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Reliable determination of ^{237}Np in environmental solid samples using ^{242}Pu as a potential tracer

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ABSTRACT

This paper reports an analytical method for rapid determination of neptunium (^{237}Np) in environmental solid samples exploiting automated sequential injection (SI)-based anion exchange separation. Pivotal issues on analytical method performance were investigated including sorption behavior of ^{237}Np onto various AG 1-type anion exchangers; suitability of ^{242}Pu as a tracer for ^{237}Np determination in environmental solid samples; and long-term chemical stability of tetravalent Np. Experimental results revealed that the degree of resin cross-linking has a significant influence on the separation efficiency in terms of chemical yields of ^{237}Np and removal of interfering nuclides. Although ca. 30% of sorbed Np onto AG 1-×4 was stripped out during HCl rinsing step for the removal of Th, chemical yield ratios of ^{237}Np to ^{242}Pu were proven steady with an average value of 0.67 ± 0.04 ($n = 15$) under selected experimental conditions. Disulfite-8 M HNO_3 was selected as a redox pair for valence adjustment to Np(IV) and the tetravalent Np in the sample solution was demonstrated to be stabilized for up to 5 days under 3 °C. The analytical results for reference materials showed a good agreement with the expected values, thereby demonstrating the usefulness of ^{242}Pu as a non-isotopic tracer for ^{237}Np chemical yield monitoring. The on-column separation procedure fosters rapid analysis as required in emergency situations since each individual sample can be handled within 2.5 h, and leads to a significant decrease in labor intensity compared to conventional batch-wise protocols.

1. Introduction

Neptunium is the first transuranium element (TRU) with ^{237}Np as the most important long-lived isotope, which is an alpha emitter with half-life of $(2.144 \pm 0.007) \times 10^5$ years. The main sources of ^{237}Np in the environment are nuclear weapon tests, controlled releases from nuclear reprocessing plants, especially at La Hague (France) and Sellafield (UK), and nuclear accidents, e.g., Chernobyl in 1986 [1]. Due to the considerably longer half-life compared with other actinides, for example ^{239}Pu and ^{240}Pu, the activity of ^{237}Np is relatively low. However, it will be the prevailing TRU element in nuclear waste after a few hundred years, where most of plutonium and uranium are removed while neptunium together with other transuranics and fission and activation products go to the high active waste fraction for final disposal [1]. Besides, neptunium is one of the most hazardous radionuclides in spent nuclear fuel due to the relatively high mobility especially under oxic conditions. Therefore, accurate determination of ^{237}Np in environmental samples is important for radioecological studies, environmental risk assessment, emergency preparedness and nuclear waste treatment.

A number of analytical methods including co-precipitation, solvent extraction, ion exchange chromatography and extraction chromatography have been reported for the determination of ^{237}Np in environmental samples [2–15] and the analytical features thereof have been critically ascertained in recent review articles [16,17]. The major obstacle in accurate ^{237}Np determination lies in the need to obtain a reliable chemical yield isotopic tracer. In fact, no such ideal tracer is available as of yet because the short-lived ^{239}Np ($t_{1/2} = 2.3565 \pm 0.0004$ d) imposes stringent demands on its production and sample handling times during analysis [18]; the long-lived ^{236}Np ($t_{1/2} = (1.54 \pm 0.06) \times 10^5$ years) is not easy to generate and still not available commercially in a suitable purity; the applicability of ^{235}Np ($t_{1/2} = 396.1 \pm 1.2$ d) is hampered by frequent ^{237}Np impurities and the need of sufficient amount of ^{235}Np to obtain a reliable signal with liquid scintillation counting (LSC) [19]. In theory, ^{237}Np as an alpha emitter could be measured by alpha spectrometry. In practice, however, this is not a straightforward task due to the ultra-trace level of ^{237}Np in non-contaminated environmental samples plus the low specific activity of the isotope. Accordingly, long measurement times, from 24 h to weeks, are required. Besides, spectrometric interferences from ^{226}Ra, ^{229}Th,

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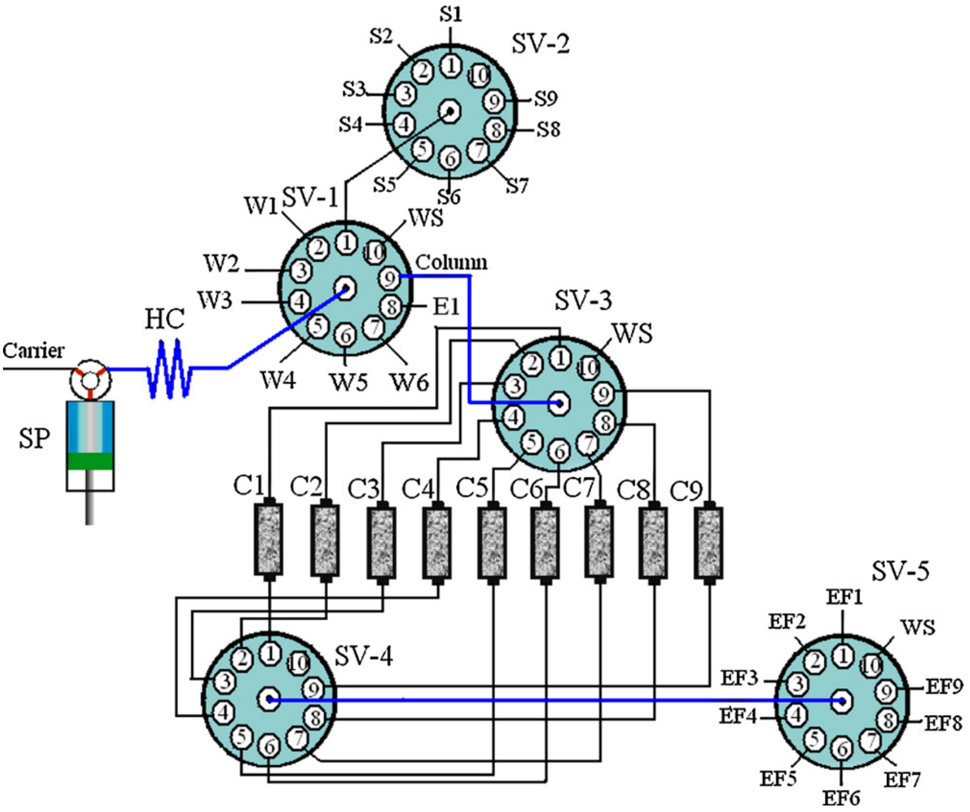

Fig. 1. Schematic diagram of the sequential injection (SI) system for automated separation of ultra-trace levels of ^{237}Np in environmental solid samples. S1-S9: samples; W1: 8 M HNO_3; W2: 6 M HNO_3; W3: 4 M HNO_3; W4: 2 M HNO_3; W5: 1 M HNO_3; W6: 9 M HCl; E1: 0.5 M HCl; C1–C9: anion exchange columns; EF1–EF9: eluate fractions; SV1–SV5: multi-position selection valves.

^{230}Th, ^{233}U, ^{234}U, and ^{242}Pu set high demands on the chemical separation when measuring ^{237}Np by alpha spectrometry.

To overcome the abovementioned problems, a potential avenue would be to exploit a non-isotopic tracer (e.g., ^{242}Pu) to monitor the chemical yield of ^{237}Np in radiochemical analysis combined with ICP-MS for the detection of ^{237}Np, since ICP-MS offers advantages of fast measurement and low detection limits over alpha spectrometry [20]. However, articles associated with the application of non-isotopic tracers for ^{237}Np are scarce. To the best of our knowledge, the reported separation methods are up to date limited to the publications of Chen et al. [7] and Kim et al. [21] using anion exchange and extraction chromatography, respectively. Kim et al. [21] reported a flow injection system coupled to ICP-MS for expedient separation of Np and Pu, yet only applicable to the analysis of small sized samples (≤4 g of soil). In our former work [22], we succeeded in Np determination using a non-isotopic Pu tracer via extraction chromatography (TEVA), however, as compared with anion exchange chromatography, extraction chromatography is more costly and less feasible for widespread use in radiochemical laboratories for routine assays. Notwithstanding the fact that quantitative isolation of Np was reported by Chen et al. [7] using anion exchange chromatography, the chemical separation protocol was labor-intensive and time-consuming since several separation techniques were combined in a batch-wise fashion including precipitation, solvent extraction and anion exchange chromatography.

In this work, we aim to investigate the suitability and actual applicability of ^{242}Pu as a non-isotopic tracer for rapid determination of ^{237}Np using SI-anion exchange separation and ICP-MS detection. Sorption performances of ^{237}Np and ^{242}Pu onto anion exchangers are investigated in detail for a variety of column dimensions and sorbent materials. To the best of our knowledge, no automatic flow-based method using gel-type anion exchanger has been reported to date for the determination of ^{237}Np at environmentally relevant levels.

2. Experimental

2.1. Experimental setup

A schematic illustration of the automated separation set-up is shown in Fig. 1. It consists of an FIAlab-3500B SI system (FIAlab Instruments, Bellevue, WA, USA) furnished with a syringe Pump (SP, Cavro, Sunnyvale, CA, USA, 25 ml capacity), an internal 10-port multi-position selection valve (SV-1), four external 10-port multi-position section valves, SV-2 to SV-5 (Valco Instruments, Houston, TX, USA), and nine separation columns. Operation of the system was computer controlled via FIALab software. All outlets of the selection valve (SV-1) were connected through PEEK ferrules with rigid PTFE tubing (2.4 mm i.d./3.2 mm o.d.) and all 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 i.d./1.6 mm o.d.). The central port of the SV-1 was connected to the holding coil (HC), which consists of a 6.6 m-long PTFE tubing with an inner capacity of 30 ml (2.4 mm i.d./3.2 mm o.d.). In order to improve the sample throughput, nine columns were implemented in the SI system at a time and thus nine samples were able to be processed consecutively in a fully automated fashion. Each column was proven to be reused up to three times.

2.2. Standards, reagents and samples

All reagents, including nitric acid (HNO_3), hydrochloride acid (HCl), ammonia ($NH_3{\cdot}H_2O$), potassium disulfite ($K_2S_2O_5$) and sodium hydroxide (NaOH) used in the experiment were of analytical reagent grade. ^{242}Pu standard solution (0.1037 Bq g^{-1} in 2 M HNO$_3$) was diluted from NBL-CRM 130 purchased from New Brunswick Laboratory (Argonne, IL, USA). ^{237}Np solution of 0.01175 Bq g^{-1} in 2 M HNO$_3$ was diluted from a stock solution supplied by Risø National Laboratory for Sustainable Energy (Denmark). Standard solutions of uranium and thorium were purchased from NIST (Gaithersburg, MD, USA). ^{239}Np was separated from a ^{243}Am stock solution as follows: the ^{243}Am solution was first loaded onto an anion exchange column, after washing with 9 M HCl to remove all ^{243}Am, ^{239}Np (the daughter of ^{243}Am) was eluted with 2 M HCl. All solutions used in the experiments were prepared with deionised water (18 MΩ cm, purified using a water purification system from Sartorius Stedim Biotech, Aubagne Cedex, France).

AG 1-type anion exchangers are the resins of choice for Np separation in most of radioanalytical laboratories [2,3,6,7,15,23,24]. In this work, AG 1-type resins with different cross-linkages and particle sizes were explored including AG 1-×2 (2% cross-linkage, 50–100 mesh), AG 1-×4 (4% cross-linkage, either 50–100 mesh or 100–200 mesh) and AG 1-×8 (8% cross-linkage, 50–100 mesh) in chloride form (Bio Rad Laboratories Inc., Hercules, CA, USA). Resin beads were swelled in water and poured into a cylindrical Econo-Column® (Bio-Rad Laboratories Inc.), followed by pre-conditioning with 25 ml of 8 M HNO$_3$ prior to use. The effect of column size and aspect ratio on the separation of ^{237}Np was investigated exploiting columns with the following dimensions: ∅ 1.0 × 20 cm (ca. 16 ml), ∅ 0.7 × 20 cm (ca. 8 ml), ∅ 0.7 × 10 cm (ca. 4 ml), ∅ 0.5 × 10 cm (2 ml), ∅ 0.7 × 5 cm (ca. 2 ml) and ∅ 0.5 × 5 cm (ca. 1 ml).

Method development and investigation of key parameters were performed using 10 g of a laboratory round-robin inter-comparison material, *namely*, Danish soil, (unless otherwise stated) spiked with ^{237}Np. One certified reference material (IAEA-135 sediment) and one reference sample from an inter-comparison exercise (Irish Sea sediment) were utilized as well for evaluation of method trueness. A Danish seaweed (Fucus vesiculosus) collected from the Klint, Danish coast was also analysed. The seaweed was first air-dried and then oven-dried at 70–80 °C for 2 days, whereupon the sample was ground and sieved through a 0.4 mm sieve.

2.3. Sample pre-treatment

10 g of Danish soil (or 1.0 g of IAEA-135 sediment/Irish Sea sediment or 20 g of Danish seaweed) was placed in a beaker and ashed at 550 °C overnight to decompose organic matter. The treated sample was spiked with 5.0 mBq of ^{242}Pu as a chemical yield tracer and, in the cases of Danish soil and seaweed, with 0.50 mBq of ^{237}Np as well. A detailed explanation of the preliminary sample pretreatment protocol can be found in our previous publication [22]. In brief, after aqua regia digestion, Np and Pu were co-precipitated with iron oxyhydroxides and thus isolated from the major components of the sample matrix.

2.4. Valence adjustment to Pu(IV) and Np(IV)

The redox pair K$_2$S$_2$O$_5$–8 M HNO$_3$ was utilized for valence adjustment of the target radionuclide and tracer to Np(IV) and Pu(IV), respectively. The complete analytical sequence has been described elsewhere [22].

2.5. Automated separation scheme

The SI-anion exchange chromatographic procedure consists of four steps as follows: (I) rinsing the holding coil with 50 ml of deionised water, and overall manifold tubing with in total 50 ml of 8 M HNO$_3$ at a flow rate of 10 ml min^{-1}; (II) loading the sample (14 ml per assay) onto the anion exchange column at 1.0 ml min^{-1}; (III) rinsing the column with 100 or 200 ml (100 ml for 2 ml-column and 200 ml for 4, 8, 16 ml-column, respectively) of 8 M HNO$_3$ at 2.5 ml min^{-1} to remove most of the matrix elements and uranium, followed by 100 ml of 9 M HCl to remove thorium; (IV) eluting Np and Pu with 40 or 100 ml of 0.5 M HCl (40 ml for 2, 4, 8 ml-column and 100 ml for 16 ml-column, respectively) at 2.5 ml min^{-1}.

The eluate was evaporated to dryness on a hot-plate to eliminate hydrochloric acid. The residue was dissolved in 5 ml of 0.5 M HNO$_3$ and the resultant solution was analysed by ICP-MS for quantification of ^{237}Np, ^{242}Pu and interfering nuclides.

2.6. ICP-MS detection of ^{237}Np and ^{242}Pu

To 5 ml of processed sample (diluted in 0.5 M HNO$_3$), 50 μl of 100 μg l^{-1} In(III) (as InCl$_3$) were added as an internal standard to correct the potential transmission variations in ICP-MS instrument. The concentrations of ^{237}Np, ^{242}Pu, ^{238}U and ^{232}Th were determined by X Series^{II} inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an Xs-skimmer core and a concentric nebulizer under hot plasma conditions. The typical operational conditions for ICP-MS detection of the above radionuclides are given elsewhere [22].

3. Results and discussion

In brief, this work aimed at setting an automated SI-based chromatographic procedure where both Pu and Np are sorbed strongly and equally well in the separation platform. To facilitate measurement using a sensitive detection method (ICP-MS) the protocol should be able to remove matrix elements which might cause serious spectral and non-spectral interfering effects. This mainly holds true to uranium but thorium needs to be kept to minimum levels as well.

3.1. Selection of separation protocol and column dimensions

The main challenge whenever using ^{242}Pu as a non-isotopic tracer for ^{237}Np determination is to obtain similar uptake and elution behavior for Pu and Np during the separation process and to ensure closely equal chemical yields. Column dimensions and physicochemical properties of anion exchangers including cross-linkage and particle size were investigated as core parameters for expedient uptake of both radionuclides. Fig. 2 shows the chemical yields of Np and Pu in connection with columns of varied dimensions packed with diverse anion exchangers, *namely*, AG 1-×2 (50–100 mesh), AG 1-×4 (50–100 mesh), AG 1-×8 (50–100 mesh) and AG 1-×4 (100–200 mesh). Because of the need of quantitative removal of uranium to reduce the interference of tailing of ^{238}U at $m/z = 237$ in ICP-MS, the decontamination factor for uranium, i.e. the ratio of total amount of uranium in the sample loading solution and that in the eluate, was also compared among distinct resins (see Fig. 3).

Experimental results revealed the existence of significant differences between the chemical yields of ^{237}Np and ^{242}Pu regardless of column dimensions and cross-linkage. The chemical yields ratio ^{237}Np to ^{242}Pu in AG 1-×2 decreased dramatically when reducing the column size. On the other hand, chemical yield ratios of ^{237}Np/^{242}Pu in AG 1-×4 and AG 1-×8 were unrelated to column size, with steady values at ca. 0.7, even employing small-sized (2 ml) columns for separation. However, AG 1-×4 resin was superior to AG 1-×8 regarding decontamination of uranium with factors within the range of 10^3–10^4 for AG 1-×4 vs. 10^2–10^3 for AG 1-×8 when using 2 mL (∅ 0.5 × 10 cm) of columns. The small sized AG 1-×4 column (∅ 0.5 × 10 cm) was regarded as the most suitable choice because of elevated Pu chemical yields (>95%) and fairly high

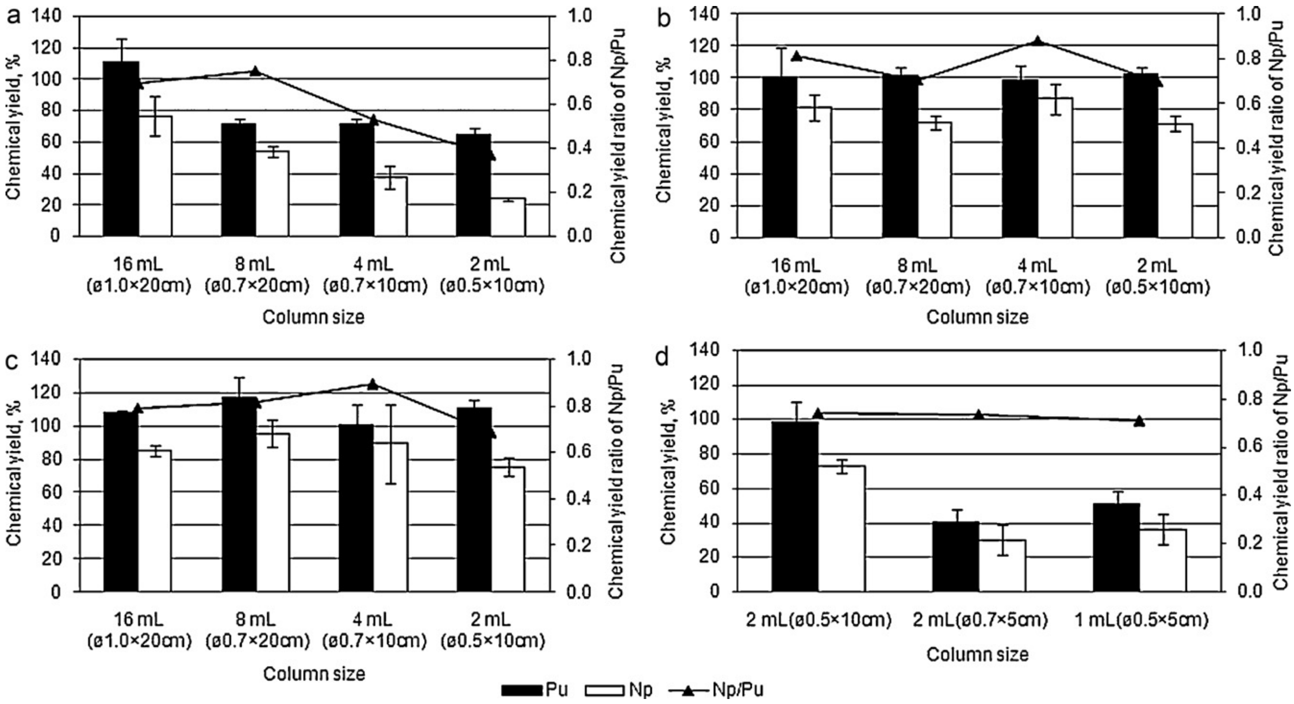

Fig. 2. Chemical yields of Np and Pu using distinct strong basic anion exchangers including (a) AG 1-×2 (50–100 mesh), (b) AG 1-×4 (50–100 mesh), (c) AG 1-×8 (50–100 mesh) and (d) AG 1-×4 (100–200 mesh) with columns of different capacity including 1 ml (∅ 0.5 × 5 cm), 2 ml (∅ 0.7 × 5 cm or ∅ 0.5 × 10 cm), 4 ml (∅ 0.7 × 10 cm), 8 ml (∅ 0.7 × 20 cm) and 16 ml (∅ 1.0 × 20 cm) (sample: 10 g of Danish soil; flow rate: 1.0 ml min^{-1} for sample loading and 2.5 ml min^{-1} for column rinsing and elution).

ratios of ^{237}Np/^{242}Pu chemical yields and decontamination factors for uranium, with minimal pressure drop in the flow system, and consequently was selected for further investigation.

The influence of particle surface area and column aspect ratio on the performance of 4% cross-linkage resins is presented in Fig. 2b and d. Although improved decontamination factors for uranium (see Fig. 3) and slightly higher ratios of ^{237}Np/^{242}Pu chemical yields were obtained whenever smaller beads were used, undue back pressure was observed which hindered the application of high flow rates in the low-pressure SI network. The column aspect ratio affected the separation efficiency as well: the larger the aspect ratio, the better were the chemical yields of both ^{242}Pu and ^{237}Np (re., ∅ 0.5 × 10 cm vs. ∅ 0.7 × 5 cm in Fig. 2d).

To further improve the decontamination factors of ^{238}U, varied concentrations of nitric acid and flow rates were investigated in the isolation of ^{237}Np onto AG 1-×4 resin using 10 g of Danish soil as a sample. Experimental results (see Fig. 4) demonstrated that the lower the concentration of nitric acid, the better the decontamination factor for U. However, chemical yields of ^{242}Pu and ^{237}Np as well as the ratio thereof dropped dramatically with the decrease in the concentration of nitric acid, which makes low concentration of nitric acid impracticable in the rinsing step due to significant losses of target radionuclides. An 8 M HNO_3 solution was thus chosen for the remainder of the work, which is in a good agreement with previously published works [7,25,26]. To evaluate the applicability of the analytical protocol proposed, measurement of the background signal at $m/z = 237$ was carried out with increasing concentrations of ^{238}U. Within the concentration range tested (10–1000 ng l^{-1} ^{238}U), the background signal barely changed, thereby confirming the reliability of the protocol for ^{237}Np assays at environmentally relevant concentration levels. When high concentrations of thorium are not removed from the sample, an interfering signal at $m/z = 242$ which

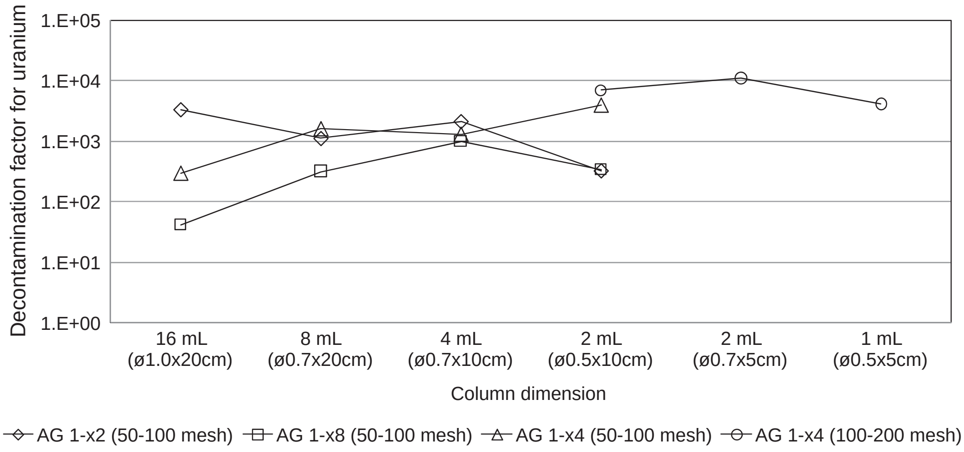

Fig. 3. Variation of decontamination factors for uranium on the basis of column dimensions and anion exchanger type (sample: 10 g of Danish soil; Flow rate: 1.0 ml min^{-1} for sample loading and 2.5 ml min^{-1} for column rinsing and elution).

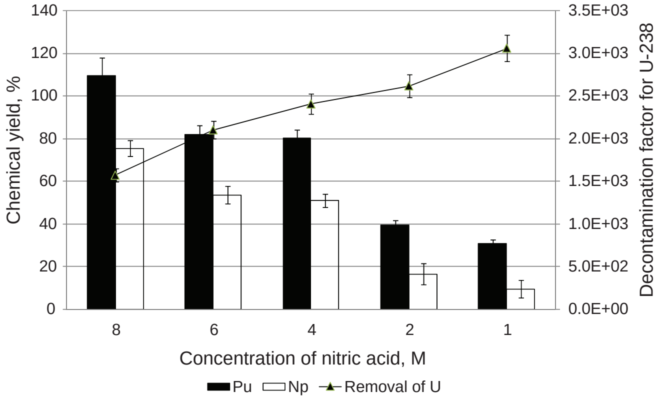

Fig. 4. Effect of the concentration of nitric acid on the removal of uranium from AG 1-×4 (50–100 mesh) (sample: 10 g of Danish soil; separation protocol: column rinsing with 100 ml of a given concentration of HNO_3 followed by 100 ml of 9 M HCl, elution of ^{237}Np and ^{242}Pu with 40 ml of 0.5 M HCl. Flow rate: 1.0 ml min^{-1} for sample loading and 2.5 ml min^{-1} for column rinsing and elution).

is cause by the polyatomic ion $^{230}Th^{12}C$ might overlap with ^{242}Pu. To minimize Th interfering effect, a 9 M HCl rinsing step was hence adopted after 8 M HNO_3 washing, rendering decontamination factors up to 10^4–10^5 for Th.

Flow rates for the two-step rinsing were varied from 2.5 to 5.0 ml min^{-1} aimed at increasing the sample throughput and improving the analytical efficiency. At 5.0 ml min^{-1} the chemical yields of ^{242}Pu and ^{237}Np were relatively low, therefore, the washing and elution flow rates were affixed to 2.5 ml min^{-1}. The sample loading flow rate was however set to 1.0 ml min^{-1} to ensure quantitative uptake of ^{242}Pu and ^{237}Np.

3.2. Suitability of ^{242}Pu as a tracer for Np determination

Experimental results compiled in Figs. 2 and 4 demonstrated that losses of ^{237}Np were still significant (ca. 20–30%) whenever ^{242}Pu was quantitatively retrieved from the sample under all investigated experimental conditions. Further experiments were therefore designed to unravel the physicochemical behavior of Np and Pu onto AG 1-×4 utilizing 10 g of soil spiked with a given amount of ^{237}Np, ^{239}Np and ^{242}Pu. All effluents from the column separation procedure were collected and measured for ^{239}Np using gamma spectrometry while ^{237}Np and ^{242}Pu were quantified by ICP-MS. ^{239}Np was added to the sample for better ascertainment of the fate of Np during the overall chemical separation procedure since effluents from sample loading and column rinsing might contain high amounts of interfering species deteriorating the reliable ICP-MS quantification of ^{237}Np. Fig. 5 compiles the overall results as obtained from four assay replicates of 10 g of Danish soil. No appreciable losses of ^{242}Pu were observed during sample loading and column rinsing using 8 M HNO_3 and 9 M HCl, respectively, while 30 ± 5% of ^{237}Np (and ^{239}Np) was found in the 9 M HCl fraction. The discrepancies in chemical yields between ^{237}Np (or ^{239}Np) and ^{242}Pu are therefore caused by the loss of ^{237}Np (or ^{239}Np) occurring in the 9 M HCl rinsing step. Published values for distribution coefficients of Pu and Np on anion exchangers in HCl media indicate a slightly higher affinity for Pu relative to Np [25], which might be accentuated when operating in a dynamic flow-through mode in lieu of steady-state conditions. The loss of Np might also be encountered during the on-column transformation of nitrate complexes of Np(IV) and Pu(IV) into their chloride complexes, because the stability of chloride complexes of Pu might be better than those of Np. Oxidation of Np to the pentavalent oxidation state is yet another possibility and should in this case be mediated by some intermediate product formed when mixing nitric and hydrochloric acids on-column. In principle, the valence state change of Np during 9 M HCl rinsing step might be detected with spectrophotometry at sufficiently high concentration, but unfortunately standards with the high concentration of Np are not readily available for the authors.

Interestingly, the cumulative losses of Np followed a linear correlation against the volume of 9 M HCl from 20 ml and onwards up to 100 ml. This effect has not been earlier discussed in the literature in the use of AG 1-type resins for the uptake and isolation of Np. This linear correlation reveals a constant bleeding of Np from the anion exchanger in a dynamic flow-through mode, which might be a consequence of the lower distribution coefficients of Np chlorocomplexes onto gel-type anion exchange resins as compared with Pu chlorocomplexes. The losses of Np could be thus minimized by reducing the volume of 9 M HCl. Repeated assays exploiting 2 ml of AG 1-×4 (50–100 mesh) for 10 g of Danish soil however demonstrated a relatively steady $^{237}Np/^{242}Pu$ chemical yield ratio with an average value of 0.67 ± 0.04 (n = 15) when using 100 ml of 9 M HCl for column rinsing. This implies that under well-

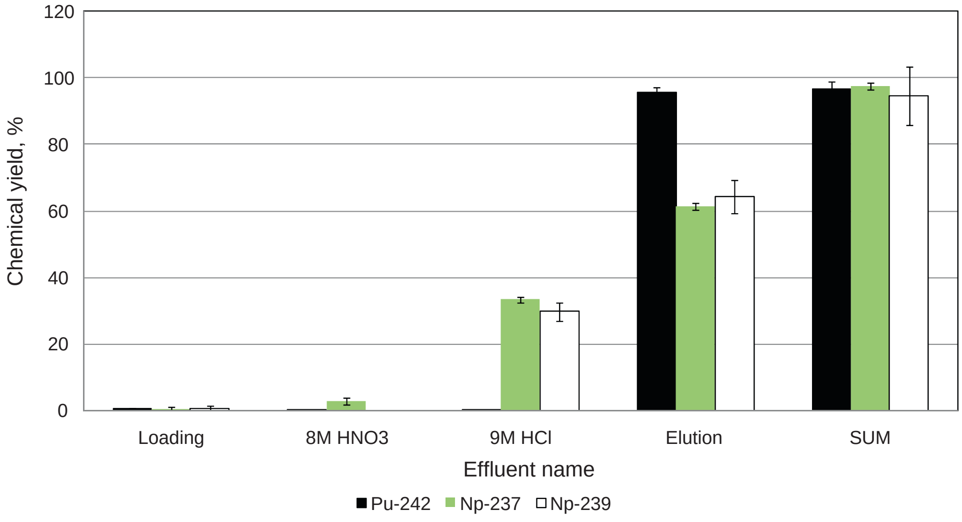

Fig. 5. Breakdown of ^{237}Np, ^{239}Np and ^{242}Pu chemical yields in different fractions of the overall steps in the SI-column separation protocol (sample: 10 g of Danish soil; resin: AG 1-×4 (50–100 mesh); separation protocol: column rinsing with 100 ml of 8 M HNO_3 followed by 100 ml of 9 M HCl, elution of ^{237}Np and ^{242}Pu with 40 ml of 0.5 M HCl. Flow rate: 1.0 ml min^{-1} for sample loading and 2.5 ml min^{-1} for column rinsing and elution).

Table 1
Determination of ^{237}Np activity in reference materials and spiked environmental samples using the proposed SI method in combination with ICP-MS.

Sample	Amount (g)	^{237}Np spiked (mBq)	Measured activity of ^{237}Np (Bq kg^{-1})	Literature or expected activities of ^{237}Np, (Bq kg^{-1})
IAEA-135 sediment	1.0	–	0.93 ± 0.05 (2.91)	0.846 ± 0.045 [21]
Irish sea sediment	1.0	–	0.99 ± 0.04 (0.13)	0.987 ± 0.048 [7]
Spiked Danish soil	10	0.50 ± 0.02	0.049 ± 0.003 (0.58)	0.050 ± 0.002
Spiked Danish seaweed	20	0.50 ± 0.02	0.026 ± 0.002 (0.87)	0.025 ± 0.001

Results are expressed as the mean of four replicates ± standard deviation. Numbers in brackets are $|t|_{\text{exp}}$ values, at the 95% confidence interval, the critical t-value (t_{crit}) is 3.18 for $n = 4$.

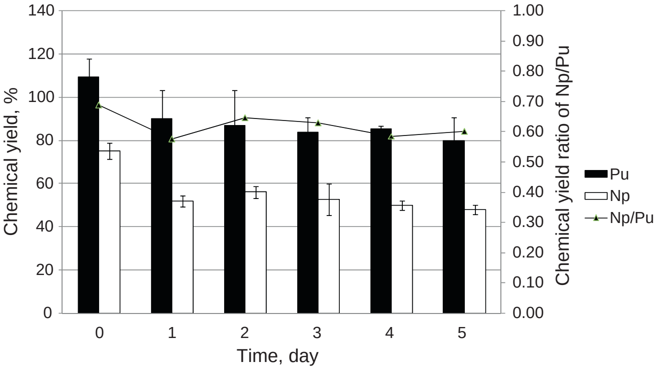

Fig. 6. Temporal stability of Pu(IV) and Np(IV) in the sample loading solution containing 8 M HNO_3 at 3 °C (sample: 10 g of Danish soil; resin: AG 1-×4 (50–100 mesh); separation protocol: column rinsing with 100 ml of 8 M HNO_3 followed by 100 ml of 9 M HCl, elution of ^{237}Np and ^{242}Pu with 40 ml of 0.5 M HCl. Flow rate: 1.0 ml min^{-1} for sample loading and 2.5 ml min^{-1} for column rinsing and elution).

defined experimental conditions as provided by SI manifolds, ^{242}Pu should be regarded as a viable tracer for ^{237}Np chemical yield monitoring.

3.3. Temporal stability of Pu(IV) and Np(IV) in the sample loading solution

In our previous work [22], we compared various methods for valence adjustment and stabilization of Pu(IV) and Np(IV). The redox pair $K_2S_2O_5$–8 M HNO_3 was proven the most effective reagent for simultaneous valence adjustment to Pu(IV) and Np(IV). The stability of Pu(IV) and Np(IV) in this solution is of major importance when preparing several samples to be analysed with the aid of an automated method where samples are not run in parallel. The valence states for both elements should be kept unaffected until the last sample has been loaded onto the column. To determine the time span to which Pu(IV) and Np(IV) are stable in the sample loading milieu, we conducted tests employing $K_2S_2O_5$–8 M HNO_3 redox reagents and keeping the sample loading solution in 8 M HNO_3 at 3 °C. The experimental results (see Fig. 6) reveal that Pu(IV) and Np(IV) could be stabilized in an 8 M HNO_3 medium for up to 5 days at 3 °C since the ^{237}Np/^{242}Pu chemical yield ratios were relatively constant in the range of 0.6–0.7, with no statistically significant differences in chemical yields at the 95% confidence.

It should be noted that remarkable decreases in chemical yields of Pu and Np were observed for the samples kept under 3 °C for 1–5 days compared with the ones immediately loaded onto the column after valence adjustment. This might be a consequence of lower distribution coefficients of Pu and Np onto the anion exchanger under lower reaction temperature, because those sample solutions were not re-warmed up to room temperature before loading onto the column.

3.4. Application of the proposed SI-separation method to environmental solid analysis

To explore the potential applicability of the present method for ^{237}Np determination in a variety of environmental solids, analyses were performed on a standard reference material (IAEA-135 sediment), an in-house reference sample (Irish Sea sediment) and spiked seaweed and soil samples. The analytical results are listed in Table 1. A good agreement was found for all samples between experimental results and literature reported, certified or estimated values, suggesting the applicability of the proposed method for the determination of ^{237}Np when utilizing ^{242}Pu as a non-isotopic tracer combined with the use of a normalization coefficient (viz., 0.67) for calculation of actual chemical yields of ^{237}Np.

On-column separation of a single sample in this work could be accomplished within 2.5 h, thus nine samples can be sequentially processed in a fully automated mode within one day. Because of the automation of column separation, sample treatment and chromatographic separation are allowed to be undertaken in parallel for a given number of samples, which is otherwise not straightforward (e.g., in the conventional methods). There are three distinctive benefits of using a fast automated separation procedure capitalized on SI when analysing ^{237}Np. First, the improved sample throughput compared with manual separation methods fosters Pu and Np to be preserved as Pu(IV) and Np(IV), respectively, in the course of the assays. Secondly, the rapid separation in the automated procedure also opens the possibility of utilization of the short-lived ^{239}Np as isotopic tracer. Last but not least, the automated processing of samples in a programmable sequence leads to improved reproducibility, decrease of measurement uncertainty, minimization of sample cross-contamination and improved safety due to minimum analyst intervention in the overall column separation procedure.

4. Conclusion and outlook

A flow-based anion exchange method was developed in this work for the determination of ^{237}Np at environmentally relevant levels. The detection of target radionuclides was performed using ICP-MS, offering advantages over alpha spectrometry of expeditious assays and low detection limits. The analytical results herein reported for ^{237}Np assays using AG 1-×4-type anion exchangers nested to a multi-position valve of the SI setup demonstrate that ^{237}Np to ^{242}Pu chemical yield ratios were almost steady within the range of 0.6–0.7 under certain experimental conditions. Although losses of Np occurred during column separation, the good agreement between experimental results and expected values for ^{237}Np in reference materials and spiked real-life samples reveals that ^{242}Pu is suitable as a non-isotopic tracer for ^{237}Np provided that normalization is taken into account.

Further work is underway to improve the chemical yields of ^{237}Np via multivariate optimization of the overall analytical procedure. A simple means to alleviate differences in chemical yields of Np and Pu is to decrease the volume of rinsing 9 M HCl yet at expenses of increased amounts of Th in the eluate. Whenever not feasible, alternative anion exchange resins, e.g., macro-porous AG

MP-1 M, might be evaluated as well as the modulation of chemical composition of the washing solution via addition of a redox reagent, such as $NaNO_2$, to prevent the on-column changeover of Np(IV).

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