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MINES BRANCH INVESTIGATION REPORT IR 61-70

IMPURITIES IN REFRACTORY METALS POWDERS

by

**L. G. RIPLEY, ELSIE M. PENNER, A. H. GILLIESON,
W. R. INMAN & R. H. DONAHOE**

MINERAL SCIENCES DIVISION

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L.G. Ripley^{*}, Elsie M. Penner^{**}, A.H. Gillieson^{*},
W.R. Inman^{***} and R.H. Donahoe^{****}

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GENERAL INTRODUCTION

In July, 1959, the Analytical Chemistry Subdivision of the Mineral Sciences Division was requested to undertake certain work for the Advisory Group on Aeronautical Research and Development (AGARD) to NATO.

Specifically the work involved the determination of traces of certain other elements in high purity molybdenum, niobium, tantalum and tungsten metal powders. These powders were prepared by NATO countries participating in the work of AGARD.

The work to date of this Division has been the determination of nitrogen in samples of molybdenum, niobium, tantalum and tungsten from the United Kingdom, France and the United States; iron in samples of molybdenum, niobium, tantalum and tungsten from the United Kingdom; and spectrographic analyses of four tungsten samples, two from the United States and one each from France and the United Kingdom.

* Senior Scientific Officers, ** Scientific Officer, *** Head, and **** Technician, Analytical Chemistry Subdivision, Mineral Sciences Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

The results and the methods used were issued as Mineral Sciences Division Internal Reports MS-60-87, September 14, 1960 and MS-61-40, May 2, 1961. These reports were given to Mr. H.V. Kinsey, Canadian Materials representative on the Structures and Materials Panel, for the use of the panel coordinator.

The above reports are now being reissued, with minor editorial changes, as Parts I, II and III of the present Investigation Report. Copies of this report are being sent to the member countries of the Structures and Materials Panel of AGARD (NATO).

PART I DETERMINATION OF IRON IN HIGH PURITY MOLYBDENUM, NIOBIUM, TANTALUM AND TUNGSTEN METALS

1. Principle

Bathophenanthroline (4,7-diphenyl - 1, 10 - phenanthroline) forms a complex with ferrous iron that can be extracted into N-amyl alcohol. The optical density of the complex in N-amyl alcohol is measured in a spectrophotometer at a wavelength of 536 millimicrons.

2. Reagents

Standard Iron Solution

Weigh 0.1000 g of electrolytic iron into a 250 ml flask. Add 30 ml of distilled water and 5 ml of concentrated sulphuric acid (H_2SO_4 sp gr 1.84). Heat as necessary until the iron is dissolved.

Cool and make up to 500 ml. Store in polyethylene bottle.

5 ml = 1.000 mg Fe.

Bathophenanthroline (4,7 - Diphenyl - 1, 10-Phenanthroline)
0.001 M Solution

Weigh 0.167 g of the reagent into a 400 ml polyethylene beaker. Add 250 ml of ethyl alcohol (cologne spirits) and allow to stand overnight to ensure complete solution. Make up to 500 ml with distilled water and store in polyethylene bottle.

Hydroxylamine Hydrochloride, 50% Solution (Iron Free)

Weigh 250 g of the reagent ($\text{NH}_2\text{OH}\cdot\text{HCl}$) into a 1000 ml beaker and add approximately 300 ml of distilled water. When solution is complete add 50 ml of the 0.001 M bathophenanthroline solution and stir for several minutes. Let stand for two hours. Transfer to a 500 ml separatory funnel and extract with 15 ml portions of a 3:1 mixture of chloroform and N-amyl alcohol until both aqueous and organic solvent layers are white. Discard the chloroform-N-amyl alcohol fractions. Then extract three times with 10 ml portions of chloroform to remove the dissolved N-amyl alcohol. Filter the aqueous solution into a 500 ml volumetric flask, make to volume with distilled water and store in polyethylene bottle.

Ammonium Tartrate, 25% Solution (Iron Free)

Weigh 125 g of the reagent $(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ into a 1000 ml beaker and add approximately 350 ml of distilled water. When the ammonium tartrate is dissolved add 2 ml of the 50% hydroxylamine hydrochloride solution and mix well. Then add 10 ml of 0.001 M bathophenanthroline solution, stir thoroughly and allow to stand for two hours. Extract with chloroform and N-amyl alcohol as for the hydroxylamine hydrochloride solution. Filter into a 500 ml volumetric flask, make to volume with distilled water and store in polyethylene bottle.

Boric Acid, 5% Solution (Iron Free)

Weigh 50 g of the reagent H_3BO_3 into a 1000 ml beaker and add approximately 800 ml of distilled water. Heat until solution is complete. Cool, add 2 ml of 50% hydroxylamine hydrochloride solution and stir thoroughly. Then add 20 ml of 0.001 bathophenanthroline solution, mix well and allow to stand for two hours. Extract with chloroform and N-amyl alcohol as for the hydroxylamine hydrochloride solution. (Because of the volume it is convenient to do this in two portions using a 500 ml separatory funnel). Filter into a 1 litre volumetric flask, make to volume and store in polyethylene bottle.

3. Standard Curve

Dilute 5 ml of the standard iron solution to 500 ml.

Then 1 ml of the diluted iron solution = 2 micrograms of Fe.

To a 250 ml polyethylene beaker add 20 ml of the 25% ammonium tartrate solution, 40 ml of the 5% boric acid solution and 20 ml of the 50% hydroxylamine hydrochloride solution. Adjust the pH of the contents of the beaker to 5.5 with concentrated ammonium hydroxide (NH_4OH sp gr 0.90), using a pH meter. Make to a volume of 100 ml. To each of six 60 ml separatory funnels, which are marked at 25 ml, add a 10 ml aliquot of this solution. Then by burette add to the first separatory funnel 2.5 ml of the diluted standard iron solution, to the second 5.0 ml, to the third 7.5, to the fourth 10.0 ml and to the fifth 12.5 ml. The sixth is the blank. Dilute the contents of each funnel to 25 ml with distilled water, mix and allow to stand for 30 minutes. Add to each funnel, by pipette, 4 ml of 0.001 M bathophenanthroline solution. Mix by swirling and allow to stand a further 15 minutes. Add to each funnel, by pipette, 10 ml of N-amyl alcohol, stopper and shake for 2 minutes, then let stand for 5 minutes for the layers to separate. Drain off, and discard, the lower (aqueous) layer. Transfer the N-amyl alcohol layers to 15 ml centrifuge tubes. Centrifuge for 30 seconds, transfer to cuvettes and measure the optical density at 536 millimicrons using a Beckman Du spectrophotometer. Plot micrograms of iron vs optical density.

4. Procedure for Niobium and Tantalum

Weigh a 0.500 g sample into a 250 ml Teflon beaker (Teflon = Tetra fluorethylene-Dupont). Add 5 ml of distilled water, 2 ml hydrofluoric acid (48% HF) and cover with a polyethylene watch glass. Add concentrated nitric acid (HNO_3 sp gr 1.42) dropwise, slowly, until metal is in solution. Usually 1 ml of nitric acid is sufficient. Wash down plastic watch glass with small volume of distilled water. Add 3 ml of formic acid (HCOOH 88%) and heat gently on the hot plate until the evolution of brown nitrogen gases ceases and the solution becomes colourless. Wash down sides of beaker with the minimum amount of water that will suffice, and continue heating gently for fifteen minutes. Remove from the hot plate and add to the hot solution 10 ml of the 25% ammonium tartrate solution. (This is added by pipette and the solution is run down the sides of the beaker to wash down any solution adhering thereto). Let stand 10 minutes, add 20 ml of the 5% boric acid solution, by pipette, washing down the sides of the beaker, and let stand 20 minutes. Add, by pipette, 10 ml of the 50% hydroxylamine hydrochloride solution and let stand 30 minutes. Adjust the pH to 5.5 by the slow addition of concentrated ammonium hydroxide (NH_4OH sp gr 0.90). Use a pH meter in this adjustment. Transfer to a 100 ml flask, make to volume and let stand for 3 hours to complete the reduction of the iron. A reagent blank is carried through the same procedure. Transfer 20 ml aliquots of the samples and blank to 60 ml separatory funnels. Make to 25 ml with

distilled water, add 4 ml of the 0.001 M bathophenanthroline solution and proceed as for the standard curve.

1 microgram Fe = 0.001% when 20 ml aliquots are taken.

5. Procedure for Molybdenum and Tungsten

Weigh a 0.500 g sample into a 250 ml Teflon beaker. Add 5 ml of distilled water and 2 ml of hydrofluoric acid (48% HF). Cover the beaker with a polyethylene watch glass and add concentrated nitric acid dropwise (HNO_3 sp gr 1.42) until solution is complete. Wash down watch glass with minimal amount of distilled water and then add exactly 2 ml of concentrated hydrochloric acid (HCl sp gr 1.19). Heat on hot plate for several minutes. In the case of molybdenum heat until the solution becomes very pale yellow in colour. Then add 3 ml of formic acid (HCOOH 88%) and proceed as for niobium and tantalum.

6. Notes

1. Reduction of iron in the presence of tartrate is slow.
2. The solutions of niobium, tantalum and tungsten may be allowed to stand overnight. In the case of the molybdenum solution, overnight standing results in lower values for iron.
3. The niobium and tantalum solutions may exhibit some turbidity. This will not affect the iron results.
4. The N-nyl alcohol extracts are stable for at least 24 hours. (Tests were not extended beyond this).

7. Values Obtained by the Above-described Procedures

<u>Sample</u>	<u>% Iron</u> <u>Replicate Values</u> *	<u>Average</u>
Molybdenum-HM-85	0.0066, 0.0064, 0.0066	0.0065
Niobium -HJ-57	0.0218, 0.0219, 0.0246, 0.0247, 0.0224, 0.0226, 0.0224	0.0229
Tantalum -HM-84	0.0145, 0.0145, 0.0151, 0.0151	0.0148
Tungsten -HM-86	0.0114, 0.0116, 0.0120, 0.0121	0.0118

* Replicates were obtained on at least two different days.

PART II DETERMINATION OF NITROGEN IN HIGH PURITY
MOLYBDENUM, NIOBIUM, TANTALUM AND TUNGSTEN METALS

1. Principle

Nitrogen is determined by a modified Kjeldahl procedure. The ammonia is steam distilled into dilute acid and estimated spectrophotometrically after being reacted with Nessler reagent.

2. Reagents

The various reagents used were of "analytical grade" and meet with ACS specifications. No special purification was attempted to remove the small amounts of nitrogen present in them, as reagent blanks were always carried.

Distilled water, prepared in a system fabricated of glass and block tin was used throughout.

The Nessler reagent was prepared from elemental mercury, elementary iodine and potassium iodide by the method of Koch and McMeekin - J.A.C.S., 46, 2066 (1924). This reagent gives a very stable compound with ammonia and no protective colloid is required.

3. Apparatus

The steam distillation apparatus is constructed so that the sample is dissolved and distilled from the same flask. The flask connects to the steam distillation train by a $\frac{45}{50}$ ground glass joint.

Optical density was measured by a Coleman MK XIV spectrophotometer.

4. Solution of the Samples

Because these metals are refractory, and since nitric acid was of course proscribed, the problem of solution was difficult. For this reason the methods of solution vary somewhat with the metals.

Molybdenum

Weigh a 1.000 g sample into a 250 ml reaction flask, add 15 ml of concentrated sulphuric acid (H_2SO_4 sp gr 1.84), 3 g of potassium sulphate (K_2SO_4) and 0.3 g copper sulphate ($CuSO_4$ anhydrous). Fume until the reaction is complete. Cool, wash down the flask with a

small amount of water and add 3 ml of hydrogen peroxide (H_2O_2 30%).

Let stand at room temperature for five minutes, boil to remove excess hydrogen peroxide, cool, dilute to 100 ml with distilled water and distil, Nesslerize and measure the optical density as described below.

Niobium

Weigh 1.000 g into a 250 ml reaction flask. Add 15 ml of concentrated sulphuric acid (H_2SO_4 sp gr 1.84), 3 g of potassium sulphate and 0.3 g of copper sulphate ($CuSO_4$ anhydrous). Fume until reaction is complete (between 30 and 60 minutes) - see note (a). Cool, dilute to 100 ml with distilled water and distil, Nesslerize and measure the optical density as described below.

Note (a):

If a slight insoluble residue persists, cool, dilute with 20 ml distilled water, cool, add 3 ml hydrogen peroxide (30% H_2O_2) and proceed as for molybdenum.

Tantalum

Weigh a 1.000 g sample into a 250 ml reaction flask. Add 15 ml concentrated sulphuric acid (H_2SO_4 sp gr 1.84), 3 g potassium sulphate and 0.3 g copper sulphate ($CuSO_4$ anhydrous). Fume for 1 hour. Cool (note (b)). Dilute with 20 ml distilled water; cool. Add 2 ml of hydrofluoric acid (HF 48%) (note (c)). Allow to stand at room temperature for 5 minutes. Add 3 ml hydrogen peroxide (H_2O_2 30%) (note (d)). Allow to stand at room temperature

for a further 5-10 minutes. Boil to remove excess hydrofluoric acid and hydrogen peroxide. Cool, dilute with distilled water.

Distil, Nesslerize and measure optical density as described below.

Note (b):

The sample is only partly dissolved at this point.

Note (c):

The hydrofluoric acid will dissolve the greater part of the undecomposed metal.

Note (d):

The hydrogen peroxide should complete the decomposition.

If it does not at first, the hydrofluoric acid and hydrogen peroxide treatment should be repeated.

Tungsten

Weigh a 1.000 g sample into a 250 ml reaction flask.

Add 10 ml concentrated sulphuric acid (H_2SO_4 sp gr 1.84) and 15 ml concentrated orthophosphoric acid (H_3PO_4 85%). Fume until the metal is completely dissolved (1-2 hours). Cool, dilute to 100 ml with distilled water. Distil, Nesslerize and measure the optical density as described below.

5. Distillation

Connect the reaction flask to the steam distillation train.

Add to the reaction flask sufficient 50% sodium hydroxide solution (NaOH 50% solution) to neutralize and then 10 ml in excess. Steam,

distil, collecting the distillate in a 100 ml volumetric flask containing 15 ml distilled water and 1 ml of N/10 sulphuric acid. ($0.1\text{ N H}_2\text{SO}_4$). Distil until 60 ml of distillate have been collected, then remove the volumetric flask, washing the delivery tube with a small amount of water.

6. Nesslerization

To the volumetric flask now add 10 ml of Nessler solution (Koch and McMeekin), mix and dilute to 100 ml with distilled water. Let stand 10 minutes for full colour development.

7. Measurement of Optical Density

Measure the optical density using a Coleman MK XIV spectrophotometer, (square cuvettes with 1.3 cm light path) at a wavelength of 410 millimicrons, comparing with a reagent blank.

Find the amount of nitrogen in the sample by reading the value from a curve that has been prepared by Nesslerizing known amounts of ammonium sulphate and plotting optical density against milligrams of nitrogen.

It is convenient to check the standard curve by running appropriate U.S. National Bureau of Standards steel samples along with the samples under examination.

8. Nitrogen Values for High Purity Molybdenum, Niobium, Tantalum and Tungsten by the Above-described Methods

<u>Molybdenum</u>			
<u>Code No.</u>	<u>Source of Material</u>	<u>Nitrogen % Replicate Values</u>	<u>Mean</u>
FR/Mo/3	France	0.0050, 0.0060, 0.0070, 0.0080, 0.0080	0.007
US-Mo-P2E Lot #CR2966RM	General Electric Co., Cleveland, Ohio, U.S.A.	0.0045, 0.0045, 0.0045, 0.0050, 0.0080	0.005
US-Mo-P2F Lot # 200	Wah Chang Corp., Glen Cove, New York, U.S.A.	0.0045, 0.0045, 0.0050, 0.0065, 0.0085	0.006
HM-85	Murex Ltd., U.K.	0.0010, 0.0015, 0.0015, 0.0020, 0.0020, 0.0027	0.0018
<u>Niobium</u>			
FR/Nb/1	France	0.0060, 0.0070, 0.0077, 0.0080, 0.0080, 0.0100, 0.0107	0.008
US-Nb-P3B	Fansteel Metallurgical Corp., U.S.A.	0.0260, 0.0260, 0.0270, 0.0280, 0.0310	0.028
HJ-57	Murex Ltd., U.K.	0.128, 0.134, 0.134, 0.136, 0.138, 0.146	0.136
<u>Tantalum</u>			
FR/Ta/1	France	0.0155, 0.0160, 0.0160, 0.0165	0.016
US/Ta/P3A Lot #T-560	National Research Corp., Cambridge, Mass., U.S.A.	0.0040, 0.0045, 0.0045, 0.0060	0.005
US/Ta/P3B	Fansteel Metallurgical Corp., U.S.A.	0.0025, 0.0030, 0.0035, 0.0040	0.003
HM-84	Murex Ltd., U.K.	0.060, 0.064, 0.064, 0.066, 0.066, 0.074	0.066

(cont' d)

<u>Code No.</u>	<u>Source of Material</u>	<u>Nitrogen % Replicate Values</u>	<u>Mean</u>
		<u>Tungsten</u>	
FR/W/3	France	0.0005, 0.0010, 0.0015,	0.001
US-W-P2D	U.S.A.	0.0017, 0.0020, 0.0035, 0.0038	0.003
US-W-P2F Lot #1139	Wah Chang Corp., Glen Cove, New York, U.S.A.	0.0020, 0.0025, 0.0027	0.002
HM-86	Murex Ltd., U.K.	0.0000 , 0.0000 , 0.0005, 0.0010, 0.0011, 0.0019, 0.0026	0.0010

PART III QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF
TUNGSTEN METAL BY SELECTIVE DISTILLATION
OF IMPURITIES IN THE DC ARC

1. Introduction

Direct spectrographic impurity determination in tungsten by the arc is rendered impracticable because tungsten has a very complex line spectrum, and in addition gives rise to an intense continuum. The heavy background and extensive line interference render measurement of impurity line intensities inaccurate or impossible.

Dyck and Veleker (1) avoided these difficulties by mixing the tungsten powder with high purity graphite before arcing. The heat of the arc causes the rapid formation of the highly refractory tungsten carbide, which does not volatilize into the arc and produce the tungsten spectrum until all more volatile impurities have been driven out of the sample. Thus the method relies, for effective separation of the impurities from the tungsten, on a process of selective or differential volatilization in the arc.

The above-mentioned workers recommended, and used, as source unit, an intermittent ac arc giving 2200 volts at 2.5 to 15 amperes, since with this type of excitation the impurities are much more completely volatilized out of the sample before the tungsten begins to enter the excitation zone in significant amount, and tungsten line interference can be rendered minimal by limiting exposure time.

Such a source unit was not available in the Mines Branch at the time the present work was done, and a conventional dc arc was employed. The suppression of the tungsten spectrum, although not as complete as with the ac arc, was nevertheless adequate and, in the wavelength range studied, prevented the estimation of only two (calcium and molybdenum) out of the sixteen impurity elements investigated.

2. Apparatus

Excitation Source: Applied Research Laboratories
(A.R.L.) dc Arc Source Unit Type No. 02825 A (Modified).

Spectrograph: Baird 3-metre grating instrument.

Recording Equipment: Eastman Kodak S.A.2 plates.

Densitometer: Sturrock Cathode-Ray Instrument.

(R.F. Sturrock, Can. Chem. Processing, Nov. 1955, pp. 99-100).

Developing Equipment: A.R.L. Rocking Tray Developer
and Fixer. A.R.L. Plate Dryer.

Sample Preparation Equipment: Wig-L-Bug Mixer
(obtainable from SPEX Industries Ltd.). Hydrogen Reduction
Tube-Furnace.

3. Procedure

Standard Samples: Since no spectroscopically pure tungsten powder was available to serve as the base for standards, it was necessary to carry out a simplified qualitative examination

of the samples on hand, by this selective distillation method, to discover which of the samples was the purest, and could therefore most suitably be used for the preparation of standards by addition of known quantities of the impurity elements of interest.

This preliminary qualitative examination also served to indicate the ranges of standards which should be prepared.

For the samples examined, the ranges of standards shown in Table 1 were prepared. Only three standards could be prepared because of the limited amount of sample material available. The concentration ranges of the three standards were in the ratio 1:10:100, but it is recommended that where possible at least five standards be prepared with concentration ratio of 1:3:10:30:100.

TABLE 1

Ranges of Standards
Parts per million

Element	Std # 1	Std # 2	Std # 3
K, Na, Si	1000	100	10
Th	500	50	5
As, Fe, P, Zn	200	20	2
Al	150	15	1.5
Ag	68	7	0.7
Ba, Ca, Cd, Cr, Mg, Sn, Cu, Nb	50	5	0.5
Pb, Mn, Mo, Ti, V	10	1	0.1

Preparation of Standards: The standards were prepared by adding, volumetrically, solutions of the impurity elements to tungsten powder, drying at 105°C, and reducing under a stream of hydrogen for 1 to 2 hours at about 300°C. Spectroscopically pure materials were used whenever possible, normally as oxides; failing these, reagent grade materials were employed, as detailed in Table 2. Hydrochloric acid solutions (1:1 HCl) containing 1 mg/ml of the element were first made up for the majority of the elements, and appropriate volumes combined to produce four master standard solutions each of which was diluted 10-fold twice.

The four master standard solutions A, B, C, D and E were made by combining the volumes of the element solutions shown in Table 3.

One millilitre of master standard "A", 10 ml of "B", 8.85 ml of "C", 12.7 ml of "D" and 1 ml of "E" were added to 10 g of tungsten powder in a silica or vitreosil boat, in such a manner, and in such a quantity at one time, that the sides of the boat were not wetted by the solution.

The same volumes of the 10-fold dilutions were added in the same way to another 10 g portion of powder, and the procedure repeated on a third 10 g quantity using the 100-fold dilutions of the master standards.

TABLE 2

Materials Employed for Standard Solutions

Element	Compound	Grade	Dissolved in	
Ag	AgNO ₃	reagent	distilled water	
Al	metal	Specpure*	1:1 HCl	
As	As ₂ O ₃	"		
Ba	BaCO ₃	"		
Ca	CaCO ₃	"		
Cd	CdO	"		
Cr	Cr ₂ O ₃	"		
Cu	CuO	"		
Fe	Fe ₂ O ₃	"		
K	KOH	reagent		distilled water
Mg	MgO	Specpure		1:1 HCl
Mn	Mn ₃ O ₄	"		
Mo	MoO ₃	"	HCl, tartrate + tr HF	
Na	Sodium silicate	reagent		
Nb	Nb ₂ O ₅	Specpure		
P	(NH ₄) ₂ HPO ₄	"	1:1 HCl	
Pb	PbO	"	1:1 HCl	
Si	Sodium silicate	reagent		
Sn	metal	Specpure		
Th	Th(NO ₃) ₄	reagent		
Ti	TiO ₂	Specpure	H ₂ SO ₄	
V	V ₂ O ₅	"	1:1 HCl	
Zn	ZnO	"		

* Johnson Matthey and Co. Ltd., Hatton Garden, London, England.

TABLE 3

Master Standard Solutions

Element	Vol of 1 mg/ml element solution (ml)	Master Standard
K Na Si	1	A (volume 1 ml)
As Cr Cu P	6 3 15 6	B (total volume 30 ml)
Mo Nb Sn Ti V	0.75 21 1.5 0.3 3	C (total volume 26.55 ml)
Al Ba Ca Cd Fe Pb Mg Mn Ni Th Zn	4.5 0.75 0.75 3 3 0.3 1.5 3 0.3 15 6	D (total volume 38.1 ml)
Ag	1	E (total volume 1 ml)

Between additions of the solutions to the powder, the boat and its contents were dried in an oven at 105°C.

After all additions were made, the three silica boats and their powder contents were treated with hydrogen in a tube furnace at 300°C for 1 to 2 hours.

The resulting powder standards were each thoroughly mixed in a "Wig-L-Bug" Mixer, and transferred to labelled bottles.

Preparation of Samples: The samples of tungsten powder were mixed thoroughly and 1.25 g of each and 0.20 g of a graphite powder - nickel oxide mixture (fifteen parts high purity graphite to one part of "Specpure" nickel oxide) weighed and thoroughly mixed.

Electrode System: The sample mixtures were tamped into the electrode cup (National Carbon Co. No. L 3918) and the weight of mixture in the cup recorded. The amount of mixture prepared was sufficient to fill 2 electrodes. A 1/8 in. diameter pointed counter electrode (National Carbon Co. No. L 4036) was used as cathode, the sample and cup forming the anode.

Excitation: The samples were arced in duplicated in the dc arc at 7 amp.

Exposure Conditions: The following exposure conditions were employed:-

Spectral Region	2300 - 3600 A (1st order)
Slit Width	0.025 mm
Sector Ratio	1:10:100
Arc burn period	none
Arc exposure period	30 sec

Photographic Processing:

Emulsion	Eastman Kodak SA-2
Development	Eastman Kodak D-19 for 6 min
Stop bath	running water for 15 sec
Fixing	Eastman Kodak F-10 for 10 min
Washing	running water for 30 min
Drying	blower and heater

Photometry: The intensities of the nickel and the impurity element lines were read directly on the Sturrock Cathode-Ray Densitometer, whose scale had been previously calibrated for the SA-2 plate.

The wavelengths of the lines used are shown in Table 4. The averages of the duplicate ratios of analytical line intensity to internal standard line intensity were plotted on 5 cycle x 3 cycle log-log graph paper to produce a family of working curves.

The majority of the curves were essentially straight lines, but those for Na, Fe, Al, Pb, Sn and Mn showed an inflection towards a constant intensity ratio. This deviation from linearity was caused by the presence of amounts of the elements in question in the tungsten powder used as a base for the standards, of comparable order to the amounts of the elements added. The procedure of Duffendack and Wolfe (2) was employed to determine the concentrations of these elements in the matrix of the standards.

Accuracy: Since no analysed tungsten standards were available in the concentration range studied, the only check on the accuracy of the method was a comparison of spectrographic results with those obtained by the spectrophotometric method described in MS-60-87, see Table 5.

The precision of the method based on the average deviations of the duplicates is approximately 10 per cent and is considered reasonable for a dc arc method.

TABLE 4
Analytical Lines

Element	Analytical Line, A	Internal Standard Line, A
Ag	3280.683	
Al	3092.713	
Ba	2335.269	
Cd	3261.057	
Cr	3021.558	
Cu	3273.962	
Fe	3020.640	
Mg	2795.53	Ni 3080.755
Mn	2794.817	
Na	3302.323	
Pb	2833.07	
Si	2516.123	
Sn	3175.019	
Th	3290.59	
Ti	3341.875	
Zn	3345.020	

TABLE 5
Iron Content

Sample	Spectrographic %	Colorimetric %
Fr-W-3	0.004	0.007
H.M. 86	0.010	0.012

4. Results

The analytical results obtained by this method are given in Table 6.

TABLE 6
Quantitative Spectrographic Analyses of Tungsten Metal Powders
 (Results in parts per million)

Element	Sample Description			
	American: Wah Chang Corp. US-W-P2F	American: US-W-P2D	British: Murex Ltd. H.M. 86	French: FR-W-3
Ag	<0.1	<0.1	<0.1	<0.1
Al	<0.1	<0.1	1.1	1.6
Ba	3	3	<0.1	<0.1
Cr	0.4	<0.1	0.2	<0.1
Cu	<0.1	<0.1	<0.1	<0.1
Fe	10	5	120	41
Mg	<0.1	0.5	0.3	<0.1
Mn	<0.01	<0.01	0.3	0.4
Na	55	55	75	50
Pb	0.4	0.8	0.5	0.2
Si	<0.1	0.8	1.0	50
Sn	<0.1	2	0.4	<0.1
Th	n.d.	n.d.	n.d.	n.d.
Ti	<0.01	0.03	1.2	0.11
Zr	7	10	3	4

n.d. = none detected

5. References

- (1) Dyck, R. and Veleker, T.J., Anal. Chem.,
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- (2) Duffendack, O.S. and Wolfe, R.A., Ind. Eng.
Chem., Anal. Ed. 10, 161, (1938).

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LGR:EMP:AHG:WRI:RHD/DV