

# Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26

# ***Rapid determination of plutonium in water samples using vacuum box system separation and low background liquid scintillation counter measurement***

Bo Liu<sup>1,3</sup>, Keliang Shi<sup>1,2</sup>\*, Gaoyang Ye<sup>1</sup>, Yaming Li<sup>1</sup>, Wangsuo Wu<sup>1,2\*</sup>

1. Radiochemistry Lab, School of Nuclear Science and Technology, Lanzhou University, Lanzhou, 730000, China.

2. Key Laboratory of Special Function Materials and Structure Design, Ministry of Education.

3. Northwest Nuclear and Radiation Safety Supervision Station, Department of Environmental Protection, Lanzhou, 730000, China.

## **Abstract**

27 An analytical method for rapid determination of <sup>239+240</sup>plutonium in  
28 environmental liquid sample was developed. The separation of plutonium from  
29 matrix and interfering elements was performed using anion exchange  
30 chromatographic columns executed in a vacuum box system. Under the optimized  
31 conditions, the chemical yield of plutonium is better than 90% and the  
32 decontamination factors for uranium, thorium and americium ranged from 10<sup>3</sup> to 10<sup>4</sup>  
33 for 5 L water samples. The concentrations of plutonium were measured by detecting  
34  $\alpha$  decay of <sup>239+240</sup>plutonium using low background liquid scintillation counter (LSC).  
35  
36 The analytical results of plutonium in water samples were in good agreement with  
37 the values obtained by conventional method, indicating that the proposed method is  
38 reliable and can be used for low level plutonium analysis in environmental water  
39 samples.  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56

\* Corresponding author: Tel.: +86 931 8913278; Fax: +86 931 8913551  
E-mail address: [shikl@lzu.edu.cn](mailto:shikl@lzu.edu.cn) (K. Shi) and [wuws@lzu.edu.cn](mailto:wuws@lzu.edu.cn) (W. Wu)

**Keywords**

Plutonium, environmental liquid samples, vacuum box system, LSC, analysis

**1. Introduction**

Plutonium (Pu), as an important artificial nuclide, has been released into the environment through human nuclear activities such as reprocessing of spent nuclear fuel, nuclear weapons testing and nuclear accidents<sup>1-4</sup>. Its isotopes are considered as highly radiological and biological toxic pollutants because of their long half-lives (<sup>236</sup>Pu:  $3.5 \times 10^9$  yr, <sup>238</sup>Pu:  $4.3 \times 10^{10}$  yr, <sup>239</sup>Pu:  $5.5 \times 10^{15}$  yr, <sup>240</sup>Pu:  $1.2 \times 10^{11}$  yr, <sup>244</sup>Pu:  $2.5 \times 10^{10}$  yr) and  $\alpha$  emission associated with their decay<sup>5</sup>. Isotopes of Pu can be migrated into water and soil under the action of monsoon and ocean current, and enter into human body through food chain and cause damage to human<sup>6,7</sup>. Therefore, there is a strong requirement of developing rapid and robust techniques for the determination of Pu in the environment.

Since the 1950s, many methods for separation and purification of Pu from water samples have been developed, including co-precipitation, solvent extraction, and anion exchange and extraction chromatography<sup>8-11</sup>. Based on the high ionic potential and the chemical property of forming anionic complexes, Pu can be easily taken up by anion exchange resins and anion exchange chromatography is thus often used in the determination of Pu in various environmental samples<sup>12,13</sup>. However, in order to obtain the high purity of Pu for accurate analysis, large-size ion exchange columns were often applied for the removal of matrices, which will produce a large amount of radioactive wastes and cause difficulties for subsequent disposal<sup>9-11</sup>. In addition, the

1  
2  
3  
4 traditional anionic chromatography is usually operated under the condition of normal  
5  
6 pressure, which is time consuming and labor intensive especially for the samples with  
7  
8 complex matrices. The development of a separation system with which a fast column  
9  
10 separation can be carried out is significant. Vacuum box executed in chromatography  
11  
12 approach is regarded as an appealing tool for convenient separation of trace level of  
13  
14 radionuclides from water samples<sup>14,15</sup>. The flow rate of column can be controlled by a  
15  
16 vacuum pump. To our best knowledge, the reported methods are mainly related to the  
17  
18 vacuum box executed in extraction chromatography<sup>16,17</sup>. The application of anionic  
19  
20 chromatography, especially the small sized chromatographic column for the  
21  
22 separation of Pu from environmental samples, is still limited.  
23  
24  
25  
26  
27

28  
29 Both radiometric methods such as  $\alpha$  spectrometry and liquid scintillation counting  
30  
31 (LSC) and mass spectrometric techniques like inductively coupled plasma mass  
32  
33 spectrometry (ICP-MS) can be used for Pu measurement. Based on the advantages of  
34  
35 short analytical time and relatively high sensitivity, Pu is often measured by  
36  
37 ICP-MS<sup>18,19</sup>. The major challenge of this method for Pu measurement is the isobaric  
38  
39 and spectrometric interferences of  $^{238}\text{U}$ ,  $^1\text{H}^{238}\text{U}^+$  and  $^{241}\text{Am}$ . In addition, high  
40  
41 concentration of matrix elements may lead to the signal suppression. The  
42  
43 concentration of total dissolved solid in the sample solution generally needs to be kept  
44  
45 below 0.1%<sup>20</sup>. Accordingly, effective separation and purification, especially for  $^{238}\text{U}$ ,  
46  
47 is particularly critical for accurate determination of  $^{239}\text{Pu}$ , which in some case increase  
48  
49 the analytical time and lead to a poor accuracy of measurement. As  $\alpha$ -emitter,  
50  
51  $^{239+240}\text{Pu}$  can also be measured by  $\alpha$ -spectrometry with advantages of easy application  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 and relatively low instrument expenses<sup>21,22</sup>. However, the detection of Pu with  
5  
6  $\alpha$ -spectrometry requires relatively long counting times (usually 1~4 days) and is not  
7  
8 suitable for emergency situations. With the improvement of instrument detectors, LSC  
9  
10 could offer the function of  $\alpha/\beta$ -discrimination and can be applied for Pu measurement  
11  
12 <sup>23-25</sup>. Compared with  $\alpha$ -spectrometry, simple source preparation and short counting  
13  
14 time are the main advantages and thus LSC can be used for emergency preparedness.  
15  
16  
17 In addition, with the aid of scintillation cocktail as the media of radiation energy  
18  
19 transfer, the self-absorption of sample source is negligible and the absorption of  
20  
21 detector walls, windows and air absorption is also limited. Accordingly, the accurate  
22  
23 analysis of trace level Pu in environmental samples using LSC is achievable.  
24  
25  
26  
27

28  
29 Aiming at rapid determination of trace level Pu in water samples, a vacuum box  
30  
31 system executed in small sized anion exchange columns followed by detecting  $\alpha$   
32  
33 decay of <sup>239+240</sup>Pu using low background LSC which could discriminate  $\alpha/\beta$  emission  
34  
35 was proposed in the present work. The parameters of anion exchange column which  
36  
37 affect the separation speed and efficiency of Pu were optimized. The analytical results  
38  
39 proved that the proposed method can be used for routine analysis of Pu in daily  
40  
41 monitoring and rapid analysis for emergency preparedness.  
42  
43  
44  
45

## 46 **2. Experimental**

### 47 *2.1. Experimental setup*

48  
49 The vacuum box anion exchange chromatographic setup is composed of a vacuum  
50  
51 box system (Eichrom Technologies, Inc., USA) furnished with 24 anion exchange  
52  
53 columns (C1-C24). The system consists of a polycarbonate trough with lid and 24  
54  
55  
56  
57  
58  
59  
60

ports and a gauge is used to monitor the vacuum pressure. All the outlets of chromatographic columns were connected through PEEK ferrules with rigid PTFE beaker. Within the system, 24 samples can be separated synchronously.

All measurements of Pu were performed using  $\alpha/\beta$ -LSC (Tri-Carb 3180TR/SL, PerkinElmer LifeScience, Boston, MA, USA) with Optiphase HiSafe3 scintillation cocktails (PerkinElmer LifeScience, Boston, MA, USA). Am and Th were measured by  $\alpha$  spectrometer; and U was measured with trace uranium analyzer.

### 2.2. Standards, reagents and samples

All reagents, including HNO<sub>3</sub>, HCl, NH<sub>3</sub>·H<sub>2</sub>O, NH<sub>2</sub>OH·HCl, NaOH and NaNO<sub>2</sub> used were of analytical grade. High purity water (18 M $\Omega$  cm) (Milli-Q 50, Millipore, Bedford, MA, USA) was applied for the solution preparation throughout the experiment.

The Pu standard solution was provided by the 404 Company Limited., China National Nuclear Group (Lanzhou, China). Standard solutions of uranium (U), americium (Am) and thorium (Th) were obtained from China Institute of Atomic Energy (Beijing, China). Simulation solution was prepared by mixing known amounts of Pu, U, Am and Th in water. Three water samples (5 L waste water collected from Yumen Area, China) were analyzed for testing the accuracy of the method.

Anion exchange resins used were of AG 1 series with different crosslinkage and particle sizes, including AG 1- $\times$ 2 (2% crosslinked, 50-100 mesh), AG 1- $\times$ 4 (4% crosslinked, 50-100 mesh and 100-200 mesh) and AG 1- $\times$ 8 (8% crosslinked, 50-100 mesh) in chloride form (Eichrom Technologies LLC., USA). The resins were swelled

1  
2  
3  
4 in water firstly, and then dispersed in 8 mol L<sup>-1</sup> HCl and transferred into a column  
5  
6 which was pre-conditioned with 8 mol L<sup>-1</sup> HCl. The performance of columns with  
7  
8 ratios were investigated and compared, including 10 mm i.d.×20 cm long (ca. 16 mL),  
9  
10 8.8 mm i.d.×20 cm long (ca. 12 mL), 7 mm i.d.×20 cm long (ca. 8 mL), 7 mm i.d.×10  
11  
12 cm long (ca. 4 mL), 5 mm i.d.×10 cm long (ca. 2 mL), 7 mm i.d.×5 cm long (ca. 2 mL)  
13  
14 and 5 mm i.d. ×5 cm long (ca. 1 mL).  
15  
16  
17

### 18 *2.3. Sample pre-treatment*

#### 19 *2.3.1. Filtration and acidification*

20  
21 Water samples (e.g., waste water, freshwater and groundwater) were acidized to pH  
22  
23 2-3 immediately after collection. Then the samples were filtered using Millipore MF  
24  
25 membrane filters (0.45 mm, 47mm diameter) and a polysulfon filtration unit DSO320  
26  
27 Series (Nalgene, Rochester, NY, USA) before analysis.  
28  
29  
30  
31

#### 32 *2.3.2. Pre-concentration of Pu*

33  
34 The content of Pu is usually at trace level in water sample (typically within the  
35  
36 femtograms per litre range). To get accurate analytical results, Pu must be  
37  
38 concentrated from sample matrix using some pre-concentration techniques<sup>13</sup>. In the  
39  
40 present work, a co-precipitation method was applied for the enrichment of Pu in water  
41  
42 samples. The procedure is as follows, a calculated amount of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (1 mol/L) and  
43  
44 FeCl<sub>3</sub> (1 mol/L) were added to the water samples. The pH of sample solution was  
45  
46 adjusted to 6 to get Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> precipitates (Pu can be co-precipitated at  
47  
48 the same time)<sup>26</sup>. The sample was then kept overnight (>8 h) for settlement. After  
49  
50 removal of supernatant, the slurry containing Pu was separated by centrifugation. The  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 residue was finally dissolved with 8 mol L<sup>-1</sup> HCl for further purification of Pu.  
5

#### 6 7 *2.4. Valence adjustment to Pu(IV)*

8  
9 Since anion exchange resins have high exchange capacities for Pu(IV) in  
10 nitric/hydrochloric acid media<sup>27,28</sup>, a two-step valence adjustment method was thus  
11 utilized during the separation procedure. 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl was firstly added  
12 into sample solution with gently stirring for 15 min to reduce the overall Pu to Pu(III),  
13 then NH<sub>3</sub>·H<sub>2</sub>O was used to adjust pH to 9~10. The precipitate obtained was dissolved  
14 with concentrated HCl and Pu(III) was oxidized to Pu(IV) using 1.0 mol L<sup>-1</sup> NaNO<sub>2</sub>.  
15  
16 The sample solution was finally diluted to 8 mol L<sup>-1</sup> HCl media prior to loading onto  
17 anion exchange column.  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27

#### 28 29 *2.5. Separation scheme and source preparation*

30  
31 The separation procedure contains four steps as following: (i) pre-conditioning anion  
32 exchange column with 8 mol L<sup>-1</sup> HCl; (ii) transferring the sample in 8 mol L<sup>-1</sup> HCl  
33 media (about 10 mL) and loading it on the anion exchange column at 0.8 mL min<sup>-1</sup> to  
34 exchange the target analytes as anionic hydrochloric complexes<sup>29</sup>; (iii) washing  
35 column with 5 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> to remove U and Fe ions, and 5 mL of 8 mol  
36 L<sup>-1</sup> HCl to desorb Am and Th as well as other matrix elements respectively; (vi)  
37 eluting Pu with 5 mL of 0.5 mol L<sup>-1</sup> HCl containing 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl. (v)  
38  
39 Regeneration the anion exchange column with 5 mL of 0.1 mol/L NH<sub>2</sub>OH·HCl-0.5  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

60  
The eluant obtained was evaporated to dryness and the residue was dissolved in 5mL  
of 0.01 mol L<sup>-1</sup> HNO<sub>3</sub>. The solution contained Pu was then transferred into a 20 mL



1  
2  
3  
4 polyethylene bottle and 10 mL scintillation cocktail was added. The Pu in samples  
5  
6 was finally measured by low background LSC.  
7

### 8 9 *2.6. Detection of Pu using LSC*

10  
11 In the present work, Pu was determined by detecting  $\alpha$  decay of  $^{239+240}\text{Pu}$  using low  
12  
13 background LSC. Prior to sample analysis, the LSC instrument was tuned for  
14  
15 minimum sensitivity of Am using  $^{241}\text{Am}$  standard solution ( $0.01 \text{ mol L}^{-1} \text{ HNO}_3$  as  
16  
17 media) and the instrumental parameters were further adjusted for Pu. It is important to  
18  
19 note that these parameters were optimized each time when the instrument was  
20  
21 initialized. The method allows achievement of a detection limit of  $1.6 \times 10^{-2} \text{ Bq L}^{-1}$  for  
22  
23 5 L water samples in 60 min counting time. The analytical procedure is illustrated in  
24  
25 Fig.1.  
26  
27  
28  
29  
30

## 31 **3. Results and discussion**

### 32 33 *3.1. Parameters optimization of chromatographic column*

34  
35 In general, sufficient amount of anion exchange resins are often regarded as an  
36  
37 essential factor for separation of target radionuclides in water samples. The column  
38  
39 volumes of 10-20 mL are usually employed to ensure satisfactory recoveries and  
40  
41 appropriate separation efficiencies of radionuclides<sup>30</sup>. In this work, the parameters  
42  
43 which affect the separation abilities of chromatographic column were optimized for 5  
44  
45 L water samples. The results (Fig.2) show that the chemical yields of Pu (>85%) and  
46  
47 the decontamination factors (>10<sup>3</sup>) for U, Th and Am obtained from the anion  
48  
49 exchange chromatographic columns ( $0.5 \times 10 \text{ cm}$ , ca. 2 mL) are similar as the larger  
50  
51 volumes of 16mL ( $1.0 \times 20 \text{ cm}$ ), 12mL ( $0.88 \times 20 \text{ cm}$ ), 8mL ( $0.7 \times 20 \text{ cm}$ ), 4mL ( $0.7 \times 10$   
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 cm), indicating that the small sized column (containing 2 mL resin) is enough for Pu  
5  
6 purification in 5 L water samples. It should be pointed out that when smaller sized  
7  
8 column (0.5×5 cm, ca. 1 mL) was explored, the chemical yield of Pu dropped  
9  
10 dramatically to less than 40% (Fig.3). Therefore, considering the advantages of low  
11  
12 consumption of resins and reagents, an appropriate volume of column (0.5×10 cm, ca.  
13  
14 2 mL resin) was selected for separation and determination of Pu.  
15  
16  
17  
18

19 Crosslinkage is an important parameter of anion exchange resin, which determines the  
20  
21 internal structure of resin and affects its uptake and elution properties. In this work,  
22  
23 three kinds of resins with different crosslinkage, namely AG 1-×2, AG 1-×4 and AG  
24  
25 1-×8, were investigated. The results (Fig.4(a)) show that the chemical yields of Pu  
26  
27 increased with the increasing of the resin crosslinkage. The main reason for such a  
28  
29 phenomenon would be that the higher exchange crosslinkage means there are more  
30  
31 functional groups in the interior of the resin and the specific surface area of the resins  
32  
33 are larger, leading to higher uptake ability for Pu<sup>3+</sup>. Among the three kinds of resins,  
34  
35 the decontamination factor of AG 1-×8 for U was reduced obviously (Fig. 4(b)). To  
36  
37 overcome the problems, the volumes of washing solutions must be increased to  
38  
39 remove the sorbed U from AG 1-×8 columns, which will decrease the chemical yield  
40  
41 of Pu because some amount of Pu can be washed with the large volume of solution.  
42  
43 For AG 1-×4 resin, different particle size (AG 1-×4(a), 50-100 mesh; AG 1-×4(b),  
44  
45 100-200 mesh) were also investigated (Fig.4(b)). It is found that the chemical yields  
46  
47 of Pu with smaller particle size of resin are a little higher than larger ones. However,  
48  
49 the decontamination factors for U, Th and Am obtained from the bigger particle size  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 of resins (AG 1- $\times$ 4(a)) are better. Combining these two factors, we choose AG 1- $\times$ 4 (a)  
5  
6 as the adsorbent for Pu separation.  
7

8  
9 The flow rate is another important parameter for anion exchange resin during column  
10  
11 separation. The high flow rate is in favor for fast separation of nuclides from water  
12  
13 samples. However, the chemical yields of Pu and decontamination factors for U, Th  
14  
15 and Am were deteriorated when the flow rate is higher than 1.0 mL min<sup>-1</sup> (see Fig.5).  
16  
17 To get high recovery of Pu and fast processing of samples, the flow rate of 0.8 mL  
18  
19 min<sup>-1</sup> was chosen during the sample loading and column washing.  
20  
21  
22

### 23 24 3.2. Media for Pu separation

25  
26 For Pu separation by anion exchange chromatography, the oxidation state of Pu is  
27  
28 very important, which will affect the separation efficiency as well as the accuracy of  
29  
30 analytical results. The redox states of Pu can be stabilized by complexation with  
31  
32 various ligands<sup>32</sup>. In this case, the choice of suitable media becomes significant.  
33  
34 Because the distribution coefficients of Pu on anion exchange resins in concentrated  
35  
36 HNO<sub>3</sub> or HCl media are very high, Pu isotopes can generally be separated from other  
37  
38 nuclides<sup>33,34</sup>. To our best knowledge, Pu separation has mainly been carried out in  
39  
40 HNO<sub>3</sub> media because most of the handling processes of nuclear fuels were dissolved  
41  
42 by HNO<sub>3</sub><sup>33</sup>. However, it should be noticed that Th can form strong nitrate complex  
43  
44 and U can also form weak complex with NO<sub>3</sub><sup>-</sup> in HNO<sub>3</sub> media. Consequently, most of  
45  
46 Th and a small quantity of U can be retained on anion exchange column and easily  
47  
48 eluted with Pu, which causes the interference for accurate analysis of Pu. It is reported  
49  
50 that Th cannot form strong complex like Pu(IV) in HCl media. Furthermore, trivalent  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 actinides show practically no retention ( $K < 1$ ) in HCl solutions of up to approximately  
5  
6  $5 \text{ mol L}^{-1}$ , while tetravalent actinides remain strongly retained under these conditions,  
7  
8 with  $K > 10^3$  in  $4 \text{ mol L}^{-1} \text{ HCl}^{34}$ . In this case, all of the retained actinides can be eluted  
9  
10 using complexant eluents. To develop the optimal separation procedure, the amount of  
11  
12 HCl used during sample loading and column washing was investigated. Our  
13  
14 experimental results (see Fig.6(a)) show that the chemical yield of Pu increases  
15  
16 gradually (90%~95%) with the increase of HCl concentration from 7 mol/L to 10  
17  
18 mol/L, indicating that Pu can be easily retained on the AG1- $\times$ 4 resin at high  
19  
20 concentration of HCl. Compared to Pu, the retention of Th and Am by AG1- $\times$ 4 resin  
21  
22 in higher concentration of HCl is very limited, and the decontamination factors for  
23  
24 these nuclides are all higher than  $10^4$  (Fig.6(b)). It should be mentioned that the  
25  
26 decontamination factor of U is decreased with the increase of HCl concentration  
27  
28 (Fig.6(b)). In addition, some amount of  $\text{Fe}^{3+}$  is also sorbed on the column after sample  
29  
30 loading in HCl media. A further washing step with 1 mol/L  $\text{HNO}_3$  is thus applied for  
31  
32 the removal of U as well as Fe in the analytical procedure. Considering the high  
33  
34 recovery of Pu as well as efficient removal of Th and Am,  $8 \text{ mol L}^{-1} \text{ HCl}$  was selected  
35  
36 as the solution media during sample loading in the present work.  
37  
38  
39  
40  
41  
42  
43  
44  
45

### 46 3.3. Elution of Pu

47  
48 Two types of methods have been reported for Pu elution from anion exchange  
49  
50 columns<sup>18,19</sup>. One of them is named direct elution method based on the low adsorptive  
51  
52 capacity of Pu(IV) complexes with these eluents (e.g., diluted HF along with  $\text{HNO}_3$  or  
53  
54 HCl, diluted HCl, or diluted  $\text{H}_2\text{C}_2\text{O}_4$  along with  $\text{HNO}_3$  solution) on anion exchange  
55  
56  
57  
58  
59  
60

1  
2  
3 chromatography without reducing Pu(IV) to Pu(III). Another is called reduction  
4  
5 elution method based on the reduction of Pu(IV) to the non-adsorbable Pu(III), and  
6  
7 retrieval of Pu(III) from the column. In our present work, 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl in  
8  
9 certain concentration of HCl was used to elute Pu from anion exchange columns. To  
10  
11 get the appropriate concentration of HCl, the concentration range of 0.1~1.0 mol L<sup>-1</sup>  
12  
13 was assessed. The experimental results (Fig.7) show that the decontamination factors  
14  
15 of Th and Am were enhanced with the increase of HCl concentration. However, the  
16  
17 decontamination factors of U and the chemical yields for Pu were worsened when the  
18  
19 concentration of HCl is increased up to 1.0 mol L<sup>-1</sup>. Accordingly, 0.1 mol L<sup>-1</sup>  
20  
21 NH<sub>2</sub>OH·HCl in 0.5 mol L<sup>-1</sup> HCl was selected for Pu elution.  
22  
23  
24  
25  
26  
27

28  
29 Traditionally, a large amount of reagent (such as 50~100 mL) was used to elute Pu,  
30  
31 which makes the analytical procedure time consuming. The analytical cost of samples  
32  
33 is also enhanced because more chemical reagents were consumed. In this work,  
34  
35 different volumes of eluents were investigated. The results (see Fig. 8) show that 5  
36  
37 mL of eluent is sufficient for Pu desorption from 2 mL column, and the recoveries of  
38  
39 Pu are all above 95% for different kinds of anion exchange resins. Compared to AG  
40  
41 1-×2 and AG 1-×4 resins, the elution of Pu from AG 1-×8 is a little difficult,  
42  
43 indicating that the sorption abilities of AG 1-×8 for Pu is stronger than others. The  
44  
45 result is in good agreement with our experiment data mentioned above (results and  
46  
47 discussion section 3.1).  
48  
49  
50  
51  
52

### 53 54 *3.4. Sample throughput*

55  
56 Based on the application of the vacuum box system, 5 L water samples can be  
57  
58  
59  
60

1  
2  
3 processed with a 2mL of AG 1- $\times$ 4 columns within 2 h for total on-column separation.  
4  
5 Because the vacuum box used in the system consists of 24 ports and 24 small-size  
6  
7 chromatographic columns can be used under the same conditions, 24 water samples  
8  
9 can be analyzed at one time (one batch) and 3 batches samples can be successfully  
10  
11 processed within one day. As a result, the sample throughput is significantly improved  
12  
13 compared with the traditional method, wherein 1~2 days are usually needed for  
14  
15 processing a batch of samples<sup>35,36</sup>.  
16  
17

18  
19 The reusability of anion exchange chromatographic column is also investigated (the  
20  
21 results are not shown here). It is found that the 2mL of AG 1- $\times$ 4 column can be reused  
22  
23 more than 20 times under the premise of ensure the chemical yield of Pu (>85%) and  
24  
25 the decontamination factors of Th, U and Am (>10<sup>3</sup>).  
26  
27  
28  
29

### 30 31 *3.5. Method validation and application*

32  
33 To assess the accuracy and applicability of the proposed analytical method for  
34  
35 handling environmental samples with different levels of Pu, three water samples were  
36  
37 analyzed. The analytical results of Pu (Table 1) for the samples agree well with the  
38  
39 values obtained by the certified method of China G B11225-89, indicating that the  
40  
41 proposed analytical method is reliable and can be used for Pu determination in  
42  
43 environmental water samples.  
44  
45  
46  
47

48  
49 With the vacuum box system, column separation can be carried out within 2.0 h and  
50  
51 24 samples were analyzed simultaneously. Compared with the traditional methods, the  
52  
53 separation efficiency is improved evidently. The proposed method is therefore better  
54  
55 suited for the rapid determination of Pu isotopes in environmental risk assessment and  
56  
57  
58  
59  
60

radiological emergencies. Besides the satisfactory recoveries of Pu, appropriate decontamination factors for interferences, and the low cost of analysis, the stability of vacuum box system is another advantage with which the operation can be continuous for a long time (up to 5 months had been confirmed) without any problem.

#### 4. Conclusion

The present paper focused on the development of analytical method for rapid determination of Pu in environmental water samples with vacuum box system separation and LSC measurement. The parameters which affect the separation abilities of anion exchange resins were optimized. Based on our experimental results, the following conclusions can be drawn: (i) considering the high recovery of Pu as well as efficient removal of interferences, 8 mol/L HCl was selected as the solution media during sample loading. For Pu elution, 0.1 mol L<sup>-1</sup> NH<sub>2</sub>OH·HCl in 0.5 mol L<sup>-1</sup> HCl was used; (ii) with the application of one small sized chromatographic anion exchange column (AG 1-×4, 2.0 mL), the decontamination factors of >10<sup>3</sup> for U and >10<sup>4</sup> for Am and Th, and recovery of >90% for Pu was achieved for 5 L water samples, reaching a detection limit of 1.6×10<sup>-2</sup> Bq L<sup>-1</sup> in 60 min counting time by low background LSC; (iii) based on the application of vacuum box system and LSC measurement, the developed method remarkably reduced the analytical time, and a batch of samples (n=24) can be analyzed within one day; (iv) the analytical procedure is validated by analysis of the same water samples using a conventional method and can be used for the determination of Pu in routine analysis for daily monitoring and rapid analysis for emergency preparedness.

### Acknowledgements

Bo Liu is grateful to Radiochemistry Lab, School of nuclear Science and technology, Lanzhou University of China; China National Nuclear Corporation; Northwest Nuclear and Radiation Safety Supervision Station, Department of Environmental Protection and The 404 limited Company for all supports in his Ph.D. project. Financial supports from National Natural Science Foundation of China (J1210001, 21301083), Specialized Research Fund for the Doctoral Program of Higher Education (20130211120032), Special Foundation for High Level Waste Disposal in China (2012-494) are acknowledged.

### References

- 1 A. T. Sroor, S. M. Darwish and M. Samia, *Environmental Protection*, 2013, 4, 1-5.
- 2 O. C. Lind, B. Salbu and K. Janssens, *J. Environ. Radioact.*, 2005, 81, 21-32.
- 3 P. Lindahl, P. Roos and E. Holma, *J. Environ. Radioact.*, 2005, 82, 285-301.
- 4 Z. Jian, T. Keiko, W. Yoshito, U. Shigeo, A. Tatsuo, I. Nobuyoshi, Y. Satoshi, K. Yoshihisa, F. Shoichi and I. Sadao, *Scientific Reports* 2, Article number 304.
- 5 W. J. Weber and R. C. Ewing, *Science*, 2000, 289, 2051-2052.
- 6 S. M. L. Asbury, S. P. Lamont and S. B. Clark, *Environ. Sci. Technol.*, 2001, 35, 2295-2300.
- 7 T. Missana, Ú. Alonso, M. G. Gutiérrez and M. Mingarro, *Appl. Geochem.*, 2008, 23, 1484-1497.
- 8 J. X. Qiao, X. L. Hou, M. Miró and P. Roos, *Anal. Chim. Acta*, 2009, 652, 66-84.



- 1  
2  
3  
4 9 S. Bürger, S. D. Balsley, S. Baumann, J. Berger, S. F. Boulyga, J. A. Cunningham,  
5  
6 S. Kappel, A. Koepf and J. Poths, *Int. J. Mass Spectrom.*, 2012, 311, 40-50.  
7  
8  
9 10 D. Lariviere, V. F. Taylor, R. D. Evans and R. J. Cornett, *Spectrochimica Acta*  
11  
12 *Part B: Atomic Spectroscopy*, 2006, 61, 877-904.  
13  
14 11 Z. Varga, G. Surányi, N. Vajda and Z. Stefánka, *Radiochim. Acta*, 2007, 95,  
15  
16 81-87.  
17  
18  
19 12 S. Lee, J. Gastaud, J. L. Rosa, L. Kwong, P. Povinec, E. Wyse, L. Fifield, P.  
20  
21 Hausladen, L. D. Tada and G. Santos, *J. Radioanal. Nucl. Chem.*, 2001, 248,  
22  
23 757-764.  
24  
25  
26 13 E. Hrnccek, P. Steier and A. Wallner, *Appl. Radiat. Isot.*, 2005, 63, 633-638.  
27  
28  
29 14 S. L. Maxwell, *J. Radioanal. Nucl. Chem.*, 2006, 267, 537-543.  
30  
31  
32 15 S. L. Maxwell and B. K. Culligan, *J. Radioanal. Nucl. Chem.*, 2006, 270,  
33  
34 699-704.  
35  
36  
37 16 S. L. Maxwell, *J. Radioanal. Nucl. Chem.*, 2008, 275, 395-402.  
38  
39  
40 17 S. L. Maxwell and V. D. Jones, *Talanta*, 2009, 80, 143-150.  
41  
42  
43 18 J. X. Qiao, X. L. Hou, P. Roos and M. Miró, *J. Anal. At. Spectrom.*, 2010, 11,  
44  
45 1769-1779.  
46  
47  
48 19 J. X. Qiao, X. L. Hou, P. Roos and M. Miró, *Anal. Chim. Acta*, 2011, 685,  
49  
50 111-119.  
51  
52  
53 20 K. L. Shi, X. L. Hou, P. Roos and W. S. Wu, *Anal. Chim. Acta*, 2012, 709, 1-20.  
54  
55  
56 21 R. Jakopič, P. Tavčar and L. Benedik, *Appl. Radiat. Isot.*, 2007, 65, 504-511.  
57  
58  
59 22 Z. Varga, G. Surányi, N. Vajda and Z. Stefánka, *J. Radioanal. Nucl. Chem.*, 2007,  
60

- 1  
2  
3  
4 274, 87-94.  
5  
6 23 P. Li, Z. Liu, J. F. Lin, F. Ma, Q. L. Shi, Z. J. Guo and W. S. Wu, *J. Radioanal.*  
7  
8  
9 *Nucl. Chem.*, 2014, 299, 1973-1978.  
10  
11 24 S. Happel, P. Letessier, W. Ensinger, J. H. Eikenberg, A. H. Thakkar and E. P  
12  
13 Horwitz, *Appl. Radiat. Isot.*, 2004, 61, 339-344.  
14  
15  
16 25 S. R. Ruberu, Y. G. Liu and S. K. Perera, *Health Phys.*, 2008, 95, 397-406.  
17  
18  
19 26 T. Gäfvert, C. Ellmark and E. Holm, *J. Environ. Radioact.*, 2002, 63, 105-115.  
20  
21 27 D. Arginelli, G. Berton, S. Bortoluzzi, G. Canuto, F. Groppi, M. Montalto, M.  
22  
23 Nocente, S. Ridone and M. Vegro, *J. Radioanal. Nucl. Chem.*, 2008, 277, 65-71.  
24  
25  
26 28 M. H. Lee, J. Y. Kim, W. H. Kim, E. C. Jung and K. Y. Jee, *Appl. Radiat. Isot.*,  
27  
28  
29 2008, 66, 1975-1979.  
30  
31 29 B. Maria, *Microchem J.*, 2000, 67, 363-373.  
32  
33  
34 30 Q. J. Chen, A. Aarkrog, S. Nielsen, H. Dahlgard, H. Nies, Y. X. Yu and K.  
35  
36 Mandrup, *J. Radioanal. Nucl. Chem.*, 1993, 172, 281-288.  
37  
38  
39 31 S. Lee, J. Gastaud, J. L. Rosa, L. Kwong, P. Povinec, E. Wyse, L. Fifield, P.  
40  
41 Hausladen, L. D. Tada and G. Santos, *J. Radioanal. Nucl. Chem.*, 2001, 248,  
42  
43 757-764.  
44  
45  
46 32 S. S. Hecker, *MRS Bull.*, 2001, 26, 672-678.  
47  
48  
49 33 M. H. Lee, Y. J. Park and W. H. Kim, *J. Radioanal. Nucl. Chem.*, 2007, 273,  
50  
51 375-382.  
52  
53  
54 34 D. Solatie, P. Carbol, M. Betti, F. Bocci, T. Hiernaut, V. V. Rondinella and J.  
55  
56 Cobos, *J. Anal. Chem.*, 2000, 386, 88-94.  
57  
58  
59  
60

1  
2  
3  
4 35 O. Farmer, K. Olsen, M. Thomas and S. Garofoli, *J. Radioanal. Nucl. Chem.*,  
5  
6 2008, 276, 489-492.  
7

8  
9 36 S. K. Hanson, A. H. Mueller and W. J. Oldham, *Anal. Chem.*, 2014, 86,  
10  
11 1153-1159.  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

**Figure captures:**

**Fig. 1** Analytical procedure for the determination of Pu in environmental water samples;

**Fig.2** Chemical yields of Pu (a) and the decontamination factors for U, Th and Am (b) obtained in anion exchange chromatographic columns with different volume;

**Fig. 3** Chemical yields of Pu (a) and the decontamination factors for U, Th and Am (b) obtained in anion exchange chromatographic columns with volume of 1-2mL;

**Fig. 4** Chemical yields of Pu (a) and the decontamination factors for U, Th and Am (b) obtained in small sized anion exchange chromatographic columns with different crosslinkage and particle size of resin;

**Fig. 5** Effects of flow rate of column to chemical yields of Pu (a) and the decontamination factors for U, Th and Am (b) obtained in anion exchange chromatographic columns (2 mL resin);

**Fig. 6** Effect of HCl concentration to chemical yields of Pu (a) and the decontamination factors for U, Th and Am (b) obtained in anion exchange chromatographic columns (2 mL resin) during sample loading;

**Fig. 7** Chemical yields of Pu (a) and the decontamination factors for U, Th and Am (b) obtained in anion exchange chromatographic column (2 mL resin) with different concentration of HCl contained  $0.1 \text{ mol L}^{-1} \text{ NH}_2\text{OH}\cdot\text{HCl}$ ;

**Fig. 8** Accounts of Pu in different stages of eluent obtained in different chromatographic columns (volume: 2 mL).

Fig.1

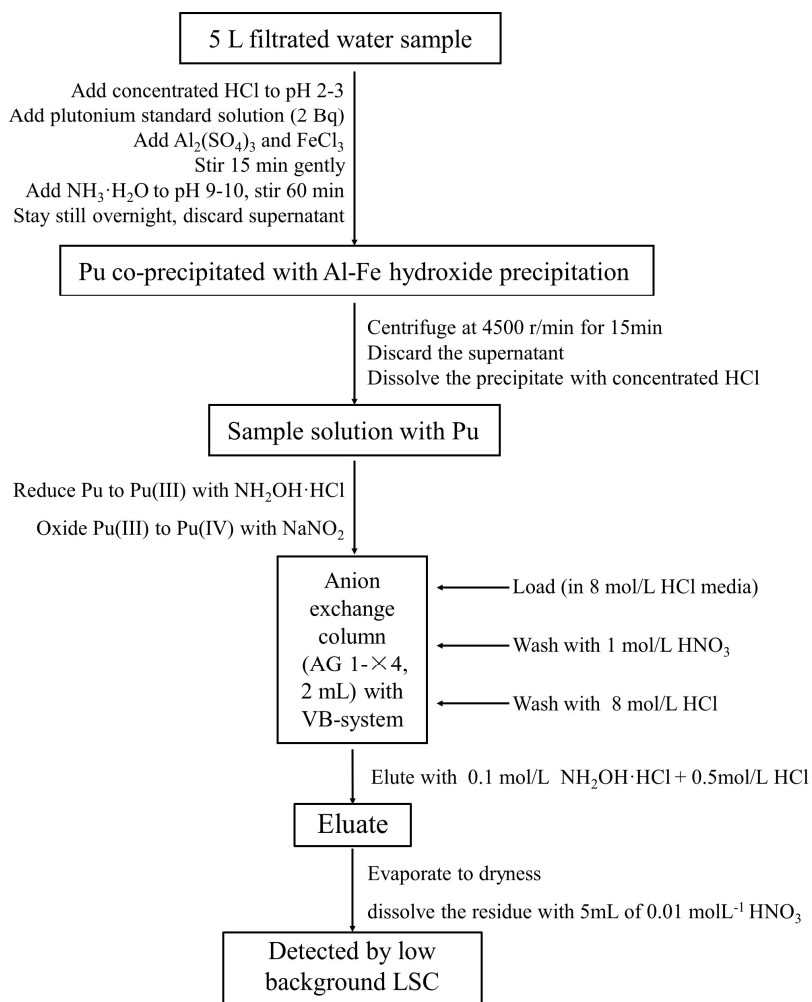


Fig.2

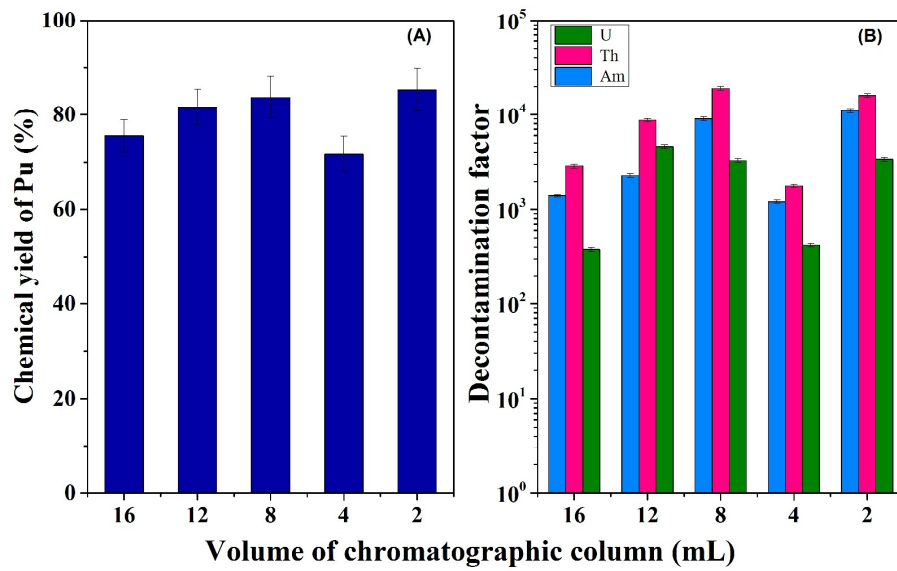


Fig.3

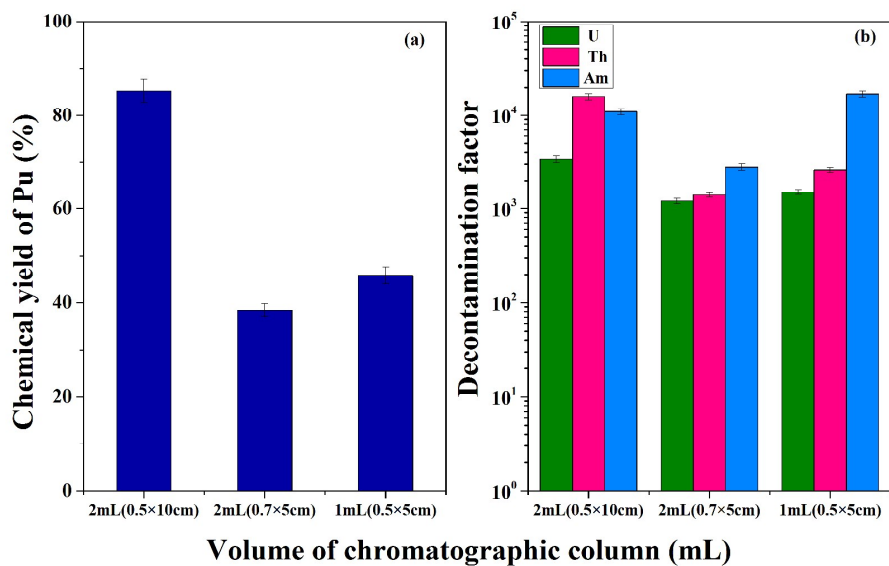


Fig.4

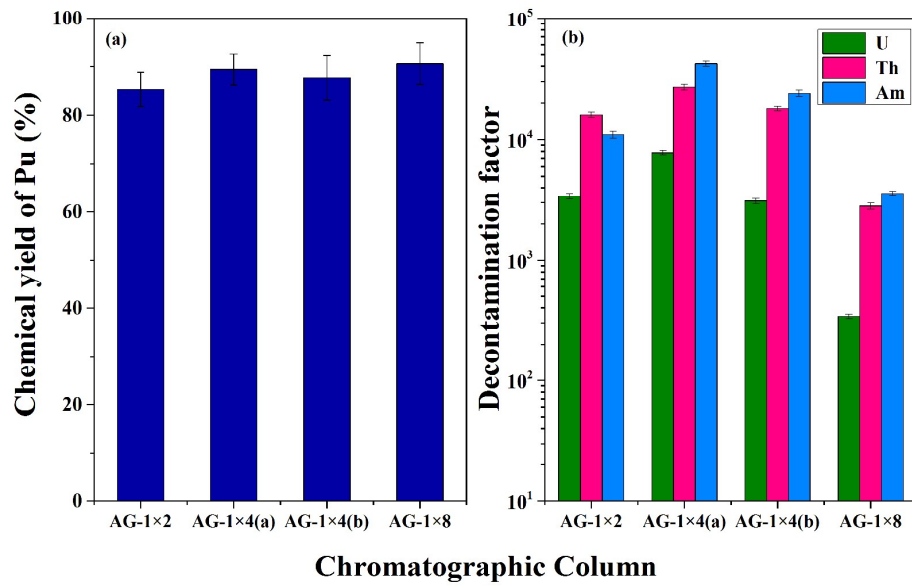




Fig.5

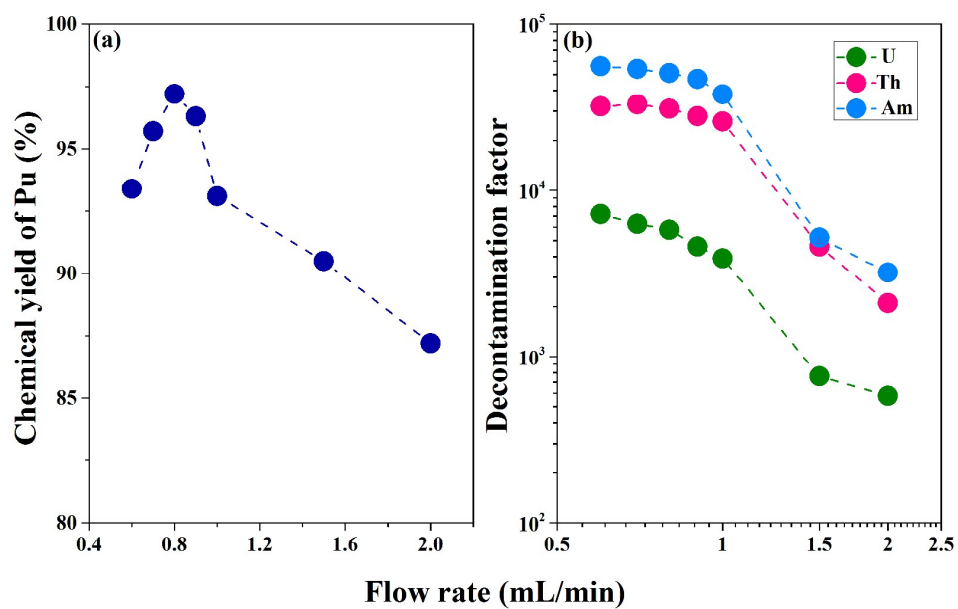


Fig.6

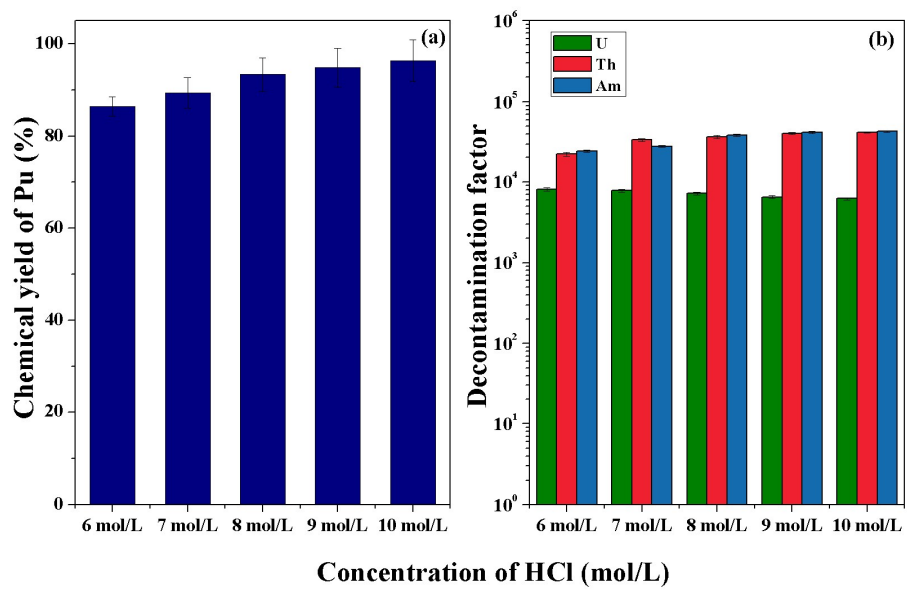


Fig.7

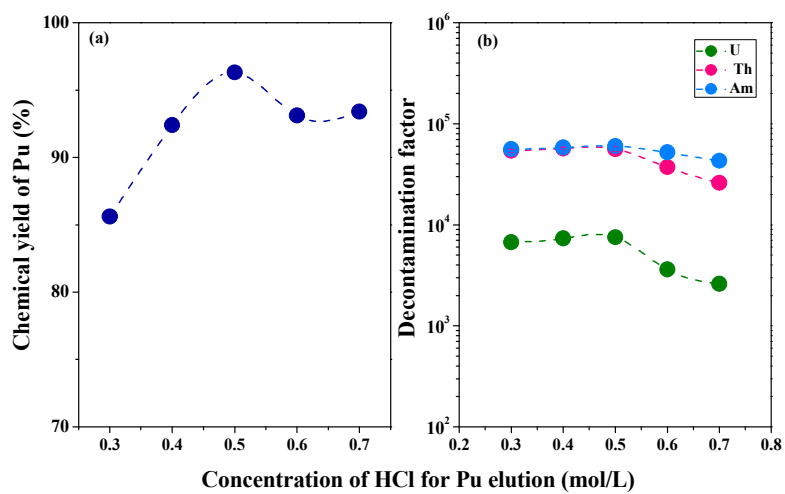
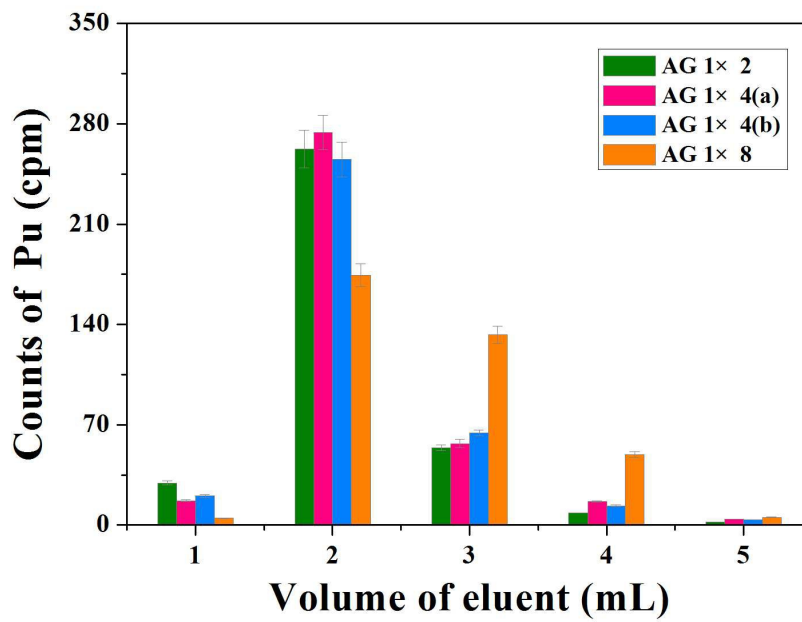


Fig.8



Analytical Methods Accepted Manuscript

Table 1, Analytical results of Pu in three water samples using the developed method and conventional method <sup>a</sup>

Samples	Chemical yield, %	Pu measured, Bq L <sup>-1</sup>	Pu measured by conventional method <sup>b</sup> , Bq L <sup>-1</sup>
1	90.0± 4.6	0.09 ± 0.03	0.10 ± 0.03
3	92.5± 3.8	0.37 ± 0.04	0.40 ± 0.05
5	96.3± 4.2	1.54 ± 0.04	1.60 ± 0.04

a: values are the average of six replicates (±standard deviation) for water samples.

b: values were obtained using a conventional method of China G B11225-89.