R. C. McAdam

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OTTAWA

ZINC-TIN-COPPER-LEAD ORE, MP-1: ITS CHARACTERIZATION AND PREPARATION FOR USE AS A STANDARD REFERENCE MATERIAL

Members of the Staff of the Mineral Sciences Division

(Compiled by G. H. Faye)

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by

Members of the Staff of the Mineral Sciences Division

(Compiled by G. H. Faye*)

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SYNOPSIS

The Mines Branch of the Department of Energy, Mines and Resources has undertaken a program to prepare a number of ores of metallic minerals for use as standard reference materials. This report describes the characterization and preparation of the second ore in the program, a zinc-tin-copper-lead ore, MP-1, from New Brunswick.

The mineralogical, geological and chemical characteristics of MP-1 are given as well as some details of methods used for its comminution, blending, and for assessing its homogeneity. Nineteen laboratories participated in the program by providing analyses for selected elements. The recommended mean values for these are: Zn - 16.33%; Sn - 2.50%; Cu - 2.15%; Pb - 1.93%; Mo - 0.014%: In - 0.071%; Bi - 0.025%; As - 0.79%; Ag - 59.5 ppm. The analytical results and the evaluation of statistical parameters for the above elements are reported.

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Direction des mines

Bulletin Technique TB 155

LE MINERAI DE ZINC-ÉTAIN-CUIVRE-PLOMB, MP-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)*

RÉSUMÉ

La Direction des mines du ministère de l'Énergie, des Mines et des Ressources a entrepris un programme pour un nombre de minerais de minéraux métalliques utilisés comme matériaux types de référence. Ce rapport décrit la caractérisation et la préparation du second minerai dans le programme, un minerai de zinc-étain-cuivre-plomb, MP-1, du Nouveau Brunswick.

Les caractéristiques minéralogiques, géologiques et chimiques du MP-1 sont données ainsi que quelques détails des méthodes utilisées pour sa pulvérisation, son mélange et pour l'évaluation de sa homogénéité. Dix-neuf laboratoires ont participé dans le programme en fournissant les analyses pour les éléments choisis. La moyenne recommandée pour ceux-là sont: Zn-16.33%; Sn-2.50%; Cu-2.15%; Pb-1.93%; Mo-0.014%: In-0.071%; Bi-0.025%; As-0.79%; Ag-59.5 ppm. Les résultats analytiques et l'évaluation des paramètres statistiques pour les éléments ci-dessus sont donnés.

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INTRODUCTION

This report is the second in a series describing the preparation and characterization of standard reference ores of metallic minerals in a program of the Mines Branch of the Department of Energy, Mines and Resources. The first ore to be standardized was a molybdenum-bismuth ore, PR-1; the details of its characterization and certification have been given in Technical Bulletin TB 139 (1). A similar approach has been taken in the acquisition, preparation and analysis of the second ore, MP-1.

MP-1 is a zinc-tin-copper-lead ore from the Brunswick Tin Mines Limited deposit in southwestern New Brunswick and was selected because of its mineralogical and chemical complexity. For many years analysts have complained about problems associated with the analysis of material that is similar to MP-1. No doubt inter-element interferences and the refractory nature of some of the minerals have contributed to these difficulties.

Nineteen laboratories mainly commercial and industrial, participated in the program to standardize MP-1 by providing analyses for zinc, tin, copper, lead, arsenic, indium, bismuth, molybdenum, tungsten, and silver. Each laboratory was asked to perform 10 determinations of each element; however, some submitted more replicate determinations than requested. Despite the complexity of MP-1 and the relatively low concentrations of certain of the ten selected elements, the results were sufficiently satisfactory, in a statistical sense, to permit the assignment of preferred values for nine of these elements.

Interestingly, the analytical results show that there is a significant difference between the results of volumetric and instrumental methods for determining tin; also, that there is a significant difference between the silver results obtained by fire-assay methods and those obtained by other methods.

This report describes the work that was done to prepare and characterize MP-1 as a standard reference ore. All the analytical results are reported, so that, if desired, the reader may make his own evaluations, as well as consider the conclusions of the authors.

MINERALOGICAL COMPOSITION OF MP-1

The material for ore standard MP-1 was taken from the 900-foot adit of the deposit of Brunswick Tin Mines Limited in southwestern New Brunswick, Canada. It consists of material from two sulphide veins blended with a small amount of mineralized rock. The sulphide veins contain large amounts of fluorite, sphalerite, chalcopyrite, galena, stannite, and cassiterite, and small amounts of arsenopyrite, wolframite, molybdenite, and native bismuth. The mineralized rock, the main ore material in this deposit, consists largely of quartz, topaz, kaolinite, chlorite, and fluorite; is enriched in wolframite, molybdenite, native bismuth, and arsenopyrite, and contains small amounts of sphalerite, chalcopyrite, tennantite, stannite, and galena. The calculated mineralogical composition of MP-1 is given in Table 1.

COMMINUTION, BLENDING, AND BOTTLING OF MP-1

The coarse ore was crushed and dry-ground to minus 200 mesh using conventional milling equipment. The material, weighing approximately 350 lb was blended in a 45-gallon, baffled, mixing drum for 20 hours. Upon emptying the blender, the bulk ore was randomly sampled and tested for homogeneity by techniques described below. These tests indicated a uniform product. Subsequently, the ore was packaged in 782 bottles each containing 200 g of material; these were stored in 24-bottle cases. A record was kept of bottle and case numbers, with the object of detecting possible bottle-to-bottle or case-to-case heterogeneity after distribution

TABLE 1

Calculated Mineralogical Composition of MP-1

Minerals		Calculated Mineralogical Composition (wt %)
Sphalerite*	ZnS-24.0, FeS-0.8, CdS-0.1, InS-0.1, MnS-0.07	25.1
Chalcopyrite	Cu-1.3, Fe-1.2, S-1.3	3.8
Stannite-Kesterite	Cu-0.8, Sn-0.8, Fe-0.2, Zn-0.2, S-0.9	2.9
Galena	Pb-1.9, S-0.3	2.2
Cassiterite	Sn-1.6, O-0.4	2.0
Arsenopyrite	As-0.8, Fe-0.6, S-0.3	1.7
Pyrite	Fe-0.6, S-0.7	1.3
Bismuth		0.03
Wolframite	WO_3-0.03, FeO+MnO-0.01	0.04
Molybdenite	Mo-0.01, S-0.01	0.02
Quartz	SiO_2-34.7	34.7
Chlorite	SiO_2-1.9, Al_2O_3-1.7, FeO-3.0, MgO-0.1, H_2O-0.3	7.0
Fluorite	Ca-3.4, F-3.2	6.6
Topaz	SiO_2-1.8, Al_2O_3-2.9, F-0.9, H_2O-0.5	6.1
Kaolinite	SiO_2-2.7, Al_2O_3-2.3, H_2O-0.8	5.8
Feldspar	SiO_2-0.5, Al_2O_3-0.1, K_2O-0.1, Na_2O-0.1	0.8
Rutile	TiO_2-0.05	0.05
Total		100.14

*The metals Fe, Cd, In and Mn are incorporated in the lattice of sphalerite, but some In also occurs as the mineral roquesite.

to the laboratories participating in the analytical aspect of the program.

TESTS FOR HOMOGENEITY

After blending, six 200-g random samples of the bulk ground ore were taken for homogeneity tests before bottling. These samples were analyzed for tin and lead by an X-ray fluorescence technique. Five replicate analyses were performed on each sample. One-way analysis of variance of the results showed that there was no significant difference between the samples with respect to their tin and lead contents.

To verify the apparent homogeneity of MP-1, five bottles were selected, at random, from the total stock of bottles. Six samples from each of the five bottles were analyzed for tin and zinc by the Analytical Chemistry Section of the Mineral Sciences Division (Lab 17). The sample weights used were 1.000 and 0.5000 g, respectively, for these determinations. A one-way analysis of variance of the 30 results for each element showed that, chemically, there was no significant difference between the bottles insofar as tin and zinc contents were concerned.

Having found ore MP-1 to be suitably homogeneous, randomly-selected bottles of the ore were sent to the participating laboratories, a list of which is given on pages 9 and 10.

Most laboratories received two bottles of MP-1 and were requested to analyze five samples from each bottle for zinc, tin, copper, lead, arsenic, indium, bismuth, molybdenum, tungsten, and silver, by methods of their own choice. The reported results 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 11 to 20. It is apparent that the analyses from the majority of laboratories do not show evidence of inhomogeneity between the bottles they received. It is concluded, therefore, that MP-1 is suitable for the purpose for which it was intended, i.e., for reference purposes in analytical methods in which the sample weights used are $\gtrsim 0.5$ g.

TABLE 2

Summary of the *t*-Test Results between Bottles within Each Laboratory

Laboratory Number	Elements									
	Zn	Sn	Cu	Pb	Mo	W	In	Bi	As	Ag
1	A	A	A	A	A	A	A	A	A	A
2	A	A	A	A	A	A	A	A	A	A
3	R	A	-	-	A	-	-	-	A	A**
4	A	A	A	A	A	-	A	A	A	A
5	R	-	R	-	A	A	R	-	-	A
6	A	A	-	A	-	-	-	-	A	A
7	A	A	A	A	A	A	-	A	A	A
8	A	A	A	A	A	-	-	A	A	A
9	A	A	A	A	R	A	A	A	A	A
10	A	-	-	A	A	-	-	-	A	A
11	A	A	R	A	A	A	R	A	A	-
12	A*	A	R	A	A	A	A	-	A	-
13	A	A*	A	A	A	R	-	A	A	-
14	A	A	R	A	A	A	A	A	R	-
15	A	-	A	A	A	-	-	-	A	A
16	-	A	A	A	-	-	A	-	-	-
17	A	A	A	A	A	A	-	A	A	R***
18	A	-	A	A	-	-	-	A	A	A
19	-	R	-	R	-	-	-	-	R	-

A = Null hypothesis accepted, i.e., there is no evidence of inhomogeneity.
R = Null hypothesis rejected, i.e., there is evidence of inhomogeneity.
\- = Insufficient results available for a meaningful statistical analysis.
* = AA method rejects the null hypothesis.
** = Fire-assay method rejects the null hypothesis.
*** = Fire-assay method accepts the null hypothesis.

CONTRIBUTION OF THE ANALYTICAL CHEMISTRY SECTION MINERAL SCIENCES DIVISION (Lab-17)

In addition to contributing the results of 10 replicate determinations for each element to be certified, Lab-17 performed the analyses in the homogeneity tests described above. This accounts for the inordinately large number of results for zinc and tin listed under Lab-17 in Table 4.

It is realized that this gives undue statistical weight to the contribution of Lab-17 for zinc and tin. However, because the results lie close to the mean values for all laboratories, the overall effect of this 'anomaly' is small. This 'weight problem' arises because it is not possible to select meaningfully only 10 of the 30 results reported for zinc and tin.

The situation is similar for the silver results obtained by Lab-17. Here, however, it is a matter of results obtained by more than one method that are being reported.

A complete analysis of a reference material such as MP-1 is desirable, Therefore, Lab-17 provided additional analytical results for this purpose. These results are presented in Table 3, together with a few analyses from certain other participating laboratories. It is to be noted that the recommended values (Table 8) for the "certified" elements have been included in Table 3. Each entry in Table 3 is the average of at least two determinations. Because the procedural details of the methods used by Lab-17 were similar to those of well-established methods, these are not presented here.

TABLE 3

Provisional Chemical Analyses for MP-1

O	-	26.8[a] wt %	Zn	-	16.3 wt %
Si	-	19.4	Sn	-	2.50
Al	-	3.63	Cu	-	2.15
Fe	-	5.68	Pb	-	1.93
Mg	-	0.04	As	-	0.79
Ca	-	3.36	Cd	-	0.07[c]
K	-	0.10	In	-	0.07
Na	-	0.01	Bi	-	0.03
Ti	-	0.07	W	-	0.02
Mn	-	0.05	Mo	-	0.01
S	-	11.8			
H_2O at 980°C	-	1.57			
C	-	0.10			
F	-	4.04[b]			

Total	-	100.5
Corrected for O in H_2O	-	1.4
Corrected Total		99.1

a - Determined by neutron-activation analysis in Mineral Sciences Division.

b - Analysis by Lab-11.

c - Average of results from Labs 11 and 19.

THE CERTIFICATION OF MP-1 FOR SELECTED ELEMENTS

The names of the laboratories that participated in the program to certify ore MP-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-17, 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
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
Falconbridge Nickel Mines Limited, Metallurgical Laboratories, Thornhill, 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
Noranda Research Centre, Pointe Claire, Quebec
Ontario Department of Mines and Northern Affairs, Toronto, Ontario
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

The participating laboratories, with the exception of those within the Mineral Sciences Division of the Mines Branch, each received two randomly selected bottles of MP-1. These "outside" laboratories were requested to determine, in quintuplicate, as many as possible of the elements: zinc, copper, tin, lead, arsenic, bismuth, molybdenum, tungsten, indium, and silver, by methods of their own choice. It is known that for some determinations, certain laboratories processed the samples of MP-1 together with batches of other samples undergoing 'routine' analysis. Other laboratories, however, treated the samples of MP-1 separately, and perhaps with care that might not be excercised during the analysis of 'routine' samples. The importance of the 'approach' taken by the various laboratories cannot be assessed easily. However, on the basis of the results listed in Table 4, this matter seems subordinate to the nature of the methods used.

Table 4 also shows that certain laboratories performed the required five analyses for each element on each bottle, but used different methods for each bottle. Also, in certain cases 'extra' results, obtained by a second method, were reported. Although these laboratories did not follow the program instructions completely, all results were used in the evaluation of statistical parameters, because there were no objective criteria available for rejecting any of the analyses. Indeed, as will be seen, the reporting of the results obtained by more than one method of analysis is useful in detecting biases associated with specific methods.

A number of laboratories submitted information on sample weights with their analytical results; these are included in Table 4. Although the information is not complete, it can be concluded that the reporting laboratories chose sufficiently large sub-sample weights so that their sub-sampling errors (2), which is one component of the within-laboratory error, are substantially less than the laboratory-to-laboratory variations, and, consequently, they do not affect the recommended values given in Table 8.

EVALUATION OF STATISTICAL PARAMETERS

The results reported by all participating laboratories are presented in Table 4. 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 to 10 show the cumulative distribution of the results for each of the ten 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 overall 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 5. It is seen that the results that deviate from the mean by more than twice the standard deviation are about 7% 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:

$$m_j = \frac{\sum_{i=1}^{i=N} (x_i - \bar{x})^j}{N}$$

and is the mean of the jth moment of the x values about their own mean value.

A closer examination of the results of the analyses revealed that there was a substantial variation between laboratories, thereby rendering the results not totally independent of each other. Table 6 shows that all the laboratories reported lower coefficients of variation than the overall coefficient of variation. Figures 11 to 20 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, 3). 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 results of the analyses are strongly dependent on the laboratory from which they come. For this reason, considering the data as a set of independent variables results in confidence intervals that are unrealistic, although this 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(4):

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

where
- x_{ij} = the jth result reported by Laboratory i;
- μ = the true value that will be estimated by the overall 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 ω^2 and σ^2, respectively. The existence of ω^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 7.

The true value, μ, in the above model can be estimated by the overall mean, $\bar{x}_{..}$, thus:

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

with variance of this overall mean being given by:

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

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

k = the number of laboratories; and

ω and σ 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 6 and Figures 11 to 20 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 σ_i^2. The weighted mean, $\bar{x}_{..}$, was then computed from the following formula(4):

$$\bar{x}_{..} = \sum_{i=1}^{i=k} a_i \bar{x}_{i.}$$

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

and is the weighting factor for Laboratory i. and

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

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

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

The results of these various schemes of computation are summarized in Table 7 under the corresponding notations, A, B, and C. The values of parameters under A were computed after rejecting all results that deviated from the overall mean by more than twice the standard deviation. The parameters under B and C were computed after rejecting the results of entire laboratories whose laboratory means deviated from the overall mean by more than twice the inter-laboratory standard deviation.

TABLE 4

Results of Analysis of MP-1

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-1	16.29(polar.)	2.35(polar.)	2.17(polar.)	1.97(a.a.)	0.013(a.a.)	0.016(color.)	0.069(a.a.)	0.024(a.a.)	0.71(vol.)	66.9(a.a.)
	16.27	2.34	2.18	1.97	0.013	0.015	0.070	0.025	0.74	67.2
	16.33	2.33	2.17	1.98	0.012	0.016	0.065	0.025	0.71	66.2
	16.26	2.34	2.18	1.96	0.014	0.015	0.072	0.024	0.74	66.5
	16.35	2.33	2.17	1.97	0.014	0.014	0.072	0.024	0.71	66.5
	16.29	2.34	2.17	1.97	0.014	0.014	0.066	0.023	0.71	67.2
	16.28	2.33	2.18	1.98	0.014	0.015	0.065	0.026	0.74	66.5
	16.30	2.34	2.17	1.97	0.012	0.016	0.072	0.025	0.71	66.5
	16.32(a.a.)	2.35	2.18(a.a.)	1.97	0.012	0.016	0.070	0.025	0.71	66.2
	16.27	2.33	2.18	1.97	0.014	0.015	0.070	0.024	0.71	66.5
Sample wt, g	-	-	-	-	-	-	-	-	-	-

a.a. = atomic absorption; amp = amperometric; color. = colorimetric; e.f.p. = emission flame photometry; grav. = gravimetric;
x.r.f. = X-ray fluorescence

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-2	16.38(vol.)	2.486(a.a.)	2.15(a.a.)	1.92(a.a.)	0.0132(a.a.)	0.028(color.)	0.074(a.a.)	0.0260(a.a.)	0.77(vol.)	58 (a.a.)
	16.38	2.486	2.15	1.92	0.0118	0.028	0.074	0.0250	0.77	58
	16.33	2.512	2.20	2.00	0.0134	0.029	0.074	0.0275	0.78	62
	16.38	2.460	2.20	2.00	0.0128	0.026	0.073	0.0250	0.78	60
	16.40	2.390	2.15	1.98	0.0120	0.030	0.073	0.0260	0.80	58
	16.40	2.475	2.18	1.98	0.0131	0.029	0.073	0.0260	0.80	56
	16.38	2.486	2.20	1.92	0.0132	0.027	0.074	0.0250	0.78	57
	16.38	2.486	2.25	1.96	0.0138	0.028	0.076	0.0230	0.78	57
	16.33	2.491	2.25	2.00	0.0140	0.025	0.072	0.0250	0.78	60
	16.38	2.491	2.15	1.98	0.0128	0.025	0.072	0.0235	0.78	60
	16.30	2.462	2.15	2.00	0.0125		0.074	0.0260	0.79	60
	16.40	2.48	2.18	2.00	0.0136		0.074	0.0260	0.79	58
		2.26(vol.)	2.11(vol.)	2.00(vol.)	0.0130(color.)					57 (f.a.)
		2.29	2.11	2.00	0.0125					60
		2.29		1.98	0.0120					58
		2.26		2.00	0.0130					57
				1.96	0.0138					58
				2.01	0.0136					
				1.95	0.0136					
				1.97	0.0128					
				1.98	0.0125					
				1.95	0.0125					
				1.96	0.0128					
				2.01	0.0128					
Sample wt, g	-	-	0.5	0.5	-	-	0.5	0.5	-	-

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-3	16.42(vol.)	2.15(vol.)	2.28(a.a.)	1.79(a.a.)	0.015(a.a.)			0.035(a.a.)	0.83(vol.)	58 (a.a.)
	16.42	2.15	2.28	1.79	0.016			0.035	0.83	58
	16.42	2.15	2.28	1.79	0.015			0.035	0.83	57
	16.40	2.18	2.28	1.79	0.015			0.035	0.83	57
	16.40	2.15	2.28	1.79	0.015			0.035	0.83	57
	16.47	2.16	2.28	1.79	0.015			0.030	0.83	57
	16.47	2.16	2.28	1.79	0.015			0.030	0.83	58
	16.45	2.16	2.28	1.79	0.015			0.030	0.83	58
	16.47	2.16	2.28	1.79	0.016			0.030	0.83	57
	16.45	2.15	2.28	1.79	0.015			0.030	0.83	57
										56.6(f.a.)
										56.3
										56.6
										56.6
										56.3
										55.9
										55.9
										55.6
										55.9
										55.9
Sample wt, g	1.0	1.0	0.5	0.5	2.0			1.0	1.0	0.5

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-4	16.44(a. a.)	2.15(x. r. f.)	2.04(a. a.)	2.04(a. a.)	0.040(a. a.)		0.094(a. a.)	0.056(a. a.)	0.89(x. r. f.)	65.9(a. a.)
	16.56	2.20	2.01	1.99	0.041		0.090	0.051	0.88	59.7
	16.63	2.17	2.10	1.98	0.038		0.091	0.051	0.83	58.3
	16.52	2.16	2.02	2.03	0.040		0.095	0.050	0.86	59.3
	16.45	2.18	2.07	2.01	0.039		0.093	0.048	0.87	58.7
	16.33	2.10	2.04	1.97	0.041		0.090	0.050	0.88	60.0
	16.47	2.10	2.04	2.08	0.038		0.091	0.049	0.89	59.7
	16.49	2.15	2.02	2.02	0.035		0.090	0.051	0.90	59.0
	16.53	2.20	2.01	2.08	0.039		0.092	0.050	0.84	58.3
	16.54	2.20	2.08	2.02	0.041		0.093	0.048	0.85	61.7
Sample wt, g	1.0	-	1.0	1.0	1.0		1.0	1.0	-	1.0

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-5	15.59(vol.)	2.21(vol.)	2.15(polar.)	1.74(polar.)	0.042(color.)	0.012(color.)	0.066(color.)	0.019(color.)	0.924(color.)	60 (color.)
	15.59	2.21	2.17	1.73	0.045	0.016	0.066	0.019	0.924	64
	15.62	2.21	2.15	1.73	0.045	0.013	0.068	0.019	0.924	65
	15.59	2.21	2.17	1.75	0.046	0.011	0.065	0.019	0.924	65
	15.62	2.21	2.15	1.74	0.042	0.011	0.067	0.013	0.924	65
	15.38	2.25	2.11	1.78	0.045	0.011	0.062	0.013	0.910	62
	15.41	2.25	2.11	1.78	0.045	0.013	0.065	0.013	0.910	63
	15.41	2.25	2.12	1.78	0.046	0.011	0.061	0.014	0.910	64
	15.38	2.25	2.13	1.78	0.048	0.015	0.060	0.014	0.910	62
	15.41	2.25	2.13	1.78	0.048	0.015	0.065		0.910	64
Sample wt, g	0.5	0.5	0.5	2.0	0.25	0.25	1.0	1.0	-	1.0

	Zn(%)	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-6	16.2(a.a.)	2.55(a.a.)	2.13(a.a.)	1.90(a.a.)	0.013(a.a.)	0.03(color.)		0.027(a.a.)	0.77(vol.)	62 (a.a.)
	16.3	2.59	2.13	1.88	0.013	0.03		0.027	0.77	62
	16.2	2.61	2.10	1.90	0.013	0.03		0.027	0.79	62
	16.3	2.57	2.13	1.90	0.013	0.03		0.027	0.78	62
	16.2	2.61	2.13	1.88	0.013	0.03		0.027	0.79	62
	16.3(vol.)	2.58(vol.)	2.09	1.92(vol.)	0.014	0.03		0.027	0.77	62
	16.2	2.65	2.12	1.94	0.014	0.03		0.027	0.80	62
	16.1	2.67	2.09	1.90	0.014	0.03		0.027	0.79	61.5
	16.1	2.58	2.12	1.90	0.014	0.03		0.027	0.79	61.5
	16.3	2.55	2.09	1.92	0.014	0.03		0.027	0.79	62.
Sample wt, g	0.5	1.0	2.0	1.0	2.0	1.0		2.0	1.0	5.0

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-7	16.12(vol.)	2.08(vol.)	2.12(vol.)	1.93(vol.)	0.012(a.a.)	0.016(color.)		0.025(a.a.)	0.78(vol.)	59.0(f.a.)
	16.22	2.05	2.13	1.98	0.014	0.019		0.026	0.77	60.0
	16.15	2.12	2.11	1.92	0.014	0.021		0.026	0.78	58.3
	16.12	2.23	2.08	1.94	0.012	0.019		0.026	0.77	58.7
	16.20	2.22	2.08	1.97	0.014	0.021		0.027	0.76	58.7
	16.12	2.01	2.12	1.90	0.014	0.019		0.025	0.77	58.0
	16.07	2.07	2.12	1.94	0.014	0.021		0.025	0.77	59.0
	16.05	2.21	2.13	1.92	0.013	0.024		0.026	0.77	56.6
	16.15	2.16	2.12	1.94	0.014	0.019		0.026	0.78	59.0
	16.22	2.21	2.08	1.95	0.013	0.022		0.027	0.76	58.7
Sample wt, g	1.0	1.0	1.0	1.0	1.0	2.0		1.0	2.0	14.0

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-8	16.21(vol.)	2.65(vol.)	2.16(vol.)	1.96(a.a.)	0.01(a.a.)	0.01(color.)		0.03(volor.)	0.78(vol.)	51.5(f.a.)
	16.21	2.62	2.16	1.96	0.02	0.01		0.02	0.76	52.8
	16.23	2.67	2.19	1.94	0.02	0.01		0.03	0.80	53.5
	16.19	2.64	2.19	1.96	0.01	0.01		0.03	0.78	54.2
	16.24	2.64	2.18	1.94	0.01	0.01		0.02	0.80	54.2
	16.19	2.68	2.16	1.88	0.01	0.01		0.02	0.80	54.9
	16.24	2.64	2.18	1.94	0.01	0.01		0.03	0.76	51.5
	16.16	2.62	2.16	1.92	0.02	0.01		0.03	0.78	53.5
	16.21	2.62	2.19	1.96	0.02	0.01		0.03	0.78	52.8
	16.21	2.64	2.18	1.96	0.02	0.01		0.03	0.76	54.2
Sample wt, g	1.0	1.0	1.0	1.0	2.0	1.0	-	1.0	1.0	14.6

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-9	16.31(vol.)	2.15(vol.)	2.24(a.a.)	1.97(a.a.)	0.017(color.)	0.034(color.)	0.076(a.a.)	0.024(a.a.)	0.76(vol.)	61.7(a.a.)
	16.36	2.19	2.24	1.97	0.018	0.036	0.076	0.024	0.77	61.7
	16.37	2.22	2.27	1.97	0.018	0.036	0.076	0.025	0.77	62.4
	16.39	2.24	2.27	1.98	0.019	0.037	0.076	0.026	0.77	62.4
	16.44	2.25	2.27	2.00	0.020	0.037	0.078	0.027	0.77	62.4
	16.26	2.19	2.23	1.95	0.016	0.035	0.076	0.024	0.76	62.1
	16.31	2.20	2.25	1.95	0.016	0.036	0.076	0.025	0.76	62.4
	16.31	2.22	2.25	1.95	0.016	0.036	0.078	0.026	0.76	62.4
	16.31	2.25	2.25	2.00	0.017	0.036	0.078	0.026	0.76	62.8
	16.37	2.27	2.27	2.00	0.017	0.037	0.078	0.026	0.77	62.8
Sample wt, g	1.0	2.0	1.0	1.0	5.0	2.0	1.0	2.0	2.0	2.0

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-10	16.21(polar.)		2.15(vol.)	1.90(a.a.)	0.012(a.a.)			0.025(a.a.)	0.863(vol.)	56.1(a.a.)
	16.21		2.15	1.90	0.012			0.025	0.842	56.0
	16.12		2.14	1.89	0.012			0.025	0.833	56.1
	16.18		2.14	1.89	0.012			0.025	0.829	56.1
	16.21		2.14	1.89	0.012			0.025	0.842	56.1
	16.23		2.13	1.90	0.012			0.025	0.833	56.1
	16.21		2.13	1.89	0.012			0.025	0.853	56.1
	16.19		2.13	1.89	0.012			0.025	0.833	56.1
	16.19		2.13	1.89	0.013(color.)			0.025	0.838	56.0
	16.18		2.13	1.88	0.013			0.025	0.839	55.9
			2.15(a.a.)	1.886(polar.)						
			2.16(polar.)	1.888						
Sample wt, g	-	-	-	-	-	-	-	-	-	-

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-11	16.24(vol.)	2.29(polar.)	2.10(polar.)	1.85(polar.)	0.013(a.a.)	0.021(x.r.f.)	0.068(a.a.)	0.024(a.a.)	0.73(vol.)	
	16.14	2.41	2.12	1.83	0.014	0.021	0.068	0.024	0.74	
	16.14	2.31	2.09	1.85	0.014	0.018	0.069	0.024	0.73	
	16.17	2.41	2.12	1.83	0.014	0.018	0.068	0.023	0.73	
	16.17	2.37	2.09	1.87	0.015	0.018	0.067	0.023	0.74	
	16.17	2.39	2.12	1.85	0.014	0.020	0.069	0.023	0.77	
	16.14	2.34	2.13	1.84	0.015	0.020	0.068	0.024	0.76	
	16.20	2.31	2.14	1.84	0.014	0.018	0.070	0.023	0.0	
	16.14	2.43	2.12	1.84	0.014	0.021	0.070	0.023	0.73	
	16.17	2.35	2.12	1.83	0.014	0.021	0.069	0.024	0.75	
	16.12(polar.)		2.11(a.a.)							
			2.11							
			2.11							
			2.09							
			2.10							
			2.09							
			2.09							
			2.13							
			2.15							
			2.15							
Sample wt, g	-	-	-	-	1.0	-	-	-	-	-

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-12	16.10(amp.)	2.72(a.a.)	2.23(color.)	1.85(vol.)	0.0131(color.)	0.0205(color.)	0.068(vol.)		0.768(vol.)	
	16.10	2.76	2.21	1.90	0.0131	0.0218	0.968		9.770	
	16.10	2.76	2.20	1.88	0.0128	0.0223	0.071		0.769	
	16.15	3.00	2.27	1.87	0.0132	0.0208	0.072		0.760	
	16.18	2.74	2.19	1.85	0.0127	0.0218	0.0685(e.f.p.)		0.775	
	16.16	2.42	2.25	1.97	0.0125	0.0208	0.0675		0.772	
	16.11	2.77	2.12	1.98	0.0127	0.0208	0.0715		0.768	
	16.20	2.55	2.10	1.82	0.0126	0.0223	0.0728		0.775	
	16.12	2.39	2.13	1.93	0.0126	0.0208	0.0708		0.774	
	16.14	2.58	2.12	1.895(a.a.)	0.0123	0.0215	0.0695		0.763	
	16.19(polar.)	2.85	2.19	1.885	0.0128		0.0715			
	16.37	2.79	2.15	1.895	0.0129		0.0715			
	15.97	2.75	2.190(a.a.)	1.920	0.0128		0.0715			
	16.30	3.02	2.180	1.920	0.0132		0.0728			
	16.08	2.74	2.185	1.855	0.0133		0.0708			
			2.185	1.880	0.0126					
			2.195	1.870	0.0123					
				1.885	0.0125					
					0.0133					
					0.0129					
	15.78(a.a.)	2.23(a.a.)	2.160(a.a.)	1.895(a.a.)			0.0702(a.a.)			
	15.73	2.25	2.160	1.845			0.0749			
	15.83	2.70	2.160	1.925			0.0752			
	15.73	2.45	2.155	1.890			0.0750			
	15.80	2.63	2.155	1.890			0.0718			
	15.70	2.33(vol.)	2.105	1.885			0.0715			
	15.65	2.35	2.170				0.0730			
	15.70	2.37	2.195				0.0780			
	15.73	2.40	2.160				0.0688			
	15.73	2.37	2.185				0.0673			
		2.40	2.145				0.0673			
		2.36	2.185				0.0718			
		2.37	2.140				0.0733			
		2.37	2.170				0.0768			
Sample wt, g	1.0	0.5-1.0	0.5	0.5-1.0(a.a.) 1.0(vol.)	2.0	2.0	0.5-1.0	-	0.2	-

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-13	16.27(vol.)	2.405(vol.)	2.129(vol.)	2.000(grav.)	0.016(color.)	0.015(color.)		0.022(color.)	0.768(vol.)	64.8(a.a.)
	16.23	2.375	2.127	1.999	0.015	0.016		0.022	0.762	64.8
	16.28	2.394	2.137	1.999	0.015	0.018		0.022	0.773	64.8
	16.27	2.394	2.130	1.989	0.014	0.015		0.021	0.764	64.8
	16.28	2.433	2.138	1.993	0.020	0.016		0.022	0.750	64.8
	16.31	2.417	2.134	2.008	0.015	0.014		0.021	0.750	64.8
	16.29	2.390	2.127	1.987	0.016	0.015		0.021	0.769	64.8
	16.29	2.382	2.136	1.981	0.017	0.015		0.022	0.761	64.8
	16.27	2.394	2.130	1.989	0.017	0.014		0.022	0.763	64.8
	16.29	2.390	2.132	1.981	0.019	0.014		0.023	0.769	64.8
		2.377(grav.)								
		2.376								
		2.381								
		2.59(a.a.)								
		2.62								
		2.59								
		2.53								
		2.53								
		2.53								
		2.53								
Sample wt, g	-	-	-	-	-	-	-	-	-	-

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-14	16.50(a.a.)		1.923(a.a.)	1.923(a.a.)			0.070(a.a.)	0.028(a.a.)	0.66(x.r.f.)	
	16.10		1.913	1.953			0.070	0.027	0.66	
	16.50		1.903	1.871			0.070	0.027	0.62	
	16.50		1.913	1.932			0.072	0.026	0.64	
	16.50		1.923	1.891			0.074	0.026	0.62	
	16.75		1.910	1.898			0.072	0.026	0.63	
	16.10		1.898	1.903			0.072	0.026	0.60	
	16.10		1.913	1.891			0.074	0.027	0.58	
	16.10		1.895	1.884			0.073	0.028	0.59	
	16.25		1.900	1.898			0.072	0.027	0.61	
Sample wt, g	-	-	-	-	-	-	-	-	-	-

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag pppm
MP-1, LAB-15	16.6(a.a.)		2.14(a.a.)	1.89(a.a.)	0.0137(a.a.)				0.78(color.)	59.(a.a.)
	16.6		2.16	1.89	0.0137				0.76	60.
	16.7		2.14	1.89	0.0131				0.76	60.
	16.5		2.13	1.92	0.0137				0.76	60.
	16.7		2.15	1.85	0.0131				0.77	58.
	16.5		2.15	1.89	0.0137				0.76	58.
	16.6		2.16	1.92	0.0137				0.77	58.
	16.6		2.16	1.89	0.0131				0.76	59.
	16.8		2.14	1.89	0.0131				0.76	59.
	16.7		2.13	1.90	0.0124				0.77	59.
Sample wt, g	-	-	-	-	-				-	-

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-16		2.47(polar.)	2.16(polar.)	1.96(polar.)			0.068(polar.)			
		2.47	2.13	1.98			0.070			
		2.47	2.16	1.94			0.069			
		2.47	2.19	1.94			0.069			
		2.51	2.19	1.96			0.068			
		2.47	2.16	1.94			0.068			
		2.51	2.16	1.94			0.067			
		2.47	2.19	1.94			0.068			
		2.51	2.19	1.96			0.070			
		2.51	2.16	1.94			0.069			
							0.068			
							0.069			
Sample wt, g	1.0	1.0	1.0	1.0	-	-	1.0	1.0	-	-

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-17	16.57(vol.)	2.42(vol.)	2.04(color.)	1.98(a.a.)	0.013(a.a.)	0.036(color.)		0.025(color.)	0.88(vol.)	53.5(a.a.)
	16.51	2.38	2.08	1.94	0.015	0.031		0.025	0.84	54.9
	16.51	2.41	2.04	1.85	0.011	0.029		0.026	0.88	53.5
	16.57	2.41	2.04	1.92	0.011	0.054		0.027	0.84	53.5
	16.57	2.39	2.04	1.92	0.011	0.044		0.027	0.88	53.5
	16.51	2.43	2.04	1.94	0.012	0.055		0.024	0.88	56.6
	16.63	2.42	2.02	1.86	0.012	0.022		0.026	0.88	54.9
	16.45	2.41	2.02	1.89	0.011	0.036		0.024	0.88	54.9
	16.45	2.42	2.04	1.92	0.012	0.035		0.026	0.84	54.9
	16.57	2.53	2.07	2.06	0.013	0.048		0.028	0.84	54.9
	16.51	2.42								54.2(f.a.)
	16.51	2.46								55.2
	16.63	2.42								54.2
	16.51	2.39								54.2
	16.51	2.41								55.2
	16.51	2.46								52.5
	16.57	2.40								56.2
	16.57	2.49								55.2
	16.57	2.38								55.2
	16.57	2.39								54.2
	16.57	2.41								55.2
	16.45	2.43								
	16.57	2.43								
	16.45	2.49								
	16.63	2.40								
	16.57	2.41								
	16.57	2.42								
	16.57	2.47								
	16.45	2.43								
	16.51	2.48								
Sample wt, g	0.5	1.0	0.5	0.5	2.0	1.0	-	1.0	1.0	29.17

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-18	16.6(grav.)		2.11(elec.)	2.05(vol.)				0.028(a.a.)	0.82(vol.)	56.0(f.a.)
	16.6		2.11	2.09				0.028	0.82	56.2
	16.7		2.11	2.09				0.027	0.80	57.0
	16.9		2.10	2.07				0.026	0.80	56.8
	16.7		2.10	2.08				0.029	0.81	57.8
	16.6		2.10	2.10				0.027	0.81	57.0
	16.9		2.10	2.06				0.028	0.81	56.8
	16.8		2.10	2.11				0.028	0.82	55.8
	16.7		2.11	2.08				0.029	0.81	55.8
	16.8		2.10	2.09				0.025	0.81	56.8
	1.0									56.3
										57.3
Sample wt, g	1.0	-	1.0	1.0	-	-	-	1.0	1.0	29.17

	Zn%	Sn%	Cu%	Pb%	Mo%	W%	In%	Bi%	As%	Ag ppm
MP-1, LAB-19		2.62(x.r.f.)		1.91(x.r.f.)					0.80(x.r.f.)	
		2.63		1.89					0.75	
		2.62		1.91					0.77	
		2.63		1.89					0.80	
		2.64		1.88					0.76	
		2.63		1.96					0.84	
		2.58		1.94					0.83	
		2.60		1.94					0.80	
		2.58		1.93					0.85	
		2.61		1.95					0.81	
		2.63		1.89					0.77	
		2.64		1.90					0.80	
		2.63		1.90					0.81	
		2.57		1.90					0.80	
		2.59		1.89					0.77	
		2.60		2.00					0.79	
		2.59		2.00					0.76	
		2.56		1.98					0.75	
		2.57		2.01					0.82	
		2.60		2.01					0.80	
		2.61		1.87					0.81	
		2.60		1.88					0.81	
		2.60		1.88					0.82	
		2.60		1.85					0.80	
		2.59		1.87					0.77	
Sample wt, g	-	-	-	-	-	-	-	-	-	-

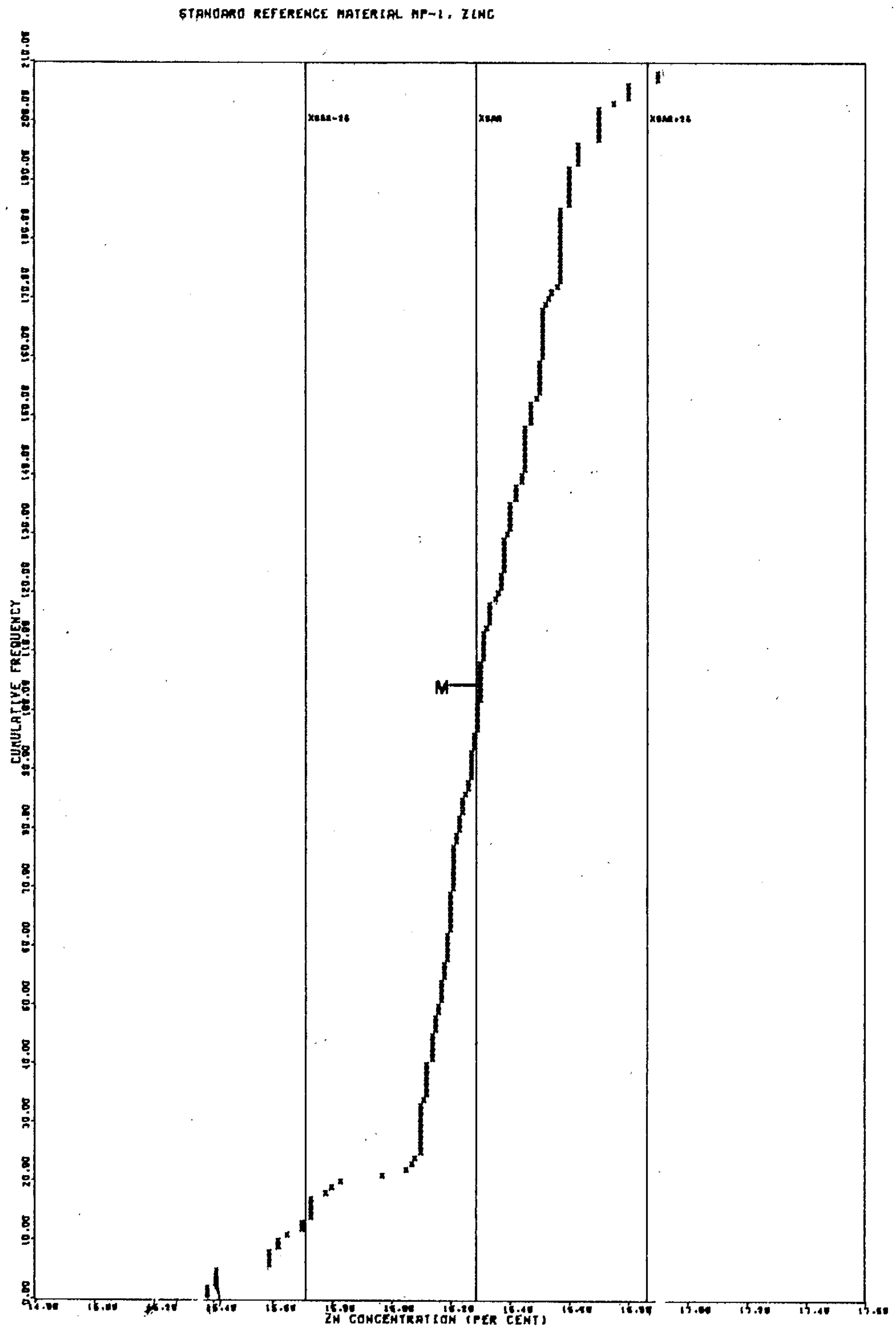
STANDARD REFERENCE MATERIAL MP-1, ZINC
CUMULATIVE FREQUENCY
ZN CONCENTRATION (PER CENT)
XBAR-2S
XBAR
XBAR+2S
M

Figure 1

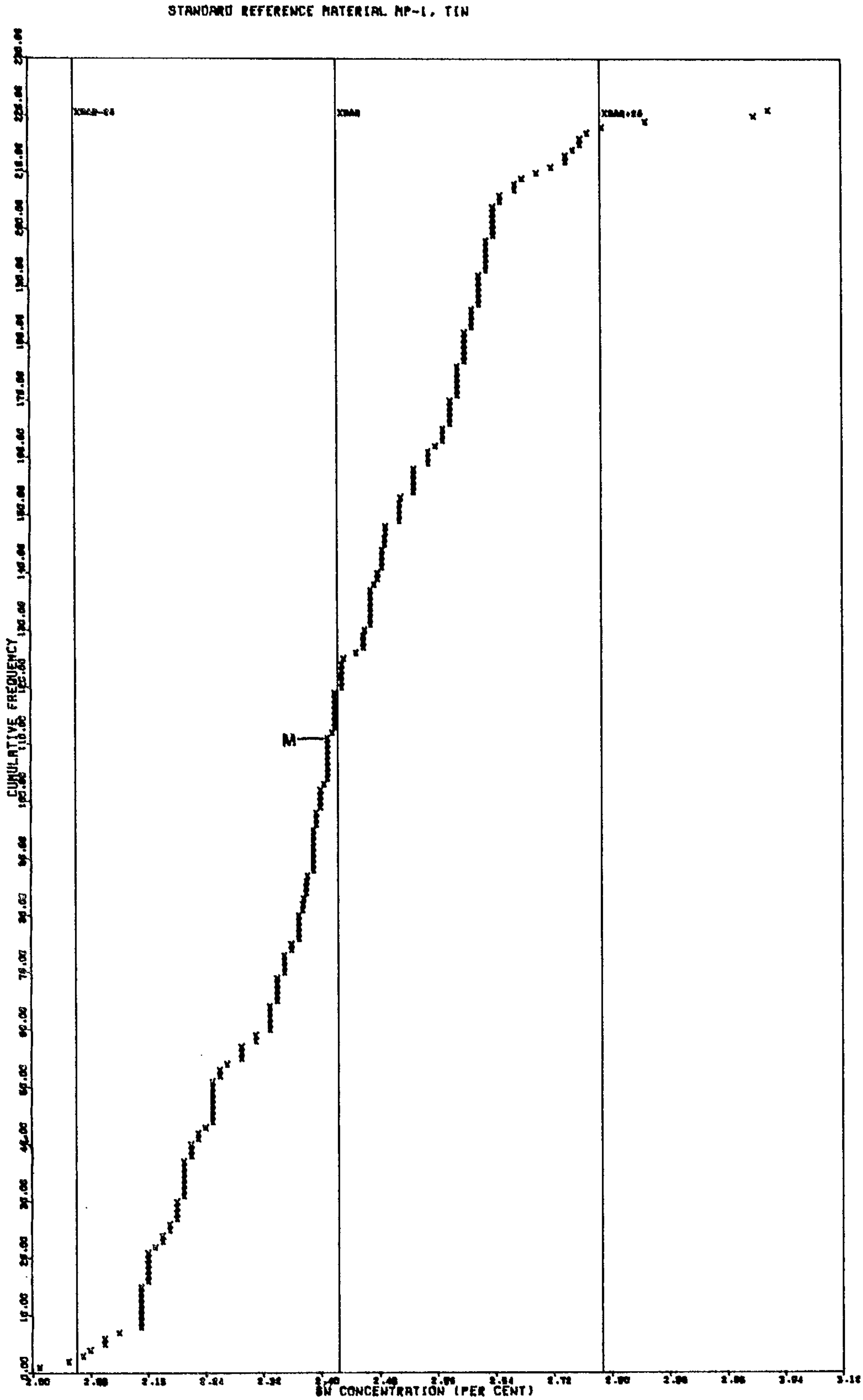
STANDARD REFERENCE MATERIAL MP-1, TIN
XBAR-2S
XBAR
XBAR+2S
M
CUMULATIVE FREQUENCY
SN CONCENTRATION (PER CENT)

Figure 2

STANDARD REFERENCE MATERIAL MP-1, COPPER

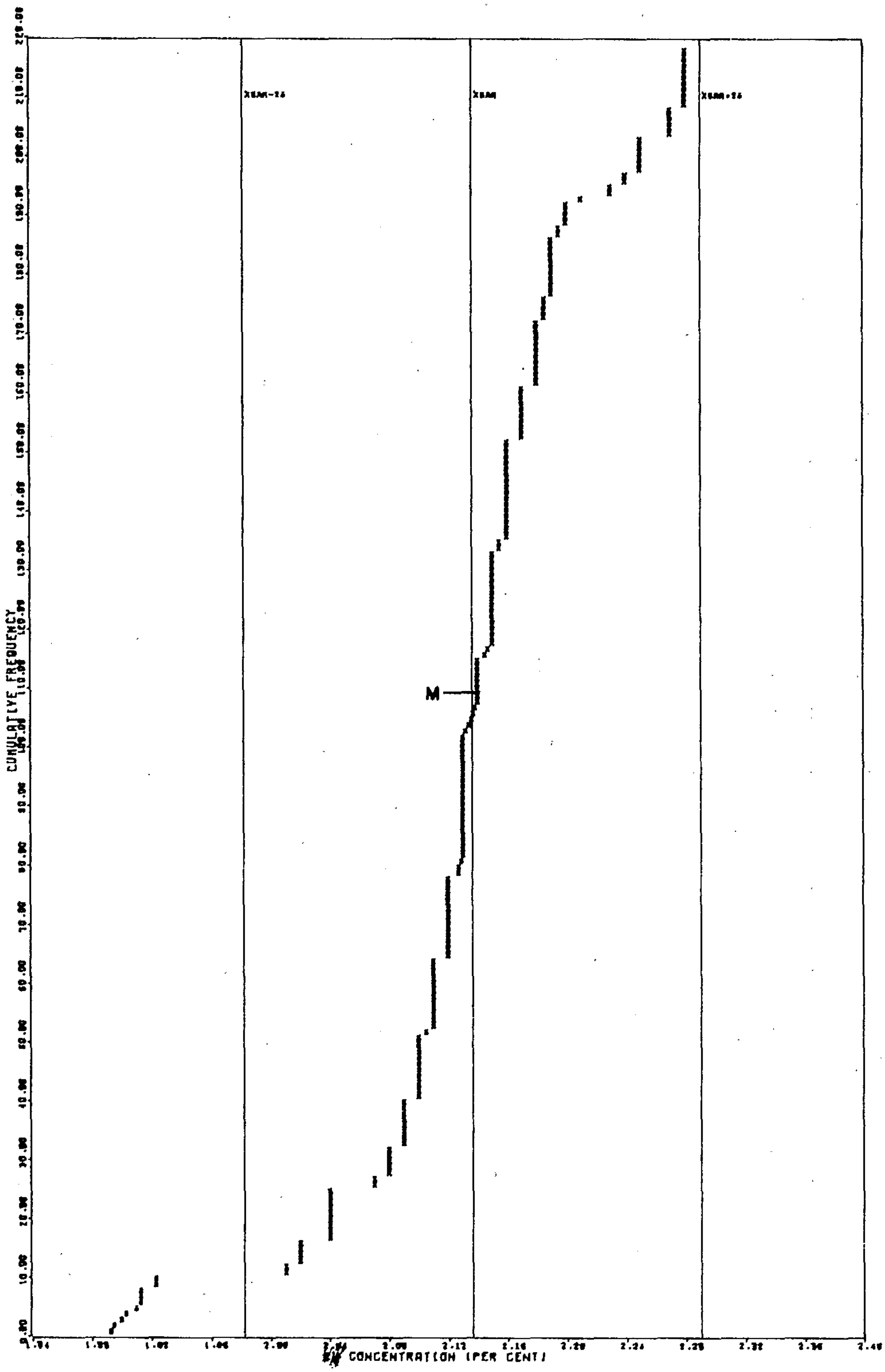

Figure 3

STANDARD REFERENCE MATERIAL NP-1, LEAD

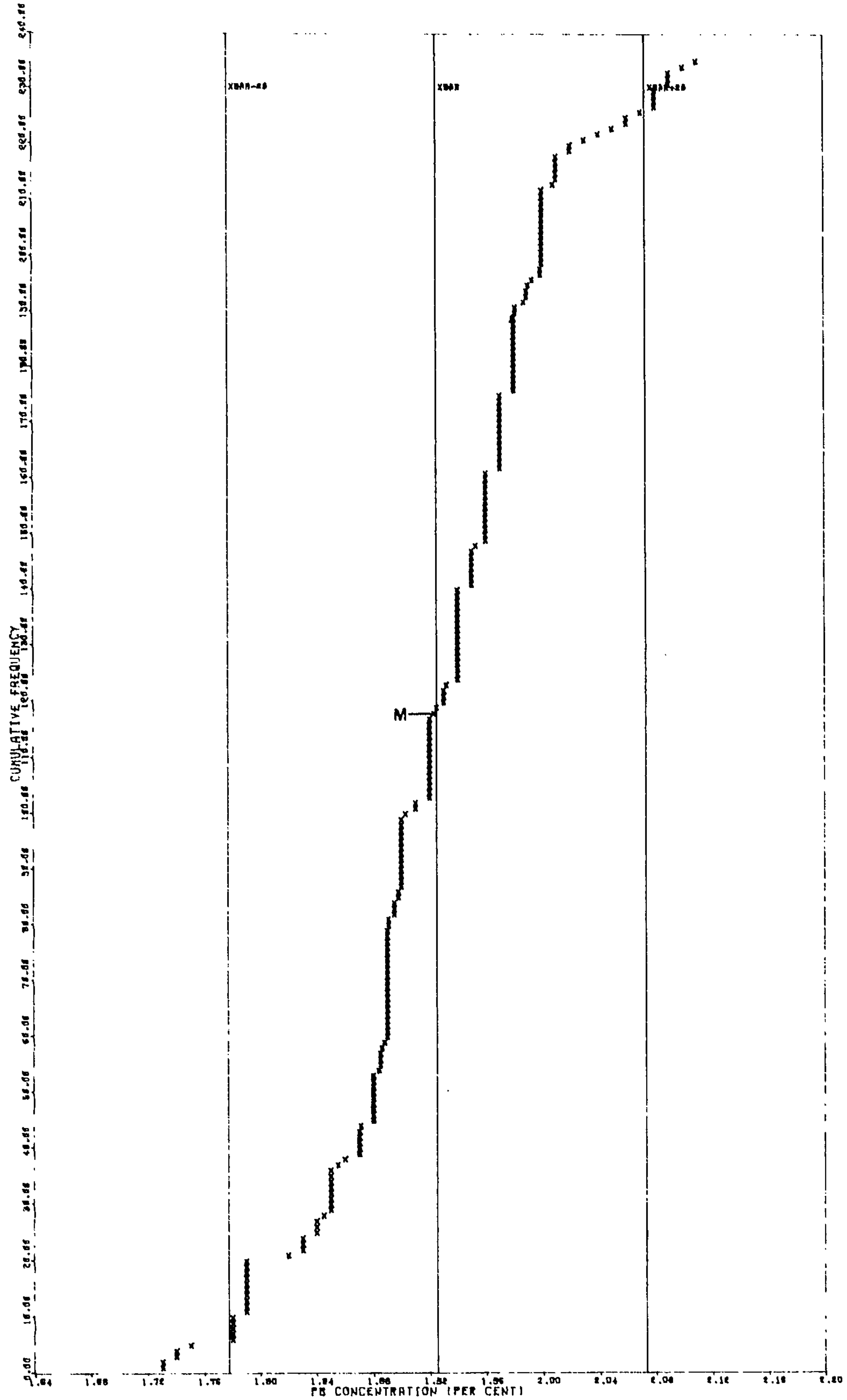

Figure 4

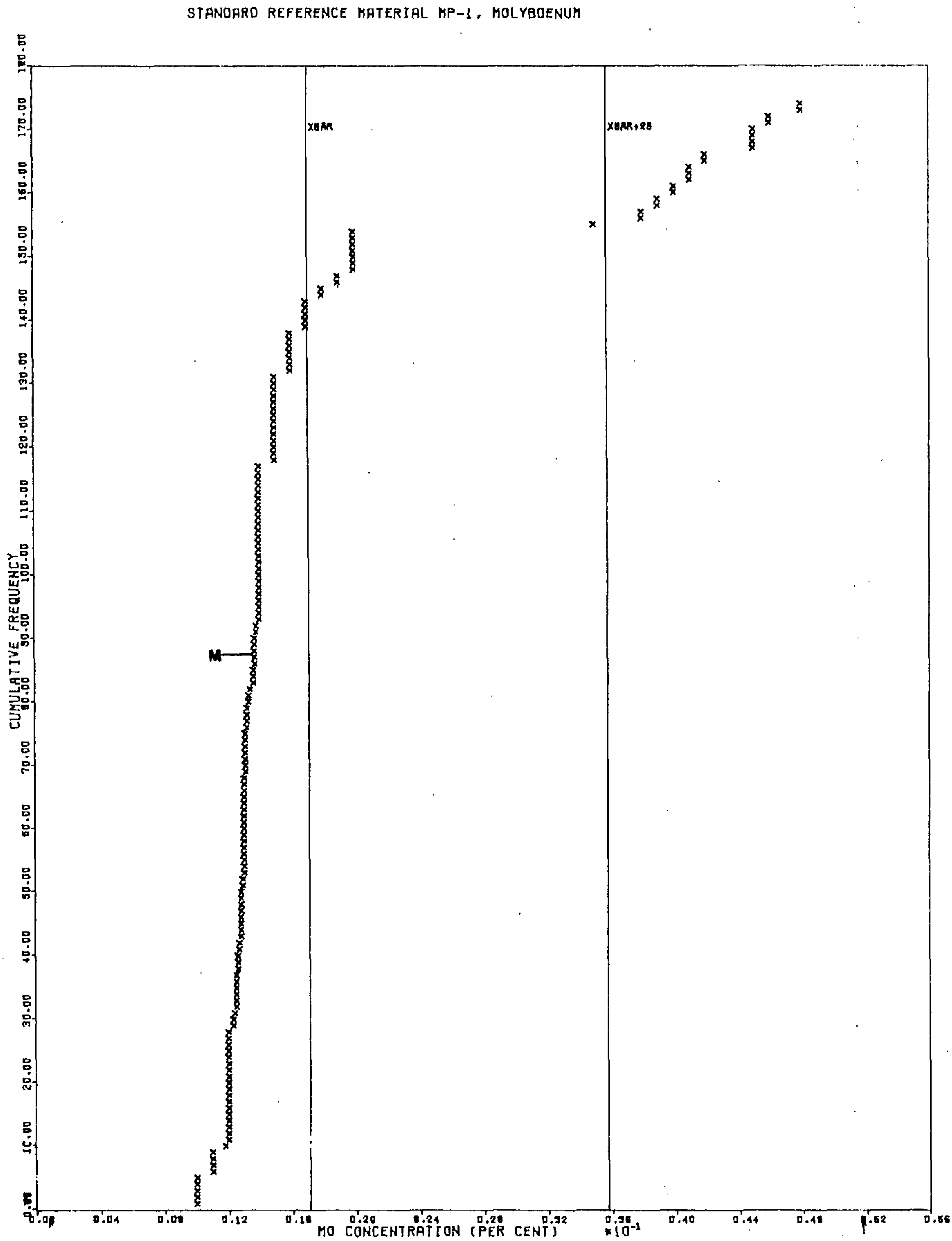
STANDARD REFERENCE MATERIAL MP-1, MOLYBDENUM
CUMULATIVE FREQUENCY
MO CONCENTRATION (PER CENT)
XBAR
XBAR+2S
M

Figure 5

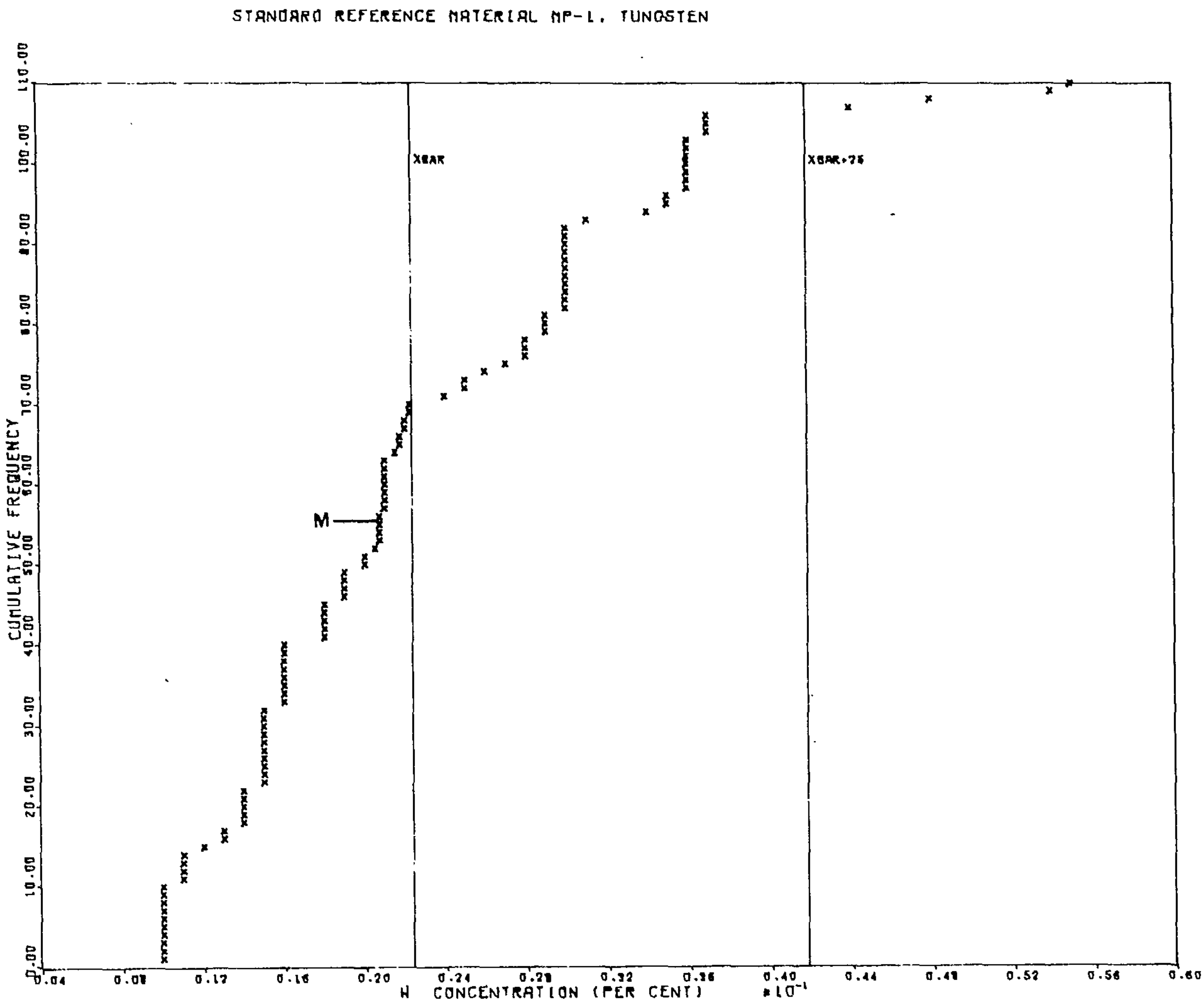
STANDARD REFERENCE MATERIAL MP-1, TUNGSTEN
CUMULATIVE FREQUENCY
W CONCENTRATION (PER CENT) *10⁻¹
XBAR
XBAR+2S
M

Figure 6

STANDARD REFERENCE MATERIAL MP-1, INDIUM

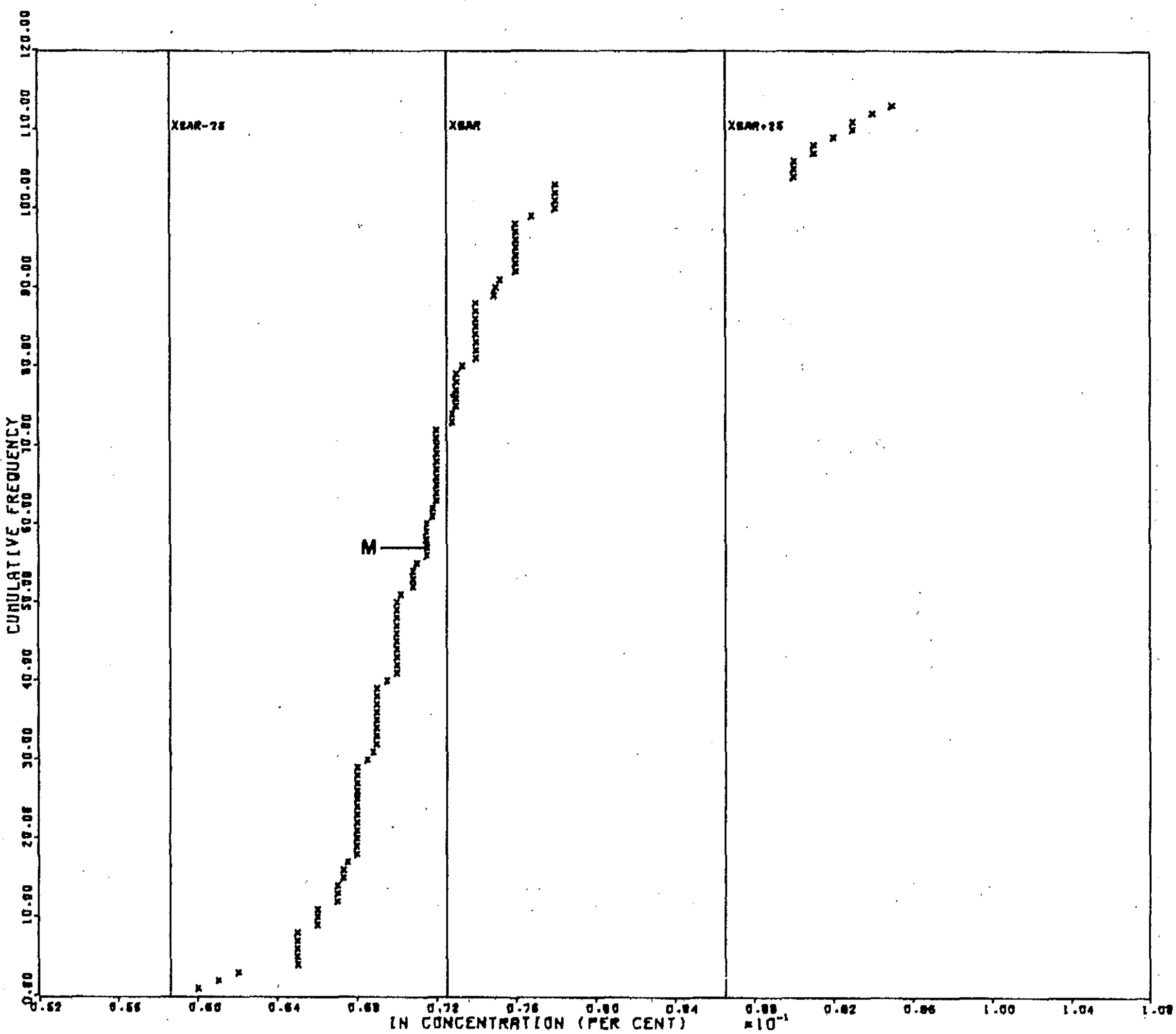

Figure 7

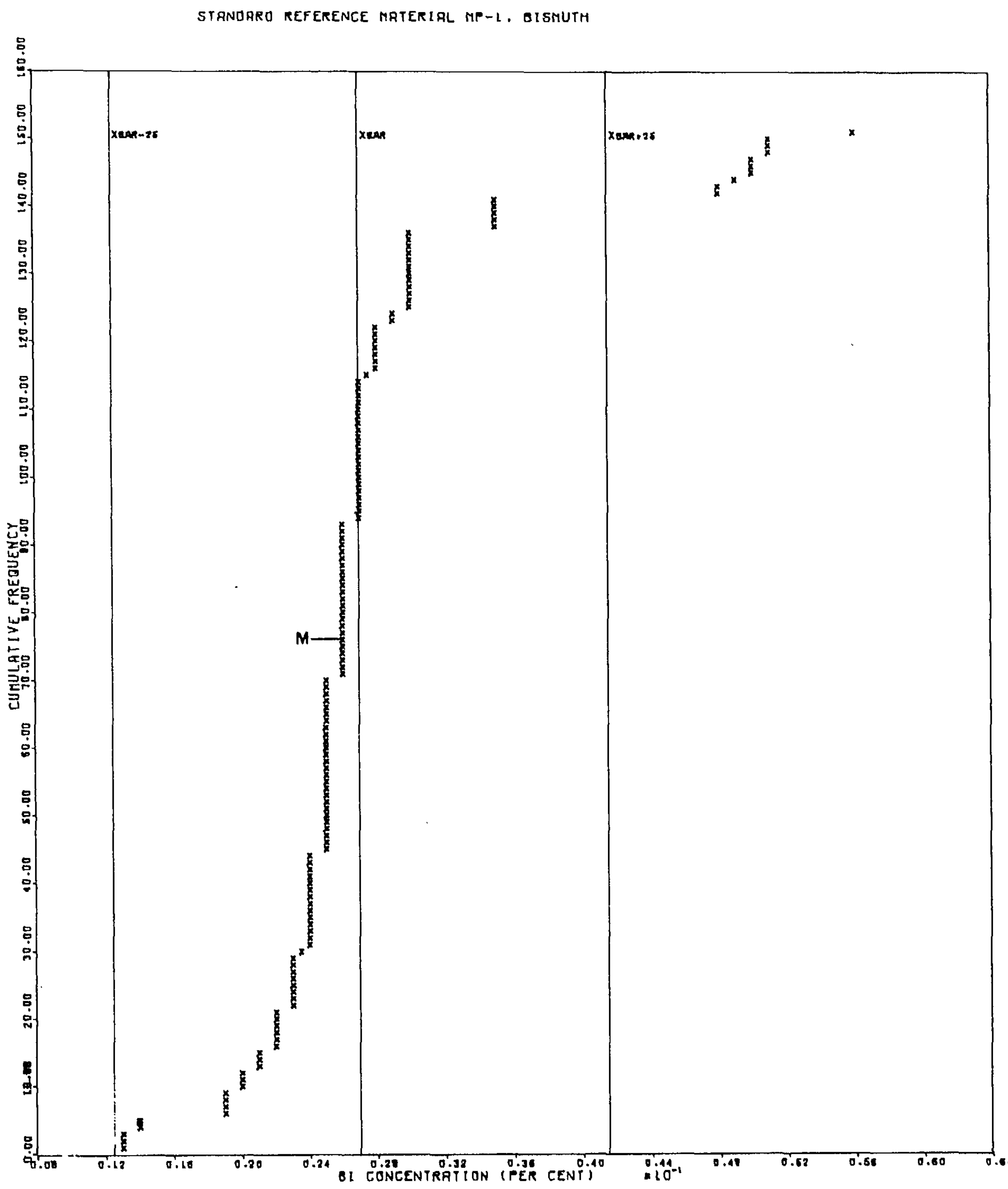
STANDARD REFERENCE MATERIAL MP-1, BISMUTH
CUMULATIVE FREQUENCY
BI CONCENTRATION (PER CENT)
x10⁻¹
XBAR-2S
XBAR
XBAR+2S
M
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00
90.00
100.00
110.00
120.00
130.00
140.00
150.00
160.00
0.08
0.12
0.16
0.20
0.24
0.28
0.32
0.36
0.40
0.44
0.48
0.52
0.56
0.60
0.64

Figure 8

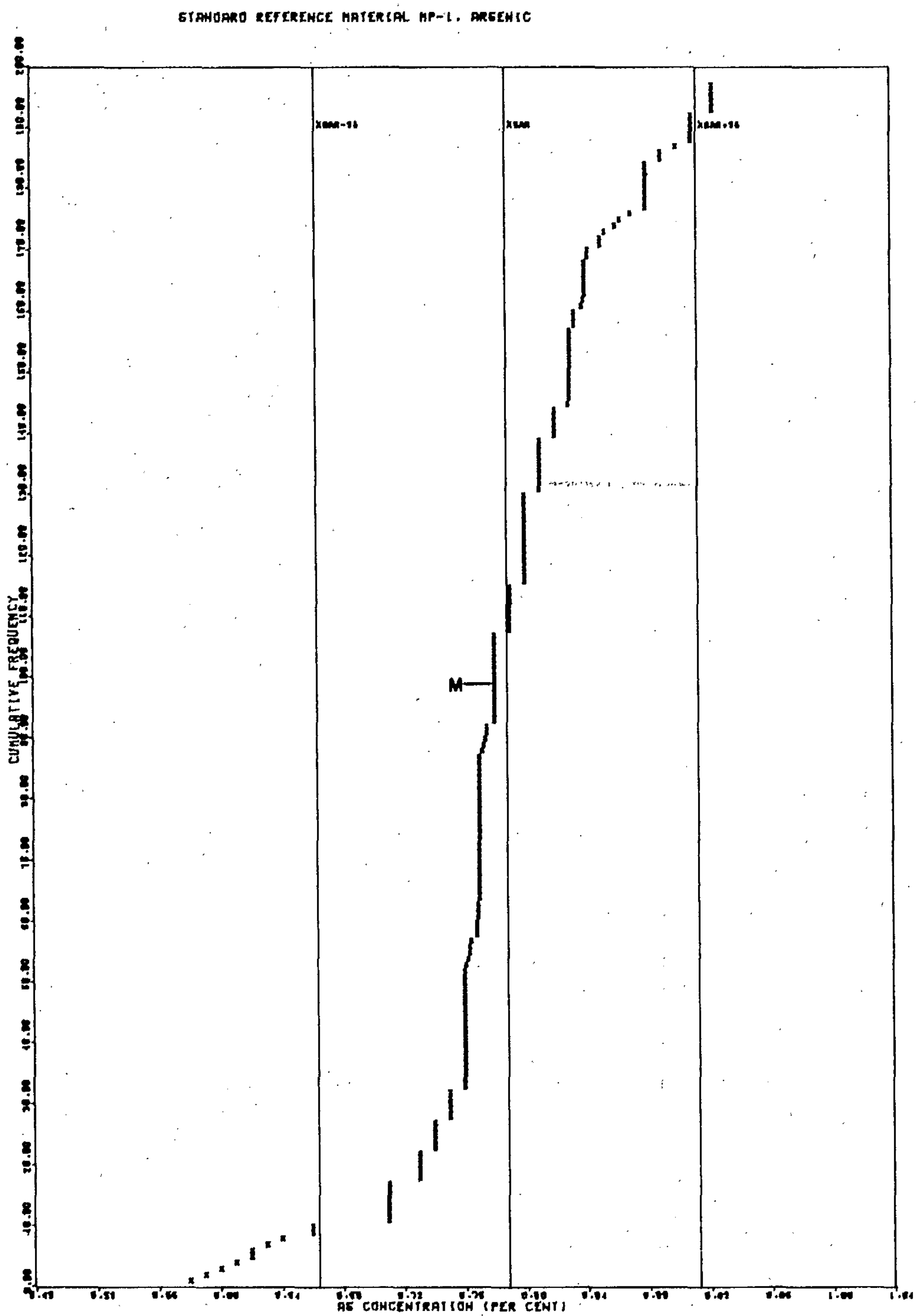
STANDARD REFERENCE MATERIAL MP-1, ARSENIC
CUMULATIVE FREQUENCY
M
AS CONCENTRATION (PER CENT)

Figure 9

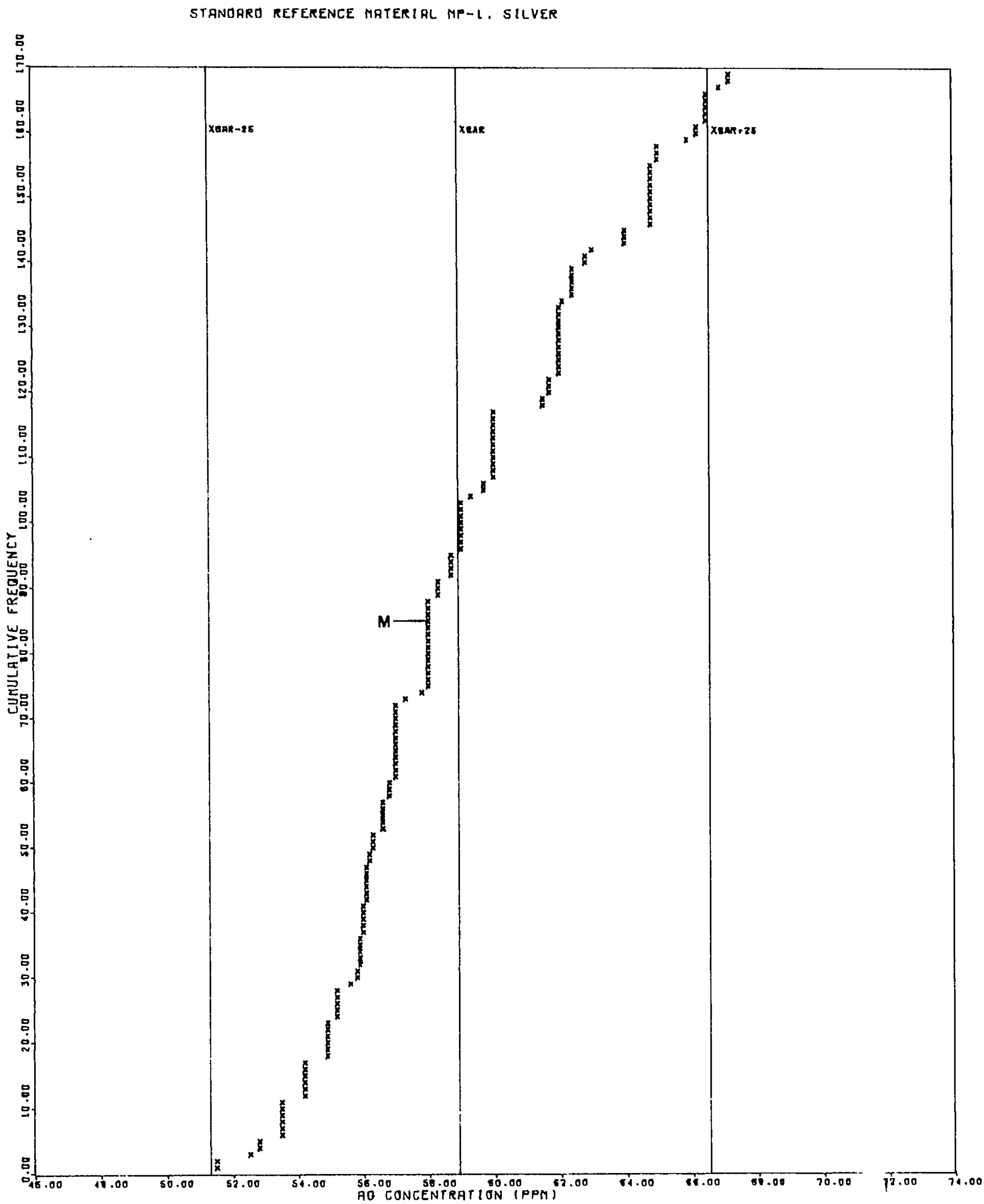
STANDARD REFERENCE MATERIAL MP-1, SILVER
CUMULATIVE FREQUENCY
AG CONCENTRATION (PPM)
XBAR-2S
XBAR
XBAR+2S
M

Figure 10

ZINC

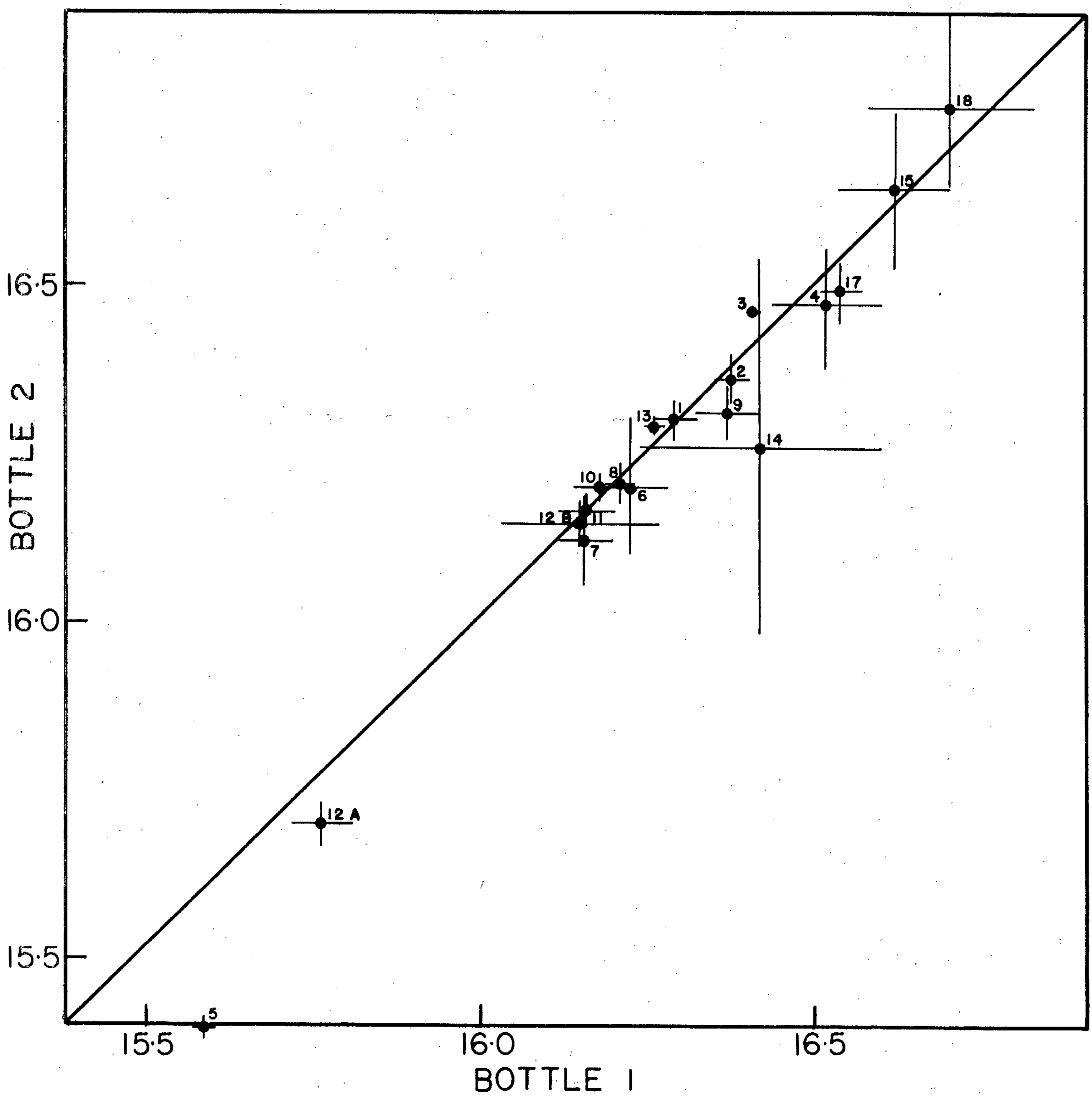

Figure 11 - SRM MP-1. Average Zinc Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

Note: A and B refer to different methods of analysis for the same laboratory.

TIN

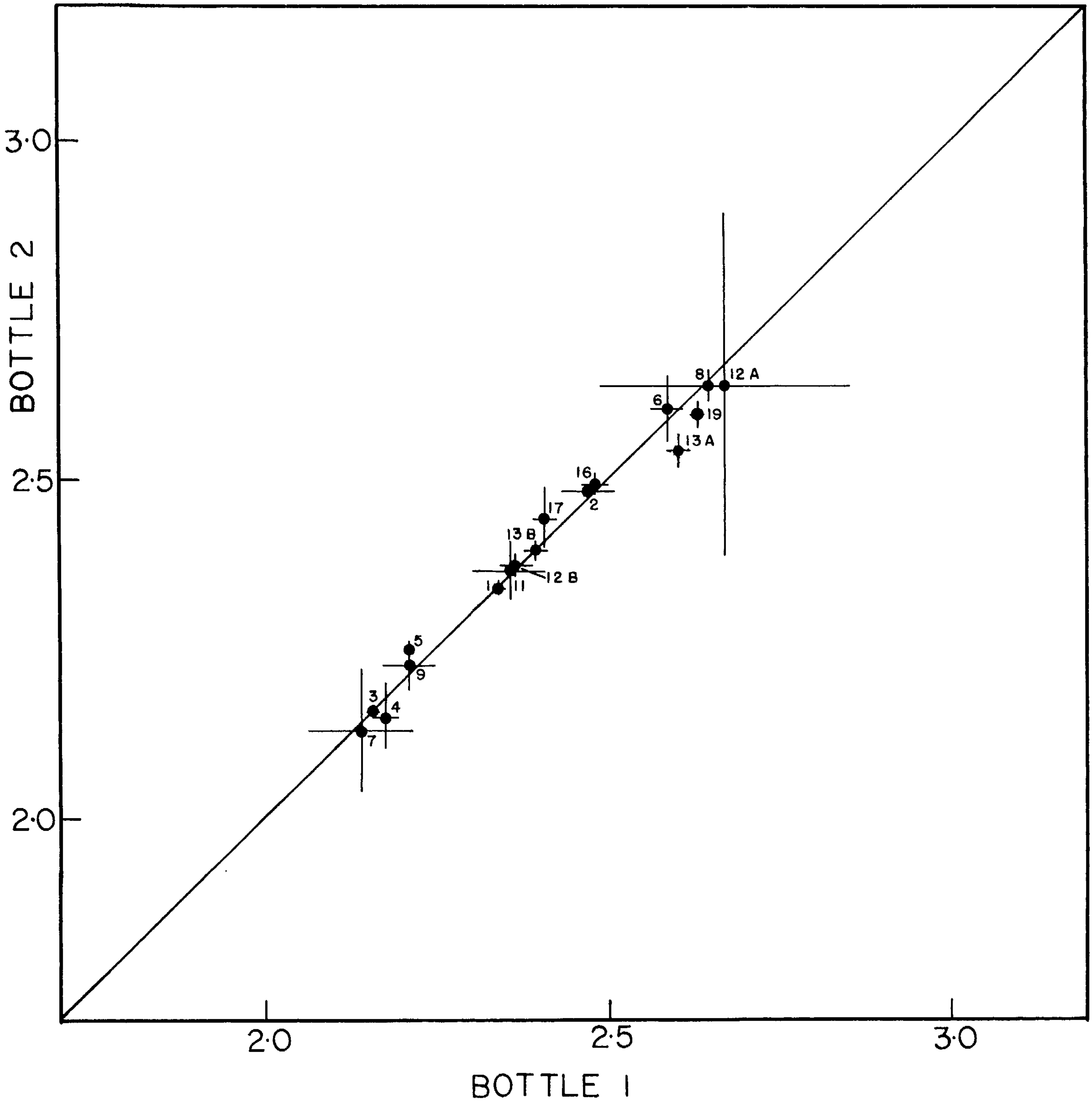

Figure 12. SRM MP-1. Average Tin Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

Note: A and B refer to different methods of analysis for the same laboratory.

COPPER

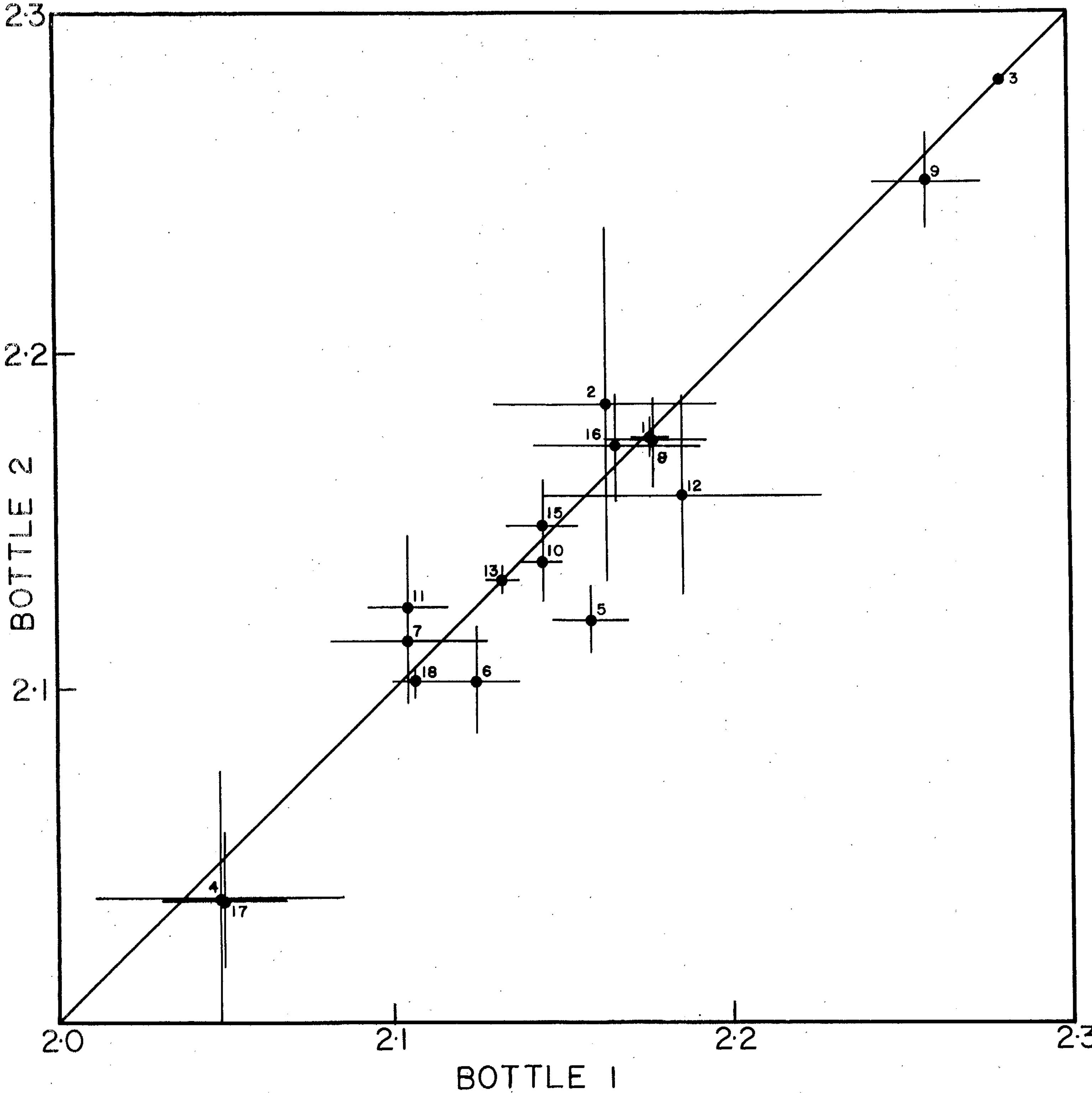

Figure 13 - SRM MP-1. Average Copper Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

LEAD

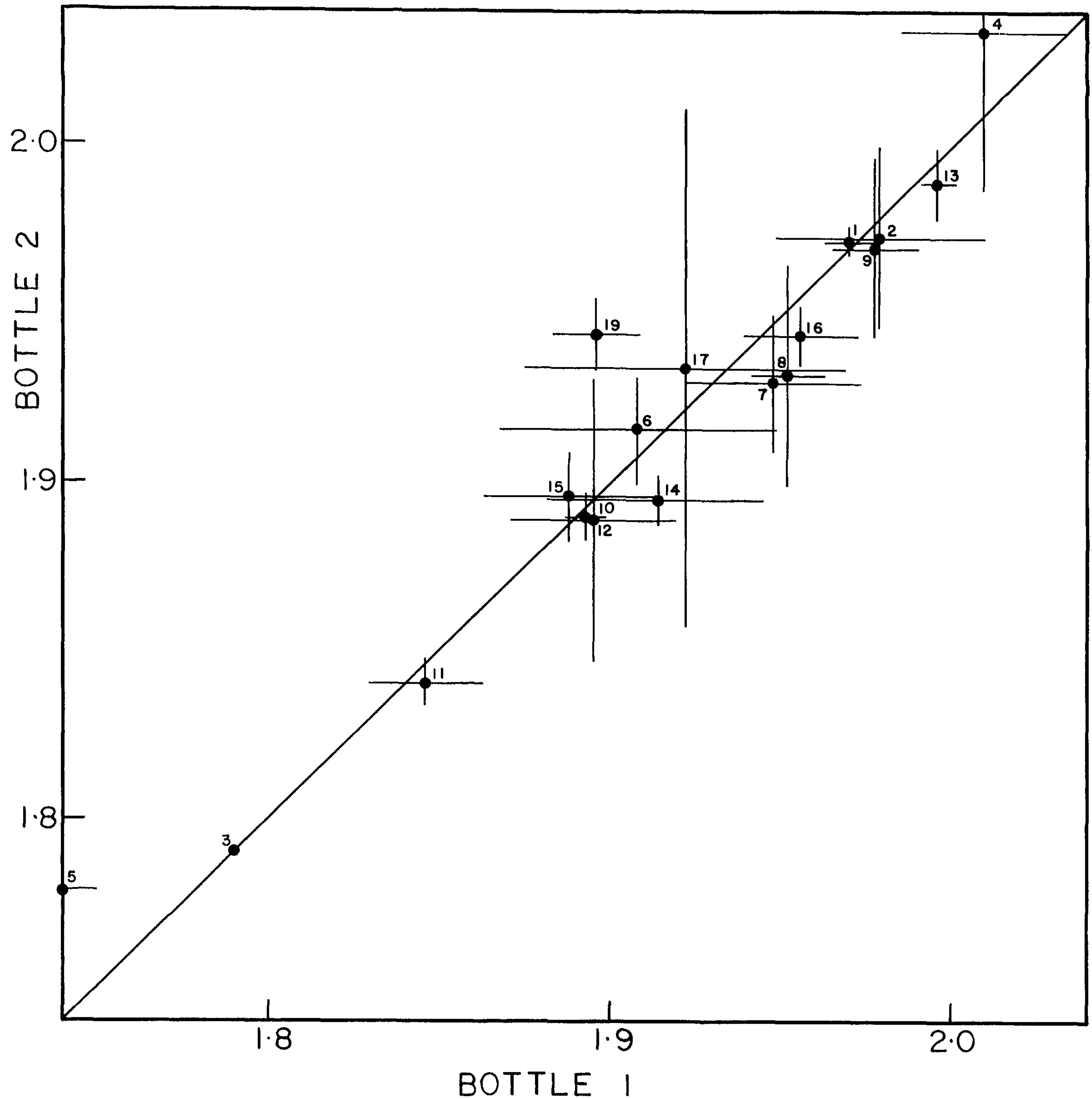

Figure 14 - SRM MP-1. Average Lead Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

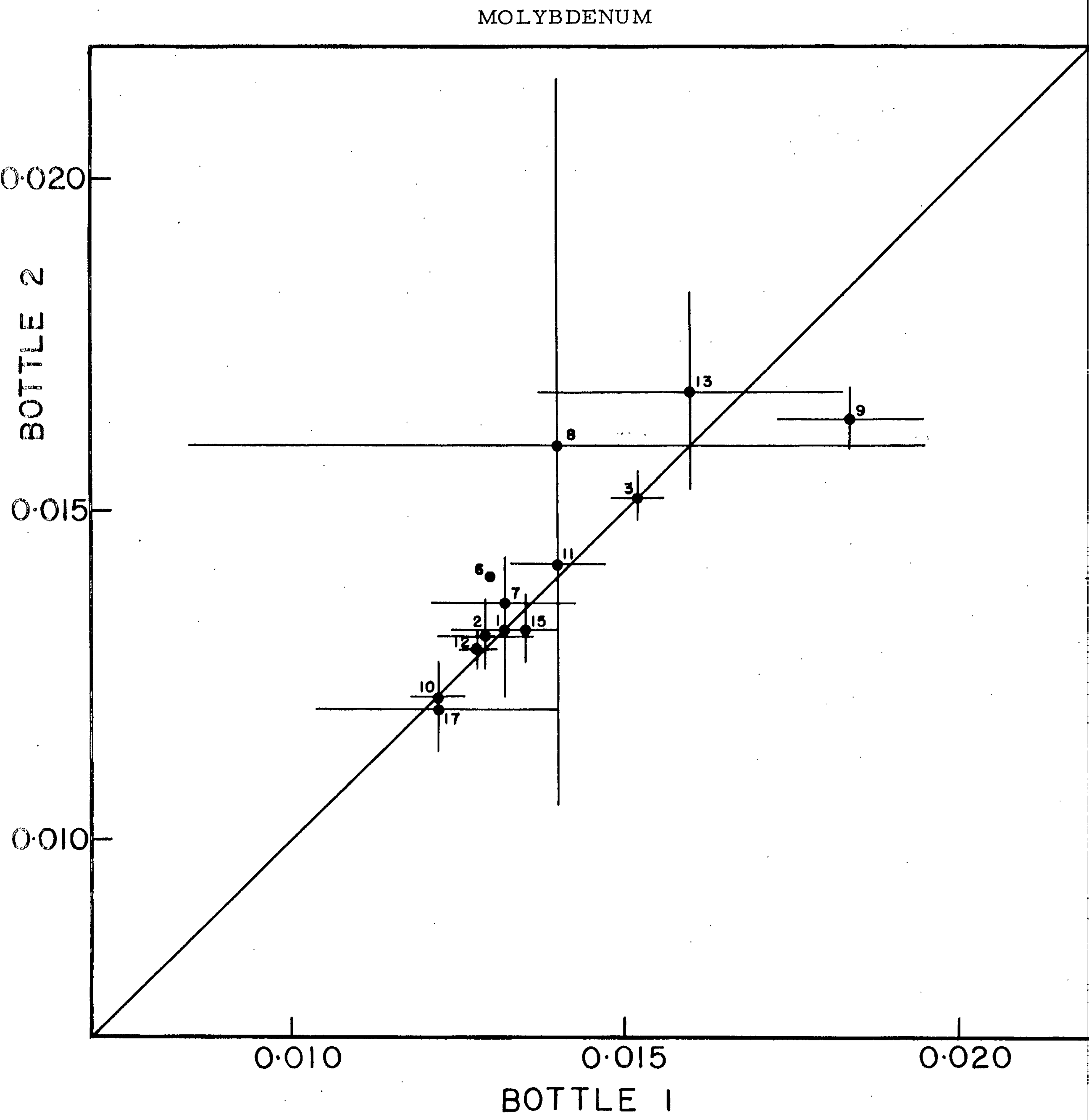

Figure 15 - SRM MP-1. Average Molybdenum Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

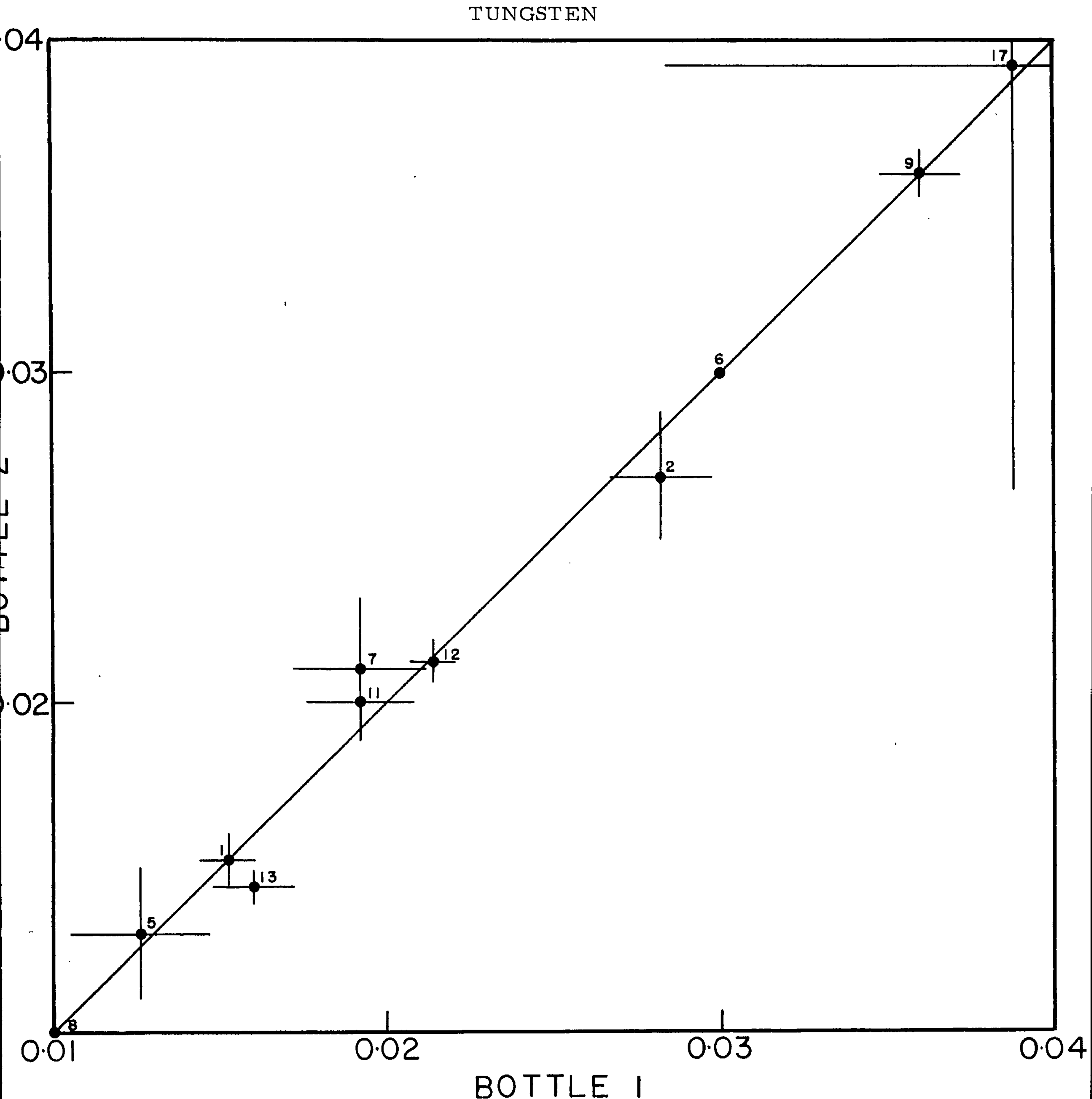

Figure 16 - SRM MP-1. Average Tungsten Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

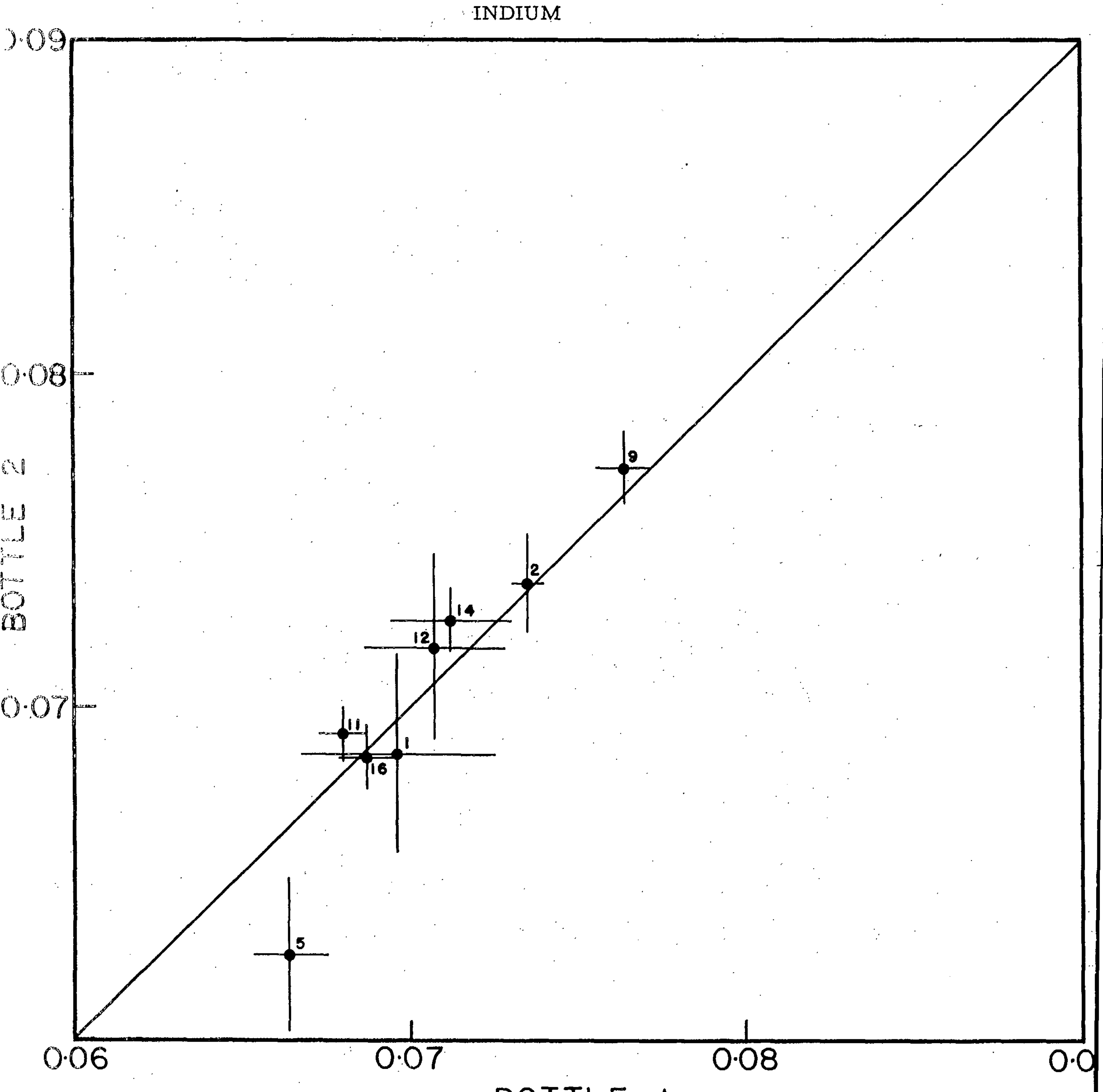

Figure 17 - SRM MP-1. Average Indium Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

BISMUTH

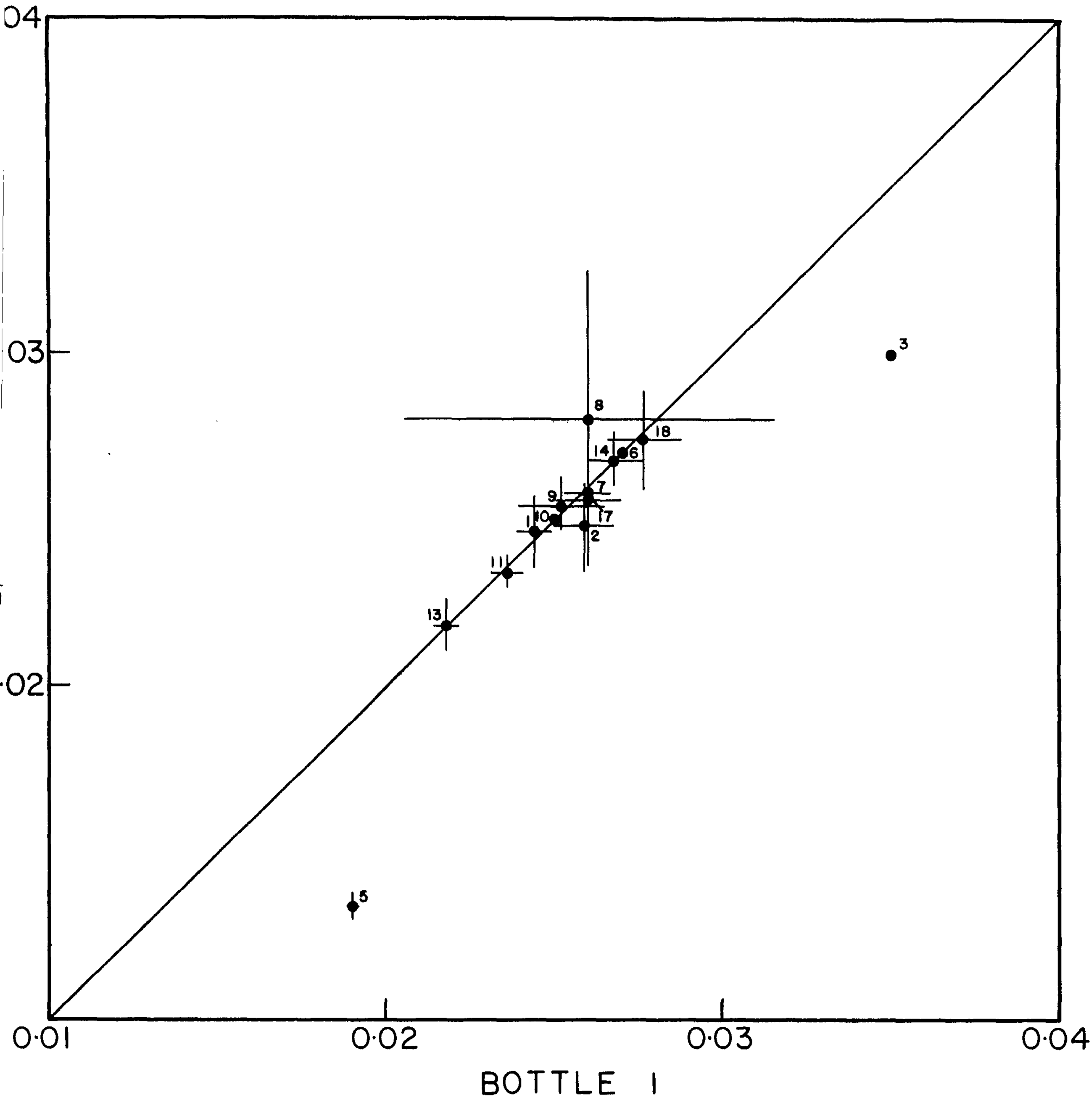

Figure 18 - SRM MP-1. Average Bismuth Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

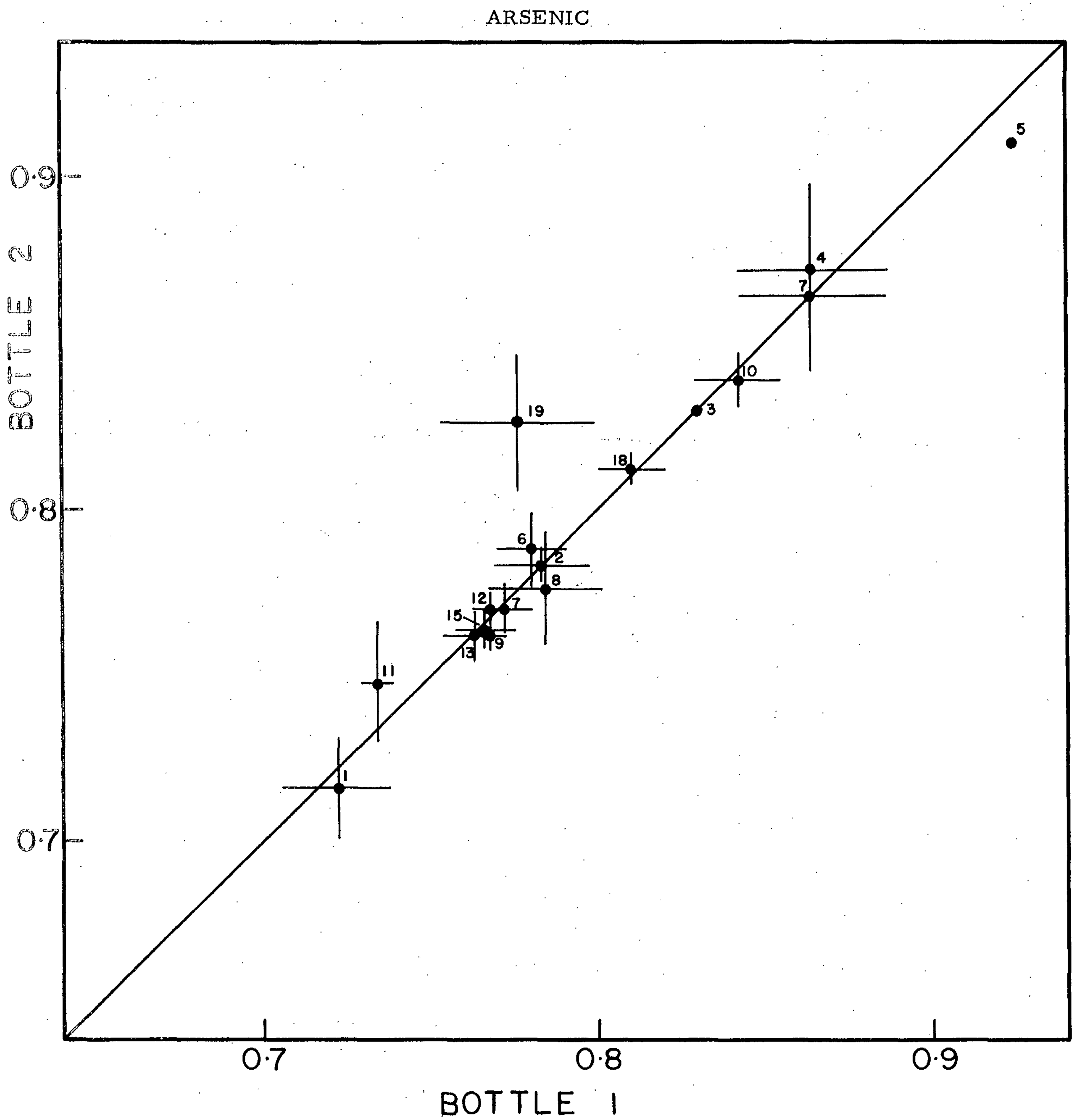

Figure 19 - SRM MP-1. Average Arsenic Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

SILVER

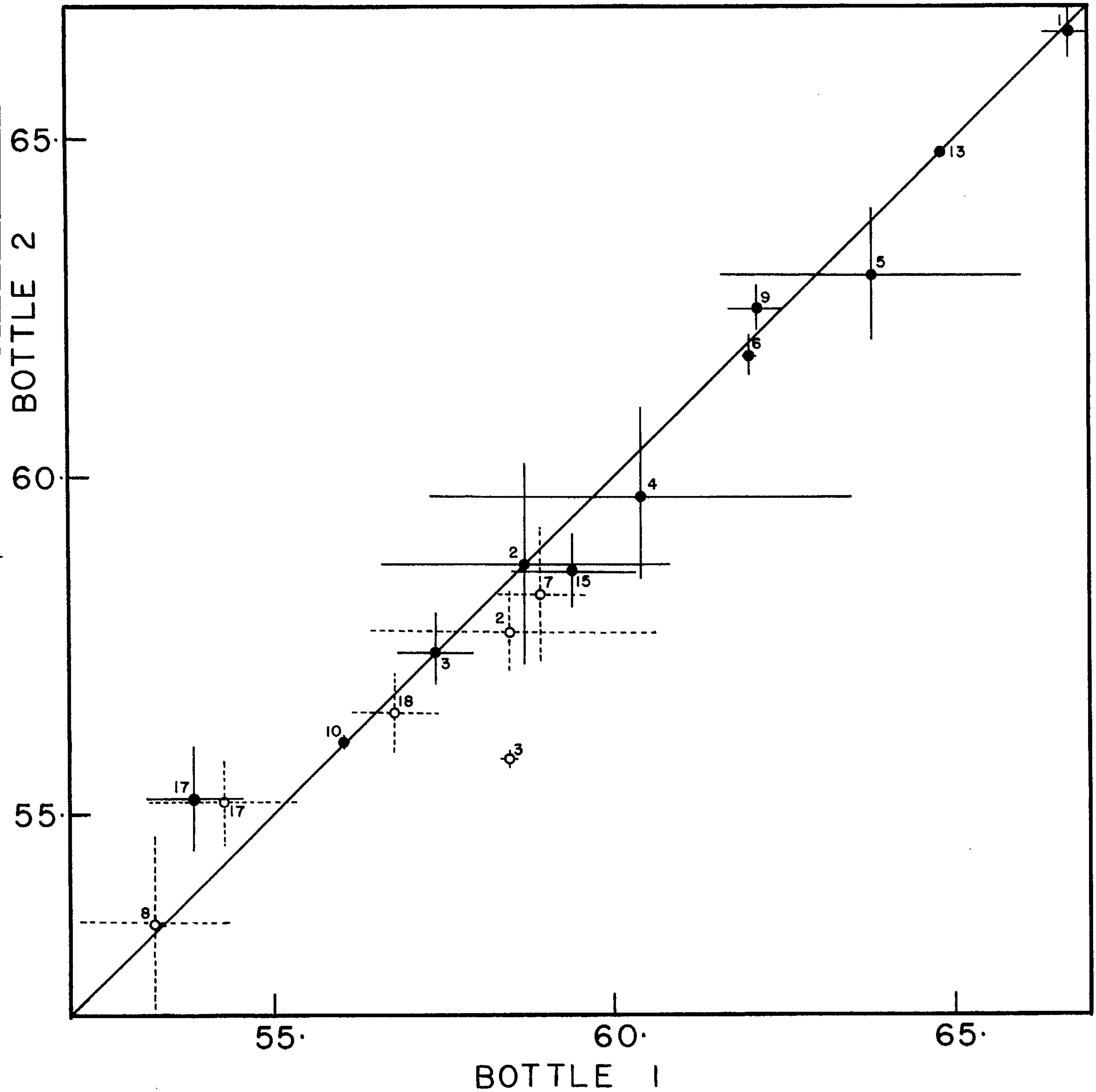

Figure 20 - SRM MP-1. Average Silver Analyses (ppm) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analyzed.)

Note: Dashed lines and open circles indicate analyses by fire-assay method.

TABLE 5

Statistical Parameters Computed, Based on the Assumption that the Analytical Results are Normally-Distributed, Random Variables*

Elements	No. of Observation N	Median M (%)	Mean, x (%)	Standard Deviation S (%)	Coefficient of Variation C.V. (%)	Skewness Factor α_3	Kurtosis Coefficient α_4
Zn	208	16.300	16.289	0.288	1.8	-0.97	4.41
	193	16.310	16.333	0.212	1.3	-0.30	3.33
Sn	221	2.410	2.424	0.182	7.5	0.20	2.90
	215	2.410	2.419	0.166	6.9	-0.05	2.15
Cu	218	2.140	2.137	0.077	3.6	-0.83	4.90
	208	2.140	2.148	0.060	2.8	0.30	3.27
Pb	235	1.923	1.925	0.074	3.8	-0.18	3.19
	221	1.920	1.923	0.063	3.3	-0.32	2.76
Mo	174	0.014	0.017	0.009	54.9	2.29	6.76
	154	0.013	0.014	0.002	15.3	1.28	4.90
W	110	0.021	0.022	0.010	43.4	0.94	3.79
	106	0.021	0.021	0.008	38.2	0.41	2.05
In	113	0.072	0.073	0.007	9.7	1.68	5.83
	103	0.071	0.071	0.004	5.2	-0.21	3.11
Bi	151	0.026	0.027	0.007	27.0	2.02	8.12
	141	0.026	0.025	0.004	15.0	-0.59	5.57
As	197	0.780	0.789	0.062	7.9	-0.45	4.57
	182	0.780	0.794	0.045	5.7	0.64	3.04
Ag	169	58.0	58.9	3.8	6.5	0.44	2.29
ppm	166	58.0	58.8	3.7	6.3	0.42	2.30

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

TABLE 6

Laboratory Means and Coefficients of Variation for MP-1

Lab. No.	Zn n_i	Zn $\overline{x}_i$	Zn C.V.$_i$(%)	Sn n_i	Sn $\overline{x}_i$	Sn C.V.$_i$(%)	Cu n_i	Cu $\overline{x}_i$	Cu C.V.$_i$(%)	Pb n_i	Pb $\overline{x}_i$	Pb C.V.$_i$(%)	Mo n_i	Mo $\overline{x}_i$	Mo C.V.$_i$(%)
1	10	16.296	0.18	10	2.338	0.34	10	2.175	0.24	10	1.971	0.29	10	0.0132	6.96
2	12	16.370	0.20	16	2.425	3.86	14	2.174	2.01	24	1.976	1.44	24	0.0130	4.61
3	10	16.437	0.17	10	2.157	0.44	10	2.280	0.00	10	1.790	0.00	10	0.0152	2.77
4	10	16.496	0.49	10	2.161	1.74	10	2.043	1.51	10	2.022	1.86	10	0.0392	4.78
5	10	15.500	0.70	10	2.230	0.95	10	2.139	1.04	10	1.759	1.30	10	0.0452	4.52
6	10	16.220	0.49	10	2.596	1.53	10	2.113	0.87	10	1.904	0.97	10	0.0135	3.90
7	10	16.142	0.36	10	2.136	3.77	10	2.109	0.99	10	1.939	1.23	10	0.0134	6.29
8	10	16.209	0.15	10	2.642	0.77	10	2.175	0.62	10	1.942	1.33	10	0.0150	35.14
9	10	16.343	0.32	10	2.218	1.63	10	2.254	0.67	10	1.974	1.05	10	0.0174	7.76
10	10	16.193	0.19	-	-	-	12	2.140	0.49	12	1.891	0.32	10	0.0122	3.46
11	11	16.164	0.21	10	2.361	2.06	20	2.114	0.93	10	1.843	0.68	10	0.0141	4.03
12	25	15.986	1.38	30	2.559	8.76	32	2.171	1.75	24	1.891	1.96	20	0.0128	2.43
13	10	16.278	0.13	20	2.451	3.50	10	2.132	0.19	10	1.993	0.44	10	0.0164	11.57
14	10	16.340	1.46	-	-	-	10	1.909	0.56	10	1.904	1.29	-	-	-
15	10	16.630	0.57	-	-	-	10	2.146	0.55	10	1.892	1.02	10	0.0133	3.32
16	-	-	-	10	2.486	0.83	10	2.169	0.93	10	1.950	0.73	-	-	-
17	30	16.538	0.33	30	2.427	1.48	10	2.043	0.92	10	1.928	3.13	10	0.0121	10.63
18	10	16.730	0.69	-	-	-	10	2.104	0.25	10	2.082	0.87	-	-	-
19	-	-	-	25	2.605	0.88	-	-	-	25	1.921	2.51	-	-	-
All Labs	208	16.289	1.77	221	2.424	7.49	218	2.137	3.60	235	1.925	3.85	174	0.0171	54.93

TABLE 6 (Cont'd)

Laboratory Means and Coefficients of Variation for MP-1

Lab. No.	W n_i	W $\bar{x}_i$	W C.V.$_i$(%)	In n_i	In $\bar{x}_i$	In C.V.$_i$(%)	Bi n_i	Bi $\bar{x}_i$	Bi C.V.$_i$(%)	As n_i	As $\bar{x}_i$	As C.V.$_i$(%)	Ag ppm n_i	Ag ppm $\bar{x}_i$	Ag ppm C.V.$_i$(%)
1	10	0.0152	5.19	10	0.0691	4.06	10	0.0245	3.47	10	0.719	2.02	10	66.6	0.54
2	10	0.0275	6.24	12	0.0736	1.47	12	0.0253	4.79	12	0.783	1.26	17	58.5	2.71
3	-	-	-	-	-	-	10	0.0325	8.11	10	0.830	0.00	20	56.8	1.36
4	-	-	-	10	0.0919	1.95	10	0.0504	4.51	10	0.869	2.68	10	60.1	3.80
5	10	0.0128	15.10	10	0.0645	4.09	9	0.0159	18.74	10	0.917	0.81	10	63.4	2.60
6	10	0.0300	0.00	-	-	-	10	0.0270	0.00	10	0.784	1.37	10	61.9	0.34
7	10	0.0201	10.86	-	-	-	10	0.0259	2.85	10	0.771	0.96	10	58.6	1.50
8	10	0.0100	0.00	-	-	-	10	0.0270	17.89	10	0.780	2.09	10	53.3	2.17
9	10	0.0360	2.62	10	0.0768	1.35	10	0.0253	4.19	10	0.765	0.69	10	62.3	0.61
10	-	-	-	-	-	-	10	0.0250	0.00	10	0.841	1.24	10	56.1	0.13
11	10	0.0196	7.30	10	0.0686	1.41	10	0.0235	2.24	10	0.741	1.96	-	-	-
12	10	0.0213	3.17	29	0.0712	3.48	-	-	-	10	0.769	0.65	-	-	-
13	10	0.0152	8.09	-	-	-	10	0.0218	2.90	10	0.763	1.02	10	64.8	0.00
14	-	-	-	10	0.0719	2.12	10	0.0268	2.94	10	0.621	4.39	-	-	-
15	-	-	-	-	-	-	-	-	-	10	0.765	0.92	10	59.0	1.38
16	-	-	-	12	0.0686	1.31	-	-	-	-	-	-	-	-	-
17	10	0.0390	28.01	-	-	-	10	0.0258	5.10	10	0.864	2.39	20	54.6	1.81
18	-	-	-	-	-	-	10	0.0275	4.62	10	0.811	0.91	12	56.6	1.10
19	-	-	-	-	-	-	-	-	-	25	0.796	3.41	-	-	-
All Labs	110	0.0224	43.36	113	0.0726	9.66	151	0.0270	26.96	197	0.789	7.89	169	58.9	6.49

TABLE 7

Statistical Parameters for MP-1

	Zn			Sn			Cu			Pb			Mo		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
No. of Participating Laboratories	16	16	16	15	15	15	17	17	17	19	17	17	13	13	13
No. of Observations	193	198	198	215	221	221	208	208	208	221	215	215	154	154	154
Median, %*	16.31	16.31	16.31	2.41	2.41	2.41	2.14	2.14	2.14	1.92	1.92	1.92	0.013	0.013	0.013
Mean, %*	16.33	16.33	16.34	2.42	2.42	2.39	2.15	2.15	2.15	1.92	1.93	1.93	0.014	0.014	0.014
95% Confidence Interval of the Mean, %*															
Low		16.20	16.22		2.32	2.30		2.12	2.12		1.90	1.90		0.013	0.012
High		16.45	16.45		2.52	2.48		2.18	2.18		1.96	1.95		0.015	0.015

TABLE 7 (Cont'd)

Statistical Parameters for MP-1

	W			In			Bi			As			Ag		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
No. of Participating Laboratories	11	11	11	8	8	8	14	14	14	17	16	16	14	13	13
No. of Observations	106	110	110	103	103	103	141	141	141	182	177	177	166	159	159
Median, %*	0.021	0.021	0.021	0.071	0.071	0.071	0.026	0.026	0.026	0.780	0.780	0.780	58.0	58.0	58.0
Mean, %*	0.021	0.022	0.022	0.071	0.071	0.071	0.025	0.025	0.025	0.794	0.791	0.790	58.8	58.5	58.9
95% Confidence Interval of the Mean, %*															
Low		0.016	0.016		0.068	0.068		0.023	0.023		0.768	0.769		56.3	56.9
High		0.029	0.029		0.074	0.073		0.027	0.027		0.814	0.812		60.6	61.0

*Silver values are in ppm; others are in wt %.

TABLE 8

Recommended Values for the Means and their Confidence Intervals for Standard Reference Material MP-1

Statistics	Content of Element % by weight								ppm
	Zn	Sn*	Cu	Pb	Mo	In	Bi	As	Ag*
Mean	16.33	2.50	2.15	1.93	0.014	0.071	0.025	0.791	59.5
95% Confidence Interval of the Mean									
Low	16.20	2.39	2.12	1.90	0.013	0.068	0.023	0.768	56.3
High	16.45	2.61	2.18	1.96	0.015	0.074	0.027	0.814	60.6

*See comments pertaining to tin and silver on pp 60-62.

DISCUSSION

Table 7 shows that, in all cases, the means computed by the four procedures are in good agreement with one another and with the medians. Therefore, any of these means should provide a good estimate of the concentration of each of the metals in this material. However, there is a strong dependence of the results on the laboratory from which they were reported. Therefore, the computation procedure A is technically incorrect. The assumption used for the computation procedures B and C are equally reasonable. Because there is no reason to prefer either one of these two methods of computation, the statistical parameters computed by procedure B are arbitrarily recommended for the certification of MP-1 for zinc, copper, lead, molybdenum, indium, bismuth, and arsenic (Table 8).

For chemical reasons a somewhat different treatment has been used in arriving at recommended values (Table 8) for tin and silver; these are explained in the following section. A recommended value was not assigned for tungsten for a statistical reason which is explained below.

COMMENTS ON ANALYTICAL METHODS AND RESULTS FOR TIN, SILVER, AND TUNGSTEN

Tin

From experience in the Mines Branch laboratories and elsewhere(5), it is known that the accurate determination of tin in ores can be troublesome. Indeed, the wide range of values for tin in MP-1 (Tables 4, 7 and 9) attests to this problem. Because tin is an important constituent of MP-1, it is desirable to critically evaluate the tin results with the object of arriving at the most meaningful preferred value.

By correlating the tin results with the type of method used (Table 9), it is readily apparent that the mean value obtained by instrumental methods (2.50%) is significantly higher than that given by the volumetric methods (2.35%). Table 9 also shows that the results of the volumetric methods may depend, in part, on the nature of the reducing agent. Three laboratories used iron powder and obtained a mean result (2.49%) which agrees closely with that of the instrumental methods but is much higher that the mean result of the Pb-reduction variation (2.22%).

It is known that, in certain applications,(6) the use of test lead may lead to low results for tin determined by the volumetric method; therefore, it is the authors' opinion that a mean value of 2.50%, for the instrumental and Fe-reduction methods, is to be preferred to the overall value of 2.42% for tin.

TABLE 9

Correlation of Tin Values with Method

Analytical Method	Number of Results	Mean (% Tin)
Instrumental	109	2.50
Volumetric - Total	109	2.35
Volumetric - Fe Reduction	45	2.49
Volumetric - Ni Reduction	10	2.40
Volumetric - Al Reduction	10	2.23
Volumetric - Pb Reduction	40	2.22
Volumetric - Unknown	4	2.28

Silver

Figure 20 clearly shows, that, generally, the silver results obtained by fire-assay methods are substantially lower than those given by the non-fire-assay (wet chemical-decomposition) methods. The respective mean values for the methods are 56.1 ppm and 60.4 ppm.

It has been reported that, in the lead-collection method of fire assay for silver, the average loss of silver is approximately 3%(7). It is noteworthy that, even if the fire-assay values are corrected by this amount, the mean value (57.8) is still significantly lower than that of the other methods.

A "corrected" overall mean of 59.5 ppm is obtained when the fire-assay results for silver are increased by 3%. This values is probably closer to the true value.

Tungsten

Because the range of values reported for tungsten (Table 4) is large and there is no obvious clustering of results, it was decided not to assign a recommended value for this element. Should the future users of MP-1 volunteer to analyze it for tungsten and submit their results to the co-ordinator of this standards program, it may be possible to certify MP-1 for tungsten after sufficient results become available.

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