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 $\pm 5\%$. 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).

Keywords: Neptunium, plutonium, ICP-MS, radionuclides, environmental soil analysis

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/m² 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 & 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; Qiao et al., 2011a; Qiao et al., 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; Qiao et al., 2011a; Qiao et al., 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 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 $^{238}\text{UH}^+ / ^{238}\text{U}$ ratio was determined from measurements of a solution of NIST SRM U960 and used to correct the ^{239}Pu count rates. The contribution of $^{238}\text{UH}^+$ to the total counts at mass 239 was typically less than 1%. A dwell time of 30 milliseconds was used at each mass unit. Mass bias was monitored periodically using a solution of NBL CRM 128 ($^{239}\text{Pu} / ^{242}\text{Pu}$, 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 hours. The samples were fully dissolved using either HF-HNO₃-HClO₄ or HF-HNO₃. A known amount of ^{242}Pu tracer (ca. 4 dpm) was added to each sample. Saturated aqueous NH₂OH·HCl (1-4 mL, depending on sample volume) and La(NO₃)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 FeCl₂·4H₂O solution (prepared fresh daily) was added. The samples were allowed to stand at room temperature for 30 minutes. HF was added to obtain a fluoride ion concentration of at least 2.5 M, and the samples were allowed to stand for 10 minutes. The samples were centrifuged and the supernatant decanted.

The LaF₃ precipitate was redissolved by addition of saturated H₃BO₃ (1 mL) and concentrated HNO₃ (1 mL). Once the mixture was fully dissolved, 0.6 M FeCl₂·4H₂O 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 minutes at room temperature. Concentrated HNO₃ (1.25 mL) and 7.2 M HNO₃ (4.5 mL) were added, followed by a saturated solution of NaNO₂ (0.25 mL). The samples were allowed to stand at room temperature for 30 minutes.

1 An anion exchange column was prepared by adding 0.75 mL AG MP-1M resin (50-100
2 mesh, chloride form) to a 2 mL disposable Biorad column. The resin was washed with deionized
3 water (6 mL). The resin was conditioned with 7.2 M HNO₃ (3 x 2 mL). The sample was loaded,
4 then the centrifuge cone washed with 7.2 M HNO₃ (2 x 5 mL), and the washings loaded onto the
5 column. The column was washed with concentrated HCl containing 1 drop HNO₃ (2 x 3 mL).
6 The column was washed with 7.2 M HNO₃ (3 x 4 mL). The plutonium and neptunium were
7 eluted with concentrated HBr (2 x 2 mL). The samples were evaporated, and then concentrated
8 HNO₃ (1 drop) was added and evaporated. The samples were redissolved in 2% HNO₃ for
9 analysis by ICP-MS.

10
11 *3.2 Uncertainty determination.* A control solution was prepared using a known concentration of
12 ²⁴²Pu (ca. 3 x 10¹³ atoms, prepared from NIST SRM 4334G) and an approximately equal known
13 concentration of ²³⁷Np (ca. 3 x 10¹³ atoms, prepared from NIST SRM 4341), diluted to a total
14 volume of ~25 mL. In a typical experiment, two aliquots (0.25 mL, containing ca. 3 x 10¹¹ atoms
15 each of ²³⁷Np and ²⁴²Pu) of the control solution were purified by anion exchange chromatography
16 in parallel to the sample and a process blank containing no added neptunium. The ²³⁷Np/²⁴²Pu
17 ratio in the processed controls was determined by ICP-MS and compared to the ²³⁷Np/²⁴²Pu ratio
18 in the stock control solution to determine the extent of fractionation that occurred between ²³⁷Np
19 and ²⁴²Pu during the anion exchange procedure. The ²³⁷Np/²⁴²Pu ratio measured in the original
20 stock control solution was also compared to the expected value to determine the extent to which
21 inter-element fractionation occurs in the mass spectrometer due to ionization or mass bias
22 effects.

23 **4. Results and Discussion.**

24 *4.1 Purification of Np and Pu*

25 A previously reported method for the purification of plutonium by anion exchange
26 chromatography was modified to allow for isolation of both neptunium and plutonium in high
27 yield. To minimize inter-element chemical fractionation, additional steps were carried out to
28 control the oxidation states of neptunium and plutonium. Initially, the actinides were
29 concentrated and separated from the matrix using a LaF₃ co-precipitation. An oxidation state
30 adjustment was then performed to regulate the oxidation states of Pu and Np prior to loading the
31 sample onto the anion exchange resin. Addition of iron(II) chloride and ascorbic acid solutions
32 was used to reduce plutonium to the +3 valence state and neptunium to +4. This step was
33 followed by addition of NaNO₂ to form Pu⁴⁺ and Np⁴⁺. Adjustment of the actinides to the 4+
34 state ensured their retention on the resin (AG MP-1M, 50-100 mesh) in 7.2 M nitric acid as
35 [Pu(NO₃)₆]²⁻ and [Np(NO₃)₆]²⁻. Thorium was removed by washing the column with concentrated
36 HCl, and uranium was removed by washing with 7.2 M nitric acid. Overall, the method provides
37 high yields of plutonium and neptunium (ca. 85-90%) and good decontamination from the
38 potentially interfering elements uranium and thorium, as well as the common matrix elements
39 that comprise the bulk of an environmental collection.

40 *4.2 Instrumental mass bias determination*

41 Instrumental mass bias was monitored periodically using a solution of NBL CRM 128
42 (²³⁹Pu/²⁴²Pu, 1:1 Atom Ratio Plutonium Isotopic Standard). Under the typical operating
43 conditions, mass bias was found to be undetectable when compared to the instrumental precision
44
45

For example, mass bias was calculated as 1.00002 ± 0.00039 per amu by comparing the observed and reference $^{239}\text{Pu}/^{242}\text{Pu}$ ratio for CRM 128 as calculated using equation 1.

$$\text{mass bias per amu} = \left[\frac{\left(^{239}\text{Pu} / ^{242}\text{Pu} \right)_{\text{observed}}}{\left(^{239}\text{Pu} / ^{242}\text{Pu} \right)_{\text{reference}}} \right]^{1/3} \quad (1)$$

An additional experiment was performed to ensure that no difference in ionization or mass bias effects was observed for neptunium compared to plutonium. A control solution was prepared containing known concentrations of ^{237}Np and ^{242}Pu tracers in a ratio of 0.956 ± 0.016 . Replicate measurements of the ratio of $^{237}\text{Np}/^{242}\text{Pu}$ in the control solution were then performed by ICP-MS. The average measured value of $^{237}\text{Np}/^{242}\text{Pu}$, 0.952 ± 0.016 , was in good agreement with the expected value, indicating that inter-element mass bias effects were insignificant compared to the uncertainty in the measurement.

4.3 Uncertainty budget estimation

Chemical fractionation occurring between neptunium and plutonium during the laboratory purification process is a major potential source of uncertainty. To determine the extent of fractionation that occurs between ^{237}Np and ^{242}Pu during the analysis, a control solution was prepared containing known concentrations of ^{237}Np and ^{242}Pu tracers (ca. 1:1 ratio). In parallel with each environmental sample, two aliquots of the control solution were purified by anion exchange as described above. The ratio of $^{237}\text{Np}/^{242}\text{Pu}$ in the control experiments after anion exchange was determined by ICP-MS and compared to the $^{237}\text{Np}/^{242}\text{Pu}$ ratio measured in the initial stock solution. The chemical fractionation is defined as follows:

$$[Np/Pu]_{\text{fractionation}} = \frac{\left[^{237}\text{Np} / ^{242}\text{Pu} \right]_{\text{control}}}{\left[^{237}\text{Np} / ^{242}\text{Pu} \right]_{\text{standard}}} \quad (2)$$

Figure 1. Chemical fractionation between ^{237}Np and ^{242}Pu occurring as a result of anion exchange chromatography. The average fractionation (0.930) is indicated by the solid blue line. The dashed lines indicate the 2σ uncertainty ($\pm 7.1\%$).

Figure 1 shows a plot of the chemical fractionation observed in 83 control experiments conducted over the course of more than one year. The average chemical fractionation is 0.930 and the standard deviation is 3.5%. For a given sample, the fractionation value determined in the control experiments run in parallel with the sample was used to correct the raw count rates at ^{237}Np . An uncertainty of 3.5% was propagated into the overall uncertainty of the ^{237}Np measurement to address the component of uncertainty arising from inter-element fractionation that occurs during the chemical purification.

Additional sources of uncertainty in the method are the uncertainty in the absolute concentration of the ^{242}Pu tracer (1%), as well as uncertainty in the raw count rates of the sample (ca. 2-5% for low level environmental samples). For a typical ^{237}Np count rate uncertainty of 2 to 3%, the overall measurement uncertainty is on the order of 4 to 5%. The uncertainty in the measured values of ^{239}Pu and ^{240}Pu is considerably lower (1-2%), as no chemical fractionation correction is needed.

4.4 Comparison to related reported methods.

Previously, Chen, Kim, and Qiao have described methods for the determination of ^{237}Np by ICP-MS using a ^{242}Pu tracer (Chen et al., 2002; Kim et al., 2004; Qiao et al., 2010; Qiao et al., 2011a; Qiao et al., 2011b). Prior reported purification schemes have involved both extraction chromatography (TEVA resin) and anion exchange chromatography (AG 1-x4 or AG MP-1M resins) (Chen et al., 2002; Qiao et al., 2011a). A number of different reagents (Fe^{2+} , ascorbic acid, $\text{K}_2\text{S}_2\text{O}_5$, H_2O_2) have been evaluated for adjusting the oxidation states of neptunium and plutonium during the chemical purification (Chen et al., 2002; Kim et al., 2004; Qiao et al.,

2011a). The method described here is similar to previously developed procedures, using Fe^{2+} and ascorbic acid, followed by NaNO_2 to ensure redox control of neptunium and plutonium.

However, prior reports indicate that the relative yields of neptunium and plutonium can vary depending on the purification conditions and type of resin (Chen et al., 2002; Kim et al., 2004; Qiao et al., 2011a). A new approach to systematically quantify the chemical fractionation occurring between neptunium and plutonium is employed in this method. Two control experiments run in parallel with each sample are used to assess the differences in chemical yields between Np and Pu. The fractionation determined from the parallel control experiments is then used to correct the raw neptunium count rates. The fractionation measured in the parallel control experiments is thought to best represent inter-element fractionation that occurs during sample purification.

4.5 Analysis of a spiked Peruvian soil sample.

As a test of the method accuracy, a sample of known ^{237}Np concentration ($8.13 \pm 0.13 \times 10^7$ atoms/g) was prepared by spiking a ^{237}Np tracer (prepared from NIST SRM 4341) into a solution of Peruvian soil (NIST SRM 4355 Activation and Fission Product blank). Four replicate measurements of the ^{237}Np concentration in the sample were performed and compared with the known value (Figure 2). The average value and propagated uncertainty of the ^{237}Np concentration measured in the solution was $8.05 \pm 0.36 \times 10^7$ atoms/g, in good agreement with the known value. The standard deviation of the measurements was 2.3%.

Figure 2. The ^{237}Np concentration measured in the spiked Peruvian Soil solution. The known concentration value (based on the amount of ^{237}Np tracer added) is shown with a solid blue line, and the uncertainty in the known concentration (based on the uncertainty in the tracer concentration) is shown with dashed blue lines.

4.6 Analysis of standard reference materials 4357, 1646a, and 2702.

Using the optimized method, neptunium and plutonium concentrations were determined in several standard reference materials. NIST standard reference material 4357 (Radioactivity

Standard) is composed of a mixture of sediment derived from the Chesapeake Bay area and sediment from the coastal UK near the Sellafield reprocessing facility. The certified range (2.5 to 97.5% confidence) of $^{239+240}\text{Pu}$ activity in SRM 4357 is 9.3-13.2 mBq/g, with an average value of 10.4 ± 0.2 . Some variability in the absolute concentration of plutonium is expected and attributable to known heterogeneity in the reference material (Inn et al., 1996; Inn et al., 2001; Lin et al., 2001).

To evaluate the consistency of the method, a sample (~6 g) of SRM 4357 was dissolved and repeatedly analyzed. Five separate aliquots of the dissolved sample were analyzed independently over the course of one month. Each analyzed portion represented ~0.26 g of reference sediment containing $\sim 1.6 \times 10^9$ atoms of ^{239}Pu per aliquot. For the five replicate analyses, the measured $^{240}\text{Pu}/^{239}\text{Pu}$ values were in good agreement within the measurement uncertainty. The average and standard deviation of the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio was 0.2339 ± 0.0033 , a variation in the results of $\pm 1.4\%$. For comparison, the total propagated uncertainty for each individual measurement ranged from 1.7 to 3.9%. Similarly, the measured values of $^{237}\text{Np}/^{239}\text{Pu}$ were also quite consistent, with an average and standard deviation of 0.1503 ± 0.0032 . In this case the standard deviation for the five measurements was $\pm 2.1\%$, as compared with a total propagated uncertainty for each individual measurement of ± 4.7 to 6.3%. In general the analytical method produces results that are reproducible within the total propagated uncertainty of the individual measurements.

Additional experiments were performed using individually dissolved portions of SRM 4357 (Table 1). Five separate dissolutions of the solid material (with masses between ca. 0.2 and 1.2 g) were performed and analyzed individually. Detailed studies of the heterogeneity of SRM 4357 have been previously reported (Lin et al., 2001). The measured concentrations of ^{239}Pu ranged from $5.43 \pm 0.06 \times 10^9$ to $5.95 \pm 0.07 \times 10^9$ atoms/g (Table 1). The $^{239+240}\text{Pu}$ activity in the sediment was calculated based on the concentrations of ^{239}Pu and ^{240}Pu determined by ICP-MS, and ranged from 9.27 ± 0.28 to 10.03 ± 0.22 mBq/g (Table 2). The average $^{240}\text{Pu}/^{239}\text{Pu}$ ratio was 0.233 ± 0.003 , in good agreement with average values for $^{240}\text{Pu}/^{239}\text{Pu}$ in SRM 4357 previously reported by Cizdziel et al. (0.237) (Cizdziel et al., 2008), Ketterer et al. (0.227) (Ketterer & Szechenyi, 2008), Zhang et al. (0.235) (Zhang et al., 2010) and Kim et al. (0.24) (Kim et al., 2004). For the largest sample (5), the plutonium instrumental count rates were high enough that ^{241}Pu could also be determined. The $^{241}\text{Pu}/^{239}\text{Pu}$ ratio measured was 0.0065 ± 0.0005 (reference date 8/23/2013), consistent with previous work by Kershaw and coworkers, who measured $^{241}\text{Pu}/^{239}\text{Pu}$ by TIMS in sediment cores collected near Sellafield (Kershaw et al., 1995). Kershaw and coworkers found that the $^{241}\text{Pu}/^{239}\text{Pu}$ ratio depended on the sampling depth, ranging from ~0.020-0.001 (reference date ca. 1995) (Kershaw et al., 1995).

The ^{237}Np concentration measured in SRM 4357 varied from $8.5 \pm 0.5 \times 10^8$ atoms/g to $1.06 \pm 0.05 \times 10^9$ atoms/g. The average calculated activity (0.0094 ± 0.0009 mBq/g, Table 2) is consistent with that reported by Kim and coworkers for ^{237}Np activity in SRM 4357 (0.0089 ± 0.0008 mBq/g) (Kim et al., 2004). The ^{237}Np activity in SRM 4357 is not certified, but an informational value is provided at 0.007 mBq/g (with a range of reported values of 0.004-0.009). For the analysis of these five samples, the average and standard deviation of the $^{237}\text{Np}/^{239}\text{Pu}$ atom ratio was 0.160 ± 0.016 . Both the measured ratios in SRM 4357 for $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{237}\text{Np}/^{239}\text{Pu}$ are consistent with the isotopic composition reported for nuclear fuel reprocessing at Sellafield (Kershaw et al., 1995).

Table 1. Plutonium and neptunium measurements of NIST SRM 4357.

Sample number	Sample dry mass (g)	²³⁹ Pu (atoms/g)	²⁴⁰ Pu (atoms/g)	²³⁷ Np (atoms/g)	²⁴⁰ Pu/ ²³⁹ Pu	²³⁷ Np/ ²³⁹ Pu
1	0.2121	5.43 ± 0.06 x 10 ⁹	1.29 ± 0.04 x 10 ⁹	8.73 ± 0.53 x 10 ⁸	0.238 ± 0.007	0.161 ± 0.010
2	0.4575	5.88 ± 0.12 x 10 ⁹	1.36 ± 0.04 x 10 ⁹	9.01 ± 0.51 x 10 ⁸	0.231 ± 0.010	0.154 ± 0.009
3	0.3764	5.95 ± 0.07 x 10 ⁹	1.37 ± 0.03 x 10 ⁹	8.48 ± 0.49 x 10 ⁸	0.231 ± 0.005	0.143 ± 0.009
4	0.3755	5.64 ± 0.09 x 10 ⁹	1.30 ± 0.02 x 10 ⁹	8.76 ± 0.53 x 10 ⁸	0.231 ± 0.003	0.155 ± 0.009
5	1.2029	5.68 ± 0.07 x 10 ⁹	1.32 ± 0.02 x 10 ⁹	1.06 ± 0.05 x 10 ⁹	0.233 ± 0.001	0.187 ± 0.008
average ± 1sd	0.5249	5.72 ± 0.21 x 10⁹	1.33 ± 0.04 x 10⁹	9.12 ± 0.86 x 10⁸	0.233 ± 0.003	0.160 ± 0.016

Table 2. Calculated activities of ²³⁹⁺²⁴⁰Pu and ²³⁷Np per gram of NIST SRM 4357.^a

Sample number	²³⁹⁺²⁴⁰ Pu activity (mBq/g)	²³⁷ Np activity (mBq/g)
1	9.27 ± 0.28	0.0090 ± 0.0005
2	9.91 ± 0.34	0.0092 ± 0.0005
3	10.03 ± 0.22	0.0087 ± 0.0005
4	9.50 ± 0.22	0.0090 ± 0.0005
5	9.60 ± 0.17	0.0109 ± 0.0005
average ± 1sd	9.66 ± 0.31	0.0094 ± 0.0009

^a Calculated using half-lives of 2.410 x 10⁴ yrs for ²³⁹Pu, 6.56 x 10³ yrs for ²⁴⁰Pu, and 2.14 x 10⁶ yrs for ²³⁷Np.

Standard reference materials 1646a (Estuarine Sediment) and 2702 (Inorganics in Marine Sediment) are sediments from the Chesapeake Bay area that are certified for inorganic elemental composition. Both materials are expected to contain plutonium and neptunium derived from global fallout from atmospheric nuclear weapons testing. Unlike SRM 4357, there is no added component of Sellafield sediment in SRM 1646a or SRM 2702, and thus the overall concentration of neptunium and plutonium radionuclides is expected to be considerably lower.

Two separate samples of SRM 1646a (~2-3 g each) were dissolved and analyzed for plutonium and neptunium. For SRM 1646a, the ratios of ²³⁷Np/²³⁹Pu (0.356 ± 0.033) and ²⁴⁰Pu/²³⁹Pu (0.171 ± 0.004) determined are consistent with those reported in northern hemisphere soils for global fallout from nuclear weapons testing (Kelley et al., 1999).

Table 3. Plutonium and neptunium measurements of NIST SRM 1646a and SRM 2702.

SRM number (sample number)	²³⁹ Pu (atoms/g)	²⁴⁰ Pu (atoms/g)	²³⁷ Np (atoms/g)	²⁴⁰ Pu/ ²³⁹ Pu	²³⁷ Np/ ²³⁹ Pu
1646a (1)	1.43 ± 0.02 x 10 ⁸	2.40 ± 0.05 x 10 ⁷	4.74 ± 0.28 x 10 ⁷	0.168 ± 0.004	0.332 ± 0.020
1646a (2)	1.38 ± 0.06 x 10 ⁸	2.39 ± 0.20 x 10 ⁷	5.21 ± 0.46 x 10 ⁷	0.174 ± 0.011	0.379 ± 0.034
1646 (average ± 1sd)	1.40 ± 0.04 x 10⁸	2.40 ± 0.01 x 10⁷	4.98 ± 0.34 x 10⁷	0.171 ± 0.004	0.356 ± 0.033

2702 (1)	$2.75 \pm 0.03 \times 10^8$	$4.70 \pm 0.24 \times 10^7$	$2.42 \pm 0.11 \times 10^8$	0.171 ± 0.009	0.880 ± 0.040
2702 (2)	$2.25 \pm 0.07 \times 10^8$	$4.09 \pm 0.14 \times 10^7$	$2.18 \pm 0.10 \times 10^8$	0.182 ± 0.007	0.971 ± 0.058
2702 (3)	$2.66 \pm 0.12 \times 10^8$	$4.22 \pm 0.28 \times 10^7$	$2.50 \pm 0.18 \times 10^8$	0.159 ± 0.013	0.942 ± 0.078
2702 (average $\pm$ 1sd)	$2.55 \pm 0.27 \times 10^8$	$4.34 \pm 0.32 \times 10^7$	$2.37 \pm 0.17 \times 10^8$	0.171 ± 0.012	0.931 ± 0.046

Table 4. Calculated activities of $^{239+240}\text{Pu}$ and ^{237}Np per gram of NIST SRM 1646a and NIST SRM 2702.^a

Sample number	$^{239+240}\text{Pu}$ activity (mBq/g)	^{237}Np activity (mBq/g)
1646 (1)	0.211 ± 0.005	0.00049 ± 0.00003
1646 (2)	0.206 ± 0.019	0.00054 ± 0.00005
1646 (average $\pm$ 1sd)	0.208 ± 0.004	0.00051 ± 0.00003
2702 (1)	0.408 ± 0.022	0.0025 ± 0.0001
2702 (2)	0.342 ± 0.016	0.0022 ± 0.0001
2702 (3)	0.384 ± 0.030	0.0026 ± 0.0002
2702 (average $\pm$ 1sd)	0.378 ± 0.034	0.0024 ± 0.0002

^a Calculated using half-lives of 2.410×10^4 yrs for ^{239}Pu , 6.56×10^3 yrs for ^{240}Pu , and 2.14×10^6 yrs for ^{237}Np .

Three different samples of SRM 2702 (~2 g each) were dissolved and analyzed for plutonium and neptunium. While the average $^{240}\text{Pu}/^{239}\text{Pu}$ ratio measured for SRM 2702 (0.171 ± 0.012) is consistent with global fallout, the average ratio of $^{237}\text{Np}/^{239}\text{Pu}$ (0.931 ± 0.046) is considerably higher than values reported by Kelley and coworkers for $^{237}\text{Np}/^{239}\text{Pu}$ in northern hemisphere soils (Kelley et al., 1999). The higher $^{237}\text{Np}/^{239}\text{Pu}$ ratio in SRM 2702 may reflect different chemical behaviors and mobility of plutonium and neptunium in the environment (Morris et al., 2000). For example, previous neptunium and plutonium measurements of aquatic sediment cores off the coastal UK near Sellafield suggest a higher mobility of neptunium, with ^{237}Np concentrating relative to plutonium in surface sediment layers (Hursthouse et al., 1991; Morris et al., 2000).

The overall average ^{239}Pu concentration for both SRM 1646a ($1.40 \pm 0.04 \times 10^8$ atoms/g) and SRM 2702 ($2.55 \pm 0.27 \times 10^8$ atoms/g) was found to be significantly lower than in SRM 4357 ($5.72 \pm 0.21 \times 10^9$ atoms/g). The measured ^{239}Pu concentrations, $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{237}\text{Np}/^{239}\text{Pu}$ isotopic ratios are all consistent with global fallout being the source of the plutonium in SRM 1646a and SRM 2702. The higher $^{240}\text{Pu}/^{239}\text{Pu}$ and lower $^{237}\text{Np}/^{239}\text{Pu}$ ratios in SRM 4357 are consistent with transuranic contamination from nuclear fuel reprocessing releases. This industrial source term from Sellafield discharge effectively overwhelms background contamination from atmospheric fallout as detected in the SRM 1646a and 2702 reference materials.

5. Conclusions.

A new method was developed to analyze environmental samples simultaneously for ^{237}Np , ^{239}Pu , and ^{240}Pu by ICP-MS using a ^{242}Pu tracer. 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 the uncertainty arising from inter-element fractionation occurring during the method suggest that the overall precision 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.

Neptunium and plutonium concentrations were determined in several standard reference materials. NIST SRM 4357, a radioactivity standard containing sediment collected off the coast of the UK near Sellafield, was found to have isotopic signatures consistent with nuclear fuel reprocessing. Measurements of $^{240}\text{Pu}/^{239}\text{Pu}$ and ^{237}Np were in good agreement with previously reported values. Different isotopic signatures were measured for NIST SRM 1646a and SRM 2702, sediment standards collected within the Chesapeake Bay. The measured values of $^{240}\text{Pu}/^{239}\text{Pu}$ and $^{237}\text{Np}/^{239}\text{Pu}$ are consistent with global fallout from atmospheric nuclear weapons testing. The ability to measure the low levels of fallout-derived neptunium and plutonium in SRM 1646a and SRM 2702 underscores promise of this method for determining neptunium and plutonium in a range of environmental solid samples.

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References

- Chen C., Dahlgaard H., Nielsen S. P., Aarkrog A. 2002. ^{242}Pu Tracer for Simultaneous Determination of ^{237}Np and $^{239,240}\text{Pu}$ in Environmental Samples. *Journal of Radioanalytical and Nuclear Chemistry* 253, 451-458.
- Cizdziel J. V., Ketterer M. E., Farmer D., Faller S. H., Hodge V. F. 2008. $^{239,240,241}\text{Pu}$ Fingerprinting of Plutonium in Western US Soils Using ICP-MS: Solution and Laser Ablation Measurements. *Analytical and Bioanalytical Chemistry* 390, 521-530.
- Cochran J. K., Moran S. B., Fisher N. S., Beasley T. M., Kelley J. M. 2000. Sources and Transport of Anthropogenic Radionuclides in the Ob River System, Siberia. *Earth and Planetary Science Letters* 179, 125-137.
- Efurd D. W., Roensch F. R., Drake J., Perrin R. E. 1991. Production, Separation, and Purification of ^{236}Np and ^{236}Pu . *Radiochimica Acta* 54, 159-161.
- Hunt G. J., Smith B. D. 1999. The Radiological Impact of Actinides Discharged to the Irish Sea. *Journal of Environmental Radioactivity* 44, 389-403.
- Hursthouse A. S., Baxter M. S., Livens F. R. 1991. Transfer of Sellafield-Derived ^{237}Np to and within the Terrestrial Environment. *Journal of Environmental Radioactivity* 14, 147-174.
- Inn K. G. W., Lin Z., Liggett W. S., Schima F. J., Krey P., et al. 1996. Low-level Radioactivity Ocean Sediment Standard Reference Material. *Applied Radiation and Isotopes* 47, 967-970.
- Inn K. G. W., Lin Z., Wu Z., McMahon C., Filliben J. J., et al. 2001. The NIST Natural-Matrix Radionuclide Standard Reference Material Program for Ocean Studies. *Journal of Radioanalytical and Nuclear Chemistry* 248, 227-231.
- Kelley J. M., Bond L. A., Beasley T. M. 1999. Global Distribution of Pu Isotopes and ^{237}Np . *The Science of the Total Environment* 237-238, 483-500.
- Kenna T. C. 2002. Determination of Plutonium Isotopes and Neptunium-237 in Environmental Samples by Inductively Coupled Plasma Mass Spectrometry with Total Sample Dissolution. *Journal of Analytical Atomic Spectroscopy* 17, 1471-1479.

- 1 Kershaw P. J., Sampson K. E., McCarthy W., Scott R. D. 1995. The Measurement of the Isotopic
2 Composition of Plutonium in an Irish Sea Sediment by Mass Spectrometry. *Journal of*
3 *Radioanalytical and Nuclear Chemistry* 198, 113-124.
- 4 Ketterer M. E., Szechenyi S. C. 2008. Determination of Plutonium and Other Transuranic Elements by
5 Inductively Coupled Plasma Mass Spectrometry: A Historical Perspective and New Frontiers in
6 the Environmental Sciences. *Spectrochimica Acta B* 63, 719-737.
- 7 Kim C. S., Kim C. K., Lee K. J. 2004. Simultaneous Analysis of ^{237}Np and Pu Isotopes in Environmental
8 Samples by ICP-SF-MS Coupled with Automated Sequential Injection System. *Journal of*
9 *Analytical Atomic Spectroscopy* 19, 743-750.
- 10 Lin Z., Inn K. G. W., Filliben J. J. 2001. An Alternative Statistical Approach for Interlaboratory
11 Comparison Data Evaluation. *Journal of Radioanalytical and Nuclear Chemistry* 248, 163-173.
- 12 MacKenzie A. B., Scott R. D., Allan R. L., Shaban Y. A. B., Cook G. T., Pulford I. D. 1994. Sediment
13 Radionuclide Profiles: Implications for Mechanisms of Sellafield Waste Dispersal in the Irish
14 Sea. *Journal of Environmental Radioactivity* 23, 39-69.
- 15 Morris K., Butterworth J. C., Livens F. R. 2000. Evidence for the Remobilization of Sellafield Waste
16 Radionuclides in an Intertidal Salt Marsh, West Cumbria, UK. *Estuarine, Coastal, and Shelf*
17 *Science* 51, 613-625.
- 18 Qiao J., Hou X., Roos P., Miró M. 2010. Rapid and Simultaneous Determination of Neptunium and
19 Plutonium Isotopes in Environmental Samples by Extraction Chromatography Using Sequential
20 Injection Analysis and ICP-MS. *Journal of Analytical Atomic Spectroscopy* 25, 1769-1779.
- 21 Qiao J., Hou X., Roos P., Miró M. 2011a. High-Throughput Sequential Injection Method for
22 Simultaneous Determination of Plutonium and Neptunium in Environmental Solids Using
23 Macroporous Anion-Exchange Chromatography, Followed by Inductively Coupled Plasma Mass
24 Spectrometric Detection. *Analytical Chemistry* 83, 374-381.
- 25 Qiao J., Hou X., Roos P., Miró M. 2011b. Reliable Determination of ^{237}Np in Environmental Solid
26 Samples Using ^{242}Pu as a Potential Tracer. *Talanta* 84, 494-500.
- 27 Vanhaecke F., Wannemacker G. d., Moens L., Dams R., Latkoczy C., et al. 1998. Dependence of
28 Detector Dead Time on Analyte Mass Number in Inductively Coupled Plasma Mass
29 Spectrometry. *Journal of Analytical Atomic Spectroscopy* 13, 567-571.
- 30 Zhang Y., Zheng J., Yamada M., Wu F., Igarashi Y., Hirose K. 2010. Characterization of Pu
31 Concentration and Its Isotopic Composition in a Reference Fallout Material. *Science of the Total*
32 *Environment* 408, 1139-1144.