LA-11167

UC-10

Issued: December 1987

LA--11167

DE88 005089

Determining Zirconium in 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

THIS DOCUMENT IS UNCLASSIFIED

DETERMINING ZIRCONIUM IN URANIUM BY X-RAY FLUORESCENCE

by

Calvin J. Martell and James M. Hansel

ABSTRACT

Various concentrations of zirconium in uranium are determined by dissolving 2.5 g of the uranium sample. We add an aliquot of sample solution plus the internal standard, yttrium, to a 10-ml volumetric flask and pour this solution into an x-ray cell that is covered with Mylar film. Standards and samples in x-ray cells are placed in an x-ray fluorescence wavelength instrument where the K_{α} line for both zirconium and yttrium are read. We then compare the ratio of the intensities of zirconium and yttrium for a sample with those for standards. The relative standard deviation for 1% and 5% zirconium is 0.6% and 0.08%, respectively, with an accuracy of 100.3%.

INTRODUCTION

Zirconium, a detector element in uranium, is used to measure neutron energies of underground nuclear explosions. To properly determine the strength of the nuclear device, we must know the concentration of the zirconium in the uranium. We are able to determine the zirconium in the uranium without doing a separation because of the relatively high levels of zirconium. Previously, chemists¹ had been able to determine 5% to 50% zirconium in uranium. A uranium L_{β_6} line coincides with the zirconium K_{α} line, and a correction factor is applied for this. We add yttrium as an internal standard at the beginning of the analysis to achieve the best precision possible. The yttrium compensates for any changes that may occur in the sample during processing. We transfer the solution containing uranium, zirconium, and yttrium to a 10-ml volumetric flask and add a portion of this solution to an x-ray cell for the analysis.

Equipment and Reagents

In this work, we used the following equipment:

- Aluminum cell holder, 50-mm o.d.
- Analytical balance
- Mylar film, 6- μ m thick
- Sample cells, x-ray, Chemplex, plastic, number 1430, 32-mm o.d.
- X-ray spectrometer: Siemens SRS 300 micro-processor-controlled sequential x-ray spectrometer system; rhodium-target x-ray tube

We also used the following reagents:

- Hydrochloric acid, 12M
- Hydrofluoric acid, 10M

- Nitric acid, 15.7M
- Yttrium solution, 0.500 mg/ml
- Zirconium solution, NBS SRM 2129, 10.00 ± 0.01 mg/ml
- Zirconium solution, 0.500 mg/ml, from NBS SRM 2129
- Zirconium solution, 1.000 mg/ml, from NBS SRM 2129

PROCEDURE FOR DISSOLUTION OF URANIUM-ZIRCONIUM ALLOY SAMPLES

1. Dissolve 2.5 g of the U-Zr alloy to avoid problems with heterogeneity.
2. Take an appropriate aliquot for the sample cut. (This work should be done in a hood using a hot plate and a heat lamp. Gloves should be worn for this work.)
3. Put the accurately weighed 2.5 g of sample in a 250-ml beaker, add 5 ml of 12M HCl, and cover the beaker. After the vigorous reaction has stopped, a large amount of black material, uranium and zirconium, will remain.
4. Cool, rinse the cover glass and beaker walls with water, then add approximately 1 ml of 15.7M HNO₃. Swirl the beaker and heat with the heat lamp for several minutes. We are trying to dissolve the finely divided uranium at this step, but it is difficult to see when this has been completed because of the presence of the dark metallic zirconium.
5. Rinse the cover glass and beaker walls with water and evaporate the sample to incipient dryness.
6. Add 5 ml of 15.7M HNO₃ after cooling.
7. Cover the beaker, place on a hot plate, and heat until reaction almost ceases and brown fumes are gone.
8. Remove beaker from hot plate and allow to cool.
9. Transfer the uranium solution and the undissolved zirconium particles to a 50-ml Teflon beaker using a wash bottle. It will be necessary to put some 10M HF in the 250-ml beaker and heat briefly to dissolve

the small amount of zirconium that creeps up the beaker wall. This HF-Zr solution should be added to the Teflon beaker. Repeat this step three times to ensure the dissolution of all remaining zirconium particles.

10. Place the Teflon beaker under a heat lamp to evaporate excess liquid. As the evaporation takes place, the HNO₃ and HF should dissolve the zirconium. If it appears that all the zirconium will not dissolve, add more 10M HF.
11. Allow the solution to stand until it has been clear for some time, then transfer it to a volumetric flask of the appropriate size.

ANALYSIS OF SAMPLES

We pipet 2 ml of the 0.500-mg/ml yttrium solution into each 20-ml sample beaker, add the appropriate size aliquot of the sample, and evaporate this solution so that it fits into a 10-ml volumetric flask. We then transfer a portion of this solution to an x-ray cell and cover the cell with 6- μ m-thick Mylar film. Next, we place the covered x-ray cell containing our sample solution in an aluminum cell holder, which also has a Mylar cover. The sample solution is excited by the rhodium-target x-ray tube. We measure the following 2θ settings for 60 s each:

2θ	Measurement
22.16	Background 1
22.56	Zr K α
23.80	Y K α
24.40	Background 2
22.16	Background 3
23.04	U L α
24.40	Background 4

We analyze the samples with the spectrographic parameters shown in Table I:

TABLE I. 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

Low Zirconium Levels Using 500 mg of Uranium Sample

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

Standard No.	Zirconium (mg)	Yttrium (mg)	Uranium (mg)
Zr-1	0.000	2.000	500
Zr-2	0.000	2.000	500
Zr-3	2.000	2.000	500
Zr-4	2.000	2.000	500
Zr-5	5.000	2.000	500
Zr-6	5.000	2.000	500

Figure 1 shows a plot of intensity ratios (Zr/Y) vs concentration for low percentage levels of zirconium.

Higher Levels of Zirconium Using 100 mg of Uranium Sample

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

Standard No.	Zirconium (mg)	Yttrium (mg)	Uranium (mg)
Zr-1	0.000	2.000	100
Zr-2	0.000	2.000	100
Zr-3	3.000	2.000	100
Zr-4	3.000	2.000	100
Zr-5	5.000	2.000	100
Zr-6	5.000	2.000	100

Figure 2 shows a plot of intensity ratios (Zr/Y) vs concentration for high percentage levels of zirconium.

CALCULATIONS

Low Zirconium Levels Using 500 mg of Uranium Sample

The Siemens spectrometer gives net intensity values for the zirconium K_{α} , yttrium K_{α} , and uranium L_n peaks. Standards Zr-1 and Zr-2 contain no zirconium so the intensity values at the zirconium K_{α} setting for these two will be due solely to uranium L_{β_6} . The ratio of the uranium lines L_{β_6}/L_n is about 2.7500. With this ratio and the intensity of the uranium L_n line, a correction can be made for the presence of the weak uranium line under the zirconium line. We multiply the ratio of the two uranium lines (L_{β_6}/L_n) times the intensity of the uranium L_n line and subtract the result from the intensity of the zirconium K_{α} plus the uranium L_{β_6} line. The corrected zirconium intensity is then divided by the intensity of the yttrium line. The values are expressed as counts per second. We do a least squares fit for the standards relating Zr/Y ratios vs the zirconium concentrations. To calculate the concentrations of zirconium in the analyzed samples, we use the coefficients for the equation representing this standard curve.

Higher Levels of Zirconium Using 100 mg of Uranium Samples

At these higher intensities for zirconium and with much lower amounts of uranium, we read only the zirconium and yttrium lines without backgrounds and do

Fig. 1. Intensity vs concentration of low percentage levels of zirconium.

Fig. 2. Intensity vs concentration of high percentage levels of zirconium.

not make any correction for the weak uranium line underlying the zirconium line. We do a least squares fit for the standards relating Zr/Y ratios vs the zirconium concentrations. To calculate the concentration of zirconium in the analyzed samples, we use the coefficients for the equation representing this standard curve.

PRECISION

To establish the precision of the method, we prepared four sets of zirconium samples using solutions prepared from the NBS SRM 2129 zirconium standard. Next, we pipetted the appropriate amount of the zirconium solution into six beakers and added yttrium, the internal standard, and then the uranium solution. These samples were then analyzed according to the Analysis of Samples section. The results are shown in Table II. The average relative standard deviation for 0.5% to 5.0% zirconium is 0.85%.

TABLE II. Precision of Method (Low-Level Zirconium)

Zirconium (%)	Number of Determinations	Relative Standard Deviation (%)
0.5	6	1.60
1.0	6	0.73
3.0	6	0.53
5.0	6	0.50

ACCURACY

The accuracy of the method was determined with solutions prepared from the NBS SRM 2129 standard. We prepared four levels of zirconium samples

and treated them as described in the Analysis of Samples section; the results are given in Table III. The average recovery for the range of 0.5% to 5.0% zirconium is 100.3%.

TABLE III. Accuracy of Method

Zirconium Added (%)	Number of Determinations	Zirconium Recovery (%)
0.5	6	99.89
1.0	6	100.88
3.0	6	99.76
5.0	6	100.73

DISCUSSION

We have described the analysis of uranium for 0.5% to 5.0% zirconium using two sets of standards, low and high levels of zirconium, and are attempting to match standards with samples as closely as possible. We could have taken other amounts of sample, say 50 mg, for a different combination of zirconium in uranium. The actual amount of zirconium may be similar in each set, but the important difference is that the low-level set of standards contains 500 mg of uranium and the high-level set contains only 100 mg of uranium.

REFERENCE

1. E. A. Hakkila, R. G. Hurley, and G. R. Waterbury, "X-ray Fluorescence Spectrometric Determination of Zirconium and Molybdenum in the Presence of Uranium," *Analytical Chemistry* **36**, 2094-2097 (1964).