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Simultaneous analysis of ^{237}Np and Pu isotopes in environmental samples by ICP-SF-MS coupled with automated sequential injection system

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A simultaneous analytical method for ^{237}Np, ^{239}Pu and ^{240}Pu has been developed using sector field inductively coupled plasma mass spectrometry (ICP-SF-MS) detection combined with an automated sequential injection (SI) separation system. The chemical purification of these actinides was carried out on an actinide-specific extraction chromatographic resin, TEVA-Spec, in an automated SI system. The similar chemical behaviors of Np and Pu on TEVA-Spec was confirmed by recovery test after treating with ascorbic acid in 5 M HNO_3. TEVA-Spec maintained its re-usability, giving high and consistent chemical recovery, and showed good selectivity for Np and Pu and a low memory effect during the consecutive analysis of nine replicate samples. The high chemical recovery ($>90\%$), reliable accuracy and repeatability of ^{237}Np and Pu isotope purification using the SI system were proved using standard reference materials. Low detection limits of 2.5, 2.1 and 0.42 fg ml^{-1} were obtained for ^{237}Np, ^{239}Pu and ^{240}Pu, respectively, which make it possible to analyze these nuclides in samples of soil and sediment as low as 1 g. With the exception of the preparation process required prior to loading a sample, all chemical purifications were carried out automatically by the programmed SI system, and were completed within 1 hour, which included measurement by ICP-SF-MS. This method was successfully applied to the analysis of the environmental levels of ^{237}Np and Pu in soil, sediment and in biological samples.

Introduction

A number of radionulides have been released into the environment by nuclear weapon testing, nuclear facilities and nuclear accidents. Among these radionulides, ^{237}Np ($T_{1/2} = 2.14 \times 10^6$ y), ^{239}Pu ($T_{1/2} = 2.41 \times 10^4$ y) and ^{240}Pu ($T_{1/2} = 6.56 \times 10^3$ y) are important isotopes from the viewpoint of their extremely long half-lives and their radiological toxicities. Accurate and rapid analysis of these isotopes in environmental samples is significant in the understanding of their behaviors in the environment and monitoring of their concentrations around nuclear facilities.

From the point of view of their rapid measurement and its low detection limit, ICP-MS is an attractive measurement tool, as opposed to radiometric methods such as alpha spectrometry, which have generally been used for the analysis of alpha radionuclides. Kim *et al.*[1] measured ^{237}Np and Pu isotopes in the soil and sediment using HR-ICP-MS, Truscott *et al.*[2,3] analyzed these actinides in soil (NIST 4353) and a biological sample (NIST 4352) by ICP-SF-MS, and Egorov *et al.*[4] developed an on-line ICP-MS method for the determination of the several actinides, including Np and Pu, in a dissolved vitrified nuclear waste sample. TIMS (thermal ionization mass spectrometry)[5] and AMS (accelerator mass spectrometry)[6] have also been used to measure ^{237}Np in environmental samples, and have the merit of a low detection limit and high accuracy compared with ICP-SF-MS. However, although TIMS and AMS are more sensitive than ICP-MS for the analysis of ^{237}Np, they require a complicated sample preparation procedure. For Pu analysis, ^{242}Pu (3.8×10^5 y) and ^{244}Pu (8.2×10^7 y)[7] are used as tracers, but there is no an available tracer having a long half-life for ^{237}Np analysis. Although ^{236}Np (1.2×10^5 y) has been used as a Np tracer in the determination of ^{237}Np by ICP-MS[8] and TIMS,[9] it is not easy to prepare because ^{236}Np is produced by deuteron bombardment of ^{235}U.

To overcome this difficulty, Chen *et al.*[10] developed a way of measuring ^{237}Np using a ^{242}Pu tracer; however, the method still involves much time to separate ^{237}Np from the bulk sample matrix. Recently, Kenna[8] and Rosa *et al.*[11] developed new analytical methods for the determination of ^{237}Np and Pu isotopes in environmental samples by ICP-SF-MS. They purified Np and Pu using same chemical separation procedure and calculated the concentration of ^{237}Np and Pu isotopes by the isotope dilution technique, where ^{236}Np, ^{239}Np and ^{242}Pu standard were added as a tracer for Np and Pu. However, both methods are indispensable for a stringent and tedious chemical purification in the analysis of ^{237}Np and Pu isotopes.

During the past 10 years, solid phase extraction chromatography resins have been commonly used to purify actinide elements in environmental samples.[12,13] Among these resins, TEVA-Spec has been shown to have a high affinity for tetravalent actinides in strong nitric acid, but a low affinity in weak hydrochloric acid.[14] Thus, TEVA-Spec could be applied to the simultaneous separation of ^{237}Np and Pu, and ^{242}Pu could be used as a tracer for the quantitative determination of both actinides. For a successful application of TEVA-Spec to the simultaneous analysis of ^{237}Np and Pu, first the chemical recovery of the two actinides by the separation process should be similar. Secondly, prior to loading samples into TEVA-Spec, both actinides in solution should be converted to the tetravalent state. Finally, the ^{238}U level in the purified solution should be reduced to less than about 100 pg ml^{-1} to minimize its spectral (^{238}U/^{237}Np, ^{238}U/^{239}Pu) and polyatomic (^{238}UH/^{239}Pu) interferences in the quantitative analysis of ^{237}Np and ^{239}Pu.[15–17]

Recently, SI techniques have been applied to save analysis time and labour in the determination of actinides,[18,19] and are useful for developing automating chemical procedures for small sample quantities. These SI techniques, coupled with a simple separation method involving a single column,

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Table 1 Operating conditions of ICP-MS and the sample introduction system

	ICP and plasma conditions				
Rf plasma power/W	1350				
Coolant gas flow rate/l min^{-1}	14				
Auxiliary gas flow rate/l min^{-1}	1.7				
Carrier gas flow rate/l min^{-1}	0.77				
Expansion pressure/mbar	1.6				
Intermediate pressure/mbar	5.0×10^{-4}				
Analyzer pressure/mbar	8.0×10^{-8}				
	Sample introduction system (Aridus)				
Sweeping gas flow rate/l min^{-1}	1.85				
Spray chamber temp./°C	80				
Membrane desolvator temp./°C	160				
Sample uptake rate/ml min^{-1}	0.10				
Type of nebulizer	T1-H microconcentric nebulizer				
	Data acquisition parameters				
Element	^{237}Np	^{238}U	^{239}Pu	^{240}Pu	^{242}Pu
Mass range/amu	236.4–237.6	237.8–238.6	238.4–239.6	239.4–240.6	241.4–242.6
Dwell time/ms	200	20	200	400	40
Width points	100	100	100	100	100
Peak widths	1.5	1.3	1.5	1.5	1.5
Runs	3	3	3	3	3
Resolving power			430		
Total analysis time/s	90	7.8	90	180	18

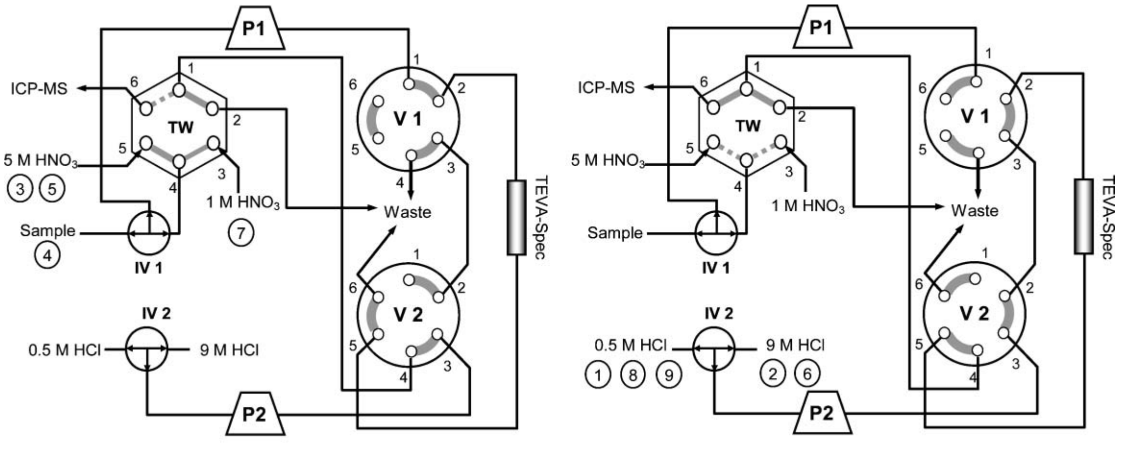
and their combination with TEVA-Spec resin, offer a useful means of automating to the analysis of ultra-trace levels of ^{237}Np and Pu isotopes in environmental samples. The aim of this study was to determine the optimum separation conditions required for the simultaneous analysis of ^{237}Np and Pu isotopes by coupling ICP-SF-MS with an automated SI system.

Experimental

ICP-MS and sequential injection (SI) system

A PlasmaTrace2 (Micromass, Manchester, UK) was equipped with an ASX 100 microautosampler and an Aridus desolvating introduction system (Cetac Technologies, Omaha, NE, USA) involving a T1-H microconcentric nebulizer. The operation conditions used for ICP-SF-MS and the sample introduction system are listed in Table 1. The isotopes of interest were measured three times in peak hopping mode to calculate the mean and standard deviation of measurement. All data acquisitions were carried out in low-resolution mode with different dwell times for actinides based on the difference of concentration in the sample. Mass bias correction was used to correct for different mass responses instead of internal standard normalization to calculate ^{237}Np and Pu isotope concentrations using the isotope dilution (ID) method.

An automated SI system, shown schematically in Fig. 1, was equipped with a PrepLab (Fison, Manchester, UK) liquid handing system and a Rheodyne two-way valve, which was used to divert the final pathway of eluent to the ICP-MS. With the exception of peristaltic tubing, which was of 0.95 mm id Tygon®, all transport lines were of 0.8 mm id poly(tetrafluoroethylene) (PTFE) tubing (Upchurch Scientific, WA, USA), and the final line from the column to the microautosampler was of 0.1 mm id polyether ether ketone (PEEK) tubing to minimize the dead volume. The size of the micro borosilicate column located in the PrepLab was 3 mm id × 25 mm (Omnifit, Cambridge, England).



(a) Valve position 1 (b) Valve position 2

Fig. 1 Schematic diagram of the sequential injection (SI) system for the simultaneous analysis of ^{237}Np and Pu isotopes. P1 and P2, peristaltic pump; V1 and V2, dual two-way six-port valve; TW, two-way valve; IV1 and IV2, isolation valve. The circled numbers indicate the procedure order, as described in Table 2.

Reagents and materials

Deionized water (18 MΩ cm^{-1}) was obtained from a Milli-Q Plus System (Millipore, Bedford, MA, USA) and was used for all dilutions. Super-pure HCl (AA-100, Tama Chemicals. Japan) was used as an eluant in the SI system. Electronic grade concentrated nitric acid (Dongwoo Pure Chemicals, Iksan, Korea) was also used for the preparation of the loading sample and for resin rinsing. The TEVA-Spec was purchased from the Eichrom Inc. (Darien, IL, USA) in powder form, and swollen for at least 7 days with 1 M high purity nitric acid before packing. H_2O_2 (Merck, Darmstadt, Germany), sodium nitrite (Aldrich, Milwaukee, WI, USA) and ascorbic acid (Merck) were of GR grade. ^{242}Pu standard solution (SRM 4334G) and ^{237}Np standard solution (SRM 4341) were supplied by the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). For the validation test, one soil (IAEA-Soil-6), three kinds of sediment (IAEA-135, NIST-4350B, NIST-4357) and one biological reference material (IAEA-307) were purchased from the International Atomic Energy Agency (IAEA, Vienna, Austria) and NIST, respectively.

Sample preparation and chemical purification using the SI system

Prior to chemical treatment, approximately 1 g of four standard reference materials (IAEA-Soil-6, IAEA-307, NIST-4350B, NIST-4357) and 50 mg of IAEA-135 were weighted in a 20 ml quartz beaker, and then ashed ashed at 500 °C in a muffle furnace for 1 hour to decompose organic matter. After a ^{242}Pu tracer and concentrated nitric acid had been added, the mixture was boiled with stirring on a hot-plate for 1 hour. The filtrate obtained by passing this mixture through a glass fiber filter (GF/C, Whatman, USA) was heated and dried on a hot-plate until it became sludge-like. The resulting solution was then adjusted to 5 M HNO_3 and refiltered using a membrane filter under the 20 ml Teflon vial. Ascorbic acid was added to the filtered solution and the solution stood for 1 hour to allow the redox reaction to go to completion prior to injecting the loading solution into the SI system. The detailed operation of the SI system is described in Table 2.

The purification processes were designed with a total of 9 steps, from the rinsing step of resin once used in a previous sample to the final elution step. 5 M HNO_3, 1 M HNO_3 and 9 M HCl were used as a rinsing solution for U, Th and bulk elements in the sample solution. The upper pump delivered the loading solution and 5 M HNO_3 at a flow rate of 1.6 ml min^{-1} and the lower pump was used for the 1 M HNO_3, 9 M HCl and 0.5 M HCl at a flow rate of 0.8 ml min^{-1}. An additional two-way valve system allows an alternative route for the eluant in the fully automatic separation system. The whole procedure was performed automatically using an ICP-MS operation program and the two-way valve control system. In the final separation step, that is step 9, the purified Np and Pu from the column were transferred to a 2 ml conical Teflon vial placed in a microautosampler, and then transferred to the plasma using the sample introduction system.

Results and discussion

Sensitivity of actinides by ICP-SF-MS

Because ^{242}Pu was used as a tracer for the simultaneous determination of ^{237}Np and Pu isotopes by the ID method, sensitivity differences for the two actinide determinations by ICP-MS should be corrected for. Sensitivities for actinide elements were investigated using four actinides, *i.e.*, ^{237}Np, ^{238}U, ^{242}Pu, and ^{243}Am, as described in Table 1. As is demonstrated in Fig. 2, the sensitivity difference between these four nuclides is not significant, which agrees with the findings of Jones,[20] because of their similar ionization energies and atomic masses. Moreover, the sensitivity difference of approximately 1% between ^{237}Np and ^{242}Pu is not significant considering the variablity associated with the recovery ratio of ^{237}Np/^{242}Pu at chemical separation. However, this difference was included as a mass bias correction factor when calculating the sample ^{237}Np concentration.

Table 2 SI system program and description of program steps

Step	Pumped medium	Dual two-way valve position	Two-way valve position	Flow rate/ml min^{-1}		Isolation valve 1	Isolation valve 2	Time/s
				Pump 1	Pump 2			
1	0.5 M HCl	2	1	0	0.83	—	Left	150
2	9 M HCl	2	1	0	0.83	—	Right	40
3	5 M HNO_3	1	2	1.6	0	Right	—	120
4	5 M HNO_3	1	1	1.6	0	Left	—	420
5	5 M HNO_3	1	2	1.6	0	Right	—	240
6	9 M HCl	2	1	0	0.83	—	Right	240
7	1 M HNO_3	1	1	1.6	0	Right	—	180
8	0.5 M HCl	2	1	0	0.83	—	Left	19
9	0.5 M HCl	2	2	0	0.83	—	Left	60

Description of step	
1	0.5 M HCl is pumped through resin to rinse residual elements.
2	9 M HCl is pumped through resin to fill up the bottom tube.
3	5 M HNO_3 is pumped through column to pre-treat resin at 1.6 ml min^{-1}.
4	Sample is loaded to TEVA-Spec at 1.6 ml min^{-1}.
5	5 M HNO_3 is pumped to rinse residual sample and interference materials.
6	9 M HCl is pumped through resin to clean Th in resin.
7	1 M HNO_3 is pumped to rinse residual U.
8	0.5 M HCl is pumped through TEVA-Spec to elute Np at 0.83 ml min^{-1} for 19 s until 0.5 M HCl reaches the two-way valve.
9	About 0.83 ml of 0.5 M HCl is pumped to elute Np and Pu on TEVA-Spec.

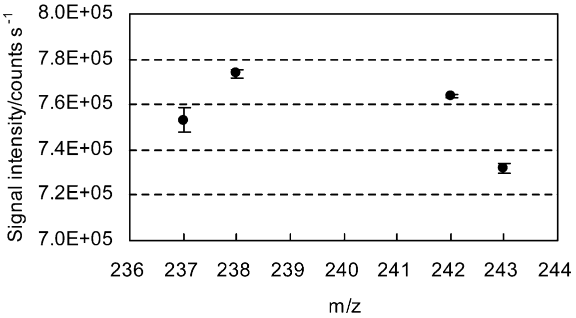


Fig. 2 Sensitivity of several actinides by ICP-SF-MS.

Spectral interference of ^{238}U

The polyatomic interference induced by ^{238}U in the measurement of Pu isotopes by ICP-MS is well known.[15,16] An Aridus desolvating introduction system greatly lowered this interference by removing solvent from the eluate. Furthermore, high level ^{238}U in a sample also affects the quantitative analysis of ^{237}Np by ICP-MS. To quantify the interference induced by ^{238}U, the pseudo concentration of ^{237}Np defined as 'the concentration of ^{237}Np corresponding to the down-mass tailing of ^{238}U peak on the 237 mass peak' was calculated with ^{238}U standard solutions at two mass resolutions.

As is shown in Fig. 3, 1 ng ml^{-1} of U caused a positive error corresponding to approximately 20 fg ml^{-1} of ^{237}Np at the two mass resolutions without large difference. The influence of spectral interference by ^{238}U at 237 *m/z* was similar to that due to molecular interference at 239 *m/z*, as we reported previously.[21] Even though the use of high mass resolution can help with the suppressing effect of the peak tailing from the high abundant neighboring isotopes without a reduction in the limit of detection (LOD), it also decreases signal intensity for the ^{237}Np peak. Consequently, applying high mass resolution is impractical to the measurement of ultra-low levels of ^{237}Np in the environmental samples as well as the elimination U in the chemical separation procedure is the best way to minimize the spectral interference of ^{238}U.

Behavior of Np and Pu in TEVA-Spec

In order to examine whether ^{242}Pu could be used as a tracer for the simultaneous analysis of ^{237}Np and Pu isotopes in the present separation scheme, the elution patterns of Np and Pu were plotted (Fig. 4). Eluate fractions were collected at 10 s intervals and the chemical recoveries of Np and Pu were calculated with the activity spiked, respectively. This experiment was performed with a standard solution containing ^{237}Np, ^{242}Pu and 30 mg of Fe^{III} in 5 M HNO$_3$. Although Np eluted a little faster than Pu from the TEVA-Spec resin, as depicted in Fig. 4, the total chemical recoveries of Np and Pu were nearly identical, about 98% and 99% in 0.83 ml of eluate, respectively. These high and similar chemical recoveries imply that ^{242}Pu could be used as a common tracer for simultaneous analysis by ICP-SF-MS. As shown in the elution curve, most of the Np and Pu retained in the TEVA-Spec could be recovered with only 0.83 ml of eluant, which corresponded to running the SI system for 60 s.

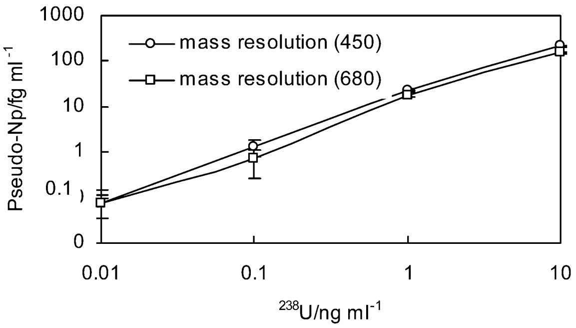


Fig. 3 Spectral interference of ^{238}U at two mass resolutions.

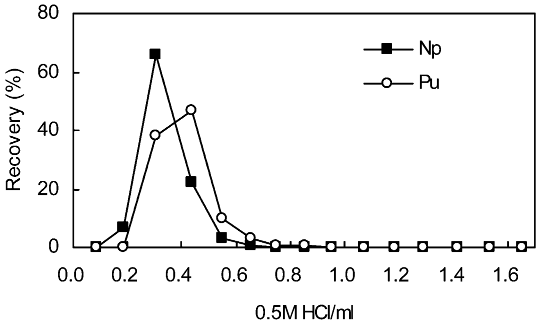


Fig. 4 Elution profile for Np and Pu in TEVA-Spec.

The similar recoveries of both actinides by TEVA-Spec was reconfirmed by spike testing. Six spiked solutions with the same concentrations of ^{237}Np and ^{242}Pu were separated by the SI system described in the experimental section. Although the chemical recovery of each nuclide ranged from 87 to 95%, the average ^{237}Np/^{242}Pu ratio was 0.99 with a little variation, which supports the notion that ^{242}Pu is a suitable tracer for the simultaneous analysis of ^{237}Np and Pu using the SI system in combination with TEVA-Spec.

Effect of nitric acid concentration on the purificaiton of Np and Pu by TEVA-Spec

According to the elution profiles of radionuclides by TEVA-Spec, strong Np and Pu retention was observed in nitric acid media at *ca.* 3 M HNO$_3$.[22] However, the elution patterns of Np and Pu may be changed by the sample matrix composition and redox treatment. Furthermore, it is difficult to maintain the nitric acid concentration in the loading solution after volume reduction by evaporating off the filtered acid extractant in order to reduce the volume of the loading solution. For this reason, the recovery test for both actinides was performed with increasing concentration of nitric acid in the loading solution, *i.e.*, from 3 M to 8 M. As plotted in Fig. 5, the chemical recoveries of Np and Pu were high in the ranges 3–6 M and 4–7 M, respectively. The recovery ratio of ^{237}Np/^{242}Pu was maintained with a unit value in the concentration range 4–6 M and recovery was sufficiently high. Thus, 5 M was chosen as an optimum nitric acid concentration for the loading and rinsing solution in the SI system. In addition, U was eliminated with an average decontamination value of 5 × 10^5 in a consistent manner for all the concentrations tested. The decontamination factor was defined as 'the total amount of an atom in the loading solution divided by the total amount of the atom in the final eluate'.

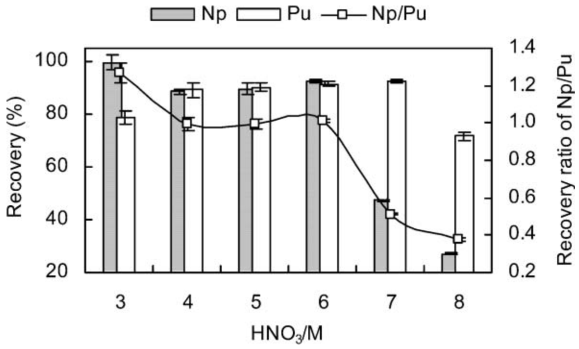


Fig. 5 Effect of the concentration of nitric acid on separation of Np and Pu in TEVA-Spec.

Effect of ascorbic acid on the oxidation states of Np and Pu

According to the pH of the sample solution, Np can exist as Np^{IV}, Np^{V} or Np^{VI}, and Pu as Pu^{III}, Pu^{IV}, Pu^{V} or Pu^{VI}. In strong nitric acid, Pu^{V} is very unstable and tend to disproportionate to +3, +4 and +6, whereas for Np, Np^{V} predominates.[23,24]

As described by Holwitz *et al.*,[22] TEVA-Spec shows a high affinity only for the tetravalent actinide in the nitric acid matrix: therefore, Np and Pu in the loading sample should be adjusted to this state for both to be retained during the ion exchange step. Meanwhile, ^{238}U, the most important element related to the interference effect in the analysis of ^{237}Np and ^{239}Pu by ICP-MS, can be easily removed by nitric acid treatment, since the hexavalent state of U, the dominant oxidation state in environment samples, has very low capacity factor (k') on TEVA-Spec. Consequently, the manipulation of oxidation state is an important procedure in the selective separation of target nuclides from bulk and interference elements.

Perna *et al.*[19] and Kenna[8] sequentially used several redox agents, *i.e.*, Mohr's salt and $NaNO_2$, to prepare Pu^{IV} and Np^{IV}. However, these methods are sensitive to reaction time, especially $NaNO_2$, and require a complicated separation procedure. In order to find a redox agent capable of guaranteeing similar recoveries of both actinides with simple treatment, three reagent types frequently used for the redox reaction of these actinides were examined with respect to chemical recovery. All investigations were carried out in a working solution (3 mg ml^{-1} Fe, ^{237}Np and ^{242}Pu tracer in 5 M HNO_3) using the same separation procedure as used for real samples. Table 3 shows that ascorbic acid was best in this respect, and that the recoveries of both actinides were similar. Pu recovery after $NaNO_2$ treatment was similar to that obtained with no added redox agent. The absorption peak of Pu^{VI} at 830 nm in the UV-Vis spectra was confirmed in the loading solution containing no redox agent. The absorption peak for Pu^{VI} completely disappeared after treatment with ascorbic acid, whereas $NaNO_2$ had no effect on the reduction of Pu^{IV}. So, in the present study, only ascorbic acid was used, because it effectively reduces Np^{V} to Np^{IV} and Pu^{VI} to Pu^{IV} in the loading solution.

Fig. 6 presents that the recoveries of ^{237}Np and ^{242}Pu and the recovery ratio of $^{237}Np/^{242}Pu$ with elapsed time after treating the loading solution with ascorbic acid. As can be seen from Fig. 6, both actinides were recovered at around 90% after 20 min and the recovery increased slightly with reaction time. Thus, the loading solution was treated with ascorbic acid for at least 20 min. In the case of no treatment of ascorbic acid, the recoveries of Np and Pu were 0.4% and 60%, respectively.

To determine the optimum amount of ascorbic acid that should be added to the loading solution, the chemical recoveries of Np and Pu were examined *versus* ascorbic acid concentration. After adding ascorbic acid, 10 ml of the working solution (3 mg ml^{-1} Fe, ^{237}Np and ^{242}Pu tracer in 5 M HNO_3) were left for 30 min, and then both actinides were separated on the SI system. As presented in Fig. 7, the recoveries of both actinides reached about 90% in 10 mg of ascorbic acid, and did not increase further up to 200 mg.

Table 3 Chemical recovery of Np and Pu using different redox agents

Redox agent	Concentration/ M	Recovery (%) Np	Recovery (%) Pu
None	—	1.1 ± 0.4	62 ± 4
Hydrogen peroxide (H_2O_2)	1.0	25 ± 13	35 ± 12
Sodium nitrite ($NaNO_2$)	0.2	6.2 ± 2	67 ± 3
Ascorbic acid	0.06	89 ± 1	88 ± 1

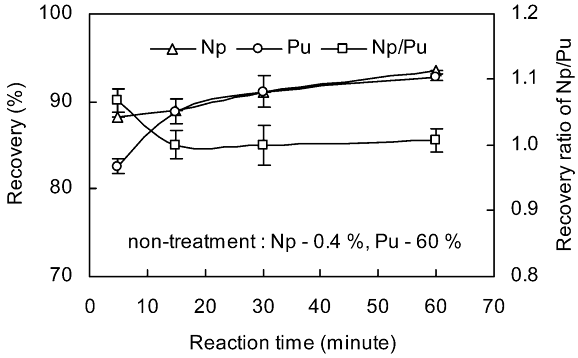


Fig. 6 Chemical recovery of Np and Pu with 0.06 M ascorbic acid reaction time.

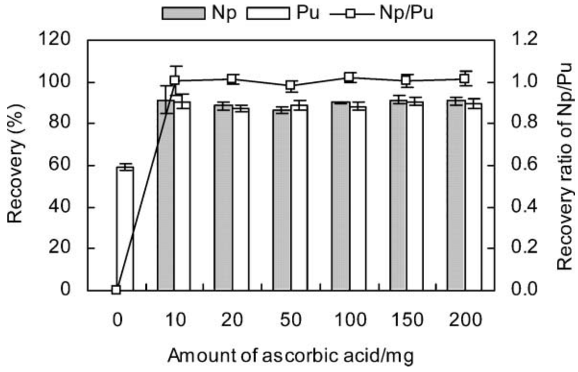


Fig. 7 Effect of the amounts of ascorbic acid on the chemical recovery of Np and Pu.

Removal of Th and U

^{232}Th and ^{238}U are naturally abundant in soil and sediment. Accordingly, large amounts of ^{232}Th in the sample solution can interfere with the quantitative determination of ^{237}Np and Pu isotopes because a huge ^{232}Th ICP-MS spectrum increases the background noise in the spectra of the Np and Pu isotopes. Whereas U is easily removed in the sample loading and rinsing step by 5 M HNO_3, Th is not removed by nitric acid medium in the TEVA-Spec. Fortunately, the capacity factor for Th is very low over a wide hydrochloric acid concentration range, whereas Np and Pu have higher capacity factors at high hydrochloric acid concentrations. Thus, 9 M HCl was selected as a rinsing solution for Th removal. In the case of U, although U was almost eliminated in the early two separation stages, the residual amounts of ^{238}U retained on the TEVA-Spec resin were not small enough to be negligible in the determination of the ^{237}Np and Pu isotopes at the fg ml^{-1} levels required in environmental samples. For this reason, the supplementary rinsing step with 1 M HNO_3 was followed by 9 M HCl rinsing. Table 4 shows the percentages of Th and U removed by 9 M HCl and 1 M HNO_3 with eluent volume in the rinsing steps.

Table 4 Removal of Th and U through TEVA-Spec separation steps

Separation steps	Volume/ ml	Th removal (%)	U removal (%)
Sample loading	12	1.1	89.9
Rinsing with 5 M HNO_3	7	1.5	10.5
Rinsing with 9 M HCl	1.4	93.1	0.03
	2.8	1.6	0.01
	4.3	0.5	0.01
	5.7	0.2	0.02
Rinsing with 1 M HNO_3	0.9	2.5	0.64
	1.7	0.2	0.07
	2.6	0.1	0.02
	3.4	0.1	0.01

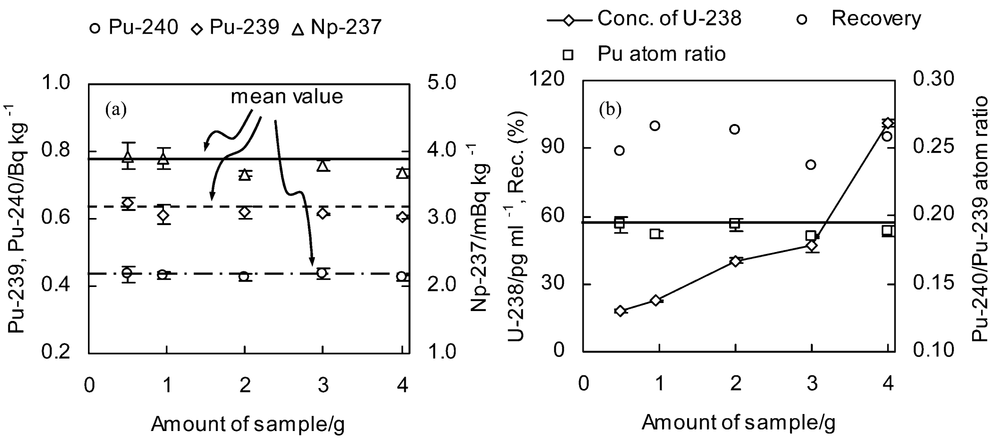


Fig. 8 Variations of precision and accuracy for ^{237}Np and Pu isotopes (a) and chemical recovery and U concentration (b) with the sample amount. Error bars on individual analysis are ± 1σ of the mean value for 3 replicates.

The decontamination factor of U was 8.8 × 10^5, which is similar to that obtained by dual column sequential separation.[19]

Effect of sample amount on the SI system

The concentrations of ^{237}Np and Pu isotopes in environmental samples ranged widely according to the sample location and matrix. Occasionally, 1 g of soil or sediment was too small to obtain reliable data in terms of accuracy and precision. In such cases, to improve result reliability, the sample size should be increased. However, the separation of large samples on a small TEVA-Spec column could cause unexpected problems, *e.g.*, serious interference and reduced chemical recovery. In order to examine the separation capability of the SI system for large samples, we compared the accuracy, precision, chemical recovery and the ^{238}U concentration in different IAEA-Soil-6 sample sizes.

According to the result shown in Fig. 8, test precision for the three radionuclides improved slightly on increasing the count number in ICP-MS as well as the concentration of ^{238}U increased with sample amount. Although, the ^{238}U concentration in the final eluate was over 100 pg ml^{-1} when a 4 g sample was used, the interference effect of ^{238}U on the final concentration of ^{237}Np and ^{239}Pu was less than 0.3%. The concentrations of ^{239}Pu and ^{240}Pu were within a relative error of 10% of from the certified value,[25] and the ^{240}Pu/^{239}Pu atom value was the same as those obtained by Muramatsu *et al.*[26] and Nygren *et al.*[27] Furthermore, the concentrations of ^{237}Np, ^{239}Pu and ^{240}Pu were similar in all samples and no degradation of chemical recovery was found. As a result, the described scale of the SI system could be used to treat up to 4 g of soil with good accuracy and high chemical recovery.

Re-usability test of TEVA-Spec

The re-usability of the TEVA-Spec in the SI system in a consecutive separation process is of interest, due to its high cost and the need for protracted resin exchange. The extended use of resin can lead to degradation of resin performance with the loss of immobilized stationary organic phase and hydrolysis of extractant and polymer support. Judgements concerning the re-use of resins can be based on the level of chemical recovery and the success of decontamination of residual interference caused by successive use.

Table 5 shows the chemical recoveries and the concentrations of ^{237}Np and Pu isotopes in nine replicates of NIST-4357, obtained after consecutive separation procedures using the same resin. Blank samples were treated using the same resin after completing the consecutive separation of three NIST replicates. Prior to injecting the next sample, the resin was rinsed with about 5 ml of 0.5 M HCl to minimize the memory effect. The memory effect in TEVA-Spec was calculated in relation to the activity of the blank sample against the spiked activity of the previous replicate sample. Although about 2% of the Pu in the sample was found in the blank solution, the memory effect did not increase gradually in three blanks. In addition, the results for ^{237}Np and Pu obtained using a blank effect correction were within the certificate interval of NIST.[28] Even if the memory effect is not significant, it should be checked using a blank sample whenever TEVA-Spec is used repeatedly.

Validity test and its application to the environmental samples

The reliability of the proposed analytical method was also examined using NIST-4357, which is a valuable standard

Table 5 Re-usability and memory effect of TEVA-Spec in NIST-4357

NIST-4357 replicate	^{238}U conc./pg ml^{-1a}	Recovery (%)	^{237}Np/mBq kg^{-1b}	$^{239+240}$Pu/Bq kg^{-1b}	^{240}Pu/^{239}Pu atom ratio
1	1.8	89	10.3	9.05	0.24
2	7.4	94	9.7	9.30	0.24
3	0.2	99	9.2	9.29	0.23
Blank-1	1.2	2.4			
4	10.5	92	8.8	9.99	0.24
5	0.4	97	8.8	9.29	0.24
6	2.0	89	9.0	10.68	0.24
Blank-2	26.3	2.5			
7	7.5	91	8.4	8.88	0.24
8	19.0	96	8.0	10.33	0.25
9	20.9	92	7.8	9.92	0.24
Blank-3	7.4	1.8			
Mean	8.84	2.2	8.9 ± 0.77	9.64 ± 0.62	0.24 ± 0.006

[a] The average decontamination factor of U was 8.8 × 10^5. [b] Confidence intervals for ^{237}Np and $^{239+240}$Pu by NIST were 4–9 mBq kg^{-1} and 9.3–13.2 Bq kg^{-1}, respectively.

reference material containing a certified ^{237}Np level. To verify the applicability of this method to the samples from different matrices, three standard reference materials (SRM) of IAEA and NIST, including a biological sample, were analyzed. As is shown in Table 6, the analytical results of total Pu in IAEA-135 fell within the IAEA certified range,[29] and the ^{240}Pu/^{239}Pu atom ratio agreed well with value reported by the MEL laboratory.[27,30]

Additionally, the concentrations of ^{237}Np, ^{239}Pu and ^{240}Pu agreed within a 10% deviation with that reported by Chen *et al.*[10] For NIST-4350B, the ^{237}Np and Pu isotope results were similar to those found by Kenna[8] and Kim *et al.*,[16] and agreed with the NIST certified $^{239+240}$Pu values.[31]

In the case of the biological reference sample, IAEA-307, although the accuracy of the analytical result for ^{237}Np was unverifiable, because the actual ^{237}Np level was not known, the $^{239+240}$Pu concentration was within the confidence interval of IAEA,[32] and the ^{237}Np value near identical for 4 replicates. Furthermore, the chemical recoveries for all testing replicates of the three SRMs were sufficiently high and the concentration of U in the final eluate was less than 50 pg ml^{-1}, thus enabling the quantitative determination of ^{237}Np and Pu isotopes by ICP-SF-MS in combination with the SI system.

Table 6 Comparison of the analytical results to recommended or informational values available for standard reference materials. The ± values give one standard deviation

Sample	Replicate no.	Rec. (%)	^{237}Np/Bq g^{-1}	Rec. or info. value (95% C.I.)	^{239}Pu/Bq g^{-1}	^{240}Pu/Bq g^{-1}	$^{239+240}$Pu/Bq g^{-1}	Rec. or info. value (95% CI)	^{240}Pu/^{239}Pu atom ratio	Rec. or info. value (95% CI)
IAEA-135	6	86	0.79 ± 0.03	0.85 ± 5.3	121 ± 5.68	92 ± 7.3	212 ± 12.4	213 (205–225.8)	0.21 ± 0.01	0.207 ± 0.006
NIST-4350B	4	94	0.000 20 ± 0.000 02	0.000 18 ± 0.000 01	0.36 ± 0.04	0.14 ± 0.01	0.51 ± 0.05	0.508 (0.479–0.528)	0.11 ± 0.01	0.11 ± 0.01
IAEA-307	4	96	0.000 78 ± 0.000 08	Not available	0.45 ± 0.02	0.32 ± 0.01	0.77 ± 0.01	0.72 (0.66–0.79)	0.20 ± 0.01	Not available

Conclusions

We have described a new simultaneous analytical method for ^{237}Np and Pu isotopes in various environmental samples by ICP-SF-MS combined with the SI system. This method is very fast and convenient by virtue of straightforward sample pretreatment and an automated separation procedure. Thus, this method is compatible with the requirements of an emergency situation demanding rapid analysis of ^{237}Np and Pu isotopes, and is able to analyze small sample volumes. Moreover, it is an economic analytical tool as only a small volume of resin is packed into the micro-column, because of its sustained separating ability in real situations. This method was successfully applied to soil, sediment and biological samples, and showed high chemical recovery, a satisfactory accuracy, and a low level of interference from ^{238}U.

However, further study for the rapid simultaneous determination of ^{237}Np and Pu isotopes in water samples is required, especially in sea-water, as the present separation scheme is unsuitable for water samples.

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