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by

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ABSTRACT

Uranium and neptunium in plutonium are determined using an anion exchange x-ray fluorescence method. After a 500-mg plutonium sample is dissolved with 10M HCl and ascorbic acid is added, the solution is passed through an anion-exchange column. At least 99.8% of the plutonium passes through the column. The uranium, neptunium, and remaining plutonium, both tetravalent and trivalent, are eluted from the column and evaporated. The small amount of tetravalent plutonium in the eluate solution is reduced to the trivalent state by adding ascorbic acid in 10M HCl to the solution. The resulting solution is pipetted onto a filter paper impregnated with anion-exchange resin. The plutonium, now all in the trivalent state, is washed from the resin paper with 10M HCl, leaving the uranium and neptunium essentially plutonium-free. The Lα1 x-ray lines for the two elements are read and compared with standards prepared in the same way. The recovery of uranium and neptunium is 98% and 91%, respectively. The average relative standard deviation for uranium is 4.6% and for neptunium, 4.1%.

INTRODUCTION

Analytical methods exist that can be used to determine uranium[1-3] or neptunium[4] in high-purity plutonium metal. However, these methods cannot be used to determine both elements simultaneously. An x-ray fluorescence method,[5] which can be used to determine both uranium and neptunium simultaneously, has recoveries of only 35% for both elements. The low recoveries result from efforts to reduce the plutonium concentration to noninterfering levels. In the anion-exchange x-ray fluorescence method described here, we have essentially eliminated plutonium interference, yet maintained high recoveries for both uranium and neptunium.

APPARATUS

Columns, ion-exchange, 19- by 200-mm.
Flask, filtering, micro, with tubulation, 125-mℓ.
Funnel, Hirsch, size 000A.
Heat lamps, infrared, borosilicate glass, red end, 250-W.
Hot plate, Corning or equivalent.
Laboratory glassware, beakers, pipets, volumetric flasks, etc.
Micropipet, with syringe, 200-μℓ.
Mylar film, 6-μm-thick.
Sample cells, x-ray, Chemplex or equivalent, 32-mm-diam.
Slides, glass, moated.

Spatula, porcelain, spoon at one end.

X-ray spectrograph, vacuum, Philips Electronics, Inc., LiF crystal, tungsten-target x-ray tube, scintillation detector with associated electronic counting circuitry, or equivalent spectrograph.

REAGENTS

Acid, ascorbic, Eastman Organic Chemicals, L-ascorbic acid or equivalent.

Acid, hydrochloric, 12M, 10M, and 0.1M.

Ion-exchange papers, Reeve-Angel anion-exchange resin-loaded papers, designated SB-2 or equivalent.

Ion-exchange resin, analytical grade anion-exchange resin, designated by Bio-Rad Laboratories as AG1X4, 50- to 100-mesh chloride or equivalent.

X-RAY OPERATING CONDITIONS

X-ray tube, tungsten-target.
Potential, 50-kV.
Current, 35-mA.
Counter, scintillation.
Analyzing crystal, LiF.
Counting time, 60 s.

SAMPLE ANALYSIS PROCEDURE

Place an accurately weighed plutonium sample (500-mg) in a 20-mℓ beaker, cover with a watch glass, and add 5 mℓ of 10M HCl. After plutonium is dissolved, add approximately 10 mℓ of 10M HCl to 20-mℓ beaker, rinsing the watch glass in the process. To ensure that as much of the plutonium as possible is in the trivalent state, add 150 mg of ascorbic acid and stir to dissolve.

Condition the ion-exchange column with approximately 30 mℓ of 10M HCl. Transfer the 10M HCl solution of plutonium to the ion-exchange column using an additional 25 mℓ of 10M HCl to rinse the beaker and wash the trivalent plutonium through the column.

Elute the uranium, neptunium, and small amount of remaining plutonium through the column with 20 mℓ of 0.1M HCl. Evaporate the eluate solution to approximately 2 mℓ and transfer to a 5-mℓ beaker using 0.1M HCl. Evaporate this solution to incipient dryness, add 200 μl of 10M HCl containing 10 mg ascorbic acid per milliliter of HCl, and swirl the beaker to dissolve the residue. Pipet the solution onto a 25-mm-diam anion-exchange resin-loaded paper that is supported by a moated glass slide. Rinse the 5-mℓ beaker twice with 100 μℓ of 10M HCl. Place the moist resin paper onto a Hirsch funnel which is under a slight vacuum. Gently and slowly drip 2.0 mℓ of 10M HCl onto the resin paper to wash the blue trivalent plutonium from the resin paper into the filtering flask.

Allow the resin paper to air dry slowly. Place a 50-mm square of Mylar film over a 32-mm x-ray sample cell, place the dried resin paper on the Mylar film, then position a second 50-mm square of Mylar film over the resin paper. Attach the x-ray cell rings to hold the resin paper firmly in position. Place the cell in a cell holder and put into the x-ray spectrograph. Excite the sample using the tungsten target x-ray tube. Measure for 60 s each the intensity for a background, the neptunium Lα1, the uranium Lα1, and a second background. The 2θ settings are as follows.

2θ	Measurement
24.00	Background
25.50	Neptunium Lα1
26.14	Uranium Lα1
27.14	Background

WORKING STANDARDS

High-purity plutonium is treated as described in the Sample Analysis Procedure section to remove any uranium or neptunium that may be present. Approximately 0.5 g of trivalent plutonium in 10M HCl is added to each of six 20-mℓ beakers containing uranium and neptunium in the following amounts.

Beaker No.	Uranium (μg)	Neptunium (μg)	Plutonium (mg)
1	0	100	500
2	0	100	500
3	50	50	500
4	50	50	500
5	100	0	500
6	100	0	500

These standards, containing known amounts of uranium and neptunium, are then analyzed, as described in the Sample Analysis Procedure section.

CALCULATIONS

The intensities for the two backgrounds, neptunium, and uranium are converted to counts per second (c/s). The c/s from the two backgrounds are averaged, and this average is subtracted from both the uranium c/s and the neptunium c/s. Next a correction of 0.0115 c/s is made to the neptunium x-ray intensity for each c/s of uranium intensity. A correction of 0.0289 c/s is made to the uranium x-ray intensity for each c/s of neptunium intensity. A least squares fit is made relating corrected c/s vs concentration for both neptunium and uranium. The coefficients for the equation that represents the calibration curve for the neptunium standards are used to calculate the concentration of neptunium in the analyzed samples. Similarly, the coefficients for the equation that represents the calibration curve for the uranium standards are used to calculate the concentration of uranium in the analyzed samples.

EXPERIMENTS

The chemistry of uranium, neptunium, and plutonium is similar; there are only minor differences that may be exploited to achieve total separation of uranium and neptunium from much larger amounts of plutonium. We know that anion-exchange resins sorb tetravalent plutonium. Also, we have found that significant amounts of trivalent plutonium will sorb from strong HCl solutions.

We found that approximately 1000 μg of plutonium from a 500-mg plutonium sample, which was reduced with ascorbic acid, was sorbed by AG1X4 anion exchange resin. Most of this 1000 μg of plutonium was trivalent plutonium. Tests indicated that all but 30 to 50 μg of the plutonium was removed by washing the resin paper with 2.0 mℓ of 10M HCl. When this is done, the intense blue color of the trivalent plutonium disappears from the resin paper. When ascorbic acid is added to the eluate solution before pipetting onto the resin paper, the plutonium concentration on the paper is further reduced to 10 μg or less.

The presence of 1000 μg of plutonium would prevent the determination of neptunium and would interfere with the determination of uranium. The presence of 100 μg of plutonium, although acceptable, would increase the detection limit of neptunium. Therefore, we have tried to reduce the plutonium concentration on the resin paper to less than 10 μg without lowering the recovery of uranium and neptunium. This is done by using ascorbic acid to reduce the tetravalent plutonium in the anion-exchange column eluate solution. Then we did a second separation of uranium and neptunium from plutonium using SB-2 resin paper. The 10M HCl environment enables the uranium and neptunium to be sorbed by the resin, whereas the trivalent plutonium is merely deposited on the paper by evaporation. When the 100 μℓ of 10M HCl washings are added to the resin paper, the trivalent plutonium is washed to the outer edges of the paper, which indicates that it is not sorbed by the resin paper. Transfer of the resin paper to the Hirsch funnel, which is under slight vacuum, permits the trivalent plutonium on the paper to be washed off the disk and into the Hirsch flask with 10M HCl while the uranium and neptunium remain firmly sorbed by the resin paper.

DISCUSSION

The method described in this report is for relatively pure plutonium metal. Samples of PuO_2 that require dissolution in a sealed-reflux system[6] using 12M HCl, 15M HNO_3, and 1.3M HF also may be analyzed by this method. The presence of HNO_3 may result in a less complete, but acceptable, separation of uranium and neptunium from plutonium. If a significant amount of plutonium is

TABLE I

PRECISION FOR THE DETERMINATION OF NEPTUNIUM AND URANIUM IN A 500-mg PLUTONIUM SAMPLE

Sample Type	Neptunium (μg)	Relative Standard Deviation (%)	Uranium (μg)	Relative Standard Deviation (%)
Natural	20	3.5	40	4.9
Natural	15	3.0	125	6.8
Spiked	10	4.9	10	2.9
Spiked	50	5.6	45	5.1
Spiked	100	3.5	100	3.3

present (>10 μg), a correction factor of 0.034 c/s must be applied to neptunium for each c/s of plutonium. This method also may be used to determine uranium and neptunium in $^{238}PuO_2$.

RELIABILITY

We established the reliability of this method by repeated analysis of both "spiked" and "natural" plutonium samples. Spiked samples contain known amounts of uranium and neptunium, whereas natural samples contain no added amounts of uranium or neptunium. The relative standard deviation for 10 to 100 μg of neptunium is 4.1%; that for 10 to 125 μg of uranium is 4.6% (Table I).

ACCURACY

In the absence of standard reference materials, the bias of this method could not be unquestionably determined. By using chemical working standards similar to the samples to calibrate the method, one should effectively eliminate any bias.

INTERFERENCES

The two possible sources of interference are (1) the presence of significant amounts of elements that have high distribution coefficients between 10M HCl and the anion-exchange resin, and (2) the presence of elements that have x-ray lines overlapping the measured x-ray lines. Elements that would be of the first type of interference are iron, gallium, zirconium, and molybdenum. Large amounts of these elements would cause interference by competing with uranium and neptunium for available resin sites. Elements having x rays that overlap the $L\alpha 1$ x rays for uranium and neptunium are rubidium, gold, thallium, and thorium. We found that there is no interference caused by up to 1000 μg of iron, gallium, zirconium, rubidium, gold, thallium, or thorium, nor by 100 μg of molybdenum on the determination of uranium and neptunium.

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