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ANALYSIS FOR Pu(III) AND Pu(IV) ON A TRACER SCALE

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ABSTRACT

Several different procedures for the tracer scale analysis of solutions of plutonium have been investigated. The purpose of these procedures has been the determination of the fraction of the plutonium present in the +3 oxidation state in solutions containing mainly Pu(III) and Pu(IV).

Procedures involving the use of columbium oxide and lanthanum ammonium oxalate were not feasible. Preliminary experiments indicated that Pu(IV) is carried by ThP_2O_7 while Pu(III) is not carried. Further investigation might prove the use of a procedure involving ThP_2O_7 to be highly feasible.

The use of zirconium phenylarsonate to carry Pu(IV) and at the same time leave Pu(III) in the supernatant solution has been investigated quite thoroughly. Difficulties were encountered in the prevention of the reduction of Pu(IV) to Pu(III) during the course of the analysis. It was found that Cl_2 present at a concentration of 2×10^{-4} N prevented the reduction of Pu(IV) and at the same time did not oxidize Pu(III). Successful analyses of solutions containing Pu(III) and Pu(IV) were carried out using Cl_2 as an oxidant.

In connection with the work on the zirconium phenylarsonate procedure, the formulas of plutonium(IV) phenylarsonate and zirconium(IV) phenylarsonate were found to be $Pu(C_6H_5AsO_3)_2 \cdot xH_2O$ and $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ respectively.

A procedure is proposed involving the use of zirconium phenylarsonate and LaF_3 to determine the amount of Pu(III), Pu(IV) and Pu(VI) in solutions containing all three oxidation states. Although the analysis did not prove successful, the discrepancy may have been due to a trace of Fe(III) in the plutonium solution. It is proposed that the Fe(III) may have catalyzed the oxidation of Pu(III) to Pu(IV) by Cl_2.

1. Introduction

Plutonium is known to exist in four oxidation states in aqueous solution: Pu(III), Pu(IV), Pu(V) and Pu(VI). The problem of determining the oxidation number of plutonium in various solutions is indeed an important and interesting one.

Each of the oxidation states has a characteristic absorption spectrum in solution. When dealing with solutions in which the plutonium has a "macro" concentration (greater than 10^{-4} M), the spectrum often furnishes a convenient means of analyzing for the various oxidation states. The applicability of this

method to quantitative measurements is complicated because the absorption spectra of the various oxidation states are not independent of the anions in solution due to complex formation. Therefore, in order to analyze solutions for the amount of the different oxidation states present one has to know the spectrum of each oxidation state in the medium under consideration. These quantitative measurements must be made with a spectrophotometer while a qualitative determination of what oxidation states are present can be made by merely viewing the solution with a spectrometer. The use of the absorption spectrum as an analytical method becomes inconvenient at very low concentrations because of the excessive length of absorption cell necessary to give appreciable amounts of absorption.

A tracer scale analysis for the determination of the amount of Pu(VI) in a solution can be made by the "LaF$_3$ holding oxidant" method developed by W. H. McVey of this laboratory.[1]

A good semi-micro method for determining the amount of Pu(III) in a solution which contains largely Pu(III) and Pu(IV) at tracer concentrations had not yet been developed. It has been the purpose of the present work to find such a method.

The fact that an element at tracer concentrations is often carried by a precipitate of another similar element in the same oxidation state is well established.[2] In two of the procedures to be presented, Pu(IV) is carried by precipitates of Zr(IV) and Th(IV) while in another the possibility of carrying Pu(III) with a precipitate of La(III) is discussed.

Certain restrictions are placed on the method if it is to be a practical one. The analysis should involve reagents which are not capable of oxidizing or

reducing plutonium in any of its oxidation states at an appreciable rate. The solution in which the analysis is to be carried out should be one in which the air oxidation of Pu(III) is slow. The analysis should be carried out at room temperature for it may frequently be necessary to analyze solutions in which oxidation (or reduction) would certainly occur if heated.

In attempting to check on whether or not a given oxidation state of plutonium is or is not carried by a certain precipitate, it is desirable to have a solution of plutonium entirely in the oxidation state to be tested. With this in mind a few important facts concerning the chemistry of plutonium will be reviewed.

Solutions of Pu(III) in HCl solution prepared by H_2 reduction are known to build up a certain concentration of Pu(IV) upon long standing.[3] Presumably this oxidation is due to the ion pairs produced in the solution by the alpha particles.

Plutonium in the +3 oxidation state is oxidized at an appreciable rate by O_2 of the air in the presence of certain anions which complex Pu(IV) and therefore reduce the Pu(III) - Pu(IV) potential. An example of such behavior is noted in the case of sulfate solutions of Pu(III). Pu(IV) forms a sulfate complex and Pu(III) is more readily oxidized to Pu(IV) in the presence of sulfate than in the presence of chloride. Plutonium in the +4 oxidation state is known to exist in a colloidal form which may behave quite differently with respect to being carried by certain precipitates than does the ionic form (so-called "normal" form). Plutonium in the +4 oxidation state is capable of disproportionating into Pu(III) and Pu(VI), the equilibrium amounts of Pu(III) and Pu(VI) increasing as the acidity is decreased. For these reasons, a solution of Pu(IV) to be used in

experiments designed to determine the behavior of "normal" Pu(IV) should be prepared in such a manner as to eliminate as far as possible the formation of colloidal Pu(IV) and should be kept in a medium in which the disproportionation is as small as possible.

2. Analytical Procedures

2.1 Columbium Oxide Separation. It was found by G. C. Pimentel and J. W. Gofman[4] that whereas plutonium, in what was then known as the reduced state, was carried by $Cb_2O_5 \cdot xH_2O$, this carrying was reduced to a very low value ($\sim 2.5\%$) in the presence of $NH_2OH \cdot HCl$. This "anomalous" behavior is now known to have been due to the fact that the plutonium in the presence of $NH_2OH \cdot HCl$ was Pu(III), whereas in the solution from which it was carried by $Cb_2O_5 \cdot xH_2O$ it was Pu(IV) The difference in the carrying of Pu(III) and Pu(IV) by an oxide may be correlated with the difference in the tendency of these two ions to precipitate as hydroxides. The Pu(IV) precipitates as a hydroxide at a pH of about 2 while a pH of about 7 is necessary before Pu(III) precipitates; that is, Pu(IV) has a greater tendency to become attached to the oxygen of OH^- than Pu(III). Similarly, it has a greater tendency to become attached to the oxygen of the $Cb_2O_5 \cdot xH_2O$ than Pu(III). This should be a possible Pu(III) - Pu(IV) separation for analysis; experiments using this method were tried.

Difficulty was experienced in getting the $Cb_2O_5 \cdot xH_2O$ to coagulate when a columbate solution was acidified and stirred at room temperature. The $Cb_2O_5 \cdot xH_2O$ was not completely centrifugable if formed in HCl solution but was found to coagulate and centrifuge out nicely if precipitated from a HSO_4^- solution. It was found that from 0.20 ml of $HSO_4^- - SO_4^-$ solution, 200 µg of

Cb(V) precipitated as the oxide carried only 1-2% of Ce(III) tracer;* under similar conditions 3-4% of Pu(III) in $NH_2OH \cdot HCl$ was carried. This higher carrying of Pu(III) may have been due to incomplete reduction of the plutonium. The carrying of Pu(IV) was about 90% under similar conditions. This approach to the Pu(III) - Pu(IV) separation and analysis problem was dropped because it was learned that the rate of air oxidation of Pu(III) in the presence of sulfate was appreciable. Since it appeared that the presence of sulfate was necessary to obtain an easily centrifugable precipitate, the possibility of the successful use of this method for analysis is doubtful. However, it was not actually proven that the rate of oxidation was great enough to render the method useless.

2.2 _Oxalate Separation._ The use of an oxalate separation in a Pu(III) - Pu(IV) analysis was investigated. Whereas Th(IV) dissolves in an $(NH_4)_2C_2O_4$ solution to form an oxalate complex, La(III) forms an insoluble precipitate of $La_2(NH_4)(C_2O_4)_5 \cdot 6H_2O$[5] in an $(NH_4)_2C_2O_4$ solution. Such facts might lead one to expect Pu(III) to be carried from an $(NH_4)_2C_2O_4$ solution by $La_2(NH_4)_4(C_2O_4)_5 \cdot 6H_2O$, while Pu(IV) would remain in solution as an oxalate complex. However, it has been

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* 100 μg of Ce(III) was present. In this procedure as in two of the other procedures discussed, Pu(IV) was carried by some precipitate while the Pu(III) was expected to remain in the supernatant solution. In all such experiments La(III) or Ce(III) was added to act as a "holdback" agent for Pu(III). The advantages of adding a "holdback" agent are evident. If Pu(III) behaves exactly the same as does La(III) and the amount of La(III) carried by the precipitate does not increase as the amount of La(III) in solution increases, the amount of Pu(III) carried can be reduced by increasing the amount of "holdback" agent.

shown that Th(IV) is coprecipitated with La(III) when La(III) is precipitated from an $(NH_4)_2C_2O_4$ solution.[6] The formula of the compound precipitating was found to be $La_3Th_2(NH_4)_8(C_2O_4)_{12.5} \cdot 16H_2O$.[7] It has also been shown that Pu(IV) is slowly incorporated into this compound when precipitated from an $(NH_4)_2C_2O_4$ solution.[6] This factor would invalidate the use of this procedure.

2.3 Separation of Pu(III) and Pu(IV) by Thorium Pyrophosphate. The precipitation of thorium pyrophosphate, leaving the +3 ions in solution[9] is a means of separating Th(IV) from the +3 rare earth ions. The formula of the compound which is precipitated under conditions similar to those used by Carney and Campbell has been reported as $ThP_2O_7 \cdot 2H_2O$.[10] This compound dissolves in an excess of sodium pyrophosphate, indicating that Th(IV) forms a pyrophosphate complex. Compounds of Ce(IV) and Zr(IV) pyrophosphate are also known to be insoluble in dilute acid. Compounds of the +3 rare earth ions and pyrophosphate are known.[9] These, like the compounds of the +4 ions of thorium, zirconium and cerium, are soluble in excess sodium pyrophosphate, indicating complex formation but unlike the +4 ion pyrophosphates, these are soluble in dilute HCl solution.

These facts would lead one to believe that Pu(IV) could be carried from an acid solution by a precipitate of thorium pyrophosphate at the same time leaving any Pu(III) in the supernatant solution.

The procedure of Carney and Campbell[9] involves heating the solution after the addition of the sodium pyrophosphate. Since heating is to be avoided if possible, experiments were run to determine the rate and completeness of precipitation of thorium pyrophosphate at room temperature. To determine the

behavior of Th, Io tracer was used; Io is the alpha particle emitting Th isotope, Th^{230}. To a solution containing Th(IV), HCl, La(III), and Io tracer was added a solution of $Na_4P_2O_7$. A white crystalline precipitate formed immediately. The precipitate was stirred with the mother liquor for varying lengths of time. The precipitate was then centrifuged off, and an aliquot of the supernatant solution was mounted directly on a Pt dish for counting. In some of the experiments the precipitate was suspended in dilute HNO_3 and transferred to a Pt dish for counting of the alpha activity. In the other experiments the amount of Th precipitated was calculated from the amount remaining in the supernatant solution and the known amount of Io used. The results of these experiments are presented in Table 1.

The results indicate that Th(IV) is precipitated quite rapidly and fairly completely under the conditions chosen. Increasing the concentration of HCl to 1.8 $\underline{M}$ decreases the amount of Th(IV) precipitated in 2 hours. Several experiments were performed to check on the behavior of Pu(III) and Pu(IV) under the conditions which lead to 97.5 percent of Th(IV) being precipitated as thorium pyrophosphate. In these experiments the results were variable and quite inconsistent with the idea that Pu(IV) might behave like Th(IV) and Pu(III) like La(III). It was found that the plutonium in the presence of a reducing agent such as SO_2 or $NH_2OH \cdot HCl$ was carried to a variable extent ranging from 5% to almost 100%. No apparent correlation existed between the experimental results and the conditions used. The tracer used in these experiments was prepared under conditions which would lead to the presence of some Pu(VI) in the solution, although this was not realized at the time. If such was the case, the results of experiments

TABLE 1

PRECIPITATION OF THORIUM PYROPHOSPHATE

Th(IV)	200 micrograms
La(III)	500 micrograms
NH_3OHCl	0.03 millimoles (a)
$Na_4P_2O_7$	1.0 micromole
Room temperature	

Volume (ml)	HCl (moles/l)	Time of Stirring (intermittent) (min)	%Th(IV) precipitated
0.12	1.0	2	91.
0.12	1.0	6	97.5
0.12	1.0	120	98.
0.13	1.8	135	95.

(a) Present to duplicate conditions used in concurrently run experiments on the carrying of Pu(III).

in which the plutonium was supposedly Pu(IV) would be anomalous if Pu(VI) is not carried by thorium pyrophosphate, and in those in which it was treated with a reducing agent to prepare Pu(III) the results would also be anomalous if Pu(V) is carried, for the reducing agents tried (SO_2 and NH_3OHCl) are known to reduce Pu(VI) to Pu(V) fairly rapidly while further reduction is slow.[11]

More recently two sets of experiments were run in which the oxidation state of the plutonium was more carefully controlled. The Pu(III) solution was prepared on a five milligram scale by reduction with NH_3OHCl. The blue color of Pu(III) was observed visually; however, the presence of several percent Pu(IV) would not change this color appreciably. Aliquots of this solution were delivered into a cone containing the Th(IV), La(III), NH_3OHCl and HCl for treatment with the $Na_4P_2O_7$ solution. The Pu(IV) solution was prepared by precipitating Pu(III) hydroxide from the above prepared Pu(III) solution; this precipitate was washed with H_2O and dissolved in concentrated HNO_3. This solution was warmed and diluted to 2 $\underline{M}$ HNO_3. Such a procedure is known to give Pu(IV). Aliquots of this solution were delivered into a solution containing Th(IV), La(III), HCl and a very low concentration of $Cr_2O_7^{-}$. The $Cr_2O_7^{-}$ in 1 $\underline{M}$ HCl acts as a "holding oxidant" to insure that no reduction to Pu(III) takes place. Thorium pyrophosphate was precipitated from these solutions. The amount of Pu(III) carried by thorium pyrophosphate was determined by direct mounting of the precipitate and counting for alpha activity. The amount of Pu(IV) not carried by the thorium pyrophosphate was determined by removing an aliquot of the supernatant solution, reducing the $Cr_2O_7^{-}$ with NH_3OHCl and precipitating LaF_3 by the addition of HF. The resulting

LaF_3 precipitate was mounted for alpha counting. The percent of plutonium carried in each case was calculable since the amount of activity introduced into each sample was known. The results of these experiments are presented in Table 2.

The results presented in Table 2 indicate that Pu(IV) is carried to an extent of better than 95 percent under conditions where about 97 percent of Th(IV) is precipitated. Under similar conditions about one percent of the Pu(III) is carried. These results would lead one to believe that a satisfactory analytical procedure could be developed utilizing the precipitation of thorium pyrophosphate. Such a procedure, however, should offer no advantages over the zirconium phenylarsonate method which is described in a later section of this report.

2.3 Separation of Pu(III) and Pu(IV) by Zirconium Phenylarsonate.

(a) Preliminary Work. The fact that plutonium (presumably in the +4 oxidation state) is carried by zirconium phenylarsonate was first shown by S. G. Thompson.[12] More recently A. Kant[13] has shown that the +3 rare earth ions are not carried by zirconium phenylarsonate. This would lead one to believe that Pu(IV) could be separated from Pu(III) when both existed in solution by the precipitation of zirconium phenylarsonate, the precipitate carrying the Pu(IV) while the Pu(III), which behaves similarly to the +3 rare earth ions in many respects, would remain in solution.

Some experiments were run to determine how well zirconium phenylarsonate carries Pu(IV) when precipitated at room temperature. In the preparation of the plutonium tracer solution used in these experiments, measures were taken to

TABLE 2

CARRYING OF PU(III) AND PU(IV) BY

THORIUM PYROPHOSPHATE

Th(IV)	200 micrograms (as NO_3^-)
La(III)	500 micrograms (as Cl^-)
(HCl)	1.0 $\underline{M}$
$Na_4P_2O_7$	1.0 micromole
Volume	0.12 ml
Time of stirring	8 minutes

Room Temperature

Oxidation State	NH_3OHCl moles/l	$Na_2Cr_2O_7$ moles/l	Percent Plutonium Carried by Ppt.
+3	0.3	----	1.4
+3	0.3	----	0.8
+4	---	0.006	95.2
+4	---	0.006	98.4

insure that the Pu(IV) was in the "normal" form. The behavior of the colloidal form of Pu(IV) in a zirconium phenylarsonate precipitation is discussed in a later section of this paper. The tracer solution used in most of these experiments was analyzed for Pu(VI) by the "LaF$_3$ holding oxidant" method;[1] it was found to contain approximately 0.2 percent Pu(VI).

The phenylarsonic acid solution was added to a solution containing the Pu(IV), La(III), Zr(IV) and acid. The precipitate, which appears immediately, was stirred intermittently with the mother liquor for varying lengths of time; the precipitate was then centrifuged off. The supernatant solution was analyzed for plutonium by precipitating LaF$_3$. The amount of plutonium carried by the zirconium phenylarsonate could be calculated from the activity in the supernatant solution since a known amount of plutonium was used in each experiment. The results of these experiments are presented in Table 3.

At 0.033 $\underline{M}$ phenylarsonic acid the amount of Pu(IV) carried by the zirconium phenylarsonate increases as the time of stirring of the precipitate with the mother liquor is increased. Under these conditions the zirconium is not completely precipitated rapidly. This was ascertained in the following way: the supernatant solution, after being separated from the centrifuged precipitate with which it had been stirred for about 10 minutes, was allowed to stand. Within an hour a visible amount of precipitate had appeared in this solution. Using this same type of experiment it was found that at a higher concentration of phenylarsonic acid the rate of precipitation is more rapid. From the results presented in Table 3, it can be seen that for a given time of stirring, the zirconium phenylarsonate which is precipitated from a more concentrated solution

TABLE 3

CARRYING OF PU(IV) BY ZIRCONIUM PHENYLARSONATE

La(III)   100 micrograms
Zr(IV)   30 micrograms
Room temperature except
where noted otherwise.

Volume (ml)	$C_6H_5AsO_3H_2$ (moles/l)	HCl (moles/l)	NO_3^- (moles/l)	Pu(IV) Micrograms	Time of Stirring (min)	%Pu(IV) Carried
0.19	0.033	2.5	0.02	0.055	11	92. (a)
"	"	"	"	"	40	96.
"	"	"	"	"	260	98.4
"	"	"	"	"	1020	99.8
"	"	"	"	"	6	97. (b)
"	"	"	"	"	30	99. (b)
"	"	"	"	"	420	99.9 (b)
0.28	0.022	6.4	"	"	12	16.
0.28	0.022	6.4	"	"	220	11.
0.29	0.049	2.5	"	"	9	98.0 (c)
"	"	"	"	"	110	99.1
"	"	"	"	"	320	99.4
0.27	"	2.7	0.1	0.68	10	95.5 (d)
0.28	0.049	2.1	0.6	1.5	10	97.8
0.35	"	2.5	0.7	4.2	10	95.9
0.10	0.054	2.5	0.2	4.2	8	98.8
0.28	0.046	2.1	0.6	11.6	10	94.2
0.33	0.049	2.3	0.2	15.5	10	82.

(a) 5 experiments: 81, 91, 92, 94 and 94 percent carried.
    81% value omitted from average
(b) 70°C instead of room temperature
(c) 2 experiments: 98.1% and 97.9%
(d) 2 experiments: 95.1% and 96.3%; tracer solution of
    plutonium used was analyzed for Pu(VI) by "LaF$_3$-holding
    oxidant" method. 1.3% of plutonium was Pu(VI).

of phenylarsonic acid carries the Pu(IV) to a greater extent. The experimental results also reveal that the Pu(IV) is carried to a greater extent after a given time of stirring if the solution is at 70°C. The results show that the carrying of plutonium is greater than that observed by A. Kant[13] under similar conditions. In view of the fact that he observed better carrying in a HCOOH - HCOONH$_4$ buffer than in a HCl solution of the same hydrogen ion concentration, it is suggested that the tracer used by Kant contained some Pu(VI) which is not carried by zirconium phenylarsonate (see later section of this paper); in the formate buffer the Pu(VI) might be reduced to Pu(IV).

The carrying of Pu(IV) by zirconium phenylarsonate at higher Pu(IV)/Zr(IV) ratios was also tested. It is seen that at high ratios the carrying decreases as this ratio increases. Conditions exist, however, under which more than four micrograms of Pu(IV) can be carried to an extent of 98 percent by thirty micrograms of zirconium when precipitated as the phenylarsonate if the precipitate is stirred with the mother liquor for ten minutes before centrifugation.

It is seen that at 6.4 $\underline{M}$ HCl and 0.022 $\underline{M}$ C$_6$H$_5$AsO$_3$H$_2$ the carrying is quite poor. This much lower carrying is not due to a correspondingly lower percentage of the zirconium being precipitated, for it is known that zirconium phenylarsonate is not appreciably soluble under these conditions.*

The behavior of a +3 ion which should resemble Pu(III) was investigated. Ce(III) tracer was used; the ionic radius of Ce(III) in CeF$_3$ is only 0.011 $\overset{o}{A}$

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*No conclusion correlating the percent of the plutonium carried with the amount of the zirconium precipitated can be drawn if this is not an example of the type of carrying in which equilibrium is established at each new crystal face as it forms.

greater than that of Pu(III) in LaF_3. [14] The experiments were performed in much the same fashion as described previously. The precipitate was washed in each case with a solution of approximately the same composition as that from which it was precipitated. No La(III) was present in the wash solution. In these experiments both the precipitate and supernatant solution were analyzed. The precipitate was analyzed by first dissolving the zirconium phenylarsonate in hydrofluoric acid and then adding La(III) carrier; the resulting LaF_3 carries the rare earth activity. The results which are presented in Table 4 indicate that less than 1% of the Ce(III) is carried by zirconium phenylarsonate under conditions that result in a carrying of greater than 98% of Pu(IV).

The carrying of Pu(III) by zirconium phenylarsonate was next investigated. A Pu(III) tracer solution was prepared by diluting (with a NH_3OHCl solution) a Pu(III) solution prepared on a milligram scale by NH_3OHCl reduction. The procedure was similar to that used in the experiment on the carrying of Ce(III) tracer by zirconium phenylarsonate reported in Table 4. The results of these experiments are presented in Table 5. These results indicate that Pu(III) is carried to the extent of about one percent under conditions where Ce(III) was carried to a slightly lower extent and Pu(IV) was carried to the extent of about 98%. A. Kant of the Ames group reported the results of experiments on the carrying of plutonium which had been heated in a $NH_2OH \cdot HCl$ solution for some time. [15] Since he found much higher carrying one would conclude that the plutonium was not completely in the +3 oxidation state. This is interesting, for the reduction of Pu(IV) to Pu(III) by $NH_2OH \cdot HCl$ on a macro scale is known to proceed quite rapidly. Perhaps the slow rate was due to Pu(IV) being present

TABLE 4

CARRYING OF CE(III) BY ZIRCONIUM PHENYLARSONATE

La(III)　　　100 micrograms

Zr(IV)　　　30 micrograms

Room temperature except where noted

Volume (ml)	$C_6H_5AsO_3H_2$ (moles/l)	HCl (moles/l)	Time of Stirring (min)	%Ce^{+3} Carried
0.20	0.033	2.4	6	0.8 (a)
0.20	0.033	2.4	30	1.2 (a)
0.19	0.035	2.5	12	0.4
0.28	0.024	6.4	12	0.4
0.29	0.046	2.5	10	0.08
0.10	0.054	2.5	9	0.6

(a) 70°C

TABLE 5

CARRYING OF PU(III) BY ZIRCONIUM PHENYLARSONATE IN

THE PRESENCE OF NH$_2$OH·HCl

Zr(IV)   30 micrograms

Room temperature

Volume (ml)	$C_6H_5AsO_3H_2$ (moles/l)	HCl (moles/l)	NH$_2$OH·HCl (moles/l)	La(III) (µg)	Pu(III) (µg)	Time of Stirring (min)	%Pu(III) Carried
0.17	0.039	1.4	0.12	100	0.10	140	4.2 (a)
0.17	0.039	1.4	0.12	100	0.10	60	1.0
0.17	0.039	1.4	0.12	400	0.10	60	1.3
0.19	0.035	2.6	0.12	100	0.10	60	0.6
0.22	0.030	1.1	0.12	100	0.10	60	1.1
0.20	0.033	2.4	0.10	200 µg. Y(III)	0.10	150	0.9
0.29	0.046	2.5	(b)	100	0.06	11	0.5
0.28	0.046	2.5	0.05	100	0.73	10	0.8

(a) Precipitate not washed.
(b) NH$_2$OH·HCl concentration unknown but
appreciably higher than 0.1 $\underline{M}$.

in a colloidal form.

Thus far it has only been shown that Pu(IV) is carried by zirconium phenylarsonate in the presence of NO_3^- which would oxidize Pu(III) slowly under similar conditions, and it has also only been shown that the Pu(III) is not carried in the presence of $NH_2OH \cdot HCl$ which will certainly reduce Pu(IV) under the conditions used. To check on the applicability of the procedure to analysis, experiments similar to those reported in Tables 3 and 5 were run in the absence of NO_3^- and $NH_2OH \cdot HCl$. It was found that in the absence of NO_3^-, plutonium which was originally Pu(IV) was not carried to a very great extent; results ranged from practically quantitative non-carrying to carrying of 80%. This indicated that the Pu(IV) was being reduced by one of the reagents used or by an impurity contained therein. The phenylarsonic acid used (Eastman Kodak Co. No. 2020) was tested for reducing impurity by treatment with I_3^- solution. It was found that when such a test was carried out in a $NaHCO_3$-CO_2 buffer solution, an appreciable amount of I_3^- was used up, whereas, if the test was performed in 0.1 $\underline{M}$ H^+ much less I_3^- was used up. One method of preparation of $C_6H_5AsO_3H_2$ is the reaction of phenyldiazonium chloride with Na_3AsO_3.[16] It is not known if this is the method of preparation utilized by Eastman Kodak Co., but if such were the case it would not be surprising to find that As(III) was an impurity. Since As(III) is oxidized quantitatively by I_3^- in a $NaHCO_3$-CO_2 buffer whereas in 0.1 $\underline{M}$ H^+ there are approximately equal concentrations of As(III) and As(V) present in a solution which is 0.1 molar in I^- and 10^{-4} molar in I_3^-, it appears likely that one of the reducing impurities present is As(III).

Attempts were then made to purify all of the chemicals used. The pheny-

larsonic acid was purified by recrystallization from water three times; decolorizing carbon (trade-name Nuchar-00) was used in each recrystallization. The purified product was crystalline and very white. Attempts to purify the phenylarsonic acid by recrystallization without using the carbon black proved futile; the product obtained had an odor and was not pure white in color. A solution of purified $LaCl_3$ was prepared by precipitating some City Chemical lanthanum chloride as the hydroxide with NH_2OH, dissolving in HCl, precipitating as potassium lanthanum sulfate with K_2SO_4, dissolving in dilute HCl and then precipitating the hydroxide three times, each time redissolving in HCl. Pure $ZrOCl_2 \cdot 8H_2O$ was prepared by recrystallization from concentrated HCl of Eimer and Amend's zirconium chloride. Since some of the zirconium chloride purified in this manner had an odor of an organic nature, decolorizing carbon was also used in the first recrystallization of the material; this eliminated the odor.

Using these purified reagents, experiments on the carrying of Pu(III) and Pu(IV) by zirconium phenylarsonate were performed. The solution of Pu(IV) chloride was prepared on a milligram scale. A solution of plutonium was reduced with $NH_2OH \cdot HCl$ to Pu(III); the hydroxide was precipitated with NaOH and was washed with H_2O. This hydroxide was dissolved in conc. HNO_3, a treatment which is known to produce Pu(IV). The +4 hydroxide was then precipitated several times with NaOH, each time being dissolved with concentrated HCl. By never allowing the Pu^{+4} to be in a solution of low H^+ concentration for appreciable lengths of time, the disproportionation of Pu(IV) into Pu(III) and Pu(VI) was minimized. The final solution was diluted to $\sim$ 4 $\underline{M}$ in HCl; in such a solution the equilibrium amount of Pu(III) and Pu(VI) is very low. The solution of Pu(III)

chloride free of reducing agents was prepared by W. H. McVey by H_2 (on platinized Pt) reduction of Pu(IV).[17]

This solution was used over a considerable period of time. Since Pu(IV) is slowly formed in this solution upon standing, the percent Pu(IV) was determined spectrophotometrically for the experiments and is tabulated along with the percent carried. The experiments on the Pu(III) and Pu(IV) solutions prepared in this manner were carried out in a fashion similar to that used in the previously described experiments. Since the concentration of plutonium was known in these solutions and known volume aliquots were used, it was only necessary to analyze one of the fractions; in the case of analysis of Pu(IV) solutions the supernatant solution was analyzed, and in the case of analysis of Pu(III) solutions the zirconium phenylarsonate precipitate was analyzed. The results of such experiments are presented in Table 6 and Table 7.

It is seen that even with the repurified reagents the carrying of the plutonium is not as complete as one would expect if the plutonium were all Pu(IV). The carrying seems to be erratic; that is, the results of experiments which are performed under conditions which are identical as far as reagents used and general technique employed vary quite appreciably. This same type of erratic behavior was noted in the many experiments performed using reagents which were not as highly purified as those used in these later experiments. In these cases the carrying was lower and it was quite irreproducible. This variation must be due to the fact that the plutonium in the experiments which show low carrying does not remain completely in the +4 oxidation state. Since erratic behavior was observed when experimental conditions and reagents employed

TABLE 6

CARRYING OF PU(IV) BY ZIRCONIUM PHENYLARSONATE

Plutonium — 4 micrograms
La(III) — 100 micrograms
Zr(IV) — 30 micrograms
Volume — 0.21 ml
(HCl) = 2.3 $\underline{M}$
$(C_6H_5AsO_3H_2)$ = 0.054 $\underline{M}$
Room temperature
Precipitate stirred approximately 10
  minutes with mother liquor before
  centrifugation.

Experiment	% plutonium carried
1	75. (a)
2	98.5
3	82. (b)
4	92.
5	97.6
6	94.4
7	98.2
8	96.5
9	93.8
10	93.8
11	94.6
12	91.2

(a) Stood 45 min with all reagents present
except $C_6H_5AsO_3H_2$; $C_6H_5AsO_3H_2$
then added.

(b) Stood 18 min with all reagents present
except $C_6H_5AsO_3H_2$; $C_6H_5AsO_3H_2$ then
added. In all other experiments the pheny-
larsonic acid was added right after the
other reagents were mixed.

TABLE 7

CARRYING OF PU(III) BY ZIRCONIUM PHENYLARSONATE

Plutonium	2.5 micrograms
La(III)	100 micrograms
Zr(IV)	30 micrograms
Volume	0.21 ml
(HCl) =	2.3 M
$(C_6H_5AsO_3H_2)$ =	$0.0\overline{54}$ M

Room temperature

Precipitates stirred approximately 10 minutes with mother liquor before centrifugation.

Percent plutonium Carried	Percent present as Pu(IV) as determined spectrophoto- metrically using Pu(IV) (in HCl) peak at 4700 Å	Percent Pu(III) Carried (a)
1.5	(b)	$\leqslant$ 1.5
3.2	4.7	0
3.3	4.7	0
8.2	5.5	2.7
6.9	5.5	1.4
5.6	5.5	0.1
5.0	5.5	0

(a) Assuming that Pu(IV) is carried quantitatively.

(b) Not determined

were the same, one seems forced to the conclusion that the erratic behavior is due to traces of reducing impurities introduced independent of the reagents. It would require 4×10^{-3} microequivalents of reducing agent to reduce one microgram of Pu(IV) to Pu(III). It seems possible that such a small quantity of reducing impurity might inadvertently be introduced from the air (i.e., dust, laboratory gases, etc.).

The results in Table 7 indicate that the +3 plutonium is not carried to a very great extent (i.e., $<1\%$) in the absence of hydroxylamine hydrochloride. This is about the same as was indicated in the analysis carried out in the presence of $NH_2OH \cdot HCl$. Here too, there is a certain amount of erratic behavior; in some cases it could be explained on the basis of the Pu(IV) misbehaving (i.e., becoming reduced and therefore not carried).

(b) The Use of Cl_2 at Low Concentrations as a Holding Oxidant to Prevent the Reduction of Pu(IV). Since the main problem which exists is the prevention of the reduction of Pu(IV) by some unknown substance which is introduced into some samples to a greater extent than into others, it would be desirable to find an oxidizing agent which would destroy this unknown substance (or substances) and at the same time not oxidize Pu(III) at an appreciable rate under the conditions of the experimental procedure. R. E. Connick and W. H. McVey have found that Cl_2 oxidizes Pu(III) only slowly in 0.5 $\underline{M}$ HCl.[18] Since it has been observed qualitatively that Cl_2 oxidizes Pu(III) more rapidly at a higher acid concentration, analyses in the presence of Cl_2 were carried out at a lower HCl concentration than in the previously reported experiments. Experiments performed in the presence of Cl_2 are reported in Table 8. The Pu(IV) and Pu(III) solutions used

Table 8

CARRYING OF PU(III) AND PU(IV) BY ZIRCONIUM

PHENYLARSONATE IN THE PRESENCE OF 1.7×10^{-4} N Cl$_2$

Plutonium		2.5 micrograms
Zr(IV)		30 micrograms
La(III)		100 micrograms
Volume		0.21 ml
(HCl)	=	0.57 M (1.1 M before addition of $C_6H_5AsO_3H_2$)
$(C_6H_5AsO_3H_2)$	=	0.054 M
(Cl_2)	=	1.7×10^{-4} N

Room temperature

Precipitates stirred approximately 10 minutes before centrifugation.

Pu(IV) solution used:				
Percent Pu(IV) carried	98.3	98.6	98.8	98.6
Pu(III) solution used:				
Percent plutonium carried	3.7	10.2	11.2	7.6
Percent present as Pu(IV) as determined spectrophotometrically using the Pu(IV) (in HCl) peak at 4700 Å.	7.6	7.6	7.6	7.6
Percent Pu(III) carried (a)	1.1	2.6	3.6	0

(a) Assuming that Pu(IV) is carried quantitatively.

in these analyses were the same as those used in the analyses reported in Tables 6 and 7.

One can see that the presence of Cl_2 at very low concentrations eliminates the trouble which was formerly so prevalent in the carrying of Pu(IV) by zirconium phenylarsonate. The behavior in the case of the Pu(III) is still a little irreproducible.

A mixture of Pu(III) and Pu(IV) in HCl was prepared by mixing measured volumes of the Pu(III) and Pu(IV) stock solutions used in the previously reported experiments. Correcting for the amount of Pu(IV) in the Pu(III) (the determination of the amount of Pu(IV) being made spectrophotometrically) the percent of Pu(IV) in the mixed solution was 66%. Analyses of this solution were performed by the zirconium phenylarsonate procedure. The experimental conditions were identical with those used in the experiments reported in Table 8. Only the zirconium phenylarsonate precipitates were analyzed, the percent +4 being calculated on the basis of the known amount of activity used in each sample. In eight experiments (run at two different times in sets of four) the percentages of the plutonium carried by the zirconium phenylarsonate were 64, 63, 64 and 64 in the first set and 68, 66, 68 and 71 in the second set. These results agree fairly well with the calculated 66% Pu(IV) if one assumes that Pu(IV) was carried quantitatively and Pu(III) remained completely in the supernatant solution. Thus, it appears that mixtures of Pu(III) and Pu(IV) in an HCl solution can be analyzed by the zirconium phenylarsonate method if Cl_2 is present at a concentration of 1.7×10^{-4} N.

(c) Oxidation of Pu(III) by NO_3^-. Since in the presence of NO_3^- no anomalous results on the carrying of Pu(IV) by zirconium phenylarsonate were obtained

(see Table 3), it seemed worthwhile to check on whether or not Pu(III) is rapidly oxidized by NO_3^- under these conditions. A solution containing HCl, $ZrOCl_2$, $LaCl_3$, HNO_3 and Pu(III) was treated with a $C_6H_5AsO_3H_2$-HCl solution. The precipitate was analyzed as before. The results of these experiments are presented in Table 9. It is seen that the rate of oxidation by NO_3^- is not very rapid.* At the lower concentration of HNO_3 no oxidation occurred but rather it appears that at this low concentration of HNO_3, Pu(IV) may not be "held" in the +4 oxidation state. To check on this, four duplicate experiments were run identical to those at the lower HNO_3 concentration reported in Table 9 using the Pu(IV) stock solution which was used in the experiments reported in Tables 6 and 7. It was found that only 87, 82, 92 and 89 percent of the Pu was carried. This indicates that at this lower concentration of HNO_3, the Pu(IV) is not effectively "held" in the +4 oxidation state. The fact that the rate of oxidation of Pu(III) to Pu(IV) by HNO_3 at 0.02 $\underline{M}$ HNO_3 and 4.8 $\underline{M}$ HCl isn't exceedingly rapid indicates that the effectiveness of NO_3^- in "holding" the Pu(IV) in the +4 oxidation state must be due to its oxidation of the "reducing impurities" which caused so much trouble. The results of these experiments indicate that NO_3^- would not be an effective "holding oxidant" for use in solutions of Pu(III) and Pu(IV). However,

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* R. E. Connick and W. H. McVey present experiments run at a higher concentration of plutonium which show a lower rate of oxidation.[17] The discrepancy between the results reported here and those reported by Connick and McVey may be due to the fact that in the experiments reported here, HNO_3 solutions were the source of NO_3^- whereas in those reported in CN-2330 $NaNO_3$ was used, the acid being furnished by HCl. Since HNO_3 solutions are known to contain small amounts of the oxides of nitrogen, the more rapid rate may be due to oxidation by these oxides or a catalytic action of the oxides of nitrogen on the rate of oxidation of Pu(III) by NO_3^-.

it is possible that using conditions intermediate between those tried, Pu(III) would not be oxidized at an appreciable rate and at the same time the Pu(IV) would be effectively held in the +4 oxidation state.

(d) _Carrying of Pu(IV) in Colloidal Form by Zirconium Phenylarsonate._

Plutonium in the +4 oxidation state is known to exist in a colloidal form the properties of which differ markedly from those of the "normal form". This colloidal form of Pu(IV) is believed to be a peptized hydroxide. Certain characteristics of the absorption spectrum of the colloidal form of Pu(IV) are also present in the spectrum of the hydroxide suspended in water. The Pu(IV) solution used in the experiments described in the earlier sections of this report was prepared in a manner which would prevent the formation of the colloidal form. In order to check on the behavior of the colloidal form, a solution of Pu(IV) was prepared in a manner which should give colloidal Pu(IV): a solution of Pu(III) was prepared by $NH_2OH \cdot HCl$ reduction; Pu(III) hydroxide was precipitated and washed. The hydroxide was dissolved in concentrated HNO_3, a treatment known to give Pu(IV). The +4 hydroxide was precipitated from this solution with NaOH and "redissolved"[*] in small volumes of 0.23 $\underline{M}$ HCl; this was repeated three times. At the end of this procedure, the presence of normal Pu(IV) could not be detected when the solution was viewed with a spectrometer. Two aliquots of this solution were delivered into a solution containing 100 micrograms La(III), 30 micrograms Zr(IV), 0.22 $\underline{M}$ HCl and 5×10^{-4} $\underline{N}$ Cl_2. To this solution was added an equivalent volume of a solution, the composition of which was

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[*]Actually, the hydroxide is mainly peptized rather than dissolved by this treatment. The amount of HCl added was insufficient to react quantitatively with $Pu(OH)_4$. Also, the spectrum of the material corresponded to the colloidal Pu(IV) and not the "normal" Pu(IV).

TABLE 9

OXIDATION OF PU(III) TO PU(IV) BY NO_3^-

Plutonium	2.5 micrograms
La(III)	100 micrograms
Zr(IV)	30 micrograms
(HCl)	4.8 $\underline{M}$ before addition of $C_6H_5AsO_3H_2$
	2.4 $\underline{M}$ after " " "
Volume	0.10 ml before " " "
	0.20 ml after " " "
$(C_6H_5AsO_3H_2)$	0.057 $\underline{M}$

HNO₃ (moles/l)		Time before addition of $C_6H_5AsO_3H_2$ (min)	% Plutonium Carried	% Plutonium originally Pu(IV) (spectrophotometric)	% Pu oxidized assuming 1% Pu(III) carried
before [a]	after [a]				
0.0025	0.0012	5	6.3	7.6	0
0.0025	0.0012	11	7.0	7.6	0
0.02	0.01	13	20.2	8.1	11.3
0.02	0.01	18	25.0	8.1	16.1

(a) Before and after addition of $C_6H_5AsO_3H_2$.

which was 0.11 $\underline{M}$ $C_6H_5AsO_3H_2$ and 0.75 $\underline{M}$ HCl; the precipitate was stirred with the mother liquor for 10 minutes and then centrifuged off. The supernatant solution and precipitate were analyzed as previously described. The percent of the plutonium carried by the zirconium phenylarsonate precipitate in the two experiments was 94.2 and 95.5. These figures are not quite as high as those reported for "normal" Pu(IV) but at the concentration of HCl existing in the plutonium stock solution there might well be some Pu(III) and Pu(VI) due to the disproportionation of Pu(IV).

(e) **Carrying of Pu(VI) by Zirconium Phenylarsonate.** Since Pu(III), Pu(IV) and Pu(VI) can all exist in the same solution, it seemed desirable to check on the behavior of Pu(VI) with respect to its carrying by zirconium phenylarsonate. A tracer solution of Pu(VI) was prepared by heating a solution containing Pu(IV) with $Cr_2O_7^{=}$ in dilute HNO_3; this solution was used in two experiments, in one of which UO_2^{++} was added to act as a "holdback agent" for Pu(VI). The results of these experiments are presented in Table 10.

It is seen that Pu(VI) is not carried by zirconium phenylarsonate and further, that no "holdback agent" is necessary to prevent the carrying of Pu(VI).

(f) **Attempts to Analyze Solution Containing Pu(III), Pu(IV) and Pu(VI).** Since neither Pu(III) nor Pu(VI) is carried by zirconium phenylarsonate, it should be possible to analyze solutions containing Pu(III), Pu(IV) and Pu(VI) for the percentage of each of these three constituents. First a zirconium phenylarsonate precipitate would be removed. This would carry the Pu(IV). If then, the supernatant solution from the precipitation of zirconium phenylarsonate were treated with $Cr_2O_7^{=}$ and H_2SO_4, which would prevent both the reduction of Pu(VI) and the

TABLE 10

CARRYING OF PU(VI) BY ZIRCONIUM PHENYLARSONATE

Zr(IV)   30 micrograms
La(III)   100 micrograms
Pu(VI)   0.055 micrograms
Volume   0.23 ml
$(Na_2Cr_2O_7)$ 0.03 $\underline{M}$
$(C_6H_5AsO_3H_2)$ 0.029 $\underline{M}$
(HCl)   2.0 $\underline{M}$
Room temperature
Precipitate stirred with mother liquor for
  17 minutes before centrifugation.

$UO_2(NO_3)_2$ moles per liter	% Pu(VI) carried
0	< 0.25 %
0.0043	< 0.5 %

further oxidation of Pu(IV) which would be formed by the action of $Cr_2O_7^-$ on the Pu(III) originally present, and a LaF_3 precipitate were removed, the plutonium carried by the LaF_3 would correspond to that which was originally Pu(III). The supernatant solution from this fluoride precipitation could then be reduced with $NH_2OH \cdot HCl$ and LaF_3 precipitated again. The plutonium carried by this precipitate would correspond to the plutonium originally present as Pu(VI). Several experiments designed to check this method were tried. They are described in Table 11. The solutions of Pu(III), Pu(IV) and Pu(VI) used, were equilibrium disproportionation mixtures prepared and analyzed spectrophotometrically by M. Kasha and G. E. Sheline.

It is seen from the results presented in Table 11 that the zirconium phenylarsonate carries too large a percentage of the plutonium; that is, there is more plutonium carried by the zirconium phenylarsonate precipitate than there is Pu(IV) in the original solution. This apparent increase in the amount of Pu(IV) takes place mainly at the expense of the Pu(III), the Pu(VI)   entage being but slightly lower than the value determined spectrophotometrically. If the higher amount of Pu(IV) was due to reproportionation of the Pu(III) and Pu(VI), the amount of Pu(VI) would be quite a bit lower than was found to be the case. Also, the concentration of plutonium is quite low, and therefore the rate of reproportionation would be very low.[19] The acid into which the aliquot was delivered was approximately the same concentration as in the aliquot itself and therefore reproportionation would not tend to take place until the Pu(IV) had been removed from the solution by the zirconium phenylarsonate. There was present in the

TABLE 11

ANALYSIS OF Pu(III) - Pu(IV) - Pu(VI)

MIXTURES BY THE ZIRCONIUM PHENYLARSONATE METHOD

La(III)	100 micrograms
Zr(IV)	30 micrograms
(Cl$_2$)	5.0x10^{-4} N before addition of C$_6$H$_5$AsO$_3$H$_2$
	2.5x10^{-4} N after " " "
Volume	0.090 ml before " " "
	0.19 ml after " " "
(C$_6$H$_5$AsO$_3$H$_2$)	0.050 M

Total micrograms plutonium present	HCl concentration in plutonium stock solution (moles/l)	HCl concentration before addition of C$_6$H$_5$AsO$_3$H$_2$ HCl mixture (moles/l)	HCl concentration during precipitation of zirconium phenylarsonate (moles/l)	Percent plutonium carried by zirconium phenylarsonate	Percent plutonium carried by LaF$_3$ from supernatant solution of zirconium phenylarsonate pptn. (a)	Percent plutonium carried by LaF$_3$ from supernatant solution of previous LaF$_3$ pptn. (reducing agent present)	Percentages as determined spectrophotometrically		
							Pu(IV)	Pu(III)	Pu(VI)
0.20	0.20	0.21	0.59	44.5	27.8	27.7	27.6	46.6	26.1
0.20	0.20	0.21	0.59	41.8	31.9	26.3	27.6	46.6	26.1
0.97	0.50	0.67	0.57	70.1	17.7	12.2	57.6	28.2	13.0
0.97	0.50	0.67	0.57	72.2	17.3	10.5	57.6	28.2	13.0

(a)   (Cr$_2$O$_7$--) = 7x10^{-3} M
    (UO$_2$++) = 2x10^{-2} M
    (H$_2$SO$_4$) = 0.17 N
    (HF) = 3 M

disproportionation mixture used in these experiments a small but unknown concentration of Fe(III). It is possible that iron acts as a catalyst in the oxidation of Pu(III) to Pu(IV) by Cl_2. This has not been investigated. If this is not the reason one would conclude that the difference in behavior was due to the presence of Pu(VI). Since Pu(VI) is not used up, the mechanism must involve Pu(VI) as a catalyst for the oxidation of Pu(III) to Pu(IV) which does not seem very reasonable.

(g) Formula of Pu(IV) Phenylarsonate. In connection with the work on the carrying of Pu(IV) by zirconium phenylarsonate, it seemed worth while to investigate qualitatively the behavior of Pu(IV) phenylarsonate. The apparent solubility and rate of precipitation under a single set of conditions was determined. The composition of the solution before precipitation was: 1.97 micrograms Pu(IV)/ml and approximately 2.0 $\underline{M}$ HCl; the solution was then made 0.038 $\underline{M}$ in $C_6H_5AsO_3H_2$ (or 0.021 $\underline{M}$ if the Pu was precipitated quantitatively as Pu $(C_6H_5AsO_3)_2 \cdot xH_2O$). A white precipitate formed immediately. At various times aliquots of the supernatant solution were removed and analyzed for plutonium. No attempt was made to keep the temperature uniform nor was the precipitate kept suspended by agitation or frequent stirring. The results are given in Table 12.

Since the solubility of plutonium(IV) phenylarsonate is relatively low, it should be possible to determine the ratio of Pu(IV) to phenylarsonate in the precipitate in a relatively simple manner. To 1.1 mg of Pu(IV) in 0.60 ml of 1 $\underline{M}$ HCl were added measured volumes of 0.12 $\underline{M}$ $C_6H_5AsO_3H_2$; the precipitate was stirred with the supernatant solution and allowed to stand for a period of time. The supernatant solution was then analyzed for plutonium by mounting

TABLE 12

RATE OF PRECIPITATION OF PU(IV)

PHENYLARSONATE

$(HCl) = 2.0 \underline{M}$

$(C_6H_5AsO_3H_2)$ final $= 0.021 \underline{M}$

Time of Standing	Solubility (μg plutonium/ml)
40 min	130
24 hours	18
13 days	10

an aliquot of the solution on a platinum dish and counting for alpha activity. If one assumes that the phenylarsonate is quantitatively removed from the solution by the excess Pu(IV), such measurements will give the ratio of Pu(IV) to phenylarsonate in the precipitate. The results of this experiment are presented in Table 13.

From the results of this experiment one would conclude that the formula of the compound which precipitates under the conditions used is $Pu(C_6H_5AsO_3)_2 \cdot xH_2O$.

(h) Formula of Zr(IV) Phenylarsonate. An experiment was run to determine whether Zr(IV) precipitates as $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ or $ZrO(C_6H_5AsO_3) \cdot yH_2O$. To a solution 0.80 M in HCl containing 5.5 micromoles of Zr(IV) was added 6 micromoles of $C_6H_5AsO_3H_2$; the precipitate which formed was stirred with the supernatant solution for 30 minutes and then centrifuged off. Another portion of 6 micromoles of $C_6H_5AsO_3H_2$ was added to the supernatant solution and a considerable bulk of precipitate appeared. This would indicate that the precipitate which forms under these conditions is not $ZrO(C_6H_5AsO_3) \cdot yH_2O$. The addition of a third 6 micromole portion of $C_6H_5AsO_3H_2$ caused no further precipitation. Therefore, the precipitate does not contain three $C_6H_5AsO_3^-$ groups per Zr(IV) atom. One would conclude that Zr(IV) forms $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ when precipitated under the conditions used.

(i) Pu(III) in Phenylarsonic Acid Solutions. In view of the results obtained with respect to the carrying of Pu(III) by zirconium phenylarsonate, it does not seem likely that Pu(III) would form an insoluble phenylarsonate. To check on this, an experiment was run; a solution of Pu(III) was prepared by $NH_2OH \cdot HCl$ reduction; the final composition of the solution was 0.44 M HCl, 0.0034 M Pu(III), 0.02 M $C_6H_5AsO_3H_2$

TABLE 13

PRECIPITATION OF PU(IV) PHENYLARSONATE

Moles Pu(IV) in solution x 10^6	4.7	2.4	0.4
Moles Pu(IV) precipitated x 10^6	0	2.3	4.3
Moles $C_6H_5AsO_3H_2$ added x 10^6	0	4.8	9.6
Ratio Pu(IV) /$C_6H_5AsO_3^{=}$ in precipitate		2.1	2.2

and 0.16 $\underline{M}$ $NH_2OH \cdot HCl$. No precipitate appeared. One week later there was a very

small amount of solid present in the cone; this may have been Pu(IV) phenylarsonate,

the Pu(IV) being formed by O_2 oxidation or by the interaction of ion pairs formed by

the α-particles from plutonium.

Some experiments were also run to show that La(III) did not form an insoluble

phenylarsonate as would be predicted from the behavior of Ce(III) tracer and Pu(III)

with respect to carrying by zirconium phenylarsonate in the presence of La(III)

"hold-back agent". Four hundred micrograms of La(III) was added to 0.3 ml of

0.06 $\underline{M}$ $C_6H_5AsO_3H_2$ in one case and 0.3 ml of a solution the composition of which

was 0.06 $\underline{M}$ $C_6H_5AsO_3H_2$ and 0.16 $\underline{M}$ HCl in another case. No precipitate appeared

in 24 hours in either case. Thus one would conclude that the phenylarsonates of

the +3 rare earths and +3 plutonium are moderately soluble in dilute HCl as one

would predict from the behavior of tracers of those +3 ions in the zirconium phenyl-

arsonate precipitation.

3. Discussion

In discussing the significance of the carrying of Pu(IV) by $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$

one must consider the nature of the ions in solution as well as the nature of the

solid phase.

The ionic species of Pu(IV) present in HCl solution has been studied by Hindman, [20]

He has measured the potential of the Pu(III) - Pu(IV) couple in solutions containing

NaCl and HCl at different concentrations of HCl maintaining the ionic strength

constant. The potential is independent of the hydrogen ion concentration in the range

1 $\underline{M}$ to 0.3 $\underline{M}$. That Pu(III) is not hydrolyzed in this acid range is concluded from its

similarity to the +3 rare earth ions as well as the fact that its absorption spectrum does not change as the acid concentration is varied from 0.1 $\underline{M}$ to 1.0 $\underline{M}$.[21] Therefore, one would conclude that Pu(IV) is not oxygenated in the acid range 0.3 $\underline{M}$ - 1.0 $\underline{M}$. Hindman[20] has also made use of the absorption spectra of solutions of Pu(IV) to study the hydrolysis of Pu(IV) in acid solution. From these data he concludes that Pu(IV) is 100% Pu^{+4} (hydrated) in 1.1 $\underline{M}$ HCl and 94% Pu^{+4} (hydrated) in 0.36 $\underline{M}$ HCl. The absorption spectrum of Pu(IV) in solutions of 1 to 2 $\underline{M}$ HCl is the same as that of Pu(IV) in solutions of 1 to 9.4 $\underline{M}$ HClO$_4$. Perchlorate is generally not considered to be a strong complex forming ion. Thus, these data are interpreted by Hindman as indicating that Pu(IV) in HCl solutions in which the HCl concentration is less than 2 $\underline{M}$ does not have chloride ions attached. The absorption spectrum at higher HCl concentration indicates that some new species is predominant in 6 $\underline{M}$ HCl.[22]
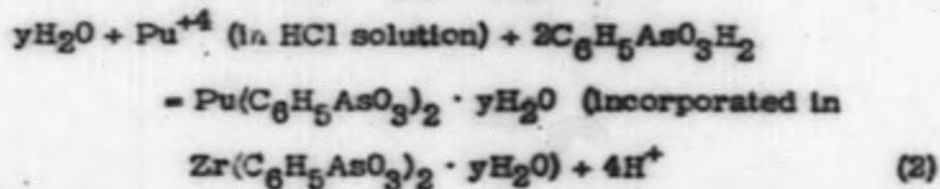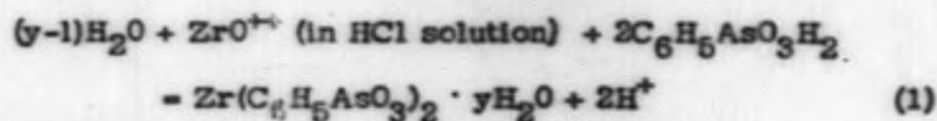
The ionic species of Zr(IV) present in acid solution is not completely settled. B. H. Ketelle and G. E. Boyd[23] have made a thorough review of the literature of zirconium in an effort to establish the species of Zr(IV) in solution. It appears that at lower hydrogen ion concentrations (0.1 $\underline{M}$) the Zr(IV) is hydrolyzed to an extent greater than ZrO^{++}. At higher hydrogen ion concentrations no good quantitative work on the hydrolysis of Zr(IV) exists. Most authors seem to write Zr(IV) as ZrO^{++} in

fact that the radius of Zr^{+4} is lower than that of Pu^{+4} would lead one to expect Zr(IV) to be less basic than Pu(IV). No quantitative measurements on the stability of chloride complexes of Zr(IV) exist. However, qualitative measurements of the dissolving power of certain acids for zirconium phosphate indicate that chloride forms less stable complexes with Zr(IV) than does nitrate, sulphate, phosphate, oxalate or fluoride. (24)

The precipitate of $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ is extremely finely divided when precipitated at room temperature. When viewed under a magnification of 430 fold, the particles appear to be crystalline, although no definite crystalline form can be discerned because of the small particle size. The precipitate of $Pu(C_6H_5AsO_3)_2 \cdot xH_2O$ was not examined with a microscope; the crystalline form of this compound may well be the same as that of the zirconium compound.

The determination of the actual mechanism of the carrying of a microcomponent by some macroscopic precipitate is a difficult problem that requires many different types of experimental evidence which were not acquired in the present work. It was shown that the rate of precipitation of the zirconium phenylarsonate is not very rapid and also that the Pu(IV) is carried more completely when the solutions and solid have been stirred together for longer periods of time. Thus, it is apparent that in most of the experiments reported, equilibrium conditions did not exist. However, certain conclusions regarding the mechanism of carrying of Pu(IV) by $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ may be drawn from existing data. That the process is not merely an absorption phenomenon is shown conclusively by the fact that the carrying is still fairly good when there are present in the precipitate 1 atom of Pu(IV) for every 8 atoms of Zr(IV). The most reasonable mechanism for the carrying of Pu(IV) by $Zr(C_6H_5AsO_3)_2 \cdot yH_2$ in the light of the known facts is the isomorphous replacement of Zr(IV) in the $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ by Pu(IV). It has not been shown that $Pu(C_6H_5AsO_3)_2 \cdot xH_2O$ is isomorphous with $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$. However, even if the two compounds were not isomorphous the mechanism of carrying of the plutonium might well be an isomorphous replacement of Zr(IV) by Pu(IV) in the crystal. The carrying of Pu(IV)

was seen (in Table 3) to drop to 62% as the number of Zr(IV) atoms per Pu(IV) atom in the crystal became 6. Such a behavior is not surprising in view of the difference in ionic radii of Pu^{+4} and Zr^{+4}. The metal-oxygen distance in PuO_2 is 2.333 Å while in ZrO_2 it is 2.20 Å.[25] At a ratio in the crystal of Zr(IV)/Pu(IV) of 6 the forces and the character of the crystal might very well be different than that of a crystal in which the metal atoms are very predominantly Zr(IV). Another factor which one would have to consider in experiments run at higher concentrations of Pu(IV) is the possibility of the precipitation of a phase in which Pu(IV) is the macro-component. The solubility of $Pu(C_6H_5AsO_3)_2 \cdot xH_2O$ is low enough that even at the conditions of most of the experiments reported in Table 3 the solubility of $Pu(C_6H_5AsO_3)_2 \cdot xH_2O$ may be exceeded.

If the isomorphous replacement of Zr(IV) by Pu(IV) in $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ is the true mechanism of carrying, one could represent what is happening by the following equations:

$$(y-1)H_2O + ZrO^{++} \text{ (in HCl solution)} + 2C_6H_5AsO_3H_2$$

$$= Zr(C_6H_5AsO_3)_2 \cdot yH_2O + 2H^+ \tag{1}$$

$$yH_2O + Pu^{+4} \text{ (in HCl solution)} + 2C_6H_5AsO_3H_2$$

$$= Pu(C_6H_5AsO_3)_2 \cdot yH_2O \text{ (incorporated in}$$

$$Zr(C_6H_5AsO_3)_2 \cdot yH_2O) + 4H^+ \tag{2}$$

An examination of equation (2) indicates that the carrying of Pu(IV) by $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ (for a constant amount of $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$) would drop off as the hydrogen ion concentration was increased. This was actually observed. The solubility of the $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ would increase as the hydrogen ion

concentration was increased. The amount of $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ precipitated at the higher acidity was essentially the same as that at the lower acidity and thus the decreased carrying of Pu(IV) could not be accounted for on that basis. Changing the chloride ion concentration would have an effect on reaction (2) for, as was mentioned previously, Pu(IV) is known to form a chloride complex in the region of 6 $\underline{M}$ HCl. Equation (1) may also have a chloride ion dependence. Thus, in changing the HCl concentration these factors about which little is really known would have to be considered in writing valid net reactions.

The possibility exists that the species of Pu(IV) and Zr(IV) in solutions which contain phenylarsonic acid (i.e., the supernatant solutions from the precipitations) are complex ions involving metal ions and phenylarsonate ions. If such were the case the equations (1) and (2) would be incorrect. These equations would all have to be modified when referring to the precipitation and carrying processes if the ratio of Zr(IV) to Pu(IV) is not very large, for the solid phase would no longer be $Zr(C_6H_5AsO_3)_2 \cdot yH_2O$ but rather a mixed crystal. That the mixed crystal in which the ratio of Zr(IV) to Pu(IV) is 6 behaves differently than one in which the Pu(IV) is very dilute was shown by the dropping in its carrying power for Pu(IV).

The slight carrying of plutonium from solutions in which it was supposedly Pu(III) and Pu(VI) may have been due to the presence of some Pu(IV) in these solutions. The carrying of Ce(III) could also be due to a small amount of Ce(IV) in the solution. The fact that the carrying of these +3 ions was observed to vary would give weight to the idea that the carrying was due to the presence of small amounts of Pu(IV). Experiments on the carrying of an ion such as La(III) should

indicate the true carrying of a +3 ion by zirconium phenylarsonate. Similarly, the true carrying of a Pu(VI) type ion could better be determined by use of U(VI). It would be interesting to run such experiments.

The practical use of the zirconium phenylarsonate method for the analysis of solutions of Pu(III) and Pu(IV) at tracer concentrations seems to be limited by the extreme care which one must exercise to prevent the reduction of Pu(IV). However, it has been shown that a HCl solution containing Pu(III) and Pu(IV) can be analyzed with fair accuracy if Cl_2 is present at $8x10^{-5}$ $\underline{M}$. In the absence of Cl_2, there was some irreproducibility in experiments in which the same repuri-fied reagents were used. The fact that the same repurified reagents were used in different experiments in which irreproducibility was observed would indicate that the reagents could not be the sole cause of the discrepancies observed when Cl_2 was absent. If inadvertently added impurities (i.e., laboratory gases, dust, etc.) are the cause of the irreproducibility, one would expect no better results from any similar analytical procedure in which the plutonium was present at very low concentrations. The use of a "holding oxidant" such as Cl_2, which does not o   e Pu(III) at an appreciable rate and at the same time prevents the re-duction of Pu(IV) by oxidizing the troublesome reducing impurities, is necessary when working with low concentrations of plutonium.

The use of the zirconium phenylarsonate method coupled with the "LaF_3 holding oxidant" method for distinguishing Pu(VI) [and Pu(V)] from the lower oxidation states as a means of determining Pu(III), Pu(IV) and Pu(VI) in a solution containing all three oxidation states did not prove workable. The difficulty may

have been due to the presence of a trace of Fe(III) which may have catalyzed the oxidation of Pu(III) to Pu(IV) by Cl_2. It does not seem very likely that the presence of Pu(VI) in the solution could affect the rate of oxidation by Cl_2 of Pu(III) to Pu(IV).

A tracer scale analysis of the type of the zirconium phenylarsonate procedure is applicable to many types of solutions of plutonium which can not be analyzed spectrophotometrically and for that reason is very important. In the use of this procedure (or any similar procedure) blank experiments should be run on solutions of Pu(III) and Pu(IV) similar to those which are to be analyzed. Such blank experiments would indicate whether or not a procedure of this type is applicable to the particular analytical problem under consideration.

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Analysis for Pu(III) and Pu(IV)

on a Tracer Scale *

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