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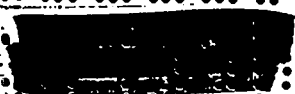
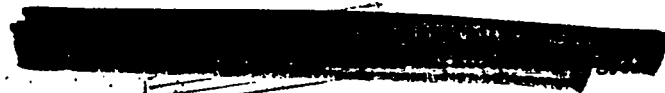
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### THE EFFECT OF GALLIUM ON PLUTONIUM ASSAY



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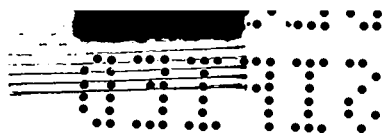
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CHEMISTRY AND CHEMICAL ENGINEERING  
M-3679 (29th Ed.)

This document consists of 20 pages



LOS ALAMOS SCIENTIFIC LABORATORY  
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

REPORT WRITTEN: November 1962

REPORT DISTRIBUTED: August 23, 1963

THE EFFECT OF GALLIUM ON PLUTONIUM ASSAY



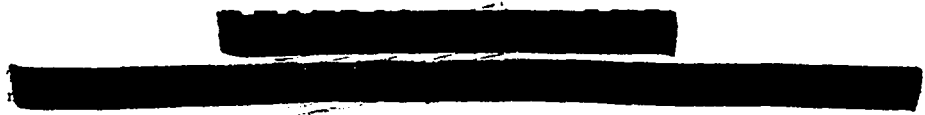
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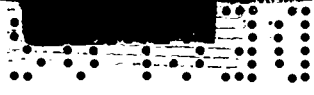
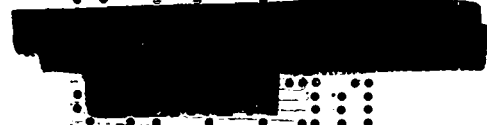
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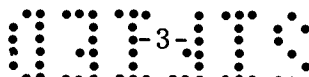

## ABSTRACT

In a general investigation of plutonium assay methods, all of the methods gave essentially identical results except in the case of a few samples analyzed by a photometric titration method. Slightly low assay values were obtained for delta-stabilized plutonium containing gallium when a visible precipitate of lead sulfate formed during the titration. Evidently, a pretitration step involving reduction of the hydrochloric acid solution of the metal with a lead reductor occasionally introduced sufficient lead to form a precipitate when sulfuric acid was added prior to the titration of plutonium(III) with ceric sulfate. Omission of the pretitration step caused high assays. An extensive search for impurity elements in a sample of delta-stabilized plutonium revealed no interfering elements in concentrations that would have a noticeable effect on the assays.


It was found that gallium(II), in variable, unknown quantities, was formed during dissolution of delta-stabilized plutonium in hydrochloric acid. The gallium(II) is titratable with ceric sulfate and causes a positive bias in the assay. Lead(II) ion in the lead reductor presumably oxidizes gallium(II) to the noninterfering (III) oxidation state. Evaporation of the hydrochloric acid solution of the metal to fumes with sulfuric acid and reduction with zinc amalgam also are effective in eliminating gallium(II) and provide a solution in which the plutonium is present quantitatively in the (III) oxidation state. By exercising care in the use of the lead reductor, or by using the fuming operation followed by reduction with zinc amalgam, precise and accurate assays of delta-stabilized plutonium containing gallium were obtained by the photometric titration method.

## ACKNOWLEDGMENTS

The authors are indebted to R. G. Bryan, D. C. Croley, J. W. Dahlby, G. B. Nelson, R. T. Phelps, J. C. Walden, and A. Zerwekh for their assistance in the analyses for impurities and to C. F. Metz for his supervision of the investigation.

  
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## INTRODUCTION

Several of the plutonium assay methods<sup>(7)</sup> were reexamined as part of a continuing effort to make improvements in these frequently used analyses. This investigation included a study of the controlled-potential coulometric,<sup>(9)</sup> amperometric,<sup>(4)</sup> potentiometric,<sup>(1, 10)</sup> and photometric<sup>(3)</sup> titration methods and their applications to assays of delta-stabilized and alpha plutonium metal. The photometric titration method included the recommended reduction of solutions of the delta-stabilized metal by use of a lead reductor.<sup>(2)</sup> All of the methods were found to give essentially identical plutonium compositions for both types of plutonium metal. Many successful applications of these proven methods are described elsewhere and need not be covered here in detail.

However, in the course of the investigation, it was found that in a few cases results from the photometric titration method were slightly low for delta-stabilized plutonium as compared to the assays by other methods. These low assays resulted when a visible precipitate of lead sulfate formed during the determination. This led to an investigation of the need for the reduction with the lead reductor. In this work one of the potentiometric methods<sup>(1)</sup> was used as a referee or reference method to ascertain occurrence of erroneous results during testing of modifications to the photometric titration method. The investigation finally showed that formation of gallium(II) during dissolution of plutonium in the presence of gallium made necessary a pretreatment of the solution before titration and also provided an

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explanation for one of the functions of the lead reductor in the photometric titration of delta plutonium, stabilized with gallium.

## ANALYTICAL METHODS

### Rocky Flats (RF) Method

The fundamental step in this method is the titrimetric oxidation of plutonium(III) to (IV) with standard ceric sulfate in sulfuric acid medium. <sup>(3, 7)</sup> In the case of alpha plutonium, the (III) oxidation state is obtained quantitatively by dissolution of the metal in 6 N hydrochloric acid. For delta-stabilized plutonium an additional step, reduction of the hydrochloric acid solution of the metal in a lead reductor, is included. <sup>(2)</sup> Because plutonium(III) is subject to air oxidation, it is essential to proceed directly to the final titration. The endpoint of the titration is detected with an interference-filter photometer which indicates the disappearance of the color of ferroin indicator as it is oxidized. The use of a color indicator makes a blank determination essential.

Some changes were made to attain more rapid and precise determinations. Smaller samples, ranging between 100 and 200 mg., were used; weighings were made with a semi-micro analytical balance (Ainsworth Model TCX); and the titrant was added from a special 18-ml. volume buret or a 12-gram capacity weight buret. In addition, the use of a lead reductor was omitted in several assays of delta-stabilized plutonium in order to evaluate the effect of this pretreatment step.

The borosilicate-glass volume-buret was fabricated from the bulb of a 20-ml. transfer pipet and a 1-ml. measuring pipet which was graduated in 0.01-ml. intervals to permit estimation of the titrant volume to 0.001 ml. The bulb forming the upper section of the buret was calibrated by weighing the quantity of water it contained. Only the

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final 1 ml. of volume, made from the measuring pipet, was graduated, making it necessary to use plutonium metal samples which could be titrated with a volume of ceric sulfate in the range between the bulb volume, 17.298 ml., and 18.298 ml. Fabrication of the volume buret was completed by adding a Teflon-plug stopcock with a needle valve (Fischer & Porter Catalog No. 790-006). The weight buret was similar to the one illustrated in Figure 61, Reference (6), but larger in capacity. The fine-bore tips of both burets were coated with wax to permit the transfer of very small increments of titrant to the plutonium solution by merely touching the surface of the solution.

The filter photometer was assembled according to published information<sup>(3, 8)</sup> except for a few minor changes. The wiring diagram for the instrument used for this investigation is shown in Figure 1. The power supply unit and the sensing unit were each assembled in 3 x 5 x 7-inch aluminum Miniboxes. The power to the sensing unit was usually turned on about 30 minutes before titration. Then just before use the 30,000-ohm potentiometer was adjusted to give full-scale (100- $\mu$ amp.) reading on the microammeter, with no beaker placed in the sensing unit. This adjustment of the potentiometer normally supplied about 15 volts to the cadmium sulfide photoconductive cell.

The blank determination was 0.121 ml. when the volume buret was used, and 132.0 mg. for the weight buret. When titrations were made with the latter buret it was convenient, near the endpoint, to transfer small increments from the buret tip to the plutonium solution with a stirring rod. The endpoint approach described by Caldwell et al.<sup>(3)</sup> was followed, and when 100-mg. plutonium samples were used, the endpoint consistently occurred at 80 to 82  $\mu$ amp. Also, the recommended standardization of titrant with primary standard  $As_2O_3$  was followed.

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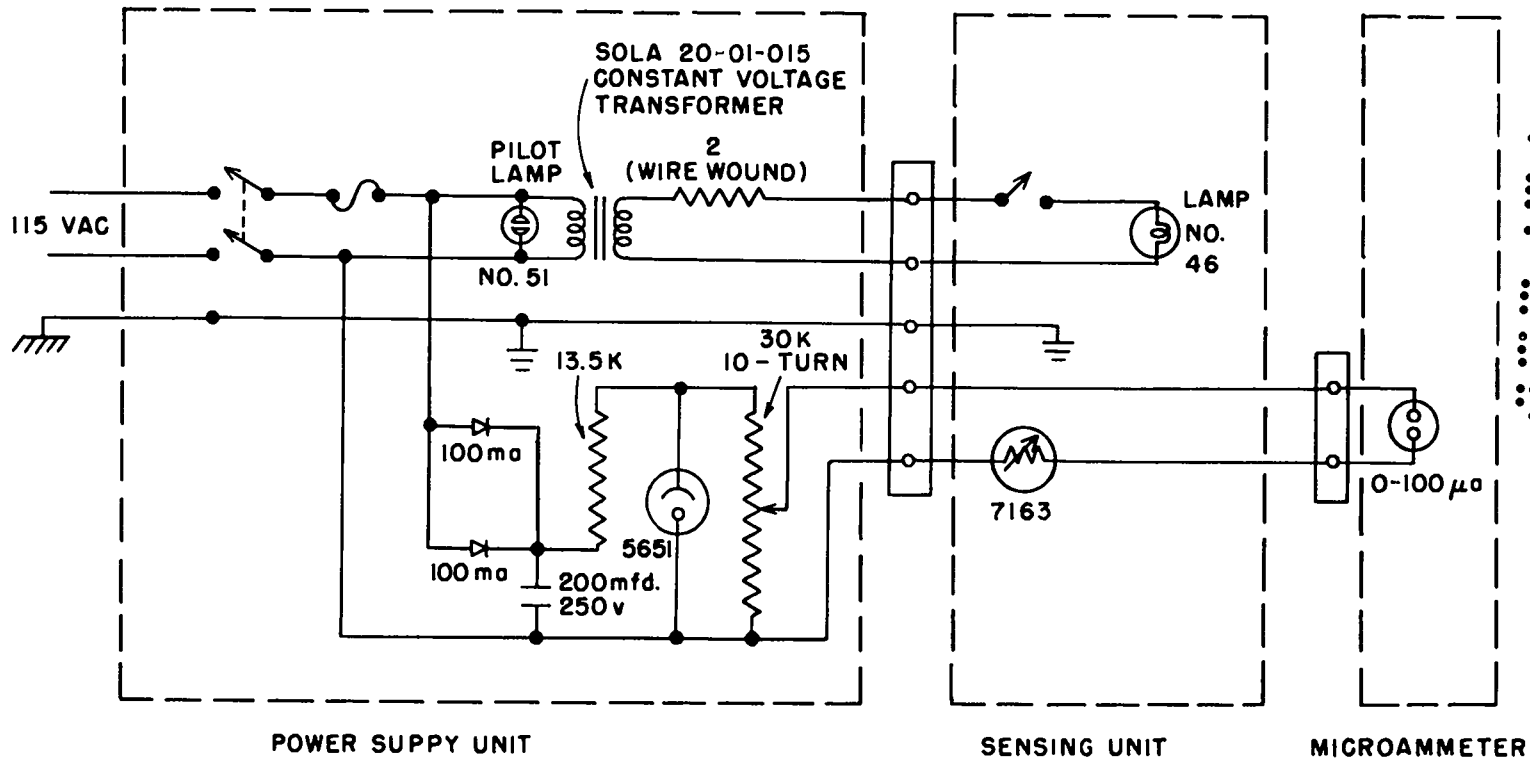



Figure 1. Schematic diagram for filter photometer

  
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### Los Alamos (LA) Method


The basic step in this method also is the titrimetric oxidation of the plutonium(III) to (IV) by ceric sulfate in sulfuric acid medium. The metal is dissolved in hydrochloric acid, the solution is evaporated to fumes with sulfuric acid, and then the plutonium is reduced to the (III) oxidation state with liquid zinc amalgam immediately before the titration. The endpoint is detected by the change in potential between calomel and platinum electrodes. Details of this method are described elsewhere. (1, 6, 7)

Ordinarily a sample in the range of 22 to 28 mg. of plutonium is taken as a weighed aliquot from a solution containing 0.6 gram of original metal. In some cases for this investigation, it was more practical to use approximately 100-mg. samples for analysis. These were either reduced with zinc amalgam in the normal manner, or the plutonium formed quantitatively during dissolution in hydrochloric acid was titrated directly, as in the RF method for alpha plutonium. For most samples no changes from the published LA method were made, including the recommended standardization of 0.05 N ceric sulfate against primary sodium oxalate.

### RESULTS AND DISCUSSION

The excellent agreement for assays of alpha plutonium and the low relative standard deviation by the LA and RF methods are shown by the data in Table I. The excellent precision obtained by the RF method probably results from the use of a weight buret or the special volume buret in place of the 50-ml. buret prescribed in the original method.<sup>(3)</sup>

The two methods of assay also gave identical results for plutonium in the presence of gallium when the lead reductor is used routinely as recommended in the RF method. On the other hand, high results are

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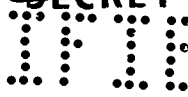
  
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TABLE I  
ASSAY DATA FOR SAMPLE A (ALPHA METAL)

LA method			RF method		
Sample wt., mg.	Wt. Ce soln., <sup>a</sup> g.	Percent Pu	Sample wt., mg.	Vol. Ce soln., <sup>b</sup> ml.	Percent Pu
25.253	2.4625	99.99	193.47	18.036	100.01
27.271	2.6578	99.93	192.46	17.942	100.01
25.208	2.4580	99.98	191.50	17.849	99.99
25.187	2.4561	99.99	184.98	17.245	100.01
23.611	2.3032	100.03	192.73	17.967	100.01
23.053	2.2497	100.07	187.84	17.516	100.04
22.628	2.2052	99.93	191.17	17.819	99.99
22.447	2.1891	100.00	188.32	17.560	100.03
24.420	2.3805	99.96	188.70	17.575	99.92
24.387	2.3793	100.04	189.49	17.666	100.02
24.636	2.4017	99.96	188.53	17.569	99.97
24.624	2.4017	100.01	189.43	17.653	99.97
			189.72	17.686	100.01
			191.91	17.889	100.00
			189.13	17.636	100.04
			188.62	17.573	99.95
	Average	99.99			100.00
	Rel. st. dev.	± 0.04			± 0.03

<sup>a</sup>Titer is 10.254 mg. plutonium per gram of ceric solution.

<sup>b</sup>Titer is 10.728 mg. plutonium per milliliter of ceric solution.

A blank of 0.121 ml. has been subtracted from the volume of ceric solution.

  
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obtained by the RF method when the lead reductor is not used. This can be observed with the data in Table II in which the difference between averages for percent plutonium in Sample B is 0.96%. This difference is much greater than the observed relative standard deviations of the methods and is significant. Consequently, an analysis for impurities that might cause the discrepancy was made.

#### Impurity Elements in Sample B (Delta-Stabilized Metal)

In the extensive search for impurity elements (any element other than plutonium or gallium) in Sample B, solvent extractions and separations with ion-exchange resins were employed to concentrate impurities. Portions of metal as large as 10 grams were used for these impurity separations prior to spectrochemical or spectrophotometric determinations. The data from this search for impurities are given in Table III.

There is no single element, with the possible exception of carbon, or combination of elements with the concentration levels listed in Table III which can explain the 0.96% difference in assays by the two methods, unless the difference involves some type of catalytic effect. In the case of carbon-containing plutonium, dissolving the metal might produce carbonaceous compounds, for example, acetylene. The direct reaction of this organic substance with ceric sulfate during the titration could lead to abnormally high assay values. A sensitive qualitative test did not reveal the presence of acetylene in the gas evolved during dissolution.

#### Effect of Gallium on Plutonium Assay

When the search for interfering impurity elements in Sample B was not successful, three additional samples of delta-stabilized metal were assayed by both the LA and RF methods. As in the previous determinations, the lead reductor treatment was omitted from the RF

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Table II

ASSAY DATA FOR SAMPLE B (RF DELTA-STABILIZED METAL)

LA method			RF method		
Sample wt., mg.	Wt. Ce soln., <sup>a</sup> g.	Percent Pu	Sample wt., mg.	Vol. Ce soln., <sup>b</sup> ml.	Percent Pu
26.143	2.4699	99.03	193.21	17.992	99.91
26.394	2.4916	98.95	189.23	17.631	99.96
25.819	2.4405	99.08	188.22	17.518	99.85
27.608	2.6093	99.07	191.32	17.823	99.94
27.425	2.5921	99.07	194.36	18.149	100.17
27.975	2.6428	99.02	192.61	17.963	100.05
29.078	2.7454	98.97	191.02	17.806	100.00
26.989	2.5498	99.03	192.45	17.946	100.04
27.198	2.5685	98.99	192.78	17.962	99.96
27.394	2.5855	98.93	188.15	17.526	99.93
25.731	2.4301	99.00	193.60	18.029	99.91
27.908	2.6376	99.06	192.94	17.979	99.97
			193.48	18.027	99.95
			194.12	18.085	99.95
			193.46	18.057	100.13
	Average	99.02			99.98
	Rel. st. dev.	± 0.05			± 0.08

<sup>a</sup>Titer is 10.482 mg. plutonium per gram of ceric solution.

<sup>b</sup>Titer is 10.728 mg. plutonium per milliliter of ceric solution.

A blank of 0.121 ml. has been subtracted from the observed volume of ceric solution.

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TABLE III  
 IMPURITY ELEMENTS IN SAMPLE B (DELTA METAL)  
 (All data in p. p. m.)

Ag	< 1.5	Hf	< 1.5	Pt	< 1.5
Al	100	Hg	< 6	Re	< 1.5
As	< 6	In	< 1.5	Rh	< 1.5
Au	< 1.5	Ir	< 1.5	Ru	< 1.5
B	0.8	La	< 10	Sb	< 6
Be	< 0.1	Li	< 0.2	Si	90
Bi	< 1	Mg	< 5	Sn	10
C	400	Mn	50	Ta	12
Ca	< 10	Mo	29	Ti	< 1.5
Cd	< 1.5	Na	< 10	Tl	< 1.5
Co	< 10	Nb	< 1.5	Th	24
Cr	120	Ni	400	Zn	< 10
Cu	50	O <sub>2</sub>	100	Zr	< 1.5
F	< 2	Pb	15	V	< 1.5
Fe	1000	Pd	< 1.5	W	< 10
Ge	< 1.5				

Note: For some elements, such as C, Fe, Ni, and O<sub>2</sub>, the analytical data indicated a varying degree of nonhomogeneity, but these variations were not significant for the problem under investigation.

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method. The average percent plutonium and the relative standard deviation calculated from the data obtained in this manner, along with the corresponding values for Samples A and B from Tables I and II, are listed in Table IV. This latter table also shows the differences between average percent plutonium obtained by the two methods.

In order to explain this difference in results, the possible oxidation states of gallium and plutonium were considered. When the use of a lead reductor is omitted from the RF assay method, the (III) oxidation state of plutonium is obtained simply by dissolution of the metal sample in dilute hydrochloric acid. If the reducing action of the dissolving plutonium reduces some of the gallium to gallium(II) instead of the normally expected gallium(III), then some ceric sulfate would be consumed in oxidizing the gallium(II), and high assay values would result. In the LA method the addition of sulfuric acid and evaporation to fumes evidently oxidizes any gallium(II), and the gallium(III) is not reduced by the dilute zinc amalgam.

A series of experiments was performed to determine if a lower oxidation state of gallium causes abnormal assays for plutonium. High purity gallium from three sources, in the form of metal, oxide, and anhydrous chloride salt, was used. It was added, after an appropriate conversion to a usable form when necessary, to the dilute hydrochloric acid required for plutonium dissolution. The amount of gallium thus added to the acid used for dissolving a 100-mg. sample was usually in the range of 2 to 10 mg. Portions of Sample C (delta-stabilized metal) were dissolved in this manner and immediately titrated as described in the RF assay method for alpha plutonium. The assays were 100.10 and 100.69%, compared with the average of 99.76% for Sample C (Table IV) which was obtained by using hydrochloric acid initially containing no gallium chloride. Alpha metal samples also gave abnormal assays if a few milligrams of gallium first were added

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TABLE IV  
 COMPARISON OF ASSAY DATA FOR DELTA METAL  
 BY RF AND LA METHODS

Sample No.	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>A<sup>a</sup></u>
Origin of sample	RF	RF	LA	LA	LA
Ave. percent gallium	1.05	0.99	0.68	2.97	None
<u>RF method</u>					
Ave. percent Pu	99.98	99.76	99.64	97.95	100.00
Rel. stand. dev.	0.08	0.01	0.04	0.13	0.03
<u>LA method</u>					
Ave. percent Pu	99.02	99.06	99.25	96.95	99.99
Rel. stand. dev.	0.05	0.02	0.01	0.04	0.04
<u>Difference for methods</u>					
Ave. percent Pu	0.96	0.70	0.39	1.00	0.01

<sup>a</sup>Sample A is alpha metal; results included for comparison purposes.

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to the dilute acid used in dissolving the sample. For example, portions of Sample A assayed 100.11 and 100.07%, compared to a normal assay value of 99.99%.

It was possible to reduce the magnitude of the error in the abnormal assays for delta-stabilized metal samples in several ways other than passing the plutonium solution through a lead reductor. If the dilute hydrochloric acid was cooled with dry ice during metal dissolution, the assay for Sample C was reduced from an average of 99.76 to 99.53%. If the volume of dilute hydrochloric acid was increased (see Table V), the observed assay value was found to decrease. The various volumes of acid indicated on Table V were added at different rates. One sample of alpha metal (Sample A) did not show significant change in assay when the volume of acid was decreased. These effects were assumed to be the result of varying amounts of gallium(II) produced under the different conditions for dissolution.

If the assumption is true that gallium is partially converted to the (II) oxidation state by plutonium when it dissolves in hydrochloric acid, then other strong reducing metals might have the same effect.

Magnesium was selected to replace plutonium because it has only one oxidation state in solution. Direct titration as described in the RF method for alpha metals, of a solution containing 100 mg. of high-purity magnesium metal dissolved in dilute hydrochloric acid, required the same weight of ceric sulfate, 132.4 mg., as a blank determination. Likewise, a blank determination made on a hydrochloric acid solution of gallium remained within the range of normal blanks at 134.6 mg. However, if high-purity magnesium was dissolved in gallium-containing hydrochloric acid, the blanks observed were 152.5 and 210.2 mg. of ceric solution. It is assumed that under the latter conditions the reducing action of magnesium forms some gallium(II) which is titrated along with the usual ferroin indicator added in controlled amounts.

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TABLE V  
EFFECT ON ASSAY FROM VOLUME OF DISSOLUTION ACID

Sample No.	Volume of 6 N HCl, ml.	Percent Pu
B	0.3	101.29
"	0.3	99.76
"	0.5	99.90
"	1.0	99.96
"	1.0	99.41
C	5.0	99.22
A	0.3	100.02

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Similar evidence for conversion of gallium to the (II) oxidation state by the dissolution of high-purity magnesium metal was found by potentiometric titration of such samples. Titrations began at potential around +150 mv. (instead of the -350 mv. for plutonium samples in the LA method), but they were concluded at the usual -760 mv. for cerium(IV) titrations of plutonium(III). A blank, starting with dilute hydrochloric acid containing 40 mg. of gallium in the form of dissolved chloride, required 1.4 mg. of ceric sulfate titrant, but a similar acid solution in which 100 mg. of magnesium was previously dissolved required 57.0 mg. of the titrant.

#### Methods for Eliminating Gallium(II)

The recommended RF method for assay of delta-stabilized plutonium includes the lead reductor treatment and, therefore, must oxidize any gallium(II) formed in the dissolution of the metal. Because the potential<sup>(5)</sup> of the  $Pb-Pb^{+2}$  couple is -0.13 volt and the potentials of the  $Ga-Ga^{+2}$  and  $Ga^{+2}-Ga^{+3}$  couples are -0.45 and -0.65 volt, respectively, it is assumed that lead(II) ions in the lead "reductor" actually oxidize the limited amounts of gallium(II) formed in dissolution of the sample.

However, care must be exercised in the use of the lead reductor. As an illustration, Sample B, which averaged 99.02% plutonium when the LA method was employed, also gave a value of 99.01% for each of two portions of metal assayed with the RF method, but at times, with no apparent change in technique, a small amount of insoluble lead sulfate was observed just after dilution of the dissolved sample to 75 ml. with 1 N sulfuric acid, and the assays were low (98.88 and 98.08%). A low assay (99.83%) was obtained also for a sample of alpha plutonium (Sample A) when a small amount of lead sulfate was present in the solution being titrated. This was assumed to be due to the lead sulfate acting as a carrier for some of the plutonium.

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Other oxidants for gallium(II) were sought. The potentials for the gallium couples given above indicate that the oxidant for gallium(II) must have a potential within a narrow range of values. For example, these potentials indicate that a zinc reductor cannot be used in place of a lead reductor. The  $Zn-Zn^{+2}$  potential is -0.76 volt, or slightly less negative than this when amalgamated, and is too close to the potentials of the gallium couples. This conclusion was verified experimentally. It was found that addition of metallic zinc to a solution of delta-stabilized plutonium, just after dissolution in hydrochloric acid, was not effective in eliminating abnormal assays by direct titration. The evaporation to fumes with sulfuric acid followed by reduction with zinc amalgam, as in the LA method, was effective in eliminating high results when either a potentiometric or photometric determination of the endpoint was used in the direct titration. Therefore, the ceric sulfate titration to a photometric endpoint is definitely not the cause for any error in assay of plutonium.

The potentials of the gallium couples indicate that nickel with a potential of -0.24 volt for the  $Ni-Ni^{+2}$  half reaction might oxidize the gallium(II) with no deleterious side reactions. However, addition of nickel chloride to a plutonium solution containing gallium(II) did not eliminate abnormal assay results.

This investigation of possible methods for eliminating gallium(II), following dissolution of delta-stabilized plutonium, led to the conclusion that the pretreatment described in the LA method [evaporation of the solution to fumes with sulfuric acid and reduction to the (III) oxidation state with zinc amalgam] is a reliable technique. The lead reductor treatment gives equally reliable results unless a precipitate of lead sulfate forms. No other method of eliminating gallium(II) was found to be satisfactory.

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## CONCLUSIONS

- (1) Gallium(II), which is formed in variable, unknown quantities during dissolution of delta-stabilized plutonium, is titratable with cerium(IV).
- (2) Pretreatment of dissolved delta-stabilized plutonium to eliminate gallium(II) is essential before titrimetric determinations. This pretreatment may involve use of a lead reductor, or sulfuric acid fuming followed by reduction with liquid zinc amalgam.
- (3) Care must be exercised in the use of a lead reductor to prevent precipitation of plutonium-carrying lead sulfate. Therefore, there is no advantage in modifying the pretreatment operation in the LA method.
- (4) No impurities in delta-stabilized plutonium metal other than those such as iron, previously known to interfere in the respective analytical methods, were found in concentrations that would have marked adverse effect on either the LA or RF assay method.

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