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October 9, 1972

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PREPARATION OF HIGH PURITY AMERICIUM OXIDE

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U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

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Printed in the United States of America

Available from the

National Technical Information Service

U. S. Department of Commerce

Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.95

Printed
October 9, 1972

RFP-1857
UC-4 CHEMISTRY
TID-4500 (56th Ed.)

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Prepared under Contract AT(29-1)-1106
for the
Albuquerque Operations Office
U. S. Atomic Energy Commission

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PREPARATION OF HIGH PURITY AMERICIUM OXIDE

Stephen G. Proctor

Abstract. Americium oxide has been purified using a fluoride precipitation of the rare earth impurities from a solution of hexavalent americium. Additional purification was obtained by successive oxalate precipitations of the americium. The total impurity content of the purified AmO_2 averaged 600 ppm, none of which was contributed by the rare earth elements.

INTRODUCTION

Americium-241 has been considered a troublesome impurity in plutonium process streams. In recent years, however, there has been an increasing interest in americium-241 as a product in itself. Americium-241 is introduced into the plutonium as a result of the radiolytic decay of plutonium-241 which is present in minor quantities.

Plutonium-241 has a 13 year half-life and decays by beta emission to americium-241. The americium-241 derived from this source is therefore isotopically pure which enhances its value. For many years, americium-241 has been recovered from the Rocky Flats plutonium stream and has been shipped to the Research Isotope Pool at the Oak Ridge National Laboratory (ORNL).

The routine production grade AmO_2 recovered by Rocky Flats will ordinarily contain from 0.5- to 5.0- wt% impurities. These impurities will generally consist of lead, calcium, and the rare earth elements which constitute the major proportion of the impurity content. With the new interest in high purity AmO_2 , a purification procedure was developed to upgrade the production grade AmO_2 to a 99.9% level.

Many methods for purifying AmO_2 have been reported. Weaver and Kappelmann used the Talspeak¹ method of solvent extraction which used the highly preferential complexing of the americium by an aminopolyacetic acid. Many similar methods using the complexing of americium by organophosphorous chelating agents have been reported. By using an ion exchange technique, Ryan and Pringle² were able to purify americium by making use of the americium thiocyanate complex which will load onto anion exchange resin. This procedure is currently used by Rocky Flats for the recovery and purification of americium.

Since the majority (75%) of the impurities in the production grade AmO_2 are rare earth elements, a method had to be used which would selectively separate the rare earths from

americium. The similarities in the chemistries of the rare earths and americium make an effective separation difficult and most purification procedures do not yield a quantitative separation. Therefore, a new method of purification was developed. This method consisted of a fluoride precipitation of the rare earths from a solution of hexavalent americium, which does not form an insoluble fluoride.

The americium is initially oxidized from Am(III) to Am(VI) using ammonium persulfate and argentic oxide. Following oxidation, the rare earths are precipitated by introducing fluoride ion and the insoluble rare earth fluorides are removed from solution by filtration. The oxalate precipitation of the americium with oxalic acid will separate americium from most of the common elemental impurities which form soluble oxalate complexes.

EXPERIMENTAL

The AmO_2 was divided into batches of approximately 20 grams, and each batch was treated identically for rare earth separation. The work was performed in one liter Pyrex beakers using a Thermolyne stirring hot plate. The calcination of the material was accomplished using a Thermolyne-type 1300 furnace.

Each batch was dissolved initially in 250 ml of 8M HNO_3 to give an americium concentration of 0.28M. Following dissolution, the acidity of the solution was adjusted to 0.1M with 8M NH_4OH . The solution was then heated to 80°C and made 0.25M in ammonium persulfate $[(\text{NH}_4)_2 \text{S}_2\text{O}_8]$ and 0.002M in argentic oxide (Ag_2O). The solution temperature was maintained at 80°C for 40 minutes to allow for complete oxidation of the americium to the hexavalent state. The solution volume at this point should be kept at 0.5 liter. The rare earths were then precipitated by making the solution 0.2M in HF. After mixing for approximately 3 minutes, the insoluble fluoride material was removed from solution by filtration and washed with water. The fluoride residue was calcined and set aside for recycling or discard. The americium in the resulting filtrate was reduced to the trivalent state by adding ascorbic acid until the brown color disappeared. The americium was then precipitated as an oxalate by adding a 0.1M stoichiometric excess of oxalic acid and heating the solution to 60°C. After an over-night-digestion period at room temperature, the americium oxalate $[\text{Am}_2(\text{C}_2\text{O}_4)_3]$ was filtered, washed with water, and calcined at 600°C for

6 hours. The resulting AmO_2 was sampled for a rare earth impurity analysis.

Following the rare earth separation, the oxide was divided into ~50-gram batches for lead and silver removal and a final oxalate precipitation. The AmO_2 was dissolved in 500 ml of 6M HNO_3 and made 0.1M in NH_4Cl . The

resulting insoluble silver chloride (AgCl) and lead chloride (PbCl_2) were removed from solution by filtration, washed with water, and discarded. The filtrate was subsequently treated with the previously described oxalate precipitation technique. The $\text{Am}_2(\text{C}_2\text{O}_4)_3$ was again calcined to an oxide which was analyzed for impurities. A process flowsheet is shown in Figure 1.

Figure 1. Process Flowsheet.

RESULTS

The AmO_2 used in the first seven batches contained 5520 ppm of detectable impurities, of which 3300 ppm was contributed by 2500 ppm of lead and 800 ppm of certain rare earths. The remaining ~1700 ppm of impurities were distributed fairly evenly among several common elemental impurities. The rare earth concentrations were erbium (Er) 100 ppm, thulium (Tm) 300 ppm, yttrium (Y) 300 ppm, and ytterbium (Yb) 100 ppm. The AmO_2 used in the eighth and ninth batches contained large amounts of rare earth impurities. The rare earth concentration in these batches totaled 47,000 ppm, of which thulium contributed the bulk of 40,000 ppm. The individual rare earth concentrations in this AmO_2 were thulium (Tm) 40,000 ppm; cerium (Ce) 700 ppm; neodymium (Nd) 3,000 ppm; yttrium (Y) 3,000 ppm; and ytterbium (Yb) 300 ppm. The non-rare earth impurities in this AmO_2 totaled 3,160 ppm with lead and iron composing the bulk of this total. The results of the analysis after the rare earth removal for all nine batches are shown in Table 1.

Table 1. Rare Earth Impurities after Purification (ppm).

Batch No.	Ce	Er	Tm	Y	Yb	Nd
1	<500	<50	<50	<5	<5	<50
2	<500	<50	<50	<5	<5	<50
3	<500	<50	<50	<5	<5	<50
4	<500	<50	<50	<5	<5	<50
5	<500	<50	<50	<5	<5	<50
6	<500	<50	<50	<5	<5	<50
7	<500	<50	<50	<5	<5	<50
8	<500	<50	<50	<5	<5	<50
9	<500	<50	<50	<5	<5	<50

Notes: < - Indicates less than detectable limit of the emission spectrographic analysis.
ppm - μg of impurity/gram of AmO_2 .

The analysis of the final AmO_2 product is shown in Tables 2, 3, and 4. These results show that the detectable impurities for the first batch totaled 500 ppm, and the impurities for the second and third batches totaled 630 ppm and 620 ppm, respectively. These three batches were made up by combining the nine batches into three batches. The impurity analyses were accomplished by optical emission spectroscopy. The calorimetric assay for each of the three batches is shown in Table 5. All three batches compared favorably with the theoretical value of 0.8828 g Am/g AmO_2 .

The average batch recovery as high purity AmO_2 was 90.8%, which was considered quite acceptable compared to Rocky Flats production losses of 10 to 15 percent. Individual batch recoveries ranged from 88 to 93 percent.

Table 2. Sample Analysis (ppm). Batch No. HP-71-1.

Element	Impurity	Element	Impurity	Element	Impurity
Ag	< 5	Hf	< 50	Ru	<500
Al	< 100	Hg	< 50	Sb	< 50
As	< 100	Ho	<500	Sc	< 50
Au	< 50	In	< 50	Si	< 50
B	< 1	Ir	< 50	Sm	<500
Ba	< 5	K	<500	Sn	< 50
Be	< 1	La	< 50	Sr	<100
Bi	< 10	Li	<500	Ta	<100
Ca	300	Lu	< 5	Tb	<500
Cb	< 100	Mg	< 1	Te	< 50
Cd	< 10	Mn	< 1	Th	< 50
Ce	< 500	Mo	< 50	Ti	< 10
Co	< 100	Na	<500	Tl	<100
Cr	< 50	Nd	< 50	Tm	< 50
Cs	<1000	Ni	< 50	U	<100
Cu	< 10	P	<500	V	< 10
Dy	< 50	Pb	<100	W	<100
Er	< 50	Pd	< 50	Y	< 5
Eu	< 50	Pt	< 50	Yb	< 5
Fe	200	Pu	<100	Zr	< 50
Ga	< 50	Rb	<500	Zn	<100
Gd	< 50	Re	<500		
Ge	< 50	Rh	<500		

Notes: < - Below detectable limit of analysis.
ppm - μg of impurity/gram of AmO_2 .
Total detectable impurities - 500 ppm.

Table 3. Sample Analysis (ppm). Batch No. HP-71-2.

Element	Impurity	Element	Impurity	Element	Impurity
Ag	80	Hf	< 50	Rh	<500
Al	< 100	Hg	<100	Ru	<500
As	< 100	Ho	<500	Sb	< 50
Au	< 50	In	< 50	Sc	< 50
B	< 1	Ir	< 50	Si	< 10
Ba	< 5	K	< 30	Sm	<500
Be	< 1	La	<500	Sn	< 5
Bi	< 10	Li	<500	Sr	< 25
Ca	500	Lu	< 5	Ta	<100
Cb	< 50	Mg	< 10	Tb	<500
Cd	< 10	Mn	< 1	Te	< 50
Ce	< 500	Mo	< 50	Th	< 50
Co	< 10	Na	<500	Ti	< 10
Cr	< 10	Nd	< 50	Tl	<100
Cs	<1000	Ni	< 50	Tm	< 50
Cu	< 50	P	<500	U	<100
Dy	< 500	Pb	<100	V	< 10
Er	< 50	Pd	< 50	W	<100
Eu	< 50	Pt	< 50	Y	< 5
Fe	50	Pu	<100	Yb	< 5
Ga	< 500	Rb	<500	Zr	< 50
Ge	< 5	Re	<500	Zn	< 50

Notes: < - Below detectable limit of analysis.
ppm - μg of impurity/gram of AmO_2 .
Total detectable impurities - 630 ppm

Table 4. Sample Analysis (ppm). Batch No. HP-72-1.

Element	Impurity	Element	Impurity	Element	Impurity
Ag	80	Hf	< 50	Rh	<500
Al	< 100	Hg	<100	Ru	<500
As	< 100	Ho	<500	Sb	< 50
Au	< 50	In	< 50	Sc	< 50
B	< 1	Ir	< 50	Si	50
Ba	< 5	K	< 30	Sm	<500
Be	< 1	La	<500	Sn	< 5
Bi	< 10	Li	<500	Sr	< 25
Ca	440	Lu	< 5	Ta	<100
Cb	< 50	Mg	< 10	Tb	<500
Cd	< 10	Mn	< 1	Te	< 50
Ce	< 500	Mo	< 50	Th	< 50
Co	< 10	Na	<500	Ti	< 10
Cr	< 10	Nd	< 50	Tl	<100
Cs	<1000	Ni	< 50	Tm	< 50
Cu	< 50	P	<500	U	<100
Dy	< 500	Pb	<100	V	< 10
Er	< 50	Pd	< 50	W	<100
Eu	< 50	Pt	< 50	Y	< 5
Fe	50	Pu	<100	Yb	< 5
Ga	< 500	Rb	<500	Zr	< 50
Ge	< 5	Re	<500	Zn	< 50

Notes: < - Below detectable limit of analysis.
 ppm - μg of impurity/gram of AmO_2 .
 Total detectable impurities - 620 ppm.

Table 5. Calorimetric Assays of AmO_2 .

Batch No.	Grams of AmO_2	Grams of Am	Grams Am/ Grams AmO_2
HP-71-1	50.1	44.2	0.882
HP-71-2	50.0	44.2	0.884
HP-72-1	50.2	44.3	0.883

DISCUSSION

The procedure used for americium purification is rapid and can be easily carried out with a minimal amount of equipment and space. In contrast, any solvent extraction purification process would have required a considerable amount of extraction equipment (such as extractors and separatory devices). Additionally, any solvent extraction process which utilizes organic solvents should be carried out in an inert atmosphere to minimize the fire hazard associated with organic solvents in a glovebox system. Ion exchange processes, such as used at Rocky Flats, generate large volumes of waste solutions and are better suited for bulk separation and purification of americium. The method which was used is designed for a small scale batch-type operation capable of handling batches of americium as large as 20 grams each. The rare earth separation technique which was used yields a rare-earth-

free product with a single precipitation except in cases where the rare earth concentration is extremely high. In this case, a double precipitation is required. The oxalate purification step often requires more than one precipitation to obtain a pure product. Both the fluoride and oxalate purification steps, however, can be carried out quickly and with a minimal amount of equipment.

Lead and Silver Removal

For the three batches processed, the lead removal step worked well. The original contamination was reduced from 2500 ppm to <100 ppm in each batch. The silver, which was introduced into the process as an oxidizing agent, was also efficiently removed. The silver contamination in the AmO_2 will run as high as 5000 ppm prior to its removal. As the results show, the silver was reduced to 80 ppm in two batches and to <5 ppm in the other batch.

Oxalate Precipitation

The oxalate precipitation step of the procedure reduced the elemental impurity level from 1200 ppm to an average of 575 ppm. The bulk of the remaining impurities was contributed by calcium (300 ppm, 440 ppm, and 500 ppm for the three batches). Calcium contamination in americium is difficult to separate by oxalate precipitation because calcium also forms a moderately insoluble oxalate (CaC_2O_4). The calcium contamination was therefore not expected to be reduced significantly by this technique.

Calorimetry

The calorimetric assay on the final product gave results which were nearly identical with the theoretical assay of AmO_2 (88.3%). The second batch of AmO_2 actually exceeded the theoretical assay of AmO_2 , but the margin of error involved amounted to only 0.1%. This small error can be attributed to analytical error since the method is known to be accurate only to $\pm 0.1\%$. Three 50-gram batches of AmO_2 have been purified using this purification technique and have been shipped to the ORNL Research Isotope Pool for sale and distribution.

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