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MA-2: A CERTIFIED GOLD REFERENCE ORE

H.F. STEGER AND W.S. BOWMAN

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MA-2: A CERTIFIED GOLD REFERENCE ORE

by

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

SYNOPSIS

A 341-kg sample of a gold ore MA-2 from Kirkland Lake, Ontario was prepared as a compositional reference material. MA-2 was ground to minus 74 μm, blended in one lot and bottled in 400-g units. Its homogeneity was confirmed by a combined fire assay-atomic absorption procedure for gold.

In a "free choice" analytical program, 22 laboratories contributed results for gold in one bottle of MA-2. Based on a statistical analysis of the data, a recommended value was assigned for Au at 1.86 μg/g or 0.0543 oz/ton. A value for silver is provided for information purposes.

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

MA-2: MINERAI DE REFERENCE CERTIFIE D'OR

par

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

SYNOPSIS

Un échantillon de 341 kg d'un minerai d'or, MA-2, provenant de Kirkland Lake en Ontario, a été préparé comme matériau de référence de composition. Le MA-2 a été broyé à une granulométrie de moins 74 µm, mélangé en lot de minerai et embouteillé en unités de 400 g. L'homogénéité de MA-2 a été confirmée pour l'or par une méthode analytique qui combine des techniques pyrognostique et d'absorption atomique.

En vertu d'un programme analytique de "libre choix", 22 laboratoires ont fourni des résultats sur un flacon de MA-2 pour l'or. L'analyse statistique des donnés fut utilisée pour assigner une valeur recommandée de 1,86 µg/g ou 0,0543 oz/tonne pour l'or. Une valeur pour l'argent est donnée à titre de renseignements.

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Note: Avec la collaboration de d'autres membres du personnel des Laboratoires des sciences minérales.

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INTRODUCTION

The preparation, characterization and certification of gold ore MA-2 is a further contribution by 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 reference materials certified by CCRMP are described in a catalogue available from CANMET, Energy, Mines and Resources Canada, Ottawa (1).

MA-2 was chosen because of three independent requests made to CCRMP in 1980 for a relatively simple siliceous ore containing gold at 1-2 µg/g. Certified gold ore MA-1 available from CCRMP is too high in gold at 17.8 µg to serve as a useful reference material in the analysis of relatively low-grade gold deposits currently of interest (2).

An interlaboratory program was conducted to obtain results for gold from 22 commercial, industrial and government laboratories using analytical methods of their choice. The results should therefore be indicative of the "state-of-the-art" of the analysis for gold.

NATURE AND PREPARATION

The raw material for MA-2 was donated to CCRMP in July 1980 by Willroy Mines Limited and is typical of the waste rock of the Macassa mine at Kirkland Lake, Ontario. The geology and mineralogy of the gold ores of the Kirkland Lake District are well known and have been described conveniently in a field excursion guidebook of the Canadian Institute of Mining and Metallurgy (3,4).

The gold in MA-2 exists mainly as native metal, containing approximately 7 wt % silver; it occurs as inclusions both in gangue and in pyrite, the principal sulphide mineral. Some calaverite ($AuTe_2$) is also present which occurs only as inclusions in some pyrite grains. The gangue constituents of the ore are, in decreasing order of abundance: quartz, feldspar, dolomite, muscovite and chlorite. Other minerals present in trace amounts are: chalcopyrite, sphalerite, hematite, magnetite, altaite (PbTe) and melonite ($NiTe_2$).

MA-2 was dry-ground in February 1981 to pass a 74-µm screen. The powdered ore weighing approximately 341 kg was tumbled in a 570-L conical blender for 20 h and bottled in 400-g units. MA-2 was found to be sufficiently homogeneous for gold by a combined fire assay-atomic absorption procedure to qualify as a reference material (5). Results of the confirmation of the homogeneity of MA-2 are summarized in Appendix A.

The approximate chemical composition and particle size analysis are given in Tables 1 and 2.

Table 1 - Approximate chemical composition of MA-2

Element	wt %*
Si	24.0
Al	8.6
K	4.9
Fe	4.6
Ca	3.7
Na	2.6
C (Total)	1.6
S	0.54
L.O.J.	6.0
H_2O (105°C)	0.1

*Mean of duplicate determinations

Table 2 - Particle size analysis of MA-2 (wet screen)

Size of fraction (µm)	wt %*
-104 + 74	0.0
- 74 + 55	0.5
- 55 + 37	17.1
- 37	82.4

*Mean of duplicate determinations

INTERLABORATORY PROGRAM FOR CERTIFICATION

Participating laboratories in the certification program for MA-2 are listed alphabetically in Appendix B. Each was assigned a code number which bears no relation to its alphabetical order.

Each laboratory was requested to contribute five replicate results for gold on one bottle of MA-2 by a method of its choice and to report the results on an "as is" basis. Some laboratories, however, deviated from the request for five results or contributed results by more than one method. In the latter instance, each set was considered statistically independent.

The results of CANMET's assessment of the homogeneity of MA-2 were included in the program. However, to avoid any biasing of the statistics, only five results, chosen at random out of the 45 available, were used in subsequent calculations. The recommended value for gold is given in Table 3. Analytical and methodological information is presented in Tables 4 and 5. Analytical results for silver are given in Table 6 for convenience.

Table 3 - Recommended value and associated statistical parameters for gold in MA-2

No. of laboratories	20
No. of results	125
Mean	1.86 µg/g; 0.0543 oz/ton
95% confidence limits,	
low	1.81 µg/g; 0.0527 oz/ton
high	1.92 µg/g; 0.0560 oz/ton
σ_A*	0.07 µg/g; 0.0020 oz/ton

*Average within-laboratory standard deviation

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

Laboratory 17 analyzed its bottle of MA-2 in triplicate on consecutive days. The discrepancy between the two sets of results suggests a methodological problem; therefore they were excluded from further consideration. Both sets of results from Laboratory 3 and the set obtained by atomic absorption by Laboratory 7 were rejected

Table 4 - Summary of analytical methods for gold (outliers excluded)

Method	Decomposition, separation, etc	Laboratory	n	$\bar{x}$ (µg/g)
Fire assay - atomic absorption	Lead button collection; dissolution in HNO_3 + HCl	CANMET, 1b, 5, 8, 9, 13b	34	1.81
	Lead button collection; cupellation to silver bead; dissolution in HNO_3 + HCl	10, 12, 19, 22	20	1.80
	Sample roasted; tin button collection; tin volatilized	21b	2	1.68
Fire assay - gravimetry	Lead button collection; HNO_3 treatment	6, 13a, 14, 15a, 20	30	1.87
	Sample roasted; silver added; lead button collection; HNO_3 treatment	18	5	1.89
Fire assay - ICP-AES	Lead button collection; aqua regia to dryness; taken up in 30% HCl	16	5	2.02
Fire assay - emission spectro.	Sample roasted; lead button collection and cupellation; Method ASTM E-400-71	21a	5	1.68
Atomic absorption	Aqua regia; gold extracted into MIBK	4b, 15b	10	1.84
	HCl + HBr + Br_2; gold extracted into MIBK	2, 4a	10	2.00
Colorimetry	Sample roasted at 600°C; digested in aqua regia; gold extracted into toluene as Thio-Michler's ketone complex	7a	5	1.88

Table 5 - Analytical results, laboratory means and standard deviations for gold

			wt %				Mean	S.D.
Lab 1	(FA-G)*	1.54	1.47	1.54	1.65	1.37	1.514	.103
Lab 1	(FA-AA)	1.68	1.61	1.65	1.71		1.662	.042
Lab 2	(AA)	2.13	2.34	2.14	2.08	2.10	2.158	.104
Lab 3	(FA-AA)*	1.70	1.70	2.10	2.10	2.40	2.000	.300
Lab 3	(COLOR)*	1.70	1.70	2.10	2.40	2.10	2.000	.300
Lab 4	(AA)	1.88	1.89	1.99	1.96	1.93	1.930	.046
Lab 4	(AA)	1.75	1.80	1.72	2.15†	1.75	1.834	.179
Lab 5	(FA-AA)	1.84	1.89	1.86	1.82	1.89	1.860	.030
Lab 6	(FA-G)	1.89	1.89	1.89	1.89	1.89	1.890	.000
Lab 7	(COLOR)	1.92	1.78	1.84	1.82	2.02	1.876	.095
Lab 7	(AA)*	1.86	1.70	1.72	1.60	2.24	1.824	.250
Lab 8	(FA-AA)	1.70	1.86	1.74	1.79	1.64	1.746	.084
Lab 9	(FA-AA)	1.85	1.85	1.71	1.82	1.71	1.810	.067
		1.85	1.82	1.75	1.82	1.92		
Lab 10	(FA-AA)	1.71	1.75	1.78	1.71	1.75	1.740	.030
Lab 12	(FA-AA)	1.88	1.98	1.96	1.81	1.96	1.918	.071
Lab 13	(FA-G)	1.92	1.96	1.89	1.89	1.92	1.916	.028
Lab 13	(FA-AA)	2.05	1.90	1.95	1.80	1.90	1.92	.090
Lab 14	(FA-G)	1.85	1.89	1.65	1.68	1.78	1.800	.105
		1.68	1.78	1.82	1.95	1.92		
Lab 15	(FA-G)	2.13	1.89	1.92	1.89	1.85	1.936	.111
Lab 15	(AA)	1.68	1.78	1.78	1.78	1.68	1.740	.054
Lab 16	(FA-ES)	1.92	1.89	2.13	2.19	1.95	2.016	.134
Lab 17	(FA-AA)*	1.78	1.86	1.75	1.87	2.19	1.905	.161
		1.98						
Lab 18	(FA-G)	1.81	1.906	1.875	1.875	1.978	1.888	.060
Lab 19	(FA-AA)	1.83	1.92	1.90	1.80	1.91	1.892	.053
Lab 20	(FA-G)	1.78	2.02	1.95	1.82	1.95	1.904	.100
Lab 21	(FA-ES)	1.71	1.65	1.75	1.68	1.61	1.680	.053
Lab 21	(FA-AA)	1.74	1.62				1.680	.084
Lab 22	(FA-AA)	2.17	2.08	2.26	2.10	2.27	2.176	.087
CANMET	(FA-AA)	1.82	1.87	1.73	1.78	1.73	1.786	.060

*Outlying set

†Outlying results

Table 6 - Analytical results for silver in MA-2

Laboratory	Details	No. of results	Mean µg/g
CANMET	Fire Assay; HNO_3 dissolution; atomic absorption finish	9	0.65
16	Fire Assay; aqua regia dissolution; ICP - emission spectrometric finish	5	0.51

because of high variance. One set of results was rejected because its mean differed from the overall mean of gold by more than twice the standard deviation.

ESTIMATION OF CONSENSUS VALUE AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and its 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 (6)

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

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 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 with 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 $\bar{x}..$:

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

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

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

is a measure of the quality of the certification data for the reference materials of CCRMP (7). 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%.

For MA-2, a value of 1.94 for σ_B/σ_A was obtained for all results. Therefore, RP = 0% and this reference material can be certified for its gold content. The calculation of σ_B/σ_A did not take into account the four sets of results which were rejected because of methodological cause or high variance. Their inclusion would have lowered the value of σ_B/σ_A appreciably.

DISCUSSION

Table 4 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. As expected, the fire assay pre-concentration procedure followed by either a gravimetric or atomic absorption finish predominated. An attempt to detect a statistical significance between the overall means of the fire assay-gravimetric and the fire assay-atomic absorption procedures was not made because of the overlap in the respective 95% confidence intervals.

Figure 1 illustrates the plot of the relative frequency against the gold interval for all results. The slightly skewed distribution observed is frequently obtained in interlaboratory programs.

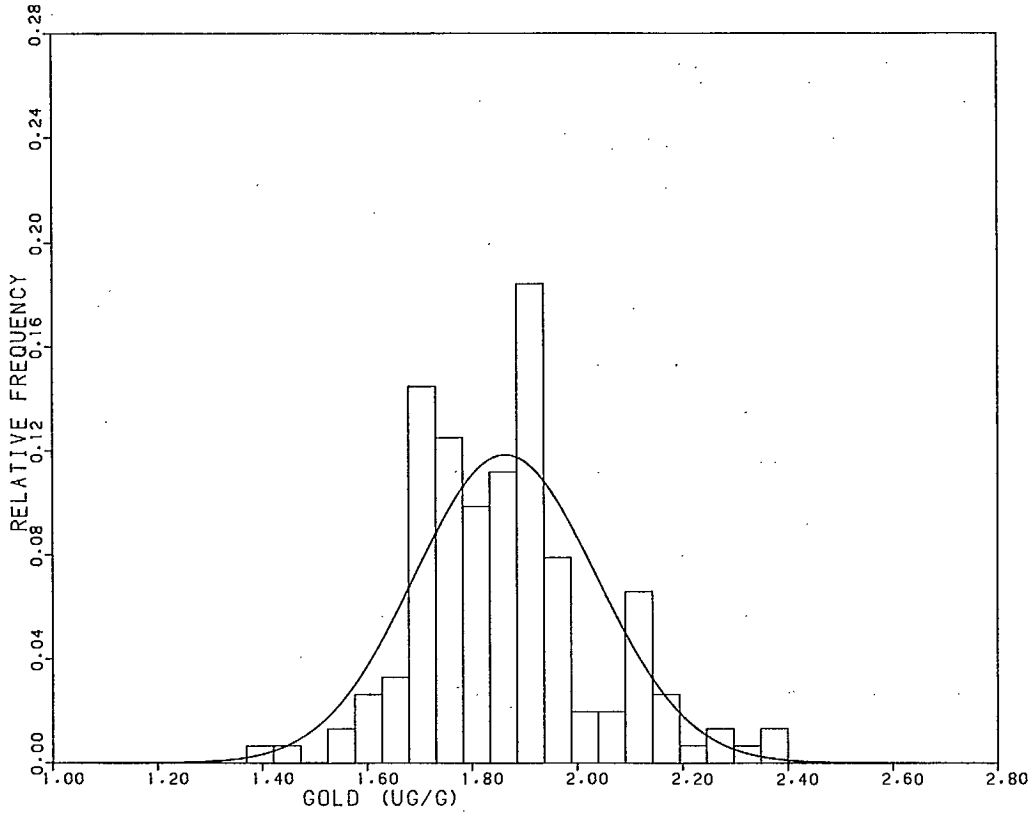

Fig. 1 - Reference ore MA-2

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APPENDIX A

Confirmation of Homogeneity

HOMOGENEITY OF MA-2

The homogeneity of MA-2 was confirmed at CANMET by analyzing 15 bottles for gold in triplicate using a combined fire assay-atomic absorption procedure (5). These bottles were selected as follows. The stock of 840 bottles was divided into 15 lots of 56 bottles. The code numbers of the first bottle was selected at random out of the first lot. The code numbers of the other 14 bottles were given by the code number of the preceding bottle plus 56. The results of the analysis are shown in Table 7.

A one-way analysis of variance technique was used to assess the homogeneity (6). 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.

Table 7 - Confirmation of homogeneity of MA-2

	Au µg/g			
Bottle	Individual			Mean
32	1.82	1.77	1.72	1.77
88	1.78	1.80	1.69	1.76
144	1.72	1.75	1.77	1.75
200	1.70	1.87	1.72	1.76
256	1.72	1.75	1.68	1.72
312	1.67	1.73	1.82	1.74
368	1.70	1.80	1.73	1.74
424	1.82	1.82	1.77	1.80
480	1.82	1.72	1.68	1.74
536	1.78	1.82	1.78	1.79
592	1.72	1.69	1.68	1.70
648	1.78	1.72	1.78	1.76
704	1.72	1.73	1.72	1.72
760	1.73	1.78	1.70	1.74
795	1.72	1.80	1.70	1.74
		Overall mean:		1.749

Analysis of variance table for gold

Source of variation	Degrees of freedom	Mean square
Between bottles	14	2.275×10^{-3}
Within bottles	30	2.496×10^{-3}
Total	44	

Calculated F statistic = 0.9117
F.95 (14, 30) = 2.0374

Null hypothesis of no difference between bottles is accepted.

APPENDIX B

Participating Laboratories

Atlantic Analytical Services Ltd., St. John, New Brunswick.
A. Graham

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

British Columbia Department of Energy, Mines and Petroleum Resources, Victoria, British Columbia.
W.M. Johnson

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

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

Dome Mines Limited, Assay Office, South Porcupine, Ontario.
W. Clifford

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

Falconbridge Nickel Mines Ltd., Sudbury Division, Falconbridge, Ontario.
R.J. Wiseman

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

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

Inco Ltd., J. Roy Gordon Research Laboratory, Sheridan Park, Ontario.
St. J.H. Blakely

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

National Institute for Metallurgy, Randburg, South Africa.
E.J. Ring

Noranda Mines Ltd., Noranda, Quebec.
M.G. Caris

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

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

Sherritt Gordon Mines Ltd., Mining Division, Lynn Lake, Manitoba.
R. Klassen

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

Swastika Laboratories Limited, Swastika, Ontario.
G. Lebel

U.S. Bureau of Mines, Reno Metallurgy Research Center, Reno, Nevada.
K.G. Broadhead