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ZINC-LEAD-TIN-SILVER ORE KC-1:

Its Preparation and Characterization for Use as a Certified Reference Material

Members of the Staff of the
MINERAL SCIENCES DIVISION

Compiled by
G. H. Faye, W. S. Bowman and R. Sutarno

CANADIAN CERTIFIED REFERENCE MATERIALS PROJECT

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ZINC-LEAD-TIN-SILVER ORE KC-1: ITS PREPARATION AND CHARACTERIZATION FOR USE AS A CERTIFIED REFERENCE MATERIAL

by

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

SYNOPSIS

A zinc-lead-tin-silver ore, KC-1, has been prepared and characterized for use as a certified reference material.

This report describes the nature and origin of KC-1, and gives information on procedures used for its preparation and for assessing its homogeneity. Twenty-five laboratories provided analytical results for zinc, lead, tin, copper and silver; the recommended values are, respectively: 20.37%, 6.98%, 0.68%, 0.114% and 0.114%. The analytical results and the estimation of statistical parameters for the five selected elements are reported.

MINERAI DE ZINC-PLOMB-ETAIN-ARGENT KC-1:
LA PREPARATION ET LA CARACTERISATION DE CE MINERAI
UTILISE COMME MATERIAU DE REFERENCE CERTIFIE

par

Les membres du personnel de la division des Sciences Minérales. (Compilé par G.H. Faye, W.S. Bowman et R. Sutarno)

SYNOPSIS

Un minerai de zinc-plomb-étain-argent, KC-1, a été préparé et caractérisé pour son utilisation comme matériau de référence certifié. Les auteurs décrivent, dans ce rapport, la nature et l'origine de KC-1, et donnent l'information quant aux procédés utilisés pour sa préparation et pour l'évaluation de son homogénéité. Des résultats analytiques pour le zinc, le plomb, l'étain, le cuivre et l'argent ont été fournis par vingt-cinq laboratoires; les valeurs recommandées sont, respectivement, de 20.37%, 6.98%, 0.68%, 0.114% et 0.114%. On a donné les résultats analytiques et l'estimation des paramètres statistiques pour les cinq éléments sélectionnés.

INTRODUCTION

This report describes the preparation and characterization of a zinc-lead-tin-silver ore, KC-1, for use as a certified reference material. The work is a facet of the Canadian Certified Reference Materials Project (CCRMP) to certify materials that are representative of major Canadian ore deposits. Certified reference ores and related materials previously prepared by the Ores Task Force of the CCRMP are described in an Information Circular (see Appendix) available from the Mines Branch, and in Technical Bulletins that are issued with the purchase of each reference material[1-6].

KC-1 was prepared from material hand-picked at the Kidd Creek deposit of Ecstall Mining Limited, and was chosen to represent a typical high-grade base-metal ore. KC-1 also acts as a complement to the previously certified base-metal ore MP-1[3], which contains lower zinc, lead and silver values but higher copper and tin values than KC-1.

Twenty-five laboratories analyzed KC-1 for one or more of zinc, lead, tin, copper and silver. As in previous interlaboratory programs of the CCRMP, a substantial proportion of the results for the base metals were obtained by atomic absorption methods. However, a sufficient number were also obtained by other means so that various between-method comparisons could be made. These showed that for all elements except tin there was not a significant difference between atomic-absorption results and those obtained by other methods. Similarly, no significant differences were found between variations in a particular class of method, e.g., volumetric methods for zinc and lead. In the case of tin, it was found that the various modifications of the volumetric (iodometric) method tended to yield lower results than did methods having an instrumental finish. A similar finding was made previously for tin in MP-1[3].

The recommended values for the selected elements in KC-1, zinc, lead, tin, copper, and silver are respectively 20.37%, 6.98%, 0.68%, 0.114% and 0.114%.

It is now the practice of the Canadian Certified Reference Materials Project to use the term 'certified' rather than 'standard' to describe reference materials such as KC-1. It is considered that 'certified' can be translated to other languages with less ambiguity than 'standard'.

MINERALOGICAL COMPOSITION OF KC-1

The material for reference ore KC-1 was hand-picked at the Kidd Creek mine of Ecstall Mining Limited and was transported in lump form to the Mines Branch where it was processed as described below. The detailed mineralogy of ore from the Kidd Creek deposit has been described by Petruk and Owens[7]. With the aid of chemical analyses from Table 2, the mineralogical composition of KC-1 was calculated and is given in Table 1.

TABLE 1

Calculated mineralogical composition of KC-1

Minerals	Composition wt %
Sphalerite, Zn-20.4, Fe-1.4, Cd-0.08, Mn-0.02, S-10.8,	32.7
Pyrite, Fe-13.9, S-16.0	29.9
Galena, Pb-7.0, S-1.1	8.1
Cassiterite, Sn-0.7, O-0.2	0.9
Siderite, Fe-0.24, CO_2-0.15	0.4
Pyrrhotite, Fe-0.2, S-0.1	0.3
Chalcopyrite, Cu-0.1, Fe-0.1, S-0.1	0.3
Silver	0.1
Tetrahedrite + Stephanite	0.05
Quartz	20.6
Feldspar, K_2O-0.1, Na_2O-0.3, CaO-0.4, Al_2O_3-1.3, SiO_2-2.9	5.0
Chlorite, FeO-0.3, MgO-0.1, Al_2O_3-0.15, SiO_2-0.25, H_2O-0.1	.9
Carbon	0.2
Total	99.5

COMMINUTION, BLENDING, AND BOTTLING of KC-1

The coarse ore was crushed and dry-ground to minus 200 mesh using conventional milling equipment. The material, weighing approximately 275 lb was blended in a 45-gallon, baffled, mixing drum for eight hours. Upon opening the blender, the bulk ore was sampled and tested for homogeneity by techniques described below; these tests indicated a satisfactory product. Subsequently, KC-1 was bottled in 200-g lots. The approximate chemical composition of the material is given in Table 2 and its screen analysis is given in Table 3.

TABLE 2

Approximate chemical composition of KC-1

O - 14[a] wt %	S - 28
Si - 11	C - 0.2
Al - 0.8	Zn - 20.37[b]
Fe - 16	Pb - 6.98[b]
Ca - 0.3	Sn - 0.68[b]
Mg - 0.05	Cu - 0.114[b]
Na - 0.2	Ag - 0.114[b]
K - 0.1	H_2O (1800°F) - 0.7
Mn - 0.05	

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

b - Certified values from Table 10.

TABLE 3

Screen analysis of KC-1

Mesh size (Tyler)	wt %
+100	0.1
-100 +150	0.2
-150 +200	1.4
-200 +250	15.6
-250 +325	46.8
-325 +400	11.8
-400	24.1

TESTS FOR HOMOGENEITY

Prior to the distribution of samples to participating laboratories, X-ray fluorescence and chemical methods were used to establish that KC-1 was sufficiently homogeneous to be used for the purpose for which it was intended. As is mentioned below under Interlaboratory Program, each participating laboratory analyzed two bottles of KC-1; consequently, its homogeneity could be confirmed subsequently by comparing the reported results (Table 4) between bottles within each laboratory, using the t-test at a 5% significance level. The results of these tests are summarized in Table 5 and are illustrated in Figures 6 to 10. Table 5 shows that the majority of laboratories did not find any evidence of a difference between the two bottles they received.

INTERLABORATORY PROGRAM FOR CERTIFICATION OF KC-1

The names of the laboratories that participated in the program to certify KC-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.

Participating Laboratories

Bondar-Clegg & Company Limited, Ottawa, Ontario.

Bondar-Clegg & Company Limited, Vancouver, British Columbia.

British Columbia Dept. of Mines & Petroleum Resources, Victoria, British Columbia.

Can-Test Limited, Vancouver, British Columbia.

Chemex Labs Limited, North Vancouver, British Columbia.

Cominco Limited, 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.

Hudson Bay Mining & Smelting Company Limited, Flin Flon, Manitoba.

Inorganic and Analytical Research Group (two independent analysts), Mineral Sciences Division, Mines Branch, EMR, Ottawa, Ontario.

Lakefield Research of Canada Limited, Lakefield, Ontario.

Loring Laboratories Limited, Calgary, Alberta.

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

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

Noranda Mines Limited, Noranda, Ontario.

Sherritt Gordon Mines Limited, Research & Development Division, Fort Saskatchewan, Alberta.

Sherritt Gordon Mines Limited, Mining & Milling Division, Lynn Lake, Manitoba.

Special Projects Group (two independent analysts), 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.

Thunder Bay Testing Limited, Thunder Bay, Ontario.

The participating laboratories, with the exception of one within the Mineral Sciences Division of the Mines Branch, each received two randomly-selected bottles of KC-1. They were requested to determine as many as possible of zinc, lead, tin, copper and silver in each bottle, in quintuplicate, by methods of their choice. A number of laboratories voluntarily submitted analytical results by more than one method (Table 4). As in previous interlaboratory programs[2,4,6] of the CCRMP to certify reference ores, atomic absorption spectrophotometry was the most widely used analytical technique.

In cases where a laboratory submitted more than one set of results for an element, by different methods, each method set was considered to be independent of the other(s) for statistical purposes (Table 7) i.e., each set was treated as originating in a separate 'laboratory'.

ESTIMATION OF STATISTICAL PARAMETERS

The results reported by all participating laboratories are presented in Table 4. The following procedures were used to estimate the best values for the statistical parameters.

A. All results treated as though they were independent

Figures 1 to 5 show the cumulative distributions of the results for the five selected elements. The normal parameters, the median, mean, variance, standard deviation, skewness factor, and kurtosis coefficients were estimated twice, first from all the results and then from those results that deviate from the overall mean ($\overline{x}..$) by no more than twice the standard deviation. 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 6. For the five selected elements it is seen that the results that deviate from the mean by more than twice the standard deviation range between 3 and 10% of the total frequency. This is a reasonable proportion for normally distributed independent variables. By rejecting these results, both the skewness 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:

$$m_r = \frac{\sum_i^k \sum_j^{n_i} (x_{ij} - \bar{x}_{..})^r}{\sum_i^k n_i}$$

where m_r is the mean of the r^{th} moment of the x values about their mean.

In this and in other interlaboratory programs conducted by the authors[2-4,6], it is evident that there were substantial variations between laboratories and, indeed, between sets for the same laboratory and that, therefore, the results were not completely independent of each other. Table 7 shows that most of the laboratories reported coefficients of variation lower than the overall coefficient of variation. Figures 6 to 10 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[8]. 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 8 for completeness, are unrealistic; their narrowness emphasizes this point.

B. Analysis of variance technique

Because interlaboratory variations were expected, the results were then treated as though they satisfied the following model[9]:

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

where

x_{ij} = the j^{th} result reported by laboratory (set) i;

μ = the true value that is estimated by the overall mean $\bar{x}_{..}$;

y_i = the discrepancy between the mean of results from laboratory i and the true value; and

e_{ij} = the discrepancy of x_{ij} from the mean of results from laboratory i.

The assumption in this analysis is that both y_i and e_{ij} are normally distributed, with 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 degree of freedom. The true value, in the above model can be estimated by the overall mean, $\bar{x}_{..}$, thus:

$$\bar{x}_{..} = \frac{\sum_i^k \sum_j^{n_i} x_{ij}}{\sum_i^k n_i}$$

with the variance of this overall mean being given by:

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

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. The results of these calculations are presented in Table 8.

C. Weighted mean to give minimum variance

Further examination of Table 7 and Figures 6 to 10 shows that there is a wide range in the degree of precision obtained by the various laboratories. For this reason, weighting the data by a 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, $\bar{\bar{x}}_{..}$, was then computed from the following formula[9]:

$$\bar{\bar{x}}_{..} = \sum_i^k \frac{a_i}{n_i} \sum_j^{n_i} x_{ij}$$

in which

$$a_i = \frac{w_i}{\sum_i^k w_i}$$

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

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

The results of these various schemes of computation are summarized in Table 8 under the corresponding notations, A B, and C. The estimates of parameters under A were computed after rejecting all results that deviated from the overall mean by more than twice the standard deviation. The estimated parameters under B and C were computed after rejecting complete sets of results whose means deviated from the overall mean by more than twice the standard deviation.

TABLE 4

Results of analysis of KC-1

	Zinc (%)		Lead (%)		Tin (%)		Copper (%)		Silver (%)	
Lab-1	(a.a.)	(vol-a)	(a.a.)	(grav)	(a.a.)	(vol)	(a.a.)	(color)	(a.a.)	(f.a.)
	19.59	20.40	7.06	7.09	0.69	0.60	0.109	0.114	0.1115	0.1108
	19.72	20.30	7.06	7.08	0.71	0.58	0.110	0.112	0.1080	0.1114
	19.45	20.30	6.93	7.04	0.68	0.60	0.107	0.113	0.1080	0.1113
	19.72	20.40	6.93	6.92	0.71	0.61	0.109	0.110	0.1098	0.1117
	19.72	20.30	6.93	7.12	0.69	0.60	0.109	0.109	0.1080	0.1111
	19.59	20.40	6.87	7.24	0.69	0.60	0.108	0.115	0.1115	0.1105
	19.59	20.30	6.87	7.30	0.71	0.59	0.111	0.114	0.1108	0.1104
	19.86	20.30	6.87	7.17	0.69	0.59	0.108	0.113	0.1101	0.1103
	19.59	20.24	7.04	7.32	0.71	0.61	0.111	0.113	0.1101	0.1118
	19.59	20.19	7.04	7.33	0.68	0.60	0.108	0.109	0.1142	0.1101
		(vol-b)								
		20.23								
		20.23								
		20.22								
		20.23								
		20.17								
		20.30								
		20.30								
		20.22								
		20.17								
		20.10								
Sample wt, g	0.5	0.5	0.5	0.5	1	1	0.5	0.5	3	0.5 A.T.
Lab-2		(vol-a)	(a.a.)		(a.a.)		(a.a.)		(a.a.)	(f.a.)
		20.1	6.88		0.62		0.115		0.114	0.1133
		20.3	6.86		0.62		0.115		0.111	0.1132
		20.3	6.86		0.63		0.115		0.116	0.1133
		20.2	6.88		0.62		0.114		0.115	0.1133
		20.2	6.87		0.62		0.115		0.115	0.1132
		20.2	6.87		0.62		0.115		0.116	0.1133
		20.2	6.85		0.62		0.114		0.110	0.1132
		20.2	6.87		0.63		0.115		0.115	0.1133
		20.2	6.87		0.63		0.115		0.115	0.1134
		20.2	6.88		0.63		0.114		0.113	0.1133

a.a. = atomic absorption; vol = volumetric; polar = polarographic; grav = gravimetric; f.a. = fire assay; xrf = X-ray fluorescence; color = colorimetric (spectrophotometric).

vol-a = volumetric-ferrocyanide; vol-b = volumetric-EDTA; vol-c = volumetric-molybdate; vol-d = volumetric-thiosulphate.

NOTE: For each laboratory-entry, results from different bottles are separated by horizontal lines.

Table 4 (continued)

	Zinc (%)	Lead (%)	Tin (%)	Copper (%)		Silver (%)	
Lab-3	(vol-b)	(vol-b)	(a.a.)	(a.a.)	(vol)	(a.a.)	(f.a.)
	20.57	6.96	0.66	0.107	0.11	0.1150	0.1153
	20.57	6.96	0.66	0.112	0.11	0.1150	0.1150
	20.57	6.96	0.65	0.112	0.11	0.1125	0.1138
	20.62	6.86	0.69	0.112	0.11	0.1100	0.1142
	20.62	7.01	0.68	0.112	0.11	0.1125	0.1145
	20.57	7.07	0.66	0.116	0.10	0.1125	0.1151
	20.57	6.96	0.66	0.109	0.10	0.1100	0.1127
	20.62	7.07	0.68	0.112	0.10	0.1049	0.1131
	20.57	7.04	0.68	0.109	0.10	0.1135	0.1141
	20.62	7.04	0.67	0.112	0.10	0.1135	0.1149
	(vol-a)	6.93	0.66				0.1158
	20.54	7.04	0.65				0.1162
	20.59	7.04	0.66				
	20.54	(vol-c)	0.67				
	20.54	7.07	0.66				
	20.54	7.07	0.63				
	20.34	7.07	0.66				
	20.29	7.07	0.67				
	20.39	7.07	0.66				
	20.39	7.08	0.68				
	20.39	7.05					
		7.10					
		7.05					
		7.10					
		7.05					
		7.05					
		7.10					
		7.05					
		7.05					
Sample wt, g	0.5-1	1	0.25	0.5	5	1	0.5 A.T.
Lab-4	(vol-b)	(vol-b)		(a.a.)	(vol)	(a.a.)	(f.a.)
	20.06	7.01		0.12	0.12	0.1080	0.1135
	20.13	6.96		0.12	0.12	0.1110	0.1122
	20.17	7.01		0.12	0.12	0.1130	0.1128
	20.14	7.01		0.12	0.12	0.1050	0.1134
	20.19	7.01		0.12	0.12	0.1060	0.1119
	20.19	6.96		0.12	0.13	0.1140	0.1117
	20.20	7.01		0.13	0.12	0.1130	0.1130
	20.13	7.04		0.12	0.12	0.1110	0.1133
	20.17	6.96		0.12	0.12	0.1100	0.1123
	20.21	7.04		0.12	0.13	0.1080	0.1125
Sample wt, g	1	1		1	2	1	0.5 A.T.

Table 4 (continued)

	Zinc (%)		Lead (%)		Tin (%)	Copper (%)		Silver (%)	
Lab-5				(xrf)	(xrf)				(xrf)
				6.90	0.71				0.14
				6.88	0.71				0.14
				6.89	0.70				0.14
				6.97	0.70				0.13
				6.88	0.71				0.13
				6.96	0.70				0.13
				6.88	0.69				0.13
				7.06	0.69				0.13
				7.01	0.69				0.13
				7.11	0.69				0.12
Lab-6						(a.a.)		(a.a.)	
						0.117		0.119	
						0.118		0.115	
						0.118		0.115	
						0.117		0.114	
						0.118		0.116	
						0.118		0.115	
						0.118		0.114	
						0.119		0.116	
						0.119		0.116	
						0.118		0.118	
Sample wt, g						0.5		1	
Lab-7	(a.a.)	(vol-a)	(a.a.)	(vol-c)		(a.a.)	(vol)	(a.a.)	(vol)
	20.84	20.89	6.86	6.77		0.109	0.111	0.109	0.106
	20.37	20.75	6.59	6.69		0.104	0.106	0.108	0.114
	20.82	20.53	6.86	6.54		0.106	0.107	0.107	0.112
	20.47	20.35	6.80	6.70		0.104	0.111	0.112	0.106
	20.37	20.74	6.57	6.79		0.110	0.105	0.113	0.107
	20.69	20.70	6.67	6.63		0.106	0.110	0.114	0.111
	20.85	20.66	6.59	6.67		0.110	0.111	0.107	0.110
	20.77	20.48	6.77	6.71		0.108	0.108	0.110	0.108
	20.38	20.30	6.90	6.69		0.105	0.105	0.109	0.110
	20.40	20.81	6.87	6.79		0.110	0.107	0.113	0.109
Sample wt, g	0.5	1	1	1		2	2	2	2

Table 4 (continued)

	Zinc (%)		Lead (%)		Tin (%)		Copper (%)		Silver (%)	
Lab-8	(a.a.)	(vol-a)	(a.a.)	(vol-b)			(a.a.)	(vol)	(a.a.)	(f.a.)
	20.53	20.34	7.00	6.65			0.120	0.112	0.122	0.116
	20.42	20.19	7.01	6.67			0.123	0.114	0.121	0.112
	20.46	20.34	7.01	6.59			0.120	0.113	0.122	0.110
	20.42	20.24	7.00	6.62			0.119	0.114	0.123	0.113
	20.30	20.19	6.95	6.68			0.120	0.110	0.121	0.112
	20.42	20.39	7.00	6.61			0.121	0.112	0.120	0.113
	20.37	20.26	6.94	6.55			0.119	0.113	0.123	0.113
	20.34	20.34	7.00	6.63			0.119	0.110	0.122	0.111
	20.38	20.39	6.98	6.66			0.118	0.110	0.122	0.113
	20.37	20.29	6.97	6.64			0.118	0.110	0.121	0.114
Sample wt, g	0.5	0.5	1	1			1	3	2	6
Lab-9		(vol-a)	(a.a.)	(vol-c)	(a.a.)		(a.a.)			(f.a.)
		20.4	7.0	6.94	0.77		0.11			0.116
		20.3	7.0	6.97	0.78		0.11			0.116
		20.4	7.0	6.94	0.78		0.11			0.116
		20.3	7.0	6.97	0.78		0.11			0.117
		20.4	7.1	6.94	0.79		0.11			0.117
		20.4	7.0	6.94	0.79		0.11			0.116
		20.4	7.0	6.97	0.79		0.11			0.116
		20.4	7.0	6.97	0.78		0.11			0.116
		20.3	7.1	6.92	0.78		0.11			0.118
		20.4	7.0	6.99	0.78		0.11			0.116
Sample wt, g		1	0.25	2	2		2			0.5 A.T.
Lab-10	(a.a.)	(polar)	(a.a.)	(vol-d)		(vol)	(a.a.)	(polar)	(a.a.)	(f.a.)
	20.66	20.68	6.98	7.04		0.67	0.114	0.116	0.1166	0.1168
	20.50	20.68	7.00	7.01		0.68	0.113	0.117	0.1157	0.1160
	20.66	20.74	6.97	6.98		0.682	0.114	0.115	0.1160	0.1162
	20.48	20.74	7.01	6.96		0.68	0.114	0.117	0.1160	0.1156
	20.70	20.66	7.01	6.98		0.678	0.115	0.115	0.1162	0.1159
	20.60	20.70	7.00	7.00		0.67	0.114	0.112	0.1166	0.1169
	20.68	20.74	7.01	6.99		0.68	0.112	0.117	0.1160	0.1166
	20.49	20.64	6.98	6.96		0.682	0.116	0.115	0.1162	0.1163
	20.66	20.68	7.04	6.97		0.67	0.114	0.115	0.1160	0.1159
	20.72	20.66	6.96	7.00		0.684	0.116	0.116	0.1160	0.1155
				(polar)		(polar)				
				6.96		0.672				
				7.02		0.674				
				6.97		0.68				
				6.96		0.684				

(continued)

Table 4 (continued)

	Zinc (%)	Lead (%)	Tin (%)	Copper (%)	Silver (%)
			0.68		
			0.684		
			0.685		
			0.68		
			0.673		
			0.675		
Sample wt, g	0.5 1	0.5 1	1	1 1	2 5
Lab-11	(vol-b)	(vol-b)	(vol)	(a.a.)	(a.a.)
	20.35	6.92	0.60	0.11	0.118
	20.41	6.95	0.59	0.11	0.114
	20.40	6.96	0.58	0.11	0.116
	20.29	6.96	0.59	0.11	0.114
	20.30	6.97	0.58	0.11	0.117
	20.38	6.97	0.59	0.11	0.118
	20.33	6.98	0.58	0.11	0.117
	20.36	6.95	0.59	0.11	0.114
	20.29	6.96	0.59	0.11	0.113
	20.36	6.94	0.59	0.11	0.113
Sample wt, g	0.5	1	2	1	0.25
Lab-12	(vol-b)	(vol-b)	(vol)	(color)	
	20.38	6.90	0.667	0.118	
	20.32	6.95	0.668	0.119	
	20.36	6.97	0.668	0.117	
	20.40	6.95	0.680	0.117	
	20.44	6.93	0.678	0.117	
	20.36	6.98	0.675	0.115	
	20.38	6.90	0.682	0.123	
	20.37	7.00	0.701	0.118	
	20.39	6.91	0.670	0.122	
	20.37	6.96	0.683	0.114	
	20.32	6.98	0.663		
	20.37	6.96	0.673		
	20.34	6.97	0.662		
	20.38	6.96	0.673		
	20.31	7.01	0.662		
	20.35	7.01	0.681		
	20.32	6.99	0.671		
	20.39	7.00	0.687		
	20.26	7.01	0.660		
	20.38	6.99	0.673		
Sample wt, g	0.5	0.5	2	1	

Table 4 (continued)

	Zinc (%)		Lead (%)		Tin (%)	Copper (%)		Silver (%)
Lab-13	(a.a.)		(a.a.)		(a.a.)	(a.a.)		(a.a.)
	20.4		6.982		0.74	0.115		0.1158
	20.3		7.101		0.71	0.114		0.1156
	20.4		7.025		0.71	0.116		0.1154
	20.3		7.018		0.70	0.114		0.1161
	20.3		7.072		0.70	0.116		0.1158
	20.1		7.056		0.73	0.117		0.1160
	20.2		7.109		0.70	0.118		0.1160
	20.3		7.109		0.71	0.117		0.1158
	20.4		7.077		0.67	0.116		0.1150
	20.3		6.982		0.71	0.116		0.1172
Sample wt, g	2		2		2	1		2
Lab-14	(a.a.)	(polar)	(a.a.)	(vol-c)		(a.a.)	(polar)	(f.a.)
	20.6	20.84	6.85	6.858		0.122	0.118	0.1128
	20.2	20.45	6.90	6.858		0.116	0.114	0.1107
	20.3	20.52	6.90	6.807		0.114	0.114	0.1117
	20.3	20.52	6.90	6.858		0.114	0.114	0.1118
	20.2	20.52	6.85	6.858		0.112	0.111	0.1117
	20.3	20.64	6.85	6.807		0.112	0.112	0.1115
	20.2	20.64	6.85	6.883		0.110	0.107	0.1123
	20.4	20.52	6.90	6.807		0.110	0.109	0.1112
	20.3	20.52	6.90	6.858		0.110	0.109	0.1116
	20.2	20.52	6.90	6.833		0.108	0.106	0.1142
Sample wt, g	0.5	0.5	0.5	1		0.5	2	0.5 A.T.
Lab-15		(vol-b)		(vol-b)	(polar)		(polar)	
		20.26		7.04	0.69		0.11	
		20.23		7.04	0.68		0.11	
		20.29		7.04	0.68		0.12	
		20.29		7.07	0.70		0.11	
		20.29		7.03	0.69		0.11	
		20.26		7.07	0.69		0.11	
		20.23		6.99	0.68		0.11	
		20.29		7.04	0.68		0.11	
		20.26		7.04	0.68		0.11	
		20.29		7.05	0.69		0.11	
Sample wt, g		1		2	1		1	

Table 4 (continued)

	Zinc (%)		Lead (%)		Tin (%)	Copper (%)	Silver (%)	
Lab-16					(vol)			
					0.681			
					0.679			
					0.681			
					0.682			
					0.680			
					0.680			
					0.684			
					0.684			
					0.682			
					0.682			
Sample wt, g					2			
Lab-17	(a.a.)	(vol-a)	(a.a.)		(a.a.)	(a.a.)	(a.a.)	(f.a.)
	20.4	20.2	7.02		0.672	0.116	0.118	0.114
	20.1	20.1	6.95		0.671	0.116	0.119	0.115
	20.3	20.3	6.94		0.670	0.115	0.119	0.115
	20.5	20.1	6.98		0.667	0.115	0.118	0.116
	20.1	20.3	6.95		0.667	0.114	0.119	0.115
			6.93		0.667	0.112		
			6.91		0.664	0.110		
			6.94		0.670	0.113		
			6.97		0.680	0.113		
			7.01		0.669	0.114		
Sample wt, g	1	0.5	1		1	1-2	0.5 A.T.	0.5 A.T.
Lab-18		(vol-a)		(vol-c)	(a.a.)	(a.a.)		(f.a.)
		20.33		7.00	0.71	0.11		0.1161
		20.37		7.01	0.72	0.11		0.1159
		20.36		7.01	0.72	0.11		0.1166
		20.34		7.00	0.72	0.11		0.1164
		20.32		7.02	0.73	0.11		0.1164
		20.35		6.98	0.71	0.11		0.1165
		20.37		7.04	0.72	0.11		0.1161
		20.31		7.01	0.72	0.11		0.1161
		20.38		6.98	0.72	0.11		0.1166
		20.39		6.98	0.73	0.11		0.1162
Sample wt, g		0.5		1	0.5	1		0.5 A.T.

Table 4 (continued)

	Zinc (%)	Lead (%)	Tin (%)	Copper (%)	Silver (%)	
Lab-19			(color)			
			0.683			
			0.685			
			0.680			
			0.706			
			0.700			
			0.697			
			0.690			
			0.692			
			0.695			
			0.709			
Sample wt, g			0.25			
Lab-20	(a.a.)	(a.a.)	(a.a.)	(a.a.)	(a.a.)	(f.a.)
	20.5	7.02	0.70	0.117	0.106	0.117
	20.5	6.90	0.71	0.119	0.103	0.117
	20.4	6.90	0.69	0.119	0.107	0.117
	20.5	7.02	0.72	0.117	0.107	0.117
	20.4	7.02	0.66	0.116	0.107	0.115
	20.4	6.91	0.70	0.116	0.107	0.117
	20.3	7.04	0.70	0.116	0.106	0.118
	20.4	6.85	0.70	0.117	0.106	0.117
	20.5	6.91	0.68	0.118	0.108	0.118
	20.4	6.98	0.70	0.119	0.105	0.117
Lab-21			(vol)			
			0.689			
			0.683			
			0.693			
			0.683			
			0.675			
			0.681			
			0.679			
			0.685			
			0.682			
			0.675			
Sample wt, g			1.5			

Table 4 (continued)

	Zinc (%)	Lead (%)		Tin (%)	Copper (%)	Silver (%)
Lab-22	(vol-a)	(a.a.)	(vol-c)		(a.a.)	(f.a.)
	20.15	7.20	7.20		0.12	0.1138
	20.18	7.20	7.20		0.12	0.1140
	20.18	7.15	7.15		0.12	0.1131
	20.13	7.15			0.12	0.1132
	20.16	7.15			0.12	0.1138
	20.16	7.20			0.12	0.1129
	20.18	7.20			0.12	0.1131
	20.18	7.15			0.12	0.1131
	20.16	7.20			0.12	0.1130
	20.13				0.12	0.1136
	20.13				0.12	0.1131
	20.16				0.12	0.1135
Sample wt, g	0.5		1		0.5	0.5 A.T.
Lab-23	(vol-a)		(vol-c)	(vol)	(a.a.)	(f.a.)
	20.23		6.93	0.55	0.103	0.1121
	20.23		6.93	0.55	0.106	0.1131
	20.13		6.98	0.55	0.104	0.1126
	20.23		7.03	0.60	0.103	0.1127
	20.18		6.98	0.55	0.104	0.1128
	20.28		6.93	0.50	0.104	0.1122
	20.28		7.03	0.51	0.103	0.1125
	20.28		6.88	0.53	0.103	0.1122
	20.23		7.03	0.54	0.104	0.1129
	20.28		7.03	0.55	0.104	0.1123
			(grav)			
			6.77			
			6.81			
			6.84			
			6.78			
			6.86			
			6.88			
			6.77			
			6.92			
			6.85			
			6.85			
Sample wt, g	1		1	1	1	0.5 A.T.

Table 4 (concluded)

	Zinc (%)	Lead (%)		Tin (%)		Copper (%)		Silver (%)
Lab-24	(vol-a)	(a.a.)	(vol-d)	(a.a.)	(vol)	(a.a.)	(color)	(f.a.)
	20.24	7.04	6.98	0.65	0.656	0.127	0.118	0.1168
	20.23	7.00	6.94	0.67	0.666	0.123	0.121	0.1177
	20.25	7.04	6.96	0.60	0.650	0.117	0.118	0.1168
	20.31	7.06	6.95	0.67	0.662	0.122	0.113	0.1163
	20.25	7.07	7.01	0.60	0.652	0.123	0.120	0.1182
	20.25	7.06	7.00	0.65	0.656	0.123	0.116	0.1155
	20.27	7.12	7.00	0.63	0.647	0.120	0.117	0.1181
	20.27	6.98	6.93	0.65	0.676	0.122	0.111	0.1188
	20.25	7.06	6.96	0.65	0.662	0.120	0.116	0.1171
	20.27	7.00	6.98	0.63	0.652	0.122	0.116	0.1187
Sample wt, g	1	0.5	1	1	1	1	1	0.5 A.T.
Lab-25	(vol-a)	(a.a.)	(vol-c)		(vol)	(a.a.)		(f.a.)
	20.26	7.26	7.33		0.608	0.112		0.1102
	20.41	7.30	7.33		0.612	0.112		0.1108
	20.26	7.26	7.33		0.608	0.112		0.1103
	20.26	7.26	7.35		0.618	0.112		0.1110
	20.46	7.28	7.33		0.616	0.112		0.1113
	20.26	7.34	7.23		0.620	0.112		0.1105
	20.36	7.32	7.23		0.610	0.112		0.1102
	20.21	7.30	7.17		0.612	0.112		0.1108
	20.31	7.30	7.12		0.616	0.112		0.1106
	20.31	7.30	7.12		0.608	0.111		0.1109
Sample wt, g	0.5	0.25	1		2	1		0.5 A.T.

TABLE 5

Summary of the t-tests on results between bottles for each laboratory

Lab. No.	Zinc		Lead		Tin		Copper		Silver	
1	a.a.	A	a.a.	A	a.a.	A	a.a.	A	a.a.	A
	vol.	A	grav.	R	vol.	A	color.	A	f.a.	A
2	vol.	A	a.a.	A	a.a.	A	a.a.	A	a.a.	A
									f.a.	A
3	vol.	R			a.a.	A	a.a.	A	a.a.	A
							vol.	R	f.a.	A
4	vol.	A	vol.	A			a.a.	A	a.a.	A
							vol.	A	f.a.	A
5			xrf.	R	xrf.	R			xrf.	R
6							a.a.	R	a.a.	A
7	a.a.	A	a.a.	A			a.a.	A	a.a.	A
	vol.	A	vol.	A			vol.	A	vol.	A
8	a.a.	A	a.a.	A			a.a.	A	a.a.	A
	vol.	A	vol.	A			vol.	A	f.a.	A
9	vol.	A	a.a.	A	a.a.	A	a.a.	A	f.a.	A
			vol.	A						
10	a.a.	A	a.a.	A	vol.	A	a.a.	A	a.a.	A
	polar.	A	vol.	A	polar.	A	polar.	A	f.a.	A
			polar.	A						
11	vol.	A	vol.	A	vol.	A	a.a.	A	a.a.	A
12	vol.	R	vol.	R	vol.	A	color.	A		
13	a.a.	A	a.a.	A	a.a.	A	a.a.	R	a.a.	A
14	a.a.	A	a.a.	A			a.a.	R	f.a.	A
	polar.	A	vol.	A			polar.	R		
15	vol.	A	vol.	A	polar.	A	polar.	A		
16					vol.	A				
17			a.a.	A	a.a.	A	a.a.	R		
18	vol.	A	vol.	A	a.a.	A	a.a.	A	f.a.	A
19					color.	A				
20	a.a.	A	a.a.	A	a.a.	A	a.a.	A	a.a.	A
									f.a.	A
21					vol.	A				
22	vol.	A	a.a.	A			a.a.	A	f.a.	A
23	vol.	R	grav.	A	vol.	R	a.a.	A	f.a.	A
			vol.	A						
24	vol.	A	a.a.	A	a.a.	A	a.a.	A	f.a.	A
			vol.	A	vol.	A	color.	A		
25	vol.	A	a.a.	R	vol.	A	a.a.	A	f.a.	A
			vol.	R						

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

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

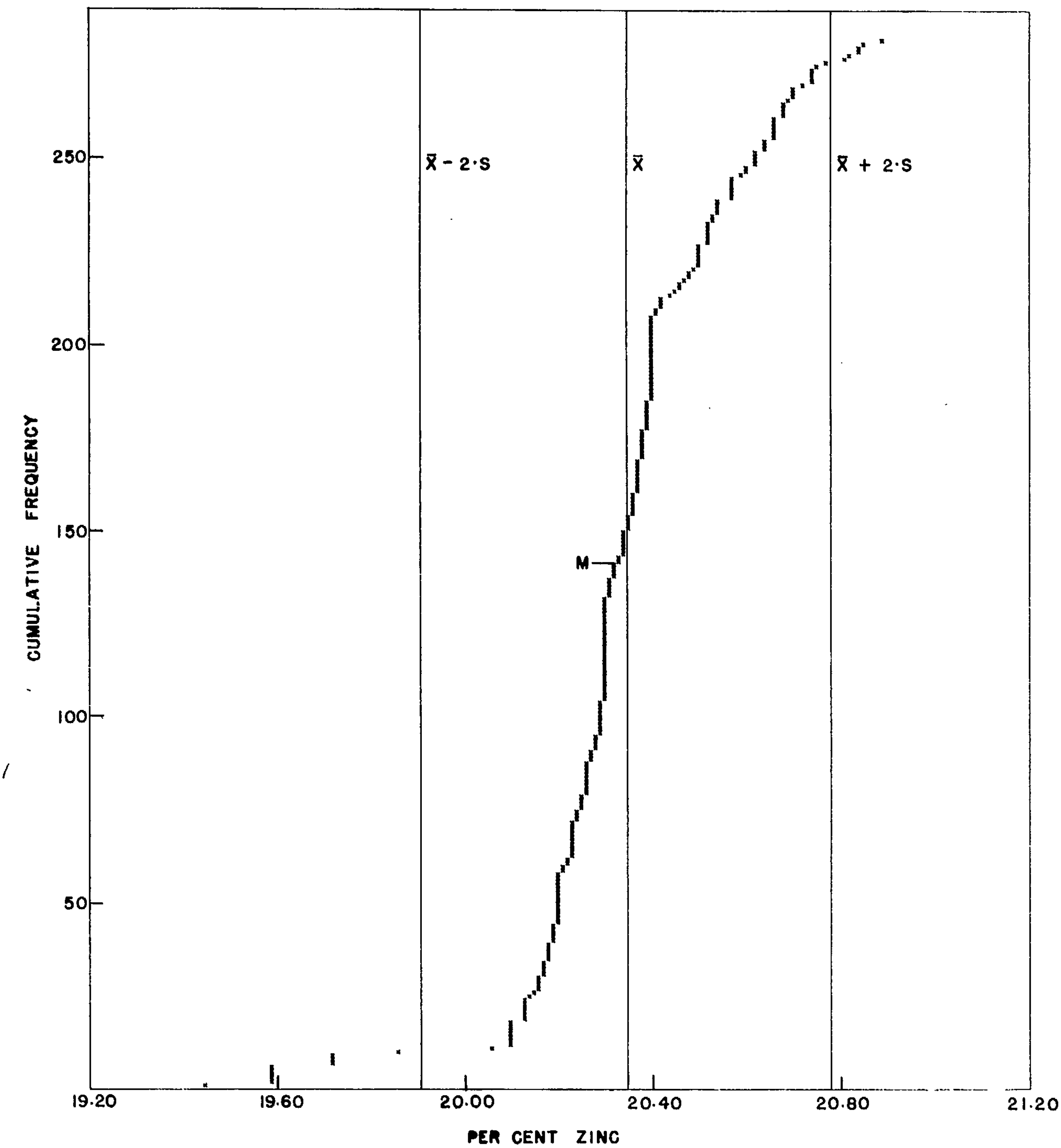

Fig. 1. Cumulative distribution for zinc results.

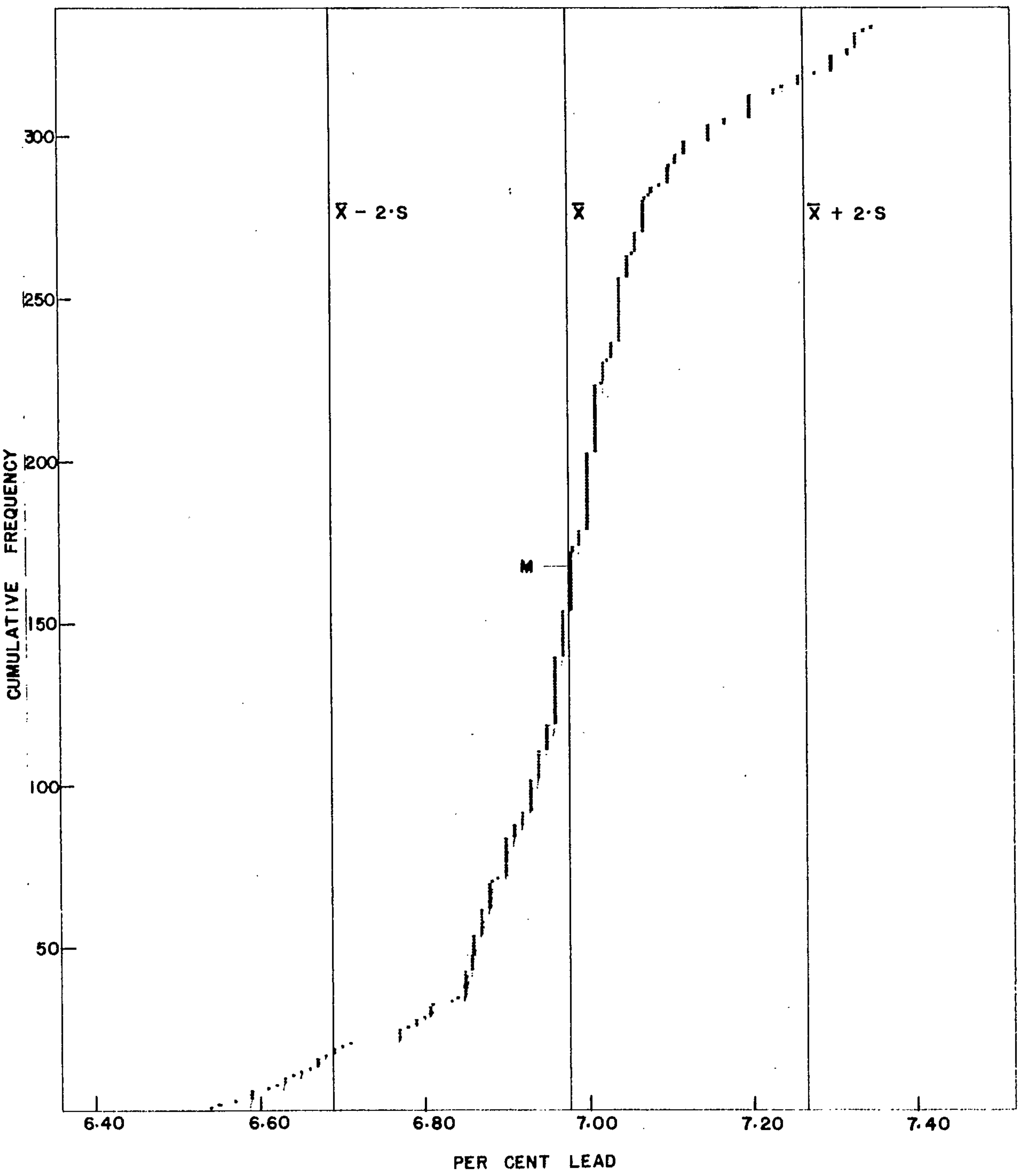

Fig. 2. Cumulative distribution for lead results.

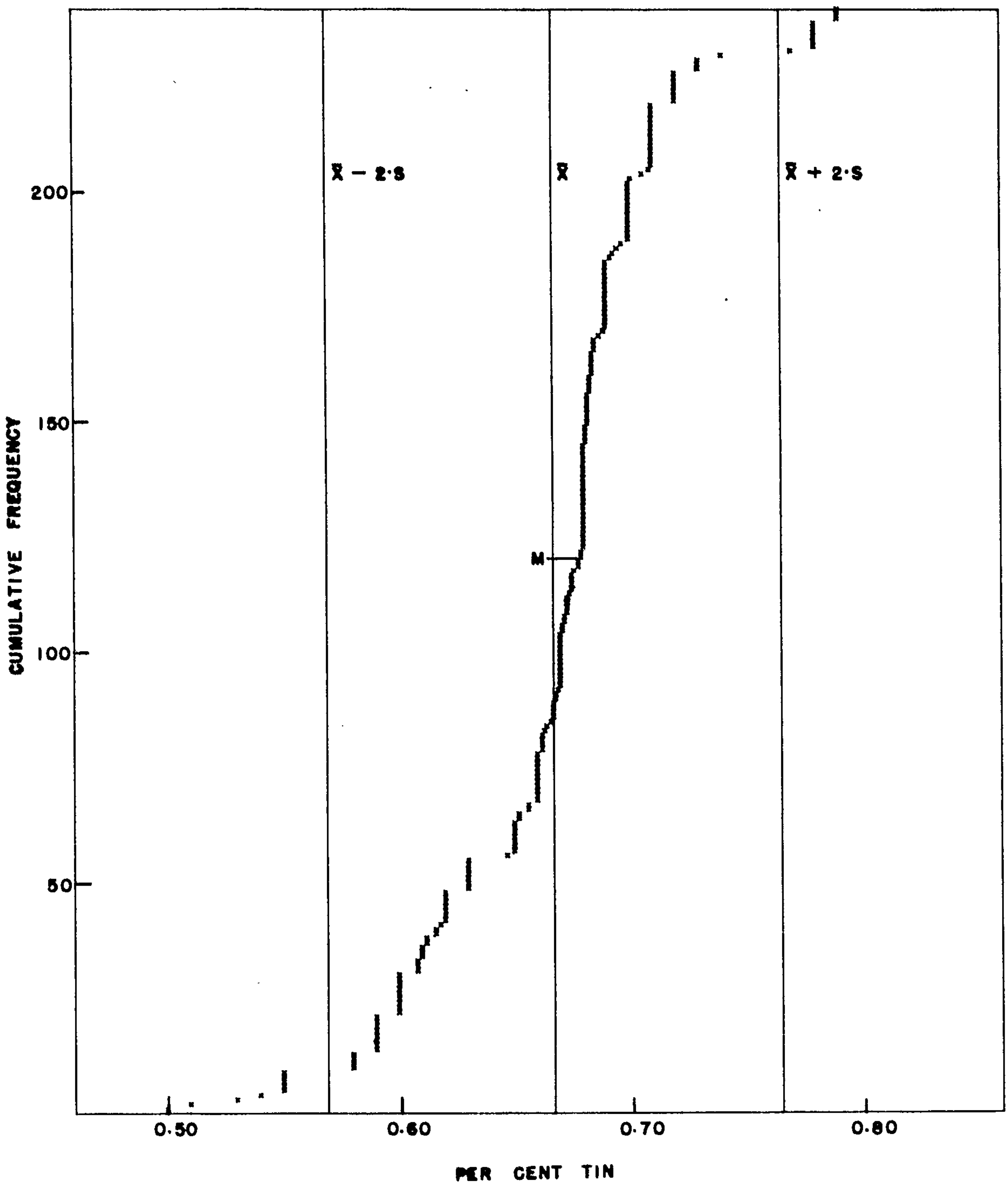

Fig. 3. Cumulative distriburion for tin results.

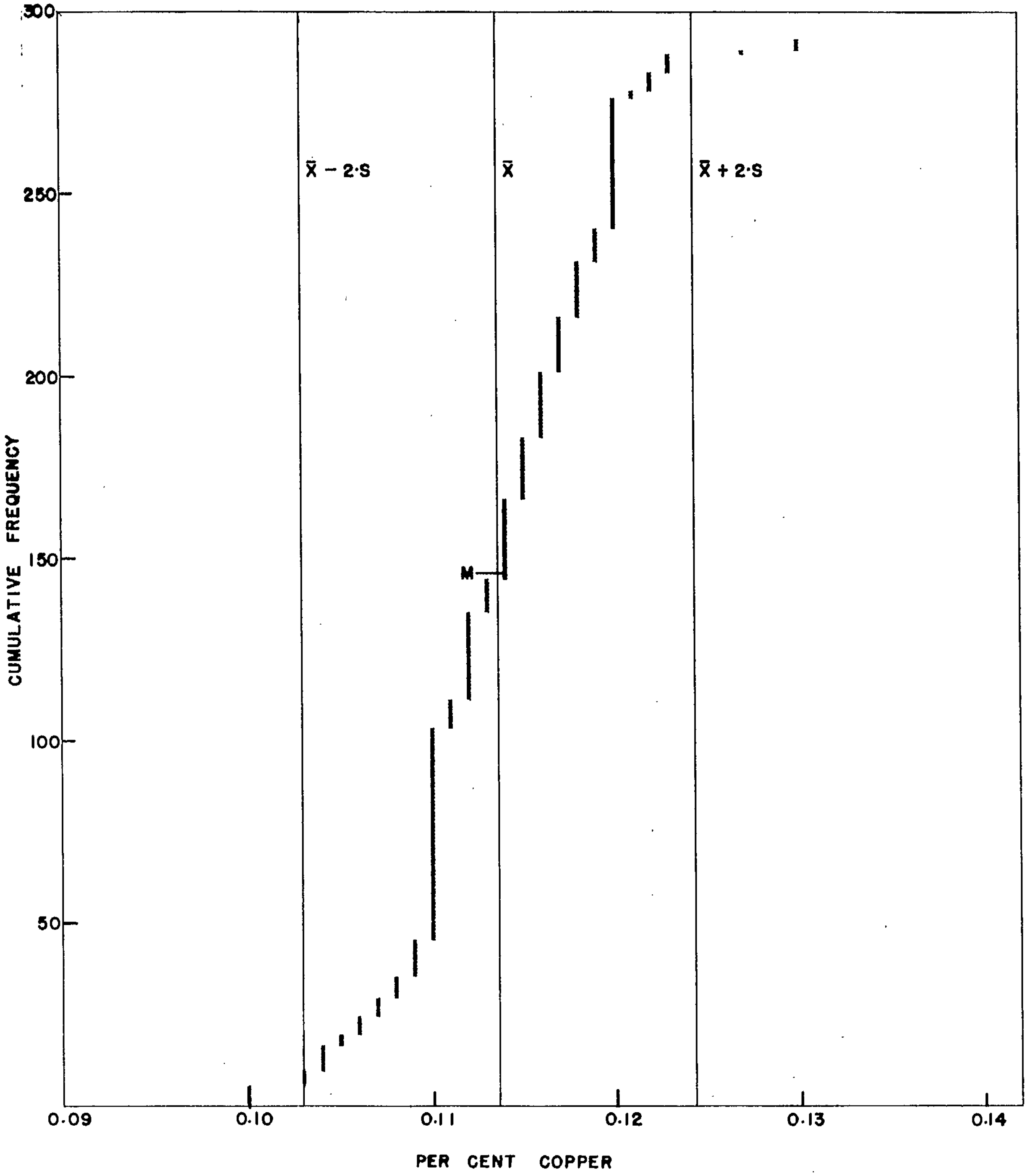

Fig. 4. Cumulative distribution for copper results.

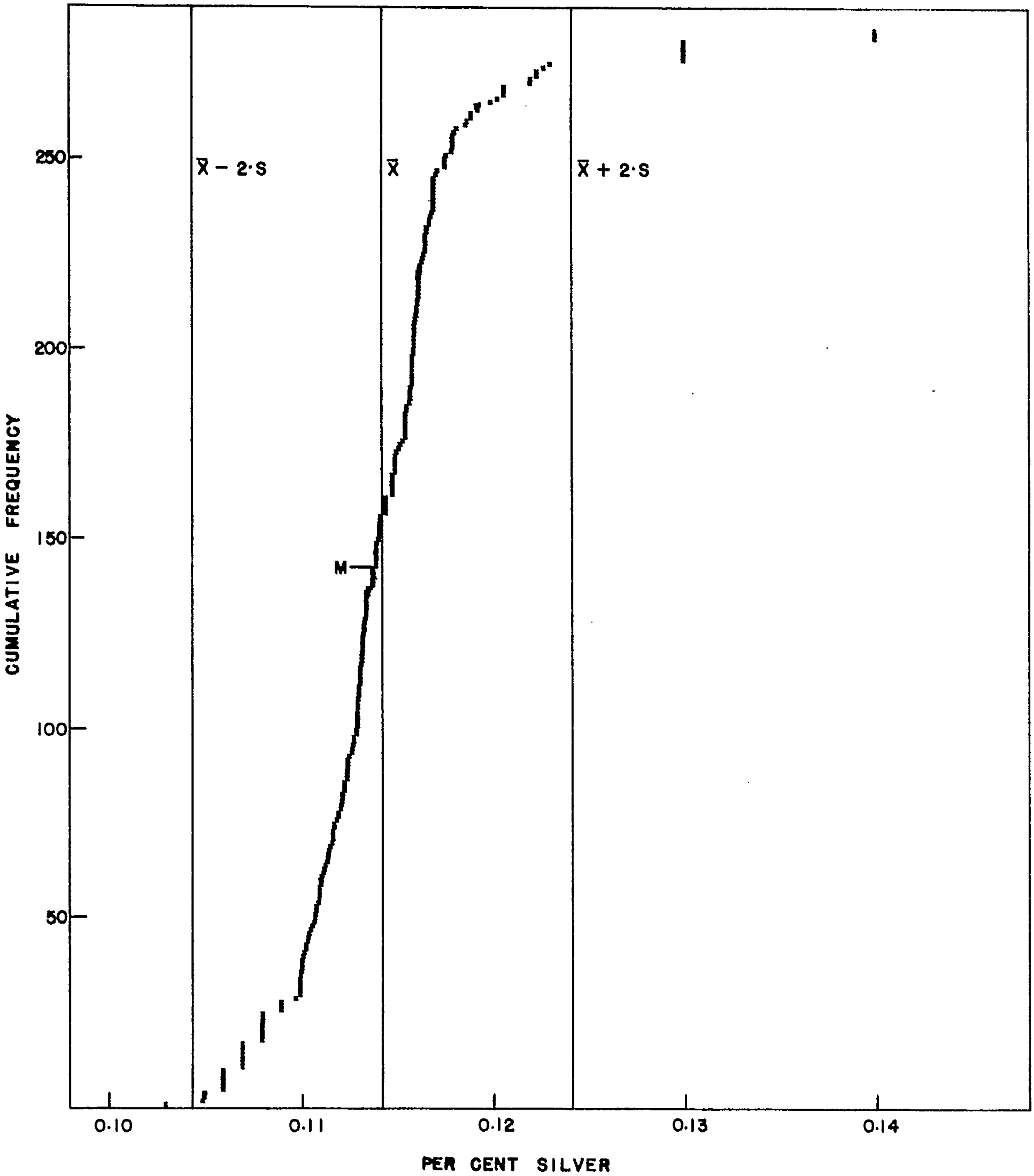

Fig. 5. Cumulative distribution for silver results.

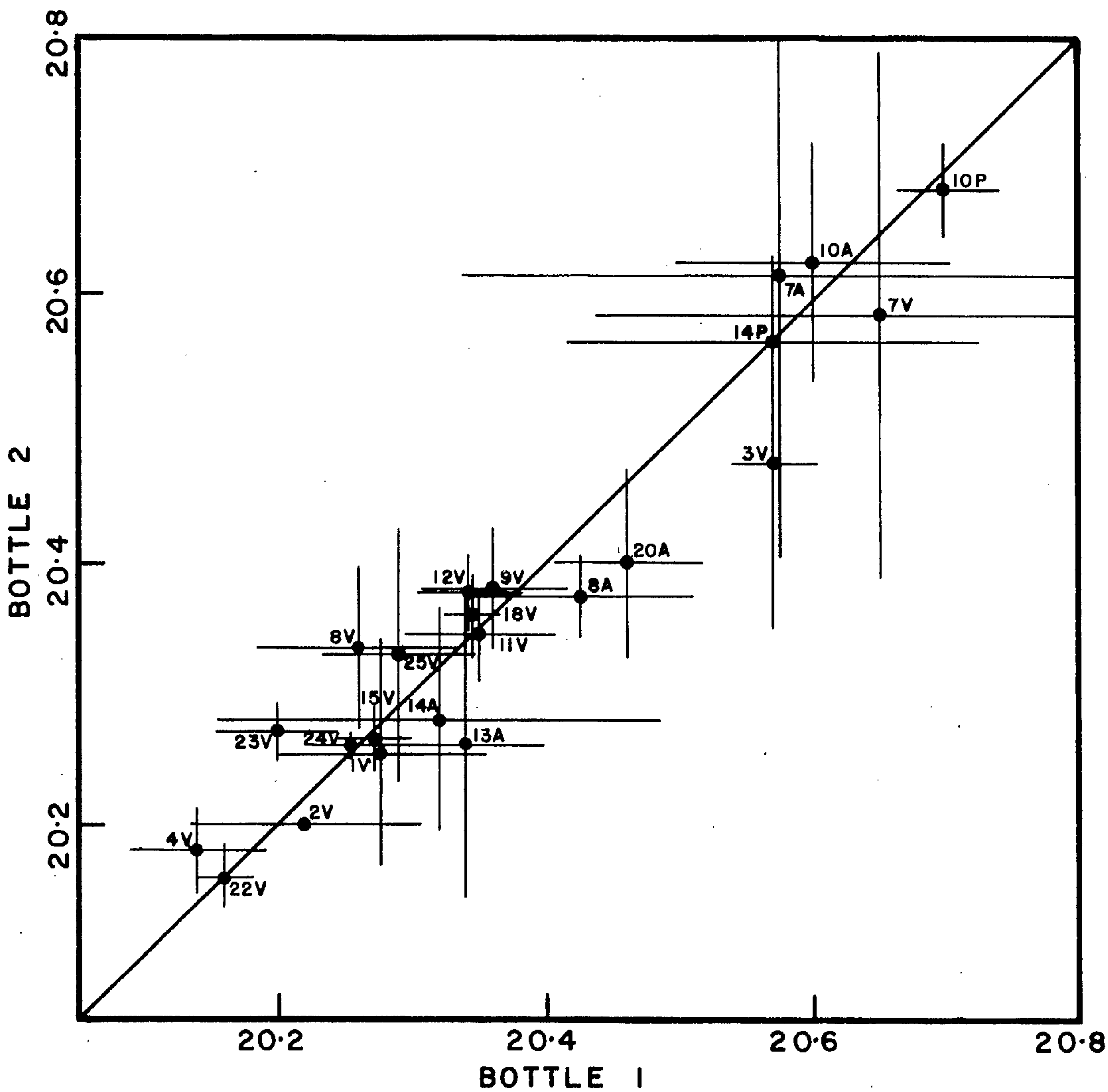

Fig. 6. Average zinc analyses (%) from each participating laboratory. (The crosses indicate one standard deviation on either side of the average for both bottles analyzed.)

NOTE: A = atomic absorption; V = volumetric; P = polarographic.

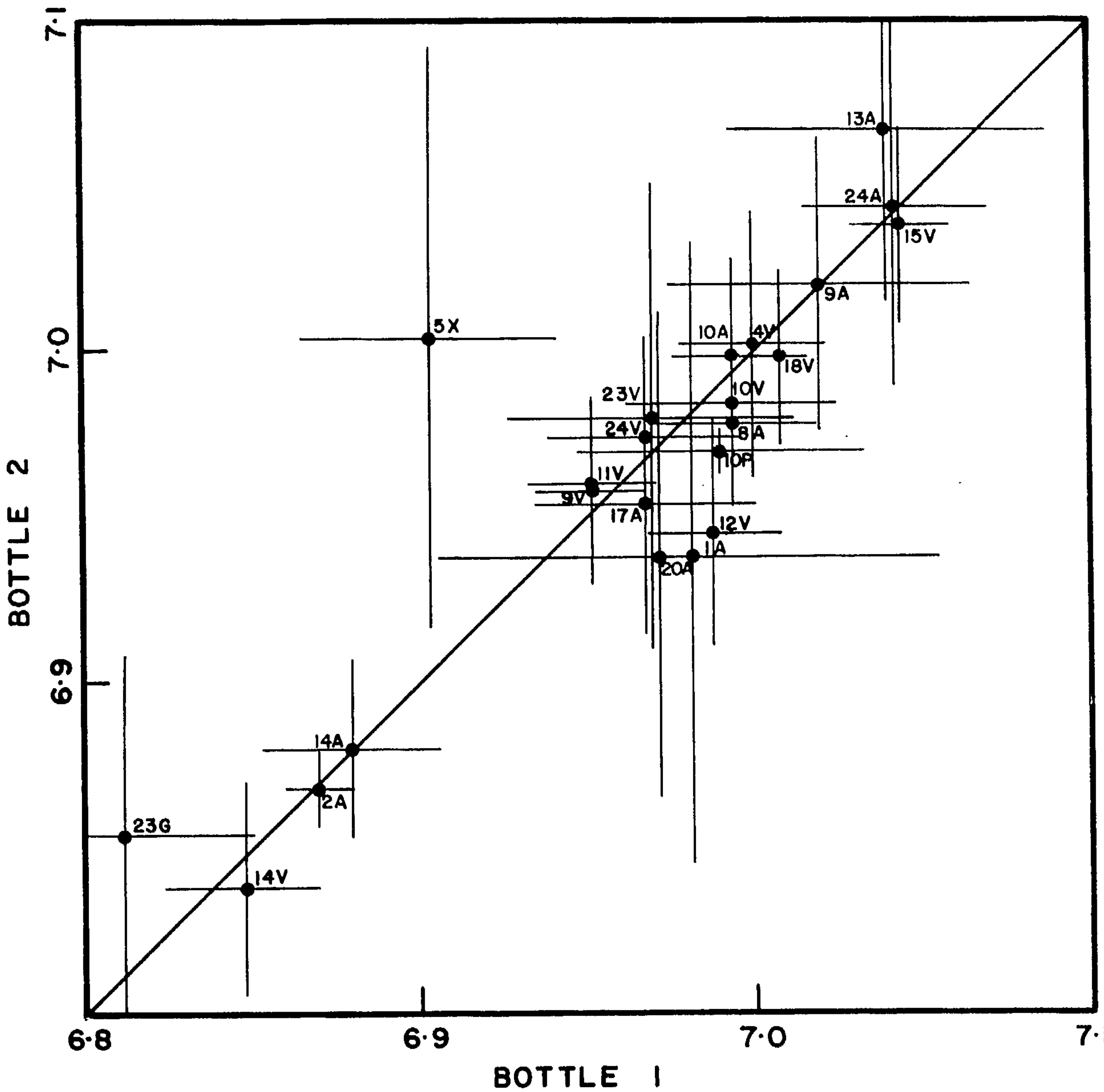

Fig. 7. Average lead analyses (%) from each participating laboratory. (The crosses indicate one standard deviation on either side of the average for both bottles analyzed.)

NOTE: A = atomic absorption; V = volumetric; P = polarographic; G = gravimetric; X = X-ray fluorescence.

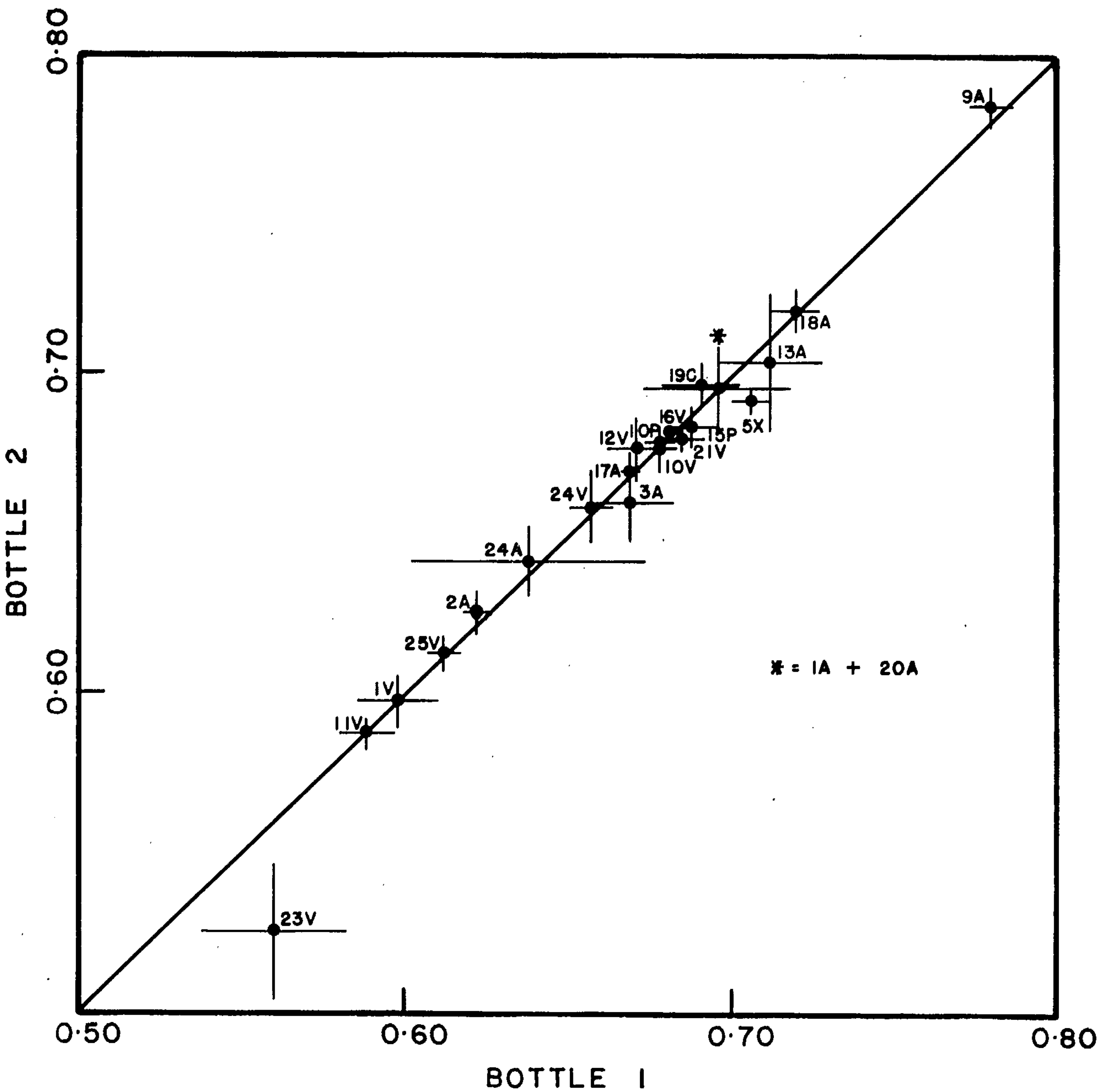

Fig. 8. Average tin analyses (%) from each participating laboratory. (The crosses indicate one standard deviation on either side of the average for both bottles analyzed.)

NOTE: A = atomic absorption; V = volumetric; P = polarographic; X = X-ray fluorescence; C = colorimetric (spectrophotometric).

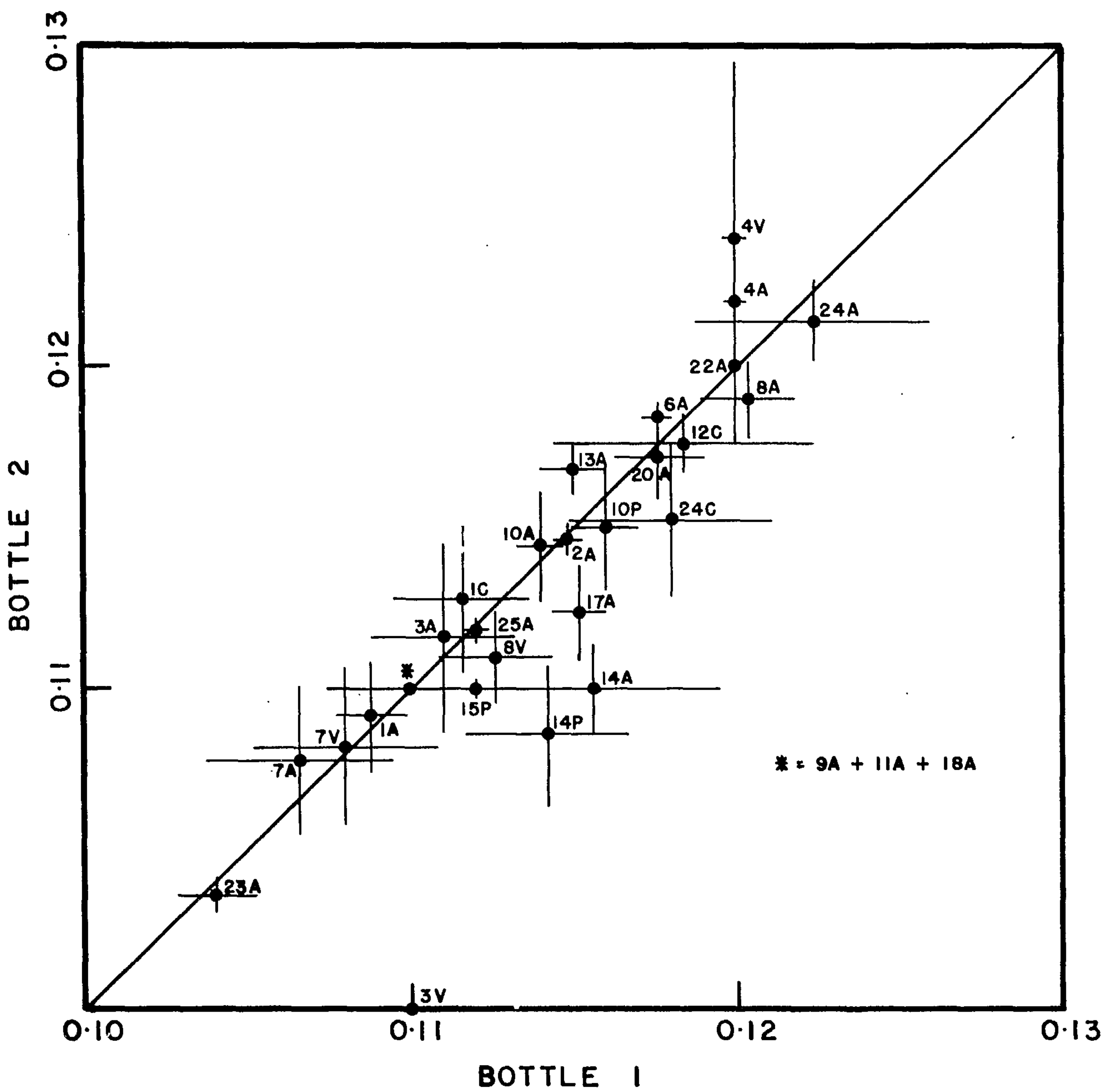

Fig. 9. Average copper analyses (%) from each participating laboratory. (The crosses indicate one standard deviation on either side of the average for both bottles analyzed.)

NOTE: A = atomic absorption; V = volumetric; P = polarographic; C = colorimetric.

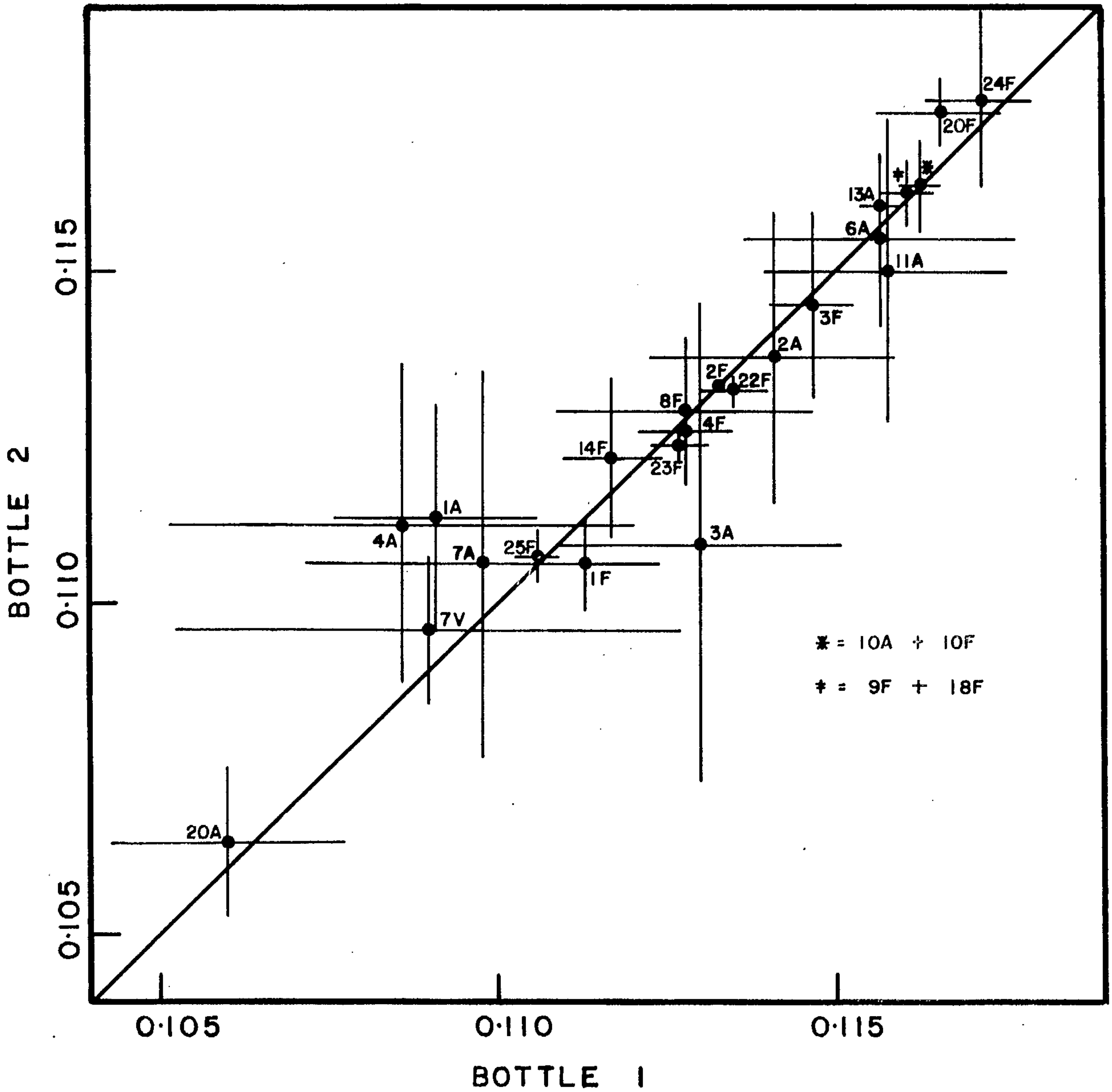

Fig. 10. Average silver analyses (%) from each participating laboratory. (The crosses indicate one standard deviation on either side of the average for both bottles analyzed.)

NOTE: A = atomic absorption; F = fire assay; V = volumetric.

TABLE 6

Estimates of statistical parameters for KC-1, based on the assumption that the analytical results are all independent*

Elements	No. of Obs. N	Median M (%)	Mean $\bar{x}$ (%)	Std. Dev. s (%)	Coeff. of Var. c.v. (%)	Skewness Factor α_3	Kurtosis Coeff. α_4
Zinc	282	20.33	20.34	0.22	1.1	-0.7	5.9
	266	20.34	20.36	0.16	0.8	0.7	2.9
Lead	334	6.98	6.98	0.14	2.1	-0.2	4.3
	302	6.98	6.98	0.10	1.4	0.1	3.7
Tin	240	0.68	0.67	0.05	7.3	-0.5	4.2
	220	0.68	0.67	0.04	5.4	-0.8	2.9
Copper	292	0.114	0.114	0.005	4.7	0.0	3.2
	283	0.114	0.114	0.005	4.2	-0.1	2.3
Silver	284	0.114	0.114	0.005	4.3	1.9	10.8
	273	0.114	0.114	0.003	3.0	-0.2	3.3

*The first set of values 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 7

Means and coefficients of variation for KC-1

Lab No.	Zinc n_i	Zinc $\bar{x}_i$ (%)	Zinc c.v.$_i$ (%)	Lead n_i	Lead $\bar{x}_i$ (%)	Lead c.v.$_i$ (%)	Tin n_i	Tin $\bar{x}_i$ (%)	Tin c.v.$_i$ (%)	Copper n_i	Copper $\bar{x}_i$ (%)	Copper c.v.$_i$ (%)	Silver n_i	Silver $\bar{x}_i$ (%)	Silver c.v.$_i$ (%)
1	10(a.a.) 10(vol.) 10(vol.)*	19.64 20.31 20.22	0.6 0.3 0.3	10(a.a.) 10(grav.)	6.96 7.16	1.2 1.9	10(a.a.) 10(vol.)	0.70 0.60	1.8 1.5	10(a.a.) 10(col.)	0.109 0.112	1.2 1.9	10(a.a.) 10(f.a.)	0.110 0.111	1.8 0.5
2	10(vol.)	20.21	0.3	10(a.a.)	6.87	0.1	10(a.a.)	0.62	0.8	10(a.a.)	0.115	0.4	10(a.a.) 10(f.a.)	0.114 0.113	1.7 0.0
3	10(vol.) 10(vol.)*	20.59 20.46	0.1 0.5	13(vol.) 15(vol.)*	7.00 7.07	0.9 0.3	20(a.a.)	0.66	2.0	10(a.a.) 10(vol.)	0.111 0.105	2.2 5.0	10(a.a.) 12(f.a.)	0.112 0.115	2.7 0.9
4	10(vol.)	20.16	0.2	10(vol.)	7.00	0.4				10(a.a.) 10(vol.)	0.121 0.122	2.6 3.5	10(a.a.) 10(f.a.)	0.110 0.113	2.8 0.6
5				10(xrf)	6.95	1.2	10(xrf)	0.70	1.3				10(xrf)	0.132	4.8
6										10(a.a.)	0.118	0.6	10(a.a.)	0.116	1.4
7	10(a.a.) 10(vol.)	20.60 20.62	1.0 1.0	10(a.a.) 10(vol.)	6.75 6.70	1.9 1.1				10(a.a.) 10(vol.)	0.107 0.108	2.3 2.3	10(a.a.) 10(vol.)	0.110 0.109	2.4 2.4
8	10(a.a.) 10(vol.)	20.40 20.30	0.3 0.4	10(a.a.) 10(vol.)	6.99 6.63	0.4 0.6				10(a.a.) 10(vol.)	0.120 0.112	1.2 1.5	10(a.a.) 10(f.a.)	0.122 0.113	0.8 1.3
9	10(vol.)	20.37	0.2	10(a.a.) 10(vol.)	7.02 6.96	0.6 0.3	10(a.a.)	0.78	0.8	10(a.a.)	0.110	0.0	10(f.a.)	0.116	0.5
10	10(a.a.) 10(pol.)	20.62 20.69	0.4 0.2	10(a.a.) 10(vol.) 4(pol.)	7.00 6.99 6.98	0.3 0.4 0.4	10(vol.) 10(pol.)	0.68 0.68	0.8 0.7	10(a.a.) 10(pol.)	0.114 0.116	1.1 1.3	10(a.a.) 10(f.a.)	0.116 0.116	0.2 0.4
11	10(vol.)	20.35	0.2	10(vol.)	6.96	0.2	10(vol.)	0.59	1.1	10(a.a.)	0.110	0.0	10(a.a.)	0.115	1.7
12	20(vol.)	20.36	0.2	20(vol.)	6.97	0.5	20(vol.)	0.67	1.5	10(col.)	0.118	2.4			
13	10(a.a.)	20.30	0.5	10(a.a.)	7.05	0.7	10(a.a.)	0.71	2.6	10(a.a.)	0.116	1.1	10(a.a.)	0.116	0.5
14	10(a.a.) 10(pol.)	20.30 20.57	0.6 0.5	10(a.a.) 10(vol.)	6.88 6.84	0.4 0.4				10(a.a.) 10(pol.)	0.113 0.111	3.6 3.3	10(f.a.)	0.112	0.9
15	10(vol.)	20.27	0.1	10(vol.)	7.04	0.3	10(pol.)	0.69	1.0	10(pol.)	0.111	2.8			
16							10(vol.)	0.68	0.2						
17	5(a.a.) 5(vol.)	20.28 20.20	0.9 0.5	10(a.a.)	6.96	0.5	10(a.a.)	0.67	0.6	10(a.a.)	0.114	1.6	5(a.a.) 5(f.a.)	0.119 0.115	0.7 0.5
18	10(vol.)	20.35	0.1	10(vol.)	7.00	0.3	10(a.a.)	0.72	0.9	10(a.a.)	0.110	0.0	10(f.a.)	0.116	0.2
19							10(col.)	0.69	1.4						
20	10(a.a.)	20.43	0.3	10(a.a.)	6.96	1.0	10(a.a.)	0.70	2.4	10(a.a.)	0.117	1.1	10(a.a.) 10(f.a.)	0.106 0.117	1.3 0.7
21							10(vol.)	0.68	0.8						
22	12(vol.)	20.16	0.1	9(a.a.) 3(vol.)	7.18 7.18	0.4 0.4				12(a.a.)	0.120	0.0	12(f.a.)	0.113	0.3
23	10(vol.)	20.24	0.2	10(grav.) 10(vol.)	6.83 6.98	0.7 0.8	10(vol.)	0.54	5.0	10(a.a.)	0.104	0.9	10(f.a.)	0.113	0.3
24	10(vol.)	20.26	0.1	10(a.a.) 10(vol.)	7.04 6.97	0.6 0.4	10(a.a.) 10(vol.)	0.64 0.66	3.9 1.3	10(a.a.) 10(col.)	0.122 0.117	2.1 2.6	10(f.a.)	0.117	0.9
25	10(vol.)	20.31	0.4	10(a.a.) 10(vol.)	7.29 7.25	0.4 1.3	10(vol.)	0.61	0.7	10(a.a.)	0.112	0.3	10(f.a.)	0.111	0.3
Total	282	20.34	1.1	334	6.98	2.1	240	0.67	7.3	292	0.114	4.7	284	0.114	4.3

*Two different volumetric techniques used by the same laboratory.

TABLE 8

Estimates of statistical parameters for KC-1

	Zinc			Lead			Tin			Copper			Silver		
	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
No. of participating laboratories	20	20	20	21	21	21	17	17	17	21	21	21	19	19	19
No. of sets of results	27	27	27	32	31	31	20	20	20	29	29	29	28	28	28
No. of observations	266	272	272	302	314	314	220	220	220	283	292	292	273	274	274
Median, %	20.34	20.34	20.34	6.98	6.98	6.98	0.68	0.68	0.68	0.114	0.114	0.114	0.114	0.114	0.114
Mean, %	20.36	20.37	20.36	6.98	6.98	6.98	0.67	0.67	0.67	0.114	0.114	0.114	0.114	0.114	0.114
95% confidence interval of the mean, %															
Low	20.34	20.31	20.30	6.97	6.94	6.94	0.66	0.65	0.65	0.113	0.112	0.112	0.113	0.112	0.113
High	20.38	20.43	20.43	6.99	7.02	7.02	0.67	0.68	0.68	0.114	0.116	0.115	0.114	0.115	0.115

DISCUSSION

Table 8 shows that, in all cases, the means computed by the three 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 the selected elements in KC-1. However, there is a strong dependence of the results on the laboratory from which they were reported, and in the case of tin, on the analytical methods used (see below); therefore, the computation procedure A is technically incorrect. The assumptions 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 estimated statistical parameters computed by procedure B are arbitrarily recommended for the certification of KC-1 for zinc, lead, copper and silver (Table 10). The treatment used in arriving at the recommended value for tin takes into account chemical factors and is given below.

Statistical treatment of tin results

In a previous interlaboratory program to certify reference ore MP-1 for tin, it was found that certain modifications of the volumetric (iodometric) method gave appreciably lower results than did the methods involving an instrumental finish (approximately half of which were atomic absorption methods) [3,10]. An examination of the results in Table 7 indicates that a similar pattern prevails for the tin results for KC-1.

A detailed unpublished study in this laboratory has shown that, although the iodometric method for tin in ores is prone to several kinds of negative errors, certain modifications of it are nevertheless capable of yielding satisfactory results under optimum conditions. This is borne out by certain sets of results given in Table 9, and in the documents pertaining to MP-1[3,10].

TABLE 9

Results of *t*-test, and estimated statistical parameters for volumetric tin results

Lab. No.	$\overline{x}_i$	s_i	n_i	t	Test of null hypothesis
1	0.598	0.0092	10	2.9	R
10	0.678	0.0055	10	0.1	A
11	0.588	0.0063	10	3.3	R
12	0.674	0.0100	20	0.2	A
16	0.682	0.0016	10	0.05	A
21	0.683	0.0056	10	0.1	A
23	0.543	0.0271	10	4.7	R
24	0.658	0.0087	10	0.8	A
25	0.613	0.0044	10	2.4	R

A = null hypothesis accepted.
R = null hypothesis rejected.

To evaluate objectively the volumetric tin results for certification purposes, a preliminary consensus value, $\overline{x}_{inst}$ for the non-volumetric results was computed. Then the mean volumetric tin result, $\overline{x}_i$, for each laboratory, was compared with $\overline{x}_{inst}$ (0.68) using the following formula for the *t*-test at the 5% significance level:

$$t = \frac{\left|\overline{x}_{inst} - \overline{x}_i\right|}{\left(\frac{s_i^2}{n_i} + \frac{\omega^2_{inst}}{k_{inst}} + \omega^2_{inst}\right)^{\frac{1}{2}}}$$

where

k_{inst} is the number of sets of instrumental results (12);

ω_{inst} is estimated from the analysis of variance of these results (0.027);

n_i and s_i are the number and standard deviation, respectively, of the volumetric results reported by laboratory i.

The results of these calculations are given in Table 9. In four cases the *t*-test showed that the volumetric results were not from the acceptable population; accordingly, they were rejected from further consideration. The acceptable volumetric results and the instrumental ones were then used to compute the recommended value for tin (Table 10).

Multi-element analysis

In only six cases did the participating laboratories determine more than one element in the solution obtained from a single subsample of KC-1; in five of these zinc and copper were determined in aliquots of the same solution.

Inter-method comparisons

Using appropriate statistical tests, the results of different methods of analysis for a given element were compared with the object of detecting significant differences at the 5% level. Only in the case of tin (described above) was a notable difference detected.

TABLE 10

Recommended values and their confidence intervals for standard reference material, KC-1

	% Zinc	% Lead	% Tin*	% Copper	% Silver	oz/ton Silver
Recommended value	20.37	6.98	0.68	0.114	0.114	33.2
95% confidence intervals						
Low	20.31	6.94	0.67	0.112	0.112	32.8
High	20.43	7.02	0.69	0.116	0.115	33.5

*See discussion of tin results on p. 30.

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A P P E N D I X

An information circular (catalogue) describing all certified reference materials that are available from the Mines Branch can be obtained by writing to:

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