

SEPARATION OF AMERICIUM AND CURIUM BY CHROMATOGRAPHIC TECHNIQUE USING TERTIARY PYRIDINE TYPE RESIN

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Abstract

The group separation of trivalent actinides and lanthanides and the mutual separation of americium and curium are necessary for the transmutation of americium. We have proposed the separation system based on the chromatography using the tertiary pyridine-type resin. In this separation system, the complete separation method of the trivalent actinides and lanthanides are already established using the hydrochloric acid and methanol mixed solvent. In the present work, the separation of americium and curium was investigated. It was found that the americium can be almost completely separated from curium by using the nitric acid and methanol mixed solvent.

Introduction

Various types of separation processes [1] have been proposed for the purpose of nuclear fuel reprocessing. Among them, almost all the modern reprocessing plants employ the PUREX. In spite of the successful implementation of the PUREX reprocessing, the mutual separation of fission products is beyond the scope of current PUREX plants. For the partitioning of actinides, a lot of new separation methods have been proposed. They are the molten salt electrorefining [2], advanced solvent extraction [3,4], ion exchange [5,6], and so on. However, the group separation of trivalent actinides and lanthanides and the mutual separation of minor actinides still remain as unsolved problems. The partitioning of trivalent actinides and lanthanides and the mutual separation of minor actinides are, especially, critical issue to create the innovation process for actinide burning and transmutation. The difficulty of separation of their elements is due to that the lanthanides and minor actinides have the same valence level in solution and the similar ion radii. We have proposed the separation system based on the chromatography using the tertiary pyridine-type resin. In this separation system, the complete separation method of the trivalent actinide and lanthanide are already established using the hydrochloric acid and methanol mixed solvent [7]. The mutual separation of trivalent actinides, i.e., americium and curium, is still an important problem at the present time. The following many studies were carried out. Hale and Lowe employed cation exchange chromatography using DTPA to separate americium and curium [8]. On the other hand, several studies tried to separate oxidized americium (Am(IV)) from other trivalent actinides [9,10]. This technique had been developed by the CEA, France as the "SESAME" process in the 1990's [11]. However, further study is still required for establishing a simpler and milder separation technique of these elements.

In the present study, we apply the chromatographic technique using the tertiary pyridine-type resin to the mutual separation of trivalent actinides, i.e. americium and curium, using a mixture of nitric acid and methanol.

Experimental

Tertiary Pyridine Resin

The resin used in the present experiment was highly porous tertiary pyridine-type resin embedded in silica beads. This resin was produced by the present research group of Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology [12]. The pyridine resin was made by synthesizing 4-vinylpyridine of 80weight% and m/p-divinylbenzene of 20weight% dissolved in mixed solvent of 60vol.% acetone and 40vol.% diethylphthalate in high porous silica beads. 2,2'-azobisisobutyronitrile (AIBN) and 1,1'-azobiscyclohexane-1-carbonitrile was used synthesis initiator. The chemical structure of this resin is presented in Figure 1. This resin has been confirmed to have the high radiation resistance [13]. By using the silica beads support, since the mechanical distortion doesn't occur, the pressure loss in chromatography operation is considerably suppressed. The high porous structure enables ions to easily diffuse into the resin. The average diameter of this resin is 60 μm . The total exchange capacity of the resin is 1.94 meq/g(dry) in Cl⁻ form. The cross-linkage is 20%.

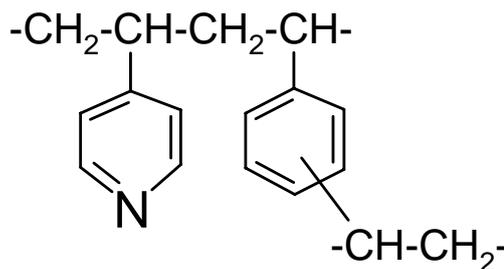


Fig.1 Chemical structure of tertiary pyridine type resin.

Materials

The trivalent actinides used in this study were ^{241}Am and ^{242}Cm . A mixed sample of ^{241}Am and ^{242}Cm was produced by irradiation of shielded $^{241}\text{AmO}_2$ in the Japan Materials Testing Reactor (JMTR) and was separated from fission products [7]. The sample in the solutions with a 40vol.%-conc. nitric acid and 60vol.%-methanol mixed solution included some amounts of $^{249,252}\text{Cf}$, because the sample used californium in other experiment was included. All solvents used in the present study were reagent grade and supplied by Wako Pure Chemical Ind., Ltd., Japan.

Chromatography Experiments

A mixture of trivalent actinides was dissolved into a concentrated nitric acid solution and the desired methanolic nitric acid solution. A 0.5 cm^3 portion of this solution was fed into a 10cm bed-height column packed with the 8 cm^3 of tertiary pyridine-type resin. This column was preliminarily conditioned with the same concentration of nitric acid solution or methanolic nitric acid solution. Then, the elution experiment was carried out by using the same concentration of nitric acid solution or methanolic nitric acid solution at room temperature at flow rate of $100\text{ cm}^3/\text{h}$. The effluent from the bottom of the column was collected in fractions of $2\sim 5\text{ cm}^3$. The identification of nuclear species and the evaluation of their relative concentrations in fractions were conducted by using an α -ray spectroscopy and a γ -ray spectroscopy; the elution curve of americium was drawn by result of γ -ray spectroscopy, the elution curve other elements was drawn by result of α -ray spectroscopy.

Results and Discussion

The elution chromatogram of americium and curium with concentrated nitric acid solution is shown in Figure 2. The open circles and the solid circles indicate the relative intensities of americium and curium, respectively. Although a slight peak separation between americium and curium was observed, their elution curves overlapped for the most part. Next, the chromatography experiment was carried out with methanol in addition to the nitric acid solution. The chromatogram with a 70vol.-%-conc.HNO₃ and 30vol.-%-MeOH mixed solution is shown in Figure 3. The separation of americium and curium is not sufficient, although the amounts of adsorption of both americium and curium increase. Furthermore, we carried out the chromatography with an additional increase of the methanol ratio until 60vol.%. Figure 4 shows the result of chromatographic experiment with a 40vol.-%-conc.HNO₃/60vol.-%-MeOH mixed solution. Three actinides, americium, curium, and californium, were included in the feed sample used in this experiment. As mentioned in subsection of *materials*, californium was regarded as a sort of impurity. But it was unexpected good fortune, because we obtain the adsorption behavior of californium on the tertiary pyridine resin in methanolic nitric acid solution. However, unfortunately, the amount of ²⁴⁹Cf ($E_{\alpha}=5.81$ MeV) in the sample was too small to identify its α peak. Although the amount of ²⁵²Cf seemed to be enough large to identify, the α peaks of ²⁵²Cf (6.12 MeV) were detected so closely to those of ²⁴²Cm (6.11 MeV) that it was difficult to distinguish them individually. Therefore, the elution curves of curium and californium were drawn by the gross using the α -peaks of ²⁵²Cm and ²⁴²Cf. The solid circles indicate the sum peak of curium and californium. The retention volume of the actinides in the chromatograph shown in Figure 4 became larger in comparison with cases of Figs. 2 and 3. It can be confirmed in Figure 4 that the elution curve of americium was clearly separated from those of curium and californium. It should be noted that the lump elution curve of curium and californium had two peaks at about 50 cm³ and 100 cm³ of effluent volume. These two peaks probably attribute to the individual elution of curium and californium. In order to identify these two peaks, γ -ray spectra were measured for the fraction samples around these peaks. A sharp peak of ²⁵²Cf ($E_{\gamma} = 43.4$ keV) was observed in the spectra of fraction around the first peak of elution curve obtained by α -spectrometer, while no considerable peak was observed in the spectra of the fractions around the second elution peak. The open squares indicate the relative intensities of γ -ray

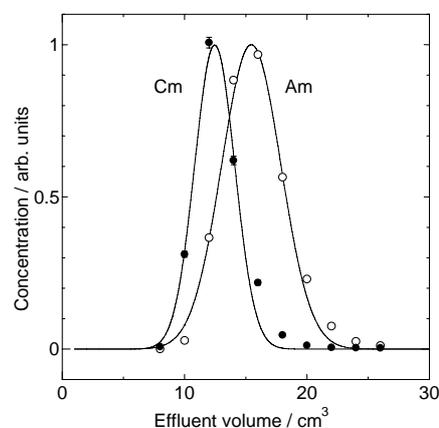


Fig. 2 Chromatogram of americium and curium with concentrated nitric acid solution.

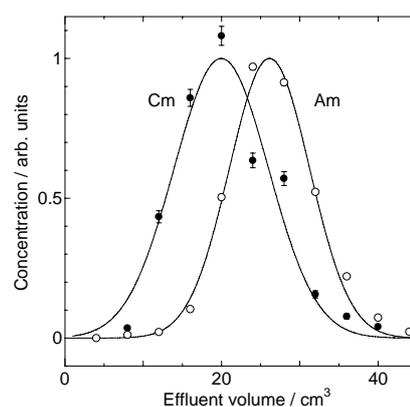


Fig. 3 Chromatogram of americium and curium with 70vol.-%-conc.HNO₃ and 30vol.-%-MeOH mixed solution.

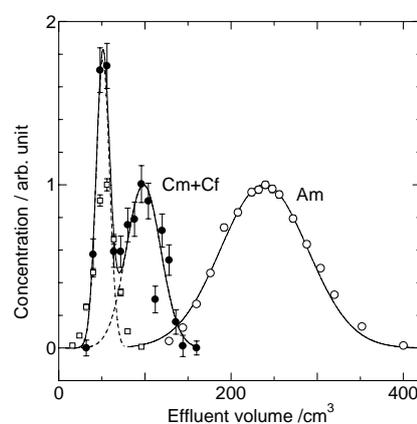
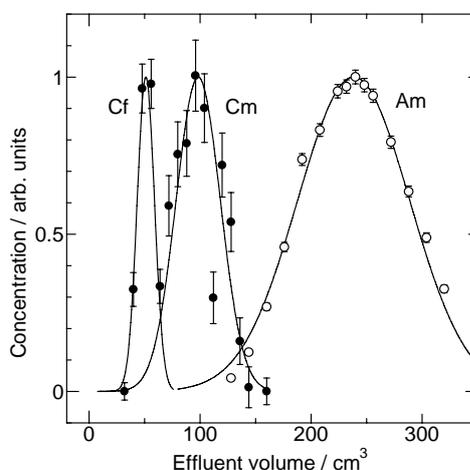


Fig. 4 Chromatogram of americium and curium with 40vol.-%-conc.HNO₃ and 70vol.-%-MeOH mixed solution.

peaks emitted from ^{252}Cf . The shape of the first elution peak is in good agreement with the elution curve drawn from the γ -peaks of ^{252}Cf . Furthermore, a peak of another californium isotope, ^{249}Cf (387.95keV), was also observed in the same fraction of first peak. Thus, we concluded that the first elution peak in Figure 4 attributed to californium and the second one ascribed to curium. The peak separation of curium and californium were carried out. The solid line on the curve of curium and californium in Figure 4 represents the fitting curve using summation of two Gaussian peaks to the experimental data obtained by α -ray spectroscopy. The dashed lines are the separated Gaussian curves. The result of peak-separation for the overlapped elution curves of curium and californium in Figure 4 by two peaks Gaussian curve fitting are anew shown in Figure 5. The actinides, americium, curium and californium, are confirmed to be individually separated. The trivalent actinides are eluted in the reverse order of atomic numbers.

Fig.5 Separation result of trivalent actinide.



The separation behaviour with concentrated nitric acid solution and methanolic nitric acid solution was compared. The separation factors of americium and curium ($S_{\text{Am/Cm}}$), the numbers of theoretical plates (N), and the resolution of americium and curium ($R_{\text{Am/Cm}}$) in the case of conc. HNO_3 solution and 40vol.% conc. HNO_3 /60vol.% MeOH mixed solution are shown in Table I.

Table I. Methanol effect. Comparison of concentrated nitric acid solution and methanolic nitric acid solution.

	$S_{\text{Am/Cm}}$	N_{Am}	N_{Cm}	$R_{\text{Am/Cm}}$
conc. HNO_3	1.47	40.9	58.4	0.367
40vol% HNO_3 /60vol% MeOH	2.52	22.2	24.2	0.992

These parameters are calculated using the parameter of the Gaussian fitted chromatogram profile, $C \sim \exp[-(V - V_r)^2 / 2\sigma^2]$, where C , V , and V_r are concentration, effluent volume, and retention volume, respectively. These factors about the separation are defined following as,

$$S_{\text{Am/Cm}} = (V_{r,\text{Am}} - V_0) / (V_{r,\text{Cm}} - V_0),$$

$$N = (V_r / \sigma)^2,$$

$$R_{\text{Am/Cm}} = (V_{r,\text{Am}} - V_{r,\text{Cm}}) / (2\sigma_{\text{Am}} + 2\sigma_{\text{Cm}}),$$

where V_0 is dead volume of column. The separation factor of americium and curium by using 40vol.%HNO₃/60vol.%MeOH mixed solution is about 1.7 times as large as by using only conc.HNO₃, while the numbers of theoretical plates by conc.HNO₃ are about 1.5-2.4 times as large as 40vol%HNO₃/60vol%MeOH mixed solution. The decrease of the number of theoretical plates means that ion exchange rate, or adsorption-desorption rate of ions on pyridine resin, is suppressed by methanol. That is, the methanol addition increases the adsorption of ions, but decreases the rate of adsorption-desorption of ions. The separation factor increases as a result of the deference of the adsorption increase. We speculate that the increase of adsorption by methanol addition is due to the dehydration effect of methanol, and that the decrease of rate is due to the bulky of solvated methanol substitute for water molecule. The resolution is proportional to $S-1$ and to the square root of R . According to this law, the resolution of americium and curium is increase to about 2.4 times with methanol addition. The experimentally obtained resolution is 2.7 times. According to the definition of resolution, if the resolution is over 1, the complete separation is achieved. Since the obtained separation factor is 0.992, we concluded that the americium and curium are able to be almost completely separated in our separation system. We expect that the higher resolution will be achieved by choice of ratio of appropriate concentration of nitric acid and alcohols.

Conclusion

Americium and curium were separated individually by using a tertiary pyridine resin embedded in silica beads with the mixed solvent composed of concentrated nitric acid solution and methanol. The adsorption of these elements on the resin was confirmed to be promoted by an increase of methanol ratio in the mixed solvent. It was confirmed that americium and curium are able to be almost completely separated by using a 10 cm resin column with the mixture of 40 vol.% conc. HNO₃ and 60 vol.%-methanol. The behavior of adsorption and separation of californium was also obtained. The elution order of the trivalent actinides in the present system is in the reverse order of atomic numbers.

Appendix: group separation of trivalent actinides and lanthanides

The group separation of trivalent actinides and lanthanides are already achieved by using the tertiary pyridine-type resin embedded in silica beads with concentrated hydrochloric acid and methanol mixed solution [7]. The resin using this separation system is exactly the same as the resin using in the present experimental system, and the experimental condition except for the solvents is also same. The result of the trivalent actinides and lanthanides separation with 70vol% concentrated hydrochloric acid and 30vol% methanol mixed solution is shown in Figure 6. The elution profile of americium and curium are fitted by asymmetrical Gaussian curve. We can see the complete group separation of trivalent actinides and lanthanides. The lanthanides and actinides are eluted in each group.

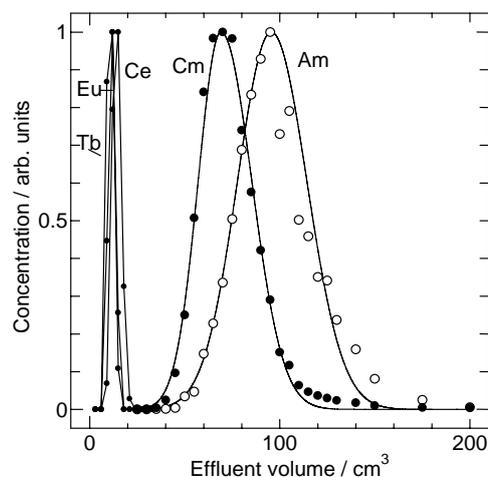


Fig.6 Chromatogram of trivalent actinides and lanthanides with 70vol.%conc.HCl/ 30vol.% MeOH mixed solution.

The mutual separation of elements in each group is not sufficient.

Furthermore, we carried out the chromatographic experiments with changing the hydrochloric acid concentrations [14] and with varying the adding ratio of methanol [15]. If the lower concentration of hydrochloric acid solutions than the concentrated hydrochloric acid is used, the adsorptions of both actinides and lanthanides drastically decrease. As a result, the group separation of actinides and lanthanides is not almost achieved. The addition of the methanol increases the amount of adsorption of actinides and lanthanides on pyridine resin and the separation factor. However, the group separation is confirmed to be achieved without methanol, although the distribution coefficients and the separation factor small.

In conclusion, the complete group separation of trivalent actinides and lanthanides can be achieved by chromatography using the tertiary pyridine resin in the hydrochloric acid solution system. While, nitric acid solution system is appropriate for the mutual separation of americium and curium.

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