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THE SPECTROPHOTOMETRIC DETERMINATION OF CERIUM IN PLUTONIUM

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ABSTRACT

A method is described for the determination of cerium in plutonium alloys containing 3 percent cobalt. A separation of the cerium is made by oxidizing the plutonium to the (VI) oxidation state with persulfate and precipitating the cerium as the fluoride using lanthanum fluoride as a carrier. After conversion of the fluoride precipitate to the sulfate, the cerium is again oxidized with persulfate and the amount present determined by measuring the absorbance of the sulfate solution at 320 millimicrons. Molybdenum, tantalum, iron, zirconium, neodymium and ruthenium present in small amounts do not interfere with the determination.

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INTRODUCTION

The high molecular extinction coefficient of cerium(IV)in solution has often been used in spectrophotometric methods for its determination, and conditions for the spectrophotometric determination of cerium in sulfate solutions have been recently described in the literature.(7,3,6,12) This method has the advantage of simplicity and specificity at least as far as the rare earth metals are concerned. The absorbance of cerium(IV) in alkaline peroxide solutions has also been widely used.(13,5,2,11) Several reagents have been suggested as a means of further increasing the sensitivity of the determination. These include ferrous orthophenanthroline,(4) oxine,(9) cupferron,(14) Sunchrome Pure Blue B,(8) and benzidine.(10) .

The method suggested by Medalia and Bryne(7) for determining cerium in sulfate solutions was used in the procedure described in this report for determining cerium in plutonium solutions after a preliminary separation from the plutonium. The use of absorption cells of longer light path increased the sensitivity satisfactorily and simply, thus eliminating the need for a more elaborate procedure. In practical analysis the large amounts of plutonium present interfered with the direct spectrophotometric determination of cerium, thereby requiring a preliminary separation of the two elements. This was accomplished by precipitating the cerium as the fluoride from a plutonium(VI) solution using lanthanum fluoride as a carrier. The precipitate was then converted to the soluble sulfate and the cerium oxidized to the (IV) state and determined spectrophotometrically. This method gave satisfactory results with plutonium solutions containing small amounts of several other elements and is the basis for the procedure described in this report.

CAUTION

Any work involving the handling of plutonium-containing materials should be done under approved conditions and in laboratories designed for the adequate protection of the worker. Rules recommended by the Health Group for the safe handling of such materials should be rigidly followed.

APPARATUS AND REAGENTS

Apparatus

1. Spectrophotometer, Beckman Model DU, equipped with holders for absorption cells of 1- and 10-cm. light path.

2. Absorption cells, quartz, 1-cm. light path, 3-ml. capacity; and 10-cm. light path, 6-ml. capacity.

3. Centrifuge, clinical, 110-volt, 60-cycle, equipped with glass centrifuge tubes of 50-ml. capacity.

4. Heating block, aluminum, with a built-in 750-watt heating unit, equipped with holes for holding 50-ml. centrifuge tubes and a hole for inserting thermometer.

5. Micropipets, with syringe, 200- and 100-μl. capacities.

6. Pipet, polyethylene, 0.5-ml. capacity, for use with 49% hydrofluoric acid.

7. Pipets, volumetric, inter-joint with syringe.

8. Measuring scoop, glass, made to contain approximately 1 gram of amonium persulfate.

9. Flasks, volumetric, pyrex, 10-ml. capacity.

Reagents

1. Standard Ceric Sulfate Solution (0.1 M). Add slowly with stirring 85.6 grams of $Ce(HSO_4)_4$ (G. Frederick Smith Chemical Co.) to 200 ml. of 0.6 N sulfuric acid. On solution, add 50 ml. of 36 N sulfuric acid and make up to 2 liters. (The solution used was approximately 1 N in sulfuric acid and was found to be 0.0973 M in total cerium by volumetric analysis.)

2. Standard Cerous Sulfate Solution (0.7 gram Ce/ml.). Prepare by reducing 5.00 ml. of the standard ceric sulfate solution with 0.1 N hydrogen peroxide, added dropwise until the solution turns colorless, then add 3 ml. of 36 N sulfuric acid and dilute to 100 ml. with distilled water. (Standard cerous solutions for use in obtaining calibration data may be prepared from this stock solution by appropriate dilution).

3. Plutonium Sulfate Stock Solution (10 mg. Pu/ml.). Add 1.00 ± 0.01 grams of pure plutonium metal to 33 ml. of 3 N sulfuric acid and heat on a steam bath until solution is complete. After cooling, dilute to 100 ml. with distilled water. (It is advisable to centrifuge this solution before using to avoid introduction of undissolved foreign material.)

4. Silver Nitrate Solution (0.25%). Dissolve 0.25 gram of silver nitrate (Mallinckrodt Chemical Works, analytical reagent grade) in distilled water and dilute to 100 ml. Store in low actinic glass bottle.

5. Potassium Persulfate Solution (2.4%). Dissolve 2.4 grams of $K_2S_2O_8$ (Mallinckrodt analytical reagent grade) in distilled water and dilute to 100 ml.

6. Lanthanum Nitrate Solution (10 mg. La/ml.). Dissolve 2.34 grams of $La(NO_3)_3$ (Lindsay Chemical Co.) in distilled water and dilute to 100 ml.

7. Ammonium Persulfate $(NH_4)_2S_2O_8$. Mallinckrodt Chemical Works, analytical reagent grade.

8. Hydrofluoric Acid (49%). "Baker Analyzed" reagent.

All other reagents used were of analytical reagent grade. Distilled water of low conductivity (<0.1 p.p.m. salinity) and free from organic material was used in the preparation of all solutions.

RECOMMENDED PROCEDURE

Sulfate or nitrate solutions of the sample may be used for analysis. Chloride ion interferes with the persulfate oxidation and should not be present. Small amounts of hydrofluoric acid added to ensure solution of the sample do not interfere.

1. Add a known aliquot of a plutonium-cerium solution containing 50 mg. of plutonium to a 50-ml. centrifuge tube and adjust the volume to approximately 10 ml. with 1 N sulfuric acid.

2. Add 0.2 ml. of silver nitrate solution (0.25) and approximately 1 gram of ammonium persulfate and heat in a steam bath for 15 minutes.

3. Remove from the steam bath, add 0.1 ml. of lanthanum nitrate solution (1 mg. of La) and 0.5 ml. of 49% hydrofluoric acid, stir, and allow to stand for 5 minutes.

4. Centrifuge the solution for 5 minutes, decant by suction, and invert the tube to allow the remaining solution to drain. (Remove the small amount of liquid collected at the rim of the tube by suction into a container suitable for the storage of plutonium residues.)

5. Add approximately 2 ml. of 1 N hydrofluoric acid to the precipitate in the tube and stir with a platinum rod.

6. After rinsing the rod with 1 N hydrofluoric acid, again centrifuge the solution for 5 minutes and decant in the manner described in Step 4.

7. Add 0.1 ml. of 36 N sulfuric acid to the precipitate in the tube and heat in an aluminum block at 200° C for 30 minutes.

8. After removing the tube from the block, cool slightly and add 7 ml. of 1 N sulfuric acid, 0.2 ml. of silver nitrate solution (0.25%) and 1 ml. of potassium persulfate solution (2.4%).

9. Place the tube in the steam bath and heat for 15 minutes.

10. Remove from the steam bath, cool to room temperature, and transfer the solution quantitatively to a 10-ml. volumetric flask using 3 or 4 rinses with distilled water.

11. Adjust the volume to 10 ml. with distilled water, mix well, and transfer a portion to a quartz absorption cell of appropriate length.

12. Measure the absorbance of the solution at 320 mμ against a reference solution containing the same amount of sulfuric acid, silver, and persulfate (see Step 8) and treated according to Steps 9-11 of the RECOMMENDED PROCEDURE.

13. Determine the cerium content by means of a calibration curve prepared by treating standard plutonium-cerium solutions according to Steps 1-12 of the RECOMMENDED PROCEDURE.

EXPERIMENTAL

Ceric Sulfate Solutions

A series of solutions containing varying known amounts of cerium were treated according to Steps 8-11 of the RECOMMENDED PROCEDURE. This was done in order to check the method for determining cerium and to aid in the estimation of the recovery of cerium from plutonium solutions. The solutions were prepared by appropriate dilution of the cerous sulfate stock solutions (see Reagents), and absorption cells with 1- and 10-centimeter light paths were used. The data obtained are shown in Tables I and II and the average absorbance values are plotted versus the cerium concentration in Figures 1 and 2. The lines connecting

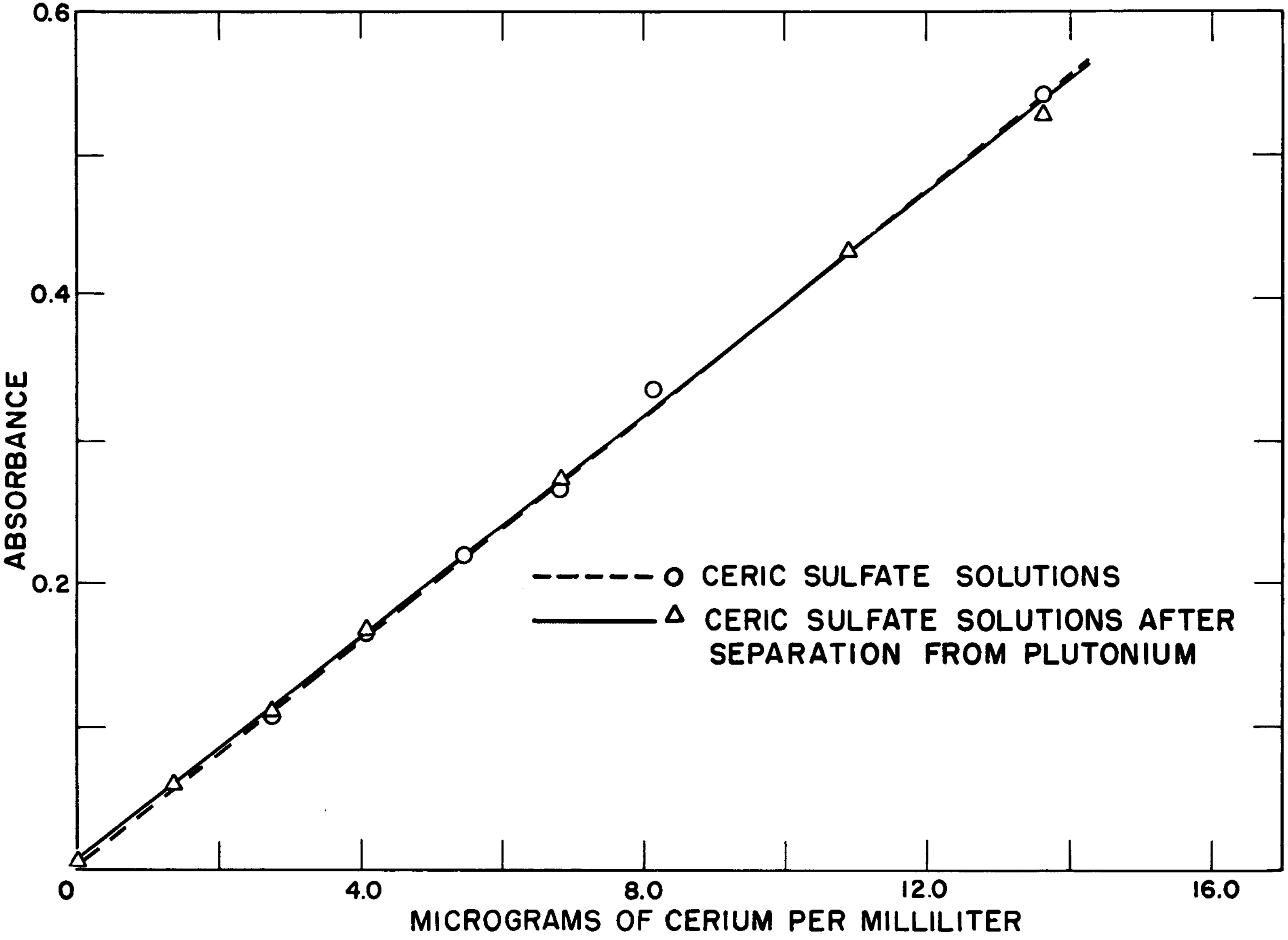

Figure 1. Absorbance of ceric sulfate solutions (1-cm. cells).

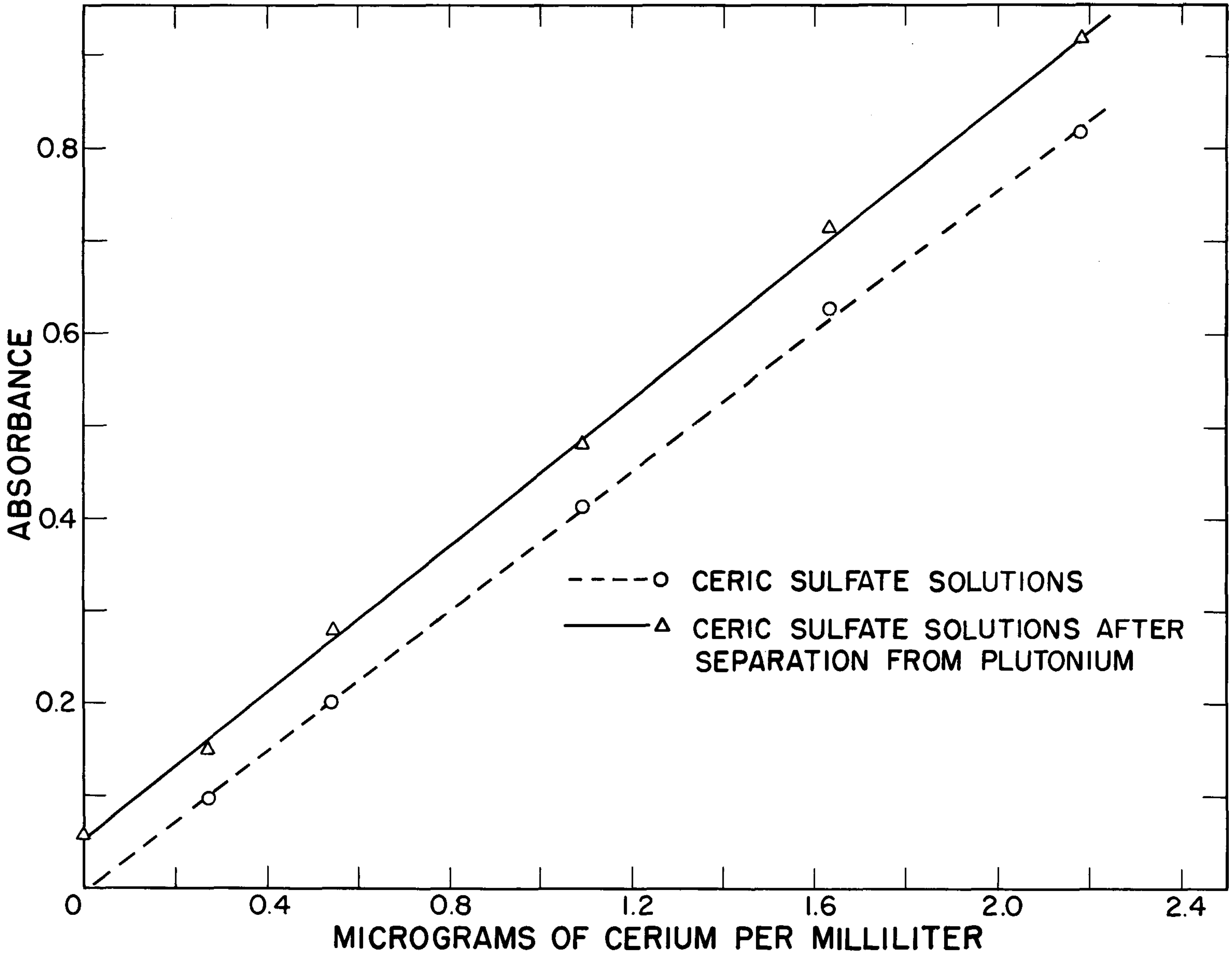

Figure 2. Absorbance of ceric sulfate solutions (10-cm. cells).

the points were drawn according to the statistical method of least squares. The value for the molar extinction coefficient for cerium(IV) in 1 N sulfuric acid at 320 millimicrons was calculated from the data in Table I to be 5560 in good agreement with the value 5580 reported in the literature.(7)

Table I

ABSORBANCE OF CERIC SULFATE SOLUTIONS
(1-cm. cells, λ = 320 mμ, total volume 10 ml.)

μg. of Ce/ml.	2.72	4.09	5.45	6.81	8.17	13.62
Absorbance	0.107	0.168	0.221	0.266	0.338	0.540
	0.108	0.166	0.218	0.266	0.337	0.540
Average Absorbance	0.108	0.167	0.219	0.266	0.338	0.540

Table II

ABSORBANCE OF CERIC SULFATE SOLUTIONS
(10-cm. cells, λ = 320 mμ, total volume 10 ml.)

μg. of Ce/ml.	0.272	0.545	1.09	1.63	2.18
	0.097	0.199	0.410	0.620	0.819
Absorbance	0.101	0.196	0.405	0.637	0.818
	0.098	0.210	0.427	0.630	0.817
Average Absorbance	0.099	0.202	0.414	0.629	0.818

Cerium-Plutonium Solutions

A series of plutonium sulfate solutions containing 50 milligrams of plutonium and known amounts of cerium were treated according to Steps 1-12 of the RECOMMENDED PROCEDURE. These solutions were prepared by mixing aliquots from standard cerous and plutonium sulfate solutions (see Reagents). The plutonium solution was centrifuged before using to prevent the addition of any insoluble material that might be present. Absorption cells of both 1- and 10-centimeter light path were used. The results obtained are shown in Tables III and IV. The average absorbance values are plotted versus the cerium concentration in Figures 1 and 2. The line through the points was drawn according to the statistical method of least squares.

Table III

ABSORBANCE OF CERIC SULFATE SOLUTIONS AFTER SEPARATION FROM PLUTONIUM
(1-cm. cells, $\lambda = 320$ mµ, total volume 10 ml.)

µg. of Ce/ml.	0	1.36	2.72	4.09	6.81	10.90	13.62
Absorbance	(0.005	0.063	0.119	0.167	0.275	0.435	0.530
	(0.006	0.056	0.110	0.168	0.274	0.431	0.535
	(0.007	0.060	0.111	0.168	0.272	0.434	0.519
	(0.005	0.060	0.111	0.171	0.276	0.435	0.526
Average Absorbance	0.006	0.060	0.113	0.169	0.274	0.434	0.528

Table IV

ABSORBANCE OF CERIC SULFATE SOLUTIONS AFTER SEPARATION FROM PLUTONIUM

(10-cm. cells, λ = 320 mμ, total volume 10 ml.)

μg. of Ce/ml.	0	0.272	0.545	1.09	1.63	2.18
Absorbance	0.056	0.156	0.269	0.475	0.724	0.918
	0.058	0.149	0.284	0.491	0.708	0.918
	0.057	0.152	0.282	0.492	0.715	0.912
	0.068	0.153	0.284	0.466	0.716	0.914
Average Absorbance	0.060	0.153	0.280	0.481	0.716	0.916

STATISTICAL RESULTS

A standard deviation for each cerium concentration used was calculated from the data in Tables III and IV based on the total number of determinations.(1) The results of these calculations are shown in Tables V and VI.

Table V

RESULTS OF STATISTICAL TREATMENT OF DATA

(1-cm. cells, 50-mg. Pu sample, 28 det'ns)

Cerium (μg.)	Cerium (wt. %)	Standard Deviation (relative %)
13.6	0.027	10.7
27.2	0.054	5.3
40.9	0.082	3.5
68.1	0.136	2.1
109.0	0.218	1.3
136.2	0.272	1.1

Table VI

RESULTS OF STATISTICAL TREATMENT OF DATA
(10-cm. cells, 50-mg. Pu sample, 24 det'ns)

Cerium (µg.)	Cerium (wt. %)	Standard Deviation (relative %)
2.72	0.0054	10.0
5.45	0.0109	5.1
10.90	0.0218	2.5
16.34	0.0326	1.7
21.79	0.0436	1.4

The percent recovery of the cerium as calculated from comparison of the slopes of the absorbance-concentration curves is 97 and 104 relative percent for the 1- and 10-centimeter cells respectively.

EFFECT OF VARIOUS IONS ON THE PROCEDURE

Cations

Because the procedure was devised for use with plutonium alloys which were expected to contain several elements, it was necessary that the effect of these elements be investigated. The following elements listed in Table VII, present either singly or collectively in the original solution in the amounts indicated, were found to change the absorbance readings less than 0.005 of an absorbance unit.

Table VII

NON-INTERFERING ELEMENTS

Element Added	Element/Ce (wt. ratio)	Weight % (based on Pu)
Potassium	44	3.6
Cobalt	36	3.0
Tantalum	36	3.0
Iron	36	3.0
Neodymium	24	2.0
Molybdenum	12	1.0
Zirconium	12	1.0
Ruthenium	12	1.0

Ruthenium, when present, is distilled off in the first persulfate oxidation and causes annoyance by coating the glassware with a black oxide. This situation may be alleviated by evaporating the sample to dryness with perchloric and sulfuric acids prior to analysis.

Increasing the plutonium sample size from 50 to 100 milligrams increased the size of the absorbance blank from 0.006 to 0.012 unit (using 1-cm. cells).

Interference of various metal ions with the absorbance of ceric sulfate solutions is discussed by Medalia and Byrne.(7) Since many of these ions would probably be separated from the cerium by the lanthanum fluoride precipitation step, they are not serious considerations.

Anions

Sulfate and nitrate ions do not interfere with the method; however, appreciable amounts of chloride hinder the persulfate oxidation due to the formation of silver chloride. Chloride ions can be effectively removed by evaporating the solution to dryness two or three times with sulfuric acid. It was found that fluoride ions could be tolerated when they were present in the solution in small amounts such as is necessary to prevent tantalum from precipitating.

CONCLUSIONS

By choosing absorption cells of appropriate length, cerium in plutonium solutions may be determined by the method described in this report in concentrations of approximately 0.01 to 0.3 weight percent with a standard deviation of 5 to 1 percent, respectively. The determination of higher concentrations of cerium with comparable precision is possible by reduction of the sample size. The presence of several metals as impurities does not appreciably interfere with the determination.

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