

Sequential anion-exchange separation of trace U, Th, Pb and lanthanides in environmental samples

By Y. Miyamoto^{1,*}, K. Yasuda¹, M. Magara¹, T. Kimura¹ and S. Usuda²

¹ Research Group for Radiochemistry, Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency (JAEA), Tokai-mura, Naka-gun, Ibaraki, 319-1195 Japan

² Cyclotron and Radioisotope Center, Tohoku University, Aoba 6-3, Aramaki, Aoba-ku, Sendai, 980-8578 Japan

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Summary. The sequential separation technique of U, Th, Pb, and the lanthanides with a single anion-exchange column was applied to analysis of the geochemical reference sample, JB-1. The separation technique was previously developed by the authors and reported. The sample was digested and dissolved in nitric acid. Five solutions of different volume containing 0.1–1 mg of the JB-1 were loaded on the separate columns, and the elements of interest in the solution were sequentially separated. The concentrations of the elements were measured with an ICP-MS. The elements were successfully separated and alkaline metals and alkaline earth metals were effectively eliminated from the elements. The elemental concentrations were concordant with the literature values within the deviation except for that of Th. The elemental concentrations were accurately determined in $\geq 500 \mu\text{g}$ of the JB-1 without subtraction of processing blanks.

1. Introduction

Uranium (U), Thorium (Th), lead (Pb), and the lanthanides are key elements in geo- and cosmo-chemistry. Abundance and isotopic ratios of these elements in rocks, meteorites, and airborne dust are used for estimating their origin [1], dating of mineral formation [2], history on mineralization [3], and age determination of nuclear materials [4, 5].

Mass spectrometry is a powerful analytical method in these studies. Quantitative and isotopic analyses of these samples are carried out with many types of instruments such as high resolution inductively-coupled plasma mass spectrometer (HR-ICP-MS), secondary ionization mass spectrometer (SIMS), and isotope microscope [6]. High concentration of major elements, such as Na and K, in environmental samples affects ion intensity of analytes in ICP-MS measurement [7, 8]. Chemical separation of the elements of interest is classically done and is time-consuming, but for precise analysis separations must be done. Uranium, Th, Pb, and the lanthanides can be separated with ion-exchange columns as well as with solvent extraction [9].

Almost all these techniques require many complicated steps and various types of reagents. In the precise analysis of μm -size samples, the chosen separation procedures should be thought out to avoid contamination of the elements of interest during the sample treatment. To be effective at avoiding contamination from foreign environment, 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. In addition to the simplified separation, use of a clean laboratory and highly pure reagents are the most important countermeasures for the contamination. Many excellent ligands and extractants for the chemical separation have been developed [10–13]. Many of these reagents are often difficult to purify and they decompose. Highly pure HCl and HNO₃ are commercially available, and these are conventionally used as the eluents in the ion-exchange separations.

The authors developed the techniques of sequential separation of U, Th, Pb, and the lanthanides using a single anion-exchange column and mixed media consisting of HCl, HNO₃, CH₃COOH, and HF [14]. These elements in an ICP-MS calibration solution (50 ng each) were successfully separated. To evaluate feasibility of this separation in environmental samples, the elements in a geochemical reference sample were separated and determined with ICP-MS.

2. Experimental

A geochemical reference sample, JB-1, was used in this study. This sample is powdered basalt, and issued from Advanced Industrial Science and Technology (AIST), formerly Geological Survey of Japan (GSJ). The reference sample was digested with the acids, and the sample solution was prepared. Five samples of different volume were loaded onto separate anion-exchange columns, and the elements of interest were sequentially separated. The elution fractions were separately collected, and the concentrations in the fractions were determined with an ICP-MS.

Water was deionized and purified (resistivity, 18.2 M Ω cm) with Milli-Q water system (Millipore Corp.). All labwares such as beakers and bottles used in this study

* Author for correspondence
(E-mail: miyamoto.yutaka@jaea.go.jp).

were made of Teflon (PTFE and PFA). The labwares were immersed in 8 M HNO₃ for a few days, then rinsed with Milli-Q water before the use.

Highly pure grade of HCl, HNO₃, HF (TAMA-Pure AA-10 or 100, TAMA Chemicals), and CH₃COOH (Extra pure grade for trace analysis (URG), Kanto Chemicals Co. Ltd.) used in this study were not further purified. The HI (Wako Pure Chemical Industries, Ltd.) used in this study was Wako special grade and the concentration was 55–58 wt %.

2.1 Sample and digestion

The geochemical reference sample, JB-1 was dried for 12 h at 110 °C in an oven, then weighed 200 mg of the sample. The sample was heated and digested with a mixture of 2 mL of conc. HNO₃, 4 mL of HF, and 4 mL of HCl in a PTFE bottle with a screw cap. The bottle was heated in a microwave oven (ETHOS 900, Milesotone S.r.l.). The digestion in the closed vessel was carried out in a room for various non-radioactive experiments where the oven has been installed. The digested sample was brought in the clean-room, then the solution was transferred into a PTFE beaker and 1 mL of HClO₄ was added to the sample. The solution was heated and evaporated to dryness on a heater to completely decompose the digestion residue. The evaporation residue was dissolved in 20 mL of 2 M HNO₃. The concentration of JB-1 in the solution was 8.8 mg/g, which was calculated from the weights of the sample and the solution.

2.2 Ion-exchange separation

About 550 mg (in dry weight) of anion-exchange resin (Muromac 1 × 8, Cl⁻ form, 100–200 mesh, Muromachi Chemicals Inc.) was packed into a polyethylene column (5.5 mm i.d., 42 mm height, 1.0 mL of column volume). The anion-exchange column was rinsed with conc. HCl and Milli-Q water. Finally, the column was conditioned with 5 mL of the mixture of 90 vol % (15.7 M) CH₃COOH and 0.2 M HNO₃. Five different volumes (10, 25, 50, 75, and 100 μL) of the sample solution were pipetted into separate 10 mL beakers, and 1 ml of the ²³³U solution (2.3 ng/g) was added into each beaker to correct the recovery yield of U.

The spike should be added at the beginning of the sample digestion step to avoid analytical bias, if the radioactive ²³³U is allowed to use in the room for the sample digestion. The sample solutions were evaporated to dryness. The resulting residues were dissolved in 1 mL of the mixture of 90 vol % (15.7 M) CH₃COOH and 0.2 M HNO₃. The five samples were loaded on the respective columns. The elements of interest were sequentially separated by following the procedure described in our previous report [14]. The volume and composition of the eluents for the separation were shown Table 1.

Each fraction of the effluents was collected into a separate beaker. The effluents were evaporated to dryness on a heater. The resulting residues were dissolved in 2 mL of conc. HNO₃, then the solutions were evaporated again. Finally, the residues dissolved in 5 mL of 0.3 M HNO₃. 10 μg of the internal spike solution (concentration: 1 ppm each of In and Bi) was added to the sample solutions to compensate for the variation of peak intensity in ICP-MS measurement [15].

2.3 Determination of concentration in the fraction

The concentration of U, Th, Pb, and the lanthanides in the elution fractions were measured with an ICP-MS (Agilent 7500 a, Agilent Technologies Inc.). The operation condition of the ICP-MS was optimized to obtain both low production rate of oxide ions (¹⁴⁰Ce¹⁶O⁺/¹⁴⁰Ce⁺ = 0.7%) and low doubly charged ions (¹⁴⁰Ce²⁺/¹⁴⁰Ce⁺ = 0.6%). For the determination of Th, Pb, and the lanthanides, two ICP-MS calibration solutions (XSTC-13 and XSTC-1, SPEX CertiPrep, Inc.) were used for the standard. These solutions were mixed and diluted to eight solutions of different concentrations to make the working curves (ppb–cps). For the determination of U, one natural U solution (11.5 ng of U/g) was used as standard. The solution was prepared by diluting the U standard solution certified at IRMM (IRMM-148). The processing blanks were not subtracted from the analytical results.

All treatments were carried out in clean rooms (ISO Class 5 and 6) at the clean laboratory “CLEAR” in JAEA [16] except for the sample digestion by using the microwave oven.

Table 1. Volume and composition of the eluents for the sequential anion-exchange separation.

Eluted element	Volume (ml)	Composition of the eluent
Alkaline metals and alkaline earth metals (for elimination)	11 + 1 ^a	90 vol % (15.7 M) CH ₃ COOH + 0.2 M HNO ₃
Lanthanides	32	85.3 vol % (14.8 M) CH ₃ COOH + 0.89 M HCl + 0.8 M HNO ₃ + 0.01 M NH ₂ OH·HCl
Th	20	70 vol % (12.2 M) CH ₃ COOH + 1 M HCl + 0.005 M HF
Pb	12	9 M HCl
Fe (for elimination)	24	9 M HCl + 0.1 M HI
U	12	0.2 M HCl + 1 M HF (0.5 M HCl + 0.005 M HF) ^b

a: The volume includes 1 ml of the feed solution;

b: The eluent consisting of the composition in the parenthesis was used for the U separation in case of the 100 μL sample.

Table 2. Concentrations of the elements of interest in JB-1.

Sample volume/ μL		10	25	50	75	100	Imai ^b
Weight of JB-1/ μg^a		94.4	239	476	718	943	
Ho	ppm	1.41(4)	0.90(3)	0.87(3)	0.82(2)	0.79(3)	0.79(9)
	ng ^c	0.075	0.19	0.38	0.57	0.75	
Lu	ppm	0.93(2)	0.52(1)	0.407(9)	0.361(9)	0.32(2)	0.31(3)
	ng	0.029	0.074	0.15	0.22	0.29	
Th	ppm	7.8(3)	9.0(2)	7.8(2)	7.7(2)	8.2(1)	9.3(7)
	ng	0.88	2.2	4.4	6.7	8.8	
Pb	ppm	34.1(9)	15.7(4)	9.2(2)	11.9(3)	9.8(3)	10(4)
	ng	0.94	2.4	4.8	7.2	9.4	
U	ppm	2.05(6)	1.95(6)	1.73(5)	1.63(4)	1.82(4)	1.67(28)
	ng	0.16	0.40	0.80	1.2	1.6	
	Recovery/%	95	95	92	91	75	

The numbers in parentheses indicate standard deviation (1σ) of the last significant figures. The deviations include the following components of uncertainty; weighting (RSD: $\sim 1\%$) and ICP-MS counting statistics (RSD: 2–3%). The uncertainties of concentration in the standards were not assessed.

a: The weight calculated from the concentration of JB-1 in the feed solution (8.8 mg/g);

b: The recommended values and reported value of Pb compiled by Imai *et al.* [17];

c: The weight of elements was calculated from the literature values and the weight of JB-1.

3. Results and discussion

The elements of interest in the sample solutions of 10–100 μL , which were equivalent to 0.094–0.94 mg of the geological reference sample (JB-1), were successfully separated. Most of total Rb (as a representative of alkaline metals) and total Sr (as a representative of alkaline earth metals) were eliminated, and only 0.2–0.4% of total Rb and 2–4% of total Sr were eluted into the lanthanides fraction due to the tailing of elution. The percentages were constant in the range of 10–100 μL feed solutions. When a sample containing much amount of alkaline earth metals (*e.g.* Ca in calcites and corals) is analyzed by means of this separation technique, a bigger ion-exchange column should be used to successfully eliminate the alkaline earth metals.

In this technique, 50% of total Sc and 80% of total Y were eluted together with the lanthanides. It is due to the similarities of chemical behavior between these elements and the lanthanides.

The representative elemental concentrations in the JB-1 measured by this technique and the recommended values (the reported value of Pb) compiled by Imai *et al.* [17] are shown in Table 2. All elemental concentration in the 75 μL and 100 μL of samples were concordant with the recommended values within the 1σ , except for Th. The $\geq 75 \mu\text{L}$ results for Lu and the $\geq 25 \mu\text{L}$ results for Ho were concordant with the recommended value within the deviation. These volumes were equivalent to 0.2 ng of Ho and Lu. The limit of lanthanides determination in this work was 0.2 ng in the weight of lanthanide. All results seem to increase with decreasing the sample volume, *i.e.* amount of the element. Especially, all the 10 μL results were high and clearly outside the 1σ . It shows that the processing blank cannot be ignored to determine sub-ng of the elements. The blank may originate from impurities in the reagents. The amount of blanks was estimated from the calculation of the difference between the analytical results and the recommended values.

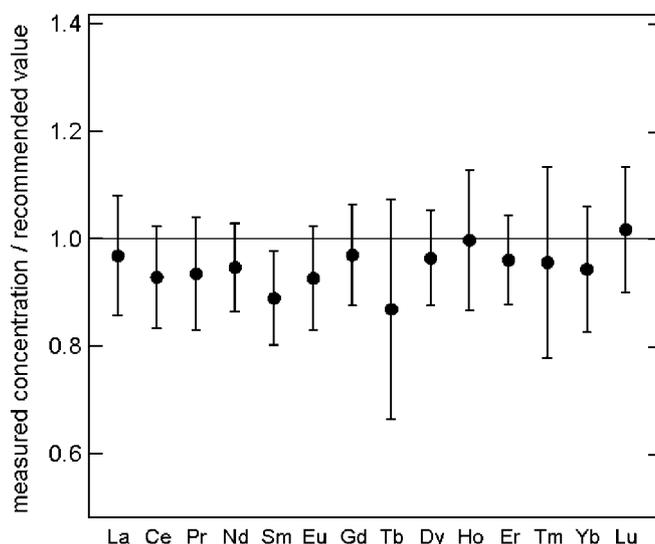


Fig. 1. Ratios of the concentration of the lanthanides measured by using 100 μL of the feed solution and the recommended value. The deviation (1σ) of ratios was combined with the deviations of the measured values and those of recommended values [17].

The amount of processing blanks for each 5 element in the 5 samples was almost constant and was not related to the sample volume (10 μL to 100 μL). The average blanks of Ho and Lu were coincidentally same, 63 pg.

The ratios of measured concentration of the lanthanides to the recommended values were shown in Fig. 1. The ratios seem to be 5% lower than the recommended values for the lanthanides, but the measured values were equal to the recommended values within the deviation. There was no significant difference in the ratios among the lanthanides. It implies that it is possible to accurately determine each lanthanide in a sample without recovery corrections. The chemical recoveries were not corrected for the lanthanides because radioactive lanthanide tracers cannot be handled in

our “CLEAR” due to the Japanese regulation. More accurate analytical result will be expected by using the radioactive tracers when the tracers free from the stable isotopes of these elements of interest are available. They should be added and brought into equilibrium with the analyte as early as possible.

All concentrations of Th in this study were 17% lower than the recommended value. When 50 ng of Th in an ICP-MS calibration solution was separated with this technique, 95% of the Th was recovered. The low Th recovery in the rock samples may be due to the difference in the elemental composition. The composition of eluent will be improved in the future examinations.

The $\geq 50 \mu\text{L}$ results for Pb ($\geq 4.8 \text{ ng of Pb}$) were concordant with the reported value within the deviation as shown in the Table 2. The $10 \mu\text{L}$ result (0.94 ng of Pb) was 3.4 times higher than the reported value. About 2.2 ng of Pb blank was estimated from the blank calculation. Suppression of the Pb blank is expected by using purified reagents and carefully washed labwares.

The $\geq 25 \mu\text{L}$ results for U were concordant with the recommended value within the deviation (Table 2). About 35 pg of U blank was estimated from the blank calculation. The recovery yields of U in the samples measured with ^{233}U spike were 91–95%, but the recovery yield in the $100 \mu\text{L}$ result was exceptionally low (75%). It was due to the use of eluent consisting of different composition reported in our previous study [14] as shown in the Table 1. The revised composition, $0.2 \text{ M HCl} + 1 \text{ M HF}$ of the eluent was effective in improvement of the U recovery yield.

Uranium, Th, Pb, and the lanthanides in the geological reference sample were successfully separated by this sequential anion-exchange method. The concentrations of these elements (except for Th) were accurately analyzed when $\geq 50 \mu\text{L}$ of the feed solution ($\geq 476 \mu\text{g of JB-1}$) was used.

4. Summary

Uranium, Th, Pb, and the lanthanides in the geochemical reference sample, JB-1 which is the powdered basalt, were sequentially separated with a single anion-exchange column and the mixtures of CH_3COOH , HNO_3 , HCl , and HF . Alkaline metals and alkaline earth metals which are major elements in environmental samples were eliminated, and the elements of interest were successfully separated and fully recovered, except for Th. The concentrations of the elements in $\geq 500 \mu\text{g}$ of JB-1 were accurately determined without subtraction of processing blanks. The estimated processing blanks of lanthanides, Pb and U in this study were 63 pg , 2.2 ng and 35 pg , respectively. These blank will decrease by using purified reagents and carefully washed labwares, and it will be possible to analyses the order of less than $500 \mu\text{g}$ of the environmental samples. The recovery correction of Th should be required in this study. More accurate analyses can be expected by adding chemical yield tracers in the sample digestion process. The improvement of Th recovery is under consideration. Application of this sequential separation technique to an automatic separation system has been examined. The details of the system will be reported in the

future. This simplified separation technique will be applied to the analyses for environmental samples such as minerals and airborne dusts.

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