CH-1 AND CH-2:

CERTIFIED REFERENCE GOLD ORES

H.F. STEGER AND W.S. BOWMAN

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by

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

SYNOPSIS

A 228-kg sample of copper-silver-gold sulphide ore from Chibougamau, Quebec, has been prepared as a compositional reference material for gold. The material, encoded CH-1, was ground to minus 74 µm and mixed in one lot; approximately 96 kg were bottled in 200-g units. The remaining 132 kg of CH-1 were blended with 17 kg of gold reference ore MA-1, screened to pass minus 46 µm and bottled in 200-g units. The latter, encoded CH-2, was tested for homogeneity with respect to gold content by a fire assay-atomic absorption procedure.

In a "free choice" analytical program, 17 laboratories contributed results for gold in CH-1 and for one or more of iron, sulphur, copper, silver and gold in CH-2. Based on a statistical analysis of the data, the following recommended values were assigned: Au, 0.24 µg/g for CH-1; and Fe, 25.7%; S, 17.4%; Cu, 2.43%; Ag, 24.2 µg/g; and Au, 1.33 µg/g for CH-2.

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Note: Major contributions were also made by other staff members of the Mineral Sciences Laboratories.

MINERAIS D'OR DE RÉFÉRENCE CERTIFIÉS: CH-1 ET CH-2

par

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

SYNOPSIS

Un échantillon de 228 kg de minerai de soufre de cuivre-argent-or de Chibougamau au Québec a été préparé comme matériau de référence de composition pour l'or. Le minerai, désigné CH-1, a été broyé à une granulométrie de moin 74 µm et mélangé en lot de minerai; approximativement 96 kg ont été embouteillés en unités de 200 g. Les restant 132 kg du CH-1 ont été mélangés avec 17 kg du matériau de référence type d'or MA-1, tamisés afin de passer 46 µm et embouteillés en unités de 200 g. Celui-ci, désigné CH-2, a été soumis à des essais d'homogénéité quant à l'or par une méthode qui combine l'analyse pyrognostique et la spectrométrie d'absorption atomique.

En vertu d'une campagne analytique de "libre choix", 17 laboratoires ont soumis des résultats pour l'or en le CH-1 et pour un ou plusieurs du fer, du soufre, du cuivre, de l'argent et de l'or en le CH-2. Suite à l'analyse statistique des données, les valeurs recommandées suivantes ont été assignées: Au, 0,24 µg/g en le CH-1; et Fe, 25,7%; S, 17,4%; Cu, 2,43%; Ag, 24,2 µg/g; et Au, 1,33 µg/g en le CH-2.

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Nota: D'autres membres du personnel des Laboratoires des sciences minérales ont également apporté une grande contribution à ce projet.

CONTENTS

TABLES

TABLES (Cont'd)

FIGURES

INTRODUCTION

The preparation, characterization and certification of ores CH-1 and CH-2 is a continuing contribution of the Canadian Certified Reference Materials Project (CCRMP) in its endeavour to provide 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).

CH-1 and CH-2 are gold-bearing reference materials having a high sulphide matrix and are intended to complement the much less complex siliceous matrix gold reference materials such as MA-1 (2), MA-2 (3) and GTS-1 (4).

An interlaboratory program was conducted to obtain analytical results for gold only in CH-1 and for iron, sulphur, copper, silver and gold in CH-2 from laboratories using methods of their choice. The results should be indicative of the practical state of the art of the analysis for these elements in this type of material matrix.

NATURE AND PREPARATION

The raw material for CH-1 was hand-picked in 1970 by Dr. W. Petruk of CANMET at the Campbell Chibougamau copper mine near Chibougamau, Quebec (5). The mineralogy of the orebody has been described by J.Y. Cote et al. (6). The host rock is meta-anorthosite; sulphide mineralogy (in order of abundance) is pyrrhotite, pyrite and chalcopyrite and small amounts of sphalerite, galena and molybdenite. Copper, gold and silver are the economic metals.

The raw material was dry-ground in May of 1983 to pass a 74-µm screen. The powdered ore weighing 228 kg was tumbled in a 570-L conical blender for 9 h. Ninety-six kilograms of the blended material were bottled in 200-g units which were heat-sealed in polyester-aluminum foil-polyethylene pouches to prevent oxidation while in storage at CANMET.

One hundred and thirty-two kg of the powdered ore were mixed with 17.1 kg of gold reference ore MA-1 for 15 h to prepare reference ore CH-2. The analysis of 15 randomly selected bottles of CH-2 for gold demonstrated the material and CH-1 by inference to be statistically sufficiently homogeneous for use as a reference material (Appendix A). CCRMP, however, was not satisfied with the magnitude of the within-bottle variance assuming this to be due to a random distribution of the larger gold particles from MA-1. The mixture was passed through a 46-µm screen and subsequent analysis indicated a much smaller within-bottle variance. Approximately 103 kg of this screened material, encoded CH-2, were blended for 14 h and bottled in 200-g units.

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

Table 1 - Mineralogical composition of CH-1

Mineral	Mass %
Pyrrhotite	39.3
Anorthosite	29.0
Albite	16.5
Pyrite	8.0
Chalcopyrite	5.7
Ferro-aluminosilicates	2.0
Hematite-magnetite	1.0
Sphalerite	0.3
Galena	trace
Quartz	trace
Orthoclase	trace

Table 2 - Approximate chemical composition

	Mass %	
Element	CH-1	CH-2
Fe	28.23	25.7
S	19.00	17.4
Si	12.96	13.6
Al	6.86	6.8
Cu	2.44	2.4
Zn	0.20	-
Ni	0.08	-
C, total	0.04	0.1
Co	0.02	-
Pb	0.02	-
Ag	26.2 µg/g	24.2 µg/g
Au	0.24 µg/g	1.3
H_2O (105°)	0.17	0.1

Table 3 - Particle size analysis (wet screen)

	Mass %	
Size of fraction (µm)	CH-1	CH-2
-104 + 74	0.2	-
-74 + 46	9.4	0.1
-46 + 37	10.1	12.0
-37	80.3	87.9

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 openly.

Each laboratory was requested to contribute five replicate results for gold in CH-1 and for iron, sulphur, copper, silver and gold in CH-2 by methods of its own choice and to report the results on an "as is" basis. When a laboratory submitted results for an element by more than one method, each set was considered to be statistically independent. The recommended values for CH-1 and CH-2 are presented in Tables 4 and 5. Methodological and analytical information is reported in Tables 6a through 7f.

Table 4 - Recommended values and statistical parameters for CH-1

No. of laboratories	17
No. of sets of results	18
No. of results	88
Mean	0.24 µg/g, 0.0070 oz/ton
95% confidence limits,	
low	0.22 µg/g, 0.0064 oz/ton
high	0.26 µg/g, 0.0076 oz/ton
σ_A*	0.022 µg/g

*Average within-laboratory standard deviation.

Table 5 - Recommended values and statistical parameters for CH-2

Element	No. of laboratories	No. of sets of results	No. of results	Overall mean	95% CL low	95% CL high	σ_A
				mass %			
Fe	12	13	67	25.7	25.3	26.0	0.09
S	13	15	85	17.4	17.2	17.6	0.13
Cu	14	15	80	2.43	2.38	2.48	0.02
Ag	11	15	73	24.2 µg/g	23.7 µg/g	24.7 µg/g	0.37 µg/g
Au	17	19	94	1.33 µg/g	1.28 µg/g	1.38 µg/g	0.07 µg/g

Table 6a - Summary of analytical methodology for gold in CH-1 and CH-2 (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	CH-1 $\bar{x}$ (µg/g)	CH-2 $\bar{x}$ (µg/g)
Fire assay-atomic absorption	Fire assay concentration to Pb button; acid dissolution	CANMET (a), CANMET (b), 3, 6, 8, 9, 12a, 13	41	0.26	1.31
	Fire assay concentration (silver added) to silver bead	2, 15	10	0.23	1.41
	Fire assay concentration (palladium added) to palladium bead; dissolution in aqua regia; Au extracted into MIBK	14	5	0.24	1.36
Fire assay-gravimetry	Fire assay concentration to silver bead; silver dissolved; Au weighed	1, 16	10	0.29	1.32
Fire assay-ICP-AES	Fire assay concentration to silver or doré bead; dissolution in aqua regia	4, 7	10	0.19	1.23
Fire assay-DC-AES	Fire assay concentration to silver bead; dissolution in aqua regia	11	5	0.20	1.28
Neutron activation analysis		12b	5	0.22	1.32
No details		10	5	0.23	1.50
Colorimetry	Roasting; taken up in HCl + HNO_3 + HF + Br_2; Au extracted as bromide complex into 7% trioctylamine in toluene; cola developed with thio-Michler's ketone solution	5	5	0.23	1.45

Table 6b - Summary of analytical methodology for iron in CH-2 (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (mass %)
Titrimetry	One or more of HCl + HNO_3 + HF + $HClO_4$ + H_2SO_4; single or double precipitation of hydrous oxides; taken up in dil. HCl; reduced with $SnCl_2$; titrated with dichromate	7, 13a, 15	17	25.42
	Na_2O_2 + NaOH fusion; single or double hydrous oxide precipitation; taken up with dil. HCl; reduced to Fe(II); titrated with dichromate	1, 3, 12	15	25.51
	HCl + HNO_3 + Br_2; silica dehydrated; taken up in dil. HCl and filtered; precipitate treated with HF to remove silica; residue fused with Na_2CO_3 and added to filtrate; double hydrous oxide precipitation; taken up in dil. HCl; reduced to Fe(II) and titrated with dichromate	CANMET(a)	5	26.34
	Na_2O_2 + NaOH fusion; hydrous oxide precipitation; taken up in dil. HCl; reduced with test lead; titrated with cerric ammonium sulphate	8	5	25.72
Atomic absorption	One or more of HCl + HNO_3 + HF + $HClO_4$ + H_2SO_4 to dryness; taken up in dil. HCl	CANMET(b), 9, 11 14	20	25.90
Xrf	$K_2S_2O_7$ fusion; ground and pelletized	4	5	25.54

Table 6c - Summary of analytical methodology for sulphur in CH-2 (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (mass %)
Gravimetry	One or more of HCl + HNO_3 + Br_2 to dryness; taken up in dil. HCl; sulphate precipitated with $BaCl_2$	9, 12, 15, 16	20	17.22
	One or more of HCl + HNO_3 + $KClO_3$ + $NaClO_3$ + Br_2; silica dehydrated and filtered off; Fe precipitated with $(NH_4)_2CO_3$ and filtered off; sulphate precipitated with $BaCl_2$	CANMET(b), CANMET(c)	15	17.67
	As previous but soluble $BaSO_4$ recovered; filtrate from $BaSO_4$ precipitation reduced to low volume to recover $BaSO_4$	CANMET(a)	5	17.79
	Fusion with Na_2O_2 + NaOH; Fe removed with NH_4OH; sulphate precipitated with $BaCl_2$	8	5	17.07
Combustion-titrimetry	Leco Induction Furnace decomposition; iodimetric finish with KI-KIO3	3, 6	15	17.19
	Leco Induction Furnace decomposition; NaOH acidimetric titration	11	5	17.40
Combustion-colorimetry	Leco Induction Furnace decomposition; IR measurement	7, 13	10	17.81
Xrf	1:3 sample: sand pressed into pellet	4	5	17.05

Table 6d - Summary of analytical methodology for copper in CH-2 (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (mass %)
Atomic absorption	One or more of HCl + HNO_3 + HF + $HClO_4$ to dryness; taken up in dil. HCl or HNO_3	CANMET 1, 3, 7, 9, 11, 12, 13, 15b	45	2.43
Titrimetry	HCl + HNO_3 + H_2SO_4 + Br_2 to dryness; taken up in dil. acid; NH_4F and sodium acetate are added; titrated with $Na_2S_2O_3$	15a	5	2.42
———	HCl + HNO3 + H2SO4 to dryness; taken up in dil. acid; Cu precipitated as sulphide by addition of $Na_2S_2O_3$ and boiling; filtered off and ignited; dissolved in HNO_3; pH adjusted and KI added; titrated with $Na_2S_2O_3$	8	5	2.50
ICP-AES	HCl + $HClO_4$ to dryness; taken up in dil. HCl	6	10	2.45
	Fusion with Na_2O_2 + Na_2CO_3; taken up in dil. HCl; scandium added as internal standard	16	5	2.44
Xrf	$K_2S_2O_7$ fusion; ground and pelletized	4	5	2.54
No details		10	5	2.29

Table 6e - Summary of analytical methodology for silver in CH-2 (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (µg/g)
Fire assay-gravimetry	Fire assay concentration to silver bead; weigh; dissolve silver; weigh gold bead; silver by difference	1, 3, 6, 15	18	24.6
Fire assay-atomic absorption	Fire assay concentration to lead button; taken up in HNO_3	CANMET(a), CANMET(b), 7, 11	20	24.5
Atomic absorption	One or more of HCl + HNO_3 + HF to dryness; taken up in HCl or HNO_3	8, 9, 12, 16	20	24.0
	HNO_3 + HF + H_2SO_4 + Br_2 to dryness; silver extracted as bromide into chloroform containing tribenzylamine; stripped with conc'd HBr; treated with HNO_3 + $HClO_4$ to dryness; taken up in 10% HCl - 1% diethylenetriamine	CANMET(c)	5	24.8
	HCl + $HClO_4$ + Br_2 to dryness; silver extracted as bromide into MIBK; stripped with conc'd HCl + 1% thiourea to dryness; taken up in HCl	CANMET(d)	5	23.5
	HCl + $HClO_4$ + Br_2 to dryness; silica removed with HF; to dryness; taken up in 20% HCl - 1% diethylenetriamine	CANMET(e)	5	23.4

Table 7a - Analytical results, laboratory means and standard deviations for gold in CH-1

						MEAN	S.D.
CANMET (FA-AA)	0.30	0.32	0.33	0.32	0.33	0.3200	0.0122
LAB- 1 (FA-G)	0.34	0.34	0.34	0.34	0.34	0.3400	0.0000
LAB- 2	0.19	0.19	0.23	0.20	0.21	0.2040	0.0167
LAB- 3 (FA-AA)	0.21	0.23	0.22	0.23	0.21	0.2200	0.0100
LAB- 4 (FA-DCP)	0.185	0.175	0.135	0.175	0.200	0.1740	0.0241
LAB- 5 (COLOR)	0.239	0.220	0.226	0.230	0.226	0.2282	0.0070
LAB- 6 (AA)	0.24	0.28	0.44			0.3200	0.1058
LAB- 7 (FA-DCP)	0.20	0.22	0.22	0.21	0.22	0.2140	0.0089
LAB- 8 (FA-G)	0.309	0.309	0.309	0.274	0.274	0.2950	0.0192
LAB- 9 (FA-AA)	0.206	0.206	0.240	0.206	0.240	0.2196	0.0186
LAB-10	0.21	0.24	0.24	0.21	0.24	0.2280	0.0164
LAB-11 (FA-DCP)	0.196	0.202	0.209	0.223	0.182	0.2024	0.0152
LAB-12 (FA-AA)	0.250	0.250	0.250	0.240	0.240	0.2460	0.0055
LAB-12 (FA-NAA)	0.238	0.207	0.220	0.203	0.210	0.2156	0.0140
LAB-13 (FA-AA)	0.260	0.222	0.232	0.214	0.296	0.2448	0.0335
LAB-14 (FA-AA)	0.207	0.204	0.243	0.265	0.290	0.2418	0.0371
LAB-15 (FA-AA)	0.24	0.27	0.24	0.24	0.24	0.2460	0.0134
LAB-16 (FA-G)	0.252	0.230	0.237	0.235	0.255	0.2418	0.0110

Table 7b - Analytical results, laboratory means and standard deviations for gold in CH-2

						MEAN	S.D.
CANMET (FA-AA)	1.30	1.26	1.23	1.26	1.28	1.2888	0.0380
	1.34	1.33	1.31				
CANMET (FA-AA)	1.20	1.33	1.22	1.30	1.28	1.2660	0.0546
LAB- 1 (FA-G)	1.30	1.30	1.30	1.30	1.30	1.3000	0.0000
LAB- 2	1.38	1.40	1.45	1.41	1.42	1.4120	0.0259
LAB- 3 (FA-AA)	1.40	1.39	1.48	1.49	1.39	1.4300	0.0505
LAB- 4 (FA-DCP)	1.180	1.225	1.270	1.335	1.338	1.2696	0.0689
LAB- 5 (COLOR)	1.44	1.45	1.41	1.48	1.48	1.4520	0.0295
LAB- 6 (AA)	1.17	1.23	1.11			1.1700	0.0600
LAB- 7 (FA-DCP)	1.09	1.22	1.28	1.13	1.20	1.1840	0.0750
LAB- 8 (FA-G)	1.371	1.371	1.406	1.337	1.337	1.3644	0.0288
LAB- 9 (FA-AA)	1.234	1.167	1.029	1.029	1.097	1.1112	0.0893
LAB-10	1.51	1.51	1.44	1.51	1.51	1.4960	0.0313
LAB-11 (FA-DCP)	1.31	1.26	1.35	1.29	1.21	1.2840	0.0527
LAB-12 (FA-AA)	1.45	1.60	1.45	1.40	1.50	1.4800	0.0758
LAB-12 (FA-NAA)	1.248	1.371	1.293	1.376	1.310	1.3196	0.0542
LAB-13 (FA-AA)	1.30	1.40	1.40	1.31	1.38	1.3580	0.0492
LAB-14 (FA-AA)	1.276	1.064	1.740			1.3600	0.3457
LAB-15 (FA-AA)	1.30	1.41	1.44	1.41	1.47	1.4060	0.0643
LAB-16 (FA-G)	1.317	1.317	1.367	1.340	1.325	1.3332	0.0211

Table 7c - Analytical results, laboratory means and standard deviations for iron in CH-2

						MEAN	S.D.
CANMET (TITR)	26.29	26.33	26.27	26.41	26.41	26.3420	0.0657
CANMET (AA)	25.82	25.75	26.23	26.35	25.92	26.0140	0.2625
LAB- 1 (TITR)	25.65	25.67	25.64	25.61	25.65	25.6440	0.0219
LAB- 3 (TITR)	25.52	25.47	25.26	25.59	25.40	25.4480	0.1260
LAB- 4 (XRF)	25.50	25.40	25.58	25.62	25.60	25.5400	0.0906
*LAB- 6 (ICP)	26.22	26.94	27.18	26.52	26.58	26.4300	0.4012
	26.56	25.96	26.04	26.20	26.10		
LAB- 7 (TITR)	25.51	25.48	25.64	25.34	25.49	25.4920	0.1066
LAB- 8 (TITR)	25.7	25.7	25.7	25.7	25.8	25.7200	0.0447
LAB- 9 (AA)	25.6	25.3	25.6	25.4	25.3	25.4400	0.1517
*LAB-10	28.4	28.0	27.8	28.0	27.6	27.9600	0.2966
LAB-11 (AA)	27.2	27.2	27.0	27.2	27.4	27.2000	0.1414
LAB-12 (TITR)	25.43	25.46	25.40	25.46	25.41	25.4320	0.0277
LAB-13 (TITR)	25.29	25.34	25.34	25.34	25.29	25.3357	0.0378
	25.35	25.40					
*LAB-13 (ICP)	27.97	27.83	28.03			27.9433	0.1026
LAB-14 (AA)	24.97	24.80	24.83	25.01	25.02	24.9260	0.1036
LAB-15 (TITR)	25.39	25.44	25.49	25.44	25.49	25.4500	0.0418
*LAB-16 (ICP)	24.1	24.1	24.1	23.9	24.0	24.0400	0.0894

*Outlying set

Table 7d - Analytical results, laboratory means and standard deviations for sulphur in CH-2

						MEAN	S.D.
CANMET (GRAV)	17.81	17.79	17.79	17.81	17.73	17.7860	0.0329
CANMET (GRAV)	17.48	17.53	17.51	17.51	17.57	17.5200	0.0332
CANMET (GRAV)	17.90	17.88	17.73	17.89	17.78	17.7390	0.1311
	17.79	17.57	17.57	17.69	17.59		
LAB- 2 (GRAV)	17.54	17.57	17.52	17.58	17.58	17.5580	0.0268
LAB- 3 (COMB)	16.71	16.79	16.72	16.94	16.86	16.8040	0.0971
LAB- 4 (XRF)	17.08	16.88	17.12	17.16	17.00	17.0480	0.1110
LAB- 6 (COMB)	17.92	17.40	17.65	17.83	17.93	17.3780	0.4855
	17.29	16.44	17.36	16.84	17.12		
LAB- 7 (COMB)	17.7	17.5	17.3	17.1	17.2	17.3600	0.2408
LAB- 8 (GRAV)	17.08	17.05	17.06	17.08	17.07	17.0680	0.0130
LAB- 9 (GRAV)	17.1	17.2	17.2	17.1	17.2	17.1600	0.0548
LAB-11 (COMB)	17.5	17.3	17.2	17.4	17.6	17.4000	0.1581
LAB-12 (GRAV)	17.20	17.25	17.26	17.24	17.23	17.2360	0.0230
LAB-13 (COMB)	17.8	18.3	18.2	18.8	18.2	18.2600	0.3578
*LAB-14 (COMB)	15.07	14.95	14.98	15.17	15.10	15.0540	0.0896
LAB-15 (GRAV)	17.64	17.66	17.49	17.39	17.57	17.5500	0.1116
LAB-16 (GRAV)	16.89	17.00	17.09	16.78	16.88	16.9280	0.1195

*Outlying set

Table 7e - Analytical results, laboratory means and standard deviations for copper in CH-2

						MEAN	S.D.
CANMET (AA)	2.21	2.23	2.22	2.22	2.23	2.2220	0.0084
LAB- 1 (AA)	2.52	2.50	2.52	2.50	2.50	2.5080	0.0110
LAB- 3 (AA)	2.45	2.46	2.46	2.46	2.46	2.4580	0.0045
LAB- 4 (XRF)	2.538	2.526	2.526	2.556	2.548	2.5388	0.0133
LAB- 6 (ICP)	2.40	2.44	2.41	2.43	2.49	2.4490	0.0448
	2.44	2.53	2.48	2.48	2.39		
LAB- 7 (AA)	2.44	2.44	2.48	2.46	2.46	2.4560	0.0167
LAB- 8 (TITR)	2.47	2.52	2.51	2.49	2.50	2.4980	0.0192
LAB- 9 (AA)	2.37	2.36	2.37	2.38	2.39	2.3740	0.0114
LAB-10	2.27	2.48	2.26	2.27	2.15	2.2860	0.1197
LAB-11 (AA)	2.51	2.50	2.49	2.50	2.49	2.4980	0.0084
LAB-12 (AA)	2.51	2.50	2.50	2.51	2.51	2.5060	0.0055
LAB-13 (AA)	2.39	2.37	2.38	2.38	2.38	2.3800	0.0071
*LAB-14 (AA)	2.13	2.09	2.26	2.21	2.25	2.1880	0.0750
LAB-15 (TITR)	2.39	2.41	2.40	2.39	2.41	2.4000	0.0100
LAB-15 (AA)	2.40	2.44	2.44	2.44	2.40	2.4240	0.0219
LAB-16 (ICP)	2.42	2.46	2.42	2.45	2.45	2.4400	0.0187

*Outlying set

Table 7f - Analytical results, laboratory means and standard deviations for silver in CH-2

						MEAN	S.D.
CANMET (FA-AA)	24.00	23.83	23.75	23.83	23.75	23.8320	0.1021
CANMET (FA-AA)	26.33	26.58	26.33	25.92	25.83	26.1980	0.3136
CANMET (AA)	24.4	25.4	25.3	24.6	24.2	24.7800	0.5404
CANMET (AA)	23.5	24.3	24.1	23.2	22.3	23.4800	0.7950
CANMET (AA)	23.2	23.6	23.2	23.3	23.6	23.3800	0.2049
LAB- 1 (FA-G)	24.	24.	25.	25.	25.	24.6000	0.5477
LAB- 3 (FA-G)	24.51	24.71	24.76	24.66	24.64	24.6560	0.0940
*LAB- 4 (FA-G)	17.2	16.5	18.2			17.3000	0.8544
LAB- 6 (FA-G)	23.2	23.8	23.4			23.4667	0.3055
LAB- 7 (FA-AA)	24.2	24.0	24.1	24.1	24.1	24.1000	0.0707
LAB- 8 (AA)	24.0	24.3	24.7	24.7	24.3	24.4000	0.3000
LAB- 9 (AA)	24.	25.	24.	24.	24.	24.2000	0.4472
*LAB-10	21.1	20.9	20.3	21.5	21.1	20.9800	0.4382
LAB-11 (FA-AA)	23.7	23.7	23.7	23.8	23.5	23.6800	0.1095
LAB-12 (AA)	25.0	25.0	25.0	25.0	25.0	25.0000	0.0000
*LAB-13 (AA)	21.5	21.3	21.8	21.5	21.8	21.5800	0.2168
LAB-14 (AA)	20.2	20.7	20.2	20.6	20.9	20.5200	0.3114
*LAB-15 (FA-G)	24.3	26.4	24.7	24.7	25.4	25.1000	0.8276
LAB-16 (AA)	22.	22.	23.	23.	22.	22.4000	0.5477

*Outlying set

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

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

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 (7).

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

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 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 to the within-laboratory standard deviation, σ_B/σ_A, where

$$\sigma_B = \sqrt{\left[\sum_i^k \left(\bar{x}_i. - \left(\sum_i^k \bar{x}_i.\right)/k\right)\right]^2 \Big/ k-1}$$

is a measure of the quality of the certification data for the reference materials of CCRMP (8). 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 the overall mean, σ_B/σ_A and RP for CH-1 and CH-2 are reported in Table 8.

Table 8 - Values of the overall mean, σ_B/σ_A and RP

Material	Element	Mean	σ_B/σ_A	RP
CH-1	Au	0.24 µg/g	2.1	0.0
CH-2	Fe	25.7%	2.2	41
	S	17.4%	2.8	6.3
	Cu	2.43%	2.9	31
	Ag	23.7 µg/g	2.4	21
	Au	1.33 µg/g	1.6	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. No attempt was made for any element to detect a statistically significant difference between the overall means of the more popular methods because there was generally not a sufficient number to warrant the test.

Table 8 indicates that only gold in both materials and sulphur in CH-2 were sufficiently well characterized by the interlaboratory program to be assigned certified status. The histograms for all elements are shown in Figs. 1a-1f.

COPPER

An examination of the results on the basis of chemical or methodological considerations indicated that a further rejection of results was not warranted.

IRON

A comparison of the quality of results by methodology indicated that the ICP-AES procedures were least desirable because of either relatively poor within-laboratory or between-laboratories agreement. CCRMP therefore considered it justifiable to reject these three sets of results and to recalculate the appropriate statistical parameters. As a consequence, there was no change in the overall mean but an improvement in its uncertainty.

Future users of CH-2 as a reference material for ICP-AES are advised to do so only with great care.

SILVER

An examination of the results illustrated that one set was clearly an outlier (Laboratory 4). The overall mean of results for which a fire assay concentration step was used was 24.45 µg/g Ag whereas that for which a multi-acid decomposition was used was 23.07 µg/g Ag. For the latter, there are three sets out of the 10 which are appreciably lower than the remaining seven. If these three are rejected, the seven have an overall mean of 23.95 µg/g Ag, which is in good agreement with the fire assay results. CCRMP therefore decided to recalculate the mean value and associated statistical parameters after rejecting the results from Laboratories 4, 10, 13 and 14. The new overall mean is 24.2 µg/g.

STATUS OF IRON, COPPER AND SILVER

The initial mean value for copper and recalculated means for iron and silver cannot be assigned certified value status because of the magnitude of their uncertainty or the intercession in their calculation. These elements are, however, sufficiently well characterized to be assigned recommended value status.

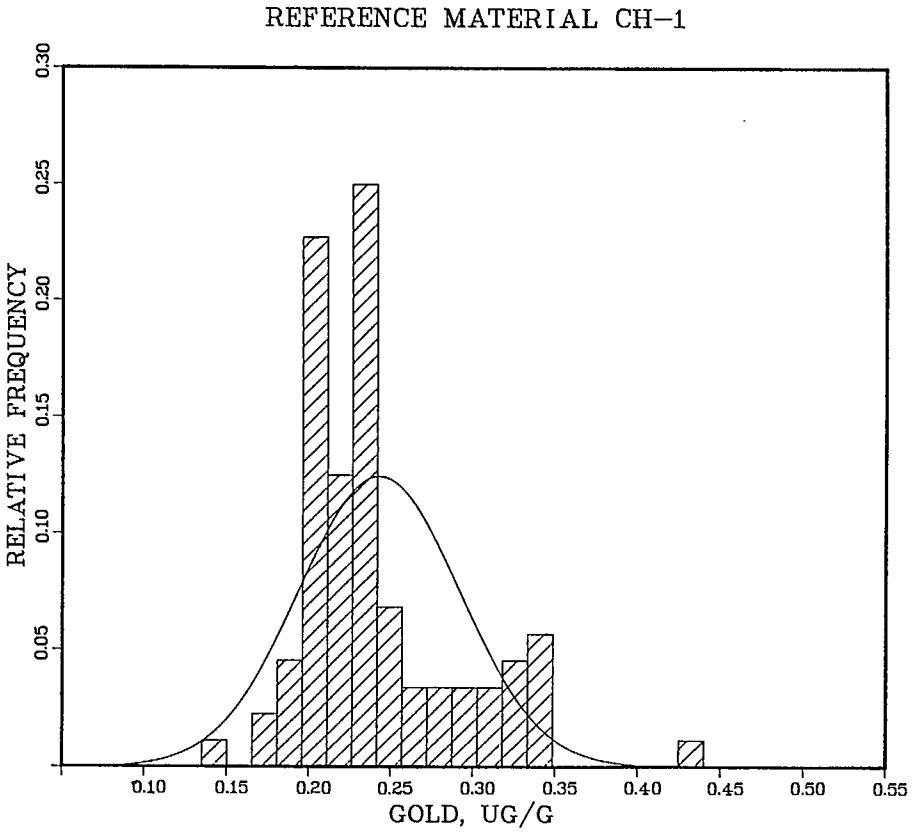

FIG. 1a — Histogram for gold in CH-1

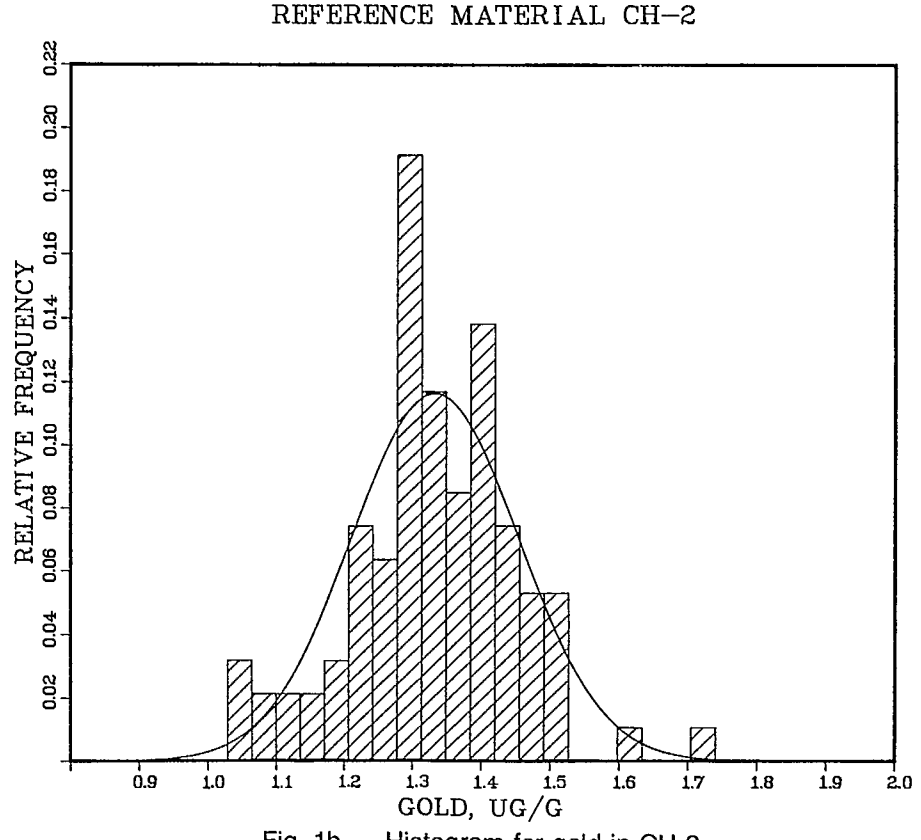

Fig. 1b — Histogram for gold in CH-2

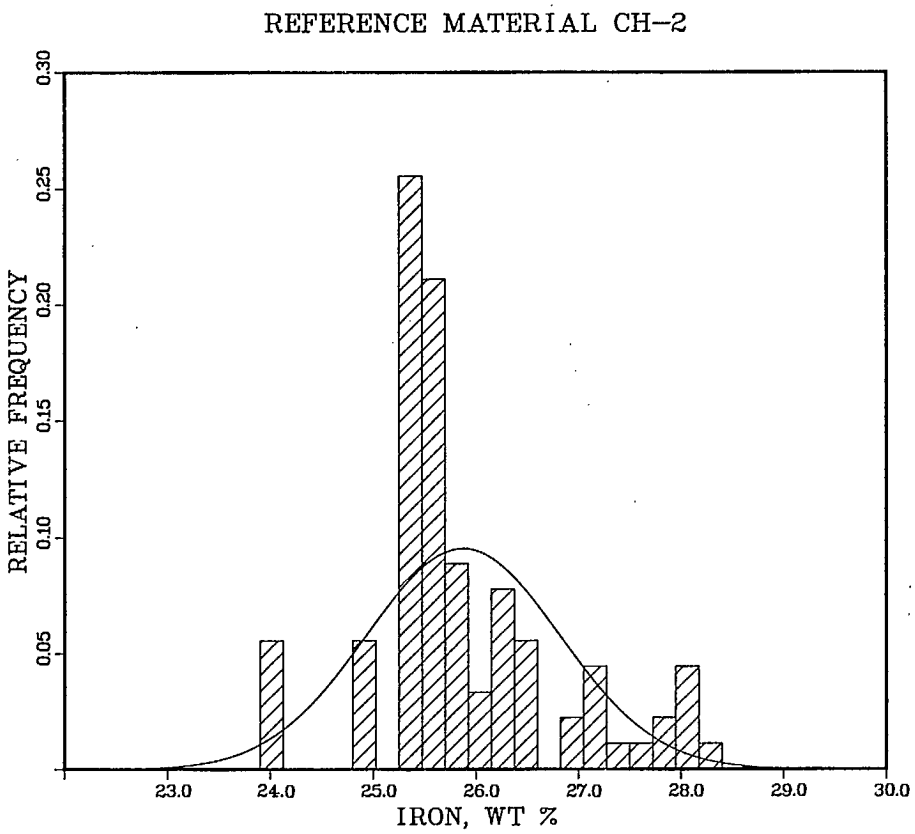

Fig. 1c — Histogram for iron in CH-2

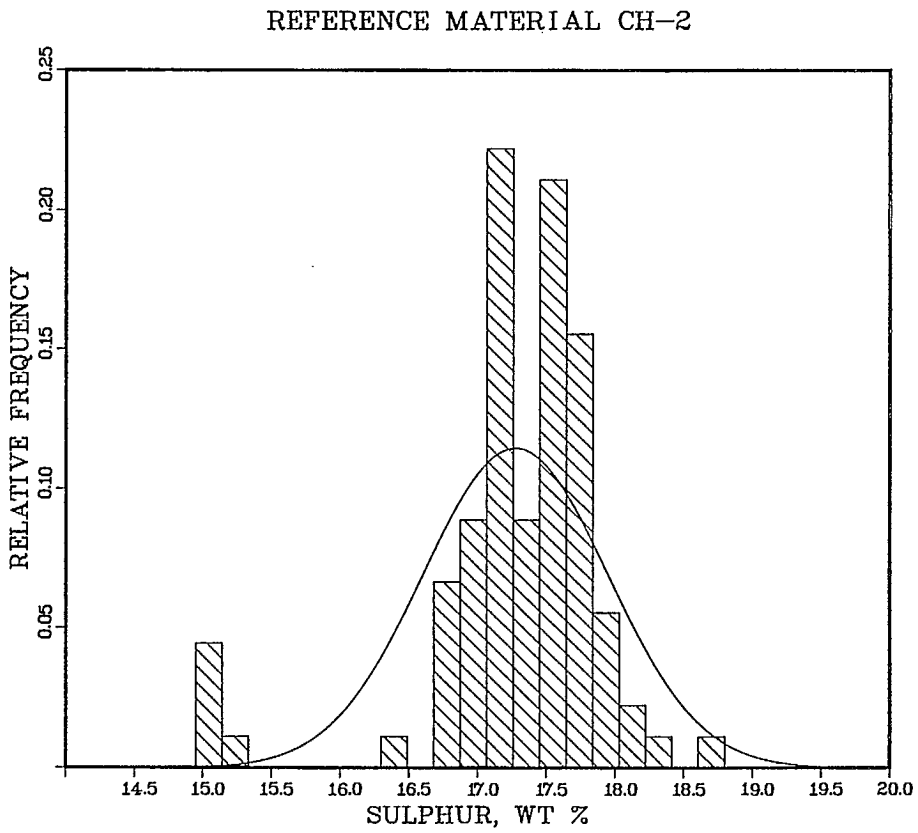

Fig. 1d — Histogram for sulphur in CH-2

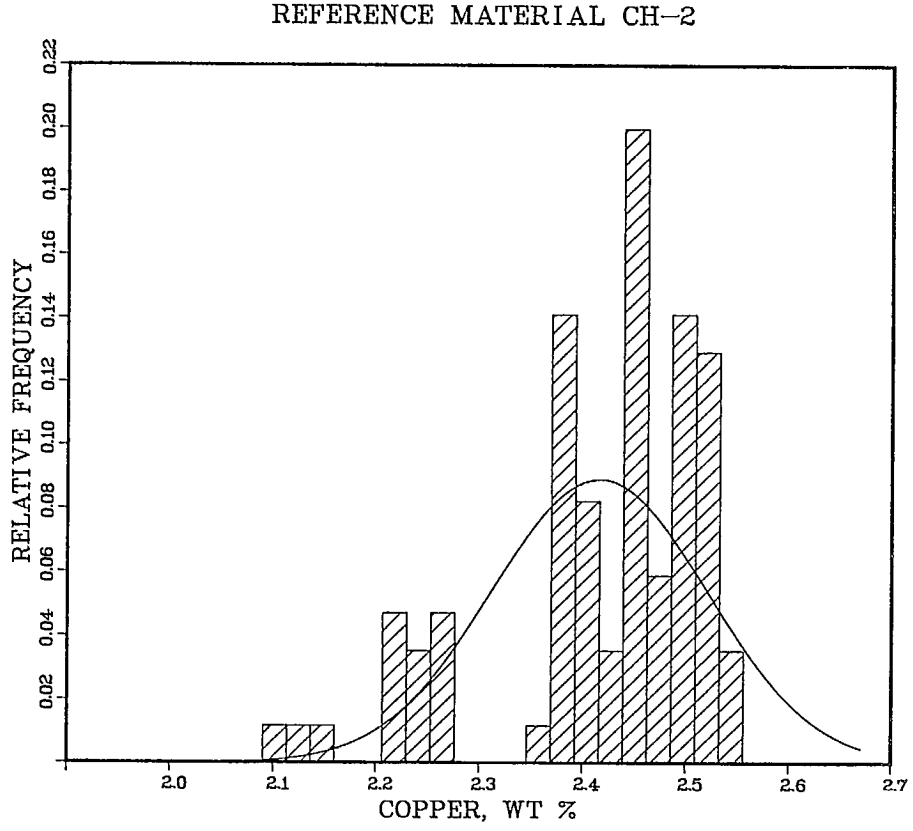

Fig. 1e — Histogram for copper in CH-2

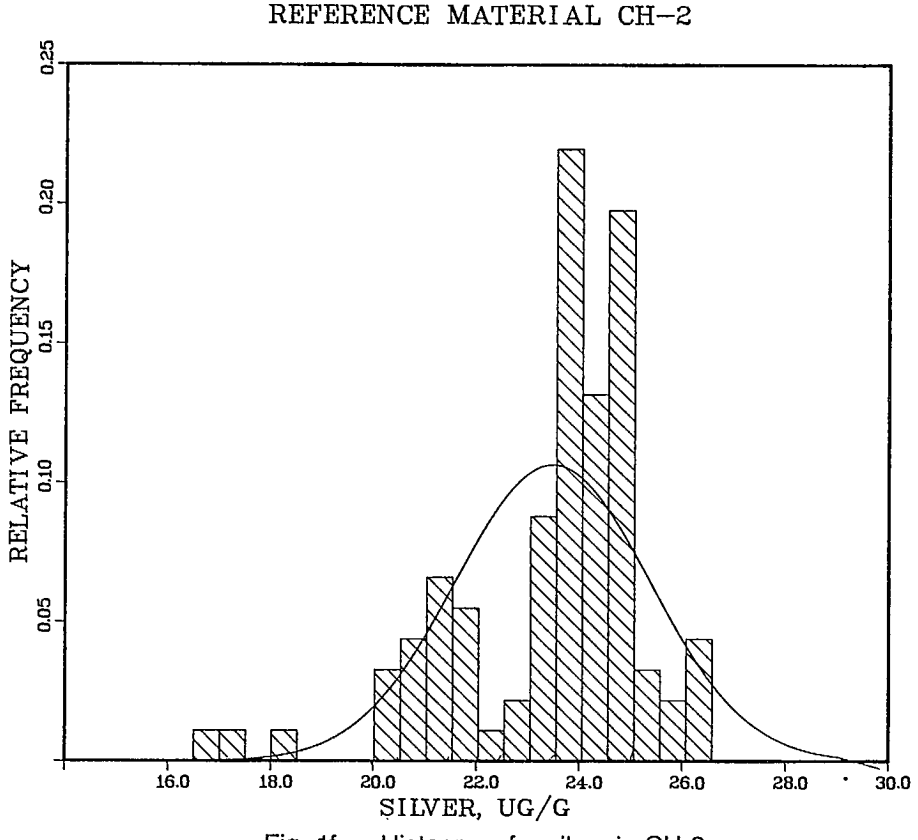

Fig. 1f — Histogram for silver in CH-2

PROCEDURE FOR CHECKING AN ANALYTICAL METHOD USING CH-1 AND CH-2

Perform n replicate determinations (from separate sub-samples) using the analytical method that is being tested. It is suggested that n = 10 for a one-time investigation. For a periodic check of accuracy of an analytical method, n = 2 for each period is sufficient; however, the total number of replicates should be greater than 10.

Compute the following statistics

$$\bar{X} = \sum_{i=1}^{n} X_i/n \text{ - mean}$$

$$S_W = \sqrt{\sum_{i=1}^{n} (X_i - \bar{X})^2 \Big/ n-1} \text{ - estimated within-laboratory standard deviation i.e., precision of the method}$$

n is the number of analytical results remaining after rejection of outliers.

a) Verification of precision

Compute

$$F = \frac{(S_W)^2}{(S_{rc})^2}$$ where the value of S_{rc} is the within-laboratories standard deviation for CH-1 and CH-2.

Compare F against $F_o = F_{0.95, n-1, DF_c}$ which is obtainable from any statistics book. If the degree of freedom DF_c is not given in the certificate, use $DF_c = 60$.

$F \leq F_o$: the analytical method is sufficiently precise

$F > F_o$: the analytical method is not as precise as those used for certification of RM

b) Verification of accuracy

$$\text{If } \left| \bar{X} - A_c \right| \leq 2\, S_{Lc}$$

then the analytical method has sufficient accuracy. Otherwise, it is not considered to be as accurate as the laboratories accepted in the certification program.

Values of A_c are presented as the "overall mean" in Tables 4 and 5 and values of S_{rc} and the between-laboratories standard deviation, S_{Lc}, are reported in Table 9.

Table 9 - Values of S_{rc} and S_{Lc} for CH-1 and CH-2

Material	Element	S_{rc}	S_{Lc}
CH-1	Au	0.025 µg/g	0.043 µg/g
CH-2	Fe	0.18%	0.71%
	S	0.22%	0.35%
	Cu	0.036%	0.083%
	Ag	0.43 µg/g	0.89 µg/g
	Au	0.024 µg/g	0.097 µg/g

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APPENDIX A
CONFIRMATION OF HOMOGENEITY

CONFIRMATION OF HOMOGENEITY

The homogeneity of CH-2 and of CH-1 by inference was confirmed at CANMET by analyzing 15 bottles for gold in triplicate using a combined fire assay-atomic absorption procedure (A10). The stock was divided into 14 lots of 38 bottles and a 15th lot of 32 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 38. The results are shown in Table A10.

Table A10 - Confirmation of homogeneity of CH-2 for gold

	Au (µg/g)			
Bottle No.	Individual			Mean
10	1.45	1.30	1.30	1.350
48	1.45	1.48	1.37	1.433
85	1.31	1.33	1.37	1.337
123	1.37	1.35	1.27	1.330
161	1.55	1.33	1.40	1.427
199	1.40	1.27	1.30	1.323
236	1.27	1.23	1.30	1.267
274	1.40	1.43	1.37	1.400
312	1.33	1.40	1.51	1.413
349	1.40	1.27	1.27	1.313
387	1.47	1.27	1.40	1.380
425	1.27	1.40	1.43	1.367
462	1.27	1.29	1.27	1.277
500	1.47	1.43	1.33	1.410
538	1.40	1.31	1.27	1.327
			Overall mean is	1.357

Analysis of variance

Source of variation	Degrees of freedom	Sum of squares	Mean squares
Between sets	14	0.11670	8.3356×10^{-3}
Within sets	30	0.15007	5.0022×10^{-3}
Total	44	0.26676	

Calculated F statistic = 1.666

F.95(14,30) = 2.037

Null hypothesis of no difference between bottles is accepted for gold

A one-way analysis of variance technique was used to assess the homogeneity (8). 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 gold. The within-bottle standard deviation, σ = 0.0707 µg/g Au is acceptable at this concentration but was judged by CCRMP to be too large, particularly in view of the within-bottle precision found for CH-1. It was concluded that the poorer precision observed for CH-2 was due to the presence of larger particles of native gold from the admixed MA-1. Consequently, CH-2 was screened and only the material passing 46 µm was retained for use as a reference material. Subsequent analyses of CH-2 indicate a within-bottle precision that is more acceptable on chemical grounds.

REFERENCE

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APPENDIX B
PARTICIPATING LABORATORIES

PARTICIPATING LABORATORIES

Atlantic Analytical Services Ltd.
Saint John, New Brunswick
W. Wilson

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

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

CANMET, Mineral Sciences Laboratories
Energy, Mines and Resources Canada
Ottawa, Ontario

Chemex Labs Alberta Ltd.
Calgary, Alberta
R.B. Pang

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

Hudson Bay Mining and Smelting Company Ltd.
Flin Flon, Manitoba
D. Allen

Inco Ltd.
J. Roy Gordon Research Laboratory
Mississauga, Ontario
V.J. Zatka

Inco Ltd.
Process Technology
Copper Cliff, Ontario
J. Bozic

Kamloops Research and Assay Laboratory Ltd.
Kamloops, British Columbia
D. Blundell

Kidd Creek Mines Ltd.
Timmins, Ontario
J.M. Labreque

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

MINTEK
Randburg, South Africa
E.J. Ring

Noranda Mines Ltd.
Noranda, Quebec
M. Bédard

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

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

Technical Services Laboratories
Mississauga, Ontario
A.H. Debnam

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