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ANION EXCHANGE X-RAY FLUORESCENCE DETERMINATION OF URANIUM IN PLUTONIUM

by

Calvin J. Martell and James M. Hansel

ABSTRACT

An improved method is described for the determination of uranium in plutonium metal and plutonium compounds using x-ray fluorescence following two anion-exchange separations. Uranium (as the chloride complex) is first separated from most of the 500-mg plutonium sample using anion-exchange resin in glass columns with 8*M* HCl and ascorbic acid. The eluate solution from this separation contains uranium as $(UO_2Cl_3)^-$, Pu^{+3}, and a small amount of Pu^{+4}. This solution is dried and redissolved in 8*M* HCl and ascorbic acid to reduce the Pu^{+4} to Pu^{+3}; it is then pipetted onto filter paper impregnated with anion-exchange resin. The plutonium is washed from the resin filter paper with 8*M* HCl, leaving uranium adsorbed on the paper. The $L_{\alpha 1}$ x-ray line for the uranium is measured and compared to standards. The precision is 4% relative standard deviation for the concentration range from 5 to 200 μg uranium. The minimum detection limit is 1 μg uranium.

INTRODUCTION

In the original method,[1] 12*M* HCl was used to dissolve the plutonium sample, which was then dried and redissolved in 6*M* HCl to perform the anion-exchange separation of uranium from plutonium. The lower the molarity of HCl used in the anion-exchange separation, the lower the recovery is for uranium.[2] Higher molarity of HCl results in greater amounts of Pu^{+3} adsorbing with uranium on the resin during the anion-exchange separation.

The original method accepted 92% uranium recovery and whatever amount of plutonium (as much as 1000 μg) that remained with uranium during the anion-exchange separation step. In the improved method, 8*M* HCl is used both to dissolve the plutonium sample and carry out the anion-exchange separation. This simplification saves time and eliminates the use of the very corrosive 12*M* HCl in our dry boxes.

In the original method, the uranium was pipetted onto the resin filter paper disc with 0.1*M* HCl. At this acid molarity, uranium did not adsorb onto the resin but was merely transferred to the resin disc by evaporation. The uranium tended to migrate to the outer edge of the disc, resulting in a poor presentation for x-ray excitation. In the improved method, the uranium solution is transferred to the resin disc with 8*M* HCl. The uranium is adsorbed by the resin in the center of the disc while the nonadsorbing trivalent plutonium migrates to the edge of the disc[3] where it can be easily removed by a 1-mℓ wash with 8*M* HCl. The uranium centered on the disc is then well positioned for x-ray excitation.

APPARATUS

- Aluminum cell holder, 50-mm o.d.
- Aluminum foil, 28- by 80-mm, rolled into a cylinder
- Columns, glass, ion-exchange, 19- by 200-mm
- Flask, filtering, micro, with tubulation, 125-mℓ
- Funnel, Hirsch, size 000A
- Heat lamps, infrared, red end, 250-W
- Hot plate, 150- by 180-mm
- Micropipet, glass with syringe, 200-μℓ
- Mylar film, 6-μm thick
- Sample cells, x-ray, Chemplex, plastic, series 1400, 32-mm-o.d.
- Slide, glass, moated
- Spatula, porcelain, spoon at one end
- X-ray spectrograph; vacuum, Philips Electronics, Inc., LiF crystal; molybdenum-target x-ray tube; and scintillation detector with associated electronic counting circuitry.

REAGENTS

- Anion-exchange resin-loaded paper, Reeve-Angel SB-2
- Ascorbic acid, Eastman Organic Chemicals, L-ascorbic acid
- Hydrochloric acid, 12*M*, 8*M*, and 0.1*M*
- Ion-exchange resin, analytical grade anion-exchange resin, AG1×4, 50- to 100-mesh, chloride form, Bio-Rad Laboratories
- Nitric acid, 15.7*M*
- Uranium reference solution (5 mg/mℓ): Dissolve 1250 mg of NBS SRM 960 uranium metal in 12*M* HCl. (Use H_2O_2 to help dissolve the uranium.) Dilute to a volume of 250 mℓ with 1*M* HCl.
- Uranium reference solution (25 μg/mℓ): Pipet 5 mℓ of the 5-mg/mℓ uranium solution into a 1000-mℓ volumetric flask and dilute with 1*M* HCl.

DISSOLUTION OF PLUTONIUM COMPOUNDS

Plutonium oxide is dissolved using the sealed tube dissolution system.[4] The resulting solution is transferred to a 20-mℓ beaker and evaporated to dryness. The residue is dissolved in 5 mℓ 8*M* HCl.

Plutonium fluoride is heated and dissolved with 15.6 *M* HNO_3 in a covered 20-mℓ beaker. After all the pink PuF_4 has been dissolved and converted to $Pu(NO_3)_4$, the solution is evaporated to dryness and 5 mℓ of 8*M* HCl are added to dissolve the $Pu(NO_3)_4$. The solution is then dried. The addition of 8*M* HCl and the drying of the solution are done three times to ensure complete conversion of the $Pu(NO_3)_4$ to $PuCl_4$.

Plutonium nitrate solution is evaporated in a 20-mℓ beaker and dissolved in 5 mℓ 8*M* HCl and dried. This is repeated three times to ensure complete removal of HNO_3.

Plutonium metal is dissolved with 5 ml 8*M* HCl in a covered 20-mℓ beaker. After the plutonium metal is dissolved, the watch glass and sides of beaker are rinsed with 8*M* HCl.

SEPARATION OF URANIUM

To the plutonium chloride sample obtained by the treatment described in the previous section, add 8*M* HCl to a total volume of 15 mℓ in a beaker containing the plutonium sample. Add 150 mg of ascorbic acid and stir to dissolve (ensuring that as much of the plutonium as possible is in the trivalent state).

Condition the resin in the ion-exchange column with approximately 30 mℓ of 8*M* HCl. Transfer the 8*M* HCl solution of plutonium to the ion-exchange column. Use an additional 15 mℓ of 8*M* HCl to rinse the beaker and wash the blue trivalent plutonium through the column.

Elute the uranium and the small amount of remaining plutonium from the column with 20 mℓ of 0.1*M* HCl. Evaporate the eluate solution to approximately 2 mℓ and transfer to a 5-mℓ beaker using 0.1*M* HCl. Evaporate this solution to incipient dryness; add 200 μℓ of 8*M* HCl-ascorbic acid and swirl the beaker to dissolve the residue. Pipet the solution onto a 25-mm-diam anion-exchange resin-loaded paper supported by a moated glass slide. Pipet approximately 15 μℓ of the uranium solution at a time. Rinse the 5-mℓ beaker twice with 100 μℓ of 8*M* HCl and pipet onto the resin paper also. Place the moist resin paper onto a Hirsch funnel that is under a slight vacuum. Gently and slowly drip 1 mℓ of 8*M* HCl onto the outer edge of the resin paper to wash the blue trivalent plutonium from the resin paper into the filtering flask. Allow the resin paper to air-dry while remaining on the Hirsch funnel. (A heat lamp speeds the drying.)

X-RAY FLUORESCENCE MEASUREMENT

Place a 50-mm square of Mylar film over a 30-mm-diam x-ray sample cell; place the dried resin paper on the Mylar film; then position a second 50-mm square of Mylar film over the resin paper. Attach the x-ray cell rings to hold the resin paper firmly in position between the two layers of Mylar film.

Remove the bottoms from the cells to be used and place a thin sheet of aluminum, rolled into a cylinder, into the cell from the bottom. The aluminum cylinder reduces background noise from the plastic x-ray cells.

Next place the cell containing the resin paper and the aluminum cylinder in an aluminum cell holder and put it into the x-ray spectrograph. Excite the sample using the molybdenum-target x-ray tube. Measure for 60 s each, (1) the intensity for a background, (2) the uranium $L_{\alpha 1}$, and (3) a second background. The 2θ settings are as follows:

2θ	MEASUREMENT
24.00	Background
26.14	Uranium $L_{\alpha 1}$
27.14	Background

X-RAY OPERATING PARAMETERS

X-ray tube	Molybdenum
Potential	50 kV
Current	30 mA
Counter	Scintillation
Analyzing crystal	LiF
Counting time	60 s

REFERENCE MATERIALS

Treat high-purity plutonium metal as described in the section, *Separation of Uranium,* to remove any uranium that may be present in the plutonium. Add 0.5 g of this freshly anion exchanged trivalent plutonium to each of six 20-mℓ beakers, and pipet the appropriate amounts of the uranium reference solution (25 μg U/mℓ). The reference materials should have the following makeup:

Beaker No.	Uranium (μg)	Plutonium (mg)
1	0	500
2	0	500
3	100	500
4	100	500
5	200	500
6	200	500

Analyze these reference materials, containing known amounts of uranium, as described in the *Separation of Uranium section.*

CALCULATIONS

Convert the intensities for the two backgrounds and the uranium line to counts per second (c/s). Average the c/s for the two backgrounds and subtract this average from the uranium c/s. Do a least squares fit relating uranium c/s vs uranium concentration. Use the coefficients for the equation (representing the calibration curve for the uranium reference materials) to calculate the concentration of uranium in analyzed samples.

MINIMUM DETECTABLE LIMIT

The minimum detectable limit (MDL) of an element is defined as the lowest concentration detectable in a given matrix. The MDL can be obtained in different ways, three of which are discussed.

In x-ray fluorescence, primary factors affecting the MDL are the peak-to-background (P/B) ratio and the precisions of the peak-line and background-intensity measurements. The difficult operation of determining the background intensity may be done several ways: (1) the total continuous spectrum is calculated; (2) in a sample containing the desired element, the background under the element peak is interpolated from high- and low-background measurements; and (3) the line intensity of the desired element is measured on a matrix free of the desired element (which would be a blank).

Once the background is determined, the MDL may be calculated by

$$\mathrm{MDL} = (3\sqrt{C_b})/S \ , \tag{1}$$

in which 3 equals the factor to convert standard deviation to the 99% confidence level, C_b is the number of counts in background, $\sqrt{C_b}$ is an approximation of the standard deviation of the background counts, and S is the number of counts per unit amount of element (commonly known as the slope of a calibration curve).

Some experimenters calculate the MDL by

$$\mathrm{MDL} = (3\sqrt{2C_b})/S \ . \tag{2}$$

The use of $2C_b$ rather than C_b is based on Heinrich's contention[5] that, near the detection limit, counting errors for both line and background intensities must be considered.

Our calculation of MDL is

$$\mathrm{MDL} = (3\sigma)/S \ , \tag{3}$$

where σ is the actual standard deviation of the desired element measured at zero concentration. To use Eq. (3), the intensities of the desired element are measured on several blanks and the standard deviation calculated. This equation implies that a line intensity equal to three times the standard deviation for measuring blanks should be measurable above the background 99% of the time.

We feel Eq. (3) is the best one to use because we could obtain the actual standard deviation of the line intensity on several blanks. The alternative is to use the less desirable square root of the background counts, which is only an approximation to the standard deviation of the line intensity.

In other situations, it may not be possible to have blanks completely free of the desired element, thus it would be necessary to use the square root of the background counts as in Eqs. (1) and (2).

Our calculated MDL using Eq. (3) is 1 µg of uranium.

PRECISION

The precision of the method was established by repeated analysis of plutonium samples, some with added amounts of uranium. The results are shown in Table I.

TABLE I. Precision of Method

Uranium (µg)	Number of Determinations	Relative Standard Deviation (%)
4.5	10	5.4
41.4	4	2.1
104.1	5	2.0
14.6	10	6.6
18.4	10	3.8
186.5	10	3.2

The average relative standard deviation for 5 to 200 µg uranium is 3.9%.

ACCURACY

To assess accuracy, a uranium reference solution (25 µg/mℓ) was used to add known amounts of uranium to pure samples of plutonium, which were then treated as described in the section entitled *Separation of Uranium.* The results are given in Table II.

TABLE II. Accuracy of Method

Uranium Added (µg)	Uranium Measured (µg)	Uranium Recovery (%)
9.9	9.9	100.0
61.4	63.0	102.6
112.9	116.0	102.8
216.0	214.0	99.1
422.1	419.3	99.3

The average recovery for the range from 10 to 400 µg uranium is 100.8%.

DIVERSE ION EFFECTS

Interfering elements are those that sorb and elute on anion-exchange resin partially or completely with uranium, particularly those having common x-ray lines that overlap the uranium $L_{\alpha 1}$ line. Elements that sorb and elute with uranium are iron and gallium. Large amounts can interfere by using resin sites, thereby causing loss of uranium. An element that has overlapping x-rays and also sorbs and elutes with uranium on anion exchange resin is gold. At the highest levels studied, of 1000 µg each of iron, gallium, and gold, no x-ray intensities were detected at the uranium $L_{\alpha 1}$ line.

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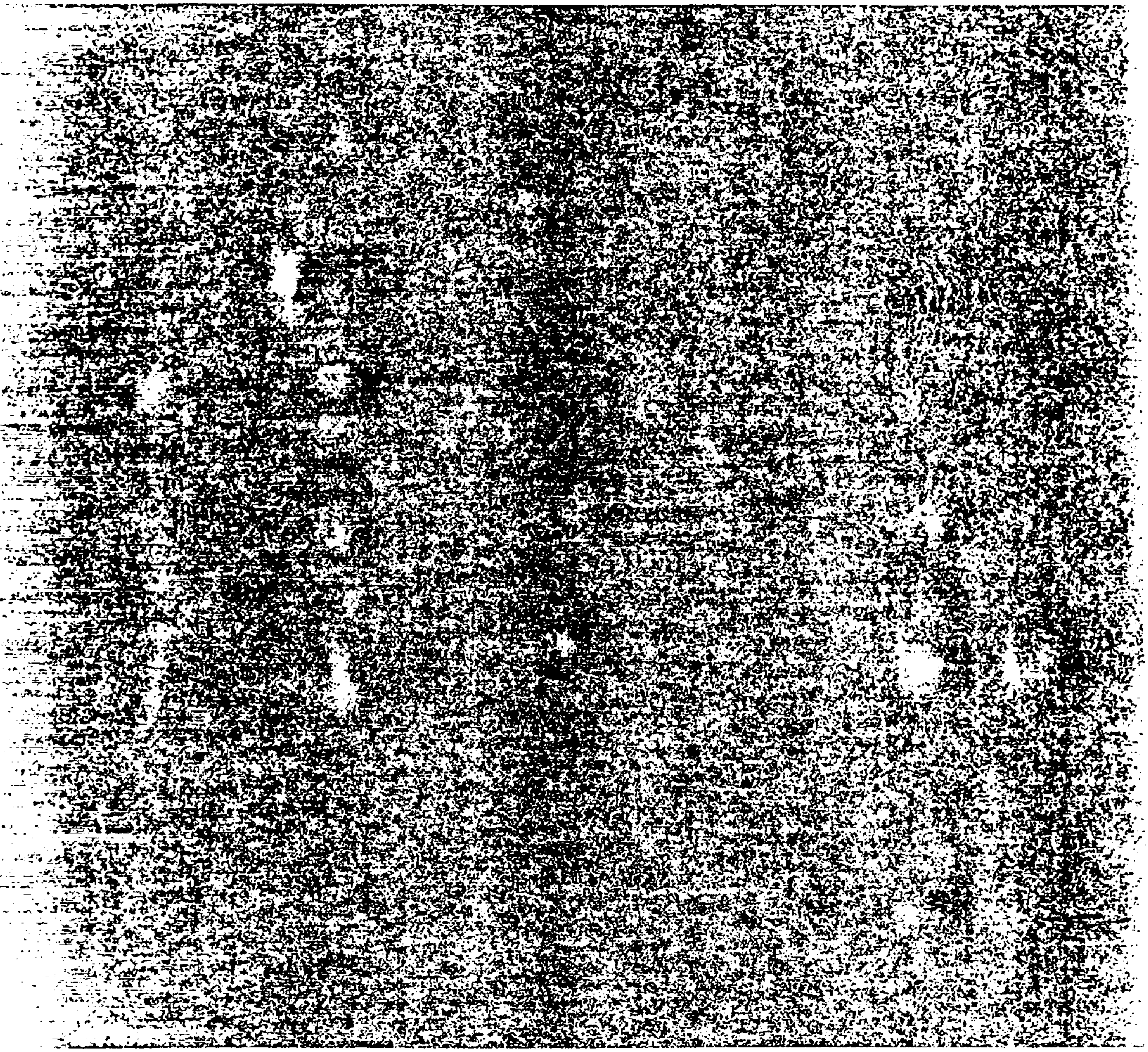

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