Purification of Plutonium

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ABSTRACT

Plutonium is now being purified on a routine basis by the following scheme: 1) oxidation to \( \text{PuO}_2^{2+} \), 2) two \( \text{NaPuO}_2\text{Ac}_3 \) precipitations, 3) two ether extractions of \( \text{PuO}_2(\text{NO}_3)_2 \) (the second extraction in the absence of salting-out agents), 4) reduction to \( \text{Pu}^{4+} \). The average yield through this procedure has been 86 per cent. The purity of the final product is very satisfactory for present requirements (1 gram metal reduction) and is surprisingly close to tolerance requirements considering that no precautions have been taken (i.e., ordinary C.P. reagents and pyrex containers are used and solutions are left exposed to the air caring and after purification).
PURIFICATION OF PLUTONIUM

Two months ago while looking for a method to purify the product from X so it would be suitable for metal reduction, we performed the following experiment on 10 mg of Pu.

1) 10 mg Pu oxidized to PuO$_2^{+}$ with Na$_2$Cr$_2$O$_7$ in HNO$_3$ at 85° C (sealed in 1 ml cone during oxidation).

2) NaPuO$_2$Ac$_3$ precipitated with NaAc·3H$_2$O and NaNO$_3$ and washed with Na$^+$, Ac$^-$, HAc solution.

3) NaPuO$_2$Ac$_3$ dissolved in HNO$_3$ and evaporated to ~10 μl. (NaNO$_3$ and PuO$_2$(NO$_3$)$_2$·xH$_2$O crystallized out on cooling.)

4) ~100 μl. diethyl ether added, the ether frozen in liquid N$_2$, the cone sealed, warmed to room temperature and shaken. PuO$_2$(NO$_3$)$_2$ dissolved to give reddish brown ether solution.

5) The solution centrifuged to the bottom of the cone, the ether frozen in liquid N$_2$, the cone opened, and after melting the ether solution, the NaNO$_3$ separated from the ether solution by centrifuging through a fritted funnel into another 1 ml cone. The NaNO$_3$ was washed several times with ether.

6) 1 μl H$_2$O added to the ether solution, the solution frozen, the top of the cone pulled into a capillary and sealed. The cone was warmed to room temperature, shaken and centrifuged to the capillary end of the cone (the capillary being supported in a 0.5 ml cone - see Fig. 1). The H$_2$O phase in the tip of the capillary.
capillary was frozen in a CO₂-acetone mixture and the ether solution gently centrifuged away from the solid water phase.

7) Tip containing H₂O phase broken off and step (6) repeated.

8) H₂O added to ether and ether evaporated (reddish brown water solution of PuO₂(NO₃)₂).

9) HNO₃ and HI added to PuO₂(NO₃)₂ solution, heated to oxidize HI to I₂ and to sublime I₂. Resulting solution Pu(NO₃)₄ in HNO₃ called lot 5 (see Table II for purity).

Encouraged by the results of the above run, we devised techniques to purify Pu on the 1 gram scale. The method is described on the following pages.
PROCEDURE FOR PURIFYING ONE GRAM OF PLUTONIUM

Pu(NO₃)₄ soln. in HNO₃
in 40 ml grad. cone
+ 6.26 ml 0.5 M Na₂Cr₂O₇
+ HNO₃
Dil. to 20.9 ml
Place 30 ml beaker over cone
Heat at 85°C for ~10 hrs
Dil to 20.9 ml
Composition of soln.

PuO₂⁺⁺ = 0.2 M
HNO₃ = 2.0 M
Cr₂O₇⁻⁻ = 0.083 M
Cr³⁺ = 0.133 M
Na⁺ = 0.3 M

+ 11.6 g NaAc·3H₂O
Stir
Cent.
Wash twice 25 ml 5 M Na⁺
0.2 M Ac⁻, 0.35 M HAc
Supernatant + washes

\[ R = 1 \]

Comp. of S.N. (vol. = ~26 ml)

\begin{align*}
\text{Na}^+ &= 3.4 \text{ M} \\
\text{Ac}^- &= 1.2 \text{ M} \\
\text{HAc} &= 1.6 \text{ M}
\end{align*}

NaPuO₂Ac₃ ppt.
+ 10.9 ml 5 M HNO₃
Dil. to 20.9 ml
Comp. of soln.

\begin{align*}
\text{PuO}_2^{2+} &= 0.2 \text{ M} \\
\text{HNO}_3 &= 2.0 \text{ M} \\
\text{Na}^+ &= 0.2 \text{ M} \\
\text{HAc} &= 0.6 \text{ M}
\end{align*}

+ 11.6 g NaAc·3H₂O
Stir
Cent.
Wash once 25 ml 5 M Na⁺
0.2 M Ac⁻, 0.35 M HAc
Evap. to ~1.3 ml
PROCEDURE FOR PURIFYING ONE GRAM OF PLUTONIUM (cont.)

1. Dissolve residue in 3 mL HNO₃.
2. Heat to sublimation and dissolve.
3. Reextract.
4. Evaporate.
5. Filter.
6. Repeat.
7. Wash, neutralize, and discard.

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Pu₂(NO₃)₄ in HNO₃.

Final Product.
Fig. 1
10 mg. ether extraction

Fig. 2
Apparatus to withdraw supernatant and washes from NaPuO₃Ac₃.

Fig. 3
Apparatus to transfer PuO₂(NO₃)₂ solution to extraction thimble.

Fig. 4
Apparatus to transfer solutions to 40 ml. cone.

Fig. 5
Ether extractor (designed by J.W. Kennedy)
Table I

YIELD DATA ON FOUR RUNS

<table>
<thead>
<tr>
<th></th>
<th>Fraction</th>
<th>Lot 7 (mg)</th>
<th>Lot 9 (mg)</th>
<th>Lot 12* (mg)</th>
<th>Lot 14* (mg)</th>
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<td>R-1</td>
<td>S-N. + washes</td>
<td>1460</td>
<td>1300</td>
<td>2160</td>
<td>1460</td>
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<td>R-2</td>
<td>Aq. phase 1st ether extraction</td>
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<td>Yield</td>
<td>Final product</td>
<td>94.0</td>
<td>87.2</td>
<td>83.0</td>
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* NaBrO₃ used for oxidizing agent (see discussion p. 10 for procedure).
## Table II

SPECTROGRAPHIC ANALYSIS FOR IMPURITIES IN FINAL PRODUCT

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<th>Tolerance</th>
<th>Lot 5</th>
<th>Lot 7</th>
<th>Lot 9</th>
<th>Lot 12</th>
<th>Lot 14</th>
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* Lots 12 and 14 oxidized by NaBrO₃ and the final Pu(NO₃)₄ solution converted to PuCl₄ soln by two hydroxide precipitations.
* Possible 49 interference.
† Element known to be present before purification.
‡ Element added before purification (1% as much impurity as U).
Discussion

The purity of the product from the procedure described is quite satisfactory for our present requirements (plutonium pure enough for 1 gram metal reduction experiments), and the basic chemistry (NaPuO$_2$Ac$_3$ precipitations and ether extractions) looks promising for purification to tolerance limits.

The 11 per cent of the product that does not follow through the scheme is not lost since all but R-1 (NaPuO$_2$Ac$_3$ supernatants and washes) can be thrown directly into the next batch and reworked. R-1 requires a hydroxide precipitation before reworking.

The techniques described are not wholly satisfactory. The worst objection to them is that they allow the room in which the work is done to become contaminated, and this is a health hazard. Solutions are also left exposed to the air (mainly during evaporations and during the HI reduction) which results in the introduction of impurities during and after the purification.

Improvements which have been or are being made in the procedure are described below.

1) NaBrO$_3$ has been substituted for Na$_2$Cr$_2$O$_7$ as an oxidizing agent. Na$_2$Cr$_2$O$_7$ gave trouble by precipitating Th, Zr, etc., chromates upon addition of the NaAc. The conditions before oxidation on the 1 gram scale are: 0.2 M NaBrO$_3$, 1 M HNO$_3$, and 0.2 M Pu$^4+$. After oxidation at 85° C (which we know to be complete in four hours) 1.9 g NaN$_2$O$_3$ and 9.0 g NaAc$\cdot$3H$_2$O are added. This gives

Yield: 99 g
a supernatant of the following composition: 3.4 M Na⁺, 1.0 M Ac⁻,
1.1 M HAc.

2) Electrolytic reduction of PuO₂⁺⁺ to Pu⁺⁺ will be substituted for the
HI reduction. The HI reduction is messy and probably substantially con-
tributes to room contamination and contamination of the product with
impurities because of the bubbling and exposure to air during the HNO₃
oxidation of the HI. The electrolytic reduction has not been applied to
the 1 gram scale. However, 50 g of 0.16 M PuO₂⁺⁺ in 1 M HNO₃ has been
successfully reduced in about one hour using Pt electrodes, 1.6 volts
across the cell, and a current of 20 milliamperes. Successful reduction
was determined by the color change and the absence of PuO₂⁻ (failure to
precipitate Na₂Pu₂O₃ upon addition of Na₂CO₃ - had all the Pu been
PuO₂⁻, 99.5 per cent would have precipitated).

3) Techniques are being revised, substituting filtering for centrifuging
using larger extractors and in general keeping solutions covered at all
times and minimizing transfers. The new apparatus and techniques have
not been thoroughly tested so are not reported here.