研究論文

76. Solvent Extraction of Plutonium in the System of Tri-*n*-butyl Phosphine Oxide-carbon Tetrachloride and Nitric Acid Solution

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The distribution ratio of Pu(IV) and Pu(III) between nitric acid solution and tri-*n*-butyl phosphine oxide solution diluted with carbon tetrachloride was determined in the range of nitric acid concentration from 0.5 M to 10 M and tri-*n*-butyl phosphine oxide concentration from 1×10^{-4} M to 3×10^{-1} M. It was found that plutonium can be easily extracted from the irradiated uranium under the suitable conditions of extraction.

INTRODUCTION

It was found that the tri-*n*-butyl phosphine oxide, TBPO, was the excellent extraction solvent for the tetravalent metals during our previous extraction study with organophosphorus compounds from nitric acid solution⁽¹⁾. It was suggested that Pu(IV) could be well extracted with TBPO, since the tetravalent metals such as Zr(IV), Th(IV) and Ce(IV), can be extracted very well from nitric acid solution with TBPO diluted in carbon tetrachloride.

Some extraction studies with tri-alkyl phosphine oxide have been reported⁽²⁾⁻⁽⁴⁾. Almost all studies were carried out with tri-*o*-octyl phosphine oxide by which uranium can be extracted effectively from acidic solution. However, the details of the extraction of plutonium with tri-alkyl phosphine oxide have not been reported.

The present article describes the details of the extraction of plutonium with tri-*n*-butyl phosphine oxide and the procedure of separating plutonium from irradiated uranium.

I. EXPERIMENTAL

1. Sources of materials

TBPO was obtained from the Tama Chem. Co., Tokyo, Japan which was used without any purification. Reagent grade carbon tetrachloride was used as diluent. Plutonium was obtained by the irradiation of

the depleted uranium in the JRR-1 reactor, and purified by means of the usual TBP extraction method followed by anion exchange⁽⁵⁾. Pu(IV) was prepared by adding sodium nitrite while Pu(III) was prepared by the reduction of Pu(IV) with hydroxylamine. The behavior of Pu(III) in the range of nitric acid concentration over 1 M was not studied, as hydroxylamine would not work well as a reductant in this range.

2. Determination of distribution ratio

The techniques employed were the similar to the usual method⁽⁶⁾⁽⁷⁾. In order to eliminate the effect caused by very small amounts of Pu(III) in the Pu(IV) tracer or of Pu(IV) in the Pu(III) tracer, the following procedure was carefully employed: First, organic and aqueous phases containing plutonium tracer added with sodium nitrite were equilibrated, and very small amounts of Pu(III) in the Pu(IV) tracer were mostly remained in the aqueous phase, whereas the greater part of Pu(IV) tracer was extracted in the organic phase. This organic phase was then equilibrated with a fresh portion of nitric acid solution. For Pu(III) tracer, as small amounts of Pu(IV) contained in the Pu(III) tracer was mostly extracted into the organic phase through the first contact, a fresh portion of organic solvent was equilibrated after removing the first organic phase.

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Amounts of plutonium were determined radiochemically with an internal proportional counter. The uranium concentration was determined by the hydrogen peroxide method colorimetrically⁽⁸⁾.

All partitions were carried out at $25^\circ \pm 0.2^\circ \text{C}$ in a thermostat.

3. Extraction of plutonium from irradiated uranium

The 300~500 ml separating funnels were used for the procedure, which was carried out at room temperature ($20^\circ \sim 23^\circ \text{C}$). The anion exchange resin column, Dowex 1 X-8, 200~400 mesh, 5 mm ϕ $\times$ 60 mm, was used for final purification of plutonium solution which was obtained by back-extraction from the organic solvent.

II. RESULTS AND DISCUSSION

1. Distribution of plutonium between nitric acid solution and TBPO-carbon tetrachloride solution

Fig. 1 shows the variation of distribution ratio, K_d , in the range of 1×10^{-4} to 3×10^{-1}

Fig. 1 Distribution ratio of Pu(V), (III) and U(VI) between 1 M HNO₃ and various TBPO concentration solution

M TBPO concentration in the organic phase keeping the acidity of the aqueous phase at 1 M HNO₃. In the plots log K_d values of plutonium for log TBPO concentration, the slope of the lines is two for both Pu(V) and Pu(III). According to Nomura and Hara, U(VI) is supposed to have the same result as far as uranium concentration is very dilute compared to TBPO⁽⁹⁾. The dotted line in Fig. 1 shows calculated K_d value for U(VI) which was obtained on the basis of the assumption of square law. As shown in Fig. 1, Pu(V) nitrate is extracted very well with TBPO highly diluted in carbon tetrachloride.

Fig. 2 shows the variation of K_d values of Pu(V), Pu(III) and U(VI) in the range of 0.5 to 10 M nitric acid keeping the TBPO concentration 1×10^{-2} M. Maximum extractions of these species from nitric acid solutions were observed at about 1 M HNO₃.

It is noteworthy that Pu(V) nitrate can be extracted better than uranyl nitrate by a factor of about 50. Pu(V) extracted into 1×10^{-2} M TBPO is easily stripped with 1 M HNO₃ containing 5% hydroxylamine as plutonium is reduced to Pu(III).

- I : Pu(V) TBPO concn. = 0.01M
- Δ : Pu(III) TBPO concn. = 0.01M
- : U(VI) TBPO concn. = 0.01M
initial U concn. = 0.005M
- : U(VI) TBPO concn. = 0.732M
initial U concn. = 0.1M

Fig. 2 Distribution ratio of Pu(V), (III) and U(VI)

2. Separation of plutonium from uranium irradiated in JRR-1

Plutonium was extracted from uranium irradiated in the JRR-1 with TBPO-carbon tetrachloride. As mentioned above, both Pu(IV) and U(VI) were extracted with TBPO from nitric acid solution, but these K_d values were affected by the uncomplexed free TBPO concentration in the organic phase. In the system of very small amounts of plutonium coexisting with very large amounts of uranium, the extractability of plutonium is limited by the uranium concentration contained in the organic phase. If 1×10^{-2} M TBPO solution is used, TBPO concentration uncomplexed with uranium is calculated as 4×10^{-3} M for initial uranium concentration of 5×10^{-3} M or 6.4×10^{-3} M for 3×10^{-3} M. Therefore, the extraction of plutonium is expected as 95% for initial uranium concentration of 5×10^{-3} M or 98% for 3×10^{-3} M.

(1) Extraction of plutonium with one extraction stage

As Fig. 3 shows, the plutonium oxidized to Pu(IV) by sodium nitrite was extracted with the equal volume of 1×10^{-2} M TBPO solution from 3×10^{-3} M irradiated uranium solution. The irradiation of uranium was carried out at $2 \sim 5 \times 10^{11}$ n/sec·cm² neutron flux in JRR-1 for about 60 hr. Free nitric acid concentration in the aqueous phase was kept 1 M through the extraction process. Plutonium extracted in the organic phase was stripped with 0.5 M HNO₃ containing 5% hydroxylamine by reducing plutonium to Pu(III). Then plutonium back-extracted was coprecipitated with the 10~20 mg aluminium carrier and was purified with the anion exchange cycle in the nitric acid medium.

Fig. 4 shows the amounts of plutonium obtained from different amounts of uranium. Three points obtained fall on a straight line through the origin, showing the good reproducibility of the present method. The dotted lines in the Fig. 4 show the calculated values for $4 \times$ and 5×10^{11} n/sec·cm² neutron flux and the experimental data are roughly agreed with these values.

After plutonium was back-extracted from organic solution, the decontamination factor

Fig. 3 Plutonium separation scheme

Fig. 4 The amount of plutonium produced in uranium

was 10 for uranium and was 10^2 for γ -activity.

(2) Extraction of plutonium with small volume of solvent

Plutonium can be extracted from a large volume of irradiated uranium solution with the small volume of TBPO solution by contacting both phases repeatedly. As TBPO is slightly soluble to nitric acid solution, the freshly contacting aqueous solution should contain the equilibrium amount of TBPO in order to prevent the loss of TBPO. For the system of 1 M nitric acid solution and 1×10^{-2} M TBPO-carbon tetrachloride solution, the equilibrium concentration of TBPO in aqueous phase was determined as 6.5×10^{-4} M (0.14 g/l). The aqueous phase was prepared to be 1×10^{-3} M uranium, 1 M nitric acid and 6.5×10^{-4} M TBPO concentration. The 50 ml of 1×10^{-2} M TBPO was contacted with an equal volume of the aqueous phase and was separated, then the organic phase was successively contacted with the fresh aqueous phase and similar procedures were repeated. After six times of contacts, the organic phase was scrubbed with 0.5 M HNO_3 containing 5 % hydroxylamine. 2.5×10^3 cpm of plutonium was found for 0.14 g of irradiated uranium from this scrub solution and was well agreed with the result of one stage extraction process shown in Fig. 4. This result suggests the possibility of concentration of plutonium from the large volume of irradiated uranium solution with the small volume of TBPO solution.

3. Recovery yield of plutonium

Recovery yield of plutonium was determined for the separation process shown in Fig. 3 by adding plutonium to uranium solution. As Fig. 5 shows, three data for different amounts of plutonium added fall on a straight line through the origin. Recovery yield can be calculated by the slope of line. The dotted line in Fig. 5 shows the value of 100 % recovery yield, so the recovery yield is 75 %. This value, however, is including the yield of the ion exchange process that is about 90 %⁽¹⁰⁾. The yield can be increased by using of a multiple extraction process.

--- : Calculated values for 100% recovery

Fig. 5 Recovery yield of plutonium

4. Extraction of fission products

The fission products have very low extractability for this extraction process because the concentration of TBPO is very low. Tetravalent metals of the fission products, for example $\text{Zr(IV)}^{(11)}$, have comparatively high extractability but those elements can be removed through the back-extraction process.

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REFERENCE

- (1) K. OSHIMA, *et al.* : (to be published).
- (2) J. C. WHITE : TID-7555, (1957).
- (3) C. A. BLAKE, K. B. BROWN, C. F. COLEMAN : ORNL-1964, (1955).
- (4) W. J. ROSS, J. C. WHITE : *Anal. Chem.*, **31**, 1847 (1959).
- (5) K. KIMURA, T. ISHIMORI, K. NAITO, H. UMEZAWA, {K. WATANABE : *This Journal*, **2**, 328, (1960).
- (6) K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK, H. A. C. MCKAY : *J. Inorg. Nucl. Chem.*, **4**, 100 (1957).
- (7) G. F. BEST, H. A. C. MCKAY : *ibid.*, **4**, 315 (1957).
- (8) C. J. RODDEN, J. C. WARF : "Analytical Chemistry of the Manhattan Project" (NNES IV-1), (1950).

- (9) S. NOMURA, R. HARA : (to be published).
(10) K. WATANABE : (unpublished).
(11) H. UMEZAWA, R. HARA : *Anal. Chim. Acta*,
(1960), (in press).

Tri-*n*-butyl Phosphine Oxide による
プルトニウムの抽出

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Tri-*n*-butyl Phosphine Oxide (TBPO) の四塩化炭素溶液と硝酸の系において、TBPO の濃度 1×10^{-4} M から 3×10^{-1} M, 硝酸濃度 0.5 M から 10 M の範囲にわたって Pu(Ⅲ) と Pu(Ⅳ) の分配平衡が測定された。その結果、ウラン濃度が 0.005 M 以下であれば中性子照射したウランからプルトニウムを容易に抽出できることが明らかになった。