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X-RAY FLUORESCENCE SPECTROGRAPHIC DETERMINATION OF
ZIRCONIUM AND MOLYBDENUM IN THE PRESENCE OF URANIUM

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ABSTRACT

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Zirconium and molybdenum in uranium-zirconium-molybdenum carbide are determined without chemical separation using an x-ray fluorescence spectrographic procedure. The mixed carbide is dissolved in nitric-hydrofluoric acid, niobium is added to serve as an internal standard, and the solution is irradiated using a tungsten-target x-ray tube. The ratios of the intensities of the $K\alpha$ lines for zirconium and niobium and of the $K\beta$ lines for molybdenum and niobium are measured. Corrections, which were found to be a linear function of uranium concentration in the range between 30 and 100 percent of uranium, are applied to each intensity ratio. The procedure is applicable to the determination of 5 to 50 percent each of zirconium and molybdenum with a relative standard deviation of 1 to 2 percent. Foreign elements of high mass absorption coefficient interfere when present in concentrations greater than approximately 10 percent for the determination of molybdenum, or 20 percent for the determination of zirconium.

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INTRODUCTION

A rapid analytical method was required for determining 5 to 50 percent of molybdenum and zirconium with a standard precision of about 1 percent in mixtures of uranium, molybdenum, and zirconium carbides. X-Ray fluorescence techniques without chemical separations are well-suited for determinations of this type and offer the required precision. However, the x-ray fluorescence determination of molybdenum and zirconium in the presence of large and variable amounts of uranium is complicated by the overlap of the L series lines for uranium with the K series spectra for these elements. Flikkema and Schablaske⁽¹⁾ determined 0.5 to 5 percent of molybdenum in uranium using a high resolution topaz analyzing crystal and measuring the intensity of the K_{α} line for molybdenum (plus the contribution of the L_{β_3} line for uranium) and applying a correction factor for background. Peed, Wright, and Rogosa⁽⁴⁾ determined 1 to 5 percent of zirconium in uranium by measuring the intensities of the K_{α} line for zirconium and the L_{β_2} line for uranium. The contribution of the L_{β_6} line for uranium to the K_{α} line for zirconium was determined as a function of the L_{β_2} line intensity using uranium metal as a sample. It was possible to apply a correction to the measured intensity for the K_{α} line for zirconium from the sample and then to plot the intensity ratio of the L_{β_2} line for uranium to the K_{α} line for zirconium as a function of concentration. A log-log plot of this function is a straight line which may be used as a

calibration curve. Attempts to use these techniques for determining higher zirconium and molybdenum concentrations in the present investigation did not yield straight line calibration curves using log-log, semi-log, or linear graph paper. Therefore, a method utilizing niobium as an internal standard for determining zirconium and molybdenum was developed.

INSTRUMENTATION

A Philips Electronic Corporation x-ray spectrophotograph with a three position head, lithium fluoride analyzing crystal, and Machlett FA60 tungsten-target x-ray tube were used. A multiplier phototube with a sodium iodide-thallium iodide scintillation crystal was used as the detector. The x-ray tube was operated at 50 KV and 30 MA and the phototube was operated at 680 volts. The inside of the stainless steel sample cell provided with the instrument was coated with paraffin to prevent corrosion by the nitric-hydrofluoric acid solution used for determinations. Mylar windows for the sample cell were coated with Desicote to reduce bubble formation during irradiation.

RECOMMENDED PROCEDURE

Samples that weighed between 150 and 250 mg. and contained greater than 50 mg. of uranium were dissolved by heating with nitric acid until reaction ceased, then adding hydrofluoric acid and heating again until the reaction subsided. Reacting the sample with nitric acid first was necessary to prevent formation of insoluble tetravalent uranium fluorides. Free carbon, if present, was removed by filtration. Twenty mg. of niobium were added to serve as an internal standard, the solutions were evaporated and diluted with distilled water to a final volume

of 10.0 ml. and transferred immediately to 1 ounce polyethylene bottles. The sample solution was placed in the wax-coated sample cell, which was positioned in the x-ray spectrograph, and the intensities of the K_{α} lines for zirconium and niobium and the K_{β} lines for molybdenum and niobium were measured. A minimum of 32,000 counts were accumulated at each line. To obtain correction factors for the zirconium and molybdenum, uranium was determined using a standard x-ray absorption edge procedure⁽²⁾. Zirconium and molybdenum concentrations were calculated using equations (1) and (2), respectively, under DISCUSSION.

DISCUSSION

The x-ray fluorescence determination of zirconium and molybdenum in the presence of uranium is complicated by the overlap of the L series x-ray lines for uranium with the K series lines for these elements.

Wavelengths of spectral lines and their relative intensities are summarized in Table I. The spectrum of niobium which was selected as an internal standard is included.

Table I

X-Ray Spectra for Uranium, Zirconium, Molybdenum, and Niobium in the Wavelength Region between 0.6 and 0.82 Å.

Element	Line	Wavelength, Å.	2θ angle, degrees (LiF crystal)	Relative intensity(3)
Zr	K_{α}	0.788	22.57	100
	K_{β}	0.701	20.05	20
Mo	K_{α}	0.710	20.31	100
	K_{β}	0.631	18.03	20
Nb	K_{α}	0.748	21.41	100
	K_{β}	0.664	18.98	20
U	$L_{\beta 1}$	0.720	20.60	50
	$L_{\beta 2}$	0.755	21.61	20
	$L_{\beta 3}$	0.710	20.31	6
	$L_{\beta 4}$	0.748	21.41	4
	$L_{\beta 6}$	0.789	22.59	1
	$L_{\gamma 1}$	0.615	17.57	10
	L_{η}	0.806	23.09	1

The $K\beta$ line for zirconium cannot be used for analysis because of overlap from the $K\alpha$ line for molybdenum and the $L\beta_{1,3}$ line for uranium. Similarly, use of the $K\alpha$ line for molybdenum determinations is precluded. The analysis is limited therefore to the use of the $K\alpha$ line for zirconium and the $K\beta$ line for molybdenum. However, the weak $L\beta_6$ line for uranium overlaps the $K\alpha$ line for zirconium and a suitable means is required to eliminate effects of large variations in uranium concentration. Besides line overlap, large uranium concentrations can interfere by absorbing the intensity of the measured x-ray line and by reducing the scattered primary radiation from the x-ray tube target, hence reducing background intensity.

The internal standard technique for eliminating these interferences was considered. The criteria of an internal standard are that it provide straight line calibration curves and also reduce effects produced by matrix elements. Scattered background radiation, the $K\alpha$ line for niobium, and the $L\eta$ and $L\beta_4$ lines of uranium were investigated as possible internal standard lines for the determination of zirconium. For the determination of molybdenum, scattered background radiation, the $L\gamma_1$ line for uranium, and the $K\beta$ line for niobium were considered as internal standard lines. Of these, the $K\alpha$ line of niobium, for the determination of zirconium, and the $K\beta$ line of niobium, for the determination of molybdenum, provided straight line calibration curves with least interference from uranium over the desired concentration ranges. Therefore, further investigation was limited to the use of niobium as an internal standard.

Determination of Zirconium:

Plotting the ratio of intensities of the $K\alpha$ line of zirconium (plus the contribution of the $L\beta_6$ line for uranium) to the $K\alpha$ line for niobium (plus the

contribution of the $L\beta_3$ line for uranium) against zirconium concentration yields a straight line calibration curve. However, the slope of this curve changes with varying uranium concentration. The slope and change in slope are described by the equation:

$$\text{Zr concentration, mg. / 10 ml.} = \frac{R - b}{a - c(d - 100)} \quad (1)$$

where

R is the measured intensity ratio
a is the slope of the curve for samples containing 100 mg. of uranium
b is the intercept on the Y (ratio) axis and is constant over the uranium concentration range investigated
c is the change in slope per 10 mg. of uranium, and
d is the uranium concentration in mg. / 10 ml. in the sample solution.

This equation is applicable to determining zirconium concentrations in the range between 0.05 and 100 mg. per 10 ml. in the presence of uranium concentrations in the range between 50 and 175 mg. per 10 ml.

Determination of Molybdenum:

Upon plotting the ratio of intensities of the $K\beta$ line for molybdenum to the $K\beta$ line for niobium against molybdenum concentration a straight line calibration curve is obtained for molybdenum concentrations up to 40 mg. per 10 ml. The slope of this curve remains constant with varying uranium concentration but the intercept on the Y (ratio) axis changes.

The slope and change in intercept of this curve are described by the equation:

$$\text{Mo concentration, mg. / 10 ml.} = \frac{R - b + c(100 - d)}{a} \quad (2)$$

where

R is the measured intensity ratio
a is the slope of the curve, and remains constant over the uranium concentration range investigated
b is the intercept on the Y (ratio) axis for solutions containing 100 mg. of uranium per 10 ml.
c is the change in intercept per 10 mg. of uranium, and
d is the uranium concentration in mg. / 10 ml. in the sample.

Precision and Accuracy:

The precision of the method for measuring zirconium and molybdenum was determined at several zirconium and molybdenum concentration levels. Results (Tables II and III) are based upon a minimum of fourteen determinations at each concentration level and indicate that relative standard deviations approaching the required 1 to 2 percent can be obtained for molybdenum and zirconium, each in the concentration range between 5 and 50 percent.

Table II

Precision of the X-Ray Fluorescence Procedure for Determining Zirconium in the Presence of Uranium

Zr added, mg. / 10 ml.	U added, mg. / 10 ml.	Zr concen- tration range, percent	Standard devia- tion, mg.	Relative stand- ard deviation, percent
0	100 to 175	0	0.09	---
10.00	60 to 175	5 to 12	0.16	1.6
20.00	60 to 175	10 to 25	0.25	1.2
40.00	60 to 175	19 to 40	0.45	1.1
100.00	60 to 175	36 to 63	1.2	1.2

Table III

Precision of the X-Ray Fluorescence Procedure for Determining Molybdenum in the Presence of Uranium

Mo added, mg. / 10 ml.	U added, mg. / 10 ml.	Mo concen- tration range, percent	Standard de- viation, mg.	Relative stand- ard deviation, percent
0	100 to 175	0	0.13	---
20.00	60 to 175	10 to 30	0.33	1.7
40.00	60 to 175	18 to 40	0.40	1.0

The interelement effects of molybdenum and zirconium were found to be very small, amounting to -0.06 mg. of molybdenum per 10 mg. of zirconium, and 0.06 mg. of zirconium per 10 mg. of molybdenum. These effects are negligible except for samples containing large amounts of zirconium which require an intercept correction in the determination of molybdenum.

Results of typical determinations of zirconium (Table IV) and molybdenum (Table V) in the presence of various amounts of uranium are generally within two relative standard deviations of the method. Each value shown is the result of a single determination.

Table IV

Determination of Zirconium in the Presence of Various Amounts of Uranium

U added, mg. / 10 ml.	O mg. added	Zr found, mg. / 10 ml.					Ave. Zr recovery, percent (b)
		20 mg. added	40 mg. added	60 mg. added	80 mg. added	100 mg. added	
150	0.19	19.7	40.4	59.3	81.0	101.7	100.7
125	0.15	20.2	39.3	59.6	79.4	99.8	99.4
100	0	20.3	39.8	60.1	78.3	100.1	99.5
80	-0.06	20.3	40.2	60.1	76.6(a)	98.9	99.8
60	-0.22	20.2	----	61.0	79.0	99.9	100.0
Average found	0.00	20.1	39.9	60.0	79.4	100.1	

(a) Omitted in determination of average found

(b) Data for Zr found in reagent blank are not included in calculations of recoveries.

Table V

Determination of Molybdenum in the Presence of Various Amounts of Uranium

U added, mg. / 10 ml.	O mg. added	Mo found, mg. / 10 ml.			Ave. Mo re- covery, percent(a)
		20 mg. added	40 mg. added		
150	0.12	20.3	40.3		101.0
125	0.05	19.7	40.1		99.7
100	0.00	20.1	39.6		99.5
80	-0.10	20.4	39.9		101.0
60	-0.09	20.1	40.0		100.1
Average found	-0.02	20.1	40.0		

(a) Data for Mo found in reagent blank are not included in calculations of recoveries.

Interferences:

This procedure is designed to eliminate the serious interference caused by line overlap of uranium in the x-ray fluorescence determination of zirconium and molybdenum. Other elements that may interfere due to overlap of either the analytical lines used for zirconium or molybdenum or the lines for the internal standard, niobium, are summarized in Tables VI and VII. Only first order lines having a relative intensity greater than 5 were considered, and possible overlap was assumed if the wavelength of the lines were within approximately 0.017 Å or a 2θ angle of 0.5° of the analytical line. Many of the elements listed are rare and would not be expected to be present in most samples.

Table VI

Elements which May Interfere with the Determination of Zirconium
Due to Line Overlap

<u>Element</u>	<u>X-Ray Line</u>	<u>Wavelength, Å.</u>
Zr	K_α	0.788
Pa	$L\beta_2$	0.774
Sr	K_β	0.783
Po	$L\gamma_1$	0.788
Bi	$L\gamma_3$	0.790
Th	$L\beta_2$	0.794
Nb	K_α	0.748
Pa	$L\beta_3$	0.732
Np	$L\beta_2$	0.735
Y	K_β	0.740
Pa	$L\beta_1$	0.742
Th	$L\beta_3$	0.755
Bi	$L\gamma_4$	0.761

Table VII

Elements which May Interfere with the Determination of Molybdenum

Due to Line Overlap

<u>Element</u>	<u>X-Ray Line</u>	<u>Wavelength, A.</u>
Mo	$K\beta$	0.631
Rh	$K\alpha$	0.613
Pa	$L\gamma_2$	0.624
Th	$L\gamma_6$	0.632
Pa	$L\gamma_1$	0.634
Ru	$K\alpha$	0.643
Nb	$K\beta$	0.664
Th	$L\gamma_1$	0.653
Tc	$K\alpha$	0.673

In addition to line overlap, interference in using the internal standard procedure may arise also from enhancement and absorption. Enhancement is caused by an element having a strong x-ray line between the x-ray absorption edges of the element determined and the internal standard element. Interference by enhancement is expected to be caused only by ruthenium in the determination of molybdenum and only by technetium in the determination of zirconium.

Absorption interference may be of two types: preferential absorption of the shorter wavelength x-ray line used in the analysis by an element having an absorption edge between the analytical lines measured, and general absorption of both lines by material which greatly increases the mass absorption coefficient of the sample. Preferential absorption is expected in the x-ray fluorescence determination of molybdenum only by the L1 edge of radium using the $K\beta$ lines for molybdenum and niobium. Interference in the determination of zirconium using the $K\alpha$ x-ray lines for zirconium

and niobium is expected by the K edge of strontium, the LI edges of bismuth and lead, and the L III edge of thorium. General absorption becomes serious when the ratio of line intensity to internal standard intensity deviates significantly from unity. Hence, it would be most pronounced for samples containing little or no molybdenum or zirconium.

The effects of various elements on the determination of molybdenum and zirconium were studied. Solutions were prepared to contain 0 or 40 mg. of molybdenum and zirconium, 100 mg. of uranium, and various amounts of lead, mercury, copper, cadmium, or sulfuric acid. Mercury, cadmium, and copper were selected as typical elements having high, medium, and low mass absorption coefficients, respectively, for the K series radiation of zirconium and molybdenum, and various sulfuric acid concentrations were used in order to study the effect of variable solvent concentration. Lead is expected to give high recoveries for the determination of zirconium due to selective absorption of the K_{α} line for niobium. Large concentrations of elements having high mass absorption coefficients interfere with the determination of zirconium, as do large concentrations of sulfuric acid (Table VIII), and with the determination of low concentrations of molybdenum (Table IX). Each value shown is the result of duplicate determinations on one solution. No interference was assumed if the average of duplicate determinations was within two standard deviations of the quantity added.

Table VIII

Effect of Mercury, Cadmium, Copper, Sulfuric Acid on the X-Ray Fluorescent Determination of Zirconium in Uranium

Element added	(μ/ρ) Zr $K\alpha$	Amount added, mg. / 10 ml.	Zr found, mg. / 10 ml.	
			O mg. added	40.0 mg. added
Pb	140	20	0.06	41.5
		40	0.16	----
Hg	160	40	0.00	39.4
		80	-0.10	38.9
Cu	67	50	-0.06	39.9
		100	-0.10	39.8
Cd	38	50	-0.06	39.9
		100	-0.06	39.6
H_2SO_4	---	1750	0.10	39.7
		3500	0.22	38.1

Table IX

Effect of Lead, Mercury, Cadmium, Copper, and Sulfuric Acid on the X-Ray Fluorescent Determination of Molybdenum in Uranium

Element added	(μ/ρ) Mo $K\beta$	Amount added, mg. / 10 ml.	Mo found, mg. / 10 ml.	
			O mg. added	40.0 mg. added
Pb	105	20	-0.04	41.0
		40	0.12	40.3
		80	0.60	----
Hg	97	40	0.65	41.1
		80	0.73	39.7
Cu	38	50	-0.22	41.4
		100	0.30	40.9
Cd	21	50	-0.17	40.5
		100	0.30	40.1
H_2SO_4	---	1750	1.1	41.0
		3500	2.0	40.2

CONCLUSIONS

The use of niobium as an internal standard, and application of empirically determined correction factors, provided a rapid method for the x-ray fluorescence determination of zirconium and molybdenum in the presence of uranium. Using this technique, interference caused by variations in the uranium concentrations in the sample is eliminated effectively. For the determination of not greater than 50 percent of molybdenum or zirconium, the uranium content may vary between 30 and 100 percent. One analyst can analyze approximately eight to ten samples daily for both elements.

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