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Concurrent determination of ^{237}Np and Pu isotopes using ICP-MS: analysis of NIST environmental matrix standard reference materials 4357, 1646a, and 2702

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ABSTRACT

An optimized method was developed to analyze environmental soil and sediment samples for ^{237}Np, ^{239}Pu, and ^{240}Pu by ICP-MS using a ^{242}Pu isotope dilution standard. The high yield, short time frame required for analysis, and the commercial availability of the ^{242}Pu tracer are significant advantages of the method. Control experiments designed to assess method uncertainty, including variation in inter-element fractionation that occurs during the purification protocol, suggest that the overall precision for measurements of ^{237}Np is typically on the order of ±5%. Measurements of the ^{237}Np concentration in a Peruvian Soil blank (NIST SRM 4355) spiked with a known concentration of ^{237}Np tracer confirmed the accuracy of the method, agreeing well with the expected value. The method has been used to determine neptunium and plutonium concentrations in several environmental matrix standard reference materials available from NIST: SRM 4357 (Radioactivity Standard), SRM 1646a (Estuarine Sediment) and SRM 2702 (Inorganics in Marine Sediment).

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1. Introduction

Neptunium-237 is a long-lived radionuclide that decays by alpha emission ($t_{1/2} = 2{,}144{,}000$ yrs). Fallout from atmospheric nuclear weapons testing has deposited significant quantities of ^{237}Np in the environment, with typical soil concentrations ranging between 1×10^{12} and 3×10^{13} atoms/m^2 in the northern hemisphere (Kelley et al., 1999). Nuclear fuel reprocessing and plutonium production facilities have also released considerable amounts of ^{237}Np into the environment (Cochran et al., 2000; Hunt and Smith, 1999; Hursthouse et al., 1991; MacKenzie et al., 1994; Morris et al., 2000). The ability to rapidly and accurately assess the concentration of ^{237}Np in a solid sample is critical from the perspective of environmental monitoring and safety, as well as for nuclear forensics applications.

Inductively coupled plasma mass spectrometry (ICP-MS) is a useful technique for determining the concentration of ^{237}Np in a sample. In mass spectrometry, isotope dilution is a powerful technique for concentration measurements of an element, but standard methods rely on a suitable tracer, typically a relatively long-lived, non-interfering isotope of the same element. The isotope ^{236}Np ($t_{1/2} = 154{,}000$ yrs) has been traditionally used for this purpose (Kenna, 2002), but ^{236}Np is not commercially available. Moreover, the production of ^{236}Np is difficult and low-yielding, involving the bombardment of a highly enriched and purified ^{235}U foil with deuterons (Efurd et al., 1991).

In the absence of a ^{236}Np tracer, an alternative strategy would be to use an isotope of plutonium, which has similar chemical behavior to neptunium. The isotope ^{242}Pu is commercially available in high purity, and has previously been investigated for use as a tracer for the determination of ^{237}Np (Chen et al., 2002; Kim et al., 2004; Qiao et al., 2010, 2011a, 2011b). Several automated sample analysis techniques have been developed for determining ^{237}Np in seawater, seaweed, and soil samples using a ^{242}Pu tracer (Kim et al., 2004; Qiao et al., 2010, 2011a, 2011b). A major challenge of this approach is that greater uncertainty in the measured ^{237}Np concentration could arise from variability in chemical fractionation that occurs between Np and Pu during the analysis. A successful analysis method would aim to both minimize and quantify the chemical fractionation that occurs between the two elements.

In this work, our goal was to develop a well-defined method to analyze environmental soil and sediment samples simultaneously

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for ^{237}Np, ^{239}Pu, and ^{240}Pu using a ^{242}Pu tracer. Specific aims were to optimize the chemical purification in order to minimize the inter-element separation of Np and Pu, and to quantify the uncertainty that arises due to fractionation between the elements. The method was then applied to measure plutonium and neptunium in the radioactivity standard NIST SRM 4357, which is composed of a mixture of sediment collected from the Chesapeake Bay area and sediment collected from the coastal UK near the Sellafield reprocessing facility. Plutonium and neptunium derived from global fallout from nuclear weapons testing were also measured in two other standard reference materials collected within the Chesapeake Bay, NIST SRM 1646a and NIST SRM 2702.

2. Material and methods

2.1. Chemicals and reagents

Optima grade acids were purchased from Fisher Scientific and trace metals grade ascorbic acid was purchased from Sigma Aldrich. All other chemicals were of analytical reagent grade and used as received.

2.2. Instrumentation

The analysis was performed using a Thermo Fisher Scientific X-series II ICP-MS. The instrument dead time was calibrated using a previously published procedure (Vanhaecke et al., 1998). The ^{238}UH^{+}/^{238}U ratio was determined from measurements of a solution of NIST SRM U960 and used to correct the ^{239}Pu count rates. The contribution of ^{238}UH^{+} to the total counts at mass 239 was typically less than 1%. A dwell time of 30 ms was used at each mass unit. Mass bias was monitored periodically using a solution of NBL CRM 128 (^{239}Pu/^{242}Pu, 1:1 Atom Ratio Plutonium Isotopic Standard).

3. Experimental

3.1. Sample purification procedure

A solid sample was transferred to a quartz cone, dried as recommended by the certificate (40 °C, 90 °C, or 110 °C for SRMs 4357, 2702, and 1646a, respectively), and a dry mass was obtained. The samples were then heated in a furnace at 550 °C for at least 12 h. The samples were fully dissolved using either $HF-HNO_3-HClO_4$ or $HF-HNO_3$. A known amount of ^{242}Pu tracer (ca. 4 dpm) was added to each sample. Saturated aqueous $NH_2OH \cdot HCl$ (1–4 mL, depending on sample volume) and $La(NO_3)_3$ (0.5 mL of a 10 mg/mL standardized solution) were added to each sample. The samples were allowed to equilibrate for at least 12 h, after which time one drop of a 0.6 M $FeCl_2 \cdot 4H_2O$ solution (prepared fresh daily) was added. The samples were allowed to stand at room temperature for 30 min. HF was added to obtain a fluoride ion concentration of at least 2.5 M, and the samples were allowed to stand for 10 min. The samples were centrifuged and the supernatant decanted.

The LaF_3 precipitate was redissolved by addition of saturated H_3BO_3 (1 mL) and concentrated HNO_3 (1 mL). Once the mixture was fully dissolved, 0.6 M $FeCl_2 \cdot 4H_2O$ solution (1 mL, prepared fresh daily) was added. Ascorbic acid (0.25 mL of a 100 mg/mL solution) was also added to each sample, and the samples were allowed to stand for 10 min at room temperature. Concentrated HNO3 (1.25 mL) and 7.2 M HNO_3 (4.5 mL) were added, followed by a saturated solution of $NaNO_2$ (0.25 mL). The samples were allowed to stand at room temperature for 30 min.

An anion exchange column was prepared by adding 0.75 mL AG MP-1M resin (50–100 mesh, chloride form) to a 2 mL disposable Biorad column. The resin was washed with deionized water (6 mL). The resin was conditioned with 7.2 M HNO_3 (3 × 2 mL). The sample was loaded, then the centrifuge cone washed with 7.2 M HNO_3 (2 × 5 mL), and the washings loaded onto the column. The column was washed with concentrated HCl containing 1 drop HNO_3 (2 × 3 mL). The column was washed with 7.2 M HNO_3 (3 × 4 mL). The plutonium and neptunium were eluted with concentrated HBr (2 × 2 mL). The samples were evaporated, and then concentrated HNO_3 (1 drop) was added and evaporated. The samples were redissolved in 2% HNO_3 for analysis by ICP-MS.

3.2. Uncertainty estimation

A control solution was prepared using a known concentration of ^{242}Pu (ca. 3×10^{13} atoms, prepared from NIST SRM 4334G) and an approximately equal known concentration of ^{237}Np (ca. 3×10^{13} atoms, prepared from NIST SRM 4341), diluted to a total volume of ~25 mL. In a typical experiment, two aliquots (0.25 mL, containing ca. 3×10^{11} atoms each of ^{237}Np and ^{242}Pu) of the control solution were purified by anion exchange chromatography in parallel to the sample and a process blank containing no added neptunium. The ^{237}Np/^{242}Pu ratio in the processed controls was determined by ICP-MS and compared to the ^{237}Np/^{242}Pu ratio in the stock control solution to determine the extent of fractionation that occurred between ^{237}Np and ^{242}Pu during the anion exchange procedure. The ^{237}Np/^{242}Pu ratio measured in the original stock control solution was also compared to the expected value to determine the extent to which inter-element fractionation occurs in the mass spectrometer due to ionization or mass bias effects.

4. Results and discussion

4.1. Purification of Np and Pu

A previously reported method for the purification of plutonium by anion exchange chromatography was modified to allow for isolation of both neptunium and plutonium in high yield. To minimize inter-element chemical fractionation, additional steps were carried out to control the oxidation states of neptunium and plutonium. Initially, the actinides were concentrated and separated from the matrix using a LaF_3 co-precipitation. An oxidation state adjustment was then performed to regulate the oxidation states of Pu and Np prior to loading the sample onto the anion exchange resin. Addition of iron (II) chloride and ascorbic acid solutions was used to reduce plutonium to the +3 valence state and neptunium to +4. This step was followed by addition of $NaNO_2$ to form Pu^{4+} and Np^{4+}. Adjustment of the actinides to the 4+ state ensured their retention on the resin (AG MP-1M, 50–100 mesh) in 7.2 M nitric acid as $[Pu(NO_3)_6]^{2-}$ and $[Np(NO_3)_6]^{2-}$. Thorium was removed by washing the column with concentrated HCl, and uranium was removed by washing with 7.2 M nitric acid. Overall, the method provides high yields of plutonium and neptunium (ca. 85–90%) and good decontamination from the potentially interfering elements uranium and thorium, as well as the common matrix elements that comprise the bulk of an environmental collection.

4.2. Instrumental mass bias determination

Instrumental mass bias was monitored periodically using a solution of NBL CRM 128 (^{239}Pu/^{242}Pu, 1:1 Atom Ratio Plutonium Isotopic Standard). Under the typical operating conditions, mass bias was found to be undetectable when compared to the instrumental precision For example, mass bias was calculated as 1.00002 ± 0.00039 per amu by comparing the observed and

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