

# **A Rapid and Efficient Automated Method for the Sequential Separation of Plutonium and Radiostrontium in Seawater**

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## Abstract

In this work, a novel method for the simultaneous separation of Pu and  $^{90}\text{Sr}$  in seawater is proposed that is based on precipitation and extraction chromatography with an automated radionuclide separator. In particular, Pu from seawater is co-precipitated with  $\text{Fe}(\text{OH})_2$ ;  $^{90}\text{Sr}$  is precipitated as  $\text{SrCO}_3$ . The precipitates are then dissolved in  $\text{HNO}_3$  and sequentially separated using TEVA and Sr-resin columns on an automated radionuclide separator (MARS, Modular Automated Radionuclide Separator). The yield of Pu and Sr from 1 L and 10 L of seawater ranged between 50 and 74 %, and between 77 and 95 %, respectively. The separation time for 1 L and 10 L seawater samples was estimated as 3.2 h and 9.4 h, respectively.

## 1 Introduction

2 Dangerous artificial radionuclides such as cesium, plutonium and  $^{89/90}\text{Sr}$  are released into the  
3 environment as a result of accidents in nuclear facilities or of nuclear weapon testing [1, 2]. To achieve a  
4 full radiological protection of the environment, it is crucial to develop efficient methods that allow the  
5 monitoring of these artificial radionuclides. After the Fukushima Daiichi Nuclear Power Plant (FDNPP)  
6 accident, the dramatic increase in  $^{134/137}\text{Cs}$  concentration in seawater has been well documented [3]. In  
7 contrast, plutonium and  $^{89/90}\text{Sr}$  concentrations in seawater have been rarely reported [4]. This may be due  
8 to i) the difficulty of achieving an efficient separation of these radionuclides; ii) the tedious sample  
9 treatment needed to determine the alpha/beta emitters as opposed to the analysis of gamma emitters in  
10 seawater. Thus, the development of a rapid and valid analytical method is essential to assess the potential  
11 hazards, and to allow early decision-making in case of a nuclear accident.

12 Sequential separation of Pu and Sr in environmental samples is a promising technique that can address  
13 these issues. The great advantage is that chemical separation is performed only once for the two  
14 radionuclides. To perform the sequential separation, several approaches have been proposed including  
15 combined procedures of the anion-exchange resin and Sr-resin [5] or TRU and Sr resin [6]. Although the  
16 above mentioned methods are normally reliable and accurate, most of them are operated manually and are  
17 therefore labor intensive and time-consuming because of employing the gravity flow method. Maxell [7]  
18 reported a sequential separation method for actinides and  $^{89/90}\text{Sr}$  in environmental aqueous samples. The  
19 method was based on the use of TEVA and Sr resins stacked on a vacuum box, which could reduce just  
20 the analytical time as compared to the gravity-flow method. However, it still needs much manual  
21 operations such as handling reagents.

22 In this study, we propose a sequential separation of Pu and  $^{90}\text{Sr}$  from seawater using automated  
23 separation system with minimal operational work. Pu and  $^{90}\text{Sr}$  from seawater were concentrated by co-  
24 precipitation/precipitation like  $\text{Fe}(\text{OH})_2$  and  $\text{SrCO}_3$ . Then they were purified by TEVA and Sr resin. The  
25 behavior of Pu on TEVA and Sr on Sr-resin was investigated to optimize the operational procedure. The  
26 performance of this method was tested for 1 L and 10 L seawater samples spiked with  $^{238}\text{Pu}$  and  $^{90}\text{Sr}$ . This  
27 is the intermediate study to develop the fully automated sequential separation system for radionuclides.

## 29 **Experimental**

### 30 *Reagents*

31 Powders for TEVA (100~150  $\mu\text{m}$ ) and Sr resin (100~150  $\mu\text{m}$ ) were obtained from Eichrom  
32 [Technologies](#), Inc. (Illinois, USA). The resins were swollen in water for 2 h prior to use. All solutions  
33 were prepared using de-ionized water ([DIW](#), MilliQ-Plus, 18M $\Omega$ ).  $^{241}\text{Pu}$ ,  $^{242}\text{Pu}$  and  $^{90}\text{Sr}$  were purchased  
34 from the National Institute of Standards and Technology (NIST, Gaithersburg, MA, USA).  $^{238}\text{Pu}$  was  
35 obtained from [Korea Research Institute of Standards and Science](#) (KRISS, Daejeon, Korea).  $^{241}\text{Pu}$  was  
36 used to estimate the behavior of Pu on the TEVA.  $^{242}\text{Pu}$  was used as a tracer in the whole procedure.  $^{85}\text{Sr}$   
37 was obtained from Eckert & Ziegler Analytics Inc (GA, USA) and used as a tracer.

38

### 39 *Determination*

40 Cations such as Sr, Ca and Mg ions were measured by Inductively Coupled Plasma Optical Emission  
41 Spectrometers (ICP-OES, Varian, USA).  $^{85}\text{Sr}$  was analyzed by [gamma spectrometer \( \$\gamma\$ -spectrometer,](#)  
42 [HPGe detector, Canberra, USA\)](#). Alpha spectrometer ( $\alpha$ -spectrometer, Ortec, USA) was used for the  
43 analysis of  $^{238/242}\text{Pu}$ .  $^{238/242}\text{Pu}$  in 30 ml 1M HCl was taken in 100 ml Teflon beaker. It was evaporated to  
44 dryness at 150  $^{\circ}\text{C}$  and dissolved in NaHSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> solution. Then it was electrodeposited on  
45 stainless steel discs at a constant current of 0.9 A from (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution for 2 h. Liquid Scintillation  
46 Counter (LSC, Quantulus 1220, Perkin Elmer, USA) was used for the analysis of  $^{241}\text{Pu}$ ,  $^{90}\text{Y}$  ingrowth  
47 from  $^{90}\text{Sr}$ .  $^{241}\text{Pu}$  in 30 ml 1M HCl was transferred in 20 ml glass vial and evaporated to dryness at 110  $^{\circ}\text{C}$ .  
48 8 mL of a 0.05 M HNO<sub>3</sub> solution was added to each glass vial and mixed with 12 mL of Ultima Gold  
49 LLT. For analysis of  $^{90}\text{Sr}$  by LSC, 0.5 ml of Sr carrier (10 mg ml<sup>-1</sup>) was taken in 50 ml volume of conical  
50 tube. The pH of the solution was adjusted to 10 with 25 % ammonia. Then, 5 mL of a saturated Na<sub>2</sub>CO<sub>3</sub>  
51 solution was added to precipitate SrCO<sub>3</sub>. The precipitate was transferred in a 20 mL glass vial and washed  
52 with ethanol. It was dried at 80  $^{\circ}\text{C}$  and dissolved in 8 mL of 0.05 M HNO<sub>3</sub>. Unfortunately SrCO<sub>3</sub>  
53 containing stable Sr 70 mg was not dissolved in 8 ml of 0.05 M HNO<sub>3</sub>. Therefore, 8 ml of 0.5 M HNO<sub>3</sub>  
54 was used to dissolve SrCO<sub>3</sub>. Then  $^{90}\text{Y}$  fraction from  $^{90}\text{Sr}$  was determined on LSC using Cerenkov  
55 counting.

56

57 *Samples*

58 Seawater samples (salinity 3.2 %) were collected in the East Sea. All seawater samples were filtered  
59 through a cellulose filter (0.45  $\mu\text{m}$ ). The samples were acidified to pH 2 with HCl and spiked with  $^{90}\text{Sr}$   
60 (94 Bq) and  $^{238}\text{Pu}$  (0.0117 Bq).  $^{242}\text{Pu}$  (0.029 Bq) and  $^{85}\text{Sr}$  (1 Bq) were added as tracers for Pu and Sr,  
61 respectively. The concentrations of Ca, Mg and Sr were 350  $\text{mg L}^{-1}$ , 1150  $\text{mg L}^{-1}$  and 6.5  $\text{mg L}^{-1}$ ,  
62 respectively.

63

64 *Column preparation*

65 The powders of TEVA and Sr resin swollen in DIW were packed into a borosilicate glass column  
66 (BenchMark, Omnifit, USA). The Sr resin was packed in a 10 mm  $\times$  100 mm column and in a 15 mm  $\times$   
67 400 mm column to achieve the desired resin volume. 4 ml (BV) of Sr resin (1.2 g) was used for the  
68 purification of Sr in 1 L of seawater. 35 mL (BV) Sr resin (12 g) was used to separate Sr from 10 L of  
69 seawater. TEVA resin was packed in a 10mm  $\times$  100mm column to obtain a BV of 4 mL (1.2 g) for 1 L  
70 seawater or 6 mL (1.8 g) for 10L seawater, respectively.

71

72 *Apparatus – automated radionuclide separator*

73 The entire purification procedure was performed with MARS developed in our laboratory [8]. It is based  
74 on fluidic systems using column and can control the flow rate and the types of the reagents in the system.  
75 This allows a significant reduction of working labor. MARS was originally designed for the automated  
76 single-radionuclide separation of four samples. In this study, it was modified to allow the sequential  
77 separation of two radionuclides in a single sample with a minimum manual work. The sample was loaded  
78 on TEVA/Sr resin (Figure 1-a). After all Sr in sample was eluted from TEVA column, Sr resin column  
79 was manually disconnected from MARS (Figure 1-b). Washing solutions and eluent for Pu were passed  
80 through TEVA column. Then, TEVA column was replaced by Sr resin column (figure 1-(c)). Washing  
81 solutions and eluent for Sr were passed through Sr resin. Except connection/disconnection of columns, all  
82 operational conditions (e.g., loading, washing and elution flow rates and the chemical composition of  
83 reagents) were controlled via software developed in our laboratory [8]. The 6-inlet ports flow selection  
84 valve (6I-FSV) is used to select different reagents, and the 2-inlet ports flow selection valve (2I-FSV) is

85 used to select a sample or a reagent. A 3-way flow distribution valve (3W-FDV) was used to obtain the  
86 optimized volume of eluents in the elution step.

87

#### 88 *Concentration of Pu and Sr in seawater*

89 The filtered seawater samples were acidified to pH 2 using HCl to avoid loss of actinides. This point is  
90 crucial because hydrolyzed actinides have a great affinity to the surfaces of containers [9]. 1 g of  $\text{Na}_2\text{S}_2\text{O}_5$   
91 was added per 1 L seawater to adjust to oxidize all Pu to Pu(III). After that, 30 mg of  $\text{Fe}^{3+}$  as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$   
92 was added with stirring. It adjusted to pH 10 by 25 % ammonia to precipitate  $\text{Fe}(\text{OH})_2$ . 15g of  $\text{Na}_2\text{CO}_3$   
93 was added to precipitate  $\text{SrCO}_3$  with intense mixing for 30 min. Concentrated  $\text{HNO}_3$  was added to  
94 dissolve the precipitate. Pu(III) can be oxidized to Pu(IV) with  $\text{HNO}_3$  [10]. The concentration of  $\text{HNO}_3$  in  
95 the sample medium was adjusted to 6 M, before introducing it into the TEVA and the Sr-resin columns.

96 Concerning the recovery of Sr, 1 L seawater samples were tested using different amounts of  $\text{Na}_2\text{CO}_3$   
97 (from 5 g to 15 g), as described above. The precipitates were filtered by a glass fiber filter (GF/F,  
98 Whatman). Concentration of Ca, Mg and Sr in the filtrate were analyzed by ICP-OES and compared with  
99 the initial concentration. Recovery of Sr in 1 L seawater was increased with the amount of  $\text{Na}_2\text{CO}_3$  and  
100 was over 90 % with 15 g  $\text{Na}_2\text{CO}_3$  (table 1). Most of divalent cations such as Ca and Mg were precipitated  
101 as hydroxide and carbonate salt, also.

102

#### 103 *Behavior of Sr and Pu on TEVA*

104 For efficient sequential separation of Pu and Sr, it is important to determine when Sr is eluted from  
105 TEVA. TEVA and Sr resin column should be separated at that time. 25 mL of a 6 M  $\text{HNO}_3$  solution,  
106 containing  $^{85}\text{Sr}$  and 10 mg of stable Sr, was passed through the 4 ml TEVA at  $2 \text{ ml min}^{-1}$ . After passing  
107 the sample, 30 ml of 8 M  $\text{HNO}_3$  was added to remove Sr at  $2 \text{ ml min}^{-1}$ . Every 3ml of solution coming  
108 from TEVA was taken in 20 ml plastic vial and  $^{85}\text{Sr}$  was determined (Fig 2-a). Sr was stripped from  
109 TEVA resin with additional 15 ml of 8 M  $\text{HNO}_3$ .

110 The elution behavior of Pu on TEVA 4 ml (BV) and 6 ml (BV) column was determined by LSC using  
111  $^{241}\text{Pu}$  (Fig 2-b). 20 mL of a 6 M  $\text{HNO}_3$  solution spiked with  $^{241}\text{Pu}$  was passed through the TEVA at  $2 \text{ ml}$   
112  $\text{min}^{-1}$ .  $^{241}\text{Pu}$  was eluted with 2 ml of 1 M HCl using about 36 ml 1 M HCl at  $1 \text{ ml min}^{-1}$ .

113

114 *Behavior of Sr on Sr resin*

115 Fig. 3 shows the elution behavior of Sr on Sr resin column. 10 mg and 70 mg of stable Sr in 8 M HNO<sub>3</sub>  
116 was passed through Sr resin 4 ml (BV) and 36 ml (BV) column at 2 ml min<sup>-1</sup>, respectively. DIW was used  
117 to elute Sr from Sr resin at 2 ml min<sup>-1</sup>.

118

119 *Purification of Pu and Sr on MARS*

120 Processing standards were prepared to test purification steps of Pu and Sr on MARS. It contains <sup>241</sup>Pu,  
121 <sup>85</sup>Sr and 7 mg stable Sr in 20 ml of 6 M HNO<sub>3</sub>. It was loaded on 4 ml TEVA/4 ml Sr resin columns at 2  
122 ml min<sup>-1</sup>. Additional 15 ml 8 M HNO<sub>3</sub> was used to strip Sr from TEVA at 2 ml min<sup>-1</sup>. As previously  
123 described, Sr resin was removed from MARS. 20 ml of 1 M HNO<sub>3</sub> solution and 30 mL of 9 M HCl  
124 solution were in order used to wash TEVA at 2 ml min<sup>-1</sup>. 24 ml of 1 M HCl was used to elute Pu at 1 ml  
125 min<sup>-1</sup>. Sr resin column was then reconnected on MARS instead of TEVA column. 20 ml of 8 M HNO<sub>3</sub>  
126 was used to wash Sr resin at 2 ml min<sup>-1</sup>. Sr was eluted with 20 ml DIW at 2 ml min<sup>-1</sup>.

127

## 128 **Results and discussion**

129 *Recommend procedure for simultaneous Pu and Sr from seawater*

130 Based on above results, we propose the sequential separation of Pu and Sr from seawater as follows:

- 131 1. Add 1 g of Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and 30 mg of Fe<sup>3+</sup> with stirring
- 132 2. Adjust of pH to 10 by ammonia and then add 15 g of Na<sub>2</sub>CO<sub>3</sub> with mixing for 30 min
- 133 3. Filter the sample by GF/F and dissolve the precipitates in concentrated HNO<sub>3</sub>
- 134 4. Pre-condition TEVA (4 ml)/Sr resin (4ml) with 8M HNO<sub>3</sub> and load sample at 2 ml min<sup>-1</sup>
- 135 5. Wash TEVA/Sr resin with 15 ml of 8 M HNO<sub>3</sub> at 2 ml min<sup>-1</sup> and then disconnect Sr resin column  
136 from MARS
- 137 6. Wash TEVA with 15 ml 1 M HNO<sub>3</sub> and 30 ml 9 M HCl at 2 ml min<sup>-1</sup>
- 138 7. Elute Pu from TEVA with 24 ml of 1 M HCl at 1 ml min<sup>-1</sup>
- 139 8. Disconnect TEVA column and re-connect Sr resin column on MARS
- 140 9. Wash Sr resin with 20 ml 8 M HNO<sub>3</sub> and elute Sr with 20 ml DIW at 2 ml min<sup>-1</sup>

141 The amount of reagents and bed volume of TEVA/Sr resin for 10 L seawater was written in Fig 4. The  
142 separation time of Pu and Sr for 1 L and 10 L seawater was measured as 3.2 h and 9.4 h, respectively.

143

144 *Determination of <sup>90</sup>Sr and <sup>238</sup>Pu in spiked seawater by proposed procedure*

145 Table 2 shows the analytical results for five samples of 1 L seawater and two samples of 10 L, spiked  
146 with 94.2 Bq of <sup>90</sup>Sr and 0.0115 Bq of <sup>238</sup>Pu. The average <sup>90</sup>Sr result was  $91.6 \pm 2.1$  Bq L<sup>-1</sup> (1 SD,  
147 standard deviation) with an average bias of -2.7 %. The average <sup>238</sup>Pu was  $0.0116 \pm 0.0008$  Bq L<sup>-1</sup> (1 SD)  
148 with an average bias of -1.1 %. These excellent results confirmed that the proposed procedure is very  
149 reliable. The recovery of Sr and Pu was  $87.8 \pm 6.5$  % and  $62.5 \pm 10.4$  % (1 SD) for sets of seawater,  
150 respectively.

151 The recovery of Pu in this method is relatively lower than obtained by Maxwell et al. ( $87.7 \pm 6.4$  %)  
152 [11]. When the processing standards were followed just the purification steps on MARS, the recovery of  
153 Pu was higher than 90 %. The discrepancy mentioned above may result from incomplete valence  
154 adjustments of Pu in concentration step before introducing to TEVA resin. The step for the valence  
155 adjustments of Pu should be improved for better recovery of Pu. For 10 L seawater, the recovery of Sr  
156 was lower than that in 1 L seawater. Although Sr recovery on Sr resin was quantitative for Ca level up to  
157 320 mg per Sr resin 2 ml (BV), chemical yields declined above that level [12]. Most of Ca in seawater  
158 was precipitated with Sr in the concentration step (table 1). It is shown that high level of Ca in sample  
159 loaded on Sr resin results in a small deterioration of Sr recovery for 10 L seawater.

160 The minimum detectable activity (MDA) for radionuclides using this method with alpha spectrometry  
161 and LSC was calculated with the equations from Currie [13]:

$$MDA = \frac{(2.71 + 4.65\sqrt{BKG \cdot C_T})}{60 \times C_T \times R \times E_C \times V_{SMP}}$$

162 where BKG is the background count rate; C<sub>T</sub> is the counting time; R is the chemical recovery; V<sub>SMP</sub> is  
163 the sample volume (L); E<sub>C</sub> is the detector counting efficiency; 60 is the conversion factor from dpm to Bq.  
164 The MDA for <sup>90</sup>Sr is 5.2 mBq L<sup>-1</sup> with 100 min counting, V<sub>SMP</sub> 10 L, BKG 10 cpm, E<sub>C</sub> 60% and R 80.0 %.  
165 MDA for <sup>238</sup>Pu is 39 μBq L<sup>-1</sup> with 2 days counting, V<sub>SMP</sub> 10 L, BKG 1 count, E<sub>C</sub> 20% and R 54.2 %.

166

167 A large-volume sampling (typically 50 ~ 200 L) is necessary for a reliable analysis of Pu and Sr in  
168 seawater because of their low concentration [14, 15]. However, in an emergency scenario, such as the  
169 FDNPP accident, smaller amounts of seawater can be used to estimate the radiological activity. This is  
170 because the concentration of a radionuclide increases drastically after an accident. Casauberta et al. [16]  
171 reported that the level of  $^{90}\text{Sr}$  ranged between 8 and 85  $\text{mBq L}^{-1}$  in surface water which was 10 times  
172 larger than the pre-Fukushima level ( $1.2 \text{ mBq L}^{-1}$ ). In this study, the target sample aliquot is about 10 L,  
173 which is 1/10 of a typical sample volume for background-level analysis. In emergency situation,  $^{89}\text{Sr}$  level  
174 is high, also. The analysis of  $^{89}\text{Sr}$  was not shown in this work. However, if  $^{89/90}\text{Sr}$  results are required,  
175 Cerenkov counting is useful technique for determination of  $^{89/90}\text{Sr}$  [17].

176

## 177 **Conclusion**

178 A procedure based on an automated radionuclide separator was proposed to simultaneously separate  
179  $^{238}\text{Pu}$  and  $^{90}\text{Sr}$  from seawater with a reliable performance. The separation time was measured to be 3.2 h  
180 and 9.4 h, for the 1 L and 10 L seawater samples, respectively. Although MDA in this approach is higher  
181 than that of the background levels of  $^{238}\text{Pu}$  and  $^{90}\text{Sr}$  in the ocean, our method is suitable in the event of  
182 emergencies, in which concentration of plutonium and  $^{89/90}\text{Sr}$  drastically increases. Our results show that  
183 MARS has a small limit such as column replacements. The development of a fully automated procedure  
184 is currently being investigated in our laboratory for a safe and rapid sequential separation of several  
185 radionuclides.

186

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249

**Table 1. Removal of Sr in 1L of seawater with amount of Na<sub>2</sub>CO<sub>3</sub>**

Na <sub>2</sub> CO <sub>3</sub>	Removal of Sr <sup>a</sup> (%)	Removal of Ca <sup>b</sup> (%)	Removal of Mg <sup>b</sup> (%)
5g	55.0 ± 3.9	99.1	97.9
10g	84.9 ± 1.2	99.5	96.9
15g	92.3 ± 4.5	98.7	96.3

<sup>a</sup> sample number = 3, “average ± 1 standard deviation”; <sup>b</sup> sample number = 1

**Table 2. <sup>90</sup>Sr and <sup>238</sup>Pu results in a set of seawater samples**

Seawater	Recovery (%)	<sup>90</sup> Sr reference value (Bq) <sup>a</sup>	<sup>90</sup> Sr measured value (Bq)	Difference (%)	Recovery (%)	<sup>238</sup> Pu reference value (Bq) <sup>b</sup>	<sup>238</sup> Pu measured value (Bq)	Difference (%)
1L	94.9	94.3	90.3	-4.2	73.7	0.0117	0.0128	9.4
	85.4	94.3	89.2	-5.4	51.5	0.0117	0.0107	-8.5
	95.0	93.9	95.2	1.4	58.0	0.0117	0.0117	-0.2
	90.1	94.3	92.0	-2.4	72.8	0.0117	0.0125	6.8
	89.5	94.3	91.2	-3.3	73.5	0.0117	0.0107	-8.5
10L	82.5	94.1	93.2	-1.0	56.5	0.0117	0.0114	-2.6
	77.5	94.2	90.2	-4.2	51.8	0.0117	0.0112	-4.3
Avr.	87.8		91.6	-2.7	62.5		0.0116	-1.1
SD	6.5		2.1		10.4		0.0008	
Processing standard <sup>c</sup> (n=3)	92.1 ± 1.2				91.9 ± 0.6			

<sup>a</sup> uncertainty 3.0 % (1 SD)

<sup>b</sup> uncertainty 5.0 % (1 SD)

<sup>c</sup> Processing standards are used to test the purification step (1 SD)

Figure 1. Schematic flow diagram of MARS (R1: 8 M HNO<sub>3</sub>, R2: 1 M HNO<sub>3</sub>, R3: 9 M HCl, R4: DIW, In the column section: solid line (1), connection of TEVA and Sr-resin column; dash line (2), connection only with TEVA column; dot line (3), connection only with Sr-resin column.

Figure 2. Behavior of (a) Sr and (b) Pu on the TEVA column (open triangle: Sr on TEVA 4 ml (BV); open circle: Pu on TEVA 6 ml (BV); closed circle: Pu on TEVA 4 ml (BV)).

Figure 3. Elution behavior of Sr on Sr resin (open circle: Sr resin 35 ml (BV); closed circle: Sr resin 4 ml (BV)).

Figure 4. Flow chart of simultaneous separation of Pu and Sr in seawater using TEVA and Sr resin columns.

Figure 1

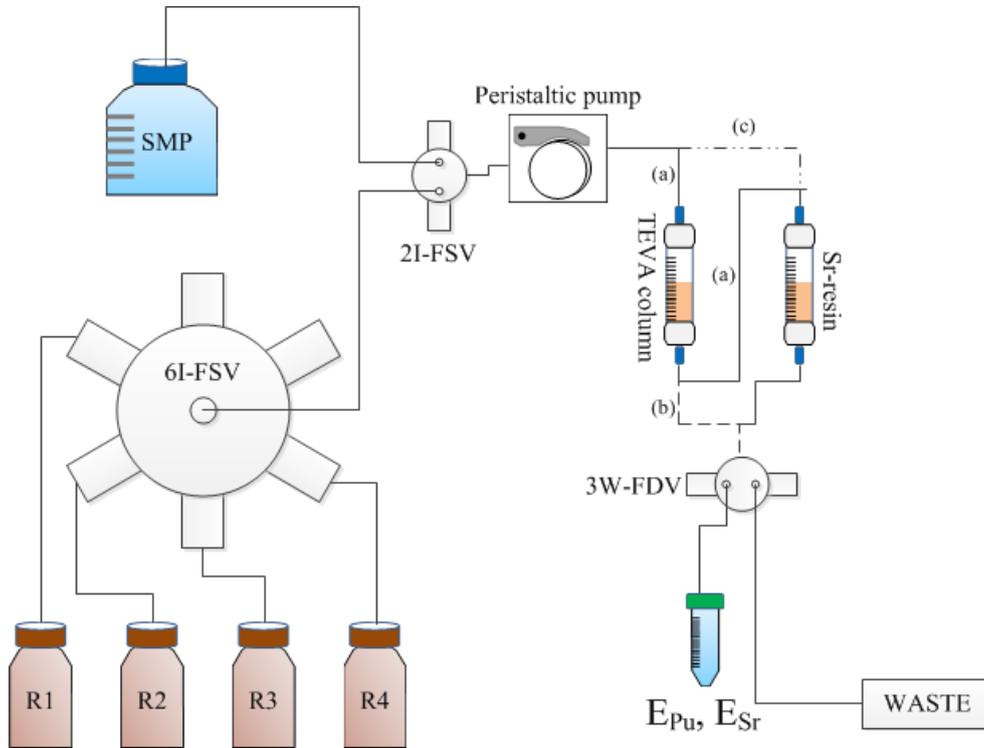


Figure 2

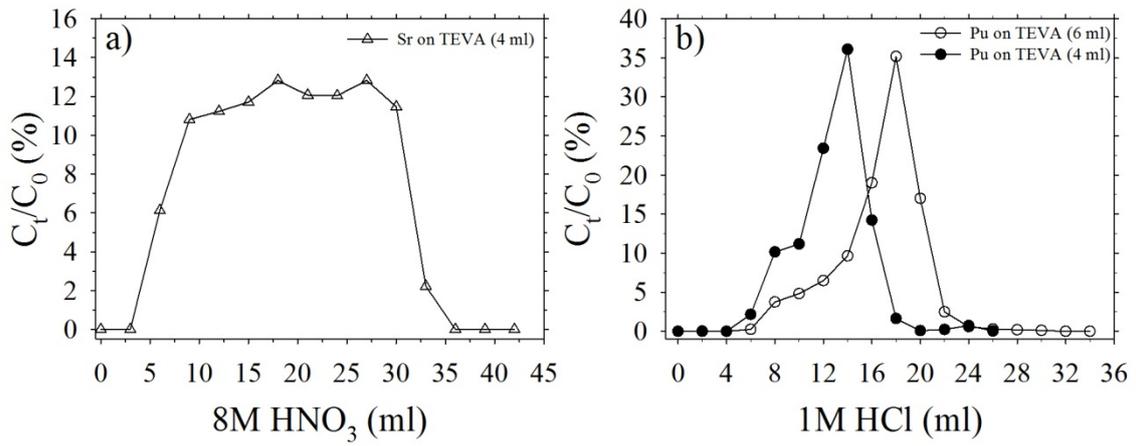


Figure 3

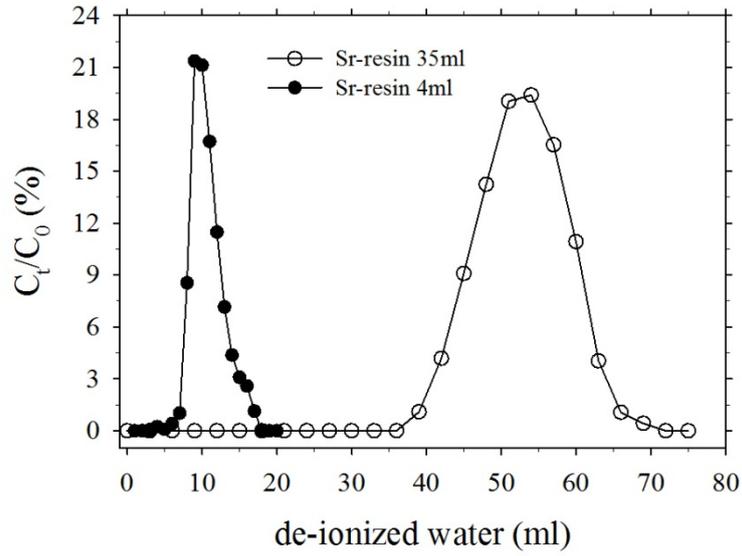


Figure 4

