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NOTE

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Abstract

A solvent-extraction method has been developed to separate uranium and plutonium from an aqueous solution containing phosphoric, sulfuric, and nitric acids by extracting them into 0.5 *M* TOPO in xylene followed by stripping with ammonium carbonate solution. In the case of plutonium, spectral evidence reveals that the complex species extracted into TOPO is predominantly the neutral nitrate complex of Pu(IV).

INTRODUCTION

Extraction of uranium and plutonium from aqueous phosphoric acid enables their recovery from aqueous wastes containing phosphoric acid. The most frequently used volumetric method (*1*) for the determination of uranium in nuclear fuel samples results in aqueous wastes, containing phosphoric, sulfuric, and nitric acids and appreciable quantities of uranium and plutonium. If the fuel contains high concentrations of fissile isotopes of uranium (^{235}U or ^{233}U), as is the case with FBTR fuels, the recovery of uranium and also of plutonium from such waste becomes necessary.

Although both uranium and plutonium can be extracted with a variety

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of organic extractants from a nitrate medium, the presence of sulfuric and phosphoric acids usually suppresses their extraction. The present work was undertaken to develop a solvent-extraction method for the separation of uranium and plutonium from an aqueous solution containing phosphoric, sulfuric, and nitric acids, and the results obtained are reported here.

EXPERIMENTAL

Material

Uranium-233 obtained from the Fuel Reprocessing Division, BARC, was purified by anion exchange in a HCl medium, and its radiochemical purity was checked by alpha spectrometry. Plutonium was purified by TTA extraction. A stock solution of uranyl nitrate was prepared by dissolving nuclear grade uranium oxide in nitric acid and was used for experiments with natural uranium.

Primene JM-T and Amberlite LA-2 were obtained from Rohm and Haas Co., TOA from K & K Laboratories, Aliquat 336 from General Mills, TOPO from Eastman Kodak Co., and HDEHP from B.D.H. All were used without further purification. All other chemicals used were of A.R. grade.

Distribution Coefficient Experiments

Equal volumes of a xylene solution of the extractant and an aqueous solution of 1 *M* each of phosphoric, sulfuric, and nitric acids (assumed to be a typical composition of the waste) containing either ^{233}U(VI) or Pu(IV) were pipetted into ground glass stoppered tubes which were subsequently shaken at room temperature for about 30 min. At the end of equilibration the phases were separated by centrifuging, and suitable aliquots from both phases were pipetted into vials containing 5 ml of liquid scintillator solution for the radioassay of the actinides.

Similar experiments with macro amounts of uranium were carried out by taking ~100 mg of natural uranium.

Analysis

Phosphoric and sulfuric acids in the mixture were titrated potentiometrically. Uranium in miligram amounts was estimated volumetrically (*1*) and microgram amounts spectrophotometrically using a Cary-14 recording spectrophotometer.

RESULTS

Extraction of Phosphoric Acid

It was felt that if H_3PO_4 could be selectively extracted from the aqueous mixture into a suitable extractant, both uranium and plutonium from the remaining aqueous phase could be recovered relatively easily. The extraction of phosphoric acid by a variety of extractants has been reported (*2–4*). In the present work, when the extraction of H_3PO_4 alone was attempted using different amines, the maximum extraction was found to be into Amberlite LA-2. When 1 *M* aqueous phosphoric acid was contacted with 20% of this amine in xylene, about 50% of the H_3PO_4 was extracted into the amine. However, in the presence of 1 *M* H_2SO_4 in the aqueous phase, practically no H_3PO_4 was found to be extracted into the amine. By resorting to multiple extractions with a fresh organic phase each time, it was found that H_3PO_4 could be extracted into the amine only after the complete extraction of H_2SO_4. However, both U and Pu were also found to be extracted into the amine (Table 1). Thus the separation of Pu and U from phosphoric acid could not be achieved by this approach.

Attempts were therefore made to find a suitable extractant for selective extraction of U and Pu directly from an aqueous solution of phosphoric, sulfuric, and nitric acids.

Extraction of Uranium and Plutonium

Preliminary experiments which indicated that U(VI) could be quantitatively extracted by TOPO in xylene were carried out with a number of

TABLE 1

Extraction of Acids, Uranium, and Plutonium by 20% Amberlite LA-2 in CCl_4

No. of extractions	Percentage extracted			
	H_2SO_4[a]	H_3PO_4[a]	U(VI)[b]	Pu(IV)[b]
1	39.0	0.75	0.24	0.017
2	70.0	5.7	1.3	0.024
3	98.0	14.0	34.0	43.0
4	99.4	79.0	98.4	94.0
5	—	—	98.5	99.0

[a] Aqueous phase, 1 *M* H_2SO_4 + 1 *M* H_3PO_4.

[b] Aqueous phase, 1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 1 *M* HNO_3.

extractants. The extraction of uranium was subsequently studied at varying concentrations of TOPO and the results are given in Table 2. These data show that ~98% of U can be extracted from the aqueous mixture by 0.5 *M* TOPO in xylene. Similar extraction studies were also carried out for Pu(IV) by using a number of extractants. The distribution coefficient data obtained are given in Table 3, and they indicate that Pu can be extracted almost quantitatively by 0.5 *M* TOPO in xylene.

The distribution coefficient data for U(VI) and Pu(IV) obtained using 0.5 *M* TOPO in xylene and various aqueous media are given in Table 4. The results show that the extraction of both U(VI) and Pu(IV) from 1 *M* H_2SO_4, and especially from 1 *M* H_3PO_4, is much less than that from 1 *M* HNO_3. It has been reported that the extraction of U(VI) from a sulfate medium by TOPO is markedly increased by addition of nitric acid or a nitrate salt (*5*). A few data included in Table 4 show that the addition

TABLE 2

Extraction of ^{233}U(VI) with TOPO Concentration in Xylene ([^{233}U] = ~20 μg/ml)

TOPO (*M*)	Distribution coefficient (*D*)
0.05	3.0
0.1	9.5
0.2	25.0
0.3	42.0
0.4	57.0
0.5	73.0

TABLE 3

Extraction of Pu(IV) by Different Extractants ([Pu] = ~20 μg/ml, time of equilibration = 30 min., diluent: xylene)[a]

Extractants	Concentration	Distribution coefficient (*D*)
Primene JM-T	10%	0.0014
Amberlite LA-2	10%	0.00015
TOA	10%	0.0027
Aliquat 336	10%	0.112
HDEHP	5%	0.60
TOPO	0.5 *M*	371
TOPO + HDEHP	0.5 *M* each	198

[a] Aqueous phase, 1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 1 *M* HNO_3.

TABLE 4

Extraction of U(VI) and Pu(IV) by 0.5 *M* TOPO in Xylene[a]

Aqueous phase	Distribution coefficient (*D*)	
	U(VI)	Pu(IV)
1 *M* HNO_3	199	1493
1 *M* H_2SO_4	9.8	6.3
1 *M* H_3PO_4	0.083	0.25
1 *M* H_2SO_4 + 1 *M* H_3PO_4	1.6	1.7
1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 1 *M* HNO_3	56.0	371
1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 2 *M* HNO_3	49.0	—
1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 4 *M* HNO_3	34.4	—
1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 0.5 *M* NO_3^-	67.0	—
1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 1.0 *M* NO_3^-	63.0	—
1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 2.0 *M* NO_3^-	60.0	—
1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 4.0 *M* NO_3^-	59.0	—

[a] NO_3^- ion concentration obtained using $NaNO_3$.

of nitric acid or nitrate ions increases the extraction of both U(VI) and Pu(IV). This suggests that the species of U(VI) or Pu(IV) extracted from an aqueous phase containing HNO_3, H_2SO_4, and H_3PO_4 is probably predominantly the neutral nitrate complex of U(VI) or Pu(IV) solvated by TOPO. In an attempt to substantiate this, the absorption spectra of Pu(IV) in 0.5 *M* TOPO in xylene extracted from aqueous media containing (a) 1 *M* HNO_3, (b) 1 *M* HNO_3 + 1 *M* H_2SO_4, (c) 1 *M* HNO_3 + 1 *M* H_2SO_4 + 1 *M* H_3PO_4, (d) 1 *M* H_2SO_4, and (e) 1 *M* H_2SO_4 + 1 *M* H_3PO_4 were recorded. The spectra of Pu(IV) extracts from (a), (b), and (c) were identical, as were the spectra of the remaining two extracts. Typical spectra of both types are shown in Fig. 1. Comparison of the two spectra thus supports the view that the species of Pu(IV) extracted from a mixture of nitric, sulfuric, and phosphoric acids is essentially the nitrate complex of Pu(IV).

Back-Extraction of Uranium and Plutonium

It was found that U(VI) can be quantitatively stripped from TOPO solutions with 0.5 *M* ammonium carbonate. Back-extraction of plutonium from TOPO solutions was studied using a number of stripping agents, and the results are summarized in Table 5. The data show that Pu could only be quantitatively stripped with a mixture of HF and nitric acid. The

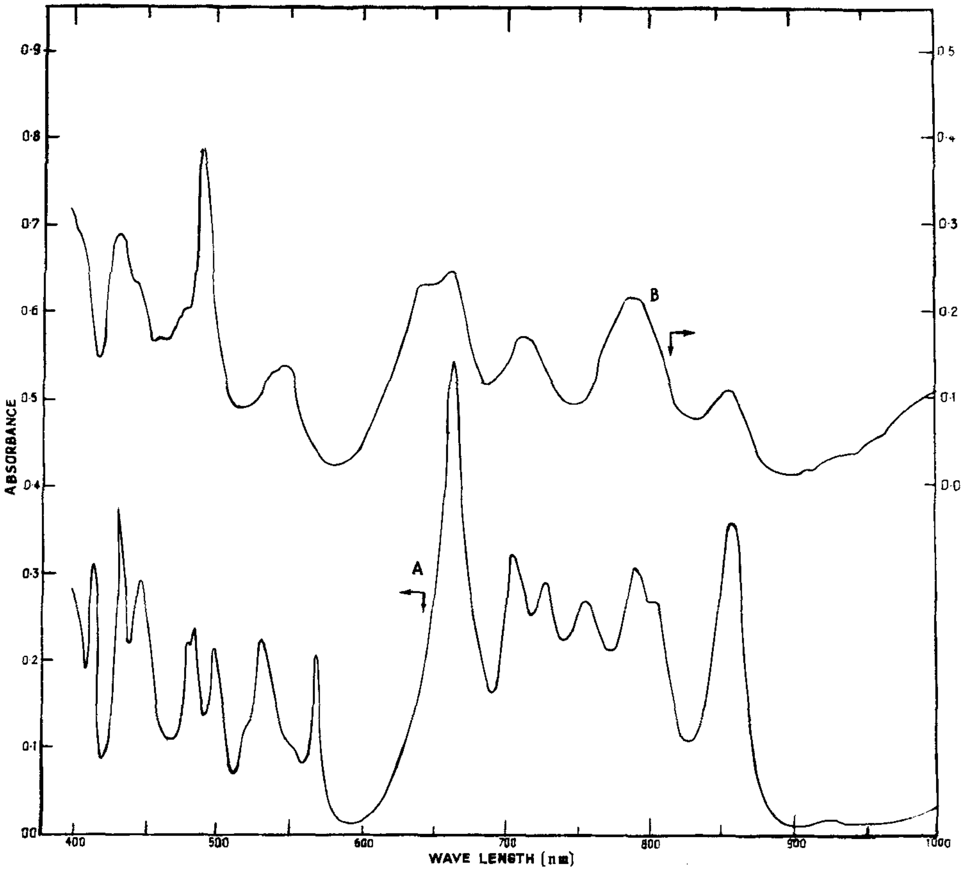

FIG. 1. Absorption spectra of Pu(IV) in TOPO–xylene from (A) 1 *M* H_2SO_4 + 1 *M* H_3PO_4 and (B) 1 *M* H_2SO_4 + 1 *M* H_3PO_4 + 1 *M* HNO_3.

presence of a reducing agent favors the stripping. However, when experiments were carried out with macroconcentrations of Pu (mg/ml), it was found that Pu was quantitatively back-extracted with ammonium carbonate solution. This behavior is contrary to that observed earlier (Table 5), and could possibly be due to the change of oxidation state of Pu(IV) which results more rapidly at a higher concentration of Pu. The absorption spectrum of Pu in 0.5 *M* $(NH_4)_2CO_3$ was recorded after acidifying with perchloric acid. The spectrum revealed that Pu in the stripped solution was present mainly as Pu(III), which was inferred from the presence of the

TABLE 5

Back-Extraction of Plutonium from TOPO Solutions

Stripping agents	Percentage of Pu stripped
0.5 *M* $(NH_4)_2CO_3$	12.0
1 *M* oxalic acid	35.0
0.2 *M* HF	5.0
1 *M* HF + 1 *M* HNO_3	82.0
1 *M* HF + 1 *M* HNO_3 + 0.05 *M* ferrous sulfamate + 0.05 *M* $NH_2OH \cdot HCl$	89.0
2 *M* HF + 1 *M* HNO_3 + 0.05 *M* ferrous sulfamate + 0.05 *M* $NH_2OH \cdot HCl$	97.0

characteristic peak at 600 nm. The effective stripping of Pu(IV) from TOPO with $(NH_4)_2CO_3$ at macroconcentration can thus be attributed to its reduction to Pu(III).

Finally, the separation of U and Pu from an aqueous mixture by extracting them into 0.5 *M* TOPO followed by stripping with 0.5 *M* $(NH_4)_2CO_3$ was successfully tried with 100 mg U and 10 mg Pu. Plutonium and uranium from the back-extracted $(NH_4)_2CO_3$ solution could be further purified by the usual methods such as TBP or TTA extractions or anion exchange after adjusting the acidity of the aqueous phase with nitric acid and the oxidation state of Pu to Pu(IV).

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REFERENCES

1. W. Davis and W. Gray, *Talanta*, *11*, 1203 (1964).
2. F. G. Zharovskii and V. F. Melnik, *Zh. Neorg. Khim.*, *6*, 466 (1961).
3. F. L. Moore, *Anal. Chem.*, *29*, 1660 (1957).
4. C. E. Higgins, *J. Inorg. Nucl. Chem.*, *24*, 415 (1962).
5. J. White and W. Ross, NAS-NS-3102, 1961, p. 44.

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