and addition of a suited internal standard. LSC measurements were performed using either a TriCarb 1600TR (Packard) or a 1220 Quantulus (PerkinElmer) and ProSafe HC (Meridian) as liquid scintillation cocktail.

### Determination of weight distribution ratios $D_w$

For Ag and selected elements weight distribution ratios were determined. 50 mg of the Cl resin were weighted into 2 mL centrifugation tubes and 0.3 mL of the acid for which the  $D_w$  was to be determined was added. The tubes were closed and shaken for 30 min in order to precondition the resin. 1 mL of a solution of a well defined pH value, containing defined amounts of selected cations, in general 1  $\mu$ g per cation, was then added (A<sub>0</sub> sample). The tubes were again closed, shaken for 30 min and finally centrifuged. A 1 mL aliquot was withdrawn from the tube using a micro-pipette (A sample). The aliquot was diluted appropriately using 3% HNO<sub>3</sub> and measured by ICP-MS. Measurements were performed relative to the A<sub>0</sub> sample.

I<sup>-</sup> and Cl<sup>-</sup> weight distribution ratios were determined using Ag<sup>+</sup> loaded Cl resin prepared as described before and

A<sub>0</sub> samples containing known activities of <sup>36</sup>Cl or <sup>129</sup>I. Conditions tested included 1 M H<sub>2</sub>SO<sub>4</sub> as well as varying KSCN (0.01–0.2 M) and Na<sub>2</sub>S (0.04–0.35 M) concentrations. The withdrawn aliquots were mixed with 10 mL of liquid scintillation cocktail and measured by liquid scintillation counting (counting time  $t = 10$  min) relative to A<sub>0</sub> samples. All  $D_w$  values were determined in triplicate.

$D_w$  values were calculated according to Eq. 1, net count rates refer to ICP-MS count rates as well as to LSC count rates:

$$D_w = \frac{(N_{A0} - N_A)}{N_A} \times \frac{V}{m_R} \quad (1)$$

where  $N_{A0}$  = net count rate in the A<sub>0</sub> sample;  $N_A$  = net count rate in the A sample;  $V$  = Volume of the aqueous phase (1.3 mL) and  $m_R$  = amount of the resin in g.

### Maximum uptake

First, the Ag<sup>+</sup> uptake of the Cl resin was examined in batch experiment. 50 mg of the resin were preconditioned as described before and contacted in a 2 mL centrifuge tube with 1 mL of a Ag<sup>+</sup> standard solution (A<sub>0</sub> sample; 1 M H<sub>2</sub>SO<sub>4</sub> containing 5 mg Ag<sup>+</sup> mL<sup>-1</sup>) under shaking for 30 min. A 1 mL aliquot was withdrawn using a micro-pipette. The aliquot was diluted appropriately using 3% HNO<sub>3</sub> and measured by ICP-MS. Measurements were performed relative to the A<sub>0</sub> sample. The Ag<sup>+</sup> uptake ( $K$ ) of the resin was calculated according to Eq. 2:

$$K = \frac{(c_{Ag,A0} \cdot V_{A0}) - (c_{Ag,A} \cdot V_A)}{m_R} \quad (2)$$

where  $c_{Ag,A0}$  = silver concentration in the A<sub>0</sub> sample,  $c_{Ag,A}$  = silver concentration in the A sample,  $V_{A0}$  = volume of the A<sub>0</sub> sample,  $V_A$  = volume of the A sample,  $m_R$  = mass of the resin in g.

Additionally the silver uptake was also examined by column elution experiments. Several columns were prepared in order to allow estimating the influence of the contact time on the Ag<sup>+</sup> uptake. The columns used for the uptake studies were prepared by soaking 0.65 g of Cl resin in 10 mL 1 M H<sub>2</sub>SO<sub>4</sub> for 2 h under shaking; the resin was subsequently transferred into an empty 2 mL column. The packed columns were then loaded with a small volume (2 mL) of a 1 M H<sub>2</sub>SO<sub>4</sub> silver nitrate solution with a well known Ag<sup>+</sup> concentration (10 mg Ag<sup>+</sup> mL<sup>-1</sup>) and allowed to stand for 0.5, 2.5, 10 h, respectively. The columns were then rinsed three times with 10 mL 1 M H<sub>2</sub>SO<sub>4</sub>, the rinsing solutions were collected in a volumetric flask, appropriately diluted and analyzed by ICP-MS for Ag content.

Cl<sup>-</sup> and I<sup>-</sup> uptake behaviours were also examined via column experiments using Cl resin columns previously loaded with Ag<sup>+</sup>. In case of Cl<sup>-</sup> uptake, the columns were

loaded with 5 mg of  $\text{Cl}^-$ , in case of  $\text{I}^-$  with 20 mg of  $\text{I}^-$  (both as sodium salts). Loaded columns were rinsed three times with 1 M  $\text{H}_2\text{SO}_4$ , all rinsing solutions were collected, diluted and analyzed by ICP-MS. Calculations were performed analogous to Eq. 2, obtained experimental results were compared to theoretical values (quantitative precipitation of  $\text{I}^-/\text{Cl}^-$  by 13 mg of  $\text{Ag}^+$ ).

### Elution studies

The columns used during the elution studies were prepared similarly as described above. The resin was soaked in 1 M  $\text{H}_2\text{SO}_4$  for 2 h and then transferred into the column. The columns were then loaded with 2 mL of 1 M  $\text{H}_2\text{SO}_4$  solution containing 13 mg of  $\text{Ag}^+$  and allowed to stand for 2.5 h. The main aim of the elution study was to determine optimum volumes of the respective rinsing and elution steps. The loading solutions were collected directly, whereas rinsing and elution steps were collected in 5 mL fractions.

Elution studies on  $\text{Cl}^-$  and  $\text{I}^-$  were performed using sample load solutions that were 1 M in  $\text{H}_2\text{SO}_4$  and that contained either 50 Bq  $^{36}\text{Cl}$  and 1 mg of  $\text{Cl}^-$  (as sodium chloride) or 50 Bq  $^{129}\text{I}$  and 1 mg of  $\text{I}^-$  (as sodium iodide). The elution studies were first performed separately for  $\text{Cl}^-$  and  $\text{I}^-$ . Elution conditions evaluated included 0.1 M KSCN (for  $\text{Cl}^-$  elution) and 0.35 M  $\text{Na}_2\text{S}$  (for  $\text{I}^-$  elution), both at pH 7, as well as several different rinsing steps upfront to the  $\text{I}^-$  elution with the focus of evaluating their influence on the  $\text{I}^-$  elution yield.

The best suited elution conditions obtained from the elution studies were applied to a loading solution containing known activities of both,  $^{36}\text{Cl}$  and  $^{129}\text{I}$ , in order to confirm its suitability for the foreseen separation.

### Decontamination factors

Data obtained during the  $\text{Cl}^-/\text{I}^-$  elution studies using the optimized method were also used to calculate decontamination factors ( $D_f$ ) for  $\text{Cl}^-$  and  $\text{I}^-$  in the respective  $\text{I}^-$  and  $\text{Cl}^-$  fractions. These were calculated according to Eq. 3:

$$D_f = \frac{N_0}{N_a} \tag{3}$$

where  $N_0$  = net count rate of the element in the  $A_0$  sample;  $N_a$  = net count rate of the element in the respective fraction.

In case the count rate in the respective fraction was lower than the decision level (DL), the decontamination factor  $D_f$  was calculated according to Eq. 4

$$D_f \geq \frac{N_{A0}}{\text{DL}} \tag{4}$$

where DL is calculated for LSC measurements using Eq. 5:

$$\text{DL} = (k_{1-\alpha} + k_{1-\beta}) \cdot \sqrt{N_0 \cdot \left(\frac{1}{t_0} + \frac{1}{t_m}\right)} + \frac{1}{4}(k_{1-\alpha} + k_{1-\beta})^2 \cdot \left(\frac{1}{t_0} + \frac{1}{t_m}\right) \tag{5}$$

wherein:  $k_{1-\alpha}$  and  $k_{1-\beta}$  = quintiles of the normal distribution,  $N_0$  = background count rate,  $t_0$  = background counting time and  $t_m$  = sample counting time.

The optimized elution conditions and volumes were further applied to loading solutions containing a number of different elements (Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Cd, Cs, Ba, Pb, U; all 10  $\mu\text{g}$  in 10 mL loading solution).  $\text{Cl}^-$  and  $\text{I}^-$  fractions were collected and analyzed by ICP-MS; decontamination factors for these elements were calculated as indicated above, in case the concentration of an element was below the decision limit of the ICP-MS the decontamination factors were calculated according to Eq. 4 with DL being three times the standard deviation of the background count rate of the element in the blank sample.

Finally loading solutions containing known activities of  $^{90}\text{Sr}/^{90}\text{Y}$ ,  $^{60}\text{Co}$  or  $^{137}\text{Cs}$  were prepared and separated on the Cl resin columns, chloride and iodide fractions were collected and analyzed by LSC, decontamination factors were calculated according to Eqs. 3 and 4.

### Precision

In order to get some first information on the precision of the method a 300 mL tap water sample was spiked with  $^{36}\text{Cl}$  and  $^{129}\text{I}$  (activity level of the final sample: each 0.5 Bq  $\text{mL}^{-1}$ ); homogenized and divided into 30 subsamples. The samples were analyzed over 3 days, 10 samples per day. Standard deviations were calculated according to Eqs. 6–8, wherein the total combined standard deviation  $s_t$  was calculated from the intra-day standard deviation  $s_b$  and the inter-day standard deviation  $s_w$ .

$$s_t = \sqrt{s_w^2 + s_b^2} \tag{6}$$

$$s_w = \sqrt{\frac{\sum s_j^2}{n}} \tag{7}$$

$$s_b = \sqrt{\frac{\sum (\bar{x}_j - \bar{x})^2}{n - 1}} \tag{8}$$

### Simulated real sample

A simulated real sample was prepared by adding well known activities of  $^{36}\text{Cl}$  ( $47.2 \pm 2.4$  Bq) and  $^{129}\text{I}$  ( $41.1 \pm 3.1$  Bq), as well as known activity levels of  $^{60}\text{Co}$ ,

$^{90}\text{Sr}/^{90}\text{Y}$  and  $^{137}\text{Cs}$  (each 85 Bq) to 50 mL of a tap water sample previously adjusted to 1 M  $\text{H}_2\text{SO}_4$ . 10 mL aliquots of this solution were analyzed in triplicate following the optimized separation method, and the  $\text{Cl}^-$  and  $\text{I}^-$  fractions were analyzed by LSC. Mean yields and contributions of the precision to the overall uncertainty were taken from the results of the precision experiments and used for activity and uncertainty calculation. Results were evaluated according to Eqs. 9 and 10.

$$\text{Bias } B [\%] = \frac{A_D - A_R}{A_R} \cdot 100 \quad (9)$$

$$E_n = \frac{|A_D - A_R|}{\sqrt{U(A_D)^2 - U(A_R)^2}} \quad (10)$$

wherein  $U = u_c \times k$  with  $k = 2$ ,  $A_R$  = reference activity,  $A_D$  = determined activity.

## Results and discussion

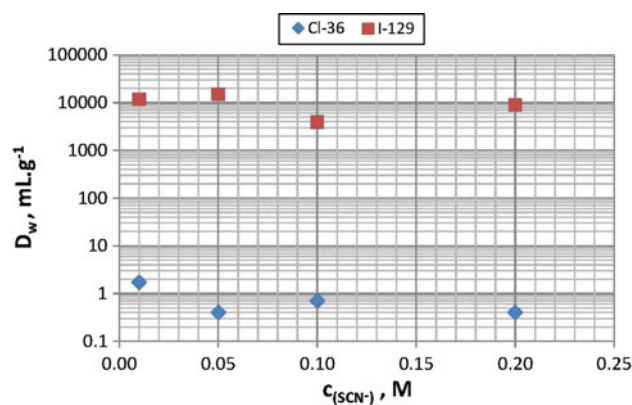
### Weight distribution ratios $D_w$

In order to evaluate the suitability of the resin for the foreseen use, the  $D_w$  of  $\text{Ag}^+$  was first determined for a number of acids and acid concentrations; however, for practical reasons the main focus was set on sulfuric acid. The  $D_w$  values of  $\text{Ag}^+$  in  $\text{H}_2\text{SO}_4$  on the Cl resin were found to be: 65,000  $\text{mL g}^{-1}$  in 1 M  $\text{H}_2\text{SO}_4$ , 60,000  $\text{mL g}^{-1}$  at pH 3 and 35,000 at pH 5.  $\text{Ag}^+$  is thus very well extracted over a wide range of pH values with a maximum in 1 M  $\text{H}_2\text{SO}_4$ . At this concentration the resin has, as Table 1 shows, high selectivity for Ag and Pd whereas none of the other elements tested show relevantly high  $D_w$  values. The resin's selectivity is thus overall suited for the purpose.

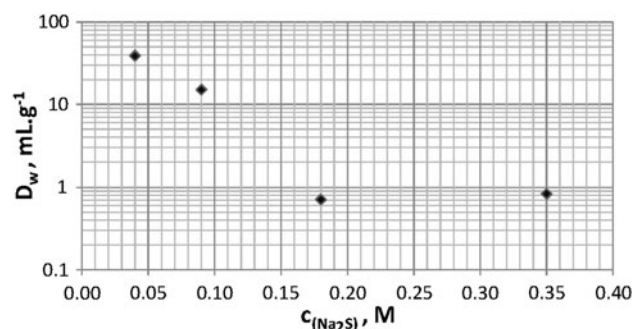
$D_w$  values were determined for  $\text{Cl}^-$  and  $\text{I}^-$  in 1 M  $\text{H}_2\text{SO}_4$ , in 0.01, 0.05, 0.1 and 0.2 M KSCN; in addition  $\text{I}^-$   $D_w$  values were determined in 0.04, 0.09, 0.18 and 0.35 M

**Table 1**  $D_w$  values of various elements on Cl resin in 1 M  $\text{H}_2\text{SO}_4$

Analyte	$D_w, \text{mL g}^{-1}$
Ag	65,000
Cd	<1
Ce	4
Co	<1
Cu	<1
Fe	<1
Mn	<1
Ni	<1
Pd	87,000
Zn	25



**Fig. 1**  $D_w$  of  $\text{Cl}^-$  and  $\text{I}^-$  on  $\text{Ag}^+$  loaded Cl resin at pH 7 and varying  $\text{SCN}^-$  concentrations



**Fig. 2**  $D_w$  of  $\text{I}^-$  on  $\text{Ag}^+$  loaded Cl resin at pH 7 and varying  $\text{Na}_2\text{S}$  concentrations

$\text{Na}_2\text{S}$ . For both  $\text{Cl}^-$  and  $\text{I}^-$ , the  $D_w$  values in 1 M  $\text{H}_2\text{SO}_4$  were greater than 1,000 (Cl: 1,600, I: 2,000). These conditions thus allow not only excellent  $\text{Ag}^+$  retention, but also very good chloride and iodide uptake. Accordingly 1 M  $\text{H}_2\text{SO}_4$  was chosen as sample loading condition for all further testing. Figures 2 and 3 summarize the  $D_w$  values obtained for  $\text{Cl}^-$  and  $\text{I}^-$  under varying KSCN and  $\text{Na}_2\text{S}$  concentrations. Figure 1 shows that even small amounts of KSCN interfere very strongly with the  $\text{Cl}^-$  uptake whereas  $\text{I}^-$  remains very well retained. The  $\text{Cl}^-/\text{I}^-$  separation seems thus easily possible using a dilute KSCN solution. For further testing 0.1 M KSCN was used.  $\text{I}^-$  can, as Fig. 2 shows, be eluted with  $\text{Na}_2\text{S}$  solutions of elevated concentration. For further testing 0.35 M was chosen.

### Maximum uptake

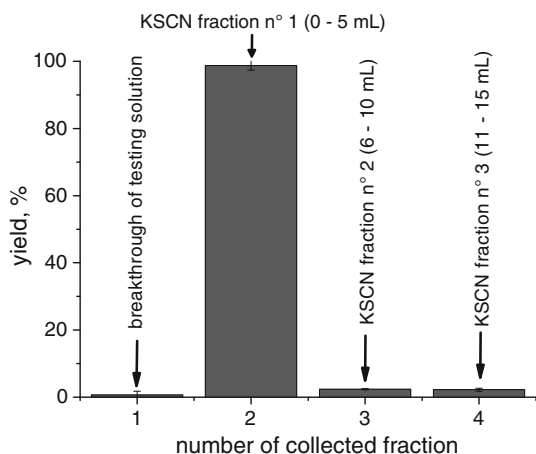
The  $\text{Ag}^+$  uptake of the Cl resin was determined to be  $38.5 \pm 1.3 \text{ mg Ag}^+ \text{ g}^{-1}$  resin under the described batch extraction conditions.  $\text{Ag}^+$  uptake in column geometry was found to be lower under the chosen conditions; additionally it was found that the uptake is time dependent: after 30 min  $16.5 \pm 0.8 \text{ mg}$  of  $\text{Ag}^+$  were extracted, after 2.5 h  $19.5 \pm 1.0 \text{ mg}$  of  $\text{Ag}^+$ . Longer contact times did not result

in a further increase of the  $\text{Ag}^+$  uptake. For all further experiments, the resin was contacted with the  $\text{Ag}^+$  for about 2 h in order to assure maximum uptake, for routine use a time of 30 min would seem sufficient.

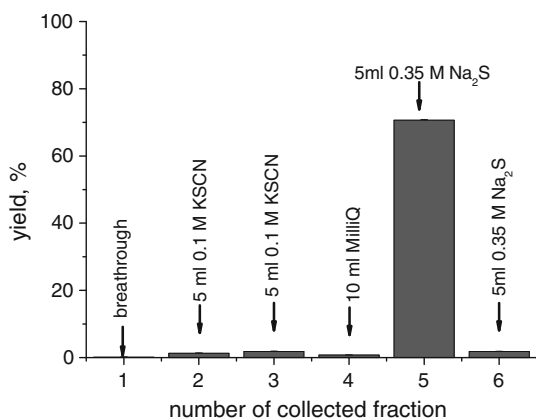
The  $\text{Cl}^-$  and  $\text{I}^-$  uptake of the Cl resin under the chosen conditions were found to be  $4.3 \pm 0.2 \text{ mg Cl}^- \text{ g}^{-1}$  resin and  $16.3 \pm 1.6 \text{ mg I}^- \text{ g}^{-1}$  resin, which agrees well with the theoretical values of  $4.2 \text{ mg Cl}^- \text{ g}^{-1}$  resin and  $14.9 \text{ mg I}^- \text{ g}^{-1}$  resin.

#### Elution studies

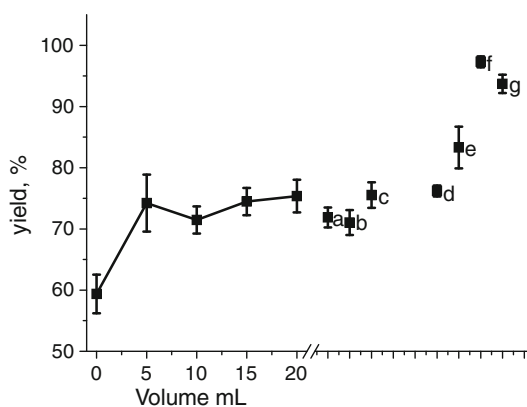
Figures 3 and 4 show the results of the initial elution studies; Fig. 3 shows that 5 mL 0.1 M KSCN quantitatively remove  $\text{Cl}^-$  from the column, whereas, as Fig. 4 shows, no  $\text{I}^-$  is eluted; it further shows that  $\text{I}^-$  is mainly eluted in the first 5 mL of 0.35 M  $\text{Na}_2\text{S}$ , almost none being eluted in the later fractions. Nevertheless, the  $\text{I}^-$  yield was



**Fig. 3**  $\text{Cl}^-$  elution with 0.1 M  $\text{SCN}^-$  (fractions 2–4, fraction size: 5 mL), 2 mL Cl resin column ( $\text{Ag}^+$  loaded)



**Fig. 4**  $\text{I}^-$  elution, all fractions, fraction sizes: 5 mL, 2 mL Cl resin column ( $\text{Ag}^+$  loaded)



**Fig. 5** Influence of the rinsing step upfront to the  $^{129}\text{I}$  elution with  $\text{Na}_2\text{S}$ : Rinsing with various volumes of deionized water; **a** 10 mL 0.01 M  $\text{NaHSO}_3$ , **b** 10 mL 0.1 M  $\text{NaHSO}_3$ , **c** 10 mL 1 M  $\text{NaHSO}_3$ , **d** 10 mL 1 M  $\text{NaNO}_2$ , **e** 10 mL 30%  $\text{H}_2\text{O}_2$ , **f** 10 mL 1%  $\text{NH}_3$  and **g** 10 mL 1%  $\text{NaOH}$ ; 2 mL Cl resin column ( $\text{Ag}^+$  loaded)

found to be only in the order of 70%. Follow up studies were performed using various additional rinsing steps between the  $\text{Cl}^-$  and the  $\text{I}^-$  elution step including increasing amounts of deionized water, reducing and oxidizing agents and alkaline solutions. Figure 5 shows the  $\text{I}^-$  yield in the  $\text{I}^-$  fraction in function of the rinsing step performed before the elution. 1%  $\text{NH}_3$  and 1%  $\text{NaOH}$  solutions proved to be the best choice, resulting in near quantitative  $\text{I}^-$  elution. For practical reasons 1%  $\text{NaOH}$  was retained as additional rinsing step, since  $\text{NH}_3$  complexed and eluted parts of the  $\text{Ag}^+$  retained on the Cl resin column. The best suited separation method can thus be summarized as follows:

The sample loading solutions are adjusted to 1 M  $\text{H}_2\text{SO}_4$  (in order to assure that iodine and chlorine are present as chloride and iodide a strong reducing agent, e.g.  $\text{Sn(II)}$  might be added to the sample loading solution) and loaded onto the  $\text{Ag}^+$  loaded Cl resin column. The column loading is followed by a first rinsing step with 10 mL deionized water in order to increase the pH on the column and to remove matrix elements and potential interferences.  $\text{Cl}^-$  is eluted with 5 mL 0.1 M KSCN. The column is then further rinsed with 10 mL 1%  $\text{NaOH}$  in order to optimize the  $\text{I}^-$  elution and finally  $\text{I}^-$  is eluted using 5 mL 0.35 M  $\text{Na}_2\text{S}$ . Figure 6 summarizes the method.

In order to verify that the  $\text{Cl}^-/\text{I}^-$  separation is working sufficiently well for the foreseen use a solution containing  $^{36}\text{Cl}$  and  $^{129}\text{I}$  was separated using the described method, the observed separation is very clean, as Fig. 7 shows.

#### Decontamination factors

The determined decontamination factors  $D_f$  are summarized in Table 2. In all cases the net count rates in the  $\text{Cl}^-$  and  $\text{I}^-$  fractions were below the respective decision limits,



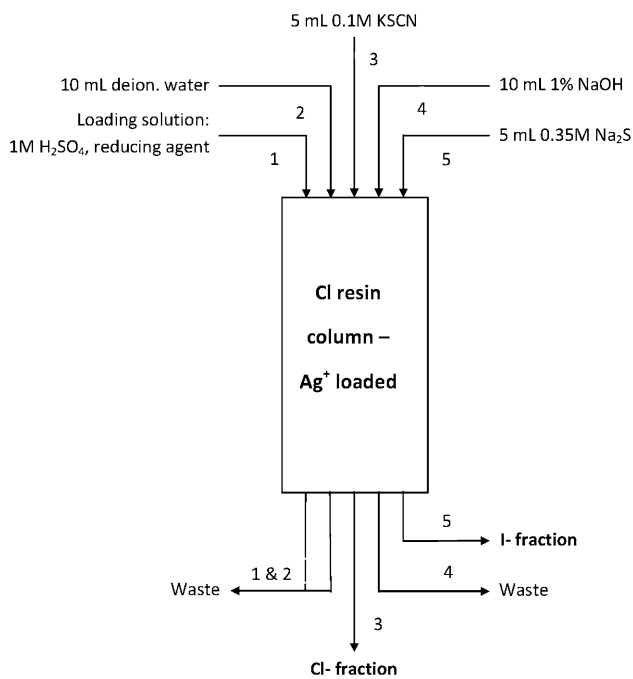


Fig. 6 Scheme of optimized Cl<sup>-</sup>/I<sup>-</sup> separation method

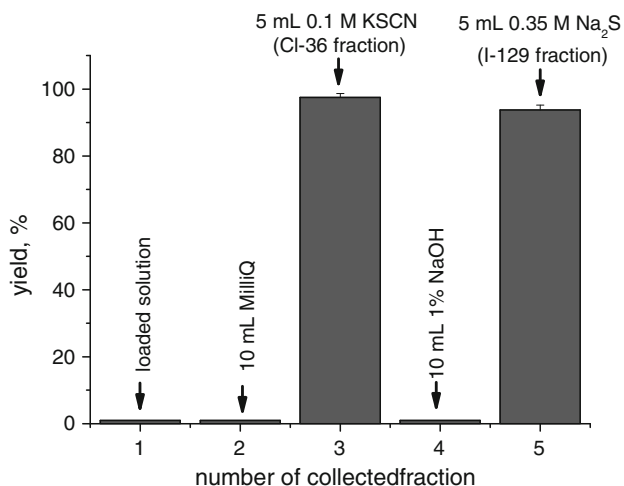


Fig. 7 Elution profile, elution study of combined <sup>36</sup>Cl and <sup>129</sup>I with optimized method, 2 mL Cl resin column (Ag<sup>+</sup> loaded)

accordingly all  $D_f$  values are given as being “greater than”. Overall the results indicate that the Cl resin and the chosen separation method show a suitable selectivity for the intended use. These results will have to be confirmed by the analysis of real samples.

Precision

Table 3 shows the results of the precision experiments. The Cl<sup>-</sup> elution shows very good precision with a  $s_t < 3\%$ . The precision of the I<sup>-</sup> elution on the other hand is acceptable,

Table 2 Decontamination factors  $D_f$  of various elements in Cl<sup>-</sup> and I<sup>-</sup> fractions

Analyte	$D_f$ in Cl <sup>-</sup> fraction	$D_f$ in I <sup>-</sup> fraction
Ba	>1,000	>600
Cd	>6,900	>7,700
Co	>170	>1,500
Cr	>29	>430
Cs	>200	>6,200
Cu	>210	>190
Mn	>210	>370
Ni	>170	>320
Pb	>300	>720
Rb	>16	>2,300
Sr	>180	>17,000
U	>1,900	>200
Zn	>32	>11
<sup>60</sup> Co	>320	>320
<sup>137</sup> Cs	>150	>150
<sup>90</sup> Sr/ <sup>90</sup> Y	>180	>160
<sup>36</sup> Cl	NA	>160
<sup>129</sup> I	>420	NA

Table 3 Results of precision experiments: mean <sup>36</sup>Cl and <sup>129</sup>I yields ( $M_t$ ), intra-day standard deviation ( $N = 10$ )  $s_b$ , inter day standard deviation ( $N = 3$ )  $s_w$ , combined total standard deviation  $s_t$

Analyte	$M_t$ (%)	$s_w$ (%)	$s_b$ (%)	$s_t$ (%)
<sup>36</sup> Cl	96.98	2.39	0.20	2.40
<sup>129</sup> I	91.66	5.20	7.62	9.22

but with a  $s_t$  in the order of 9% significantly lower than the Cl<sup>-</sup> precision. In any case it is advisable to use stable Cl<sup>-</sup> and I<sup>-</sup> as internal standards.

Simulated real samples

Table 4 compares the results obtained experimentally with the expected results. The determined and reference activities agree well, because the  $E_n$  values are below 1. The determined results are thus not deviating significantly from the expected ones. The bias between determined and expected results is well below 10%, nevertheless the <sup>36</sup>Cl results show a slight negative bias, the use of an internal standard, for <sup>36</sup>Cl as well as for <sup>129</sup>I, is thus advisable. The results are regrouped rather well, the  $s_b$  value is 2.5% for <sup>129</sup>I results (number of replicates  $N = 3$ ) and 0.95% for <sup>36</sup>Cl results ( $N = 3$ ), further confirming the good precision of the method.

**Table 4** Comparison of determined and reference activities, three replicates, bias and  $E_n$ ,  $k = 2$ 

	Determined activities		Reference activities		Bias (%)	$E_n$
	$A(^{129}\text{I}), \text{Bq}$	$U_{A(^{129}\text{I})}, \text{Bq}$	$A(^{129}\text{I}), \text{Bq}$	$U_{A(^{129}\text{I})}, \text{Bq}$		
$^{129}\text{I}$						
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
	Determined activities		Reference activities		Bias (%)	$E_n$
	$A(^{36}\text{Cl}), \text{Bq}$	$U_{A(^{36}\text{Cl})}, \text{Bq}$	$A(^{36}\text{Cl}), \text{Bq}$	$U_{A(^{36}\text{Cl})}, \text{Bq}$		
$^{36}\text{Cl}$						
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

## Conclusions and outlook

An extraction chromatographic resin showing very good selectivity for silver and platinum group metals was characterized and tested with respect to its use as a Cl selective resin after loading with  $\text{Ag}^+$ . The resin showed overall good  $\text{Cl}^-$  and  $\text{I}^-$  uptake under loading conditions. Elution conditions were identified allowing separate elution of  $\text{Cl}^-$  and  $\text{I}^-$ . Through elution studies the best suited separation conditions and elution volumes were identified. The developed method was tested for  $^{36}\text{Cl}$  and  $^{129}\text{I}$  containing solutions, as well as for solutions containing numerous elements/potential interferents in order to get information on respective decontamination factors. Results indicated a good selectivity of the method and no major interferent could be identified. The method showed, at least for water samples, a very good precision for the  $\text{Cl}^-$  separation, and an acceptable precision for the  $\text{I}^-$  separation, nevertheless the use of internal standards is advisable. The analysis of a simulated real sample showed good agreement between obtained and expected results, though a slight negative bias was observed in the case of  $^{36}\text{Cl}$ . Results obtained so far indicate that the resin and the method have a good potential towards the foreseen use. Further development of the method with respect to the analysis of environmental and decommissioning samples (e.g. filter, soil and concrete samples) will be performed in the future. The suggested method will only allow the extraction and determination of iodine and chlorine in  $\text{I}^-$  and  $\text{Cl}^-$  form, oxoanions of these elements present in the sample solutions will thus have to be reduced before the separation in order to be also extracted; this fact will be addressed in further experiments. The so developed methods will then be validated

with respect to precision, linearity, and especially accuracy by analyzing real samples in comparison to already validated methods and by analyzing reference materials.

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