Canada Centre for Mineral and Energy Technology Centre canadien de 22. technologie des minéraux et de l'énergie

# HCC-1 AND INM-1 -PYROMETALLURGICAL CRM<sub>S</sub> FOR SULPHUR

**Henry F. Steger** 



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by

Henry F. Steger



Canadian Certified Reference Materials Project

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# HCC-1 and INM-1 - Pyrometallurgical CRMs for Sulphur

Henry F. Steger\*

# SYNOPSIS

Two pyrometallurgical feed materials were considered for certification for sulphur to serve as reference materials. HCC-1 is a copper concentrate from Hudson Bay Mining and Smelting Limited in Flin Flon, Manitoba and INM-1 is a nickel-copper sulphide matte from INCO Limited in Copper Cliff, Ontario.

HCC-1 and INM-1 were ground to pass a 106  $\mu$ m screen, blended and bottled in 50-g units. Sufficiency of homogeneity was assumed.

In an interlaboratory analytical program, eleven laboratories provided five or more results for sulphur in each material by a barium sulphate precipitation method. Based on statistical analysis of the data, a recommended value and 95% confidence interval of  $33.92 \pm 0.12\%$  and  $22.17 \pm 0.20\%$  for HCC-1 and INM-1, respectively, were assigned.

Methodological and statistical information regarding the interlaboratory analytical program is provided.

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# HCC-1 et INM-1 - Matériaux de référence pyrométallurgiques pour le soufre

Henry F. Steger<sup>\*</sup>

# RÉSUMÉ

On a pris en considération la certification de deux matériaux pyrométallurgiques alimentaires pour le soufre afin de servir comme matériaux de référence. Le HCC-1 est un concentré de cuivre provenant de la compagnie Hudson Bay Mining and Smelting Limited à Flin Flon au Manitoba et le INM-1 est une matte des sulphides de nickel-cuivre provenant de la compagnie INCO Limited à Copper Cliff en Ontario.

Les HCC-1 et INM-1 ont été broyés pour passer un tamis de -106  $\mu$ m et embouteillés en unités de 50-g. On a assumé que l'homogénéité des matériaux soit acceptable.

Dans le cadre d'une campagne inter-laboratoire analytique, onze laboratoires ont soumis cinq résultats ou plus pour le soufre pour chaque matériau en appliquant une technique de précipitation de sulphate de baryum. Lors de l'analyse statistique des données, on a assigné une valeur recommandée et une intervalle de confiance de 95% de 33,92  $\pm$  0,12% et 22,17  $\pm$  0,20% pour le HCC-1 et INM-1, respectivement.

De l'information méthodologique et statistique en ce qui concerne la campagne interlaboratoire analytique est pourvue.

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#### **INTRODUCTION**

The preparation, characterization and certification for sulphur of the pyrometallurgical materials, HCC-1 and INM-1, is a contribution of the Canadian Certified Reference Materials Project (CCRMP) to make available to the Canadian smelting industry reference materials that are representative of its feed stream materials. Other CCRMP reference materials typical of Canadian deposits for use in analytical laboratories associated with mining, metallurgy, and the earth sciences are described in a catalogue available from CANMET, Energy, Mines and Resources Canada, K1A 0G1 (1).

The emission of sulphur dioxide in the pyrometallurgy of sulphide concentrates and mattes is a serious problem that is common to all Canadian mining and smeltering companies and to government Ministries of the Environment through their regulatory responsibility.

The current widespread concern with acid rain has led to increasing political, public and regulatory pressure on the smelting industry to reduce its level of sulphur dioxide output. The compliance with, or rather the failure to achieve, prescribed regulatory emission levels can lead to serious financial loss and/or even penalty. Some companies base their calculation of the quantity of sulphur dioxide emissions on the sulphur content of the smelter feed stream materials. Others use such calculations to verify the direct measurement of sulphur dioxide in up-the-stack emissions. For this reason, it is important that the analysis for sulphur in solids can be carried out as accurately and precisely as possible.

CCRMP offers several reference materials certified for sulphur that are used in this application. However, the uncertainty of the sulphur value of these materials is "relatively" large because certification is based on interlaboratory programs in which the participants had free choice of method.

To minimize the between-methods variance, certification of the pyrometallurgical reference materials was carried out by interlaboratory program in which participating laboratories were restricted to the "classical" barium sulphate precipitation method. An assessment of the degree of consensus achievable with this method was first established by interlaboratory program on the CCRMP certified copper concentrate, CCU-1a (2). The results of this program, compared with the corresponding parameter values determined in the 1988 certification program for CCU-1a, showed that restricting the analysis to barium sulphate precipitation decreased the between-laboratories and withinlaboratory standard deviation and thus reduced the overall uncertainty. The mean value for sulphur of the method assessment program was somewhat lower than the certified value in CCU-1a but the overlap of 95% confidence limits implied that there was no statistical difference between them.

Radioisotope studies on sulphur distribution/losses in barium sulphate precipitation were carried out concurrently at CANMET. The study with Ba-133 tracer was inconclusive (3). The study with  $S^{35}$ labeled sulphate pointed out that the loss of sulphur in CCU-1a by barium sulphate precipitation at CANMET amounted to 0.4% of total sulphur (4), i.e., 0.04x30.08 = 0.13%S absolute. Of this, almost 94% reported to the filtrates in the various steps of the method. It is likely that the loss and distribution of sulphur varies with the laboratory. The chemical composition of the filtrates affects the solubility of barium sulphate and the volume of the filtrates determines the magnitude of the loss of sulphur.

An interlaboratory certification program was conducted in late 1989 and early 1990 to obtain measurements for sulphur on two pyrometallurgical materials, HCC-1 and INM-1, from 11 laboratories using an in-house barium sulphate precipitation method or that provided by CANMET. Participating laboratories included two government laboratories and eight from five Canadian mining and smelting companies, Cominco, Falconbridge, Hudson Bay Mining and Smelting, International Nickel, and Noranda.

## NATURE AND PREPARATION

HCC-1 was donated in July 1989 by Hudson Bay Mining and Smelting Limited, Flin Flon, Manitoba, and is typical of the copper concentrate mill feed which was also the source for CCRMP certified copper concentrates, CCU-1 and CCU-1a. In general, the concentrate is a little above 80% chalcopyrite with 5-10% of each of pyrite and sphalerite with a trace of pyrrhotite. The raw material weighing about 46 kg was passed through a Denver roller and screened. Forty-five kg of -106  $\mu$ m particulate was recovered. The material was blended for 3 hours and bottled in 50-g units.

INM-1 was donated in October 1989 by the International Nickel Company Limited, Copper Cliff, Ontario, and is a typical sample of nickel-copper sulphide matte.

Constituent wt %	HCC-1	INM-1
2	26.0	0.5 5
Cu	26.9	25.5
Fe	29.8	5.1
Ni		48.0
Pb	1.0	
s*	33.92	22.17
SiO <sub>2</sub>	1.1	0.1
Zn	4.6	

# **Table 1 - Approximate chemical composition**

\*certified value

Size	HCC-1 wt	INM-1
+ 74 μm	4.4	13.4
44 - 74 μm	15	18
37 - 44 μm	10	9.2
- 37 μm	70.6	59.4

#### Table 2 - Screen size analysis (wet screen)

The raw material weighing about 43 kg was passed through a Denver roller and screened. Forty kg of 106  $\mu$ m particulate was recovered. The material was blended for 3 hours and bottled in 50-g units.

The nominal composition of HCC-1 and INM-1 is reported in Table 1. The particle-size analysis is given in Table 2.

A formal homogeneity-testing program was not carried out for these materials. It was assumed that the successful previous experience in preparing homogeneous lots of several hundred kilograms of the similar materials, CCU-1 and CCU-1a for HCC-1 and PTM-1 for INM-1, without problem was sufficient to expect homogeneity in lots of 45 kg and less.

# INTERLABORATORY PROGRAM FOR CERTIFICATION

Ten laboratories participated in the certification program by contributing a minimum of five results for sulphur for the sample of HCC-1 and INM-1 by an inhouse barium sulphate precipitation method or that provided by CANMET. Participants are listed alphabetically in Appendix A. Each one was assigned a code number that bears no relation to the alphabetical order. One laboratory provided results by the same method by two different analysts. These were treated as independent sets of results for statistical purposes. A summary of the barium sulphate precipitation procedures is given in Tables 3. The analytical results are given in Tables 4 and 5. The recommended values for sulphur and associated statistical parameters are reported in Table 6.

# STATISTICAL TREATMENT OF ANALYTICAL DATA

# **Detection of Outliers**

Two of the sets of results from one analyst in Laboratory-2 and two of the sets of results from Laboratory-9 were determined to be outliers on statistical grounds and excluded from the calculation of the recommended value and associated parameters. For Laboratory-9, the mean of the set for HCC-1 differed from the grand mean by more than twice the overall standard deviation of the individual results. The sets of results from Laboratory-9 and Laboratory-2 for INM-1 had inordinately high variance in comparison with the peer sets as detected by the Cochran's Test (5). Because of the high frequency of rejection, the decision was taken to exclude all sets of results from Laboratories-2 and -9.

# Estimation of Consensus Value 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 certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (5)

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

where  $x_{ij}$  = the j <sup>th</sup> result in set i,  $\mu$  = the true consensus value,  $y_i$  = the discrepancy between the mean of the results in the set i ( $\hat{x}_i$ ) and  $\mu$ and  $e_{ij}$  = the discrepancy between  $x_{ij}$ and  $\hat{x}_i$ .

It is assumed that both  $y_i$  and  $e_{ij}$  are normally distributed with means of zero and variances of  $\sigma^2$  and  $\omega^2$ , respectively. The significance of  $\omega^2$  is detected by comparing the ratio of between-sets 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:

$$\overline{x} ... = \frac{\underset{\Sigma\Sigma}{kn}_{i}}{\underset{i j}{\overset{k}{\sum}} x_{ij}} / \underset{i}{\overset{k}{\sum}} n_{i}$$

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

The value of  $\sigma^2$  is estimated by  $s_1^2$ , which is given by:

$$s_1^2 = \frac{k n_i}{\sum \sum (x_{ij} - \overline{x}_i)^2 / (\sum n_i - k).}_{i j}$$

The value of  $\omega^2$  is estimated by:

$$\omega^{2} = (k-1) \cdot (s_{2}^{2} - s_{1}^{2}) / (\sum_{i=1}^{k} n_{i} - \sum_{i=1}^{k} n_{i}^{2} / \sum_{i=1}^{k} n_{i})$$

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

The variance of the overall mean is given by:

$$V[\overline{x}..] = \left( \begin{array}{cc} k & k \\ \sum n_{i}^{2} / (\sum n_{i})^{2} \right) \omega^{2} + \sigma^{2} / \sum n_{i} \\ i & i \end{array} \right)^{k}$$

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

$$\overline{\mathbf{x}} ... \pm t_{0.975,(k-1)} \{ \mathbf{V}[\overline{\mathbf{x}} ..] \}^{\frac{1}{2}}.$$

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 instances would fall within the prescribed limits. The average within-set standard deviation,  $\sigma_A$ , 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  $\sigma_A$ .

## Criterion for Certification

The ratio of the between-laboratories to the within-laboratory standard deviation,  $\sigma_{\rm B}/\sigma_{\rm A}$ , where

$$\sigma_{\rm B} = \left\{ \sum_{i}^{\rm k} (\bar{x}_{i} - \bar{x}_{..})^2 / (k - 1) \right\}^{\frac{1}{2}}$$

is a measure of the quality of the certification data used by CCRMP (6). The acceptable upper limit of  $\sigma_B/\sigma_A$  is 3. The criterion for certification is RP, the percentage of sets of results that must be removed to yield a value of  $\sigma_B/\sigma_A$  equal to less than the acceptable upper limit. The value of RP may not exceed 15% for an element to be considered certifiable. When this is true, the overall mean is assigned as the recommended value.

This criterion is applicable only to those interlaboratory programs where the number of participants exceeds ten. This is not the case for these pyrometallurgical materials and therefore the data was not subjected to this criterion.

# Stability of Reference Materials

Samples of HCC-1 and INM-1 were subjected to accelerated oxidation condi-

tions at 50°C and 70% relative humidity to assess their stability. Subsamples were removed at 7, 29 and 42 days and the test was halted after 56 days. A total sulphate analysis was performed on the untreated materials and on the different oxidized subsamples. In addition, untreated samples and those oxidized for 56 days were analyzed for elemental sulphur and sulphate. The results are shown in Tables 7 and 8.

#### DISCUSSION

The histograms in Figures 1 and 2 for HCC-1 and INM-1, respectively, show that the analytical results for sulphur are evenly distributed about the mean value. This is substantiated by the good agreement between the median and mean values for sulphur for HCC-1 and INM-1 in Table 6.

The first phase of this project demonstrated that the restriction of the methodology to barium sulphate precipitation and ICP-AES for the determination of sulphur in reference material CCU-1a reduced the uncertainty of the mean value by more than 50% of that of the certified value. The average withinlaboratory standard deviation also decreased slightly. This same smaller uncertainty of the mean value and better within-laboratory standard deviation have been attained for HCC-1. The uncertainty of the mean value of sulphur in INM-1 is also lower than that for the certified value for sulphur in CCU-1a. This project has therefore succeeded in preparing two reference materials for use by analytical laboratories.

The results of the stability study indicate that HCC-1 is vulnerable to oxidation leading to decreasing sulphur content. Sulphate appears to be the main oxidation product. The formation of elemental sulphur cannot be ruled out because of its volatility at 50°C. INM-1 also appears to be subject to ambient oxidation but to a lesser degree than HCC-1. It must be noted that the conditions of 50°C and 70% relative humidity used to accelerate the oxidation of these pyrometallurgical materials are very severe and it is unlikely that the changes observed would ever be realized under normal laboratory conditions. It is nevertheless recommended that bottles of these materials once opened be stored in a dessicator to minimize the extent of ambient oxidation.

The materials, HCC-1 and INM-1 together with CZN-1, a zinc concentrate (7), provide analysts with a suite of reference materials certified for sulphur and which are representative of some of the more important mineral concentrates and process products of the Canadian pyrometallurgical industry.

### ACKNOWLEDGEMENT

The author wishes to thank the participating laboratories listed in the Appendix for their contribution to this project. In CANMET, acknowledgement must be extended to R.J. Guillas for the determination of sulphur, M.C. Blanchette for the radiotracer studies, E.H. MacEachern for the stability study and W.S. Bowman for the statistical analyses.

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Laboratory	Description
Laboratory-1	Fuse 0.5g of the sample with 1:3 sodium hydroxide:sodium peroxide. Acidify with hydrochloric acid and precipitate hydrous oxides with ammonium hydroxide. Filter and wash with hot water. Precipitate sul- phate with barium chloride. Filter barium sulphate and ignite in tared clay crucible.
Laboratory-2	See CANMET method, Lab-5.
Laboratory-3	Decompose 0.3g of the sample with bromine in carbon tetrachloride and nitric acid. Add hydrochloric acid and evaporate to dryness to dehydrate silica. Add 10% sodium carbonate, let boil and filter. Acidify with hydrochloric acid, and add barium chloride. Filter off barium sulphate and calcine at 950 $^{\circ}$ C in a tared crucible.
Laboratory-4	Fondre 0.5-1g de l'échantillon avec de 2:1 peroxyde de sodium:carbonate de sodium andryde. Faire précipiter les oxydes de fer avec de carbonate d'ammonium. Filtrer et laver avec une solution chaude d'hydroxyde de sodium (1%). Retraiter le précipité avec de carbonate d'ammonium et filtrer et laver avec la solution d'hydroxyde de sodium. Combiner les deux filtrats. Acidifier avec l'acide chlorhydrique et ajouter de chlorure de baryum. Filtrer le précipité de sulfate de baryum et le calciner dans un creuset de porcelaine pesé à 950°C.
Laboratory-5	Decompose 0.5-1g of the sample with bromine in carbon tetrachloride and nitric acid. Add hydrochloric acid and bake to dryness to dehydrate silica. Take up in hydrochloric acid and filter. Precipitate ferric hydrous oxide with ammonium hydroxide. Add barium chloride and acidify with hydrochloric acid to dissolve iron hydrous oxides. Filter barium sulphate and wash with dilute hydrochloric acid and hot water to remove chlorides. Ignite at 800-900°C in a tared platinum crucible.
Laboratory-6	Decompose 0.15-0.2g of the sample with a bromine solution in potassium bromide and nitric acid and dry on low heat. Add hydrochloric acid and dehydrate silica which is filtered off. Precipitate hydrous iron oxides with sodium peroxide and lead and calcium with sodium carbonate and filter off. Acidify with hydrochloric acid and add barium chloride. Filter off barium sulphate and ignite at 900°C in a tared porcelain crucible.

# Table 3 - Summary of Barium Sulphate Methods for Sulphur

- Laboratory-7 Décomposer 0.5g de l'échantillon avec de brome, d'acide nitrique et d'acide chlorhydrique. Précipiter les oxydes de fer par d'hydroxyde d'ammonium et le filtrer et laver à l'eau. Redissoudre le précipité avec l'acide chlorhydrique et faire reprécipiter par d'hydroxyde d'ammonium. Filtrer et combiner les filtrats des deux précipitations. Acidifier par l'acide chlorhydrique et ajouter de la solution de chlorure de baryum. Filtrer le sulfate de baryum et le calciner à 1000°C dans un creuset pesé.
- Laboratory-8 See CANMET method, Lab-5.
- Laboratory-9 Decompose 0.40g of INM-1 with a bromine solution in potassium bromide and nitric acid. Add hydrochloric acid and dehydrate silica and filter off. Acidify with hydrochloric acid and add barium chloride in hot solution. Filter barium sulphate and ignite.
- Laboratory-10 Decompose 0.25g of HCC-1a and CZC-1 with a bromine solution in potassium bromide and nitric acid. Precipitate iron and lead with ammonium hydroxide and carbonate. Re-dissolve and reprecipitate with ammonium hydroxide. Filter and combine with original filtrate. Add hydrochloric acid and dehydrate silica and filter off. Acidify with hydrochloric acid and add barium chloride in hot solution. Filter barium sulphate and ignite.
- Laboratory-11 Fuse 0.5g of the sample with a mixture of 2g of each of sodium peroxide and sodium carbonate. Quench in dilute hydrochloric acid. Add ammonium carbonate and heat to affect solution and filter. Acidify with hydrochloric acid, add hydroxylamine hydrochloride and boil to reduce residual ferric and chromate. Precipitate sulphate with barium chloride and allow to digest overnight. Filter and ignite at 800-900°C in a tared clay crucible.

Laborato	ry	Sulphur Results (%)					Mean	s.D.
Lab-1	33.9	33.7	33.6	33.8	33.7		33.740	0.114
Lab-2 *	33.47	33.28	33.13	33.45	33.15	33.51	33.332	0.168
	33.64	33.72	34.03	33.77	33.77		33.786	0.146
Lab-3	34.07	34.02	34.08	34.08	34.09		34.068	0.028
Lab-4	34.04	34.10	34.13	34.09	34.11	34.03	34.083	0.040
Lab-5	34.04	34.23	33.96	34.14	34.02		34.078	0.107
Lab-6	33.96	33.72	33.80	33.74	33.92	33.78		
	33.79	33.77	33.75	33.86	33.88		33.802	0.080
Lab 7	33.87	33.72	33.92	33.73	33.88		33.824	0.092
Lab-8	34.17	33.89	33.89	33.80	33.85	33.73	33.888	0.151
Lab-9 *	32.71	33.13	32.94	33.15	33.13		33.012	0.189
Lab-11	34.04	33.98	34.22	34.20	34.18		34.124	0.107

Table 4 - Analytical Results for Sulphur (%) in HCC-1

\*Suspected outlier

Table 5 - Analytical Results for Surphul (%) in finite	Table 5 -	Analytical	Results	for	Sulphur	(%)	ın	INM-1	
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Laboratory		Sulphur Results (%)					Mean	S.D.
Lab-1	22.1	22.2	22.1	22.1	22.1		22.120	0.045
Lab-2 *	21.63	21.40	21.92	21.75	21.85	22.03	21.763	0.225
	22.11	22.12	22.21				22.147	0.055
Lab-3	22.60	22.61	22.51	22.46	22.51	22.55	22.540	0.058
Lab-4	22.19	22.31	22.23	22.14	22.19	22.21	22.212	0.057
Lab-5	22.15	22.23	22.22	22.24	22.20		22.208	0.036
Lab-6	21.75	21.87	21.82	21.75	21.84	21.97		
	21.97	21.89	21.89	21.90	21.93	21.93	21.875	0.074
Lab 7	22.53	22.52	22.57	22.55	22.59		22.552	0.029
Lab-8	21.98	22.20	22.03	22.10	21.98	22.12	22.068	0.087
Lab-9 *	22.42	22.57	22.47	22.67	22.29		22.484	0.145
Lab-11	22.17	22.14	22.19	22.21	22.17		22.176	0.026

\*Suspected outlier

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Parameter	HCC-1	INM-1
Recommended Value, %	33.92	22.17
95% Conf. Limits Low, % High, %	33.80 34.03	21.97 22.37
Standard Deviation, % Between-laboratories Within-laboratories	0.14 0.095	0.24 0.051
No. of sets No. of results	9 53	9 53

 Table 6 - Mean Values and Statistical Parameters for Sulphur

ſ	Time	HCC-1	INM-1
	Untreated	33.35	22.27
	7 days	33.12	22.22
	29 days	33.25	22.12
	42 days	32.20	21.26
	56 days	31.56	21.76

Table / - Results for Total Sulphur in Oxidized Materials	Tab	le	7	-	Results	for	<b>Total</b>	Sulphur	in	Oxidized	Materials (	%)
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Table 8 - Results for Elemental Sulphur and Sulphatein Oxidized Materials (%)

	HCC-1	INM-1
Elemental Sulphur		
Untreated 56 days	0.36	0 0
Sulphate		
Untreated 56 days	0.58 1.33	0 0



REFERENCE MATERIAL HCC-1

Figure 1 - Histogram of results for sulphur in HCC-1



Figure 2 - Histogram of results for sulphur in INM-1

#### **APPENDIX A**

## **PARTICIPATING LABORATORIES**

Canada Centre for Mineral and Energy Technology Energy, Mines and Resources Canada Ottawa, Ontario H.F. Steger

Centre de recherches minérales Ministère de l'Energie et des Ressources(Mines) Québec Sainte-Foy, Québec M. Pichette

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