Separation of Uranium and Protactinium from Thorium by Amine Extraction

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(Received September 18, 1959)

Preuss and Saunders⁽¹⁾ reported the extraction of uranium from sulfuric acid solution with amines. The use of primary amine as an extractant for thorium from sulfuric acid was reported by Crous and Denis⁽²⁾. Moore and his coworkers studied the liquid-liquid extraction of protactinium, niobium, tantalum, cobalt and zinc by amine⁽³⁻⁵⁾.

In this paper, the extraction of thorium, protactinium and uranium from hydrochloric, nitric and sulfuric acid of various concentrations with secondary amine is studied. Amberlite LA-1 in kerosene diluent is used as an extractant.

The free-base form of Amberlite LA-1 removes acids from aqueous solutions by neutralization as illustrated by reaction 1,

$$(\mathrm{RR'NH})_{\mathrm{org}}+\mathrm{H}^{+}+\mathrm{A}^{-}\rightleftarrows(\mathrm{RR'NH_2A})_{\mathrm{org}} \quad (1)$$

where the ions, H^+ and A^-, refer to the aqueous phase and "org" refers to the amine salt dissolved in the organic solvent. When the amine salt formed through neutralization is brought into contact with an aqueous solution which contains another anion, the exchange of anions associated with the amine salt takes place as shown by reaction 2,

$$(\mathrm{RR'NH_2A})_{\mathrm{org}}+\mathrm{B}^{-}\rightleftarrows(\mathrm{RR'NH_2B})_{\mathrm{org}}+\mathrm{A}^{-} \quad (2)$$

where A^- and B^- represent two different anions.

When an element exists as a complex anion in an aqueous medium, it will be extracted by the amine according to this exchange process. Then it is of interest to compare the acid dependency of the extraction coefficient of an element by the amine with that of the distribution coefficient of the same element by the anion exchange resin. From the result of the extraction study, it is found that under the optimum conditions uranium, protactinium and thorium can be separated from each other. This separation procedure will be suitable for the recovery of uranium-233 from irradiated thorium blanket fuel. Consequently, the radiation damage of Amberlite LA-1 and LA-2 is studied by two methods.

The Extraction Coefficient of Thorium, Protactinium and Uranium from Hydrochloric, Nitric and Sulfuric Acid of Various Concentrations by Amberlite LA-1

Experimental.—Two milliliters each of 5% Amberlite LA-1 in a kerosene diluent is shaken in a small glass-stopped tube for 1 min. with the same volume of an acid solution of the sample. After centrifuging, 1 ml. each of the aqueous and the organic phases are pipetted out and the concentration of the element is measured as follows. Thorium-234 (UX_1) and protactinium-233 are used as tracers for thorium and protactinium, and the γ-ray activity is measured with a well-type scintillation counter. Uranium nitrate is used as the starting material

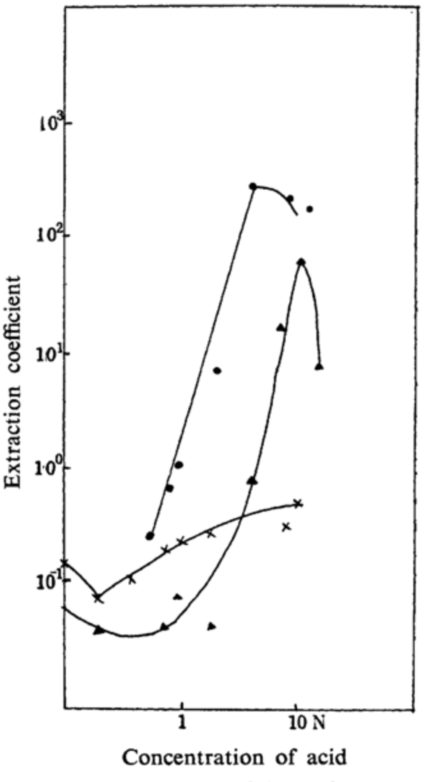

Fig. 1. Extraction coefficient of Th, Pa and U from HCl with Amberlite LA-1.
U —●—, Pa —▲—, Th —×—

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1) A. Preuss and J. Saunders, RMO-2533 (1955).
2) D. J. Crous and J. O. Denis, ORNL-1859 (1955).
3) J. Y. Ellenburg, G. W. Leddicotte and F. L. Moore, *Anal. Chem.*, 26, 1045 (1954).
4) H. A. Mahlman, G. W. Leddicotte and F. L. Moore, ibid., 26, 1939 (1954).
5) F. L. Moore, ibid., 27, 70 (1955).

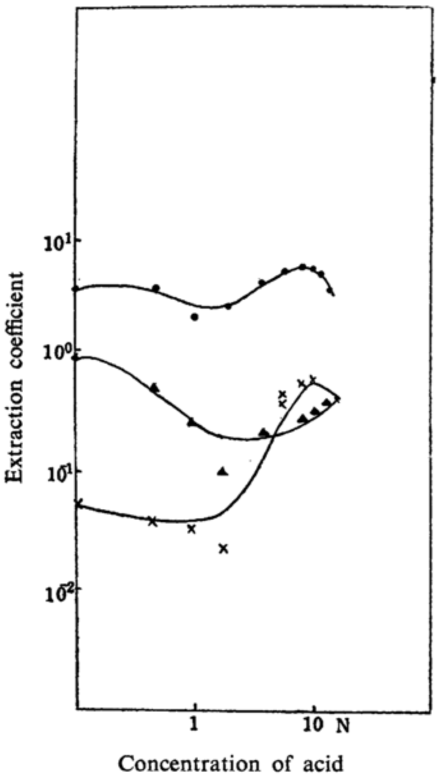

Fig. 2. Extraction coefficient of Th, Pa and U from HNO_3 with Amberlite LA-1.

U —●—, Pa —▲—, Th —×—

for extraction and its concentration is determined colorimetrically with hydrogen peroxide. The extraction coefficient is calculated by the following equation,

$$E=\frac{\text{Concentration of U, Th or Pa in organic phase/ml.}}{\text{Concentration of U, Th or Pa in aqueous phase/ml.}}$$

where E is the extraction coefficient. The results are shown in Figs. 1—3.

Results.—The maximum extraction coefficient of uranium is about 200 at 6∼12 N hydrochloric acid and below this concentration the extraction coefficient decreases with a slope of 3. From nitric acid solution, uranium is extractable in all the concentration ranges examined, giving an extraction coefficient of 2∼5. The extraction coefficient of 1∼3 is also found from 1∼12 N sulfuric acid solution. Thorium is not extracted from these acids except 6∼15 N nitric acid, but the extraction coefficient is only 0.5 even under this condition. Protactinium is favorably extracted from hydrochloric acid of higher concentration with a maximum extraction coefficient of 60. From nitric or sulfuric acid the extraction coefficient of protactinium is very low.

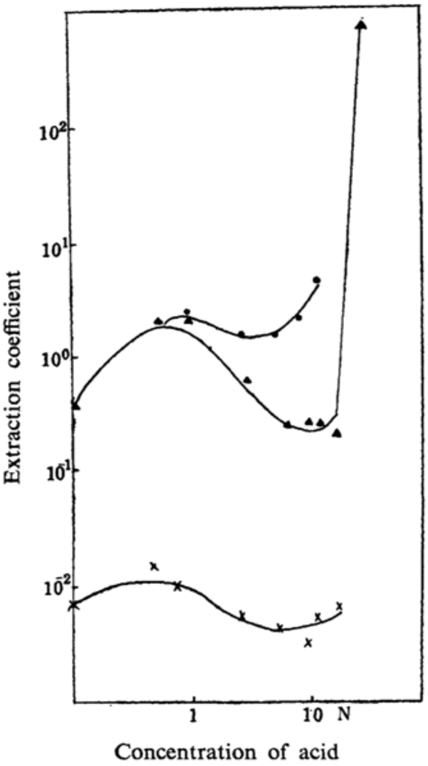

Fig. 3. Extraction coefficient of Th, Pa and U from H_2SO_4 with Amberlite LA-1.

U —●—, Pa —▲—, Th —×—

Comparison of Extraction Coefficient with Distribution Coefficient

If the amine extraction is based on the anion exchange mechanism, it is valuable to compare the amine extraction curve with the acid dependency of the distribution coefficient of these elements by anion exchange resin. From this view-point, the distribution coefficient (Kd) of thorium, protactinium and uranium between hydrochloric, nitric and sulfuric acids of various concentrations and anion exchange resin are measured by the following method.

Experimental.—Dowex 1 ×8 (100∼200 mesh) is used as an anion exchange resin. It is treated with 10% sodium hydroxide solution, washed with water and then converted into the desired form with hydrochloric, nitric or sulfuric acid. Half a gram of dried resin is placed for 24 hr. in 5 ml. of the acid solution of thorium, protactinium or uranium. The solution is filtered and the concentration of 1 ml. of filtrate is compared with that of the reference solution which contains no resin. Kd is calculated by the following equation,

$$Kd=\frac{\text{C(1 g. of resin)}}{\text{C(1 ml. of solution)}}=\frac{\text{C(reference)}-\text{C(filtrate)}}{\text{C(filtrate)}}\times 10$$

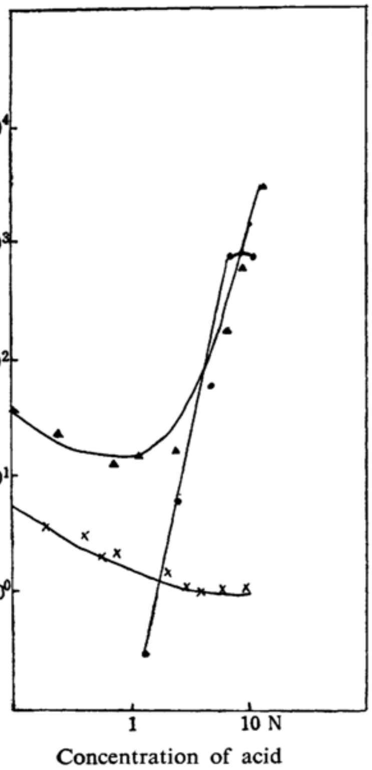

Fig. 4. Distribution coefficient of Th, Pa and U between Dowex 1 and HCl.

U —●—, Pa —▲—, Th —×—

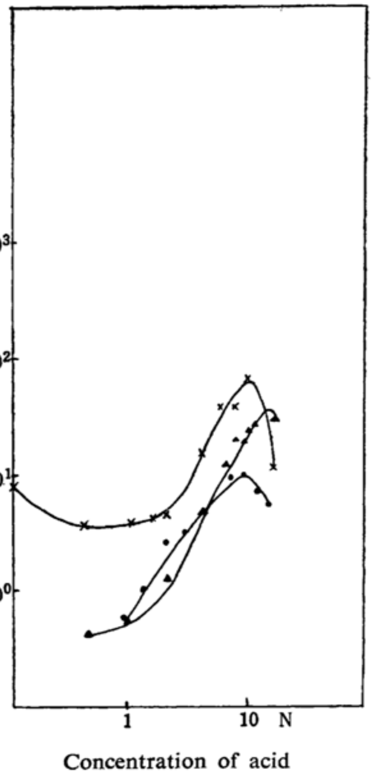

Fig. 5. Distribution coefficient of Th, Pa and U between Dowex 1 and HNO_3.

U —●—, Pa —▲—, Th —×—

where C means the concentration.

UX_1 and Pa-233 are used as tracers for thorium and protactinium, respectively. Their γ-ray activities are measured to determine the concentration. The concentration of uranium is determined by the colorimetric method.

Results.—The results are shown in Figs. 4—6. Concerning the anion exchange of these elements, some studies have already been reported by Kraus, Nelson and Danon[6,7]. In hydrochloric acid solution, the shapes of *K*d curves resemble those of extraction curves by LA-1, but the extraction coefficient of uranium is relatively very high. In a more concentrated nitric acid, Fig. 5 shows the order of adsorption as Th> Pa>U, but Fig. 2 shows the order of extraction as U>Th>Pa. In sulfuric acid, uranium is most favorably extractable with the amine, but Fig. 6 shows nearly the same *K*d value of uranium and protactinium.

These facts show that Amberlite LA-1 is selective in the extraction of uranium. It is not clear from these data whether or not this selectivity is due to the difference in the mechanism of amine extraction and anion exchange.

The Separation of Uranium, Protactinium and Thorium by Amberlite LA-1

According to the study of the extraction coefficient, uranium and protactinium are sufficiently extracted from 8 N hydrochloric acid, but thorium is not extracted from hydrochloric acid of any concentration. At 3 N hydrochloric acid, the extraction coefficients are about 35, 0.1 and 0.05 for uranium, protactinium and thorium, respectively. From these facts, the separation of these elements is studied as follows.

Experimental.—*a*) *The separation of thorium and protactinium from 8 N hydrochloric acid.*—Fifty milligrams of thorium nitrate is irradiated in the J. R. R.-1 Reactor for 2 hr. at a flux of 10^{11} neutrons/cm^2/sec. The irradiated sample is dissolved in 2 ml. of 8 N hydrochloric acid and extracted with 5% Amberlite LA-1 (HCl form) in kerosene. The organic phase is scrubbed three times with 3 ml. each of 8 N hydrochloric acid, then stripped three times with 2 ml. each of 0.1 N hydrochloric acid. γ-Ray activity of about 3.8×10^6 c. p. m. of protactinium is collected in the stripping solution and thorium is not detected by thorin in this solution. The recovery of protactinium is about 80%.

b) *The effect of kerosene diluent on the extraction coefficient.*—The effect of kerosene diluent is tested

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[6] K. A. Kraus and F. Nelson, A/Conf. 8/P/837 (1955).
[7] J. Danon, *J. Am. Chem. Soc.*, 78, 5935 (1956).

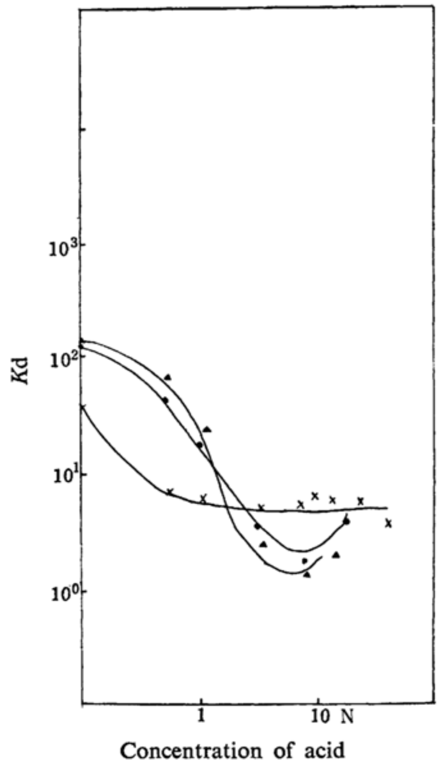

Fig. 6. Distribution coefficient of Th, Pa and U between Dowex 1 and H_2SO_4.

U —●—, Pa —▲—, Th —×—

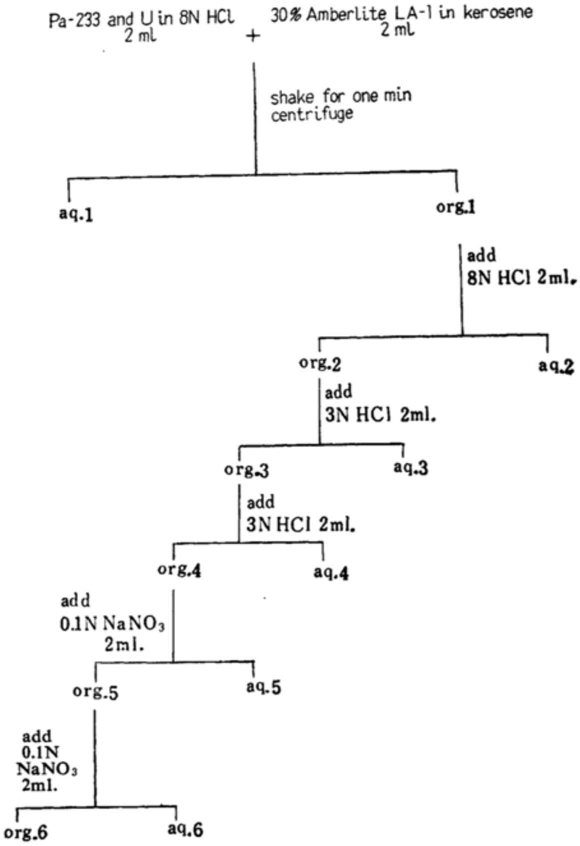

Fig. 7. Procedure of separating uranium and protactinium.

by calculating the extraction coefficient of protactinium from 8 N hydrochloric acid. From zero to 37.5% LA-1 in kerosene is used as an extractant. Two milliliters each of aqueous and organic phases are shaken for 1 min. and centrifuged. The extraction coefficient is determined as explained above. The results are shown in Table I. The effect of the diluent is negligible within the concentration of 2.5 to 37.5% LA-1 in kerosene.

TABLE I. THE EFFECT OF DILUENT TO THE EXTRACTION COEFFICIENT OF PROTACTINIUM FROM 8 N HCl

The concentration of Amberlite LA-1 in kerosene	Extraction coefficient of Pa from 8 N HCl
0 %	0.05
0.5	27
2.5	194
5.0	150
7.5	158
12.5	256
17.0	143
37.5	197

c) Stripping of uranium.—About 10 mg. of uranium is extracted from 2 ml. of 8 N hydrochloric acid with 2 ml. of 30% Amberlite LA-1 in kerosene. Then, uranium is stripped from the organic phase with sodium nitrate, ammonium sulfate and sodium carbonate of various concentrations. The concentration of uranium in aqueous phase is measured colorimetrically with hydrogen peroxide. The results are shown in Table II.

Table II shows that uranium is completely stripped from the organic phase with 0.1 N sodium nitrate.

TABLE II. RECOVERY OF URANIUM FROM 30% AMBERLITE LA-1 IN KEROSENE

Concentration of stripping agent	Distilled water	$NaNO_3$	$(NH_4)_2SO_4$	Na_2CO_3
0 N	106%	—	—	—
〃	119	—	—	—
〃	120	—	—	—
0.1	—	100 %	88.4%	82.0%
〃	—	102	—	—
〃	—	105	—	—
0.5	—	94.0	89.4	75.0
1.0	—	89.8	54.3	94.0
2.0	—	80.5	60.5	—
4.0	—	54.6	—	—
5.0	—	30.5	54.3	87.6

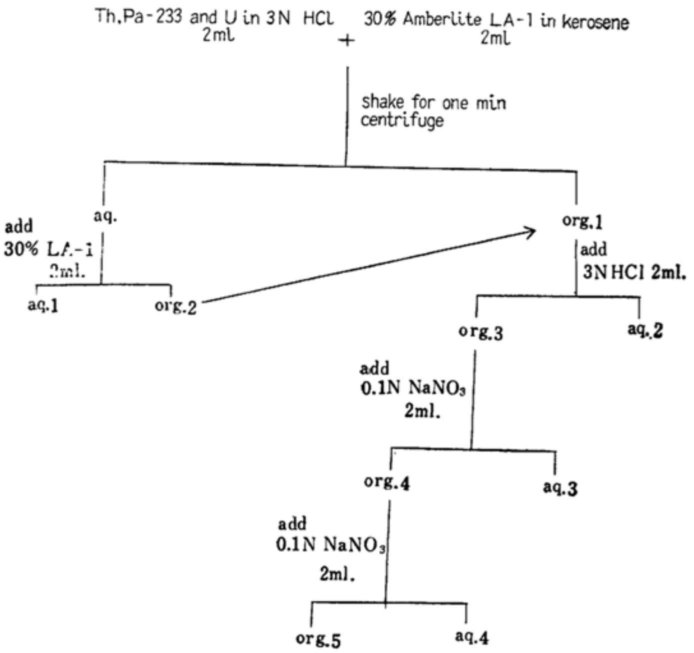

Fig. 8. Procedure of separating uranium from irradiated thorium.

Recovery with 0.1 N ammonium sulfate is 88.4%. The recovery of uranium decreases with the increase of the concentration of sodium nitrate or ammonium sulfate. Recovery with sodium carbonate is 75∼94 %. When distilled water is used as a stripping agent, two phases do not separate even after centrifugation and colorimetric data show a higher value. Consequently, the best stripping agent is 0.1 N sodium nitrate.

d) *The separation of protactinium and uranium by 3N hydrochloric acid scrubbing.*—The separation scheme is shown in Fig. 7. Two milliliters of 8 N hydrochloric acid solution of protactinium-233 and uranium is shaken with 2 ml. of 30% Amberlite LA-1 in kerosene for 1 min. Most of the protactinium and uranium are extracted in this procedure. The organic phase is scrubbed with 2 ml. of 8 N hydrochloric acid, then protactinium is stripped twice with 3 N hydrochloric acid. Finally uranium is stripped twice with 0.1 N sodium nitrate. The results are shown in Table III. It is seen from these results that protactinium-233 is sufficiently extracted from 8 N hydrochloric acid and easily stripped with 3 N hydrochloric acid and that uranium is also sufficiently extracted from 8 N hydrochloric acid and about 40% of uranium is stripped with 3 N hydrochloric acid. Sixty per cent of the uranium is recovered with a slight contamination of protactinium-233 in this procedure. Thorium is not extracted under the condition explained above.

TABLE III. RECOVERY* OF PROTACTINIUM AND URANIUM

Sample No.	Medium	Recovery of Pa-233	Recovery of U
aq. 1+aq. 2	8 N HCl	1.3%	8.4%
aq. 3+aq. 4	3 N HCl	98.0	35.7
aq. 5+aq. 6	0.1 N NaNO$_3$	0.3	70.0
org. 6	30% Amberlite LA-1 in kerosene	0.4	—

* This ratio is calculated by two experiments.

e) *The extraction of uranium from thorium and protactinium in 3N hydrochloric acid solution.*— About 50 mg. of thorium nitrate is irradiated in the J. R. R.-1 Reactor. After irradiation, 20 mg. of uranium is added to this sample and the mixture is dissolved in 2 ml. of 3 N hydrochloric acid. Two milliliters of Amberlite LA-1 in kerosene is added to this solution and the solution is shaken for 1 min. After centrifuging, the aqueous phase is re-extracted with 2 ml. of 30% LA-1 solution. Two organic phases are scrubbed with 2 ml. of 3 N hydrochloric acid. Uranium is stripped twice with 2 ml. each of 0.1 N sodium nitrate. The activity of protactinium-233 is measured by γ-ray counting. The Recovery of uranium is determined by the colorimetric method. Fig. 8 shows the separation scheme. Results are shown in Table IV.

Table IV. RECOVERY* OF PROTACTINIUM AND URANIUM

Sample No.	Medium	Recovery of Pa-233	Recovery of U
aq. 1+aq. 2	3 N HCl	98.5%	0%
aq. 3+aq. 4	0.1 N NaNO$_3$	0.5	100
Org. 5	30% Amberlite LA-1 in kerosene	0.7	—

* This ratio is calculated by two experiments.

TABLE V. RADIATION DAMAGE OF AMBERLITE LA-1 AND LA-2

Sample No.	Amine	Distance from Co-60	Dose rate	Irradiation time		Total dose	Exchange capacity	Extraction coefficient of Pa from 8 N HCl
		cm.	r/hr.	hr.	min.	r	meq./ml.	
1	Amberlite LA-1	12.5	5.6×10^5	89	20	5×10^7	2.03	130
2	〃	〃	〃	17	50	1×10^7	2.03	125
3	〃	10	8.1×10^5	6	16	5×10^6	2.03	134
4	〃	〃	〃	1	15	1×10^6	2.03	124
5	〃	15	4.2×10^5	1	12	5×10^5	2.01	122
6	〃	30	1.3×10^5		48	1×10^5	2.01	152
7	〃	50	4.4×10^4	1	08	5×10^4	2.01	173
8	〃	—	0	0		0	2.03	183
9	Amberlite LA-2	12.5	5.6×10^5	89	20	5×10^7	2.03	83
10	〃	〃	〃	17	50	1×10^7	2.03	92
11	〃	10	8.1×10^5	6	16	5×10^6	2.03	110
12	〃	〃	〃	1	15	1×10^6	2.03	87
13	〃	15	4.2×10^5	1	12	5×10^5	2.01	86
14	〃	30	1.3×10^5		48	1×10^5	2.01	86
15	〃	50	4.4×10^4	1	08	5×10^4	2.03	87
16	〃	—	0	0		0	2.03	85

Uranium is completely recovered from the first solution by this procedure.

Radiation Damage of Amberlite LA-1 and LA-2

If these amines are used in reactor fuel reprocessing, radiation damage may occur on the action of high level γ-rays. Amberlite LA-1 and LA-2 are irradiated by γ-rays from Co-60 under various conditions (Table V). The degree of radiation damage is measured by extraction of protactinium-233 from 8 N hydrochloric acid and by potentiometric titration in dioxane. Two milliliters of irradiated sample is dissolved in 50 ml. of dioxane and is titrated with 0.2 N perchloric acid in dioxane. The end point is determined by drawing the potentiometric titration curve. A pH meter is used as a potentiometer. A calomel electrode, of which the aqueous solution of potassium chloride is displaced by saturated methanol solution of potassium chloride[8], is used as a reference electrode. A platinum electrode is used as an indicating electrode. The typical titration curve is shown in Fig. 9. The results are shown in Table V. Another method is to measure the extraction coefficient of protactinium-233 from 8 N hydrochloric acid by 30% irradiated amine in kerosene. The extraction coefficient is determined as mentioned above. Results are also shown in Table V. The radiation damage of Amberlite LA-1 and LA-2 is negligible under these conditions (dose rate is 8.1×10^5 r/h, maximum total dose is 5×10^7 r).

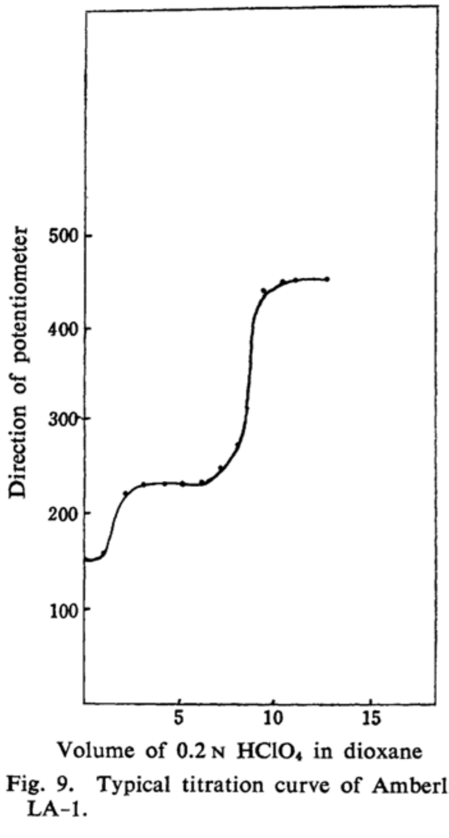

Fig. 9. Typical titration curve of Amberlite LA-1.

Summary

Uranium, protactinium and thorium are satisfactorily separated from each other by secondary amine extraction. Amberlite LA-1 in kerosene diluent is used as the extractant. Separation from hydrochloric acid solution is superior to that from systems using other acids. The acid

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[8] J. S. Fritz, A. U. Moye and M. J. Richard, *Anal. Chem.*, **29**, 1685 (1957).

dependency of the extraction coefficient by amine fairly resembles that of the distribution coefficient by anion exchange resin, but the former has a selectivity for uranium. Under the total dose of 5×10^7 *r*., the radiation damage of Amberlite LA-1 is negligibly small. From these results, it is evident that there is a possibility of applying the amine extraction to the recovery of uranium-233 from reactor blanket fuel.

The authors wish to express sincere thanks to Dr. Toshio Nakai for his guidance.

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