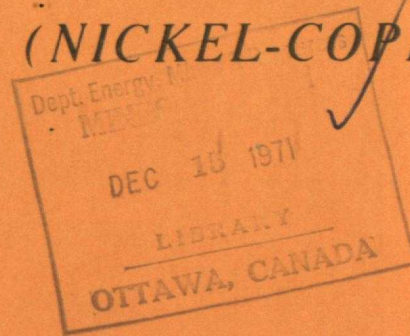


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DEPARTMENT OF  
ENERGY, MINES AND RESOURCES  
MINES BRANCH  
OTTAWA

*CHARACTERIZATION AND PREPARATION  
OF STANDARD REFERENCE MATERIALS  
THAT CONTAIN NOBLE METALS:  
(A) PTA (ORES) AND  
(B) PTM (NICKEL-COPPER MATTE)*



R. C. MCADAM, SUTARNO AND P. E. MOLOUGHNEY

MINERAL SCIENCES DIVISION

JUNE 1971

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CHARACTERIZATION AND PREPARATION OF STANDARD REFERENCE MATERIALS THAT CONTAIN NOBLE METALS: (A) PTA (ORES) AND (B) PTM (NICKEL-COPPER MATTE)

by

R. C. McAdam\*, Sutarno\*\* and P. E. Moloughney\*\*\*

SYNOPSIS

Two reference materials containing platinum-group metals have been certified as standards. A concentrate from an alluvial material (containing platinum alloys) from the Tulameen River area of British Columbia has been analyzed for platinum; a nickel-copper matte from the Sudbury area of Ontario has been analyzed for platinum, palladium, rhodium, and gold. The sample preparation and characterization of the reference materials are described and a statistical evaluation of the "round-robin" analytical values has been performed. These reference standards are now available from the Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa.

A program for analyzing the nickel-copper matte for iridium, ruthenium, silver, and, possibly, osmium is to be undertaken. If sufficient satisfactory results are obtained, these constituents will also be certified for this material.

---

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Direction des mines Bulletin technique TB 138

LA CARACTÉRISATION ET LA PRÉPARATION D'ÉTALONS  
DE RÉFÉRENCE CONTENANT DES MÉTAUX PRÉCIEUX:  
(a) PTA (MINÉRAI) ET (b) PTM (MATTE DE NICKEL ET DE CUIVRE)

by

R. C. McAdam\*, Sutarno\*\* et P. E. Moloughney\*\*\*

RÉSUMÉ

Deux matériaux de référence contenant des métaux de groupe platine ont été établis comme étalons. Un sable noir alluvial (contenant des alliages de platine) de la région de la Rivière Tulameen en Colombie Britannique a été analysé pour le platine; une matte de nickel et de cuivre de la région de Sudbury en Ontario a été analysée pour le platine, le palladium, le rhodium et l'or. La préparation de l'échantillon et la caractérisation des matériaux de référence sont décrites et une évaluation statistique des valeurs analytiques obtenus anonymement des différents laboratoires a été effectuée. Maintenant, on peut obtenir ces étalons de référence en s'adressant à la Division des sciences minérales, Direction des mines, ministère de l'Énergie, des Mines et des Ressources, Ottawa.

On entreprendra un programme pour l'analyse de la matte de nickel et de cuivre pour l'iridium, le ruthénium, l'argent et, possiblement, l'osmium. Si les résultats sont suffisants et satisfaisants, ces constituants seront aussi certifiés pour ce matériel.

---

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## INTRODUCTION

The Mineral Sciences Division of the Mines Branch has initiated a programme for the certification of several standard reference materials containing the platinum-group metals in an attempt to overcome the difficulties encountered by commercial laboratories over past years in obtaining reliable assay results for these metals. The programme was conducted under the auspices of the Standards Committee of the Spectroscopy Society of Canada, with Dr. A.H. Gillieson, Head, Spectrochemistry Group, Mineral Sciences Division, as the chairman of this committee. This committee has been responsible for the certification of several reference materials, including a sulphide ore, four syenite rock samples, five phosphor-bronzes and four commercial-purity copper standards.

Three materials considered suitable for certification as precious-metals-group standards have been obtained. These included a flotation (sulphide) concentrate and a nickel-copper matte produced from the Sudbury ore of Ontario and provided by the International Nickel Company of Canada and by Falconbridge Nickel Mines Limited, respectively, together with a concentrate from an alluvial material (containing platinum alloys), from the Tulameen River area of British Columbia, supplied by B.H. Levelton and Associates of Vancouver. The senior author of this report has acted as the leader of a Task Force that was set up to organize and implement this phase of the programme.

The reference materials were prepared at the Mines Branch and distributed to laboratories in Canada and in the United States that had agreed to participate in the "round-robin" analytical programme required for certification of the materials as standards. Appendix I to this report (see page 29) gives a list of the participating organizations. They will be referred to in this report as Laboratories "A" to "K", respectively. It must be clearly understood, however, that the code letter bears no relation whatever to the order in which these organizations are listed in



Appendix A. This procedure has been adopted to preserve the anonymity of the participants' particular analytical results.

Subsequent to the distribution and analysis of the flotation concentrate, it was noted that "agglomeration" or "pelletizing" of the material had occurred. For this reason, further work is being done on this sample before it can be certified as a standard. This report, therefore, will deal only with the work conducted on the Tulameen concentrate and on the nickel-copper matte.

The original programme called for the certification of the reference materials for platinum, palladium, rhodium, and gold. However, preliminary analyses of the Tulameen sand indicated that platinum was the only precious metal present in amounts suitable for certification under this programme. The participating laboratories were instructed accordingly. The sampling of the ore materials and its distribution into bottles will be described later in the report.

Two bottles of each of the reference materials, selected at random, were submitted to each of the laboratories with the request that analyses for platinum, palladium, rhodium, and gold be performed on five separate bottles of the matte and that each result for each element be reported. For the Tulameen black sand samples, platinum analyses only were requested. Several of the laboratories did not report the number of analyses requested, therefore a statistical method of evaluation had to be devised to meet this situation. The results of this evaluation and the values assigned for the precious metals determined in the reference materials are given in this report.

The standard samples are now available to commercial, industrial, and other laboratories for assessing analytical methods used for the determination of precious metals. The standards may also prove valuable in identifying some of the difficulties encountered in analyzing for these metals.

PREPARATION, SAMPLING AND CHARACTERIZATION  
OF THE REFERENCE MATERIALS

1. The Tulameen Sand

Three samples of black sand from the Tulameen area of British Columbia were collected by sluicing and subsequent magnetic separation. Two samples, weighing 216 pounds and 47 pounds respectively, were pure magnetic fractions, and the third sample, weighing 257 pounds, was a mixed non-magnetic and magnetic material but with the nuggets removed by tabling.

A super-panner concentrate was made from the magnetic concentrate of the Tulameen placer-sand material. A mineralogical examination<sup>(1)</sup> of a polished section of this concentrate showed that the platinum was present as large flakes (or grains) and also in a finely disseminated form. Two large flakes were isolated and submitted to X-ray diffraction examination. The X-ray diffraction patterns were found to correspond to those of a platinum alloy. Microprobe analysis of some of the flakes indicated the contents - 71% platinum, 15% iron, and 20% copper<sup>2</sup>. The flakes examined were 0.3 and 0.5 millimeters in diameter, but the rest of the sample consisted of grains 0.1 to 0.3 millimeters in diameter. These large flakes, although relatively few in number, would be impossible to predict as to distribution and, because of their size and platinum content, would exert a great effect if present in any sample taken for analysis. For this reason, it was decided that the Tulameen reference material, after mixing of the three sample portions, should be ground so that the size differential between the flakes of platinum alloy and the finely disseminated platinum would be increased. This would occur because the flakes are very malleable and would not suffer any appreciable reduction in size by reason of the additional comminution; rather, they would tend to be flattened out.

---

For References, see page 28.

This procedure made possible the removal of the large flakes by screening. After removal of the large flakes of platinum alloy, the Tulameen material was divided into sixteen (16) equal-weight lots by continuous splitting. Each lot was further split into thirty-two (32) sub-lots. These were bottled and labelled to identify the lot number and the bottle number.

The procedure used for sampling of the Tulameen material is schematically depicted in Figure 1.

A chemical analysis for the major components, conducted on material taken from one of these bottles, gave the following contents:

63.0% Fe, 1.20% Ca, 2.91% Al, 3.63% SiO<sub>2</sub>, 0.62% Mg, Cr - none detectable, see Mineral Sciences Division Internal Report MS-AC-71-278, by J.C. Cloutier and R.R. Craig.

The absence of detectable chromium, in the form of chromite, was fortunate. If this refractory mineral is present in appreciable amounts, it must be decomposed prior to the analysis of the sample.

## 2. The Nickel-Copper Matte

The nickel-copper matte was ground to minus 100 mesh and tumbled in a 45-gallon drum for approximately ten hours to ensure thorough mixing. The material was then bottled in one-pound lots and random sample bottles taken from the total lot for distribution to the laboratories participating in the round-robin programme.

A chemical analysis for major constituents was made on material from a randomly selected bottle. The following results were obtained:

30.24% Cu, 44.75% Ni, 1.58% Fe, 21.6% S, see Mineral Sciences Division Internal Reports MS-AC-71-278 and 285, by J.C. Cloutier and R.R. Craig.

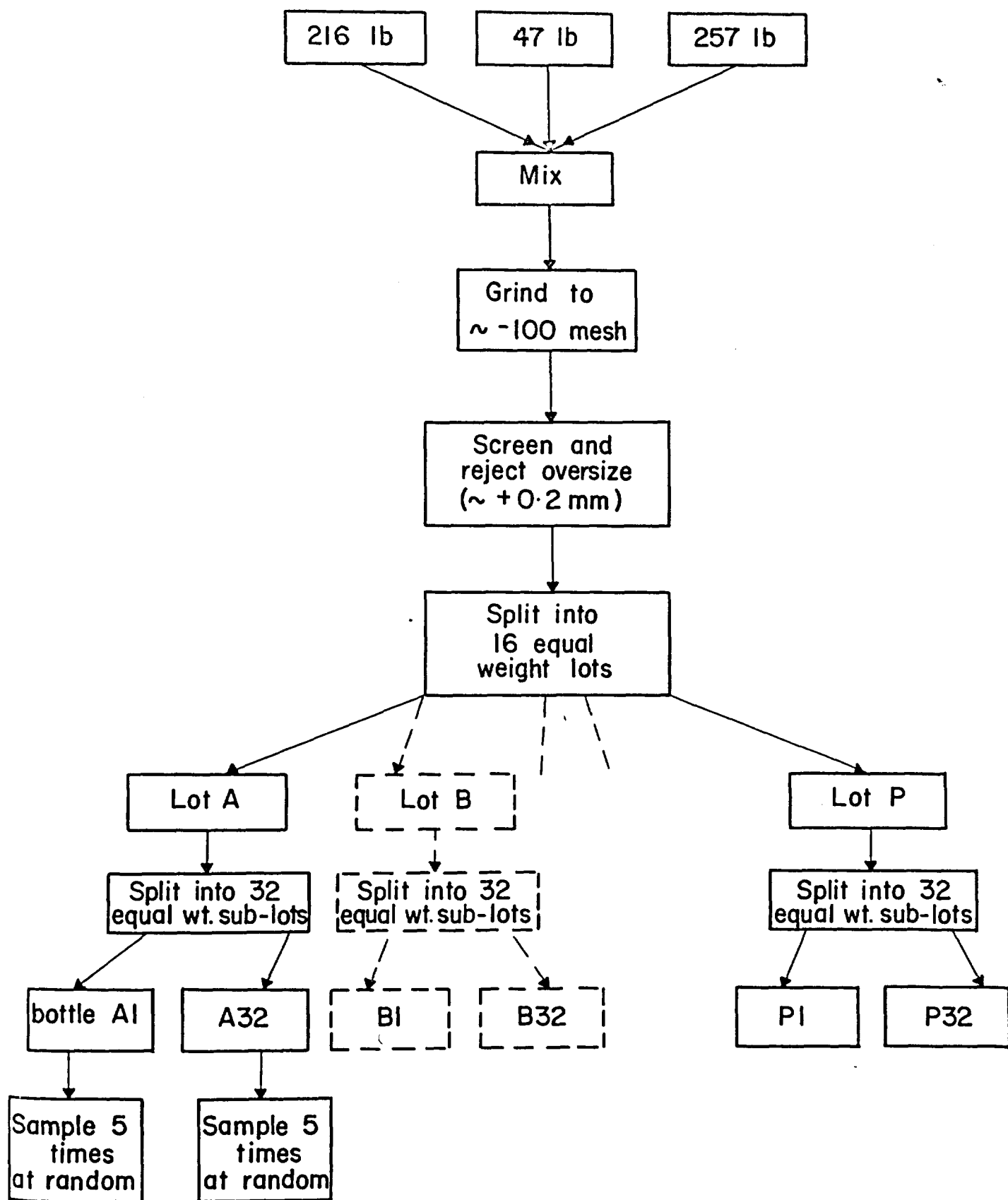


Figure 1. Sampling Procedure for the Tulameen Sand Concentrate.

## ANALYTICAL METHODS USED BY THE PARTICIPATING LABORATORIES

Several different analytical methods were used by the laboratories that collaborated in the round-robin analytical work required for the certification of the precious metals in these reference materials.

The assay methods employed by the various laboratories, designated "A" to "K", will now be mentioned in sequence.

Laboratory "A" collected the precious metals in molten tin by fusing the sample at 1200°C to 1250°C with a flux containing stannic oxide, sodium carbonate, silica, borax, and powdered coke. The resultant tin alloy was dissolved and the individual precious metals were isolated by ion-exchange and solvent-extraction processes and determined by either optical or atomic-absorption spectrophotometry.

Laboratories "B" and "H" collected the platinum, palladium, rhodium, gold, and silver in a lead button by fire assay and determined the individual elements spectrographically according to the proposed ASTM method by Lewis, Ott and MacMillan<sup>(3)</sup>. Laboratory "B" also collected the platinum, palladium, and gold into a silver bead and determined them spectrographically.

Laboratory "C" collected the platinum, palladium, rhodium, and gold in a silver bead and determined the individual elements by atomic-absorption spectrophotometry. Only one determination was made for rhodium by combining the five samples.

Laboratory "D" performed the initial assays using the fire-assay collection into a silver bead followed by spectrographic determination of the individual elements. However, the matte samples were checked by leaching with hydrochloric acid, roasting at 650°C, followed by fire-assay collection and spectrographic determination. The filtrates were also analyzed and the results corrected accordingly. Higher values for platinum and palladium were obtained by including the leaching procedure.

Laboratory "E" collected the platinum by the fire-assay method and completed the determination spectrographically.

Laboratory "F" used thermal neutron-activation analysis but did not provide any results for the platinum-group metals in the standard reference materials described in this present report, see NOTE, below.

Laboratory "G" collected the precious metals into a silver bead and determined the individual metals spectrographically.

Laboratory "H" followed the same procedure as Laboratory "B".

Laboratory "I" decomposed the sample by aqua regia treatment and by alkaline fusion. The platinum-group metals were then concentrated into a tellurium precipitate formed by the reduction of tellurite with stannous chloride. The platinum, palladium, and rhodium were then determined by atomic-absorption spectrophotometry according to procedures described in Talanta, 16, pp. 591-595 and pp. 1461-1465 (1969) by M. M. Schnepfe and F. S. Grimaldi.

Laboratory "J" collected the gold by fire assay and finished the determination by atomic-absorption spectrophotometry. The platinum, palladium, and rhodium were determined by the method described in Talanta, see previous paragraph.

Laboratory "K" treated the Tulameen material by fire assay and determined the platinum in the precious-metal bead by a spectrophotometric method using stannous chloride.

The nickel-copper matte was treated by an acid attack. The soluble platinum-group metals were recovered from the leach liquor (and separated from nickel) by hydrogen sulphide ( $H_2S$ ) precipitation. This precipitate was then combined with the original leach residue for fire assay. The gold, platinum, and palladium were determined by atomic-absorption spectrophotometry, and the platinum by the stannous chloride photometric method. The rhodium was collected into a gold bead and eventually determined by atomic-absorption spectrophotometry.



NOTE: Laboratory "F" provided results for palladium in the Sudbury concentrate using thermal neutron-activation analysis. The accuracy of this method is limited due to the small amount of sample (100 to 250 milligrams) that can be used for the analysis. These values will be reported after the work on the copper-nickel concentrate is completed.

#### RESULTS OBTAINED .

The platinum-group and gold assays reported by the participating laboratories are listed in Tables 1, 2(a), 2(b), 2(c), and 2(d).

TABLE 1

Platinum Assays (oz/ton) on Standard Reference Material PTA (Tulameen Concentrate)  
 (oz/ton x 34.3 = ppm)

Sample	Lab "A"	Lab "B"	Lab "C"	Lab "D"	Lab "E"	Lab "G"	Lab "H"	Lab "J"	Lab "K"
PTA-1	0.087	0.084	0.093	0.052	0.14	0.100	0.094	0.072	0.108
	0.094	0.096	0.087	0.056		0.077	0.083	0.050	0.102
	0.073	0.102	0.079	0.068		0.093	0.086	0.120	
	0.095	0.078	0.086	0.060		0.080	0.087	0.059	
	0.100	0.096	0.084	0.080		0.065	0.100		
				0.160		0.110			
			0.080	0.082					
			0.100						
PTA-2	0.090	0.093	0.083	0.152	0.14	0.073	0.078	0.095	0.094
	0.102	0.093	0.081	0.124		0.094	0.087	0.050	0.105
	0.089	0.084	0.084	0.112		0.087	0.087	0.069	
	0.084	0.113	0.094	0.120		0.090	0.072	0.089	
	0.089	0.096	0.081	0.108		0.072	0.066		
		0.096		0.080		0.100			
		0.096		0.056		0.082			
		0.096		0.080					
PTA-3	0.083								
	0.090								
	0.099								
	0.090								
	0.089								

TABLE 2(a)

Platinum Assays (oz/ton) on Standard Reference Material PTM (Nickel-Copper Matte)  
 (oz/ton x 34.3 = ppm)

Sample	Lab "A"	Lab "B"	Lab "C"	Lab "D"	Lab "G"	Lab "H"	Lab "I"	Lab "K"
PTM-1	0.168	0.163	0.168	0.184	0.19	0.190	0.145	0.180
	0.185	0.154	0.168	0.170	0.16	0.178	0.145	0.175
	0.180	0.163	0.168	0.180	0.14	0.170		
	0.168	0.169	0.168	0.180	0.19	0.168		
	0.171	0.163	0.160		0.13	0.186		
	0.166							
	0.164							
	0.172							
	0.160							
	0.170							
PTM-2	0.187	0.160	0.170	0.200	0.17	0.172	0.15	0.175
	0.182	0.158	0.158	0.180	0.13	0.176	0.15	0.182
	0.168	0.173	0.168	0.190	0.13	0.186		
	0.168	0.170	0.168		0.18	0.156		
	0.160	0.164	0.168		0.15	0.174		
	0.172							
	0.178							
	0.164							
	0.172							
	0.164							

TABLE 2(b)

Palladium Assays(oz/ton) on Standard Reference Material PTM (Nickel-Copper Matte)  
(oz/ton x 34.3 = ppm)

Sample	Lab "A"	Lab "B"	Lab "C"	Lab "D"	Lab "G"	Lab "H"	Lab "I"	Lab "K"
PTM-1	0.251	0.255	0.231	0.200	0.21	0.288	0.23	0.231
	0.243	0.236	0.236	0.200	0.21	0.262	0.23	0.236
	0.236	0.255	0.237	0.172	0.19	0.258		0.225
	0.254	0.249	0.242	0.192	0.24	0.248		0.220
	0.241	0.245	0.232	0.224	0.22	0.278		
	0.256			0.204				
	0.244			0.158				
	0.256			0.171				
	0.244			0.168				
	0.256							
PTM-2	0.265	0.249	0.231	0.176	0.22	0.214	0.23	0.225
	0.241	0.252	0.235	0.180	0.20	0.266	0.23	0.230
	0.233	0.267	0.236	0.216	0.19	0.288		0.234
	0.233	0.274	0.240	0.216	0.23	0.242		0.230
	0.240	0.231	0.232	0.160	0.19	0.266		
	0.244			0.220				
	0.248			0.192				
	0.238			0.164				
	0.238							
	0.238							

TABLE 2(c)

Rhodium Assays (oz/ton) on Standard Reference Material PTM (Nickel-Copper Matte)  
(oz/ton x 34.3 = ppm)

Sample	Lab "A"	Lab "B"	Lab "C"	Lab "D"	Lab "G"	Lab "H"	Lab "I"	Lab "K"
PTM-1	0.024		0.06	0.022		0.034	0.023	0.032
	0.022			0.026		0.030	0.024	0.030
	0.025			0.028		0.029		
	0.021			0.026		0.028		
	0.021			0.023		0.032		
	0.021							
	0.024							
	0.024							
	0.024							
	0.024							
PTM-2	0.022		0.05	0.024		0.030	0.024	0.032
	0.021			0.029		0.032	0.024	0.028
	0.025			0.024		0.032		
	0.022					0.028		
	0.024					0.030		
	0.022							
	0.022							
	0.022							
	0.023							
	0.023							

TABLE 2(d)

Gold Assays (oz/ton) on Standard Reference Material PTM (Nickel-Copper Matte)

(oz/ton x 34.3 = ppm)

Sample	Lab "A"	Lab "B"	Lab "C"	Lab "D"	Lab "G"	Lab "H"	Lab "I"	Lab "K"
PTM-1	0.049	0.050	0.052	0.056	0.064	0.054	0.046	0.064
	0.049	0.049	0.054	0.056	0.067	0.052	0.046	0.062
	0.048	0.051	0.054	0.044	0.058	0.050	0.046	
	0.049	0.050	0.053	0.044	0.076	0.046	0.041	
	0.050	0.051	0.060	0.048	0.064	0.054	0.041	
PTM-2	0.047	0.049	0.055	0.038	0.073	0.048	0.044	0.061
	0.048	0.048	0.050	0.056	0.058	0.048	0.044	0.065
	0.050	0.052	0.050	0.056	0.055	0.048	0.044	
	0.048	0.051	0.051	0.052	0.073	0.040	0.041	
	0.048	0.050	0.051	0.036	0.093	0.048	0.041	



## EVALUATION OF THE RESULTS

The results of the analyses received from the participating laboratories have been listed in Table 1 for the Tulameen concentrate and in Table 2 for the nickel-copper matte. The number of replicate determinations reported varied over the participating laboratories from one to ten per bottle of sample instead of the five, as was originally requested. Statistically, the results were treated in two steps: the test of homogeneity of the samples from bottle to bottle, and the evaluation of their means and spread.

### 1. Homogeneity of the Samples

The basis of this test is the assumption that the samples are homogeneous enough for the analytical methods used in this programme to be meaningful, unless there is statistical evidence to the contrary. This assumption is based both on the preliminary mineralogical studies of the samples<sup>(1)</sup> and also on the physical preparation conditions such as during grinding, screening and mixing. The standard t-test with a 5% level of significance was used to detect the possibility of inhomogeneity<sup>(4)</sup>. Normal distribution of the results was assumed throughout the statistical analyses. The results are summarized, in Table 3, for the Tulameen concentrate and for the nickel-copper matte samples. For the Tulameen concentrate, the results from only one laboratory in seven led to rejection of the assumption that the sample was homogeneous. For the nickel-copper matte sample, none of the laboratories gave any reason to reject the assumption.

TABLE 3

Summary of the Between-Bottles Homogeneity Tests on the Samples\*

Laboratory	Tulameen Concentrate	Nickel-Copper Matte			
	Platinum	Platinum	Rhodium	Palladium	Gold
A	Ac	Ac	Ac	Ac	Ac
B	Ac	Ac	-	Ac	Ac
C	Ac	Ac	-	Ac	Ac
D	Ac	Ac	Ac	Ac	Ac
E	-	-	-	-	-
F	-	-	-	-	-
G	Ac	Ac	-	Ac	Ac
H	Re	Ac	Ac	Ac	Ac
I	-	-	-	-	Ac
J	Ac	-	-	-	-
K	-	-	-	Ac	-

\*Ac = Null hypothesis accepted; no evidence of inhomogeneity between bottles.

Re = Null hypothesis rejected; possible inhomogeneity between bottles.

- = Insufficient data to enable a meaningful statistical analysis to be made.

## 2. Computation of the Over-all Means of the Results

In view of the above evidence of homogeneity for both the Tulameen concentrate and the nickel-copper samples, the results reported for each element by each laboratory were combined to form a "laboratory result", and the differences among results within each laboratory were considered to be random errors. The 95% confidence intervals were computed for each laboratory and compared with each other graphically in Figures 2 to 6. The estimated over-all means of these laboratory results for each metal-content of the samples were calculated by three different methods designated as (a), (b), and (c). The results of these computations are summarized in Table 4. These methods of calculation will now be described.

### (a) Analysis-of-Variance Method

This method is similar to the one described in the "ASTM Manual for Conducting an Inter-Laboratory Study of a Test Method"<sup>(5, 6)</sup>.

The mathematical details of this method are described in Appendix B. The basic approach of the analysis-of-variance method is to find the means by averaging all observations, giving equal weight to each of them. Two sources of variation were considered in this method. The first source was the inter-laboratory variation; the second was the within-laboratory variation.

### (b) Weighted Means to Give a Minimum Variance

The mathematical details of this method are given in Appendix C. The mean values for each laboratory were combined with those of the other laboratories to arrive at an over-all mean that gave a minimum variance. The following formulae were used:

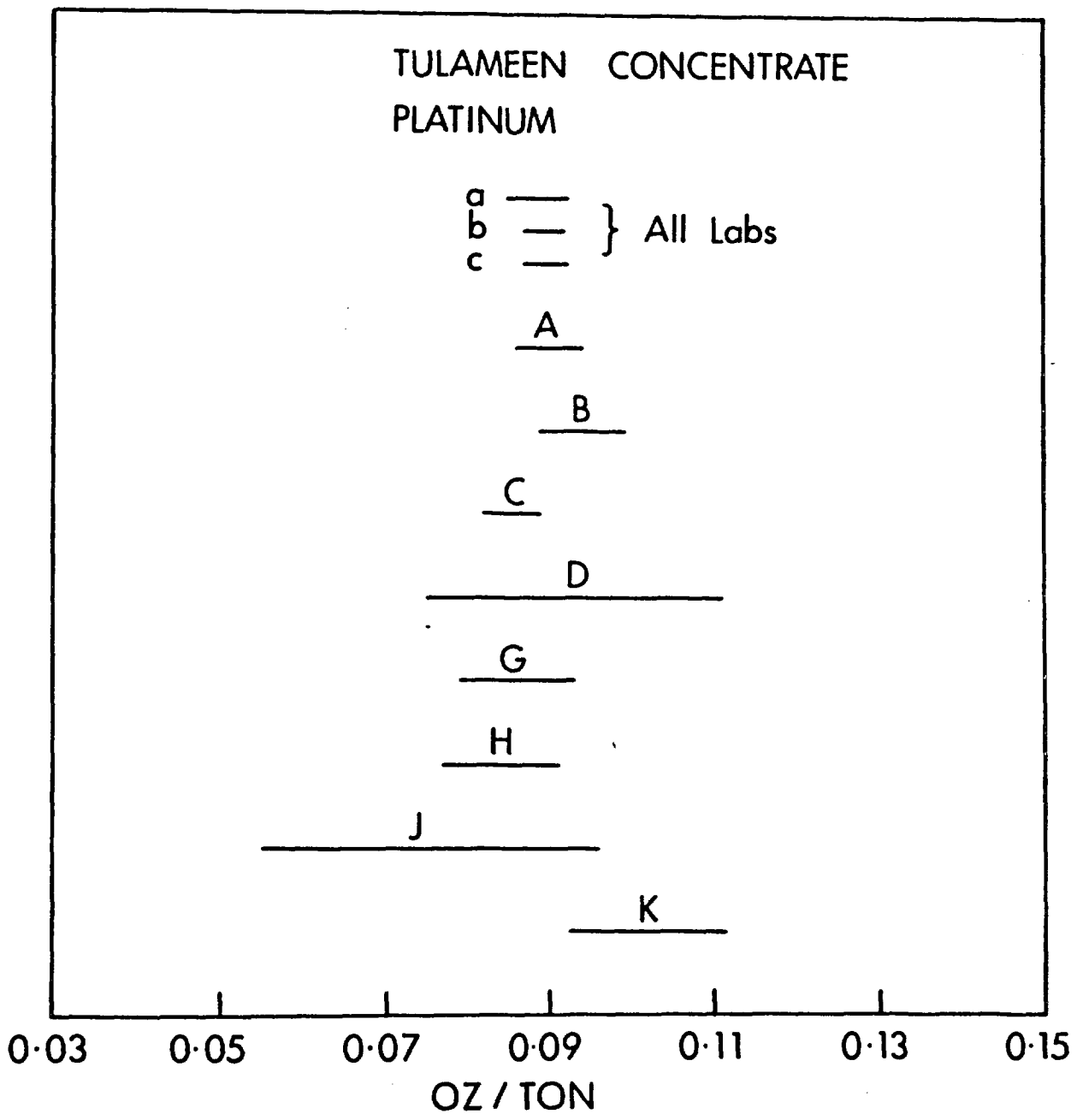


Figure 2. 95% Confidence Intervals of Platinum Content of the Tulameen Concentrate as Reported by Various Laboratories.

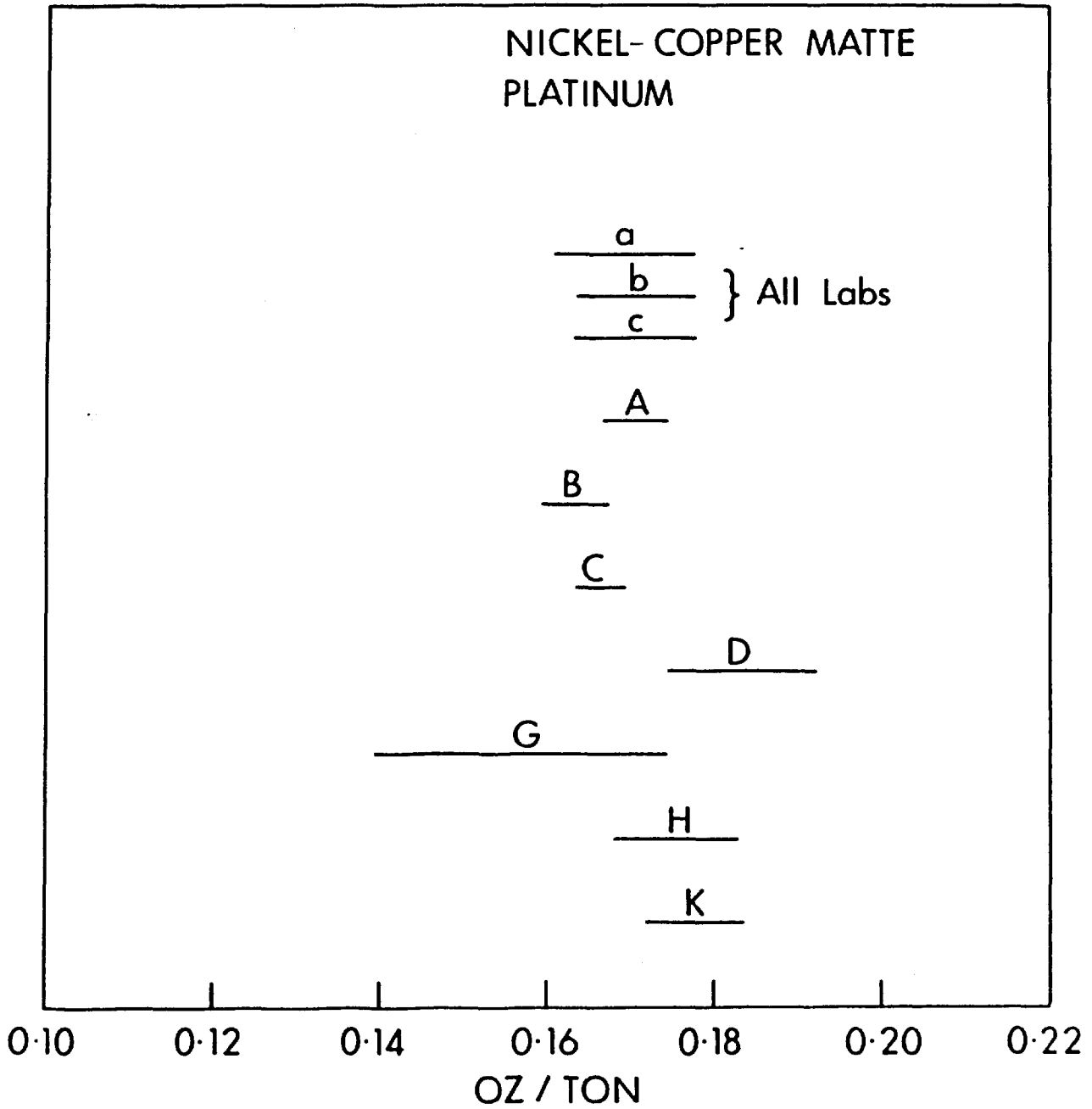


Figure 3. 95% Confidence Intervals of Platinum Content of the Nickel-Copper Matte Samples as Reported by Various Laboratories.

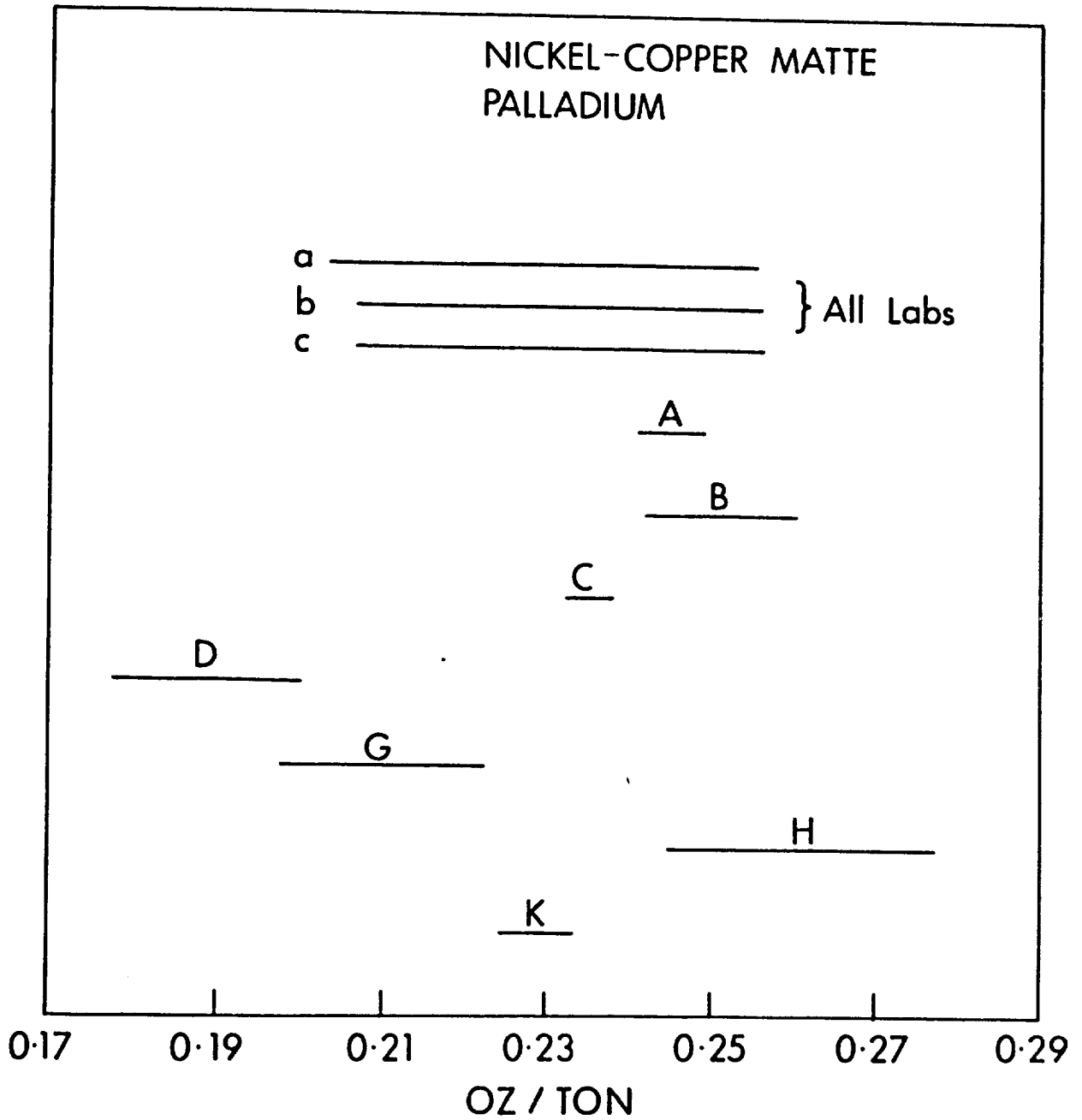


Figure 4. 95% Confidence Intervals of Palladium Content of the Nickel-Copper Matte Samples as Reported by Various Laboratories.



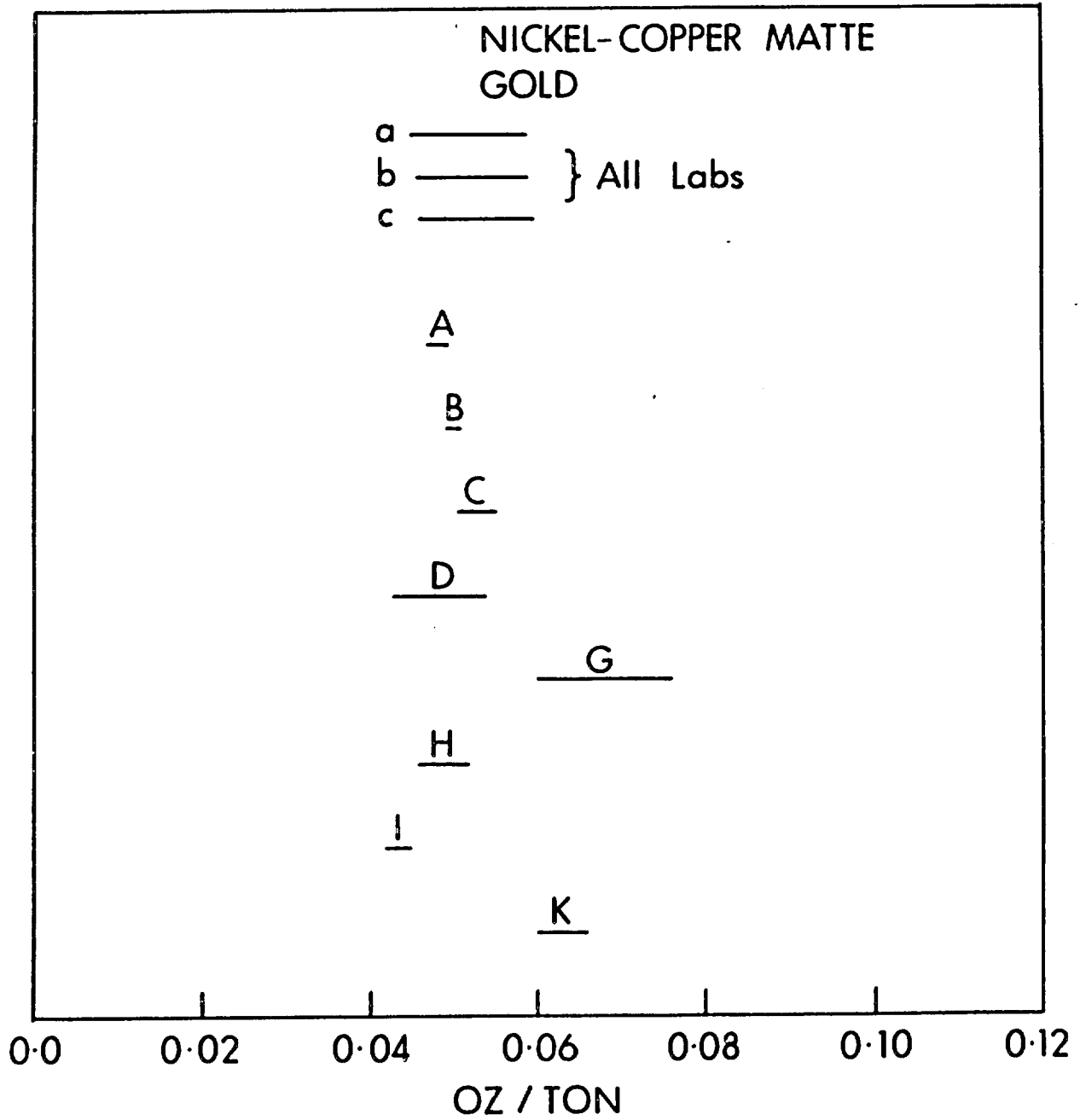


Figure 5. 95% Confidence Intervals of Gold Content of the Nickel-Copper Matte Samples as Reported by Various Laboratories.

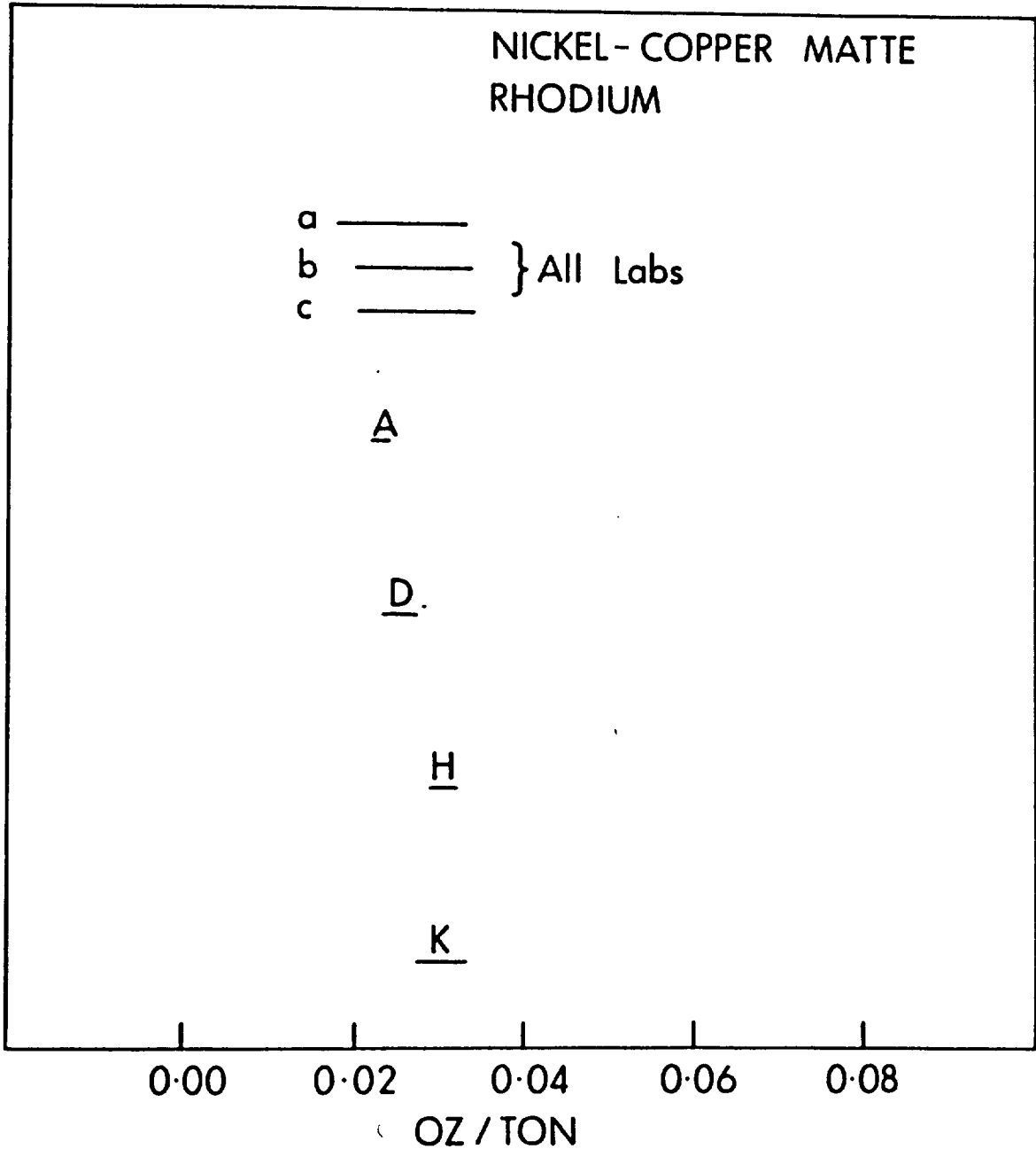


Figure 6. 95% Confidence Intervals of Rhodium Content of the Nickel-Copper Matte Samples as Reported by Various Laboratories.

TABLE 4

Estimated Parameters for the Tulameen Concentrate and for the Nickel-Copper Matte Samples

Sample	Element	Method of Computation	Mean (oz/ton)	95% Confidence Intervals of the Means		Median (oz/ton)	No. of Results
				Low (oz/ton)	High (oz/ton)		
Tulameen Concentrate	Platinum	(a)	0.089	0.085	0.092	0.088	90
		(b)	0.089	0.087	0.091		
		(c)	0.089	0.087	0.092		
Nickel-Copper Matte	Platinum	(a)	0.170	0.161	0.178	0.170	71
		(b)	0.171	0.164	0.179		
		(c)	0.171	0.164	0.179		
	Rhodium	(a)	0.026	0.018	0.033	0.024	42
		(b)	0.027	0.021	0.034		
		(c)	0.027	0.021	0.034		
	Palladium	(a)	0.230	0.203	0.256	0.236	85
		(b)	0.231	0.207	0.256		
		(c)	0.231	0.207	0.256		
Gold	(a)	0.052	0.045	0.059	0.050	74	
	(b)	0.053	0.046	0.059			
	(c)	0.053	0.046	0.060			

$$\bar{x}_{..} = \sum_{i=1}^{i=k} \frac{w_i}{\sum_{i=1}^{i=k} w_i} \bar{x}_i. \quad \dots \quad (\text{Eq. 1})$$

$$\bar{x}_i. = \sum_{v=1}^{v=n_i} x_{iv}/n_i \quad \dots \quad (\text{Eq. 2})$$

$$V[\bar{x}_{..}] = \frac{1}{\sum_{i=1}^{i=k} w_i} \quad \dots \quad (\text{Eq. 3})$$

Where  $\frac{1}{w_i}$  = the estimated variance of the means of each laboratory;

$\bar{x}_i.$  = the mean of each laboratory;

$\bar{x}_{..}$  = over-all mean;

$x_{iv}$  = individual results reported by laboratory i;

$n_i$  = number of results reported by laboratory i;

$k$  = number of participating laboratories;

and  $V[\bar{x}_{..}]$  = variance of the over-all mean,  $\bar{x}_{..}$ .

The confidence intervals were then computed, based on the (k-1) degrees of freedom.

(c) Weighted Means by the Inverse of the Square Root of the Variance

This is a compromise between the two methods described in (a) and (b). The over-all means were obtained by averaging all the laboratory means, giving weights inversely proportional to the square root of their own variance. Using the same notation as in (b):

$$\bar{x}_{..} = \frac{\sum_{i=1}^{i=k} w_i \bar{x}_i}{\sum_{i=1}^{i=k} w_i} \quad \dots \quad \text{(Eq. 4)}$$

$$w_i = \left( \omega^2 + \frac{s_i^2}{n_i} \right)^{-\frac{1}{2}} \quad \dots \quad \text{(Eq. 5)}$$

where  $\omega^2$  is the between-laboratory variance

$$V[\bar{x}_{..}] = \frac{k}{\left( \sum_{i=1}^{i=k} w_i \right)^2} \quad \dots \quad \text{(Eq. 6)}$$

The confidence intervals were then computed in the same manner as in (b). In this scheme  $1/w_i$  is the square root of the estimated variance of the means of each laboratory.

DISCUSSION

1. The Tulameen Concentrate

The analysis of variance of the results for this sample showed no inter-laboratory variations. The means estimated by all three methods, [(a), (b), and (c)], are all equal to the third decimal place (viz., 0.089 oz/ton) and were very close to the grand median (viz., 0.088 oz/ton). The 95% confidence intervals are 0.085-0.092, 0.087-0.091 and 0.087-0.092 oz/ton for Methods (a), (b), and (c), respectively (see Table 4 and Figure 2).

All of these intervals are considered to be reasonable physically. For this reason, any of these estimates would be reasonable for this sample. The authors would suggest that the estimate obtained by Method (a), the most conservative, be used for certification purposes.

## 2. The Nickel-Copper Matte

The analytical problems associated with the nickel-copper matte sample were more complicated than those of the Tulameen concentrate. For each sample, the determination of four elements was required. Consequently, fewer results were reported. The number of results reported for rhodium was too small to yield any useful estimate of the statistical parameters with any reasonable degree of certainty. There are only 42 results reported by four participating laboratories. These results were almost homogeneously distributed (see Table 4 and Figure 6), so no further statistical study of them was made. Although a still-relatively-small number of results was reported for the other three elements (platinum, palladium and gold), these results were more favourably distributed and were reported by more laboratories.

It can be shown, in Figures 3 to 5, that, in general, laboratories reported results with wider-than-average within-laboratory spreads, and with larger deviations from the over-all means. For this reason, the weighted averages, as an estimate of the means, are more reasonable for these results than is the un-weighted average (Table 4). As in the case of Tulameen concentrate, all these intervals are considered reasonable. However, in this case, the authors recommend that the results computed by Method (b) (i. e., minimum variance) be used for certification purposes. These estimate are summarized in Table 5.



TABLE 5

The Best Estimate of the Concentration of Platinum, Palladium and Gold  
in the Nickel-Copper Matte Sample

Statistic \ Element	oz/ton Platinum	oz/ton Palladium	oz/ton Gold
Mean	0.171	0.231	0.053
95% Confidence Interval for the Mean	0.164-0.179	0.207-0.256	0.046-0.059

GENERAL REMARKS

The work described in this report represents another in the series of investigations conducted in the Mines Branch designed to establish reference materials against which analytical procedures and laboratory performance in the minerals/metals field can be measured. As mentioned in the Introduction, several such materials have been authenticated under the auspices of the Standards Committee of the Spectroscopy Society of Canada. These earlier examples were mostly concerned with reference metallic materials and more emphasis was placed on the analytical procedures with rather less on the validity of the sampling procedures.

In the present study, both the validity of the sampling procedure to produce homogeneous samples and the attainable precision of the analyses have formed essential aspects.

The use of such standard reference materials will, it is hoped, be of use to the relevant mineral industries, both in their analytical work on precious-metal ores and in the commercial aspect of their enterprises. It was felt that this type of study could be extended to cover other types of ore minerals, containing different combinations of metals. Therefore, a continuing project has been set up in the Mineral Sciences Division, under the over-all coordination of Mr. G.H. Faye, Head, Inorganic Chemistry Group, to develop a series of Standard Reference Ore Minerals, covering, it is hoped, a wide variety of metallic minerals and ore types and a wide range of metallic contents. This study could, in fact, be considered as the first in this series, although the work was largely done before the series, as such, was established.

#### ACKNOWLEDGEMENTS

The authors wish to thank the participating organizations listed in Appendix A for performing the "round-robin" analyses required for the certification programme. They would also like to thank: Mr. R. Klymowsky, Mineral Processing Division, and Mr. Y. Bourgoïn, for sample preparation; Dr. E.H. Nickel for mineralogical examination; Dr. D.C. Harris for electron-microprobe analyses; Mr. R.R. Craig and Mr. J.C. Cloutier for chemical analyses for the major constituents; Mr. W.S. Bowman for assistance in the statistical evaluation of results; Mr. J.A. Graham for assistance in analyzing for the precious metals. The above are all members of the staff of the Mineral Sciences Division except where otherwise stated. Finally, Wright Engineers Limited of Vancouver, B.C. for providing the Tulameen material supplied by B.H. Levelton and Associates.

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APPENDIX A

Participating Organizations in the Certification of Platinum-Metals Ore Samples as Standard Reference Materials.

1. U. S. Geological Survey, Denver, Colorado, U.S.A.
2. U. S. Bureau of Mines, Reno, Nevada, U.S.A.
3. U. S. Geological Survey, Washington, D.C., U.S.A.
4. Ledoux and Company, Teaneck, New Jersey, U.S.A.
5. Englehard Industries Inc., Newark, New Jersey, U.S.A.
6. Mineral Sciences Division, Mines Branch, Ottawa.
7. Ministry of Natural Resources, Quebec.
8. Department of Geology, McMaster University, Hamilton.
9. Ontario Department of Mines, Provincial Assay Office, Toronto.
10. Falconbridge Nickel Mines Ltd., Thornhill, Ontario.
11. International Nickel Company of Canada, Toronto.

These laboratories are referred to in the Report as Laboratories "A" to "K", but not respectively.

## APPENDIX B

### One-Way Analysis of Variance

This method is based on the following model:

$$x_{iv} = u + y_i + z_{iv} \quad \dots \quad (\text{Eq. 7})$$

where  $x_{iv}$  = the  $v$ th result of laboratory  $i$ ;

$u$  = the true element concentration in the sample;

$y_i$  = the variation of results between laboratories;

and  $z_{iv}$  = the variation of results within laboratories.

Both  $y_i$  and  $z_{iv}$  are assumed to have expected values of zero and to have variances of  $\omega^2$  and  $\sigma^2$ , respectively. To compute the confidence intervals, it is necessary to further assume that both  $y_i$  and  $z_{iv}$  follow normal frequency distributions.

If  $n_i$  is the number of replicate analyses reported by laboratory  $i$  for a given element, and  $k$  is the number of participating laboratories, then the splitting of sums of squares leads to the following summary:

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Square	Average Mean Square
Between Laboratories	$\sum_{i=1}^{i=k} n_i (\bar{x}_i - \bar{x}_{..})^2$	$(k-1)$	$S_2^2$	$\sigma^2 + \frac{1}{k-1} \left( \sum_{i=1}^{i=k} n_i - \frac{\sum_{i=1}^{i=k} n_i^2}{\sum_{i=1}^{i=k} n_i} \right) \omega^2$
Within Laboratories	$\sum_{i=1}^{i=k} \sum_{v=1}^{v=n_i} (x_{iv} - \bar{x}_i)^2$	$\sum_{i=1}^{i=k} n_i - k$	$S_1^2$	$\sigma^2$
Total	$\sum_{i=1}^{i=k} \sum_{v=1}^{v=n_i} (x_{iv} - \bar{x}_{..})^2$	$\sum_{i=1}^{i=k} n_i - 1$		

where

$$\bar{x}_i = \sum_{v=1}^{v=n_i} x_{iv} / n_i \text{ is the average results of each laboratory; and}$$

$$\bar{x}_{..} = \sum_{i=1}^{i=k} \sum_{v=1}^{v=n_i} x_{iv} / \sum_{i=1}^{i=k} n_i \text{ is the overall mean of the results which}$$

provides an unbiased estimate of  $\mu$ ;

$$S_1^2 = \left\{ \sum_{i=1}^{i=k} \sum_{v=1}^{v=n_i} (x_{iv} - \bar{x}_i)^2 \right\} / \left\{ \sum_{i=1}^{i=k} n_i - 1 \right\} \text{ is an estimate of } \sigma^2;$$

$$\text{and } S_2^2 = \left\{ \sum_{i=1}^{i=k} n_i (\bar{x}_i - \bar{x}_{..})^2 \right\} / \{k-1\} \text{ is an estimate of the following quantity:}$$

$$\sigma^2 + \frac{1}{k-1} \left\{ \sum_{i=1}^{i=k} n_i - \frac{\sum_{i=1}^{i=k} n_i^2}{\sum_{i=1}^{i=k} n_i} \right\} \omega^2.$$

The variance of  $\bar{x}_{..}$ ,  $V[\bar{x}_{..}]$ , can be estimated as follows:

$$V[\bar{x}_{..}] = \frac{1}{\left( \sum_{i=1}^{i=k} n_i \right)^2} \sum_{i=1}^{i=k} V \left[ \sum_{v=1}^{v=n_i} x_{iv} \right] \quad \dots \quad (\text{Eq. 8})$$

$$\text{Since } \sum_{v=1}^{v=n_i} x_{iv} = n_i \mu + n_i y_i + \sum_{v=1}^{v=n_i} z_{iv} \quad \dots \quad (\text{Eq. 9})$$

$$V \left[ \sum_{v=1}^{v=n_i} x_{iv} \right] = n_i^2 V[y_i] + n_i \sigma^2$$

$$= n_i^2 \omega^2 + n_i \sigma^2 \quad \dots \quad (\text{Eq. 10})$$

Substituting Eq. 10 in Eq. 8, we get

$$\begin{aligned} V[\bar{x}..] &= \frac{\sum_{i=1}^{i=k} n_i^2 \omega^2}{\left(\sum_{i=1}^{i=k} n_i\right)^2} + \frac{\sigma^2}{\sum_{i=1}^{i=k} n_i} \\ &= \frac{\sum_{i=1}^{i=k} n_i^2 \omega^2}{N^2} + \frac{\sigma^2}{N} \quad \dots \quad (\text{Eq. 11}) \end{aligned}$$

where  $N = \sum_{i=1}^{i=k} n_i$  is the total number of results reported by all laboratories.

In the case where the null hypothesis is accepted, the first term in the right-hand side of Eq. 11 will vanish and we get

$$V[\bar{x}..] = \frac{\sigma^2}{N} \quad \dots \quad (\text{Eq. 12})$$

This method of computation was used to evaluate the results by Method (a) in the section on "Evaluation of the Results".



## APPENDIX C

### Weighted Mean to Give Minimum Variance

Suppose there are k participating laboratories, each reporting  $n_i$  results for a particular element with means of  $\bar{x}_i$  and variances of  $\sigma_i^2$ . Let all  $\bar{x}_i$ 's have an expected value of u; then the grand mean,  $\bar{x}_{..}$ , can be computed in such a way that it will be an unbiased estimate of u and will have a minimum variance, by the use of a correct set of weighting factors,  $a_i$ 's, such that

$$\bar{x}_{..} = \sum_{i=1}^{i=k} a_i \bar{x}_i. \quad \dots \quad (\text{Eq. 13})$$

For  $\bar{x}_{..}$  to be an unbiased estimate of u, it must have an expected value of u, thus:\*

$$\begin{aligned} E[\bar{x}_{..}] &= E \left[ \sum_{i=1}^{i=k} a_i \bar{x}_i \right] \\ &= \sum_{i=1}^{i=k} a_i E[\bar{x}_i] \\ &= u \sum_{i=1}^{i=k} a_i \\ &= u \end{aligned}$$

Therefore,  $\sum_{i=1}^{i=k} a_i = 1 \quad \dots \quad (\text{Eq. 14})$

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\*  $E[\bar{x}_{..}]$  is the expected value of  $\bar{x}_{..}$ ; all other terms have the same definitions as in Appendix II, unless otherwise stated.

The variance of  $\bar{x}_{..}$  is given by  $V[\bar{x}_{..}]$  where

$$\begin{aligned} V[\bar{x}_{..}] &= V \left[ \sum_{i=1}^{i=k} a_i \bar{x}_i \right] \\ &= \sum_{i=1}^{i=k} a_i V[\bar{x}_i] \\ &= \sum_{i=1}^{i=k} a_i \sigma_i^2 \quad \dots \quad (\text{Eq. 15}) \end{aligned}$$

Eq. 14 can be rewritten as

$$\begin{aligned} a_k + \sum_{i=1}^{i=(k-1)} a_i &= 1 \\ \text{or } a_k &= 1 - \sum_{i=1}^{i=(k-1)} a_i \quad \dots \quad (\text{Eq. 16}) \end{aligned}$$

Substituting Eq. 16 into Eq. 15, we get:

$$\begin{aligned} V[\bar{x}_{..}] &= \sum_{i=1}^{i=(k-1)} a_i \sigma_i^2 + \left( 1 - \sum_{i=1}^{i=(k-1)} a_i \right)^2 \sigma_k^2 \\ &= \sum_{i=1}^{i=(k-1)} a_i^2 \sigma_i^2 + \left\{ 1 - 2 \sum_{i=1}^{i=(k-1)} a_i + \left( \sum_{i=1}^{i=(k-1)} a_i \right)^2 \right\} \sigma_k^2 \quad \dots \quad (\text{Eq. 17}) \end{aligned}$$

In order for  $V[\bar{x}_{..}]$  to be a minimum, its derivatives with respect to the weighting factors must all be zero, thus:

$$\frac{\partial V[\bar{x}_{..}]}{\partial a_i} = 0 \text{ for all values of } i = 1, 2, \dots, k \quad \dots \quad (\text{Eq. 18})$$

For  $i=j$ , where  $1 \leq j \leq k$ , we get

$$\begin{aligned} \frac{\partial V[\bar{x}..]}{\partial a_j} &= 2 a_j \sigma_j^2 - 2 \sigma_k^2 + 2 \sum_{i=1}^{i=(k-1)} a_i \sigma_k^2 \\ &= 2 \left[ a_j \sigma_j^2 - \left( 1 - \sum_{i=1}^{i=(k-1)} a_i \right) \sigma_k^2 \right] = 0 \quad \dots \text{(Eq. 19)} \end{aligned}$$

Substituting Eq. 16 into Eq. 19, we get:

$$a_j \sigma_j^2 - a_k \sigma_k^2 = 0 \quad \dots \text{(Eq. 20)}$$

whence

$$a_j = a_k \frac{\sigma_k^2}{\sigma_j^2} \quad \dots \text{(Eq. 21)}$$

Eq. 21 is valid for all values of  $j = 1, 2 \dots k$ , thus:

$$\sum_{j=1}^{j=k} a_j = \sum_{i=1}^{i=k} a_i = 1 \quad \dots \text{(Eq. 22)}$$

also

$$\sum_{j=1}^{j=k} a_j = a_k \sigma_k^2 \cdot \sum_{j=1}^{j=k} \frac{1}{\sigma_j^2} \text{ (from Eq. 21)} \quad \dots \text{(Eq. 23)}$$

Substituting Eq. 22 into Eq. 23, we get:

$$a_k = \frac{1}{\sigma_k^2 \sum_{j=1}^{j=k} \frac{1}{\sigma_j^2}} \quad \dots \text{(Eq. 24)}$$

Substituting Eq. 24 into Eq. 21, we get:

$$a_j = \frac{1}{\sigma_j^2 \sum_{j=1}^{j=k} \frac{1}{\sigma_j^2}} \quad \dots \text{(Eq. 25)}$$

Since Eq. 25 is valid for all values of  $j = 1, 2, \dots, k$ , it can be generalized as:

$$a_i = \frac{1}{\sigma_i^2 \sum_{i=1}^{i=k} \frac{1}{\sigma_i^2}} \quad \dots \text{ (Eq. 26)}$$

If we define  $W_i = \frac{1}{\sigma_i^2}$ , Eq. 26 becomes

$$a_i = \frac{W_i}{\sum_{i=1}^{i=k} W_i} \quad \dots \text{ (Eq. 27)}$$

Substituting Eq. 27 into Eq. 13, we get:

$$\bar{x}_{..} = \sum_{i=1}^{i=k} \frac{W_i}{\sum_{i=1}^{i=k} W_i} \bar{x}_{i.} \quad \dots \text{ (Eq. 28)}$$

Eq. 7 can be rewritten as:

$$\sum_{v=1}^{v=n_i} x_{iv} = n_i u + n_i y_i + \sum_{v=1}^{v=n_i} z_{iv}$$

Since

$$\begin{aligned} \bar{x}_{i.} &= \sum_{v=1}^{v=n_i} x_{iv} / n_i \\ V[\bar{x}_{i.}] &= V \left[ \sum_{v=1}^{v=n_i} x_{iv} / n_i \right] \\ &= \omega^2 + \frac{s_i^2}{n_i} \end{aligned}$$

where  $\omega^2$  = the between-laboratory variance,

and  $\frac{s_i^2}{n_i}$  = the variance of the mean of the within-laboratory  $i$  values, which can be estimated as:

$$\frac{s_i^2}{n_i} = \sum_{v=1}^{v=n_i} \left( x_{iv} - \bar{x}_i \right)^2 / n_i (n_i - 1)$$

A reasonable estimate of  $w^2$  can be computed from Appendix II, thus:

$$w^2 = \left( S_2^2 - S_1^2 \right) \frac{(k-1)}{\left( N - \frac{\sum_{i=1}^{i=k} n_i^2}{N} \right)} \quad \dots \text{(Eq. 29)}$$

From Eq. 28, the variance of the grand mean  $V[\bar{x}_{..}]$  can be estimated as:

$$\begin{aligned} V[\bar{x}_{..}] &= \sum_{i=1}^{i=k} V \left[ \frac{W_i}{\sum_{i=1}^{i=k} W_i} \bar{x}_i \right] \\ &= \sum_{i=1}^{i=k} \left( \frac{W_i}{\sum_{i=1}^{i=k} W_i} \right)^2 V[\bar{x}_i] \\ &= \sum_{i=1}^{i=k} \left( \frac{W_i}{\sum_{i=1}^{i=k} W_i} \right)^2 \frac{1}{W_i} \\ V[\bar{x}_{..}] &= \frac{1}{\sum_{i=1}^{i=k} W_i} \quad \dots \text{(Eq. 30)} \end{aligned}$$

The confidence interval can then be estimated, based on  $(k-1)$  degrees of freedom<sup>(7)</sup>.

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