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Determination of U isotope ratios in sediments using ICP-QMS after sample cleanup with anion-exchange and extraction chromatography

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Abstract

The determination of uranium is important for environmental radioactivity monitoring, which investigates the releases of uranium from nuclear facilities and of naturally occurring radioactive materials by the coal, oil, natural gas, mineral, ore refining and phosphate fertilizer industries, and it is also important for studies on the biogeochemical behavior of uranium in the environment. In this paper, we describe a quadrupole ICP-MS (ICP-QMS)-based analytical procedure for the accurate determination of U isotope ratios (^{235}U/^{238}U atom ratio and ^{234}U/^{238}U activity ratio) in sediment samples. A two-stage sample cleanup using anion-exchange and TEVA extraction chromatography was employed in order to obtain accurate and precise ^{234}U/^{238}U activity ratios. The factors that affect the accuracy and precision of U isotope ratio analysis, such as detector dead time, abundance sensitivity, dwell time and mass bias were carefully evaluated and corrected. With natural U, a precision lower than 0.5% R.S.D. for ^{235}U/^{238}U atom ratio and lower than 2.0% R.S.D. for ^{234}U/^{238}U activity ratio was obtained with less than 90 ng uranium. The developed analytical method was validated using an ocean sediment reference material and applied to an investigation into the uranium isotopic compositions in a sediment core in a brackish lake in the vicinity of U-related nuclear facilities in Japan.

Keywords: Uranium; Isotope ratio; Sediments; Quadrupole ICP-MS; Environmental radioactivity

1. Introduction

Uranium is ubiquitous in the environment due to natural processes and anthropogenic activities. It has three naturally occurring isotopes: ^{234}U, ^{235}U, and ^{238}U, with corresponding natural isotopic abundances (at.%) of 0.00548, 0.7200, and 99.2745 [1]; this means the ^{235}U/^{238}U and ^{234}U/^{238}U ratios in uranium of natural origin are 0.00725 and 0.0000552. Emissions of U from anthropogenic nuclear sources can, however, significantly alter the isotopic ratios in environmental samples. Uranium that is enriched in ^{235}U is indicative of weapons production, while the depleted U, which shows low ^{235}U/^{238}U ratios, is indicative of nuclear fuels that have been burnt up, reprocessed, or are waste from fuel enrichment processes [2–5]. The release of naturally occurring radioactive material (NORM) by the coal, oil, natural gas, mineral, ore refining and phosphate fertilizer industries could enhance the radioactivity level in the environment, but keep the isotopic compositions of uranium unaltered, in particular the ^{235}U/^{238}U ratio. The ^{234}U/^{238}U may vary due to the natural causes. It has been found that the ^{234}U/^{238}U activity ratio ($AR_{234/238}$) varies considerably in many water, soil, sediment and uranium ore samples of different geographical origins [6–10]. The $AR_{234/238}$ values in water reportedly vary from 0.5 to 40 [11,12], while those in soil typically range from 0.5 to 1.2 [13]. The mechanism of such variation is preferential leaching of ^{234}U compared with ^{238}U from the solid phase, caused by radiation damage of the crystal lattice upon alpha decay of ^{238}U, oxidation of insoluble tetravalent ^{234}U to soluble hexavalent ^{234}U during decay, and alpha recoil of ^{234}Th (and its daughter ^{234}U) into solution phase [14]. Uranium isotope ratios, therefore, give information regarding the source of the uranium in the environment, and are important for studying its biogeochemical behavior.

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For the determination of uranium isotopic ratios, thermal ionization mass spectrometry (TIMS) has been widely used for high precision analysis. This technique, however, is time consuming and expensive. Another traditional analytical approach involving alpha spectrometry suffers from low sample throughput and poor counting statistics for low-activity samples, although it is effective and widely available. In recent years, quadrupole ICP-MS (ICP-QMS) has become increasing popular in environmental studies for the analysis of samples containing low activity uranium. Compared with TIMS and alpha spectrometry techniques, ICP-QMS offers a number of advantages for isotope ratio measurement due to easier sample preparation steps, excellent detection limits (usually less than 0.1 pg/ml, or 1.2×10^{-9} Bq/ml for ^{238}U) [15], shorter measurement time and the capability to carry out precise isotope ratio measurements. The determination of ^{235}U/^{238}U ratio with ICP-QMS in a variety of environmental samples has been reported in the literature [16,17], however, there is very little study on the capability of ICP-QMS for ^{234}U/^{238}U activity ratios in environmental samples due mostly to the extremely low ^{234}U mass concentration in these matrices [18–20], although the high precision analysis of U isotopes with multi-collector sector field ICP-MS (MC-ICP-MS) has been well established [16,21].

For the accurate determination of ^{234}U/^{238}U ratio in environmental samples using ICP-QMS, it is important to have a sufficiently clean sample, as the ^{234}U analysis may experience interference from the sample matrix and polyatomic ions, such as $^{232}ThH_2^+$ due to the low atom abundance of ^{234}U. In this paper, we describe an analytical procedure for the accurate determination of uranium isotope ratios (^{235}U/^{238}U and $AR_{234/238}$) in sediment samples using ICP-QMS. We employed a two-stage chromatographic separation and purification process; first, the uranium was separated from the sediment matrix using an AG 1 × 8 anion-exchange column, then the obtained U fraction was further purified with TEVA extraction chromatography. The factors that affect the accurate and precise U isotope ratio analysis, such as the detector dead time correction, abundance sensitivity, dwell time and mass bias were carefully evaluated and corrected. High precision analysis for $AR_{234/238}$ was achieved with only 90 ng U with R.S.D. of 2–3% for a short-term measurement, and less than 2% for a long-term measurement. The developed analytical procedure was applied to the investigation into the uranium isotopic compositions in a sediment core collected in a brackish lake in the vicinity of several U-related nuclear facilities.

2. Experimental

2.1. Instrumentation

A HP-4500 quadrupole ICP-MS (Yokogawa Analytical Systems, Tokyo, Japan) was employed for the determination of U isotopes. The sample introduction system included a Scott-type spray chamber fitted with a Babington-type nebulizer. The mass bias was evaluated and corrected with IRMM-184 uranium isotope standard. The determination was performed under normal plasma conditions (Table 1). Concentrations of ^{234}U, ^{235}U and ^{238}U were calculated from the results of isotopic ratios relative to the ^{233}U spike based on the isotope dilution principle.

Table 1
Instrument and data acquisition settings for ICP-QMS measurements

Instrument settings	ICP-QMS
RF power	1200 W
Nebulizer	Babington type
Spray chamber	Glass, double pass
Sample cone	Nickel, 0.8 mm orifice diameter
Skimmer cone	Nickel, 0.4 mm orifice diameter
Sample uptake rate	0.4 ml/min
Argon flow rates	
Plasma gas	16 l/min
Auxiliary gas	1.0 l/min
Carrier gas (nebulizer gas)	1.14–1.18 l/min (optimized daily to highest intensity of $^{238}U^+$)
Data acquisition settings	
Acquisition mode	Isotope ratio
Monitored isotopes	^{233}U, ^{234}U, ^{235}U and ^{238}U
No. of scans	No. of sweeps: 1000
Samples per peak	Points/mass: 3
Dwell time (ms)	50 for ^{234}U; 15 for ^{235}U; 5.0 for ^{238}U and 3.0 for ^{233}U
Total acquired time per sample	390 s (no. of replicates 5)
Integration type	Average

2.2. Chemical and reagents

All commercial chemicals were of analytical-reagent grade and were used without further purification. Nitric and hydrochloric acids were obtained from Kanto Chemicals (Tokyo, Japan). Uranium-233 tracer (92/233/23) was obtained from AEA Technology, UK. The purity of the ^{233}U tracer has been checked and the result showed that the ^{233}U spike did not add any significant quantities of other U isotopes. The natural uranium isotope standard (IRMM-184) was purchased from Institute for Reference Materials and Measurements (Geel, Belgium). Standard solutions of other elements (e.g., U, Th, Fe, Pb) were prepared from Multi-element Plasma Standards (SPEX Industries). The anion-exchange resin used in this study was AG 1-X8 (100-200 mesh, Bio-Rad). The resin was pre-treated according to the procedure described by Muramastu et al. [22]. The certified reference material employed for the study of elution profiles of U and Fe on AG 1-X8 resin was IAEA-368 (ocean sediment from Mururoa Atoll). The TEVA resin (100–150 μm, 2 ml column) was purchased from Eichrom Technologies Inc.

2.3. Analytical procedure

An aliquot of 1 g dried sediment was weighed out, and spiked with ^{233}U (10 ng) as yield monitor. Uranium was leached from the sediment samples using 8 M HNO_3 at 180 °C for at least 4 h. The warm supernatant (leachate) was filtered through a glass-fiber filter. The filtrates were heated on a hotplate until a thick wet paste was obtained. The wet paste was dissolved by adding concentrate HNO_3 while warming on the plate. The sample solution was adjusted to the acidity of 8 M HNO_3 by adding de-ionized water to a volume of 10 ml. After loading on the AG 1 × 8 anion-exchange column (10 cm × 1.0 cm, i.d.), the column was washed with 8 M HNO_3 (40 ml) and 10 M HCl (40 ml) to remove cationic matrices and Th. Finally, U was eluted from the column with 0. 1 M HCl (50 ml). The U fraction (0.1 M HCl) obtained from the AG 1-X8 column was further purified with the Eichrom TEVA resin using a procedure described by Tagami and Uchida [15]. In brief, the U fraction 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 the TEVA column (2 ml), which was pre-treated with 10 ml of 0.1 M HNO_3 followed by 10 ml 6 M HCl. The column was washed with 20 ml of 6 M HCl, and finally, U was eluted with 20 ml of 1 M HCl. The eluate was evaporated to dryness and the residue was dissolved in 5 ml of 4% HNO_3 solution. The solution was diluted to an appropriate concentration for ICP-QMS measurements. The whole procedure is summarized in Fig. 1. To avoid any cross contamination, no columns were re-used; for all the samples, the separation and purification was done with newly prepared columns.

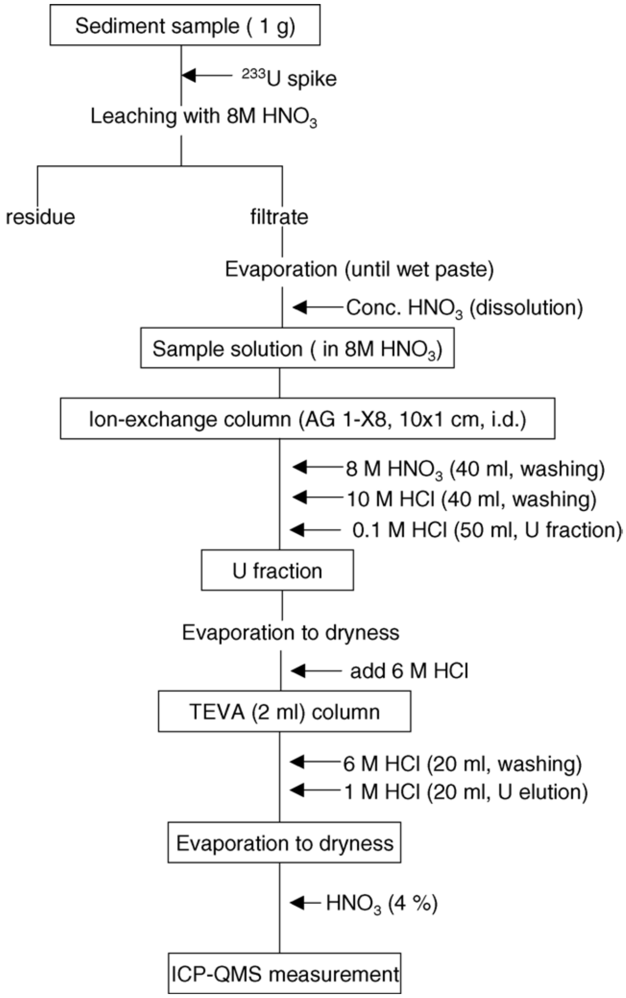

Fig. 1. Analytical procedure for the determination of U isotopes in sediments by ion-exchange and extraction chromatography combined with ICP-QMS.

3. Results and discussion

3.1. *Separation and purification of U from sample matrix*

Sediment samples have a complicated matrix that makes it difficult to obtain accurate U isotope ratios with ICP-MS. Many chromatographic methods have been reported for the separation and purification of U. Among them, UTEVA and TRU resins have been widely used in the literature [21,23–28]. Recently, Tagami and Uchida [15] described a simple procedure for the separation and pre-concentration of U based on the Eichrom TEVA extraction chromatography because the U adsorbability by TEVA resin is higher than that of UTEVA resin in hydrochloric acid media [24]. Using HCl with different concentrations for the washing and elution U from TEVA resin, they demonstrated that U could be separated from many other elements (Li, Be, Na, Mg, Al, K, Ca, Mn, Ni, Rb, Sr, Y, Cs, Ba, Pb, Th, Co, Cu, Zn, Fe, Cd, and Sn) with a high U recovery (ca. 90%), resulting in a very “clean” final solution for accurate U isotope ratio analysis with ICP-QMS. However, when this method was applied to the soil samples, it was found that the high content of Fe in soil samples severely affected U extraction behavior by TEVA resin, resulting in a drop of U recovery.

In the present work, we adopted a two-stage chromatographic separation and purification approach. First, we used an anion-exchange column, AG 1-X8, to separate U from sample matrix, in particular this meant from the large amount of Fe in the sediment. In addition, U was also separated from Th. This is essential for the determination of $^{234}U/^{238}U$ isotope ratio by ICP-MS, as $^{232}ThH_2{}^+$ may interfere with ^{234}U determination, considering the fact that the mass concentration of ^{234}U is extremely low in the environmental samples due to its low atom abundance. As shown in Fig. 2, Fe in the IAEA-368 ocean sediment reference material was removed from the AG 1-X8 column during the sample loading and the 8 M HNO_3 washing step. Th was eluted with the following washing using 10 M HCl. Finally, U was eluted with 0.1 M HCl. The obtained U fraction from AG 1-X8 was purified by the second TEVA extraction chromatography as described in detail in Section 2. It is noted that, although a loss of U (ca. 20–30%) took place during the removal of Fe in AG 1-X8 column, the overall yield of U was 60 ± 5% in the whole procedure. Luo et al. [21] have presented a highly

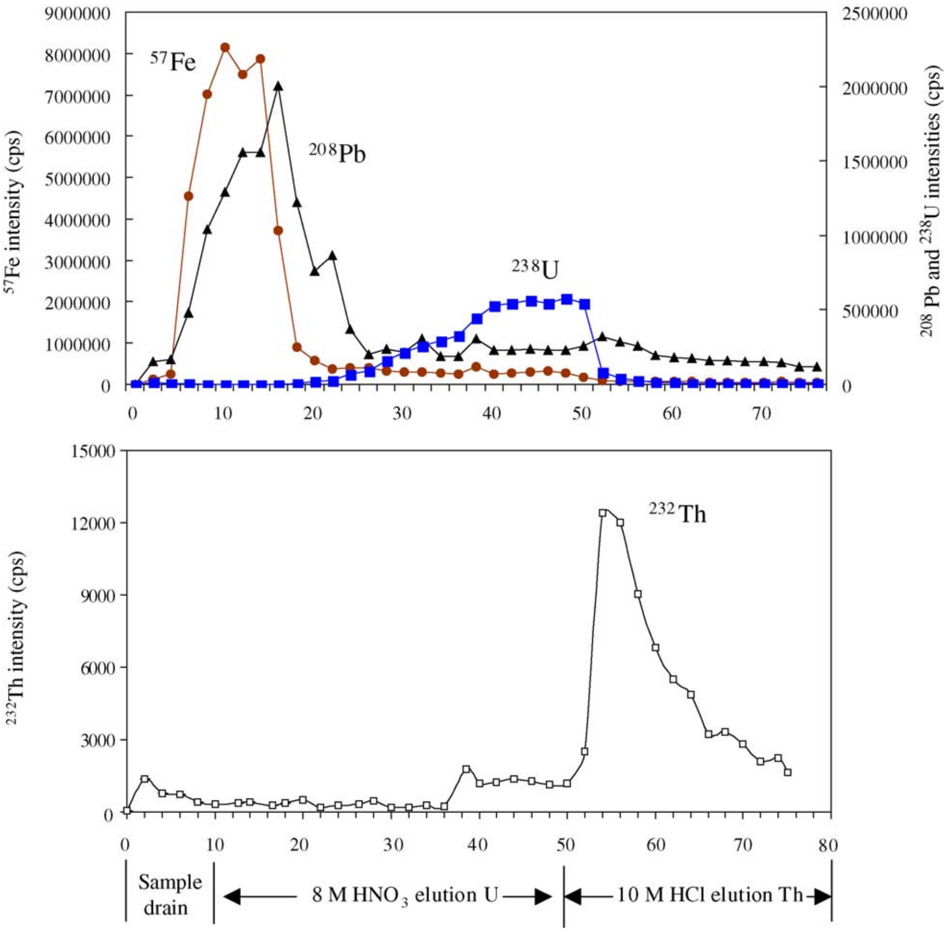

Fig. 2. Elution profile of separation of U, Fe and Pb from sediment matrix (IAEA 368, ocean sediment) with anion-exchange chromatography (AG 1 × 8).

effective chemical procedure using TRU resin for the separation of U and Th from rock matrix for high precision U and Th isotope ratio analysis using MC-ICP-MS. Considering the limited sensitivity of ICP-QMS, it is desirable to have the purity of U fraction in the sample solution as high as possible to avoid any possible matrix effect for the determination of ^{234}U isotope due to its extremely low abundance. Therefore, for the samples with complicated matrix, such as sediments, we chose the combination of anion-exchange (AG 1-X8) chromatography and extraction chromatography (TEVA) which we think provides an ideal U separation and purification method for accurate isotope ratio measurement with ICP-QMS.

3.2. Accurate determination of U isotope ratios with ICP-QMS

In order to achieve accurate and precise isotopic ratio results, the ICP-QMS instrumental parameters were optimized to maximize ion sensitivity with high stability, that is, lowest relative standard deviation (R.S.D.). This was achieved by the measurement of U isotope ratios using IRMM-184 U standard solution before routine measurement. In quadrupole ICP-MS, the $(m-1)$ overlap of $^{235}\mathrm{U}^+$ on $^{234}\mathrm{U}^+$ has been a concern for the accurate determination of $^{234}\mathrm{U}^+$ signal. To evaluate the magnitude of this overlap, the abundance sensitivity was estimated with IRMM-184 U standard solution to be 8×10^{-7} at m/z 236 and 1×10^{-6} at m/z 237. Considering the fact that the ratio of $^{235}\mathrm{U}/^{234}\mathrm{U}$ is only 137.58 for U of natural origin, the influence of $^{235}\mathrm{U}^+$ on $^{234}\mathrm{U}^+$ signal is negligible, and no correction is needed for the $(m-1)$ overlap of $^{235}\mathrm{U}^+$ on $^{234}\mathrm{U}^+$ in our instrument. The possible interference of $^{232}\mathrm{ThH_2}^+$ polyatomic ion on $^{234}\mathrm{U}^+$ determination was investigated using a Th standard solution at a concentration of 100 ng/ml. It was observed that the $^{232}\mathrm{ThH_2}^+/^{232}\mathrm{Th}^+$ signal ratio was 7.6×10^{-6} under the measurement conditions. In addition, in this work, the instrumental interferences on the accurate determination of U isotopic ratios, which includes the detector dead time and the mass bias of the ion current, were carefully evaluated and corrected.

3.2.1. Detector dead time

Detector dead time is normally defined as the time before and after each pulse registered by the detector used but which cannot be recorded. This means that the actual count rate is higher than that observed. In addition, such an effect is more significant for isotopes of high abundance, for example, the ^{238}U. We estimated the detector dead time (τ) experimentally through measurements of ^{235}U/^{238}U ratio for natural U solution (IRMM-184). The corrected ^{235}U/^{238}U was calculated using values of τ which produce a plateau of constant ^{235}U/^{238}U which is independent of ^{238}U signal intensity. The dead time was corrected by the following equation [29]:

$$I_{\text{corr}} = \frac{I_{\text{meas}}}{1 - I_{\text{meas}} \times \tau}$$

where I_{corr} is the corrected intensity (cps), I_{meas} is the measured intensity (cps) and τ is the detector dead time (s). We obtained a τ value of 27 ns for our HP-4500 ICP-QMS. This value is slightly larger than the value of 9.09 ns estimated using Pb isotopes for HP-4500 [30], but smaller than that of Elan-500 ICP-QMS (i.e., 80 ns) using U isotopes as reported by Ketterer et al. [19]. In contrast to the sector field ICP-MS, the detector dead time was mass-dependent, and normally a larger detector dead time will be established for the heavier ion [31]. Since the detector dead time is not a fixed parameter but varies with the aging of the detector, it is recommended to make the correction at regular intervals.

3.2.2. Mass bias correction

Besides the effect of detector dead time, the appropriate correction of mass bias also significantly affects the accuracy of isotope ratio results. The mass bias is a measure of the deviation between the measured and true isotopic ratios. It is well known that different transmission efficiencies and the space charge effect are the two most important potential sources of mass bias [32]. The observed isotope ratios can be distorted due to the counteraction of these two types of mass bias. Therefore, in order to perform accurate isotope ratio measurement, the isotope ratios have to be corrected for mass bias. In this work, we used the U isotope standard solution (IRMM-184, 10 ng/ml in 1 M HNO_3) which consists of naturally occurring U (^{235}U/^{238}U = 0.00726) to determine the mass bias coefficient (MBC). Mass bias correction was applied using the following equation:

$$\text{MBC} = \left[\frac{(^{235}\text{U}/^{238}\text{U})_{\text{meas}}}{(^{235}\text{U}/^{238}\text{U})_{\text{true}}}\right]^{1/3}$$

The mass bias coefficient determined for the standard solution on the ^{235}U/^{238}U ratio ranged from 0.9949 to 1.015, indicating a maximum bias around 4.6 or 1.5% per amu in our instrument. The mass bias coefficient may vary within a single determination sequence at fixed instrumental parameters, therefore, when the analysis for lake sediment samples was done, the U isotope standard solution was analysed before and after the real sample. The obtained U isotope ratios of IRMM-184 (before and after the real sample) were averaged and used to calculate the mass bias coefficient for the real sample to obtain reliable isotope ratio results.

3.2.3. Effect of dwell time

When the analysis is performed with the isotope ratio mode, a high-speed scanning rate (1000 times per mass) should be selected for HP 4500 ICP-QMS. A suitable dwell time, the length of time spent by the instrument in measuring the signal at each mass during repetitive scans, is essential for precision of isotope ratio measurement. A shorter dwell time can result in more sweeps per replication. As Furuta [33] indicated, a very short dwell time, e.g., <0.1 ms, however, resulted in distorted mass spectra and consequently in low precision.

An experiment has been conducted with the isotopically-known U solution (IRMM-184, 10 ng/ml) in order to optimize the dwell time ranging from 0.3 to 21 ms in terms of the precision of ^{235}U/^{238}U isotopic ratios. The dwell time of ^{235}U was set as three times that of ^{238}U due to the difference of relative abundance. As shown in Fig. 3A, the R.S.D.% decreases with

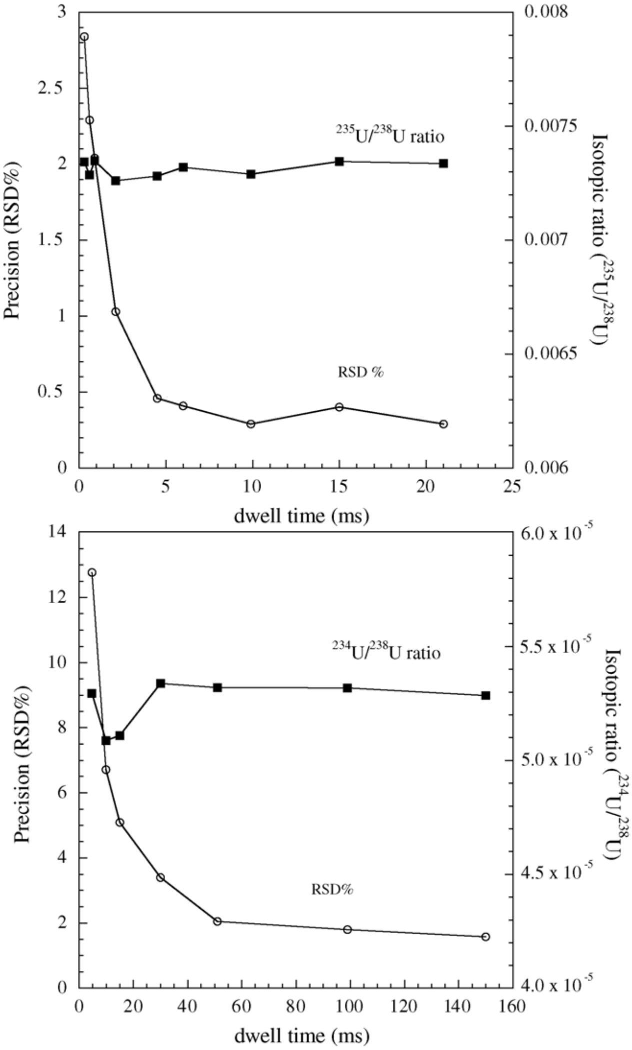

Fig. 3. Effect of dwell time (10 ng/ml IRMM-184 U standard solution; dwell time ^{235}U set as three times that for ^{238}U) on the precision (R.S.D.%) of isotopic ratio of ^{235}U/^{238}U (A), and on the precision (R.S.D.%) of isotopic ratio of ^{234}U/^{238}U (B).

increasing dwell time. For instance, the R.S.D.% was 2.8% for a dwell time of 0.3 ms, and 0.3% for 21 ms. The isotopic ratio ^{235}U/^{238}U showed fluctuations when short dwell times (0.3–2 ms) were employed, but was relatively constant above 4.5 ms. Therefore, in our measurements, the dwell times were set at 5 and 15 ms for ^{238}U and ^{235}U, respectively. After the optimization of dwell times for ^{238}U and ^{235}U measurements, the effect of the dwell time of ^{234}U on the precision of ^{234}U/^{238}U ratio analysis was investigated by fixing the dwell time of ^{238}U as 5 ms while changing the dwell time of ^{234}U. As shown in Fig. 3B, the precision was improved by increasing ^{234}U dwell time; with a dwell time of 50 ms, the R.S.D.% could be lowered to 2%. Further increase of dwell time did not show significant improvement for the precision. In general, a longer dwell time could increase the total counts for the low abundance isotope ^{234}U, thus reducing the error due to counting statistics. However, as quadrupole mass spectrometry is a sequential measurement device for different isotopes, a longer dwell time would increase the total measurement time for the isotope ratio analysis, hence increasing the error resulting from the fluctuation of plasma conditions which offsets the precision improvement provided by better counting statistics. We also noted that the ^{234}U/^{238}U ratios showed a fluctuation when shorter dwell times (5–30 ms) were set for ^{234}U isotope. A relatively constant ^{234}U/^{238}U ratio was obtained when a dwell time longer than 30 ms was employed. Therefore, as a compromise between good precision and longer measurement time, a dwell time of 50 ms was selected for ^{234}U isotope. Under the optimized dwell time settings for U isotope ratio analysis, the total measurement time was about 7 min with five replicates.

3.2.4. Accuracy and precision of U isotope ratio measurement

Fig. 4 shows the effect of U concentrations on the precision (R.S.D.%, based on a short-term measurement, $n = 3$) of U isotope ratio analysis. The concentrations of U investigated were 2, 5, 10, 40, 70 and 100 ng/ml. For ^{235}U/^{238}U ratio, the R.S.D.% was less than 1% in all the investigated U concentrations. Better R.S.D.% lower than 0.5% could be obtained when U concentration was increased to 10 ng/ml. For ^{234}U/^{238}U ratio, due to the low abundance of ^{234}U isotope (0.00524%), the R.S.D.% obtained was generally higher than that of ^{235}U/^{238}U. Nevertheless, with a U concentration of 10 ng/ml, a R.S.D.% lower than 3% (Fig. 4B) could be obtained for ^{234}U/^{238}U ratio in our ICP-QMS.

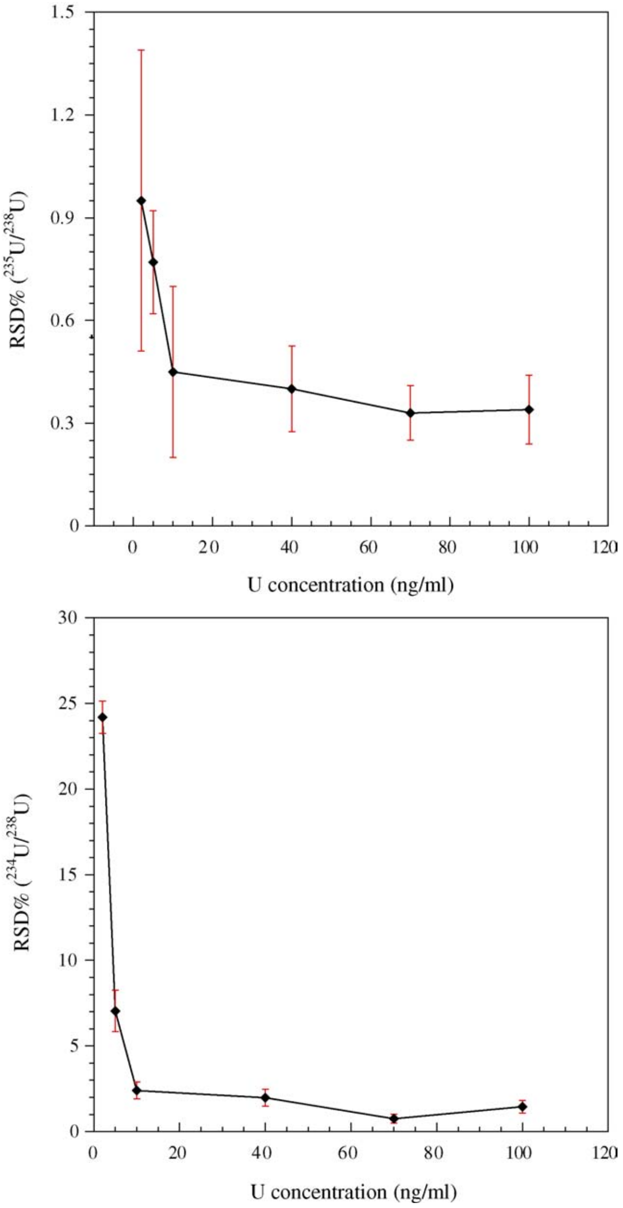

Fig. 4. Relative standard deviation (R.S.D.%) for isotopic ratios of ^{235}U/^{238}U (A) and ^{234}U/^{238}U (B) in IRMM-184 measured by ICP-QMS plotted against U concentrations.

The accuracy and precision of U isotope ratio analysis for the long-term measurement ($n = 10$) was estimated using IRMM-184 U isotope standard solution (with natural U isotopic composition) at U concentration of 10 ng/ml. The results are summarized in Fig. 5. We saw that good accuracy and precision were obtained for U isotope ratios. For ^{235}U/^{238}U ratio, the mean of 10 measurements was 0.00725; compared to the certified value of 0.00726, the accuracy was −0.14% with a precision (R.S.D.%) of 0.3. For ^{234}U/^{238}U activity ratio (a unity activity ratio corresponding to a ^{234}U/^{238}U atom ratio of 0.00005472), 10 measurements resulted in a mean of 0.962, compared to the certified value of 0.965, the accuracy was −0.3% with a precision (R.S.D.%) of 1.7.

In studies on environmental radioactivity and geochemistry of U, $AR_{234/238}$, the ^{234}U/^{238}U activity ratio, is usually used to differentiate secular equilibrium U and disequilibrium U [34]. For example, Zielinski et al. [12] found that U milling-affected groundwaters near a former uranium mill site in Canon City, Colorado had an $AR_{234/238}$ of 1.0 ± 0.1, while “background” water had significantly higher $AR_{234/238}$ values of 1.3–1.5. In addition, it has been reported that $AR_{234/238}$ values in soil typically ranged from 0.5 to 1.2 [13]. Therefore,

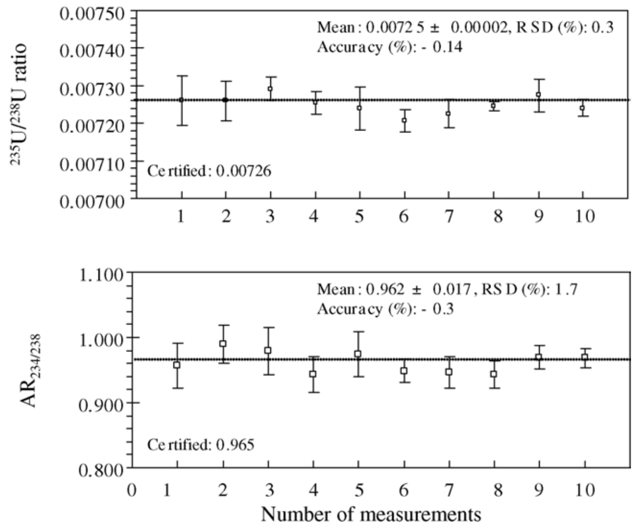

Fig. 5. The accuracy and precision of isotopic ratios of ^{235}U/^{238}U and ^{234}U/^{238}U obtained from IRMM-184 with a long-term measurement using ICP-QMS.

with a precision less than 2% for ^{234}U/^{238}U ratio, it is sufficient to differentiate the origin of U of natural weathering and U in a closed environment with secular equilibrium.

3.3. Application to lake sediments

The developed analytical procedure was validated by measuring the U isotopes in an ocean sediment reference material (IAEA-368). The results are summarized in Table 2. As can be seen in the table, a good agreement between the obtained results and the certified values was obtained for the activities of ^{234}U, ^{235}U and ^{238}U. The ^{235}U/^{238}U ratio indicated a natural U origin for this sediment reference material.

As an important application, we investigated the isotopic compositions of U in a sediment core collected from Obuchi Lake, Japan. The basic physical and chemical characteristics of Obuchi Lake can be found in the literature [35]. The lake is bordered by several nuclear fuel-related facilities: a uranium enrichment facility, a low-level radioactive waste disposal facility, and a storage center for vitrified high-level waste. These facilities have been operating since 1992. Currently, a spent fuel reprocessing facility is under construction. From the viewpoint of environmental radioactivity monitoring, it is important to determine the U concentration and isotopic compositions in this lake.

Table 2
Determination of uranium isotopes in ocean sediment reference material (IAEA-368)

Sample	IAEA-368 (this work)	IAEA-368 (certified)
^{235}U/^{238}U ($\times 10^{-3}$)	7.24 ± 0.03	–
$AR_{235/238}$	0.0460 ± 0.0002	–
^{234}U/^{238}U ($\times 10^{-5}$)	6.13 ± 0.21	–
$AR_{234/238}$	1.12 ± 0.04	–
^{238}U (μg/g)	2.54 ± 0.16	2.49 (2.01–2.65)[a]
^{238}U (mBq/g)	31.6 ± 1.9	31 (25–33)[a]
^{234}U (mBq/g)	35.4 ± 2.1	35.7 (21.5–44.8)[a]
^{235}U (mBq/g)	1.5 ± 0.1	1.9 (1.6–2.6)[a]

AR stands for the activity ratio.

[a] Values shown inside the parentheses are the range with 95% confidence interval. The uncertainty is 1σ.

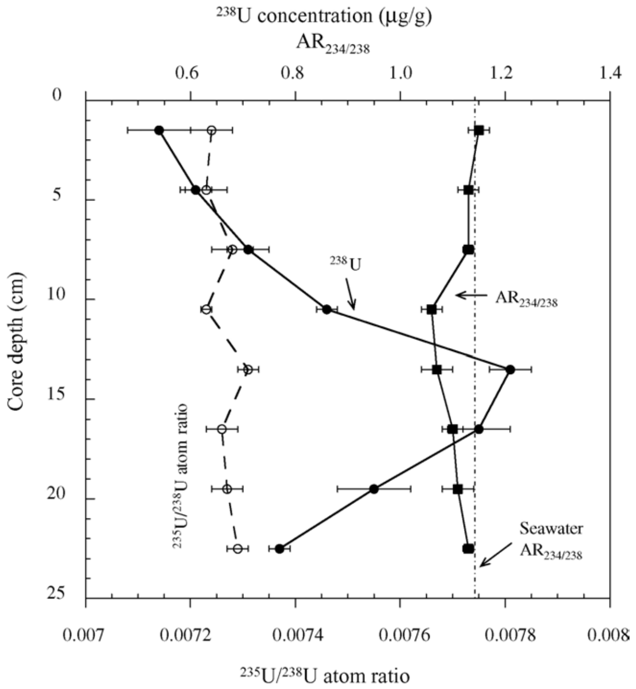

Fig. 6. Sediment core depth profiles of ^{238}U concentration, ^{234}U/^{238}U activity ratio ($AR_{234/238}$) and ^{235}U/^{238}U atom ratios.

After the JCO criticality accident in 1999 in Japan, a survey on the U isotopes in soils indicated that the acid-extractable U showed high ^{235}U/^{238}U ratios. These ratios which were for U released due to the accident were in contrast to U in the silicate fractions which had the natural isotope ratio [36]. Therefore, in order to evaluate the possible environmental impact on the Obuchi Lake area due to the operation of nuclear facilities, this work focused on the acid-extractable fraction in the investigated sediment samples. The concentrations of ^{238}U and the U isotopic ratios of ^{235}U/^{238}U and ^{234}U/^{238}U (activity ratio, $AR_{234/238}$) are shown in Fig. 6. The ^{235}U/^{238}U atom ratios were almost constant throughout every layer in this sediment core, ranging from 0.00723 (±0.00001) to 0.00731 (±0.00002) with the precision (R.S.D.%) of 0.2–0.5%. The mean of ^{235}U/^{238}U ratios in this sediment core was 0.00726, which was nearly the same as that of natural U. The concentrations of ^{238}U observed in Obuchi sediment samples ranged from 0.5 to 1.2 μg/g, which were comparable to the U values for common Japanese soils (0.17–4.6 μg/g) [37]. Therefore, both the ^{235}U/^{238}U atom ratio and the ^{238}U concentration data indicated that the operation of U enrichment facility and radioactive waste disposal facility since 1992 did not result in observable U release into the nearby Obuchi Lake. The activity ratios of ^{234}U/^{238}U ($AR_{234/238}$) in Obuchi Lake sediments ranged from 1.06 to 1.15. The obtained precision (R.S.D.%) for $AR_{234/238}$ determination ranged from 0.9 to 2.8%. The mean of $AR_{234/238}$ in this sediment core was 1.11 ± 0.03, which was slightly higher than the $AR_{234/238}$ value of 1.0 under the secular equilibrium condition. Obuchi Lake is a brackish lake; its salinity of the lake is 10–15 psu in the surface layer and 20–30 psu in the bottom layer due to the inflow of seawater from the Pacific Ocean by tidal action [35]. The modern seawater value of $AR_{234/238}$ is 1.14 ± 0.03 [38], and the $AR_{234/238}$ value for rocks in central Japan has been reported to be 0.99 [39]. Therefore, the observed $AR_{234/238}$ values in the acid-extractable fraction of sediments could be attributed to mixing of seawater U supplied by the tidal action and the lithogenic U of sands in the sediments.

4. Conclusions

In this work, an analytical procedure based on quadrupole ICP-MS was developed. Separation and purification of U from sample matrix was achieved with two-stage anion-exchange and TEVA extraction chromatography. For sediment samples, the whole procedure offered a U yield of 60%. The accurate and precise analysis of U isotope ratios ($^{235}U/^{238}U$ atom ratio and $^{234}U/^{238}U$ activity ratio) was achieved with ICP-QMS by controlling and correcting the factors that affect the accuracy and precision, such as the detector dead time, dwell time and mass bias. With natural U, a precision lower than 0.5% R.S.D. for $^{235}U/^{238}U$ atom ratio and lower than 2.0% R.S.D. for $^{234}U/^{238}U$ activity ratio was obtained with only 90 ng uranium. This precision was comparable or better than that of conventional alpha spectrometry, which normally needs 10 μg uranium to achieve a similar precision with a counting time of tens of hours. The method was successfully applied to the investigation of U isotope compositions in sediment samples, and we expected it to be applicable to other environmental samples.

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