

Study on the combined analytical method for separation of uranium and plutonium by TEVA+DGA and TEVA+UTEVA resin ICP-MS

Chen Long, Li Sufen*, Cai Xinfu, Huo Yonggang

School of Nuclear Engineering, Rocket Force University of Engineering, Xi'an, 710025, China

*Corresponding author

Abstract: The efficient separation method of nuclides is an important proof for the accurate measurement of trace uranium-plutonium radionuclides by ICP-MS. In this paper, based on the adsorption characteristics of the resin, the separation effect of uranium and plutonium between TEVA+DGA resin series scheme and TEVA+UTEVA resin series scheme was compared and analyzed, and the sample column and elution conditions were optimized. The results show that the recovery efficiency of uranium and plutonium by TEVA+UTEVA resin is 93%~100% and 97%~111%, respectively. The recovery efficiency of uranium and plutonium by TEVA+DGA resin is 91%~96% and 98%~115%, respectively. In contrast, TEVA+UTEVA resin has a higher recovery efficiency for uranium plutonium.

Keywords: Resin series, nuclide separation, mass spectrometry measurement

1. Introduction

The distribution of U and Pu in environmental samples is very different, and the concentration of U in soil and sediment is 106~109 times higher than that of Pu. In seawater, the concentration ratio of U/Pu is as high as 1010, and the content of Pu in the air is about $0.4\sim 400\times 10^{-16}$ g/m³, which is far less than the content of U. During the sample preparation process, radionuclides such as U, Pu, Ra, Pb and Th in the environment will be transferred indiscriminately to the acid system. When the U and Pu radionuclides in the samples are measured by ICP-MS, the presence of ²³⁸UH⁺ will cause strong interference to ²³⁹Pu⁺, and the concentration value of the two radionuclides cannot be accurately measured. In addition, due to the large number of elements contained in the sample, in order to avoid the influence of polyatomic ions and matrix on the measurement and analysis, it is necessary to carry out radiochemical separation of the sample to accurately measure and analyze the concentration of trace uranium and plutonium radioactive aerosol in the environment, so as to minimize the interference factors.

At present, there are two main analytical methods for trace elements in the laboratory: extraction separation method and resin separation method. In the process of sample separation, the extraction separation method needs to use a large number of extractants, and the operation process is complicated. The resin separation method is simple to operate and uses less solvents, which has the selectivity of solvent extraction and the high efficiency of chromatographic separation, and is especially suitable for the sample separation of low concentration components. Therefore, this paper selects the resin separation method to realize the rapid separation and purification of samples.

2. Extraction chromatography

Extraction chromatography (EXC) is a common technique for separation of radionuclides in laboratory. Using its good separation characteristics, researchers have established a series of diverting processes. Shan Xing et al^[1], established a combined analysis method of Pu, Np and Am using TK200+DGA resin in series. Ling Zhang et al^[2], successfully used TK200 resin to separate U from the complex seawater matrix, realizing rapid measurement and analysis of U isotopes in seawater. Zhongtang Wang^[3] et al. used TK200 resin in series to separate Pu in soil samples after digestion from the matrix, so that the decontamination coefficient of uranium reached 7.5×10^7 . Meanwhile, in the research work, it was proved that the sample separation effect of multi-column resin in series was better than that of single column. Wu Men et al^[4], proposed a combined analysis method of U and Pu in seawater with TEVA+UTEVA+DGA three-column series, and verified through experiments that resin has a high

recovery efficiency for U and Pu in seawater samples.

The extraction chromatographic resin was prepared by physical impregnation and combination of extractant and stationary phase with inert carrier as support. Figure 1 Surface structure of extractive chromatographic resin. Usually, the mobile phase is an inorganic aqueous solution, such as hydrochloric acid or nitric acid solution, or a complexing agent, such as oxalic acid or hydrofluoric acid solution. When the inorganic aqueous solution flows through the fixed phase, the separated nuclides in the solution are repeatedly and continuously extracted and de-extracted in the fixed phase, and different partition coefficients of different substances on the resin are used to achieve the purpose of substance separation.

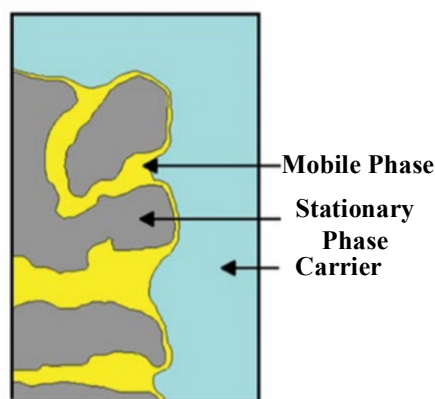


Figure 1: Extractive chromatography resin surface.

3. Resin series scheme

According to the resin technical documents provided by TRISKEM company, the resins that can be used for separation of uranium and plutonium are mainly TEVA, UTEVA, DGA, TRU and TK200. TRU resin is a mixture, which will emulsify for a long time, leading to the blockage of the resin. Meanwhile, TRU resin has a high adsorption capacity for iron ions. When the sample liquid passes through the column, the resin column will preferentially adsorb higher concentration of iron ions, resulting in poor separation effect of the resin. TK200 resin has a strong retention of U, and it needs to use oxalate ammonia to eluate it from the resin, resulting in a large amount of insoluble compounds in the eluent, which needs to be further treated. In this paper, only three resins, TEVA, UTEV and DGA, are used for the series combination of resins. Figure 2 shows the diagram of resin series.

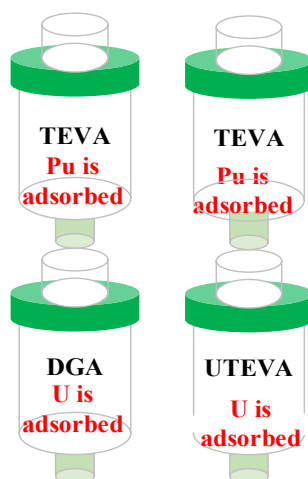


Figure 2: Resin series diagram.

4. Experimental reagents and instruments

The resin used in the experiment is TEVA resin, UTEVA resin and DGA resin produced by TRISKEM company, and the particle size of the resin is 100~150 μm . Deionized water (greater than 18 $\text{M}\Omega/\text{cm}^3$)

from the Milli-Q water purification system. Nitric acid, hydrochloric acid, hydrofluoric acid, all purchased from Sinopod Group, excellent pure. The standard solution of uranium and plutonium comes from the Chinese Academy of Radiation Protection, of which the concentration of ^{238}U standard solution is 17.743 ng/g, and the concentration of ^{242}Pu standard solution is 31.051 pg/g. In order to prevent contamination of the ICP-MS torch and ion detector by the high concentration sample solution, the standard solution was diluted. 15mL of ^{242}Pu containing 3.105pg 8 M HNO_3 matrix and 15mL of ^{242}Pu containing 3.105pg and ^{238}U containing 3.5486 ng 8 M HNO_3 matrix were configured respectively. The measurement and analysis instrument is the NexION 5000 ICP-MS produced by PerkinElmer (PE) Company, USA.

The instrument adopts dynamic reaction cell technology and multiple four-pole technology, with excellent anti-interference ability, which can effectively reduce the strong interference generated by $^{238}\text{UH}^+$ to $^{239}\text{Pu}^+$ measurement, and also has low background concentration and excellent matrix tolerance, which can realize the rapid measurement of uranium and plutonium under trace or ultra-trace conditions.

The measurement process adopts the standard curve method, and the recovery efficiency of uranium plutonium by different resins can be used in formula (1):

$$\varphi = \frac{m_c \cdot (c_c - c_b)}{m_a \cdot c_a} \quad (1)$$

Where φ is the recovery efficiency of U or Pu, m_a is the mass number when the sample is loaded into the column, c_a is the mass concentration of U or plutonium in the product, m_c is the mass concentration of the collected leach, c_c is the mass concentration of U or Pu in the leach, and c_b is the mass concentration of U or Pu in the blank sample. Since the chemical reagent used contains only a very small amount of ^{238}U and does not contain Pu, $c_b=0$ when calculating Pu recovery efficiency.

5. Sample separation and purification

5.1. Separation and purification of uranium plutonium with TEVA+UTEVA

Install the syringe, TEVA resin column, UTEVA resin column, white flow guide tube, yellow flow guide tube and 50 mL centrifuge tube successively on the empty box. A total of 6 resin columns in series are numbered 1~6#, as shown in Figure 3.

The resin column in series was pretreated with 15 mL 8 M HNO_3 , and the flow rate was controlled to be 1 mL/min. When the liquid flowed through the resin column, the pump pressure was increased to drain the resin.

15 mL of ^{242}Pu samples containing 3.1051 pg 8 M HNO_3 matrix were respectively loaded into 1~3# pre-treated chromatographic columns, and the flow rate was adjusted to 1 drop /s. After the liquid passed through the resin column, the pump pressure was increased to drain the resin.

15 mL of samples containing 3.1051 pg/g ^{242}Pu and 3.5486 ng 8 M HNO_3 matrix with ^{238}U were respectively loaded into 4~6# pre-treated chromatographic columns, and the flow rate was adjusted to 1 drop /s. After the liquid passed through the resin column, the pump pressure was increased to drain the resin.

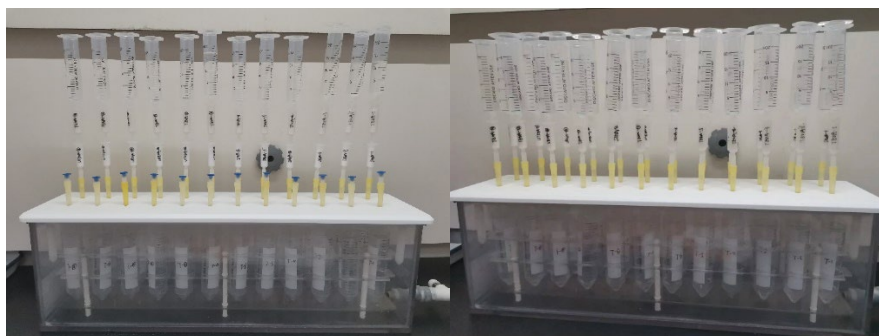


Figure 3: Resin series installation diagram (Left)

Figure 4: Resin series installation diagram Resin separation installation diagram (Right)

When the sample liquid is completely passed through the resin, use 15 mL 8 M HNO₃ to wash the resin. After the washing is completed, increase the pressure of the air pump to drain the resin.

Disconnect the TEVA resin column and UTEVA resin column in series, reinstall the TEVA resin column and UTEVA resin column for sample adsorption, open the vacuum box, use the marked 50 mL centrifuge tube to collect the eluent, and replace the flow tube and syringe, as shown in Figure 4.

The TEVA resin column was rinsed with 12 mL 0.1M HCl-0.01M HF and the flow rate was adjusted to 1 drop /s. When the liquid completely passed through the resin, the pump pressure was increased, the resin was drained, Pu eluent was taken out, weighed and filtered to be measured.

The UTEVA resin was rinsed with 30 mL 0.01M HCl and the flow rate was adjusted to 1 drop /s. When the liquid passed through the resin completely, the pump pressure was increased, the resin was drained, and the eluent containing U was taken out and weighed and filtered to be measured. The separation and purification process of TEVA+UTEVA uranium plutonium is shown in Figure 5.

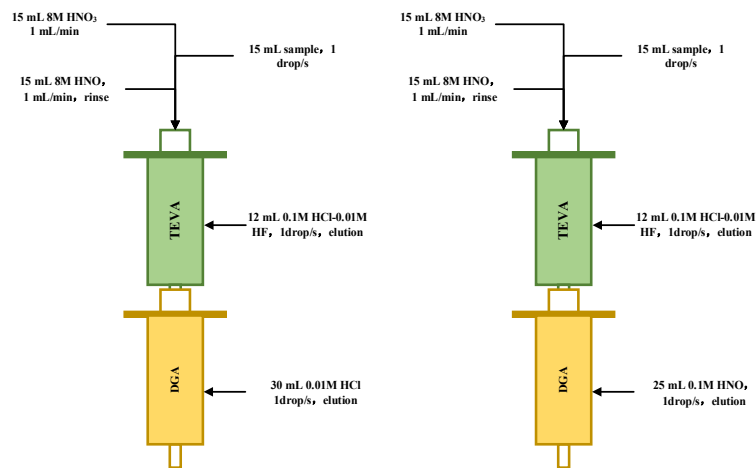


Figure 5: Flow chart of separation and purification of uranium and plutonium TEVA+UTEVA (Left)

Figure 6: Flow chart of separation and purification of uranium and plutonium TEVA+DGA (Right)

5.2. Separation and purification of uranium plutonium with TEVA+DGA

Refer to the method in 5.1 to complete the installation, numbering, pretreatment, sample loading and resin column washing of TEVA+DGA resin column; After the series resin column is disconnected, the treatment of TEVA resin column is the same as in 5.1; The DGA resin column was washed with 25 mL 0.1M HNO₃ and the flow rate was adjusted to 1 drop /s. When the liquid passed through the resin completely, the pressure of the pump was increased, the resin was drained, and the U eluting liquid was taken out and weighed and filtered to be measured. The separation and purification process of TEVA+DGA uranium and plutonium is shown in Figure 6.

6. Analysis of experimental results

6.1. Analysis of TEVA+UTEVA uranium plutonium experiment results

Table 1: TEVA+UTEVA resin uranium plutonium separation test record

NO.	Standard solution adding quality(g)		²⁴² Pu Elution quality(g)	²³⁸ U Elution quality (g)	²⁴² Pu Concentration (ppt)	²³⁸ U Concentration (ppt)	²⁴² Pu recovery efficiency	²³⁸ U recovery efficiency
	²⁴² Pu	²³⁸ U						
1#	0.103	/	11.49	29.458	0.2689	7.657	97%	/
2#	0.101	/	12.12	28.48	0.2787	7.856	108%	/
3#	0.102	/	12.028	28.568	0.2801	6.775	106%	/
4#	0.101	0.198	11.685	28.609	0.2983	122.3266	111%	100%
5#	0.103	0.195	11.582	28.8	0.2932	125.9476	106%	105%
6#	0.102	0.198	11.74	29.144	0.2901	112.1282	108%	93%

TEVA+UTEVA resin in series, uranium plutonium separation experiment results are shown in Table 1. The serial resin columns numbered 1[#]~3[#] in the table are the ²³⁸U background blank of the serial resin columns numbered 4[#]~5[#], which is used to calculate the amount of ²³⁸U introduced into the reagent during the experiment. From the measurement results of eluent in 1-3 #UTEVA resin, the concentration of ²³⁸U introduced by reagent is 6.775-7.856 ppt, accounting for about 5% to 7% of the actual concentration, and the background introduction is relatively low.

The recovery efficiency of UTEVA resin for ²³⁸U is 93%~100%. The ²³⁸U in the mixed solution of ²³⁸U and ²⁴²Pu was washed by the upper column and 15mL of 8M HNO₃ solution, and almost all of the ²³⁸U solution in the UTEVA resin was eluted by 30mL 0.01M HCl, which achieved a good sample recovery effect. The relative error produced in the measurement process of the instrument is 0.5%~0.9%, and the measurement results are accurate and reliable.

In addition to the 1[#] resin, the recovery efficiency of other resins for ²⁴²Pu is more than 100%, which is related to the error generated in the sample preparation and measurement analysis. As can be seen from the error bar in the figure, the relative error generated by ICP-MS measurement and analysis of the first four groups of data is relatively large, about 1.2%~2.9%, and the relative error of the last two groups of data is 0.3%~0.8%, which may be related to the change of ICP-MS sensitivity in the measurement process.

Except for the 4[#] resin column, the difference between the measured value and the expected value is less than 10%. From the experimental results, 12 mL 0.1M HCl-0.01M HF can completely adsorb ²⁴²Pu in TEVA resin, especially after adding HF, the recovery efficiency of ²⁴²Pu has been significantly improved. Compared with the research work done by Yang Yuning^[5], The recovery efficiency of the method used in this paper is improved by nearly ten percentage points, which may have a great relationship with the addition of HF. Adding a small amount of HF acid to the elution solution can form a complex with ²⁴²Pu in the resin, making it easier to eluate from the resin and achieve higher recovery efficiency. This separation method can effectively reduce the loss of Pu in the sample preparation process, and a small amount of HF can be directly sent to ICP-MS for measurement and analysis, which reduces the related work of acid removal and volume determination in the later stage, and improves the sample separation efficiency.

6.2. Analysis of TEVA+DGA uranium plutonium experiment results

Table 2: TEVA+DGA resin uranium plutonium separation test record

NO.	Standard solution adding quality(g)		²⁴² Pu Elution quality(g)	²³⁸ U Elution quality (g)	²⁴² Pu Concentration (ppt)	²³⁸ U Concentration (ppt)	²⁴² Pu recovery efficiency	²³⁸ U recovery efficiency
	²⁴² Pu	²³⁸ U						
1 [#]	0.099	/	12.117	24.896	0.2928	10.777	115%	/
2 [#]	0.102	/	12.084	24.658	0.2863	8.200	109%	/
3 [#]	0.111	/	12.107	24.815	0.2782	8.299	98%	/
4 [#]	0.102	0.191	11.941	24.731	0.3033	131.112	114%	96%
5 [#]	0.100	0.198	11.798	24.740	0.2926	86.746	111%	61%
6 [#]	0.102	0.196	11.662	24.511	0.2911	128.781	107%	91%

TEVA+DGA resin in series, uranium plutonium separation experiment results are shown in Table 2. Similar to TEVA+UTEVA resin ²³⁸U and ²³⁹Pu nuclide separation experiments, the first three groups of samples are background blank, used to calculate the content of ²³⁸U introduced by the experimental reagent. The concentration of ²³⁸U in the eluent of 1[#]~3[#] DGA resin ranged from 8.2 to 10.77 ppt, which was significantly higher than the background content of ²³⁸U in the eluent of UTEVA resin, which may be caused by the different substrates of the two eluents. The eluent used in UTEVA resin is hydrochloric acid solution, and DGA resin is nitric acid solution, so it can be seen that the content of ²³⁸U in nitric acid solution is higher than that in hydrochloric acid solution.

5[#] DGA resin is the outlier, the recovery efficiency of ²³⁸U is only 61%, and nearly 40% of ²³⁸U is lost. The count rate of ²³⁸U in the corresponding TEVA resin column is 167663.4 cps, which is not much different from the count rate of ²³⁸U in 4[#] and 6[#] TEVA resin. Therefore, ²³⁸U is not lost in TEVA resin, that is to say, all ²³⁸U in TEVA resin has been transferred to DGA resin during resin washing. From the ICP-MS measurement error point of view, the 5[#] DGA resin ²³⁸U measurement relative error is 1.2%, so it is not caused by the instrument measurement. Therefore, there may be two reasons for the loss of ²³⁸U. First, during the sample loading process, there was leakage when the flow passed through the interface of TEVA resin and DGA resin, so that part of the sample did not enter the DGA resin; Second, in the

process of leaching, the speed of the leaching liquid flowing through the DGA resin was not strictly controlled, which made the flow rate too fast, and the ^{238}U adsorbed in the DGA resin could not react with the nitric acid solution in time, resulting in part of the ^{238}U adsorbed on the DGA resin failed to elute. In addition to the 5[#] DGA resin, the recovery efficiency of the other two resin columns for ^{238}U is above 90%, and the recovery efficiency of the 4[#] resin column is the highest, which is 96%. Comparing the recovery efficiency of the two separation schemes for ^{238}U , the recovery efficiency of TEVA+UTEVA resin separation scheme seems to be higher than that of TEVA+DGA resin separation scheme, which may be caused by the difference of impregnating extractant on the inert carrier of UTEVA and DGA resin.

The recovery efficiency of ^{242}Pu is 98%~111%, which is basically similar to the recovery efficiency of TEVA+UTEVA series resin. By comparing the relative errors generated during the measurement of U and Pu by ICP-MS, it is found that the relative errors generated during the measurement of U by ICP-MS are 0.4%~1.8%, and the relative errors generated during the measurement of Pu are 0.2%~3.2%, which shows that the measurement of U by the instrument is relatively more stable.

7. Conclusion

The experimental results show that the two resins can achieve better separation effect in series. TEVA+UTEVA series resin separation scheme has a recovery rate of 93%~100% for U and a recovery efficiency of 97%~111% for Pu. The recovery efficiency of TEVA+DGA resin series scheme for U is 91%~96%, and the recovery efficiency of Pu is 98%~115%. Compared with that, TEVA+UTEVA resin has a higher recovery rate for U, and this resin series scheme is more economical. Therefore, this paper selects TEVA+UTEVA series scheme to realize the separation of nuclides.

References

- [1] XING S, ZHANG W, QIAO J, et al. Determination of ultra-low level plutonium isotopes (^{239}Pu , ^{240}Pu) in environmental samples with high uranium [J]. *Talanta*, 2018, 187: 357-64.
- [2] ZHANG L, LEVY I, VASSILEVA E. Determination of uranium isotopes in marine sediments and seawaters by SF ICP-MS after rapid chemical separation using TK200 resin [J]. *Environmental science and pollution research international*, 2023.
- [3] WANG Z, HUANG Z, XIE Y, et al. Method for determination of Pu isotopes in soil and sediment samples by inductively coupled plasma mass spectrometry after simple chemical separation using TK200 resin [J]. *Analytica Chimica Acta*, 2019, 1090.
- [4] MEN W, ZHENG J, WANG H, et al. Establishing rapid analysis of Pu isotopes in seawater to study the impact of Fukushima nuclear accident in the Northwest Pacific [J]. *Rep.*, 2018, 8(1): 1892.
- [5] Yang Yuning, WU Junhong, ZHANG Hailing, et al. Analysis method of $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratio in soil based on TOA extraction chromatographic layer [J]. *Nuclear chemistry and radiochemistry*, 2020, 42(4): 9.