

Redox speciation method for neptunium in a wide range of concentrations

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(Received June 24, 2002; accepted in revised form September 27, 2002)

Neptunium / Redox speciation / Chemical separation / Impregnated resin / Bismuth phosphate

Summary. The adsorption method for determination of the distribution of neptunium among its oxidation states by the use of solvent impregnated resins and bismuth phosphate precipitates as adsorbents is described. For neptunium in concentration ranging from $\sim 10^{-10}$ to $\sim 10^{-2.5}$ M, Np(IV) and Np(VI) were quantitatively adsorbed on the impregnated resin in a solution of the acidity 1.0–0.1 M HClO₄, while Np(V) remained in the liquid phase. In the same condition, the precipitate of bismuth phosphate absorbed Np(IV) selectively, leaving Np(V) and Np(VI) in the liquid phase. By carrying out these adsorption methods in Ultrafree-MC Microporous Centrifugal Filter Units (Millipore Corporation), the oxidation state distribution of neptunium in acid solution can be determined in a simple manner with a small sample volume (500 μ l) regardless of its concentration.

Introduction

Since uranium, neptunium, and plutonium can exist in various oxidation states with different chemical behavior in aqueous solution, it is necessary to know not only the concentration, but also the oxidation state of elements in each sample. There are various spectroscopic methods that can be used to determine the concentration and oxidation state of the actinide in a solution [1]. However, these techniques are not applicable to the low concentrations under $\sim 10^{-7}$ M, which are to be encountered in many conditions such as in environmental systems. The radiochemical separation based on the two-phase distribution is the only method capable of redox speciation of these elements at trace-level concentrations. So far, several reports have been published on solvent extraction [2–8], co-precipitation [2, 3, 6, 8–13] and adsorption methods [14–17]. The extraction with TTA (thenoyltrifluoroacetone) is widely used for actinide redox speciation, but, as observed for Pu(VI), the photosensitive nature of TTA necessitates the avoidance of light exposure in the extraction of reducible species [18]. The co-precipitation with lanthanum fluoride has a weak point that fluoride ions may

kinetically take part in the reduction of actinides [19], the adsorption with silica gel needs careful pretreatment of silica gel and long contact time (2–4 h) and the adsorption with CaCO₃ also needs careful pretreatment and its separation efficiency is poor [20]. Moreover, a limitation common to these chemical separations is that these methods require experiences and skills. Therefore, it is to be desired to develop a simple method which permits any person to reliably determine the oxidation state of actinide in aqueous solution at any concentration.

The present study is an attempt to establish an easy and simple method which needs neither experience nor skill for discriminating between the oxidation states of neptunium at tracer and macro concentrations. The adsorption on resins impregnated with organophosphorus extractants and on bismuth phosphate precipitate are the most promising of various adsorbents so far examined in our laboratory. This method is easy and simple in handling, applicable to a wide range of concentrations and exerts no influence on the redox reaction in solution. In addition, the redox speciation can be carried out in relatively short time (10 min) with a very small volume of sample solution (500 μ l). The method has been developed for solutions of the acidity of 1 \sim 0.1 M where Np(IV), Np(V) and Np(VI) exist in their non-complexed forms as Np⁴⁺, NpO₂⁺ and NpO₂²⁺. The method is based on the two-phase distributions. For the method to be successful to the system where more than one oxidation states of neptunium coexist, the rate of distribution should be sufficiently faster than the rate of redox reaction, and the sorption capacity of the system should be high enough to deal with the total metal ion concentration to assume the fast attainment of the equilibrium. To check these conditions, the solid-liquid distributions were therefore evaluated at low ($C_M \sim 10^{-10}$ M) and high ($C_M \cong 10^{-2.5}$ M) neptunium concentrations.

Experimental

Isotopes

For the experiments at a total neptunium concentration of $C_M \cong 10^{-2.5}$ M, the isotope ²³⁷Np was used. With addition of small amounts of HClO₄ and HNO₃, an aliquot of

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Table 1. Redox reagents for the preparation of specified oxidation state solutions.

	Np(IV)	Np(V)	Np(VI)
$C_{\text{Np}} \cong 10^{-2.5}$ M Np-237	H ₂ -gas reduction to Np(III) and air oxidation to Np(IV)	HONH ₃ Cl 5×10^{-3} M	fume with c.HNO ₃ + c.HClO ₄ dissolve in acid
$C_{\text{Np}} \sim 10^{-10}$ M Np-239	FeSO ₄ 0.02 M	Fe(NO ₃) ₃ 0.02 M	KMnO ₄ 0.002 M

the stock solution of ²³⁷Np (in 1.0 M HNO₃) was evaporated to near dryness and dissolved in 0.1 or 1.0 M HClO₄. After this treatment, the oxidation state of this solution was confirmed to be Np(VI). Np(V) solution was prepared by reduction of this Np(VI) with hydroxylammonium chloride whose concentration in the experiment is listed in Table 1. Np(IV) solution was prepared by the combination of hydrogen reduction and air oxidation [21], *i.e.*, Np(VI) was reduced to Np(III) by bubbling with hydrogen gas on a platinum black catalyst for 2 h, and then oxidized to Np(IV) by contacting with air. The oxidation state distribution of these neptunium solutions were determined by absorption spectrophotometry. Photoabsorption spectra of the neptunium solutions were obtained using a Shimadzu model UV-3100 PC UV-VIS-NIR spectrophotometer (Japan). Concentrations of ²³⁷Np were determined from its α -activity measured with a liquid scintillation spectrometer (Perals Spectrometer, Ordella Model 8100B with Ultima Gold AB Scintillator), discriminating the β -activity of its daughter nuclide ²³³Pa.

For the experiments at a tracer concentration of ²³⁹Np ($\sim 10^{-10}$ M), ²³⁹Np tracer was prepared by milking from ²⁴³Am by the method of Sill [22]. ²⁴³Am was obtained from Commissariat à l'Énergie Atomique (France). The solutions of ²³⁹Np in oxidation states IV, V and VI were prepared by the addition of suitable redox reagents listed in Table 1 [14]. Relative concentrations of ²³⁹Np were determined by γ -activity measurement with a well-type NaI(Tl) scintillation counter.

Materials

The resin for impregnation of the extractant, SEPABEADS SP825 was obtained from Mitsubishi Chemical Corporation (Japan). This is a nonpolar macroporous styrene/divinyl benzene polymer, supplied as spherical particles (particle diameter > 0.25 mm) with a mean pore size of approximately 5.7 nm and a specific surface area of about 1000 m² g⁻¹. Before the use, this resin was mixed with enough volume of methanol and washed by ultrasonic clean-

ing to remove organic impurities and the monomer. Then, it was dried at 80 °C for 2 h and kept in a calcium chloride desiccator.

H-DEHP (di (2-ethylhexyl) phosphoric acid, purity > 95.0%), DBP (di-*n*-butyl phosphoric acid, purity > 97.0%), and CMP (dihexyl N,N-diethyl carbamoyl methyl phosphonic acid, purity > 97.0%) were obtained from Tokyo Kasei Kogyo Co., Ltd. (Japan) and were used without further purification. Other chemicals were obtained from Wako Pure Chemical Industries (Japan) and used as received. The solutions of reductants and oxidants, such as hydroxylammonium chloride, iron(II) sulfate and potassium permanganate, were prepared just before use.

Four kinds of organophosphorus extractants (DBP, CMP, H-DEHP and Al-DEHP) were impregnated into the resin to examine their adsorption characteristics, where Al-DEHP means that a part of protons in H-DEHP were substituted with aluminum ions. To prepare Al-DEHP, an organic solution that was a 1 : 1 (wt/wt) mixture of H-DEHP and benzene was contacted with a same volume of 1 M Al(NO₃)₃ aqueous solution. The mixture was shaken for 5 min in a separatory funnel. The pH of the aqueous solution shifted from the initial 1.67 to final 0.36, indicating a certain degree of ion exchange between proton and aluminum ion. After this extraction, the organic phase was air-dried for 10 h to remove benzene from Al-DEHP.

To impregnate the extractants into the resin, pretreated SEPABEADS SP825 (1.0 g) was mixed with 6 ml of CMP or DBP. In the case of H-DEHP and Al-DEHP, the extractant was diluted with benzene to the proportions as listed in Table 2 in order to make the impregnation smooth, and SP825 (1.0 g) was mixed with 6 ml of these diluted extractants. The mixture was stirred for 1 h and then kept standing for 24 h. Then, the excess extractant in the micro-pores of the resin was removed from the resin by filtration under reduced pressure, and the resin was rinsed with distilled water several times. Finally, the resin was dried at 75 °C for 2 h to remove residual water and benzene, and kept in a calcium chloride desiccator.

Table 2. Impregnated resin and reagent composition.

Name of impregnated resin	Proportions of impregnating solution
H-DEHP-75	H-DEHP 75 vol. % + benzene 25 vol. %
H-DEHP-60	H-DEHP 60 vol. % + benzene 40 vol. %
Al-DEHP-75	Al-DEHP 75 vol. % + benzene 25 vol. %
Al-DEHP-60	Al-DEHP 60 vol. % + benzene 40 vol. %
DBP	DBP (di- <i>n</i> -butyl phosphate) 100 vol. %
CMP	CMP (dihexyl N,N-diethyl carbamoyl methyl phosphonate) 100 vol. %

Procedures

Solvent impregnated resin

The operation of the adsorption of neptunium onto the resin was conducted in the Ultrafree-MC Microporous Centrifugal Filter Unit (UFC30GV pore size 0.22 μm) made by Millipore Corporation U.S.A. As shown in Fig. 1, this unit is composed of an outer tube and inner filter tube. By preparing the sample solution in the inner tube, the composed unit can be subjected to centrifugation. After the centrifugal filtration, the inner content (precipitate) can be taken out separately from the filtrate. With this filter unit, solid and liquid phase can be easily separated by centrifugation with using a very small sample volume (500 μl). The experiment for the adsorption of neptunium in each oxidation state was conducted following the procedure mentioned below.

- 0.1 g of the impregnated resins was put on the filter in the filter unit and then 500 μl of a sample solution containing neptunium was added.
- The mixture in the filter unit was shaken for 1 or 10 min with the micro mixer shaker (TITEC Micro Mixer E-36) made by TAITEC Co. Japan.
- The unit was centrifuged by 10 k rpm for 3 min. The phases were separated by the micro bench centrifuge (CHIBITAN-II XX42 CF0 0T) made by Millipore Corporation Japan.

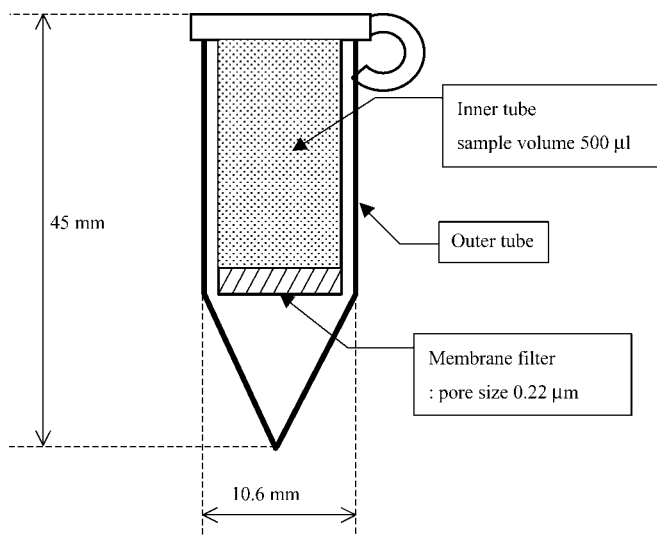


Fig. 1. Ultrafree-MC Microporous Centrifugal Filter Unit (UFC30GV pore size 0.22 μm) made by Millipore Corporation USA.

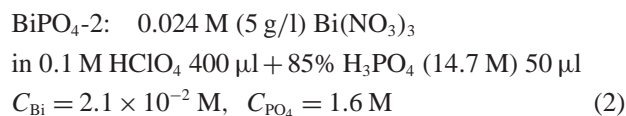
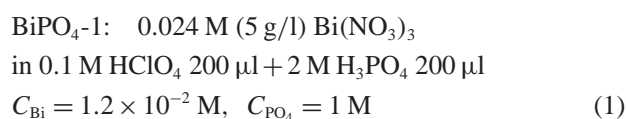
Table 3. The adsorption of Np(IV), Np(V) and Np(VI) on the impregnated resins (1). Acidity: 1.0 M HClO_4 , Shaking time: 10 min.

	Np adsorbed/%					
	Np-237, $C_{\text{Np}} \cong 10^{-2.5}$ M			Np-239, $C_{\text{Np}} \sim 10^{-10}$ M		
	Np(IV)	Np(V)	Np(VI)	Np(IV)	Np(V)	Np(VI)
H-DEHP-60	81.0	2.0	91.0	98.3	3.0	99.7
H-DEHP-75	96.2	0.5	96.1	98.1	-0.1	99.1
Al-DEHP-60	96.0	2.8	96.6	99.1	3.2	99.6
Al-DEHP-75	99.1	0.6	97.8	99.2	0.0	99.6
DBP	98.9	33.2	77.7	98.5	5.6	91.2
CMP	93.7	15.3	67.1	-	-	-

- At a tracer concentration of ^{239}Np ($\sim 10^{-10}$ M), a 200 μl portion of liquid phase was pipetted and the γ -activity of ^{239}Np was measured. At a macro concentration of ^{237}Np ($\cong 10^{-2.5}$ M), a 100 μl portion of liquid phase was pipetted and the total volume of the solution was adjusted to be 2 ml by diluting with 1 M HClO_4 . Then α -activity (of ^{237}Np) in 50 μl of the diluted solution was measured as described above.
- The adsorption ratio of neptunium was calculated from the difference between the initial and liquid phase's activities.

Bismuth phosphate

To prepare the precipitate of bismuth phosphate, bismuth nitrate solution and phosphoric acid solution were pipetted into a centrifugal filter unit. The following two conditions for the precipitation were examined.



Each mixture was gently shaken and allowed to stand for 10 min to complete precipitation, and then the filter unit was centrifuged. Bismuth phosphate precipitate ($\text{BiPO}_4\text{-1}$, $\text{BiPO}_4\text{-2}$) remaining on the filter surface was obtained and the filtrate was discarded. The experiment for the adsorption of neptunium was conducted in the same manner as in the case of the impregnated resin, using bismuth phosphate precipitate as solid phase.

Results and discussion

Adsorption on the impregnated resin

The adsorption behavior of macro ($C_{\text{Np}} \cong 10^{-2.5}$ M) and trace ($C_{\text{Np}} \sim 10^{-10}$ M) concentrations of Np(IV), Np(V) and Np(VI) on the impregnated resin was examined at acidities 1.0 M and 0.1 M HClO_4 . Table 3 shows the adsorption ratio at the acidity of 1.0 M HClO_4 for the shaking time of 10 min. Except the case of H-DEHP-60, both macro and trace concentrations of Np(IV) and Np(VI) are quantitatively adsorbed on H-DEHP and Al-DEHP resins at the acidity of

Table 4. The adsorption of Np(IV), Np(V) and Np(VI) on the impregnated resins (2). Acidity: 0.1 M HClO₄, Shaking time: 10 min.

	Np adsorbed/%					
	Np-237, $C_{Np} \cong 10^{-2.5}$ M			Np-239, $C_{Np} \sim 10^{-10}$ M		
	Np(IV) ^a	Np(V)	Np(VI) ^b	Np(IV)	Np(V)	Np(VI)
H-DEHP-60	80.3	2.6	89.0	99.8	7.9	100.0
H-DEHP-75	91.6	2.6	90.2	100.0	5.3	100.0
Al-DEHP-60	91.2	-0.1	90.3	99.6	4.3	100.0
Al-DEHP-75	92.1	2.6	90.0	99.7	3.7	99.9

a: Np(IV): 93.5%, Np(V): 6.5%;

b: Np(VI): 92%, Np(V): 8%.

1.0 M, while Np(V) is not adsorbed on these resins. This indicates that H-DEHP and Al-DEHP impregnated resin can be used to discriminate Np(IV) and Np(VI) from Np(V). On the other hand, DBP and CMP impregnated resins do not have such high capability as H-DEHP and Al-DEHP impregnated resin to separate three oxidation states of neptunium at a macro concentration. Table 4 shows the adsorption ratio of neptunium on the H-DEHP and Al-DEHP impregnated resins at the acidity of 0.1 M HClO₄. The absorption spectra of Np(IV) and Np(VI) sample solutions indicated the gradual formation of Np(V) in these sample solutions under this condition, *i.e.*, macro concentration of Np and the acidity of 0.1 M, as described in the footnote of Table 4. Therefore, except for the H-DEHP-60 case, the result in Table 4 means that Np(IV) and Np(VI) quantitatively adsorb on the all DEHP resins and Np(V) does not adsorb at the acidity of 0.1 M HClO₄. The adsorption percentages on H-DEHP-60 are lower compared with other resins at both acidities. This is probably due to a smaller amount of impregnated extractant in the resin which may decrease the rate of the adsorption. On the other hand, there is no adverse effect in the adsorption percentages on Al-DEHP-60. Perhaps the ion exchange of Np(IV) and Np(VI) with Al(III) in Al-DEHP is kinetically more favorable than with proton in H-DEHP.

With the intention of making the time for the procedure shorter, the adsorption on Al-DEHP was examined with the shaking time of 1 min. However, as shown in Table 5, the

adsorption percentages of macro concentration of Np(IV) and Np(VI) did not reach quantitative values, although those at trace concentration reached quantitative values. Since the adsorption percentages on Al-DEHP-75 are larger than on Al-DEHP-60 resin, the rate of adsorption is considered to depend on the amount of Al-DEHP impregnated into the resin.

In conclusion, the adsorption on Al-DEHP-75 resin with the shaking time of 10 min can be used to discriminate Np(IV) and Np(VI) from Np(V) regardless of the concentration of neptunium.

Adsorption on bismuth phosphate

The adsorption behavior of macro ($C_{Np} \cong 10^{-2.5}$ M) and trace ($C_{Np} \sim 10^{-10}$ M) concentrations of Np(IV), Np(V) and Np(VI) on bismuth phosphate precipitate was investigated at acidities 1.0 M and 0.1 M HClO₄. Table 6 shows the adsorption percentages of neptunium in each oxidation state for the shaking time of 10 min. Both macro and trace concentrations of Np(IV) are quantitatively adsorbed on bismuth phosphate precipitate at acidities 1.0 M and 0.1 M HClO₄. On the other hand, Np(V) and Np(VI) are not adsorbed under these conditions. The difference between the precipitation of (BiPO₄-1) and (BiPO₄-2) has no influence upon the adsorption behaviour of neptunium. Thus, it is better to adopt (BiPO₄-2) preparation method since larger amount of precipitate is formed than in (BiPO₄-1) and a commercial

Table 5. The adsorption of Np(IV), Np(V) and Np(VI) on the impregnated resins (3).

	Acidity: 1 M HClO ₄ , Shaking time: 1 min					
	Np adsorbed/%					
	Np-237, $C_{Np} \cong 10^{-2.5}$ M			Np-239, $C_{Np} \sim 10^{-10}$ M		
	Np(IV) ^a	Np(V)	Np(VI)	Np(IV)	Np(V)	Np(VI)
Al-DEHP-60	19.3	-3.2	61.7	98.1	0.9	97.2
Al-DEHP-75	75.7	-1.8	96.5	97.8	1.1	97.7

a: Np(IV) > 98.6%, Np(V) < 1.4%.

	Acidity: 0.1 M HClO ₄ , Shaking time: 1 min					
	Np adsorbed/%					
	Np-237, $C_{Np} \cong 10^{-2.5}$ M			Np-239, $C_{Np} \sim 10^{-10}$ M		
	Np(IV)	Np(V)	Np(VI)	Np(IV)	Np(V)	Np(VI)
Al-DEHP-60	8.6	-0.6	62.1	98.0	0.1	99.4
Al-DEHP-75	40.8	-0.3	94.6	98.2	2.1	99.4

Table 6. The adsorption of Np(IV), Np(V) and Np(VI) on bismuth phosphate precipitate. Shaking time: 10 min.

	Np adsorbed/%					
	Np-237, $C_{Np} \cong 10^{-2.5}$ M			Np-239, $C_{Np} \sim 10^{-10}$ M		
	Np(IV) ^a	Np(V)	Np(VI)	Np(IV)	Np(V)	Np(VI)
	1 M HClO ₄					
BiPO ₄ -1	98.2	1.6	0.5	98.9	1.5	1.8
BiPO ₄ -2	98.6	0.7	0.0	99.4	1.9	2.4
	0.1 M HClO ₄					
BiPO ₄ -1	98.7	1.7	0.5	99.5	0.9	4.4
BiPO ₄ -2	98.7	2.0	2.4	100	0.6	3.7

a: Np(IV) > 98.6%, Np(V) < 1.4%.

Table 7. Adsorption behavior of neptunium on the impregnated resin and BiPO₄.

	IV	V	VI
Al-HDEHP impregnated resin	O	X	O
Bismuth phosphate precipitate	O	X	X

phosphoric acid reagent can be used directly for the preparation of precipitate. In conclusion, the adsorption on bismuth phosphate precipitate with the shaking time of 10 min can be used to discriminate Np(IV) from Np(V) and Np(VI) regardless of the concentration of neptunium.

Discrimination of Np(IV), Np(V) and Np(VI)

Table 7 summarizes the adsorption behavior of neptunium (IV), (V) and (VI) onto Al-DEHP impregnated resin and bismuth phosphate precipitate, where 'O' and 'X' represent the quantitative adsorption ($\geq 98\%$) and quantitative non-adsorption ($\leq 4\%$), respectively, at the concentrations of $10^{-10} \leq C_{Np} \leq 10^{-2.5}$ M. Table 7 indicates that the combination of the adsorption onto the impregnated resin and the adsorption onto the bismuth phosphate precipitate makes possible to distinguish between Np(IV), Np(V) and Np(VI) in a wide range of neptunium concentrations.

Conclusion

This study develops a simple neptunium redox speciation method that is composed of adsorption reactions using the impregnated resin and the bismuth phosphate precipitate as adsorbent. Since uranium and plutonium behave similarly to neptunium, the present method is expected to be able to be applied also to the discrimination of the oxidation states of uranium and plutonium. The operation can be conducted in a simple manner with a small volume (500 μ l) of the sample in the filter unit. The adsorbent, Al-DEHP impregnated resin or bismuth phosphate precipitate can be prepared in advance and separately from the radioactivity handling. The main separation process is composed of sample addition, shaking and centrifugation with using the small size filter unit. These handlings can be carried out in a simple and compact manner such as needed for experiments in a glove box system. The procedure developed in this study needs a rather long shaking time of 10 min due to the slower rate of

the solid-liquid distribution as compared with liquid-liquid distribution. However, since the existence of unnecessary chemical reagents in the aqueous solution is avoided with using the solid adsorbents, there observed no shift in the oxidation state of neptunium during the separation procedure.

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