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Ultra-trace plutonium determination in small volume seawater by sector field inductively coupled plasma mass spectrometry with application to Fukushima seawater samples

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ABSTRACT

Long-term monitoring of Pu isotopes in seawater is required for assessing Pu contamination in the marine environment from the Fukushima Dai-ichi Nuclear Power Plant accident. In this study, we established an accurate and precise analytical method based on anion-exchange chromatography and SF-ICP-MS. This method was able to determine Pu isotopes in seawater samples with small volumes (20–60 L). The U decontamination factor was 3×10^7–1×10^8, which provided sufficient removal of interfering U from the seawater samples. The estimated limits of detection for ^{239}Pu and ^{240}Pu were 0.11 fg mL^{-1} and 0.08 fg mL^{-1}, respectively, which corresponded to 0.01 mBq m^{-3} for ^{239}Pu and 0.03 mBq m^{-3} for ^{240}Pu when a 20 L volume of seawater was measured. We achieved good precision (2.9%) and accuracy (0.8%) for measurement of the ^{240}Pu/^{239}Pu atom ratio in the standard Pu solution with a ^{239}Pu concentration of 11 fg mL^{-1} and ^{240}Pu concentration of 2.7 fg mL^{-1}. Seawater reference materials were used for the method validation and both the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios agreed well with the expected values. Surface and bottom seawater samples collected off Fukushima in the western North Pacific since March 2011 were analyzed. Our results suggested that there was no significant variation of the Pu distribution in seawater in the investigated areas compared to the distribution before the accident.

1. Introduction

Plutonium isotopes (^{239}Pu, $t_{1/2}$ = 24,100 y; ^{240}Pu, $t_{1/2}$ = 6561 y) have been released into the marine environment as a result of global fallout from the atmospheric nuclear weapons testing, reprocessing of nuclear fuels, accidents of military nuclear facilities and accidents in nuclear plants [1]. Studying the concentration of plutonium isotopes in marine environment is important because Pu presents a potential threat to human health due to its radiotoxicity and its chemical toxicity. In addition, Pu isotopes play important roles as tracers for understanding ocean processes, such as sediment mixing and particle scavenging in the water column, and the atom ratio of ^{240}Pu/^{239}Pu, which varies from different sources, serves as a key fingerprint for Pu source identification [2,3]. From these viewpoints, determination of Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater is highly necessary to understand fully the behavior and fate of Pu in marine environment. Although the total amount of Pu input to the ocean is large (8.6 PBq $^{239+240}$Pu by the year 2000 [4]), the concentration of Pu in seawater is extremely low. The $^{239+240}$Pu concentrations in the surface waters of the world ocean decreased exponentially over recent decades [5,6]. For instance, the $^{239+240}$Pu concentrations in the surface seawater of the North Pacific ranged from 8.1 to 35 mBq m^{-3} in the early 1970s, while in 2000, values were estimated to be 0.3–2.7 mBq m^{-3} [7]. This decrease of more than ten-fold has made it more difficult to make Pu measurements in seawater nowadays.

Conventionally, alpha spectrometry has usually been used for Pu measurement in seawater. With alpha spectrometry, large volumes of seawater (~200 L) and long counting times (days to several weeks) are normally needed. Moreover, alpha spectrometry cannot

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distinguish ^{239}Pu and ^{240}Pu due to their close alpha radiation energies (5.16 Mev and 5.17 MeV for ^{239}Pu and ^{240}Pu, respectively); thus the ^{240}Pu/^{230}Pu atom ratio fingerprint cannot be given. Recently, the application of inductively coupled plasma mass spectrometry (ICP-MS) to the measurement of $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio in various environmental samples at trace and ultra-trace levels has been widely studied [8–10]. The advantages of ICP-MS for the determination of Pu isotopes include easy sample preparation, short measurement time, and high sensitivity, precision and accuracy [11–13].

When ICP-MS is used for Pu determination, polyatomic interferences, especially from uranium hydrides, need to be carefully checked. The average ^{238}U concentration in seawater in the oceans is ca. 3 μg L^{-1}, nine to ten orders of magnitude higher than that of Pu [1,14]. Thus the severest interferences for the determination of Pu in seawater by ICP-MS come from the tailing effect of the $^{238}U^+$ peak and the uranium hydrides ($^{238}UH^+$ and $^{238}UH_2^+$), which cannot be resolved from $^{239}Pu^+$ and $^{240}Pu^+$ even with the HR mode ($m/\Delta m$ = 10,000). Although efforts have been made to reduce the intensity ratio of $^{238}UH^+/^{238}U^+$ detected by sector field ICP-MS (SF-ICP-MS) to become as low as $1–3 \times 10^{-5}$ when proper sample introduction systems are used [14–17], complicated chemical procedures for the separation of Pu in seawater are still strongly needed prior to the ICP-MS analysis. If we assume a 20 L volume of seawater is used for the determination of Pu and the final sample is prepared in a 1 mL solution, a U decontamination factor greater than 1×10^7 is needed to reduce the ^{238}U concentration in the final sample solution to become less than 5 pg mL^{-1}, which is required to make the effect of ^{238}U negligible. In order to eliminate the troublesome interferences from seawater samples, efforts such as co-precipitation, anion-exchange chromatography, extraction chromatography and the combination of these methods have been taken in recent years [18–21].

The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident caused the release of large amounts of radionuclides into the ocean [22,23]. The radioactive contamination status in the marine environment is of great concern. Intensive investigations of radioactivity in the marine environment focusing on fission radionuclides, such as ^{134}Cs, ^{137}Cs, ^{131}I and ^{90}Sr, have been carried out since the FDNPP accident [24–26]; however, corresponding studies about the actinides, especially Pu isotopes in seawater are limited. Normally, only 20–60 L seawater is collected for environment monitoring at a marine station due to the difficulty of seawater sampling and transportation. Thus in order to assess the possible Pu contamination in seawater from the FDNPP accident, an accurate and precise analytical method is highly desired for the measurement of Pu isotopes in small-volume seawater samples.

As Pu is an important element involved in the GEOTRACES program, six laboratories participated in its inter-calibration exercise on Pu determination in seawater samples [27]. The reported values showed measurement of $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater at current concentration levels with a sample volume of 20 L remains a challenge. In this work, an analytical method based on anion-exchange chromatography using Dowex 1X8 resin and SF-ICP-MS for the determination of plutonium isotopes at the ultra-trace level in seawater was established. The aim of this study was to establish and validate the required analytical method for Pu measurement in small-volume (20–60 L) seawater as part of the on-going project for long-term and continuous assessment of the oceanic Pu contamination from the FDNPP accident. The analytical merits of this method, including U decontamination, analytical precision and accuracy were discussed. Seawater reference materials were measured for validation of the method. Finally, this method was applied to determine $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in seawater collected off the FDNPP site in the western North Pacific since March 2011 to identify the possible Pu contamination from the accident in the marine environment.

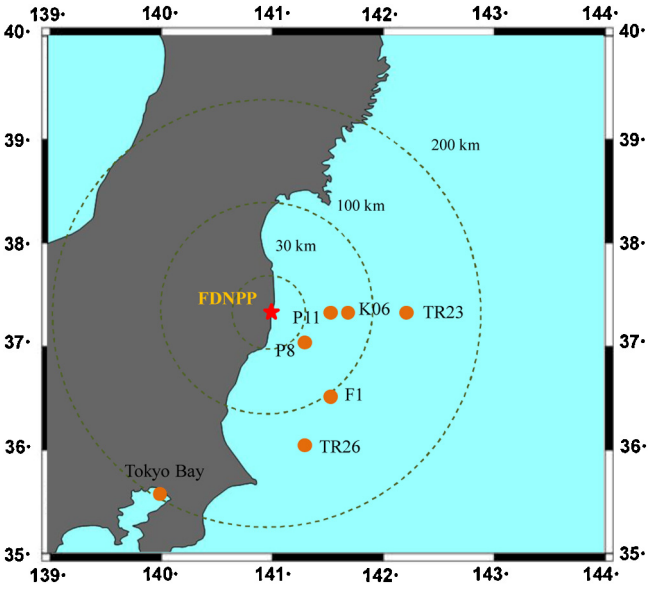

Fig. 1. Map showing seawater collection stations from the western North Pacific and Tokyo Bay since the FDNPP accident.

2. Materials and methods

2.1. Reagents and seawater samples

A Millipore Milli-Q-Plus water purification system was used for the preparation of high-purity water (18 MΩ cm^{-1}). All commercial chemicals used were of analytical grade except for source preparation prior to ICP-MS measurement, in which ultrapure grade 68% HNO_3 (Tama Chemicals, Japan) was used. Fe-carrier (20 mg mL^{-1} Fe in 1 M HNO_3) was prepared from iron (III) chloride hexahydrate. The anion exchange resins used in this study were Dowex 1X8 (100–200 mesh, Wako Chemical, Ltd., Japan), AG 1X8 (100–200 mesh, Bio-rad Laboratories, Inc., USA and Eichrom Technologies, LLC., USA) and AG MP-1 M (100–200 mesh, Bio-rad Laboratories, Inc., USA). ^{242}Pu (CRM 130, plutonium spike assay and isotopic standard, New Brunswick Laboratory, USA), as a yield tracer, was used to spike the seawater samples.

Two certified seawater reference materials IAEA-381 and IAEA-443 were obtained from International Atomic Energy Agency (IAEA, Vienna, Austria). Surface seawater samples (20 L for each sample) were collected from Tokyo Bay in April 2013 for the method optimization. Surface and bottom seawater samples (20–60 L for each sample) were gotten 30 km off the FDNPP site in the western North Pacific during the cruises of MR 11-05, KH 11-07 and KT-13-1 from July 2011 to January 2013 from the following stations: K06 (37°20′ N 141°40′ E), F1 (36°29′ N 141°30′ E), P8 (37°00′ N 141°17′ E), P11 (37°20′ N 141°28′ E), TR23 (37°20′ N 142°10′ E) and TR26 (36°00′ N 141°20′ E). These locations for the seawater collection are shown in Fig. 1.

2.2. Uranium extraction from anion-exchange resins

In order to choose the proper anion-exchange resin for the separation of Pu in seawater samples, we compared the extracted U by 8 M HNO_3 from the four different kinds of resins. About 2.0 g resin was weighed out into a 15 mL centrifuge tube and 5 mL 8 M HNO_3 was added for the extraction of U from the resin. The centrifuge tubes were put on a shake stage and shook for 2 h. The slurry was