



# Development and characterisation of a new Sr selective resin for the rapid determination of $^{90}\text{Sr}$ in environmental water samples



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## ABSTRACT

A new resin selective for Sr has been developed and characterised for the direct binding of  $^{90}\text{Sr}$  from environmental waters with minimal pre-treatment. The new selective resin comprises of a mixture of two extractants, 4,4'(5')-bis-*t*-butylcyclohexano-18-crown-6 and di(2-ethyl-hexyl)phosphoric acid, sorbed onto Amberchrom CG-71. Sr uptake is shown to be high (the distribution weight coefficient  $D_w > 100 \text{ mL g}^{-1}$ ) across a range of environmentally realistic conditions (pH 2–8 and up to  $11,500 \text{ mg L}^{-1}$  NaCl,  $500 \text{ mg L}^{-1}$  Ca,  $400 \text{ mg L}^{-1}$  K and  $1300 \text{ mg L}^{-1}$  Mg). The Sr capacity of the resin is shown to be  $7.7 \pm 0.4 \text{ mg g}^{-1}$ , meaning that the resin has a sufficient capacity to quantitatively remove Sr from most environmental water samples. The reasonably fast uptake kinetics of the resin ( $95 \pm 4\%$  of strontium bound within 30 min) results in a resin that is applicable to both batch- and column-type separation procedures. A range of potentially co-extracted radio-elements have been identified and an elution scheme has been developed to separate interferences, including  $^{90}\text{Y}$ , from  $^{90}\text{Sr}$ . The clean elution of  $^{90}\text{Sr}$  permits immediate measurement by radiometric means, with no need for complicated spectral processing or waiting for secular equilibrium between  $^{90}\text{Sr}$  and  $^{90}\text{Y}$ . The characterised resin is applicable for use in rapid determination procedures, enabling the swift analysis of water samples required by monitoring schemes at contaminated nuclear sites and in the aftermath of nuclear accidents.

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## 1. Introduction

The anthropogenic,  $\beta$ -emitting radionuclide  $^{90}\text{Sr}$  poses a high health risk as it is easily metabolised by the body and incorporated into the skeletal system. Permitted and accidental releases from nuclear facilities have resulted in contamination of environmental waters around the world [1–5]. Such contamination requires long-term monitoring plans, for which rapid, streamlined procedures are necessary to enable the required, large sample throughput. Additionally,  $^{90}\text{Sr}$  is a key radionuclide in emergency post-incident monitoring [6,7], where the extent of contamination needs to be rapidly determined. Strontium-89 ( $t_{1/2}=50.5$  days) can also be released into the environment following reactor exposure accidents (e.g. Chernobyl), however  $^{90}\text{Sr}$  ( $t_{1/2}=28.8$  years) is the more important radionuclide long term [6]. Consequently, the discussion will be directed towards  $^{90}\text{Sr}$ , but much is relevant to  $^{89}\text{Sr}$  as well.

Determination of  $^{90}\text{Sr}$  requires separation from interfering matrix constituents and interfering radionuclides. A variety of

different methods have been developed, aiming to create simpler and more rapid procedures [8]. The development of Sr Resin in the 1990s [9–12] was a major step forward in chromatographic separation of  $^{90}\text{Sr}$ . Sr Resin consists of a 1 M 4,4'(5')-bis-*t*-butylcyclohexano-18-crown-6 (DtBuCH18C6) in 1-octanol solution sorbed onto an inert, polymeric support resin [11,12]. The crown ether extractant has a cavity size of 260 to 320 pm and the diameter of  $\text{Sr}^{2+}$  is 226 pm [13]; consequently the  $\text{Sr}^{2+}$  ion can be size-selectively separated by retention in the crown ether cavity. Sr Resin is widely used for the extraction of strontium from environmental waters, however it requires the acidification of the sample prior to separation (e.g. to 5 M  $\text{HNO}_3$ ) as strontium binding is dependent on acid concentration [12]. The most efficient method for converting a large volume ( $\geq 1$  L) environmental water sample to a higher acid concentration matrix is by precipitation, e.g. carbonate precipitation of alkaline earth metals, which is time consuming and invariably leads to loss of the analyte [14]. Therefore, a resin that can directly bind strontium from environmental water samples, with no prior sample preparation, has been developed in this work.

Mixtures of organic-soluble cation exchangers, such as di(2-ethyl-hexyl)phosphoric acid (HDEHP), and crown ethers have previously been used in the organic phase of liquid solvent

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extraction systems, eliminating the necessity of transferring an inorganic anion to the organic phase [15]. In such a mixture of HDEHP and crown ether, the cation in the aqueous phase is exchanged at the organic phase interface for the  $H^+$  of the HDEHP. The metal cation then exists as an organic phase soluble salt with which the crown ether can bind. As HDEHP binds strontium at environmental pH values [16,17], a mixture of HDEHP and DtBuCH18C6 has the potential to facilitate metal binding directly from environmental waters. We have therefore investigated the uptake and elution behaviour of Sr on a Sr Resin modified with the addition of HDEHP sorbed to the inert polymer support structure.

## 2. Materials and methods

### 2.1. Candidate resins

Sr Resin consists of an extractant solution (1 M DtBuCH18C6 dissolved in 1-octanol) sorbed onto Amberchrom CG-71 polymeric support beads. Five different resins were produced by gradually replacing the 1-octanol with increasing amounts of HDEHP. The support beads were impregnated using solutions containing given ratios of the non-volatile extractants. To ensure that the required extractant content had been achieved, the masses of the impregnated support beads were evaluated. On the basis of preliminary tests, the resin with the highest HDEHP content was chosen for further characterisation (in the following referred to as TK100 Resin). All further work was conducted solely with this resin.

### 2.2. Strontium uptake

Strontium uptake on the TK100 Resin was assessed using the distribution weight coefficient ( $D_w$ , mL  $g^{-1}$ ):

$$D_w = [(A_0 - A_s)/M_r]/(A_s/V_s)$$

where  $A_0$ =initial activity or mass concentration in the solution (Bq  $L^{-1}$  or mg  $L^{-1}$ ),  $A_s$ =final activity or mass concentration in the solution (Bq  $L^{-1}$  or mg  $L^{-1}$ ),  $V_s$ =volume of the solution (mL) and  $M_r$ =mass of the resin (g). The higher the  $D_w$  the higher the proportion of analyte that binds to the resin. A screening criterion of 100 mL  $g^{-1}$  was used; above this value the resin binding was deemed effective.

### 2.3. Instrumentation and reagents

Elemental concentrations of Sr, U, Y, Pb, Bi, Cs, Co and Ba (Section 2.4.1.–2.4.6.) were measured using either a Perkin-Elmer ELAN 6000 ICP-MS or a Thermo Scientific Elemental X-Series ICP-MS. Element concentrations of Sr, Ca, K, Mg, Ba and Pb (Section 2.5.3) were measured on a Thermo Scientific iCAP 6000 Series ICP-OES. Radium-226 was measured using a Packard 1600TR liquid scintillation analyser (Section 2.4.6) or a Tri-Carb 3170 liquid scintillation analyser (Section 2.5.4). All  $^{90}Sr/^{90}Y$  and  $^{233}U$  (Section 2.5.4) measurements were made with a Tri-Carb 3170 liquid scintillation analyser. Americium-241 was measured using a Tri-Carb 3170 liquid scintillation analyser (Section 2.4.6) or an Ortec HPGe gamma-spectrometer (Section 2.5.4). Bismuth-207 measurements were made using an Ortec HPGe gamma-spectrometer (Section 2.5.4).

All reagents used were of analytical grade and Milli-Q (MQ) water was used throughout as the background matrix for all water solutions. Resins were provided by TrisKem International. Ultima Gold LLT (Perkin Elmer) liquid scintillation cocktail was used for scintillation counting, apart from the measurement of  $^{226}Ra$  in Section 2.4.6 where ProSafe HC was used (Meridian Biotechnologies). All experiments were conducted in triplicate.

### 2.4. Uptake characterisation

#### 2.4.1. Effect of pH

The effect of pH on Sr uptake was investigated over a range of environmentally realistic values. Experimental solutions consisting of 1 mg  $L^{-1}$  Sr in 1 mM NaCl, were adjusted to between pH 2 and pH 8 using dilute NaOH or dilute  $HNO_3$  solutions. Ten mg of resin were weighed out into 15 mL centrifuge tubes and 10 mL of experimental solution were added. The resin-solution system was allowed to equilibrate for 24 h, then the pH was adjusted back to its starting value (the solutions become acidic following prolonged contact with the resin). After shaking for an hour and allowing the resin to settle, an aliquot of supernatant was extracted and the Sr concentration determined ( $A_s$ ). Blank samples were prepared in parallel, with no Sr added to the solution. An aliquot of the experimental solution was taken to determine the initial Sr mass concentration ( $A_0$ ).

#### 2.4.2. Major ion interference

The potential interferences investigated were calcium, potassium, magnesium and barium. For each potentially interfering element, solutions were made up over a range of environmentally realistic concentrations [18], from freshwater to seawater concentrations. Calcium concentrations ranged up to 500 mg  $L^{-1}$ , K up to 400 mg  $L^{-1}$  and Mg up to 1300 mg  $L^{-1}$ . Interference from Ba was investigated at a single concentration of 200  $\mu g L^{-1}$  [19]. For each experimental solution a Sr blank and a spiked Sr solution (100 mg  $L^{-1}$ ) was made up. Fifty mg of TK100 Resin were weighed into a 2 mL micro-centrifuge tube and 300  $\mu L$  of the experimental solution (Sr blank) were added. The tubes were shaken by hand and then placed on a shaker for 30 min to condition the resin, hydrating the resin and removing air bubbles. Then 1 mL of either the 100 mg  $L^{-1}$  Sr solution or the Sr blank solution was added. The samples were again shaken by hand and placed on a shaker for a further 1 h. The samples were centrifuged to separate the resin and supernatant. An aliquot of supernatant ( $A_s$ ) was taken from each sample and from each experimental solution ( $A_0$ ) to determine the Sr concentration by ICP-MS.

#### 2.4.3. Effect of ionic strength

The effect of ionic strength was investigated by making solutions of up to 500 mM NaCl. An aliquot was removed from each for use as a Sr blank solution, whilst the remaining experimental solutions were made up to a concentration of 100 mg  $L^{-1}$  Sr. The same experimental procedure as for the major ion interference experiment was then followed.

#### 2.4.4. Capacity

The resin capacity was determined by shaking 10 mg of resin with 10 mL of 1 mM NaCl, with Sr concentrations ranging from 0.5 mg  $L^{-1}$  to 19 mg  $L^{-1}$  for 24 h. A fraction of the supernatant was then removed and measured by ICP-MS to obtain  $A_s$ . The supernatant concentration was compared with the directly analysed experimental solution ( $A_0$ ) to calculate the uptake in terms of mg Sr  $g^{-1}$  resin.

#### 2.4.5. Uptake kinetics

Resin uptake kinetics were characterised by conditioning 10 mg of resin in 5 mL of 1 mM NaCl solution (Sr blank) for 30 min, then adding 5 mL of 1 mg  $L^{-1}$  Sr in 1 mM NaCl experimental solution and shaking for a range of time periods (2, 5, 10, 30, 60 and 120 min). After the allotted time period the sample was removed from the shaker and a fraction of the supernatant was extracted ( $A_s$ ) and measured by ICP-MS. The supernatant concentration was

compared with the directly analysed experimental solution ( $A_0$ ) to calculate the percentage uptake.

#### 2.4.6. Radio-element uptake

A 50 mL bulk solution of potential interferences was prepared consisting of  $10 \mu\text{g mL}^{-1}$  of each of U, Y, Pb, Bi, Cs, Co and Ba in MQ water. The same experimental procedure as for the major ion interference experiment was followed, with sample aliquots being measured by ICP-MS.

The potential interferences from Ra and Am were assessed in two different experiments. In both the resin was shaken with 1 mL spiked experimental solution for 1 h ( $^{226}\text{Ra} \sim 240 \text{ Bq mL}^{-1}$  and  $^{241}\text{Am} \sim 45 \text{ Bq mL}^{-1}$ ). The samples were centrifuged to separate the supernatant. One mL of solution was then removed (for  $A_s$ ) and transferred into a scintillation vial. Ten mL of scintillation cocktail were added to the vials, which were then measured by liquid scintillation counting (LSC). A comparison sample ( $A_0$ ) was prepared by pipetting 1 mL of the spiked experimental solution directly into a scintillation vial and adding cocktail. Blank samples were prepared by shaking the resin with unspiked solutions. All samples in the  $^{226}\text{Ra}$  experiment were counted quickly after preparation to avoid issues with ingrowth of  $^{226}\text{Ra}$  daughters.

### 2.5. Elution characterisation

#### 2.5.1. Elution reagents

To identify the optimum HCl and  $\text{HNO}_3$  wash and elution concentrations, a range of acid concentrations were made up consisting of 0.01, 0.1, 0.5, 1, 2, 3, 4, 6, 8 and 10 M. Aliquots of each acid concentration were taken and spiked with  $^{90}\text{Sr}/^{90}\text{Y}$  to give  $\sim 30 \text{ Bq mL}^{-1}$  experimental solutions. The same procedure as per the radium interference experiment was followed to the point where a 1 mL aliquot of the supernatant is removed (for  $A_s$ ). Here, the 1 mL supernatant aliquot was placed into a scintillation vial and dried down to incipient dryness on a hot plate. One mL of concentrated  $\text{H}_2\text{O}_2$  was then added and heated on the hot plate to decompose any colour. After allowing the  $\text{H}_2\text{O}_2$  to decompose, 3 mL of 1 M HCl were added to the scintillation vials and the vials gently shaken. Twenty mL of scintillation cocktail were added prior to measurement by LSC. Comparison samples (for  $A_0$ ) were prepared by pipetting 1 mL of the  $^{90}\text{Sr}/^{90}\text{Y}$  acid solution directly into a scintillation vial and following the same drying down procedure, prior to adding cocktail. Blank samples were prepared in the same way as unspiked acid solutions. Strontium and yttrium binding to TK100 Resin were calculated by counting the samples straight away and then again when secular equilibrium had re-established (after 3 weeks).

#### 2.5.2. Alternative elution reagents

In order to identify potential eluents, other than HCl and  $\text{HNO}_3$ , strontium uptake was characterised in the presence of a number of different reagents. For each reagent (0.1 M citric acid, 0.1 M oxalic acid and 0.05–0.4 M EDTA), 50 mg of resin were weighed into round-ended micro-centrifuge tubes and the same experimental procedure as the radium interference experiment was followed, with  $\sim 10 \text{ Bq}$  of  $^{90}\text{Sr}/^{90}\text{Y}$  being added. The samples were measured by LSC after leaving the samples for  $\sim 3$  weeks to allow secular equilibrium to re-establish.

#### 2.5.3. Element separation

To test a potential elution scheme on the resin,  $3 \times 2 \text{ mL}$  columns were made up by slurring TK100 Resin with MQ water and wet loading it onto the column until the resin volume of the column had reached the 2 mL mark ( $\sim 0.7 \text{ g}$  of dry resin). The columns were then pre-conditioned with 5 mL of MQ water. An

experimental loading solution consisting of  $100 \text{ mg L}^{-1}$  Sr, Ca, K, Mg, Ba, and Pb in MQ water was made up, 5 mL of which ( $\sim 500 \mu\text{g}$  of each element) were pipetted onto the column. The eluent fraction was collected in a vial. The column was then washed with  $5 \times 5 \text{ mL}$  of 8 M  $\text{HNO}_3$  and  $5 \times 5 \text{ mL}$  of 2 M HCl, with each 5 mL fraction collected separately. Aliquots of the collected fractions were then diluted with 0.1 M  $\text{HNO}_3$  and analysed by ICP-OES. The concentration of each element in each fraction was then compared with the concentration of each element in the experimental loading solution, which was directly analysed.

#### 2.5.4. Americium, bismuth, radium and uranium

The elution profiles of Am, Bi, Ra and U, were assessed in four separate experiments. For the Am and Bi experiments, 5 mL of 1 mM NaCl in loading solution spiked with either  $\sim 30 \text{ Bq } ^{241}\text{Am}$  or  $\sim 25 \text{ Bq } ^{207}\text{Bi}$  tracer was added to a 2 mL resin filled column. The column was then washed with  $5 \times 5 \text{ mL}$  of 8 M  $\text{HNO}_3$  and then  $5 \times 5 \text{ mL}$  of 2 M HCl. The resultant fractions were counted by gamma-spectrometry. In the Ra and U experiments, elution profiles were created by adding 5 mL of 1 mM NaCl loading solution, spiked with  $^{226}\text{Ra}$  ( $\sim 20 \text{ Bq}$ ) or  $^{233}\text{U}$  ( $\sim 5 \text{ Bq}$ ), to a 2 mL column and counting aliquots of the 5 mL eluent fractions by LSC.

#### 2.5.5. $^{90}\text{Sr}/^{90}\text{Y}$ separation

To assess  $^{90}\text{Sr}/^{90}\text{Y}$  separation, 5 mL of 1 mM NaCl loading solution spiked with  $\sim 50 \text{ Bq}$  of  $^{90}\text{Sr}/^{90}\text{Y}$  tracer was added to a pre-filled 2 mL column. The column was then washed with  $5 \times 5 \text{ mL}$  of 8 M  $\text{HNO}_3$ , and  $5 \times 5 \text{ mL}$  of 2 M HCl and the fractions collected. Aliquots of the collected eluent fractions were taken and measured by LSC. The samples were measured straight after the experiment and, again, after secular equilibrium had re-established.

### 3. Results and discussion

#### 3.1. Uptake characterisation

##### 3.1.1. Effect of pH

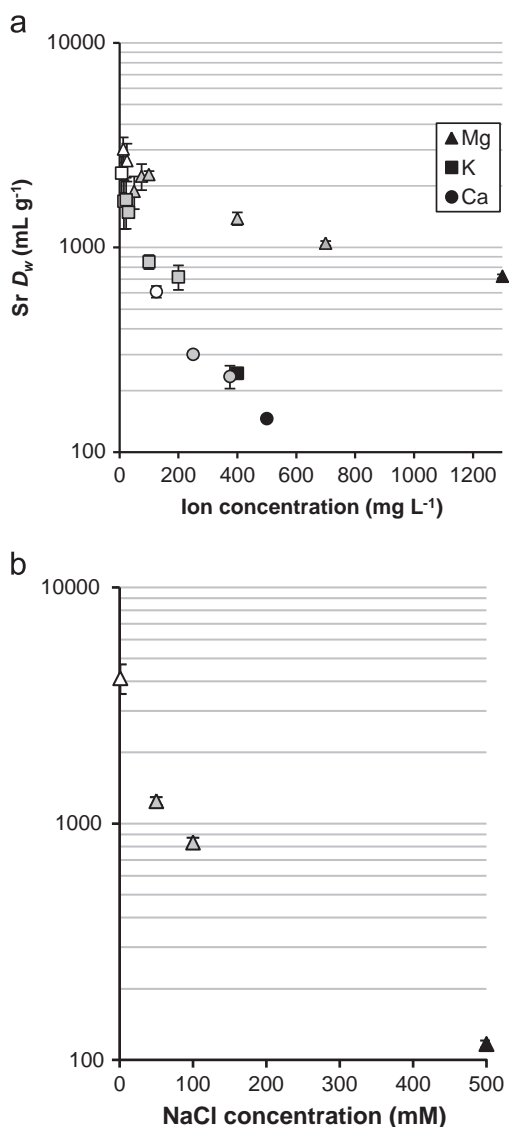
Strontium binding to the TK100 Resin is high across the pH values investigated with all  $D_w$  values  $> 10000 \text{ mL g}^{-1}$ , apart from pH 2 ( $3305 \pm 358 \text{ mL g}^{-1}$ ) and pH 6 ( $8897 \pm 1077 \text{ mL g}^{-1}$ ). This indicates the applicability of the resin to the typical range of pH values found in environmental waters ([Supplementary material 1](#)).

##### 3.1.2. Major ion interference

Calcium and potassium were shown to have the most significant effect on the strontium  $D_w$  ([Fig. 1a](#)), whilst magnesium had less of an effect. Calcium is usually present in higher concentrations in environmental waters than potassium, so is the more significant interference. However, for the environmentally realistic ion concentrations investigated, the strontium  $D_w$  values remained sufficiently high for the resin to function usefully, i.e.  $> 100 \text{ mL g}^{-1}$ . Additionally, strontium uptake was not affected by the presence of barium, with the strontium  $D_w$  value being  $5313 \pm 729 \text{ mL g}^{-1}$  (at  $200 \mu\text{g L}^{-1}$  Ba). The upper values of the ion concentration ranges used are similar to or greater than the most common 'high' ion concentration environmental water, namely seawater, meaning that the TK100 Resin is suitable for use with most environmental waters with respect to their major ion compositions [[18,20](#)].

##### 3.1.3. Effect of ionic strength

The strontium  $D_w$  decreases with increasing NaCl concentration ([Fig. 1b](#)). However, the  $D_w$  value is  $> 100 \text{ mL g}^{-1}$  for all tested



**Fig. 1.** (a) Strontium uptake on TK100 Resin in the presence of an increasing concentration of potassium, magnesium and calcium. (b) Strontium uptake on TK100 Resin in the presence of an increasing NaCl concentration (mean from triplicate experiments  $\pm$  standard error). For both parts, data are mean from triplicate experiments  $\pm$  standard error. Freshwater ion concentration values are open symbols, seawater values are closed symbols and values between these are coloured grey. Where error bars are not visible, they are smaller than the symbol size. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ionic strengths and as such the resin is applicable for use with the majority of environmental waters samples with respect to their ionic strength [18].

### 3.1.4. Capacity

It is possible to estimate the capacity of the resin by examining the Sr uptake in the presence of increasing Sr concentrations. Capacity is reached at the point where the resin uptake plateaus and no further Sr is bound. Using this method, the capacity of the resin can be estimated as being  $7.7 \pm 0.4$  mg Sr g<sup>-1</sup> resin (Supplementary material 2a). The capacity is lower than conventional Sr Resin (27 mg Sr g<sup>-1</sup>), but similar to other commercially available extraction chromatographic resins, e.g. TRU Resin (7 mg Nd g<sup>-1</sup>) [12,21]. Although the capacity of TK100 Resin

should be sufficient for the majority of terrestrial waters, care may have to be taken to ensure enough resin is used when separating <sup>90</sup>Sr from seawater samples, as seawater has a stable strontium concentration range of 7.2–7.8 mg L<sup>-1</sup> [22]. Care may also have to be taken to ensure the resin capacity is not exceeded if stable Sr is being used to determine the chemical recovery.

### 3.1.5. Uptake kinetics

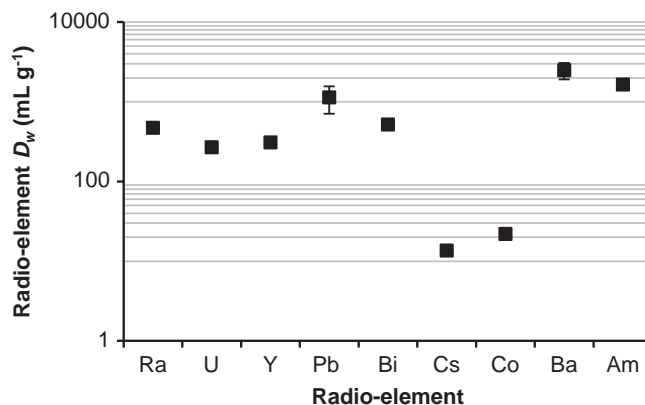
The kinetics of strontium uptake (adsorption rate) by the resin can be estimated by determining the time that it takes for equilibrium to be established between the resin and the solution. This occurred after 30 min, with  $95 \pm 4\%$  of strontium bound to the resin after this time (Supplementary material 2b). This adsorption rate is slower than conventional Sr Resin, which reaches equilibrium in around 3 min when using 5 M HNO<sub>3</sub> solutions [23]. Nonetheless, it is still similar to other commercially available extraction chromatographic resins that are used in column experiments [e.g. AC Resin], [24]. The results indicate that the resin is also suitable for batch experiments lasting longer than 30 min.

### 3.1.6. Radio-element uptake

Barium, lead and americium show a particularly high affinity for TK100 Resin ( $D_w$  values  $\geq 1000$  mL g<sup>-1</sup>, Fig. 2), whilst radium, bismuth, uranium and yttrium also exhibit significant binding ( $D_w$  values  $> 100$  mL g<sup>-1</sup>, Fig. 2). If procedures using the TK100 Resin analyse <sup>90</sup>Sr by radiometric methods, then radionuclides of these co-extracted elements (e.g. <sup>226</sup>Ra, <sup>210</sup>Pb, <sup>241</sup>Am or <sup>238</sup>U) could interfere with the measurement. Consequently, chromatographic separation of Sr from these radio-elements has been investigated (Section 3.2.2.).

Of particular significance is the low affinity of TK100 Resin for Cs and Co, as both <sup>137</sup>Cs and <sup>60</sup>Co are often co-present with <sup>90</sup>Sr at contaminated sites and after nuclear accidents [25–27]. As Cs and Co binding is low, chromatographic separation does not need to be considered.

The half-life of <sup>90</sup>Sr is much longer than the half-life of its daughter radionuclide <sup>90</sup>Y, meaning that <sup>90</sup>Y comes into secular equilibrium with separated <sup>90</sup>Sr after a period of  $\sim 3$  weeks. As <sup>90</sup>Y is also a pure  $\beta$ -emitter ( $E_{\max} = 2.28$  MeV) it has the potential to affect <sup>90</sup>Sr measurement if radiometric methods are used. Therefore, for these methods, the analyst requires either 100% separation of Sr and Y or none at all. Partial separation delays the analysis as it is necessary to wait for secular equilibrium prior to analysis (see Section 3.2.3.).



**Fig. 2.** Radio-element  $D_w$  values on TK100 Resin (mean from triplicate experiments  $\pm$  standard error). Where error bars are not visible, they are smaller than the symbol size.

### 3.2. Elution characterisation

As a range of radio-elements bind to TK100 Resin, the ability of the resin to chromatographically separate strontium from other interferences has been investigated.

#### 3.2.1. Elution reagents

In  $\text{HNO}_3$  media,  $^{90}\text{Y}$  binding decreases with increasing acid concentration from 0.01 M to 10 M  $\text{HNO}_3$  and the  $D_w$  is  $< 20 \text{ mL g}^{-1}$  in 1 M  $\text{HNO}_3$  and above (Fig. 3b). Strontium-90 binding decreases to  $D_w < 30 \text{ mL g}^{-1}$  in 0.5 M  $\text{HNO}_3$ , but then increases to  $D_w \sim 100 \text{ mL g}^{-1}$  in concentrations of 8 M  $\text{HNO}_3$  and above. The high affinity of  $^{90}\text{Sr}$  and low affinity of  $^{90}\text{Y}$  in  $\geq 8 \text{ M HNO}_3$  therefore makes it possible to retain  $^{90}\text{Sr}$  on the TK100 Resin whilst  $^{90}\text{Y}$  is eluted. Consequently, 8 M  $\text{HNO}_3$  can be used as a column wash reagent for the chromatographic separation of strontium from co-extracted radio-elements (see Section 3.2.2.). Compared to  $\text{HNO}_3$  there is less difference in the binding of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  in  $> 1 \text{ M HCl}$  (Fig. 3a) and as such  $\text{HCl}$  is less applicable for the separation of  $^{90}\text{Y}$  from  $^{90}\text{Sr}$ . However,  $^{90}\text{Sr}$  binding was lowest in 2 M  $\text{HCl}$  ( $10.8 \pm 0.9 \text{ mL g}^{-1}$ ), making it a suitable reagent for the chromatographic elution of  $^{90}\text{Sr}$ , provided that any co-extracted radio-elements have already been washed off (with 8 M  $\text{HNO}_3$ ) or are retained (see Section 3.2.2.).

A number of alternative reagents were also investigated. The  $D_w$  for Sr uptake was found to be  $38.1 \pm 1.1 \text{ mL g}^{-1}$  and  $1511.3 \pm 108.2 \text{ mL g}^{-1}$  in 0.1 M oxalic acid and 0.1 M citric acid respectively, making both organic acids unsuitable for use as elution reagents. Strontium uptake in 0.05–0.2 M EDTA was found to be negligible ( $D_w < 1 \text{ mL g}^{-1}$ ). However, mineral acids present fewer issues than EDTA as a sample matrix for both radiometric and mass spectrometric measurements. Therefore 2 M  $\text{HCl}$  was used as an elution agent to test chromatographic separation [28].

#### 3.2.2. Chromatographic separation

The alkali and alkaline earth metals calcium, potassium, magnesium and barium were all washed off the 2 mL column with 15 mL of 8 M  $\text{HNO}_3$  (Fig. 4). A range of radio-elements were shown to have a high affinity for the TK100 Resin (Fig. 2). Of these radium, bismuth and americium were eluted with 15 mL of 8 M  $\text{HNO}_3$  (Fig. 5). No uranium or lead was detected in any of the fractions analysed, indicating that uranium and lead are strongly retained on the resin. Strontium was eluted separately to all the other

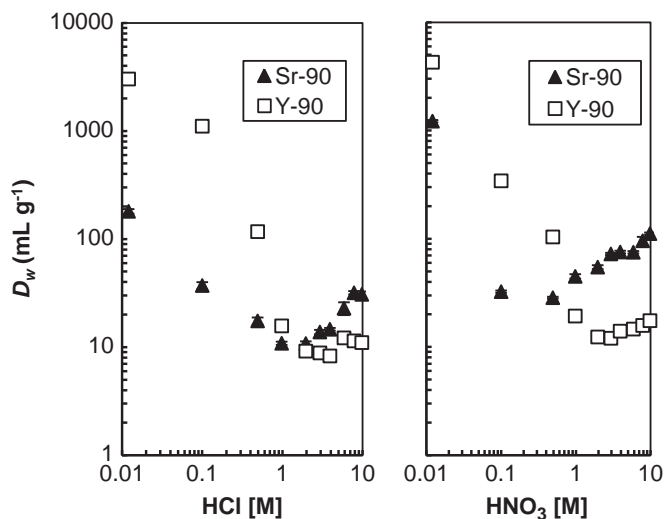


Fig. 3. Strontium-90/yttrium-90 binding on TK100 Resin over a range of  $\text{HCl}$  and  $\text{HNO}_3$  acid concentrations (mean from triplicate  $\pm$  standard error). Where error bars are not visible, they are smaller than the symbol size.

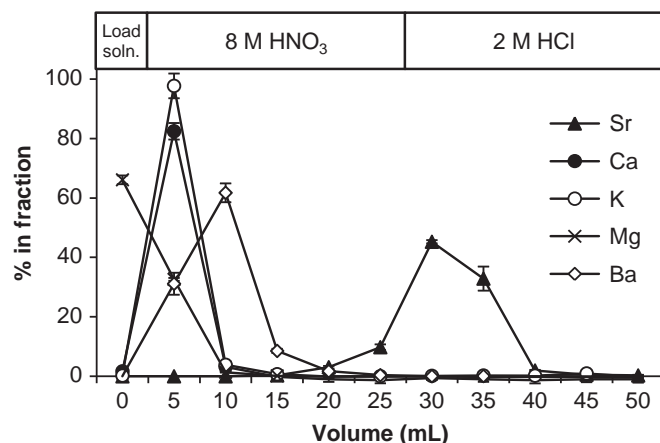


Fig. 4. An elution profile for 5 elements loaded onto a 2 mL TK100 Resin column. Data are mean from triplicate  $\pm$  standard error. Where error bars are not visible, they are smaller than the symbol size.

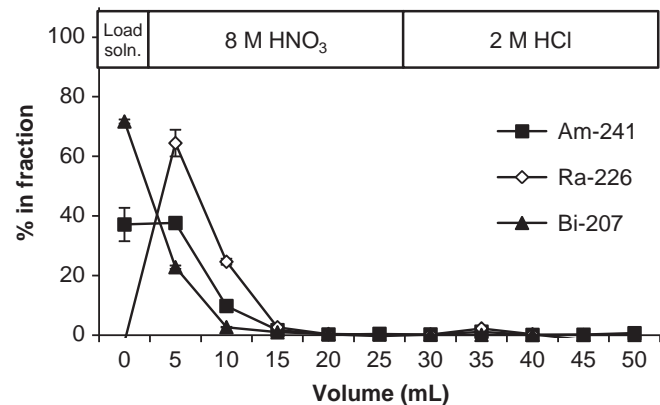


Fig. 5. An elution profile for Am, Ra and Bi loaded onto a 2 mL TK100 Resin column. Data are mean from triplicate  $\pm$  standard error. Where error bars are not visible, they are smaller than the symbol size.

elements, with 20 mL of 2 M  $\text{HCl}$  (Fig. 4). The strontium recovery was  $93.0 \pm 3.0\%$  (mean  $\pm$  standard error).

The ability of the TK100 Resin to separate strontium from potassium, lead, americium, radium and uranium is important, as the radionuclides  $^{40}\text{K}$ ,  $^{210}\text{Pb}$ ,  $^{241}\text{Am}$ ,  $^{226}\text{Ra}$  and the isotopes of U occur at contaminated nuclear sites and after nuclear accidents and can interfere with the radiometric measurement of  $^{90}\text{Sr}$  [4,29].

Figs. 4 and 5 show that strontium can be successfully separated from a range of elements on TK100 Resin to give a clean fraction, free from possibly interfering radio-elements. The TK100 Resin should enable the creation of simple procedures with samples that can be readily measured radiometrically.

#### 3.2.3. $^{90}\text{Sr}/^{90}\text{Y}$ separation

Fig. 6 shows that the applied elution scheme successfully separates  $^{90}\text{Sr}$  from  $^{90}\text{Y}$ . Most  $^{90}\text{Y}$  passes straight through the column in the load solution ( $60.2 \pm 1.5\%$ ) whilst all remaining  $^{90}\text{Y}$  is washed off the column in 10 mL 8 M  $\text{HNO}_3$ . The total separation of  $^{90}\text{Y}$  from  $^{90}\text{Sr}$  was confirmed by re-counting the samples after 3 weeks when secular equilibrium had re-established. As the elution scheme is capable of separating  $^{90}\text{Y}$  from  $^{90}\text{Sr}$ , the TK100 Resin is applicable to rapid determination procedures, as  $^{90}\text{Sr}$  samples can be measured immediately after separation, with no need to wait  $\sim 3$  weeks for secular equilibrium to re-establish. The authors have used TK100 Resin in the development of a new, rapid

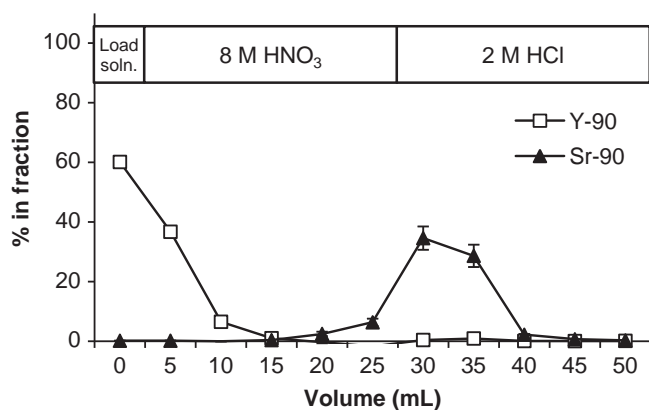


Fig. 6. An elution profile for  $^{90}\text{Sr}$  and  $^{90}\text{Y}$ , loaded onto a 2 mL TK100 Resin column. Data are mean from triplicate  $\pm$  standard error. Where error bars are not visible, they are smaller than the symbol size.

determination procedure which was tested on both spiked and contaminated real environmental samples [30].

#### 4. Conclusions

A new Sr selective resin has been produced for the direct binding of  $^{90}\text{Sr}$  from environmental water samples. The resin consists of a mixture of di(2-ethyl-hexyl)phosphoric acid (HDEHP) and 4,4' (5')-bis-t-butylcyclohexano-18-crown-6 (DtBuCH18C6) sorbed onto Amberchrom CG-71 polymeric support beads (TK100 Resin). The TK100 Resin was characterised over a range of environmentally realistic pH values, ionic strengths and potential competing ion interferences and was shown to have a sufficient strontium uptake to permit the binding of  $^{90}\text{Sr}$  from the majority of environmental water samples. The resin capacity was found to be high enough for the majority of environmental waters and binding of strontium was found to have reached equilibrium in 30 min. Potentially interfering co-extracted radioelements have been identified and the complete chromatographic separation of  $^{90}\text{Sr}$  from the co-extracted radio-elements, including  $^{90}\text{Y}$ , has been shown to be possible. The elution characteristics of the resin can thus be used to create a clean  $^{90}\text{Sr}$  sample that can be measured straight away by radiometric means, with no need for complicated spectral processing or waiting for secular equilibrium to be reached.

Unlike conventional Sr Resin, TK100 Resin has the necessary characteristics to enable the direct binding and simple separation of  $^{90}\text{Sr}$  from a range of environmental waters. Thus TK100 Resin is applicable to the development of rapid determination procedures. Such rapid determination procedures would enable the high through-put of water samples required by monitoring schemes at contaminated nuclear sites and importantly, the rapid analysis of water samples in cases of nuclear accidents.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2014.06.041>.

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