

## Interaction of Humic Acid and Am(III) in Aqueous Solution

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### Americium/Humic acid/Stability constant

Laboratory experiments using radiotracer of americium ( $^{241}\text{Am}$ ) and humic acid isolated from natural surface soil have been conducted to evaluate the effect of added humic acid on the behavior of Am(III) in aqueous solution and the stability constant of the complex formed between Am(III) and humic acid. The former experiments were performed in the synthetic aqueous medium containing Ca or in fresh rain water at pH 6.5 and 4.5. At pH 6.5 in the absence of humic acid, Am(III) in both solutions [(Ca: 10 ppm) or rain water] was almost adsorbed on the wall of the polyethylene vial used, and the major fraction of Am left in the solution was retained on the filter of 0.45- $\mu\text{m}$  pore size. On the other hand, in the presence of humic acid (100 ppm), the adsorption of Am on the vial was not observed, and the decrease of the retention of Am on the same filter suggests its complex formation with humic acid. At pH 4.5, the behavior of Am(III) in the solution (Ca: 10 ppm) was not influenced by the addition of humic acid (100 ppm). When the quantities of Ca were increased in the solution at a constant amount of humic acid, insoluble complexes were formed according to the increase of Ca to humic acid, and Am was scavenged over 90% as the insoluble complexes. The study of stability constant indicated that Am(III) had the strong interaction with humic acid.

### INTRODUCTION

The behavior of the long-lived artificial radionuclides, especially transuranic elements such as plutonium and americium, in the terrestrial environment, is nowadays becoming a matter of concern from the view of long-term safety<sup>1)</sup>.

As for the interaction of transuranic elements with soil, it is very important to know what role do the soil organic acids, *i.e.*, humic and fulvic acids, play in the behavior of these elements. The knowledge so far obtained on the behavior of them with soil organic acids is limited<sup>2-5)</sup>. Bertha and Choppin<sup>3)</sup> noted from the studies of the binding constants of humic and fulvic acids with Am(III) and Eu(III) that Am(III) was strongly held by the humic materials. Concerning the solubilization of Pu and Am by humic compounds, Cleveland and Rees<sup>4)</sup> showed that soil humic compounds were not a major factor in the solubilization of Pu and

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Am in Rocky Frats soil, and Yamamoto *et al.*<sup>5)</sup> also showed that fallout Pu in soil is unlikely to be leached with humic and fulvic acids.

Since it seems still important to understand the interaction of transuranic elements with soil organic acids to predict their behaviors in soil, we have conducted the laboratory experiments on the interaction of Am(III) with humic acid isolated from natural surface soil. The effect of the addition of humic acid on the behavior of Am(III) in aqueous solution and the stability constant of the Am(III)-humic acid complex were investigated by using radiotracer of <sup>241</sup>Am(III).

#### MATERIALS AND METHODS

##### 1) Materials

All the reagents used here were prepared from analytical grade reagents. Dowex 50x8 (20-50 mesh) cation exchange resin supplied from BIO-RAD laboratories was prepared by washing it in a glass column with KCl solution, and then with distilled water until Cl<sup>-</sup> ion became undetectable. The resin obtained was dried at 105°C. By the following way, <sup>241</sup>Am tracers obtained from RCC Amersham, England, were adjusted to valence state of III: aliquot portion of <sup>241</sup>Am was evaporated to dryness with 2 M NH<sub>2</sub>OH·HCl and the residue was dissolved with 1.5 M HCl.

##### 2) Isolation and purification of humic acid

The surface soil sample rich in organic materials (about 50%) was collected from the flat ridge of Mt. KANMURI (35°36' N by 136°29' E) about 1100 m above sea levels in Fukui Pref., Japan. The soil sample was air-dried, and ground

**Table 1.** Analytical Characteristics of Humic Acid extracted from the Surface Soil of Mt. KANMURI

Elementary composition (%)		Functional group	
Carbon	51.20	Total acidity (meq/g)	6.0
Hydrogen	4.54	COOH (meq/g)	3.4
Oxygen	40.12	Phenolic OH (meq/g)	2.6
Nitrogen	3.77	No. of COOH per M.W*	6.1
Ash	0.37	No. of phenolic OH per M.W*	4.7
M.W*	1.8 x 10 <sup>3</sup>		

\*: Number-average molecular weight.

to pass through a standard sieve (32-mesh). The humic acid was extracted with 0.5 M NaOH solution (an extractant to soil ratio of 10:1) for 24 hours with occasional shaking. The method of pulification of humic acid is almost the same as described by Bertha and Choppin<sup>3</sup>). The characteristics of the humic acid thus obtained are shown in Table 1. Elemental analyses of this humic acid were done by using Perkin-Elmer Elemental Analyzer, Model 240. The number-average molecular weight was measured by the freezing-point depression method in sulfolane (*tetra*-methylene sulfone)<sup>6</sup>). The accuracy of this method was also checked by measuring the known molecular weights of benzoic and trimellitic acids. The values obtained were within the errors of 5% of the theoretical molecular weights. As for the functional group analyses<sup>7</sup>), total acidity was determined by barium hydroxide adsorption method, and carboxyls by the calcium acetate method. Phenolic hydroxyls were assumed to be equal to the difference between total acidity and carboxyl groups. The infrared spectrum was similar to those by Kumada and Aizawa<sup>8, 9</sup>). This humic acid was found to be B-type according to the classification of humic acid by Kumada<sup>10</sup>).

### 3) Effect of humic acid (H.A) on the behavior of Am(III) in aqueous solution

Two kinds of water samples were used: one consists of the synthetic aqueous medium containing 10 ppm Ca, and another is a fresh rain water filtered through a 0.45- $\mu$ m pore size filter, containing 0.6 ppm Ca+Mg originally. The water samples (50 or 100 ml) spiked with <sup>241</sup>Am(III) were continuously shaken mechanically in the polyethylene vials, with or without H.A (100 ppm) at a given pH for several days. An aliquot portion (1 ml) of sample solutions were taken at several time-intervals to determine the total activity in the sample solutions. Another 2 ml was filtered through a superimposed two sheets of 0.45- $\mu$ m filters and then sucked by aspirator for 5 minutes without washing. Each sample thus obtained was counted in the same geometry by NaI(Tl) detector with thin beryllium window. The percentage retention of <sup>241</sup>Am on filter was calculated on the basis of these gamma-activity measurements.

Furthermore, as the H.A coagulates with increasing metal-H.A ratio in the solution, the following experiments were carried out to know the effect of the scavenging of the <sup>241</sup>Am from the sample solution. That is, to 5 ml aliquots of H.A (0.15 mM) solution containing <sup>241</sup>Am, the increasing quantities of Ca were added at pH of 6.5. And each system was diluted exactly 6 ml with distilled water and stood at room temperature for 4 hours after shaking vigorously. The precipitate was separated from the supernatant solution with a centrifuge, and then each fraction was subjected to radioactivity measurement in the same geometry by the above-mentioned detector. The content of H.A in the supernatant solution was also determined spectrophotometrically using the absorption at 350 nm.

#### 4) Measurements of stability constants

The ion-exchange equilibrium method of Schubert<sup>11)</sup> was used to determine the stability constants of complexes formed between Am and H.A. To compare the stability constants of Am-H.A complex with those of another metal ions, the stability constants were further measured for two divalent metal ions, *i.e.*, Mn(II) and Co(II), by using the same H.A. To avoid a carrier-free state of Am in the stability constant study, gadolinium (GdCl<sub>3</sub>·HCl) was used as a carrier of Am because of the similarity for the chemical properties between Am and Gd ions<sup>12)</sup>. Thus, Gd solution spiked with radiotracer <sup>241</sup>Am was used for the experiment. On the other hand, the divalent metal solutions were prepared from chemical grade reagents: MnCl<sub>2</sub>·4H<sub>2</sub>O and CoCl<sub>2</sub>·6H<sub>2</sub>O, and then solution was spiked with radiotracer of <sup>54</sup>Mn or <sup>60</sup>Co, respectively.

To each 5 ml volumetric flask, the required volume of H.A stock solution with a few drops of 0.1 M KOH was added along with 5 ml of M KCl solution, followed by the addition of the aqueous metal stock solution. Then, the pH was adjusted to be exactly 6.5 by addition of a few drops of 0.1 M KOH or 0.1 M HCl solution. Finally, the volume of each flask was made to 50 ml with distilled water. Each final solution (50 ml) has the concentration of  $0.1 \times 10^{-5}$  M for Gd and that ranging from  $0.2 \times 10^{-5}$  to  $1.5 \times 10^{-5}$  M for H.A, while for the divalent metal systems  $1 \times 10^{-5}$  M for metal ions and from  $1 \times 10^{-5}$  to  $20 \times 10^{-5}$  M for H.A, respectively. For each experiment, one-gram of K-saturated Dowex 50x8 resin was weighted into polyethylene vial and then the solution containing the metal and H.A was transferred to this vial, followed by the shaking at  $25 \pm 0.1^\circ\text{C}$  for at least 50 hours. The exchange resin was then separated from the solution by filtration, and the resin and the filtrate of 2 ml were counted respectively using NaI(Tl) detector with thin beryllium window.

### RESULTS AND DISCUSSION

#### I. Effect of H.A on the behavior of Am in aqueous media

The experiments were mainly performed in the synthetic water media (Ca: 10 ppm) or in the fresh rain water media (Ca+Mg: 0.6 ppm originally) at pH 6.5 close to natural system to simulate the Am migration in soil by groundwater and rain water. Comparative experiments were also performed at pH of 4.5.

In Fig. 1, the time dependencies of the Am left in the solution in the absence or the presence of H.A at pH 6.5 and 4.5 are shown respectively. As seen from this figure, the Am left in the solution of pH 6.5 are remarkably different in the absence or the presence of H.A. The contents of Am in the absence of H.A decrease quickly for both media due to the adsorption of Am on the wall of the polyethylene vial, reaching about 10% of added Am after 20 hours, and afterward decreasing slightly. Among the content of Am left in the solution, the percentage of Am retained on the filter of 0.45- $\mu\text{m}$  pore size was from 81 to 90% for Ca

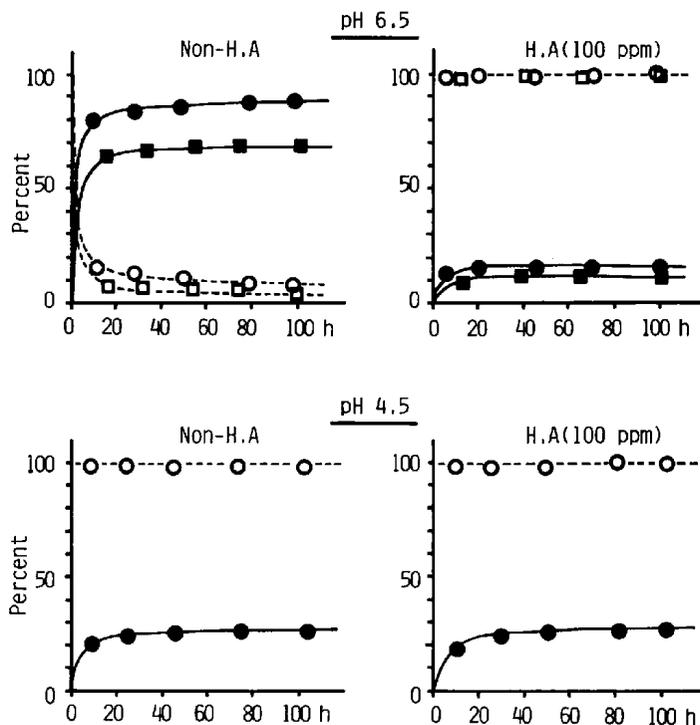


Fig. 1. Radioactivity changes of Am in aqueous media in the absence or the presence of H.A (humic acid) at pH 6.5 and 4.5 [circle symbols (Ca: 10 ppm) and square symbols (rain water, Ca+Mg: 0.6 ppm)].

—○—□— : %Am in the solution to the total Am activity added initially.

—●—■— : %Am retained on filter (0.45- $\mu$ m) to the amount of Am left in the solution.

media and 63-73% for rain water. Previously, Murray and Fukai<sup>13)</sup> have demonstrated by the laboratory experiments using river water and sea water samples that major fraction of Am is likely to become particulate in natural conditions. In our experiments, the similar tendency as Murray's observation is recognized in the media at pH 6.5 in the absence of H.A.

On the other hand, in the presence of H.A, no adsorption of Am on the wall of the polyethylene vial was observed for both solutions, and Am retention on the filter decreases remarkably. These facts suggest the possible formation of complex with added H.A and Am. The difference between Ca medium and rain water was not found clearly in our experiments.

The behaviors of Am at pH 4.5 as shown in the lower part of Fig. 1 are similar notwithstanding the absence and the presence of H.A. In this cases, the adsorption of Am on the wall of the vial was not observed, and the retention of Am on the filter was approximately 20-30%. These facts indicate that in the case of low pH such as pH 4.5, H.A used here was not effective in the formation of complex with Am, as the complex formation of metal with soil organic acid are largely dependent on the pH of solution and become higher at increased pH<sup>14</sup>).

Furthermore, to know the size of particulate Am formed in the Ca or rain water media, the retention of Am on filters of various pore size (0.1-, 0.45- and 1.0- $\mu$ m) were examined by taking the media after 100 hours time-interval. The results are presented in Fig. 2 for various solutions having different Ca-H.A ratios. In the media at pH 4.5, Am retentions by filters of various pore size were not different in the absence of H.A as well as in the presence of H.A. In the media at pH 6.5, Am retentions by filters in all cases tend to increase with decreasing pore size of filter. The behaviours of Am were not different among the Ca-H.A ratio of 1:100 (0.45:1 in terms of mole ratio) and 10:100 (4.5:1), and Ca+Mg-H.A ratio of 0.6:100. However, for the Ca-H.A ratio of 100:100 (45:1), the percentage retentions of Am on filters are higher than those for the above-men-

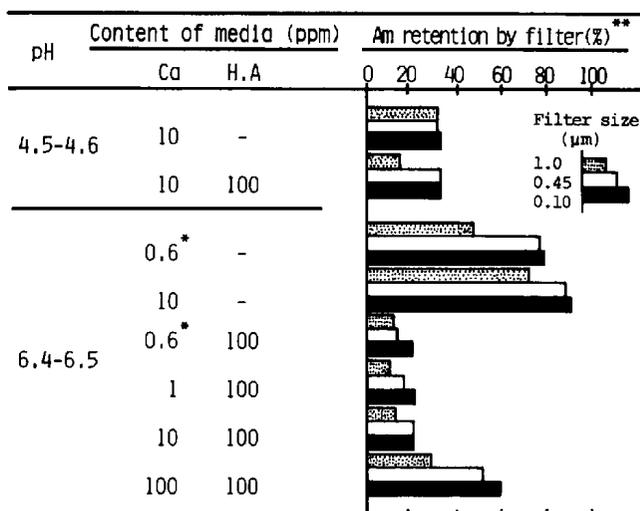


Fig. 2. Size distributions of particulate Am formed in the Ca or rain water media with or without H.A (humic acid).

\* : Rain water

\*\* : %Am retained on filter to the amount of Am left in the solution after 100-hour period.

tioned three kinds of ratios. These results show that H.A is subjected to coagulate with increasing Ca-H.A ratio, and precipitates insoluble complexes<sup>15</sup>).

In order to determine how Am is distributed among the soluble and insoluble fractions, the following experiments were carried out: various quantities of Ca were added to 5 ml aliquots of H.A solution containing <sup>241</sup>Am radiotracer at pH 6.5, and then each system was diluted exactly to 6 ml with distilled water. The results are presented in Fig. 3. As found in Fig. 3, the contents of H.A in soluble fraction decrease rapidly from about  $1.8 \times 10^{-2}$  m mole Ca, and over about  $3 \times 10^{-2}$  m mole Ca, its decrease become slight, while an increase of Am in the insoluble fraction is found corresponding to the decrease of the content of H.A in the soluble fraction. Most of Am (81~95%) was scavenged as the insoluble complexes formed in the range of  $3 \sim 6 \times 10^{-2}$  m mole Ca, which corresponds to the Ca-H.A mole ratio of 45:1 ~ 82:1. It may be very important that, though the particulate or collidal formation of Am is prevented by the addition of H.A, most of Am in the solution is scavenged by the insoluble complexes formed between Ca and H.A as Ca-H.A ratio increases. These facts, the formation of soluble metal complex, and the subsequent scavenging of trace metals with insoluble complexes formed by various electrolytes, may contribute to explain the fact that Pu and Am in soil are unlikely to be leached under simulated natural conditions even with natural soil organic substances.

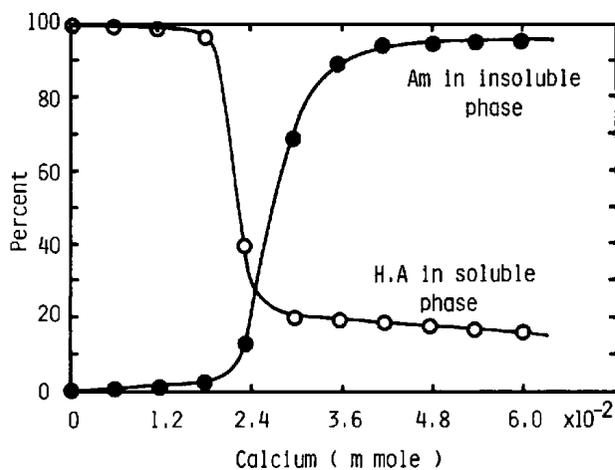


Fig. 3. Scavenging of Am due to the coagulation of H.A (humic acid) with calcium (constant amount of humic acid =  $7.4 \times 10^{-4}$  m mole).

## II. Stability constants

The quantitative investigations of complexes between H.A and metal ions are very difficult because the H.A is a heterogeneous polyelectrolytic materials and the characteristics of H.A are dependent on its original source and the methods of isolation and purification. The measurement of the number-average molecular weight of this H.A used here prompted us to estimate the stability constants of the Am(III)-humic complexes. The Co(II) and Mn(II) complexes of the same H.A were also studied to compare the results with that for Am(III), because the radioactive  $^{60}\text{Co}$  and  $^{54}\text{Mn}$  are important in the environmental studies as representative corrosion products in reactor coolant water system<sup>16</sup>.

If the metal-humic complexes are not adsorbed by the resin and exist in the solution, the stability constants of these complexes,  $k_i$ , are calculated from the following equation<sup>11</sup>):  $(Dm^\circ/Dm)-1 = k_1[L] + k_1k_2[L]^2 + \dots$  (1), where  $Dm^\circ$

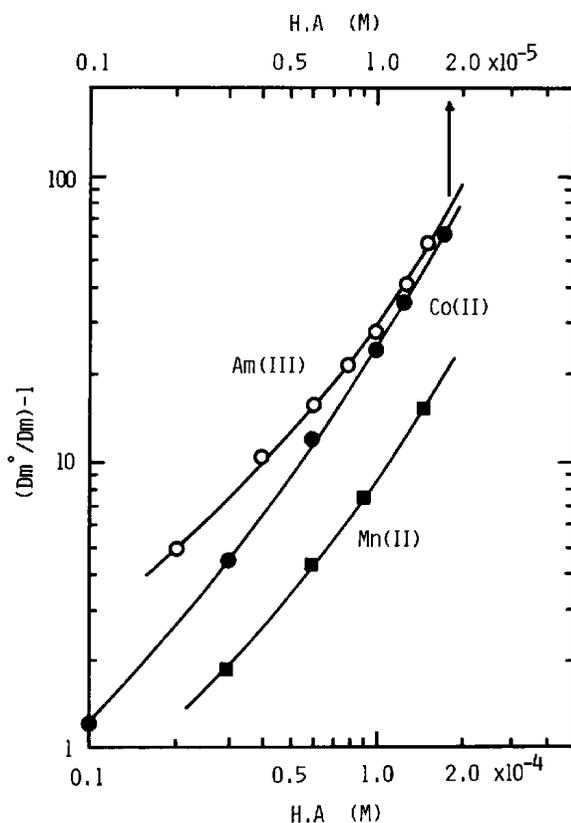


Fig. 4. Plots of  $(Dm^\circ/Dm)-1$  as a function of H.A (humic acid) concentration: each point is plotted as the average of 2~3 experimental results. [ $\mu = 0.1$  (KCl),  $T = 25 \pm 0.1^\circ\text{C}$ ,  $\text{pH} = 6.5$ ]

and  $D_m$  are the distribution coefficients of metal ion between resin and solution phases in the absence and the presence of humate ion  $[L]$ , respectively. If a plot of  $(D_m^\circ/D_m)-1$  vs.  $[L]$  gives a straight line, it may be considered that only one complex exists. On the other hand, if its plot doesn't give straight line, it may be considered that multiple complexes may also exist. In this case, the following equation was used generally:  $[(D_m^\circ/D_m)-1]/[L] = k_1 + k_1k_2[L] + \dots$  (2). Then, the values of  $k_1$  and  $k_1k_2$  may be obtained from the intercept and slope of the straight line of a plot of  $[(D_m^\circ/D_m)-1]/[L]$  vs.  $[L]$ .

The plots of  $(D_m^\circ/D_m)-1$  vs.  $[L]$  for Am(III), Co(II) and Mn(II) are shown in Fig. 4. The line for each metal ion doesn't give straight line. On the other hand, if the data were plotted according to the equation (2), straight line for each metal was obtained as shown in Fig. 5, from which the stability constants were calculated. These values thus obtained are also presented in the terms of  $\log k_1$  and  $\log k_1k_2$  in this figure.

It is seen in Fig. 5 that the values of  $\log k_1 = 6.4$  and  $\log k_1k_2 = 10.6$  for Am(III) are higher than those for Co(II) and Mn(II). Even from these observed values, we can not directly assume that complexed species are  $ML$  and  $ML_2$  ( $M$ : metal) as a simple stepwise formations of complexes, because H.A used here is not

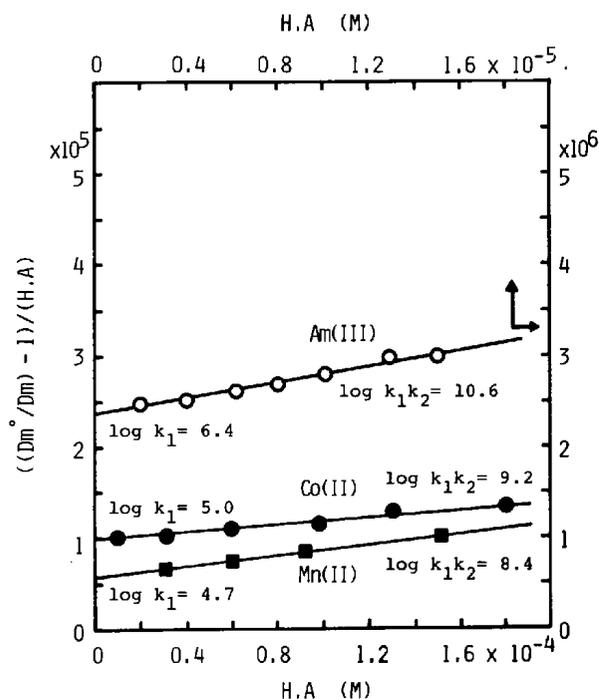


Fig. 5. Plots of  $[(D_m^\circ/D_m)-1]/[H.A]$  as a function of H.A (humic acid) concentration.

a monomer, and in addition has many active groups responsible for complex formation such as carboxyl, carbonyl and phenolic-OH, and the measurements are done at pH of 6.5 where hydrolyses of Am, Co and Mn are likely to occur. At any way, these observations indicate that Am(III) has strong interaction with humic acid as reported previously by Bertha and Choppin<sup>3)</sup>.

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