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Separation of Trace Uranium from Plutonium for Subsequent Analysis

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ABSTRACT

Trace uranium quantities are separated from plutonium metal and plutonium oxide for subsequent analysis. Samples are dissolved in hydrobromic acid or a hydrobromic acid-hydrofluoric acid mixture. The U(VI)-halide complex is separated from nonsorbed Pu(III) on an anion exchange column using sequential washes of 9M HBr, a 0.1M HI-12M HCl mixture, and 0.1M HCl.

I. INTRODUCTION

Uranium is an ever-present element in plutonium materials as daughters from alpha decay of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{242}Pu. Uranium also can be present, mainly as ^{238}U, from incompletely separated, reactor-irradiated material that produced the plutonium. In recently prepared plutonium materials that have a low abundance of the ^{238}Pu isotope, the uranium content often is below 100 ppm. Most chemical methods for determining microgram amounts of uranium are subject to interference by plutonium at a ratio of 10^4 and greater. Thus, a quantitative preseparation of uranium is required that has a high separation factor for plutonium. Such a separation also provides a uranium fraction for analysis by isotope-dilution mass spectrometry, a technique used in our laboratory.

The developed procedure gives 97.5% recovery of uranium and a separation factor of $> 10^6$ for plutonium. It involves dissolution of plutonium metal in 9M HBr or plutonium oxide in a 0.05M HF-9M HBr mixture, addition of a small quantity of bromine to ensure that uranium is hexavalent, anion exchange of the U(VI)-bromide complex but not the Pu(III), final elution of plutonium with a 0.1M HI-12M HCl mixture, and elution of uranium with 0.1M HCl.

II. EXPERIMENTAL AND DISCUSSION

A. Dissolution of Samples

When separating a trace component by ion exchange, it is advantageous to sorb it rather than the matrix components. This permits use of a small column and small reagent volumes to elute the matrix components before the trace component.

As the dissolvent, hydrobromic acid for plutonium metal or hydrobromic acid plus hydrofluoric acid for plutonium oxide converts the plutonium almost completely to Pu(III). The dissolution is rapid and complete for plutonium metal at ambient temperature and is complete within 8 h for plutonium oxide at sub-boiling temperature.

B. Ion Exchange

Uranium sorbs strongly, whereas plutonium, which is reduced to Pu(III) by hydrobromic acid, sorbs negligibly on anion exchange resin from hydrobromic acid concentrations above 6M.[1] Because the elution rate of plutonium from anion exchange resin is slow in hydrobromic acid media,[2] it is eluted quantitatively with a 0.1M HI-12M HCl mixture.[3] Uranium then is eluted with 0.1M HCl. The selected ion exchange resin is macroporous Dow MSA-1, 50 to 100 mesh, chloride form, which was obtained from the Dow Chemical Company. This resin also is available in small quantities as AGMP-1 from Bio-Rad Laboratories. The greater surface area of macroporous resin provides rapid equilibrium.

When we use the recommended procedure for 100-mg PuO_2 samples, the recovery of 25 ppm of uranium is 97.5 ± 1.5%, accompanied by $< 0.0001\%$ of the initial plutonium. This corresponds to a separation factor of $> 10^6$ for plutonium. These recovery and separation factors were computed from isotope-dilution mass spectrometric analyses of uranium and plutonium added to and recovered from ion exchange columns.

III. RECOMMENDED PROCEDURE

A. Reagents

The acids, 9M HBr, 7.4M HI, and 6M HCl, are purified of trace uranium by distillation in a quartz apparatus. The HCl is reconcentrated to 12M by bubbling HCl gas into it using quartz or polyethylene components with the receiver cooled in an ice bath. A nitrogen sparge during distillation of HI and its storage in sealed ampoules prevents air oxidation. Reagents are stored in quartz containers to minimize natural uranium contamination.

1. **Dissolvent, 0.05M HF-9M HBr.** Dilute 0.17 ml of 27M HF to 100 ml with distilled 9M HBr.
2. **Eluting solution, 0.1M HI-12M HCl.** Dilute 1 ml of 7.4 M HI to 74 ml with the specially prepared 12M HCl. Prepare this mixture immediately before use.
3. **Eluting Solution, 0.1M HCl.** Dilute 1 ml of the specially prepared 12M HCl to 120 ml with distilled or deionized water.
4. **Bromine,** Analytical Reagent grade.

B. Ion Exchange Column

Prepare columns from disposable, 6-mm-i.d., 60-mm-long, polyethylene droppers with 2-ml reservoirs. (Suitable droppers can be obtained from the Nalge Co., Rochester, New York, article No. 6219.) Cut off the top of the dropper to form an open reservoir and insert a small wad of quartz wool in the tip. Transfer a water slurry of Dow MSA-1, 50 to 100 mesh, chloride-form resin into the column until the settled height is just below the reservoir. Immediately before use, pass 8 ml of 0.1M HCl and then 6 ml of the specially prepared 12M HCl through the column.

C. Sample Processing

1. Transfer a weighed protion of plutonium metal or plutonium oxide to a Teflon beaker. (The sample size is dependent on the uranium content and the analytical method to be used. The ion exchange column handles 100-mg plutonium portions.)
2. Dissolve the plutonium metal in 9M HBr without heat or the plutonium oxide in 0.05M HF-9M HBr with heat, using 20 ml of acid per gram of either type sample; cover the beaker to prevent loss.
3. Add an amount of bromine equal to 1 mol% of the plutonium to oxidize the uranium completely to U(VI).
4. Transfer a portion containing 100 mg or less of plutonium to a freshly prepared ion exchange column having a receptacle beneath it.
5. Rinse the Teflon beaker with two 0.5-ml volumes of 9M HBr and transfer each quantitatively to the column.
6. Pass 5 ml of 0.1M HI-12M HCl through the column to reduce any higher oxidation states of plutonium to Pu(III).
7. Wait 10 min and pass another 10 ml of 0.1M HI-12M HCl through the column to complete the reduction and elution of plutonium.
8. Place a new receptacle free of uranium contamination under the column for collection of the uranium fraction.
9. Pass 5 ml of 0.1M HCl through the column to elute the uranium.

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