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This document contains 11 pages

PURIFICATION OF PLUTONIUM

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Technology - Plutonium

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ABSTRACT

Plutonium is now being purified on a routine basis by the following scheme: 1) oxidation to PuO_2^{++}, 2) two $NaPuO_2Ac_3$ precipitations, 3) two ether extractions of $PuO_2(NO_3)_2$ (the second extraction in the absence of salting-out agents), 4) reduction to 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 during and after purification).

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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 $Na_2Cr_2O_7$ in HNO_3 at 85° C (sealed in 1 ml cone during oxidation).
2) $NaPuO_2Ac_3$ precipitated with $NaAc \cdot 3H_2O$ and $NaNO_3$ and washed with Na^+, Ac^-, HAc solution.
3) $NaPuO_2Ac_3$ dissolved in HNO_3 and evaporated to ~10 μl. ($NaNO_3$ and $PuO_2(NO_3)_2 \cdot xH_2O$ 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_2O 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_2O phase in the tip of the

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capillary was frozen in a CO_2-acetone mixture and the ether solution gently centrifuged away from the solid water phase.

7) Tip containing H_2O phase broken off and step (6) repeated.

8) H_2O added to ether and ether evaporated (reddish brown water solution of $PuO_2(NO_3)_2$.

9) HNO_3 and HI added to $PuO_2(NO_3)_2$ solution, heated to oxidize HI to I_2 and to sublime I_2. Resulting solution $Pu(NO_3)_4$ in HNO_3, 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.

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PROCEDURE FOR PURIFYING ONE GRAM OF PLUTONIUM

[redacted]

$Pu(NO_3)_4$ soln. in HNO_3
in 40 ml grad. cone

+ 6.26 ml 0.5 M $Na_2Cr_2O_7$

+ HNO_3

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.

PuO_2^{++}	=	0.2 M
HNO_3	=	2.0 M
Cr_2O_7	=	0.083 M
Cr^{+3}	=	0.133 M
Na^+	=	0.3 M

+ 11.6 g $NaAc \cdot 3H_2O$

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)

Na^+	=	3.4 M
Ac^-	=	1.2 M
HAc	=	1.6 M

$NaPuO_2Ac_3$ ppt.

+ 10.9 ml 5 N HNO_3

Dil. to 20.9 ml

Comp. of soln.

PuO_2^{++}	=	0.2 M
HNO_3	=	2.0 M
Na^+	=	0.2 M
HAc	=	0.6 M

+11.6 g $NaAc \cdot 3H_2O$

Stir

Cent.

Wash once 25 ml 5 N Na^+,
0.2 M Ac^-, 0.35 M HAc

Supernatant + washes

R = 1

Comp. of S.N. (vol. = 20 ml)

Na^+	=	3.3 M
Ac^-	=	1.2 M
HAc	=	2.1 M

$NaPuO_2Ac_3$ ppt.

+ 2.5 ml 5 N HNO_3

Transfer soln. to extraction cup

Evap. to ~1.3 ml

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$PuO_2(NO_3)_2 \cdot xH_2O$ and $NaNO_3$ in extraction cup

Extract with ether in micro soxhlet extractor ~1.5 hrs at ~2 min/cycle (Flask filled with 3 ml H_2O and 15 ml ether.)

Water phase $NaNO_3$ and unextracted $PuO_2(NO_3)_2$

R - 2

Ether phase

Ether evap. from flask leaving H_2O soln. of $PuO_2(NO_3)_2$.

Trans. to extraction cup

Evap. to ~1.0 ml

Extract with ether in micro soxhlet extractor 1.5 hrs at 2 min/cycle.

Water phase

Unextracted $PuO_2(NO_3)_2$

R - 3

Ether phase

Ether evap. from flask

Trans. to 40 ml cone

+ 2 ml 5 N HNO_3

+ 3 ml 6 N HI

+ 3 ml 5 N HNO_3

Heat (to oxid. excess I^- to I_2)

Cent.

Trans. S.N. soln to another 40 ml cone

Wash I_2 three times ~1 ml H_2O

S.N. + wash

Heat to eliminate dissolved I_2

Final Product

$Pu(NO_3)_4$ in HNO_3

I_2 ppt.

Heat to sublime I_2

Dissolve residue in HNO_3

R - 4

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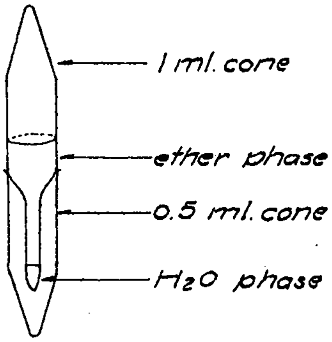

Fig. 1
10 mg. ether extraction

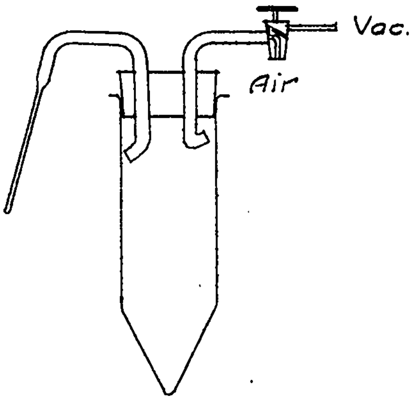

Fig. 4
Apparatus to transfer solutions to 40 ml. cone

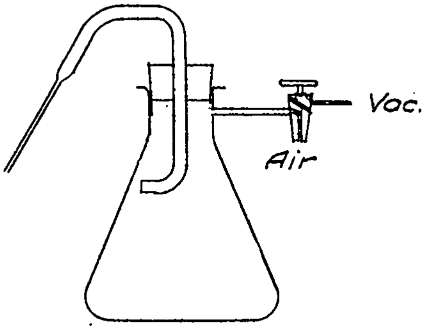

Fig. 2
Apparatus to withdraw supernatant and washes from $NaPuO_2Ac_3$.

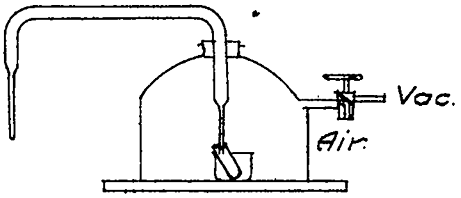

Fig. 3
Apparatus to transfer $PuO_2(NO_3)_2$ solution to extraction thimble.

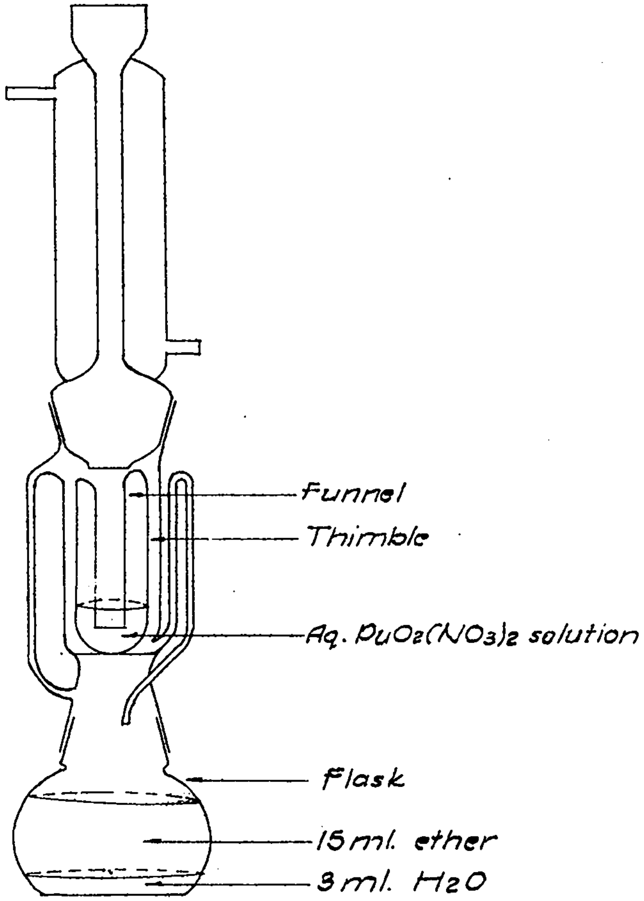

Fig. 5
Ether extractor
(designed by J. W. Kennedy)

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Table I

YIELD DATA ON FOUR RUNS

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	#	Fraction	Lot 7	Lot 9	Lot 12*	Lot 14*
Original Amount			1460 mg	1300 mg	2160 mg	1460 mg
% in Residues	R-1	S.N. + washes	0.8%	0.8%	5.8%	1.3%
	R-2	Aq. phase 1st ether extraction	1.1	2.3	4.6	3.7
	R-3	Aq. phase 2nd ether extraction	3.2	9.3	4.5	13.2
	R-4	I_2 residue	0.9	0.4	2.1	0.5
	Yield	Final product	94.0	87.2	83.0	81.3

* $NaBrO_3$ used for oxidising agent (see discussion p. 10 for procedure).

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Table II

SPECTROGRAPHIC ANALYSIS FOR IMPURITIES IN FINAL PRODUCT

Element	Tolerance	Lot 5	Lot 7	Lot 9	Lot 12△	Lot 14△	U Stand-in (HI red. omitted) After one other ext.	U Stand-in (HI red. omitted) Final Product
Li	1.2		<15		5	<.4	<0.5	0.5
Be	0.06	<10	10	<20†	<0.5	.4	1‡	50‡
B	0.22						1	0.5
Na	5.2		<160			25	20‡	4‡
Mg	6	<100†	20*†	<200†	6	50	15‡	3‡
Al	11	≤500	120	<2000	<4	<4	<2‡	<2‡
Si	50						500	8
P	≤350							<50
Ca	2000	100	<80†	200	<100†	200	20‡	5‡
Cr					<1000	≤200	35‡	20
Mn							<1	<1
Fe	4000		≤200	<2000	<1000†	<200		<5‡
Ni							<5	<5
Cu								<20
Zr		<1000†	<2000†	<2000	<200†	1000		
Mo	15000						<5	<10
Ag							0.2	0.4
Cd							0.2	0.2
In							<1	<1
Sn								<5
La		<1000†	<2000†	<2000	<1000†	≤1000		
Ce		<5000	<10000	<10000	<2000	<4000		
Au							<0.2	0.2
Pb							1	<1
Bi		<1000	<2000†	<2000	<1000†	<1000		
Th		<5000	2000†*	<10000	<2000†			

△ Lots 12 and 14 oxidized by $NaBrO_3$ and the final $Pu(NO_3)_4$ solution converted to $PuCl_4$ 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).

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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 ($NaPuO_2Ac_3$ precipitations and ether extractions) looks promising for purification to tolerance limits.

The 14 per cent of the product that does not follow through the scheme is not lost since all but R-1 ($NaPuO_2Ac_3$ supernatants and washes) can be thrown directly into the next batch and reworked. R-1 requires a hydroxide precipitation beofre 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 $Na_2Cr_2O_7$ as an oxidizing agent. $Na_2Cr_2O_7$ 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 N 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 $NaNO_3$ and 9.0 g $NaAc \cdot 3H_2O$ are added. This gives

[redacted]

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a supernatant of the following composition: 3.4 M Na^+, 1.0 M Ac^-, 1.1 M HAc.

2) Electrolytic reduction of PuO_2^{++} to Pu^{+4} will be substituted for the HI reduction. The HI reduction is messy and probably substantially contributes to room contamination and contamination of the product with impurities because of the bubbling and exposure to air during the HNO_3 oxidation of the HI. The electrolytic reduction has not been applied to the 1 gram scale. However, 50 g of 0.16 M PuO_2^{++} in 1 N HNO_3 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 PuO_2 (failure to precipitate $NaPuO_2Ac_3$ upon addition of $NaAc\cdot 3H_2O$ - had all the Pu been PuO_2, 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.

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