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Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

REVISION OF RECOMMENDED VALUES FOR REFERENCE ORES MP-1 AND KC-1

G.H. Faye and W.S. Bowman

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FOREWORD

The work described in this report contributes to the Canadian Certified Reference Materials Project (CCRMP). The CCRMP in turn contributes to the Mineral Technology Development Activity (Utilization Sub-Activity) of CANMET's Minerals Research Program by producing mineralogical and metallurgical reference materials (RM's) for use in industrial, commercial and government laboratories in Canada.

The CCRMP was initiated in the early seventies in response to a demand from such laboratories for RM's that were not then available. Many of these laboratories now willingly contribute analytical information which is ultimately used in the CCRMP to certify RM's.

Now that a relatively large number of reference ores and related materials have been made available, they are being used in a "feed-back" fashion to critically assess analytical methods that are essential for quality-control and research in Canadian enterprises.

R.L. Cunningham
Chief

AVANT-PROPOS

Le travail qui est décrit dans le présent rapport apporte une contribution au Programme canadien des matériaux de référence certifiés (CCRMP). De son côté, le CCRMP collabore aux travaux de l'Activité de la mise au point des techniques minérales (Sous-activité de l'utilisation) du Programme de recherche sur les minéraux de CANMET en normalisant des matériaux minéralogiques et métallurgiques pour les différents laboratoires industriels, commerciaux et gouvernementaux au Canada.

Le CCRMP a été créé au début des années '70 pour répondre à la demande formulée par les différents laboratoires qui voulaient de tels matériaux de référence qui n'étaient pas disponibles auparavant. Ainsi, plusieurs laboratoires effectuent maintenant des travaux analytiques et par la suite léguent volontairement les informations nécessaires au CCRMP pour certifier des matériaux de référence.

Maintenant qu'une quantité relativement abondante de minerais de référence et apparentés sont disponibles, on les utilise rétro-activement afin d'évaluer les méthodes analytiques employées par les compagnies canadiennes pour contrôler la qualité et faire de la recherche.

/

R.L. Cunningham
Chef

CANMET REPORT 78-2

REVISION OF RECOMMENDED VALUES FOR REFERENCE ORES MP-1 AND KC-1

by

G.H. Faye* and W.S. Bowman**

SYNOPSIS

The composition of CCRMP reference ores MP-1 and KC-1 has altered by oxidation since their original certification in 1972 and 1974 respectively. Because of the continuing demand for these reference materials, an inter-laboratory program was undertaken to re-certify the remaining stock.

Statistical evaluation of results for total zinc, obtained from 10 independent analysts, indicated that bottle-to-bottle homogeneity had remained satisfactory and that the new means and corresponding 95% confidence intervals for zinc are 15.90 ± 0.06% and 20.07 ± 0.07% for MP-1 and KC-1 respectively.

The recommended values for constituents other than zinc have been revised by using correction factors of 0.974 and 0.985 for MP-1 and KC-1 respectively. These factors are the ratios of the new zinc values to the original values for the two reference materials.

To prevent further oxidation, all bottles of MP-1, KC-1, and of other CCRMP reference materials containing appreciable concentrations of sulphide minerals, will be fitted with improved cap closures and sealed in gas-tight laminated foil pouches under nitrogen.

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RAPPORT DE CANMET 78-2

LA REVISION DES VALEURS RECOMMANDEES POUR LES MINERAIS DE REFERENCE MP-1 ET KC-1

par

G. H. Faye* et W.S. Bowman**

SYNOPSIS

La composition des minerais de référence MP-1 et KC-1 du PCMRC a été modifiée par l'oxydation depuis leur certification initiale effectuée en 1972 et 1974 respectivement. Comme la demande de ces matériaux certifiés s'est maintenue, un programme inter-laboratoire a été mis sur pied afin de recertifier les stocks qui restent.

L'évaluation statistique des résultats d'essais sur le zinc total provenant de 10 analystes indépendants, a démontré que l'homogénéité d'un flacon à l'autre a été maintenue d'une façon suffisante. Les nouvelles moyennes et les marges d'erreur (calculées à 95%) correspondantes pour le zinc sont de 15.90 ± 0.06% pour le MP-1 et 20.07 ± 0.07% pour le KC-1.

On a revisé les valeurs recommandées pour les constituants autres que le zinc en employant des facteurs de correction de 0.974 pour le MP-1 et 0.985 pour le KC-1. Ces facteurs représentent les ratios des nouvelles valeurs du zinc sur les valeurs initiales pour les deux matériaux de référence.

Afin de prévenir une nouvelle oxydation, tous les flacons contenant du MP-1, du KC-1 et tout autre matériau de référence du PCMRC qui contient des concentrations appréciables de minéraux sulfureux seront munis de capsules de bouchage améliorées et scellés dans des sacs de feuille de métal lamellaire étanches aux gaz et emmagasinés sous l'azote.

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REVISION OF RECOMMENDED VALUES FOR REFERENCE ORES MP-1 AND KC-1

INTRODUCTION

The high-zinc reference ores MP-1 and KC-1 were each certified by the CCRMP for a number of constituents in 1972 and 1974 respectively and are widely used because of their mineralogical and chemical complexities and metals at useful concentration levels. A detailed description of the ore samples and an account of the original certification procedures are supplied to users of each reference ore.[1,2]

When MP-1 and KC-1 were first prepared and issued, it was recognized that, as with any high-sulphide ore, there was potential danger of oxidation with resulting change in composition during storage and use. However, it was assumed that 200-g units of the low-moisture ore materials, stored in well-capped 250-ml bottles, would not be significantly oxidized during their life expectancy of up to 10 years. This was subsequently supported by the results of experiments in which samples of MP-1 and KC-1 were analyzed for oxidation products after exposure to air at various relative humidities (40-82%) and temperatures (34-67°C) for periods up to seven weeks.[3] From this it was inferred by extrapolation that at approximately 20-25°C the two reference ores would be essentially stable in tightly-capped bottles.

However, in mid 1976 it was found that arbitrarily selected bottles of both MP-1 and KC-1, that had been in use in certain CANMET and commercial laboratories for several years yielded total zinc values that were less than their original lower 95% confidence limits of 16.20% and 20.31% respectively. The zinc analyses were obtained mainly by a widely-used titrimetric method in which ethylenediaminotetra-acetic acid (EDTA) is used as titrant.[4]

Because of the possibility that the method might have produced results that were biased with respect to the original recommended zinc values, it was again thoroughly assessed at CANMET and found not to give low results when applied to materials such as MP-1 and KC-1. It was therefore concluded that alteration of the selected samples had indeed occurred.

To establish whether the condition of the stocks of MP-1 and KC-1 stored at CANMET warranted continued distribution to users, a comprehensive analytical program was undertaken to determine the current zinc values of the ores and the corresponding within-bottle and between-bottle components of variance as measures of their homogeneity.

This report presents the analytical results of the program and their statistical treatment, and shows that the assignment of revised zinc values is justified. Moreover, the original recommended values and corresponding confidence intervals for the minor certified constituents can also be revised by applying a correction factor derived from the new zinc results.

MP-1 and KC-1 will be protected from further oxidation by sealing each bottle, under nitrogen, in a gas-tight pouch.

ANALYTICAL PROGRAM

Selection and distribution of samples

Fifty bottles of each of the two reference ores were selected at random from the stock in June 1977. Because the fine grained ores had settled significantly during storage, each bottle was shaken by hand to dislodge material packed near the bottom and then homogenized for two hours with a Fisher-Kendall mixer. Ten bottles of each reference ore were then distributed to each of five laboratories which agreed to perform two determinations for zinc on each bottle received using separate 0.5 to 1.0-g subsamples, for a total of 20 determinations for each ore.

Table 1 also includes zinc results obtained by several CANMET analysts for a number of additional bottles each of MP-1 and KC-1 that had previously been taken from stock between June and October, 1976, for special studies of oxidation products.

In Tables 1 and 2, the analysts are designated as "laboratories"; of these, three were from industrial or commercial laboratories and the remainder from CANMET.

Analytical methods and results

Although the program permitted analysts to choose their own methods, it was known that the titrimetric method using EDTA would predominate because it is widely used by CANMET analysts, and is also being considered for use in ASTM standards (recommended analytical methods). As Table 1 shows, about 65% of the results were obtained using this method; the remainder were obtained amperometrically with ferrocyanide, by atomic absorption spectrophotometry, or by polarography. Results by the common titrimetric method using ferrocyanide with an external indicator are conspicuously absent, although it should be noted that nearly one half of the total zinc results in the original certification of MP-1 and KC-1 were by this method.

A comparison of the overall means of results of the titrimetric EDTA method and those by non-EDTA methods (Table 2) does not reveal any significant difference in results of the two methods.[1] Thus all results are taken to be valid measures of the zinc content of the two reference ores.

Homogeneity assessment of MP-1 and KC-1

A two-way analysis of variance using nested design was performed on the zinc results obtained on the 50 bottles of both MP-1 and KC-1 selected in June 1977. The F-ratios of between-bottle to within-bottle mean squares are 0.68 and 0.85 for MP-1 and KC-1, respectively. The critical value of the F-distribution at 95% probability for 45 and 50 degrees of freedom is 1.62, therefore, the between-bottle inhomogeneity is insignificant for both reference ores.

Computation of revised means, confidence limits and related statistics for zinc in MP-1 and KC-1

As mentioned above, zinc results were also available for six bottles of each ore taken from stock in 1976. Because there was no evidence that this set differed from the larger 1977 set in extent of oxidation, all zinc results for each reference ore were combined for purposes of computation. Accordingly, a one-way analysis of variance was performed to compute pertinent statistical parameters, which, in Table 3, are compared with those obtained in the original certification.

The certifiability of CCRMP reference materials for a particular constituent requires its certification factor to be 4 or less. This factor is the ratio of the 95% confidence interval for the mean, expressed as a percentage, to the average coefficient of variation.[6] For zinc in MP-1 and KC-1, the certification factors are 1.74 and 2.55 respectively, clearly confirming the acceptability of the new means.

Assignment of correction factor for revision of certified values

The analysis of variance mentioned above indicates that between-bottle inhomogeneity is insignificant at the 95% level for the selected bottles of both MP-1 and KC-1. Thus, it can be concluded that oxidation of the ores has been relatively uniform. Confirmation is given by Table 3 which clearly shows that the precision of the new means for zinc is as good as or better than that of the original means.

The ratios of the revised to original means for zinc are 0.974 and 0.985 for MP-1 and KC-1 respectively. These factors were used to correct the original certified values for elements other than zinc; the revised values and their corrected 95% confidence limits are given in Tables 4 and 5. It is realized that except for zinc, these revised confidence limits are contrived. However, because the homogeneity of MP-1 and KC-1 has not been affected by oxidation, it is reasonable to assume that the precision of the original results still applies, i.e., that the magnitude of the confidence intervals has not changed. Some confirmatory analyses for copper in MP-1 and lead in KC-1 are given in Table 6. It is evident that they fall within the corresponding confidence limits.

Stability of MP-1 and KC-1

From the foregoing it is clear that the bakelite caps on the bottles of MP-1 and KC-1 did not provide an air-tight seal and thus significant oxidation of sulphide minerals occurred. Although the actual mechanism of oxidation has not been completely elucidated, it is known that the principal oxidation product is sulphate. It can be speculated that as the oxygen of the air in the free space (~100 ml) above the ore material in the bottle was consumed in forming sulphate, a negative pressure was created inside the bottle which in turn induced outside air to enter the bottle to effectively continue the process. No doubt, changes in atmospheric pressure also contributed to the diffusion of gases in and out of the imperfectly capped bottles. It is probable that such processes would lead to gradation in oxidation from top to bottom within the bottle. However, this effect would be overcome by the user who, in keeping with good practice, would normally blend the contents of the bottle before opening it to take subsamples.

When it became apparent in late 1976 that the entire stock of MP-1 and KC-1 had been affected by oxidation, friction tape was placed around the caps of all bottles. Although such a closure was not expected to be completely air-tight, experiments showed that it had reduced the rate of oxidation of the two reference materials to a relatively low level. For example, during the 12 months of 1977, tested bottles containing 200 g of ore gained approximately 0.2% by weight in the case of MP-1, and essentially zero in the case of KC-1.

At the time of preparing this report, arrangements were being made to seal all bottles of the two reference ores in laminated polyester-aluminum foil-polyethylene bags containing nitrogen; this should ensure that the recommended values of the stock at CANMET will be valid indefinitely.

It is strongly recommended, however, that users store opened bottles of MP-1 and KC-1 under a dry inert gas such as nitrogen. Also, when taking subsamples, the bottles should be exposed to the air for the shortest time possible.

ACKNOWLEDGEMENT

The analytical contribution of analysts from both CANMET and outside laboratories is acknowledged with gratitude.

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TABLE 1(a) - Zinc results for reference ore MP-1

Laboratory	Method	Zinc (wt %)									
* LAB- 1	EDTA	15.93	15.99	15.99	15.96	15.93	15.93	16.06	16.05	15.98	15.96
		15.96	15.95	15.92	15.95	15.88	15.92	15.85	15.82	15.95	15.95
LAB- 1	EDTA	15.88	15.95	15.85							
* LAB- 2	EDTA	15.88	15.90	15.86	15.87	15.93	15.88	15.83	15.83	15.95	15.90
		15.95	15.94	15.81	15.83	15.80	15.81	15.88	15.90	15.97	15.82
LAB- 2	EDTA	16.03	16.05	16.07	16.07	15.98	15.99	16.01	16.02	16.01	16.04
LAB- 2	EDTA	15.85	15.88	15.85	15.89	15.89					
LAB- 2	EDTA	16.11	16.12	15.77	15.85						
* LAB- 3	EDTA	16.14	16.14	15.99	15.99	15.87	15.82	15.93	15.85	15.96	15.92
		15.88	16.01	15.99	15.92	15.91	15.93	15.80	15.85	15.85	15.90
LAB- 3	EDTA	16.03	16.07	16.06	16.08	16.10					
* LAB- 4	(A.A.)	15.81	15.74	15.89	15.94	15.85	15.77	15.87	15.84	15.96	15.80
		15.87	15.80	15.80	15.68	15.81	15.88	15.68	15.83	15.85	15.82
LAB- 4	A.A.	16.00	16.13	16.10	16.05	16.00					
LAB- 6	EDTA	15.84	15.85	15.86	15.90	15.84	15.92	16.00	15.95	15.91	15.93
LAB- 7	FERRO-A	15.81	15.80	15.80	15.66	15.79	15.73	15.72	15.78	15.70	15.72
LAB- 7	EDTA -IX	15.73	15.72	15.77	15.75	15.82	15.76	15.79	15.81	15.82	15.80
LAB- 8	POLAR	15.75	15.71	15.82	15.81	15.83	15.80	15.89	15.77	15.95	15.85
* LAB-10	(A.A.)	15.80	15.95	16.05	16.05	16.05	16.45	16.00	16.00	16.05	16.05

TABLE 1(b) - Zinc results for reference ore KC-1

Laboratory	Method	Zinc (wt %)									
*LAB- 1	EDTA	20.07	20.09	20.37	20.41	20.35	20.02	20.04	20.17	19.69	20.07
		20.11	19.91	20.02	20.02	20.10	20.11	20.11	20.22	20.11	20.11
		19.94	20.14	20.17	20.22						
*LAB- 2	EDTA	20.11	20.12	20.05	20.09	20.16	20.11	20.17	20.21	20.18	20.17
		20.05	20.05	20.13	20.14	20.12	20.15	20.12	20.10	20.16	20.17
LAB- 2	EDTA	20.15	20.14	20.13							
LAB- 2	EDTA	20.07	20.05	20.00	20.04						
*LAB- 3	EDTA	20.10	20.11	20.14	20.18	20.13	20.14	20.08	20.11	20.13	19.97
		20.05	20.10	20.13	20.09	20.07	20.09	20.10	20.08	20.14	20.12
LAB- 3	EDTA	20.08	20.04	20.09	19.99	20.09					
*LAB- 4	(A.A.)	19.92	19.89	19.94	19.95	19.98	19.92	19.95	19.92	19.94	19.89
		19.91	19.92	19.88	19.88	19.94	20.00	19.77	19.89	19.83	19.79
LAB- 6	EDTA	19.89	19.88	19.97	19.85	19.86	20.03	19.96	20.08	20.03	20.03
LAB- 7	EDTA-IX	20.08	20.05	20.04	20.14	20.11	20.09	20.09	20.08	20.10	20.09
LAB- 8	POLAR	20.19	20.17	20.25	20.23	20.30	20.21	20.27	20.20	20.16	20.19
LAB- 9	FERRO-A	20.08	20.06	20.09	20.05	20.01	19.98	20.01	20.03	19.98	20.04
*LAB-10	(A.A.)	20.25	20.15	20.15	20.10	20.15	20.15	20.10	20.10	20.10	20.15

Multiple entries for particular labs indicate results for samples chosen from stock for different purposes.

* Results for samples chosen at random in June 1977, other results for samples originally chosen for other purposes.

IX - separation by ion exchange

FERRO-A - amperometric titration with ferrocyanide

POLAR - polarographic

TABLE 2

Laboratory mean values and coefficients of variation for MP-1

Reference material	Lab. No.	Method	n	Mean	cv(%)
MP-1	Lab- 1	EDTA	20	15.9465	0.36
	Lab- 1	EDTA	3	15.8933	0.32
	Lab- 2	EDTA	20	15.8770	0.33
	Lab- 2	EDTA	10	16.0270	0.19
	Lab- 2	EDTA	5	15.8720	0.13
	Lab- 2	EDTA	4	15.9625	1.12
	Lab- 3	EDTA	20	15.9325	0.58
	Lab- 3	EDTA	5	16.0680	0.16
	Lab- 4	a.a.	20	15.8245	0.46
	Lab- 4	a.a.	5	16.0560	0.36
	Lab- 6	EDTA	10	15.9000	0.33
	Lab- 7	ferro-amp	10	15.7510	0.33
	Lab- 7	EDTA	10	15.7770	0.23
	Lab- 8	polar.	10	15.8180	0.44
	Lab-10	a.a.	10	16.0450	1.01
		Total	162	15.9031	0.72
KC-1	Lab- 1	EDTA	24	20.1071	0.75
	Lab- 2	EDTA	20	20.1280	0.22
	Lab- 2	EDTA	3	20.1400	0.05
	Lab- 2	EDTA	4	20.0400	0.15
	Lab- 3	EDTA	20	20.1030	0.22
	Lab- 3	EDTA	5	20.0580	0.22
	Lab- 4	a.a.	20	19.9055	0.29
	Lab- 6	EDTA	10	19.9580	0.42
	Lab- 7	EDTA	10	20.0870	0.14
	Lab- 8	polar.	10	20.2170	0.22
	Lab- 9	ferro-amp	10	20.0330	0.19
	Lab-10	a.a.	10	20.1400	0.23
		Total	146	20.0721	0.57

ferro-amp - amperometric titration with ferrocyanide

polar. - polarographic

n - number of determinations

TABLE 3

Revised and original means for zinc and their precision

	Zn (wt %)	95% Confidence limits	Average within-lab cv(%)	Certification factor
MP-1				
1972 original values	16.33	16.20 - 16.45	0.46	3.36
1977 revised values	15.90	15.84 - 15.96	0.42	1.74
KC-1				
1974 original values	20.37	20.31 - 20.43	0.38	1.61
1977 revised values	20.07	20.01 - 20.14	0.26	2.55

TABLE 4

Recommended values and confidence limits for selected constituents in MP-1 (1978)

Constituent	Recommended value	95% Confidence limits
	(wt %)	
Zn	15.90	15.84 - 15.96
Sn	2.43	2.32 - 2.54
Cu	2.09	2.06 - 2.12
Pb	1.88	1.85 - 1.91
Mo	0.014	0.013 - 0.015
In	0.069	0.066 - 0.072
Bi	0.024	0.022 - 0.026
As	0.77	0.75 - 0.79
Ag	57.9 ppm	55.7 - 60.1

TABLE 5

Recommended values and confidence limits for selected constituents in KC-1 (1978)

Constituent	Recommended value	95% Confidence limits
	(wt %)	
Zn	20.07	20.01 - 20.14
Pb	6.87	6.83 - 6.91
Sn	0.67	0.66 - 0.68
Cu	0.112	0.110 - 0.114
Ag	0.112	0.110 - 0.113

TABLE 6

Confirmatory analyses for MP-1 and KC-1

Reference material	Cu (wt %)	Pb (wt %)
MP-1	2.11 a.a.	-
	2.12 a.a.	
KC-1	-	6.84 a.a.
		6.85 a.a.
		6.87 titrimetric (EDTA)
		*6.80 " "

Except where indicated by asterisk, each entry is the mean of five replicate determinations by the indicated method on a different bottle taken directly from stock in early 1977.

*Mean of duplicate results on each of five bottles that had been opened and kept unprotected from laboratory atmosphere from June-December 1977.