# The Chemistry of Americium. II. The Behavior of Am(III), Am(V), and Am(VI) in Column Chromatography, with Bis(2-ethylhexyl)phosphoric Acid Used as the Extractant

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The behavior of Am(III), Am(V), and Am(VI) in column chromatography with bis(2-ethylhexyl)phosphoric acid(HDEHP) used as the extractant were investigated in comparison with that of Np(IV), Np(V), and Np(VI). When the solution of Am(VI) was submitted to the column chromatography, it was found that Am(VI) was rapidly reduced to Am(V) and partially to Am(III) by HDEHP, irrespective of the conditions, such as the flow rate, the acidity, and the composition and temperature of the influent. The optimum conditions for the separation of Am(V) and Am(III) and for the preparation of the Am(V) solution were established by utilizing the difference in the adsorbability on the column bed between Am(III) and Am(V). When a freshly-prepared Am(V) solution was submitted to column chromatography, it was found that Am(V) was also reduced to Am(III) as well as Am(VI) by HDEHP. The percentage of the Am(V) fraction eluted strongly depended on the conditions in the column chromatography, but it was found to be constant within the limits of experimental error under definite conditions as long as the same column was used. This fact was applied to the determination of the Am(V) content in the mixed solution of Am(III) and Am(V). The content of Am(V) decreased slowly in the nitrate, acetate, sulfate, and perchlorate solutions at lower temperatures, but it rapidly decreased in the chloride, iodide, sulfite, and hydrogen peroxide solutions even at 0 °C. The content of Am(V) decreased more rapidly at higher temperatures, and the kinetic analysis showed that the reduction of Am(V) apparently followed the first-order kinetics in the acetate solutions.

Americium is the heaviest of the actinoid element which are known to have penta- and hexa-valent states. In the solution involving higher concentrations of americium, the disproportionation reaction of Am(V) is remarkable, but it is negligible at lower concentrations of americium. The α-decay of $^{241}$Am leads to the radiolytic reduction of both Am(V) and Am(VI) at rates of 1.2 and 3.1%/h respectively, irrespective of the concentration of $^{241}$Am.[1)] Therefore, the stabilities of Am(V) and Am(VI) must be discussed in connection with the participation of these reactions.

It is well known that Am(VI) is relatively stable in strongly acidic solutions,[2)] but Stokely and Moore have reported that the addition of an acetate buffer to a cooled solution of Am(VI) causes the reduction of Am(VI) to Am(V).[3)] It has also been reported that Am(VI) in a dilute nitric acid solution not containing silver ion was rapidly reduced to Am(V) in the absence of such stabilizing anions as fluoride.[4)] Zangen investigated the solvent extraction of Am(VI) with several extractants such as HDEHP in $CCl_4$ from nitric acid solutions containing $(NH_4)_2S_2O_8$ and $AgNO_3$ as holding oxidants, but he gave no information about the stability of Am(VI) during the extraction.[5)]

The standard potentials for the Am(III)–Am(V) and Am(V)–Am(VI) couples are 1.74 and 1.60 volts respectively.[6)] It can be expected from these potentials that Am(V) and Am(VI) are powerful oxidants and that they are easily reduced by normal reductants and organic materials. Our information concerning the instabilities of Am(V) and Am(VI) in both the aqueous and organic phases is rather poor, especially at lower concentrations of americium. Only a little information was obtained by the previous work in which the rates of reduction of Am(V) in several media were investigated by means of solvent extraction with 2-thenoyltrifluoroacetone(TTA).[7)]

In this work the behavior of Am(III), Am(V), and Am(VI) in column chromatography, using HDEHP as an extractant, has been studied in comparison with that of neptunium in various valency states. Furthermore, the instabilities of Am(V) and Am(VI) with respect to reduction by HDEHP and by some coexisting materials have been investigated.

## Experimental

*Reagents.* The nuclides used in this study were $^{241}$Am (433 y), $^{243}$Am(7400 y), $^{237}$Np($2.14\times10^6$ y), and $^{239}$Np (2.355 d); their radiochemical purities were certified by γ-ray and α-particle spectrometry. The solutions of Am(III) and Am(VI) were prepared in a manner which has been described before using $^{241}$Am,[7)] and the concentration of americium was adjusted to about $10^{-6}$M. $^{243}AmO_2$, obtained from the Oak Ridge National Laboratory, was dissolved in concentrated nitric acid, and a 10M nitric acid solution of $^{243}$Am was used for the tri-*n*-octylamine (T-*n*-OA) extraction to isolate $^{239}$Np,[8)] which was a daughter of $^{243}$Am and which was used as a tracer of neptunium. $^{237}$Np in a 1M nitric acid solution, obtained from the Radiochemical Centre, Amersham, England, was purified by the TTA extraction method[9)] and was used as a carrier of neptunium within two hours after the purification in order to minimize the interference from its daughter. The solutions of Np(IV), Np(V), and Np(VI) were prepared by the literature methods.[10-12)]

HDEHP, obtained from Tokyo Kasei, was purified by the solvent extraction method[13)] and diluted with distilled acetone. The TTA, T-*n*-OA, and other chemicals were of a G. R. grade. Celite 545, obtained from Jones-Mannville, was used as a supporting medium for the extractant. It had been washed with acid, treated with dimethyldichlorosilane, and sized in 80—100 meshes.

*Apparatus.* A Kobe Kogyo Model PS-500 flat-type NaI(Tl) scintillation probe connected with a Toshiba 800-channel pulse-height analyzer was used for the measurement of the γ-ray spectra, while an Osaka Dempa Gridded Ionization Chamber connected with the same pulse-height analyzer was used for the measurement of the $\alpha$-particle spectra. The $\gamma$-ray assay was performed by the use of the scintillation probe connected with a Kobe Kogyo Model SA-400 scaler.

A Toa-Dempa-Kogyo pH meter Model PE-2 was used for the pH measurements. A Shimadzu Ozone Generator was used to bubble ozone gas through the testing solutions in order to eliminate the reducing materials as much as possible. Most of the column chromatographic experiments were performed at a temperature determined with an accuracy of ±0.5 °C in an Ohishi Netsu-Kagaku thermostatted box.

*Procedure. Column Preparation*: 5 grams of Celite 545 and 20 ml of 1M HDEHP-acetone were mixed in a beaker. The mixture was allowed to settle overnight, and then the excess solution was decanted. After air drying at room temperature, the powder was suspended in distilled water; the mixture was then added to a glass tube plugged with glass wool to the desired height. The column was subsequently washed with a 2M nitric acid solution and with water.

*Column Chromatography*: 50—100 μl portions of sample solutions were fed onto the top of the column bed, which had preliminarily been washed with the influent. The column was operated by the usual chromatographic procedures. Suitable aliquots of the effluent were put in polyethylene test tubes or on aluminium dishes for $\gamma$-ray measurements.

If the separation of Am(III) and Am(V) was desired, it was done as follows: Am(V) was eluted from the column with a few milliliters of an influent whose acidity was lower than 0.1M; then the Am(III) was eluted with a few milliliters of a 2M nitric acid solution. After the measurement of the total $\gamma$-ray activity in both the Am(V) and Am(III) fractions, the percentage of Am(V) was calculated.

## Results and Discussion

*Elution of Am(III), Am(VI), Np(IV), Np(V), and Np(VI).* The Am(III), Am(VI), and Np(V) in the nitric acid solutions were fed onto the top of a column bed and then eluted with nitric acid solutions of various acidities. Some typical elution curves are shown in Fig. 1. The peak of Np(V) in the elution curve did not shift in the $10^{-4}$—0.5 M acidity range; Np(V) passed through the column without adsorption. On the other hand, the peak of Am(III) shifted remarkably with the change in the acidity of the influent. In the case of the Am(VI) sample solution, the major part of the americium was eluted within two column volumes of the influent, while the minor part was eluted with the same volume of the influent as Am(III); the major peak did not shift in the $10^{-4}$—0.5 M acidity range like the peak of Np(V), and the minor peak showed the same behavior as that of Am(III).

The Np(IV) and Np(VI) fed onto the column bed could not be eluted with the nitric acid solution in the 0.01—2 M acidity range. However, Np(VI) was gradually eluted with influents of acidities higher than 5 M, though Np(IV) was not eluted at all with the nitric acid solution of the acidity up to 10 M adsorbed tightly on the column bed.

It is known that the actinoid(III, IV, VI) ions are adsorbed tightly on the column bed containing HDEHP.[4] Therefore, it may be concluded that the species which passed through the column without adsorption in the elution of the Am(VI) sample solution was Am(V), since it showed a behavior in the column chromatography similar to that of Np(V) among the various valency states of neptunium.

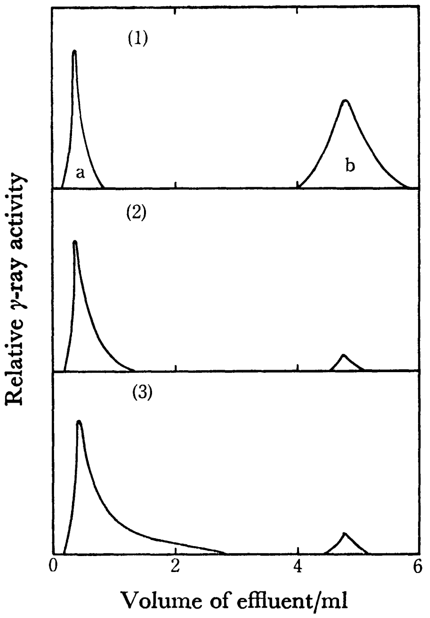

Fig. 1. Behaviors of Am(III), Am(VI) and Np(V) in column chromatography.
Column: 5 mmφ×30 mm, Influent: 0.2 M $HNO_3$, Flow rate: 80 μl/min
1. a) Np(V), b) Am(III). 2. Am(VI) sample solution. 3. Am(VI) sample solution (Influent: 0.2 M $HNO_3$, 0.1 M peroxydisulfate, trace $AgNO_3$).

*Reduction of Am(VI) during the Column Chromatography.* Before the Am(VI) sample solution was submitted to the column chromatography, the valency state of americium had been confirmed as hexavalent by means of the $LaF_3$ coprecipitation method.[14] Therefore, it is clear that Am(VI) was rapidly reduced to Am(V) during the column chromatography. It is well known that Am(VI) is relatively stable in the presence of such holding oxidants as $(NH_4)_2S_2O_8$ with an $AgNO_3$ catalyst and without any contact with organic materials.[14] In the elution curve with an influent containing the holding oxidant (Fig. 1(3)), the peak corresponding to Am(V) had a tail. The rate of reduction decreased somewhat in the presence of the holding oxidant, but it was found that most of the americium was eluted in the pentavalent state.

As causes of the reduction of Am(VI), two factors are possible: the supporting medium and the extractant (HDEHP) in the column bed. In the preliminary experiments, it was confirmed that the powder used as the supporting medium was inert to the redox reaction of americium. Thus, the Am(VI) was probably reduced by the extractant even though the holding oxidant was added. The rapid reduction of Am(VI) by the extractant was also observed in the column chromatography with the Am(VI) solutions of acetate, sulfate, perchlorate, bromate, chloride and hypochlorite in the acidity range of $10^{-4}$—0.1 M.

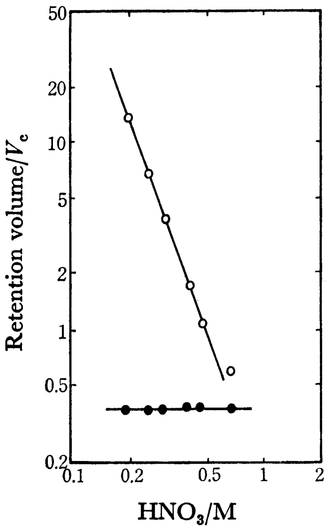

Fig. 2. Dependence of the retention volume on the acidity of the influent.
○: Am(III) ●: Am(V)

*Reduction of Am(V) during the Column Chromatography.* The log-log plot of the retention volume (the volume of the effluent at the peak position in the elution curve) *vs.* the acidity of the influent is shown in Fig. 2, where the retention volume, subtracted by one column volume ($V_c$), is expressed in $V_c$ units. The difference between Am(III) and Am(V) in their adsorbability on the column bed suggests that the recommended procedure for the separation of Am(V) from Am(III) should be as follows: using a column more than 1 ml in bed volume, the Am(V) should be eluted with an influent with an acidity of less than 0.1 M and a volume of less than two column volumes, and the Am(III) should be rapidly stripped with a 2 M nitric acid solution.

TABLE 1. ELUTION OF Am(VI) SAMPLE SOLUTION WITH 0.1 M NITRATE SOLUTION

| pH | Temperature °C | Am(V) fraction % | |
|---|---|---|---|
| 2.0 | 0 | 86.5±0.8[a)] | |
| 2.5 | 0 | 85.1±0.8 | |
| 3.0 | 0 | 84.1±1.0 | |
| 3.5 | 0 | 84.7±0.8 | |
| 2.0 | 0 | 89.8±0.8[b)] | 77.7[c)] |
| 2.0 | 10 | 87.8±1.0 | 70.5 |
| 2.0 | 20 | 88.9±1.0 | 69.5 |
| 2.0 | 30 | 87.4±1.0 | 68.6 |
| 2.0 | 40 | 80.8±1.0 | 61.0 |

Oxidant a) and b): $(NH_4)_2S_2O_8+AgNO_3$ c): $(NH_4)_2S_2O_8$
Column a): 6 mmϕ×30 mm b) and c): 6 mmϕ×25 mm

Following the procedure described above, Am(VI) sample solutions were eluted with nitrate solutions under various conditions and the percentage of the Am(V) fraction was determined radiometrically. As is postulated in Table 1, the percentage of the Am(V) fraction was almost constant in the 2.0—3.5 pH range at 0 °C, but it decreased with a rise in the temperature at a constant acidity. The percentage of the Am(V) fraction did not reach 100% even at 0 °C. These findings are probably the result of the instability of Am(V) during the column chromatography.

TABLE 2. ELUTION OF Am(V) SAMPLE SOLUTION WITH 0.01 M NITRATE SOLUTION (pH 2.5) AT 0 °C

| Bed volume mmϕ, mm | Flow rate ml/min | Am(V) fraction % |
|---|---|---|
| 8×50 | 0.1 | 3.0 |
| 8×40 | 0.4 | 15.1 |
| 8×35 | 1.0 | 42.4 |
| 8×30 | 1.1 | 60.3 |
| 8×30 | 1.6 | 64.8 |
| 10×20 | 2.0 | 91.5 |
| 10×15 | 2.5 | 95.0 |

The Am(V) solution freshly prepared by the elution of the Am(VI) solution was submitted to column chromatography, and the percentage of the Am(V) fraction was measured with respect to the different volume of the column bed. It is clear from the results presented in Table 2 that the bigger the column bed, the smaller the percentage of the Am(V) fraction. These results can be explained easily in connection with the duration of passing over the column bed: Am(V) was obviously reduced by the extractant to Am(III) just like Am(VI). The percentage of the Am(V) fraction depended on the conditions of the column chromatography, such as the temperature, the flow rate, the composition of the influent, and the volume of the column bed. However, it was found that the percentage of the Am(V) fraction was constant within limits of experimental error, as is shown in Fig. 3, when the same column was used in the elution

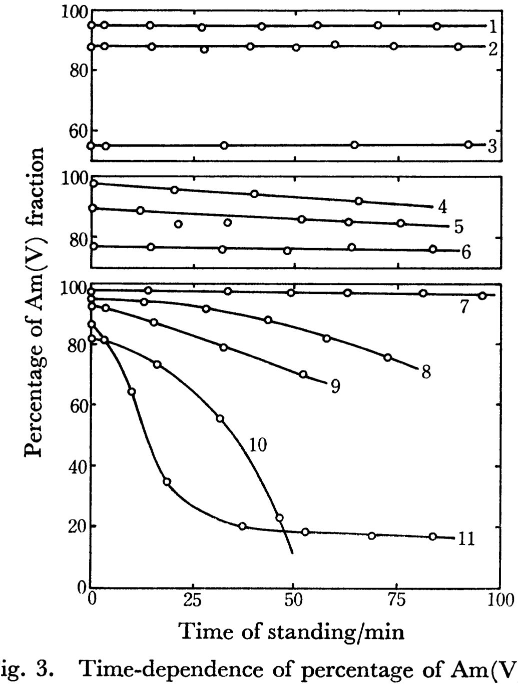

Fig. 3. Time-dependence of percentage of Am(V) fraction in 0.1 M solutions of pH 2.5 at 0 °C
1–3: Nitrate, 4: Acetate, 5: Sulfate, 6: Perchlorate, 7: Peroxydisulfate, 8: Chloride, 9: Hydrogen peroxide, 10: Potassium bromate, 11: Peroxydisulfate freshly prepared (The different column was used except for two couples, 1–8 and 2–11)

of Am(V) in a 0.1 M nitric acid solution. This finding suggests that Am(V) is stable in the nitrate solutions and that the rate of Am(V) decreased by the column chromatography is constant so long as the same column is used. Thus, the content of Am(V) in the mixed solution of Am(III) and Am(V) can be determined by a simple correction for the percentage of the Am(V) fraction obtained by the column chromatography under definite conditions using the same column.

*Stability of Am(V) in Several Kinds of Solutions.* Aliquots of an Am(V) solution kept at various temperatures were submitted to column chromatography at 0 °C in order to investigate the dependence of the percentage of the Am(V) fraction on the standing time. Some of the results are shown in Fig. 3. The percentage of the Am(V) fraction in the perchlorate, sulfate, acetate, and aged peroxydisulfate solutions decreased slowly, but it readily decreased in the chloride, iodide, sulfite, hydroxylamine, hydrogen peroxide, bromate, and freshly-prepared peroxydisulfate solutions, even at 0 °C. The unexpected results with the common oxidant, the bromate, and the freshly-prepared peroxydisulfate solutions can be explained in terms of the following phenomena: the bromate obviously eluted a portion of the extractant and the peroxydisulfate formed bubbles in the column bed. The decreases in the percentage of the Am(V) fraction in the solution kept at lowered temperatures did not result from the oxidation of Am(III) and Am(V), but from the reduction of Am(V) to Am(III) because of the higher redox potentials for two couples, Am(III)–Am(V) and Am(V)–Am(VI).

Then, the dependence of the content of Am(V) in the acetate solutions on the standing time was investigated at various temperatures. As is shown in Fig. 4, the semilog arithmic plot of $[Am(V)]_t/[Am(V)]_0$ *vs.* the standing time showed a linearity, where $[Am(V)]_0$ and $[Am(V)]_t$ were the concentrations of Am(V) at the standing times of 0 and $t$ respectively. The slope of the straight line somewhat increased with an increase in the pH in the 2—3 range examined at the same temperature. Consequently, the reduction of Am(V) in an acetate solution apparently follows the first-order kinetics. The reduction rate of Am(V) to Am(III) decreased to as low as a few percentages per hour at 0 °C, though the radiolytic reduction rate of 1.2%/h should remain even at sufficiently lowered temperatures. Therefore, the experiments using Am(V) solutions have to be performed at lower temperatures and have to be finished within a few hours after the preparation of Am(V) solutions in order to minimize the interference from Am(III).

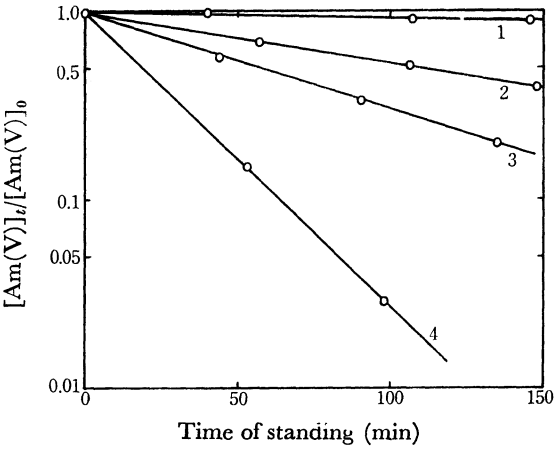

Fig. 4. Time-dependence of $[Am(V)]_t/[Am(V)]_0$ in 0.1 M acetate solution of pH 2.0
1: 0 °C, 2: 40 °C, 3: 60 °C, 4: 80 °C.

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