Rapid Chemical Separation for Bk

T. Maruyama,[a] D. Kaji,[a] T. Kaneko,[a] S. Goto,[a] K. Tsukada,[b] H. Haba,[b] M. Asai,[b] S. Ichikawa,[b] Y. Nagame,[b] and H. Kudo*,[a]

[a]*Department of Chemistry, Faculty of Science, Niigata University, Niigata 950-2181, Japan*
[b]*Advanced Science Research Center, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan*

An anion exchange in mineral acid and methanol system was examined in view of rapid chemical separation. An elution behavior of Bk in hydrochloric acid–methanol system was obtained using ^{250}Bk. An elution behavior of Bk in nitric acid–methanol system was predicted from the relationship between an elution position and an ionic radius. The separation was completed for nitric acid–methanol system and for hydrochloric–methanol system within 40 and 25 min, respectively.

1. Introduction

There are a number of nuclides which have not been discovered even though they are expected to have fairly long half-lives especially in the neutron-rich region of actinides. Many new isotopes of actinides may be produced by use of neutron-rich targets such as ^{248}Cm, ^{249}Cf, and ^{254}Es. Neutron-rich Bk isotopes belong to such isotopes. The purpose of the present investigation is to develop a rapid separation method for the observation of neutron-rich berkelium isotopes. Discovery of such a nuclide needs separation from many kinds of nuclides which will be produced at the same time. Most separation methods for lanthanides and actinides have been based on the use of cation exchanger with eluents containing organic complexing agents. These methods are fairly rapid and the mutual separation is also good.[1–4] However, measurement of α particles and fission fragments are obscured by the residue of the organic agents which are not easily decomposed. Most solvent extraction methods also utilize organic complexing agents.[5] Therefore new chemical methods which enable the rapid separation of the actinide elements and the immediate preparation of counting sources suitable for α spectrometry are desired, so that we examined an anion exchange in mineral acid–alcohol system in which no residue and fast evaporation are expected.

2. Experimental

A strongly basic anion-exchange resin, MCI GEL CA08S (Mitsubishi Chemical Industries Ltd.), was used in the present work. The particle size of the resin is 11 ± 2 μm and the degree of cross-linking is 8%. The exchange capacity is larger than 1.2 meq/mL. The Teflon tube column of 2 mm inner diameter filled with the resin is illustrated in Figure 1(a). As eluent, methanol was selected for its properties of low viscosity and high vapor pressure. Figure 1(b) shows a schematic diagram of loading a sample solution and passing the eluent through the column. After conditioning the resin by methanol mixed with either conc. HNO$_3$ or conc. HCl in a volume ratio of 9 : 1, the eluent was stored in a reservoir, Spiral-II, by using a tube pump. By manipulating valves, 300 μL of the sample solution was introduced into the top of the column. Then the eluent was passed through the column and chromatograms were developed. The flow rate was controlled by a nitrogen gas pressure.

The elution behaviors of lanthanide and actinide elements were examined with varying the flow rate, methanol contents, and acid concentration. Tracers used in this work were ^{152}Eu, ^{148}Gd, ^{160}Tb, ^{241}Am, ^{242}Cm, ^{252}Cf, and fission products from ^{252}Cf. The effluent was collected either on a Ta dish for α-

particle measurement or into a plastic tube for γ-ray measurement.

An isotope of ^{250}Bk was used as a Bk tracer, which was produced from ^{248}Cm(^{18}O, X)^{250}Bk reaction by the tandem accelerator of Japan Atomic Energy Research Institute. About 400 μg/cm^2 thick ^{248}Cm was electrodeposited together with ^{152}Gd-enriched Gd of 50 μg/cm^2 thickness on a Be backing foil. As the target was originally prepared for rutherfordium chemistry, gadolinium was mixed to check the chemical behavior of rutherfordium homologue, Hf. The target was irradiated for about 50 min with the ^{18}O beam of 300 pnA in current. The incident energy of ^{18}O was 94 MeV on target. Nuclear reaction products were transported with an aerosol loaded gas-jet system, and collected on membrane filter of a 0.1 μm pore diameter. After collection the membrane filter was washed with a loading solution to prepare for the sample solution, to which ^{241}Am was added as a tracer.

An HPGe detector coupled with a multichannel pulse height analyzer was used for the measurement of γ-ray radioactivity. An automatic γ counting system with an NaI(Tl) scintillation detector, COBRA (PACKARD), was also employed when only
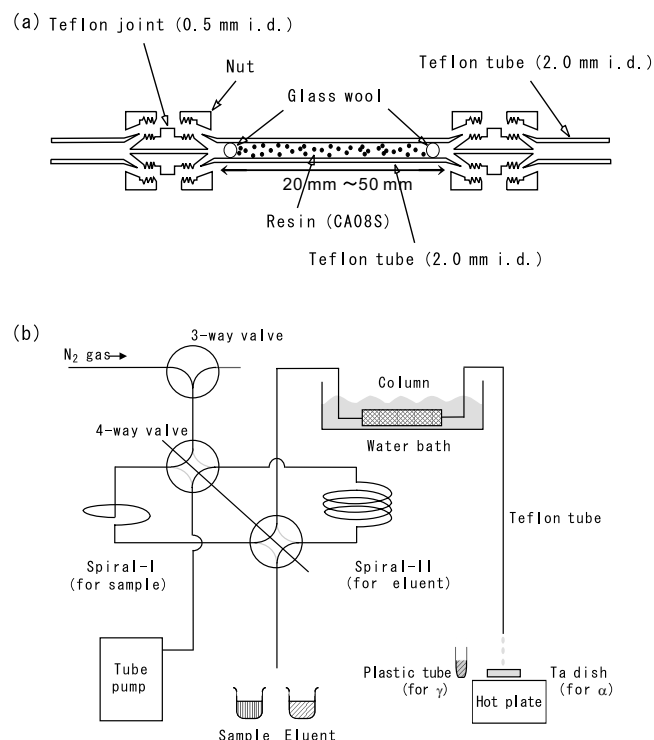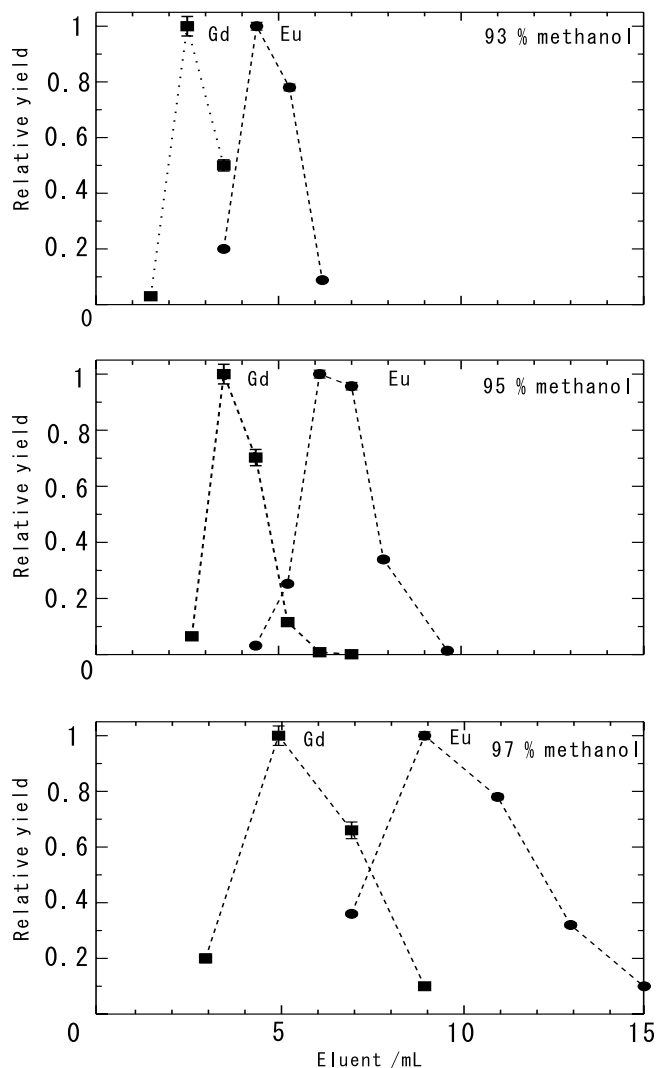

Figure 1. (a) Anion exchange column used in this work. (b) Schematic drawing of apparatus for anion exchange separation.

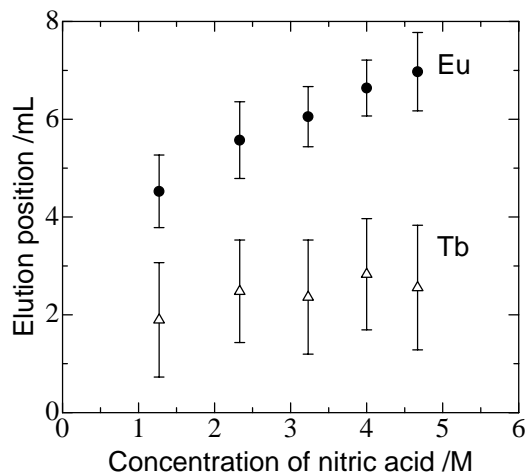*Corresponding author. E-mail: hkudo@curie.sc.niigata-u.ac.jp. FAX: +81-25-262-6171.

Figure 2. Effect of methanol content in 3.2 M HNO$_3$–methanol anion exchange system.

Figure 3. Peak position vs. nitric acid concentration. The attached error bars indicate the widths (FWHM) of the elution curves.

Figure 4. Elution curves of some lanthanides and actinides in nitric acid–methanol anion exchange system. The estimated elution curves for Bk and Sm are also shown.

a single tracer was used. A silicon surface barrier detector with a multichannel pulse height analyzer was used for the measurement of α radioactivity.
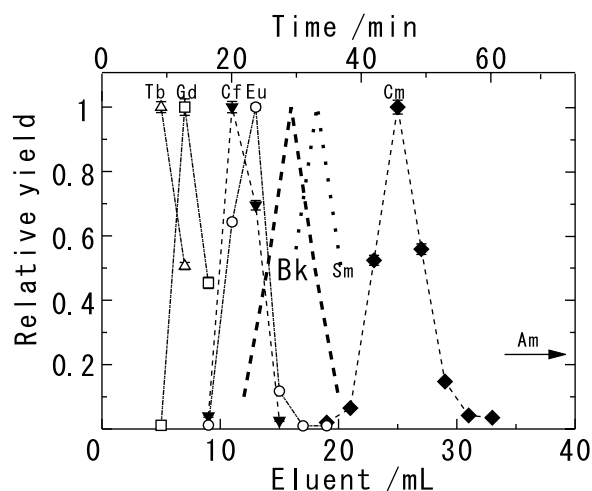
3. Results and Discussion

3.1. Nitric Acid–Methanol System. It is known that the elution positions for lanthanide and actinide elements are correlated with their ionic radii in an anion exchange in the nitric acid–methanol system.[6] This means that the elution position of a given element of actinide is easily predictable, if its trivalent ionic radius is known. Therefore, the nitric acid–methanol system was firstly examined by using several tracers. Essentially a rapid separation requires fast flow rate, so that the effect of the flow rate was examined. The peak position was found to be not influenced by the change of the flow rate, but the elution curves became broader as the flow rate got faster. The optimum flow rate was determined from the elution time and the peak broadening to be around 0.5–0.8 mL/min.

When the column temperature was kept at room temperature, peak broadening, serious tailings, and overlapping elution curves were observed in the chromatograms. This is caused by slow attainment of an exchange equilibrium at room temperature. In addition, the flow rate was slow compared with the cases at elevated temperatures under the same pressure. This is because the viscosity of the eluent is higher at low temperature. Therefore, the column temperature was kept at 80–85 °C. Although this temperature was almost an upper limit for the resin, the deterioration of the resin was not recognized after more than 20 runs of experiments.

In general, ions are more strongly adsorbed at higher methanol content,[7] so that good separation is expected at higher methanol content. On the other hand, the stronger the adsorption, the longer the elution time. In this point of view, the effect of methanol content was examined using ^{152}Eu and ^{148}Gd tracers. The results are shown in Figure 2. As is expected, higher methanol content gives a stronger adsorption. But at the highest methanol content examined, the width of the elution curve is considerably large. We define the figure of merit (FOM) as the difference of the peak positions divided by the sum of the widths of two elution curves. The best FOM was obtained at 95% methanol content. At this methanol content, the elution time for Eu was fairly short, about 20 min.

It was reported that adsorption on the resin is enhanced by an increase in nitric acid concentration.[7] Considering the separation time, the concentration of nitric acid was examined up to 4.7 M at 95% of methanol content. The results are shown in Figure 3. The best separation was achieved at the highest concentration of nitric acid. The elution time for Eu was about 25 min in 4.7 M nitric acid. This value of the elution time is still applicable to the separation for nuclides of a few tens minutes half-life.

Under the best condition obtained in nitric acid–methanol system, the chromatograms for several lanthanide and actinide elements were developed and displayed in Figure 4. The sequence of the elution was Tb < Gd < Cf < Eu < Cm < Am. Americium remained on the resin under the present condition. As the peak positions and the widths of the elution curves are found to be well correlated with the ionic radii of trivalent ions,[8] the chromatogram for Bk was predicted from these correlations
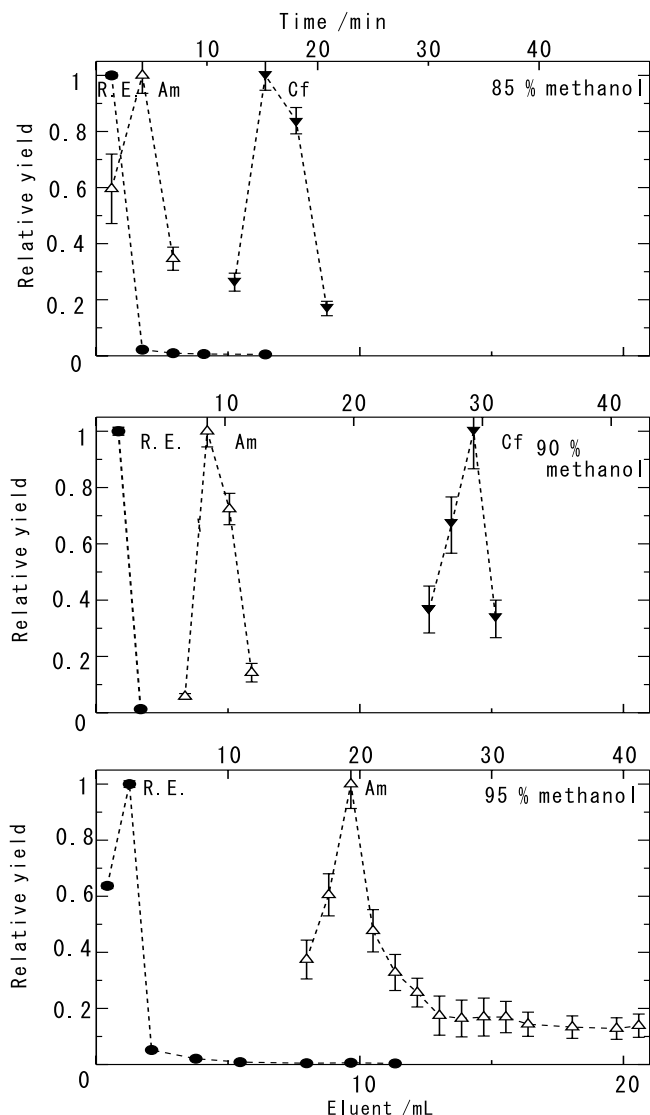
Figure 5. Effect of methanol content in 12 M HCl–methanol anion exchange system.
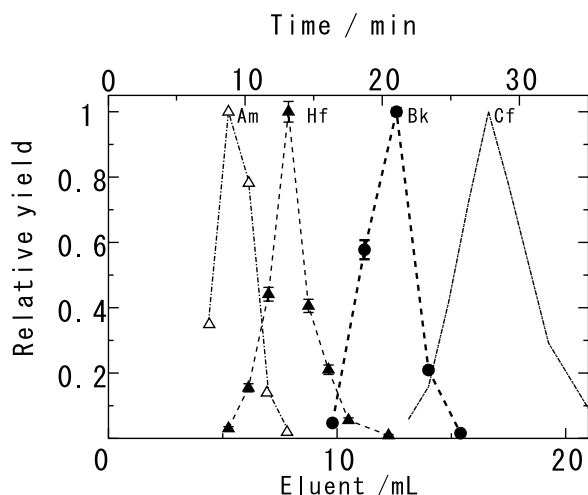
Figure 6. Elution curves of Hf, Am, Cf, and Bk in hydrochloric acid–methanol system.

and depicted in Figure 4. The values of the ionic radii given by Shannon[9] were used. As the ionic radius of Sm is close to that of Bk, the predicted chromatogram for Sm is also drawn in the figure. It is expected that the separation for Bk is completed in about 35 min and the separated fraction of Bk will be contaminated by small amounts of Cf, Eu, and Sm if exist.

3.2. Hydrochloric–Methanol System. Group separation of actinides from lanthanides has been made by an anion ex-

change in the hydrochloric acid–methanol system.[10] And it was reported that in the hydrochloric acid–methanol system is efficient the separation of Bk from other actinides. However, the elution time is quite long and the reported separation scheme cannot be used for a rapid separation as it is.

In the present work the fast flow rate for this system was examined whether it is applicable in rapid separation. The elution curves at fast flow rate over 1.0 mL/min became broad remarkably. It was found that the flow rate should be below 0.7 mL/min. At room temperature, demerits similar to those in the nitric acid system were encountered. All the neighboring elution curves overlapped each other and the tailing was considerably large. Therefore the experiments should be performed at about 85 °C. When the concentration of hydrochloric acid was less than 12 M, the adsorption on the resin was too weak and Am and Cf could not be separated. The concentration of hydrochloric acid was fixed to 12 M thereafter.

The effects of methanol content are shown in Figure 5, where the chromatographic behaviors of Am and Cf were displayed. It is clear from the figure that the best result was obtained at 90% of methanol content. In this condition, Am and Cf were well separated and the elution time for Bk was expected to be about 25 min judging from the elution position in Reference 7. The hydrochloric acid–methanol system seems to be more suited for the Bk separation, because no contamination from lanthanides and actinides were expected.

In order to examine the behaviors of other elements, such as fission products which will be produced at the same time with the Bk production, fission products from ^{252}Cf spontaneous fission were used as tracers. It was found that lanthanides (La, Ce, Nd, Pm, Sm), Ba, and Rh were observed only for the first fraction in a similar manner as seen in Figure 5, while Ru, Cd, and Te remained in the column. Small amounts of Ru were observed for all fractions. The elution curves of such elements as Zr, Ag, and I, were seen near the expected position of Bk. Accordingly the Bk fraction may be contaminated with small amounts of Ru, Zr, Ag, and I. However Bk can be separated from most of elements in this system.

Under the optimum condition in the HCl–methanol system, the chromatographic behavior of Bk was examined using ^{250}Bk which was produced from ^{248}Cm + ^{18}O reaction. The elution curve for Bk is shown in Figure 6 together with that for ^{241}Am which was added as a tracer. The elution curve of Cf which was obtained under the same conditions in the tracer experiment was also depicted in the figure. The elution curve for Hf is also depicted in the figure. Hafnium isotopes were produced from Gd + ^{18}O reaction. As is expected, the Hf behavior is about the same with that of its homologue, Zr. The chemical yield for whole procedure was about 80% including a wash-out efficiency from the membrane filter which was used as a collector in the gas-jet transport system. The Bk fraction was measured within 30 min from the end of bombardment. As the separation time is comparable to the theoretically predicted half-lives[11] of ^{252}Bk (23.3 min) and ^{253}Bk (51.3 min), the present separation method can be utilized to the observation of these nuclides.

4. Conclusion

Hydrochloric acid–methanol system is found to be more efficient compared with nitric acid–methanol system for the rapid separation of Bk. The elution behavior of Bk in the anion exchange with hydrochloric acid–methanol was obtained, which can be effectively utilized to the observation of unknown isotopes of Bk.

References

(1) S. G. Thompson, B. G. Harvey, G. R. Choppin, and G. T. Seaborg, J. Am. Chem. Soc. **76**, 6229 (1954).

(2) M. M. Zeligman, Anal. Chem. **37**, 524 (1965).

(3) K. Reagan and W. W. Meinke, Anal. Chem. **36**, 157 (1964).

(4) P. Dufek, M. Vobecky, J. Holik, and J. Valasek, J. Chromatography **435**, 249 (1988).

(5) L. Yuan-Fang, L. Chemg, K. J. Moody, D. Lee, G. T. Seaborg, and H. R. Von Gunten, J. Radioanal. Chem. **76**, 119 (1983).

(6) Y. Marcus and F. Nelson, J. Phys. Chem. **63**, 77 (1959).

(7) S. Usuda, JAERI 1315 (1989).

(8) T. Maruyama, Master Thesis, Niigata University, 2002.

(9) R. D. Shannon, Acta Crystallorg. A **32**, 751 (1976).

(10) E. K. Hulet, R. G. Gutmacher, and M. S. Coops, J. Inorg. Nucl. Chem. **17**, 350 (1961).

(11) T. Tachibana, M. Yamada, and Y. Yoshida, Prog. Theor. Phys. **84**, 641(1990); T. Tachibana and M. Yamada, *Proceedings of the International Conference on Exotic Nuclei and Atomic Masses, Arles, 1995*, edited by M. de Saint Simon and O. Sorlin (Editions Frontières, Gif-sur-Yvette, 1995), p. 763.