

Anion-exchange separation of americium and the lanthanides using a single column

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A sequential separation technique using an anion-exchange column developed in the previous works has the potential to completely separate picograms of Am from the lanthanides using mixtures of acetic acid, hydrochloric acid, and nitric acid as the eluents, without any functional ligands or special columns. This experimental result implies that ultra-trace actinides, including Am, Pu, U, and Th in environmental samples can be sequentially separated by combination of these mixed-media eluents and an anion exchange column.

1. Introduction

Americium is an anthropogenic actinide produced in nuclear power plants and from the explosion of Pu atomic bombs. Americium-241 can be produced as a decay product of ^{241}Pu . The increase of ^{241}Am due to ^{241}Pu decay may significantly enhance the alpha-activity level in a contaminated area for a certain period of time¹. Using the $^{241}\text{Am}/^{241}\text{Pu}$ ratio, the purification age, which is defined as the time elapsed since the last chemical separation, can be estimated. The Pu purification age was accurately determined by measuring the $^{241}\text{Am}/^{241}\text{Pu}$ ratio in a Pu-only sample and a U-Pu particle mixture synthesized from a reference sample^{2,3}. For the determination of ^{241}Am and ^{241}Pu by ICP-MS, it is necessary to chemically separate these elements, because the mass difference between these isobars ($\Delta m = 2.3 \cdot 10^{-5}$ amu) is too small to be separated by ICP-MS. Many analytical techniques based on ion chromatography and solvent extraction have been developed for the chemical separation of Am and Pu from matrix elements. Americium is a member of the actinides, whose chemical properties are very similar to those of the lanthanides. Ultra-trace levels of Am may co-exist with micro-grams of lanthanides in environmental samples, including soils and sediments.

For these samples, chemical separation of Am from the lanthanides must be incorporated in separation process, as high concentrations of lanthanides in the sample may interfere with the accurate measurement of ultra-trace quantities of Am. This interference occurs due to the matrix-effect, which leads to a loss of sensitivity and deposition of salts on the orifice, sampling cone, and skimmer cone of the ICP-MS instrument. Lanthanides and actinides can be effectively separated using some selective ligands^{4,5}, including thiocyanate salts⁶ and extractants on Eichrom resins, including DGA⁷ and TEVA⁸. However, some of these acid-resistant ligands may elute with the target elements, which is a severe issue for radiochemical analyses, besides they may be very expensive compared with conventional ion-exchange resins. In some cases, several tandem columns and/or systematic separation procedures are required to remove other matrix elements⁸. The sequential anion-exchange separation of U, Pu, Th, Pb, and the lanthanides was successfully achieved by using a suitable combination of acetic acid, nitric acid, hydrochloric acid, and the hydrofluoric acid for selective elution of each element in our previous works⁹⁻¹¹. In the current work, elution behavior

of Am in this separation system was investigated by separating an ^{243}Am spike solution.

2. Experimental

The elements of interest were separated using a sequential system known as the clean and automatic separation system for ultra-trace analysis (CASSUAL)⁹⁻¹¹. This system consists of a small anion-exchange column, automatic inert valves, a fraction collector, and Teflon tubes. The eluents for this sequential separation were stored in the thick Teflon tubes, and they were extruded using pressurized argon gas at 0.45 MPa. The eluent change and effluent collection were automatically controlled by a computer program. The flow rate of the eluents ranged from 0.03 to 0.07 mL/min, depending on the concentration of the acid component. An anion-exchange resin (MCI-GEL CA08S, resin size: $11 \pm 2 \mu\text{m}$, Mitsubishi Chemical Corp., Japan) that was strongly basic (8% cross linkage, Cl⁻ form) was used for the separation. The MCI-GEL products have been developed for high performance liquid chromatography (HPLC), and the resin size is well-controlled to obtain high resolution of eluents with excellent reproducibility because the resins are essentially spherical and have a controlled, narrow particle size distribution. This resin had the same composition as Dowex 1×8 (Dow Chemical Company, USA). Some varieties of Dowex 1×8 in resin size are available. Particle size is roughly controlled, and the particle size of the finest Dowex 1×8 resin ranges from 200 mesh to 400 mesh (equivalent to 38–75 μm). More fine resin such as the CA08S in resin size isn't available from this company. Fresh resin (dried weight: 72 mg) was packed into a PFA tube (2 mm inner diameter) to make a 50-mm-long column (column volume (CV): 0.158 mL).

A solution containing 4 pg of ^{243}Am (ORNL, USA) was used to investigate the Am separation profile. Water was deionized and purified (resistivity: 18.2 M Ω -cm) using a Milli-Q water system (Millipore Corp., USA). Highly pure HCl, HNO₃, HF (TAMA-Pure AA-10 or AA-100 grade, Tama Chemicals, Co. Ltd., Japan), acetic acid (ultra-pure grade; >99.9% purity, Kanto Chemical Co. Ltd., Japan), and hydrochloric hydroxylamine (NH₂OH·HCl) (guaranteed reagent (GR) grade; 99.0% purity, Merck Co., Germany) were used without further purification. The ^{243}Am spike solution was pipetted into a Teflon beaker, and dried with a hot-plate. The residue after evaporation was dissolved in 500 μL of a mixture of 16M acetic acid and 0.2M HNO₃; the composition of this mixture was the same as that of the first eluent. The feed solu-

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tion was then loaded on the separation column via a sample loop. The effluent was collected periodically in separate vials, and each fraction was dried using a hot-plate. The evaporation residues were dissolved in 1 mL of 15M HNO₃ and then dried again. Finally, the evaporation residue was dissolved in 5 mL of 0.3M HNO₃. The ²⁴³Am intensity in each elution fraction was measured using sector-field ICP-MS (SF-ICP-MS) (ELEMENT-2, ThermoFisher Scientific Inc., Germany). The recovery yield of Am was calculated from the ratio of the intensity of ²⁴³Am in the fraction of interest to the sum of the intensities of all fractions. The standard deviation of the Am recovery yield was calculated from variation of the ion intensity in 5 repeats of ICP-MS measurement. All treatments were carried out in clean rooms (ISO class 5 and 6) at the Clean Laboratory for Environmental Analysis and Research (CLEAR) of Japan Atomic Energy Agency (JAEA)¹².

3. Results and discussion

The calculated recovery yields of each fraction are summarized in Table 1. Americium was retained on the column in the first two fractions, which were indicated as M-1 and M-2 fractions in the Table 1, and then gradually eluted in the fractions Ln-4 (Am recovery yield; 0.4%) and Ln-5 (1.1%) after passing through the 11.6 CV of the eluent used for lanthanide separation. By the end of this step, total Am loss was 1.7%. All the remaining Am was eluted in the subsequent fractions Th-1 (89.3%) and Th-2 (8.9%). In previous works⁹⁻¹¹, alkaline metals and alkaline earth metals were completely eluted in the first mixed-media equivalent to the M-1 and M-2 fractions, and then the lanthanides were completely eluted with the first two fractions of the second eluent, which corresponds to the first 2 fractions (total 7.5 CV), Ln-1 and Ln-2 in this work. These results imply that Am can be simply and sequentially separated from lanthanides and also alkaline metals and alkaline earth metals, by only elution with this mixed acid. Kimura *et al.*¹³ reported the calculated inner sphere hydration number of Cm³⁺ and several other lanthanide (III) species

decreased remarkably with increasing the mole fraction of the non-aqueous component of the water/non-aqueous solvent mixture, including the water/methanol mixture. Their experimental results showed that the hydration number of Cm³⁺ was smaller than that of the lanthanide (III) species in the solvent containing a greater amount of the non-aqueous component, and also indicated that the H₂O molecules in the first coordination sphere of the ions were replaced to a considerable degree by the non-aqueous molecules.

The mechanism by which Am eluted at a different position than the lanthanides in this work might be explained by the difference of their inner-sphere hydration number in the first coordination sphere in a water/non-aqueous solvent mixture. In this scenario, acetic acid plays as the role of a polarized non-aqueous solvent, similarly to methanol in their report. In future works, sequential separation of Am, Pu, U, Th and the lanthanides using an anion-exchange column will be reported, and the chemical behavior of the lanthanides and Am in mixed media composed of mineral acids and acetic acid mixed media will be investigated.

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References

- (1) J. Zheng, K. Tagami, S.H. Takeda, W. Bu, *J. Anal. Atom. Spectrom.* 28, 1676 (2013).
- (2) Y. Miyamoto, F. Esaka, D. Suzuki, M. Magara, *Radiochim. Acta* 101, 745 (2013).
- (3) Y. Miyamoto, D. Suzuki, F. Esaka, M. Magara, *Anal. Bioanal. Chem.* 407, 7165 (2015).

TABLE 1: Recovery yields of Am by sequential anion-exchange separation using acetic acid-based mixed media

Fraction No.	Elution volume, [cumulative volume] ^{*1} (CV)	Recovery yield of ²⁴³ Am (%) ^{*2}	Composition of the eluent	Eluted element in the previous work ^{*3}
M-1	9.1 [9.1]	0.1 ± 0.1	16 M CH ₃ COOH, and 0.2 M HNO ₃	Mg, Rb, Sr, Cs, Ba, Be, Sc, Cr, Mn, Te
M-2	11.1 [20.2]	0.0 ± 0.0		
Ln-1	3.7 [3.7]	0.0 ± 0.0	15 M CH ₃ COOH, 0.80 M HCl, 0.9 M HNO ₃ , and 0.03 M NH ₂ OH·HCl	Lanthanides, Y, Co
Ln-2	3.8 [7.5]	0.1 ± 0.1		
Ln-3	4.1 [11.6]	0.0 ± 0.0		
Ln-4	4.2 [15.8]	0.4 ± 0.1		
Ln-5	6.0 [21.8]	1.1 ± 0.1		
Th-1	2.5 [2.5]	89.3 ± 4.2	12 M CH ₃ COOH, and 2 M HCl, 0.1 M HF	Th
Th-2	3.2 [5.7]	8.9 ± 0.6		
Th-3	3.5 [9.2]	0.0 ± 0.0		
Th-4	3.6 [12.8]	0.0 ± 0.1		
Th-5	6.5 [19.3]	0.0 ± 0.1		
Pb	14.5 [14.5]	0.0 ± 0.1	9M HCl	Pb, Cu, In, Ag
Fe	3.0 [3.0]	0.0 ± 0.0	8M HNO ₃	Fe, Zn, Ga, Cd
Pu	14.8 [14.8]	0.0 ± 0.1	6M HCl, and 0.1M HF	
U	11.8 [11.8]	0.1 ± 0.1	0.2M HCl, and 1M HF	U, Sn, Bi
Total	105.4	100.0 ± 4.3		

*1: Cumulative volume expressed in column volume (CV) unit of the fractions of interest. 1 CV is equivalent to 0.158 mL.

*2: The standard deviation of the recovery yields was calculated from variation of the ion intensity in 5 repeats of ICP-MS measurement.

*3: The elements which >50% of the total amount was eluted in the fraction of interest in the previous work¹¹.

- (4) A.K. Sengupta, A.M. Bruce, *Ion Exchange and Solvent Extraction*, Vol.19 (CRC Press, Boca Raton, 2010).
- (5) M. Nilsson, C. Ekberg, M. Foreman, M. Hudson, J.O. Liljenzin, G. Modolo, G. Skarnemark, *Solvent Extr. Ion Exch.* 24, 823 (2006).
- (6) T.S. Rudisill, D.P. Diprete, M.C. Thompson, *J. Radioanal. Nucl. Chem.* 296, 631 (2013).
- (7) K. Dasthaiah, B.R. Selvan, A.S. Suneesh, K.A. Venkatesan, M.P. Antony, R.L. Gardas, *Sep. Sci. Technol.* 52, 2308 (2017).
- (8) U. Nygren, I. Rodushkin, C. Nilsson, D. C. Baxter, *J. Anal. Atom. Spectrom.* 18, 1426 (2003).
- (9) Y. Miyamoto, K. Yasuda, M. Magara, *Analyst* 140, 4482 (2015).
- (10) Y. Miyamoto, K. Yasuda, M. Magara, *Analyst* 140, 4720 (2015).
- (11) Y. Miyamoto, K. Yasuda, M. Magara, *J. Radioanal. Nucl. Chem.* 309, 303 (2016).
- (12) S. Usuda, K. Yasuda, Y.S. Kokubu, F. Esaka, C.G. Lee, M. Magara, S. Sakurai, K. Watanabe, F. Hirayama, H. Fukuyama, K. T. Esaka, K. Iguchi, Y. Miyamoto, J.Y. Chai, *Int. J. Environ. Anal. Chem.* 86, 663 (2006).
- (13) T. Kimura, R. Nagaishi, Y. Kato, Z. Yoshida, *Radiochim. Acta* 89, 125 (2001).