S 53. *The Separation of Protoactinium.*

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A method of separation of protoactinium based on its absorption on manganese dioxide precipitates followed by solvent extraction of the " cupferron " complex is described.

CONCENTRATES of natural protoactinium (^{231}Pa) usually contain the other naturally radio-active substances, in particular, ionium and polonium, together with tantalum, niobium, zirconium, titanium, and silica derived from the original ore. The principal separation procedures described are the original method of Hahn and Meitner (*Physikal. Z.*, 1918, **19**, 208), the more recent process due to von Grosse (*Nature*, 1927, **120**, 621), and variants of these schemes. The former depends on co-deposition of the protoactinium with tantalic acid, and the latter on zirconium phosphate. Recently, Thompson has published a new method (U.S.A.E.C. Declassified Document AECD-1897, April 15th, 1948) depending on the adsorption of the protoactinium on manganese dioxide precipitates, a phenomenon first reported by von Grosse and Agruss (*J. Amer. Chem. Soc.*, 1935, **57**, 438), followed by separation from the manganese by ion exchange of the complex protoactinium fluoride anion on an anion-exchange resin. Thompson (*loc. cit.*) mentions the solvent extraction of protoactinium from chloride and nitrate solutions, but details, including the identity of the solvents used, are omitted.

Tracer experiments on the chemistry of protoactinium (see preceding paper) proved that losses of material by adsorption can only be avoided if all the stages of a separation are conducted in strongly acid solution or by means of the soluble complex fluorides, citrates, or tartrates. The experience of other investigators suggests that the later stages of the isolation of proto-actinium will be facilitated if zirconium and titanium carriers are avoided. Finally, methods of separation which are not essentially dependent on the total concentration, such as solvent extraction and other partition processes, are most reliable.

The method of separation described avoids the use of zirconium or tantalum as carrier and ensures that all aqueous protoactinium solutions are at least 3N. in mineral acid. The procedure consists in dissolution of the material and production of a fluoride-free solution, adsorption of the protoactinium on a manganese dioxide precipitate formed *in situ* in three successive portions by warming the solution after the addition of solutions of potassium permanganate and a manganous salt, solution of the manganese precipitate, and extraction of protoactinium " cupferronate " by amyl acetate, destruction of the " cupferronate," and a repetition of the separation cycle. All the aqueous solutions used were 3N. in hydrochloric, sulphuric, or nitric acid.

For complete recovery of the protoactinium from a mineral concentrate, it is necessary to bring the whole of the material into solution by a combination of bisulphate and alkali carbonate fusions. The tenacious adsorption of protoactinium on the smallest silica precipitates, and its anomalous behaviour in the presence of soluble silica, make it obligatory to drive off the silicon as tetrafluoride by treatment with excess of hydrofluoric acid. Since neither the manganese dioxide adsorption nor the cupferronate extraction can be carried out in the presence of fluoride ions, the mixture must then be converted into sulphates or perchlorates by the appropriate acids. Alternatively, the fluorides may be dissolved in boric and nitric acids, and the protoactinium may then be co-deposited with ferric hydroxide by addition of iron and ammonium hydroxide (Newton, *Physical Rev.*, 1949, **75**, 23). The separation of an undesired precipitate or of insoluble materials at any stage almost always leads to loss of protoactinium by adsorption, and each such insoluble fraction needs separate solution and treatment. Even in the acidic solutions used, some adsorption on to the walls of containing vessels occurred, but recovery by treatment with hot 1M-citric acid solution can be made.

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The manganese dioxide stage was found to be very efficient with respect to protoactinium recovery and insensitive to fluctuations in the conditions, but it may not be used in the presence of citric acid, chlorides, or fluorides. This stage effects separation of the protoactinium from most of its macroscopic contaminants; separation from thorium is fairly good and from zirconium and hafnium quite appreciable. Little or no separation from polonium is achieved.

The manganese dioxide precipitate may be dissolved in 3N-mineral acid in the presence of hydrogen peroxide or sodium nitrite. The latter is preferred since the peroxide occasionally gives rise to insoluble precipitates in the presence of thorium, and the precipitate adsorbs a large percentage of the protoactinium.

In the presence of a reducing agent, such as sulphurous acid, it was found that amyl acetate extraction of the cupferron complex of protoactinium from a 3N-mineral acid solution separates the protoactinium from most elements except zirconium, hafnium, titanium, and polonium. The extraction coefficient is about 30 under these conditions. Solvent extraction of the complex increases the selectivity of this reagent, since elements that form insoluble cupferronates in aqueous solution under similar conditions are not always noticeably extracted (see, *e.g.*, Furman *et al.*, U.S.A.E.C. Declassified Documents MDDC-1619, 1620, 1623). In the case of thorium and tantalum it appears that this is because the reduction in the cupferron concentration in the aqueous layer taking place on shaking with the solvent allows the less stable cupferronates to dissociate and prevents any considerable extraction of the complex. Thus an aqueous suspension of thorium cupferronate is partly converted into thorium hydroxide by shaking with amyl acetate.

The protoactinium cupferronate can be extracted from citric acid solutions, but not in the presence of fluoride ions. The ready oxidation of both cupferron and the protoactinium complex requires the stabilisation of the cupferron reagent by the addition of a little quinol.

The protoactinium can be recovered from the organic phase by washing with ammonium fluoride solution or by thermal destruction of the complex at 100° and extraction of the protoactinium by an aqueous mineral acid or 1M-citric acid solution.

This method of separation has been applied to the isolation of tracer [233]Pa from irradiated thorium carbonate and of [231]Pa from an ore concentrate. In the latter case the polonium was separated first by deposition on silver foil, and the last traces removed by ignition of the product.

The identity and radiochemical purity of the [231]Pa was established by comparing its coprecipitation behaviour with the [233]Pa. It was found that mixtures of [233]Pa and [231]Pa in 3N-mineral acids appeared to take some time to reach isotopic equilibrium at room temperature.

Experimental.

(All experiments were carried out using [233]Pa unless otherwise stated.)

Preliminary experiments showed that more than 90% of the protoactinium in a solution could be carried down by the addition of a pre-formed lead or manganese dioxide precipitate, but that a considerably better efficiency was attained by precipitation of the manganese *in situ*. The most convenient method was to add an excess of manganous sulphate solution to the protoactinium-bearing solution and to determine the amount of manganese dioxide precipitated by the amount of potassium permanganate solution subsequently added. The manganese dioxide was precipitated by heating the solution to 80° for 20 minutes on a water-bath. The efficiency of separation was not noticeably dependent on the concentration of the manganese solutions used or on the excess of manganous salt present. It was, however, improved by agitation of the solution while heating. Increased time of contact of the precipitate and the solution occasionally decreased the efficiency of co-deposition. The quantity of carrier precipitated is not critical :

Mass of MnO_2 precipitated, mg./ml.	1	3	4	5
Pa, %, carried down from 3N-HNO_3	92	97	97·5	98

Since the separation can be repeated after solution of the oxide in the minimum volume of acid, a smaller quantity of carrier being used, the process effects a very rapid concentration of protoactinium.

The co-deposition is most effective and selective in strongly acidic solutions. The following results were obtained by precipitating 5 mg./ml. of manganese dioxide in the manner described above :

pH	1·85	1·75	1·66	1·34	0·6	1N-HNO_3	3N-solns.
Pa, %, carried down	86	82	92·5	97	98	98	96·5

The relevant elements accompanying the protoactinium on the manganese dioxide were found to be thorium, bismuth, zirconium, and polonium. The percentages of these elements removed from solution, when present at a concentration of 0·05M. in 3N-nitric acid, by the manganese dioxide precipitate was determined by precipitating 5 mg./ml. of carrier under the conditions described : (*a*) Thorium; ionium was used as tracer for the thorium, $2 \pm \frac{1}{2}$% carried down. (*b*) Bismuth; radium-*E* was used as tracer, 13% carried down. (*c*) Polonium; radium-*F* was used as tracer, at tracer concentration only, the

manganese dioxide effects quantitative removal of polonium at 3N. in nitric acid and 80% in 6N. nitric acid. (*d*) Zirconium (hafnium), using the zirconium–hafnium tracer (^{95}Zr $+$ ^{181}Hf) described in the preceding paper, 15% carried down.

The solvent extraction of protoactinium cupferronate from strongly acidic solutions, recorded in the previous paper, appeared suitable for the separation of the protoactinium from the manganese.

Early experiments in which the protoactinium in each phase was determined before and after extraction revealed serious losses of protoactinium; further, on storage, the organic solution of the complex steadily lost activity. The protoactinium was found to be adsorbing on to the walls of the containing vessel from the organic phase. The fresh cupferron extract was unaffected by 1M-citric acid solution, but after storage, citric acid removed a fraction of the protoactinium depending on the time elapsed since extraction. Thus it appeared that the adsorption followed decomposition of the cupferronate. Since cupferron is very susceptible to oxidation, this seemed a possible explanation of the observations. The hypothesis was tested by comparing the stability of extracts of the cupferronate prepared with and without the addition of quinol by determining the amount of activity removed by equal portions of 1M-citric acid solutions at various times after the extraction. The extracts made in the presence of quinol were found to be stable for 24 hours, losing none of their activity when washed with 1M-citiric acid after one day had elapsed since extraction. In the absence of quinol, 66% of the activity was removed by an equal volume of 1M-citric acid 2 hours after preparation of the extract. In addition, it was shown that short periods of aeration of the organic phase rapidly destroyed the complex. Subsequent experiments were conducted with a saturated aqueous solution of cupferron stabilised by the addition of quinol and stored in a dark bottle. Fresh preparations from pure cupferron were made every few days.

The suitability of various solvents was assessed by measuring the percentage of protoactinium extracted by equal volumes of the different solvents from equal aliquots of 3N-nitric acid solution containing protoactinium and cupferron :

Amyl acetate	98	Ether	96
Chloroform	92	Methyl *iso*butyl ketone	98
Benzene	77	Nitromethane...........................	98

The last two solvents were rejected in view of their strong solvent properties for a variety of inorganic salts. Amyl acetate was chosen from the remainder because of its technical convenience.

The essentially complete extraction was not markedly affected by the amount of cupferron used, except that larger amounts are less readily oxidised. A concentration of 2 mg./ml. of cupferron was adopted in these experiments.

The effect of the pH of the aqueous solution on the extraction was investigated, ammonium acetate–acetic acid and ammonium chloride–hydrochloric acid being used at various pH values and various normalities of hydrochloric acid containing protoactinium. Each extraction was made by shaking 1 vol. of amyl acetate with 1 vol. of the protoactinium solution and 0·1 vol. of the cupferron solution, and the percentage of protoactinium passing into the solvent layer determined :

	Acetate solutions.				Chloride solutions.						
pH	5·3	3·5	1·6	1·4	5·2	2·9	1·8	1·5	0·8	0·7	0·25
Pa extracted, %	88	87	90	92	73	73	87	93	93	93	97

	Hydrochloric acid.		
Normality	1·2	2·3	3·5
Pa extracted, %	88	94·5	97·5

The extraction was not noticeably influenced by small changes in temperature, and equilibrium between the two phases was reached quickly.

No attempt was made to determine partition coefficients accurately. Typical values obtained in different experiments with a 3N-hydrochloric acid solution containing protoactinium and cupferron and amyl acetate as solvent were 22, 32, 28, 18, 32, 40. The average of a larger number of extractions from 3N-acid was 32. Repetition of the extraction on the aqueous layer after separation and addition of more cupferron gave the same partition coefficient; 38 and 32; 32 and 28.

The dissociation of the citrate, oxalate, tartrate, and fluoride complexes was compared with that of the cupferronate by determining the percentage of protoactinium extracted as cupferronate from 0·5M-solutions of these anions by an equal volume of amyl acetate :

	Oxalic acid.	Tartaric acid.	Citric acid.	Ammonium fluoride.
Activity of amyl acetate	255	455	510	0
Activity of aqueous layer.....................	165	0	0	460

The extraction of the complex from 3N-acid given a good separation from all uni- and bi-valent cations. Under these conditions the amount of lead extracted by an equal volume of amyl acetate from 0·1M-lead nitrate solution containing cupferron could not be detected by the colour with dithizone; neither could the amount of manganese extracted from 0·1M-manganous sulphate be detected by its colour on oxidation to permanganate.

The extraction of thorium and bismuth as a function of the pH or normality of the aqueous phase was investigated by means of uranium-*X* and radium-*E* as tracers, respectively :

Composition of solution.	NH$_4$OAc–HOAc.			NH$_4$Cl–HCl.			HCl.
pH (or normality) of aqueous phase ...	5·8	3·2	1·3	0·7	0·6	0·4	3
U-*X*, %, in organic phase.................	37	69	26	1·6	1·2	1·1	

Ammonium chloride was added so that the first two series of experiments were conducted in solutions of roughly the same ionic strength :

	Hydrochloric acid solutions.			
Normality of solution	0·1	0·3	1·5	3
Ra-*E* extracted, %	50*	55*	0·3	<0·01

* Some loss by hydrolysis took place.

Amyl acetate was found to decompose the insoluble tantalum cupferronate. [182]Ta being used as tracer, the amount extracted by an equal volume of amyl acetate from a solution of the tartrate complex of tantalum, to which cupferron and nitric acid to 3N. had been added, was less than 1%.

Zirconium (hafnium) and polonium were shown to give rise to cupferronates which were nearly as readily extracted as the protoactinium complex. The partition coefficients, determined by means of [95]Zr + [181]Hf and Ra-*F* as tracers, were about 10 in each case for extraction from aqueous solutions between 0·1N. and 3N. in acid.

Interference by iron, tin, uranium, and vanadium was avoided by oxidation or reduction to states giving cations with the minimum charge.

A combination of these two separation stages provided a satisfactory process for the isolation of carrier-free [233]Pa from irradiated thorium " carbonate " (acid-soluble product of the precipitation of thorium nitrate by ammonium carbonate solutions). For instance, on applying the method to 5 ml. of a solution containing 6050 α-counts/minute due to thorium and 23,000 β-counts/minute due to [233]Pa, 10 mg. of manganese dioxide precipitated in two stages, without separation of the first half of the precipitate from the solution, contained 170 α-counts/minute and 22,400 β-counts/minute. After extraction of the cupferron complex the amyl acetate contained less than 10 α-counts/minute and 21,000 β-counts/minute. A similar separation on a larger scale with duplication of each stage and repetition of the separation on the residues gave a 95% yield of [233]Pa and a reduction to 10^{-5} in thorium content.

A similar procedure, but involving greater repetition of the separations, was successfully applied to the isolation of 2×10^6 α-disintegrations/minute of [231]Pa from a concentrate on thorium oxalate containing 40 α-counts/minute/mg. [231]Pa with 3200 α-counts/minute/mg. due to thorium isotopes and 500 α-counts/minute/mg. due to radium and its decay products. The chemical identity of the product was established by its co-deposition on zirconium phosphate, iodate, and phenylarsonate and on manganese dioxide. Its freedom from polonium was established by showing that its α-activity was not reduced by ignition to 800°. Finally, a mixture of solutions of the [233]Pa and [231]Pa in 3N-nitric acid was prepared, and the ratio of β/α activity determined. (The [231]Pa solution used contained a few mg./ml. of zirconium carrier.) Various precipitations were carried out, and the ratio of β/α activity of the precipitates measured. Preliminary experiments revealed little connection between the two ratios. However, when the experiments were repeated with a mixture in 6N-nitric acid that had been heated to 100° for 4 hours before the precipitations, the β/α activity ratios in the solution and precipitates became equal :

Nature of precipitate.	β/α Ratio of solution.	β/α Ratio of precipitate.
Zirconium oxalate	1·06	1·11
Zirconium phenylarsonate	0·77	0·78
Manganese dioxide...................................	0·77	0·74
Zirconium phosphate................................	1·06	1·20

It would appear that, under these conditions, isotopic equilibrium is but slowly established.

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