A Valence Control Method Based on a Pt-Aided Hydrogen Peroxide Treatment for Yielding Tetravalent Neptunium and Plutonium in Nitric Acid Solutions

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There are several possible causes of the recovery decrease sometimes encountered in the chemical separation procedures for actinides. Although the interferences present in the samples could be related to the recovery decrease in the actinide separations, an incomplete valence control of the actinides in the sample solution conditioning step often causes problems of a significant loss of them in the subsequent sample loading step. Thus, control of the valence states of the actinides in the sample solutions is a basis for the separation methods such as anion exchange, extraction chromatography, solvent extraction and precipitation. In some chromatographic separation procedures for actinides, both Np and Pu are required to be adsorbed as their tetravalent state on the sorption media such as anion exchange resins or UTEVA-resin.[1,2] The most prominent factor influencing the individual separation of actinides may be an adjustment of the valences of Pu to a desired one, which is nearly the same as in the case of Np. Therefore, special attention must be given to a completion of a valence control for Pu and Np together in a sample solution prior to its loading on a separation column.

Various reducing agents such as ferrous sulfate, hydroxylamine, hydrazine, SO_2 and $SnCl_2$ are used to reduce Np(VI) to Np(IV) and all the Pu to Pu(III).[3] Ferrous sulfamate reduces Np in higher valence states to Np(IV), while it reduces all the Pu to Pu(III).[4] Np and Pu can be adjusted to Np(IV) and Pu(IV) by the use of sodium nitrite following an addition of ferrous ammonium sulfate.[5] However, these reagents introduce foreign ions into sample solutions which would complicate the subsequent separation steps. Reduction of Np(VI) to Np(IV) and Pu(VI) to Pu(IV) with H_2O_2 has sometimes been adopted in the valence control step of the actinide separation procedures used to determine individual actinides.[1,3,6] However, poor and inconsistent recoveries for Np and/or Pu were often observed when using H_2O_2 as a valence control agent in HNO_3 media samples.[7-11]

The purpose of this study is to develop a simple and efficient method that affords a valence adjustment of both Np and Pu to a tetravalent state for an effective adsorption onto the UTEVA-resin and the anion exchange resins from HNO_3 media. A H_2O_2-based sample solution treatment followed by a Pt-metal catalytic decomposition of the excess H_2O_2 was investigated to adjust both the Np and Pu to the required tetravalent state. The effectiveness of the H_2O_2-based valence control method proposed in this study was assessed by its adaptation to an UTEVA-resin chromatography for an individual separation of U, Np, Pu, and Am by using a synthetic mixture of their isotopes.

Experimental Section

Reagents and instruments. ^{237}Np solution (AEA Technology, Harwell, UK) was purified using an anion exchange procedure.[4] ^{241}Am (Amersham Internal), ^{239}Pu (North American Scientific), ^{233}U (IRMM), and the purified ^{237}Np were used to prepare the synthetic samples of the actinides. Alpha liquid scintillation counting of the extraction chromatographic eluates was made using a Packard 2500TR/AB, TRI-CARB liquid scintillation counter. A high resolution type inductively coupled plasma mass spectrometer (ICP-MS, Finnigan MAT, ELEMENT) was used for a measurement of the individual isotopes in the eluates. The absorption spectra of the Np solutions were measured with a Varian CARY5 UV-Vis-NIR spectrophotometer, using a 1.0 cm semi-micro quartz cell (Hellma).

Valence control of Np. Several 2.0 mL aliquots of the Np stock solution (5.0 mM Np/2.0 M HNO_3) were evaporated to dryness on a hot plate. After taking up one of the residues in 2.0 mL of 8.0 M HNO_3, 0.1 M H_2O_2 was added to the solution, and then a variation of its absorption spectrum was measured with the standing time. The other residues were separately dissolved in 2.0 mL of HNO_3 solutions with varying concentrations, after which the absorption spectrum was measured for each solution.

After an addition of 20 μL of 30% H_2O_2 to 2.0 mL of 5.0 mM Np in 8.0 M HNO_3, the solution was allowed to stand for 3 hours. Following this, the solution in which a coil of Pt-wire, 1.0 (D.) × 110 mm (L.), was immersed, was stirred intermittently with the very same Pt-wire coil until no oxygen bubbles evolution was observed on the surface of the Pt-wire. Absorption spectrum of the solution containing a Pt-wire coil was also measured at various time intervals for 3 days.

Actinide separation on UTEVA-resin. The UTEVA-resin (Eichrom Industries Inc.), 100-150 μ, was slurried in 1 M HNO_3 and soaked for one day. Aliquots of the slurry were then poured into a disposable syringe (4.7 mm I.D., 60 mm L.) to give a bed height of 50 mm. The flow rate was maintained at about 0.15 mL/min by a gravity elution. The column was preconditioned prior to its use by washing it with several column volumes of 8.0 M HNO_3.

The sample load solution was typically prepared as follows: One milliliter of the synthetic mixture solution [15 Bq (Becquerel)/mL of each of ^{233}U, ^{237}Np, ^{239}Pu, and ^{241}Am in 1 M HNO_3] was taken in a 10 mL glass beaker. The solution was evaporated to dryness on a hot plate. The residue was taken up in 2.0 mL of 8.0 M HNO_3. Ten microliters of 30% H_2O_2 were added to the solution and it was left to stand for 3 hours. A Pt-wire coil was immersed in the solution for 2 hours, with intermittent stirrings. This sample load solution was applied to the top of the preconditioned UTEVA-resin column. The beaker was rinsed with four 0.5 mL fractions of 8.0 M HNO_3 and the rinses were poured onto the column. After Am was washed off the column with 4 mL of 8.0 M HNO_3, 1 mL of 2.0 M HNO_3 was passed through the column, and then Pu, Np, and U were sequentially eluted with 2.0 M HNO_3-0.005 M $NH_2OH \cdot HCl$-0.005 M ascorbic acid, 2.0 M HNO_3-0.1 M $H_2C_2O_4$, and 0.02 M HNO_3-0.02 M HF, respectively.

Results and Discussion

Stabilization of Np(IV). Environmental solid samples are usually converted to dissolved sample solutions through a sample pretreatment process consisting of a digestion of the solid samples with mineral acids, a subsequent evaporation of the digest solutions to dryness, and a dissolution of the resulting residues in HNO_3. Usually, by using concentrated HNO_3, these sample solutions are prepared, in which Pu is predominantly present in the (VI) state.[12] Considering Koch's report[13] of the fact that all the Np in HNO_3 solutions is finally converted to Np(VI) by a heating, it could be assumed that Np is present in the dissolved solution mainly as Np(VI). At the separation step, the dissolved solutions of the solid samples are diluted with deionized water in order to adjust the medium acidity to 8.0 M HNO_3. Following this, both Np and Pu are adjusted to a tetravalent state for an anion exchange or UTEVA-resin chromatography. Therefore, it is important to know the distribution of the Np valence states and their stability in HNO_3 solutions while undergoing processes such as heating the sample solutions to dryness and dissolving the resulting residues. Thus, an absorption spectrometric investigation was conducted on the Np solutions which were obtained by heating the pure Np solutions of HNO_3 to dryness followed by re-dissolving the residues in HNO_3 solutions. The identification of the respective valence states of Np can be achieved by recording the absorption spectra over the wavelength range of 400 to 1300 nm. The most suitable absorption peaks for identification of the valence states are situated at 960 and 723 nm for Np(IV), 980 and 617 nm for Np(V), and 1223 nm for Np(VI). Figure 1 shows the spectra of the residue dissolved solutions. As seen in Figure 1, Np was predominantly present as Np(VI) in the dissolved solutions in the HNO_3 ranged from 2.0 to 15.5 M. With increasing the HNO_3 concentration, Np(V) decreased, while Np(VI) increased. Above 8.0 M HNO_3, Np(V) was not observed. Although the absorption peak of 980 nm Np(V) for 2.0 M HNO_3 in Figure 1 was intense due to its high molar absorptivity (370 $M^{-1}cm^{-1}$ at 1 M HNO_3) when compared with that (40 $M^{-1}cm^{-1}$ at 1 M HNO_3) of the 1223 nm Np(VI) peak,[14] the concentration of the two valence states was found to be 15% Np(V) and 85% Np(VI). This result supports the assumption that Np(VI) solely exists in the dissolved solutions originating from the sample pretreatment step for solid samples such as soils and sediments. It was also found that the intensity of the Np(VI) peak at 1223 nm decreased with increasing HNO_3 concentration due to the dependency of the molar absorptivity on the HNO_3 concentration and the formation of a new nitrate complex of Np(VI). As seen in Figure 1, when increasing the HNO_3 concentration, a new absorption peak appeared at 1120 nm and its intensity increased, indicating the formation of a new nitrate complex of Np(VI). Based on the suggestion by Vasil'ev *et al.*,[15] the absorption peaks at 1223 nm and 1120 nm can be attributed to $NpO_2(H_2O)_6^{2+}$ and $NpO_2(NO_3)_2$, respectively.

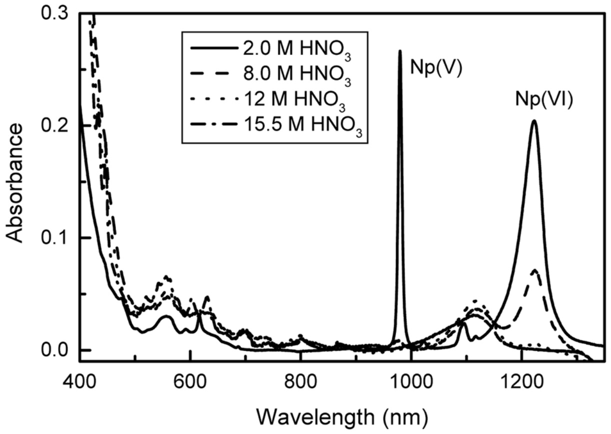

Figure 1. Spectra of the Np solutions prepared by heating the nitric acid solutions of Np to dryness and dissolving the residues with 2.0, 8.0, 12.0, and 15.5 M HNO_3; [Np] = 5.0 mM for all the samples.

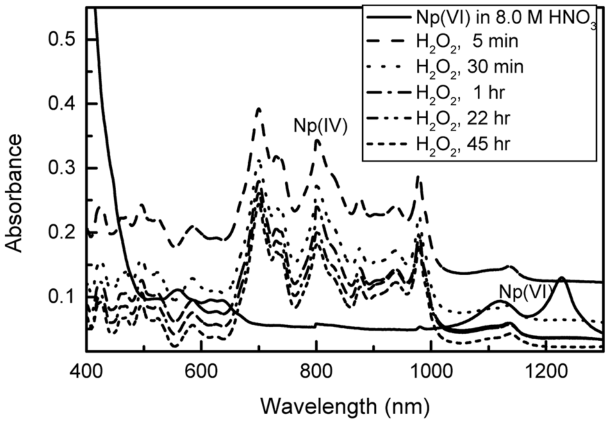

Figure 2. Variation of the neptunium spectrum of the residue dissolved solution in 8.0 M HNO_3 vs. the standing time after an addition of H_2O_2; [Np] = 5.0 mM, initial [H_2O_2] = 0.1 M.

An aliquot of the Np stock solution was heated to dryness, and the residue was dissolved in 12.0 M HNO_3, and then the absorption spectrum of the solution was measured with diluting the HNO_3 concentration down to 2.0 M. No significant spectral changes were observed for the diluted solutions over a period of a week, but the absorption spectra obtained 3 weeks later indicated a slow increase in the 980 nm Np(V) peak for all the solutions. The lower the HNO_3 concentration used, the greater the tendency toward a Np(V) formation was found as well. This result indicates that Np(VI) is not stable in dilute HNO_3. It thus appears that the HNO_3 concentration is a very important factor in determining the distribution of Np valence states.

The variation in the absorption spectrum of the dissolved solution in 8.0 M HNO_3 measured over a period of 2 days after an addition of H_2O_2 is shown in Figure 2. As might be expected from the literature,[16] H_2O_2 rapidly reduced the Np(VI) to Np(IV) in 8.0 M HNO_3. Although the spectrophotometric observations in this study also indicated that a stabilization of the Np(IV) state with H_2O_2 could be achieved above 6 M HNO_3, our investigation was limited only to 8.0 M HNO_3 solutions of Np where the maximum adsorptions of Np(IV) and Pu(IV) by anion exchange resins as well as UTEVA-resin occur.

Co-stabilization of Np(IV) and Pu(IV). When H_2O_2 is added in excess to the HNO_3 solutions of Pu(VI), Pu(VI) is slowly reduced, through a mixture of Pu(IV) and Pu(III), to Pu(III). The resulting Pu(III) becomes stable as long as H_2O_2 is present due to its reducing power. However, since Pu can exist as Pu(III) in HNO_3 solutions with concentrations of below 5 M, Pu(III) is immediately oxidized to Pu(IV) with increasing the HNO_3 concentration to a value greater than 5 M under the condition without any reducing agent.[17] Therefore, it seems highly likely that an oxidation of Pu(III) to Pu(IV) in 8.0 M HNO_3 can be achieved by decomposing the excess H_2O_2 after converting Pu to a mixture of Pu(IV) and Pu(III) by an addition of H_2O_2. The major difficulty in the simultaneous valence control of Np and Pu is how to decompose the excess H_2O_2 without changing the Np(IV) state. H_2O_2 decomposes slowly in pure HNO_3 solutions. Krot *et al.*[16] reported that the rate of a H_2O_2 decomposition in about 8 M HNO_3 was less than 1.5% per hour under the conditions without any catalytic impurity. Although H_2O_2 can be decomposed by a simple heating, its thermal decomposition was not considered in this study due to the possibility of an oxidation of Np(IV) by a heating to Np(VI). Iron and other transition metal ions have been known to catalyze a decomposition of H_2O_2. It is also well known that Pt metal catalytically decomposes the H_2O_2 dissolved in aqueous solutions.[18] We expected that the Pt catalytic decomposition of an excess H_2O_2 would accompany a spontaneous oxidation of Pu(III) to Pu(IV) by nitrate in relatively high concentrated HNO_3 solutions such as 8 M HNO_3 without changing the Np(IV) state which was adjusted by the H_2O_2. A spiral of Pt-wire was immersed into the H_2O_2-treated dissolved solution in 8.0 M HNO_3 until oxygen bubbles did not occur on the surface of the Pt-wire. All the excess H_2O_2 was almost completely decomposed in 1 hour by a stirring with the very same Pt-wire as judged by the visual observations of an oxygen bubbling. Decomposition reaction without stirring the H_2O_2-treated dissolved solution with the Pt-wire was completed in about one day. The decomposition time can be remarkably shortened by an intermittent swirling with the same Pt-wire, which produced a clean Pt surface by immediately removing the oxygen bubbles at the moment of their occurrence at the Pt surface. Absorption spectrophotometric measurements on the H_2O_2-treated Np-containing solution before and after an immersion of the Pt-wire revealed that the decomposition of H_2O_2 produced no change in the Np(IV) spectrum. No change in the Np(IV) state in this solution was also observed during a 3-day standing time after decomposition of the excess H_2O_2 using the Pt-wire. This result indicates that the Np(IV) state is remarkably stable in 8.0 M HNO_3 even without any holding reductant such as H_2O_2.

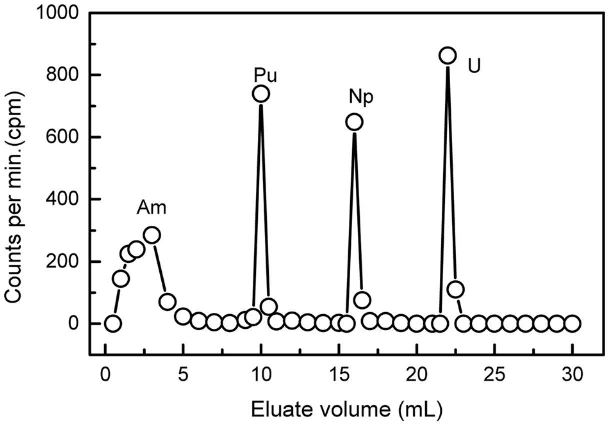

Figure 3. Elution sequence of Am, Pu, Np, and U from the UTEVA extraction chromatographic resin; Column: UTEVA-resin (100-150 μ), 4.7(I.D.) × 50 mm (H.); Sample: 2 mL of 8.0 M HNO_3 containing 15 Bq each of ^{241}Am, ^{239}Pu, ^{237}Np, and ^{233}U; Eluents: 8.0 M HNO_3 for Am, 2.0 M HNO_3-0.005 M $NH_2OH{\cdot}HCl$-0.005 M ascorbic acid for Pu, 2.0 M HNO_3-0.1 M $H_2C_2O_4$ for Np, 0.02 M HNO_3-0.02 M HF for U.

Effectiveness of a valence control. In order to confirm a stabilization of Np(IV) and Pu(IV) by the above-described method for the samples containing actinides at below μg levels, their recoveries for the UTEVA-resin chromatographic separation were measured.

The extraction chromatographic procedure was followed according to the conditions proposed by Morgenstern *et al.*,[1] with some modifications. Figure 3 shows a typical chromatogram obtained from the UTEVA-resin column separation with the H_2O_2-Pt treated synthetic sample solution containing 15 Bq each of ^{233}U, ^{237}Np, ^{239}Pu and ^{241}Am (which corresponds to 43 ng, 575 ng, 6.6 ng and 0.12 ng, respectively) in 2.0 mL of 8.0 M HNO_3. Am(III) showed a somewhat broad band because of the additional loading of the rinse of the sample beaker on the column, while each of the other elements was eluted in a reasonably sharp band. Pu was not observed in the Am-fraction, while about 20% of the initial Np was found. This result indicates that the Pu in the loading sample could be quantitatively adjusted to the Pu(IV) state, but a part of Np(IV) adjusted by H_2O_2 was reoxidized to the Np(V) state after the Pt-catalytic H_2O_2 decomposition.

For the quantitative results, three 1.0 mL aliquots of the synthetic sample solution containing 15 Bq each of ^{233}U, ^{237}Np, ^{239}Pu and ^{241}Am in 8.0 M HNO_3 were subjected to the separate columns followed by the subsequent separation steps as described above. The recoveries, based on the concentrations of the isotopes in each isotope fraction determined using ICP-MS, were found to be 99.2 ± 0% for ^{233}U, 77.3 ± 1.1% for ^{237}Np, 90.1 ± 1.2% for ^{239}Pu, and 99.6 ± 0.6% for ^{241}Am, where the deviations indicate one-sigma values. The amount of Np which was not recovered into the Np-fraction was found to be almost equal to that of Np leaked into the Am-fraction at the sample loading step. The Pu-, Np-, and U-fractions were found to be nearly free of contaminations from other isotopes. The valence control method proposed in this study produced high recoveries and showed a good reproducibility for U, Pu and Am in the UTEVA-resin chromatography, while for Np, it was reproducible but somewhat low recoveries.

The Np recoveries were also measured for a constant sample volume of 2.0 mL (8.0 M HNO_3), by varying the ^{237}Np amounts from 5.01 Bq to 465 Bq. The amount of H_2O_2 added was 0.1 mmole for all the samples. The Np recovery increased from 61.5% to 74.2%, 82.6% and 92.6% with an increasing ^{237}Np amount from 5.01 Bq (0.192 μg ^{237}Np) to 15 Bq (0.575 μg ^{237}Np), 46.5 (1.78 μg ^{237}Np) and 465 Bq (17.8 μg ^{237}Np), respectively. It should be noted that the significant Np loss into the Am-fraction occurred for the sample solutions containing lower concentrations of Np. This result appears to show that the dissolved oxygen in the sample solution after a decomposition of the excess H_2O_2, reoxidizes a part of the Np(IV) to Np(V).

Dependency of the Np recovery on the sample volume was also investigated with a constant amount of 15 Bq ^{237}Np only in 8.0 M HNO_3. The amount of H_2O_2 added into all the samples was 0.1 mmole. The Np recovery decreased from 76.6% to 74.2% and 66.8% as the sample volume increased from 1.0 mL to 2.0 mL and 5.0 mL, respectively. This result is to be expected when considering the increase in the concentration ratio of [dissolved oxygen]/[Np] with an increase in the sample volume. Therefore, in order to improve the Np recovery, the sample volume must be reduced to as little as possible. On the other hand, it was found that the use of H_2O_2 without a successive decomposing of the excess H_2O_2 provided a good Np recovery, in excess of 90% at as low as a 15 Bq level of Np. However a considerable amount of Pu leaked out into the Am-fraction. This finding indicates that Np was maintained at the Np(IV) state in the presence of H_2O_2 in 8.0 M HNO_3, while a part of Pu existed at the Pu(III) state. Therefore, when a Pu separation is not required, a high Np recovery could be achieved by only an addition of H_2O_2 to a sample solution by omitting a Pt-wire immersion.

In conclusion, the use of a H_2O_2-Pt treatment as a valence control method for Pu(IV) and Np(IV) in 8.0 M HNO_3 led to a complete stabilization of the Pu(IV), along with a downward trend of the ratio of [Np(IV)] to $[Np]_{total}$ with a decrease in the Np concentration of a sample solution.

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