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Separation and Spectrophotometric Measurement of 0.5 to 10 Parts per Million of Thorium in Plutonium

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Separation and Spectrophotometric Measurement of 0.5 to 10 Parts per Million of Thorium in Plutonium

by

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ABSTRACT

Trace concentrations (0.5 to 10 ppm) of thorium in plutonium are measured spectrophotometrically as the Arsenazo III complex, following separation by a two-step precipitation-anion exchange resin method. In the first separation step, the plutonium is oxidized to the (VI) oxidation state in fuming perchloric acid, and the thorium, with lanthanum carrier, is precipitated as the fluoride while the plutonium (VI) remains in solution. In the second step, the precipitate is dissolved in 7.8 N nitric acid and passed through an anion exchange resin column which adsorbs only the thorium and remaining traces of plutonium. The thorium is eluted selectively with 12 N hydrochloric acid, and the thorium-Arsenazo III complex is formed in 4 N perchloric acid. At a wavelength of 665 mμ, the molar absorptivity of the complex is 113,000. Relative standard deviations calculated from 12 or more determinations each of 0.5, 2, 3, 5, and 10 μg. of thorium added to 1-gram samples of plutonium are 4.7, 3.7, 3.9, 2.3, and 2.2%, respectively. Of 45 other elements investigated, only aluminum, antimony, calcium, lanthanum, molybdenum, tin, and tungsten cause interference when present in 100-mg. quantities. Of these interfering elements, only antimony interfers when the quantity is reduced to 10 mg.

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INTRODUCTION

As part of a general program to develop methods which will be capable of measuring lower concentration levels of impurity elements in plutonium, the application of the color-forming reagent Arsenazo III [1, 8-dihydroxynaphthalene-3, 6-disulfonic acid-2, 7-bis(azo-2)-phenylarsonic acid] to the spectrophotometric measurement of thorium was investigated. Formation of intensely colored complexes that contain Arsenazo III and thorium, zirconium, rare earths, plutonium, or several other metals have been reported.[3, 5, 7, 8, 14, 16-18, 21, 24, 25, 27, 28] This nonselectivity of Arsenazo III makes separation of thorium from interfering metals necessary. The intended application required quantitative separation of submicrogram quantities of thorium from gram amounts of plutonium that also contained trace concentrations of several of the interfering metals. A large number of separation methods have appeared in the literature.[4, 6, 9, 11, 12, 20, 22, 23, 26] Various solvent extraction[13, 19] and ion exchange resin[1] methods were investigated, but a simple one-step separation was not found.

In an existing method applicable to the separation of 5 to 80 micrograms of thorium from 0.5 gram of plutonium,[15] the thorium is coprecipitated with lanthanum carrier as the insoluble fluorides while plutonium is oxidized to the fluoride-soluble (VI) oxidation state. Although this separation is satisfactory for the less-sensitive measurement using Thoron as the color-forming reagent, the contamination of the separated thorium with milligram amounts of lanthanum carrier and traces of unseparated plutonium makes this separation wholly inadequate when

Arsenazo III is the color-forming reagent. However, thorium is not lost during the coprecipitation, and this separation method could serve as a first step to eliminate most of the plutonium and to reduce the sample essentially to 10 milligrams of lanthanum contaminated with the small quantities of thorium and plutonium. Then the thorium could be separated more readily using exchange resin or liquid-liquid extraction techniques. By following this approach a two-step separation was developed in which the thorium is coprecipitated with lanthanum as the fluorides and then separated from lanthanum and trace impurities using anion exchange resin. Coupling this separation to the spectrophotometric measurement as thorium-Arsenazo III led to a reliable method applicable to measuring 0.5 to 10 parts per million of thorium in plutonium.

During the preparation of this manuscript, another two-step method for separating 2 to 80 micrograms of thorium from plutonium, neptunium, and uranium was published.[10] In this method, plutonium (IV) is adsorbed on anion exchange resin from 4 N hydrochloric acid, and the thorium is collected in the wash solution. A trioctylphosphine oxide extraction completes the separation, and the thorium is measured spectrophotometrically using Thoron as the color-forming reagent. This separation method offers no advantage over the coprecipitation-anion exchange resin separation and requires many operations. The method described in this report is more widely applicable to plutonium alloys containing up to 10 percent of other elements as investigations showed no interference from 38 elements at the 10 percent concentration level. In addition, Arsenazo III forms a more highly colored complex with thorium than Thoron does, and better sensitivity is obtained using the method described here.

APPARATUS AND REAGENTS

Apparatus

Centrifuge, International, clinical model.

Hot plate, Thermostatic, Fisher Autemp heater or equivalent.

Infrared heat lamp, 250-watt, hard glass.

Normal laboratory glassware, including beakers, volumetric flasks, pipets, and centrifuge cones.
Note: All glassware, including beakers and pipets, was cleaned before each set of analyses in hot nitric acid and thoroughly rinsed with water to avoid contamination by thorium or any other heavy metal.

Resin columns, borosilicate glass. These columns were made by sealing a 9-cm. piece of 6-mm. i.d. tubing to a 9-cm. piece of 10-mm. i.d. tubing, and drawing out the end of the smaller tubing to a blunt fine tip. The small opening was plugged with glass wool and filled to a depth of 8.5 cm. with equilibrated Dowex 1 x 2 anion exchange resin.

Sand bath, half-fill 20-ml. beakers with fine white sand.

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

Steam bath.

Stirring rod, platinum.

Reagents

Arsenazo III, 0.05%, [1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis(azo-2)-phenylarsonic acid], prepared by dissolving 0.5 gram of Arsenazo III in 950 ml. of water, filtering, and diluting the solution to one liter with water. (See EXPERIMENTAL for method of preparing this reagent).

Hydrochloric acid, 12 N, reagent grade.

Hydrofluoric acid, 1 N, prepared by diluting 7.4 ml. of 27 N hydrofluoric acid to 200 ml. with water.

Hydrofluoric acid, 27 N, reagent grade.

Hydroxylamine hydrochloride, 25%, prepared by dissolving 250 grams of $NH_2OH.HCl$ in one liter of water.

Lanthanum carrier solution, 10 mg./ml., prepared by dissolving 23.4 grams of lanthanum nitrate, $La(NO_3)_3$, in 15 ml. of 7.8 N nitric acid and passing this solution through a column containing equilibrated resin as described under Apparatus. The column was washed with four 30-ml. portions of 7.8 N nitric acid, and the eluent solution was diluted to one liter with water.

Nitric acid, 15.6 N, reagent grade.

Nitric acid, 7.8 N, prepared by diluting one liter of 15.6 N nitric acid to 2 liters with water.

Perchloric acid, 12 N, reagent grade.

Perchloric acid, 1 N and 5 N, prepared by diluting 41.8 ml. and 208 ml., respectively, of 12 N perchloric acid to 500 ml. with water.

Resin, Dowex 1 x 2, 100 to 200 mesh. The chloride form of the resin was washed with one liter of 12 N hydrochloric acid followed by one liter of water. The resin was then washed with 15.6 N nitric acid until small portions of the wash solution remained clear when silver ion was added. The chloride-free resin was washed with one liter of 7.8 N nitric acid and air dried in a Buchner funnel. The dried resin was then stored until needed.

Sulfuric acid, 36 N, reagent grade.

Sulfuric acid, 1 N, prepared by adding 14 ml. of 36 N sulfuric acid to 300 ml. of water, and diluting to 500 ml. with water.

Thorium stock solution, 2 mg./ml., prepared by dissolving 2 grams of high purity thorium metal in hydrochloric and perchloric acids, and diluting to 1 liter with 1 N perchloric acid. The metal used in this work was obtained from Metal Hydrides Co., Beverly, Mass., and contained less than 70 ppm total detected metal impurities.

Thorium solution, 100 μg./ml., prepared by diluting 5 ml. of the thorium stock solution to 100 ml. with 1 N perchloric acid.

Thorium solution, 1 μg./ml., prepared by diluting 5 ml. of 100 μg./ml. thorium solution to 500 ml. with 1 N perchloric acid.

Thorium solution, 0.25 μg./ml., prepared by diluting 25 ml. of 1 μg./ml. thorium solution to 100 ml. with 1 N perchloric acid.

RECOMMENDED PROCEDURE

Duplicate determinations are made on each sample, on a solution that contains a known quantity of thorium (known solution), and on the reagent blank solution. The reagent blank and known solutions are prepared by adding 3 ml. of 12 N hydrochloric acid and a few drops of 15.6 N nitric acid to each of four 40-ml. centrifuge cones. To two of the cones, 5 μg. of thorium (5 ml. of the solution containing 1 μg./ml. of thorium) are added. The other two solutions are the reagent blanks.

From each plutonium metal sample, two accurately weighed portions, each not greater than 1 gram and containing less than 10 μg. of thorium, are taken, placed in 40-ml. centrifuge cones, and dissolved in 12 N hydrochloric acid. A few drops of nitric acid are added to oxidize the plutonium to the (IV) state. Each solution is transferred to a 20-ml. beaker, 2.5 ml. of 12 N perchloric acid is added, and the solution is evaporated to fumes. The beakers containing plutonium samples are covered with watch glasses and heated under a heat lamp until a deep red color indicates that the plutonium is oxidized to the (VI) oxidation state. Each solution, including the reagent blank and known solution, is transferred with 1 N sulfuric acid to a 40-ml. centrifuge cone to which 10 mg. of lanthanum (1 ml. lanthanum nitrate solution) has been added, and then 2.5 ml. of 27 N hydrofluoric acid are added. The solutions are stirred with a platinum rod and centrifuged for 5 min. Using suction, the supernatant solutions are withdrawn into a container for disposal of radioactive solutions (residue bottle).

The precipitates are washed with 1 N hydrofluoric acid, the solutions centrifuged, and the wash solutions discarded. To each residue, 1/2 ml. of 12 N perchloric acid is added, and the cone is placed in a sand bath and heated to 225 to 275° C. for a few minutes until the precipitate is loosened or dissolved. The contents of the cone are transferred to a 10-ml. beaker and evaporated to dryness. The residue is redissolved in 5 ml. of 7.8 N nitric acid containing 1 drop of 30% hydrogen peroxide and heated on the steam bath for 30 min. (If plutonium can be seen after the first separation, add enough equilibrated resin to the samples to adsorb the plutonium.) The solution in the beaker is diluted to 5 ml. with water and transferred to an anion exchange resin column. The column is washed with three 5-ml. portions of warm 7.8 N nitric acid, and then the thorium is eluted with 10 ml. of 12 N hydrochloric acid into a 10-ml. beaker. The eluate solution is evaporated slowly to dryness, and a few drops of 12 N perchloric acid are added and then fumed off.

The residue is dissolved in 5 N perchloric acid and transferred to a 5-ml. volumetric flask containing 1 drop of 25% hydroxylamine hydrochloride solution. One ml. of 0.05% Arsenazo III solution is added to each flask containing a reagent blank, standard, or sample, and also to each of two other 5-ml. flasks that contain only 4 ml. of 5 N perchloric acid to prepare two reference solutions. Each flask is diluted to the mark with 5 N perchloric acid and shaken immediately prior to measuring the absorbance at a wavelength of 665 mμ.

The absorbances of the blanks, A_B, and known solutions containing 5 μg. of thorium, A_K, are compared with the absorbances shown in Table I. If there is a significant difference, the determinations must be repeated using freshly prepared reagents. If there is not a significant difference, the ppm of thorium in each sample is calculated using Equation (1) and the measured absorbance, A_S.

$$\text{Th, ppm} = \frac{(5\ \mu\text{g. of Th})(A_S - A_B)}{(A_K - A_B)(\text{Sample Wt., grams})} \qquad (1)$$

EXPERIMENTAL

Preparation of Arsenazo III

At the time this investigation was started Arsenazo III was not commercially available. Therefore, the reagent was prepared by the azo addition of concentrated solutions of diazotised o-aminophenylarsonic acid and chromotropic acid in excess calcium hydroxide as described in Savvin.[24]

Fifteen grams of o-aminophenylarsonic acid were dissolved in 30 milliliters of water and 15 milliliters of concentrated hydrochloric acid. After the solution was cooled, 50 grams of crushed ice were added. To this mixture was added, with constant stirring, a solution of 5 grams of sodium nitrite in 10 to 15 milliliters of water and 7.8 N nitric acid until a small excess of the acid showed when the solution was tested with iodized starch paper. The small excess of nitric acid was subsequently removed with sulphamic acid.

To a solution containing 6.5 grams of the disodium salt of chromotropic acid in 20 milliliters of water, a mixture of 10 grams of calcium oxide and 30 milliliters of water was added. The mixture was cooled in an acetone-dry ice mixture, and 50 grams of crushed ice and the previously prepared diazonium solution were added with constant stirring. The solution turned a blue-violet color and was allowed to stand for 30 minutes to 2 hours at room temperature.

The following tests were made to ascertain the success of the reaction. One drop of the reaction mixture was added to 50 to 100 milliliters of water, and 5 to 10 milliliters of the resulting blue solution were placed in a test tube. Then 2 to 3 drops of concentrated hydrochloric acid were added. The color of the solution turned pink-crimson. Five drops of the thorium stock solution were added, and the solution acquired the emerald green color of the thorium-Arsenazo III complex. The solution was divided into two portions, and 0.5 milliliter of 36 N sulfuric acid was added to one portion while it was being mixed and cooled. The other portion was retained as a color reference. If the reaction was incomplete, the sulfuric acid caused the solution to turn red-violet, crimson, or muddy colored. In this case the product was a mixture of Arsenazo I and Arsenazo III, and the preparation was repeated. If the solution turned dark green, the reaction was complete, and one liter of hot water and 100 milliliters of 12 N hydrochloric acid were added to the entire reaction mixture that had stood for 30 minutes to 2 hours. The solution was stirred to dissolve the calcium salts, allowed to settle, and filtered through a coarse fritted-glass filter funnel. The black precipitate was washed with 50 to 100 milliliters of 1 N hydrochloric acid and the filtrate discarded. The crude product was dissolved in one liter of hot water containing 50 milliliters of 40 percent sodium hydroxide solution, and the solution was filtered and then acidified with 100 milliliters of 12 N hydrochloric acid. The solution was left overnight, and then the precipitate was filtered and washed successively with 50 milliliters each of water and

ethanol. The air-dried product was quite stable, but solutions of Arsenazo III are not and should be discarded after 2 to 3 months.

Optimum Conditions for Formation of the Thorium-Arsenazo III Complex

Optimum conditions for the formation of the thorium-Arsenazo III complex were determined by investigating the effects of several variables, including acid anion, acid concentration, and Arsenazo III concentration on the absorbance of the complex. In the investigation of the effects of various acid anions, the thorium-Arsenazo III complex was formed in 4 N hydrochloric, nitric, sulfuric, and perchloric acid solutions that contained 2 milliliters of 0.05 percent Arsenazo III solution and 10 micrograms of thorium in 10 milliliters. A green color formed in the sulfuric acid solution and interfered with the measurement of the absorbance of the thorium-Arsenazo III complex. Nitric acid greatly reduced the absorbance of the complex, presumably because of oxidation of the organic reagent. Hydrochloric or perchloric acid were satisfactory solutions in which to form the colored complex, but 4 N perchloric acid was preferred because the absorbance was about 5 percent greater in this solvent than in the 4 N hydrochloric acid solution. All subsequent measurements were made using perchloric acid solutions.

To determine the effect of acid concentration on the absorbance of the colored complex, two quantities of thorium were reacted with Arsenazo III in each of eight perchloric acid concentrations ranging from 1 to 7 N. The measured absorbances (Table I), when compared to absorbances of corresponding reagent blanks, show that an acid concentration between 4 and 4.5 N gives the best combination of low blank and high absorbance for the thorium complex.

Table I

Effect of Acid Concentration on the Absorbance of the Reagent Blank and Thorium-Arsenazo III Complex

$HClO_4$, N	Absorbance at 665 mμ., of		
	Reagent Blank	1 μg./ml. Th	2 μg./ml. Th
1	---	0.404	0.705
2	0.029	0.500	0.960
3	0.028	0.545	1.045
3.5	0.031	0.562	1.074
4	0.035	0.577	1.103
4.5	0.040	0.580	1.126
6	0.110	0.660	1.200
7	---	0.771	1.240

Table II shows the effect of variations in the Arsenazo III concentration on the absorbance of the complex formed in 4 N perchloric acid solutions containing each of two thorium concentration levels, 0.4 and 2 micrograms per milliliter. The data show that at each thorium concentration level the absorbance is essentially constant when greater than 78 micrograms of Arsenazo III per milliliter are used; therefore a concentration of 0.1 milligram per milliliter was considered sufficient for the determination of not greater than 2 micrograms per milliliter of thorium.

During the investigation, it became apparent that scrupulous care in cleaning glassware and obtaining pure reagents was needed to prevent a rapid decrease in the absorbance of the thorium-Arsenazo III complex and also a high absorbance for the blank solutions. When the absorbance cells became dirty, the absorbance of the complex decreased as much as 50 percent in 15 minutes. In order to measure the rapid decrease in absorbance, the Arsenazo III was carefully added such that the color-forming reagent solution floated on top of the other solution. Then each sample was shaken immediately before being transferred to the

Table II

Variation of Absorbance with Arsenazo III Concentration at Each of Two Thorium Concentrations

Th Taken, μg./ml.	Arsenazo III Taken, μg.	Absorbance
0.4	120	0.100
	360	0.180
	520	0.200
	780	0.200
	1000	0.200
2.0	120	0.260
	360	0.750
	520	0.900
	780	0.950
	1000	0.950

absorbance cells. Often the only agents that would clean the cells were detergents. When the absorbance of a blank was high, generally the reagents were found to be contaminated with thorium or some other heavy metal ion. The lanthanum salts available generally were slightly contaminated. Therefore the lanthanum carrier solution was made 7.8 N in nitric acid and was passed through an anion exchange resin column before the solution was diluted to volume. This removed thorium contamination.

Separation of Thorium

Several liquid-liquid extraction separations of thorium[13,19,20,22,23] were considered for this application. The most promising were the extraction of the thorium-Arsenazo III complex into amyl alcohol,[13] and the extraction of thorium into high molecular weight amines or phosphorus-containing compounds.[19,20] It was found that the amyl alcohol extraction was nonselective; the zirconium-Arsenazo III complex was extracted, and the other heavy metal complexes including the lanthanides,[5] protactinium,[18] plutonium,[16] titanium,[3] and

uranium[17] were expected to be coextracted. The use of liquid ion exchange systems seemed promising, but involved lengthy methods of reagent purification. For these reasons ion exchange resin techniques seemed preferable.

The first separation method investigated was an anion exchange resin system in which thorium (IV) is adsorbed from 0.1 N sulfuric acid solution while plutonium is passed through the column in the reduced (III) oxidation state. Four methods of reducing the plutonium to the (III) oxidation state were tried. Addition of hydroxylamine sulfate, hydrogen peroxide, or sulfurous acid to the plutonium solution left visible amounts of plutonium (IV) on the columns. In the fourth reduction method, plutonium solutions were heated with hydroxylamine sulfate and then passed through a Jones reductor directly onto the columns. This method was most effective, leaving only 170 to 1300 micrograms of plutonium with the thorium. However this was still too much to be tolerated in the sensitive spectrophotometric measurement with Arsenazo III. In addition, it was found that the thorium absorbed on the resin from 0.1 N sulfuric acid was only 85 to 88 percent eluted by 4 N perchloric acid. Therefore this separation method was not pursued further.

Another ion exchange resin system which seemed to have promise was the cation exchange of thorium as a simple four-valent ion. The thorium (IV) was absorbed on the cation exchange resin from 9 N hydrochloric acid. Plutonium forms a negatively charged ion, $PuCl_6^{=}$, which passes through the column. The thorium was then eluted with oxalic acid. It was found, however, that the thorium failed to absorb completely and appeared in the first washes off the column.

At this point it was obvious that a simple one-step separation would not be found readily. Therefore consideration was given to a two-step separation that combines: (1) the precipitation of the thorium as the fluoride

using lanthanum as a carrier, while plutonium (VI) remains in solution; and (2) dissolution of the fluoride precipitate in 7.8 N nitric acid and selective adsorption of the thorium and remaining traces of plutonium on an anion exchange resin. Then the thorium is eluted with concentrated hydrochloric acid. The reliability of the fluoride precipitation method has been proved adequately by repeated use in other methods for measuring thorium in plutonium.[15] The loss of thorium in this operation is less than 0.4 percent.[2] The reliability of the two-step separation was thoroughly tested by making repeated separations of 0.5 to 10 micrograms of thorium from 1.0-gram samples of plutonium and measuring the thorium spectrophotometrically as the Arsenazo III complex. The results of these measurements (Table III) showed that the loss of thorium was quite low.

RELIABILITY

The precision of the method is based upon the determination of thorium in solutions containing 0.5 to 10 micrograms of thorium and 1.0 gram of plutonium, or 2.5 to 10 micrograms of thorium and no plutonium. These solutions were prepared by combining aliquots of the thorium solutions that have known concentrations and 1.0-gram portions of high-purity plutonium. Each was analyzed by the method described, along with two 1.0-gram portions of the plutonium metal without added thorium. The two-step separation was not performed on the samples without plutonium. The relative standard deviations for the measurement of thorium after separation from 1.0 gram of plutonium are in the range of 4.7 to 2.2 percent, while those for the thorium measurement without separation are 0.7 to 1.3 percent (Table III). The thorium found after separation varies from 96 to 100 percent, showing that a slight negative bias exists at the higher (5 to 10 ppm) thorium concentration levels.

This bias is reflected in the lower molar absorptivity of 111,000 following separation of thorium as compared to 113,000 when a separation is not required.

Table III

Determination of Microgram Quantities of Thorium in Plutonium

Th Taken, μg.	Pu Taken, grams	No. of Detn.	Av. Corrected Absn.* at 665 mμ.	Rel. Std. Dev., %	Th Found, %	Av. Molar Absorptivity
0.5	1.0	12	0.034	4.7		
2	1.0	13	0.186	3.7	100	
3	1.0	17	0.294	3.9	99	111,000
5	1.0	15	0.483	2.3	97	
10	1.0	16	0.964	2.2	96	
2.5	0.0	15	0.232	1.3		
5	0.0	15	0.497	0.7		113,000
10	0.0	15	1.006	0.8		

*Reagent blank subtracted

The effects of 45 other ions on this determination were investigated. Approximately 100 milligrams of each ion were added individually to aliquots containing 1.0 gram of plutonium and 5 micrograms of thorium which were then measured by this spectrophotometric method. The elements that are insoluble in either hydrofluoric acid or 7.8 N nitric acid caused the greatest difficulties (Table IV). It was found that several evaporations to fumes with perchloric acid, in place of the one evaporation usually required, were necessary to decompose the fluoride precipitates of calcium, cerium, lanthanum, scandium, and yttrium. The perchlorate salts dissolved in 7.8 N nitric acid, and the metal ions passed through the anion exchange resin. Surprisingly, calcium and lanthanum still caused some interference.

Table IV

Effects of Various Ions on the Determination of Thorium in Plutonium
(1.0 gram of plutonium and 5 micrograms of thorium taken in each case)

Quantity of Element Added, mg.	Noninterfering Elements*	Interfering Elements
100	Ag, As, Au, B, Ba, Be, Bi, Ce, Cd, Cl, Co, Cr, Cu, Fe, Ga, Hf, Hg, In, K, Li, Mg, Mn, Na, Ni, Pb, Pd, Pt, Ru, Sc, Si, Sr, Ta, Ti, U, V, Y, Zn, Zr	Al, Ca, La, Mo, Sb, Sn, W
50	Al, Ca, La	Mo, Sb, Sn, W
10	Mo, Sn, W	Sb

*An element was considered to interfere if there was an error greater than 6 percent in the thorium found.

Special treatment also was required for barium and strontium which form insoluble sulfates in the dilute sulfuric acid solution from which the thorium is precipitated with hydrofluoric acid. However, when the sulfuric acid was omitted from this solution, the barium and strontium neither precipitated nor caused interference. One-hundred-milligram quantities of molybdenum, tin, and tungsten formed precipitates that could not be dissolved in 7.8 N nitric acid, and these clogged the anion exchange resin column. However, smaller amounts of these elements (10 milligrams) did not interfere; antimony was the only element that caused interference at the 10-milligram level.

It was concluded that the method is sufficiently reliable, selective, and sensitive for measuring thorium in the high-purity plutonium metal now

being produced. The concentrations of other elements in this metal should be much less than those required to cause interference with this method.

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