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MICROVOLUMETRIC ASSAY OF PLUTONIUM

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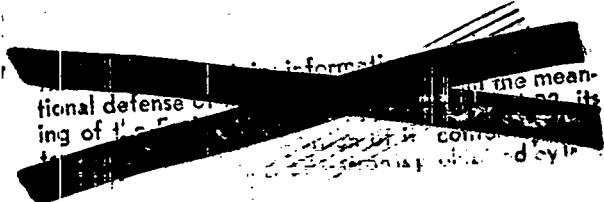
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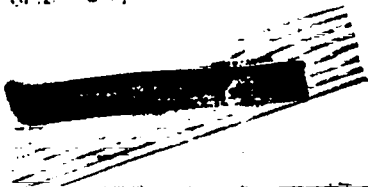
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Abstract

Plutonium as sulfate in 2N sulfuric acid is reduced to +3 valence with zinc amalgam under a carbon dioxide atmosphere and is titrated potentiometrically to +4 valence with ceric sulfate.<sup>1)</sup> An accuracy of 0.1 per cent is obtained in the range of 2 to 10 mg.

LOS ALAMOS NATL. LAB. LIBS.



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- 1) Pepokowitz, LA-462, December 3, 1945; I. M. Kolthoff and N. H. Furman, Potentiometric Titrations, John Wiley & Sons, Inc., 1931.

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Introduction

A microvolumetric method for the estimation of plutonium was one of several methods requested to supplement the existing physical method of counting.<sup>2)</sup> The request was made in August 1944 in anticipation of the production program started at Los Alamos in 1945. The desired accuracy was 0.1 per cent.

When the problem was begun the existence of such a method was not known. A micro-iodometric method had been attempted here. Work was begun done at another project laboratory on the reduction of plutonium to +3 valence with titanium trichloride and its potentiometric titration in dilute sulfuric to +4 valence with ceric sulfate.<sup>3)</sup>

Procedure

For method of sampling, reagents, apparatus, procedure, calculations, and figures, see LA-416A.

Discussion

The sample size was limited at the outset by the amount of relatively pure material available. With the knowledge that under production conditions 10 mg or more would be available per determination, work was started on a 1-mg (in 2 ml) scale in order to exaggerate some of the errors and interferences.

Throughout this work ceric ion has been the only standard oxidizing agent used (excepting the data, Table V). Standardization of the ceric solution will be discussed in the next section.

The ionic system of 2N sulfuric acid is especially favorable to the quantitative oxidation of plutonium to the +4 valence. The potential

2) Bradford, Roberts, and Wahl, LA-469, January 11, 1946.

3) CN-1791 refers to this work in progress. No further reference was found in a search of the project literature.

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of the reaction  $\text{Pu}^{+3} \rightarrow \text{Pu}^{+4} + e^-$  in 1N perchloric acid, in which both states are presumed to be relatively non-complexed,<sup>4)</sup> is about -0.95 volt.<sup>5)</sup> The potential of the reaction  $\text{Pu}^{+4} + 2\text{H}_2\text{O} \rightarrow \text{PuO}_2^{+2} + 4\text{H}^+ + 2e^-$  in the same system is about -1.1 volts. The observed potential of the first reaction in 2N sulfuric acid is about -0.75 volt. Assuming this difference in potential to be caused by the formation of a sulfate complex of plutonium  $+6$ ,<sup>6)</sup> the potential of the second reaction in 2N sulfuric acid might be expected to be about -1.2 volts subject to the difference in hydrogen ion concentration of the two acid systems and to any effect of sulfate on plutonium  $+6$ . In actual practice a break of 0.5 volt in the titration curve occurs at the  $+4$  valence equivalence point. No attempt has been made to show the presence of plutonium  $+6$  upon the addition of excess ceric ion.

During the development of the method, titration curves and end points were determined potentiometrically with a saturated potassium chloride-calomel electrode and a platinum electrode. All solution measurements were made by weight. A satisfactory color indicator for 0.1 per cent accuracy has not been found. With ferrous-ortho-phenanthroline the color change at the end point is from red-brown to brown.

All routine assay work has been done potentiometrically with weight rather than volume measurements (Table I). The data of three operators plotted as ( $\Delta$  millivolts) / ( $\Delta$  weight of ceric solution) versus the mean potential of the increment concerned. The maximum was estimated at 760

4) Gofman and Connick, CN-261, p. 4, August 15, 1942.

5) Hindman, Kraus, and Howland, CK-1371, p. 8, March 1, 1944.

6) Gofman and Connick, CN-239, p. 5, July 15, 1942.

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millivolts. In a titration of 5 mg of plutonium the average slope from 700 to 820 millivolts is about 10 millivolts per  $\gamma$  of plutonium. The rate of attaining an equilibrium potential in 2N sulfuric appears to be faster with plutonium than with iron or uranium.

Of the several possible reducing agents, liquid zinc amalgam was selected. The ease with which the amalgam can be separated from the reduced solution quite outweighs the disadvantage of its comparatively slow rate of reduction of plutonium in 2N sulfuric acid (15 to 45 minutes, depending upon the ratio of plutonium in the several valence states, the ratio of amalgam surface to solution volume, and the rate of stirring). High and variable blanks ( $6 \times 10^{-4}$  milliequivalents corresponding to 140  $\gamma$  of plutonium) obtained in the initial work with zinc amalgam led to the temporary consideration of other reducing agents. A silver microreductor was first used with the plutonium in 1N hydrochloric acid, but was abandoned because of the large rinse volume and the variation ( $\pm 2 \times 10^{-4}$  milliequivalents) of the blank. Reduction with stannous chloride under various conditions followed by oxidation of the excess reducing agent with mercuric chloride gave rather poor precision.

At this point an attempt was made to determine the nature of the blank obtained with liquid zinc amalgam and to eliminate it or obtain satisfactory reproducibility. When 2 ml of 2N sulfuric acid were stirred with zinc amalgam for 1/2 hour or longer in air, a blank of about  $6 \times 10^{-4}$  milliequivalents was observed.<sup>7)</sup> From different reductions this value varied as much as 50 per cent. If the blank were caused by impurities in the sulfuric acid, it might be expected that other acids should produce a blank of different magnitude. However, with dilute hydrochloric acid, perchloric acid, or even

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distilled water instead of sulfuric acid, a blank of comparable magnitude was obtained under similar conditions. The same observation was made with dilute hydrochloric acid on mercury alone. There seemed to remain only water and oxygen from which the reducing substance might be formed. Reduction under an atmosphere of carbon dioxide was immediately undertaken and was found to give a low and sufficiently reproducible blank of about  $2 \times 10^{-5}$  milliequivalents (Table II).

Hillebrand and Lundell<sup>8)</sup> mention the hydrogen peroxide explanation of the blank obtained with a Jones reduction, but state that they have found no evidence for the formation of peroxide. They further state that hydrogen peroxide is completely destroyed when a sulfuric acid solution of it is passed through the reductor. Mason and Pekola<sup>9)</sup>, working with dilute sulfuric acid and liquid zinc amalgam on a macro scale, observe a blank in the presence of air. They consider it to be caused by hydrogen peroxide. Their estimate is 8 ppm. The blank observed above on a micro scale ( $6 \times 10^{-4}$  milliequivalents in 2 ml) would correspond to 5 ppm.

There are several reasons for believing the blank to be hydrogen peroxide. The potentiometric titration curve of a blank is very similar to one of reagent hydrogen peroxide in the same acid system. Equal aliquots of a single blank react with the same number of equivalents of ceric ion as with iodide ion (titrated with thio-sulfate). The rate of reduction of the blank with iodide is within 10 per cent of the rate of reduction of reagent peroxide with iodide under the same conditions. Starting with 2 ml

- 8) W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, p. 103, John Wiley and Sons, Inc., 1929.
- 9) Mason and Pekola, A-1061, p. 2, November 17, 194

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of 2N sulfuric acid heavily spiked with reagent peroxide, the previously observed value of  $6 \times 10^{-4}$  milliequivalents is obtained after the usual reduction time.

It would appear that the blank obtained with liquid zinc amalgam and dilute acids (or water) in the presence of air is caused by a peroxide intermediate in the reduction of oxygen to water. Plutonium has little effect upon the value of the blank in the presence of air. Iron greatly decreases the blank as might be expected from its potential and rate of reaction with peroxide.

In order to include possible effects of plutonium upon the blank (in carbon dioxide atmosphere), blanks were determined in the presence of small but known amounts of plutonium (10 to 100 $\mu$ ). An average of  $2 \pm 1 \times 10^{-5}$  milliequivalents was found both in the presence of plutonium and with 2N sulfuric acid alone (Table II).

A study of interferences was necessary since the method was intended to be used for relatively impure plutonium nitrate from Hanford. Analyses of this material showed between 0.2 and 1.0 per cent iron (colorimetric) and usually less than 100 ppm uranium (fluorimetric). Stainless-steel apparatus and shipping containers were thought to be responsible for the high iron content. Spectrographic chromium and nickel estimates did not contradict the assumption. Other substances expected to interfere (see below) seemed from spectrographic estimates to be below objectionable limits except as possible catalysts.

Standard macrovolumetric procedures for titanium, vanadium, iron, molybdenum, tungsten, and uranium indicate their certain interference. These elements with the exception of tungsten were studied both alone and

in the presence of plutonium. (Attempts to prepare a standard tungsten solution were unsuccessful. The reported differences in energy between its various oxidation states would not permit it to be a catalyst for air oxidation of plutonium.) Titanium, vanadium, and molybdenum show the characteristic valence changes of one, two and three respectively. All three are reasonably quantitative on the milligram scale but are quite susceptible to air oxidation. Combinations with plutonium give results between the calculated sum and the calculated value for plutonium, depending upon the extent to which air is excluded during the reduction and titration. No evidence for catalysis of air oxidation of plutonium was found. At least semiquantitative separate estimations of titanium, plutonium, and vanadium can be obtained from the same titration. Distinction almost certainly be improved by the proper acidity and anion.

Reduction of uranium under carbon dioxide atmosphere followed by immediate titration gives results that are several percent high. In more concentrated solutions the brown color caused by the presence of uranium +3 is distinctly visible after extended reduction.<sup>11)</sup> With combinations of uranium and plutonium in dilute hydrochloric acid, a very sharp break of about 300 millivolts occurs in the titration curve at the equivalence point uranium +6 - plutonium +3. More work is planned to obtain an accuracy of 0.5 per cent or better in the assay of uranium-plutonium alloys by a single titration.

The method for plutonium without modification is quantitative for iron. (Table III) The combination is quantitative. Plutonium in 2N

11) LA-462, p. 5, Pepkowitz observed no uranium +3 after reduction for 15 minutes in his type of apparatus.



sulfuric acid is air oxidized faster than iron. Attempts to distinguish quantitatively between the two in the same titration were unsuccessful in 2N sulfuric acid. A small but insensitive and useless break in the titration curve occurs in dilute hydrochloric acid. Correction for iron is very simply and accurately made from the colorimetric analysis.<sup>12)</sup> Separation need not be considered for iron content less than 2.0 weight per cent. (2.00 weight per cent of iron is a correction of 8.56 per cent in the titration.)

A number of other ions were studied. The selection was made from a consideration of valence states, potentials, catalytic possibilities, complex formation, and ionic strength effects. Copper, cadmium, mercury, tin, arsenic, antimony, and bismuth are either reduced into the amalgam or reduced to an oxidation state incapable of being precipitated by sulfide or oxidized by ceric. Chromium, manganese, cobalt, and nickel do not interfere. High concentrations of ammonium ion, sodium, magnesium, and aluminum have very little effect upon the titration curve. Nitrate gives high results. It appears to be removed by a single fuming with sulfuric acid. (Table IV). Samples containing nitrate are fumed twice with sulfuric acid before reduction.

For the error arising from air oxidation see Table III. The potential reading of a solution quantitatively reduced to plutonium +3 under a carbon dioxide atmosphere is observed to rise from -0.2 volt to +0.3 volt in about one minute of stirring after separation from the amalgam and exposure to air. The titer of this change is of the order of 0.1 per cent or less.

12) LA-416, III.D.

### Standardization of the Ceric Solution

A micro method for standardization has the advantage of using the same technique and equipment. The ceric solution is added slowly with stirring to oxalate in 2 ml of 2N sulfuric acid. The temperature throughout the titration is kept at about 80°C. More than an equivalent amount of ceric is consumed if the solution is added too rapidly or at room temperature. The titration at no time should contain enough ceric to give a visible yellow color. The end point is determined potentiometrically. Short of the end point the potential rises sharply with each addition of ceric solution and then falls slowly to equilibrium. Beyond the end point the potential rises slowly to equilibrium. The change from a falling to a rising potential occurs at about 900 millivolts (calomel versus platinum) and can be caused by as little as 0.03 per cent ( $10^{-5}$  milliequivalents) of the equivalent amount of ceric solution. The blank appears to be zero, since results from aliquots varying by a factor of five are indistinguishable. The data of Tables V and VI support this method of standardization.<sup>13)</sup>

The primary standard (Bureau of Standards 99.95 per cent sodium oxalate) has been observed to decrease in weight of the order of 0.02 per cent when dried at 120°C for two hours. A solution containing about 10mg/g is prepared by dissolving the standard in 1N sulfuric acid. Each titration contains about 200 mg. of this solution. All dilutions and aliquots are made by weight to 0.01 per cent.

The ceric solution decreases in concentration about 0.05 per cent per month (Table VII). An atomic weight of 239.05 has been used for plutonium

13) Furman, J. Am. Chem. Soc., 50, 755 (1928).

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containing one per cent of isotope 240.<sup>14)</sup>

Precision and Accuracy

In the routine assay of Hanford material, sampling is probably the most exacting operation. Forty milligram aliquots of solution are weighed to 0.01 mg on an Ainsworth TC type analytical balance.

A critical discussion of precision and accuracy will not be given. The known contributing factors appear in the preceding sections; results appear in the tables of data.

14) Bartlett and Swinehart, LA-327, p. 24, July 11, 1945.

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TABLE I

## ROUTINE ASSAY

Sample Number	Operator	Pu Assay* (uncorrected)	Maximum Deviation	Iron Correction	Deviation** (Pu Assay)
255	D	210.81 mg/g		3.45 mg Pu/g	0.000/0
	A	212.26		3.45	
	B	211.21	0.69%		
256	A	218.58		5.05	.05
	A	218.48		4.95	
	B	218.18	.18		
257	D	203.21		4.13	.03
	D	203.14	.03	4.13	
258	D	211.33		3.52	.02
	D	211.99	.31	3.56	
259	D	213.79		3.23	.02
	D	214.65		3.19	
	B	214.48	.40		
260	D	216.72		4.59	.05
	D	216.69	.01	4.47	
261	C	209.80		3.60	.02
	C	209.45	.17	3.64	
262	D	211.99		3.01	.05
	C	212.03	.02	3.12	
263	D	205.95		5.11	.05
	C	205.96	.00	5.19	
				5.22	
264	D	209.15		4.01	.00
	D	208.57	.28	4.02	
265	B	207.90		4.99	.00
	B	207.62	.13	4.99	
266	D	207.72		4.27	.02
	A	208.01	.14	4.32	

\* All results obtained on these samples appear in this table.

\*\* Maximum deviation of the iron corrections.

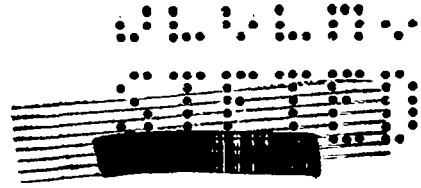


TABLE I (continued)

SPECIAL SAMPLES

Sample Number	Operator	Pu Assay* (uncorrected)	Maximum Deviation	Iron Correction	Deviation (% Pu Assay)
SSW	B	14.085 mg/ml		0.005 mgPu/ml	
	C	14.093			
	C	14.076			
	B	14.087			
	B	14.104			
	C	14.102	0.20%		
WB-1	B	100.22		.221	
	B	100.17		.229	0.01%
	B	100.13			
	B	100.11	.11		
WB-2	B	174.42		.103	
	B	174.59		.105	.00
	B	174.49			
	B	174.51	.10		

\* All results obtained on these samples appear in this table.

TABLE II

ESTIMATIONS OF THE BLANK IN 2ML OF 2N SULFURIC ACID

Iron taken	Plutonium taken	Calculated weight of 0.02044 N ceric solution	Observed weight of ceric solution	Blank (mg of ceric) solution
2.3		2.0 mg	3.7 mg	1.7 mg
8.5		7.4	8.1	0.7
2.4		2.1	3.3	1.2
5.3		4.6	5.5	0.9
6.5		5.7	6.3	0.6
3.7		3.2	3.9	0.7
6.6		5.8	6.7	0.9
1.1		1.0	1.5	0.5
	26.0	5.3	6.1	0.8
	41.9	8.6	9.5	0.9
	33.0	6.8	7.3	0.5
	47.1	9.6	10.5	0.9
	29.0	5.9	8.0	2.1
	18.5	3.8	5.5	1.7
	22.7	4.6	5.2	0.6
	21.1	4.3	4.6	0.3

Average

Average

Deviation

3.9
0.4



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TABLE III

## TITRATIONS OF IRON AND PLUTONIUM\*

## A. Iron

1. Concentration of iron solution from the weight of standard (assay 99.8%)	0.901	mg Fe/g
2. Concentration as determined by titration with ceric	0.9014	mg Fe/g
a. Regular procedure	.9005	
	.9011	
	Average	.9010
b. Syphoned directly into ceric solution	.9001	
	.9009	
c. Stirred in air for 70 minutes after separation from the amalgam	.9009	
	.9019	

## B. Plutonium

Concentration as determined by titration with ceric

a. Regular procedure	6.477	mg Pu/g
	6.487	
	6.479	
	Average	6.481
b. Syphoned directly into ceric solution	6.484	
	6.481	
c. Allowed to stand without stirring after separation from the amalgam		
10 minutes	6.483	
12	6.466	
15	6.486	
20	6.465	
25	6.464	
d. Stirred in air for 70 minutes after separation from the amalgam	6.225	

\* This data was taken according to the procedure described in LA-416, IV c. A blank of 0.001 Omg of ceric solution was used.

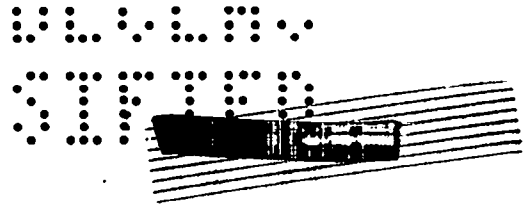


TABLE III (continued)

C. Iron and Plutonium

	Iron taken	Plutonium taken	Calculated weight* of ceric solution	Observed weight	Deviation
<u>a. Regular procedure</u>					
	.0277 mg	6.305 mg	1.3190g	1.3187g	-0.0003
	.0678	6.738	1.4429	1.4434	+ .03
	.0484	6.863	1.4516	1.4509	- .06
	.0874	6.376	1.3859	1.3844	- .11
<u>b. Syphoned directly into ceric solution</u>					
	.0241 mg	5.406	1.1313g	1.1332g	+ .17
	.0399	6.310	1.3307	1.3319	+ .09
<u>c. Allowed to stand 20 minutes without stirring after separation from the amalgam</u>					
	.0549 mg	6.204 mg	1.3221g	1.3114g	- .81
	.0432	6.381	1.3481	1.3397	- .62
<u>d. Stirred in air for 96 minutes after separation from the amalgam</u>					
	.0536 mg	6.305 mg	1.3416g	1.2377g	-7.74

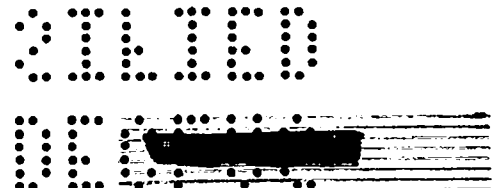
\*The calculated weights include a blank of 0.001 Omg of ceric solution and are based upon the concentrations: 0.901Omg Fe/g, 6.481mg Pu/g, 4.874mg Pu/g of ceric solution.

TABLE IV

NITRATE INTERFERENCE

Eight aliquots of sample 202, 1.0 M in nitric acid  
 Number of fumings with 150 of concentrated sulfuric acid:

<u>None</u>	<u>One</u>	<u>Two</u>	<u>Three</u>
206.0mg/g	197.93mg/g	197.88mg/g	197.92mg/g
266	197.63	197.83	198.07



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TABLE V

DIRECT AND INDIRECT STANDARDIZATIONS OF CERIC SOLUTION

A. Titer of ceric solution, direct titration of oxalate		.02040 N
		.02039 N
		.02038 N
		.02038 N
	Average	.02038 N
B. Titer of permanganate solution, direct titration of oxalate		.05888 N
		.05896 N
		.05891 N
	Average	.05892 N
C. Ratio of ferrous solution to ceric solution		.5991g/g
		.5991
		.5993
		.5998
	Average	.5994
D. Ratio of permanganate solution to ferrous solution		.5773g/g
		.5773
		.5778
	Average	.5775

(average B.) (average C.) (average D.) = 4.875mg Pu/g of ceric solution

TABLE VI

ASSAY\* OF PLUTONIUM METAL SAMPLES

#JR-1	99.97% Pu	#JR-2	100.01% Pu
	100.05		99.98
	99.94		99.99
			100.11
			100.05
Average	99.99% Pu	Average	100.03% Pu

\*These results are corrected for iron which was present in amounts between 80 and 150 ppm. (colorimetric)

\*\*Spectrographic analysis showed other determinable impurities to be very low.

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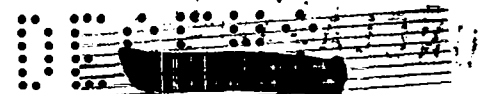



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TABLE VII

## STABILITY OF CERIC SOLUTION

Solution Number	Date	Average Titer
I	August 8	5.453 + 002mg Pu/g of ceric solution
	August 19	5.448 ± 001
	September 24	5.447 ± 002
	November 7	5.444 ± 003
	January 3	5.435 ± 002
II	September 27	5.096 + 002
	January 4	5.091 ± 001

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