

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, SO₂ and SnCl₂ 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 H₂O₂ 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 H₂O₂ as a valence control agent in HNO₃ 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 HNO₃ media. A H₂O₂-based sample solution treatment followed by a Pt-metal catalytic decomposition of the excess H₂O₂ was investigated to adjust both the Np and Pu to the required tetravalent state. The effectiveness of the H₂O₂-

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. ²³⁷Np solution (AEA Technology, Harwell, UK) was purified using an anion exchange procedure.⁴ ²⁴¹Am (Amersham Internal), ²³⁹Pu (North American Scientific), ²³³U (IRMM), and the purified ²³⁷Np 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 HNO₃) were evaporated to dryness on a hot plate. After taking up one of the residues in 2.0 mL of 8.0 M HNO₃, 0.1 M H₂O₂ 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 HNO₃ solutions with varying concentrations, after which the absorption spectrum was measured for each solution.

After an addition of 20 μ L of 30% H₂O₂ to 2.0 mL of 5.0 mM Np in 8.0 M HNO₃, the solution was allowed to stand for 3 hours. Following this, the solution in which a coil of Pt-wire, 1.0 (D.) \times 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 HNO₃ 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 HNO₃.

The sample load solution was typically prepared as follows: One milliliter of the synthetic mixture solution [15 Bq (Becquerel)/mL of each of ²³³U, ²³⁷Np, ²³⁹Pu, and ²⁴¹Am in 1 M HNO₃] 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 HNO₃. Ten microliters of 30% H₂O₂ 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 HNO₃ and the rinses were poured onto the column. After Am was washed off the column with 4 mL of 8.0 M HNO₃, 1 mL of 2.0 M HNO₃ was passed through the column, and then Pu, Np, and U were sequentially eluted with 2.0 M HNO₃-0.005 M NH₂OH·HCl-0.005 M ascorbic acid, 2.0 M HNO₃-0.1 M H₂C₂O₄, and 0.02 M HNO₃-0.02 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 HNO₃. Usually, by using concentrated HNO₃, these sample solutions are prepared, in which Pu is predominantly present in the (VI) state.¹² Considering Koch's report¹³ of the fact that all the Np in HNO₃ 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 HNO₃. 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 HNO₃ 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 HNO₃ to dryness followed by re-dissolving the residues in HNO₃ 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 HNO₃ ranged from 2.0 to 15.5 M. With increasing the HNO₃ concentration, Np(V) decreases-

ed, while Np(VI) increased. Above 8.0 M HNO₃, Np(V) was not observed. Although the absorption peak of 980 nm Np(V) for 2.0 M HNO₃ in Figure 1 was intense due to its high molar absorptivity (370 M⁻¹cm⁻¹ at 1 M HNO₃) when compared with that (40 M⁻¹cm⁻¹ at 1 M HNO₃) 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 HNO₃ concentration due to the dependency of the molar absorptivity on the HNO₃ concentration and the formation of a new nitrate complex of Np(VI). As seen in Figure 1, when increasing the HNO₃ 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 NpO₂(H₂O)₆²⁺ and NpO₂(NO₃)₂, respectively.

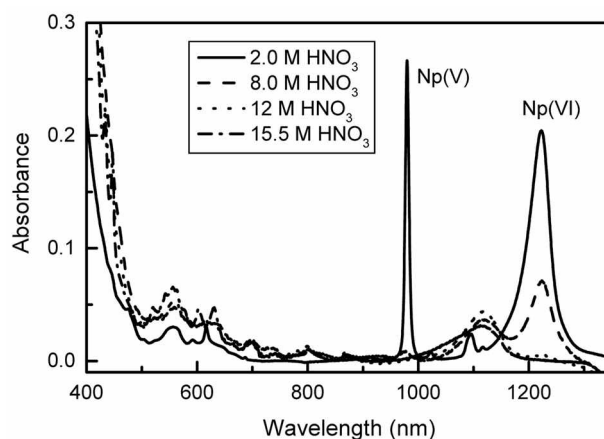


Figure 1. Spectra of the Np solutions prepared by heating the nitric acid solutions of Np to dryness and dissolving the residues with 2.0, 8.0, 12.0, and 15.5 M HNO₃; [Np] = 5.0 mM for all the samples.

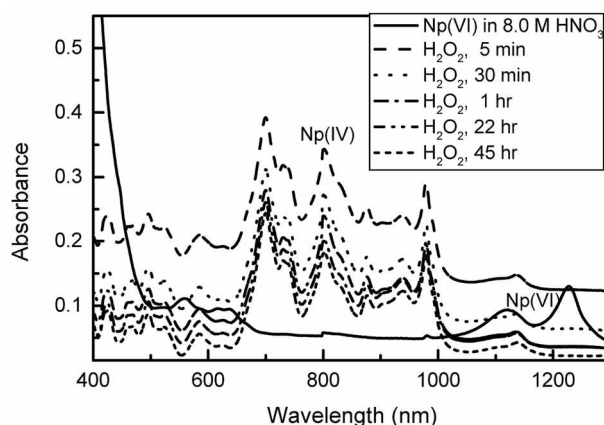


Figure 2. Variation of the neptunium spectrum of the residue dissolved solution in 8.0 M HNO₃ vs. the standing time after an addition of H₂O₂; [Np] = 5.0 mM, initial [H₂O₂] = 0.1 M.

An aliquot of the Np stock solution was heated to dryness, and the residue was dissolved in 12.0 M HNO₃, and then the absorption spectrum of the solution was measured with diluting the HNO₃ 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 HNO₃ 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 HNO₃. It thus appears that the HNO₃ 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 HNO₃ measured over a period of 2 days after an addition of H₂O₂ is shown in Figure 2. As might be expected from the literature,¹⁶ H₂O₂ rapidly reduced the Np(VI) to Np(IV) in 8.0 M HNO₃. Although the spectrophotometric observations in this study also indicated that a stabilization of the Np(IV) state with H₂O₂ could be achieved above 6 M HNO₃, our investigation was limited only to 8.0 M HNO₃ 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 H₂O₂ is added in excess to the HNO₃ 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 H₂O₂ is present due to its reducing power. However, since Pu can exist as Pu(III) in HNO₃ solutions with concentrations of below 5 M, Pu(III) is immediately oxidized to Pu(IV) with increasing the HNO₃ 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 HNO₃ can be achieved by decomposing the excess H₂O₂ after converting Pu to a mixture of Pu(IV) and Pu(III) by an addition of H₂O₂. The major difficulty in the simultaneous valence control of Np and Pu is how to decompose the excess H₂O₂ without changing the Np(IV) state. H₂O₂ decomposes slowly in pure HNO₃ solutions. Krot *et al.*¹⁶ reported that the rate of a H₂O₂ decomposition in about 8 M HNO₃ was less than 1.5% per hour under the conditions without any catalytic impurity. Although H₂O₂ 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 H₂O₂. It is also well known that Pt metal catalytically decomposes the H₂O₂ dissolved in aqueous solutions.¹⁸ We expected that the Pt catalytic decomposition of an excess H₂O₂ would accompany a spontaneous oxidation of Pu(III) to Pu(IV) by nitrate in relatively high concentrated HNO₃ solutions such as 8 M HNO₃ without changing the Np(IV) state which was adjusted by the H₂O₂. A spiral of Pt-wire was immersed into the H₂O₂-treated dissolved solution in 8.0 M HNO₃ until oxygen bubbles did not occur on the surface of the Pt-wire. All the

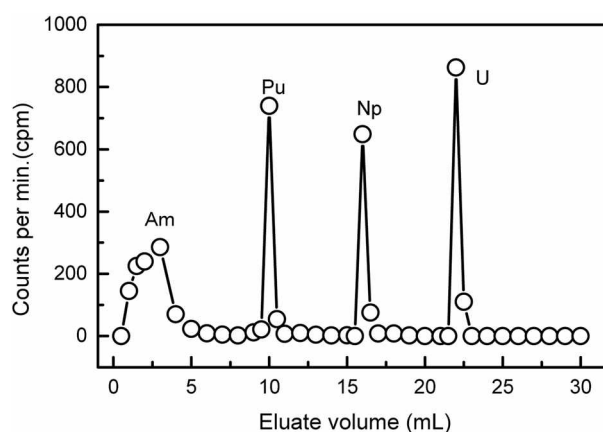


Figure 3. Elution sequence of Am, Pu, Np, and U from the UTEVA extraction chromatographic resin; Column: UTEVA-resin (100-150 μ i), 4.7(I.D.) \times 50 mm (H.); Sample: 2 mL of 8.0 M HNO₃ containing 15 Bq each of ²⁴¹Am, ²³⁹Pu, ²³⁷Np, and ²³³U; Eluents: 8.0 M HNO₃ for Am, 2.0 M HNO₃-0.005 M NH₂OH-HCl-0.005 M ascorbic acid for Pu, 2.0 M HNO₃-0.1 M H₂C₂O₄ for Np, 0.02 M HNO₃-0.02 M HF for U.

excess H₂O₂ 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 H₂O₂-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 H₂O₂-treated Np-containing solution before and after an immersion of the Pt-wire revealed that the decomposition of H₂O₂ 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 H₂O₂ using the Pt-wire. This result indicates that the Np(IV) state is remarkably stable in 8.0 M HNO₃ even without any holding reductant such as H₂O₂.

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 μ g levels, their recoveries for the UTEVA-resin chromatographic separation were measured.

The extraction chromatographic procedure was followed according to the conditions proposed by Morgenstem *et al.*,¹ with some modifications. Figure 3 shows a typical chromatogram obtained from the UTEVA-resin column separation with the H₂O₂-Pt treated synthetic sample solution containing 15 Bq each of ²³³U, ²³⁷Np, ²³⁹Pu and ²⁴¹Am (which corresponds to 43 ng, 575 ng, 6.6 ng and 0.12 ng, respectively) in 2.0 mL of 8.0 M HNO₃. 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 H₂O₂ was reoxidized to the Np(V) state after the Pt-catalytic H₂O₂ decomposition.

For the quantitative results, three 1.0 mL aliquots of the synthetic sample solution containing 15 Bq each of ²³³U, ²³⁷Np, ²³⁹Pu and ²⁴¹Am in 8.0 M HNO₃ 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 ²³³U, 77.3 ± 1.1% for ²³⁷Np, 90.1 ± 1.2% for ²³⁹Pu, and 99.6 ± 0.6% for ²⁴¹Am, 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 HNO₃), by varying the ²³⁷Np amounts from 5.01 Bq to 465 Bq. The amount of H₂O₂ 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 ²³⁷Np amount from 5.01 Bq (0.192 μg ²³⁷Np) to 15 Bq (0.575 μg ²³⁷Np), 46.5 (1.78 μg ²³⁷Np) and 465 Bq (17.8 μg ²³⁷Np), 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 H₂O₂ 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 ²³⁷Np only in 8.0 M HNO₃. The amount of H₂O₂ 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 H₂O₂ without a successive decomposing of the excess H₂O₂ 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 H₂O₂ in 8.0 M HNO₃, 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 H₂O₂ to a sample solution by omitting a Pt-wire immersion.

In conclusion, the use of a H₂O₂-Pt treatment as a valence control method for Pu(IV) and Np(IV) in 8.0 M HNO₃ 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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