



Determination of ultra-trace level plutonium isotopes in soil samples by triple-quadrupole inductively coupled plasma-mass spectrometry with mass-shift mode combined with UTEVA chromatographic separation

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ABSTRACT

Although triple-quadrupole inductively coupled plasma-mass spectrometry (ICP-MS/MS) has become an attractive technique for the measurement of long-lived radionuclides, the abundance sensitivity, isobaric and polyatomic ions interferences seriously restrict the application. The spectral peak tailing and uranium hydrides (UH^+ , UH_2^+) from ^{238}U have a serious influence on the accurate measurement of ^{239}Pu and ^{240}Pu , especially for the ultra-trace level plutonium isotopes in the higher uranium sample. A new method was developed using ICP-MS/MS measurement in mass-shift mode with collision-reaction gas combined with a chemical separation procedure. As O_2 readily converted Pu^+ ion to PuO_2^+ , while disassociated the interfering diatomic ions of interfering elements (U, Pb, Hg, Tl, etc.), the interferences from these elements were completely eliminated if plutonium was detected as PuO_2^+ at the m/z more than 270. By the mass filter in MS/MS mode combined with O_2 as reaction gas the lower peak tailing of $^{238}\text{U}^+$ ($<5 \times 10^{-12}$) was significantly suppressed. By this way, the $^{238}\text{UO}_2\text{H}^+/^{238}\text{UO}_2^+$ atomic ratio was reduced to 4.82×10^{-9} , which is significantly lower than that of other collision-reaction gas modes. Interferences from Pb, Hg and Tl polyatomic ions were also completely eliminated. Thus, accurate measurement of ultra-trace level ^{239}Pu in high uranium sample solutions with the $^{239}\text{Pu}/^{238}\text{U}$ concentration ratio of 10^{-10} was achieved by the mass-shift mode with 0.15 mL/min O_2/He + 12.0 mL/min He as collision-reaction gas, and high elimination efficiency of uranium interferences up to 10^{14} can be obtained by combination with the chemical separation using a single UTEVA resin column. The developed method can be applied to accurately determine the fg level ^{239}Pu in high uranium samples, such as large-size deep seawater, deep soil and sediment, uranium debris of nuclear fuel.

1. Introduction

As one of the most important anthropogenic radionuclides, plutonium (Pu) is widely utilized or produced in human nuclear activities including nuclear weapons and nuclear power reactors. Due to the high chemical and radioactive toxicity, long-term stay ($T_{1/2}$ for ^{239}Pu and ^{240}Pu are 2.41×10^4 y and 6.56×10^3 y, respectively) in the

environment, plutonium could be accumulated in the liver and bones and bring about the long-term health risk for the human body [1]. Human nuclear activities, such as atmospheric nuclear weapons testing, nuclear fuel reprocessing and nuclear accidents, are the main sources of plutonium in the environment [2]. Among them, the atmospheric nuclear weapons tests in 1945–1980 have released 6.5×10^{15} Bq of ^{239}Pu and 4.4×10^{15} Bq of ^{240}Pu , much higher than other sources [2]. The

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$^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios are different from their origins. A ratio of 0.178 ± 0.023 is well accepted for the global fallout of the nuclear weapons tests [3], compared to the lower ratio of 0.01–0.07 for plutonium in nuclear weapons [4,5] and the higher ratio for release from the nuclear accidents in Chernobyl (0.396 ± 0.014) and Fukushima ($0.323\text{--}0.330$) [6–8]. Therefore, as an important fingerprint, the $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio is often used to identify the source of the plutonium and estimate the effect of human nuclear activities on the environment [9,10]. For this point, it is very critical to accurately determine ^{239}Pu and ^{240}Pu of very low levels in environmental samples (air samples, soil samples, water samples, etc.) and nuclear forensic samples.

For the measurement of ^{239}Pu and ^{240}Pu , α -spectrometry is the prevailing instrument, but the $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio is hard to be obtained due to the close alpha energies of ^{239}Pu (5.15 MeV) and ^{240}Pu (5.16 MeV) [11]. Also, the relatively long measurement time (day to weeks) for ^{239}Pu and ^{240}Pu hinders this technique practicable for analysis of ultra-low level plutonium in the environment samples [12,13]. In the past decades, the development of mass spectrometric techniques makes it possible to measure ultra-trace plutonium isotope. Among types of mass spectrometric techniques, inductively coupled plasma mass spectrometry (ICP-MS) is the most widely used technique and more and more attractive for the measurement of ultra-trace level plutonium isotopes due to its short analytical time (minutes), easy operation, low cost and easy maintenance, and easy sample pretreatment besides the advantages of high sensitivity, low detection limit (^{239}Pu and ^{240}Pu : 0.01–0.1 mBq) [11,14–22].

However, accurate measurement of plutonium isotopes in the environmental samples is always a huge challenge. Firstly, the plutonium ($^{239,240}\text{Pu}$) concentration in environmental samples is very low, namely $(0.04\text{--}400) \times 10^{-16} \text{ g/m}^3$ [14,23], $(1\text{--}900) \times 10^{-15} \text{ g/g}$ [9,19,21], $(0.5\text{--}22) \times 10^{-16} \text{ g/L}$ [24] in the atmosphere, soil (sediment), and seawater samples, respectively. Secondly, high matrix and interference elements (Pb, Hg, Tl and U, etc.) in large-size samples give rise to great difficulties in plutonium measurement using ICP-MS [25]. Besides interference from Pb, Hg, and Tl, the interference from peak tailing and hydrides of ^{238}U is a decisive factor in the detection limit and plays a crucial role in the accurate detection of ^{239}Pu and ^{240}Pu . To effectively remove uranium and the matrix element, the combined multi-resin procedures, including TEVA + AG 1- \times 4 [21], UTEVA + TRU [26,27], TRU + AG 1- \times 4 [28] and TEVA + UTEVA + DGA [19], have been used and the decontamination factors of uranium (U) is high to 10^7 . However, the ultra-trace plutonium isotopes in some special samples with high uranium ($^{238}\text{U}/^{239}\text{Pu} > 3 \times 10^{10}$), such as deep sea water, deep soil and sediment, uranium debris of nuclear fuel, can not be accurately measured by ICP-MS even combined with the effective clean-up procedures.

However, the collision/reaction cell (CRC) technology introduced to the ICP-MS can further lessen the interfering effects of $^{238}\text{UH}^+$ and $^{238}\text{UH}_2^+$ ions on $^{239}\text{Pu}^+$ and $^{240}\text{Pu}^+$ in measurement. Up to now, different collision/reaction gases (He, O_2 , N_2O , NH_3 and CO_2 , etc.) have been tried to remove the uranium hydrides and other polyatomic ions interference [15,16,29–33]. According to the previous works on the measurement of plutonium isotopes using ICP-MS/MS, the introduction of He may triple the sensitivity of plutonium of the traditional model (Q-ICP-MS) [16], but the signals of uranium hydrides are also enhanced about 3 times. NH_3 as reaction gas could improve the elimination efficiency of uranium hydrides compared to the traditional model without reaction-collision gas [15], but the UH^+/U^+ ratio is still too high to meet the need of measurement for the ultra-low level plutonium in the high uranium sample. The use of CO_2 as reaction gas decreases the UH^+/U^+ ratio to 10^{-8} [16], but the low sensitivity for plutonium hinders the measurement of ultra-trace plutonium isotopes. It is well accepted that O_2 would readily react with plutonium as well as uranium hydrides and uranium [16], thus decreasing the portion of UH^+ (UH_2^+) ion. However, the sensitivity based on PuO or Pu is very low because Pu is mostly

converted to PuO_2 in the collision cell. As the m/z for PuO_2 (>271) is beyond the detection range for most ICP-MS, the commonly used measurement of Pu by ICP-MS is on-mass mode up to now. The new type of ICP-MS/MS (such as Agilent 8900) extends the m/z detection range to 275. Therefore, quantitative analysis of femtogram level plutonium in high uranium samples may be realized using ICP-MS/MS (Agilent 8900) with mass-shift mode with the suitable collision-reaction gas based on the higher sensitivity and elimination efficiency for the interference than that of Agilent 8800.

To achieve the rapid and accurate measurement of femtogram level of ^{239}Pu and ^{240}Pu in special samples with the high uranium, parameters including the instrumental parameters and the collision gas flow rate were investigated and optimized for a mass-shift measurement based on an ICP-MS/MS (Agilent 8900). The corresponding chemical separation procedure was also modified to balance between the time consumption and accuracy of the measurement.

2. Material and methods

2.1. Instrument and setup

Inductively coupled plasma tandem quadrupole mass spectrometry (ICP-MS/MS, Agilent 8900) was equipped with high m/z (maximum: 275) and a CRC between two fully functioning mass filters (Q1, Q2) (Fig. S1). While Q1 and Q2 as the mass selection play important roles in the selection of target ions as well as the rejection of all non-target masses/elements, the CRC is another key component for interference elimination via the reaction between the reaction gas and the target ion or interference ions. Standard solutions (^{238}U , 1 $\mu\text{g/L}$; ^{239}Pu , 1 ng/L) were used to tune the ICP-MS/MS and the optimized parameters are listed in Table S1. The mass filters (Q1, Q2) settings were shown in Table S2 for ICP-MS measurement. The standard solution and sample solutions, which were dissolved in 0.5 mol/L HNO_3 , were introduced into the ICP-MS/MS using a T-valve at 0.1 mL/min and the In^{3+} (InCl_3 , 1 $\mu\text{g/L}$) solution was used to monitor the instrument stability. Pt skimmer cone, s-lens, PFA concentric nebulizer and hot plasma were chosen in the measurement of plutonium isotopes. CO_2 , He and O_2/He gas (10% O_2), (all 99.999% purities) were used as collision gas respectively to eliminate the polyatomic interferences.

2.2. Chemical reagents and samples

^{242}Pu standard solution (11.98 pg/mL in 2 mol/L HNO_3) was prepared from ^{242}Pu standard reference material of NIST-SRM-3443I (National Institute of Standard Technology, Gaithersburg, Maryland, USA). The standard solutions of U and interfering elements such as Pb, Tl, and Hg (1.000 g/mL) were purchased from the National Center of Analysis and Testing for Non-ferrous Metals & Electronic Materials in Beijing. The chemical reagents, including $\text{NH}_3\cdot\text{H}_2\text{O}$, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, NaOH , NaNO_2 , HNO_3 , HCl and ascorbic acid, which were purchased from China National Pharmaceutical Group Co., Ltd. (Sinopharm), were guaranteed reagent. UTEVA extraction chromatographic resin (100–150 μm) was purchased from TrisKem International in Bruz of France.

Two soil standard reference materials including IAEA-375 and IAEA-Soil-6 were used to validate the analytical method. Meanwhile, 6 deep layer soil samples (12–40 cm) from two soil profiles (C1-1/2/3/4, C2-1/2), which were collected in 2014 in the Xilingol region in China, were analyzed to verify the practicability of the method.

2.3. Chemical separation of plutonium from environmental samples

The detailed chemical separation and purification procedure of plutonium isotopes in soil or sediment samples were showed in Fig. S2 and presented in Supporting Information. Briefly, the ashed soil or sediment samples were leached with 8 mol/L HNO_3 solutions after a known amount of ^{242}Pu was spiked. The acid leachate was neutralized

with ammonium to precipitate plutonium with hydroxide-iron hydroxide and washed with 2 mol/L NaOH solution and water. Plutonium in the precipitate contained was dissolved and the solution was adjusted to 3 mol/L HNO₃ medium before the sample solution was loaded to a UTEVA column ($\Phi 5 \times 10$ mm). Following washing with 80 mL 3 mol/L HNO₃ solution, plutonium isotopes were eluted by 20 mL 0.1 mol/L ascorbic acid – 1 mol/L HNO₃ solution. After removing the organic matter and diluting in 3 mL 0.5 mol/L HNO₃, ICP-MS/MS was used to measure the plutonium isotopes.

3. Results and discussion

3.1. Effectiveness of different collision/reaction gas to eliminate the interference

Preliminary results showed that NH₃/He + He can significantly improve the sensitivity of plutonium isotopes using Agilent 8900, but the $^{238}\text{UH}^+/^{238}\text{U}^+$ ratio of 10^{-6} does not satisfy the determination of plutonium isotopes in high uranium samples. Therefore, the discussion about NH₃/He + He mode is neglected in this work.

Fig. 1 shows that the $^{238}\text{U}^+$ and $^{238}\text{UH}^+$ signals increased with the increment of He flow rate, but the interference from uranium has not been suppressed. At a He flow rate of 12.0 mL/min, the sensitivity of Pu⁺ is 2170 Mcps/(mg/L), improved by a factor of 6.3 times compared to the CRC of ICP-MS/MS without collision-reaction gas, but the $^{238}\text{UH}^+/^{238}\text{U}^+$ ratio is 3.49×10^{-5} , little changed compared to 6.44×10^{-5} for the no-gas mode.

CO₂ is an effective reaction gas on the elimination of the interference from uranium including $^{238}\text{U}^+$ and $^{238}\text{UH}^+$ [16,30,33,34]. The reactions of CO₂ with presence and absence of helium were investigated in our work. Fig. 2 shows that the $^{238}\text{UH}^+/^{238}\text{U}^+$ ratio is 1.00×10^{-8} using ICP-MS/MS (Agilent 8900), but the sensitivity of $^{242}\text{Pu}^+$ for each species of $^{242}\text{Pu}^+$ (at $^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$ or $^{242}\text{PuO}_2^+$) is lower than 350 Mcps/(mg/L) and 540 Mcps/(mg/L) for the single CO₂ mode and CO₂+He mode, respectively (see Fig. 2).

The CO₂/He as the collision-reaction gas has high elimination efficiencies for U⁺ and UH⁺ (Fig. S3), but the sensitivity of Pu⁺ is too low to meet the measurement requirements of the ultra-trace level plutonium with the high concentration of uranium. At the same time, the sensitivity

of Pu⁺ using O₂/He as the collision-reaction gas is investigated. The single O₂/He mode shows (Fig. 3) that the $^{242}\text{PuO}^+$ and $^{242}\text{PuO}_2^+$ ions signal increased while the signals of $^{242}\text{Pu}^+$ ions remarkably decreased with the O₂/He (10%) flow rate increases. The sensitivity of Pu at m/z 242 ($^{242}\text{Pu}^+$), 258 ($^{242}\text{PuO}^+$) and 274 ($^{242}\text{PuO}_2^+$) are lower than 200 Mcps/(mg/L), also not suitable to measure the ultra-trace level plutonium isotopes in the uranium samples, although the interference from uranium, especially the UH⁺, is effectively eliminated at m/z 258 and 274 using O₂/He as the collision/reaction gas.

It has been demonstrated that the presence of He as the collision gas can remarkably enhance the sensitivity of isotopes [16]. Therefore, intense attention was paid to the combination of He and O₂/He as collision-reaction gases for the elimination of uranium interference based on the high m/z with Agilent 8900.

3.2. Elimination of uranium interference using O₂/He + He as reaction/collision gases

It was observed in Fig. 4 that the maximal sensitivity of $^{242}\text{Pu}^+$ (880 Mcps/(mg/L)) at m/z 274 ($^{242}\text{PuO}_2^+$) was obtained at the O₂/He flow rate of 0.09 mL/min with 12.0 mL/min He, and the signal of $^{238}\text{UHO}_2^+$ was 0.068 cps/(μg/L) in comparison. With the O₂/He flow rate increased to a maximum of 0.15 mL/min, the sensitivity of $^{242}\text{Pu}^+$ at m/z 274 ($^{242}\text{PuO}_2^+$) was 813 Mcps/(mg/L), slightly lower than the maximum sensitivity (880 Mcps/(mg/L)). However, the interference signals of $^{238}\text{UHO}_2^+$ (0.034 cps/(μg/L)) was half of that for the O₂/He flow rate of 0.09 mL/min with 12.0 mL/min He. Therefore, the O₂/He of 0.15 mL/min was selected as the optimal reaction gas flow rate.

It is clear from Fig. 4 that the intensities of $^{238}\text{UO}_2^+$ ions significantly increased by almost 4 orders of magnitude, while the $^{238}\text{U}^+$ ions intensities decreased exponentially by almost 3 orders of magnitude when the flow rate O₂/He increased to the maximum value (0.15 mL/min). As the O₂/He flow rate increased from 0 to 0.15 mL/min, the intensity of $^{238}\text{UH}^+$ signal exponentially decreased by more than 3 orders of magnitude, while the $^{238}\text{UHO}^+$ and $^{238}\text{UHO}_2^+$ signals reduced by more than 300 and 84 times, respectively. The results indicated that $^{238}\text{U}^+$ and $^{238}\text{UH}^+$ preferred to react with O₂ to form $^{238}\text{UO}_2^+$ as illustrated by reactions 1 to 3.



At the same time, the intensity of $^{242}\text{Pu}^+$ signal decreases exponentially by more than 600 times at the O₂/He flow rate of 0.15 mL/min with 12 mL/min He compared to that for He mode (only 12.0 mL/min He without O₂/He gas) (Fig. 4). But it was observed that the signal of $^{242}\text{PuO}_2^+$ (at m/z = 274) gradually increases with the injection of O₂/He and is significantly higher than that of $^{242}\text{PuO}^+$ (at m/z = 258) and $^{242}\text{Pu}^+$ (at m/z = 242) when the flow rate of O₂/He reaches 0.03 mL/min (Fig. 4). The phenomenon can be attributed to the formation of $^{242}\text{PuO}_2^+$ with a relatively high level of O₂ in the CRC.

It is attractive that the change of He flow rate has a significantly effect on the signal intensity of three $^{242}\text{Pu}^+$ species ($^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$ and $^{242}\text{PuO}_2^+$) with 0.15 mL/min O₂/He as shown in Fig. 5. The Pu⁺ ion signal reaches a maximum value of 7.7 Mcps/(mg/L) at 4 mL/min He, while the intensity of $^{242}\text{PuO}^+$ ion reaches its maximum value of 292 Mcps/(mg/L) when He flow rate increased to ~2 mL/min. However, the intensity of PuO₂⁺ ion increases with He flow rate and the measured sensitivity of $^{242}\text{PuO}_2^+$ ion is relatively constant (810–890 Mcps/(mg/L)) when the helium flow rate increases from 6.0 to 12.0 mL/min. Meanwhile, the interference of $^{238}\text{UHO}_2^+$ signal was reduced to the lowest value (0.034 cps/(μg/L)) at He flow rate of 12.0 mL/min (Fig. 5). Therefore, the He of 12.0 mL/min was selected as assistant/collision gas. These results indicate that the formation of $^{242}\text{PuO}^+$ and $^{242}\text{PuO}_2^+$ causes

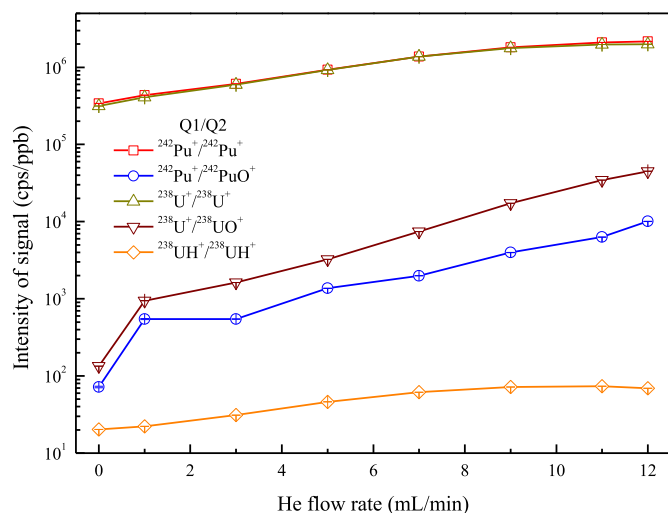


Fig. 1. Variation of the intensities of $^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$, $^{238}\text{U}^+$, $^{238}\text{UH}^+$ and $^{238}\text{UO}^+$ ions (for 1 ng/L ^{242}Pu and 10 μg/L ^{238}U standard solution) with the flow rate of helium injected to the CRC. For $^{242}\text{Pu}^+$ and $^{242}\text{PuO}^+$, m/z = 242 was selected in the Q1 (first quadrupole) and m/z = 242 and 258 in the Q2 (second quadrupole); for $^{238}\text{U}^+$ and $^{238}\text{UO}^+$, m/z = 238 was selected in the Q1 and m/z = 238 and 254 in the Q2; for $^{238}\text{UH}^+$, m/z = 239 was selected in both Q1 and Q2.

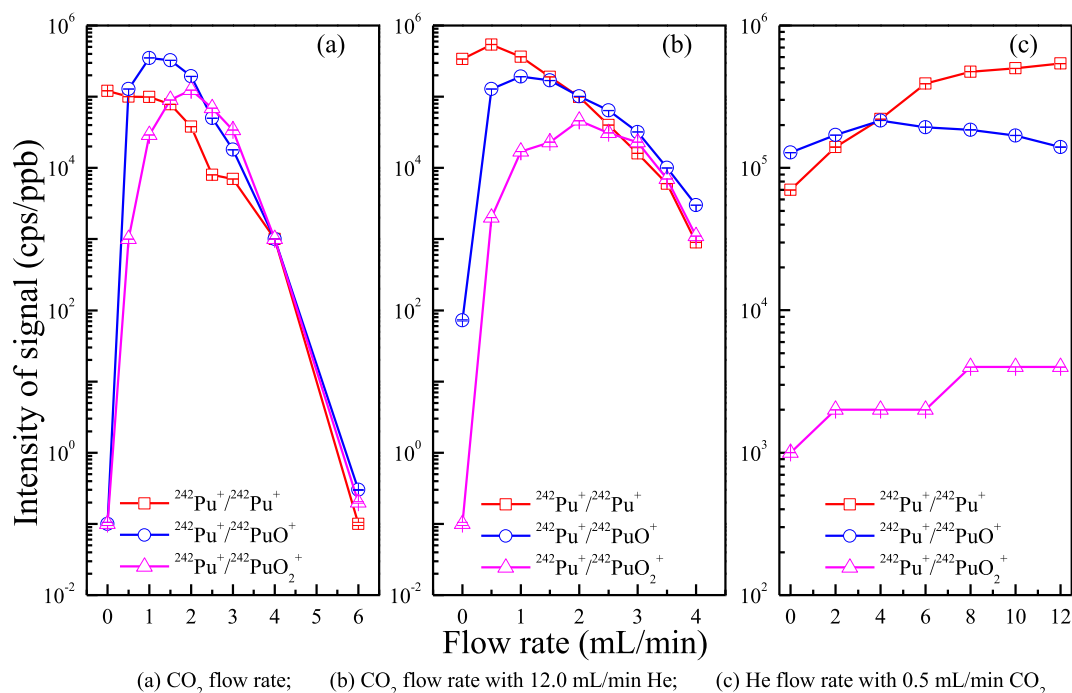


Fig. 2. Variation of the intensities of $^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$ and $^{242}\text{PuO}_2^+$ ions (for 1 ng/L ^{242}Pu standard solution) with the flow rate of CO_2 with helium injected to the CRC. For $^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$ and $^{242}\text{PuO}_2^+$, $m/z = 242$ was selected in Q1 and $m/z = 242, 258$ and 274 in Q2, respectively.

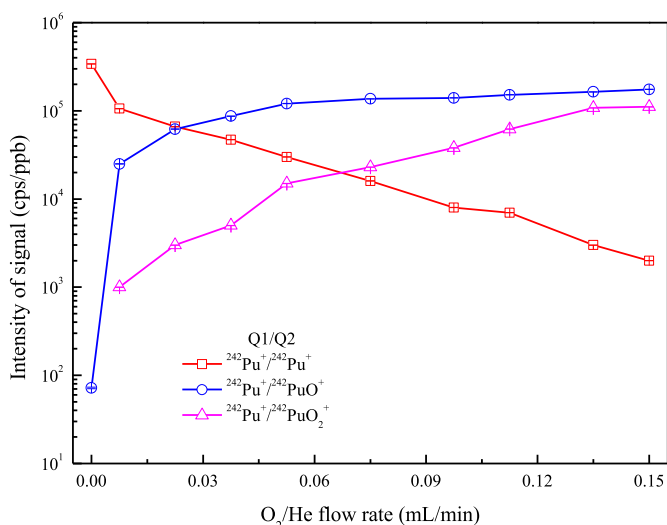


Fig. 3. Variation of the intensities of $^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$ and $^{242}\text{PuO}_2^+$ ions using 1 ng/L ^{242}Pu standard solution with the flow rate of O_2/He injected to the CRC. For $^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$ and $^{242}\text{PuO}_2^+$, $m/z = 242$ was selected in Q1 and $m/z = 242, 258$ and 274 in Q2, respectively.

the loss of $^{242}\text{Pu}^+$ ion signal as illustrated by reactions 4 to 5.



Compared with the sensitivity of $^{242}\text{PuO}_2^+$ ion only using O_2/He of 0.15 mL/min in the CRC, the sensitivity of $^{242}\text{PuO}_2^+$ ion is enhanced about 8 times with the introduction of He. Therefore, He plays a crucially important role in the enhancement in sensitivity of $^{242}\text{PuO}_2^+$ ion signal.

When $^{242}\text{Pu}^+$ ion reacts with O_2 , $^{242}\text{PuO}_2^+$ ion could have a relatively large kinetic energy ranges (0–20 eV), which hinders $^{242}\text{PuO}_2^+$ passing

through the Q2. When He was introduced into the CRC, however, the kinetic energy of $^{242}\text{PuO}_2^+$ ion was reduced to about 2 eV with a narrowed distribution (0–3 eV) due to the elastic collision between $^{242}\text{PuO}_2^+$ ion and He atoms [6,35]. On the other hand, the presence of helium as the buffer layer could decrease the loss of ions by preventing the $^{242}\text{PuO}_2^+$ ion from reaching the octupole in CRC. By these two mechanisms, more $^{242}\text{PuO}_2^+$ ions could enter the detector and the sensitivity of plutonium isotopes would be improved [15,16]. The sensitivity of plutonium ion as $^{242}\text{PuO}_2^+$ (813 Mcps/(mg/L)) with 0.15 mL/min O_2/He + 12.0 mL/min He is two times higher than that in no gas mode (340 Mcps/(mg/L)), while the signal intensities of interfering $^{238}\text{UHO}_2^+$ ion was reduced to the lowest value (0.034 cps/(μg/L)), capable for ultra-trace level plutonium measurement with high uranium matrix.

The results also indicate that a strong reaction occurs between O_2 and Pu^+ , U^+ and UH^+ . It can be explained by the reaction thermodynamics of U^+ and Pu^+ with the O_2 . The reaction efficiencies of U^+ and Pu^+ with O_2 , which react to form the UO^+ and PuO^+ , are respectively 0.72 and 0.27, and higher than that of CO_2 (0.29 for UO^+ , 0.003 for PuO^+) [32]. Moreover, the reaction efficiencies of UO^+ and PuO^+ with O_2 to form the UO_2^+ and PuO_2^+ are 0.45 and 0.07, respectively, much higher than that of CO_2 (0.004 for UO_2^+ , <0.001 for PuO_2^+) [32]. The reaction efficiencies of U^+ and Pu^+ with O_2 are higher than that of CO_2 according to the measured results. This can be explained by the bond dissociation energies (BDE) of the oxidizing reagents. The reported BDE of O_2 by 498.4 kJ/mol is lower than BDE of CO_2 by 532.2 kJ/mol [32]. At the same time, the BDE of UO^+ (801–807 kJ/mol) and UO_2^+ (764–772 kJ/mol) is also significantly higher than that of PuO^+ (618–683 kJ/mol) and PuO_2^+ (498–520 kJ/mol) [32]. Moreover, the ionization energy of UO_2 (5.4–5.5 eV) is lower than that of PuO_2 (7.03–10.1 eV) [32]. Besides, the different reaction efficiencies of U^+ and Pu^+ with O_2 also depend on the promotion energies from the ground-state configurations to reactive-state configurations of the An^+ ions. The promotion energy of U^+ (0.04 eV) from $5f^37s^2(^4\text{F}_{9/2})$ to $5f^36d7s(^6\text{L}_{11/2})$ is higher than that of Pu^+ (1.08 eV) from $5f^67s(^8\text{F}_{1/2})$ to $5f^36d7s(^8\text{K}_{7/2})$ [36], and shows a higher activation energy barrier of Pu^+ to the reaction with oxidizing reagents than that of U^+ . All of the above discussion indicates that the U^+ is easier to react with oxidizing reagents than the Pu^+ .

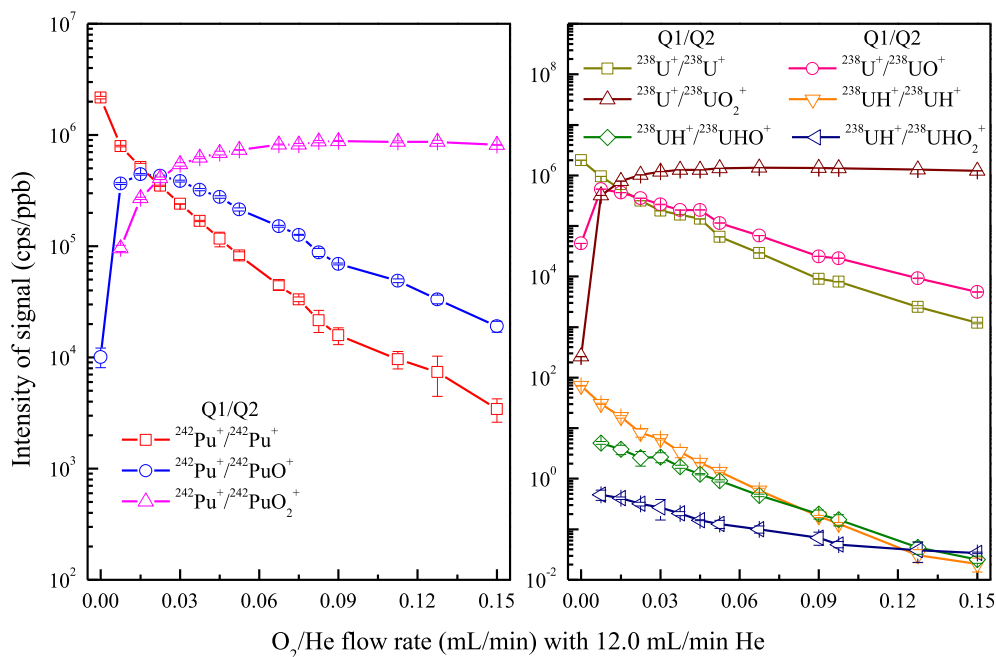


Fig. 4. Variation of the intensities of $^{238}\text{U}^+$, $^{238}\text{UO}^+$, $^{238}\text{UO}_2^+$, $^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$ and $^{242}\text{PuO}_2^+$ ions (for 1 ng/L ^{242}Pu and 10 $\mu\text{g/L}$ ^{238}U standard solution) with the flow rate of O_2/He with 12.0 mL/min helium injected to the CRC. For U^+ , $^{238}\text{UO}^+$ and $^{238}\text{UO}_2^+$ ions, $m/z = 238$ was selected in Q1 (first quadrupole) and $m/z = 238, 254$ and 270 in the Q2 (second quadrupole). For $^{238}\text{UO}^+$, $m/z = 239$ was selected in Q1 and $m/z = 239, 255$ and 271 in Q2, respectively. For $^{242}\text{Pu}^+$, $m/z = 242$ was selected in Q1 and $m/z = 242, 258$ and 274 in Q2, respectively. ^{242}Pu standard solution of 1.0 ng/L, and uranium standard solution of 10 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$ (for UO^+) were used in this measurement.

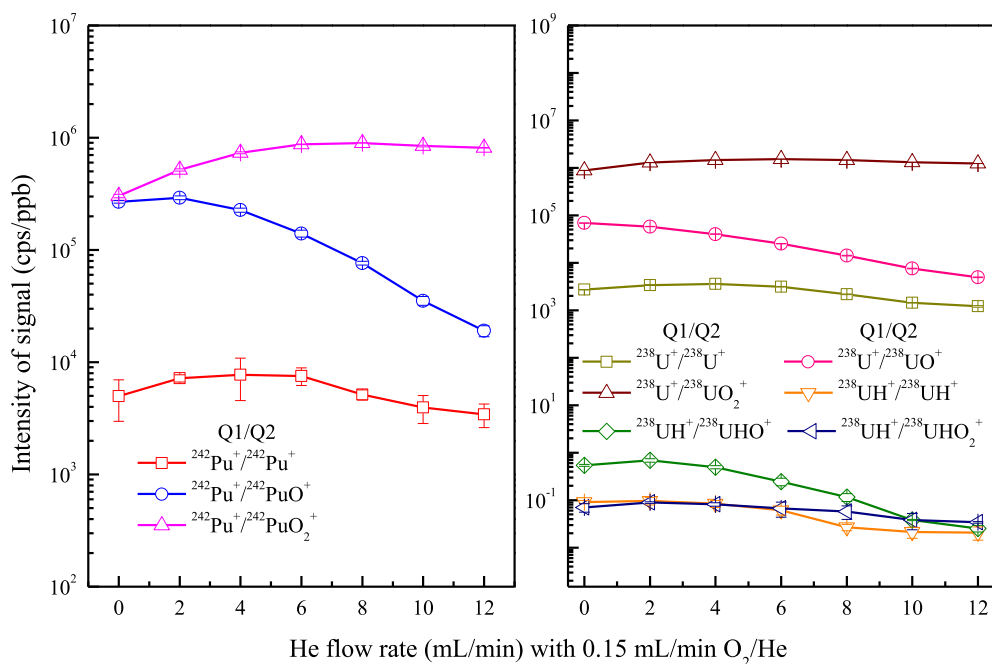


Fig. 5. Influence of flow rate of helium injected to the CRC with 0.15 mL/min O_2/He on the intensities of the $^{242}\text{Pu}^+$, $^{242}\text{PuO}^+$, $^{242}\text{PuO}_2^+$, $^{238}\text{U}^+$, $^{238}\text{UO}^+$, $^{238}\text{UO}_2^+$, $^{238}\text{UH}^+$, $^{238}\text{UHO}^+$ and $^{238}\text{UHO}_2^+$ ions (for 1 ng/L ^{242}Pu and 10 $\mu\text{g/L}$ ^{238}U standard solution). $^{238}\text{UHO}_2^+ / ^{238}\text{UO}_2^+$ in the legend means that $m/z = 239$ ($^{238}\text{UH}^+$) was selected for the first quadrupole (Q1) and $m/z = 271$ ($^{238}\text{UHO}_2^+$) was selected in the second quadrupole (Q2) mass separator; others are a similar meaning. (Left) Measurement of a ^{242}Pu standard solution and (right) measurement of a uranium standard solution. ^{242}Pu standard solution of 1.0 ng/L, and uranium standard solution of 10 $\mu\text{g/L}$ and 100 $\mu\text{g/L}$ (for UO^+) were used in this measurement.

The interference for the measurement of ^{239}Pu using ICP-MS comes mostly from the spectral peak tailing of ^{238}U and uranium hydride ion ($^{238}\text{UH}^+$), and interference is hard to completely discriminate and quantify. The spectral peak tailing at the low (237) and the high (238) from the mass spectrum of ^{238}U both affect the abundance sensitivity, and the contribution at $m-1$ is usually higher than that at $m+1$ according to published literature [6]. Therefore, the contribution from spectral peak tailing of $^{238}\text{UO}_2^+$ at m/z 271 can be conservatively estimated by monitoring the signal at m/z 269. According to Table 1, the best abundance sensitivity is 1.01×10^{-7} in the single quadrupole mode (ICP-MS) with the injection of $\text{O}_2/\text{He} + \text{He}$ in CRC. Moreover, with the application of two quadrupoles for ICP-MS/MS using 0.15 mL/min $\text{O}_2/\text{He} + 12.0$ mL/min He as collision-reaction gas, the contributions from the

spectrum peak tailing of $^{238}\text{UO}_2^+$ at m/z 269 and 271 are further suppressed to less than 5×10^{-12} . This is mainly attributed to the double mass selection from MS/MS, as the MS/MS mode only allows the specified m/z ion including the analyte ion and the interfering ions with the same m/z to enter the detector. And then, the signal at m/z 269 is minor and extremely close to the value from procedure blank when 10 $\mu\text{g/L}$ uranium standard solution (then the counts of UO_2 is out of range of the ICP-MS/MS) is measured by ICP-MS/MS using 0.15 mL/min $\text{O}_2/\text{He} + 12.0$ mL/min He as collision-reaction gas. The result infers that the contributions of $^{238}\text{UO}_2$ spectrum peak tailing at m/z 271 and 272 are very negligible. In a word, the interferences from the uranium hydride ($^{238}\text{UHO}_2^+$ and $^{238}\text{UH}_2\text{O}_2^+$) are a major contribution to the measurement of ^{239}Pu and ^{240}Pu using ICP-MS/MS. The results (Table 2) indicate that

Table 1Abundance sensitivity of ^{238}U ($I_{m/z237}/I_{m/z238}$) of ICP-MS in different mode.

Mode	Agilent 8800 ^a [16]		Agilent 8900 ^b	
	ICP-MS	ICP-MS/MS	ICP-MS	ICP-MS/MS
No Gas	2.36×10^{-4}	3.47×10^{-8}	1.36×10^{-4}	5.69×10^{-8}
He	8.08×10^{-5}	8.19×10^{-9}	4.08×10^{-5}	5.29×10^{-10}
O ₂ /He + He	1.76×10^{-5}	2.29×10^{-11}	1.01×10^{-7}	$<5 \times 10^{-12}$
CO ₂ + He	4.14×10^{-7}	$<2 \times 10^{-11}$	1.54×10^{-7}	1.05×10^{-11}

Note.

^a No gas—no collision/reaction gas in CRC; He—8.0 mL/min; NH₃/He + He: 1.2 mL/min NH₃/He-8 mL/min He; O₂—2.0 mL/min O₂; CO₂ + He—1.2 mL/min CO₂-8.0 mL/min He.

^b No gas—no collision/reaction gas in CRC; He—12.0 mL/min; O₂/He + He—0.15 mL/min O₂/He + 12.0 mL/min He; CO₂ + He—0.5 mL/min CO₂-12.0 mL/min He.

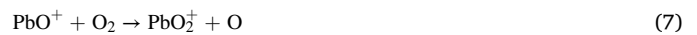
great suppression of uranium hydride was achieved using ICP-MS/MS with 0.15 mL/min O₂/He + 12.0 mL/min He as collision-reaction gas compared to the other modes including no gas mode, He mode and O₂/He mode, giving a very low $^{238}\text{UHO}_2^+/^{238}\text{UO}_2^+$ ratio of 4.82×10^{-9} and $^{238}\text{UH}_2\text{O}_2^+/^{238}\text{UO}_2^+$ ratio of 2.22×10^{-11} . Meanwhile, the elimination of uranium hydride using Agilent 8900 with O₂/He + He is better than that of Agilent 8800 with CO₂ + He, and UH^+/U^+ ratio is 2–3 orders of magnitude lower than the previously reported values from the other types ICP-MS including Q-ICP-MS, MC-ICP-MS and SF-ICP-MS (Table 2). More important, compared to our previous work using Agilent 8800 with CO₂-He, the sensitivity of plutonium isotopes using Agilent 8900 with O₂/He + He improved by 2.4 times. Based on the above discussion, the developed method for the accurate measurement of ^{239}Pu in a higher uranium matrix ($^{238}\text{U}/^{239}\text{Pu} > 10^8$) is feasible and the measured result for ultra-trace level ^{239}Pu is reliable.

3.3. Validation of the developed method for measurement of low-level ^{239}Pu and ^{240}Pu in high uranium matrix

The ^{239}Pu concentration in the simulated solution containing high concentration of uranium (0.01–10000 µg/L) of was measured by ICP-MS/MS using 0.15 mL/min O₂/He + 12.0 mL/min He as the collision-reaction gas. The results (Table 3) show that the ultra-trace level ^{239}Pu with the concentration of 0.01 ng/L can be accurately measured in the high uranium solution of 10000 µg/L ($^{239}\text{Pu}/^{238}\text{U}$ concentration ratio up to 1.0×10^{-9}) using 0.15 mL/min O₂/He + 12.0 mL/min He. Meanwhile, both of the lower uncertainties (<8%) and lower deviations also suggest that the measured values of ultra-trace level ^{239}Pu containing high uranium concentration are reliable and accurate. The measured result confirms that the developed measurement method can

be successfully applied to measure the ultra-trace level ^{239}Pu in the high uranium matrix. Combined with the chemical separation using UTEVA resin, it was inferred the ultra-trace level ^{239}Pu in the $^{239}\text{Pu}/^{238}\text{U}$ concentration ratio of 10^{-13} could also be accurately measured by the developed method.

Except for the interference from uranium including spectral peak tailing and uranium hydride, other polyatomic ions from Pb, Hg and Tl, such as $^{206}\text{Pb}^{33}\text{S}^+$, $^{207}\text{Pb}^{16}\text{O}_2^+$, $^{208}\text{Pb}^{31}\text{P}^+$, $^{205}\text{Tl}^{34}\text{S}^+$, $^{205}\text{Hg}^{35}\text{Cl}^+$, $^{202}\text{Hg}^{37}\text{Cl}^+$, $^{199}\text{Hg}^{40}\text{Ar}^+$, $^{203}\text{Tl}^{36}\text{Ar}^+$, $^{204}\text{Pb}^{35}\text{Cl}^+$ for ^{239}Pu , and $^{204}\text{Pb}^{36}\text{Ar}^+$, $^{206}\text{Pb}^{34}\text{S}^+$, $^{207}\text{Pb}^{33}\text{S}^+$, $^{208}\text{Pb}^{32}\text{S}^+$, $^{203}\text{Tl}^{36}\text{Ar}^+$, $^{205}\text{Tl}^{35}\text{Cl}^+$, $^{203}\text{Tl}^{37}\text{Cl}^+$, $^{200}\text{Hg}^{40}\text{Ar}^+$, $^{208}\text{Pb}^{16}\text{O}_2^+$ for ^{240}Pu [37], also have obvious effects on the measurement of ^{239}Pu and ^{240}Pu . The 200 µg/L Pb, Hg and Tl in the 0.5 mol/mL HNO₃ and 0.5 mol/mL HNO₃+0.1 mol/mL HCl were analyzed, and the results (Table S3) showed that the signals at both m/z 239 (271) and 240 (272) are less than 0.01 cps in the HCl and HNO₃ media by ICP-MS/MS using 0.15 mL/min O₂/He + 12.0 mL/min He as collision-reaction gas. This might be attributed to the mechanism that Pb, Hg and Tl are difficult to react with O₂ to form new polyatomic ions at m/z 271 or 272, instead oxidation products such as PbO^+ , HgO^+ , TlO^+ , PbO_2^+ , HgO_2^+ , and TlO_2^+ might be produced, away from m/z 271 or 272 as illustrated by reactions 6 to 11.

**Table 3**Determination of low concentration ^{239}Pu with high concentration uranium by ICP-MS/MS using 0.15 mL/min O₂/He + 12.0 mL/min He.

Sample solution			Measurement results of ^{239}Pu	
U concentration (10 ⁻⁹ g/mL)	^{239}Pu concentration (10 ⁻¹⁵ g/mL)	$^{239}\text{Pu}/^{238}\text{U}$ concentration ratio	^{239}Pu concentration (10 ⁻¹⁵ g/mL)	Deviation (%)
0.01	10.1	1.0×10^{-3}	10.1 ± 0.59	0.52
0.10	10.1	1.0×10^{-4}	10.3 ± 0.84	2.33
1.00	10.1	1.0×10^{-5}	9.66 ± 0.67	-4.23
10.0	10.1	1.0×10^{-6}	10.2 ± 0.80	1.41
100	10.1	1.0×10^{-7}	9.97 ± 0.79	-1.02
1000	10.0	1.0×10^{-8}	9.68 ± 0.82	-3.65
10,000	10.1	1.0×10^{-9}	9.51 ± 0.57	-6.56

Table 2Estimated ratios of $^{238}\text{UH}^+/\text{U}^+$ and $^{238}\text{UH}_2^+/\text{U}^+$ ratio, and sensitivity of ^{242}Pu in ICP-MS/MS measurement with the different reaction gas in comparison with the reported data by other works.

ICP-MS mode		$^{238}\text{UH}^+/\text{U}^+$ ratio ^a	$^{238}\text{UH}_2^+/\text{U}^+$ ratio ^a	^{242}Pu sensitivity (Mcps/(mg/L))	Reference
ICP-MS/MS –8900	No Gas	6.44×10^{-5}	3.01×10^{-8}	340	This study
	He	3.49×10^{-5}	6.35×10^{-9}	2170	
	O ₂ /He + He	4.82×10^{-9}	2.22×10^{-11}	813 ($^{242}\text{PuO}_2$)	
	CO ₂ + He	1.00×10^{-8}	1.80×10^{-11}	540	
ICP-MS/MS –8800	No Gas	3.09×10^{-5}	8.50×10^{-9}	320	[16]
	He	1.88×10^{-5}	4.05×10^{-9}	1030	
	NH ₃ /He + He	1.29×10^{-6}	2.78×10^{-10}	1170	
	O ₂	1.09×10^{-6}	1.54×10^{-10}	200 (^{242}PuO)	
	CO ₂ + He	1.15×10^{-8}	$<2.00 \times 10^{-11}$	340	
Q-ICP-MS		$(1.4\text{--}3.2) \times 10^{-5}$		80–250	[43,44]
MC-ICP-MS		1.8×10^{-5}	$(1.4\text{--}3.1) \times 10^{-7}$	1.8×10^4	[45]
SF-ICP-MS		$(1.1\text{--}40) \times 10^{-6}$		280–2800	[19,46,47]

Note.

^a The ratios were estimated based on the measured signal intensities at $m/z = 239$ and 240 as the contribution of $^{238}\text{UH}^+$ and $^{238}\text{UH}_2^+$ ions in comparison with the intensity of ^{238}U in the corresponding condition; For modes of no gas and with helium as reaction gas, the intensity of $^{238}\text{U}^+$ signal was used; for CO₂ + He and O₂/He + He modes, the intensity of $^{238}\text{U}^+$ signal at 12.0 mL/min He was used.

Furthermore, the chemical separation procedure of plutonium can also remove the interference ions from the matrix. As mentioned above (Fig. S2), Pu was separated from the sample by leaching and co-precipitation, purified by UTEVA extraction chromatography, and the sample solution containing plutonium was diluted in a small volume of 3 mL 0.5 mol/L HNO_3 before ICP-MS/MS measurement. According to the measured result, most of the inferring elements can be removed by the chemical procedure. For 20 g soil samples, the concentration of U, Pb, Hg and Tl in the final solution are lower than $<0.1 \mu\text{g/L}$, $<40 \mu\text{g/L}$, $<0.001 \text{ ng/L}$ and $<0.2 \mu\text{g/L}$, respectively. It can be deduced that the high decontamination factor of $(1-2) \times 10^5$ was achieved for U in the large-size environmental samples (1–2 mg/L uranium).

The soil certified reference materials including IAEA-375 and IAEA-SOIL-6 were used to confirm the accuracy of the developed method for the measurement of ^{239}Pu and ^{240}Pu in the samples. The analytical results (Table 4) indicate that the measured concentrations of ^{239}Pu and ^{240}Pu agreed well with the reference values of those two certified reference materials. Therefore, the determination of ultra-trace levels ^{239}Pu and ^{240}Pu with high concentration interference elements (U, Pb, Hg, Tl, etc.) by the developed method is reliable.

Besides, the procedure blank was used to calculate the limit of detection and evaluate the interference introduction from the separation procedure. Table 4 shows that the very low signals of $0.20 \pm 0.09 \text{ cps}$ at $m/z = 271$ and $0.10 \pm 0.08 \text{ cps}$ at $m/z = 272$ ($n = 3$) in procedure blank are obtained, only 3 times higher than those measured in 0.5 mol/L HNO_3 solutions. With the sensitivity (813 Mcps/(mg/L)) and chemical yield (65–95%, average 80%) for plutonium isotopes, based on 3 times standard deviation of signal intensity for procedure blank samples ($n = 3$), the limit of detection (LOD) of the analytical method for ^{239}Pu and ^{240}Pu in 20 g soil samples were respectively 0.062 fg/g (0.14 $\mu\text{Bq/g}$) and 0.055 fg/g (0.47 $\mu\text{Bq/g}$), lower than those reported with different collision-reaction gas modes, such as $\text{NH}_3/\text{He} + \text{He}$ (0.55 fg/g and 0.09 fg/g) and $\text{CO}_2 + \text{He}$ (0.11 fg/g and 0.071 fg/g) using ICP-MS/MS (Agilent 8800) [15,16], also lower than those values for Q-ICP-MS (8.26 fg/g and 8.45 fg/g) [38] and SF-ICP-MS (0.6 fg/g and 0.07 fg/g) without collision cells [39].

3.4. Application of the developed method for determination of ^{239}Pu and ^{240}Pu in environmental samples

The developed method was applied to analysis of the ^{239}Pu and ^{240}Pu in five deep layer samples (20–40 cm) and one sub-surface layer sample (12–14 cm) collected from Xilingol region in China, far from human nuclear activities. The ^{239}Pu and ^{240}Pu activity concentrations (Table 4)

in the C1 profile show a gradual drop tendency from 0.054 mBq/g to $0.55 \times 10^{-3} \text{ mBq/g}$ and 0.031 mBq/g to $0.71 \times 10^{-3} \text{ mBq/g}$, respectively. At the same time, the ^{239}Pu and ^{240}Pu activity concentrations (Table 4) in the C2 profile were close to those values in the C1 profile with the same deep layer. The declining trend of $^{239,240}\text{Pu}$ concentrations with the depth in soil profile has also been reported for other undisturbed soil profiles, and the low $^{239,240}\text{Pu}$ level ($<0.01 \text{ mBq/g}$) have also been observed in the deep layer soil ($>20 \text{ cm}$) [40–42]. It is attributed to the low vertical migration of deposited plutonium due to its high association with organic matter and fine soil particles [40–42]. Moreover, the measured $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios in the six samples ranged from 0.151 ± 0.026 to 0.214 ± 0.080 , which is in agreement with the reported value from global fallout plutonium (0.178 ± 0.023) [3], suggest that the global fallout plutonium is the major source in the sampling sites.

Based on the pre-experiment about the measurement of uranium concentration, the uranium concentrations in the deep layer ($<20 \text{ cm}$) soil samples ranged from 2.5 $\mu\text{g/g}$ to 4.0 $\mu\text{g/g}$. This means that the ultra-trace level plutonium ($(0.55-5.28) \times 10^{-3} \text{ mBq/g}$ ^{239}Pu , corresponding to 0.22–2.2 fg/g ^{239}Pu) present in the deep layer soil samples with high uranium level up to 2.5–4.0 $\mu\text{g/g}$ gives a $^{238}\text{U}/^{239}\text{Pu}$ concentration ratio as high as 10^{10} . The measured results once again prove that the developed method including ICP-MS/MS measurement and chemical separation is reliable and accurate to determine the ultra-trace concentration ^{239}Pu and ^{240}Pu ($\leq 1 \mu\text{Bq}$) in the high uranium sample with the high $^{238}\text{U}/^{239}\text{Pu}$ concentration ratio of 10^{10} .

4. Conclusions

A CRC-ICP-MS/MS method in combination with chemical separation to accurately determine the ultra-trace level plutonium isotopes in the high uranium samples was developed. The interferences from the elements (U, Pb, Hg and Tl) on the measurement of ^{239}Pu and ^{240}Pu can be effectively suppressed by using an ICP-MS/MS with 0.15 mL/min $\text{O}_2/\text{He} + 12.0 \text{ mL/min He}$ as the collision-reaction gas. Based on the mass-shift mode of ICP-MS/MS, the interferences of the elements (Pb, Hg and Tl) of 200 $\mu\text{g/L}$ can be neglected. More important, as the dominant interferences, $^{238}\text{UHO}_2^+/^{238}\text{U}^{16}\text{O}_2^+$ ratio was reduced to 4.82×10^{-9} , 2–3 orders of magnitude lower than the previously reported values, and the abundance sensitivity (effect of the spectral peak tailing of $^{238}\text{UO}_2$ at $m/z = 271$) was improved to $<5 \times 10^{-12}$, 7 orders of magnitude better than that of other types of ICP-MS method. At the same time, the sensitivities of U and Pu were improved by a factor of 6.3 due to the ion focusing and buffer layer of He in the CRC. According to the measured result for the

Table 4

Determination of $^{239,240}\text{Pu}$ in certified reference material (IAEA-375 and IAEA-SOIL-6) and deep layer environmental samples using ICP-MS/MS under tandem- $\text{O}_2/\text{He} + \text{He}$ mode after UTEVA extraction chromatography.

Sample	Count for ^{239}Pu (cps) ^a	Count for ^{240}Pu (cps) ^b	^{239}Pu concentration (mBq/g)	^{240}Pu concentration (mBq/g)	$^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio	$^{239,240}\text{Pu}$ concentration (mBq/g)
0.5 mol/mL HNO_3	0.07 ± 0.06	0.03 ± 0.03				
Procedure blank	0.20 ± 0.09	0.10 ± 0.08				
IAEA-375	Measured value 24.5 ± 1.18	Measured value 7.14 ± 0.44	0.145 ± 0.020	0.129 ± 0.020	0.241 ± 0.019	0.274 ± 0.056
	Reference value [48–50]	Reference value [48–50]	0.113 ± 0.010	0.124 ± 0.020	0.299 ± 0.140	$0.26-0.34$
IAEA-SOIL-6	Measured value 177 ± 3.72	Measured value 33.8 ± 0.81	0.596 ± 0.077	0.415 ± 0.061	0.189 ± 0.006	1.011 ± 0.198
	Reference value [21,51]	Reference value [21,51]	0.645 ± 0.020	0.452 ± 0.027	$0.171-0.196$	$0.96-1.11$
C1-1	12–14 cm 40.3 ± 2.01	12–14 cm 6.33 ± 0.32	0.054 ± 0.008	0.031 ± 0.005	0.155 ± 0.011	0.085 ± 0.019
C1-2	20–22 cm 3.60 ± 0.32	20–22 cm 0.87 ± 0.21	$(5.28 \pm 0.82) \times 10^{-3}$	$(4.20 \pm 1.19) \times 10^{-3}$	0.159 ± 0.042	$(9.48 \pm 3.06) \times 10^{-3}$
C1-3	22–24 cm 2.13 ± 0.22	22–24 cm 0.78 ± 0.30	$(2.43 \pm 0.40) \times 10^{-3}$	$(3.21 \pm 1.34) \times 10^{-3}$	0.191 ± 0.077	$(5.64 \pm 2.53) \times 10^{-3}$
C1-4	38–40 cm 1.73 ± 0.23	38–40 cm 0.37 ± 0.07	$(0.55 \pm 0.10) \times 10^{-3}$	$(0.71 \pm 0.17) \times 10^{-3}$	0.214 ± 0.080	$(1.26 \pm 0.38) \times 10^{-3}$
C2-1	20–22 cm 1.95 ± 0.29	20–22 cm 0.47 ± 0.12	$(2.42 \pm 0.47) \times 10^{-3}$	$(1.85 \pm 0.54) \times 10^{-3}$	0.208 ± 0.061	$(4.27 \pm 1.50) \times 10^{-3}$
C2-2	22–24 cm 8.30 ± 0.46	22–24 cm 0.96 ± 0.16	$(1.59 \pm 0.22) \times 10^{-3}$	$(0.88 \pm 0.20) \times 10^{-3}$	0.151 ± 0.026	$(2.47 \pm 0.66) \times 10^{-3}$

Note.

^a —the count at m/z 271.

^b —the count at m/z 272.

simulation samples solutions, the ultra-trace level ^{239}Pu with the $^{239}\text{Pu}/^{238}\text{U}$ concentration ratio as low as 10^{-10} was accurately measured, suggesting that the elimination efficiency of uranium interference of 10^{-13} can be achieved in combination with the chemical separation using UTEVA resin. The developed analytical method has been validated by certified reference materials (IAEA-375 and IAEA-SOIL-6) and successfully applied to determine the ultra-trace level plutonium isotopes in the large-size soil samples. The results indicated that the developed method is practicable to the analysis of fg level ^{239}Pu in mg level uranium samples with U/Pu concentration ratio up to 10^{14} .

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2021.122652>.

Author contributions

The manuscript was written through the contributions of all authors. Weichao Zhang, Xiaolin Hou, Haitao Zhang, Yihong Xu and Haijun Dang designed the experiment, draft and revised the manuscript, Weichao Zhang, Jianfeng Lin, Sui Fang, Chen Li, Xiaowei Yi, Ning Chen, Wei Wang and Jiang Xu implemented the experiment including the chemical separation and ICP-MS/MS measurement. All authors have given approval to the final version of the manuscript.

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