

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 ($^{235}\text{U}/^{238}\text{U}$ atom ratio and $^{234}\text{U}/^{238}\text{U}$ 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 $^{234}\text{U}/^{238}\text{U}$ 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 $^{235}\text{U}/^{238}\text{U}$ atom ratio and lower than 2.0% R.S.D. for $^{234}\text{U}/^{238}\text{U}$ 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.

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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 $^{235}\text{U}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ 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 $^{235}\text{U}/^{238}\text{U}$ 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 $^{235}\text{U}/^{238}\text{U}$ ratio. The $^{234}\text{U}/^{238}\text{U}$ may vary due to the natural causes. It has been found that the $^{234}\text{U}/^{238}\text{U}$ activity ratio ($\text{AR}_{234/238}$) varies considerably in many water, soil, sediment and uranium ore samples of different geographical origins [6–10]. The $\text{AR}_{234/238}$ 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 $^{235}\text{U}/^{238}\text{U}$ 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 $^{234}\text{U}/^{238}\text{U}$ 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 $^{234}\text{U}/^{238}\text{U}$ 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 $^{232}\text{ThH}_2^+$ 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 ($^{235}\text{U}/^{238}\text{U}$ and $\text{AR}_{234/238}$) 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 \times 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 $\text{AR}_{234/238}$ 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

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 $^{238}\text{U}^+$)
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

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.

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

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