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Mutual actinides separation by column separation method using impregnated resin for high accurate actinides analysis

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A new simplified method through chromatograph using impregnated resin under low concentration of HCl was accomplished for separation of Am(III)/Cm(III) as pretreatment for highly precise and accurate actinide analyses. The isotopic composition and elemental composition of actinides play a crucial role in understanding the characteristics of spent fuel and nuclear debris. In recent times, mass spectrometry techniques such as Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) have seen widespread use for the analysis of actinides. ICP-MS enables the simultaneous determination of multiple elements based on their mass numbers. To ensure precise and accurate analysis of actinides, it is essential to perform mutual separation of actinides performing isotopic determination using ICP-MS. This separation is necessary to eliminate isobaric interferences that exist in actinides series such as ²³⁸U and ²³⁸Pu, ²⁴¹Pu and ²⁴¹Am, and ²⁴³Am and ²⁴³Cm. While previous studies have successfully achieved the mutual separation of trivalent actinides from Plutonium and Uranium, this study focuses on the separation of Am/Cm. The separation of americium (III) from curium (III) was achieved through extraction chromatography using resin impregnated with Octyl (Phenyl)-N,N-Diisobutyl Carbamoyl Methyl Phosphine Oxide (CMPO) and N,N,N',N'-tetra octyl Diglycolamides (TODGA).

Keywords: americium; curium; TODGA; chromatograph; HCl

1. Introduction

The separation of Am and Cm have been studied extensively, in order to develop the nuclide separation methods as pre-treatment for high precise and accurate analyses of actinides in spent fuels and nuclear fuel debris by using mass-spectrometry such as ICP-MS/MS. Application of inductively coupled plasma-mass spectrometry (ICP-MS) in elemental analysis and isotope analysis of actinides have been massively studied in many fields of study included nuclear application [1-5].

ICP-MS allows multiple elements determination based on their mass number. Concerning that some isotopes in actinides series have similar mass number or isobar, chemical separation becoming mandatory before performing the isotopic determination in order to increase precise and accuracy of the isotopic determination using mass spectrometry. The aim of chemical separation is eliminating the potential isobaric interferences that exist in actinides series, such as ²³⁸U and ²³⁸Pu, ²⁴¹Pu and ²⁴¹Am, ²⁴³Am and ²⁴³Cm. Some studies shows that ion chromatographic separation is the most effective methods for ion interference removal [6,7]. In addition, The result

of study for the quantitative actinide analysis by using a triple quadrupole ICP-MS/MS (tandem ICP-mass spectrometry) also suggests for removing the interfering ions by chemical separation [8]. However, separation of Am from Cm is quite challenging study owing to their very similar chemical behaviour, same oxidation state and similar ionic radii, especially in the nitric acid solutions used in nuclear applications.

Regarding study of Am/Cm separation, increasing the oxidation state of americium from 3+ to 5+ or 6+ and followed by chemical separation in nitric acid solution was successfully done by some researchers [9-11]. However, changing the oxidation number of Am and Cm is not easy work because it naturally stables as trivalent actinides. Complete separation of Am from Cm was achieved by Suzuki et al with the nitric acid/methanol mixed solvent on pyridine resin as ion exchange resin [12]. Involving methanol and high concentration of HNO₃ in the separation process has safety and environmental disadvantages. Am/Cm separation by using cation exchange, Dowex 50, in hydrochlorides (HCl) solution was investigated with slight separated peak of Am and Cm as a result [13], better resolution of separation is required.

In the field of nuclear reprocessing, a hydrometallurgical process known as EXAm (Extraction of Americium) was developed to specifically isolate Americium (Am) from

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Curium (Cm) and other fission products using organic extractants. To improve the separation of Am from Cm during the extraction and scrubbing phases of this process, a complexing agent called N,N,N',N'-tetraethyl-diglycolamide (TEDGA) is introduced into the aqueous phase. Several strong diamide-type extractants with ether oxygen in their central structure have been developed and employed for the recovery of Am and Cm in nitric acid solutions. Notably, Diglycolamides (DGA) as an extractant have shown significant potential for the separation of trivalent actinides from lanthanides and, in particular, the separation of Am from Cm [15-18].

In the realm of nuclear technology, chemical separation within a nitric acid system is preferred because HNO₃ does not cause corrosion to facilities, unlike HCl. This is one of the reasons why most chemical separation studies are conducted using HNO₃, while separation in HCl remains an area for further exploration. In our previous study, separation of trivalent actinides (AnIII), Plutonium (Pu) and Uranium (U) is successfully done through column separation by using Tributyl Phosphate (TBP) resin and combining HNO₃ and HCl system [19]. In this study, we investigate the separation of Am/Cm in HCl using TODGA-resin. Unlike conventional methods like EXAm, where Am/Cm separation in spent fuel reprocessing is typically accomplished through solvent extraction, our approach focuses on solid-liquid separation for analytical purposes. The study commences by investigating the distribution coefficient on DGA resin in HCl solution through batch experiments, followed by chromatograph separation experiments.

A novel method for the separation of Am/Cm was developed using straightforward chromatographic techniques. This method utilizes normal DGA resin, which is commercially provided by Triskem Int. It enables high-resolution separation of Am/Cm, even at low concentrations, making it suitable for application in nuclear facilities with safety considerations in mind. Remarkably, this separation process consumes less than 50 mL of a low-concentration HCl solution, which offers environmental benefits.

Throughout the experiment, measurements of all elements were conducted using a gamma spectrometer and a triple quadrupole inductively coupled plasma mass spectrometer (ICP-MS/MS: Agilent 8900, Agilent Technologies, Japan) in IMR Tohoku University facilities, Oarai, Ibaraki.

2. Experimental

2.1. Material and instrumental

TRU-resin (TBP and CMPO impregnated resin) and DGA-normal-resin (TODGA impregnated resin) were obtained from Triskem. With particle size 100-150µm for TRU-resin, and 50-100µm for DGA-resin. Radioisotopes that used in this study are ²⁴¹Am and ²⁴⁴Cm newly bought in 2020 from Eckert & Ziegler. All of radioisotopes are stored in facilities of IMR Tohoku University. Stable isotopes that used in this are Cerium (Ce), Neodymium (Nd) and Gadolinium (Gd) as lanthanides ion are obtained from

ICP-MS standard solution manufactured by AccuStandard. Other materials were used in this study are HNO₃ and HCl solution by Ultrapur. A triple quadrupole inductively coupled plasma mass spectrometer (ICP-MS/MS: Agilent 8900, Agilent Technologies, Japan) was used for all element measurements in this study. This ICP-MS/MS is placed in Actinide Experiment Building, International Research Center for Nuclear Materials Science, Institute for Materials Research, Tohoku University.

2.2. Batch experiment

The adsorption behaviors of actinides on the impregnated resins, TRU-resin and DGA-normal-resin, in HCl and HNO₃ solution were investigated by batch experiments. We obtained the distribution coefficient of trivalent actinides and lanthanides in HCl and HNO₃ solutions with the different acid concentrations from 0.5 mol/L to 10 mol/L. In this experiment, each initial solution (before absorption) was prepared in 3 mL of acid solution contained 2 ppm of each lanthanide (Ce, Nd, and Eu) and 1 kBq of each trivalent actinide (Am and Cm). The amount of resin for each sample is 0.05 gr for batch experiment with DGA resin and 0.1 gr for batch experiment with TRU resin. Distribution coefficients were determined using where A₀ is the initial activity concentration before absorption, A is the activity concentration after absorption, V is the total volume of the solution and m is the mass of the resin.

$$K_d = \frac{A_0 - A}{A} \times \frac{V}{m} \quad (1)$$

2.3. Chromatograph separation

The feed preparation and chromatographic separation using two different resins (TRU and DGA) were conducted separately. Initially, Ce, Nd, Eu, Am, and Cm were prepared in 1 mL of 4 mol/L HNO₃ as an initial sample (feed) for chromatographic separation using TRU resin. The column separation experiment was carried out with approximately 8.5 mL of resin packed into a Muromac mini column L with a 10 cm column height. Extraction of An(III) and Ln from other impurity elements was conducted as the second step using TRU resin. Next, 1 mL of feed was injected, followed by a 4 mol/L HNO₃ solution to elute the impurities. And then, 0.1 mol/L HNO₃ solution was injected as the second solvent, followed by a 0.1 mol/L HCl solution. Each solvent was injected for approximately 15 mL, and every 1 mL of effluent volume was collected in a vial and measured using ICP-MS/MS, Agilent 8900.

The separation of Am and Cm was conducted as the final separation step in the study using DGA resin. Basically, the feed for Am/Cm separation using DGA-resin was prepared by collecting the last 3 mL sample of previous separation using TRU-resin in 0.1 mol/L HCl and adding Gd, Ce, Nd, Am, Cm into the feed solution to increase the concentration of the elements to 10 ppm for each lanthanide, and the amount of Am and Cm was increased nearly 20 times compared to what was

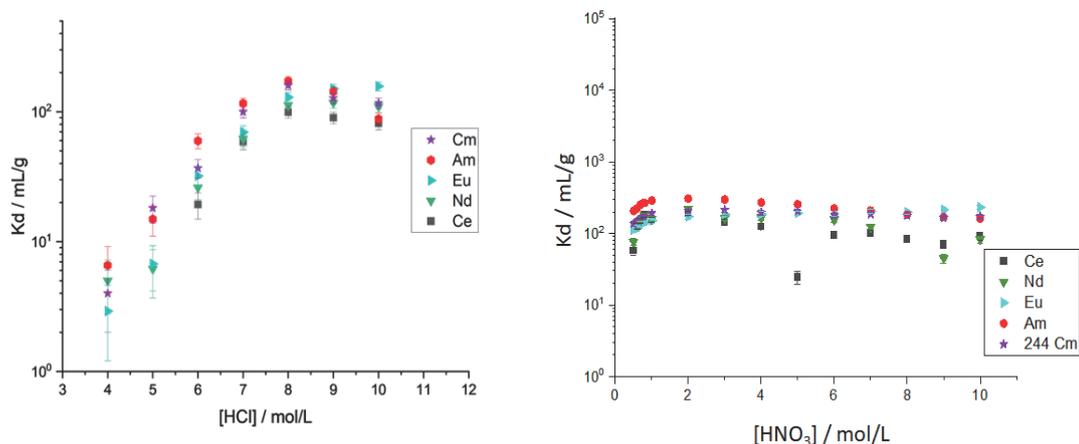


Figure 1. Behaviour of An(III) and Ln on CMPO (TRU) resin in HCl solution (left) and HNO₃ solution (right).

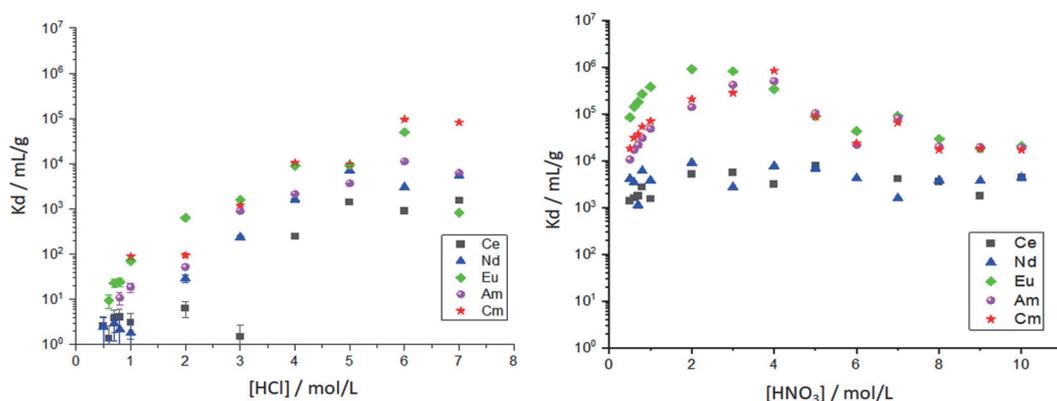


Figure 2. Behaviour of An(III) and Ln on DGA resin in HCl solution (left) and HNO₃ solution (right).

contained in the feed of TRU resin. Not only was the concentration increased, but the concentration of HCl was also raised from 0.1 mol/L to 1 mol/L HCl. Sample preparation was necessary before injecting the feed into the DGA resin column. After adjusting the concentration of HCl of feed solution to separation condition, 1 mol/L HCl was also injected into the resin for a conditioning process of approximately 20 mL. Next, 0.5 mL of feed was injected into the column, followed by approximately 30 mL of 1 mol/L HCl solution. Every 1 mL of effluent volume was collected in a vial for measurement using ICP-MS/MS, Agilent 8900.

3. Result and Discussion

3.1. Absorption behavior of An(III) and Ln in CMPO (TRU) resin and DGA resin

Before chromatograph separation, some batch experiments are conducted by using TRU-resin and DGA-resin to obtain the distribution coefficient (Kd) of trivalent actinides and lanthanides in HCl and HNO₃ solutions with the different acid concentrations from 0.5 mol/L to 10 mol/L. Kd showed the absorption behavior of An(III) and Ln elements on the resin. In the batch experiment, Ce, Nd,

and Eu were used to represent Ln elements in this system. To decide the next step of actinides separation, batch experiment was conducted to investigate the behavior of trivalent actinides and lanthanides in TRU resin and DGA resin.

Figure 1 shows trivalent actinides and lanthanides strongly absorbed into TRU resin and as we can see from **Figure 2**, the absorption of An(III) and Ln are even stronger on DGA resin in HNO₃ solution. On the other hand, affinity of An(III) and Ln went down in decreasing of concentration of HCl on TRU and DGA resin. This is clear, separation of Am and Cm will be difficult in HNO₃ solution due a strong bonding between the An(III) and Ln with both of resin in this condition. Based on batch experiment result, TRU resin will be used as An(III) and Ln extraction by using HNO₃ solution to extract An(III) and Ln and low concentration of HCl solution to recover the elements. In addition, Remarkable gap between Kd of Am and Cm in 1 mol/L HCl on DGA resin was obtain, this condition will be used for Am and Cm separation.

3.2. An(III) and Ln extraction by using TRU-resin

An(III) and Ln extraction is necessary separation of Am from Cm. The aims of extraction of An(III) and Ln is to

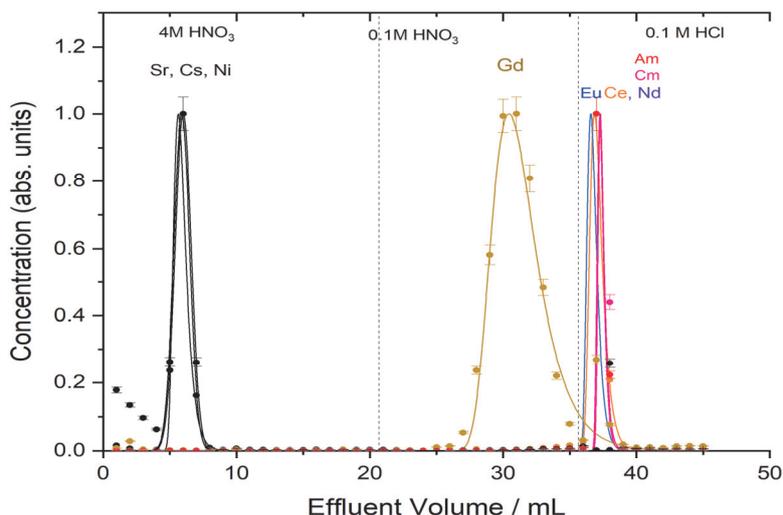


Figure 3. Chromatograph separation result of An (III) and Ln extraction by using TRU-resin

separate An(III) and Ln(III) from other impurities that might be contained in the feed solution and acid conversion. Acid conversion here means, the changing of acid condition of An(III) and Ln solution. Refer to PUREX process, extraction of uranium and plutonium process are commonly conducted in HNO_3 process, so we assume that An(III) and Ln solution will be obtained in HNO_3 solution. Before the separation by using TRU resin, feed preparation is required by adjusting the condition of feed solution in 4 mol/L HNO_3 . At this time, gadolinium (Gd) was added as additional of Ln elements. TRU-resin In extraction of An(III) and Ln experiment, diluted HNO_3 was used to check the absorption of An(III) and Ln in the very low concentration of HNO_3 solution, before the recovery of An(III) and Ln by using HCl solution.

0.5 mL of feed solution was injected into the column packed with TRU-resin and followed by 20mL of 4 mol/L of HNO_3 as the first solvent, 0.1 mol/L HNO_3 and 0.1 mol/L HCl solution as second and third solvent, respectively. The result shown in **Figure 3**, it confirmed that TRU-resin has strong absorption towards An (III) and all of trivalent Ln in high concentration of HNO_3 . Meanwhile, Other elements, such as Sr, Cs, and Ni shows no adsorption on TRU resin in HNO_3 solution. Sr, Cs, and Ni were contained in the feed from XSTC-311 standard solution by SPEX CertiPrep that was used as a source of U and Th element for actinides separation experiment by using TBP resin. The next step, 0.1 mol/L of HNO_3 was injected as second solvent to confirm the absorption behavior of An(III) and Ln in low concentration of HNO_3 . An(III), Ce and Nd as light lanthanides still strongly absorbed on the resin, while Gd which has higher mass number compare to Ce and Nd, eluted together with 0.1 mol/L. In this condition, separation of Gd and Nd seems possible on TRU-resin. Last, 0.1 mol/L HCl was injected to recover remains elements, which are An(III), Ce and Nd from TRU-resin.

The whole process of An(III) and Ln extraction by

using TRU resin could be simplify by removing the second solvent or diluted HNO_3 from the process. recovery of An(III) and Ln can be done by using 0.1 mol/L of HCl after separate An(III) and Ln from other elements in 4 mol/L HNO_3 .

3.3. Am/Cm separation by using DGA-resin

As the result of batch experiment of DGA resin, 1 mol/L of HCl was used for Am/Cm separation by using DGA resin. After adjusting the concentration of feed solution in 1 mol/L of HCl and conditioning process of column packed with DGA-resin, 0.5 mL of feed contained Am, Cm, Gd, Nd and Ce in 1 mol/L was injected into the column followed by ~35 mL of 1 mol/L HCl solution. every 1 mL of effluent volume was collected in the Vial and checked by using ICP-MS as mentioned in experimental section.

The result of separation is shown by **Figure 4**. We confirmed separation of Am and Cm was achieved in 1 mol/L of HCl. The elution order started from Ce, Gd, and Nd as lanthanides groups, respectively. Am and Cm as trivalent actinides group eluted after lanthanides group. the elution order of trivalent actinides is reverse to ionic radii.

4. Conclusion

The adsorption behaviors of trivalent actinides and lanthanides on TRU resin and DGA resin in HCl and HNO_3 solutions were investigated by batch-wise experiment and column chromatography. We obtained co-extraction of trivalent actinides and lanthanides from other elements in spent fuels and nuclear debris in 4 mol/L HNO_3 solution, and elution of trivalent actinides and lanthanide at a time in diluted HCl solution. This elution has also a role of acid conversion for next step. Mutual Am/Cm separation by using DGA impregnated resin by Triskem is achieved in 1 mol/L HCl solution through chromatography. Trivalent actinides are eluted before lanthanides group and the

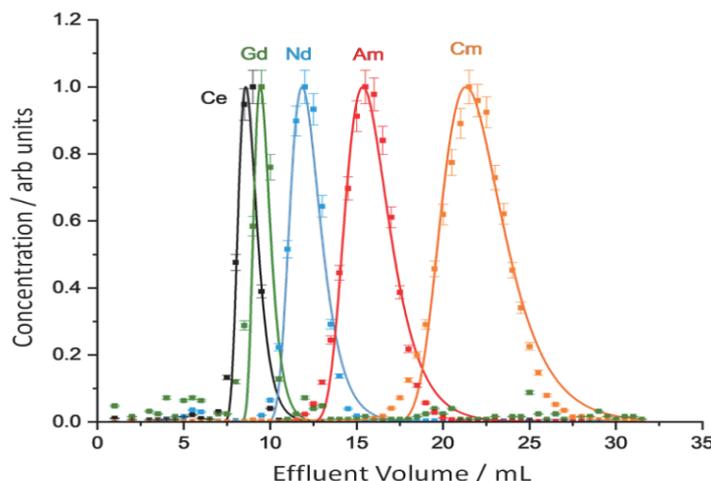


Figure 4. Chromatograph separation result of Am/Cm Separation

elution order of trivalent actinides is reverse to ionic radii. In terms of behavior of lanthanides, it is influenced by its ionic radii, smaller ionic radii such as Ce, Nd and Eu, tends to strongly absorbed into TRU-Resin and DGA-resin, while, lanthanides with bigger ionic radii such as Gd, has weaker affinity compare to Ce, Nd and Eu. this phenomenon can be seen clearly in the result of chromatograph using TRU-resin. additionally, in general, trivalent actinides and lanthanides are strongly absorbed into resin in HNO₃ system compare in HCl system.

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