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Published in:
Talanta

Link to article, DOI:
[10.1016/j.talanta.2018.05.051](https://doi.org/10.1016/j.talanta.2018.05.051)

Publication date:
2018

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Xing, S., Zhang, W., Qiao, J., & Hou, X. (2018). Determination of ultra-low level plutonium isotopes (^{239}Pu , ^{240}Pu) in environmental samples with high uranium. *Talanta*, 187, 357-364.
<https://doi.org/10.1016/j.talanta.2018.05.051>

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Determination of Low-level Plutonium Isotopes (^{239}Pu , ^{240}Pu) in Environmental Samples with High Uranium

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ABSTRACT

In order to measure trace plutonium and its isotopes ratio ($^{240}\text{Pu}/^{239}\text{Pu}$) in environmental samples with a high uranium, an analytical method was developed using radiochemical separation for separation of plutonium from matrix and interfering elements including most of uranium and ICP-MS for measurement of plutonium isotopes. A novel measurement method was established for extensively removing the isobaric interference from uranium ($^{238}\text{U}^1\text{H}$ and $^{238}\text{UH}_2^+$) and tailing of ^{238}U , but significantly improving the measurement sensitivity of plutonium isotopes by employing NH_3/He as collision/reaction cell gasses and MS/MS system in the triple quadrupole ICP-MS instrument. The results show that removal efficiency of uranium interference was improved by more than 15 times, and the sensitivity of plutonium isotopes was

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increased by a factor of more than 3 compared to the conventional ICP-MS. The mechanism on the effective suppress of ^{238}U interference for ^{239}Pu measurement using NH_3 -He reaction gas was explored to be the formation of UNH^+ and UNH_2^+ in the reactions of UH^+ and U^+ with NH_3 , while no reaction between NH_3 and Pu^+ . The detection limits of this method were estimated to be 0.55 fg mL^{-1} for ^{239}Pu , 0.09 fg mL^{-1} for ^{240}Pu . The analytical precision and accuracy of the method for Pu isotopes concentration and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio were evaluated by analysis of sediment reference materials (IAEA-385 and IAEA-412) with different levels of plutonium and uranium. The developed method were successfully applied to determine ^{239}Pu and ^{240}Pu concentrations and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios in soil samples collected in coastal areas of eastern China.

Keywords: ICP-MS/MS, Collision/reaction cell, NH_3/He model, Plutonium isotopes, Environmental samples, isobaric interference of uranium

1. Introduction

Plutonium (Pu) isotopes especially ^{239}Pu ($t_{1/2}=24100 \text{ y}$) and ^{240}Pu , ($t_{1/2}=6561 \text{ y}$) are anthropogenic radionuclides with high radiological toxicity and long-term retention in the environment [1-7]. Plutonium was released to the environment as a result of human nuclear activities including atmospheric nuclear weapons testing, nuclear fuel reprocessing and nuclear accidents. Global fallout of the atmospheric nuclear weapons testing during 1950s-1970s is the main source of plutonium in the environment, with an estimated total amount of $1.26 \times 10^{16} \text{ Bq}$ of $^{239+240}\text{Pu}$, which is more than 2 orders of magnitude higher than that released from all other sources [8-11]. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios carry important signature reflecting the source terms of plutonium [5, 6, 12, 13],

and thus it was considered to be an excellent indicator for identification of the source term and for nuclear forensics.

Due to the ultralow Pu concentration in environmental samples down to 0.01-2 mBq g⁻¹ ((4-900)×10⁻¹⁵ g g⁻¹) for ²³⁹Pu concentrations in environmental soil [14-16], 0.001-10 μBq m⁻³ ((0.04-400)×10⁻¹⁶ g m⁻³) for ²³⁹Pu concentrations in the atmosphere [10, 17, 18], 0.02-5 μBq L⁻³ (0.9-22)×10⁻¹⁶ g L⁻¹) for ²³⁹Pu concentrations in the water [19], it is a challenge to accurately measure Pu isotopes in the environmental samples, which requires to analyze the large sample and using high sensitivity measurement instrument. Traditionally, alpha spectrometry is the major technique used for the measurement of ²³⁹⁺²⁴⁰Pu total activity in most radiochemistry labs [20-23], wherein the isotopic composition of ²³⁹Pu and ²⁴⁰Pu is difficult to be obtained because of similar energies of ²³⁹Pu and ²⁴⁰Pu. In the recent years, with the development of mass spectrometric techniques [7, 15, 24, 25] (e.g., ICP-MS, AMS, TIMS and RIMS) in combination with modern radiochemical separation techniques (e.g., extraction chromatography), the determination of individual ²³⁹Pu and ²⁴⁰Pu activity in different environmental samples can be achieved. Although the determination of Pu isotopes has been undertaken by the high sensitivity and low detection limit of AMS [24, 26], TIMS [27] and RIMS [28], due to less availability and high cost, it is not yet applied for analysis of large number of environmental samples.

Due to the significantly improved sensitivity and the ability for measurement of isotope ratio, precision and accuracy for isotope ratio measurements ICP-MS has been successfully applied to the determination of Pu isotopes in environmental samples [15, 29-31]. In this measurement technique, due to resolution of ICP-MS is not sufficient to discriminate ²³⁹Pu⁺ (²⁴⁰Pu⁺) from ²³⁸UH⁺ (²³⁸UH₂⁺) the interference of the uranium

hydride interferences ($^{238}\text{UH}^+$ and $^{238}\text{UH}_2^+$) and the peak tailing from $^{238}\text{U}^+$ (abundance sensitivity) is the major challenge for accurate measurement of Pu isotopes in environmental samples. Because, the uranium concentration in environmental sample is more than 7 orders of magnitude higher than the Pu concentration, a chemical separation with a sufficiently high decontamination factor (10^5 - 10^7) for uranium have to be applied before measurement using ICP-MS.

Collision/reaction cell technology applied to ICP-MS has shown a great potential to remove these interferences [32-36]. This work aims to develop a high sensitive and accurate analytical method for determination low level plutonium isotopes (^{239}Pu and ^{240}Pu) using a triple quadrupole ICP-MS equipped with collision/reaction cell using NH_3/He as reaction gasses, combined with radiochemical separation of plutonium from sample matrix and purification it against from uranium. The developed method was validated by analysis of reference materials with different level of plutonium and uranium, and applied to determine plutonium isotopes in soil samples collected in coastal areas of eastern China.

2. Materials and methods

2.1. ICP-MS/MS instrument and measurement parameters

A triple quadrupole ICP-MS (Agilent 8800 ICP-MS/MS, Agilent Technologies, Tokyo, Japan) with an octapole collision/reaction cell situated between two quadrupole mass filters (Q1 and Q2) was used to measure plutonium isotopes. A schematic diagram of the ICP-MS instrument is presented in Fig. 1. NH_3 -He mixture gasses were introduced into the reaction cell at a flow rate of 1.2 mL min^{-1} for NH_3 and 8 mL min^{-1} for He. The sample uptake rate was 0.4 mL min^{-1} . The instrument was tuned each time using $\sim 2 \text{ } \mu\text{g L}^{-1}$ uranium and $\sim 1 \text{ ng L}^{-1}$ plutonium (^{242}Pu) standard solution, the optimized instrumental parameters are shown in Table 1. 3.5 mL of sample solution in

0.5 mol L⁻¹ HNO₃ containing 1 µg L⁻¹ In(III) (in the form of InCl₃) as internal standard was measured. A 0.5 mol L⁻¹ HNO₃ solution was used as a washing solution between consecutive samples. No memory effects were observed for consecutive measurement of different level samples. The regression line of measured standard series of ²⁴²Pu was proven to be linear over a large range of 0.01 ng L⁻¹ to 30 ng L⁻¹ (R²=0.999).

2.2. Chemical reagents and Samples

A stock solution of ²⁴²Pu (0.1037 Bq g⁻¹ in 2 mol L⁻¹ HNO₃) used as a chemical yield tracer of plutonium was prepared by dilution of NBL-CRM 130 purchased from New Brunswick Laboratory (Argonne, IL). Uranium standard solutions was purchased from NIST (Gaithersburg, MD). TEVA extraction chromatographic resin (100-150 µm particle size) was purchased from TRISKEM International (Bruz, France). AG 1-X4 anion exchange resins (100–200 mesh particle size) in chloride form was purchased from Bio-Rad Laboratories Inc. (California, USA). All reagents, including HNO₃, HCl, NaOH, NH₃·H₂O, NH₂OH·HCl, K₂S₂O₅ and FeCl₃·6H₂O used in this work were of analytical reagent grade. All solutions were prepared using Milli-Q water (18 MΩ·cm, Sartorius Stedim Biotech, Aubagne Cedex, France).

Two standard reference materials including Irish Sea sediment (IAEA-385) and Pacific Ocean sediment (IAEA-412) were analyzed in this work for plutonium isotopes for method validation. The Irish Sea sediment IAEA-385 was collected from the Irish Sea in 1995 [37]. The Pacific Ocean sediment (IAEA-412) was collected at 22°22'N, 152°40'E (water depth 5600 m) in the northwest Pacific Ocean in 1997 [38].

23 surface soil samples (0-5 cm) was collected from coastal area in northeast China. After removal of small stones and root of vegetation, all soil samples were air-dried, grounded and sieved through a 200-mesh sieve. Before analysis, the sample was

dried in an oven at 100°C for overnight, which was used for determination of $^{239+240}\text{Pu}$ activities and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios.

2.3. Chemical separation of plutonium from environmental samples

Plutonium isotopes in environmental solid samples were separated and purified by anion exchange chromatography and extraction chromatography[25, 30], respectively. Fig. 2 shows the schematic diagram of the chemical procedure for separation of plutonium using two chromatographic methods. Briefly, 10-20 g of sample was first ashed at 450 °C overnight to decompose the organic matter. After spiking 5 mBq ^{242}Pu as a chemical yield tracer, 200-400 mL of *aqua regia* was added, and the sample was acid leached for 2 hours at 200°C on a hot plate. The leaching step was repeated once for 30 min at 200 °C. Plutonium in the leachate was coprecipitated with iron hydroxides by adding $\text{NH}_3 \cdot \text{H}_2\text{O}$ to adjust pH 8-9 in order to remove major matrix components (e.g. Ca, Mg, etc.). After centrifugation, the precipitate was washed with 6 mol/L NaOH to remove amphoteric components (e.g. V, Al, etc.). The precipitate was dissolved with a few milliliters of concentrated HCl, 300 mg of $\text{K}_2\text{S}_2\text{O}_5$ was added to the sample solution and stirred for 20 min. to reduce the overall plutonium to Pu(III). $\text{NH}_3 \cdot \text{H}_2\text{O}$ was then added to adjust pH 8-9. The obtained precipitate was separated by centrifuge and once again dissolved with a few milliliters of concentrated HCl. 5-10 mL of concentrated HNO_3 was added to oxidize Pu(III) to Pu(IV) by NO_2^- contained in the HNO_3 solution. For separation of plutonium using anion-exchange chromatography using AG 1-X4 resin, the sample solution was prepared in 8 mol/L HNO_3 medium and loaded to an AG 1-X4 resin column (1 cm in diameter and 15 cm in length). After sequentially rinsing the column with 100 mL of 8 mol L^{-1} HNO_3 and 100 mL of 6 mol L^{-1} HCl, to remove uranium, thorium and matrix elements, Pu was finally eluted with 100 mL of 0.5 mol L^{-1} HCl. For separation of plutonium using extraction chromatography using TEVA

resin, the sample solution was prepared in 1 mol L⁻¹ HNO₃ medium and loaded to a TEVA resin column (2 mL, 8 mm in diameter and 40 mm in height). After rinsing the column with 100 mL of 1 mol L⁻¹ HNO₃ and 60 mL of 6 mol L⁻¹ HCl, plutonium was finally eluted with 40 mL solution of 0.1 mol/L NH₂OH·HCl in 2 mol L⁻¹ HCl. Both eluates were evaporated to dryness on a hot-plate followed by addition of few drops of concentrated HNO₃ and heating to decompose the hydroxylamine and eliminate the hydrochloric acid.

The residue was finally dissolved in 0.5 mol L⁻¹ HNO₃ and transferred to a 5 mL plastic tube in a final volume of 3.5 mL. ²³⁹Pu, ²⁴⁰Pu, ²⁴²Pu as well as ²³⁸U were measured by ICP-MS/MS. Chemical yields of plutonium in the procedures were measured using ²⁴²Pu to be 80–90%.

3. Results and discussion

3.1. Elimination of interference of uranium using NH₃/He as reaction gas in the collision/reaction cell

The ²³⁸U⁺ peak tailing and the uranium hydrides (²³⁸UH⁺ and ²³⁸UH₂⁺) formation are the primary interference for measurement of ²³⁹Pu and ²⁴⁰Pu. Compared to conventional ICP-MS, the ICP-MS/MS equips an additional quadrupole mass filter (Q1) in front of the octopole reaction cell, which can be used to select only analyte mass (m/z=239), so almost all matrix and interfering ions can be removed/rejected. The selected ions is then transferred to the collision cell for further elimination of interfering ions (e.g. ²³⁸U¹H⁺). Afterwards, the second quadrupole mass filter (Q2) is used to allow only the selected ions after reactions in the collision/reaction cell enter to the detector. Therefore, this approach has a potential to efficiently solve the problem of conventional ICP-MS that the complicated matrix ions can produce new interferences after directly entering the reaction/collision cell.

Fig. 3 shows the measured intensities of possible ions transmitted/formed in the reaction cell filled with NH₃/He gasses at a flow rate of 0.6 mL min⁻¹ for NH₃ and 8 ml/min for He. When 19.77 µg L⁻¹ of ²³⁸U standard solution was injected to the ICP-MS, the mass 238 was selected in Q1 and ions with m/z of 238 (U⁺), 239 (UH⁺), 240 (UH₂⁺), 250 (UC⁺), 252 (UN⁺), 253(UNH⁺), 254(UNH₂⁺) and 255 (UOH⁺) was selected in Q2 and measured in the detector. The measured intensities of these ions (counts/s) and their relative proportions are shown in Fig. 3a. It can be seen that the dominant species of uranium formed in collision cell is UNH⁺, accounting for 59.47% of all uranium species, followed by UNH₂⁺ (8.29%), indicating ²³⁸U⁺ ion can react with NH₃ to form UNH⁺ and UNH₂⁺ ions. While, U⁺ ion still accounts for 31.36% of all species of uranium, indicating the reaction of U⁺ with NH₃ is sufficiently high enabling to completely eliminate U⁺. It is also observed that other species such as UH⁺ (0.17%), UH₂⁺ (<0.01%), UC⁺ (<0.01%), UN⁺ (0.44%), UOH⁺ (0.26%) , are minor, indicating the low formation of UH⁺ and other ions in the reaction cell. Based on this result, the reactions of U⁺ with NH₃ in the reaction cell filled with NH₃-He can be proposed as:

When 19.78µg L⁻¹ of ²³⁸U standard solution was injected and the mass 239 was selected in Q1 and ions with m/z of 238 (U⁺), 239 (UH⁺), 250 (UC⁺), 252 (UN⁺), 253(UNH⁺) and 254(UNH₂⁺) was selected in Q2 and measured in the detector. When the m/z 239 was selected for both Q1 and Q2, the measured intensity of mass 239 was only 1.61 cps ppb⁻¹ U (Fig. 3b), which is 8.17% of the intensity of 239 mass (19.7 cps/ppb⁻¹ U) when only He gas (with the same flow rate) was applied. Indicating that NH₃ can eliminate more than 90% UH⁺ in the reaction cell. The possible reactions are:

This is confirmed by the increased intensity of m/z 253 (UNH^+) and 254 (UNH_2^+) observed in the NH_3 -He model compared to He model.

When 0.97 ng L^{-1} of ^{239}Pu standard solution was injected and the 239 mass was selected in Q1, the formed species in the reaction cell filled with NH_3 -He is dominated by 239 (Pu^+) with a intensity of 1080 cps/ppt ^{239}Pu , accounting for >98.6% of all species of Pu, other species of plutonium such as PuN^+ (<0.01%), PuNH^+ (0.56%), PuNH_2^+ (0.56%) and PuNH_3^+ (0.28%) are minor (Fig. 3c). This result indicates that Pu^+ is inert to NH_3 in the reaction cell. The reaction of plutonium ion in the reaction cell can be therefore proposed to be:

Fig. 4 shows the variation of measured intensities (cps) of m/z 238 and 239 with the concentration of ^{238}U standard solution by using ICP-MS/MS at a flow rate of 1.2 mL min^{-1} for NH_3 and 8 mL min^{-1} for He (a) and conventional signal quadrupole ICP-MS without reaction gas (b). In the ICP-MS/MS with NH_3 -He reaction gas, the measured sensitivity of ^{239}Pu is $\sim 490 \text{ Mcps ppm}^{-1}$, which is about 1.5 times higher than that of the conventional ICP-MS without reaction gas ($330 \text{ Mcps ppm}^{-1}$). In this condition, the abundance sensitivity of ^{238}U to m/z 239 (tailing of $^{238}\text{U}^+$ plus $^{238}\text{U}^1\text{H}^+$) was estimated to be 2.2×10^{-6} , which is one order of magnitude better than that of the conventional ICP-MS (3.2×10^{-5}). These results show that the $^{238}\text{U}^+$ peak tailing at m/z 239 and the $^{238}\text{UH}^+$ interference can be significantly improved by using ICP-MS/MS with NH_3 -He as reaction gas.

Measurements using ICP-MS with He as collision gas show that the sensitivity of ^{239}Pu can be improved to $1020 \text{ Mcps ppm}^{-1}$, which is the same as that of ICP-MS/MS with NH_3 -He as reaction/collision gas, but 3 times higher than that of ICP-MS without collision gas. The significantly improved sensitivity for plutonium isotopes should be attributed to focusing feature of collision gas in the collision/reaction cell. However, the abundance sensitivity of ^{238}U to m/z 239 (tailing of ^{238}U peak and $^{238}\text{U}^1\text{H}$) of the

ICP-MS with He collision gas (2.8×10^{-5}) was not significantly improved compared to the ICP-MS/MS with NH_3 -He as reaction gas. This indicates that UH^+ ion is not easily decomposed by collision with He in the collision cell.

In brief, with effective mass filters (Q1 and Q2) and ion/molecule ion reaction with NH_3 , the interference of $^{238}\text{U}^+$ peak tailing and $^{238}\text{UH}^+$ ion interference can be removed, which is important for the accurate measurement of ^{239}Pu and ^{240}Pu . The detection limit of the method, based on six times the standard deviation of the blank solution ($0.5 \text{ mol L}^{-1} \text{ HNO}_3$), were estimated to be 0.55 fg mL^{-1} for ^{239}Pu and 0.092 fg mL^{-1} for ^{240}Pu in 3.5 mL of sample solution respectively. These values are lower than those reported for HR-ICP-MS (4 fg mL^{-1} for ^{239}Pu and 3 fg mL^{-1} for ^{240}Pu in the 2.4 mL sample solution) [39], but slightly higher than those reported for SF-ICP-MS equipped with an APEX-Q high-efficiency sample introduction system (0.11 fg mL^{-1} for ^{239}Pu and 0.08 fg mL^{-1} for ^{240}Pu in the 0.5 mL sample solution) [40-42]. If the ICP-MS/MS is equipped with an APEX-Q high-efficiency sample introduction system, the detection limit could be improved to 0.1 fg mL^{-1} for ^{239}Pu and 0.02 fg mL^{-1} for ^{240}Pu .

3.2. Measurement of Pu isotopes in standards, environmental samples

The reliability and detection limit of the method for the measurement of Pu isotopes, especially low-level Pu isotopes, are affected by many parameters, such as the chemical yield of Pu isotopes, instrument background, procedure blank and removal of interferences. The chemical yield of plutonium during the separation procedure was measured to be more than 80% by using ^{242}Pu as yield tracer, which was spiked into the sample at the beginning of the chemical separation, this is sufficient to ensure accurate measurement of ^{239}Pu and ^{240}Pu in low-level environmental sample. The instrumental background was assessed using $0.5 \text{ mol L}^{-1} \text{ HNO}_3$, and the procedure blank was prepared using the same procedure as the sample. The results of ^{238}U , ^{239}Pu

and ^{240}Pu count rates in background, procedure blanks, samples, and reference materials are presented in Table 2. The measured ^{238}U and ^{239}Pu count rates in $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ by ICP-MS/MS are 3.00 cps and 0.10 cps, which are at least 1-2 orders of magnitude lower than those in the procedure blanks, environmental samples and reference materials (IAEA-385 and IAEA-412). The ^{239}Pu and ^{240}Pu count rates in the procedure blank are 0.55 cps and 0.04 cps, which are 1-3 orders of magnitude lower than those in the samples and reference materials. This low instrument background and procedure blank level ensure the reliability of the analytical results of ^{239}Pu and ^{240}Pu in the low-level samples. The activity concentration of ^{239}Pu and ^{240}Pu in different level environmental samples and reference materials range from 0.05 to 1.01 mBq g^{-1} . With the low-level counts rate of procedure blank, this results shows that no cross-contamination during the chemical separation and measurement. In addition, the measured constant low count rate of ^{239}Pu and ^{240}Pu in the blanks between each sample indicate no significant memory effects for consecutive measurement of different level samples by using 0.5 mol/L HNO_3 as washing solution.

The analytical results of reference materials show that the measured activity concentration of ^{239}Pu and ^{240}Pu and are $1.81 \pm 0.07 \text{ mBq g}^{-1}$ and $1.17 \pm 0.10 \text{ mBq g}^{-1}$ in the IAEA-385 and $0.37 \pm 0.01 \text{ mBq g}^{-1}$ and $0.23 \pm 0.01 \text{ mBq g}^{-1}$ in the IAEA-412, respectively (Table 2), which are in a good agreement with the certified values of $1.79 \pm 0.28 \text{ mBq g}^{-1}$ and $1.15 \pm 0.14 \text{ mBq g}^{-1}$ of IAEA-385 [37] and $0.36 \pm 0.016 \text{ mBq g}^{-1}$ and $0.24 \pm 0.016 \text{ mBq g}^{-1}$ of IAEA-412 [38], respectively. All these features prove that the developed method for determination of low level ^{239}Pu and ^{240}Pu in the environmental samples is reliable and accurate.

3.3. Determination of Pu isotopes in ocean sediment reference material (IAEA-385 and IAEA-412) treated by anion exchange chromatography and extraction chromatography

Although ICP-MS/MS with $\text{NH}_3\text{-He}$ as reaction gas can significantly improve the elimination of the interferences, the accurate determination of ^{239}Pu and ^{240}Pu in low-level sample is still not possible without chemical separation because of extremely high concentration of uranium compared to plutonium and complicated and high salt environmental samples such as soil and sediment. The most often applied techniques for separation and purification of plutonium from sample matrix and uranium are ion exchange chromatography and extraction chromatography using TEVA resin [25, 30, 43-45]. The measured ^{238}U count rates and Pu isotopes concentration in the separated solutions of IAEA-385 and IAEA-412 sediment using anion-exchange chromatography and TEVA extraction chromatography using the developed method with ICP-MS/MS are presented in the Table 3. The results show that the measured ^{238}U count rate (674 cps for IAEA-385 and 390 cps for IAEA-412) by using TEVA extraction chromatography were 1-2 orders of magnitude lower than those by using anion-exchange chromatography (10000 cps for IAEA-385 and 49400cps for IAEA-412). For the analysis of high plutonium level samples such as IAEA-385, the discrepancy between the measured values and the certified values of ^{239}Pu and ^{240}Pu by using anion-exchange chromatography were only 2.79% for ^{239}Pu and 0.87% for ^{240}Pu , which are similar with the discrepancy by using TEVA extraction chromatography (1.12% for ^{239}Pu and 1.74% for ^{240}Pu). However, for analysis of low plutonium sample such as IAEA-412, the discrepancy of ^{239}Pu and ^{240}Pu by using anion-exchange chromatography were 16.7% for ^{239}Pu and 8.37% for ^{240}Pu , which are much bigger than the discrepancy of TEVA extraction chromatography (2.78% for ^{239}Pu and 4.17% for ^{240}Pu). This results indicate that the less decontamination factor for uranium in the separation procedure using anion-exchange chromatography cause a higher

interference of uranium in the measurement of plutonium isotopes, and therefore less reliable of the analytical results. In this case, a high performance extraction chromatography using TEVA resin is preferred to provide reliable analytical results, especially for low plutonium and high uranium level samples. However, both chemical separation method can be well applied for determination of plutonium isotopes in samples with low uranium and relative high plutonium concentrations.

3.4. Distribution of plutonium in surface soil and its source in the coastal region of East China

The developed method was applied to measure ^{239}Pu and ^{240}Pu in surface soil samples collected from the coastal areas of eastern China, where most of Chinese nuclear power plants are located. The $^{239+240}\text{Pu}$ activity concentrations (Fig. 5a) in the surface soil samples in this area ranged from 0.011 to 0.27 mBq g^{-1} , with the average of 0.11 mBq g^{-1} , which are close to that in Northern China (0.04-0.15 mBq g^{-1}) [46]. From the perspective of $^{239+240}\text{Pu}$ activities, there is no significant environmental influence during the operation nuclear power plants in this area. The $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio of soil samples ranged from 0.16 to 0.22 (Fig. 5b), with the average of 0.19, which are typical global fallout value of 0.180 ± 0.014 in the northern hemisphere (71–30°N) [47] and similar to the measured $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio of 0.186 ± 0.008 in soils of Hubei in central China [24], indicating a predominantly global atmospheric fallout source. These results provide an important baseline data for assessment of the possible influence of Chinese nuclear power plants in the future in this region.

4. Conclusion

Based on the chemical reaction between uranium and NH_3 in the collision/reaction cell and effective mass selection by mass filters (Q1 and Q2), the interferences of $^{238}\text{U}^+$ peak tailing and uranium hydrides can be suppressed by more than 2 orders of magnitude compared to conventional ICP-MS. The measured ^{239}Pu and ^{240}Pu concentrations in the reference materials (IAEA-385 and IAEA-412) are in a good agreement with the certified values. The separation method of TEVA extraction chromatography is more effective for determination of plutonium in low-level samples compared to the anion-exchange chromatography. The $^{239+240}\text{Pu}$ concentrations and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios in environmental soil samples collected from the coastal area of eastern China was determined using the developed method. The measured $^{239+240}\text{Pu}$ concentrations ($0.011\text{--}0.27\text{ mBq g}^{-1}$) and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios ($0.16\text{--}0.22$) indicate a global atmospheric fallout source of plutonium in this region.

Acknowledgement

Financial supports from the Ministry of Science and Technology of China (2015FY110800), the National Natural Science Foundation of China (11605206), as well as State Key Laboratory of Loess and Quaternary Geology are gratefully acknowledged.

Conflicts of interest

Authors declare no conflicts of interest.

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Caption of tables:

Table 1 Instrument parameters and data acquisition settings for ICP-MS/MS measurement of plutonium isotopes.

Table 2 Analytical results of ^{238}U , ^{239}Pu and ^{240}Pu count rate and $^{239+240}\text{Pu}$ concentrations in background, procedure blanks, samples and standard reference materials separated using TEVA-extraction method and measured by ICP-MS/MS at a flow rate of 1.2 mL min^{-1} for NH_3 and 8 mL min^{-1} for He.

Table 3 Analytical results of ^{238}U count rates and Pu isotopes concentrations in IAEA-385 and IAEA-412 certified reference materials separated by anion-exchange chromatography and TEVA extraction chromatography, respectively.

Table 1

Instrument parameters and data acquisition settings for ICP-MS/MS measurement of plutonium isotopes.

<i>ICP conditions</i>	Sample uptake rate	0.4 mL min ⁻¹		
	RF power	1500 W		
	Sampling depth	7 mm		
	Carrier gas	1.2 L min ⁻¹		
	Spray chamber	2 °C		
<i>Lens</i>	Extraction lens 1	-180V		
	Extraction lens 2	-10 V		
	Omega bias	-120 V		
	Omega	20 V		
	Q1 entrance	4 V		
	Q1 outlet	-7 V		
	Cell entrance	-130 V		
	Cell outlet	-80 V		
<i>Q1</i>	Q1 bias	2 V		
<i>Collision/reaction cell</i>	He flow	8 mL min ⁻¹		
	NH ₃ flow	1.2 mL min ⁻¹		
	Octapole bias	-4 V		
	Octapole RF power	200 V		
	KED	-13 V		
<i>Data acquisition</i>				
Isotope	²³⁸ U	²³⁹ Pu	²⁴⁰ Pu	²⁴² Pu
Dwell time s ⁻¹	0.5	20	30	5
Scans	100	100	100	100
Times	5	5	5	5

Table 2

Analytical results of ^{238}U , ^{239}Pu and ^{240}Pu count rate and $^{239+240}\text{Pu}$ concentrations in background, procedure blanks, samples and standard reference materials separated using TEVA-extraction method and measured by ICP-MS/MS at a flow rate of 1.2 mL min⁻¹ for NH₃ and 8 mL min⁻¹ for He.

Sample	^{238}U , cps	^{239}Pu , cps	^{240}Pu , cps	^{239}Pu , mBq g ⁻¹	^{240}Pu , mBq g ⁻¹
Background	3.00±2.00	0.10±0.10			
Procedure Blank	265.96±20.78	0.55±0.22	0.04±0.03		
S-1	556.91±24.04	115.02±5.09	20.03±0.83	0.61±0.04	0.39±0.02
S-2	489.26±34.02	7.50±0.65	1.42±0.02	0.03±0.003	0.02±0.001
S-3	323.95±5.66	63.28±0.6	11.73±0.32	0.41±0.02	0.28±0.01
IAEA-385	673.59±18.27	86.62±2.21	14.98±1.19	1.81±0.07	1.17±0.10
IAEA-412	389.55±19.81	89.57±1.53	15.46±0.76	0.37±0.01	0.23±0.01

Table 3

Analytical results of ^{238}U count rates and Pu isotopes concentrations in IAEA-385 and IAEA-412 certified reference materials separated by anion-exchange chromatography and TEVA extraction chromatography, respectively.

		^{238}U , cps	^{239}Pu , mBq g $^{-1}$	^{240}Pu , mBq g $^{-1}$
IAEA-385	Anion-exchange	10000±70	1.74±0.08	1.14±0.1
	TEVA extraction	674±18	1.81±0.07	1.17±0.10
	Certified value	—	1.79±0.28	1.15±0.14
IAEA-412	Anion-exchange	49400±900	0.30±0.01	0.26±0.02
	TEVA extraction	389±20	0.37±0.01	0.23±0.01
	Certified value	—	0.36±0.016	0.24±0.016

Caption of figures:

Fig. 1. Schematic diagram of the triple quadrupole ICP-MS.

Fig. 2. Schematic diagram of the chemical procedure for separating plutonium by anion-exchange chromatography and TEVA extraction chromatography.

Fig. 3. Potential mechanism for removing interferences of UH^+ in ICP-MS/MS measurement of plutonium isotopes at a flow rate of 0.6 mL min^{-1} for NH_3 and 8 mL min^{-1} for He. (a) Reactions in the collision/reaction cell, molecular ion reactions of U^+ with NH_3 ; (b) reactions of UH^+ with NH_3 in the reaction cell; (c) reactions of Pu^+ with NH_3 . Target ion is selected in the first mass spectrometer (Q1) and entered the collision/reaction cell (ORS³), Q2 is then set to scan and measure desired U and Pu species.

Fig. 4. Variation of the measured intensities of m/z 238/238 and 239/239 with the concentration of ^{238}U standard solution by using ICP-MS/MS at a flow rate of 1.2 mL min^{-1} for NH_3 and 8 mL min^{-1} for He (a) and conventional ICP-MS without reaction cell (b). The error bars showed in the figures are too small to be seen, all measurement uncertainty in this figure are less than 3%.

Fig. 5. Distribution of $^{239+240}\text{Pu}$ concentration and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio in surface soil in the coastal areas of eastern China.

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