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Spectrophotometric Determination of Microgram Amounts of Thorium in Plutonium

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Spectrophotometric Determination of Microgram Amounts of Thorium in Plutonium

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ABSTRACT

Thorium when present in the concentration range of 15 to 140 ppm in plutonium-containing materials is measured spectrophotometrically as the thorium-thorin complex. This measurement is made following separation of thorium by precipitation as thorium fluoride, with lanthanum fluoride carrier, while plutonium is oxidized to the fluoride-soluble (VI) oxidation state. The molar absorptivity of the thorium-thorin complex is 15,600 at 545 mμ. The relative standard deviations in determining 5 and 17 μg. (10 and 34 ppm) of thorium are 11 and 4%, respectively. In the range of 33 to 73 μg. (66 to 146 ppm) of thorium, the relative standard deviation is not greater than 1.8%. The average for the thorium found in 91 determinations of 5 to 73 μg. of thorium is 99 ± 1%.

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INTRODUCTION

Recent improvements in the production of high-purity plutonium[3] have necessitated the development of a method for the measurement of microgram quantities of thorium in plutonium-containing materials. Previous investigators[1] described a method for the determination of 0.01 to 0.8 percent of thorium in plutonium-thorium alloys, but this method is not sufficiently sensitive to apply to the determination of the low concentrations of thorium found in plutonium metals of recent production. One approach to improving the sensitivity of the method was the use of larger samples, but this change involved several modifications in the method. In the previous work, samples that weighed not more than 100 milligrams were dissolved in 70 percent perchloric acid, and the solution was evaporated to strong fumes to oxidize the plutonium to the (VI) oxidation state. The reaction between plutonium metal and 70 percent perchloric acid is very rapid, and larger samples may react violently. Therefore, the 500-milligram samples analyzed in the present method are dissolved in hydrochloric acid; then perchloric acid is added and the solution evaporated to fumes to remove all chloride ions which would interfere in subsequent operations in the method. The thorium is then precipitated by adding hydrofluoric acid, and the plutonium remains in solution as the fluoride-soluble plutonium (VI). Early experiments with 500-milligram samples showed that the fuming perchloric acid oxidation was not satisfactory. Apparently some reducing substances in the hydrofluoric acid, added to precipitate the thorium, caused some of the plutonium (VI) to be reduced to the fluoride-insoluble (IV) oxidation state. To avoid this, an extra oxidation utilizing peroxydisulfate and silver ions was

included to ensure complete oxidation of the plutonium and to provide a holding oxidant during the precipitation of thorium. Following the separation, the fluoride precipitate is dissolved in fuming perchloric acid, and the thorium is reacted with thorin, o-(2-hydroxy-3, 6-disulfo-1-naphthylazo) benzenearsonic acid, at a pH in the range of 0.3 to 1.0.[4] This report describes the modified method and the experimental work done in proving the reliability of the method in measuring 15 to 140 parts per million of thorium in plutonium.

SAMPLING

Samples of plutonium metal, salts, or alloys are usually received as turnings, powders, or small pieces. The samples are carefully inspected and any extraneous material, such as lint or foreign metal chips that may have been introduced in the sampling or machining operations, is removed. If a metal sample is contaminated with cutting oil, the turnings are washed with Vythene (methyl chloroform) or trichloroethylene and dried in air at room temperature. Hygroscopic plutonium compounds are protected from atmospheric moisture during sampling. Plutonium-containing solutions, generally in nitric or hydrochloric acid, are carefully examined for solid material, and solutions containing residues are rejected. Metal or solution aliquots containing not greater than 500 milligrams of plutonium are analyzed. However, the thorium content should not exceed 70 micrograms.

APPARATUS AND REAGENTS

Apparatus

Balance, analytical, Ainsworth, model BCT or equivalent.

Beakers, 20-ml., borosilicate glass.

Centrifuge, International Clinical Model, with head for 15-ml. centrifuge tubes, and a head for 40-ml. centrifuge tubes.

Centrifuge tubes, graduated, 12-ml. and 40-ml., heavy duty borosilicate glass. The 12-ml. tubes should be calibrated at the 0.5-ml. mark.

Dish, platinum, 30-ml.

Flasks, volumetric, 10-ml., borosilicate glass.

Heat lamps, infra-red, Pyrex, red-end, 250-W.

Heating apparatus, aluminum. A cylindrical aluminum block approximately 15 cm. high and 15 cm. in diameter was drilled to provide suitable sized holes, about 4-1/2 in. deep, to hold sixteen 12-ml. centrifuge tubes and a thermometer. The block was heated with an electric hot plate that is 4 in. in diameter. A shallow circular depression was milled in the bottom of the block to leave a lip that fitted around the hot plate surface. The block was wrapped with asbestos tape.

Hot plate, electric, 4-in. diameter.

Pipet, Mohr, 1-ml., with 1/100-ml. subdivision marks.

Pipet, 1-ml., polypropylene.

Pipet, transfer, various sizes, borosilicate glass.

Rack, polyethylene, for the support of the 12-ml. centrifuge tubes.

Rod, platinum, stirring, 160- x 1-mm.

Spatula, porcelain, with spoon of a size that will hold approximately 1 gram of ammonium peroxydisulfate.

Spectrophotometer, Beckman, model DU, with a set of four matched fused-silica cells that have 1-cm. light paths.

Steam bath, stainless steel, 15- x 8- x 3-in.

Timer, interval.

Vacuum transfer device (See Figure 1.)

Reagents

Acid hydrochloric, 12 M (specific gravity 1.19), reagent grade.

Acid hydrofluoric, 48%, reagent grade.

Acid hydrofluoric, 1 M; 3.7 ml. of 48% hydrofluoric acid were diluted with distilled water to 100 ml. and stored in a polyethylene wash bottle.

Acid nitric, 15.6 M (specific gravity 1.42 to 1.50), reagent grade.

Acid perchloric, 70%, reagent grade.

Acid perchloric, 0.1 M; 8 ml. of 70% perchloric acid were diluted to 1 liter with water.

Acid sulfuric, 18 M (specific gravity approximately 1.84), reagent grade.

Acid sulfuric, 0.5 M; 14 ml. of 18 M sulfuric acid were diluted to 500 ml. with water and stored in a polyethylene wash bottle.

Ammonium peroxydisulfate, reagent grade crystals.

Hydroxylamine hydrochloride solution, 25% aqueous solution.

Lanthanum nitrate solution, 10 mg. of lanthanum per ml.; 3.12 grams of $La(NO_3)_3 \cdot 6H_2O$, reagent grade, were dissolved in distilled water, diluted to 100 ml., and stored in a dropping bottle.

Plutonium solution, 250 mg. of plutonium per ml.; 25 grams of high-purity plutonium metal were dissolved in 12 M hydrochloric acid and diluted to 100 ml. with 25 ml. of 12 M hydrochloric acid and water. The plutonium used in this work contained 2.4 ppm of thorium and not greater than 200 ppm total known impurities.

Silver nitrate solution, 0.25%, aqueous, stored in a low-actinic glass bottle.

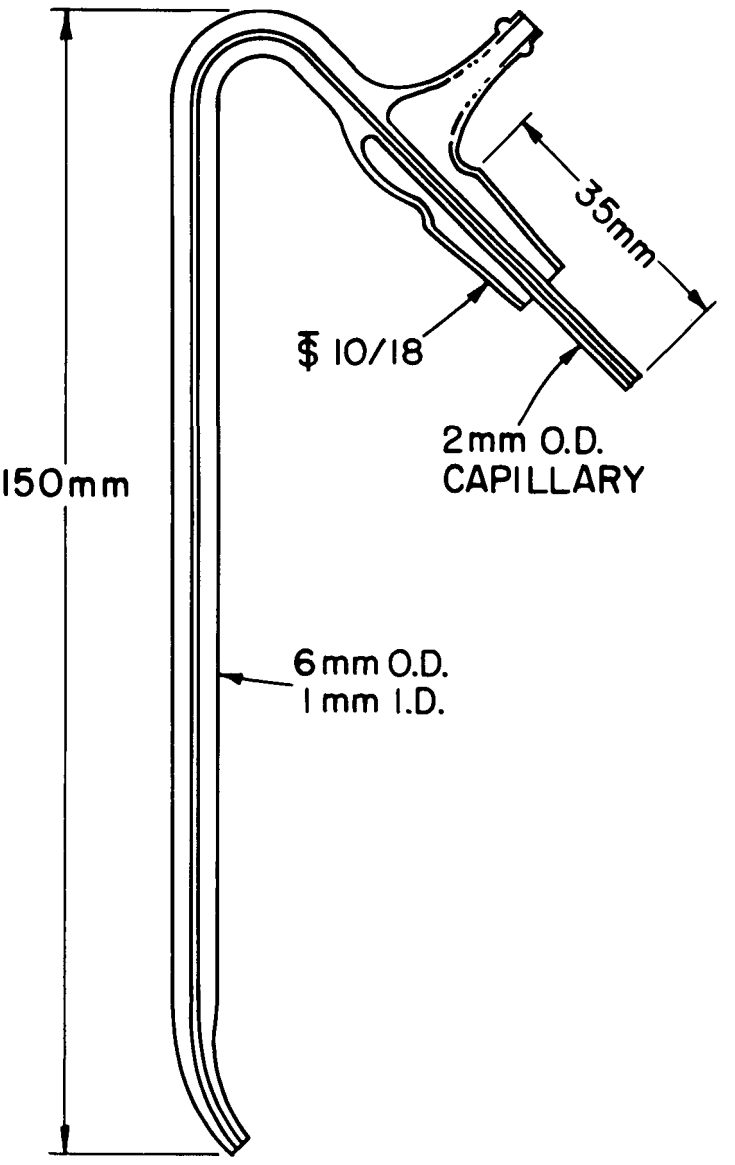

Figure 1. Vacuum transfer device.

Thorin solution, 0.1%; 1.000 gram of the sodium salt of o-(2-hydroxy-3, 6-disulfo-1-naphthylazo) benzenearsonic acid was dissolved in distilled water and diluted to 1 liter.

Thorium stock solution, 2 mg. of thorium per ml.; 2 grams of high-purity thorium metal were accurately weighed, dissolved in hydrochloric and perchloric acids, and diluted to 1 liter with 0.1 M perchloric acid. If high-purity thorium metal is not available, then reagent grade $Th(NO_3)_4 \cdot 4H_2O$ may be used to make the stock solution, which should be analyzed for thorium gravimetrically.[2]

Thorium solution, 20 μg. of thorium per ml.; an accurately pipetted, 2.00-ml. aliquot of the thorium stock solution was diluted to 200 ml. with 0.1 M perchloric acid.

RECOMMENDED PROCEDURE

For plutonium metal, alloy, or salt samples an accurately weighed 500-mg. portion was dissolved cautiously in a 40-ml. centrifuge tube with a watch-glass cover by dropwise addition of 12 M hydrochloric acid and water. The watch-glass cover and walls of the tube were washed with distilled water, and the solution was centrifuged for 5 min. and inspected to determine if the dissolution was complete. If a residue was not found, the solution was transferred to a 20-ml. beaker. If a residue was present, the supernatant solution was decanted into a 20-ml. beaker, and the residue was transferred to a 30-ml. platinum dish. The hydrochloric acid was evaporated, and the residue was fumed with 1 ml. each of hydrofluoric, nitric, and sulfuric acids using an infra-red heater and a hot plate. The dish was cooled, the residue dissolved in a few ml. of water, and this solution combined with the supernatant solution in the 20-ml. beaker. Samples received in solution form were carefully examined and rejected if insoluble material was visible. If a residue was not found, an aliquot containing not greater than 500 mg. of plutonium or 70 μg. of thorium was transferred to a 20-ml. beaker. Duplicate analyses of each sample were performed.

Duplicate determinations were made of reagent blanks, starting with 1 ml. of 12 M hydrochloric acid, and of "known" solutions, starting with 3-ml. (60 μg.) aliquots of the thorium solution. The thorium and reagent blank solutions were processed with the samples.

To each beaker were added 1 ml. of 15.6 M nitric acid and 2 ml. of 70% perchloric acid. The solutions were evaporated on the steam bath to a volume of approximately 2 ml. and then on a hot plate under infra-red heaters to near dryness. The beakers were cooled, and the residues

were dissolved in 2 ml. of 0.5 M sulfuric acid dispensed from the polyethylene wash bottle. The solutions were transferred quantitatively to 12-ml. centrifuge tubes using three 2-ml. rinses of 0.5 M sulfuric acid to make the transfer. To each tube were added 5 drops of lanthanum nitrate solution, 0.1 ml. of 0.25% silver nitrate solution, and one scoop (1 gram) of ammonium peroxydisulfate. The tubes were heated in a steam bath for 15 min. and cooled, and 1 ml. of 48% hydrofluoric acid was added from a polypropylene pipet directly to each solution without allowing the acid to contact the wall of the tube. The mixtures were thoroughly stirred with the platinum stirring rod, and the rod was rinsed with 1 M hydrofluoric acid after each stirring. The precipitates were allowed to settle for 5 min., then the tubes were centrifuged for 5 min. The supernatant solutions containing the fluoride-soluble plutonium (VI) were drawn off by suction through a fine-tipped polyethylene tube into a plutonium residue bottle. The centrifuge tubes were inverted on a tissue for 2 or 3 min., and any solution that drained down the inner wall of the tubes was sucked into the residue bottle.

The precipitates were stirred with 3 ml. of 1 M hydrofluoric acid, using the platinum rod, and the rod was rinsed with the acid after each stirring. Then the tubes were centrifuged and the supernatant solutions removed as described above. One ml. of 70% perchloric acid was added to each tube which was then heated to 220° C. for 30 min. in the aluminum heating apparatus. The tubes were cooled, and 70% perchloric acid was added to adjust the volume in each tube to 0.5 ml. Using the vacuum transfer device and three 2-ml. water rinses, the solutions were transferred to 10-ml. volumetric flasks. Reference solutions were prepared by adding 6 ml. of water and 0.5 ml. of 70% perchloric acid to each of two 10-ml. volumetric flasks. To each reference, sample, blank, and "known" (60 μg. of thorium) solution, 0.5 ml. of 25% hydroxylamine hydrochloride solution was added, and the solutions were heated on the steam bath for 30 min. Then the flasks were allowed to cool to room temperature, 1.00 ml. of 0.1% thorin solution was added, and each flask was diluted to volume with distilled water. The flasks were stoppered and shaken to mix the solutions.

Using a Beckman DU spectrophotometer and fused silica cells having 1-cm. light path lengths, the absorbances were measured versus the reference solution at a wavelength of 545 mμ. The average absorbances, A_b, of the two blank solutions; A_k, of the two known solutions; and A_s, of each sample were used in Equation 1 to calculate the concentration of thorium in ppm.

$$\text{Th, ppm} = \frac{(A_k - A_b)(A_s - A_b)}{(\mu\text{g. of Th})(\text{Sample wt., grams})} \qquad (1)$$

where μg. of Th is approximately 60.

RELIABILITY

The reliability of the method was established by repeated analysis of solutions that contained known thorium concentrations and 500 milligrams of plutonium. These solutions were prepared by adding from 3.8 to 72 micrograms of thorium to 2-milliliter aliquots of the plutonium solution and analyzing these solutions according to the recommended procedure. In addition, nine aliquots of the plutonium solution to which thorium was not added were analyzed. The results of these determinations (Table I) showed that 1.2 ± 0.6 micrograms of thorium were added in each 500 milligrams of plutonium, and that the relative standard deviations of the method for measuring 5 and 17 micrograms of thorium were 11 and 4 percent, respectively. In the range of 33 to 73 micrograms of thorium, the relative standard deviation was less than 2 percent. The average value for the thorium found in 91 measurements of 5 to 73 micrograms of thorium was 99 ± 1 percent. These data also show that the method is quite reliable for the measurement of 34 to 146 parts per million of thorium, and that 10 parts per million of thorium may be measured with a standard deviation of 1 part per million.

The absorbance of the thorium-thorin complex is a linear function of the thorium concentration in the range of 0 to 73 micrograms of thorium per 10 milliliters of solution. The molar absorptivity of the colored complex is 15,600.

Table I

Analytical Results for the Determination of Thorium
(500 mg. of plutonium in each solution)

Number of Determinations	Th Added, μg.	Total Th, μg.	Th Found, μg.	Th Found, %	Std. Dev., μg.	Rel. Std. Dev., %
9	0.0	1.2*	1.2		0.6	50
14	3.8	5.0	4.9	98	0.5	11
14	16.0	17.2	17.1	99	0.7	4.0
14	32.0	33.2	33.1	100	0.6	1.7
14	48.0	49.2	49.4	100	0.8	1.7
21	64.0	65.2	64.8	99	1.2	1.8
14	72.0	73.2	72.2	99	1.3	1.7

*1.2 μg. of thorium present in 500 mg. of plutonium

The applicability of this method to the measurement of greater than 73 micrograms of thorium was investigated by analyzing a series of solutions containing 80 or 100 micrograms of thorium. The results of these analyses showed that the method has a slight negative bias in measuring 80 micrograms of thorium and that this bias increases as the quantity of thorium increases. Throughout the recommended range of the method, 15 to 140 parts per million of thorium in 500-milligram samples, there is a linear relationship between absorbance and micrograms of thorium.

An investigation of the effects of other metal ions on this method was not undertaken because this had been done in previous work.[1,4] However, it is obvious that metals which coprecipitate with thorium fluoride and also form colored compounds with thorin at pH 0.3 to 1.0 will interfere. Most anions, except phosphate, that may cause interference are volatilized by the initial fuming with perchloric acid. The method has

been applied to the analysis of microgram amounts of thorium in high-purity plutonium metal; plutonium-iron and plutonium-gallium alloys; inorganic solutions of plutonium; and chlorides, fluorides, and oxides of plutonium.

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