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SEPARATION AND DETERMINATION OF PLUTONIUM IN PLUTONIUM-URANIUM FUEL ELEMENTS

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ABSTRACT

Plutonium is separated from uranium in plutonium-uranium oxide and plutonium-uranium carbide reactor fuel element samples by cation exchange. Initially the refractory oxides or carbides are dissolved by refluxing in concentrated nitric acid-6N hydrofluoric acid solution. After separation, plutonium is determined by potentiometric titration at constant current with potassium dichromate; uranium may be determined similarly. At least 99.9% recovery of both plutonium and uranium was obtained on synthetic samples.

SEPARATION AND DETERMINATION OF PLUTONIUM IN PLUTONIUM-URANIUM FUEL ELEMENTS

C. E. Pietri

Reactor fuel elements with plutonium-uranium oxide or carbide cores have been considered advantageous for power reactors.[1, 2] The carbide elements are produced by reacting mixtures of plutonium dioxide, uranium dioxide, and carbon. The exact chemical composition of the oxide base material and the final carbide product is necessary as a check of the manufacturing process. The method under study provides for a separation of plutonium from uranium (and excess carbon) by cation exchange prior to the determination of plutonium by constant current potentiometry.

By adapting an existing plutonium concentration process,[3] a cation-exchange separation from uranium on an analytical scale has been achieved. After separation, the plutonium is determined by titration with potassium dichromate[4] while the uranium content may be assayed similarly.[5]

REAGENTS AND APPARATUS

Sulfuric Acid, concentrated, reagent-grade.

Sulfuric Acid, 1N, reagent-grade.

Sulfuric Acid, 4N, reagent-grade.

Nitric Acid, concentrated, reagent-grade.

Nitric Acid, 4N, reagent-grade.

Nitric Acid, 8M, reagent-grade.

Hydrofluoric Acid, concentrated, reagent-grade.

Nitric Acid (0.3M)-Hydroxylamine Sulfate (0.05M) Solution. Add 20 ml. of concentrated nitric acid to a 1000-ml. volumetric flask, dilute with distilled water to about 950 ml., shake, and allow to cool. Add 4.1 g. of hydroxylamine sulfate ($NH_2OH.1/2H_2SO_4$) to the solution, dilute to 1000 ml. with water and shake.

Sulfuric Acid (0.3M)-Hydroxylamine Sulfate (0.05M) Solution. Prepare similarly to the above nitric acid-hydroxylamine sulfate solution using 16.6 ml. of concentrated sulfuric acid.

Nitric Acid (6M)-Sulfamic Acid (0.05M) Solution. Prepare similarly to the above nitric acid-hydroxylamine sulfate solution using 380 ml. of nitric acid and 4.9 g. of sulfamic acid, ($NH_2SO_3H_2$).

Ion-Exchange Resin. Wash 100 g. of wet AG-50W cation resin (a highly purified analytical grade of Dowex-50, X-10, 200-400 mesh, hydrogen-form, obtained from Bio-Rad Laboratories, Richmond, California) free of "fines" with water and store in a plastic bottle.

Ion-Exchange Column. The design and operation of this column is described in another report.[6] Use the Dowex-50 cation resin to load the column (1-cm. diameter) to a height of 8 cm. and wash the prepared resin bed with 15 ml. of 0.3M HNO_3-0.05M $NH_2OH.1/2H_2SO_4$ solution prior to use.

Weight Buret, 30-ml. capacity.

Titration Apparatus. Connect a small 45-volt "B" battery and a 20-megohm resistor (1/4-watt) in series to two bright gold electrodes spaced 1 cm. apart in a 150-ml. beaker. Connect another lead from each of the gold electrodes to a vacuum tube voltmeter (such as Leeds and Northrup Model 7664 pH Indicator). Agitation of the solution in the titration beaker is produced by a Teflon-covered magnetic stirring bar and a variable speed magnetic stirrer.

Jones Reductor. Fill a Jones reductor tube with a column (2.5-cm. diameter and 12-cm. long) of granulated zinc amalgam. Wash with two 10-ml portions of 4N sulfuric acid prior to use.

Potassium Dichromate Solution, 0.7 mg. $K_2Cr_2O_7$/g. Solution. Dry National Bureau of Standards primary standard potassium dichromate, sample No. 136a, for 2 hours at 110°C and cool in a desiccator. Weigh a 1000-ml. volumetric flask to the nearest 10 mg. Weigh 0.7 g. of the dried potassium dichromate to ± 0.05 mg., add to the flask, dissolve in 4N sulfuric acid, and dilute to 1 liter with the acid. Cool and reweigh the flask and contents. Calculate the concentration of potassium dichromate as milligrams of potassium dichromate per gram of solution.

PROCEDURE

Sample Preparation. Weigh an oxide or carbide sample containing about 100 mg. plutonium into a platinium dish and dissolve by heating in a minimum amount of 10M HNO_3. (Pyrophoric carbides require somewhat different initial treatment which is not described here.) Samples which do not dissolve readily are treated as follows: Evaporate the mixture to dryness, add 30-ml. of concentrated nitric acid and 7-ml. of concentrated hydrofluoric acid for every 0.5 g. of sample, cover with a tight-fitting cover, and heat overnight at 80-90°C. The fluoride of plutonium and uranium may precipitate during this period. For the more refractory samples, it may be necessary to repeat this treatment. After the sample has dissolved, evaporate the solution to incipient dryness; dissolve any precipitatedfluorides with 8M nitric acid. Evaporate again, add 10-ml. of concentrated nitric acid, and evaporate to a moist residue to remove fluoride. Dissolve the residue in 20 ml. of 0.3M nitric acid-0.05M hydroxylamine sulfate solution.

Ion-Exchange Separation. Warm the covered solution under heat lamps for 20-30 minutes, cool, and add to the prepared ion-exchange column. Regulate the flow rate to about 0.3 ml./min. Wash the column with 10 ml. of 0.3M nitric acid-0.05M hydroxylamine sulfate solution. Elute the uranium quantitatively from the column overnight with 150 ml. of 0.3M sulfuric acid-0.05M hydroxylamine sulfate solution at a rate of 0.3-0.5 ml./min. Collect the effluent for uranium analysis, if so desired. Elute the plutonium at the same rate with 75 ml. of 6M nitric acid-0.05M sulfamic acid, collecting all the effluent in a 150-ml. beaker. Add 1 ml. concentrated sulfuric acid to the solution, evaporate to dryness and repeat the fuming with 0.5 ml. of concentrated sulfuric acid. Cool the residue and dissolve in a minimum amount of 1N sulfuric acid.

Plutonium Analysis. While the residue is dissolving, pour 30 ml. of the standard potassium dichromate solution into a clean, dry weight buret and weigh to ± 1 mg.

Pour the dissolved plutonium sample into the Jones reductor. Collect the reduced plutonium(III) solution from the reductor in a 150-ml. beaker containing a Teflon-coated magnetic stirring bar. Adjust the flow rate to about 15 ml./min. When the liquid level of the sample reaches 5 mm. above the amalgam bed, rinse the original beaker, in which the sample was dissolved, twice, with 4N sulfuric acid, adding the washings to the reductor. Wash the reductor three times with 10-ml. portions of 4N sulfuric acid and finally with 10 ml. of water.

Set up the titration apparatus with the electrodes inserted in the plutonium solution. Rapidly add the titrant from the weight buret until the blue color of the sample solution changes to pale orange. Turn on the magnetic stirrer so that it gently agitates the solution. Adjust the pH meter to zero on the +700 scale. Quickly add the titrant in 5-drop portions until the potential of the system reverses itself. Continue the titration until a meter change of 10 mv. is noted. At this point add the titrant in 2-drop portions until the first increment of greater than 10 mv. in noted. Weigh the buret and continue the titration while recording the change in potential for each weighed increment of titrant added. The titration should be continued until the addition of one drop of titrant results in a meter deflection of 10 mv. or less. The end point (E.P.) is indicated by the maximum value derived from the ratio of the potential increase (ΔE) obtained to each weight increment of titrant added (ΔW) or:

$$\text{E.P.} = \frac{\Delta E}{\Delta W} = \text{maximum value}$$

EXPERIMENTAL

Sample Dissolution. The high-fired oxides and carbides are difficult to dissolve. Fusion with sodium bisulfate or ammonium bifluoride usually accomplishes the job but introduces excess solids. Dissolution with concentrated nitric acid containing a small amount of hydrofluoric acid (0.05-0.005M) has been successful at times. When this latter technique was tried, incomplete solution of plutonium-uranium oxides was experienced even after long heating times (>72 hours). Plutonium-uranium carbides (which had been pressed into pellets and were thereby rendered non-pyrophoric) initially reacted in this acid mixture but apparently insoluble compounds (other than free carbon) also formed.

When a mixture of 15.7N nitric acid and 6N hydrofluoric acid was used under semi-reflux conditions at 80°C, relatively rapid and quantitative dissolution of both carbide and oxide samples was obtained.

Ion-Exchange Studies. Although the cation exchange separation of plutonium and uranium is used in plant-scale processing operations, little information on the analytical applications of this method has been reported. In present tests, synthetic solutions containing approximately 15% plutonium and 85% uranium were used to determine the recovery for these elements using the outlined procedure. Radiometric analysis of the effluent from the sample adsorption stage indicated <0.001% total alpha activity. Elution of the uranium from the column and determination as U_3O_8 gave 100.0% recovery. Again, radiometric analysis of an additional 150 ml. wash solution following this elution showed <0.001% activity. Subsequent titration of the eluted plutonium indicated 99.9% recovery while an additional 75-ml. wash disclosed <0.001% activity. Other experiments indicated that a small amount of plutonium (<0.1%) is tenaciously held on the resin in spite of repeated washings.

"Gassing" in the resin bed during the elution of plutonium with 6N nitric acid has been a problem on plant-scale levels even with sulfamic acid present to retard the nitric acid-hydroxylamine reactions. In only one sample during the present work was severe "gassing" a problem and its suspected cause could be traced to improper preparation of reagents.

Plutonium Analysis. The constant current potentiometric titration of plutonium based on National Bureau of Standards potassium dichromate was modified for routine sample analysis by reducing the analysis time with a slight loss in precision. The uncertainty in the final plutonium value contributed by this modification was considered to be no more significant than the possible plutonium bias sustained in the ion-exchange separation.

RESULTS

The results of analyses for several samples from three different types of materials, plutonium-uranium oxides, plutonium-uranium carbides, and pure plutonium sesquicarbide are shown in Table 1. The precision obtained for the latter compound (not requiring prior separation from uranium) was better than that for the oxide or carbide mixtures. The relatively poorer precision obtained for the (PuU)C mixtures was attributed to difficulty in handling these samples, some of which were pyrophoric in nature.

TABLE 1

DETERMINATION OF PLUTONIUM IN OXIDE AND CARBIDE SAMPLES

	Plutonium Content, %			
	Theoretical	Experimental	Standard Deviation	Relative Standard Deviation, %
PuO_2-UO_2-C	15.6	15.5	0.04	0.3[a]
(PuU)C	19.3	19.3	0.20	1.0[b]
Pu_2C_3	93.0	92.9	0.09	0.1[c]

a. Based on six determinations.
b. Based on three determinations.
c. Based on eight determinations.

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