ORNL-1419
Cy. 1

APPLICATION OF X-RAY FLUORESCENCE TO ANALYSIS OF ZIRCONIUM IN URANIUM

By

W. F. Peed
W. B. Wright, Jr.
G. L. Rogosa

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
OAK RIDGE, TENNESSEE

cy-1
C-R. Lit.

[redacted]

Index No. ORNL-1419

Subject Category: Chemistry
General

Application of X-Ray Fluorescence to Analysis of Zirconium in Uranium

W. F. Peed, W. B. Wright, Jr., and G. L. Rogosa

December 6, 1952

Stable Isotope Research and Production Division

C. P. Keim, Director

[redacted]

OAK RIDGE NATIONAL LABORATORY

Operated by

CARBIDE AND CARBON CHEMICALS COMPANY
A Division of Union Carbide and Carbon Corporation
Oak Ridge, Tennessee

Contract No. W-7405-eng-26

[redacted]

[redacted]

Index No. ORNL-1419
Chemistry General

Distribution, Series A:

1-28.	Carbide and Carbon Chemical Company
29.	American Cyanamid Company (Watertown)
30-37.	Argonne National Laboratory
38.	Armed Forces Special Weapons Project (Sandia)
39.	Armed Forces Special Weapons Project, Washington
40.	Army Chemical Center
41-45.	Atomic Energy Commission, Washington
46.	Battelle Memorial Institute
47-49.	Brookhaven National Laboratory
50-51.	California Research and Development Company
52-53.	Carbide and Carbon Chemicals Company (C-31 Plant)
54-56.	Carbide and Carbon Chemicals Company (K-25 Plant)
57-64.	Carbide and Carbon Chemicals Company (ORNL) [redacted]
65.	Catalytic Construction Company
66.	Chicago Patent Group
67.	Chief of Naval Research
68.	Dow Chemical Company, Pittsburg
69.	Dow Chemical Company (Rocky Flats)
70-74.	duPont Company
75-77.	General Electric Company (ANPP)
78-83.	General Electric Company, Richland
84.	Hanford Operations Office
85-88.	Idaho Operations Office
89.	Iowa State College
90-93.	Knolls Atomic Power Laboratory
94-96.	Los Alamos Scientific Laboratory
97.	Mallinckrodt Chemical Works
98.	Massachusetts Institute of Technology (Kaufmann)
99-101.	Mound Laboratory
102.	National Advisory Committee for Aeronautics, Cleveland
103.	National Bureau of Standards
104.	National Lead Company of Ohio
105.	Naval Medical Research Institute
106.	Naval Research Laboratory
107.	New Brunswick Laboratory
108-109.	New York Operations Office
110-111.	North American Aviation, Inc.
112.	Patent Branch, Washington
113.	RAND Corporation
114.	Savannah River Operations Office, Augusta
115.	Savannah River Operations Office, Wilmington
116.	Sylvania Electric Products, Inc.
117.	Tennessee Valley Authority

[redacted]

[redacted]

118.	U. S. Naval Radiologican Defense Laboratory
119.	UCLA Medical Research Laboratory (Warren)
120-123.	University of California Radiation Laboratory
124-125.	University of Rochester
126-127.	Vitro Corporation of America
128.	Western Reserve University (Friedell)
129-130.	Westinghouse Electric Corporation
131-132.	Wright Air Development Center
133-147.	Technical Information Service, Oak Ridge

Carbide and Carbon Chemicals Company internal distribution as follows:

1.	C. E. Center
2.	C. E. Larson
3.	L. B. Emlet
4.	A. M. Weinberg
5.	W. B. Humes
6.	E. D. Shipley
7.	C. P. Keim
8.	C. E. Normand
9.	Russell Baldock
10.	Boyd Weaver
11.	J. M. Herndon
12.	F. E. Clark
13.	R. F. Hibbs
14.	L. A. Stephens
15.	W. C. Jackson
16.	D. Zucker
17.	R. Lafferty
18.	W. A. Burns
19.	H. G. King
20.	R. C. McIlhenny
21.	H. W. Dunn
22.	W. F. Peed
23.	W. B. Wright, Jr.
24.	J. R. McNally, Jr.
25-28.	Reports Office, TID

Issuing Office
Technical Information Department, Y-12 Plant
Date Issued: JAN 23 1953

[redacted]

[redacted]

Application of X-Ray Fluorescence to Analysis of Zirconium in Uranium

W. F. Peed, W. B. Wright, Jr.* and G. L. Rogosa**

ABSTRACT

A rapid instrumental method of analysis for the determination of zirconium in uranium has been developed and applied to a number of samples. Sources of error have been investigated and it is shown that the precision and accuracy compare favorably with conventional methods. Time of analysis for a single sample is less than twenty minutes and the effects of impurities are negligible.

INTRODUCTION

During the history of application of X-ray methods to analytical chemistry, attention has been given primarily to diffraction techniques. More recently, Liebhafsky[1] has discussed other applications of X-rays to analytical chemistry. If a sample of material is subjected to X-radiation and the resulting fluorescence analyzed with a crystal of known lattice dimensions, the intensity of characteristic X-rays diffracted at specific angles may be measured. Intensity measurements may then be correlated with established working curves resulting in an analysis of the material.

---

* Y-12 Analytical Laboratory
**Research Participant, Florida State University, Tallahassee, Florida

1. Liebhafsky, H. A., Anal. Chem. (Jan. 1949, 1950, 1951).

[redacted]

The fluorescence method can be very rapid. Mortimore and Romans[2] report that a single analysis, including sample preparation and calculation, requires only 5 to 10 minutes. Samples of the order of one gram are sufficient and recovery of the sample after analysis is essentially 100 per cent. Excellent agreement between X-ray fluorescence measurements and conventional chemical methods is obtained.

Since the intensity of the secondary radiation above background is the limiting factor, the X-ray fluorescence method has found widest application in the regions above the upper limits of spectrographic methods.

EXPERIMENTAL

Samples for fluorescence examination were prepared from mixed oxides of zirconium and uranium by the method of Mortimore and Romans, which consists of grinding 1.0 gram of the mixed oxides with 1.0 gram of cornstarch and then briquetting into pellets about 1-1/4 inch in diameter at 8000 p.s.i. The standards varied from 1 per cent to 5 per cent zirconium. Impurities were added to samples in the amounts discussed later. For one set of data the weight of mixed oxides was varied in order to determine the effect of cornstarch ratio on the fluorescence.

Fluorescence X-ray intensities were measured with a General Electric XRD-3 spectrometer with fluorescence attachments which use a bent mica crystal as a monochromator. Counting equipment was modified as described

---

2. Mortimore, D. M. and P. A. Romans, J. Opt. Soc. Am. 42, 673-77 (1952).

in ORNL-1265.[3] A T-section resistance-capacitance filter was used in the X-ray tube high voltage power supply to minimize counting losses.

Intensities of the uranium Lβ_2 and zirconium Kα_1,α_2 (plus U Lβ_6 contribution) lines were determined by measuring the time required to record 32,768 counts at the respective goniometer positions of 29.00° and 30.40°. (The peaks are flat over a range of more than $\pm$ 0.10°). Where background determinations were needed, the time required for 4096 counts in the line-free region on the long wavelength side of the zirconium peak was measured. Determination of the U Lβ_6 peak was made by measuring the time required for 32,768 counts at the 2θ position of 30.40° using a pure uranium oxide (U_3O_8) sample.

DISCUSSION

In order to interpret the intensities of zirconium and uranium radiation for an analysis of the material, it is necessary to know the variation of the intensity ratio with the zirconium content. If the ratio is corrected for both background and U Lβ_6 contribution to the Zr Kα_1,α_2 peak, a straight line will result in a log log plot. (See Figure 2.) However, as shown in Figure 1, a plot without correction results in a slightly bowed curve. Such a curve has the advantage that it may be determined easily and constructed rapidly, and permits direct and rapid calculation of the zirconium content of the sample; whereas the corrected curve requires somewhat lengthy calculation before the zirconium content is ascertained.

Although the uncorrected curve appears less desirable it yields excellent results for samples in which the impurity content is less than 10 per cent. A comparison of data obtained by X-ray fluorescence and calculated from the uncorrected curve with analysis of the same samples by the colorimetric method

3. Peed, W. F. and H. W. Dunn, "Preliminary Investigation of Monochromatic X-Ray Absorption as a Method of Analysis for Uranium", ORNL-1265, April 8, 1952.

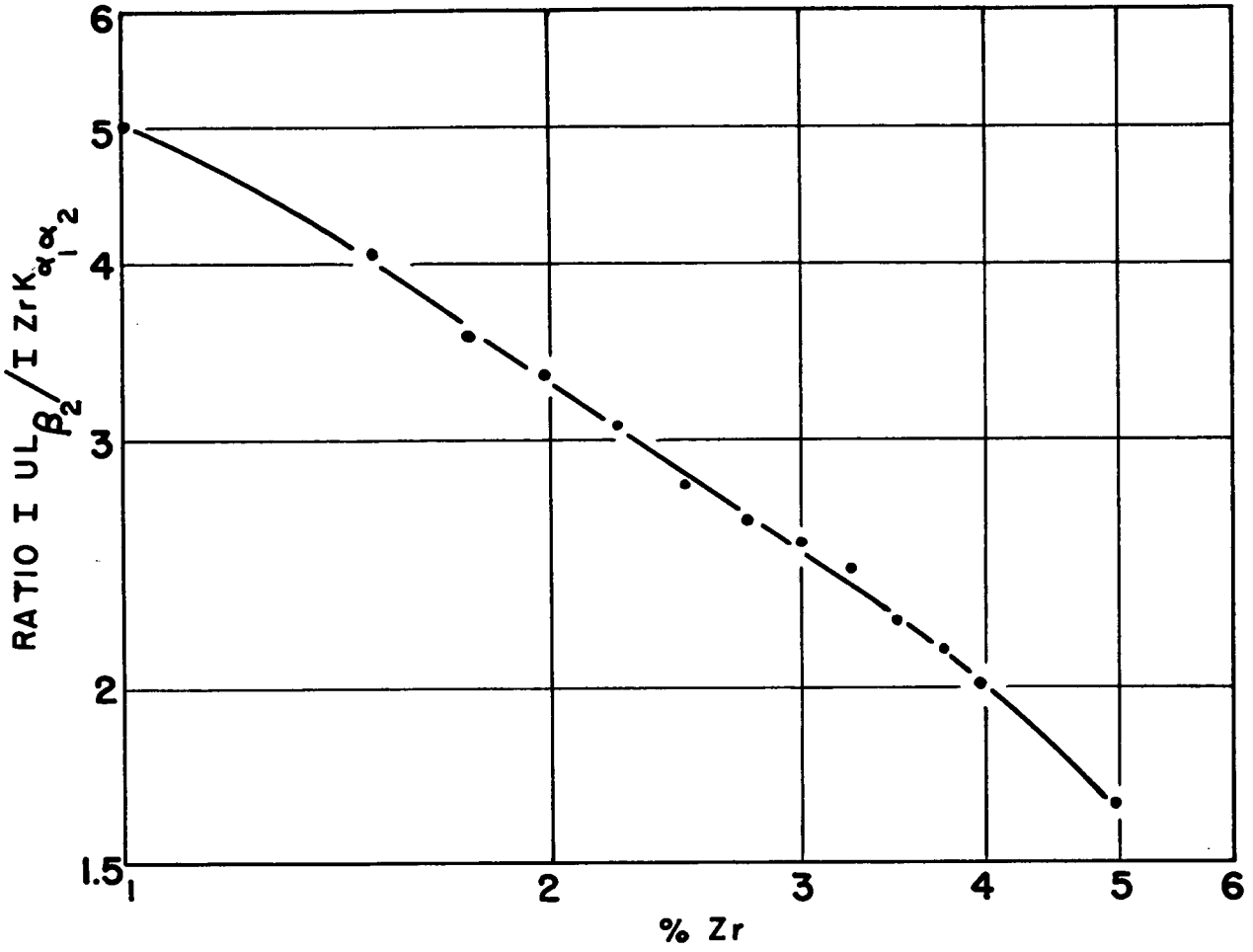

FIGURE I. CALIBRATION CURVE
(UNCORRECTED)

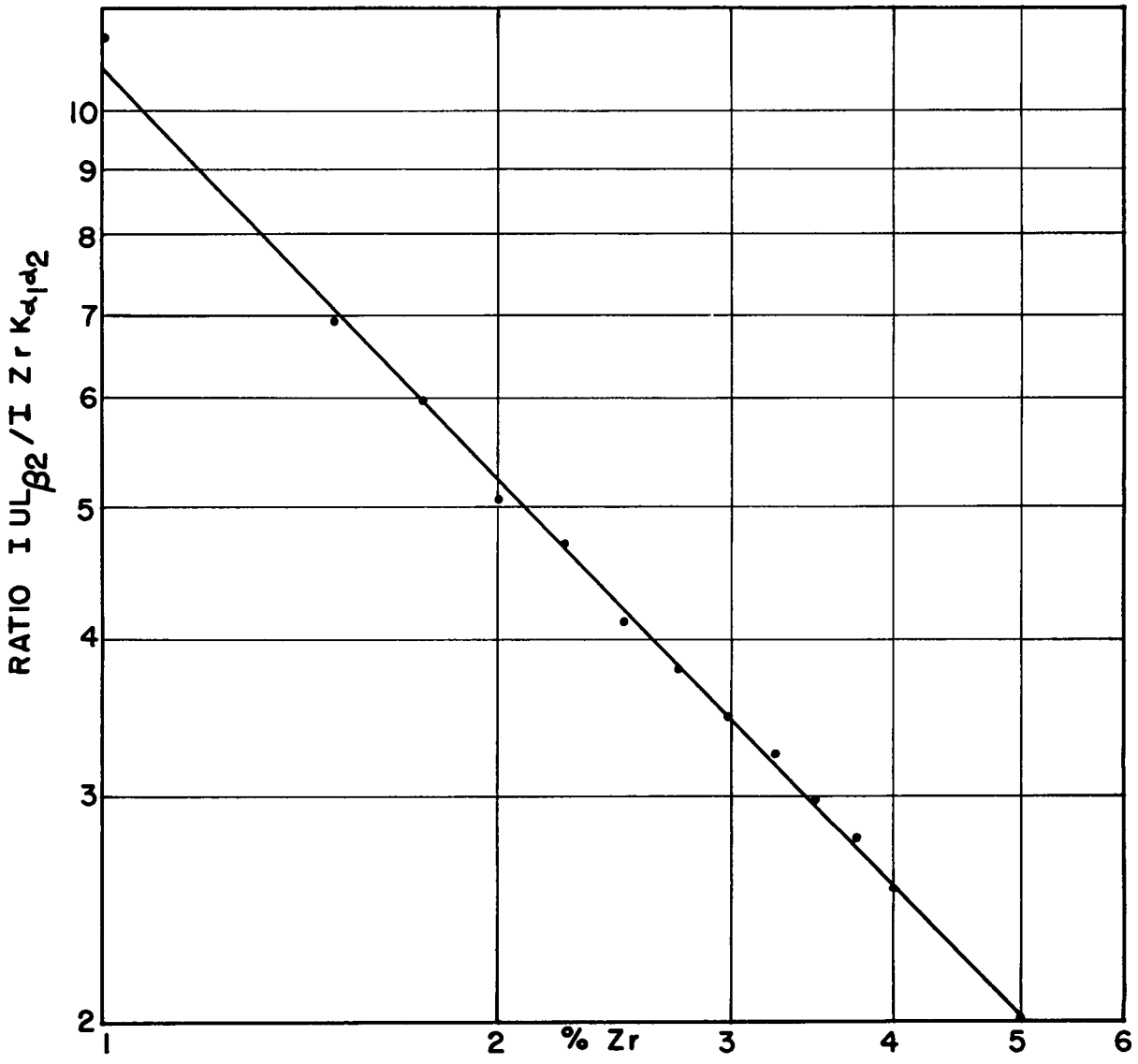

FIGURE 2. CALIBRATION CURVE
(CORRECTED FOR BACKGROUND AND UL$_{\beta 6}$)

of King and Burns[4] is given in Table I. The bias and limit of error of the X-ray data are + 0.53 per cent and ± 3.62 per cent, respectively, or no significant bias with respect to the colorimetric method.

To evaluate the instrumental contribution to the precision, one pellet was counted 18 times yielding a limit of error of ± 3.8 per cent. It should be noted that the instrumental L.E. is essentially the same as the experimental L.E. By increasing the number of counts the instrumental limitations could be reduced if more precise measurements were required.

TABLE I

COMPARISON OF CHEMICAL AND X-RAY ANALYSES

Sample No.	% Zirconium	
	Colorimetric	X-Ray Fluorescence
1	2.36	2.39
2	2.42	2.42
3	2.41	2.45
4	2.00	1.97
5	2.90	3.00
6	2.17	2.18
7	2.94	2.93
8	2.76	2.79
9	2.27	2.25

In both the corrected and uncorrected curve the U $L\beta_2$ peak is used as an internal standard. In this way it is possible to correct for small amounts of impurities and minor variations in pellet preparation. Difficulties encountered with large changes in sample size, U $L\beta_6$ contribution to the zirconium peak, and large amounts of impurities are not resolved with the uncorrected curve.

4. King, H. G. and W. A. Burns, Y-12 Analytical Laboratory, unpublished work.

Measurement of the intensities are subject to background which arises largely by scattering from the cornstarch. Uranium and zirconium absorb this scattered radiation considerably and thereby reduce the background intensity. Impurities complicate the situation since they introduce more scattering in some cases and more absorption in others. The background then is a function of the components of the cornstarch pellet.

Since the background distorts the measured intensities, the effect is particularly noticeable in the presence of large amounts of impurities and when the sample to cornstarch ratio is reduced drastically. The effect of the latter is illustrated by the data in Table II.

TABLE II

EFFECT OF OXIDE/STARCH RATIO ON ANALYSES FOR ZIRCONIUM

g Oxide/ g Cornstarch	% Zr Uncorrected Curve	% Zr Corrected Curve
1.0	2.15	2.16
1.0	2.25	2.22
0.8	2.20	2.16
0.8	2.25	2.23
0.6	2.25	2.22
0.4	2.30	2.22
0.2	2.40	2.24
0.2	2.37	2.21

For the construction of the corrected curve, the uranium-zirconium fluorescence spectrum was scanned and a line free region on the long wavelength side of the zirconium peak was selected for the determination of background (see Figures 3 and 4). The U $L\beta_6$ contribution to the zirconium peak was measured by determining the ratio of the U $L\beta_6$ to U $L\beta_2$ intensities from a pellet containing only uranium after subtraction of background from both peaks. The effect of U $L\beta_6$ contribution in a sample

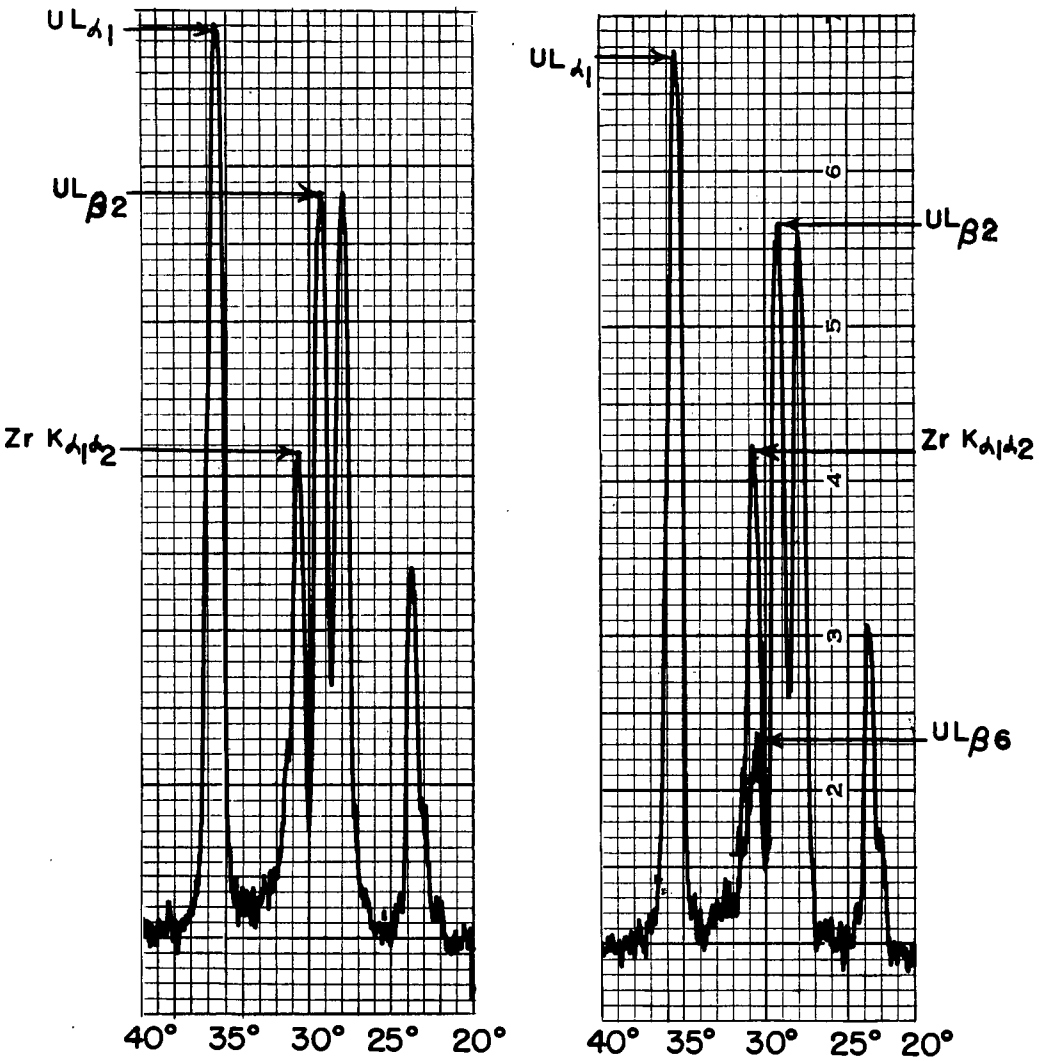
UL α1
UL β2
Zr Kα1α2
40° 35° 30° 25° 20°
ZIRCONIUM IN URANIUM
24 % Sn ADDED
UL α1
UL β2
Zr Kα1α2
UL β6
6
5
4
3
2
40° 35° 30° 25° 20°
ZIRCONIUM IN URANIUM

FIGURE 3

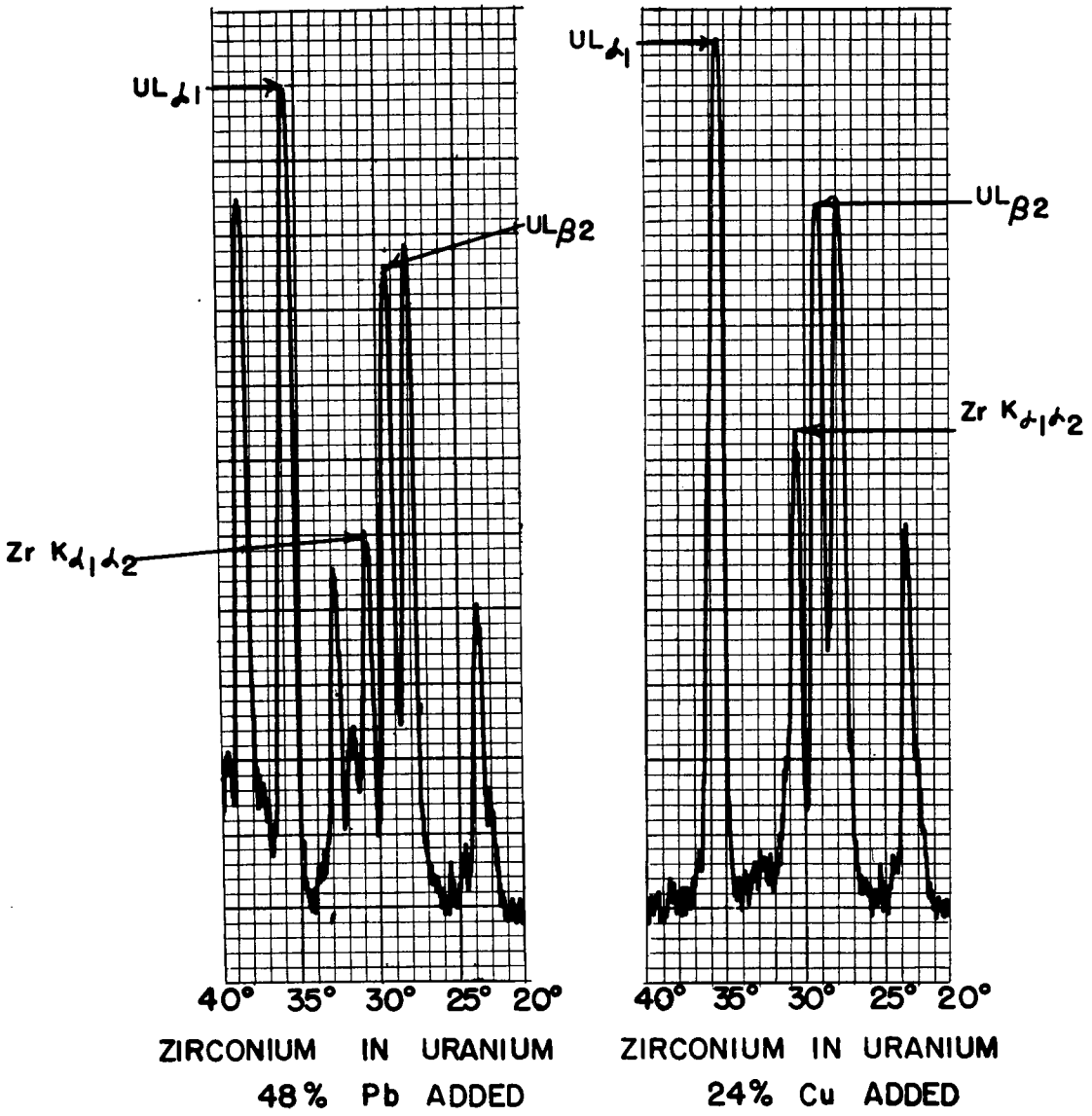
ULα_1
ULβ_2
Zr K$\alpha_1\alpha_2$
40° 35° 30° 25° 20°
ZIRCONIUM IN URANIUM
48% Pb ADDED
ULα_1
ULβ_2
Zr K$\alpha_1\alpha_2$
40° 35° 30° 25° 20°
ZIRCONIUM IN URANIUM
24% Cu ADDED

FIGURE 4

is then calculated simply by multiplying the observed uranium peak by this factor and subtracting the result from the Zr intensity. When these corrections are applied to the measured intensities of the Zr-U standards, a log log plot of the resulting ratios versus zirconium concentration yields a straight line over the region investigated. (See Figure 2.)

It is seen in Table II that corrected intensity ratios when read from the corrected curve, negate the effect of large changes in the sample to cornstarch ratio. This implies that the sample size may be varied over large ranges. Table III illustrates the effect of several impurities on the measured zirconium concentration. Again it is indicated that correction of the intensities negates the effects of impurities. This will be true for all impurities except those that yield lines in the region used for intensity measurements. Elements expected to seriously interfere include lead, thorium, and bismuth. In Figures 3 and 4 scans of the spectrum of this region are reproduced at a concentration level of 2.22 per cent zirconium. In the pure Zr-U scan the U $L\beta_6$ peak was superimposed on the spectrum to indicate the magnitude of the contribution. It is noted that the scans of the pure U-Zr sample and those containing copper and tin are identical except for changes in peak height due to changes in background. In the presence of lead, however, lines appear in the region which evidently interfere seriously with the zirconium determination from the uncorrected curve. Correction for background reduces the error considerably, even in the case of lead. (See Table III).

TABLE III

IMPURITY EFFECTS

Impurity in %	Uncorrected Curve % Zr	Uncorrected Curve % Error	Corrected Curve % Zr	Corrected Curve %Error
2 % Sn	2.28	2.73	2.31	4.09
14 % Sn	2.23	0.45	2.22	0.00
24 % Sn	2.25	1.36	2.22	0.00
5 % Cu	2.22	0.00	2.18	1.82
24 % Cu	2.25	1.36	2.20	0.91
2 % Pb	2.30	3.64	2.23	0.45
48 % Pb	2.55	15.00	2.32	4.54

To obtain a limit of error for the method, the results listed in Tables II and III were considered as repeated analyses of one sample under drastic changes in conditions. The value of $\pm$ 4.35 per cent represents the maximum limit of error of the method when correcting for background effects. The L.E. $\pm$ 11.5 per cent, calculated from the uncorrected measurements, indicates the advisability of background correction with unknown samples.

The variation in the intensity ratios as a function of voltage is shown in Table IV. It is seen that the variation is negligible within an increment of a thousand volts at 50 KV.

TABLE IV

EFFECT OF TUBE VOLTAGE ON OBSERVED PER CENT ZIRCONIUM

Voltage (in KV)	% Zr
50	2.22
47	2.26
44	2.32
41	2.50

[redacted]

CONCLUSIONS

This method has been applied to a number of samples of zirconium in uranium. It is rapid and the precision and accuracy compare favorably with the more time consuming colorimetric method. In samples that are relatively free from impurities no background corrections need be made. In all other cases background corrections permit an accurate analysis. The time required for a single sample is approximately 10 minutes if background corrections are not made. Background correction increases the time required to 15-20 minutes per determination.

The method seems applicable to practically any element above titanium in the periodic table. The only requirement is that an internal standard be introduced with a peak fairly close to the measured intensity. It seems reasonable to assume that the above application can be extended to low uranium concentrations in zirconium, and also to the determination of uranium in nonfluorescing matrices such as aluminum.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to F. E. Clark and members of the Y-12 Analytical Laboratory, in particular to W. A. Burns for preparation of the standard zirconium sample, to H. G. King for the colorimetric analytical results and to R. C. McIlhenny for assistance in the preparation of the manuscript. We also wish to thank J. R. McNally, Jr. of this laboratory, under whose direction the work was done.

[redacted]