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TUNGSTEN ORES CT-1, BH-1, AND TLG-1: THEIR CHARACTERIZATION AND PREPARATION FOR USE AS CERTIFIED REFERENCE MATERIALS

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G.H. Faye, W.S. Bowman and R. Sutarno*

SYNOPSIS

Three low-grade tungsten ores, two of scheelite (CT-1 and TLG-1) and one of wolframite (BH-1), have been characterized and prepared for use as certified reference materials.

This report is a detailed account of the inter-laboratory program for obtaining the analytical results for tungsten, and the statistical treatment used to assign the recommended values, which are 1.04%, 0.42% and 0.083%, respectively, for CT-1, BH-1 and TLG-1. Information is also given on the nature and origin of the three ores, and on the procedures used for their preparation and for assessing their homogeneity.

* Note: The certification scheme involved major contributions by members of the staff of the Mineral Sciences Laboratories and by numerous laboratories in other organizations (see p 2).

RAPPORT DE CANMET 76-5

MINERAIS DE TUNGSTENE CT-1, BH-1 ET TLG-1: LEUR CARACTERISATION ET LEUR PREPARATION POUR ETRE UTILISES COMME MATERIAUX DE REFERENCE CERTIFIES

par

G.H. Faye, W.S. Bowman et R. Sutarno*

SYNOPSIS

Trois minerais de tungstène à basse teneur, deux de scheelite (CT-1 et TLG-1) et un de wolframite (BH-1) ont été caractérisés et préparés pour être utilisés comme matériaux de référence certifiés.

Ce rapport est un compte rendu détaillé du programme inter-laboratoire pour l'obtention des résultats analytiques pour le tungstène ainsi que le traitement statistique utilisé pour assigner les valeurs recommandées, qui sont de 1.04%, 0.42% et 0.083% respectivement, pour CT-1, BH-1 et TLG-1. D'autres renseignements sont donnés concernant la nature et l'origine de ces trois minerais, et sur les procédés utilisés pour leur préparation et pour évaluer leur homogénéité.

* Note: Plusieurs membres du personnel des Laboratoires des sciences minérales et des nombreux laboratoires d'autres organismes ont collaboré à la certification (voir page 2).

INTRODUCTION

This report describes the characterization and preparation of samples of three tungsten ores for use as certified compositional reference materials. The work is a facet of the Canadian Certified Reference Materials Project (CCRMP) to certify materials that are representative mainly of Canadian ore deposits, and that have potential value in conventional analytical or earth sciences laboratories. Certified reference ores prepared previously by the CCRMP are described in a catalogue that is available from the Canada Centre for Mineral and Energy Technology, and in technical reports that are issued with the purchase of each reference material[2-8].

At the outset it was intended to certify one scheelite ore (CT-1) and one wolframite ore (BH-1); however, the timely donation of a low-grade scheelite ore of American origin made it convenient to treat the three ores as a suite covering the range 0.1 to 1% tungsten. Seventeen participants analyzed one or more of the three ore samples for tungsten by a method of their choice. As expected, as many as 15 contributors used an absorptiometric method involving thiocyanate as the chromogenic reagent; two laboratories used an X-ray fluorescence method.

NATURE AND PREPARATION OF CT-1, BH-1 AND TLG-1

CT-1 was obtained in 1973 from Canada Tungsten Mining Corporation, Tungsten, N.W.T. BH-1 was hand-picked, in 1973, from a stockpile at the Burnt Hill deposit near Fredericton, New Brunswick; the deposit is owned by the International Paper Company Limited. TLG-1 is from Browne's Lake Mine, Beaverhead County, Montana, and was donated to the CCRMP by the General Electric Company, Cleveland, Ohio.

The mineralogical composition, the approximate chemical composition, and the wet screen analysis for each ore are given in Tables 1, 2, and 3 respectively.

The two Canadian ore samples were dry-ground by ball-milling, ostensibly to minus 200 mesh. TLG-1 did not require comminution and therefore was screened only to remove a small amount of +200 mesh material. A wet screen analysis was subsequently done on samples of each of the three materials (Table 3). Each of the powdered ores was then tumbled separately in a 20 cu ft conical blender for approximately eight hours. Upon opening the blender the bulk ores were systematically sampled and, by an X-ray fluorescence technique, were found to be sufficiently homogeneous to be bottled in 200-g units.

TABLE 1

Calculated mineralogical composition

Mineral	CT-1	BH-1	TLG-1
		wt%	
scheelite	1.6	--	0.1
wolframite	--	0.8	--
quartz	18	73	>10
pyroxene	40	--	--
amphibole	10	--	>10
feldspar	2	2	1-10
chlorite	tr	5	1-10
biotite	--	11	--
muscovite	--	4	--
mica	5	--	1-10
clay minerals	0.5	--	1-10
calcite	8	--	>10
dolomite	2	--	1-10
beryl & topaz	--	1.0	--
hydrogarnet	--	--	>10
cassiterite, rutile, apatite	--	0.4	--
pyrrhotite	12	2	--
pyrite	tr	0.2	--
chalcopyrite	0.5	0.01	tr
bismuth	--	0.04	--
bismuthinite & galena	--	0.03	--

TABLE 2

Approximate chemical composition

	CT-1	BH-1	TLG-1
		wt %	
W	1.04*	0.442*	0.083*
Si	17.2	38.0	21.5
Al	2.9	3.5	3.0
Fe (total)	8.6	3.2	17.5
Ca	12.2	0.5	16.6
Mg	2.0	0.4	2.7
Na	0.2	0.1	0.2
K	0.7	1.7	0.4
Ti	0.2	0.4	0.1
Mn	0.7	0.2	1.3
S	8.1	0.8	0.1
Mo	0.03	0.02	<0.01
C (total)	1.7	0.1	1.4
H_2O (950°C)	0.9	0.9	2.2
H_2O^- (105°C)	0.5	0.08	1.6

* Recommended value from Table 9.

TABLE 3

Wet screen analyses

Mesh size (Tyler)	CT-1	BH-1	TLG-1
		wt %	
+ 150	1.3	0.1	--
-150 + 200	1.7	0.1	--
-200 + 270	2.5	1.0	1.6
-270 + 325	3.3	3.0	8.2
-325 + 400	2.7	2.8	4.2
-400	88.8	92.2	85.1

INTERLABORATORY PROGRAM FOR CERTIFICATION OF CT-1, BH-1 AND TLG-1

The names of the laboratories that participated in the program to certify the tungsten ores are given below in alphabetical order. Each of these was arbitrarily assigned a code number so that analytical results could be recorded while preserving the anonymity of the laboratory. The code numbers bear no relation to the alphabetical order of the laboratory name.

Participating Laboratories

Bondar-Clegg & Company Limited,
Ottawa, Ontario.

Bondar-Clegg & Company Limited,
Vancouver, British Columbia.

Chemex Labs Limited,
North Vancouver, British Columbia.

Cominco Limited,
Trail, British Columbia.

Commercial Laboratory, U.S.A.

General Electric Company,
Cleveland, Ohio.

Hudson Bay Mining & Smelting Company Limited,
Flin Flon, Manitoba.

Lakefield Research of Canada Limited,
Lakefield, Ontario.

Mineral Research Branch,
Ministry of Natural Resources,
Toronto, Ontario.

Mineral Sciences Laboratories, CANMET,
Ottawa, Ontario (five independent analysts).

Sherritt Gordon Mines Limited,
Research & Development Division,
Fort Saskatchewan, Alberta.

Sherritt Gordon Mines Limited,
Mining & Milling Division,
Lynn Lake, Manitoba.

United Keno Hill Mines Limited,
Elsa, Yukon.

The participating laboratories (or independent analysts at CANMET) received two randomly-selected bottles of one or more of the three ore samples, and were requested to determine tungsten in each bottle, in quintuplicate, by a method of their choice. More than 85% of the results (Table 4) were obtained by an absorptiometric method using thiocyanate as reagent. Among the laboratories using the thiocyanate method, several provided results obtained after various methods of sample decomposition (see Discussion); in such cases each set of results was considered to be independent for statistical purposes, i.e., each set was treated as if it originated in a separate laboratory.

Confirmation of homogeneity using interlaboratory results

Using the *t*-test at the 5% significance level, a comparison of reported results for both bottles from each set confirmed that the degree of homogeneity of CT-1 and TLG-1 is satisfactory (Tables 5(a) and 5(c)). However, six of eighteen sets of results for BH-1 indicated a significant difference between the means of the two bottles (Table 5(b)). Because this rejection rate of the null hypothesis is abnormally high and is not consistent with the previously mentioned test of homogeneity by X-ray fluorescence method, additional chemical analyses (Table 6) were performed by two independent analysts at CANMET. The results of this "extra" work are discussed in detail below; they support the X-ray fluorescence results and the conclusion that BH-1 is suitably homogeneous.

The degree of homogeniety of the three reference ores is also illustrated in Figure 1, in which, for each set, the difference between the means of the results for the two bottles is plotted against the corresponding mean of the results for both bottles. The vertical bar represents the 95% confidence interval of the former. If a bar intersects the abscissa, the null hypothesis is accepted, i.e., there is no evidence of inhomogeneity between bottles according to that particular set of results.

ESTIMATION OF CONSENSUS VALUES

To avoid the introduction of bias to the estimated mean and confidence interval for a particular element, it is normal practice in CCRMP certification schemes to reject sets of results whose means differ from the consensus value by more than twice the overall standard deviation (identified in Table 4).

Analysis of variance (ANOVA)

A one-way ANOVA technique was used to calculate the consensus values for tungsten in CT-1, BH-1 and TLG-1. The analytical results were treated as though they satisfied the following model[9]:

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

where:

x_{ij} = the j^{th} result reported in set i;

μ = the true value that is estimated by the overall mean $\overline{x}_{..}$;

y_i = the discrepancy between the mean of the results from set i and the true value; and

e_{ij} = the discrepancy of x_{ij} from the means of the results from set i.

It is assumed in this analysis that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2, respectively. The existence of ω^2 can be 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 magnitude of ω^2 and σ^2 can be estimated from the ANOVA table (page 4).

Analysis of variance and expected mean squares for the one-way classification

Source of variance	Sums of squares	Degrees of freedom	Mean squares	E [Mean squares]
Between-sets	$\sum_{i}^{k} n_i (\bar{x}_{i.} - \bar{x}_{..})^2$	k-1	s_2^2	$\sigma^2 + \frac{1}{k-1}\left(\sum_{i}^{k} n_i - \frac{\sum_{i}^{k} n_i^2}{\sum_{i}^{k} n_i}\right)\omega^2$
Within-sets	$\sum_{i}^{k} \sum_{j}^{n_i} (x_{ij} - \bar{x}_{i.})^2$	$\sum_{i}^{k} n_i - k$	s_1^2	σ^2
Total	$\sum_{i}^{k} \sum_{j}^{n_i} (x_{ij} - \bar{x}_{..})^2$	$\sum_{i}^{k} n_i - 1$		

The concensus value, in the above model, can be estimated by the overall mean $\bar{x}_{..}$, thus:

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

with the variance of the overall mean being given by:

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

where:

n_i = the number of results reported in set i;

k = the number of sets;

The 95% confidence limits were then calculated according to the number of laboratories. The results of these calculations are presented in Table 7.

Certification factor

A recently conceived measure for evaluating the quality of reference materials is the 'certification factor'[10]. This factor can be computed from the following expression:

$$CF = \frac{2\left[t_{0.975,(k-1)} \cdot V[\bar{x}_{..}]^{\frac{1}{2}}\right] \times 100}{\overline{cv}}$$

where:

$\overline{cv}$ is the average of the within-set coefficients of variation and is given by

$$\overline{cv} = \sum_{i}^{k} cv_i / k$$

The certification factors for CT-1, BH-1 and TLG-1 are given in Table 7.

DISCUSSION

Table 7 shows that the certification factors for all three materials are well below the critical value of 4[10]. This indicates that CT-1, BH-1 and TLG-1 are suitable for use as reference materials because the precision of their consensus values for tungsten is as good as the average precision obtained by the contributors of the analytical results. Thus the consensus values given in Table 7 are accepted as recommended values for CT-1, BH-1, and TLG-1. For the convenience of the reader the recommended values and their 95% confidence limits are also given in Table 8.

Chemical confirmation of homogeneity of BH-1

Because the rejection of the null hypothesis for six sets of results for BH-1 (Table 5(b)) was inconsistent with previously obtained X-ray fluorescence data, two independent analysts at CANMET were asked to provide additional data for testing the homogeneity of BH-1. They were each given five randomly-selected bottles and were requested to perform tungsten analyses on five separate sub-samples from each bottle (i.e., 25 determinations) by the absorptiometric thiocyanate method following a mixed-acid decomposition.

Each analyst performed five series of analyses in which one sub-sample was taken from each bottle in each series (Table 6). This scheme permitted within-bottle, between-bottle and between-series (day to day) comparisons to be made by an analysis of variance. The results of this analysis showed that the between-series effects were the largest source of variance, and that bottle to bottle variance was not significant at the 5% level. Consequently, the original conclusion that BH-1 is suitably homogeneous is supported.

Each of the two CANMET analysts had previously contributed results for the two bottles of BH-1 in the initial round-robin program. Their second set of results were used as separate contributions for the estimation of the consensus value and 95% confidence limits for BH-1. One of these analysts (LAB-16 in Table 5(b)) originally gave results that implied a real difference between the two bottles, thus accounting for a rejection of the null hypothesis. However, as stated above, the overall results for the 10 bottles used in the extra work on BH-1 show no evidence of inhomogeneity. It is probable, therefore, that the between-bottle disparity found by LAB-16 in the original program is a function of the analytical method rather than a measure of inhomogeneity in BH-1. This conclusion is supported by a knowledge that the variability and magnitude of the blank associated with the tungsten-thiocyanate method could account for differences between series of analyses similar to those in Table 6 or between bottle sets such as those found by LAB-16 in Table 5(b).

Effect of method of decomposition

A large majority of tungsten results were obtained by the thiocyanate-absorptiometric method after sample decomposition by a sodium peroxide fusion, a potassium (sodium) pyrosulphate fusion, or a hydrofluoric-hydrochloric-phosphoric acid attack. From Table 7 it is evident that these methods of decomposition account for 45%, 30% and 25%, respectively, of the chemical results for the three ores. As expected, results by the fusion methods predominate as they are the ones most widely known by ore and rock analysts. The mixed-acid decomposition, devised in 1962, is described in a technical bulletin[11] of the former Mines Branch (now CANMET).

From a consideration of Table 7 it appears that, for all three ores, there is a consistent trend with the means increasing in the order peroxide < pyrosulphate < acid. Although all three methods probably result in complete sample decomposition, the above correlation implies that there are different chemical effects associated with each, especially between peroxide and acid. However, statistically it cannot be said that there is a significant difference in the overall results of the three methods; as Figure 2 clearly shows, there is appreciable overlap of the 95% confidence intervals of the means for the three methods — an exception being the case of peroxide fusion vs. acid attack for BH-1 in Figure 2(b).

From the chemical evidence available at this time, it is not certain whether a small negative bias is associated with the peroxide fusion method relative to the other two methods. Because this possibility exists however, the statistical parameters for tungsten in CT-1, BH-1, and TLG-1 have been computed after exclusion of all results obtained by the peroxide fusion method. These are given in Table 9 and can be used by those who may be concerned about the lower peroxide values.

It is to be emphasized that the recommended means are those derived from the acceptable data (Table 4) generated from all three methods of decomposition, as these values more completely reflect the "state of the art" for determining tungsten in low-grade ores.

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TABLE 4(a)

Tungsten results for CT-1

TUNGSTEN (WEIGHT PERCENT)

													SAMPLE WT. G
	LAB- 1 (THIOCY.)	pyro	1.040	1.050	1.050	1.020	1.050	1.050	1.050	1.010	1.020	1.040	0.5
	LAB- 1 (THIOCY.)	acid	1.070	1.060	1.070	1.080	1.070	1.060	1.070	1.070	1.070	1.070	0.5
	LAB- 2 (THIOCY.)	perox	1.040	.990	.980	1.040	1.030	1.000	1.000	1.020	1.040	1.040	1.0
	LAB- 3 (THIOCY.)	pyro	1.054	1.053	1.058	1.067	1.070	1.050	1.058	1.041	1.049	1.054	1.0
	LAB- 4 (XRF)	–	.947	1.000	1.016	1.064	.977	.890	1.019	1.015	.966	.970	–
*	LAB- 5 (THIOCY.)	other	1.350	1.330	1.180	1.200	1.190	1.200	1.280	1.250	1.290	1.330	0.5
	LAB- 6 (THIOCY.)	acid	1.080	1.100	1.090	1.110	1.080						1.0
	LAB- 6 (THIOCY.)	pyro	1.040	1.050	1.080	1.050	1.020						0.5
	LAB- 7 (THIOCY.)	perox	.983	.944	1.030	.944	.975	.991	1.040	.952	1.000	1.040	0.5
	LAB- 8 (THIOCY.)	perox	1.040	1.040	1.000	1.020	1.000	1.020	1.000	1.010	1.000	1.020	0.5
			1.000	1.010	1.040	1.040	1.010	1.020					
	LAB- 9 (THIOCY.)	perox	1.097	1.106	1.092	1.089	1.091	1.089	1.097	1.093	1.097	1.110	0.5
	LAB-10 (THIOCY.)	pyro	1.080	1.080	1.130	1.100	.980	1.020	1.100	1.050	1.080	1.100	0.2
			1.090	1.050									
	LAB-11 (THIOCY.)	perox	1.019	1.046	1.078	1.078	1.059	1.037	1.065	1.078	1.058	1.046	1.0
	LAB-12 (THIOCY.)	pyro	1.040	1.040	1.052	1.044	1.032	1.056	1.036	1.040	1.048	1.024	0.5
	LAB-13 (THIOCY.)	perox	1.040	1.000	1.010	.980	1.020	1.010	1.040	.970	1.010	1.020	1.0
	LAB-14 (X.R.F.)	–	.970	1.010	1.020	1.020	1.010	.990	.980	.950	.970	1.000	–
	LAB-15 (THIOCY.)	perox	1.050	1.030	1.050	1.100	1.020	1.000	1.070	1.130			–
	LAB-16 (THIOCY.)	acid	1.030	1.020	1.030	1.040	1.020	1.050	1.060	1.070	1.070	1.060	0.5
	LAB-16 (THIOCY.)	pyro	1.070	1.070	1.070	1.100	1.090	1.100	1.100	1.140	1.100	1.110	0.5
	LAB-16 (THIOCY.)	perox	1.030	1.050	1.040	1.050	1.030	1.060	1.070	1.060	1.060	1.070	0.5
*	LAB-17 (THIOCY.)	pyro	.920	.880	.900	.880	.920	.900	.920	.880	.900	.880	1.0

* set rejected as outlier

TABLE 4(b)

Tungsten results for BH-1

TUNGSTEN (WEIGHT PERCENT)

												SAMPLE WT, G
LAB- 1 (THIOCY.)	pyro	.460	.440	.440	.440	.440	.430	.440	.440	.420	.440	0.5
LAB- 1 (THIOCY.)	acid	.420	.420	.420	.430	.420	.420	.440	.470	.440	.440	0.5
LAB- 2 (THIOCY.)	perox	.418	.417	.420	.420	.420	.412	.413	.412	.412	.417	1.0
LAB- 3 (THIOCY.)	pyro	.451	.464	.458	.448	.460	.459	.469	.464	.467	.458	1.0
* LAB- 4 (XRF)	-	.352	.344	.353	.346	.351	.321	.343	.344	.341	.344	-
* LAB- 5 (THIOCY.)	other	.530	.520	.510	.525	.530	.530	.500	.520	.515	.520	0.5
LAB- 6 (THIOCY.)	acid	.431	.440	.434	.428	.435						1.0
LAB- 6 (THIOCY.)	pyro	.438	.435	.440	.442	.435						0.5
LAB- 7 (THIOCY.)	perox	.412	.425	.425	.412	.412	.428	.416	.428	.416	.412	0.5
LAB- 8 (THIOCY.)	perox	.400	.400	.400	.400	.410	.410	.400	.400	.400	.410	0.5
		.400	.400	.410	.410	.400	.400					
LAB- 9 (THIOCY.)	perox	.423	.432	.426	.419	.417	.427	.427	.430	.416	.420	1.0
LAB-10 (THIOCY.)	pyro	.420	.410	.420	.410	.410	.420	.420	.420	.420	.420	0.5
LAB-11 (THIOCY.)	perox	.413	.413	.408	.444	.424	.408	.381	.393	.389	.420	1.0
LAB-12 (THIOCY.)	pyro	.414	.408	.414	.404	.408	.412	.410	.412	.410	.407	1.0
LAB-13 (THIOCY.)	perox	.420	.410	.410	.420	.420	.410	.420	.420	.420	.420	1.0
LAB-14 (X.R.F.)	-	.427	.426	.432	.433	.427	.400	.399	.403	.398	.400	-
LAB-15 (THIOCY.)	perox	.414	.407	.398	.409	.404	.359	.402	.401			-
LAB-16 (THIOCY.)	acid	.422	.424	.420	.422	.424	.430	.428	.430	.430	.433	1.0
LAB-16 (THIOCY.)	pyro	.431	.424	.429	.427	.419	.442	.437	.439	.439	.437	1.0
LAB-17 (THIOCY.)	pyro	.420	.400	.400	.390	.400	.400	.400	.400	.380	.380	1.0
LAB-12 (THIOCY.)	acid	.434	.437	.432	.424	.433	.433	.438	.426	.423	.426	1.0
		.425	.428	.432	.428	.421	.437	.431	.421	.423	.421	
		.431	.433	.428	.428	.425						
LAB-16 (THIOCY.)	acid	.436	.429	.423	.426	.423	.434	.429	.433	.421	.428	1.0
		.439	.431	.423	.425	.426	.434	.431	.423	.425	.428	
		.431	.433	.423	.429	.426						

* set rejected as outlier

TABLE 4(c)

Tungsten results for TLG-1

TUNGSTEN (WEIGHT PERCENT)

												SAMPLE WT, G
LAB- 1 (THIOCY.)	pyro	.089	.086	.082	.086	.086	.077	.082	.085	.084	.087	1.0
LAB- 1 (THIOCY.)	acid	.085	.091	.093	.075	.079	.089	.091	.075	.077	.075	1.0
LAB- 2 (THIOCY.)	perox	.095	.097	.097	.092	.094	.092	.094	.095	.094	.097	1.0
LAB- 3 (THIOCY.)	acid	.087	.091	.091	.093	.090	.088	.088	.088	.093	.091	1.0
LAB- 4 (XRF)	-	.084	.090	.089	.088	.088	.084	.086	.086	.087	.090	-
* LAB- 5 (THIOCY.)	other	.105	.105	.098	.103	.098	.105	.100	.098	.100	.103	0.5
LAB- 6 (THIOCY.)	acid	.090	.094	.093	.094	.094						1.0
LAB- 6 (THIOCY.)	pyro	.090	.090	.090	.090	.094						0.5
LAB- 7 (THIOCY.)	perox	.073	.078	.078	.073	.071	.073	.073	.076	.076	.078	1.0
LAB- 8 (THIOCY.)	perox	.075	.075	.070	.075	.075	.075	.075	.075	.075	.075	1.0
		.070	.075	.075	.075	.070	.075					
LAB- 9 (THIOCY.)	perox	.079	.078	.077	.078	.079	.075	.079	.078	.078	.079	1.0
LAB-10 (THIOCY.)	pyro	.084	.084	.084	.084	.081	.086	.081	.084	.084	.086	1.0
LAB-11 (THIOCY.)	perox	.086	.083	.069	.075	.083	.075	.072	.083	.075	.072	2.0
LAB-12 (THIOCY.)	pyro	.076	.076	.080	.080	.080	.080	.074	.080	.082	.082	1.0
LAB-13 (THIOCY.)	perox	.081	.098	.089	.088	.089	.090	.086	.095	.081	.088	1.0
LAB-14 (X.R.F.)	-	.075	.073	.073	.075	.075	.076	.076	.077	.076	.075	-
LAB-15 (THIOCY.)	perox	.094	.094	.096	.096	.093	.093	.100	.096			-
LAB-17 (THIOCY.)	acid	.085	.085	.080	.090	.080	.085	.090	.085	.085	.090	1.0

* set rejected as outlier

TABLE 5(a)

Laboratory means, coefficients of variation, and summary of *t*-test on between-bottle results for CT-1

Tungsten, wt %

		BOTTLE 1			BOTTLE 2			NULL HYPOTH.	OVERALL			
		N	MEAN	ST.DEV.	N	MEAN	ST.DEV.		N	MEAN	ST.DEV.	C.V.(%)
LAB- 1	(THIOCY.)	5	1.0420	.0130	5	1.0340	.0182	A	10	1.0380	.0155	1.49
LAB- 1	(THIOCY.)	5	1.0700	.0071	5	1.0680	.0045	A	10	1.0690	.0057	.53
LAB- 2	(THIOCY.)	5	1.0160	.0288	5	1.0200	.0200	A	10	1.0180	.0235	2.31
LAB- 3	(THIOCY.)	5	1.0604	.0077	5	1.0504	.0063	A	10	1.0554	.0085	.80
LAB- 4	(XRF)	5	1.0008	.0438	5	.9720	.0520	A	10	.9864	.0478	4.85
* LAB- 5	(THIOCY.)	5	1.2500	.0828	5	1.2700	.0485	A	10	1.2600	.0648	5.14
LAB- 6	(THIOCY.)	THERE IS ONLY 1 BOTTLE							5	1.0920	.0130	1.19
LAB- 6	(THIOCY.)	THERE IS ONLY 1 BOTTLE							5	1.0480	.0217	2.07
LAB- 7	(THIOCY.)	5	.9752	.0354	5	1.0046	.0370	A	10	.9899	.0375	3.79
LAB- 8	(THIOCY.)	8	1.0162	.0169	8	1.0175	.0158	A	16	1.0169	.0158	1.55
LAB- 9	(THIOCY.)	5	1.0950	.0068	5	1.0972	.0079	A	10	1.0961	.0070	.64
LAB-10	(THIOCY.)	6	1.0650	.0550	6	1.0783	.0232	A	12	1.0717	.0409	3.81
LAB-11	(THIOCY.)	5	1.0560	.0247	5	1.0568	.0160	A	10	1.0564	.0196	1.86
LAB-12	(THIOCY.)	5	1.0416	.0073	5	1.0408	.0121	A	10	1.0412	.0094	.91
LAB-13	(THIOCY.)	5	1.0100	.0224	5	1.0100	.0255	A	10	1.0100	.0226	2.24
LAB-14	(X.R.F.)	5	1.0060	.0207	5	.9780	.0192	A	10	.9920	.0239	2.41
LAB-15	(THIOCY.)	4	1.0575	.0299	4	1.0550	.0580	A	8	1.0562	.0427	4.05
LAB-16	(THIOCY.)	5	1.0280	.0084	5	1.0620	.0084	REJECT	10	1.0450	.0196	1.87
LAB-16	(THIOCY.)	5	1.0800	.0141	5	1.1100	.0173	REJECT	10	1.0950	.0217	1.98
LAB-16	(THIOCY.)	5	1.0400	.0100	5	1.0640	.0055	REJECT	10	1.0520	.0148	1.40
* LAB-17	(THIOCY.)	5	.9000	.0200	5	.8960	.0167	A	10	.8980	.0175	1.95
								TOTAL	206	1.0452	.0708	6.77

* set rejected as outlier

TABLE 5(b)

Laboratory means, coefficients of variation, and summary of *t*-test on between-bottle results for BH-1

Tungsten, wt %

		BOTTLE 1			BOTTLE 2			NULL HYPOTH.	OVERALL			
		N	MEAN	ST.DEV.	N	MEAN	ST.DEV.		N	MEAN	ST.DEV.	C.V.(%)
LAB- 1	(THIOCY.)	5	.4440	.0089	5	.4340	.0089	A	10	.4390	.0099	2.27
LAB- 1	(THIOCY.)	5	.4220	.0045	5	.4420	.0179	REJECT	10	.4320	.0162	3.75
LAB- 2	(THIOCY.)	5	.4190	.0014	5	.4132	.0022	REJECT	10	.4161	.0035	.84
LAB- 3	(THIOCY.)	5	.4562	.0066	5	.4634	.0048	A	10	.4598	.0066	1.44
* LAB- 4	(XRF)	5	.3492	.0040	5	.3386	.0099	A	10	.3439	.0090	2.63
* LAB- 5	(THIOCY.)	5	.5230	.0084	5	.5170	.0110	A	10	.5200	.0097	1.87
LAB- 6	(THIOCY.)	THERE IS ONLY 1 BOTTLE							5	.4336	.0045	1.04
LAB- 6	(THIOCY.)	THERE IS ONLY 1 BOTTLE							5	.4380	.0031	.70
LAB- 7	(THIOCY.)	5	.4172	.0071	5	.4200	.0075	A	10	.4186	.0070	1.68
LAB- 8	(THIOCY.)	8	.4025	.0046	8	.4037	.0052	A	16	.4031	.0048	1.19
LAB- 9	(THIOCY.)	5	.4234	.0059	5	.4240	.0058	A	10	.4237	.0055	1.31
LAB-10	(THIOCY.)	5	.4140	.0055	5	.4200	.0000	***R**	10	.4170	.0048	1.16
LAB-11	(THIOCY.)	5	.4204	.0144	5	.3982	.0156	REJECT	10	.4093	.0184	4.49
LAB-12	(THIOCY.)	5	.4096	.0043	5	.4102	.0020	A	10	.4099	.0032	.78
LAB-13	(THIOCY.)	5	.4160	.0055	5	.4180	.0045	A	10	.4170	.0048	1.16
LAB-14	(X.R.F.)	5	.4290	.0032	5	.4000	.0019	REJECT	10	.4145	.0155	3.74
LAB-15	(THIOCY.)	4	.4070	.0067	4	.3915	.0217	A	8	.3992	.0170	4.26
LAB-16	(THIOCY.)	5	.4224	.0017	5	.4302	.0018	REJECT	10	.4263	.0044	1.04
LAB-16	(THIOCY.)	5	.4260	.0047	5	.4388	.0020	REJECT	10	.4324	.0076	1.75
LAB-17	(THIOCY.)	5	.4020	.0110	5	.3920	.0110	A	10	.3970	.0116	2.92
LAB-12	(THIOCY.)	THERE ARE MORE THAN 2 BOTTLES							25	.4287	.0052	1.21
LAB-16	(THIOCY.)	THERE ARE MORE THAN 2 BOTTLES							25	.4284	.0047	1.11
								TOTAL	244	.4229	.0300	7.09

* set rejected as outlier

TABLE 5(c)

Laboratory means, coefficients of variation, and summary of *t*-test on between-bottle results for TLG-1

Tungsten, wt %

		BOTTLE 1			BOTTLE 2			NULL HYPOTH.	OVERALL			
		N	MEAN	ST.DEV.	N	MEAN	ST.DEV.		N	MEAN	ST.DEV.	C.V.(%)
LAB- 1	(THIOCY.)	5	.0858	.0025	5	.0830	.0038	A	10	.0844	.0034	4.00
LAB- 1	(THIOCY.)	5	.0846	.0077	5	.0814	.0079	A	10	.0830	.0075	9.09
LAB- 2	(THIOCY.)	5	.0950	.0021	5	.0944	.0018	A	10	.0947	.0019	1.99
LAB- 3	(THIOCY.)	5	.0904	.0022	5	.0896	.0023	A	10	.0900	.0022	2.40
LAB- 4	(XRF)	5	.0878	.0023	5	.0866	.0022	A	10	.0872	.0022	2.52
* LAB- 5	(THIOCY.)	5	.1018	.0036	5	.1012	.0028	A	10	.1015	.0030	2.98
LAB- 6	(THIOCY.)	THERE IS ONLY 1 BOTTLE							5	.0930	.0017	1.86
LAB- 6	(THIOCY.)	THERE IS ONLY 1 BOTTLE							5	.0908	.0018	1.97
LAB- 7	(THIOCY.)	5	.0746	.0032	5	.0752	.0022	A	10	.0749	.0026	3.47
LAB- 8	(THIOCY.)	8	.0744	.0018	8	.0737	.0023	A	16	.0741	.0020	2.72
LAB- 9	(THIOCY.)	5	.0782	.0008	5	.0778	.0016	A	10	.0780	.0012	1.60
LAB-10	(THIOCY.)	5	.0834	.0013	5	.0842	.0020	A	10	.0838	.0017	2.01
LAB-11	(THIOCY.)	5	.0792	.0070	5	.0754	.0045	A	10	.0773	.0059	7.64
LAB-12	(THIOCY.)	5	.0784	.0022	5	.0796	.0033	A	10	.0790	.0027	3.43
LAB-13	(THIOCY.)	5	.0890	.0060	5	.0880	.0051	A	10	.0885	.0053	6.01
LAB-14	(X.R.F.)	5	.0742	.0011	5	.0760	.0007	REJECT	10	.0751	.0013	1.71
LAB-15	(THIOCY.)	4	.0950	.0012	4	.0955	.0033	A	8	.0952	.0023	2.43
LAB-17	(THIOCY.)	5	.0840	.0042	5	.0870	.0027	A	10	.0855	.0037	4.31
								TOTAL	174	.0845	.0085	10.10

* set rejected as outlier

TABLE 6

Chemical confirmation of homogeneity of BH-1

CANMET Analyst A

	Tungsten, wt %					
	Bottle 191	Bottle 477	Bottle 813	Bottle 822	Bottle 1094	Mean
Series 1	0.434	0.433	0.425	0.437	0.431	0.432
2	0.437	0.438	0.428	0.431	0.433	0.433
3	0.432	0.426	0.432	0.421	0.428	0.428
4	0.424	0.423	0.428	0.423	0.428	0.425
5	0.433	0.426	0.421	0.421	0.425	0.425
Mean	0.432	0.429	0.427	0.427	0.429	

CANMET Analyst B

	Tungsten, wt %					
	Bottle 315	Bottle 378	Bottle 610	Bottle 826	Bottle 970	Mean
Series 1	0.436	0.434	0.439	0.434	0.431	0.435
2	0.429	0.429	0.431	0.431	0.433	0.431
3	0.423	0.433	0.423	0.423	0.423	0.425
4	0.426	0.421	0.425	0.425	0.429	0.425
5	0.423	0.428	0.426	0.428	0.426	0.426
Mean	0.427	0.429	0.429	0.428	0.428	

TABLE 7

Estimation of statistical parameters for tungsten ores (after rejection of outliers)

		No. of Participating Laboratories	No. of Sets of Results	No. of Observations	Median, %	Mean, %	Av. Within-lab cv, %	95% Confidence Limits for the Mean, %		Certification Factor
								Low	High	
CT-1	Perox	8	8	84	1.040	1.035	2.2	1.006	1.064	
	Pyro	6	6	57	1.050	1.060	1.8	1.036	1.083	
	Acid	3	3	25	1.070	1.064	1.2	1.007	1.121	
	XRF	2	2	20	--	0.989	-	--	--	
	Overall	15	19	186	1.041	1.042	2.1	1.025	1.058	1.54
BH-1	Perox	7	7	74	0.412	0.412	2.1	0.404	0.420	
	Pyro	7	7	65	0.424	0.427	1.6	0.406	0.447	
	Acid	4	5	75	0.428	0.429	1.6	0.427	0.431	
	XRF	1	1	10	--	0.415	-	--	--	
	Overall	15	20	224	0.423	0.422	1.9	0.415	0.430	1.86
TLG-1	Perox	7	7	74	0.078	0.082	3.7	0.073	0.091	
	Pyro	4	4	35	0.084	0.084	2.9	0.077	0.091	
	Acid	4	4	35	0.089	0.087	4.4	0.080	0.094	
	XRF	2	2	20	--	0.081	-	--	--	
	Overall	15	17	164	0.084	0.083	3.5	0.080	0.087	2.57

TABLE 8

RECOMMENDED TUNGSTEN VALUES FOR REFERENCE ORES

	CT-1	BH-1	TLG-1
RECOMMENDED VALUE	1.042 WT%	0.422 WT%	0.083 WT%
95% CONFIDENCE LIMITS			
LOW	1.025	0.415	0.080
HIGH	1.058	0.430	0.087

TABLE 9

PROVISIONAL TUNGSTEN VALUES AFTER EXCLUSION OF RESULTS BY PEROXIDE FUSION

	CT-1	BH-1	TLG-1
PROVISIONAL VALUE	1.061 WT%	0.428 WT%	0.085 WT%
95% CONFIDENCE LIMITS			
LOW	1.045	0.418	0.082
HIGH	1.077	0.438	0.089

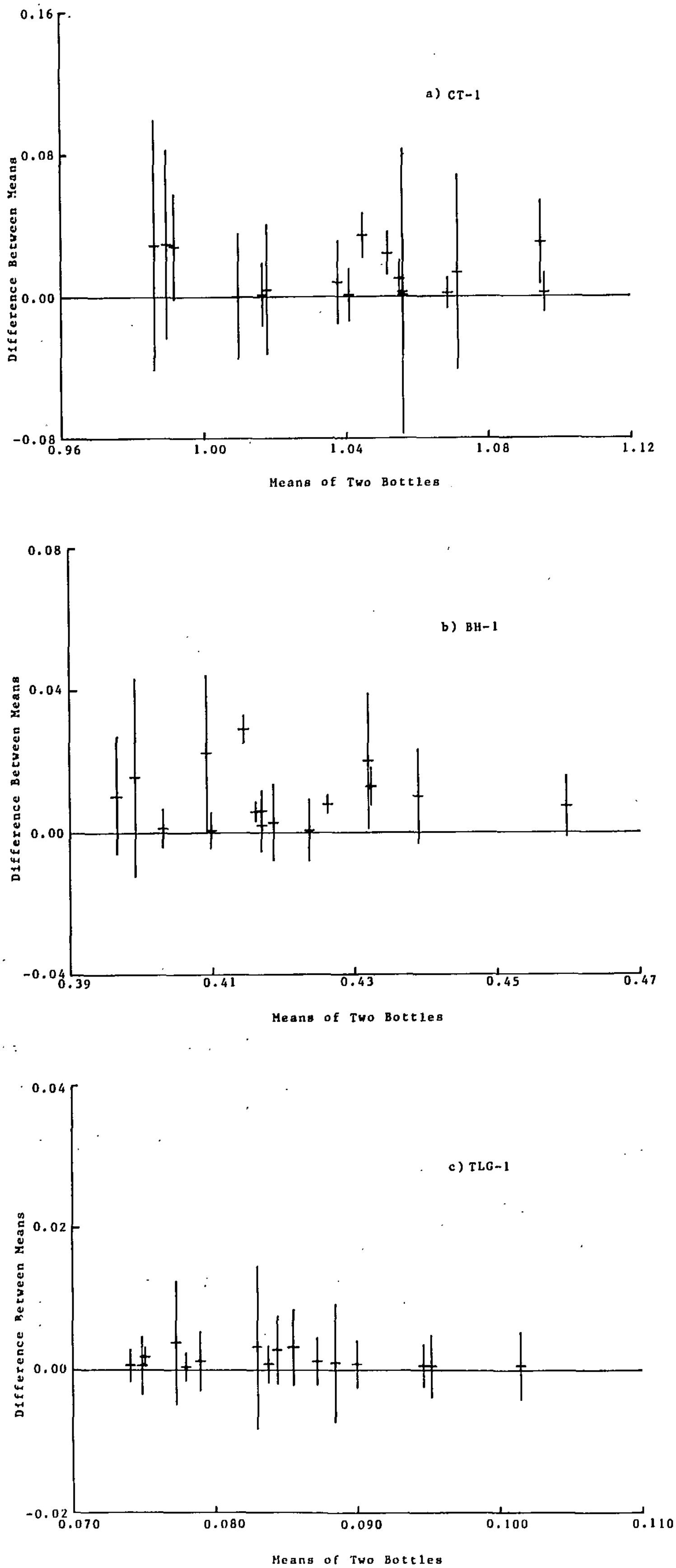

Figure 1. Illustration of degree of homogeneity

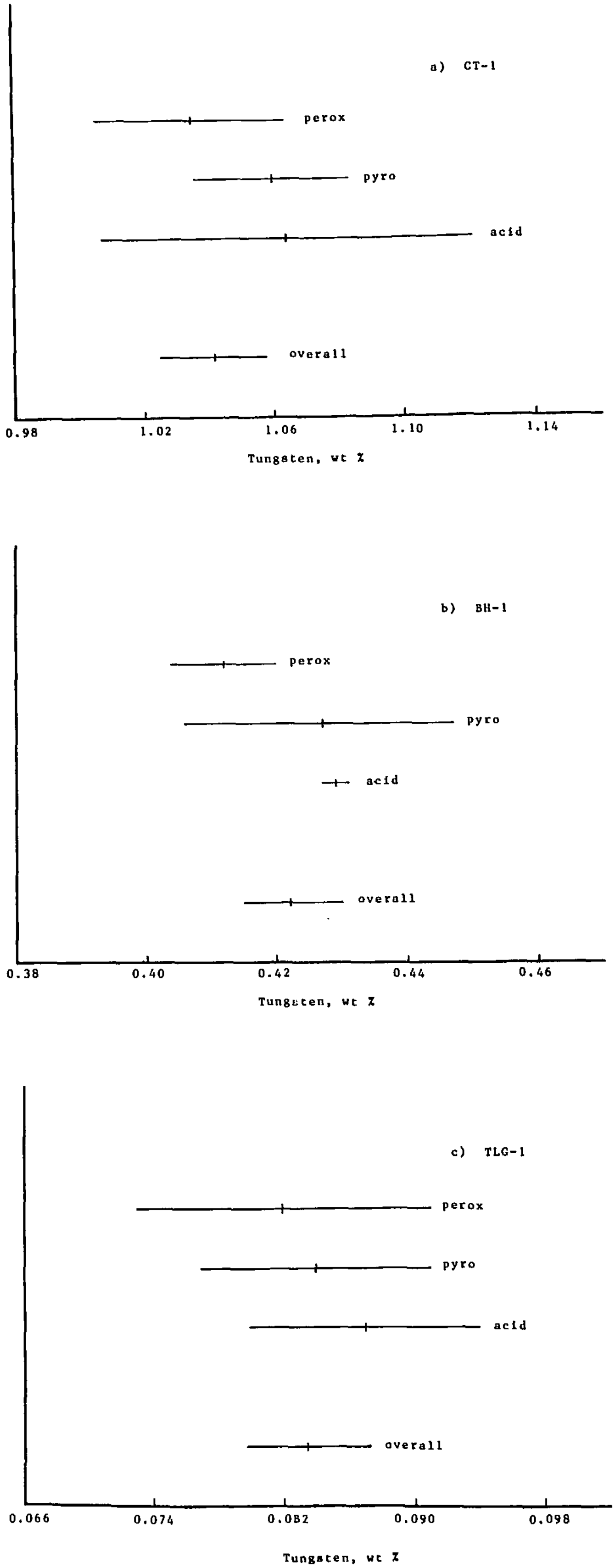

Figure 2. Overall means and 95% confidence intervals in CT-1, BH-1, and TLG-1 after various methods of decomposition