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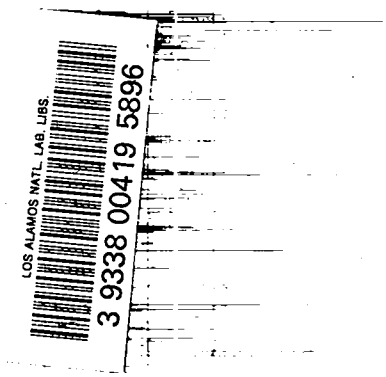
THE SPECTROPHOTOMETRIC DETERMINATION OF PLUTONIUM IN SOLUTIONS CONTAINING LARGE AMOUNTS OF ALUMINUM, CALCIUM, AND MAGNESIUM

by

Glendall L. King



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TECHNOLOGY - PLUTONIUM

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CHEMISTRY AND METALLURGY DIVISION

ANALYTICAL GROUP

Charles F. Metz, Group Leader

ABSTRACT

A spectrophotometric procedure for the determination of plutonium has been applied to solutions that contain much aluminum, calcium, and magnesium. It was found necessary to separate the plutonium from the contaminating materials before analyzing for the plutonium. A double sequence of ammonia and strong alkali precipitations was found successful in separating the plutonium. For solutions that were originally 0.001 M in plutonium(IV), 2.0 M in aluminum(III), 0.5 M in calcium(II), and 0.5 M in magnesium(II), the plutonium content was determined with a standard deviation of ± 2.1 percent.

INTRODUCTION

It became necessary for this Laboratory to analyze for plutonium in solutions which contained relatively large amounts of aluminum, calcium, and magnesium. Since a spectrophotometric procedure for plutonium had been developed[1], and since the plutonium content of the aluminum-calcium-magnesium solutions was in the range of this procedure, it was logical that an attempt be made to apply this procedure to these solutions.

Of the ions aluminum(III), calcium(II), and magnesium(II), it was anticipated that aluminum(III) would probably offer the most interference, since sodium alizarinsulfonate, under different conditions, has been used as a colorimetric reagent for small amounts of aluminum[5]. Subsequently, it was found that aluminum did interfere strongly with the plutonium determination, and it became necessary to develop a procedure for its removal. A double sequence of ammonia and strong alkali precipitations removed the calcium and magnesium as well as most of the aluminum. The interference caused by the small amount of aluminum that carried through the precipitation procedure was eliminated by complexing the aluminum with fluoride ion.

Standard Health-Safety Rules of the Laboratory should be strictly followed in employing any of the following procedures.

APPARATUS AND REAGENTS

Apparatus

A Beckman Model DU Quartz Spectrophotometer with Corex cells of one centimeter path length was used for all measurements.

Modified Melaven cells[4] were used for electrolysis. An actual cell consisted of a three way stopcock (oblique bore, 1 mm) sealed onto the bottom of a small test tube (15 x 125 mm) with a coiled, perforated platinum sheet serving as the anode and a pool of mercury as the cathode. The electrolysis arrangement is shown in Figure 1. A Fischer Electroanalyzer served as the power supply.

Calibrated micropipettes of 0.10, 0.20, and 0.5 milliliter capacity equipped with syringe-controls were used for transferring all plutonium solutions. These items are shown in Figure 2.

An International Clinical Centrifuge, with 5 milliliter cones, was used for the separation procedure.

Reagents

Stock plutonium(IV) solutions were prepared by dissolving pieces of pure plutonium metal that had been previously electropolished[2] and then weighed. Approximately 0.4 milliliter of 6 N hydrochloric acid was used to dissolve 50 milligrams of the metal, 0.5 milliliter of

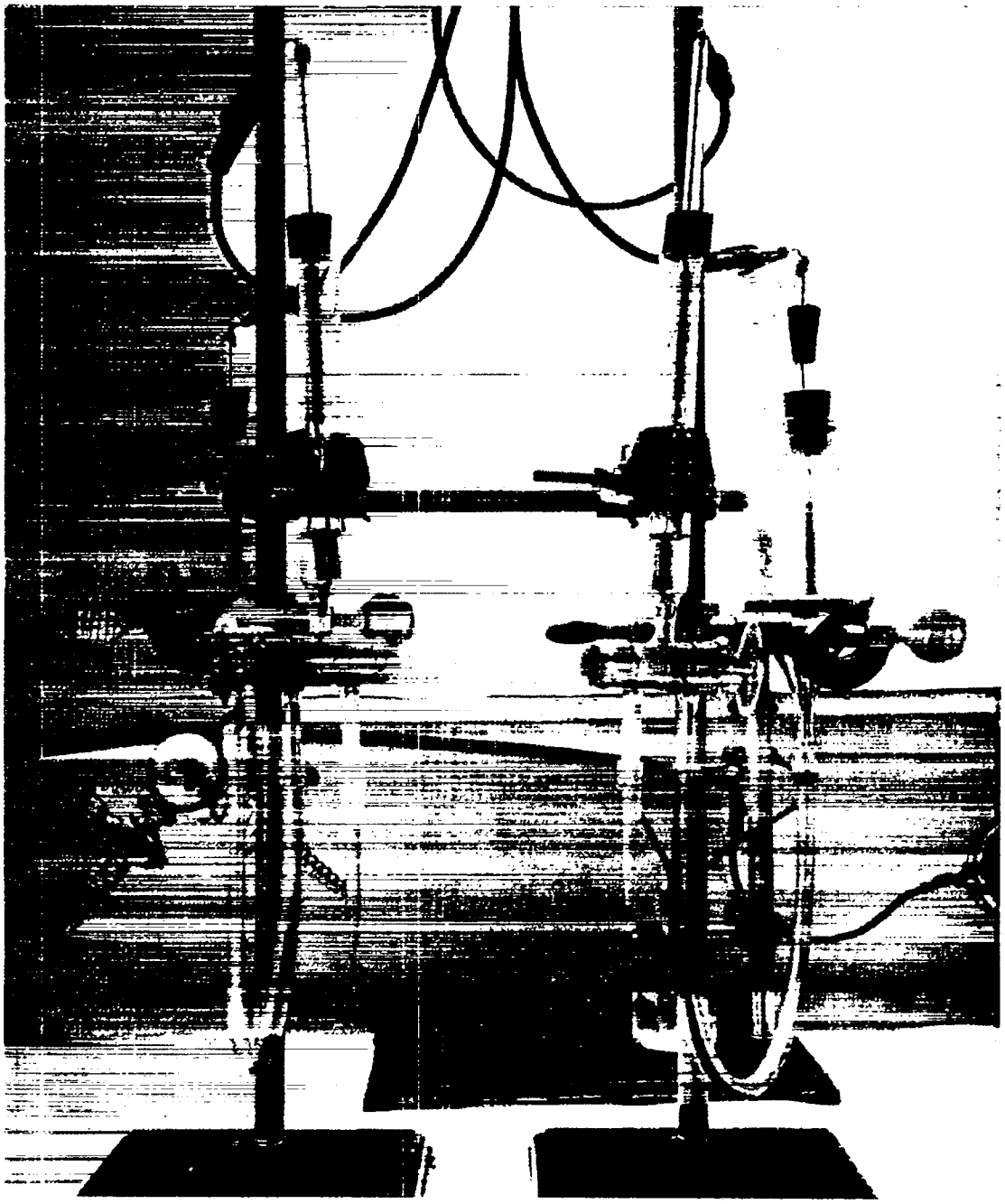

Figure 1

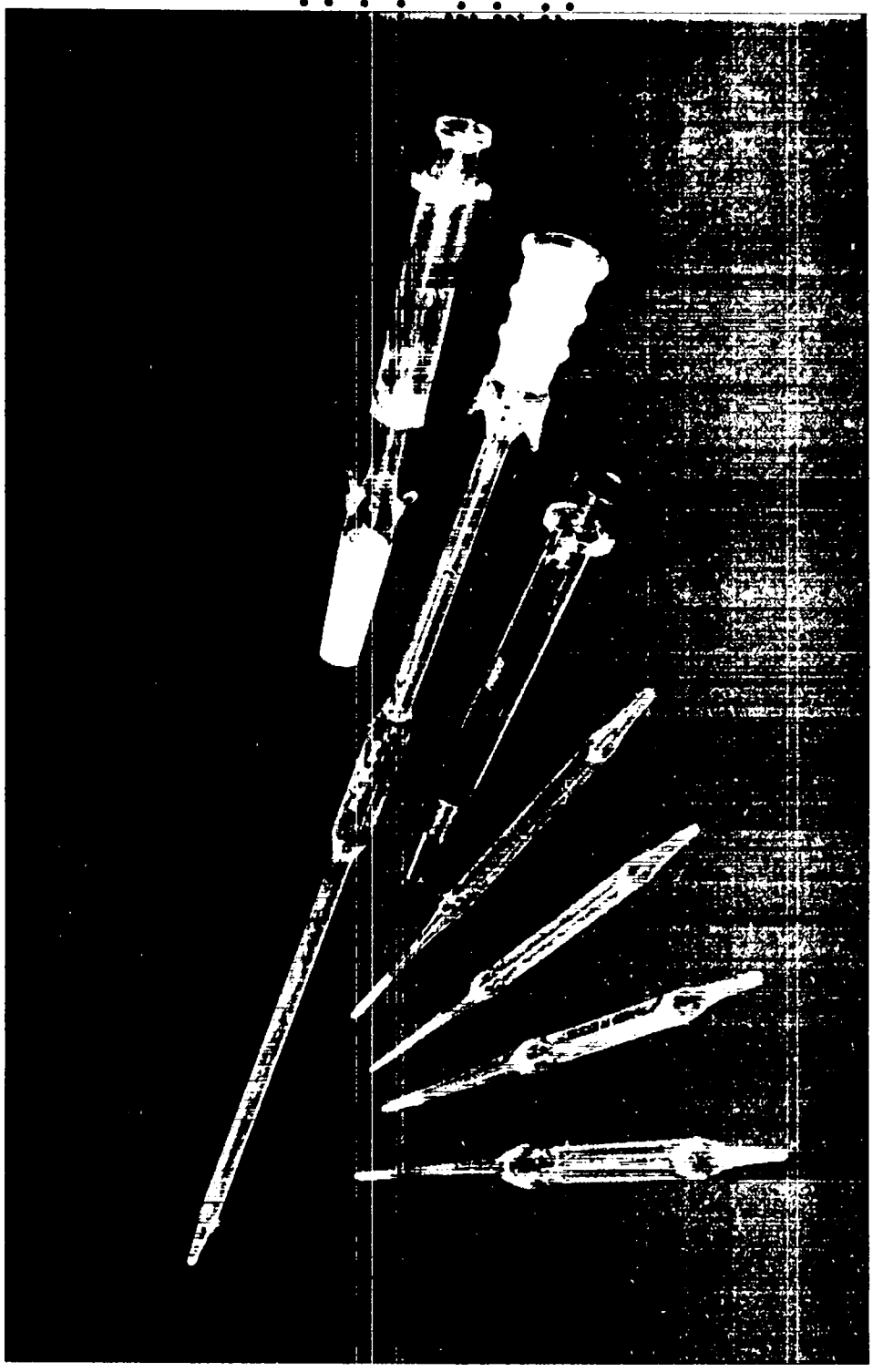

Figure 2

6 N sulfuric acid and a few drops of 6 N nitric acid were added to oxidize the plutonium to the +4 state, and the resulting solution evaporated to dryness under an infra-red lamp. The residue was dissolved in water and enough 6 N sulfuric acid to make the final volume 0.05 N in this acid. Volume aliquots of these solutions, measured and transferred by means of micropipettes with attached syringe-controls, were used in subsequent experiments.

A stock aluminum-calcium-magnesium solution was prepared by dissolving the necessary amount of the corresponding nitrate in water to produce a final solution that was approximately 2.0 M in aluminum(III), 0.5 M in calcium(II), and 0.5 M in magnesium(II).

A 0.2 percent aqueous solution of sodium alizarinsulfonate.

A formate buffer, 3.0 N in formic acid and 0.6 M in sodium formate.

2 M ammonia; prepared by diluting the C.P. reagent with distilled water.

5 M potassium hydroxide; prepared by dissolving the C.P. reagent in distilled water.

2 N and 6 N sulfuric acid; prepared by diluting the C.P. reagent with distilled water.

A dilute solution of sodium fluoride, containing 400 micrograms of

fluoride ion per milliliter, which had been adjusted to a pH of three with 6 N sulfuric acid.

RECOMMENDED PROCEDURE

1. Transfer, using a micropipette with syringe-control, a sample containing 25 to 150 micrograms of plutonium to a 5 milliliter centrifuge cone. Add about one milligram of iron(III) to insure the complete precipitation of all plutonium.

2. Add 2 M ammonia with stirring until the methyl red endpoint is reached. Centrifuge, siphon the supernatant into a waste residue bottle, wash the precipitate once with water, centrifuge, and again siphon the supernatant into a waste residue bottle.

3. To the precipitate from step 2, add 2 milliliters of 5 M potassium hydroxide and thoroughly stir the precipitate. Centrifuge, siphon the supernatant into a waste residue bottle, wash the precipitate once with water, centrifuge, and again siphon the supernatant into a waste residue bottle.

4. Dissolve the precipitate from step 3 in a few drops of 6 N sulfuric acid, and then repeat step 2.

5. Repeat step 3 on the precipitate from step 4.

6. Dissolve the final precipitate from step 5 in the minimum amount

of 6 N sulfuric acid (two drops are usually sufficient), and quantitatively transfer the solution, by means of a 0.5 milliliter micropipette with syringe-control, to a platinum crucible. Fume the contents to dryness using an infra-red heating lamp.

7. Dissolve the crucible-contents in a few drops of water plus 50 microliters of 2 N sulfuric acid. Keep the volume as small as possible, preferably below 0.5 milliliters. Then quantitatively transfer the solution, using a 0.5 milliliter micropipette with syringe-control, to one of the mercury cathode cells. Electrolysis is carried on for thirty minutes at an applied voltage of 7 volts and a current of 0.2 ampere.

8. After electrolysis to remove iron and other impurities, wash the solution into a 10 milliliter volumetric flask, taking care that the final volume is less than 5.8 milliliters.

9. Add 0.2 milliliter of the sodium fluoride solution (80 micrograms of fluoride ion), 2.0 milliliters of formate buffer solution, 2.0 milliliters of sodium alizarinsulfonate solution, and then dilute to 10 milliliters with distilled water.

10. After mixing thoroughly, heat the solution to incipient boiling (usually 10-15 minutes) under an infra-red heating lamp.

11. Cool to room temperature, transfer an aliquot of this solution,

using a 2 milliliter pipette with syringe-control, to a clean one centimeter absorption cell, and measure the optical density at 530 millimicrons. Compare with a blank containing the same amount of acid, buffer, and reagent, as the reference solution.

12. The optical density divided by 0.00413 (or multiplied by 242) gives the number of micrograms of plutonium present in the 10 milliliter aliquot.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Interference of Aluminum, Calcium, and Magnesium.

Of the ions aluminum(III), calcium(II), and magnesium(II), it was anticipated that aluminum(III) would offer more interference in the plutonium determination since sodium alizarinsulfonate, under different conditions, has been used as a colorimetric reagent for small amounts of aluminum[5]. In order to see how these materials behaved under the conditions of the plutonium determination, 0.5 milliliter aliquots of the aluminum-calcium-magnesium solution (27 milligrams of aluminum, 10 milligrams of calcium and 6 milligrams of magnesium) were treated with the buffer and reagent and a deep red color developed. Since the aluminum was thought to be most responsible for this color, it seemed desirable to make a quantitative study of the reaction of aluminum(III) and sodium alizarinsulfonate under the same conditions. A solution containing 100 micrograms of aluminum(III) per milliliter was prepared,

and aliquots of this solution were treated exactly as the plutonium solutions. The results obtained are listed in Table I.

Table I

Aluminum Interference in the Sodium Alizarinsulfonate Procedure for Plutonium

Micrograms of Al in 10 ml	Optical Density (Ave. of 2)	Pu Equivalent in Micrograms
50	0.060	14.5
100	0.123	29.9
150	0.183	44.3
200	0.243	58.8

It is obvious from the data in Table I that even small amounts of aluminum(III) would cause considerable error in the plutonium determination. That magnesium interference is considerably less is shown by the data in Table II. These data were obtained using aliquots of a magnesium sulfate solution and following the same procedure as used for the plutonium solutions.

Table II

Magnesium Interference in the Sodium Alizarinsulfonate Procedure for Plutonium

Milligrams of Mg in 10 ml	Optical Density (Ave. of 2)	Pu Equivalent in Micrograms
5.0	0.002	0.5
10.0	0.004	1.0
15.0	0.006	1.5
20.0	0.016	4.0

A quantitative study of the calcium interference was not made because this would have necessitated the preparation of a calcium solution in a sulfate medium, with the calcium content being greater than that allowed by the solubility product of calcium sulfate.

2. Elimination of Interferences.

In view of the marked interference by aluminum, the mild interference of magnesium, and the insolubility of calcium sulfate, it was necessary to seek a working procedure whereby most of the calcium and magnesium and all of the aluminum could be separated from the plutonium. Electrolysis using the mercury cathode would be of no value since none of the above elements can be deposited in the mercury(3).

Chemical considerations of the aluminum, calcium, and magnesium ions present, as well as knowledge of the fact that plutonium can be precipitated from solution quite completely by making use of iron(III) hydroxide as a collecting agent, led to the belief that separation of the plutonium from the impurities could be accomplished by a series of precipitations at carefully controlled pH values, and at the same time prevent losses of the plutonium by coprecipitation.

The main difficulty in the quantitative separation of micro quantities of an element from macro quantities of impurities by precipitation of the macro constituents of the solution, lies in the fact that many precipitates tend to coprecipitate other ions present in the solution.

Although such tendencies may be quite small in some cases, significant percentages of the micro constituent may thus be removed and lost in the procedure. To avoid such losses of plutonium, consideration was given to the possibility of precipitating the plutonium away from the impurities, and to insure a quantitative separation by using iron(III) hydroxide to collect the plutonium.

The addition of one milligram of iron(III) as the sulfate followed by ammonia to the methyl red endpoint would precipitate the aluminum, iron, and plutonium as hydroxides and leave nearly all of the calcium and magnesium in solution. Treatment of this precipitate with an excess of strong potassium hydroxide would result in a precipitate of iron and plutonium as hydroxides with the aluminum left in solution. This precipitate could be dissolved and the iron readily separated from the plutonium by electrolysis into a mercury cathode. This procedure was tried and found to be generally satisfactory although the precipitations had to be repeated in order to remove all but traces of aluminum being carried by the iron(III) precipitates.

These traces of aluminum apparently were causing some trouble since erratic results were often obtained on the subsequent plutonium determinations. A study of the complexing of aluminum indicated that small amounts of fluoride ion could eliminate the interference of small amounts of aluminum in the sodium alizarinsulfonate procedure and yet not interfere appreciably with the plutonium determination.

Tables III and IV illustrate these findings. In view of these results it seemed advisable to add fluoride ion to all solutions obtained from the precipitation procedure.

Table III

Elimination of the Aluminum-Alizarinsulfonate Color Using Fluoride Ion

Micrograms of Al in 10 ml	Micrograms of Fluoride in 10 ml	Optical Density (Ave. of 2)
50	0	0.068
50	80	0.012
50	160	0.002
50	240	0.001

Table IV

Effect of Various Amounts of Fluoride Ion on Mixtures of Aluminum and Plutonium

Micrograms of Pu in 10 ml	Micrograms of Al in 10 ml	Micrograms of Fluoride in 10 ml	Optical Density (Ave. of 2)
122.2	0	0	0.500
122.2	0	80	0.496
122.2	50	0	0.600
122.2	50	80	0.509
122.2	50	160	0.499
122.2	50	240	0.480

3. Analysis of Aluminum-Calcium-Magnesium Solutions.

To check upon the reproducibility of this procedure, aliquots of the standard plutonium(IV) solution were added to aliquots of the aluminum-calcium-magnesium solution and the resulting solutions subjected to the various precipitations, and then to the color development. Eighty

micrograms of fluoride ion were added immediately preceding the addition of the buffer and the reagent. The results obtained when 19 duplicate samples were analyzed are listed in Table V.

Table V

Determination of Plutonium in Solutions Which Contained 2.0 M Aluminum(III), 0.5 M Calcium(II), and 0.5 M Magnesium(II)

Micrograms Pu Taken	Micrograms Pu Found (Ave. of 2)	Percent Difference
122.2	121.5	- 0.6
122.2	124.4	+ 1.8
122.2	118.5	- 3.0
122.2	121.5	- 0.6
122.2	122.9	+ 0.6
122.2	126.8	+ 3.8
122.2	123.4	+ 1.0
122.2	126.4	+ 3.4
122.2	121.0	- 1.0
122.2	126.8	+ 3.8
122.2	123.2	+ 0.8
122.2	121.2	- 0.8
122.2	121.5	- 0.6
122.2	125.6	+ 2.8
122.2	118.0	- 3.4
122.2	120.7	- 1.2
122.2	123.9	+ 1.4
122.2	121.0	- 1.0
122.2	121.7	- 0.4

A standard deviation of ± 2.1 percent was calculated for the determined plutonium content of those samples in Table V. Although this value is somewhat high, as compared to the standard deviation of pure plutonium solutions[1], it would appear that these results represent the best that can be obtained on these highly contaminated

solutions. Mechanical errors in treatments of the solutions and precipitates, and variations in the amount of aluminum entrapped by the gelatinous iron precipitates could cause considerable variation in the determined amount of plutonium.

CONCLUSIONS

1. A method for determining plutonium in solutions containing large amounts of aluminum, calcium and magnesium has been developed. It was found necessary to remove aluminum, and desirable to remove calcium and magnesium before determining plutonium with sodium alizarinsulfonate.

2. The plutonium content of 19 synthetic samples was determined, after separating the aluminum, calcium, and magnesium by a sequence of ammonia and strong alkali precipitations, with a standard deviation of ± 2.1 percent.

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