

이온크로마토그래피에 의한 PuO_2^{2+} , Pu^{4+} 및 Pu^{3+} 의 분리

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Separation of PuO_2^{2+} , Pu^{4+} and Pu^{3+} by Ion Chromatography

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요 약. 이온크로마토그래피를 이용하여 Pu 화학종의 분리방법을 검토하였다. 환원제(KI, NaNO_2) 또는 산화제(KBrO_3)를 사용하여 Pu의 산화수를 조절한 후 1-octanesulfonate 와 α -HiBA 용리액을 사용하는 동적계에서 PuO_2^{2+} , Pu^{4+} 및 Pu^{3+} 의 화학종을 각각 안정하게 개별분리하였다. Iodide와 nitrite 를 동시에 사용하여 Pu 화학종들을 Pu^{3+} 까지 환원한 다음 이온크로마토그래피로 안정하게 분리하였다.

ABSTRACT. Separation of plutonium species was studied by ion chromatography installed in a glove box for the determination of plutonium element. The plutonium species, PuO_2^{2+} , Pu^{4+} and Pu^{3+} , were stably separated on dynamically equilibrated cation exchanger using 1-octanesulfonate and α -HiBA eluant after controlling the plutonium oxidation states with KI, NaNO_2 or KBrO_3 based on the oxidation-reduction potentials. For the separation of plutonium from other matrix, PuO_2^{2+} and Pu^{4+} were reduced to Pu^{3+} with KI and NaNO_2 followed by cation exchange chromatography.

INTRODUCTION

Separation of plutonium species was studied by ion chromatography in order to determine each species in the solution. Generally, plutonium speciation is performed by the methods such as spectrophotometry, potentiometry, ion exchange technique and solvent extraction method.¹ The plutonium species complexed with ligand can be identified by a characteristic UV-Visible absorption spectra of the plutonium complexes. Potentiometry is also used for the determination of each species by measurement of the oxidation-reduction potential. Solvent extraction and ion exchange technique are mostly applicable to the separation of each species by controlling the oxidation states. Tetravalent plutonium is extracted into tributylphosphate (TBP) phase after treatment of PuO_2^{2+} with nitrite ion. The extracted plutonium is back-extracted from TBP by reduction to the trivalent

state with ferrous sulfamate.¹ However, ion exchange chromatography has an advantage to separate the chemical species simultaneously compared to solvent extraction. Anion exchange chromatography has been reported being effective for the separation of plutonium from other elements in high concentration of hydrochloric acid.² Negatively charged plutonium(VI) complexes with chloride are adsorbed on anion exchange column at $\text{pH} < 1$. The plutonium species adsorbed are individually separated after selective reduction by iodide ion on the column. Separations of plutonium species by ion chromatography were reported^{3,4} for the separation of each species such as Pu(VI), Pu(IV) and Pu(III). However, three species were not separated at the same time. In this experiment, high performance liquid chromatography using cation exchanger was chosen for the separation of these species because anion

exchange chromatography is tedious and time-consuming. However, metallic components of HPLC system are likely to be damaged by high concentration of acid medium. Consequently, the eluant of low concentration of acid is preferred for this purpose on cation exchange column. Equilibrated cation exchange column using 1-octanesulfonate as an ion exchanger was used because this system can give an advantage to control ion exchange capacity otherwise the ion exchange capacity can be gradually decreased by radiolysis of functional group.⁵

In this study three plutonium species are individually and simultaneously separated by cation exchange ion chromatography after controlling the oxidation states of plutonium species with reductants prior to sample injection so that one of the plutonium species can be used for burnup measurement in irradiated nuclear fuels if it is purely separated from other elements.

EXPERIMENTAL

Reagents and Apparatus. Solvent delivery pump was SP 8800 of Spectra-physics Co. consisting of Rhedyne injection valve with 20 μL sample loop. UV/Vis detector of Waters Associates M481 was used for the detection of metal elements at 651 nm by post-column reaction with coloring reagent delivered from LC-5000 syringe pump(ISCO Co.). An integrator of SP 4270 of Spectraphysics Co. was used. The elements in samples were separated by a reversed phase column LC-18(15 cm L \times 0.46 cm ID, 5 μm pore size) and collected by a solenoid valve(Cole-Parmer Inst. CP#N-01367-7230), respectively. α -hydroxyisobutyric acid(α -HiBA)(Aldrich Co.) and 1-octanesulfonate(Aldrich Co.) were used as an eluant and an ion exchanger, respectively, for the dynamically equilibrated cation exchange system. PuO_2^{2+} stock solution was prepared by dissolving 4 g of PuO_2 powder(ORNL, Pu-242) with (1+1) HNO_3 -0.01 M HF solution and diluted to 50 mL. This solution was diluted to 6 μg Pu/mL for standard solution. Coloring reagent was Arsenazo III(2.2-[1.8-dihydroxy-3.6-disulfo-

2.7-naphthalene-bis-(azo)] dibenzene arsonic acid) (Merck GR) for post-column reaction.

Ion Chromatographic System. Ion chromatographic system consisting of a separating column, an injection valve and a solenoid valve was installed inside a glove box.⁶ A solvent delivery pump, an integrator, a syringe pump and a detector were installed outside the glove box. The analytes separated on the column passed through the detector and re-entered into the glove box and were stored for waste disposal. A visible line of 651 nm was selected for the detection of plutonium in ion chromatography by post-column reaction using Arsenazo III as a coloring reagent. The plutonium fraction collected using solenoid valve was identified by α -spectrometric method.

Control of Plutonium Oxidation States.

About 2 mL of PuO_2^{2+} solution(6 ppm) in (1+1) HNO_3 medium was dried on hot plate. The residue was dissolved with 10 mL of 0.1 M HCl and with about 0.1 g of granular KBrO_3 to oxidize plutonium of any lower oxidation state. This solution was chromatographed by α -HiBA eluant to give only a oxidized plutonium peak, PuO_2^{2+} , at the retention time of 1.7 min as shown in Fig. 1. For the reduction treatment, the dried residue of nitric acid medium solution was dissolved by addition of

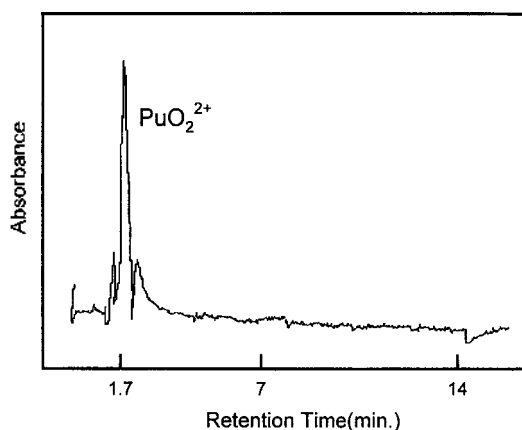


Fig. 1. Chromatogram of PuO_2^{2+} by α -HiBA Eluant. Column: C18(15 cm L \times 0.46 cm ID), Eluant: 0.0225 M α -HiBA/0.01 M 1-Octanesulfonate, pH 3.80, Flow Rate: 1.0 mL/min. Detection: Arsenazo III, 651 nm by Post-Column Reaction, Sample Loop: 20 μL .

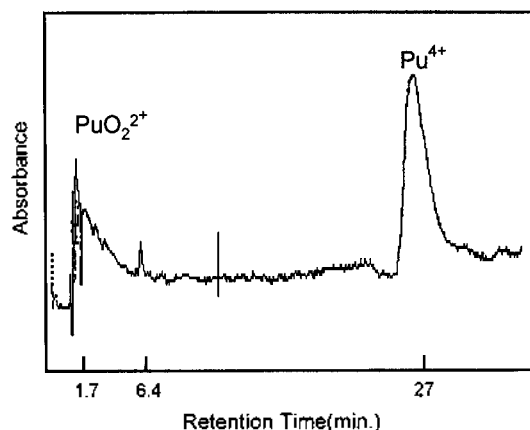


Fig. 2. Chromatogram of plutonium species produced by hydrogen iodide reduction treatment. Column: C18(15 cm L×0.46 cm ID), Eluant: 0.0225 M α -HiBA/0.01 M 1-Octanesulfonate, pH 3.80, Flow Rate: 1.0 mL/min. Detection: Arsenazo III, 651 nm by Post-Column Reaction, Sample Loop: 20 μ L.

5 mL of 6 M HCl and 1 mL of concentrated HI and dried again. The dried residue was redissolved by 0.1 M HCl solution. This solution was also chromatographed as shown in Fig. 2. In Fig. 2, two peaks were separated at the retention times of around 6 min. and 27 min., respectively.

In order to identify these peaks, excess amount of KI (~0.2 g) was added at the final dissolving step with 0.1 M HCl at the above procedure. This solution was injected into the column. Two different peaks appeared at 27 min. and 32 min. as shown in Fig. 3. Both of the peaks were gradually increased at each injection as a function of time after reduction treatment until about one hour. As a next step, a nitrite ion effect was studied on plutonium oxidation states. The plutonium solution of 0.1 M HNO₃ medium was dried on hot plate. The residue was dissolved with 5 mL of 0.4 M HCl and small amount of granular NaNO₂. This solution was dried again. The residue was redissolved with 5 mL of 0.4 M HCl and 2 mL of 0.1 M KI. The final solution was injected into the column (Fig. 4). Finally for the quantitative reduction to Pu³⁺, 2 mL of PuO₂²⁺ (6 ppm) in nitric acid medium was dried on hot plate. 5 mL of 0.1 M HCl and about 0.2 g of NaNO₂ were added to

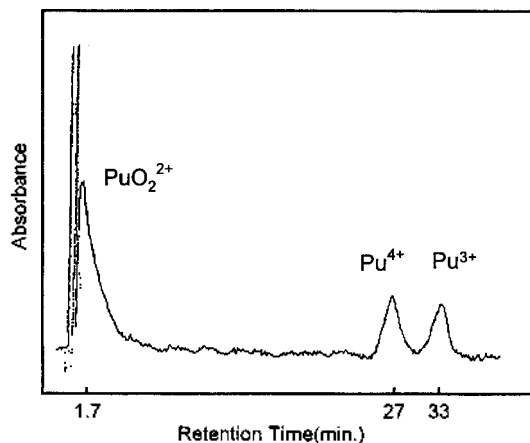


Fig. 3. Chromatogram of plutonium species reduced by iodide treatment. Column: C18(15 cm L×0.46 cm ID), Eluant: 0.0225 M α -HiBA/0.01 M 1-Octanesulfonate, pH 3.80, Flow Rate: 1.0 mL/min. Detection: Arsenazo III, 651 nm by Post-Column Reaction, Sample Loop: 20 μ L.

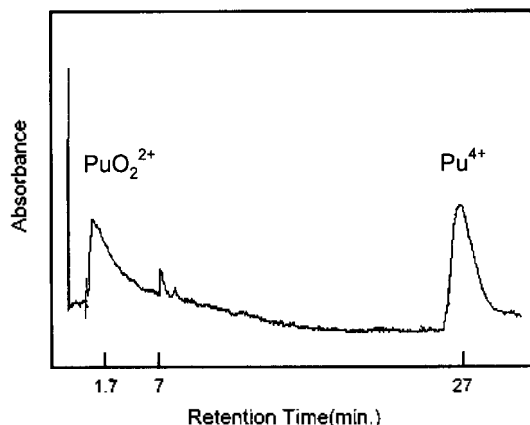


Fig. 4. Chromatogram of Pu species reduced by sodium nitrite reductant. Column: C18(15 cm L×0.46 cm ID), Eluant: 0.0225 M α -HiBA/0.01 M 1-Octanesulfonate, pH 3.80, Flow Rate: 1.0 mL/min. Detection: Arsenazo III, 651 nm by Post-Column Reaction, Sample Loop: 20 μ L.

the residue for dissolution and valency adjustment. This solution was dried again, and the residue was redissolved with 5 mL of 0.4 M HCl and an excess of KI (~0.2 g). The final solution was chromatographed to have a peak at 33 min. as shown in Fig. 5.

RESULTS AND DISCUSSION

Control of plutonium oxidation states by chemi-

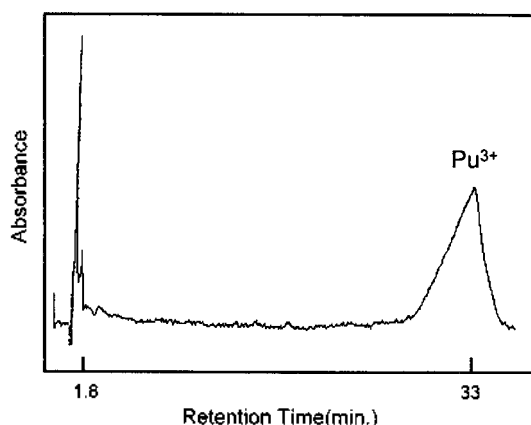


Fig. 5. Chromatogram of Pu^{3+} reduced by sodium nitrite and potassium iodide. Column: C18(15 cm L \times 0.46 cm ID), Eluant: 0.0225 M α -HiBA/0.01 M 1-Octanesulfonate, pH 3.80, Flow Rate: 1.0 mL/min. Detection: Arsenazo III, 651 nm by Post-Column Reaction, Sample Loop: 20 μ L.

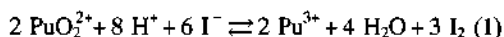
cal reagents was studied for the separation of plutonium species by ion chromatography. Separation of plutonium species was tried by cation exchange ion chromatography using α -HiBA eluant based on the stability constants of these species with different ligands^{7,8,9}(Table 1). α -HiBA was used as a complexing agent because it has been successfully used for the separation of lanthanide and actinide elements by ion chromatography.⁵ Generally, the reductants such as I^- ,

Table 1. Stability Constants of Pu-Ligand Complexes^{1,7,8,9}

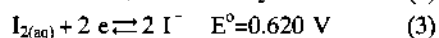
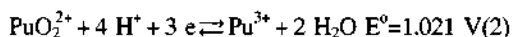
Species	$\log\beta_1$	$\log\beta_2$	$\log\beta_3$	Condition*
PuO_2^{2+}	3.04	5.00	5.00	1
Pu^{3+}	2.60	4.57	4.57	1
PuO_2^{2+}	6.63	11.46	11.46	2
Pu^{4+}	8.75	16.9	16.9	2
Pu^{4+}	5.3	9.0	9.0	3
Pu^{3+}	2.02	3.34	3.34	3
Pu^{3+}	-0.10 ± 0.05			4
Pu^{3+}	0.10 ± 0.05			5
Pu^{3+}	1.3 ± 0.1			6
Pu^{4+}	0.15 ± 0.1			4
Pu^{4+}	0.4 ± 0.2			5
Pu^{4+}	2.0 ± 0.5			6

*1: α -HiBA, 2: Oxalic acid, $\mu=1$ M, 20 $^\circ$ C, 3: Acetic acid, $\mu=2$ M, 20 $^\circ$ C, 4: Cl^- , $\mu=1$ M, 25 $^\circ$ C, 5: Cl^- , $\mu=0.5$ M, 25 $^\circ$ C, 6: Cl^- , $\mu=0$ M, 25 $^\circ$ C

NO_2^- , Fe^{2+} , H_2O_2 have been used for the reduction of PuO_2^{2+} to Pu^{3+} . The reductants^{3,10} such as hydroquinone, I^- , $\text{NH}_2\text{OH}\cdot\text{HCl}$ are used for the reduction of Pu^{4+} to Pu^{3+} . At a certain condition all plutonium oxidation states can be existed simultaneously because its oxidation-reduction potentials are similar one another.³ One of the reduction equations of PuO_2^{2+} by I^- is as follows.

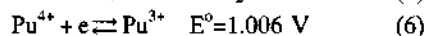
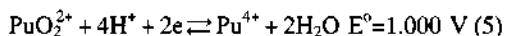


The reaction equation (1) was derived from the reaction (2) and (3), and the equilibrium constant (K) of the reaction (1) can be calculated from the Nernst equation (4) using standard reduction potentials of PuO_2^{2+} and I_2 in equation (2) and (3).



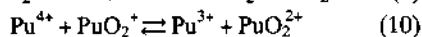
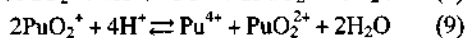
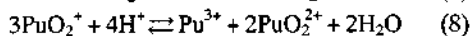
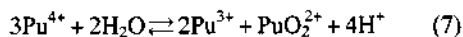
$$E = E^\circ - (RT/nF) \ln K \quad (4)$$

The equilibrium constant(K) calculated from the reaction (1) was 5.13×10^{40} . This means that the reduction of PuO_2^{2+} by I^- undergoes thermodynamically spontaneous reaction, and the PuO_2^{2+} is quantitatively reduced to Pu^{3+} .



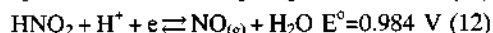
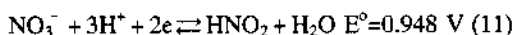
The reduction of PuO_2^{2+} to Pu^{4+} by I^- was also predicted by calculation of an equilibrium constant using equation (3), (4) and (5). In this case the equilibrium constant(K) was 7.2×10^{12} . This value also means that the reduction occurs spontaneously even though the value is smaller than that of equation (1). Accordingly, controlling of plutonium oxidation states was performed based on the above results. First of all, plutonium was oxidized by bromate to identify the oxidized species. Only a PuO_2^{2+} peak appeared as shown in Fig. 1. This means that all the plutonium species were oxidized by bromate to PuO_2^{2+} at earlier retention time. In the reduction treatment, two chromatograms by treatments with HI and excess amount of KI, respectively, were obtained as shown in Fig. 2 and Fig. 3. Based on the Fig. 2 and Fig. 3, it is supposed that the peak at 27 min. seems to be Pu^{4+}

and the peak at 32 min. be Pu^{3+} based on the reduction conditions in this experiment and the stability constants in Table 1. It is reported^{1,3} that a charge density of plutonium species decreases as following order; $\text{Pu}^{4+} > \text{PuO}_2^{2+} > \text{Pu}^{3+}$, so the stability constants with α -HiBA also decrease with the same order. The elution order of the chemical species in ion chromatography depends on the competition between complexing force in the eluant and attraction force with ion exchanger on the stationary phase. PuO_2^{2+} is thought to be eluted earlier than Pu^{4+} in this experiment because PuO_2^{2+} is more weakly adsorbed on the surface of ion exchanger due to steric effect even though it complexes more weakly with complexing agent in the eluant (Table 1). Pu^{4+} seems to be eluted earlier than Pu^{3+} because Pu^{4+} complexes more strongly with eluant than Pu^{3+} , and the complexing force in the eluant is dominant effect compared to attraction force with ion exchanger. The peak at around 6 min. in Fig. 2 is presumed to be PuO_2^+ , but not clear by this experiment. These results suggest that PuO_2^{2+} is continuously reduced to Pu^{4+} and Pu^{3+} by I^- . The relative peak height of PuO_2^{2+} over Pu^{4+} in Fig. 3 was shown higher than that in Fig. 2. This means that PuO_2^{2+} in Fig. 3 was not sufficiently reduced to lower oxidation states because of earlier injection compared to in Fig. 2. However, stoichiometric study on plutonium reduction was not performed in this experiment. Four kinds of plutonium species such as Pu^{3+} , Pu^{4+} , PuO_2^+ and PuO_2^{2+} were reported to exist at the same time due to disproportionation reaction and slow reaction between bonding and cleavage of metal-oxygen.¹ That is, the plutonium species are not quantitatively reduced to Pu^{3+} by only I^- because of disproportionation reaction as follows.

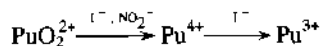


Consequently, the effect of nitrite, NaNO_2 , was additionally studied as well as I^- . A nitrite ion, NO_2^- , plays a role to oxidize Pu^{3+} to Pu^{4+} and to

reduce PuO_2^{2+} to Pu^{4+} as a valence adjuster¹ because the oxidation and reduction potentials are almost same as shown in equation (11) and (12). In Fig. 4, the peak of Pu^{4+} was obtained by nitrite treatment.



This phenomenon means that small amount of KI and NaNO_2 can reduce PuO_2^{2+} to Pu^{4+} . This result is similar to that in Fig. 2. Finally, all the plutonium species, PuO_2^{2+} and Pu^{4+} , were reduced to Pu^{3+} by extreme condition such as both of a nitrite and an excess of iodide as shown in Fig. 5. This means that NaNO_2 and excess amount of KI reduced all the plutonium species to Pu^{3+} quantitatively. That is, Pu^{4+} reduced by NaNO_2 is reduced again to Pu^{3+} by I^- as following sequence. The Pu^{3+} reduced in this condition was stable and not oxidized to a higher oxidation state. In this reduction step of Pu^{4+} to Pu^{3+} the equilibrium constant ($K = 1.15 \times 10^{13}$) was calculated from equation (3) and (6). This large equilibrium constant confirms that the reduction reaction is also thermodynamically spontaneous and the reduced Pu^{3+} species is stable.



CONCLUSION

The reduction of PuO_2^{2+} and Pu^{4+} to Pu^{3+} by I^- or NO_2^- was proved to be spontaneous reaction based on the equilibrium constants. Three plutonium species such as PuO_2^{2+} , Pu^{4+} and Pu^{3+} were stably separated by dynamically equilibrated cation exchange. In the case of PuO_2^{2+} treatment with iodide ion, two species, Pu^{4+} and Pu^{3+} , co-existed. Using NaNO_2 with excess of KI, all plutonium species were quantitatively reduced to Pu^{3+} which was stably separated on the column and also makes it allow to separate plutonium element from interfering matrix. The chromatographic separation in this study will be much easily applicable to the speciation of plutonium oxidation states compared

to other methods such as potentiometry and spectrophotometry.

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