

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/49648986>

# High-Throughput Sequential Injection Method for Simultaneous Determination of Plutonium and Neptunium in Environmental Solids Using Macroporous Anion-Exchange Chromatography, Follo...

ARTICLE in ANALYTICAL CHEMISTRY · JANUARY 2011

Impact Factor: 5.64 · DOI: 10.1021/ac102567b · Source: PubMed

CITATIONS

8

READS

135

4 AUTHORS, INCLUDING:



Jixin Qiao

Technical University of Denmark

22 PUBLICATIONS 161 CITATIONS

SEE PROFILE



Xiaolin Hou

Technical University of Denmark

171 PUBLICATIONS 2,328 CITATIONS

SEE PROFILE



Manuel Miro

University of the Balearic Islands

182 PUBLICATIONS 2,665 CITATIONS

SEE PROFILE

# High-Throughput Sequential Injection Method for Simultaneous Determination of Plutonium and Neptunium in Environmental Solids Using Macroporous Anion-Exchange Chromatography, Followed by Inductively Coupled Plasma Mass Spectrometric Detection

Jixin Qiao,<sup>\*,†</sup> Xiaolin Hou,<sup>†</sup> Per Roos,<sup>†</sup> and Manuel Miró<sup>‡</sup>

Radiation Research Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark, and Department of Chemistry, Faculty of Sciences, University of the Balearic Islands, Carretera de Valldemossa km. 7.5, E-07122 Palma de Mallorca, Illes Balears, Spain

This paper reports an automated analytical method for rapid and simultaneous determination of plutonium and neptunium in soil, sediment, and seaweed, with detection via inductively coupled plasma mass spectrometry (ICP-MS). A chromatographic column packed with a macroporous anion exchanger (AG MP-1 M) was incorporated in a sequential injection (SI) system for the efficient retrieval of plutonium, along with neptunium, from matrix elements and potential interfering nuclides. The sorption and elution behavior of plutonium and neptunium onto AG MP-1 M resin was compared with a commonly utilized AG 1-gel-type anion exchanger. Experimental results reveal that the pore structure of the anion exchanger plays a pivotal role in ensuring similar separation behavior of plutonium and neptunium along the separation protocol. It is proven that plutonium-242 ( $^{242}\text{Pu}$ ) performs well as a tracer for monitoring the chemical yield of neptunium when using AG MP-1 M resin, whereby the difficulties in obtaining a reliable and practicable isotopic neptunium tracer are overcome. An important asset of the SI setup is the feasibility of processing up to 100 g of solid substrates using a small-sized (ca. 2 mL) column with chemical yields of neptunium and plutonium being  $\geq 79\%$ . Analytical results of three certified/standard reference materials and two solid samples from intercomparison exercises are in good agreement with the reference values at the 0.05 significance level. The overall on-column separation can be completed within 3.5 h for 10 g of soil samples. Most importantly, the anion-exchange mini-column suffices to be reused up to 10-fold with satisfactory chemical yields ( $> 70\%$ ), as demanded in environmental monitoring and emergency scenarios, making the

proposed automated assembly well-suited for unattended and high-throughput analysis.

Plutonium (Pu) and neptunium (Np) were released into the environment by nuclear activities including the nuclear weapons testing from the 1940s to the 1980s, nuclear accidents and discharges from nuclear power plants, and spent nuclear fuel reprocessing plants.<sup>1</sup> They are regarded as highly radiologically and biologically hazardous pollutants in the environment, because of alpha emission and long half-lives of their most important isotopes (e.g.,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{237}\text{Np}$ ), respectively. From the viewpoint of environmental risk assessment and radiological emergency preparedness, as well as nuclear waste treatment, there is a current requirement in accurate determination of Pu and Np in various environmental compartments.<sup>2</sup>

In principle, it is possible to perform simultaneous isolation of Pu and Np, because the chemical behaviors of tetravalent Pu and Np anionic complexes are similar in nitric and hydrochloric acid media.<sup>3,4</sup> Plutonium isotopes (viz.,  $^{242}\text{Pu}$ ,  $^{236}\text{Pu}$ , or  $^{244}\text{Pu}$ ) might be selected as nonisotopic tracers to monitor the chemical yield of Np. The remarkable advantage would be the avoidance of difficulties in obtaining isotopic Np tracers ( $^{239}\text{Np}$ ,  $^{236}\text{Np}$ , or  $^{235}\text{Np}$ ), which are not commercially available and are not easily produced and purified in most laboratories.<sup>5,6</sup> Moreover, the analytical time would be shortened, because there would be no need for chemical separation of Np (namely,  $^{237}\text{Np}$ ) from Pu, and the consumption of samples and chemicals would also be reduced to a large extent. A handful of analytical methods have

\* Author to whom correspondence should be addressed. Tel.: +45 4677 5454. Fax: +45 4677 5330. E-mail: jiqi@risoe.dtu.dk (official), qiaojixin2004@gmail.com (private).

<sup>†</sup> Technical University of Denmark.

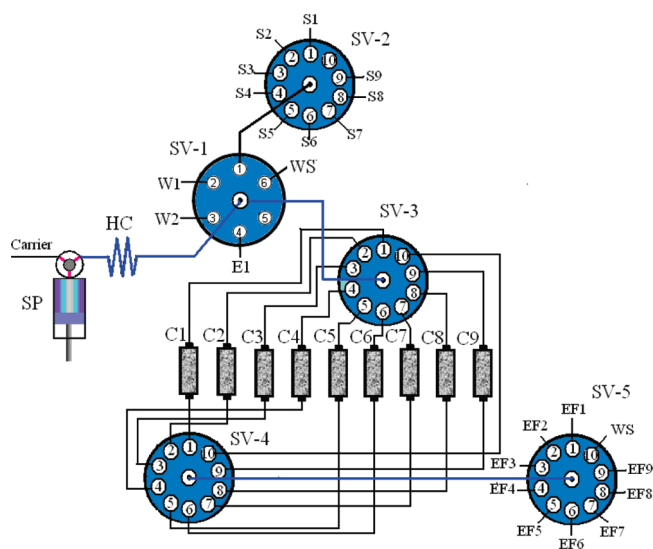
<sup>‡</sup> University of the Balearic Islands.

- (1) Morss, L. R.; Edelstein, N. M.; Fuger, J. *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Springer: Dordrecht, The Netherlands, 2006.
- (2) Qiao, J.; Hou, X.; Miró, M.; Roos, P. *Anal. Chim. Acta* **2009**, *652*, 66–84.
- (3) Burney, G. A.; Harbour, R. M. *Radiochemistry of Neptunium*, NAS-NS 3060, Technical Information Center, Office of Information Service, United States Atomic Energy Commission, VA, 1974.
- (4) Lehto, J.; Hou, X. *Chemistry and Analysis of Radionuclides*, 1st ed.; Wiley-VCH: Weinheim, Germany, 2010.
- (5) Qiao, J. X.; Hou, X. L.; Roos, P.; Miró, M. *J. Anal. At. Spectrom.* **2010**, *25*, 1769–1779.
- (6) Qiao, J. X.; Hou, X. L.; Roos, P.; Miró, M. Submitted to *Talanta*, **2010**.

been reported to date for the simultaneous determination of Pu and Np in environmental samples;<sup>5–10</sup> however, only a few works have exploited a Pu isotope as a tracer for both Pu and Np.<sup>5,7,10</sup>

Difficulties in using Pu isotopes as tracers for <sup>237</sup>Np determination might arise from the fact that the tetravalent Np (Np(IV)), being easily oxidized, may behave differently from Pu(IV) onto the sorptive resin during separation. The first application of extraction chromatography (TEVA) for the simultaneous separation of Pu and Np, using a Pu isotopic tracer, was reported by Kim et al., but it was only devoted to small-sized samples ( $\leq 4$  g of soil).<sup>10</sup> In our previous work, larger-sized samples (10 g of soil) were successfully analyzed for Pu and Np using a TEVA column,<sup>5</sup> but chemical yields, in some instances, were  $<60\%$ , as a consequence of the low distribution coefficients of Pu and Np onto TEVA in highly concentrated nitric acid.<sup>11</sup> Compared with extraction chromatography, anion-exchange chromatography is cost-effective and has widespread use in routine radiochemical assays. AG 1 gel-type (also called microporous) resins are the sorbent of choice and are commonly utilized for the anion-exchange separation of Pu and/or Np in a variety of analytical protocols.<sup>7,12–22</sup> Large-sized gel-type (AG 1-X4) anion-exchange columns have also been exploited for simultaneous isolation of Pu and Np, using <sup>242</sup>Pu as a tracer;<sup>7</sup> yet, the procedure is tedious and operated in a manual fashion, so it is time-consuming and labor-intensive. Moreover, our previous investigation, implementing AG 1-gel-type exchangers in a flow-based network for the dynamic separation of <sup>237</sup>Np using <sup>242</sup>Pu as a nonisotopic tracer, revealed poor chemical yields for Np.<sup>6</sup>

For the purpose of developing a high-throughput analytical method for simultaneous determination of Pu isotopes (namely, <sup>239</sup>Pu and <sup>240</sup>Pu) and <sup>237</sup>Np, a paradigm shift is proposed in this work, to exploit macroporous anion exchangers, which have been barely used in radiochemical assays. To our best



**Figure 1.** Schematic diagram of the sequential injection (SI) anion-exchange column manifold for simultaneous determination of Pu and Np in environmental solids. W1, 8 mol/L HNO<sub>3</sub>; W2, 9 mol/L HCl; E1, 0.5 mol/L HCl; WS, waste; S1–S9, ports for sample loading; EF1–EF9, ports for eluate collection; SP, syringe pump; SV-1–SV-5, selection valves; HC, holding coil; and C1–C9, nine anion-exchange columns.

knowledge, this is the first automated flow-based method using macroporous anion-exchange column separation for concurrent determination of trace levels of Pu and Np in environmental solid samples (viz., soil, sediment, and seaweed).

## EXPERIMENTAL SECTION

**Flow-Based Setup.** The automated separation setup consisted of an FIALab-3500B sequential injection (SI) system (FIALab Instruments, Bellevue, WA) that was furnished with the following: a syringe pump (SP, Cervo, Sunnyvale, CA, 25 mL capacity); one 6-port multiposition selection valve (SV-1); four 10-port multiposition section valves, identified as SV-2 to SV-5 (Valco Instruments, Houston, TX); and nine anion-exchange columns. A schematic illustration of the SI analyzer is shown in Figure 1. Within the system, nine samples can be sequentially processed by computer control via FIALab-associated software. All the outlets of the selection valve (SV-1) were connected through PEEK ferrules with rigid poly tetrafluoroethylene (PTFE) tubing (2.4 mm inner diameter (id)/3.2 mm outer diameter (od)), and all the outlets of the external selection valves (SV-2 to SV-5) were connected through PEEK ferrules with rigid PTFE tubing of smaller diameter (0.8 mm id/1.6 mm od). The central port of the SV-1 was connected to the holding coil (HC), which consisted of a 6.6-m-long PTFE tubing with an inner capacity of 30 mL (2.4 mm id/3.2 mm od). Hereby, it should be mentioned that two of the external selection valves, i.e., SV-2 and SV-5, might be replaced by an autosampler and eluate autocollector, respectively.

**Standards, Reagents, and Samples.** All reagents used in the experiment were analytical reagent grade and prepared using deionized water (18 M $\Omega$ ·cm). A <sup>242</sup>Pu standard solution (0.1037 Bq/g in 2 mol/L HNO<sub>3</sub>) diluted from NBL-CRM 130 (New Brunswick Laboratory, Argonne, IL) was used as a chemical yield tracer for both Pu and Np. <sup>237</sup>Np (0.01175 Bq/g in 2 mol/L HNO<sub>3</sub>) and <sup>239</sup>Pu solutions (0.100 Bq/g in 2 mol/L HNO<sub>3</sub>) were

- (7) Chen, Q. J.; Dahlgard, H.; Nielsen, S. P.; Aarkrog, A. *J. Radioanal. Nucl. Chem.* **2002**, *253*, 451–458.
- (8) Perna, L.; Betti, M.; Moreno, J. M. B.; Fuoco, R. *J. Anal. At. Spectrom.* **2001**, *16*, 26–31.
- (9) Kenna, T. C. *J. Anal. At. Spectrom.* **2002**, *17*, 1471–1479.
- (10) Kim, C. S.; Kim, C. K.; Lee, K. J. *J. Anal. At. Spectrom.* **2004**, *19*, 743–750.
- (11) Horwitz, E. P.; Dietz, M. L.; Chiarizia, R.; Diamond, H.; Maxwell, S. L.; Nelson, M. R. *Anal. Chim. Acta* **1995**, *310*, 63.
- (12) Pentreath, R. J.; Harvey, B. R. *Mar. Ecol. Prog. Ser.* **1981**, *6*, 243–247.
- (13) Rosner, G.; Winkler, R.; Yamamoto, Y. *J. Radioanal. Nucl. Chem.* **1993**, *173*, 273–281.
- (14) Beasley, T. M.; Kelley, J. M.; Maiti, T. C.; Bond, L. A. *J. Environ. Radioact.* **1998**, *38*, 133–146.
- (15) Chen, Q. J.; Dahlgard, H.; Nielsen, S. P.; Aarkrog, A.; Christensen, I.; Jensen, A. *J. Radioanal. Nucl. Chem.* **2001**, *249*, 527–533.
- (16) Lindahl, P.; Roos, P.; Eriksson, M.; Holm, E. *J. Environ. Radioact.* **2004**, *73*, 73–85.
- (17) Lee, M. H.; Jung, E. C.; Kim, W. H.; Jee, K. Y. *J. Alloys Compd.* **2007**, *444–445*, 544–549.
- (18) Kelley, J. M.; Bond, L. A.; Beasley, T. M. *Sci. Total Environ.* **1999**, *237/238*, 483–500.
- (19) Lindahl, P.; Keith-Roach, M.; Worsfold, P.; Choi, M.; Shin, H.; Lee, S. *Anal. Chim. Acta* **2010**, *671*, 61–69.
- (20) Paxton, W. F.; O'Hara, M. J.; Peper, S. M.; Petersen, S. L.; Grate, J. W. *Anal. Chem.* **2008**, *80*, 4070–4077.
- (21) Chamizo, E.; Jiménez-Ramos, M. C.; Wacker, L.; Vioque, I.; Calleja, A.; García-León, M.; García-Tenorio, R. *Anal. Chim. Acta* **2008**, *606*, 239–245.
- (22) Li, C.; Larivière, D.; Kiser, S.; Moodie, G.; Falcomer, R.; Elliot, N.; Burchart, L.; Paterson, L.; Epov, V.; Evans, D.; Pappas, S.; Smithe, J.; Cornetta, J. *J. Anal. At. Spectrom.* **2008**, *23*, 521–526.

supplied by Risø National Laboratory for Sustainable Energy (Denmark). Standard solutions of uranium and thorium were purchased from NIST (Gaithersburg, MD).

The anion-exchange resins explored in this work were AG MP-1 M macroporous resins with particle sizes of 50–100 and 100–200 mesh, as well as AG 1-X4 gel-type resin with particle size of 100–200 mesh, both in chloride form (Bio Rad Laboratories Inc., Hercules, CA). AG MP-1 resin is the macroporous equivalent of AG 1-gel-type resin with an effective surface area of ca. 23 m<sup>2</sup>/g and porosity as large as 20%. The resin was swelled in deionized water and poured into a ca. 2 mL (5 mm id × 10 cm long) Econo-column (Bio Rad Laboratories, Inc.) and preconditioned with an 8 mol/L HNO<sub>3</sub> solution. Three certified reference materials including two sediments (IAEA-385 and IAEA-135), and one seaweed (NIST-4359), and two reference materials from a laboratory round-robin intercomparison (namely, a Danish soil<sup>23</sup> and an Irish Sea sediment) were employed to evaluate the trueness of the method. Unless otherwise stated, the Danish soil was selected for method development.

**Sample Pretreatment.** A certain amount (0.5–100 g, depending on the concentration of Pu and Np) of a given solid sample was placed in a beaker and ashed at 550 °C overnight to decompose the organic matter. The sample was spiked with 5 mBq of <sup>242</sup>Pu as a tracer. With regard to the Danish soil, 0.5 mBq of <sup>237</sup>Np was added to increase the signal of <sup>237</sup>Np in ICP-MS measurement, because of the negligible concentration of <sup>237</sup>Np in the original sample. Aqua regia was then added to the sample (in a ratio of 10 mL of aqua regia to 1 g of sample) and the mixture was digested on a hot plate at 150 °C for 30 min and then 200 °C for 2 h, respectively. During the digestion, the beaker was covered with a watchglass, to prevent significant evaporation of the solution. After cooling, the supernatant was filtered through a GF/A filter into a centrifuge tube, and the beaker and filter paper were washed with 30 mL of 0.2 mol/L HCl. Concentrated ammonia was added to the supernatant to adjust the pH to a value of 8–9, to coprecipitate Pu and Np with iron hydroxides and remove concomitant matrix components, whereupon the coprecipitate was separated by centrifugation. For small-sized samples (e.g., ≤ 1 g soil or sediment), the overall Np must be adjusted to a tetravalent state with K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> prior to the above step, to ensure the quantitative precipitation of Np, because of potential losses of the target radionuclide, as a consequence of the relatively high solubility of Np(V). Thirty milliliters (30 mL) of 6 mol/L NaOH was added to the coprecipitate to dissolve amphoteric elements, such as aluminum and vanadium, and then remove them by centrifugation.

A few milliliters of concentrated HCl were added to dissolve the precipitate from the pretreatment step above, and then 300 mg of K<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was added to convert the overall Pu and Np to Pu(III) and Np(IV), respectively. NaOH (6 mol/L) was added to the solution to adjust the pH to a value of 10. After centrifugation, a few milliliters of concentrated HCl were added to dissolve the resulting precipitate. Concentrated HNO<sub>3</sub> was then added to oxidize Pu(III) to Pu(IV), and, finally, the solution

was adjusted to 8 mol/L HNO<sub>3</sub> to stabilize the target species as Pu(IV) and Np(IV) prior to injection into the SI setup.

For large sample sizes (viz., 20 g of seaweed and 20–100 g of soil), the sample was initially divided into 2–10 aliquots with a mass of 10 g each to facilitate separation of analytes by coprecipitation. Pretreatment of the aliquots was performed simultaneously in a batchwise approach. After pretreatment, subsample solutions were combined and the composite sample was subjected to the automated column separation.

**Automated Separation Scheme.** The SI anion-exchange chromatographic procedure consists of the following five steps:

(I) Rinse the holding coil with 50 mL of deionized water and wash the sample inlet and manifold tubing with 8 mol/L HNO<sub>3</sub> at a flow rate of 10 mL/min;

(II) Precondition the anion-exchange resin with 20 mL of 8 mol/L HNO<sub>3</sub> at a flow rate of 2.4 mL/min;

(III) Load the sample (from 15 to 150 mL, depending on the sample size (e.g., 15 mL for 10 g of Danish soil)) in a 8 mol/L HNO<sub>3</sub> medium onto the anion-exchange column;

(IV) Rinse the column with 80 mL of 8 mol/L HNO<sub>3</sub> to remove most of the uranium and matrix elements, followed by 60 mL of 9 mol/L HCl to remove thorium; and

(V) Elute Pu and Np with 40 mL of 0.5 mol/L HCl.

Unless otherwise stated, the flow rate for the overall column separation procedure was 1.2 mL/min. In case the anion-exchange column is reused, 60 mL of 0.05 mol/L H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> is used for column cleanup between samples.

The eluate was evaporated to dryness on a hot plate to eliminate HCl. The residue was redissolved in 5 mL of 0.5 mol/L HNO<sub>3</sub>, and the reconstituted solution was analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) for quantification of the Pu isotopes and <sup>237</sup>Np and interfering elements, such as U, Th, and Pb.

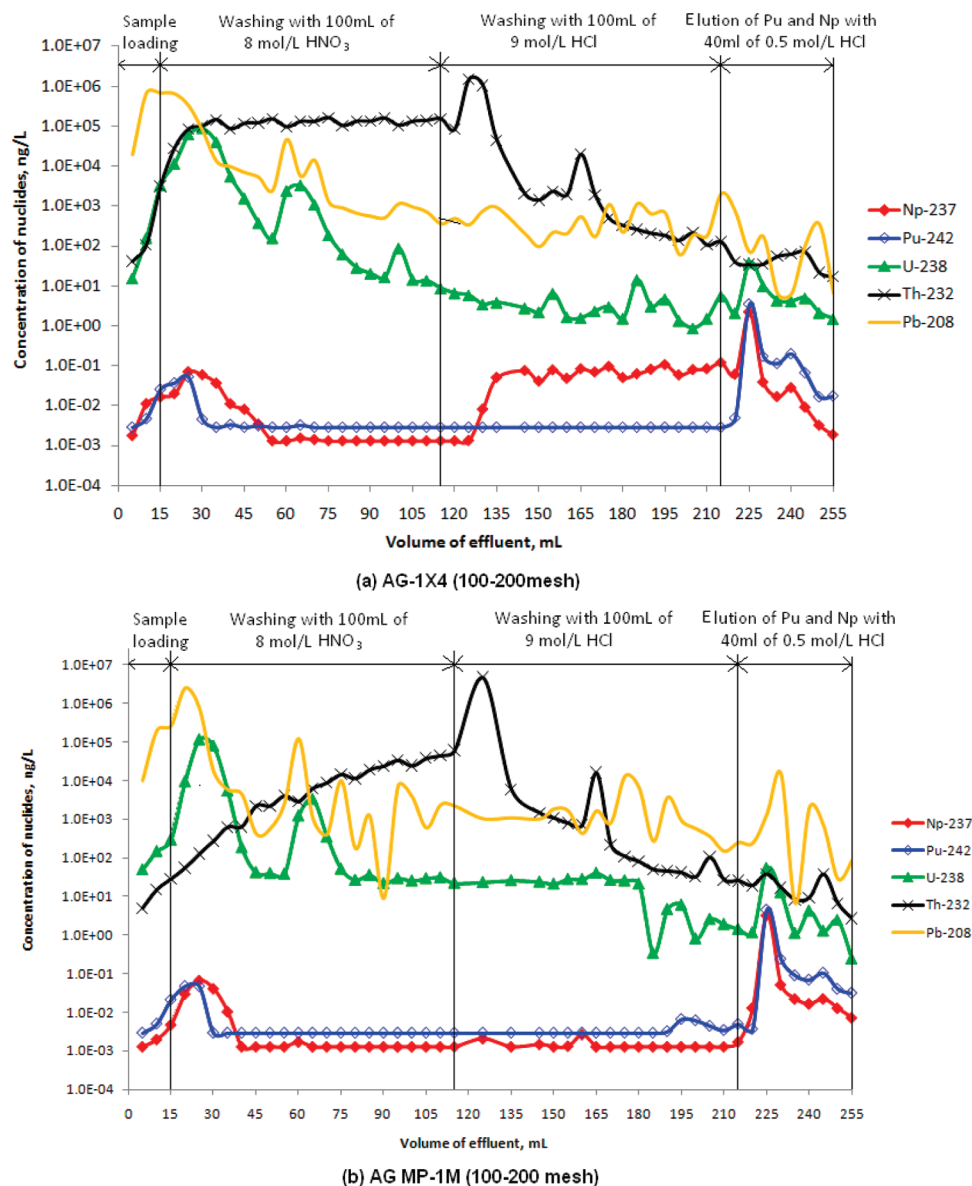
**Determination of Plutonium and Neptunium Using ICP-MS.** Prior to sample measurement, the ICP-MS instrument was tuned using a 1.0 µg/L solution of <sup>238</sup>U in 0.5 mol/L HNO<sub>3</sub>. The typical operational conditions of the instrument have been given elsewhere.<sup>5,24</sup> Note that the instrumental parameters were optimized each time the instrument was initialized. Typical sensitivities of plutonium (i.e., <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>242</sup>Pu) and neptunium (<sup>237</sup>Np) ranged from 2 × 10<sup>5</sup> to 4 × 10<sup>5</sup> cps per µg/L.<sup>5</sup>

To 5 mL of processed sample solution in 0.5 mol/L HNO<sub>3</sub>, 50.0 µL of 100 µg/L In(III) (in the form of InCl<sub>3</sub>) was added as an internal standard. The concentrations of <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>242</sup>Pu, and <sup>237</sup>Np, as well as <sup>238</sup>U, <sup>232</sup>Th, and <sup>208</sup>Pb, were determined using an ICP-MS system (X Series<sup>II</sup>, Thermo Fisher Scientific, Waltham, MA) that was equipped with an Xs-skimmer cone and a concentric nebulizer under hot plasma conditions. <sup>239</sup>Pu and <sup>237</sup>Np standard solutions were prepared in 0.5 mol/L HNO<sub>3</sub> containing 1.0 µg/L In(III). Detection limits, calculated as three times of the standard deviations (3σ) of the processing blank, were 1.5 pg/L for <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>242</sup>Pu, and <sup>237</sup>Np. A 0.5 mol/L HNO<sub>3</sub> solution was used as a washing solution between consecutive assays. No carry-over effects were observed for consecutive analysis of samples differing in Pu and Np concentration by up to 3 orders of magnitude. The

(23) Roos, P.; Nygren, U.; Appelblad, P.; Skipperud, L.; Sjögren, A. *NKS-Norcmass reference material for analysis of Pu-isotopes and <sup>237</sup>Np by mass spectrometry*, Nordic Nuclear Safety Research Report No. NKS-135, Roskilde, Denmark, 2006, pp 1–12.

(24) Qiao, J.; Hou, X.; Roos, P.; Miró, M. *Anal. Chem.* 2009, 81, 8185–8192.





**Figure 2.** Sorption and elution behavior of Pu, Np, U, Th, and Pb on different anion exchangers: (a) gel-type anion exchanger AG 1-X4 (100–200 mesh) and (b) macroporous anion exchanger AG MP-1 M (100–200 mesh). (Sample = 10 g of Danish soil, flow rate in the entire procedure = 1.2 mL/min.)

regression line was proven to be linear over the range of 0.01 ng/L to 100 ng/L for both Pu and Np.

*CAUTION! Safety concerns in handling radioactive nuclides of Pu and Np should be stressed here. In this work, a semihot laboratory was specifically used for storage of the radioactive stock solutions, and care was taken whenever samples were spiked with radionuclides of Pu and Np and the spikes were measured gravimetrically.*

## RESULTS AND DISCUSSION

**Comparison of the Analytical Performance of Macroporous AG MP-1 M against Gel-Type AG 1-X4 for Isolation of Target Species.** To the best of our knowledge, no studies have yet compared, in detail, the analytical performance of macroporous anion exchangers with gel-type resins for simultaneous determination of Pu isotopes and <sup>237</sup>Np in environmental solid samples. In this work, 10 g of Danish soil spiked with ca. 5 mBq of <sup>242</sup>Pu and 0.5 mBq of <sup>237</sup>Np was used to investigate the influence of

resin type on the separation efficiency. The sorption and elution profiles of Pu, Np, U, Th, and Pb onto anion exchangers are shown in Figure 2a and 2b for the gel-type anion exchanger AG 1-X4 (100–200 mesh) and macroporous AG MP-1 M (100–200 mesh), respectively. The contents of <sup>242</sup>Pu and <sup>237</sup>Np in the four fractions collected from the column separation procedure, including sample loading, rinsing with 8 M HNO<sub>3</sub> and 9 M HCl, and elution with 0.5 M HCl, are summarized in Table 1. With regard to the gel-type AG 1-X4, minute amounts (<5%) of <sup>242</sup>Pu and <sup>237</sup>Np were observed in either the sample loading or the 8 M HNO<sub>3</sub> rinsing fractions. However, ~20% of <sup>237</sup>Np was lost in the 9 M HCl rinsing fraction. As a result, a notable difference between the chemical yields of <sup>242</sup>Pu (60.6%) and <sup>237</sup>Np (45.4%) in the eluate was detected with a <sup>237</sup>Np/<sup>242</sup>Pu chemical yield ratio of 0.75, which is consistent with our previous investigations.<sup>6</sup>

**Table 1. Comparison of the Distribution of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  in Various Stages of the SI-Based Analytical Procedure Exploiting AG 1-X4 and AG MP-1M Anion Exchangers<sup>a</sup>**

step	AG 1-X4 Resin (100–200 mesh)		AG MP-1 M Resin (100–200 mesh)	
	$^{242}\text{Pu}$ (%)	$^{237}\text{Np}$ (%)	$^{242}\text{Pu}$ (%)	$^{237}\text{Np}$ (%)
sample loading	$0.5 \pm 0.1$	$0.6 \pm 0.1$	$1.0 \pm 0.1$	$0.4 \pm 0.1$
8 M $\text{HNO}_3$ rinsing	$2.2 \pm 0.1$	$4.3 \pm 0.2$	$2.3 \pm 0.1$	$3.4 \pm 0.2$
9 M $\text{HCl}$ rinsing	$1.3 \pm 0.1$	$23.6 \pm 1.2$	$0.4 \pm 0.1$	$0.2 \pm 0.1$
elution	$60.6 \pm 3.0$	$45.4 \pm 2.3$	$79.3 \pm 4.0$	$82.6 \pm 4.1$
SUM	$64.5 \pm 3.2$	$73.9 \pm 3.7$	$83.0 \pm 4.1$	$86.6 \pm 4.3$

<sup>a</sup> All values are the average of two replicates  $\pm$  uncertainty.

On the other hand, minute amounts ( $\leq 4\%$ ) of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  were concurrently found in the sample loading and rinsing steps when using the AG MP-1 M anion exchanger. Most importantly, the chemical yields of  $^{242}\text{Pu}$  (79.3%) and  $^{237}\text{Np}$  (82.6%) in the elution were significantly improved with a  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yield ratio of 1.04. This means  $^{242}\text{Pu}$  performs well as a tracer for monitoring the chemical yield of  $^{237}\text{Np}$ . Note that the summation of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  chemical yields in the four fractions of the separation procedure is  $<100\%$ , yet better in the AG MP-1 M anion exchanger (see Table 1), which should be a consequence of the loss in sample pretreatment, sample reconstitution prior to ICP-MS measurement and/or remains of target analytes in the anion-exchange column that were not completely eluted with 40 mL of 0.5 M  $\text{HCl}$ .

Although AG 1-X4 resin has a nominal anion-exchange capacity identical to that of AG MP-1 M (1.0 meq/mL), AG 1-X4 beads are characterized by a dense internal structure with no discrete pores, in contrast with AG MP-1 M beads, which bear a porous, multichannelled structure.<sup>25</sup> Experimental results stated above and compiled in Figure 2 reveal that pore structure—and, thus, bead permeability—plays a remarkable role in the sorption and elution behavior of Np. Pre-elution of Np in 9 M  $\text{HCl}$  on AG 1-X4 resin might arise from the fact that less-functional moieties remain available in a dynamic flow-through solid-phase extraction mode, compared with AG MP-1M, and the lower distribution coefficients of  $^{237}\text{Np}$  chlorocomplexes onto anion-exchange beads as compared with that of Pu chlorocomplexes.<sup>3,25</sup> Figure 2 also shows that potential interfering nuclides (including U, Th, and Pb) behave similarly on both anion exchangers. In fact, both U and Pb could be quantitatively removed from the columns with 8 M  $\text{HNO}_3$ , whereas Th could be removed with 9 M  $\text{HCl}$ . In the eluate, the decontamination factors for U and Th were in the range of  $10^3$ – $10^4$  and  $10^4$ – $10^5$ , respectively, while those of Pb varied widely, from  $1 \times 10^3$  to  $1 \times 10^6$ , because of external contamination from the vessels and reagents. However, no severe interferences from U, Th, and Pb in the ICP-MS measurement of Pu isotopes and  $^{237}\text{Np}$  in the SI eluates were detected in any case.

**Effect of Particle Size and Flow Rate.** Because resins with large particle size could be compatible with high flow rates and, therefore, expedite sample analysis, the effects of particle size and flow rate on the separation efficiency were investigated and summarized in Table 2. The analytical comparison of two particle-size distributions (50–100 mesh and 100–200 mesh) of AG MP-1

**Table 2. Effect of Particle Size and Flow Rate on the Separation Efficiency of AG MP-1M in an SI-Based Mode<sup>a</sup>**

particle size (mesh)	flow rate (mL/min)	Chemical Yield		
		$^{242}\text{Pu}$ , %	$^{237}\text{Np}$ , %	$^{237}\text{Np}/^{242}\text{Pu}$ ratio
50–100	1.2	$73.6 \pm 3.8$	$70.2 \pm 4.2$	0.95
100–200	1.2	$84.7 \pm 4.5$	$82.3 \pm 5.1$	0.97
100–200	2.4	$75.6 \pm 5.0$	$62.2 \pm 4.9$	0.82

<sup>a</sup> All values are the average of three replicates  $\pm$  standard deviation.

M reveal that the larger the particle surface area, the better the chemical yields were. Yet, increasing the flow rate above 1.2 mL/min for the simultaneous separation of Pu along with Np was proven inappropriate, because the chemical yield ratio of  $^{237}\text{Np}/^{242}\text{Pu}$  deviated significantly from 1.0 when the flow rate was increased from 1.2 mL/min to 2.4 mL/min. Therefore, flow rates in the overall separation protocol were fixed to 1.2 mL/min throughout this work.

#### Valence Adjustment and Stability of Pu(IV) and Np(IV).

A pivotal step in the separation scheme is the adjustment of oxidation states of target radionuclides to Pu(IV) and Np(IV), for ensuring similar separation behavior of Pu and Np onto the anion exchanger. Our previous exploration and comparison of various methods for valence adjustment led us to conclude that the redox pair  $\text{K}_2\text{S}_2\text{O}_5$ –8 M  $\text{HNO}_3$  was the most effective agent.<sup>5</sup>

The same redox pair was employed in this work and the stability of Pu(IV) and Np(IV) after valence adjustment was investigated thereafter. Experimental results (see Table 3) demonstrate that Pu(IV) and Np(IV) might be stabilized in a 8 mol/L  $\text{HNO}_3$  milieu (sample solution) at room temperature for up to 24 h with acceptable chemical yields ( $>65\%$ ) for both Pu and Np and with satisfactory  $^{237}\text{Np}/^{242}\text{Pu}$  chemical yield ratios within the range of 0.93–1.05. The stabilization of Pu(IV) and Np(IV) in solution for  $\geq 5$  days at 3 °C with chemical yields of Pu and Np  $\geq 77\%$  and  $^{237}\text{Np}/^{242}\text{Pu}$  ratios from 0.96 to 1.00 is noteworthy.

**Separation Capability and Reusability of AG MP-1 M Resin.** To the best of our knowledge, no studies on the separation capability and reusability of AG MP-1 M anion exchanger have been reported so far for the processing of large-sized solid samples. Our analytical results (see Table 4) in the exploration of column separation capability showed that ca. 2 mL of AG MP-1 M resin can process a soil sample with a mass of up to 100 g with equally satisfactory chemical yields for Pu (85.2%) and Np (79.4%). However, undue back pressure was observed during sample loading when processing a 200-g soil sample. This suggests that

(25) Thompson, G. H.; Burney, G. A. *Processing of  $^{238}\text{Pu}$  and  $^{237}\text{Np}$  with macroporous anion exchange resin*, DP-1333 Chemical Separations Processes for Plutonium and Uranium, Report No. TID-4500-R61, UC-10, E. L. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC, 1973.

**Table 3. Variation of Chemical Yields of Pu and Np with the Time Interval between Valence Adjustment and Beginning of Column Separation**

Room Temperature				3 °C			
time (h)	Chemical Yield <sup>a</sup>			time (day)	Chemical Yield <sup>a</sup>		
	<sup>242</sup> Pu (%)	<sup>237</sup> Np (%)	ratio of <sup>237</sup> Np/ <sup>242</sup> Pu		<sup>242</sup> Pu (%)	<sup>237</sup> Np (%)	ratio of <sup>237</sup> Np/ <sup>242</sup> Pu
0	80.7	79.3	0.98	0	80.7	79.3	0.98
3.5	79.5	74.6	0.94	1	83.9	84.0	1.00
7.0	69.2	71.9	1.04	2	85.6	84.0	0.98
10.5	70.7	74.4	1.05	3	80.7	79.4	0.98
17.5	73.0	73.7	1.01	4	86.5	85.3	0.99
21.0	69.1	68.8	1.00	5	79.8	77.0	0.96
24.5	70.0	65.3	0.93				

<sup>a</sup> The uncertainties in the chemical yields of <sup>242</sup>Pu and <sup>237</sup>Np are all <10% (uncertainty is estimated considering the counting uncertainty in ICP-MS and sample, blank, tracer, and standard preparation).

**Table 4. Influence of Sample Size on the Analytical Performance of a ca. 2 mL Column Packed with AG MP-1M (100–200 Mesh) Resin for the Separation of Pu and Np from Soil Samples<sup>a</sup>**

sample size, g	Chemical Yield			Measured Value <sup>b</sup> (Bq/kg)	
	<sup>242</sup> Pu (%)	<sup>237</sup> Np (%)	ratio of <sup>237</sup> Np/ <sup>242</sup> Pu	<sup>239</sup> Pu	<sup>240</sup> Pu
10	87.8 ± 5.0	86.8 ± 6.0	0.99	0.14 ± 0.01	0.09 ± 0.01
20	84.8 ± 4.8	85.0 ± 5.6	1.00	0.14 ± 0.01	0.09 ± 0.01
50	75.2 ± 6.3	77.6 ± 7.2	1.03	0.14 ± 0.02	0.09 ± 0.01
100	85.2 ± 10.0	79.4 ± 9.5	0.93	0.14 ± 0.02	0.10 ± 0.01

<sup>a</sup> All values are the average of two replicates (± uncertainty). <sup>b</sup> The reference values of <sup>239</sup>Pu and <sup>240</sup>Pu concentrations in the Danish soil were reported to be 0.140 ± 0.008 and 0.098 ± 0.006 Bq/kg, respectively.

the small-sized AG MP-1 resin is not suitable for loading large amounts (>150 mL) of sample solution, as a consequence of resin shrinking in intimate contact with large volumes of highly concentrated nitric acid. Nevertheless, the volume of sample solution can be reduced through the improvement of the sample pretreatment procedure, for example, with the application of oxalate precipitation to remove most of the matrix elements and therefore minimize the size of the coprecipitate containing the target radionuclides.

Analytical results for evaluation of AG MP-1 M column reusability when handling 10 g of Danish soil spiked with different amounts of <sup>237</sup>Np are summarized in Table 5. Note that a ca. 2-mL column packed with AG MP-1 M resin could be reused up to 10 times with satisfactory chemical yields (>70%). Although it was still feasible to further reuse the column for three more assays, chemical yields started to decrease significantly and the interfering effects of uranium in the ICP-MS readouts became severe. Therefore, a 10-fold column reuse limitation is suggested to ensure accurate analysis. One should keep in mind that the on-column separation procedure might be completed within 3.5 h per sample, whereby 10 samples can be processed within 1.5 days using merely one chromatographic column. Accordingly, the SI system herein proposed and furnished with nine separation columns would be able to operate unattended for two weeks with a nominal workload of 90 samples when replacing SV2 and SV5 by an autosampler and fraction collector, respectively. In this case, the consumption of resin and analysis costs would be reduced to a large extent and the sample throughput improved significantly.

However, subtle deviations of measured <sup>237</sup>Np and Pu isotopes values from the expected concentrations were noted in some instances during the course of investigation of column reusability. This might be a consequence of the incomplete removal of Pu and Np from the anion exchanger, even with the usage of 60 mL of 0.05 mol/L H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> for column cleanup between samples. In further investigations of sample cross-contamination, a maximum analyte carryover of 5% for <sup>242</sup>Pu and 0.5% for <sup>237</sup>Np was detected in the consecutive processing of two Danish soil samples spiked with ca. 20 mBq of <sup>242</sup>Pu and ca. 2 mBq of <sup>237</sup>Np. Therefore, attention should be paid when reusing the AG MP-1 M resin for processing a variety of samples with different concentration levels of analytes, wherein stronger cleanup chemicals (e.g., hydrofluoric acid (HF) or ethylenediamine tetraacetic acid (EDTA)) might be needed to minimize carry-over effects.

**Method Validation.** Three certified reference materials, including two sediments (IAEA-385 and IAEA-135) and one seaweed (NIST-4359), and two reference materials from a laboratory round-robin intercomparison (namely, a Danish soil and an Irish Sea sediment) were analyzed by resorting to the proposed SI anion-exchange chromatographic method. Four aliquots of the reference samples were analyzed to test the trueness of the proposed method. This is determined under the criterion of the significant test score (*t*).<sup>26</sup> This parameter is calculated from the reference activity (*A*<sub>ref</sub>), the measured activity (*A*<sub>mea</sub>), the number of replicates (*n*), and the measured standard deviation (*s*<sub>mea</sub>), as follows:

$$t = \frac{|A_{\text{ref}} - A_{\text{mea}}| \sqrt{n}}{s_{\text{mea}}}$$

At the 0.05 significance level, the critical *t*-value (*t*<sub>crit</sub>) is 3.18 for *n* = 4. According to the *t*-test, all the *t*-values are below *t*<sub>crit</sub> (see Table 6); therefore, the overall experimental results are not significantly different from the reference or indicative values at the 95% probability level.

**Analytical Performance of the SI Anion-Exchange Chromatographic Manifold.** The SI manifold, using the AG MP-1 anion exchanger presented herein, is able to handle notably larger

(26) Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, 3rd ed.; Ellis Horwood Limited: West Sussex, U.K., 1993.

**Table 5. Reusability of AG MP-1M (100–200 Mesh) Anion-Exchange Resin in a ca. 2 mL Column for the Separation of Pu and Np from Soil Samples<sup>a</sup>**

sequence number of sample	chemical yield of <sup>242</sup> Pu <sup>d</sup> (%)	Concentration of <sup>237</sup> Np <sup>b,d</sup> (Bq/kg)		Concentration of Pu Isotopes <sup>c,d</sup> (Bq/kg)	
		measured	expected	<sup>239</sup> Pu	<sup>240</sup> Pu
1	83.5	0.30	0.29	0.14	0.11
2	96.0	0.16	0.18	0.15	0.10
3	91.0	0.07	0.08	0.12	0.12
4	83.6	0.04	0.04	0.15	0.12
5	90.2	0.16	0.19	0.15	0.10
6	87.8	0.16	0.13	0.14	0.12
7	81.1	0.07	0.07	0.15	0.12
8	86.4	0.04	0.04	0.15	0.12
9	79.1	0.25	0.28	0.15	0.13
10	70.6	<DL <sup>e</sup>	0.00	0.15	0.10
11	63.8	0.04	0.05	0.14	0.11
12	66.0	0.13	0.12	0.15	0.11
13	62.0	<DL	0.00	0.14	0.12

<sup>a</sup> Sixty milliliters (60 mL) of 0.05 mol/L H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> was used for column cleanup between samples. <sup>b</sup> Different amounts of <sup>237</sup>Np were used to enrich the Danish soil, inducing different concentrations of <sup>237</sup>Np in the samples (the original <sup>237</sup>Np concentration in the soil is below the detection limit (DL)). <sup>c</sup> The reference values of <sup>239</sup>Pu and <sup>240</sup>Pu concentrations in the Danish soil were reported to be 0.140 ± 0.008 and 0.098 ± 0.006 Bq/kg, respectively. <sup>d</sup> The uncertainties in chemical yields of <sup>242</sup>Pu and activity concentrations of <sup>237</sup>Np and <sup>239</sup>Pu are all <10%. <sup>e</sup> The detection limit (DL) of <sup>237</sup>Np is 1.5 pg/L (or 15 fg in 10 mL of eluate, corresponding to 0.00039 mBq of <sup>237</sup>Np).

**Table 6. Analytical Results of Environmental Solids by Resorting to the Proposed SI Anion-Exchange Method<sup>a</sup>**

sample	IAEA-135 sediment	Irish Sea sediment	IAEA-385 sediment	Danish soil	NIST-4359 seaweed <sup>c</sup>
weight (g)	0.5	0.5	1.0	10.0	20.0
chemical yield (%)	72.1 ± 4.2	69.0 ± 5.1	74.4 ± 4.2	88.9 ± 4.7	68.4 ± 3.3
measured value <sup>b</sup> (Bq/kg)					
<sup>237</sup> Np	0.91 ± 0.06 [1.85]	0.99 ± 0.05 [0.10]	0.023 ± 0.006 [1.27]	0.103 ± 0.002 [1.73]	0.00020 ± 0.00006 [0.75]
<sup>239</sup> Pu	127 ± 5 [1.39]	230 ± 7 [1.73]	1.7 ± 0.2 [1.91]	0.148 ± 0.009 [1.54]	0.081 ± 0.002 [2.60]
<sup>240</sup> Pu	97 ± 3 [1.85]	173 ± 2 [1.73]	1.1 ± 0.1 [1.39]	0.100 ± 0.008 [0.43]	0.055 ± 0.006 [0.58]
<sup>239</sup> + <sup>240</sup> Pu	224 ± 7 [2.72]	403 ± 9 [3.08]	2.8 ± 0.2 [1.56]	0.25 ± 0.02 [1.04]	0.136 ± 0.008 [0.14]
expected value <sup>d</sup> (Bq/kg)					
<sup>237</sup> Np	0.846 ± 0.045 <sup>h</sup> (ref 7)	0.987 ± 0.048 <sup>h</sup> (ref 7)	0.0186 ± 0.0038 <sup>h</sup> (ref 28)	0.101 ± 0.002 <sup>i</sup>	0.000173 (0.000152–0.000198) <sup>g</sup>
<sup>239</sup> Pu	123.0 ± 3.8 <sup>h</sup> (ref 7)	237.0 ± 5.0 <sup>h</sup> (ref 7)	1.92 (1.30–2.07) <sup>g</sup>	0.140 ± 0.008 <sup>h</sup> (ref 23)	0.0840 ± 0.0033 <sup>e</sup>
<sup>240</sup> Pu	93.8 ± 2.3 <sup>h</sup> (ref 7)	171.0 ± 4.9 <sup>h</sup> (ref 7)	1.18 (0.97–1.32) <sup>g</sup>	0.098 ± 0.006 <sup>h</sup> (ref 23)	0.057 (0.049–0.066) <sup>g</sup>
<sup>239</sup> + <sup>240</sup> Pu	213 (205–226) <sup>f</sup>	419.0 ± 10.6 <sup>h</sup> (ref 7)	2.98 (2.81–3.13) <sup>f</sup>	0.238 ± 0.014 <sup>h</sup> (ref 23)	0.1296 ± 0.0075 <sup>e</sup>

<sup>a</sup> All values are the average of four replicates (±standard deviation). <sup>b</sup> Numbers in brackets are  $|t|_{\text{exp}}$  values at the 95% probability level. The critical  $t$ -value ( $t_{\text{crit}}$ ) is 3.18 for  $n = 4$ . <sup>c</sup> The information value of <sup>237</sup>Np in the certification of NIST-4359 seaweed was provided by Risø-DTU; however, the units for <sup>237</sup>Np activity were presented incorrectly in the certification datasheet. The correct value should be 0.17 mBq/kg, with a range of 0.152–0.198 mBq/kg. <sup>d</sup> Expected values include the certified value, the recommended value, the information value, the literature value, and that added to the sample. <sup>e</sup> Includes only the certified value. <sup>f</sup> Includes only the recommended value. <sup>g</sup> Includes only the information value. <sup>h</sup> Includes only the literature value. <sup>i</sup> Includes only that added to the sample.

amounts of solid samples (up to 100 g of soil), in comparison with almost all the previously published works for the simultaneous determination of Pu isotopes and <sup>237</sup>Np wherein ≤10 g of soil were processed,<sup>7,9,10,17,27</sup> and, therefore, sample enrichment factors might be improved by a factor of 10 or better. Compared with previous publications devoted to either nuclear fuel<sup>8,27</sup> or highly contaminated environmental samples,<sup>10</sup> the developed method is more suitable for determination of ultratrace levels of <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>237</sup>Np, as a result of the low ICP-MS detection limits of <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>237</sup>Np (viz., 1.5 pg/L) and the likelihood of handling large-sized samples. Chemical yields, especially for <sup>237</sup>Np (85 ± 6.0%), are significantly improved, compared to those of former reports.<sup>5,6,9</sup>

The automated processing of samples in a programmable SI sequence leads to not only expeditious assays of Pu and Np

(different steps in the analytical procedure can be executed concurrently), compared with the conventional batch-wise method using large-sized anion-exchange columns,<sup>7</sup> but also to simplicity, reliability, a decrease in uncertainty measurements (because of minimal human intervention), and improved safety of the analyst as well. Last but not least, enhanced repeatability is obtained, as a consequence of the precise control of sample and reagent volumes and flow rates within the SI network. The reuse of separation columns following appropriate washing sequences gives rise to cost-effective approaches. In addition, the SI system might be reconfigured at will for the simultaneous processing of several samples via multicolumn designs.

## CONCLUSION

A sequential injection (SI)-based anion-exchange chromatographic method is proposed herein for the automated and simultaneous determination of <sup>239</sup>Pu, <sup>240</sup>Pu, and <sup>237</sup>Np in environmental solids, using a macroporous anion exchanger (AG MP-1 M). Our analytical results demonstrate that (i) <sup>242</sup>Pu performs well as a chemical yield tracer for <sup>237</sup>Np because

(27) Perna, L.; Bocci, F.; de las Heras, L. A.; De Pablo, J.; Betti, M. *J. Anal. Spectrom.* **2002**, *17*, 1166–1171.

(28) Pham, M. K.; Sanchez-Cabeza, J. A.; Povinec, P. P. *Report on the worldwide intercomparison exercise IAEA-385 Radionuclides in Irish Sea sediment*, Report No. IAEA/AL/151 IAEA/MEL/7, International Atomic Energy Agency, Monaco, 2005; pp 12–13.



excellent agreement between chemical yields of  $^{242}\text{Pu}$  and  $^{237}\text{Np}$  is obtained throughout this work; (ii) a small sized column packed with ca. 2 mL of AG MP-1 M resin suffices to process up to 100 g of soil; (iii) the separation column can be reused up to 10-fold with no appreciable deterioration of chemical yields; and (iv) the automated method simplifies the analytical workloads, compared to error-prone batch-wise methods.

#### **ACKNOWLEDGMENT**

J.Q. is grateful to the Radioecology and Tracers Programme (headed by Sven P. Nielsen), Radiation Research Department, Risø National Laboratory for Sustainable Energy, Technical University of Denmark for all of the support in her Ph.D. project. M.M.

acknowledges financial support from Spanish Ministry of Science and Innovation, through Project No. CTM 2010-17214.

#### **NOTE ADDED AFTER ASAP PUBLICATION**

This manuscript originally posted ASAP December 1, 2010 with an error in the Results and Discussion section. The corrected manuscript posted ASAP on December 7, 2010.

Received for review September 29, 2010. Accepted November 7, 2010.

AC102567B