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A SPECTROPHOTOMETRIC DETERMINATION OF MULTIMICROGRAM AMOUNTS OF PLUTONIUM

by

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CHEMISTRY AND METALLURGY DIVISION

ANALYTICAL GROUP

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ABSTRACT

A spectrophotometric method for the determination of plutonium using sodium alizarinsulfonate has been developed. The red plutonium-alizarinsulfonate color is developed in solutions having a pH of about three in the presence of a formic acid-sodium formate buffer, and the resulting absorption is measured at 530 millimicrons. Most interfering cations, particularly iron(III), are removed from the plutonium solutions by means of electrolysis using a mercury cathode. Aluminum(III), in quantities up to 3 percent of the plutonium content, may be tolerated in this procedure. Chloride and nitrate ions produce no interference over the concentration range studied, while tartrate, citrate, oxalate, and fluoride ions cause low results. The analysis of a large series of pure plutonium solutions, ranging from about 25 to 150 micrograms of plutonium in 10 milliliters, gave a standard deviation of ± 0.92 percent for the determined plutonium content.

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INTRODUCTION

The need for a method of plutonium analysis that would fill the void between the optimum range of the potentiometric titration procedure(3) and the radiochemical analysis procedure(1) has long been desired. Thus, the ultimate purpose of this work has been to develop a precise chemical method for the determination of multimicrogram amounts of plutonium. It seemed not unlikely that a colorimetric procedure could be quite successful for such a determination, and the foremost problem then developed into a search for a reagent that would form a highly-colored, soluble complex with small amounts of plutonium.

A survey of plutonium literature(e.g.4) failed to uncover a plutonium compound that was sufficiently colored to be suitable for the colorimetric determination of microgram amounts of this element. Procedures have been developed for the colorimetric determination of uranium(IV)(8) and thorium(IV)(9), and it seemed quite possible that one of the reagents used in these procedures might be suitable for the determination of plutonium(IV). Both of these reagents, namely, sodium alizarinsulfonate and 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, were tested with plutonium(IV), and both reagents gave fairly highly colored complexes. However, the color produced with sodium alizarinsulfonate seemed to be more stable and somewhat more intense. Consequently the spectrophotometric procedure was developed with this

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reagent.

Iron(III) was found to be a very serious interference, and it became necessary to remove it before attempting the plutonium determination. Removal of the iron was readily effected by electrolysis using a mercury cathode, and in fact, many metallic impurities could be removed from plutonium solutions by this same procedure(5).

Standard Health-Safety Rules of the Laboratory should be 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(6) 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 0.05, 0.10, 0.20, and 0.50 milliliter capacity were used with syringes attached for transfer of all plutonium solutions. These items are shown in Figure 2.

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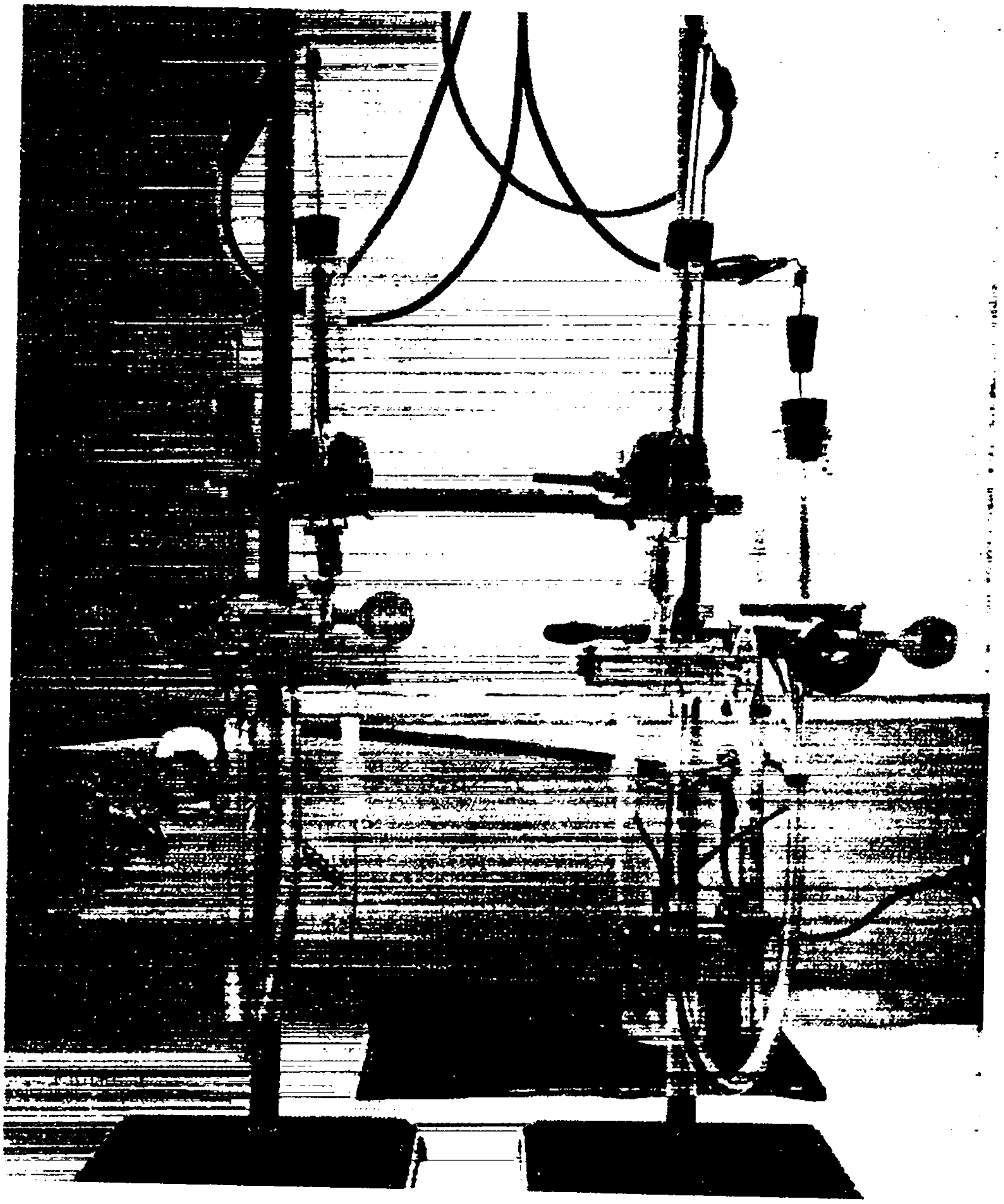

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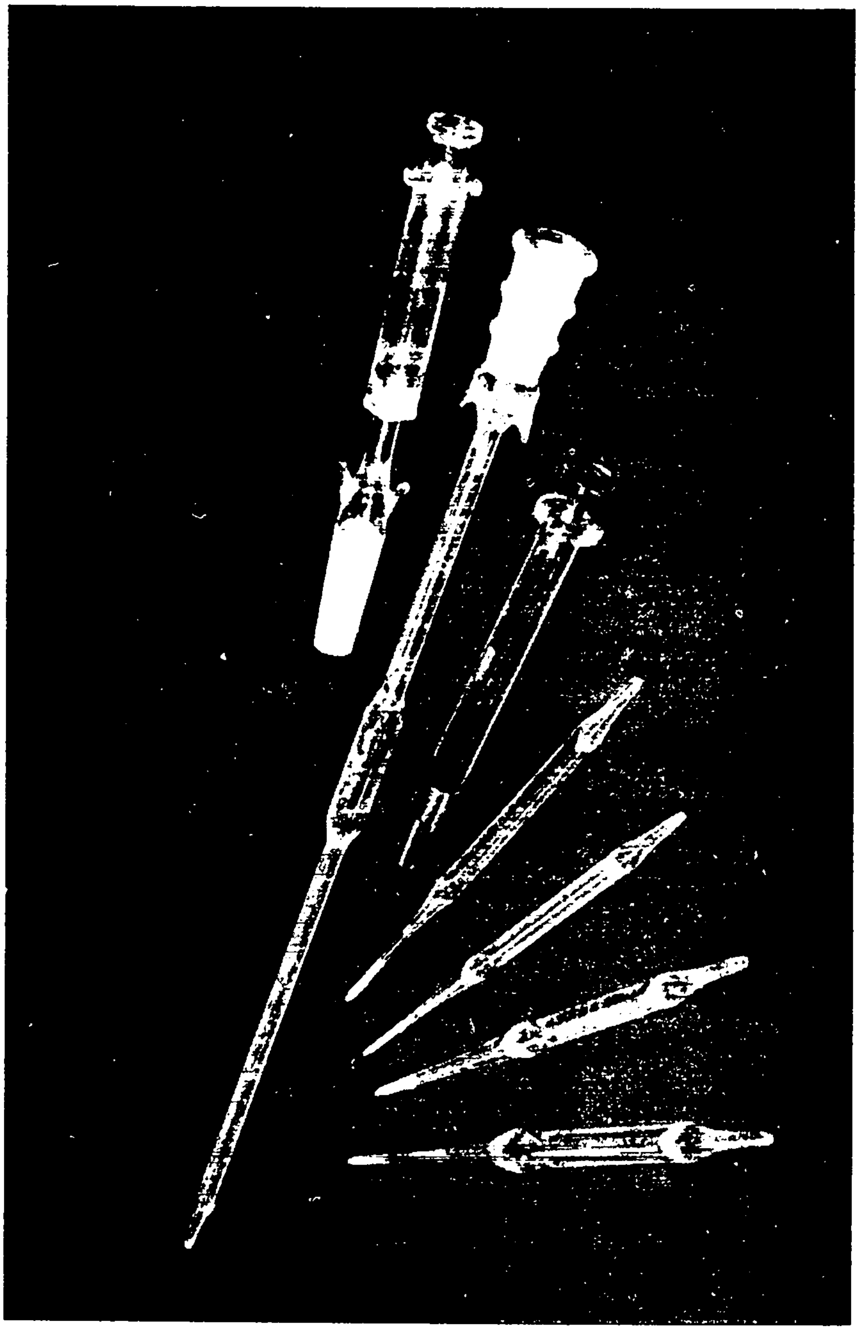

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Reagents

Stock plutonium 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 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 stock solutions, measured and transferred by means of micropipettes with attached syringe-controls, were used in subsequent experiments.

0.2 percent sodium alizarinsulfonate; prepared by dissolving 1.00 gram of the solid in 500 milliliters of water and filtering the solution free of suspended matter.

Formate buffer, 3.0 N in formic acid and 0.6 M in sodium formate; prepared by dissolving 56.5 milliliters of reagent formic acid and 20.4 grams of reagent sodium formate in distilled water and diluting to 500 milliliters.

6 N sulfuric acid; prepared by dilution of the C.P. reagent solution with distilled water.

2 N sulfuric acid; prepared by dilution of the C.P. reagent solution

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with distilled water.

RECOMMENDED PROCEDURE

1. Evaporate to dryness, under an infra-red heating lamp, a sample containing 25 to 150 micrograms of plutonium to remove any chloride, nitrate, or excessive amounts of sulfate. If only small amounts of sulfate are present as the anion, then steps 1 and 2 may be eliminated.
2. Dissolve the residue in a small amount of water and one drop (50 microliters) of 2 N sulfuric acid. Keep the volume at 0.5 milliliter or less.
3. Transfer this solution, using a 0.5 milliliter micropipette with syringe-control, to the electrolysis cell and electrolyze to remove iron and other interfering impurities. Electrolysis is carried on for thirty minutes at an applied voltage of 7 volts and a current of 0.2 ampere.
4. Wash the electrolyzed solution directly into a 10 milliliter volumetric flask, taking care that the final volume is not more than 6.0 milliliters.
5. Add 2 milliliters of the formate buffer solution, 2 milliliters of the sodium alizarinsulfonate solution, and dilute to 10 milliliters with distilled water.
6. After mixing thoroughly, heat the solution to incipient boiling (usually 10-15 minutes) under an infra-red heating lamp.

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7. After cooling to room temperature, transfer an aliquot of this solution, using a two milliliter pipette with syringe control, to a clean one-centimeter absorption cell. Measure the optical density at 530 millimicrons, using a blank containing the same amount of acid, buffer, and reagent, as the reference solution.
8. 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. Absorption Characteristics of Plutonium Alizarinsulfonate.

When an aqueous solution of sodium alizarinsulfonate is added to a solution of plutonium(IV) at a pH of 2.8, a reddish-brown color is developed. Solutions of this reddish-brown complex (to be compared with the bright yellow of the blank) were examined spectrophotometrically and 530 millimicrons was found to be the wavelength of maximum absorption. Figure 3, obtained using 78.7 micrograms of plutonium in 10 milliliters, illustrates these findings. Figure 4 indicates that the system does follow Beer's law, at least over the concentration range studied. An average molecular extinction coefficient of 9,871 was calculated in the usual manner(7).

2. Effect of pH, Buffer, and Reagent.

Some time was spent in investigation of the factors that related to maximum color formation. Variations in pH, amount of formate buffer

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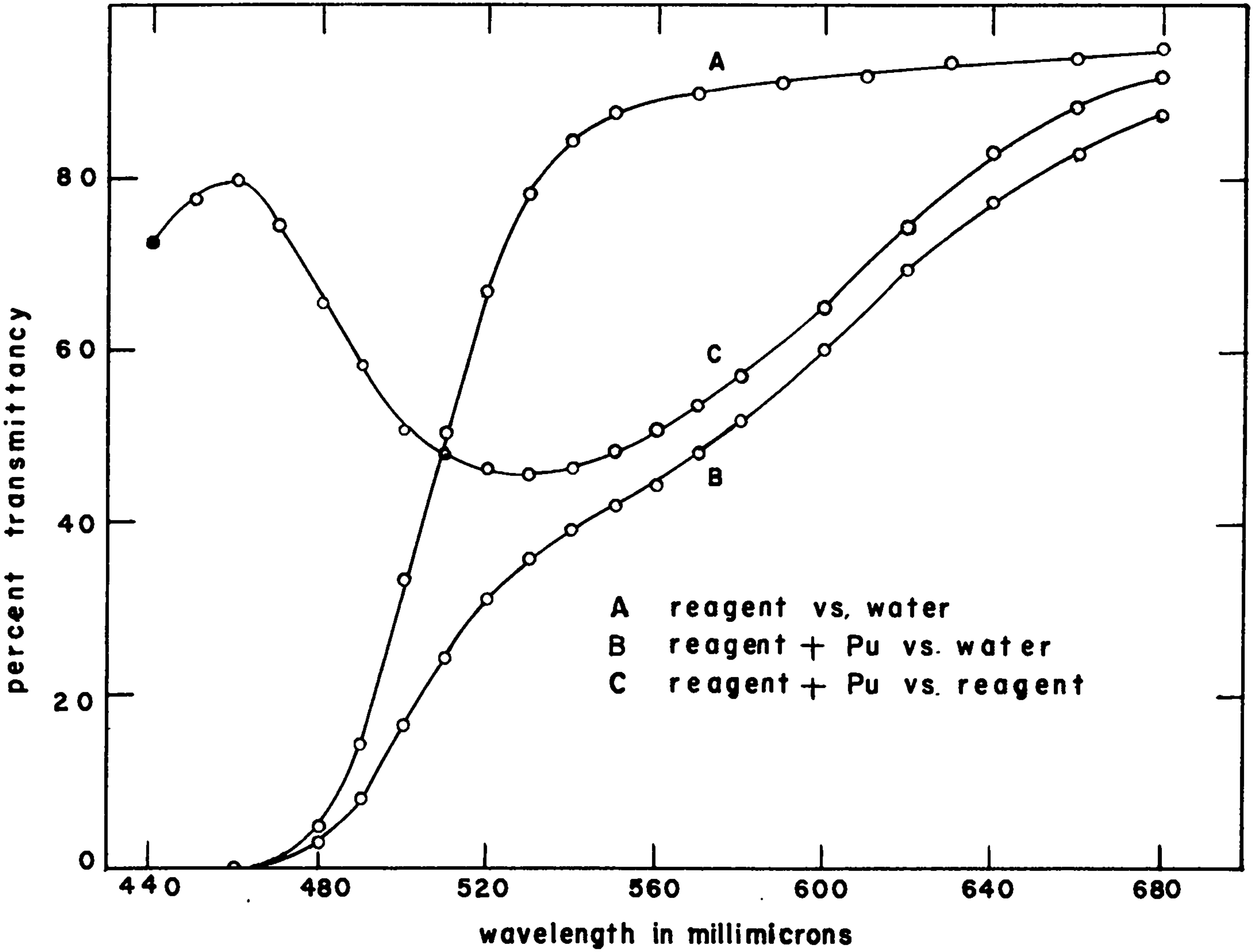

Fig. 3 Spectral Examination of the Plutonium— Alizarin Sulfonate Complex

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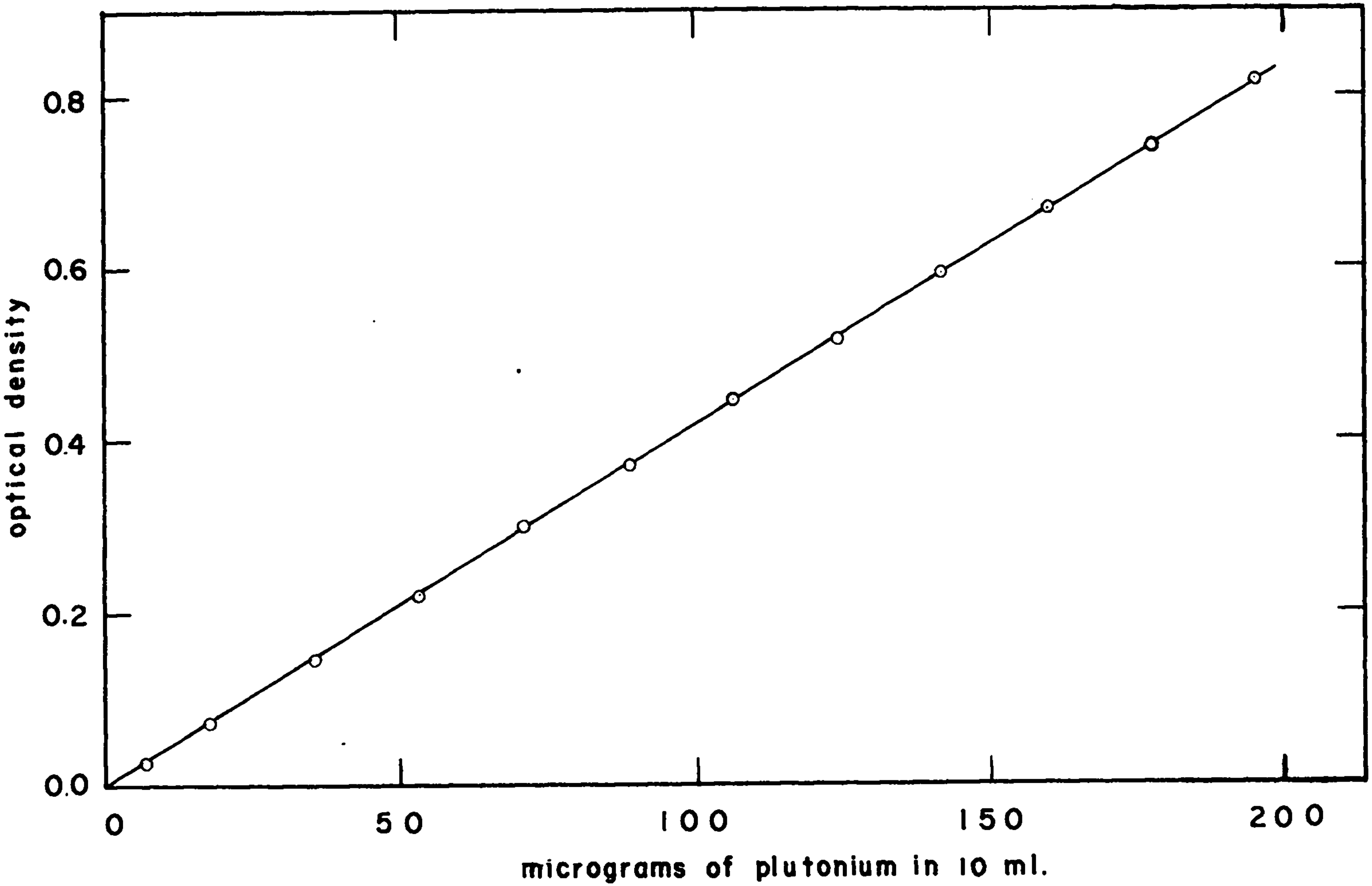

Fig. 4 Spectral Transmittancy of the Plutonium-Alizarin Sulfonate Complex at 530 mμ

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used, and amount of reagent used, all caused some variations in the amount of absorption. It was then necessary to arbitrarily choose one set of experimental conditions and follow them at all times. Two milliliters of the buffer solution and two milliliters of the reagent solution were selected as being the best, since with these amounts the best compromise of color formation, buffering capacity, and freedom of interference seemed to be obtained. Control of pH is particularly important and the pH of all final solutions should be as near 2.8 as possible. The amount of acid and buffer recommended in the procedure is very satisfactory in this respect.

3. Effect of Foreign Ions.

It was found early in the work that iron(III) caused very serious interference in the plutonium procedure. The magnitude of this interference is well illustrated by the data in Table I.

Table I

Iron(III) Interference in the Determination of Plutonium With Sodium Alizarinsulfonate

Micrograms of Fe(III) in 10 ml	Optical Density	Plutonium Equivalent in Micrograms
0.48	0.035	8.5
0.96	0.072	17.4
1.43	0.110	26.6
1.91	0.148	35.8
3.82	0.293	70.9
5.73	0.449	108.7
7.64	0.578	140.0
9.55	0.698	168.9

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It was thought that the serious interference of iron(III) could be overcome by making a suitable iron correction. Such a procedure would have necessitated a separate iron(III) analysis on each sample, but this was not considered to be too detrimental to the method. However, when such a technique was applied in attempting to analyze a series of nitrate solutions, the results were very poor. It was not until all solutions were electrolyzed with a mercury cathode that the iron difficulties were overcome. Table II compares the analysis results obtained when an iron correction was made and when aliquots of the same solutions were analyzed following an electrolytic separation of the iron. It is readily apparent that only the results obtained on the electrolyzed solutions check very closely with the results obtained by potentiometric titration.

In the nitrate solutions discussed in Table II, the amount of iron present is quite small as compared to the amount of plutonium. It seemed of interest to see how readily large amounts of iron could be removed from plutonium solutions. For these studies the general procedure involved pipetting definite volumes of standard iron(III) and plutonium(IV) solutions into the electrolysis cells, electrolyzing for 30 minutes, and then making the color development. The results obtained are tabulated in Table III and indicate clearly that the electrolytic separation procedure can be successfully applied to plutonium solutions containing high or low percentages of iron.

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Table II

Analysis of Nitrate Solutions

Potentiometric Titration Results(A) (mg Pu/g of soln)	Spectrophotometric Results			
	Using the iron Correction Factor	Percent Variance From A	From Electrolyzed Solutions	Percent Variance from A
217.7	219.9	+ 1.01	216.0	- 0.78
214.4	208.8	- 2.85	213.7	- 0.33
229.1	210.8	- 7.99	231.9	+ 1.22
214.4	206.3	- 3.78	215.6	+ 0.56
213.9	208.0	- 2.76	211.8	- 0.98
211.8	191.5	- 9.11	214.8	+ 1.42
224.3	222.8	- 0.69	223.8	- 0.22
212.3	209.6	- 1.27	211.2	- 0.52

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Table III

Determination of Plutonium in Solutions Containing High Percentages of Iron

Micrograms Pu Taken	Micrograms Fe Added	Weight Percent of Fe Present	Micrograms Pu Found	Percent Difference
99.26	23.44	19.1	97.80	- 1.47
99.26	46.88	32.1	98.29	- 0.98
99.26	70.32	41.5	99.02	- 0.25
99.26	100.9	50.3	98.77	- 0.49
99.26	201.8	66.9	99.50	+ 0.25
99.26	403.6	80.2	100.23	+ 0.98
99.26	1009.	91.0	100.23	+ 0.98

The effect of the ions aluminum(III), americium(III), chromium(III), cobalt(II), copper(II), nickel(II), manganese(II), uranium(VI), and zinc(II), in the sodium alizarinsulfonate procedure were also investigated. Table IV indicates the seriousness of the interference of each ion as well as listing the iron interference for comparative purposes.

Table IV

Summary of Certain Metal Ion Interferences in the Plutonium Determination

Ion	Micrograms of Ion/100 Micrograms of Plutonium necessary to Cause a One Percent Error in the Plutonium Determination
Al(III)	3.3
Am(III)	19.5
Cr(III)	244.
Co(II)	346.
Cu(II)	25.
Fe(III)	0.06
Ni(II)	> 3000.
Mn(II)	> 3000.
U(VI)	82.
Zn(II)	> 3000.

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It is readily apparent that, compared to the iron(III) interference, none of the other ions produces a serious interference if present in amounts less than indicated. Aluminum(III) produces the most serious interference of the ions not removed by the mercury cathode, and the method can only be directly applied to solutions that do not contain more than 3 percent as much aluminum as plutonium.

Limited studies were made of the effect of tartrate, citrate, oxalate, and fluoride ions on the color produced with a fixed amount of plutonium and sodium alizarinsulfonate. All of these caused low results. The amount of interference decreased in the order oxalate, tartrate, citrate, and fluoride. When present in equal molar quantities with plutonium, errors of five percent or less were obtained.

Chloride and nitrate ions, in amounts up to 20 milligrams in 10 milliliters, produce no interference in the plutonium determination. However, due to the adverse effect that these ions have on the electrodes during electrolysis(5), they should be removed from the plutonium solutions. Evaporation to dryness (step 1 of the Recommended Procedure) is sufficient for their removal.

4. Application of the Procedure to Analysis of Concentrated Nitrate Solutions.

In order to check upon the usefulness and accuracy of the method in actual analysis, it was decided to analyze a series of concentrated solutions and compare the results obtained with those obtained by the

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potentiometric titration procedure. Although such tests necessitated diluting the solutions a considerable amount before a volume aliquot could be used directly, it was felt that the results obtained would be quite valuable.

In preparing these solutions an amount of the nitrate solution necessary to give about 5 milligrams of plutonium was weighed into platinum cups and treated in the same manner as those for the potentiometric titrations(3). The contents of the cups were transferred, using a 0.5 milliliter pipette with syringe-control, to 25 milliliter volumetric flasks and, after adding enough 6 N sulfuric acid to make the total volume 0.05 N in this acid, were diluted to volume with distilled water. For the spectrophotometric analysis, 0.5 milliliter aliquots of these solutions were pipetted into the electrolysis cells, and the procedure followed as usual. The results obtained are shown in Table V and they appear to be quite good, since in a majority of the cases only one weighed aliquot of the nitrate solution was received, and also since the results from the potentiometric titrations often vary appreciably.

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Table V

Analysis of Concentrated Nitrate Solutions

Potentiometric Titration Results (mg Pu/g soln.)	Micrograms Pu Found in Color Aliquots	Pu Calculated from Colorimetric Results (mg Pu/g soln.)	Percent Difference
100.5	93.98	99.1	- 1.39
106.8	94.70	104.6	- 2.06
219.5	144.5	220.4	+ 0.41
89.1	88.67	89.4	+ 0.34
93.6	97.83	94.3	+ 0.75
92.5	90.12	90.9	- 1.73
60.1	54.46	60.8	+ 1.17
211.8	114.7	209.7	- 0.99
216.4	127.4	219.9	+ 1.62
210.0	118.6	208.3	- 0.81
220.4	118.3	220.4	0.00
219.7	149.2	220.9	+ 0.55
217.1	122.7	216.1	- 0.46
220.6	155.7	221.7	+ 0.50
226.8	106.8	225.1	- 0.75
217.7	78.67	216.0	- 0.78
216.6	147.7	217.4	+ 0.37
214.4	97.47	213.7	- 0.33
229.1	102.3	231.9	+ 1.22
214.4	102.1	215.6	+ 0.56
213.9	130.0	211.8	- 0.98
211.8	91.08	214.8	+ 1.42
224.3	91.20	223.8	- 0.22
212.3	112.3	211.2	- 0.52
222.2	136.9	224.0	+ 0.81
213.7	131.1	214.0	+ 0.14
221.5	148.7	220.5	- 0.45

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REPRODUCIBILITY

In order to get an idea of the reproducibility of this method for plutonium, a large series of pure plutonium solutions, having accurately known amounts of plutonium present, were analyzed. As mentioned in the section on reagents, specimens of pure plutonium metal dissolved in 0.05 N sulfuric acid served as stock solutions. For these studies definite volume aliquots of the plutonium solutions were electrolyzed and treated in the usual manner. Table VI gives some representative data that were selected at random from the 114 duplicate solutions that were analyzed.

Table VI

Analysis of Pure Plutonium Solutions

Micrograms of Pu Taken	Micrograms of Pu Found (Ave. of 2 Aliquots)	Percent Difference
25.97	26.82	+ 3.30
25.97	25.60	- 1.42
25.97	25.73	- 0.94
52.27	52.75	+ 0.92
52.27	52.03	- 0.46
52.27	52.27	0.00
74.62	74.82	+ 0.27
74.62	74.14	- 0.64
74.62	74.74	+ 0.16
99.26	99.75	+ 0.49
99.26	98.77	- 0.49
99.26	99.50	+ 0.24
122.2	122.1	- 0.10
122.2	122.3	+ 0.10
122.2	121.5	- 0.60
153.3	153.3	0.00
153.3	151.8	- 0.96
153.3	153.5	+ 0.16

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For this series of 114 duplicate samples a standard deviation of ± 0.92 percent was calculated. If instead of duplicate samples quadruplicate samples were considered, the standard deviation would be ± 0.52 percent. It seems rather over-optimistic to expect standard deviations of smaller magnitude from a spectrophotometric procedure. The calculated standard deviation as a function of the plutonium content is shown in Table VII.

Table VII

Variation of Standard Deviation with Plutonium Content

Micrograms of Pu in 10 ml	No. of Duplicates	Standard Deviation (%)
25.97	18	1.84
52.27	17	0.69
74.62	20	0.67
99.26	18	0.70
122.2	20	0.50
153.3	21	0.46

It seems apparent that if the determined amount of plutonium decreased below 25 micrograms in 10 milliliters the standard deviation would increase quite rapidly.

CONCLUSIONS

1. A spectrophotometric method for the determination of multimicrogram amounts of plutonium has been developed.
2. For best results certain interfering cations, namely iron(III), must be removed from the sample solution. Electrolysis using

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the mercury cathode is very successful in removing such ions.

3. This method should be directly applicable to any plutonium solution that contains interfering ions that are removable by the mercury cathode.
4. A standard deviation of ± 0.92 percent was calculated for duplicate results on 114 synthetic plutonium solutions.

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