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COMPARISON OF FOUR TITRIMETRIC METHODS FOR ASSAYING PLUTONIUM

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COMPARISON OF FOUR TITRIMETRIC METHODS FOR ASSAYING PLUTONIUM

by

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ABSTRACT

Four plutonium assay methods were compared by applying each to the assay of high-purity plutonium metal. These methods are the redox titration using photometric end point detection, amperometric titration, and two potentiometric titrations. No difficulties were experienced using any of the methods, but high americium concentrations were found to cause a slight effect on the amperometric titration. For lower concentrations of americium, 200 to 300 ppm, this effect was not discerned. Essentially the same assays of the high-purity plutonium metal were obtained by the four methods.

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CONTENTS

INTRODUCTION

Four plutonium assay methods (5) were compared as part of a continuing evaluation of these frequently used analyses. The methods included in this investigation were the amperometric, (6) photometric, (4) and two potentiometric (3, 7) titrations. Applicability of each method to the assay of alpha-phase plutonium metal was the basis of comparison.

This comparison was not intended to be a comprehensive evaluation of all applicable plutonium assay methods. Of the several good methods available, only those were included for which a current capability existed. Omission of a particular method from this comparison should not be construed as disapproval of the method.

The first part of this work was an intercomparison of the amperometric and the two potentiometric titration methods. This was done by assaying two solutions prepared by dissolving cleaned high-purity plutonium metal in hydrochloric acid and analyzing weighed aliquots of these solutions by each of the three methods. The metal from which the solutions were prepared had a total known impurity content less than 300 ppm (Table I). At a later date one of the potentiometric titration methods (3) was compared with the photometric titration method.(4) In this comparison, weighed pieces of plutonium metal, having the same impurities shown in Table I, were assayed by each method. No difficulties were experienced with any of the methods, and essentially the same assays of the high-purity plutonium were obtained by each.

Table I

Concentrations of Impurities in High-Purity Plutonium Metals

Elements determined spectrochemically, ppm				Elements determined spectrophotometrically, ppm		Other elements, ppm	
Li,	< 0.2	Ni,	< 10	Fe,	< 20	Am,	119
Be,	< 0.1	Cr,	< 5	U,	< 30	O,	30
Na,	< 10	B,	< 0.5	Ga,	20	C,	35
Mg,	< 10	Mn,	< 2	Ta,	< 35	F,	< 2
Ca,	< 10	Sn,	< 1	Mo,	< 1		
Al,	10	Bi,	< 1	Zr,	< 10		
La,	< 10	Co,	< 10	Th,	< 15		
Si,	< 10	Zn,	< 10	W,	44		
Pb,	< 2						
Cu,	< 2						

ANALYTICAL METHODS

Each of these methods is described in detail elsewhere,(3-7) and only the main operations are given here briefly in order to identify the methods. Any minor changes in the methods to make them compatible to our equipment and general operating philosophy are included in these brief descriptions.

Los Alamos (LA) Potentiometric Method (Zn-Hg reduction - Ce(IV) oxidation)

The main step in this method(3, 5) is the titrimetric oxidation of plutonium (III) to (IV) with cerium (IV) sulfate solution. Six-hundred mg. of cleaned plutonium metal is dissolved in 3 N to 6 N hydrochloric acid, and weighed aliquots containing approximately 25 mg. of plutonium are analyzed. Organic material and undesirable anions are removed by two evaporations with sulfuric acid. The plutonium is reduced with zinc amalgam under a carbon dioxide atmosphere, and the plutonium (III) is titrated with standard ceric sulfate solution. The end point is detected potentiometrically using a platinum and a saturated calomel electrode. Using weight burets, the relative standard deviation in determining 25 mg. of plutonium is found to be 0.06%.

Los Alamos (LA) Potentiometric Method ($HClO_4$ oxidation - Fe(II) reduction)

The fundamental step in this method is the reduction of plutonium (VI) to (IV) by iron (II) and titrimetric oxidation of the excess iron (II) with cerium (IV) sulfate.(5, 7) This method requires a larger sample (2 grams) of the plutonium metal to ensure very accurate weighing. This metal is dissolved in 3 N hydrochloric acid, and weighed aliquots each containing greater than 200 mg. of plutonium are evaporated to incipient dryness. A few drops of nitric acid and 5 to 10 ml. of 70% perchloric acid are added, and the solutions are fumed strongly to oxidize the plutonium. The fuming operation is repeated, and evaporation is continued until the final volume is 2 to 3 ml. This is cooled rapidly and immediately diluted with water to prevent formation of reduction products of perchloric acid. Sulfuric acid is added to stabilize the (IV) oxidation state of plutonium when it is formed in the titration. Then the plutonium (VI) is reduced by a slight excess of standard iron (II) solution added from a weight buret. This slight excess is back titrated with standard cerium (IV) solution. A relative standard deviation of 0.03% is obtained for this method using a sample of approximately 300 mg.

Argonne (ANL) Amperometric Method
(Ag(II) oxidation - Fe(II) reduction)

This method also is based on the titrimetric reduction of plutonium (VI) by iron (II) in a sulfate medium.(5, 6) A 600-mg. sample of the cleaned plutonium metal is dissolved in 3 N hydrochloric acid, and weighed aliquots containing 10 to 20 mg. of plutonium are converted to a sulfate medium by fuming with sulfuric acid. Then the plutonium is oxidized to the (VI) oxidation state by argentic oxide, the excess oxidant is destroyed by heating, and the plutonium (VI) is titrated with standard iron (II) solution. The end point is detected amperometrically using a rotating platinum electrode and a mercurous sulfate electrode. The relative standard deviation of this method has been found to be 0.03% in determining 10 to 20 mg. of plutonium.

Rocky Flats (RF) Photometric Method
(Ce(IV) oxidation of Pu(III)

This method is based upon the quantitative formation of plutonium (III) when the metal is dissolved in hydrochloric acid, followed by the rapid titration of this oxidation state with cerium (IV) using photometric detection of the end point. A 500-mg. sample of plutonium metal is dissolved in 6 N hydrochloric acid. One hundred ml. of 0.5 M sulfuric acid and 0.25 ml. of ferrion indicator are added, and the plutonium (III) is titrated immediately with standard cerium (IV) solution. The end point in the titration is determined using a filter photometer to detect the change in color of the indicator. A reagent blank, mostly due to the indicator, must be determined. The method as used in the comparison was essentially the same as that developed at Rocky Flats,(4) but a few minor changes made the operations more compatible to our equipment. These changes consisted of using smaller samples, ranging between 100 and 200 mg. as compared to the recommended 500 mg. Weighings of the smaller samples were made on a semimicro balance to obtain the necessary accuracy. In addition, the titrant was added from a special 18-ml. volume buret or a 12-gram capacity weight buret; the original method recommends a 50-ml. volume buret.

RESULTS AND DISCUSSION

In considering the results of the comparisons of the assay methods, it is important to realize that all data were obtained by trained chemists thoroughly familiar with the various limitations, operations requiring especial care, and other facets of the assay methods. Proper functioning and calibration of all instruments and careful standardization of reagent solutions were proved by preliminary assays of known plutonium solutions before the comparative analyses were performed. It is doubtful that the excellent results reported here would be obtained by analysts less familiar with the methods.

The data in the comparison of the two LA potentiometric titrations and the ANL amperometric titration (Table II) were obtained by three analysts during an interval of about two weeks. Each analyst used one assay method exclusively in this comparison. The results in the comparison of the RF photometric titration with the LA potentiometric titration (Zn-Hg reduction - Ce(IV) oxidation) method (Table III) were obtained by one analyst during an investigation lasting several weeks.

The assay results corroborate the reported high precision and accuracy of each method. In some cases, notably the results obtained by the RF method, the precision is better than that reported for the method.(4) This is presumed to be a consequence of application of weight burets or special volume burets to this titration. The RF method and the LA potentiometric method in which plutonium (VI) is titrated with iron (II)

Table II

Assays of High-Purity Plutonium by Three Methods

Method	No. of titrations	Solution	Av. Pu content, %	Rel. std. dev., %
Amperometric Ag(II)-Fe(II)	10	A	99.98	0.04
	10	B	99.95	0.03
Potentiometric Zn(Hg)-Ce (IV)	10	A	100.00	0.06
	10	B	99.96	0.03
Potentiometric $HClO_4$-Fe (II)	6	A	99.97	0.02
	10	B	99.96	0.03

are potentially the most accurate and precise because the large quantity of plutonium (greater than 100 mg.) assayed minimizes the effects of small errors in weighings and measurements of titrants. However, choice of method on the basis of reliability alone is extremely difficult in view of the excellent results obtained by each method. In this comparison, in which reliability is the main criterion, it must be concluded that the four methods are essentially equal.

For application to specific analyses, other factors assume importance. For example, the two methods in which iron (II) is the titrant require daily standardization and careful storage of this reagent. However, titrating with iron (II) eliminates interference caused by iron, a common impurity in plutonium. The interference of several other ions on these determinations also should be considered in view of the requirements of the specific application. Of the four methods, the LA potentiometric titration of plutonium (VI) with iron (II) probably is subject to interference by fewer metals than the other methods. For routine operations, either the RF method, if relatively pure plutonium is to be assayed, or the LA method (Zn-Hg reduction-Ce(IV) oxidation) may prove the most convenient and rapid.

Table III

Assay Data for High-Purity Plutonium Metal(1)

LA method			RF method		
Sample wt., mg.	Wt. Ce soln.,[a] g.	Percent Pu[c]	Sample wt., mg.	Vol. Ce soln.,[b] ml.	Percent Pu[c]
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

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[a] Titer is 10.254 mg. plutonium per gram of ceric solution.

[b] Titer is 10.728 mg. plutonium per ml. of ceric solution. A blank of 0.121 ml. has been subtracted from the volume of ceric solution.

[c] Percentages are based upon the calculated plutonium content of the metal and not upon the sample weight.

The effects on an assay method of a low concentration of a particular impurity may be insidious and go undetected unless an intensive investigation of the method is made. This was pointed out during a recent comparison of the LA potentiometric (Zn-Hg reduction - Ce(IV) oxidation) and the ANL amperometric methods.(2) A large number of results for high-purity plutonium accumulated over a long time gave some indication that the amperometric titration method might be biased very slightly. For this reason, every possible cause for a bias in this method was considered. The only likely reason was that the strong oxidant, argentic oxide, might oxidize the americium impurity which would then react with some of the standard iron (II) solution during the titration. If the iron (II) had been standardized against potassium dichromate, then the results for the plutonium would be slightly high, by an amount relative to the concentration of americium in the plutonium. To test this theory, the amperometric titration method was used to determine the plutonium in a solution of the high-purity metal. Then aliquots of this same solution to which small quantities of americium had been added were titrated. As shown in Table IV, the americium did cause the results to be high, but the effect was not linear and did not seem to be quantitative. In addition to these titrations, the americium solution itself was titrated. Based upon an oxidation change of two, about 25% of the americium was titrated. Although this effect becomes significant for large concentrations of americium, the usual concentrations found in plutonium (not greater than 300 ppm) would not have a significant effect on the amperometric titration. In most cases the bias is of about the same magnitude as the relative standard deviation of the titration or smaller. No other difficulties with the amperometric method have been encountered.

Table IV(2)

Effect of Americium on the Amperometric Titration of Plutonium

Am added, ppm	Number of determinations	Av. Pu found,[a] %	Standard deviation
0	6	100.00_0	0.0002
500	4	100.05_8	0.0003
1000	3	100.06_9	0.0002
2000	4	100.10_9	0.0001

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[a] Approximately 12 mg. Pu titrated in each case.

CONCLUSIONS

1. The four assay methods for plutonium included in this comparison are essentially equal in reliability for the analysis of high-purity plutonium metal.
2. High americium concentrations cause a slight effect on the amperometric titration of plutonium, but for lower concentrations (200 to 300 ppm) this effect is insignificant.
3. Difficulties were not experienced in using any of the methods in this application.
4. This comparison of methods for the assay of high-purity plutonium metal should not be considered an evaluation of the methods for any other application.

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