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Centre canadien de la technologie des minéraux et de l'énergie

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MP-2: A CERTIFIED TUNGSTEN-MOLYBDENUM REFERENCE ORE

H.F. STEGER AND W.S. BOWMAN

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MP-2: A CERTIFIED TUNGSTEN-MOLYBDENUM REFERENCE ORE/ MP-2: MINERAI DE RÉFÉRENCE TYPE DE TUNGSTÈNE-MOLYBDÈNE

by/par

H.F. Steger* and/et W.S. Bowman**

SYNOPSIS

A 170-kg sample of a tungsten-molybdenum ore from Mount Pleasant, New Brunswick, has been prepared as a compositional reference material. MP-2 was ground to minus 74 µm, mixed in one lot, bottled in 200-g units and tested for homogeneity with respect to its bismuth and silver contents by chemical methods.

In a "free-choice" analytical program, 16 laboratories contributed results for one or more of tungsten, molybdenum, bismuth, silver and tin in one bottle of MP-2. Based on a statistical analysis of the data, the following recommended values were assigned: W, 0.65%; Mo, 0.281%; Bi, 0.246%; and Ag, 4.9 µg/g.

A provisional value of 0.043% was assigned for tin.

Un échantillon de 170-kg de minerai de tungstène-molybdène provenant de Mount Pleasant au Nouveau-Brunswick a été préparé comme matériau de référence de composition. Le MP-2 a été broyé à une granulométrie de moins 74 µm, mélangé en lot de minerai, embouteillé en unités de 200-g et soumis à des essais d'homogénéité quant au bismuth et à l'argent par des méthodes chimiques.

En vertu d'un programme analytique de "libre choix", 16 laboratoires ont soumis les résultats pour un ou plusieurs des éléments suivants: tungstène, molybdène, bismuth, argent et étain dans une bouteille du MP-2. Suite à analyse statistique des données, les valeurs recommandées suivantes ont été assignées: W, 0,65%; Mo, 0,281%; Bi, 0,246%; et Ag, 4,9 µg/g.

Une valeur provisiore de 0,043% a été assignée à l'étain.

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Note: Major contributions were also made by other staff members of the Mineral Sciences Laboratories./ D'autres membres du personnel des Laboratoires des sciences minérales ont également apporté une grande contribution à ce projet.

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INTRODUCTION

The preparation, characterization and certification of base metal ore MP-2 is another contribution of the Canadian Certified Reference Materials Project (CCRMP) in providing compositional reference ores, concentrates and related products typical of Canadian deposits and generally unavailable from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. Other certified reference materials are described in a catalogue available from CANMET, Energy, Mines and Resources, Ottawa, Canada (1).

The raw material for MP-2 was originally gathered for preparation as a spike to increase the content of tungsten, molybdenum and bismuth in reference ore MP-1a (2). The subsequent commencement of the exploitation of the source of this raw material for tungsten and molybdenum suggested that the remaining, fully prepared sample, now encoded as MP-2, be certified as a reference ore for the appropriate elements in the current operations at the Mount Pleasant deposit.

An interlaboratory program was conducted to obtain results for 5 elements from 16 commercial, industrial and government laboratories using analytical methods of their choice. The results should therefore be indicative of the practical current state of the analysis for these elements.

NATURE AND PREPARATION

The raw material to prepare MP-2 was donated to CCRMP in October 1978 by Billiton Exploration Company Limited and is representative of the wolframite-molybdenite-bismuth mineralization deposits at Mount Pleasant, New Brunswick. The material was hand-picked at the mine site by CANMET geologists (3).

The sample was dry-ground in March 1980 to pass a 74-µm screen. The powdered ore, weighing 170 kg, was tumbled in a 570-L conical blender for 8 h and bottled in 200-g units.

The analysis of 15 randomly-selected bottles of MP-2 for bismuth and silver by two independent methods demonstrated it to be sufficiently homogeneous for use as a reference material. The results of the confirmation of the homogeneity of MP-2 are reported in Appendix A.

The approximate mineralogical and chemical compositions and the particle size analysis are given in Tables 1 to 3.

Table 1 - Approximate mineralogical composition

Mineral	wt %
Quartz	70.0
Chlorite	10.0
Topaz	5.0
Lepidocrocite	5.0
Fluorite	2.0
Calcite	1.0
Wolframite	1.0
Loellingite	1.0
Sphalerite	0.7
Molybdenite	0.4
Bismuth	0.25
Chalcopyrite	0.23
Rutile	0.2
Bismuthinite	0.2
Pyrite	0.1
Monazite	0.1
Zircon	0.1
Galena	0.05

Table 2 - Approximate chemical composition

Element	wt %*
SiO_2	76.1
Al	5.4
F	4.1
Fe	3.7
Ca	2.7
W	0.65
S	0.7
Zn	0.4
Mo	0.28
Bi	0.25
Cu	0.9
As	0.2
Sn	0.04
Mg	0.04
Pb	0.04
Ag	4.9 µg/g
C (total)	0.02
H_2O (105°C)	<0.1

*Mean of minimum of two determinations or certified value

Table 3 - Particle size analysis (wet screen)

Size of fraction (µm)	wt %*
-104 + 74	0.3
-74 + 55	17.0
-55 + 46	4.3
-46 + 37	11.0
-37	67.4

*Mean of duplicate determinations

INTERLABORATORY PROGRAM FOR CERTIFICATION

The laboratories that participated in the certification program are listed in Appendix B. Each was assigned a code number which bears no relation to its alphabetical order. The results from CANMET are reported as Laboratory 1.

Each laboratory was requested to contribute five replicate results for tungsten, molybdenum, bismuth and silver for one bottle of MP-2 by methods of its choice and to report the results on an "as is" basis. Some laboratories also agreed to submit results for tin. When a laboratory submitted results by more than one method for an element, each set was considered to be statisticlly independent.

The results of the confirmation of the homogeneity of MP-2 were included in the program. However, to avoid any biasing of the statistics, only five results, chosen at random out of the one set for bismuth and each of the two sets of 45 results for silver were used in subsequent calculations. The recommended values for tungsten, molybdenum, bismuth and silver are reported in Table 4. The provisional value for tin is reported in Table 5.

Methodological and analytical information is presented in Tables 6 and 7.

Table 4 - Recommended values and statistical parameters (outliers excluded)

	No. of	No. of	Overall mean	95% CL		σ_A
				Low	High	
Element	laboratories	results	wt %			
W	13	75	0.65	0.63	0.67	0.009
Mo	15	90	0.281	0.271	0.291	0.004
Bi	11	65	0.246	0.239	0.252	0.003
Ag	11	74	4.9+	4.6+	5.2+	0.2+

+ µg/g

Table 5 - Provisional value and statistical parameters for tin (outliers excluded)

No. of laboratories	5
No. of results	30
Overall mean ± 95% CI	0.043 ± 0.005%
σ_A	0.002%

Table 6a - Summary of analytical results for tungsten (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Colorimetry	Fusion with Na_2O_2 or $Na_2O_2 + Na_2CO_3$; W reduced with $SnCl_2$ and determined as thiocyanate complex	1b, 2, 13, 14	20	0.655
	Fusion with $NaHSO_4$; Mo removed by extraction with xanthate from 1.5 M HCl into $CHCl_3$; W reduced with $SnCl_4$ and determined as thiocyanate complex	1a	5	0.663
	Fusion with $K_2S_2O_7$; W reduced with SnO_2 and determined as thiocyanate complex	12, 15	10	0.677
	One or more of $HCl + HF + HNO_3 + H_2SO_4 + H_3PO_4$; W reduced with $SnCl_2$ and determined as thiocyanate complex	6, 7la, 7b	15	0.628
	$HCl + HF + HNO_3 + HClO_4$; extracted with tetraphenylarsonium chloride - A.E. Affsprung and J.W. Murphy; Anal. Chim. Acta. 30, 501; (1964)	16	5	0.695
X-ray fluorescence analysis	Somar mix	5	5	0.640
	Briquetted with 75% SiO_2 + 5% Fe_2O_3 + 20% Al_2O_3	10	6	0.584
Neutron activation analysis		3, 11	10	0.645

Table 6b - Summary of analytical results for molybdenum (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption analysis	One or more of HCl + HNO_3 + HF + $HClO_4$ + H_2SO_4; taken up in dilute HCl or HNO_3	2, 4, 7a, 7b 9c, 11, 12, 14,16	45	0.275
	HCl + HNO_3 + $KClO_3$; taken up in dilute HCl + $AlCl_3$	6, 13	10	0.299
	HCl + HNO_3 + HF + $HClO_4$; Mo separated by double precipitation with NaOH; taken up in dilute HCl	1b	5	0.298
	HCl + HNO_3 + HF + H_2SO_4 + Br_2; Sn and As volatilized with HBr; Mo and W extracted together with α-benzoinoxime into $CHCl_3$; back-extracted with ammonia; Mo extracted as xanthate complex into $CHCl_3$; stripped with HNO_3 + $HClO_4$ + H_2SO_4; final solution is 15% HCl	1a	5	0.286
	Fusion with Na_2O_2; taken up in 20% HCl + $AlCl_3$	10	5	0.294
	No details	8b	5	0.252
X-ray fluorescence analysis	Somar mix	5	5	0.287
	No details	8a	5	0.266
Neutron activation analysis		3	5	0.300

Table 6c - Summary of analytical results for bismuth (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption analysis	One or more of HCl + HNO_3 + HF + $HClO_4$ + H_2SO_4; final solution is 4 to 20% of either HCl or HNO_3	2, 4, 6, 7a, 7b, 11, 13, 14	40	0.245
	One or more of HCl + HNO_3 + HF + $HClO_4$ + H_2SO_4; Bi co-precipitated with hydrous Fe_2O_3; dissolved in dilute HCl	1a, 16	10	0.240
	Fusion with Na_2O_2 - Na_2CO_3; dissolved in dilute H_2SO_4	1b	5	0.255
	No details	8	5	0.248
Atomic absorption analysis - flameless	HNO_3 + HF + $HClO_4$; taken up in 20% HCl; BiH_3 evolution with $NaBH_4$; heated quartz tube	12	5	0.255

Table 6d - Summary of analytical results for silver (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (µg/g)
Fire assay-atomic absorption analysis	Fire assay; Pb button dissolved in HNO_3	1a, 2b, 16	15	4.87
Fire assay	No details on Ag determination	14a	4	3.98
Atomic absorption analysis	One or more of HCl + HF + HNO_3; final solution is 20-25% HCl	1b, 2a, 6, 7a, 7b, 11, 13, 14b	40	5.10
	HNO_3 + HF; final solution is 1M HNO_3	12	5	4.60
	Roasted at 600°C; HBr + Br_2; Ag extracted from KI - ascorbic acid solution into TOPO - MIBK	9	5	4.44
DC plasma	Digested HNO_3	5	5	5.00

Table 6e - Summary of analytical results for tin (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption analysis	Fusion with Na_2O_2 + Na_2CO_3 ; Sn precipitated as hydrous oxide; redissolved in dilute HCl	1b	5	0.0488
	Fusion with Na_2O_2 + Na_2CO_3; Sn extracted as iodide into toluene; stripped with 10% H_2SO_4 - 50% HNO_3 - 10% HCl	1a	5	0.0404
	Fusion with Na_2O_2; taken up in 4% HCl	13	5	0.0488
Atomic absorption analysis - flameless	Roasted at 650°C; fusion with $LiBO_2$; taken up in 2% HCl; tin hydride evaluation; heated quartz tube	12	5	0.0379
X-ray fluorescence analysis	Somar mix	5	5	0.0402
	No details	2	5	0.0436

Table 7a - Laboratory results, means and standard deviations for tungsten

						Mean	S.D.
Lab 1 (COLOR)	.664	.662	.673	.657	.659	.6630	.0062
Lab 1 (COLOR)	.634	.643	.648	.641	.651	.6434	.0066
Lab 2 (COLOR)	.654	.662	.658	.658	.646	.6556	.0061
Lab 3 (NAA)	.6610	.6290	.6390	.6240	.6320	.6370	.0145
Lab 5 (XRF)	.653	.631	.637	.622	.657	.6400	.0148
Lab 6 (COLOR)	.65	.63	.65	.64	.72†	.6580	.0356
Lab 7 (COLOR)	.604	.599	.617	.609	.610	.6078	.0068
Lab 7 (COLOR)	.608	.599	.629	.633	.628	.6194	.0150
*Lab 8 (XRF)	.48	.50	.55	.52	.47	.5040	.0321
*Lab 9 (XRF)	.80	.86	.84	.84	.78	.8240	.0329
Lab 10 (XRF)	.603	.595	.568	.578	.584	.5838	.0131
	.575						
Lab 11 (NAA)	.670	.674	.671	.664	.671	.6700	.0037
Lab 12 (COLOR)	.72	.72	.73	.73	.72	.7240	.0055
Lab 13 (COLOR)	.668	.670	.671	.671	.673	.6706	.0018
Lab 14 (COLOR)	.634	.642	.653	.662	.661	.6504	.0122
Lab 15 (COLOR)	.64	.63	.62	.65	.61	.6300	.0158
Lab 16 (COLOR)	.694	.686	.709	.689	.697	.6950	.0089

*Outlying set

†Outlying result

Table 7b - Laboratory results, means and standard deviations for molybdenum

						Mean	S.D.
Lab 1 (AA)	.289	.288	.280	.287	.288	.2864	.0036
Lab 1 (AA)	.298	.285	.294	.299	.312	.2976	.0098
Lab 2 (AA)	.316	.317	.317	.321	.316	.3174	.0021
Lab 3 (NAA)	.3010	.2990	.3010	.2980	.3010	.3000	.0014
Lab 4 (AA)	.263	.257	.264	.255	.261	.2600	.0039
Lab 5 (XRF)	.286	.287	.288	.285	.287	.2866	.0011
Lab 6 (AA)	.29	.29	.29	.29	.29	.2900	.0000
Lab 7 (AA)	.273	.275	.283	.279	.281	.2782	.0041
Lab 7 (AA)	.281	.279	.281	.278	.283	.2804	.0019
Lab 8 (XRF)	.25	.26	.27	.29	.26	.2660	.0152
Lab 8 (AA)	.2389	.2529	.2558	.2577	.2562	.2523	.0077
Lab 9 (AA)	.27	.28	.28	.28	.28	.2780	.0045
*Lab 9 (XRF)	.75	.78	.78	.75	.78	.7680	.0164
Lab 10 (AA)	.29	.30	.29	.30	.29	.2940	.0055
Lab 11 (AA)	.274	.272	.278	.274	.271	.2738	.0027
Lab 12 (AA)	.244	.249	.244	.242	.238	.2434	.0040
Lab 13 (AA)	.310	.306	.312	.309	.307	.3088	.0024
Lab 14 (AA)	.265	.263	.265	.255	.258	.2612	.0045
Lab 15 (AA)	.23	.23				.2300	.0000
Lab 16 (AA)	.285	.287	.287	.285	.288	.2864	.0013

*Outlying set

Table 7c - Laboratory results, means and standard deviations for bismuth

						Mean	S.D.
Lab 1 (AA)	.246	.249	.248	.250	.250	.2486	.0017
Lab 1 (AA)	.246	.254	.257	.252	.251	.2520	.0041
Lab 2 (AA)	.233	.240	.235	.238	.238	.2368	.0028
Lab 4 (AA)	.260	.254	.256	.257	.257	.2568	.0022
*Lab 5 (XRF)	.292	.302	.290	.296	.291	.2942	.0049
Lab 6 (AA)	.25	.25	.25	.25	.25	.2500	.0000
Lab 7 (AA)	.235	.231	.233	.232	.236	.2334	.0021
Lab 7 (AA)	.250	.242	.243	.250	.245	.2460	.0038
Lab 8 (AA)	.2448	.2442	.2531	.2469	.2500	.2478	.0037
*Lab 9 (XRF)	.36	.35	.35	.35	.35	.3520	.0045
Lab 11 (AA)	.246	.246	.244	.244	.244	.2448	.0011
Lab 12 (AA)	.260	.256	.260	.250	.250	.2552	.0050
Lab 13 (AA)	.265	.263	.263	.264	.262	.2634	.0011
Lab 14 (AA)	.230	.230	.230	.225	.230	.2290	.0022
Lab 16 (AA)	.230	.227	.231	.232	.232	.2304	.0021

*Outlying set

Table 7d - Laboratory results, means and standard deviations for silver

						Mean	S.D.
Lab 1 (FA-AA)	4.75	4.78	4.88	4.80	4.83	4.8080	.0497
Lab 1 (AA)	5.2	5.4	5.5	5.4	5.8	5.4600	.2191
Lab 2 (AA)	4.8	5.0	4.9	4.8	4.7	4.8400	.1140
Lab 2 (FA-AA)	4.8	5.1	4.1	5.1	5.1	4.8400	.4336
Lab 5 (PLASMA)	4.8	4.9	5.1	5.1	5.1	5.0000	.1414
Lab 6 (AA)	4.0	3.9	4.0	4.0	4.0	3.9800	.0447
Lab 7 (AA)	5.3	5.3	5.2	5.3	5.4	5.3000	.0707
Lab 7 (AA)	5.2	5.2	5.2	5.2	5.2	5.2000	.0000
*Lab 8 (AA)	8.3	4.8	5.2	8.6	8.5	7.0800	1.9071
Lab 9 (AA)	5.1	5.1	4.1	4.1	3.8	4.4400	.6148
Lab 11 (AA)	5.97	5.98	5.96	5.98	5.96	5.9700	.0100
Lab 12 (AA)	4.75	4.50	4.62	4.50	4.62	4.5980	.1040
Lab 13 (AA)	5.44	5.44	5.59	5.82	5.41	5.5400	.1716
Lab 14 (FA-G)	3.8	3.8	3.8	4.5		3.9750	.3500
Lab 14 (AA)	4.1	4.6	4.5	4.6	4.6	4.4800	.2168
Lab 16 (FA-AA)	5.0	4.9	4.9	5.0	5.0	4.9600	.0548

*Outlying set

Table 7e - Laboratory results, means and standard deviations for tin

						Mean	S.D.
Lab 1 (AA)	.044	.039	.041	.039	.039	.0404	.0022
Lab 1 (AA)	.044	.047	.054	.048	.051	.0488	.0038
Lab 2 (XRF)	.045	.044	.044	.042	.043	.0436	.0011
Lab 5 (XRF)	.040	.042	.040	.039	.040	.0402	.0011
*Lab 9 (XRF)	.12	.13	.12	.11	.12	.1200	.0071
Lab 12 (AA)	.0389	.0377	.0372	.0372	.0383	.0379	.0007
Lab 13 (AA)	.050	.048	.049	.050	.047	.0488	.0013

*Outlying set

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

Any sets of results obviously suspect for methodological reasons were rejected. Also, the sets of results whose means differed by more than twice the overall standard deviation from the initially calculated mean value were not used in subsequent computations to avoid biasing of the statistics. All results that were rejected are identified in Table 7.

ESTIMATION OF CONSENSUS VALUES AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and variance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (4):

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in set i,
μ = the true consensus value,
y_i = the discrepancy between the mean of the results in the set i ($\bar{x}_i.$) and μ, and
e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i.$

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2, respectively. The significance of ω^2 is detected by comparing the ratio of between-set mean squares to within-set mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The consensus value of the assumed model is estimated by the overall mean $\bar{x}..$ by:

$$\bar{x}.. = \sum_{i}^{k} \sum_{j}^{n_i} x_{ij} \Big/ \sum_{i}^{k} n_i$$

where n_i = the number of results in set i, and
k = the number of sets.

The value of σ^2 is estimated by s_1^2 which is given by:

$$s_1^2 = \sum_{i}^{k} \sum_{j}^{n_i} (x_{ij} - \bar{x}_i.)^2 \Big/ \sum_{i}^{k} n_i - k.$$

The value of ω^2 is estimated by

$$\omega^2 = (s_2^2 - s_1^2) \Big/ \frac{1}{k-1} \left(\sum_{i}^{k} n_i - \sum_{i}^{k} n_i^2 / \sum_{i}^{k} n_i \right)$$

where

$$s_2^2 = \sum_{i}^{k} n_i (\bar{x}_i. - \bar{x}..)^2 \Big/ k-1.$$

The variance of the overall mean is given by

$$V[\bar{x}..] = \left(\sum_{i}^{k} n_i^2 / (\sum_{i}^{k} n_i)^2 \right) \omega^2 + \left(1/\sum_{i}^{k} n_i \right) \sigma^2$$

and the 95% confidence limits for $\bar{x}..$ are

$$\bar{x}.. \pm t_{0.975,\,(k-1)} \sqrt{V[\bar{x}..]}$$

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 cases would fall within the prescribed limits.

The average within-set standard deviation, σ_A, is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better reproducibility should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A.

Criterion for Certification

The ratio of the between-laboratory mean to the within-laboratory standard deviation σ_B/σ_A, where

$$\sigma_B = \sum (\bar{x}..-x_i.)^2/k-1$$

is a measure of the quality of the certification data for the reference materials of CCRMP (5). The acceptable upper limit for σ_B/σ_A is 3 for all elements except uranium for which an upper limit of 2 is more realistic.

The criterion for the certification of an element in a reference material is RP, the percentage of sets of results that must be rejected to give a value of σ_B/σ_A equal to or less than the acceptable upper limit. RP should not exceed 15%.

The values of σ_B/σ_A and RP for tungsten, molybdenum, bismuth, silver and tin in MP-2 are reported in Table 8.

Table 8 - Values of σ_B/σ_A and RP for MP-2

Element	Number of sets of results	σ_B/σ_A All results	σ_B/σ_A Final	RP %
W	17	4.79	2.47	17.6
Mo	20	5.01	2.77	26.3
Bi	15	10.50	2.53	33.3
Ag	16	2.55	2.55	0.0
Sn	6	2.71	2.71	0.0

DISCUSSION

Table 6 is a summary of a methodological classification of accepted analytical results where there is a clear-cut distinction between types of methods in decomposition, separations and determination steps.

It is evident therein that one analytical technique was predominantly used for tungsten, molybdenum and bismuth, i.e., colorimetry for tungsten and atomic absorption spectrometry for the other two. The average within-laboratory standard deviation is therefore essentially pertinent only to this predominant technique.

TUNGSTEN, MOLYBDENUM AND BISMUTH

The values of σ_B/σ_A and RP in Table 8 suggest that these elements should not be certified in MP-2. Table 9 summarizes the values of the between-laboratories spread given by

$$2\left(t_{0.975,\,(k-1)}\sqrt{V[\bar{x}..]}\right) \times 100\% \Big/ \bar{x}..$$

and the mean within-laboratory coefficient of variation given by

$$\sigma_A \times 100\% \,/\, \bar{x}..$$

for the interlaboratory programs for tungsten, molybdenum and bismuth in reference materials MP-1 (6), its recently prepared replacement MP-1a (2) and MP-2. They are all from the same complex wolframite-molybdenum-bismuth mineralization deposit with zones of sphalerite-galena. The chemical complexity of these materials makes possible the occurrence of inter-element interferences that could affect adversely the between-laboratory agreement but not the within-laboratory precision. Moreover, the mineralogical composition requires extreme care for complete decompositions to be achieved.

Tungsten is not certifiable on the basis of RP criterion for MP-1 or MP-2, but while it is so for MP-1a it was not because there is an evident lack of consensus observable in the histogram of the analytical results. For MP-1, molybdenum and bismuth are certifiable according to RP but this is due to poor within-laboratory precision. For MP-1a, the between-laboratory agreement improved compared with MP-1, but the much greater improvement in the within-laboratory precision renders molybdenum and bismuth uncertifiable according to RP.

A similar situation exists for MP-2, the between-laboratory agreement is acceptable for these elements as well as for tungsten but the very good within-laboratory precision renders them uncertifiable according to RP. Although there is

Table 9 - Between-laboratory spread and within-laboratory coefficient of variation

Element	RM	$\bar{x}$ %	Between-lab spread (%)	Within-lab coeff. of variation (%)
W	MP-1*	0.021	57.09	7.07
	MP-1a*	0.040	20.61	4.65
	MP-2	0.65	6.01	1.46
Mo	MP-1	0.014	13.16	7.62
	MP-1a	0.029	8.00	1.98
	MP-2	0.281	6.88	1.53
Bi	MP-1	0.024	16.02	5.56
	MP-1a	0.032	11.82	2.70
	MP-2	0.246	5.20	1.00

*Not certified

no evidence to dispute the low values of σ_A found for MP-2, it is unfortunate that a significant number of results for tungsten, molybdenum and bismuth were not obtained by at least one method other than the predominantly used one.

CANMET has analyzed numerous samples from the Mount Pleasant area, the source of the MP series, since the 1960's. They are difficult samples, especially for tungsten, molybdenum and bismuth. This is of course substantiated by the results of the certification programs for these elements in MP-1, MP-1a and MP-2. For this reason, CCRMP considers that the strict application of RP criterion for the certification of MP-2 is unwarranted and that tungsten, molybdenum and bismuth should be certified. The histograms of the results for these elements are depicted in Fig. 1a-1c.

SILVER

Table 8 illustrates that silver can be certified according to RP criterion. The histogram for the silver results is shown in Fig. 1d.

TIN

Only a provisional value can be reported for tin because only five laboratories reported results. A minimum of 10 is necessary for consensus (5). The histogram for the tin results is depicted in Fig. 1e.

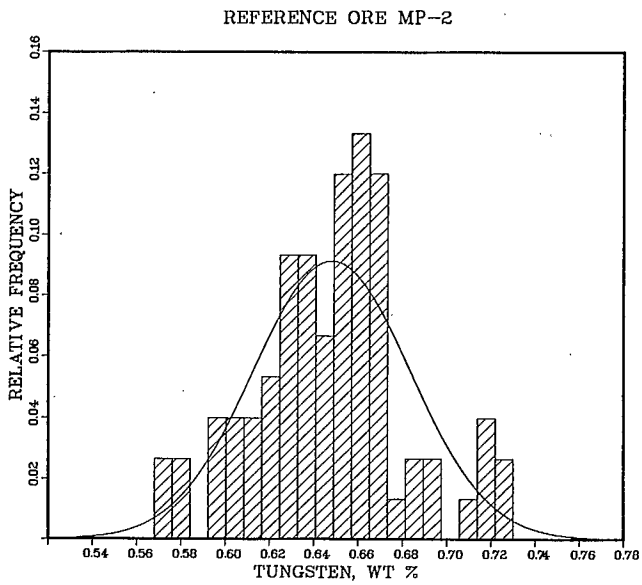

Fig. 1a - Histogram for tungsten

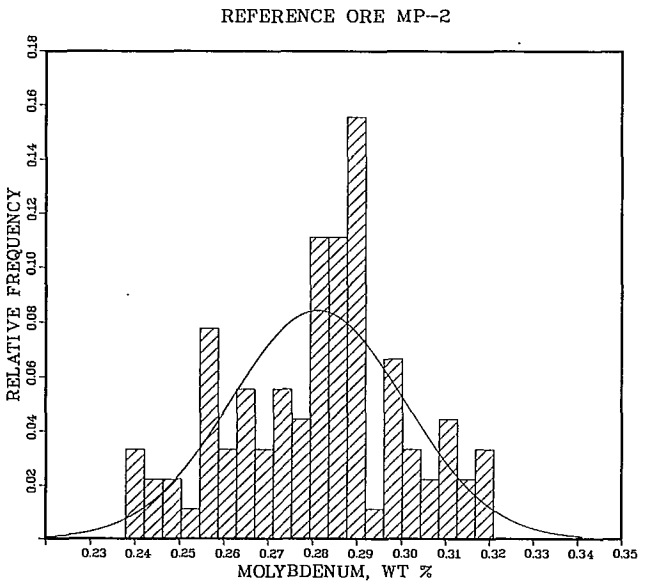

Fig. 1b - Histogram for molybdenum

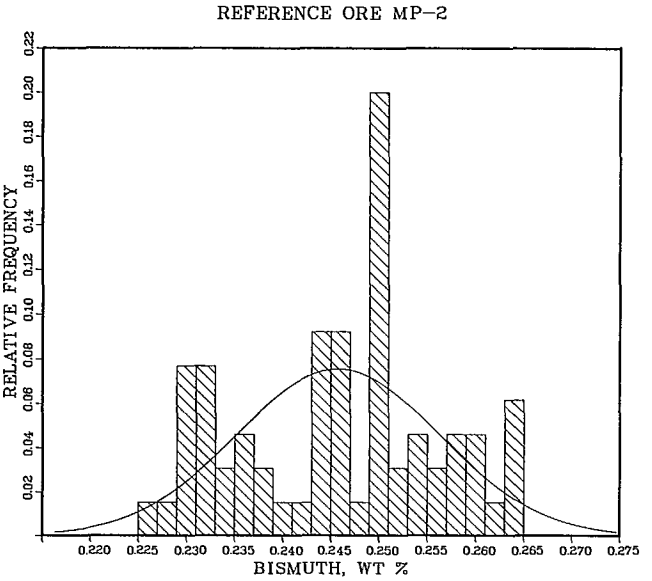

Fig. 1c - Histogram for bismuth

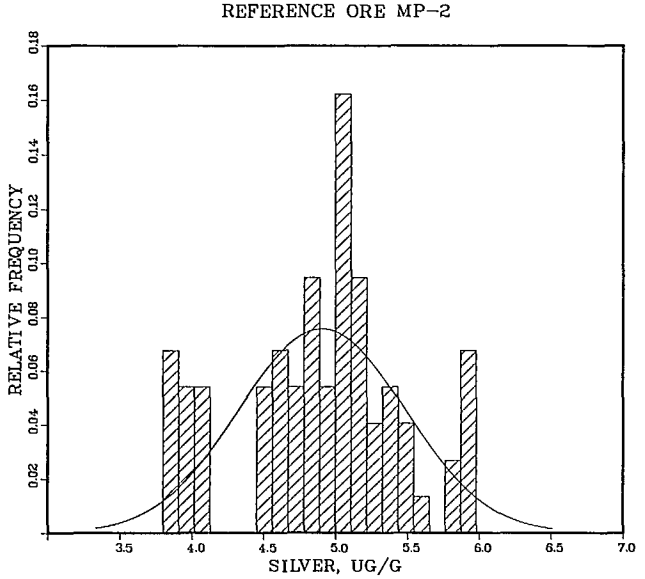

Fig. 1d - Histogram for silver

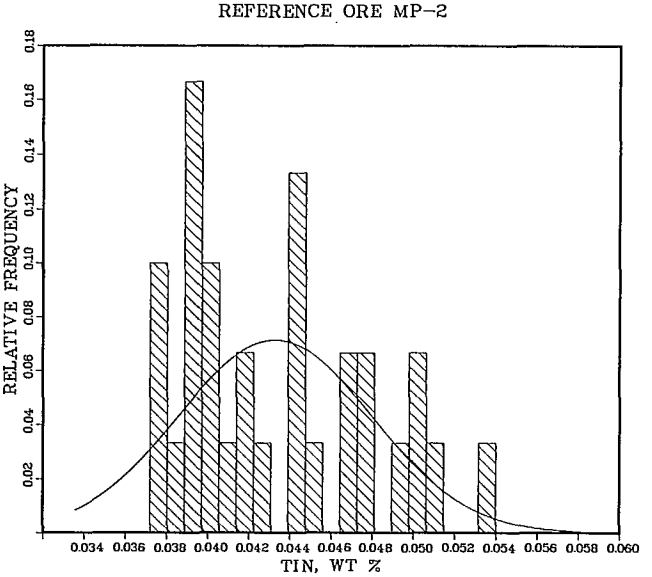

Fig. 1e - Histogram for tin

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APPENDIX A

CONFIRMATION OF HOMOGENEITY

CONFIRMATION OF HOMOGENEITY

The homogeneity of MP-2 was confirmed by Bondar-Clegg & Company Limited, Ottawa, Ontario, by analyzing in triplicate 15 bottles selected from a stock of 780 for bismuth and silver. The stock was divided into 15 lots of 52 bottles. The code number of the first bottle was selected at random out of the first lot. The code numbers of the remaining bottles selected were given by the code number of the preceding bottle plus 52. The results are shown in Tables 10 to 12.

A one-way analysis of variance technique was used to assess the homogeneity (4). Herein, the ratio of the between-bottle to within-bottle mean square is compared with the F statistic at the 95% level of probability. No evidence of bottle-to-bottle inhomogeneity was found for either bismuth or silver.

Table 10 - Confirmation of homogeneity of MP-2 for bismuth

	Bi (wt %)			
Bottle No.	Individual			Mean
42	.242	.244	.244	.243
94	.239	.233	.238	.236
146	.236	.244	.240	.240
198	.243	.233	.237	.237
250	.240	.234	.236	.237
302	.235	.234	.235	.235
354	.233	.234	.234	.234
406	.237	.240	.241	.239
458	.243	.243	.237	.241
510	.241	.238	.239	.239
562	.238	.233	.243	.238
614	.233	.235	.238	.235
666	.238	.238	.240	.239
718	.239	.239	.239	.239
770	.237	.233	.242	.237
			Overall mean =	.238

Analysis of variance table for bismuth

Source of variation	Degrees of freedom	Mean square
Between bottles	14	1.807×10^{-5}
Within bottles	30	9.222×10^{-6}
Total	44	
Calculated F statistic =	1.96	
F.95(14,30) =	2.037	

Null hypothesis of no difference between bottles is accepted for bismuth

Table 11 - Confirmation of homogeneity of MP-2 for silver (fire assay-atomic absorption)

	Ag (µg/g)			
Bottle No.	Individual			Mean
42	4.5	4.5	4.8	4.6
94	4.1	4.8	4.8	4.6
146	4.5	4.5	4.8	4.6
198	4.5	4.8	4.8	4.7
250	5.1	5.1	4.1	4.7
302	5.1	5.5	5.5	5.4
354	5.1	4.8	5.5	5.1
406	4.8	4.5	4.8	4.7
458	5.5	4.5	4.1	4.7
510	5.1	4.5	4.8	4.8
562	4.8	4.8	4.8	4.8
614	5.5	4.8	4.5	5.3
666	5.5	4.8	4.1	4.8
718	4.8	4.8	4.1	4.6
770	4.5	4.5	5.1	4.7
			Overall mean =	4.8

Analysis of variance table for silver

Source of variation	Degrees of freedom	Mean square
Between bottles	14	1.707×10^{-1}
Within bottles	30	1.673×10^{-1}
Total	44	
Calculated F statistic =	1.020	
F.95(14,30) =	2.037	

Null hypothesis of no difference between bottles is accepted for silver

Table 12 - Confirmation of homogeneity of MP-2 for silver (acid decomposition-atomic absorption)

	Ag (µg/g)			
Bottle No.	Individual			Mean
42	4.8	4.8	4.8	4.8
94	4.8	4.9	4.9	4.9
146	4.8	4.8	5.0	4.9
198	4.9	4.8	4.9	4.8
250	4.8	4.9	4.8	4.8
302	4.9	4.9	4.8	4.9
354	4.9	4.8	4.8	4.8
406	4.8	5.0	5.0	4.9
458	4.9	4.8	4.9	4.8
510	4.9	4.8	4.8	4.8
562	4.8	4.8	4.9	4.8
614	4.9	4.9	4.8	4.9
666	4.8	4.9	4.8	4.8
718	4.9	4.8	4.7	4.8
770	4.8	4.9	4.8	4.8
			Overall mean =	4.8

Analysis of variance table for silver

Source of variation	Degrees of freedom	Mean square
Between bottles	14	4.262×10^{-3}
Within bottles	30	5.278×10^{-3}
Total	44	
Calculated F statistic =	0.808	
F.95(14,30) =	2.037	

Null hypothesis of no difference between bottles is accepted for silver

APPENDIX B

PARTICIPATING LABORATORIES

PARTICIPATING LABORATORIES

Atlantic Analytical Services Ltd.
St. John, New Brunswick
M.L. Harley

Bondar-Clegg and Company Ltd.
North Vancouver, British Columbia
R.K. Rogers

Bondar-Clegg and Company Ltd.
Ottawa, Ontario
P. Haulena

Brenda Mines Limited
Peachland, British Columbia
D. Perkins

CANMET, Energy, Mines and Resources Canada
Mineral Sciences Laboratories
Ottawa, Ontario
(3 independent analysts)

Chemex Labs. Ltd.
North Vancouver, British Columbia
B.L. Twaites

Falconbridge Nickel Mines Ltd.
Metallurgical Laboratories
Thornhill, Ontario
W.L. Ott

Geological Survey of India
Central Chemical Laboratory
Calcutta, India
A.N. Chowdbury

Hudson Bay Mining and Smelting Company Ltd.
Flin Flon, Manitoba
W.W. Henderson

Lakefield Research of Canada Ltd.
Lakefield, Ontario
D.M. Wyslouzil

MINTEK
Randburg, South Africa
E.J. Ring

Noranda Research Centre
Pointe Claire, Quebec
J.D. Kerbyson

Nuclear Activation Services Ltd.
Hamilton, Ontario
E.L. Hoffman

Ontario Ministry of Natural Resources
Geoscience Laboratories
Toronto, Ontario
C. Riddle

Surinam Government Geological and Mining Services
Paramaribo, Surinam
K.E. Burke

X-ray Assay Laboratories Ltd.
Don Mills, Ontario
E.J. Brooker