NBS SPEC. PUBL. 260-16

Standard Reference Materials:

HOMOGENEITY CHARACTERIZATION OF NBS SPECTROMETRIC STANDARDS IV: PREPARATION AND MICROPROBE CHARACTERIZATION OF W-20 PERCENT Mo ALLOY FABRICATED BY POWDER METALLURGICAL METHODS

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Standard Reference Materials:

Homogeneity Characterization of NBS Spectrometric Standards IV: Preparation and Microprobe Characterization of W-20 Percent Mo Alloy Fabricated by Powder Metallurgical Methods

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Preface

Within the framework of the NBS Institute for Materials Research the area of standard reference materials is a broad and important one, including the preparation, characterization and distribution of a wide variety of materials in such diverse fields as metallurgy, polymers and inorganic materials. In carrying out such a program there is much interaction with representatives of industry and science, beginning with discussions as to which primary standard materials will do most to advance technology, the furnishing of materials and fabrication of samples, and the characterization and certification of the materials by cooperative efforts. The many groups participating in a standards program are very interested in detailed information on specific aspects of the program -- but to date there has been no publication outlet for such written discussions.

To meet this need, NBS Miscellaneous Publication 260 has been reserved for a series of papers in the general area of "standard reference materials". This series will present the results of studies and investigations undertaken within the Institute for Materials Research with emphasis on the preparation and characterization of standard reference materials. This subject-oriented series will provide a means for rapid dissemination of this detailed information and we hope will stimulate the use of standard reference materials in science and industry.

W. Wayne Meinke, Chief
Office of Standard Reference Materials

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Contents

The purpose of this report is to present a detailed account of the preparation for the W-20% Mo material and the results of the critical evaluation of homogeneity by the electron microprobe. Results of studies for atomic number correction and effects of operating voltage on the microprobe absorption correction also are given.

2. GENERAL DESCRIPTION OF STANDARD REFERENCE MATERIAL 480 (W-20% Mo)

This standard is a composite consisting of a core of W-20% Mo alloy wire embedded in pure Mo rod, onto which there has been electroplated a layer of pure W. The alloy wire has been extensively characterized by means of the electron microprobe and is satisfactory for use as a standard from the standpoint of homogeneity.

Chemical analyses were performed by the Analytical Coordination Chemistry Section, Analytical Chemistry Division, NBS, with the following recommended values for the provisional Certificate of Analysis: Mo 21.5 wt % and W 78.5 wt %. Two independent methods were employed, the first of which utilized an ion exchange separation followed by gravimetric determinations of the ignited oxides. An average value of 78.5 was determined for W, with an uncertainty of 0.5 wt % (n=4). (The reported uncertainties are 95% confidence intervals.) For Mo, the average value was determined to be 21.5 with an uncertainty of 0.3 wt % (n=4). A spectrophotometric thiocyanate method was used for the determination of Mo only. In this method Mo was reduced with Sn^{+2} and the color system stabilized with butyl cellosolve. An average value of 21.7 wt % Mo was obtained with an uncertainty of 0.2 wt % Mo (n=6).

SRM 480 is issued as an unmounted slug of composite about 10 mm in diameter by 1 mm thick. The outer W layer is about 1 mm thick, the Mo rod is about 6 mm diameter and the W-Mo alloy wire is about 1 mm diameter. The composite can be metallurgically mounted and polished according to a procedure outlined in this report so that the standard is ready for insertion into the microprobe in about one hour.

3. CHOICE OF MATERIAL

Several factors contributed to the choice of W-20% Mo to be the first trial powder metallurgically prepared NBS microprobe standard. First, the Office of Standard Reference Materials at NBS believed that if the W-Mo refractory metal combination, with its attendant difficulties such as high annealing temperature, high hot working temperature, and rapid reaction rate at these temperatures, could be successfully prepared, the way would be immediately open to prepare several other standards by powder metallurgical techniques.

Next, General Electric's Lamp Metals and Components Department, the fabrication contractor, had a great deal of experience in preparing tungsten base alloys. The particular composition 80% W-20% Mo was chosen as a starting point since the fabrication contractor had considerable experience with this alloy and its behavior. Finally, the W-Mo alloy system is interesting from the point of view of quantitative microprobe analysis. This interest arises from the fact that when the W Lα lines are used for analysis, there is virtually no absorption correction [2] required for the tungsten microprobe data. Furthermore, no characteristic fluorescence correction is required [3]. Thus, the atomic number correction [4] is isolated and can be studied. On the other hand, a large absorption correction and an atomic number correction are required when using the Mo Lα lines for analysis. Decreasing the operating voltage decreases the absorption correction as well as the uncertainty in the absorption correction [5] without affecting the atomic number correction appreciably [6]. Thus, the Mo results can be studied as a function of operating voltage and the superimposed effects of absorption correction and atomic number uncertainty can be observed. Finally, if the Mo Kα line can be used, say in conjunction with an operating voltage of 30 kV, the absorption correction for Mo is only 2% while the atomic number correction is about 10%. Hence, the atomic number correction can be nearly isolated on both elements of the system.

The choice of W-Mo was to some degree dictated by the constitution diagram for W-Mo alloys. This particular refractory metal system forms a continuous series of solid solutions [7]. Therefore, by heat treating at suitable temperatures, for suitable times, homogenization should occur. However, as will be explained later, heat treatment alone was insufficient to produce the desired homogeneity; severe working of the material was also necessary.

As to the final standard, it was decided that any useful microprobe specimen should contain the pure end member materials as well as the alloy. Thus, all investigators would have the same pure metals in order to minimize confusion arising from the possible use of impure "pure end members." Therefore, SRM 480 (W-20% Mo) is a composite with W-20% Mo alloy wire embedded in a Mo rod onto which pure W has been plated.

4. ALLOY PREPARATION

The powders chosen were one micrometer size W and two micrometer size Mo. The analyses of the powders are shown in Table 1. Some 2800 g of W and 700 g of Mo were weighed out on a balance having a sensitivity of 1 mg and which had been calibrated versus Class S weights. The powders were preblended in a twin shell blender equipped with an intensifier bar. Final mixing was done by jet milling; the powders were collected by a cyclone collector. Some 233 g of very fine powder, collected at the upper orifice of the cyclone collector, differed in composition from the main powder and was discarded. This precluded the using of the weighed powders for accuracy of composition.

The blended powder was hydrostatically pressed at about 35,000 PSI (241 MN/m^2) in rubber boots to prepare five green ingots. These ingots were sintered for 2 hours at 2800 °C at a pressure of 10^{-5} torr. The resulting ingots were machined to 2.5 cm (one inch) diameter by 5 cm (two inch) long billets and extruded in a Dynapak at 2050 °C at 10:1 extrusion ratio to 8.9 mm (0.35 inch) diameter rod.

The rods were self-resistance heated for one hour at 2500 to 2600 °C at a pressure of 10^{-5} torr. One rod was swaged to 5.1 mm (0.20 inch) diameter and given a homogenizing anneal for one hour at 2500 °C. This rod was designated Sample 10.

Samples taken at each stage in the fabrication process were examined metallographically at NBS. The results showed that only Sample 10 had a single phase microstructure. Even so, Sample 10 had large grains (ASTM 1 to 2) and porosity at grain boundaries. Furthermore, interference microscopy of the polished-etched-polished surface revealed marked surface relief which we attributed to very high grain boundary energy.

For these reasons, Sample 10 was annealed again for 12 hours at 2800 °C which did not noticeably improve the structure. Finally, Sample 10 was extruded from 5.1 mm (0.20 inch)

Table 1. The analyses of the W and Mo powders.

Spectrographic Analysis

Tungsten powder				Molybdenum powder			
Element	ppm	Element	ppm	Element	ppm	Element	ppm
Al	6	Ni	27	Al	24	Ni	18
Ca	29	Cu	3	Ca	11	Cu	17
Si	7			Si	58	W	215
Mo	68	Mn	6			Mn	10
Fe	19	Mg	4	Fe	52	Mg	<10
Cr	8	Sn	6	Cr	28	Sn	28

LECO Analysis

Oxygen	Carbon	Oxygen	Carbon
1730	15	1780	29

Flame photometry analysis

Sodium	Potassium
24	35

Apparent density by Scott-Schaeffer-White volumeter (ASTM B-329-58)

1.98 g/cm^3	1.19 g/cm^3

Average particle diameter by Fisher sub-sieve sizer

	As supplied	Lab milled	Lab milled
Number (μm)	1.05	1.00	2.1
Porosity	.770	.640	.726

Wt % particle size distribution by photelometer

Micrometer range	Wt %	Micrometer range	Wt %	Micrometer range	Wt %
0 - 1	58.1	0 - 2	5.1	11 - 12	0.7
1 - 2	40.2	2 - 3	16.1	12 - 13	.8
2 - 3	1.6	3 - 4	22.3	13 - 14	.8
		4 - 5	12.4	14 - 15	---
		5 - 6	5.8	15 - 20	9.5
		6 - 7	3.4	20 - 25	7.0
		7 - 8	0.9	25 - 30	7.0
		8 - 9	.5	30 - 35	2.0
		9 - 10	1.7	35 - 40	2.3
		10 - 11	.6		

diameter to about 1.1 mm (0.045 inch) diameter in one pass with the aid of the Dynapak. The resulting material showed no grain boundaries and no voids even when deeply etched as shown in Figure 1. This material is the final form of the W-Mo alloy standard. Analysis for metallic impurities in the alloy is given in Table 2.

The alloy wire was sheathed in pure Mo and the entire rod was electrodeposited from fused salt solution with high purity tungsten to make the final composite standard which is shown in Figure 2. The final diameter of the composite is about 6 mm (1/4 inch). The alloy yield was only 69 cm. Therefore, the total yield of composite standards numbered only about 475.

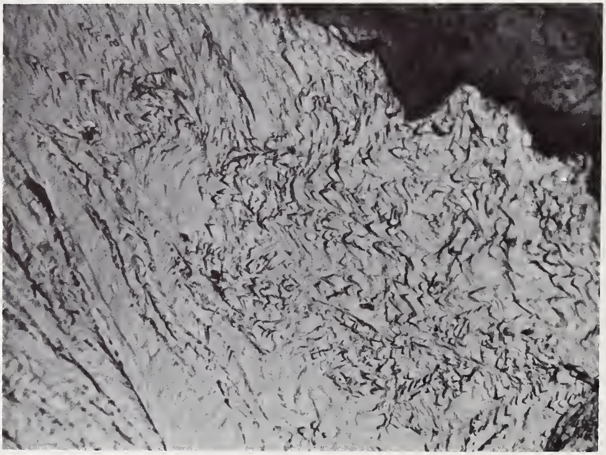

Figure 1. Micrograph of the heavily etched alloy wire. Note highly strained material and absence of inclusions and voids. Interface between Mo and the alloy wire is at upper right. X1000

Table 2. Trace analysis, sample 10 of W-20% Mo.

Element		Element	
Ag	.001 - .01[a]	Mg	>.001
Al	.001 - .01	Mo	>10
B	>.001	Ni	.001 - .01
Ca	>.001	Pb	>.001
Cu	>.001	Si	.01 - .1
Fe	.01 - .1	W	>10

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[a] Values given as weight percent.

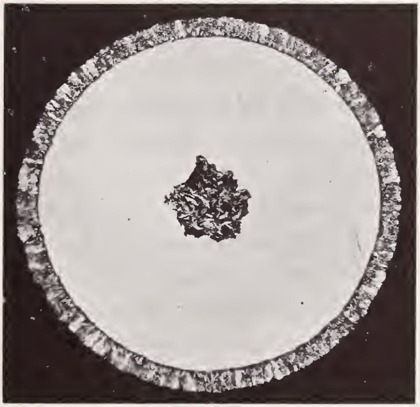

Figure 2. Overall view of SRM 480 showing the alloy wire at center encased in pure Mo (white) and pure W at the outer rim. X10

5. SUGGESTED METALLOGRAPHIC PREPARATION FOR MICROPROBE ANALYSIS

The following method of mechanical polishing provides a finished, satisfactory, sample in about 30 minutes. Mounting with a stainless steel ring around the specimen minimizes rounding.

Rough grinding is carried out on wet SiC papers through 80, 160, 400 and 600 grit respectively. On the 600 grit paper, the specimen is polished in several directions with as little pressure as possible to completely remove coarse scratches.

Fine grinding is done with 9 µm diamond on a silk or nylon lap rotating at 250 rpm. Medium hand pressure is applied. The lap should be nearly dry; a wet lap causes the specimen to pit. Fine grinding should not require more than two minutes to completely remove all scratch directionality.

The specimen is rough polished with 6 µm diamond on a canvas covered wheel rotating at 250 rpm. The canvas is again maintained nearly dry. Light to moderate hand pressure gives the best results.

Next, fine polishing is accomplished using 0.25 µm diamond on a microcloth covered wheel. Again the lap is nearly dry and only light hand pressure is used. At this point the specimen is etched for about five seconds in Murakami's reagent [8].

Final polishing is carried out with 0.05 µm γ-Al_2O_3 on Gamal cloth. Here an etch-polish-etch method is used to provide the final surface. At least three etchings are usually required. A typical specimen is shown in Figure 2. Once prepared, the surface should need only light final polishing from time to time.

6. HOMOGENEITY TESTING BY MEANS OF THE MICROPROBE

Four samples were selected from the cut composite rod. These were chosen by mixing the samples, choosing one, mixing, choosing another and so on. Two different metallographers prepared two specimens each following the procedure outlined previously. Two samples were inserted into the microprobe in the lightly etched condition while two were unetched. In all cases, a bridge of silver based paint was used to provide a conducting path from the sample to ground. Vacuum metallized (coated) specimens were not run.

Three of the four selected samples designated EMS-72, 73, 74 respectively, were chosen for homogeneity testing. The fourth sample (EMS-75) was retained for independent microprobe analysis to check the results of the other three samples. Thus, the fourth sample was treated typically as any piece of material which might have been issued as representative of the final standard.

Homogeneity testing by means of the microprobe was carried out using an operating voltage of 20 kV, a monitor current (proportional to beam current) of two microamperes corresponding to a specimen current of 0.22 microamperes. The $L\alpha$ lines of the W and Mo were monitored by means of LiF (W) and EDDT (Mo) monochromator-proportional counter channels. The dead time in each channel was 2.3 microseconds. The x-ray emergence angle was 52.5°.

As a preliminary check, the specimen was driven at 96 μm per minute and ratemeter traces were obtained going all the way across the specimen along three diameters at about 120° to each other. Except for the extreme edges, no gross inhomogeneities were observed; the specimens were deemed suitable for final homogeneity characterization.

The method used to obtain the required homogeneity data in a digital form was that of quantitative raster scanning (QRS). The QRS method is a point-by-point analysis within a given raster in which the information obtained at each point is retained in digital form. Either the specimen or the electron beam can be displaced to obtain the desired raster. The device available at the National Bureau of Standards displaces the beam while the specimen remains stationary.

Heinrich has concluded that in any QRS procedure, the most serious limitations are counting statistics and instrumental instability. In addition, if the beam is displaced, defocusing of the x-ray optics is a distinct possibility because the x-ray source may no longer be on the focusing (Rowland) circle [9].

To obtain satisfactory counting statistics, count rates were used corresponding to 70,000 counts/sec in pure W and 30,000 counts/sec in pure Mo for the homogeneity tests. With a dwell time per point of 10 seconds, some 500,000 counts from W and 50,000 counts from Mo were obtained from the W-20 Mo alloy. With such high count rates, it is necessary to apply appropriate deadtime corrections [10].

To reduce the effects of instrumental instability, the monitor current was allowed to control the dwell-time per point. This was done by means of a voltage-to-frequency converter which enabled the monitor current to be scaled. The monitor current scaler was made the master controller and a fixed increment of monitor current was used to obtain counts for points. This is equivalent to saying that the same number of incident electrons were used to obtain data for all points.

Finally, defocusing effects were checked by observing counts at the extreme positions of the raster. By focusing the spectrometer with the beam in a very slow scanning mode and observing the ratemeter output on a recorder the best results were obtained. With our instrument; the widest raster which showed no defocusing was a square about 48 μm on an edge. The raster scanner was made to dwell at 100 points within this square using a 10 x 10 matrix.

Five such raster scans were taken for one specimen and four scans for the other two specimens. The data were delivered directly on punched paper tape with the values for W, Mo, and dwell time per point being printed out. Each separate raster was well removed on the specimen from any other raster so that representative sampling was obtained from each sample. These data were subjected to analyses testing for trends and other non-random behavior. No significant departure from randomness was observed.

Coefficients of variation were computed from these data for both W and Mo; the results are shown in Table 3. Based on these results, it is concluded that the overall coefficient of variation in percent can be conservatively taken to be 2.5% for Mo and 1.5% for W. These figures then can be applied to the entire lot of alloy available.

Table 3. Homogeneity characterization results, SRM 480 (W-20% Mo).

Specimen	Condition	%CV-Mo[a]	%CV-W[a]	Determinations (each element)
EMS-72	lightly etched	2.47	1.24	400
EMS-73	unetched	2.37	1.55	400
EMS-74	lightly etched	2.54	1.34	500

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[a] $\%CV = \frac{(100)\ (\text{Std dev})}{\text{Mean number of counts}}$

Approximate mean number of counts accumulated for W = 500,000.
Approximate mean number of counts accumulated for Mo = 45,000.

Since almost all microprobe quantitative analysis is based on repetitive determinations, the expected width of a 95% confidence interval is of interest. Table 4 shows the expected width of the 95% confidence interval as a function of the number of repeat determinations. From Table 4, it can be seen that 16 repetitions are sufficient to obtain an analysis interval (95% confidence) of about ±1% relative. The time required for such an analysis including the pure element and background determinations is about one hour based on our experience in analyzing each of the four W-Mo specimens.

Table 4. Relative 95% confidence interval expressed in percent of the amount of W or Mo present.

$$(t_{n-1})\ (\%CV)/(n)^{1/2}$$

(n = number of determinations)

n	W	Mo
10	±1.1	±1.9
16	±0.8	±1.3
25	±0.6	±1.0

As a final check, the pure W and Mo in the composites were compared with NBS pure W and Mo. For an accumulation of 300,000 Mo counts and 900,000 W counts, differences between the two pairs of materials were not observed.

7. QUANTITATIVE MICROPROBE ANALYSIS OF W-20% Mo

From the standpoint of homogeneity, the intensity ratio of the alloy to the respective pure metal (the k value) should be the same within the limits predicted by Table 4 from sample to sample at a given operating voltage. Let us call this the k-criterion.

The foregoing postulate was investigated by performing microprobe analysis on each of three specimens as well as the one not checked for micro-homogeneity. The operating voltages were 15 and 10 kV respectively. The specimens concerned were one etched and two unetched samples respectively. In addition, one of the etched specimens was checked at 20 kV using all of the 500 points obtained for homogeneity characterization. The Lα line of W was measured for 20 and 15 kV, the Mα line at 10 kV. Count rates were adjusted to about 10,000 counts/sec for the pure elements in determining k values. Results are given in Table 5 for k. The results show the k criterion definitely is satisfied. The conclusion is that SRM 480 is suitable for use as a microprobe standard from the standpoint of sample-to-sample homogeneity.

Table 5. Results of electron probe microanalysis of SRM 480 (W-20% Mo).

Specimen	Operating voltage (kV)	k^a_{Mo}	k^a_{W}
EMS 74	20	0.143	0.772
EMS 72	15	0.163	0.742
EMS 73	15	0.164	0.744
EMS 75	15	0.166	0.739
EMS 72	10	0.210	0.723
EMS 73	10	0.212	0.729
EMS 75	10	0.213	0.726

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[a] Dead time and background corrected intensity ratio.

The computations to obtain the mass fractions by microprobe analysis were performed with the multi-access computer following a program by Heinrich and Rasberry [11]. The following corrections were performed:

1. Absorption correction by the method of Philibert [12] and Duncumb [13] with the Duncumb expression for electron retardation, σ, modified by Heinrich [6]. The mass absorption coefficients used will be discussed later.

2. Atomic number correction by the method of Thomas [14] as modified by Heinrich [11]. In addition, for this study, the effective voltage suggested by Thomas was modified to agree with results of numerical integration [15] for the stopping power portion of the correction. Backscatter factors [4] and mean ionization potentials [4] used will be discussed. No fluorescence corrections were applied.

The program follows the iteration procedure of Criss and Birks [16] but does not normalize the intensity ratios. Iteration stops when variations for all elements are less than 0.001%. In our case, this required only three iterations for all the analyses. The data were input as background- and dead- time corrected intensity ratios. One run using the correction procedure of Brown based on the electron transport equation was also performed using the Naval Research Laboratory's computer through the courtesy of Dr. Brown.

To determine the uncertainty of the calculated composition (C) value as a function of input parameters, such as mass absorption coefficients and backscatter factors, the data were corrected using various input parameter data. Mass absorption coefficients for W and Mo listed in Table 6 were obtained from the tables of Dewey [17], Frazer [18], and Heinrich [19] respectively. These tabulations show a range of about 25% in the value of the mass attenuation coefficient of W for Mo Lα radiation.

Table 6. X-ray mass absorption coefficients for tungsten and molybdenum (cm^2/g).

Emitter Absorber	Mo Lα	W Lα	Reference
Mo	705.5	140.4	17
Mo	686	139	18
Mo	728	139.8	19
W	4049	137.3	17
W	3251	149	18
W	3145.2	150.8	19

Using the same atomic number correction parameters and varying the mass absorption coefficients gives a spread of about 10% relative for Mo for any atomic number correction at 15 kV. There is no spread for W. At 20 kV, the situation is a spread of about 15% relative for Mo for any atomic number correction and no spread for W. At 10 kV, W Mα and Lα lines were used for the respective analysis. Dewey does not give mass absorption coefficient values for W Mα. Still at 10 kV, the spread is 7.5% relative for Mo. For W, only Heinrich and Frazer's data were available; there is no spread of results.

Holding the mass absorption coefficients constant and varying the atomic number correction parameters gives the spread due to the atomic correction. Here, backscatter factors were used as given by Duncumb-Bishop [4], Duncumb-Kulenkampff [4] and Springer [20] respectively. For any set of mass absorption coefficients, the spread at 15 kV for Mo was 4.5% relative for Mo and 0.6% for W. At 10 kV, the spread for Mo was still 5% relative but was 0.7% for W. The atomic number results are not altered by more than 0.3% by the averaging procedure of Duncumb-Reed [4] (separating the stopping power and backscatter portions of the correction) rather than that of Castaing [14] (use of α factor).

Therefore, the uncertainty in the mass absorption coefficient of W for Mo Lα is primarily responsible for the large spread of results for Mo when Mo Lα lines are used for analysis. The major contributor to uncertainties in the atomic number correction term is the backscatter factor; the stopping power portion of the correction had little effect on the uncertainty. For Mo analysis, using the Lα lines, both the absorption and atomic number corrections contribute to the overall uncertainty. As an example, the results for one sample are given in Table 7.

Table 7. Computed results for EMS-75 run at an operating voltage of 15 kV.

Input parameters	Mo	W	Normalized Mo	Normalized W	$f(\chi)$ Mo	$f(\chi)$ W
F,D-B	0.202	0.790	0.204	0.796	0.568	0.980
H,D-B	0.197	0.790	0.200	0.799	0.575	0.980
DEW,D-B	0.221	0.790	0.219	0.781	0.518	0.982
DEW,D-K	0.216	0.791	0.215	0.785	0.517	0.982
DEW,S	0.211	0.794	0.210	0.790	0.516	0.982
H,S	0.189	0.794	0.192	0.808	0.573	0.980
H,D-K	0.193	0.791	0.196	0.804	0.574	0.980
BROWN	0.225	0.768	0.227	0.773	---	---

Note: All stopping power values calculated using an effective voltage of 9.18 kV for Mo and 13.2 kV for W. Mean ionization potentials from reference [21]. Other combinations of input data for the stopping power portion of the correction varied from that used by less than 0.7%.

Input parameter legend

H: Mass absorption coefficients due to Heinrich [19].
F: Mass absorption coefficients due to Frazer [18].
DEW: Mass absorption coefficients due to Dewey [17].
D-B: Backscatter factor due to Duncumb-Bishop [4].
D-K: Backscatter factor due to Duncumb-Kulenkampff [4].
S: Backscatter factor due to Springer [20].
BROWN: Computer program due to D. B. Brown using calculated correction parameters. Run by Dr. Brown using our data.

Table 8 gives results for each sample using Heinrich's mass absorption coefficients and the Duncumb-Reed [4] data for backscatter factors in the atomic number correction.

Table 8. Calculated concentrations for W-20 weight percent Mo[a,b,c].

Specimen	Operating voltage (kV)	Molybdenum C	Molybdenum C norm	Tungsten C	Tungsten C norm
EMS 74	20	0.202	0.199	0.812	0.801
EMS 72	15	0.194	0.197	0.792	0.803
EMS 73	15	0.195	0.197	0.794	0.803
EMS 75	15	0.197	0.200	0.790	0.800
EMS 72	10	0.228	0.232	0.754	0.768
EMS 73	10	0.230	0.233	0.758	0.767
EMS 75	10	0.231	0.234	0.757	0.766

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[a] Mass absorption coefficients from Heinrich [19].
[b] Backscatter factors from Duncumb-Reed [4].
[c] Mean ionization potentials from Caldwell [21].

The challenge for microprobe analysis represented by SRM 480 is clearly shown by the spread in the analytical data. At operating voltages down to 10 kV, the absolute percentage deviation from the chemical analysis is far greater for Mo than for W despite the fact that the concentration of W is four times that of Mo. The large Mo range is due to the uncertainties in both the absorption correction and the atomic number correction. As predicted [5], lowering the operating voltage reduces the spread in the results for Mo and improves the accuracy since the $f(\chi)$ value is correspondingly raised. Table 9 shows $f(\chi)$ for Mo and W as a function of voltage. The variation of the W results with voltage is a function of uncertainties in the atomic number correction--most likely in the backscatter portion of the correction. SRM 480 shows that even under the best experimental conditions, an accurate microprobe analysis for Mo is extremely difficult to obtain. In fact, it is probable that simultaneous determination of W and Mo using the respective Lα lines is not feasible at a single operating voltage.

Table 9. Values of $f(\chi)$ for Mo and W in SRM 480 as a function of operating voltage.

Analytical line	Operating voltage (kV)	$f(\chi)$
Mo Lα	20	0.44
Mo Lα	15	0.57
Mo Lα	10	0.75
Mo Lα	5	0.90
W Lα	20	0.96
W Lα	15	0.98
W Mα	10	0.84

The foregoing results clearly show that more work on correction procedures and input parameters is urgently needed. Standards such as SRM 480 will be useful in evaluating such correction procedures. Such a study is beyond the scope of this paper.

8. CONCLUSIONS

SRM 480 (W-20% Mo) is satisfactory for use as a microanalytical standard from the standpoint of homogeneity. For microprobe analysis, 16 determinations are sufficient to provide a 95% confidence interval of about ±1% relative.

The need for microprobe standards is clearly shown by the very large spread of computed concentrations using the same correction method with different input parameters. As predicted [5], the spread in the Mo analysis decreases with decreasing operating voltage since the effect of the uncertainty of the mass absorption coefficient of W for Mo Lα is thereby diminished. The uncertainty due to the atomic number correction remains remarkably constant as a function of operating voltage; this spread is largely due to uncertainties in the backscatter factor.

SRM 480 is versatile in that the atomic number correction can be isolated for W or for both W and Mo. The latter can be done by using the Mo-Kα line for analysis. In such a case, the absorption correction for Mo is only 2% but high background and fluorescence by continuum will be encountered. It is probably better to first meet these problems which include the use of high operating voltages but low overvoltages, and high background rates when using a well characterized standard rather than an unknown.

If good stability can be obtained, analysis should be carried out at 5 kV. Then the absorption correction, even when using the Mo Lα line for analysis, is only 7% while the atomic number correction is about 20%. Hence, the problems associated with low voltage operation can be attacked while using a well characterized standard.

SRM 480 is relatively easy to prepare for examination. Once prepared, little further preparation work is required. For the W-20 Mo alloy, it was found that lightly etched and unetched specimens gave the same results. Light etching is recommended as a convenience. No inclusions or inherent voids were observed in the final microstructure during routine metallographic examination ranging up to a magnification of 1500 diameters.

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