S **55**. *The Solvent Extraction of Protoactinium.** By A. G. MADDOCK and L. H. STEIN.

R. C. THOMPSON (U.S. Atomic Energy Commission Declassified Documents MDDC-1770, January 1948, and MDDC-1897, February 1948) has recorded the extraction of protoactinium from aqueous chlorides and nitrates by various organic solvents, but no details of the procedure are given nor are the solvents used identified.

Such a method of separation would provide a desirable final stage to the isolation of macroscopic amounts of natural protoactinium using the procedure previously described (A. G. Maddock and G. L. Miles, this vol., p. S 253). Preliminary experiments showed that a variety of solvents gave efficient extraction of trace concentrations of protoactinium from strong chloride solutions.

Approximate extraction coefficients for the protoactinium, present at trace concentrations (these experiments were conducted using ^{233}Pa), between the solvent and an approximately 4M-solution of aluminium chloride were found to be : amyl alcohol 9·0, 2 : 2′-dichlorodiethyl ether 8·0, *iso*butyl alcohol 7·0, n-butyl alcohol 7·0, methyl *iso*butyl ketone 3·7, diethyl ketone 2, methyl n-propyl ketone 2, and methyl n-hexyl ketone 2·6. Amyl acetate, ethyl ether, chloroform, methyl ethyl ketone, nitromethane, and ethyl-n-hexyl alcohol gave poor extractions. The extraction coefficient for 2 : 2′-dichlorodiethyl ether appeared favourable and the greater selectivity of this solvent, subsequently discovered, suggested its further investigation. The following data refer exclusively to this solvent.

The extraction coefficient was increased with the normality of the aqueous phase with respect to hydrochloric acid. With use of 6M-calcium chloride as the aqueous phase, the following results were obtained :

Concn. of hydrochloric acid solution	2N.	4N.	6N.
Extraction coefficient	<0·01	1·2	5·0

In addition the extraction coefficient increased with the salt concentration in the aqueous phase. Thus, when various dilutions of saturated calcium chloride solution, all 6N. in respect of hydrochloric acid were used, the following values were determined :

Dilution by volume	0 ×	1·33 ×	1·5 ×	2 ×
Extraction coefficient	8	2·3	1·6	0·5

It appeared probable, too, that the extraction coefficient increased as the activity of the water in the solution decreased. Approximately 8M-magnesium chloride solution, 6N. with respect to hydrochloric acid, was eventually chosen for the aqueous phase because the preparation of stable solutions was easier than with the calcium and aluminium chlorides.

Moderate concentrations (0·5N.) of sulphate, nitrate, perchlorate, tartrate, and citrate ions reduced the extraction coefficient but did not render extraction impracticable. Using 6N-hydrochloric acid saturated with calcium chloride, and ignoring precipitates formed on addition of the interfering anion, added as the acid, we found extraction coefficients as follows :

Anion (0·5N.)	None	Sulphate	Nitrate	Perchlorate	Citrate	Tartrate
Extraction coefficient	9	*ca.* 2	*ca.* 2	*ca.* 5	*ca.* 2	*ca.* 5

Presence of fluorides, however, reduced the coefficient to a value too low for satisfactory extraction.

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* Contribution to the Discussion of papers No. S **53**, " The Separation of Protoactinium," by A. G. Maddock and G. L. Miles, and No. S **54**, " A New Valency of Protoactinium," by G. Bouissières and M. Haissinsky.

The separation from various other elements with 6N-hydrochloric acid, saturated with hydrated aluminium chloride at 15° and containing the contaminating element, as the aqueous phase, was influenced as follows. (*a*) Uranyl ions. Approximately 0·2N-uranyl nitrate and chloride were without effect on the extraction of protoactinium, and the extraction coefficient for uranium was less than 0·01 in each case. (*b*) Manganous ions. Approximately 0·2M-manganous chloride was without effect on the extraction of the protoactinium and the amount of manganese extracted was not detectable by the colour developed on oxidation to permanganate. (*c*) Zirconium. Approximately 0·1M-zirconyl chloride was without effect on the extraction of protoactinium and the extraction coefficient for zirconium was less than 0·02. Zirconium was determined colorimetrically by alizarin and by using tracer zirconium. This separation was repeated in nearly saturated solutions of calcium and magnesium chloride in 6N-hydrochloric acid. (*d*) Titanium (studied in magnesium chloride solutions only). Quadrivalent titanium, about 0·05M., was without effect on the extraction of protoactinium and was not appreciably extracted itself, but tervalent titanium at the same concentration gradually reduced the extraction coefficient for protoactinium from 9·0 to *ca.* 1·0 without being noticeably extracted itself.

When kept for 8 hours or longer, the organic solution of protoactinium complex lost activity appreciably by adsorption on the walls of the containing vessel, presumably following decomposition of the complex. The results suggest that solvent extraction of protoactinium by 2 : 2′-dichlorodiethyl ether from an aqueous solution, 6N. with respect to hydrochloric acid and saturated with magnesium chloride, provides a valuable method of separation of the element from zirconium and titanium as well as many other elements.