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Development of a Separation Method for Uranium Isotopic Mass Ratio Measurement in Environmental Samples by ICP-MS

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A separation method using TEVA Spec resin (Eichrom Industries Inc.) was studied for a simple and rapid measurement of uranium isotopic mass ratio in environmental soil samples by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS). The resin, charged in a minicolumn, retained U from a 20-mL sample solution adjusted to 6 M HCl. After washing the column with 6 M HCl, U was eluted with 20 mL of 1 M HCl. Through this separation process, U in a standard solution was purified from major and minor elements including Fe. Subsequently, the method was also applied to actual soil sample solutions, but U could not be separated from Fe. This was possibly attributed to Fe contents in the samples being higher than in that in the standard solution, and Fe would affect U sorption onto the resin. However, the separation method could separate U from major matrix elements in soil and the isotopic mass ratios of $^{235}U/^{238}U$ and $^{234}U/^{238}U$ could be measured by Q-ICP-MS using a 0.1 g sample of dried soil.

KEYWORDS: rapid separation method, uranium isotopic mass ratio, Q-ICP-MS, TEVA resin, soil samples

I. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has been used for measurements of long-lived radionuclides in environmental samples. For example, the concentrations of ^{238}U can be measured with the detection limit of less than 0.1 pg/mL (1.2×10^{-9} Bq/mL) in a few minutes. Thus, the concentrations of U have been determined by ICP-MS without any radiochemical separation in natural water samples or in soil samples by just dissolving them in a solution using mineral acids.[1-2] Recently, the ICP-MS has also been used for the measurement of U isotopic ratios.[3, 4] Although thermal ionization mass spectrometry (TIMS) has a higher precision for this purpose,[5] ICP-MS needs less chemical separation and the measurement time is much shorter. Thus, ICP-MS has become a powerful tool for rapid environmental monitoring. Quadrupole (Q-) ICP-MS is especially attractive because the instrument is widely used for the measurement of elements at trace levels in environmental samples.

For a precise isotope ratio measurement of U by Q-ICP-MS, it is necessary to separate U from the matrix elements. Generally, anion exchange resins and liquid-liquid extractions are used for U separation.[6, 7] Recently, U/TEVA and TRU resins have come into popular use to separate actinide elements sequentially.[8] The TRU and U/TEVA resins could absorb U (VI) with k' values (retention volume) of 10000 and 300 in 10 M HNO_3, respectively.[9] However, the k' for U/TEVA seems small in 10 M HNO_3 and that for TRU in 0.04 M HNO_3 is big as 50, that means 50 mL of 0.04 M HNO_3 is necessary to remove U from 1-g of the resin. On the other hand, the U absorbability by TEVA resin (k'=3000) is higher than those of U/TEVA (k'=200) in HCl solution,[5,9] thus, we have developed a simple and rapid separation method for U with the TEVA resin for Q-ICP-MS.[4] The method was sufficiently useful enough to separate and concentrate U from sample matrixes, however, a high Fe concentration was found in the final solution for Q-ICP-MS because the resin is a strongly basic anionic exchange resin. Although high Fe concentrations, i.e., 100 mg/L (ppm), do not affect the counts of U isotopes, it is preferable to avoid any contamination of matrix elements to keep instrumental stability and sensitivity during the measurement. In this study, we paid attention to U separation from Fe in soil samples. Moreover, the extraction behaviors of other matrix elements were checked regarding their influence on U separation in the TEVA resin separation step.

II. Experimental

1. Reagents

Nitric acid, hydrochloric acid and hydrofluoric acid were ultra-pure analytical grade (Tama Chemicals, AA-100). Deionized water (>18 MΩ) was obtained from a Milli-Q water system (Millipore Co.). Pre-packed minicolumns of Tc-selective chromatographic resin, TEVA (Eichrom Industries, Inc.) were used for separation of U. The column was pretreated with 10 mL of 0.1 M HNO_3 followed by 10 mL of 6 M HCl.

To make a standard curve for Q-ICP-MS measurements, multi-element standard solutions including 10 ppm of U, XSTC-355 and XSTC-640 (SPEX Industries Inc.), were used. The XSTC-355 was also used in a preliminary test to set suitable chemical separation conditions.

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2. Samples

Six soil samples collected in Japan, two standard rock samples, JG-1 and JCp-1, and two soil samples collected in the Marshall Islands were used. The soil samples were air-dried, passed through a 2 mm sieve to remove rocks and plant roots, and then ball milled into a fine powder.

3. Method

(1) Test-1

The XSTC-355 solution (1 mL) and Fe(III) solution including 2 mg of Fe were transferred into a PFA beaker and 10 mL of acid mixture (HNO_3, HCl and HF) were added. The solution was evaporated to dryness on a hot plate at 120-140°C. The residue was dissolved with 20 mL of 6 M HCl. The solution was passed through a TEVA Spec resin column to extract U on the resin. Iron was also extracted on the resin at the same time presumably as chloro complexes. The load solution was allowed to drain. The column was then washed with 20 mL of 6 M HCl. The U retained on the resin was eluted with 0.5, 1 or 2 M HCl. During the extraction, the eluates were collected in 5-10mL aliquots. Finally, 10 mL of 0.1 M HNO_3 were used to extract all the U and Fe remaining in the column. Each extraction with 0.5, 1, or 2 M HCl was repeated 3 times. All the eluates from the column had their the U and Fe concentrations measured by Q-ICP-MS (Yokogawa, Agilent-7500a).

(2) Test-2

A 0.2 g amount of soil sample was dissolved with 15 mL of acid mixture (HNO_3, HCl and HF) after heating the two in a PFA beaker covered with a PFA watchglass on a hot plate for 3 h. Then the solution was evaporated to dryness. Next 5 mL of concentrated HCl were added to the residue and the solution was evaporated to dryness again. Then, the residue was dissolved in 20 mL of 6 M HCl and the solution was passed through a preconditioned TEVA resin minicolumn. The column was washed with 20 mL of 6 M HCl and U fraction was extracted with 25 mL (5 mL x 5) of 1 M HCl. The column was finally washed with 10 mL of 0.1 M HNO_3. The XSTC-355 was also treated as described in this test-2 for comparison.

III. Results and Discussion

1. Identification of U Separation Conditions from Fe Using a TEVA Resin Column

Previously, we used 30 mL of 0.1 M HNO_3 to remove U from a TEVA resin column after washing the column with 6 M HCl.[4] Under this set of elution separation conditions, Fe was also eluted as Fe^{3+} showing almost 100% recovery. Thus, to separate U from Fe, the elution behaviors using 0.5-2 M HCl solution with the resin column were studied (Test-1). The elution behavior was described as relative amount, defined as "the amount of an element in the fraction (C)" divided by "the total amount of the element in the sample (C_0)". As shown in **Fig.1**, the 0.5M HCl could not separate U from Fe because the U peak was followed by the Fe peak within 5 mL: The elution behaviors of U and Fe in 0.5 M HCl were almost the same. However, the use of 1 M HCl allowed most of the U to be eluted in the in first 20-mL eluate. After that, the Fe peak was followed but both peaks were completely separated. When 2 M HCl was used, U could be removed faster than Fe from the column, since Fe was strongly absorbed by the resin. However, the U band was wider than that for 1 M HCl elution; therefore, to extract U, at least 140 mL of 2 M HCl was necessary. The 1 M HCl extraction was the best for U separation from Fe while minimizing the amount of Fe and the separation time.

The separation conditions were then set as follows. The sample solution was adjusted to 6 M HCl and passed through the TEVA resin column. After washing the column

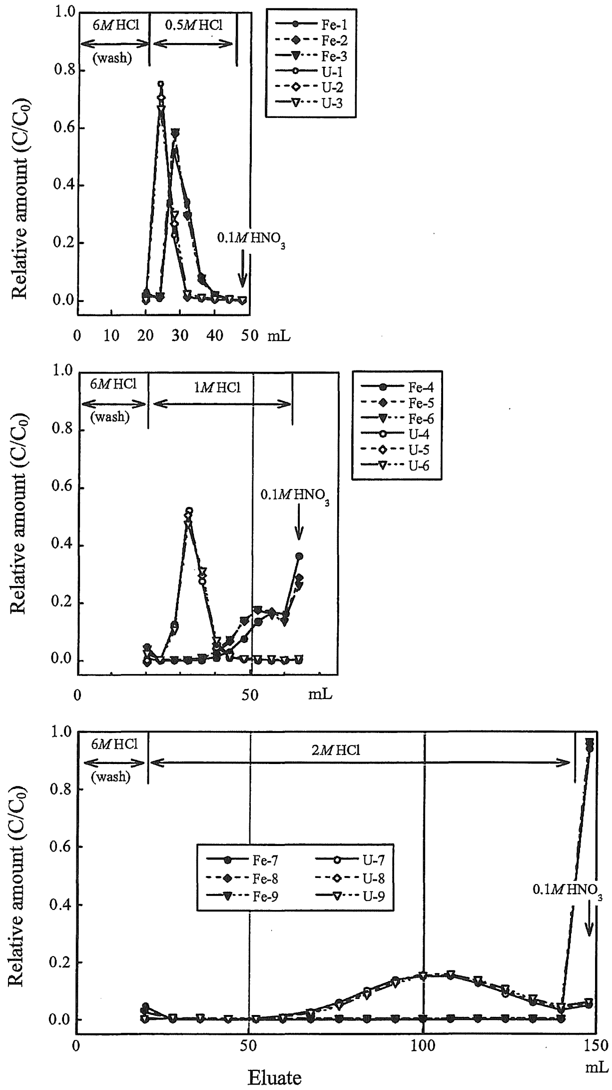

Fig. 1 The elution behaviors of U and Fe with the TEVA resin column when 0.5, 1, and 2M hydrochloric acid solutions were used after washing the column with 20 mL of 6M hydrochloric acid. Each treatment was repeated three times.

with 20 mL of 6 M HCl, the U retained on the resin was extracted with 20 mL of 1 M HCl. The U fraction was evaporated once to near dryness to decrease the acid content. Finally, the residue was dissolved into a 10-mL amount of 2% HNO_3 for Q-ICP-MS measurement. The recovery obtained with this standard solution was 90-100%. It was not necessary to collect all the U from the TEVA resin column because a rapid isotopic mass ratio measurement by Q-ICP-MS was the purpose of this method.

2. Separation and Measurement of U in Rock and Soil Samples

The method was applied to environmental soil and rock samples (Test-2). The elution behaviors of U and Fe are shown in **Fig. 2**. The elution behaviors of Li, Be, Na, Al, V, Mn, Ni, Rb, Sr, and Pb were also measured, but the results were the same as those of Cs, therefore, only the results of Cs are shown in the same figure. As was expected, U in the standard solution could be separated from Fe and from the other elements (**Fig.2-a**). However, the method could not separate U completely from Fe when actual soil samples were used (**Fig.2-b**). The U elution peak for the soil sample shifted backwards, away from that for the standard solution. Iron content in the standard solution was a maximum of 2 mg, however, the sample contained about 4-10 mg of Fe. Although the resin can possibly extract up to 40 mg Fe/g resin, the Fe concentration seemed to be so high that iron chloride complexes were interfering with U extraction on the resin and U elution behavior. When Fe contents were lower than 2 mg, U in actual soil samples would be separated from Fe. However, not all the Fe was found in the 1 M HCl fraction, thus, the method can still decrease Fe content in the final solution for Q-ICP-MS.

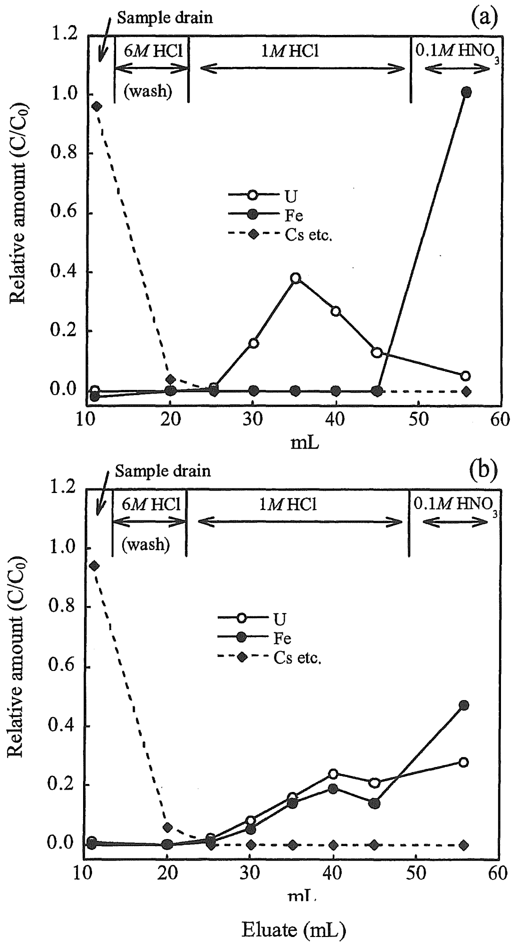

Fig. 2 The elution behaviors of U, Fe, and Cs with the TEVA resin column from (a) a standard solution and (b) a soil sample. The behaviors of Li, Be, Na, Al, V, Mn, Ni, Rb, Sr, Ba and Pb were the same as that for Cs.

3. Uranium Isotopic Mass Ratio Measurement by Q-ICP-MS

The separation method was used for all the samples for U isotopic ratio measurement by Q-ICP-MS. All U fractions included some Fe (in ppm order). During the measurement by Q-ICP-MS, three replicate measurements were done for every sample, looking for 1, 50, and 150 s counting times for ^{238}U, ^{235}U and ^{234}U, respectively, in each run. The U isotopic ratios of $^{235}U/^{238}U$ are plotted in **Fig. 3**. The activity ratio expected in natural samples was 0.00725. The observed values indicated the natural ratio, that is, no contamination with enriched U or depleted U was observed even for the soil samples collected in the Marshall Islands. The ^{234}U counts were also measured and the ratios of $^{234}U/^{238}U$ calculated were almost the natural one as well (the data not shown). There was no data for uranium isotopic mass ratio for the Marshall Islands' soil samples. The uranium concentrations in the samples were 1-2 µg/g and the $^{235}U/^{238}U$ ratios were natural one; these results implies that the amounts of U from the nuclear weapon explosions in that area would be small, though further studies are needed in the future to clarify the effect.

For total U concentration measurement, a 0.1 g soil sample was digested using just mixed acid reagents; then,

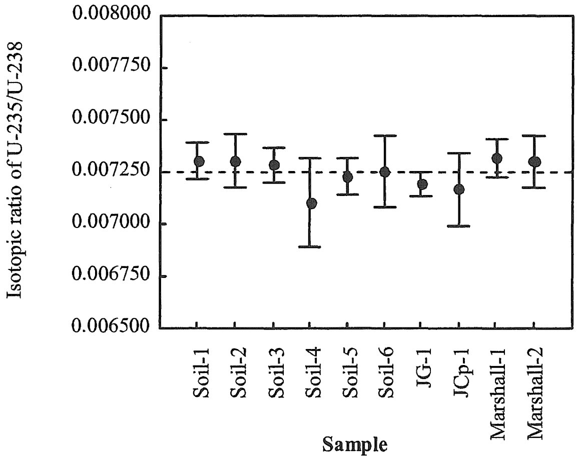

Fig. 3 Isotopic ratio of $^{235}U/^{238}U$ in soil and rock samples measured by Q-ICP-MS after separation of U using the TEVA resin separation method. The broken line shows the natural isotopic ratio (0.00725).

the residue was diluted to at least 200 mL due to instrumental limitation. Therefore, the U concentration observed under the usual Q-ICP-MS operation conditions was <0.2 ng/mL. In practice, to obtain good precision under the measurement conditions, U concentration should be more than 2 ng/mL. With application of the proposed method, U could be concentrated to the 2-10 ng/mL level without any other matrix element contamination in the final solution for Q-ICP-MS, though some Fe might be present. However, the Fe contamination does not interfere with the counts of U isotopes by Q-ICP-MS. In Japanese soil samples, the U concentration ranges from 0.17-4.6 mg/kg with an average of 2.3 mg/kg.[2)] Thus, to measure the isotopic ratio of U by Q-ICP-MS, 0.05-0.1 g of totally digested soil sample are necessary for this separation method.

In conclusion, the proposed method could separate U from Fe in the standard solution for U isotopic mass ratio measurement by Q-ICP-MS, however, Fe could not separated when actual soil samples were used. Further studies are needed to identify the limitation factors for U separation from Fe.

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