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Keiji Naito

November 1959

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A METHOD OF PURIFICATION OF AMERICIUM^{*}

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November 1959

I. INTRODUCTION

Since the first isolation of Am²⁴¹ by B. B. Cunningham in 1945,¹ the purification of americium has been performed by many researchers. The methods of purificiation or separation of americium can be divided roughly into three methods: precipitation methods, ion exchange methods, and solvent extraction methods. Table I gives a classification of the methods of separation and purification of americium which have been used to date.

It can be observed from Table I that each method has its own purpose and is not applicable generally -- so that one or more methods should be utilized according to the kinds and amounts of impurities in the sample.

However, it is desirable to have a general method of purification which is applicable independent of the kinds of impurities in case many different impurities exist. The author tried to purify americium using the following methods which constitute a general procedure for purification.

II. OUTLINE OF PURIFICATION

The author chose the ion exchange method as a general purification method, because ion exchange seems to be the method by which one can get high purity most easily in the laboratory.

^{*} Work done under the auspices of the U S. Atomic Energy Commission.

^{**} On leave from the Japanese Atomic Energy Research Institute, Tōkai-mura, Naka-gun, Ibaraki-ken, Japan.

Method	Materials from which Am is to be separated	Procedure	Reference number	Remarks
Precipitation	U, Pu	Oxidation of solution, then coprecipitation or precipitation of Am as ${\rm AmF}_3$	2	Rare earth fluorides (such as LaF_3 , CeF_3) are used as carriers.
<i>,</i>	General impurities	Carbonate precipitation and sulfide precipi- tation together are used with fluoride precipitation, or oxalate precipitation	3	Rare earths cannot be separated.
		Dowex-50 resin and 13.3 <u>M</u> HCl eluant	4	Group separation of lanthanides (III) and actinides (IV) is possible.
• • •	Trivalent lanthanides	Dowex-50 resin and ammonium citrate (or malate or glycolate or lactate or EDTA) eluant.	· 3	Group separation of lanthanides (III) and actinides (III) is not possible.
on exchange		Dowex-l resin and ammonium thiocyanate eluant	5,6	Separation of Am from lighter rare earths.
•		Dowex-l resin and 8 <u>M</u> LiCl - 0.1 <u>M</u> HCl eluant	7	Group separation of lanthanides (III) and actinides (III) is possible; Li (a, n) hazard.
• • • •	Trivalent actinides	Dowex-50 resin and ammonium a-hydroxy isobutyrate (or EDTA or lactate or glycolate or malate or citrate eluant)	8	•
	U, Pu, Np	Dowex-1 resin and 6 to 10 \underline{M} HCl or 8 to 10 \underline{M} HNC ₃ eluant	7	U(VI), Pu(IV,VI), Np(IV,VI)
	Triválent lanthanides	TBP extraction (from 12 \underline{M} HCl or 15 \underline{M} HNO ₃ aqueous solution)	9 [.]	Salting-out agent is frequently used. Counter current extraction is usually used.
· ·	Trivalent actinides	TBP extraction (from 12 <u>M</u> HC1 or 15 <u>M</u> HNO ₃ aqueous solution)	10, 11	The same as above.
	La	TTA extraction (pH \simeq 33)	11	
	Pu	Cupferron extraction	12	Pu(IV)

.

Table I. Methods of separation or purification of americium

u U U -4-

However, if impurities exist in large amounts, it is not suitable to use the ion exchange method directly, because a great quantity of ion exchanger will be necessary to absorb the large amount of impurities. Accordingly, in such a case, it is preferable to separate the large amounts of impurities roughly prior to using the ion exchange purification.

The author chose the precipitation method as a rough method for separating the large amounts of impurities.

1. Rough separation of impurities by means of the precipitation method.

Various precipitation methods in Table I will be applicable for the crude separation of impurities. In many cases, however, the addition of a carrier (such as La, Ce, etc.) is necessary in order to avoid the loss of americium during the separation process. Generally speaking, all impurities except rare earth elements can be separated by applying the precipitation method.

2. Purification by means of the ion exchange method.

Among the various ion exchange methods in Table I, the anion exchange separation using 6 - 10 \underline{M} HCl eluant seems to be the most attractive method as a general means of purification.

Anion exchange separation using HCl eluant has been studied carefully by K. A. Kraus and F. Nelson.¹³ It can be found from the results of Kraus and Nelson that nearly all impurities except alkali, alkali-earth, and rare earth elements can be separated from americium using concentrated HCl eluant. Where 9 <u>M</u> HCl eluant is used, Figure 1 shows the elements which can be separated from americium. In this case, americium passes through a Dowex-1 resin column but the elements within the lines in Figure 1 are adsorbed on the resin strongly, so that the separation of these impurities from americium can be achieved easily. (For those elements with more than one oxidation state, the most stable oxidation state in usual aqueous solution is shown in Table I.)

Since rare earth elements, which usually accompany americium, are not separated by the anion exchange with 9 M HCl eluant, the author intended ł

0 в С N Li Be а1⁺³ Si Р s Na Mg .Ga⁺³ Fe⁺³ C,0⁺² Ge⁺⁴ v+5 <u>C</u>r⁺³ <u>N</u>i⁺² Zn⁺² +3 Ti⁺⁴ <u>M</u>n⁺² Cu^{+2} K CaSc⁺³ 5n⁺² .In⁺³ Ag^{+1} 55⁺³5 Te⁺⁴ Cd⁺² Zr⁺⁴ Rh⁺³Pd⁺² Mo⁺⁶ Tc⁺⁷ Ru⁺⁴ Rb Sr Y⁺³ NЪ Pb⁺² HI+6 Hg⁺² Ta⁺⁵ Ir⁺³ Ta^{+1} Bi⁺³ Po⁺⁴ w⁺⁶ $Pt^{+4} Au^{+3}$ Re⁺⁷ Ós⁺³ Cs Ba Lanthanides⁺³ u[‡]4 Pa⁺⁵ Fr Ra Actinides +3 Th⁺⁴

+6 Np⁺⁴ +6 Pu⁺⁴

Figure 1. Anion exchange separation with 9 M HCl eluant. Elements within the lines are strongly adsorbed. Elements outside the lines are not adsorbed or are only weakly adsorbed. -6-

to use anion exchange with 5 M NH₄SCN eluant for this purpose. In this separation, americium is adsorbed strongly on Dowex-1 resin and the rare earth elements are adsorbed very weakly. Although this method was used extensively by the Los Alamos group, the behavior of most elements except trivalent actinides and lanthanides is not clear during the elution process. It is estimated, however, that many elements, such as alkali and alkaline earth elements, which cannot be separated by anion exchange with 9 M HCl can be separated by this method. Accordingly, anion exchange separations with 9 M HCl eluant and with 5 M NH₄SCN eluant were tried as a general method of purification of americium.

3. Americium sample.

About 6.5 liters of waste solution from Hanford containing large amounts of many impurities was used as the sample solution for the purification of americium.

The alpha assay of this solution indicated about 56 mgs of americium and about 3.1 gms of plutonium in the solution, and the spectrographic analysis showed that aluminum, bismuth, lanthanum, plutonium, iron, calcium, manganese and chromium were present as main impurities.

The amounts of these impurities relative to americium are given in the column of "Before Separation" in Table II. (The figures in Table II were obtained from the spectrographic analysis and, in the case of americium and plutonium, from alpha assay.) -7-

)

Main Impurities	Before Separation	After Rough Separation	After Purification
Am	1. 0	1. 0	1. 0
Al	590	2.0	6×10^{-4}
Bi	29.0	0.8	$<1 \times 10^{-3}$
La	180(420)**	80(420)**	$<2 \times 10^{-4}$
\mathbf{Pu}	50	5.8	$<2 \times 10^{-2}$
Fe	6	20	$<2 \times 10^{-4}$
Ca	1. 2	0.2	$<4 \times 10^{-4}$
Mn	0.6	2.8	2×10^{-6}
Cr	0.3	2.0	$<2 \times 10^{-4}$

Table II. Comparison of relative amounts of impurities.*

* Ratio in weight.

** These results should be interpreted considering the error of the spectrographic analysis. For example, the relative amounts of La in "Before Separation" and "After Rough Separation" should be the same value but both are not the same. A precise value for La was obtained later by weighing lanthanum oxide.

4. Reagents.

Though chemically pure reagents were used during the separation, ' in the purification process special care was taken to avoid the introduction of impurities from the reagents. HCl gas was passed into conductivity water to prepare HCl aqueous, and ammonium thiocyanate was pretreated by passing a solution of it through a Dowex-1 resin column in order to separate iron from the reagent. The ion exchange resin was used after pretreating it with 1 M NaOH and 1 - 13 M HCl.

III. ROUGH SEPARATION OF IMPURITIES

1. Procedure of separation.

The impurities which are found in large amount in the sample solution are aluminum, bismuth, lanthanum, and plutonium, as shown by Table III. In order to separate roughly all of these impurities except lanthanum, the following procedure was used:

- a. <u>Separation of aluminum</u>: Aluminum was precipitated as hydroxide with americium by introducing NH₃ gas; the aluminum hydroxide was dissolved by adding concentrated NaOH solution.
- b. <u>Separation of bismuth</u>: After aluminum was separated, the hydroxide precipitate was dissolved with HCl and H_2S gas was introduced into the solution after making the solution weakly acidic. Bismuth was precipitated from the solution as the form of sulfide.
- c. Separation of plutonium: After bismuth was removed, the solution was heated to expel H_2S gas and NH_3 gas was introduced into the solution to precipitate the hydroxide again. The hydroxide precipitate was dissolved in nitric acid and plutonium was precipitated in the form of peroxide by adding H_2O_2 .

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2. Results.

**

The sample solution (a total of 6.5 liters) was divided into four parts of nearly equal volume and the above procedure was repeated four times in a standard Berkeley Box. The reason for dividing the solution into four parts was that the box was not large enough to treat the entire amount of solution at once. Therefore 1.6 to 1.8 liters of the sample solution were treated at a time.

Table III. Result of spectrographic analysis for pure americium.

	Impurities										
Sample	Ca	A1	Mg	Fe	Am	Ľa	Mn	Bi	Na	Ni	
Am Sample	0.02	0.05	0.02	<0.01	>>10**	<0.01	0.01	<0.05	<1	<0.05	
Blank	0.03	0.02	0.02	<0.01	<0.05	<0.01	<0.01	<0.05	<1	<0.05	

* µgs per entire sample (100 λ).

The amount of Am is about 50 μ g.

After rough separation of the impurities, an 870 ml americium fraction (alpha activity ratio: americium 90.0% and plutonium 10.0%) and 310 ml plutonium fraction (alpha activity ratio: plutonium 96.8% and americium 3.2%) were obtained.

The relative amounts of impurities after the rough separation are shown in Table II. This shows that the amounts of all impurities except lanthanum were reduced to nearly the same order as the amount of americium. The amount of iron is believed to have increased, compared with the amount before separation, as a result of contamination by the reagents (NaOH solution especially was used in very large quantity).

The recoveries of americium and plutonium were 108% and 104%, respectively. The reason the recoveries appear to exceed 100% is probably due to a decrease in the self-absorption of alpha particles in the alpha-assay sample.

3. Discussion

The following points were noticed during the rough separation:

- a. The separation of aluminum using excess NaOH is not effective when the concentration of NaOH is low. The solubility of aluminum in excess NaOH increases rapidly with the increase of the NaOH concentration but suddenly decreases at around 7 <u>M</u> NaOH concentration as a result of a phase change.¹⁴ Therefore it may be desirable to use about 5 <u>M</u> NaOH solution in order to obtain effective separation.
- b. It is preferable to keep the acidity of solution as low as possible in order to precipitate bismuth completely as a sulfide. In case plutonium exists in solution, however, polymeric plutonium hydroxide is easily formed with decrease of the acidity of the solution. If the acidity of solution is more than 1 to 1.5 M, polymeric plutonium hydroxide is not formed but the precipitation of bismuth sulfide is very incomplete. Accordingly, the acidity of the solution was kept at 0.3 M and complete precipitation of bismuth sulfide was obtained, although a small amount of polymeric plutonium hydroxide was formed (about 1% of the total plutonium).
- c. The condition for precipitation of plutonium peroxide was that suggested by J. W. Hamaker <u>et al</u>¹⁵, the concentration of hydrogen ion $[H] \simeq 1.0$ <u>M</u> and that of hydrogen peroxide $[H_2 \Phi_2] \simeq 10\%$. Plutonium peroxide was separated by centrifugation at room temperature, but the amount of plutonium in the supernatant solution was about ten times as high as expected from the solubility data¹⁵ on plutonium peroxide. This may be attributed to the suspension of the precipitate in the supernatant solution as a result of

of decomposition of hydrogen peroxide. Accordingly, if necessary, it may be preferables to ice the precipitate during the separation of plutonium peroxide.

IV. PURIFICATION

1. Procedure of purification.

- The procedure of purification using ion exchange was the following:
- Separation of plutonium, iron, and other impurities. a. From the americium portion which was obtained from the rough separation, a 9 M HCl sample solution was prepared by the by adding 13 M HCl. This sample solution was poured into a Dowex-1 x 8 resin (200-400 mesh) column. The ion exchange column used was 3,2 cm diameter x 12 cm height, and the flow rate was about 0.25 cm/min, although the flow rate was not controlled. After the 9 M HCl sample solution was passed through the column, the column was washed with a volume of 9 M HCl three to four times as large as the volume of resin bed. The eluting solution and washing solution were combined and this was designated as americium portion (total volume was 1470 ml). The impurities adsorbed on Dowex-1 resin, such as plutonium, iron, bismuth, etc., were eluted with 0.1 M HCl.

b. <u>Preparation of the feed solution for americium-lanthanum</u> separation.

The americium portion which was obtained after the anion exchange separation with 9 <u>M</u> HCl eluant was diluted to 2 <u>M</u> HCl solution with conductivity water and this solution was poured into a Dowex-50 x 4 resin (200-400 mesh) column. Four ion exchange columns were used and each column was 3.2 cm diameter x 20 cm height, the flow rate being about 0.2: cm/min. The americium adsorbed on Dowex-50 resin was eluted with a volume of $5 \text{ M} \text{ NH}_4 \text{SCN}$ which was three to four times larger than the volume of resin bed, and a $5 \text{ M} \text{ NH}_4 \text{SCN}$ feed solution was obtained (total volume was about 2000 ml).

c. Separation of lanthanum.

The 5 \underline{M} NH₄SCN feed solution (pH \simeq 1.0) was passed into a Dowex-1 x 8 resin (200-400 mesh) column and americium and lanthanum were adsorbed on the resin. Then 5 \underline{M} NH₄SCN eluant was used continuously. The elution position of lanthanum could be found easily by adding NH₃ to the eluting solution. After the complete elution of lanthanum was confirmed, americium was eluted with a volume of $0.1 \underline{M}$ HCl which was three to four times larger than the volume of resin bed.

Two 3.2 cm diameter x 25 cm height columns were used initially for this separation. Though the separation was incomplete because the height of the column was not sufficient (J. S. Coleman et al. recommended using a column of 40 cm height⁵), the major part of the lanthanum was separated by this elution. Then the same procedure was repeated with a 2.0 cm diameter x 3.5 cm height column, and a 300 ml americium portion completely free of lanthanum was obtained. The flow rate was about 0.4 cm/min and the necessary volume of anion exchanger to perform the complete separation of lanthanum from americium was found to be about 20 ml for 1 gram of rare earth as suggested by Coleman et al.⁵

d. Separation of aluminum.

The result of spectrographic analysis of the americium portion which was obtained from the above-mentioned procedures showed that only aluminum (and a small -13-

amount of manganese) was not separated completely. Then NaOH dissolution and 2 \underline{M} NH₄SCN elution were tried in order to remove aluminum (and manganese) from americium. Though the details of these methods will be mentioned later, both are especially convenient only in combination with the above-mentioned procedures. The procedure for the separation of aluminum (and manganese) was as follows:

When the 5 \underline{M} NH₄SCN feed solution for americiumlanthanum separation was prepared on Dowex-50 resin, 2 \underline{M} NaOH was poured into the Dowex-50 resin column prior to elution with 5 \underline{M} NH₄SCN. Aluminum was dissolved into excess NaOH solution and americium remained on the resin as americium hydroxide. After americium hydroxide was dissolved with 0.1 \underline{M} HCl, 2 \underline{M} NaOH was poured on again to dissolve aluminum completely (NaOH dissolution method).

After lanthanum was eluted from Dowex-1 resin with $5 \underline{M} \text{ NH}_4 \text{SCN}$ eluant, $2 \underline{M} \text{ NH}_4 \text{SCN}$ was poured into the same column, then aluminum and manganese were eluted before americium was eluted ($2 \underline{M} \text{ NH}_4 \text{SCN}$ elution method).

2. Results.

As a result of the above-mentioned purification, 95 ml of pure americium solution (0.1 <u>M</u> HCl) was obtained. It was found that the total amount of americium was 51 mg and the recovery of americium during the purification process was nearly 100%.

The result of spectrographic analysis of about 50 μ g of americium is shown in Table III. No impurities except aluminum and manganese could be detected. The relative amounts of impurities are shown in the "After Purification" column in Table II. It should be understood that the relative amounts of aluminum and manganese are quite small although both were detected in spectrographic analysis.

3. Discussion.

 a. Separation of plutonium, iron, and other impurities. In the anion exchange separation with 9 M HCl eluant, the alpha assay of the eluting solution and washing solution showed that all the americium passed through the column; on the other hand, all the plutonium (its oxidation state was believed to be +4) was adsorbed on Dowex-1 resin.

Table IV shows an example of the relative amounts of the impurities after the anion exchange separation with 9 <u>M</u> HCl eluant. It should be observed that aluminum, lanthanum, calcium, manganese, and chromium are not separated as expected, but bismuth, plutonium, and iron are reduced below the detection limit of spectrographic analysis.

Table IV.	Relative amounts	of	impurities	after	anion	exchange
	separation with 9	М	HCl.			

Main impurities	Am	A1	Bi	La	Pu	Fe	Ca	Mn	Cr
Relative amount	1. 0	1.1	<0.017	110	<0.34	<0.0003	0.017	1.1	1.1

b. <u>Preparation of the feed solution for americium-lanthanum</u> separation.

As suggested by Coleman⁵, the 5 <u>M</u> NH₄SCN feed solution can be obtained by eluting the Dowex-50 resin column after the sample is adsorbed on the column. The lower the acidity of the solution is, the more strongly americium and lanthanum are adsorbed on Dowex-50 resin.⁶ Since americium and lanthanum are more strongly adsorbed on Dowex-50 at low acidity, it is necessary to dilute the 9 \underline{M} HCl sample solution (which was obtained from the anion exchange separation with 9 M HCl) below 2 M HCl solution.

When americium and other ions adsorbed on Dowex-50 are eluted with 5 \underline{M} NH₄SCN, the following three elution parts are observed:

Color Activity

(1) The first elution portion _____none _____none

(2) The second elution portion red none

(3) The third elution portion none strong. Table V shows the result of spectrographic analysis for these elution parts. In this case, americium was adsorbed on Dowex-50 x 4 resin column from 1 <u>M</u> HC1 solution and eluted with 5 <u>M</u> NH₄SCN (column 1.1 cm diameter x 20 cm height, flow rate \simeq 0.2 cm/min).

Table V.	Amounts of impurities in eluting solution in *
	5 M NH ₄ SCN elution from Dowex-50 column.

	Vol. of elution	1					Impurit	ies		· · ·		
Samples	(ml)	Ca	A1	Mg	Fe	Mn	Am	Cr	Pu	La	Ni	Bi
Elution portion (1)	7.5	05	1	0.1	<0.01		<0.5	0.5	<1	<0.01	<0.01	<0.05
Elution portion (2)	6.0	0.5	3	0.05	0.2	5	<0.5	0.5	<1	<0.01	<0.01	<0.05
Elution portion (3)	20.0	0.1	0.5	0.03	<0.01	0.05	<0.5**	0.5	<1	20	<0.01	<0.05
Blank		0.2	0.05	0.05	<0.01	<0.01	<0.5	<0.01	<1	<0.01	<0.01	<0.05

* μ gs per entire sample (100 λ), 100 λ of sample solution was obtained by mixing 50 λ of aliquot from each elution portion and 50 λ of pure HCl.

** Amount of americium is $1.8 \mu g$ from the result of alpha assay.

From Table V the following facts can be observed:

- Nearly all the lanthanum and americium are contained in portion (3).
- (2) Nearly all the iron is contained in portion (2).
- (3) Major part of manganese is contained in portions (2) and (1).
- (4) Aluminum is contained in portions (2) and (1).

Accordingly, the following interesting conclusion is derived from the above-mentioned facts.

In the case of elution from cation exchange resin with 5 MNH₄SCN, iron and manganese can be separated from americium and aluminum will be separated from americium; on the other hand, the behavior of lanthanum is the same as that of americium. The behavior of chromium is not clear but the separation of chromium from americium seems to be difficult.

c. Separation of lanthanum.

(1) 5 <u>M</u> NH₄SCH elution.

It was confirmed that the anion exchange separation of americium and lanthanum with 5 <u>M</u> NH₄SCN eluant was perfect. Table VI shows the behavior of this elution; in this case the sample containing about 1.85 mg of americium was treated (column 1.1 cm diameter x 35 cm height, resin Dowex-1 x 8, flow rate $\simeq 0.4$ cm/min). As shown in Table VI, the entire lanthanum is eluted; on the other hand, americium could not be detected by alpha activity in this eluting solution, so that the following conclusion is obtained: in the case of anion exchange separation with 5 <u>M</u> NH₄SCN eluant, lanthanum can be separated from americium perfectly and iron, aluminum, and manganese seem to be adsorbed on the resin with americium.

Sample	Fraction		,]	[mpurit:	ies			
No.	(ml)	La	Fe	Am	Ca	A1	Mg	Mn	Bi	Cr
1	0-40	<0.01	<0.01	<0.1	0.01	<0.01	<0.01	<0.01	≼0.05	<0.01
3	80-120	10	<0.01	<0.1	0.03	<0.01	<0.01	<0.01	<0.05	<0.01
5	160-200	5	<0.01	<0.1	0.02	<0.01	<0.01	<0.01	<0.05	<0.01
7	240-280	3	<0.01	<0.1	0.01	<0.01	<0.01	<0.01	<0.05	<0.01
9	320-360	0.5	<0.01	<0.1	0.01	<0.01	<0.01	<0.01	<0.05	<0.01
11	400-440	<0.01	<0.01	<0.1	<0.01	<0.01	<0.01	<0.01	<0.05	<0.1
13	480-520	<0.01	<0.01	<0.1	<0.01	<0.01	<0.01	<0.01	<0.05	<0.1
15	560-600	<0.01	<u><</u> 0.01	<0.1	0.02	0.05	<0.01	<0.01	<0.05	<0.01

Table VI. Amounts of impurities in eluting solution in 5 \underline{M} NH₄SCN elution from Dowex-1 column^{*}

*

 μ gs per entire sample (100 λ) which was obtained from each fraction.

When 5 <u>M</u> NH₄SCN solution containing americium is left standing, the solution begins to be colored yellow and if the solution is left for a long time, a yellow precipitate is formed. This is considered to be a result of the formataion of a decomposition product of NH₄SCN by alpharadiation of americium. Consequently, the eluting solution passing through the column sometimes has a yellow color.

(2) 0.1 M HCl elution,

Americium adsorbed on Dowex-l resin can be eluted easily with 0.1 M HCl. Table VII shows the behavior of this elution; in this case the sample containing 1.85 mg of americium was treated (column 1.1 cm diameter x 35 cm height, resin Dowex-l x 8).

Sample	Fraction		Impurities								
No.	(ml)	La	Fe	Am	Ca	Al	Mg	Mn	Bi	Cr	
1	0-15	<0.01	<0.01	<0.1	0.03	0.01	0.02	<0.01	<0.05	<0.01	
2	15-30	<0.01	<0.01	10	0.1	7	0.05	<0.01	<0.05	<0.01	
3	30-45	<0.01	<0.01	2	0.2	2	0.05	<0.01	<0.05	<0.01	
4	45 - 60	<0.01	<0.01	0.4	0.1	0.5	0.05	<0.01	<0.05	<0.01	
5	60-100	0,01	<0.01	0.1	0.1	0.5	0.1	2	<0.05	<0.01	
6	100-140	<0.01	<0.01	<0.01	0.1	0.07	0.05	1	<0.05	<0.01	

Table VII.Amounts of impurities in eluting solution in0.1 M HCl elution from Dowex-l column.

 μ gs per entire sample (100 λ) which was obtained from each fraction.

The following conclusion was obtained from Table VII: in the case of elution with 0.1 M HCl from an anion exchange column, americium is eluted easily; aluminum is also eluted easily and its behavior is quite similar to that of americium. As manganese is eluted a little after americium, manganese is separable from americium. Iron is eluted after americium is eluted, so that iron can be separated completely.

d. Separation of aluminum.

All impurities except aluminum (and manganese) were separated completely by applying the anion exchange separation with 9 <u>M</u> HCl eluant and 5 <u>M</u> NH₄SCN eluant. Although there are several methods for the separation of aluminum from americium, a method combined with the above-mentioned procedures is desirable. The following two methods were tried from this viewpoint.

(1) NaOH dissolution method.

When the 5 \underline{M} NH₄SCN feed solution for americiumlanthanum separation is prepared on Dowex-50 resin, if 2 <u>M</u> NaOH is passed into the column prior to eluting it with 5 <u>M</u> NH₄SCN, aluminum should be dissolved into excess NaOH solution and would pass through the column. On the other hand, americium is precipitated as the form of hydroxide and will remain on the column because the resin serves as a filter bed.

Though it is desirable to use about 5 \underline{M} NaOH solution in order to dissolve aluminum, as discussed previously, the viscosity and density of 5 \underline{M} NaOH seemed to be too high, so that 2 M NaOH was used.

(2) 2 M $NH_{A}SCN$ elution method.

It was found that the use of 5 \underline{M} NH₄SCN in the anion exchange separation was very effective for the separation of lanthanum from americium, but was not effective for the separation of aluminum from americium. This means that the concentration of 5 \underline{M} NH₄SCN is strong enough to adsorb both americium and aluminum on a column. However, the complexes of both ions with SCN ion are not the same and complexing of americium ion must be stronger than that of aluminum ion. Accordingly, the separation of aluminum from americium must be possible by eluting with NH_4SCN solution of low concentration. On the other hand, it has been found that the use of $2 \underbrace{M}{M}$ NH₄SCN is effective for the separation of aluminum from iron using an anion exchange column¹⁷ (in this case, iron remains on the resin and aluminum passes through the column by eluting with 2 M NH_4SCN). The use of 2 \underline{M} NH₄SCN was tried for this separation. Comparing the results of both methods, Table VIII is obtained. From Table VIII the following conclusions

were observed:

- (a) In the case of NaOH dissolution method, it appears that part of the aluminum does not dissolve in excess NaOH, probably due to co-precipitation with americium, so that it is desirable to repeat the dissolution of aluminum with 2 <u>M</u> NaOH after dissolving the first precipitate with diluted HCl.
- (b) In the case of 2 <u>M</u> NH₄SCN elution, the separation of aluminum from americium is not complete. However, the reason the separation was not complete may be the use of a short column (15 cm height), so it may be necessary to use a column of height 30 cm or longer in order to get complete separation.
- (c) It is very interesting and important that manganese, which cannot be separated in the case of NaOH dissolution method, is separated completely in the case of 2 \underline{M} NH₄SCN elution method. Therefore, the 2 \underline{M} NH₄SCN elution method is effective in separating both aluminum and manganese.
- (d) In the case of the NaOH method, the concentration of sodium is very high, but this is not a problem because sodium can be removed by sufficient washing with water.

	Impurities									
Samples	Al	Am	Bi	Ca	Cr	Fe				
NaOH dis- solution	0.5	>10	<0.05	0.05	<0.01	<0.01				
2 M NH ₄ SCN elution	0.7	~ 10	<0.05	0.05	<0.01	<0.01				
Blank	0.03	<1	<0.05	0.1	<0.01	<0.01				

Table VIII. Separation of aluminum (comparison of NaOH method and 2 \underline{M} NH₄SCN elution method).*

	Impurities								
Samples	Mg	Mn	La	Na	Ni	Np			
NaOH dis- solution	0.03	0.5	<0.01	10	<0.01	<1			
2 M NH ₄ SCN elution	0.03	<0.01	<0.01	<1	<0.01	<1			
Blank	0.03	<0.01	<0.01	<1	<0.01	<1			

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Samples	Pb	Pu	Si	Ū	Yb	Y
NaOH dis- solution	<0.1	<1	<001	<0.5	<0.01	<0.01
$2 \text{ M NH}_4 \text{SCN}$	<0.1	<1	<0.01	<0, 5	<0.01	<0.01
Blank	<0.1	<1	<0.01	<0. 5 🦂	<0.01	<0.01

* μ gs per entire sample (100 λ).

V. SUMMARY

As one of the general methods of purification of americium the rough separation of the impurities by using precipitation method and the purification by using ion exchange method were tried and satisfactory results were obtained. In this experiment, all impurities except aluminum and manganese were separated from americium using the anion exchange separation with 9 <u>M</u> HCl eluant and with 5 <u>M</u> NH₄SCN eluant. Aluminum and manganese can be separated using NaOH dissolution and 2 <u>M</u> NH₄SCN elution: methods which are applicable together with the above-mentioned anion exchange methods.

Some interesting facts were observed during the process of elution with $NH_{A}SCN$ from the cation and anion exchange columns.

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