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Separation and Spectrophotometric Measurement
of 0.1 to 5 ppm of Zirconium in Plutonium

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Separation and Spectrophotometric Measurement
of 0.1 to 5 ppm of Zirconium in Plutonium

by

R. G. Bryan
G. R. Waterbury

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SEPARATION AND SPECTROPHOTOMETRIC MEASUREMENT
OF 0.1 TO 5 PPM OF ZIRCONIUM IN PLUTONIUM

by

R. G. Bryan and G. R. Waterbury

ABSTRACT

Zirconium in trace concentrations (0.1 to 5 ppm) in plutonium is separated and determined spectrophotometrically as the Arsenazo III complex. To separate the zirconium, it is extracted from an 8 to 10 N hydrochloric acid solution of plutonium(III) into N-phenylbenzohydroxamic acid (PBHA) in chloroform, and any traces of plutonium(IV) are washed from the organic phase with 5% ascorbic acid in 9N hydrochloric acid. The zirconium is then back-extracted into a hydrochloric-hydrofluoric acid solution which is evaporated to fumes with perchloric acid, and the zirconium-Arsenazo III complex is formed in 7.2N hydrochloric acid. At a wavelength of 665 m μ , the molar absorptivity of the complex is 120,000. Relative standard deviations calculated from 24 or more determinations each of 0.2, 0.5, 2.0, and 5.0 μ g. of zirconium added to 1-gram samples of plutonium are 43, 22, 6.2, and 2.7%, respectively. Two-gram samples of plutonium can be analyzed satisfactorily for zirconium by this method. Of 52 other elements (ions) investigated, beryllium, fluoride, germanium, hafnium, molybdenum, tantalum (niobium), titanium, and tungsten caused interference when present in 100-mg. quantities. Of these elements, only hafnium and titanium interfere when the quantity is reduced to 1 mg.

INTRODUCTION

As part of a general program to develop methods for measuring very low concentrations of impurity elements in high purity plutonium metal and alloys, Arsenazo III [1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis(azo-2)-phenylarsonic acid] was applied to the determination of zirconium. Previous work associated with a method for measuring thorium in plutonium ⁽¹⁹⁾ showed that the molar absorptivity of the zirconium-Arsenazo III complex was

of the order of 100,000, which would be adequate for the present purpose. A comparison ⁽⁷⁾ of 13 chromogenic reagents for the spectrophotometric measurement of zirconium showed that Arsenazo III provided the best sensitivity and independence of pH. However, the selectivity of this reagent is not adequate unless a quantitative separation of the zirconium is made from plutonium and also from impurity and alloying elements.

The method currently employed here for separating zirconium from plutonium is the precipitation of zirconium *p*-bromomandelate. (24) Although this separation is very selective, the solubility of the precipitate limits application of this method to separation of not less than 10 micrograms of zirconium. Many liquid-liquid extraction methods have been applied to separation of zirconium from various materials. (9, 10, 21) Extraction of zirconium into 2-thenoyltrifluoroacetone (TTA) (14, 15) is a widely used separation, but it is not very selective. Zirconium also is extracted into bis-(2-ethylhexyl) hydrogen phosphate, (2) but this reagent is not readily available. Of the methods reported, the most promising for a fast selective separation was the extraction of zirconium into *N*-phenylbenzohydroxamic acid (PBHA). (23) Earlier work with this reagent described the separation of niobium, tantalum, titanium, vanadium, and zirconium by PBHA extraction from uranium, and the spectrographic determination of these elements. This extraction was adapted to separate zirconium from plutonium, and Arsenazo III was then applied to measure the zirconium spectrophotometrically. Thus a highly sensitive and selective method for determining zirconium in plutonium was developed.

APPARATUS AND REAGENTS

Apparatus

Beakers, Teflon TFE, 50-ml. These beakers were cleaned prior to each analysis in hot nitric and hydrofluoric acid mixture and thoroughly rinsed with water to remove contamination by zirconium or other heavy metals.

Covers, Teflon TFE, 50-mm.

Extractors, fused-silica. See Fig. 1.

Hot plate, thermostatic, Fisher Autemp heater or equivalent.

Infrared heat lamp, 250-watt, hard glass.

Manifold, borosilicate glass. See Fig. 2.

Normal laboratory glassware, including beakers, pipets, syringes, and volumetric flasks.

Spectrophotometer, Beckman Model DU, with matched fused-silica cells having 1-cm. light paths.

Fig. 1. Fused-silica extractor.

Spectrophotometer, recording, Cary Model 11 MS or equivalent, with matched fused-silica cells having 1-cm. light paths.

Steam bath

Reagents

Arsenazo III, 0.1% [1, 8-dihydroxynaphthalene-3, 6-disulfonic acid-2, 7-bis(azo-2)-phenylarsonic acid], prepared by dissolving 1.0 gram of Arsenazo III in 950 ml. of water by mixing for about 12 hrs., and then diluting to 1 liter with water.

Ascorbic acid, 5%, prepared by dissolving 250 mg. of ascorbic acid in 5 ml. of 9N hydrochloric acid. This solution must be made immediately prior to use.

Ascorbic acid, 5%, PBHA-washed, prepared by dissolving 3 grams of ascorbic acid in 60 ml. of 9N hydrochloric acid in a 100-ml. volumetric flask. The solution is washed by shaking it with 10 ml. of 1.2% PBHA in CHCl_3 and allowing the

Fig. 2. Extractor manifold.

phases to separate. This solution must be made fresh each day.

p-Bromomandelic acid, Delta Chemical Works No. CO-2218 or equivalent.

Chloroform, CHCl_3 , reagent grade.

Hexone, (4-methyl-2-pentanone) redistilled.

Hydrochloric acid, 12N, reagent grade.

Hydrochloric acid, 12N, PBHA-washed, prepared by washing 12N hydrochloric acid with 1.2% PBHA in CHCl_3 .

Hydrochloric acid, 9N, prepared by diluting 375 ml. of 12N hydrochloric acid to 500 ml. with water.

Hydrochloric acid, 9N, PBHA-washed, prepared by washing 9N hydrochloric acid with 1.2% PBHA in CHCl_3 .

Hydrochloric-hydrofluoric acid, prepared by diluting 250 ml. of 12N PBHA-washed hydrochloric acid and 30 ml. of 27N hydrofluoric acid to 500 ml. with water.

Hydrofluoric acid, 27N, reagent grade.

Hydroxylamine hydrochloride, 25%, prepared by dissolving 250 grams of $\text{NH}_2\text{OH} \cdot \text{HCl}$ in 1 liter of water and washing the solution with 1.2% PBHA in CHCl_3 .

PBHA, 1.2% in chloroform, prepared by dissolving 12 grams of N-phenylbenzohydroxamic acid (Eastman Organic Chemical No. 7297 or equivalent) in 1 liter of CHCl_3 .

Perchloric acid, 12N, reagent grade.

Sulfuric acid, 36N, reagent grade.

Zirconium stock solution, 10 mg./ml., prepared by dissolving 10 grams of high-purity zirconium metal in hydrochloric and hydrofluoric acids and diluting the solution to 1 liter. This solution was standardized by precipitating the zirconium with p-bromomandelic acid and weighing the zirconium as the oxide after ignition. ⁽¹⁷⁾

Zirconium solution, 100 $\mu\text{g.}/\text{ml.}$, prepared by fuming 10 ml. of the stock solution in 30 ml. of perchloric acid, to remove the fluoride ion, and diluting to 1 liter with 9N hydrochloric acid.

Zirconium solution, 1 $\mu\text{g.}/\text{ml.}$, prepared by dilut-

ing 5 ml. of the 100 $\mu\text{g.}/\text{ml.}$ solution and 250 ml. of 12N hydrochloric acid to 500 ml. with water.

Zirconium solution, 0.1 $\mu\text{g.}/\text{ml.}$, prepared by diluting 10 ml. of 1 $\mu\text{g.}/\text{ml.}$ solution and 50 ml. of 12N hydrochloric acid to 100 ml. with water. The three zirconium solutions, 0.1, 1.0, and 100 $\mu\text{g.}/\text{ml.}$, should be made fresh every 3 to 4 weeks.

SAMPLE PREPARATION

High purity plutonium metal and alloys are received as turnings or small pieces. Inspect the sample carefully and remove extraneous material, such as lint and foreign metal chips, that may have been introduced in the sampling or machining operations. If the sample is contaminated with cutting oil, wash the metal in methyl chloroform and dry at room temperature. If the surface is oxidized and analysis of the entire sample, including the oxide, is not requested, clean the surface by filing or electropolishing. From each plutonium metal sample, take two accurately weighed portions, each not greater than 2 grams and containing less than 5 $\mu\text{g.}$ of zirconium. Duplicate determinations are made on each sample, on a solution containing a known quantity of zirconium (known solution), and on the reagent blank solution.

RECOMMENDED PROCEDURE

Caution: Health safety rules for handling plutonium must be rigidly followed, and adequate protection for the operator must be ensured by the use of suitable dryboxes and protective clothing.

- (1) Place each accurately weighed portion of the sample in a covered 50-ml. Teflon beaker and add 3 ml. PBHA-washed 12N hydrochloric acid to dissolve the sample. Then add one ml. of 25% hydroxylamine hydrochloride. (Note: All reagents used during the separation are washed with PBHA.)
- (2) Prepare the blank and known solutions in duplicate by adding 3 ml. of 9N hydrochloric acid and 1 ml. of 25% hydroxylamine hydrochloride to each of four Teflon beakers. To two of the beakers, add 2 $\mu\text{g.}$ of zirconium (2 ml. of the 1 $\mu\text{g.}/\text{ml.}$ zirconium solution) to prepare the known solutions.
- (3) Heat the samples, blanks, and known solu-

tions for 20 to 30 min. on a steam bath, and then treat each solution as described in the following steps.

(4) Add 5 ml. of PBHA in chloroform to an extraction vessel and then add the solution using 10 ml. of 12N hydrochloric acid for the transfer.

(5) Mix the phases by drawing air through the extraction vessel for 10 min., and then allow the phases to separate for 5 min. NOTE: At the start and finish of each mixing step, clear the arm of the extraction vessel by drawing either chloroform or 9N hydrochloric acid through it. During each mixing step, add chloroform to maintain the organic phase volume at 5 to 10 ml.

(6) Force the PBHA-chloroform (bottom) layer into a second extraction vessel using air pressure, and add 5 ml. of PBHA-chloroform to the aqueous phase in the first extraction vessel.

(7) Repeat step No. 5.

(8) Force the PBHA-chloroform phase into the second extraction vessel that contains the initial extract, and draw the aqueous layer, that contains the plutonium, into a container (residue bottle) for disposal of radioactive solutions.

(9) Wash the combined zirconium-PBHA-chloroform phases successively with 5 ml. each of 9N hydrochloric acid, 5% ascorbic acid, and 9N hydrochloric acid for 3 min. each. Follow each wash by a 3-min. settling period, and draw off and discard the aqueous (top) layer with a syringe pipet.

(10) Add 10 ml. of the hydrochloric-hydrofluoric acid solution to the organic phase, mix the layers for 10 min., and then allow the phases to separate for 5 min.

(11) Remove the organic phase (bottom) from the vessel with air pressure, and discard.

(12) Add 5 ml. of hexone to the vessels, mix the layers for 3 min., and then allow the phases to separate for 3 min.

(13) Force the aqueous phase (bottom) into a 50-ml. Teflon beaker containing 0.5 ml. of perchloric acid and one drop of sulfuric acid.

(14) Wash the hexone with 2 ml. of the hydrochloric-hydrofluoric acid mixture and add this aqueous

phase to the Teflon beaker.

(15) Evaporate the aqueous phase until fumes of perchloric acid are evolved, and fume until the liquid volume is reduced to one drop.

(16) Add 0.2 ml. of 5% ascorbic acid to a 5-ml. volumetric flask and transfer the solution from step No. 15 to this flask using 9N hydrochloric acid.

(17) Add 1 ml. of 0.1% Arsenazo III, dilute to 5 ml. with 9N hydrochloric acid, and wait 15 min. for full color development. NOTE: Reagents for the color development should not be washed with PBHA.

(18) Measure the absorbance of the solution in cells having 1-cm. light paths at a wavelength of 665 mμ.

(19) Compare the absorbances of the blank, A_B , and the known solutions (2 μg. of zirconium), A_K , to the absorbances shown in Table IV. If there is a significant difference, repeat the analyses using freshly prepared reagents. If there is not a significant difference, calculate the ppm of zirconium in each sample using Equation (1) and the measured absorbance, A_S , for each sample.

$$\text{Zr, ppm} = \frac{(A_S - A_B)(2 \mu\text{g. of Zr})}{(A_K - A_B)(\text{Sample wt, grams})} \quad (1)$$

EXPERIMENTAL

Spectrophotometric Measurement of Zirconium

The optimum conditions for the formation of the zirconium Arsenazo III complex were found by using various acids, various acid and Arsenazo concentrations, and various lengths of time for the color development. To determine the best acid concentration, aliquots containing 2 micrograms of zirconium were pipetted into 10-milliliter flasks, and sufficient hydrochloric, perchloric, or sulfuric acid was added to make the final acidity 1 to 10N. Then a 2-milliliter aliquot of the Arsenazo III solution was added to provide a concentration of 0.2 milligrams per milliliter, which in all of these

tests was held constant, and the absorbances were measured at regular intervals over a period of 1 hour. The maximum absorbance per microgram of zirconium was obtained when the colored complex was formed during a period of 15 minutes in 10 milliliters of 7.2N hydrochloric acid, and the minimum absorbance resulted when sulfuric acid was the solvent. The absorbance per microgram of zirconium in perchloric acid was about equal to that in hydrochloric acid.

The hydrochloric acid concentration was then held constant at 7.2N while the Arsenazo III concentration was varied from 0.5 to 3 milligrams in 10 milliliters. The maximum absorbance per microgram of zirconium was obtained when the Arsenazo III concentration was 0.2 milligrams per milliliter.

The absorbances obtained for repeated measurements of various zirconium concentrations under these controlled conditions showed that the relative standard deviation in measuring 0.2 to 5 micrograms of zirconium in the absence of plutonium is no greater than 3.0 percent (Table I). The molar absorptivity of 120,000 calculated from these data indicated that as little as 0.04 microgram per milliliter of zirconium may be measured reliably.

A wavelength of 665 millimicrons was recommended^(7, 19) for the measurement of the absorbance of the zirconium-Arsenazo III complex. Using the optimum conditions described earlier for the formation of the complex, 4- and 12-microgram quantities of zirconium were reacted with Arsenazo III, and the absorption spectra of the resulting complexes were recorded by means of a recording spectrophotometer (Fig. 3). A very sharp peak was found at 665 millimicrons, confirming the earlier reports.

Fig. 3. Absorption spectra for zirconium-Arsenazo III; 1, 4 μ g. zirconium in 10-ml. volume; 2, 12 μ g. zirconium in 10-ml. volume.

Zr Taken, μ g./ml. (a)	No. of Detn.	Av. Absn. at 665 $m\mu$	Std. Dev., μ g.	Rel. Std. Dev., %
0.04	6	0.057	0.006	3.0
0.20	6	0.271	0.020	2.0
0.40	6	0.523	0.012	0.6
0.80	6	1.040	0.032	0.8
1.00	6	1.310	0.070	1.4

(a) Total volume of 5 ml.

The range through which Beer's law was obeyed was also investigated. Zirconium concentrations of 0.2 to 1.3 micrograms per milliliter were measured under the optimum conditions for forming the complex. The results (Table II) show that Beer's law is followed at least to an absorbance of 1.770.

The various oxidation states of plutonium are known to form colored complexes with Arsenazo III, ⁽¹⁶⁾ and any plutonium that follows zirconium through the extraction separation interferes with the method. However, the absorbance per microgram of plutonium was found to be only 0.005 for plutonium(III)-Arsenazo III as compared to 0.080 for the plutonium(IV) complex. Therefore, ascorbic acid was added to the solution in which the Arsenazo III complex was formed to hold plutonium in the (III) oxidation state and thereby minimize the effect of any traces of plutonium that accompanied the zirconium.

Separation of Zirconium

Conditions for the quantitative extraction of zirconium, niobium, tantalum, titanium, and vanadium from hydrochloric acid solutions into PBHA-chloroform are adequately described by Vita. ⁽²³⁾ Zirconium extracts quantitatively from 1N or 8 to 11N hydrochloric acid into 0.5 percent PBHA-chloroform during a 5- to 10-minute contact. At hydrochloric acid concentrations from 2 to 8N, the extraction efficiency is slightly lower, with a minimum of 93 percent extraction at 5N hydrochloric acid. These results were verified here for zirconium, and a hydrochloric acid concentration from 8 to 10N was used in all further extractions. Although 5 minutes was adequate for extrac-

tion of zirconium under optimum conditions, an extraction time of 10 minutes was selected to ensure complete extraction from plutonium solutions on a routine basis.

Removal of Contamination from Extraction Reagents. Application of the extraction method to separation of zirconium, followed by spectrophotometric measurement as described previously, resulted in high absorbances for reagent blanks and solutions containing known amounts of zirconium. Contamination of the various reagents with zirconium or other heavy metals was suspected. As each of the impurities must be extractable into PBHA-chloroform to cause interference, the simplest means of purifying the reagent solutions was to wash them with the organic extractant. When this was done, high absorbances for reagent blanks and known solutions were no longer obtained. This was especially beneficial for the reagents used in large volume during the extraction. However, it was found that the 9N hydrochloric acid used to transfer the final zirconium solution into 5-milliliter flasks for color development must not be washed with PBHA. Any PBHA left in the acid destroyed the zirconium Arsenazo III complex, and extremely low absorbances resulted.

Back-Extraction of Zirconium. The lack of dependence of the zirconium extraction on the hydrochloric acid concentration precluded back-extraction into dilute hydrochloric acid and increased the difficulty of finding a suitable aqueous medium for back-extracting the zirconium and forming the zirconium Arsenazo III complex. Attempts were made first to back-extract the zirconium by reacting it with reagents that form water-soluble com-

TABLE II
Spectrophotometric Measurement of Zirconium
(Each solution in 7.2N HCl and 0.2 mg./ml. Arsenazo III)

<u>Zr Taken,</u> <u>μg./ml.</u>	<u>Absn.</u> <u>at 665 mμ</u>	<u>Absn./μg.</u>
0.2	0.271	0.136
1.0	1.310	0.131
1.1	1.465	0.133
1.2	1.620	0.135
1.3	1.770	0.136

Av. 0.134 ± 0.002

plexes. Aqueous phases consisting of Arsenazo III in 7.2N hydrochloric acid, Arsenazo III in 2N perchloric acid, or various concentrations of ethylenediaminetetraacetic acid were not effective in back-extracting the zirconium. Other reagents, such as oxalic acid, also were considered but not tried because they would have to be destroyed before the zirconium-Arsenazo III complex could be formed. The problem was solved by back-extracting the zirconium into 6N hydrochloric-1.6N hydrofluoric acid. This particular solvent was selected because tantalum and niobium, which co-extract with zirconium, (3, 12, 22) can be extracted from the hydrochloric-hydrofluoric acid solution into hexone. In these measurements 0.2 to 5.0 micrograms of zirconium were extracted into PBHA-chloroform by mixing for 10 minutes, and the organic phase was washed with an equal volume of 6N hydrochloric-1.6N hydrofluoric acid for 10 minutes. The aqueous phase was washed for 5 minutes with 10 milliliters of hexone which was then discarded. The aqueous phase was transferred to a Teflon beaker, 0.5 milliliter of 70% perchloric acid was added, and the solution was evaporated to one drop. The zirconium-Arsenazo III complex was formed and the absorbance measured as described in steps 16 through 19 in the RECOMMENDED PROCEDURE. The results were compared with the absorbances obtained for known quantities of zirconium that had not been through the separation method (Table I). The efficiency of the separation was 98 to 102 percent (Table III) for 2 to 5 micrograms of zirconium and 91 percent for 0.2 micrograms.

Elimination of Plutonium. Application of this extraction into PBHA-chloroform and back-extraction into hydrochloric-hydrofluoric acid to the separation of known quantities of zirconium from gram quantities of plutonium showed that some plutonium coextracted. When the final aqueous phases were evaporated and the zirconium-Arsenazo III color formed, high and erratic absorbances were obtained. Radiochemical analyses of the final solutions showed that they contained 5 to 10 micrograms of plutonium. As plutonium(IV) is known to extract into PBHA, (16) a reducing agent was needed to hold the plutonium in the (III) oxidation state. Several reagents, including hydroxylamine hydrochloride, hydrozine, sulfurous acid, stannous chloride, zinc, and zinc-mercury (Jones reductor), were tried unsuccessfully as holding reductants for the plutonium during the extraction. However, it was found that washing the organic extract with a 5 percent solution of ascorbic acid in 9N hydrochloric acid removed the small quantities of co-extracted plutonium but not the zirconium. Incorporation into the method of the ascorbic acid wash of the PBHA-chloroform layer eliminated the high and erratic absorbances. However, the practice of adding ascorbic acid to the final color solution was continued to ensure that the effect of plutonium was minimized.

RELIABILITY

The reliability of this separation and spectrophotometric method was found by determining 0.2 to 5.0 micrograms of zirconium in solutions that also contained 1.0 gram of plutonium. These

TABLE III
Zirconium Recovered by Back-Extraction
From PBHA Into Hydrochloric-Hydrofluoric Acids

Zr Taken, μg.	No. of Detn.	Av. Absn. (Following Separation)	Zr Found, %
0.0	18	0.012	-
0.2	14	0.064	91
2.0	5	0.535	100
4.0	5	1.074	102
5.0	15	1.291	98

results were compared to values obtained for equal quantities of zirconium in solutions that did not contain plutonium. A minimum of 24 determinations at each of five zirconium concentration levels in plutonium showed that the standard deviations were about 0.1 microgram for the quantities of zirconium measured. Therefore, the relative standard deviations were 6.2 and 2.7 percent, respectively, in measuring 2 and 5 parts per million of zirconium, but increased to 22 and 43 percent for the submicrogram quantities (Table IV). In the absence of plutonium the method is more precise. The relative standard deviation did not exceed 3.0 percent in measuring 0.2 to 5.0 micrograms of zirconium.

The effects of 52 other ions on the method were determined by adding 100 milligrams of the ion being tested and 1 gram of plutonium to 2 micrograms of zirconium and then analyzing for the zirconium. Of these ions, beryllium, fluoride, germanium, hafnium, molybdenum, tantalum (niobium), titanium, and tungsten caused an error greater than 5 percent in the results for zirconium (Table V). Then smaller quantities of the interfering ions were tested in a similar manner. Ten-milligram amounts of beryllium, germanium, and molybdenum, or 1 milligram amounts of tantalum (niobium), and tungsten did not cause an error in the zirconium found. Germanium was

reported to be extracted by PBHA;⁽¹¹⁾ however, neither germanium nor beryllium interfered when 10-milligram quantities were present. Molybdenum formed a precipitate which mechanically interfered with the separation of the phases. Tantalum and niobium reportedly extract into PBHA-chloroform,^(3, 12, 13, 20, 22, 23) and each was expected to back-extract into the hydrochloric-hydrofluoric acid mixture and then be washed out by hexone. However, when large quantities of tantalum (10 or 100 milligrams) were present, tantalum oxide precipitated and was carried mechanically through the separation as a solid. This interfered with the color formation. Titanium⁽²³⁾ and tungsten,⁽⁸⁾ also extracted into PBHA-chloroform and back-extracted into hydrochloric-hydrofluoric acid. However, these elements do not cause interference when present in approximately one-milligram quantities. Hafnium was tested by adding 2- and 4-microgram quantities to solutions containing 1 gram of plutonium and then analyzing the plutonium for zirconium. As was expected, hafnium can be quantitatively measured by this method. The absorbance of the hafnium after separation from plutonium indicated a molar absorptivity of 113,000 for the hafnium-Arsenazo III complex. However, hafnium is a rare impurity in plutonium and its alloys, and it is not expected to be a problem.

TABLE IV
Determination of Zirconium Following Separation Using PBHA

Zr Taken, μg.	Pu Taken, grams	No. of Detn.	Av. Absn. at 665 mμ	Std. Dev., μg.	Rel Std. Dev., %	Zr Found, %
0.0	0.0	18	0.012	0.023	-	-
0.2	0.0	14	0.064	0.006	3.0	91
2.0	0.0	5	0.535	0.042	2.1	100
4.0	0.0	5	1.074	0.085	2.1	102
5.0	0.0	15	1.291	0.130	2.6	98
0.0	1.0	55	0.051	0.088	-	-
0.2	1.0	28	0.106	0.086	43	96
0.5	1.0	26	0.191	0.109	22	103
2.0	1.0	36	0.583	0.124	6.2	102
5.0	1.0	24	1.406	0.135	2.7	103

Nitric and hydrofluoric acid interfere in the procedure when they are present in the initial solution. Nitric acid interferes if greater than 0.25 milliliters is present when the plutonium is first extracted. The interference apparently is a result of the oxidation of the PBHA by the nitric acid. Hydrofluoric acid, in greater than 0.1-milliliter quantities, interferes by precipitating the plutonium which mechanically follows through the separation and gives high results. Either acid can be removed by adding perchloric acid, evaporating the solution to dryness, and redissolving the residue in hydrochloric acid.

Vanadium, chromium, and iron extract into the PBHA (4, 5, 18, 23) forming highly colored complexes. The iron is washed out by the 9N hydrochloric acid. Neither vanadium nor chromium are

back-extracted by the hydrochloric-hydrofluoric acid mixture, and, therefore, do not interfere. Several elements including gallium, indium, lanthanum, lead, thallium, and tin are extracted into PBHA at lower acid concentrations. (1, 6, 11) However, these elements did not interfere, and therefore were probably not extracted at the higher acidity.

In order to lower the detection limit of the method, the effects of larger amounts of plutonium on the separation were determined. Five grams of plutonium precipitated as the chloride and mechanically prevented separation of the phases. Three grams of plutonium did not cause obvious difficulties in the separation, but the results obtained for the blanks and standards were erratic. However, 2 grams of plutonium did not have a deleterious effect. The reagent blanks were small, and

TABLE V
Effects of Various Ions on the Determination of Zirconium in Plutonium
(1.0 gram of plutonium and 2 μ g. of zirconium taken in each case)

Quantity of Element (ion) Added, mg.	Noninterfering Elements(ions)	Interfering Elements(ions) (a)
245 (0.25 ml. 8M HNO_3)	NO_3^-	
100	Ag, Al, Au, Ba, Bi, Ca, Cd, Ce, ClO_4^- , Co, Cr, Cu Cs, Fe, Ga, Hg, In, K, La, Li, Mg, Mn, Na, NH_4^+ , Ni, Pb, Pd, Pt, Rb, Ru, Sb, Sc, Si, Sn, SO_4^{2-} , Sr, Te, Th, Tl, U, V, Y, Zn	Be, F^- , Ge, Hf, Mo, Ta(Nb), Ti, W
60 (0.1 ml. 50% HF)	F^-	
10	Be, Ge, Mo	Hf, Ta(Nb), Ti, W
1	Ta(Nb), W	Hf, Ti
0.9	Ti	Hf

(a) An element was considered to interfere if the Zr found deviated by more than 5% from the known value.

96 to 105 percent of the zirconium was recovered (Table VI) at the 0.1- to 2-parts per million concentration level.

The method is sufficiently reliable and sensitive for measuring zirconium in high purity plutonium as well as in most of the plutonium alloys now being produced.

TABLE VI
Effect of Two Grams of Plutonium on the
Determination of Zirconium

Zr Taken, <u>μg.</u>	Absorbance at 665 mμ	Zr Found, %
0.0	0.062	-
0.2	0.120	105
2.0	0.596	100
4.0	1.086	96

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