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Sequential Injection Method for Rapid and Simultaneous Determination of ^{236}U, ^{237}Np, and Pu Isotopes in Seawater

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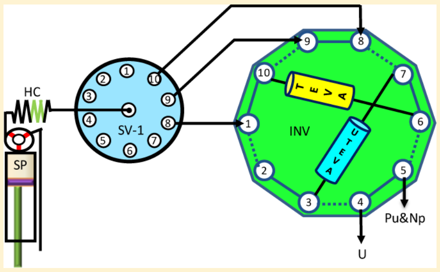
Supporting Information



ABSTRACT: An automated analytical method implemented in a novel dual-column tandem sequential injection (SI) system was developed for simultaneous determination of ^{236}U, ^{237}Np, ^{239}Pu, and ^{240}Pu in seawater samples. A combination of TEVA and UTEVA extraction chromatography was exploited to separate and purify target analytes, whereupon plutonium and neptunium were simultaneously isolated and purified on TEVA, while uranium was collected on UTEVA. The separation behavior of U, Np, and Pu on TEVA–UTEVA columns was investigated in detail in order to achieve high chemical yields and complete purification for the radionuclides of interest. ^{242}Pu was used as a chemical yield tracer for both plutonium and neptunium. ^{238}U was quantified in the sample before the separation for deducing the ^{236}U concentration from the measured ^{236}U/^{238}U atomic ratio in the separated uranium target using accelerator mass spectrometry. Plutonium isotopes and ^{237}Np were measured using inductively coupled plasma mass spectrometry after separation. The analytical results indicate that the developed method is robust and efficient, providing satisfactory chemical yields (70–100%) of target analytes and relatively short analytical time (8 h/sample).

As anthropogenic radionuclides, ^{236}U ($t_{1/2}$ = 23.4 Myr), ^{237}Np ($t_{1/2}$ = 2.1 Myr), ^{239}Pu ($t_{1/2}$ = 24.1 kyr), and ^{240}Pu ($t_{1/2}$ = 6.5 kyr) are among the most significant ones because these isotopes are α-particle emitters with long half-lives and are radiologically and chemically toxic. ^{236}U is mainly produced from the omnipresent ^{235}U by thermal neutron capture via (n, γ)-reactions, but can also be produced by ^{238}U (n, 3n) ^{236}U reactions with fast neutrons. On the surface of the earth, a very minor amount of ^{236}U (ca. 35 kg) exists from natural production, mainly in uranium ores,[1] while the majority (more than 1000 kg) of ^{236}U in the current environment was produced by anthropogenic processes (e.g., nuclear weapons testing[3] and in U-fission reactors).[2] Due to the low specific activity, significant amounts of ^{236}U might be released from nuclear fuel reprocessing facilities without violating health protection regulations.[2]

On the other hand, it has been estimated that 1746 kg of ^{237}Np, 2835 kg of ^{239}Pu, and 518 kg of ^{240}Pu have been released into the environment during the past nuclear activities.[4] Global fallout from atmospheric nuclear weapons testing is the main source of ^{237}Np, ^{239}Pu, and ^{240}Pu inventories.[5,6] Regional contaminations of ^{237}Np, ^{239}Pu, and ^{240}Pu originated from accidents with nuclear weapons (Palomares, 1966 and Thule, 1968), accidents at nuclear facilities (Chernobyl, 1986 and Fukushima, 2010) and reprocessing operations (La Hague, France and Sellafield, U.K.).[4]

Besides the need for environmental risk monitoring and nuclear safeguards, determination of ^{236}U, ^{237}Np, ^{239}Pu, and ^{240}Pu is also of great significance for radioecology and tracer studies. ^{237}Np, ^{239}Pu, and ^{240}Pu are of special interest for tracing regional radioactive sources and investigating water mass circulation and particulate matter scavenging.[7,8] In recent years, the potential of ^{236}U as an environmental proxy has also been promisingly recognized because ^{236}U/^{238}U isotopic ratios carry key signatures to differentiate uranium sources.[2,9]

However, the environmental distribution of anthropogenic ^{236}U, ^{237}Np, ^{239}Pu, and ^{240}Pu is not well-assessed yet.[9−11] Data of ^{237}Np and ^{236}U in seawaters taken from the open sea are especially limited, and their application as oceanic tracers is even scarcer.[1] This is mainly due to the fact that accurate measurements of very low levels of ^{236}U, ^{237}Np, ^{239}Pu, and ^{240}Pu even with modern mass spectrometers require complicated radiochemical separation, which were normally performed in manual fashion and thus are highly labor intensive with low sample throughput.[12−18]

In the recent years, several rapid analytical methods have been developed through the use of a vacuum box for determination of multiradionuclides,[19,20] and some research groups have reported flow-based automated analytical protocols, which significantly reduce analytical time and labor intensity.[21−31] Although the application of these flow-based

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methods offers great advantages in radiochemical assays, at present their development is still limited to a few laboratories.[21−31] Moreover, most established flow-based protocols are integrating single chromatographic columns for single radionuclide assays, and few of them have flexible applications in multiradionuclide determinations via multi-column tandems.[21−31]

In this work, we aim to develop a rapid analytical method being capable of simultaneously determining ^{236}U, ^{237}Np, ^{239}Pu, and ^{240}Pu in seawater samples. Extraction chromatographic (TEVA−UTEVA) columns were tactfully integrated in an SI manifold for automated purification of radionuclides of interest. ^{242}Pu was used as a tracer for ^{237}Np, ^{239}Pu, and ^{240}Pu, while ^{236}U was traced by endogenic ^{238}U. ICP-MS and AMS were exploited for the quantification of target isotopes throughout the method development and application.

■ EXPERIMENTAL SECTION

SI-Based Setup. The automated sequential injection (SI) analyzer (see Figure 1) consisted of a syringe pump (SP, Cavro, Sunnyvale, CA), one 10-port multiposition selection valve (SV-1), one 6-port multiposition section valve (SV-2), and one 10-port injection valve (INV) (Valco Instruments, Houston, TX). Two Econo-Columns (Bio-Rad Laboratories, Inc., Hercules, CA) packed with TEVA and UTEVA resin (100−150 μm particle size, Triskem International, Bruz, France) were integrated with the INV (see Figure 1), whereupon the isolation and connection of the TEVA and UTEVA columns was freely controlled through the programmable INV position regulation (position 1: TEVA and UTEVA were isolated; position 2: TEVA and UTEVA were connected).

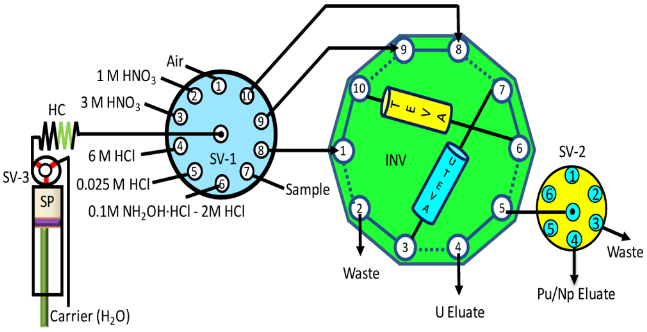

Figure 1. Schematic diagram of the SI system for simultaneous determination of U, Th, Pu/Np in seawater (HC: holding coil; INV: injection valve (position 1 shown as dotted line, position 2 shown as solid line); SP: syringe pump; SV: selection valve).

The central port of SV-1 was connected to the syringe pump through a holding coil (HC), which consisted of an 8 m long PTFE tubing with an inner capacity of 25 mL (2.0 mm inside diameter (i.d.)/2.8 mm outside diameter (o.d.)). The syringe pump was equipped with a 25 mL gastight glass syringe and a three-way solenoid valve (SV-3) at the head to facilitate the application of multicommutation schemes (out: to HC; in: to H_2O). All outlets of SV-2 and INV and partial outlets of SV-1 (i.e., port 7−10 for sample uptake and connection with INV) were connected through PEEK ferrules and fittings with rigid PTFE tubing of 0.8 mm i.d./1.6 mm o.d., while the remaining outlets (i.e., port 1−6 of SV-1 and carrier (H_2O) outlet of SV-3) of the SI-manifold were connected with PTFE tubing of larger diameter (2.4 mm i.d./3.2 mm o.d.). The SI manifold was fully automatically controlled via the aid of the user-friendly FIAlab software (FIAlab Instruments, Bellevue, WA)

Standards, Reagents, and Samples. A ^{242}Pu standard solution (0.1037 Bq/g in 2 mol/L HNO_3) diluted from NBL-CRM 130 (New Brunswick Laboratory, Argonne, IL) was used as a chemical yield tracer for both plutonium and neptunium. ^{237}Np (0.01175 Bq/g in 2 mol/L HNO_3) and ^{239}Pu (0.0833 Bq/g in 2 mol/L HNO_3) standard solutions were supplied by Center of Nuclear Technologies, Technical University of Denmark (DTU). Standard solutions of uranium and thorium (both 1.000 g/L in 2 mol/L HNO_3) were purchased from NIST (Gaithersburg, MD). All reagents used in the experiment were of analytical reagent grade and prepared using ultrapure water (18 MΩ·cm). Econo-Columns with different inner volumes were utilized for chromatographic separation, including 0.5 cm i.d. × 5 cm length (1 mL volume) and 0.5 cm i.d. × 10 cm length (2 mL volume).

For the method development, seawater samples collected at Roskilde Fjord, Denmark (55°41′N, 12°5′E) in 2012 were used throughout the work. For method application and evaluation, seawater samples collected from North Atlantic (69°64′N, 6°89′E) in 2011 and from Kattegat, Denmark (55°58′N, 11°34′E) in 2013 were analyzed.

Sample Pretreatment. To optimize the iron hydroxide coprecipitation condition, 200 mL of seawater spiked with known amounts of ^{242}Pu (ca.10 mBq) and ^{237}Np (ca.1 mBq) was used, and 0.2−2 mL of concentrated HCl was added to acidify the seawater to a pH of 0.9−1.9 (see Figure S-1). In addition, 0.03−0.2 mL of 0.1 g/mL Fe (as $FeCl_3$) was added to an Fe concentration of 15−100 mg/L. The details for the following operations are summarized in the Supporting Information.

To further optimize the preconcentration procedure for 10 L of filtrated seawater, 10 mL of concd HCl was added to adjust the pH to 2. Known amounts of ^{237}Np and ^{242}Pu were spiked, and 2−5 mL of 0.1 g/mL Fe solution and 2−20 g of $K_2S_2O_5$ were added. The sample was stirred by N_2 bubbling for 20 min, and then a two-step coprecipitation or one-step coprecipitation combining acid digestion was applied (see the experimental details in the Supporting Information and the results in Table 1). The sample was finally constituted to 3 mol/L HNO_3 for the automated chromatographic separation performed in the SI system.

Chromatographic Separation. *Investigation on Separation Behavior of Radionuclides on UTEVA Column.* To investigate the separation behavior of radionuclides on a UTEVA column, an artificial solution in HCl or HNO_3 media spiked with ca. 0.5 mBq of ^{237}Np, 5 mBq of ^{242}Pu, 62 μBq (5 ng) of ^{238}U, 20 μBq (5 ng) of ^{232}Th, and 30 mg of Fe was prepared. After valence adjustment and sample loading, the UTEVA column was rinsed with different solutions, and uranium was finally eluted with 0.025 mol/L HCl. The detailed experimental operations are demonstrated in the Supporting Information.

Investigation on Separation Performance of TEVA−UTEVA Columns. To investigate the effect of nitric acid concentration on the separation behavior of tandem TEVA−UTEVA columns, 100 mL of 0.2 mol/L HCl was spiked with ca. 20 mBq of ^{242}Pu, 1.0 Bq (80 μg) of ^{238}U, and 800 mg of Fe. After valence adjustment, the sample was prepared in 1−4 mol/L HNO_3 for the TEVA−UTEVA column separation (see Figure 2). The detailed experimental operations for the column separations are also detailed in the Supporting Information.

Table 1. Comparison of Analytical Performance in Different Pretreatment and Column Separation Conditions for Simultaneous Determination of U, Pu, and Np[a]

	experimental condition			chemical yield (%)				
group no.	pretreatment	column separation sequence	analytical time (h)	^{242}Pu	^{237}Np	^{237}Np/^{242}Pu ratio	^{238}U	DU
1	two-step coprecipitation	1. sample loading in 6 mol/L HCl 2. wash TEVA–UTEVA with 40 mL of 6 mol/L HCl 3. wash TEVA–UTEVA with 60 mL of 1 mol/L HNO_3 4. elute Pu/Np from TEVA with 20 mL of 0.025 mol/LHCl 5. elute U from UTEVA with 20 mL of 0.025 mol/L HCl	20	0.1 ± 0.1	0.1 ± 0.1		0.6 ± 0.2	(9.1 ± 0.9) × 10^3
2	two-step coprecipitation	1. sample loading in 3 mol/L HNO_3 2. wash TEVA–UTEVA with 40 mL of 3 mol/L HNO_3 3. wash TEVA with 20 mL of 1 mol/L HNO_3 and 20 mL of 6 mol/L HCl 4. elute Pu/Np from TEVA with 20 mL of 0.025 mol/L HCl 5. elute U from UTEVA with 20 mL of 0.025 mol/L HCl	20	6.1 ± 8.1	36.8 ± 17.3	0.13 ± 0.16	88.9 ± 8.9	(1.3 ± 0.5) × 10^3
3	One-step coprecipitation + acid digestion	1. sample loading in 3 mol/L HNO_3 2. wash TEVA–UTEVA with 40 mL of 3 mol/L HNO_3 3. wash TEVA with 20 mL of 1 mol/L HNO_3 and 20 mL of 6 mol/L HCl 4. elute Pu/Np from TEVA with 20 mL of 0.025 mol/L HCl 5. elute U from UTEVA with 20 mL of 0.025 mol/L HCl	8	76.7 ± 7.7	77.8 ± 7.8	0.99 ± 0.16	61.6 ± 2.6	(1.9 ± 0.2) × 10^4
4	one-step coprecipitation + acid digestion	1. sample loading in 3 mol/L HNO_3 2. wash TEVA–UTEVA with 20 mL of 3 mol/L HNO_3 and 20 mL of 1 mol/L HNO_3 3. wash TEVA with 20 mL of 1 mol/L HNO_3 and 20 mL of 6 mol/L HCl 4. elute Pu/Np from TEVA with 20 mL of 0.025 mol/L HCl 5. elute U from UTEVA with 20 mL of 0.025 mol/L HCl	8	73.6 ± 9.8	73.9 ± 5.6	1.01 ± 0.21	97.6 ± 20.6	(5.3 ± 0.5) × 10^4

[a] Values are the average of two replicates ± uncertainty.

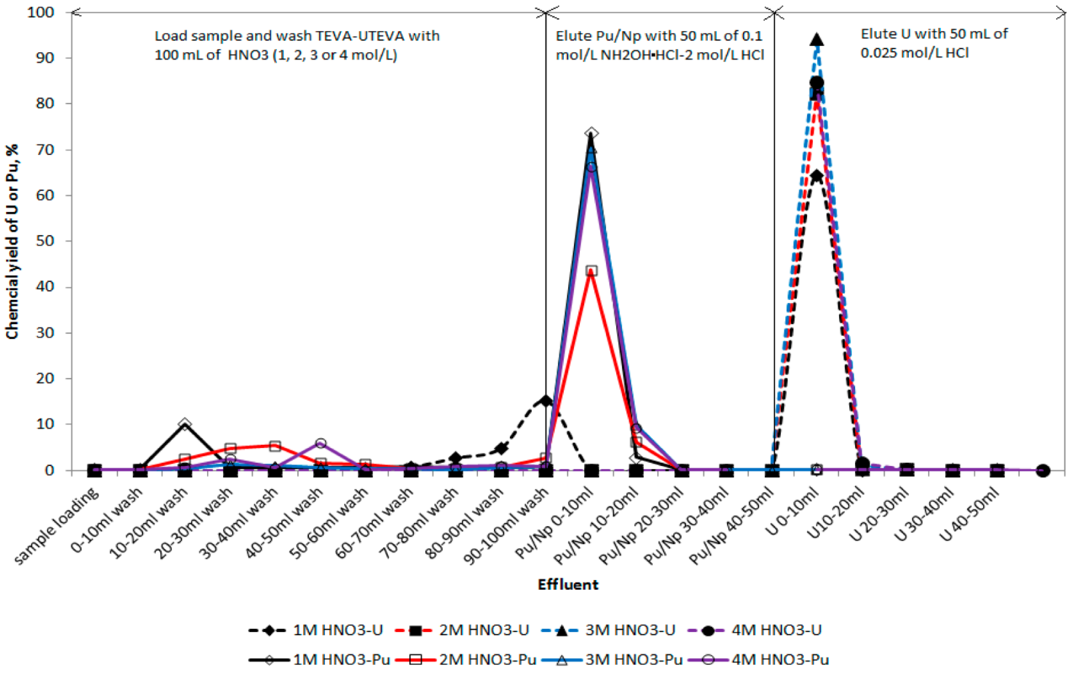

Figure 2. Sorption and elution behavior of uranium and plutonium on tandem TEVA−UTEVA columns under different concentrations of nitric acid washing (sample loading solution: 5−20 mL of 1−4 mol/L HNO_3; column washing: 100 mL of 1−4 mol/L HNO_3; Pu/Np elution: 50 mL of 0.1 mol/L $NH_2OH·HCl$−2 mol/L HCl; U elution: 50 mL of 0.025 mol/L HCl).

Automated SI Chromatographic Separation Scheme. The optimized SI extraction chromatographic procedure for simultaneous determination of uranium, neptunium, and plutonium consists of six steps as follows: (I) Rinse the holding coil with 25 mL of deionized water and wash sample inlet and eluates outlets tubing with 3 mol/L HNO_3 at a flow rate of 10 mL/min; (II) Precondition the connected TEVA−UTEVA columns with 20 mL of 3 mol/L HNO_3 at 3.0 mL/min; (III) Load the sample solution (ca. 15 mL) onto the connected TEVA−UTEVA columns at 1.2 mL/min; (IV) Rinse the connected TEVA−UTEVA columns with 40 mL of 3 mol/L HNO_3 at 1.2 mL/min; (V) Disconnect the TEVA and UTEVA columns and rinse the TEVA column with 20−40 mL of 1 mol/L HNO_3, followed by 20 mL of 6 mol/L HCl at 2.4 mL/min; (VI) Elute neptunium and plutonium from TEVA with 20 mL of 0.1 mol/L $NH_2OH·HCl$−2 mol/L HCl and elute uranium from UTEVA with 20 mL of 0.025 mol/L HCl at 1.2 mL/min. The detailed operations in the SI analyzer and corresponding positions of SV-1, SV-2, and INV at each step are compiled in the Supporting Information in Table S-2.

Each eluate was evaporated to dryness on a hot-plate to eliminate hydrochloric acid. To the neptunium and plutonium eluate, a few milliliters of concentrated HNO_3 were added to decompose $NH_2OH·HCl$. The residue was reconstituted in 5 mL of 0.5 mol/L HNO_3 for ICP-MS measurement and/or target preparation for AMS measurement.

Detection of Uranium, Neptunium, and Plutonium with ICP-MS and AMS. *ICP-MS Measurement.* The concentrations of ^{232}Th, ^{238}U, ^{239}Pu, ^{242}Pu, and ^{237}Np were determined by an X series^{II} ICP-MS (Thermo Fisher Scientific, Waltham, MA) equipped with an Xt-skimmer core and a concentric nebulizer under hot plasma conditions. Indium (as $InCl_3$) was used as an internal standard and added into each sample to a final concentration of 1.0 μg/L for measurement of efficiency calibration. The analytical sensitivities ranged between 1 and 5 × 10^6 cps per μg/L for ^{232}Th, ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, and ^{242}Pu. In the case of ^{238}U quantification, samples were diluted by 10−10 000 times (depending on the uranium concentration) to ensure the measured values were within the linear response range (0.01−100 ng/L). A 0.5 mol/L HNO_3 solution was used as a washing solution between consecutive assays. The typical operational conditions of the instrument have been given elsewhere.[32] It is important to note that the instrumental parameters were optimized each time when the instrument was initialized.

AMS Measurement. The AMS measurement of $^{236}U/^{238}U$ was carried out at the 3 MV tandem accelerator facility VERA (Vienna Environmental Research Accelerator) at the University of Vienna, Austria. To the reconstituted uranium eluate in 0.5 mol/L HNO_3, ca. 1 mg of Fe (as $FeCl_3$ solution) was added, and the sample was adjusted to pH > 9 with ammonia to coprecipitate uranium. The precipitate was dried in an oven under 100 °C and then was baked in a furnace for 2−3 h at 700 °C to convert the hydroxides to Fe_2O_3 and uranium oxides. The sample was then ground to fine powder, mixed with a similar volume of silver powder, and pressed into aluminum target holders suitable for the cesium sputter ion source of VERA. The detailed AMS instrumental condition has been reported elsewhere.[33]

Briefly, uranium was sputtered as UO^-. After acceleration and gas stripping, a charge state 5+ (5% yield for $^{238}U^{5+}$ using O_2 as stripper gas) or 3+ (25% yield for $^{238}U^{3+}$ using He as stripper gas) was chosen.[34] After separation by the "high-energy" mass spectrometer, the particle energy is measured in an ionization chamber, which allows the separation of background ions with lower charge states. The overall efficiency of the instrument in the configuration used for this measurement was about 5 × 10^{-4}, and the abundance sensitivity for ^{236}U is better than $^{236}U/^{238}U = 10^{-12}$.

RESULTS AND DISCUSSION

Preconcentration by Iron Hydroxide Coprecipitation. Iron hydroxide coprecipitation was used to preconcentrate uranium, neptunium, and plutonium. In this step, the coprecipitation efficiency of the analytes are the major concern. Therefore, the principal parameters influencing the coprecipitation efficiency were investigated, and results are discussed below.

Release of Uranium from Carbonate Complexes. In open seawater samples, uranium mainly exists as soluble carbonate complexes, and decomposition of the carbonate complex is the key issue for effective preconcentration of uranium using iron hydroxide coprecipitation. In acidic conditions, carbonate complexes are not stable and can be decomposed to form CO_2; therefore, uranium can be released as free ions into the seawater sample. Analytical results (Figure S-1a) show that chemical yields of uranium during the coprecipitation are all around 80−85%, which reveal that pH ca. 2 is low enough to decompose carbonate complexes and release uranium as free ions. A further increase of acidity (lower pH) does not increase the chemical yield of uranium. About a 10−15% loss of uranium during the coprecipitation step might be caused by insufficient addition of Fe (15 mg/L) carrier. Preliminary investigations indicate that slightly higher chemical yield of uranium can be obtained with the aid of N_2 bubbling to degas the dissolved carbon dioxide in seawater compared with magnetic stirring (results are not shown here). Nevertheless, in the case of processing larger volumes (e.g., >10 L), where mechanical stirring is not easily performed, N_2 bubbling is a relatively convenient approach and additionally ensures the complete release of uranium from carbonate complexes.

Effect of Iron Concentration on the Coprecipitation Efficiency. An increased amount of iron could improve the coprecipitation efficiency of radionuclides but at the cost of increased workload in the following sample treatment. Thus, the selection of appropriate Fe concentration is important to ensure good analytical performance of the entire protocol. The results (Figure S-1b) show that uranium, plutonium, and neptunium can be quantitatively coprecipitated when NaOH was used to adjust the pH to 10−11, regardless of the variation of Fe concentrations within 15−100 mg/L. However, when $NH_3 \cdot H_2O$ was used to adjust the sample pH in the second step of coprecipitation, the chemical yields of uranium, plutonium, and neptunium increase with the increasing amount of Fe added to the solution. This might be attributed to the fact that Ca and Mg can be coprecipitated when NaOH is used instead of $NH_3 \cdot H_2O$. To ensure sufficiently high chemical yield of uranium, plutonium, and neptunium in the preconcentration step, 50 mg/L Fe was selected for coprecipitation in this work. Chemical yields over 100% obtained in this investigation (especially for plutonium) might be an artifact of matrix effects in the ICP-MS measurement.

Separation Behavior of Radionuclides on UTEVA. *Removal of Thorium and Elution of Uranium.* It has been reported that thorium (as Th(IV)) has very low affinity to UTEVA in medium-concentrated HCl (e.g., 4−6 mol/L) solution, while U(VI), Np(IV), and Pu(IV) have high distribution factors onto UTEVA under this condition.[35] Our analytical results (Table S-1) demonstrate that >90% of thorium can be removed from the UTEVA column with 10−20 mL of 6 mol/L HCl washing. When the sample was loaded in 6 mol/L HCl and washed with 10 mL of 6 mol/L HCl, more than 99% of thorium can be removed (condition A, Table S-1).

Uranium adsorbed onto the UTEVA column can be effectively eluted with diluted HCl solution (e.g., 0.025 mol/L HCl), and almost quantitative uranium recoveries were obtained for 1 mL of UTEVA with solely 10 mL of 0.025 mol/L elution (see conditions A and B, Table S-1).

Separation of Uranium from Plutonium/Neptunium. Pu(IV) and Np(IV) have very similar sorption behavior as U(VI) onto UTEVA in both HNO_3 and HCl solutions.[35] However, Pu(III) (similar to Am(III)) has very low affinity onto UTEVA in HNO_3 or HCl media and can be easily separated from U(VI). It is clear from our data that when plutonium was reduced to Pu(III) and loaded onto UTEVA in 6 mol/L HCl, the separation between plutonium and uranium was well-performed and >90% of plutonium flowed through the column during the sample loading process (see Table S-1, condition A). However, only around 50% of neptunium (condition A, Table S-1) flowed through the UTEVA column during sample loading, and this might be a consequence of incomplete reduction of Np to Np(III).

Under condition B and C (see Table S-1), $NH_2OH \cdot HCl$ was employed to reduce both plutonium and neptunium to trivalent, in order to elute Pu and Np from UTEVA column in 6 mol/L HCl solution. However, ca. 50% of neptunium and >90% of plutonium were observed in the uranium fraction under condition B (Table S-1), indicating that the on-column reduction of neptunium and plutonium with $NH_2OH \cdot HCl$ could not be well-performed in a timely manner due to the slow kinetic processes of the redox reactions. When increasing the concentration of $NH_2OH \cdot HCl$, however, uranium was pre-eluted in the plutonium and neptunium fraction (condition C in Table S-1), which might be attributed to the reduction of U(VI) to U(IV) based on the redox potentials of UO_2^{2+}/U^{4+} and NH_2OH/N_2O:

$$N_2O + 5H_2O + 4e^- = 2NH_2OH + 4OH^- \qquad E°N_2O/NH_2OH = -1.05 \tag{1}$$

$$UO_2^{2+} + 4H^+ + 2e^- = U^{4+} + 2H_2O \qquad E°UO_2^{2+}/U^{4+} = 0.334 \tag{2}$$

It has been reported[35] that a possible way to separate Pu(IV)/Np(IV) from U(VI) via the UTEVA column is to employ an appropriate aqueous complexing agent (e.g., oxalic acid) to dramatically reduce the sorption of Pu(IV)/Np(IV) while keeping U(VI) absorbed. This approach was also used in the analytical procedures of Eichrom Technologies[36] to remove neptunium from UTEVA in HCl solution. Under condition D, 0.05 mol/L $H_2C_2O_4$−6 mol/L HCl was exploited to elute Pu(IV) and Np(IV) from UTEVA. Disappointedly, the separation of Pu(IV) from U(VI) is relatively slow and only 20% of plutonium is eluted in the 20 mL 0.05 mol/L $H_2C_2O_4$−6 mol/L HCl fraction. It is also surprising that ca. 90% of neptunium is bleeding from UTEVA during sample loading and 2 mol/L HNO_3 washing, which is probably attributed to the oxidation of Np(IV) to Np(V) by the elevated $[NO_3^-]$ due to the extra addition of $Al(NO_3)_3$, and thus inducing the equilibrium $2NO_3^- = 2NO_2^- + O_2$ to move rightward.

The overall results in Table S-1 allow us to conclude that the very similar absorption behavior of Np(IV) and Pu(IV) to U(VI) onto UTEVA in both HNO_3 and HCl media make the separation between plutonium/neptunium and uranium using a single UTEVA column somewhat troublesome. In all the cases studied in this work, neptunium and plutonium do not behave consistently, and thus a separate neptunium isotopic tracer has to be used for ^{237}Np determination, which makes the work more complicated. Moreover, a single UTEVA column separation could not provide sufficiently high removal of uranium from the plutonium/neptunium fraction; therefore, further purification is still needed in most cases to eliminate the interferences of ^{238}U in the ICP-MS measurement of ^{237}Np, ^{239}Pu, and ^{240}Pu through tailing of ^{238}U and polyatomic interferences of ^{238}U^{1}H and ^{238}U^{2}H.

For simultaneous separation of plutonium and neptunium using ^{242}Pu as a yield tracer meanwhile obtaining highly purified target analytes, a dual-column separation procedure in the conjunction of TEVA and UTEVA was finally selected; in this procedure, plutonium and neptunium were simultaneously separated via a TEVA column, and uranium was purified by UTEVA.

Performance of TEVA–UTEVA Tandem Columns for U, Pu, and Np Separation. A preliminary investigation using the TEVA–UTEVA tandem columns (Table 1, group 1) indicated that the chemical yield of ^{238}U, ^{237}Np, and ^{242}Pu were extremely low (<1%) when the sample was loaded in 6 mol/L HCl. This might be attributed to the competitive adsorption of iron (as $FeCl_4^-$) in 6 mol/L HCl medium onto TEVA and UTEVA. Therefore, HNO_3 was selected as sample loading media in the further investigation.

Figure 2 shows the sorption and elution behavior of plutonium and neptunium onto TEVA–UTEVA tandem columns under different nitric acid concentration for sample loading. Uranium starts to bleed when it is washed with 60 mL of 1 mol/L HNO_3, which causes a low chemical yield (ca. 65%) of uranium in the eluate. When it is rinsed with 2–4 mol/L HNO_3, the bleeding of uranium is not obvious within the 100 mL washes, and the highest uranium chemical yield (ca. 95%) is achieved using 3 mol/L HNO_3 for sample loading and column washing.

Plutonium was somehow lost when the column was rinsed with 1–2 mol/L HNO_3, especially under condition of 2 mol/L HNO_3. The relatively low chemical yield of plutonium might be a joint effect of the lower distribution factor of Pu(IV) on the UTEVA column in 2 mol/L HNO_3 and the interference of matrix elements. Similar to uranium, the highest plutonium chemical yield (ca. 80%) was also achieved when employing 3 mol/L HNO_3 as a sample loading and column washing solution. The slightly decreased chemical yields of plutonium (ca. 75%) and uranium (ca. 90%) in the case of using 4 mol/L HNO_3 might be related to the prompted matrix interferences in this smaller volume (5 mL) sample. On the basis of this observation, 3 mol/L HNO_3 was finally selected as the optimal sample loading solution and was used throughout the work.

Pu and Np Behavior Coherence and U Decontamination. In the beginning of the method development, a two-step coprecipitation was used for the sample pretreatment, and the sample solution was directly loaded onto the connected TEVA–UTEVA columns after valence adjustment. Although satisfactory chemical yields (80–90%) of uranium were achieved, very low chemical yields of plutonium and neptunium were encountered (see group 2, Table 1), and inconsistent separation behavior between plutonium and neptunium made the utilization of ^{242}Pu as a trace for neptunium infeasible. The adsorptions of organic substances/colloids contained in the sample solution for TEVA chromatographic separation might be responsible for the low retention of plutonium and neptunium onto the columns, which induce inferior anion exchange capacity and/or insufficient amount of functional groups for plutonium and neptunium uptake by TEVA. Meanwhile, the decontamination factors for uranium (DU) in this case were also low (1×10^3), which could not completely eliminate the interferences of ^{238}U to the measurement of ^{237}Np, ^{239}Pu, and ^{240}Pu by ICP-MS. Besides, the two-step coprecipitation operation was rather time-consuming, taking ca. 1 day for a single sample.

To overcome this problem, a one-step coprecipitation procedure in combination with acid digestion to decompose organic substances contained in the sample was proposed, and the analytical performance was investigated. It was noticed that addition of salts (e.g., NaCl or KCl) after the formation of iron hydroxide precipitation is very effective to prompt the settlement of the precipitate. This might be related to the increase in the ionic strength, thus prompting the aggregation of the small iron hydroxide particles to form large flocs and quicker sedimentation. As shown in groups 3 and 4 in Table 1, the chemical yields of plutonium and neptunium and the coherence of their separation behavior are significantly improved. Meanwhile, the DU is also 10–50-fold increased, and with rinsing the TEVA using 1 mol/L of HNO_3, instead of 3 mol/L of HNO_3, better DU (5×10^4) is achieved (see group 4, Table 1). On the basis of overall investigation, an optimized analytical procedure for simultaneous determination of uranium, neptunium, and plutonium in 10 L of seawater was established (Figure 3).

Application of the Developed Method for Seawater Analysis. Seawater samples collected from the North Atlantic, Kattegat, and Roskilde Fjord were processed using the established procedure. The analytical results (Table 2) show that chemical yields of uranium and plutonium/neptunium range from 65 to 100% with average values of 91.1% (^{238}U) and 72.3% (^{242}Pu). For the seawater samples spiked with known amounts of ^{239}Pu and ^{237}Np, the measured ^{239}Pu and ^{237}Np activities agree well with the expected values with a mean relative deviation ($\bar{D}_i$) of −1.2% for ^{239}Pu and −3.7% for ^{237}Np, demonstrating the satisfactory trueness of the proposed analytical method. Here, the relative deviation (D_i) for each radionuclide was calculated according to the equation $D_i = ((A_i - A_{ei})/A_{ei}) \times 100\%$, where A_{ei} and A_i are the expected and measured values for individual samples, respectively.

With respect to the ^{236}U concentrations in different samples, it is noted that the levels of the ^{236}U/^{238}U atomic ratio are higher in Kattegat seawater ($(7-15) \times 10^{-8}$) than those from North Atlantic ($(2-9) \times 10^{-8}$) and Roskilde Fjord ($(1-2) \times 10^{-8}$), which might be explained by the fact that the distances from the ^{236}U discharge points of European reprocessing plants in La Hague (France) and Sellafield (UK) to Kattegat are shorter compared with the distances to the North Atlantic and the Roskilde Fjord. A higher dilution factor of the distant site in the North Atlantic and the fresh water dilution of ^{236}U that entered the Roskilde Fjord reduced the concentration of ^{236}U in these water samples. This work is mainly focused on method development, and therefore, analytical results of ^{236}U in additional water samples and detailed discussions about the ^{236}U distribution characters will be published elsewhere.

The overall analytical procedure is rather rapid providing an analysis turn-around time of ca. 8 h. With the merit of automation, the lab intensity was reduced to a significant degree; batch-wise (4–8 samples or replicates) sample

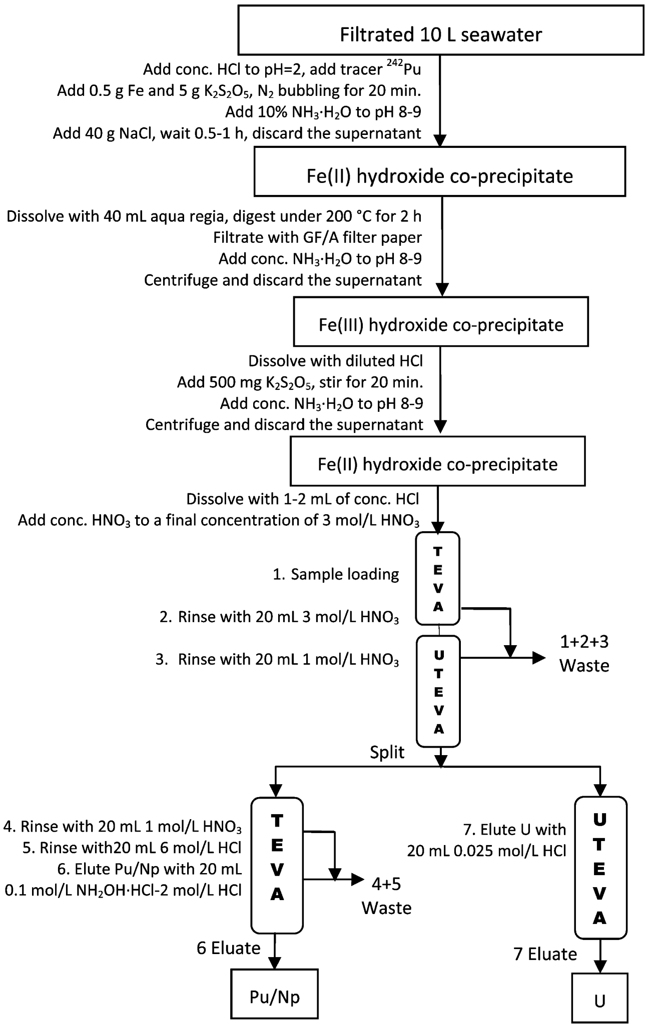

Figure 3. Schematic flowchart of analytical procedure for simultaneous determination of uranium, neptunium, and plutonium in 10 L of seawater.

pretreatment can be performed concurrently with the automated column separation. Therefore, the sample throughput was improved notably compared with the conventional manual method used in our lab (consuming >1 days/sample), and we were able to analyze four samples in a continuous 24 h run period.

■ CONCLUSIONS AND PERSPECTIVES

A novel dual-column tandem SI analytical method was developed for simultaneous determination of uranium, plutonium, and neptunium in seawater samples. The developed flow setup is miniaturized and capable of assembling dual chromatographic columns and switching their connections at will. One-step coprecipitation is efficient to scavenge target radionuclides, and acid digestion is important to ensure coherent analytical behavior of plutonium and neptunium and satisfactory chemical yields. Under the optimal experimental condition, ^{242}Pu performed well as a nonisotopic tracer for ^{237}Np, thus the difficulties of obtaining a neptunium isotopic tracer were avoided. The proposed analytical procedure is rather simple and straightforward, providing satisfactory chemical yields (70−100%) and the capability of multi-radionuclide determination in a timely manner (8 h/sample).

In this work, we encountered difficulties in measuring the actual concentrations of ^{239}Pu, ^{240}Pu, and ^{237}Np with ICP-MS detection due to their extremely low levels in open seawater. To overcome these difficulties, future work would be dedicated to improve the separation capacity of the analytical method to larger volume samples, for example ≥200 L of seawater, or to employ AMS for the quantification of plutonium isotopes and ^{237}Np.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

Table 2. Analytical Results of ^{236}U, ^{237}Np, ^{239}Pu, and ^{240}Pu in Different Seawater Samples Applying the Proposed Method (10 L)

	chemical yield[a] (%)					measured value (mBq/L)		expected or spiked value (mBq/L)	
sample ID	^{238}U	^{242}Pu	$^{236}U/^{238}U^{c}$ ($\times 10^{-8}$)	^{238}U (μg/L)	$^{236}U^{c}$ (atom/L)	^{237}Np	^{239}Pu	^{237}Np	^{239}Pu
North Atlantic-1	100.5	66.8	8.88 ± 1.33	2.76 ± 0.41	$(6.21 \pm 0.93) \times 10^{8}$	<0.001	<0.005		
North Atlantic-2	82.6	69.9	2.03 ± 0.30	2.17 ± 0.33	$(1.11 \pm 0.17) \times 10^{8}$	0.18 ± 0.03	1.02 ± 0.10	0.20 ± 0.01	1.12 ± 0.06
Kattegat-1	112.1	78.4	14.5 ± 2.18	2.26 ± 0.34	$(8.28 \pm 1.24) \times 10^{8}$	<0.001	0.005 ± 0.001		
Kattegat-2	83.0	70.3	7.01 ± 1.05	2.26 ± 0.34	$(4.01 \pm 0.60) \times 10^{8}$	0.12 ± 0.02	1.24 ± 0.12	0.13 ± 0.01	1.24 ± 0.06
Roskilde Fjord-1	95.2	77.8	1.40 ± 0.21	1.65 ± 0.28	$(6.88 \pm 1.03) \times 10^{7}$	<0.001	0.03 ± 0.01		
Roskilde Fjord-2	72.7	70.7	1.65 ± 0.25	1.65 ± 0.28	$(5.85 \pm 0.88) \times 10^{7}$	0.16 ± 0.02	1.18 ± 0.12	0.15 ± 0.01	1.12 ± 0.06
procedure blank		75.5	22.11 ± 1.82	0.004 ± 0.003[b]	$(2.24 \pm 1.68) \times 10^{6}$	<0.001	<0.005		
average	91.0	72.3				$\bar{\bar{D}}_{\mathrm{Np}} = -3.7\%$	$\bar{D}_{\mathrm{Pu}} = -1.2\%$		

[a] The uncertainties for all chemical yields values are less than 10%. [b] The value is calculated assuming the sample volume of 10 L. [c] Procedure blank has already been subtracted for the values of all the seawater samples reported here.

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