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The Chemistry of Protactinium. I. The Preparation of Protactinium-233 and the Purification of Protactinium-231

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Many methods, such as the co-precipitation method, the solvent extraction method and the ion exchange method, had previously been proposed for the separation and the purification of protactinium. However, these methods have some defects for the separation of Pa-233 produced by the thermal neutron irradiation of thorium dioxide and the purification of commercial Pa-231, when an attempt is made to study the chemistry of protactinium. From the above point of view, a combined method of solvent extraction and anion exchange was investigated. In the present paper, the detailed conditions for the TBP extraction of protactinium from a hydrochloric acid solution and the method for its final purification by anion exchange were described. The present method is comparatively simple and rapid, and chemically- and radiochemically-pure protactinium can thus be obtained.

Although protactinium has been known for a long time, its chemical properties are still far from having been thoroughly investigated; this is because of its comparative natural scarcity, its lack of usefulness, and the difficulties involved in its separation due to the remarkable similarity of its chemical properties to such Vb elements as niobium and tantalum, which usually accompany protactinium. This backwardness in the investigation is also attributable to its unstability in an aqueous solution; that is, it has a strong tendency to hydrolyze and to precipitate, even in a relatively strong acid solution. Recently, however, the chemistry of protactinium has become of interest in nuclear reactor technology because one of its isotopes, ^{233}Pa, is an intermediate in the thorium-uranium breeding cycle, being the parent of the fissionable isotope ^{233}U. Some investigations have therefore been carried out on the chemistry of protactinium.[1-3] However, the results are not always acceptable because the unstability in aqueous solution has resulted in some confusion in published works. Therefore, we have attempted to study its chemistry exhaustively, using the various methods available.

In this paper simple and relatively rapid methods will be described for the preparation of ^{233}Pa and for the purification of commerical ^{231}Pa.

Protactinium-233 can be produced by the $^{232}\mathrm{Th}(n, \gamma)\ ^{233}\mathrm{Th} \xrightarrow[\beta^-]{} {}^{233}\mathrm{Pa}$ reaction. Many methods for the separation of protactinium from neutron-irradiated thorium have been proposed, but they are not satisfactory because of the necessity for the special reagents or because of the complexity of the procedures. Among these, the ion exchange method is excellent in this respect, but it is generally most useful in the treatment of a microamount of materials, so that its direct application to the complete separation of a large amount of materials will make for a cumbersome procedure. Therefore, it is desirable to use a preliminary separation method before ion exchange. For this purpose, McCormack and his co-workers[4] used diisopropylcarbinol extraction from a nitric acid solution, but this reagent is not easily available. Will[5] used diisopropyl ketone after the ion exchange separation and finally purified ^{233}Pa by the use of another small anion exchange column. His procedure, however, is complicated.

In this experiment, tri-*n*-butyl phosphate was chosen for its easy availability, its ease of handling and its powerful extractability. This reagent was used for the separation of thorium, protactinium and uranium by the countercurrent extraction method from a hydrochloric acid solution;[6] its behavior toward the accompanying fission products will not be given. In this paper the conditions for the TBP extraction of ^{233}Pa from a hydrochloric acid solution and the method for its final purification by anion exchange will be described in detail.

For the purification of commercial ^{231}Pa, this anion exchange method was modified on the basis of its chemical and radiochemical purity.

Experiments

Reagents.—*Radioactive Isotopes.*—The kinds of radioactive isotopes, their suppliers, the commercial forms

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[1] H. W. Kirby, "The Radiochemistry of Protactinium," NAS-NS 3016, U. S. A. E. C., Washington D. C. (1959).

[2] M. Haissinsky and G. Bouissières, "Protactinium," Nouveau Traité de Chimie Minérale, XII, Ed. by P. Pascal, Masson et Cie., Paris (1958), p. 617.

[3] R. E. Elson, "The Chemistry of Protactinium," The Actinide Elements, Ed. by G. T. Seaborg and J. J. Katz, McGraw-Hill Book Co., New York (1954), p. 103.

[4] J. J. McCormack, F. H. Cripps and W. A. Wiblin, *Anal. Chim. Acta*, **22**, 408 (1960).

[5] M. W. Will, U. S. A. E. C., UCRL-8423 (1958).

[6] D. F. Peppard, G. W. Mason and M. V. Gergel, *J. Inorg. Nucl. Chem.*, **3**, 370 (1957).

TABLE I. RADIOACTIVE ISOTOPES USED IN THIS WORK

Nuclide	Supplier	Commercial form	Pre-treatment
^{106}Ru	Radiochemical Center, England	Trichloride	
^{95}Zr-^{95}Nb	Oak Ridge National Laboratory, U. S. A.	Oxalate	If necessary, each nuclide is separated by means of TTA extraction; Converted to HCl form
^{137}Cs	Oak Ridge National Laboratory, U. S. A.	Chloride	
^{144}Ce	Radiochemical Center, England	Trichloride	
^{90}Sr-^{90}Y	N. V. Philips-Roxane Pharmaceutisch-Chemische Industrie " Duphar ", Holland	Chloride	
^{231}Pa	Radiochemical Center, England	Pentoxide	
^{233}Pa	Prepared by this method		

and the methods of pretreatment are shown in Table I. Their radiochemical purities were certified by γ-ray and α-ray spectrometries, or by analyses of their β-ray absorption curves, before use.

Ion Exchanger.—A strong basic anion exchange resin, Dowex-1, 100—200 mesh, was used. It was conditioned in the usual manner and converted to the chloride form before use.

Solvent.—Highest purity-grade TBP was washed with a diluted sodium hydroxide solution and then with distilled water in order to remove any hydrolysis product. Immediately before use, it was then equilibrated with the aqueous solution to be used.

The other chemicals, such as thorium dioxide, hydrochloric acid and hydrofluoric acid, were of highest purity grade.

Apparatus.—The β- and γ-rays were measured by a Hitachi G. M. counter and a Hitachi well-type scintillation counter respectively. A Kobe-Kogyo Model PS-400 well-type scintillation probe and a Osaka-Dempa Model 4 gridded ionization chamber, both of them connected to a TMC-400 channel pulse height analyzer, Model 406-6, were used for the measurements of the γ- and α-ray spectra respectively. For the solvent extraction procedures, a Iwaki universal mechanical shaker, Model V-S, was used. The ion exchange column, the separatory funnel and the centrifuge cone were made of polyethylene in order to minimize the adsorption of protactinium on the wall.

Procedures.—The experimental procedure was as follows unless otherwise stated.

Solvent Extraction.—Ten-milliliter portions of the aqueous phase which had been adjusted to the desired condition and of the organic phase were mixed for 10 min. with a mechanical shaker. After the two phases had been completely separated, an aliquot of each phase was taken for the measurement of its gamma radioactivity by the use of a scintillation counter. Each value given is the average of the results of at least two determinations. Care was taken to check the material balance in each case.

Ion Exchange.—The column was prepared as follows. Ten milliliters of an exchanger immersed in distilled water was poured into a polyethylene column, 9 mm. in internal diameter, using finely-cut polyethylene cloth as a column support. The column thus prepared had a height of about 150 mm. After that, the column was treated passing through 30 ml. of the solution to be used at the flow rate of 0.2—0.3 ml./min. When the level of the solution reached the top of the exchanger bed, the sample solution was introduced and ion exchange separation was started. The flow rate of the influent was kept nearly constant, 0.2—0.3 ml./min., throughout this experiment.

For making elution curves, effluents were received in polyethylene test tubes for every suitable aliquot; their radioactivities were measured with the well-type scintillation counter.

The Preparation of the Sample for the Measurement of the α-Ray Spectra.—The method recommended by Kirby[7] was used: An aliquot of a diluted acidic sample solution was transferred to a stainless-steel disk coated with a thin collodion film. The solution was then evaporated to dryness under an infrared lamp, with the plate tilted as necessary to retain the solution in the center of the plate. The plate was then cooled, and the residue was covered with one milliliter of 0.1 N nitric acid. One drop of concentrated ammonium hydroxide solution was added, and the solution was again evaporated to dryness. The position of the lamp was lowered sufficiently to drive off all the ammonium nitrate, and then the plate was ignited over a flame until the organic coating had burned off. This was used for the measurement of the α-ray spectrum.

The Determination of Thorium and Uranium.—The thorium and uranium were determined by the neothorone[8] and the peroxide methods[9] respectively.

Results

I. The Preparation of Protactinium-233.—The Irradiation and Dissolution of the Target.

—Two-tenths grams of thorium dioxide, sealed in a quartz ampoule under reduced pressure, was irradiated with thermal neutrons for 20 min. in the

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[7] p. 33 of Ref. 1.

[8] M. Ishibashi and S. Higashi, *Japan Analyst* (*Bunsekikagaku*). **4**, 14 (1955).

[9] Y. Inoue, S. Suzuki and H. Gotô, This Bulletin, **37**, 1547 (1964).

pneumatic tube of the JRR-2 atomic pile (total flux; 6.4×10^{13}) of the Japan Atomic Energy Research Institute, or, if circumstances did not permit, this 2 g. of thorium dioxide, sealed in a polyethylene bag, was irradiated with thermal neutrons for 2 hr. in the pneumatic tube of the JRR-1 atomic pile (total flux; 3×10^{11}). The sample was allowed to decay for one day for the complete conversion of ^{233}Th into ^{233}Pa, and then dissolved by heating it with a concentrated hydrochloric acid solution containing several drops of diluted hydrofluoric acid (1 : 30) as a catalyst. Care must be taken not to add excess hydrofluoric acid solution, because too much fluoride ions prevent the complete dissolution of the target.

Conditions for the TBP Extraction.—*The Effect of the Shaking Time.*—The effect of the shaking time on the extraction of protactinium from a 6 N hydrochloric acid solution was investigated. It was found that 10 min. shaking is sufficient, therefore, extraction will hereafter be performed by shaking for 10 min.

The Effect of the Hydrochloric Acid Concentration.—The effect of the hydrochloric acid concentration on the extraction of protactinium was also investigated. It is apparent from Fig. 1 that the extraction is almost complete at hydrochloric acid concentration above 5 N.

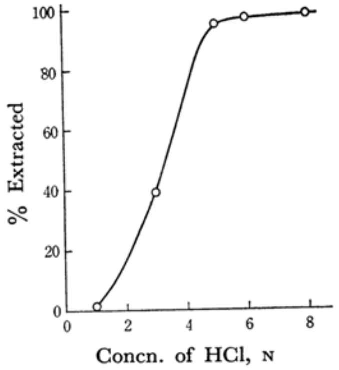

Fig. 1. The effect of hydrochloric acid concentration on the extraction of protactinium.
Shaking time: 10 min.

The Effect of the Hydrofluoric Acid Concentration.—The effect of the hydrofluoric acid concentration on the stripping of protactinium was investigated at a hydrochloric acid concentration of 6 N. The results presented in Fig. 2 show that the extraction percentage is constant over a hydrofluoric acid concentration of 0.4 N, so a 6 N HCl - 0.5 N HF solution is sufficient for the stripping of ^{233}Pa.

The Effect of the Thorium Concentration.—The effect of thorium on the extraction of protactinium was investigated at a hydrochloric acid concentration of 6 N, as is shown in Table II. With the increase in the concentration of thorium, the extraction of protactinium was somewhat decreased, but the effect was not very great.

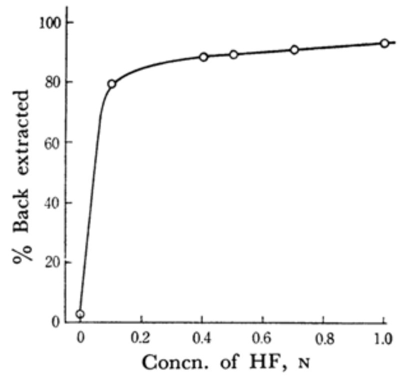

Fig. 2. The effect of hydrofluoric acid concentration on the stripping of protactinium.
Shaking time: 10 min., Acidity: 6 N HCl

TABLE II. THE EFFECTS OF THORIUM ON THE EXTRACTION OF ^{233}Pa

Amount of Th added as ThO$_2$, mg.	Per cent extracted of ^{233}Pa
None	97.1
400	95.4
800	94.4

The Masking of Fluoride Ions by Means of Aluminium Chloride.—If re-extraction is needed, it is essential to mask the fluoride ions added for the back extraction of protactinium. Aluminum chloride and boric acid are efficient for this purpose. In this experiment aluminum chloride was chosen, and the effect of its concentration was examined. The experiments were performed by the addition of a 3 M aluminium chloride solution to 10 ml.

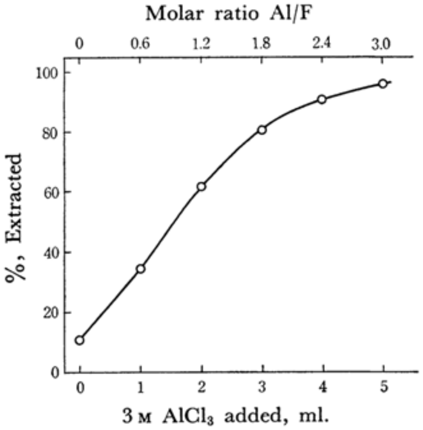

Fig. 3. The masking of fluoride ion with aluminum chloride.
Shaking time: 10 min.
Acidity: 6 N HCl - 0.5 N HF

of an aqueous solution which had the same composition as the stripping solution, 6 N HCl - 0.5 N HF. As is clearly shown in Fig. 3, the addition of 5 ml. or more of the aluminum chloride solution was needed for the complete extraction of protactinium from the stripping solution. This corresponds to the aluminum to fluoride molar ratio of 3.0.

The Extraction of Ions to Co-exist.—The main impurities in the irradiated thorium dioxide are considered to be ^{233}U and long-lived fission products; ^{95}Zr-^{95}Nb, ^{137}Cs, ^{106}Ru, ^{90}Sr-^{90}Y and rare earths (mainly ^{144}Ce). The separation of them from protactinium by the TBP extraction was examined, with the results shown in Table III. It is clear from the table that ^{137}Cs, ^{90}Sr-^{90}Y and ^{144}Ce can be separated from protactinium in the forward extraction, and uranium, in the backward one. The separation of ^{95}Zr-^{95}Nb and ^{106}Ru, was, however, incomplete. For their decontaminations, it is necessary to use other separation techniques.

TABLE IIIa. EXTRACTION OF LONG-LIVED FISSION PRODUCTS

Nuclide	Condition	Per cent extracted
^{95}Zr-^{95}Nb	6 N HCl	68.2
^{137}Cs	6 N HCl	1.40
^{106}Ru	6 N HCl	70.8
^{90}Sr-^{90}Y	6 N HCl	0.91
^{144}Ce	6 N HCl	0.73
^{95}Zr-^{95}Nb	6 N HCl - 0.5 N HF	56.0
^{137}Cs	6 N HCl - 0.5 N HF	0.87
^{106}Ru	6 N HCl - 0.5 N HF	67.2
^{90}Sr-^{90}Y	6 N HCl - 0.5 N HF	0.21
^{144}Ce	6 N HCl - 0.5 N HF	0.10

TABLE IIIb. EXTRACTION OF THORIUM AND URANIUM

Element	Added mg.	Condition	Per cent extracted
Th	400	6 N HCl	0.0
Th	800	6 N HCl	7.8
Th	1.6	6 N HCl	0.0
Th	1.6	6 N HCl-0.5 N HF	91.9
U	2.38	6 N HCl	98.7
U	2.38	6 N HCl-0.5 N HF	98.7

Anion Exchange Separation.—Referring to Moore's method[10] the anion exchange method was investigated. After protactinium was adsorbed on the resin bed, elution was performed with a 9 N HCl-0.004 N HF solution and then a 9 N HCl - 0.2 N HF solutions. At the same time, the behaviour of ^{95}Zr-^{95}Nb and of ^{106}Ru was investigated under the same conditions as for protactinium. These results are presented in Fig. 4. ^{95}Zr-^{95}Nb could be separated quantitatively, but the separation of ruthenium was not complete. The removal of ruthenium, however, can be more easily and completely attained by the distillation from a perchloric acid solution[11] than by ion exchange, so no further experiments were conducted. It may be assumed from the investigation by Kraus[12] that the ions, which are almost all removed by solvent extraction, will not be adsorbed on the exchanger bed from a 10 N hydrochloric acid solution except uranium. Uranium, however, cannot be eluted by the eluant at all. Therefore, these elements may be separated again by this procedure, and so the decontamination factor may be extremely high. As is shown in Fig. 4a the elution curve of protactinium shows some tailing and a large volume of eluant is necessary for the complete recovery of protactinium. When the yield of fission products is considered to be extremely low, as in this case,[2] the use of an eluant with a higher fluoride concentration, such as 9 N HCl - 1 N HF, is convenient, because it hardly affects the behavior of any of the ions except zirconium and niobium, while the elution curve of protactinium becomes sharp, with a resultant decrease in the volume of eluant necessary for protactinium.

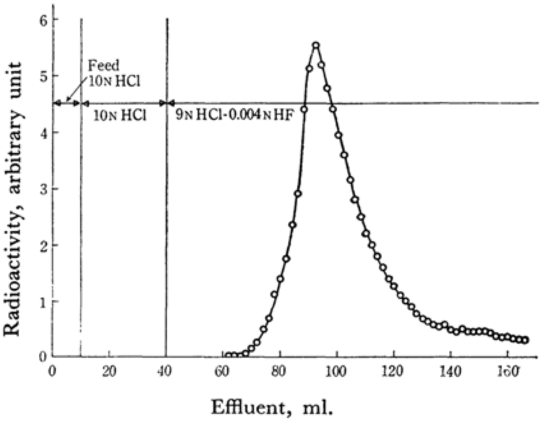

Fig. 4a. Elution of protactinium.

Recommended Procedure for the Separation of ^{233}Pa from Neutron-irradiated Thorium.—By putting the above results together, the best conditions for the separation of protactinium from thorium dioxide were decided upon. The irradiated thorium dioxide was dissolved by heating it in a platinum dish with concentrated hydrochloric acid containing several drops of a diluted hydrofluoric acid solution (1 : 30) to serve as a catalyst. This solution was initially evaporated almost to dryness, on a hot plate and then on a water bath. The residue was dissolved in possibly a small amount of a concentrated hydrochloric acid solution and

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[10] K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **73**, 2900 (1951).

[11] Y. Inoue, This Bulletin, **36**, 1316 (1963)

[12] K. A. Kraus and F. Nelson, 1st International Conferences on the Peaceful Uses of Atomic Energy, Geneva, p. 837 (1955).

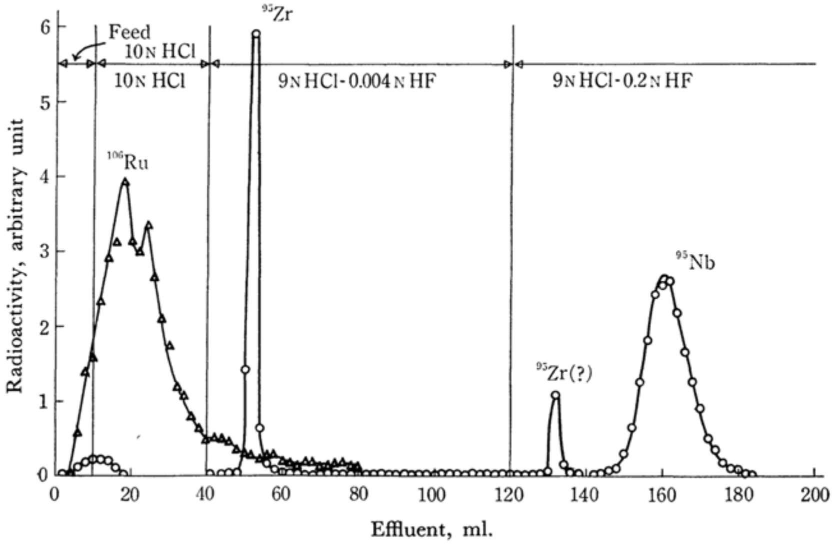

Fig. 4b. Elution of ^{95}Zr, ^{95}Nb and ^{106}Ru.
○: ^{95}Zr-^{95}Nb △: ^{106}Ru

again evaporated to dryness in the same manner. This was repeated a few times in order to eliminate the hydrofluoric acid completely. Then the residue was dissolved in 10 ml. of 6 N hydrochloric acid, and the solution was transferred to a separatory funnel. Ten milliliters of TBP was added, and the funnel was shaken mechanically for 10 min. After the two phases had separated, the aqueous layer (the lower) was run off and discarded. The TBP layer was then scrubbed with 10 ml. of a 6 N hydrochloric acid solution and its aqueous layer discarded. Then 10 ml. of a 6 N HCl - 0.5 N HF solution was added to the TBP extract, and the mixture was shaken mechanically for 10 min. The aqueous layer was run into another separatory funnel and scrubbed with fresh TBP. The aqueous layer was then transferred into another separatory funnel and washed with 10 ml. of distilled benzene in order to remove the remaining TBP. The aqueous layer was then placed in a platinum dish and heated almost to dryness, initially on a hot plate and finally on a water bath. After it had been cooled, 10 ml. of 10 N hydrochloric acid was added; the solution was heated in order to dissolve the residue and then poured into an ion exchanger bed; when the level of the solution reached the top of the exchanger bed, 50 ml. of a 10 N hydrochloric acid solution and 30 ml. of a 10 N HCl - 1.0 N HF solution were passed through the column successively. The protactinium-233 obtained in a 10 N HCl - 1.0 N HF solution was not only free from any thorium but also free from any solid materials. To make sure of its radiochemical purity, the γ-ray spectrum was measured. As is shown in Fig. 5, the spectrum completely coincided with the published data.[1]

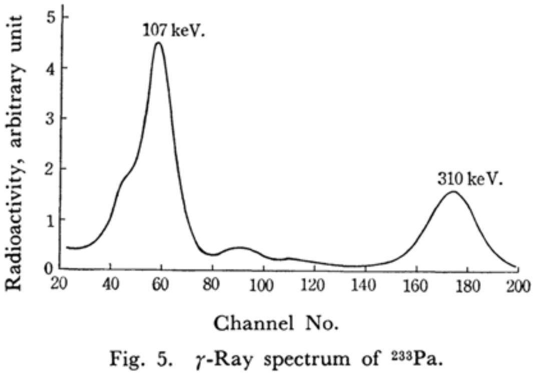

Fig. 5. γ-Ray spectrum of ^{233}Pa.

II. The Purification of Protactinium-231. —Basic considerations and Preliminary Experiments.—As is shown in Table I, ^{231}Pa was purchased in the form of protactinium pentoxide from the Radiochemical Center, Amersham, England. To check its chemical purity, emission spectrographic analysis was performed; a little niobium was detected in some cases. Although it was difficult to detect rare earths, they, as well as niobium, should be considered as chemical impurities. As to radiochemical impurities, it is assumed that ^{227}Ac, ^{227}Th and ^{233}Ra, the daughters of ^{231}Pa, are important enough to take consideration of their half lives. All the impurities listed above except niobium were considered not to be adsorbed on the anion exchange column from the concentrated hydrochloric acid solution, so the separation of niobium and protactinium was the main problem. The separation seems to be possible by means of the above-mentioned anion exchange procedures, but in the treatment of macroamounts of protactinium, the hydrofluoric acid concentration of 0.004 N is so small that tailing may

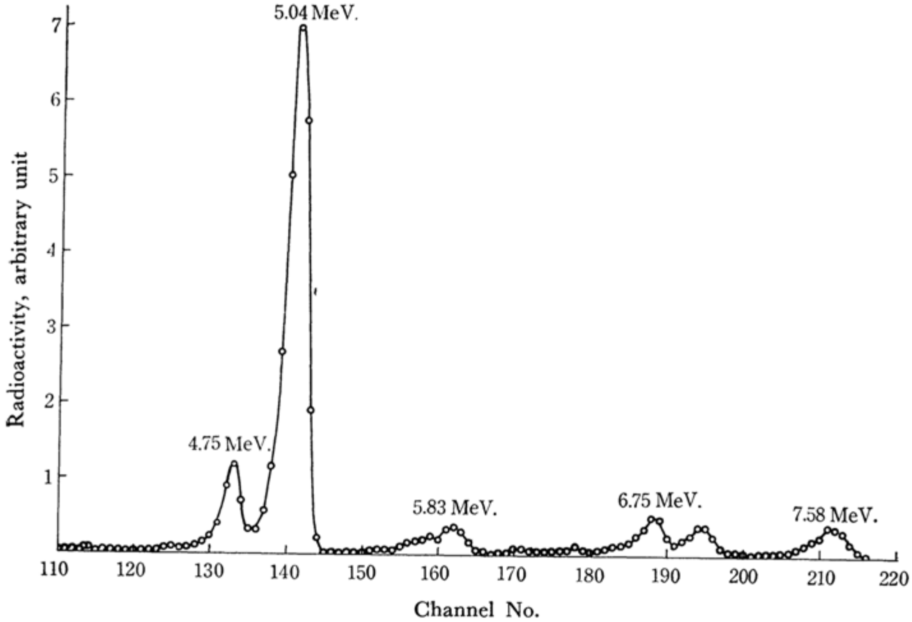

Fig. 6a. α-Ray spectrum of commercial ^{231}Pa.

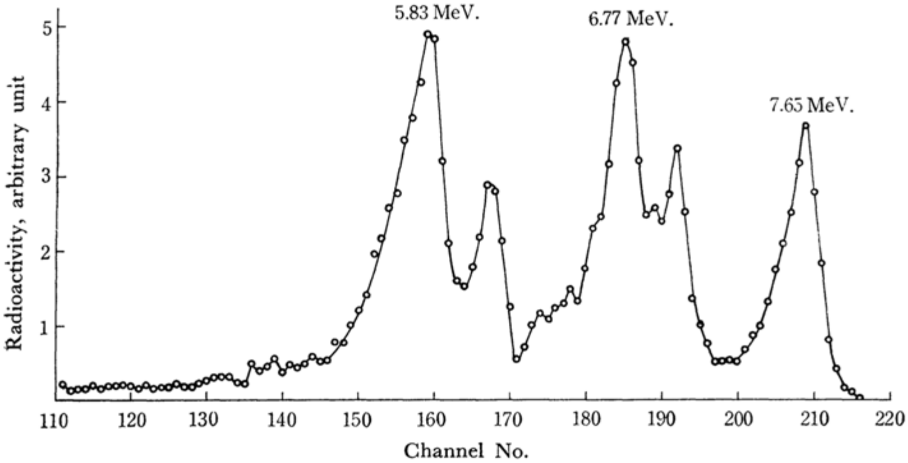

Fig. 6b. α-Ray spectrum of HCl washings.

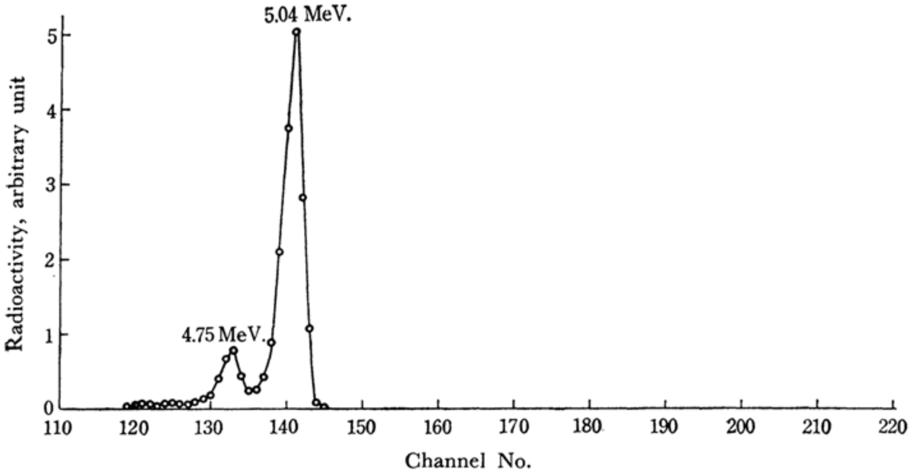

Fig. 6c. α-Ray spectrum of purified ^{231}Pa.

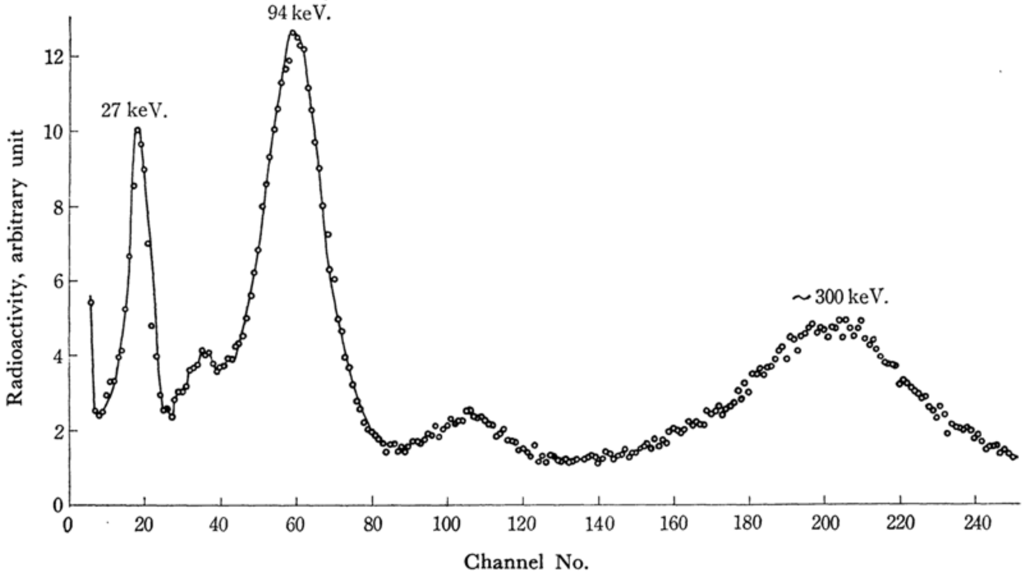

Fig. 7a. γ-Ray spectrum of commercial ^{231}Pa.

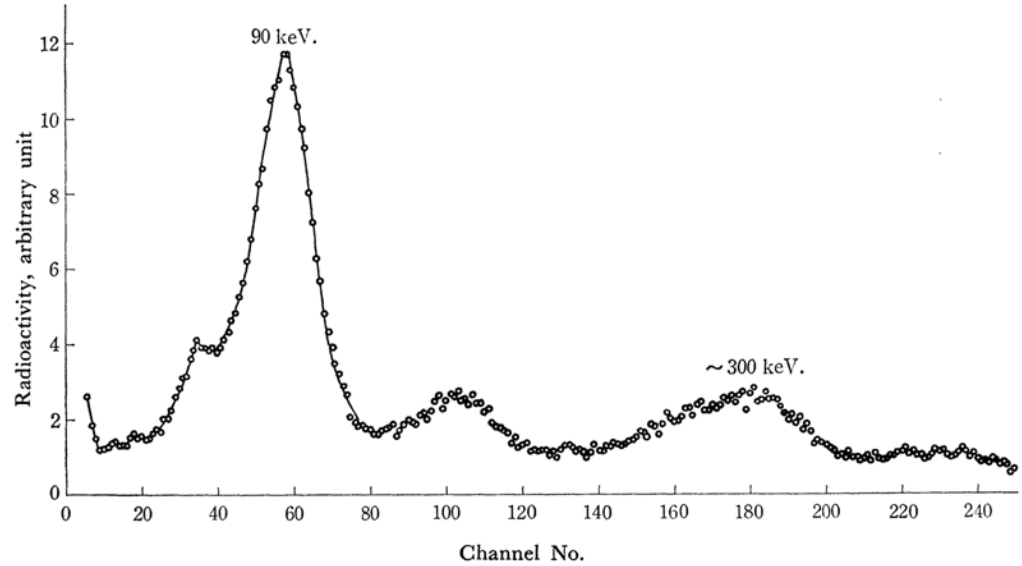

Fig. 7b. γ-Ray spectrum of HCl washings.

increase markedly. Furthermore, the ion exchange capacity should be large because a good separation is desired. Therefore, a high concentration of hydrofluoric acid and a large column are necessary for this purpose. Bearing this in mind, the preliminary separation of ^{95}Nb and ^{233}Pa was performed using 20 ml. of anion exchange resin and a 9 N HCl - 0.1 N HF solution as an eluant. In this case, niobium began to elute after 40 ml. of eluant had passed through. The elution of protactinium was complete before 30 ml. of eluant had passed through, so the complete mutual separation of these elements seemed possible.

Recommended Procedure for the Purification of Commercial Protactinium-231. — Putting the above results together, the recommended procedure for the purification of commercial protactinium was decided upon.

Protactinium pentoxide was dissolved in concentrated hydrochloric acid, containing possibly a small amount of hydrofluoric acid, in a platinum dish, the solution was then evaporated almost to dryness. This process was repeated until the hydrofluoric acid was completely expelled. The residue was dissolved in concentrated hydrochloric acid and diluted to 9 N with distilled water. This

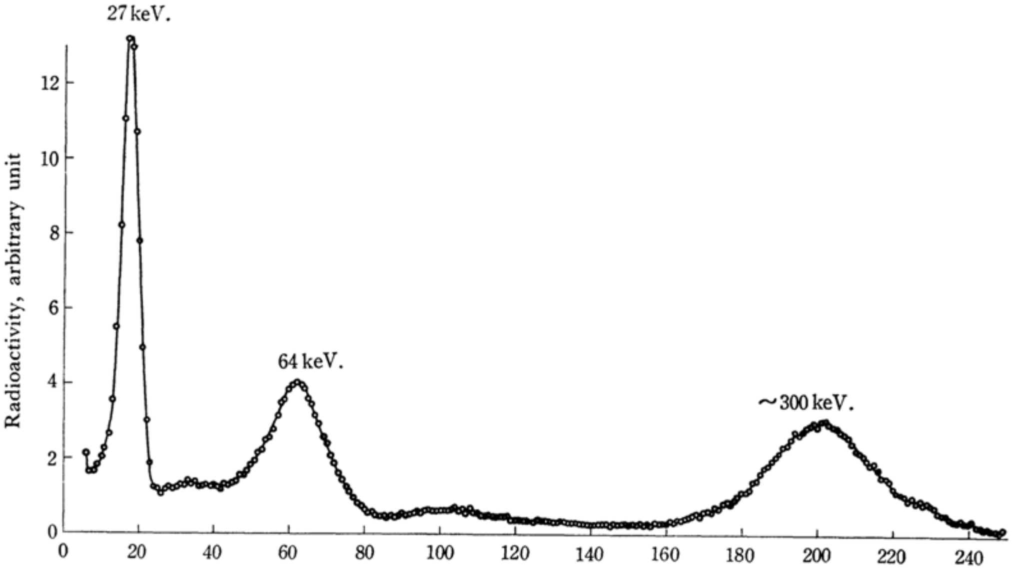

Fig. 7c. γ-Ray spectrum of purified ^{231}Pa.

solution was percolated into the ion exchange column; when the level of the solution reached the top of the exchanger bed, 20 ml. of a 9 N hydrochloric acid solution was introduced in order to remove any radiochemical impurities. Then protactinium was eluted with 30 ml. of a 9 N HCl - 0.1 N HF solution. Care must be taken to check the characteristic γ-ray of 27 keV. throughout the ion exchange process in order to prevent any accidental loss due to the incomplete elimination of fluoride ions from the sample solution. The protactinium solution thus prepared was then evaporated almost to dryness and diluted with distilled water, and enough ammonium hydroxide solution was added to precipitate protactinium hydroxide. This precipitate was filtered, washed thoroughly, and ignited in a platinum crucible in the usual manner. For example, 29.8 mg. of pure protactinium pentoxide was obtained from 35.0 mg. of the crude sample. To check its radiochemical purity and to see the course of purification, the α- and γ-ray spectra of the original sample, the hydrochloric acid washings and the purified sample were measured, as is shown in Figs. 6 and 7. In Fig. 6 α-ray peaks more energetic than 5 MeV. are observed in the original sample. They have their origin in the decay products of ^{231}Pa. The α-ray spectrum of the hydrochloric acid washings shows no peaks of protactinium except those of daughters. On the contrary, the purified sample shows no peaks above 5 MeV., so it can be considered to be completely pure. In the γ-ray spectra, the circumstances are not as clear as in the α-ray spectra because of the complex overlapping of peaks, but the characteristic peak of ^{231}Pa (27 keV.) is not observed in the spectrum of hydrochloric acid washings, and that of the purified sample shows good agreement with the standard one.[1] Moreover, no niobium was detected in the purified sample by emission spectrographic analysis.

Summary

The methods for the separation of the ^{233}Pa produced by the thermal-neutron irradiation of thorium dioxide and the purification of commercial ^{231}Pa have been investigated. The separation of ^{233}Pa has been achieved by the combination of TBP extraction from a hydrochloric acid solution and anion exchange separation by a hydrochloric acid - hydrofluoric acid eluant. ^{231}Pa has been purified by a modification of the above anion exchange. Both processes can be conducted comparatively simply and rapidly, with the result that both isotopes are chemically and radiochemically pure enough for research work.

A part of the expense has been defrayed by a grant-in-aid by the Ministry of Education.