研究論文

83. *Determination of Neptunium-239 in Various Aqueous Samples*

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All neptunium of (IV), (V) and (VI) states in urine is quantitatively coprecipitated onto basic phosphates of calcium and magnesium which are formed when the sample is treated with sodium hydroxide. In the present paper, the determination method of neptunium is studied by using this coprecipitation procedure.

Neptunium can be concentrated by the coprecipitation from large volumes of aqueous samples such as urine, tap water and sea water. Separation from other radioactive nuclides which are simultaneously coprecipitated onto the precipitate can be attained by the anion exchange.

For urine sample, basic phosphates of calcium and magnesium were directly precipitated by adding sodium hydroxide solution. For tap water, phosphoric acid and small amount of the calcium carrier were added in order to carry neptunium down. In the case of sea water, phosphoric acid was added and a small portion of calcium and magnesium phosphates were precipitated by adding a small amount of sodium hydroxide. The precipitate was dissolved with nitric acid. The resultant solution should contain 7.5 N nitric acid-0.1 M semi-carbazide-0.01 M ferrous sulfamate. The solution was passed through 1.00 g of Dowex 1, X 8 resin column and washed with the nitric acid-reductants solution, then eluted the adsorbed neptunium with a small amount of 0.2 N nitric acid-0.005 M ceric sulfate solution.

The recoveries of neptunium-239 are $97.0 \pm 2.6\%$ for 300 ml of human urine, $97.9 \pm 3.1\%$ for 1,000 ml of tap water and $96.4 \pm 2.2\%$ for 1,000 ml of sea water, respectively.

INTRODUCTION

Many studies on the analysis of neptunium are reported by many workers. However, most of those studies are the reports on the separation and recovery procedure from irradiated uranium or reactor wastes, and studies from the viewpoint of health physics are very rare.

Neptunium-239 and 237 are very important isotopes among many neptunium isotopes. The former isotope is the daughter nuclide of uranium-239 which is produced by $^{238}\text{U}(n,\gamma)^{239}\text{U}$ reaction, whereas the latter is the daughter nuclide of uranium-237 which is produced by $^{238}\text{U}(n,2n)^{237}\text{U}$ or $^{235}\text{U}(n,\gamma)^{236}\text{U}(n,\gamma)^{237}\text{U}$ re-

actions. Neptunium-239 is a beta emitter and its half-life is 2.33 days, and a large amount of it is produced in the natural or slightly enriched uranium reactor. Neptunium-237 is an alpha emitter of a very long half-life (2.2×10^6 years), and the rate of production of it by $(n, 2n)$ reaction on uranium-238 reaches about 0.3% of the plutonium production rate⁽¹⁾.

For the soluble form of neptunium-239, gastro-intestine is the critical organ and the maximum permissible concentrations in air and water are $3 \times 10^{-7} \mu\text{C/cc}$ and $10^{-3} \mu\text{C/cc}$ respec-

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tively for 168 hr week⁽²⁾. Thus, it is considered that the neptunium-239 is one of the most important nuclide from the viewpoint of the radiation control.

The author⁽³⁾ already reported that neptunium is completely coprecipitated with the basic phosphates of calcium and magnesium. In this paper, the further study on the determination of neptunium using the coprecipitation is described.

Many studies on the coprecipitation of neptunium are carried out. It is concluded that, in the oxidized state, neptunium is coprecipitated onto sodium uranyl acetate⁽⁴⁾⁽⁵⁾ and in the reduced state, it is coprecipitated onto lanthanum trifluoride⁽⁶⁾⁽⁷⁾. Recently, the detail study was carried out on the coprecipitation of neptunium onto lanthanum trifluoride and zirconium phosphate⁽⁸⁾. Those precipitates can carry down neptunium in the selected valence state, also, it has the oxidation states of (IV), (V) or (VI). However, any quantitative coprecipitation of neptunium without regards to the valence states have not been reported.

The author found that all neptunium of these three valence states is completely coprecipitated onto basic phosphates of calcium and magnesium, and developed further study on the determination of neptunium in the various aqueous samples such as urine, tap water and sea water.

I. EXPERIMENTAL

1. Preparation of neptunium-239 stock solution

Uranyl nitrate (40~100 mg) was irradiated in the nuclear reactor, JRR-1, and let stand for one day. It was then dissolved in 2 ml of 1 N hydrochloric acid. Neptunium was reduced by adding a small amount of ascorbic acid as a reductant. The solution was dried up by a heating lamp and the residue was dissolved in

a 1 ml of 7.5 N nitric acid. The solution was poured onto the Dowex 1 column (resin 2.0 g, 6.7 mm in diameter, 10 cm in length) at the flow rate of 1.5 ml/min. The column was washed with 100 ml of 7.5 N nitric acid. Adsorbed neptunium was eluted with 0.2 N nitric acid. The purify of this neptunium solution was examined both by the gamma-ray spectrum and by the decay curve, and no impurity was detected.

2. Preparation of Dowex 1 column

Dowex 1, X8 resin (100~200 mesh) was adequately washed with demineralized water, stood over night in 2 N sodium hydroxide solution, and was washed with demineralized water till the washing water does not indicate alkalinity. Then, 7.5 N nitric acid solution was added and stood over night. After washing with demineralized water, the resin was dried up at $35^{\circ}\pm 1^{\circ}\text{C}$ for 24 hr and stored in a desiccator.

3. Preparation of ferrous sulfamate solution

Ferrous sulfamate stock solution was prepared by dissolving electrolytic iron powder in a slight excess of sulfamic acid solution and supernatant solution was used.

4. Preparation of Np (IV), (V) and (VI) solution

Neptunium (IV) was prepared as follows; the semicarbazide and ferrous sulfamate solution was added to the neptunium stock solution and the concentration of the solution was adjusted to 0.1 M for semicarbazide and 0.01 M for ferrous sulfamate. By this treatment, neptunium was instantly reduced to (IV) state⁽⁹⁾.

Neptunium (V) was prepared by the reduction of neptunium (VI) with excess hydroxylamine in 1 N nitric acid solution. Hydroxylamine reduces (VI) state instantly to (V) state, but the reduction of (V) state to (IV) state is very slowly in 1 M acidic solution⁽⁹⁾.

Neptunium (VI) was prepared by the oxi-

elation of stock solution. Ceric sulfate was added to the stock solution of neptunium and the concentration was adjusted to 0.005 M for ceric sulfate. By this treatment, neptunium was oxidized very rapidly⁽⁹⁾⁽¹⁰⁾.

All chemicals used in this experiment are of the analytical grade, and experiments were carried out at the room temperature.

(1) Coprecipitation with basic phosphate precipitate

Twenty-five millilitres of synthetic urine* was taken in a centrifugal tube, and the neptunium (IV), (V) or (VI) solution was added. The basic phosphates of calcium and magnesium were precipitated by adding 6 N sodium hydroxide. After standing for a few minutes, the solution was centrifuged at about 4000 r.p.m. for 5 min. The supernatant solution was decanted and discarded. To the precipitate remaining in the centrifugal tube, 1 ml of 2 N nitric acid was added to dissolve it. The nitric acid solution was transferred quantitatively with 1 ml of 2 N nitric acid into a small polyethylene tube, and the gamma-activity was observed with a pulse height analyzer (well-type scintillator).

The result is shown in Table 1. Table 1 clearly indicates that all Np (IV), (V) and (VI) are quantitatively coprecipitated onto basic phosphates of calcium and magnesium.

Table 1 Coprecipitation factor of Np(IV), (V) and (VI) with basic phosphates of calcium and magnesium

Valence	Added activity (cpm)	Amount of precipitate (mg)	Coprecipitated activity (cpm)	Coprecipitation factor (%)
Np(IV)	768±11	20	771±11	100.3±2.0
Np(V)	753±11	20	731±11	97.1±2.0
Np(VI)	768±11	20	765±11	99.7±2.0

† Standard deviation based on the counting error.

(2) Adsorption of neptunium on Dowex-1 resin in the presence of basic phosphate precipitate

Many studies have been carried out on the adsorption of neptunium on an anion exchange resin^{(10)~(16)}, but in the case of the anion exchange of neptunium which coprecipitated onto the basic phosphate, considerable amounts of calcium, magnesium and phosphate ions exist together. So that, the following experiment was carried out;

Twenty millilitres of Np(IV)-7.5N nitric acid-0.1 M semicarbazide solution was taken into a conical flask, the standard phosphoric acid-7.5 N nitric acid solution or basic phosphate-7.5 N nitric acid solution was added. Dowex-1 resin was then added and the flask was shaken for 20 hr.

Resin adsorption was determined by comparing the activity of an aliquot of the solution with that of a control solution. Activity was measured using an ordinary G-M counter after the sample solution was dried up in a glass counting dish. The degree of adsorption for neptunium by the resin is expressed in the equilibrium distribution coefficient Kd , which is defined by the following equation:

$$Kd = \frac{\% \text{Np adsorbed}}{100 - \% \text{Np adsorbed}} \times \frac{\text{volume of solution (ml)}}{\text{amount of resin (g)}}$$

The result is shown in Table 2.

The existence of phosphoric acid decreases the adsorption degree of neptunium in 7.5 N nitric acid-0.1 M semicarbazide solution, while the presence of basic phosphate increases the adsorption degree. The decrease of the adsorption degree caused by phosphoric acid may be considered

* The chemical composition of human urine is widely varied, so that, synthetic urine was prepared and used in some experiments of this work (see, This Journal., 2, No.7, 381(1960).)

Table 2. Distribution coefficient of neptunium on Dowex 1, X 8 resin from 7.5N nitric acid-0.1M semicarbazide solution in the coexistence of different amounts of phosphoric acid or basic phosphate precipitate

Added material	Amount of added material (mg)	Amount of resin (g)	Volume of solution (ml)	% of adsorbed activity	Kd
-	-	0.219	20.0	89.9	880
Phosphoric acid	10	0.219	22.4	91.5	1,070
"	20	0.224	24.8	90.1	890
"	50	0.220	21.2	89.5	830
"	101	0.220	22.4	88.7	770
"	201	0.226	24.8	80.6	410
"	420	0.205	30.0	74.2	280
-	-	0.208	20.0	89.9	890
Basic phosphate ppt.	21	0.204	20.3	90.4	940
"	43	0.216	20.5	91.4	1,010
"	85	0.218	21.5	92.0	1,140
"	170	0.209	22.0	92.3	1,190
"	340	0.223	24.0	92.4	1,190

to be due to the oxidation of neptunium.

Many other active nuclides are coprecipitated with basic phosphate precipitate (3) (17). Therefore the distribution coefficient values of several radioactive nuclides were measured in a similar way, but only increasing the amount of the resin to 2.00 g. The amount of the basic phosphate added to the experimental solution was 170 mg. Both semicarbazide and ferrous sulfamate were used as the reductant. The result is shown in Table 3.

As is seen from Table 3, the distribution coefficient values of those nuclides indicate that the adsorption onto the resin is very weak or does not occur at all.

Table 3. Distribution coefficient of several radioactive nuclides on Dowex 1 resin from 7.5N nitric acid-0.1M semicarbazide-0.01M ferrous sulfamate in the presence of the basic phosphate precipitate

Nuclide	F.P. †	⁹⁵ Zr- ⁹⁵ Nb	¹⁰⁶ Ru- ¹⁰⁶ Rh	¹⁴⁷ Pm	⁹⁰ Sr- ⁹⁰ Y
Kd	2.4	9.5	1.0	Not adsorbed	Not adsorbed

† Mainly composed of ¹⁰⁶Ru-¹⁰⁶Rh, ¹³⁷Cs-^{137m}Ba, ⁹⁰Sr-⁹⁰Y, ¹⁴⁷Pm and ¹⁴⁴Ce-¹⁴⁴Pr.

It is qualitatively observed that uranium (VI) is adsorbed on the resin very weakly and easily washed out by small amounts of 7.5N-nitric acid-0.1M semicarbazide-0.01M ferrous sulfamate solution from the resin column.

(3) Elution of neptunium from Dowex 1 resin column

The elution of neptunium from the Dowex 1 resin can be attained with the dilute acid solution, but the elution with 0.2 N nitric acid is rather slow and required comparatively large volumes of elutriant for quantitative recovery. The rate of elution was increased by oxidizing neptunium (IV) to the higher valence state with

resin: Dowex 1, X 8, 100~200 mesh 1.0g (volume 2.0ml)

column: 6.7 mm in diameter, 63 mm in length

elute: 0.2 N nitric acid-0.005 M ceric sulfate

elution rate: 0.30 ml/min

Fig. 1 Elution curve of neptunium-239

ceric sulfate⁽¹⁰⁾.

The elution curve of neptunium with 0.2 N nitric acid-0.005 M ceric sulfate from Dowex 1, X 8 resin column is shown in Fig. 1. Neptunium was eluted with 5 column volumes of elutriant. In this case, the washing of the resin column with minute amounts of demineralized water prior to the elution is very favorable, and by this treatment, neptunium was eluted quantitatively with 3 column volumes of elutriant. On the other hand, only 60 % of neptunium was eluted with 10 column volumes of 0.2 N nitric acid.

(4) Recovery of neptunium from human urine, tap water and sea water

(i) Human urine: Three hundred millilitres of urine was taken in a beaker and added 1.00 ml of neptunium stock solution. Excess of 6 N sodium hydroxide solution was added and the basic phosphate of calcium and magnesium was precipitated. After standing for 30 min, the supernatant solution was discarded by decantation and the slurry was centrifuged at 3,600 r.p.m. for 5 min. The precipitate was dissolved with small amounts of concentrated nitric acid and then transferred into a small evaporating dish. The solution was heated until all organic substances were destroyed. The residue was dissolved with 12 ml of 7.5 N nitric acid-0.1 M semicarbazide-0.01 M ferrous sulfamate solution. The resultant solution was put aside for about 30 min, and passed through the Dowex 1, X 8 resin column (6.7 mm in diameter, 6.3 cm in length, resin 1.0 g) at the flow rate of 0.3-0.4 ml/min. The column was washed with 15 ml of the 7.5 N nitric acid-reductants solution at the flow rate of 0.5 ml/min. Neptunium was then eluted with 1.0 ml of demineralized water and 6.0 ml 0.2 N nitric acid-0.005 M ceric sulfate solution at the flow rate of 0.33 ml/min. A total 7.0 ml of eluates was evaporated in a

small evaporating dish, and transferred quantitatively with small amount of 2 N nitric acid into a glass counting dish, dried up and counted the radioactivity using an ordinary G-M counter.

(ii) Tap water: Into 1 l of tap water taken in a beaker, were added 2.0 ml of 6 N phosphoric acid, 2.2 ml of calcium chloride solution (100 mg as Ca), and 1.00 ml of neptunium stock solution. The basic phosphates of calcium and magnesium were precipitated by adding excess of 6 N sodium hydroxide solution. Further treatment was carried out as the same method with mentioned in (i).

(iii) Sea water: Into 1 l of sea water taken in a beaker, were added the 6.0 ml of 6 N phosphoric acid and 1.00 ml of neptunium stock solution. Then 7.0 ml of 6 N sodium hydroxide solution was slowly added under constant stirring in order to precipitate the basic phosphate. The stirring was continued for 10 min, and further treatments was carried out as the same method as that mentioned above, but in the cases of tap water and sea water, the destruction procedure by nitric acid was omitted. The results are shown in Table 4.

Table 4 Recovery of neptunium-239 from human urine, tap water and sea water

Sample	Sample amount (ml)	Added activity (cpm)	Detected activity (cpm)	Recover yield (%)
Human urine	300	1,008 ± 20	979 ± 16	97.0 ± 2.6†
Tap water	1,000	1,008 ± 20	986 ± 23	97.9 ± 3.1
Sea water	1,000	436 ± 7	420 ± 7	96.4 ± 2.2

† Standard deviation based on the counting error.

II. DISCUSSION

The coprecipitation of neptunium onto the basic phosphate precipitate is very suitable in the determination of neptunium in various aqueous samples. However, the present method requires the separation of neptunium from many

other active nuclides such as rare earth elements, zirconium, niobium, strontium, ruthenium, uranium, etc. which are simultaneously coprecipitated onto the basic phosphate precipitate. The separation of neptunium from those nuclides can be carried out rather easily by the anion exchange from nitric acid solution.

Besides neptunium (N), it is known that plutonium (Pu)⁽¹⁸⁾ forms stronger anionic nitrate complex in nitric acid. Thorium is rather strongly adsorbed on the anion exchange resin (Kd-300)⁽¹⁹⁾ and uranium (U)⁽²⁰⁾, ruthenium (Ru)⁽²¹⁾, protoactinium (Pa)⁽²¹⁾, praseodymium (Pr)⁽¹⁹⁾ and neptunium (Np)⁽²¹⁾ are very weakly adsorbed, zirconium (Zr)⁽²⁰⁾ is slightly adsorbed, plutonium (Pu)⁽²¹⁾, aluminium (Al)⁽²⁰⁾, iron (Fe)⁽²⁰⁾ and rare earth element⁽²⁰⁾ are not adsorbed.

It is considered that the adsorption degree of those nuclides is not changed by the presence of the basic phosphate precipitate.

The experimental results showed that ⁹⁰Sr-⁹⁰Y, ⁹⁵Zr-⁹⁵Nb, ¹⁰⁶Ru-¹⁰⁶Rh and ¹⁴⁷Pm are weakly adsorbed or not adsorbed on the Dowex 1 resin. Uranium (U) is also weakly adsorbed and easily eluted out from the resin column by washing.

Thorium is rather strongly adsorbed on the anion exchange resin. Besides that, the coprecipitation behavior of thorium with basic phosphate is not clear. However the separation of thorium from neptunium is not investigated because of the following reason. In the determination of neptunium-239, however, the measurement of neptunium is carried out by beta-counting, therefore, if any thorium were coprecipitated with neptunium, it would not interfere the determination of neptunium. Plutonium is easily separated by the column operation⁽¹⁰⁾.

For the determination of neptunium in human urine and sea water, no carrier is

required, but calcium is required as the carrier in the case of tap water (generally non-saline water). In the case of sea water, very large amounts of precipitate is formed by addition of sodium hydroxide in the presence of phosphoric acid, so that, the amount of the precipitate is controlled by adding the insufficient amounts of sodium hydroxide. In such case, the coprecipitation of neptunium is also completed quantitatively.

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各種水溶液試料中の ^{239}Np の定量法

赤石 準

カルシウムおよびマグネシウムの塩基性リン酸塩沈殿へⅣ, Ⅴ, Ⅵ価のネプツニウムが共沈することを利用し, 多量の水溶液試料(尿, 水道水, 海水)よりネプツニウムを濃縮し, ついで陰イオン交換樹脂を用いて同時に共沈する他の多くの放射性核種と分離する方法を検討した。

尿については試料に直接水酸化ナトリウムを加え, 水道水についてはリン酸と担体としてカルシウムを加えたのち, 水酸化ナトリウムを加えて沈殿を生成させる。海水はリン酸を加え, かくはんしながら水酸化ナトリウムを徐々に加えて沈殿を生成させる。多量の水酸化ナトリウムを加えると沈殿の生成量は多くなるので, この場合は少量を加えて生成する沈殿を一部分にとどめる。沈殿は遠心分離し, 少量の硝酸にとかし, 硝酸 7.5 N, セミカルバジド 0.1 M, スルファミン第一鉄 0.01M の溶液になるようにおのおのを加えてネプツニウムをⅣ価に還元する。この溶液を Dowex 1, X8 樹脂のカラムに通し, 吸着したネプツニウムを 0.2 N の硝酸と 0.005 M の硝酸第二セリウムの混合溶液で溶離する。ネプツニウムの収率は尿 300 ml につき $97.0 \pm 2.6\%$, 水道水および海水 1l につき, それぞれ $97.9 \pm 3.1\%$, $96.4 \pm 2.2\%$ であった。

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