

# Use of TEVA resin for the determination of U isotopes in water samples by Q-ICP-MS

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## Abstract

In order to measure uranium isotopic mass ratio in natural water samples by Q-ICP-MS, an application of TEVA resin (Eichrom) was studied to separate and concentrate U. After being evaporated to dryness, the sample residue was dissolved in 6 M HCl, then, TEVA extraction was carried out. U extracted on the resin could be removed with 20 ml of 1 M HCl (U fraction) when Fe content was lower than 2 mg. U recovery in U fraction showed a negative correlation with Fe content in the samples.

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## 1. Introduction

Radiation measurement methods, such as alpha spectrometry, have been used for environmental monitoring of U; however, recently, inductively coupled plasma mass spectrometry (ICP-MS) has become a powerful tool because of its sensitivity and short measurement time. Indeed, direct measurement of U concentrations in terrestrial water samples using <sup>238</sup>U is possible by ICP-MS in a few minutes, because the detection limit is usually less than 0.1 pg/ml ( $1.2 \times 10^{-9}$  Bq/ml) (Yamasaki and Tsumura, 1991; Muramatsu et al., 1994; Shiraishi et al., 1994; Karpas et al., 1996). In addition, ICP-MS needs less chemical separation work-up and the measurement time is much shorter than that for thermal ionization mass spectrometry. It has been used successively for the measurement of U isotopic mass ratios (Shiraishi et al., 1994; Becker and Dietze, 1999; Uchida et al., 2000; Yoshida et al., 2000). In this study, we focus on using quadrupole (Q-) ICP-MS, because the instrument is widely used in

environmental studies for trace elements and long-lived radionuclides.

To measure U isotopic mass ratios by Q-ICP-MS, it is necessary to concentrate U from the environmental samples, since the element concentration is usually found at low pg/ml levels in terrestrial water samples. Although U/TEVA and TRU resins have been used for sequential extraction of actinide elements (Horwitz et al., 1992, 1995; Yokoyama et al., 1999; Warwick et al., 1999; Fujikawa et al., 2002), Horwitz et al. (1995) reported that the U adsorbability by TEVA resin is higher than that of U/TEVA resin in hydrochloric acid solution. Consequently, it would be better to use TEVA resin when a rapid U isotopic mass ratio monitoring is necessary in an emergency situation.

In this study, we applied a simple separation method using TEVA resin, which was modified from our previous method (Uchida et al., 2000) to measure U isotopic mass ratio of <sup>235</sup>U/<sup>238</sup>U in water by Q-ICP-MS. Although all U on the resin was removed with 0.1 M HNO<sub>3</sub> in our previous method, Fe was also found in the fraction because the resin is a strongly basic anionic exchange resin. Although Fe contents in natural water samples are expected to be low, it was not clear whether

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Fe content affects U elution behavior from the resin or not. There are many reports on U separation methods using anion exchange resins solvent extraction (e.g., Korkisch and Sorio, 1975; Brits and Smit, 1977; Rosenberg et al., 1991), however, no data dealing with Fe content effect on U elution behavior are available. Thus, another fundamental experiment was carried out to clarify whether the resin can separate U from Fe during the separation process.

## 2. Experimental

### 2.1. Instruments

Measurements of U isotopes and 23 other major and trace elements in sample solutions were carried out with an Agilent Model 7500 ICP-MS, (Yokogawa, Japan). The basic operation conditions with a Babington nebulizer were applied. For determination of the 24 major and trace elements, scanning was repeated 3 times with 100 sweeps for each scan. Total counting time was 3 min for one sample. For U isotopic ratio determination, Bi was used as an internal standard. Uranium isotopes were scanned 1000 times for one scanning, which was repeated 5 times. Total counting time of this measurement was 15 min.

To make a standard curve for Q-ICP-MS measurements, multi-element standard solution XSTC-355 (SPEX Industries Inc.) was used. The Q-ICP-MS sensitivity for U isotopes was checked using another standard solution, XSTC-640 (SPEX Industries Inc.).

### 2.2. Separation method

Three natural water samples which contained 0.5–30 g/kg total dissolved solids were used. Each sample was filtered through a 20- $\mu$ m pore size filter, then, 5 ml of conc. HCl were added to a 200–500 ml amount of water sample. The solution was evaporated to about 50 ml in a 500-ml glass beaker on a hot plate at 120–140°C. The solution was transferred into a 50-ml PTFE beaker and was evaporated to dryness at 120°C. The residue was dissolved in 10–20 ml of 6 M HCl. After removing particles by filtration (GF-A, Whatman), the solution was passed through a mini-column charged with the TEVA resin (Eichrom Industries, Inc.), which was pretreated with 10 ml of 0.1 M HNO<sub>3</sub> followed by 10 ml of 6 M HCl. The column was washed with 20 ml of 6 M HCl, and U was stripped with 20 ml of 1 M HCl (U fraction). Finally, elements retained on the resin were removed with 0.1 M HNO<sub>3</sub>. Hydrochloric acid and nitric acid used were ultra-pure analytical grade (Tama Chemicals, AA-100). Deionized water (>18 M $\Omega$ ) obtained from a Milli-Q water system (Millipore Co.) was

used for dilution of reagents and rinsing the laboratory-ware.

All the eluates from the resin column were collected to check the elution behaviors of major and trace elements by ICP-MS, by comparing the concentrations in each fraction (*C*) with those in the initial solution (*C*<sub>0</sub>). Before the ICP-MS measurement, each eluate was evaporated to dryness and the residue was dissolved in 5 ml of 2% HNO<sub>3</sub> solution. The solution was diluted to a suitable concentration (<1000  $\mu$ g/ml in total) for ICP-MS measurement.

## 3. Results and discussion

### 3.1. Elution behaviors of U and other major and trace elements with the TEVA resin

The separation method was modified from our previous study for sediment samples (Uchida et al., 2000). The original method was useful enough to separate and concentrate U from sample matrixes, however, a high Fe concentration was found in the final eluate of 0.1 M HNO<sub>3</sub> for ICP-MS. It would be better to avoid any contamination, thus keeping better instrumental stability and sensitivity during the ICP-MS measurement. Solvent extractions could separate U from Fe as Okafor and Uzoukwu (1990) reported, but introduction of the step is time consuming. Thus, in this study, reagent strength for U separation was changed to simplify the method. In our previous experiment, the use of 1 M HCl as U strip solution allowed most of the U to be eluted in the first 20-ml eluate followed by the Fe elution (Tagami and Uchida, 2003). Thus, 20 ml of 1 M HCl was used to separate U from Fe (U fraction) after washing the column with first 20 ml of 6 M HCl.

The extraction behaviors of U and other elements from the TEVA resin column using standard solutions are listed in Table 1. The values are “relative content” defined as *C/C*<sub>0</sub>. As can be seen from the table, Fe was not found in the U strip fraction under the separation conditions. It was observed that almost all the elements, including Th, were completely eliminated through this procedure. Thirty to fifty percent of the added W was found in the U fraction; however, the presence of W does not affect counting of uranium isotopes by Q-ICP-MS.

The method was also used for soil samples to identify any elements interfering with U separation behavior. A 0.2 g amount of soil sample was dissolved in aqua regia, then, after removing the precipitate, elution behavior of U and Fe in the solution was studied. In Fig. 1, U recovery in the U strip fraction (1 M HCl) is plotted against Fe content in the samples. The U recovery showed a high negative correlation with Fe content (*p*<0.01), that is, Fe affected the U separation. The

Table 1  
Elution behaviors of U and 23 other elements from TEVA resin under the U separation conditions

Elements	Sample drain (6 M HCl) 10–20 ml	Wash (6 M HCl) 20 ml	U strip (1 M HCl) 20 ml	0.1 M HNO <sub>3</sub> 10 ml
Li, Be, Na, Mg, Al, K, Ca, Mn, Ni, Rb, Sr, Y, Cs, Ba, Pb, Th	90–100	<10	<1	—
Co	30–40	60–70	<5	—
Cu	10–20	50–70	<30	—
Fe, Zn, Cd	<1	<1	<5	95–100
Sn	<10	<1	<1	90–100
W	<10	30–50	30–50	<10
U	—	—	80–100	<20

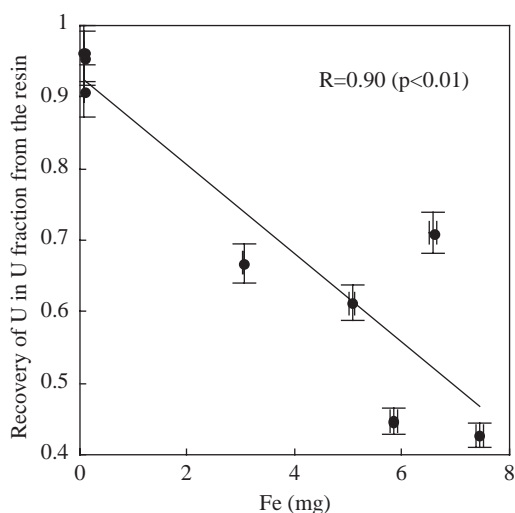


Fig. 1. Percentage of U found in the U fraction by the proposed method plotted against Fe content in the samples.

elution behaviors of Fe and U under the separation conditions are shown in Fig. 2. Uranium in standard and sample solutions which were adjusted to 6 M HCl was completely extracted onto the resin. Then, for the standard solution (about 0.1 mg Fe content), U was separated from Fe as expected, but U was not removed with 20 ml of 1 M HCl when the Fe content was increased to 4–10 mg. The rest of the U retained on the resin was found in the 0.1 M HNO<sub>3</sub> fraction. By contrast, some Fe could be removed with 1 M HCl when a high Fe content solution was applied. The high Fe content affected U extraction behavior by the resin.

The TEVA resin has the highest adsorption factor for U in 6 M HCl as reported by Horwitz et al. (1995). Therefore, a fundamental experiment on the extractability of U with the TEVA resin from 6 M HCl solution was carried out while changing Fe content. The standard solution XSTC-355, which contained 10 µg/ml of U was diluted 100 times with a 6 M HCl solution. FeCl<sub>3</sub> was

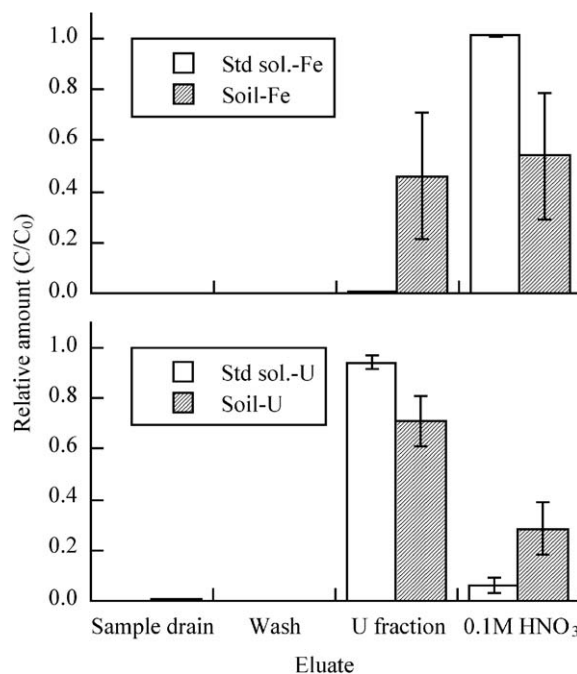


Fig. 2. Elution behaviors of Fe and U with the resin in standard solution (ca. 0.1 mg Fe) and high Fe content solutions (4–10 mg).

dissolved in 50 ml of deionized water and added at different Fe(III) strength (0.6–110 mg of Fe) to the standard solution. A batch technique was used in this experiment. The U extraction reaction by the resin is a fast process, but the mixture of the prepared solution and the TEVA resin was shaken for 4 h, which would be long enough to reach reaction equilibrium.

The percentages of U and Fe extracted on the resin are shown in Fig. 3. The U content in a sample was about 2 µg, which would be low enough to retain all the U by the resin in 6 M HCl. No U extraction onto the resin was observed when the Fe content was about 100 mg. The resin could retain about 40 mg of Fe per

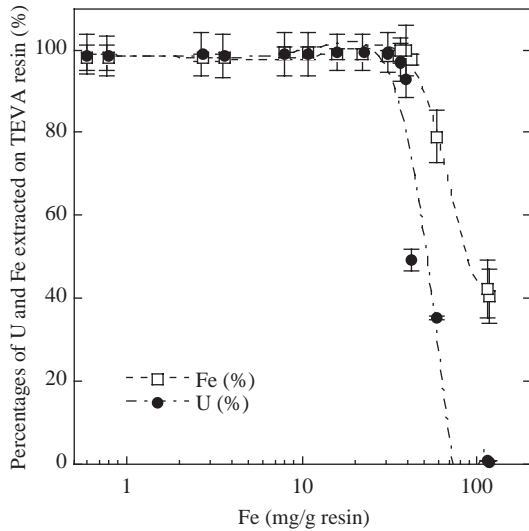


Fig. 3. Adsorptions of Fe and U by TEVA resin from 6 M HCl solutions containing 0.6–110 mg of Fe.

g-resin; however, the Fe content higher than 2 mg could cause low U recovery in the U fraction from the resin. Thus, it would be better to check the Fe content in the solution samples prior to U separation with the resin.

### 3.2. U isotopic mass ratio measurement in water samples by Q-ICP-MS

Since U concentrations in natural water samples are at pg/ml levels, it is necessary to concentrate a sample to a suitable concentration for Q-ICP-MS of the isotopic mass ratio. Fig. 4 shows example results of relative standard deviation (RSD, %) of  $^{235}\text{U}/^{238}\text{U}$  isotopic mass ratios as measured by Q-ICP-MS. The errors were mainly counting errors, but, clearly, the errors decreased with increasing U concentration. From the results, it was estimated that the preferable U concentration for U isotopic ratio measurement by Q-IP-MS was between 2–20 ng/ml. When the U concentration level is high, i.e., 100 ng/ml, the instrument automatically switches the counting method from pulse counting to analogue counting only for  $^{238}\text{U}$ . Additionally, even the counting time at mass 238 was shortened (i.e., <0.1 s per mass) to avoid counting above > 10 M counts; thus the counting time would become too short to obtain better precision for the isotopic mass ratio measurement. Uranium concentration should be increased, but having a value lower than 100 ng/ml would be better for the measurement.

The modified separation method was applied to U isotopic abundance measurement in water samples. The results are listed in Table 2. The measured  $^{235}\text{U}/^{238}\text{U}$  atomic ratios were almost the same as that calculated

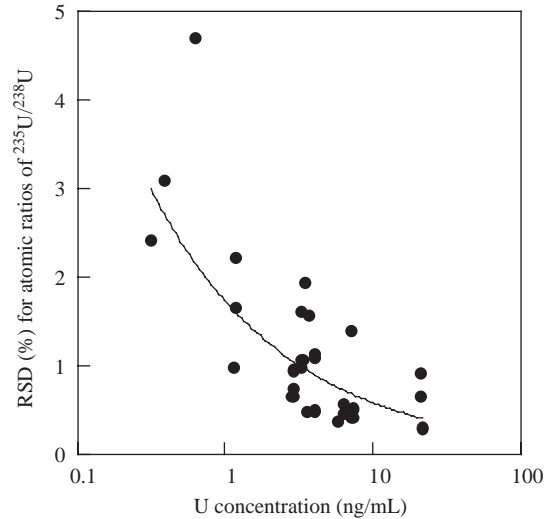


Fig. 4. Relative standard deviation (RSD, %) for isotopic ratio of  $^{235}\text{U}$  to  $^{238}\text{U}$  measured by Q-ICP-MS plotted against U contents in the samples.

Table 2

Recoveries and  $^{235}\text{U}/^{238}\text{U}$  isotopic ratios of the water samples measured by Q-ICP-MS

Sample	<i>n</i>	Recovery (%)	$^{235}\text{U}/^{238}\text{U}$
A	3	94 ± 20	0.00727 ± 0.00027
B	3	57 ± 6	0.00730 ± 0.00002
C	1	92	0.00734 ± 0.00010

from natural abundance, 0.00725. About 90% recoveries were observed except for Sample-B, which had the highest dissolved solid content among the samples. No significant amount of Fe in the U fraction of the samples was observed by Q-ICP-MS, thus, no influence of Fe on the U extraction by the resin was suspected. The low recovery in the U fraction could be affected by the concentration step of the water, i.e. U removal by coprecipitation with other elements or a low U extractability with the resin due to the high salinity. Further study is necessary to minimize the U loss during the separation steps.

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