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R. E. Bradbury

LA 404 - C. 1

Correction to LA-404.

Please make the following corrections to your copy of LA-404.

Line 9 on page 5 should read "sodium uranyl acetate" rather than sodium uranyl nitrate. All subsequent references to sodium uranyl nitrate should read " sodium uranyl acetate."

Shirley Alldredge,
Document Room

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CHEMICAL RESEARCH

BUILDING D PLUTONIUM PURIFICATION

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ABSTRACT

This report summarizes and explains the chemical research leading to the development of various processes for the purification of plutonium. The purification efficiency of the steps and processes used is summarized in Table VI, Purification Factors for Impurities.

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FIGURES AND TABLES

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CHEMICAL RESEARCH
BUILDING D PLUTONIUM PURIFICATION

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I. History---Development of Various Purification Processes

In the summer of 1943, the CM-5 group was organized for the purpose of wet chemistry purification and dry conversion preparatory to metal reduction of plutonium and uranium-235.

The first plutonium received at Los Alamos consisted of about 0.5 milligram of cyclotron irradiated material from Berkeley mixed with several hundred grams of uranium and about 30 micrograms of neptunium-237. The plutonium and neptunium were separated from the uranium by the use of successive sodium uranyl acetate precipitations. Such a precipitation only "carries" Pu and Np when they are in the oxidized state. Then the Pu was removed from Np by several lanthanum and cerium flouride carrier precipitations and finally purified by an iodate precipitation. Both the Pu and Np, after purification, were used for measurements by the Physics division.

In February, 1944, the first 5 milligram shipment of Pu arrived at this site from Clinton and first purification research on appreciable amounts of material began. Shipments of Clinton plutonium gradually increased in number and amount of material so that the design of a completely enclosed glass apparatus for safely handling purification was begun.

All lots of material, except three, were purified by the recovery phase of CM-5 under F. K. Pittman until August, 1944, when the construction of an enclosed glass apparatus was completed which could handle one gram of material per run. Then in September, 1944, all purification runs were standardized to an eight gram scale, these runs being used for both production and research (see Fig. 1 for apparatus used). Finally, in January, 1945, when large (80 and 160g. shipments) quantities of plutonium became available from Hanford all production runs were standardized to the 160 gram scale while

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research was continued on the 8 gram scale.

The necessity for stringent purification because of the α-n reaction involving plutonium and lighter elements, purity tolerances for metallurgical reasons, and our complete lack of knowledge as to what impurities would be present in future incoming material from Hanford, has already been explained in another report (LA-403, part I). It is sufficient to mention here that the purity tolerances which had to be met were extremely low and the elements present in incoming material which had to be removed nearly completely, involved the entire periodic table.

The first purification procedures were suggested by analogy with known uranium purification Chemistry. Both the ether extraction and sodium uranyl acetate ~~nitrate~~ precipitation of uranium as UO_2^{+2} had proven sufficient to purify this element from all other known elements. Thus, the first process used consisted in oxidizing the Pu to the +6 state, making two sodium plutonyl acetate precipitations, each of which was washed several times, and then twice extracting plutonyl nitrate with ether. This purification scheme was satisfactory except that it obviously would not remove uranium which was present to the extent of about 1% in Clinton material. Also, the metallurgists were using uranium sulfide crucibles and any recovered Pu contained large amounts of uranium which must be removed. For these reasons, a means of removing the uranium present was developed. The best removal found was through the use of an oxalate precipitation of Pu (III). This was incorporated into a new process, designated Procedure A, which consisted of a Pu (III) oxalate precipitation, and acetate precipitation after oxidation to Pu (VI), an ether extraction, reduction to Pu (III), and a final Pu (III) oxalate precipitation.

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The results of many analysis proved that a single ether extraction was sufficient to remove all the elements except U, Cr, and probably Np well below tolerance limits, so the next process developed, designated Procedure B, utilized a single ether extraction, after oxidation to Pu (VI), followed by the Pu (III) oxalate precipitation. (See LA-405 for complete flow sheets of all processes). This procedure has been adopted for future production.

The major purpose of future research on any further purification processes will probably attempt to do away with the ether extraction as the use of ether constitutes a dangerous industrial hazard and inevitably involves the use of specially built equipment and many protective safety devices. So far, the only promising methods involve the use of Pu (III) oxalate precipitations or Pu (IV) peroxide precipitations. We still have no analytical date to prove that either of these methods will meet the tolerance limits for impurities in the final product.

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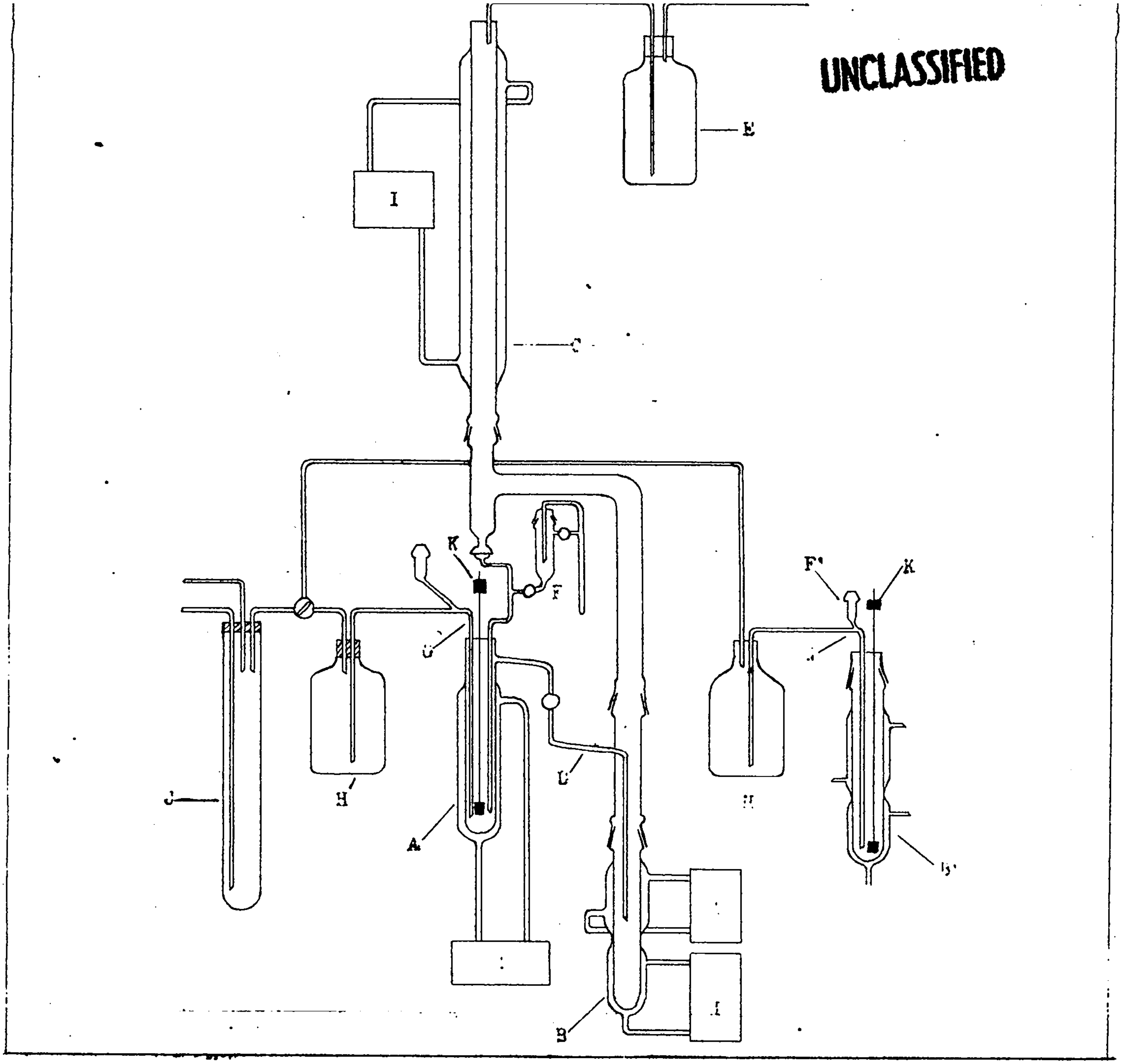

Figure 1. PURIFICATION APPARATUS

A - First precipitation and extraction tube
B - Second precipitation tube and ether boiler, in position for ether extraction
B' - B in position for second oxalate precipitation
C - Ether condenser
D - Loaded ether return
E - Ether storage
F - Product and reagent introduction tube
F' - Reagent introduction tube
G - Supernatant and wash solution withdrawal - 3 inch vertical motion
H - Supernatant and wash solution collection bottle
I - Heat exchanger and water circulating pump
J - Constant vacuum device
K - Motor driven stirrer

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II. Development of Purification Chemistry.

A. Ether Extraction Research

Diethyl ether extraction of plutonyl nitrate from dilute nitric acid using NH_4NO_3 or, later, $Ca(NO_3)_2$ as salting out agents proved to be the most satisfactory purification step used. When the total impurities present in the plutonyl nitrate solution did not exceed 5%, a single ether extraction lowered the concentrations of all impurities at least to tolerance limits, with only few exceptions. Uranium was quantitatively extracted, about 10% of the Cr as $H_2Cr_2O_7$ was extracted, and possibly neptunium, although there is no concrete evidence other than general chemical behavior that the latter would extract.

The first partial evidence of the purification efficiency and the technique of operating the ether extraction was obtained from an experiment using 10 mg. of plutonium (see report LA-75). The plutonium was oxidized to Pu (VI) with $Na_2Cr_2O_7$-HNO_3 and twice precipitated as $NaPuO_2Ac_3$. Two ether extractions followed these precipitations. The first extraction was in the presence of $NaNO_3$ (from the dissolution of $NaPuO_2Ac_3$) as a salting out agent. The second extraction was made without using any salting out agent. The purity of the final product from this experiment and four one gram experiments using the same procedure is given in LA-406 (Table III, lots No. 5, 7, 9, 12, 14) or LA-75 (Table II).

As soon as gram amounts of Pu were available the extraction was carried out in a standard Soxhlet extractor provided with a non-porous cup which was operated until as much Pu (VI) as possible was removed. At first it was feared that the use of any salting out agent (even dilute $NaNO_3$ present after dissolving $NaPuO_2Ac_3$) while producing faster, more complete Pu (VI) extraction would also force out light element impurities. After the analysis on the initial runs, it

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was found that $NaNO_3$ as a salting out agent gave as good purification and much better extraction than no salting out agent. However, up to this time there was no evidence that more concentrated salting out agents could be used other than 0.4M $NaNO_3$ present after dissolving $NaPuO_2Ac_3$.

Uranyl nitrate "stand-in" research by M. Kahn proved that using NH_4NO_3 in concentrations up to 9.0M as a salting out agent gave a 99.5% yield of $UO_2(NO_3)_2$ and as pure a product, within the limits of analytic detection, as was obtained using no salting out agent. To all appearances, one ether extraction was as good as several in removing light element impurities, with the exception of boron. However, this may have been partly due to the analysis of background amounts of these elements. Shortly after this work was made known, NH_4NO_3 was used as a salting out agent in the extraction of Pu (VI) nitrate as part of the purification process. Also, only one extraction was used in the process and the product purity was satisfactory.

The Soxhlet extraction apparatus was used until an all-glass, enclosed apparatus was constructed which would take care of <u>all</u> chemical operations in the purification process without ever removing the Pu being purified from the apparatus until finally ready to transfer the pure $Pu_2(C_2O_4)_3$ precipitate to dry conversion. This apparatus was first built to accommodate one gram of Pu per run but after only one run was reconstructed to purify material in eight gram lots (Fig. 1). This eight gram apparatus was used for the principal portion of all the research done on both purification chemistry and production problems.

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Uranyl Nitrate "Stand-In" Research

Uranyl nitrate was used as a "stand-in" to obtain some of the preliminary ether extraction data, i.e., to determine effect of concentration of salting out

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agents and of HNO_3 on the extraction rate, extraction rate of uranyl nitrate and of HNO_3 against time, effect of $HC_2H_3O_2$ (which would be left from dissolving a previous acetate precipitate) and the rate of extraction. The various experiments made and the results obtained are summarized in Table I and in Figures 2 and 3, which are graphs representing extraction rates of uranyl nitrate and of HNO_3 against time. Two analyses were used to obtain these extraction rates:

U analysis: To a measured aliquot of the solution being extracted was added enough 6M NH_4OH to ppt. all the UO_2^{+2}, and about 2 ml. excess. This mixture was centrifuged about 15 min. at 2600 r.p.m. The clear supernatant was then drawn off and discarded. The ppt. remaining was dissolved in 2M HNO_3 and reprecipitated with 6M NH_4OH several times (supernatants, after centrifuging, were drawn off and discarded) to remove all salts. Finally the salt-free diuranate ppt. was dissolved in 2M HNO_3 and slowly ignited to U_3O_8 in a weighed platinum crucible. The crucible was weighed, after cooling, to determine amount of U_3O_8 obtained from original aliquot.

HNO_3 analysis; HNO_3 remaining in the extracted solution was determined at the same time intervals as UO_2^{+2} by removing the later with potassium ferrocyanide and titrating against standard base using methyl red indicator1).

The ether distillation rate was kept at 20 to 24 ml/min. throughout all the extractions and the apparatus used was of the continuous ether recycle type shown in Fig. 1 (8 g. apparatus) except that the extractor was not kept colder than room temperature and an outlet was provided at the bottom of it so that samples could be withdrawn at definite time intervals. Rate of stirring in the extractor was kept constant.

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1) C. W. Hammond, April 21, 1944, CC1432, Determination of Free Nitric Acid in UNH Solutions.

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Analysis after single extractions had indicated that the acetate precipitation was probably unnecessary for satisfactory purification, so that the possibility of going directly from oxidation of either the incoming stock material or the first oxalate precipitate was considered. When this was attempted with NH_4NO_3 as a salting out agent, such copious quantities of Br_2 were evolved that the corrosion problem became too great. Also considerable quantities of "gunk" were formed which carried into the ether layer and clogged the ether carry-off tube. Therefore, if the acetate precipitation was to be omitted, some salting out agent other than NH_4NO_3 had to be used. Previous reports from other sites (A-1022, A-1029, A-1037, A-1052, A-1059) had described the effects of various nitrates, e.g., sodium, calcium, ferric, cupric, aluminum, magnesium, and zinc on the distribution of uranyl nitrate between water and ether. Of these, calcium nitrate was chosen as the most likely substitute. If any cation impurity were to be carried over with the ether, Ca would <u>probably</u> be the least objectionable not only because it would be introduced into the plutonium metal during reduction but also because it could be removed rather well during remelting of the metal. It was fortunate that very <u>little,</u> Ca^{+2} was carried over (about .01%) because it was found that 0.1% or greater Ca as an impurity produced lower yields during reduction of PuF_4 to the metal. The seventh run of this series (Table I) was the first attempt to use $C_a(NO_3)_2$ as a salting out agent.

Conclusions drawn from the date on Table I and the graphs in Figs. 2 and 3 indicate that when NH_4NO_3 is used for uranyl nitrate extraction the main factor is the total nitrate concentration rather than the conc. of either HNO_3 or NH_4NO_3 independently and that $Ca(NO_3)_2$ with low HNO_3 conc. is a much better salting out agent than NH_4NO_3 under the best conditions. Further, the extraction of HNO_3

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coincided closely with that of $UO_2(NO_3)_2$ on all the extractions except the one using $Ca(NO_3)_2$ where the acid was extracted more slowly until the principal portion of uranyl nitrate had been carried over. Calculations indicate that these extraction curves approximate the exponential formula at fairly high concentrations of UO_2^{+2} i.e., the rate of extraction varies directly as the concentration of uranyl nitrate present.

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Table I

Ether Extraction of Uranyl Nitrate

Run No.	Chemical Conditions Previous to Extraction	Remarks and Observations
1.	0.33 M $UO_2(NO_3)_2$ 9.0 M NH_4NO_3 2.0 M HNO_3	Extraction run for 205 minutes--proceeded normally. High HNO_3 concentration used.
2.	0.33 M $UO_2(NO_3)_2$ 9.0 M NH_4NO_3 0.45 M HNO_3	Extraction run for 220 minutes--proceeded normally. Fairly low HNO_3 concentration used.
3.	0.33 M $UO_2(NO_3)_2$ 9.4 M NH_4NO_3 0.09 M HNO_3	Extraction run for 225 minutes--proceeded normally. Low HNO_3 concentration but total NO_3^- concentration same as in preceding run.
4.	0.11 M $UO_2(NO_3)_2$ 8.25 M NH_4NO_3 0.57 M HNO_3 0.34 M $HC_2H_3O_2$	Extraction run for 183 minutes. An initial $NaUO_2Ac_3$ precipitation was made, then HNO_3 and NH_4NO_3 was added to simulate actual purification process conditions using low HNO_3 concentration.
5.	0.11 M $UO_2(NO_3)_2$ 8.53 M NH_4NO_3 2.2 M HNO_3 0.34 M $HC_3H_3O_2$	Extraction run for 158 minutes. Used as check on Run No. 4 this time using high HNO_3 concentration before extraction. Copious quantities of nitrogen oxides were evolved.
6.	0.11 M $UO_2(NO_3)_2$ 8.25 M H_4NO_3 0.28 M HNO_3	Extraction run for 174 minutes. Low HNO_3 concentration and lower NH_4NO_3 concentration as encountered in the two previous runs. No $HC_2H_3O_2$ present.
7.	0.11 M $UO_2(NO_3)_2$ 4.0 M $Ca(NO_3)_2$ 0.3 M HNO_3	Extraction run for 33 minutes, after which time it was as complete as previous runs. Low HNO_3 concentration although total NO_3^- concentration was nearly as great as in previous runs. Only 60 parts of Ca per million of 9L carried over with ether.

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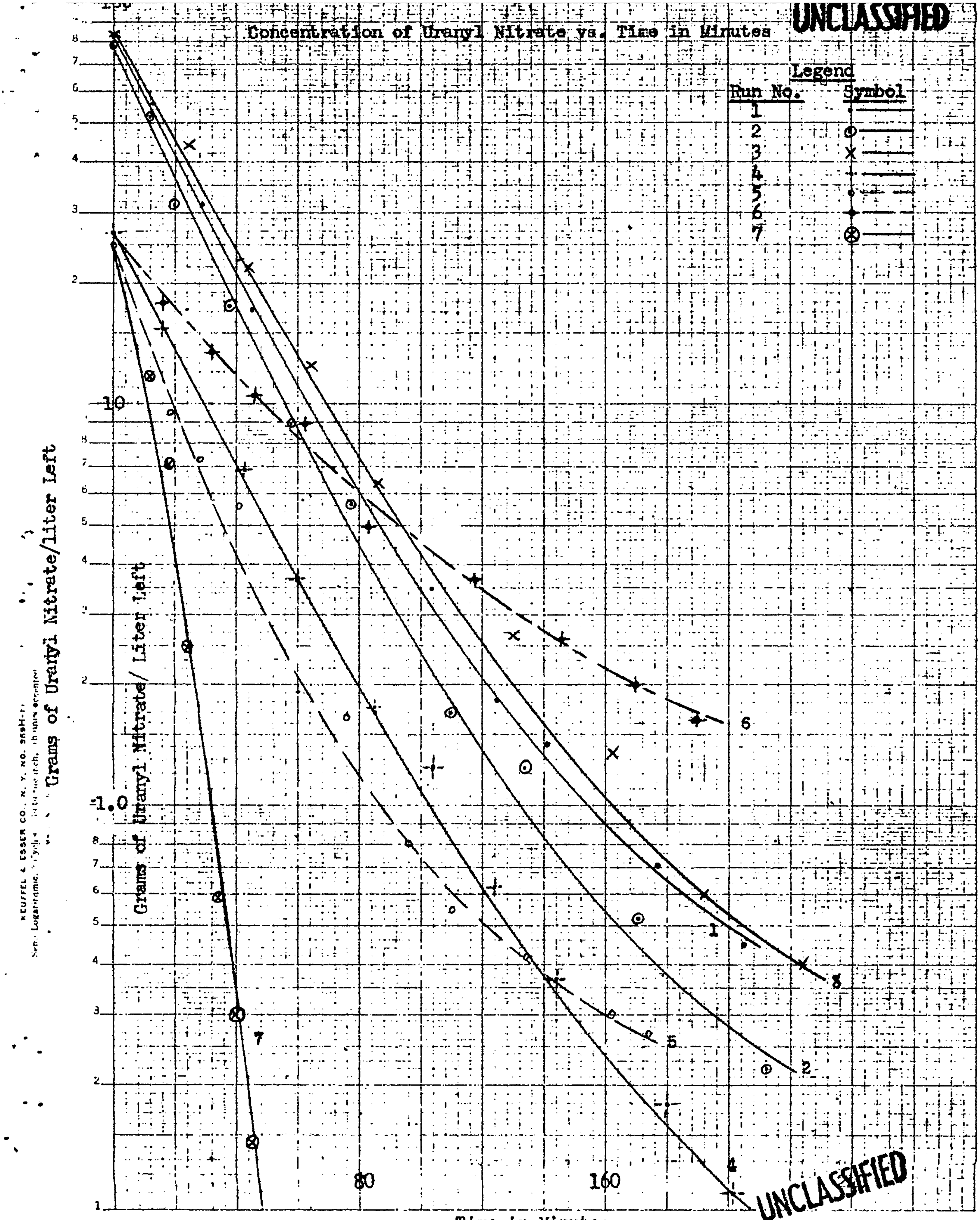

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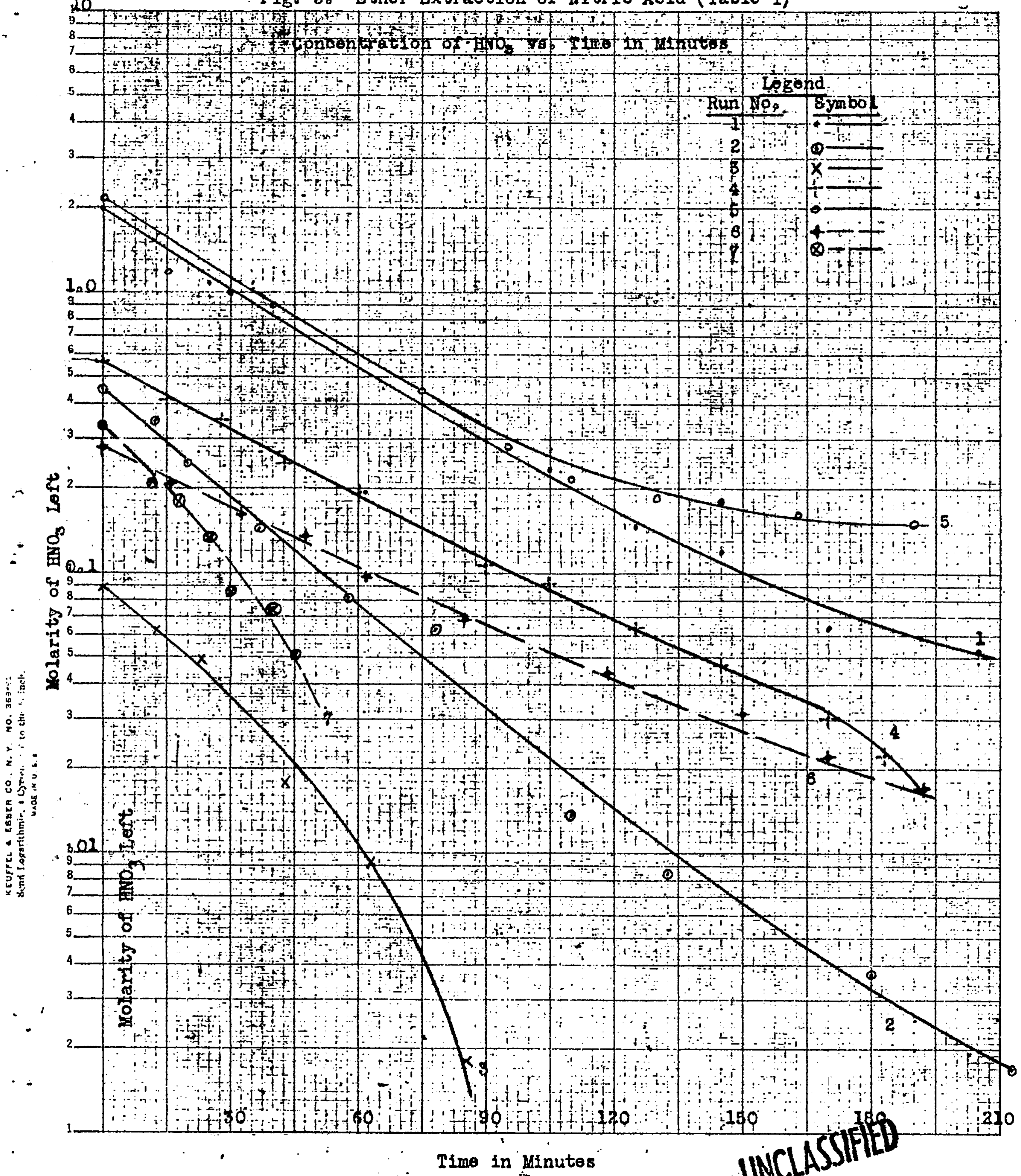
Fig. 3. Ether Extraction of Nitric Acid (Table I)



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Plutonyl Nitrate Extraction Rates

The first extractions made, using NH_4NO_3-HNO_3 as a salting out agent for plutonyl nitrate (obtained by dissolving $NaPuO_2Ac_3$) had initial concentrations of $NH_4NO_3 = \sim 6.5M$, $HNO_3 = < 0.8M$, Pu(VI) $= \sim 0.14M$, $NaNO_3 = \sim 0.14M$, $HC_2H_3O_2 = \sim 0.42M$. With these starting chemical conditions, it took at least 30-40 minutes for 8 grams of Pu (VI) to be extracted from the aqueous medium into ether using a continuous ether distillation rate of ~25 ml. per minute in the 8 gram apparatus. On several runs, the initial HNO_3 concentration was not greater than 0.3M and the extractions would not go to completion unless more HNO_3 was added. So research was begun to find the optimum conditions for quick complete extraction still retaining product purity. First indications were that the HNO_3 concentration should be as high as possible but not so high that the amount carried over with the plutonyl nitrate would interfere with the subsequent HI reduction and oxalate precipitation.

Table II is a summary of the extraction rate work using NH_4NO_3-HNO_3 as a salting out agent. Runs numbered thru 230 P were made to determine the best conditions for fast, complete extraction. The best conditions found started with NH_4NO_3 = 8.0M, HNO_3 = 1.5M at the beginning of extraction. These conditions were achieved on future production runs by dissolving the sodium plutonyl acetate with 9.0M NH_4NO_3-2.2M HNO_3 reagent.

Runs Nos. 244P, 245P, 246P, 249P, 250P, 251P give data for suns from which extraction curve data was obtained. Aliquots were taken of the aqueous solution at definite time intervals and the Pu determined by radioassay. There is no data available on the extractions of HNO_3 during these extractions as there is still no good method of determining H^+ in the presence of Pu (VI). The extraction curves obtained from this data are contained in Figs. 4 and 5. Fig. 5 is

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especially significant as it shows graphically the important part HNO_3 plays in the extraction of plutonyl nitrate whereas in the extraction of uranyl nitrate it was found that the material kept extracting without "sloping off" to any great extent even after the HNO_3 concentration was very low.

Table II gives data for extractions made using $Ca(NO_3)-HNO_3$ as a salting out agent. It should be noted here that the initial HNO_3 concentrations are considerably lower than in the previous NH_4NO_3 runs yet the extractions obtained were a good deal better. Figs. 6 and 7 are the extraction curves obtained from this data. $Ca(NO_3)_2$ served as an excellent salting out agent when used to proceed directly from oxidation of the $Pu_2(C_2O_4)_3$ or the incoming material to Pu (VI) solution by $NaBrO_3-HNO_3$. It is assumed that all extractions listed in Table III were preceded by an oxalate precipitation unless otherwise indicated. The ether distillation rate was kept at ~25ml/min. and the temperature of the extractor at 8°C.

The efficiency of the ether extraction may be judged from the fact that, at the most, only several hundred parts of Ca per million of Pu were carried over during the extraction from a solution which contained about 40 times as much Ca (~4.0M Ca, ~0.1M Pu).

Conclusions which may be drawn from the data in Tables II and III and their accompanying graphs (Figs. 4, 5, 6, and 7):

(1) For best extraction the total NO_3^- concentrations in the aqueous solution containing Pu (VI) should be as high as possible. If NH_4NO_3 is used as a salting out agent, the HNO_3 concentration should be at least 1.0-1.5M initially or HNO_3 should be "bled" in occasionally to obtain a fast, complete (i.e., >99% yield of purified Pu) extraction. If $Ca(NO_3)_2$ is used as a salting out

agent, the HNO_3 concentration can be $<0.5M$. In actual practice the following sets of initial concentrations were found to be best:

$$\left\{\begin{array}{l} \text{7.5M } NH_4NO_3 \\ \text{1.5M } HNO_3 \\ \text{0.12M Pu (VI)} \end{array}\right\} \text{ or } \left\{\begin{array}{l} \text{4.0M } Ca\,(NO_3)_2 \\ \text{0.5M } HNO_3 \\ \text{0.12M Pu (VI)} \end{array}\right\}$$

(2) When NH_4NO_3 is used as a salting-out agent, the HNO_3 concentration is very important and the speed of extraction depends more on the ${}^{C}HNO_3$ than on the ${}^{C}NH_4NO_3$ or total NO_3 - concentration (compare 249P which used high ${}^{C}HNO_3$ and low ${}^{C}NH_4NO_3$ with 250P which used medium HNO_3 but very high NH_4NO_3 concentration).

(3) When $Ca(NO_3)_2$ is used as a salting-qut agent, rate of extraction is dependent principally on the total NO_3^- concentration in the aqueous solution.

(4) $Ca(NO_3)_2$ with low HNO_3 concentration is considerably better than NH_4NO_3 with high HNO_3 concentration.

The purification achieved on all these runs was satisfactory for the production of good plutonium metal.

Plutonyl Nitrate Ether Extractions. (NH$_4$NO$_3$ salting out agent)

Run No.	Time for dissapp. of Pu (VI) color in aqueous phase	$C_{NH_4NO_3}$	C_{HNO_3}	Pu loss (mg. left in aq. phase)	Method of Addn. of Salting-out Reagents.	Remarks
Average 200P-222P	about 30-40 min.	~6.5M	<0.8M	70 mg.	As single soln. Usually necessary to add 10-20 ml. additional 10N HNO$_3$	Ext. duration, 1-1 1/2 hrs.
223-P	10 min.	6.7M	0.93M	24 mg.	160 ml. of 10M NH$_4$NO$_3$, then 20 ml. 16M HNO$_3$	Ext. duration, 3/4 hrs.
225P	<5 min.	7.5M	1.75M	52 mg.	As single soln. of 10M NH$_4$NO$_3$-2.08M HNO$_3$	Ext. duration, 3/4 hrs. Some NH$_4$NO$_3$ pptd. initially but gradually re-dissolved.
227P	<10 min.	7.5M	1.10M	15 mg.	As single soln. of 10M NH$_4$NO$_3$-2.08M HNO$_3$	Ext. duration,
228P	<15 min.	7.26M	1.5M	18 mg.	As single soln.	Ext. duration, 60 min.
229P	<5 min.	8.25M	1.73M	11 mg.	As single soln., then addn. 13ml. of 10M HNO$_3$	Ext. duration, 50 min. NH$_4$NO$_3$ pptd. initially but gradually dissolved
230P	<25 min.	6.6M	1.66M	50 mg.	As single soln. then 10 ml. 16M HNO$_3$ additional	Ext. duration, 80 min. No acetate washes.

Table II (Cont.)

Run No.	Time for dissapp. of Pu (VI) color in aqueous phase	$C_{NH_4NO_3}$	C_{HNO_3}	Pu loss (mg. left in aq. phase)	Method of Addn. of Salting-out Reagents.	Remarks
244P	≤20 min.	8.24M	~0.27M (est.)	16 mg.	Single soln. 9.5M NH_4NO_3-0.83M HNO_3	Ext. duration, 80 min.
245P	≤60 min.	7.37M	~0.18M (est.)	47 mg.	Single soln. after oxidation-10M NH_4NO_3	Ext. duration, 120 min. No acetate ppt. Poor oxalate ppt. after extraction. No acetate. Gray ppt. formed during extraction.
246P	≤25 min.	8.15M	~0.19M (est.)	14 mg.	Single soln. after oxidation-10M NH_4NO_3	Ext. duration, No acetate ppt. Excessive Br_2 liberated.
249P	≤5 min.	7.61M	1.49M	9 mg.	Single soln. 9M NH_4NO_3-2.2M HNO_3	Ext. duration, 60 min.
250P	≤30 min.	8.64M	0.97M	5 mg.	Single soln. 10.2M NH_4NO_3-1.4M HNO_3	Ext. duration, 55 min.
251P	≤15 min.	8.4M After [illegible] min. 8.4M	~0.75M After 35 min. ~0.75M	4 mg.	Single soln. 10.2M NH_4NO_3-1.4M HNO_3	Ext. duration, 75 min. 19 ml. of 10M HNO_3 added after 35 min. of ext.

Fig. 4 Plutonyl Nitrate Ether Extractions (Table II)

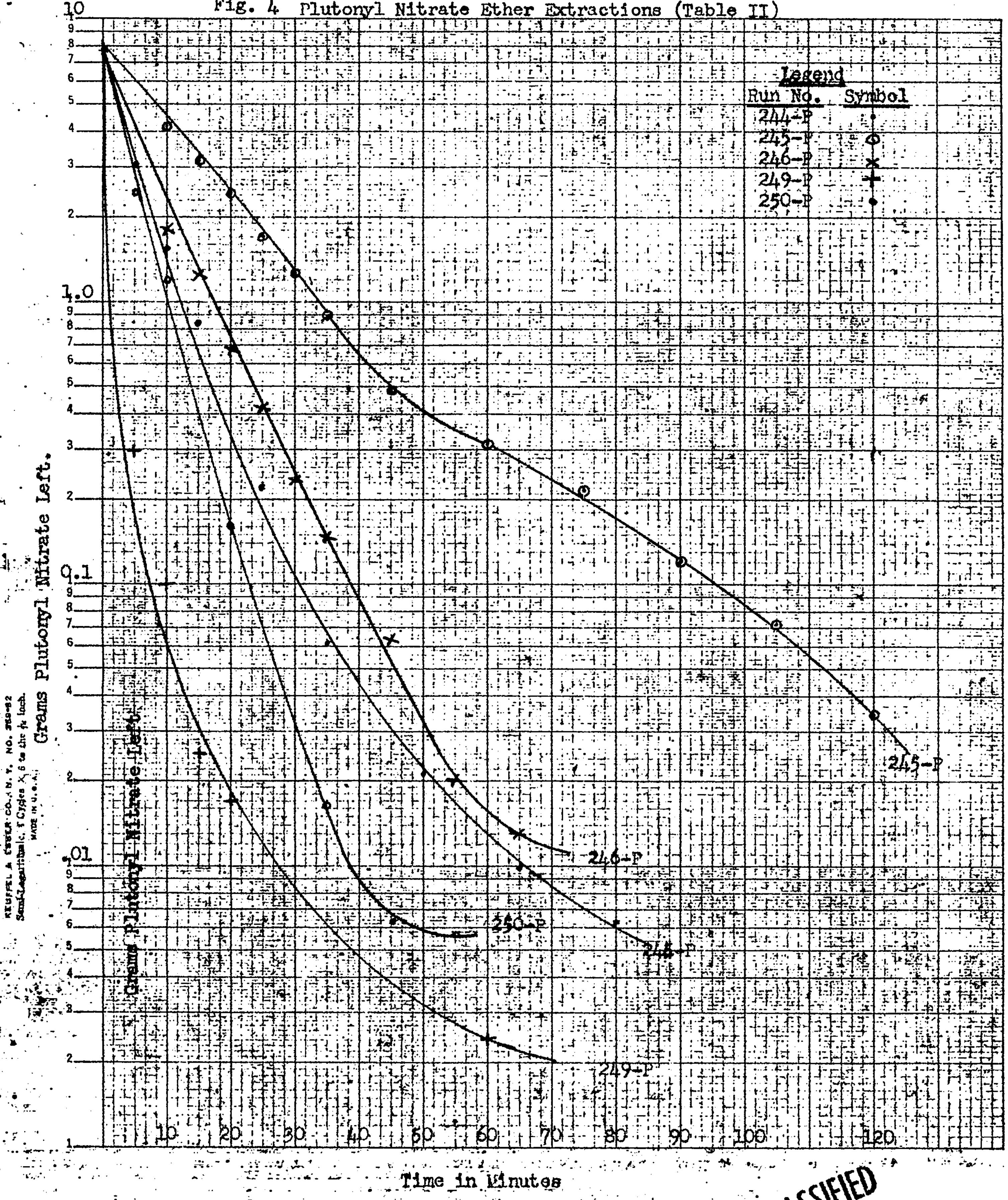

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Fig. 5 Plutonyl Nitrate Ether Extraction (251-P from Table II)

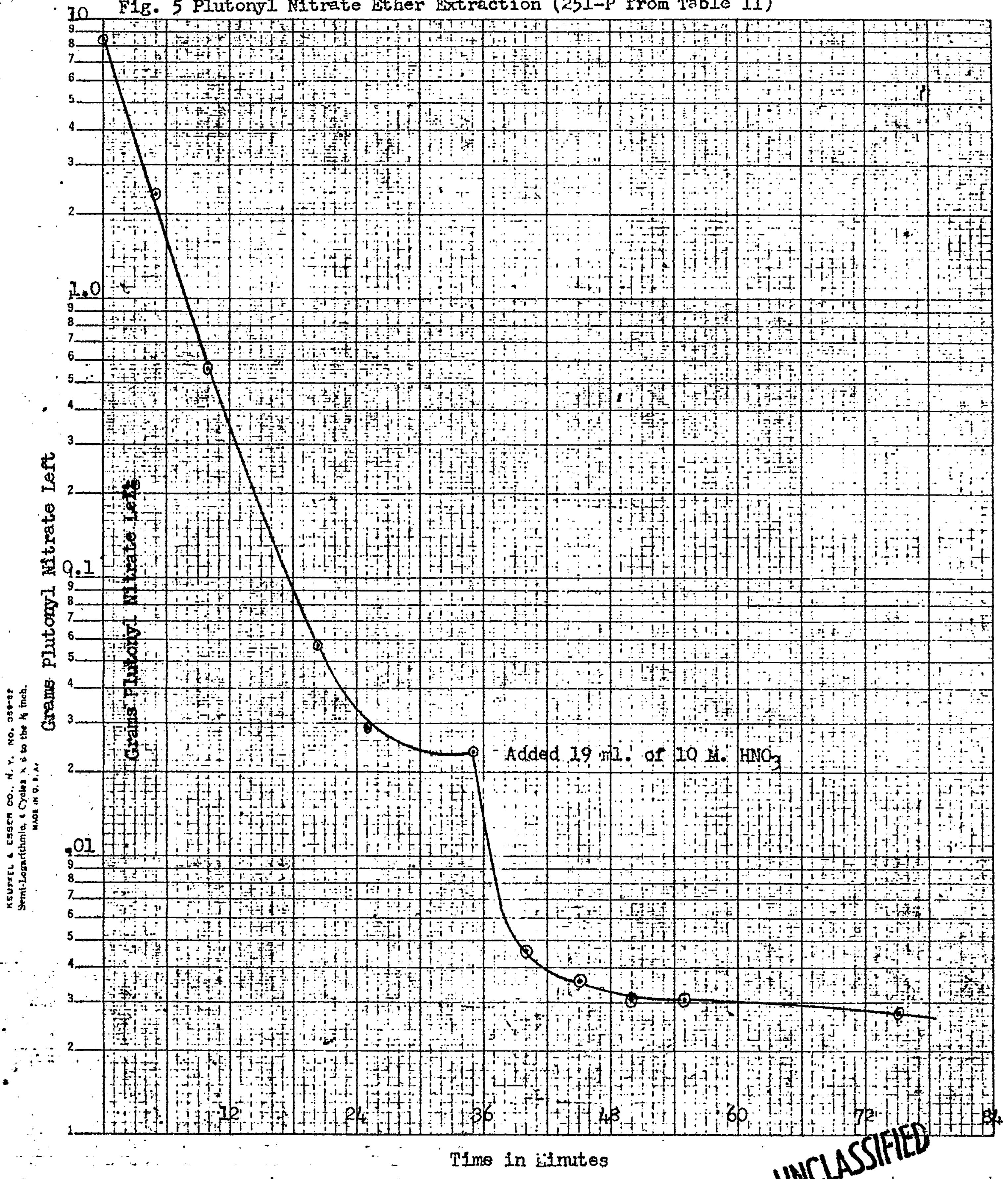

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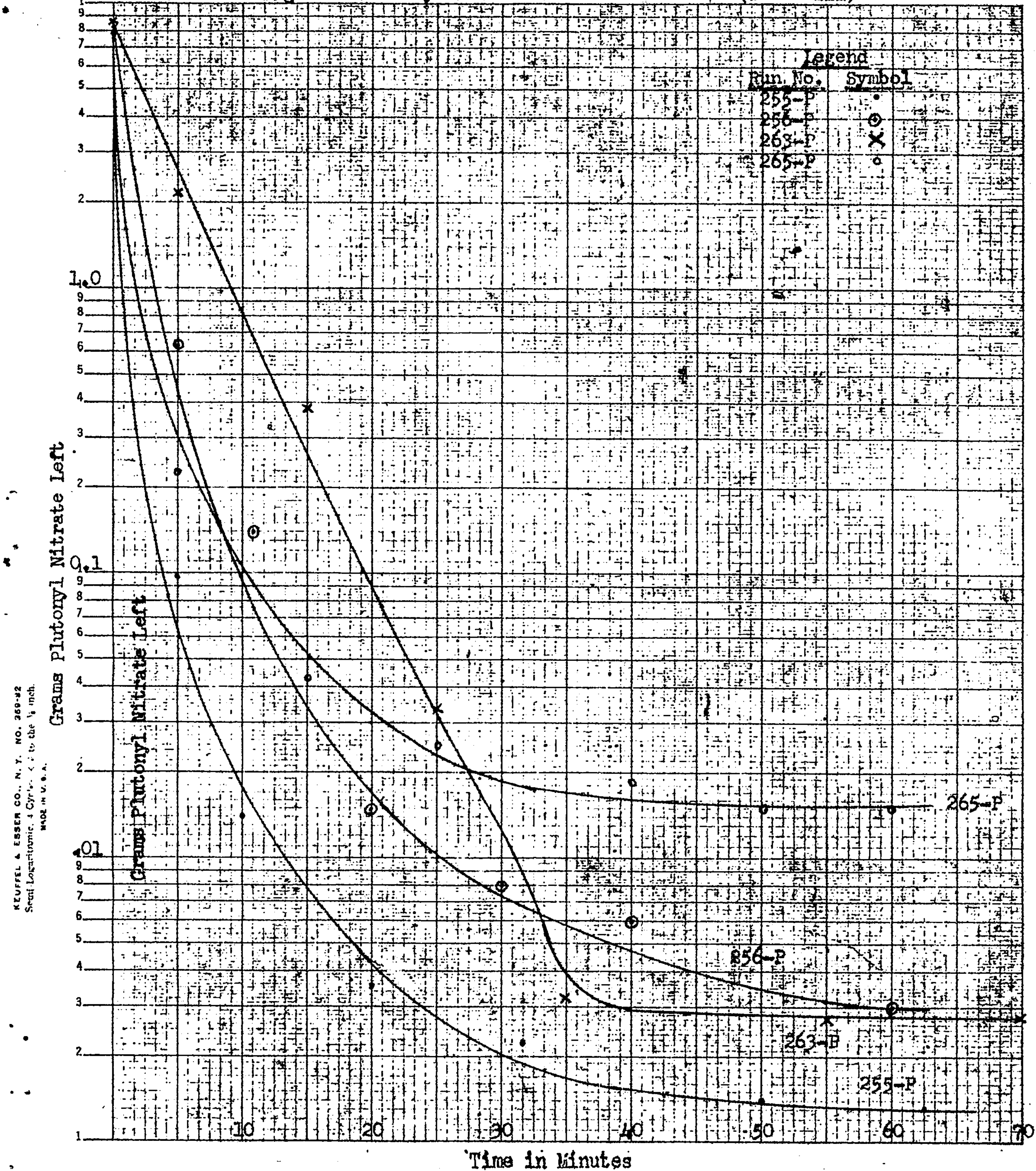
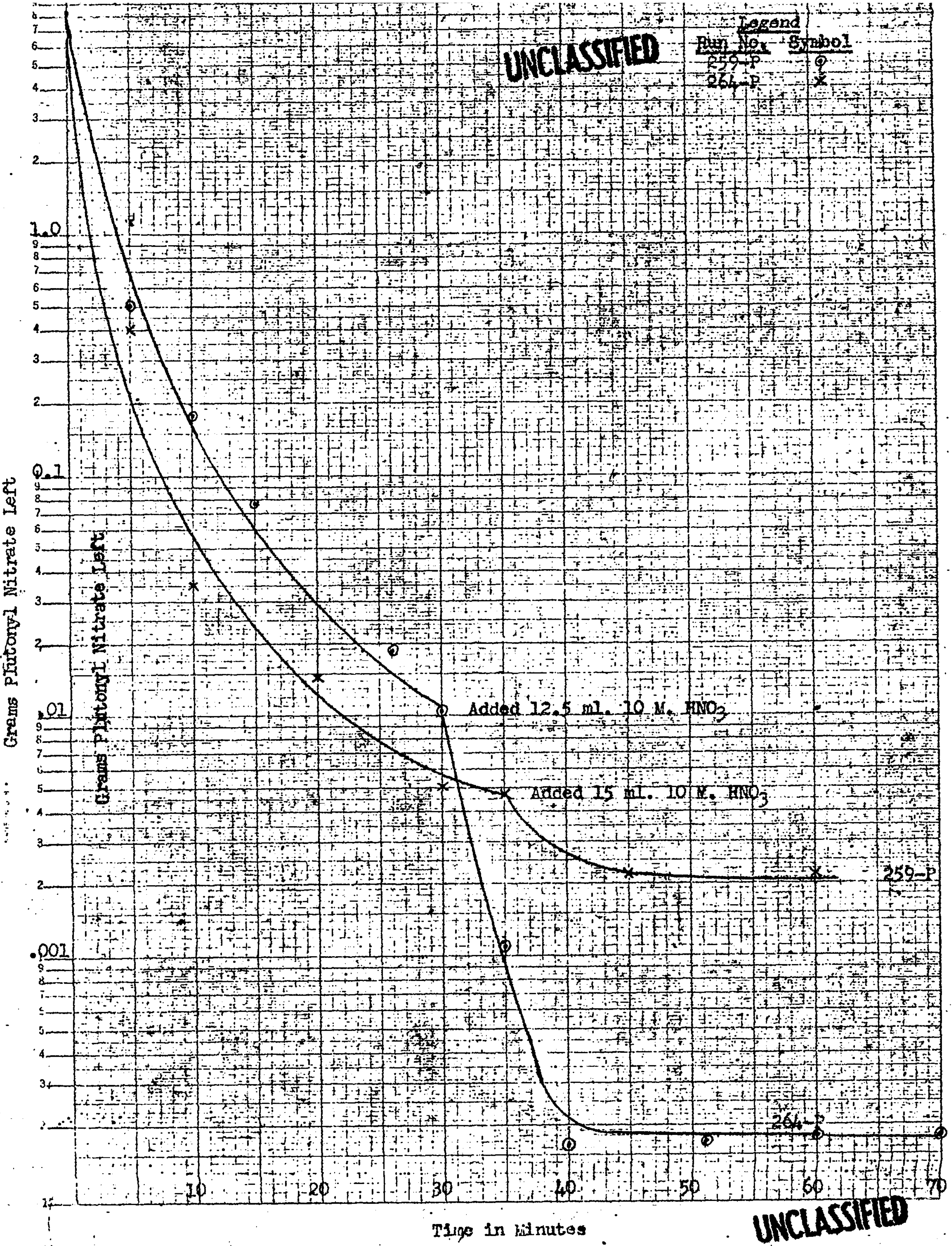
Table III

Plutonyl Nitrate Ether Extraction-($Ca(NO_3)_2$ salting out agent

Time for dissapp. of Pu (VI) color in aqueous phase	$C_{Ca(NO_3)_2}$	C_{HNO_3}	Pu loss	Remarks
$\leq$5 min.	4.28M	~.24M	2 mg.	Ext. duration, 70 min. 300 parts of Ca per million of Pu carried over with pure product.
$\leq$12 min.	3.0M	~.24M	7 mg.	Ext. duration, 80 min.
$\leq$10 min.	3.75M	0.55M	4 mg.	Ext. duration, 70 min. No oxalate pptn. Direct oxidation, then extraction.
$\leq$6 min.	3.75M	~0.5M	4 mg.	Ext. duration, 100 min. No oxalate pptn. 125 ml. 10M HNO_3 added after 60 min. Brown solid formed at H_2O-ether interface.
$\leq$18 min.	3.75M	~1.05M	3 mg.	Ext. duration, 70 min. No oxalate pptn.
$\leq$10 min.	3.75M	~0.4M	4 mg.	Ext. duration, 60 min. No oxalate pptn.
$\leq$8 min.	3.75M	~0.5M	16 mg.	Ext. duration, 60 min.

Fig. 6. Plutonyl Nitrate Ether Extractions (Table III)




Legend
Run No.
Symbol
259-P
264-P
Grams Plutonyl Nitrate Left
1.0
0.1
.01
.001
Added 12.5 ml. 10 M. HNO$_3$
Added 15 ml. 10 M. HNO$_3$
259-P
264-P
10
20
30
40
50
60
70
Time in Minutes

Purity Achieved by Process Involving Single Ether Extraction With $Ca(NO_3)_2$ as Salting-Out Agent.

Results of many previous analysis had indicated that a single ether extraction of Pu (VI) gave excellent purification. For this reason it was hoped that a shorter, more simple process could be used on a production scale which would depend only on an ether extraction and oxalate precipitation for complete purification. Two 160-gram runs, 576-P, and 577-P, were made to see if such a process would be satisfactory for purifying Hanford material as it was sent to this site in June, 1945. The procedure used was to oxidize the mixture of Pu (IV) and Pu (VI) nitrates (previously dissolved in 1M HNO_3) with excess $NaBrO_3$, then ether-extract the Pu (VI) nitrate using $Ca(NO_3)_2$ as a salting-out agent and finally precipitate $Pu_2(C_2O_4)_3$ after reduction of Pu (IV) with 5.5M HI. This was known as the B-1 purification process. The $Pu_2(C_2O_4)_3$ precipitate was washed three times and after the final wash-supernatant was drawn off, samples were taken for analysis. Further analyses were made after the Pu had been converted to metal and remelted by Hammel. (For detailed conditions for this process, see B-1 procedure in LA-405.)

Table IV is a summary of the purification achieved on these two runs listing elements analyzed for immediately after purification and after the metal was remelted. The metal produced was found sufficiently pure to meet all the requirements of the metallurgists and physicists.

These two 160-gram runs had proved that the B-1 process was sufficient to purify Hanford material received at that time. However, there was a definite possibility that certain impurities, viz. Cr, Fe, Ni, La, Sn, $SO_4^{=}$, and $PO_4^{\equiv}$, might be increased in the future. $SO_4^{=}$ and $PO_4^{=}$ had been reported as interfering ions which would hinder extractions of $UO_2(NO_3)_2$ by complexing the UO_2^{+2} strongly so it was feared that if they appeared in high concentrations, the extraction of Pu (VI) would likewise not go to completion. Also, if either $SO_4^{=}$ or $PO_4^{=}$ were carried over by ether with the Pu (VI) the complexing action might interfere with HI reduction or the oxalate precipitation. So to test the efficiency of extraction (using $Ca(NO_3)_2$ as a salting out agent) in removing these impurities and in overcoming the complexing effect of $SO_4^{=}$ and $PO_4^{\equiv}$, a series of extractions were made on the eight-gram scale in which the impurities in question were added in excess over any amount expected with Hanford Pu.

Table IV

Summary of Purification Runs 576P and 577P

Run No.		576P	577P
Date		6-18-45	6-21-45
Source of Pu		75-H	76-H
Elements Left After Purification (parts per million part of Pu)#	Li	<0.6 -----	<0.8 -----
	Be	----- -----	<.08 -----
	B	----- (<0.3)	----- (<0.3)
	Na	----- -----	3 -----
	Mg	<6 -----	<2 -----
	Al	9 -----	<2 -----
	Si	<120 (~[illegible]000)	<120 (~200)
	Pu	<43 -----	<65 -----
	K	----- -----	<73 -----
	Ca	220 -----	24 -----
	V	<60 (<30)	<60 (<60)
	Cr	<22 (<60)	<2 (<60)
	Mn	<6 (<10)	<2 (<10)
	Fe	[illegible] -----	118 -----
	Co	<22 -----	<8 -----
	Ni	<22 (<10)	8 (~10)
	Zn	----- -----	<33 -----
	Cu	----- (<60)	----- (<60)
	Sr	≤2 -----	<0.8 -----
	In	<30 (<30)	<30 (<30)

Numbers in parenthesis indicate ppm. of the element after the converted metal was remelted.

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Table IV (Cont.)

Run No.		476		577P	
Date		6-18-45		6-21-45	
Source of Pu		75-H		76-H	
Elements Left after Purification (parts per million part of Pu)#	Sn	-----	(15)	<8	(15)
	Sb	<60	(<60)	<60	(<60)
	Ba	43	-----	<2	-----
	La	<5	-----	<2	-----
	Ca	-----	-----	<17	-----
	Au	<150	(<150)	<150	-----
	Hg	-----	(<150)	<17	-----
	Tl	35	(<15)	<100	-----
	Pb	-----	-----	<8	(<15)
	U	-----	(40)	-----	(20)

Numbers in parenthesis indicate ppm. of the element after the converted metal was remelted.

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Table V is a summary of the data obtained from these runs. In all, seven 8-gram extractions were made using 21-W as starting material. Each run consisted of the following steps:

(1) Impurities were added to each 8g batch to bring the impurity concentration of the starting material up to the amounts indicated in Table V.

(2) The Pu (IV) - Pu (VI) starting mixture present was oxidized with $NaBrO_3$-HNO_3. To do this, temperature was raised slowly to 92°C, and held there for one hour, while stirring vigorously. Br_2 started coming off at ~65°C but by the time the temperature had reached 92°C no more Br_2 was apparent. After oxidation, the solution was quite cloudy (probably because of SnO_2 and SiO_2).

(3) Extraction was then carried out using $Ca(NO_3)_2$ as a salting-out agent. Ether was carried continuously through the aqueous solution. Initial concentrations and extraction conditions:

$C_{Pu} = 0.12M$

$C_{Ca(NO_3)_2} = 3.7M$

$C_{HNO_3} = \sim 0.3M$

$C_{NaBrO_3} = \sim 0.06M$

Temp. = 6.5° -- 8.5°C

Distillation rate of ether ~ 25 ml/min. Extractions were visually complete in less than 15 minutes (no Pu (VI) color in ether layer) but total extraction time was 45 minutes. Br_2 was present in the ether layer during some runs but no reason for this or correlation with other data could be found.

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(4) Samples were taken for analysis after extraction. Results are summarized in Table V. Losses of Pu in the aqueous layer did not exceed 14 mg (>99.8% recovery of purified Pu).

The only elements which appeared to any extent were Ca, Cr and Sn. The oxalate precipitation which follows this should remove a good deal of each of these impurities. The B-1 process was adopted for use on a production scale a short time after this research was done and the metal produced has been satisfactory from every standpoint.

Table V

Summary of Purification Achieved by Ether Extractions

Using $Ca(NO_3)_2$ as Salting Out Agent

Run No. (Date)	Initial Impurities	Impurities After Extraction (ppm.) (Separation factors given in parenthesis)							
		Ca	Cr	Ni	Sn	La	Fe	$SO_4^{=}$	$PO_4^{\equiv}$
273P (7-3-45)	Soln. A[3] 18.2 % $SO_4^{=}$ .09% $PO_4^{\equiv}$	170	220 (23)	[illegible] (715)	120	≤3 (>6,675)	130 (154)	<18,000 (>10)	<25 (>36)
274P (7-5-45)		70	220 (23)	10 (500)	70	≤3 (>5,675)	240 (080)	<18,000 (>10)	<25 (>36)
275P (7-5-45)	Soln. A[3] 50% $SO_4^{=}$ 0.5% $PO_4^{\equiv}$	60	300 (17)	10 (500)	100	<2 ([illegible]00)	157 (127)	<15,000 (>32)	<50 ([illegible])
27[illegible]P (7-6-45)		60	240	8 ([illegible]25)	100	<2 (>10,000)	[illegible]3 (228)	<15,000 (>32)	<50 (>100)
277P (7-6-45)	Soln. A[3] 50% $SO_4^{=}$ 2.0% $PO_4^{\equiv}$	160	300 (17)	20 (250)	200	<2 (>10,000)	140 (143)	<15,000 (>32)	<50 (>400)
278P (7-9-45)		270	450 (11)	≤23 (>217)	160	<5 ([illegible]00)	274 (73)	<14,000 (>35)	<64 (>310)
279P (7-9-45)	Soln. A[3] 18.2% $SO_4^{=}$ 2.0% $PO_4^{\equiv}$	250	400 (12.5)	≤26 (>200)	150	<5 (>4000)	100 (200)	<15,000 (>12)	<50 (>400)

1. "ppm." refers to parts by weight of element present per million parts of Pu.
2. %, given is with respect to Pu.
3. Soln. A brought impurities in starting material up to following amounts with respect to Pu.
   Fe=2.0%. Cr=0.5%, Ni=0.5%, La=2.0%, Sn= saturated soln. of Sn^{+4} with respect to 1M HNO_3.
4. Limits of sensitivity on the $SO_4^{=}$ analysis in presence of Pu (VI).

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Loss of Pu During Extraction

No matter how long any extraction was carried out there was always a residue of Pu (as determined by radioassay) which would not extract. This is clearly shown in several of the graphs (Figs. 4, 5, 6, 7) where the curve of extraction slopes off to a straight line at some low Pu concentration. After several extractions, the ether layer and aqueous layer were separated and assayed separately. It was found that only about one tenth of the residual Pu was left in the ether layer and, therefore, the bulk of it was still unextracted in aqueous solution.

There are several possible reasons for this. First of all, oxidation may have been incomplete and any Pu (IV) still in the solution would not extract from the solution which was very low in HNO_3. Secondly, it is evident that HNO_3 is extracted with the ether and may be depleted to such an extent that the pH of the aqueous solution approaches 7. It is feasible that at such a pH, basic complexes of Pu (VI) are formed that will not extract. Finally, there may be complexing ions present, e.g. acetate, sulfate, phosphate, that hinder the extraction of the last traces of Pu (VI).

Excessive Bromine Liberation During Extraction

During a large percentage of the extractions made, a great deal of Br_2 was present in the distilling ether and as vapor throughout the apparatus. Presumably, the Br_2 was either formed during the extraction from the interaction of $NaBrO_3$ with HNO_3 and NH_4NO_3 or was left in the apparatus after oxidation to Pu (VI) by $NaBrO_3$. It has already been mentioned that the use of NH_4NO_3 as a salting-out agent in the presence of $NaBrO_3$ liberated copious quantities of Br_2 and formed a paste-like emulsion in the ether layer which prevented the Pu (VI)

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from being carried over into the boiler (Fig. 1). When $Ca(NO_3)_2$ was used as a salting-out agent in the presence of $NaBrO_3$ and low HNO_3 concentrations, the liberation of Br_2 was reduced to such an extent that the yellow Br_2 color in the ether layer was hardly perceptible. This was partly due to the fact that nearly all $Ca(NO_3)_2$ extractions could be carried out using very low HNO_3 concentrations. When it was necessary to add additional HNO_3 to obtain complete oxidation (thereby leaving a relatively high HNO_3 concentration at the beginning of extraction) there was a great deal of Br_2 liberated even using $Ca(NO_3)_2$ as a salting-out agent. A special research problem indicated that considerable Br_2 was liberated just from the interaction of $NaBrO_3$ and HNO_3 (see section on "Oxidation", this report) even at the low temperature present during extraction.

Because much of the large-scale production apparatus had to be constructed of metal, presence of Br_2 constituted a very serious corrosion problem. The only metals which would withstand Br_2 vapor were platinum and tantalum. So as long as NH_4NO_3 was used as a salting-out agent it was more necessary to retain the acetate precipitation to remove the $NaBrO_3$ after oxidation than as a purification step. The problem of Br_2 corrosion has been minimized by the use of $Ca(NO_3)_2$ as a salting-out agent, by the use of poly-TFE plastic gaskets, and both platinum and tantalum metal on parts of the purification equipment exposed to Br_2 vapors.

Separation of Impurities by Ether Extraction

A large number of analyses were made after Pu (VI) had been extracted from aqueous solutions containing a large number of metal impurities. This work has been summarized in Table VI of this report.

B. Sodium Plutonyl Acetate Precipitation

Use of the sodium plutonyl acetate precipitation as a purification step

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was suggested by analogy with uranium chemistry. There are so few insoluble acetates that such a precipitation should lower the concentrations of all elements present with the plutonium except Np, U, Na and probably some of the heavier elements that would tend to hydrolyze at a pH = 5.

The first precipitation made at Site Y with tangible amounts of material was done as part of the purification scheme used on the first 10 mg of Clinton Pu purified here (see LA-75). The precipitant used was excess 2.4M NaAc-2.9M $NaNO_3$ which was added to the HNO_3 solution of Pu (VI) immediately after oxidation. This gave a supernatant above the precipitate with the following composition:

$Na^+ = 3M$

$Ac^- = 0.6M$

$HAc = 0.5M$

It was already known that $UO_2Ac_3^-$ was a strong complex ion and the solubility of the $NaUO_2Ac_3$ compound principally dependent on the mass action law. Therefore, the excess Na^+ used would be expected to greatly repress the solubility of the $NaPuO_2\ Ac_3$ precipitate. The precipitate was centrifuged and after the supernatant was drawn off, washed twice with 5M Na^+--0.2M Ac^- -- 0.35M HAc solution. The concentrations of Ac^- and HAc were adjusted to give a wash solution of pH = 5.

As long as acetate precipitations were carried out on the one-gram scale in centrifuge cones, no difficulty due to settling of precipitate was encountered as the precipitate could be easily separated by centrifuging it down to a small volume. However, as soon as the all-glass enclosed eight-gram purification apparatus was used, there was considerable difficulty in obtaining a precipitate that would settle to a reasonably low volume in a short time. Most of the

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precipitates settled so poorly that it was impossible to obtain satisfactory washing.

In order to determine qualitatively the best conditions for precipitation, one gram of Pu (VI) as the nitrate was precipitated under varying conditions of temperature and rate of addition of the precipitating reagent. The settling rate of $NaPuO_2Ac_3$ in each case was observed. It was found best to precipitate the $NaPuO_2Ac_3$ at a temperature of 60 to 65° C, adding the precipitating reagent at a rate of 4 ml/min. Using these conditions, it was still impossible to consistently obtain satisfactory precipitations so the chemical conditions at which the acetate precipitate initially formed were varied. It was finally found that good precipitates could always be obtained by diluting the Pu (VI) immediately after $NaBrO_3$ oxidation, to 0.24M and then using a precipitating reagent of 2.75M NaAc-2.4M $NaNO_3$.

The original conditions using a temperature of 60°C and a precipitating reagent addition rate 4 ml/min in the eight gram apparatus or 50 ml/min in the 60-gram production apparatus were still retained. The general procedure for such an acetate precipitation can be represented schematically as follows:

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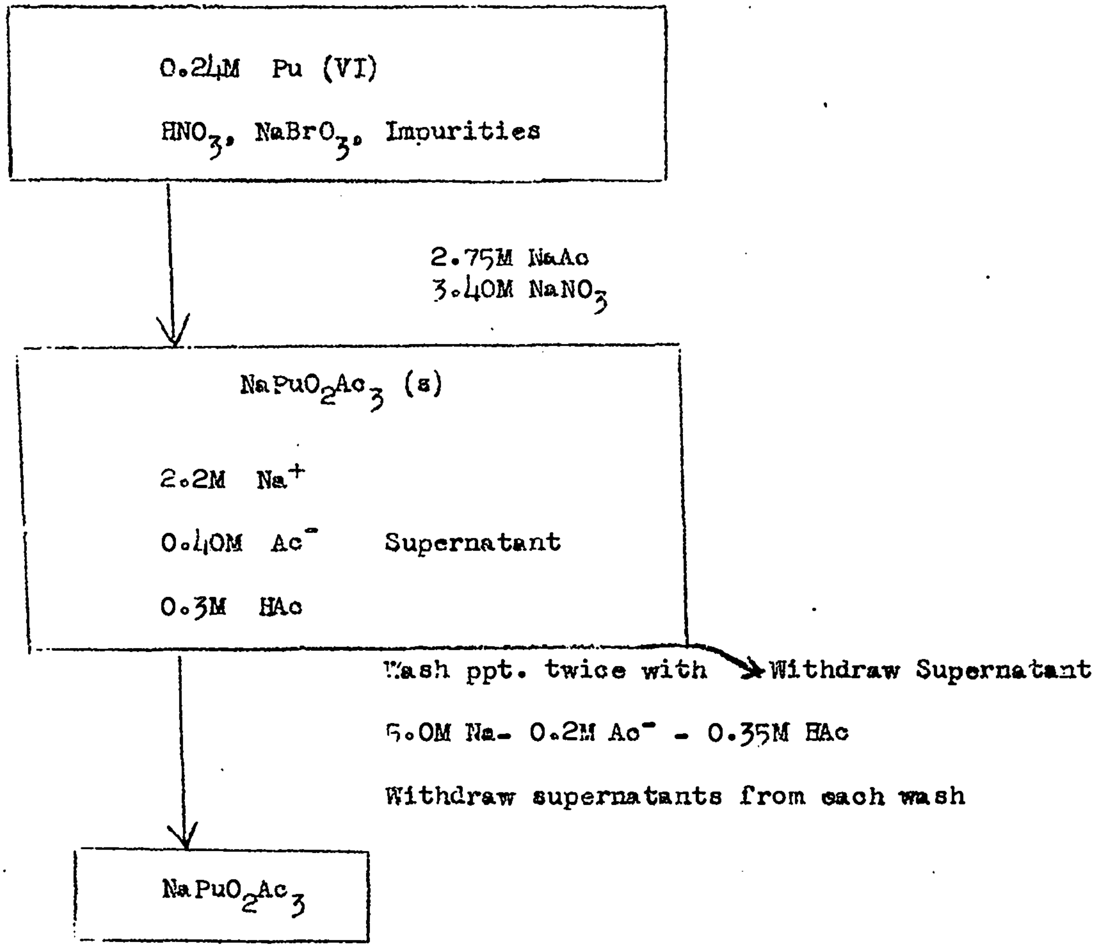

Sodium plutonyl acetate, as usually formed in this process is pink to light red color. When pure crystals are formed, they are bright red.

Solubility of $NaPuO_2Ac_3$

The solubility of $NaPuO_2Ac_3$ has been reported in another publication (LA-154). The figures given in this report, 19.5 grams/liter at 25°C, and 37.5 grams/liter at 95°C., indicate that one of the principle disadvantages of using the acetate precipitation in the purification process would be the high loss of Pu in the supernatant and washes. Although the high concentration of Na^+ (3 to 4M) used, cut down the solubility to 75 mg Pu/liter there was an even greater loss (150 mg Pu liter) due to samll suspended particles of the precipitate which could not settle, even after many hours, and were removed with the supernatant.

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The total loss incurred due to the acetate step in the procedure was at least 1% of the total Pu involved in the process. This made the $NaPuO_2Ac_3$ precipitation the highest Pu loss step in the process. It was natural, then, that when the ether extraction and $Pu_2(C_2O_4)_3$ precipitation was found to be successful in removing all impurities below tolerance limits that the acetate precipitation was dropped from the process (see use of $Ca(NO_3)_2$ as salting-out agent under extraction data in this report).

Impurity Removal by $NaPuO_2Ac_3$ Precipitation

The acetate precipitation followed by two washes of the ppt. was most useful in removing La and a fair percentage of most other elements. All the available data obtained here is presented in Table VI (part F, Summary of Purification Factors).

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C. Pu (III) Oxalate Precipitation

The purification process first used, (acetate precipitation and ether extraction) possessed no means of removing U from Pu. There were two reasons why a means of removing U was necessary in the process; (1) uranium sulfide crucibles were used for reduction and remelting of Pu metal and recovered Pu from these sources was highly contaminated with U, and (2) there was no way of knowing just how much U would be present in future Clinton or Hanford plutonium. It would be very difficult, because of the chemical similarity of UO_2^{+2} and PuO_2^{+2}, to effect a separation if both elements were in their highest oxidation state. For this reason, it was considered best to reduce the plutonium to one of the lower oxidation states and then precipitate it with an ion which would form an insoluble Pu compound but a fairly soluble UO_2^{+2} compound. After a great deal of research, the best precipitation found for this purpose has been the oxalate precipitate, $Pu_2(C_2O_4)_3$, formed by adding 0.67M $H_2C_2O_4$ to a solution of Pu (III) nitrate after reduction with iodide ion.

So far, this report has dealt with two useful purification steps. Now, with the advent of a third step, a workable process had to be developed which would proceed smoothly from one step to the next. It was necessary that dry conversion be given a Pu compound which could readily be converted to PuO_2. $Pu_2(C_2O_4)_3$ met this requirement very well so an oxalate precipitation had to be the last step in the process. It was considered best to have an oxalate precipitation as the first step because the separation factor of U from Pu was quite low (10 to 50), therefore necessitating two oxalate precipitations to obtain adeq [redacted] purification. Furthermore, after the $Pu_2(C_2O_4)_3$ precipitate was obtai the rest of the process could be planned using a starting compound of known composition.

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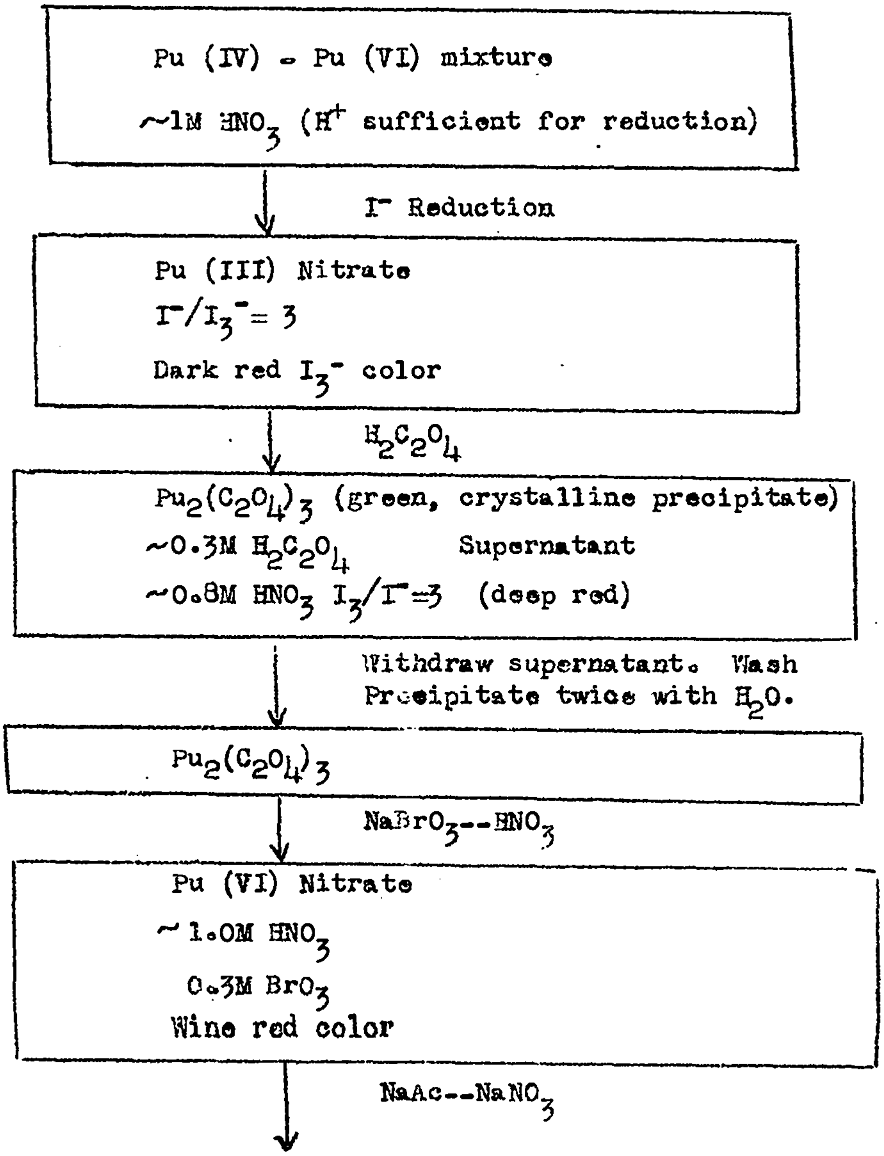
It was fairly easy to oxidize the $Pu_2(C_2O_4)_3$ to Pu (VI) nitrate and CO_2 using $NaBrO_3$-HNO_3. After oxidation, the $NaPuO_2Ac_3$ precipitation was made, then, after dissolving the precipitate in HNO_3 and ether extraction was made in the presence of NH_4NO_3 as a salting-out agent. The Pu (VI)-laden ether was carried into a boiler where the last oxalate precipitation was carried out. This process was used on a production scale from April, 1944 until August 1945 and is represented schematically as follows (see LA-405, "A" Process) ;



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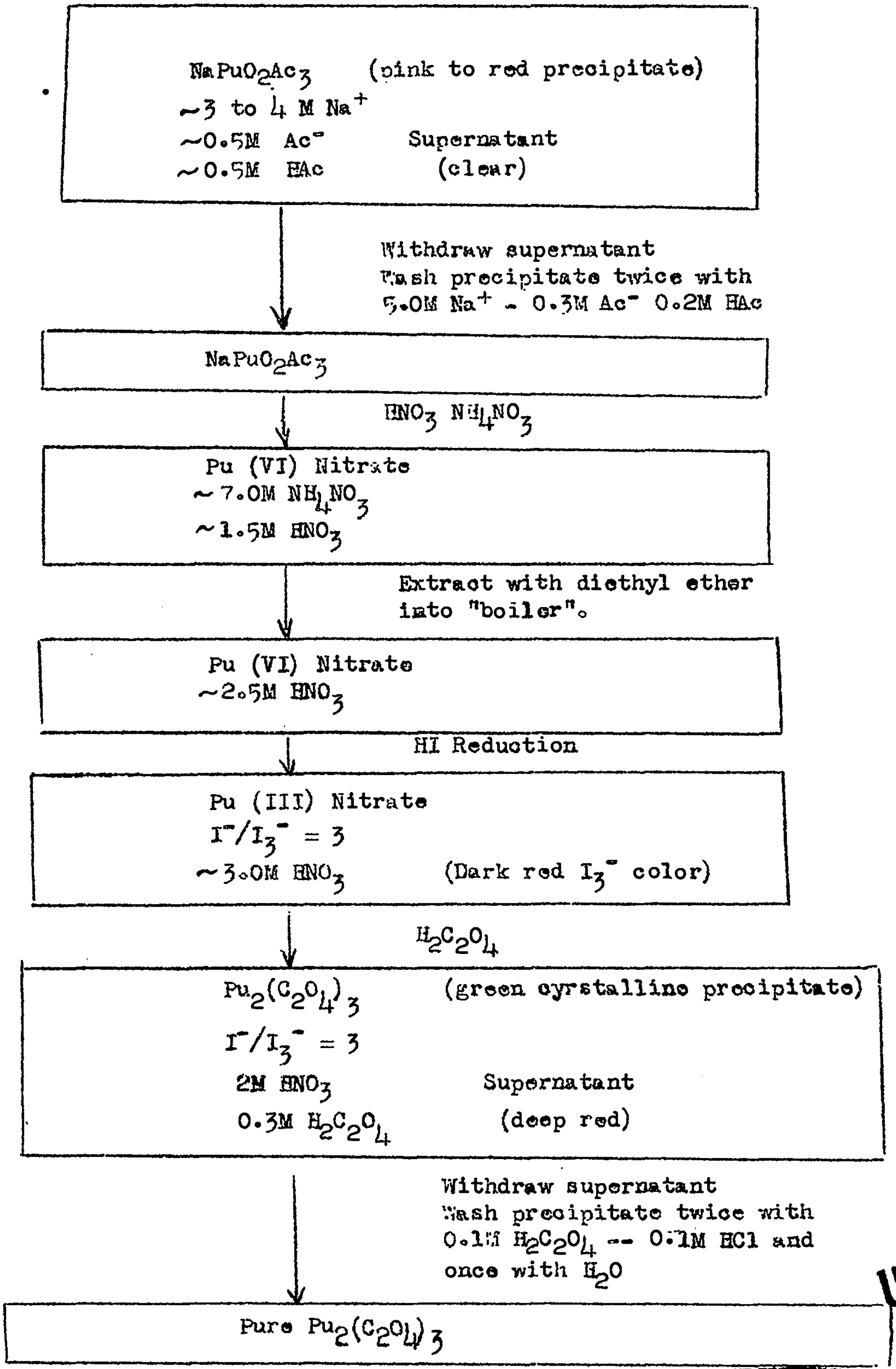

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Initial Studies on Use of the Oxalate Precipitate

The first problem entailed a determination of the comparative solubilities of $Pu_2(C_2O_4)_3$ and of $UO_2C_2O_4$. Further, the possibility that the $Pu_2(C_2O_4)_3$ precipitate would carry down the major portion of the UO_2^{+2} with it was not out of the question, so the actual separation factor of U from Pu under the conditions used in a purification process must be found.

Menker has already determined the Ksp of $UO_2C_2O_4 = (^{C}UO_2^{+2})\ (^{C}C_2O_4^{=})$ $= 1.73 \times 10^{-8}$. For purposes of comparison it was necessary to determine the Ksp of $Pu_2(C_2O_4)_3$.

$$Ksp = (^{C}Pu)^2\ (^{C}C_2O_4^{=})^3$$

Two determinations, made by independent workers, gave values of $\underline{1 \times 10^{-26}}$ and $\underline{1.12 \times 10^{-26}}$ for Ksp of $Pu_2(C_2O_4)_3$. Both of these experiments were made immediately after HI reduction of Pu (IV) so that the supernatant above the precipitate contained I^-/I_3^- ratio equal to 3, a known molority of H^+ and of $H_2C_2O_4$, and a known concentration of Pu^{+3} in equilibrium with the precipitate (determined by radio assay). The concentration of $C_2O_4^{=}$ was calculated from the dissociation equation.

$$^{C}C_2O_4 = \frac{K_1\ K_2\ (^{C}H_2C_2O_4)}{(CH^+)^2}$$

Later, experiments were performed to check these data. This time, pure $Pu_2(C_2O_4)_3$ was mixed with H_2O and the dissolved Pu^{+3} concentration determined by radioassay. Under these conditions, $Ksp = 3.38\ (^{C}Pu^{+3})^5$ as $^{C}C_2O_4 = (3/2)\ ^{C}Pu^{+3}$. The value of Ksp obtained by this method after allowing <u>15 minutes</u> for the system to come to equilibrium was $\underline{1.08 \times 10^{-26}}$, an exceedingly good check on the previous

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two values. An interesting fact was brought out during this work. Samples of the supernatant were taken at time intervals and it was found that the concentration of Pu present in the supernatant increased gradually, finally reaching a maximum amount after about 2-1/2 hours. This either indicates that it takes this long for the equilibrium,

$$Pu_2(C_2O_4)_3 \rightleftarrows 2Pu^{+3} + 3C_2O_4^{-2}$$

to be established, or that slight oxidation of the Pu (III) to form Pu (IV) and Pu (VI) is taking place thus allowing dissolution of additional Pu^{+3} from the precipitate. Because of the excellent correlation with previous data, the latter was taken as the most logical explanation.

Under the conditions used for the oxalate precipitation, $UO_2C_2O_4$ would have a solubility of $\sim$ 28g of U per liter, while $Pu_2(C_2O_4)_3$ would have a solubility of only $\sim$0.45 g of Pu^{+3} per liter. This great difference in solubility indicated the possibility of a good separation of U from Pu. Experiments were performed in which known amounts of $UO_2(NO_3)_2$ were added to samples of Pu (III) nitrate and then an oxalate precipitation carried out. As determined by analyses, the concentration of UO_2^{+2} was cut down by factors of about 20 to 50 after a single oxalate precipitation.

Pu^{+3} was found to complex readily in saturated $K_2C_2O_4$ or $H_2C_2O_4$ solution to give a very soluble green oxalate complex. For this reason, the excess of $H_2C_2O_4$ used for precipitation had to be controlled rather well. It was found best to keep the concentration of excess $H_2C_2O_4 < 0.4M$ and have the H^+ concentration $> 0.5M$ to keep the dissociation of $H_2C_2O_4$ down to a minimum.

In actual practice the oxalate precipitation proved to be a very

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satisfactory step in the purification process. Once a satisfactory reduction was obtained, it was very easy to obtain a precipitate which would settle exceedingly well even after several washes. Besides removing uranium, a fair percentage of many other impurity elements were removed by the first oxalate. This lightened the load considerably on the following purification steps in the process. All of the precipitations used were carried out at room temperature. No particular advantage could be found in precipitating at higher temperatures. As in the case of the $NaPuO_2Ac_3$ precipitate, slow addition of the precipitating reagent ($\sim$3ml/min) produced a somewhat better precipitate.

Purity Achieved by Single Pu (III) Oxalate Precipitation

By the summer of 1945, the Hanford Pu received at Site Y had become low enough in impurities (less than 1%, excepting $SO_4^=$ and $PO_4^=$) to consider the possibility of using a single Pu (III) oxalate precipitation followed by three washes as a satisfactory purification process (see "C" Process, LA - 405, for detailed procedure). Four 8-gram runs and two 160-gram runs were made following this procedure but the analyses obtained are not sufficient to warrant its immediate use. After a single Pu (III) precipitation, the conversion to Pu F_4, reduction of Pu F_4 to Pu metal, and the α-n background count of the metal were all satisfactory. The main disadvantage of this process is its inability to remove La. Both Clinton and Hanford Pu contain about 1% of this impurity and it must be removed to meet purity tolerances. Furthermore, if any of the impurities now present in Hanford material were to be increased without warning, a considerable quantity of unsatisfactory metal might be produced.

Purification achieved by the oxalate precipitation can be found in this report in Table VI; Summary of Purification Factors.

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Loss of Pu During $Pu_2(C_2O_4)_3$ Precipitation

Losses of Pu incurred during the oxalate precipitation from Pu^{+3} in solution and solid suspended particles of $Pu_2(C_2O_4)_3$ in the supernatants and washes was never excessively great. The total loss during the first oxalate precipitation and two washes was about 0.3% of the total Pu in the process. The total loss during the last oxalate precipitation and three washes was about 0.7% of the total Pu in the process. Loss during the last oxalate precipitation is higher not only because of the extra H_2O wash of the precipitate involved, but also because 5.5M <u>HI</u> was used for reduction of the plutonium to Pu^{+3} instead of KI which was used for the first oxalate precipitation. The extra H^+ in the last oxalate would necessarily increase the solubility of $Pu_2(C_2O_4)_3$. It is possible to use $K_2C_2O_4$ as a precipitating reagent instead of $H_2C_2O_4$ and obtain satisfactory results. This would cut down the H^+ concentration considerably and thereby reduce the loss due to solubility of $Pu_2(C_2O_4)_3$. This procedure has not been adopted on a production scale. Despite the additional loss involved, it was found best to keep the H^+ at least 0.5M. This produced a much more crystalline precipitate which would settle better, and achieve better purification than when a lower H^+ concentration was used.

Effect of Leaving $Pu_2(C_2O_4)_3$ in Boiler after Ether Extraction

It was impossible to remove all traces of the $Pu_2(C_2O_4)_3$ precipitate left in the boiler after the purification process (Fig. 1 Apparatus). On the following "run" in that apparatus, the first use of the boiler would be to receive $PuO_2(NO_3)_2$ - HNO_3-laden ether and boil off the ether to be recycled while retaining the $PuO_2(NO_3)_2$ and HNO_3 in solution. It was thought that the traces of $Pu_2(C_2O_4)_3$ in the boiler might react with these substances to give a troublesome compound or precipitate which might interfere with the subsequent HI reduction and oxalate precipitation. A number of runs were made on the 3-gram

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scale in which $Pu_2(C_2O_4)_3$ was left in the boiler mixed with water or dilute HNO_3 ($< 1.5M$) during an ether extraction. In every case the precipitate dissolved to give a clear solution of plutonium nitrate. When 1.0 to 1.5M HNO_3 was left in the boiler with the precipitate, dissolution occurred in 5 to 20 minutes depending on the amount of precipitate. In H_2O, dissolution of the precipitate was complete in 30 to 40 minutes after it was exposed to Pu (VI) nitrate and HNO_3 carried over by the ether. Presumably, the $Pu_2(C_2O_4)_3$ was oxidized by the Pu (VI) and HNO_3 present in the boiler:

$$Pu_2(C_2O_4)_3 + 12H^+ + 4PuO_2^{+2} \longrightarrow 5Pu^{+4} + 6CO_2 + 8\,H_2O$$

D. Reduction of Pu (IV) and Pu (VI)

The plutonium received at Site Y was a mixture of Pu (IV) and Pu (VI) nitrates. If this material were to be purified by the "A" process, in which the first step is a $Pu_2(C_2O_4)_3$ precipitation, a satisfactory production scale reduction to Pu^{+3} had to be developed. Various reagents tested for this use were $HCOOH$, H_2CO, H_2S, electrolysis, H_2 and Pt black and I^- (from either KI or HI). The most satisfactory reducing agent found for use on a production scale was I^-. Either KI or HI was added directly to the mixture of plutonium nitrates while stirring vigorously. 15 to 20 minutes were allowed for complete reduction. A crude colorimetric determination indicated that the half-time for I^- reduction of a Pu (IV) - Pu (VI) nitrate mixture was about one-half minute, so the time used for reductions (15-20 minutes) gave essentially complete reduction. After ether extraction, the Pu (VI) nitrate in the boiler must also be reduced to Pu^{+3} before the last $Pu_2(C_2O_4)_3$ precipitation can be made. HI was always used for this reduction to avoid contamination of the pure product with K^+.

The following reactions represent the reduction of Pu (IV) - Pu (VI) by I^-:

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(1) $2Pu^{+4} + 3I^{-} \longrightarrow 2Pu^{+3} + I_3^{-}$

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

Besides the I^- used to reduce the plutonium nitrate, there must be sufficient excess present to complex the I_2 formed, by the reaction.

(3) $I_2 + I^- \rightarrow I_3^-$

Using given values of K and the known molarities for the solubility of I^- and I_2 in the equation

$$K = \frac{(I^-)\ \ (I_2)}{(I_3^-)}$$

it was possible to calculate the I^-/I_3^- ratio just necessary to keep the I_3^- complex stable (no I_2 precipitate). For temperatures of 20 to 30° this ratio equals 1.06. Further there are .670 equivalents of oxidizing power in reaction (1) and 3x.670 = 2.01 equivalents of oxidizing power in reaction (2). Thus for each .670 equivalents of oxidizing power for plutonium, 0.335 moles of I_3^- are formed and 1.005 moles of I^- are necessary <u>just</u> for reduction. A total of 1.340 moles of I^-, then, is the minimum amount required for reduction of each .670 equivalents of oxidizing power of plutonium nitrate. It was decided to add one mole excess of I^- thereby bringing the I^-/I_3^- ratio of the supernatant to 3. This excess of I^- was considered adequate to meet all possible changing conditions.

H^+ Necessary for Reduction

By chemical analysis, Hanford material was found to contain about 50% Pu (IV) and 50% Pu (VI). The Pu (VI) was assumed to be PuO_2^{+2} because of its similarity to UO_2^{+2}. Then if Pu (IV) is assumed to be Pu^{+4} (which requires no H^+ for reduction) it should be possible to base all H^+ calculations on the 50% PuO_2^{+2} present. When this was done, there wasn't sufficient H^+ present to enable the reduction to go to completion. Several factors may be involved here; (1) it

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was impossible to do more than estimate the H^+ concentration present and all our estimates may have been high, (2) the actual formula for the Pu (IV) ion may be PuO^{+2}. <u>If</u> the latter is true reaction (1) becomes

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

This would account for the consumption of H^+ not calculated for but we have no evidence that PuO^{+2} is the actual complex ion form.

In order to avoid the necessity for relying on H^+ calculations, it was decided to use 5.5M HI for all reductions on a production scale. Then the reducing agent alone supplies ample H^+.

<u>Temperature During Iodide Reduction</u>

When put on a production scale, the last HI reduction after ether extraction caused a great deal of corrosion trouble from I_2 liberation. This was believed due to the oxidation of I^- by the excess HNO_3 present. In order to find a method by which I_2 liberation could be avoided, an experiment was made using the same chemical conditions in the process, 4M HNO_3 - 1.5M I^- - 0.5M I_3^-. This solution was held at known temperatures and the I_2 liberated determined by thiosulfate titration and collecting the I_2 formed on a "cold finger". Below 30°C, there was practically no I_2 liberated, but above this temperature oxidation of the I^- by HNO_3 rose sharply and a great deal of I_2 was given off. Further, it was found that the reduction of Pu (VI) by I^- liberated 50 Kcal per mole of Pu. On a 160-g scale, this would mean the temperature during reduction would rise 27°C, if 100% Pu (VI) were present and 14°C, if 50% Pu (VI). Therefore, in order to keep the temperature during reduction below 30°C, it was necessary to lower the temperature of the Pu (VI) - HNO_3 mixture to 15°C before reduction and keep coolant circulating around the boiler (or extractor, if it were first HI reduction) all during reduction. Also the rate of reaction had to be kept low

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by controlled addition of HI. Reduction of the Pu (VI) by I^- was just as complete in the same time as at a higher temperature (based on comparison of yields).

Effect of Various Reducing Agents on Pu (VI)

SO_2 was used to produce very satisfactory reduction of Pu (VI) to Pu (III).

$$2PuO_2^{+2} + 3SO_2^{+2} + 2H_2O \longrightarrow 2Pu^{+3} + 3SO_4^{=} + 4H^+$$

It was only necessary to bubble SO_2 gas through the Pu (VI) nitrate solution or add cold, saturated SO_2 solution to it. In about 5 minutes, reduction to blue-violet Pu $(NO_3)_3$ solution was complete.

Formaldehyde, H_2CO, reduced Pu (VI) nitrate to its lowest valence state quantitatively.

$$2PuO_2^{+2} + 3H_2CO + 2H^+ \longrightarrow Pu^{+3} + 3HCOOH + H_2O$$

The reduction was carried out in a sealed container (to keep all the H_2CO in solution) at 90°C. Under these conditions and with ~150% excess H_2CO, reduction was complete (1.0-mg scale) after about 15 minutes. On several reductions using 60 to 80 mg of Pu, a green precipitate of unknown constitution was formed. It usually took several days to dissolve this precipitate and thereby complete the reduction.

Hydrogen sulfide, H_2S, produced complete reduction of Pu (VI) nitrate in less than 5 hours at room temperature.

$$2PuO_2^{+2} + 3H_2S + 2H \longrightarrow 2Pu^{+3} + 3S^o + 4H_2O$$

The free S^o formed in this reaction was centrifuged off and the excess H_2S removed by boiling on a steam bath.

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Electrolysis of a Pu (VI) nitrate solution produced Pu (IV) nitrate. Using about 20 milliamperes and 1.6 volts, reduction to Pu (IV) was complete in 35 minutes.

$$PuO_2^{+2} + 2H^+ + 2e^- \longrightarrow PuO^{+2} + H_2O$$

After reduction, no precipitate was obtained upon the addition of either NaAc or HF so it was estimated that there could not be greater than 5% of PuO_2^+ and Pu^{+3} present. It is possible that the use of different electrolysis conditions would further reduce PuO^{+2} to Pu^{+3} but research on this problem was discontinued.

H_2 will reduce Pu (IV) to Pu (III) in ~10 minutes using a Pt° black catalyst and a fast stream of H_2.

$$2PuO^{+2} + H_2 + 2H^+ \xrightarrow{Pt^{o}\ black} 2Pu^{+3} + 2H_2O$$

Because of the mechanical difficulties involved and uncertainty of consistent reduction, none of these procedures were ever used on a production scale.

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E. Oxidation Research

Oxidation of Pu (III) and Pu (IV) to Pu (VI) nitrate was necessary as a preliminary to either a $NaPuO_2Ac_3$ precipitation or other extraction. The first oxidant used was 0.2M $Na_2Cr_2O_7$ - 1M HNO_3 and the oxidation was made on dissolved plutonium nitrate from Clinton (principally Pu^{+4}). $Na_2Cr_2O_7$ was not a satisfactory oxidizing agent for several reasons. The oxidation required from 3 to 10 hours at 93°C depending on how long it took for in insoluble plutonium chromate compound initially formed to dissolve. Often, it was impossible to dissolve the last traces of this compound. Also when the $Na_2Cr_2O_7$ oxidation was followed by a $Na\ PuO_2Ac_3$ precipitation, insoluble chromates of the impurities present also precipitated at the pH of 5 attained. This meant, of course, that there was virtually no removal of such impurities. After investigation of various oxidizing agents, $NaBrO_3$ was chosen as the best agent on a production and research basis. The Br_2 formed during oxidation was driven off, no further metal ion impurities were introduced, no insoluble bromates were formed and oxidation was faster.

$NaBrO_3$ could be used to oxidize the solution of Pu (IV) nitrate in 1-2M HNO_3 prepared at Site Y by dissolving the plutonium nitrate paste received from Clinton or Hanford (first step in "B" Process);

$$5PuO^{+2} + 2BrO_3^- + 2H^+ \longrightarrow 5PuO_2^{+2} + Br_2 + H_2O.$$

This oxidation was complete after heating at 93°C (boiling temperature) for one hour. A 100% excess of $NaBrO_3$ was used.

For the "A" process, $NaBrO_3$--HNO_3 was used to oxidize the first $Pu_2(C_2O_4)_3$ precipitate to $PuO_2(NO_3)_2$ solution

$$5Pu_2(C_2O_4)_3 + 12BrO_3^- + 32H^+ \longrightarrow 10PuO_2^{+2} + 6Br_2 + 30CO_2 + 16H_2O$$

This oxidation was complete after heating at 93°C for one hour. Temperature had to be raised slowly to avoid violent Br_2 liberation and CO_2 foaming which, if uncontrolled, would carry the oxidizing mixture over into the reactor. The first step in this reaction may be oxidation (at room temperature) of $Pu_2(C_2O_4)_3$ to $Pu(C_2O_4)_2$ by the HNO_3. This was indicated by an immediate color change of the precipitate from green to light tan and the fact that no Br_2 was liberated. Then, as the temperature was raised, the tan Pu $(C_2O_4)_2$ precipitate gradually dissolved. Accompanied by copious evolution of Br_2 about 30% excess $NaBrO_3$ and 100% excess HNO_3 were used in the reaction mixture. After oxidation, the $PuO_2(NO_3)_2$ solution in 1M HNO_3 was a clear wine-red color.

On a production scale (160g Pu) there was considerable difficulty in consistently obtaining satisfactory oxidation of Pu (VI) - Pu (IV) nitrates in 1M HNO_3. ("B" Process). In many cases an insoluble precipitate of unknown composition was formed which was very difficult to dissolve. This precipitate was undoubtedly a plutonium compound so it must be dissolved before an ether extraction, the next step in the process, could be made. It was found possible to complete the oxidation by adding an additional 50% excess of $NaBrO_3$ and HNO_3 and continue heating at 93°C until the precipitate was in solution. Often this required several hours. A possible explanation for this difficulty can be found in the fact that the starting plutonium nitrate solution before such a troublesome oxidation was usually an intense green color. This green color has been associated with a polymerized form of Pu (IV) nitrate which contains at least several thousand Pu (IV) atoms in each molecule of the polymer. The polymer may form a precipitate which is very hard to dissolve.

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Oxidation of BrO_3^- by HNO_3

Because a troublesome oxidation could be completed by adding further excess of BrO_3^- and HNO_3, it was thought possible that reaction between these two compounds might be sufficient to destroy each other, thus necessitating replenishment of these reagents to complete the oxidation to Pu (IV). An experiment was performed in which 0.335M $NaBrO_3$ was reacted with 0.5M, 1.0M, 2.0M and 4M HNO_3 at 93°C (temperature and concentration of $NaBrO_3$ used in the process). Aliquots were taken at definite time intervals and the BrO_3^- determined by titration against standard thiosulphate. With 0.5M HNO_3, there was practically no reaction after several days. With 1.0M HNO_3, there was slight, noticeable Br_2 liberation but it was not sufficient to detect by the titration used in this experiment. With 2.0M HNO_3, the half-time for the decomposition of the BrO_3^- present was $\sim$50 minutes. With 4M HNO_3, the half-time for BrO_3^- decomposition was $\sim$20 minutes. As the usual H^+ concentration used during oxidation is about 1M, there is probably very little loss of $NaBrO_3$ and HNO_3 due to their interactions.

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F. Summary of the Purification Achieved by Various Processes and by Single Steps in each Process.

Table VI is a summary of the impurity separation data obtained while working on various chemical processes for the purification of plutonium. Results have been given in "Purification Factors" (referred to by the abbreviation P.F.) where purification factor equals the parts by weight of the impurity per million parts by weight of Pu (ppm) before purification divided by the parts by weight of the same impurity per million parts by weight of Pu after purification, for one or a given combination of purification steps used. As referred to in the table, these steps are:

Oxalate Precipitation -- $Pu_2(C_2O_4)_3$ precipitation followed by two or three washes,

Acetate Precipitation -- $NaPuO_2Ac_3$ precipitation followed by two washes,

Ether Extraction NH_4NO_3 -- Diethyl ether extraction of plutonyl nitrate using NH_4NO_3 as a salting-out agent,

Ether Extraction, $Ca(NO_3)_2$ -- Diethyl ether extraction of plutonyl nitrate using $Ca(NO_3)_2$ as a salting-out agent.

Any combination of the above steps is known as a "Process". As referred to in the table, these processes are:

"A" Process -- consists of an oxalate precipitation, an acetate precipitation, and an ether extraction, NH_4NO_3 if P.F. is obtained from experimental data; if P.F. is obtained from the calculated best estimated P.F. (see notes following Table VI), it includes another oxalate precipitation,

"B" Process -- consists of an ether extraction, $Ca(NO_3)_2$ and an oxalate precipitation,

"C" Process -- consists of a single oxalate precipitation.

See LA-405 and the special sections of this report for details of all the above steps and processes mentioned.

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Other terms used in Table VI which require explanation are:

Best Estimated P.F. -- Best estimated purification factor refers to the best average factor obtainable from consideration of all the data presented for a particular impurity element under the step or process listed. Presumably, this P.F. could be used to predict the impurity separation possible for the step or process given if it were to be incorporated into a new purification scheme. For the "A" Process, the best estimated P.F. is obtained, where possible, by multiplying the purification factors obtained for each of the steps in the process, or using the actual P.F. obtained experimentally, whichever was the higher factor. For the individual steps, the best valid purification factor is given. It is assumed that an ether extraction, NH_4NO_3 is equivalent to an ether extraction, $Ca(NO_3)_2$.

Element and State Tested -- Lists the impurity element being separated from plutonium and the oxidation state or compound in which the element appears at the time of analysis. E.g., after an oxalate precipitation, the element would be present in a reduced state, after either type of ether extraction, the element would be present in the oxidized state existing after treatment with $NaBrO_3$-HNO_3 oxidant at 93°C.

Precipitation -- parts by weight of the impurity element per million parts by weight of Pu present.

All the data presented are dependent, of course, on the limits of sensitivity of the analyses used. In the case of some of the earlier runs, made about a year ago, these sensitivities were not nearly so low as at the present time. In short, as the methods of analysis were improved, the purification factors obtained became greater. This accounts for a good deal of the

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irregular data obtained and substantiates the assumption that the highest purification factors obtained (almost always later than the original factor to which it is compared) for any step or process are valid. The methods of analysis used and their sensitivity limits have been outlined in LA-406, Table II-A.

Footnotes used in Table VI.

1) Boron separations on the four "special" runs listed were made using $UO_2(NO_3)_2$ as a stand-in for $PuO_2(NO_3)_2$. It is assumed that the removal of boron from Pu would be the same or at least closely comparable. Data were obtained from M. Kahn.

2) Zr-Cb mixture used was 65-day Zr^{95} and 35-day Cb^{95} tracers in equilibrium in oxalic acid solution. Run No. 214-P and 217-P were made starting only with tracer quantities detectable by a γ-meter. Additional quantities of Zr and Cb (5% Zr and .02% Cb with respect to Pu) were added as carriers during Run No. 215-P. The best estimated P.F. given for the "A" Process is the lowest factor possible and applies only when total Zr-Cb impurity content exceeds 5%. If only tracer quantities of Zr-Cb were present, this factor would be greater than 200, the additional separation being due to the acetate precipitation.

3) Since Na^+ is introduced in the "A" and "B" Processes, the best estimated P.F. is calculated using only the steps following the introduction of Na^+. From the amounts of Na^+ introduced and the best estimated P.F., one would expect < 2 ppm of Na left at the end of the "A" Process and < 0.3 ppm left at the end of the "B" Process if the plutonium were not further contaminated.

4) Ca^{+2} is introduced in the "B" Process before the first purification step. From the amount of Ca^{+2} introduced and the best estimated P.F. one would

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$<$300 ppm Ca left at the end of the "B" Process if there were no further contamination.

5) A considerable portion of the Sn present was added as a precipitate at the beginning of the process.

6) Run No. 205-P (first one listed) was made using radioactive La^{140} tracer. Purification factors were calculated from data obtained from γ-meter readings.

7) From known chemistry, it is assumed that there will be no U separation during either an acetate precipitation or an ether extraction.

*All analyses of these elements may be inaccurate due to contamination from impurities in dust, Pyrex-glass sample containers and purification equipment, and C.P. reagents used in the process. Thus, it may be assumed that all the purification factors given for these elements are somewhat lower than the true values.

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TABLE VI. PURIFICATION FACTORS FOR IMPURITIES

Element and State Tested	Amount Present-Ppm.		Purification Factor							Run Number
	Before Purif.	After Purif.	Oxalate Pptn.	Acetate Pptn.	Ether Extraction		"A" Process	"B" Process	"C" Process	
					NH_4NO_3	$Ca(NO_3)_2$				
Li Li^+	10,000	<5	-	-	-	-	>2000	-	-	243-P
Best Est. P.F.	-	-	-	-	-	-	>2000	-	-	-
Be Be^{+2}	50	<0.4	-	-	-	-	>125	-	-	206-P
"	50	<0.4	-	-	>125	-	-	-	-	207-P
Best Est. P.F.	-	-	-	-	>125	>125	>125	>125	-	-
$B^{(1)}$ H_3BO_3	1.4	<0.3	>5	-	-	-	-	-	>5	570-P
"	2.7	<0.3	>9	-	-	-	-	-	>9	571-P
"	10,000	200	-	-	50	-	-	-	-	Special[1]
"	200	35	-	-	57	-	-	-	-	Special[1]
"	10,000	300	-	33	-	-	-	-	-	Special[1]
"	60	0.1	-	60	-	-	-	-	-	Special[1]
Best Est. P.F.	-	-	>5	>30	>50	>50	>30,000	>250	>5	-
Na*(3) Na^+	50,000	35	-	-	-	-	1430	-	-	243-P
"	1×10^5	35	-	-	2860	-	-	-	-	243-P
"	1×10^5	32	-	-	3120	-	-	-	-	245-P
"	1×10^5	120	835	-	-	-	-	-	835	Special
Best Est. P.F.	-	-	>800	-	>2800	>2800	$>2\times10^5$	$>2\times10^5$	>800	-
Mg* Mg^{+2}	1280	<8	-	-	-	-	>163	-	-	206-P
"	1000	<8	-	-	>125	-	-	-	-	207-P
"	129	10	-	-	-	-	13	-	-	209-P
"	100	4	-	-	-	-	25	-	-	245-P
"	100	<5	-	-	-	-	>20	-	-	246-P
"	100	<2	-	-	-	-	>80	-	-	266-P
Best Est. P.F.	-	-	-	-	>125	>125	>150	>125	-	-
Al* Al^{+3}	2000	20	-	-	-	-	100	-	-	206-P
"	2000	40	-	-	50	-	-	-	-	207-P
Best Est. P.F.	-	-	-	-	50	50	>100	>50	-	-
Si SiO_2	340	250	1.4	-	-	-	-	-	-	570-P
"	790	<120	-	-	-	-	-	>6.6	-	576-P
Best Est. P.F.	-	-	1	-	>6	>6	>6	>6	1	-

TABLE VI (Cont.)

Element and State Tested	Amount Present-Ppm.		Purification Factor							Run Number
	Before Purif.	After Purif.	Oxalate Pptn.	Acetate Pptn.	Ether Extraction		"A" Process	"B" Process	"C" Process	
					NH_4NO_3	$Ca(NO_3)_2$				
Ce Ce^{+4}	11,400	<400	-	-	-	-	>29	-	-	206-P
"	10,000	<400	-	-	>25	-	-	-	-	207-P
"	1000	<31	-	-	-	-	>32	-	-	229-P
"	1000	<31	-	-	>32	-	-	-	-	230-P
Best Est. P.F.	-	-	-	-	>25	>25	>30	>25	-	-
Hg Hg^{+2}	290	<38	-	-	-	-	>7	-	-	220-P
"	1000	<31	-	-	-	-	>32	-	-	229-P
"	1000	130	-	-	7.7	-	-	-	-	230-P
"	1000	<50	-	-	>20	-	-	-	-	242-P
Best Est. P.F.	-	-	-	-	>8	>8	>30	>8	-	-
Tl Tl^{+3}	1000	<3	-	-	-	-	>333	-	-	229-P
"	1000	3-30	-	-	>30	-	-	-	-	230-P
Best Est. P.F.	-	-	-	-	>30	>30	>300	>30	-	-
Pb PbO_2	16,000	<80	-	-	-	-	>125	-	-	206-P
"	10,000	<40	-	-	>250	-	-	-	-	207-P
"	1000	47	-	-	-	-	21	-	-	229-P
"	1000	130	-	-	7.7	-	-	-	-	230-P
"	1000	<50	-	-	>20	-	-	-	-	242-P
Best Est. P.F.	-	-	-	-	>10	>10	>>20	>10	-	-
U(7) UO_2^{+2}	1×10^5	1800	55	-	-	-	-	-	55	Special
"	1×10^5	2000	50	-	-	-	-	-	50	Special
"	20,000	2000	-	-	-	-	10	-	-	231-P
"	40,000	2500	-	-	-	-	16	-	-	242-P
"	2000	100	20	-	-	-	-	-	20	232-P
Best Est. P.F.	-	-	>20	1	1	1	>100	>20	>20	-

TABLE VI (Cont.)

Element and State Tested	Amount Present-Ppm.		Purification Factor							Run Number
	Before Purif.	After Purif.	Oxalate Pptn.	Acetate Pptn.	Ether Extraction NH_4NO_3	Ether Extraction $Ca(NO_3)_2$	"A" Process	"B" Process	"C" Process	
Cr $Cr_2O_7^=$	5000	<4	-	-	-	-	>1250	-	-	231-P
"	5000	450	-	-	-	-	-	11	-	232-P
"	1000	<2.5	-	-	>40	-	-	-	-	242-P
"	2100	<4	-	-	-	-	>525	-	-	245-P
"	2100	5	-	-	-	-	420	-	-	246-P
"	1500	<2	-	-	-	-	>750	-	-	266-P
"	5000	220	-	-	-	23	-	-	-	275-P
"	5000	300	-	-	-	17	-	-	-	276-P
"	5000	300	-	-	-	17	-	-	-	277-P
"	5000	450	-	-	-	11	-	-	-	278-P
Cr^{+3}	4000	<60	>67	-	-	-	-	-	>67	570-P
"	700	<60	>12	-	-	-	-	-	>12	571-P
"	4000	<22	-	-	-	-	-	>550	-	576-P
"	2000	<2	-	-	-	-	-	>1000	-	577-P
Best Est. P.F.	-	-	>60	-	15	15	$>5x10^4$	>900	>60	-
Mn MnO_2	2000	<40	-	-	>50	-	-	-	-	207-P
"	2000	<4	-	-	-	-	>500	-	-	231-P
"	2000	<5	-	-	>400	-	-	-	-	232-P
"	210	<4	-	-	-	-	>53	-	-	245-P
"	210	<5	-	-	-	-	>42	-	-	246-P
"	150	<2	-	-	-	-	>75	-	-	266-P
Mn^{+2}	65	<4.4	>15	-	-	-	-	-	>15	570-P
"	35	<4.4	>8	-	-	-	-	-	>8	571-P
"	38	<5	-	-	-	-	-	>7.6	-	576-P
"	36	<2	-	-	-	-	-	>18	-	577-P
Best Est. P.F.	-	-	>6	-	>200	>200	>9000	>1000	>8	-
Co Co^{+2}	5000	<40	-	-	-	-	>125	-	-	206-P
"	5000	<40	-	-	>125	-	-	-	-	207-P
"	2000	<18	-	-	-	-	>118	-	-	231-P
"	5000	<23	-	-	>217	-	-	-	-	232-P
Best Est. P.F.	-	-	-	-	>150	>150	>150	>150	-	-

State Tested	Purif.	Purif.	Pptn.	Pptn.	NH_4NO_3	$Ca(NO_3)_2$	Process	Process	Process	Number
Fe* Fe^{+3}	10,000	145	-	-	-	-	69	-	-	206-P
"	10,000	42	-	-	240	-	-	-	-	207-P
"	17,400	60	-	-	-	-	290	-	-	209-P
"	6250	40	-	-	-	-	156	-	-	245-P
"	6250	22	-	-	-	-	284	-	-	246-P
"	6000	52	-	-	-	-	115	-	-	266-P
"	20,000	130	-	-	-	154	-	-	-	273-P
"	20,000	240	-	-	-	84	-	-	-	274-P
"	20,000	157	-	-	-	127	-	-	-	275-P
"	20,000	88	-	-	-	228	-	-	-	276-P
"	20,000	140	-	-	-	143	-	-	-	277-P
"	20,000	100	-	-	-	200	-	-	-	279-P
Fe^{+2}	4980	300	17	-	-	-	-	-	17	570-P
"	3610	125	29	-	-	-	-	-	29	571-P
"	2720	163	-	-	-	-	-	17	-	576-P
"	2300	118	-	-	-	-	-	20	-	577-P
Best Est. P.F.	-	-	20	-	100	100	>40,000	2000	20	-
Ni Ni^{+2}	5000	<40	-	-	-	-	>125	-	-	206-P
"	5000	<40	-	-	>125	-	-	-	-	207-P
"	5000	<9	-	-	>560	-	-	-	-	232-P
"	1250	<25	-	-	-	-	>63	-	-	245-P
"	750	<10	-	-	-	-	>75	-	-	246-P
"	1100	<25	>44	-	-	-	-	-	>44	570-P
"	700	<48	>14	-	-	-	-	-	>14	571-P
"	5000	7	-	-	-	715	-	-	-	273-P
"	5000	10	-	-	-	500	-	-	-	274-P
"	5000	10	-	-	-	500	-	-	-	275-P
"	5000	8	-	-	-	625	-	-	-	276-P
"	5000	20	-	-	-	250	-	-	-	277-P
Best Est. P.F.	-	-	>30	-	>200	>200	$>1x10^5$	>6,000	>30	-
Zr-Cb(2)	?	?	3.3	20	>3	-	>200	-	-	214-P
	?	?	4	2.8	1.5	-	17	-	-	215-P
	?	?	-	-	2.3	-	-	-	-	217-P
Best Est. P.F.	-	-	>3	>2	>2	-	>36	>6	>3	-

State Tested	Purif.	Purif.	Pptn.	Pptn.	NH_4NO_3	$Ca(NO_3)_2$	Process	Process	Process	Number
<u>Zn</u> Zn^{+2}	10,000	<40	-	-	-	-	>250	-	-	206-P
"	10,000	<40	-	-	>250	-	-	-	-	207-P
"	5000	9	-	-	-	-	555	-	-	229-P
"	5000	10	-	-	500	-	-	-	-	230-P
Best Est. P.F.	-	-	-	-	>300	>300	>300	>300	-	-
<u>Cd</u> Cd^{+2}	5000	<40	-	-	-	-	>125	-	-	206-P
"	5000	<40	-	-	>125	-	-	-	-	207-P
"	1000	9	-	-	-	-	111	-	-	229-P
"	1000	10	-	-	100	-	-	-	-	230-P
"	1000	<25	-	-	>40	-	-	-	-	242-P
Best Est. P.F.	-	-	-	-	>100	>100	>100	>100	-	-
<u>Sn</u>(5) Sn^{+4}	90	<4	-	-	-	-	>20	-	-	220-P
"	5000	120	-	-	-	42	-	-	-	273-P
"	5000	70	-	-	-	71	-	-	-	274-P
"	5000	100	-	-	-	50	-	-	-	275-P
"	5000	100	-	-	-	50	-	-	-	276-P
"	5000	200	-	-	-	25	-	-	-	277-P
"	5000	160	-	-	-	31	-	-	-	278-P
"	5000	150	-	-	-	33	-	-	-	279-P
Best Est. P.F.	-	-	-	-	>30	>30	>30	>30	-	-
<u>La</u>(6) La^{+3}	300	?	1	>165	7500	-	-	-	1	205-P
"	57,000	<40	-	-	-	-	>1420	-	-	206-P
"	20,000	<3	-	-	-	>6675	-	-	-	273-P
"	20,000	<3	-	-	-	>6675	-	-	-	274-P
"	20,000	<2	-	-	-	$>1x10^5$	-	-	-	275-P
"	20,000	<2	-	-	-	$>1x10^5$	-	-	-	276-P
"	20,000	<2	-	-	-	$>1x10^5$	-	-	-	277-P
"	20,000	<5	-	-	-	>4000	-	-	-	278-P
"	20,000	<5	-	-	-	>4000	-	-	-	279-P
Best Est. P.F.	-	-	1	>150	>5000	>5000	$>5x10^5$	>5000	1	-

TABLE VI (Cont.)

Element and State Tested	Amount Present-Ppm.		Purification Factor							Run Number
	Before Purif.	After Purif.	Oxalate Pptn.	Acetate Pptn.	Ether Extraction		"A" Process	"B" Process	"C" Process	
					NH_4NO_3	$Ca(NO_3)_2$				
P $H_2PO_4^-$	900	<25	-	-	-	>36	-	-	-	273-P
"	900	<25	-	-	-	>36	-	-	-	274-P
"	5000	<50	-	-	-	>100	-	-	-	275-P
"	5000	<50	-	-	-	>100	-	-	-	276-P
"	20,000	<50	-	-	-	>400	-	-	-	277-P
"	20,000	<64	-	-	-	>310	-	-	-	278-P
"	20,000	<50	-	-	-	>400	-	-	-	279-P
"	1,185	<40	>30	-	-	-	-	-	>30	570-P
"	1,260	<48	>26	-	-	-	-	-	>26	571-P
"	1,100	<43	-	-	-	-	-	>26	-	576-P
"	1,320	<65	-	-	-	-	-	>20	-	577-P
Best Est. P.F.	-	-	>25	-	>300	>300	>1x10^5	>7000	>25	-
S HSO_4^-	182,000	<18,000	-	-	-	>10	-	-	-	273-P
"	182,000	<18,000	-	-	-	>10	-	-	-	274-P
"	500,000	<15,000	-	-	-	>32	-	-	-	275-P
"	500,000	<15,000	-	-	-	>32	-	-	-	276-P
"	500,000	<15,000	-	-	-	>32	-	-	-	277-P
"	500,000	<14,000	-	-	-	>35	-	-	-	278-P
Best Est. P.F.	-	-	-	-	>>30	>>30	>>30	>>30	-	-
K K^+	50,000	<440	-	-	-	-	>114	-	-	243-P
"	430	<44	>10	-	-	-	-	-	>10	570-P
Best Est. P.F.	-	-	>10	-	-	-	>100	-	>10	-
Ca*(4) Ca^{+2}	1000	<20	-	-	-	-	>50	-	-	206-P
"	1000	<20	-	-	>50	-	-	-	-	207-P
"	290	35	-	-	-	-	8.3	-	-	220-P
"	1048	30	-	-	-	-	35	-	-	209-P
"	2x10^6	300	-	-	-	6,670	-	-	-	255-P
"	1.2x10^6	170	-	-	-	7,060	-	-	-	273-P
"	1.2x10^6	70	-	-	-	17,100	-	-	-	274-P
"	1.2x10^6	60	-	-	-	20,000	-	-	-	275-P
"	1.2x10^6	220	-	-	-	-	5,450	-	-	576-P
"	1.2x10^6	24	-	-	-	-	50,000	-	-	577-P
Best Est. P.F.	-	-	-	-	>6000	>6000	>5000	>6000	-	-

G. Special Research Problems.

This part of the report is a summary of the special research problems the results of which never affected the purification processes used. Most of the work was done in the spring of 1944 before a routine procedure for purification had been adopted.

Iodate Precipitation:

The Pu (IV) iodate precipitation was considered as a possible purification step, especially as a means of removing uranium. There were several difficulties, however, which prevented it from being used on a routine production basis.

The most successful method for obtaining a good Pu (IV) iodate precipitate consisted of the following steps:

(1) Reduce the plutonium present in HNO_3 solution to Pu^{+3} with SO_2 gas or cold SO_2 saturated solution.

(2) Oxidize the Pu^{+3} just to Pu^{+4} by heating on a steam bath in the presence of 1M HNO_3 solution.

(3) Add HIO_3--HNO_3 to precipitate the Pu^{+4} as Pu (IV) iodate. Enough precipitant was added to give a supernatant above the precipitate of 2M HNO_3--0.2M HIO_3.

Once formed, Pu (IV) iodate was very hard to dissolve even by the use of oxidizing agents such as BrO_3^- or $Cr_2O_7^=$. Oxidation with $Na_2Cr_2O_7$-HCl required at least 3 hours at 93°C ("tracer" scale). When a $NaPuO_2Ac_3$ precipitation was made after such an oxidation, I_2 precipitate also. This was probably due to the decomposition of ICl present at the pH of 5 achieved in the buffered acetate solution. Various complexing ions were used in attempts to dissolve Pu (IV)

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iodate precipitate. Of these $CO_3^=$ and Ac^- were useless but excess sodium citrate could be used to effect dissolution. However, any further treatment of a solution formed in this way, caused reprecipitation of $Pu\ (IO_3)_4$.

The iodate precipitation was quite successful in removing U from Pu. Several experiments were made in which two iodate precipitations were found to lower the U present from 10% to < .01% (with respect to Pu).

The solubility of Pu (IV) iodate in various media has already been reported in LA-63. In 2M HNO_3--0.2M HIO_3 solubility of Pu (IV) iodate was found to be 20 to 40 mg Pu/liter depending on the method of precipitation.

Pu (IV) Peroxide Precipitation.

Solubilities for Pu (IV) peroxide in various media have already been reported on LA-63. In 0.43M HNO_3--1.6M H_2O_2, solubility of Pu (IV) peroxide was about 30 mg Pu/liter at room temperature. A few preliminary investigations were made to determine if a peroxide precipitation could be used in removing U from Pu. It was found that very poor U removal was effected. Furthermore, it was very difficult to consistently obtain good precipitants.

Pu (III) Fluoride Precipitation.

The solubility of Pu (III) fluoride in various media has been reported in LA-63. In 1M HCl--1NHF the solubility of Pu (III) fluoride is about 50 mg Pu/liter at room temperature. In 0.6M HNO_3-0.5M HF, the solubility of Pu (IV) fluoride is greater than 1300 mg Pu/liter at room temperature.

The Pu (III) fluoride precipitation was used principally as an indication of the extent of reduction to Pu^{+3} obtained with various reducting agents. Pu (VI) fluoride and Pu (IV) fluoride are very soluble while Pu (III) fluoride is very insoluble. HF was added to the plutonium solution in HCl or HNO_3 after reduction. The precipitate obtained was centrifuged and the solubility of the plutonium precipitate present determined by radioassay. Later it was found

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that Pu (IV) fluoride is carried by any Pu (III) fluoride precipitate present. This made the above method of determining extent of reduction to Pu^{+3} useless.

Pu (IV) Oxalate Precipitation

The solubility of Pu (IV) oxalate in various media has already been reported in LA-63. In 0.6M HNO_3 to 0.25M $H_2C_2O_4$, the solubility was 360 mg Pu/liter at room temperature. The principal reason for research on the Pu (IV) oxalate precipitation was for the purpose of determining solubility under various conditions. It was not considered to be of any use in a purification scheme.

Plutonium Complexes

While engaged in research on various problems, the following complex compounds of plutonium were observed:

Pu (III) Oxalate - Green solution formed by adding excess $K_2C_2O_4$ to $Pu_2(C_2O_4)_3$.

Pu (IV) Oxalate - Orange solution formed by adding excess $K_2C_2O_4$ to $Pu_2(C_2O_4)_2$.

Pu (IV) Acetate - Orange solution formed by adding 3.5M Na^+-1.5M Ac^--1.5M HAc to Pu^{+4} nitrate solution.

Pu (IV) Phosphate - Pink solution formed by adding H_2PO_4 to Pu^{+4} nitrate solution.

Pu (IV) Citrate - Orange solution formed by adding excess sodium citrate to a Pu (IV) iodate precipitate.

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