# *Coprecipitation of Neptunium with Lanthanum Trifluoride*

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It is well known that oxidized neptunium does not coprecipitate with lanthanum trifluoride whereas reduced neptunium is carried down almost quantitatively. Although this process is studied and often utilized for the practical separation of neptunium[1-3], its oxidation state is not clearly defined. Some believe that both neptunium(IV) and -(V) are carried down by lanthanum trifluoride[4], whereas others believe that neptunium(V) is not[5]. Sometimes the expression the " lanthanum fluoride carriable state " is used in place of the " oxidation state "[6]. Thus, the coprecipitation behavior of neptunium (V) is open to question.

In the present study, the different modes of coprecipitation behavior of neptunium(IV), -(V) and -(VI), are studied with the aids of the tracers for neptunium(IV), -(V) and -(VI). The oxidation state of the neptunium tracer used is determined according to the solvent extraction behavior as well as to the coprecipitation behavior with zirconium phosphate.

## Experimental

**Materials.**—Neptunium-239 separated from neutron irradiated uranyl nitrate[7] is used as the tracer for neptunium. Prior to use, the tracer is treated chemically in order to confirm the fact that neptunium(IV), -(V) and -(VI) tracer is radiochemically pure.

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[1] G. T. Seaborg and A. C. Wahl, *J. Am. Chem. Soc.*, **70**, 1128 (1948).

[2] L. B. Magnusson and T. J. LaChapelle, ibid., **70**, 3534 (1948).

[3] L. B. Magnusson, S. G. Thompson and G. T. Seaborg, *Phys. Rev.*, **78**, 363 (1950).

[4] L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, AEC Report ANL-4066 (1947).

[5] G. T. Seaborg and J. J. Katz, " The Chemistry of the Actinide Elements "; Methuen and Co., Ltd., London (1957), Chap. VI.

[6] E. K. Hyde, First United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. VII, P/728, United Nations Publication, New York (1956).

[7] T. Ishimori and E. Nakamura, This Bulletin, 32, 713 (1959).

These chemical treatments are as follows.

*Tetravalent neptunium.*—(A) *In nitirc acid system.* The tracer reduced by granulated zinc in 1 N nitric acid is extracted by TTA*-benzene, stripped by 3 N nitric acid washed with benzene and diluted with distilled water to 2 N. (B) *In hydrochloric acid system.* The tracer is reduced by granulated zinc in 1 N HCl, extracted by TTA-benzene solution, stripped by 1 N HCl in a large volume and washed with benzene.

*Pentavalent neptunium.*—In the nitric acid system, neptunium(V) tracer is prepared in the following four ways. (C) The tracer is prepared as perchloric acid solution and pipetted into 2 N nitric acid. Neptunium is almost all pentavalent in perchloric acid⁷⁾, and the neptunium(VI) which might be present is removed by 100% TBP**. (D) The tracer is oxidized with ceric ammoium nitrate⁵⁾ in 7 N nitric acid, extracted with 100% TBP, stripped by distilled water after the organic layer is diluted with a large volume of benzene, and reduced by hydrazine⁵⁾. The acid concentration is about 2 N. Neptunium distribution ratios in the TBP nitric acid system are measured when neptunium is treated with oxidizing or reducing agent. (E) The tracer is reduced with sulfur dioxide in perchloric acid solution in order to change all of neptunium into neptunium(V), and pipetted in volume of a few lambda (0.001ml.). The distribution ratio is measured between 100% TBP and 1.7 N perchloric acid tracer solution saturated with sulfur dioxide. (F) The tracer is treated as (D), but reduced with sulfur dioxide instead of with hydrazine⁵⁾. The distribution ratio of this tracer solution is checked between 1.7 N perchloric acid and TBP.

(G, H) In the hydrochloric acid system, the tracer is obtained in perchloric acid solution and a few lambda of it are pipetted into the acid. The acid concentration is 1 N(G) or 4 N(H) of hydrochloric acid.

(I, J) In the perchloric acid system, a perchloric acid tracer solution is used. The perchloric acid concentration is 4.6 N(I) or 1.2 N(J).

*Hexavalent neptunium.*—(K) In nitric acid system. The tracer solution is warmed and oxidized with ceric ammonium netrate in 7 N $HNO_3$⁵⁾. Oxidized neptunium is extracted with 100% TBP. The organic phase obtained is shaken with 7 N nitric acid in order to remove Np(IV) and -(V). Neptunium is backextracted with distilled water and washed with benzene. The acid concentration is about 2 N. The distribution ratio of neptunium between 7 N nitric acid and TBP is measured. (L) In hydrochloric acid system. The tracer is oxidized by potassium chlorate⁵⁾ in 8 N hydrochloric acid during the heating of the solution, extracted with 100% TBP, backextracted with a large volume of distilled water, and washed with benzene. The distribution ratio of tracer between 8 N hdyrochloric acid and 100% TBP is checked. (M) In perchloric acid system. Tracer is oxidized with silver peroxide in 1.2 N perchloric acid⁵⁾. Experiments are carried out in the presence of silver peroxide powder. Without silver peroxide, the tracer is carried down with lanthanum fluoride.

The lanthanum carrier solution contains 2 mg. of the lanthanum ion per ml. in acid solution. In order to avoid complexities, lanthanum carrier is dissolved in the same acid as that used for nuptunium tracer solution in every case.

The zirconium carrier solution contains 10 mg. zirconium per ml.

Hydrofluoric acid (47.1%) is used without dilution as precipitant for lanthanum fluoride. It will be seen in Table I that high hydrofluoric acid concentration in the precipitant causes marked coprecipitation of neptunium(V) in nitric acid medium. Thus, the coprecipitation behavior is supposed to be dependent on the concentration of hydrofluoric acid. However, not considering this effect, hydrofluoric acid is used without any dilution or purification in the present study.

1 M diammonium hydrogen phosphate solution is used as precipitant for zirconium phosphate.

**Procedure.**—The coprecipitation experiments are carried out as follows. Two milliliters of acid solution containing neptunium-239 in a desired oxidation state, 1 ml. of carrier solution and 1 ml. of precipitant solution are mixed thoroughly in a centrifuge tube. The hydrofluoric acid corrosion of glass is avoided by using an polyacrylic acid tube. After the white precipitate is removed by centrifugation, 2 ml. of the supernatant solution is taken in a glass tube for the measurement of the gamma activity. This is measured by Philips' scintillation counter.

## Results

The reproducibility is checked by repeating experiments under the same conditions. As is seen in Table I, most values coincide well with

TABLE I. THE EFFECT OF HYDROFLUORIC ACID CONCENTRATION

| Acid concn. | Activity remaining / Activity taken | Mean |
|---|---|---|
| conc. HF(47.1%) | 0.0067 | 0.0073 |
| | 0.0068 | |
| | 0.0082 | |
| | 0.0074 | |
| 1 : 1 HF | 0.010 | 0.010 |
| | 0.011 | |
| | 0.0096 | |
| | 0.0096 | |
| 1 : 3 HF | 0.057 | 0.057 |
| | 0.044 | |
| | 0.060 | |
| | 0.060 | |

Given activity for 2 ml. of solution is 61486 cpm. Nitric acid concentration is 2 N. Tracer is Np(V).

TABLE II. THE EFFECT OF NITRIC AND CONCENTRATION

| $HNO_3$, N | Activity remaining / Activity taken |
|---|---|
| 0.5 | 0.0138 |
| 1.0 | 0.0116 |
| 2.0 | 0.0124 |
| 5.0 | 0.0110 |

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* Thenoyltrifluoroacetone.

** Tri-*n*-butyl phosphate.

TABLE III. COPRECIPITATION OF NEPTUNIUM

| Acid | Tracer | | $LaF_3$ pptn. | | $ZrH_2(PO_4)_2$ pptn. | |
|---|---|---|---|---|---|---|
| | Solution | Treatment | Ratio* | % Np pptd. | Ratio* | % Np pptd. |
| $HNO_3$ | Np(IV) | A | 0.0096 | 99 | 0.084 | 92 |
| | Np(V) | B | 0.012 | 99 | 0.70 | 30 |
| | Np(V) | C | 0.0064 | 99 | 0.77 | 23 |
| | Np(V) | D | 0.017 | 98 | 0.78 | 22 |
| | Np(V) | E | 0.021 | 98 | 0.85 | 15 |
| | Np(VI) | F | 0.99 | 1 | 0.45 | 55 |
| HCl | Np(IV) | G | 0.016 | 98 | 0.018 | 98 |
| | Np(V) | H | 0.011 | 99 | 0.96 | 4 |
| | Np(V) | I | 0.0099 | 99 | 0.87 | 13 |
| | Np(VI) | J | 0.72 | 28 | 0.75 | 25 |
| $HClO_4$ | Np(V) | K | 0.028 | 97 | 0.97 | 3 |
| | Np(V) | L | 0.026 | 97 | 0.82 | 18 |
| | Np(VI) | M | 0.89 | 11 | 0.66 | 34 |

$* \ \frac{\text{Activity remaining in solution}}{\text{Activity taken}}$

one another. However, experiments are repeated four times under the same conditions and the mean value of the ratio between the neptunium remaining and the neptunium taken, is calculated.

On the other hand, it is likely that the acidity of the tracer solution would not cause a strong effect on the coprecipitation. Table II shows that the tracer solution of 0.5~5.0 N nitric acid gives reproducible results. All results obtained are summarized in Table III.

The tracers were prepared by solvent extraction with TBP and/or TTA, as described in the experimental part and the oxidation state of the neptunium was determined according to the solvent extraction behavior and also the coprecipitation behavior with zirconium phosphate.

The oxidation state of neptunium(IV) was ascertained by TTA-extraction and zirconium phosphate coprecipitation. It is well known that only neptunium(IV) is extracted by TTA[4-6], and is carried down by zirconium phosphate[3,5,6]. Results show that neptunium(IV) coprecipitates with lanthanum fluoride in nitric and hydrochloric acid solutions. No experiment was carried out in perchloric acid solution, because neptunium(IV) is unstable in perchloric acid solution.

In the series of experiments for neptunium(V) and -(VI), the distribution ratios of the neptuium tracer were measured between mineral acid and 100% TBP. The distribution of neptunium(IV), -(V) and -(VI) between tributyl phosphate and some kinds of mineral acid had been betermined in the previous study[7]. The distribution ratio being measured, the oxidation state is assigned by comparing the distribution ratio measured and that reported. On the other hand, zirconium phosphate can not carry down neptunium(V) and -(VI) quantitatively. These results show that neptunium(V) is carried down with lanthanum fluoride whereas neptunium(VI) is not. An uncertainty may be found in the preparation of $ZrH_2(PO_4)_2$ precipitate, because it is not aged in order to prevent any change in the oxidation state of neptunium.

It will be noted in Table III that both neptuium(IV) and -(V) are carried down by lanthanum fluoride almost completely, while a remarkable amount of neptunium(VI) remains in the supernatant solution. As far as lanthanum fluoride precipitation is concerned, the difference between the behavior of neptunium(IV) and that of neptunium(V) can not be identified separately, but these two oxidation states behave quite differently in TBP-acid solution systems. It is also seen in Table III that they behave differently in coprecipitation with zirconium phosphate.

Results show that neptunium(IV) and -(V) can not be separately identified according to their behavior in being carried down with lanthanum trifluoride, whereas they are identified by the behavior in the solvent extractions or in the coprecipitation with zirconium phosphate. Thus it is presumed that both neptunium(IV) and -(V) are carried down almost completely with lanthanum trifluoride while neptunium(VI) remains in the supernatant solution.

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