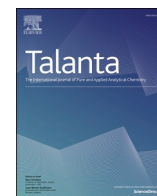




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Determination of ultra-low ^{236}U in environment samples using ICP-MS/MS measurement and chemical separation

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ABSTRACT

^{236}U in the environment mainly originates from human nuclear activities. Based on the unique properties of uranium, ^{236}U can be used as a powerful tracer for investigation of oceanographic and environmental processes. This requires sensitive measurement of ^{236}U in various environmental samples. Due to the ultra-low radioactive level of ^{236}U in the environment, its measurement is only possible by mass spectrometry. Because of the low atomic ratio of $^{236}\text{U}/^{235}\text{U}$ down to 10^{-7} – 10^{-5} in the environment, the interferences of $^{235}\text{U}^{1}\text{H}^{+}$ and peak tailings of ^{235}U and ^{238}U are critical challenges in the measurement of ^{236}U by ICP-MS. This work developed a sensitive ICP-MS/MS method for measurement of ultra-low ^{236}U by employing reaction cell technique and sequential quadrupole mass separators. By using $0.6\text{ mL min}^{-1}\text{ CO}_2$ - 7 mL min^{-1} helium as collision/reaction gas to convert U^{+} and UH^{+} to UO^{+} , the interferences of UH^{+} ($\text{UOH}^{+}/\text{UO}^{+}$ ratio) were significantly reduced to less than 2.4×10^{-7} . A minimum detectable $^{236}\text{U}/^{238}\text{U}$ ratio of 3.0×10^{-10} was achieved, which is one order of magnitude better than reported values. By using collision focusing with helium in the reaction cell and APEX sample introduction system, the measurement sensitivity for ^{236}U ($^{236}\text{UO}^{+}$) was improved to $7.5 \times 10^6\text{ cps ppb}^{-1}$. In combination with an effective chemical separation of uranium from sample matrix and interferences using total borate fusion following extraction chromatography with UTEVA resin, a detection limit of $7.2 \times 10^{-16}\text{ g g}^{-1}$ for ^{236}U was achieved. The developed method was verified by analysis of certified reference materials and by comparison with AMS measurement method. Soil samples collected from Northwest China were successfully analyzed. $^{236}\text{U}/^{238}\text{U}$ ratios down to 9×10^{-10} were measured in these samples, and the sources of ^{236}U in different sites were discussed.

1. Introduction

^{236}U is a long-lived radionuclide (2.35×10^7 years), which is mainly produced through $^{238}\text{U}(\text{n}, 3\text{n})^{236}\text{U}$ and $^{235}\text{U}(\text{n}, \gamma)^{236}\text{U}$ reactions. The dominant source of ^{236}U in the environment is the human nuclear activities. About 900 kg ^{236}U had been released to the environment from atmospheric nuclear weapons testings in 1945–1980 and the spent nuclear fuel reprocessing plants have discharged about 100 kg ^{236}U to the seas, compared to only 35 kg naturally occurred ^{236}U in the earth [1–3].

The release from the nuclear accidents is another source of ^{236}U in the surface reservoir. An enhanced level of ^{236}U has been observed in the soil contaminated by the Chernobyl accident [4]. Unlike most of metals, uranium is a conservative element in the ocean because of the formation of soluble complex of uranium with carbonate, and the anthropogenic ^{236}U deposited and discharged to the seas is also conservative. Due to the specific source term and environmental behavior, anthropogenic ^{236}U becomes a powerful tracer for oceanographic and environmental process studies. In combination with other radionuclides, it was also used as a

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fingerprint for identification of sources of radioactive pollution and investigation of transport pathways of air pollution and seawater circulation, as well as for nuclear safety assessment by detection of possible releases and leakage from nuclear facilities [4–7].

In order to carry out ^{236}U tracing application, a reliable and effective analytical method is necessary to accurately determine ultra-low ^{236}U in environmental samples. Due to the very low specific radioactivity of ^{236}U (2.4 MBq g^{-1}) and the similar energies of α -particles of ^{236}U (4.45–4.49 MeV) with that of ^{235}U (4.37–4.60 MeV), it is therefore impossible to measure the environmental ^{236}U using α spectrometry, even in the contaminated environmental samples.

Mass spectrometry, such as thermal ionization mass spectrometry (TIMS) and secondary ion mass spectrometry (SIMS), has been used for ^{236}U measurement in samples with relatively high ^{236}U content, e.g. hot particles [8,9], while accelerator mass spectrometry (AMS) is a more sensitive method for ^{236}U measurement, and the only technique for measurement of ^{236}U in samples with $^{236}\text{U}/^{238}\text{U}$ atomic ratio less than 1×10^{-10} [2,3,10]. However, only a few AMS instruments are available for the measurement of ^{236}U , highly limiting the application of ^{236}U in the environmental researches. Inductively coupled plasma mass spectrometry (ICP-MS) is becoming the most commonly used technique for the measurement of long-lived radionuclides including ^{236}U because of its high sensitivity and low capital costs [11–14]. However, the peak tailings of ^{235}U and ^{238}U ions and polyatomic ions (e.g. $^{235}\text{U}^+\text{H}^+$) highly hinder its application in the measurement of ^{236}U in environmental samples [11,15,16]. ICP-MS/MS equipped with two quadrupole mass separators and an octopole collision/reaction cell (CRC) has shown good potential to improve the abundance sensitivity to less than 10^{-10} , and to strongly suppress $^{235}\text{U}^+\text{H}^+$ ion signal [12,17,18]. By using O_2 as reaction gas, a UOH^+/UO^+ ratio of 4×10^{-7} was reported recently [18], which makes this technique suitable to measure ^{236}U in Fukushima accident contaminated environmental samples with $^{236}\text{U}/^{238}\text{U}$ atomic ratios down to 7×10^{-9} . However, the application of O_2 as reaction gas also significantly reduces the measurement sensitivity of ^{236}U to $(4\text{--}6) \times 10^5 \text{ cps ppb}^{-1}$ even using Apex introduction system, which makes it insufficient to analyze environmental samples from the areas without direct exposure to contaminations.

Determination of ultra-trace amount of ^{236}U in environmental solid samples (e.g. soil, sediment) requires release of uranium from solid samples prior to separation of uranium from sample matrix and interferences. Alkaline and borate fusion [19,20], acid digestion [5] and total acid dissolution [21] are often used for decomposition of soil and sediment sample to release uranium into solution. Our preliminary experiment showed that the melted sample was often spilled over the crucible during alkaline fusion using NaOH as fusion flux reagent, causing a loss of the sample and increasing the risk of cross-contamination. Acid leaching can only release ^{236}U adsorbed on the surface of sample grains, but is not valid for uranium present in refractory hot particles and inside the mineral crystal. It was reported that less than 60% of the total uranium in soil and sediment can be leached out by acid leaching using HNO_3 or *aqua regia*, and the leaching rates of uranium vary with the acids and sample types, temperature and leaching time [22,23]. The partial release of ^{236}U and naturally occurred uranium also make the yield monitoring with isotope tracer (e.g. ^{233}U) invalid. Consequently, the ^{236}U concentrations in the samples might be underestimated and the measured $^{236}\text{U}/^{238}\text{U}$ ratios might vary with the experiment conditions. Total dissolution using HF mixed with other acids (e.g. HNO_3) can release all uranium, but the process is time consuming and uses large amount of highly toxic and volatile HF, which is not practically applicable for handling large size sample ($>3 \text{ g}$) [24, 25]. Borate fusion has been shown to be the most advantageous for decomposition of silicate and oxide-rich samples as it can completely decompose these types of samples and relatively rapid [20].

This work aims to develop a sensitive and powerful ICP-MS analytical method to determine ultra-low ^{236}U with $^{236}\text{U}/^{238}\text{U}$ atomic ratios down to 10^{-9} in ordinary environmental samples. The effort focused on

further eliminating interference of ^{235}U hydride, and improving measurement sensitivity of ^{236}U by selecting an effective collision/reaction gas and employing high efficiency sample introduction system. Meanwhile, method for chemical separation of uranium from soil and sediment samples has been improved to obtain reliable analytical results of ^{236}U concentration and $^{236}\text{U}/^{238}\text{U}$ atomic ratio in ordinary environmental samples without direct radioactive contamination.

2. Materials and methods

Instrumentation and setup. A triple quadrupole ICP-MS (Agilent 8800, Agilent Technologies, Japan) equipped with an octopole CRC and two quadrupole mass separators, was used for the measurement of ^{236}U . The first quadrupole (Q1) acts as an ion-guide to select the target ions (e.g. $^{236}\text{U}^+$). The reaction gas reacts with the entered ions for eliminating the interfering ions by forming new ions in the CRC. The newly formed ions in the CRC enter the second quadrupole (Q2) and the target ions are selected for measurement in the following detector.

The instrument was tuned using a ^{238}U (1.0 ng mL^{-1} natural uranium) standard solution to obtain optimal conditions. The procedure blanks, standards and the final purified samples were prepared in $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ for measurement. In^{3+} (InCl_3 , 1.0 ng mL^{-1}) solution was used as an internal standard. The samples and internal standard solutions were introduced using an Apex Ω desolvating nebulizer (Elemental Scientific, Omaha, NE, USA) at 0.4 mL min^{-1} or MicroMist Micro Flow 200 nebulizer at 0.5 mL min^{-1} (for measurement of ^{238}U concentration). Pt skimmer cone, s-lens and hot plasma were used in the measurement of uranium isotopes. Three gas lines (He, 9.86% O_2 in He, and CO_2 gas, 99.999% purities) connected to the CRC were used in this work. The optimized parameters of the ICP-MS operation for the measurement of ^{236}U are shown in Table 1.

Reagents and standards. A standard solution of ^{238}U from Spex CertiPrep (Metuchen, NJ, USA), a ^{233}U tracer solution from the Institute for Reference Materials and Measurements (IRMM-051) at Geel, Belgium, and an extraction chromatographic resin UTEVA from Triskem International, France were purchased. HNO_3 and HCl (analytical reagent) were purified by distillation using DST-4000 (Saville, US). All other reagents used in the experiment were of analytical-reagent grade and prepared using deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$). Standard reference materials IAEA-375 (soil) and IAEA-385 (sediment) were

Table 1

Instrumental settings of ICP-MS/MS (Agilent 8800) for measurement of ^{236}U using double quadrupole mass separators and $\text{CO}_2\text{--He}$ ($0.6 \text{ mL min}^{-1}\text{--}7 \text{ mL min}^{-1}$) as reaction gas.

Conditions	Parameter	Value
ICP	RF Power	1530 W
	RF Matching	1.91 V
	Sampling Depth	3.4 mm
	Carries Gas	1.17 L min^{-1}
	Temperature of Spray Chamber	7°C
Lens	Extraction Lens 1	-169.0 V
	Extraction Lens 2	-0.5 V
	Omega Bias	-152 V
	Omega Lens	20.3 V
	Q1 Entrance	2.5 V
	Q1 Exit	3.5 V
	CRC focus	5.1 V
	CRC Entrance	-100 V
	CRC Exit	-109 V
	Deflect	5.0 V
	Plate Bias	-120 V
	Q1 Bias	-0.5 V
	Q1 Prefilter Bias	-3.7 V
CRC	Q1 Postfilter Bias	-14.7 V
	Octopole Bias	-8.1 V
	Octopole RF	187 V
	Energy Discrimination	-20 V

purchased from IAEA. Seven surface soil samples (0–5 cm) were collected using a stainless-steel cylinder sampler from undisturbed sites in Northwest China in 2018. The samples were sealed in plastic bags and transported to laboratory for analysis. The sampling sites are shown in Fig. 1.

Separation of uranium from samples. The soil samples were firstly air-dried, and stones (>3 mm in diameter) and vegetation roots were manually removed. The samples were then dried at 100 °C in an oven to a constant weight, weighed, ground and sieved through an 80-mesh sieve. About 3 g sample was weighed in a 30 mL high purity graphite crucible and mixed with lithium metaborate and sodium persulfate in a mass ratio of 1:0.5:0.2. About 30 pg ^{233}U solution was spiked into the sample as a tracer for monitoring chemical yield of uranium during chemical separation. The sample in crucible was fused in a muffle oven using a temperature increasing protocol of 100 °C for 30 min to remove water/moisture, 650 °C for 1 h to remove organic substances and finally 1000 °C for 30 min to completely decompose and fuse sample. After cooling to room temperature, the sample as glassy bead was dissolved with a mixed acid solution of 4 mol L⁻¹ HNO₃ and 6 mol L⁻¹ HCl by heating on a hot plate at 200 °C. One gram of polyethylene glycol was added as a flocculant into the sample solution to remove silicic acid as precipitate. The precipitate was separated from the supernatant by centrifugation at 4500 rpm for 5 min, and washed with 0.1 mol L⁻¹ HNO₃ twice. The washes were combined with the supernatant for the following purification of uranium.

Ammonia solution (25% v/v) was slowly added into the supernatant to adjust pH to 8–9 to co-precipitate uranium with Fe(OH)₃. The precipitate was separated by centrifugation, washed with deionized water, and then dissolved with concentrated HNO₃. The dissolved solution was diluted with H₂O to adjust HNO₃ concentration to 3.0 mol L⁻¹.

The prepared sample solution was loaded onto a UTEVA resin column (2 mL) which was pre-conditioned with 30 mL of 3.0 mol L⁻¹ HNO₃. The UTEVA column was rinsed with 40 mL of 3.0 mol L⁻¹ HNO₃ and 30 mL of 6 mol L⁻¹ HCl to remove matrix elements and thorium. Uranium on the UTEVA column was finally eluted with 30 mL of 0.025 mol L⁻¹ HCl solution, and the eluate was evaporated to dryness at 180 °C on a hotplate. The residue was dissolved and prepared in 3.0 mL of 0.5 mol L⁻¹ HNO₃ solution for measurement of uranium isotopes by ICP-MS.

Measurement of ^{238}U and ^{236}U by ICP-MS. The signal intensities of $^{236}\text{U}^{16}\text{O}^+$, $^{235}\text{U}^{16}\text{O}^+$ and $^{238}\text{U}^{16}\text{O}^+$ in the sample solutions were measured at $m/z = 252$, 251 and 254 (Q2), respectively. The ICP-MS/MS instrument was first tuned for optimal condition (the best sensitivity for $^{238}\text{U}^+$ derived at the moment) using 1.0 ng g⁻¹ uranium solution at no

gas mode (without collision/reaction gases) prior to analysis.

Due to the extremely high concentration of ^{238}U in the final sample solution (>1 µg mL⁻¹), a 0.1 mL aliquot was taken from the sample solution and diluted by a factor of 100–1000 using 0.5 mol L⁻¹ HNO₃ for measurement of ^{238}U to ensure the measured value within the linear correlation range.

Sufficient counts of $^{238}\text{UHO}^+$ are critical to minimize measurement uncertainty of $^{238}\text{UHO}^+ / ^{238}\text{UO}^+$ ratio. However, extremely high ion current of $^{238}\text{UO}^+$ will be harmful to the detector. Thus, the $^{238}\text{U}^{16}\text{O}^{16}\text{H}^+ / ^{238}\text{U}^{16}\text{O}^+$ ratio was calculated indirectly by measurement of $^{238}\text{U}^{16}\text{O}^{16}\text{H}^+ / ^{235}\text{U}^{16}\text{O}^+$ ratio in a uranium standard solution (ST) of high concentration (1.0 µg mL⁻¹) and of $^{238}\text{U}^{16}\text{O}^+ / ^{235}\text{U}^{16}\text{O}^+$ in a diluted uranium standard solution (diluted ST) (1.0 ng mL⁻¹) in the same instrument conditions.

$$\left(\frac{^{238}\text{U}^{16}\text{O}^{16}\text{H}^+}{^{238}\text{UO}^+} \right)_{\text{estimated}} = \left(\frac{^{238}\text{U}^{16}\text{O}^{16}\text{H}^+}{^{235}\text{U}^{16}\text{O}^+} \right)_{\text{ST}} \times \left(\frac{^{235}\text{U}^{16}\text{O}^+}{^{238}\text{U}^{16}\text{O}^+} \right)_{\text{diluted ST}}$$

The contribution of $^{235}\text{U}^{16}\text{O}^{16}\text{H}^+$ to the count rates at $m/z = 252$ ($^{236}\text{U}^{16}\text{O}^+$) was calculated using the estimated $^{238}\text{U}^{16}\text{O}^{16}\text{H}^+ / ^{238}\text{U}^{16}\text{O}^+$ ratio (supposed to be the same as $^{235}\text{U}^{16}\text{O}^{16}\text{H}^+ / ^{235}\text{U}^{16}\text{O}^+$ ratio) and the measured $^{235}\text{U}^{16}\text{O}^+$ intensity in the sample solution. The contribution of $^{235}\text{U}^{16}\text{O}^{16}\text{H}^+$ and the procedure blank were subtracted from the measured count rate at $m/z = 252$ to derive the intensity of net $^{236}\text{U}^{16}\text{O}^+$ signal in the samples.

$$\left(^{236}\text{UO}^+ \right)_{\text{net}} = \left(^{236}\text{UO}^+ \right)_{\text{measured}} - \left(^{235}\text{UO}^+ \right)_{\text{measured}} \times \left(\frac{^{238}\text{U}^{16}\text{O}^{16}\text{H}^+}{^{238}\text{U}^{16}\text{O}^+} \right)_{\text{estimated}} - \left(^{236}\text{UO}^+ \right)_{\text{blank}}$$

The $\left(^{236}\text{UO}^+ / ^{235}\text{UO}^+ \right)_{\text{net}}$ atomic ratios in the samples were calculated using the $\left(^{236}\text{UO}^+ \right)_{\text{net}}$ and $^{235}\text{UO}^+$ ion intensity, and the $^{236}\text{U} / ^{238}\text{U}$ atomic ratios in the samples were calculated as:

$$^{236}\text{U} / ^{238}\text{U} = \left(^{236}\text{UO}^+ \right)_{\text{net}} / \left(\left(\frac{^{238}\text{U}^{16}\text{O}^+}{^{235}\text{U}^{16}\text{O}^+} \right)_{\text{diluted solution}} \times ^{235}\text{UO}^+ \right)$$

The ^{236}U concentration in the sample was calculated using the $^{236}\text{U} / ^{238}\text{U}$ atomic ratios and the ^{238}U concentration in the sample.

For the measurement of $^{236}\text{U}^{16}\text{O}^+$ and $^{238}\text{U}^{16}\text{O}^{16}\text{H}^+$ signals, 3 points per peak, 20 replicates of 500 sweeps, and integration time of 45 s were applied to obtain a better statistic of the count rates of these ions and reasonable measurement uncertainty. For $^{238}\text{U}^{16}\text{O}^+$, $^{235}\text{U}^{16}\text{O}^+$ and $^{233}\text{U}^{16}\text{O}^+$ signals, 3 points, 100 sweeps, 5 replicates, and integration time of 0.5 s, 1 s, 2 s, respectively were applied due to the relatively higher count rates of the corresponding species. For most of the samples, the count rates of $^{236}\text{UO}^+$ were more than 10 cps, which is more than 40

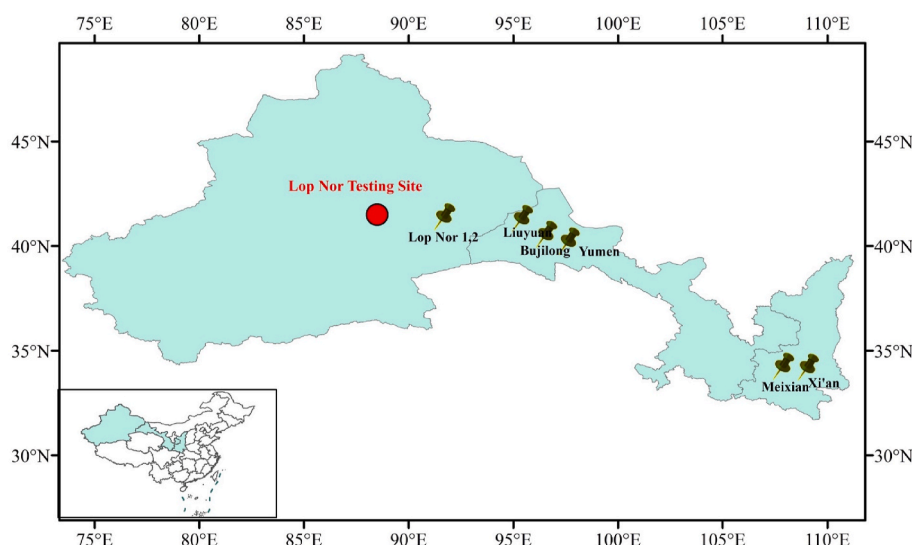


Fig. 1. Sampling sites of surface soil in the northwest China.

times higher than procedure blank (Table 2). The measurement uncertainties for $^{236}\text{U}^{16}\text{O}^+$ in most of the samples were less than 5%.

3. Results and discussion

In the ICP-MS measurement of ^{236}U in the environmental samples, the major challenge is elimination of the interferences of $^{235}\text{UH}^+$ due to its similar m/z as $^{236}\text{U}^+$ ($\Delta m/m = 2.6 \times 10^{-5}$). Based on the feature of sequential mass separators and CRC of the Agilent 8800 ICP-MS, different reaction gases were investigated and optimized for elimination of UH^+ interference and obtaining high measurement sensitivity of uranium. The method for separation of uranium from soil sample was also investigated to improve separation efficiency and to simplify the chemical procedure, in order to develop a sensitive and reliable analytical method for determination of ^{236}U in ordinary environmental samples.

3.1. Separation of uranium from environmental solid samples

The fusion method with lithium metaborate (LiBO_2) and lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) has been reported for decomposition of soil and sediment samples to release transuranic elements [20,26,27]. Here, this method was used to completely decompose the large-size soil and sediment samples (>3 g) for uranium separation. Organic substances cannot be easily decomposed by LiBO_2 fusion. Therefore, ashing with addition of $\text{Na}_2\text{S}_2\text{O}_8$ as an oxidant prior to fusion was applied for decomposition of organic substance. At the conditions of mass ratio of sample: LiBO_2 : $\text{Na}_2\text{S}_2\text{O}_8 = 1:0.5:0.2$ and ashing at 650°C for 1 h followed by fusion at 1000°C for 0.5–1 h, soil and sediment samples could be completely decomposed. After fusion, the melted sample beads were easily dissolved in the mixed acid solution of $4.0\text{ mol L}^{-1}\text{HNO}_3$ and $6.0\text{ mol L}^{-1}\text{HCl}$. The whole procedure for treatment of 3–5 g of sample needs less than 4 h, which is much faster than other methods (>4–24 h) (Table 3). In addition, less than 20 mL mixed acid solution (HNO_3 and HCl) and no HF are required for each gram sample, comparable to or less than the consumption amount of acid in other methods.

An extraction chromatography with UTEVA resin was used to separate uranium from the matrix and other elements based on high affinity of uranium on this resin. The results showed that the uranium recoveries monitored by the spiked ^{233}U were higher than 80%, and no visible amount of salt was observed in the separated uranium sample. The

Table 2

Measurement results of ^{236}U in the procedure blanks, certified reference materials and environmental samples.

Sample	Sample type or sampling site	Sample mass (g)	Chemical yield, ^{233}U (%)	^{236}U ($^{236}\text{U}^{16}\text{O}^+$) count rates (cps)
0.5 mol $\text{L}^{-1}\text{HNO}_3$	Instrument blank	–	–	0.04 ± 0.03
Blank	Procedure blank	–	–	0.24 ± 0.06
IAEA-375, soil	Reference material	0.5–0.6	82.6–87.4	10.5 ± 2.1
IAEA-385, sediment	Reference material	2.9–3.0	85.0–89.3	55.1 ± 7.6
Surface soil-1	Meixian, Shaanxi China	2.9–3.0	83.3–90.1	19.0 ± 4.6
Surface soil-2	Xi'an, Shaanxi, China	2.9–3.0	87.1–91.2	16.3 ± 3.3

Note: The results were presented here as the average of three replicate experiments. The uncertainties were estimated in consideration of measurement of three replicate samples and the contribution from other steps in all analytical procedure, and presented as the expanded uncertainty using a coverage factor of $k = 1$. The $^{236}\text{U}^{16}\text{O}^+$ count rates were measured using ICP-MS/MS in the optimized condition. The contribution from procedure blank was negligible and subtracted; the contribution of $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ from the sample was estimated and subtracted from the measured values in the analyzed samples. All samples were prepared in $3.0\text{ mL } 0.5\text{ mol L}^{-1}\text{HNO}_3$ solution for ICP-MS/MS measurement.

decontamination factors for possible interfering elements which might form polyatomic ions with the similar m/z as ^{236}U (e.g. Hg , Tl , Pb) were higher than 10^5 .

The analytical results of the two standard reference materials IAEA-375 (soil) and IAEA-385 (sediment) (Table 4) showed that the determined ^{238}U concentrations ($2.10 \pm 0.17\text{ }\mu\text{g g}^{-1}$ for IAEA-375, and $2.37 \pm 0.14\text{ }\mu\text{g g}^{-1}$ for IAEA-385) were in good agreement with the certified/recommended values ($1.86\text{ }\mu\text{g g}^{-1}$ with range of 1.66–2.05 for IAEA-375; $2.36\text{ }\mu\text{g g}^{-1}$ for IAEA-385). This indicates that this method is reliable for completely releasing uranium from soil and sediment samples.

3.2. Elimination of interferences

The dominant interferences for the measurement of ^{236}U by ICP-MS are the $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ ions interference, tailings of $^{235}\text{U}^+$ and $^{238}\text{U}^+$ peaks to $^{236}\text{U}^+$, and other polyatomic ions, e.g. $^{196}\text{Hg}^{40}\text{Ar}^+$, $^{205}\text{Tl}^{31}\text{P}^+$, $^{204}\text{Pb}^{32}\text{S}^+$, $^{199}\text{Hg}^{37}\text{Cl}^+$. Collision reaction technique with different gases was investigated to eliminate the interferences of polyatomic ions, especially $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ ions. Our preliminary experiment showed that most of uranium standards contain some extent of ^{236}U , with $^{236}\text{U}/^{238}\text{U}$ atomic ratios higher than 10^{-9} . It is therefore impossible to evaluate the interference of $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ ions by measurement of the uranium standard solution at m/z 236. Alternatively, the signal of $^{238}\text{U}^{16}\text{O}^+\text{H}^+$ was measured for evaluation of $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ elimination based on the similar feature in the formation of UH^+ for ^{235}U and ^{238}U , and no measurable ^{239}Pu in the uranium standard.

Helium as the collision gas. Helium as a commonly used collision gas was investigated. The results (Fig. 2) show that the $^{238}\text{U}^{16}\text{O}^+\text{H}^+/^{238}\text{U}^+$ ratios do not significantly reduce with the injection of helium into the CRC, indicating that helium could not effectively destroy UH^+ ion and reduce the $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ interference. In contrast, the ratio of $^{238}\text{U}^{16}\text{O}^+\text{H}^+/^{238}\text{U}^+$ increased with the flow rates of helium of over 9 mL min^{-1} .

However, it was observed that the intensities of $^{238}\text{U}^+$ signals significantly increased with the increased helium flow rate and reached a maximum of $6.3 \times 10^6\text{ cps}$ for $1\text{ ng mL}^{-1}\text{U}$ at $7\text{ mL min}^{-1}\text{He}$ (Fig. 2). This phenomenon was also reported in the ICP-MS measurement of plutonium isotopes [28]. The enhanced $^{238}\text{U}^+$ ion intensity with the injection of helium in the CRC is due to the ion focusing effect, which reduced the repulsion among the ions by the collision in the CRC [28] and improved the transmission efficiency of ions to the detector. The significantly decreased intensities of U^+ ions with further increasing flow rate of helium above 7 mL min^{-1} might be attributed to the scattering of ions at high flow rate of the injected helium gas, which hindered the transmission of U^+ ions to the Q2 detector. In addition, the energy loss of U^+ ions during elastic collision becomes significant at high flow rate of helium, causing a declined transfer efficiency of U^+ ions due to kinetic energy discrimination at high flow rate of collision gas [29].

It was also observed that the intensities of $^{238}\text{U}^{16}\text{O}^+\text{H}^+$ ($m/z = 254$) signals increased with the increasing flow rate of helium over 6 mL min^{-1} . Meanwhile, the lost U^+ signal was partly compensated by the increased UO^+ signal at the high flow rates of helium, indicating some U^+ ions were converted to UO^+ . A similarly increased trend of $^{238}\text{U}^{16}\text{O}^+\text{H}^+/^{238}\text{U}^{16}\text{O}^+$ ratios with increasing flow rates of helium was also observed at the high flow rates of helium (Fig. 2). This indicates that helium could not eliminate the interferences of UH^+ and UOH^+ , but increase UH^+ and UOH^+ signals at the high flow rates of helium. Nevertheless, these results suggest that helium is useful to improve the analytical sensitivity of ^{236}U due to ion focusing effect in the CRC.

Oxygen (O_2) as the reaction gas. Oxygen as reaction gas has been reported for elimination of $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ ion interference in the measurement of ^{236}U by ICP-MS/MS [12,17,18]. This is based on the assumption that $^{236}\text{U}^+$ and $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ can be converted to $^{236}\text{U}^{16}\text{O}^+$ and $^{235}\text{U}^{16}\text{O}^+$, respectively, by strongly oxidative O_2 in the reaction cell [17]. Our preliminary experiment showed that UH^+ and UOH^+ signals were significantly suppressed, and the UOH^+/UO^+ ratios were significantly reduced when high purity O_2 was injected to the CRC. Meanwhile, the

Table 3

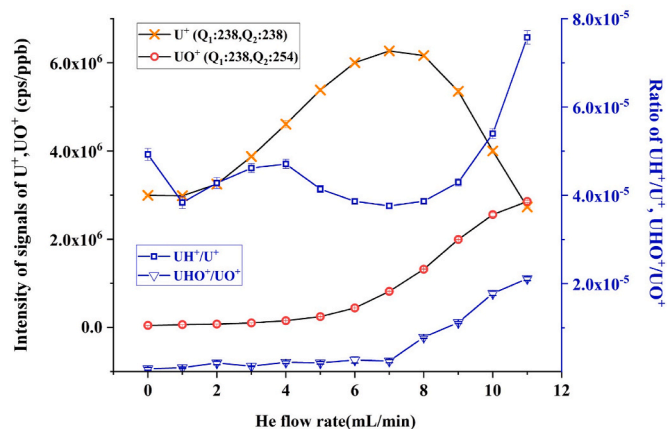
Comparison of performance of the developed method with the reported methods for sample pretreatment to release uranium from solid to solution.

Decomposition Method	Acids used	Sample mass, (g)	Time consumption (hour)	Acids consumption (mL g ⁻¹)	Reference
Acid leaching	16 M HNO ₃	1	16–24	–	[6]
	8 M HNO ₃	1	>4 h	10	[41]
Dissolution	HCl + HNO ₃ + HF	2	>5 h	100	[42]
	HNO ₃ +HF + HClO ₄	3–5	12 h	10	[43]
	HNO ₃ +HF	1	>24	>10	[25]
LiBO ₂ Fusion	4 M HNO ₃ +6 M HCl	3–5	4 h	20	This work

Table 4Analytical results of ²³⁸U and ²³⁶U concentrations and ²³⁶U/²³⁸U atomic ratios in certified reference materials IAEA-375 and IAEA-385 and two samples and comparison with the reported values by other methods.

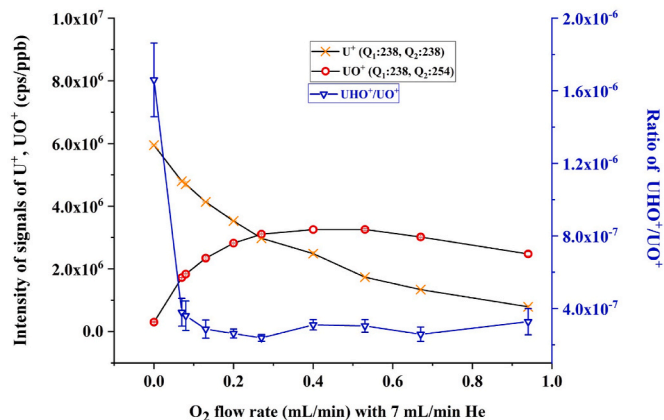
Sample	Sampling region	²³⁸ U concentration (μg g ⁻¹)	²³⁶ U concentration (× 10 ⁶ atoms g ⁻¹)	²³⁶ U/ ²³⁸ U ratio (× 10 ⁻⁹)	Separation Method	Measurement method	Reference
IAEA-375 soil	Farm close to Chernobyl NPP	1.97				α-spectrometry	[44]
		2.26 ± 0.29				α-spectrometry	[45]
			402 ± 24			AMS	[32]
			12000	2450 ± 120		AMS	[34,35]
IAEA-385 sediment	Sea sediment from Irish Sea	2.10 ± 0.17	67.2 ± 12.9	13.1 ± 0.17	LiBO ₂ Fusion	ICP-MS	This work
		2.26–2.42				α-spectrometry	[46]
			≤106	≤20	HNO ₃ +HCl + HF	AMS	[33]
			138 ± 32	26.9 ± 7.1	HNO ₃ leaching	ICP-MS/MS	[17]
Surface soil	Meixian, Shaanxi	–	39.4 ± 3.5	–	HNO ₃ +HF	AMS	[32]
		2.37 ± 0.14	42.6 ± 7.0	5.90 ± 0.43	LiBO ₂ Fusion	AMS	This work
		–	–	6.34 ± 1.01	LiBO ₂ Fusion	ICP-MS	This work
		1.86 ± 0.04	4.80 ± 0.56	0.96 ± 0.07	LiBO ₂ Fusion	AMS	This work
Surface soil	Xi'an, Shaanxi, China	–	–	0.92 ± 0.32	LiBO ₂ Fusion	ICP-MS	This work
		–	–	1.33 ± 0.10	LiBO ₂ Fusion	AMS	This work
		2.56 ± 0.08	9.78 ± 1.34	1.41 ± 0.31	LiBO ₂ Fusion	ICP-MS	This work

*The uncertainties of analytical results in this work are expended uncertainties using a coverage factor of k = 1.

**Fig. 2.** Variation of intensities of ²³⁸U⁺ and ²³⁸U¹⁶O⁺ ions and ²³⁸U¹⁶O¹H⁺/²³⁸U¹⁶O⁺ ratios with the flow rates of helium injected to the CRC. Uranium standard solutions (1.0 ng mL⁻¹ for U⁺ and UO⁺ and 100 ng mL⁻¹ for UH⁺ and UOH⁺ measurement) were used for the experiment.

intensities of U⁺ ions significantly decreased but UO⁺ ions increased with injection of O₂ into the CRC. However, the intensities of the UO⁺ and U⁺ signals were much lower compared to U⁺ ions at no gas mode. This might be attributed to the further conversion of the formed UO⁺ to UO₂⁺ due to the high oxidation capacity of O₂. However, UO₂⁺ ion could not be measured in Agilent 8800 ICP-MS, because it is beyond the measurement scale of the instrument (up to *m/z* = 260). A diluted O₂ gas in helium (9.86% O₂) at low flow rate (0.07–1.0 mL min⁻¹) was therefore applied to reduce further conversion of UO⁺ to UO₂⁺ and to eliminate ²³⁵U¹H⁺ ion interference.

The experimental results (Fig. 3) show that the

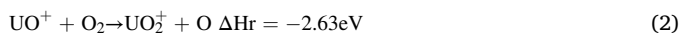
**Fig. 3.** Variation of the intensities of ²³⁸U⁺ and ²³⁸U¹⁶O⁺ ions and ²³⁸U¹⁶O¹H⁺/²³⁸U¹⁶O⁺ ratios with the flow rates of O₂ with 7.0 ml min⁻¹ helium injected to the CRC. Uranium standard solutions (1.0 ng mL⁻¹ for ²³⁸U⁺, ²³⁸U¹⁶O⁺ and 100 ng mL⁻¹ for ²³⁸U¹⁶O¹H⁺-measurement) were used for the experiments.

²³⁸U¹⁶O¹H⁺/²³⁸U¹⁶O⁺ ratios dramatically decreased to less than 4 × 10⁻⁷ when O₂-He gas (0.07–1.0 mL/min) was injected to the CRC, compared to about 8 × 10⁻⁵ for ²³⁸U¹H⁺/²³⁸U⁺ at helium mode. In consideration of the maximal intensity of UO⁺ ions, the flow rate was optimized to be 0.53 ml min⁻¹ O₂/He - 7 ml min⁻¹ He. At this condition, UOH⁺/UO⁺ ratio of 3.1 × 10⁻⁷ and ²³⁸U¹⁶O⁺ sensitivity of 3.6 × 10⁶ cps ppb⁻¹ were achieved using a dissolving nebulizer (Apex Ω). A similar method using only O₂ as reaction gas was recently reported [18], in which a UOH⁺/UO⁺ ratio of 4 × 10⁻⁷ and ²³⁸U¹⁶O⁺ sensitivity of only (4–6) × 10⁵ cps ppb⁻¹ were obtained using Apex Ω system. The UOH⁺/UO⁺ ratio achieved in this work is slightly better than the reported one, but the measurement sensitivity of this method is more than

6 times higher than the reported value. This should be attributed to the collision focusing of helium gas as the collision gas in combination with O₂ as reaction gas in our method, as well as the optimization of other parameters. It was also noted that Apex Ω system did not only improve the measurement sensitivity of ²³⁶U by a factor of about 8, but also suppressed UH⁺ ion formation (Table 5).

As shown in Fig. 3, it is apparent that the U⁺ ion signal decreased dramatically but UO⁺ ion signal increased rapidly with the increased flow rate of O₂. Meanwhile, the increased UO⁺ signal roughly compensated the loss of U⁺ ion signal, indicating the conversion of U⁺ to UO⁺ ion by the diluted O₂ in the CRC. The UO⁺ ion signal slightly decreased at the O₂ flow rate of over 0.53 mL min⁻¹. This might be attributed to the formation of UO₂⁺ at higher flow rate of O₂. Compared with the intensities of U⁺ signals at helium gas mode, the highest intensity of the formed UO⁺ ions at the O₂ flow of 0.53 mL min⁻¹ accounts for only 52% of the total uranium species (Table 6).

The easy formation of UO⁺ and UO₂⁺ with O₂ as reaction gas should be attributed to the exothermic reactions of U⁺ and UO⁺ with O₂ ($\Delta H_r < 0$) [30]:



Due to the formation of UO₂⁺, the analytical sensitivity of ²³⁶U was reduced although uranium hydride interference was effectively suppressed (Table 5). Therefore, the detection limit for ²³⁶U was not sufficiently improved with O₂ as the reaction gas.

CO₂ as the reaction gas. CO₂ as a reaction gas can also effectively converts U⁺ to UO⁺, which allows elimination of the UH⁺ ion interference in the measurement of plutonium isotopes by ICP-MS [28]. Our experimental results using CO₂ as reaction gas (Fig. 4) show that the intensities of U⁺ signals dramatically decreased with the increased flow rates of CO₂. Meanwhile, the intensities of UO⁺ ions significantly increased and reached to the maximum of 7.5×10^6 cps for 1 ng mL⁻¹ U at 0.6 mL min⁻¹ CO₂-7.0 mL min⁻¹ He. The observed intensity under this condition was about 3 times higher than that derived using O₂ as the reaction gas at the correspondingly optimal condition in this work (Table 5). The intensity of UO⁺ ions is also over one order of magnitude higher than the reported sensitivity of UO⁺ in the pure CO₂ or O₂ mode on the same instrument system [18], suggesting a significantly increased intensity by combination with helium gas, probably due to instrumental parameter setting of the ICP-MS.

Unlike O₂, the reactions of CO₂ with U⁺ and UO⁺ are endothermic reaction due to the higher bond energy of CO₂ (799 kJ mol⁻¹) compared to O₂ (498 kJ mol⁻¹) [30]. This makes these reactions thermodynamically unfavorable, and needs external kinetic energy. The kinetic energy of U⁺ in the cell can be provided from the bias voltage (negative voltage) during its flight in the collision/reaction cell, allowing U⁺ ions to react with CO₂ in a slightly endothermic process ($\Delta H_r = 0.31\text{eV}$). The relatively high reaction enthalpy for the reaction of CO₂ with UO⁺ to form UO₂⁺ ($\Delta H_r = 0.57\text{eV}$) [30] reduced the formation of UO₂⁺ from UO⁺. Therefore, the higher intensities of UO⁺ signals appeared compared to that observed under O₂-He mode.

Table 5

Elimination of uranium hydride interference (UH⁺ or UOH⁺) and the sensitivity of ²³⁶U⁺ signal at different experiment conditions and comparison with the reported values.

Reaction gas	Flow rate (mL min ⁻¹)	Sample introduction systems	Sensitivity (UO ⁺ , cps per ng mL ⁻¹ U)	Ratio of ²³⁸ U ¹⁶ O ¹ H ⁺ / ²³⁸ U ¹⁶ O ⁺	Reference
O ₂	0.1	MicroMist nebulizer	6.0×10^5	1.0×10^{-6}	[12]
O ₂	0.1	Apex-Q nebulizer	3.0×10^5	1.0×10^{-5}	[17]
CO ₂ or O ₂	0.7–1	Apex Ω nebulizer	$(4-6) \times 10^5$	4.0×10^{-7}	[18]
O ₂ -He	0.53–7	MicroMist nebulizer	9.0×10^4	$(1.1 \pm 0.05) \times 10^{-6}$	This work
O ₂ -He	0.53–7	Apex Ω nebulizer	3.3×10^6	$(3.1 \pm 0.18) \times 10^{-7}$	This work
CO ₂ -He	0.6–7	MicroMist nebulizer	3.7×10^5	$(1.0 \pm 0.06) \times 10^{-6}$	This work
CO ₂ -He	0.6–7	Apex Ω nebulizer	7.5×10^6	$(2.4 \pm 0.14) \times 10^{-7}$	This work

*the results of UOH⁺/UO⁺ ratios are the average and 1SD of the 3 replicates experiment for the signals of ²³⁸U¹⁶O¹H⁺ and ²³⁸U¹⁶O⁺.

Table 6

Variation of the proportions of different uranium species with the flow rate of O₂ injected to the CRC as reaction gas in the measurement of ²³⁶U using ICP-MS/MS.

O ₂ flow (mLmin ⁻¹)	²³⁸ UO ⁺	²³⁸ U ⁺	Others
0.07	25.4%	74.4%	0.2%
0.40	48.3%	39.1%	12.6%
0.53	52.1%	27.8%	20.0%
0.94	39.7%	12.7%	47.6%

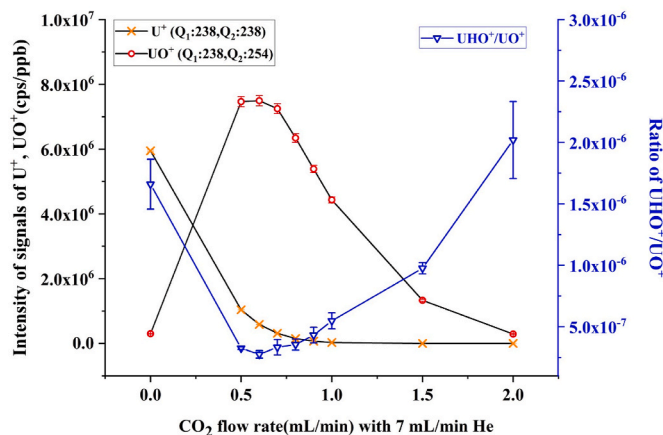
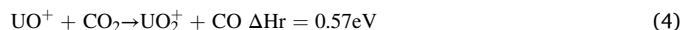
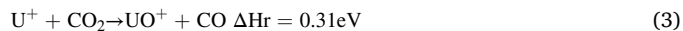


Fig. 4. Variation of the intensities of the ²³⁸U⁺ and ²³⁸U¹⁶O⁺ ions and ²³⁸U¹⁶O¹H⁺/²³⁸U¹⁶O⁺ ratios with the flow rate of CO₂ with 7.0 ml min⁻¹ helium injected to the CRC. Uranium standard solutions (1.0 ng mL⁻¹ for ²³⁸U⁺ and ²³⁸U¹⁶O⁺ and 100 ng mL⁻¹ for ²³⁸U¹⁶O¹H⁺ measurement) were used for the experiments.



It was observed that the UOH⁺/UO⁺ ratios significantly decreased with the increased flow rates of CO₂ and reached to the minimum of 2.4×10^{-7} at the CO₂ flow rate of 0.6 mL min⁻¹, and then gradually increased with the further increased flow rates of CO₂ (Fig. 4). This might be attributed to the sharply decreased intensities of UO⁺ ions with the increased flow rates of CO₂ over 0.6 mL min⁻¹, which results from the conversion of UO⁺ to UO₂⁺, but the intensities of UOH⁺ ion did not significantly decrease with the flow rates of CO₂ over 0.6 mL min⁻¹. This is the lowest ratio of UOH⁺/UO⁺ compared with all reported values, and about 2 times lower than the recently reported value of 4×10^{-7} using single CO₂ or O₂ as reaction gas [18].

The maximum sensitivity of UO⁺ of 7.5×10^6 cps ppb⁻¹ and the minimum of ²³⁸U¹⁶O¹H⁺/²³⁸U¹⁶O⁺ ratio of $(2.4 \pm 0.14) \times 10^{-7}$ were achieved at 0.6 mL min⁻¹ CO₂ - 7.0 mL min⁻¹ He using Apex Ω for samples introduction. This condition was selected as the optimal

condition for the measurement of ^{236}U . At this condition, the measured count rate of $^{238}\text{U}^{16}\text{O}^+\text{H}^+$ was 1.8×10^3 cps with relative uncertainty of only 1.2%. The average and 1SD of $^{238}\text{U}^{16}\text{O}^+\text{H}^+ / ^{238}\text{U}^{16}\text{O}^+$ ratios of three replicate samples were measured to be $(2.4 \pm 0.14) \times 10^{-7}$. The variation of the measured values was not only from the measurement uncertainty of $^{238}\text{U}^{16}\text{O}^+\text{H}^+$, but also from all other factors including the stability of the instrument.

Peak tailings effects of ^{235}U and ^{238}U . The tailings of ^{235}U and ^{238}U peaks are another challenge in the measurement of low-level ^{236}U by ICP-MS, because the $^{236}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{235}\text{U}$ atomic ratios in the environmental samples are normally down to 10^{-11} – 10^{-5} . Tandem quadrupole mass separators equipped in Agilent 8800 ICP-MS can greatly decrease this interference. Due to the formation of uranium hydride ($^{235}\text{U}^{16}\text{O}^+\text{H}^+$), the direct evaluation of the tailing contribution of $^{235}\text{U}^{16}\text{O}^+$ and $^{238}\text{U}^{16}\text{O}^+$ peaks to the counts at m/z 252 ($^{236}\text{U}^{16}\text{O}^+$ ions) is impossible. Since the peak tailing occurs on both sides at mass ($n-1$) and ($n+1$), and the tailing to the low mass side is normally higher than that to the higher mass side, the tailing of $^{238}\text{U}^{16}\text{O}^+$ ($m/z = 254$) to $m/z = 253$ was used to evaluate this interference. At the optimal conditions of $0.6 \text{ mL min}^{-1} \text{ CO}_2$ - $7.0 \text{ mL min}^{-1} \text{ He}$ as reaction gas, the signal intensity at $m/z = 253$ for Q2 (Q1 was set at m/z 237) was measured to be less than 0.1 cps for 1000 ng mL^{-1} uranium, corresponding to an abundance sensitivity (the ratio of the intensity at $m/z = 253$ to that at $m/z = 254$) of $<1.2 \times 10^{-11}$. The contribution of the $^{235}\text{U}^{16}\text{O}^+$ peak tailing to the m/z 252 can be therefore estimated to be $<1.2 \times 10^{-11}$. Since the tailing of a peak to m/z of $n-2$ is one order of magnitude lower than that to m/z of $n-1$, the tailing of $^{238}\text{U}^{16}\text{O}^+$ to $m/z = 252$ is also $<1 \times 10^{-12}$. The overall tailing contribution of ^{235}U and ^{238}U to ^{236}U measurement can be estimated to be $<1.3 \times 10^{-11}$ for both ^{238}U and ^{235}U . This is more than three orders of magnitude lower than the interference of uranium hydride ($^{235}\text{U}^{16}\text{O}^+\text{H}^+$) in the measurement of ^{236}U , and therefore the tailing effect of ^{235}U and ^{238}U could be neglected.

The extremely low abundance sensitivity achieved in this work is mainly attributed to the employment of the two sequential quadrupole mass separators. In the first quadrupole, when m/z 236 was set, ions of $^{236}\text{U}^+$, $^{235}\text{U}^+\text{H}^+$ and scattering tailings of $^{235}\text{U}^+$ and $^{238}\text{U}^+$ ions passed through Q1 and entered the CRC. In this stage, the contributions of the $^{235}\text{U}^+$ and $^{238}\text{U}^+$ peaks tailing are similar to the normal single quadrupole ICP-MS at level of 10^{-6} – 10^{-7} . In the octupole collision/reaction cell, U^+ and UH^+ were converted to UO^+ and minor UOH^+ at the optimal flow rate of CO_2 –He. In the second quadrupole mass separator, where m/z 252 was set, ions of $^{236}\text{U}^{16}\text{O}^+$, $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ and the scattered tailing of $^{235}\text{U}^{16}\text{O}^+$ and $^{238}\text{U}^{16}\text{O}^+$ passed through and entered to the detector. Since only a very few number of ions resulted from the scattered $^{235}\text{U}^{16}\text{O}^+$ (converted from scattered $^{235}\text{U}^+$ and decomposed $^{235}\text{U}^{16}\text{O}^+\text{H}^+$) and $^{238}\text{U}^{16}\text{O}^+$ ions (converted from the scattered $^{238}\text{U}^+$) could enter the detector, the overall tailing from ^{235}U and ^{238}U was almost completely suppressed.

Interference of other polyatomic ions. Besides the uranium hydride ($^{235}\text{U}^{16}\text{O}^+\text{H}^+$ or $^{235}\text{U}^{16}\text{O}^+\text{H}^+$), other polyatomic ions with similar m/z as $^{236}\text{U}^+$ ion might also interfere with the measurement of ^{236}U by ICP-MS. They are mainly the polyatomic ions of Hg, Pb and Tl isotopes with isotopes of light elements in the separated sample solution and plasma. Among them, $^{196}\text{Hg}^{40}\text{Ar}^+$, $^{208}\text{Pb}^{28}\text{Si}^+$, $^{205}\text{Tl}^{31}\text{P}^+$, $^{204}\text{Pb}^{32}\text{S}^+$, $^{204}\text{Hg}^{32}\text{S}^+$, $^{199}\text{Hg}^{37}\text{Cl}^+$, $^{201}\text{Hg}^{35}\text{Cl}^+$ are the key species [31]. Pb, Tl, Hg solutions ($0.5 \mu\text{g mL}^{-1}$) in $0.1 \text{ mol L}^{-1} \text{ HCl}$ – $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ media were measured using ICP-MS/MS at the optimal condition using $0.6 \text{ mL min}^{-1} \text{ CO}_2$ – $7 \text{ mL min}^{-1} \text{ He}$ as collision/reaction gas and setting m/z 236 at Q1 and m/z 252 at Q2. The measured signal intensities were less than 0.05 cps at m/z 252 for each single element solution, which is similar to the blank (0.04 cps) of $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ solution. The negligible interference of these elements to the measurement of ^{236}U in the optimal measurement conditions in this work should be attributed to the reactions in the CRC. The CO_2 –He gas injected into the CRC also decomposed the polyatomic ions of Hg, Pb and Tl. Meanwhile, the measurement of the formed $^{236}\text{U}^{16}\text{O}^+$ ions excludes any possible

polyatomic ions from these elements, because they could not form ions of m/z 252 in the CRC. In addition, Hg, Pb and Tl were also well removed during the chemical separation of uranium using extraction chromatography. The measured concentrations of these three elements in the final separated samples solution are less than 0.03 ng g^{-1} , more than 10^4 times lower than the test solutions. Therefore, the interference of these elements for ^{236}U measurement is negligible.

Detection limit of the developed method for ^{236}U . Under the optimal condition, the measurement sensitivity of the developed ICP-MS/MS method for ^{236}U was 7.5×10^6 cps per $1 \text{ ng mL}^{-1} \text{ }^{236}\text{U}$, and the count rate at m/z 252 was 0.24 ± 0.06 cps for the procedure blanks when $0.6 \text{ mL min}^{-1} \text{ CO}_2$ – $7 \text{ mL min}^{-1} \text{ He}$ as reaction gas and Apex Ω sample introduction were used (Table 2). The absolute detection limit of the developed method for ^{236}U can be calculated using three-fold of standard deviation (3 SD) of the count rates for procedure blanks (0.24 ± 0.06 cps) to be $3 \times 10^{-17} \text{ g g}^{-1}$ for 3 g sample (prepared in 3 ml solution, with a chemical yield of 80%). However, the detection limit of ^{236}U in the samples was mainly restricted by the interference of $^{235}\text{U}^{16}\text{O}^+\text{H}^+$ ions, because large amount of uranium was present in the separated samples compared to the procedure blanks. Based on the measured $^{238}\text{U}^{16}\text{O}^+\text{H}^+ / ^{238}\text{U}^{16}\text{O}^+$ ratios of $(2.4 \pm 0.14) \times 10^{-7}$ using $1 \mu\text{g mL}^{-1}$ uranium standard solution, the minimum detectable $^{236}\text{U}/^{238}\text{U}$ ratio can be estimated to be 3.0×10^{-10} using 3 SD of the measured $\text{UOH}^+ / \text{UO}^+$ ratios in three replicate measurements, in consideration of a natural atomic ratio of 7.2×10^{-3} for $^{235}\text{U}/^{238}\text{U}$. A practical detection limit of the developed method for ^{236}U can be estimated using the equation below:

$$DL = R \left(\frac{^{236}\text{U}}{^{238}\text{U}} \right) \times [U] \times \rho \times m \times V^{-1}$$

Where, $R \left(\frac{^{236}\text{U}}{^{238}\text{U}} \right)$ is the minimum detectable $^{236}\text{U}/^{238}\text{U}$ ratio (3.0×10^{-10}), $[U]$ is the uranium concentration in the sample ($\mu\text{g g}^{-1}$), ρ is the chemical yield (80% in this work), m is the mass of sample (g) and V is the volume of final solution for measurement (mL). For analysis of 3 g soil or sediment sample with uranium concentration of $3 \mu\text{g g}^{-1}$ and the final separated uranium in 3 mL ($\sim 3 \text{ g}$) solution, the detection limit of the method for ^{236}U can be estimated to be $7.2 \times 10^{-16} \text{ g g}^{-1}$ or $1.7 \times 10^{-9} \text{ Bq g}^{-1}$. The detection limit achieved in this work is one order of magnitude lower than the reported values in the literatures [17,18]. This method can be therefore used to determine ^{236}U in ordinary environmental samples (soil, sediment) without direct nuclear contamination ($^{236}\text{U}/^{238}\text{U} < 10^{-8}$).

3.3. Method validation

Since standard reference material with certified ^{236}U value is not commercially available, reference materials IAEA-375 (soil) and IAEA-385 (sediment) with reported ^{236}U values in the literatures were analyzed for method validation. The samples were first decomposed with the fusion method using LiBO_2 , and the fused beads were dissolved in HNO_3 – HCl . The uranium in the solution was separated using extraction chromatography with UTEVA resin, and the chemical yield of uranium of over 85% was achieved in this process. The separated ^{236}U in 3.0 ml of 3% HNO_3 solution was measured by ICP-MS/MS under the optimized condition using CO_2 –He as reaction gas. Meanwhile, the separated uranium from IAEA-385 was also prepared as oxides with Fe_2O_3 powder and measured using 300 kV AMS (MILEA) in ETH Zurich, Switzerland. The analytical results (Table 4) showed that the measured $^{236}\text{U}/^{238}\text{U}$ atomic ratio ($(6.34 \pm 1.01) \times 10^{-9}$) in the sediment reference material (IAEA-385) is similar to the value measured by AMS ($(5.90 \pm 0.43) \times 10^{-9}$). The measured ^{236}U concentration in IAEA 385 ($(42.6 \pm 7.0) \times 10^6 \text{ atoms g}^{-1}$) agrees well with the reported value of $(39.4 \pm 3.5) \times 10^6 \text{ atoms g}^{-1}$ measured by AMS [32] and fell within the reported range [33], but is lower than another reported value of $(138 \pm 32) \times 10^6$

atoms g^{-1} by ICP-MS/MS [17], which might be attributed to the overestimation of ^{236}U signal due to the insufficient elimination of $^{235}\text{U}^{1}\text{H}^{+}$ interference (with $\text{UOH}^{+}/\text{UO}^{+} = 10^{-6}$). For IAEA-375 soil, the measured concentration of ^{236}U is lower than the reported values [32, 34, 35], but the reported values in these literatures are also different from each other by more than one order of magnitude. The highest value $((2450 \pm 120) \times 10^{-9})$ for $^{236}\text{U}/^{238}\text{U}$ atomic ratio is even 2 orders of magnitude higher than our measured value. Besides the analytical accuracy, the inhomogeneity of ^{236}U in this sample might be a major reason. This standard was prepared from a sample collected from Chernobyl accident highly contaminated area, and hot particles with refractory actinides and fission products have been observed in this sample. In addition, two soil samples collected from Shaanxi, China were also analyzed for $^{236}\text{U}/^{238}\text{U}$ atomic ratio using the developed ICP-MS/MS method and AMS. The sampling sites of these two samples are far from any nuclear facilities, reflecting the global fallout level of ^{236}U . The analytical results (Table 4) show that the measured $^{236}\text{U}/^{238}\text{U}$ ratios using the developed ICP-MS method $((9.2 \pm 3.2) \times 10^{-10}$ and $(1.41 \pm 0.31) \times 10^{-9}$) agree well with the results of AMS $((9.6 \pm 0.7) \times 10^{-10}$ and $(1.33 \pm 0.10) \times 10^{-9}$), confirming the developed ICP-MS/MS method is reliable for determination of ^{236}U in environmental samples.

3.4. Analysis of the environmental soil samples from northwest China

The analytical results of ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios in seven surface soil samples from Northwest China are presented in Table 7. The ^{236}U concentrations in the surface soils from Shaanxi, China (Meixian and Xi'an) were $(4.80\text{--}9.78) \times 10^6$ atoms g^{-1} (corresponding to $4.5\text{--}9.2$ nBq g^{-1}) with $^{236}\text{U}/^{238}\text{U}$ atomic ratios of $((0.92\text{--}1.41) \times 10^{-9})$. This level is close to the reported values in the background region, which received only global fallout (Mozambique, Chile, Australia, Italy, Japan and Hunan in China) [21, 36–39], indicating that the source of ^{236}U in these areas in Shaanxi, China are mainly from global fallout. The ^{236}U concentrations of $(109\text{--}198) \times 10^6$ atoms g^{-1} (or $102\text{--}186$ nBq g^{-1}) and $^{236}\text{U}/^{238}\text{U}$ atomic ratios of $(16\text{--}19) \times 10^{-9}$ in two samples collected near the Lop Nor nuclear weapons tests site (Lop Nor 1 and 2) are more than one order of magnitude higher than those from Shaanxi, China. This might be attributed to the contribution of the close-in (proximal) fallout of the atmospheric nuclear weapons tests at Lop Nor, China in 1964–1980 at the sampling sites, which are less than 200 km distance away from the tests site in Lop Nor. A similar high concentration of ^{236}U (128×10^6 atoms g^{-1} or 120 nBq g^{-1}) and $^{236}\text{U}/^{238}\text{U}$ atomic ratio (21×10^{-9}) with those in the Lop Nor were observed in the surface soil from Yumen, about 500 km downwind direction (southeast) from the Lop Nor tests site. The close-in fallout of the nuclear weapons tests at Lop Nor might be an important source of ^{236}U

in this region as well. The ^{236}U concentrations $((30\text{--}48) \times 10^6$ atoms g^{-1} or $28\text{--}45$ nBq g^{-1}) and $^{236}\text{U}/^{238}\text{U}$ atomic ratios $((4.4\text{--}5.4) \times 10^{-9})$ in surface soil samples from Liuyuan and Bujilong, China are 3–4 times higher than those from Shaanxi, China, but 4–5 times lower than that from Lop Nor and Yumen, although these two sampling sites are close to Yumen. This might be attributed to different deposition rate or less retention of ^{236}U deposited from the Chinese nuclear weapons tests. The similar distribution pattern of plutonium isotope was also reported in these areas [40]. These results demonstrated the successful application of the developed method in the analysis of environmental soil samples for ^{236}U , even in the background areas.

4. Conclusion

A sensitive analytical method was developed for determination of ultra-low ^{236}U in environmental samples. Based on this study, it can be concluded that: (1) A rapid and easy operation method using total fusion with LiBO_2 as fusion flux followed by acid dissolution and extraction chromatographic separation using UTEVA resin was developed. The uranium recovery can reach up to 80%. The decontamination factors of more than 1×10^5 for most of interfering elements and a sample treatment time of less than 4 h were achieved; (2) $\text{CO}_2\text{--He}$ was demonstrated as a powerful reaction/collision gas for elimination of uranium hydride interference by converting $^{236}\text{U}^{+}$ and $^{235}\text{U}^{1}\text{H}^{+}$ ions to $^{236}\text{U}^{16}\text{O}^{+}$ and $^{235}\text{U}^{16}\text{O}^{+}$ and by measuring ^{236}U as $^{236}\text{U}^{16}\text{O}^{+}$ ions. The $^{235}\text{U}^{16}\text{O}^{1}\text{H}^{+}/^{235}\text{U}^{16}\text{O}^{+}$ ratio was significantly reduced to 2.4×10^{-7} , and the minimum detectable $^{236}\text{U}/^{238}\text{U}$ atomic ratio was improved to 3×10^{-10} under the optimal condition. The interferences of polyatomic ions of Hg, Pb and Tl were almost completely eliminated. (3) By employment of the sequential quadrupole mass separators, the tailings of ^{235}U and ^{238}U (abundance sensitivity) were significantly reduced to $<1.3 \times 10^{-11}$. By the ion focusing with He gas injected into the CRC and desolvation with Apex for sample introduction, the measurement sensitivity of ^{236}U was significantly improved to 7.5×10^6 cps for 1 ng mL^{-1} ^{236}U , so that the absolute detection limit of the method for ^{236}U can reach $3 \times 10^{-17} \text{ g g}^{-1}$ for 3 g solid sample. In consideration of the contribution of uranium hydride, a detection limit of $7.2 \times 10^{-16} \text{ g g}^{-1}$ for ^{236}U for 3 g sample was achieved. (4) The developed method was validated by analysis of standard reference materials and comparable with the measurement values by AMS, confirming its reliability and accuracy. The analytical method has been successfully applied for determination of ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios in surface soil samples collected from Northwest China. A significantly high ^{236}U level at sites of Lop Nor and Yumen compared to the background region in Xi'an was observed, which is attributed to the close-in deposition from nuclear weapons test at Lop Nor and the dispersion of

Table 7

Analytical results of ^{236}U concentrations and $^{236}\text{U}/^{238}\text{U}$ atomic ratios in surface soil samples from Northwest China and comparison with the reported values in other locations.

Sample species	^{238}U Conc. ($\mu\text{g g}^{-1}$)	^{236}U Conc. ($\times 10^6$ atoms g^{-1})	$^{236}\text{U}/^{238}\text{U}$ atomic ratio ($\times 10^{-9}$)	Sample decomposition method	Reference
Chile		2.06–9.10		$\text{HNO}_3+\text{H}_2\text{O}_2+\text{HF}$	[36]
Mozambique		0.56 ± 0.21			
Italy	0.85–4.93	7.7–54.9	0.94–11.70	$\text{HNO}_3+\text{H}_2\text{O}_2+\text{HF}$	[38]
North Queensland Australia		4.09–10.06		8 M HNO_3	[37]
Austria		148 ± 11		8 M $\text{HNO}_3+\text{H}_2\text{O}_2$	[32]
Ishikawa, Japan	0.99–2.54	892–3760	18.5–109	8 M $\text{HNO}_3+\text{H}_2\text{O}_2$	[41]
Near FDNPP, Japan	–	5.0–260	9.9–135	$\text{HNO}_3+\text{HClO}_4+\text{HF}$	[39]
Hunan, China	0.53–2.31	16.1–213	4.7–49.1	HNO_3 leaching	[21]
Meixian, Shanxi	1.86 ± 0.04	4.80 ± 0.56	0.92 ± 0.32	LiBO_2 Fusion	This work
Xi'an, Shaanxi	2.56 ± 0.08	9.78 ± 1.34	1.41 ± 0.31	LiBO_2 Fusion	This work
Bujilong, Gansu	2.69 ± 0.10	29.7 ± 2.8	4.36 ± 0.40	LiBO_2 Fusion	This work
Liuyuan, Gansu	3.55 ± 0.08	48.3 ± 3.7	5.38 ± 0.51	LiBO_2 Fusion	This work
Lop Nor 1, Xinjiang	2.70 ± 0.09	109 ± 8	15.9 ± 1.2	LiBO_2 Fusion	This work
Lop Nor- 2, Xinjiang	4.08 ± 0.16	198 ± 14	19.2 ± 1.4	LiBO_2 Fusion	This work
Yumen, Gansu	2.42 ± 0.07	128 ± 13	20.9 ± 2.2	LiBO_2 Fusion	This work

*The uncertainties of analytical results in this work are expanded uncertainties using a coverage factor of $k = 1$.

the radioactive plume in this region.

Credit author statement

Yanyun Wang, Methodology, Investigation, Validation, Visualization, Writing - original draft; Writing - review & editing, Visualization. Xiaolin Hou, Conceptualization, Methodology, Data curation, Supervision, Funding acquisition, Resources, Writing - review & editing. Weichao Zhang, Methodology, Investigation, Writing - review & editing. Luyuan Zhang, Data curation, Writing - review & editing. Yukun Fan, Writing - review & editing.

Notes

The authors declare no competing financial interest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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