Sequential Separation of U, Th, Pb, and Lanthanides with a Single Anion-Exchange Column

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With a combination of a single anion-exchange column and mixed media of CH_3COOH and other acids (HCl and/or HNO_3), 50 ng each of U, Th, Pb, and the lanthanides were sequentially separated. The mixed media including CH_3COOH were effective for the sequential separation. All of the elements were more than 95% recovered, and the decontamination factor was more than 100. Major elements in geological samples such as alkali metals, alkaline earth metals, and Fe were eliminated from the column. This separation technique reduces separation time and simplifies the complicated traditional processes without any special reagents or equipments. The technique has potential for use in pg (10^{-12} g) level trace analysis.

1. Introduction

Uranium (U), thorium (Th), lead (Pb), and the lanthanides are key elements in geochemistry and cosmochemistry. Abundance ratios and isotopic ratios of these elements in rocks, meteorites, and airborne dust are used for estimating their origin,[1-3] dating of mineral formation,[4] history of mineralization,[5-8] and age determination of nuclear materials.[9-11]

Mass spectrometry is a powerful analytical method for these studies. Quantitative and isotopic analyses of these samples are carried out with many types of mass spectrometers. Secondary ion mass spectrometry (SIMS)[12] and isotope microscopy[13] provide isotopic analysis without any pre-treatments for μm-size samples.[4,5] They are the main analytical tools in geochemistry. The total mass of some polyatomic ions, which are originated in co-existing with other elements, sometimes overlap with that of an isotope of interest and lead to systematic error in the measurement of isotopic ratios (*e.g.* $^{208}Pb^{12}C^{16}O^+$ for ^{236}U and $^{195}Pt^{40}Ar^+$ for ^{235}U). Magara et al reported that the formation rate of $^{195}Pt^{40}Ar^+$ measured by inductively-coupled plasma mass spectrometry (ICP-MS) is 1.5×10^{-5}.[14] The formation rate is defined as the ratio of the count rate of $^{195}Pt^{40}Ar^+$ to ^{195}Pt. When the concentration ratio of Pt/U in an analytical sample is 10, the atomic ratio of $^{235}U/^{238}U$ will include 0.7% of the systematic error. The amount of Pt should be reduced to < 1/10 of the U amount by means of a chemical separation to measure the isotopic ratios of U precisely. The contribution from the polyatomic ions may be subtracted if both the concentration of interfering elements and the formation rate can be measured precisely. Esaka et al reported the technique of isolation of U particles from Pb particles with a needle for analysis of U minor isotopes by SIMS.[15] The technique may be powerful for particle analysis.

High concentrations of matrix elements, such as Na and K, affect the ion intensity of analytes in ICP-MS measurements.[16] Chemical separation of the elements of interest is classically done and is time-consuming, but precise analysis can only be done by eliminating these interferences. Uranium, Th, Pb, and the lanthanides can be separated with ion-exchange columns[17-] [19] as well as with solvent extraction.[20] Almost all these techniques require many complicated steps and various eluents. In the precise analysis of μm-size samples, the chosen separation procedures should be thought out to avoid contamination of the elements of interest from foreign environments. This type of contamination creates serious uncertainties in trace analyses. Use of a clean laboratory and highly pure reagents are the most important countermeasures for avoiding the contamination. Many excellent ligands and extractants for the chemical separations are synthesized and available.[21-24] Many of these reagents are often difficult to purify and they decompose, whereas highly pure acids such as HCl, HNO_3, CH_3COOH, and HF are readily available, and it is easy to purify them. Hydrochloric acid and HNO_3 are well known as eluents for anion-exchange separation. The ion-exchange characteristics of all elements in these acids and mixture of some reagents such as alcohols have been systematically studied since the 1960s.[25-30]

To be effective at avoiding contamination from foreign environments, the separation procedure must be simplified. The combination of multiple exchange columns for tasks such as the evaporation of effluents increases the number of separation steps, resulting in increase of a chance of contamination.

The authors developed a simplified separation technique for U, Th, Pb, and the lanthanides using a single anion-exchange column and mixed media consisting of CH_3COOH and other acids. An anion-exchange column was used in this study. Anion-exchange columns do not retain the elements of interest from water and/or concentrated acids. It is therefore easy to clean anion-exchange columns. Cation-exchange columns retain Th and the lanthanides over a wide range of HCl concentration (1–12 M). It is difficult to clean this type of column completely.

There are few papers on the separation of these elements with a single anion-exchange column. In this work, suitable compositions of mixed media consisting of CH_3COOH and other acids for the separations were investigated. Acetic acid is a good medium for an anion-exchange separation. It was reported that the partial replacement of aqueous solution with CH_3COOH enhances the adsorption of many elements such as Th, U, Pb, and the lanthanides.[31-35] Kim and Born reported that the distribution coefficients of U, Th, and Pa increase with increasing concentration of CH_3COOH and HCl in mixed media of these acids.[35] They explained that the hydration field

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around the uranium ion becomes weakened in the presence of CH_3COOH, and the water dipoles in coordination may be replaced by acetate as well as chloride ions. The ion-exchange characteristics of all the elements[31-34] and the interaction of actinides[36] were studied, but only a few applications with CH_3COOH media were reported.[37-41]

2. Experimental

Uranium, Th, Pb, and the lanthanides in a mixture of three ICP-MS calibration solutions were separated with an anion-exchange column and the mixed media consisting of CH_3COOH and other acids. The elution profiles of these elements were examined, and the composition and volume of the mixed media were optimized to achieve the sequential separation of the elements of interest. All the fractions of the effluent were collected. The recovery of the elements in the fractions was measured with an ICP-MS. The reagents and detailed procedures are described below.

2.1. Reagents. Three ICP-MS calibration solutions (XSTC-13, XSTC-1, and XSTC-7, SPEX CertiPrep, Inc.) were mixed, and a stock solution of 0.3 M HNO_3 containing 103 ppb of U, Th, Pb, lanthanides, etc. (57 elements) was prepared. The concentrations of these elements are shown in Table 1. Water was deionized and purified (resistivity: 18.2 MΩ·cm) with a Milli-Q water system (Millipore Corp.). All labware such as vials and stock bottles used in this study was made of Teflon (PFA). The following commercially available reagents were used without further purification in this study.

HCl: concentration 30 wt.%, TAMA-Pure AA-100 grade, TAMA Chemicals.

HNO_3: concentration 68 wt.%, TAMA-Pure AA-10 grade, TAMA Chemicals.

HF: concentration 38 wt.%, TAMA-Pure AA-10 grade, TAMA Chemicals.

CH_3COOH: concentration >99.7wt.%, Extra pure grade for trace analysis (UGR), Kanto Chemical Co. Ltd.

HI: concentration 55–58wt.%, Wako Pure Chemical Industries, Ltd.

2.2. Ion Exchange Separation. About 550 mg (in dry weight) of an anion-exchange resin (Muromac 1x8, Cl⁻ form, 100–200 mesh, Muromachi Chemicals Inc.) was packed into a polyethylene column (5.5 mm i.d., 42 mm height, column volume: 1.0 mL). The column was washed with concentrated HCl and H_2O. Finally, the column was conditioned with 5 mL of the mixture of CH_3COOH and HNO_3, which is the eluent for the elimination of alkali metals and alkaline earth metals. Stock solution (500 μl) was pipetted into a 10 mL vial and evaporated to dryness. About 50 ng of each element was contained in the solution. The dried sample was dissolved in 1 mL of the mixture of CH_3COOH and HNO_3 and loaded onto the column. The flow rate of the effluents was 0.1–0.2 mL/min for the mixed media and 0.3–0.4 mL/min for the HCl media.

Each 4 mL of the effluent was collected into a separate vial. The effluents were weighed and evaporated to dryness. The resulting residues were dissolved in 1 mL of concentrated HNO_3, and the solutions were evaporated to dryness. Finally, the residues were dissolved in 2 mL of 0.3 M HNO_3 to analyze the elemental concentration with an ICP-MS (Agilent 7500a, Agilent Technologies Inc.). The stock solution was diluted, and six standards of different concentrations were prepared to make a working curve. The variation of ion intensity among the samples in the ICP-MS measurement was corrected by bracketing the measurement of samples with those of the standard solutions. The concentration of Fe was determined with the ion intensity of mass 57, and the recovery of Fe from the column was indicated as a relative value normalized to the total recovery of Fe in all effluent vials. All treatments were carried out in clean rooms (ISO class 5 and 6) at the clean laboratory "CLEAR" in JAEA.[42]

3. Results and Discussion

The appropriateness of the eluent mixture, which consisted of mixture of CH_3COOH and HCl and/or HNO_3, was investigated by dividing the study into four parts, described in the following sections 3.1–3.4. Finally, the elements in interest were sequentially separated with the optimized eluents, and the recoveries were evaluated (see section 3.5.).

3.1. Elimination of alkali metals and alkaline earth metals. Alkali metals and alkaline earth metals such as Na, K, Ca, and Mg are present in high concentrations in environmental samples such as rocks, soils, and plants. A high concentration of these elements may cause matrix effects in ICP-MS analysis.[16] By using mixed media consisting of CH_3COOH and HNO_3 as the eluent, these elements were eliminated effectively. The analytes—U, Th, Pb, and the lanthanides—were retained.

Figure 1 shows the effect of HNO_3 concentration in the mixed media on the elution of Lu. The mixture of 90 vol.% CH_3COOH and 0.2 M HNO_3 effectively suppressed the elution of Lu. Lutetium (as a representative of the heavier lanthanides) was eluted with more than 15 mL of the mixture. Lanthanum (as a representative of the lighter lanthanides), Th, Pb, and U were retained after more than 30 mL of any mixture of
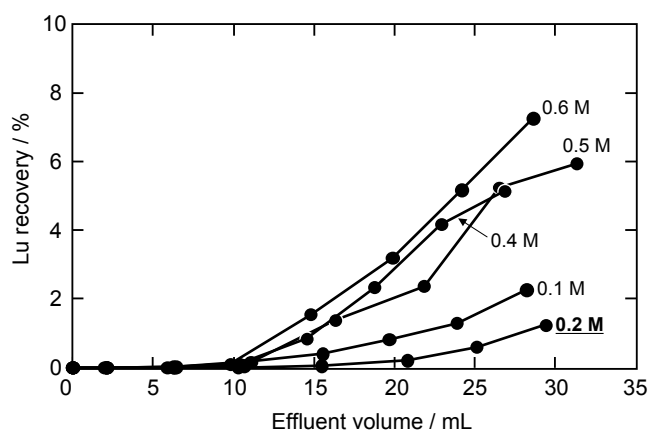

Figure 1. Effect of HNO_3 concentration in the mixed media of 90 vol.% CH_3COOH and HNO_3 on suppression of Lu elution. The column volume (CV) is equivalent to the effluent volume.

TABLE 1: Elemental concentration in the mixture of three ICP-MS calibration solutions

Concentration (ppb)	Composition	Calibration solution
103	(Li), Be, (Na), (Mg), (Al), (K), (Ca), V, Cr, Mn, Fe, Co, Ni, Cu, (Zn), Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, (Hg), Tl, Bi, Pb, Th, U	XSTC-13 (10 μg/mL)
103	Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	XSTC-1 (10 μg/mL)
103	Ru, Rh, Pd, (Sn), Sb, Te, Hf, Ir, Pt, Au	XSTC-7 (10 μg/mL)

Note: The calibration solutions were mixed and diluted with 0.3 M HNO_3. The elements in parentheses were contained in the solution, but those were not determined in this work.

CH_3COOH and HNO_3. Thirteen mL (13 column volumes, CV) of the mixture was used for the elimination of alkali metals and alkaline earth metals from the column.

The heavier lanthanides—Lu, Yb, Tm, Er, Ho, Dy, Tb, and Gd—were eluted with more than 15 mL of the mixture in that order (*i.e.* the inverse order of their atomic number). This implies that the distribution coefficients (K_d) of the heavier lanthanides decreased in the order of their atomic number. Korkisch reported the K_d of U, Th, Pb, La, and Gd on Dowex 1x8 with a mixed media consisting of glacial CH_3COOH and HNO_3.[43] The K_d of these elements increase with increasing concentration of CH_3COOH, and these elements are strongly retained by the resin from a mixture of 90 vol.% CH_3COOH and 10 vol.% 5 M HNO_3. He also reported that the K_d of La slightly increases with increasing acidity, and the K_d of Gd is one tenth that of La. The trend on the elution profiles of lanthanides in this work was consistent with his results and the experimental results on the anion-exchange separation with HNO_3 media.[44-47]

3.2. Separation of lanthanides. It is known that U and Pb are retained by anion-exchange columns in HCl media, and Th and the lighter lanthanides (La) are retained in HNO_3 media.[48] We found that a mixed media solution consisting of CH_3COOH, HCl, and HNO_3 was a good eluent for the separation of lanthanides from U, Th, and Pb.

Figure 2 shows the effect of HNO_3 concentration on the recovery of Th. The concentrations of CH_3COOH and HCl were 78–90 vol.% and 0.76–0.95 M, respectively. The recoveries of Th in 9 mL of the effluent decreased with increasing HNO_3 concentration in the mixed media. Thorium was not eluted when the HNO_3 concentration was more than 0.5 M. The mixture of 85.0 vol.% CH_3COOH, 0.89 M HCl, and 0.80 M HNO_3 was the best composition for separation of the lanthanides. Figure 3 shows the cumulative recoveries of La and Th. The recovery of La reached 100% with 35 mL of this mixture, and Th was eluted with more than 35 mL. Therefore, lanthanides were separated from Th, Pb, and U with 37 mL (37 CV) of this eluent.

The recovery of Ce was irregularly low (35%) compared with that of the other lanthanides (95%). To improve the recovery of Ce, some reducing agents ($NH_2OH \cdot HCl$, HI, H_2O_2, NH_4NO_2) were added to the eluents, and Ce^{4+} was changed into Ce^{3+}. Hydroxylamine chloride ($NH_2OH \cdot HCl$) was the most effective of these four reagents for improving the recovery of Ce. Cerium recovery increased with the reducing agents in the following order: $NH_2OH \cdot HCl$ > HI > H_2O_2 > NH_4NO_2. This order is the same as that of their standard electrode potential, and may depend on the strength of reduction of Ce^{4+} to Ce^{3+}. Cerium in the ICP-MS solution was prepared from $Ce(NO_3)_3$. The valence of Ce in the initial feed solution may be mainly trivalent, and it is the same as that of other lanthanides. Some of Ce^{3+} ions might be oxidized to Ce^{4+} during the chemical treatments, and this oxidation may cause the anomalously low recovery of Ce.

By using the mixture of 85.0 vol.% CH_3COOH, 0.89 M HCl, 0.80 M HNO_3, and 0.01 M $NH_2OH \cdot HCl$, all of the lanthanides were fully recovered (99.7 ± 0.7%) as shown in Figure 4. There was no difference in recovery among the lanthanides. It is possible to determine each lanthanide in a sample without individual recovery correction.

3.3. Separation of Th from Pb and U. Thorium was separated with the mixture of CH_3COOH and HCl. The elution profile of Th was affected by the concentrations of both HCl and CH_3COOH. The elution shape of Th became sharper with decreasing CH_3COOH concentration, as shown in Figure 5(a). The elution position of Th was shifted to the front with increasing HCl concentration, as shown in Figure 5(b). It seems to be preferable to use the mixture of 60 vol.% CH_3COOH and 1 M HCl for the Th separation, but 2–4% of the Pb was eluted
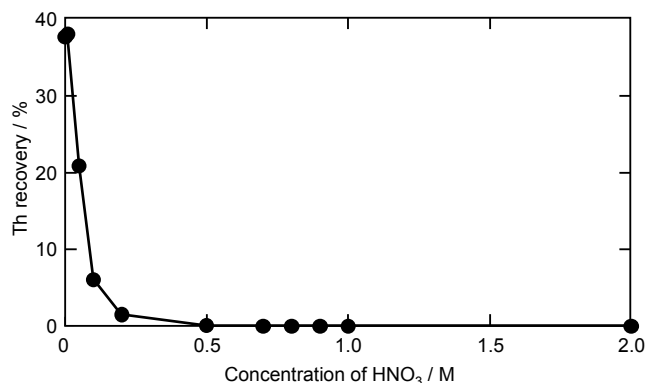

Figure 2. Effect of HNO_3 concentration in the mixed media of CH_3COOH, HCl, and HNO_3 on suppression of Th elution. The recovery of Th in 9 mL of effluent is indicated. The concentrations of CH_3COOH and HCl were 78–90 vol.% and 0.76–0.95 M, respectively.
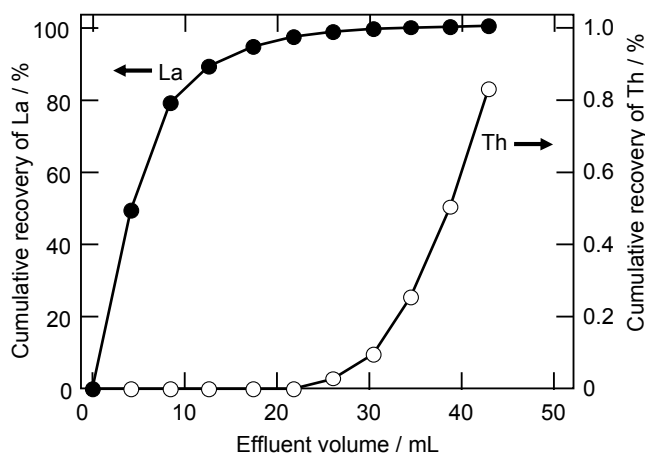

Figure 3. Cumulative recovery of La and Th eluted with the mixed media of 85.0 vol.% CH_3COOH + 0.89 M HCl + 0.80 M HNO_3. The column volume (CV) is equivalent to the effluent volume.
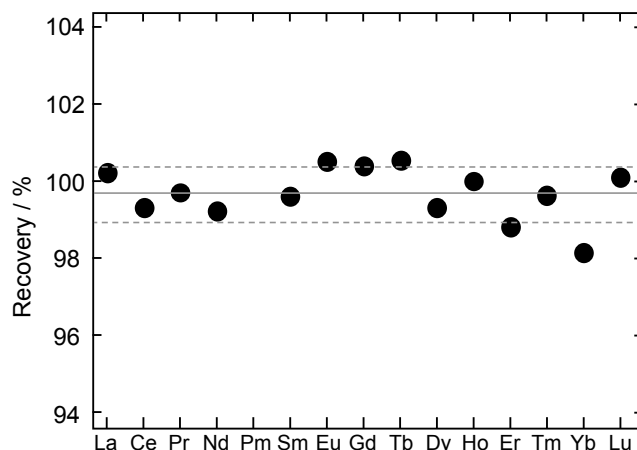

Figure 4. Variation in the recovery of lanthanides eluted with the mixed media of 85.0 vol.% CH_3COOH + 0.89 M HCl + 0.80 M HNO_3 + 0.01 M $NH_2OH \cdot HCl$. The solid line and the broken lines show the average and standard deviation (1σ) of recovery of lanthanides, respectively; (99.7 ± 0.7) %.

together with the Th for this composition. We found that 22 mL of the mixture of 70 vol.% CH_3COOH and 1 M HCl worked well for the Th separation in this work. Lead was not eluted with this eluent mixture.

To improve the elution shape of Th, 0.005 M HF was added to the eluent. The shape became sharp, and 99% of Th was

eluted with 10 mL of the eluent. The formation of cationic fluoro complexes of Th may reduce the absorbability of Th in an anion-exchange column.

   3.4. Separation of Pb, U, and Fe. Lead, Fe, and U were separated with the conventional eluents. Thirteen mL of 9 M HCl, 24 mL of 9 M HCl + 0.1 M HI, and 25 mL of 0.5 M HCl + 0.005 M HF were used for Pb separation, Fe elimination, and U separation, respectively. Iron was eliminated from the column by reducing Fe^{3+} to Fe^{2+} with 9 M HCl + 0.1 M HI. The column stood for 10 hours after eluting with 2 mL of the eluent to ensure the reduction, then Fe was eliminated with 22 mL of the eluents. The elution shape of U was sharpened with a mix-
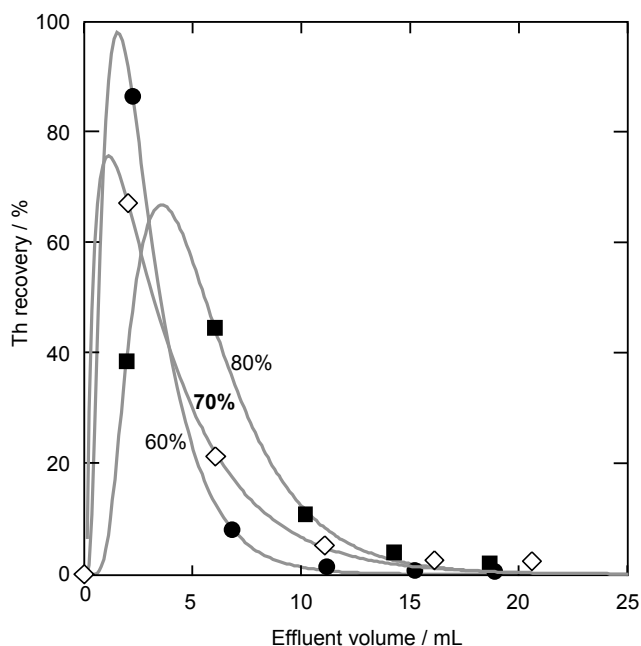
ture of HCl and HF. This probably occurs for the same reason as the Th elution. Schumann et al. reported that UO_2^{2+} and UO_2F^+ are the main cation species of U in a mixture of 0.001–0.1 M HF and 0.1 M HCl.[50]

   3.5. Sequential separation with the optimized eluents. By using the eluents optimized in sections 3.1. to 3.4., sequential separation of the elements of interest was carried out. Figure 6 shows elution curves of the elements of interest and representative interfering and matrix elements. Table 2 shows the eluted elements whose recovery was more than 20% in the fractions. The recovery of U, Th, Pb, and the lanthanides in each fraction (fraction No.6, fraction No.3, fraction No.4, and fraction No.2 in Figure 6) were 82%, 97%, 100%, and 100%, respectively. The recovery of U was more than 95% without the Fe separation using HCl + HI. This variation of U recovery might be caused by iodine adsorption on a portion of the surface of the resin, which is an oxidized product of HI. The recovery of Pb was estimated as 100% in this sequential separation, but 500 pg of Pb was contained in all of the fractions as a process blank, especially 2 ng (equivalent to 4% of total Pb) in the fraction No.5. The excess Pb may originate from the labware, the reagents such as HI and very fine (< 0.3 μm in diameter) Pb aerosols which are passed through the HEPA filters built in the clean rooms and clean hoods. A portion of Fe was eluted in the Th fraction (fraction No.3 in Figure 6) (14%) and the U fraction (fraction No.6 in Figure 6) (10%). Decontamination factors (DF) are shown in Table 3. The DF of lanthanides to Th, Th to Pb, and Pb to U were more than 100. Less than 1% of the alkali metals and 4% of the alkaline earth metals were contained in the lanthanides fraction (fraction No. 2 in Figure 6). We found that each element of interest was satisfactorily separated and fully recovered by this technique.

4. Conclusion

   With a single anion-exchange column, sequential separation of 50 ng each of U, Th, Pb, and the lanthanides in an ICP-MS calibration solution was successfully carried out. Using a mixture of CH_3COOH and other mineral acids (HCl and/or HNO_3)

Figure 5(a). Effect of the concentration of CH_3COOH in the mixed media of CH_3COOH (60 vol.%, 70 vol.%, and 80 vol.%) and 1 M HCl on the elution profile of Th. The elution curves indicate the results of the fits by the Glueckauf equation.[49] The column volume (CV) is equivalent to the effluent volume.
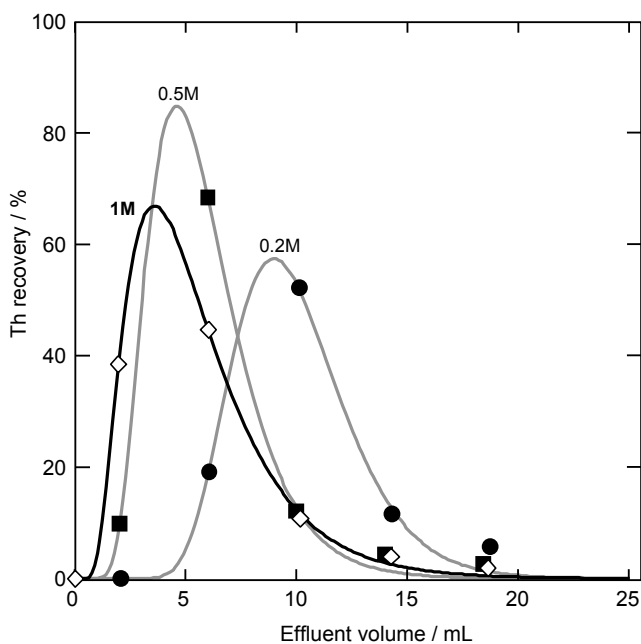

Figure 5(b). Effect of the concentration of HCl in the mixed media of HCl (0.2 M, 0.5 M, and 1.0 M) and 80 vol.% CH_3COOH on the elution profile of Th. The elution curves indicate the results of the fits by the Glueckauf equation.[49] The column volume (CV) is equivalent to the effluent volume.
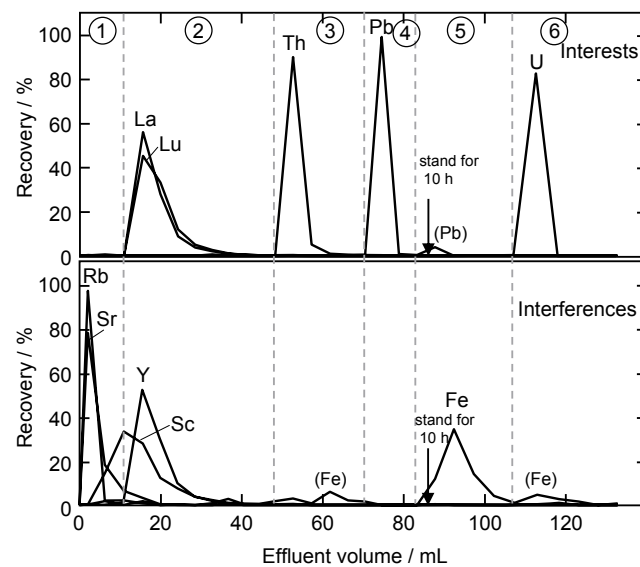

Figure 6. Sequential elution curves of U, Th, Pb, and the lanthanides (La and Lu) (upper), and elution curves of some interfering elements, Rb (representative of alkaline metals), Sr (representative of alkaline earth metals), Sc, Y, and Fe (bottom). Eluents; No.1: 90 vol.% CH_3COOH + 0.2 M HNO_3 (13 mL); No.2: 85.0 vol.% CH_3COOH + 0.89 M HCl + 0.80 M HNO_3 + 0.01 M $NH_2OH \cdot HCl$ (37 mL); No.3: 70 vol.% CH_3COOH + 1 M HCl + 0.005 M HF (22 mL); No.4: 9 M HCl (13 mL); No.5: 9 M HCl + 0.1 M HI (2 mL and stand for 10 hours, then 22 mL); No.6: 0.5 M HCl + 0.005 M HF (25 mL). The column volume (CV) is equivalent to the effluent volume.

TABLE 2: Eluted elements in each fraction

Fraction No.	Eluents	Eluted elements
1	90 vol.% CH_3COOH + 0.2 M HNO_3 (13 mL)	**Be**, Sc, (V), Cr, Mn, Ni. (As), Se, **Rb**, **Sr**, (Ru), Te, **Cs**, **Ba**, (Tl)
2	85.0 vol.% CH_3COOH + 0.89 M HCl + 0.80 M HNO_3 + 0.01 M $NH_2OH\cdot HCl$ (37 mL)	Sc, V, Cr, Mn, Ni, Se, Y, (Ba), **lanthanides**, (Ir)
3	70 vol.% CH_3COOH + 1 M HCl + 0.005 M HF (22 mL)	Mn, Co, **Th**
4	9 M HCl (13 mL)	Co, Cu, (Rh), In, **Pb**
5	9 M HCl + 0.1 M HI (24 mL)	**Fe**
6	0.5 M HCl + 0.005 M HF (25 mL)	Ga, As, **U**

Note: The elements whose recovery was more than 20% of the fraction are tabulated. The elements whose recovery was in the range of 15–20% are shown in parentheses. The elements expected to be eluted in the fraction are indicated in bold type.

TABLE 3: Decontamination factors of representative elements in the effluents

Fraction No.2		Fraction No.3		Fraction No.6	
La / Th	> 540	Th / La	720	U / Pt	> 130
La / Rb	130	Th / Pb	> 110	U / Pb	> 140
La / Sr	22	Th / Fe	7	U / Fe	10
La / Sc	1.8				
La / Y	1.0				

Note: The decontamination factor is calculated from the recovery ratio of the element of interest to the co-existing element in the fraction.

enabled complete separation of the elements of interest. The absorption of the elements of interest on the column was enhanced in the mixture of CH_3COOH compared with simple HCl and HNO_3 media. Alkali metals, alkaline earth metals, and Fe which are representative interferences for isotopic analysis in geological samples were eliminated from U, Th, Pb, and the lanthanides. The recovery of the elements of interest was more than 95%. The elution shapes of Th and U became sharp by adding 0.005 M HF to the eluents. The recovery of Ce increased by adding 0.01 M $NH_2OH\cdot HCl$ to the eluent for the lanthanide separation, and all of the lanthanides, including Ce, were fully recovered. Due to the tailing of the Fe elution, 10% of the Fe was eluted in the U fraction. The separation performance (*e.g.*, peak resolution) may be improved by controlling the column size and the grain size of the resin. This simplified separation technique can be applied for pg (10^{-12} g) level trace analysis with highly pure reagents. This separation technique has potential of applications in many research and development field, such as geochemistry, cosmochemistry, and analysis for non-proliferation.

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