Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Desorption Behavior of Plutonium from Anion-Exchange Resin with HNO_3-HI Mixed Acid Solution

Shigekazu Usuda[a]; Satoshi Sakurai[a]; Masaru Hirata[b]; Hirokazu Umezawa[c]
[a] Department of Fuel Safety Research, Japan Atomic Energy Research Institute, Ibaraki-Ken, Japan [b] Department of Administrative Services, Japan Atomic Energy Research Institute, Ibarakiken, Japan [c] Department of Radioisotopes, Japan Atomic Energy Research Institute, Ibaraki-Ken, Japan

To cite this Article Usuda, Shigekazu , Sakurai, Satoshi , Hirata, Masaru and Umezawa, Hirokazu(1990) 'Desorption Behavior of Plutonium from Anion-Exchange Resin with HNO_3-HI Mixed Acid Solution', Separation Science and Technology, 25: 11, 1225 — 1237

To link to this Article: DOI: 10.1080/01496399008051850

URL: http://dx.doi.org/10.1080/01496399008051850

SEPARATION SCIENCE AND TECHNOLOGY, 25(11 & 12), pp. 1225–1237, 1990

Desorption Behavior of Plutonium from Anion-Exchange Resin with HNO_3–HI Mixed Acid Solution

SHIGEKAZU USUDA and SATOSHI SAKURAI
DEPARTMENT OF FUEL SAFETY RESEARCH
JAPAN ATOMIC ENERGY RESEARCH INSTITUTE
TOKAI-MURA, NAKA-GUN, IBARAKI-KEN 319-11, JAPAN

MASARU HIRATA
DEPARTMENT OF ADMINISTRATIVE SERVICES
JAPAN ATOMIC ENERGY RESEARCH INSTITUTE
OARAI-MACHI. HIGASHI-IBARAKI-GUN, IBARAKIKEN 311-13, JAPAN

HIROKAZU UMEZAWA
DEPARTMENT OF RADIOISOTOPES
JAPAN ATOMIC ENERGY RESEARCH INSTITUTE
TOKAI-MURA, NAKA-GUN. IBARAKI-KEN 319-11, JAPAN

Abstract

The effect of HI on the desorption behavior of Pu from strongly basic anion-exchange resin in HNO_3 solutions was investigated. The desorption of Pu increased with increasing concentration of HNO_3 in HNO_3–HI mixed acid solutions. On the other hand, it was difficult to elute Pu with the mixed acid solution containing more than 2.5 *M* HNO_3 since HI decomposed vigorously in the resin column as the HNO_3 concentration increased. The valence state of Pu in the effluent was a mixture of tri- and tetra-valences. The mixed acid solution, 1 *M* HNO_3–0.1 *M* HI, was found to be adequate as an eluent for effective desorption of Pu from the anion-exchange resin in HNO_3 media. Purification procedures for Pu were developed for both micro- and macroamounts.

INTRODUCTION

For the separation and purification of Pu, anion-exchange methods have often been applied (*1–9*). Anion-exchange with HCl solutions enables the separation of Pu quantitatively for analytical purposes (*1–6*), but it is undesirable to operate in a glove box made of stainless steel due to the corrosiveness of HCl. The anion-exchange method with HNO_3 solutions has been also used for the purification process of macroamounts of Pu in a glove box (*3–9*). In such a process, quantitative recovery of Pu from the column is difficult due to the following reasons: The Pu(IV) ions adsorb strongly on the anion-exchange resins in HNO_3 solution ($K_d > 10^3$) at moderate concentrations of HNO_3 (*10*), and in low HNO_3 concentrations the hydroxide precipitation of Pu might occur in the resin phase even though the K_d values become smaller (*9*, *11*). To recover all the Pu by anion-exchange with the only solutions of HNO_3, an extremely large volume of eluent is required.

Since Pu(III) does not adsorb on the resin (*10*), reducing Pu(IV) to Pu(III) leads to effective recovery of Pu. Solutions of 9–12 *M* HCl containing 0.1 *M* HI have been used as the eluent to achieve quantitative separation (*3*). Dilute solutions of HCl or HNO_3 containing reducing agent of Pu, such as $NH_2OH \cdot HCl$ or $FeSO_4$, have also been used. The latter eluents frequently have problems, such as disturbed flow of the eluent due to gassing and the introduction of metal-ion impurities from the reducing reagents.

In this work, HI was employed in the HNO_3 eluent as an alternative reducing agent which could be easily eliminated by evaporation. The effective desorption of Pu from an anion-exchange resin in HNO_3 solution was examined for the elution of trace and macroamounts of Pu.

EXPERIMENTAL

Materials

Glass columns of 1-mL capacity (ϕ 4 mm × 8 cm) were used, and they were usually packed with a strongly basic anion-exchange resin, MCI GEL CA08P or DIAION SA#100 (Mitsubishi Chemical Industries Ltd., 8% crosslinking, 100–200 mesh, anion-exchange capacity > 1.2 meq/mL). Some other anion-exchange resins, DOWEX 1-X4 (4% crosslinking, 100–200 mesh) and BIORAD AG MP-1 (macroporous type, 100–200 mesh), were also used for comparison. All resins were thoroughly washed with concentrated HCl, distilled water, and 7 *M* HNO_3 before use.

Hydroiodic acid, HI (55–58%), and nitric acid, HNO_3 (60–62%), were used as eluents. Hydroxylamine hydrogen chloride ($NH_2OH \cdot HCl$), nitrogen dioxide gas (NO_2), and hydrogen peroxide (H_2O_2) were used as redox agents of Pu. All chemicals were of reagent grade and used without further purification.

For experiments with microamounts of Pu, Pu extracted from spent fuel specimens was used. It was dissolved in concentrated HNO_3 solution and adjusted to the tetra-valence state by redox treatment with concentrated HNO_3 and $NH_2OH \cdot HCl$ (*3*). Aged plutonium oxide powder (PuO_2) was used as the source for macroamounts of Pu samples, and it was dissolved in 4 *M* HNO_3 solution by oxidizing with electrolytically generated Ag^{2+} (*13*) and prepared as Pu(IV) by introducing NO_2 gas at 40°C (*14*).

Uranium tracer, ^{237}U, was prepared by the $^{238}U(r,n)$ reaction on a U target followed by purification by anion-exchange with HCl solutions and solvent extraction with 20% TBP–CCl_4 at 7 *M* HNO_3.

Measurements of Activity and Valence States

In the experiment for microamounts of Pu, a drop or an aliquot of effluent was mounted on a Ta disk (ϕ 24 mm × 0.05 mm thick). The alpha-ray spectrum was measured with a Si-surface barrier detector and gross α counting with a 2 π-gas-flow-proportional counter.

In the experiment eluting macroamounts of Pu, 1 mL of effluent was taken into a glass tube and measured for the Pu concentration by γ-ray spectrometry on the γ-rays of 129 keV for ^{239}Pu and 149 keV for ^{241}Pu with a high-purity Ge coaxial detector (EG&G ORTEC, Inc., LO-AX detector) at constant geometry.

An optical waveguide spectrum analyzer (Guided Wave, Inc., Model 200), which is based on the light transmission capabilities of broadband fiber optics, was used for measurement of the absorption spectrum of Pu (400–900 nm). The valence state of Pu was directly detected with the fiberhead dipped into sample solutions.

RESULTS AND DISCUSSION

Desorption of Microamounts of Pu (μg order)

Figure 1 shows fractions of Pu eluted from a 1-mL column of anion-exchange resin (DIAION SA#100) with HNO_3 solutions of various concentrations with and without 0.1 *M* HI. In this experiment, Pu adjusted to tetra-valence was charged to the resin column and washed with 30 column bed volumes (CV) of 4 *M* HNO_3 solution. Desorbed fractions of Pu with HI-free solutions decreased with increasing HNO_3 concentration. About 90% of Pu was eluted with 35 CV of 0.1 *M* HNO_3 solution, but the Pu might form an insoluble tetra-valent polymer in the resin phase and/or hydrolyze in the effluent (*9*, *11*). To avoid such polymerization and/or hydrolysis, it is necessary to keep the HNO_3 concentration in the eluting solution at least 0.3 *M* or higher. With 35 CV of 1 *M* HNO_3 solution, only

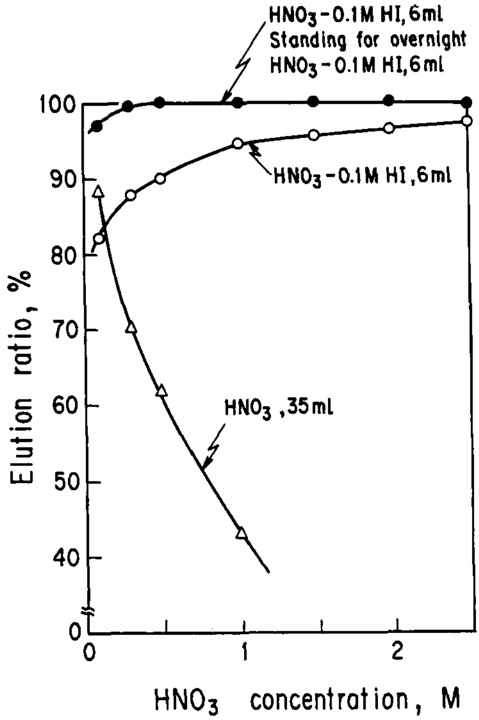

FIG. 1. Fractions of Pu eluted from the anion-exchange resin column with HNO_3 solutions of various concentrations with and without 0.1 *M* HI included. (DIAION SA#100: 1 mL, at room temperature.)

43% of Pu was recovered. On the other hand, more than 90% of Pu was eluted with 6 CV of 0.5 *M* or higher concentrations of HNO_3 containing 0.1 *M* HI. The recovery yields increased with increasing HNO_3 concentration. Complete elution was attained only in the case where 6 CV of HNO_3 containing 0.1 *M* HI was first added to the column and allowed to stand overnight. Then elution was repeated with 6 CV of the same solution at HNO_3 concentrations of 0.5 to 2 *M*.

Figure 2 shows the elution curves of Pu with 0.1, 1.0, 2.0, and 2.5 *M* HNO_3 solutions containing 0.1 *M* HI. Tailing was remarkable in the 0.1 *M* HNO_3–0.1 *M* HI solution. There was a dark purple color at the top of the column, indicating that the deposition of decomposition products of HI increased with increasing HNO_3 concentration. At HNO_3 concentrations over 2.5 *M*, the eluent flow was blocked by bubbles from HI decomposition. From measurements of the gross α activity on the ashed resin of

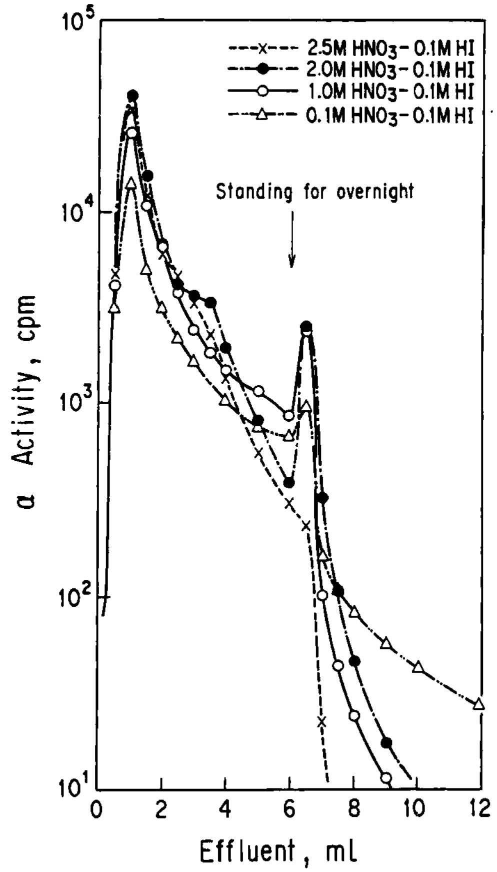

FIG. 2. Elution curves for microamounts of Pu with 0.1, 1, 2, and 2.5 *M* HNO_3 solutions containing 0.1 *M* HI after washing the column with 30 CV of 4–7 *M* HNO_3 solutions. (DIAION SA#100: 1 mL, at room temperature.)

each column, it was confirmed that the remaining Pu on the resin column was less than 0.2%.

Desorption of macroamounts of Pu (mg order)

Fifteen milligrams of tetra-valence Pu prepared in 4 *M* HNO_3 solution was transferred to a 1-mL column. About 40% of the capacity of the column was loaded with the Pu, giving a green color. The column was washed with 5 CV of the solution to eliminate more than 99% of the ^{241}Am from the column. When 1 CV of 1 *M* HNO_3–0.1 *M* HI solution flowed down through the column, desorption of Pu was not effective because HI rapidly reacted with the Pu(IV) on the resin and decomposed, coloring the column brown.

To recover Pu effectively from the resin phase, a large portion of Pu was first eluted with 3 CV of 0.3 *M* HNO_3, then the remained small portion (colored pale green) was well desorbed with 6 CV of a 1 *M* HNO_3–0.1 *M* HI solution. The elution profile is shown in Fig. 3. About 97% of Pu in macroamounts was recovered. Further elution with 6 CV of the same solution after the column was allowed to stand overnight resulted in quantitative recovery of the rest of the Pu (about 3%). No γ activity of Pu was observed on the resin, indicating there was less than about 0.03 g Pu/L, corresponded to $\leq$ 0.2% of the total Pu as determined from the lower limit of detection by γ-ray spectrometry.

Valence State of Pu in the Effluents

Figure 4(a) and 4(b) shows the absorption spectra of Pu(III) in 1 *M* HNO_3–0.1 *M* HI and 3.8 *M* HNO_3–0.1 *M* H_2O_2 solutions at room temperature. The upper spectrum was taken within a few seconds after adding HI to a solution of about 3 g Pu(IV)/L in 1 *M* HNO_3. It was observed that the tetra-valence material was rapidly reduced to tri-valence in 1 *M* HNO_3–0.1 *M* HI mixed acid solution. Large absorbance at a wavelength of less

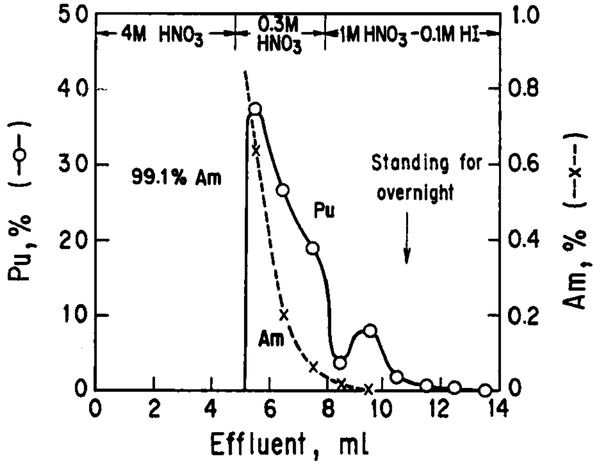

FIG. 3. Elution profile for macroamounts of Pu (14 mg) with 0.3 *M* HNO_3 and 1 *M* HNO_3–0.1 *M* HI solutions. (MCI GEL CA08P: 1 mL, at room temperature.)

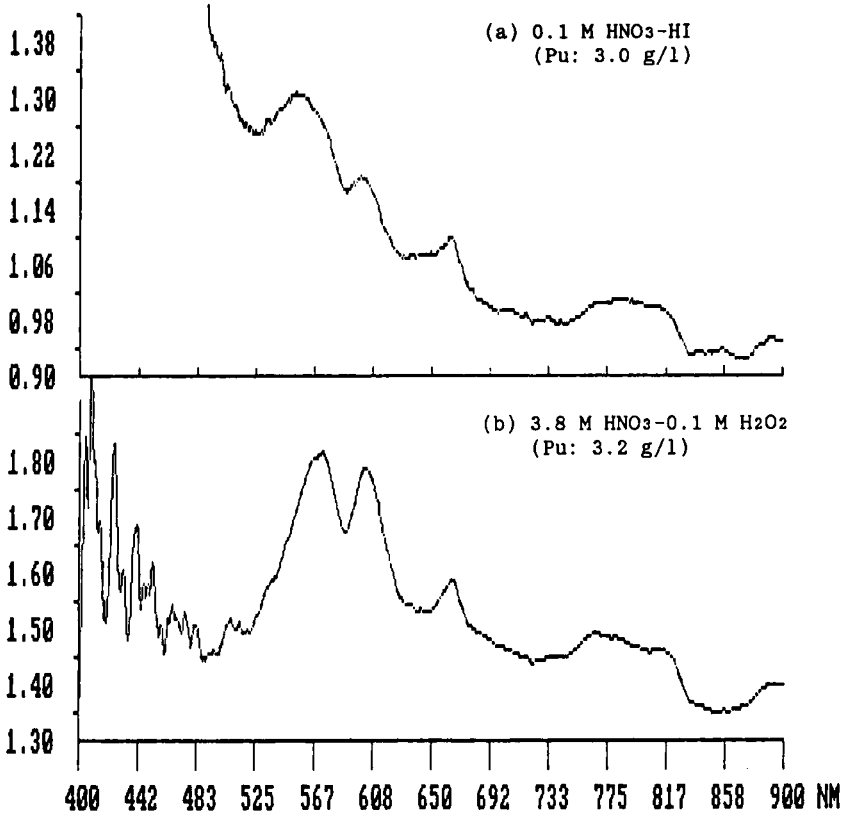

FIG. 4. Absorption spectra of Pu(III) in HNO_3 solution containing reductants at room temperature. (a) 3.0 g/L of Pu in 1 *M* HNO_3–0.1 *M* HI solution. (b) 3.2 g/L of Pu in 3.8 *M* HNO_3–0.1 *M* H_2O_2 solution.

than 600 nm occurred as time passed, owing to an increase in the decomposition products of HI. Therefore, it was difficult to observe the absorption band at 470 nm for Pu(IV). For comparison, a typical absorption spectrum of Pu(III) is shown in Fig. 4(b); it was obtained a few hours later after adding H_2O_2 to the solution.

Most of the Pu in the 0.3 *M* HNO_3 effluent was tetra-valent, as shown in Fig. 5(a), 5(b) and 5(c). Only a very small portion of Pu was detected in Pu(VI) just after the elution (see the 830-nm absorption band in Fig. 5b).

On the other hand, the Pu in the 1 *M* HNO_3–0.1 *M* HI effluent was a mixture of tri- and tetra-valent, as shown in Fig. 6(a), 6(b), and 6(c). It

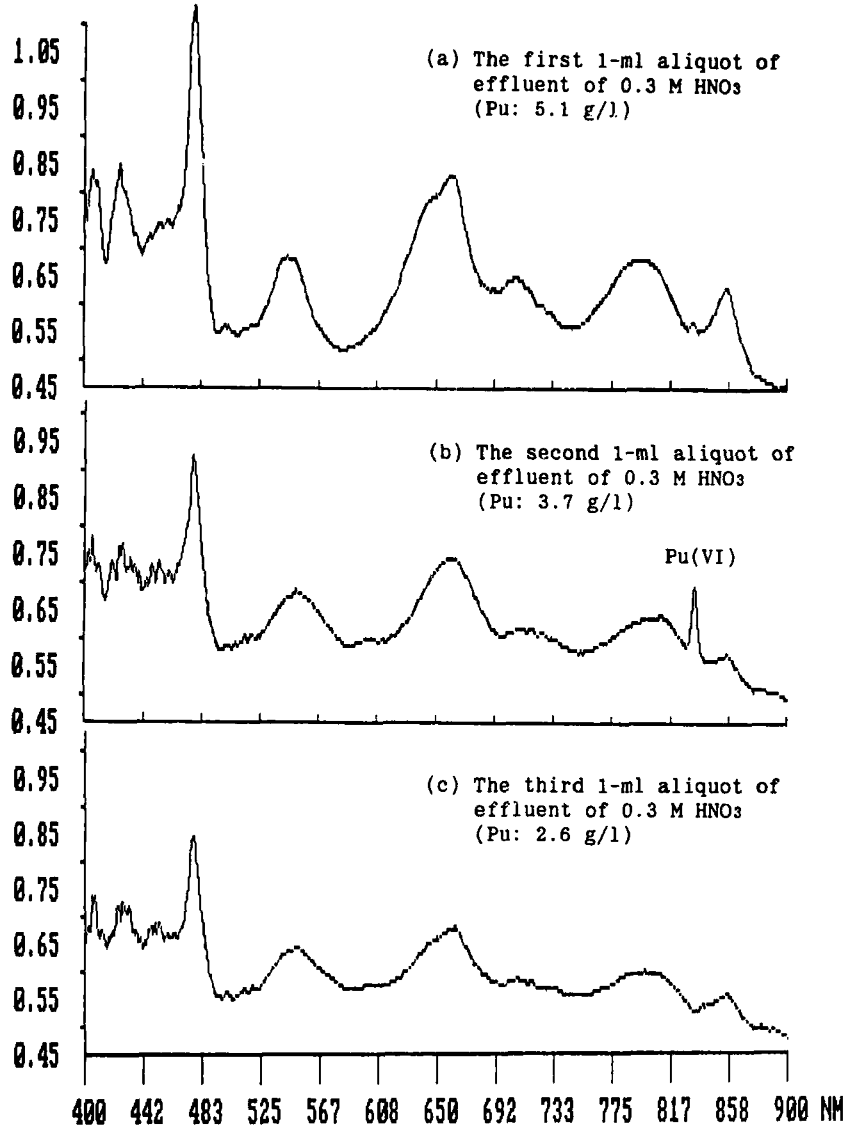

FIG. 5. Absorption spectra of Pu(IV) in 0.3 *M* HNO_3 effluent at room temperature. (a) 5.1 g/L of Pu in the first 1-mL aliquot of effluent. (b) 3.7 g/L of Pu in the second 1-mL aliquot of effluent. (c) 2.6 g/L of Pu in the third 1-ml aliquot of effluent.

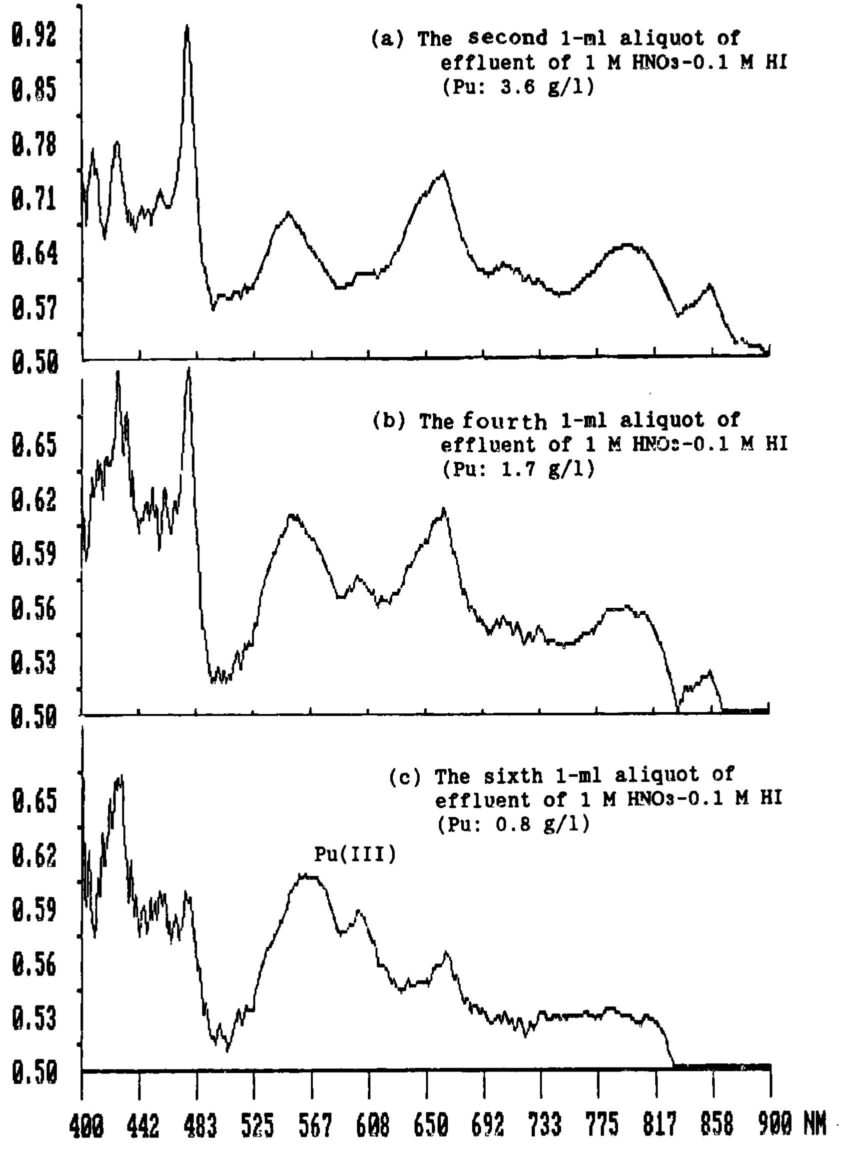

FIG. 6. Absorption spectra of Pu(III) and Pu(IV) in 1 *M* HNO_3–0.1 *M* HI effluent at room temperature. (a) 3.6 g/L of Pu in the second 1-mL aliquot of effluent. (b) 1.7 g/L of Pu in the fourth 1-mL aliquot of effluent. (c) 0.8 g/L of Pu in the sixth 1-mL aliquot of effluent.

was observed that the ratio of Pu(III) to Pu(IV) in the effluent became larger in the latter part of the effluent.

It has been reported that Pu(IV) retained strongly on an anion-exchange resin is desorbed by reducing it to Pu(III) with HCl solutions containing a reducing agent such as HI, NH_4I, $FeSO_4$, and $NH_2OH \cdot HCl$ (*1–8*). In such a system, Pu was first eluted as tetra-valent and later as tri-valent.

The elution behavior may be explained as follows: With macroamounts of Pu, reduction of Pu(IV) to Pu(III) is restricted, and Pu(IV) is gradually eluted in accordance with its decreased K_d value in 1 M HNO_3 during the first part of the elution. Later, Pu(III) in the effluent increases as the reduction of Pu(IV) to Pu(III) proceeds in the resin column.

Purification Procedures of Pu

Based on the above results, purification procedures for Pu by the anion-exchange method with HNO_3 and HNO_3–HI solutions were developed as shown in Fig. 7. To determine the behavior of U, ^{237}U tracer was used for

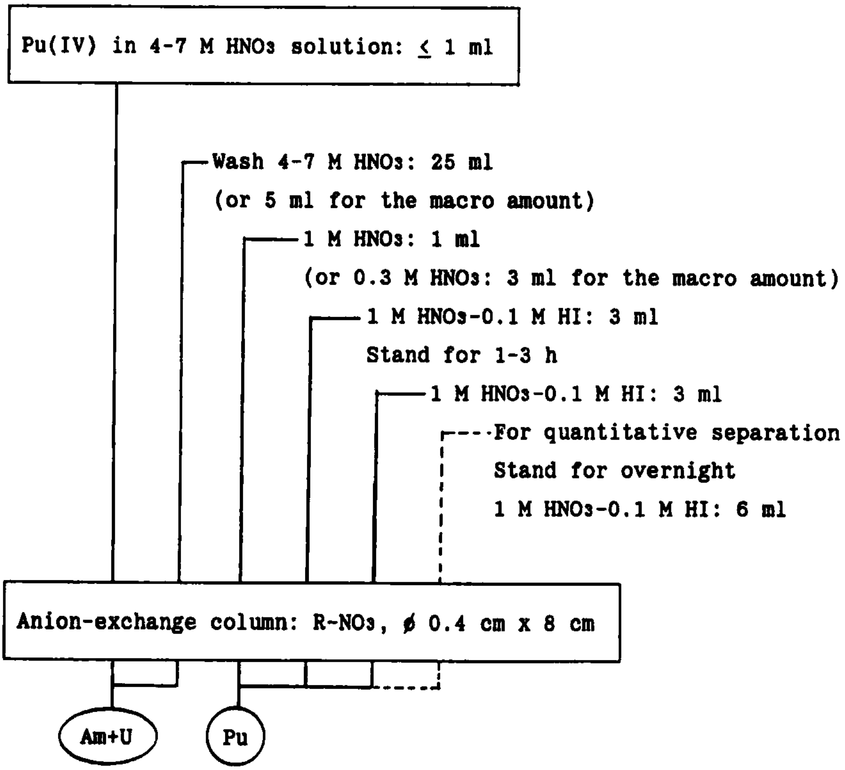

FIG. 7. Puritication procedures for Pu by the anion-exchange method with HNO_3 and HNO_3–HI solutions.

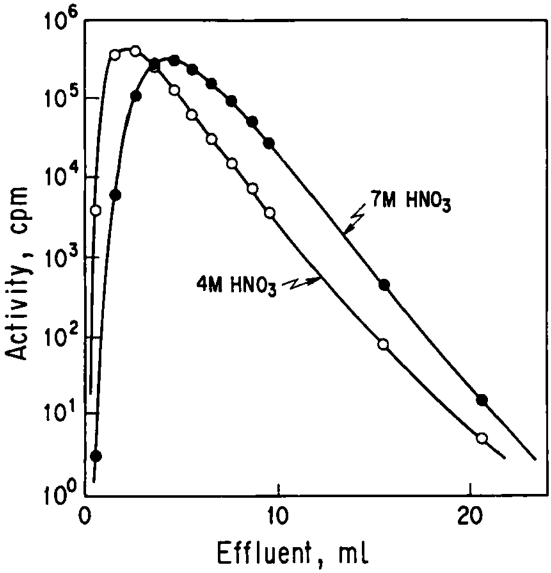

FIG. 8. Elution curves of U with 4 and 7 *M* HNO_3 solutions. (BIORAD AG MP-1: 1 mL, at room temperature.)

elution with 4 and 7 *M* HNO_3 solutions as shown in Fig. 8. More than 99.9% of U could be eliminated from the column with 20 CV of the eluting solutions. Plutonium samples for the isotope dilution method can be obtained from elution with 6 CV of a 1 *M* HNO_3–0.1 *M* HI solution. It is necessary to apply an additional 6 CV of the solution when quantitative recovery of Pu is required.

Unless Pu is completely adjusted to Pu(IV), Pu(III) and Pu(VI) may be eluted with 4–7 *M* HNO_3 (Am + U fraction). As shown in Table 1, only very small amounts of Pu leaked out of the column of DIAION, BIORAD, and DOWEX resin in the first 5-mL elution (Am fraction). However, several percent of Pu leaked in the succeeding elution with 1 *M* HNO_3 (U fraction) from the DIAION resin column but not with BIORAD and DOWEX. This may be due to partial oxidation of Pu(IV) to Pu(VI) on the resin. The elution behavior of microamounts of Pu was well reproduced within about ±2% for repeated runs where all the conditions were kept the same; column conditioning, operating temperature, and the use of freshly prepared HNO_3–HI eluent.

CONCLUSIONS

Desorption of Pu from a strongly basic anion-exchange resin was studied by using HNO_3–HI mixed acid solutions. Plutonium recovery increased

TABLE 1
Elution Distributions of Microamounts of Pu with DIAION, DOWEX, and BIORAD Resin Columns[a]

Effluent	DIAION	DOWEX	BIORAD
Sample solution: 1 ml			
7 *M* HNO_3: 5 mL	0.07 ± 0.01%	0.08 ± 0.01%	0.07 ± 0.01%
7 *M* HNO_3: 25 mL	5.8 ± 1.6	0.004 ± 0.002	0.003 ± 0.001
1 *M* HNO_3: 1 mL			
1 *M* HNO_3–0.1 *M* HI: 3 mL (stand for 1 h)	78.6 ± 1.6	92.6 ± 0.1	84.3 ± 1.9
1 *M* HNO_3–0.1 *M* HI: 3 mL (stand for overnight)	12.1 ± 1.7	6.5 ± 0.1	12.5 ± 1.4
1 *M* HNO_3–0.1 *M* HI: 6 mL	3.3 ± 0.6	0.65 ± 0.01	3.0 ± 0.6
Column	0.17 ± 0.06	0.08 ± 0.02	0.13 ± 0.02

[a] Error: 1σ (*n*: 3–5). DIAION: SA#100 (8% crosslinking, 100–200 mesh). DOWEX: 1-X4 (8% crosslinking, 100–200 mesh). BIORAD: AG MP-1 (macro porous, 100–200 mesh).

with increasing HNO_3 concentration, and HI decomposed vigorously at higher HNO_3 concentrations. The optimum eluting solution for Pu was a 1 *M* HNO_3–0.1 *M* HI mixed acid solution. Desorption conditions were studied for both micro- and macroamounts of Pu, and purification procedures were established. The decomposition products of HI deposited slightly at the top of column, but Pu was successfully purified from more than 99% of Am and U.

The present procedures have the following advantages: complete desorption of Pu from the resin column, use of a relatively small volume of eluents involving simply evaporating and salt-free reagents, and adaptability for the purification of micro- and macroamounts of Pu.

Acknowledgment

The authors are grateful to Mr. S. Wakamatsu of the Department of Fuel Safety Research, JAERI, for his assistance in the measurement of γ-ray and absorption spectra of Pu.

REFERENCES

1. F. Nelson, D. C. Michelson, and J. H. Holloway, *J. Chromatogr.*, *14*, 258 (1964).
2. R. M. Abernathey, G. M. Matlack, and J. E. Rein, IAEA/SM-149/37, 1971.
3. H. Natsume, H. Umezawa, S. Okazaki, T. Suzuki, T. Sonobe, and S. Usuda, *J. Nucl. Sci. Technol.*, *9*, 737 (1972).
4. R. P. Roberts and F. P. Brauer, HW-60552, 1959.

5. *Annual Book of ASTM Standards,* Vol. 12.02, Designation: E321-79, 1987, p. 135.
6. K. Watanabe, *J. At. Energy Soc. Jpn., 11,* 687 (1969).
7. G. M. Allison and R. G. Hart, AECL-1372, 1961.
8. H. C. Hodge, J. N. Stannard, and J. B. Hursh (eds.), *Handbook of Experimental Pharmacology, New Series XXXVI, Uranium, Plutonium, Transplutonic Elements,* Springer Verlag, 1973, p. 569.
9. J. L. Ryan and E. J. Wheelwright, *Ind. Eng. Chem., 51,* 60 (1959).
10. J. P. Faris and R. F. Buchanan, *Anal. Chem., 36,* 1157 (1964).
11. D. B. James, LA-3357, 1965.
12. Y. Suzuki et al., Private Communication, 1980.
13. S. Sakurai, S. Tachimori, J. Akatsu, T. Kimura, Z. Yoshida, H. Mutoh, T. Yamashita, and K. Ohuchi, *J. At. Energy Soc. Jpn., 31,* 1243 (1989).
14. S. Sakurai et al., Unpublished Results.

Received by editor October 3, 1989.