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Inductively coupled plasma-sector field mass spectrometry with a high-efficiency sample introduction system for the determination of Pu isotopes in settling particles at femtogram levels

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Abstract

An analytical method for the determination of plutonium concentration and its isotope ratio ($^{240}Pu/^{239}Pu$) for settling particle samples by inductively coupled plasma mass spectrometry (ICP-MS) is presented. The generally used approach for Pu preconcentration by increasing the amount of samples is not applicable because of the small size of settling particle samples available for the analysis for Pu isotopes. Efforts were made to improve the sensitivity of a sector-field ICP-MS (SF-ICP-MS) and reduce the $^{238}UH^+$ interference for Pu analysis by combining a high-efficiency sample introduction system (APEX-Q). An extremely low detection limit of 0.07 fg Pu was achieved, which allowed the determination of Pu isotope ratio at femtogram levels. The precision and accuracy of $^{240}Pu/^{239}Pu$ isotope ratio analysis were carefully examined with a certified Pu isotope standard (NBS-947) and an ocean sediment reference material (IAEA-368). Simple anion-exchange chromatography for the separation and purification of Pu was combined with the APEX-Q/SF-ICP-MS system to determine Pu isotopes in settling particles collected in the East China Sea continental margin. The obtained results supported a previous observation on the lateral transport of Pu containing particles in this continental margin.

Keywords: Plutonium; Isotope ratio; Settling particles; ICP-SFMS; Marine environment

1. Introduction

Plutonium isotopes have been introduced to the oceans mainly as a consequence of atmospheric nuclear weapons testing. There are two major sources of plutonium in the Pacific Ocean: global (stratospheric) fallout and the close-in (tropospheric) fallout from nuclear weapons testing at the Pacific Proving Ground (PPG). Depending on the emission sources, Pu isotope ratios, in particular $^{240}Pu/^{239}Pu$ atom ratios, vary significantly in the environment, which allows the transport of Pu from different sources to be studied. Consequently, the $^{240}Pu/^{239}Pu$ atom ratio was considered to be an excellent tracer for investigation of the particle transportation and scavenging processes in the oceans.

Plutonium from the global fallout has been drastically reduced since the 1980s, and the close-in fallout signature in recent decades has become more significant in the western North Pacific [1,2]. The fallout from the PPG close-in fallout source is characterized by an elevated $^{240}Pu/^{239}Pu$ ratio (>0.20) relative to global stratospheric fallout (0.18–0.19). A series of studies on Pu inventories and $^{240}Pu/^{239}Pu$ atom ratios in the water column and sediments in the Pacific have revealed the wide presence of PPG close-in fallout Pu in the western North Pacific and its marginal seas [2–6]. In our previous work, we observed PPG source Pu in sediments in the Okinawa Trough [4], in the Japan Sea [7], and in Sagami Bay [3]. Lee et al. [5] also found higher $^{240}Pu/^{239}Pu$ ratios in sediments from the southern Okinawa Trough. Kim et al. [2,8] further reported the presence of PPG source Pu in seawater and sediments near the Korean Peninsula. Although the oceanic current transportation of Pu from the PPG and the early direct tropospheric fallout have been proposed to be responsible for the wide presence of PPG close-in fallout Pu signature [2,3,5,9], details for the Pu transportation are not well understood. Studying the Pu scavenging process by biogenic and inorganic particles using a sediment trap sampling technique is essential to elucidate the details of the oceanic Pu transportation

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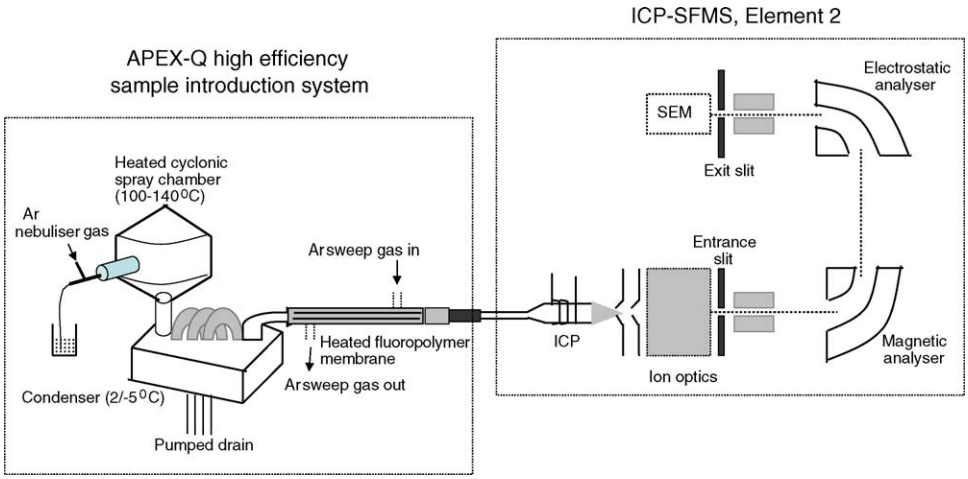

Fig. 1. Schematic diagram of SF-ICP-MS coupled to a high-efficiency sample introduction system.

process, because sinking particulate material has been regarded as the primary means by which surface-introduced transuranics, for instance, Pu are transported to the sediments [10,11].

The conventional and most widely used method to determine Pu in marine samples is alpha spectrometry [12,13]. This method, however, is not able to provide information on the isotope ratio of $^{240}Pu/^{239}Pu$, which is important for the study of Pu transport and scavenging processes in the ocean. On the other hand, thermal ionization mass spectrometry (TIMS), which has been widely applied in the determination of fallout Pu in marine samples for many decades [6,14–17], is being replaced increasingly by inductively coupled plasma mass spectrometry (ICP-MS) because ICP-MS generally offers good sensitivity, precision and accuracy for isotope ratio measurements and higher sample throughput with the easiness of the sample introduction [18]. Also, in particular for Pu isotope ratio measurements, a simple chemical treatment procedure can be employed for the separation and purification of Pu from a marine sample matrix [19,20]. ICP-MS has been successfully applied to the determination of Pu isotopes in marine samples, such as sediments [21–24], seawater [2,25–27], squid [28], and sea ice [29], the determination of Pu isotopes in settling particle samples by ICP-MS, however, is still a challenging task for analytical chemistry due to the limited sample size available for analysis. It is expensive and technically difficult to obtain samples of settling particles from the deep, open ocean. The sample size available for Pu isotope analysis, in most cases, is in the range of a few milligrams to some hundreds of milligrams. The amount of Pu isotopes, especially ^{240}Pu for an analysis could be as low as a few femtograms (10^{-15} g) in the sample. Therefore, in order to measure $^{240}Pu/^{239}Pu$ isotope ratio at femtogram levels, a highly sensitive analytical method is required.

The aim of the present work was to develop an accurate analytical method for Pu isotopes in settling particle samples using sector-field ICP-MS. Efforts were made to improve the instrument sensitivity and reduce the UH^+ interference for Pu analysis by using a high efficiency sample introduction system (APEX-Q). The precision and accuracy of $^{240}Pu/^{239}Pu$ isotope ratio analysis at ultratrace levels were carefully examined with a certified Pu isotope standard and an ocean sediment reference material. Finally, this method was applied to the determination of Pu isotopes in settling particles collected in the East China Sea continental margin.

2. Experimental

2.1. ICP-MS instrumentation

To determine Pu isotopes in settling particle samples, a SF-ICP-MS (Finnigan Element 2, Bremen, Germany) was used in the low resolution (LR) mode in order to utilize the maximal instrument sensitivity. An APEX-Q high-efficiency sample introduction system (Elemental Scientific Inc., Omaha, NE, USA) with membrane desolvation unit (ACM) and a conical concentric nebulizer (hereafter called a conical nebulizer, CN) were used as sample introduction systems. A schematic diagram of the SF-ICP-MS coupled to the APEX-Q system is presented in Fig. 1. Additionally, the normal skimmer cone was replaced by a high-efficiency cone (X-cone, Thermo Finnigan) further increasing sensitivity of SF-ICP-MS for the settling particle samples. All the measurements were made in the self-aspirating mode to reduce the risk of contamination by the peristaltic pump tubing. The SF-ICP-MS was optimized daily using a 1 ng ml^{-1} U standard solution (Merck standard) when using the CN sample introduction, and 0.1 ng ml^{-1} U standard solution when using the APEX-Q system. Optimized instrument conditions for the determination of Pu isotopes are listed in Table 1.

2.2. Chemical and reagents

All commercial chemicals were of analytical-reagent grade and were used without further purification. Nitric acid, HCl, H_2O_2, $NaNO_2$, $HClO_4$, NH_4I and HF were obtained from Kanto Chemicals (Tokyo, Japan). Plutonium-242 (CRM 130, plutonium spike assay and isotopic standard, New Brunswick Laboratory, USA) was used to spike the samples. The mixed Pu isotope standard solution (NBS-947) was provided by Dr. Y. Muramatsu

Table 1
Instrument and data acquisition settings for SF-ICP-MS and APEX-Q system

SF-ICP-MS	
Instrument settings	
Forward power	1200 W
Nebulizer	Conical concentric
Sample cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.8 mm orifice diameter or X-cone
Torch	Fassel
Cool gas	16 l min^{-1}
Auxiliary gas	0.8 l min^{-1}
Sample gas (nebulizer gas)	0.97–0.99 l min^{-1} (optimized daily to highest intensity of $^{238}U^+$ and lowest possible oxide formation rate)
Data acquisition settings	
Low resolution ($m/\Delta m = 300$)	
Acquisition mode	E-scan (peak jumping)
Monitored isotopes	$^{238}U^+$, $^{239}Pu^+$, $^{240}Pu^+$, $^{242}Pu^+$
No. of scans (runs × passes)	17 × 3
Mass window	10%
Samples per peak	80
Sample time	10 ms for $^{238}U^+$; 30 ms for $^{242}Pu^+$; 100 ms for $^{239}Pu^+$ and $^{240}Pu^+$
Integration type	Average
Total time of analysis	150 s
Medium resolution ($m/\Delta m = 4000$)	
Acquisition mode	E-scan (peak jumping)
Monitored isotopes	$^{238}U^+$, $^{239}Pu^+$, $^{240}Pu^+$, $^{242}Pu^+$
No. of scans (runs × passes)	17 × 3
Mass window	80%
Samples per peak	10
Sample time	10 ms for $^{238}U^+$; 30 ms for $^{242}Pu^+$; 100 ms for $^{239}Pu^+$ and $^{240}Pu^+$
Integration type	Average
Total time of analysis	150 s
APEX-Q system	
Sample uptake rate	0.2 ml min^{-1} (with conical nebulizer)
Spray chamber temperature	140 °C
Condenser temperature	2 °C
Sweep gas (Ar)	3 l min^{-1}
Additional gas (Ar)	0.1 l min^{-1}
N_2 gas	∼10 ml min^{-1}

(Gakushuin University, Japan). The anion-exchange resin used in this study was AG 1-X8 (100–200 mesh, Bio-Rad).

2.3. Sediment trap sampling

Settling particle samples were collected at four stations. On the continental margin of the East China Sea, three moorings of sediment traps (Stns. F-4, F-6, F-8) were deployed from 26 October to 4 November 1995, and one mooring of a sediment trap (SST-2) was deployed from 1 March 1993 to 22 February 1994 in the Okinawa Trough area. The sample bottles of the cylindrical traps were filled before deployment with 2% formaldehyde solution and sodium chloride in filtered seawater. Formalin was buffered by saturation with sodium tetraborate. Sodium chloride was added to increase the density of the solution in the sampling bottle slightly. Details about the sediment trap mooring strategy were described elsewhere [13].

2.4. Sample preparation

After recovery of the sediment traps, sample bottles were stored in a refrigerator (5 °C). In the laboratory, the sediment trap samples were first wet-sieved through a 1-mm nylon mesh to exclude large zooplankton and other swimmers. The samples were then split into four aliquots by a rotating wet-sample splitter (WSD-4). The divided samples were filtered onto pre-weighed Nuclepore polycarbonate membrane filters (0.6 μm pore size, 47 mm diameter) and rinsed with deionized water to remove salts.

The dried and weighed settling particle samples (0.03–0.5 g) were spiked with yield monitors of ^{242}Pu (2 pg), digested in a covered 30 ml Teflon beaker with the addition of a mixture of concentrated HNO_3 (4 ml), $HClO_4$ (2 ml) and HF (2 ml) on a hotplate at 180–200 °C. The tracer addition was performed at the beginning of the digestion procedure to ensure complete radioactive equilibrium between tracer and sample solution. After digestion, the sample was then evaporated to near dryness, whereupon 3 ml of 70% $HClO_4$ were added, and heating was continued until the $HClO_4$ fumed. This fuming process was repeated two or three times to remove traces of HF. This is important, because plutonium can form a stable fluoride complex which could interfere at later stages of the ion chromatographic separation. Then, 2 ml of concentrated nitric acid were added and the sample was evaporated to dryness. This nitric acid addition and evaporation step was repeated a second time. After the final evaporation, the sample was brought up in 20 ml of 8 M HNO_3, along with 0.3 g of $NaNO_2$. The sample was warmed to 40 °C for 10–15 min to prepare the sample for the ion-exchange column separation. This digestion procedure is also useful for the determination of U and Th isotopes in settling particle samples.

If only Pu isotopes are of interest, an acid leaching procedure using 8 M HNO_3 could be employed. The details of this leaching procedure have been described previously [21], except that the amount of spiked Pu-242 tracer was reduced to 2 pg. Lee et al. [30] have made a comparison between a total digestion method and the acid leaching method for sediment and biological samples. For Pu chemical recoveries, they found that no remarkable differences between acid leaching (8 M HNO_3) and the total digestion using the combination of HNO_3, HCl and HF. Similarly, other workers also demonstrated that the acid leaching was sufficient to recover non-global fallout Pu from sediment samples. For example, Oktay et al. [31] used simple acid leaching to find clearly recognizable Nevada Test Site Pu signatures in sediments. Ketterer et al. [20] resolved global and regional Pu sources in soils and lake sediments using acid leaching. Therefore, the acid leaching method is generally acceptable to analyze the fallout-derived radionuclides in marine environmental samples. The advantage of using acid leaching method for Pu isotope analysis in marine environmental samples is not only the simplification and shortening of time for sample preparation, but also its advantage in separation of Pu and U, which is important for the accurate determination of ^{239}Pu using the ICP-MS technique because of the possible interference by $^{238}UH^+$, because much less U (only ca. 50% of the total U in the samples) will be leached out with the acid leaching procedure [32,33].

2.5. Separation and purification of Pu for ICP-MS measurement

An anion-exchange chromatographic method described by Muramatsu et al. [19] was employed for the separation and purification of Pu. It was characterized as a simple separation and purification method for Pu with a high Pu chemical recovery (70–90%) and a high U decontamination factor (in the order of 10^4–10^5). In brief, the filtered sample solution (8 M HNO_3) was passed through an anion-exchange resin (AG 1 × 8, 100–200 mesh, Cl^-) column (2.5 ml, packed in Muromac mini-column M, 6.5–8.5 mm × 58 mm, i.d.), which was pre-conditioned with 40 ml of 8 M HNO_3. The column was washed with 50 ml of 8 M HNO_3 to remove U (VI) from the column. Thorium was stripped with 40 ml of 10 M HCl, which also converted the resin back into the chloride form. Plutonium(IV) was converted to an anionic chloro-complex and was retained on the resin. Finally, Pu was eluted with 50 ml of NH_4I (5%)–HCl (29 + 71) solution, where iodide reduced Pu(IV) to Pu(III). HNO_3 (4 ml), $HClO_4$ (0.2 ml) and H_2O_2 (1 ml) were added to the eluate, which was heated on the hotplate to decompose any organic material and to expel excess iodine. After the solution had been boiled off, the residue was dissolved in 4% HNO_3 (0.7 ml) for the SF-ICP-MS measurement. The Pu background of the used chemicals and the ion exchange resin was examined using the operational blank sample. It was found that the background concentrations of ^{239}Pu and ^{240}Pu are 0.6 and 0.07 fg/ml, respectively. The chemical recovery of ^{242}Pu tracer ranged from 70% to 90%.

3. Results and discussion

Plutonium concentration ($^{239+240}$Pu) in settling particles normally ranges from 1.0 to 10 Bq kg^{-1} in the marine environment [10,12,14]. Considering a typical sample size of 0.1 g, and assuming a ^{240}Pu/^{239}Pu atom ratio of 0.18 (global fallout), the amount of ^{240}Pu per sample is in the range of 4.5–45 fg. In contrast to other marine samples, such as sediments and seawaters, the limited sample size of settling particles does not allow any pre-concentration by increasing the amount of samples for analysis. Therefore, to measure the ^{240}Pu/^{239}Pu isotope ratio with acceptable precision (less than 10% error) at the low concentration level for settling particle samples, a highly sensitive ICP-MS analytical method is indispensable; this requires a detection limit at least in the lower sub-femtogram level for measurement of Pu isotopes.

Previously, we have successfully applied quadrupole ICP-MS (ICP-QMS) with a shield torch system and SF-ICP-MS to the determination of Pu isotopes in sediment samples [21,34]. Using ICP-QMS, we obtained a detection limit of 42 fg (or 8 fg ml^{-1}) for Pu isotopes, which allowed us to make Pu isotope ratio measurements in about 10 g sediment samples. Further improvement was achieved using SF-ICP-MS with a conical nebulizer; the obtained low detection limit of 0.35 fg (or 0.7 fg ml^{-1}) for Pu isotopes made it possible to determine Pu isotope ratios in 1 g sediment samples. However, taking into account the small size settling particle samples (0.03–0.5 g), the determination of Pu isotopes was not achievable with the above-mentioned methods.

Inspired by a recent work by Krachler et al. [35], which demonstrated a sensitivity improvement of one order of magnitude for Pb determination by using the APEX sample introduction system, we investigated the analytical performance of the APEX-Q high-efficiency sample introduction system (with a desolvator-ACM) for Pu isotope analysis. We compared the sensitivity improvement using the APEX-Q system with different nebulizers. We carefully evaluated the effect of UH^+ interference on ^{239}Pu determination. In addition, the accuracy and precision of ^{240}Pu/^{239}Pu isotope ratio measurement at femtogram levels were investigated when the APEX-Q system was combined with SF-ICP-MS.

3.1. Sensitivity improvement using SF-ICP-MS with the APEX-Q system

We used an APEX-Q sample introduction system to improve the sensitivity for the analysis of long-lived radionuclides. This system consisted of a heated cyclonic spray chamber, a Peltier cooled condenser and an ACM Nafion fluoropolymer membrane desolvation module. This system can be used with different nebulizers operating over a wide range of sample uptake rates from 20 μl min^{-1} to over 1 ml min^{-1}. The nebulizers can be either self-aspirated or pumped. In this work, all the measurements were made in the self-aspirating mode in order to reduce the risk of contamination by the peristaltic pump tubing. The spray chamber was heated to 140 °C whereas the chiller was set to 2 °C, thereby generating a more uniform aerosol and significantly reducing the moisture in the generated aerosols. In addition, the ACM desolvation module removed residual solvent vapor in the sample aerosol stream, thus, only dry aerosols were loaded to the plasma. Using a U standard solution, we evaluated the sensitivity improvement of the APEX-Q system combined with different nebulizers, namely, the PFA-100 microflow nebulizer (100 μl min^{-1}), the ST-nebulizer (this nebulizer is identical to the PFA-100 microflow nebulizer, but has a removable sample capillary which controls the sample uptake rate, 400 μl min^{-1}) and the conical nebulizer (200 μl min^{-1}). The results are shown in Fig. 2. For comparison, the sensitivities obtained with a quadrupole ICP-MS (HP 4500) with and without the use of a shield torch, and with the SF-ICP-MS without the use of the APEX-Q system are also shown in this figure. The APEX-Q system used a small flow of nitrogen to increase transport efficiency and the signal stability. This N_2 flow rate has to be carefully adjusted because the overall sensitivity is affected by it. We found that the maximal sensitivity was obtained when the N_2 flow was set to around 10 ml min^{-1}. The flow rate of Ar sweep gas for the ACM membrane desolvation module was found to have no significant effect on the sensitivity, and we set it to 3 l min^{-1} as suggested by the instrument manufacturer.

As shown in Fig. 2, compared with the sensitivity obtained with SF-ICP-MS without using the APEX-Q system, we achieved sensitivity improvements with the PFA-100 microflow nebulizer, the ST-nebulizer, and the conical nebuliser of 3.3, 12.5 and 5.4 times, respectively. For the conical nebulizer, a

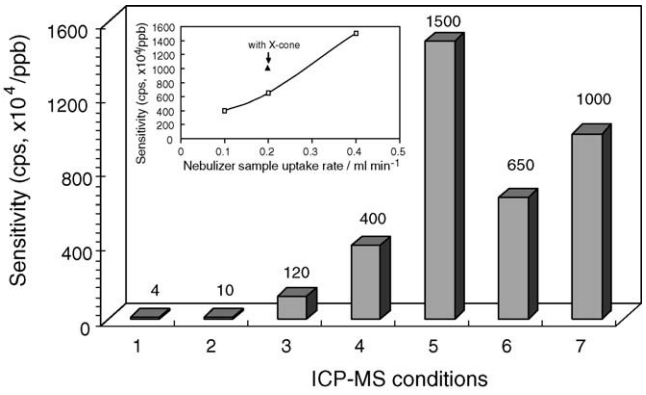

Fig. 2. Comparison of sensitivity for ^{238}U in ICP-MS using different sample introduction systems. ICP-MS conditions: (1) HP-4500 ICP-QMS with a Babington type nebulizer; (2) HP 4500 ICP-QMS with a Babington type nebulizer using shield torch; (3) Element 2 SF-ICP-MS with a conical nebulizer; (4) Element 2 SF-ICP-MS with APEX-Q using PFA-100 nebulizer (100 μl min^{-1}); (5) Element 2 SF-ICP-MS with APEX-Q using ST-nebulizer (400 μl min^{-1}); (6) Element 2 SF-ICP-MS with APEX-Q using conical nebulizer (200 μl min^{-1}); (7) Element 2 SF-ICP-MS with APEX-Q using conical nebulizer (200 μl min^{-1}) and with X-skimmer cone. The insert shows the effect of nebulizer sample uptake rate on the sensitivity using the APEX-Q system.

further sensitivity improvement by using the X-skimmer cone by a factor of 8.3 was achieved. Using the APEX-Q system, as shown in the insert in Fig. 2, the sensitivity increased with the increasing sample uptake rate. Although the highest sensitivity was obtained using a ST-nebulizer, the sample uptake rate of 400 μl min^{-1} was relatively high for our determination for Pu isotopes in settling particle samples. As shown in Table 1, for Pu isotope ratio analysis, the total time was 150 s, and required more than 1 ml of sample solution. Considering the small sample size (0.03–0.5 g) of settling particles, it is preferable to do the analysis with as small a volume as possible, in order to avoid dilution of the samples. With the conical nebulizer, only 0.5 ml sample solution was required for Pu isotope ratio analysis. Therefore, as a compromise between the sensitivity and the required sample volume for analysis, we considered the conical nebulizer using the X-cone as the best arrangement for the APEX-Q system.

Under the best operating conditions using the conical nebuliser with the X-cone, we evaluated the detection limit for Pu analysis using ^{242}Pu tracer. The detection limit, defined as three times the standard deviation of the blank solution (4% HNO_3), was 0.14 fg ml^{-1} Pu, or 0.00032 mBq ml^{-1} for ^{239}Pu and 0.0012 mBq ml^{-1} for ^{240}Pu, respectively, for a counting time of 150 s. Since only 0.5 ml of sample solution was needed for the analysis, the absolute detection limit for Pu was 0.07 fg, which was among the lowest detection limits reported for Pu analysis in the literature [18,36].

3.2. Effect of UH^+ interference

The presence of uranium in the sample may hamper the accurate determination of Pu isotopes, especially for ^{239}Pu, due to the uranium hydride formation ($^{238}UH^+$) and the peak tailing effect from $^{238}U^+$. The sample introduction system is recognized as the most important factor affecting formation of uranium hydride ions in a plasma compared with other factors, such as gas flow rate, and the distance of the torch from the cone [25,27]. Using a 1 ng ml^{-1} U standard solution, we evaluated the uranium hydride formation rate in the APEX-Q system using the conical nebulizer and coupled with the ACM membrane desolvation module. We found that the $^{238}UH^+$ ion formation rate was less than 2×10^{-5} (Table 2). Kim et al. [23] have investigated the influence of the interference effect of ^{238}U at 239 *m/z* with various sample introduction systems, and found that the MCN-6000 microconcentric nebulizer coupled with the membrane desolvation system showed the lowest hydride formation. As shown in Table 2, the $^{238}UH^+$ ion formation rate obtained with the APEX-Q system was comparable with that of the MCN-6000 sample introduction system, and was among the lowest values reported in the literature. The overall influence of U concentration on the background signal on *m/z* 239 is presented in Fig. 3. The background signal at 239 *m/z* was less than 10 cps if the uranium concentration was lower than 50 pg ml^{-1}. In our settling particle samples collected in the East China Sea continental margin, the concentration of U was typically in the range of 1–2 μg g^{-1}. Considering a typical sample size of 0.1 g settling particles and the high decontamination factor (described in Section 2) of the employed chromatographic separation and purification system, the U concentration in the final solution (0.5–1.0 ml) was around 10–20 pg ml^{-1}. Therefore, after background subtraction, the influences of uranium hydride molecular ions, as well as the peak tailing effect from ^{238}U were considered negligible.

Table 2
Comparison of interference effect of $^{238}UH^+$ on the determination of ^{239}Pu by SF-ICP-MS with different sample introduction systems

Sample introduction system	UH^+/U^+	Reference
Pneumatic nebulizer	$7.59–8.39 \times 10^{-5}$	[23]
MCN-100	$4.05–4.73 \times 10^{-5}$	[23]
MicroMist	1.8×10^{-4}	[36]
Q-DIHEN	$1–5 \times 10^{-4}$	[36]
USN-5000$^+$	$3.20–4.00 \times 10^{-5}$	[23,36]
USN+MINI-GASS	$2.33–2.79 \times 10^{-5}$	[23]
MCN-6000	$1.35–1.80 \times 10^{-5}$	[23]
Aridus	3.2×10^{-5}	[36]
APEX-Q with ACM unit	$1.16–1.95 \times 10^{-5}$	This study

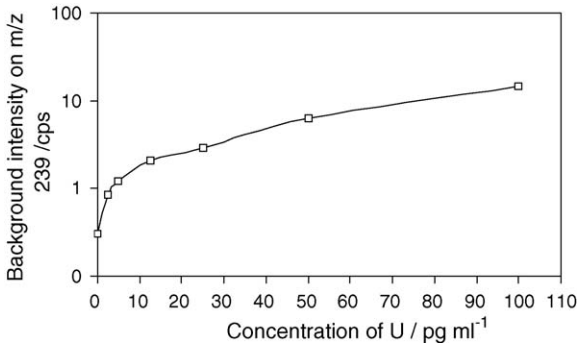

Fig. 3. Influence of U concentration on the background signal at *m/z* 239 in SF-ICP-MS combined with the APEX-Q sample introduction system.

Table 3
$^{240}Pu/^{239}Pu$ isotope ratio in certified standard solution (NBS-947) measured by SF-ICP-MS with and without using the APEX-Q system

Analytical system	$^{240}Pu/^{239}Pu$ isotope ratio		^{239}Pu concentration (pg ml^{-1})	Precision (%)	Accuracy (%)	ε-Value[a]
	Measured	Certified				
A	0.2418 ± 0.0014	0.2420	15	0.6	−0.08	0.0008
B	0.2413 ± 0.0011	0.2420	1.5	0.4	−0.29	0.0029
B	0.2427 ± 0.0034	0.2420	0.15	1.4	0.30	−0.0029

A: SF-ICP-MS using a conical nebulizer without using the APEX-Q system; B: SF-ICP-MS with the APEX-Q system using a conical nebulizer and an X-cone.
[a] The ε stands for the mass discrimination per unit, defined as $R_{certified}/R_{measured} = 1 + \Delta m\varepsilon$.

3.3. Accuracy and precision for Pu isotope ratio measurement

The precision and accuracy of the $^{240}Pu/^{239}Pu$ isotope ratio of the APEX-Q system were studied using a certified Pu isotope standard solution (NBS-947) at ^{239}Pu concentrations of 1500 and 150 fg ml^{-1}, respectively (Table 3). The obtained results showed good agreement with the certified value of the $^{240}Pu/^{239}Pu$ isotope ratio. For a long-term measurement ($n = 10$) at a ^{239}Pu concentration of 150 fg ml^{-1}, the precision (R.S.D.) and accuracy were 1.4% and 0.3%, respectively. As shown in Fig. 4, for a single measurement (runs × passes, 17 × 3), the precision (R.S.D.) ranged from 0.5% to 1.7% at ^{239}Pu concentration of 1500 fg ml^{-1} (Fig. 4A), and 2.1% to 3.8% at ^{239}Pu concentration of 150 fg ml^{-1} (Fig. 4B). In addition, when compared with the $^{240}Pu/^{239}Pu$ isotope ratios and the ε values obtained by SF-ICP-MS without using the APEX-Q system, we considered that using the APEX-Q sample introduction system and X-cone did not introduce an additional mass bias for the $^{240}Pu/^{239}Pu$ isotope ratio determination at the ultratrace level. The ε stands for the mass discrimination per unit, defined as $R_{certified}/R_{measured} = 1 + \Delta m \times \varepsilon$, by Taylor et al. [37] and Heumann et al. [38].

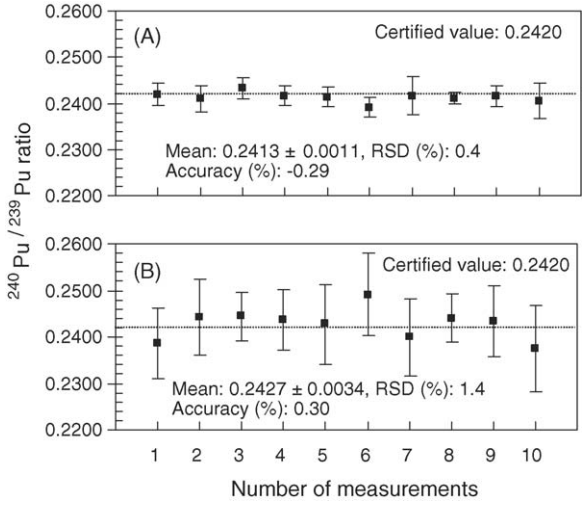

Fig. 4. The accuracy and precision of isotopic ratio of $^{240}Pu/^{239}Pu$ obtained from NBS 947 standard using SF-ICP-MS with the APEX-Q sample introduction system: (A) NBS 947 at a concentration of 1500 fg ml^{-1} for ^{239}Pu and 363 fg ml^{-1} for ^{240}Pu; (B) NBS 947 at a concentration of 150 fg ml^{-1} for ^{239}Pu and 36.3 fg ml^{-1} for ^{240}Pu.

3.4. Determination of Pu isotopes in ocean sediment reference material (IAEA-368) with a sample size of 0.1 g

Since no settling particle reference material is available for Pu isotope analysis, an ocean sediment reference material (IAEA-368) was used to assess the accuracy of the determination of total Pu ($^{239+240}Pu$) activity and the isotope ratio of $^{240}Pu/^{239}Pu$. Although this reference material was only certified for the total Pu activity, its $^{240}Pu/^{239}Pu$ isotope ratio has been investigated by several research groups, and the reported $^{240}Pu/^{239}Pu$ ratios ranged from 0.03 to 0.04 [19,21,23]. The experimentally established Pu activity (29.1 ± 0.2 mBq g^{-1}, $n = 6$), and the isotope ratio of $^{240}Pu/^{239}Pu$ (0.037 ± 0.003, $n = 6$) were in good agreement with the certified Pu activity of 31 mBq g^{-1} (ranging from 29 to 34) and the literature ratios.

3.5. Determination of Pu isotopes in settling particles collected in the East China Sea continental margin

Table 4 presented the results of Pu concentration (mBq g^{-1}) and isotope ratios in settling particle samples collected in the East China Sea and Okinawa Trough area. Previously [13], another set of F-series settling particle samples (Stns. F-4 to F-8) was analyzed using α-spectrometry for total Pu activity ($^{239+240}Pu$) after wet digestion using a mixture of HNO_3, $HClO_4$ and HF. The good agreement between the results obtained with α-spectrometry and SF-ICP-MS demonstrated the applicability of the present analytical method for the accurate determination of Pu isotopes in small size marine settling particle samples.

Settling particle samples were generally too small to allow duplicate analyses for Pu isotopes. However, sample sizes from Stns. F-4U and F-4L were sufficiently large to allow duplicate analyses of $^{240}Pu/^{239}Pu$ isotope ratio using the medium resolution mode (MR). For analysis using LR mode, the $^{240}Pu/^{239}Pu$ isotope ratios were 0.250 ± 0.014 for Stn. F-4U and 0.225 ± 0.009 for Stn. F-4L. Using the MR mode, the obtained $^{240}Pu/^{239}Pu$ isotope ratios were 0.255 ± 0.031 and 0.226 ± 0.042 for Stns. F-4U and F-4L, respectively. It should be noted that the uncertainties were larger for the results using the MR mode, because the sensitivity was lower than that of the LR mode. For the determination of Pu isotope ratio at ultratrace level using the LR mode, the presence of lead in the final sample solution may also affect the $^{240}Pu/^{239}Pu$ ratio accuracy due to the formation of polyatomic ions of $^{204}Pb^{35}Cl^+$ and $^{204}Pb^{36}Ar^+$. To resolve these interferences from Pu isotopes, a resolution of 3000 is required. Therefore, these interferences could not

Table 4
Results of Pu concentrations (mBq g^{-1}) and atom ratios in settling particle samples

Sample	Location	Water depth (m)	$^{239+240}$Pu α-spectrometry[a]	$^{239+240}$Pu SF-ICP-MS	^{240}Pu/^{239}Pu
Stn. F-8L	29°36.01′N, 125°04.90′E	120	3.00 ± 0.26	3.16 ± 0.13	0.241 ± 0.014
Stn. F-6U	28°53.29′N, 126°41.41′E	241	3.18 ± 0.20	3.16 ± 0.21	0.251 ± 0.016
Stn. F-6L		289	3.97 ± 0.28	3.77 ± 0.31	0.226 ± 0.024
Stn. F-4U	28°40.86′N, 127°04.47′E	494	3.56 ± 0.13	2.79 ± 0.09	0.250 ± 0.014 (0.255 ± 0.031)[b]
Stn. F-4M		569	3.17 ± 0.14	3.05 ± 0.24	0.245 ± 0.026
Stn. F-4L		592	3.55 ± 0.11	3.29 ± 0.11	0.225 ± 0.009 (0.226 ± 0.042)[b]
SST-2-A8U	28°08.20′N, 127°11.40′E	606	n.d.[c]	4.93 ± 0.59	0.263 ± 0.036
SST-2-A8M		813	n.d.	5.96 ± 0.37	0.236 ± 0.019
SST-2-A8L		1019	n.d.	4.10 ± 0.23	0.244 ± 0.015

The errors quoted are 1S.D.
[a] Settling particle samples were digested using a mixture of HNO_3, $HClO_4$ and HF, and measured with alpha spectrometry (data cited from Yamada and Aono [13]).
[b] Isotope ratio of ^{240}Pu/^{239}Pu measured under medium resolution mode.
[c] n.d. stands for "not determined".

be resolved under the LR mode ($m/\Delta m = 300$), but they could be resolved from ^{239}Pu and ^{240}Pu masses under the MR mode ($m/\Delta m = 4000$). The excellent agreement between the results obtained under LR and MR modes indicated that the possible interference resulting from Pb was negligible in our analytical procedure for settling particles. Indeed, in our previous work [39], we have found that the anion-exchange chromatography was capable of separating of Pb and Pu. Lead present in the sample was eluted together with Fe from the resin during the washing step using 8 M HNO_3.

The ^{240}Pu/^{239}Pu isotope ratios in the settling particles ranged from 0.225 to 0.263 in the East China Sea and Okinawa Trough. These ratios are significantly higher than that of global fallout ratio of 0.18, and are comparable with those in the underlying surface sediments (0.21–0.26) reported by Wang and Yamada [4], confirming the presence of the PPG close-in fallout Pu in this region. In previous work using α-spectrometry to study the particle flux of $^{239+240}$Pu, Yamada and Aono [13] observed a clear tendency for $^{239+240}$Pu fluxes to increase with depth, and the highest $^{239+240}$Pu fluxes were observed near the bottom in the East China Sea continental margin. The large fluxes of $^{239+240}$Pu were attributed to episodic lateral transport of particles that flow down the continental slope with the nepheloid layer. The similarity of ^{240}Pu/^{239}Pu isotope ratios of settling particles collected in the continental shelf (Stn. F-8), shelf edge (Stn. F-6), the slope (Stn. F-4) and the Okinawa Trough (SST-2) obtained in the present work provided additional evidence to support the observation of lateral transport of plutonium in the continental margin, and suggested that the transported particles may subsequently be removed to the underlying sediments in the Trough region. Detailed studies on the deposition of Pu in the sediments through scavenging by settling particles in Okinawa Trough are in progress.

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