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THE PREPARATION OF PLUTONIUM TRICHLORIDE

WORK DONE BY:

- T/3 S. E. Bakes
- C. S. Garner
- I. B. Johns
- G. H. Moulton
- B. Weinstock

REPORT WRITTEN BY:

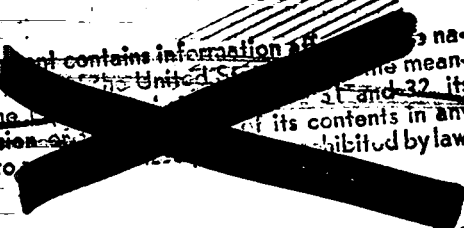
C. S. Garner

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ABSTRACT

The following methods for the preparation of plutonium trichloride have been developed and their relative advantages and difficulties described:

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- 1) Dehydration of Pu(III) chloride solutions,
 - 2) Hydrochlorination of plutonium hydride,
 - 3) Dehydration of Pu(IV) chloride solutions, followed by reduction with hydrogen,
 - 4) Hydrochlorination of plutonium dioxide in the presence of hydrogen,
 - 5) Hydrochlorination of plutonyl nitrate in the presence of hydrogen,
 - 6) Chlorination of plutonium dioxide in the presence of carbon tetrachloride vapor,
 - 7) Hydrochlorination of plutonium(III) oxalate in the presence of hydrogen.

The favored method at present is No. 7 which can be carried out relatively rapidly on the present scale of operations (1-10 grams Pu) and which appears to offer the least probability of giving trouble on a 200-gram scale. Some of the properties of the trichloride are indicated, such as the melting point, vapor pressure and hydroscopicity.

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CONFIDENTIALTHE PREPARATION OF PLUTONIUM TRICHLORIDE

Because of the low tolerance limit for fluorine in plutonium for E-1, the use of plutonium trifluoride or tetrafluoride in the preparation of plutonium metal has been considered undesirable. Consequently, methods for the preparation of plutonium trichloride have undergone intensive study by the "dry" chemistry staff of Group C-5. Some of these findings have been reported very briefly in the monthly progress reports of the Division of Chemistry and Metallurgy, but it seems worthwhile to describe the various methods in greater detail.

First attempts to prepare PuCl_3 involved dehydration of Pu(III) chloride solutions in the presence of anhydrous hydrogen chloride and volatile substances used in the reduction of the Pu(IV) to Pu(III). Consult Table I for the details of the treatment involved. This process appears to result in reasonably pure PuCl_3 , but it would probably be difficult to execute on a 200-gram scale. 7

Good PuCl_3 may be made by the action of hydrogen chloride on plutonium hydride (Table II). However, at present the hydride can be made only from the metal, and this process for preparing PuCl_3 would be feasible only if it were decided to make metal first from the fluoride (or some other way). Since the hydriding and hydrochlorination steps are expected to be inefficient for removing light element impurities this plan seems to have little value.

Attempts to prepare PuCl_4 by dehydration of Pu(IV) chloride solutions, followed by reduction of the PuCl_4 to PuCl_3 with hydrogen, have resulted in a nearly black, water-insoluble product of varying composition. From the results obtained in these studies (see Table III) it is not clear that anhydrous PuCl_4 exists, but if it does it probably is unstable with respect to dissociation into

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PuCl_3 and Cl_2 . Careful control of the rate of dehydration probably would permit the use of this process as may be judged by the relatively good material prepared in run 89-56, but the generally discouraging results have prompted the development of better methods.

The relative difficulty of obtaining Pu(III) and Pu(IV) chloride solutions after the purification procedure (see LA-75 for a description of the procedure in use up until recently), without the introduction of light element impurities, led to a study of the direct use of the $\text{PuO}_2(\text{NO}_3)_2$ solution as it normally came out of the purification scheme in use. The procedure found satisfactory on a small scale involved evaporation of the viscous $\text{PuO}_2(\text{NO}_3)_2$ solution to crystals, an operation somewhat difficult and slow to carry out on a 200-gram scale because of the health hazard, ignition of the nitrate to PuO_2 , and heating of the dioxide in a stream of approximately 50-mol percent H_2 , 50-mol percent HCl . Tables IV and V present the results of these studies. The use of PuO_2 ignited only to 350-400° C has a definite advantage over that of highly-ignited dioxide as far as speed of reaction is concerned. On the other hand, $\text{PuO}_2(\text{NO}_3)_2$ apparently does not decompose quantitatively to PuO_2 at these low temperatures, a fact which necessitates the taking of a small weighed aliquot for ignition at 1000° in order to determine the percent conversion to chloride in the subsequent hydrochlorination. This general method can certainly be made to work on a 200-gram scale, but there is plenty of evidence suggesting that the reaction is increasingly difficult to carry out in a reasonable time as the scale goes up from 1 to 200 grams. The direct treatment of $\text{PuO}_2(\text{NO}_3)_2$ with $\text{H}_2 + \text{HCl}$, without conversion to dioxide first, appears to offer no advantage over the use of PuO_2 (see Table VI).

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Experiments on treating PuO_2 with $\text{Cl}_2 + \text{CCl}_4$, S_2Cl_2 , etc., have not been intensively pursued at Los Alamos owing to the considerable effort being devoted to this problem at Chicago. Some of the results obtained here, using $\text{Cl}_2 + \text{CCl}_4$ in the vapor phase, are presented in Table VII. Unless sublimation of PuCl_3 is desirable from a purification point of view this process has little to recommend it, for it is difficult to get quantitative conversion without appreciable sublimation of the PuCl_3 .

The process which is favored at this time consists of the partial drying of a slurry of " $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ " in water by passage of air over the slurry at about 50° , followed by heating slowly in a stream of $\text{H}_2 + \text{HCl}$ from room temperature to about 600° . Drying of the slurry proceeds rapidly because plutonium (III) oxalate is very insoluble in water (LA-63) and, hence, the water present is substantially at its normal vapor pressure. On a gram scale the hydrochlorination has been carried out extremely rapidly with success, but on a 5-10 gram scale it has been found necessary to carry out slowly the initial part of the hydrochlorination (i.e., heating to about 250° chiefly to dehydrate the hydrated oxalate). In general, there is still a considerable saving of time over the best method formerly in use, and experiments suggest that a much greater rate of flow of the $\text{H}_2 + \text{HCl}$ mixture, particularly during the early part of the hydrochlorination, will allow very rapid conversion to chloride. Studies made with relatively slow rates of flow are presented in Table VIII.

Use of the plutonium(III) oxalate as a starting material in the preparation of trichloride has the added advantage that the oxalate precipitation fits conveniently into the "wet" purification procedure, giving good separation of uranium from the plutonium (which the rest of the "wet" procedure does not) and

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being capable of giving additional purification from light elements. The extra time required to convert the $\text{PuO}_2(\text{NO}_3)_2$ to the oxalate (by HI reduction and addition of $\text{H}_2\text{C}_2\text{O}_4$) is only of the order of two hours, so the net saving in time over the older dioxide process of making the trichloride is of the order of a day. A considerable amount of work remains to be done in engineering the process on a 200-gram scale.

In general, the preparations tabulated were carried out using platinum or porcelain containers placed in a quartz tube electrically heated and through which the desired gas could be passed. Temperatures were measured with chromel-alumel thermocouples. The yields were generally followed by careful weighings which were checked from time to time by chemical analysis for chlorine (Group C-9) and by X-ray analysis (Group C-8).

Several attempts have been made to sublime PuCl_3 in a high vacuum because of the possible use in freeing the trichloride from traces of dioxide or oxychloride. These experiments have demonstrated that PuCl_3 can be sublimed in vacuum, compact blue-green crystals being obtained in contrast to the very fine granules normally obtained in the "dry" preparations from oxide or oxalate. The exact optimum conditions for obtaining highly pure trichloride have not been ascertained as yet.

Pure plutonium trichloride appears to be a blue-green substance, melting at about 760°C , with a vapor pressure (as measured by molecular effusion) of approximately 5×10^{-6} mm Hg at 600° , 3×10^{-4} mm at 700° and 2×10^{-3} mm at 750° . The vapor pressure values are probably not sufficiently accurate to allow calculation of a reliable value of the heat of sublimation. The trichloride is somewhat hygroscopic, slowly hydrating in air (R.H. = 30-40 percent) to form what appears

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to be $\text{PuCl}_3 \cdot 6\text{H}_2\text{O}$. The water of hydration may be removed by heating in a stream of hydrogen chloride for several hours at 250° . The trichloride is converted to dioxide upon heating in air to about 400° , but is stable with respect to oxidation at room temperature.

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TABLE I. PREPARATION OF PuCl₃ BY DEHYDRATION OF Pu(III) CHLORIDE SOLUTION

Sample No.	Amount of Pu, mg	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
69-12	65	Pu(IV) chloride solution	1) NH ₂ OHCl reduction of Pu ⁺⁴ 2) Dehydration in dry HCl, 6 hrs. at ~200° C	Low	Slate-blue color; gave complex X-ray pattern. Low yield of metal in electrolytic reduction (first electrolytic attempt on PuCl ₃).
89-31	71	Ditto	1) HCHO reduction of Pu ⁺⁴ 2) Dehydration in H ₂ at 70° 3) Dry HCl, ~1 hr. at Rt → 400°	High, but material had poor appearance	Slate-blue; 31.0% Cl (theor. for PuCl ₃ = 30.7% Cl). Low metal yield in electrolytic reduction (second reduction attempt).
89-34	68	Ditto	1) H ₂ S reduction of Pu ⁺⁴ 2) H ₂ and HCl treatment as for 89-31	Unknown	Slate-blue. Reduction not attempted.

TABLE II. PREPARATION OF PuCl₃ FROM "PuH₃"

Sample No.	Amount of Pu, mg	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
90-38	4	"PuH ₃ "	1) Dry HCl, ~1 hr. at 400°	~83%	Blue-green. Reduction not attempted.
90-39	75	Ditto	1) Dry HCl, ~14 hrs. at 400°	~100%	Blue-green. Fair yield of metal in electrolytic reduction.

TABLE III. PREPARATION OF PuCl₃ BY REDUCTION OF "PuCl₄" WITH H₂

Sample No.	Amount of Pu, mg	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
89-35	37	Pu(IV) chloride solution	1) Evap. in dry HCl at 85° 2) Dried to dark brown solid in dry HCl, ~2 hrs. at RT→300° 3) Reduced with H ₂ , 3 hrs. at RT→420°	Unknown. Probably some PuOCl or PuOCl ₂ .	Almost black. Complex X-ray pattern. No reduction attempt.
89-41	191	Ditto	Ditto	Ditto	Almost black. Oxygen content 1%. Low metal yield in electrolytic reduction. ~13% Pu in +3 state before H ₂ reduction.
89-45	600	Ditto	1) Evap. in air at 50° 2) Dehydrated in dry HCl, ~4 hrs. at RT→300°, plus 1/2 hr. at 300° in high vacuum 3) Reduced with H ₂ , 4 hrs. at RT→400°, plus H ₂ + HCl, 3 hrs. at RT→400°	High	Dark blue-green. Oxygen content 0.43%. X-ray indicated PuCl ₃ plus small amount of a second phase. Gave metal in electrolytic and bomb reactions.
89-49	1780	Ditto	Ditto, except no vacuum treatment	Ditto	Ditto, except no oxygen analysis. 27.4% Cl.
89-56	780	Ditto	Ditto	Ditto	Gray-blue. 31.1% Cl. Gave metal in reductions.

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TABLE IV. PREPARATION OF PuCl₃ BY ACTION OF H₂ + HCl ON HIGHLY-IGNITED PuO₂

Sample No.	Amount of Pu, mg.	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
90-43	9	Pu(VI) nitrate solution	1) Evap., ignited to PuO ₂ at 1000° 2) Dry HCl, ~60 hrs. at 400-700° 3) Dry H ₂ + HCl, 48 hrs. at 500-600°	~100%	Light Blue. No reduction attempt.
127-8	11	Ditto	1) Evap., ignited to PuO ₂ at 1000° 2) Dry H ₂ + HCl, 700°	Ditto	Ditto
89-63	593	Ditto	Ditto, 16 hrs. H ₂ + HCl at 700-770°	64%	Material was U-contam., dark color. Molten at 770°. Returned for recovery.
89-65	105	Ditto	Ditto, except 600-700° for H ₂ + HCl	~97%	Ditto, except sample not melted. 0.2% U.
89-66	2110	Ditto	1) Evap., ignited to PuO ₂ at 820° 2) Dry H ₂ + HCl, 19 hrs. at 600-780°	99%	Good yields in metal preparation.
89-72	1070	Ditto	Ditto	~100%	Ditto
89-76	1620	Ditto	Ditto	53%	U-contam. Returned for recovery.
89-78	4400	Ditto	Ditto, except H ₂ + HCl for 58 hrs. at 600-740°	92%	U-contam. Gave metal in reductions.

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TABLE IV. PREPARATION OF PuCl₃ BY ACTION OF H₂ + HCl ON HIGHLY-IGNITED PuO₂ (Cont'd.)

Sample No.	Amount of Pu, mg.	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
89-83	1800	Pu(VI) nitrate solution	1) Evap., ignited to PuO ₂ at 1000° 2) Reduced with H ₂ at 1000° for 2 days; wt. decreased below Pu ₂ O ₃ , some Pu-Pt alloy formed 3) Ignited in air to PuO ₂ at 900° 4) Dry H ₂ + HCl, 39 hrs. at 600-730°	93%, poor quality	Dark colored. Returned for recovery
89-85	788	Ditto	1) Evap., ignited to PuO ₂ at 1000° 2) Dry H ₂ + HCl, 45 hrs. at 730°	60%, poor quality	Returned for recovery.
89-86	1130	Ditto	Ditto	88%	>1% U. Returned for recovery.

TABLE V. PREPARATION OF PuCl₃ BY ACTION OF H₂ + HCl ON GENTLY-IGNITED PuO₂

Sample No.	Amount of Pu, mg.	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
127-6	14	Pu(IV) nitrate solution	1) Evap., ignited to PuO ₂ at 300° 2) Dry H ₂ + HCl, ~4 hrs. at 500°	~100%	Light blue. No reduction attempt.
89-57	1440	Pu(VI) nitrate solution	1) Evap., ignited to PuO ₂ at 400° 2) Dry H ₂ + HCl, ~19 hrs. at 500-700°	Ditto	Ditto. 31.1% Cl. Good yields of metal in reductions.

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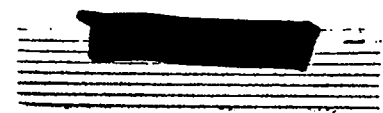
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TABLE V. PREPARATION OF PuCl₃ BY ACTION OF H₂ + HCl ON GENTLY-IGNITED PuO₂ (Cont'd.)

Sample No.	Amount of Pu, mg.	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
89-89	1350	Pu(VI) nitrate solution	1) Evap., ignited to PuO ₂ at 350° 2) H ₂ + HCl, 36 Hrs. at 600-720°	~100%	Blue-green. Good yield of metal in electrolytic reduction.
89-90	1470	Ditto	Ditto	~92%	Good metal yield in bomb reduction.
89-92	1230	Ditto	1) Evap., ignited to PuO ₂ at 390° 2) H ₂ + HCl, 25 hrs. at 350-710°	99%	Poor yield in bomb reduction.
89-93	1260	Ditto	1) Evap., ignited to PuO ₂ at 350° 2) H ₂ + HCl, 26 hrs. at RT → 710°	>96%	Good metal yield in bomb reduction.
89-94	404	Ditto	Ditto, except H ₂ + HCl for 38 hrs.	95%	0.1% U. Returned for recovery.
89-95	3960	Ditto	As for 89-93	99%	0.1% U. Used in metal production.
89-97	349	Ditto	As for 89-93, except ~2 g HAc added to original solution to test for its interference with dry reactions	98%	HAc appeared to have no effect. Used in "dry" research.
89-101	760	Ditto	As for 89-93	~71%	0.1% U. Returned for recovery.



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TABLE VI. PREPARATION OF PuCl₃ BY ACTION OF H₂ + HCl ON "PuO₂(NO₃)₂"

Sample No.	Amount of Pu, mg	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
89-98	1760	Pu(VI) nitrate solution	1) Evap. to dry crystals 2) Heated in dry H ₂ + HCl slowly, 17 hrs., RT → 700°	95%	More trouble than process involving ignition to PuO ₂ . Used in "dry" research.

TABLE VII. PREPARATION OF PuCl₃ BY ACTION OF Cl₂ + CCl₄ ON PuO₂

Sample No.	Amount of Pu, mg	Starting Material	Treatment	% Conversion to PuCl ₃	Remarks
119-39	10	PuO ₂ (1000°)	1) Cl ₂ + CCl ₄ vapor, ~1.5 hrs. at 600-720°. Appreciable sublimation	High	Blue-green. Material including sublimate, assayed PuCl _{2.98} .
119-41	15	Ditto	Ditto	~97%	Blue-green.
89-102	175	Ditto	1) Cl ₂ + CCl ₄ vapor, 2 hrs. at 620° gave 49% conversion 2) 3 hrs. more gave 98% conv. Some sublimation	98%	Blue-green. Used in "dry" research.

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TABLE VIII. PREPARATION OF PuCl_3 BY ACTION OF H_2 + HCl ON $\text{Pu}_2(\text{C}_2\text{O}_4)_3$

Sample No.	Amount of Pu, mg.	Starting Material	Treatment	% Conversion to PuCl_3	Remarks
69-26	150	" $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ "	1) Evap. slurry to dryness in air at $\sim 50^\circ$ 2) H_2 + HCl , 6 hrs. at $\text{RT} \rightarrow 550^\circ$	100%	Light blue. Used in "dry" research.
69-28	240	Ditto	1) Ditto 2) H_2 + HCl , 2 hrs. at $\text{RT} \rightarrow 700^\circ$	$\sim 99\%$	Light blue; X-ray like 89-35. 29.1% Cl. Used in "dry" research.
69-30	970	Ditto	Ditto	100%	Light blue. X-ray pattern indicated PuCl_3 , no second phase. Good yield of metal in bomb reduction.
69-32	12,000	Ditto	1) Ditto 2) Heated rapidly in H_2 + HCl , 5 hrs. at $\text{RT} \rightarrow 700^\circ$	Gave PuOCl	Blue-black. Returned for recovery.
89-30	8500	Ditto	1) Ditto 2) H_2 + HCl , 4 hrs. at $\text{RT} \rightarrow 680^\circ$	Gave " $\text{PuO}_2 \cdot \text{PuCl}_3$ "	Dark Gray-blue. X-ray indicated PuOCl . Part gave very poor metal yield, rest returned for recovery.
89-105	5850	Ditto	1) Ditto 2) H_2 + HCl , 13 hrs. at $\text{RT} \rightarrow 625^\circ$	$\sim 100\%$	Blue-green. X-ray indicated PuCl_3 only. 30.7% Cl. Gave good yields of metal in bomb and electrolytic reductions.
89-107	7180	Ditto	1) Ditto 2) H_2 + HCl , 19 hrs. at $\text{RT} \rightarrow 625^\circ$	$\sim 100\%$	Blue-green. 30.5% Cl. Used in 9.3 g metal production together with 89-105

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