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PURIFICATION PROCESSES

Q-BUILDING PLUTONIUM PURIFICATION

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ABSTRACT

The details of the flow of materials through the D-Building Plutonium Purification Process and related operations are given. Sample procedure sheets giving detailed instructions for the operation of each process are included. The conditions prevailing before and after each chemical operation and the reactions involved in each step are shown in flow sheets for each process. During production operations modifications of each process made for greater ease of operation and higher yields. The reasons for and the details of each modification are given.

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Methods, Cut

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PURIFICATION PROCESSES

D-BUILDING PLUTONIUM PURIFICATION

I. Introduction

The following section presents the details of the flow of plutonium through the purification process and related operations.

Plutonium arrived at this site in the form of a thick paste of Pu (IV) and (VI) nitrates, contained in a specially constructed stainless-steel "bomb". (Construction of bomb shown in LA - 409). This material and a Pu (IV) nitrate solution from D-Building Recovery Group were the starting materials for purification operations.

When received at this site, the "bombs" were checked by the Monitoring and Decontamination Group for leakage and resulting external contamination. If found satisfactory, or after decontamination, the "bomb" was sent to storage through the Quantity Control Group. This group authorized and supervised the transfer of plutonium between designated space units.

The first set of operations performed by the Plutonium Purification Group consisted of the preparation of the solution used as starting material for the actual purification operations. These operations were termed Cut Operations. The equipment used during cut operations is shown in LA - 409.

Purification of plutonium was by one of three procedures, designated A, B, and C. Each modification was developed to effect simplification, reduction in operation time, and higher yields. The various changes were adopted as the

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kind and magnitude of the impurities present in the incoming material became known and as the purification obtained by large scale operation became better understood.

After purification the main charge of plutonium was in the form of a slurry of Pu (III) oxalate. This was sent to the Plutonium Dry Conversion Group for further processing. The supernatant and wash solutions from precipitation reactions and the residue from ether extraction contained appreciable amounts of plutonium. These solutions were acidified, to dissolve plutonium compounds, samples taken for plutonium assay, and the solutions sent to D-Building Recovery Group.

The continuity between, cut operations, purification, and treatment of supernatant solutions is shown in Fig. 1. The details of these operations are given in the sections which follow.

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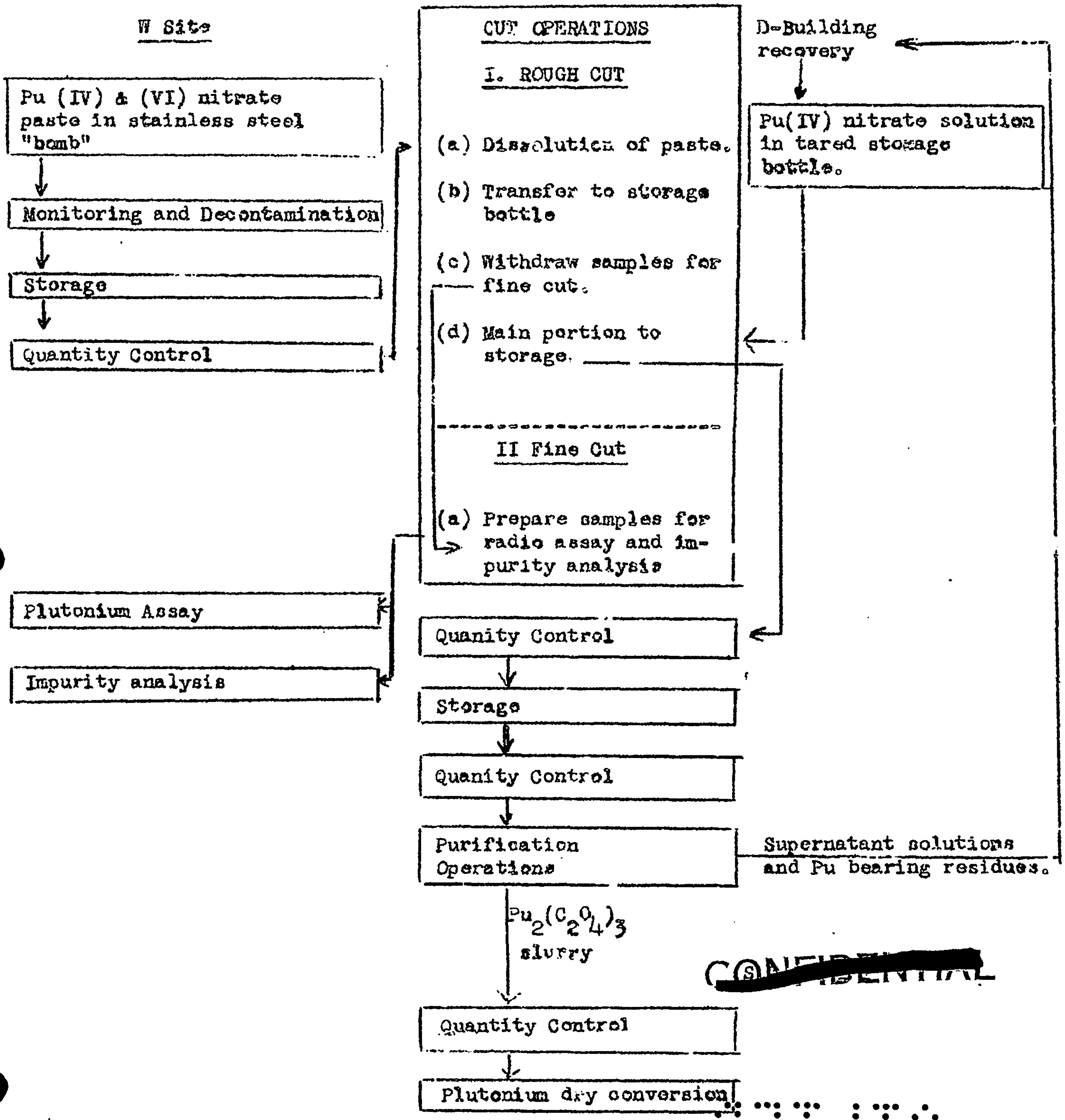
FIGURE - I

Flow of Plutonium through Purification and Related Operations



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II. Methods

Rough Cut Procedure "H" Batches

(1) Request authorization from Quantity Control Group to move "bomb" from storage to cut room.

(2) Open "bomb" and add 300 to 350 ml of 1.0M HNO_3.

(3) Stir for 30 minutes.

(4) Weigh storage bottle (with cap) empty. (Record on sheet #1)

(5) Transfer solution from "bomb" to storage bottle and wash "bomb" with M-HNO_3 until volume in bottle ≅ 800 ml.

(6) Weigh storage bottle (with cap) full. (Record on sheet #1)

(7) Stir solution in storage bottle for 30 minutes.

(8) (a) Take 1-ml cut with pipette calibrated "to deliver" and add to tared sample bottle (1-ml volumetric flask), marked with batch number (Record calibration of pipet on sheet #1)

(b) On every tenth batch, stop stirring, take a 10-ml cut with a clean, dry pipette and deliver into a clean, dry 12-ml graduated centrifuge cone.

(9) Place storage bottle in boron can and request Quantity Control for authorization to move it to storage vault.

(10) Transfer samples (1-ml, and 10-ml if taken) to Fine Cut room.

Rough Cut Procedure "R" Batches

(1) Deliver to the Recovery Group a tared, empty storage bottle, with cap and lucite liner, in a boron can. (Record weight on sheet #1)

(2) Receive storage bottle from Recovery with solution in it.

[redacted]

(3) If assay indicates the amount of plutonium is not in the range of 152-168 grams, calculate amount to be added or removed.

(4) Add or remove calculated amount from storage bottle.

(5) Dilute to 800 ml with M-HNO_3 and proceed according to steps to 6 to 8 (a) inclusive under Rough Cut for "H" Batches. (Record data on sheet #1)

(6) Proceed according to (9) and (10) above.

Fine Cut Procedure

(1) Weigh sample bottle from step 8 (a) of Rough Cut. (Record weight on sheet #1)

(2) Weigh 100 microliter calibrated pipet and holder empty. (Record weight on sheet #1)

(3) Take 100-microliter cut from sample bottle, wipe end of pipet with Kleenex and place pipet in holder.

(4) Weigh 100-microliter pipet and holder, full. (Record weight on sheet #1)

(5) Transfer 100-microliter sample to a 10-ml volumetric flask marked with batch number and letter A.

(6) Wash pipet three times with 5M HNO_3 into flask.

(7) Wash and dry pipet on vacuum pipet cleaner.

(8) Repeat steps (2) to (7) inclusive, except volumetric flask is labeled with batch number and letter B. Tolerance weighing of ± .03 between duplicate aliquots of A and B.

(9) On every twentieth "H" batch take a 100-microliter cut and deliver with 5M HNO_3 into 1 ml volumetric flask. Mark with batch number and the letter S. (Record on sheet #1 that cut has been taken.)

[redacted]

Disposition of Samples Taken During Cut Operations

The main portion of the solution remained in a storage vault until results of plutonium assay indicated plutonium present was in the range 140 to 170 grams of Pu. It then was ready for purification operations.

After fine cut operations the 1-ml sample, taken in step 8 (a) of Rough Cut, was in three portion. (With every twentieth lot, in four portions) Two 100-microliter samples plus pipet wash were in 10-ml flasks marked with batch number and letter A and B. These two samples together with an assay request (sheet #2) were delivered to the Radio Assay Group. These samples were used for assay of plutonium by a radio chemical counting technique. The 800 microliters (700 microliter with every twentieth batch) remaining in the sample bottle, were delivered to the analytical laboratory. At the same time, a request for analysis (sheet #4) was given to the analytical office. The sample was used for assay of plutonium by a titration method, for the colorimetric determination of iron, and for quantitative determination of all elements detectable by direct copper spark. With every twentieth batch the 100-microliter sample, worked with batch and letter S, was sent to group R-4, and used for the determination of spontaneous fission rate.

The 10-ml cut, taken on every tenth "R" batch was centrifuged, and 2 ml of the supernatant transferred to a clean dry test tube, marked with batch number and the letter M. This sample was taken to the analytical laboratory for boron analysis. The remaining supernatant, ~7.5 ml, was transferred to a clean dry volumetric flask. This sample was delivered to the analytical laboratory and used for "complete" analysis by the best method available at the time. The solids remaining in the centrifuge cone, were transferred and washed with small portions of N HNO_3, to a tared-2ml Gooch-Monroe crucible. The crucible and contents were taken to the analytical laboratory, where it was dried and weighed. The solids were later analyized by spectro-chemical methods.

Data Obtained by Cut Operations

(Data recorded on sheet #1). From the weight of storage bottle empty and full, one obtained the total weight of solution for the batch. (Rough Cut Procedure #4 & #6). The density of the solution was obtained from the weight of the 1-ml cut (taken with calibrated pipet) and also from the weights of the two 100 microliter cuts. Densities calculated from 1-ml and 100-microliter cuts usually checked to better than 0.5%. Originally, densities were calculated from duplicate 1-ml samples and duplicate 100-microliter samples to determine which would be the more precise method. There appeared to be little difference between the methods, but since two 100-microliter samples were taken for radio assay, calculation of density from these samples afforded a means of obtaining duplicate density determinations. However, the weight of the 1-ml cut when sampled and its weight when used in the analytical laboratory was a convenient check on the extent of evaporation. Therefore, the weights of the 1-ml and the two 100-microliter samples were taken, and density calculated from each.

The total volume of solution was calculated from the total weight of solution and its density. This was more convenient than attempting to measure the volume of such a highly active solution.

Only calculations from radio assay data required a knowledge of the density. The chemical titration of plutonium was on a weight basis, i.e. determined and reported as grams of plutonium per gram of solution.

[redacted]

[redacted]

Explanation of Data Sheets

The following eight sheets are examples of the sheets used to record and accumulate data for each batch processed by the purification group.

Sheet #1. Data from Fine Cut and Rough Cut.

This sheet was taken into the cut room and the data recorded as the steps were finished. When the fine cut procedure and rough cut procedure had supplied the data through step (10), the sheet was turned over to the Recorder.

Sheet #2. Assay Request Sheet.

An estimate of the product concentration was made and this sheet made out accordingly, by the Recorder. The cuts, plus the request sheet, were then taken to the Assay Group. The remainder of the sheet was filled out with the Assay data.

If, on sheet #2, the deviation was less than, or equal to, the total error, and the product concentration was within the limits 140 to 170 grams Pu., the Recorder accept the assay by initialling the sheet. This sheet was retained by the Assay Group.

Sheet #3. Data from Assay.

Upon completion of the determination of the plutonium concentration by the Assay group, the data sheet #3 was returned to the Recorder. This sheet contained only the information from sheet #2 that was pertinent for calculating the total present in a batch.

Sheet #3, was retained by the Recorder and filed under the Run Number.

[redacted]

With this data, sheet #1 was completed, and the total amount of plutonium in the batch calculated.

<u>Sheets #4, #5, #6. Analysis Request Sheets.</u>

These sheets were used to request analyses of the cuts taken during Fine Cut. Requests were made on Sheet #4 for all but every tenth batch. On every tenth batch which required a "complete" analysis, sheets #5 and #6 were used.

<u>Sheet #7. Report of Spectrochemical Analysis.</u>

The results of direct copper spark, pyroelectric analysis, and cupferron analysis were reported by the analytical laboratory on this sheet.

<u>Sheet #8. Analytical Laboratory Report.</u>

All constitments not determined by spectrochemical methods were reported on the sheet.

#1

CUT DATA SHEET Lot # 90-H

1. Initial Container:
(a) Safe # 86-L
(b) Container # 13

2. Storage Container:
(a) Safe # 80-L
(b) Container # S-21

3. Sample Bottle and Pipet:
(a) Bottle # 90H
(b) Pipet # II
(c) Pipet Vol. 1.001 ml.

4. R.A. Cut Bottles and Pipets:

	(1)	(2)
(a) Bottle #	90 H_A	90 H_B
(b) Pipet #	B	B
(c) Pipet Vol #	99.8	99.8

5. Special Sample Bottles and Pipets:
(a) Bottle #
(b) Pipet #
(c) Pipet Vol. ml.

6. Storage container:
(a) Wt. cont. full 2167
(b) " " empty 1122
(c) " solution 1045

7. Time of Soln min.

8. Wt. of Cut:
(a) Wt. of sample bottle full 2.4658
(b) Wt. of sample bottle empty 1.1127
(c) Wt. sample 1.3531

9. Wt. of R.A. Cuts:

	(1)	(2)
(a) Wt. of pipet full	1540.3 mg	1540.3 mg
(b) Wt. of pipet empty	1405.7 mg	1406.9 mg
(c) Wt. sample	134.6 mg	134.4 mg

10. Wt. Special Cuts 10 ml, 100 λ

11. Amount

		Density	g/l	g/g soln	Total	To Purif	Tom	To R.A.	Segre'
g soln		X	X	X	1045	1030.2	14.42	.27	.14
W or R		X	X	.1531	160.0	157.730	2.208	.041	.021
Density	I ml	1.352	X				X	X	X
	100λ	1.348	X			X	X	X	X
	Boaz		X			X	X	X	X
R A		100λ	200.4	.1487	155.392	153.191	X	X	X
Chem TIT		Boaz		.1441	150.585	148.448	2.078	.039	.020

200 ml SAMPLE # 70 H

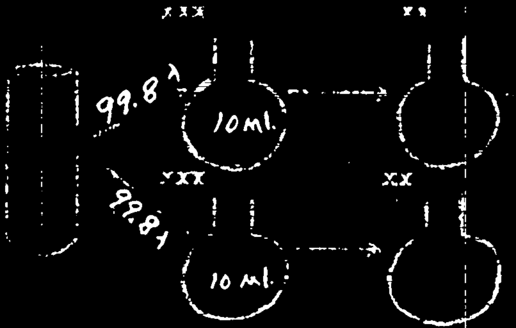
.400 DATE June 26-45

VOL OF SAMPLE 20 NAME Atherton

RUSH

OK.
NLB

#2



1
DIL. FACT. ______
x D.F./S.A. ______
→ PRODUCT CONC. ______ g./l
SOLIDS ON PLATE ______ µg.

x
DIL. FACT. ______
D.F./S.A. ______
PRODUCT CONC. ______ g./l
SOLIDS ON PLATE ______ µg.

COUNTING ERROR ______
ABS. ERROR ______
TOTAL ERROR ______
DEV. ______
AVE. PROD. CONC. ______ g./l

AIR ______ N_2 ______ ______ # ______ COUNT ______ DATE ______

SAMPLE #				BKG			
TIME							
△ TIME							
SCALE							
FINAL READING							
INITIAL READING							
FINAL - INITIAL							
TOTAL COUNTS							
c/m							
AVERAGE							
COIN CORR.							
BKG							
TRUE c/m ± S.D.							

* Total solids = all material that is not volatile at 80° (Includes H_2SO_4, $H_2C_2O_4$, NH_4Cl and NH_4NO_3)

1st CALC. ______
PIPETTING ______
COUNTING ______
2nd CALC. ______
FINAL CHECK ______

3

2473

PRODUCT CONC. 200.4 g./l.

EST. ERROR 2. %

DEV. 0.4 %

SAMPLE # 90-H

DATE 6-26-45

NAME Atherton

VOL. OF SOL'N. ______ ml.

DESCRIPTION

REQUEST FOR ANALYSIS
to
ANALYTICAL LABORATORY
CM-9

SAMPLE NO. CM-5-NLB-85-H

Date Submitted June 25-45

DESCRIPTION + 4 49 nitrate in 1.0

Date Reported

CONCENTRATION 200.4 g/1

(Figure furnished by radio assay)

Analysis Requested	Analysis Reported
Assay by Titration	
Colormetric Fe	
All elements detectable by Direct Cu Spark	

REMARKS :

Sample Vol. = 0.8 ml
Total wt. Sol'n. = 1.0784
Density = 1.348

(Figures furnished by purification on basis of Fine-Cut data)

N. L. Brown
Submitted by

Analyst

REQUEST FOR ANALYSIS
TO
ANALYTICAL LABORATORY

CM-9

SAMPLE NO. CM-5NLB-90H

Date Submitted June 26, 45

Date Reported

DESCRIPTION +4 49 Nitrate in 1.0M HNO_3

ANALYSIS

Constituent	Analysis Requested (x) *	Expected Percent	Percent by Analysis
Suspended Solids	a. Total b. Semi-quant.	0.1 — 1.0% Si and Sn.	

* If only spectroscopic estimation is desired indicate by writing "spec. est.". This is to show presence or absence of traces.

METHOD:

REMARKS:

N. S. Brown

Submitted by

Analyst

REQUEST FOR ANALYSIS
to
ANALYTICAL LABORATORY
CM-9

Date Submitted June 25-45

SAMPLE NO. CM-5

DESCRIPTION +4 nitrate in 1.0 M. HNO_3

ANALYSIS

Constituent	Analysis Requested	Expected Percent	Percent by Analysis
	Assay by titration. Density.	200 g/l	
Fe B	Colorimetric Fe B	0.5% 1 ppm	
~~All elements detectable, not detected by cupferron or Pyroelectric analysis~~	~~Direct Cu Spark~~	~~Limit of Detection~~	
All elements detectable	Cupferron Analysis		
All elements detectable	Pyroelectric Analysis		
~~Suspended Solids~~	~~Suspended Solids a. Total b. Semi-Quant.~~ Separate Request	~~0.1 - 1.0 % Si and Sn~~	
U	Flourimetric U	Limit of Detection	
Th + Zr	Hexone	100 ppm.	
$SO_4^=$	$SO_4^=$	25 %	
P	Colorimetric P	1000 ppm.	

REMARKS:

Concentration: 200.4 g/l

N. S. Brown
Submitted by

SPECTROCHEMICAL ANALYSIS

Date July 3 1945

Plate # 2215

#

Li		Sr.	≮20	Dy	
Be	ND<10	Y		Ho	
B		Zr	ND<200	Er	
C		Cb		Tm	
Na		Mo		Yb	
Mg	≮20	Ma		Lu	
Al	<200	Ru		Hf	
Si		Rh		Ta	
P		Pd		W	
K		Ag		Re	
Ca	≮20	Cd	ND<1000	Os	
Sc		In		Ir	
Ti		Sn	≮400	Pt	
V	ND<1000	Sb		Au	
Cr	1200	Te		Hg	ND<4000
Mn	<200	Cs		Tl	
Fe		Ba	ND<1000	Pb	ND<200
Co	ND<1000	La	2000	Bi	ND<1000
Ni	2000	Ce	ND<2000	Po	
Cu		Pr		Ab	
Zn		Nd		Vi	
Ga		Il		Ra	
Ge		Sm		Ac	
As	ND<2000	Eu		Th	ND<4000
Se		Gd		Pa	
Rb		Tb		U	

Sample # CM-5-NLB-90 H

Date Received June 25 1945

Submitted by Brown

Description -4 49 nitrate

Work by McCall

Reported by Nachtrieb

Key:

FT	< .001%	S	> 1%
T	.001-.01%	VS	> 10%
W	.01-0.1%	ND	Not Detected
M	0.1-1%	I	Interference

FIGURES EXPRESS PPM. UNLESS OTHERWISE INDICATED

FORM 58

ANALYTICAL LABORATORY REPORT

Date June 29, 1945

#8

SAMPLE NO. CM-5NLB-90-H

DESCRIPTION -4 49 nitrate in 1.0M HNO_3

SUBMITTED BY NL Brown

DATE SUBMITTED June 25, 1945

REPORT OF ANALYSIS

CONSTITUENT	ANALYSIS REQUESTED ( )	EXPECTED PER CENT	PER CENT BY ANALYSIS
P			247 P/ml 249 P/ml 248 P/ml 1232 P/ml 1242 P/ml 1237 P/ml

METHODS USED

REMARKS

Smith
ANALYST

[redacted]

Purification Methods

Three processes were developed for the purification of plutonium. Each process consisted of one or more of the following chemical operations, each of which had desirable separation factors of plutonium from various impurities; (1) precipitation of Pu (III) oxalate. (2) of sodium plutonyl acetate, and (3) extraction of Pu (VI) nitrate from aqueous solution with diethyl ether.

The first process to be developed, designated Procedure A, consisted of the following chemical operations: (1) reduction of Pu (IV) or a mixture of Pu (IV) and Pu (VI) to Pu (III) with KI or HI, (2) precipitation of Pu (III) oxalate with oxalic acid, (3) oxidation of Pu (III) oxalate with HNO_3 and $NaBrO_3$, (4) precipitation of sodium plutonyl acetate. (5) dissolution of sodium plutonyl acetate into HNO_3 and NH_4NO_3, (6) diethyl ether extraction of Pu (VI) nitrate, NH_4NO_3 as salting out agent, (7) reduction of Pu (VI) to Pu (III) with HI, and (8) precipitation of Pu (III) oxalate with oxalic acid.

In the first three modification of the A-Procedure, the first reduction was carried out with KI. It was first assumed that the starting material was essentially all Pu (IV) and the reduction reaction could be represented by:-

$$(1)\quad 2Pu^{++} + 3I^{-} \longrightarrow 2Pu^{+3} + I_3^{-}$$

Spectrophotometric analysis of the starting material indicated that from 30 to 70% was Pu (VI), assumed to be $2PuO_2^{++}$. The reduction of this ion, with iodide, was assumed to proceed according to:-

$$(2)\quad 2PuO_2^{++} + 9I^{-} + 8H^{+} \longrightarrow 2Pu^{+3} + 3I_3^{-} + 4H_2O$$

[redacted]

[redacted]

Reaction according to (2) requires the presence of hydrogen ion in order that reduction be complete. In that no satisfactory method of determining hydrogen ion concentration in concentrated plutonium solutions had been devised, the requirements of (2) were satisfied by substituting HI for KI in A-4 and latter procedures.

Experience indicated that the reduction of Pu (IV) and Pu (VI) more closely follows the following equations than (1) and (2) :-

$$(3)\quad 2PuO^{++} + 3I^- + 4H \longrightarrow 2Pu^{+3} + I_3^- + 2H_2O$$

$$(4)\quad 2PuO_2^{++} + 9I^- + 8H^+ \longrightarrow 2Pu^{+3} + 3I_3^- + 4H_2O$$

No experimental evidence exists to indicate the predominence of Pu (IV) as $2PuO^{++}$ over any other possible form of ion. However, the behavior of the system during reduction and subsequent operations indicated that (3) and (4) are a good approximation of the reduction reactions.

To insure as complete reduction as practical (~99.9%) and to complex the I_2 formed during reaction, as I_3^-, the following conditions were adopted. HI, in the ratio of 8 moles per mole of plutonium, was added to the solution to be reduced, at a temperature of 17°C., or less. Reaction was complete in twenty minutes. Specification of a maximum starting temperature was necessary in order that the peak temperature during reaction be below the point where volitalization of I_2 became appreciable, and that a reaction between I^- and HNO_3 be prevented.

Precipitation of Pu (III) oxalate was the most trouble free purification step used. Addition of a nearly saturated solution of $H_2C_2O_4$ (0.67M) to a solution immediately following HI reduction and allowing twenty minutes for the

[redacted]

[redacted]

precipitate to form, with stirring, produced a precipitate which settled readily. The prime function of the Pu (III) oxalate precipitation was the removal of uranium. Under operating conditions uranium was removed by a factor of approximately 20. Lanthanium, present the extent of approximately 30,000 parts per million of Pu, was practically quantitatively precipitated during this step.

Preparatory to acetate precipitation and ether extraction the plutonium was oxidized to Pu (VI). Oxidation was accomplished by the action of HNO_3 and $NaBrO_3$ on a slurry of Pu (III) oxalate, at elevated temperatures. After addition of HNO_3 and a solution of $NaBrO_3$ to the slurry, the temperature of the mixture was raised to 75°C., and maintained at that temperature until the precipitate was dissolved, (approximately a half hour). The temperature was then raised to 93°C., and maintained for one hour. The reactions involved during oxidation were assumed to proceed according to:-

$$(5) \quad 5Pu_2(C_2O_4)_3 + 12BrO_3^- + 32H^+ \longrightarrow 10PuO_2^{++} + 6Br_2 + 30CO_2 + 16H_2O$$

$$(6) \quad 5La_2(C_2O_4)_3 + 6BrO_3^- + 36H^+ \longrightarrow 10La^{+3} + 3Br_2 + 30CO_2 + 16H_2O$$

The dissolution of the Pu (III) oxalate at an intermediate temperature controlled the rate of evolution of Br_2 and CO_2.

Several cases of incomplete oxidation were experienced. This was evidenced by inability to dissolve the oxalate precipitate, even with prolonged heating at 93°C. The only satisfactory method of resolving the system was by addition of a two-fold excess of HNO_3 and $NaBrO_3$ and heating for several hours at 93°C.

The precipitation of sodium plutonyl acetate followed the oxidation.

[redacted]

[redacted]

The conditions for precipitation with acceptable yields were much more critical than during the formation of the Pu (III) oxalate. The precipitation reaction was assumed to proceed according to:-

(7) $PuO_2^{++} + 3Ac^- + Na^+ \longrightarrow NaPuO_2Ac_3$

The solubility of the compound was studied as a function of sodium ion concentration. In the presence of sodium ion concentrations up to approximately 3M, the solubility shows a marked decrease with increased sodium ion concentration. At approximately 20°C, in water, the solubility is 19.5g Pu per liter, in 4M sodium ion 0.07g Pu per liter. Precipitation was from an HAc-Ac⁻ buffer (~0.25M HAc & 0.5M Ac⁻) with a pH ~ 5. Because the hydrogen ion concentration was not precisely known after oxidation it was necessary to titrate the oxidized solution with the acetate precipitant, in order that the composition of the supernatant be within prescribed limits. By slowly adding precipitant, with stirring, the excess acid from oxidation was neutralized, the end point being the appearance of permanent precipitate of sodium plutonyl acetate.

After neutralization of excess acid, an amount of precipitant sufficient to form the precipitate and establish optimum conditions in the supernatant was added. In order to form a precipitate having desirable settling properties, control of temperature and of rate of addition of precipitant was necessary. Addition of the precipitant, as dilute as practical, at a rate of 50 ml. per minute, or less, to a solution at 65°C. formed a precipitate having desirable properties. Precipitation above 65°C., increased the settling rate but also increase the loss through increased solubility. The function of acetate precipitate was to remove

[redacted]

[redacted]

lanthaum, and to reduce the volume of solution to be ether extracted.

After washing, the sodium plutonyl acetate was dissolved in HNO_3 containing NH_4NO_3:-

(8) $NaPuO_2Ac_3 + 3HNO_3 \longrightarrow Na^+ + PuO_2^{++} + 3HAc + 3NO_3^-$

The NH_4NO_3 acted as a salting out agent for the ether extraction to follow. Excess reagent was added so that the hydrogen ion concentration was approximately 1.5M, and the ammonium nitrate approximately 8.0M.

Ether extraction while being the most efficient overall purification operation was the most difficult step to engineer to large-scale operations. For satisfactory production work it was required that the operation be continuous, completely enclosed, and relatively fast. The first two requirements were met by building a modification of the common Soxlet extractor. The mechanism of extraction was unknown and partition coefficients were only qualitatively determined so that optimum conditions for fast extraction were determined more or less by trial and error. The results of experiments using $UO_2(NO_3)_2$ as a "stand-in" and finally with $PuO_2(NO_3)_2$ indicated that high nitrate ion activity and low temperatures increased the ratio $PuO_2(NO_3)_2$ in ether to $PuO_2(NO_3)_2$ in water. High nitrate ion activity was achieved by the addition of concentrated solutions of NH_4NO_3 (in all A produces) and of $Ca(NO_3)_2$ (in all B prosedures). Nitric acid was extracted with $PuO_2(NO_3)_2$ and if below a certain initial value, extraction of $PuO_2(NO_3)_2$ stopped before complete removal from the aqueous phase. Optimum initial hydrogen ion concentration appeared to differ with the salting out agent used with NH_4NO_3 (A-procedure) initial hydrogen ion concentration greater than approximately 1.3M, and with $Ca(NO_3)_2$ (B-procedure) greater than approximately

[redacted]

[redacted]

0.4M, gave satisfactory extraction. The rate of ether pass was run at the maximum attainable with the equipment. The limiting factor was the heat transferred into the boiler. Extraction gave the greatest purification from a greater number of element than any other operation. Only uranium, which was presumably quantitatively extracted and chromium extracted to approximately 10% of that present, were the only elements observed to follow plutonium. Production equipment attained approximately 99% extraction in three hours.

Following extraction the plutonium was reduced to Pu (III) equation (4), and Pu (III) oxalate precipitated. The final oxalate precipitation served two purposes. As well as being a purification operation, it was a compound which could be conveniently dried, ignited to the dioxide and hydro fluorinated by the plutonium dry-conversion operations.

When purity tolerances were partially lifted, it seemed probable that a quicker and simpler procedure would yield plutonium of satisfactory purity. The first major change in purification operations, consisted in elimination of the first Pu (III) oxalate and the sodium plutonyl acetate precipitations. The process was designated as Procedure B., and consisted of the following steps:- (1) oxidation of the starting material with HNO_3 and $NaBrO_3$, (2) ether extraction, using $Ca(NO_3)_2$ as a salting out agent, (3) reduction with HI, and (4) precipitation of Pu (III) oxalate.

A third revision of the purification operations, designated Procedure C., consisted only of HI reduction and Pu (III) oxalate precipitation. Only two semi-production runs were made using the C-procedure.

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A summary of the yields and purification attained in all production runs is given in LA - 406.

Flow sheets, giving the details of all purification procedures, are given in the following sections.

[redacted]

Flow Sheet

+2.00 L H_2O to Boiler

+Product to Ext.

Extractor [Initial Product]

0.80 L

0.42M	PuO^{++}	(0.34)(a)	≅ 160 g Pu	(b)
0.41M	PuO_2^{++}	(0.33)		
0.60M	H^+	(0.48)(c)		
0.02M	Fe^{+3}	(0.02) ≅ 1.0g		(d)
0.005M	Cr^{+3}	(0.004) ≅ 0.2g		
0.004M	Ni^{+2}	(0.003) ≅ 0.2g		
0.02M	La^{+3}	(0.02) ≅ 3.0g		
0.39M	HSO_4^-	(0.31) ≅ 30.0g		
0.009M	$H_2PO_4^-$	(0.007) ≅ 0.7g		
2.05M	NO_3^-	(1.64)		

$SnO_2 \cdot X H_2O$, $SiO_2 \cdot X H_2O$ ≅ 0.3g

+0.20 L 1M HNO_3 (0.20) Storage bottle
wash to Ext.

Cool Ext to 17°C

+1.00 L 5.5M HI (5.50) to Ext. (e)

Allow 20 min for reduction

$$\left\{\begin{array}{l} 2\,PuO_2^{++} + 9\,I^- + 8\,H^+ \cong 2\,Pu^{+3} + 3\,I_3^- + 4\,H_2O \\ 2\,PuO^{++} + 3I^- + 4H^+ \cong 2\,Pu^{+3} + I_3^-\ 2H_2O \\ 2\,Fe^{+3} + 3I^- \cong 2\,Fe^{+2} + I_3^- + \end{array}\right\}$$

~ 15 Kcal. heat liberated

Cool Ext. to 25°C

Extractor [After Reduction]

2.00 L.

0.34M	Pu^{+3}	(0.67)
2.09M	H^+	(4.18)
0.01M	Fe^{+2}	(0.02)
0.002M	Cr^{+3}	(0.004)
0.002M	Ni^{+2}	(0.003)
0.01M	La^{+3}	(0.02)
0.16M	HSO_4^-	(0.31)
0.004M	$H_2PO_4^-$	(0.007)
0.62M	NO_3^-	(1.84)
1.75M	I^-	(3.49)
0.34M	I_3^-	(0.67)

$SnO_2 \cdot X H_2O$, $SiO_2 \cdot X H_2O$ ≅ 0.3g

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3.20 L 0.67M $H_2C_2O_4$ (2.14) to Ext.

Allow ppt. to form 20 min.

$2\,Pu^{+3} + 3\,H_2C_2O_4 = Pu_2(C_2O_4)_3 + 6H^{+1}$
$2\,La^{+3} + 3\,H_2C_2O_4 = La_2(C_2O_4)_3 + 6H^{+1}$

Allow ppt. to settle 15 min.

Withdraw S. N. →

P=146 [S.N. of 1st. Ox.]

4.60 L

1.22M	H^+	(5.62)
0.004M	Fe^{+2}	(0.02)
0.0009M	Cr^{+3}	(0.004)
0.0007M	Ni^{+2}	(0.003)
0.06M	HSO_4^-	(0.28)
0.02M	$H_2PO_4^-$	(0.007)
0.36M	NO_3^-	(1.66)
0.68M	I^-	(3.15)
0.13M	I_3^-	(0.60)
0.22M	$H_2C_2O_4$	(1.00)

640 mg Pu

Extractor [1st Ox. Ppt., No Wash]

0.50 L S.N. (f)

1.22M	H^+	(0.61)
0.06M	HSO_4^-	(0.03)
0.36M	NO_3^-	(0.18)
0.68M	I^-	(0.34)
0.13M	I_3^-	(0.07)
0.22M	$H_2C_2O_4$	(0.11)

0.10 L Ppt.

$Pu_2(C_2O_4)_3$	(0.33)
$La_2(C_2O_4)_3$	(0.01)

$SnO_2 \cdot X\ H_2O,\ SiO_2 \cdot X\ H_2O = 0.3g$

$+4.5$ L H_2O to Ext.

Suspend ppt. in wash solution

Allow ppt. to settle 15 min.

Withdraw wash →

P=146 [1st. Wash of 1st Ox.]

4.50 L

0.12M	H^+	(0.55)
0.006M	HSO_4^-	(0.03)
0.04M	NO_3^-	(0.16)
0.07M	I^-	(0.31)
0.01M	I_3^-	(0.06)
0.02M	$H_2C_2O_4$	(0.10)

100 mg Pu

Extractor [1st Ox. Ppt., After 1st wash]

0.50 L S.N.

0.12M	H^+	(0.06)
0.04M	NO_3^-	(0.02)
0.07M	I^-	(0.03)
0.01M	I_3^-	(0.007)
0.02M	$H_2C_2O_4$	(0.01)

0.10 L Ppt.

$Pu_2(C_2O_4)_3$	(0.33)
$La_2(C_2O_4)_3$	(0.01)

$SnO_2 \cdot X\ H_2O,\ SiO_2 \cdot X\ H_2O = 0.3g$

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$+4.5L\ H_2O$ to Ext.

Suspend ppt. in wash solution.

Allow ppt. to settle 15 min.

Withdraw wash → P-146 [2nd wash of 1st. Ox.]

Extractor [1st. Ox. Ppt., After 2nd wash]

0.50 L S.N.		
0.01M	H^+	(0.006)
0.002M	NO_3^-	(0.002)
0.006M	I^-	(0.003)
0.001M	I_3^-	(0.001)
0.002M	$H_2C_2O_4$	(0.001)

0.10 L Ppt.	
$Pu_2(C_2O_4)_3$	(0.33)
$La_2(C_2O_4)_3$	(0.01)

$SnO_2 \cdot X\ H_2O,\ SiO_2 \cdot X\ H_2O = 0.3g$

$+0.30$ L 10M HNO_3(3.00) to Ext.

$+0.90$ L 1.54M $NaBrO_3$(1.39) to Ext.

Heat Ext. to 75°C. and hold at 75°C. until reaction is complete

$$\left\{\begin{array}{l} 5\ Pu_2(C_2O_4)_3 + 12BrO_3^- + 32H^+ \\ \quad = 10\ PuO_2^{++} + 6Br_2 + 30\ CO_2 + 16H_2O g \\ 5\ La_2(C_2O_4)_3 + 6BrO_3^- + 36H^+ \\ \quad = 10\ La^{+3} + 3Br_2 + 30CO_2 + 18H_2O \\ H_2O(1) = H_2O(g)\ [0.20\ L\ H_2O(1)\ evap] \end{array}\right\}$$

$+0.375$ L 1M HNO_3(0.375) to Ext. from wash ring.

Heat Ext. to 93°C and hold at 93°C for 1 hr.

$+H_2O$ to Ext. to dilute solution to 2.8 L [~0.875 L H_2O]

Extractor [After Oxidation]

2.80 L		
0.24M	PuO_2^{++}	(0.67)
0.40M	H^+	(1.13)
0.007M	La^{+3}	(0.02)
0.50M	Na^+	(1.39)
0.21M	BrO_3^-	(0.58)
1.19M	NO_3^-	(3.33)

P-146 [2nd wash of 1st. Ox.]

4.50L		
0.01M	H^+	(0.05)
0.004M	NO_3^-	(0.02)
0.006M	I^-	(0.03)
0.001M	I_3^-	(0.007)
0.002M	$H_2C_2O_4$	(0.01)

100 mg Pu

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Alkaline Bubbler (i)

1.50 L Before Oxid.			1.50 L After Oxid.		
4.50M	Na^+	(6.75)	4.50M	Na^+	(6.75)
1.00M	$SO_3^=$	(1.50)	0.73M	SO_3	(1.09)
2.50M	OH^-	(3.75)	0.27M	$SO_4^=$	(0.41)
			0.55M	Br^-	(0.82)
			0.60M	$CO_3^=$	(0.90)
			0.77M	HCO_3^-	(1.16)

$$\left\{\begin{array}{lcl} Br_2 + SO_3^= + 2OH^- & = & 2Br^- + SO_4^= + H_2O \\ CO_2 + 2OH^- & = & CO_3^= + H_2O \\ CO_2 + CO_3^= + H_2O & = & 2HCO_3^- \end{array}\right\}$$

CO_2 (2.06)
Br_2 (0.41)

Acid Bubbler (h)

1.50 L Before Oxid.			1.70 L After Oxid.		
1.00M	H^+	(1.50)	0.88M	H^+	(1.50)
1.00M	NO_3^-	(1.50)	0.88M	NO_3^-	(1.50)
				~1 mg Pu	

Br_2 (0.41)
CO_2 (2.06)
H_2O (11.10)

[redacted]

$SnO_2 \cdot X\ H_2O,\ SiO_2 \cdot X\ H_2O$ (0.3g)

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+2.00 L [2.75M NaAc^(j) (5.50), 3.4M $NaNO_3$ (6.30)] to Ext. [add at rate of < 50 ml/min.]
$H^+ + Ac^- = HAc$
Adjust temp. to 65°C.

{$PuO_2^{++} + 3\ Ac^- + Na^+ = NaPuO_2Ac_3$
Permanent ppt. should form when 300-700 ml reagent has been added.}

Allow ppt. to settle 15 min.

Withdraw S.N. →

P-2 [Acetate S.N.]

4.20 L, 65°C		
2.77M	Na^+	(11.63)
0.50M	Ac^-	(2.11)
0.24M	HAc	(1.01)
0.12M	BrO_3^-	(0.52)
2.16M	NO_3^-	(9.06)
0.004M	La^{+3}	(0.02)
	1.40g Pu	

Extractor [Acetate Ppt., No Wash]

0.50 L S.N. 65°C^(k)		
2.77M	Na^+	(1.40)
0.50M	Ac^-	(0.25)
0.24M	HAc	(0.12)
0.12M	BrO_3^-	(0.06)
2.16M	NO_3^-	(1.07)
0.10 L Ppt. 65°C		
$NaPuO_2Ac_3$ (0.66)		
$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ = 0.3g		

+4.00 L [4.8M $NaNO_3$ (19.2), 0.2M NaAc (0.8) 0.35M HAc (1.40)] to Ext.

Suspend ppt. in wash solution.

Allow ppt. to settle 15 min.

Withdraw wash →

P-2 [Acetate 1st wash]

4.00 L, 65°C		
4.76M	Na^+	(19.02)
0.23M	Ac^-	(0.95)
0.34M	HAc	(1.35)
0.01M	BrO_3^-	(0.05)
4.50M	NO_3^-	(18.02)
	250mg Pu	

Extractor [Acetate Ppt. 1st wash]

0.50 L S.N. 65°C		
4.76M	Na^+	(2.40)
0.23M	Ac^-	(0.12)
0.34M	HAc	(0.17)
0.01M	BrO_3^-	(0.007)
4.50M	NO_3^-	(2.26)
0.10 L Ppt., 65°C $NaPuO_2Ac_3$ (0.66)		
$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ = 0.3g		

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Continued -

+4.00 L [4.8M $NaNO_3$ (19.2) 0.2M NaAc(0.8)
0.35M HAc (1.40)] to Ext.

Suspend ppt. in wash solution.

Allow ppt. to settle 15 min.

Withdraw wash →

P-2 [Acetate 2nd wash]

4.00 L, 65°C

4.97M	Na^+	(19.88)
4.76M	NO_3^-	(19.08)
0.35M	HAc	(1.42)
0.0015M	BrO_3^-	(0.006)
0.20M	Ac^-	(0.82)

250mg Pu

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Extractor [Acetate Ppt. After 2nd wash]

0.50 L S.N. 65°C		
4.97M	Na^+	(2.48)
4.76M	NO_3^-	(2.38)
0.35M	HAc	(0.17)
0.005M	BrO_3^-	(0.001)
0.20M	Ac^-	(0.10)

0.10 L Ppt. 65°C	
$NaPuO_2Ac_3$	(0.66)

+4.50 L [9.0M NH_4NO_3 (40.5) 2.2M HNO_3 (9.90)] to Ext.

$$\left\{\begin{array}{l} NaPuO_2Ac_3 + 3H^+ = PuO_2^{++} + Na^+ + 3HAc \\ H^+ + Ac^- = HAc \end{array}\right\}$$

+10M NH_4NO_3 to Ext. mark, ~0.4 L (4.00)

Cool Ext. to 10 to 15°C.

Extractor [Before Extraction]

5.5 L		
0.12M	PuO_2^+	(0.66)
0.59M	Na^+	(3.14)
10.32M	NO_3^-	(56.78)
8.09M	NH_4^+	(44.50)
0.41M	HAc	(2.25)
1.42M	H^+	(7.82)
0.0002M	BrO_3^-	(0.001)

$SnO_2 \cdot X H_2O$, $SiO_2 \cdot X H_2O$ = 0.3g

Heat Boiler

+Diethyl ether to Ext. (Run Extraction 3 hrs. keeping Boiler at 45-50°C. Wash Ext. walls with ether from wash ring after 1 hrs. extraction

$$\left\{\begin{array}{lll} 99.5\% & PuO_2(NO_3)_2 & \text{extracted} \\ 99\% & HNO_3 & \text{extracted} \\ 99\% & HAc & \text{extracted} \end{array}\right\}$$

Withdraw liquid from Ext.

Wash Ext. 1.675 L 1M HNO_3 (1.675)
0.175 L from Wash Ring
1.50 L from Ext. Res.

Withdraw wash

P-3 [Extraction Residue]

1.50 L
Ether
Br_2 (trace)

5.0 L		
0.02M	H^+	(0.08)
8.90M	NH_4^+	(44.50)
0.63M	Na^+	(3.14)
9.55M	NO_3^-	(47.72)
0.0002M	BrO_3^-	(0.001)
0.004M	HAc	(0.02)

$SnO_2 \cdot X H_2O$, $SiO_2 \cdot X H_2O$ = 0.3g

800 mg Pu

P-3 [Extractor Wash]

1.675 L		
1M	H^+	(1.675)
1M	NO_3^-	(1.675)

Traces NH_4^+, Na^+, BrO_3^-, Pu, etc.

[redacted]

Heat Boiler to 93°C and keep at 93°C for 0.5 hrs.

Cool Boiler to 15°C

[redacted]

Boiler [After Extraction]

2.50 L		
0.26M	PuO_2^{++}	(0.65)
3.10M	H^+	(7.74)
0.89M	HAc	(2.23)
3.62M	NO_3^-	(9.00)

+1.1 L 5.5M HI (6.05) to Boiler

Allow 20 min for reduction.

$\left\{ 2\,PuO_2^{++} + 9I^- + 8H^+ = 2Pu^{+3} + 3I_3^- + 4H_2O \right\}$
~30 Kcal heat liberated

Cool Boiler to 25°C

Boiler [After Reduction]

3.60 L		
0.18M	Pu^{+3}	(0.65)
3.11M	H^+	(11.19)
0.87M	I^-	(3.12)
0.27M	I_3^-	(0.98)
2.52M	NO_3^-	(9.06)
0.62M	NAc	(2.23)

+3.2 L 0.67M $H_2C_2O_4$ (2.14) to Boiler

Allow ppt. to form 20 min.

$2\,Pu^{+3} + 3H_2C_2O_4 = Pu_2(C_2O_4)_3 + 6H^+$

Allow ppt. to settle 15 min.

Withdraw S.N. ⟶

P-146 [2nd Ox. S.N.]

6.20 L		
1.96M	H^+	(12.16)
0.47M	I^-	(2.90)
0.15M	I_3^-	(0.90)
1.35M	NO_3^-	(8.37)
0.33M	HAc	(2.06)
0.17M	$H_2C_2O_4$	(1.07)

800 mg Pu

[redacted]

Boiler [2nd Ox. After 2nd wash]

0.50 L S.N.

0.11M	H^+	(0.055)
0.003M	I^-	(0.0015)
0.001M	I_3^-	(0.0005)
0.009M	NO_3^-	(0.0045)
0.003M	HAc	(0.0015)
0.10M	Cl^-	(0.05)
0.10M	$H_2C_2O_4$	(0.05)

0.10 L Ppt.

$Pu_2(C_2O_4)_3$(0.33)

+5.50 L H_2O to Boiler

Suspend ppt. in wash solution.

Allow ppt. to settle 15 min.

Withdraw wash →

Boiler [2nd Ox. After 3rd wash]

0.70 L S.N. (1)

0.009M	H^+	(0.006)
0.0003M	I^-	(0.0002)
0.0001M	I_3^-	(0.00007)
0.0008M	NO_3^-	(0.0006)
0.0003M	HAc	(0.0002)
0.008M	Cl^-	(0.006)
0.008M	$H_2C_2O_4$	(0.006)

0.10 L Ppt.

$Pu_2(C_2O_4)_3$ (0.33)

Transfer slurry to transfer bottle and return excess S.N. to Boiler →

Wash transfer tube with 0.1 L 12M HCl (1.20) →

P-146 [2nd Ox. 3rd Wash]

5.30L L

0.009M	H^+	(0.049)
0.0003M	I^-	(0.0013)
0.0001M	I_3^-	(0.0004)
0.0008M	NO_3^-	(0.004)
0.0003M	HAc	(0.0013)
0.008M	Cl^-	(0.04)
0.008M	$H_2C_2O_4$	(0.04)

160 g Pu

Transfer Bottle [Ox. Ppt. After Transfer]

0.30 L S.N.

0.009M	H^+	(0.001)
0.0003M	I^-	(0.00004)
0.0001M	I_3^-	(0.00002)
0.0008M	NO_3^-	(0.0001)
0.0003M	HAc	(0.00004)
0.008M	Cl^-	(0.001)
0.008M	$H_2C_2O_4$	(0.001)

0.10 L Ppt.

$Pu_2(C_2O_4)_3$ (.329) = 155.18 gms. Pu

P-146 [Transfer Tube wash]

0.10 L

12M	H^+	(1.20)
12M	Cl^-	(1.20)

Pu trace

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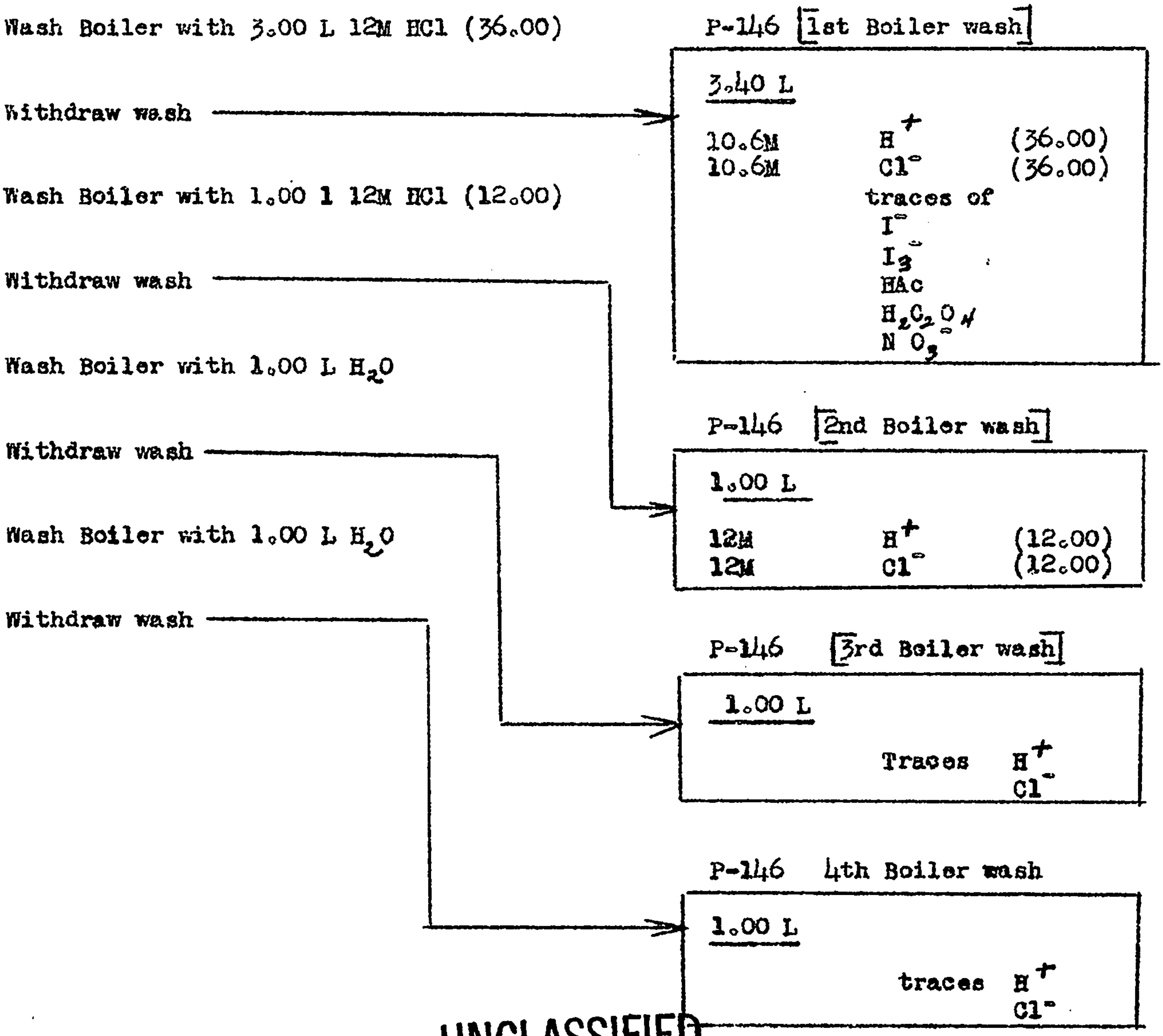

Wash Boiler with 3.00 L 12M HCl (36.00)

Withdraw wash

Wash Boiler with 1.00 l 12M HCl (12.00)

Withdraw wash

Wash Boiler with 1.00 L H_2O

Withdraw wash

Wash Boiler with 1.00 L H_2O

Withdraw wash

P-146 [1st Boiler wash]

3.40 L

10.6M	H^+	(36.00)
10.6M	Cl^-	(36.00)
	traces of	
	I^-	
	I_3^-	
	HAc	
	$H_2C_2O_4$	
	NO_3^-	

P-146 [2nd Boiler wash]

1.00 L

12M	H^+	(12.00)
12M	Cl^-	(12.00)

P-146 [3rd Boiler wash]

1.00 L

Traces H^+ Cl^-

P-146 4th Boiler wash

1.00 L

traces H^+ Cl^-

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STANDARD PROCEDURE A-8 RESIDUES

P-146

42.60 L

1.72M	H^+	(69.66)
0.0005M	Fe^{++}	(0.02)
0.0001M	Cr^{++}	(0.004)
0.00007M	Ni^+	(0.003)
0.008M	HSO_4^-	(0.31)
0.0002M	$N_2PO_4^-$	(0.007)
0.27M	NO_3^-	(10.88)
0.16M	I^-	(6.60)
0.01M	I_2^-	(1.65)
0.08M	$H_2C_2O_4$	(3.37)
0.05M	HAc	(2.22)
1.24M	Cl^-	(50.30)

Pu ≅ 2120 mg (0.009) 0.0002M

P-3

1.50 L $(C_2H_5)_2O$

6.675 L

0.26M	H^+	(1.76)
6.66M	NH^+	(44.50)
0.47M	Na^+	(3.15)
7.38M	NO_3^-	(49.40)
0.0002M	BrO_3^-	(0.001)
0.003M	HAc	(0.02)

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ ≅ 0.3g

Pu ≅ 800 mg (0.003) 0.0006M

Evaporated ether in stream of air in hood

6.675 L

0.26M	H^+	(1.76)
6.66M	NH_4^+	(44.50)
0.47M	Na^+	(3.14)
7.38M	NO_3^-	(49.40)
0.0002M	BrO_3^-	(0.001)
0.003M	HAc	(0.02)

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ ≅ 0.3g

Pu ≅ 800 mg (0.003)--0.0006M

P-5 Acid Bubbler (f)

1.70 L

0.88M	H^+	(1.50)
0.88M	NO_3^-	(1.50)

Pu ~1mg

P-9 Alkaline Bubbler (i)

1.50 L.

4.50M	Na^+	(6.75)
0.73M	$SO_3^=$	(1.09)
0.27M	$SO_4^=$	(0.41)
0.55M	Br^-	(0.82)
0.60M	$CO_3^=$	(0.90)
0.77M	HCO_3^-	(1.16)

P-2

12.20 L

4.14M	Na^+	(50.53)
0.32M	Ac^-	(3.88)
0.31M	HAc	(3.78)
0.05M	BrO_3^-	(0.58)
3.78M	NO_3^-	(46.16)
0.002M	La^{+3}	(0.02)

Pu ≅ 1900 mg (0.004) 0.0003M

+0.50 L 16M HNO_3(8.00)

12.70 L

0.32M	H^+	(4.12)
3.98M	Na^+	(50.53)
0.60M	HAc	(7.66)
0.05M	BrO_3^-	(0.58)
4.27M	NO_3^-	(54.16)
0.002M	La^{+3}	(0.02)

Pu ≅ 1900 mg (0.004) 0.0003M

[redacted]

STANDARD PROCEDURE A-8 REAGENTS

Amount per Run

Reagent	Volume (liters)	Density (g/cc)	Gram Moles
H_2O	19.375	0.997	
HNO_3, 1 M(a)	3.700	1.032	3.70
HNO_3, 10 M	0.300	1.295	3.00
HNO_3, 16 M	0.500	1.418	8.00
HCl, 12 M	4.100	1.178	49.20
HI, 5.5 M	2.100	1.50	11.55
$H_2C_2O_4$, 0.67M	6.400	1.027	4.288
$H_2C_2O_4$, 0.1 M HCl, 0.1 M	11.000	1.005	1.10 1.10
NH_4NO_3, 9.0M HNO_3, 2.2M	4.500	1.320	40.50 9.90
NH_4NO_3, 10 M	0.400	1.294	4.00
$NaBrO_3$, 1.54 M	0.900	1.171	1.386
NaAc, 2.75M $NaNO_3$, 3.40M	2.000	1.260	5.50 6.80
$NaNO_3$, 4.45 M NaAc, .55M HNO_3, .35M	8.000	1.255	35.60 4.40 2.80
NaOH, 2.50 M Na_2SO_3, 1.00 M	1.500	1.200	3.75 1.50
Diethyl Ether.(a)	3.20 L	0.71	------
Total Aq. Solutions	67.975	------	------

[redacted]

STANDARD PROCEDURE A-8 REAGENTS

Amount per Run

Reagent	Gram Moles	Mol. Wt.	Grams	Pounds
HNO_3, 70% $^{(m)}$	27.40	63.0	1726	3.81
HCl, 38%	50.30	36.5	1836	4.05
HI, 47%	11.55	127.9	1477	3.26
$H_2C_2O_4 \cdot 2H_2O$	5.388	126.1	679	1.50
NH_4NO_3	44.50	80.05	3562	7.85
$NaBrO_3$	1.386	150.9	209	0.46
$NaAc \cdot 3H_2O$	9.90	136.1	134.74	0.30
NaOH	3.75	40.0	150.00	0.33
$NaNO_3$	42.40	85.0	3604	7.95
Na_2SO_3	1.50	126	189	0.42
$(C_2H_5)_2O^{(n)}$	-----	-----	-----	5.00

[redacted]

Standard Procedure A-8

Notes:

(a) A number in parenthesis following the formula of an ion or compound represents the number of gram moles of the ion or compound.

(b) It is believed that the process can handle a charge containing from 140 to 170g of Pu without the conditions being sufficiently changed to cause abnormal losses.

The form of the Pu when it is received is rather uncertain. After solution, spectrophotometric analysis has shown the Pu to be about half in the $+6$ oxidation state and about half in the $+4$ oxidation state. When the solution is allowed to stand the amount of Pu in the $+6$ state decreases, so it appears that the $+6$ state is not formed by dismutation of the $+4$ state after the slurry is dissolved. Because of its chemical similarity to UO_2^{++} the $+6$ state of Pu is assumed to be PuO_2^{++}. The $+4$ state is assumed to be PuO^{++} only because assuming this form helps explain the apparent loss of H^+ during the oxidation in the "B" procedure and during the first reduction in "A" procedure.

(c) The amount H^+ present is very uncertain. The amount stated in the flow sheet (0.48) moles of free H^+) is calculated from the arbitrary assumption that the slurry received from W is 1M in total available H^+. The solution could be as low as 0.30 moles of free H^+ if there were no available H^+ in the slurry and as high as 1.40 moles if the molecular weight of the plutonium nitrate were 500 and the remaining weight of the slurry was due to 70% HNO_3.

[redacted]

(d) The amounts of impurities listed give high averages of the impurities found in Hanford material processed in Bldg. D. The table below gives the ranges through which the impurities have fluctuated.

Impurity	high (g)	low (g)
Fe	4.	0.4
Cr	0.6	0.06
Ni	0.4	0.04
La	16.	0.1
$SO_4^=$	48.	16.
$PO_4^{\equiv}$	1.	0.3
Solids	1.	0.05

(e) Sufficient HI is added to properly reduce the Pu even if it were all in the $+6$ oxidation state.

(f) The oxalate precipitate usually settles to a volume of 300 to 500 ml and 100 to 200 ml of supernatant is left over the precipitate. Here it is assumed that 600 ml of precipitate plus supernatant is left in the reactor and that the actual volume occupied by the precipitate is 100 ml. This volume would predict a density of the oxalate with ten waters of hydration of 3g/cc, which is reasonable.

(g) The equations written for the oxidation are not known to be correct. It is quite possible the NO_3^- plays some part in the oxidation for the color of the oxalate precipitate has been observed to change color on the addition of the 10M HNO_3.

The purpose of the bubbler is to remove from the reactor and absorb the Br_2, CO_2, H_2O vapor and any Pu carried in the spray. The acid bubbler absorbs most of the H_2O and Pu in a solution from which the Pu may be recovered. The alkaline bubbler absorbs the Br_2, and CO_2 and

[redacted]

remaining traces of Pu. Air is pulled through the bubbler by means of a mechanical pump.

The usual amount of H_2O evaporated during the oxidation is about 200 ml but may be much more if the solution is allowed to boil (about 96°C at an elevation of 7500 ft.)

Probably very little BrO_3^- decomposes since the H^+ concentration is reduced to less than 1M before the temperature reaches 93°C.

(h) The acid bubbler need not be changed every run. It need be changed only when condensed H_2O from the oxidation increases the volume sufficiently to interfere with the operation of the bubblers.

(i) The alkaline bubbler needs to be changed every run.

(j) Ac^- refers to the Acetate ion ($C_2H_5O_2^-$).

(k) The $NaPuO_2\,Ac_3$ precipitate usually settles to a volume of 300 to 500 ml and 100 to 200 ml of supernatant is left over the precipitate. Here it is assumed that 600 ml of precipitate plus supernatant is left in the reactor and that the actual volume occupied by the precipitate is 100 ml. This volume would predict a density of 3g/cc for the $NaPuO_2Ac_3$, which is reasonable (density of $NaUO_2Ac_3$ = 2.6g/cc)

(l) When a clean transfer bottle is used the flow sheet is accurate. When a transfer bottle which has not been cleaned is returned by Dry Conversion (normal procedure) it will contain 150 ml of solution plus precipitate. Therefore a volume of only 650 ml should be left in the boiler for the transfer. This means that 150 ml more of this last wash solution will

[redacted]

go into P-146 and only 550 ml of supernatant will be left in the boiler with the precipitate.

(m) About 0.65L of 1M HNO_3 (0.65) is used in the cut operation and is not included in the figures given in the table. Figure given in the table allow for changing the bubblers after every run.

(n) The amount of ether used can be variable. In a tight system only 1.5 to 2.0 L are used. If a system leaks, as much as 15L have been used. It is assumed here that one 5-lb can of ether is used per run.

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STANDARD PROCEDURE A-8

Operating Instructions

Boron Can No.	Bottle No.	Lot No.	Wgt. Soln.	Pu Assay gms. Pu Radio	Chem.

General Instructions

1. Operators initial procedure at beginning and end of shift.

2. Leave reagent reservoir tube in reagent bottle after reagent has been drawn into reservoir until ready to use next reagent.

3. Gloves, masks and coveralls must be worn during entire process. Face shields must be worn during ether extraction and while handling ether.

4. Do not move plutonium out of space unit without permission of Quantity Control.

Procedure

Step

0. Check controls (use check list attached). Request Boron Can from Quantity Control.

1. Add 2L H_2O to boiler.

2. Turn reservoir stopcock to off.

3. Turn coolant into extractor jacket.

4. Transfer product to reservoir and add to extractor.

5. Turn reservoir stopcock to off.

6. With vac on reservoir, wash product bottle with 200 ml 1M HNO_3. Transfer wash to extractor, with extractor stirrer [illegible] slowly.

[redacted]

7. Turn reservoir stopcock to off.

8. When extractor temp. ≅ 20°C, turn coolant off.

9. Transfer 1.0L 5.5M HI to reservoir.

10. Add HI to extractor.

11. Operators change gloves.

12. Allow 20 min from time of addition of HI, for reduction.

13. Transfer 3.2L 0.67M $H_2C_2O_4$ to reservoir.

14. Connect extractor supernatant tube to P-146 bottle.

15. After 20 min. reduction time, add $H_2C_2O_4$ to reservoir.

16. Turn reservoir stopcock to off.

17. After $H_2C_2O_4$ is in, burp extractor supernatant line to agitate, and stir for 20 min.

18. Transfer 4.5L H_2O to reservoir.

19. After solution has been stirred 20 min, stop stirrer and allow ppt. to settle 5 min. Blow out supernatant tube and allow to settle 10 min more.

20. After ppt. has settled for 15 min set supernatant tube 100 ml above ppt. (~600 ml) and suck supernatant into P-146.

21. Rack supernatant tube up when supernatant is over.

22. Close pinchcock on extractor supernatant line and open pinchcock on extractor "burper" line.

23. Add water to extractor. Start stirrer when 1 liter H_2O is in.

24. Close reservoir stopcock.

25. Stop stirrer, allow ppt. to settle for 5 min, blow out supernatant line, and allow ppt. to settle for 10 min more.

26. Transfer 4.5 liters of H_2O to reservoir.

27. Open extractor supernatant line pinch clamp and close extractor "burper" line.

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28. When ppt. has settled for 15 min, set supernatant tube 100 ml above ppt.(~800 ml) and suck supernatant into P-146.

29. Back supernatant tube up, close extractor supernatant line pinch clamp and open extractor "burper" pinch clamp.

30. Add water to extractor. Start stirrer when 1 liter H_2O is in.

31. Repeat 23 to 28 inclusive, omitting 25.

32. Transfer 300 ml 10M HNO_3 to reservoir.

33. Add acid to extractor.

34. Close reservoir stopcock.

35. Transfer 900 ml 1.54M $NaBrO_3$ to reservoir.

36. Add $NaBrO_3$ to extractor.

37. Close reservoir stopcock.

38. Start extractor stirrer, turn extractor steam on and start circulating pump.

39. When extractor temp = 50°C, turn steam off.

40. Allow temp. to rise to 75°C and hold at 75°C until ppt. has dissolved.

41. When ppt. has dissolved add 375 ml M HNO_3 through wash ring, raise temp. to 91°C and hold at 91°C for 1 hour.

42. After heating for 1 hour at 91°C, dilute to 2.8 liters and adjust temp. to 65°C.

43. Transfer 2.00 liters 2.75M NaAc, 3.4M $NaNO_3$ to reservoir.

44. Add solution, with stirring, to extractor, add a rate of 50 ml per/min. or less. (Permanent ppt. should form at 300 to 700 ml).

45. Turn reservoir stopcock to off.

46. Continue stirring 5 min after reagent is in.

47. Stop stirrer, allow ppt. to settle for 5 min, blow out supernatant line, allow ppt. to settle 10 min, more.

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48. Transfer 4.00 liter 4.8M $NaNO_3$, 0.2M NaAc, 0.35M HAc to reservoir.

49. Change supernatant bottle from P-146 to P-2

50. When ppt. has settled 15 min, open supernatant line pinch clamp, close extractor "burper" pinch clamp, set supernatant tube 100 ml above ppt. and suck supernatant into P-2.

51. Close supernatant line pinch clamp, open extractor "burper" pinch clamp.

52. Add solution from reservoir to extractor.

53. Keep temperature of extractor at 65°C during washing of ppt.

54. When 1 liter of solution has been added, start stirrer. Stir for 5 min after solution is in.

55. Allow ppt. to settle 5 min and blow out supernatant line. Allow ppt. to settle 10 min more.

56. Transfer 4.0 liters of 4.8M $NaNO_3$, 0.2M NaAc, 0.35M HAc to reservoir.

57. Repeat 49 to 54 inclusive.

58. Repeat 49.

59. Close the supernatant line pinch clamp and open the extractor "burper" pinch clamp.

60. Transfer 4.50 liters of 9.0M NH_4NO_3, 2.2M HNO_3 to reservoir.

61. Turn coolant into condenser, and extractor.

62. Add solution to extractor. Start stirrer when 1 liter has been added.

63. Turn reservoir stopcock to off.

64. Transfer sufficient 10M NH_4NO_3 to reservoir to dilute extractor to 5.6 liters.

65. Add NH_4NO_3 to extractor.

66, Turn reservoir stopcock off.

67. When extractor is 15°C or less turn coolant and pump off.

68. Turn Br_2 bubbler off.

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69. Turn steam into boiler and pump on.

70. Turn extractor stirrer off and fill ether reservoir, turn extractor and boiler stirrers on.

71. When boiler temperature is 50°C or greater, add ether to extractor until ether runs through extractor side arm.

72. Bleed ether (continuously or in spurts) to keep boiler temperature between 45°C to 50°C.

73. After extraction has run one hour blow out extractor supernatant tube.

74. After extraction has run two hours blow out extractor supernatant tube and wash extractor walls down with ether from wash ring.

75. Change supernatant bottle from P-2 to P-3.

76. Open extractor supernatant pinch clamp and close extractor "burper" pinch clamp.

77. When extraction has run three hours, suck H_2O into P-3.

78. Turn I_2 bubbler on and maintain boiler at 93°C for 30 min.

79. Transfer 1.5 liters of M HNO_3 to reservoir.

80. Add HNO_3 to extractor.

81. Turn reservoir stopcock off.

82. Wash walls of extractor with 175 ml M HNO_3 from wash ring.

83. Suck acid from extractor with P-3.

84. Remove P-3 to hood, blow air over surface to evaporate ether.

85. When boiler has been heated for 30 min turn off steam and turn on coolant. Cool boiler to 15°C.

86. Transfer 1.1 liters of 5.5M HI to reservoir.

87. When boiler is 15°C add HI, and stir for 20 min.

88. Turn reservoir stopcock to off.

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89. When boiler is 20° to 25°C turn coolant and pump off.

90. Transfer 3.2 liters of 0.67M $H_2C_2O_4$ to reservoir.

91. After stirring HI solution 20 minutes, add $H_2C_2O_4$.

92. When $H_2C_2O_4$ has been added, close reservoir stopcock, work boiler "burper" approx. 20 times, and stir for 20 minutes.

93. After stirring 20 minutes, stop stirrer, allow ppt. to settle 5 min, blow out boiler supernatant line, and allow to settle for 10 min more.

94. Attach P-146 to boiler supernatant line.

95. Transfer 5.5 liters of 0.1M $H_2C_2O_4$, 0.1M HCl to reservoir.

96. When ppt. has settled for 15 min open boiler supernatant pinch clamp, close boiler "burper" pinch clamp, set supernatant tube 100 ml. above ppt. and withdraw supernatant into P-146.

97. Rack supernatant tube up, close supernatant line pinch clamp, open boiler "burper" pinch clamp, add wash to boiler.

98. After 1 liter of wash has been added, start stirrer. Stir for 5 min after wash has been added. Close reservoir stopcock.

99. Stop stirrer, allow ppt. to settle for 5 min blow out supernatant line, and allow to settle for 10 min more.

100. Transfer 5.5 liters of 0.1M $H_2C_2O_4$, 0.1M HCl to reservoir.

101. Repeat 95 to 98 inclusive.

102. Transfer 5.5 liters H_2O to reservoir.

103. Repeat 95 to 98.

104. When ppt. has settled for 15 minutes, open boiler supernatant pinch clamp, close "burper" pinch clamp, set supernatant tube at 800 ml and suck supernatant into P-146.

105. Rack supernatant tube up.

106. Disconnect boiler supernatant line and connect transfer bottle.

107. Suspend ppt. in supernatant. With stirrer running suck slurry into transfer bottle.

[redacted]

108. Allow ppt. to settle for 2 - 3 minutes in transfer bottle, tap bottle to pack ppt. Blow supernatant back into boiler.

109. Repeat 106 and 107 four times.

110. On last pass allow ppt. to settle in transfer bottle for 15 minutes before returning supernatant to boiler. Leave calcm. of supernatant over ppt. in transfer bottle.

111. Remove storage bottle and leucite liner to boron can. Notify Quantity Control that batch is ready for transfer to storage.

112. Wash transfer tube with 100 ml 12M HCl, into P-146.

113. Transfer 3.0 liters of 12M HCl to reservoir.

114. Add acid to boiler.

115. Close reservoir stopcock.

116. Stir for 2 to 3 minutes or until remaining ppt. has dissolved.

117. Suck acid with P-146.

118. Transfer 1.0 liter of 12M HCl to reservoir.

119. Add acid to boiler.

120. Close reservoir stopcock.

121. Stir for 2 to 3 minutes.

122. Suck acid with P-146.

123. Transfer 1.0 liter H_2O to reservoir.

124. Add H_2O to boiler.

125. Stir for 2 to 3 minutes.

126. Suck H_2O into P-146.

127. Transfer 1.0 liter H_2O to reservoir.

128. Add H_2O to boiler.

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129. Stir for 2 to 3 minutes.

130. Suck H_2O into P-146.

131. Remove supernatants, P-146, P-2 & P-3 to supernatant cut room.

132. Add 0.5 liters 16M HNO_3 to P-2, stir throughly.

133. Take ca/ml cut from each solution into a 10-mm test tube, marked with batch number and supernatant no. Seal test tubes with parafilm.

134. Transfer supernatants to Recovery. Obtain a temporary receipt for difference between W-Site assay and 140g.

135. Check and decontaminate room.

136. Oil motors and bearings. Grease stopcocks. Put glycerine in transfer head slide.

137. Drain alkaline bubbler into P-9, transfer to Recovery with no receipt or assay.

138. Refill reagent bottles.

[redacted]

[redacted]

Several minor modifications of the A procedure were adopted from time to time. These changes, designated A-1 to A-9 served to make the basic A procedure easier to operate. The details of the A-8 procedure are given in the flow sheet. The essential differences between the A-8 and earlier modification are given below.

Procedure A-1 Same as A-8 except:--

(1) Volume initial Pu solution 1.2 liters. (A-8,-0.8 liters)

(2) Storage bottle washed with 400 ml. 6M KI and 200 ml M HNO_3, and wash added to extractor. (A-8 -- Storage bottle washed with 200 ml M HNO_3 and added to extractor. One liter 5.5M HI added directly to extractor).

(3) Volume in extractor after oxidation 3.1 liter (A-8 2.8 liters)

(4) Sodium plutonyl acetate precipitant:--1.7 liters of 3.24 M NaAc and 4.00M $NaNO_3$. (A-8--2.00 liters of 2.75M $NaNO_3$ and 3.40M $NaNO_3$).

(5) Ether extraction at room temperature ~22°C (A-8 extraction at 10° to 15°C.)

(6) Reduction after extraction with 800 ml 7.5M HI (A-8, 1.1 liters 5.5M HI)

(7) Boiler wash, after transfer of Pu (III) oxalate:- 100 ml 12M HCl (to wash transfer tube), 500 ml 12M HCl, 2 - 1 liter portions of water (A-8, 100 ml 12M HCl, 3 liters 12M HCl, 1 liter 12M HCl, 2 - 1 liter portions of water.)

(8) Supernatant solutions were not combined, designation as follows:--

P-1 Supernatant and washes from 1st. oxalate precipitate, treated with 1 liter 12N HCl.

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P-2	Supernatant and washes from sodium plutonyl acetate precipitate, treated with 0.5M liters 16M HNO_3.
P-3	Ether extraction aqueous residue. Plus 1.68 liters of M HNO_3 used as extractor wash.
P-4A	Supernatant and 1st. wash of 2nd. oxalate precipitate, treated with 1 liter of 12M HCl.
P-4B	Second and 3rd wash of 2nd. oxalate precipitate, treated with 0.5 liter of 12M HCl.
P-5	Acid bubbler residue.
P-6	Boiler supernatant tube and boiler wash.
P-9	Alkaline bubbler residue.

Procedure A-2, Same as A-1 except:-

(1) Solution after oxidation was diluted to 2.8 liters, instead of 3.1 liters.

(2) Sodium plutonyl acetate was precipitated with 2.0 liters of 2.75M NaAc, 3.40M $NaNO_3$ instead of 1.7 liters 3.24M NaAc, 4.0M $NaNO_3$.

(3) Final reductant was 1.1 liters of 5.5M HI instead of 0.8 liters of 7.5M HI. The sodium plutonyl acetate precipitant was changed (2) because it was found that the precipitate formed by addition of a more dilute precipitant had better settling properties.

The change in volume of solution after oxidation (1) was necessary in order that the larger volume of acetate precipitant (2) not make the total volume of solution greater than the capacity of the vessel.

The change in HI volume and concentration (3) was because of a change in brand of reagent used.

Procedure A-3, Same as A-2 except:-

(1) Residues P-1, P-4A, P-4B, and P-6 were combined and called P-146. These residues were combined in order to facilitate recovery processing.

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Procedure A-4, Same as A-3 except:-

(1) One liter of 5.5M HI was used as first reductant rather than KI.

This change eliminated the introduction of potassium ion and also insured sufficient H^+ for the reduction should these be appreciable Pu (VI).

Procedure A-5, Same as A-4 except:-

(1) The extractor was washed first with 1.5 liters 10M HNO_3, then with 180 ml M HNO_3, instead of 1.68 liters of M HNO_3.

(2) The boiler was washed first with 3 liters 12M HCl. then with 1 liter 12M HCl, instead of 500 ml 12M HCl.

(3) No acid was added to P-146.

These changes provided more adequate washing of both the boiler and extractor. The increase in acid wash to boiler eliminated the need of acidifying, P-146.

Procedure A-6, Same as A-5 except:-

(1) Nitric acid was substituted for HCl throughout the process.

This change allowed the combination of all residues, in recovery, and anticipated the change from D building operations to D.P. site, where stainless lines prohibited the use of HCl.

Procedure A-7, Same as A-5 except:-

(1) During extraction 10M NH_4NO_3 (~1.5 liters) was bled into extractor to keep the volume of the aqueous phase constant.

This change made for faster extraction.

Procedure A-8,

Details given into flow sheets, pages 21 to 32.

Procedure A-9, Same as A-8 except:-

(1) Nitric acid was substituted for HCl throughout the process.

STANDARD PROCEDURE B-2
FLOW SHEETS

Add 2.00L H_2O to Boiler

Add product to extractor

Extractor [Initial Product]

0.80L

0.42M	PuO^{++}	(0.34)[a]	≅ 160g Pu[b]
0.41M	PuO_2^{++}	(0.33)	
0.22M	H^+	(0.18)[c]	
0.03M	Fe^{+++}	(0.02)	≅ 1.0g[d]
0.005M	Cr^{+++}	(0.004)	≅ 0.2g
0.004M	Ni^{++}	(0.003)	≅ 0.2g
0.03M	La^{++}	(0.02)	≅ 3.0g
0.39M	HSO_4^-	(0.31)	≅ 30.0g
0.009M	$H_2PO_4^-$	(0.007)	≅ 0.7g
1.67M	NO_3^-	(1.34)	

SnO ·X H O, SiO ·H O ≅ 0.3g

Wash storage bottle with 0.20L 1M HNO_3, (0.20) add to Ext.

Add 0.10L 10M HNO_3 (1.00)

0.30L 1.54M $NaBrO_3$ (0.46) to Ext.

Heat Ext. to 93°C, keep at 93°C for 1 hr.

$$\left.\begin{cases} 5PuO^{++} + 2BrO_3^- + 2H^+ = 5\ PuO_2^{++} + Br_2 + H_2O \\ 4BrO_3^-\ (0.10) + 4H^+ = 2\ Br_2 + 5O_2 + 2H_2O \\ 10Cr^{+++} + 5BrO_3^- + 17H_2O = 5Cr_2O_7^{=} + 34H^+ + 3Br_2 \end{cases}\right\} (e)$$

$H_2O\ (l) \longrightarrow H_2O_{(g)}$ [0.20L H_2O (l) evap.]

Cool Ext. to 25°C.

Br_2 (0.12)
O_2 (0.13)
H_2O 0.20L

Acid Bubbler[f]

1.50L Before Oxid.			1.70L After Oxid.		
1.00M	H^+	(1.50)	0.88M	H^+	(1.50)
1.00M	NO_3^-	(1.50)	0.88M	NO_3^-	(1.50)
			~1mg Pu		

$Br_2 + SO_3^{=} + 2OH^- \longrightarrow 2Br^- + SO_4^{=} + H_2O$

Alkaline Bubbler

1.50L Before Oxid.			1.50L After Oxid.		
4.50M	Na^+	(6.75)	4.50M	Na^+	(6.75)
2.50M	OH^-	(3.75)	0.92M	$SO_3^{=}$	(1.38)
1.00M	$SO_3^{=}$	(1.50)	2.34M	OH	(3.51)
			0.08M	$SO_4^{=}$	(0.12)
			0.16M	Br^-	(0.24)

[redacted]

Extractor [After Oxidation]

<u>1.20L</u>

0.56M	PuO_2^{++}	(0.67)
0.96M	H^+	(1.13)
0.38M	Na^+	(0.46)
0.02M	Fe^{+3}	(0.02)
0.002M	Ni^{++}	(0.003)
0.02M	La^{+++}	(0.02)
0.26M	HSO_4^-	(0.31)
0.006M	$H_2PO_4^-$	(0.007)
0.002M	$Cr_2O_7^=$	(0.002)
2.12M	NO_3^-	(2.54)
0.18M	BrO_3^-	(0.21)

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot XH_2O \cdot 3$g

Add 5.0M $Ca(NO_3)_2$ to Ext. mark ~4.15L (20.75)

Add 0.1 L 10M HNO_3 (1.00) to Ext.

Add 0.05L H_2O to Ext.

Cool to 15°C

Extractor [Before Extraction]

<u>5.5L</u>

0.12M	PuO_2^{++}	(0.67)
0.44M	H^+	(2.44)
0.08M	Na^+	(0.46)
3.72M	Ca^{++}	(20.44)
0.004M	Fe^{+++}	(0.02)
0.0005M	Ni^{++}	(0.003)
0.004M	La^{+++}	(0.02)
0.001M	$H_2PO_4^-$	(0.007)
0.0004M	$Cr_2O_7^=$	(0.002)
8.18M	NO_3^-	(45.04)
0.04M	BrO_3^-	(0.21)

$CaSO_4$----(0.81)

$SnO_2 \cdot S\ H_2O$, $SiO_2 \cdot X\ H_2O$ 0.3g

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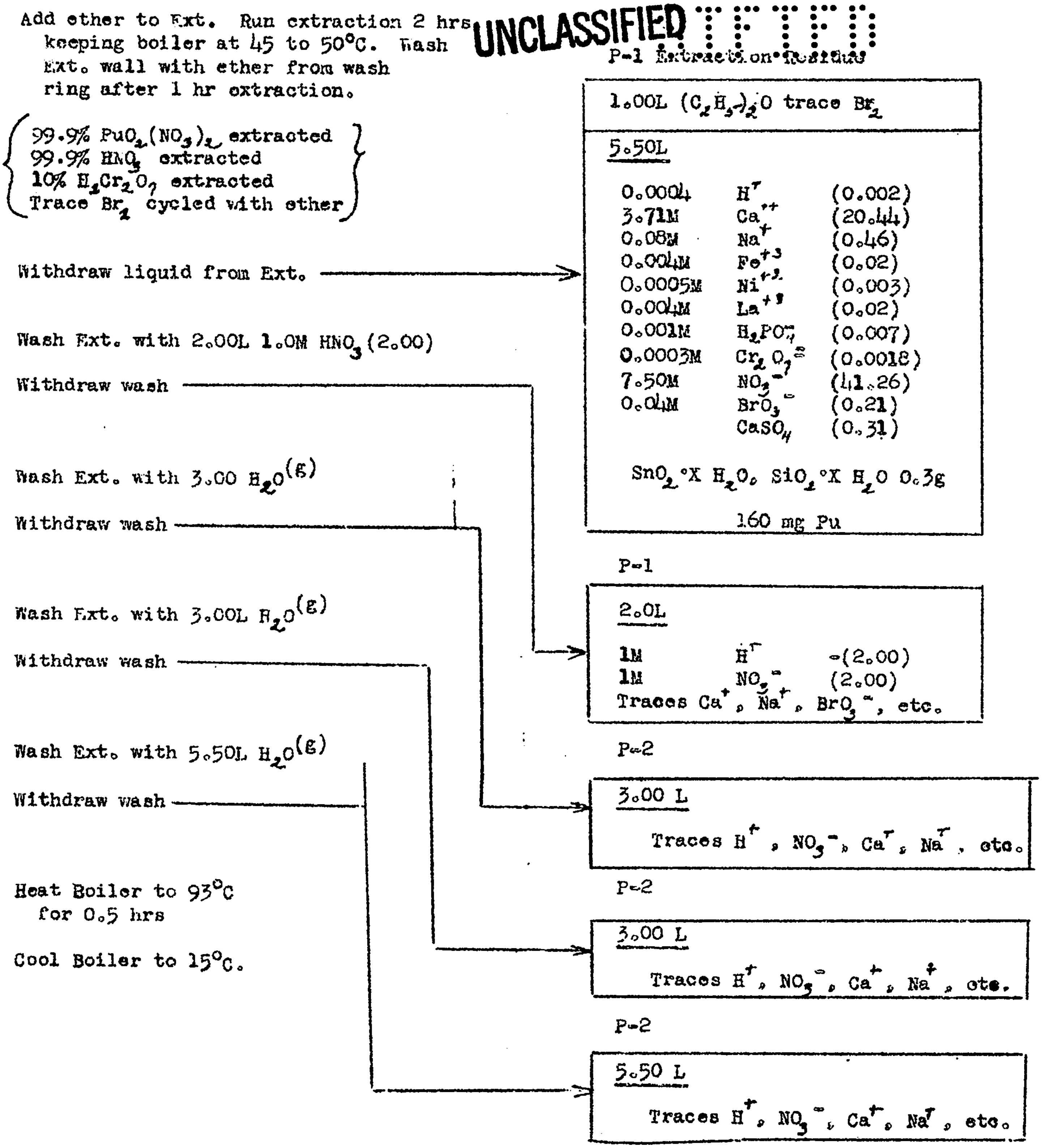

Add ether to Ext. Run extraction 2 hrs keeping boiler at 45 to 50°C. Wash Ext. wall with ether from wash ring after 1 hr extraction.

99.9% $PuO_2(NO_3)_2$ extracted
99.9% HNO_3 extracted
10% $H_2Cr_2O_7$ extracted
Trace Br_2 cycled with ether

Withdraw liquid from Ext.

P-1 Extraction Residue

1.00L $(C_2H_5)_2O$ trace Br_2

5.50L

0.0004	H^+	(0.002)
3.71M	Ca^{++}	(20.44)
0.08M	Na^+	(0.46)
0.004M	Fe^{+3}	(0.02)
0.0005M	Ni^{+2}	(0.003)
0.004M	La^{+3}	(0.02)
0.001M	$H_2PO_4^-$	(0.007)
0.0003M	$Cr_2O_7^{=}$	(0.0018)
7.50M	NO_3^-	(41.26)
0.04M	BrO_3^-	(0.21)
	$CaSO_4$	(0.31)

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ 0.3g

160 mg Pu

Wash Ext. with 2.00L 1.0M HNO_3 (2.00)

Withdraw wash

P-1

2.0L

1M	H^+	(2.00)
1M	NO_3^-	(2.00)

Traces Ca^+, Na^+, BrO_3^-, etc.

Wash Ext. with 3.00 $H_2O^{(g)}$

Withdraw wash

P-2

3.00 L

Traces H^+, NO_3^-, Ca^+, Na^+, etc.

Wash Ext. with 3.00L $H_2O^{(g)}$

Withdraw wash

P-2

3.00 L

Traces H^+, NO_3^-, Ca^+, Na^+, etc.

Wash Ext. with 5.50L $H_2O^{(g)}$

Withdraw wash

P-2

5.50 L

Traces H^+, NO_3^-, Ca^+, Na^+, etc.

Heat Boiler to 93°C for 0.5 hrs

Cool Boiler to 15°C.

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Boiler [After Extraction]

2.00 L		
0.34M	PuO_2^{++}	(0.67)
1.22M	H^+	(2.44)
1.89M	NO_3^-	(3.78)
0.0001M	Cr_2O_7	(0.0002)

Add 1.10 L 5.5M HI(6.05) to Boiler

Allow 20 min for reduction

$$\left\{\begin{array}{l}2PuO_2^{++} + 9I^- + 8H^+ \longrightarrow 2Pu^{+3} + 3I_3^- \pm 4H_2O \\ Cr_2O_7 + 9I^- + 14H^+ \longrightarrow 2Cr^{+3} + 3I_3^- + 7H_2O\end{array}\right\}$$

~30 KCal. heat liberated

Cool Boiler to 25°C.

Boiler [After reduction]

3.10 L		
0.21M	Pu^{+3}	(0.67)
1.87M	H^+	(5.81)
1.22M	NO_3^-	(3.78)
0.0001M	Cr^{+3}	(0.0004)
0.98M	I^-	(3.03)
0.33M	I_3^-	(1.01)

Add 3.2 L 0.67M $H_2C_2O_4$(2.14) to Boiler

$$\left\{2Pu^{+3} + 3H_2C_2O_4 \longrightarrow Pu_2(C_2O_4)_3 + 6H^+\right\}$$

Allow ppt. to form 20 min.

Allow ppt. to settle 15 min.

With S.N. ⟶

P-3 [Oxalate S.N.]

5.70 L		
1.26M	H^+	(7.20)
0.00005M	Cr^{+3}	(0.0003)
0.49M	I^-	(2.78)
0.16M	I_3^-	(0.94)
0.61M	NO_3^-	(3.48)
0.18M	$H_2C_2O_4$	(1.05)
	840 mg Pu	

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Boiler [Oxalate ppt., no wash]

0.60 L total(h)
0.50 L S.N.

1.26M	H^+	(0.63)
0.49M	I^-	(0.25)
0.16M	I_3^-	(0.08)
0.61M	NO_3^-	(0.30)
0.18M	$H_2C_2O_4$	(0.09)

0.1 L

$Pu_2(C_2O_4)_3$ (0.33)

Add 5.50 L 0.1M $H_2C_2O_4$ (0.55)
0.1M HNO_3 (0.55)
to Boiler

Suspend ppt. in wash solution

Allow ppt. to settle 15 min.

Withdraw wash →

P-3 [Oxalate 1st wash]

5.50 L

0.20M	H^+	(1.08)
0.04M	I^-	(0.24)
0.01M	I_3^-	(0.07)
0.14M	NO_3^-	(0.78)
0.11M	$H_2C_2O_4$	(0.60)

200 mg Pu

Boiler Oxalate ppt. after 1st wash

0.60 L total
0.50 L S.N.

0.20M	H^+	(0.10)
0.04M	I^-	(0.02)
0.01M	I_3^-	(0.01)
0.14M	NO_3^-	(0.07)
0.11M	$H_2C_2O_4$	(0.05)

0.10 L

$Pu_2(C_2O_4)_3$ (0.33)

Add 5.50 L 0.1M $H_2C_2O_4$ (0.55)
0.1M HNO_3 (0.55)
to Boiler

Suspend ppt. in wash solution

Allow ppt. to settle 15 min.

Withdraw wash →

P-3 [Oxalate, 2nd wash]

5.50 L

0.11M	H^+	(0.61)
0.003M	I^-	(0.018)
0.002M	I_3^-	(0.009)
0.10M	NO_3^-	(0.57)
0.10M	$H_2C_2O_4$	(0.55)

200 mg Pu

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Boiler [Oxalate ppt. after 2nd wash]

0.60 L total

0.50 S.N.

0.11M	H^+	(0.05)
0.003M	I^-	(0.002)
0.002M	I_3^-	(0.001)
0.10M	NO_3^-	(0.05)
0.10M	$H_2C_2O_4$	(0.05)

0.10 L

$Pu_2(C_2O_4)_3$ (0.33)

Add 5.50 L H_2O to Boiler

Suspend ppt. in wash solution

Allow ppt. to settle 15 min.

Withdraw wash

P-3 [Oxalate 3rd wash]

5.30 L

0.008M	H^+	(0.04)
0.0003M	I^-	(0.0017)
0.0002M	I_3^-	(0.00088)
0.008M	NO_3^-	(0.04)
0.008M	$H_2C_2O_4$	(0.04)

100 mg Pu

Boiler [Oxalate ppt. after 3rd wash]

0.80 L total

0.70 L SN

0.008M	H^+	(0.01)
0.0003M	I^-	(0.0003)
0.0002M	I_3^-	(0.0001)
0.008M	NO_3^-	(0.01)
0.008M	$H_2C_2O_4$	(0.01)

$Pu_2(C_2O_4)_3$ (0.33)

Transfer slurry to transfer bottle and return excess S.N. to Boiler

Transfer Bottle [Oxalate ppt.]

0.40 L total

0.30 L S.N.

H^+	(0.004)
I^-	(0.0001)
I_3^-	(0.00004)
NO_3^-	(0.004)
$H_2C_2O_4$	(0.004)

$Pu_2(C_2O_4)_3$ (158.500 g Pu) (0.33)

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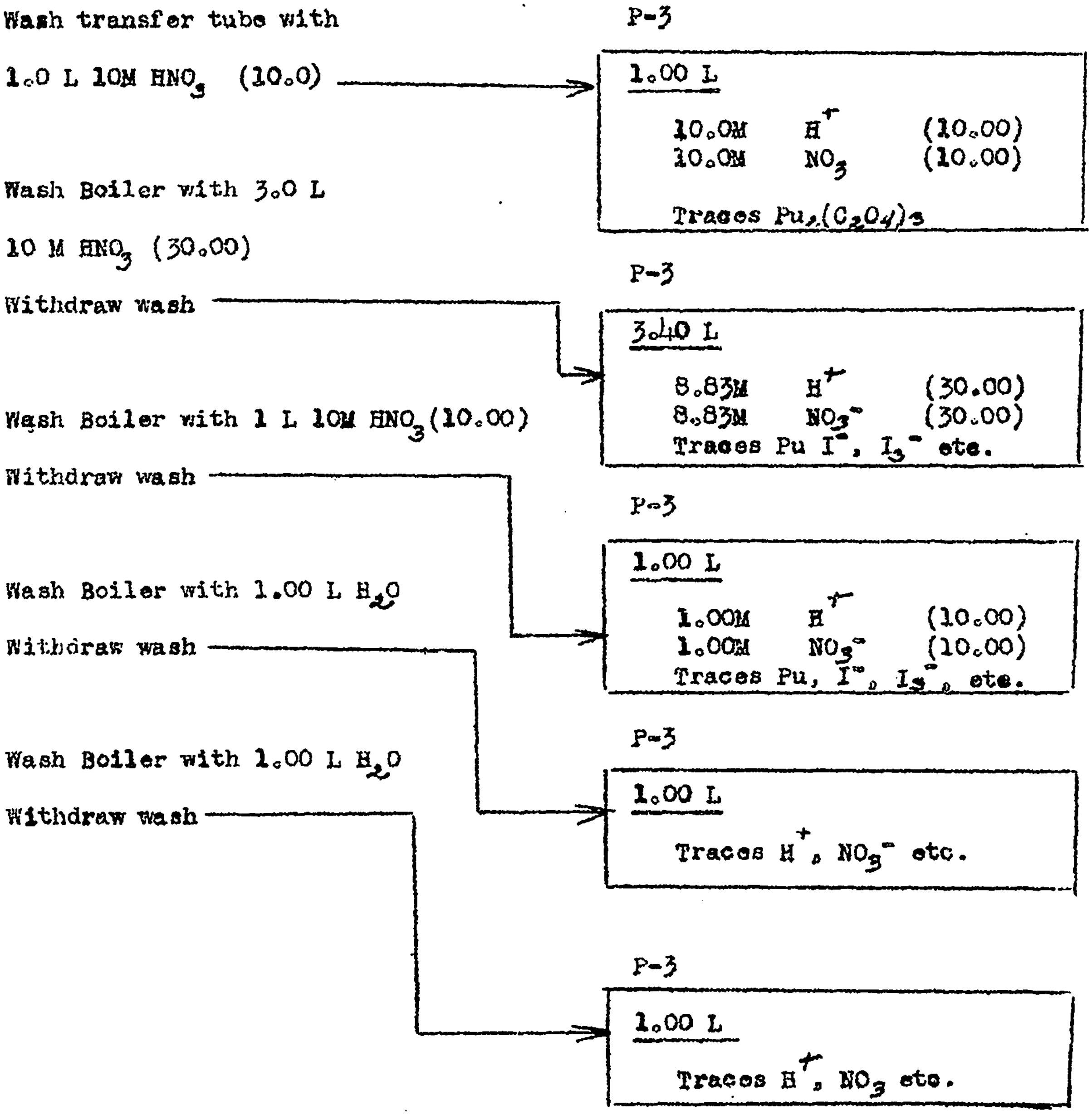

Wash transfer tube with

1.0 L 10M HNO_3 (10.0)

P-3

1.00 L

10.0M H^+ (10.00)

10.0M NO_3 (10.00)

Traces $Pu_2(C_2O_4)_3$

Wash Boiler with 3.0 L

10 M HNO_3 (30.00)

Withdraw wash

P-3

3.40 L

8.83M H^+ (30.00)

8.83M NO_3^- (30.00)

Traces Pu I^-, I_3^- etc.

Wash Boiler with 1 L 10M HNO_3 (10.00)

Withdraw wash

P-3

1.00 L

1.00M H^+ (10.00)

1.00M NO_3^- (10.00)

Traces Pu, I^-, I_3^-, etc.

Wash Boiler with 1.00 L H_2O

Withdraw wash

P-3

1.00 L

Traces H^+, NO_3^- etc.

Wash Boiler with 1.00 L H_2O

Withdraw wash

P-3

1.00 L

Traces H^+, NO_3 etc.

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STANDARD PROCEDURE B-2 RESIDUES

P-1

7.50 L

0.27M	H^+	(2.00)
2.72M	Ca^{++}	(20.44)
0.06M	Na^+	(0.46)
0.003M	Fe^{+3}	(0.02)
0.0004M	Ni^{+2}	(0.003)
0.003M	La^{+3}	(0.02)
0.0009M	$H_2PO_4^-$	(0.007)
0.0002M	$Cr_2O_7^=$	(0.0018)
5.77M	NO_3^-	(43.26)
0.03M	BrO_3^-	(0.21)
0.04M	$CaSO_4$	(0.31)

$SiO_2 \cdot X\ H_2O$, $SnO_2 \cdot X\ H_2O$ 0.3g

160 mg Pu

P-5 [Acid Bubbler] (f)

1.70 L

0.88M	H^+	(1.50)
0.88M	NO_3^-	(1.50)

Pu ~ 1mg

P-9 [Alkaline Bubbler]

1.50 L

4.50M	Na^+	(6.75)
0.92M	$SO_3^=$	(1.38)
2.34M	OH^-	(3.51)
0.08M	$SO_4^=$	(0.12)
0.16M	Br^-	(0.24)

P-2

11.50 L

Traces H^+, NO_3^-, Ca^{++}, Pu etc.

P-3

29.40 L

2.00 M	H^+	(58.93)
0.0001M	Cr^{+3}	(0.003)
0.10M	I^-	(3.04)
0.003M	I_3^-	(1.01)
1.87M	NO_3^-	(54.88)
0.07M	$H_2C_2O_4$	(2.24)

Pu 1340 mg.

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STANDARD PROCEDURE B-2

REAGENTS

Amount per Run

Reagent	Volume (L.)	Density g/cc	Gram Moles
H_2O	21.05	0.997	
HNO_3 -M (i)	3.70	1.032	3.70
HNO_3 10M	5.20	1.295	52.00
HI -5.5M	1.10	1.50	6.05
$H_2C_2O_4$ -0.67M	3.20	1.027	2.14
$H_2C_2O_4$ -0.1M HNO_3 -0.1M	11.00	1.008	1.10 1.10
$Ca(NO_3)_2$ 5M	4.15	1.520	20.75
$NaBrO_3$ 1.54M	0.30	1.171	0.462
NaOH - 2.50M Na_2SO_3 - 1.00M	1.50	1.200	3.75 1.50
Diethyl ether (j)	3.20	0.71	

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STANDARD PROCEDURE B-2

REAGENTS

Reagent	Gm. Moles	Mol. Wgt.	Gms.	Lbs.
HNO_3 70% (i)	56.80	63.0	3578	7.89
HI 47%	6.05	127.9	774	1.71
$H_2C_2O_4 \cdot 2H_2O$	3.24	126.1	409	0.90
$Ca(NO_3)_2 \cdot 4H_2O$	20.75	236.16	4900	10.80
$NaBrO_3$	0.462	150.9	70	0.15
NaOH	3.75	40.0	150	0.33
Na_2SO_3	1.50	85.0	128	0.28
Diethyl Ether (j)	-----	-----	-----	5.00

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Standard Procedure B-2

Notes:

(a) A number in parenthesis following the formula of an ion or compound represents the number of gram moles of the ion or compound.

(b) It is believed that the process can handle a charge containing from 130 to 180g without the conditions being sufficiently changed to cause abnormal losses.

The form of the Pu when it is received is rather uncertain. After solution, spectrophotometric analysis has shown the Pu to be about half in the +6 oxidation state and about half in the +4 oxidation state. When the solution is allowed to stand the amount of Pu in the +6 state decreases, so it appears that the +6 state is not formed by dismutation of the +4 state after the slurry is dissolved. Because of its chemical similarity to UO_2^{++} the +6 state of Pu is assumed to be PuO_2^{++}. The +4 state is assumed to be PuO^{++} only because assuming this form helps explain the apparent loss of H^+ during the oxidation in the "B" procedure and during the first reduction in "A" procedure.

(c) The amount of H^+ present is very uncertain. The amount stated in the flow sheet (0.18 moles of free H^+) is calculated from the arbitrary assumption that the slurry is 1 M in total available H^+. The solution could be as low as 0.30 moles of free H^+ if there were no available H^+ in the slurry and as high as 1.40 moles if the molecular weight of the plutonium nitrate were 500 and the remaining weight of the slurry was due to 70% HNO_3.

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(d) The amounts of impurities listed give high averages of the impurities found in Hanford material processed in Bldg. D. The table below gives the ranges through which the impurities have fluctuated.

Impurity	high (g)	low (g)
Fe	4.	0.4
Cr	0.6	0.06
Ni	0.4	0.04
La	16.	0.1
$SO_4^{=}$	48.	16.
$PO_4^{\equiv}$	1.	0.3
Solids	1.	0.05

(e) At the end of the oxidation the solution is usually a clear deep red color by transmitted light. When this has not been the case it has been the practice to cool the solution to ~50°C, add about 200 ml. of 1.54M $NaBrO_3$ and 100 ml of 10M HNO_3 and continue heating. No further HNO_3 is added before the ether extraction in this case. Sometimes even more BrO_3^- is required to get a clear solution. This extra treatment may not be necessary, but it is known that when used satisfactorily ether extractions are obtained.

The decomposition of BrO_3^- at 93°C. is rather slow in 1M HNO_3, has a half time of 45 min. in 2M HNO_3, and half time of <5 min. in 4M HNO_3.

The usual amount of H_2O evaporated is ~200 ml. but may be much higher if the solution is allowed to boil (96°C).

If only the amount of BrO_3^- indicated in the flow sheet is consumed the alkaline bubbler solution is 8% used, if all the BrO_3^- is consumed 16% of the alkaline bubbler solution is used, and if in the abnormal case where 0.31 extra moles of BrO_3^- are added, the BrO_3^- is all consumed 26% of the alkaline bubbler solution is used. Probably for safety the

[redacted]

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alkaline bubbler solutions should be changed every two runs.

(f) The acid bubbler need not be changed every run. It need by changed only when condensed H_2O from the oxidation increases the volume sufficiently to interfere with the operation of the bubblers.

(g) These washes are to remove $Ca(NO_3)_2$ from the reagent reservoir so the $Ca(NO_3)_2$ will not be introduced into the Boiler. These washes are omitted in B-3 the recommended D.P. procedure because the D.P. Boiler has a separate reservoir.

(h) The oxalate precipitate usually settles to a volume of 300-500 ml and 100-200 ml of supernatant is left over the precipitate. Here it is assumed that 600 ml of precipitate plus supernatant is left in the boiler and that the actual volume occupied by the precipitate is 100 ml. This volume would predict a density of the oxalate with ten water of hydration of 3 g/cc, which is reasonable.

(i) About 0.65L of M HNO_3 (0.65) is used in the cut operation and is not included in the figure given in the table. Figures given in the table allow for changing the bubblers every run.

(j) The amount of ether used can be variable. In a tight system only 1.5-2.0 L are used. If a system leaks, as much 15 L have been used. It is assumed here that one 5 lb. can of ether is used per run.

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STANDARD PROCEDURE B-2

Operating Instructions

Boron Can No.	Bottle No.	Lot No.	Wgt. Soln.	Pu Assay (gms. Pu)	
				Radio	Chem.

General Instructions

1. Operators initial procedure at beginning and end of shift.
2. Leave reagent reservoir tube in reagent bottle after reagent has been drawn into reservoir until ready to use next reagent.
3. Gloves, masks and coveralls must be worn during entire process. Face shields must be sorn during ether extraction and while handling ether.
4. Do not move plutonium from space unit without permission of Quantity Control.

Procedure

Step

1. Request boron can from Quantity Control.
2. Check controls.
3. Transfer 2.0 liters of H_2O to reservoir.
4. Add H_2O to boiler.
5. Close reservoir stopcock.
6. Transfer plutonium solution from storage bottle to reservoir.
7. Close reservoir stopcock.
8. With vac. on reservoir, wash product bottle with 200 ml. M HNO_3, and then 100 ml of 10M HNO_3.

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9. With stirrer running, add acid to extractor.

10. Transfer 300 ml 1.54M $NaBrO_3$ to reservoir.

11. Start extractor bubblers.

12. Attach extractor supernatant to P-1.

13. Add $NaBrO_3$ to extractor.

14. Close reservoir stopcock.

15. Turn steam into extractor and circulating pump on. Heat extractor to 93°C. Maintain at 92°C. to 94°C. for 1 hour.

16. Turn coolant into condenser.

17. After heating for 1 hour, turn coolant into extractor and circulating pump on. Cool to 15°C.

18. Transfer 100 ml of 10M HNO_3 to reservoir.

19. Add acid to extractor.

20. Close reservoir stopcock.

21. Transfer 3.5 liters of 5.0M $Ca(NO_3)_2$ to reservoir.

22. Add $Ca(NO_3)_2$ to extractor.

23. Close reservoir stopcock.

24. Transfer sufficient 5.0M $Ca(NO_3)_2$ to reservoir to dilute extractor to 5.5 liters.

25. Add $Ca(NO_3)_2$ to extractor.

26. Close reservoir stopcock.

27. Transfer 50 ml H_2O to reservoir.

28. Add H_2O to extractor.

29. Close reservoir stopcock.

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30. Cool extractor to 15°C.

31. Turn steam into boiler and circulating pump on.

32. Operators put on face shields.

33. Turn off stirrers, fill ether reservoir.

34. Turn on extractor and boiler stirrers.

35. When boiler temperature is 50°C or greater, bleed ether into extractor until it runs through side arm.

36. Bleed ether into extractor slowly, until ether returns from condenser. Observe temperature drift for 2 minutes.

If temperature is above 50°C. and is rising or remaining constant, bleed in ether slowly until the temperature in the boiler falls to 50°C., taking into account the temperature lag of the system.

If the temperature is falling, observe the drift until it becomes steady. Then proceed as above. If the temperature falls below 38°C., turn on bubbler in boiler.

Maintain boiler temperature at 45°C. to 50°C.

37. After extraction has run 1 hour, blow out extractor supernatant tube.

38. After extraction has run 1 1/2 hours blow out extractor supernatant tube, wash extractor walls with ether from wash ring.

39. When extraction has run 2 hours, open extractor supernatant pinchclamp, close extractor "burper"-- pinchclamp, suck residue into P-1.

40. Continue heating boiler until temperature is 90°C., then turn off pump and start bubbler. Maintain temperature at 90°C. to 94°C. for 1 1/2 hour.

41. Transfer 1.5 liters of M HNO_3 to reservoir, add acid to extractor.

[redacted]

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42. Close reservoir stopcock.

43. Wash extractor walls with 500 ml of M HNO_3 from wash ring.

44. With extractor stirrer running suck acid into P-1.

45. Transfer 1.5 liters of M HNO_3 to reservoir.

46. Add acid to extractor.

47. Close reservoir stopcock.

48. With stirrer running, suck acid into P-1.

49. Transfer extractor supernatant tube from P-1 to P-2.

50. Transfer 3.0 liters of H_2O to reservoir.

51. Add H_2O to extractor.

52. Close reservoir stopcock.

53. With stirrer running, suck H_2O into P-2.

54. Repeat 50 to 53 inclusive.

55. Transfer 5.5 liters of H_2O to reservoir.

56. Repeat 51 to 53 inclusive.

57. Remove P-1 to hood, blow air over surface to evaporate ether.

58. When boiler has been heated for 1/2 hour, turn off steam, turn on coolant and pump and cool to 15°C.

59. Transfer 1.1 liters of 5.5M HI to reservoir.

60. When boiler is 15°C., add HI to boiler. Stir for 20 minutes after HI is in.

61. When boiler has cooled to 25°C., turn off coolant and pump.

62. Transfer 3.2 liters of 0.67M $H_2C_2O_4$ to reservoir.

63. When HI solution has been stirred for 20 minutes, add $H_2C_2O_4$. Stir for 20 minutes, "burp" to agitate.

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64. Close reservoir stopcock.

65. After stirring 20 minutes, stop stirrer, allow ppt. to settle for 5 minutes, blow out boiler supernatant tube and allow ppt. to settle for 10 minutes more.

66. Transfer 5.5 liters of 0.1M $H_2C_2O_4$, 0.1M HNO_3 to reservoir.

67. Attach boiler supernatant tube to P-3.

68. After ppt. has settled for 15 minutes, open supernatant line pinchclamp, close "burper" pinchclamp; set supernatant tube 200 ml above ppt. and suck supernatant into P-3.

69. Transfer 5.5 liter of 0.1M $H_2C_2O_4$, 0.1M HNO_3 to reservoir. Close supernatant line pinchclamp and open "burper" line pinchclamp.

70. Add wash to boiler.

71. When 1 liter has been added start stirrer. Stir until ppt. has been throughly suspended. Stop stirrer.

72. Allow ppt. to settle for 5 minutes, blow out supernatant line and allow ppt. to settle for 10 minutes more.

73. Transfer 5.5 liters of H_2O to reservoir.

74. Add H_2O to boiler. When 1 liter of H_2O has been added start stirrer. Stir until the ppt. is throughly suspended.

75. Close reservoir stopcock.

76. When ppt. is throughly suspended, stop stirrer and allow ppt. to settle for 5 minutes. Blow out supernatant line and allow ppt. to settle, 10 minutes more.

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77. When ppt. has settled for 15 minutes, open supernatant line pinchclamp, close "burper" pinch clamp. Set supernatant tube 200 ml above ppt. and suck supernatant into P-3.

78. Rack supernatant tube up.

79. Disconnect boiler supernatant line and connect transfer bottle.

80. Suspend ppt. in supernatant and with stirrer running suck slurry into transfer bottle.

81. Allow ppt. to settle 2-3 minutes in transfer bottle, tap bottle to pack ppt. Blow supernatant back into boiler.

82. Repeat 80 & 81 four times.

83. On last pass allow ppt. to settle for 15 minutes in transfer bottle before returning supernatant to boiler. Leave ca 1cm. of supernatant over ppt. in transfer bottle.

84. Remove storage bottle and leucite liner to boron can and notify Quantity Control that batch is ready for transfer to storage.

85. Wash transfer tube with 1 liter of 10M HNO_3 into P-3.

86. Transfer 3 liters of 10M HNO_3 to reservoir.

87. Add acid to boiler. Stir for 2-3 minutes.

88. Suck acid into P-3.

89. Transfer 1 liters of 10M HNO_3 to reservoir.

90. Add acid to boiler. Stir for 2-3 minutes.

91. Suck acid into P-3.

92. Transfer 1 liter H_2O to reservoir.

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93. Add H_2O to boiler. Stir for 2-3 minutes.

94. Suck wash into P-3.

95. Transfer 1 liter H_2O to reservoir.

96. Add H_2O to boiler. Stir for 2-3 minutes.

97. Suck wash into P-3.

98. Transfer supernatant bottles to supernatant cut room. Stir each throughly, take a 1 ml cut from each into a 10 mm test tube marked with batch no. and residue no. Seal test tubes with parafilm.

99. Transfer supernatant solutions to recovery and obtain temporary receipt for difference between W-site assay and 140 g.

100. Transfer supernatant cuts and assay request sheets (sheet #2) to Radio Assay group.

101. Check and decontaminate room.

102. Oil motors and bearings. Grease stopcocks. Put glycerine in transfer head slide.

103. Drain alkaline bubbler into P-9, transfer to Recovery with no receipt or assay.

104. Refill reagent bottle.

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STANDARD PROCEDURE C-1

product to Boiler

Boiler [Initial Product]

0.60 L

0.43M	PuO^{++}	(0.34)[a]	160 gr.[b]
0.41M	PuO_2^{++}	(0.33)	
0.60M	H^+	(0.48)[c]	
0.03M	Fe^{+3}	(0.02)	≈ 1.0g [d]
0.005M	Cr^{+3}	(0.004)	≅ 0.2 gr.
0.004M	Ni^{+2}	(0.003)	≅ 0.2 gr.
0.03M	La^{+3}	(0.02)	≅ 3.0 gr.
0.39M	HSO_4^-	(0.31)	≅ 30.0 gr.
0.009M	$H_2PO_4^-$	(0.007)	≅ 0.7 gr.
2.05M	NO_3^-	(1.64)	

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ ≅ 0.3 gr.

+ 0.20 L 1M HNO_3 (0.2) Storage bottle

Wash to boiler

Cool boiler to 20°C

1.00 L 5.5M HI (5.5) to boiler[e]

Allow 20 min for reduction

$$\left\{\begin{array}{l} 2PuO_2^{++} + 9I^- + 8H^+ \longrightarrow 2Pu^{+3} + 3I_3^- + 4\,H_2O \\ 2PuO^{++} + 3I^- + 4H^+ \longrightarrow 2Pu^{+3} + I_3^- + 2\,H_2O \\ \qquad 2Fe^{+3} + 3I^- \longrightarrow 2Fe^{+2} + I_3^- \\ \qquad\quad \sim 15\ \text{Kcal heat liberated} \end{array}\right\}$$

Cool Boiler to 25°C.

[redacted]

[redacted]

Boiler [After Reduction]

2.00 L

0.34M	Pu^{+3}	(0.67)
2.09M	H^{+}	(4.18)
0.01M	Fe^{+2}	(0.02)
0.002M	Cr^{+3}	(0.004)
0.002M	Ni^{+2}	(0.003)
0.01M	La^{+3}	(0.02)
0.16M	HSO_4^{-}	(0.31)
0.004M	$H_2PO_4^{-}$	(0.007)
0.92M	NO_3^{-}	(1.84)
1.75M	I^{-}	(3.49)
0.34M	I_3^{-}	(0.67)

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ = 0.3g

+3.20 L 0.67M $H_2C_2O_4$ (2.14) to boiler

Allow ppt. to form 20 min

$$2Pu^{+3} + 3H_2C_2O_4 \longrightarrow Pu_2(C_2O_4)_3 + 6H^{+}$$
$$2La^{+3} + 3H_2C_2O_4 \longrightarrow La_2(C_2O_4)_3 + 6H^{+}$$

Allow ppt. to settle 15 min.

Withdraw S.N. ⟶

P-146 S.N. (Ox. ppt.)

4.60 L

1.22M	H^{+}	(5.63)
0.004M	Fe^{+2}	(0.02)
0.0009M	Cr^{+3}	(0.004)
0.0007M	Li^{+2}	(0.003)
0.06M	HSO_4^{-}	(0.28)
0.002M	H_2PO_4	(0.007)
0.36M	NO_3^{-}	(1.66)
0.68M	I^{-}	(3.15)
0.13M	I_3^{-}	(0.60)
0.22M	$H_2C_2O_4$	(1.00)

640 mg Pu

[redacted]

[redacted]

Boiler 1st Ox. Ppt. (No wash)

0.5 L S.N.(f)

1.22M	H^+	(0.62)
0.06M	HSO_4^-	(0.03)
0.36M	NO_3^-	(0.18)
0.68M	I^-	(0.34)
0.13M	I_3^-	(0.07)
0.22M	$H_2C_2O_4$	(0.11)

0.10 L ppt.

$Pu_2(C_2O_4)_3$	(0.33)
$La_2(C_2O_4)_3$	(0.01)

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ = 0.3 g

5.5 L 0.1M $H_2C_2O_4$ (.55) 0.1 M HCl (.55)
to Boiler

Allow Ppt. settle 15 min.

Withdraw S.N. ————→

P-146 First wash

5.5 L S.N.

0.19M	H^+	(1.07)
0.03M	NO_3^-	(0.17)
0.03M	HSO_4^-	(0.03)
0.06M	I^-	(0.31)
0.01M	I_3^-	(0.06)
0.11M	$H_2C_2O_4$	(0.61)
0.09M	Cl^-	(0.50)

Pu 160 mg

Boiler Ppt. after 1st wash

0.5 L S.N.

0.19M	H^+	(0.10)
0.03M	NO_3^-	(0.01)
0.06M	I^-	(0.03)
0.01M	I_3^-	(0.01)
0.11M	$H_2C_2O_4$	(0.05)
0.09M	Cl^-	(0.05)

0.1

$Pu_2(C_2O_4)_3$	(0.33)
$La_2(C_2O_4)_3$	(0.01)

$SnO_2 \cdot X\ H_2O$ $SiO_2 \cdot X\ H_2O$ = 0.3 g

[redacted]

+5.5 L 0.1M $H_2C_2O_4$ (0.55)
        0.1M HCL (0.55)

Suspend ppt. Allow ppt to settle

Withdraw wash →

P-146 Ox. 2nd wash

5.50 L S.N.

0.11M	H^+	(0.60)
0.002M	NO_3^-	(0.009)
0.004M	I^-	(0.02)
0.002M	I_3^-	(0.009)
0.10M	$H_2C_2O_4$	(0.55)
0.10M	Cl^-	(0.55)

Pu 160 mg

Boiler Ppt. after 2nd wash

0.50 L S.N.

0.11M	H^+	(0.05)
0.002M	NO_3^-	(0.001)
0.004M	I^-	(0.01)
0.002M	I_3^-	(0.001)
0.10M	$H_2C_2O_4$	(0.05)
0.10M	Cl^-	(0.05)

0.10 L Ppt.

$Pu_2(C_2O_4)_3$	(0.33)
$La_2(C_2O_4)_3$	(0.01)

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$, 0.3g

+5.50 L H_2O suspend ppt.

Allow ppt to settle

Withdraw wash →

P-146

5.30 L S.N.

0.008M	H^+	(0.04)
0.0002M	NO_3^-	(0.0009)
0.002M	I^-	(0.009)
0.0002M	I_3^-	(0.0009)
0.008M	$H_2C_2O_4$	(0.04)
0.008M	Cl^-	(0.04)

Pu 160 mg

Boiler Ppt. after 3rd wash

0.70 L S.N.

0.008M	H^+	(0.01)
0.0002M	NO_3^-	(0.0001)
0.002M	I^-	(0.001)
0.0002M	I_3^-	(0.0001)
0.008M	$H_2C_2O_4$	(0.01)
0.008M	Cl^-	(0.01)

0.10 L Ppt.

$Pu_2(C_2O_4)_3$	(0.33)
$La_2(C_2O_4)_3$	(0.01)

$SnO_2 \cdot X\ H_2O$, $SiO_2 \cdot X\ H_2O$ 0.3g

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Transfer slurry to Transfer Bottle and return excess SN to Boiler

Transfer Bottle Ox. pt. after transfer

0.30 L S.N.

0.008M	H^+	(0.004)
0.0002M	NO_3^-	(0.00004)
0.002M	I^-	(0.0004)
0.0002M	I_3^-	(0.00004)
0.008M	$H_2C_2O_4$	(0.004)
0.008M	Cl^-	(0.004)

$Pu_2(C_2O_4)_3$ (0.33) (158.88 g Pu)
$La_2(C_2O_4)_3$ (0.01)

$SiO_2 \cdot X H_2O$, $SiO_2 \cdot X H_2O$ 0.3g

Wash transfer tube with
0.10 L 12M HCL (1.2)

Withdraw wash

P-146

0.50 L

2.4M	H^+	(1.2)
2.4M	Cl^-	(1.2)

Traces I^-, I_3^-, $H_2C_2O_4$, Pu etc.

Wash Boiler with
0.50 L 12M HCL (6.0)

Withdraw wash

P-146

0.50 L

12M	H^+	(6.0)
12M	Cl^-	(6.0)

Traces $H_2C_2O_4$, Pu etc.

Wash Boiler with
1.0 L H_2O

Withdraw wash

P-146

1.0 L

Traces H^+, Cl^-, $H_2C_2O_4$ etc.

Wash Boiler with
1.0 L H_2O

Withdraw wash

P-146

1.0 L

Traces H^+, Cl^-, $H_2C_2O_4$ etc.

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STANDARD PROCEDURE C-1

RESIDUES

P-146

23.90 L

0.61M	H^+	(14.54)
0.0008M	Fe^{+3}	(0.02)
0.0002M	Cr^{+3}	(0.004)
0.0001M	Ni^{+2}	(0.003)
0.01M	HSO_4^-	(0.31)
0.0003M	$H_2PO_4^-$	(0.007)
0.08M	NO_3^-	(1.84)
0.15M	I^-	(3.49)
0.03M	I_3^-	(0.67)
0.09M	$H_2C_2O_4$	(2.20
0.35M	Cl^-	(8.29)

Pu 1120 mg

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[redacted]

STANDARD PROCEDURE A-8

REAGENTS

Reagent	Volume (liters)	Density g/cc	Gram Moles
H_2O	7.50	0.997	
HI 5.5 M	1.00	1.50	5.50
$H_2C_2O_4$ 0.1 M HCl 0.1 M	11.00	1.005	1.10 1.10
$H_2C_2O_4$ 0.67 M	3.20	1.027	2.14
HCl 12M	0.60	1.178	7.20
HNO_3 1 M(g)	0.20	1.032	0.20
Total aq.Solutions	23.50 L.	----	----

Substance	Gm. Moles	Mol. Wgt.	Gms.	Lbs.
HI 47%	5.50	127.9	703.5	1.55
HNO_3 70%(g)	0.20	63.0	12.6	0.028
HCl 38%	8.30	36.5	303.0	0.67
$H_2C_2O_4 \cdot 2H_2O$	3.24	126.1	408.6	0.90

[redacted]

[redacted]

Standard Procedure C-1

Notes:

(a) A number in parenthesis following the formula of an ion or compound represents the number of gram moles of the ion or compound.

(b) It is believed that the process can handle a charge containing from 130 to 180g of Pu without the conditions being sufficiently changed to cause abnormal losses.

The form of the Pu when it is received is rather uncertain. After solution, spectrophotometric analysis has shown the Pu to be about half in the +6 oxidation state and about half in the +4 oxidation state. When the solution is allowed to stand the amount of Pu in the +6 state decreases, so it appears that the +6 state is not formed by dismutation of the +4 state after the slurry is dissolved. Because of its chemical similarity to UO_2^{++} the +6 state of Pu is assumed to be PuO_2^{++}. The +4 state is assumed to be PuO^{++} only because assuming this form helps explain the apparent loss of H^+ during the oxidation in the "B" procedure and during the first reduction in "A" procedure.

(c) The amount of H^+ present is very uncertain. The amount stated in the flow sheet (0.48 moles of free H^+) is calculated from the arbitrary assumption that the slurry received from W is 1M in total available H^+. The solution could be as low as 0.30 moles of free H^+ if there were no available H^+ in the slurry and as high as 1.40 moles if the molecular weight of the plutonium nitrate were 500 and the remaining weight of the slurry was due to 70% HNO_3.

[redacted]

[redacted]

(d) The amounts of impurities listed give high averages of the impurities found in Hanford material processed in Bldg. D. The table below gives the ranges through which the impurities have fluctuated.

Impurity	high (g)	low (g)
Fe	4.	0.4
Cr	0.6	0.06
Ni	0.4	0.04
La	16.	0.1
$SO_4^{=}$	48.	16.
$PO_4^{\equiv}$	1.	0.3
Solids	1.	0.05

(e) Sufficient HI is added to properly reduce the Pu even if it were all in the +6 oxidation state.

(f) The oxalate precipitate usually settles to a volume of 300 to 500 ml and 100 to 200 ml of supernatant is left over the precipitate. Here it is assumed that 600 ml. of precipitate plus supernatant is left in the reactor and that the actual volume accupied by the precipitate is 100 ml. This volume would predict a density of the oxalate with ten waters of hydration of 3g/cc, which is reasonable.

(g) About 0.65L of IM HNO_3 (0.65) is used in the cut operation and is not included in the figures given in the table. Figures given in the table allow for changing the bubblers after every run.

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STANDARD PROCEDURE C-1

Operating Instructions

Boron Can No.	Bottle No.	Lot No.	Wgt. Soln.	Pu Assay (g. Pu)	
				Radio	Chem.

General Instructions

1. Operators initial procedure at beginning and end of shift.
2. Leave reagent reservoir tube in reagent bottle after reagent has been drawn into reservoir until ready to use next reagent.
3. Gloves, masks, and coveralls must be worn during entire process. Face shields must be worn during ether extraction and while handling ether.
4. Do not move plutonium out of space unit without permission of Quantity Control.

Procedure

Step

1. Turn coolant into boiler and pump on.
2. Transfer product to reservoir and add to boiler.
3. Close reservoir stopcock.
4. With vacuum on reservoir, wash storage bottle with 200 ml M HNO_3.
5. Transfer 1.0 liter of 5.5M HI to reservoir.
6. When boiler is 15°C., add HI to boiler. Stir for 20 minutes after HI is in.
7. When boiler has cooled to 25°C., turn off coolant and pump.
8. Transfer 3.2 liters of 0.67M $H_2C_2O_4$ to reservoir.

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9. When HI solution has been stirred for 20 minutes, add $H_2C_2O_4$. Stir for 20 minutes, "burp" to agitate.

10. Close reservoir stopcock.

11. After stirring 20 minutes, stop stirrer, allow ppt. to settle for 5 minutes, blow out boiler supernatant tube and allow ppt. to settle for 10 minutes more.

12. Transfer 5.5 liters of 0.1M $H_2C_2O_4$, 0.1M HCl to reservoir.

13. Attach boiler supernatant tube to P-3.

14. After ppt. has settled for 15 minutes, open supernatant line pinchclamp, close "burper" pinchclamp; set supernatant tube 200 ml above ppt. and suck supernatant into P-3.

15. Transfer 5.5 liters of 0.1M $H_2C_2O_4$, 0.1M HCl to reservoir. Close supernatant line pinchclamp and open "burper" line pinchclamp.

16. Add wash to boiler.

17. When 1 liter has been added start stirrer. Stir until ppt. has been throughly suspended. Stop stirrer.

18. Allow ppt. to settle for 5 minutes, blow out supernatant line and allow ppt. to settle for 10 minutes more.

19. Transfer 5.5 liters of H_2O to reservoir.

20. Add H_2O to boiler. When 1 liter of H_2O has been added start stirrer. Stir until the ppt. is throughly suspended.

21. Close reservoir stopcock.

22. When ppt. is throughly suspended, stop stirrer and allow ppt. to settle for 5 minutes. Blow out supernatant line and allow ppt. to settle, 10 minutes more.

[redacted]

23. When ppt. has settled for 15 minutes, open supernatant line pinchclamp, close "burper" pinchclamp. Set supernatant tube 200 ml above ppt. and suck supernatant into P-3.

24. Rack supernatant tube up.

25. Disconnect boiler supernatant line and connect transfer bottle.

26. Suspend ppt. in supernatant and with stirrer running suck slurry into transfer bottle.

27. Allow ppt. to settle 2-3 minutes in transfer bottle, tap bottle to pack ppt. Blow supernatant back into boiler.

28. Repeat 26 and 27 four times.

29. On last pass allow ppt. to settle for 15 minutes in transfer bottle before returning supernatant to boiler. Leave ca 1cm. of supernatant over ppt. in transfer bottle.

30. Remove storage bottle and leucite liner to boron can and notify Quantity Control that batch is ready for transfer to storage.

31. Wash supernatant tube with 100 ml 12M HCl into P-146.

32. Transfer 500 ml 12M HCl to reservoir.

33. Add HCl to boiler and stir.

34. Close reservoir stopcock.

35. When ppt. had dissolved suck acid into P-146.

36. Transfer 1.0 liter H_2O to reservoir.

37. Add H_2O to boiler, close reservoir stopcock. Stir.

38. Suck H_2O into P-146.

39. Repeat 35 to 37 inclusive.

[redacted]

[redacted]

40. Transfer supernatant bottles to supernatant cut room. Stir each throughly, take a 1 ml cut from each into a 10 mm test tube marked with batch no. and residue no. Seal test tubes with parafilm.

41. Transfer supernatant solutions to recovery and obtain temporary receipt for difference between W-site assay and 140 g.

42. Transfer supernatant cuts and assay request sheets (sheet #2) to Radio Assay group.

43. Check and decontaminate room.

44. Oil motors and bearings. Grease stopcocks. Put glycerine in transfer head slide.

45. Drain alkaline bubbler into P-9, transfer to Recovery with no receipt or assay.

46. Refill reagent bottle.

[redacted]

[redacted]

Treatment of Supernatant Solutions, A-Procedure

The supernatant solutions withdrawn after precipitation reactions, the solutions used to wash precipitate and the aqueous residue from ether extractions were returned to the D building recovery group, for more complete removal of plutonium. During experimental runs, each residue was sampled for plutonium assay, to determine the amount of plutonium "lost" during each operation. On strictly production runs several of the solutions were combined during operations, and sampled for plutonium assay before being turned over to recovery. The designation of solutions sent to Recovery were as follows;-

P-1 The supernatant and wash solutions from the first Pu (III) oxalate precipitation.

P-2 The supernatant and wash solutions from the sodium plutonyl acetate.

P-3 The aqueous residue from ether extraction.

P-4 The supernatant and wash solutions from the second oxalate precipitation.

P-5 Acid bubbler residue.

P-6 Boiler wash.

P-7 Iodine bubbler residue.

P-8 Wash from transfer bottle.

P-9 Alkaline bubbler residue.

P-10 Solution obtained as the result of an operational difficulty or error. eg;- If the first oxalate could not be oxidized, it was sent to D-Building Recovery as P-10.

During production runs P-1, P-4 and P-6 were combined and designated P-146.

[redacted]

Supernatants were sampled, for plutonium assay, before being sent to D-Building Recovery. If sufficient acid had not been added during extractor or boiler wash to dissolve all plutonium compounds, the solutions were acidified, well stirred, and a 1 ml sample withdrawn and sent to Radio Assay. From either the assay of the original plutonium entering the purification process, or the oxide weight obtained by ignition of the final oxalate and the sum of the supernatant assays, the yield for a run was calculated.

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DOCUMENT ROOM

REC. FROM L. B.

DATE 3-13-47

REC. NO. REC. ✓

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