

ADAPTATION OF AN ANALYTICAL PROCEDURE FOR CONCURRENT DETERMINATION OF Np AND Pu IN CLAY SAMPLES



TOBIAS RENZ^{1,2*}, MARKUS PLASCHKE¹, FRANCESCA QUINTO¹, ANDREAS BAUER¹,
MARKUS LAGOS³, HEINRICH TAUBALD², AND HORST GECKEIS¹

¹Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

²Department of Geoscience, University of Tuebingen, Wilhelmstraße 56, 72074 Tübingen, Germany

³Steinmann Institute, University of Bonn, Poppelsdorfer Schloss, 53115 Bonn, Germany

Abstract—Np and Pu are two important actinides of concern for the safe long-term disposal of nuclear waste. Both actinides are, in addition, constituents of global nuclear fallout. Investigation of their environmental behavior requires ultra-sensitive analytical methods, but current methods for a concurrent determination in clay minerals are lacking. In the present study, a Pu isotope was investigated for use as a non-isotopic yield tracer for Np in extraction, purification, and mass spectrometric determination of Np and Pu isotopes in clay materials. Inductively coupled plasma mass spectrometry was used in this developmental study, but the method is intended for future ultra-trace analysis of global-fallout Np and Pu in clay-rich soil materials by the more sensitive accelerator mass spectrometry. Another field of application may be the investigation of diffusion patterns of actinides in compacted clay liners and potential host rocks for radioactive waste disposal. The analytical procedure includes the following steps: (1) extraction of Np and Pu from clay samples; (2) adjustment of Np and Pu to Np(IV) and Pu(III); (3) pre-concentration of Np and Pu by co-precipitation with iron hydroxide; (4) adjustment of Pu to Pu(IV); (5) extraction chromatographic separation of Pu and Np from iron and matrix elements; and (6) determination of Np and Pu by mass spectrometry. The analytical procedure was applied successfully to spiked montmorillonite and illite test portions of up to 1 g. High chemical yields near 90% were obtained for both Np and Pu. The suitability of Pu as a non-isotopic tracer for Np was indicated by Np/Pu chemical yield ratios close to unity. Accurate pH adjustment during the reductive co-precipitation and short processing times are vital to obtain high chemical yields and Np/Pu yield ratios close to unity.

Keywords—Clay · Extraction Chromatography · ICP-MS · Neptunium · Non-isotopic Tracer · Plutonium

INTRODUCTION

Np and Pu in the environment are mostly anthropogenic, coming from sources such as nuclear weapon testing, discharges from nuclear facilities, and nuclear accidents. Only minute amounts are of natural origin, generated by spontaneous fission in uranium ores. Np and Pu isotopes are also constituents of spent nuclear fuel, and those with long half-lives are main contributors to the long-term radiotoxicity of high-level radioactive waste (Kim, 2006). Clay or clay-rich materials are considered in many countries as potential host rocks for nuclear waste repositories, and they also serve as major constituents of technical barriers in repository systems. Knowledge of the migration behavior of Np and Pu in these materials is, therefore, crucial for the safe, long-term disposal of nuclear waste. Depending on the redox potential, Np and Pu form species that are mobile under repository conditions or in the natural environment. Reactions, notably redox reactions, of actinides in trace concentrations in natural environments are often so slow that their geochemical behavior cannot be assessed fully in laboratory and field studies extending over relatively short time periods. Actinides released in nearly 500 atmospheric nuclear weapon tests between 1945 and 1980 were deposited as radioactive fallout. Starting in 1951,

thermonuclear devices were detonated in the atmosphere and global fallout, namely the deposition of radioactive debris over the Earth's entire surface, occurred (Denecke et al. 2018). Concentration gradients of fallout actinides along drill cores can be used as measures of their migration behavior under natural conditions over the many decades since their deposition (Quinto et al. 2013a, 2013b). Such studies, as well as investigation of the diffusion behavior of actinides in compacted clay liners and in clay formations, could help to understand migration and retention of actinides in these materials. So far, no study has addressed the determination of Np at ultra-trace concentrations in clay or mudrock in the course of radionuclide migration experiments. Moreover, no investigation of migration patterns of global-fallout Np in environmental clay-rich materials has been carried out.

The Np and Pu contents of soils or rocks containing global nuclear fallout are extremely small (attograms to femtograms per gram). Similar contents are expected in natural rock or clay liners to which Np and Pu were added for diffusion experiments carried out in the context of nuclear waste repository research. Measuring these low contents requires a procedure

* E-mail address of corresponding author: tobias.renz@web.de
DOI: 10.1007/s42860-019-00018-z

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42860-019-00018-z>) contains supplementary material, which is available to authorized users.

for quantitative separation of Np and Pu from the sample matrix and a highly sensitive determination method, such as accelerator mass spectrometry (AMS).

Determination of ^{237}Np with mass spectrometric methods ideally requires an isotopic yield tracer that has the same chemical behavior as the analyte without being present in the sample. In the case of Np, however, no such ideal tracer is available. The short-lived ^{239}Np ($t_{1/2} = 2.35$ d) would allow only a short time for sample preparation and analysis, which is not feasible for the extensive sample preparation needed for ultra-trace mass spectrometry. Furthermore, the introduction of ^{239}Pu produced by the decay of ^{239}Np would impede determination of ^{239}Pu inherent to the sample. ^{235}Np ($t_{1/2} = 396$ d) is another possible tracer, but typically contains trace amounts of ^{237}Np which make it unsuitable as a yield tracer. Very low count rates are expected when Np in environmental samples is determined by ultra-trace analysis with AMS; hence even a tiny amount of ^{237}Np in the yield tracer could affect the accuracy of such a measurement. Of the long-lived ^{236}Np , only in-house working standards that contain ~27% of ^{237}Np are presently available, but the production of more suitable ^{236}Np reference material is being investigated at the Idaho and Los Alamos National Laboratories (USA) and at the National Physical Laboratory (UK) (Jerome et al. 2017). A long-lived isotope of a different actinide, similar in chemical behavior to the analyte and not present in the sample, might serve as a non-isotopic yield tracer, however.

Chen et al. (2002) were the first to use ^{242}Pu as a non-isotopic yield tracer to overcome the lack of a suitable isotopic tracer for Np in concurrent determination of ^{237}Np and $^{239,240}\text{Pu}$ by inductively coupled plasma mass spectrometry (ICP-MS) and α -spectrometry. They developed a procedure in which Np and Pu were pre-concentrated by reduction and co-precipitation with $\text{Fe}(\text{OH})_2$. They then stabilized Np and Pu as tetravalent nitrate-complexes and together separated them from iron and other elements by ion exchange chromatography, taking advantage of the very similar chemical behavior of tetravalent Np and Pu. Kim et al. (2004) developed a related procedure based on extraction chromatographic separation with TEVA[®] resin (Eichrom Technologies, Lisle, Illinois, USA) instead of ion exchange chromatography. These procedures were further developed, adapted, and optimized to particular applications and various sample matrices (Qiao et al. 2010, 2011a, 2011b, 2013a, 2013b, 2013c). Types of samples included sediments, groundwater, seawater, and biological samples such as urine and seaweed, with sample sizes up to several grams or liters. More recently, Matteson et al. (2015) developed a method for concurrent determination of ^{237}Np and Pu isotopes with ICP-MS using the ion exchange resin AG[®] MP-1 M (Bio-Rad, Hercules, California, USA). The first oxidation state adjustment was performed with iron(II) chloride and ascorbic acid to reduce Pu to Pu(III) and Np to Np(IV); later, NaNO_2 was added to form Pu(IV) and to stabilize Np(IV).

The studies mentioned above proved that Pu can be used as a non-isotopic yield tracer for determination of Np. ^{242}Pu has

been used by Dai et al. (2015) and Qiao et al. (2013b) for determination of Np by AMS, demonstrating that it has potential as a non-isotopic yield tracer for ultra-trace analysis of Np. In the work of Qiao et al. (2013b), however, determination of low-femtogram amounts of ^{237}Np with ^{242}Pu as a yield tracer was hampered by contamination, probably from earlier work with ^{237}Np .

The method proposed here has been developed, in particular, with future ultra-trace analysis of Np and Pu in clay or clay-rich material by means of AMS in mind. It was further designed for high chemical yields of Np and Pu in all separation steps so that the overall yields of the two elements will be virtually the same.

EXPERIMENTAL SECTION

The analytical procedure used in the present study consisted of the following steps: (1) extraction of Np and Pu from spiked clay test portions with *aqua regia*; (2) oxidation-state adjustment of Np and Pu; (3) pre-concentration of Np and Pu by iron hydroxide co-precipitation; (4) oxidation state adjustment of Pu prior to column separation; (5) chromatographic co-extraction of Pu and Np; and (6) determination of Np and Pu by quadrupole ICP-MS (Fig. 1).

Starting material and reagents

Two different clays were used in the study: illite from an Oligocene lacustrine sediment sequence in Le Puy-en-Velay region of France (Illit du Puy, IdP), and montmorillonite from a Cretaceous bentonite deposit in Wyoming, USA, obtained as the SWy-2 source clay material (Source Clays Repository of The Clay Minerals Society, www.clays.org). Portions of SWy-2 and IdP were purified and converted into their homoionic sodium forms, to test the presented procedure with well characterized material, such as that used in laboratory diffusion experiments. The <63 μm and <1 μm fractions of the clays were isolated by sieving and sedimentation techniques. Portions of these fractions were treated with a 1 mol/L NaCl solution (p.a. grade, Merck, Darmstadt, Germany) at pH 3.5 and washed several times with a 1 mol/L NaCl solution at pH~8 to remove soluble constituents and to transform the clays to their homoionic sodium form. The excess NaCl was removed by dialysis against deionized water. The conditioned clay materials were freeze-dried and stored. The starting materials for the experiments were conditioned fractions of SWy-2 and IdP with particle sizes of <1 μm and <63 μm , respectively.

A Np-Pu spike solution was prepared from in-house ^{237}Np and ^{242}Pu solutions (for isotopic composition of the solutions the reader is referred to Table S1 in the Supplemental Materials section) diluted with 2% HNO_3 (Ultrapure[®] grade, Merck, Darmstadt, Germany) for use in the experiments. The ^{237}Np and ^{242}Pu concentrations in the resulting spike solution were determined by quadrupole ICP-MS of two tenfold diluted aliquots of the spike solution (see measurement protocol Table S2 in the Supplemental Materials section). For each aliquot, the concentrations for the masses of ^{237}U , ^{238}U , and

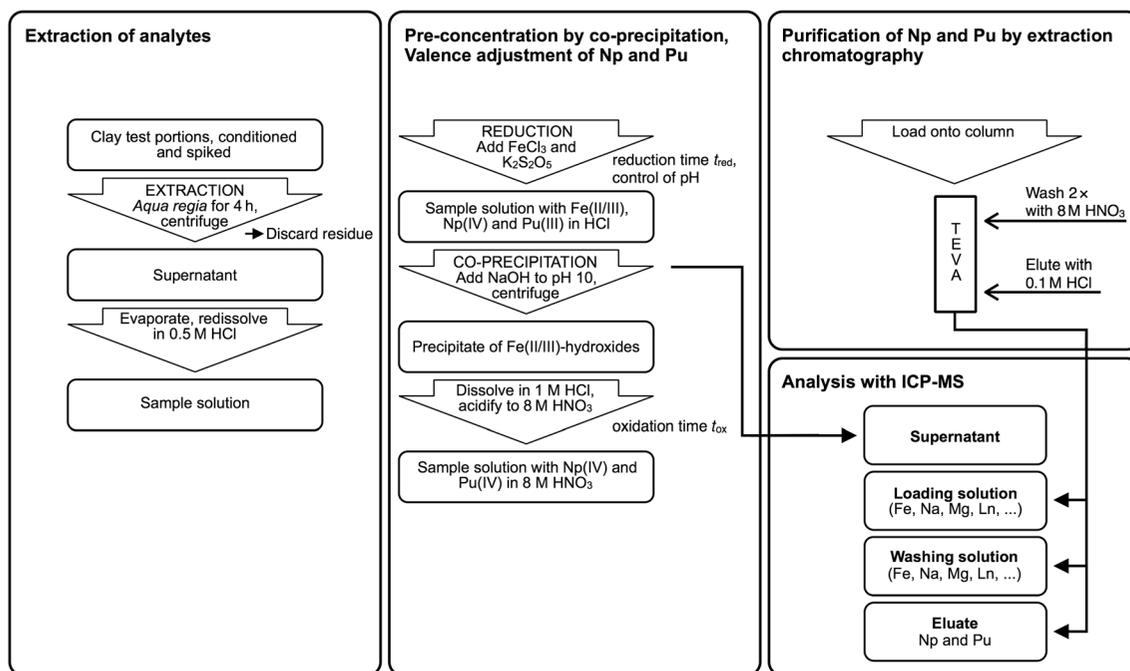


Fig. 1 Analytical procedure for the concurrent determination of Np and Pu in clay samples. Ln symbolizes the lanthanides

^{242}U were determined in five measurement cycles. The average values were calculated from these measurements, and the standard deviations represent the short-term precision of the ICP-MS. The final ^{237}Np and ^{242}Pu concentrations in the spike solution, calculated as the weighted means for the two aliquots with the corresponding uncertainty of each weighted mean, were $10.95 \pm 0.34 \mu\text{g/L}$ ^{237}Np and $8.71 \pm 0.29 \mu\text{g/L}$ ^{242}Pu (equations S1–S3 in the [Supplemental Materials](#) section). HCl, HNO_3 , and HF (Suprapur[®] grade, Merck, Darmstadt, Germany), used in various concentrations throughout the sample treatment and analytical procedure, were diluted with deionized water (18 M Ω cm) from a Milli-Q Element System (Millipore, Billerica, Massachusetts, USA). For the reductive co-precipitation, potassium metabisulfite ($\text{K}_2\text{S}_2\text{O}_5$; p.a. grade, Merck, Darmstadt, Germany), aqueous solutions of NaOH (1 mol/L and 6 mol/L; p.a. grade, Merck, Darmstadt, Germany), and a 10 g/L aqueous solution of iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$; ACS reagent grade, Sigma-Aldrich, St. Louis, Missouri, USA) were used. The extraction chromatography was done with TEVA-Spec resin (TrisKem International, Bruz, France) with a particle size of 50–100 μm .

Test portion preparation and extraction of analytes

Six test portions of the conditioned clays were suspended in Milli-Q water in glass beakers: two 100 mg portions of SWy-2 (S1, S2), two 100 mg portions of IdP (S3, S4), and two 1 g portions of SWy-2 (S5, S6). Each was spiked with 100 μL of the Np-Pu spike solution and dried. The amount of spike was determined gravimetrically. The spiked test portions were each treated with 12 mL of boiling *aqua regia* on a hotplate at 120°C for 4 h to release Np and Pu into the solution. To prevent evaporation of the solution, the beaker was covered with a

watch glass. Each test portion plus another 4 mL *aqua regia* used to rinse the beaker was transferred to a 50 mL centrifugation vial. After centrifugation at $\sim 2218 \times g$ for 10 min (Biofuge Primo, Heraeus Instruments, Hanau, Germany), the supernatant was decanted and the clay residue was washed with 3–5 mL *aqua regia* and centrifuged. Both the washing and centrifuging of the clay residue was then repeated once. The supernatants were combined and evaporated to dryness, and the residue was re-dissolved in 10 mL of 0.5 mol/L HCl. This solution, plus another 10 mL of 0.5 mol/L HCl employed to rinse the beaker, was then transferred to a 50 mL centrifuge tube.

Oxidation-state adjustments and pre-concentration of Np and Pu

Principles Because TEVA[®] resin is selective for tetravalent actinides, it is mandatory that Np and Pu exist as Np(IV) and Pu(IV) before the extraction chromatography. According to Chen et al. (2001, 2002) Np and Pu are reduced by $\text{HSO}_3^- - \text{Fe}^{3+}$ in weak hydrochloric acid solution to Np(IV) and Pu(III). In this case, the redox-couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E_0 = +0.771 \text{ V}$) acts as a redox buffer and prevents Np(IV) from being oxidized to Np(V) ($E_0 = +0.789 \text{ V}$) or reduced to Np(III) ($E_0 = +0.147 \text{ V}$). While the solution is later basified to pH 10 with NaOH, Np and Pu are scavenged by the forming iron(II/III) (oxyhydr)oxides. When concentrated HNO_3 is added after the co-precipitation, Pu(III) is oxidized to Pu(IV) by the redox couple $\text{HNO}_3/\text{HNO}_2$ while Np remains as Np(IV). Np(IV) and Pu(IV) coexist in HNO_3 solution as tetravalent nitrate-complexes $\text{Np}(\text{NO}_3)_6^{2-}$ and $\text{Pu}(\text{NO}_3)_6^{2-}$.

Procedure For the reductive co-precipitation, 0.5 mL of an iron chloride solution (corresponding to ~ 1 mg Fe^{3+}) and 25 mg of $\text{K}_2\text{S}_2\text{O}_5$ (the $\text{S}_2\text{O}_5^{2-}$ hydrolyzes into HSO_3^-) were added to each test portion to reduce Np and Pu to Np(IV) and Pu(III), respectively. After 20 min (reducing time, t_{red}) the solution was basified to pH 10 by adding first 6 mol/L of NaOH and then 1 mol/L of NaOH dropwise. The pH was monitored with a semi-micro Ross electrode (81–03, Orion Co., Thermo Fisher Scientific, Waltham, Massachusetts, USA) in combination with a digital pH meter (720 A, Orion Co., Thermo Fisher Scientific, Waltham, Massachusetts, USA). Six commercial buffer solutions (Merck, Darmstadt, Germany) were used for pH calibration. Np and Pu were co-precipitated with the iron(II/III) (oxyhydr)oxides which were forming. In this reductive co-precipitation, the pH must not exceed 10.1 to avoid oxidation of Np(IV) to Np(V) at higher pH (see results below). After separation by centrifugation, each precipitate was dissolved in 0.5 mL of 1 mol/L HCl. Finally, 10 mL of 8 mol/L HNO_3 was added to stabilize Np(IV) and to oxidize Pu(III) to Pu(IV). In this way, both Np and Pu were converted to nitrate-complexes in the tetravalent state.

Extraction chromatography

Guidance from preliminary experiments Preliminary experiments indicated a correlation between Np found in the loading and washing fractions and the time between co-precipitation and chromatographic separation. The longer this oxidation time (t_{ox}), the more Np was oxidized to Np(V) by both nitric acid and dissolved oxygen in the solution and was, therefore, not retained on the resin. This effect was not observed for Pu, which resulted in Np/Pu yield ratios considerably smaller than unity. The oxidation time for the present sample series was, therefore, kept to ~ 30 min, needed after co-precipitation to prepare (by centrifugation, dissolution of the precipitate, and oxidation of Pu) for the extraction chromatography. Significantly different yields for Np and Pu had also been observed when concentrated HNO_3 was added first and subsequently diluted to 8 mol/L (Qiao et al. 2010). Conversely, Np chemical yields were greatly increased when 8 mol/L HNO_3 , a milder oxidation agent, was applied directly (Chen et al. 2002).

Pu yields, on the other hand, were affected by the way the iron hydroxide precipitates were dissolved. Precipitates dissolved in pure 8 mol/L HNO_3 led to brownish discoloration of the upper frit and the resin upon loading of the columns. Even though the discoloration disappeared when elution with weak HCl began, the Pu yields were 40% lower than in the present study. Apparently, the precipitate was not fully dissolved in the preliminary experiments and remaining colloids or fine solids were retained by the resin. The Pu yields were increased to $>80\%$ by dissolving the iron hydroxide precipitates in 0.5 mL of 1 mol/L HCl prior to the oxidation with 8 mol/L HNO_3 , ensuring complete and fast dissolution of the precipitate. Furthermore, this approach reduced t_{ox} and thereby prevented Np(IV) from being oxidized. The extraction chromatographic separation was not affected by the presence of chloride in the loading solution at the given concentration.

Procedure TEVA[®] resin was suspended in 2 mol/L HNO_3 and soaked for at least one day. A volume of 1 mL resin was loaded into a column (volume: 2 mL, diameter: 7 mm) equipped with a 10 mL reservoir. An additional frit, placed above the resin, prevented disturbance during loading and completed the packing of the column. The resin was conditioned with two 5 mL portions of 8 mol/L HNO_3 prior to loading. The procedure to separate Np and Pu by extraction chromatography on TEVA[®] resin employed four steps: (1) loading the test portion onto the conditioned TEVA[®] column; (2) washing the column twice with 5 mL 8 mol/L HNO_3 to strip iron and other elements; (3) eluting Np and Pu with a total of 20 mL of 0.1 mol/L HCl in portions of 5, 5, and 10 mL; and (4) eluting again with 4 mL of a solution containing HF and HCl (0.1 mol/L each) to prove that the elution was complete after step 3. Step 4, used for validation in the present study, will not be necessary in future application of the procedure for analysis of ultra-trace Np and Pu with AMS.

Strong complexing of Np and Pu by agents such as fluorides or organic compounds has the potential to enhance their elution. Such agents can compete for actinides with $\text{Fe}(\text{OH})_3$ during co-precipitation of Np and Pu in target preparation for AMS and will, therefore, not be used in the procedure for analysis of ultra-trace Np and Pu.

Determination of Np and Pu by ICP-MS

All fractions collected from a column (loading and washing solutions, eluate, second eluate) were evaporated to dryness, as were the supernatants from the reductive co-precipitations. To remove all chloride, and in the case of the second eluate, fluoride, the residues were dissolved in concentrated HNO_3 and evaporated to dryness three times. The residues from the supernatant were then re-dissolved in 5 mL, and each residue from the column separation in 6 mL, of 2% ultrapure HNO_3 . For ICP-MS measurement a defined volume was taken and ^{103}Rh (Alfa Aesar, Ward Hill, Massachusetts, USA) was added to a final concentration of 0.01 $\mu\text{g}/\text{mL}$ as an internal standard. The concentrations of ^{237}Np and ^{242}Pu were determined with an Elan 6100 quadrupole inductively coupled plasma mass spectrometer (Perkin Elmer, Waltham, Massachusetts, USA) equipped with an auto sampler and a Rytan[®] cross-flow nebulizer. Standard solutions diluted from NIST SRM 4321c (0.1–10 $\mu\text{g}/\text{L}$ U) were used for multipoint calibration. The certified reference materials SPS-SW1 (Spectrapure, Oslo, Norway) and SLRS5 (National Research Council, Ottawa, Canada) were used to verify the calibration. Diluted (2%) ultrapure HNO_3 was used as the blank solution and measured repeatedly in the series (see Table S2 in the Supplemental Materials section). Average values and standard deviations were calculated from five measurement cycles for each test solution. The detection limits for the masses ^{237}U and ^{242}U were each calculated as three times the standard deviation of the blank solution readings multiplied by a calibration factor. Both detection limits were ~ 1 ng/L. The uncertainties of the yields and yield ratios are the propagated errors from the spike-solution and test-solution measurements (equations S4 and S5 in the Supplemental Materials section).

Table 1 Yields of ^{237}Np and ^{242}Pu and yield ratios, $y_{\text{Np}}/y_{\text{Pu}}$, for the test portions S1–S6

Test portion		Initial mass (ng)			Recovered mass (ng)		Yield (%)		Yield ratio
Identifier	Clay	Mass (g)	^{237}Np	^{242}Pu	^{237}Np	^{242}Pu	^{237}Np	^{242}Pu	$y_{\text{Np}}/y_{\text{Pu}}$
S 1	SWy-2	0.102	1.08 ± 0.03	0.859 ± 0.029	0.83 ± 0.05	0.80 ± 0.04	76.8 ± 4.9	92.8 ± 5.6	0.83 ± 0.08
S 2	SWy-2	0.103	1.08 ± 0.03	0.862 ± 0.029	0.95 ± 0.05	0.78 ± 0.05	88.0 ± 5.1	90.5 ± 6.2	0.97 ± 0.09
S 3	IdP	0.102	1.08 ± 0.03	0.854 ± 0.029	0.91 ± 0.05	0.79 ± 0.04	85.1 ± 4.7	92.1 ± 5.3	0.92 ± 0.08
S 4	IdP	0.105	1.09 ± 0.03	0.864 ± 0.029	0.91 ± 0.04	0.69 ± 0.03	83.4 ± 4.3	80.1 ± 4.2	1.04 ± 0.08
S 5	SWy-2	1.003	1.08 ± 0.03	0.861 ± 0.029	0.96 ± 0.05	0.76 ± 0.04	88.8 ± 4.8	88.2 ± 4.7	1.01 ± 0.08
S 6	SWy-2	1.003	1.08 ± 0.03	0.857 ± 0.029	0.98 ± 0.04	0.79 ± 0.05	91.0 ± 4.1	91.6 ± 6.2	0.99 ± 0.09

RESULTS AND DISCUSSION

The aim of the present study was to establish a separation scheme optimized in terms of chemical yields of ^{237}Np (y_{Np}) and ^{242}Pu (y_{Pu}), defined as $y_i = m_{i,\text{eluate}}/m_{i,\text{added}}$, where m_i is the mass of actinide i and the yield ratio is $y_{\text{Np}}/y_{\text{Pu}}$. A yield ratio close to unity indicates that Np and Pu were concentrated and purified with almost equal efficiency throughout the procedure, which is a prerequisite for using a Pu isotope as non-isotopic tracer for the determination of ^{237}Np . The separation scheme described previously was applied to six spiked clay test portions (S1–S6). High chemical yields of $>80\%$ were obtained for both Np and Pu (Table 1), except for Np in S1, which was an outlier (see below). Chemical yields for Np and Pu in S2–S6 ranged from $83.4\% \pm 4.3\%$ to $91.0\% \pm 4.1\%$ and $80.1\% \pm 4.2\%$ to $91.6\% \pm 6.2\%$, respectively. Excluding S1, the average yields for Np and Pu were near 90%. Even more important was that the yield ratios of S2–S6 were consistent with one another and their average was close to unity (Table 1).

To quantify actinide losses throughout the various steps of the procedure, the supernatants of the reductive co-

precipitations, the loading and washing solutions of the column separations, and the solutions from an additional elution (step 4 in Extraction chromatography of the Experimental section) were analyzed by ICP-MS. Np and Pu concentrations in the supernatants of the reductive co-precipitations were below the ICP-MS detection limits, corresponding to maximum Np and Pu losses of 0.5% and 0.6%, respectively (Table S2 in the Supplemental Materials section). The scavenging of Np and Pu by the iron(II/III) hydroxides is, therefore, quantitative.

Some Np loss, $12.2\% \pm 1.6\%$ and $0.6\% \pm 0.2\%$, occurred during loading of S1 and S2 (Fig. 2), respectively, and an additional $1.7\% \pm 0.3\%$ of the Np was lost during washing of S1, although t_{ox} was kept to ~ 30 min and 8 mol/L nitric acid was used for acidification. During co-precipitation the pH was, for a short time, adjusted to values of >11.7 and >10.8 for S1 and S2, respectively, and had to be reduced by adding 0.1 mol/L HCl dropwise. This pH elevation may have caused some Np to be re-oxidized and not retained on the TEVA[®] resin. Whether or not the Np was oxidized immediately or later during the procedure, however, is not clear.

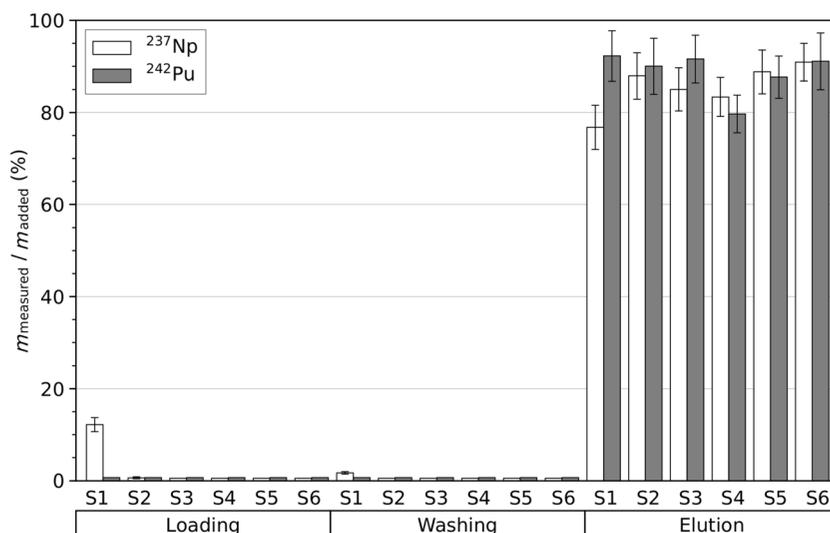


Fig. 2 ^{237}Np and ^{242}Pu in the various fractions from the extraction chromatographic separation with TEVA[®] resin, as fractions of the amounts added to the clay. Error bars indicate the propagated error from the determination of these nuclides in the spike solution and in the various fractions

The Np and Pu concentrations in the loading and in the washing solutions of S3–S6 were below the detection limit. The combined losses during the loading and washing steps of S3–S6 could be no more than 1.2% and 1.4% of the overall Np and Pu, respectively (Table S3 in the Supplemental Materials section). For S3–S6 the pH during co-precipitation was kept between 9.9 and 10.1. The retention of tetravalent Np and Pu complexes on TEVA[®] is, therefore, considered to be quantitative.

For the simultaneous elution of Np and Pu, some studies (Qiao et al. 2010, 2013b) relied on weak hydrochloric acid in combination with hydroxylamine hydrochloride (NH₂OH·HCl) as a complexing agent. As mentioned earlier, strong complexing agents may be troublesome for further AMS target preparation. These should be avoided, or if employed they should then be completely oxidized or vaporized, which would make the further sample preparation more demanding. Np and Pu yields using only weak HCl (0.1 mol/L) as eluent ranged from 83% to 91% and 80% to 93%, respectively (S1 Np excluded, Table 1). The Np and Pu concentrations from a second elution with HCl-HF solution (0.1 mol/L each) were below or at the detection limits, which correspond to maximum additional recoveries for Np and Pu of 0.6% and 0.7%, respectively (Table S3 in the Supplemental Materials section). Experiments with NH₂OH·HCl led to the same result. These results indicate that the elution of Np and Pu with 0.1 mol/L HCl was nearly quantitative in all cases.

A certain proportion of the unrecovered Np and Pu might have been retained in the clay residue after the *aqua regia* treatment and subsequent centrifugation, although the residue was washed twice with *aqua regia*. The residue was not further analyzed because of the overall good yields of the method. Digestion of the clay test portions with a HF-*aqua regia* mixture, instead of the *aqua regia* treatment used in the present procedure, was not applied, mainly because it would have produced an undesired high concentration of matrix elements from which Np and Pu would have had to be separated. Such digestion might also require an additional step to remove amphoteric matrix elements before the co-precipitation, as they would impede pH adjustment.

In order to avoid re-oxidation of Np(IV) to Np(V), several steps of the procedure (including reductive co-precipitation and column chromatography) must be carried out directly one after another, which limits the sample throughput to around four samples per day.

CONCLUSION

An analytical procedure was successfully adapted for mass spectrometric determination of ²³⁷Np in clay or clay-rich materials using ²⁴²Pu as a non-isotopic tracer. High chemical yields near 90% for both Np and Pu and yield ratios close to unity were obtained. Accurate control of pH and minimization of the processing times are crucial for the proposed procedure. The method is capable of handling samples of up to 1 g of montmorillonite and illite, two clay minerals that are relevant for nuclear waste disposal. No strong complexing agents were used anywhere within the procedure, which makes it

particularly promising for future AMS ultra-trace analysis of Np and Pu in environmental samples.

ACKNOWLEDGEMENTS

The authors are grateful to Cornelia Walschburger for assistance with the ICP-MS measurements and thank David Fellhauer for sharing his experience regarding the speciation of actinides. They are also very grateful to the associate editor, J. M. Wampler, and the two anonymous reviewers for their essential comments and suggestions which greatly improved the quality of the manuscript.

REFERENCES

- Chen, Q., Dahlgaard, H., Nielsen, S. P., & Aarkrog, A. (2002). ²⁴²Pu as tracer for simultaneous determination of ²³⁷Np and ^{239,240}Pu in environmental samples. *Journal of Radioanalytical and Nuclear Chemistry*, 253, 451–458.
- Chen, Q., Dahlgaard, H., Nielsen, S. P., Aarkrog, A., Christensen, I., & Jensen, A. (2001). Determination of ²³⁷Np in marine sediment and seawater. *Journal of Radioanalytical and Nuclear Chemistry*, 249, 527–533.
- Dai, X., Christl, M., Kramer-Tremblay, S., & Synal, H.-A. (2015). Ultra-trace determination of neptunium-237 and plutonium isotopes in urine samples by compact accelerator mass spectrometry. *CNL Nuclear Review*, 4, 125–130.
- Denecke, M. A., Bryan, N., Kalmykov, S., Morris, K., & Quinto, F. (2018). Sources and behaviour of actinide elements in the environment. In J. K. Gibson & W. A. de Jong, (Eds.), *Experimental and theoretical approaches to actinide chemistry* (pp. 378–444) New Jersey, USA: Wiley, Hoboken
- Jerome, S. M., Carney, K., Essex, R., Fassbender, M. E., Goldberg, S., Kinlaw, M., LaMont, S. P., Mackney, D., Morrison, J. J., & Nortier, F. M. (2017). Reference materials for neptunium determination. *Applied Radiation and Isotopes*, 126, 44–48.
- Kim, C. S., Kim, C. K., & Lee, K. J. (2004). Simultaneous analysis of ²³⁷Np and Pu isotopes in environmental samples by ICP-SF-MS coupled with automated sequential injection system. *Journal of Analytical Atomic Spectrometry*, 19, 743–750.
- Kim, J.-I. (2006). Significance of actinide chemistry for the long-term safety of waste disposal. *Nuclear Engineering and Technology*, 38, 459–482.
- Matteson, B. S., Hanson, S. K., Miller, J. L., & Oldham, W. J., Jr. (2015). Concurrent determination of ²³⁷Np and Pu isotopes using ICP-MS: Analysis of NIST environmental matrix standard reference materials 4357, 1646a, and 2702. *Journal of Environmental Radioactivity*, 142, 62–67.
- Qiao, J., Hou, X., Roos, P., & Miró, M. (2010). Rapid and simultaneous determination of neptunium and plutonium isotopes in environmental samples by extraction chromatography using sequential injection analysis and ICP-MS. *Journal of Analytical Atomic Spectrometry*, 25, 1769–1779.
- Qiao, J., Hou, X., Roos, P., & Miró, M. (2011a). High-throughput sequential injection method for simultaneous determination of plutonium and neptunium in environmental solids using macroporous anion-exchange chromatography, followed by inductively coupled plasma mass spectrometric detection. *Analytical Chemistry*, 83, 374–381.
- Qiao, J., Hou, X., Roos, P., & Miró, M. (2011b). Reliable determination of ²³⁷Np in environmental solid samples using ²⁴²Pu as a potential tracer. *Talanta*, 84, 494–500.
- Qiao, J., Hou, X., & Roos, P. (2013a). Method for determination of neptunium in large-sized urine samples using manganese dioxide

- coprecipitation and ^{242}Pu as yield tracer. *Analytical Chemistry*, *85*, 1889–1895.
- Qiao, J., Hou, X., Roos, P., Lachner, J., Christl, M., & Xu, Y. (2013b). Sequential injection approach for simultaneous determination of ultratrace plutonium and neptunium in urine with accelerator mass spectrometry. *Analytical Chemistry*, *85*, 8826–8833.
- Qiao, J., Hou, X., Steier, P., & Golser, R. (2013c). Sequential injection method for rapid and simultaneous determination of ^{236}U , ^{237}Np , and Pu isotopes in seawater. *Analytical Chemistry*, *85*, 11026–11033.
- Quinto, F., Hrnccek, E., Krachler, M., Shotyk, W., Steier, P., & Winkler, S. R. (2013a). Determination of ^{239}Pu , ^{240}Pu , ^{241}Pu and ^{242}Pu at femtogram and attogram levels – evidence for the migration of fallout plutonium in an ombrotrophic peat bog profile. *Environmental Science: Processes & Impacts*, *15*, 839–847.
- Quinto, F., Hrnccek, E., Krachler, M., Shotyk, W., Steier, P., & Winkler, S. R. (2013b). Measurements of ^{236}U in ancient and modern peat samples and implications for postdepositional migration of fallout radionuclides. *Environmental Science & Technology*, *47*, 5243–5250.

[Received 10 March 2018; revised 28 January 2019; AE: J.M. Wampler]