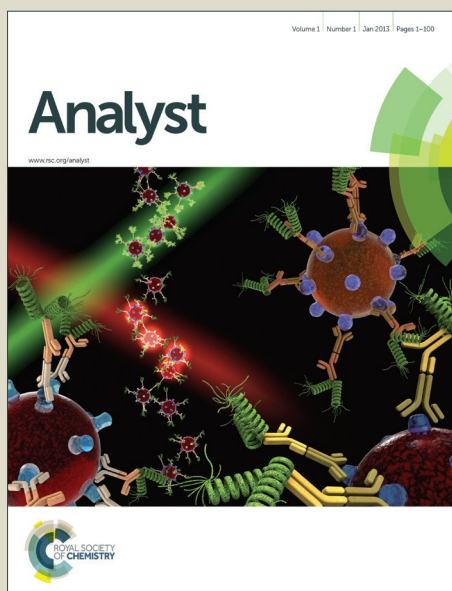


Analyst

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Sequential Separation of Ultra-trace U, Th, Pb, and Lanthanides using a Simple Automatic System

Cite this: DOI: 10.1039/x0xx00000x

Yutaka Miyamoto*, Kenichiro Yasuda, Masaaki Magara

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Uranium, Thorium, lead, and the lanthanides were automatically and sequentially separated with a single anion-exchange column. This separation was achieved using eluents consisting of simple and highly pure acid mixture of HCl, HNO₃, acetic acid, and HF. The elements of interest were separated from the major constituents, which included alkaline metal elements, alkaline earth metal elements, and iron. This simple, automatic system is driven with pressurized nitrogen gas, and controlled by a computer program. An optimized separation was accomplished under the following conditions: a 50 mm long and 2 mm diameter column, 11 μm diameter anion-exchange resin, and a 35 μL/min flow rate. Using this system, 50 ng of varied elements in a 100 μL feed solution were perfectly separated within 5 h with >400 decontamination factors and >95% yield. In order to evaluate the performance of this system, a reference powdered rock sample was separated by using this system. Abundances of objective elements, including 0.23 ng of lutetium, were accurately determined without corrections of chemical recovery yield or subtraction of processing blank. This separation technique saves time and effort for chemical processing, and it is useful for ultra-trace quantitative and isotopic analyses of elements in small environmental samples.

1. Introduction

Uranium, thorium, lead, and the lanthanides are key elements in geochemistry and cosmochemistry. Their abundance and isotope ratios in rocks, meteorites, and airborne dust are used to estimate their origin¹, dating of mineral formation², mineralization history³, and age determination of nuclear materials^{4,5}. Their separation is required for a precise analysis, but their chemical separation is time consuming. Uranium, Th, Pb and lanthanides can be separated by ion-exchange columns as well as through solvent extraction^{6,7}. Virtually all these techniques require several complicated steps and various types of reagent. To effectively avoid contamination from a foreign environment, this separation procedure must be simplified. Several excellent ligands and extractants have been developed for chemical separation⁸⁻¹¹, but some of these are frequently difficult to purify; moreover, they can also decompose. Extremely pure HCl and HNO₃ are commercially available, and these are conventionally used as the eluents in ion-exchange separation systems. We successfully developed sequential separation techniques for U, Th, Pb, and lanthanides using a single anion-exchange column and mixed media consisting of HCl, HNO₃, acetic acid, and HF^{12,13}. This technique was applied to determine the elemental abundance in a reference rock sample, and abundances in ≥500 μg of sample were accurately determined¹³.

*Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki 319-1195, Japan.

E-mail: miyamoto.yutaka@jaea.go.jp; Tel: +81-29-282-5518; FAX: +81-29-284-3658

The elements of interest were separated using a gravimetric flow in a conventional sized (1 mL) anion-exchange column. This conventional separation method can be applied to various samples, but it takes a considerable volume (10–30 mL) of eluents and time (2 d) to accomplish the separation. Usuda reported on the rapid separation of trans-plutonium elements with a pressurized gas and anion-exchange column¹⁴. To overcome the shortcoming in our previous technique, an automatic sequential separation utilizing a small anion-exchange column and pressurized gas has been developed. In column chromatography, the representative and effective parameters for achieving the highest elution peak resolution in the shortest possible time are the column size, resin particle size, eluent flow rate, and column temperature. In this work, the separation was optimized for the resin particle size, column length, and eluent flow rate to completely separate each element of interest in a short time. Abundance of elements of interest in a reference rock sample was determined to evaluate the performance of this separation technique.

2. Experimental

2.1. Apparatus and reagents

A simple system consisting of an ion exchange column, inert valves, and Teflon tubes was assembled to perform the sequential separation. Figure 1 shows a diagram of this system. The sample solution and eluents pass through the Teflon parts of the system, but they do not make contact with metals or movable parts, such as plungers in the high-performance liquid chromatography (HPLC), to reduce the process blank level. A

100 μL sample solution was loaded into a sample loop. The volume of eluents required for each element separation were collected and stored in large Teflon (PFA) tubes (4 mm inner diameter (i.d.), 80 cm long). The chemical composition and volume of eluents are listed in Table 1. The stored solutions were extruded by pressurized nitrogen gas charged at 1 MPa in a small metal gas cylinder (capacity: 300 mL) attached to a regulator. The flow rate of the eluents was adjusted by varying the gas pressure with the regulator. The gas pressure was kept constant during a series of sequential separations, with the eluents automatically and sequentially switched by a solvent selector equipped with an inert valve (SV-5008AM, GL Sciences Inc., Japan). A flow sensor (FX-301F, Panasonic Corp. SUNX Ltd., Japan) attached to the outlet tube of the selector detects when the eluent source is empty, and then the solvent valve is switched to the next position.

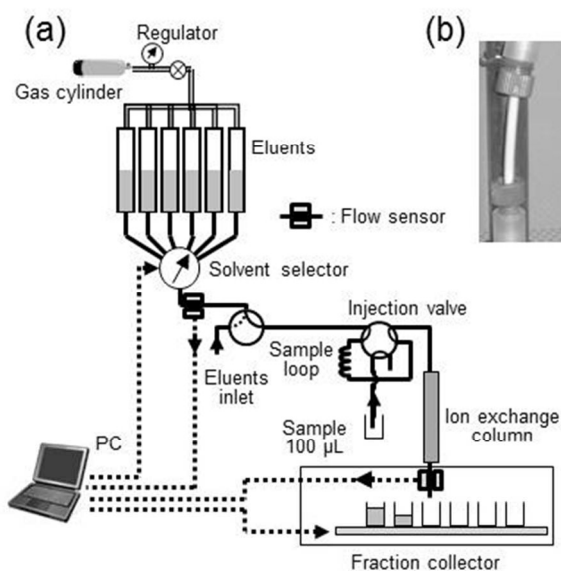


Fig. 1. (a) Diagram of the automatic sequential separation system driven by pressurized gas. The bold, broken, and double lines indicate the eluent flow lines, control signals, and gas flow lines, respectively. (b) Anion exchange column for the sequential separation. The anion exchange resin was packed into a PFA tube (1 mm inner diameter, 2 mm outer diameter). The PEEK fittings were attached to both ends of the tube.

The eluent flow detection and valve switching were controlled by an analog to digital converter (ADC) interface (USB-6221, National Instruments Co., USA) and LabVIEW program (National Instruments Co., USA). This entire system, including the software program working on the LabVIEW, was assembled by us. The effluents in each fraction were collected by hand in this experiment. A fraction collector (CHF122SC, ADVANTEC MFS, Inc., Japan) was also available for their automatic collection. A PFA tube (1 mm i.d., 2 mm outer diameter) was used as the column by cutting it to an appropriate length. Teflon wool was packed into the end of the tube, ensuring it was 22 mm long, and used to prevent leaking of the resin. An anion-exchange resin was packed into a column with a glass reservoir (15 mm i.d., 30 cm long). The resin suspended in deionized water was stored in the reservoir. An empty column was attached to one end of this reservoir with a PEEK fitting, and the other end of the reservoir was connected to the gas cylinder. The compressed nitrogen gas pressure was adjusted to 0.5 MPa with a regulator to pack the slurry into the column. The appearance of column was shown in Fig.1.

Columns were prepared in lengths of 42, 50, 80, 100, and 120 mm. The column was connected to the separation system with the resin, then rinsed with Milli-Q water and concentrated HCl. Finally, each column was conditioned with five times their column volume of an acetic acid and HNO_3 mixture, which is an identical composition to the feeding solution (*i.e.*, eluent No.1 listed in the Table1). An anion-exchange resin with two different particle sizes, MCI-GEL (Mitsubishi Chemical Corp., Jpn), CA08Y ($23.5 \pm 4 \mu\text{m}$), CA08S ($11.0 \pm 2 \mu\text{m}$) was used. These are strongly basic anion-exchange resins (8% cross linkage, Cl^- form), and the base material consists of styrene-divinyl benzene (DVB) copolymer. It has the same composition as Dowex 1X8 (The Dow Chemical Company, USA). The MCI-GEL packing materials are used for high performance liquid chromatography (HPLC). High resolution separations are obtained, because the beads are perfect spheres and their size distribution is tight. Three Inductively coupled plasma mass spectrometry (ICP-MS) calibration solutions (XSTC-13, XSTC-1, and XSTC-7, SPEX CertiPrep, Inc., USA) 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 detailed element quantities in the calibration solutions are described in our previous work^{12,13}. Water was deionized and purified (resistivity: 18.2 $\text{M}\Omega \cdot \text{cm}$) with a Mill-Q water system (Millipore Corp., USA). All labware, including the vials and stock bottles used in this work was made of Teflon (PFA). Highly pure acids: HCl, HNO_3 , HF (TAMA-Pure grade, Tama Chemicals Co. Ltd., Japan), acetic acid (precision analysis (UGR) and Ultrapur grade; >99.0% purity, Kanto Chemical Co. Ltd., Japan) and $\text{NH}_2\text{OH} \cdot \text{HCl}$ (guaranteed reagent (GR) grade; 99.0% purity, Merck Co., Germany) were used without further purification.

2.2. Ion exchange separation

Five hundred microliters of the stock solution containing 50 ng of each element was pipetted into a 10 mL vial and fully evaporated. The dried sample was dissolved in 100 μL of the acetic acid and HNO_3 mixture, which is the same composition as eluent No.1, and loaded onto the column via the sample loop shown in Fig. 1. Each 0.5 mL of the effluent was collected into a separate vial. The effluents were weighed and evaporated to dryness. The resultant residues were dissolved in 1 mL of concentrated HNO_3 , and the solutions were evaporated again. Finally, the residues were dissolved in 2 mL of a 0.3 M HNO_3 solution to analyze the elemental concentration by ICP-MS (Agilent 7500a, Agilent Technologies Inc., USA). Reference curves (counts per second (cps) vs. ppb) were drawn using five reference solutions to determine the sample concentrations. The recovery yield of the elements was calculated from the measured elemental concentration in the fractions. All treatments were performed in clean rooms (ISO Class 5 and 6) of the clean laboratory for environmental analysis and research "CLEAR" at the Japan Atomic Energy Agency (JAEA)¹⁵. The average flow rate ($\mu\text{L}/\text{min}$) in each fraction was calculated from the weight and density of the effluent and the elapsed time for the elution.

2.3. Determination of a reference rock sample

Elemental abundances of a geochemical reference sample were determined to evaluate the performance of this separation technique. Two hundreds milligrams of a powdered basalt sample, JB-1 which was prepared in Advanced Industrial Science and Technology (AIST)¹⁶ was digested with the mixture of HCl, HNO_3 , HF, and HClO_4 . Finally, the acid

residue was dissolved in 100 mL of 2 M HNO₃ solution. The concentration of JB-1 in the solution was 1.92 mg/g, which was calculated from the weights of the sample and the solution. A portion (370 μL, equivalent to 519 μg of JB-1) of this sample solution was pipetted into a beaker, and 2.3 ng of ²³³U was spiked to the sample for the correction of recovery yield of U. This spiked solution was evaporated to dryness. Finally, the resulting residue was dissolved in 100 μL of the eluent No.1, and the feed solution was loaded on a column, and then the elements of interest were separated. The separation fractions were evaporated to dryness, and were dissolved in 2 mL of 0.3 M HNO₃. The concentration of U, Th, Pb, and the lanthanides in the elution fractions were measured with the ICP-MS. Two ICP-MS calibration solutions (XSTC-331 and XSTC-1, SPEX CertiPrep, Inc., USA) were used for the reference standards to determine the concentration of elements of interest. These solutions were mixed and diluted to five solutions of different concentrations to draw reference curves (cps vs. ppb).

3. Results and discussion

3.1. Optimization of the resin particle size

It is expected that smaller resins will improve the separation performance, since the smaller size increases the reactive surface area in a column. Figure 2 shows the elution profiles of a reference sample on columns packed with different sizes of anion-exchange resin (23.5 μm and 11 μm). The gas pressure was set at 0.4 MPa. The eluent flow rates for Th separation were 19 μL/min for the 11- μm resin column and 140 μL/min for the 23.5- μm resin column. The elements of interest were completely separated on the column packed with the 11- μm resin. In the case of the 23.5- μm resin column, the Th and lanthanide peak shapes were broadened, with the peak tails extending to the next fraction even when using a 120 mm long column. Separations using a column with the 23.5- μm resin at a lower pressure (*i.e.*, a decreased flow rate) of 0.2 MPa (65 μL/min for the Th elution) and 0.3 MPa (84 μL/min) were examined to obtain their retention times, but at complete separation was not accomplished under these conditions. A complete sequential separation was accomplished using the 11- μm resin column; however, this required a long time (19 h) for the 100-mm column. Objective elements were selectively separated by combination of anion exchange resin in acetic acid–mineral acids mixed media^{17–25}, but chemical forms of the elements and absorption mechanism are not precisely discussed. Kim and Born suggested the hydration field around the interested ion becomes weakened in the presence of acetic acid, and the water dipoles in coordination may be replaced by acetate as well as chloride¹⁷. Guseva *et al.* suggested the possibility of formation of uranium hydroxoacetate complex [UO₂Ac(OH)]⁻ and [UO₂Ac₂(OH)]²⁻ (Ac = CH₃COO⁻) for the anion exchange behaviour of actinides in acetic acid¹⁸. In our work, the objective elements may form anionic species of nitrate, chloride, and/or acetate in the eluents. In addition to the formation of anionic species, partial replacement of aqueous solution with acetic acid enhances the absorption of many elements as reported in many works^{19–22}. The alkaline metals and alkaline earth metals in a sample were eliminated with the eluent No.1 listed in Table 1, because these elements do not form any anionic species. The lanthanides may be changed the chemical form to cationic ions by changing the composition of eluents from acetic acid–HNO₃ to the acetic acid–HCl–HNO₃ mixed media of eluent No.2. Anionic Th nitrate complex in the eluent No.1, 2 and 3 was changed to cationic Th ions (Th⁴⁺) by

a lack of NO₃⁻ ions in the mixed media of eluent No.3. Lead, Fe, and U were eluted with concentrated HCl, concentrated HNO₃, and diluted HCl, respectively in the same manner as conventional anion-exchange separation techniques. Investigations about chemical form of absorbed elements in the mixture of concentrated acetic acid and inorganic acids may be helpful to construct sophisticated sequential separation techniques.

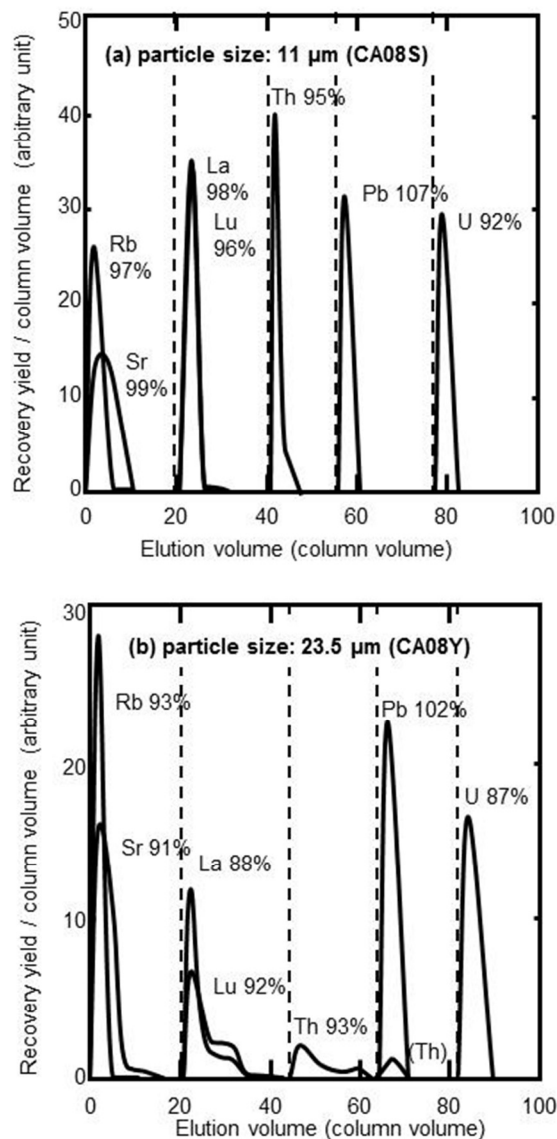


Fig. 2. Elution profile comparison between the different column particle sizes. The chemical yields are indicated next to the element symbols. The broken lines indicate the change of elution composition. (a) Separation with particle size: 11 μm (CA08S), column size: 100 mm × 0.2 mm i.d., column volume: 314 μL, gas pressure: 0.4 MPa, and total process time: 18.7 h. (b) Separation with particle size: 23.5 μm (CA08Y), column size: 120 mm × 0.2 mm i.d., column volume: 377 μL, gas pressure: 0.4 MPa, and total process time: 3.1 h.

3.2. Optimization of the column length and flow rate

The flow rate increased proportionally with increasing gas pressure and decreased inversely with increasing column length in this sequential separation system. Therefore, these two parameters should be considered for flow rate optimization.

The resolution of the elution peak improves with increasing column length, but it is costly in terms of increased analysis time. In order to examine the effect of column length, sequential separations were performed with three columns: 42 mm, 80 mm, and 100 mm long with 11- μm resin under 0.4 MPa gas pressure. As expected, the shorter column lengths resulted in shorter separation times: 3 h, 12.3 h, and 19 h for the 42 mm, 80 mm, and 100 mm long columns, respectively. Figure 3 shows Th the peak profiles separated with the three different column lengths.

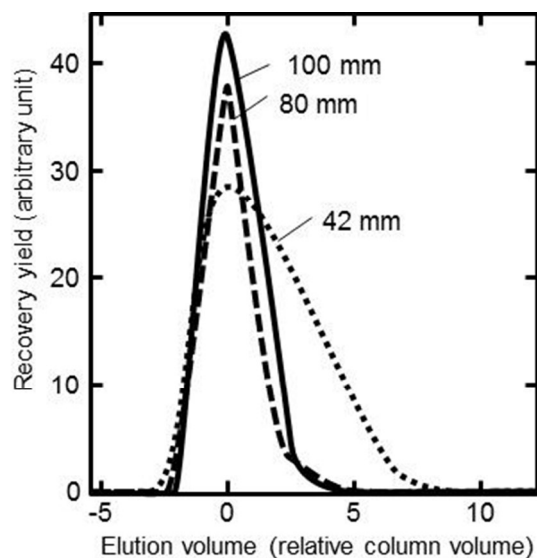


Fig. 3. Comparison of Th elution profiles between the different column length. The horizontal positions of the elution profiles were aligned relative to the peak maximas. The recovery yield in a fraction was normalized relative to the elution volume and complete Th recovery. This separation used a particle size of 11 μm (CA08S); column size of 0.2 mm i.d. \times lengths of 42, 80, and 100 mm (column volume: 132, 251, and 314 μL , respectively); gas pressure of 0.4 MPa (46, 21, 19 $\mu\text{L}/\text{min}$ flow rate for Th elution, respectively); and total process times of 3.2, 12.3, and 18.7 h, respectively.

In the case of the 42- mm column, a 46 $\mu\text{L}/\text{min}$ flow rate was too fast to the Th exchange anion species in equilibrium, and the peak profile was worse than for the longer columns. The 80- mm and 100- mm columns both produced a complete separation of the analytes. The column length and flow rate were optimized by the width of the Th peak. Van Deemter *et al.* reported a mechanism of band broadening in non-ideal chromatography to explain the relationship between flow rate and band width²⁶. They suggested the following Eq.1:

$$H = A + \frac{B}{v} + C \cdot v \quad (1)$$

where, v is the flow rate, H is the height equivalent to a theoretical plate (HETP), and the variables A , B , and C are the coefficients for the Eddy diffusion, longitudinal diffusion, and equilibration time, respectively. This equation was applied to optimize the flow rate by minimizing the value of H , which is a function of the peak width. It is expected that the peak resolution increased with a decrease in the HETP. The relative H value was obtained from the column length divided by the number of theoretical plates. This number was obtained from the results of an elution curve fitting using a formula described by Glückauf²⁷. Figure 4 shows a comparison of the HETP

values relative to the two resin sizes. The HETPs of 11- μm resin column were approximately 10 times less than the 23.5- μm one, suggesting that the smaller resin is effective for improving the Th peak resolution. The optimal flow rate was found to be 35 $\mu\text{L}/\text{min}$ from a fitting result for the column with the 11- μm resin. This flow rate was achieved by adjusting the gas pressure to 0.45 MPa for a 50 mm column length, to not exceed the upper limit of the gas pressure in this system (0.5 MPa). The experimental result of this optimized condition was also plotted in Fig.4. Figure 5 shows the elution profiles of the representative elements. Fifty nanograms of each element was fed into the column and separated under these optimized conditions: 2 mm ϕ \times 50 mm long column (volume: 0.158 mL), 11 μm resin size, and 0.45 MPa gas pressure. A portion of Fe can contaminate the U fraction, but each element of interest was completely separated. In this work, 8 M HNO_3 was used to eliminate the Fe contamination instead of the 9 M HCl and 0.1 M HI mixture reported previously^{12,13}, which does not require long standing times to reduce the Fe^{3+} ion reaction. A series of sequential separations was completed in 5 h. The chemical recovery yields and decontamination factors are listed in Table 2. The recovery yield of the elements of interest were all $>95\%$.

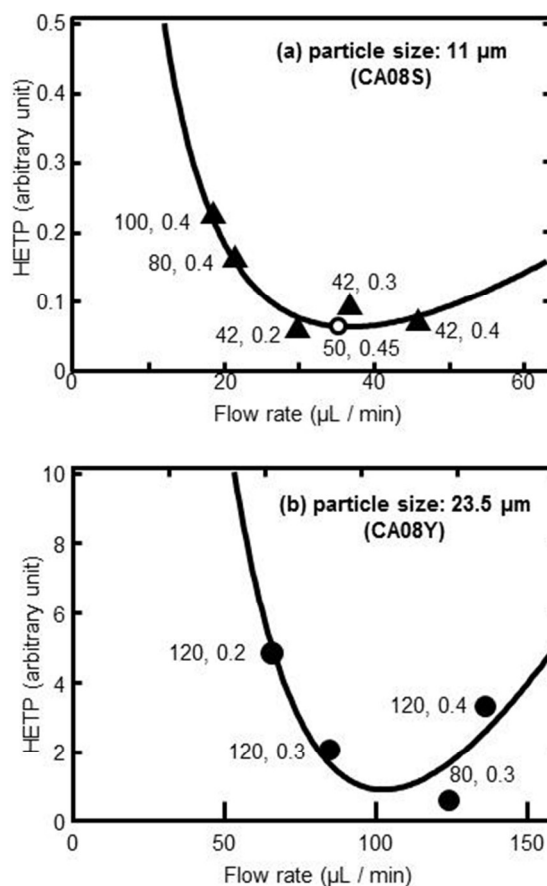


Fig. 4. Optimization of the flow rate for Th separation. Separation with (a) particle size: 11 μm (CA08S), (b) 23.5 μm (CA08Y). The numbers indicate the column length (mm) and gas pressure (MPa) used in the sequential separation. The bold lines indicate the fitting results of the model equation²⁶. The open circle indicates the experimental result of the optimized condition.

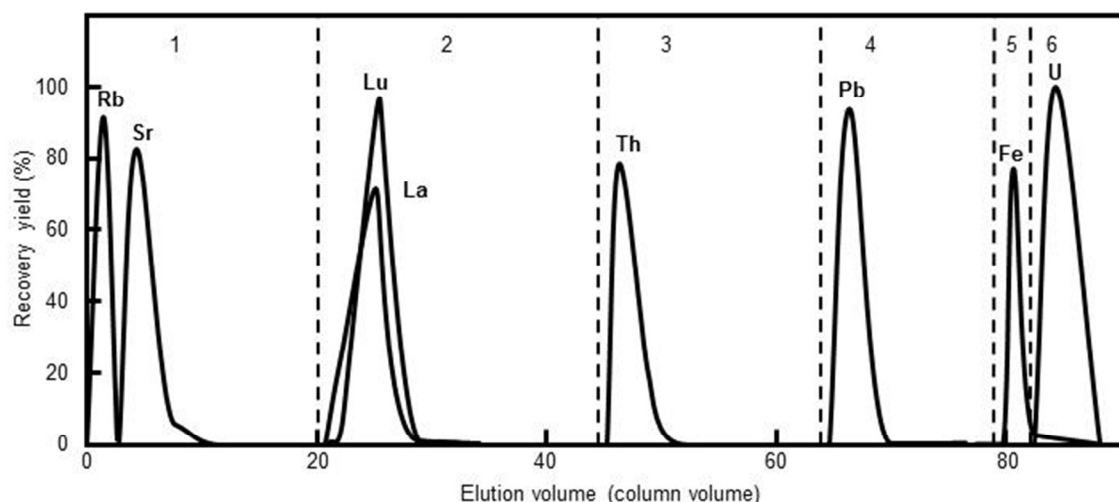


Fig. 5. Elution profile of representative elements separated under the optimized condition. The numbers indicate the fraction No. listed in Table 1. The broken lines indicate the change of elution composition. This separation used a particle size of 11 μm (CA08S), column size of 0.2 mm i.d. \times 50 mm long, (column volume: 157 μL), gas pressure of 0.45 MPa (35 $\mu\text{L}/\text{min}$ flow rate for Th elution), and total process time of 5 h.

Figure 6 reveals a chemical fractionation beyond the uncertainty was not found for each lanthanide member. This lanthanide fraction can be directly served as an analytical sample to determine abundance of lanthanide elements without corrections of recovery yield of each lanthanide member and interferences from major constituents of environmental samples, including the alkaline metals, the alkaline earth metals, and Fe. Each lanthanide member can be obtained from this separation fraction by further separation using the effective eluents such as 2-hydroxy-2-methylpropanoic acid (2-HIBA) solution on demand. Decontamination factors >400 were obtained for the elements of interest. The small contamination of Fe in the U fraction can be suppressed by modifying the eluent composition to effectively eliminate Fe. The procedure of this modification will be reported in a future paper.

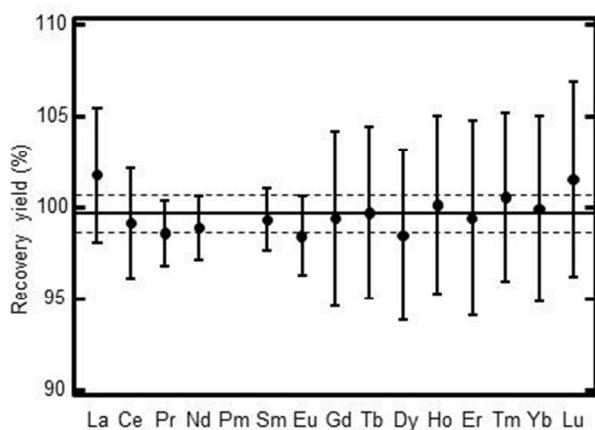


Fig. 6. Chemical recovery yield variation for each lanthanide members. The solid and broken lines indicate the average and standard deviation of the yield for all lanthanide members, respectively.

3.3. Application to analysis of elemental abundances in an environmental sample

The elements of interest in a sample solution of 370 μL which was equivalent to 749 μg of the reference powdered basalt sample (JB-1)²⁷, were successfully separated and fully recovered with the automatic sequential separation system under the optimized conditions: 0.45 MPa gas pressure (35 $\mu\text{L}/\text{min}$ flow rate for Th separation), 11 μm diameter anion-exchange resin (CA08S), 2 mm diameter \times 50 mm long column. Figure 7 shows the elemental abundance of the JB-1 sample solution. The reference values were obtained from the sample mass served to this analysis and the compiled concentrations¹⁶. The recovery yield of U determined using the ²³³U spike was 101 ± 2 (%). The abundance of objective elements ranged from 0.23 ng of Lu to 51 ng of Ce. These ultra-trace elements were automatically and sequentially separated without contamination at sub-ng level. The analytical results were in good agreement with the recommended values within the uncertainty. It is notable that the sequential separation of ultra-trace multiple elements without separation loss or contamination of process blank was achieved with this technique. More accurate analyses can be expected by adding chemical yield tracers in sample digestion processes or by using the isotope dilution technique.

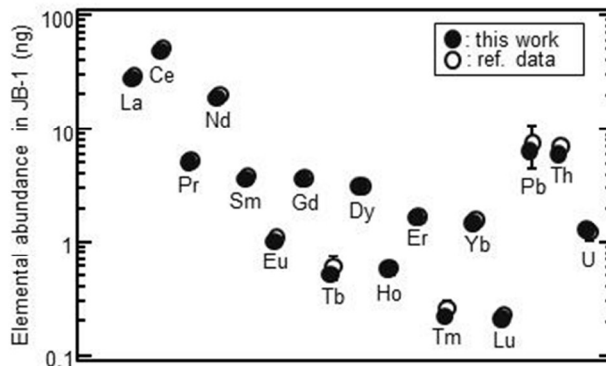


Fig. 7. Application of the automatic sequential separation system to ultra-trace analysis of elemental abundance. The sample solution of basalt reference sample (JB-1) of 749 μg was separated, and then the elements were determined by ICP-MS. The closed and open circles indicate the analytical results in this work and the recommended values (except for reported value of Pb)¹⁶, respectively.

This application examination indicates that the samples for ultra-trace analysis can be prepared without time consuming or complicated chemical separation. This simple sequential separation technique has outstanding potential for analysing the elemental abundance and isotope ratios of ultra-trace elements at sub-ng level in environmental samples. Additionally these features enabled us to perform a chemical separation of multiple elements at the ultra-trace level, regardless of operator skill, as compared with conventional techniques.

4. Conclusions

The separation performance herein reveals that this separation technique is useful for the ultra-trace analysis of small samples with elemental and isotopic composition. The sequential and automatic anion-exchange separation of 50 ng of U, Th, Pb, and lanthanides was accomplished with the highly pure acid mixture and a simple system driven by a pressurized gas within 5 h. By optimization of separation conditions; particle size of anion-exchange resin, column length, and flow rate of eluents, the elements of interest were perfectly separated with recovery yields of >95% and decontamination factors of 100–5000. In this system, major constituents including alkaline metals, alkaline earth metals, and iron were eliminated from the elements of interest. High separation performance was proved by analysing the abundance of objective elements ranging from 0.23 ng of Lu to 51 ng of Ce in a reference rock sample. This advantage is considerably helpful in analysing accurate abundances and isotope ratios of elements at sub-ng level in environmental samples without the interferences of these major constituents or complicated separation recipes. Numerous samples could be processed in a short time without requiring special skills by modifying this system to separate samples in parallel.

Acknowledgements

The authors are grateful to Shigekazu Usuda for his valuable idea on the pressurized separation system. This work was supported by financial aid from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan (Scientific Research (C), Grant No. 25340078).

Notes and references

- 1 A. Bollhöfer, K. J. R. Rosman, *Geochim. Cosmochim. Acta*, 2001, **65**, 1727-1740.
- 2 I. G. Alvarez, M. A. Kusiak, R. Kerrich, *Chem. Geol.*, 2006, **230**, 140-160.
- 3 E. Pelt, F. Chabaux, C. Innocent, A. K. Navarre-Sitchler, P. B. Sak, S. L. Brantley, *Earth Planet. Sci. Lett.*, 2008, **276**, 98-105.
- 4 A. W. Knight, E. S. Eitheim, A. W. Nelson, S. Nelson, M. K. Schultz, *J. Environm. Radioactiv.*, 2014, **134**, 66-74.
- 5 L. A. Mayers, S. E. Glover, S. P. LaMont, A. M. Stalcup, H. B. Spitz, *J. Radioanal. Nucl. Chem.*, 2014, **299**, 1833-1837.
- 6 G. Shimoda, *J. Mass Spectrom. Soc. Jpn.*, 2004, **52**, 213-218.
- 7 M. Mola, A. Neito, A. Peñalver, F. Borrull, C. Aguilar, *J. Environm. Radioactiv.*, 2014, **127**, 82-87.
- 8 A. N. Turanov, V. K. Karandashev, V. E. Baulin, *Solvent Extr. Ion Exch.*, 2012, **30**, 244-261.
- 9 A. K. Dinkar, S. K. Singh, S. C. Tripathi, P. M. Gandhi, R. Verma, A. V. R. Reddy, *J. Radioanal. Nucl. Chem.*, 2013, **298**, 707-715.

- 10 E. P. Horwiz, M. L. Dietz, S. Rhoads, C. Felinto, N. H. Gale, J. Houghton, *Anal. Chim. Acta*, 1994, **292**, 263-273.
- 11 E. P. Horwiz, M. L. Dietz, R. Chiarizia, H. Diamond, *Anal. Chim. Acta*, 1992, **266**, 25-37.
- 12 Y. Miyamoto, K. Yasuda, M. Magara, T. Kimura, S. Usuda, *J. Nucl. Radiochem. Sci.*, 2009, **10**, 7-12.
- 13 Y. Miyamoto, K. Yasuda, M. Magara, T. Kimura, S. Usuda, *Proc. Radiochim. Acta*, 2011, **1**, 209-212.
- 14 S. Usuda, JAERI 1315, JAEA, 1989.
<http://www.jaea.go.jp/english/publication/index.html>
- 15 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, *Intern. J. Environ. Anal. Chem.*, 2006, **86**, 663-675.
- 16 N. Imai, S. Terashima, S. Ito, A. Ando, *Geostand. Newslett.*, 1995, **19**, 135-213.
- 17 J. I. Kim, H. -J. Born, *Radiochim. Acta*, 1970, **14**, 35-39.
- 18 L. I. Guseva, G. S. Tikhomirova, P. A. Korovaikov, *Radiochemistry (Radiokhimiya)*, 1999, **41**, 229-232.
- 19 J. P. Faris, R. F. Buchanan, *Anal. Chem.*, 1964, **36**, 1157-1158.
- 20 P. Van Acker, *Anal. Chim. Acta*, 1980, **113**, 149-158.
- 21 J. I. Kim, H. -J. Born, *Radiochim. Acta*, 1970, **14**, 65-72.
- 22 G. S. Tikhomirova, L. I. Guseva, P. A. Korovaikov, *Radiochemistry (Radiokhimiya)*, 1999, **41**, 233-235.
- 23 Van den Winkel, F. De Corte, J. Hoste, *J. Radioanal. Chem.*, 1972, **10**, 139-143.
- 24 Van den Winkel, F. De Corte, J. Hoste, *Anal. Chim. Acta*, 1971, **56**, 241-259.
- 25 P. Van den Winkel, F. De Corte, A. Speecke, J. Hoste, *Anal. Chim. Acta*, 1968, **42**, 340.
- 26 J. J. Van Deemter, F. J. Zuiderweg, A. Klinkenberg, *Chem. Eng. Sci.*, 1956, **5**, 271-289.
- 27 E. Glückauf, *Trans. Faraday Soc.*, 1953, **51**, 34-44.

Table 1. Chemical Composition and volume of eluents.

Fraction No.	Eluted element	Volume (mL) [CV] ^a	Composition of the eluent
1	Alkali metals, alkali earth metals (for elimination)	0.10 [0.64] ^b 3.14 [20]	16 M CH ₃ COOH–0.2 M HNO ₃
2	Lanthanides	3.93 [25]	15 M CH ₃ COOH–0.80 M HCl–0.9 M HNO ₃ – 0.03 M NH ₂ OH·HCl
3	Th	3.14 [20]	12 M CH ₃ COOH–1 M HCl–0.1 M HF
4	Pb	2.36 [15]	9 M HCl
5	Fe (for elimination)	0.47 [3]	8 M HNO ₃
6	U	1.88 [12]	0.2 M HCl–1 M HF

a: Column volume (CV) unit for 2mmφ × 50 mm long column (0.158 mL); b: Volume for feeding the sample solution.

Table 2. Recovery yields and decontamination factors of representative elements in the effluents

Fraction No.	Recovery yield (%) ^a	Eluted element ^b	Decontamination factor ^c
1	89 ± 11 (for Rb) 94 ± 4 (for Sr)	Mg, Rb, Sr, Cs, Ba, Be, Sc, Cr, Mn, Te	Rb / La 280
2	96 ± 4 (for lanthanides)	lanthanides, Y, Co	La / Rb > 9x10 ³ La / Th > 7x10 ⁴ La / U > 2x10 ⁵
3	95 ± 10 (for Th)	Th	Th / La 420 Th / U > 4x10 ⁵
4	109 ± 14 (for Pb)	Pb, Cu, In, Ag	Pb / Th 5x10 ³ Pb / U 1x10 ⁴
5	84 ± 9 (for Fe)	Fe, Zn, Ga, Cd	
6	103 ± 11 (for U)	U, Sn, Bi	U / Fe 40 – 170

a: The average and standard deviation in 4 runs, and the Fe recovery was normalized relative to the complete recovery of all fractions;

b: The elements whose recovery was >50 % of the fraction are listed. The elements expected to be eluted in the fraction are indicated in bold type;

c: The decontamination factors were calculated from the chemical recovery ratios.