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Los Alamos

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DETERMINING CERIUM IN PLUTONIUM BY ANION EXCHANGE AND X-RAY FLUORESCENCE

by

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ABSTRACT

This report describes a procedure for determining cerium in plutonium using an anion-exchange separation and x-ray fluorescence. We add lanthanum to the plutonium solution as an internal standard, oxidize the plutonium to Pu^{+4}, and pass the solution through an anion-exchange column with 8M HCl. The Pu^{+4} sorbs to the resin, and the cerium and lanthanum pass through the column completely. We evaporate the solution containing the cerium and the lanthanum to 0.5 mL for pipetting onto a resin paper disc. The Pu^{+4} is eluted off the column using 0.1M HCl. We then measure the K_α x-ray line for both cerium and lanthanum. The ratio of cerium to lanthanum for the sample is then compared with those from the standards. This method has a precision of 2.8% relative standard deviation for cerium over a concentration range of 0.1 to 5% cerium.

INTRODUCTION

It is difficult to determine accurately cerium in the presence of plutonium. Therefore, we separate the cerium from the plutonium. The sample can then be handled more easily and safely with the plutonium removed.

To achieve the best precision possible, we add lanthanum as an internal standard at the beginning of the analysis. Because it behaves like cerium, lanthanum compensates for any changes that may occur in the sample during processing.

We evaporate the solution containing the cerium and the lanthanum to ≈0.5 mL and pipet it onto a resin disc paper. This process greatly improves the x-ray intensity for cerium and lanthanum over that obtained from reading solutions.

Equipment and Reagents

In this work, we use the following equipment:

- Aluminum cell holder, 50-mm o.d.
- Columns, glass, ion-exchange (32 by 200 mm)
- Glass rod, bent and flattened on one end
- Heat lamps, infrared, red end, 250 W
- Hot plate, 150 by 180 mm
- Mylar film, 6 μm thick
- Sample cells, x-ray, Chemplex, plastic, number 1430, 32-mm o.d.

- Teflon disc, perforated; to fit inside ion-exchange column

- X-ray spectrometer; Siemens SRS 300 microprocessor-controlled sequential x-ray spectrometer system; rhodium-target x-ray tube

We also use the following reagents:

- Anion-exchange resin-loaded paper, Reeve-Angel SB-2

- Hydrochloric acid, 12M, 8M, and 0.1M

- Hydrofluoric acid, 1.3M

- Ion-exchange resin, analytical grade anion-exchange resin, AG1x4, 50 to 100 mesh, chloride form, Bio-Rad Laboratories

- Nitric acid, 15.7M

- Cerium solution, 1.000 mg/mL

- Lanthanum solution, 1.000 mg/mL

PROCEDURE

For determining cerium in plutonium, we

1. Place a 1-g sample of plutonium in a 20-mL beaker, add 5 mL of 8M HCl, and transfer the dissolved plutonium to a 100-mL volumetric flask.

2. Pipet 2 mL of the lanthanum solution into a 20-mL beaker and add the appropiate amount of plutonium solution to the beaker.
   Note: If the cerium concentration is relatively high, 10 mL of the plutonium solution (10 mg Pu/mL) should give sufficient cerium for analysis. However, if the cerium level is low, it may be necessary to take the entire 1-g sample of plutonium. It is advisable to keep the amount of cerium to moderate quantities. We want enough cerium to produce a strong x-ray signal but not so much that it will pile up on the resin disc. The ideal amount may be 2-3 mg.

3. Add 1.0 mL 15.7M HNO_3 by pipet to convert the Pu^{+3} to Pu^{+4}, let the beaker set for 2 hours or overnight if possible to reduce the effervescence of HCl, and heat gently to evaporate the solution to ≈1 mL volume.
   Note: This evaporation procedure should be done only once. Additional drying may convert Pu^{+4} to Pu^{+6}, which will come through the column with the cerium and lanthanum.

4. Add 8-10 mL of 8M HCl to the beaker and dissolve the sample; heat if necessary.

5. Fill the anion exchange column with resin to within 2-3 cm of the top and condition the column with 8-10 mL of 8M HCl four times, place a 20-mL beaker under the column to catch the solution that will pass through, and place the perforated Teflon disc on top of the resin.

6. Add the plutonium solution to the top of the column by pouring the solution down a bent and flattened glass rod onto the Teflon disc, rinse the 20-mL sample beaker with 2-3 mL of 8M HCl, and add this to the column after the plutonium solution has stopped flowing. We continue to rinse with the 8M HCl until 20 mL of solution is collected in the beaker under the column.
   Note: By passing the sample through the column, we have sorbed the Pu^{+4} to the resin and have allowed the cerium and lanthanum to pass completely through the solution. The flattened glass rod and perforated Teflon disc help keep the plutonium near the top of the column so more resin is available to sorb the plutonium. This has achieved our separation, and we need only start the evaporation of the cerium and lanthanum solution and recover the plutonium from the column.

7. Add 0.1M HCl to the column to elute the Pu^{+4} from the column.

8. Transfer the solution to a 5-mL beaker when the 20 mL of cerium and lanthanum has evaporated to about 2 mL and continue evaporating until only about 0.5 mL is left.

9. Pipet the solution onto a 25-mm-diam anion-exchange resin-loaded paper supported on a clean 5-mL beaker. We then pipet ≈15 μL of the cerium-lanthanum solution at a time, rinse the 5-mL beaker once with 100 μL of 8M HCl, and add the solution to the resin disc.

10. Use a heat lamp to help speed the drying process during the pipetting. When the resin disc is dry after pipetting, we place the disc between two 50-mm squares of Mylar film over a 32-mm-diam x-ray

sample cell and attach the cell rings to hold the film in place.

11. Put the sample cell into an aluminum cell holder, place in the Siemens spectrograph, and read each of the following 2θ settings:

2θ	Measurement
13.93	Background 1
14.41	Ce K_{α}
14.74	Background 2
14.75	Background 3
14.97	La K_{α}
15.41	Background 4

Figure 1 shows a plot of intensity vs 2θ for cerium and lanthanum after separation from a 500-mg sample of plutonium by anion exchange. The intensity of cerium is ≈2800 c/s.

We analyze the sample with the spectrographic parameters shown in Table I.

Table I. X-Ray Operating Parameters

X-ray tube	Rhodium
Voltage	60 kV
Current	50 mA
Counters	Scintillation and Flow
Analyzing Crystal	LiF 220
Soller slit	Fine
Counting time	30 s

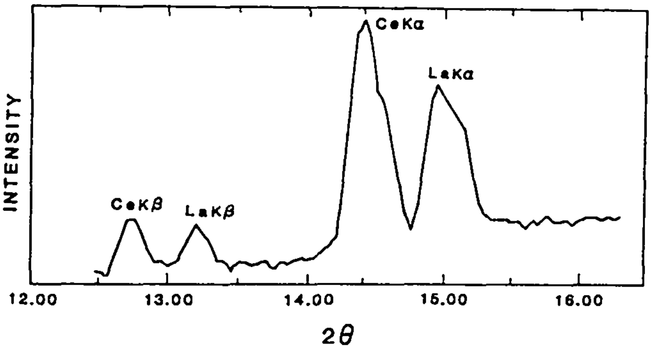

Fig. 1. Wavelength scan for cerium and lanthanum.

STANDARDS

The standards contain known amounts of cerium and lanthanum as listed below:

Standard No.	Cerium (mg)	Lanthanum (mg)	Plutonium (mg)
Ce-1	0.000	2.000	500
Ce-2	0.000	2.000	500
Ce-3	1.000	2.000	500
Ce-4	1.000	2.000	500
Ce-5	3.000	2.000	500
Ce-6	3.000	2.000	500
Ce-7	5.000	2.000	500
Ce-8	5.000	2.000	500

We place 10 g of high-purity plutonium in a covered 250-mL beaker and dissolve with 8M HCl and a small amount of 1.3M HF. Next, we transfer the plutonium solution to a 100-mL volumetric flask and add 5 mL of 15.7M HNO_3 to the flask to oxidize the plutonium to Pu^{+4}.

At this point, we pipet the appropriate amounts of the cerium solution into each of the eight 20-mL beakers and add 2.000 mg of the internal standard, lanthanum, and 500 mg of plutonium to each beaker.

These standards are analyzed as described in the "Procedure" section. Figure 2 shows a plot of intensity ratios (Ce/La) vs concentration of cerium.

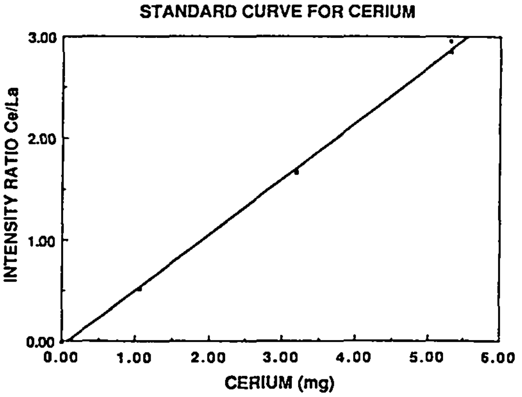

Fig. 2. Plot of intensity ratios (Ce/La) vs concentration of cerium.

CALCULATIONS

The Siemens spectrometer gives the net intensity values. To obtain the Ce/La ratios, we divide the cerium counts per second by the lanthanum counts per second.

We do a least squares fit for the standards, relating Ce/La ratios to the cerium concentrations. To calculate the concentration of cerium in the analyzed samples, we use the coefficients for the equation representing this standard curve.

PRECISION

We established the precision of the method by analyzing prepared samples repeatedly. Known amounts of the well-characterized cerium solution were pipetted into beakers, and the appropriate amounts of lanthanum and plutonium were added. We then treated the samples as described in the "Procedure" section. The results are shown in Table II. The average relative standard deviation for 0.1 to 5% cerium is 2.80%.

TABLE II. Precision of Method

Cerium (%)	Number of Determinations	Relative Standard Deviation (%)
0.1	6	3.47
0.5	6	2.64
1.0	6	3.08
2.5	6	1.59
5.0	6	3.01

ACCURACY

The accuracy of the method was determined by preparing five levels of cerium solutions and treating them as described in the "Procedure" section. The results are given in Table III. The average recovery for the range 0.1 to 5% is 100.7%.

DISCUSSION

The selection of an internal standard for cerium was difficult. Lanthanum was initially selected and rejected because it overlapped with cerium when the LiF(200) crystal was used. Next, barium was considered but was rejected because its K_β line interferred with the cerium K_α line. Cessium was tried but was found to be chemically incompatible with our system.

A second consideration of lanthanum but this time with the LiF(220) crystal proved promising. The dispersion was sufficient although significant intensity was lost by switching from the LiF(200) to the LiF(220) crystal.

TABLE III. Accuracy of Method

Cerium Added (%)	Number of Determinations	Cerium Recovery (%)
0.1	6	99.5
0.5	6	99.7
1.0	6	101.5
2.5	6	100.3
5.0	6	102.6

The recommended lines for cerium and lanthanum are the L lines, and for relatively high concentrations, this is correct. However, the L lines are much weaker than the corresponding K lines and, at low levels of cerium, are inadequate.

Our observation was that the intensity of the cerium and lanthanum K lines, although significantly stronger than that of the L lines, was still much weaker than would be obtained with a corresponding amount of yttrium.

From previous work,[1] we know that yttrium has abundant intensity, sufficient to read yttrium and its internal standard in solutions. In this case, cerium and its internal standard could only be analyzed by drying the solution onto a resin disc. Part of this reduction of intensity is due to using LiF(220), which gives greater dispersion but at a cost of reduced intensity. Still the loss of intensity between yttrium and cerium was greater than can be explained by the use of LiF(220) crystal alone.

Jenkins and DeVries[2] offer the explanation that the lower limit of a spectrometer is determined by the angle (2θ) at which the analzying crystal no longer reflects most of the sample x-rays. This 2θ lower limit is typically around 22 for our type of spectrometer. The 2θ angles we are using are $\approx$15, so we are below the limit for getting the best intensity from our desired element, cerium. However, the internal standard, lanthanum, has a very similar 2θ setting; thus it is able to compensate for this condition.

In studying the precision of this method, we observed that recovering 5% cerium from 1000-mg of plutonium gave a precision of 5 to 6% and that recovering 5% cerium from smaller amounts of plutonium, e.g., 500-mg, gave a precision of ≈3%. For this reason, we suggest that the sample size be adjusted to avoid getting 4 to 6-mg of cerium in 1000-mg of plutonium.

An important consideration is the amount of plutonium that comes off the column with the cerium and the lanthanum. The procedure, as described here, gave an average of 6 μg of plutonium for each of six replicates containing 1040 mg of plutonium before the anion exchange.

Another group of six replicates, containing 540 mg of plutonium before the anion exchange, gave an average of 12 μg of plutonium on each disc.

We believe the important feature in this excellent separation of plutonium from cerium and lanthanum is control of the conversion of Pu^{+3} to Pu^{+4} only. The factors of significance are the addition of 1.0 mL of 15.7M HNO_3 to the plutonium, the slow evaporation to ≈1 mL of volume done only once, and no addition of 1.3M HF to the plutonium solution.

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2. R. Jenkins and J. L. DeVries, "Dispersion," in *Practical X-Ray Spectrometry* (Springer-Verlag, New York, 1967), Chap. 2, pp. 26-34.

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