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Article

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Determination of femtogram level plutonium isotopes in environmental and forensic samples with high-level uranium using chemical separation and ICP-MS/MS measurement

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Abstract: ICP-MS is becoming a competitive technique for the measurement of plutonium isotopes. However, the abundance sensitivity (tailing of ^{238}U to $m/z=239$ and 240), isobaric and polyatomic ions interferences (e.g. $^{238}\text{U}^1\text{H}^+$) are the most critical challenges for determination of low-level plutonium in high uranium samples. This work presents a new method to solve this problem using ICP- MS with two tandem quadrupole separators and dynamic collision/reaction cell combined with chemical separation. The interference of uranium hydrides ($^{238}\text{U}^1\text{H}^+$ and $^{238}\text{U}^1\text{H}_2^+$) was effectively eliminated using CO_2 as reaction gas by converting hydrides to oxides of uranium ions ($\text{UO}^+/\text{UO}_2^+$), but still keep the intensity of Pu^+ signal. The tailing interference of $^{238}\text{U}^+$ (abundance sensitivity) was intensively eliminated by significantly suppressing the $^{238}\text{U}^+$ signal using CO_2 as reaction gas and using two tandem quadrupole mass separators in the ICP-MS/MS. With these approaches, the overall interference of uranium was reduced to $<1 \times 10^{-8}$, which is 3 orders of magnitude better than the conventional ICP-MS. Combined with chemical separation with a decontamination factor of 10^5 for uranium, an overall factor of 10^{12} for elimination of uranium interference was achieved. The developed method was demonstrated to enable accurate determination of $<10^{-15}$ g/g level plutonium isotopes in environmental samples even in uranium debris sample with a U/Pu atomic ratio up to 10^{12} . The developed method was validated by the analysis of spiked solution and certified reference materials of soil.

Keyword: ICP-MS/MS, Collision/Reaction cell, reaction gas, $\text{CO}_2\text{-He}$, Plutonium isotopes, Uranium interference

INTRODUCTION

Plutonium is one of the most important transuranic elements in the environment due to its widely utilization and production in nuclear weapons and nuclear power reactors. Among plutonium isotopes, ^{239}Pu ($t_{1/2}=2.41\times 10^4$ y) and ^{240}Pu ($t_{1/2}=6.56\times 10^3$ y) are long-lived alpha-emitting radionuclides and the most important ones in the nuclear fuel and environment due to their high production and releases. Plutonium is a critical hazardous environmental pollutant due to its highly radiological toxicities and long-term persistent in the environment. Plutonium in the environment mainly originates from atmospheric nuclear weapons tests, nuclear fuel reprocessing plants and nuclear accidents ¹. The atmospheric nuclear weapons tests in 1945-1980 had released 6.5×10^{15} Bq of ^{239}Pu and 4.4×10^{15} Bq of ^{240}Pu into the environment, making it the major source of plutonium in the environment ^{1,2}. It is important to monitor it for evaluation of environmental impact of nuclear activities and possible radiological attack. The atomic ratios of $^{240}\text{Pu}/^{239}\text{Pu}$ vary with its sources depending on the production and release model, a ratio of 0.18 in the global fallout was observed all over the world ³, while, much lower ratios of 0.02-0.07 in nuclear weapons ^{4,5} and higher ratios of 0.23-0.47 in the releases from the nuclear accidents in Chernobyl and

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3 Fukushima and reprocessing plants of nuclear spent fuel of power reactors⁶⁻⁸ were measured. The
4 $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio can therefore be used as a fingerprint to identify the source term of the
5 plutonium and estimate the contribution of different nuclear activities to the environment⁹, as well
6 as for nuclear forensic investigation¹⁰. For these purposes, an analytical method for accurate
7 determination of low level ^{239}Pu and ^{240}Pu is necessary and very critical.
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10 ^{239}Pu and ^{240}Pu are conventionally measured by α -spectrometry, but it is unable to provide
11 $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio, because alpha spectrometry could not distinguish the alpha rays of ^{239}Pu
12 (5.15 MeV) and ^{240}Pu (5.16 MeV)¹¹. Meanwhile, it cannot measure ultra-low level ^{239}Pu and ^{240}Pu
13 of less than 0.1 mBq (or 5×10^{-14} g $^{239}\text{Pu} + ^{240}\text{Pu}$). With the rapid development of mass spectrometry,
14 it has being become an attractive technique for determination of long-lived radionuclides including
15 plutonium isotope in the past decades. Among them, AMS and TIMS have high sensitivity and
16 low detection limit, but they are not easily accessible and high cost¹⁰⁻¹³. ICP-MS has become a
17 widely used technique for the measurement of plutonium isotopes in environmental samples with
18 a comparable or better sensitivity compared with alpha spectrometry, low cost and ability to
19 measure $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio^{2,9,11,14,15}.
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38 The concentrations of plutonium isotopes ($^{239}, ^{240}\text{Pu}$) in environmental samples are normally
39 very low, to be $(0.04-400) \times 10^{-16}$ g/m³ in the atmosphere^{16,17}, $(1-900) \times 10^{-15}$ g/g in soil and sediment
40 ^{9,18-21}, and $(0.5-22) \times 10^{-16}$ g/L in seawater samples^{22,23}. The accurate determination of trace amount
41 of plutonium isotopes requires a high enrichment of plutonium from a large size of sample and
42 separation from matrices and interfering substances, as well as a sensitive measurement method.
43 The matrix elements (salt), peak tailing and hydrides of ^{238}U and the polyatomic ions^{2,24} are the
44 major interference in the measurement of plutonium isotopes using ICP-MS. Among them, the
45 interference of uranium including peak tailing and hydride ions of ^{238}U ($^{238}\text{U}^1\text{H}^+$ and $^{238}\text{U}^1\text{H}_2^+$) is
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the most critical one limiting the accurate measurement of ^{239}Pu and ^{240}Pu . Co-precipitation, ion exchange chromatography and extraction chromatography are often applied for separation and purification of plutonium in environmental samples, especially for removal of uranium¹⁵. Multi-steps separation, e.g. combination of ion exchange and extraction chromatography using different resins, such as TEVA+AG1- $\times 4$ ²⁰, UTEVA+TRU²⁵, TRU+ AG1- $\times 4$ ²⁶ and TEVA+UTEVA+DGA¹⁸ has been used, and a decontamination factors of 10^5 - 10^7 for uranium have been achieved. However, this is still not sufficient for the determination of ultra-trace level of plutonium in high uranium samples (with U/Pu atomic ratio $>10^{10}$), e.g. deep seawater, deep soil and sediment, uranium debris and scrap sample of nuclear fuel for forensics ($^{238}\text{U}/^{239}\text{Pu} > 1 \times 10^{10}$). In addition, the multi-columns combination also make the chemical separation more complicated and time consuming.

HR-ICP -MS and ICP-MS-MC have been used for determination of plutonium isotopes and other actinides^{18, 45}. The most attractive feature of these instruments for measurement of plutonium isotope is its high sensitivity, a count rate of 6×10^7 cps/ppb U was reported by using Apex-ICP-SF-MS in low resolution model¹⁸, which is nearly one order of magnitude higher than ICP-MS or ICP-MS/MS instrument. Although an improved abundance sensitivity (up to 10^{-6} - 10^{-7}) can be reached in high resolution model, but still much lower than ICP-MS/MS instrument. Due to the small difference of mass between $^{238}\text{U}^1\text{H}$ and ^{239}Pu ($\Delta m/m = 2.7 \times 10^{-5}$), the HR-ICP-MS instrument could not effectively remove the interference of uranium hydrides in the measurement of plutonium isotopes. The dynamic collision/reaction cell (DRC) technology in the ICP-MS has shown a powerful feature to eliminate polyatomic ions. Different reaction gasses, such as He, O_2 , N_2O , NH_3 and CO_2 have been proposed for removing uranium hydride²⁷⁻³¹. We had investigated the application of NH_3 -He as reaction gas in the ICP-MS measurement of plutonium isotopes, and

found that the elimination efficiency of uranium hydrides was improved by a factor of 15 compared to the ordinary method without reaction gas¹⁴, which is still not sufficient for the determination ultra-low level plutonium in the presence of high uranium. No detailed report on the application of other reaction gasses for ICP-MS measurement of femtogram level plutonium isotopes in samples containing high-level uranium is available. Desolvation technique (e.g. APEX) was often applied for reduced uranium hydride and improve the counting efficiency in the ICP-MS measurement of plutonium and other actinides^{6, 18, 45}. It was found that this system can significantly improve the counting sensitivity by a factor of 7-10. Although an improvement on removal of uranium hydrides was observed in our experiment, but only 2-3 times suppression of UH^+ ions signal, which is not sufficient for the determination of plutonium isotopes in high uranium samples. ICP-MS/MS with two quadrupole mass separators has been applied for determination of plutonium isotopes^{14, 31}. With this instrument, a better abundance sensitivity of up to 10^{-10} can be achieved, which can significantly remove the interference of the ^{238}U peak tailing in the measurement of ^{239}Pu and ^{240}Pu ¹⁴.

This work aims to develop a rapid and accurate analytical method for determination ultra-trace level plutonium isotopes in high-level uranium samples by using a simple chemical separation combined with ICP-MS/MS equipped with DRC, in order to determine femtogram level ^{239}Pu and ^{240}Pu in high uranium samples such as seawater, soil, sediment and nuclear fuel debris. The most effort is dedicated to effectively eliminate interference of uranium using DRC with different reaction/collision gasses.

EXPERIMENTAL SECTION

Instrument and setup. Triple quadrupole ICP-MS (Agilent 8800, Agilent Technologies, Japan)

was used for the measurement, it equips with an octopole DRC between two quadrupole mass separators. The first quadrupole (Q1) acts as an ion-guide to select the target ions (isotopes). The collision/reaction gas is introduced into the DRC, to reacts with the entered ions for eliminating the interfering ions by forming new ions. The second quadrupole (Q2) acts as another mass-filter for selecting the target ions after the reactions in the DRC for their measurement in the followed detector (Figure S1). The instrument was tuned using ^{238}U (1.0 ppb natural uranium) and plutonium (^{239}Pu , 1.0 ppt) standard solutions, the optimized parameters are shown in Table S1. The standard, simulated solution (isotope spiked) and separated plutonium samples were prepared in 0.5 mol/L HNO_3 for measurement, In^{3+} (InCl_3 , 1.0 ppb) solution was used as an internal standard which was injected to the nebulizer using a T-valve. The sample and internal standard solution were introduced using peristaltic pump at 0.5 mL/min. Pt skimmer cone, s-lens, MicroMist Micro Flow 200 nebulizer and hot plasma were used in the measurement of plutonium isotopes. Four gas lines (CO_2 , He, NH_3 -He (9.88% NH_3), and O_2 gas, 99.999% purities) to the DRC were used in this work.

Chemical reagents and samples. ^{242}Pu standard solution (70.0 pg/mL in 2.0 mol/L HNO_3) was prepared from ^{242}Pu standard reference materials of NIST-SRM-3443I (National Institute of Standard Technology, Gaithersburg, Maryland, USA). ^{239}Pu working solution (398 pg/mL in 2 mol/L HNO_3) was prepared from a calibrated ^{239}Pu solution supplied by DTU Nutech (Denmark), and the standard solution of uranium was prepared from IRMM-184 uranium standard solution (Institute for reference materials and managements, Geel, Belgium). AG 1- $\times$ 4 anion exchange resin (100–200 mesh, chloride form, Bio-Rad Laboratories Inc., California, USA) was used for separation of plutonium. All chemical reagents used in this work were high pure analytical grade reagents and prepared using deionized water (18.2 $\text{M}\Omega\cdot\text{cm}$).

To investigate the possible reactions in the reaction cell with different reaction gasses and to

optimize parameters for effectively eliminating interference of $^{238}\text{U}^1\text{H}^+$ for measurement of $^{239}\text{Pu}^+$, uranium (20 and 1000 ng/mL) and ^{239}Pu (10 pg/mL) standard solutions were prepared, some m/z values were selected in Q1 and Q2 as shown in Table S2 for ICP-MS measurement.

Two standard reference materials, Irish Sea sediment (IAEA-385) and soil (IAEA-327) were analyzed for verification of the method. Meanwhile, 4 surface soil samples (0–5 cm) and 2 deep soil samples (25–30 cm) collected from background areas in China were analyzed in this work.

Chemical separation of plutonium from environmental samples. A chemical separation procedure using acid leaching, co-precipitation and chromatographic separation (Figure S2) was used for separation of plutonium from the sample matrix and interfering radionuclides, the detailed method has been reported elsewhere¹⁴ and presented in the Supporting Information. In brief, a known amount of ^{242}Pu (3.4 pg) was spiked as chemical yield tracer to soil or sediment sample, the sample was leached with *aqua regia*. Ammonium was added to the leachate precipitate plutonium with iron and other metals as hydroxides. Plutonium in the precipitate was dissolved, converted to Pu^{4+} and prepared in 1.0 mol/L HNO_3 solution, which was loaded to a TEVA column. After rinsed the column with 1.0 mol/L HNO_3 and 6 mol/L HCl , plutonium on the column was eluted with 40 mL of 0.1 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 2 mol/L HCl . After decomposed $\text{NH}_2\text{OH}\cdot\text{HCl}$ and prepared in 3.0 mL of 0.5 mol/L HNO_3 solution, plutonium isotopes were measured using ICP-MS/MS.

RESULTS AND DISCUSSION

The collision/reaction gasses including He , $\text{NH}_3\text{-He}$, O_2 and CO_2 were investigated for elimination of uranium hydride ($^{238}\text{U}^1\text{H}^+$ and $^{238}\text{U}^1\text{H}_2^+$). The results (Figure 1) show that injection of helium gas into the DRC could not suppress the intensities of $^{238}\text{U}^+$ and $^{238}\text{U}^1\text{H}^+$ signal, but even

increased $^{238}\text{U}^+$ and $^{238}\text{U}^1\text{H}^+$ signal intensities with the increased flow rate of helium (Figure 1). This indicates that UH^+ ion could not be destroyed through collision reaction with helium.

Figure 1 Variation of the intensities of Pu^+ , PuO^+ , U^+ , UH^+ , UO^+ ion with the flow rate of helium injected to the DRC. For Pu^+ and PuO^+ , the $m/z=239$ was selected in the Q1 (first quadrupole) and $m/z=239$ and 255 in the Q2 (second quadrupole), respectively; for U^+ and UO^+ , the $m/z=238$ was selected in the Q1 and $m/z=238$ and 254 in the Q2, respectively; for UH^+ , $m/z=239$ was selected in both Q1 and Q2.

The results using O_2 as a reaction gas (Figure S3) show that the intensity of $^{238}\text{U}^+$ signal was significantly reduced with the increased flow rate of O_2 . Meanwhile, intensive signals of $^{238}\text{U}^{16}\text{O}^+$ ($m/z=254$) was measured when the flow rate of O_2 was increased to 0.5 ml/ml , and then decreased

with an increased flow rate of O_2 . This implies that $^{238}U^{16}O_2^+$ was formed with increased O_2 flow rate²⁹. The intensity of $^{238}U^1H^+$ ion also significantly reduced with the increased flow rate of O_2 . The remarkably increased intensity of $^{238}U^{16}O^+$ was observed when $m/z = 239$ ($^{238}U^1H$) was selected in Q1, but UHO^+ ions (Q1(238)/Q2(255)) was still measurable (Table S3). This indicates that U^+ and UH^+ ions react with O_2 to form UO^+ and UO_2^+ , and a small fraction of UH^+ ion was converted to UHO^+ . However, the intensity of Pu^+ ion also decreased in the same order of magnitude as $^{238}U^+$ with the injection of O_2 . Meanwhile, the intensities of PuO^+ signal increased with the increased flow rate of O_2 (Figure S3). This indicates that Pu^+ can also react with O_2 to form PuO^+ . In this case, the peak tailing of $^{238}U^{16}O^+$ and $^{238}U^{16}O^1H^+$ and $^{238}U^{16}O^1H_2^+$ become the dominant interferences for measurement of $^{239}Pu^{16}O^+$ and $^{240}Pu^{16}O^+$ ions, causing a less efficient elimination of the uranium interference.

Ammonia as a reaction gas has been investigated for the elimination of uranium interference¹⁴. It was observed that the intensity of UH^+ signal decreased with the flow rate of NH_3 (Figure S4) due to the formation of UNH_2^+ ions ($m/z=255$) (Table S3)¹⁴. While, the intensity of Pu^+ was not significantly reduced with the increased flow rate of NH_3 (Figure S4, Table S4) due to no reaction of Pu^+ with NH_3 . Therefore, NH_3 was successfully used to eliminate uranium interference¹⁴. However, UH^+ could not be completely removed, makes it not sufficient for the determination of low-level ^{239}Pu in high uranium samples.

CO_2 has also been proposed as a reaction gas for the elimination of the uranium interference^{27,28,30}. The results show that CO_2 highly suppressed the signals of $^{238}U^+$ and $^{238}U^1H^+$, while only part of Pu^+ reacted with CO_2 to form PuO^+ ions (Figure 2).

Elimination of uranium interference using CO_2 -He as reaction/collision gasses. It was observed that the intensities of U^+ ions decreased exponentially with the increased flow rate of

CO₂ injected to the DRC by 3 orders of magnitude when the flow rate of CO₂ was increased to 1.2 ml/min (Figure 2). Meanwhile, extensive UO⁺ signal was observed (Figure 2, Table S3), indicating U⁺ and UH⁺ react with CO₂ to form UO⁺. Following a rapidly increased intensity of UO⁺ signal with the injection of CO₂, the intensity of UO⁺ signal gradually decreased with the increased flow rate of CO₂ from 0.5 ml/min (Figure 2), this should be attributed to the formation of UO₂⁺ ions, and the intensity of UO₂⁺ ion increased with the increased flow rate of CO₂²⁷.

Figure 2 Variation of the intensities of U⁺, UH⁺, UO⁺, Pu⁺ and PuO⁺ ions with the flow rate of CO₂ with 8 ml/min helium injected to the DCR. For U⁺ and UO⁺ ions, m/z=238 was selected in Q1 (the first quadrupole) and m/z = 238 and 254 in the Q2 (second quadrupole), respectively; For UH⁺, Pu⁺ and PuO⁺, m/z=239 was selected in Q1 and m/z=239, 239, and 255, respectively. ²³⁹Pu standard solution of 2.0 pg/ml and Uranium standard solution of 20 ng/mL and 1000 ng/mL (for UH⁺/UH⁺) were used in this measurement.

It is interesting that the intensity of UH^+ ion shows the same exponentially decreased trend as U^+ ion with the increased flow rate of CO_2 (Figure 2), indicating that UH^+ can be destroyed by reaction with CO_2 in the DRC through the formation of UO^+ and UO_2^+ . About 10^4 reduction of UH^+ signal was achieved at 1.3 ml/min. CO_2 injection, further increasing flow rate of CO_2 does not significantly reduce the UH^+ signal.

It was observed that the intensity of Pu^+ signal decreases slowly with the increased flow rates of CO_2 , and reach to about 1/3 intensity of the original one (without CO_2 but only 8 ml/min He) at 1.2 ml/ml CO_2 (Figure 2). Meanwhile, the increased signal of $^{239}\text{Pu}^{16}\text{O}^+$ (at $m/z=255$) was observed with the injection of CO_2 . However, with the increased flow rate of CO_2 , the intensity of PuO^+ signal showed a similar declining trend as Pu^+ signal (Figure 2). This should be attributed to the enhanced formation of PuO_2^+ at a high flow rate of CO_2 in the DRC ²⁷.

It was found that the flow rate of helium has a significant influence on the intensity of Pu^+ signal (Figure 3). With 1.2 ml/min CO_2 , the intensity of Pu^+ signal increased with the increased flow rate of helium and reaches to a maximum value at 8 ml/min, and then decreases. Therefore, the flow rate of 8 ml/min for helium was selected as assistant/second gas. Meanwhile, the intensity of PuO^+ ions decreases significantly with the increased flow rate of helium. This might be attributed to the reduced reactivity of CO_2 with Pu^+ ion to form PuO^+ in the increased flow rate of helium, and consequently causing the increased Pu^+ signal intensity. It was also observed that the intensities of Pu^+ and U^+ signals increased for about 3 times when only helium was injected from 0 to 8.0 ml/min and then keep relative constant when further increasing the flow rate of He (Figure 1). Therefore, the increased intensity of Pu^+ with the increased flow rate of helium in the presence of CO_2 should be attributed to the helium injected to the DRC. Pu^+ ions from the plasma through the first quadrupole has a relatively high and large expanded kinetic energy (0-20 eV), elastic

collision of these ions with helium atoms reduced their kinetic energy to about 2 eV and narrowed distribution of the ion kinetic energy (0-3 eV), which significantly improved ion focusing, and consequently increased the numbers of ions counted in the detector, i.e. measurement sensitivity^{8,31}. The improved intensity of Pu^+ by collision focusing of the injected helium gas compensate the loss of Pu^+ signal intensity by partly forming PuO^+ in the DRC, and makes the intensity of Pu^+ signal in the same level (about 3.4×10^5 cps/ppb) at the reaction gasses of 1.2 mL/min CO_2 -8 mL/min He as that in no gas mode. It was also observed that the intensities of UH^+ signal significantly decreased with the increased flow rate of helium (Figure 3), which helps the elimination of uranium hydride interference. Based on the above experimental results, 1.2 mL/min CO_2 – 8.0 mL/min He was selected as the optimal condition for the elimination of uranium interference and sensitive measurement of plutonium isotopes.

Figure 3 Influence of flow rate of helium injected to the DRC with 1.2 ml/min CO_2 on the intensities of the Pu^+ , PuO^+ , U^+ , UH^+ and UO^+ ions. $^{238}\text{UH}^+ / ^{238}\text{UO}^+$ in the legend means that $m/z=239$ ($^{238}\text{UH}^+$) was selected for the first Quadrupole (Q1) and $m/z=255$ ($^{238}\text{U}^{16}\text{O}^+$) was

selected in the second quadrupole (Q2) mass separator, others are the similar meaning. The left figure is the measurement of a uranium standard solution, and the right figure is the measurement of a ^{239}Pu standard solution. Note: the uncertainties presented in some data points are too small to be clearly visible.

These observations also indicate that CO_2 has high reactivity with U^+ and UH^+ compared to Pu^+ , this can be explained by the thermodynamics of oxidation reaction of U^+ and Pu^+ with oxidizing reagents (i.e. NH_3 , CO_2 and O_2). The reported efficiencies of the reactions of Pu^+ (related to the bond dissociation energy of PuO^+ and the oxidizing reagents of CO_2 and O_2) are 0.003 for CO_2 and 0.27 for O_2 . While the efficiencies of reactions of U^+ with CO_2 and O_2 are 0.29 and 0.72, respectively ³². The higher of the reaction efficiency is the stronger of the reactivity, this explains why only fraction of Pu^+ was oxidized to PuO^+ by CO_2 , but almost all U^+ was oxidized to UO^+ and UO_2^+ by CO_2 and O_2 . The relative high reaction of CO_2 with U^+ compared to Pu^+ could be also explained by the reaction kinetics ³². The oxidation of U^+ and Pu^+ requires to promote the ground-state ions to a reactive configuration containing two unpaired non-f-orbital electrons. U^+ requires only 0.04 eV energy to promote a 7s electron to 6d orbit, while Pu^+ needs to promote a 5f electron to 6d orbit, which requires higher energy of 1.08 eV, and shows an activation energy barrier to the reaction. Therefore, only a fraction of Pu^+ could be oxidized to PuO^+ by CO_2 and the formation of PuO^+ increases with the increased flow rate of CO_2 .

Both peak tailing of ^{238}U and the uranium hydride ion ($^{238}\text{U}^1\text{H}^+$) contribute to the signal at $m/z = 239$ in ICP-MS measurement of ^{239}Pu . But it is impossible to discriminate and directly measure these two contributions. Since the ^{238}U peak causes tailings to both low (m-1) and high (m+1) sides in the mass spectrum (abundance sensitivity), and the low side (m-1) normally receives a higher

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3 tailing contribution compared to the high ($m+1$) side⁸. Monitoring the signal intensity at $m/z=237$
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5 can estimate the contribution of ^{238}U tailing to the $m/z=239$. Table 1 shows the measured
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7 abundance sensitivities of ^{238}U to $m/z=237$ in single quadrupole mode (the Q1 was closed and only
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9 Q2 was used) and tandem quadrupoles modes ($m/z=237$ was selected in both quadrupoles) and
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11 using different collision/reaction gasses in the DRC. The best abundance sensitivity of 4×10^{-7} in
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13 the single quadrupole mode was achieved by using $\text{CO}_2\text{-He}$ as reaction gas. This is mainly
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15 attributed to the highly removal of $^{238}\text{U}^+$ ions by oxidizing it to UO^+ and UO_2^+ , collision focusing
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17 of $^{238}\text{U}^+$ by helium atoms in the DRC also helps to reduce the tailing contribution to $m/z=237$ and
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19 239⁸. An extensive suppression of tailing effect (abundance sensitivity) down to $<1.6\times 10^{-11}$ was
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21 achieved by using two tandem quadrupole mode and 1.2 mL/min CO_2 -8.0 mL/min He as the
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23 reaction/collision gas. The intensity of signal at $m/z=237$ was reduced to undetectable (not
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25 significant difference compared to the procedure blank) when measuring a 1×10^{-6} g/mL uranium
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27 solution. It means that the interference of $^{238}\text{U}^+$ tailing to the measurement of ^{239}Pu and ^{240}Pu is
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29 negligible, and the major interference should be the hydrides of uranium ($^{238}\text{U}^1\text{H}^+$ and $^{238}\text{U}^1\text{H}_2^+$).
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36 The level of elimination of uranium hydride ($^{238}\text{U}^1\text{H}^+$ and $^{238}\text{U}^1\text{H}_2^+$) using ICP-MS/MS with
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38 different reaction gas was estimated by measurement of a 1×10^{-6} g/mL uranium standard solution
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40 and monitoring the intensity of signals at $m/z=239$ and 240. The signal intensities at $m/z=239$ and
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42 240 were compared with the highest intensity of $^{238}\text{U}^+$ in the corresponding condition, i.e. the $^{238}\text{U}^+$
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44 ion intensity in no gas was used for the modes of no gas and O_2 , and the $^{238}\text{U}^+$ ion intensity in 8.0
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46 mL/min helium gas was used for the modes of He, $\text{NH}_3\text{-He}$ and $\text{CO}_2\text{-He}$. The results (Table 2)
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48 shows that both O_2 and $\text{NH}_3\text{-He}$ mode can reach to $^{238}\text{U}^1\text{H}^+/^{238}\text{U}^+$ ratio of 1×10^{-6} , and the best
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50 elimination of uranium hydride was achieved by using 1.2 mL/min CO_2 -8.0 mL/min He as reaction
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52 gas in ICP-MS/MS measurement, reach to 1.2×10^{-8} for $^{238}\text{U}^1\text{H}^+/^{238}\text{U}^+$ ratio and $< 2\times 10^{-11}$ for
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$^{238}\text{U}^1\text{H}_2^+/^{238}\text{U}^+$. They are 50-1000 times improvement compared to the previously reported values in the ICP-MS measurement of ^{239}Pu using different instruments and setups (Table 2). This value is also 100 times better than the newly reported ICP-MS/MS using $\text{NH}_3\text{-He}$ as reaction gas ¹⁴. This result suggests that this method can measure ^{239}Pu in a sample solution containing at least 10^7 times higher uranium. In summary, the developed method for determination of ^{239}Pu and ^{240}Pu using ICP-MS/MS is more than 10^4 times better than the ordinary single quadrupole mass separator in view of elimination of the $^{238}\text{U}^+$ tailing and more than 1000 times better in view of the elimination of uranium hydrides interference by employing $\text{CO}_2\text{-He}$ as reaction gas in the DRC, which is also effective for removal of interference of other polyatomic ions.

Verification of the developed method for determination of low-level ^{239}Pu and ^{240}Pu in high uranium solution. Simulated solution containing 1×10^{-14} g/mL of ^{239}Pu and $(0.010\text{-}988)\times 10^{-9}$ g/mL of uranium was analyzed using the developed ICP-MS/MS method. The results (Table 3) show that the ^{239}Pu in a concentration as low as 1×10^{-14} g/mL can be accurately measured in a solution containing 1×10^{-7} g/mL uranium (i.e. Pu/U atomic ratio of 1×10^{-7}) using 1.2 mL/min $\text{CO}_2\text{-}8.0$ ml/min He as reaction gas. This confirms that the developed method can be successfully used to measure ultra-low level ^{239}Pu in more than 10^7 times higher uranium solution. Even for a solution with Pu/U atomic ratio down to 1×10^{-8} , ^{239}Pu was measured to be $(13.0\pm 2.4)\times 10^{-15}$ g/mL after a correction by subtraction of the contribution of uranium hydride ($^{238}\text{U}^1\text{H}^+$), which is reasonably good agreement compared with the spiked ^{239}Pu of 10.1×10^{-15} g/mL. While, for the ICP-MS/MS methods using other reaction gas, ^{239}Pu of 10×10^{-15} g/mL can be only accurately measured in the sample with less than 1×10^{-9} g/mL uranium, i.e. with Pu/U atomic ratio higher than 1×10^{-5} . This demonstrated that the elimination efficiency of uranium hydride was improved

by a factor of more than 100 in the developed method compared to the previously reported methods.

In ICP-MS measurement, other polyatomic ions with $m/z=239$ and 240 also interfere with the measurement of ^{239}Pu and ^{240}Pu . The most important ones are those polyatomic ions of Hg, Tl and Pb with Ar, Cl, S and O, 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 ²⁴. The analysis of 5×10^{-7} g/mL Pb and Tl in 0.1 mol/L HCl and 0.5 mol/L HNO₃ solution showed that the signal intensities observed at $m/z=239$ are less than 0.07cps and 0.03 cps for HCl and HNO₃ media, respectively, which is not significantly higher than that observed in the blank of only 0.5 mol/L HNO₃ solution (Table S5). This indicates that the developed ICP-MS/MS method can also sufficiently eliminate the interferences of these polyatomic ions of Pb and Tl. However, a remarkable interferences of polyatomic ions of Hg was observed when no reaction gas or helium gas was applied. A significant elimination of this interference for the measurement of ^{239}Pu and ^{240}Pu was achieved when CO₂-He and NH₃-He were applied as reaction gas. The measurement of 5×10^{-7} g/mL Hg in 0.1 mol/L HCl - 0.5 mol/L HNO₃ solution showed an signal intensity of 1.9 ± 0.3 cps at $m/z=239$, but not significant increased signal at $m/z=239$ for Hg-3% HNO₃ compared to the 3% HNO₃ blank was observed. Meanwhile, no significantly increased signal at $m/z=240$ was observed for Hg-0.1 M HCl-3%HNO₃ and Hg-3% HNO₃, compared to 3% HNO₃ blank solution was observed. The 27 times higher signal intensity at $m/z=239$ observed in Hg-0.1M HCl-3% HNO₃ solution compared to that in Hg-3% HNO₃ and 3% HNO₃ blank (0.07 cps) indicates that $^{202}\text{Hg}^{37}\text{Cl}^+$ polyatomic ion cannot be completely eliminated in the reaction cell using CO₂-He gas. The measurement results also showed that Hg does not form HgO^+ in the presence of CO₂ in the reaction cell, implying a less efficiency to decompose the HgCl^+ ions in the reaction cell by oxidation reaction. Therefore,

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3 Cl⁻ or HCl should be avoid/eliminated in the finally prepared plutonium solution for ICP-MS
4 measurement. In the HNO₃ media, no measurable interference of Hg, Tl and Pb to the measurement
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6 of plutonium isotopes was observed in the developed method.
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10 Chemical separation was applied to pre-concentrate plutonium from big samples and remove
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12 matrix and interfering elements. In this work, plutonium was first leached by acids followed by
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14 separation of plutonium using co-precipitation and extraction chromatography using TEVA resin
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16 (Figure S2), and finally prepared in a small volume (3 mL) of HNO₃ solution without salt (< 1 mg)
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18 for ICP-MS measurement. Meanwhile, uranium and other interfering elements (Pb, Hg, Tl, Cl)
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20 can also highly removed. A decontamination factor of (1-2)×10⁵ for uranium was achieved.
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24 A simulated solution containing 4 mg/mL ²³⁸U and 4×10⁻¹⁵ g/mL ²³⁹Pu (²³⁹Pu/²³⁸U = 1×10⁻¹²)
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26 was analyzed using the developed method employing chemical separation for determination of
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28 ²³⁹Pu and ²⁴²Pu. The analytical results (Table S6) show that the measured ²³⁹Pu value
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30 ((4.12±0.31)×10⁻¹⁵, (4.23±0.32)× 10⁻¹⁵ g/mL and (4.16±0.35)× 10⁻¹⁵ g/mL) agree well with the spiked
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32 value ((4.10±0.05)×10⁻¹⁵ g/mL), confirmed that the developed analytical method including chemical
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34 separation and ICP-MS/MS measurement is reliable for determination of femtogram level ²³⁹Pu in
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36 an extremely high uranium samples (with a U/Pu ratio up to 1×10¹²).
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40 Two certified reference materials (soil IAEA-327 and sediment IAEA-385) were analyzed for
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42 ²³⁹Pu and ²⁴⁰Pu using the developed method. The analytical results (Table 4) show that the
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44 measured concentrations of ²³⁹Pu and ²⁴⁰Pu agree well with the reference values and the reported
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46 values³³ in IAEA-385 (p<0.01). ²³⁹Pu and ²⁴⁰Pu were not certified in IAEA-327, but the analytical
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48 results in this work agree very well with the reported values in the literature for IAEA-327 ³⁴
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50 (p<0.01). These analytical results confirmed that the analytical method presented in this paper is
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52 reliable for the determination of low-level ²³⁹Pu and ²⁴⁰Pu in environmental and forensic samples
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with high-level uranium.

Procedure blanks were prepared and analyzed using the same method as the samples, the analytical results (Table 4) show constantly small signals of 0.15 ± 0.03 cps at $m/z=239$ and 0.04 ± 0.02 cps at $m/z=240$ ($n=3$, procedure blanks), only 2 times higher than those measured in 0.5 mol/L HNO_3 solution (used for preparing samples). The signal at $m/z=239$ and 240 might be attributed to trace amount of plutonium contamination in the laboratory environment and chemical reagents, instrumental memory of plutonium as well as the contribution of hydride of uranium in the blanks. The analytical results of plutonium in the samples were always corrected by subtraction of the procedure blanks prepared and measured in the same batch as the samples.

Using the measured sensitivity of 340 cps/ppt for plutonium isotopes by the developed ICP-MS/MS method and the chemical yield of plutonium (average 85%) in the entire separation procedure, the limit of detection of the method can be calculated as 3 times of standard deviation of the signal intensity of the procedure blanks to be 0.93 fg for ^{239}Pu and 0.62 fg for ^{240}Pu (for 3.0 mL sample solution), which are corresponding to 2.1 μBq for ^{239}Pu and 5.2 μBq for ^{240}Pu . The limit of detection was further improved by employing a high efficiency introduction system of APEX Ω for about 5 times to 0.2 fg for ^{239}Pu and 0.1 fg for ^{240}Pu , because the counting efficiency of plutonium was increased by a factor of 8 (2650 cps/ppt ^{239}Pu) and uranium hydrides was further suppressed by a factor of 2. Although the count rates of $^{239}\text{Pu}^+$ (0.65 ± 0.15 cps) and $^{240}\text{Pu}^+$ (0.25 ± 0.08 cps) in the procedure blank also enhanced, but the variations/relative standard deviations of signal intensities of blanks were improved.

Application of the developed method for determination of ^{239}Pu and ^{240}Pu in environmental samples. Two deep (25-30 cm) and four surface (0-5 cm) soil samples collected from the

background areas at sites without visible disturbance in China were analyzed using the developed method for ^{239}Pu and ^{240}Pu . The analytical results (Table 4) show a big variation of concentrations of ^{239}Pu and ^{240}Pu in the surface soil ranging from 0.07 to 0.13 mBq/g for ^{239}Pu and 0.048-0.087 mBq/g for ^{240}Pu , corresponding to a range of 0.12-0.22 mBq/g for $^{239,240}\text{Pu}$, which fall into the reported range of $^{239,240}\text{Pu}$ concentrations in the surface soil in the background areas in China (0.07-0.85 mBq/g for $^{239,240}\text{Pu}$)^{35,36}. The concentrations of ^{239}Pu and ^{240}Pu in the deep soil are more than 50 times lower than that determined in the surface soil in the same site. Exponentially decreased plutonium concentrations with the depth in soil core and much low concentrations of $^{239,240}\text{Pu}$ (<0.01 mBq/g) in the deep soil (> 25 cm) in undisturbed soil profiles have reported in many locations^{19,37,38}. This is attributed to the high association of fallout plutonium with organic substance and minerals, causing a low vertical migration of fallout plutonium in soil core³⁹. The measured $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios in these samples are around 0.18, which agree well with the reported ratio of the global fallout plutonium³, indicating the dominant global fallout source of plutonium in these samples.

For accurate determination of low-level plutonium isotopes in deep soil samples, 30 g soil sample was analyzed. In this case, a large amount of uranium presents in the samples. The uranium concentrations in the deep soil samples were measured to be 3.0-3.5 $\mu\text{g/g}$, meaning more than 90 μg uranium presents in these samples with ultra-low level plutonium ($(1-5) \times 10^{-3}$ mBq/g ^{239}Pu , corresponding to 0.4-2 fg/g ^{239}Pu), with $^{238}\text{U}/^{239}\text{Pu}$ atomic ratios up to 10^{10} . This demonstrates that the developed method enables to accurately determine as low as 1 μBq ^{239}Pu and ^{240}Pu in such a 10^{10} folds higher uranium samples.

Conclusions

An analytical method based on chemical separation and ICP-MS measurement was developed for accurate determination of ultra-low level plutonium isotopes in high uranium samples. The most critical interference of uranium to the measurement of ^{239}Pu and ^{240}Pu was effectively eliminated by using an ICP-MS/MS instrument and 1.2 mL/min CO_2 -8.0 mL/min helium as reaction gas. The interference of uranium to the measurement of ^{239}Pu ($^{238}\text{U}^1\text{H}^+/^{238}\text{U}^+$ ratio) was reduced to 10^{-8} , which is more than 2 orders of magnitude better than the previously reported ICP-MS methods. Combined with the chemical separation using extraction chromatography with TEVA resin, an overall elimination efficiency of uranium interference reaches 10^{12} , making it enable to accurately determine femtogram level plutonium isotopes in samples containing milligram uranium. Uranium hydride interference was efficiently eliminated by reaction with CO_2 in the DRC to completely convert U^+ and UH^+ to UO^+ and UO_2^+ ions. While, plutonium reacts only partly with CO_2 , enabling it to be measured as Pu^+ ion. The abundance sensitivity (tailing of ^{238}U at $m/z=239$) was improved to $< 2 \times 10^{-11}$, which is 10^6 times better than the conventional ICP-MS method. The measurement sensitivity for plutonium isotopes was improved by a factor 3 by collision focusing using high flow rate of helium into the DRC. Analysis of spiked samples demonstrated the reliability of the developed method for accurate determination of femtogram of ^{239}Pu in high uranium samples with U/Pu atomic ratio up to 10^{12} . The developed method has been verified by the analysis of certified reference materials, and successfully applied for the determination of environmental samples with femtogram level plutonium isotopes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information, which is available free of charge on the ACS Publications website. A detailed analytical method, 6 tables and 4 figures are presented.

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Notes

The authors declare no competing financial interest.

Author Contributions

The manuscript was written through contributions of all authors. XH designed the experiment, drafted and revised the manuscript, WZ and YW implemented the experiment, and WZ also participated in draft preparation and prepared all figures. All authors have given approval to the final version of the manuscript.

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Table 1 Results of abundance sensitivity of ²³⁸U at m/z=237 in different mode of ICP-MS

Mode #	ICP-MS (single quadrupole)	ICP-MS/MS (tandem quadrupoles)
No Gas	2.36×10 ⁻⁴	3.47×10 ⁻⁸
He	8.08×10 ⁻⁵	8.19×10 ⁻⁹
NH ₃ -He	6.88×10 ⁻⁶	5.50×10 ⁻¹⁰
O ₂	1.76×10 ⁻⁵	2.29×10 ⁻¹¹
CO ₂ -He	4.14×10 ⁻⁷	< 2×10 ⁻¹¹

No gas: no collision/reaction gas was applied; He: 8.0 mL/min helium as collision gas; NH₃/He: 1.2 mL/min NH₃ – 8 mL/min He; O₂: 2.0 mL/min O₂; CO₂-He: 1.2 mL/min – 8.0 mL/min He.

Table 2 Efficiency of uranium hydrides elimination ($^{238}\text{UH}^+ / ^{238}\text{U}^+$ and $^{238}\text{UH}_2^+ / ^{238}\text{U}^+$ ratios) and ^{239}Pu sensitivity in ICP-MS/MS measurement with the different reaction gas and comparison with the reported data of other methods

ICP-MS mode		$^{238}\text{UH}^+ / ^{238}\text{U}^+$ ratio #	$^{238}\text{UH}_2^+ / ^{238}\text{U}^+$ ratio #	^{239}Pu sensitivity (Mcps/ppm)	Reference
No Gas		3.09×10^{-5}	8.50×10^{-9}	320	
He		1.88×10^{-5}	4.05×10^{-9}	1030	
ICP-MS/MS	NH ₃ /He	1.29×10^{-6}	2.78×10^{-10}	1170	This study
	O ₂	1.09×10^{-6}	1.54×10^{-10}	200 (^{239}PuO)	
	CO ₂ /He	1.15×10^{-8}	$< 2.00 \times 10^{-11}$	340	
Q-ICP-MS		$(1.4-3.2) \times 10^{-5}$		80-250	40,41
HR-ICP-MS		4×10^{-5}		~350	42
ID-HR-ICP-MS		$(1.35-1.78) \times 10^{-5}$		~500	43
MC-ICP-MS		1.8×10^{-5}	$(1.4-3.1) \times 10^{-7}$	1.8×10^4	44
SF-ICP-MS		$(1.1-19.5) \times 10^{-6}$		280-2800	45,46

The ratios were estimated using the measured signal intensities at $m/z=239$ and 240 as the contribution of $^{238}\text{U}^1\text{H}^+$ and $^{238}\text{U}^1\text{H}_2^+$ ions in comparison with the intensity of $^{238}\text{U}^+$ in the corresponding condition; For modes of no gas and helium as reaction gas, the intensity of $^{238}\text{U}^+$ signal was used; for CO₂-He and NH₃-He modes, the intensity of $^{238}\text{U}^+$ signal at 8 ml/min He as collision gas, and for O₂ mode, the intensity of $^{238}\text{U}^+$ signal of no gas mode was used.

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Table 3 Determination of ²³⁹Pu in simulated high uranium solution using ICP-MS/MS with different reaction gasses

Sample solution			Measurement results of ²³⁹ Pu							
U conc.	²³⁹ Pu conc.	²³⁹ Pu/ ²³⁸ U	No gas		He gas ¹⁾		NH ₃ -He gas ²⁾		CO ₂ -He gas ³⁾	
10 ⁻⁹ g/mL	10 ⁻¹⁵ g/mL	atomic ratio	²³⁹ Pu conc.	Division	²³⁹ Pu conc.	Division	²³⁹ Pu conc.	Division	²³⁹ Pu conc.	Division
			10 ⁻¹⁵ g/mL		10 ⁻¹⁵ g/mL	%	10 ⁻¹⁵ g/mL	%	10 ⁻¹⁵ g/mL	%
0.010	10.1	1.01×10 ⁻³	10.0±0.6	-1.0%	10.8±0.8	6.9%				
0.10	10.1	1.01×10 ⁻⁴	11.7±0.7	15.8%	10.7±0.9	5.9%	9.92±0.71	-2.0%		
1.00	10.1	1.01×10 ⁻⁵	47.1±1.4	370%	22.3±1.6	120%	11.4±0.7	13.9%	10.0±0.8	-1.0%
10.0	10.1	1.01×10 ⁻⁶					22.3±1.6	121%	10.4±0.9	3.0%
100.0	10.1	1.01×10 ⁻⁷							11.1±0.8	11.9%
988.0	10.1	1.01×10 ⁻⁸							24.4±1.6	140%

1) 8.0 mL/min helium gas as reaction gas; 2) 1.2 mL/min NH₃-8.0 mL/min helium; 3) 1.2 mL/min CO₂-8.0 mL/min He.

Table 4 Determination of certified reference materials (IAEA-327 and IAEA-385) and environmental soil samples using ICP-MS/MS under tandem- CO_2/He mode with anion exchange chromatography

Sample Code	Sampling location/depth	Sample mass, g	Chemical yield	^{239}Pu counts (cps)	^{240}Pu counts (cps)	^{239}Pu concentration (mBq/g)	^{240}Pu concentration (mBq/g)	$^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio	Reference
3% HNO_3	Instrument blank			0.072±0.023	0.021±0.012				
Blank	Procedure blank			0.153±0.033	0.042±0.023				
IAEA-327	Certified reference	1.9-2.0	85-90%	23.7±0.9	4.54±0.21	0.333±0.019	0.232±0.017	0.191±0.018	This study
soil	material					0.35±0.02	0.25±0.02	0.19±0.02	34
IAEA-385	Certified reference	1.7-1.8	85-90%	92.6±2.5	16.6±0.5	1.77±0.09	1.13±0.08	0.175±0.015	This study
sediment	materials					1.92	1.18		Reference value
						1.79±0.28	1.15±0.14	0.174±0.032	14,33
GDHY-1	Guangdong (25-30 cm)	20.0-20.5	85-90%	1.10±0.11	0.193±0.022	$(1.30\pm0.22)\times10^{-3}$	$(0.852\pm0.145)\times10^{-3}$	0.178±0.043	This study
GDHY-2	Guandong (0-5 cm)	2.0-2.1	85-90%	5.75±0.23	0.923±0.111	0.074±0.005	0.048±0.007	0.177±0.028	This study
NMTL	Inner Mongolia (25-30 cm)	10.0-10.1	82-87%	2.05±0.12	0.172±0.018	$(5.10\pm0.71)\times10^{-3}$	$(3.42\pm0.52)\times10^{-3}$	0.183±0.038	This study
SXXA	Shaanxi, (0-5 cm)	3.5-3.6	82-87%	11.4±0.5	2.17±0.21	0.090±0.009	0.061±0.009	0.184±0.033	This study
FJND	Fujian, (0-5 cm)	4.0-4.1	82-87%	15.7±0.8	2.35±0.25	0.109±0.009	0.075±0.012	0.187±0.034	This study
ZJWZ	Zhejiang (0-5 cm)	2.0-2.1	85-90%	10.3±0.7	1.87±0.19	0.132±0.018	0.087±0.014	0.180±0.038	This study

Note: the results presented here are average of three replicates of each certified reference material, and the uncertainties are estimated from the all analytical process with coverage factor of $k=1$

TOC

222x121mm (150 x 150 DPI)

Figure 1 Variation of the intensities of Pu^+ , PuO^+ , U^+ , UH^+ , UO^+ ion with the flow rate of helium injected to the DRC. For Pu^+ and PuO^+ , the $m/z = 239$ was selected in the Q1 (first quadrupole) and $m/z = 239$ and 255 in the Q2 (second quadrupole), respectively; for U^+ and UO^+ , the $m/z = 238$ was selected in the Q1 and $m/z = 238$ and 254 in the Q2, respectively; for UH^+ , $m/z = 239$ was selected in both Q1 and Q2.

220x168mm (300 x 300 DPI)

Figure 2 Variation of the intensities of U+, UH+, UO+, Pu+ and PuO+ ions with the flow rate of CO2 with 8 ml/min helium injected to the DCR. For U+ and UO+ ions, m/z=238 was selected in Q1 (the first quadrupole) and m/z = 238 and 254 in the Q2 (second quadrupole), respectively; For UH+, Pu+ and PuO+, m/z=239 was selected in Q1 and m/z=239, 239, and 255, respectively. ²³⁹Pu standard solution of 2.0 pg/ml and Uranium standard solution of 20 ng/mL and 1000 ng/mL (for UH+/UH+) were used in this measurement.

221x165mm (300 x 300 DPI)

Figure 3 Influence of flow rate of helium injected to the DRC with 1.2 ml/min CO₂ on the intensities of the Pu⁺, PuO⁺, U⁺, UH⁺ and UO⁺ ions. $^{238}\text{UH}^+ / ^{238}\text{UO}^+$ in the legend means that $m/z=239$ ($^{238}\text{UH}^+$) was selected for the first Quadrupole (Q1) and $m/z=255$ ($^{238}\text{U}^{16}\text{O}^+$) was selected in the second quadrupole (Q2) mass separator, others are the similar meaning. The left figure is the measurement of a uranium standard solution, and the right figure is the measurement of a ^{239}Pu standard solution. Note: the uncertainties presented in some data points are too small to be clearly visible.

264x178mm (300 x 300 DPI)