

*Dr. N. H. A. Bright*



DEPARTMENT OF  
ENERGY, MINES AND RESOURCES  
MINES BRANCH  
OTTAWA

*COPPER-MOLYBDENUM ORE, HV-1:  
ITS CHARACTERIZATION AND PREPARATION  
FOR USE AS A STANDARD  
REFERENCE MATERIAL*

G. H. FAYE, W. S. BOWMAN AND SUTARNO

MINERAL SCIENCES DIVISION

MARCH 1973

017991376

© Crown Copyrights reserved

Available by mail from Information Canada, Ottawa,  
and at the following Information Canada bookshops:

HALIFAX  
1687 Barrington Street

MONTREAL  
640 St. Catherine Street West

OTTAWA  
171 Slater Street

TORONTO  
221 Yonge Street

WINNIPEG  
393 Portage Avenue

VANCOUVER  
800 Granville Street

or through your bookseller

Price 75 cents    Catalogue No.    M34-20/167

Price subject to change without notice

Information Canada  
Ottawa, 1973

Mines Branch Technical Bulletin TB 167

COPPER-MOLYBDENUM ORE HV-1:  
ITS CHARACTERIZATION AND PREPARATION FOR USE AS A  
STANDARD REFERENCE MATERIAL

by

Members of the Staff of the Mineral Sciences Division  
(Compiled by G. H. Faye, W. S. Bowman and Sutarno)

- - -  
SYNOPSIS

A copper-molybdenum ore, HV-1, has been prepared and characterized for use as a standard reference material. HV-1 is the third ore of metallic minerals to be issued for sale as part of the Canadian Standard Reference Materials Project, of the Mines Branch, Department of Energy, Mines and Resources.

This report gives the mineralogical, geological and chemical characteristics of HV-1, as well as some details of methods used for its comminution and blending, and for assessing its homogeneity. Twenty-three laboratories provided analyses for copper and molybdenum; the recommended mean values for these are: 0.52% and 0.058%, respectively. The analytical results and the evaluation of statistical parameters for copper and molybdenum are reported.

Direction des mines  
Bulletin technique TB 167

MINERAI DE CUIVRE-MOLYBDÈNE, HV-1: LA  
CARACTÉRISATION ET LA PRÉPARATION DE CE MINERAI  
UTILISÉ COMME MATÉRIAU TYPE DE RÉFÉRENCE

par

Les membres du personnel de la  
Division des sciences minérales  
(Compilé par G.H. Faye, W.S. Bowman et Sutarno)\*

RÉSUMÉ

Les auteurs ont préparé et caractérisé un minerai de cuivre-molybdène, HV-1 utilisé comme matériau type de référence. HV-1 est le troisième minerai des minéraux métalliques qui sera disponibles pour achat comme partie du Projet canadien des matériaux types de références de la Direction des mines du ministère de l'Énergie, des Mines et des Ressources.

Dans ce rapport, les auteurs donnent les caractéristiques minéralogiques, géologiques et chimiques du HV-1, ainsi que quelques détails des méthodes utilisées pour sa pulvérisation, son mélange et pour l'évaluation de sa homogénéité. Vingt-trois laboratoires ont fourni les analyses pour le cuivre et le molybdène; la moyenne recommandée pour ceux-là sont: 0.52% et 0.058% respectivement. Ils donnent aussi les résultats analytiques et l'évaluation des paramètres statistiques pour le cuivre et le molybdène.

---

\*Division des sciences minérales, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada.

CONTRIBUTIONS FROM MINERAL SCIENCES DIVISION

(in alphabetical order)

Principal Contributors

Bowman, W.S.  
Faye, G.H.  
Petruk, Dr. W.  
Sutarno, Dr.

Other Contributors

Churchill, T.R.  
Cloutier, J.C.  
Dalton, J.L.  
Hargreaves, I.  
Hole, J.C.  
Kobus, R.S.  
Lanthier, P.  
Lefebvre, J.M.  
McAdam, R.C.  
McDiarmid, Mrs. V.M.  
McMahon, C.  
McMaster, C.H.  
Nebesar, B.

## INTRODUCTION

This report describes the preparation and characterization of a copper-molybdenum ore, HV-1, as a standard reference material. HV-1 is the third ore of metallic minerals to be certified as part of the Canadian Standard Reference Materials Project, of the Mines Branch, Department of Energy, Mines and Resources. Previously issued materials are molybdenum ore, PR-1 (see Ref. 1), and a zinc-tin-copper-lead ore MP-1 (see Ref. 2).

HV-1 is a mixture of materials taken from large, low-grade, copper-molybdenum porphyry deposits in the Highland Valley area of British Columbia; it is intended to be representative of samples analyzed in large numbers by enterprises associated with the exploitation of these deposits. At least one inter-laboratory analytical study, on a sample similar to HV-1, yielded discordant results for copper and molybdenum (3). It is felt, therefore, that a standard reference ore such as HV-1, with well-established values for these two elements, would be valuable to commercial and industrial laboratories, especially in Western Canada.

For certification purposes, twenty-three laboratories analyzed HV-1 for molybdenum and copper; most of these provided results that were obtained by both atomic absorption spectrophotometry and by an alternative method of their choice. Considering all results collectively, statistical tests indicated that, for both elements, there was no significant difference between the atomic absorption results and those obtained by other methods.

This report describes the procedures used to obtain the recommended values for copper and molybdenum in HV-1; these are 0.52% and 0.058%, respectively.

COMMINUTION, BLENDING, AND MINERALOGICAL COMPOSITION  
OF HV-1

To prepare HV-1, approximately equal quantities of materials taken from the ore deposits of Highmont Mining Corporation Limited and Valley Copper Mines Limited were combined. Both deposits are located in the Highland Valley area of British Columbia. The coarse ore was crushed and dry-ground to minus 200 mesh in conventional milling equipment. The material, weighing approximately 400 lb, was blended in a 45-gallon, baffled, mixing drum for 8 hours. Analysis of grab samples indicated that the copper content of the ore was close to the target value of 0.5%; however, the molybdenum content of 0.015% was far short of the target value of 0.05%.

To up-grade the ore, 0.4 lb of a 96% molybdenite concentrate (90% minus 200 mesh) from Brenda Mines Limited, near Peachland, British Columbia, was added and the whole was blended in the mixing drum for 16 hours. Upon emptying the blender, the bulk ore was randomly sampled and tested for homogeneity by techniques described below. Subsequently, the ore was packaged in 854 bottles each containing 200 g of material; these were stored in 24-bottle cases.

The mineralogical composition of HV-1 is given in Table 1 and was calculated from the chemical analyses given in Table 3 and the previously established, detailed mineralogy of the ore.

TABLE 1

Calculated Mineralogical Composition of HV-1

Minerals	Calculated Mineralogical Composition (wt %)
Bornite	0.6
Chalcopyrite	0.3
Pyrite	0.1
Molybdenite	0.1
Quartz	40.7
Plagioclase	26.9
Orthoclase	10.6
Sericite	12.3
Biotite	2.3
Amphibole and pyroxene	2.0
Clay minerals	1.0
Zircon	Trace
Calcite	1.5
Hematite and magnetite	0.6
Rutile	0.3
Barite	0.1
Tramp iron (presence indicated from polished section; calculated by difference)	0.4
Total	99.8



## TESTS FOR HOMOGENEITY

After blending, two 200-g grab samples of the ore were taken for homogeneity tests. Chemical analyses of these samples for copper and molybdenum suggested that HV-1 was sufficiently homogeneous to be bottled.

To verify the apparent homogeneity of HV-1, five bottles were selected at random from the total stock of bottles. Six 0.5-g samples from each of these bottles were analyzed for copper by the Analytical Chemistry Section of the Mineral Sciences Division (Lab 5). A one-way analysis of variance of the 30 results showed that there was no significant difference between the bottles insofar as the copper contents was concerned.

With the exception of Lab 5, each participating laboratory (page 11) received two randomly selected bottles of HV-1; most of these laboratories were requested to analyze five samples from each bottle for copper and molybdenum. The reported results (Table 6) were compared between bottles, within each laboratory, using the  $t$ -test at a 5% significance level. The results of these tests are summarized in Table 2 and are illustrated in Figures 3 and 4. Table 2 shows that the majority of the laboratories do not find any evidence of difference between the bottles they received.

TABLE 2

Summary of the *t*-Tests on Results Between Bottles for Each Laboratory

Lab. No.	Copper	Molybdenum
1	A	R
2	A	A
3	A	A
4	A	A
5	A	A
6	A	R
7	A	A
8	A	A
9	A	A
10	A	A
11	A	A
12	A	A
13	A	A
14	R	A
15	A	R
16	A	A
17	A	A
18	A	A
19	A	A
20	-	-
21	A	A
22	A	A
23	A	A

A = Null hypothesis accepted, i. e., there is no evidence of inhomogeneity.

R = Null hypothesis rejected, i. e., there is evidence of inhomogeneity.

CONTRIBUTION OF THE ANALYTICAL CHEMISTRY SECTION  
MINERAL SCIENCES DIVISION (Lab 5)

In addition to contributing the results of 10 replicate determinations for the certification of HV-1 for copper and molybdenum, Lab 5 performed analyses for copper in the homogeneity tests described above. This accounts for the inordinately large number of atomic absorption analyses, for copper listed under Lab 5 in Table 6. The mean of these results (0.528% Cu) differs by 0.006% from the over-all mean (0.522% Cu), and, therefore, the additional 20 analyses do not unduly influence the recommended value for copper, which is 0.52%.

To provide a more complete chemical characterization of HV-1, Lab 5 provided additional analyses for major and minor constituents. These results are presented in Table 3, along with results of emission spectrographic analysis by Lab 17.

TABLE 3

Provisional Chemical and Spectrographic Analyses of HV-1

Chemical <sup>a</sup> (Mineral Sciences Division, Mines Branch)	Spectrographic <sup>b</sup> (Geological Survey of Canada)
O - 49.2 <sup>c</sup> wt %	Ba - 0.081 wt %
Si - 33.9	Mg - 0.35
Al - 6.61	Mn - 0.026
Fe (total) - 1.88	Sr - 0.041
Ca - 1.40	Ti - 0.13
Mg - 0.34	V - 0.007
Na - 2.26	Zr - 0.008
K - 2.82	Cu - 0.51
Ti - 0.16	Mo - 0.06
Mn - 0.03	
Cu - 0.52	
S (comb) - 0.34	
S (grav) - 0.35	
C (total) - 0.20	
H <sub>2</sub> O (98°C) - 1.42	
Total 101.1	
Correction for O in H <sub>2</sub> O 1.3	
Adjusted total 99.8	

a - Average of at least two determinations for each constituent.

b - Average of 10 replicate determinations made on 5 separate 40-mg aliquots from each of two bottles.

c - Determined by neutron-activation analysis in the Mineral Sciences Division.

d - See Table 4.

The results in Table 3 were used in the calculation of the mineralogical composition of HV-1.

#### Determination of Sulphur by Combustion Method

Although the sulphur content of HV-1 was determined gravimetrically by Lab 5 (Tables 3 and 4), it was considered worthwhile to provide a well-established provisional value by the combustion method also, especially because the sulphur content of HV-1 is in the optimum range for this determination. It is hoped that the mean sulphur value by the combustion method, given in Table 4, will be useful to those who wish to use HV-1 as a provisional reference material for this element.

The two sets of results by Analyst No. 1, given in Table 4, are related to the use of two reference materials -- a standard reference ore, PR-1 (see Ref. 1) and an analyzed molybdenite concentrate. Both materials were diluted with vanadium pentoxide to prepare a series of calibration standards.

Analyst No. 2 analyzed HV-1 by a gravimetric method and by the combustion method, in which a standard iron ore was used as a reference material.

It is evident from Table 4 that good precision was obtained by the combustion method by Analyst No. 1, and that his mean result of 0.34% agrees well with the mean result of 0.35% obtained independently by Analyst No. 2.

TABLE 4

Sulphur Contents Reported by Lab 5

Combustion Method, Analyst No. 1

PR-1 as reference (% Sulphur)		MoS <sub>2</sub> concentrate as reference (% Sulphur)
Bottle 1	0.335	0.336
	0.345	0.346
	0.344	0.345
	0.335	0.335
	0.341	0.342
Bottle 2	0.343	0.344
	0.337	0.337
	0.336	0.337
	0.339	0.340
	0.343	0.344
Mean	0.340	0.341
Standard Deviation	0.004	0.004
<u>Gravimetric and Combustion Methods, Analyst No. 2</u>		
Gravimetric		Combustion (Iron Ore BCS #301 as reference)
Bottle 3	0.36	0.35
	0.35	0.35
Bottle 4	0.35	0.35
	0.34	0.35
Mean	0.35	0.35

## THE CERTIFICATION OF HV-1 FOR COPPER AND MOLYBDENUM

The names of the laboratories that participated in the program to certify ore HV-1 are given below, in alphabetical order. Each of these was arbitrarily assigned a code number so that analytical results could be recorded while preserving the anonymity of the laboratory. The code numbers bear no relation to the alphabetical order of the laboratory names.

The reader will have noted already that no attempt has been made to hide the identity of Lab 5 which is the Metallic Ores Group of the Analytical Chemistry Section of the Mineral Sciences Division, Mines Branch.

### Participating Laboratories

Assayers Limited, Rouyn, Quebec  
Bondar Clegg and Company Limited, Ottawa, Ontario  
Bondar Clegg and Company Limited, Vancouver, British  
Columbia  
Can Test Limited, Vancouver, British Columbia  
Central Laboratories and Technical Services Division,  
Geological Survey of Canada, EMR, Ottawa, Ontario  
Chemex Labs Limited, North Vancouver, British Columbia  
Cominco, Trail, British Columbia  
Crest Laboratories (B.C.) Limited, Vancouver, British  
Columbia  
Extraction Metallurgy Division, Mines Branch, EMR,  
Ottawa, Ontario  
General Testing Laboratories, Vancouver, British Columbia  
Lakefield Research of Canada Limited, Lakefield, Ontario  
Loring Laboratories Limited, Calgary, Alberta

Metallic Minerals Group, Analytical Chemistry Section,  
Mineral Sciences Division, Mines Branch, EMR, Ottawa,  
Ontario

Ontario Department of Mines and Northern Affairs, Toronto,  
Ontario

Sherritt Gordon Mines Limited, Research and Development  
Division, Fort Saskatchewan, Alberta

Sherritt Gordon Mines Limited, Mining and Milling Division,  
Lynn Lake, Manitoba

Special Projects Group, Analytical Chemistry Section,  
Mineral Sciences Division, Mines Branch, EMR, Ottawa,  
Ontario

Spectrochemistry Section, Mineral Sciences Division, Mines  
Branch, EMR, Ottawa, Ontario

Swastika Laboratories Limited, Swastika, Ontario

Technical Services Laboratories, Toronto, Ontario

The New Brunswick Research and Productivity Council,  
Fredericton, New Brunswick

Thunder Bay Testing Limited, Thunder Bay, Ontario

The participating laboratories, with the exception of those within the Mineral Sciences Division of the Mines Branch, each received two randomly selected bottles of HV-1. These "outside" laboratories were requested to determine both total copper and total molybdenum in each bottle, in quintuplicate, by methods of their choice. Although it was not considered a necessity of the standardization program, the participating laboratories were asked to perform the analyses by two different methods. It is evident from Table 6 that most laboratories that had the facilities for a second method complied with the request. As expected, atomic absorption spectrophotometry was the most popular technique for the determination of both elements. Comments on the results by different methods will be made later (page 37). Table 6 also shows that the majority of laboratories submitted the requested number of replicate determinations; only three, including Lab 5, submitted more than 10 results for a particular element and method. These "extra" results were found subsequently



to have a negligible effect on the recommended values that were ultimately assigned for copper and molybdenum (Table 10).

It is to be noted that the laboratories were asked to use a sub-sample of at least two grams for the determination of molybdenum by chemical methods -- most laboratories complied with this request. Where known, the magnitude of the sub-sample weights used by the participants is given in Table 6. This information justifies the conclusion that the contributing laboratories chose sufficiently large sub-sample weights that their sub-sampling errors were substantially less than the laboratory-to-laboratory variations and, consequently, do not affect significantly the recommended values given in Table 10.

Most of the methods used by the participating laboratories were chemical ones which involved an acid decomposition. Because the methods were intended to give total values for copper and molybdenum, it was thought worthwhile to record the acid mixtures used by the laboratories for particular determinations (Table 5). Ten of the sixteen laboratories reporting information on methods of decomposition used hydrofluoric acid to decompose siliceous constituents of the samples. However, by correlating Tables 5 and 6, it can be determined that this treatment did not lead to values that were significantly different from those obtained in laboratories that did not use hydrofluoric acid. This is consistent with the observation, by microscope, that only a negligible fraction of the sulphide minerals in HV-1 remained completely entrapped by silicates.

TABLE 5

Acid Mixtures Used for Decomposition of Sample

Lab No.	Copper		Molybdenum	
	a. a.	other	a. a.	other
Lab 1	Cl, N, S	Cl, N, S	Cl, N, S	--
Lab 2	Cl, N, P	Cl, N, P	Cl, N, P	Cl, N, P
Lab 3	F, Cl, N, P	F, Cl, N, P	F, Cl, N, P	F, Cl, N, P
Lab 4	F, Cl, N	N, Br <sub>2</sub>	F, Cl, S	F, Cl, S
Lab 5	F, Cl, N, P	F, Cl, N, P	F, Cl, N, P	F, Cl, N, P
Lab 6	F, Cl, N, S	F, Cl, N, S	F, Cl, N, S,	F, Cl, N, S
Lab 7	--	F, Cl, P	--	F, Cl, P
Lab 8	N, P	Cl, N, Br <sub>2</sub> , S	N, P	N, P, S
Lab 9	unknown	unknown	unknown	unknown
Lab 10	"	"	"	"
Lab 11	Cl, N, P	Cl, N, P	Cl, N, P	Cl, N, P
Lab 12	unknown	unknown	unknown	unknown
Lab 13	F, Cl, N, P	unknown	F, Cl, N, P	F, Cl, N, P
Lab 14	total decomp.	total decomp.	total decomp.	total decomp.
Lab 15	N	--	--	--
Lab 16	F, Cl, N, P	F, Cl, N, S	F, Cl, N, P	F, Cl, N, P
Lab 17	--	--	--	--
Lab 18	unknown	unknown	unknown	unknown
Lab 19	N, P	--	N, P	Cl, N, S
Lab 20	unknown	--	--	unknown
Lab 21	F, Cl, P	F, Cl, P	F, Cl, P	F, Cl, P
Lab 22	F, Cl, N, S	F, Cl, N, S	F, Cl, N, S	F, Cl, N, S
Lab 23	--	--	--	--

Legend: F = hydrofluoric;  
 Cl = hydrochloric;  
 N = nitric;  
 P = perchloric;  
 S = sulphuric;  
 a. a. = atomic absorption.

## EVALUATION OF STATISTICAL PARAMETERS

The results reported by all participating laboratories are presented in Table 6. The following procedures were used to compute the best values for the statistical parameters.

### A. All Results Treated as Though They Were Independent

Figures 1 and 2 show the cumulative distribution of the results for the two selected elements. The normal parameters, the median, mean, variance, standard deviation, skewness factor, and kurtosis coefficients were computed twice, firstly from all the results, and secondly from those results that deviate from the over-all mean ( $\bar{x}..$ ) by no more than twice the standard deviation ( $s$ ), i. e.  $[(\bar{x}.. - 2s) \leq x_{ij} \leq (\bar{x}.. + 2s)]$ . This rejection was considered necessary to prevent the possible introduction of bias to the estimated means. The results of these computations are presented in Table 7. It is seen that the results that deviate from the mean by more than twice the standard deviation are about 4% of the total frequency. This is a reasonable proportion for normally distributed independent variables. By rejecting these results, both the skewness factor and the kurtosis coefficient were brought nearer to the values of a normal distribution for most elements. The kurtosis coefficient,  $\alpha_4 = m_4/m_2^2$ , is a measure of the sharpness of the peak of the probability density curve; for an ideal distribution  $\alpha_4 = 3$ . The skewness factor,  $\alpha_3 = m_3/\sqrt{m_2^3}$ , is a measure of the symmetry of the curve. Ideally,  $\alpha_3 = 0$ .

In computing these quantities, use is made of the formula:

$$m_r = \frac{\sum_{i=1}^k \sum_{j=1}^{n_i} (x_{ij} - \bar{x}..)^r}{\sum_{i=1}^k n_i}$$

and is the mean of the rth moment of the x values about their mean.

In this, and other inter-laboratory programs conducted by the authors (1,2) it is evident that there were substantial variations between laboratories thereby rendering the results not totally independent of each other. Table 8 shows that most of the laboratories reported lower coefficients of variation than the over-all coefficient of variation. Figures 3 and 4 illustrate this point more clearly. In these figures, the average results by each laboratory for the first bottle were plotted against the average results for the second bottle (1,4). The length of the arms of the crosses represent the estimated standard deviation of the results for the corresponding bottles. These figures show that the analytical results are strongly dependent on the laboratory from which they come. For this reason, the confidence limits, given under A in Table 9 for completeness, are unrealistic; their narrowness emphasizes this point. This type of analysis, however, gives a good estimate of the mean.

#### B. Analysis of Variance Technique

Having suspected the existence of inter-laboratory variations, the results were then treated as though they satisfy the following model (5):

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

where  $x_{ij}$  = the jth result reported by Laboratory i;

$\mu$  = the true value that will be estimated by the over-all mean  $\bar{x}..$ ;

$y_i$  = the discrepancy between the mean of the Laboratory i and the true value; and

$e_{ij}$  = the discrepancy of  $x_{ij}$  from the mean of Laboratory i.

The assumption in this analysis is that both  $y_i$  and  $e_{ij}$  are normally distributed with the means of zero and variances of  $\omega^2$  and  $\sigma^2$ , respectively. The existence of  $\omega^2$  can be detected by comparing the ratio of "between-laboratory" mean squares to "within-laboratory" mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom. The results of this analysis are presented in Table 9. The true value,  $\mu$ , in the above model can be estimated by the over-all mean,  $\bar{x}..$ , thus:

$$\bar{x}.. = \frac{\sum_{i=1}^k \sum_{j=1}^{n_i} x_{ij}}{\sum_{i=1}^k n_i}$$

with variance of this over-all mean being given by:

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

where  $n_i$  = the number of results reported by Laboratory i;

$k$  = the number of laboratories; and

$\omega$  and  $\sigma$  can be estimated from "between-laboratory" and "within-laboratory" mean squares.

The 95% confidence intervals were then calculated according to the number of laboratories.

C. Weighted Mean to Give Minimum Variance

Further investigation of Table 8 and Figures 3 and 4 shows that there is a wide range in the degree of precision obtained by the various laboratories. For this reason, weighting the data by the weighting factor as a function of within-laboratory variance was tried. In this scheme, the results reported by each laboratory were considered as a set of independent variables with a mean of  $\bar{x}_i$ , and a variance of  $\sigma_i^2$ . The weighted mean,  $\bar{x}..$ , was then computed from the following formula (5):

$$\bar{x}.. = \sum_{i=1}^k \frac{a_i}{n_i} \sum_{j=1}^{n_i} x_{ij}$$

in which

$$a_i = \frac{w_i}{\sum_{i=1}^k w_i}$$

and is the weighting factor for Laboratory i, and

$$w_i = \left( w^2 + \frac{\sigma_i^2}{n_i} \right)^{-1}$$

and is the reciprocal of the variance of  $\bar{x}_i$ . This scheme will provide a mean value with a minimum variance of

$$V[\bar{x}..] = \frac{1}{\sum_{i=1}^k w_i}$$

The results of these various schemes of computation are summarized in Table 9 under the corresponding notations, A, B, and C. The values of parameters under A were computed after rejecting all results that deviated from the over-all mean by more than twice the standard deviation. The parameters under B and C were computed from all results submitted.

TABLE 6  
Copper and Molybdenum Analyses of HV-1

	Copper (%)		Molybdenum (%)	
	(a. a.)	(vol.)	(a. a.)	(color.)
HV-1, Lab 1	(a. a.)	(vol.)	(a. a.)	
	0.526	0.53	0.056	
	0.525	0.53	0.056	
	0.523	0.53	0.055	
	0.523	0.53	0.059	
	0.526	0.53	0.056	
	0.526	0.53	0.054	
	0.529	0.52	0.053	
	0.529	0.52	0.053	
	0.533	0.53	0.052	
	0.529	0.53	0.053	
Sample wt, g	2	2	2	
HV-1, Lab 2	(a. a.)	(electro.)	(a. a.)	(color.)
	0.522	0.52	0.06	0.063
	0.526	0.52	0.06	0.059
	0.528	0.515	0.06	0.063
	0.525	0.52	0.06	0.059
	0.526	0.525	0.06	0.059
	0.524	0.52	0.06	0.063
	0.528	0.52	0.06	0.059
	0.526	0.51	0.06	0.059
	0.526	0.51	0.06	0.065
	0.530	0.52	0.06	0.063
Sample wt, g	1	2	5	2
HV-1, Lab 3	(a. a.)	(color.)	(a. a.)	(color.)
	0.523	0.532	0.0567	0.0535
	0.530	0.540	0.0581	0.0537
	0.521	0.536	0.0550	0.0523
	0.528	0.538	0.0592	0.0536
	0.526	0.539	0.0580	0.0547
	0.522	0.531	0.0550	0.0512
	0.528	0.531	0.0539	0.0532
	0.517	0.521	0.0560	0.0528
	0.522	0.536	0.0562	0.0523
	0.530	0.544	0.0564	0.0524
Sample wt, g	3	3	3	3

a. a. = atomic absorption; color. = colorimetric (spectrophotometric);  
 electro. = electrolytic; polar. = polarographic; spect. = emission  
 spectrographic; vol. = volumetric; x. r. f. = X-ray fluorescence.

	Copper (%)		Molybdenum (%)	
	(a. a.)	(vol.)	(a. a.)	(color.)
HV-1, Lab 4	0.533	0.523	0.060	0.061
	0.527	0.532	0.059	0.060
	0.531	0.520	0.063	0.059
	0.529	0.522	0.061	0.060
	0.530	0.524	0.060	0.062
	0.537	0.522	0.057	0.063
	0.533	0.522	0.064	0.058
	0.529	0.524	0.063	0.064
	0.528	0.523	0.061	0.060
	0.539	0.526	0.062	0.063
Sample wt, g	1	0.5-1	2	2
HV-1, Lab 5	(a. a.)	(color.)	(a. a.)	(color.)
	0.526	0.571	0.057	0.055
	0.526	0.529	0.057	0.053
	0.529	0.531	0.055	0.055
	0.529	0.533	0.055	0.063
	0.526	0.535	0.057	0.056
	0.529	0.531	0.054	0.054
	0.526	0.528	0.059	0.056
	0.526	0.555	0.053	0.060
	0.532	0.532	0.055	0.059
	0.529	0.521	0.055	0.057
	0.526			
	0.526			
	0.526			
	0.530			
	0.529			
	0.532			
	0.526			
	0.526			
	0.530			
	0.526			
	0.529			
	0.529			
	0.529			
	0.526			
	0.526			
	0.530			
	0.532			
	0.529			
	0.526			
	0.526			
Sample wt, g	5	5	2	2



	Copper (%)		Molybdenum (%)	
	(a. a.)	(polar.)	(a. a.)	(color.)
HV-1, Lab 6	0.51	0.51	0.055	0.055
	0.51	0.52	0.055	0.056
	0.50	0.52	0.056	0.056
	0.51	0.53	0.055	0.056
	0.50	0.50	0.056	0.056
	0.52	0.53	0.056	0.058
	0.51	0.51	0.057	0.056
	0.52	0.52	0.055	0.057
	0.51	0.52	0.056	0.056
	0.51	0.51	0.056	0.056
Sample wt, g	2	1	2	2
HV-1, Lab 7		(polar.)		(polar.)
		0.54		0.055
		0.54		0.055
		0.53		0.055
		0.54		0.054
		0.53		0.056
		0.54		0.054
		0.54		0.056
		0.54		0.056
		0.54		0.055
		0.54		0.055
Sample wt, g		1		1
HV-1, Lab 8	(a. a.)	(electro.)	(a. a.)	(color.)
	0.52	0.519	0.06	0.062
	0.52	0.512	0.06	0.062
	0.52	0.516	0.06	0.061
	0.52	0.514	0.06	0.062
	0.52	0.517	0.06	0.062
	0.52	0.512	0.06	0.060
	0.52	0.518	0.06	0.061
	0.52	0.514	0.06	0.062
	0.52	0.519	0.06	0.060
	0.52	0.516	0.06	0.062
Sample wt, g	1	5	2	1

	Copper (%)		Molybdenum (%)	
	(a. a.)	(color.)	(a. a.)	(color.)
HV-1, Lab 9	0.500	0.501	0.056	0.055
	0.510	0.501	0.056	0.055
	0.510	0.505	0.056	0.055
	0.510	0.510	0.056	0.055
	0.504	0.510	0.056	0.055
	0.510	0.500	0.057	0.055
	0.500	0.505	0.056	0.055
	0.504	0.500	0.057	0.055
	0.510	0.510	0.056	0.055
	0.504	0.510	0.056	0.055
Sample wt, g	-	-	-	-
HV-1, Lab 10	0.525	0.520	0.054	
	0.524	0.522	0.053	
	0.524	0.521	0.053	
	0.524	0.523	0.054	
	0.524		0.055	
	0.522		0.055	
			0.053	
			0.053	
			0.053	
			0.054	
Sample wt, g	-	-	-	-
HV-1, Lab 11	0.510	0.518	0.054	0.056
	0.505	0.520	0.054	0.055
	0.505	0.519	0.057	0.055
	0.500	0.513	0.055	0.056
	0.505	0.512	0.055	0.055
	0.510	0.516	0.055	0.057
	0.505	0.518	0.054	0.056
	0.510	0.515	0.057	0.057
	0.510	0.518	0.057	0.057
	0.510	0.519	0.057	0.057
			0.057	
			0.055	
			0.057	
			0.057	
			0.056	
			0.056	
			0.057	
			0.057	
			0.056	
			0.056	
Sample wt, g	1	5	1.2	2

	Copper (%)		Molybdenum (%)	
	(a. a.)	(vol.)	(a. a.)	(color.)
HV-1, Lab 12	0.523	0.520	0.056	0.055
	0.522	0.520	0.056	0.057
	0.522	0.515	0.057	0.056
	0.520	0.544	0.056	0.055
	0.519	0.524	0.056	0.056
	0.518	0.524	0.056	0.057
	0.522	0.559	0.056	0.054
	0.518	0.520	0.057	0.055
	0.518	0.534	0.056	0.055
	0.518	0.524	0.056	0.056
		0.500		
		0.525		
		0.525		
		0.475		
		0.525		
		0.520		
		0.525		
		0.522		
		0.517		
		0.520		
Sample wt, g	1	1	2	2
HV-1, Lab 13	(a. a.)	(vol.)	(a. a.)	(color.)
	0.525	0.525	0.0575	0.0567
	0.525	0.524	0.0575	0.0590
	0.530	0.521	0.0588	0.0567
	0.530	0.525	0.0575	0.0582
	0.530	0.523	0.0563	0.0561
	0.525	0.522	0.0575	0.0561
	0.525	0.522	0.0563	0.0590
	0.530	0.524	0.0575	0.0577
	0.542	0.522	0.0563	0.0551
	0.525	0.520	0.0575	0.0577
Sample wt, g	1	2.5	2	1
HV-1, Lab 14	(a. a.)		(a. a.)	
	0.513		0.059	
	0.510		0.059	
	0.513		0.059	
	0.515		0.058	
	0.515		0.058	
	0.520		0.058	
	0.517		0.058	
	0.517		0.059	
	0.522		0.058	
	0.522		0.058	
Sample wt, g	1		1	

	Copper (%)		Molybdenum (%)	
HV-1, Lab 15	(a. a.)	(x. r. f.)		(x. r. f.)
	0.525	0.54		0.04
	0.525	0.56		0.05
	0.525	0.54		0.05
	0.525	0.55		0.05
	0.525	0.52		0.05
	0.538	0.57		0.06
	0.525	0.60		0.06
	0.525	0.59		0.07
	0.525	0.55		0.05
	0.525	0.58		0.06
Sample wt, g	1	-		-
HV-1, Lab 16	(a. a.)	(electro.)	(a. a.)	(color.)
	0.516	0.526	0.055	0.061
	0.519	0.528	0.056	0.062
	0.519	0.528	0.056	0.063
	0.519	0.529	0.059	0.063
	0.525	0.531	0.059	0.063
	0.516	0.529	0.054	0.062
	0.516	0.529	0.057	0.062
	0.525	0.530	0.057	0.063
	0.525	0.531	0.059	0.063
	0.533	0.531	0.060	0.063
Sample wt, g	2	5	5	2
HV-1, Lab 17		(spect.)		(spect.)
		0.495		0.0558
		0.480		0.0548
		0.515		0.062
		0.520		0.070
		0.470		0.0578
		0.515		0.0563
		0.510		0.0738
		0.550		0.0683
		0.510		0.0585
		0.500		0.0525
Sample wt, mg		4		4

	Copper (%)		Molybdenum (%)		
	(a. a.)	(color.)	(a. a.)	(color.)	(grav.)
HV-1, Lab 18	0.522	0.521	0.060	0.057	0.0605
	0.522	0.517	0.056	0.057	0.055
	0.525	0.516	0.056	0.0565	0.059
	0.525	0.519	0.057	0.057	0.0595
	0.522	0.526	0.058	0.0555	0.060
	0.526	0.519	0.058	0.057	0.062
	0.515	0.523	0.057	0.055	0.0625
	0.520	0.519	0.056	0.055	0.055
	0.525	0.517	0.058	0.057	0.057
	0.522	0.517	0.057	0.057	0.054
Sample wt, g	2	2	2	4	2
HV-1, Lab 19	(a. a.)		(a. a.)	(color.)	
	0.509		0.056	0.058	
	0.509		0.057	0.055	
	0.509		0.058	0.058	
	0.509		0.057	0.058	
	0.505		0.056	0.056	
	0.509				
	0.509				
	0.510				
	0.510				
	0.510				
Sample wt, g	2		2	2	
HV-1, Lab 20	(a. a.)			(color.)	
	0.546			0.063	
	0.543			0.064	
	0.549			0.064	
	0.550			0.065	
	0.542			0.063	
Sample wt, g	-			-	
HV-1, Lab 21	(a. a.)	(color.)		(color.)	
	0.536	0.504		0.0571	
	0.528	0.505		0.0557	
	0.525	0.503		0.0572	
	0.533	0.505		0.0557	
	0.523	0.502		0.0559	
	0.530	0.506		0.0572	
	0.526	0.508		0.0557	
	0.528	0.506		0.0559	
	0.527	0.508		0.0570	
	0.531	0.507		0.0557	
Sample wt, g	2	2		2	

	Copper (%)		Molybdenum (%)	
	(a. a.)	(color.)	(a. a.)	(color.)
HV-1, Lab 22	0.505	0.500	0.0600	0.0606
	0.505	0.499	0.0592	0.0600
	0.500	0.504	0.0592	0.0583
	0.500	0.508	0.0592	0.0610
	0.510	0.504	0.0592	0.0587
	0.503	0.508	0.0583	0.0580
	0.483	0.504	0.0613	0.0587
	0.493	0.500	0.0592	0.0585
		0.503		0.0583
		0.503		0.0591
Sample wt, g	1	5	1	5
HV-1, Lab 23		(x. r. f.)		(x. r. f.)
		0.513		0.060
		0.526		0.061
		0.515		0.062
		0.518		0.061
		0.505		0.060
		0.515		0.061
		0.516		0.061
		0.514		0.060
		0.513		0.061
		0.521		0.061
		0.524		
		0.518		

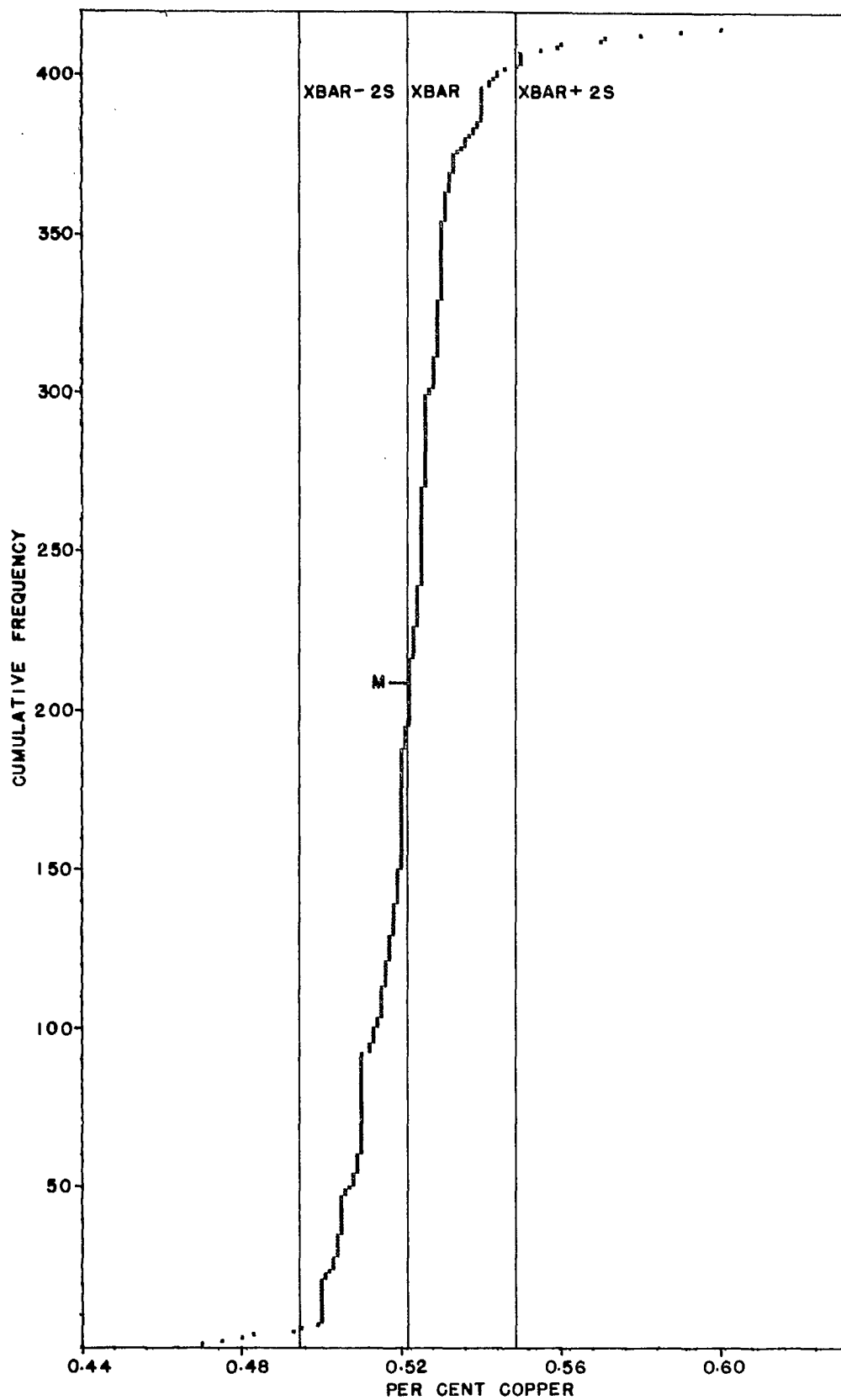


Figure 1. Cumulative Distribution for Copper.

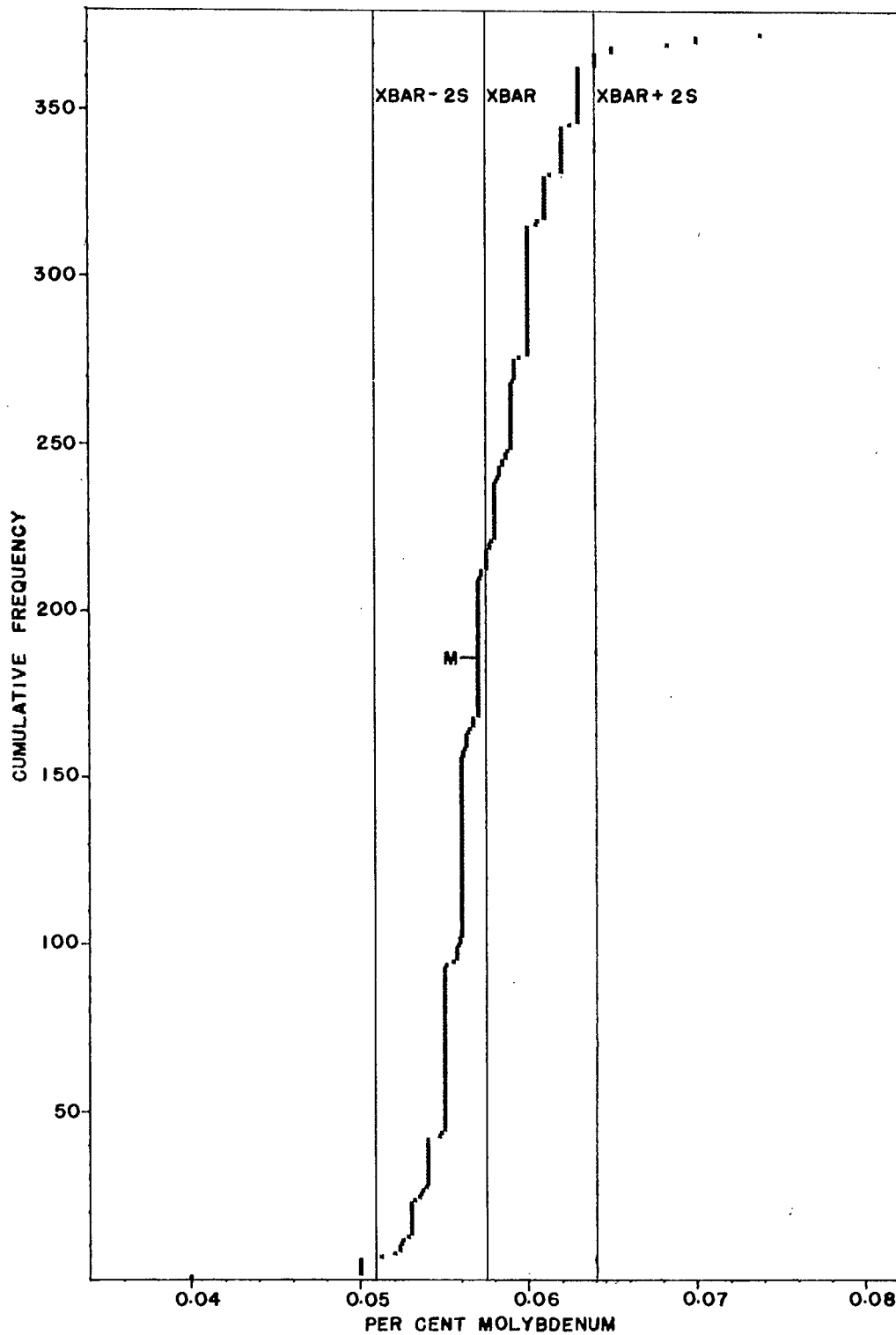


Figure 2. Cumulative Distribution for Molybdenum.



COPPER

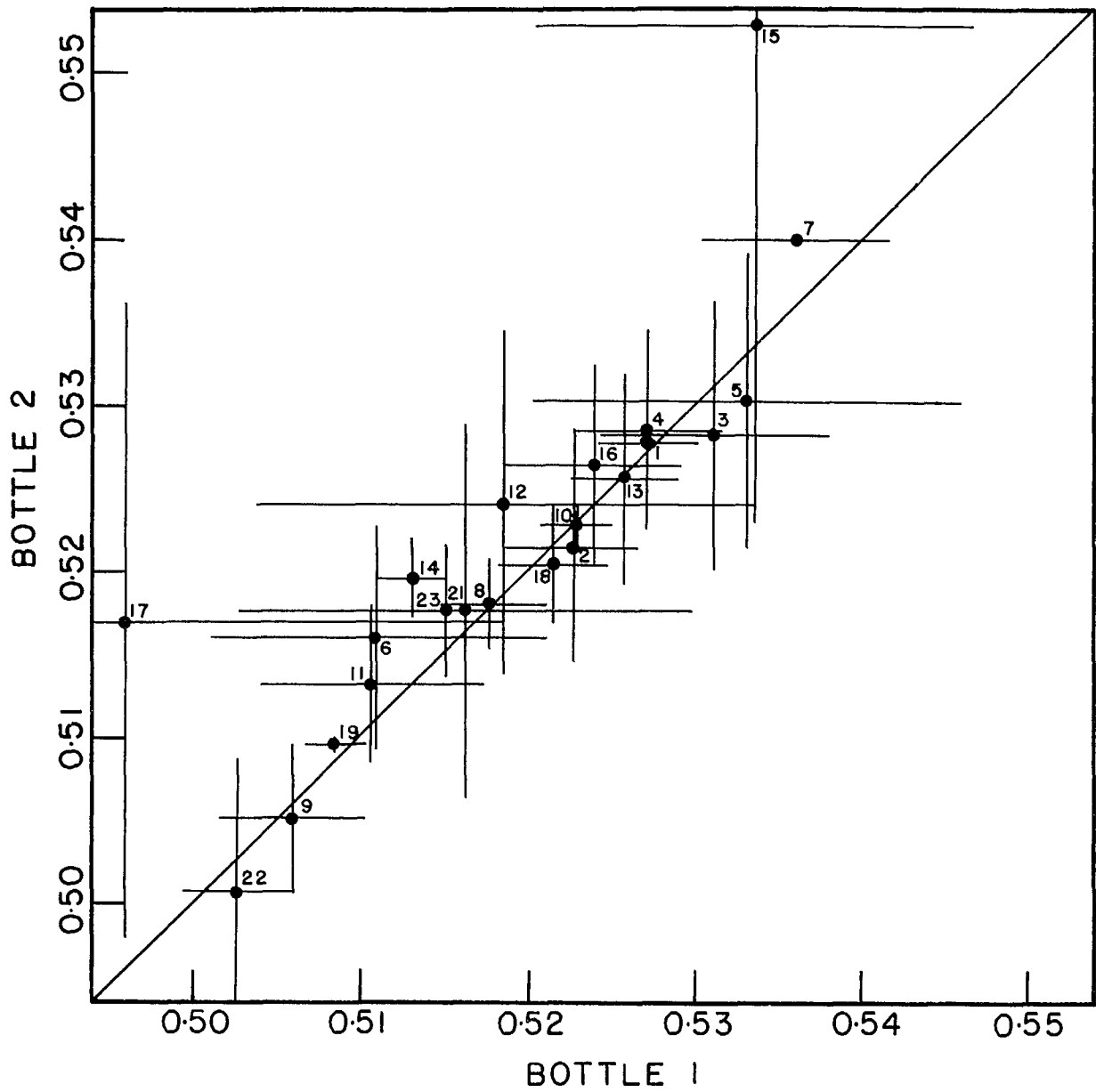


Figure 3. Average Copper Analyses (%) From Each Participating Laboratory. (The crosses indicate one standard deviation on either side of the average for both bottles analyzed.)

MOLYBDENUM

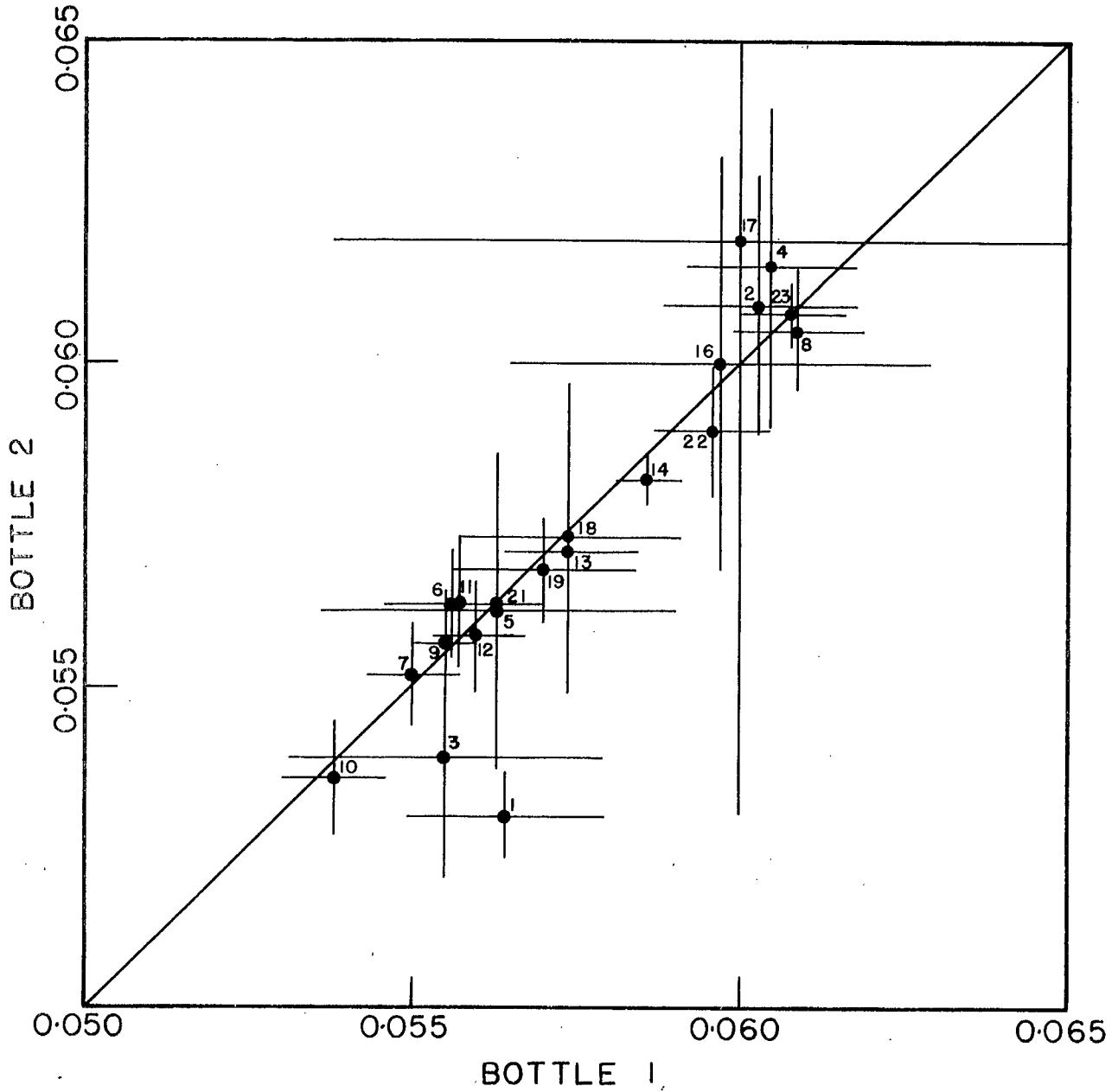


Figure 4. Average Molybdenum Analyses (%) From Each Participating Laboratory. (The crosses indicate one standard deviation on either side of the average for both bottles analyzed).

TABLE 7

Statistical Parameters for HV-1, Based on the Assumption that the Analytical Results are Normally Distributed Random Variables\*

Elements	No. of Observations N	Median M (%)	Mean $\bar{x}$ (%)	Standard Deviation s (%)	Coefficient of Variation c.v. (%)	Skewness Factor $a_3$	Kurtosis Coefficient $a_4$
Cu	415	0.522	0.522	0.014	2.59	0.88	8.67
	397	0.522	0.521	0.010	1.92	-0.24	2.71
Mo	373	0.057	0.058	0.003	5.74	0.41	6.75
	361	0.057	0.057	0.003	4.73	0.41	2.50

\*The first set of parameters for each element was computed from all results; the second set was computed from results that deviate from the over-all means by no more than twice the standard deviation.

TABLE 8

Laboratory Means and Coefficients of Variation for HV-1

Lab. No.	Copper			Molybdenum		
	$n_i$	$\bar{x}_i$	c. v. $_i$ (%)	$n_i$	$\bar{x}_i$	c. v. $_i$ (%)
1	20	0.527	0.69	10	0.055	3.86
2	20	0.522	1.06	20	0.061	2.90
3	20	0.530	1.40	20	0.055	4.04
4	20	0.528	1.01	20	0.061	3.24
5	40	0.530	1.57	20	0.056	4.43
6	20	0.514	1.70	20	0.056	1.36
7	10	0.538	0.78	10	0.055	1.34
8	20	0.518	0.55	20	0.061	1.52
9	20	0.506	0.85	20	0.056	1.22
10	10	0.523	0.31	10	0.054	1.53
11	20	0.512	1.15	30	0.056	1.91
12	30	0.521	2.49	20	0.056	1.41
13	20	0.526	0.93	20	0.057	1.83
14	10	0.516	0.78	10	0.058	0.88
15	20	0.543	4.52	10	0.054	15.62
16	20	0.525	1.08	20	0.060	5.15
17	10	0.507	4.39	10	0.061	11.92
18	20	0.521	0.67	30	0.057	3.62
19	10	0.509	0.29	10	0.057	1.93
20	5	0.546	0.65	5	0.064	1.31
21	20	0.517	2.38	10	0.056	1.26
22	18	0.502	1.22	18	0.059	1.62
23	12	0.517	1.08	10	0.061	1.49
Total	415	0.522	2.59	373	0.058	5.74

TABLE 9  
Statistical Parameters for HV-1

Statistical Parameters	Copper			Molybdenum		
	A	B	C	A	B	C
No. of Participating Laboratories	23	23	23	23	23	23
No. of Observations	397	415	415	361	373	373
Median (%)	0.522	0.522	0.522	0.057	0.057	0.057
Mean (%)	0.521	0.522	0.522	0.057	0.058	0.058
95% Confidence Interval for the Mean (%)						
Low	0.520	0.517	0.517	0.057	0.056	0.057
High	0.522	0.526	0.526	0.058	0.059	0.059

TABLE 10  
Recommended Values for the Means and their Confidence Intervals for Standard Reference Material HV-1

Statistical Parameters	% Copper	% Molybdenum
Mean	0.522	0.058
95% Confidence Interval for the Mean		
Low	0.517	0.056
High	0.526	0.059

## DISCUSSION

It was mentioned previously that most laboratories were asked to obtain analyses for copper and molybdenum by two different methods. It was hoped to determine by this means whether or not significant methodological biases existed. The response to this request was good, as shown in Tables 6 and 11. As expected, most laboratories obtained one set of results by atomic absorption methods and a second set by an alternative method which, for molybdenum, in most cases was a spectrophotometric (colorimetric) one. Table 11 gives the means of the results obtained by specific methods and the corresponding coefficients of variation.

Statistically, there is a significant difference (i. e., 0.0008%) between the a. a. results for molybdenum and the non-a. a. results, however, in practical terms, this difference is trivial.

The recommended value is, of course, the rounded mean of all 373 results.

It is to be noted that the entries in Table 11 under Analytical Method include laboratory-to-laboratory variations; nevertheless, the magnitude of the coefficients of variation are relatively small; this emphasizes the suitability of HV-1 as a reference ore. The larger coefficients of variation, associated with the spectrographic and x. r. f. results for molybdenum, could be due to the relatively small amount of "signal-generating" sample material involved in the method.

It is realized that, in some cases, the results reported in Table 6 imply an unrealistic degree of sensitivity and accuracy for the analytical methods. However, for completeness, all digits in the reported results have been retained. Ultimately, the recommended values for copper and molybdenum are given to two significant figures only.

TABLE 11

Comparison of Atomic Absorption and Other Results for  
Copper and Molybdenum

Analytical Method	Copper			Molybdenum		
	N	$\bar{x}$	c. v. (%)	N	$\bar{x}$	c. v. (%)
Atomic absorption	209	0.521	1.9	173	0.057 <sub>1</sub>	4.0
Spectrophotometric (colorimetric)	60	0.517	3.0	150	0.058	5.5
Volumetric	50	0.524	2.0	-	-	-
Electrolytic	40	0.520	1.2	-	-	-
Polarographic	24	0.527	2.3	10	0.055	1.3
X-ray fluorescence	22	0.536	5.2	20	0.057	11.8
Emission spectro- graphic	10	0.507	4.4	10	0.061	11.9
Gravimetric	-	-	-	10	0.058	5.2
Total, non-a. a.	206	0.522		200	0.057 <sub>9</sub>	
All results	415	0.522		373	0.058	

REFERENCES

1. Staff of Mineral Sciences Division, Molybdenum Ore, PR-1: Its Characterization and Preparation for Use as a Standard Reference Material. Mines Branch Technical Bulletin, TB 139 (1971).
2. Members of the Staff of the Mineral Sciences Division (compiled by G. H. Faye), Zinc-Tin-Copper-Lead Ore, MP-1: Its Characterization and Preparation as a Standard Reference Material. Mines Branch Technical Bulletin, TB 155 (1972).
3. Hanson, G.R., Let's talk about assaying. Northern Miner, p. 7 (Oct. 15, 1970).
4. Youden, W.J., Graphical Diagnosis of Interlaboratory Test Results. Ind. Qual. Control., 15, 1-5 (1959).
5. Brownlee, K.A., Statistical Theory and Methodology in Sciences. John Wiley and Sons, Inc., New York (1961).



