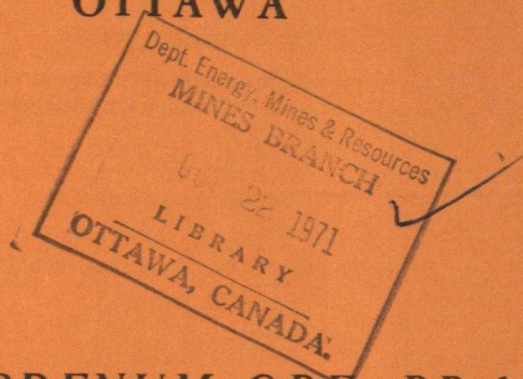


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DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA



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

THE STAFF OF THE MINERAL SCIENCES DIVISION

AUGUST, 1971

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

by

Members of the Staff of the Mineral Sciences Division*

- - -

SYNOPSIS

To fulfil a need of Canadian industrial and commercial laboratories, the Mines Branch of the Department of Energy, Mines and Resources has undertaken a program to produce a number of standard reference ores of metallic minerals. This report describes the characterization of molybdenum ore, PR-1, and its preparation for use as a standard reference material.

The mineralogical, geological and chemical characteristics of PR-1 are given as well as the details of the methods used for its comminution and blending and for assessing its homogeneity. Nineteen laboratories participated in the program by providing analytical results for molybdenum, bismuth, iron, and sulphur. All these results and the evaluation of their statistical parameters are reported for each of the four elements. Recommended values of the means and their confidence limits are given.

*This report has been compiled and is authored, in part, by G.H. Faye, Group Leader, Inorganic and Analytical Chemistry Research Group, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada, who is the co-ordinator of the program to standardize ores of metallic minerals.

Direction des mines

Bulletin technique TB 139

LE MINERAI DE MOLYBDÈNE, PR-1: SA CARACTÉRISATION ET SA PRÉPARATION POUR SON USAGE COMME ÉTALON DE RÉFÉRENCE

par

Des membres du personnel de la Division des sciences minérales*

RÉSUMÉ

Afin de répondre aux besoins des laboratoires industriels et commerciaux canadiens, la Direction des mines du ministère de l'Énergie, des Mines et des Ressources a entrepris la réalisation d'un programme visant à produire un certain nombre de minerais de référence normalisés pour les minéraux métalliques. Le présent rapport décrit les caractéristiques du minerai de molybdène, PR-1, et sa préparation pour son usage comme étalon de référence.

On donne les caractéristiques minéralogiques, géologiques et chimiques du PR-1, ainsi que des précisions sur les méthodes utilisées pour le pulvériser et le mélanger, et pour évaluer son homogénéité. Dix-neuf laboratoires ont participé au programme en fournissant des résultats d'analyse du molybdène, du bismuth, du fer et du soufre. Tous ces résultats, ainsi que l'évaluation de leurs paramètres statistiques, sont fournis pour chacun des quatre éléments. On donne les valeurs moyennes recommandées, ainsi que la valeur des limites acceptables et fiables.

* Le présent rapport a été compilé et rédigé, en partie, par G.H. Faye, chef de groupe, Groupe de recherche sur la chimie inorganique et analytique, Division des sciences minérales, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa, Canada; il est le coordonnateur du programme de normalisation des minerais de minéraux métalliques.

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INTRODUCTION

In 1970, the Mines Branch, Department of Energy, Mines and Resources, undertook a program to prepare and characterize a number of standard reference ores of metallic minerals. This was in response to the expressed needs of a number of Canadian industrial and commercial laboratories as revealed through visits by personnel of the Mineral Sciences Division of the Mines Branch to such laboratories and through a nationwide survey by questionnaire.

The need for standard reference samples of metallic ores arises from the usual desire of the analysts to have standard materials on which analytical methods may be tested and evaluated within a laboratory and which would be useful in inter-laboratory studies that could involve umpires and the interest of clients.

Though many types of standard reference materials are prepared and sold by institutions such as the U. S. National Bureau of Standards, the U. S. Geological Survey, and the British Bureau of Analysed Samples, Ltd., few ores are available -- in fact, most of the so-called ores are concentrates.

Therefore, to fill this void and to serve Canadian interests, it was apparent that the Mines Branch could serve a useful role in preparing standard samples of some typical metallic ores of Canada. It was recognized that these materials should contain metal values that would be consistent with those in raw ores and that their mineralogical complexity should realistically reflect the materials that confront the analyst or worker in the earth sciences.

Though it is anticipated that the proposed standard ores will be used primarily in analytical laboratories, it is felt that ores whose chemical and mineralogical characteristics have been thoroughly established will also be of interest to earth scientists in general.

At this time, it is difficult to predict the number of materials that will be prepared and characterized in this standards program. No doubt this will depend on factors such as the response accorded to the first two or three standard reference ores, the readiness of laboratories to provide the analytical data necessary to adequately characterize the ores, and special needs that arise unexpectedly. If there is a demand, it is also possible that the Mines Branch standards program could be extended to include the preparation of certain types of mineral concentrates that are not available from other sources.

This report describes the preparation and characterization of molybdenum ore, PR-1, the first ore of the standards program. The report is comprehensive in the sense that essentially all the information and data obtained on PR-1 have been included so that the reader may make his own interpretations as well as consider the comments of the writers. The certificate of analysis that will be issued with the sample bottles, at the time of sale of PR-1, will be prepared from material selected from this report.

BACKGROUND INFORMATION

In May, 1970, Dr. W. Petruk, Acting Group Leader, Mineralogy Group, Mineral Sciences Division, collected approximately 600 pounds of a high-molybdenum, low-bismuth ore from the Preissac molybdenum mine near Cadillac, Quebec, specifically for use in this standards program. This material, subsequently labelled PR-1, was taken from various parts of the Preissac mine to yield a material that contained most of the elements found in the ore deposit. The geology of the deposit was communicated to Dr. Petruk by Preissac's Chief Geologist, Mr. D.S. Rogers. The mineralogy of the ore was determined by microscopical and X-ray diffraction studies of samples taken from various parts of the deposit.

MINERALOGICAL AND GEOLOGICAL CHARACTERISTICS OF PR-1

(W. Petruk, Research Scientist, Mineralogy Group)

a) Geology

The Preissac molybdenum deposit is a vein-type deposit in a sericite granite that may be part of the Lacorne Batholith. The granite in the mine area occurs adjacent to a sericite schist and is cut by a strong north-northeast trending fault. The molybdenum orebody occurs on both sides of the fault and extends from the surface down to the tenth level, with the highest grade of ore being near the sericite schist.

The granite is fairly coarse-grained but, locally, micro-granitic and pegmatitic phases are present. It consists of feldspar, sericite, and quartz and contains trace amounts of chlorite, rutile and, locally, spessartite. In some places near ore veins, the rutile is altered to anatase and some of the anatase is finely intergrown with calcite to form large, irregular grains that are steel-grey in hand specimens. The granite in the upper parts of the mine is talcose and that near ore veins is weakly to strongly altered, containing saussuritized feldspar and, locally, talc.

The ore consists of ore minerals in quartz veins, in quartz stringers, and in granite. The quartz veins are up to several feet wide and consist of quartz and some muscovite, fluorite, feldspar, and calcite. The muscovite occurs as bundles of crystals in stringers parallel to the veins; the fluorite occurs as irregular grains and as masses along the veins; the feldspar and calcite occur as irregular grains and masses. The ore minerals in the veins are molybdenite, pyrite, native bismuth, bismuthinite, sphalerite, galena, chalcopryite, hematite, magnetite, rutile, and anatase. Molybdenite is the main ore mineral in the veins and is commonly associated with muscovite but not with significant quantities of other ore minerals. Some veins, however, contain significant amounts of bismuth-bearing

minerals with the molybdenite; some contain pockets of massive hematite; some contain large pyrite and/or chalcopyrite grains; and some contain vugs lined with quartz, feldspar, pyrite, galena, molybdenite, native bismuth, and bismuthinite.

The ore minerals in granite occur near the mineralized quartz veins and stringers and consist largely of disseminated molybdenite and pyrite. The molybdenite is present as small grains and as large crystals and is generally associated with the sericite.

b) Mineralogy

Molybdenite (MoS_2)

The molybdenite is present in quartz veins and stringers and, to a small extent, in altered granite near the veins. It occurs as disseminated grains and as nearly globular masses composed of molybdenite crystals radiating outward from a centre. It is generally associated with muscovite and sericite, and some contains inclusions of native bismuth and bismuthinite. X-ray diffraction studies show that it is of the normal hexagonal variety.

Native Bismuth (Bi) and Bismuthinite (Bi_2S_3)

Native bismuth and bismuthinite occur as minute grains, generally associated with molybdenite and pyrite in the quartz veins and stringers. Some quartz veins contain relatively high proportions of bismuth and bismuthinite whereas others do not. Both Bi-bearing minerals occur in the same parts of the veins and in some places are intergrown with each other.

Pyrite (FeS_2)

Pyrite is present in granite and in quartz veins. It is generally present as disseminated grains but some of that in granite occurs in veinlets. Some of the pyrite in quartz occurs separately, some is

associated with hematite and magnetite, and some is partly replaced by galena, sphalerite, and chalcopyrite.

Chalcopyrite (CuFeS_2)

One large chalcopyrite grain and several small ones were found in massive fluorite in a quartz vein. This chalcopyrite contained minute inclusions of pyrite.

Sphalerite (ZnS), Galena (PbS) and Pyrrhotite (Fe_{1-x}S)

Minute grains and veinlets of sphalerite and galena were found in quartz veins and in vugs. The galena is generally present as veinlets in pyrite. A few grains of pyrrhotite were found in a polished section of a metallic mineral concentrate.

Hematite (Fe_2O_3) and Magnetite (Fe_3O_4)

Hematite is present as masses, up to five inches in size, and as disseminated grains in quartz veins and granite. The hematite masses are composed of prismatic crystals oriented more or less radially and they contain a few magnetite grains.

c) Material Selected for the Preparation of PR-1

The material selected for the preparation of PR-1 was taken from three locations and blended to provide a sample that was thought to contain most of the elements that are present in the Preissac ore. This material was taken from:

- (1) Quartz vein - stope 573: this consists largely of quartz and contains muscovite, fluorite, feldspar, calcite, and ore minerals (largely molybdenite).
- (2) Quartz vein - vein 8 - 20S: this consists largely of quartz and contains muscovite and ore minerals (largely molybdenite).

- (3) Mineralized granite and microgranite near vein 8 - 05S: this contains molybdenite and pyrite.

d) Mineralogical Composition of the Selected Material

An approximate mineralogical composition of an unblended grab sample of PR-1 was determined by X-ray diffractometry and by grain counting under the microscope. The mineralogical composition of the ore was then calculated from the chemical analyses reported in Table 5. Finally, the calculated and approximate values were compared to determine whether the calculated values are reasonable or not. The compositional calculations were made in the following sequence.

- The Si, Al, Mg, Na, K, Mn, and Ti contents were converted to the appropriate oxides.
- Fluorite was calculated by combining all the F with an appropriate amount of Ca.
- Calcite was calculated by combining all the CO_2 with appropriate amounts of Ca and O; (the fluorite and calcite account for all the Ca).
- Garnet was calculated by combining all the MnO with appropriate amounts of Al_2O_3 and SiO_2 .
- Na-feldspar was calculated by combining all Na_2O with appropriate amounts of Al_2O_3 and SiO_2 .
- Chlorite was calculated on the assumption that it contains equal amounts of MgO and FeO. MgO plus FeO were combined with appropriate amounts of Al_2O_3 , SiO_2 , and H_2O .
- All K_2O and the remaining Al_2O_3 were assumed to be contained in muscovite and K-feldspar; the distribution of K_2O and Al_2O_3 in each mineral was calculated.
- Muscovite was calculated from the preceding values of K_2O and Al_2O_3 , adding the appropriate amounts of SiO_2 and H_2O .
- K-feldspar was calculated by combining the remaining K_2O and Al_2O_3 with an appropriate amount of SiO_2 .

- The remaining SiO_2 was assumed to be quartz.
- All the TiO_2 was assumed to be present as rutile and anatase.
- Molybdenite was calculated from the Mo analysis, using the appropriate amount of S.
- Sphalerite was calculated from the Zn analysis.
- Galena was calculated from the Pb analysis.
- Chalcopyrite was calculated from the Cu analysis, together with the appropriate amounts of Fe and S.
- Half of the Bi was assumed to be native bismuth.
- Bismuthinite was calculated from the remaining Bi and the appropriate amount of S.
- Pyrite was calculated from the remaining S, together with the appropriate amount of Fe.
- The elements remaining after these calculations were: Fe = 0.87%, O = 0.31%, Ni = 0.004%, and H_2O = 0.08%. These elements are present as hematite, magnetite, nickeliferous iron from the crusher, and goethite. It is judged that relatively large errors could be introduced by calculating the quantities of these individual minerals.

The calculated mineralogical composition of PR-1 is given in Table 1 which also includes the approximate mineralogical composition for the unblended samples of PR-1. The comparison of the calculated and approximate composition indicates that the calculated mineralogical composition is reasonable and probably represents the true mineralogical composition.

The distribution of the elements in various minerals is given in Table 2.

TABLE 1
Mineralogical Composition of PR-1

Minerals	Approximate mineralogical composition of a grab sample (Wt %)	Calculated mineralogical composition of PR-1 (Wt %)
Fluorite	0.25	0.96
Calcite	not analysed	2.37
Garnet	0.12	0.07
Chlorite	0.1	1.29
Muscovite	2.5	2.30
Feldspar	31.0	
Na-feldspar		6.17
K-feldspar		12.29
		18.46
Quartz	64.0	70.27
Rutile	0.003	0.05
Molybdenite	1.25	1.02
Sphalerite	0.03	0.03
Galena	0.01	0.04
Chalcopyrite	0.004	0.03
Bismuth	0.02	0.06
Bismuthinite	0.01	0.08
Pyrite	0.60	0.58
Pyrrhotite	0.002	not calculated
Hematite	0.01	not calculated
Magnetite	0.002	not calculated
Fe+O+Ni+H ₂ O		<u>1.264</u>
TOTAL		98.47*

*The total for the calculated composition corresponds to the total for the chemical analysis reported below by Buckmaster et al. (Table 5) but corrected for the O in CO₂ and H₂O.

TABLE 2
Distribution of Elements in PR-1

Element	Minerals	Total Wt %
F	Fluorite 0.47%	0.47
Ca	Fluorite 0.49%, calcite 0.95%	1.44
O	SiO ₂ 44.66%, Al ₂ O ₃ 2.12%, MgO 0.06%, Na ₂ O 0.19%, K ₂ O 0.40%, CaO 0.38%, CO ₂ 0.76%, H ₂ O 0.27%, MnO 0.01%, TiO ₂ 0.02%, FeO 0.11% unaccounted 0.23%	49.21
MnO	Garnet 0.03%	0.03
Na ₂ O	Na-feldspar 0.73%	0.73
MgO	Chlorite 0.15%	0.15
K ₂ O	Muscovite 0.27%, feldspar 2.08%	2.35
Al ₂ O ₃	K-feldspar 2.26%, muscovite 0.89%, Na-feldspar 1.21%, chlorite 0.15%, garnet 0.01%	4.52
SiO ₂	Quartz 70.27%, K-feldspar 7.96%, Na-feldspar 4.24%, muscovite 1.04%, chlorite 0.33%, garnet 0.03%	83.87
Fe	Pyrite 0.27%, chlorite 0.37%, chalcopryrite 0.008%, magnetite 0.60%, (hematite plus iron) < 0.05%	1.27
TiO ₂	Rutile 0.05%	0.05
Mo	Molybdenite 0.612%	0.612
Bi	Bismuth 0.059%, bismuthinite 0.058%	0.117
Zn	Sphalerite 0.022%	0.022
Pb	Galena 0.038%	0.038
Cu	Chalcopryrite 0.009%	0.009
Ni	Nickeliferous iron	
S	Molybdenite 0.41%, sphalerite 0.01%, pyrite 0.31%, galena 0.006%, chalcopryrite 0.009%, bismuthinite 0.03%	0.77

Not detected by spectrographic analysis: Be, B, Sb, Ge, As, W, Sn, Cr, Ga, Nb, Ta, V, Ag, Zr, Co, Sr.

COMMINUTION, BLENDING, AND BOTTLING OF PR-1
(Y. Bourgoïn, Laboratory Helper, Analytical Chemistry Group)

The coarse molybdenum ore, PR-1, was crushed and dry-ground to minus 200 mesh in the mill of the Mineral Processing Division under the supervision of Mr. H. Renaud, Mill Foreman. On receipt of the ground ore by the Mineral Sciences Division, a 25-lb portion was rejected inadvertently. The remainder was then blended for six hours in a 45-gallon, baffled, mixing drum in the mill of the Extraction Metallurgy Division.

The ore was bottled in 780 bottles, each containing 200 g of ore; these were stored in 24-bottle cases. Bottles and cases were numbered, and a record kept of each, with the object of detecting possible case-to-case and/or bottle-to-bottle heterogeneity after distribution to the laboratories participating in the analytical aspect of the program.

TESTS FOR HOMOGENEITY
(Sutarno, W.S. Bowman, J.L. Dalton, R.W. Buckmaster)*

After the blending operation described above, the ore was temporarily stored in three boxes. Subsequently, the content of each box was placed in bottles where box origins were recorded. Two bottles were taken at random from each of the boxes and five 15- to 20-g samples were taken from each bottle. A total of 30 samples was analysed for molybdenum and bismuth by the X-ray fluorescence technique. The sampling scheme is illustrated in Figure 1. One-way analysis of variance of these results showed that there was no significant difference between the bottles insofar as molybdenum and bismuth contents were concerned.

*Research Scientist and Technical Officer, Physical Chemistry Group; Scientific Officer, Spectrochemistry Group; and Chemist, Analytical Chemistry Group, Mineral Sciences Division, respectively.

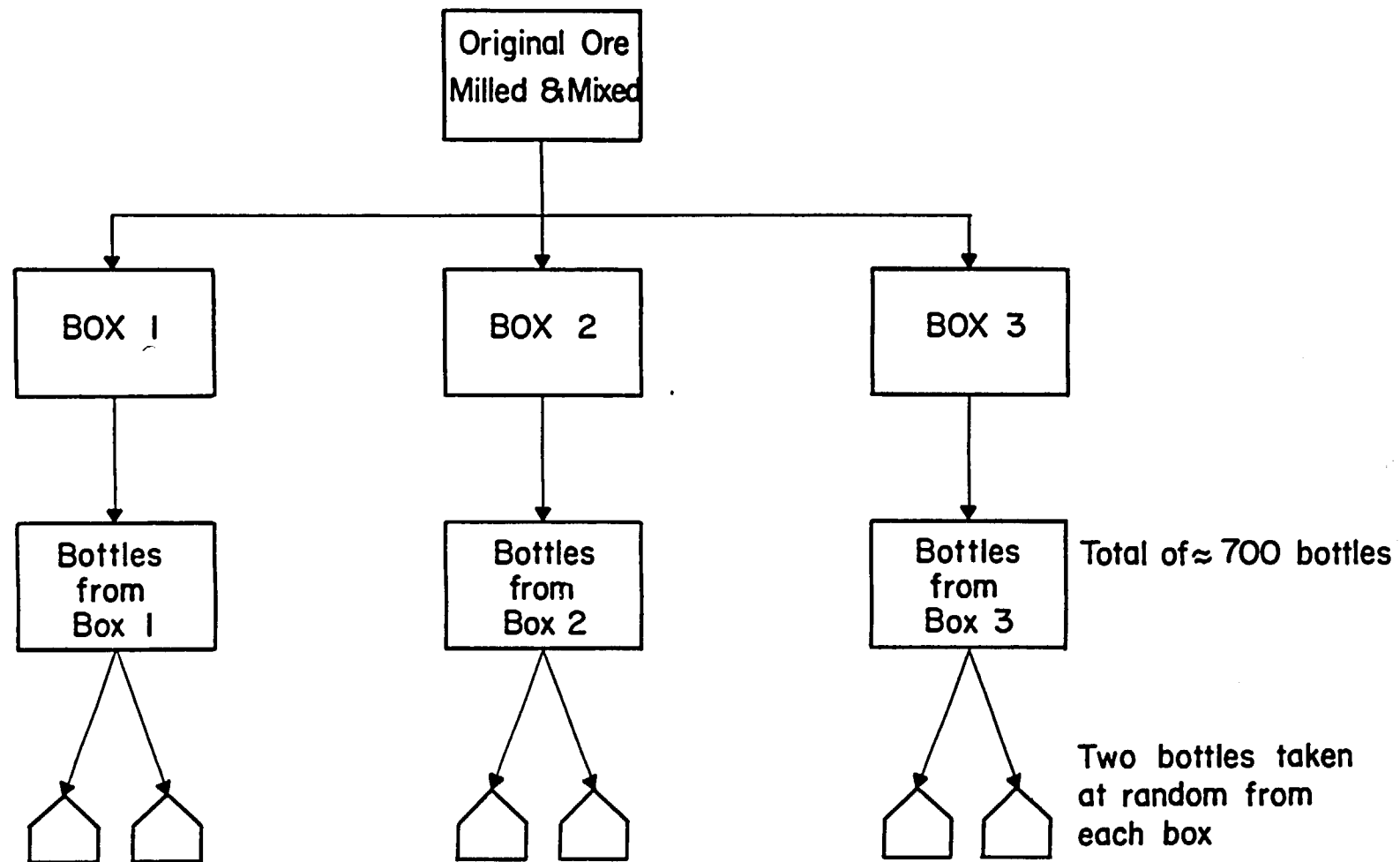


Figure 1. Sampling Scheme.

To verify the homogeneity of PR-1, six bottles were selected at random from the total stock of bottles. Five samples from each of the six bottles were analysed chemically for bismuth, molybdenum, and sulphur -- a total of thirty determinations for each element (separate samples were used for each element). One-way analysis of variance of these results showed that, chemically, there was no significant difference between the bottles insofar as molybdenum, bismuth, and sulphur contents are concerned.

The summary of these analyses of variance is given in Table 3. The results of these chemical analyses were then used as the contribution of the Mineral Sciences Division to the "round-robin" series of analyses (Table 6).

TABLE 3

Summary of One-Way Analyses of Variance for the Results of Homogeneity Tests Conducted by the Mineral Sciences Division Laboratories

Method of Analyses	N	F _{observed}			F _{0.95} (5,24) (from Table)
		Mo	Bi	S	
X-Ray Fluorescence	30	0.45	2.03	-	2.62
Chemical Analyses	30	1.01	0.77	0.97	2.62

N = number of samples.

F_{observed} = ratio of estimated between-bottles mean square to the within-bottle mean square.

F_{0.95}(5,24) = F-statistic, based on degrees of freedom of 5 and 24 at the 5% significance level.

- - - -

Having found ore, PR-1, to be suitably homogeneous, randomly-selected sample bottles of the ore were sent to the various participating laboratories, the identity of which are given on page 21.

Each laboratory received two bottles and was requested to analyse five samples from each bottle for molybdenum, bismuth, iron, and sulphur. The results reported were compared between bottles within each laboratory by t-test at a 5% significance level. These tests would provide further evidence of the homogeneity of the sample. The results of these tests are summarized in Table 4. It is shown in this table that the majority of the participating laboratories did not detect any evidence of inhomogeneity between the bottles they received.

TABLE 4

Summary of the t-Tests at the 5% Significance Level of the Results,
Between-Bottles and Within-Laboratory

Laboratory Number	Elements				Laboratory Number	Elements			
	Mo	Bi	Fe	S		Mo	Bi	Fe	S
1	A	A	A	A	11	A	R	A	A
2	A	A	A	A	12	A	A	A	A
3	A	A	A	A	13	A	R	R	R
4	A	A	-	-	14	A	R	A	A
5	A	A	A	A	15	A	A	A	A
6	A	A	A	A	16	A	A	A	A
7	A	A	A	A	17	-	-	-	A
8	A	A	A	A	18	R	A	A	A
9	A	-	A	A	19	A	-	-	-
10	A	A	A	A					

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

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

- = Insufficient data available for a meaningful statistical analysis.

CHEMICAL ANALYSIS BY THE ANALYTICAL CHEMISTRY SECTION,
MINERAL SCIENCES DIVISION, FOR THE CHARACTERIZATION AND

CERTIFICATION OF PR-1

(R. W. Buckmaster, J. C. Hole, P. Lanthier, and B. Nebesar)*

It was mentioned previously that the Analytical Chemistry Section of the Mineral Sciences Division received six randomly selected bottles of PR-1 for chemical analysis. As a contribution to the certification of PR-1, each bottle was analysed in quintuplicate for molybdenum, bismuth, iron, and sulphur. The results of these analyses appear in Table 6 under PR-1 LAB-1. Certain of these results were used in testing for homogeneity. The analytical methods used are described briefly below.

It was considered desirable to have an essentially complete chemical analysis of PR-1. Therefore, two bottles were selected from the original six; on these, at least two determinations were made for each element or constituent.

The results of these analyses are presented in Table 5 and the analytical methods used are also given below.

*Chemist, Group Leader and Technician, Analytical Chemistry Section; and Research Scientist, Inorganic and Analytical Chemistry Research Group, Mineral Sciences Division, respectively.

TABLE 5

Complete Provisional Chemical Analysis of PR-1

O	-	49.2	Wt %	Bi	-	0.12	Wt %
Si	-	39.2		Ti	-	0.03	
Al	-	2.39		Pb	-	0.04	
Fe	- -	1.27		Zn	-	0.02	
Ca	-	1.44		Mn	-	0.02	
Mg	-	0.09		Ni	-	<0.01	
Na	-	0.54		Cu	-	0.01	
K	-	1.95		F	-	0.47	
S	-	0.77		H ₂ O	-	0.29	
Mo	-	0.61		Total C			
				as CO ₂	-	1.08	
				CO ₂	-	1.04	

Methods of Analysis Used by the Analytical Chemistry Section, Mineral Sciences Division (LAB-1)

Molybdenum

The samples were completely decomposed with hydrochloric, hydrofluoric, perchloric, and sulphuric acids. Iron and copper were removed by a double precipitation using sodium hydroxide. Molybdenum was determined by a spectrophotometric method using potassium thiocyanate.

Bismuth

The samples were decomposed with nitric acid, and the insoluble residues filtered off. Bismuth was determined on a suitable aliquot of the filtrates by a spectrophotometric method using potassium iodide. Any cloudiness caused by copper or lead was removed by filtering before the absorbance was read.

The insoluble residues and filter papers from the first set of samples were completely dissolved with nitric, hydrofluoric, perchloric, and sulphuric acids, and assayed for bismuth. No bismuth was detected in the residues.

Sulphur

The samples were decomposed using bromine water and carbon tetrachloride followed by nitric acid saturated with potassium chlorate, and the insoluble residues were filtered off. Any loss of sulphur due to the presence of lead was eliminated by leaching with ammonium carbonate before filtering. Sulphur was determined gravimetrically with barium chloride. Molybdenum was eliminated by washing the barium sulphate precipitate with dilute ammonium hydroxide.

The insoluble residues and papers from the first set of samples were completely dissolved with hydrochloric, hydrofluoric, and perchloric acids, and the sulphur contents were determined in the above manner. Sulphur was not detected in the residues.

Combustion Sulphur

The sample, contained in a pre-ignited boat and cover, was ignited in a resistance-type furnace for five minutes at 2600°F to which oxygen was admitted at the rate of 1 litre/min. The combustion gases were bubbled into an acidified solution of potassium iodide containing starch indicator. The solution was titrated during the combustion with potassium iodate solution.

The two reference materials used for standardization were N.B.S. 129b (0.22% S) and B.C.S. 301 (0.47% S).

Iron

The samples were completely decomposed with hydrochloric, hydrofluoric, and perchloric acids. Iron was determined by a spectrophotometric method using 1, 10-phenanthroline.

Silicon

The samples were fused with sodium carbonate, dissolved with hydrochloric acid, and dehydrated with perchloric acid. The solutions were filtered, the filtrates dehydrated a second time, and filtered again. Silicon in the combined residues was determined by the common method involving its volatilization with hydrofluoric acid.

Aluminum

The R_2O_3 group of elements was precipitated from the filtrates from the silicon determination and dissolved with hydrochloric acid. After a cupferron-chloroform extraction from a sulphuric-acid medium, the aluminum was precipitated by ammonium hydroxide, ignited, and weighed.

Calcium

The samples were completely dissolved by treatment with hydrochloric, hydrofluoric, and perchloric acids. The R_2O_3 group of elements was removed by precipitation. Calcium was precipitated as the oxalate, ignited, and weighed.

Magnesium

Magnesium was determined by atomic-absorption spectrophotometry in the filtrates from the calcium determination, after the destruction of ammonium salts with nitric acid.

Sodium

The samples were completely dissolved with hydrochloric, hydrofluoric, and perchloric acids. Sodium was determined by atomic-absorption spectrophotometry.

Potassium

Potassium, in the solutions prepared for the sodium determination, was determined by atomic-absorption spectrophotometry.

Water

Water of constitution was determined gravimetrically after combustion at 1800°F.

Total Carbon

Total carbon was determined gravimetrically after combustion at 2600°F.

Carbon Dioxide

Carbon dioxide was determined gravimetrically after treatment with boiling perchloric acid.

Titanium

The samples were completely decomposed by hydrochloric, hydrofluoric, perchloric, and sulphuric acids; titanium was determined spectrophotometrically with hydrogen peroxide.

Lead

The samples were decomposed by hydrochloric, hydrofluoric and perchloric acids. Lead was determined by atomic-absorption spectrophotometry using a standard-addition technique.

Zinc

The zinc was determined in the same manner as the lead. in the same sample solutions.

Manganese

Manganese was determined in the same manner as the lead and zinc, in the same sample solutions.

Nickel

The samples were completely decomposed by hydrochloric, hydrofluoric, and perchloric acids. Nickel was determined spectrophotometrically using dimethylglyoxime.

Copper

The copper was determined spectrophotometrically with cuproine, using the sample solutions prepared for the nickel determination.

Additional Determinations

Mr. C. McMahon, Technical Officer, Spectrochemistry Group, determined the oxygen and fluorine content of the ore, using neutron-activation analysis.

THE CERTIFICATION OF PR-1 FOR MOLYBDENUM, BISMUTH, IRON AND SULPHUR

Participating Laboratories

The following is a list, in alphabetical order, of the names of laboratories that volunteered to participate in the program to certify molybdenum ore PR-1. Each of these was arbitrarily assigned a code number so that analytical results could be recorded while preserving the anonymity of the laboratory. These code numbers bear no relation to the alphabetic order of the laboratory names.

NOTE: Because of the special involvement of the Analytical Chemistry Section, Mineral Sciences Division, in this program, no attempt has been made to hide its identity, which is LAB-1 in Table 6.

PARTICIPATING LABORATORIES

Assayers Limited, Rouyn, Quebec.
Bondar-Clegg and Company Limited, Ottawa, Ontario.
Bondar-Clegg and Company Limited, Vancouver, British Columbia.
Chemex Labs. Limited, Vancouver, British Columbia.
Cominco, Trail, British Columbia.
Core Laboratories (Canada) Limited, Calgary, Alberta.
Crest Laboratories (B.C.) Limited, Vancouver, British Columbia.
J. T. Donald and Company Limited, Montreal, Quebec.
Extraction Metallurgy Division, Mines Branch, Ottawa, Ontario.
Hudson Bay Mining and Smelting Company, Limited, Flin Flon, Manitoba.
Lakefield Research of Canada Limited, Lakefield, Ontario.
Mineral Sciences Division, Analytical Chemistry Section, Mines Branch,
Ottawa, Ontario.
Mineral Sciences Division, Inorganic and Analytical Chemistry Research
Group, Mines Branch, Ottawa, Ontario.
Noranda Research Centre, Pointe Claire, Quebec.
Ontario Department of Mines and Northern Affairs, Toronto, Ontario.
Sherritt Gordon Mines Limited, Fort Saskatchewan, Alberta.
Superintendence Company (Canada) Limited, Vancouver, British Columbia.
Swastika Laboratories Limited, Swastika, Ontario.
TSL Laboratories (B.C.) Limited, Vancouver, British Columbia.

- . . -

With the exception of PR-1, LAB-1, each laboratory received two randomly selected bottles of PR-1. Most laboratories were instructed to determine, in quintuplicate, each of the elements molybdenum, bismuth, iron, and sulphur in both bottles by methods of their choice and to report all results to the co-ordinator of the standards program (G.H. Faye) at the Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Ontario, by May 15, 1971.

It is evident from Table 6 that certain laboratories were requested either to analyze PR-1 for fewer than four elements (e.g., PR-1, LAB-19) or, alternatively, did not comply completely with the program instructions regarding the number of replicate determinations required.

EVALUATION OF STATISTICAL PARAMETERS (Sutarno and W.S. Bowman)*

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

A. All Results Treated as Though They Were Independent

The cumulative distribution of these results were plotted and are presented in Figures 2 to 5. 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 means (\bar{x}) by no more than twice the standard deviation (s), i.e., $[(\bar{x} - 2s) \leq x_{ij} \leq (\bar{x} + 2s)]$. This rejection was considered necessary to prevent the possible introduction of bias to the estimated means. The results of these computations are presented in Table 7. It is seen that the results that deviate from the mean by more than twice the standard deviation are about 5% 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 for a normal distribution. This was particularly true for the molybdenum and iron contents.

*Research Scientist and Technical Officer, respectively, Physical Chemistry Group, Mineral Sciences Division.

TABLE 6

Analyses Obtained on Standard Reference Material PR-1

	<u>Mo %</u>	<u>Bi %</u>	<u>Fe %</u>	<u>S %</u>
PR-1, LAB-1	0.611 (color.)	0.115 (color.)	1.27 (color.)	0.773 (grav.)
	0.616	0.118	1.26	0.784
	0.611	0.115	1.26	0.776
	0.609	0.117	1.30	0.771
	0.611	0.115	1.28	0.775
	0.609	0.116	1.27	0.776
	0.614	0.118	1.26	0.781
	0.611	0.118	1.30	0.776
	0.609	0.116	1.26	0.777
	0.614	0.115	1.28	0.769
	0.611	0.116		0.764
	0.614	0.115		0.776
	0.614	0.118		0.779
	0.611	0.118		0.776
	0.614	0.115		0.779
	0.611	0.116		0.767
	0.616	0.116		0.772
	0.611	0.117		0.777
	0.609	0.117		0.767
	0.611	0.117		0.771
	0.611	0.116		0.772
	0.611	0.118		0.775
	0.611	0.118		0.775
	0.611	0.118		0.776
	0.611	0.117		0.778
	0.611	0.118		0.775
	0.611	0.117		0.776
	0.614	0.115		0.775
	0.616	0.117		0.767
	0.616	0.117		0.773
				0.79 (comb.)
				0.78
				0.78
				0.78
				0.80
				0.79
				0.78
				0.79
				0.78
				0.78
				0.77
				0.78

NOTE: (color.) = by colorimetric analysis.
 (grav.) = by gravimetric analysis.
 (comb.) = by combustion technique.

(continued)

	<u>Mo %</u>	<u>Bi %</u>	<u>Fe %</u>	<u>S %</u>
PR-1, LAB-2	0.555 (a. a.)	0.120 (a. a.)	1.26 (volum.)	0.78 (grav.)
	0.550	0.121	1.26	0.75
	0.551	0.118	1.26	0.76
	0.551	0.120	1.23	0.77
	0.548	0.121	1.23	0.76
	0.548	0.120	1.23	0.77
	0.550	0.121	1.23	0.76
	0.551	0.120	1.23	0.77
	0.548	0.121	1.23	0.76
	0.550	0.121	1.26	0.77
				0.75 (comb.)
				0.76
				0.75
				0.75
				0.74
				0.75
				0.74
				0.755
				0.75
				0.75
PR-1, LAB-3	0.595 (a. a.)	0.105 (a. a.)	1.23 (volum.)	0.76 (comb.)
	0.600	0.11	1.25	0.78
	0.598	0.11	1.26	0.77
	0.596	0.105	1.24	0.78
	0.600	0.11	1.28	0.77
	0.602	0.11	1.26	0.77
	0.598	0.10	1.25	0.78
	0.600	0.105	1.28	0.79
	0.595	0.11	1.25	0.77
	0.600	0.11	1.23	0.76
PR-1, LAB-4	0.54 (a. a.)	0.10 (a. a.)	1.12 (a. a.)	
	0.55	0.10	1.08	
	0.57	0.11	1.11	
	0.51	0.12	1.09	
	0.51	0.11		
	0.49	0.10		
	0.56	0.12		
	0.53	0.13		
	0.51	0.12		
	0.45	0.12		

NOTE: (a. a.) = by atomic-absorption spectrophotometry.
(volum.) = by volumetric analysis.

(continued)

	<u>Mo %</u>	<u>Bi %</u>	<u>Fe %</u>	<u>S %</u>
PR-1, LAB-5	0.60 (a. a.)	0.10 (color.)	1.26 (volum.)	0.83 (grav.)
	0.61	0.10	1.26	0.84
	0.60	0.10	1.27	0.85
	0.61	0.10	1.26	0.84
	0.60	0.10	1.28	0.82
	0.60	0.10	1.26	0.83
	0.60	0.11	1.28	0.85
	0.60	0.10	1.26	0.83
	0.61	0.10	1.27	0.82
	0.60	0.10	1.26	0.83
PR-1, LAB-6	0.576 (a. a.)	0.113 (a. a.)	1.21 (volum.)	0.84 (grav.)
	0.590	0.113	1.19	0.79
	0.590	0.110	1.21	0.83
	0.570	0.113	1.25	0.84
	0.570	0.113	1.20	0.84
	0.570	0.110	1.17	0.86
	0.590	0.110	1.21	0.83
	0.580	0.113	1.22	0.85
	0.580	0.113	1.19	0.86
	0.570	0.113	1.24	0.82
PR-1, LAB-7	0.550 (a. a.)	0.118 (a. a.)	1.22 (a. a.)	0.813 (comb.)
	0.545	0.104	1.25	0.800
	0.565	0.106	1.22	0.825
	0.550	0.108	1.25	0.815
	0.540	0.108	1.21	0.802
	0.550	0.113	1.22	0.805
	0.560	0.110	1.22	0.811
	0.545	0.113	1.25	0.810
	0.550	0.108		0.802
	0.540	0.106		0.810
	0.550	0.108		
	0.570	0.105		
	0.563	0.113		
		0.110		

(continued)

	<u>Mo %</u>	<u>Bi %</u>	<u>Fe %</u>	<u>S %</u>
PR-1, LAB-8	0.607 (a. a.)	0.11 (a. a.)	1.242 (a. a.)	0.785 (grav.)
	0.604	0.112	1.245	0.793
	0.605	0.11	1.245	0.789
	0.608	0.11	1.26	0.786
	0.604	0.112	1.254	0.782
	0.602	0.113	1.24	0.782
	0.595 (grav.)	0.104 (color)	1.25	0.786
	0.592	0.105	1.25	0.780
	0.604 (color.)	0.105	1.258	0.792
	0.606	0.105	1.25	0.790
PR-1, LAB-9	0.580 (color.)		1.23 (color.)	0.79 (grav.)
	0.580		1.23	0.78
	0.596		1.23	0.81
	0.596		1.24	0.82
	0.572		1.23	0.82
	0.572		1.21	0.81
	0.572		1.25	0.80
	0.592		1.22	0.81
	0.588		1.23	0.82
	0.580		1.24	0.84
PR-1, LAB-10	0.60 (color.)	0.108 (color.)	1.21 (volum.)	0.77 (grav.)
	0.58	0.107	1.22	0.76
	0.59	0.107	1.21	0.79
	0.58	0.106	1.21	0.78
	0.60	0.105	1.19	0.78
	0.58	0.105	1.17	0.78
	0.60	0.106	1.22	0.77
	0.58	0.109	1.18	0.78
	0.59	0.109	1.19	0.78
	0.57	0.105	1.18	0.78
	0.61 (a. a.)			
	0.60			
	0.59			
	0.59			
	0.59			
	0.61			
	0.61			
	0.59			
	0.59			

(continued)

	<u>Mo %</u>	<u>Bi %</u>	<u>Fe %</u>	<u>S %</u>
PR-1, LAB-11	0.648 (polarog.)	0.113 (a. a.)	1.28 (volum.)	0.782 (grav.)
	0.640	0.113	1.28	0.768
	0.639	0.112	1.28	0.775
	0.640	0.113	1.30	0.771
	0.644	0.113	1.31	0.772
	0.639	0.114	1.29	0.799
	0.639	0.114	1.28	0.777
	0.633	0.113	1.29	0.780
	0.637	0.114	1.27	0.788
	0.643	0.115	1.28	0.765
PR-1, LAB-12	0.586 (color.)	0.117 (color.)	1.231 (color.)	0.793 (comb.)
	0.588	0.114	1.225	0.797
	0.579	0.119	1.212	0.805
	0.585	0.115	1.215	0.792
	0.577	0.118	1.214	0.789
	0.586	0.118	1.232	0.793
	0.582	0.118	1.233	0.806
	0.589	0.121	1.215	0.804
	0.596	0.120	1.224	0.801
	0.594	0.117	1.222	0.793
PR-1, LAB-13	0.607 (color.)	0.118 (color.)	1.28 (color.)	0.839 (grav.)
	0.598	0.112	1.30	0.833
	0.604	0.118	1.28	0.848
	0.596	0.114	1.28	0.841
	0.597	0.112	1.31	0.841
	0.598	0.109	1.31	0.825
	0.582	0.113	1.33	0.839
	0.598	0.103	1.36	0.826
	0.585	0.107	1.31	0.826
	0.595	0.113	1.31	0.839
PR-1, LAB-14	0.593 (color.)	0.122 (color.)	1.24 (volum.)	0.812 (grav.)
	0.604	0.119	1.25	0.814
	0.605	0.115	1.24	0.817
	0.594	0.115	1.26	0.829
	0.594	0.115	1.27	0.826
	0.602	0.113	1.26	0.833
	0.594	0.109	1.25	0.813
	0.597	0.109	1.24	0.819
	0.594	0.112	1.25	0.821
	0.613	0.109	1.25	0.836

NOTE: (polarog.) = by polarographic analysis.

(continued)

	<u>Mo %</u>	<u>Bi %</u>	<u>Fe %</u>	<u>S %</u>
PR-1, LAB-15	0.612 (a. a.)	0.105 (color.)	1.25 (a. a.)	0.775 (comb.)
	0.612	0.105	1.23	0.760
	0.624	0.106	1.25	0.767
	0.636	0.103	1.26	0.776
	0.624	0.104	1.23	0.777
	0.624	0.106	1.23	0.757
	0.612	0.105	1.25	0.768
	0.636	0.105	1.26	0.756
	0.636	0.103	1.25	0.784
	0.624	0.105	1.23	0.775
PR-1, LAB-16	0.612 (grav.)	0.096 (color.)	1.26 (volum.)	0.84 (grav.)
	0.605	0.094	1.26	0.84
	0.606	0.097	1.26	0.82
	0.608	0.097	1.26	0.83
	0.601	0.094	1.29	0.84
	0.629	0.095	1.26	0.83
	0.615	0.094	1.26	0.82
	0.635	0.095	1.26	0.82
	0.601	0.095	1.26	0.83
	0.621	0.096	1.26	0.84
PR-1, LAB-17				0.774 (comb.)
				0.799
				0.787
				0.818
				0.795
				0.811
				0.800
				0.811
				0.799
				0.798
PR-1, LAB-18	0.599 (volum.)	0.109 (color.)	1.236 (volum.)	0.789 (grav.)
	0.599	0.109	1.229	0.785
	0.594	0.107	1.233	0.770
	0.588	0.108	1.229	0.784
	0.604	0.107	1.234	0.781
	0.588	0.109	1.242	0.799
	0.590	0.107	1.234	0.792
	0.586	0.105	1.235	0.790
	0.580	0.104	1.224	0.781
	0.594	0.104	1.224	0.784

(concluded)

	<u>Mo %</u>	<u>Bi %</u>	<u>Fe %</u>	<u>S %</u>
PR-1, LAB-19	0.64 (color.)			
	0.65			
	0.66			
	0.69			
	0.65			
	0.66			

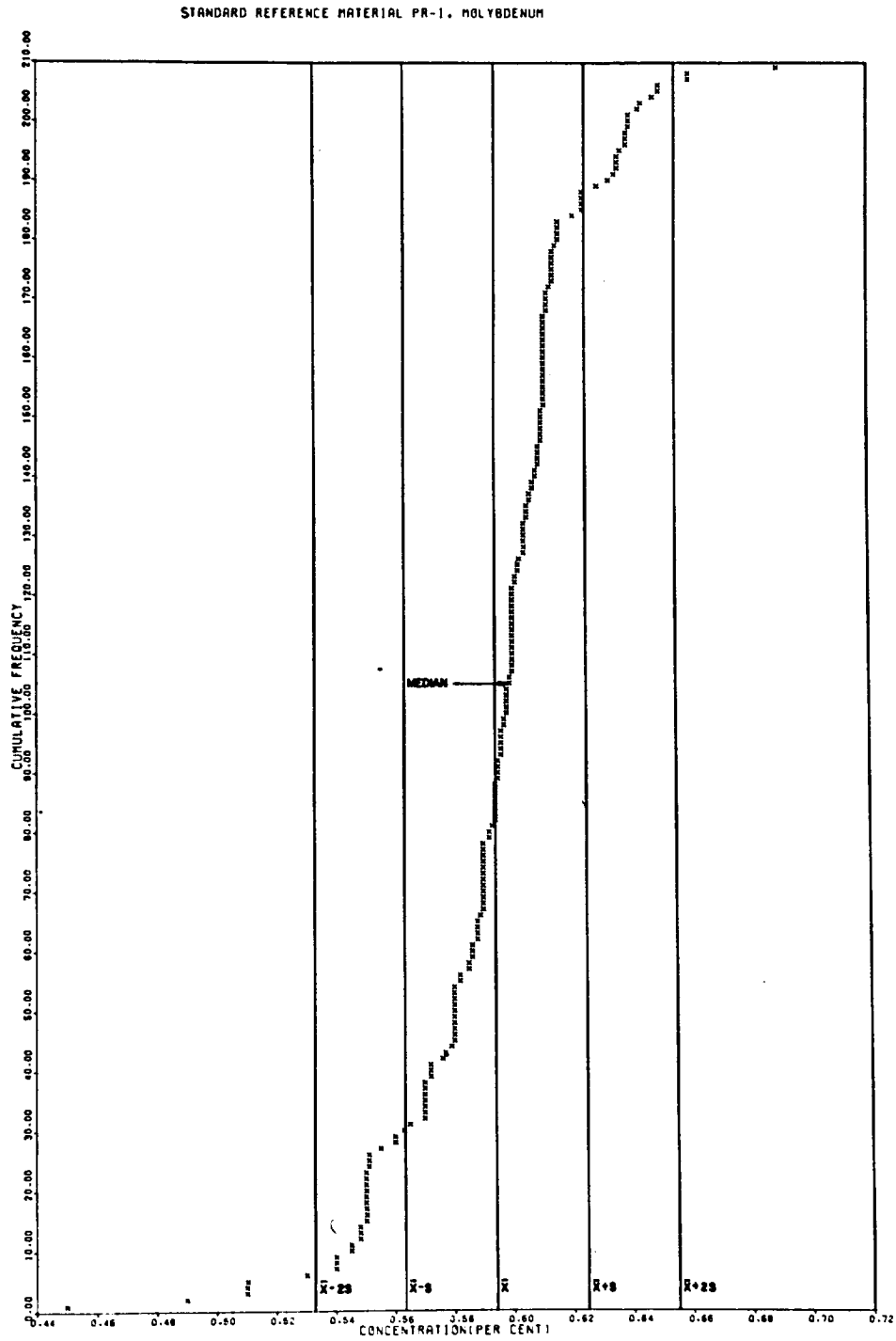


Figure 2. Standard Reference Material PR-1. Molybdenum.

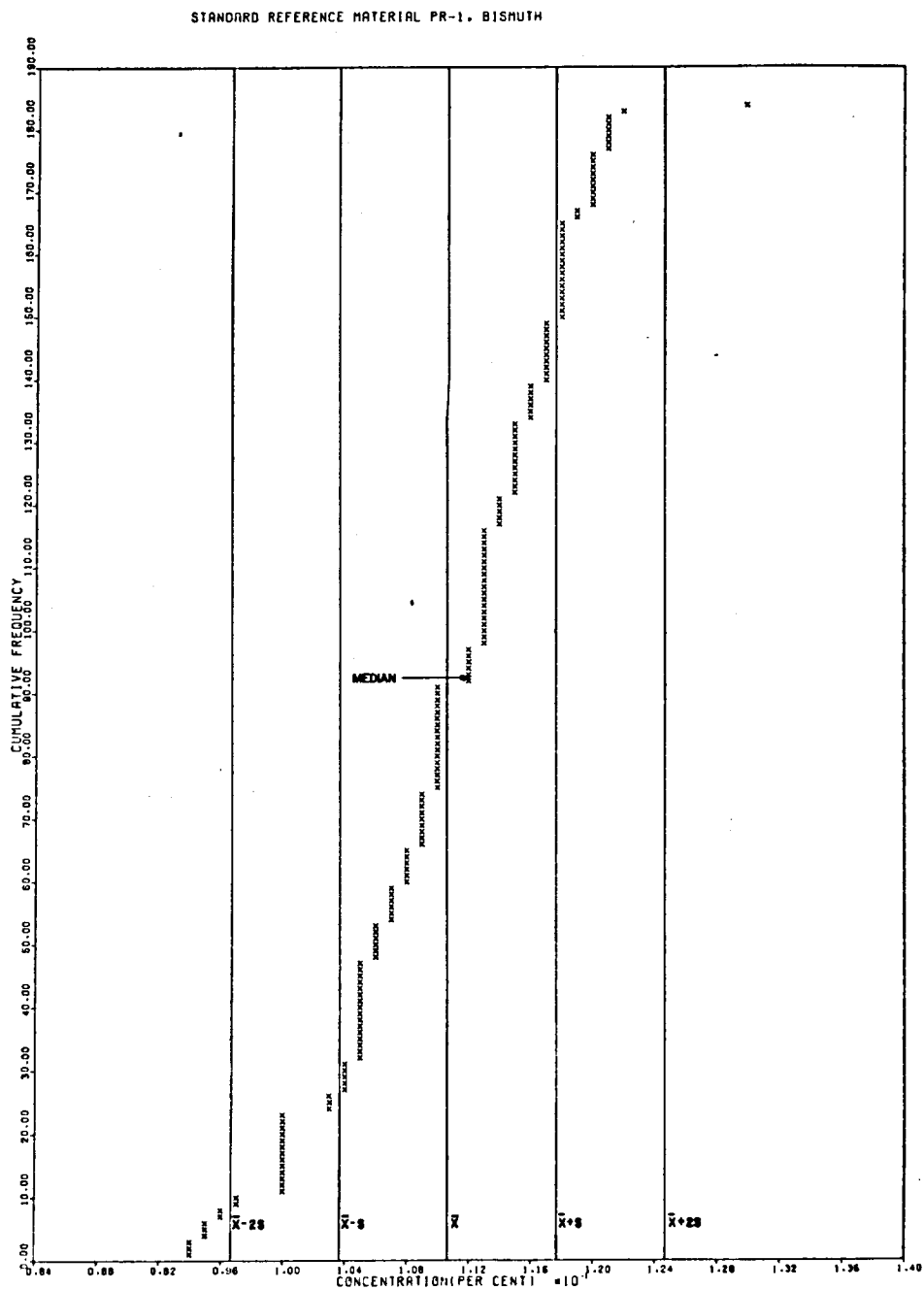


Figure 3. Standard Reference Material PR-1. Bismuth.

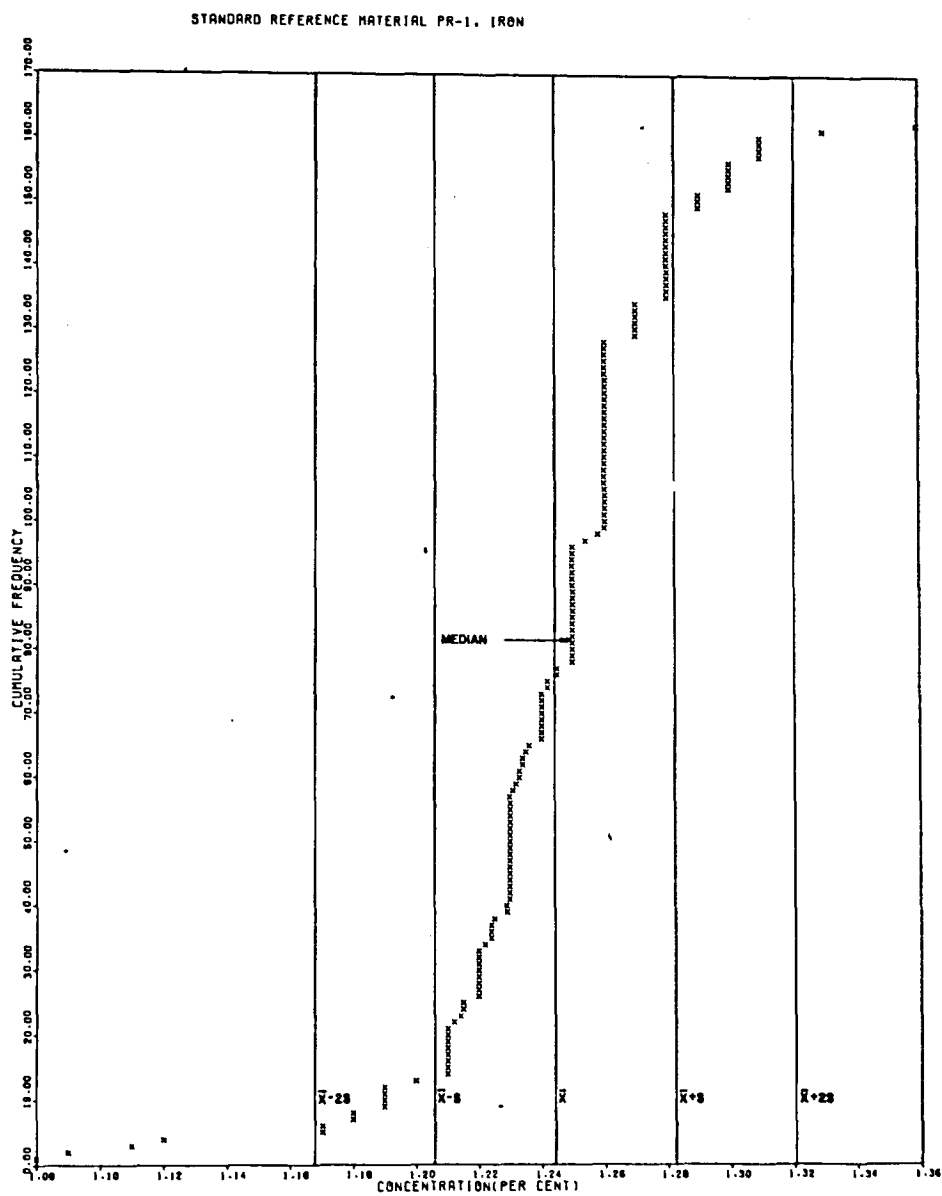


Figure 4. Standard Reference Material PR-1. Iron.

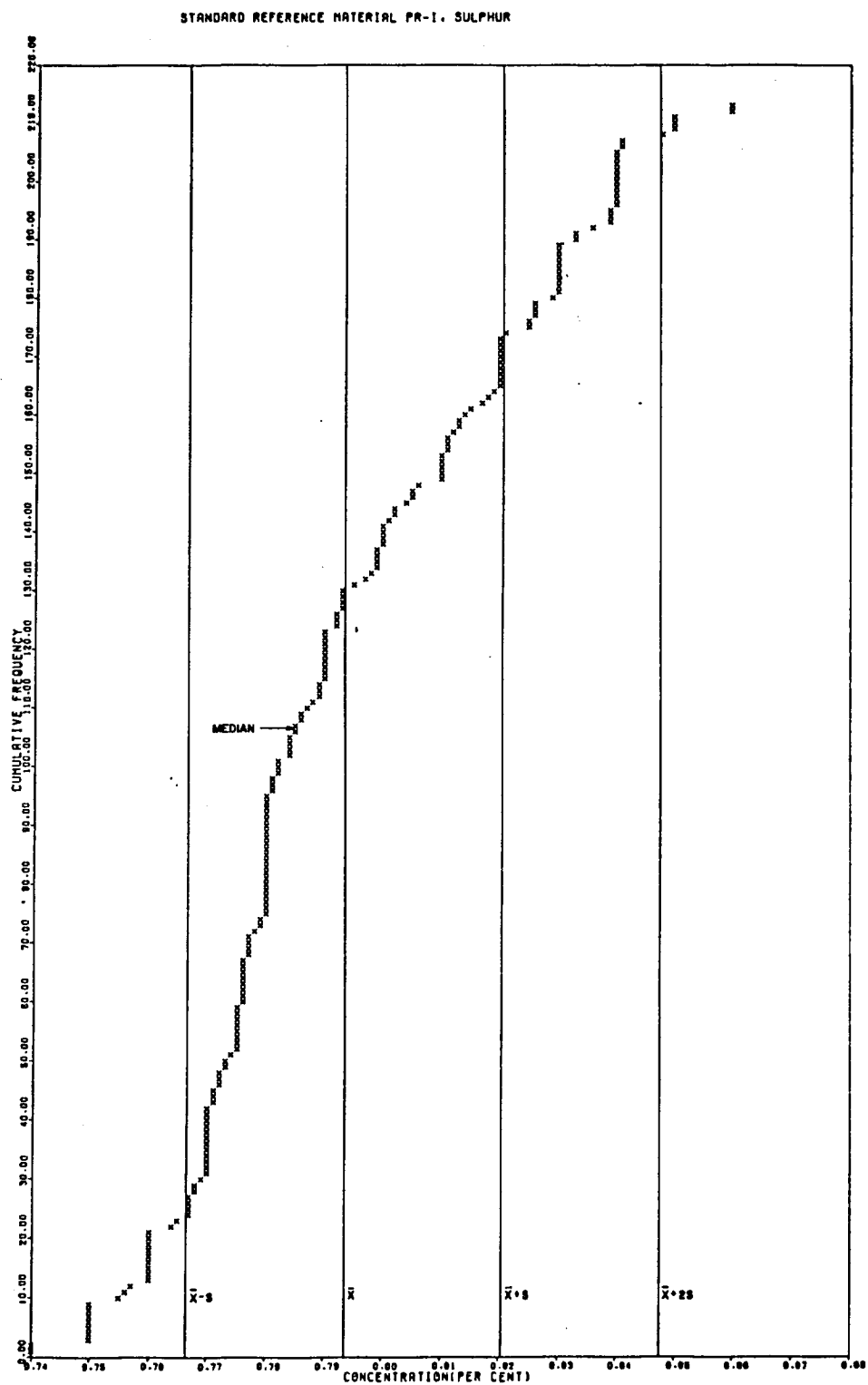


Figure 5. Standard Reference Material PR-1. Sulphur.

TABLE 7

Statistical Parameters Computed, Based on the Assumption that the
Data are Normally Distributed, Random Variables

Normal Parameters	Mo		Bi		Fe		S	
	All Data	Acc.* Data	All Data	Acc. Data	All Data	Acc. Data	All Data	Acc. Data
No. of Observations, N	209	200	184	173	162	156	213	207
Median, M (%)	0.599	0.600	0.112	0.112	1.250	1.250	0.785	0.784
Mean, \bar{x} (%)	0.594	0.596	0.111	0.111	1.244	1.246	0.793	0.792
Variance $\times 10^3$, s^2	0.920	0.582	0.049	0.035	1.442	0.817	0.727	0.641
Standard Deviation, s	0.030	0.024	0.007	0.006	0.038	0.029	0.027	0.025
Skewness Factor, α_3	-0.874	-0.318	-0.382	-0.239	-1.089	-0.094	0.490	0.425
Kurtosis Coefficient, α_4	5.940	3.025	2.660	2.093	7.188	3.073	2.327	2.231

*Accepted data, i.e., all results within twice the standard deviation about the mean

$$[(\bar{x}_{..} - 2s) \leq x_{ij} \leq (\bar{x}_{..} + 2s)].$$

s = estimated standard deviation.

M = the median of x_{ij} ;

$\bar{x}_{..}$ = the arithmetic mean of all results;

s^2 = the estimated variance of x_{ij} ;

Skewness factor, $\alpha_3 = m_3/m_2^{3/2}$ and is a measure of the skewness of the probability density curve;

for an ideal normal distribution, $\alpha_3 = 0$.

(continued)

Kurtosis coefficient, $\alpha_4 = m_4/m_2^2$, and is a measure of the sharpness of the peak of the probability density curve; for an ideal distribution $\alpha_4 = 3$.

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 j th moment of the x values about their own mean value.

Although these results, as a whole, appeared to follow normal frequency distributions, a closer examination revealed that there was a substantial variation between laboratories, thereby rendering the results not totally independent of each other. Table 8 shows that all the laboratories except Laboratory No. 4 reported lower coefficients of variation than the overall coefficient of variation. Figures 6 to 9* 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). 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 it gives a good estimate of the mean.

*The molybdenum analysis results from Laboratory No. 19 fall outside the range of Figure 6.

MOLYBDENUM

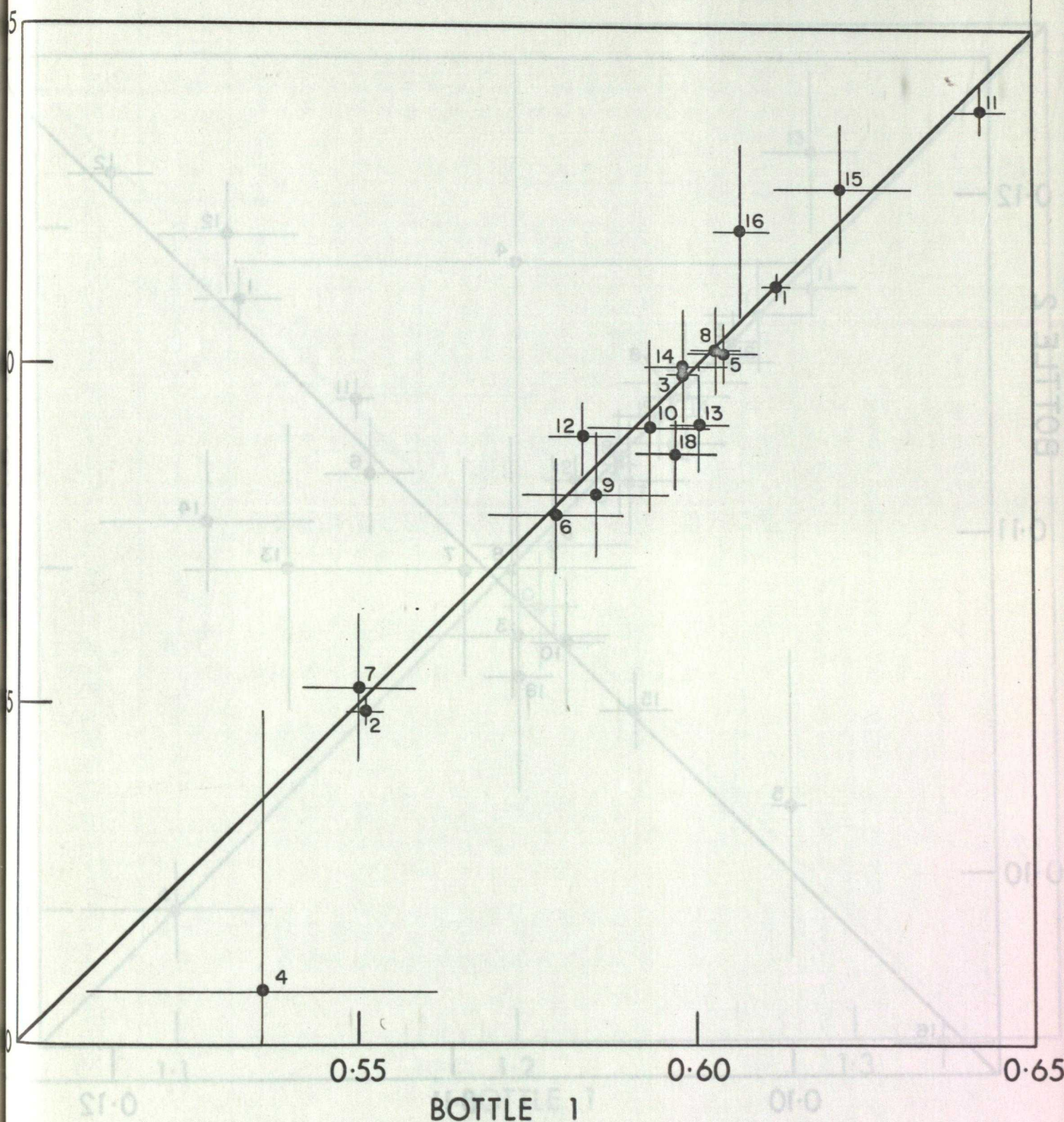


Figure 6. SRM PR-1. Average Molybdenum Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analysed.)

BISMUTH

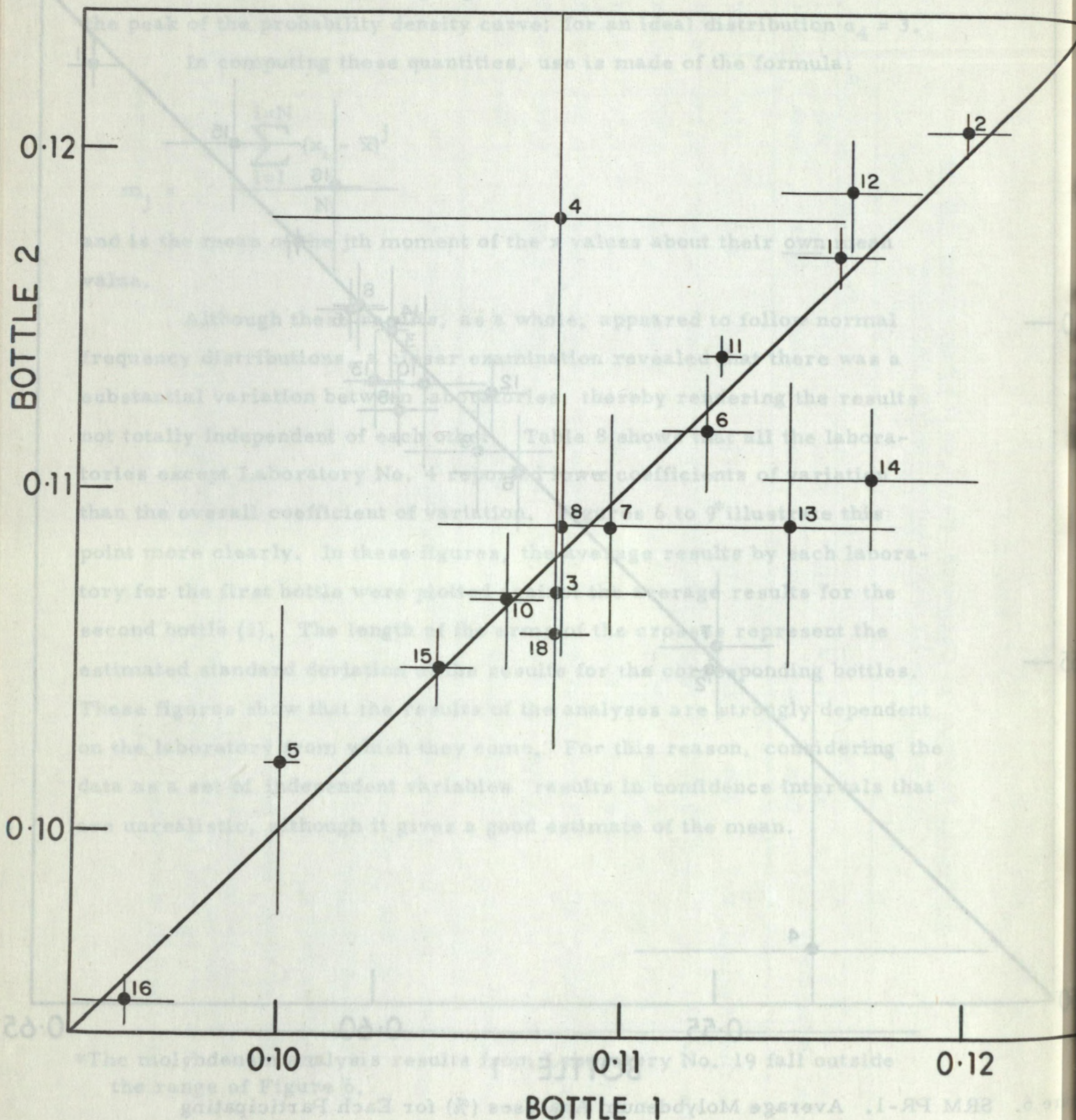


Figure 7. SRM PR-1. Average Bismuth Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analysed.)

IRON

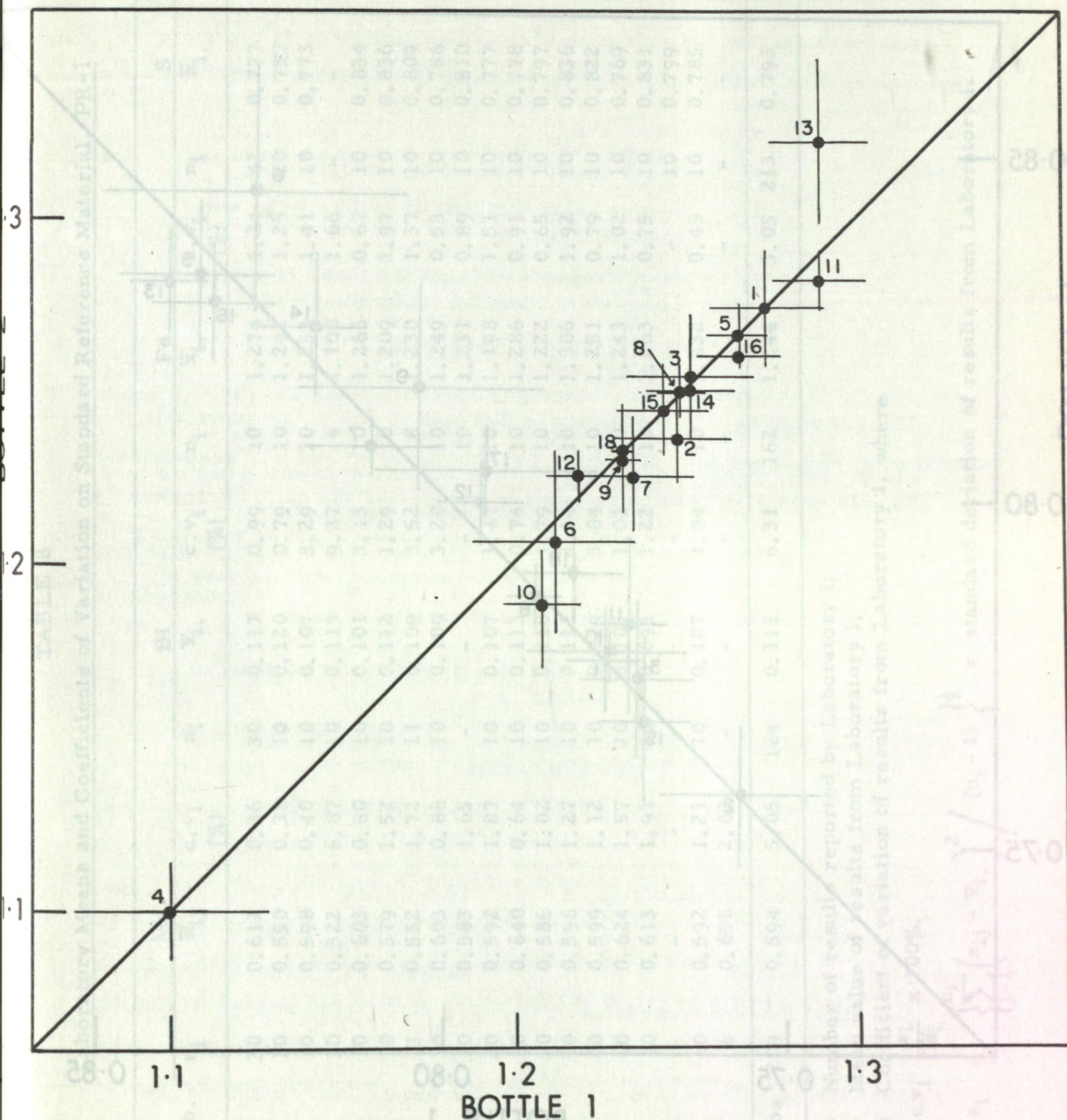


Figure 8. SRM PR-1. Average Iron Analyses (%) for Each Participating Laboratory.
(The crosses show one standard deviation on either side of the average for both bottles analysed.)

SULPHUR

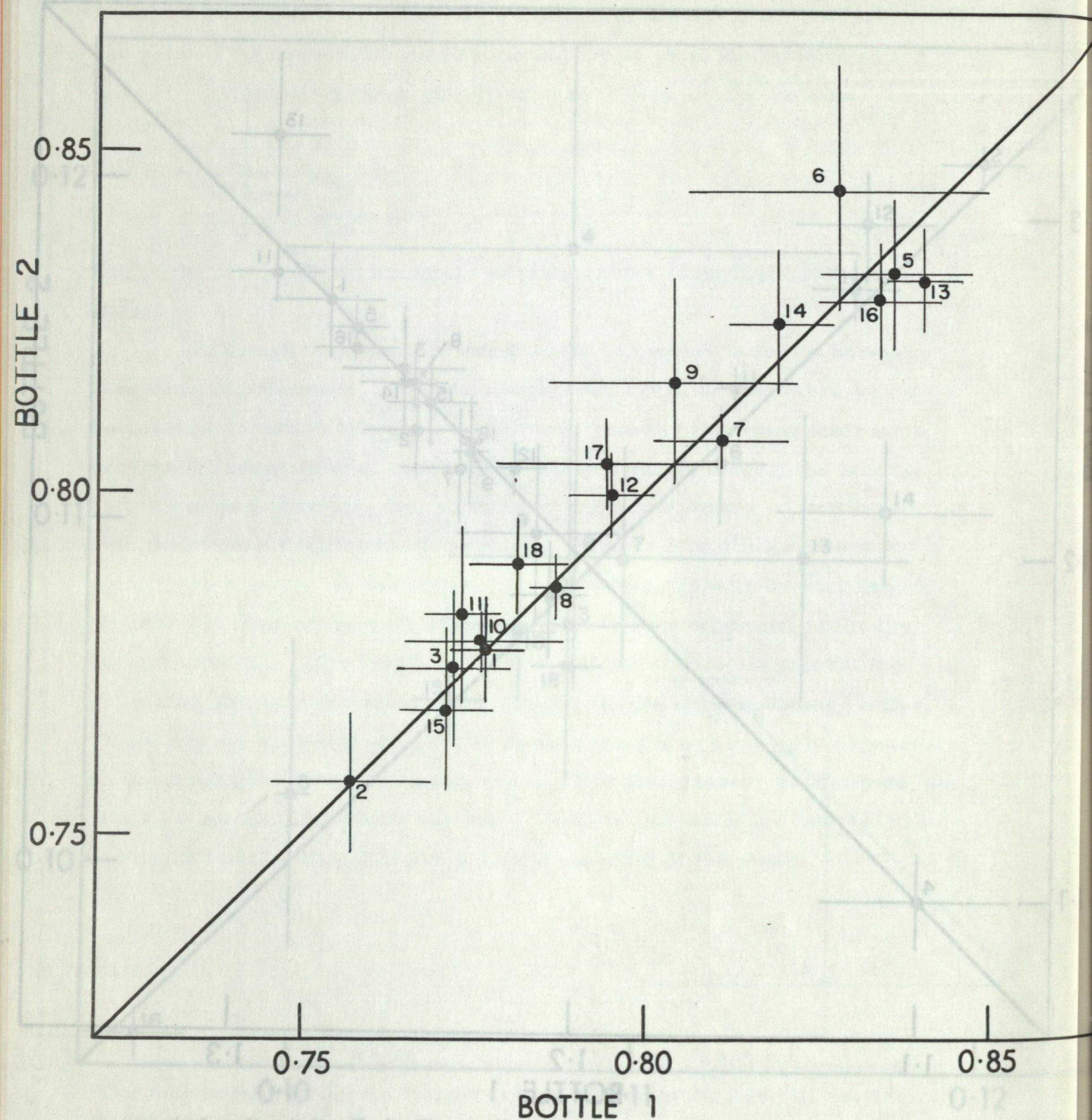


Figure 9. SRM PR-1. Average Sulphur Analyses (%) for Each Participating Laboratory. (The crosses show one standard deviation on either side of the average for both bottles analysed.)

TABLE 8

Laboratory Means and Coefficients of Variation on Standard Reference Material, PR-1

Lab. No. (i)	Mo			Bi			Fe			S		
	n_i	\bar{x}_i	c.v. _i (%)	n_i	\bar{x}_i	c.v. _i (%)	n_i	\bar{x}_i	c.v. _i (%)	n_i	\bar{x}_i	c.v. _i (%)
1	30	0.612	0.36	30	0.117	0.99	10	1.274	1.24	43	0.777	0.88
2	10	0.550	0.38	10	0.120	0.79	10	1.242	1.25	20	0.757	1.41
3	10	0.598	0.40	10	0.107	3.29	10	1.253	1.41	10	0.773	1.23
4	10	0.522	6.87	10	0.113	9.37	4	1.100	1.66	-	-	-
5	10	0.603	0.80	10	0.101	3.13	10	1.266	0.67	10	0.834	1.29
6	10	0.579	1.52	10	0.112	1.29	10	1.209	1.97	10	0.836	2.47
7	13	0.552	1.72	14	0.109	3.52	8	1.230	1.37	10	0.809	0.93
8	10	0.603	0.86	10	0.109	3.20	10	1.249	0.53	10	0.786	0.56
9	10	0.583	1.65	-	-	-	10	1.231	0.89	10	0.810	2.10
10	20	0.592	1.87	10	0.107	1.47	10	1.198	1.51	10	0.777	1.06
11	10	0.640	0.64	10	0.113	0.74	10	1.286	0.91	10	0.778	1.30
12	10	0.586	1.02	10	0.118	1.79	10	1.222	0.65	10	0.797	0.78
13	10	0.596	1.27	10	0.112	4.14	10	1.306	1.92	10	0.836	0.94
14	10	0.599	1.12	10	0.114	3.84	10	1.251	0.79	10	0.822	1.04
15	10	0.624	1.57	10	0.105	1.01	10	1.243	1.02	10	0.769	1.23
16	10	0.613	1.91	10	0.095	1.22	10	1.263	0.75	10	0.831	1.05
17	-	-	-	-	-	-	-	-	-	10	0.799	1.58
18	10	0.592	1.21	10	0.107	1.84	10	1.232	0.45	10	0.785	0.99
19	6	0.658	2.62	-	-	-	-	-	-	-	-	-
All Labs	209	0.594	5.05	184	0.111	6.31	162	1.244	3.05	213	0.793	3.40

 n_i = Number of results reported by Laboratory i; \bar{x}_i = Mean value of results from Laboratory i;c.v._i = Coefficient of variation of results from Laboratory i, where

$$c.v._i = \frac{s_i}{\bar{x}_i} \times 100\%$$

$$\text{and } s_i = \left\{ \sum_{j=1}^{n_i} (x_{ij} - \bar{x}_i)^2 / (n_i - 1) \right\}^{\frac{1}{2}} = \text{standard deviation of results from Laboratory i.}$$

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 (2):

$$x_{ij} = u + y_i + e_{ij}$$

where

- x_{ij} = the jth result reported by Laboratory i;
- u = 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 "between-laboratory" mean squares to "within-laboratory" mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom. The results of this analysis are presented in Table 9.

TABLE 9
Summary of One-Way Analyses of Variance for Standard Reference
Material PR-1

	Mo	Bi	Fe	S
No. of Participating Laboratories, k	18	16	17	17
No. of Observations, N	209	184	162	213
F statistic, calculated	83.84	37.20	58.25	83.83
$F_{0.95}(k-1, N-k)$ derived from tables	1.68	1.73	1.71	1.70

In all cases, the calculated values of the F statistic are very much larger than the value from the F distribution (i. e., the value derived from standard statistical tables). Therefore, the major source of variation of the results was procedural variation in the different laboratories.

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

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

with variance of this overall mean being given by:

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

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 8 and Figures 6 to 9 shows that there is a wide range in the degree of precision obtained by the various laboratories. The coefficients of variation range from 0.36% to 6.87% for molybdenum, from 0.74% to 9.37% for bismuth, from 0.53% to 1.97% for iron and from 0.56% to 2.47% for the sulphur data. Furthermore, many of the laboratories that reported high coefficients of variation also reported results with their means far removed from the overall mean. 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 (2):

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

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

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

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

D. Weighted Mean by the Inverse of the Square Root of the Variance

This scheme is similar to the scheme described under sub-heading C, except that $1/W_i$ is the square root of the variance of the mean of Laboratory i, therefore:

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

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

In the actual computation of the schemes described under B, C and D, the σ^2 values were, of course, replaced by s_i^2 , the estimated variance of the within-laboratory results. The value of ω^2 is estimated from the analysis of variance (method B).

The results of these various schemes of computations are summarized in Table 10 under their corresponding headings A, B, C, and D. The values of parameters under A were computed after rejecting all the results that deviated from the overall means by more than twice the standard deviations. The values of the parameters under B, C, and D were computed from all the results. In these schemes, no results were rejected because they were not considered as outlying figures by the laboratory that reported them, although they may actually be outlying results from the point of view of overall data.

TABLE 10

Estimated Statistical Parameters for Standard Reference Material PR-1

Method of Computation	Mo				Bi				Fe				S			
	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
No. of Participating Laboratories	18	18	18	18	15	16	16	16	16	17	17	17	17	17	17	17
No. of Observations (Results)	200	209	209	209	173	184	184	184	156	162	162	162	207	213	213	213
Median, %	0.600	0.599	0.599	0.599	0.112	0.112	0.112	0.112	1.250	1.250	1.250	1.250	0.784	0.785	0.785	0.785
Mean, %	0.596	0.594	0.595	0.595	0.111	0.111	0.110	0.110	1.246	1.244	1.239	1.239	0.792	0.793	0.799	0.799
Variance of the Mean $\times 10^4$	0.029	0.574	0.482	0.482	0.002	0.030	0.025	0.025	0.052	0.794	0.778	0.778	0.031	0.567	0.406	0.406
95% Confidence Interval of the Mean, % Low	0.593	0.578	0.580	0.580	0.110	0.107	0.106	0.107	1.242	1.225	1.220	1.220	0.789	0.777	0.785	0.785
High	0.599	0.610	0.610	0.610	0.112	0.114	0.113	0.113	1.251	1.263	1.258	1.258	0.795	0.809	0.812	0.812

DISCUSSION

Table 10 shows that, in all cases, the means computed by the four procedures are in very 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, since there is a strong dependence of the results on the laboratory from which they were reported, the computation procedure A is technically incorrect. The assumption used for the computation procedures B, C, and D are all equally reasonable. Because there is no reason to prefer any one of these three methods of computation, the statistical parameters computed by procedure B are recommended for the certification of this material. These statistics are presented in Table 11.

TABLE 11
Recommended Values for the Means and Their Confidence
Intervals for Standard Reference Material PR-1

Statistics	Content of Elements (% by weight)			
	Mo	Bi	Fe	S
Mean	0.594	0.111	1.244	0.793
95% Confidence Interval				
of the Mean Low	0.578	0.107	1.225	0.777
High	0.610	0.114	1.263	0.809

Most of the analytical methods used by the participating laboratories differ in detail at various stages of the analyses. It is difficult to place these methods into a meaningful classification. Therefore, in the computation of the statistical parameters, the variation of the methods used by the laboratories were included as part of the inter-laboratory variations.

For the sulphur analyses, two distinct methods were used, the combustion and the gravimetric. An attempt was made to investigate any difference between them. Seven laboratories that used the combustion method reported 73 results, and 12 laboratories that used the gravimetric method reported 140 results. Computation by method B produced the results shown in Table 12.

TABLE 12
Results of Sulphur Analyses Computed by Method B

	Analysis by gravimetry	Analysis by combustion	Overall
No. of Laboratories	12	7	19
No. of Observations	140	73	213
Mean	0.799	0.783	0.793
95% Confidence Interval of the Mean	0.779-0.818	0.764-0.802	0.777-0.809

It can be seen from Table 12 that there is no significant difference between the results of the sulphur analyses using the above two methods.

The main purpose for undertaking this "round-robin" series of analyses was to prepare and characterize as a standard reference material an ore of particular composition and mineralogical characteristics. However, as a by-product of the study, the round-robin scheme provided a reasonably comprehensive nation-wide survey on the state-of-the-art in the analytical chemistry of materials of this type. From this survey, the following information can be drawn:

1. Most laboratories are using methods that, by themselves, are both precise and consistent. This can be seen from Table 8 and from Figures 6 to 9. The coefficients of variation calculated from most sets of results are of the same order of magnitude. The laboratory means

from Bottle 1 do not differ from the means from Bottle 2 for most laboratories. This is demonstrated by the fact that, in most cases, in Figures 6 to 9 the mean points lie reasonably close to the 45° line.

2. The fact that the major cause of variation lies in the inter-laboratory variation (see Table 8) indicates that, although most laboratories reported results with a good degree of precision, some improvement of their accuracy still remains to be achieved. The overall coefficients of variation of 6% for molybdenum and bismuth and of over 3% for iron and sulphur are considered to be rather large. These coefficients of variation could, presumably, be improved if the participating laboratories, particularly those who reported results with substantial deviations from the overall means, would examine their methods of analyses for possible sources of error and communicate their findings to the co-ordinator of this project.

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