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Application of extraction chromatography to the separation of thorium and uranium dissolved in a solution of high salt concentration

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Abstract

Extraction chromatography with commercially available UTEVA resin (for uranium and tetravalent actinide) was applied for the separation of Th and U from control solutions prepared from a multi-element control solution and from sample solutions of solidified simulated waste. Thorium and U in control solutions with 1–5 mol/dm^3 HNO_3 were extracted with UTEVA resin and recovered with a solution containing 0.1 mol/dm^3 HNO_3 and 0.05 mol/dm^3 oxalic acid to be separated from the other metallic elements. Extraction behavior of U in the sample solutions was similar to that in the control solutions, but extraction of Th was dependent on the concentration of HNO_3. Thorium was extracted from 5 mol/dm^3 HNO_3 sample solutions but not from 1 mol/dm^3 HNO_3 sample solutions. We conjecture that thorium fluoride formation interferes with extraction of Th. Addition of $Al(NO_3)_3$ and $Fe(NO_3)_3$, which have higher stability constant with fluoride ion than Th, does improve extractability of Th from 1 mol/dm^3 HNO_3 sample solution.

Keywords: UTEVA resin; Low-level radioactive waste; Rapid and simple chemical separation; Thorium; Uranium; ICP-MS

1. Introduction

In order to reduce the volume of low-level radioactive waste arising from operation of research reactors and from use of radionuclides in scientific research and radiation technology development, treatment of the waste by melting with plasma heating is being planned at the Japan Atomic Energy Agency (JAEA). The products of the melting treatment are homogeneous glass-like solids (solidified products) [1]. When the solidified products are disposed of in near surface repositories, concentrations of radionuclides contained in the waste package have to be evaluated. Among α-ray emitting nuclides, ^{232}Th, ^{238}U, ^{237}Np, ^{238,239,240,242}Pu, ^{241,243}Am, and ^{244}Cm are the objects of attention because they are relatively long-lived and thus have potential risk of radiological impact on the public. The concentration of these α emitters can be measured by inductively coupled plasma mass spectrometry (ICP-MS) for ^{232}Th, ^{238}U, and ^{237}Np and by α spectrometry for ^{238,239,240,242}Pu, ^{241,243}Am, and ^{244}Cm. These detection methods have been widely used for high precision analysis for actinides because of their high detection power [2–4].

For the measurement of the α-ray emitting nuclides by ICP-MS, the solidified products are dissolved in diluted HNO_3 solutions to prepare sample solutions. Though the concentration of matrix elements of the solidified products in these solutions is high, that of the targeted nuclides is very low. In such case, suppression or enhancement of signals of targeted nuclides is often observed (matrix effect). In this case, chemical separation of the targeted nuclides is indispensable for accurate determination. α-Ray spectrometry also requires chemical separation because large amounts of matrix elements absorb α energy and change the spectrum shape and some actinide isotopes emit α-rays with energy spectra indistinguishable from the targeted nuclides.

To provide a rapid and simple chemical separation method of actinide elements, extraction chromatography technique using a column packed with resins such as UTEVA, TEVA (for tetravalent actinide) and TRU (for transuranic) has been developed [5–8], and this has been applied to sample solutions of groundwater, soil, urine, high level radioactive waste, etc. [5–15]. When the sample solution is diluted HNO_3 containing only actinide elements, these elements are identified as follows: Among these resins, TRU resin has the highest extractability for actinide

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elements of different valences. It extracts not only tetra- and hexa-valent ions but also trivalent ions from HNO_3 solutions of high concentration (>1 mol/dm^3). However, TRU resin needs a relatively large amount of stripping solution and/or stripping agent to elute tetra- and hexa-valent actinide elements. TEVA resin extracts tetravalent actinide elements from HNO_3 solutions of high concentration (>1 mol/dm^3) and elutes them with a small amount of stripping solution. However, hexa-valent uranium is hardly extracted from HNO_3 solutions with TEVA resin. UTEVA resin extracts tetra- and hexa-valent actinides from HNO_3 solution of high concentration (>1 mol/dm^3) simultaneously and elutes them with a small amount of stripping solution.

Based on this information about these resins, the separation of Th and U with UTEVA resin, Am and Cm with TRU resin and Pu and Np with TEVA resin after the solidified products were dissolved in HNO_3 solution was planned in our laboratory. In the present paper, the separation of Th and U with UTEVA resin using a control solution made from a multi-element standard solution and a solution of the above solidified products is reported, and the difference in the extraction behavior of Th and U in these solutions is discussed. Appropriate conditions for the separation of Th and U from the solution are proposed.

2. Experimental

2.1. Reagents

UTEVA resin was purchased from Eichrom Technologies, USA, as a 2-cm^3 packed column, which had a frit above a resin bed to prevent the stirring of resin during injection of the sample. A liquid layer of about 1.3 cm^3 was maintained on the resin bed in the column during operation in order to avoid absorption of air by the resin bed. Multi-element standard (MES) solution for ICP-MS measurement, containing 10 μg/cm^3 each of Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Tl, Pb, Th, and U, was purchased from Accu Standard Inc. Nitric acid (60%), perchloric acid (70%), hydrochloric acid (35%), hydrofluoric acid (47%), and oxalic acid (98%) were of analytical grade and were purchased from Wako, Japan.

2.2. Digestion of the solidified products

An aliquot of a product whose composition was 12 wt% FeO and 88 wt% concrete and which was solidified by plasma melting [1] was cut out and ground into powder with particle size less than 75 μm. One gram of the powdered sample was put in a PTFE bomb and 5 cm^3 of 13 mol/dm^3 HNO_3 and 5 cm^3 of 29 mol/dm^3 HF were added. The bomb was tightly sealed and placed in a microwave oven (ETHOS-900) to heat the sample. The microwave energy was supplied for 10 min at 300 W, 10 min at 650 W, and 10 min at 400 W sequentially. After being cooled, the contents of the bomb were transferred into a PTFE beaker and heated on a hot plate to evaporate SiF_4 and excess HF. Evaporation and dissolution in HNO_3 and HF solutions were repeated several times under appropriate conditions. After $HClO_4$ fuming treatment was carried out to remove fluorides, the residue was finally dissolved in 1 mol/dm^3 HNO_3 solution. A small amount of HCl and H_2O_2 was added to the solution to aid dissolution of iron. This solution was filtered through a paper filter (Advantec, No. 5C) to remove a small amount of the residue. The volume of the solution thus obtained containing 1 g of the solidified product was 16.65 cm^3. This solution was designated as the SPD solution.

2.3. Sample solutions

Control solutions were prepared using the MES solution. Four cubic centimeters of the MES solution was evaporated to dryness and the residue was dissolved in 4 cm^3 of 1, 3, and 5 mol/dm^3 HNO_3. The resulting solutions were termed C-1M, C-3M, or C-5M, respectively.

Sample solutions were prepared as follows: eight micro cubic centimeters of the MES solution were added to 3.3 cm^3 of the SPD solution. The solution was evaporated to dryness and the residue was dissolved in 4 cm^3 of 1, 3, and 5 mol/dm^3 HNO_3 to prepare sample solutions termed S-1M, S-3M, and S-5M, respectively. In another case, the residue was dissolved in 1 M HNO_3 solutions containing 0.5 mol/dm^3 of $LiNO_3$, $NaNO_3$, $Al(NO_3)_3$, $Ca(NO_3)_2$, and $Fe(NO_3)_3$ to prepare metal-added sample solutions termed MS-Li, MS-Na, MS-Al, MS-Ca, and MS-Fe, respectively. The concentrations of metallic elements and anions in S-1M were determined with an inductively coupled plasma atomic emission spectrometer (ICP-AES) system (Shimazu ICPS-7510 sequential plasma spectrometer), an ICP-MS (Yokogawa analytical systems HP 4500) using the standard addition method, or a high-performance liquid chromatograph (HPLC, Hitachi Co. Ltd.). The results are tabulated in Table 1. The major metallic elements contained in S-1M were Na, Al, K, Ca, and Fe. The concentrations of Th and U were, respectively, about 4 and 5 orders of magnitude smaller than those of the major metallic elements. Although $HClO_4$ treatment was carried out to remove F^-, 15 mmol/dm^3 of F^- was still observed.

2.4. Column operation procedures

First, a column of UTEVA resin was conditioned with 6–10 cm^3 of a HNO_3 solution whose concentration was the same as that of the sample solution. Next, 4 cm^3 of the sample solution was injected into the column and 4 cm^3 of the effluent was collected in a bottle (load fraction). Subsequently, 6.5 cm^3 (5 free column volumes, FCV) of HNO_3 solution with the same con-

Table 1
The concentration of metallic elements, Th, U and anions in S-1M

Element	Concentration (mmol/dm^3)	Element	Concentration (mmol/dm^3)
Na	19	Fe	114
Mg	5	Ni	0.3
Al	53	Th	0.0016
K	12	U	0.0010
Ca	69		
Ti	2	F^-	15
Cr	6	Cl^-	12
Mn	1	$NO_3{}^-$	1200