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*Preparation of Pure Neptunium Oxide
for Nondestructive Assay Standards*

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PREPARATION OF PURE NEPTUNIUM OXIDE FOR NONDESTRUCTIVE ASSAY STANDARDS

by

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ABSTRACT

Accurate nondestructive assay (NDA) measurements, particularly with gamma spectrometry, require pure material standards. The purity of materials used as standards is verified by reliable chemical techniques, and these materials are then used to calibrate and certify NDA instruments. So that they can be used for this purpose, impure NpO_2 and metal were each purified by a different procedure. The NpO_2 , which contained more than 2500 ppm plutonium, was purified by a double peroxide precipitation, followed by ion exchange and oxalate precipitation of the eluate. All impurities, including plutonium, were below 100 ppm in the product. The metal, which contained more than 10 000 ppm of tantalum, was dissolved in 12 M HCl and then precipitated as the Np(IV) oxalate. The final product was below 100 ppm of all impurities except calcium.

I. INTRODUCTION

A variety of actinide isotopes are processed at the Plutonium Facility at Los Alamos. These isotopes are used to support many ongoing activities in weapons research design and testing, studies involving the SP-100 space reactor, research into milliwatt heat sources, and other program areas. Processing these actinide materials produces waste items that must be assayed before going on to further processing or disposal. Many of these items are complex matrices, such as broken glass or plastics, for which nondestructive assay (NDA) methods provide the best and most reliable analysis. At Los Alamos, the vigorous program to develop robust NDA techniques often requires pure materials for calibrating and certifying instruments. Of the 570 g of pure NpO_2 provided for gamma assay standards, 500 g of oxide was sent to New Brunswick Laboratory so that standards could be manufactured for the DOE complex and others as required, and 70 g remained at Los Alamos to be used as part of a program to develop an accurate gamma spectrometry technique for neptunium.

II. EXPERIMENTAL EQUIPMENT AND MATERIAL

The feedstock for preparing the pure NpO_2 was impure neptunium oxide and metal. The assays for each appear in Table I.

Table I. Trace Metals Analysis of Neptunium Feedstock

Trace Metal	NpO ₂ (ppm)	Np Metal (ppm)
Aluminum	8300	—
Beryllium	30	—
Calcium	4000	>1000
Chromium	25	—
Copper	25	—
Iron	240	—
Magnesium	16000	—
Manganese	10	—
Sodium	500	—
Nickel	40	—
Lead	16500	—
Silicon	110	—
Tin	35	—
Tantalum	<5	> 10000
Plutonium	2600	< 100
Americium	6	< 100

All the chemicals, such as nitric and hydrochloric acid, hydroxylamine hydrochloride, and ascorbic acid, were reagent-grade materials from either J. T. Baker or Eastman Kodak. The equipment was standard laboratory glassware, such as 600-ml, medium-glass-filter frits and beakers. One-half-inch lead shielding wrapped with plastic tape reduced exposure to the high gamma radiation produced by the ²³³Pa daughter product from ²³⁷Np decay. The neptunium was more than 99% of the 237 isotope.

III. PROCEDURE FOR NpO₂

Because the aqueous chemistries of neptunium and plutonium are similar in many respects, we decided to use proven plutonium purification techniques to purify the NpO₂.

The particular flow sheet followed in the purification process was chosen because of the variety of contaminants in the starting oxide. The peroxide precipitation removed the cations, such as iron, that would not be removed in the chloride ion-exchange step. The chloride was used primarily to separate neptunium and plutonium. The plutonium was reduced to the nonextractable (III) state and the neptunium to the (IV) state. For the metal, plutonium was not present, so only an oxalate precipitation was used to convert the metal to a reasonably pure oxide.

A. Dissolution with Nitric Acid

Because the starting NpO₂ material was "foundry oxide" and had been derived from burning neptunium metal, we assumed that the oxide would be refractory and difficult to dissolve. Therefore, the following procedure was used: total acid volume was calculated by adding 5 ml of 15.6 M HNO₃ per gram of NpO₂. After calculating the acid volume, we determined the amount of 28 M HF to bring the total free fluoride content to 0.05 M. The HF was added in two equal-volume increments: one at the beginning of the dissolution and the second after 2 h at reflux. After the material had been at reflux for 4 h, the heat was increased to distill the mixture, reduce the volume, and increase the neptunium concentration to between 250 and 300 g/l. After distillation, the mixture was cooled and then filtered through a 600-ml medium-glass-filter frit.

The dissolution proceeded very well; essentially 100% of the material dissolved. This behavior is different from that of PuO_2 in that refractory PuO_2 is much more "ceramic" in nature and much more difficult to dissolve. Neptunium seems to behave more like uranium oxides and the high-fired material is more soluble.

B. Double Peroxide Precipitation

To prepare for the peroxide precipitation, we used the procedure developed by G. A. Burney and E. K. Dukes¹ as a guideline. The neptunium nitrate solution was titrated at 10.4 M after filtration. We adjusted the acid to 5.0 M by diluting with 0.5 M HNO_3 . No sulfate was added for the first precipitation. The solution was cooled to below 21°C and 10 M H_2O_2 was added slowly. The peroxide addition was complete when a 20:1 mole ratio of peroxide to neptunium was achieved. As the precipitation proceeded, the color changed from light green to gray to light purple. The addition rate of peroxide averaged 8 to 10 ml/min. After all the peroxide was added, the cooling water was turned off and the solution was allowed to digest for 30 min.

The material was then filtered through a 600-ml medium-glass-filter frit. The filtrate was light yellow, and the precipitate filtered reasonably well with no solids going through the filter. The precipitate was purple and was washed with four bed-volumes of 0.5 M HNO_3 /5% H_2O_2 . After the precipitate had been dried with vacuum in the frit, the material was dissolved in 12 M HCl . We calculated the volume of HCl required by using enough acid to have an ending acid concentration of 4 to 5 M after complete dissolution of the cake. The peroxide cake was reactive and was dissolved by slowly adding it to the acid. The dissolution proceeded smoothly, requiring no heating or filtration.

At this point, the solution was titrated and brought up to 0.05 M in sulfate with sulfuric acid. In plutonium peroxide precipitations the sulfate improves the filtering characteristics of the cake. The solution was cooled to below 21°C and 10 M H_2O_2 was added at 8 to 10 ml/min until a 20:1 mole ratio was achieved. Again, the solution was allowed to warm and digest for 30 min. The solution was filtered through a 600-ml medium-glass-filter frit. The solution was clear, and the material filtered reasonably well.

C. Chloride Anion Exchange

1. Feed Pretreatment. After the cake from the second peroxide was dissolved, the acid concentration was adjusted to 10 M in HCl . Then, a 1:1 mole ratio of ascorbic acid to neptunium was added to reduce the valences and allowed to digest for 30 min. A large excess was used because prior ion-exchange trials revealed that plutonium was oxidized back to the (IV) state and would follow the neptunium and not be separated.

2. Resin Pretreatment. Reillex HPQ, macroporous, strong-base anion resin—a polyvinylpyridine-based material—was selected for the neptunium ion-exchange step. The resin was obtained in the chloride form and was washed with two bed-volumes of 10 M HCl and 0.1 M hydroquinone in preparation for the ion-exchange step.

3. Batch Anion Exchange. We minimized waste volumes by using a batch equilibration step instead of a flow column. We calculated the quantity of resin needed by estimating the amount of resin required for a similar amount of plutonium and doubling that amount. The resin was gently mixed with the neptunium feed in a 4-l beaker for 30 min. Occasionally, the stirring was stopped, and the resin was allowed to settle. We visually checked the color of the solution to verify the completeness of the reaction. The resin was separated by filtration and then washed in the medium-glass-filter frit with 1.5 bed-volumes of 10 M HCl and 0.1 M ascorbic acid. The neptunium was then eluted with 1.5 bed-volumes of 0.5 M HCl .

D. Np(IV) Oxalate Precipitation

The HCl concentration of the eluate was adjusted to 3 to 4 M. A 1:1 mole ratio of hydroxylamine hydrochloride to neptunium was added to hold the neptunium in the (IV) state. The mixture was allowed to digest for 15 min and then slowly heated to between 50°C and 60°C. We then added 1 M oxalic acid at 7 to 10 ml/min until 0.1 M excess oxalic acid was present. The lime-green precipitate was filtered through a 600-ml medium-glass-filter frit. The material filtered well with a clear, light-green filtrate.

E. Calcination

The oxalate cake was dried overnight with vacuum on the frit. It was then calcined in a muffle furnace at 200°C for 2 h, 400°C for 2 h, 600°C for 2 h, and 950°C for 2 h. The final oxide product was a fine, dark-green powder.

IV. PROCEDURE FOR NP METAL

A. Metal Dissolution with HCl

The impure metal, slightly encrusted with NaCl and KCl salts from the electrorefining process, was placed in a 4-l beaker. We added 12 M HCl very slowly because the metal dissolves rapidly in HCl and because the reaction is very exothermic and evolves hydrogen. The acid volume was calculated to dissolve all of the metal and end with an acid concentration of 3 to 4 M. After adding the acid, we stirred the reaction mixture for 30 min and then filtered it through a 600-ml medium-glass-filter frit.

B. Precipitation

The solution was precipitated and calcined according to the procedure outlined above in sections III D and E.

V. RESULTS AND DISCUSSION

The analytical results for the different product oxides appear in Table II.

Both methods were reasonably successful and provided a pure NpO_2 standard. In the first method, essentially 100% of the oxide and peroxide dissolved in every case. This uniformity helped make accurate calculations of acid and neptunium concentrations for reagent make-up. The peroxide precipitations removed all trace metals except plutonium. The peroxide filtrate averaged about 400 mg of neptunium per liter. Lowering the initial acidity would decrease the solubility¹; however, doing so would have increased the volume and been more difficult to handle. In all cases, the peroxide cake was more gelatinous than was the oxalate, and the peroxide process was more sensitive to process parameters than was the oxalate.

The ion-exchange resin showed a large decrease in capacity for neptunium as compared with plutonium. Effluents averaged 6 g of neptunium per liter, a value that is much too high. Spectrophotometric data showed that essentially all of the neptunium in the effluent was in the (IV) state, and acid titrations confirmed the proper acid concentration. Therefore, we can offer no explanation for this behavior. However, the ion-exchange step did provide a complete separation of the plutonium and neptunium.

Oxalate precipitation steps in both methods were very insensitive to process conditions. Even the addition of solid oxalic acid caused a nice, crystalline precipitate to form. In all cases, filtration was rapid and the filtrate averaged 190 mg of neptunium per liter.

The oxalate cake decomposed easily and provided a dark-green, fine powder. A small sample of the NpO_2 calcined at 950°C was allowed to stand in the glovebox environment over a period of a month and was weighed every three days. It showed no appreciable weight gain over that time. Therefore, the high-fired NpO_2 was reasonably inert and did not appear to absorb gases on the surface.

Table II. Analytical Results for Product Oxides

Trace Metals	Method 1 (ppm)	Method 2 (ppm)
Aluminum	30	55
Beryllium	10	<1
Calcium	<3	1200
Chromium	10	—
Copper	<1	<1
Iron	35	<5
Magnesium	<1	<1
Manganese	<1	<1
Sodium	50	10
Nickel	15	7
Lead	<5	<5
Silicon	80	5
Tin	<5	<5
Tantalum	<1	500
Plutonium	90	20
Americium	0.1	10

VI. SUMMARY

Two methods for purifying NpO_2 have been developed: the first method is used for NpO_2 that has plutonium as an impurity, and the second method is used for oxide that has only nonplutonium metals as impurities. Both methods produced high-quality oxide for standards and can be applied on a 50- to 500-g scale. Personnel exposures should be minimized by careful shielding and using proper procedures. Even with shielding, exposures to the hands and arms can be high because of the handling requirements.

ACKNOWLEDGMENT

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REFERENCES

1. G. A. Burney and E. K. Dukes, "Precipitation of Neptunium Oxalate," DP-594, E. I. DuPont de Nemours & Co., Savannah River Laboratory, July 1961.

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