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LOS ALAMOS PROJECT HANDBOOK

CHEMISTRY OF PLUTONIUM

by Duffield, Garner
and Wahl

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Report LA-50

Series A, Edition I,

Sections I, II, III, IV, V, VIII,

containing 200 pages, and

additional sections and supple-

ment sheets shown on checklist

C. [redacted]

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LOS ALAMOS PROJECT HANDBOOK, CHEMISTRY OF PLUTONIUM

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Compiled by:

Robert B. Duffield

Clifford S. Garner

Arthur C. Wahl

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September 28, 1943

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	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET Ch-1
Ch. Checklist	Copy N[redacted] Series A Issued to:

Checklist

As additional sections are added, or as supplement sheets become available, they should be bound in this volume in the sections indicated by the symbols appearing on the sheets. A record of the sections and supplements added should be made on this checklist. Cover sheets should be bound together at the back of this volume.

Copy No.	Sections	No. of pages	Date Received
18	See cover sheet, Sup I	43	12/6/43

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Report LA-30

Series A, Edition I,

Supplement 1,

containing 43 pages (sheets

IA1f-10, g-2, i-4, j-2, 1-3, 4, n-2, p-7, 8, 9, t-1; IA2h-1; IB1b-4, h-3, i-3, 4, k-10, 11, q-3; IB2a-2, c-2, f-2, 3, i-4, 1-3, o-3, p-1; ID1-2, 4-1; IIA-5, 6, B-3, C-5, E-2, H-2; IIIA1-2; IVA-7, C-4, D-7, 8, 9, L-1, M-1.)

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LOS ALAMOS PROJECT HANDBOOK, CHEMISTRY OF PLUTONIUM

Compiled by:

Robert B. Duffield

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November 27, 1943

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Report LA-30

Series A, Edition I,

Supplement 2,

containing 33 pages (sheets

IA1f-11, 12, 1-5, m-4, u-1;
IA2d-2; IB1h-4, 5; IB21-4,
o-4; IB3d-1; ID4-1; IIA-7, 8,
B-4, 5, C-6, E-3, I-1, H-3;
IIIA3-1; IVA-8, B-6, D-10, 11,
E-5, J-4, K-2, L-2; VA-8,
B-4, 5; VIII-4.)

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Robert B. Duffield

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Report LA-30

Series A, Edition I,

Supplement 3,

containing 63 pages (sheets

IA1f-13, IA1i-5, IA1j-3, IA1l-6, IA1n-3, IA1r-2, IA1v-1, IA2a-3, IA3a-1, IA3b-1, IA3c-1, IA3d-1, IA3e-1, IA3f-1, IA3g-1, IB1h-6, IB1i-5, IB1j-4, IB1q-4, IB1r-2, IB1v-1, IB1w-1, IB2d-2, IB2e-3, IB2g-2, IB2h-2, IB2l-5, IB2o-5, IB2p-2, IB2q-1, IB2r-1, IB2s-1, IB2t-1, IB3c-2, IB3d-2, IB3l-1, IB5a-1, IC2-2, IC3-1, IC4-1, ID1-3, ID4-2,3,4; IIA-9, IIB-6, IIC-7,8; IID-4,5; IIE-4, IIF-1, IIH-4, IIIA1-3, IIIA3-2, VB-6, VC-2, VIII-5,6,7,8,9,10)

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LOS ALAMOS PROJECT HANDBOOK, CHEMISTRY OF PLUTONIUM

Compiled by:

Robert B. Duffield

Clifford S. Garner

Arthur C. Wahl

May 1, 1944

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET C-1
C. Contents	Co[redacted] Issued to:

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Compiled by C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET C-2
C. Contents	Cop[redacted] Issued to:

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Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET P -1
P. Preface	Copy [redacted] Issued to:

The handbook is divided into two parts. The first of these presents a brief introductory discussion of general information concerning plutonium which is intended to be of value in quickly orienting readers unfamiliar with this element. Also, certain conventions adopted in this handbook are stated in this part. The second part of the handbook is concerned with experimental observations. These are given in sufficient detail so that the reader may learn the general features and results of a given experiment, and need consult the original literature only when he wishes a considerably detailed account. An attempt has been made to present essentially all the data available on plutonium (except where noted to the contrary) whether a given datum has appeared consistent or not with other data. The compilers feel that very little is really known regarding plutonium chemistry and that it is too early to attempt the writing of a conventional "text-book" in which information given may usually be assumed to be reasonably close to the truth. With this in mind, the reader is encouraged to read in full each section in which he may be interested so that he may recognize the existence of conflicting experimental results and form his own conclusions regarding the most probable state of knowledge. In general, the material has been arranged in approximate chronological order within a given section.

Section IV, dealing with the principal methods for extracting 49 from a pile and decontaminating it from fission products, has been written primarily as a guide to the classified reports treating this subject. For details the reader should consult the references given.

Space has been left for a section (VI) on metallurgical experiments involving plutonium. At the time of writing, almost no data are available in this field, with the possible exception of the chemical attempts to prepare plutonium metal (which are given in IIA).

Owing to the illness of one of the compilers section VII on nuclear properties has been temporarily omitted. This section will be issued in the near future.

The effects of intense radiations on plutonium chemistry (and that of extraction and decontamination in particular) have not been discussed. The reports by Burton and co-workers should be consulted by those interested in this problem.

Inasmuch as the chemistry of plutonium is changing from day to day as new investigations are carried out, it is planned to issue (about every month) supplement sheets in an effort to keep the handbook up to date. These may be bound into the handbook in the proper place at the end of each subsection involved.

The compilers will appreciate having their attention directed to any errors or omissions which may have occurred in this compilation.

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Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET In-1
In. Introduction	Co[redacted]ries A Issued to:

Discovery of elements 93 and 94

To date two transuranic elements are known, elements 93 and 94.

The former was discovered in 1940 by McMillan and Abelson(1) and named neptunium (Np) by them. The 2.3-day β-activity which they found on bombarding uranium with neutrons they assigned correctly to 93^{239} (hereinafter generally called 39). Two other isotopes of neptunium are also known: 93^{238} and 93^{237}.(2),(3) The former is a β-emitter of 2.0-day half-life, and the latter emits alphas with an approximate half-life of 3×10^6 years.

Element 94 was discovered in January, 1941, by Seaborg, Wahl and Kennedy.(2) They bombarded uranium with deuterons and obtained the 50-year, α-emitting isotope later shown to be 94^{238} (produced by (d,2n) reaction). In March, 1941, the isotope of great interest, 94^{239} (hereinafter generally called 49), was found by Seaborg, Segre, Kennedy and Lawrence.(4) This isotope emits alphas with a half-life of 21,300 years according to the best estimate (see section VII for nuclear properties). Element 94 has been given(5) the name plutonium (Pu).

Production of neptunium and plutonium

Pu^{239} may be produced by cyclotron bombardment of uranium with neutrons, or (for large-scale production) in a uranium pile containing some moderator, such as graphite, beryllium or heavy-water, as a result of the following chain:

$$U^{238} + n \longrightarrow U^{239} \xrightarrow[\text{23-min.}]{\beta^-} Np^{239} \xrightarrow[\text{2.3-day}]{\beta^-} Pu^{239}$$

In a pile operating at 2500 kw/ton U (proposed conditions for Site W pile) for 100 days about 250 g. Pu should be manufactured per ton of uranium. It is expected that about 2.5×10^5 curies of fission product activity will be associated with this amount of Pu after a 60-day cooling period. The chemical aspects of extracting Pu from the uranium and decontaminating it from fission products is treated briefly in section IV. Some aspects of the purification of Pu from remaining fission products and light-element impurities are given in section V.

Position of neptunium and plutonium in the periodic table

It might be thought that neptunium would belong to the group of elements including Mn, 43 and Re, and plutonium to the group including Fe, Ru and Os. The evidence to date indicates rather that Np and Pu are more closely related to uranium. For example, attempts have been made to prepare a volatile "tetroxide" of Pu similar to OsO_4 and RuO_4, but they have not been successful

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Position of neptunium and plutonium in the periodic table (cont.)

(see IE1-1 and IIB-1). On the other hand, Pu (and, perhaps, Np to a lesser extent) exhibits many reactions like those which uranium undergoes, such as formation of an insoluble fluoride in the lower oxidation state (see IA1f-6) and formation of an insoluble compound with sodium acetate in the upper oxidation state (see IA2a-2). However, it must be admitted that the present information is too sketchy to be sure of this classification. It is now generally considered that Np and Pu are members of a transition series of elements in which the 5f level is progressively filled without alteration of the outer electronic configuration (similar to the situation in the rare earth series, in which the 4f level fills progressively from La to Lu), thus suggesting a group of elements chemically more or less similar. However, theoretical considerations have not succeeded at present in predicting the extent of the chemical similarity.

Oxidation-reduction reactions of Np and Pu in solution

Neptunium appears to have three oxidation states stable in acid solution, the most likely oxidation-numbers of which are +3, +5, and +6.

Plutonium in aqueous solution exists in at least two oxidation states. The lower or reduced state, abbreviated $Pu^{(r)}$, almost certainly has an oxidation-number of +4. The upper or oxidized state, abbreviated $Pu^{(o)}$, probably has an oxidation-number of +6, and the ion is probably oxygenated (e.g., PuO_2^{++}). (The nature of the ions in solution is considered in section IC.) The reduced state is more stable (unlike uranium), and, unless designated to the contrary, all references to the behavior of plutonium in this handbook concern the reduced state. The potential of the $Pu^{(r)}$, $Pu^{(o)}$ couple is probably about 1 volt, and oxidizing agents such as Ag^{+2}, $Cr_2O_7^{=}$, Ce^{+4}, MnO_4^{-} and Br_3^{-} oxidize $Pu^{(r)}$ to $Pu^{(o)}$ in acid solution. $Pu^{(o)}$ may be reduced to $Pu^{(r)}$ by such reducing agents as SO_2, Fe^{++}, U^{+4} and NH_3OH^{+}. High (H^{+}) appreciably slows the rate of oxidation of $Pu^{(r)}$ to $Pu^{(o)}$, as does $SO_4^{=}$ which forms a complex with the lower state (neither H^{+} nor $SO_4^{=}$ appears to have any pronounced effect on the rate of oxidation of $Np^{(r)}$.

The methods of analysis for the various oxidation states of Np and Pu are based upon the following experimental facts: The "+4" state of Pu and the "+3" state of Np are carried by LaF_3, but not by $NaUO_2Ac_3$, while the "+6" states of both Pu and Np are carried by $NaUO_2Ac_3$, but not by LaF_3. The intermediate ("+5") state of Np is carried by neither LaF_3 nor $NaUO_2Ac_3$.

The oxidation-reduction behavior is treated in some detail in section IB.

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HANDBOOK, CHEMISTRY OF PLUTONIUM

Date: September 23, 1943

EDITION I

SHEET In-3

In. Introduction

C[redacted]s A

Issued to:

"Tracer" versus "microgram" studies

The major portion of the chemical information now available concerning plutonium and its compounds has come out of "tracer" experiments using Pu^{238} (hereinafter generally called 48) and appropriate carriers. Such experiments are open to the objection to which tracer methods are subject in general.

Relatively recently, microgram quantities of Pu^{239} have become available, and it has been possible to study the behavior of nearly pure plutonium compounds by the methods of microchemistry. In general, such experiments are more reliable than tracer technics, and they are indicated in this handbook by the code number 49.

In general, the compositions of the various known compounds of plutonium are not definitely established, and cannot be (as a rule) until larger amounts of Pu are available. The convention has been adopted of placing arbitrary formulas in quotation marks or writing the name (rather than a formula) of compounds whose exact composition is in doubt as an added emphasis of this point.

Plutonium compounds

The following table, compiled by R. Duffield, gives the pertinent data concerning the mode of preparation, color and approximate solubility behavior of the known compounds of plutonium, based on both "tracer" and "microgram" technics. For a full account of the individual experiments, including behavior with organic precipitants, see section IA.

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Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET In-4
In. Introduction	Co[redacted]s, Series A Issued to:

Precipitation Reactions of Reduced State of Plutonium

Plutonium Compound	Color*	Solubility* g./l.	Precipitated by:	Can be carried by:
Carbonate	White	H_2O: 0.043 1M Na_2CO_3: 0.072 2.5M " : 0.140	Sat'd. Na_2CO_3	$La_2(CO_3)_3$ at pH>7
Chloride	Aqueous solutions in 6M HCl are light yellow if dilute and reddish if concentrated.	—	—	—
Chromate	Orange	H_2O: 0.02 1M HNO_3: 0.120 3M " : 0.250 10M " : 0.270	0.1M $Na_2Cr_2O_7$	$BaCrO_4$ in 0.01-0.1M HNO_3 $PbCrO_4$ in 0.1-1M HNO_3
Fluorides**	Pale green	H_2O: 0.007-0.010 3M HF: 0.012 6M " : 0.045 10M NH_4F: >0.450	HF	Rare earth fluorides. The carrying is not quantitative at high acid.
Hydroxide	Olive green	H_2O: 0.0018 Conc. NH_4OH: 0.00024	Conc. NH_4OH	$La(OH)_3$ $U(OH)_4$ at pH>7.
Iodate	White	H_2O: 0.00045 6M HNO_3: 0.0062 1M HIO_3: 0.024 5M " : 0.084 1M H_2SO_4: 0.073 5M " : 0.103 1M $(NH_4)_2SO_4$: 0.034	0.35M KIO_3	$Th(IO_3)_4$, $Ba(IO_3)_2$ $Pb(IO_3)_2$, $AgIO_3$ $Bi(IO_3)_3$, $ZrO(IO_3)_2$ $La(IO_3)_3$, $UO_2(IO_3)_2$

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET In-5
In. Introduction	C[redacted]ries A Issued to:

Precipitation Reactions of Reduced State of Plutonium (cont.)

Plutonium Compound	Color*	Solubility* g./l.	Precipitated by:	Can be carried by:
Nitrate	Lemon-yellow (solution in conc. HNO_3 is deep green.	---	---	---
Oxalate	Yellow	H_2O: 0.002(?) 1M $H_2C_2O_4$: >0.500 1M $K_2C_2O_4$: >0.700	Sat'd. $H_2C_2O_4$	$La_2(C_2O_4)_3$ in 0.006-0.5N HNO_3 $Th(C_2O_4)_2$ in 0.12M HCl
Oxide	Light yellow	Ignited oxide very insoluble; slowly soluble in hot conc. H_2SO_4	(Prepared by ignition of the nitrate)	---
Peroxide	Olive green	H_2O: 0.016 $\left.\begin{matrix}1M\ HNO_3\\20\%\ H_2O_2\end{matrix}\right\}$: 0.023 $\left.\begin{matrix}3M\ HNO_3\\15\%\ H_2O_2\end{matrix}\right\}$: 0.028	15% H_2O_2	"$UO_4 \cdot xH_2O$" and "$ThO_2 \cdot H_2O_2$" at pH = 2-3
Phosphate	White	H_2O: 0.010 1M NaH_2PO_4: 0.020 5M " : 0.029 1M HNO_3: 0.025 $\left.\begin{matrix}0.15M\ H_3PO_4\\5M\ HNO_3\end{matrix}\right\}$: ~5	$\frac{1}{2}$ sat'd. NaH_2PO_4	$BiPO_4$ "$Hf_3(PO_4)_4$", "$(ZrO)_3(PO_4)_2$" in 1N HNO_3
Sulfate[+]	White	---	Sat'd. K_2SO_4	$La_2(SO_4)_3$ pptd. by sat'd. K_2SO_4

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Date: September 28, 1943	EDITION I SHEET In-6
In. Introduction	Cop[redacted], Series A Issued to:

Precipitation Reactions of Reduced State of Plutonium (cont.)

Plutonium Compound	Color*	Solubility* g./l.	Precipitated by:	Can be carried by:
Sulfide	---	---	---	"UO_2S" ppt'd. by H_2S in 0.5M KOH

* The color and solubility of the plutonium compounds were determined by precipitating the compound with no carrier present.

** Later experiments indicate this may be a mixed fluoride of plutonium and another metal (e.g., K or La) since plutonium alone has failed to precipitate with HF. The solubility given is that determined with K^+ present.

† Probably a double sulfate with K^+.

Precipitation Reactions of the Oxidized State of Plutonium

Plutonium Compound	Color	Solubility g./l.	Precipitated by:	Can be carried by:
Acetate ("$NaPuO_2Ac_3$")	Pink(?)	0.8M Na^+: 1.0 5.7M Na^+: 0.07	NaAc	$NaUO_2Ac_3$, $NaMg(UO_2)_3Ac_9 \cdot 6H_2O$
Hydroxide*	Colorless	0.5M KOH: 0.053	1M NaOH	---

* Pu may be partly in reduced state.

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Compiled by C. S. Garner

HANDBOOK, CHEMISTRY OF PLUTONIUM

Date: September 28, 1943

EDITION I

SHEET In-7

In. Introduction

[redacted] A

Issued to:

Solvent extraction of plutonium compounds

This topic is covered in section ID. It may be noted here that certain organic complexes of Pu, such as the cupferride of the lower state, are extractible into solvents such as chloroform and ether. Also, the oxidized state of Pu, like UO_2^{++}, can be salted into diethyl ether.

Distillation of plutonium compounds from aqueous solution

Attempts to distill oxides, chlorides and bromides of plutonium from aqueous solution have met with failure (see section IE).

Volatile plutonium compounds

Certain plutonium compounds have been found which are volatile below 1000°C. A higher fluoride, volatile at 300-500°, has been prepared by the action of F_2 on plutonous fluoride. Treatment of PuO_2 with dry HCl appears to produce "$PuCl_4$", volatile at 450-650°. A compound presumably an oxychloride volatilizes at 750-950° on treatment of the oxide with Cl_2. A bromide, possibly "$PuBr_4$", made by the action of Br_2 on the "metal", is volatile to some extent at 250°. Plutonous acetylacetonate has been volatilized in one experiment at ~150°. The temperature ranges given are those used for the formation of the compounds, and the actual volatilization temperatures may be lower in some cases.

Nearly all the above information has been obtained using the tracer method, and almost nothing is known of the vapor pressures of any plutonium compounds. Further account of volatility studies is given in section II.

Plutonium metal

Attempts have been made to prepare the metal by reduction of PuO_2 with H_2 (definitely unsuccessful) and with Mg and Ba, reduction of "PuF_4" with Na, Mg and Ba, and by electrolytic reduction at a mercury cathode. Owing to the very great difficulties attending reduction on a microgram scale it has not been possible so far to prove that the metal has been obtained rather than alloys or reaction products of plutonium with the refractory materials or with MgF_2 or BaF_2. In any event sufficient "metal" has not been made to allow any determination of the density or other physical properties. It seems premature to discuss the hardness, oxidizability, etc., of the metal until larger amounts of material permit identification of the reduction product as metal. See section IIA for experimental details.

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Date: September 28, 1943	EDITION I SHEET In-8
In. Introduction	[redacted] Series A Issued to:

Electrolysis of plutonium in solution

Aside from attempts to prepare the metal by reduction at a mercury cathode (results ambiguous), it is known that plutonium can be deposited on a cathode from solution of NH_4Ac or $(NH_4)_2CO_3$, probably as a hydrated oxide.

References

(1) McMillan and Abelson, Phys. Rev., 57, 1185 (1940).

(2) Seaborg, Wahl and Kennedy, Report A-136, March 20, 1942.

(3) Wahl and Seaborg, Report CC-45, April 13, 1942.

(4) Seaborg, Segre, Kennedy and Lawrence, Report A-33, 1941.

(5) Seaborg and Wahl, Report A-135, p.15, March 19, 1942

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Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I
SHEET IA1a-1

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      a. $NaUO_2Ac_3$

Co[redacted]eries A

Issued to:

Carrying of $49^{(r)}$ by $NaUO_2Ac_3$⁽¹⁾

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
$NaUO_2Ac_3$	NaAc	$UO_2^{++} = 0.55M$ $Ac^- = 0.2-0.4$ $Na^+ = 5.0$	$HAc = 0.4-0.6M$	16	U/Pu = 120
"	"	$UO_2^{++} = 0.55M$ $Ac^- = 0.2$ $Na^+ = 2.5$	$HAc \cong 0.2M$	22	$U/Pu = 10^7$

A large part of this amount carried was probably due to retention of liquid and inadequate washing.

References

(1) Sheline and Hamaker, Report CN-522, p. 2, March 15, 1943.

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Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IA1b-1

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      b. Carbonate

[redacted], Series A

Issued to:

Carrying of $48^{(r)}$ by $La_2(CO_3)_3$

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
$La_2(CO_3)_3^{(1)}$	1M K_2CO_3	None	10^{-2}M OH^-	3	
"	0.25M $NaHCO_3$ sat'd. H_2CO_3	"	10^{-6}M H^+	81	
$La_2(CO_3)_3^{(2)}$	$NaHCO_3$	"	pH = 5.6	82	
"	"	"	6.5	94	
"	"	"	7.2	91	
"	"	"	7.8	73	
"	"	10% $UO_2(NO_3)_2 \cdot 6H_2O$	7.0	10	

Carrying of $48^{(r)}$ by "$Th(CO_3)_2$"

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
"$Th(CO_3)_2$"$^{(3)}$	$NaHCO_3$	None	pH = 8.0	1	0.025g. Th^{+4}/l.
"	"	UO_2^{++}	7.3	"	0.20g. Th^{+4}/l.

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Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IAlb-2
I. Solution chemistry A. Precipitation reactions 1. Reduced state b. Carbonate	Co [redacted] eries A Issued to:

Carrying of $48^{(r)}$ by "$U(CO_3)_2$"

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
"$U(CO_3)_2$"(3)	$NaHCO_3$	---	pH = 3.3	2	
"	"	---	3.5	1	
"	"	---	6.1	14	

Carrying of $49^{(r)}$ by "$U(CO_3)_2$"

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
"$U(CO_3)_2$"(4)	$NaHCO_3$	---	pH = 3.5	<1	U/Pu = 1000

Carrying of $48^{(r)}$ by Zr carbonate

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
"$ZrO(CO_3)$"(3)	$NaHCO_3$	None	pH = 7.9	8	

Precipitation of $49^{(r)}$ by Na_2CO_3

Compound precipitated	Precipitating agent	Other ions in solution	Acidity	Remarks
"$Pu(CO_3)_2$"(5)	Sat'd. Na_2CO_3.	None	10^{-2}M OH⁻	White gelatinous precipitate

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Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM.

EDITION I SHEET IA1b-3

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      b. Carbonate

[redacted]s A

Issued to:

Solubility of 49(x) carbonate

Compound precipitated	Precipitating agent	Other ions in solution	Acidity	Solubility of Pu compound
"$Pu(CO_3)_2$"(6)	---	None	---	43mg. Pu/l. in H_2O
"	---	"	---	72mg. Pu/l. in 1M Na_2CO_3
	---	"	---	140mg. Pu/l. in 2.5M Na_2CO_3

References

(1) Duffield, Report CN-239, p. 7, July 15, 1942.

(2) Brown, Hill and Jaffey, Report CN-405, p. 9, Dec. 16, 1942.

(3) Brown, Hill and Jaffey, Report CN-405, p. 11, Dec. 16, 1942.

(4) Cunningham and Werner, Report CN-405, p. 14, Dec. 16, 1942.

(5) Cefola, Cunningham and Werner, Report CN-282, p. 1, Sept. 16, 1942.

(6) Cunningham and Werner, Report CN-328, p. 5, Oct. 31, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IA1c-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state c. Chloride and oxychloride	Co[redacted]ies A Issued to:

$49^{(r)}$ chloride(1)

Solutions of $49^{(r)}$ chloride in 6N HCl at ~3 g. Pu/l. are light yellow. On concentrating the solution the color deepens and takes on a reddish tinge. At ~100 g. Pu/l. the solution is red brown in color.

Carrying of $48^{(r)}$ by BiOCl(2)

BiOCl carries no $39^{(r)}$, $39^{(o)}$, $48^{(r)}$, $48^{(o)}$.

References

(1) Cunningham and Werner, Report CN-419, p. 20, Jan. 15, 1943.

(2) Duffield, Report CN-282, p. 6, Sept. 16, 1942.

S[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IAld-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state d. Chromate	[redacted]ries A Issued to:

Carrying of $48^{(r)}$ by $PbCrO_4$

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
$PbCrO_4^{(1)}$	K_2CrO_4 (?)	La^{+3}	None added	95	
$PbCrO_4^{(2)}$	$Na_2Cr_2O_7$	---	0.1M HNO_3	82	Initial Pb^{++}=0.15M
"	"	---	1.0M HNO_3	78	" " =0.10M

Carrying of $48^{(r)}$ by $BaCrO_4$

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
$BaCrO_4^{(2)}$	0.20M $Na_2Cr_2O_7$	---	0.01M HNO_3	75	Initial Ba^{++}=0.15M
"	0.15M $Na_2Cr_2O_7$	---	0.10M HNO_3	83	" " =0.11M

Precipitation of $49^{(r)}$ from $Na_2Cr_2O_7$ solution

Compound precipitated	Precipitating agent	Other ions in solution	Acidity	Solubility of Pu Compound
"$PuOCrO_4 \cdot xH_2O$"(3)	0.1M $Na_2Cr_2O_7$	None	0.1M HNO_3, 0.5M HAc	Orange precipitate
"	---	---	---	0.02g. Pu/l. in H_2O
"	---	---	---	0.12g. Pu/l. in 1M HNO_3
"	---	---	---	0.25g. Pu/l. in 3M HNO_3
"	---	---	---	>0.27g. Pu/l. in 10M HNO_3

Specific activity measurement showed precipitate to be 55-60% Pu. Theoretical for $PuOCrO_4$: 64%, $PuOCrO_4 \cdot H_2O$: 61%, $PuOCrO_4 \cdot 2H_2O$: 59%.

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Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IA1d-2

I. Solution chemistry
   A. Precipitation reactions
      1. Reduced state
         d. Chromate

C[redacted]es A

Issued to:

References

(1) Stoughton, Report CN-239, p. 10, July 15, 1942.

(2) Beaufait, Report CN-723, p. 11, June 20, 1943.

(3) Sheline, Report CN-723, p. 1, June 20, 1943.

[redacted]

Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IA1e-1

I. Solution chemistry
    A. Precipitation reactions
        1. Reduced state
            e. Ferrocyanide

Co[redacted] Series A

Issued to:

Precipitation of 49(r) ferrocyanide (1)

Pu nitrate solution treated with $K_4Fe(CN)_6$ solution gave a green precipitate.

Solubility in H_2O = 10-15 mg./l.
6N HCl = " "
Conc. HCl = Readily soluble

References

(1) Cunningham, Werner and Cefola, Report CN-467, p. 6, Feb. 13, 1943.

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IA1f-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	Co[redacted], Series A Issued to:

Carrying power of "preformed" LaF_3 for $48^{(r)}$ (1),(2),(3)

Carrying power investigated under wide range of conditions. With La^{+3} = 0.5 g./l., 1N HNO_3, carrying appeared satisfactory (>95%).

Dissolving of $48^{(r)}$ fluoride contained in LaF_3 by conversion to $La_2(CO_3)_3$ or $La(OH)_3$ (4)

2M K_2CO_3 treatment for ~20 hrs. 52% of $48^{(r)}$ still in precipitate. 1M NaOH treatment for 40 min. at 20°C. left 3% of $48^{(r)}$ still in precipitate.

Carrying of $49^{(r)}$ by LaF_3 at low La/Pu ratios(5)

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
LaF_3	3N HF	None	---	99	La/Pu=50, 0.5g. La/l.
"	"	"	---	99.5	La/Pu=10, 0.5g. La/l. La added in 3 separate portions.

Carrying of $48^{(r)}$ by LaF_3 precipitated with NH_4F or KF at low acidity(6)

Pu carried quantitatively by LaF_3 precipitated by addition of KF or NH_4F, 0.16 g. La^{+3}/l. When pH>1.8, this also precipitated UO_2^{++} as fluoride.

At pH >6, U precipitated with $NaHCO_3$ and redissolved in excess; addition of KF then did not cause UO_2F_2 to precipitate. From such a solution, 75% of Pu was carried by 0.06 g. La^{+3}/l. and most of remaining 25% by a "preformed" LaF_3. At pH 7.2, much less of Pu carried by an identical double precipitation.

Dissolving of LaF_3 by NaOH or ZrO^{++} on an engineering scale(7)

Either solution process worked satisfactorily on large scale operation. Details given.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IAlf-2
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	Cop[redacted] Series A Issued to:

Effect of time of centrifugation on carrying of $48^{(r)}$ by LaF_3 (8)

Necessary to centrifuge for about 4 min. with 0.5 ml. of solution and 100 µg. of La^{+3} to get 97% of 48 carried.

Effect of Al^{+3} on carrying power of LaF_3 for $48^{(r)}$ (9)

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other conditions
LaF_3	6N HF	0.02g. Al^{+3}/l.	0.3N HNO_3	99	
"	"	0.05g. Al^{+3}/l.	"	"	
"	"	0.1g. Al^{+3}/l.	"	96	
"	3N HF	0.2g. Al^{+3}/l.	"	85	
"	"	0.4g. Al^{+3}/l.	"	62	
"	"	1.0g. Al^{+3}/l.	"	3	

Carrying of $48^{(r)}$ by zirconium fluoride or lanthanum fluozirconate (10)

Zirconium fluoride did not carry $48^{(r)}$ or $48^{(o)}$. Lanthanum fluozirconate carried 1% of $48^{(o)}$.

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Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM.
Date: September 28, 1943	EDITION I SHEET IAlf-3
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	C[redacted] Series A Issued to:

Carrying of $48^{(r)}$ by "preformed" LaF_3 in ZrO^{++} solutions(11)

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
LaF_3	0.6-1.0N HF	---	3 N HNO_3	99	0.2g. La^{+3}/l.
"	"	2.5g. Zr/l.	"	90	"
"	"	4.0g. Zr/l.	"	89,78	"
"	"	2.5g. Zr/l.	1.5N HNO_3	91,94	"
"	"	5g. Zr/l.	1.0N HNO_3	94	"
"	"	5g. Zr/l.	0.5N HNO_3	96	"

Carrying power of LaF_3 for $48^{(r)}$ in 20% and 30% $UO_2(NO_3)_2 \cdot 6H_2O$(12)

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	%Pu in ppt.	Other Conditions
LaF_3	1N HF	20% $UO_2(NO_3)_2 \cdot 6H_2O$	0.5N HNO_3	100	
"	"	"	1.5N HNO_3	"	
"	2N HF	"	0.5N HNO_3	"	
"	"	"	1.5N HNO_3	"	
"	"	30% $UO_2(NO_3)_2 \cdot 6H_2O$	"	"	

Carrying power of LaF_3 for $48^{(r)}$, effect of acids and fission products(13)

No effect due to HNO_3 (0.5N), H_2SO_4 (0.05N), H_3PO_4 (0.007N). Carrying power slightly lowered by presence of fission products at Site W concentrations, by $NaAsO_2$ + Na $HAsO_4$, and by Cr^{+3}. No quantitative data given.

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[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA1f-4
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	[redacted]es, Series A Issued to:

Carrying power of LaF_3 for $49^{(r)}$ at La/Pu ratio $\approx 1^{(14)}$

At Pu ≈150 mg./l., La/Pu ≈1, no KCl, ~75% of Pu carried. At Pu ≈150 mg./l., La/Pu ≈1, 0.1N KCl, 90-100% of Pu carried. At La/Pu = 3 to 5, the carrying was quantitative, whether KCl was present or not. Authors suggested that a mixed PuLa fluoride was being precipitated, or when KCl present a mixed PuK fluoride.

Mechanism of carrying of Pu by $LaF_3^{(15)}$

$49^{(r)}$ precipitated with La/Pu < 1. Procedure was to add La^{+3} to solution of Pu and HF, stir, let stand 10 minutes and determine activity of precipitate.

Total μg. La^{+3} used	Total μg. Pu used	Total Pu ppt'd.	Atomic ratio La/Pu in ppt.
1.0	1.12	0.89	1.82
"	1.31	0.95	1.95
2.3	1.00	0.99	---
1.5	1.54	1.20	2.00
0.5	1.00	0.25	3.5
"	1.10	0.27	3.2
0.73	1.13	0.57	2.2
0.48	1.52	0.67	"

Decided formula should be $PuF_4 \cdot 2LaF_3$.

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Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1945	EDITION I SHEET IA1f-5
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	Copy [redacted] es, Series A Issued to:

Uranium correction in ordinary LaF_3 method of analysis(28)

LaF_3 coprecipitated some U, giving a high α-count. Amount relatively independent of HF, HNO_3, $UO_2(NO_3)_2$ concentrations, but did depend on amount of LaF_3 precipitated. E.G., 10-ml. vol., lusteroid tubes, 2 washings with HF, no HNO_3, 10% $UO_2(NO_3)_2 \cdot 6H_2O$:

0.13 mg. La^{+3} gave 1 c./min. due to U.
0.4 mg. La^{+3} " 10 c./min. " " "
1.0 mg. La^{+3} " 26 c./min. " " "

Uranium correction in modified LaF_3 method of analysis(16)

	α c./min. due to uranium	
Mg. LaF_3 ppt'd.	Initial LaF_3	Reppt'd. LaF_3*
1.5	40-48	15-20
0.3	15-20	4-5

*Initial precipitate washed once with H_2O, dissolved in 5 drops of $ZrO(NO_3)_2$ solution, diluted to original volume and LaF_3 reprecipitated by addition of HF. Initial precipitation made from 10% $UO_2(NO_3)_2 \cdot 6H_2O$ solution.

Effect of time of digestion of LaF_3 on amount of uranium carried(17)

	α c./min. due to uranium
Straight precipitate digested 15 min. at room temp.	~15
"Preformed" " " 30 " 50-55°C.	~45
Straight " " " " "	~70

Carrying of $48^{(r)}$ and $39^{(r)}$ by thorium fluoride(18)

"$ThF_4 \cdot 4H_2O$" precipitated by HF carried 66% of $48^{(r)}$ and 50% of $39^{(r)}$ present. UX_1 tracer carried quantitatively, showing all thorium was precipitated.

"$KThF_5 \cdot H_2O$" precipitated by KF carried 97% of $48^{(r)}$, 50% of $39^{(r)}$.

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Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA1f-6
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	C[redacted]es, Series A Issued to:

Dissolving of 48$^{(r)}$ and 59$^{(r)}$ from "ThF$_4$" by hot concentrated NH$_4$F$^{(19)}$

				% 59$^{(r)}$		% 48$^{(r)}$	
Mg. Th^{+4}	Temp.	Time	No. of extractions with NH$_4$F	NH$_4$F insol.	NH$_4$F sol.	NH$_4$F insol.	NH$_4$F sol.
0	90°C.	4 hr.	2	87	4	91	11
"	"	"	"	91	2	101	10
0.3	"	"	"	11	59	8	46
"	"	"	"	"	"	5	50
2.0	"	6 hr.	3	6	--	~3	--
"	"	"	"	"	--	~1	--
0.3	25°	36 hr.	1	84	22	79	19

"ThF$_4$" is soluble in NH$_4$F; La F$_3$, CeF$_3$, YF$_3$ not. 49$^{(r)}$ fluoride is soluble in NH$_4$F (Cefola).(23)

Carrying of 49$^{(r)}$ by UF$_4$$^{(20)}$

UCl$_4$ made by dissolving metal in concentrated HCl.

U^{+4}/Pu	Final conc. U^{+4}	% 49 carried
10,000	5 mg./l.	92
1,000	0.5	41
10	"	14

Precipitation of 49$^{(r)}$ fluoride$^{(21)}$

Addition of HF to Pu solution gave a white or pale-yellow flocculent precipitate.

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Compiled by: R. B. Duffield. Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA1f-7
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	[redacted], Series A Issued to:

Solubility of $49^{(r)}$ fluoride(22)

Solvent	Solubility, mg.Pu/l.
H_2O	10.8
3M HF	12.3
6M HF	44.8

Solubility of $49^{(r)}$ fluoride in 10M NH_4F(23)

$49^{(r)}$ fluoride precipitated with HF and treated with 10N NH_4F. Solution contained >80% of αcounts, insoluble residue remained (fluosilicate?). Solubility of >450 mg. Pu/l. in 10N NH_4F.

Appearance of $49^{(r)}$ fluoride(24)

Pale apple-green gelatinous precipitate. No information given on method of preparation.

Solubility of $49^{(r)}$ fluoride in zirconium nitrate solution(25)

Zirconium nitrate solution (50 g./l. in 3N HNO_3) dissolved $49^{(r)}$ fluoride.

Failure of $49^{(r)}$ fluoride to precipitate in the absence of other positive ions(26)

Solution of 2 g. Pu/l., 1M in HNO_3, made 2M in HF gave no precipitate. Interpreted as due to the lack of other positive ions. 10 g./l. of KCl added and a precipitate formed.

Solubility of $49^{(r)}$ fluoride and potassium $49^{(r)}$ fluoride(27)

Checked previous result in that a solution of 200 mg. Pu/l. gave no precipitate on making 2.7N in HF but did give a precipitate when K^+ added. Two determinations of the solubility of this potassium $49^{(r)}$ fluoride gave 7.3 and 10.5 mg. Pu/l. in H_2O.

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Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET LA1f-8
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	Cop[redacted]copies, Series A Issued to:

References

(1) Sheline, Report CN-299, p.5, Oct. 5, 1942.

(2) Sheline, Report CN-328, p.7, Oct. 31, 1942.

(3) Sheline, Report CN-343, p.7, Nov. 15, 1942.

(4) Prestwood, Report CN-328, p.10, Oct. 31, 1942.

(5) Cunningham and Werner, Report CN-391, p.11, Nov. 31, 1942.

(6) Willard and Turk, Report CN-405, p.18, Dec. 16, 1942.

(7) Cooper's Group, Report CN-421, p.1, June 15, 1943.

(8) Stein, Report CN-522, p.11, Mar. 15, 1943.

(9) Ames Group, Report CN-727, p.3, June 15, 1943.

(10) Clifford, Fries, James, Knox, Koshland, Shephard and Thompson, Report CN-728, p.7, June 21, 1943.

(11) Clifford, Fries, James, Knox, Koshland, Shephard and Thompson, Report CN-728, p.8, June 21, 1943.

(12) Fries, Report CN-728, p.26, June 21, 1943.

(13) James and Knox, Report CN-728, p.20, June 21, 1943.

(14) Cefola, Report CN-728, p.48, June 21, 1943.

(15) Cefola, Report CN-813, p.31, July 17, 1943.

(16) Dixon, James, Cooper, Shepard and Thompson, Report CN-778, p.12, July 1, 1943.

(17) Struthers, Report CN-778, p.13, July 1, 1943.

(18) Duffield, Report CN-250, p.3, Aug. 16, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA1f-9
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	Cop[redacted] copies, Series A Issued to:

References (contd.)

(19) Kohman, Report CN-363, p.10, Nov. 16, 1942.

(20) Cefola, Report CN-419, p.24, Jan. 15, 1943.

(21) Cunningham, Cefola and Werner, Report CN-261, p.6, Aug. 15, 1942.

(22) Cefola, Cunningham and Werner, Report CN-282, p.2, Sept. 16, 1942.

(23) Cefola, Report CN-391, p.12, Nov. 31, 1942.

(24) Cunningham and Werner, Report CN-419, p.19, Jan. 15, 1943.

(25) Cunningham, Report CN-503, p.4, Feb. 16, 1943.

(26) Cunningham and Werner, Report CN-556, p.2, Mar. 31, 1943.

(27) Cefola, Report CN-728, p.47, June 21, 1943.

(28) Knox, Report CN-556, p.8, Mar. 16, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: November 27, 1943	EDITION I, SUPP. 1 SHEET IA1f-10
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	[redacted]eries A Issued to:

Solubility of $37^{(r)}$ fluoride

Precipitated by HF from a nitrate solution. Colorless as aqueous suspension, turned clear yellow on drying hot. Dissolved readily in warm conc. HNO_3. Solubility ~30 mg. Np/l. in 1M HF.(1)

Reference

(1) Cunningham, Report CN-991, p. 20, Oct. 9, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield, A. C. Wahl Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET IAlf-11
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	C[redacted]Series A Issued to:

Carrying of $49^{(r)}$ by CeF_3(1)

From a solution 1M HNO_3, 1M HF, 0.1M H_3PO_4, 0.02M Fe^{+2}, $Ce^{+3}/Pu = 9$. 98% of Pu was carried by CeF_3.

Precipitation of sodium plutonium fluoride(2)

$Pu^{(r)}$ (295 µg.) + HF + Na^+ gave a light green flocculent precipitate. After centrifuging and washing, the precipitate appeared crystalline.

Carrying of 48 by LaF_3

In 0.5M HNO_3 and 0.5M UO_2^{++}, the HF concentration must be $\geq$1.2M to get >95% of the 48 to follow the LaF_3.(4)

Analysis of Pu for control at X(3)

A. Sample preparation (mounted in LaF_3)
Pt plate with Zapon ring 1.2 cm in diam. LaF_3 added as slurry in 150 µl. of sol'n. Slurry stirred with Pt hook, with side to side motion. Evaporated by infra-red lamp. Ignited (ignition did not change counting rate).

B. Effect of carrying and self-absorption
<0.2 mg. La^{+3}/0.5 ml. -- incomplete carrying
>0.6 mg. La^{+3}/0.8 $cm.^2$ -- self-absorption sets in

C. Concentration of Pu from dilute sol'ns. (20% UNH)
1. $BiPO_4$ pptd., dissolved HCl, LaF_3 pptd.
2. "$U(C_2O_4)_2$" pptd, dissolved HCl and H_2O_2, LaF_3 pptd. ("$U(C_2O_4)_2$" hard to dissolve)

D. U contamination (LaF_3 from 20% UNH)

mg. La^{+3}	No. washes (N HF, 1N HNO_3)	Vol. acid wash	Vol. H_2O wash	U c/m at 8% geom.(?)
0.2-0.5	0	---	50 µl.	10-20
0.5	"	---	200	5,6
"	1	100 µl.	100	3,3
"	"	200	200	2,1
"	2	100	100	2,0

[redacted]

[redacted]

Compiled by: R. B. Duffield, A. C. Wahl Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET IA1f-12
I. Solution chemistry A. Precipitation reactions 1. Reduced state f. Fluoride	[redacted] Issued to:

Analysis of Pu for control at X (cont.)

E. β^- interference on magnetic field chamber

$\sim$8% geometry

6000 gauss field

10^9 β^- disintegrations/min. do not affect chamber

References

(1) Bradshaw, Dean, Gaarder, Johnson, Kroner, Koshland and Thompson, Report CN-1095, p. 7, December 1, 1943.

(2) Carniglia, Connick, Gofman, McVey, Sheline, Report CN-1170, p. 29, December 20, 1943.

(3) Clifford, Shepard, Knights, Lewis and Borkowski, Report CN-1025, p. 25, November 8, 1943.

(4) McVey, Report CN-1134, p. 48, December 1, 1943.

[redacted]

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Compiled by: R. S. Duffield

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION 1, SUPP. 3 SHEET IA1f-13

[redacted]

Cop[redacted] of 50 copies, Series A

Issued to:

I. Solution chemistry
    A. Precipitation reactions
        1. Reduced state
            f. Fluoride

Sol'y. of Pu^{+4} fluoride

Solvent	Sol'y. mg. Pu/l.
0.6N HNO_3 0.5N HF	$> 1300^{(1)}$

Reference

(1) Mastick and Wahl, Report LA-63, p. 8, February 22, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IA1g-1

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      g. Hydroxide

[redacted] copies, Series A

Issued to:

Carrying of $48^{(r)}$ by uranous hydroxide(1)

NH_4OH added to precipitate completely U^{+4} from solution.

pH	% $48^{(r)}$ in precipitate
2.25	10
2.65	29
7.75	97
9.20	98

Preparation of $49^{(r)}$ hydroxide(2)

Prepared by treating $49^{(r)}$ iodate with concentrated NH_4OH. Pale yellowish-green flocculent precipitate.

Solubility of $49^{(r)}$ hydroxide

Solvent	Solubility, mg. Pu/l.
H_2O	1.8(3)
Conc. NH_4OH	0.24(3)
0.4M K_2SO_4	1.7(4)
1M $(NH_4)_2SO_4$	1.1(4)

Appearance of $49^{(r)}$ hydroxide(5)

Olive green by reflected light.

References

(1) Brown, Hill and Jaffey, Report CN-405, p. 13, Dec. 16, 1942.

(2) Cunningham, Werner and Cefola, Report CN-261, p. 6, Aug. 15, 1942.

(3) Cefola, Cunningham and Werner, Report CN-282, p. 2, Sept. 16, 1942.

(4) Cunningham and Werner, Report CN-328, p. 5, Oct. 31, 1942.

(5) Cunningham and Werner, Report CN-419, p. 20, Jan. 15, 1943.

[redacted]

Compiled by: R. B. Duffield Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IA1g-2
I. Solution chemistry A. Precipitation reactions 1. Reduced state g. Hydroxide	Copy [redacted] A Issued to:

Solubility of $37^{(r)}$ hydroxide

Precipitated by NH_4OH. Reddish-yellow. Solubility ~20 mg. Np/l. in solution 2M NH_4NO_3, 5M NH_4OH.(1)

Carrying of $48^{(r)}$ by $La(OH)_3$ from potassium columbate sol'n.

From solution 0.3M KOH, 0.045M Cb, 0.2-0.8 g. La^{+3}/l., 85-93% of $48^{(r)}$ was carried by $La(OH)_3$.(2)

References

(1) Cunningham, Report CN-991, p. 20, Oct. 9, 1943.

(2) Fries and Werner, Report CN-1041, p. 13, Oct. 31, 1943.

[redacted]

Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM.

EDITION I SHEET IA1h-1

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      h. 8-hydroxyquinolate

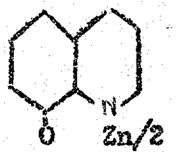
[redacted]

Issued to:

Carrying of $43^{(r)}$ by Fe^{+3}, UO_2^{++} and Zn^{++} compounds of 8-hydroxyquinoline

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	% $39^{(r)}$ in ppt.
Fe^{+3}(1)	8-hydroxyquinoline	UO_2^{++}	pH = 2.6	7	---
UO_2^{++}(1)	"	Ce^{+3}, Ce^{+4}	3.2	90	---
UO_2^{++}(2)	"	" "	3.3	37	<6
"	"	---	3.9	98	---
"	"	Ce^{+3}, Ce^{+4}	4.3	97	< 12
"	"	" "	4	95	15
Zn^{++}(2)	"	---	2.6	Not complete	---

Structure of compound:



References

(1) Apple, Knox and Perlman, Report CN-282, p. 8, Sept. 16, 1942.

(2) Thompson, Report CN-328, p. 10, Oct. 31, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA1i-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state i. Iodate	C[redacted]A Issued to:

Carrying of $48^{(r)}$ by $Th(IO_3)_4$ and by other heavy metal iodates

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
$Th(IO_3)_4$(1)	0.108M KIO_3	Ce^{+3}	2.4M HNO_3	100	16% $39^{(r)}$ in ppt.

It has also been shown(2) that carrying is essentially quantitative by $Ba(IO_3)_2$, $Pb(IO_3)_2$, $AgIO_3$, $Bi(IO_3)_3$, $ZrO(IO_3)_2$, $La(IO_3)_3$, $UO_2(IO_3)_2$.

Carrying power of $Th(IO_3)_4$ for $48^{(r)}$ in the presence of UO_2^{++} at various acidities(3),(4)

At iodate concentration of 0.108M, $Th(IO_3)_4$ precipitation and carrying of $48^{(r)}$ were essentially complete at acidities up to 3.2N. Above this acidity carrying fell off rapidly. With 10 min. standing before filtration, about 1% of uranium present also precipitated as iodate. With 1M HNO_3, three equivalents of IO_3^- per equivalent of Th^{+4} were needed to get 95% carrying of Pu.(4)

Carrying of $49^{(r)}$ by $Th(IO_3)_4$ at Th/Pu ratios of 100:1 and 600:1(4)

Carrying precipitate	Precipitating agent	Other ions in solution	Acidity	% Pu in ppt.	Other Conditions
$Th(IO_3)_4$	KIO_3	---	1N HNO_3	99	Th/Pu = 100
"	"	10% $UO_2(NO_3)_2 \cdot 6H_2O$	3N HNO_3	"	Th/Pu = 600

Carrying of $48^{(r)}$ by $UO_2(IO_3)_2$(5)

Partial precipitation of $UO_2(IO_3)_2$ at pH 2.6 carried 97% of $48^{(r)}$. Graph given in report shows effect of varying IO_3^- and UO_2^{++} concentrations.

[redacted]

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Date: September 28, 1943	EDITION I SHEET IA1i-2
I. Solution chemistry A. Precipitation reactions 1. Reduced state i. Iodate	C[redacted]A Issued to:

Carrying of $48^{(r)}$ by $UO_2(IO_3)_2$ (5) (cont.)

When $(UO_2^{++}) = 0.015M$, four or more equivalents of IO_3^- per equivalent of UO_2^{++} gave >97% carrying of $48^{(r)}$, roughly half the UO_2^{++} being precipitated. When $(UO_2^{++}) = 0.0071M$, ten or more equivalents of IO_3^- per equivalent of UO_2^{++} were necessary to give 95% carrying of $48^{(r)}$.

Precipitation of $48^{(r)}$ iodate (6)

Addition of KIO_3 to nitrate solution of Pu, gave a white bulky, crystalline precipitate.

Solubility of $49^{(r)}$ iodate

Solvent	Solubility mg. Pu/l.
Saturated KIO_3 solution	2.1 (7)
½-saturated KIO_3 solution	1.8 (7)
Saturated KIO_3, 3M HNO_3	4.8 (7)
" " 6M "	6.2 (7)
H_2O	0.45 (8)
6M HNO_3	6.2 (8)
1M HIO_3	24 (8)
5M HIO_3	84 (8)
1M H_2SO_4	73 (8)
5M H_2SO_4	103 (8)
1M $(NH_4)_2SO_4$	34 (8)

[redacted]

Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IA1i-3

I. Solution chemistry
    A. Precipitation reactions
        1. Reduced state
            i. Iodate

C[redacted] Series A

Issued to:

Composition of $49^{(r)}$ iodate

Compound weighed and then Pu content determined by weighing. Found $IO_3^-/Pu = 3.9$. Formula therefore is $Pu(IO_3)_4$.(7)

To check(10) possibility that water of hydration was making result incorrect, IO_3^- was determined by reaction with excess $S_2O_3^=$ and excess determined with standard KIO_3. Found compound to be 74.9% IO_3^-, $Pu(IO_3)_4$ is 74.5% IO_3^-.

A repetition(11) of this determination gave 77% IO_3^-.

References

(1) Duffield, Report CN-239, p. 6, July 15, 1942.

(2) Stoughton, Report CN-239, p. 9, July 15, 1942.

(3) Duffield, Report CN-250, p. 2, August 16, 1942.

(4) Duffield, Fontana, Garner, Sheline and Stoughton, Report CN-363, p. 3, November 16, 1942.

(5) Cunningham and Werner, Report CN-391, p. 12, November 31, 1942.

(6) Gofman, Report CN-391, p. 4, November 31, 1942.

(7) Cunningham, Cefola and Werner, Report CN-261, p. 5, August 15, 1942.

(8) Cefola, Cunningham and Werner, Report CN-282, p. 2, Sept. 16, 1942.

(9) Cunningham and Werner, Report CN-328, p. 5, Oct. 31, 1942.

(10) Cunningham and Werner, Report CN-299, p. 1, Oct. 5, 1942.

(11) Cunningham and Werner, Report CN-454, p. 1, Jan. 16, 1943.

(12) Cunningham and Werner, Cefola, Report CN-467, p. 6, Feb. 13, 1943.

[redacted]

Compiled by: R. B. Duffield Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IA1i-4
I. Solution chemistry A. Precipitation reactions 1. Reduced State i. Iodate	C[redacted] Series A Issued to:

Carrying of $48^{(r)}$ by "$U(IO_3)_4$"

From a sol'n. 0.4M IO_3^-, 1 g. U^{+4}/l., 5N HCl, 125 g. Bi^{+3}/l., 96% of $48^{(r)}$ was carried by "$U(IO_3)_4$". "$U(IO_3)_4$" dissolves easily in cold 10N HNO_3 without apparent oxidation of U^{+4}. Heating brings about oxidation. Fe^{+3} inhibits carrying.(1)

Reference

(1) Miller, Report CN-979, p. 29, Sept. 30, 1943.

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM.
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IA1i-3
I. Solution chemistry A. Precipitation reactions 1. Reduced state i. Iodate	Co[redacted] Series A Issued to:

Solubility of Pu^{+4} iodate(1)

Conditions	0.2M KIO_3 1N HNO_3	0.2M KIO_3 2N HNO_3	0.2M KIO_3 2N HNO_3	0.2M KIO_3 3N HNO_3	0.2M KIO_3 4N HNO_3
HNO_3 sol'n. of Pu^{+4} added to dry crystals of pp'ting. agent	20mg Pu/l.	36-39mg Pu/l.	40mg Pu/l.	44mg Pu/l.	39mg Pu/l.
Sol'n. of pp'ting. agent added to HNO_3 sol'n. of Pu^{+4}	--	18mg Pu/l.	7-20mg Pu/l.	--	--

Reference

(1) Mastick and Wahl, Report LA-63, p. 5, February 22, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM.
Date: September 28, 1943	EDITION I SHEET IA1j-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state j. Nitrate	[redacted] Issued to:

Preparation of $49^{(r)}$ nitrate(1)

Evaporation to dryness of a solution of $49^{(r)}$ nitrate left the salt as a lemon-yellow crystalline material which melted easily on warming. A solution of Pu nitrate containing 2-4 g. Pu/l. was pale yellow-green. More concentrated solutions were very deep green.(2)

Determination of relative basicities of $48^{(r)}$ and $39^{(r)}$ by precipitation of basic nitrates(3)

Basic lanthanum nitrate precipitated by addition of insufficient NH_4OH to a solution of lanthanum nitrate containing $48^{(r)}$ and $39^{(r)}$. Let stand for 5 min. at 20°C. 96% $48^{(r)}$, 35% $39^{(r)}$ carried. Concluded $39^{(r)}$ about as basic as lanthanum, $48^{(r)}$ much less so.

References

(1) Cunningham, Cefola and Werner, Report CN-261, p. 5, Aug. 15, 1942.

(2) Cunningham and Werner, Report CN-419, p. 20, Jan. 15, 1943.

(3) Duffield, Report CN-328, p. 2, Oct. 31, 1942.

[redacted]

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Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IA1j-2

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced State
      j. Nitrate

Copy [redacted]ries A

Issued to:

$37^{(r)}$ nitrate

At comparable concentrations, Np nitrate solutions are much less colored than Pu nitrate solutions. 6 g. Np/l. in $5M$ HNO_3 shows a barely detectable greenish-yellow in 0.5 µl. of solution.(1)

Reference

(1) Cunningham, Report CN-991, p. 20, Oct. 9, 1943.

[redacted]

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Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IA1j-3
I. Solution chemistry A. Precipitation reactions 1. Reduced state j. Nitrate	C[redacted] Series A Issued to:

Solubility of Pu^{+4} nitrate(1)

In 1 N HNO_3, solubility ≥ 350 g. Pu/l.

Reference

(1) Hopkins and Watt, Report CN-1258, p. 12, February 1, 1944.

[redacted]

[redacted]

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Date: September 28, 1943	EDITION I SHEET IA1k-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state k. m-nitrobenzoate	[redacted]ries A Issued to:

Carrying of 48$^{(r)}$ by Th^{+4}, Ce^{+4}, ZrO^{++} compounds of m-nitrobenzoic acid$^{(1)}$

Th^{+4}, Ce^{+4}, ZrO^{++} compounds of m-nitrobenzoic acid precipitated from an acetate buffer in the presence of La^{+3} ion as a holdback carrier carried $>$95% of 48$^{(r)}$ and only 20% of 39$^{(r)}$. UO$_2^{++}$, Y^{+3}, Sr^{++}, Ru^{+3}, MoO$_4^{=}$, Ba^{++} and La^{+3} are not precipitated under these conditions. M-nitrobenzoic acid is slightly soluble in H$_2$O (0.3 g./l.) but is much more soluble in NH$_4$Ac solutions.

References

(1) Thompson, Report CN-328, p. 10, Oct. 31, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA11-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state 1. Oxalate	C[redacted]ries A Issued to:

Carrying of $48^{(r)}$ by $La_2(C_2O_4)_3$ (1)

At an oxalic acid concentration of 0.4M, with 100 or 200 µg. La^{+3} in 160 µl., > 95% of $48^{(r)}$ was carried by $La_2(C_2O_4)_3$ at acidities from 0.006 to 0.5N HNO_3.

Carrying of $48^{(r)}$ by $Th(C_2O_4)_2$ (2)

$Th(C_2O_4)_2$, precipitated from 0.12M HCl solution by 1/6 saturated $H_2C_2O_4$, carried 95% of $48^{(r)}$.

Attempt to prepare $49^{(r)}$ oxalate(3)

Saturated solution of oxalic acid mixed with solution of Pu nitrate, evaporated to dryness, gave no precipitate.

Solubility of $49^{(r)}$ oxalate(4)

Solvent	Solubility mg. Pu/l.
H_2O	2 (?)
1M $H_2C_2O_4$	≥500
1M $K_2C_2O_4$	≥700

Determination of formula of $49^{(r)}$ oxalate by titration of oxalate with Ce^{+4} (5)

11 µg. of Pu precipitated from 1N HNO_3 with 0.1M $K_2C_2O_4$. Crystals of Pu oxalate changed overnight from yellow prismatic needles to yellowish-green rosettes. Washed with 0.25N HCl, dissolved in 6N H_2SO_4. Excess Ce^{+4} added and back-titrated with Fe^{++}, using phenanthroline as indicator.

$$C_2O_4^{=}/Pu = 2.17$$

Believe high result due to coprecipitation of $K_2C_2O_4$.

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[redacted]

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IA11-2

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      1. Oxalate

Cop[redacted]copies, Series A

Issued to:

References

(1) Gofman, Report CN-867, p. 8, Aug. 14, 1943.

(2) Cefola, Cunningham and Werner, Report CN-239, p. 25, July 15, 1942.

(3) Cefola, Cunningham and Werner, Report CN-282, p. 1, Sept. 16, 1942.

(4) Cunningham and Werner, Report CN-328, p. 5, Oct. 31, 1942.

(5) Cunningham and Werner, Report CN-556, p. 1, Mar. 31, 1943.

[redacted]

Compiled by: R. B. Duffield Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUP: 1 SHEET TA11-3
I. Solution chemistry A. Precipitation reactions 1. Reduced state 1. Oxalate	C[redacted]s A Issued to:

Carrying of $48^{(r)}$ by "$Bi_2(C_2O_4)_3$"

From a solution 1-3M HNO_3, 1.0-2.5 g. Bi^{+3}/1., 0.12M $C_2O_4^{=}$, ~90% of $48^{(r)}$ was carried by "$Bi_2(C_2O_4)_3$".(1)

Carrying of $48^{(r)}$ by "$La_2(C_2O_4)_3$" from oxalate-columbate solution

From a solution containing oxalate and columbate, 86-95% of $48^{(r)}$ was carried by "$La_2(C_2O_4)_3$" (0.2-0.8 g. La^{+3}/1.)(2)

Carrying of $48^{(r)}$ by "$Th(C_2O_4)_2$"

From a solution 1N HNO_3, 0.12M $C_2O_4^{=}$, 1 g. Th^{+4}/1. 99% of Pu was carried by "$Th(C_2O_4)_2$".(3)

Carrying of $49^{(r)}$ by "$U(C_2O_4)_2$"

From a solution 2-4M HCl, 100-300 g. Bi^{+3}/1., 0.2-0.4M $H_2C_2O_4$, 0-0.1M KCl, 1.0 g. U^{+4}/1., 0.04 mg. Pu/1. 70-85% of Pu was carried by "$U(C_2O_4)_2$".(4)

Carrying of Pu by "$U(C_2O_4)_2$"

From a solution 6M HCl, 0.4M $H_2C_2O_4$, 0.1M KCl, 150 g. Bi^{+3}/1., 2 g. U^{+4}/1., 0.04 mg. Pu/1. 95% of $49^{(r)}$ was carried by "$U(C_2O_4)_2$". When solution was also 0.1M Fe^{+3} single addition of U^{+4} to concentration of 1 g. U^{+4}/1. $\leq$67% of Pu was carried by "$U(C_2O_4)_2$". When K^+ was absent carrying was much worse ($\leq$40%). $\leq$81% of Pu carried from 10% solution of $UO_2(NO_3)_2 \cdot 6H_2O$ with one addition of U^{+4}.(5)

When U^{+4} added in two portions to give a concentration of $U^{+4} \cong 3.6$ g./1. >95% of Pu was carried by "$U(C_2O_4)_2$" from a 10% $UO_2(NO_2)_2 \cdot 6H_2O$ solution. At HNO_3 concentrations of 0.2M or less uranous phosphate precipitated when phosphate was present and the carrying was much lower.(6)

References

(1) James and Thompson, Report CN-914, p. 18, Sept. 1, 1943.

(2) Fries and Werner, Report CN-1041, p. 14, Oct. 31, 1943.

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: November 27, 1943	EDITION I, SUPP. 1 SHEET IA11-4
I. Solution chemistry A. Precipitation reactions 1. Reduced state 1. Oxalate	Copy [redacted] copies, Series A Issued To:

References (cont.)

(3) James and Thompson, Report CN-914, p. 18, Sept. 1, 1943.

(4) Dam and Fries, Report CN-914, p. 13, Sept. 1, 1943.

(5) Dam and Fries, Report CN-1041, p. 2, Oct. 31, 1943.

(6) Gearder, Halperin, James, Koshland, Kroner, Malm, Thompson, Report CN-1041, p. 19, Oct. 3, 1943.

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: January 27, 1944	EDITION I, SUPP. 2 SHEET IA11-5
I. Solution chemistry A. Precipitation reactions 1. Reduced state 1. Oxalate	[redacted]es A Issued to:

Carrying of $Pu^{(r)}$ by $La_2(C_2O_4)_3$

Carrying data indicate that $48^{(r)}$ exists in two forms, only one of which is carried by $La_2(C_2O_4)_3$. Treatment of the tracer with NH_3OHCl or oxidation by $Cr_2O_7^{=}$ followed by reduction by NH_3OHCl was found to be effective in converting the $48^{(r)}$ almost quantitatively to a form carried by $La_2(C_2O_4)_3$.(1) Cb does not affect the carrying of $Pu^{(r)}$ by $La_2(C_2O_4)_3$.(2) (See also, IB3d-1.)

References

(1) Reas, Report CN-1134, p. 5, December 1, 1943.

(2) Reas and Crandall, Report CN-1134, p. 10, December 1, 1943.

[redacted]

Compiled by: R. B. Duffield

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, Supp. 3   SHEET: IA11-6

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      1. Oxalate

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Solubility of Pu^{+4} oxalate(1)

Medium	Sol'y. mg Pu/l.
0.6N HNO_3 0.25M $H_2C_2O_4$	860
H_2O	260

Reference

(1) Mastick and Wahl, Report LA-63, p. 6, February 22, 1944.

[redacted]

Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IAlm-1

I. Solution chemistry
  A. Presipitation reactions
    1. Reduced state
      m. Oxide

Co[redacted] A

Issued to:

Carrying of $48^{(r)}$ by $Cb_2O_5 \cdot xH_2O^{(1)}$

$Cb_2O_5 \cdot xH_2O$ suspension added to $48^{(r)}$ solution carried 61% of $48^{(r)}$. (And 35% of soft γ-activity). Probably an adsorption effect.

Effect of acidity on carrying of $48^{(r)}$ by $Cb_2O_5 \cdot xH_2O^{(2)}$

No UO_2^{++} present.

(H^+)	% Pu carried
0.01M	90
0.08	85
0.2	78
0.8	57
1.5	32

Effect of UO_2^{++} on carrying of $48^{(r)}$ by $Cb_2O_5 \cdot xH_2O^{(2)}$

(UO_2^{++})	(H^+)	% Pu carried
0.12	0.1	85
0.33	0.18	83
0.5	0.16	81
1.0	0.2	70

Effect of $NaNO_3$ on carrying of $48^{(r)}$ by $Cb_2O_5 \cdot xH_2O^{(2)}$

(H^+)	(UO_2^{++})	$(NaNO_3)$	% Pu carried
0.1M	0.25M	0M	85
"	"	0.25	86
"	"	0.5	87
"	"	1.0	"
"	"	1.8	92
"	0.12	0.0	85
"	"	1.0	95

Effect of Na_2SO_4 on carrying of $48^{(r)}$ by $Cb_2O_5 \cdot xH_2O^{(2)}$

(UO_2^{++})	(Na_2SO_4)	% Pu carried
1.0M	0.2M	74
"	0.3	84
"	0.4	"
"	0.55	"

[redacted]

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Date: September 28, 1943	EDITION I SHEET IA1m-2
I. Solution chemistry A. Precipitation reactions 1. Reduced state m. Oxide	Copy [redacted] eries A Issued to:

Effect of NH_3OH^+ on carrying of $48^{(r)}$ by $Cb_2O_5 \cdot xH_2O^{(3)}$

(UO_2^{++})	(NH_3OHCl)	(HNO_3)	% Pu in ppt.
OM	OM	0.075M	85
0	0.025	"	35
0.25	0	0.05	89
"	0.005	"	5
1.0	0.03	0.23	2.5

Two $Cb_2O_5 \cdot xH_2O$ precipitations in the absence of NH_3OH^+ removed 97% of Pu. (Combination $Cb_2O_5 \cdot xH_2O$ - $NaUO_2Ac_3$ extraction-decontamination process proposed in this report.)

Effect of added salts on carrying of $48^{(r)}$ by $Cb_2O_5 \cdot xH_2O^{(4)}$

Pu carried from following solution by $Cb_2O_5 \cdot xH_2O$: $UO_2(NO_3)_2$ = 1.7M, $NaNO_3$ = 1.4M, KNO_3 = 0.1M. Cb^{+5} = 0.1M, HNO_3 = 0.17M, Na_2SO_4 = 0.1-0.3M. ~80% of Pu carried in a number of duplicate experiments. Three consecutive such precipitations removed 98% of Pu present.

0.011M ZrO^{++} reduced carrying in this solution to 61%.

Carrying of $49^{(r)}$ by $Cb_2O_5 \cdot xH_2O$

In a solution 1M in UO_2^{++}, 0.1M HSO_4^-, 0.2M $SO_4^=$, Cb/Pu = 45, $Cb_2O_5 \cdot xH_2O$ carried ~90% of $49^{(r)}$.(5)

$Cb_2O_5 \cdot xH_2O^{(6)}$ removed in two portions from solution 0.01M in Cb^{+5}, 5×10^{-4}M in $49^{(r)}$ (Cb/Pu = 20), 0.15N in HSO_4^-, 0.3M in $SO_4^=$ the following percentages of Pu:

% Pu in various fractions

First Cb_2O_5 ppt.	Second Cb_2O_5 ppt.	Total in Cb_2O_5 ppts.	Supernatant
40	-----	40	60
45	-----	45	55
47	40	87	13

Preparation of 49 oxide

Ignition of Pu nitrate in air gave a yellow-brown solid, insoluble in 6N HNO_3, soluble in hot concentrated H_2SO_4.(7)

[redacted]

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I. Solution chemistry A. Precipitation reactions 1. Reduced state m. Oxide	C[redacted] Series A Issued to:

Preparation of 49 oxide (cont.)

Later reported to be a bright lemon-yellow solid.(8)

References

(1) Gofman, Report CN-723, p. 19, June 20, 1943.

(2) Gofman, Report CN-808, p. 1, July 20, 1943.

(3) Gofman, Report CN-808, p. 6, July 20, 1943.

(4) Pimentel and Stein, Report CN-867, p. 1, August 14, 1943.

(5) Sheline and Hamaker, Report CN-808, p. 10, July 20, 1943.

(6) Sheline and Hamaker, Report CN-867, p. 6, Aug. 14, 1943.

(7) Cunningham, Cefola and Werner, Report CN-261, p. 5, Aug. 15, 1942.

(8) Cunningham and Werner, Report CN-419, p. 18, Jan. 15, 1943.

[redacted]

Compiled by: R. B. Duffield Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET IAlm-4
I. Solution chemistry A. Precipitation reactions 1. Reduced state m. Oxide	C[redacted]Series A Issued to:

Effect of Al^{+3} and Fe^{+3} on extraction of $Pu^{(r)}$ by $Cb_2O_5 \cdot xH_2O^{(1)}$

Al^{+3} ion concentrations as high as 1.2×10^{-2}M have no effect on carrying of $48^{(r)}$ by $Cb_2O_5 \cdot xH_2O$.

Fe^{+3} present at concentrations as low as 5×10^{-5}M interferes with the carrying. (See also IVK-2.)

Reference

(1) Crompton, Report CN-1134, p. 1, December 1, 1943.

[redacted]

[redacted]

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HANDBOOK, CHEMISTRY OF PLUTONIUM.

Date: September 28, 1943

EDITION I

SHEET IAln-1

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      n. Peroxide

Co[redacted]es A

Issued to:

Preparation of $49^{(r)}$ peroxide (1)

Addition of H_2O_2 to HCl solution of $49^{(r)}$ gave a white or slightly yellow precipitate.

Solubility of $49^{(r)}$ peroxide

Solvent	Solubility, mg. Pu/l.
H_2O (2), (3)	16
3M HNO_3, 15% H_2O_2 (3)	28
1M HNO_3, 20% H_2O_2 (4)	23 ± 9

Decomposition of $49^{(r)}$ peroxide (5)

Described as olive-green precipitate by reflected light. When peroxide was decomposed by HNO_3, a pink solution was obtained. Faded to a pale lavender in about three hours. Latter color persisted for two days at which time it was destroyed by heating at 100°C. for 10 min. Color may be caused by presence of $49^{(o)}$.

References

(1) Cunningham, Cefola and Werner, Report CN-261, p. 6, Aug. 15, 1942.

(2) Cunningham and Werner, Report CN-328, p. 5, Oct. 31, 1942.

(3) Cunningham and Werner, Report CN-343, p. 5, Nov. 15, 1942.

(4) Cunningham and Werner, Report CN-419, p. 23, Jan. 15, 1943.

(5) Cunningham and Werner, Report CN-419, p. 19, Jan. 15, 1943.

[redacted]

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Compiled by: R. B. Duffield
Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM
EDITION I, SUPP. 1 SHEET IA1n-2

I. Solution chemistry
   A. Precipitation reactions
      1. Reduced state
         n. Peroxide

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Issued to:

Carrying of $48^{(r)}$ by uranium peroxide

From a solution 0.001-0.25M H^+, 1.5 g. U/l. 5% H_2O_2, 89-94% of $48^{(r)}$ was carried by uranium peroxide.(1)

Carrying of $49^{(r)}$ by uranium peroxide; solubility of Pu peroxide(1)

Pu mg./l.	HNO_3 conc.	H_2O_2%	UO_2^{++} g./l.	U/Pu	% Pu ppt'd.	Sol'y. Pu mg./l.
12	0.15	5	12	1,000	96.6	---
"	"	"	6	500	95.3	---
"	"	"	1.2	100	96.4	---
"	"	"	0.6	50	96.3	---
"	"	"	0.12	10	95.5	---
"	"	"	0.012	1	87	---
"	"	"	0	---	95.5	0.7
20	0.03	6	1.5	78	97	---
"	"	"	0	---	96	1
2	0.03	6	1.5	780	69	---
"	"	"	0	---	52	1
1.5	0.5	6	15	10,000	46	---
1.2	0.15	5	0	---	91	---
"	"	0	0	---	0	---

Reference

(1) Fries & Werner, Report CN-914, p. 5, September 1, 1943

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IAIn-3
I. Solution chemistry A. Precipitation reactions 1. Reduced state n. Peroxide	Cop[redacted]ries A Issued to:

Solubility of Pu^{+4} peroxide

Solvent	Sol'y. mg Pu/l.
H_2O	21(1)
0.5N HNO_3	250-280(1)
0.8N HNO_3, 5% H_2O_2	318-533(1)
1N HNO_3	340(1)
2N HNO_3	1990-3540(1)
0.43M HNO_3 1.6M H_2O_2	5-30(2)
H_2O	90-180(2)

References

(1) Hopkins and Watt, Report CN-1258, p. 6, February 1, 1944.

(2) Mastick and Wahl, Report LA-63, p. 7, February 22, 1944.

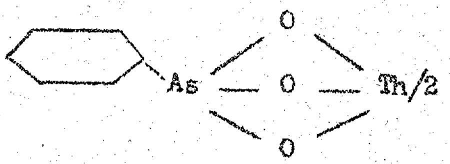
[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IA1o-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state o. Phenylarsonate	[redacted]ies A Issued to:

Carrying of $48^{(r)}$ by Th^{+4} and ZrO^{++} compounds of phenylarsonic acid(1)

Carrier	Other ions in solution	Acidity	%$49^{(r)}$ pptd.	%$39^{(r)}$ pptd.
ZrO^{++}	La^{+3}	1.7N HCl	>90	<10
(Th^{+4} and UO_2^{++} come down under these conditions.)				
ZrO^{++}	--	6N HCl	15	--
Th^{+4}	--	pH = 5	95	30

Structure of compound:



Reference

(1) Thompson, Report CN-343, p. 11, November 15, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IA1p-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state p. Phosphate	C[redacted]s, Series A Issued to:

Carrying of $48^{(r)}$ by bismuth phosphate

In ~1N HNO_3, $BiPO_4$ carried >95% of $48^{(r)}$. (1)

Carrying of $49^{(r)}$ by $BiPO_4$ at various ratios of Bi to Pu

Bi/Pu	Conditions	% $49^{(r)}$ in ppt.
17	~1N HNO_3, UO_2^{++}, 0.36M H_3PO_4	98.9(2)
120	" " " "	98.5(2)
150	" " " "	99.4(2)
1,600	" " " "	98.5(2)
28,000	" " " "	98.4(2)
150,000	" " " "	95.5(2)
25	1N H_2SO_4	89(3)
100	" "	94.6(3)
25	1N H_2SO_4, Bi added in two portions	94.7(3)
75-200	0.2-0.4N HNO_3, 0.6-1.0N H_2SO_4	97-100(4)
65	$HNO_3^* = 0.9$, $Fe^{++} = 0.02$, $H_2PO_4 = 0.6$	96(5)
50	" " " " " "	97(5)
60	" " " " " "	97(5)
75	" " " " " "	97(5)

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IA1p-2

I. Solution chemistry
A. Precipitation reactions
1. Reduced state
p. Phosphate

C[redacted]ies A

Issued to:

Carrying of $48^{(r)}$ by small amounts of $BiPO_4$ (6)

H_3PO_4 molarity	0.1	0.05	0.1	0.05	0.1	0.05	0.1	0.05	0.03
g. Bi^{+3}/1.	1.0	1.0	0.5	0.5	0.25	0.25	0.1	0.1	0.1
H^+ normality	1.5	1.5	1.3	1.3	1.2	1.2	1.1	1.1	1.1
% Pu not carried	0.7	0.9	1.0	1.1	1.2	1.5	1.2	1.3	1.0

Carrying power of $BiPO_4$ for $49^{(r)}$ (7)

Data given to show that to get a crystalline precipitate and quantitative carrying:

1. Bi^{+3} must be added in several portions in 10N HNO_3.
2. Presence of ~2N Na_2SO_4 helps.
3. High $(UO_2(NO_3)_2)$ helps.
4. Bi^{+3} must be >2 g. Bi^{+3}/1.

Effect of H_3PO_4 concentration on carrying of $48^{(r)}$ by $BiPO_4$ (8)

Carrying 98% at acid concentration up to 1.0M from 20% $UO_2(NO_3)_2 \cdot 6H_2O$ solution containing W concentration of fission products, solution stirred at 75°C. when the H_3PO_4 concentration was ~0.4M. With ratio conditions the same but the H_3PO_4 concentration equal to 0.2M, the carrying was 83%.

Effect of time of digestion on carrying of $49^{(r)}$ by $BiPO_4$ (9)

Solution 20% $UO_2(NO_3)_2 \cdot 6H_2O$

Hours of digestion at 75°C.	% Pu carried
4	88
8	92
12	95
16	96

Evidence also presented that one addition of Bi^{+3} as good as three.

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IA1p-3

[redacted] Series A

Issued to:

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      p. Phosphate

Effect of HCOOH on carrying of $48^{(r)}$ by $BiPO_4$ (10)

From a solution containing $H_3PO_4 = 0.4M$, $Bi^{+3} = 0.5$ g./l. H_2SO_4 = 1N, $UO_2(NO_3)_2 \cdot 6H_2O$ = 0.224 g./l., fission products at 2500 kw concentration, $BiPO_4$ carried the following amounts of $48^{(r)}$ at various concentration of HCOOH.

HCOOH concentration	% Pu carried
0.1M	95
0.2	96
0.4	96
0.5	93

Effect of Fe^{+2} and Fe^{+3} on carrying of $48^{(r)}$ by $BiPO_4$ (11)

		% Pu carried			
		Fe^{+2}		Fe^{+3}	
g. Bi^{+3}/l.	Fe^{+2} or Fe^{+3}	0.4M H_3PO_4	0.8M H_3PO_4	0.4M H_3PO_4	0.8M H_3PO_4
1.0	0.00	98	97	--	--
"	0.02	71,79	97	35,42	--
"	0.04	36,23	72	20,3	--
"	0.06	15	60	14	--
2.5	0.00	96,97	--	--	--
"	0.02	94	--	93	--
"	0.04	84	98	57	97
"	0.08	32	35	4	97

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Compiled by R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IA1p-4
I. Solution chemistry A. Precipitation reactions 1. Reduced state p. Phosphate	Co[redacted]s, Series A Issued to:

Effect of Ni^{++} on carrying of $48^{(r)}$ by $BiPO_4$ (12)

Solution 20% $UO_2(NO_3)_2 \cdot 6H_2O$, 1N H_2SO_4, 0.2N HNO_3, 0.8M H_3PO_4, 2.5 g. Bi/l. $BiPO_4$ precipitated and kept at 75°C. for 2 hours.

(Ni^{++})	% Pu carried
0.0000	98, 98
0.0014	98, 99
0.014	99*
0.014	98*

*Total recovery of Pu 20% below that expected.

Carrying of $48^{(r)}$ by $BiPO_4$ on engineering scale (13)

Extraction step in semi-works gave only 15-35% yield, very unreliable. No explanation for poor yield. NO seemed to have some effect. NO bubbled in during precipitation procedure on lab. scale gave loss as much as 30%.

Carrying power of hafnium phosphate for $49^{(r)}$ (14)

Hafnium phosphate at 1N HNO_3 carried 87 ± 6% of $49^{(r)}$, (20% $UO_2NO_3)_2 \cdot 6H_2O$ solution, Hf/Pu ≈100).

Carrying of $48^{(r)}$ by $LaPO_4$ (15)

$LaPO_4$ precipitated from concentrated NaH_2PO_4 solution at pH 3.8 (where zirconium phosphate just dissolves) carried 90% of $48^{(r)}$. Increase in pH decreased $48^{(r)}$ carried until at pH 8.5 only 7% of Pu was carried.

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Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I [redacted] SHEET IA1p-5
I. Solution chemistry A. Precipitation reactions 1. Reduced state p. Phosphate	Copy [redacted] copies, Series A Issued to:

Carrying of $49^{(r)}$ by zirconium phosphate at Zr/Pu ratio of 100:1(16)

HNO_3 conc.	Zr/Pu ratio	% $49^{(r)}$ carried
2N	100	16-18
1N	100	78

Precipitation of $49^{(r)}$ phosphate by NaH_2PO_4

Addition of NaH_2PO_4 solution (half-saturated) to a nitrate solution of Pu gave a white gelatinous precipitate soluble in concentrated HCl.(17)

Solubility of $49^{(r)}$ phosphate

Solvent	Solubility, mg. Pu/l.
H_2O	20(18)
1M HNO_3	25(18)
1M NaH_2PO_4	20(18)
5M NaH_2PO_4	29*(19)
0.15M H_3PO_4, 0.1M HNO_3	~ 5(20)
0.15M H_3PO_4, 1M HNO_3	~ 50(20)
0.15M H_3PO_4, 5M HNO_3	~ 5,000(20)
0.36M H_3PO_4, 5M HNO_3	~ 4,000(20)

*Very slight increase in solubility with increase in phosphate concentration evidence against a phosphate complex. Contrary to ZrO^{++}.

References

(1) Thompson, Report CN-405, p.8, Dec. 16, 1942.

(2) Cunningham and Werner, Report CN-405, p.13, Dec. 16, 1942.

[redacted]

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Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA1p-6
I. Solution chemistry A. Precipitation reactions 1. Reduced state p. Phosphate	Co[redacted]s, Series A Issued to:

References (cont.)

(3) Cefola, Report CN-454, p. 11, Jan. 16, 1943.

(4) Miller, Report CN-813, p. 7, July 17, 1943.

(5) Miller, Report CN-849, p. 14, Aug. 1, 1943.

(6) Thompson, Davidson, Miller and James, Report CN-556, p. 21, Mar. 31, 1943.

(7) Cunningham, Report CN-728, p. 37, June 21, 1943.

(8) Docher, Dixon and Dam, Report CN-813, p. 5, July 17, 1943.

(9) Miller, Report CN-849, p. 8, Aug. 1, 1943.

(10) Docher, Report CN-849, p. 7, Aug. 1, 1943.

(11) Docher, Dean and Kroner, Report CN-849, p. 6, Aug. 1, 1943.

(12) Cooper's Group, Report CN-849, p. 5, Aug. 1, 1943.

(13) Cooper's Group, Report CN-828, p.66, Aug. 26, 1943.

(14) Cunningham, Report CN-405, p. 13, Dec. 16, 1942.

(15) Thompson, Report CN-328, p. 12, Oct. 31, 1942.

(16) Cunningham and Werner, Report CN-391, p. 11, Nov. 31, 1942.

(17) Cunningham, Cefola, and Werner, Report CN-282, p. 11, Sept. 16, 1942.

(18) Cunningham and Werner, Report CN-328, p. 5, Oct. 31, 1942.

(19) Cunningham and Werner, Report CN-343, p. 4, Nov. 15, 1942.

(20) Werner, Report CN-728, p. 45, June 21, 1943.

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Compiled by: R. B. Duffield

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IA1p-7

I. Solution chemistry
  A. Precipitation reactions
    1. Reduced state
      p. Phosphate

[redacted]ies A

Issued to:

Carrying of $48^{(r)}$ by "$NH_4UO_2PO_4$"

From solution 0.5M HNO_3, 1.0M $(NH_4)_2HPO_4$, 0.0042M UO_2^{++}, 80% of $48^{(r)}$ carried by "$NH_4UO_2PO_4$".(1)

Carrying of $48^{(r)}$ by $BiPO_4$

Carrying of $48^{(r)}$ affected markedly by degree of agitation, not much by temp. of solution when H_3PO_4 added or by order of addition of Bi^{+3} and H_3PO_4.

Previously formed $BiPO_4$ precipitate added to solution carried 96% of Pu.(2)

Average yield of $BiPO_4$ method (extraction + two decontamination cycles) = 89%.(3)

Using 0.5 g. Bi^{+3}/l. (normally use 2.5 g./l.) and changing $UO_2(NO_3)_2 \cdot 6H_2O$ conc. from 19% to 15% increased per cent of Pu carried from ~85% to ~94%.

Carrying of $P_2O_7^{-4}$ in H_3PO_4 solution had slightly bad effect on carrying of Pu by $BiPO_4$ but results are somewhat uncertain.

"W" conc. of Cb has no effect on carrying of Pu by $BiPO_4$.(4)

Better decontamination but worse carrying of Pu results when precipitation was carried out by adding H_3PO_4 to Bi^{+3} solution rather than reverse method of addition.(5)

96% of Pu carried at Bi/Pu = 20

75% " " " " " = 6.4 (6)

Carrying of $48^{(r)}$ by "ThP_2O_6"

From a solution 1M HNO_3, 1 g. Th^{+4}/l. 0-20% $UO_2(NO_3)_2 \cdot 6H_2O$, 0.02-0.06M $P_2O_6^{-4}$, 80-100% of $48^{(r)}$ was carried by "ThP_2O_6". (1)

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Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: November 27, 1943	EDITION I, SUPP. 1 SHEET IA1p-8
I. Solution chemistry A. Precipitation reaction 1. Reduced state p. Phosphate	Cop[redacted]opies, Series A Issued to:

Carrying of 49$^{(r)}$ by "UP_2O_6"$^{(7)}$

HCl conc.	Bi^{+3} g./l.	U^{+4} g./l.	$P_2O_6^{-4}$ conc.	Pu mg./l.	% Pu carried
2	50	1.0	0.01	0.05	71
4	100	"	"	"	71, 90, 94
5	"	"	"	"	94
6	"	"	"	"	97
"	"	1.5	0.03	~4	~92
"	200	"	0.01	8	98
8	350	1.0	"	0.05	43(?)
10	400	2.0	0.02	"	72

Increasing conc. of Fe^{+3} or Bi^{+3} decreased carrying of Pu by "UP_2O_6". Carrying of Pu by "UP_2O_6" was at a maximum at $P_2O_6^{-4}$ conc. = 0.1M. Carrying of Pu by "UP_2O_6" dropped rapidly as U^{+4} conc. decreased below 1 g. U^{+4}/1.$^{(8)}$

Carrying of Pu by "UP_2O_6" in presence of $UO_2^{++}$$^{(7)}$

From a solution 20% $UO_2(NO_3)_2 \cdot 6H_2O$, 1M HNO_3, 1 g. U^{+4}/1., 0.02M $P_2O_6^{-4}$, ~20% of 48$^{(r)}$ was carried by "UP_2O_6".

From a solution 10% $UO_2(NO_3)_2 \cdot 6H_2O$, 6M HNO_3, 1 g. U^{+4}/1., 0.01M $P_2O_6^{-4}$, 0.05 mg. Pu/1., 93% of Pu was carried by "UP_2O_6".

From a solution 10% $UO_2(NO_3)_2 \cdot 6H_2O$, 6M HNO_3, no U^{+4}, 0.01M $P_2O_6^{-4}$, 500 mg. Pu/1., 87% of Pu precipitated. Pu hypophosphate was white and flocculent.

Carrying of Pu by "UP_2O_7"

From a solution 4-6M HCl, 100-200 g. Bi^{+3}/1., 1 g. U^{+4}/1., 0.05M $P_2O_7^{-4}$, 40-70% of Pu was carried by UP_2O_7. Fe^{+3} reduced carrying.$^{(9)}$

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Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: November 27, 1943	EDITION I, SUPP. 1 SHEET IA1p-9
I. Solution chemistry A. Precipitation reactions 1. Reduced state p. Phosphate	Copy [redacted] copies, Series A Issued to:

Solubility of 49$^{(r)}$ phosphate in presence of UO_2^{++}(10)

% $UO_2(NO_3)_2 \cdot 6H_2O$	Solubility of Pu, mg./1.
0	60
10	124
15	156
17	440
19.6	770

References

(1) James and Thompson, Report CN-914, p. 19, Sept. 1, 1943.

(2) Seaborg's Group, Report CN-931, p. 1, Sept. 11, 1943.

(3) Cooper's Group, Report CN-958, p. 1, Sept. 25, 1943.

(4) Cooper, Miller and Morris, Report CN-979, p. 8, Sept. 30, 1943.

(5) Dreher and Dean, Report CN-979, p. 16, Sept. 30, 1943.

(6) Miller, Report CN-979, p. 11, Sept. 30, 1943.

(7) James and Miller, Report CN-914, p. 10, Sept. 1, 1943.

(8) Miller, Report CN-979, p. 23, Sept. 30, 1943.

(9) Miller, Report CN-979, p. 29, Sept. 30, 1943.

(10) Johnson, Report CN-979, p. 15, Sept. 30, 1943.

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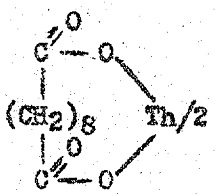
Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA1q-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state q. Sebacate	C[redacted] A Issued to:

Carrying of $48^{(r)}$ by Th^{+4} compound of sebacic acid(1)

Carrier	Other ions in solution	pH	% $48^{(r)}$ carried	% $39^{(r)}$ carried
Th^{+4}	La^{+3}	4.9	75	25

Sebacic acid precipitates Ce^{+4} and ZrO^{++} under these conditions. Sebacic acid does not precipitate Ce^{+3}, Y^{+3}, UO_2^{++} and Ba^{++} under these conditions.

Structure of compound:



References

(1) Thompson, Report CN-343, p. 10, November 15, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IA1r-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state r. Sulfate	Co[redacted]s A Issued to:

Carrying of $48^{(r)}$ by potassium lanthanum sulfate(1)

Potassium lanthanum sulfate, precipitated by saturated K_2SO_4 solution, no carrying ions present, no acid added, carried $48^{(r)}$ and $39^{(r)}$ as follows:

Element	$39^{(r)}$	$39^{(o)}$	$48^{(r)}$	$48^{(o)}$
% in ppt.	1	0	90	25*

* Reduced during experiment.

Effect of other substances on carrying of $48^{(r)}$ by potassium lanthanum sulfate(2)

Measured carrying power at various $UO_2(NO_3)_2$ concentrations and in the presence of various amounts of La^{+3}, C_2H_5OH and K_2SO_4. The important factor was the concentration of K_2SO_4, the other things did not effect carrying. The K_2SO_4 must be almost saturated.

Precipitation of $49^{(r)}$ by saturated K_2SO_4(3)

Saturated K_2SO_4 solution added to a Pu solution gave a white precipitate.

References

(1) Duffield, Report CN-282, p. 5, Sept. 16, 1942.

(2) Magel and Cefola, Report CN-405, p. 15, Dec. 16, 1942.

(3) Cefola, Cunningham and Werner, Report CN-282, p. 1, Sept. 16, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IA1r-2
I. Solution chemistry A. Precipitation reactions 1. Reduced state r. Sulfate	[redacted]ies A Issued to:

Solubility of Pu^{+4} sulfate

The solubility of Pu^{+4} in $SO_4^{=}$ solution has been found to fit the following equation over the pH range 5.4 to 2.12:

$$pH + \log\ (\text{solubility mg Pu/l.}) = 3.4$$

Since the solubility is a linear function of the H^+ concentration throughout this region, it appears that only one mole of H^+ per mole of Pu is required to dissolve the solid phase. This means the ion in solution has only one proton more or one hydroxide less than the solid phase, i.e., if the solid is $Pu(OH)_4$, $Pu(OH)_3^+$ predominates in solution over this pH range. It has been calculated that from pH 2.5 to 2.0, $Pu(OH)_2^{++}$ begins to represent an appreciable fraction of the Pu present.(1)

References

(1) Kraus, Report CN-1371, p. 12, March 1, 1944.

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[redacted]

Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IA1s-1

Co[redacted]s A

Issued to:

I. Solution chemistry
    A. Precipitation reactions
        1. Reduced state
            s. Sulfide

Carrying of 48$^{(r)}$ by uranyl sulfide and silver sulfide(1)

Carrying precipitate	Precipitating Agent	Other ions present	Acidity	% Pu in ppt.
Ag_2S	Sat'd. H_2S	None	0.25M H^+	1
UO_2S	$S^=$	"	0.5M KOH	81

References

(1) Duffield, Report CN-239, p. 7, July 15, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: November 27, 1943	EDITION I, SUPP. 1 SHEET IAlt-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state t. Arsenate	Copy [redacted] Issued to:

Carrying of Pu by $BiAsO_4$

From a solution 20% $UO_2(NO_3)_2 \cdot 6H_2O$, 0.2-0.3M HNO_3, 0.1-0.5M AsO_4^{-3}, 1.25-2.5 g. Bi^{+3}/1., 0.1N H_2SO_4, 96-100% of $48^{(r)}$ was carried by $BiAsO_4$.(1)

From a solution 20% $UO_2(NO_3)_2 \cdot 6H_2O$, 1M HNO_3, 0.1M H_3AsO_4, F.P.'s at "W" conc., 22 mg. Pu/1. 1.5 g. Bi^{+3}/1. (Bi/Pu = 69), 81-96% of $49^{(r)}$ was carried by $BiAsO_4$.(2)

Solubility of Pu arsenate

In a solution 20% $UO_2(NO_3)_2 \cdot 6H_2O$, 1M HNO_3, 0.1M H_3AsO_4, the solubility of Pu arsenate was found to be 480 mg. Pu/1. at 70°C.(2)

References

(1) James and Thompson, Report CN-914, p. 17, Sept. 1, 1943.

(2) Bradshaw, Docher, Johnson and Thompson, Report CN-1041, p. 33, Oct. 21, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: January 27, 1944	EDITION I, SUPP. 2 SHEET IAlu-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state u. Molybdate	Cop[redacted] Series A Issued to:

Carrying of $49^{(r)}$ by thorium molybdate(1)

From a solution of pH 1.30, containing 0.2 g. Th^{+4} per liter, $Th(MoO_4)_2$ carried 2.8% of $39^{(r)}$ and 99% of $49^{(r)}$.

Reference

(1) James and Thompson, Report CN-1153, p. 15, December 11, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IA1v-1
I. Solution chemistry A. Precipitation reactions 1. Reduced state v. Miscellaneous organic compounds	Copy [redacted] Series A Issued to:

Solubilities of some miscellaneous organic compounds of Pu^{+4} (1)

Ppting. agent	Appearance	Sol'y. in mother liquor
Benzoic acid	White amorphous	Very soluble
Fumaric acid	Olive-green amorphous	25 mg Pu/l. (pH = 4)
m-nitrobenzoic acid	White amorphous	4 mg Pu/l. (pH = 5) (reduced by aniline)
Salicylic acid	White	---
Pyrogallol	Dark red-brown crystalline	Very insoluble
8-hydroxyquinoline	Dark red crystalline	77 mg Pu/l. (pH = 4) 17 mg Pu/l. (pH = 8)
Picrolonic acid	Dirty pink crystalline	---
Cinnamic acid	Pale green crystalline	58 mg Pu/l. (pH = 4-5)
Acetyl-acetonate	Red-brown crystalline (2)	---

References

(1) Patton, Report CN-1371, p. 18, Mar. 1, 1944.

(2) Dixon, Smith and Hagemann, Report CN-1371, p. 19, March 1, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA2a-1
I. Solution chemistry A. Precipitation reactions 2. Oxidised state a. Acetate	Copy N[redacted]es, Series A Issued to:

Carrying of 48 and 39 by $NaMg(UO_2)_3Ac_9 \cdot 6H_2O$

Sufficient Na^+ added to a solution containing 48, 39, UO_2^{++}, and Ac^- to precipitate about 60% of UO_2^{++} present.(1)

Ion	% carried
$48^{(r)}$	4
$48^{(o)}$	60
$39^{(r)}$	2
$39^{(o)}$	64

Carrying of $48^{(o)}$ by $NaUO_2Ac_3$

99% $48^{(o)}$ carried by $NaUO_2Ac_3$ from 5M Na^+ solution.(2)

Carrying of $48^{(o)}$ by small amounts of $NaUO_2Ac_3$:(3)

(U^{+6}) before ppt'n.	Na^+	$Ac^=$	HAc	U^{+6}	Pu
0.016M	5.0M	0.75M	0.62M	3	2
0.038	2.9	0.20	0.20	4.5	5
0.008	5.0	0.75	0.61	6	4
0.008	"	0.20	0.20	7	5
0.019	2.9	"	"	9	8.7
0.0046	5.0	0.75	0.62	12	10
0.004	"	0.20	0.19	14	13

Carrying of $49^{(o)}$ by $NaUO_2Ac_3$ at various ratios of U/Pu

U/Pu	% $49^{(o)}$ carried
1000	96(4)"
100	95(4)
2×10^7	94, 97(5)
440	96(5)
210	92(5)
25	98(5)
10	99(5)
2.26	"
2 µg. Pu/µl.	96, 95, 95(5)

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I [redacted] SHEET IA2a-2
I. Solution chemistry A. Precipitation reactions 2. Oxidized state a. Acetate	Copy [redacted] copies, Series A Issued to:

Solubility of "sodium plutonyl acetate" as a function of Na^+ concentration

Na^+	Pu, g./l.	U, g./l.
0.8M	1.0	1.9
2.1	0.28	0.62
4.0	0.17	0.24
5.7	0.07	---

Report gives graph showing solubility as a function of Na^+ concentration.(6)

Crystal structure of $NaUO_2Ac_3$ and "sodium plutonyl acetate"

Formation of tetrahedral crystals characteristic of uranium. Plutonium does this too, and this is considered strong evidence for formula $NaPuO_2Ac_3$. Report has pictures of crystals of both U and Pu compounds.(7)

References

(1) Duffield, Report CN-261, p. 5, Aug. 15, 1942.

(2) Connick, Gofman, and Wahl, Report CN-363, p. 1, Nov. 16, 1942.

(3) Connick, Duffield, Garner, Gofman, Prestwood and Wahl, Report CN-419, p. 3, Jan. 15, 1943.

(4) Cunningham, Report CN-467, p. 6, Feb. 13, 1943.

(5) Sheline and Hamaker, Report CN-601, p. 3, April 15, 1943.

(6) Sheline and Hamaker, Report CN-654, p. 22, May 20, 1943.

(7) Sheline and Hamaker, Report CN-723, p. 5, June 20, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IA2a-3

I. Solution chemistry
  A. Precipitation reactions
    2. Oxidized state
      a. Acetate

Copy [redacted] ies, Series A

Issued to:

Solubility of sodium plutonyl acetate(1)

Solvent	Sol'y. mg Pu/l.
$3.3M\ Na^+$ $0.5M\ Ac$ $0.5M\ HAc$ (Oxidized by $NaBrO_3$)	71

Reference

(1) Mastick and Wahl, Report LAMS-72 p. 13, April 1, 1944.

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I [redacted] SHEET IA2b-1
I. Solution chemistry A. Precipitation reactions 2. Oxidized state b. Carbonate	Copy No. ___ of 50 copies, Series A Issued to:

Non-carrying of $48^{(o)}$ by $La_2(CO_3)_3$

$La_2(CO_3)_3$ carried only 3% of $48^{(o)}$ ($Ag^+ + S_2O_8^{=}$ used to prepare $48^{(o)}$).(1)

References

(1) Brown, Hill and Jaffey, Report CN-405, p. 10, Dec. 16, 1942.

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA2c-1
I. Solution chemistry A. Precipitation reactions 2. Oxidized state c. Fluoride	Copy No. [redacted]ies, Series A Issued to:

Non-carrying of $48^{(o)}$ by zirconium fluoride and lanthanum fluozirconate

Zirconium fluoride carried 1.5% of $48^{(o)}$. Lanthanum fluozirconate carried < 1% of $48^{(o)}$.(1)

References

(1) Clifford, Report CN-728, p. 7, June 21, 1943.

[redacted]

S[redacted]

Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IA2d-1

I. Solution chemistry
  A. Precipitation reactions
    2. Oxidized state
      d. Hydroxide

C[redacted]opies, Series A

Issued to:

Precipitation of $49^{(o)}$ by NaOH

1 µg. of Pu oxidized by $K_2Cr_2O_7$, solution made alkaline with NaOH. A nearly colorless solid precipitated. Concentration of Pu in supernatant solution = 53 mg. Pu/l. Precipitate dissolved in acid and a fluoride analysis run. Only 30% of Pu precipitated still in oxidized state. Indicates $49^{(o)}$ may not be stable in alkaline solution.(1)

References

(1) Cunningham and Werner, Report CN-556, p. 1, Mar. 31, 1943.

[redacted]

Compiled by: R. B. Duffield

Date: January 27, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 2   SHEET IA2d-2

I. Solution chemistry
    A. Precipitation reactions
        2. Oxidized state
            d. Hydroxide

C[redacted] Series A

Issued to:

Precipitation of $49^{(o)}$ by OH^- (1)

Addition of carbonate-free NH_4OH to a solution of $49^{(o)}$ gave a brown precipitate and a yellow solution. The solubility was ~ 0.5 g. Pu/l., $NH_4OH = \sim 0.8M$.

Reference

(1) Carniglia, Connick, Gofman, McVey, Sheline, Report CN-1170, p. 30, December 20, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA2e-1
I. Solution chemistry A. Precipitation reactions 2. Oxidized state e. Iodate	Copy [redacted], Series A Issued to:

<u>Non-carrying of $48^{(o)}$ by $Th(IO_3)_4$</u>

$Th(IO_3)_4$ carried < 1% of $48^{(o)}$ or $39^{(o)}$.(1)

References

(1) Duffield, Report CN-250, p. 3, Aug. 16, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA2f-1
I. Solution chemistry A. Precipitation reactions 2. Oxidized state f. Oxide	Co[redacted]ies, Series A Issued to:

Non-carrying of $48^{(o)}$ by $Cb_2O_5 \cdot xH_2O$

Solution 0.73M in UO_2^{++}, 0.26M in H^+, 2.2M in HAc, 0.04M in $Cr_2O_7^{=}$, heated to oxidize Pu. Suspension of $Cb_2O_5 \cdot xH_2O$ added and mixture heated. 0.8% of $48^{(o)}$ found in the $Cb_2O_5 \cdot xH_2O$.(1)

References

(1) Gofman, Report CN-723, p. 20, June 20, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HAND BOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IA2g-1
I. Solution chemistry A. Precipitation reactions 2. Oxidized state g. Oxychloride	Copy [redacted] copies, Series A Issued to:

Non-carrying of 48$^{(c)}$ and 39$^{(c)}$ by BiOCl$^{(1)}$

BiOCl carried no 48$^{(c)}$ from solution.

References

(1) Duffield, Report CN-282, p. 6, Sept. 16, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IA2h-1

I. Solution chemistry
  A. Precipitation reactions
    2. Oxidized state
      h. Phosphate

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Issued to:

Carrying of 48(o) by "$NH_4UO_2PO_4$"

From a solution 0.5M HNO_3, 10M $(NH_4)_2HPO_4$, 0.0042M UO_2^{+2}, 99% of 48(o) carried by "$NH_4UO_2PO_4$".(1)

Reference

(1) James and Thompson, Report CN-914, p. 19, Sept. 1, 1943.

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET: IA3a-1
I. Solution chemistry A. Precipitation reactions 3. +3 state a. fluoride	Co[redacted]pies, Series A Issued to:

Solubility of Pu^{+3} fluoride

Pu^{+3} fluoride pptd. from 1M HF sol'n. was purple-violet in color. Solubility in 1M HF 43 mg Pu/l.(1)

Solvent	Sol'y. mg Pu/l.
0.33N HNO_3 ~0.5M H_2SO_4 0.7N HF	50 (2)
1N HCl 1N HF	75-90 (2)
0.3N HCl 1N HF	5 (3)

References

(1) Smith and Patton, Report CN-1324, p. 3, February 1, 1944.

(2) Mastick and Wahl, Report LA-63, p. 8, February 22, 1944.

(3) Mastick and Wahl, Report LAMS-72 p. 13, April 1, 1944.

[redacted]

Compiled by: R. B. Duffield Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET: IA3b-1
I. Solution chemistry A. Precipitation reactions 3. +3 state b. Phosphate	Copy [redacted] copies, Series A Issued to:

Solubility of Pu^{+3} phosphate

Pu^{+3} in HCl sol'n. treated with H_3PO_4 to 1.2M. White gelatinous precipitate formed which had a solubility in 1.2M H_3PO_4 of 330 mg Pu/l.(1)

Reference

(1) Smith and Patton, Report CN-1324, p. 4, February 1, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IA3c-1
I. Solution chemistry A. Precipitation reactions 3. +3 state c. Oxalate	Copy [redacted] copies, Series A Issued to:

Solubility of Pu^{+3} oxalate

A violet crystalline precipitate was formed by addition of $H_2C_2O_4$ to a solution of Pu^{+3} in HCl. No solubility determined.(1) Solubility independently determined in sol'n. 1.1M HNO_3, 0.07M $H_2C_2O_4$, 0.17M NH_3OHCl = 210 mg Pu/l.(2)

References

(1) Smith and Patton, Report CN-1324, p. 4, Feb. 1, 1944.

(2) Connick, McVey and Sheline, Report CN-1360, p. 4, Feb. 10, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IA3d-1
I. Solution chemistry A. Precipitation reactions 3. +3 state d. Hydroxide	Copy [redacted] opies, Series A Issued to:

Solubility of Pu^{+3} hydroxide

Addition of NH_3 to an HCl solution of Pu^{+3} produced a pale blue precipitate. Solubility in ammoniacal sol'n. = 90 mg/l.(1)

References

(1) Smith and Patton, Report CN-1324, p. 4, Feb. 1, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET. IA3e-1

I. Solution chemistry
  A. Precipitation reactions
    3. +3 state
      e. Iodate

Copy [redacted] 50 copies, Series A

Issued to:

Solubility of Pu^{+3} iodate(1)

Medium	Sol'y. mg Pu/l.
1N HCl 0.25M $H_2C_2O_4$	25-90
H_2O	7

Reference

(1) Mastick and Wahl, Report LA-63, p. 6, Feb. 22, 1944.

[redacted]

Compiled by: R. B. Duffield Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IA3f-1
I. Solution chemistry A. Precipitation reactions 3. +3 state f. Sulfate	Copy [redacted] copies, Series A Issued to:

Solubility of Pu^{+3} sulfate

Addition of excess K_2SO_4 to a nitric acid solution Pu^{+3} produced a blue precipitate.

Medium	Sol'y. mg Pu/l.
0.24M $SO_4^{=}$ 0.44 HSO_4^{-} 1.4M K^{+}	120(1)
0.1M HSO_4	700(1)

Reference

(1) Connick, McVey and Sheline, Report CN-1360, p. 4, Feb. 10, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IA3g-1
I. Solution chemistry A. Precipitation reactions 3. +3 state g. Miscellaneous organic compounds	Copy [redacted]opies, Series A Issued to:

Solubilities of some miscellaneous organic compounds of Pu^{+3} (1)

Ppting agent	Appearance	Sol'y. in mother liquor
Benzoic acid	White amorphous	Very soluble
Picrolonic acid	Apple green crystalline	3-90 mg Pu/l.
Phenylarsonic acid	White crystalline	---

Reference

(1) Patton, Report CN-1371, p. 13, March 1, 1944.

[redacted]

[redacted]

Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1a-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu a. Oxidation by O_3	Copy [redacted] 50 copies, Series A Issued to:

Oxidation of 48 by O_3 in HNO_3

HNO_3	Temp.	Catalyst	48 oxidized	Other conditions
?	90° C.	Ag^+	97% in 60 min.(3,4)	Heated 30 min. at 70° before raising temperature

Oxidation of 48 by O_3 in H_2SO_4

H_2SO_4	Temp.	Catalyst	48 oxidized	Other conditions
1M	80-90° C.	1g. Ce^{+3}/1.	70% in 1 hr.(2)	O_3 was dry
"	"	"	"Quantitative" in 3 hrs.(2)	
0.5M	90°	Ce^{+3}	50% in 90 min.(1)	
"	80°	"	55% in 45 min.(1)	
"	"	Ag^+	0% in 30 min.(1)	
"	25°	---	0% in 20 min.(1)	
0.03M	22°	0.2g. Ce^{+3}/1.	99% in 30 min.(5)	
"	"	0.2g. Ag^+/1.	93% in 30 min.(5)	
"	80°	---	40-80% in 30 min.(5)	

[redacted]

[redacted]

Compiled by: A. C. Wahl

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IB1a-2

I. Solution chemistry
    B. Oxidation-reduction reactions
        1. Oxidation of Pu
            a. Oxidation by O_3

Copy [redacted] copies, Series A

Issued to:

References

(1) Perlman, Report CC-114, p. 2, June 6, 1942.

(2) Perlman, Report CC-136, p. 2, June 20, 1942.

(3) Seaborg's Group, Report CC-198, p. 6, July 18, 1942.

(4) English, Report CN-239, p. 21, Aug. 15, 1942.

(5) Hamaker, Report CN-239, p. 21, Aug. 15, 1942.

[redacted]

[redacted]

Compiled by: A. C. Wahl

Date: September 28, 1945

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB1b-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      b. Oxidation by $S_2O_8^=$, Ag^+

Copy [redacted] copies, Series A

Issued to:

Oxidation of Pu and Np by $S_2O_8^=$ and Ag^+ in HNO_3

HNO_3	Temp.	$S_2O_8^=$	Ag^+	Pu	Pu oxidized	Np oxidized	Other conditions
10M	22°C.	0.15M	0.02M	48	"Complete" in 1 hr.(10)		
1M	25°	>0.05M	>0.05M	48	"Complete" in 1 hr.(11)		5g. La^{+3}/1., 10g. Zr^{+4}/1.
1M	23°	0.09M	0.009M	48	98% in 1 min.(5,6)		

Oxidation of Pu and Np by $S_2O_8^=$ and Ag^+ in H_2SO_4

H_2SO_4	Temp.	$S_2O_8^=$	Ag^+	Pu	Pu oxidized	Np oxidized to Np(o-FS)*	Other conditions
1.5M	22°C.	0.45-2.2M	~0.025M	49	? in 20-30 min.(9)		Conditions used in Chicago to separate 220μg. 49 from >41μg. bombardment
1M	30°	0.1M	?	48	>95% in 15 min.(1,2)	>95% in 15 min.(1,2)	
"	"	0.02M	0.002M	0.15mg.49/1.	95% in 1 hr.(8)		HF ppt. more $K_2S_2O_8$ added and sol'n. allowed to stand 1-2 hrs at 22°C. 2.5g.Ce^{+3}/1. 2.5g.La^{+3}/1.
"	80°	"	"	1.5mg. 49/1.	98% in 1 hr.(8)		HF ppt.
"	80°	"	"	10mg. 49/1.	80% in 1 hr.(8)		KF ppt.
"	23°	0.09M	0.009M	48	98% in 1 min.(5,6)		
"	20°	0.1M	?	"	15-95% in 10min.(1,2)	>95% in 10 min.(1,2)	
0.5M	80°	0.02M	0.002M	48	>95% in 30 min.(4,7)		0.2g.Ce^{+3}/1.

[redacted]

Date: September 28, 1943

EDITION I

SHEET: IB1b-2

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      b. Oxidation by $S_2O_8^{=}$, Ag^{+}

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Issued to:

Oxidation of Pu and Np by $S_2O_8^{=}$ and Ag^{+} in H_2SO_4 (cont.)

H_2SO_4	Temp.	$S_2O_8^{=}$	Ag^{+}	Pu	Pu oxidized	Np oxidized to $Np^{(o-FS)}$*	Other conditions
0.3M	70°C.	0.03M	0.003M	70mg.49/1.	85% in 10 min.$^{(8)}$		3mg.La^{+3}/1.
0.055M	72°	0.09M	0.009M	48	60% in 0.5 min.$^{(3,6)}$		
"	"	"	"	"	85% in 15 min.$^{(3,6)}$		
"	22°	"	"	"	95% in 0.5 min.$^{(3,6)}$		
"	"	"	"	"	" in 50 min.$^{(3,6)}$		
"	0°	"	"	"	80% in 0.5 min.$^{(3,6)}$		
"	"	"	"	"	90% in 20 min.$^{(3,6)}$		
?	22°	0.05M	0.005M	200mg.49/1.	99% in 1 hr.$^{(12)}$		2.5g.La^{+3}/1., 5g. Zr^{+4}/1.

*$Np^{(o-FS)}$ indicates the oxidation state of Np in which the Np is not carried by LaF_3.

References

(1) Wahl, Ph.D. Thesis, Univ. of Calif., Berkeley, California, p. 29, Feb. 1942

(2) Seaborg and Wahl, Report A-135, p. 10, March 19, 1942.

(3) Hamaker, Report CC-198, p. 1, July 18, 1942.

(4) Wahl, Report CC-198, p. 3, July 18, 1942.

(5) Hamaker, Report CC-199, p. 3, July 25, 1942.

(6) Hamaker, Report CN-239, p. 25, Aug. 15, 1942.

[redacted]

[redacted]

Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1b-3
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu b. Oxidation by $S_2O_8^=$, Ag^+	Copy [redacted]opies, Series A Issued to:

References (cont.)

(7) Wahl, Report CN-239, p. 30, Aug. 15, 1942.

(8) Wahl, Report CN-336, Oct. 28, 1942.

(9) Cunningham and Werner, Report CN-419, p. 21, Jan. 15, 1943.

(10) Thompson, Report CN-503, p. 8, Feb. 28, 1943.

(11) Kohman, Report CN-601, p. 24, April 15, 1943.

(12) Cefola, Report CN-728, p. 46, June 21, 1943.

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Compiled by: A. C. Wahl

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IB1b-34

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      b. Oxidation by $S_2O_8^{=}$, Ag^+

Copy [redacted] ies, Series A

Issued to:

Oxidation of 48 by $S_2O_8^{=}$ and Ag^+ in H_2SO_4

H_2SO_4	Temp.	$S_2O_8^{=}$	Ag^+	48 oxidized	Other Conditions
1-0.5M	22°C.	0.04-0.1M	0.01M	>99% in 15-60 min.(1)	$K_2S_2O_8$ used, 1.0M Na_2SO_4, 10% $UO_2(NO_3)_2 \cdot 6H_2O$
0.5M	"	0.02-0.1M	"	>99% in 30 min.(1)	" "
"	"	0.1M	"	0% in 30 min.(1)	$(NH_4)_2S_2O_8$ used, 1.0M Na_2SO_4
0.0-0.5M	"	"	"	<10% in 30 min.(1)	$(NH_4)_2S_2O_8$ used, 0.1M Na_2SO_4, 10% $UO_2(NO_3)_2 \cdot 6H_2O$

Reference

(1) Beaton, Fields, LaChapelle, Lincoln, Sheft and Turk, Report CN-991, p. 18, Oct. 9, 1943.

[redacted]

Compiled by: A. C. Wahl

Date: September 28, 1943

HAND BOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IB1c-1

Copy [redacted] Series A

Issued to:

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      c. Oxidation by Ag^{+2}

Oxidation of 48 by Ag^{+2} in HNO_3

HNO_3	Temp.	Ag^{+2}	Ag^{+}	48 oxidized	Other conditions
11M	23°C.	0.1M	0.2M	98% in 1 min.(1,2)	
1M	"	0.01M	0.02M	"	
"	"	"	"	98% in 20 min.(1,2)	
"	"	"	---	98% in 13 min.(1,2)	

References

(1) Hamaker, Report CC-199, p. 3, July 25, 1942.

(2) Hamaker, Report CN-239, P. 26, Aug. 15, 1942.

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date : September 28, 1943	EDITION I SHEET IB1d-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu d. Oxidation by H_2O_2	Co[redacted], Series A Issued to:

Oxidation of 48 by H_2O_2 in $HClO_4$ or H_2SO_4

$HClO_4$ or H_2SO_4	Temp.	H_2O_2	48 oxidized
1M	95°C.	0.2M	Initial Half-time ≅ ~15 min.(1) (% oxidized levels off at ~80%)

Reference

(1) Hamaker, Report CN-261, p. 8, Sept. 15, 1942.

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1e-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu e. Oxidation by HO_2^-	Cop[redacted]s, Series A Issued to:

Oxidation of 48 and 39 by HO_2^- in NaOH

NaOH	Temp.	HO_2^-	48 oxidized	39 oxidized to $Np^{(o-FS)}$*	Other Conditions
0.8M	95°C.	0.2M	38% in 2 Hrs.(1)	68% in 2 hrs.(1)	Incorporation of 48,39 in very small $La(OH)_3$ ppt. may have slowed the rate.
"	22°C.	"	6% in 1 hr.(1)	6% in 1 hr.(1)	
0.001M	"	"	5% in 91 hrs.(1)	---	
"	0°C.	"	8% in 18 hrs.(1)	---	

*$Np^{(o-FS)}$ indicates the oxidation states of Np in which the Np is not carried by LaF_3.

Oxidation of 48 by HO_2^- in Na_2CO_3

Na_2CO_3	Temp.	HO_2^-	48 oxidized	Other conditions
0.33M	22°C.	0.1M	None in 9 hrs.	Pt. vessel

References

(1) Garner, Report CN-282, p. 3, Sept. 30, 1942.

(2) Gofman, Report CN-328, p. 7, Oct. 31, 1942.

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1f-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu f. Oxidation by H_5IO_6	Copy N[redacted] copies, Series A Issued to:

Oxidation of 48 by H_5IO_6 in HNO_3

HNO_3	Temp.	H_5IO_6	48 oxidized
10M	95°C.	0.022M	"Incomplete" in 1 hrs.(3)

Oxidation of 48 and 39 by H_5IO_6 in H_2SO_4

H_2SO_4	Temp.	H_5IO_6	48 oxidized	39 oxidized to $Np^{(o-FS)*}$
1M	80°C.	0.1M	>95% in 1 hr.(1,2)	>95% in 1 hr.(1,2)

$*Np^{(o-Fs)}$ indicates the oxidation states of Np in which the Np is not carried by LaF_3.

References

(1) Wahl, Ph.D. Thesis, Univ. of Calif., Berkeley, California, p. 29, Feb. 1942.

(2) Seaborg and Wahl, Report A-135, p. 10, March 19, 1942.

(3) Thompson, Report CN-503, p. 8, Feb. 28, 1942.

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Compiled by: A. C. Wahl

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IBlg-1

I. Solution chemistry
B. Oxidation-reduction reactions
1. Oxidation of Pu
g. Oxidation by MnO_4^-

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Issued to:

Oxidation of 48 by MnO_4^- in HNO_3

HNO_3	Temp.	MnO_4^-	48 oxidized	Other Conditions
10M	95°C	0.02M	"Incomplete" in 1 hr.(3)	

Oxidation of 48 and 39 by MnO_4^- in H_2SO_4

H_2SO_4	Temp.	MnO_4^-	48 oxidized	39 oxidized to $Np^{(o-FS)}$*
1M	80°C	0.1M	> 95% in 30 min.(1,2)	>95% in 30 min.(1,2)
1M	20°	"	< 15% in 10 min.(1,2)	>95% in 10 min.(1,2)

*$Np^{(o-FS)}$ indicates the oxidation states of Np in which the Np is not carried by LaF_3.

References

(1) Wahl, Ph.D. Thesis, Univ. of Calif., Berkeley, Calif., p. 29, Feb. 1942.

(2) Seaborg and Wahl, Report A-135, p. 10, March 19, 1942.

(3) Thompson, Report CN-503, p. 8, Feb. 28, 1942.

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1h-1
I. Solution Chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu h. Oxidation by Ce^{+4}	Copy [redacted] 20 copies, Series A Issued to:

Oxidation of 48 by Ce^{+4} in HNO_3

HNO_3	Temp.	Ce^{+4}	48 oxidized	Other Conditions
10M	95°C	0.5M	"Complete" in 1 hr.(3)	1M $HClO_4$
"	"	0.2M	98% in 1 hr.(4)	$BiPO_4$ dissolved in HNO_3, 25 g. Bi^{+3}/1
"	"	0.02M	84% in 20 min.(4)	
"	"	"	96% in 2 hrs.(4)	
"	"	"	99% in 12 hrs.(4)	
"	75°	"	25% in 3 hrs.(4)	
2-7M	"	0.005- 0.04M	98% in 15-180 min.(6)	Bi^{+3}, stainless steel present
4M	95°	0.002M	93% in 30 min.(5)	no $Cr_2O_7^=$ 5g. Bi^{+3}/1 H_3PO_4
2M	70-60°	"	77% in 30 min.(5)	no $Cr_2O_7^=$
"	"	"	96% in 30 min.(5)	0.01M $Cr_2O_7^=$
"	73°	"	97% in 30 min.(5)	0.02M $Cr_2O_7^=$
"	70-72°	"	86% in 15 min.(5)	0.02M $Cr_2O_7^=$, 5g. Bi^{+3}/1., H_3PO_4 "$Ce(HPO_4)_2$", "$(BiO)_2Cr_2O_7$" ppt. during oxidation.
"	"	"	90% in 45 min.(5)	
"	"	"	96% in 1 hr.(5)	
"	"	"	99% in 2 hrs.(5)	

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IB1h-2

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      h. Oxidation by Ce^{+4}

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Issued to:

Oxidation of 48 and 39 by Ce^{+4} in H_2SO_4

H_2SO_4	Temp.	Ce^{+4}	48 oxidized	39 oxidized to $Np^{(o-FS)}$*
1M	80°C	0.1M	15-95% in 30 min.(1,2)	95% in 30 min.(1,2)

* $Np^{(o-FS)}$ indicates the oxidation states of Np in which the Np is not carried by LaF_3.

References

(1) Wahl, Ph.D. Thesis, Univ. of Calif., Berkeley, Calif., p. 29, Feb., 1942.

(2) Seaborg and Wahl, Report A-135, p. 10, March 19, 1942.

(3) Thompson, Report CN-503, p. 8, Feb. 28, 1943.

(4) Thompson, Davidson, Miller, James, Report CN-556, p. 16, March 31, 1943.

(5) Miller, Report CN-633, p. 12, April 30, 1943.

(6) Dixon, James, Cooper, Shepard, Thompson, Report CN-778, p. 4, July 1, 1943.

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Compiled by: A. C. Wahl

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IB1h-3

I. Solution chemistry
B. Oxidation-reduction reactions
1. Oxidation of Pu
h. Oxidation by Ce^{+4}

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Issued to:

Oxidation of 48 by Ce^{+4} in HNO_3

HNO_3	Temp.	Ce^{+4}	48 oxidized	Other Conditions
5M	75°C.	0.02M	92% in ? time(2)	
4M	"	0.04M	97% in 3 hrs.(1)	
"	"	"	98% in 2 hrs.(1)	0.02M $Cr_2O_7^=$
2M	"	0.002M	85-90% in 2 hrs.(1)	0.02M $Cr_2O_7^=$
0.4M	"	0.002-0.01M	98% in 1 hr.(3)	40% $UO_2(NO_3)_2 \cdot 6H_2O$

References

(1) Smith's Group, Report CN-756, p. 7, June 28, 1943.

(2) Stahl, Baldwin, Faris, Olson, Stassel and Kamach, Report CN-901, p. 44, Aug. 28, 1943.

(3) Dreher, Report CN-979, p. 14, Sept. 30, 1943.

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Compiled by: A. C. Wahl

Date: January 27, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 2 SHEET IB1h-4

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      h. Oxidation by Ce^{+4}

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Issued to:

Oxidation of 48 by Ce^{+4} in HNO_3 and H_2SO_4

HNO_3	H_2SO_4	Temp.	Ce^{+4}	48 oxidized	Other conditions
3M	---	75°C.	0.7-0.9M	90-98% in 1-2 hrs.(1)	
"	0.35M	"	0.14M	94% in 1 hr.(2)	2.0 mg. Ce^{+4}/mg. Ce^{+3} (as CeF_3)
2M	0.05M	"	0.02M	93% in 1 hr.(2)	1.1 " " " (" ")
"	"	"	"	61% in 0.5 hrs.(2)	" " " " (" ")
"	"	22°	"	27% in 1 hr.(2)	" " " " (" ")
1-3M	"	75°	"	98% in 0.5-1.5 hrs.(2)	1.5 " " " (" ")
1M	0.5M	"	0.2M	86% in 1 hr.(2)	" " " " (" ")
"	0.25M	22°	0.1M	96% in 1-2 hrs.(2)	2.0 " " " (" ")
"	0.05M	75°	0.02M	98% in 0.5-1.5 hrs.(2)	" " " " (" ")
"	"	"	"	98% in 1 hr.(2)	2.5 " " " (" ")
"	"	"	"	98% in 1.5 hrs.(2)	2-2.6 mg. " La^{+3} (" LaF_3)
"	"	22°	"	31% in 1 hr.(2)	1.5 mg. " Ce^{+3} (as CeF_3)
"	"	"	"	98 % in 2 hrs.(2)	2.0 " " " (" ")
"	---	"	0.12-.6M	70-95% in 2 hrs.(1)	2.5 " " La^{+3} (as LaF_3)
0.9M	0.05M	"	0.02M	98% in 0.5-3 hrs.(2)	5 mg. Zr/ml. 0.001M $Cr_2O_7^=$ 2.5 mg. Ce/ml.
0.6M	"	22°	0.02M	97% in 2 hrs.(2)	2.5 mg. Ce^{+4}/mg. Ce^{+3} (as CeF_3)

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Compiled by: A. C. Wahl Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET IB1h-5
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu h. Oxidation by Ce^{+4}	Copy [redacted] opies, Series A Issued to:

References

(1) Werner, Fries, Dam and Covey, Report CN-1025, p. 7, November 8, 1943.

(2) Bradshaw, Dean, Gaarder, Johnson, Kroner, Koshland and Thompson, Report CN-1095, p. 4,6, December 1, 1943.

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Compiled by: A. C. Wahl Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IB1h-6
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu h. Oxidation by Ce^{+4}	Copy [redacted] copies, Series A

Oxidation of Pu^{+3} by Ce^{+4}

Ce^{+4} added to Pu^{+3} --- 24% Pu^{+3} oxidized to Pu^{+4}, 1.8% Pu^{+3} oxidized to Pu^{+6} (measured with spectrophotometer).(1)

Reference

(1) Hindman, Kraus and Howland, Report CK-1371, p. 1, March 1, 1944.

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943.	EDITION I SHEET IB1i-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu i. Oxidation by "$NaBiO_3$"	Cop[redacted] Copies, Series A Issued to:

Oxidation of 48 by "$NaBiO_3$" in HNO_3

HNO_3	Temp.	"$NaBiO_3$"	48 oxidised	Other Conditions
10M	22°C.	8g./l.	"Incomplete" in 1 hr.(2)	
6M	50°	0.005M	80% in 15 min.(3)	18-8 stainless steel present.
5M	"	"	" " " " "	
4M	"	"	" " " " "	
"	75°	"	95% in 15 min.(3)	
"	50°	"	85% in 125 min.(3)	
"	"	"	95% in 50 min.(3)	
"	"	"	90% in 25 min.(3)	
"	"	"	35% in 5 min.(3)	
"	"	0.01M	85% in 15 min.(3)	
"	"	0.008M	90% in 15 min.(3)	
"	"	0.003M	60% in 15 min.(3)	
"	"	0.001M	40% in 15 min.(3)	
"	40°	0.005M	90% in 15 min.(3)	
"	30°	"	40% in 15 min.(3)	
5M	50°	"	70% in 15 min.(3)	
2M	"	"	40% in 15 min.(3)	

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB1i-2

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      i. Oxidation by "$NaBiO_3$"

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Issued to:

Oxidation of 48 and 39 by "$NaBiO_3$" in $HClO_4$

$HClO_4$	Temp.	"$NaBiO_3$" added	48 oxidized	39 oxidized to Np(o-FS)*
0.2M	95°C.	1g./1.	87% in 15 min.(1)	88% in 15 min.(1)
"	"	"	97% in 1 hr.(1)	95% in 1 hr.(1)
"	22°	"	37% in 18 hrs.(1)	23% in 18 hrs.(1)

* Np(o-FS) indicates the oxidation states of Np in which the Np is not carried by LaF_3.

References

(1) Garner, Report CN-282, p. 4, September 30, 1942.

(2) Thompson, Report CN-503, p. 8, February 28, 1943.

(3) Dixon, James, Cooper, Shepard and Thompson, Report CN-778, p. 2, July 1, 1943.

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: November 27, 1943	EDITION I, SUPP. 1 SHEET IB1i-3
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu i. Oxidation by "$NaBiO_3$"	Copy N[redacted]copies, Series A Issued to:

Oxidation of 48 by "$NaBiO_3$" in HNO_3

HNO_3	Temp.	"$NaBiO_3$"	48 oxidized	Other Conditions
5M	50°C.	0.01M	80-95% in 1 hr.(4)	(Semi-works run)
"	"	"	>95% in 1-21 hrs.(8)	
"	"	"	80-90% in 1-21 hrs.(8)	F.P. carriers present
"	"	"	>90% in 1 hr.(5)	1st decont. cycle } 2/3 $NaBiO_3$ added at start, 1/3 after 45 min.
"	"	"	~99% in 1 hr.(5)	2nd " "
"	"	"	98% in 1 hr.(6)	Sol'n. made 0.001M in $Cr_2O_7^=$ before $BiPO_4$ and LaF_3 ppt.
"	"	"	90% in 1 hr.(6)	Sol'n. made 0.002M in "$NaBiO_3$" before $BiPO_4$ and LaF_3 ppt.
4M	"	"	98% in 1 hr.(1)	
"	"	0.005M	88% in 0.5 hrs.(1)	
"	"	0.005-0.015M	>98% in 15 min.(2)	18-8 stainless steel
0.4-2M	"	0.01-0.02M	<15% in 1 hr.(7)	40% $UO_2(NO_3)_2 \cdot 6H_2O$

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Compiled by: A. C. Wahl

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IB1i-4

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      i. Oxidation by "$NaBiO_3$"

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Issued to:

Oxidation of 48 by "$NaBiO_3$" in H_2SO_4

H_2SO_4	Temp.	"$NaBiO_3$"	48 oxidized	Other Conditions
0.2M	75°C.	0.015M	>90% in 30 min.(3) (probably ~ 98%)	0.01M $Cr_2O_7^{=}$ 0.3M HSO_4^- 1.0M $SO_4^{=}$ 2.5M Na^+

References

(1) Smith's Group, Report CN-756, p. 7, June 28, 1943.

(2) Ritter, Black and Schneller, Report CN-758, p. 5, June 26, 1943.

(3) Swartout and Ketelle, Report CN-903, p. 12, Aug. 28, 1943.

(4) Smith's Group, Report CN-906, p. 12, Aug. 28, 1943.

(5) Balthis, Olson, Peterson and Stahl, Report CN-958, p. 7 and 14, Sept. 25, 1943.

(6) Ritter and Black, Report CN-958, p. 27, Sept. 25, 1943.

(7) Dreher, Report CN-979, p. 14, Sept. 30, 1943.

(8) Peterson, Balthis and Olson, Report CN-1023, p. 30, Oct. 30, 1943.

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IB1i-5
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu i. Oxidation by "$NaBiO_3$"	Cop[redacted]opies, Series A Issued to:

Oxidation of $Pu^{(r)}$ by "$NaBiO_3$" in HNO_3

HNO_3	Temp.	"$NaBiO_3$"	Oxidation	Other conditions
>5M	35-50°C.	0.01M	Complete in 1 hr.(2)	
"	25°	"	" " 2 hrs.(2)	
3M	>50°	"	" " 1 hr.(2)	
"	25°	"	" " 2 hrs.(2)	
1M	27°	saturated	" "<1 hr.(1)	0.02-0.04M Ce^{+4} or 0.02M Zr^{+4} (trace Ce^{+4}) 0.008 M LaF_3

References

(1) Turk, Report CN-1115, p. i and 13, December 13, 1943.

(2) Ritter, Black and Johnson, Report CN-1276, p. 1, March 6, 1944.

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Compiled by: A. C. Wahl

Date: September 28, 1943.

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET I31j-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      j. Oxidation by BrO_3^-

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Issued to:

Oxidation of 48 and 39 by BrO_3^- in HNO_3

HNO_3	Temp.	BrO_3^-	48 oxidized	39 oxidized to $Np^{(o-FS)}$*	39 oxidized to $Np^{(o-Ac)}$‡	Other Conditions
1.2M	95°C	0.2M	65% in 30 min.(3)			
1.2M	"	"	94% in 60 min.(3)			
0.2M	"	"	80% in 30 min.(3)			
"	"	"	93% in 60 min.(3)			
"	23°	----	----------------	~100% in 15 min. to 5 hrs.(7)	~50% in 15 min. to 5 hrs.(7)	0.1M $Cr_2O_7^=$
0.1M	95°	0.1M	----------------	~50% in 2 hrs.(7)	~50% in 2 hrs.(7)	
0.2M	25°	0.001M - 0.1M	----------------		>95% in 7-25 min.(7)	0.1M $Cr_2O_7^=$ present 15 min. before BrO_3^- added

* $Np^{(o-FS)}$ indicates the oxidation states of Np in which the Np is not carried by LaF_3.

‡ $Np^{(o-Ac)}$ indicates the oxidation state of Np in which the Np is carried by $NaUO_2Ac_3$.

Oxidation of 48 and 39 by BrO_3^- in H_2SO_4.

H_2SO_4	Temp.	BrO_3^-	48 oxidized	39 oxidized to $Np^{(o-FS)}$*	39 oxidized to $Np^{(o-Ac)}$‡	Other Conditions
3M	25°C	0.3M	<1% in 3 min. to 74 hrs.(6)	70-98% in 3 min. to 74 hrs.(6)		
"	22°	"	5% in 0.5-1.0 hr.(5)	95% in 0.5-1.0 hr.(5)		

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1j-2
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu j. Oxidation by BrO_3^-	Copy [redacted] opies, Series A Issued to:

Oxidation of 43 and 39 by BrO_3^- in H_2SO_4 (cont.)

H_2SO_4	Temp.	BrO_3^-	43 oxidized	39 oxidized to Np(o-FS)*	39 oxidized to Np(o-Ac)*	Other Conditions
2M	25°C.	0.3M	<2% in 3-30 min.$^{(6)}$	80-94% in 3-30 min.$^{(6)}$		
"	"	"	<3% in 6-76 hrs.$^{(6)}$	93-97% in 6-76 hrs.$^{(6)}$		
1M	30°	0.1M	<15% in 20 min.$^{(1,2)}$	>95% in 20 min.$^{(1,2)}$		
"	20°	"	<15% in 10 min.$^{(1,2)}$	>95% in 10 min.$^{(1,2)}$		
"	25°	0.3M	<1% in 3 min. to 43 hrs.$^{(6)}$	80-90% in 3 min. - 43 hrs.$^{(6)}$		
"	22°	"	6% in 0.5 hrs.$^{(5)}$	87% in 0.5 hrs.$^{(5)}$		
"	"	"	11% in 1 hr.$^{(5)}$	82% in 1 hr.$^{(5)}$		
"	"	0.1M	<0.5% in 30 min.$^{(4)}$	>85% in 30 min.$^{(4)}$		Np-Pu separation used in purifying 200µg. 49 in Berkeley. (4g. La^{+3}/l.)
0.5M	25°	0.3M	<3% in 4 min.-42 hrs.$^{(6)}$	80-90% in 4 min. to 42 hrs.$^{(6)}$		
"	22°	"	10% in 0.5 hrs.$^{(5)}$	65% in 0.5 hrs.$^{(5)}$		
0.25M	95°	"	65% in 1 hr.$^{(5)}$	93% in 1 hr.$^{(5)}$		
"	"	"	36% in 2 hrs.$^{(5)}$	94% in 2 hrs.$^{(5)}$		
"	"	"	96% in 4 hrs.$^{(5)}$	96% in 4 hrs.$^{(5)}$		
"	"	"	96% in 2 hrs.$^{(5)}$	97% in 2 hrs.$^{(5)}$		UO_2^{++} present
"	"	"	97% in 2 hrs.$^{(5)}$		97% in 2 hrs.$^{(5)}$	
"	"	"	80% in 4 hrs.$^{(5)}$		100% in 4 hrs.$^{(5)}$	

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB1j-3
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu j. Oxidation by BrO_3^-	Copy [redacted] copies, Series A Issued to:

Oxidation of 48 and 39 by BrO_3^- in H_2SO_4 (cont.)

H_2SO_4	Temp.	BrO_3^-	48 oxidized	39 oxidized to $Np^{(o-FS)}$*	39 oxidized to $Np^{(o-Ac)}$*	Other Conditions
0.25M	95°C.	0.3M	92% in 5.5 hrs.(5)		94% in 5.5 hrs.(5)	
0.1M	22°	"	15% in 0.5 hrs.(5)	50% in 0.5 hrs.(5)		
0.05M	95°	"	97% in 1-4 hrs.(5)	93% in 1-4 hrs.(5)		
"	"	"	96% in 1 hr.(5)		90% in 1 hr.(5)	
"	"	"	93% in 2 hrs.(5)		91% in 2 hrs.(5)	

* $Np^{(o-FS)}$ indicates the oxidation states of Np in which the Np is not carried by LaF_3.

* $Np^{(o-Ac)}$ indicates the oxidation states of Np in which the Np is carried by $NaUO_2Ac_3$.

References

(1) Wahl, Ph.D. Thesis, Univ. of Calif., Berkeley, Calif., p. 29, Feb. 1942.

(2) Seaborg and Wahl, Report A-135, p. 10, March 19, 1942.

(3) Gofman, Report CN-250, p. 10, August 31, 1942.

(4) Wahl, Report CN-336, p. 10, October 28, 1942.

(5) Beaufait, Report CN-601, p. 10, April 15, 1943.

(6) Beaufait, Report CN-654, p. 2, May 20, 1943.

(7) King, Report CN-867, p. 14, August 14, 1943.

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IB1j-4
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu j. Oxidation by BrO_3^-	Copy [redacted] copies, Series A Issued to:

Oxidation of Pu^{+4} to Pu^{+6} by BrO_3^- in HNO_3

HNO_3	Temp.	BrO_3^- after oxid.	PuO_2^{++} after oxid.	Oxidation	
2.0M	85°C.	0.1M	0.2M	>99.5% in 4 hrs.(1)	cones sealed
1.0M	"	"	"	>99.5% in 4 hrs.(1)	
0.6M	"	"	"	99.0% in 4 hrs.(1)	

References

(1) Mastick and Wahl, Report LAMS-72, April 1, 1944.

[redacted]

[redacted]

Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1k-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^=$	Copy No [redacted] 50 copies, Series A Issued to:

Oxidation of 49 and 39 by $Cr_2O_7^=$ in HNO_3

HNO_3	Temp.	$Cr_2O_7^=$	49 oxidized	39 oxidized to Np(o-FS)*	Other Conditions
10M	95°C.	0.1M	"Incomplete" in 1 hr.(21)		
"	"	"	97% in 2.25 hrs.(27)		
8M	"	"	55% in 1 hr.(25)		
7M	"	"	75% in 1 hr.(25)		
6.4M	22°	0.02M	13% in 44 hrs.(11)		
"	"	"	79% in 140 hrs.(11)		
6.2M	95°	"	16% in 5 min.(10)		
6M	99°	?	98% in 1 hr.(21)		
"	95°	0.1M	99.7% in 2 hrs.(24)		Bi^{+3}, H_3PO_4, used in $BiPO_4$ procedure
"	"	"	98% in 2 hrs.(25)		
"	80°	?	40% in 1 hr.(21)		
"	25°	0.1M	~5% in 24 hrs.(31)	>98% in 4 min.(31)	
5.4M	22°	0.02M	13% in 40 hrs.(11)		
"	"	"	66% in 88 hrs.(11)		
5M	95°	0.1M	99% in 1 hr.(25)		
4M	"	"	98% in 45 min.(25)		
"	80°	?	90% in 1 hr.(21)		
"	25°	0.1M	~5% in 24 hrs.(31)	>98% in 3 min.(31)	
3.1M	95°	0.02M	78% in 5 min.(10)		

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1k-2
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^=$	Copy No[redacted] copies, Series A Issued to:

Oxidation of 48 and 39 by $Cr_2O_7^=$ in HNO_3 (cont.)

HNO_3	Temp	$Cr_2O_7^=$	48 oxidized	39 oxidized to Np(o-FS)*	Other Conditions
3.1M	95°C	0.02M	93% in 20 min.(10)		
3M	"	0.05M	>95% in 30 min.(28)		2.5g. La^{+3}/l. 5g. Zr^{+4}/l.
"	80°	?	"Complete" in 1 hr.(21)		
"	75°	0.05M	80% in 1 hr.(32)		
"	"	"	82% in 1 hr.(32)		0.002M Co^{++} 5g. Zr^{+4}/l. 2.5g. La^{+3}/l
"	"	"	93% in 1 hr.(32)		0.01M Co^{++}
"	"	"	96% in 1 hr.(32)		0.04M Co^{++}
"	"	0.008M	94% in 80 min.(32)		0.01M Co^{++} 5g. Zr^{+4}/l. 2.5g. La^{+3}/l
"	"	0.017 -0.006M	76% in 120 min.(32)		--------
"	"	0.017-0.008M	96% in 120 min.(32)		0.01M Co^{++}
"	"	0.017-0.008M	98% in 120 min.(32)		0.02M Co^{++}
2M	80°	?	Half-time = 24 min.(29) ("Complete" in ~3 hrs)		42% $UO_2(NO_3)_2 \cdot 6H_2O$
"	25°	0.1M	Half-time = ~45 hrs.(31)	>95% in 3 min.(31)	
1.3M	80°	?	Half-time = 12 min.(29) "Complete" in ~1 hr.)		31% $UO_2(NO_3)_2 \cdot 6H_2O$
1M	75°	0.1M	"Complete" in 1 hr.(22)		0.1M H_3PO_4
"	"	0.017M	"Complete" in 30 min.(33)		5g. Zr^{+4}/l

[redacted]

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB1k-3
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^{=}$	Copy [redacted] 50 copies, Series A Issued to:

Oxidation of 48 and 39 by $Cr_2O_7^{=}$ in HNO_3 (cont.)

HNO_3	Temp	$Cr_2O_7^{=}$	48 oxidized	39 oxidized to Np(o-FS)*	Other Conditions
1M	75°C	0.1M	98% in 10 min.(17)		0.56M UO_2^{++}
"	"	0.05M	98% in 15 min.(17)		"
"	65°	0.1M	80% in 10 min.(17)		"
"	"	"	97% in 30 min.(17)		"
"	"	"	98% in 5 min.(17)		
"	25°	"	Half-time = 5 hrs.(31)	>95% in 4 min(31)	
1-1.5M	65°-80°	"	"Complete" in 1 hr(20)		$ZrO^{++}/HF = \frac{1}{2}$ } 0.1-0.3M ZrO^{++}
"	"	"	70% in 1 hr.(20)		$ZrO^{++}/HF = 1/3$ } 0.1-0.3M ZrO^{++}
0.5M	80°	0.017M	97% in 30 min.(13)		10% $UO_2(NO_3)_2\cdot 6H_2O$
"	65°	"	96% in 15 min.(13)		" " " "
"	"	0.02M	>95% in 30 min.(16)		" " " "
"	"	0.1M	98% in 5 min.(17)		
"	65°-70°	0.02M	40-50% in 30 min.(20)		2N HF 10% $UO_2(NO_3)_2\cdot 6H_2O$
"	50°	0.017M	85% in 30 min.(13)		10% $UO_2(NO_3)_2\cdot 6H_2O$
"	?	0.02M	>90%(12)		Solid $UO_2(NO_3)_2\cdot 6H_2O$ melted + HNO_3 + $K_2Cr_2O_7$, ether extracted.
0.2M	75°	0.1M	"Complete" in 30 min.(19)		0.0177M UO_2^{++} (conditions for $N_2UO_2Ac_3$ procedure)
"	50°	0.02M	Half-time = 30 min.(6,9)		

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB1k-4
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^=$	Copy [redacted]s, Series A Issued to:

Oxidation of 48 and 39 by $Cr_2O_7^=$ in HNO_3 (cont.)

HNO_3	Temp	$Cr_2O_7^=$	48 oxidized	39 oxidized to $Np^{(o-FS)*}$	Other Conditions
0.1M	80°C	0.1M			Pu= ~5g./l. orange ppt. forms, "$PuOCrO_4$" redissolves in 3 hrs.(30)
"	75°C	"	98% in 5 min.(17)		0.56M UO_2^{++}
"	65°	"	95% in 5-50 min(17)		
"	22°	0.02M	Half-time= ~90 min.(11)		
0.074M	100°	0.1M		72% in 2 min.(26)	
"	"	"		67% in 10 min(26)	
"	22°	"		70% in 3 min(26)	

* $Np^{(O-FS)}$ indicates the oxidation states of Np in which the Np is not carried by LaF_3.

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Compiled by: A. C. Wahl

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB1k-5

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Issued to:

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      k. Oxidation by $Cr_2O_7^=$

Oxidation of 48 by $Cr_2O_7^=$ in $HClO_4$

$HClO_4$	Temp	$Cr_2O_7^=$	48 oxidized	Other Conditions
5.4M	95°C	0.02M	95% in 5 min.(11)	
"	22°	"	29% in 6 hrs.(11)	
"	"	"	55% in 46 hrs(11)	
"	"	"	60% in 143 hrs.(11)	
3.6M	95°	"	3% in 20 min(11)	3.6M H_2SO_4
0.1M	95°	"	92% in 5 min.(11)	
"	22°	"	Half-time = 90 min(11)	

Oxidation of 48 by $Cr_2O_7^=$ in HCl

HCl	Temp	$Cr_2O_7^=$	48 oxidized	Other Conditions
2.4M	65°C	0.1M	"Complete" in 30 min.(15)	Conditions for IO_3^- procedure
2.0M	75°	"	98% in 5 min(17)	
"	"	"	98% in 10 min(17)	0.56M UO_2^{++}

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB1k-6
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^=$	Co[redacted]es, Series A Issued to:

Oxidation of 48 and 39 by $Cr_2O_7^=$ in H_2SO_4

H_2SO_4	Temp.	$Cr_2O_7^=$	48 oxidized	39 oxidized to Np(o-FS)*	Other Conditions
4M	25°C	0.1M	<5% in 22 hrs(31)	>99% in 5 min(31)	
3.6M	95°	0.02M	Half-time = ~50 hrs.(4,7)	99% in 20 min(4,7)	
3M	25°	0.1M	<5% in 60 hrs(31)	>99% in 5 min(31)	
2M	"	"	<5% in 17 hrs(31)	>98% in 5 min(31)	
1M	95°	0.02M	Half-time = 20 min(3,7)		0.04M Cr^{+3}
"	80°	0.1M	>95% in 11 hrs.(1,2)	>95% in 11 hrs.(1,2)	
"	50°	0.02M	~10% in 40 hrs(4,7)	98% in 90 min.(4,7)	
"	22°	0.1M	<15% in 25 min.(1,2)	>95% in 25 min.(1,2)	
"	"	0.02M	<2% in 40 hrs.(3)		0.04M Cr^{+3}
"	"	"	25% in 10 days (4,7)		
0.5M	90°	0.1M	71% in 1 hr.(34)		1M $NaHSO_4$ 1M $NaNO_3$
"	"	"	95% in 2 hrs(34)		
"	90°	"	98% in 5 hrs.(34)		
0.1M	95°	0.02M	96% in 2 min.(5,7)	94% in 10 min.(14)	
"	"	0.002M	Half-time = ~4 min.(8)	53% in 10 min.(8)	
"	50°	0.02M	Half-time = ~1 hr(5,7)		
"	22°	"	Half-time = ~2½ days(5,7)		
pH=2.5	50°	"	90% in 109 min.(7)		
"	22°	"	90% in 21 hrs.(7)		

* Np(o-FS) indicates the oxidation states of Np in which the Np is not carried by LaF_3.

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Compiled by: A. C. Wahl

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IB1k-7

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      k. Oxidation by $Cr_2O_7^=$

Copy [redacted]ies, Series A

Issued to:

Oxidation of 48 and 39 by $Cr_2O_7^=$ in HAc

HAc	Ac^-	Temp.	$Cr_2O_7^=$	48 oxidized	39 oxidized to $Np^{(o-FS)}$*	39 oxidized to $Np^{(o-Ac)}$≠	Other Conditions
1M	--	75°C	0.1M(?)	97% in 60 min.(23)	98% in 60 min.(23)	9% in 60 min.(23)	0.01M HNO_3 0.005M UO_2^{++}
"	--	"	"	"	"	"	0.005M UO_2^{++}
"	--	95°	"	89% in 35 min.(23)	86% in 35 min.(23)	4% in 35 min(23)	
"	0.15M	"	"	63% in 60 min.(23)	98% in 60 min.(23)	12% in 60 min(23)	0.005M UO_2^{++}
0.2M	0.2M	"	"	65% in 45 min.(23)	98% in 45 min.(23)	8% in 45 min(23)	"
"	"	95°	"	67% in 15 min.(23)	98% in 15 min.(23)	6% in 15 min.(23)	0.005M UO_2^{++}
"	"	22°	"	10% in 30 min.(23)	98% in 30 min.(23)	9% in 30 min.(23)	"
0.19M	0.15M	98°	"	79% in 30 min.(18)	97% in 30 min.(18)	---------	
"	"	"	"	78% in 30 min.(18)	99% in 30 min.(18)	---------	0.005M UO_2^{++}
"	"	65°	"	63% in 30 min.(18)	98% in 30 min.(18)	---------	
"	"	60°	"	81% in 30 min.(18)	99% in 30 min.(18)	---------	0.005M UO_2^{++}
"	"	22°	"	<2% in 5 min.(18)	98% in 5 min.(18)	---------	
"	"	"	"	23% in 2.5 hrs.(18)	98% in 2.5 hrs.(18)	---------	
"	"	"	"	0% in 30 min.(18)	99% in 30 min.(18)	---------	0.005M UO_2^{++}

* $Np^{(o-FS)}$ indicates the oxidation states of Np in which the Np is not carried by LaF_3.

≠ $Np^{(o-Ac)}$ indicates the oxidation state of Np in which the Np is carried by $NaUO_2Ac_3$.

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET I B1k-8
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^{=}$	Copy [redacted], Series A Issued to:

References

(1) Wahl, Ph.D. Thesis, Univ. of Calif., Berkeley, Calif., p. 29, Feb. 1942.

(2) Seaborg and Wahl, Report A-135, p. 10, March 19, 1942.

(3) Garner, Report CC-199, p. 2, July 25, 1942.

(4) Garner, Report CC-216, p. 1, Aug. 1, 1942.

(5) Garner, Report CC-222, p. 7, Aug. 8, 1942.

(6) Garner, Report CC-222, p. 8, Aug. 8, 1942.

(7) Garner, Report CN-239, p. 14, Aug. 15, 1942.

(8) Garner, Report CN-239, p. 15, Aug. 15, 1942.

(9) Garner, Report CN-239, p. 16, Aug. 15, 1942.

(10) Gofman, Report CN-239, p. 17, Aug. 15, 1942.

(11) Garner, Report CN-250, p. 8, Aug. 31, 1942.

(12) Koshland and Nagel, Report CN-261, p. 14, Sept. 15, 1942.

(13) Apple, Knox and Perlman, Report CN-282, p. 9, Sept. 30, 1942.

(14) Garner and Sheline, Report CN-299, p. 4, Oct. 15, 1942.

(15) Duffield, Fontana, Garner, Sheline and Stoughton, Report CN-363, p. 11, Nov. 31, 1942.

(16) Perlman and Knox, Report CN-363, p. 12, Nov. 31, 1942.

(17) Prestwood, Report CN-391, p. 4, Dec. 15, 1942.

(18) Garner, Report CN-419, p. 4, Jan. 15, 1943.

(19) Connick, Duffield, Garner, Gofman and Wahl, Report CN-467, p. 17, Feb. 13, 1943.

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB1k-9
I. Solution chemistry B. Oxidation-reduction reaction 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^{=}$	Co[redacted], Series A Issued to:

References (cont.)

(20) Davidson, Koshland and Thompson, CN-503, p. 7, Feb. 28, 1943.

(21) Thompson, CN-503, p. 8, Feb. 28, 1943.

(22) Thompson, CN-503, p. 9, Feb. 28, 1943.

(23) Duffield and Gofman, CN-522, p. 9, March 15, 1943.

(24) Sutton, Report CN-544, p. 19, March 27, 1943.

(25) Thompson, Davidson, Miller and James, Report CN-556, p. 24, March 31, 1943.

(26) Connick and King, Report CN-601, p. 5, April 15, 1943.

(27) Thompson, Davidson, Dreher, Miller and James, Report CN-601, p. 15, April 15, 1943.

(28) Kohman, Report CN-601, p. 25, April 15, 1943.

(29) Clifford and Koshland, Report CN-601, p. 28, April 15, 1943.

(30) Sheline, Report CN-723, p. 1, June 20, 1943.

(31) Beaufait, Report CN-723, p. 13, June 20, 1943.

(32) Clifford, Fries, James, Knox, Koshland, Shepard and Thompson, Report CN-728, p. 3, June 21, 1943.

(33) Clifford, Fries, James, Knox, Koshland, Shepard and Thompson, Report CN-728, p. 6, June 21, 1943.

(34) Beaton, Dam, LaChapelle, Lincoln, Sheft and Turk, Report CN-894, p. 24, August 7, 1943.

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Compiled by: A. C. Wahl Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IB1k-10
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^=$	Copy [redacted]ies, Series A Issued to:

Oxidation of 48 by $Cr_2O_7^=$ in HNO_3

HNO_3	Temp.	$Cr_2O_7^=$	48 oxidized	Other Conditions
5M	85°C.	0.05M	~90% in 2 hrs.(4)	
4M	90°	0.01M	94% in 2 hrs.(2)	0.0005M Co^{+2}
"	"	"	75% in 1 hr.(2)	" "
"	"	0.005M	80% in 4 hrs.(2)	Presence of 0.0001M Co^{+2} did not change rate.
"	"	"	70% in 2 hrs.(2)	
"	"	0.001M	40% in 4 hrs.(2)	
"	"	"	25% in 2 hrs.(2)	
3M	"	0.01M	99% in 2-4 hrs.(2)	0.0005M Co^{+2}
			(only 90% in run)	
"	80°	"	98% in 2-4 hrs.(2)	" "
"	70°	"	88% in 2-4 hrs.(2)	" "
2M	90°	"	95% in 2 hrs.(2)	" "
"	75°	0.02M	90% in 45 min.(1)	
"	"	"	97% in 45 min.(1)	0.002M Ce^{+3} or Ce^{+4}
"	"	"	98% in 2 hrs.(1)	" " "
"	"	"	" " " " "	
1.2M	"	0.0167M	97% in 1 hr.(5)	(5 g. Zr^{+4}/l.
0.2-0.8M	"	0.1M	>90% in 2 hrs.(6)	

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Compiled by: A. C. Wahl Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IB1k-11
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu k. Oxidation by $Cr_2O_7^=$	Cop[redacted]ies A Issued to:

Oxidation of 48 by $Cr_2O_7^=$ in H_2SO_4

H_2SO_4	Temp.	$Cr_2O_7^=$	48 oxidized	Other Conditions
0.2M	75°C.	0.01M	>90% in 30 min.(3) (probably ~98%)	0.015M "$NaBiO_3$" 0.3M HSO_4^- 1.0M $SO_4^=$ 2.5M Na^+

References

(1) Faris and Haines, Report CN-758, p. 8, June 26, 1943.

(2) Stahl and Harris, Report CN-758, p. 12, June 26, 1943.

(3) Swartout and Ketelle, Report CN-903, p. 12, Aug. 28, 1943.

(4) Baldwin, Hoff and Sax, Report CN-958, p. 25, Sept. 25, 1943.

(5) Baldwin and Sax, Report CN-958, p. 33, Sept. 25, 1943.

(6) Gaarder, Halperin, James, Koshland, Kroner, Malm and Thompson, Report CN-1041, p. 25, Oct. 31, 1943.

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1945	EDITION I SHEET IB11-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu 1. Oxidation by Cl_2	Cop[redacted]pies, Series A Issued to:

Oxidation of 48 by Cl_2 in $HClO_4$

$HClO_4$	Temp.	Cl_2	Cl^-	48 oxidized	Other Conditions
1M	22°C.	0.025M	0.056M	18% in 41 hrs.(7)	
0.1M	95°	"	"	93% in 10 min.(7)	cones sealed
"	"	"	"	94% in 41 hrs.(7)	
"	22°	"	"	Half-time = ~2 hrs.(7)	
"	"	"	"	78% in 24 hrs.(7)	

Oxidation of 48 by Cl_2 in H_2SO_4

H_2SO_4	Temp.	Cl_2	Cl^-	48 oxidized	Other Conditions
1M	98°C.	0.025M	0.056M	<2% in 70 min.(1,5)	
"	22°	"	"	<2% in 17 days.(3)	
0.1M	95°	"	"	44% in 1 hr.(7)	cone sealed
0.0005M	80°	0.06M	--	93% in 15 min.(6)	--- Cl_2 bubbled thru solution during experiment.
0.05M	"	"	--	25% in 15 min.(6)	---
"	"	"	--	73% in 15 min.(6)	Ce^{+3}

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB11-2
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu 1. Oxidation by Cl_2	Cop[redacted]es, Series A Issued to:

Oxidation of 48 by Cl_2 (ClO^-) at higher pH

pH	Temp.	$ClO^- + HClO$	48 oxidized	Other Conditions
4-7	80°C.	0.2M	>75% in 15 min.(6)	
Slightly alkaline	?	?	>50%(2,4)	Ether extraction from nearly sat. $LiNO_3$ sol'n.

References

(1) Garner, Report CC-199, p. 2, July 25, 1942.

(2) Magel, Report CC-216, p. 8, Aug. 1, 1942.

(3) Garner, Report CC-222, p. 8, Aug. 8, 1942.

(4) Magel, Report CN-239, p. 10, Aug. 15, 1942.

(5) Garner, Report CN-239, p. 19, Aug. 15, 1942.

(6) Hemaker, Report CN-239, p. 22, Aug. 15, 1942.

(7) Garner, Report CN-261, p. 2, Sept. 15, 1942.

[redacted]

Compiled by: A. C. Wahl Date: September 28, 1945	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1a-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu a. Oxidation by $HClO_4$	Co[redacted]es, Series A Issued to:

Oxidation of 48 by $HClO_4$

$HClO_4$	Temp.	48 oxidized	Other Conditions
5.4M	95°C.	<6% in 10 min.(1)	
"	22°	<6% in 143 hrs.(1)	
1.0M	95°	~40% in 3 days(3)	
0.8M	"	0% in 87 days(4)	
0.1M	"	0% in 5 days(3)	
"	22°	< 2% in 95 hrs.(1)	
"	95°	< 2% in 2.75 hrs.(2)	$0.2M\ Br^-$

References

(1) Garner, Report CN-250, p. 8, Aug. 31, 1942.

(2) Gofman, Report CN-250, p. 11, Aug. 31, 1942.

(3) Hamaker, Report CN-261, p. 7, Sept. 15, 1942.

(4) Gofman, Report CN-867, p. 17, August 14, 1943.

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB1n-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu n. Oxidation by Tl^{+3}	Co[redacted]s, Series A Issued to:

Oxidation of 48 by Tl^{+3} in HNO_3

HNO_3	Temp.	Tl^{+3}	48 oxidized	Other conditions
0.1N	22°C.	0.01M	0% in 117 hrs.(4)	0.01M Tl^{+}

Oxidation of 48 by Tl^{+3} in H_2SO_4

H_2SO_4	Temp.	Tl^{+3}	48 oxidized	Other conditions
1M	70°C.	0.01M	<2% in 4 hrs.(1,3)	0.01M Tl^{+}
"	22°	"	<2% in 17 days(2,3)	"

References

(1) Garner, Report CC-199, p. 2, July 25, 1942.

(2) Garner, Report, CC-222, p. 8, Aug. 8, 1942.

(3) Garner, Report, CN-239, p. 19, Aug. 15, 1942.

(4) Garner, Report CN-250, p. 9, Aug. 31, 1942.

[redacted]

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB1c-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu c. Oxidation by IO_3^-	Cop[redacted]. Series A Issued to:

Oxidation of 48 by IO_3^- in HNO_3

HNO_3	Temp.	IO_3^-	48 oxidized	Other Conditions
3.1N	95°C.	0.04M	<2% in 24.5 hrs.(1)	
0.2N	"	"	<" " " " "	

Reference

(1) Gofman, Report CN-250, p. 12, Aug. 31, 1942.

[redacted]

[redacted]

Compiled by: A. C. Wahl Date: September 28, 1945	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET 13Bp-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu p. Oxidation by Br_2	Copy [redacted], Series A Issued to:

Oxidation of 48 by Br_2 in HNO_3

HNO_3	Temp.	Br_2	Br^-	48 oxidized	Other Conditions
0.2M	95°C.	0.12M	--	88% in 14 hrs.(3)	
"	"	"	--	90% in 19 hrs.(3)	
"	"	"	--	84% in 24 hrs.(3)	
0.002M	"	"	--	90% in 14 hrs.(3)	
"	"	"	--	80% in 24 hrs.(3)	

Oxidation of 48 by Br_2 in $HClO_4$

$HClO_4$	Temp.	Br_2	Br^-	48 oxidized	Other Conditions
0.1M	95°C.	0.11M	0.9M	86% in 2.75 hrs.(3)	
"	"	0.11M	--	92% in 2.75 hrs.(3)	
"	"	0.12M	--	93% in 55 min.(4)	
"	"	"	--	39% in 55 min.(4)	0.04M IO_3^-
"	"	"	--	90% in 105 min.(4)	
"	"	"	--	48% in 105 min.(4)	0.04M IO_3^-

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I   SHEET IB1p-2

I. Solution chemistry
    B. Oxidation-reduction reactions
        1. Oxidation of Pu
            p. Oxidation of Br_2

Copy [redacted] Series A

Issued to:

Oxidation of 48 and 39 by Br_2 in H_2SO_4

H_2SO_4	Temp.	Br_3^-	Br^-	48 oxidized	39 oxidized to Np(o-FS)*
1M	80°C.	0.1M	?	<15% in 15 min.(1,2)	< 15% in 15 min.(1,2)
"	20°	"	"	<15% in 2 hrs.(1,2)	< 15% in 2 hrs.(1,2)

*Np(o-FS) indicates the oxidation states of Np in which the Np is not carried by LaF_3.

References

(1) Wahl, Ph.D. Thesis, University of California, Berkeley, Calif., p. 29, Feb. 1942.

(2) Seaborg and Wahl, Report A-135, p. 10, March 19, 1942.

(3) Gofman, Report CN-250, p. 11, Aug. 8, 1942.

(4) Gofman, Report CN-261, p. 2, Sept. 15, 1942.

[redacted]

Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB1q-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu q. Oxidation by HNO_3	C[redacted], Series A Issued to:

Oxidation of Pu by HNO_3

HNO_3	Temp.	Pu	Pu oxidized	Other Conditions
13M	120°C.	48	<2% in 1 hr.$^{(4)}$	
6.4M	22°	"	<1% in 145 hrs.$^{(1)}$	
1M	100°	"	<1% in 4 hrs.$^{(4)}$	
0.2M	95°	"	5% in 14 hrs.$^{(2)}$	
"	"	"	34% in 24 hrs.$^{(2)}$	
"	"	"	50% in 33 hrs.$^{(2)}$	
0.1M	22°	"	<5% in 94 hrs.$^{(1)}$	
13-1M	120°	49	~10%$^{(3)}$	U metal containing 49 dissolved in boiling HNO_3
"	"	"	~60%$^{(4)}$	
"	"	"	15-20%$^{(5)}$	
"	"	"	14-45%$^{(6)}$	

References

(1) Garner, Report CN-250, p. 8, Aug. 31, 1942.

(2) Gofman, Report CN-250, p. 12, Aug. 31, 1942.

(3) English, Report CN-601, p. 41, April 15, 1943.

(4) Cooper, Dam, Dixon, Dreher, Gaarder, Halperin, Johnson, Knox, Lincoln, Miller, Morris, Zvolner, Koshland, and Thompson, Report CN-813, p. 1, July 17, 1943.

[redacted]

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Date: September 28, 1943	EDITION I SHEET IB1q-2
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu q. Oxidation by HNO_3	[redacted], Series A Issued to:

References (cont.)

(5) Smith's Group, Report CN-828, July 26, 1943.

(6) Knox, Report CN-849, p. 1, Aug. 1, 1943.

[redacted]

Compiled by: A. C. Wahl Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IB1q-3
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu q. Oxidation by HNO_3	Copy No. [redacted] of 50 copies, Series A Issued to:

Oxidation of 48 by HNO_3

HNO_3	Temp.	48 oxidized	Other Conditions
16 N	100°C. (?)	< 2% in 30-60 min.(1)	"$U(C_2O_4)_2$" containing 48 dis. in HNO_3

Reference

(1) Dam, Fries and Werner, Report CN-1041, p. 9, October 31, 1943.

[redacted]

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Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IB1q-4

I. Solution chemistry
    B. Oxidation-reduction reactions
        1. Oxidation of Pu
            q. Oxidation by HNO_3

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Oxidation of Pu^{+4} and Pu^{+3} by HNO_3

HNO_3	Temp.	Pu	Oxidation
0.25M	95°C.	Pu^{+4}	57% oxidized to Pu^{+6} in 30 min.(1) *
1.2M	"	"	46% " " " " " " (1) *
0.6M	~80°	Pu^{+3}	oxidized to Pu^{+4} in ~15 min.(2)

* No oxidation in 1M HCl at 95°C. for 30 min.

References

(1) Connick, McVey and Sheline, Report CN-1360, p. 9, Feb. 10, 1944.

(2) Mastick and Wahl, Report LA-63, January 22, 1944.

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IB1r-1

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Issued to:

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      r. Oxidation by Hg^{++}

Oxidation of 48 by Hg^{++} in $HClO_4$

$HClO_4$	Temp.	HG^{++}	48 oxidized
0.8M	95°C.	0.1M	0% in 87 days.(1)

References

(1) Gofman, Report CN-867, p. 17, Aug. 14, 1943.

[redacted]

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I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu r. Oxidation by Hg^{++}	~~Copy No. 18~~ of 50 copies, Series A Issued to:

Oxidation of Pu^{3} by Hg

Acid	Pu^{+3}	Hg^{++}	Oxidation
HCl	Pu^{+3}	?	No oxidation in 15 min.(1)

Reference

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB1a-1

I. Solution chemistry
 B. Oxidation-reduction reactions
  1. Oxidation of Pu
   a. Oxidation by Fe^{+++}

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Issued to:

Oxidation of 48 by Fe^{+++} in $HClO_4$

$HClO_4$	Temp.	Fe^{+++}	48 oxidised
0.8M	95°C.	0.08M	0% in 87 days.(1)

Reference

(1) Gofman, Report CN-867, p. 17, Aug. 14, 1943.

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB1t-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      t. Oxidation by I_3^-

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Issued to:

Oxidation of 48 and 39 by I_3^- in $HClO_4$

$HClO_4$	Temp.	I_3^-	I^-	48 oxidized	39 oxidized to $Np^{(o-FS)}$*
0.12M	90°C.	0.2M	0.35M	$<1\%$ in 22 hrs.(1)	$<1\%$ in 22 hrs.(1)

*$Np^{(o-FS)}$ indicates the oxidation state of Np in which the Np is not carried by LaF_3.

Reference

(1) Wahl, Report CN-419, p. 5, Jan. 15, 1943.

[redacted]

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Date: September 28, 1943	EDITION I SHEET IB1u-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu u. Electrolytic oxidation	Co~~py No. 18 of 50~~ copies, Series A Issued to:

Electrolytic oxidation of 48

Solution	Time of plating	% 48 on cathode	% 48 oxidized
0.1M $NaHCO_3$, sat. CO_2	2 hrs.	13%(1)	25%(1)
" " " "	2.5 hrs.	11%(1)	58%(1)

References

(1) Perlman, Report CC-156, p. 3, June 27, 1942.

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Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IB1v-1
I. Solution chemistry B. Oxidation-reduction reactions 1. Oxidation of Pu v. Stability of Pu^{+3}	Copy ~~No 18 of [illegible] copies~~, Series A Issued to:

Stability of Pu^{+3}

Sol'n.	Stability
6N H_2SO_4, $H_2C_2O_4$	Heated 2 hrs. 75°C. -- still purple (Pu^{+3}) (1)
OH^-	When acidified yellow green soln (Pu^{+4}) (2) (probably due to O_2)
1M H_2SO_4, Fe^{++}	No apparent oxidation in ½ hr. (3)

References

(1) Patton, Report CN-1324, p. 8, February 1, 1944.

(2) Connick, McVey and Sheline, Report CN-1360, p. 3, Feb. 10, 1944.

(3) Hindman, Kraus and Howland, Report CK-1371, p. 1, March 1, 1944.

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Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IB1w-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    1. Oxidation of Pu
      w. Stability of Pu^{+4}

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Stability of Pu^{+4} in NaOH

NaOH	Temp.	Change in oxidation state
0.25M	95°C.	24 hrs. at 22°C., 4 hrs. 25°C. -- HNO_3 added, 1% oxidized(1)
1M	"	2 hrs. -- HNO_3 added, 1% oxidized(1)

Reference

(1) Connick, McVey and Sheline, Report CN-1360, p. 8, Feb. 10, 1944.

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB2a-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu a. Reduction by $N_2H_5^+$	Cop[redacted]pies, Series A Issued to:

Reduction of $48^{(o)}$ by $N_2H_5^+$

Acid	Temp.	$N_2H_5^+$	$48^{(o)}$ reduced	Other Conditions
0.6M HNO_3	22°C.	0.015-0.06M	99% in 0.75-5.0 hrs.(1)	0.8N HF, 3g. Zr^{+4}/l., 0.02M Cr^{+3}
?	75°	0.02M	98% in 10 min.(2)	0.02M Cr^{+3}
?	22°	"	86% in 30 min.(2)	"

References

(1) Clifford, Fries, James, Knox, Koshland, Shepard and Thompson, Report CN-728, p. 14, June 21, 1943.

(2) La Chapelle, Dreher and Thompson, Report CN-728, p. 33, June 21, 1943.

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Compiled by: A. C. Wahl

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1: SHEET 132a-2

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      a. Reduction by $N_2H_5^+$

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Issued to:

Reduction of $48^{(o)}$ by $N_2H_5^+$ in HNO_3

HNO_3	Temp.	$N_2H_5^+$	$48^{(o)}$ reduced	Other Conditions
1M	75°C.	0.05M	>99% in 30 min.(1)	0.1M H_3PO_4 0.02M Cr^{+3}

Reference

(1) Ritter and Black, Report CN-758, p. 13, June 26, 1943.

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IB2b-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      a. Reduction by phenylhydrazine

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Reduction of 48$^{(o)}$ by Phenylhydrazine

HNO_3	Temp.	Phenyl-hydrazine	48$^{(o)}$ reduced	Other conditions
0.1-0.4M	22°C.	0.13M	40-50% in 1 hr.(1)	40% $UO_2(NO_3)_2 \cdot 6H_2O$

Reference

(1) Zvolner, Report CN813, p. 3, July 17, 1943.

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB2c-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      c. Reduction by HCOOH

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Reduction of $48^{(c)}$ by HCOOH in HNO_3

HNO_3	Temp.	HCOOH	$48^{(c)}$ reduced	Other conditions
~1M	90°C.	1.5-1.75M	98% in >3 min.(2)	35-45% $UO_2(NO_3)_2 \cdot 6H_2O$
0.1-0.6M	75°	0.1M	<3% in 1 hr.(1)	40% in $UO_2(NO_3)_2 \cdot 6H_2O$
0.5M	"	"	52% in 2 hrs.(1)	
0.1M	"	"	8% in 2 hrs.(1)	

References

(1) Zvolner, Report CN-813, p. 3, July 17, 1943.

(2) Cooper, Gaardner, Halperin and Knox, Report CN-849, p. 3, August 1, 1943.

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Date: November 27, 1943

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EDITION I, SUPP. 1 SHEET IB2c.2

I. Solution chemistry
    B. Oxidation-reduction reactions
        2. Reduction of Pu
            c. Reduction by HCOOH

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Issued to:

Reduction of 48$^{(o)}$ by HCOOH in HNO_3

HNO_3	Temp.	HCOOH	48$^{(o)}$ reduced	Other Conditions
1M	~100°C.	1.5M	99% in 1 hr.(1)	50% $UO_2(NO_3)_2 \cdot 6H_2O$
0.25M	"	0.1M	99% in 1 hr.(1)	"

Reference

(1) Peterson, Belthis and Olson, Report CN-1023, p. 12, October 30, 1943.

[redacted]

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Compiled by: A. C. Wahl

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB2d-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      d. Reduction by NH_3OH^+

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Issued to:

Reduction of 48(o) by NH_3OH^+

HNO_3	Temp.	NH_3OH^+	48(o) reduced	Other Conditions
0.6M	22°C.	0.1M	64% in 1 hr.(4)	40% $UO_2(NO_3)_2\cdot6H_2O$
"	"	"	53% in 1 hr.(4)	20% "
0.52M	"	0.02M	"Complete" in 1 hr.(2)	0.033M H_2SO_4, HF 0.014M Cr^{+3} 10% $UO_2(NO_3)_2\cdot6H_2O$
0.3M	"	0.1M	70% in 1 hr.(4)	40% $UO_2(NO_3)_2\cdot6H_2O$
"	"	"	50% in 1 hr.(4)	20% "
0.2M	"	"	>98% in ~30 min.(1)	0.55M UO_2^{++}, 1.65M HAc (used in $NaUO_2AC_3$ procedure)
0.1M	"	"	56% in 1 hr.(4)	40% $UO_2(NO_3)_2\cdot6H_2O$
?	75°	0.03M	61% in 90 min.(3)	0.02M Cr^{+3}

References

(1) Connick, Duffield, Garner, Gofman and Wahl, Report CN-467, p. 18, Feb. 13, 1943.

(2) Koshland, Report CN-503, p. 18, Feb. 28, 1943.

(3) La Chapelle, Dreher and Thompson, Report CN-728, p. 32, June 21, 1943.

(4) Zvolner, Report CN-813, p. 2, July 17, 1943.

[redacted]

Compiled by: A. C. Wahl Date: May 1, 1944	HANDBOOK: CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IB2d-2
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu d. Reduction by NH_3OH^+	Co[redacted]ies A Issued to:

Reduction of Pu^{+4} by NH_3OH^+

Acid	Temp.	Pu^{+4}	NH_3OH	Reduction
0.5M HNO_3	?	0.015M	0.3M	Purple color (Pu^{+3}) appeared.(1)
1.7M HNO_3	22°C.	0.14M	"	" " " " in 6 min.(2)
HCl	"	"	"	" " " ".(2)
H_2SO_4	"	"	"	" " " " (but more slowly than in HNO_3).(2)

References

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

(2) Connick, McVey and Sheline, Report CN-1360, p. 3, Feb. 10, 1944.

[redacted]

Compiled by: A. C. Wahl

Date: September 23, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB2e-1

I. Solution chemistry
    B. Oxidation-reduction reactions
        2. Reduction of Pu
            e. Reduction by SO_2

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Issued to:

Reduction of $48^{(o)}$ by SO_2 in HNO_3

HNO_3	Temp.	SO_2	$48^{(o)}$ reduced	Other conditions
1N	22°C.	0.1M	99% in 1 hr.(2)	H_3PO_4
"	"	?	>95% in 1 hr.(3)	SO_2 passed in soln. 5 min.
0.5M	25°C.	0.04M	65% in 10 min.(1)	1-2N HF 10% $UO_2(NO_3)_2 \cdot 6H_2O$ Cr^{+3}
"	"	"	80% in 20 min.(1)	
"	"	"	95%* in 30 min.(1)	
"	"	0.07M	90% in 10 min.(1)	
"	"	"	95% in 20 min.(1)	
"	"	"	95%* in 30 min.(1)	
"	"	"	95% in 20 hrs.(1)	
"	50-60°	0.02M	85% in 10 min.(1)	
"	"	"	60% in 20 min.(1)	
"	"	"	65%* in 30 min.(1)	
"	"	0.04M	97% in 10 min.(1)	
"	"	"	97% in 20 min.(1)	
"	"	"	60%* in 30 min.(1)	
"	"	0.07M	90% in 10 min.(1)	
"	"	"	92% in 20 min.(1)	
"	"	"	95%* in 30 min.(1)	
"	"	"	95% in 20 hrs.(1)	

* 99% 48 found in reduced state if two LaF_3 ppts. were removed.

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I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu e. Reduction by SO_2	Copy N[redacted]copies, Series A Issued to:

Reduction of $48^{(o)}$ by SO_2 in HNO_3 (cont.)

HNO_3	Temp.	SO_2	$48^{(o)}$ reduced	Other conditions
0.5M	50-60°C.	0.14M	95% in 30 min.(1)	1-2N HF 16% $UO_2(NO_3)_2 \cdot 6H_2O$ Cr^{+3}
"	"	0.2M	" " " " "	

References

(1) Knox, Report CN-467, p. 7, Feb. 13, 1943.

(2) Sutton's Group, Report CN-554, p. 19, March 27, 1943.

(3) Thompson, Davidson, Drsher, Miller and James, Report CN-601, p. 15, April 15, 1943.

Compiled by: A. C. Wahl

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IB2e-3

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      e. Reduction by SO_2

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Issued to:

Reduction of Pu^{+6} and Pu^{+4} by SO_2.

Acid	Pu	SO_2	Reduction
0.5M HNO_3	3.5 g. Pu^{+4}/l.	~0.15M	Purple color (Pu^{+3}) appeared(1)
0.5M HCl	5 g. Pu^{+6}/l.	~0.15M	" " " " (complete in ~15 min.)(1)
0.6M HNO_3	Pu^{+4}	?	" " " " in 5 min.(2)

References

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

(2) Mastick and Wahl, Report LA-63, February 22, 1944.

[redacted]

Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB2f-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu f. Reduction by U^{+4}	Co[redacted]pies, Series A Issued to:

Reduction of $48^{(o)}$ and $39^{(o)}$ by U^{+4} in HNO_3

HNO_3	Temp.	U^{+4}	$48^{(o)}$ reduced	$39^{(o)}$ reduced	Other Conditions
0.2M	70°C.	0.019M	>90% in 15 min.(1)	>90% in 15 min.(1)	0.3M HAc
"	22°	"	87% in 5 min.(1)	79% in 5 min.(1)	"
"	"	"	97% in 10 min.(1)	94% in 10 min.(1)	"
"	"	"	97% in 60 min.(1)	95% in 60 min.(1)	"

$48^{(o)}$ and $39^{(o)}$ precipitated with $NaUO_2Ac_3$, dissolved in HNO_3, and U^{+4} added. Analyzed by again precipitating $NaUO_2Ac_3$ except first experiment which was analyzed by LaF_3 after U^{+4} was oxidized by the HNO_3.

Reference

(1) Crandall, Report CN-601, p. 12, April 15, 1943.

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Compiled by: A. C. Wahl

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET TB2f-2

I. Solution chemistry
    B. Oxidation-reduction reactions
        2. Reduction of Pu
            f. Reduction by U^{+4}

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Reduction of $48^{(o)}$ by U^{+4} in HNO_3

HNO_3	Temp.	U^{+4}	$48^{(o)}$ reduced	Other Conditions
1M	95°-60°C.	0.005-0.01M	>90% in 2 hrs.(2)	0.1M H_3PO_4 "$U_3(PO_4)_4$" ppts. and redissolves
"	75°	0.005M	98% in 0.5 hrs.(2)	
"	"	0.0025M	75% in 5 min.(2)	
"	"	"	98% in 15 min.(2)	
"	65°	0.01M	98% in 1.25 hrs.(2)	
"	50°	0.005-0.01M	~85% in 2 hrs.(2)	
"	"	0.01M	99% in >30 min.(1)	40% $UO_2(NO_3)_2 \cdot 6H_2O$
"	"	"	50% in 15 min.(1)	
"	40°	"	97% in 1 hr.(1)	
"	35°	"	~80% in 1 hr.(1)	
"	30°	"	~70% in 1 hr.(1)	
"	22°	0.005-0.04M	>98% in 1 hr.(1)	0.002M Cr^{+3}
0.5-1.25M	50°	0.01M	>99% in 1 hr.(1)	
0.5M	"	0.001-0.02M	>98% in 1 hr.(2)	40% $UO_2(NO_3)_2 \cdot 6H_2O$
0.3-1M	"	0.01M	>99% in 1 hr.(2)	20% "
0.1-1.25M	"	"	>98% in 1 hr.(2)	40% "
0.0-0.2M	"	"	~20% in 1 hr.(2)	20% "
0.0-0.1M	"	"	~13% in 1 hr.(2)	40% "

[redacted]

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Compiled by: A. C. Wahl

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IB2f-3

I. Solution chemistry
    B. Oxidation-reduction reactions
        2. Reduction of Pu
            f. Reduction by U^{+4}

Copy [redacted], Series A

Issued to:

References

(1) Halperin and Knox, Report CN-931, p. 2, Sept. 11, 1943.

(2) Halperin, Report CN-979, p. 1, Sept. 30, 1943.

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB2g-1
I. Solution chemistry B. Oxidation-reduction reaction 2. Reduction of Pu g. Reduction by I^-	[redacted] Series A Issued to:

Reduction of $48^{(o)}$ and $39^{(o)}$ by I^- in $HClO_4$

$HClO_4$	Temp.	I^-	I_3^-	$48^{(o)}$ reduced	$39^{(o)}$ reduced
0.24M	90°C.	0.24M	0.12M	>95% in 30 min.(1)	>95% in 30 min.(1)
"	22°	"	"	>95% in 6 min.(1)	>95% in 6 min.(1)
"	"	"	"	>95% in 2 min.(1)	>90% in 2 min.(1)

Reference

(1) Wahl, Report CN-419, p. 6, Jan. 16, 1943.

[redacted]

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IB2g-2
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu g. Reduction by I^-	Co[redacted] Issued to:

Reduction of Pu^{+4} by I^-

Acid	Pu^{+4}	I^-	Reduction
0.4M H_2SO_4	0.017M	0.08M	Reduced to Pu^{+3} (I_3^- color and blue hydroxide on adding OH^-)(1)

Reference

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

[redacted]

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB2h-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu h. Reduction by $HAsO_2$	[redacted] of 50 copies, Series A Issued to:

Reduction of $48^{(o)}$ by $HAsO_2$

Acid	Temp.	$HAsO_2$	$48^{(o)}$ reduced	Other Conditions
0.52M HNO_3	22°C.	0.002M	"Complete" in 20 min.(1)	0.033M H_2SO_4, 0.014M Cr^{+3} HF, 10% $UO_2(NO_3)_2 \cdot 6H_2O$
0.3-0.6M HNO_3	"	0.14M	"Complete" in 3 hrs.(2)	0.8N HF, 0.02M Cr^{+3}
0.025M H_2SO_4	"	0.002M	98% in 1 hr.(3)	0.007M H_3PO_4, 0.012M Cr^{+3} 0.94M HF, 10% $UO_2(NO_3)_2 \cdot 6H_2O$ stainless steel
0.025M H_2SO_4	"	"	Inconsistent results(3)	0.007M H_3PO_4, 0.013M Cr^{+3}, 0.94M HF, 10% $UO_2(NO_3)_2 \cdot 6H_2O$

References

(1) Koshland, Report CN-503, p. 18, Feb. 28, 1943.

(2) Clifford, Fries, James, Knox, Koshland, Shepard and Thompson, Report CN-728, p. 13, June 21, 1943.

(3) Clifford, Fries, James, Knox, Koshland, Shepard and Thompson, Report CN-728, p. 18, June 21, 1943.

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I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu h. Reduction by $HAsO_2$	~~Copy No. 18 of 50 copies, Series~~ A Issued to:

Reduction of Pu^{+6} by $HAsO_2$

Acid	Pu^{+6}	Reduction
1M HCl	.02M	Reduced to Pu^{+4} (no reduction to Pu^{+3} in 24 hrs.)(1)

Reference

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB21-1

[redacted]

Issued to:

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      i. Reduction by H_2O_2

Reduction of $48^{(o)}$ and $39^{(o)}$ by H_2O_2 in $HClO_4$

Acid	Temp.	H_2O_2	HF	$UO_2(NO_3)_2 \cdot 6H_2O$	$48^{(o)}$ reduced	Other Conditions
1M $HClO_4$	95°C	0.04M	--	---------------	13% in 5 min.(1)	0.01M Ag^+
"	"	"	--	---------------	45% in 50 min.(1)	"
"	"	0.26M	--	---------------	20% in 10 min.(3)	"
"	"	"	--	---------------	25% in 80 min.(3)	"

Reduction of $48^{(o)}$ and $39^{(o)}$ by H_2O_2 in H_2SO_4

Acid	Temp.	H_2O_2	HF	$UO_2(NO_3)_2 \cdot 6H_2O$	48 reduced	Other Conditions
0.1M H_2SO_4	22°C	0.3M	--	---------------	0% in 75 min.(2)	90% $39^{(o)}$ red. } Cr^{+3}
"	"	"	--	---------------	60% in 16 hrs.(2)	100% $39^{(o)}$ red.

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Date: September 28, 1943	EDITION I SHEET IB21-2
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu i. Reduction by H_2O_2	[redacted] Issued to:

Reduction of 48$^{(o)}$ and 39$^{(o)}$ by H_2O_2 in HNO_3

Acid	Temp.	H_2O_2	HF	$UO_2(NO_3)_2 \cdot 6H_2O$	48 reduced	Other Conditions
1M HNO_3	75°C	0.15M	--	--------	92% in 30 min.$^{(8)}$	stainless steel present (18-8) Cr^{+3}
"	"	0.3M	--	--------	93% in 30 min.$^{(8)}$	
"	"	0.45M	--	--------	95% in 30 min.$^{(8)}$	
"	"	0.75M	--	--------	98% in 30 min.$^{(8)}$	
"	50°	0.09M	2M	--------	40% in 15 min.$^{(4)}$	Cr^{+3}
"	"	"	"	--------	50%-100% in 30 min.$^{(4)}$	
"	"	"	"	--------	95%-100% in 1 hr.$^{(4)}$	
"	"	"	"	--------	50-90% in 2.5-23 hrs.$^{(4)}$	
"	27°	"	"	--------	2% in 30 min.$^{(4)}$	
"	"	"	"	--------	60% in 1 hr.$^{(4)}$	
"	"	"	"	--------	80-90% in 2 hrs.$^{(4)}$	
"	"	"	"	--------	95% in 18 hrs.$^{(4)}$	
"	"	1.1M	"	--------	60% in 15 min.$^{(4)}$	
0.28M HNO_3	50°	0.15M	--	--------	30% in $\frac{1}{2}$-$1\frac{1}{2}$ hrs.$^{(5)}$	0.011M Cr^{+3}
"	"	"	1.7M	--------	50% in $\frac{1}{2}$-1 hr.$^{(5)}$	
"	"	"	"	6%	90-95% in $\frac{1}{2}$ hr.$^{(5)}$	
0.5M HNO_3	"	0.18M	1M	10%	>95% in 30 min.$^{(6)}$	0.04M Cr^{+3}
? HNO_3	22°	0.5M	2M	"	95% in 30 min.$^{(7)}$	
"	"	0.7M	1M	"	95% in 60 min.$^{(7)}$	

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB2i-3
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu i. Reduction by H_2O_2	C[redacted] A Issued to:

References

(1) Hamaker, Report CN-250, p. 6, Aug. 31, 1942.

(2) Garner, Report CN-250, p. 7, Aug. 31, 1942.

(3) Hamaker, Report CN-261, p. 8, Sept. 15, 1942.

(4) Apple, Knox and Perlman, Report CN-282, p. 10, Sept. 30, 1942.

(5) Hamaker, Report CN-363, p. 13, Nov. 31, 1942.

(6) Perlman and Knox, Report CN-363, p. 12, Nov. 31, 1942.

(7) Knox, Report CN-556, p. 10a, March 31, 1943.

(8) LaChapelle, Report CN-728, p. 31, June 21, 1943.

[redacted]

[redacted]

Compiled by: A. C. Wahl Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IB2i-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu i. Reduction by H_2O_2	Copy No. [redacted] of 50 copies, Series A Issued to:

Reduction of $48^{(o)}$ by H_2O_2 in HNO_3

HNO_3	Temp.	H_2O_2	$48^{(o)}$ reduced	Other Conditions
1M	75 C.	0.12M	97% in 2 hrs.	0.015M Fe^{++}, Ce^{+3}, Cr^{+3}
"	"	0.24M	99% in 1 hr.	0.015M Fe^{++}, Ce^{+3}, Cr^{+3}
0.5M	?	0.09M	99% in ? time (2)	1.0M HF, 2 g. Zr^{+4}/1.

References

(1) Smith's Group, Report CN-756, p. 8, June 28, 1943.

(2) Baldwin and Sax, Report CN-958, p. 33, September 25, 1943.

[redacted]

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Date: September, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB2j-1

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Issued to:

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      j. Reduction by HO_2^-

Reduction of $48^{(o)}$ by HO_2^- in Na_2CO_3

Na_2CO_3	Temp.	HO_2^-	$48^{(o)}$ reduced	Other Conditions
0.3M	22°C.	0.1M	"Complete" in 12 hrs.(1)	Pt vessel

Reference

(1) Gofman, Report CN-328, p. 6, Oct. 31, 1942.

[redacted]

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB2k-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu k. Reduction by hydroquinone	[redacted] es A Issued to:

Reduction of 48$^{(o)}$ by hydroquinone

HNO_3	Temp.	Hydro-quinone	48$^{(o)}$ reduced	Other Conditions
0.52M	50°C.	0.04M	"Complete" in 150 min.(1)	0.033M H_2SO_4 10% $UO_2(NO_3)_2 \cdot 6H_2O$
"	"	0.023M	>90% in 90 min.(1)	0.014M Cr^{+3} HF

Reference

(1) Koshland, Report CN-503, p. 17, Feb. 28, 1943.

[redacted]

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB21-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      1. Reduction by Fe^{++}

C[redacted] A

Issued to:

Reduction of $48^{(o)}$ by Fe^{++}

Acid	Temp.	Fe^{++}	$48^{(o)}$ reduced	Other conditions
$3M\ HNO_3$	?	?	"Complete" in 10 min.(1)	2 eq. Fe^{++}/eq. $S_2O_8^{=}$
$1M\ HNO_3$	75°C.	0.0025-0.02M	98% in 1 hr.(6)	$0.1M\ H_3PO_4$
$0.7M\ HNO_3$	"	0.0005-0.002M	98% in 1 hr.(7)	$0.06M\ H_3PO_4$
$0.6M\ HNO_3$	"	0.01M	3% in 75 min.(5)	40% $UO_2(NO_3)_2 \cdot 6H_2O$
"	"	0.02M	92% in 75 min.(5)	
"	"	0.04-0.06M	97% in 75 min.(5)	
0.5-0.75M HNO_3	?	see last column	90-97% in 2 hrs.(2)	0.4-1.0 eq. Fe/eq. $Cr_2O_7^{=}$ 1 eq. H_2O_2/eq. $Cr_2O_7^{=}$ 0.05N $Cr_2O_7^{=}$ before red. 0.7N HF 2.5g. Zr^{+4}/l.
0.1-0.6M HNO_3	75°	0.001-0.005M	~50% in 2 hrs.(5)	0.1-0.5M HCOOH 40% $UO_2(NO_3)_2 \cdot 6H_2O$
0.34-0.58M H_3PO_4	"	see last column	98% in 45 min.(4)	.25-.33 eq. Fe^{++}/eq. $Cr_2O_7^{=}$ 0.85-1.15 eq. H_2O_2/eq. $Cr_2O_7^{=}$ 1g. Bi^{+3}/l.
?	?	?	"Complete" in 12 min.(2)	Ag ppted. if $S_2O_8^{=}$; Ag^{+} used for oxidation
?	75°	0.09M	"Complete" in 30 min.(3)	$0.02M\ Cr^{+3}$

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB21-2
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu 1. Reduction by Fe^{++}	~~Copy No. 18 of 50 copies, Series A~~ Issued to:

References

(1) Kohman, Report CN-601, p. 25, April 15, 1943.

(2) Clifford, Fries, James, Knox, Koshland, Shepard and Thompson, Report CN-728, p. 15, June 21, 1943.

(3) LaChapelle, Dreher and Thompson, Report CN-728, p. 32, June 21, 1943.

(4) LaChapelle, Dreher and Thompson, Report CN-728, p. 35, June 21, 1943.

(5) Cooper, Dam, Dixon, Dreher, Gaarder, Halperin, Johnson, Knox and Lincoln, Report CN-813, p. 2, July 17, 1943.

(6) Miller, Morris, Zoolner, Koshland and Thompson, Report CN-813, p. 17, July 17, 1943.

(7) Halperin, Report CN-849, p. 13, August 1, 1943.

Compiled by: A. C. Wahl Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IB21-3
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu 1. Reduction by Fe^{++}	~~Copy No. 18 of 50 copies,~~ Series A Issued to:

Reduction of $48^{(o)}$ by Fe^{++} in HNO_3

HNO_3	Temp.	Fe^{++}	$48^{(o)}$ reduced	Other Conditions
1M	75°C.	0.015M	97% in 2 hrs.(1)	0.12M H_2O_2, Ce^{+3}, Cr^{+3}
"	"	"	85% in 1 hr.(1)	Bi^{+3}, Na^{+}
"	"	0.03M	96% in 1 hr.(1)	" "
"	"	0.015M	99% in 1 hr.(1)	0.24M H_2O_2, Ce^{+3}, Cr^{+3}
"	"	0.03M	99% in 1 hr.(4)	At 50° for 15 min. before raising temp. 0.1M H_3PO_4
"	?	0.005-0.015M	98-99% in ? time(2)	
0.5M	75°C.	0.02M	98% in >5 min.(3)	40% $UO_2(NO_3)_2 \cdot 6H_2O$ 25-12 Stainless steel
"	30-78°C.	0.02M	98% in 1 hr.(3)	

References

(1) Smith's Group, Report CN-756, p. 8, June 28, 1943.

(2) Ritter, Black, Schneller, Report CN-758, p. 5, June 26, 1943.

(3) Halperin, Report CN-931, p. 3, September 11, 1943.

(4) Bathis, Olson, Peterson and Stahl, Report CN-958, p. 7, 14, September 25, 1943.

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Date: January 27, 1944	EDITION I, SUPP. 2 SHEET IB2T-4
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu 1. Reduction by Fe	~~Copy No. 18 of 50 copies, Series A~~ Issued to:

Reduction of 48$^{(o)}$ by Fe

HNO_3	H_2SO_4	HF	Temp.	Fe^{++}	48$^{(o)}$ reduced	Other conditions
0.45M	0.025M	1M	22°C.	0.02M	98% in 0.5 hrs.(1)	Zr^{+4}, La^{+3}, Cr^{+3} present

Reference

(1) Bradshaw, Dean, Gaarder, Johnson, Kroner, Koshland and Thompson, Report CN-1095, p. 5, December 1, 1943.

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM.
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IB21-5
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu 1. Reduction by Fe^{++}	~~Copy No. 18 of 50 copies, Series A~~ Issued to:

Reduction of Pu^{+4} by Fe^{++}

The reduction in rapid but incomplete in 1M H_2SO_4

Moles Fe^{++}/mole Pu^{+4}	% Pu^{+4} reduced
0.54	50.5
1.46	92.3
2.98	98.1

Pu^{+4} concentration determined by spectrophotometer.(1)

Reference

(1) Hindman, Kraus and Howland, Report CK-1371, p. 1, March 1, 1944.

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IB2m-1

I. Solution chemistry
B. Oxidation-reduction reactions
2. Reduction of Pu
m. Reduction by HNO_2

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Issued to:

Reduction of $48^{(o)}$ by HNO_2

HNO_3	Temp.	HNO_2	$48^{(o)}$ reduced	Other Conditions
0.6M	75°C.	0.1M	17% in 1 hr.(2)	40% $UO_2(NO_3)_2 \cdot 6H_2O$
0.52M	50°	0.22M	85% in 75 min.(1)	0.033M H_2SO_4
"	22°	0.5M	"Complete" in 150 min.(1)	10% $UO_2(NO_3)_2 \cdot 6H_2O$
"	?	0.13M	51% in 30 min.(1)	0.014M Cr^{+3}
"	?	"	51% in 150 min.(1)	HF
0.3M	75°	0.1M	28% in 1 hr.(2)	40% $UO_2(NO_3)_2 \cdot 6H_2O$
0.1M	"	"	28% in 1 hr.(2)	" " " "

References

(1) Koshland, Report CN-503, p. 17, February 28, 1943.

(2) Miller, Morris, Zoolner, Koshland and Thompson, Report CN-813, p. 4, July 17, 1943.

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Date: September 28, 1943	EDITION I SHEET IB2n-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu n. Reduction by fuming H_2SO_4	~~Copy No. 18 of 50 copies, Series A~~ Issued to:

Reduction of $48^{(o)}$ and $39^{(o)}$ by fuming H_2SO_4

$48^{(o)}$ and $39^{(o)}$ are both reduced (probably completely) by fuming H_2SO_4.(1)

References:

(1) Seaborg and Wahl, Report A-135, p. 11, March 19, 1942.

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB2c-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu c. Stability of Pu(c)	~~Copy No. 18 of 50 copies, Series~~ A Issued to:

Stability of Pu$^{(c)}$ in acid solution.

Acid Solution	Temp.	Pu	Pu$^{(c)}$ reduced	Other Conditions
2M HNO_3	95°C.	48	3% in 90 hrs.$^{(2)}$	
1M HNO_3	"	"	None in 20 hrs.$^{(1)}$	
1M HNO_3, 1M $NaHSO_4$	"	"	11% in 27 hrs.$^{(2)}$	
1M HNO_3, 1M $NaHSO_4$	"	"	35% in 68 hrs.$^{(2)}$	
1M HNO_3, 0.005M H_2SO_4	"	"	7% in 12 days$^{(2)}$	Oxidized by Ag^{+2} Ag^{+2} decomposed by standing or ppting AgCl
1M H_2SO_4	"	"	95% in 40 hrs.$^{(2)}$	
0.1M H_2SO_4	"	"	12% in 5 min.$^{(2)}$	
"	"	"	95% in 40 hrs.$^{(2)}$	
1.0M $HClO_4$	"	"	~50% in 1 day$^{(3)}$	
"	"	"	85% in 5 days$^{(3)}$	
0.1M $HClO_4$	"	"	~50% in 1 day$^{(3)}$	
"	"	"	~100% in 5 days$^{(3)}$	
pH = 3.5	22°(?)	"	85% reduced$^{(7)}$	1M HNO_3 + 6M NaOH
pH = 3.6	"	"	39% reduced$^{(7)}$	1M HNO_3 + 3M NaOH
pH = 3.6	"	"	20% reduced$^{(7)}$	1M HNO_3 + 3M NaAc 0.1M $Cr_2O_7^{=}$
"	"	"	11% reduced$^{(7)}$	1M HNO_3 + 3M NH_4Ac
pH = 4.0	"	"	8% reduced$^{(7)}$	1M HNO_3 + 3M $(NH_4)_2HPO_4$
pH = 4.1-4.6	75°	"	~35% in 10 min.$^{(6)}$	
pH = 4.1-4.6	22°	"	~15% in 10 hrs.$^{(6)}$	3.2M HNO_3 + 2.5M NaAc
pH = 4.1-4.6	"	48	2-5% in 30 min.$^{(6)}$	

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Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB2c-2
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu c. Stability of $Pu^{(o)}$	~~Copy No. 18 of 50 copies, Series A~~ Issued to:

Stability of $Pu^{(o)}$ in alkaline solution

Alkaline solution	Temp.	Pu	$Pu^{(o)}$ reduced	Other Conditions
1M KOH	100°C.	48	None in 40 min.(2)	$0.03MF^-$, $0.005M\ SO_4^=$
$0.33M\ Na_2CO_3$	95°	"	50% in 5 min.(4)	In Pt
" "	"	"	90% in 11 min.(4)	" "
" "	22°	"	10% in 40 hrs.(4)	" "
" "	"	"	50% in 3 hrs.(4)	In glass or wax
$49^{(o)}$ hydroxide ppted. & dissolved in acid	?	49	70% reduced(5)	NaOH ppting. agent

References.

(1) Hamaker, Report CN-239, p. 26, Aug. 15, 1942.

(2) Hamaker, Report CN-250, p. 5, Aug. 31, 1942.

(3) Hamaker, Report CN-261, p. 7, Sept. 15, 1942.

(4) Gofman, Report CN-328, Fig. 1, Oct. 31, 1942.

(5) Cunningham and Werner, Report CN-556, p. 1, March 31, 1943.

(6) Thompson, Davidson, Miller and James, Report CN-556, p. 20, March 31, 1943.

(7) Seaton, Dam, LaChapelle, Lincoln, Sheft and Turk, Report CN-894, p. 29, Aug. 7, 1943.

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Compiled by: A. C. Wahl Date: November 27, 1943.	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IB2c-3
I. Solution chemistry B. Oxidation reduction reactions 2. Reduction of Pu c. Stability of Pu$^{(o)}$	Copy ~~No. 48 of 50 copies, Series~~ A Issued to:

Stability of 48$^{(o)}$ in HNO_3

HNO_3	Temp.	48$^{(o)}$ reduced	Other Conditions	
5M	50°C.	~1% in 1 hr.(1)		48 oxidized in 5N HNO_3 with "$NaBiO_3$" at 50° C. 2/3 $NaBiO_3$ added at start, 1/3 after 45 min. All the $NaBiO_3$ was probably not destroyed in these experiments.
"	"	~3% in 3 hrs.(1)		
"	"	~2% in 5 hrs.(1)		
"	22°	~4% in 23 hrs.(1)	1 hr. at 50°C. before lowering temp.	
"	"	~1% in 7 days.(1)		
1M	75°	1-6% in 1 hr.(1)		
"	"	2-5% in 3 hrs.(1)		
"	"	1.5% in 5 hrs.(1)		

References

(1) Baldwin, Hoff and Sax, Report CN-958, p. 24, Sept. 25, 1943.

Compiled by: A. C. Wahl
Date: January 27, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM
EDITION I, SUPP. 2 SHEET IB2c-4

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      c. Stability of $Pu^{(o)}$

C[redacted]

Issued to:

Stability of $Pu^{(o)}$ in diethyl ether

H_2O phase: 1N HNO_3, sat. NH_4NO_3, $Cr_2O_7^{=}$, ~500 mg. Pu/l.

Ether phase: previously treated with aq. $Cr_2O_7^{=}$, 50-100 mg. Pu/l.

$$\frac{H_2O}{\text{Ether}} = \frac{1}{2}, \text{ total vol.} = 2\text{-}5\ \mu\text{l.}$$

$<2\%$ $Pu^{(o)}$ reduced/hr.

Reference

(1) Patton, Report CK-1145, p. 21, Dec. 11, 1943.

[redacted]

Compiled by: A. C. Wahl

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IB2c-5

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      c. Stability of Pu$^{(c)}$

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Issued to:

Stability of Pu^{+6} in alkaline solution

Base	Reduction in alkaline solution
0.5M NH_4OH	Very little Pu^{+6} ppted -- 97% still Pu^{+6} after acidifying(1)
0.5M NaOH	Large crystals slowly formed -- 96% still Pu^{+6} after acidifying(1)

References

(1) Connick, McVey and Sheline, Report CN-1306, p. 7, Feb. 10, 1944.

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Date: November 27, 1943	EDITION I, SUPP. 1 SHEET IB2p-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu p. Reduction by $C_2O_4^=$	C[redacted] Issued to:

Reduction of $48^{(o)}$ by $C_2O_4^=$

Acid	Temp.	$C_2O_4^=$	$48^{(o)}$ reduced	Other Conditions
?	80°C.	?	99% in 45 min.(1)	48 oxidized with $C_2O_7^=$ and two-fold excess $C_2O_4^=$ was added.
?	30°	?	10% in 45 min.(1)	

Reference

(1) James and Thompson, Report CN-914, p. 18, Sept. 1, 1943.

[redacted]T

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IB2p-2
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu p. Reduction by $C_2O_4^=$	~~Copy No. 18 of 50 copies, Series A~~ Issued to:

Reduction of Pu^{+6} by $H_2C_2O_4$

Acid	Temp.	$H_2C_2O_4$	49 reduced	Other conditions
1M HNO_3	50°C.	0.03M	99% in 1 hr. at 50°C. and 0.5 hrs. at 22°C.(1)	1M HF, 0.1M H_3PO_4, 0.001M Mn^{++}
1M HNO_3	"	0.1M	96% in 1 hr. at 50°C.(1) and 0.5 hrs. at 22°C.	1M HF, 0.1M H_3PO_4
1M HNO_3	35°	0.04M	"Complete" in 1 hr.(2)	0.05M HF, 0.005M Mn^{++}

References

(1) Halperin, Report CN-1115, p. 29, December 13, 1943.

(2) Ritter, Black and Johnson, Report CN-1276, p. 4 and 6, March 6, 1944.

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IB2q-1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu q. Reduction by H_2CO	~~Copy No. 18 of 50 copies, Series A~~ Issued to:

Reduction of $Pu^{(6)}$ by H_2CO in HNO_3

HNO_3	Temp.	H_2CO	Reduction
1 N	25-35°C.	1-2%	Satisfactory in 1-2 hrs. in 0.5N HF(1)

Reference

(1) Ritter, Black and Johnson, Report CN-1276, p. 5, 6, March 6, 1944.

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Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I. SUPP. 3 SHEET IB2r-1

[redacted] Series A

Issued to:

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      r. Reduction by Sn

Reduction of Pu^{+6} and Pu^{+4} by Sn

Acid	Pu	Sn^{++}	Reduction
0.5M HCl	0.02M Pu^{+6}	0.06M Sn^{++}	Reduced to Pu^{+3} very fast (1)
?	Pu^{+6} and Pu^{+4}	eq. amount	80% $Pu^{+4} \longrightarrow Pu^{+3}$ (2)

References

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

(2) Hindman, Kraus and Howland, Report CK-1371, p. 1, March 1, 1944.

Compiled by: A. C. Wahl Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IB2a.1
I. Solution chemistry B. Oxidation-reduction reactions 2. Reduction of Pu a. Reduction by Zn	Cop[redacted]eries A Issued to:

Reduction of Pu^{+6} with Zn

Acid	Pu^{+6}	Reduction
0.5M HCl	0.02M	Reduced to Pu^{+4} (1)

Reference

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

[redacted]

Compiled by: A. C. Wahl

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET B2t-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    2. Reduction of Pu
      t. Reduction by Hg_2^{++}

Co[redacted]ies A

Issued to:

Reduction of Pu^{+4} by Hg_2^{++}

Acid	Reduction
HNO_3	No reduction (1)

Reference

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

[redacted]

[redacted]

Compiled by: A. C. Wahl

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I   SHEET IB3a-1

I. Solution chemistry
  B. Oxidation-reduction reactions
    3. Oxidation states of Pu
      a. Oxidation-number of $Pu^{(r)}$

Copy [redacted] A

Issued to:

Oxidation-number of $Pu^{(r)}$ from composition of "$Pu(IO_3)_4$"

$49^{(r)}$ precipitated as the iodate, dried and weighed. Assuming 165,000 dis./min./μg. 49 and no water of crystallization, the mole ratio $\frac{Pu}{IO_3^-} = \frac{1}{3.9}$. Therefore, oxidation-number of $Pu^{(r)} = +4.$(1)

Since the specific activity of 49 measured by weighing "PuO_2" (88% 49) and "$Pu(IO_3)_4$" (25% 49) agreed, it is likely that there are four IO_3^- per 49 as assumed. Therefore, oxidation-number of $Pu^{(r)} = +4.$(2)

6.35 μg. "$Pu(IO_3)_4$" weighed and the IO_3^- titrated with I^-, $S_2O_3^=$. Found 74.9% IO_3^- in compound (theory, assuming $Pu(IO_3)_4$, is 74.5%). Therefore, oxidation-number of $Pu^{(r)} = +4.$(3)

Above experiment repeated. Found 77% IO_3^-. Probable error = 8%. Therefore, oxidation-number of $Pu^{(r)} = +4.$(4)

Oxidation-number of $Pu^{(r)}$ from composition of "$Pu(C_2O_4)_2$"

The $C_2O_4^=$ in "$Pu(C_2O_4)_2$" was titrated with Ce^{+4}. Found 2.17 moles $C_2O_4^=$/mole Pu. Therefore, oxidation-number of $Pu^{(r)} = +4.$(5)

References

(1) Cunningham and Werner, Report CN-299, p. 1, Oct. 15, 1942.

(2) Cunningham and Werner, Report CN-419, p. 19, Jan. 15, 1943.

(3) Cunningham and Werner, Report CN-454, p. 3, Jan. 31, 1943.

(4) Cunningham, Werner and Cefola, Report CN-467, p. 6, Feb. 13, 1943.

(5) Cunningham and Werner, Report CN-556, p. 1, March 31, 1943.

[redacted]

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Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB3b-1
I. Solution chemistry B. Oxidation-reduction reactions 3. Oxidation states of Pu b. Oxidation-number of $Pu^{(o)}$	~~Copy No. 18 of 50 copies, Series A~~ Issued to:

Oxidation-number of $Pu^{(o)}$ from the similarity of "$NaPuO_2Ac_3$" to $NaUO_2Ac_3$

$Pu^{(o)}$ coprecipitates with $NaUO_2Ac_3$ at U/Pu ratios from 2×10^7 to 2.3. This indicates mixed crystal formation and similarity of UO_2^{++} and "PuO_2^{++}". Probable oxidation-number $Pu^{(o)} = +6.$(1)

$NaUO_2Ac_3$ and "$NaPuO_2Ac_3$" have similar crystal structure (both tetrahedral (cubic system) and both isotropic) indicating similarity of UO_2^{++} and "PuO_2^{++}". Probable oxidation-number $Pu^{(o)} = +6.$(2)

References

(1) Sheline and Hamaker, Report CN-601, p. 3, April 15, 1943.

(2) Sheline and Hamaker, Report CN-723, p. 10, June 20, 1943.

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[redacted]

Compiled by: A. C. Wahl Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IB3c-1
I. Solution chemistry B. Oxidation-reduction reactions 3. Oxidation states of Pu c. A Oxidation-number $Pu^{(r)} \rightarrow Pu^{(o)}$	Copy [redacted] 18 [redacted] Series A Issued to:

Difference in oxidation-number of $Pu^{(r)}$ and $Pu^{(o)}$

LaF_3 containing 49 was dissolved in H_2SO_4. 49 oxidized by Ce^{+4}. Excess Ce^{+4} titrated with Fe^{++} using ruthenium tri-dipyridyl ($E_o = -1.33V.$) as indicator. 1.1×10^{-2} μ moles Pu = 1.95×10^{-2} μ moles Ce^{+4}.(1) (Blank used 1.0×10^{-2} μ moles Ce^{+4}.)

0.035 μ moles Pu oxidized with 0.0500 μ eq. $Cr_2O_7^{=}$. Found 0.032 μ moles Pu oxidized by LaF_3 precipitation. Experiment repeated with 0.047 μ moles Pu and 0.0500 μ eq. $Cr_2O_7^{=}$. Found 0.043 μ moles oxidized. Evidence for a one step oxidation.(2)

Pu oxidized with insufficient $Cr_2O_7^{=}$. Precipitate "$PuOCrO_4$" formed. $Pu^{(o)}$ in supernatant liquid precipitated as "$NaPuO_2Ac_3$". $Pu^{(r)}$ precipitated with LaF_3. Found: equivalents $Cr_2O_7^{=}$/moles $Pu^{(o)}$ 1.9, 2.9.(3,4)

References

(1) Cunningham and Werner, Report CN-363, p. 8, Oct. 31, 1942.

(2) Cunningham and Werner, Report CN-454, p. 4, Jan. 31, 1943.

(3) Sheline and Hamaker, Report CN-654, p. 24, May 20, 1943.

(4) Sheline and Hamaker, Report CN-723, p. 5, June 20, 1943.

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IB3c-2
I. Solution chemistry B. Oxidation-reduction reactions 3. Oxidation states of Pu c. Δ Oxidation-number $Pu^{+4} \rightarrow Pu^{+6}$	Co[redacted]ies A Issued to:

Difference in oxidation number between Pu^{+4} and Pu^{+6}

a. Known excess $Cr_2O_7^=$ oxidized Pu^{+4} (1 hr. at 100°C.), ppt. $NaPuO_2Ac_3$, titrate excess $Cr_2O_7^=$ with Fe^{++}. Equivalents $Cr_2O_7^=$/mole Pu = 2.16, 2.06, av. = 2.11. (73,000 c/m/μg 49 used to calculate moles Pu)(1)

b. 1 equivalent of $Cr_2O_7^=$/mole Pu^{+4} added. % Pu oxidized analyzed by several methods.

(1) LaF_3 analysis gave	2.16 eq. $Cr_2O_7^=$/mole Pu
(2) LaF_3 analysis gave ($Cr_2O_7^=$ and H_2SO_4 present)	1.99 eq. $Cr_2O_7^=$/mole Pu
(3) $NaPuO_2Ac_3$ analysis gave (73,000 c/m/μg 49 used to calculate moles Pu)(1)	2.06 eq. $Cr_2O_7^=$/mole Pu

Reference

(1) Connick, Gofman, McVey and Sheline, Report CK-1265, Jan. 26, 1944.

[redacted]

[redacted]

Compiled by: A. C. Wahl Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET IB3d-1
I. Solution chemistry B. Oxidation-reduction reactions 3. Oxidation states of Pu d. 3rd oxidation state	Copy [redacted], Series A Issued to:

Evidence for a 3rd oxidation state of Pu

If 48 is treated with I^- or SO_2, $La_2(C_2O_4)_3$ carries ~90% of the 48.

If 48 is treated with NH_3OHCl, $La_2(Cr_2O_4)_3$ carries >95% of the 48.

Reference

(1) Reas, Report CN-1134, p. 5, December 1, 1943.

[redacted]

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Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IB3d-2

I. Solution chemistry
    B. Oxidation-reduction reactions
        3. Oxidation state of Pu
            d. 3rd oxidation state

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Issued to:

Evidence for a 3rd oxidation state of Pu

Pu^{+4} soln. (green) in 0.6 N HNO_3 + SO_2 gave purple soln.(1)

	Solubility of Oxalate (0.25M $H_2C_2O_4$, ~0.8M H^+)	Solubility of Fluoride (~1N HF, ~0.5M H^+)
From purple sol'n.	~50 mg/l.	~50 mg/l.
From Pu^{+4} green sol'n.	~850 mg/l.	>1300 mg/l.

The above data indicate an oxidation state of $Pu < +4$ (possibly +3).

Reference

(1) Mastick and Wahl, Report LA-63, February 22, 1944.

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Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IB31-1

I. Solution chemistry
    B. Oxidation-reduction reactions
        3. Oxidation states of Pu
            1. △ Oxidation-number $Pu^{+3} \rightarrow Pu^{+4}$

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Issued to:

Difference in oxidation-number of Pu^{+3} and Pu^{+4}

(a) Pu^{+3} potassium sulfate precipitated, dissolved in HNO_3, $Cr_2O_7^=$ added, $Pu(OH)_4$ ppted and reppted, excess $Cr_2O_7^=$ in OH^- supernatant titrated with Fe^{++}.

Found 1.08, 0.93 eq. $Cr_2O_7^=$/mole Pu(1)

(b) 0.54 moles Fe^{++}/mole Pu^{+4} in 1M H_2SO_4 added 50.5% Pu^{+4} reduced (measured with spectrophotometer).

Found 1.07 eq. Fe^{++}/mole Pu(2)

(c) Sn^{++} added to Pu^{+4} in 1.5M HCl. Decrease in Pu^{+4} concentration measured by spectrophotometer.

Found 1.2 eq. Sn^{++}/mole Pu(2)

(d) Ce^{+4} added to Pu^{+3} solution. Pu^{+3}, Pu^{+4}, Pu^{+6} concentrations measured with spectrophotometer.

Found .94 eq. Ce^{+4}/mole Pu(2)

References

(1) Connick, McVey and Sheline, Report CN-1360, p. 5, Feb. 10, 1944.

(2) Hindman, Kraus and Howland, Report CN-1371, p. 1, March 1, 1944.

[redacted]

Compiled by: A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IB4-1
I. Solution chemistry B. Oxidation-reduction reactions 4. Reduction of Pu$^{(r)}$ to the metal	[redacted] Issued to:

Reduction of 48$^{(r)}$ to the metal from water solutions

No 48 plated on Zn amalgam in 2 hours from acid solution (Po and Cd tracers did plate under the same conditions).(1),(2)

~20% 48 went into a 3% Na amalgam along with Ce carrier. $CeCl_3$ solution used.(3)

References

(1) Wahl, Ph.D. Thesis, Univ. of Calif., Berkeley, Calif., p. 27, Feb. 1942.

(2) Seaborg, and Wahl, Report A-135, p. 8, March 19, 1942.

(3) Nagel and Cefola, Report CN-328, p. 13, October 31, 1942.

[redacted]

[redacted]

Compiled by: A. C. Wahl Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IB5a.1
I. Solution chemistry B. Oxidation-reduction reactions 5. Pu potentials a. $Pu^{+3} \longrightarrow Pu^{+4} + e^-$	Copy [redacted]ies A Issued to:

Potential of $Pu^{+3} \longrightarrow Pu^{+4} + e^-$

Acid	Pu	E*	Method
0.4M H_2SO_4	0.017M Pu	< -0.54v.	I^- reduces Pu^{+4} to Pu^{+3} (1)
0.5M H_2SO_4	$8x10^{-8}$M Pu	< -0.65v.	Polarographic titration(2)
1M H_2SO_4	?	-0.75v.	Known amt. Fe^{++} added and relative amount Pu^{+3} and Pu^{+4} measured by spectrophotometer.(3)
1M HCl	0.02M Pu	-0.966±.005v.	Potentiometric titration of Pu^{+4} with Sn^{++}(4)
1M H_2SO_4	"	-0.75± 0.02v.	" " " " " "(4)
1M $HClO_4$	"	-0.95 ± 0.02v.	" " " " " "(4)
1M H_2SO_4	"	-0.74 ± 0.02v.	" " " Pu^{+3} with Ce^{+4} after reduction of Pu^{+4} with Fe^{++}(4)

* Referred to the Hydrogen-Hydrogen in couple as zero.

References

(1) Hindman, Kraus, Howland and Cunningham, Report CN-1324, p. 3 and 5, February 1, 1944.

(2) Watters and Orlemann, Report CN-1324, p. 7, February 1, 1944.

(3) Hindman, Kraus and Howland, Report CK-1371, p. 1, March 1, 1944.

(4) Hindman, Kraus and Howland, Report CK-1371, p. 8, March 1, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IC1-1
I. Solution chemistry C. Nature of ions in solution 1. Evidence from transference experiments	Cop[redacted]s A Issued to:

Evidence for a sulfate complex of $48^{(r)}$

In H_2SO_4 (0.1N or 0.01N):

$48^{(r)}$ A	$48^{(r)}$ M	$48^{(r)}$ C	$39^{(r)}$ A	$39^{(r)}$ M	$39^{(r)}$ C
4-33%	63-87%	11-17%	0-2%	2-13%	87-96%

A = activity found in anode compartment of cell.
M = activity found in middle compartment of cell.
C = activity found in cathode compartment of cell.

The fact that $48^{(r)}$ did not go predominately to cathode compartment showed that part of it at least must be present as a sulfate complex.(1)

Evidence against existence of NO_3^- and ClO_4^- complexes of $48^{(r)}$, $39^{(r)}$, $48^{(o)}$, $39^{(o)}$, from transference experiments

	A	M	C
1M $HClO_4$ solution			
$48^{(o)}$	0.2%	28%	71%
$39^{(o)}$	0	38	62
0.1M $HClO_4$ solution			
$48^{(r)}$	0	9	91
$39^{(r)}$	0	30	70
~0.1N HNO_3 solution			
$48^{(r)}$	0	21	79
$39^{(r)}$	2	49	49

A = % of activity found in anode compartment of cell.
M = % of activity found in middle compartment of cell.
C = % of activity found in cathode compartment of cell.

The fact that both $48^{(r)}$ and $39^{(r)}$ went quantitatively to the cathode in HNO_3 or $HClO_4$ solution showed that both exist predominately as uncomplexed positive ions in these solutions. The same is true for $39^{(o)}$ and $48^{(o)}$. This would seem to be evidence that the ions of the upper state of both are similar to UO_2^{++}.(2)

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IC1-2
I. Solution chemistry C. Nature of ions in solution 1. Evidence from transference experiments	[redacted] A Issued to:

References

(1) Gofman and Connick, Report CN-239, p. 5, July 15, 1942.

(2) Gofman and Connick, Report CN-261, p. 4, Aug. 15, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IC2-1
I. Solution chemistry C. Nature of ions in solution 2. Evidence from oxidation-reduction reactions	C[redacted], Series A Issued to:

Evidence for a sulfate complex of $48^{(r)}$

(a) From slowness of oxidation by $Cr_2O_7^=$ in H_2SO_4 solution.

(See IB1k-6.)

(b) From slowness of oxidation by BrO_3^- in H_2SO_4 solution.

(See IB1j-1, 2, 3.)

Evidence for an iodate complex of $48^{(r)}$ from slowness of oxidation by Br_2 in $NaIO_3$ solution ($HClO_4$ present)

(See IB1p-1.)

Evidence against nitrate complex of $48^{(r)}$ from fact that rate of oxidation by $Cr_2O_7^=$ in HNO_3 and $HClO_4$ are almost the same

(See IB1k-1, 2, 3, 4, 5.)

Difference in oxidation number of $49^{(r)}$ and $49^{(o)}$

(See IB3e-1)

Oxidation of $49^{(r)}$ to fluoride-soluble state

Oxidation of $49^{(r)}$ by one equivalent of $Cr_2O_7^=$ showed 93% to be oxidized to a fluoride-soluble state.

(See IB3e-1.)

[redacted]

[redacted]

Compiled by: A. C. Wahl

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM.

EDITION I, SUPP. 3 SHEET IC2-2

I. Solution chemistry
C. Nature of ions in solution
2. Evidence from oxidation reduction reactions

[redacted] A

Issued to:

Evidence for Pu^{+4} complexes from polarographic titrations

Solution	Pu	Half wave potential	Conclusion
0.5M H_2SO_4	0.0008M	-0.648	
0.05M H_2SO_4, 0.8M $K_2C_2O_4$	0.0009M	-0.082	Oxalate complex(1)
0.2M " , 0.18M "	0.0009M	-0.235	
0.1M " , 9M NH_4F	0.0006M	+0.872	Very strong fluoride complex(1)
0.2M HAc, 0.2M NaAc	0.001M	-0.281	Acetate complex(1)

Reference

(1) Watters, Report CK-1371, p. 10, March 1, 1944.

Oxidation number of Pu(c)

(See IB3c-2).

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IC3-1
I. Solution chemistry C. Nature of ions in solution 3. Evidence from precipitation reactions	[redacted] Issued to:

Similarity of $49^{(o)}$ ion to UO_2^{++} from microscopic examination of crystals of $NaUO_2Ac_3$ and "$NaPuO_2Ac_3$"

(See IA2a-2.)

Evidence for fluoride complex of $49^{(r)}$ from solubility of $49^{(r)}$ fluoride in 10N NH_4F

(See IA1f-7.)

Evidence for iodate complex of $49^{(r)}$ from solubility of $49^{(r)}$ iodate in excess HIO_3

(See IA1i-2.)

Evidence that lower state is Pu^{+4} from determination of IO_3^- in $49^{(r)}$ iodate

(See IA1i-3.)

Evidence that lower state is Pu^{+4} from determination of $C_2O_4^=$ in $49^{(r)}$ oxalate

(See IA1l-1.)

Evidence against a strong phosphate complex of $49^{(r)}$ from fact that solubility of $49^{(r)}$ phosphate increases only slightly with phosphate concentration

(See IA1p-5.)

[redacted]

Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IC3-1
I. Solution chemistry C. Nature of ions in solution 3. Evidence from precipitation reactions	Co[redacted] Series: A Issued to:

Evidence for hydrolysis of Pu^{+4} to $Pu(OH)_3^+$ from solubility of Pu^{+4} in $SO_4^=$ solution

(See IAlr-2.)

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IC4-1
I. Solution chemistry C. Nature of ions in solution 4. Evidence from absorption spectra	Co[redacted], Series A Issued to:

Nature of Pu^{+3}, Pu^{+4}, Pu^{+6} ions from absorption spectra in aqueous solution

(See VIII-6.)

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET ID1-1
I. Solution chemistry D. Extraction into organic solvents 1. Extraction into ether	C[redacted]s A Issued to:

Extraction of $48^{(r)}$ and $48^{(o)}$ into diethyl ether

Water layer containing 48 and saturated with $LiNO_3$ extracted with 1.5 times its volume of ether. Separate experiments done with 48 originally in oxidized or reduced state. % $48^{(o)}$ extracted into ether = 60-85%
% $48^{(r)}$ " " " = 2.5%
Some reduction by ether.(1)

Ether (previously shaken with $KMnO_4$ to remove reducing impurities) extracted 50% of $48^{(o)}$ from a water solution of equal volume. $48^{(o)}$ solution prepared by oxidizing Pu with sodium bismuthate in 5N HNO_3. Solution made 1N in HCl to complex Bi^{+3} and then extracted. Only 2-3% of Pu was reduced.(2) Attempts also made to extract $48^{(o)}$ into ether from a water solution prepared by oxidizing 48 in 1N HNO_3 with $K_2Cr_2O_7$ in the presence of varying amounts of $UO_2(NO_3)_2 \cdot 6H_2O$. with the following results. Fluoride analysis made on water layer for amount of Pu reduced by extraction.

$UO_2(NO_3)_2 \cdot 6H_2O$	% Pu found in ether layer	% $48^{(r)}$ in H_2O layer after extraction
0%	0.7	1.5
10	1.9	7.3
25	2.4	9.2
50	8.2	9.5

Diethyl ether also found to extract <1% of $48^{(r)}$ from a 5N HCl solution.(2)

Extraction of $49^{(o)}$ into ether from fused $UO_2(NO_3)_2 \cdot 6H_2O$

Bombarded $UO_2(NO_3)_2 \cdot 6H_2O$ melted and Pu oxidized by $Cr_2O_7^{=}$ and HNO_3. Treated with ether. 90% of $49^{(o)}$ in ether layer.(3)

References

(1) Magel and Koshland, Report CN-239, p. 10, July 15, 1942.

(2) Brady and Orlemann, Report CK-888, p. 6, Aug. 7, 1943.

(3) Magel, Report CN-261, p. 14, Aug. 15, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1　　SHEET ID1-2

I. Solution chemistry
  D. Extraction into organic solvents
    1. Extraction into ether

Copy [redacted]eries A

Issued to:

Extraction of 48$^{(o)}$ into ether$^{(1)}$

Water solution of Pu$^{(o)}$ (prepared by oxidation with "$NaBiO_3$") extracted with ether previously shaken with acid $Cr_2O_7^{=}$ solution.

HNO_3 conc. of H_2O layer	% Pu extracted
2	6
3	12
4	35
4.5	55

NH_4NO_3 conc. of H_2O layer	% Pu extracted
5	17.4
6	24.3
7	55.0 (?)
8	45.4
9	51.4
10	57.4

Reference

(1) Katz and Orlemann, Report CK-932, p. 5, Sept. 11, 1943

[redacted]

[redacted]

Compiled by: R. B. Duffield

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET ID1-3

Co[redacted]eries A

Issued to:

I. Solution chemistry
  D. Extraction into organic solvents
    1. Extraction into ether

Extraction of $Pu^{(o)}$ into diethyl ether

One ml of solution 0.07M Pu^{+4} (16 mg), 10M NH_4NO_3, 1M HNO_3, 0.02M $K_2Cr_2O_7$ (after oxidation of Pu) heated to oxidize Pu and then extracted with one ml portions of ether. Two extractions removed 67% of Pu present (74% of $Pu^{(o)}$ present). Pu then extracted back into 1M HCl sol'n. Ether solution of $Pu^{(o)}$ nitrate was pink. The extraction process gave good separation from Th, La, Pt, Bi, Ca, Cr, Na.(1)

Reference

(1) Brady, Dixon, Smith, Orlemann, Report CK-1169, p. 1, Feb. 1, 1944.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET ID2-1
I. Solution chemistry D. Extraction into organic solvents 2. Diphenylthiocarbazone-chloroform	C[redacted]ries A Issued to:

Extraction of $48^{(r)}$ into a chloroform solution of diphenylthiocarbazone

A chloroform solution of diphenylthiocarbazone did not extract $48^{(r)}$ out of water at pH 3-11.(1)

References

(1) Thompson, Report CN-328, p. 10, October 31, 1942.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET ID3-1
I. Solution chemistry D. Extraction into organic solvents 3. Cupferron-chloroform	[redacted] Issued to:

Extraction of 48$^{(r)}$ with cupferron into chloroform

Preliminary experiments showed that when a water solution (volume = 20 ml.) at pH 1.4 containing 48$^{(r)}$ and 2 drops of a 6% solution of cupferron was extracted with three 2-ml. portions of chloroform, 100% of the 48$^{(r)}$ present was found in the chloroform layer.(1)

This was checked(2) using a water solution (volume = 30 ml.) again at pH 1.4 containing 48$^{(r)}$ and three times adding to it 2 drops of 6% cupferron solution and extracting with 3 ml. of chloroform. The 48$^{(r)}$ was found distributed as follows:

First $CHCl_3$ extract - 68 c./min.
Second " " - 7 " "
Third " " - 0 " "
H_2O layer - 0 " "

The effect of the pH of the water layer on the extraction has also been determined using the above procedure.(2)

pH	% of Pu in $CHCl_3$ phase
2.0	100
1.4	93
1.1	91
0.8	91
0.5	82
0.3	67
0.2	72
0.1	72
0.0	68

When the water solution (pH 1.4) contained 10 mg. fluoride ion in 20 ml., extraction by the above procedure still took out 92% of the 48$^{(r)}$. Less than 5% of the fluoride ion was found in the chloroform layer.(1)

Extraction of 48$^{(r)}$ into 15% H_2SO_4 from cupferron-chloroform solution.

First experiments showed only 35% of 48$^{(r)}$ extracted into 15% H_2SO_4 from cupferron-chloroform.(1)

Repetition using three portions of 15% H_2SO_4 at a temperature of >30° C. showed 100% of Pu to be extracted into water layer. The chloroform layer turned green showing decomposition of cupferron.(3)

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IDS-2
I. Solution chemistry D. Extraction into organic solvents 3. Cupferron-chloroform	[redacted] A Issued to:

Extraction of Na^+, Mg^{++}, Li^+ with cupferron into chloroform

Twenty ml. of a water phase (pH 1.4), containing 50 mg. each of Na_2SO_4, Li_2SO_4, $MgSO_4$, extracted with 2 ml. of chloroform after addition of two drops of 6% solution of cupferron. No salts were detectable in the chloroform layer within the limits of sensitivity of the experiment. (0.1 mg.).(4)

Extractions of 48(r) with other organic complexing agents.

Extractions done by technique described above using a water phase of pH ~1.5 in all cases.(5)

Complexing agent	Immiscible solvent	% Pu extracted
Cupferron	Ether	100
Picrolonic acid	Ether	0
α-Nitroso β-naphthol	Chloroform	0
Ammonium thiocyanate	Ether	<10
α-Benzoin oxime	Methylisobutyl ketone	0
Tetra phenyl arsonium chloride with KI	Chloroform	0
Tetra phenyl arsonium chloride with ammonium thiocyanate	Chloroform	0

References

(1) Potratz, Report CK-733, p. 3, June 15, 1943.

(2) Anderson, Cowen, Martens and Potratz, Report CK-801, p. 7, July 17, 1943.

(3) Anderson, Cowen, Martens and Potratz, Report CK-801, p. 9, July 17, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IDS-3
I. Solution chemistry D. Extraction into organic solvents 3. Cupferron-chloroform	[redacted]es A Issued to:

References (cont.)

(4) Anderson, Cowen, Martens and Potratz, Report CK-801, p. 8, July 17, 1943.

(5) Anderson, Cowen, Martens and Potratz, Report CK-801, p. 9, July 17, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield

Date: January 27, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 2 SHEET ID4-1

I. Solution chemistry
D. Extraction into organic solvents
4. Miscellaneous solvents

C[redacted]ries A

Issued to:

Extraction of Pu into organic solvents(1)

Distribution of Pu between 10M NH_4NO_3, 1M HNO_3 solution and various organic solvents.

Solvent	% Pu$^{(r)}$ extracted	% Pu$^{(o)}$ extracted
Diethyl ether	<1	50
Dichloroethyl ether	3	---
Hexyl ether	<1	---
n-Butyl ether	<1	---
Hexanol	23	Hexanol oxidized
Methylamyl alcohol	42	---
Heptanol	15	---
Heptadecanol	10	---
2-Ethylbutyl alcohol	16	---
2-Ethyl hexanol	<1	---
2-Ethylbutyl acetate	1.5	---
2-Ethylbutyl cellosolve	71	---
" "	1.5 *	---
" "	1 **	---
Triglycoldichloride	72	---
Nitromethane	58	70
Nitroethane	34	61

* Extracted from 1M HNO_3

** " " 5M NH_4Cl, 1M HCl

A preliminary experiment to determine the distribution of light elements between nitromethane and 10M NH_4NO_3, 1M HNO_3 solution indicates satisfactory purification from S[illegible], Be, Mg, Al, K but poor separation from Na, Si, Ca. (See VB-4.)

Reference

(1) Brody and Orlemann, Report CK-1221, p. 1, Jan. 5, 1944.

The same results are given in MUC-GTS-352, p. 1, Dec. 20, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield
Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM
EDITION I, SUPP. I SHEET ID4-1

I. Solution chemistry
D. Extraction into organic solvents
4. Acetylacetonate-chloroform

[redacted]es A

Issued to:

Extraction of 48(r) acetylacetonate into $CHCl_3$ (1)

Extracted 10 ml. of aqueous solution (NH_4Ac-HAc buffered) of Pu + acetylacetone with three successive portions of $CHCl_3$ of 10-, 5- and 5-ml. volume.

pH of aqueous layer	% Pu in $CHCl_3$
2	20.8
3	79.0
4	94.0
4.5	94.4

NH_4Ac-HAc buffered solution of Pu, 1.3M in $C_2O_4^{=}$, pH 4.5 extracted with 10% $CHCl_3$ solution of acetylacetone. 1% of Pu in $CHCl_3$.

Reference

(1) Dixon and Orlemann, Report CK-932, p. 9, Sept. 11, 1943.

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION 1, SUPP. 3 SHEET ID4-2
I. Solution chemistry D. Extraction into organic solvents 4. Extraction into miscellaneous solvents	[redacted] A Issued to:

Distribution of Pu^{+4} between 10M NH_4NO_3 solution and miscellaneous organic solvents(1)

Aqueous phase	Non-aqueous phase	% Pu^{+4} in non-aqueous phase
10M NH_4NO_3 - 1M HNO_3	Methyl-n-amyl ketone	59.3
" "	Methyl-iso-butyl ketone	81.8
" "	Methyl-ethyl ketone	78.9
" "	Phenyl cellosolve	21.0
" "	Xylene	9.6
" "	Isophorone	36.5

Reference

(1) Stein, Brody and Orlemann, Report CN-1331, p. 20, March 1, 1944.

(Same data given in Report MUC-GTS-450, p. 3, February 12, 1944.)

[redacted]

[redacted]

Compiled by: R. B. Duffield

HANDBOOK, CHEMISTRY OF PLUTONIUM

Date: May 1, 1944

EDITION I, SUPP. 3 SHEET ID4-3

I. Solution chemistry
    D. Extraction into organic solvents
        4. Extraction into miscellaneous solvents

Co[redacted]

Issued to:

Summary of existing data on distribution of Pu between equal volumes of concentrated salt solutions and organic solvents(1)

Solvent	% Pu^{+4} ext'd*	% Pu^{+6} ext'd.†	% Pu^{+3} ext'd.‡
Diethyl ether	< 1	50	< 1
Dichloroethyl ether	3	10	< 1
Hexyl ether	< 1	--	< 1
n-Butyl ether	< 1	--	--
Hexanol	23	--	--
Methyl amyl alcohol	42	--	< 1
Heptanol	15	--	--
Heptadecanol	10	--	< 1
2-Ethyl butyl alcohol	16	--	< 1
2-Ethyl hexanol	< 1	--	< 1
2-Ethyl butyl acetate	1.5	--	< 1
2-Ethyl butyl cellosolve	71	--	< 1
Phenyl cellosolve	21	--	< 1
Triglycoldichloride	72	--	< 1
Nitroethane	34	61	--
Nitro methane	58	70	< 1
Nitro benzene	8	--	--
Xylene	10	--	--
Methylethyl ketone + 15% xyline	79	--	< 1

[redacted]

[redacted]

Compiled by: R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET ID4-2.
I. Solution chemistry D. Extraction into organic solvents 4. Extraction into miscellaneous solvents	Cop[redacted]s A Issued to:

Summary of existing data on distribution of Pu between equal volumes of concentrated salt solutions and organic solvents(1) (cont.)

Solvent	% Pu^{+4} ext'd.*	% Pu^{+6} ext'd.†	% Pu^{+3} ext'd.‡
Methyl isobutyl ketone	82	--	<1
Methyl-n-amyl ketone	59	--	<1
Isophorone	37	--	<1
Acetophenone	89	--	--

* Aqueous phase - 10M NH_4NO_3, 1N HNO_3

† Aqueous phase - 10M NH_4NO_3, 1N HNO_3 + 0.02M $K_2Cr_2O_7$

‡ Aqueous phase - 5M NH_4Cl, 1N HCl, sat'd. SO_2

Reference

(1) Jensen, Report CK-1512, p. 2, April 1, 1944.

[redacted]

[redacted]

Compiled by: C. S. Garner Date: September 28, 1943	HAND BOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IE1-1
I. "Solution" chemistry E. Distillation studies 1. Oxides	Ca[redacted] copies, Series A Issued to:

Non-distillation of 48 from HNO_3 solution, OsO_4 carrier

Mixture of 48, HNO_3, Ag^+, $S_2O_8^=$, OsO_4 distilled, OsO_4 caught in alkali. No 48 distilled.(1)

No 48 distilled from 48, HNO_3, OsO_4 (12 mg. Os) mixture. Addition of Ce^{+4}, $KBrO_3$ to oxidize 48 resulted in no volatilization of 48. 77% 48 left in residue in oxidized state.(2)

48, HNO_3, Ce^{+4}, O_3, OsO_4 (?) distilled. No 48 found in distillate.(3)

48, HNO_3, Ag^{+2}, O_3 mixture heated 30 min. at 70° C. Os carrier added, O_3 bubbled thru 30 min. at 90°. No 48 distilled.(4), (5)

Non-distillation of 48 from $HClO_4$ solution, RuO_4 carrier

No 48 distilled from mixture of 48, $HClO_4$, RuO_4 (7 mg. Ru). Same result when Ce^{+4}, $KBrO_3$ added to oxidize 48.(6)

References

(1) Seaborg and Wahl, Report A-135, p. 14, March 19, 1942.

(2) Seaborg's Group, Report CC-169, p. 9, July 3, 1942.

(3) Seaborg's Group, Report CC-179, p. 5, July 11, 1942.

(4) Seaborg's Group, Report CC-198, p. 6, July 18, 1942.

(5) English and James, Report CN-239, p. 21, July 15, 1942.

(6) Seaborg's Group, Report CC-169, p. 10, July 3, 1942.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IE2-1
I. "Solution" chemistry E. Distillation studies 2. Chlorides	[redacted] A Issued to:

Non-distillation of 48 from HCl-H_2SO_4 solution, $GeCl_4$ carrier

48, HCl, H_2SO_4, $GeCl_4$ (5mg. Ge) mixture distilled. No 48 distilled.(1)

Reference

(1) English, Report CC-125, p. 1, June 13, 1942.

[redacted]

[redacted]

Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IE3-1
I. "Solution" chemistry E. Distillation studies 3. Bromides	Copy [redacted] Series A Issued to:

Non-distillation of 48 from HBr solution, $SeBr_4$ carrier

48, conc. HBr, $SeBr_4$ (10 mg. Se) mixture distilled to small volume, more $SeBr_4$ added and again distilled. No 48 found in distillate.(1),(2)

References

(1) Seaborg's Group, Report CC-198, p. 7, July 18, 1942.

(2) English and James, Report CN-239, p. 21, July 15, 1942.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IIA-1
II. "Dry" chemistry A. The metal	Cop[redacted]ies A Issued to:

Attempted preparation of 48 or 49 amalgam

30 g. $CeCl_3.6H_2O$ dissolved in 10 ml. water. 48 added, solution shaken with 25 g. 3% Na amalgam. Very dilute Ce amalgam formed, separated by decantation, washed several times by shaking with water. 20% of the 48 found in Ce amalgam.(1)

49 sulfate solution electrolyzed using mercury cathode. "Yield was not complete."(2) 49 sulfate solution electrolyzed 6 hours at 12 volts (3ma.) using mercury cathode. Mercury washed three times then distilled, leaving behind 7-38% of the original 49.(3)

48 solution, 0.5M in UO_2^{++}, 0.5M in HNO_3, electrolyzed at 3.9-4.3 volts (2.5 a.) for 2 hours. No 48 found in mercury cathode.(4)

48 followed U into U amalgams prepared by treating U from decomposed UH_3 with Hg. The dilute amalgams (solid down to 8% U, completely liquid at 3% U) were separable into a liquid phase of low U content and a solid phase of higher U content. The 48 distributed with the U between these phases. On exposing an amalgam to air a powder formed which contained the 48.(13)

UH_3 similarly absorbed Hg, forming mixtures which separated on filtration into a liquid and solid phase. The mixture may be a suspension of UH_3 in Hg (active Xe not released on formation of amalgam from n-bombarded U). On standing in air a powder was released which resembled UH_3 but contained oxygen (perhaps $(UH_3)_4O$?). 48 followed UH_3 in mixture and in powder separated.(13)

Attempt to prepare 49 metal by H_2 reduction of PuO_2

49 nitrate solution evaporated on quartz, ignited to yellowish-brown oxide. Black product obtained on hydrogenation at 450°C. 2N HCl gave no gas evolution observable under a microscope (under same conditions 1 μg. U gave vigorous gas evolution).(2) (See IIB-1 for "suboxide" formation.)

Volatilization of 48 or 49 from bombarded U

Heating d-bombarded U at 1500°C. in high vacuum indicated slight volatilization of the 48. n-bombarded U heated at 1890° in high vacuum; the melted U vaporized at appreciable rate, the 49 concentrating in the vapor (1 p. 49/10^8 p. U). 49 metal more volatile than U?(5)

[redacted]

[redacted]

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Date: September 28, 1943	EDITION I SHEET IIA-2
II. "Dry" chemistry A. The metal	Copy [redacted] Series A Issued to:

Volatilization of 48 or 49 from bombarded U (cont.)

286 mg. n-bombarded U (0.5 c. 49/min./mg. U) heated at 2000°C. in ZrO_2-lined graphite crucible for 5 min. Distillate collected on a Ta condenser tube. 1.6 mg. (0.56%) of U and 70 c./min. (50%) of 49 distilled. Ratio of 49/U increased by factor of 88. Assuming vapor pressure of U at 2000° = 0.1 mm. Hg (CP-255), vapor pressure of 49 metal at 2000° $\approx$ 10 mm. Hg, if perfect solution formation occurred.(6)

Attempts to prepare 49 metal from "PuF_4" or PuO_2 and Na, Mg or Ba

About 1 µg. "PuF_4" heated with Na in Pyrex tube. Product had "metallic luster." 4 µg. "$PuF_4 \cdot xKF$" treated likewise, had "cokey appearance". 6N HCl gave gas bubbles with both products. PuO_2 similarly treated exhibited "some change in appearance of powdered oxide but no visible gas evolution" (in dil. HCl). 16 µg. "PuF_4" so treated gave a hard, flaky substance. No assurance metal produced in any case.(7)

Two samples "PuF_4", one of PuO_2, heated at 1550-1750°C. with Mg in vacuum (10^{-5} mm. Hg), using BeO crucibles. "Minute globules of metal formed." White, reflective, soft, like Pt. No tarnishing in air after 3 weeks. Gas evolution in 1N HCl. May be Pu-Mg alloy. (Th, Ce, La metals prepared similarly.)(8)

Fluxes and reducing agents studied for micropreparation of U; methods may be applicable to Pu. (No visible reaction of U with ThO_2-lined quartz vessel.)(9)

PuO_2 samples treated with Mg or Ba gave, in one case, small spheres of "metal", in other cases, BeO crucibles used appeared empty after attempted reductions. Latter interpreted as Pu-Ba or Pu-Mg alloys which wetted BeO and soaked into pores of crucibles.(10)

Reaction of 49 "metal" with H_2 and O_2

0.2 µg. 49 "metal" ("PuF_4" + Na product -- see IIA-2) heated at 500°C. in BeO crucible (vacuum of 10^{-5} mm. Hg), H_2 admitted at 650 mm., temperature lowered to room temp. over 4 hours. H_2 pumped off, air let in. No visible change. O_2 (dried with P_2O_5) let in, heated for 1 hour at 100°, 200°, 300°, 500°, 800°. No visible change up to 300°; slight tarnishing at 500° and dark brown coating at 800°.(11)

[redacted]

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IIA-3
II. "Dry" chemistry A. The metal	Co[redacted] Issued to:

Reaction of 49 "metal" with Cl_2

(See IID-3.)

Reaction of 49 "metal" with Br_2

(See IIE-1.)

Conditions for reduction of Pu halides to metal

Thermodynamic considerations and an estimated melting point of 900-1300°C. for plutonium metal suggest that of the various combinations of plutonium halides and active metals only Mg and $PuBr_4$ appears promising as means of obtaining fused Pu metal. Considerations are also presented for obtaining U and Th metals by halide reduction.(12)

Suggested methods for obtaining pure Pu metal

(See VC-1.)

References.

(1) Magel and Cefola, Report CN-328, p. 12, Oct. 31, 1942.
(2) Magel and Cefola, Report CN-328, p. 13, Oct. 31, 1942.
(3) Magel and Cefola, Report CN-343, p. 9, Nov. 15, 1942.
(4) Cook, Report CK-676, p. 3, May 15, 1943.
(5) Magel, Report CN-343, p. 16, Nov. 15, 1942.
(6) Magel, Report CN-363, p. 7, Nov. 16, 1942.
(7) Kirk and Rosenfels, Report CN&CF-591, p. 2, April 15, 1943.
(8) Baumback, Rosenfels, and Kirk, Report CK-806, p. 2, July 17, 1943.
(9) Baumback, Rosenfels and Kirk, Report CK-736, p. 5, June 21, 1943.
(10) Kirk, Rosenfels, Baumback and Zoolner, Report CK-888, p. 2, Aug. 7, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IIA-4
II. "Dry" chemistry A. The metal	[redacted] Issued to:

References (cont.)

(11) Cunningham, Davidson, Katz and Kirk, Report CK-806, p. 3, July 17, 1943.

(12) Brewer, Report CK-895, Aug. 18, 1943.

(13) Butler, Voigt, Wolter and Ayres, Report CN-925, p. 2, Sept. 8, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: November 27, 1943	EDITION I, SUPP. 1 SHEET IIA-5
II. "Dry" chemistry A. The metal	C[redacted] Issued to:

Reduction of Pu halides with metallic reducing agents

Discussion of factors involved. "Best" procedure may be "PuF_4" + Mg in ThO_2 crucibles heated a short time at ~1600°C. Pu more electropositive than Zn.(1)

Equilibria of type Metal + Pu halide $\rightleftharpoons$ Metal halide + Pu investigated. 48 added to mixture of fused metal halide and metal, its distribution determined. For U-UBr_3 system, mol-fraction 48 in salt/mol-fraction 48 in metal varied from 3 to 35 at 900 - 1140°C. For Pb-$PbCl_2$ system, ratio was 82 - 850 at 555 - 700°C.(2)

More attempts at reduction of "PuF_4" in ThO_2 crucibles, using $CaCl_2$ flux + Mg, Mg+Na, Ba+Na, Li+Na, all with no definite evidence of metal production. Recommended use of two metals (e.g., Ba, Na) which vaporize at different temperatures to have "getter" action, reduce oxidation of any metal formed. Also, have Pu compound in small crucible inside larger one which contains the reductant, vapor phase reduction.(3)

Electrolytic co-deposition of 48 with Mn(4)

(See IIIA1-2).

Notes on special meeting on metal production(5)

Non-reduction of PuO_2 by atomic hydrogen

PuO_2 (~5 μg.) in Pt boat gave no indication of reduction with H at incandescent heat. Oxides of U, Al, Be, Th also not reduced; oxides of Cu, Sb, Fe, Cb, Zn, Ti, Mn, and UF_4 were reduced under conditions used.(6)

References

(1) Baumbach, Rosenfels and Kirk, Report CK-932, p. 1, September 11, 1943.

(2) Webster, Report CK-942, p. 5, September 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IIA-6
II. "Dry" chemistry A. The metal	Copy [redacted] Issued to:

References (continued)

(3) Baumbach, Rosenfels and Kirk, Report CK-987, p. 1., October 11, 1943.

(4) Cook, Report CK-940, September 1943.

(5) Magel, Report CK-966, September 21, 1943.

(6) Manning, Report CK-987, p. 7, October 11, 1943.

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: January 27, 1944	EDITION I, SUPP. 2 SHEET IIA-7
II. "Dry" chemistry A. The metal	[redacted] copies, Series A Issued to:

Reduction of Pu halides with metallic reducing agents

Details of procedure for reducing "PuF_4" with alkali and alkaline earth metals. Attempts to prepare powdered Pu metal for Zachariasen. Technics for mounting of micro specimens of metal.(1)

Reduction of Pu halides with atomic H

"PuF_4" (~10 μg.) in Pt boat treated with atomic H for 15 min. at 700°C. Finely-divided material produced which reacted rapidly to form yellow PuO_2. Some of the pieces tested with HCl gave gas evolution. Some Pu metal may have been formed.(2)

Density of Pu metal

Micro capillary method, butyl phthalate used as immersion medium.

Metal	Weight	Method of Prep'n.	Observed density
Pu	6.73 μg.	"PuF_4" + Ba	15.5 g./cc.
"	4.22	" " "	15.0
"	21.38	" " Mg	15.5
"	27.79	" " "	15.6
U	58.75	UF_4 " Ba	18.8 (19.0 ± 0.2 handbook val.)
Cu	21.55	Remelted filing	9.3 (8.9 " ")
Pt	25.67	" globule	20.4 (21.45 " ")
"	"	Same sample	22.5

Results for Pu probably too low due to air-holes, etc. in samples.(3,4)

Slow reduction of "PuF_4" with Li at 1000°C. gave a metal powder subjected to X-ray analysis by Zachariasen and found to contain LiF, Li_2O, ThO_2 and an unknown substance, which if assumed to be Pu metal would have a density of 13.01 g./cc. This substance may be a "lower oxide" of some sort.(5)

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: January 27, 1944	EDITION 1, SUPP. 2 SHEET IIA-8
II. "Dry" chemistry A. The metal	[redacted] Issued to:

Formation of hydride from Pu metal

(See II I-1.)

References

(1) Baumbach, Fried, Kirk and Rosenfels, Report CK-1145, p. 9, December 11, 1943.

(2) Karle, Report CK-1145, p. 18, December 11, 1943.

(3) Kirk, Rosenfels, Fried and Baumbach, Report CK-1145, p. 15, December 11, 1943.

(4) Seaborg's Group, Memo MUC-GTS-296, November 15, 1943.

(5) Baumbach and Fried, Report CK-1221, p. 12, January 5, 1944.

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Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IIA-9
II. "Dry" chemistry A. The metal	Co[redacted] Issued to:

Equilibria involving Pu metal in fused metal-metal halide systems

Investigations of equilibria of the type

$$\text{Metal} + \text{Pu halide} \rightleftharpoons \text{Metal halide} + \text{Pu}$$

have continued with the aid of 48 tracer. The distribution constant K is defined as the ratio of the mol-fraction of 48 (or 49) in the salt to that in the metal (see IIA-5).

In the U-UBr_3 system at 1000°C. $K_{48} > 40$, while K_{UX_1} = 1.3-1.5; i.e., Pu appears more electropositive than U and Th.(1)

K_{48} = 8.7 (very low?) in the Mn, $MnCl_2$ system at 730°C.(1)

K_{48} = 0.16 in the Ca, $CaCl_2$ system at 800°C., Ca appearing to be more electropositive than Pu.(1)

K_{48} = 92 in the Mg-MgI_2 system at ~700°C., and is 17 in the Mg-$MgCl_2$ system at 760°C. on the basis of a single experiment. For U, K_{22} = 7.5 in the latter system. All this work was carried out in Fe crucibles. It would seem from these results that Pu is more electropositive than U and Mg, U more positive than Mg. Experiments with milligram amounts of U were in agreement with the tracer U experiments after a correction was made for the solubility of U in Mg (0.2% U by weight). Assuming Raoult's Law the K_U in terms of activities becomes 0.0022, and U is more electronegative than Mg. Since the solubility of Pu in Mg is not known it is uncertain whether a similar state exists in the case of Pu. Tracer experiments in Mg crucibles gave K_{48} = 0.92 and K_{22} = 0.72.(2)

Action of Cl_2 on Pu metal

(See IID-4.)

Action of Br_2 on U-Pu alloy

(See IIE-4.)

References

(1) Webster, Report CK-1359, February 1, 1944.

(2) Fontana and Fong, Report CK-1529, February 21, 1944.

S[redacted]

[redacted]

Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IIB-1
II. "Dry" chemistry B. Oxides	[redacted] Issued to:

Non-volatilization of 48 oxide in air or in O_2

LaF_3 containing 48 evaporated to dryness several times with HNO_3, then ignited in air. No volatilization of 48.(1)

U_3O_8 containing 48 heated at 1600°C. in Pt-lined graphite crucible. 48 did not volatilize.(2)

48, 39 (HNO_3 solutions) evaporated on Pt, heated in O_2 at 1000°C. for 1 hour in presence of 1 µg. La (as La_2O_3). No volatilization of 48. (About 22% of the 39 volatilized).(3)

Non-volatilization of 48 oxide from Na_2O_2 melt

48 (H_2SO_2 solution) evaporated on Fe. Na_2O_2 added, heated to 500°C. Melt leached with acid. 79% 48 found by LaF_3 analysis. Probably no volatilization of 48.(4)

48 (HNO_3 solution) evaporated on Ag, ignited at 500°C. Na_2O_2 added, fused state maintained in O_2 atmosphere at 500° for 5 min. Dish and contents dissolved in HNO_3; analysis gave 80% 48 present. Probably no volatilization of 48.(5)

H_2 reduction of PuO_2

(See IIA-1.)

"Reduction" of PuO_2 with Mg, Ba

(See IIA-2.)

Conversion of PuO_2 to "PuF_4"

(See IIC-1, IIC-3.)

Possible formation of 49 "suboxide"

PuO_2 (~4 µg.) heated 2 min. at 1600°C. in vacuum (10^{-5} mm. Hg). No volatilization of 49 occurred; color changed from yellow-brown to shiny black, accompanied by shrinkage in size. Product did not react with dilute HCl.(6) (See IIA-1 for data on similar-appearing material formed by H_2 reduction of PuO_2.)

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IIB-2

II. "Dry" chemistry
B. Oxides

C[redacted]s A

Issued to:

References

(1) Seaborg's Group, Report CC-179, p. 7, July 11, 1942.

(2) English and James, Report CN-239, p. 22, July 15, 1942.

(3) Garner, Report CN-282, p. 2, Sept. 16, 1942.

(4) Willard and Brown, Report CN-250, p. 3, Aug. 16, 1942.

(5) Garner, Report CN-261, p. 3, Aug. 15, 1942.

(6) Kirk, Rosenfels, Baumbach and Zoolner, Report CK-888, p. 5, Aug. 7, 1943.

[redacted]

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Compiled by: C. S. Garner
Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM
EDITION I, SUPP. 1 SHEET IIB-3

II. "Dry" chemistry
B. Oxides

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Issued to:

Non-reduction of PuO_2 by atomic hydrogen

(See IIA-5)

Conversion of PuO_2 to "$PuBr_4$" with HBr gas

(See IIE-2.)

Vapor pressure of PuO_2

About 5 µg. 49 nitrate evaporated on tantalum, coated with thin layer of collodion, ignited in vacuo (residue was black and may have been carbide rather than oxide). Effusion method used (no check on apparatus with substances of known vapor pressure). Rough values are:(1)

1400°C.	2.18×10^{-8} mm. Hg.
1600	2.40×10^{-7}
1800	6.40×10^{-6}

Reference

(1) Magel, Report CK-1040, p. 1, November 6, 1943.

[redacted]

[redacted]

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Date: January 27, 1944	EDITION I, SUPP. 2 SHEET IIB-4
II. "Dry" chemistry B. Oxides	Co[redacted] Issued to:

Relative volatility of PuO_2 and U oxides

Of the order of 50% of a 0.02 µg. PuO_2 sample volatilized from a Pt filament at 1400°C. in 30 min. in an O_2 atmosphere. U oxides under the same conditions volatilized much more readily.(1)

Possible reaction of PuO_2 with H_2

Similar experiments at 1000°C. in a H_2 atmosphere indicated that the Pu was partly buried in the Pt filament. Effect may be due to $PuO_2 + 2H_2 \longrightarrow H_2O + Pu$ reaction driven to right by formation of a Pt-Pu alloy, or, less likely, to formation of Pt hydride and adsorption of Pu in some form on the rougher surface.(1)

X-ray diffraction by PuO_2; density of PuO_2

Analysis of the pattern from a 10 µg. sample of PuO_2 indicated the crystal has the fluorite structure, cubic system, with $a = 5.370 \pm 0.002$ Å. Assuming the composition is PuO_2 the density is calculated as 11.54 ± 0.01 g./cc. Data on an unknown Pu compound are also given.(2,3)

Oxide	a	Density
PuO_2	5.370 Å	11.54 g./cc.
UO_2	5.46	10.94
ThO_2	5.587	9.99

Preparation of PuO_2

A detailed discussion of technics used for preparing PuO_2 on a 100-microgram scale preparatory to hydrofluorination and reduction to metal. Ignition of nitrate solution in lucite-lined Pt boats, final ignition at 700°C.(4)

Conversion of PuO_2 to "PuF_4"

(See IIC-6.)

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[redacted]

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Date: January 27, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 2 SHEET IIB-5

II. "Dry" chemistry

Copy No. 18 of 50 copies, Series A

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References

(1) Bradshaw and Davidson, Report CK-1072, p. 10, November 6, 1943.

(2) Mooney and Zachariasen, Report CK-1096, p. 12, November 27, 1943.

(3) Mooney and Zachariasen, Report CK-1119, December 8, 1943.

(4) Kirk and Rosenfels, Report CK-1145, p. 7, December 11, 1943.

[redacted]

Compiled by: C. S. Garner Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 5 SHEET IIB-6
II. "Dry" chemistry B. Oxides	Copy [redacted] s A Issued to:

Composition of "PuO_2"

A very pure sample of Pu^{+4} nitrate was ignited at 700°C. to the oxide. A sample submitted for O-analysis indicated the formula $PuO_{2.15}$.(1)

Attempt to prepare PuO_3

Approx. 2 mg. 49 as "$PuO_2(NO_3)_2 \cdot xH_2O$" was heated in a stream of dry air for 1 hour each at 100°, 145°, 200°, then 1.5 hours more at 200°, 4 hours at 275°, 1 hour at 350°, 2 hours each at 400°, 500°, 600°, 700°C. PuO_2 was formed above 275°. There was no evidence on the basis of weight changes of a stable PuO_3.(1)

Existence of "PuO"(?)

There is some evidence that a lower oxide, perhaps PuO, may be produced by reaction of PuO_2 with Ba at 1000° (2), and by the action of Ba, Ca or Li on "black" PuF_3.(3),(4)

Preparation of fluorides from PuO_2

(See IIC-7.)

Preparation of chlorides from PuO_2

(See IID-4.)

Preparation of bromides from PuO_2

(See IIE-4.)

References

(1) Johns, Moulton and Wahl, Report LAMS-72, p. 14, April 1, 1944.

(2) Baumbach, et al, Report CK-1372, p. 2, March 1, 1944.

(3) Seaborg, Memo MUC-GTS-450, February 12, 1944.

(4) Fried and Baumbach, Report CK-1169, p. 5, February 1, 1944.

[redacted]

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Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IIC-1
II. "Dry" chemistry C. Fluorides	[redacted] Series A Issued to:

Non-volatilization of 48 higher fluoride ("wet" preparation)

$UO_2SO_4 + Zn \longrightarrow U^{+4}$. 48 added, precipitated with UF_4 by addition of dil. HF, dried at 50°C. Portion assayed for 48. 3.6 g. heated in F_2 at 450° (Cu boat). UF_6 volatilized almost completely, <1% 48 volatilized.(1),(2) Suggested "dry" fluoride method (#1) based on this (see IVB-1). Volatilization of 48 higher fluoride when prepared by "dry" method (see below) suggests that "wet" preparation may give an oxyfluoride.

0.2 g. Se, Te, or Sb, 0.5 g. UF_4 containing 48 ("wet" prep.) treated with F_2 at 250°C. SeF_6, TeF_6, SbF_5 distilled, leaving 48 behind.(3)

Volatilization of 48 and 49 higher fluoride ("dry" preparation)

48 incorporated into UF_4 by a "dry" method:

$$UO_2(NO_3)_2 + 48 \longrightarrow U_3O_8\text{-}48$$

$$U_3O_8\text{-}48 + H_2 \longrightarrow UO_2\text{-}48$$

$$UO_2\text{-}48 + HF \longrightarrow UF_4\text{-}48$$

$$UF_4\text{-}48 + F_2 \xrightarrow{250^\circ} UF_6\uparrow\text{, 48 not volatilized.}$$

$$UF_4\text{-}48 + F_2 \xrightarrow{500^\circ} UF_6\uparrow + \text{48 higher fluoride}$$

Also, n-bombarded $UF_4 + F_2 \xrightarrow{250\text{-}300^\circ} UF_6\uparrow$. Disc counted, chemical analysis showed 21 c./min. 49 remaining.(4) Proposed new "dry" fluoride method (#2) (see IVB-1).

48, 39 in 8 mg. UF_4 treated with F_2. 48 began vaporizing appreciably at 315°, distilled completely at 520°. (UF_6 started at 145°, complete at 270°; 39 went with UF_6.)(5),(6)

0.2 µg. PuO_2, HF at 500°C. caused changed appearance but no volatilization of 49. F_2 at 250° for 30 min. volatilized about 5% of the 49. F_2 at 500° volatilized 100% of the 49 (still some visible material on plate, indicating PuO_2 not pure).(7)

Samples of UF_4 from 10^{-5} – 100 µg. (22 tracer + U) gave weight losses of 8-78% when treated with HF at 600°C. Similar treatment of Pu from 10^{-6} – 1 µg. (48 or 49) never gave more than 5% vaporized in same time. "PuF_4" less volatile than UF_4 at 600°?(8)

0.01 µg. 49, 1.5 mg. LaF_3 (how mixed?) treated with F_2 at 500°C. for 30 min. 99.8% 49 volatilized.(9)

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IIC-2

II. "Dry" chemistry
C. Fluorides

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Volatilization of 48 and 49 higher fluoride (cont.)

48 incorporated (how?) in 0.5 g. $BiPO_4$, F_2 at 600°C. for 30 min. 99.5% 48 volatilized.(10)

Stability of 48 and 49 higher fluoride

UF_4-48 + $F_2 \xrightarrow{500^\circ} UF_6\uparrow$ + 48 higher fluoride↑, trapped at -78°C. Trap warmed to 25°, dry N_2 passed thru into water reflux condenser in which UF_6 and 48 higher fluoride would be collected. All U distilled, only 15% 48. 81% 48 which distilled was in oxidized state, 9% in reduced state. 48 found in reduced state could not have volatilized in that state and must have been formed after removal of the F_2: Pu higher fluoride $\rightleftharpoons$ "PuF_4" + F_2 ?(11)

Similar experiment, except trap (at -78° originally) placed in boiling water 4 min., then recooled to -78°. 59% U swept out by N_2 stream, <1% 48 with it. Heating higher fluoride in absence of F_2 readily decomposes it to non-volatile lower fluoride. If F_2 was used as a sweeping gas, 60% 48 was swept out with 29% U at 31°C., 34% 48 with 9% U at 40°. Assuming perfect solution laws, vapor pressure of Pu higher fluoride is about 650 mm. at 31°, about 2 atm. at 40°, giving a boiling point of about 32°C. (UF_6 boils at 56°C.)(12)

n-bombarded UF_6 distilled, fractions analyzed for 49, 39, U. Following equilibria suggested (although equilibrium conditions were probably not obtained, and reactions were not established):

$$\text{"}PuF_4\text{"} + UF_6 \rightleftharpoons \text{"}PuF_6\text{"} + UF_4 \qquad K_1 \sim 3\times10^{-10}$$

$$\text{"}NpF_4\text{"} + UF_6 \rightleftharpoons \text{"}NpF_6\text{"} + UF_4 \qquad K_2 \sim 3\times10^{-12}$$

$$\text{"}PuF_6\text{"} \rightleftharpoons \text{"}PuF_4\text{"} + F_2 \qquad K_4 \sim 3\times10^{9} K_3$$

$$\text{"}NpF_6\text{"} \rightleftharpoons \text{"}NpF_4\text{"} + F_2 \qquad K_5 \sim 3\times10^{11} K_3,\ \text{where } K_3 \text{ is}$$

the dissociation constant for $UF_6 \rightleftharpoons UF_4 + F_2$, all presumably at about room temperature.(10)

Conversion of PuO_2 to "PuF_4"

About 4 µg. 49 (nitrate solution) ignited for 10 min. at 800°C. Weight of PuO_2 = 4.78 µg. Treated with HF at 550 ± 50°C. for ½ hour. Bright yellow oxide became dark, nearly black, increased in weight to 5.55 µg. Hydrofluorinated again, weight 5.54 µg. A third HF treatment caused "no significant change in weight." Percent increase in weight = 15.9; that required for $PuO_2 \rightarrow PuF_4$ is 16.3%.(13)

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IIC-3

II. "Dry" chemistry
C. Fluorides

[redacted] A

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Attempted fluorination of "PuF_4" with CoF_3, AgF_2

$UO_2(NO_3)_2$ + 49, evaporated, ignited, then H_2 (to give UO_2), HF to give UF_4-"PuF_4". Mixed with CoF_3, heated in He at 500° for 30 min. All U vaporized, but no 49.(7)

Similar experiment, except UF_4-"PuF_4" heated with CoF_3 in vacuum at 300°. Same result.(14)

0.3 g. CoF_2 slurried with 1000 c./min. 49, dried, heated with HF at 550° for several hours, then F_2 at 300°. Color changed from pink to light brown ($CoF_2 \rightarrow CoF_3$). Evacuated, heated at 300° for 1 hour, then 360° for 1 hour. All 49 remained in residue.(14)

0.3 g. Ag slurried with 48, dried, then HF at 550°, F_2 (N_2 + F_2 at 100°, then F_2 at 200°). Heated in vacuum at 320° for several hours, then at 520°. AgF_2 decomposed at 435°. >95% 48 remained in the residue.(14)

Deposition of 48 higher fluoride in metal vessels

Technic for semi-micro fluorination of 49 in Ni vessels.(14)

Below 400° deposition in Cu tubing is rapid. At about 425° the higher fluoride is carried in a F_2 stream thru Cu tubing with relatively little deposition.(15)

References

(1) Brown and Perlman, Report CC-94, p. 1, May 23, 1942.

(2) Brown, Report CC-136, p. 3, June 20, 1942.

(3) Brown, Report CC-169, p. 5, July 3, 1942.

(4) Brown and Hill, Report CC-216, p. 11, Aug. 1, 1942.

(5) Brown and Hill, Report CN-250, p. 2, Aug. 16, 1942.

(6) Brown, Hill and Webster, Report CN-282, p. 2, Sept. 16, 1942.

(7) Brown, Hill and Jaffey, Report CN-343, p. 13, Nov. 15, 1942.

(8) Brown, Hill and Bohlmann, Report CN-728, p. 66, June 21, 1943.

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Date: September 28, 1943

EDITION I

SHEET IIC-4

[redacted]

II. "Dry" chemistry
C. Fluorides

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References (cont.)

(9) Brown and Hill, Report CN-419, p. 13, Jan. 15, 1943.

(10) Brown, Hill and Jaffey, Report CN-454, p. 12, Jan. 16, 1943.

(11) Brown and Hill, Report CN-363, p. 4, Nov. 16, 1942.

(12) Brown and Hill, Report CN-391, p. 3, Nov. 31, 1942.

(13) Cunningham and Werner, Report CN-556, p. 1, March 16, 1943.

(14) Davidson and Katz, Report CK-806, p. 4, July 17, 1943.

(15) Brown, Hill Bohlmann, Lindner, Anderson and Hubble, Report CN-894, p. 1, Aug. 7, 1943.

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Compiled by C. S. Garner Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IIC-5
II. "Dry" chemistry C. Fluorides	[redacted] es A Issued to:

Volatility of "PuF_4"

About 0.01 μg. 49 spread over $\frac{1}{2}$ cm.^{2} on Pt, treated with HF for 2 hours at 600°C. Placed in Cu block inside quartz vessel. Evacuated, heated to 500°; then rapidly to 700°; held there for 1 hr. About 20% vaporized. Reheated at 700° for 3 hrs. with no further loss. Rehydrofluorinated and again heated 2 hrs. at 700° in vacuum with vaporization of about 35% more. Gases liberated from Cu block may convert some "PuF_4" to less volatile compound? (One determination of UF_4 vapor pressure by effusion method gave 1.9×10^{-4} mm. Hg at 260°C.)(1)

Volatility of Pu "higher fluoride"

Deposition temperature of "higher fluoride" may be lower in CaF_2 tubes than in Cu or Ni.(2)

Summary of previously reported results with possible explanations for behavior. Possibility "higher fluoride" is really an oxyfluoride. Appears relatively non-volatile at 200°C. Apparatus for vaporizing and collecting up to 70% in static F_2 system.(3)

References

(1) Davidson, Report CK-932, p. 4, September 11, 1943.

(2) Katz, Report CK-932, p. 11, September 11, 1943.

(3) Davidson, Katz and Orlemann, Report CK-987, p. 14, October 11, 1943.

[redacted]

Compiled by: C. S. Garner. Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2. SHEET IIC-6
II. "Dry" chemistry C. Fluorides	[redacted] Issued to:

Volatility of Pu "higher fluoride"

Studies of the passage of Pu "higher fluoride" thru long heated tubes. Once the fluoride deposits on a metal surface it cannot be revolatilized appreciably except in a F_2 stream. Essentially same results with CsF_2 tubing as with Cu tubing.(5) Pu can be volatilized as a "higher fluoride" more readily from CeF_3 than from LaF_3.(1)

With the aid of electrically-activated F_2 at room temperature, volatile compound formation was observed for UF_4, UCl_4, U_3O_8, UO_2, UO_2F_2 and UO_3. Much less volatilization (44% vol.) was observed in the case of $\sim$0.04 µg. of PuO_2 ignited on Pt and similarly treated with activated F_2.(2) 22 tracer (ignited, reduced to UO_2 with H_2, hydrofluorinated, then treated with F_2 volatilized and deposited just as Pu "higher fluoride" has done so far. Hence, at present <u>no conclusions can be drawn concerning the behavior of massive amounts of Pu "higher fluoride"</u>.(5)

Volatility of "PuF_4"

48 incorporated in $Cb_2O_5 \cdot xH_2O$ and treated with HF at a temperature which volatilized away CbF_5 was retreated with HF at 700-800°C. About 30% of the 48 volatilized at 700°, 90% at 800°. If LaF_3 or UF_4 carrier was present the volatilization was greatly impeded.(3)

Preparation of "PuF_4"

Details of a system for hydrofluorinating 100-µg. samples of PuO_2 at 550°C. Hydrofluorination for 4 hours in a slow stream of HF may be required for the conversion of 100 µg. PuO_2 to "PuF_4". Several samples were obtained of differing color: gray, purple-tinged transparent, red-brown. Possibly due to impurities, different crystal forms or oxyfluoride formation.(4)

References

(1) Lindner and Bohlmann, Report CN-1025, p. 17, Nov. 8, 1943.

(2) Florin and Davidson, Report CK-1145, p. 4, Dec. 11, 1943.

(3) Tevebaugh and Walsh, Report CN-1060, p. 2, Nov. 8, 1943.

(4) Florin, Report CK-1145, p. 8, Dec. 11, 1943.

(5) Heath and Davidson, Report CK-1221, p. 8, January 5, 1944.

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IIC-7

II. "Dry" chemistry
C. Fluorides

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Attempted fusion of "black" Pu fluoride

If "black" fluoride were PuF_4 it would be expected to fuse at a moderately high temperature. No fusion was observed below 1000°C., on heating the "black" material on Pt in a vacuum of 10^{-5} mm.(1) The "black" fluoride is now known to be PuF_3.

Volatility of PuF_4 and Pu "higher" fluoride

Pu-enriched UF_4, prepared from metal $\longrightarrow$ hydride $\longrightarrow$ UF_4 by HF, gave the same results as observed earlier by Brown with respect to treatment in F_2 at 245°C. Tracer "PuF_4" cannot be volatilized from LaF_3 or large amounts of UF_4 at 850° at which temperature "carrier-free PuF_4" is volatile.(2) (See IIC-5.)

Preparation of Pu "lower" fluorides from PuO_2, etc.

PuF_4 may be made by the action of 20% O_2 - 80% HF on PuO_2 at 550°, or by similar treatment of PuF_3. PuO_2, PuF_3 and PuF_4 all give "brown" PuF_4 when treated with HF containing 5-10% SO_2 at 550°. Weight changes observed usually indicate incomplete conversion of PuO_2 to PuF_3 or PuF_4.(3)

PuF_4 is isomorphous with green UF_4, ThF_4, HfF_4, ZrF_4. Its color is usually "pale brown".(3)

PuF_3 may be produced by a mixture of H_2 and HF on PuO_2 or PuF_4.(3)

PuF_3 is isomorphous with $PuCl_3$, UCl_3, UF_3, LaF_3. Its color is "black" or "purple". The F-Pu atom ratio has been shown by analysis to be 2.8-3.7.(3)

"Purple" PuF_3 + F_2 at 300° gave green "PuF_4" with a loss of weight. "Black" PuF_3 + F_2 at 200° gave a white substance with a greenish cast which formed "black" PuF_3 on heating in Pt to 500° in a vacuum.(3)

Preparation of PuF_3 and PuF_4 from "$Pu(NO_3)_4 \cdot xH_2O$"

Treatment of Pu^{+4} nitrate with dry HF from room temperature to 550° has given "black" PuF_3, "lavender" PuF_3, and "light tan" PuF_4, the former on two 50-mg. runs, the latter on two 1-g. runs.(4)

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HANDBOOK, CHEMISTRY OF PLUTONIUM
EDITION I, SUPP. 3 SHEET IIC-8

II. "Dry" chemistry
C. Fluorides

[redacted]

Issued to:

References

(1) Fried and Jasaitis, Report CK-1169, p. 5, February 1, 1944.

(2) Tevebaugh and Walsh, Report CN-1243, p. 6, January 8, 1944.

(3) Florin, Heath, Meyer and Katz, Report CK-1372, p. 7, March 1, 1944. (See also Report CK-1371 for an abstract of this material.)

(4) Bakes, Garner, Johns, Moulton and Walsh, Report LAMS-72, p. 13, April 1, 1944.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IID-1
II. "Dry" chemistry D. Chlorides	[redacted] Issued to:

Non-volatilization of 48 chloride (or oxide) in air

LaF_3 containing 48 evaporated to dryness several times with conc. HCl, heated on Pt dish with gas-air blast. No 48 volatilized.(1)

Non-volatilization of 48 chloride in presence of $Cl_2 + C$

$UO_2(NO_3)_2$ + 48 converted to U_3O_8-48. Heated at 350-450°C. with $C + Cl_2$. 92% U volatilized, < 7% 48 with it.(2)

Volatilization of 48 and 49 chloride (or oxychloride) in Cl_2 gas

$La(OH)_3$ containing 48, 39, dissolved in HCl, evaporated on quartz. Heated in dry Cl_2 stream for 30 min.:

Temp.	% 48 volatilized	% 39 volatilized
1100°C.	~100	~97
1000°	~96	~96
850°	~89	~89
750°	~19	~71

Probably oxychlorides rather than higher chlorides.(3)

About 0.01 µg. 49 (HNO_3 solution) evaporated to dryness with conc. HCl on quartz. 30 min. in stream of dry Cl_2:

Temp.	% 49 volatilized
1000°C.	100
900°	98
800°	11
700°	5

Results with HCl + Cl_2 same as with HCl alone (see IID-2). HCl, then Cl_2, same as Cl_2 alone. Cl_2 probably had enough O_2 in it to cause oxychloride formation.(4)

Volatilization of 48 and 49 lower chloride in HCl gas

About 0.01 µg. 49 (HNO_3 solution) evaporated on Pt, treated repeatedly with conc. HCl, or heated in dry HCl, or ignited in air to 1000°C., then in dry HCl. Heated in stream of dry HCl for 30 min.:

[redacted]

[redacted]

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Date: September 28, 1943	EDITION I SHEET IID-2
II. "Dry" chemistry D. Chloride	[redacted] A Issued to:

Volatilization of 48 and 49 lower chloride in HCl gas (cont.)

Temp.	% 49 volatilized
700°C.	~100
600°	~ 97
500°	~ 80
400°	~ 12
300°	0

Sublimed chloride retreated with HCl at 500°(30 min.) volatilized 100%.(4)

48, 39, 2 μg. La (as $LaCl_3$) gave about same results as 49 in dry HCl.(5)

Temp.	% 48 volatilized	% 39 volatilized
600°C.	73-96	40-99
500°	63-73	27-89
400°	3-27	6-32
350°	2	7
300°	0	5

Volatilization of 48 and 49 chloride in $CCl_4 + Cl_2$ gas

U_3O_8-48 + CCl_4 + Cl_2 at 400°C. gave 15-25% volatilization of 48. However, U_3O_8 + CCl_4 + Cl_2 at 400° showed non-volatile UX_1Cl_4 (m.p. of $ThCl_4$ ~820°C.) "sticks" to U_3O_8 until latter is nearly all gone, then is carried over with last traces of U. Also, "pseudovolatilization" was observed for some fission products, as follows: n-bombarded U_3O_8 + CCl_4 + Cl_2 at 400° gave 99% U volatilized with 94% γ and 80% β-emitters (should be about 75% and 25%, respectively). A glass-wool plug in the gas stream caught some of these non-volatile fission products, letting thru the U and Cb, Zr, Ru chlorides.(6) This "pseudovolatilization" of UX_1Cl_4 was reduced to ~1% by the addition of 2.2 mg. ThO_2 as a hold-back carrier to 30 mg. U_3O_8.(7) 2.1 mg. La_2O_3 added as a hold-back carrier to 349 mg. U_3O_8 containing 48 had some effect, 89% 48 remaining in the residue.(7)

0.1-0.2 μg. 49 as PuO_2 treated with Cl_2 + CCl_4 vapor in a quartz tube, volatile portion caught in a water trap, or tube washed out. 37 min. treatment gave(8):

Temp.	% 49 volatilized
710°C.	99
600°	7
425°	0

[redacted]

[redacted]

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Date: September 28, 1943	EDITION I SHEET IID-3
II. "Dry" chemistry D. Chlorides	Cop[redacted] Issued to:

Volatilization of 48 "oxychlorides" in Cl_2 or in HCl gas

22 tracer (HNO_3 solution) evaporated on quartz, ignited to U_3O_8, reduced in H_2 to UO_2, heated in Cl_2 (to give UO_2Cl_2) or in HCl (to give $UOCl_2$?). UO_2Cl_2 volatilized over range 750-1000°C., "$UOCl_2$" slightly less volatile. Similar experiments with 48 and 39 indicated 39 in Cl_2 about like UO_2Cl_2, 48 less volatile. Results probably complicated by reaction of oxides with quartz.(9)

Preparation of a 49 chloride from Cl_2 + 49 "metal"

About 0.05 µg. 49 "metal" ("PuF_4" + Na --see IIA-2) placed on sublimation plate, vacuum about 10^{-3} mm. Hg. Temperature of plate raised to 170°C., dry Cl_2 admitted at 2/3 atm., heating continued for 3-5 min., then apparatus cooled and evacuated. Collecting plate cooled to -72°, sublimation plate heated to 350° for 45 min. In three runs, 36, 13, 2% 49 sublimed.(10)

References

(1) Seaborg's Group, Report CC-179, p. 6, July 11, 1942.

(2) Brown, Report CN-250, p. 5, Aug. 16, 1942.

(3) Garner, Report CN-282, p. 1, Sept. 16, 1942.

(4) Garner, Report CN-299, p. 1, Oct. 15, 1942.

(5) Garner, Report CN-328, p. 2, Oct. 31, 1942.

(6) Brown, Hill and Jaffey, Report CN-328, p. 8, Oct. 31, 1942.

(7) Brown, Hill and Jaffey, Report CN-343, p. 15, Nov. 15, 1942.

(8) Brown, Hill and Jaffey, Report CN-454, p. 20, Jan. 16, 1943.

(9) Garner and Kent, Report CN-343, p. 1, Nov. 15, 1942.

(10) Smith and Cunningham, Report CN&CF-647, p. 3, May 15, 1943.

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET IID-4
II. "Dry" chemistry D. Chlorides	Co [redacted] Issued to:

Volatility of tracer Pu chlorides

$La(OH)_3$ precipitated from adsorption column elutriant containing Pu and F.P.s was dissolved in HCl, evaporated on Pt, counted for α- and γ-activity, then heated in a stream of dry HCl for 4 hours. Volatilization of Pu and β-activity was about the same, occuring over the range 600-800°C (95% Pu vol. at 800°).(1)

$Zr(OH)_4$ was similarly prepared and treated, two drops PCl_3 were added, the whole heated in an atmosphere of PCl_3 + HCl at 600° for 2 hours. No essential difference from behavior reported above. The same result was obtained on substitution of $POCl_3$ for PCl_3. When PCl_5 was substituted 95% of the Pu volatilized at 600°; at this temperature the PCl_5 is dissociated into $PCl_3 + Cl_2$. HCl + Cl_2 resulted in 99% volatilization of the Pu at 600°.(1)

Preparation of $PuCl_3$ by the action of Cl_2 on Pu metal

Pu metal + Cl_2 at 450° gave "blue" $PuCl_3$, not volatile at 450°. The $PuCl_3$ was identified by X-ray and chemical analyses. The Cl_2 was used at 60 mm. for 15 min., then pumped off, and the sample held at 450° for 10 min. Under the same conditions U metal formed a volatile sublimate of UCl_4. If $PuCl_4$ exists it presumably has a dissociation pressure of $Cl_2 > 60$ mm. at 450°.(2)

Preparation of Pu chlorides from PuO_2

Dry HCl does not attack massive particles of PuO_2 at 760°C. CCl_4 and Cl_2-CCl_4 react with PuO_2 at 750° to give a chloride volatile at that temperature. S_2Cl_2 vapor at 350° reacted with PuO_2, forming S and a volatile Pu compound.(2)

Preparation of $PuCl_3$ from Pu^{+4} chloride solution

65 mg. 49 as Pu^{+4} chloride solution were treated with NH_3OHCl to reduce the Pu^{+4} to Pu^{+3}, and the solution evaporated and the salt dehydrated in a stream of dry HCl at several hundred degrees. The "slate-blue" solid appeared to be $PuCl_3$.(3)

[redacted]

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Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3, SHEET IID-5

II. "Dry" chemistry
D. Chlorides

Cop[redacted]

Issued to:

Crystal structure of $PuCl_3$

$PuCl_3$ is isomorphous with UCl_3 and $CeCl_3$. The crystal is hexagonal with two molecules per unit cell, each Pu having 9 chloride neighbors. Pu-Cl distance = 2.92 A.(4)

References

(1) Wolter, Report CN-1243, p. 3, January 8, 1944.

(2) Hagemann, Karle, Katz, Hyde and Davidson, Report CK-1372, p. 11, March 1, 1944.

(3) Garner and Johns, Report LAMS-72, p. 14, April 1, 1944.

(4) Zachariasen, Report CK-1487, March 21, 1944.

[redacted]

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Compiled by: C. S. Garner
Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM
EDITION I
SHEET IIE-1

II. "Dry" chemistry
E. Bromides

Co[redacted]

Issued to:

Non-volatilization of 48 bromide (or oxide) in air

LaF_3 containing 48 evaporated to dryness several times with conc. HBr, then ignited in air with a gas-air blast. No volatilization of 48.(1),(2)

Preparation of a 49 bromide from Br_2 + 49 "metal"

About 0.05 μg. 49 "metal" treated with Br_2, sublimed in vacuo. (See details of preparing a 49 chloride, IID-3.) Bromination at 210°, sublimation at 250°. 63, 42% 49 sublimed in two runs.(3)

References

(1) Seaborg's Group, Report CC-198, p. 7, July 18, 1942.

(2) English and James, Report CN-239, p. 22, July 15, 1942.

(3) Smith and Cunningham, Report CN&CF-647, p. 3, May 15, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IIE-2

II. "Dry" chemistry
E. Bromides

Co[redacted]

Issued to:

Preparation of "$PuBr_4$" from PuO_2 + HBr gas

About 0.01 µg. 49 ignited to PuO_2 on Pt, put in quartz tube, HBr (from Br_2 + tetralin, dried by naphthalene and P_2O_5) flowed over at 850°C. for 30 min. Carbon deposited in tube. All Pu volatilized, but collection was poor. In a static system of HBr at atmospheric pressure, PuO_2 on a foil was heated to a "barely visible red heat"; 60% Pu collected on a cold finger, all volatilized.(1)

Reference

(1) Katz and Orlemann, Report CK-932, p. 7, September 11, 1943.

[redacted]

Compiled by: C. S. Garner. Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET IIE-3
II. "Dry" chemistry E. Bromides	C[redacted] Issued to:

Volatility of "Pu bromide"

$La(OH)_3$-48 dissolved in HBr, evaporated on Pt. "Some volatilization" in an HBr stream at 800-850°C.(1)

49 ignited in air on Pt to PuO_2. Treated with pure HBr gas for 30 min. (greaseless apparatus described). In case A about 0.02 µg. Pu used over a large area;(2) in case B about 1 µg. Pu used over an area of 1 mm.^{2} (3)

Temp.	% 49 vol. (case A)	% 49 vol. (case B)	% U vol. from UO_2*
300°C.	—	—	5
400	—	7	72
500	15	—	—
600	33	42	85
700	90	100	95

* "Tracer" amounts UO_2 treated in same way with HBr gas.(2) Mg. amounts UO_2 did not volatilize even at 800°C.(3)

U containing 300 c. 49/min./g. U was converted to hydride then treated with dry HBr for 1 hour at 700°C. 62% of the U and 25% of the Pu volatilized. The U probably volatilized as UBr_4: $2UBr_3 \longrightarrow UBr_4 + UBr_2$.(4)

Attempt to make "$PuBr_4$" from PuO_2 + molten CBr_4

About 0.01 µg. Pu ignited to oxide on Pt. Placed in 1 ml. Pt crucible, covered with CBr_4, put in glass tube, evacuated, dry N_2 admitted, heated slowly to 130° (CBr_4 distilled out), evacuated, heated to 500°C. No loss of Pu from crucible. Same result for $CBr_4 + HgBr_2$ treatment.(5)

References

(1) Wolter, Report CN-1060, p. 5, November 8, 1943.

(2) Katz and Davidson, Report CK-1145, p. 1, December 11, 1943.

(3) Katz and Davidson, Report CK-1221, p. 5, January 5, 1944.

(4) Ayres, Report CC-1139, p. 4, December 10, 1943.

(5) Bradshaw and Davidson, Report CK-1221, p. 7, January 5, 1944.

[redacted]

Compiled by: C. S. Garner Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IIE-4
II. "Dry" chemistry E. Bromides	Copy N[redacted] Issued to:

Action of Br_2 on U-Pu alloy

A U-Pu alloy treated with Br_2 gave a product subliming at ~450°C. The vapor pressure of "$PuBr_4$" was estimated as 0.07 mm Hg at 450°.(1)

Preparation of bromides from PuO_2

PuO_2 (50 µg.) on Pt was heated at 600° in dry HBr. 15% Pu volatilized in 30 min. The oxide was no longer visible; H_2O appeared to be taken up with formation of a blue solution. Complete volatilization occured at 750°, a blue-green deposit forming outside the heated zone.(2)

$PuO_2 \cdot xH_2O$ (hydroxide dried at 70°) was treated with HBr gas at 700° for 1 hour. The "black" hydrous oxide turned to a glassy green crystalline product, some of which sublimed. Analysis indicated the composition $PuBr_{2.70}$. The substance dissolved in H_2O giving a purple solution.(3)

$PuO_2 \cdot xH_2O$, as above, was mixed superficially with NH_4Br, the system filled with HBr gas and heated to 350°. At this temperature the NH_4Br had sublimed off. The residue had a dirty green color. No sublimation occured on heating in quartz for 1 hour at 600° (in vacuo); at 730° a light green sublimate formed, and nothing more sublimed at 800°.(4)

Crystal structure of $PuBr_3$

$PuCl_3$, UCl_3, $CeCl_3$, $LaBr_3$, $CeBr_3$ are isomorphous. Assuming $PuBr_3$ is isomorphous with them, predictions were made of the $PuBr_3$ lattice constants and density.(5)

References

(1) Smith, Report CN-1324, p. 10, February 1, 1944.

(2) Katz and Hyde, Report CK-1372, p. 15, March 1, 1944.

(3) Hyde, Davidson, Katz and Wolf, Report CK-1512, p. 5, April 1, 1944.

(4) Hyde and Davidson, Report CK-1512, p. 7, April 1, 1944.

(5) Zachariasen, Report CK-1487, March 21, 1944.

[redacted]

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Compiled by: C. S. Garner Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IIF-1
II. "Dry" chemistry F. Iodides	Copy [redacted] Issued to:

Volatility of tracer Pu iodide

Pu-enriched U was converted to hydride, treated with CH_3I vapor at 275-300°, at which temperature UI_3 is formed. On heating in a slow stream of H_2 the following results were obtained:(1)

Temp., °C.	Time, hrs.	% Pu vol.	% U vol.
750-800	1	1	4
850-900	2	31	12
900	4	45	84

Reference

(1) Ayres, Report CN-1243, p. 5, January 8, 1944.

[redacted]

[redacted]

Compiled by: C. S. Garner

Date: September 28, 1945

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IIG-1

[redacted]

II. "Dry" chemistry
G. Borohydride

Issued to:

Attempt to prepare 48 borohydride

0.54 g. UF_4 containing 48 partly converted to $U(BH_4)_4$, sublimed at 60°C. <5% 48 sublimed. Either 48 borohydride not formed or not volatile at 60°.(1)

Reference

(1) Schlesinger's Group, Report CN-441, Jan. 30, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IIH-1
II. "Dry" chemistry H. Acetylacetonate	Copy No. [redacted] A Issued to:

Preparation of "plutonous acetylacetonate"

"$Pu(OH)_4$" (~1 μg. 49) slurried with 17% acetylacetone ($CH_3COCH_2COCH_3$) in ethyl alcohol overnight. No apparent reaction.(1)

As above, except slurried with acetylacetone alone for 1 hour. Most of hydroxide precipitate disappeared. Solution evaporated nearly to dryness under reduced pressure. Red-brown material, dissolved in $CHCl_3$.(1)

Above sample volatilized (extent?) at about 150°C. under "reduced pressure".(1)

Reference

(1) Dixon and Orlemann, Report CK-932, p. 11, Sept. 11, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 1 SHEET IIH-2

II. "Dry" chemistry
H. Acetylacetonate

Copy [redacted]s A

Issued to:

Non-volatility of "plutonous acetylacetonate"

Latest attempts to volatilize the acetylacetonate were unsuccessful.(1)

Reference

(1) Katz, Report CK-1020, p. 7, October 18, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner

Date: January 27, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 2 SHEET IIH-3

II. "Dry" chemistry
H. Acetylacetonate

Co[redacted]

Issued to:

Possible preparation of "plutonous acetylacetonate"

Ten μl. Pu solution (~1 μg. Pu/μl.) treated with 25 μl. specially prepared acetylacetone, extracted after 30 min. with 10 μl. $CHCl_3$. $CHCl_3$ layer evaporated on Pt, dried in air, heated at 160-175°C. for 40 min. in a vacuum ($\sim 10^{-5}$ mm. Hg). About 0.2 μg. Pu collected on a cold finger. Also tried for Th. May be useful in preparing thin foils.(1)

Reference

(1) Dixon, Smith, Cunningham and Orlemann, Report CK-1221, p. 10, January 5, 1944.

[redacted]

[redacted]

Compiled by: C. S. Garner Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 3 SHEET IIH-4
II. "Dry" chemistry H. Acetylacetonate	[redacted] Issued to:

Preparation and properties of plutonium(IV) acetylacetonate

Approx. 1 mg. Pu precipitated as hydroxide, dissolved in 6N H_2SO_4, diluted to 0.02 ml. To this was added a solution of 25 µl. acetylacetone dissolved in 50 µl. H_2O by the addition of the minimum amount of 6N NH_4OH. More NH_4OH was added until the solution was alkaline to litmus. A red-brown precipitate formed; it was centrifuged out, washed twice with H_2O, then dried over P_2O_5. The product melted at 173°, decomposing slightly at 170°. Vapor pressure by the effusion method was 4×10^{-4} mm. at 140° (Th acetylacetonate having a vap. press. of 3×10^{-4} mm. at 100°). The compound appears suitable for making thin deposits of Pu on Al (0.13 mg./cm.^{2}). (1),(2)

Two weighed samples assayed 33, 34% Pu. Theor. for $Pu(C_5H_7O_2)_4$ is 37.7% Pu. Zachariasen's X-ray analysis indicated a complex structure not isomorphous with $Th(C_5H_7O_2)_4$.(3)

References

(1) Dixon, Smith and Hagemann, Report CK-1371, p. 19, March 1, 1944.

(2) Dixon, Report CK-1511, p. 11, April 1, 1944.

(3) Dixon, Report CK-1512, p. 5, April 1, 1944.

[redacted]

[redacted]

Compiled by: C. S. Garner Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET II I-1
II. "Dry" chemistry I. Hydride	C[redacted] Issued to:

Evidence for existence of Pu hydride

3 μg. Pu metal + $H_2 \longrightarrow$ black powder. H_2 taken up to extent $PuH_{2.97}$, a similar experiment with U giving $UH_{2.2}$. A mercury pellet in a capillary tube containing the Pu and H_2 indicated the change in volume of H_2 and moved in suddenly at about 250°C.(1,2,3)

References

(1) Baumbach, Report CK-1079, p. 4, November 15, 1943.

(2) Seaborg's Group, Memo MUC-GTS-296, p. 4, November 15, 194~~4~~3.

(3) Baumbach and Fried, Report CK-1145, p. 17, December 11, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IIIA1-1

III. Electrolysis
A. Aqueous solutions
1. Copper cathode

C[redacted]s A

Issued to:

Electrolysis of $48^{(r)}$ in nitric acid solution using copper cathode

In 0.2M HNO_3, ND_{100} = 0.15, 1.8-2.1 volts, no Pu was removed from solution in 65 minutes.(1)

Electrolysis of $48^{(r)}$ in 1M NH_4Ac solution using copper cathode

In 1M NH_4Ac, ND_{100} = 0.15, 2.3-2.4 volts, 82°C. 30% of Pu present was removed from solution in first 25 min., none in second 25 min. In 1M NH_4Ac, 0.01M UO_2^{++}, other conditions as above, 89% of Pu removed, 98% of uranium. Analysed only solution, never cathode.(1)

Electrolysis of $48^{(r)}$ in NH_4HCO_3 using copper cathode

Solution, pH of 8, 1M in NH_4HCO_3 containing $48^{(r)}$ electrolysed with platinum anode and copper cathode at 70-80°C. with current density of 0.15 amp./100 $cm.^2$ cathode at potential of 2.6-2.8 volts. Three cells used, one containing $UO_2^{++} + 48^{(r)}$, a second UO_2^{++} alone and the third $48^{(r)}$ alone. A gray precipitate formed in the cells containing uranium, which comprised 25% of the uranium present and removed 92% of the $48^{(r)}$ present in the first cell. In the cell containing $48^{(r)}$ alone, only 34% was removed from the solution by the electrolysis. Only the solution was analysed, not the electrodes.(2)

References

(1) Cook, Report CN-601, p. 16, April 15, 1943.

(2) Cook, Report CN-676, P. 3, May 15, 1943.

[redacted]

Compiled by: R. B. Duffield Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IIIA1-2
III. Electrolysis A. Aqueous solutions 1. Copper cathode	Co[redacted]es A Issued to:

Electrolysis of 48$^{(r)}$ with Mn^{+2}

Attempt made to co-deposit Pu with Mn. Mn chosen because it is the most electropositive metal yet deposited from aqueous solution.

1. Graphite anode, Cu cathode, divided cell, 8-11 volts, 0.75-1.90 amp. 27-53°C. 3% of Mn, 4% of Pu deposited.

2. Cell as above, 6 volts, 0.75 amp. 0.1M $MnSO_4$, 0.5M $(NH_4)_2SO_4$, pH 6, 38% of Mn, 8% of Pu deposited.

3. Cell as above, 9-10 volts, 1.5 amp. pH 1-3, 24% of Mn, 3% of Pu deposited.

4. Pt-H_2 anode, Cu cathode, undivided cell, 13-16 volts, 1 amp., 25-46°C. pH 2-1.5, metallic deposit. ~1 % of Mn, 1% of Pu deposited.(1)

Reference

(1) Cook, Report CK-940, p. 1, Sept. 1943.

[redacted]

Compiled by: R. B. Duffield

HANDBOOK, CHEMISTRY OF PLUTONIUM

Date: May 1, 1944

EDITION I, SUPP. 3 SHEET IIIA1-3

III. Electrolysis
A. Aqueous solution
1. Copper cathode

Copy [redacted] s A

Issued to:

Electrolysis of 48$^{(r)}$ with Mn^{+2}

Electrolysis of an aqueous sol'n. of pH 1-3 with copper cathode and manganese anode deposited on the cathode 6-10% of Pu present in the solution and 100-120% of Mn^{+2} present in solution. This is taken to indicate that the Pu couple is more electropositive than the Mn-Mn^{+2} couple.

A result was also obtained which indicated that quantitative carrying of either 48$^{(r)}$ or 48$^{(o)}$ by anodic coprecipitation with MnO_2 is not possible.(1)

Reference

(1) Cook, Report CK-1253, p. 1, January, 1944.

[redacted]

Compiled by: R. B. Duffield Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET IIIA3-1
III. Electrolysis A. Aqueous solution 3. Platinum cathode	Copy [redacted] Issued to:

Electrolysis of 49$^{(r)}$ from nitric acid(1)

A very dilute HNO_3 solution containing ~0.5 µg. of Pu nitrate was electrolysed with Pt electrodes (?). A visible dark coat was formed on the cathode, insoluble in dilute acid and having an α-count corresponding to 1/3 of Pu added to solution.

Reference

(1) Kirk and Zvolner, Report CK-1145, p. 19, December 11, 1943.

[redacted]

[redacted]

Compiled by: R. B. Duffield Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IIIA2-1
III. Electrolysis A. Aqueous solutions 2. Mercury cathode	[redacted] Issued to:

Electrolysis of $48^{(r)}$ into mercury cathode

Solution containing $48^{(r)}$, acetate-buffered to pH 5, electrolysed for two hours at 0.44 amp./cm.^{2}, 14 volts, using Pt anode. Found only 13% of $48^{(r)}$ present in mercury.(1)

Solution of "pure" (Chicago scale) $49^{(r)}$ sulfate electrolysed (no conditions given). Some Pu found in mercury (no amount given).(2)

Solution of "pure" (Chicago scale) $49^{(r)}$ sulfate electrolysed for 6 hr. at 3 milliamps with following results.(3)

Total c/m.	Activity in Hg	Activity in soln.	Volts	%Pu in Hg
3460	846	926	12	24
3460	800	928	12	23
6925	2600	1760	24	38
6925	1840	3056	24	27

Solution 0.5M HNO_3, 0.5M UO_2^{++}, $48^{(r)}$, electrolysed at 2.5 amp, 3.9-4.3 volts for 2 hr. at room temperature. No $48^{(r)}$ found in mercury.(4)

References

(1) Wolters, Report CN-315, p. 1, Oct. 15, 1942.

(2) Magel and Cefola, Report CN-328, p. 13, Oct. 31, 1942.

(3) Magel and Cefola, Report CN-345, p. 9, Nov. 15, 1942.

(4) Cook, Report CK-676, p. 3, May 15, 1942.

[redacted]

Compiled by: R. B. Duffield

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET IIIA3-2

III. Electrolysis
A. Aqueous solution
3. Platinum cathode

Co[redacted]

Issued to:

Electrolysis of Pu in aqueous solutions

Electrolysis of a sol'n. of $Pu(NO_3)_4$, 0.1 N HNO_3 gave a deposit on cathode insoluble in H_2O, soluble in conc. H_2SO_4 with no gas evolution. This deposit is assumed to be $Pu(OH)_4$. No deposit was observed when the electrolysis was done in 1 N HNO_3.(1)

Reference

(1) Zvolner, Report CK-1169, p. 6, February 1, 1944.

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Compiled by: C. S. Garner

Date: September 28, 1945

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET: IVA-1

IV. Extraction and decontamination methods
A. "Wet" fluoride method

C[redacted]A

Issued to:

Original "wet" fluoride method

Procedure used in isolating first samples of 48 and 49 from irradiated uranium.(1),(2)

Use of Fe^{+++} to dissolve LaF_3 carrier precipitates

Cycle carried out with 48 indicated Fe^{+++} satisfactory for dissolving LaF_3. Also, data on "preformed" LaF_3.(3),(4)

Carrying power of "preformed" LaF_3 for 49

(See IAlf-1.)

Carrying power of "preformed" LaF_3 for 48

(See IAlf-1.)

Fission product activity from a pile yielding 100 g. 49/day

Calculations from data on a 40-day n-bombardment of nitrate on St. Louis cyclotron.(5)

Carrying power of "preformed" LaF_3 for 48

Amount of La^{+3} in stock tracer solutions not sufficient to account for previous carrying by "preformed" LaF_3. (See IAlf-1)

Metathesis of LaF_3 to $La_2(CO_3)_3$ or $La(OH)_3$

Conversion to $La_2(CO_3)_3$ would leave Pu and Np in solution as carbonate complexes. Only about half the 48 and 39 leached out of 100 μg. LaF_3 by 0.5-2M K_2CO_3 at 20-55°C. (Pyrex vessels attacked at higher temperatures.)(6)

Conversion to $La(OH)_3$ would allow dissolving in dil. HNO_3. LaF_3 containing 48 and 39, 1M NaOH at room temperature for 3-40 min., followed by dissolving $La(OH)_3$ in dil. HNO_3 gave all but about 5% of 48 and 39 in solu-

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IV. Extraction and decontamination methods A. "Wet" fluoride method	C[redacted] A Issued to:

Metathesis of LaF_3 to $La_2(CO_3)_3$ or $La(OH)_3$ (cont.)

tion. After this, most of the 48 and 39 not oxidized by 10 mg. Cr^{+6}/ml. at 95°C. Probably not enough acid.(6)

Fission product activity in extracted 49 after 3-month shutdown

Also, consideration of waste disposal.(7)

Separation of 0.2 mg. 49 from 45 kg. U and 0.25 curie of fission products

92% yield of 49. All data and flow-sheets. Proposed application to a 1000 kw pile.(8)

Conversion of LaF_3 to $La(OH)_3$; carrying of 48 by "preformed" LaF_3

48 nearly completely oxidized by 10 mg. Cr^{+6}/ml. at 95° in 20 min. following conversion of LaF_3 to $La(OH)_3$ and solution in HNO_3, if final HNO_3 is 1M.(9) (See above. See IAlf-1 for data on "preformed" LaF_3.)

Effect of Sr^{+2}, Cb^{+5}, Zr^{+4}, Ba^{+2} as hold-back carriers

If no hold-back carriers used in first or second LaF_3 precipitations as much as 12% of γ-activity was present with 48. This activity grew, showing 12-day Ba (parent of 44-hour La) came down with second precipitate. Addition of Sr^{+2}; Cb^{+5}, Zr^{+4}, Ba^{+2} reduced "to some extent" the γ-activity going with 2d. LaF_3. Best if Ba^{+2} is removed before or along with 1st. LaF_3. No loss of 48 on removal of $BaSO_4$ if 48 in upper oxidation state.(10)

Centrifugation of LaF_3 precipitates

99.5% solids can be removed in a batch centrifuge in 4 min. at 1000 g. in 2.5 min. at 1500 g., in 1.7 min. at 2000g. 99% solids removable in a continuous centrifuge at 1800g. with a hold-up time of 12 min.(11)

Carrying of 49 by LaF_3 at La^{+3}: Pu^{+4} of 10:1 and 50:1

(See IAlf-1.)

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Date: September 28, 1943	EDITION I SHEET IVA-3
IV. Extraction and decontamination methods A. "Wet" fluoride method	[redacted] Series A Issued to:

Precipitation of LaF_3 with KF or NH_4F

Precipitation in more nearly neutral solution reduced corrosion. 48 quantitatively carried with 1.6 mg. La^{+3}/10 ml. at pH up to 1.8 using KF or NH_4F. U precipitated above pH of 1.8.(12) (See IAlf-1.)

Recovery of 48 from LaF_3; recovery of U and waste disposal

Enumeration of methods. La^{+3}, Th^{+4}, 48 as fluorides heated at 95° for about 1 hour with 10% $(NH_4)_2C_2O_4 \cdot H_2O$ solution made alkaline to methyl red with NH_4OH. 97% 48 leached out. No experiments in absence of Th^{+4}. Preliminary experiments indicated ZrO^{++}, Al^{+++}, HBO_2 may be alright for dissolving LaF_3.(13)

Carrying of 48 and 49 by UF_4

Proposal to incorporate UF_4 into LaF_3-49 precipitates in hope that 49 may be more readily dissolved from LaF_3 by oxidizing to soluble state. Data (see IAlf-6) do not support.(14)

Engineering studies: precipitating, dissolving LaF_3, etc.

Dissolving LaF_3 by ZrO^{++}, Al^{+++}. Addition of La^{+3} in several portions with centrifugation in between gave cleaner separations. Waste disposal scheme. Corrosion tests. Bad effect of SO_2 in stainless steels, giving insoluble fluorides of U^{+4} and Cr^{+3}.(15),(16),(17)

Oxidation of 48; dissolving LaF_3 by ZrO^{++}, etc.

Zr^{+4} sometimes precipitated (as a fluoride?).(18)

Fission product distribution, and heat liberation(19)

Waste disposal(20)

Coprecipitation of Ba^{+2} with product precipitates(21)

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM
EDITION I
SHEET IVA-4

IV. Extraction and decontamination methods
A. "Wet" fluoride method

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Semi-works and plant design

Corrosion not "too great a problem" with 25-12 stainless steel. Reducing agents: SO_2 too corrosive, H_2O_2 not reliable, H_3AsO_3 possibly alright.(22) (See also IB2e-1.)

ZrO^{++} decontamination cycle(23)

Semi-works: flow-sheets, fission product distribution

Decontamination factors of 10^3-10^4 for extraction plus one decontamination cycle.(24)

General considerations of this and other extraction methods(25)

Fission product distribution after cooling period of 64 days(26)

Effect of Al^{+++} on carrying of 48 by LaF_3; ZrO^{++} for dissolving LaF_3

Al^{+++} (1.2% of the U by wt.) inhibited precipitation of LaF_3 and lowered carrying of 48. "Method must be modified, or Al abandoned as coating for U." Some Zr^{+4} precipitated with LaF_3-48 in oxidation-reduction cycles when ZrO^{++} used to dissolve LaF_3.(27)

Decontamination with respect to Sr^{+2}

Sr^{+2} in tracer amounts was carried <90% by $BaSO_4$, CaF_2 or LaF_3 in extraction step, but >99% by LaF_3 from ZrO^{++} solutions such as used in decontamination cycles.(28)

Semi-works

One extraction, one decontamination cycle gave 90% yield of 49, γ decont. factor of 1500. Knox carried through two additional decont. cycles and got 59% yield of 49, decont. factor of 4 x 10^5.(29) Fission product distribution.(30)

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IV. Extraction and decontamination methods A. "Wet" fluoride method	C[redacted] Issued to:

Pu-Np separation

$Cr_2O_7^=$-HNO_3 or $Cr_2O_7^=$-H_2SO_4 gives slow rate of oxidation of 48, rapid for 39. Decont. factor for 39 may be expected to be about 100 for one $Cr_2O_7^=$-H_2SO_4 cycle.(31) (See IB1k-1,2,3,5)

Carrying of 48 by LaF_3 in presence of Al^{+++}

Negligible carrying of 48 from 3N-6N HF in presence of 1 mg. Al^{+3}/ml., poor carrying at 0.2 mg. Al^{+3}/ml.(32)

Studies of oxidation, reduction, carrying of 48, 49

(See IB1k-2, IA1f-7.)

References

(1) Wahl, Ph. D. Thesis, Univ. of Calif., Berkeley, Calif., Feb., 1942.

(2) Seaborg and Wahl, Report A-135, p. 24, March 19, 1942.

(3) Wahl, Report CC-196, p. 2, July 18, 1942.

(4) Wahl, Report CN-239, p. 29, July 15, 1942.

(5) Perlman and Brown, Report CN-328, p. 1, Oct. 31, 1942.

(6) Prestwood, Report CN-328, p. 10, Oct. 31, 1942.

(7) Perlman, Report CN-328, p. 14, Oct. 31, 1942.

(8) Wahl, Report CN-336, Oct. 28, 1942.

(9) Prestwood and Sheline, Report CN-343, p. 6, Nov. 15, 1942.

(10) Perlman and Knox, Report CN-363, p. 11, Nov. 16, 1942.

(11) Cooper's Group, Report CN-391, p. 1, Nov. 31, 1942.

(12) Willard and Turk, Report CN-405, p. 18, Dec. 16, 1942.

(13) Willard, Kohman, Petersen and Koshland, Report CN-419, p. 5, Jan. 15, 1943.

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IVA-6

IV. Extraction and decontamination methods

A. "Wet" fluoride method

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Issued to:

References (cont.)

(14) Cefola, Report CN-419, p. 24, Jan. 15, 1943.

(15) Cooper's Group, Report CN-421, p. 2, Jan. 15, 1943.

(16) Smith's Group, Report CN-486, p. 3, Feb. 20, 1943.

(17) Sutton's Group, Report CN-486, p. 16, Feb. 20, 1943.

(18) Kohman, Koshland, Thompson, Davidson and Knox, Report CN-503, p. 9, Feb. 16, 1943.

(19) Apple, Peery, Vincent and Webster, Report CN-526, March 20, 1943.

(20) Rodger, Report CN-527, March 20, 1943.

(21) Ballou, Coryell and Gest, Report CN-528, p. 9, March 13, 1943.

(22) Smith, Report CN-544, p. 3, March 27, 1943.

(23) Kohman, Knox, Shepard, Koshland and Clifford, Report CN-601, p. 23, April 15, 1943.

(24) Smith, Report CN-603, p. 3, April 24, 1943.

(25) Willard, Report, CL-606 (6), May 17, 1943.

(26) Peery, Report CN-614, May 1, 1943.

(27) James, Knox and Kohman, Report CN-633, p. 3, April 16, 1943.

(28) James, Report CN-653, p. 11, May 20, 1943.

(29) Smith, Report CN-698, p. 6a, May 31, 1943.

(30) Rubinson, Gest, Winsberg, Ballou, Leader, Campbell, Burgus, Glendenin, Steinberg and Knight, Report CN-722, June 21, 1943.

(31) Beaufait, Report CN-723, p. 12, June 20, 1943.

(32) Voigt and Tevebaugh, Report CN-727, p. 4, June 15, 1943.

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Compiled by: C. S. Garner

Date: November 27, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM.

EDITION I, SUPP. 1 SHEET IVA-7

IV. Extraction and decontamination methods
A. "Wet" fluoride method

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Liter-scale run

Following "wet" fluoride cycles, carried out in 25-12 stainless steel vessels and no fission product carriers, gave a product yield of 92.6% with a β decontamination factor of 1100 and a γ decont. factor of 1200:(1)

$Cr_2O_7^=$ oxidation of 49 in 10% UNH,

1 $BaSO_4$, 2 LaF_3 by-product precipitations,

Zr^{+4} hold-back carrier,

H_2O_2 reduction of 49,

2 LaF_3 product precipitations,

dissolved by ZrO^{++}

$Cr_2O_7^=$ oxidation of 49,

LaF_3 by-product precipitation,

H_2O_2 reduction of 49,

LaF_3 product precipitation

Reference

(1) Baldwin and Sax, Report CN-958, p. 31, September 25, 1943.

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Date: January 27, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 2 SHEET IVA-8

IV. Extraction and decontamination methods
A. "Wet" fluoride method

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Semi-works and engineering data

Clinton runs.(1)

Corrosion considerations. Dissolving of CeF_3 and LaF_3 by Ce^{+4}. Carrying of 49 by CeF_3.(2)

Separation studies.(3)

LaF_3 crossover from $BiPO_4$ method.(4)

Isolation of 49 from 700 lbs. UNH by "wet" fluoride method, followed by peroxide purification.(5)

Extraction of 1 mg. 49 from 750 lbs. U + UNH by $NaUO_2Ac_3$ process, followed by concentration and purification by "wet" fluoride cycles. (See IVE-5)

References

(1) Apple's Group, Report CN-1052, October 30, 1943.

(2) Bradshaw, Dean, Gaarder, Johnson, Kroner, Koshland and Thompson, Report CN-1095, December 1, 1943.

(3) Acken's Section, Report CN-1117, December 14, 1943.

(4) Koshland, Werner, Fries, Dam and Covey, CN-1025, p. 1, Nov. 8, 1943.

(5) Belletire, Cunningham, Hindman, Howland, Jaffey, Kraus, Magnusson, Meyer, Patton and Smith, Report CN-1153, p. 5, Dec. 11, 1943.

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IVB-1

IV. Extraction and decontamination methods
B. "Dry" fluoride methods

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Suggested extraction method (#1)

UO_2-49 + HF $\xrightarrow{500°-600°}$ UF_4-49 + H_2O

UF_4-49 + F_2 $\xrightarrow{500°-600°}$ $UF_6\uparrow$, 49 left in residue.

Leach residue with dil. HF in presence of oxidizing agent (to dissolve 49, Rb, Ag, Cs).

Reduce 49 in extract and precipitate with LaF_3 carrier. Method based on false assumption that 49 higher fluoride not volatile at 500°(see IIC-1).

Fission product behavior in method (#1)

UF_4-48 ("wet" prep.) + F_2 at 250° and at 750° gave $UF_6\uparrow$ but no volatilization of 48. Te, Ba, La, Ce, Se, Sb, Ag, Rb, U (metals, chlorides, or lower fluorides), 48 + F_2 gave quantitative volatilization of Te, Se, Sb, U.(2) About 50% of short-lived β-activity volatilized on F_2 treatment.(3) UX_1 stayed behind on treating UF_4 with F_2 at 250° or 450°. Classification of fission products according to volatility in F_2.(4) Bombarded UF_4 + F_2 at 450°, volatile products collected in trap at -78°; activities found in trap corresponded to Br, I, Sb, Cb, Te, Mo, Zr.(5)

Suggested extraction method (#2)

U-49 + O_2 $\longrightarrow$ U_3O_8-49	(Kr, Xe removed)
U_3O_8-49 + H_2 $\xrightarrow{500°}$ UO_2-49	(Br, I ")
UO_2-49 + HF $\xrightarrow{500°}$ UF_4-49	(Cb, Zr, Sb, 43? removed)
UF_4-49 + F_2 $\xrightarrow{250°}$ $UF_6\uparrow$	(Mo, Te, 43? ")
49 + F_2 $\xrightarrow{500°}$ 49 higher fluoride$\uparrow$	(None? removed)

Residue: Rb, Sr, Y, Ba, La, Ce, Cs.

Based on volatilization of 48 as a higher fluoride at 500°(see IIC-1).(6),(7)

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IVB-2

IV. Extraction and decontamination methods
B. "Dry" fluoride methods

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Fission product behavior in method (#2)

$UO_2 \longrightarrow UF_4$: volatilization of 35-40% β-, 25-30% γ-activity.

$UF_4 \longrightarrow UF_6$: no fission product vol.(?)

48 → 48 higher fluoride: no fission product vol.(?)

Residue: ~60% β-, 70% γ-activity.(8)

Volatilization of 48 higher fluoride, separation from U

UF_6 started appreciable volatilization at ~145°C., complete by 270°(39 volatilizes with UF_6).(9) LaF_3 acted as a hold-back carrier for 48 in the F_2 volatilization.(10) (See IIC-1 for more volatility data.) "Bubbling" technic for converting UO_2 to UF_4 with dry HF. $U + HF \longrightarrow UF_4 + H_2$ was rapid for powdered U.(11)

Suggested extraction method (#3)

$U\text{-}49 + HF \longrightarrow UF_4\text{-}49$

$UF_4\text{-}49 + F_2 \xrightarrow{250°} UF_6\uparrow$

$49 + F_2 \xrightarrow{500°} 49 \text{ higher fluoride}\uparrow$

First step slow with massive metal.(12)

Suggested extraction method (#4)

$U\text{-}49 + F_2 \xrightarrow{250°} UF_6$ (Cb, Zr, Ru volatilize)

$49 + F_2 \xrightarrow{500°} 49 \text{ higher fluoride}$

Requires three times as much F_2 as method (#2).(12)

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IV. Extraction and decontamination methods B. "Dry" fluoride methods	[redacted] Issued to:

Suggested combination with "dry" chloride treatments

$$U\text{-}49 + Cl_2 \xrightarrow{350^\circ\text{-}450^\circ} \text{"}UCl_5\text{"}$$

$$49 + F_2 \xrightarrow{500^\circ} 49 \text{ higher fluoride}\uparrow \text{ , or}$$

$$U\text{-}49 + O_2 \rightarrow U_3O_8\text{-}49$$

$$U_3O_8\text{-}49 + CCl_4 + Cl_2 \xrightarrow{350^\circ\text{-}450^\circ} \text{"}UCl_5\text{"}\uparrow$$

$$49 + F_2 \xrightarrow{500^\circ} 49 \text{ higher fluoride}\uparrow .^{(12)}$$

UF_6 pile

k for UF_6 in U pipes with graphite moderation might be about 1.029. No experimental data.(13)

Possibilities of decontamination by "dry" fluoride methods

Speculation on various possibilities. Three experiments on volatilization of zirconium phosphate by HF: 95% vol. in 1 hr. at 700°C.(14)

UF_6 pile, etc.

Distillation studies of UF_6, distribution of 48, 39, etc.(15),(16),(17),(18)

Suggested extraction method (#5)

Static fluorination technic. Volatilization of BiF_5 from $BiF_3 + F_2$ as function of temperature (volatilized about like UF_6). Decontamination of $BiPO_4$ precipitates.(19) Revised process:

$$U\text{-}49 + HF + \text{steam} \xrightarrow{500^\circ\text{-}700^\circ} (UF_4 + U_3O_8 + UO_2)\text{-}49$$

Small amount Bi placed in reactor

$UF_4\text{-}U_3O_8\text{-}UO_2\text{-}49 + Bi + F_2 \xrightarrow{500^\circ} UF_6\uparrow$, 49 condensed in trap at 100° with BiF_5.(17)

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HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET IVB-4

IV. Extraction and decontamination methods
B. "Dry" fluoride methods

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Suggested extraction method (#6)

Run Al-coated billets thru masticating machine to break holes in coating. Convert U to hydride at 250-300° (sift from Al shells if desired). "UH_4"-49 + HF $\xrightarrow{250^\circ}$ UF_4-49 + H_2, then fluorinate.(20),(21) "Found to work quite well."(22)

References

(1) Brown, Report CC-125, p. 1, June 13, 1942.

(2) Brown, Report CC-136, p. 3, June 20, 1942.

(3) Brown, Report CC-156, p. 3, June 27, 1942.

(4) Brown, Report CC-179, p. 1, July 11, 1942.

(5) Brown, Report CC-198, p. 2, July 18, 1942.

(6) Brown and Hill, Report CC-216, p. 11, Aug. 1, 1942.

(7) Brown and Hill, Report CN-239, p. 5, July 15, 1942.

(8) Brown and Hill, Report CC-222, p. 6, Aug. 8, 1942.

(9) Brown and Hill, Report CN-250, p. 2, Aug. 16, 1942.

(10) Brown and Hill, Report CN-261, p. 7, Aug. 15, 1942.

(11) Brown, Hill and Webster, Report CN-282, p. 2, Sept. 16, 1942.

(12) Brown, Hill and Jaffey, Report CN-328, p. 6, Oct. 31, 1942.

(13) Anderson and Brown, Report CN-362, Nov. 27, 1942.

(14) Brown and Hill, Report CN-391, p. 5, Nov. 31, 1942.

(15) Brown, Hill and Jaffey, Report CN-454, p. 12, Jan. 16, 1943.

(16) Brown, Hill and Bohlmann, Report CN-503, p. 5, Feb. 16, 1943.

(17) Brown, Bohlmann and Hill, Report CN-633, p. 13, April 16, 1943.

(18) Brown, Hill and Bohlmann, Report CN-696, May 16, 1943.

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Date: September 28, 1943	EDITION I SHEET IVB-5
IV. Extraction and decontamination methods B. "Dry" fluoride methods	Co[redacted] Issued to:

References (cont.)

(19) Brown, Hill and Bohlmann, Report CN-522, p. 6, March 15, 1943.

(20) Spedding, Newton and Johnson, Report CN-717, June 17, 1943.

(21) Newton, Spedding and Johnson, Report CN-727, p. 5, June 15, 1943.

(22) Brown, Hill, Bohlmann and Hubble, Report CN-813, p. 19, July 17, 1943.

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Date: January 27, 1944	EDITION I, SUPP. 2 SHEET IVB-6
IV. Extraction and decontamination methods B. "Dry" fluoride methods	Cop[redacted] Issued to:

Hydride modification, method (#6)

Reactions rates of H_2 with U, of HF with U or with UH_3. Decontamination studies indicated Cb and Zr do not volatilize from UH_3 during HF treatment at elevated temperatures.(1)

References

(1) Hubble, McCullough, Hill and Lindner, Report CN-1025, p. 13, November 8, 1943.

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Compiled by: C. S. Garner

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I

SHEET IVC-1

IV. Extraction and decontamination methods
C. Adsorption methods

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Adsorption of 48 by silica gel, alumina, etc.

Adsorption by Fuller's earth, silica gel, alumina, Norit A, 8-hydroxyquinoline, filter paper.(1) Alumina, silica gel, amberlite resins, Hyflo Super Cel, $BaSO_4$, $BaCO_3$.(2) Silica gel, "Zeo-Karb", alumina, titania, resins, etc.(3),(4),(5),(6),(7),(8),(9),(10),(11),(12),(13),(14),(15)

Amberlite cation exchanger and zirconium phosphate columns

Complete data and flow-sheets for an adsorption method using IR-1 and "tailor-made" zirconium phosphate adsorbents. Two runs indicated 97.5% 48 recovered with 0.06% β-activity, no U; 100% U recovered with 2.5% β-activity; 80% β-activity with 2.5% 48, no U.(16),(17),(18)

Semi-works operation of cation exchangers

"Boyd method" (see above) gave rapid adsorption of 48, some difficulty with desorption.(19)

Claimed use of IR-1 impractical owing to decomposition in 2M HNO_3. Also, some tests with HCl.(20)

Cation exchanger experiments

Separation of >95% of the 48. Desorption with 1.25M $NaHSO_4$. Gross decont. factor of 10 for extraction.(21)

Adsorption of 48 by Amberlite, Catex-234, $BiPO_4$, Cb_2O_5

Further data on Amberlite IR-1 and Catex-234. Coupling of adsorption-extraction cycle to $BiPO_4$, LaF_3 and $NaUO_2Ac_3$ decontamination cycle. Latter looks best; gave gamma decont. factor of 3 x 10^4. Use of $BiPO_4$ as adsorbent seems impractical. Cb_2O_5 when crystalline appears to be a good adsorbent for 48(r).(22)

Amberlite cation exchanger

Schumann-Furnas theory of heat transfer applied with success to transfer of 48-49 by adsorption.(23)

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IV. Extraction and decontamination methods C. Adsorption methods	C[redacted] Issued to:

Amberlite cation exchanger (cont.)

Extraction of 49 by amberlite columns studied on 120-liter scale.(23)

Coupling of $NaUO_2Ac_3$ method with column extraction. Sulfate elutriant from IR-1 column contained 95-100% 48-49, ~10% fission products, no U. Modified $NaUO_2Ac_3$ decontamination cycle ($NaBiO_3$ + $Na_2Cr_2O_7$ as oxidant, NH_3OHCl as reductant) expected to give 87-92% yield, with volume reduction of 25-35-fold, βdecont. factor about 4 x 10^3, γ decont. factor about 3 x 10^4. Flow-sheets. Also, coupling with LaF_3, $BiPO_4$ methods.(23)

References

(1) Willard, Report CC-169, p. 7, July 3, 1942.

(2) Willard, Report CC-198, p. 3, July 18, 1942.

(3) Willard, Report CC-199, p. 2, July 25, 1942.

(4) Willard and Turk, Report CC-222, p. 1, Aug. 8, 1942.

(5) Willard and Turk, Report CN-239, p. 12, Aug. 15, 1942.

(6) Willard and Turk, Report CN-261, p. 9, Sept. 15, 1942.

(7) Willard and Turk, Report CN-299, p. 5, Oct. 15, 1942.

(8) Willard and Turk, Report CN-343, p. 1, Nov. 15, 1942.

(9) LaChapelle, Fries, Orlemann, Stoughton, Turk and Willard, Report CN-522, p. 12, March 15, 1943.

(10) Turk and Fries, Report CN-556, p. 11, March 16, 1943.

(11) Beaton, Cooper, Fries, LaChapelle, Sheft and Turk, Report CN-601, p. 29, April 15, 1943.

(12) Beaton, Cooper, Fries, LaChapelle, Stoughton, Sheft and Turk, Report CN-633, p. 6, April 16, 1943.

(13) Beaton, Cunningham, Fries, LaChapelle, Sheft and Turk, Report CN-653, p. 2, May 20, 1943.

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Compiled by: C. S. Garner Date: September 23, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IVC-3
IV. Extraction and decontamination methods C. Adsorption methods	[redacted] Issued to:

<u>References (cont.)</u>

(14) Beaton, Fries, Sheft and Turk, Report CN-728, p. 50, June 21, 1943.

(15) Beaton, LaChapelle, Sheft and Turk, Report CN-813, p. 22, July 17, 1943.

(16) Adamson, Schubert, Russell and Boyd, Report CN-489, Feb. 20, 1943.

(17) Adamson, Schubert, Russell and Boyd, Report CN-502, March 4, 1943.

(18) Russell, Adamson, Schubert and Boyd, Report CN-508, March 6, 1943.

(19) Sutton's Group, Report CN-544, p. 4, March 27, 1943.

(20) Sutton's Group, Report CN-603, p. 20, April 24, 1943.

(21) Adamson, Ketelle, Russell, Schubert, Swartout, Larson and Boyd, Report CN-839, July 28, 1943.

(22) Beaton, Dam, LaChapelle, Lincoln, Sheft, Turk, Report CN-894, p. 11, Aug. 7, 1943

(23) Adamson, Brosi, Ketelle, Motta, Russell, Schubert, Swartout, Larson and Boyd, Report CN-903, Aug. 28, 1943.

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IV. Extraction and decontamination methods
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Exchange adsorbents

Further studies with Amberlite IR-1; also with "Alkalex", "R. P. Zeolite", "Titanium Zeolite #1, #2".(1)

Reference

(1) Beaton, Fields, LaChapelle, Lincoln, Sheft and Turk, Report CN-991, p. 1, October 9, 1943.

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Original phosphate method using Zr^{+4} as carrier

1 ton U as 20% $UO_2(NO_3)_2 \cdot 6H_2O$, 3N in HNO_3, 10 lbs. $ZrO(NO_3)_2 \cdot 2H_2O$, 5 lbs. $La(NO_3)_3$, 650 lbs. 85% H_3PO_4 (0.35N in H_3PO_4), heat to 65°C., let stand 1 hour. Zirconium phosphate carried about 90% 48, 40% γ-activity. Serious drawback is apparent redissolving of 48 on standing. Precipitate is "easy to filter--like aluminum hydroxide."(1)

Volume of precipitate is about five times that in "wet" fluoride method necessitating more batches or longer hold-up time. Filtration is very bad, with or without filter aids.(2)

Cunningham and Werner got only 15% 49 carried at Pu:Zr = 1:100 under conditions where 48 was carried 95%. 85% 49 carried at Pu:Zr = 1:1000 in 1N HNO_3.(3)

Proposal of a phosphate method using Bi^{+3} as carrier

Similar to above method except $BiPO_4$ used as carrier. Precipitate was crystalline, readily filterable, carried about 98% 48, about 17% γ-activity. Heating necessary to crystallise $BiPO_4$. Precipitate dissolved in HCl, then 48 carried in LaF_3 (final precipitate carried about 5% γ-activity). BiF_3 precipitated with LaF_3 unless Cl^- was present to form complex.(4)

Carrying of 49 by $BiPO_4$ at Pu:Bi ratios of 1:17 to 1:150,000

(See IAlp-1.)

Use of H_2SO_4 to prevent precipitation of uranyl phosphate(5)

Filter tests on $BiPO_4$(6),(7)

Use of HNO_3 to dissolve $BiPO_4$, etc.

Engineers objected to use of HCl because of corrosion. $BiPO_4$ dissolved in 10N HNO_3, 48 oxidized with Ag^{+2}. Erratic carrying of 39: 5-90%. "Preformed" $BiPO_4$. Fission product behavior.(8)

Carrying of 49 by $BiPO_4$ in H_2SO_4 solutions

(See IAlp-1.)

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Methods of decontamination and volume reduction(9)

Semi-works

Filtration properties, flow-sheets, etc.(10) One $BiPO_4$ precipitation gave product with 20% γ-activity.(11)

Oxidation of 48; coupling of $BiPO_4$ extraction with $NaUO_2Ac_3$ decontamination cycle

$BiPO_4$ can be dissolved in 6N HNO_3, 48 in solution oxidized by $K_2Cr_2O_7$. 48 cannot be oxidized in 3-4N HNO_3 in presence of $BiPO_4$. Decont. factor of 1000 for $BiPO_4$ extraction followed by $NaUO_2Ac_3$ cycle. (12) (See IB2c-1, 2, IB1h-1 for oxidation studies.)

Modified $BiPO_4$ extraction method

Extraction on previous basis plus three oxidation-reduction cycles gave 85% yield 48 with a decont. factor of 7×10^6 (UX + fission products).

Modified method proposed: Oxidize 49 before precipitating $BiPO_4$ in order to separate $PO_4^{\equiv}$ and $SO_4^{=}$ insoluble fission products. Reduce 49 and carry with $BiPO_4$.(13)

Semi-works

Cases of 73-85% yield of 48 for extraction plus decontamination. Excessive corrosion. Filtering problems. Aging of $BiPO_4$ affected solubility. Decont. factors of 12 after extraction, 475 after extraction plus one decont. cycle, 42,000 after additional decontamination cycle.(14),(15)

Oxidation of 48, etc.

(See IB1h-1.) Precipitation of $BiPO_4$ on dilution from 10 to 2N HNO_3 prevented by precipitation of ceric phosphate (from oxidation of 48).(16)

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Semi-works

At 0.5N H_2SO_4 >1.5N Na_2SO_4 was required to prevent precipitation of uranyl phosphate in extraction step. 99% 48 carried by $BiPO_4$ from 0.5N H_2SO_4 2N Na_2SO_4.(17)

Six separation runs, using H_2O_2 as reducing agent, $K_2Cr_2O_7 + Ce^{+4}$ as oxidizing agent (75°C.). Incomplete oxidation in some runs. 64-84% yield of 49 for extraction plus one decontamination cycle. Two decontamination cycles gave decont. factor of about 20,000.(18)

Study of reducing agents

(See IB2l-1, IB2i-1, IB2d-1, IB2a-1.)

Poor carrying of 49 by $BiPO_4$ at Pu:Bi ratio of 1:17

Earlier good carrying complicated by coprecipitation of uranyl phosphate. $SO_4^{=}$ added to keep U^{+6} in solution gave less than 90% carrying, resulting in less than 70% yield of 49 for extraction plus two decontamination cycles.(19)

$NaBiO_3$ and Ce^{+4} as oxidizing agents

(See IB1h-1, IB1i-1.)

Semi-works, etc.

Oxidation of 48 in metal-dissolving step may be as great as 60%. Fe^{++} satisfactory reducing agent for reducing in this step. 96-100% carrying of 49 at Pu:Bi = 1:75 - 1:200 under some conditions (see IAlp-2.). Alternative to dissolving $BiPO_4$ in 10N HNO_3 is to convert to hydroxide with KOH, then dissolve in 1/8th HNO_3 previously used. Waste disposal.(20)

Yields in extraction step fluctuated from 15-85% in semi-works (ran 90-95% in laboratory scale runs); reason "not known".(21)

Presence of Ni (from corrosion of stainless steels) apparently does not affect carrying of 48 by $BiPO_4$. Use of Fe^{++} and HCHO as reducing agents all right. Carrying 49 at Pu:Bi = 1:10 varied from 81-99% with three-hours digestion at 75° (see IAlp-2.).(22)

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Semi-works, etc. (cont.)

Agitation important during digestion; carrying of 48 considerably decreased if not enough agitation. 0.02M Fe^{+3} (or Fe^{+2}) no serious effect on carrying if agitation is sufficient, but 0.06M Fe^{+3} is detrimental to carrying. Reverse "hot strike" procedure gave better extraction yields: Bi^{+3} added to hot solution containing H_3PO_4, U^{+6}, 48. However, $BiPO_4$ crystals very fine, difficult to filter. Lab runs indicated 91% overall yield 48 thru two decontamination cycles, with decont. factor (γ) $\approx$11,000.(24)

Decontamination for Ce, Zr, Ru

Ce^{+3} had no appreciable effect on Ce decontamination in extraction step; Ce^{+4} was effective if >15 mg./l. in 1N HNO_3 due to precipitation of ceric phosphate. $ZrO(H_2PO_4)_2$ came down with $BiPO_4$ if Zr^{+4} = 6 mg./l. in 1N HNO_3. Ru (+3 state?) precipitated to extent of about 0.4% with $BiPO_4$; oxidation gave greater fractional precipitation of Ru with $BiPO_4$.(23)

Semi-works

Four runs gave >90% yield 48 in extraction step, but >10% losses 48 in decontamination cycles in two of the runs. $NaBiO_3$ oxidation apparently incomplete. Overall decontamination factor at end of 2d. decontamination cycle only 10^3.(25)

References

(1) Thompson, Report CN-363, p. 1, Nov. 16, 1942.

(2) Cooper's Group, Report CN-391, p. 2, Nov. 31, 1942.

(3) Thompson, Koshland and James, Report CN-391, p. 7, 11, Nov. 31, 1942.

(4) Thompson, Report CN-405, p. 7, Dec. 16, 1942.

(5) Thompson and Turk, Report CN-419, p. 1, Jan. 15, 1943.

(6) Cooper's Group, Report CN-421, p. 6, Jan. 15, 1943.

(7) Smith's Group, Report CN-483, p. 7, Feb. 20, 1943.

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D. Bismuth phosphate method

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References (cont.)

(8) Thompson, Report CN-454, p. 6, Jan. 16, 1943.

(9) Thompson, Davidson and Miller, Report CN-522, p. 8, March 15, 1943.

(10) Sutton's Group, Report CN-544, p. 11, March 27, 1943.

(11) Smith's Group, Report CN-544, p. 6, March 27, 1943.

(12) Thompson, Davidson, Miller and James, Report CN-556, p. 13, March 16, 1943.

(13) Thompson, Davidson, Dreher, Miller and James, Report CN-601, p. 10, April 15, 1943.

(14) Smith's Group, Report CN-603, p. 7, April 24, 1943.

(15) Sutton's Group, Report CN-603, p. 4, April 24, 1943.

(16) Miller, Report CN-633, p. 11, April 16, 1943.

(17) Cooper's Group, Report CN-653, p. 10, May 20, 1943.

(18) Smith's Group, Report CN-698, p. 3, May 31, 1943.

(19) Cunningham, Cefola, Patton and Werner, Report CN-728, p. 36, June 21, 1943.

(20) Cooper, Dam, Dixon, Dreher, Gaarder, Halperin, Johnson, Knox, Lincoln, Miller, Morris, Zoolner, Koshland and Thompson, Report CN-813, p. 1, July 17, 1943.

(21) Smith's Group, Report CN-828, July 26, 1943.

(22) Knox, Cooper, Gaarder, Halperin, Dreher, Dean, Kroner and Miller, Report CN-849, Aug. 1, 1943.

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IV. Extraction and decontamination methods D. Bismuth phosphate method	[redacted] Issued to:

References (cont.)

(23) Burgess, Evans, Hume, Leader and Tordella, Report CN-850, Aug. 12, 1943.

(24) Balthis, Olson and Peterson, Report CN-901, Aug. 28, 1943.

(25) Smith's Group, Report CN-906, Aug. 28, 1943.

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Process studies

Decision to use method at site W. Excess HNO_3 remaining after metal solution step reduced semi-works extraction yields to 50-75%. $NaBiO_3$ oxidation in presence of "W" fission product carriers gave only 5-10 for the γ decontamination factor per cycle. Tentative waste disposal.(1)

Studies of oxidation procedure, filtration, etc. Tentative evidence that "W" fission product carriers have no bad effect on β-decontamination after 3 decont. cycles, but have a bad effect on first two such cycles.(2)

Reduction studies with U^{+4}, Fe^{+2} (see IB2f-2, IB21-3).(3)

Carrying studies (see IAlp-7).(3)

Decontamination studied for Sr, Zr, Cb, Ru, Te, Ba, Ce, Y + La + Pr. Use of Ru^{+8}, $ZrF_6^{=}$, $CbF_7^{=}$ as hold-back carriers, and effect of $ZrO(H_2PO_4)_2$, $Cb_2O_5 \cdot xH_2O$, LaF_3 as scavengers on oxidized precipitate in first decont. cycle.(4)

Solubility of $BiPO_4$ in 0.16-10.1M HNO_3 at 30°C. Effects of temperature, added H_3PO_4, Fe^{+3}, $UO_2(NO_3)_2 \cdot 6H_2O$.(5)

Liter-scale runs gave 86.5-98.7% Pu yield thru E + 2D, overall γ-D.F. $\approx$ 10,000-35,000. Variations in single cycle D.F.s probably due to different amounts of fission products eliminated on filter. Centrifugation gave lower yields, lower D.F.s.(6)

Use of U^{+4} as reducing agent. Oxidation and carrying studies. Considerations of concentrating Pu following the decontamination.(7)

Fast methods for rough determinations of decontamination factors in $BiPO_4$ method, give lower D.F.s than by more precise methods.(8)

Solubility of $BiPO_4$ under various process conditions. Effect of washing, presence of HF, Fe^{+3}. Decont. factors for Zr and Ru.(9)

Further studies on 1-liter scale.(10)

Current site W plans indicate initial decontamination by a factor of 10^5 with the $BiPO_4$ process, followed by a combination $BiPO_4$-LaF_3 bulk-reduction cycle (3000 gal. reduced to 8 gal.). Proposed separation of ~ 250 g.

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Process studies (continued)

Pu from 2 kg. La (in 8 gal.) by precipitation of Pu peroxide without carrier.(11)

Considerations of concentration schemes such as use of $U(C_2O_4)_2$ carrier, Cb_2O_5-LaF_3 carrier. Also, discussion of use of $NaUO_2Ac_3$ for decontamination.(12)

Solubility of $BiPO_4$. Indications that precipitate is not $BiPO_4.H_2O$ or higher hydrate, may be $2BiPO_4.H_2O$. Improved Zr decontamination, and β-decont. studies. Simple method for preparation of $U(SO_4)_2$.(11)

References

(1) Smith's Group, Report CN-756, June 28, 1943.

(2) Peterson, Olson and Balthis, Report CN-758, June 26, 1943.

(3) Thompson, Koshland, Halperin, Knox, Cooper, Dean, Dreher, Gaarder, Kroner, James, Johnson, Dixon and Miller, Report CN-931, September 11, 1943.

(4) Davies, Burgus, Evans, Finkelstein, Gest, Glendenin, Leader, Mapp, Ravely, Rubinson, Steinberg, Tordella and Winsberg, Report CN-933, p. 5, September 11, 1943.

(5) Dillard, Evans, Leader, Safranski, Revinson and Bane, Report CN-933, p. 11, September 11, 1943.

(6) Balthis, Olson and Peterson, Report CN-958, p. 6, September 25, 1943.

(7) Cooper, Dean, Dreher, Halperin, Johnson, Kroner, Miller, Morris and Thompson, Report CN-979, September 30, 1943.

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IV. Extraction and decontamination methods
D. Bismuth phosphate method

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References (continued)

(8) Rubinson and Winsberg, Report CC-988, p. 3, October 11, 1943.

(9) Leader, Lassiter, Mapp, Tordella, Stanley and Evans, Report CN-989, p. 6, October 11, 1943.

(10) Sutton's Group, Report CN-1023, October 30, 1943.

(11) Dam, Fries and Werner, Report CN-1041, p. 1, October 31, 1943.

(12) Leader, Mapp, Evans, Stanley and Rubinson, Report CN-1044, p. 9, November 10, 1943.

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Date: January 27, 1944	EDITION I, SUPP. 2 SHEET IVD-10
IV. Extraction and decontamination methods D. Bismuth phosphate method	Co[redacted] Issued to:

Process studies

LaF_3 crossover studies. Concentration of Pu.(1)

Radiochemical studies on process solutions. Use of LaF_3 and MnO_2 as scavengers for F.P.s in $BiPO_4$ method.(2,3)

Decontamination, crossover steps and concentration of Pu.(4)

General separation studies, including LaF_3 studies.(5)

Decontamination studies.(5)

Coupling of an adsorption extraction cycle with $BiPO_4$ method.(7)

Decontamination improvement by use of scavengers and hold-back carriers.(8)

Clinton runs.(9)

Ru decontamination. Crystalline forms of $BiPO_4$.(10)

References

(1) Koshland, Werner, Fries, Dam and Covey, Report CN-1025, p. 1, November 8, 1943.

(2) Coryell, Hume, Ballou, Davies, Burgus and Gest, Report CN-1051, November 8, 1943.

(3) Burgus, Davies, Gest, Edwards and Coryell, Report CN-1113, December 11, 1943.

(4) Sutton's Section, Report CN-1116, December 11, 1943.

(5) Acken's Section, Report CN-1117, December 14, 1943.

(6) Leader, Evans, Mapp and Stanley, Report CN-1141, p. 9, December 18, 1943.

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IV. Extraction and decontamination methods
D. Bismuth phosphate method

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References

(7) Beaton and LaChapelle, Report CN-1153, p. 1, December 11, 1943.

(8) Olson, Stahl, Faris, Thompson, Dean, Dreher, Gaarder, Kroner, Leader and Mapp, Report CN-1153, p. 17, December 11, 1943.

(9) Acken's Section, Report CN-1209, January 11, 1944.

(10) Sugarman, Evans, Leader, Rubinson, Stanley, Report CN-1214, January 8, 1944.

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IV. Extraction and decontamination methods E. Sodium uranyl acetate method	C[redacted] Issued to:

Original extraction-decontamination method

48 is oxidized with $Na_2Cr_2O_7$. $NaAc \cdot 3H_2O$ is added to precipitate 99% of the U as $NaUO_2Ac_3$ carrying 99% $48^{(o)}$, 2% β-activity. Dissolved in HNO_3 48 reduced with $NaHSO_3$, and $NaAc \cdot 3H_2O$ added to precipitate U, leaving 96% 48 in solution. $Ce(NO_3)_3$, $UO_2(NO_3)_2$ (inactive) and NaOH added to precipitate $Ce(OH)_3$, $Na_2U_2O_7$ and 48. Dissolved in HNO_3, 48 oxidized, $NaAc \cdot 3H_2O$ added. Final $NaUO_2Ac_3$ of cycle carries 95% 48, 0.04% β-activity. Complete flow-sheets, including waste disposal plan.(1)

Solubility of $NaUO_2Ac_3$; $UO_2(IO_3)_2$ as carrier to replace hydroxide precipitates

Most U^{+6} present as $UO_2Ac_3^-$ in HAc-Ac^- buffer solutions. $NaUO_2Ac_3 \rightleftharpoons Na^+ + UO_2Ac_3^-$, $K_{S.P.} \approx 0.006$ at 25°C. Less than 0.5% U fails to precipitate from solution 0.5M in U^{+6}, 0.2M in Ac^-, 0.2M in HAc, 2.5M in Na^+ (as $NaNO_3$). Also oxidation of 48 in 0.1-1M HNO_3 and in 2M HCl (see IB1k-3,4, 5.).(2)

Modified acetate method; Np-Pu separation

Pu kept in reduced state, bulk of U precipitated as $NaUO_2Ac_3$, Pu oxidized and carried with 1/20 original amount of U. About 95% $48^{(o)}$ precipitates with smaller $NaUO_2Ac_3$. In general, same % $48^{(o)}$ carried as % U precipitated over range 3-14% U left in solution. Possibility of Np-Pu separation based on differential rate of oxidation in HAc-Ac^- buffer (see IB1k-7).(3)

Carrying of $49^{(o)}$ by $NaUO_2Ac_3$ at U:Pu ratios of 1000:1,100:1

(See IA2a-1.)

Modified acetate method in which all precipitates are $NaUO_2Ac_3$

Bulk of U removed in first step. $48^{(o)}$ carried with 1/20 of original amount of U. NH_3OHCl used as reducing agent. Oxidation-reduction cycles in which amount of U is reduced by factor of 20 per cycle. Three successive cycles gave yield of 67% 48 (no recycling), β-activity reduced overall by factor of 150,000. Flow-sheets.(4)

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Non-carrying of $49^{(r)}$ by $NaUO_2Ac_3$ at Pu:U = 1:100

Also, complete cycle carried out at initial Pu:U ratio of 1:3000 (carrying at 1:150), total recovery 49 = 92%, with 76% in final $NaUO_2Ac_3$ precipitate.(5) (See IA1a-1.)

Further runs with added fission product carriers

Two runs made with carriers at concentrations estimated for 10^6 kw pile, 100-days operation. NH_3OHAc used in one run as reducing agent, NH_3OHCl in other with about same results. 66-70% 49 + 48 recovered in final $NaUO_2Ac_3$, with an overall decont. factor of 100,000-250,000 (β-activity).(6)

Suggested Np-Pu separation

Probable existence of Np in more than one oxidation state higher than F^--insoluble state: two F^--soluble states, one in which Np is not carried by $NaUO_2Ac_3$, other in which it is. Use in separation by oxidizing with $K_2Cr_2O_7$ in pH = 2-3 ($HAc-HNO_3$), 48 oxidized, 39 oxidized but not carried by $NaUO_2Ac_3$.(7)

Carrying of $49^{(o)}$ by $NaUO_2Ac_3$; solubility of "$NaPuO_2Ac_3$"

(See IA2a-1,2.)

Np-Pu separation

Tests with freshly-bombarded nitrate showed 9% 39 carried thru one complete cycle. Flow-sheets.(8)

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Behavior of individual fission products

Generalized flow-sheet. One extraction step plus one decontamination cycle reduced over-all long lived β-activity by factor of 1-2.5 x 10^5.(9)

UX (Th) decont. factor per decont. cycle =	940 ± 70
Ru	930 ± 80
Rb	2100±300
Y	440 ± 10
Ba	7700±500
Np	1.6
La	4100±800(10)
Sr	2500±400(10)
Zr	~90 (?)(10)
Te	720± 80(10)
I	50-100(10)
Cs	3000±1600(11)

~85% yield 49 + 48 thru extraction plus two decontamination cycles. $Cb_2O_5 \cdot xH_2O$ formed can carry $48^{(r)}$ extensively but not $48^{(o)}$.(10)

Effect of Al^{+3} Hg^{+2} on extraction

95% recovery 48, >10^4 decont. factor in two cycles. Presence of anticipated concentrations of Al^{+3}, Hg^{+2} (coating problem) does not interfere. No $Al(OH)_3$ precipitation from 0.4M HAc, 0.2M Ac^-.(12)

Carrying of Np with Pu

Where desirable for special purposes about 93% 39 can be carried along with the 49 in a $NaUO_2Ac_3$ precipitate. 0.1M $Cr_2O_7^=$ in 0.2M HNO_3, 0.02M UO_2^{++} for 15 min. oxidized $39^{(r)}$ to $39^{(o-1)}$ rapidly, then solution made 0.001-0.1M in BrO_3^- and let stand 6-25 min. at room temperature to oxidize $39^{(o-1)}$ to $39^{(o)}$ which is carried by $NaUO_2Ac_3$.(13)

References

(1) Connick, Gofman and Wahl, Report CN-363, p. 1, Nov. 16, 1942.

(2) Connick, Garner, Gofman, Prestwood and Wahl, Report CN-391, p. 1 Nov. 31, 1942.

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IV. Extraction and decontamination methods E. Sodium uranyl acetate method	C[redacted]A Issued to:

References (cont.)

(3) Connick, Duffield, Garner, Gofman, Prestwood and Wahl, Report CN-419, p. 1, Jan. 15, 1943.

(4) Connick, Duffield, Garner, Gofman and Wahl, Report CN-467, p. 15, Feb. 13, 1943.

(5) Hamaker and Sheline, Report CN-522, p. 1, March 15, 1943.

(6) Connick, Duffield, Garner and Gofman, Report CN-522, p. 2, March 15, 1943.

(7) Duffield and Gofman, Report CN-522, p. 8, March 15, 1943.

(8) Gofman, Report CN-601, p. 12, April 15, 1943.

(9) Beaufait, Connick, Crandall, Evans, Gofman, Pimentel and Stein, Report CN-654, p. 7, May 20, 1943.

(10) Beaufait, Connick, Crandall, Gofman, Pimentel and Stein, Report CN-723, p. 17, June 20, 1943.

(11) Pimentel, Report CN-808, p. 12, June 20, 1943.

(12) Miller, Report CN-728, p. 64, June 21, 1943.

(13) King, Report CN-867, p. 14, Aug. 14, 1943.

[redacted]

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Compiled by: C. S. Garner Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET IVE-5
IV. Extraction and decontamination methods E. Sodium uranyl acetate method	([redacted] Issued to:

Carrying of 49 by $NaUO_2Ac_3$

20-50% 49 carried by 1st by-product precipitate on micro scale, but only 9% if 49 is first oxidized then reduced (NH_3OHCl) before precipitation.(1)

Use of $Cb_2O_5 \cdot xH_2O$ as a scavenger(2)

Operation of $NaUO_2Ac_3$ method for decontamination without volume reduction(3)

Extraction of 1 mg. 49 from 750 lbs. U + UNH

Estimated overall Pu yield for 3 cycles of acetate process was 88%, with a U reduction factor of 2400, overall γ-decontamination factor of 7800. "Wet" fluoride cycles used on 330 μg. Pu with overall γ-decontamination factor of $\sim 10^7$, including the 3 acetate cycles.(4)

References

(1) Hamaker and Sheline, Report CN-1134, p. 14, December 1, 1943.

(2) Crandall, Report CN-1134, p. 24, December 1, 1943.

(3) Beaufait, Leitz, Stein and Stevenson, Report CN-1134, p. 31, December, 1943.

(4) Carniglia, Connick, Cook, Crandall, Crompton, Gofman, Hamaker, King, King, McVey, Orr, Pimentel, Reas, Reed, Stein, Sheline, Stevenson, Stickland, Thamer and Zumwalt, Report CN-1170, December 20, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IVF-1
IV. Extraction and decontamination methods F. Iodate method	[redacted] Issued to:

Carrying of 48 by $Th(IO_3)_4$

(See IA1i-1.)

Thorium iodate method

$UO_2(NO_3)_2$, 48, fission products, 2N HNO_3 (final conc.), $Th(NO_3)_4$, KIO_3 (6 eq. IO_3^-/eq. Th^{+4}). $Th(IO_3)_4$ precipitate carried 95% 48, 5% U, 20% γ-activity. Dissolved in HCl, 48 oxidized with $Na_2Cr_2O_7$, KIO_3 added. Supernatant solution contains 92% 48, 4% γ-activity. Flow-sheets and other experimental data.(1)

Carrying of 49 by $Th(IO_3)_4$

(See IA1i-1.)

Reference

(1) Duffield, Fontana, Garner, Sheline and Stoughton, Report CN-363, p. 8, Nov. 16, 1942.

[redacted]

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Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET IVG-1
IV. Extraction and decontamination methods G. Peroxide methods	C[redacted]A Issued to:

Carrying of 48 by $UO_4 \cdot 2H_2O$

48 "quantitatively" carried. To separate 48 from U, add La^{+3} to suspension, add dil. HF, U^{+6} complexes and LaF_3 carries 48.(1)

Effect of pH on carrying.(2)

Fission product activity in $UO_4 \cdot 2H_2O$

20-30% short-lived activities came down with $UO_4 \cdot 2H_2O$ at pH = 3 (?). Reprecipitation of the peroxide reduced activity by factor of 2-4.(3),(4)

Thorium peroxide method

Suggested method. Effect of partial precipitation of Th-U peroxides, distribution of fission products.(5)

Poor yields of 48 sometimes. Very large volumes required.(6)

Optimal acidity, pH = 3.0-3.5. Minimum H_2O_2 concentration at which both Th and 48 could be precipitated about 0.6%. Product badly contaminated by fission products.(7)

Uranium peroxide method

H_2O_2 added at pH = 2.5-3.5, $UO_4 \cdot 2H_2O$ carried about 85% 48.(6)

References

(1) Perlman, Report CC-100, p. 1, May 30, 1942.

(2) Seaborg's Group, Report CC-114, p. 1, June 6, 1942.

(3) Brown, Report CC-169, p. 1, July 3, 1942.

(4) Perlman, Report CC-198, p. 1, July 18, 1942.

(5) Perlman and Knox, Report CC-216, p. 1, Aug. 1, 1942.

(6) Perlman and Knox, Report CE-289, p. 1, July 15, 1942.

(7) Kohman, Report CN-343, p. 5, Nov. 15, 1942.

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Compiled by: C. S. Garner Date: September 28, 1943.	HANDBOOK, CHEMISTRY OF PLUTONIUM. EDITION I SHEET IVH-1
IV. Extraction and decontamination methods H. "Thermal" methods	Cop[redacted] Issued to:

Preliminary survey of a "thermal" method

Bombarded metal melted in a graphite crucible (kept at 1400°C. for 1-2 hours), recast in a clean graphite mold. Kr, Xe, I, Ba, Sr, Zr, Cb(?), most of rare earths, about 70-80% γ-activity removed in one heating. "Large proportion" of 48 remained in metal. Advantages of method discussed.(1),(2)

Use of UF_4 flux, and CCl_4 treatment

Bombarded metal kept at 1400° in graphite crucible with UF_4 flux, recast at 1400°, melted, argon containing CCl_4 vapor bubbled thru. Some concentration of the 39 and 49 (or 48?) in UF_4 distilling off in first heating and in the UCl_4 formed in CCl_4 treatment.(3),(4)

References

(1) Johns, Newton, Voigt and Sullivan, Report CN-437.

(2) Voigt and Wolter, Report CN-467, p. 1, Feb. 13, 1943.

(3) Wolter and Voigt, Report CN-522, p. 1, March 15, 1943.

(4) Spedding's Group, Report CC-521, p. 1, March 15, 1943. (See also Report CC-438 for index of Ames reports thru Jan. 1, 1943.)

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IVI-1
IV. Extraction and decontamination methods I. Crystallization method	Copy [redacted] Issued to:

Preliminary crystallization extraction method

Successive crystallizations of $UO_2(NO_3)_2 \cdot 6H_2O$ from aqueous solution. 62% 48, 10% U remained in mother liquor.(1)

Liquid hold-up in crystals is problem. Phase diagram for $UO_2(NO_3)_2 - H_2O - HNO_3$ system at 25°C.(2)

About 99% fission product activity follows 48. Also, experiments in which 48 oxidized showed 53% $48^{(o)}$ went with 70% U.(3)

References

(1) Perlman, Report CN-79, May 16, 1942.

(2) James and Perlman, Report CN-405, p. 4, Dec. 16, 1942.

(3) James and Knox, Report CL-467, p. 10, Feb. 13, 1943.

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IVJ-1
IV. Extraction and decontamination methods J. "Metallurgical" methods	C[redacted]A Issued to:

Attempts to leach 49 from uranium hydride and nitride

Bombarded U hydride and nitride leached with acids showed no promise of a 49-U separation.(1)

Amount 49 extracted proportional to amount U dissolved in case of the hydride. Leaching nitride with 6N HCl removed 10% β-activity, 3% total weight, and gave concentration factor of 5.8 for the 49. Second leaching removed only 1/10th as much. Not effective for removing either 49 or fission products from U.(2)

U-49 alloyed with Misch-metal (50% Ce, 25% La), converted to nitride via hydride, extracted with HCl. 3.6% 49 extracted with 0.6% U, about same as for nitride in absence of rare earths.(3)

Partition of 48 in uranium alloys

If Pu forms stable intermetallic compound with a metal mixed in while U-Pu molten it may react completely with metal and separate from U plus extra added metal on cooling. U is then converted to hydride which is screened away from (usually) larger crystals of intermetallic compound. Nearly all U hydride went thru a 400-mesh screen, about 1/3 of added metal plus U combined with it stayed on a 270-mesh screen.(4)

2.17% Al-U alloy, 5.16% Sn-U alloy, 0.90% Bi-U alloy, converted to hydride, screened. Of Ba, Sr, Te, Mo, Zr, Ce, La, Y, UX, 39, fission products, 9-78% screened out in the case of the Al-U, 22-68% for Sn-U and 5-55% for Bi-U alloys. No data on behavior of Pu.(5)

48 only slight tendency to combine with Al; 30% 48 found with Bi-U compound; nearly all 48 separated out with Sn-U compound.(4)

U-48 alloyed with Sn, unreacted U converted to hydride (unreactive toward non-oxidizing acids), the U-Sn compound (probably U_2Sn) dissolved in H_2SO_4 or HCl, and the 48 (which concentrated in the U-Sn compound) separated from the solution. Results:

1% Sn alloy: 70% 48 separated from 95% of the U
2.4 : 93% " " " 91% " " "
5 : 93% " " " 80% " " ".(6)

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Date: September 28, 1943	EDITION I SHEET IVJ-2
IV. Extraction and decontamination methods J. "Metallurgical" methods	[redacted] Issued to:

Partition of 43 in uranium alloys (cont.)

Partial phase diagrams of U-Al, U-Bi, U-Sn systems. No Pu data.(7)

Cu-U-48 alloy (4.7% Cu), hydride conversion, screened (400-mesh); coarser fraction had 25% Cu, 71% U, 1762c. 48/min./g. U, 4990c. 48/min./g. Cu; finer fraction had 1.9% Cu, 94% U, 157c. 48/min/g. U, 8000c. 48/min./g. Cu.(8) Cu-U compound rose to top as a definite layer, contained some free U. 48 concentrated slightly in Cu-rich phase, but not removed completely from U.(9)

Au-U-48 alloy (3% Au). Au-U compound particles as fine as hydride particles. 31% Au removed by leaching with KCN, no 43 (perhaps due to cyanide acting on 48?).(8)

Ag-U-48 alloy. Presented same difficulties as Au-U-48 alloy.(8)

Hg-U-48 amalgam. (See IIA-1)

No tendency for 48 to separate from U in alloying of 5 p. Mg., 20 p. Misch-metal, 120 p. U-48 (some Mg boiled out), followed by hydride sifting.(9)

References

(1) Voigt, Wolter, Ayres and Hein, Report CN-578, p. 25, April 15, 1943.

(2) Spedding's Group, Report CC-587, p. 7, 11, April 19, 1943.

(3) Ayres, Butler, Hein, Voigt and Wolter, Report CN-678, p. 3, May 15, 1943.

(4) Johns, Butler, Tevebaugh, Wolter and Voigt, Report CN-727, p. 2, June 15, 1943.

(5) Butler, Ayres, Gladrow, Johnson, Kant and Nottorf, Report CC-725, p. 2, June 15, 1943.

(6) Butler, Wolter, Ayres, Hein, Tevebaugh and Voigt, Report CN-795, July 15, 1943.

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET IVJ-3
IV. Extraction and decontamination methods J. "Metallurgical" methods	Copy [redacted] A Issued to:

References (cont.)

(7) Carter, Snow and Ahman, Report CT-816, p. 1, July 24, 1943.

(8) Butler and Wolter, Report CN-852, p. 3, Aug. 8, 1943.

(9) Hein, Voigt and Butler, Report CN-925, p. 1, Sept. 8, 1943.

[redacted]

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HANDBOOK, CHEMISTRY OF PLUTONIUM

Date: January 27, 1944
EDITION I, SUPP. 2
SHEET IV.J-4

IV. Extraction and decontamination methods
J. "Metallurgical" methods

C[redacted]

Issued to:

Partition of Pu in uranium alloys

Melt of 5% Ag with 48-enriched U separates into 2 layers; upper contains almost all the Ag, very little U, 64% of the 48. Easily separated by conversion to hydride and sifting. Preliminary results on Au-U alloy indicated concentration of 48 in the Au-U phase.(1)

Review of technics and results up to October 15, 1943.(2)

A 20% Ag-U alloy containing 49 was found to separate 90% of the 49 in the Ag-rich cap which had 4% of the U.(3)

Addition of Au or Sn to the intermetallic system Ag-U-Pu increased the Pu in the Ag-rich cap and 300-mesh fractions to 97%, in the case of Au, and 92%, in the case of Sn, of the total Pu. 8% and 11%, respectively, of the U was extracted.(4)

References

(1) Butler, Voigt, Hein, Wolter and Ayres, Report CN-1048, October 8, 1943.

(2) Butler, Voigt, Wolter, Ayres, Hein, Tevebaugh and Johns, Report CN-1058, October 15, 1943.

(3) Butler, Voigt and Hein, Report CN-1060, p. 1, November 8, 1943.

(4) Butler, Voigt and Hein, Report CC-1199, p. 3, December 10, 1943.

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Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: C. S. Garner	EDITION I SHEET IVK-1
IV. Extraction and decontamination methods K. Columbium oxide method	Co[redacted] Issued to:

Suggested columbium oxide method

(See IVE-3 for original observation of carrying of 48$^{(r)}$ by $Cb_2O_5 \cdot xH_2O$.)

Carrying of 48 increased with decreasing acidity. UO_2^{++} and NH_3OHCl reduced carrying; $NaNO_3$ and Na_2SO_4 improved carrying. Two precipitations of $Cb_2O_5 \cdot xH_2O$ out of 1M $UO_2(NO_3)_2$ removed 97-99% 48, twice as much U per batch being handled as for other procedures to date. Precipitate dissolved in dil. $H_2C_2O_4$ which was then destroyed by $K_2Cr_2O_7$, simultaneously oxidizing 48 and reprecipitating $Cb_2O_5xH_2O$. A combined $Cb_2O_5 \cdot xH_2O$-$NaUO_2Ac_3$ procedure is also proposed.(1)

Carrying of 49 by $Cb_2O_5 \cdot xH_2O$ at Cb:Pu = 45:1 and 20:1

(See IAlm-2.)

Carrying of 48 by $Cb_2O_5 \cdot xH_2O$; effect of ZrO^{++}; oxalate variation

(See IAlm-2 for data on carrying.)

W concentrations of ZrO^{++} ($\sim 6 \times 10^{-5}$M) did not interfere with 48 carrying, but 0.001M ZrO^{++} reduced carrying to 74% and 0.011M ZrO^{++} to 61%.(2)

Possible oxalate variation: Dissolve $Cb_2O_5 \cdot xH_2O$ in $H_2C_2O_4$, precipitate $La_2(C_2O_4)_3$ carrying 48, leaving Cb^{+5} in solution. (See IAll-1 for data on carrying by $La_2(C_2O_4)_3$.)(3)

References

(1) Pimentel, Gofman, Hamaker and Sheline, Report CN-808, p. 1, July 20, 1943.

(2) Pimental and Stein, Report CN-867, p. 1, Aug. 14, 1943.

(3) Gofman, Report CN-867, p. 8, Aug. 14, 1943.

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Compiled by: C. S. Garner Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I. SUPP. 2 SHEET IVK-2
IV. Extraction and decontamination methods K. Columbium oxide method	Copy [redacted] A Issued to:

Interference of Fe^{+3} with carrying of Pu by $Cb_2O_5 \cdot xH_2O$

Fe^{+3} interferes with carrying in concentrations as low as 5×10^{-5}M, and it is so serious that this method is being discontinued unless some solution of this difficulty becomes apparent. Al^{+3} as high as 1.2×10^{-2}M has no effect on the carrying.(1)

Coupling of $La_2(C_2O_4)_3$ to $Cb_2O_5 \cdot xH_2O$ procedure(2)

References

(1) Crompton, Report CN-1134, p. 1, December 1, 1943.

(2) Crandall, Crompton, Reas and Stein, Report CN-1134, p. 11, December 1, 1943.

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Compiled by: C. S. Garner Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IVL-1
IV. Extraction and decontamination methods L. Solvent extraction methods	C[redacted] Issued to:

Ether extraction

Summary of results reported earlier. Bombarded $UO_2(NO_3)_2 \cdot 6H_2O$ treated with 0.02M $K_2Cr_2O_7$ in 0.5M HNO_3, ether-extracted, 90% $49^{(o)}$, 1% fission products in ether layer. Ether layer treated with H_2SO_3, extracted with H_2O, H_2O layer had 90% $49^{(r)}$, 1% fission products. (Report CN-261). Radiation levels of 10 times "W" level resulted in precipitate-formation. X-radiation had little or no effect. (Burton). Ether-H_2O saturated with UNH became orange, evolved gas on exposure to sunlight (Report A-519).(1)

Reference

(1) Maloney, Report CN-758, p. 53, June 26, 1943.

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Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: January 27, 1944	EDITION I, SUPP. 2 SHEET IVL-2
IV. Extraction and decontamination methods L. Solvent extraction methods	Co[redacted] Issued to:

Ether extraction

Apparatus for ether extraction, adaptable to remote operation. Runs with Argonne metal.(1)

References

(1) Jenks, Day and Boyle, Report CN-1055, p. 2, November 8, 1943.

[redacted]

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Compiled by: C. S. Garner Date: November 27, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 1 SHEET IVM-1
IV. Extraction and decontamination methods M. Bismuth arsenate method	Co[redacted]___ of 50 copies, Series A Issued to:

Carrying of 48 by $BiAsO_4$(1)

(See IAlt-1.)

Proposed extraction procedure

$Pu^{(r)}$ in 20% UNH, 1M in HNO_3, ~ 0.1M in H_3AsO_4, $BiAsO_4$ precipitated by adding 1.5 mg. Bi^{+3}/ml. to solution, digesting 1-2 hrs. at 75°C. Data on carrying of 48, 49 by $BiAsO_3$, solubility of Pu arsenate, etc. (see IAlt-1.). No H_2SO_4 needed to complex U^{+6}. HNO_3 may be greater than in $BiPO_4$ method. Indication that less Cb and Zr come down with Pu and $BiAsO_4$. One-liter scale run with 1 $BiAsO_4$ E + 2 $BiPO_4$ D cycles gave overall 48 yield of 97.4%, soft-γ-decontamination factor ~ 10^4.(2)

References

(1) James and Thompson, Report CN-914, p. 17, September 1, 1943.

(2) Bradshaw, Dreher, Johnson and Thompson, Report CN-1041, p. 30, October 31, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET VA-1
V. Purification A. Purity requirements and general aspects	Co[redacted] Issued to:

Purity requirements

For a 49 gadget (~20 kg., 10 cm. tamper (?)) the number of neutrons N from (α,n) reactions may be obtained from table by multiplying figure by weight in grams of given elemental impurity and summing for all impurities:

Element	N	Element	N	Element	N
H	0	Ne*	10^4	Ca*	10^2
He	0	Na	10^4	Ti*	5×10^1
Li*	5×10^5	Mg*	10^3	Cr*	2×10^1
Be	2×10^6	Al	5×10^3	Mo*	1×10^1
B*	10^6	Si*	2×10^2	Fe*	5
C*	10^4	P	10^3	Co*	5
N	0	S*	20	Ni*	2
O*	10^3	Cl	10^3		
F	10^5	K*	2×10^2		

*Values based on analogies, corrected for isotopic abundances and potential barriers.

The uncertainty factor is at least two.(1)

For a 23 gadget, Be emits about 7.5 times smaller N than 49 (due to six times greater α half-life, somewhat shorter α range); N for heavier impurities more strongly reduced.(1)

For a 25 gadget, N depends on amount 24. Assuming 24 separated with 25, N for Be is about 2500.(1)

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET VA-2
V. Purification A. Purity requirements and general aspects	Copy [redacted] Series A Issued to:

Purity requirements (cont.)

If neutron level corresponding to spontaneous fission half-life of 10^{15} years is considered tolerable, 2 neutrons are produced per 10^{11} α-disintegrations of 49. Since 10^4 alphas on Be produce about 2 neutrons, 1 part Be in 10^7 parts 49 is upper limit for Be. Table prepared by "similar considerations".

Element	Limit	Element	Limit	Element	Limit
Li	0.5 p.p.m.	F	5 p.p.m.	S	10,000 p.p.m.
Be	0.1	Na	20	Cl	200
B	0.2	Mg	100	K	1,000
C	20	Al	20	Ca	2,000
N	---	Si	500	Ti	4,000
O	100	P	100	Fe	40,000

Also, 2 MEV gammas of 44-hour La could produce neutrons by (γ,n) reaction with Be.(2)

Possibility of slow-n chain reaction in 49 during handling. Critical slow-n mass guessed to be about 200 g. in absence of n-absorbers. Water is chief slower; should be present to extent of 1000 times weight of 49.(2)

Another estimate of purity specifications assumes limit for any one impurity in 20 kg. 49 is 3000 neutrons/sec. from (α,n) reactions.(3) (See table, top of VA-3.)

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET VA-3
V. Purification A. Purity requirements and general aspects	[redacted] Issued to:

Purity requirements (cont.)

Element	Limit	Element	Limit	Element	Limit
Li	0.3 p.p.m.	Na	13 p.p.m.	Ca	1,500 p.p.m.
Be	0.15	Mg	14	Ti	3,000
B	0.55	Al	29	Cr	7,500
C	120	Si	130	Mo	15,000
N	----	P	1,000	Fe	30,000
O	220	S	7,500	Co	30,000
F	1.5	Cl	150	Ni	75,000
Ne	15	K	750		

Experimental thick target n yields from Po alphas(4) used to calculate specifications, assuming 3n/min./g. 49 is tolerance.(5) Limit in p.p.m. obtained from

$$\frac{(\text{tolerance n level}) \times (\text{mass range of light element } \alpha)}{(\text{n yield}/\alpha) \times (\text{specific } \alpha\text{-act. } 49) \times (\text{mass range of } 49\alpha)}$$

$$10^6 \times \frac{3}{(\text{n yield}/\alpha) \times 1.55 \times 10^{11}} \times \sqrt{\frac{A}{239}}$$

Element	Limit	Element	Limit	Element	Limit
Li*	1.2 p.p.m.	F*	0.57 p.p.m.	P*	>350 p.p.m.
Be*	0.057	Ne	----	S	----
B*	0.22	Na*	5.2	Cl	----
C*	50	Mg*	6	A	27
N	>500	Al*	11		
O*	80	Si*	50		

* According to Reports CS-746, CS-874, these limits should be multiplied by 2. The above values appear to be the most reliable to date.

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET VA-4
V. Purification A. Purity requirements and general aspects	Copy [redacted] Issued to:

Comparison of purity requirements of 49 with purity of U metal produced

Imp. in U metal according to CC-388, p.p.m.(6)

Element	Limit*	Ames	Westinghouse	Metal Hyd.	Brush
Li	1.2 p.p.m.	A(s)	A(s)	<0.5	A(s)
Be	0.057	A(s)	VW(s)	NR	A(s)
B	0.22	0.2-0.5	0.35	<0.2-0.1	0.45
C	50	~1600	180	~700	1910
O	80	NR	NR	NR	NR
F	0.57	"	"	"	"
Na	5.2	A(s)	A(s)	30	A(s)
Mg	6	~30	<10(s)	<5(s)	185(s)
Al	11	0-60	NR	A(s)	VW(s)
Si	50	~25	~10	20-50	30 (SiO_2)
P	> 350	A(s)	A(s)	A(s)	A(s)
S	10,000†	NR	NR	NR	NR
Cl	200†	2-20	<20	<5	<20
Ca	2,000†	0-20	<50(s)	<10	A(s)
Ti	4,000†	A	<5	50	5
Fe	40,000†	10-60	~45	150	50
Mo	15,000‡	A	130-205	A(s)	A(s)

*Taken from Roberts data (see VA-3), except as noted.
†Taken from CN&CF-380.
‡Taken from Bethe and Christy table (see VA-3).
(s) = spectrographic determination.
NR = not reported.
A = absent
VW = very weak.

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET VA-5
V. Purification A. Purity requirements and general aspects	Co[redacted] Issued to:

Comparison of purity requirements of 49 with analytical detection limits in U(7)

Element	49 limits*	Detection limit in U**	Method
Li	1.2 p.p.m.	0.8 p.p.m.	(s)
Be	0.057	0.03	(s)
B	0.22	0.05	(s)
C	50	10? (500-mg.)	(c)
O	80	---	---
F	0.57	---	---
Na	5.2	10	(s)
Mg	6	10	(s)
Al	11	---	---
Si	50	10	(s)
P	>350	30	(s)
S	10,000†	10 (500-mg.)	(c)
Cl	200†	5 (500-mg.)	(c)
K	750‡	30	(s)
Ca	2,000†	100	?

*Taken from Roberts data (see VA-3), except as noted.
†Taken from CN&CF-380.
‡Taken from Bethe and Christy table (see VA-3).
(s) Spectrographic determination.
(c) Chemical determination.
** 100-mg. sample, except as noted.

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Compiled by: C. S. Garner Date: September 28, 1943	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I SHEET VA-6
V. Purification A. Purity requirements and general aspects	C [redacted] Issued to:

Comparison of purity requirements of 49 with limits of analytical detection

Results in table obtained using U and Fe as "stand-ins" for Pu; impurities generally concentrated by cupferron extraction technic (see ID3-1)(8)

Element	49 limits*	Detection limit	Sample	Method
Li	1.2 p.p.m.	1 p.p.m.	1mg.	Copper A.C. arc
Be	0.057	0.2	"	Copper spark
B	0.22	0.6	10mg.	Pyroelectric
C	50	50	1mg.	Conductometric
O	80	----	----	----
F	0.57	5	1g.	Volumetric
Na	5.2	100	1mg.	Copper spark
Mg	6	5	"	" "
Al	11	"	"	" "
Si	50	"	"	" "
P	>350	10	10mg.	Pyroelectric
S	10,000†	----	----	----
Cl	200†	10	1mg.	Colorimetric
K	750‡	100	"	Copper spark
Ca	2,000	"	"	" "

* Taken from Roberts data (see VA-3), except as noted.
† Taken from CN&CF-380.
‡ Taken from Bethe and Christy table (seeVA-3).

[redacted]

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Compiled by: C. S. Garner

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET VA-7

V. Purification

A. Purity requirements and general aspects

C[redacted]

Issued to:

Effect of possible heavy isotopes on purification

Possibility of formation of 94^{238}, 94^{240}, 93^{237}, 95^{240}, etc., in the pile. Speculation on possible complications in extraction-decontamination and purification.(9)

Neutron counting of impurities

Proposed methods. Assuming permissible level of 3n/min./g. 49, a neutron counter of 1% overall efficiency, and a counting rate (above background) of 1c./min., about 30g. 49 needed for a test. Proposed use of an external alpha source.(10)

References

(1) Teller, Report CF-367, Nov. 30, 1942.

(2) Seaborg and Perlman, Report CN&CF-380, Dec. 15, 1942.

(3) Bethe and Christy, Report LA-11, p. 3, July 21, 1943.

(4) Roberts, Report CF-864, Aug. 1, 1943.

(5) Kohman, Report CK-736, p. 21, June 21, 1943.

(6) Nagel and Brown, Report CN&CF-427, p. 6, Jan. 15, 1943.

(7) Orlemann, Report CK-659, p. 3, May 15, 1943.

(8) Fred, Report CK-928, p. 1, Sept. 11, 1943.

(9) Seaborg, Report CN&CF-514, p. 1, March 15, 1943.

(10) Kohman, English and Ghiorso, Report CN&CF-591, p. 7, April 15, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET VC-2
V. Purification C. Purification of Pu	G[redacted] Issued to:

Purification of Pu by $NaPuO_2Ac_3$-ether extraction method

Two runs were made on a total of 2.5 g. Pu, using the following procedure: Oxidation with $Na_2Cr_2O_7$ in acid solution. $NaPuO_2Ac_3$ precipitated, dissolved in HNO_3 and reprecipitated, redissolved in HNO_3. The solution was diethyl ether extracted in a Soxhlet extractor in the presence of $NaNO_3$, then extracted again from H_2O solution. The Pu^{+6} was reduced with HI in HNO_3 solution, boiled to give Pu^{+4}. Overall yield was 80-93%. Spectrographic analysis for Be, Mg, Al, Ca, Fe, Zr, La, Ce, Bi, Th indicated total concentration of elements detected was 0.2%. The upper limit for the total of all impurities, including elements sought for but not detected, was about 3%.(1)

A preliminary survey of a magnetic separation of Pu from L.E.

Apparatus equivalent to one of the four units of the beta process of the Y-12 program would be needed to handle 0.6 kg. Pu/day. Construction might not be possible in 12 months. The process is discussed somewhat in the report. The method is considered only as a last resort, and might not produce anything better than possible by present known chemistry.(2)

References

(1) Mastick, Pittman and Wahl, Report LAMS-72, p. 12, April 1, 1944.

(2) Warner, Report CK-1541, p. 24, April 4, 1944.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET VIII-1
VIII. Miscellaneous data	Cop[redacted] Issued to:

Search for plutonium in natural ores

Apart from negligible amount of 49 produced by spontaneous fission of U, an amount of 1 p. 49 per 10,000 p. U would allow increasing efficiency of U in a pile by 10% if 49 were concentrated ten-fold. U might be purified too much, losing 49.(1)

Spontaneous fission of U might give 100 mg. 49 from 20 tons U, assuming (incorrectly) 49α half-life > 10^6 years.(2)

Above α half-life of 49 probably about 30,000 years, in which case 49 probably not worth looking for in ores.(3)

Search for Pu in a pitchblende concentrate (~400 g.) indicated about 3 α-disintegrations per minute. This was assumed due to 49 since the exhaustive chemical treatment should have eliminated U, Io, etc. No fission counts in 7 hours. These two data placed limit of no more than 1 p. 49 in 10^8 p. pitchblende concentrate (from fission rate), or 1 p. 49 in 10^{14} p. pitchblende concentrate (from alpha rate).(4)

Carnotite, fergusonite and hatchettolite examined for Pu by a stringent chemical cycling similar to that used in examining pitchblende.

Ore	α-dis./30 min.	fission rate
Carnotite (~5 kg.)	83	1 c./20 hrs.
Fergusonite (~0.5 kg.)	4	0 c./3 hrs.
Hatchettolite (~0.7 kg.)	12	0 c./8 hrs.

No more than 1 p. 49 in 10^{10} p. carnotite, 10^9 p. fergusonite or hatchettolite (from fission rate). Alpha rate of carnotite corresponds to about 1 p. 49 in 10^{14} p. carnotite.(5) It seems that the amount of Pu in the ores examined (which should have been the most favorable ones) is negligible for most practical purposes.

Consideration of Site W decontamination needs (6)

[redacted]

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET VIII-2

VIII. Miscellaneous data

Cop[redacted]

Issued to:

Radiation dosage from handling 49

Neutrons from (α,n) reactions:

Compound	n/min. from compound containing 1 kg. 49*
PuO_2	3×10^6
"$Pu(NO_3)_4 \cdot 8H_2O$"	6×10^6
"$Pu_2O_7 \cdot 2H_2O$"	5×10^6
"PuF_4"	8×10^7

*Assuming tolerances given in CH&CF-380 (see VA-2).

About 10^8 n/min. ≈ 0.1R dose in 8 hours at 1 foot, hence PuF_4 requires precaution.(7)

Gamma radiation from unremoved fission products: If 1 γ/1000 α (upper limit), 10 kg. 49 will have 700 millicuries γ-activity. Assuming 1 MEV average energy, about 70 mc. γ-activity escapes from 10 kg. sphere of 49. This is about 0.04 R/hr. at 1 m.(7)

Technic of charging microcrucibles with Pu

Lucite monomer distilled, partially polymerized, condensed to solid lucite lining in crucible. Nitrate solution of Pu (or U) evaporated in crucible, heated to 700°C. to convert to oxide and to remove lucite. Coherent mass of oxide in bottom of crucible (for reduction experiments, e.g.).(8)

Mounting microsamples of metal

Technic of mounting, using lucite, for purposes of metallographic examination.(9)

Analysis for Pu

(See IA1f-2, 3, 5.)

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[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET VIII-3
VIII. Miscellaneous data	Co[redacted] Issued to:

References

(1) Szilard, Report A-45, September 26, 1941.

(2) Szilard, Report A-45, Memo of September 30, 1941.

(3) Szilard, Report A-45, Memo of October 17, 1941.

(4) Seaborg and Perlman, Report A-146, April 13, 1942.

(5) Garner, Bonner and Seaborg, Report CN-246, August 26, 1942.

(6) Coryell, Report CN-576, April 15, 1943.

(7) Perlman, Report CN&CF-591, p. 12, April 15, 1943.

(8) Kirk, Rosenfels, Baumbach and Zoolner, Report CK-888, p. 1, August 7, 1943.

(9) Kirk, Rosenfels, Baumbach and Zoolner, Report CK-888, p. 5, August 7, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner, A. C. Wahl	HANDBOOK, CHEMISTRY OF PLUTONIUM.
Date: January 27, 1944	EDITION I, SUPP. 2 SHEET VIII-4
VIII. Miscellaneous data	C[redacted] Issued to:

Self-absorption of alpha particles in solid 49 metal

Calculations of the self-absorption of alphas by spherical and hemispherical pieces of Pu metal indicate it is too great to allow assay of pieces even as small as 1 μg. by alpha-counting, even after the application of corrections.(1)

Yield of 49 in Argonne pile

Measurements of the temperature rise in an uranium lump irradiated in the Argonne pile, together with chemical assay for the amount of 49 produced, gave a value for the yield of 4×10^{-5} g. 49/Kwh. On this basis operation of the Hanford pile at a power level of 2.5×10^{5} Kw. should produce 240 g. 49 per 24-hour day. The Argonne measurements also indicated that 0.88 49 atoms were produced per fission.(2)

Radiocolloid formation

At pH $\geqq 3$, 48 forms radiocolloids (i.e. concentrate at the bottom of a cone when the solution is centrifuged and sticks to the walls of glassware).(3)

At pH $\leqq 4$, 39 shows no tendency to form radiocolloids.(3)

Analysis for Pu

(See IA1f-11,12. Also, above paragraphs on radiocolloid formation.)

References

(1) Jaffey, Report CK-1072, p. 1, November 6, 1943.

(2) Anderson, Hill, Engelkemeir and Freedman, Report CN-1190, p. 10, December 25, 1943.

(3) King, Report CN-1134, p. 43, December 1, 1943.

[redacted]

Compiled by: A. C. Wahl Date: May 1, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM. EDITION I, SUPP. 3 SHEET VIII-5
VIII. Miscellaneous data	[redacted] Issued to:

Specific activity of Pu^{239}

Compound weighed	c/m/μg 49*	Geometry of counter	Half-life of 49
?	7.1×10^4 (1)	52%	24,000 y
PuO_2**	7.05×10^4 (2)	?	---
"	7.23×10^4 (2)	?	---
"	7.06×10^4 (2)	?	---

* On "50%" geometry counter.
** Assayed for oxygen and found to be PuO_2.

References

(1) Cunningham, Ghiorso and Hindman, Report CN-1241, p. 1, Jan. 5, 1944.

(2) Johns, Maxwell, Moulton and Wahl, Report LAMS-72, April 1, 1944.

[redacted]

Compiled by: C. S. Garner R. B. Duffield	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPR. 3 SHEET VIII-6
VIII. Miscellaneous data	Co[redacted]A Issued to:

Separation of Pu from slag materials

$Fe(OH)_3$, $Zr(OH)_4$, $U(OH)_4$ and $Cr(OH)_3$ have been tried as carriers for 48. The hydroxides precipitate at the pH shown: Fe^{+3} 2, Zr^{+4} 2, Ce^{+4} 2.7, U^{+4} 3, Th^{+4} 3.5, Cr^{+3} 5.3, Mg^{+2} 10.5, $Ca^{+2} > 11$, and Pu^{+4} in the range 5-6. The slags (Ca and Mg fluorides and oxides) were put into solution with fuming $HClO_4$ (more drastic treatment is needed in some cases), 48 added, then carrier and NH_4OH to precipitate the carrier. Another hydroxide precipitation is made after adding more carrier, and each hydroxide is dissolved in acid, La^{+3} added, then HF to analyze for the 48. At a pH of 5.6 - 8.2, the first $Fe(OH)_3$ precipitate carried 94 - 99.5% of the 48 (0.3 - 0.5 mg. Fe^{+3}/ml.). $U(OH)_4$ was not so good, carrying less than 90% 48 in general at pH = 5 - 8.2. $Zr(OH)_4$ carried 96 - 98.7% 48 at pH = 8. These hydroxides were sufficiently free from Ca^{+2} and Mg^{+2} to avoid precipitation of CaF_2, MgF_2 on addition of HF. "$Pu(OH)_4$ may precipitate by itself without carrier."(1)

98-100% of 48 was extracted in a single extraction from dilute $HClO_4$ of the cupferride. Details are not given.(1)

Reference

(1) Hein, Wright and Voigt, Report CK-1526, p. 5, March 23, 1944.

Absorption spectra of Pu^{+3}, Pu^{+4}, Pu^{+6} (1),(2)

The absorption spectra of the three oxidation states of Pu in aqueous solution were measured using a Beckman spectrophotometer and a band width < 100 Å. The results are given in the following curves. (See following pages.)

References

(1) Hindman, Howland, Kraus and Cunningham, Report CN-1324, p. 4, February 1, 1944.

(2) Hindman, Kraus and Howland, Report CK-1371, p. 4, March 1, 1944.

[redacted]

[redacted]

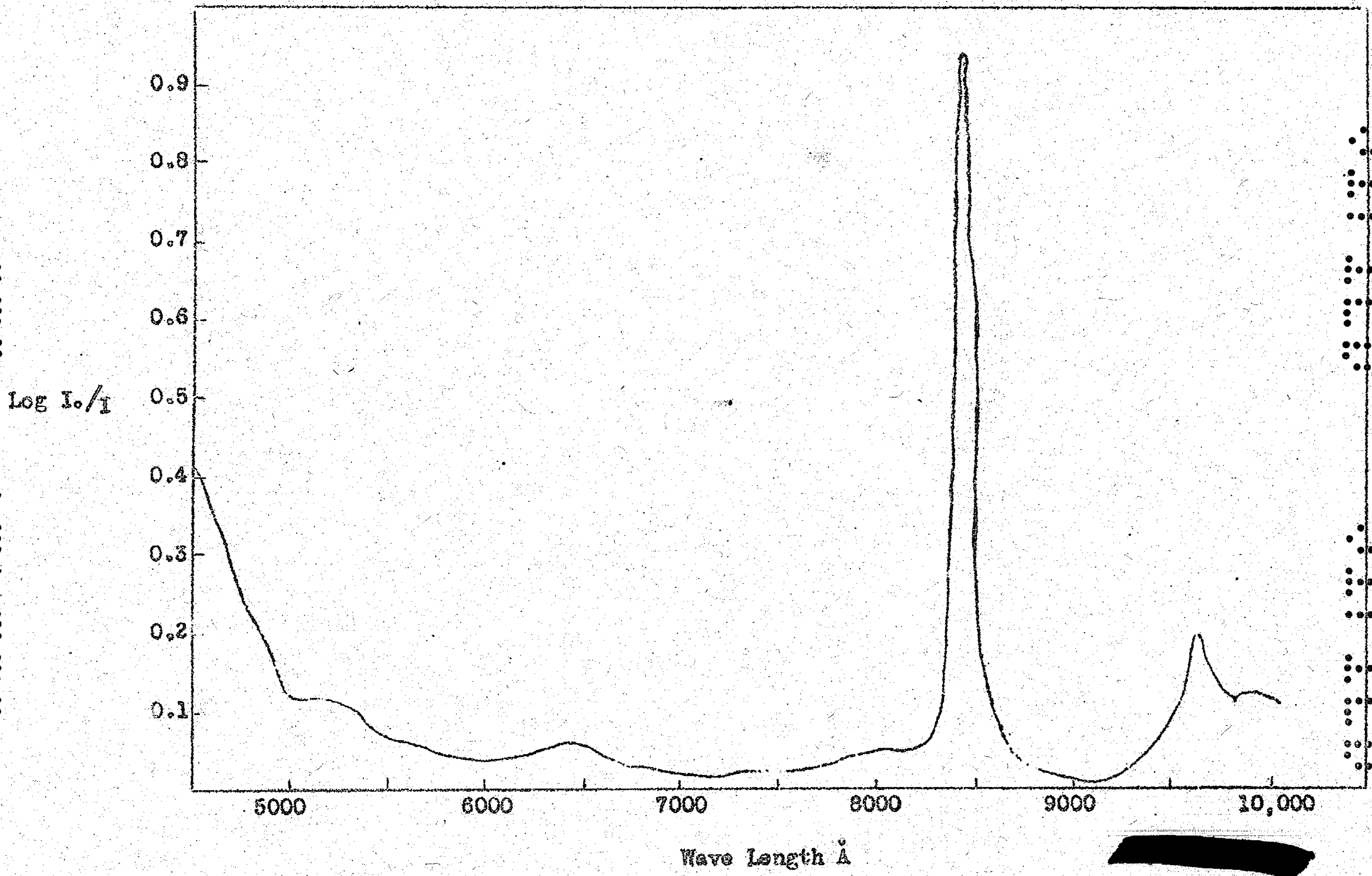
Compiled by: R. B. Duffield

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3   SHEET VIII-7

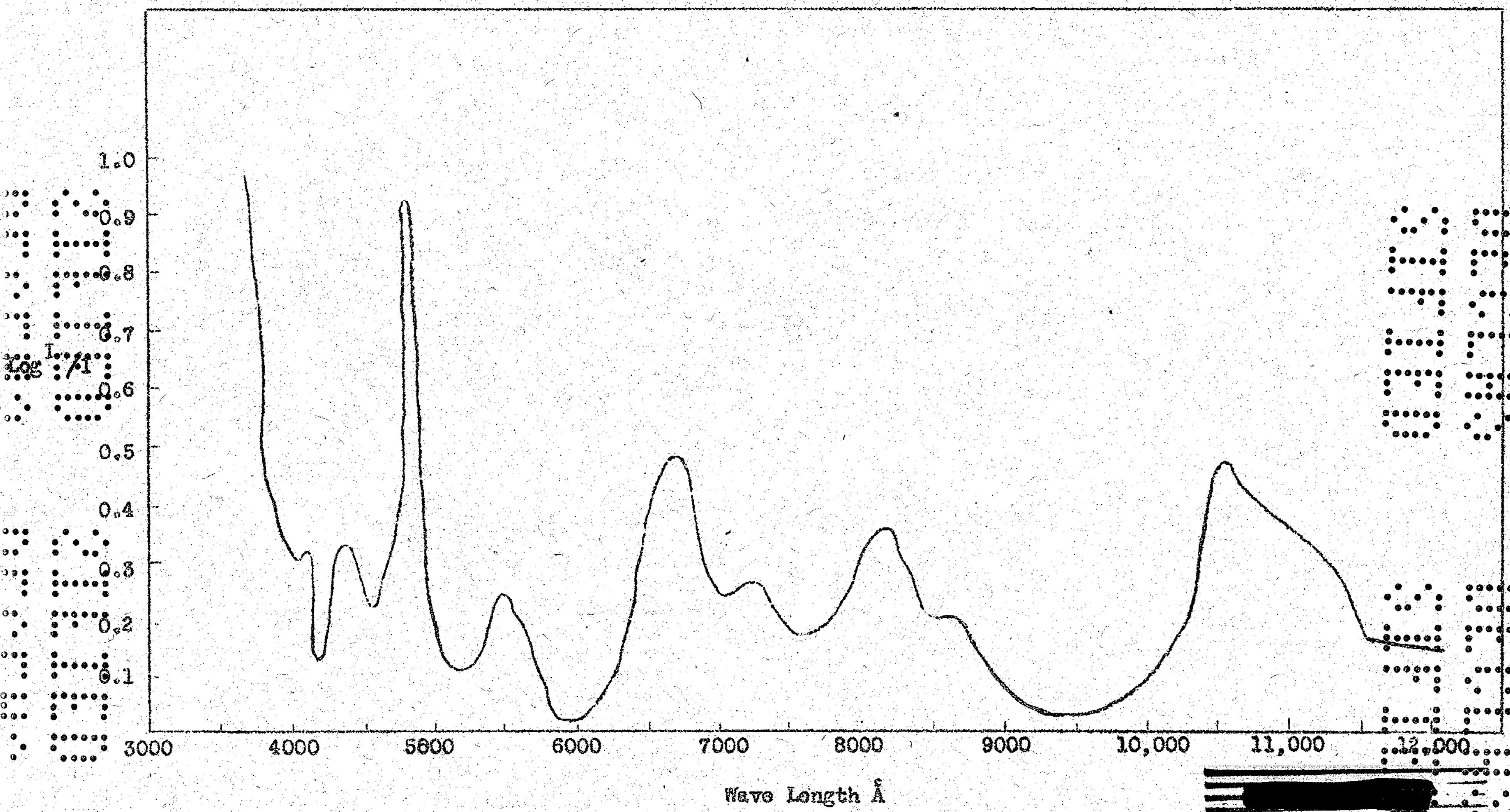
Absorption Spectrum 0.0375 M Pu^{+6} in 1.5M HCl



[redacted]

[redacted]

Absorption Spectrum 0.0521M Pu^{+4} in 1M H_2SO_4



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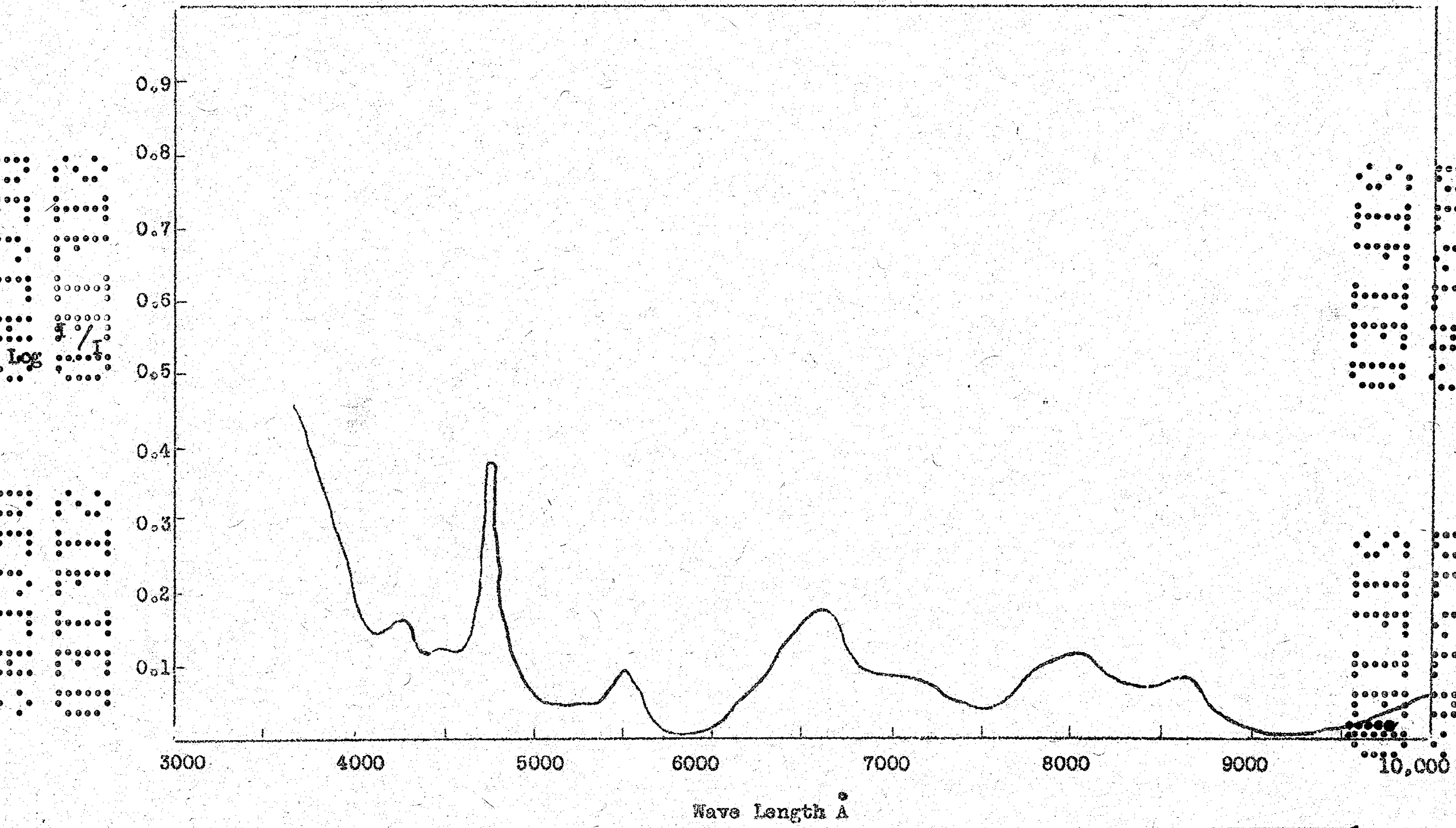
Compiled by: R. B. Duffield

Date: May 1, 1944

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I, SUPP. 3 SHEET VIII-9

Absorption Spectrum 0.038 M Pu^{+4} in 1 N HNO_3



[redacted]

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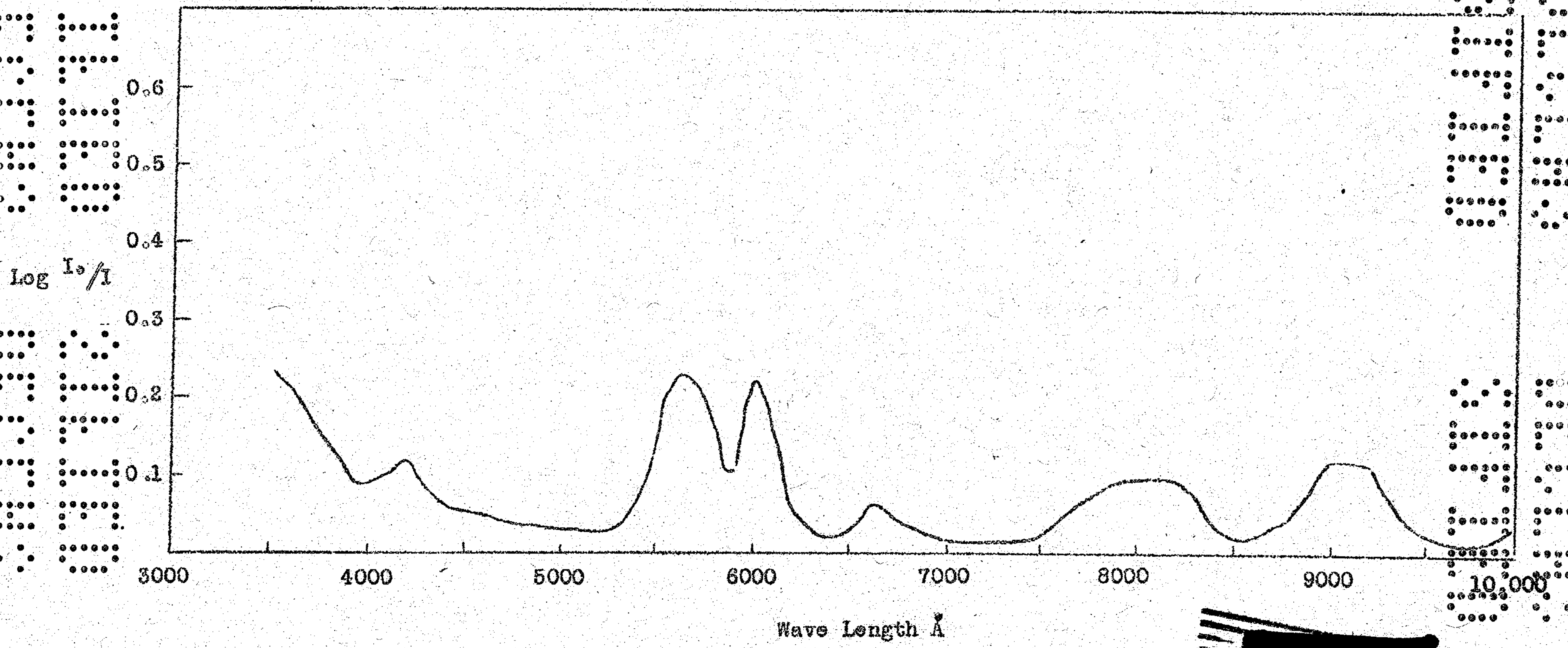
Compiled by: R. B. Duffield HANDBOOK, CHEMISTRY OF PLUTONIUM

Date: May 1, 1944 EDITION I, SUPP. 3 SHEET VIII-10

Absorption Spectrum 0.028 M Pu^{+3} in 1.37 N HCl



[redacted]

Compiled by: C. S. Garner Date: January 27, 1944	HANDBOOK, CHEMISTRY OF PLUTONIUM EDITION I, SUPP. 2 SHEET VA-8
V. Purification A. Purity requirements and general aspects	[redacted] Issued to:

Purity requirements

The data of Roberts on α,n yields from Po (see VA-3) have been used by Anderson and Roberts(1) to recalculate new α,n yields from 49 α-particles, making use of the newer value 3.68 cm. for the range of 49 α's (Pardue and Lester). On the basis of these α,n yields and assuming (1) the specific α-activity of Pu to be 155,000 dis./min./µg., and (2) the neutron tolerance level in the gadget to be 3 n/min./g.49, the following purity requirements were calculated:

Element	Limit	Element	Limit
Li	1.3 p.p.m.	Mg	5.6
Be	0.051	Al	11
B	0.20	Si	51
C	48	P	>350
O	77	S	>350
F	1.7	Cl	83
Na	4.6	A	27

Except for the values for S and Cl (new data) and for F there is no significant change from the former "best" table, values given on sheet VA-3.

Special meeting with Dr. Thomss on purification of plutonium(2)

References

(1) Anderson and Roberts, Report CN-1190, p. 12, December 25, 1943.

(2) Katz and Warner, Report CK-1185, December 20, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: September 28, 1943	EDITION I SHEET VB-1
V. Purification B. Purification of similar elements	[redacted] Issued to:

Removal of B from U by "dry fluoride" treatment

Cycle:

$$\begin{cases} U_3O_8 + H_2 \xrightarrow{700^\circ} UO_2 + H_2O \\ UO_2 + HF \xrightarrow{500^\circ} UF_4 + H_2O \\ UF_4 + O_2 + H_2O \xrightarrow{500^\circ} U_3O_8 + HF \end{cases}$$

Aqueous solution, 60 g. HBO_2 + 200 g. $UO_2(NO_3)_2 \cdot 6H_2O$, evaporated to dryness, ignited, above cycle completed twice:(1)

Step	Boron content (p.p.m.)
Initial	100,000
After 2d. hydrogenation	15 ± 3
After 2d. hydrofluorination	0.8 ± 0.2

Proposed modification for removal of B from Pu:(1)

Cycle:

$$\begin{cases} PuO_2 + HF \xrightarrow{500^\circ} \text{"}PuF_4\text{"} + H_2O \quad \text{(see IIC-2)} \\ \text{"}PuF_4\text{"} + H_2O \xrightarrow{\Delta} PuO_2 + HF \quad \text{(no data)} \end{cases}$$

Removal of Be by "dry fluoride" treatment

Be^7 tracer evaporated on Ni. HF for 3/4 hour gave 90% volatilized at 600°C., 18% at 500°. 3 mg. Be (as BeO), containing Be^7, volatilized 30-50% in HF at 600° for 3/4 hour.(2)

No volatilization of Be in F_2 at 500° for 3/4 hour.(2)

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Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET VB-2

V. Purification
B. Purification of similar elements

Co[redacted]

Issued to:

Pyroelectric concentration studies with uranium

U_3O_8 containing 15 added impurities, treated by Ga_2O_3 volatilization in an arc, followed by addition of more Ga_2O_3 to non-volatilized residue and volatilization in the arc again (method described in detail in an earlier report(3):

Element	Original conc.	Conc. after treatment
Be	0.40 p.p.m.	0.40 p.p.m.
As	40	3.0
Fe	100	100
B	1.2	0.35
Si	100	100
P	200	30
Sb	20	12
Au	0.40	0.03
Ge	4.0	0.3
Mg	100	100
Mn	20	18
Pb	"	"
Cr	40	40
Sn	20	10

For most elements the volatilization is a rate process. Not effective, in general.(4)

Critical study of the method indicated procedure probably of little use for analysis of 10 mg. (or smaller) samples of PuO_2. U_3O_8 appreciably reduced to U under conditions used; Pu may be similarly produced, may be more volatile than U, Pu spectrum may interfere. Difficulties in case of U may be due chiefly to impurities in graphite electrodes.(5)

[redacted]

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HANDBOOK, CHEMISTRY OF PLUTONIUM

Date: September 28, 1943

EDITION I

SHEET VB-3

V. Purification
B. Purification of similar elements

[redacted]

Issued to:

Purification of Th by precipitation methods

Th and U peroxides, Th iodate and oxalate precipitated, Li, Be, B, Na, Mg, Si, P, K, Fe looked for spectroscopically before and after precipitation. In general, reprecipitations of a given compound were ineffective, sometimes increasing impurities due to contamination during handling. Peroxide precipitation reduced large amounts (~10,000 p.p.m.) impurities to 10-100 p.p.m., but no further, except for Li and Be which were reduced to <0.8 and <0.05 p.p.m., respectively.(6) Peroxide precipitation appeared better than oxalate or iodate precipitation.(6)

Use of redistilled acids and water, quartz vessels, did not help. Most effective cycle was oxalate precipitation, followed by two precipitations of the peroxide, then precipitation of 10% of the hydroxide (discarded) and finally the rest of the hydroxide. Li(?), Be, Si, P, K and Fe were reduced below tolerance level; B was doubtful. Na and Mg remained too great.(7)

References

(1) Brown, Hill and Bohlmann, Report CN&CF-514, p. 4, March 15, 1943.

(2) Brown and Hill, Report CK-736, p. 5, June 21, 1943.

(3) Scribner and Mullin, Report A-123, p. 1, 1942.

(4) Marshall and Fred, Report CK-801, p. 5, July 17, 1943.

(5) Marshall, Report CK-928, p. 5, Sept. 11, 1943.

(6) Smith and Cunningham, Report CK-736, p. 9, June 21, 1943.

(7) Smith, Kroner and Cunningham, Report CK-806, p. 6, July 17, 1943.

[redacted]

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: January 27, 1944	EDITION I, SUPP. 2 SHEET VB-4
V. Purification B. Purification of similar elements	[redacted] Issued To:

Purification of Th by precipitation methods

Precipitation and recrystallization of thorium molybdate gave a good preliminary purification of Th from Li, Be, B, Na, Mg, P and K. See IAlu-1 for similarity of Pu molybdate to Th molybdate.(1)

Qualitative summary of purification of Th by precipitation:(2)

Promising precipitants*	Unpromising agents	Agents giving no precipitate with 0.0025M Th^{+4}
IO_4^-	H_3PO_4	BrO_3^-
$MoO_4^=$	H_3AsO_4	HAc (cold)
$SO_3^=$	$Fe(CN)_4^{\equiv}$	α-Nitroso-β-naphthol
H_2O_2	Sulfanilic acid	Benzidine
IO_3^-	Pyrogallic acid	Isatin
K_2SO_4	Phenylarsonic acid	Salicylaldoxime
$C_2O_4^=$	Hexamethylene tetramine (prec. of hydroxide)	Quinaldine
Tartaric acid		n-Propylarsonic acid
H_3PO_2		
Fumaric acid		
Picrolonic acid		
Phenoxyacetic acid		
m-Nitrobenzoic acid		

* In general, purification from Li, Na, K, Be, Mg and B was good, but not from Fe, P, Si. In approximate order of decreasing effectiveness for one or two precipitations.

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[redacted]

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Date: January 27, 1944	EDITION I, SUPP. 2 SHEET VB-5
V. Purification B. Purification of similar elements	C[redacted]A Issued to:

Purification of U by ether extraction

Purification of UNH by ether extraction; distribution of 22 tracer and of light element impurities between diethyl ether and 10M NH_4NO_3. Possible use to purify Pu(o) from Li, Na, K, Mg, Ca, Al, P, maybe from Be, Si, Fe, not from B.(3)

Purification of Th by solvent extraction

Th is being used as a stand-in for Pu(r). Preliminary experiment on distribution of light elements between nitromethane and 10M NH_4NO_3, 1M HNO_3 solution indicated that satisfactory purification may be expected from Si (?), Be, Mg, Al and K, but is not expected from Na, Si (?), Ca.(4) See ID4-1.2 for data on distribution of 49(r) in this and other organic solvents.(4)

References

(1) Jensen, Cunningham and Orlemann, Report CK-1072, p. 4, November 6, 1943.

(2) Jensen and Orlemann, Report CK-1221, p. 3, January 5, 1944.

(3) Brody and Orlemann, Report CK-1072, p. 7, November 6, 1943.

(4) Brody and Orlemann, Report CK-1221, p. 1, January 5, 1944.

[redacted]

Compiled by: C. S. Garner	HANDBOOK, CHEMISTRY OF PLUTONIUM
Date: May 1, 1944	EDITION I, SUPP. 3 SHEET VB-6
V. Purification B. Purification of similar elements	[redacted] Issued to:

Purification of Th^{+4} and U^{+4} by precipitation methods

A study was made of the separation of Th^{+4} and U^{+4} from added B, Be, Li, K, Na, Mg, Fe, P by multiple precipitations, including precipitation of peroxide, oxalate, molybdate, periodate, sulfite, m-nitrobenzoate and phenoxyacetate, singly and in combination. Best result was 2 X with $(NH_4)_2MoO_4$ followed by 1 X with $H_2C_2O_4$, which gave for Th: B = 0.15, Be = 0.20, Fe = 7.5, $K < 20$, $Li < 0.8$, $Mg < 5$, Na = 20, $P < 10$, $Si < 7.5$ p.p.m. (About 1000 p.p.m. of each, except Si, had been added to starting material.)(1)

Purification of U^{+4} by precipitation and extraction of U^{+6} by ether

2 X with $H_2C_2O_4$, followed by single ether extraction, reduced the added impurities (as above) to values well below the Pu tolerance limits, except for B, Na, Si. There was evidence in both this and the above work that contamination was being introduced.(1)

Size of Pu ions and its relation to stand-ins

X-ray diffraction data indicate that Pr^{+4}, Ce^{+4} and U^{+4} correspond most closely to Pu^{+4} in size. Similarly, U^{+3}, La^{+3}, Ce^{+3}, Pr^{+3}, Nd^{+3} and Sm^{+3} should be excellent stand-ins for Pu^{+3} on a crystallographic basis. Universal isomorphism of Pu^{+4} with Th^{+4}, Hf^{+4} and Zr^{+4} cannot be expected.(2)

References

(1) Stein, Jensen and Orlemann, Report CK-1372, p. 1, March 1, 1944.

(2) Zachariasen, Report CK-1453, March 6, 1944.

[redacted]

[redacted]

Compiled by: C. S. Garner

Date: September 28, 1943

HANDBOOK, CHEMISTRY OF PLUTONIUM

EDITION I SHEET VC-1

V. Purification
C. Purification of Pu

[redacted] A

Issued to:

Suggested methods for obtaining pure Pu metal

Purification from harmful impurities except F: $PuO_2 + HF \longrightarrow$ "PuF_4" + H_2O; BF_3, SiF_4, H_2O should volatilize, probably HCl also. "PuF_4" + $F_2 \longrightarrow$ "PuF_6" ↑, distill Pu away from Li, Be, Na, Mg, Al, K, Ca, Sc? Redistill, reduce to "PuF_4" and recycle. Vessels must be heavy metals; HF and F_2 must be pure.(1)

Production of Pu metal: (a) Reduction of "PuF_4" with Ca, convert crude metal to bromide or iodide, reduce with Ba in vacuo or in inert atmosphere; (b) thermal decomposition of iodide on hot W wire; (c) electrolysis "$KPuF_5$" in molten $CaCl_2$-NaCl.(1)

Refractories: graphite, BeO, Al_2O_3, MgO not good because likelihood of adding impurities. According to Creutz, SiC, B_6C, ZrO_2, ThO_2, MgO, CaO, Al_2O_3, Pt, W, Ta, Mo all react or alloy with U at 1800-2000°C. Might use "cold casting" -- recast molten metal in mold of Ta, etc., kept cold by cooling agent.(1)

Partial purification of 49 from La by peroxide precipitation

200 μg. 49, 700 μg. La, brought down to volume of 200 μl. by successive "wet fluoride" oxidation-reduction cycles. Solution 0.75M in HNO_3, 6-8 % in H_2O_2, green Pu peroxide removed by centrifugation, dissolved in 100 μl. 1M HNO_3, reprecipitated as peroxide. Dissolved in HNO_3, portion evaporated and ignited to oxide. Weighed (~4μg.), α-rate determined: specific activity = 153,000 dis./min./μg. (best value to date = 155,000. (See section VII).(2)

Extraction of 48-cupferride into $CHCl_3$

(See ID3-1,2.)

Attempts to extract other 48-organic complexes

(See ID3-2.)

References

(1) Magel and Brown, Report CN&CF-427, p. 4, Jan. 15, 1943.

(2) Perlman, Report CN&CF-514, p. 6, March 15, 1943.

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