LA-10944

UC-10

Issued: May 1987

LA--10944

DE87 009480

Rapid Determination of Uranium by X-Ray Fluorescence

Calvin J. Martell
James M. Hansel

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

RAPID DETERMINATION OF URANIUM BY X-RAY FLUORESCENCE

by

Calvin J. Martell and James M. Hansel

ABSTRACT

This report describes a method for rapidly determining the amount of uranium using x-ray fluorescence. We add an aliquot of sample solution plus the internal standard element, yttrium, to a 10-ml volumetric flask. We transfer this solution to an x-ray cell and read the $L\alpha_1$ line of uranium and the $K\alpha_1$ line of yttrium. We then compare the ratio of uranium to yttrium for the sample with the ratios obtained from standards. This rapid, highly accurate procedure has a relative standard deviation of 0.69% for samples containing 1 to 5 mg U/ml.

INTRODUCTION

The operators of the Los Alamos National Laboratory's Plutonium Processing Facility requested 24-hour turnaround on results for uranium in oxalate filtrate samples. In the recovery process, uranium oxide is dissolved away from plutonium oxide. A further effort to recover the enriched uranium is made by oxalate precipitation of uranium. Then the filtrate from this precipitation is sent to radioactive waste storage.

Before this filtrate could be sent to storage, a uranium determination was necessary for accountability purposes. However, a critical situation developed when all filtrate storage tanks were filled because a proposed gamma-counting method failed. The failure was caused by the presence of plutonium and americium.

We developed an x-ray fluorescence procedure to determine rapidly the amount of uranium present in these types of samples. In the procedure, we dilute an aliquot of the sample plus an added internal standard element to volume, transfer the sample to an x-ray cell, and then read it with the x-ray wavelength spectrometer. We compare the intensity ratio from the sample

with ratios obtained from standards and are able to phone results to the submitter within 4 hours of receiving the sample in the x-ray laboratory. The small amount of plutonium and americium present does not cause interference or pose any significant hazard in this analysis.

Equipment and Reagents

In this work, we used the following equipment:

- Aluminum cell holder, 50-mm o.d.
- Mylar film, 6- μ m thick
- Sample cells, x-ray, Chemplex, plastic, series 1400, 32-mm o.d.
- X-ray spectrometer; Siemens SRS 300 microprocessor-controlled sequential x-ray spectrometer system; rhodium-target x-ray tube

We also used the following reagents:

- Uranium solution, NBS SRM 960. 1.000 mg/ml
- Yttrium solution, 0.250 mg/ml

PROCEDURE

1. Pipet 2 ml of the internal standard yttrium solution (0.250 mg/ml) into a 10-ml volumetric flask, located inside an open-front box.
2. Pipet 1 ml of sample solution into the 10-ml volumetric flask.
3. Fill the flask to the mark with water, stopper, and shake.
4. Prepare a "cold" place inside the "hot" box using paper towels.¹
5. Transfer the sample solution from the volumetric flask to an x-ray cell, being careful to keep the exterior of the cell uncontaminated.
6. Cover the cell with mylar film. Check for leaks by turning the cell (mylar down), wait briefly, then look for leaks. Do this just before placing the cell in the spectrometer.
7. Place the covered x-ray cell containing the sample solution in an aluminum cell holder, which also has a Mylar cover.
8. Excite the sample solution with a rhodium-target x-ray tube. Measure the following 2θ settings for 60 s each:

2θ	Measurement
23.00	Background 1
23.80	Y $K\alpha_1$
24.50	Background 2
25.14	Background 3
26.14	U $L\alpha_1$
27.14	Background 4

Figure 1 shows a plot of intensity vs 2θ for yttrium and uranium. The plot shows 0.5 mg of yttrium and 2 mg of uranium.

Fig. 1. Wavelength scan for 0.5 mg yttrium and 2 mg uranium.

We analyze the samples with the spectrographic conditions shown in the following table:

X-Ray Operating Parameters	
X-ray tube	Rhodium
Potential	60 kV
Current	50 mA
Counters	Scintillation and Flow
Analyzing crystal	LiF
Soller slit	Fine
Counting time	60 s

STANDARDS

We prepare standards containing known amounts of uranium and yttrium as listed below:

Standard No.	Uranium (mg)	Yttrium (mg)
RU-1	1.000	0.500
RU-2	1.000	0.500
RU-3	2.000	0.500
RU-4	2.000	0.500
RU-5	3.000	0.500
RU-6	3.000	0.500
RU-7	4.000	0.500
RU-8	4.000	0.500

To prepare the standards, we add the above concentrations to 10-ml volumetric flasks. The level of other elements (plutonium and americium) is so low that the internal standard easily compensates for them. We analyze these standards as described in the "Procedure" section. Figure 2 shows a plot of intensity ratios (U/Y) vs concentration of uranium. These data have a correlation coefficient for fit = 0.9999.

Fig. 2. Plot of intensity ratios (U/Y) vs concentrations of uranium.

CALCULATIONS

The Siemens spectrometer gives us net intensity values. To obtain the U/Y ratios, we divide the uranium counts per second by the yttrium counts per second.

We do a least-squares fit for the standards relating U/Y ratios vs the uranium concentrations. To calculate the concentration of uranium in the analyzed samples, we use the coefficients for the equation representing this standard curve.

PRECISION

To establish the precision of the method, we analyzed samples repeatedly. Some of the samples were prepared with known amounts of NBS SRM 960 uranium solution. The results are shown in Table I. The average relative standard deviation for 1 to 5 mg uranium is 0.69%.

TABLE I. Precision of Method

Uranium (mg)	Number of Determinations	Relative Standard Deviation (%)
1.0	6	0.96
3.0	6	0.56
4.0	6	0.69
5.0	6	0.53

ACCURACY

The accuracy of the method was determined with a NBS SRM 960 uranium metal. We prepared four levels of uranium solutions and treated them as described in the "Procedure" section. The results are given in Table II. The average recovery for the range 1 to 5 mg uranium is 100.03%.

TABLE II. Accuracy of Method

Uranium Added (mg)	Number of Determinations	Uranium Recovery (%)
1.000	6	100.97
3.000	6	100.39
4.000	6	99.46
5.000	6	99.28

DISCUSSION

An energy-dispersive, x-ray fluorescence unit can also be used to read the uranium and yttrium for an even faster turnaround time in determining uranium.

If the uranium drops to very low levels or if the amount of plutonium increases significantly, another procedure will be necessary.² The alternate procedure would no longer be rapid but would be capable of determining 1 μ g of uranium in large amounts of plutonium.

REFERENCES

1. Calvin J. Martell and James M. Hansel, "Determining Yttrium in Plutonium by Anion Exchange X-Ray Fluorescence," Los Alamos National Laboratory report LA-10544 (November 1985).
2. Calvin J. Martell and James M. Hansel, "Anion Exchange X-Ray Fluorescence Determination of Uranium in Plutonium," Los Alamos National Laboratory report LA-9552 (February 1983).