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RECOVERY AND PURIFICATION OF PLUTONIUM

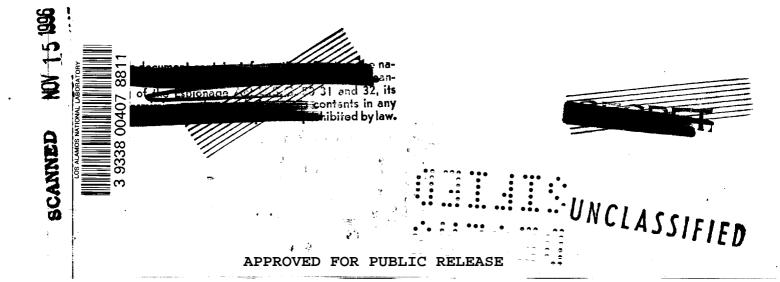
- WORK DONE BY:
- W. A. Brown
- D. Duffy
- G. B. Floming
- W. B. Gibson
- B. L. Kelchner
- F. K. Pittman
- R. Schaffer
- D. L. Wolfe

REPORT WRITTEN BY:

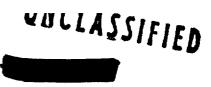
F. K. Pittman

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ABSTRACT



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The various problems of purification and recovery are discussed under the headings of preparation of solution, concentration of plutonium, and purification of plutonium. The methods used in concentration (or recovery) of the plutonium are shown to consist in all cases of one or more of the following procedures: precipitation of hydroxide, oxalate, trifluoride, tetrafluoride, or iodate; ether extraction; and certain carrier methods. A modified purification scheme is described in detail. Data are given dealing with the amounts of material handled and overall recovery efficiency. A rosume is made of phases returning material for recovery, type of material returned and impurities present. A flow sheet for the entire recovery and purification scheme is given showing impurity element removal by each step of the process. The colors of various plutonium compounds and solutions as observed on a one-to-ten-gram scale are reported.

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RECOVERY AND PURIFICATION OF PLUTONIUM

INTRODUCTION

In the process of recovery and purification of plutonium, many problems have presented themselves which deal with the separation of small amounts of plutonium from very large amounts of many of the other elements. Since most of the reported work on separations of this type has been done on a milligram scale, and since much of the work of others has dealt mainly with the separation of the last traces of impurities from the plutonium rather than the recovery of small amounts of plutonium from very large amounts of impurities, it was thought that a report of work done on a oneto-ten-gram scale would be of value to others who might encounter these same problems.

Table I gives a summation of the various phases of work returning material to be recovered. It also shows the form in which the plutonium is present, and the types of substances present as impurities with the plutonium.

The work in this laboratory may be divided into three general subheads: preparation of solution, concentration of plutonium (i.e. removal of a major portion of the impurities), and purification of plutonium (i.e. removal of last traces of the impurities). The following discussion will be based on this subdivision.

PREPARATION OF SOLUTION

Examination of Table I shows that the answer to the problems of

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this category iles, in part, in the methods which are available for dissolving plutonium metal, oxide, halides, carbides, oxalate, hydride, and peroxide. Of these compounds all except the oxide and carbide are readily soluble in the common mineral acids, HCl being best suited for the metal and the hydride, HNO₃ for the peroxide and halides, and HNO₃ + H₂SO₁ for the oxalate. When it is necessary to render the oxide or the carbide soluble, the most efficient method is a fusion with $K_2S_2O_7^{\circ}$. In this fusion a ratio of $K_2S_2O_7$ to PuO₂ (or carbide) of about 8 to 1 is used. The fused mixture is heated until the molten material turns solid. This gives a fused mass which is much more readily disintegrated by water and HCl than is possible if the heating is stopped while the fusion is still liquid. The fusion mass is greenish whilo still hot, but on cooling it turns pink. This pink color seems to be characteristic of the plus four state in the presence of sulfate, since it shows up when solutions are fumed with H₂SO₁.

However, the problem of getting plutonium into solution is not as simple as it might seem from the solubility data just stated. It is complicated by the fact that varying amounts of plutonium manage to penetrate so deeply into the refractories used in reduction and remelting that a mere leaching with acids or acid fusions does not extract all of the plutonium from the crucible materials. This mecessitates the complete dissolution of the refractories, a procedure which is disadvantageous for two reasone. In the first place many of the refractories resist dissolving to a remarkable extent, requiring long tedious treatment with various acids and with various fusion mixtures. Many of the refractories are dissolved in HF and HNO₂ when other solvents failed. In a few cases however very drastic measures have been required, and it has been found that the Na₂O₂ + C spontaneous fusion

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is very satisfactory for these materials. The second disadvantage of complete solution of the refractories lies in the fact that much greater amounts of impurities are mixed with the plutonium than would be if a leaching process were used. In order to overcome, to a certain extent, this second disadvantage, the unground crucible materials are always leached thoroughly with HCl, HNO, and aqua regia and the solutions thus obtained, containing nearly all of the plutonium and only a fraction of the crucible material (provided the crucible is insoluble in the leaching acids), are treated separately. The main portion of the crucible material is then dried, ground to approximately 100 mesh and dissolved completely. This solution contains only a small amount of plutonium, and in general is set aside until other similar solutions have been obtained, at which time it is worked up.

In these cases where the plutonium has had to be separated from metal surfaces, acid washing or $K_2S_2O_7$ fusions (depending on the form of the plutonium) will get the plutonium in solution; the metals are not much affected by these treatments.

When the plutonium is already in solution, there are three treatments that may be necessary before this solution is in a condition satisfactory for use of chemical procedures of concentration. If the volume of the solution is so large that the plutonium concentration is of the same order of magnitude as the solubilities of the compounds to be precipitated, it must be evaporated. If the plutonium is in the hexavalent state, it must be reduced before the chemistry used in concentration can be successful. This reduction is best done by passing SO_2 into the acid solution until the blue color of the trivalent plutonium becomes evident.

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The solution is then boiled to remove the excess SO_2 , and HNO_3 is added to reoxidize the trivalent plutonium to tetravalent plutonium. In this reoxidation, care must be taken that the HNO_3 does not cause a large portion of the plutonium to become hexavalent. It is probable, but not as yet proved, that the addition of small amounts of H_2SO_4 before reoxidation will prevent this. If organic matter is present, it must be removed before chemical concentration can be accomplished. The volatile organic material is removed by evaporation, and the non-volatile organic material is removed by oxidation with HNO_3 and H_2SO_4 .

THE CHEMICAL CONCENTRATION OF PLUTONIUM

The three prerequisites of a good concentration method are: 1. The major portion of the impurity must be removed in one operation. 2. The amount of plutonium removed with the impurity must be small. 3. If the operation depends upon a precipitation procedure, it should, if possible, cause the plutonium to be precipitated away from the impurity rather than the impurity to be precipitated away from the plutonium. All of the methods described here exhibit the first two characteristics, and nearly all exhibit the third.

The exact procedure which is to be used for the separation of the plutonium from other elements will naturally depend largely upon what contaminating materials are present, and to what extent. Thus, if a metal button is returned for recovery, almost no pre-purification procedures are needed. If, on the other hand, the sample for recovery consists of dry box sweepings, several separate concentration steps are required. However, in all cases, the procedure for the concentration of plutonium will consist of one or more of the following processes.

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Hydroxide precipitation

The first process after the preparation of the solution always involves the precipitation of plutonium hydroxide. This serves not only to separate many impurity elements from the plutonium, but also to give a compound which when dissolved in acid leaves a solution of approximately known acidity and plutonium concentration. For this precipitation, either NaOH or NE, OH may be used, and the choice of reagents depends upon the type of impurities present in the solution. Thus, when Be, Al, and other amphoterics are present, an excess NaOH is used to precipitate the plutonium hydroxide, leaving the impurities in solution. If Mg or other alkaline earths, alkalies, or elements which form ammonio complexes are present, NH, OH is used. In the case of alkaline earths NE OH is added until the pH of the solution is between 5 and 6 as shown by indicator paper. This gives a basicity sufficient to precipitate the plutonium hydroxide, but not to precipitate the alkaline earth hydroxides. In those cases where elements which form ammonic comploxes are present, the NH, OH is added in excess. Many times the elements of all three classes (amphoteric, complex formers, and alkaline earthe) are present in the solution, and suitable combinations of reagents and conditions are used. Whenever both NaOH and NH OH are to be used in a series of operations, NaOH is always used first, followed by NH, OH at a pH 5 to 6_{ρ} and finally followed by NH OH in excess. The precipitate from each operation is washed thoroughly and dissolved in acid before the succeeding precipitation. By using these processes, a major portion of all the elements present is removed with the exception of Ce, La, Zr, Th, Ti, Fe, Si, Ta, and Pt (of these Si and Ta are removed more or less in the preparation of the



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solution since both of these elements precipitate insoluble oxides from acid solutions; Pt is removed by means of acid H₂S in the rare cases when it is present in solution).

Oxalate Method

The solution containing the tetravalent plutonium nitrate is heated to convert all uranium to the hexavalent state. To this is added enough solid KI to give three mols of iodide per mol of plutonium, and the solution allowed to stand for thirty minutes with occasional stirring. After this enough 1M $H_2C_2O_4$ solution is added to give 1.5 mols of oxalate ion per mol of plutonium and to make the final solution 0.2 M in excess oxalio acid. The volume is then adjusted until the plutonium concentration, based on total amount present, is 0.2 M. This mixture is allowed to stand for 30 to 60 minutes, after which the green oxalate precipitate is centrifuged and washed with water until the supernatant is free of I_3° color. The precipitate is fumed with HNO₃ and H_2SO_4 to completely decompose the oxalate, and the red sulfate thus formed is dissolved in water and ECL. Plutonium hydroxide is precipitated from this solution with NH₄OH, and the precipitate is washed free of sulfate.

An alternate treatment of the precipitated oxalate may be used if no further concentration processes are necessary. The solid oxalate is treated with enough 1M NaBrO₃ solution to give 1.8 mols of bromate per mol of plutonium, and enough 16N HNO₃ to give 9.2 mols of H⁺ per mol of plutonium. The volume of the solution is then adjusted so that the plutonium concentration in the final solution will be 0.2 M, and the mixture is heated for l_1 to 6 hours at 85°C. This method of dissolution of the oxalate yields a solution of the hexavalent nitrate of plutonium.

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The oxalate procedure separates uranium (if not present in large amounts) some alkaline earths, (Zr, Th), Ti, Fe, Be, Cr, and the alkalies. It has no value as a method for separating Ce and La. The precipitation is always used as the last step prior to purification, and in many cases it is used previously to clean up solutions.

Trifluorido Mothod

A solution of the tetravalent plutonium nitrate in 1M HNO_{χ} is reduced by passing SO, into the ice-cold solution for about 20 to 30 minutes. (Reduction may also be made by means of KI as described in the previous section.) Twenty-seven normal HF is added to this blue solution until the amount added is three mols per mol of plutonium and enough excess to make the solution 1 to 2 M in HF. The mixture is allowed to stand for 30 minutes and the purple trifluoride is centrifuged, we shed, and fumed with HNOz and H2SO, to remove all fluoride. The sulfate thus formed is dissolved in water; the hydroxide is precipitated with NH,OH and washed free of sulfate.

This method accomplishes the separation of uranium to about the same extent as the oxalate. It has the advantages that the plutonium fluoride is less soluble than the oxalate, and if large amounts of uranium are present the separation is still successful. It has the disadvantages that Th and Zr are not separated from the plutonium, that the precipitate is more difficult to dissolve, and that handling of large amounts of HF solutions involves certain difficulties a

Tetrafluoride Method

A solution containing the tetravalent nitrate of plutonium in 1M HNOz is heated to oxidize all uranium to the hexavalent state, and solid KNOz is added until there are two mole of K^Tper mol of plutonium and

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LI UNCLASSIFIED the solution is 3 molar in excess. Twenty seven normal ar resthen added to give six mols of HP per mol of plutonium and to make the solution 1 to 2 molar in excess. After 30 minutes the grey potassium plutonium fluoride is centrifuged, washed, and fumed with H_2SO_4 to remove HF, and the sulfate thus formed is dissolved in water. From this solution the hydroxide is precipitated and washed free of sulfate.

This mothod has the same disadvantages and advantages as the trifluoride method, and may be used interchangeably with it. It is probably the best method for separating large amounts of uranium from plutonium. Since this does not require reduction of the plutonium it is somewhat faster. However, the trifluoride is a neater, more clean-out reaction.

Iodate Method

Procipitation of $Pu(IO_3)$ from a solution which is 2 M in HNO_3 with a O_02 molar excess of KIO_3 or HIO_3 serves to separate the plutonium from uranium in the hexavalent state. It is not nearly as satisfactory as the previously described methods for uranium separation. However, it does show promise as a method for separating cerium, which resists most other separations when present in large amounts. The iodate of trivalent cerium is soluble and should remain in solution when the plutonium is precipitated. The preliminary attempts at this separation have indicated that it will be useful, but the data are too incomplete at this time to state definitely that the method is successful. The most satisfactory method of solution of the iodate depends upon the use of HCl and SOge This reduces the indate to indide and the plutonium to the



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trivalent state. The completion of the reduction is noted by the fact that all the I₂ liberated from the iodate by SO₂ is redissolved and the solution turns blue due to trivalent plutonium. The plutonium is precipitated from this solution as $Pu(OH)_3$ by means of NH₀OH₀. It is not possible to reoxidize the plutonium to the tetravalent state before precipitation of the hydroxide because the iodide which is present prevents oxidation of the trivalent state.

Other methods for separation of cerium

All other methods which are used for the separation of cerium from plutonium involve an oxidation of the plutonium to the hexavalent state. This oxidation is achieved by means of NaBrO₃ in HNO₃ solution. Since hexavalent plutonium does not precipitate as a fluoride, the cerium can be precipitated from the oxidized solution by the addition of HF. By repeating this process, fairly complete separation can be brought about. The procedure has the disadvantage that the impurities are precipitated rather than the plutonium. A second treatment of the oxidized solution consists of ether extraction of the plutonium. This is perhaps the most efficient method of separation of plutonium from cerium, but it is also more time-consuming. If only small amounts of cerium are present, no special precautions need be taken since the regular purification scheme will effect its removal. Carrier Procedures

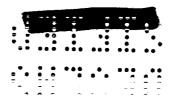
All supernatants from precipitation of hydroxides were stored until about 380 liters were on hand. Assay of these solutions showed a much higher plutonium content than would be accounted for by the solubility of $Pu(OH)_{L}$ in basic solutions. The probable explanation of this is the fact

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that tetravalent plutonium in dilute HNO3 converts to the extent of about 50 to 60 per cent to hexavalent stated. This is either a straight oxidation or a disproportionation of the tetravalent to the hexavalent and the trivalent states. Regardless of mechanism, the presence of the hexavalent plutonium in solutions from which the hydroxide is to be precipitated would cause undue loss in the supernatant since the hexavalent hydroxide is quite soluble. Since there was considerable amount of plutonium tied up in these solutions an effort was made to recover this.

These supermetants were obtained from hydroxide precipitations using both NaOH and NH, OH, and when they were mixed, precipitates formed due to the nature of the elements in the basic solution. Thus magnesium, in solution in the NH OH supernatant, was precipitated by the more basic NaOH supernatant, and beryllium, in solution in the NaOH supernatant, was precipitated by the less basic NH OH supernatant. This precipitation of hydroxides from the supernatant solutions acted as a carrier, and most of the plutonium was found to be in the precipitate. However, the concentration of the plutonium in this precipitate is so low as to make the usual precipitation methods untenable. For this reason LaFz carrier methods were used. A solution of the tetravalent plutonium nitrate in 1M HNO, was treated with SO, until the solution was saturated. Lanthanum was added in the form of $La(NO_3)_3 \circ 6H_2O_s$ and enough HF to precipitate the LaF₃ and to make the solution 1 to 2 molar in excess. The IAF_3 was centrifuged, washed, funed with $H_2SO_{1,0}$ and the IA was separated from the plutonium by one of the methods previously described. The basic supernatants after this treatment still contained enough plutonium to warrant its recovery, hence further carrier procedures are being used at the present time. Ferric nitrate



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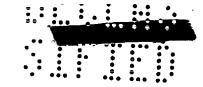
is added to the solution and the ferric hydroxide thus formed is allowed to settle through the solution. Results of this experiment are not known yet. PURIFICATION

After one or more of the concentration procedures just described have given a product which is 80 to 100 per cent plutonium, the processes of purification are carried out. The procedure used for this purification is based, with modifications, on those described in a previous report¹⁾. However, since there are certain major changes in procedure, the new method will be described in some dotail. As has been previously stated, the final procedure of concentration is an exalate precipitation in nearly all cases, and this is dissolved and oxidized according to the method described under oxalate procedure. The solution thus oxidized is treated with solid sodium acotate until the precipitation of the sodium plutonyl acotate is complete, and an excess of one third has been added. The pink $NaPuO_2Ac_3$ is centrifuged and washed twice with acetate wash solution (5M Na" 0.2M Ac", 0.35M HAc). The washed acetate is dissolved in the smallest amount of 16N HNO_3 that will give a clear solution, and the volume of this solution is reduced by evaporation until NaNOz begins to crystallize. This solution - about 1 to 2 cc per gram of plutonium - is then extracted with di-ethyl ether in a modified Soxhlet extractor having a design similar to that described in (1), but being of greater capacity. The hexavalent nitrate obtained from the ether extraction is diluted somewhat and treated with enough 7N HI to give 9 mols of I° per mol of plutonium. This mixture is allowed to stand 30 to 60 minutes, and 1 molar oxalic acid is added in sufficient amounts to

1) Mastick, Pittman, and Wahb, claMS.72

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give 1.5 mols of exalate per mol of plutonium, and to make the final solution 0.2 M in excess. The volume of the solution is then adjusted so that the plutonium concentration (total) is 0.2 M. This mixture is allowed to stand for an hour or so, and the green exalate washed free of I_{3}^{-0} . This slurry is turned over to the "dry" chemist for conversion into compounds suitable for metallurgical reduction.

During the purification processes, various solid residues are obtained. These are always removed from the solution before the succeeding procedure is carried out.

CONCLUSIONS AND DISCUSSION

Although none of the procedures described in this paper can be termed as completely quantitative, a continuous recycling of all residues and supermatants can be said to achieve quantitativeness to a large degree. For example during the past eight months about 250 individual samples have been turned in for recovery. These totaled 117_{p} 936 mg, or an average of approximately 450 mg per sample. Of this amount $109_{p}639$ mg of essentially pure plutonyl nitrate and plutonium exalate have been turned over to the "dry" chemists. About one gram is in the various supernatants and residues which will be worked up over a period of time. The apparent loss of 7.3 grams is most probably due to errors in estimations of amounts turned in for recovery, since no assays are made on any of the incoming materials, whereas all outgoing samples are assayed either by weight or by radioactive means.

Outline I may be considered to be a composite of all recovery and purification work done in this laboratory. Naturally, the entire procedure

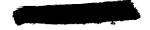


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is not followed for each individual recovery problem, but only those portions which are necessary to remove the particular elements present. It is only in case all possible impurities are present at one time that the complete scheme is followed.

COLORS OF SOLUTIONS AND PRECIPITATES

Since the colors of the various precipitates and solutions have been reported by different people as being entirely different, and since our work has dealt with large amounts of quite pure compounds, a report is made of colors of precipitates and solutions. Table II gives the colors as observed in this laboratory.



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TABLE I - MATERIAL RETURNED FOR RECOVERY

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	Phase of work returning material	Form in which Pu is present	Form of Impurity		
	METALLURGY				
1 110 0 1 3 0 0 3 0 2 3 0 2 5 0 0 5 5 5 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Bomb Reduction	Oxide, slag, metal	MgO, CaO, BeO, Al ₂ O ₃ , Ce ₂ S ₃ , UN, Ca, Pt, Cu, Ni, Co, Zn, Fe, Halogens		
	Electrolytic Reduction	Oxide, metal, trichloride	BaCl ₂ , KCl, NaCl, C, Zn, Ni, Cr, W, glass, organic Ce ₂ S ₃ , ZrN, C, BeO, Ni, BaS, MgO, CaO, UN, ThN, ZrC, TiC, ThS ₂ , Ta, Si, Mo, Ti		
	Remeit	Oxido, metal			
20100 	Physical Expts.	Oxido, motal	Fe, quartz, glass, organic, abrasivo		
	Hydride Expts.	Oxide, metal, hydride	BeO		
	Special Reduction	Oxido, metal, carbido	UN, UO ₂ , Z:N, ThO ₂ , TiN, ThN, Co ₂ S ₃ , ThS ₂ , CaO ₆ , \vdots BeO ₅ TaC, Ta, Mo ₅ W, Si, C, WC		
	Electrolytic polishing	Solutions (tri- & tetravalont)	H_PO ₄ , organic		
UN	Xoray	Oxido, metal, trihalido	None		
UNCLASSIF	Dry Box Sweepings	Oxide, metal, halides	Kleenex, rags, wood, TaO ₂ , Cr, BeO, MgO, Fe, Fe ₂ O ₃ , Ta, Cu, $2rO_2$, $2rN_0$, Ce ₂ S ₃ , brush hair		
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TABLE I - MATERIAL RETURNED FOR RECOVERY (CONTINUED)

Form of Impurity Phase of work-Form in which Pu is present returning material CHEMISTRY Organic, Cro "Wet" chemistry Solutions (trie, tetrae, hexae valent) Pt alloy, U, La, Co Oxide, metal, trihalide "Dry" chemistry Any element shown above Solutions (tri-, tetra-, hexa-Assay valent) U, Mo, W, organic, C Oxide, metal, peroxide, oxalate, Analysis gallate, cupferride None Apparatus wash Trihalides Trihalides, oxide Brush hair Dry Box Sweepings Metal, oxide None PHYSICS $2r_{o}$ La Totra-nitrate and peroxide PROJECT X

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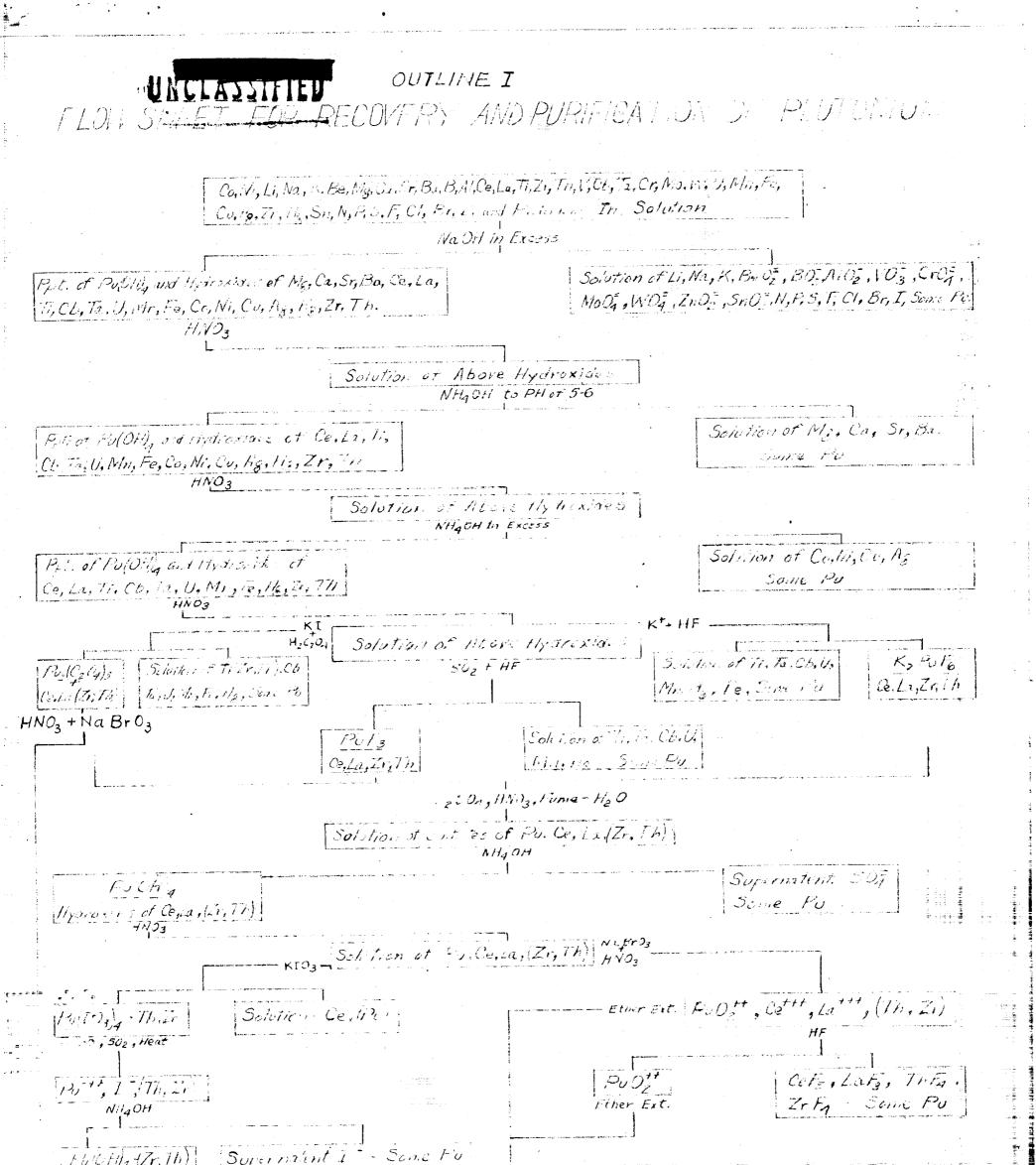
TABLE 11 - COLOR OF PRECIPITATES AND SOLUTIONS •

Name of Compound	Formula	Color
Pu ^{IV} hydroxide	Pu(OH)4	Dark green
Pu ^{III} hydroxide	Pu(OH)3	Light Blue
Pu ^{VI} hydroxide	Pu0 ₂ (OE) ₂ (?)	Brown
Sodium Pu ^{VI} acotato	Na.Pu02Ac3	Pink
Pu ^{III} flucride	PuFz	Purple
Potassium Fu ^{IV} fluoride	K2PuF6	Grey
Pu ^{III} oxalate	Pu2 (C204)3	Brilliant green
Pu ^{IV} lodate	Pu(103)4	Light pink
Pu ^{IV} sulfate	Pu(SO ₄) ₂ (?)	Pink
Pu ^{III} chloride solution		Blue
Pu ^{IV} chloride solution		Brown
Pu ^{IV} nitrate in cone HNO3		Green
Pu ^{IV} nitrate in dil. HNO3		Brown
Pu ^{VI} solutions in H ₂ O or other		Brown

*Water of hydration is not included or excluded by the formula.

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6/6+1) - {Zr, 71) - (Ce, La, Tin, Zr) Nithe: 31120 Na PUD Aca Some PuOt , (Ce, La, Th, 2) (Ce, La, Th, Zr) HNO3 P. J' (Ce. + a, 18, 2r ither Ext. $\begin{bmatrix} P_U & O_2^{++} \\ H_L & H_2 & C_2 \end{bmatrix}$ UNCLASSIFIED Some Pu Pu2(C204)3 APPROVED FOR PUBLIC RELEASE

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