

Determination of ultra-low $^{236}\text{U}/^{238}\text{U}$ isotope ratios by tandem quadrupole ICP-MS/MS

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Masaharu Tanimizu,^{*a} Naoki Sugiyama,^b Emmanuel Ponzevera^c and Germain Bayon^c

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Isotope ratios of $^{236}\text{U}/^{238}\text{U}$ were measured at levels below 10^{-7} by single collector ICPMS with a tandem quadrupole mass separation mechanism. Peak tailing of the prominent $^{238}\text{U}^+$ ion beam on the $^{236}\text{U}^+$ peak was reduced to the level of $\sim 10^{-10}$ by use of two quadrupole mass filters. The $^{235}\text{UH}^+$ interference on $^{236}\text{U}^+$ was efficiently reduced to a UH^+/U^+ ratio of 1×10^{-8} by an ion–molecule reaction between UH^+ and O_2 in a collision/reaction cell placed between the two quadrupoles. The resultant detection limit for $^{236}\text{U}/^{238}\text{U}$ measurement was better than those reported by any other ICPMS study. The $^{236}\text{U}/^{238}\text{U}$ ratios, measured as $^{236}\text{U}^{16}\text{O}^+ / ^{238}\text{U}^{16}\text{O}^+$, were determined in the range 10^{-9} to 10^{-7} without correction for spectral interference. Accurate measurements of $^{236}\text{U}/^{238}\text{U}$ to as low as 1×10^{-10} are projected.

Introduction

Inductively coupled plasma mass spectrometry (ICPMS) is a powerful analytical technique for the determination of trace elements and widely used in diverse scientific and industrial fields. ICPMS is known to suffer from background interference induced by (polyatomic) ions originating from Ar, entrained air, the solvent and/or matrix and, as a result, collision/reaction cell technology was developed to overcome this problem. Ions produced in the ICP source are introduced into a cell filled with a specific gas to induce reactions between the interfering or the analyte ions and gaseous molecules. For instance, $^{40}\text{Ar}^+$ can be neutralized by reaction with NH_3 , thereby reducing the interference at mass number 40 and permitting interference-free detection of $^{40}\text{Ca}^+$. Similarly, trace $^{75}\text{As}^+$ can be reacted with N_2O to produce $^{75}\text{As}^{16}\text{O}^+$ in order to avoid the background spectrum of $^{40}\text{Ar}^{35}\text{Cl}^+$ (e.g. Bandura *et al.*¹). Hence, collision/reaction cell ICPMS can extend the scope of ICPMS measurement, but

careful examination of mass spectra of any new species formed from reactions between co-existing elements and gaseous molecules is still required.

A newly designed quadrupole ICPMS with an octapole collision/reaction cell has been developed to reduce background spectra based on the original concept of triple quadrupole ICPMS.² Briefly, analyte ions are separated from co-existing ions by the first quadrupole mass filter, according to their mass number, before ion–molecule reactions in the cell occur. This first separation step enables the minimization of any undesirable ion–molecule reactions induced by matrix elements. Target ions transmitted through the first mass filter are subsequently screened by the second quadrupole along with the ions produced in the cell. For example, ultra-trace amounts of ^{31}P and ^{32}S can be separated from polyatomic ions originating from organic matrices at the first mass filter and detected as $^{31}\text{P}^{16}\text{O}^+$ and $^{32}\text{S}^{16}\text{O}^+$ ions after chemical reaction with O_2 gas in the cell.^{3,4} An almost interference-free background spectrum was achieved and undesirable new reactions in the cell were strictly controlled.

Another important feature of tandem quadrupole MS is the very sharp peak shapes recorded for the ions. Peak tailing from prominent isotopes can compromise measurement of adjacent masses and this characteristic is expressed as the abundance sensitivity. The tandem quadrupole ICPMS has an abundance sensitivity of better than 10^{-7} ,⁵ which is equivalent to those of a typical sector-field ICPMS operated with energy filters or under high resolution modes⁶ and a quadrupole ICPMS with a collision cell.⁷ The former mechanism filters ions with low energy and perturbed trajectories, which are produced by the collision with residual gas molecules and/or at the ICP interface region. The latter thermalizes kinetic energy of ions derived from ICP by intentional collisions with gas molecules in the collision/reaction cell through damping of their initial kinetic energy distribution. In this study, a tandem quadrupole ICPMS with an octapole collision/reaction cell (ICP-MS/MS) was applied to the determination of $^{236}\text{U}/^{238}\text{U}$ isotope ratios. The $^{236}\text{U}/^{238}\text{U}$ ratio is used as an environmental indicator to evaluate radioactive

^aKochi Institute for Core Sample Research, Japan Agency for Marine–Earth Science and Technology, Monobe-Otsu 200, Nankoku, Kochi 783-8502, Japan. E-mail: tanimizum@jamstec.go.jp; Fax: +81-88-878-2192

^bAgilent Technologies International Japan, Ltd., 9-1 Takauracho, Hachioji, Tokyo 192-0033, Japan

^cIFREMER, Unité de Recherche Géosciences Marines, F-29280 Plouzané, France

contamination, e.g. global ^{236}U fallout as a result of nuclear testing ($1\text{--}2 \times 10^{-9}$)⁸ and nuclear plant accidents (10^{-3} to 10^{-7}).⁹ For high abundance sensitivity ICPMS, spectral interference from $^{235}\text{UH}^+$ on $^{236}\text{U}^+$ remains the main obstacle for accurate measurement of ^{236}U ; therefore, the introduction of O_2 into the cell was performed to convert U^+ species to UO^+ with the aim of eliminating hydride based interference through an ion–molecule reaction involving oxygen transfer.

Experimental

Instrumentation and samples

A tandem quadrupole ICPMS featuring an octapole collision/reaction cell situated between two quadrupole mass filters (first, Q1; second, Q2) (Agilent 8800, Agilent Technologies, Tokyo, Japan) was used in this study. Oxygen was introduced into the cell at a flow rate of 0.1 mL min^{-1} . Uranium standard solutions and samples were introduced into the ICP under dry plasma conditions with a desolvating nebulizer (ARIDUS, Cetac Technologies, Omaha, NE, USA). Instrumental parameters are shown in Table 1. Typical measurement sensitivity for $^{238}\text{U}^+$ was 1.3×10^9 cps for $1 \mu\text{g g}^{-1} \text{ U}$.

Two uranium containing solutions were prepared from multielement standard solutions, XSTC-331 and XSTC-829 (SPEX CertiPrep, Metuchen, NJ, USA). XSTC-829 is a custom made solution containing $10 \mu\text{g g}^{-1} \text{ Na, K, Ca, and U}$ in 1% nitric acid, and $10 \mu\text{g g}^{-1} \text{ Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Cs, Ba, Tl, Pb, Bi, Th, and U}$ for XSTC-331 in 1% nitric acid. These solutions were suitably diluted with high purity concentrated HNO_3 (AA-100; Tama Chemical, Kawasaki, Japan) and Milli-Q water (Millipore, Billerica, MA, USA) to $500 \text{ ng g}^{-1} \text{ U}$ for U isotopic analyses. A seawater sample was collected from the western Pacific Ocean (Tosa-Bay, southwest Japan) and about 3 kg of the water,

buffered at pH 5.6, were filtered with an Empore 47 mm chelating disk (3M, St. Paul, MN, USA) for desalting and U pre-concentration. Uranium was then eluted from the disk with 3 M HNO_3 and, following evaporation to dryness, the U concentration was adjusted to approximately $1 \mu\text{g g}^{-1} \text{ U}$ with 1% HNO_3 . Finally to correct for mass discrimination of $^{236}\text{U}/^{238}\text{U}$ ratios affected at the ICP interface region, a $10 \mu\text{g g}^{-1} \text{ Tl}$ solution dissolved from a Tl isotopic reference material (NIST-SRM 997; $^{205}\text{Tl}/^{203}\text{Tl} = 2.3871$),¹⁰ was spiked into each $500 \text{ ng g}^{-1} \text{ U}$ solution to give a concentration of $100 \text{ ng g}^{-1} \text{ Tl}$.

Results and discussion

Oxygen atom transfer reaction

The ICP is an efficient ionization source for production of monovalent positively charged ions, but metal hydrides are also readily produced, especially under wet plasma conditions. Under such conditions, the rate of formation of the hydride, estimated from the $^{238}\text{UH}^+/^{238}\text{U}^+$ ratio is usually $\sim 10^{-5}$ (ref. 11) and, as such, this hydride reaction would hamper the determination of low abundance $^{236}\text{U}^+$ due to interference by $^{235}\text{UH}^+$. The extent of formation of such hydrides can be reduced by operating the ICP under dry plasma conditions, where a value of *ca.* 5×10^{-6} is typical.⁶ Dry plasma conditions permit measurements of $^{236}\text{U}/^{238}\text{U}$ by sector-field ICPMS down to *ca.* 4×10^{-8} ($^{235}\text{U}/^{238}\text{U} = 0.00725$). Thermal ionization MS (TIMS) or accelerator MS (AMS) is generally preferred for measurement of lower $^{236}\text{U}/^{238}\text{U}$ values (as compiled by Boulyga and Heumann⁹).

In this study, we have overcome the difficulty of ultra-low $^{236}\text{U}/^{238}\text{U}$ isotope ratio measurement by using collision/reaction cell technology. In essence, we have reduced the UH^+/U^+ ratio by reacting UH^+ with O_2 gas and examining the products of the ion–molecule reactions *via* the mass spectra. A uranium solution (XSTC-331) containing $1 \mu\text{g g}^{-1} \text{ U}$ in 1% HNO_3 was introduced to the ICP under wet plasma conditions to enhance the hydride species (a typical UH^+/U^+ ratio of $\sim 5 \times 10^{-5}$), and the Q1 quadrupole mass filter was set to mass number 239 to transmit $^{238}\text{UH}^+$ ions. Then the product ions from the ion–molecule reaction with O_2 in the cell were detected by scanning the Q2 quadrupole mass filter. The resultant U^+ species detected were UO^+ , UH^+ , U^+ and UOH^+ , with UO^+ being the dominant species. Almost all of the UH^+ ions introduced to the cell were transformed to the ion species listed above and their relative proportions were estimated as $\text{UO}^+ : \text{UH}^+ : \text{U}^+ : \text{UOH}^+ = 0.70 : 0.23 : 0.06 : 0.01$ (Fig. 1). This means that only $\sim 1\%$ of UH^+ ions are transformed to UOH^+ ions by simple oxidation in the cell. In contrast, U^+ ions can be readily converted to UO^+ ions with O_2 gas.¹² This partitioning of ion–molecule reactions with O_2 gas between U^+ and UH^+ ($\text{U}^+ + \text{O}_2 \rightarrow \text{UO}^+ + \text{O}$; $\text{UH}^+ + \text{O}_2 \rightarrow \text{UO}^+ + \text{OH}$) effectively reduces the contribution of the $^{235}\text{UH}^+$ interference on $^{236}\text{U}^+$ by about two orders of magnitude as a result of detecting the $^{235}\text{UOH}^+$ species at the mass number 252 for $^{236}\text{UO}^+$. Thus evaluation of ultra-low $^{236}\text{U}/^{238}\text{U}$ isotope ratios becomes possible from measurement of $^{236}\text{U}^{16}\text{O}^+/^{238}\text{U}^{16}\text{O}^+$.

Accurate determination of $^{236}\text{U}/^{238}\text{U}$ isotope ratios *via* $^{236}\text{UO}^+/^{238}\text{UO}^+$ measurement is difficult by conventional collision/reaction cell ICPMS due to the existence of stable oxygen

Table 1 Operating conditions for ICP-MS/MS. Hard extraction mode and s-lens ion optics assembly were utilized to enhance ion transmission and parameters were optimized to reduce the UH^+/U^+ ratio rather than signal intensity

ICP	RF	1600 W
	Sampling depth	6 mm
	Dilution gas flow rate	0.40 L min^{-1} (Ar)
	Option gas flow rate	0.07 L min^{-1} (10% N_2 in Ar)
Extraction lens	Extraction 1	-200 V
	Extraction 2	-10 V
	Omega	19 V
	Omega bias	-120 V
	Q1 bias	-5 V
Cell	Cell gas	O_2
	Cell gas flow rate	0.1 mL min^{-1}
	Octp bias	-40 V
	KED	15 V
Quadrupole	Mass resolution	0.7 u (at 10% height)
	Q2 pressure	$5.6 \times 10^{-4} \text{ Pa}$
Sample introduction	ARIDUS with One-Neb	
	Carrier gas flow rate	0.90 L min^{-1}
	Solution uptake	0.09 mL min^{-1} (pumped)
	Sweep Ar gas	2.0 L min^{-1}

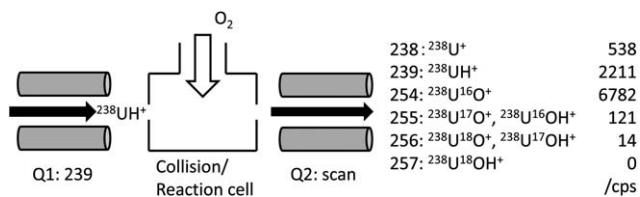


Fig. 1 Schematic of ICP-MS/MS and ion-molecule reactions for UH^+ and O_2 . Target ions are separated from matrix ions by Q1 and enter the collision/reaction cell where oxide ions are produced. Q2 is then set to measure desired U species.

isotopes (^{16}O (99.76%), ^{17}O (0.04%), ^{18}O (0.20%)), among which $^{235}\text{U}^{17}\text{O}^+$ interferes with $^{236}\text{U}^{16}\text{O}^+$ in the mass spectrum. With the ICP-MS/MS, the Q1 quadrupole is set to transmit $^{236}\text{U}^+$ (and not $^{235}\text{U}^+$) to the cell, thereby preventing the production of $^{235}\text{U}^{17}\text{O}^+$ (Fig. 2). When Q1 is set to $^{235}\text{U}^+$, $^{235}\text{U}^{17}\text{O}^+$ ions are filtered by Q2 which is set to pass $^{235}\text{U}^{16}\text{O}^+$ to the detector. Efficient separation of $^{236}\text{U}^{16}\text{O}^+$ and $^{235}\text{U}^{17}\text{O}^+$ is, therefore, achieved in this instrument without the need for high-resolution separation technology. Thus, the Q1 and Q2 mass number selections can function in such a way that a specific U^+ isotope ($^{235}\text{U}^+$, $^{236}\text{U}^+$, and $^{238}\text{U}^+$) reacts with pure $^{16}\text{O}_2$ to produce specific U^{16}O^+ species ($^{235}\text{U}^{16}\text{O}^+$, $^{236}\text{U}^{16}\text{O}^+$, and $^{238}\text{U}^{16}\text{O}^+$). A synchronized scan that transmits U mass numbers 235, 236 and 238 at Q1 and those of U + 16 u at Q2 transforms U^+ isotopes to U^{16}O^+ isotopes without alteration or degradation of the original isotopic abundances by ^{17}O and ^{18}O impurities. All isotopes referred hereafter are ^{16}O -based ions unless otherwise specified. Under the specified operating conditions (Table 1), a $^{238}\text{UH}^+ / ^{238}\text{U}^+$ ratio of $<1 \times 10^{-8}$ was obtained for a 500 ng g^{-1} U solution (XSTC-331) (actual measurement, $^{238}\text{U}^{16}\text{OH}^+ / ^{238}\text{U}^{16}\text{O}^+$) in 1% HNO_3 . This result implies that $^{236}\text{U} / ^{238}\text{U}$ measurements of 1×10^{-10} are feasible using the present instrumentation.

Abundance sensitivity

Abundance sensitivity of the instrument was estimated for measurement of U isotopes using a 500 ng g^{-1} U solution

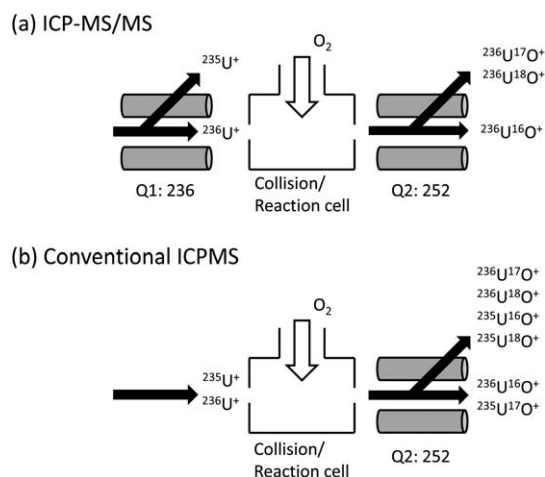


Fig. 2 Separation mechanism for $^{235}\text{U}^{17}\text{O}^+$ and $^{236}\text{U}^{16}\text{O}^+$ in (a) ICP-MS/MS, compared to (b) conventional ICPMS with a collision/reaction cell.

(XSTC-331) in 1% HNO_3 . The instrument was programmed to undertake synchronized scanning of Q1 and Q2 and to pass mass number $Q1 + 16 \text{ u}$ at Q2 by scanning Q1 in 0.05 u steps ranging from 234.5 to 239.5 u (250.5 to 255.5 u for Q2). The resultant abundance sensitivity, estimated from the ion signal at mass number 237 against $^{238}\text{U}^+$ in the mass spectrum (Fig. 3), was $<1 \times 10^{-10}$, which is better than previous values obtained for several sector-field ICPMS instruments⁶ and is almost comparable to that of TIMS.⁹ It should be noted that this value seems to be overestimated, because only background noise ($<0.01 \text{ cps}$) was observed at mass number 237 against $3 \times 10^8 \text{ cps}$ for mass number 238. Even this result, which was estimated from mass number 239 instead of 237 (Fig. 3), was affected by interference from $^{238}\text{UH}^+$ (*ca.* 1 cps); however, the value of 3×10^{-9} is still better than those obtained from other comparable studies.⁶ Peak tailing of $^{238}\text{U}^+$ was obviously not detected around 236 u, one mass unit removed from mass number 237, and the value for $^{236}\text{U} / ^{238}\text{U}$ ratio of $\sim 1 \times 10^{-10}$ was expected to be evaluated without correction for peak tailing.

$^{236}\text{U} / ^{238}\text{U}$ isotope ratio determination

The $^{236}\text{U} / ^{238}\text{U}$ ratio for a 500 ng g^{-1} U solution (XSTC-829) containing 100 ng g^{-1} Tl (NIST-SRM 997) was determined under dry plasma conditions. The resultant $^{236}\text{U} / ^{238}\text{U}$ isotope ratio after Tl-normalization was $(2.00 \pm 0.13) \times 10^{-7}$ (2se uncertainty). The sample consumption was $0.5 \mu\text{g U}$ for a measurement time of 10 minutes ($n = 9$). This value is consistent with the value of $(2.20 \pm 0.20) \times 10^{-7}$ measured with a sector-type ICP mass spectrometer equipped with an RPQ energy filter (Neptune, Thermo Instruments, Bremen, Germany) at IFREMER, France, under dry plasma conditions and using a standard-sample bracketing technique with IRMM-184 as a U isotopic reference (1.24×10^{-7}).¹³

The ability to measure ultra-low $^{236}\text{U} / ^{238}\text{U}$ ratios was tested with a natural U sample extracted from seawater. Sakaguchi *et al.*¹⁴ recently used AMS for measurement of $^{236}\text{U} / ^{238}\text{U}$ ratios for seawater samples collected in the western Pacific region ($\sim 1.5 \times 10^{-9}$) and showed that values reflected global nuclear fallout. Using the same analytical protocol mentioned above, we obtained a value of $(2.3 \pm 2.8) \times 10^{-9}$ for a 500 ng g^{-1} U solution

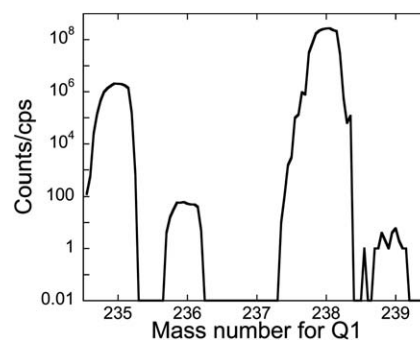


Fig. 3 Mass spectrum in the U mass range for synchronized scanning of Q1 and Q2 ($Q2 = Q1 + 16 \text{ u}$) with 0.05 u step changes. The measured signal intensity for $^{238}\text{U}^{16}\text{O}^+$ was $3 \times 10^8 \text{ cps}$ for a 500 ng g^{-1} XSTC-331 solution (1 s integration time for each step).

Table 2 Measured, Tl-normalized and expected $^{236}\text{U}/^{238}\text{U}$ isotope ratios for three synthetic mixtures, with XSTC-829 and seawater sample (two end members). Uncertainty limits were estimated from two standard error (2se) of replicate analysis ($n = 9$). Integration times for masses 203, 205, 234, 235, 236, 238, and 239 were 0.5, 0.5, 5, 1, 30, 0.1 and 10 s, respectively. Tl-normalized $^{236}\text{U}/^{238}\text{U}$ ratios were calculated from measured $^{236}\text{U}/^{238}\text{U}$ and $^{203}\text{Tl}/^{205}\text{Tl}$ ratios by a linear correction law: $(^{236}\text{U}/^{238}\text{U})_{\text{Tl-normalized}} / (^{236}\text{U}/^{238}\text{U})_{\text{measured}} = (^{203}\text{Tl}/^{205}\text{Tl})_{\text{reference}} / (^{203}\text{Tl}/^{205}\text{Tl})_{\text{measured}}$. The reference $^{203}\text{Tl}/^{205}\text{Tl}$ ratio of NIST-SRM 997 is 0.41892 ± 0.00018 .¹⁰ Precision of the $^{203}\text{Tl}/^{205}\text{Tl}$ ratio measured for each sample was typically ± 0.002 (2se, $n = 9$), and the uncertainty was propagated for the Tl-normalized $^{236}\text{U}/^{238}\text{U}$ ratios. The certification letter from SPEX indicates that U content of XSTC-829 originates from NIST 3164

	Expected $^{236}\text{U}/^{238}\text{U}$ ratio	Measured $^{236}\text{U}/^{238}\text{U}$ ratio	Tl-normalized $^{236}\text{U}/^{238}\text{U}$ ratio
XSTC-829	$2.20 \pm 0.20 \times 10^{-7}$	$1.92 \pm 0.12 \times 10^{-7}$	$2.00 \pm 0.13 \times 10^{-7}$
Synthetic mixture 1 (1 : 1)	$1.07 \pm 0.10 \times 10^{-7}$	$8.41 \pm 0.89 \times 10^{-8}$	$8.77 \pm 0.93 \times 10^{-8}$
Synthetic mixture 2 (1 : 10)	$2.00 \pm 0.22 \times 10^{-8}$	$1.67 \pm 0.99 \times 10^{-8}$	$1.73 \pm 1.03 \times 10^{-8}$
Synthetic mixture 3 (1 : 40)	$6.1 \pm 0.9 \times 10^{-9}$	$5.7 \pm 2.9 \times 10^{-9}$	$5.9 \pm 3.0 \times 10^{-9}$
Seawater	$1.5 \pm 0.5 \times 10^{-9}$	$2.2 \pm 2.7 \times 10^{-9}$	$2.3 \pm 2.8 \times 10^{-9}$

prepared from treated seawater. Most of this measurement uncertainty is attributed to acquisition of very low $^{236}\text{U}^+$ ion signals (less than 1 cps for $^{236}\text{U}^+$ versus 5×10^8 cps for $^{238}\text{U}^+$).

A set of three synthetic U isotope mixtures was next prepared using the XSTC-829 solution and the seawater sample to validate measurement capability. The two end-member 500 ng g^{-1} U solutions were mixed in various proportions (approximately 1 : 1, 1 : 10 and 1 : 40 in volume). Their $^{236}\text{U}/^{238}\text{U}$ isotope ratios are reported in Table 2 and Fig. 4 as well as those of the two end members, XSTC-829 and the seawater sample. A consistent 1 : 1 correlation between the expected and the Tl-normalized $^{236}\text{U}/^{238}\text{U}$ ratios can be recognized almost within their uncertainties, although there is a slight tendency of having lower Tl-normalized $^{236}\text{U}/^{238}\text{U}$ values compared to expected ones (Fig. 4). This may be due to the preferential scattering losses of lighter isotopes than heavy ones in the ion–molecule reaction process in the cell as observed previously,¹⁵ because Tl-normalization of $^{236}\text{U}/^{238}\text{U}$ ratios is aimed at correcting the mass discrimination effect at the ICP interface region, not in the cell. There are only a few studies concerning the isotopic discrimination process in the collision/reaction cells, and further investigations will be necessary for a wider isotopic application of this ion–molecule reaction technique with high precision. Of particular note is the fact that the results display a 1 : 1 correlation without any mass spectral correction, indicating that the potential $^{235}\text{UH}^+$ interference and $^{238}\text{U}^+$ peak tailing are negligible for $^{236}\text{U}/^{238}\text{U}$

measurement in this range. Isotopic measurement precision is simply controlled by counting statistics for the $^{236}\text{U}^+$ ion and signal stability associated with sample introduction.

Conclusion

Tandem quadrupole ICPMS with collision/reaction cell technology permits the measurement of ultra-low $^{236}\text{U}/^{238}\text{U}$ isotope ratios in the range 10^{-9} to 10^{-7} due to the high abundance sensitivity and favored ion–molecule reactions between U^+/UH^+ and O_2 . The limit of detection for ^{236}U in this study is equivalent to ca. 1×10^{-15} g. This rapid and simple analytical technique can be applied to various environmental samples for the monitoring of radioactive contamination arising from nuclear waste. The efficient reduction of hydride species with O_2 in the reaction cell could potentially be applied to other analytes, including radionuclides such as trace ^{239}Pu , in high-matrix environmental samples.

Counting statistics for the $^{236}\text{U}^+$ ion currently limit the measurement of $^{236}\text{U}/^{238}\text{U}$ ratios to the 10^{-9} range; however, this value is still an order of magnitude better than the detection limit of 1×10^{-8} ,⁶ by sector-field ICPMS. It is projected that accurate measurement of $^{236}\text{U}/^{238}\text{U}$ at the 10^{-10} level is possible without spectral interference correction, thus achieving comparable analytical performance to that of TIMS (2×10^{-10}).¹⁶

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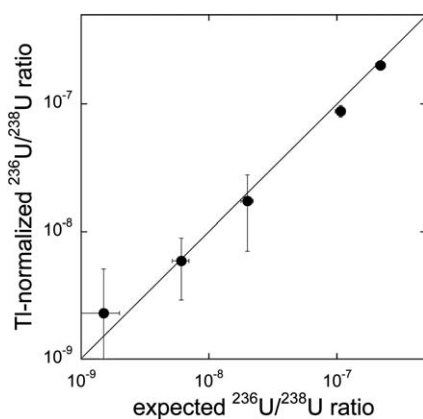


Fig. 4 Tl-normalized and expected $^{236}\text{U}/^{238}\text{U}$ ratios for three synthetic isotopic mixtures, with those of XSTC-829 and seawater.

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