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MASTER

The X-Ray Fluorescence
Spectrometric Determination
of Tantalum and Tungsten

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THE X-RAY FLUORESCENCE SPECTROMETRIC DETERMINATION OF TANTALUM AND TUNGSTEN

by

E. A. Hakkila, S. N. Deming, and R. G. Hurley

ABSTRACT

Tantalum and tungsten, when present at concentrations between 5 and 95% in various materials, are measured by x-ray spectrometric methods. For the analysis of binary mixtures, the sample is dissolved in a mixture of hydrofluoric and nitric acids, the solution is irradiated using a molybdenum-target x-ray tube, and the intensity of the $L\alpha_1$ x-ray for tantalum or tungsten is measured. The concentration of tungsten or tantalum is determined by comparing the x-ray intensity with intensities measured for solutions having known tungsten or tantalum concentrations. The relative standard deviations of the line intensity method are in the range between 2 and 1% for determining concentrations between 5 and 95% of tungsten or tantalum.

An internal standard method is used for the analysis of more complex mixtures; this method is applicable also to the analysis of binary mixtures. The sample is dissolved in hydrofluoric and nitric acids, an internal standard is added, and the solution is irradiated using a molybdenum-target x-ray tube. Zinc is added as an internal standard for the determination of tantalum or tantalum and tungsten, and copper is the internal standard for the determination of tungsten only. The ratios of the intensities of the $L\alpha_1$ x-ray for tantalum and tungsten to the $K\alpha$ x-ray for zinc, or of the $L\alpha_1$ x-ray for tungsten to the $K\alpha$ x-ray for copper, are determined. Concentrations of tantalum and tungsten are obtained by comparing the intensity ratios with equivalent ratios determined for solutions having known tantalum, tungsten, zinc, and copper concentrations. The relative standard deviations using the internal standard method are in the range between 1 and 0.6% for determining 5 to 95% of tantalum and between 2.9 and 0.4% for determining 5 to 95% of tungsten. Serious interference is caused by copper, nickel, rhenium, hafnium, iridium, or platinum in the determination of tantalum, and by nickel, hafnium, rhenium, iridium, or platinum in the determination of tungsten.

INTRODUCTION

Methods were needed for determining tantalum and tungsten in various binary and more complex mixtures, including tungsten-tantalum, tungsten-rhenium, tungsten-copper, and tungsten-uranium oxide. X-ray fluorescence spectrometric methods for measurement of major constituents generally are rapid, do not require separations, and can be applied readily to the analysis of various materials. The most rapid x-ray spectrometric method is measurement of the intensity of an x-ray for the element being determined and correction of the intensity for the counter dead time. The concentration in the sample is calculated by comparing the corrected intensity to values measured for solutions having known compositions. This method is applicable to binary mixtures, but suffers some loss in accuracy if the sample matrix is changed either by introducing a third element, varying sample size, or changing solvent composition. Compensation for matrix variations is made, to a large degree, using internal standard methods in which calculations are based upon the ratio of the intensity of the x-ray from the element being measured to the intensity of the x-ray from the internal standard. Variations in the sample composition or matrix generally affect the x-ray intensity from each element to a similar extent, but affect the ratio much less. Both of these types of x-ray methods were investigated for the measurement of tantalum and tungsten, and each method was found to have specific applications.

APPARATUS AND REAGENTS

Apparatus:

Balance, analytical, Ainsworth Model BCT or similar instrument.

Beakers, 250- and 50-ml, low-form, Teflon.

Bottles, polyethylene, various sizes, with screw caps.

Heat lamps, infrared, hard glass, with socket, switch, extension cord, and ring stand attachments.

Hot plate, thermostatic, electric (Fisher Autemp) or similar instrument, 6-in. diam.

Mylar film, 0.25-mil thick.

Normal laboratory glassware, including borosilicate glass pipets, beakers, and volumetric flasks.

Pipets, Nalgene or similar plastic ware, 5-ml with 0.1-ml graduations, calibrated to deliver.

Pulse-height analyzer, Los Alamos Scientific Laboratory Electronic Group Single-Channel Pulse-Height Analyzer, Model 10 A, or similar instrument.

Sample cell, stainless steel, as supplied with the x-ray spectrograph, but coated on the inside with paraffin. To prepare a window for the cell, place a 3-in. square of 0.25-mil-thick Mylar sheet on the inner ring of the cell window frame, and tap the outer ring in place with a small mallet. Trim off excess Mylar with scissors and screw the window onto the sample cell. The window must be replaced after 2 hr of exposure in the x-ray beam.

X-ray spectrograph, Philips Electronic, Inc., equipped with lithium fluoride analyzing crystal, molybdenum target x-ray tube, and transistorized scintillation detector with associated electron circuitry.

Reagents:

Acetone, reagent grade.

Acid, hydrofluoric, 29M, reagent grade.

Acid, nitric, 15M, reagent grade.

Copper solution, 12.5 mg/ml of copper. Dissolve 1.250 g of copper in 20 ml of 15M nitric acid and dilute to 100.0 ml with distilled water. Pure copper supplied for emission spectrographic electrodes was used in this work.

Desicote, Beckman Instrument, Inc.

Tantalum metal, 99.9% purity, or better.

Tantalum solution (A), 50.0 mg/ml of tantalum.

Dissolve 5.000 g of high-purity tantalum metal in 50 ml of 29M hydrofluoric acid and add 15M nitric acid dropwise to maintain a steady dissolution rate. Cool the solution, dilute to 100.0 ml in a borosilicate glass volumetric flask, and transfer immediately to a polyethylene bottle.

Tantalum solution (B), 10.0 mg/ml of tantalum.

Using a pipet, transfer 20.0 ml of tantalum solution (A) into a 100.0-ml borosilicate glass volumetric flask and dilute to volume with distilled water.

Transfer immediately to a polyethylene bottle.

Tungsten metal, 99.9% purity, or better.

Tungsten solution (A), 50.0 mg/ml of tungsten.

Dissolve 5.000 g of high-purity tungsten metal in 50 ml of 29M hydrofluoric acid and add 15M nitric acid dropwise to maintain a steady dissolution rate.

Allow the solution to cool, dilute with distilled water to 100.0 ml, and transfer immediately to a polyethylene bottle.

Tungsten solution (B), 10.0 mg/ml of tungsten. Transfer 20.0 ml of tungsten solution (A) into a 100.0-ml borosilicate glass volumetric flask and dilute to volume with distilled water. Transfer immediately to a polyethylene bottle.

Zinc solution, 12.5 mg/ml of zinc. Dissolve 1.250 g of zinc metal in 20 ml of 15M nitric acid. When dissolution is complete, cool, transfer to a 100-ml volumetric flask, and dilute to volume with distilled water.

SAMPLING

Samples for tungsten or tantalum analyses may be received in the form of turnings, chunks, wires, or powders. Metal samples selected for analysis should be washed in methyl chloroform and air dried to remove grease or cutting oil. Portions of the sample weighing 200 ± 10 mg should be selected for analysis.

X-RAY OPERATING CONDITIONS

X-ray tube: molybdenum-target, Philips FA 60.

Potential: 50 kV.

Current: 30 mA.

Counter: scintillation.

Counter voltage: 880.

Pulse-height analyzer: determine base line and window settings as described in the operating manual.

Rate meter scale factor: off.

Scaler input signal: positive.

S-P scale factor: 8.

Scaler scale factors: 16 and 32.

Count register: 100 or 1000 to accumulate 12,800; 25,600; 128,000; or 256,000 counts.

Analyzing crystal: LiF (2d spacing of $4.028 \text{ \AA}$)

RECOMMENDED PROCEDURE

A. Internal Standard Method

1. Place each accurately weighed 200 ± 10 mg sample in a 50-ml Teflon beaker, add 15 ml of 29M hydrofluoric acid, heat, and add 15M nitric acid dropwise to sustain dissolution at a moderate rate.
2. Add 2.00 ml of the copper internal standard solution (25.0 mg of copper) for the measurement of tungsten or 2.00 ml of the zinc inter-

nal standard solution (25.0 mg of zinc) for the measurement of tantalum or of tantalum and tungsten.

3. Evaporate each solution to approximately 1 ml, allow to cool, and then add 3.0 ml of 29M hydrofluoric acid. Transfer to a 25.0-ml volumetric flask and dilute to volume with distilled water. Transfer immediately to a polyethylene bottle.
4. Prepare solutions designated (a) through (f) to contain the amounts of tantalum or tungsten and other alloying elements shown below. For a binary alloy sample, add suitable aliquots of a solution of alloying metal, other than tantalum or tungsten, that contain the indicated quantities of the element. For a ternary alloy sample, add suitable aliquots of solutions of the alloying metals so that the ratio of the concentration of the two elements is approximately equal to that in the sample and the total quantity added is equal to that shown below.

<u>Solution</u>	<u>Ta or W added, mg</u>	<u>Total matrix elements, mg</u>
(a)	0.0 (blank)	200.0
(b)	10.00	190.0
(c)	50.0	150.0
(d)	100.0	100.0
(e)	150.0	50.0
(f)	190.0	10.0

5. Perform Steps 2 and 3 on solutions (a) through (f).
6. Fill the sample cell with solution (a), irradiate the solution with x-rays from the molybdenum-target tube, and record the time required to accumulate a minimum of 12,800 counts at the wavelengths of the $L\alpha_1$ x-rays for tantalum and/or tungsten, and also at the wavelengths of the $K\alpha$ x-ray for zinc or copper, respectively.
7. Repeat Step (6) for each of the solutions (b) through (f) and the sample solution.
8. Correct all measured count times for counter dead time by subtracting 3.8×10^{-6} sec/count.
9. Determine the count rate for each measurement using:

$$\text{Counts/sec} = \frac{\text{number of counts accumulated}}{\text{sec, corrected}} \quad (1)$$

10. Determine the intensity ratio for each solution using:

$$\text{Intensity ratio, } R = \frac{\text{counts/sec for Ta or W}}{\text{counts/sec for Zn or Cu}} \quad (2)$$

11. Determine the factors, F_i , using:

$$F_i = \frac{R_{(i)} - R_{(a)}}{\text{mg Ta or W in solution (i)}} \quad (3)$$

in which (i) is equal to (b) through (f).

12. If the values for F_i agree within 1%, determine the slope, A , using Eq. (4). (If the factors differ by more than 1%, proceed to Step 14.)

$$A = \frac{[R_{(b)} - R_{(a)}] + \dots + [R_{(f)} - R_{(a)}]}{\text{total mg of Ta or W in solutions (b)-(f)}} \quad (4)$$

13. Determine the amount of tantalum or tungsten in each sample solution using:

$$\text{Ta or W, mg} = \frac{R_{(s)} - R_{(a)}}{A} \quad (5)$$

in which (s) refers to the sample solution and A is the slope calculated by Eq. (4).

14. If the variation in factors, F_i , is greater than 1%, plot, on linear graph paper, the tantalum or tungsten concentration vs. R for solutions (a) through (f), Step 4. Determine the weight of tantalum or tungsten in the sample from this plot.
15. Determine the percent of tantalum or tungsten in each sample using:

$$\text{Ta or W, \%} = \frac{\text{weight Ta or W, mg}}{\text{sample wt, mg}} \times 100. \quad (6)$$

B. Line Intensity Method

1. Perform Steps 1, 3, and 4, Section A, on solutions (a) through (f).
2. Fill the sample cell with solution (a), irradiate the solution with x-rays from the molybdenum-target x-ray tube, and record the time to accumulate a minimum of 12,800 counts at the wavelength of the $L\alpha_1$ x-ray for tantalum and/or tungsten.
3. Perform Step 2 for each of the solutions (b) through (f) and the sample solution. Determine the count rate, I , for each solution as described in Steps 8 and 9, Section A.
4. For each of the solutions (b) through (f), determine a factor, F_i , using:

$$F_i = \frac{I_{(i)} - I_{(a)}}{\text{mg of Ta or W in standards}} \quad (7)$$

in which $I_{(i)}$ is the intensity determined for each of the solutions, (b) through (f), and $I_{(a)}$ is the intensity for solution (a).

5. If the values of F_i do not differ by more than 1%, determine the slope, A , using Eq. (8). (If the values differ by more than 1%, proceed to Step 7.)

$$A = \frac{[I_{(b)} - I_{(a)}] + \dots + [I_{(f)} - I_{(a)}]}{\text{total mg of Ta or W in solutions (b)-(f)}} \quad (8)$$

6. Determine the weight of tantalum or tungsten in each sample using:

$$\text{Ta or W, mg} = \frac{I_{(s)} - I_{(a)}}{A} \quad (9)$$

in which (s) refers to the sample solution and A is the slope determined by Eq. (8).

7. If the factors F_i differ by more than 1%, plot, on linear graph paper, the tantalum or tungsten concentration vs. intensity for solutions (a) through (f). Determine the weight of tantalum or tungsten in the sample from this plot.
8. Determine the percent of tantalum or tungsten in the sample using Eq. (6).

EXPERIMENTAL

Selection of X-Ray Tube. Previous work⁽¹⁾ showed that a tungsten-target tube was satisfactory in the determination of not greater than 10% of tungsten. The method described there was not readily applicable to measurement of tungsten at higher concentrations or of tantalum-tungsten mixtures. Use of a molybdenum-target x-ray tube eliminated overlap of first-order x-rays arising from the tube target. One disadvantage of using the molybdenum-target tube was the overlap of the second-order Compton peak for molybdenum with the tungsten L-series spectra, but a pulse-height analyzer reduced this interference significantly. It was advantageous, therefore, to use a molybdenum-target tube in conjunction with a pulse-height analyzer.

Effect of Sample Concentration. Self-absorption may cause deviations from linearity in calibration curves for x-ray fluorescence analysis if the sample solutions are too concentrated. The effects of two sample concentrations, 8 and 20 mg/ml, on the measurement of tantalum and tungsten x-ray intensities from binary mixtures were investigated by diluting solutions containing a total of 200 mg of tantalum and tungsten to either 10.0 ml (20 mg/ml) or 25 ml (8 mg/ml) and analyzing each solution. Straight-line calibration curves were obtained if the sample solution concentration was 8 mg/ml, but deviations from linearity were observed for sample concentrations of 20 mg/ml (Table I). A volume of 25.0 ml was convenient, and a sample concentration of 8 mg/ml was recommended.

Selection of Internal Standard. Several elements, including hafnium, rhenium, copper, and zinc, were considered as internal standards. Hafnium had an $L\eta$ x-ray overlapping the $L\alpha_1$ x-ray for tantalum, and rhenium had an $L\alpha_1$ x-ray overlapped by the $L\eta$ x-ray for tungsten. The $K\alpha$ x-rays from copper and zinc were relatively free of interference

Table I
Effect of Sample Concentration on Tantalum and Tungsten
X-Ray Intensities from Binary Mixtures
(200 mg of Sample)

Sample composition, %		Diluted to 10.0 ml		Diluted to 25.0 ml	
Ta	W	c/s/mg Ta	c/s/mg W	c/s/mg Ta	c/s/mg W
100	0	44.7	-	23.6	-
95	5	45.4	48.7	23.7	24.2
75	25	45.4	48.4	23.6	24.0
50	50	46.1	46.5	24.1	24.4
25	75	47.6	45.5	23.8	23.8
5	95	48.0	45.5	23.8	23.9
0	100	-	45.1	-	23.8

from tungsten and tantalum, respectively. If both tantalum and tungsten were measured, it was necessary to consider the overlapping of the $K\alpha$ line for copper at a 2θ angle of 45.02° by the $L\alpha_2$ line for tantalum at 44.74° . In addition, the $K\alpha$ line for zinc at a 2θ angle of 41.78° was overlapped by the $L\eta$ line for tungsten at 41.35° . Zinc was recommended as the internal standard when tantalum and tungsten were determined because the overlap was less serious in the case of tungsten and zinc than in that of tantalum and copper. Nonlinear calibration curves were obtained, and tantalum and tungsten concentrations were determined graphically rather than by using arithmetic factors, F.

RELIABILITY

The relative standard deviations of the line intensity and internal standard methods were determined by applying the Recommended Procedure to the analysis of solutions having known concentrations of tantalum and tungsten. Standard deviations (Tables II and III), based upon 16 measurements at each concentration, indicated that the internal standard method was more precise generally. Relative standard deviations of less than 2% were obtained in measuring each element at concentrations between 5 and 95% using the line intensity technique.

EFFECT OF OTHER IONS

Interference in the x-ray line intensity method may result (1) from elements having x-ray lines within two line-half-widths, or approximately 1° , of

the $L\alpha_1$ line for tantalum or tungsten (line overlap); (2) from elements having intense x-rays just to the short-wavelength side of the L III absorption edges for tantalum or tungsten (enhancement); or (3) from elements having mass absorption coefficients which are significantly different from those of the matrix elements in the standards at the tantalum and tungsten wavelengths (absorption). In addition to those elements having x-ray lines overlapping the $L\alpha_1$ lines for tantalum and tungsten, overlap interference in the internal standard method may result from elements having x-ray lines within a 2θ angle of approximately 1° of the internal standard line. Absorption and enhancement effects are minimized by use of an internal standard. Only elements having absorption edges between the $L\alpha_1$ x-ray for tantalum or tungsten and the internal standard x-ray cause absorption interference. Elements having an intense x-ray between the L III edge for tantalum or tungsten and the K edge for the internal standard cause enhancement. Elements which may interfere with the determination of tantalum or tungsten by x-ray line overlap, absorption, or enhancement are summarized in Table IV. Because the analyses are performed in hydrofluoric acid, the rare earths were not considered further as possible sources of interference.

The effects on the method and the maximum tolerable concentration levels of several of the elements listed in Table IV were determined. Samples were prepared to contain between 5 and 95% of tantalum and tungsten and between 1 and 25% of the added

Table II
Precision of the X-Ray Fluorescence Spectrometric
Method for Determining Tantalum
(200 mg Sample)

Ta added, %	Standard deviation, mg		Relative standard deviation, %	
	Internal standard	Line intensity	Internal standard	Line intensity
5	0.096	0.13	0.96	1.3
25	0.45	0.60	0.90	1.2
50	0.78	1.50	0.76	1.5
75	0.84	2.27	0.56	1.5
95	1.85	3.26	0.97	1.7

element. Standards contained only tantalum and tungsten. Results of these studies are summarized in Table V. Interference was assumed if the added element caused a deviation in results larger than twice the relative standard deviation of the method.

One analyst can analyze 12 samples per day using the line intensity method or nine samples per day using the internal standard method. Analysis of one sample requires 2 hr by either method.

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REFERENCE

- (1) E. A. Hakkila and G. R. Waterbury, *Talanta*, 6, 46 (1960).

Table III
Precision of the X-Ray Fluorescence Spectrometric
Method for Determining Tungsten
(200 mg Sample)

W added, %	Standard deviation, mg		Relative standard deviation, %	
	Internal standard	Line intensity	Internal standard	Line intensity
5	0.29	0.19	2.9	1.9
25	0.65	0.69	1.3	1.4
50	0.42	1.29	0.42	1.3
75	0.50	1.69	0.33	1.1
95	1.50	2.86	0.79	1.5

Table IV
Elements which May Interfere with the Measurement of
Tantalum or Tungsten

Element determined	Method	Elements interfering by		
		overlap	absorption	enhancement
Ta	Line intensity	Several rare earths; Au, Pt, Ni, Hf, Ir	Elements having atomic numbers between 1 and 18, 24 and 40, 50 and 67, and greater than 80.	Elements having atomic numbers between 31 and 37, and between 75 and 92.
W	"	Several rare earths; Ni, Ta, Re, Au	"	"
Ta	Internal standard (Zn)	Several rare earths; W, Hg, Re, Au, Pt, Ni, Hf, Ir	Ni, Er	Au, Ge, Rc
W	Internal standard (Cu)	Several rare earths; Ni, Hf, Ta, Re, Ir, Au	Ni, Ho, Er	Ga, Hg, Au, Pt, Ir

Table V
Effect of Various Elements on the Determination of
Tantalum and Tungsten

Element determined	Method	Interfering elements	Maximum tolerable concentration, %
Ta	Line intensity	Ni, Re, Hf, Ir, or Pt	1
Ta	Internal standard	Cu	1
		Ni, Re	5
		Hg	12.5
		Hf	15
W	Line intensity	Ir	1
		Re	5
		Hf	25
W	Internal standard	Hf	25