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NOBLE-METALS-BEARING SULPHIDE CONCENTRATE PTC: ITS CHARACTERIZATION AND PREPARATION FOR USE AS A STANDARD REFERENCE MATERIAL

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

MINERAL SCIENCES DIVISION

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by

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

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SYNOPSIS

A sulphide flotation concentrate from Sudbury, Ontario, has been prepared and characterized as a standard reference material for platinum, palladium, rhodium, gold, and silver. The recommended values for the contents of these elements in oz/ton are as follows: platinum 0.087, palladium 0.37, silver 0.17, rhodium 0.018, and gold 0.019. Several iridium, ruthenium, and osmium contents were reported by the laboratories that participated in the "round-robin" analytical program and these have been included in this report.

The sample preparation and characterization of the reference material are described and a statistical evaluation of the analytical values has been performed. This reference standard is now available from the Chairman of the Canadian Standard Reference Materials Project (CSRMP), Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, 555 Booth Street, Ottawa, Ontario, K1A 0G1.

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Direction des mines

Bulletin technique TB 176

LE CONCENTRÉ DE SULFURE CONTENANT DES MÉTAUX PRÉCIEUX (PTC): LA CARACTÉRISATION ET LA PRÉPARATION DE CE CONCENTRÉ UTILISÉ COMME MATÉRIAU TYPE DE RÉFÉRENCE

par

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

RÉSUMÉ

Les auteurs ont préparé et caractérisé un concentré de sulfure de Sudbury, Ontario utilisé comme matériau type de référence pour du platine, du palladium, du rhodium, de l'or et de l'argent. Les valeurs recommandées pour la teneur de ces éléments en oz/tonne sont les suivantes: le platine 0.087, le palladium 0.37, l'argent 0.17, le rhodium 0.018 et l'or 0.019. Dans ce rapport, on trouve un compte rendu de plusieur teneurs en iridium, ruthénium et osmium provenant des laboratoires qui ont participé dans le programme analytique.

Les auteurs ont décrit la préparation de l'échantillon et la caractérisation des matériaux de référence et ils ont aussi effectué une évaluation statistique des valeurs analytiques. Maintenant, on peut obtenir ses étalons de référence en s'adressant au Président du Programme canadien des produits étalons (PCPE), Division des sciences minérales, Direction des mines, ministère de l'Énergie, des Mines, et des Ressources, 555 rue Booth, Ottawa, Ontario, K1A 0G1.

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INTRODUCTION

The Mineral Sciences Division of the Mines Branch has coordinated a program for the certification of several reference materials containing platinum-group metals. This program was conducted in an attempt to overcome the difficulties encountered by commercial laboratories in obtaining reliable assay results for these metals. The first phase of the program involved the certification of an alluvial sand (PTA), from the Tulameen River area of British Columbia for platinum, and a nickel-copper matte (PTM), from Sudbury, Ontario, for platinum, palladium, and gold. A provisional value for rhodium in the matte was also reported. The results obtained in the first phase of the program have been reported (1). For the second phase of the program, a sulphide flotation concentrate, labelled PTC, from Sudbury was to be certified for platinum, palladium, rhodium, iridium, ruthenium, gold, and silver, and a nickel-copper matte PTM was to be further certified for iridium, ruthenium, and silver. This report covers the preparation and characterization of the flotation concentrate (PTC).

The sample, prepared at the Mines Branch, was distributed to laboratories in Canada, U.S.A., and South Africa that had agreed to participate in the "round-robin" analytical program required for certification of the material as a standard. The participating laboratories are listed on page 22. These laboratories will be referred to in this report as laboratories A to N, respectively. The code letters used bear no relation to the order in which these organizations are listed in Appendix A. This procedure protects the anonymity of the participating laboratories' analytical results.

The sulphide flotation concentrate had been distributed originally in the first phase of the program with the Tulameen sand and the nickel-copper matte. However, subsequent to assaying by the participating laboratories, it was noted that pelletizing of the material had occurred and the material was withdrawn pending further work on sample preparation. This work was performed and new samples of the concentrate were distributed to participating laboratories for use in the second phase of the program. NOTE: The analytical results reported on the original material, prior to further sample preparation, have proven to be as statistically acceptable as those obtained after resampling. Therefore, both sets of results have been used for the certification of the platinum-group metals and gold and silver.

Two bottles of the reference materials, selected at random, were submitted to each of the laboratories with the request that five determinations of each of the following elements be performed: platinum, palladium, rhodium, iridium, ruthenium, gold, and silver. Several laboratories did not report all the elements and/or the number of analyses requested, and so a statistical method of evaluating the results to meet this situation has been used. The

results of this evaluation and the values assigned for the precious metals determined in the reference material are given in this report.

The sulphide concentrate (PTC) is now available to commercial and other laboratories as a standard reference material with recommended values for platinum, palladium, rhodium, gold, and silver. The results obtained by several laboratories for the iridium and ruthenium content of these materials have also been included in the report for information purposes only.

PREPARATION, SAMPLING, AND CHARACTERIZATION OF THE REFERENCE MATERIAL

As previously mentioned, the sulphide concentrate was withdrawn from the first phase of the certification program when it was noted that pelletizing of the material had occurred. The material was re-ground to minus 200 mesh and blended by tumbling in a 45-gallon drum for approximately 24 hours to ensure thorough mixing. It was then re-bottled in 200-g lots and random sample bottles were taken from the total lot for distribution to the laboratories participating in the "round-robin" analytical program.

A chemical analysis for major constituents was made on material from a randomly selected bottle. The following results were obtained (2):

Copper - 5.16%

Nickel - 9.42%

Sulphur - 23.5 %

Iron - 26.9 %

ANALYTICAL METHODS USED BY THE PARTICIPATING LABORATORIES

A variety of analytical methods was used by the laboratories that collaborated in the "round-robin" analytical program for the determination of the precious metals in this reference material.

The analytical methods employed by the various laboratories, designated "A" to "N", will be mentioned in sequence.

Laboratory "A" collected the precious metals in molten tin by fire assay (3) and determined platinum, palladium, rhodium, gold, and silver by atomic-absorption spectroscopy. Ruthenium was collected by fire assay on a separate sample, isolated from the other precious metals by distillation, and determined colorimetrically with p-nitrosodimethylaniline. NOTE: The assay slag had to be re-ground and re-treated to recover all the ruthenium. Iridium was collected in a tin button which was followed by solvent extraction and determination of the iridium colorimetrically using the stannous bromide method.

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 E 400-71 (4). 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. Two determinations were made for rhodium by combining five samples for each determination.

Laboratory "D" used fire assaying, in conjunction with either optical emission spectrography or atomic-absorption spectrophotometry. Radiotracers were used to monitor the fire assay recovery of iridium, ruthenium, and osmium.

Laboratory "E" used an atomic-absorption method for the determination of silver and a spectrographic method, after pre-concentration by fire assay, for the gold, platinum, and palladium.

Laboratory "F" used thermal-neutron-activation analysis for the determination of palladium.

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

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

Laboratory "I" decomposed the sample first in aqua regia, then 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 by Schnepfe and Grimaldi (5, 6).

Laboratory "J" collected the gold by fire assay and finished the determination by atomic-absorption spectrophotometry (7). The platinum, palladium, and rhodium were determined by the method described by Schnepfe and Grimaldi (5, 6).

Laboratory "K" collected platinum and palladium into a silver bead and determined the platinum photometrically, using the stannous chloride method, and determined the palladium by atomic-absorption spectrophotometry. Rhodium was collected in a gold bead and determined by atomic-absorption spectrophotometry. Atomic-absorption methods were used for silver and gold, after collecting the former into a gold bead and the latter into a silver bead.

Laboratory "L" collected the precious metals by the nickel-sulphide collection procedure. The individual platinum-group metals were then determined by atomic-absorption spectrophotometry on the acid solutions of the prills.

Laboratory "M" collected the precious metals by fire assay, using lead as a collector, and determined the platinum and palladium by atomic-absorption spectrophotometry.

Laboratory "N" collected the precious metals into a lead button, using a fire assay procedure, and determined the individual elements by a spectrographic method (4) and by atomic-absorption spectrophotometry.

RESULTS OBTAINED

The assays of platinum-group metals and gold and silver, reported by the participating laboratories, are listed in Tables 1A and 1B.

EVALUATION OF THE RESULTS

The analytical results reported during the first phase of the program are listed in Table 1A. The number of replicate determinations reported varied from one laboratory to the other. Statistically, these results were treated in two steps.

(a) 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 program unless there is statistical evidence to the contrary. This assumption was justified in view of the method of preparing the sample, which includes grinding, screening, and mixing. The standard t-test at the 5% level of significance was used to detect the possibility of inhomogeneity (8). Normal distribution of the results was assumed throughout the statistical analyses. The results of the t-test are summarized in Table 2. Most of the available data did not show inhomogeneity, so it was assumed that the homogenization treatments of the sample were sufficient for this purpose. As mentioned before, it was noticed, during the first phase of the program, that the sample showed signs of pelletizing. The sample was then re-ground and re-analysed. The results of the second phase are listed in Table 1B. Only three laboratories reported results of analyses of two bottles during the second phase of the program. The t-tests of these results are also listed in Table 2.

TABLE 1A

Assays (oz/ton) on Standard Reference Material PTC (Sudbury Concentrate)
Obtained from Phase 1 of the Inter-Laboratory Study
(oz/ton x 34.3 = ppm)

Laboratory	Au oz/ton	Pd oz/ton	Pt oz/ton	Rh oz/ton
A	0.019	0.360	0.070	0.016
	0.018	0.380	0.076	0.015
	0.022	0.382	0.096	0.018
	0.016	0.390	0.090	0.015
	0.016	0.385	0.074	0.016
	0.018	0.394	0.077	0.014
	0.016	0.377	0.098	0.014
	0.016	0.385	0.086	0.014
	0.016	0.365	0.080	0.015
	0.020	0.370	0.068	0.016
B	0.017	0.41	0.073	0.022
	0.024	0.49	0.096	0.022
	0.018	0.44	0.104	0.021
	0.018	0.46	0.078	0.022
	0.017	0.46	0.093	0.023
	0.022	0.35	0.081	
	0.023	0.35	0.073	
	0.012	0.35	0.070	
C	0.016	0.373	0.098	0.02
	0.018	0.363	0.096	0.018
	0.018	0.360	0.100	
	0.020	0.363	0.093	
	0.015	0.360	0.093	
	0.023	0.368	0.094	
	0.031	0.368	0.101	
	0.027	0.365	0.091	
	0.029	0.365	0.089	
	0.020	0.365	0.092	
D	0.016	0.480	0.080	0.021
	0.020	0.580	0.088	0.012
	0.021	0.460	0.092	0.017
	0.028	0.720	0.092	0.014
	0.010	0.500	0.072	0.014
	0.032	0.260	0.068	0.014
	0.012	0.360	0.108	0.013
	0.010	0.372	0.072	0.014
	0.018	0.400	0.068	
	0.016	0.372	0.088	
	0.022	0.320	0.109	
	0.016	0.440	0.116	
	0.030	0.480	0.116	
	0.018	0.360	0.120	
	0.028	0.520	0.080	
	0.016	0.516	0.084	

(concluded)

TABLE 1A

(concluded)

Laboratory	Au oz/ton	Pd oz/ton	Pt oz/ton	Rh oz/ton
F		0.368		
		0.361		
		0.326		
		0.424		
		0.371		
		0.370		
		0.357		
		0.341		
		0.372		
		0.356		
		0.351		
		0.355		
		0.363		
G	0.026	0.37	0.110	
	0.016	0.38	0.097	
	0.016	0.37	0.092	
	0.019	0.35	0.090	
	0.020	0.35	0.110	
	0.024	0.35	0.099	
	0.020	0.33	0.100	
	0.034	0.34	0.110	
	0.011	0.40	0.10	
	0.020	0.34	0.097	
	0.017		0.086	
			0.120	
			0.084	
H	0.010	0.362	0.070	0.020
	0.019	0.330	0.064	0.017
	0.023	0.353	0.087	0.018
	0.014	0.360	0.089	0.018
	0.010	0.341	0.062	0.018
	0.012	0.355	0.091	0.019
	0.009	0.351	0.097	0.020
	0.017	0.371	0.088	0.020
	0.016	0.336	0.073	0.018
	0.010	0.341	0.066	0.017
I	0.016	0.34	0.081	0.017
	0.029	0.34	0.120	0.017
	0.015	0.36	0.070	
	0.027	0.35	0.070	
	0.014	0.35	0.072	
	0.014			
	0.016			
J	0.017	0.30	0.069	0.017
	0.011	0.35	0.066	0.019
		0.34	0.059	0.017
		0.31	0.052	0.018
		0.30	0.053	0.015
		0.35	0.061	0.020
K	0.010	0.355	0.098	0.015
	0.020	0.355	0.104	0.017
	0.021	0.356	0.098	0.015
	0.019	0.353	0.100	0.017
		0.353		
		0.357		
		0.356		
		0.358		

TABLE 1B

Assays (oz/ton) on Standard Reference Material PTC (Sudbury Concentrate)
Obtained from Phase 2 of the Inter-Laboratory Study
(oz/ton x 34.3 = ppm)

Laboratory	Ag oz/ton	Au oz/ton	Pd oz/ton	Pt oz/ton	Rh oz/ton	Ru oz/ton	Ir oz/ton	Os oz/ton
A	0.173	0.018	0.368	0.084	0.019	0.022	0.004	
	0.183	0.020	0.366	0.087	0.018	0.022	0.003	
	0.180	0.018	0.360	0.084	0.019	0.021	0.003	
	0.170	0.016	0.372	0.084	0.018	0.022	0.004	
	0.170	0.018	0.372	0.082	0.018	0.022	0.004	
	0.175	0.019	0.368	0.081	0.018	0.019	0.003	
	0.175	0.018	0.366	0.084	0.018	0.022	0.003	
	0.180	0.018	0.368	0.087	0.019	0.019	0.003	
	0.173	0.016	0.364	0.087	0.019	0.020	0.005	
	0.173	0.018	0.370	0.084	0.018	0.020	0.003	
C		0.028	0.356	0.110				
		0.026	0.360	0.123				
		0.032	0.353	0.110				
		0.031	0.357	0.100				
		0.029	0.363	0.110				
D	0.18	0.016	0.274	0.0875	0.022	0.021	0.0056	0.007
	0.17	0.013	0.434	0.0881	0.021	0.019	0.0066	0.008
	0.17	0.014	0.432	0.0963	0.026	0.015	0.0070	
	0.17	0.018	0.490	0.0933	0.027	0.019	0.0080	
	0.18	0.018	0.460	0.0779	0.025	0.019	0.0080	
E	0.19	0.056	0.352	0.156				
	0.14	0.024	0.448	0.100				
	0.14	0.020	0.456	0.092				
	0.14	0.024	0.396	0.136				
	0.14	0.040	0.304	0.060				
		0.020	0.320	0.061				
		0.032	0.368	0.096				
		0.024	0.404	0.056				

(continued)

TABLE 1B

(continued)

Laboratory	Ag oz/ton	Au oz/ton	Pd oz/ton	Pt oz/ton	Rh oz/ton	Ru oz/ton	Ir oz/ton	Os oz/ton
H	0.165	0.013	0.313	0.088	0.021			
	0.137	0.011	0.275	0.074	0.019			
	0.146	0.012	0.298	0.074	0.019			
	0.170	0.011	0.305	0.067	0.020			
	0.157	0.010	0.307	0.085	0.019			
	0.168	0.018	0.290	0.070	0.019			
	0.172	0.011	0.299	0.065	0.019			
	0.196	0.012	0.328	0.090	0.020			
	0.191	0.013	0.297	0.083	0.020			
	0.173	0.013	0.297	0.073	0.018			
K	0.202	0.016	0.357	0.087	0.015		0.0003*	
	0.194	0.018	0.364	0.094	0.015			
	0.200	0.019	0.369	0.099	0.019			
	0.213	0.019	0.364	0.084	0.018			
	0.204	0.019	0.360	0.089	0.017			
L		0.015	0.341	0.072	0.017	0.015	0.006	
		0.013	0.342	0.072	0.015	0.016	0.005	
		0.015	0.349	0.073	0.017	0.014	0.005	
		0.013	0.347	0.072	0.016	0.015	0.007	
		0.014	0.350	0.073	0.016	0.016	0.005	
M			0.395	0.085				
			0.399					
			0.395					
			0.395					
			0.391					
			0.349	0.086				
			0.352					
			0.349					
			0.350					
			0.346					

(concluded)

*By Mass Spectroscopy.

TABLE 1B

(concluded)

Laboratory	Ag oz/ton	Au oz/ton	Pd oz/ton	Pt oz/ton	Rh oz/ton	Ru oz/ton	Ir oz/ton	Os oz/ton
N	0.21	0.017	0.316	0.104	0.022			
	0.15	0.019	0.264	0.083	0.017			
	0.17	0.019	0.291	0.078	0.021			
	0.16	0.012	0.208	0.068	0.017			
	0.08	0.0093	0.255	0.083	0.015			
	0.09	0.017	0.268	0.096	0.016			
	0.21	0.017	0.33	0.100	0.019			
	0.25	0.013	0.36	0.084	0.020			
	0.20	0.022	0.355	0.100	0.021			
	0.20	0.015	0.360	0.100	0.020			

TABLE 2

Summary of the t-Test between Bottles within Laboratories for PTC (Sudbury Concentrate)

Phase	Labs	Ag	Au	Pd	Pt	Rh
1	A	–	Ac	Ac	Ac	Ac
	C	–	Re	Ac	Ac	–
	D	–	Ac	Ac	Re	–
	F	–	–	Ac	–	–
	G	–	Ac	Ac	Ac	Ac
2	A	Ac	Ac	Ac	Ac	Ac
	H	Re	Ac	Ac	Ac	Ac
	M	–	–	Re	–	–

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

Re = Null hypothesis rejected; possible inhomogeneity between bottles.

— = Insufficient data.

(b) Computation of the Over-All Means of the Analytical Results

After establishing that the sample was homogeneous, the results reported for each element by each laboratory were then combined to form a "laboratory result", and the differences between the results within each laboratory were considered to be caused by random error. The 95% confidence intervals for each laboratory result were estimated and compared with each other graphically in Figures 1A to 1E. The over-all means and medians for each element reported during the first and second phases of the program were computed and listed in Table 3. Both this table and Figures 1B to 1E show that there is no significant difference between the results reported during the two phases. Therefore, it is assumed that the first homogenization treatment of the sample was sufficient and that the second homogenization did not produce any significant improvement. The results obtained from both phases were then combined. NOTE: Laboratories reporting results for both the first and the second phases of the program were considered as separate laboratories for the purpose of the computation of the means. First-phase results are shown in the Figures as A', B', ---etc., and second-phase results as A, B, --- etc.

Analyses of variance of the laboratory results show that, for most elements, there is evidence of between-laboratories variation (9). This variation was physically explainable by the fact that each laboratory adopted its own choice of method. Therefore, it was considered unrealistic to treat the results as being completely independent from the reporting laboratory. The following model was then used to estimate the over-all means and their confidence limits.

$$x_{iv} = u + y_i + z_{iv}$$

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.

The detailed method of computation of the 95% confidence limit is described in Appendix B of this report.

The results of the above computation are listed in Table 4. From this table, it is reasonable to recommend that the PTC sample can be used as a standard for Ag, Au, Pd, Pt, and Rh. There were not sufficient Ru and Ir assays to arrive at useful confidence limits for these elements. The recommended values for sample PTC are listed in Table 5.

TABLE 3

Means and Medians of the Analytical Results (oz/ton) Obtained on PTC in Phase 1 and Phase 2
(oz/ton x 34.3 = ppm)

Element	Phase 1				Phase 2			
	n	N	Mean	Median	n	N	Mean	Median
Ag	–	–	–	–	6	45	0.173	0.173
Au	8	76	0.019	0.018	8	58	0.019	0.018
Pd	10	96	0.377	0.360	9	68	0.351	0.356
Pt	9	82	0.087	0.089	9	60	0.087	0.085
Rh	6	43	0.017	0.017	6	45	0.019	0.019
Ru	–	–	–	–	3	20	0.019	0.019
Ir	–	–	–	–	3	20	0.005	0.005
Os	–	–	–	–	1	2	0.007	0.007

NOTE: n = number of participating laboratories.
N = number of determinations reported.

TABLE 4

Estimated Parameters for Standard Reference Material PTC (Sudbury Concentrate) in oz/ton
(oz/ton x 34.3 = ppm)

Element	Mean (oz/ton)	95% Confidence Limits of the Mean		Median (oz/ton)	No. of	
		Low	High		Results	Labs
Silver	0.173	0.164	0.182	0.173	45	6
Gold	0.019	0.016	0.021	0.018	134	16
Palladium	0.366	0.346	0.384	0.360	164	19
Platinum	0.087	0.081	0.093	0.087	142	18
Rhodium	0.018	0.016	0.020	0.018	88	12
Ruthenium	0.019	0.011	0.027	0.019	20	3
Iridium	0.005	0.000	0.010	0.005	20	3

TABLE 5

Recommended Values and Their Confidence Intervals
for Standard Reference Material PTC

	Precious-Metals Contents of PTC									
	Ag		Au		Pd		Pt		Rh	
	oz/ton	ppm	oz/ton	ppm	oz/ton	ppm	oz/ton	ppm	oz/ton	ppm
Recommended Value	0.17	5.8	0.019	0.65	0.37	12.7	0.087	3.0	0.018	0.62
95% Confidence Intervals										
Low	0.16	5.5	0.016	0.55	0.35	12.0	0.081	2.8	0.016	0.55
High	0.18	6.2	0.021	0.72	0.38	13.0	0.093	3.2	0.020	0.69

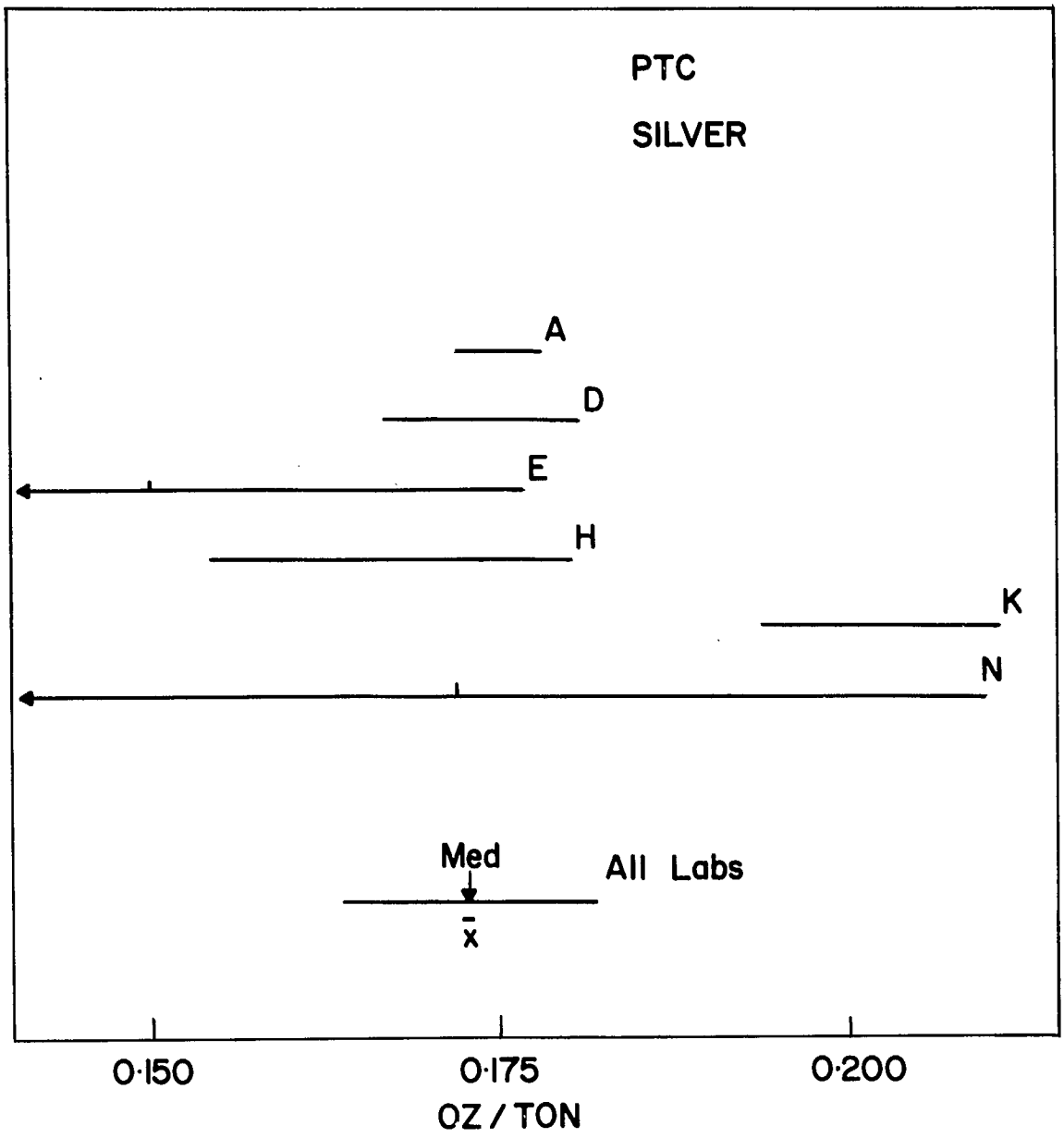

Figure 1A. 95% Confidence Intervals for Silver Contents of the Standard Reference Material PTC, Reported by Various Laboratories.

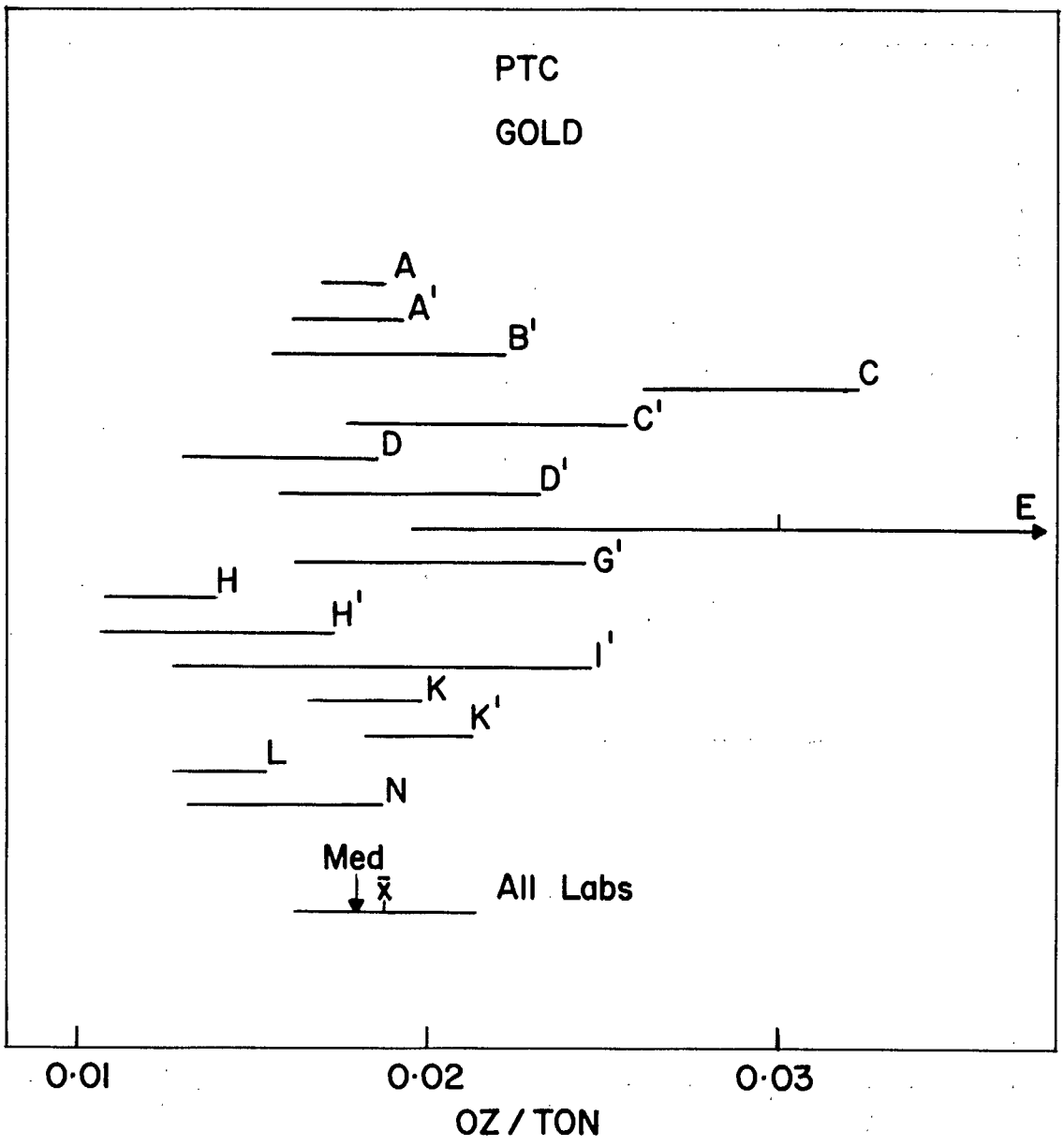

Figure 1B. 95% Confidence Intervals for Gold Contents of the Standard Reference Material PTC, Reported by Various Laboratories.

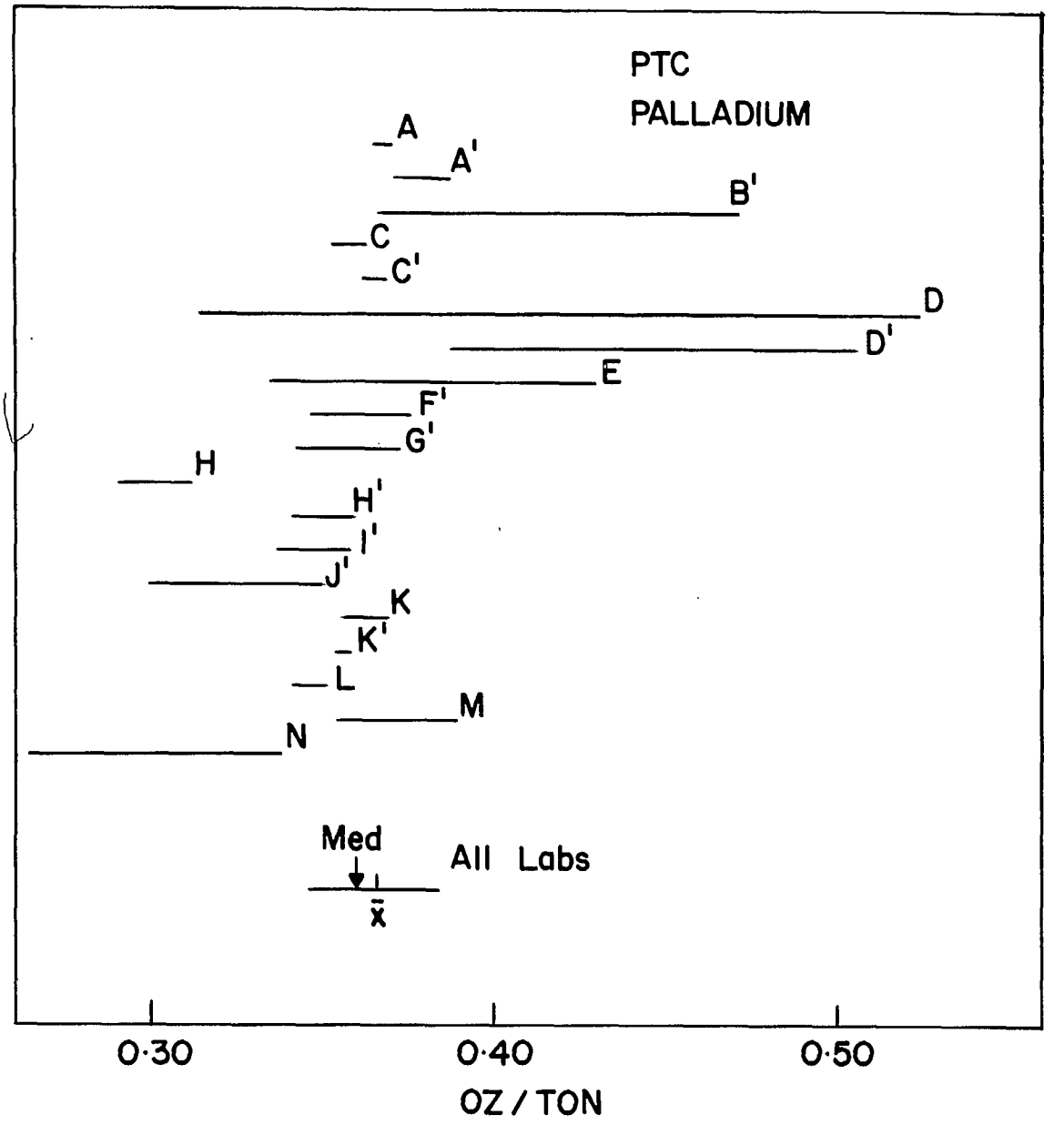

Figure 1C. 95% Confidence Intervals for Palladium Contents of the Standard Reference Material PTC, Reported by Various Laboratories.

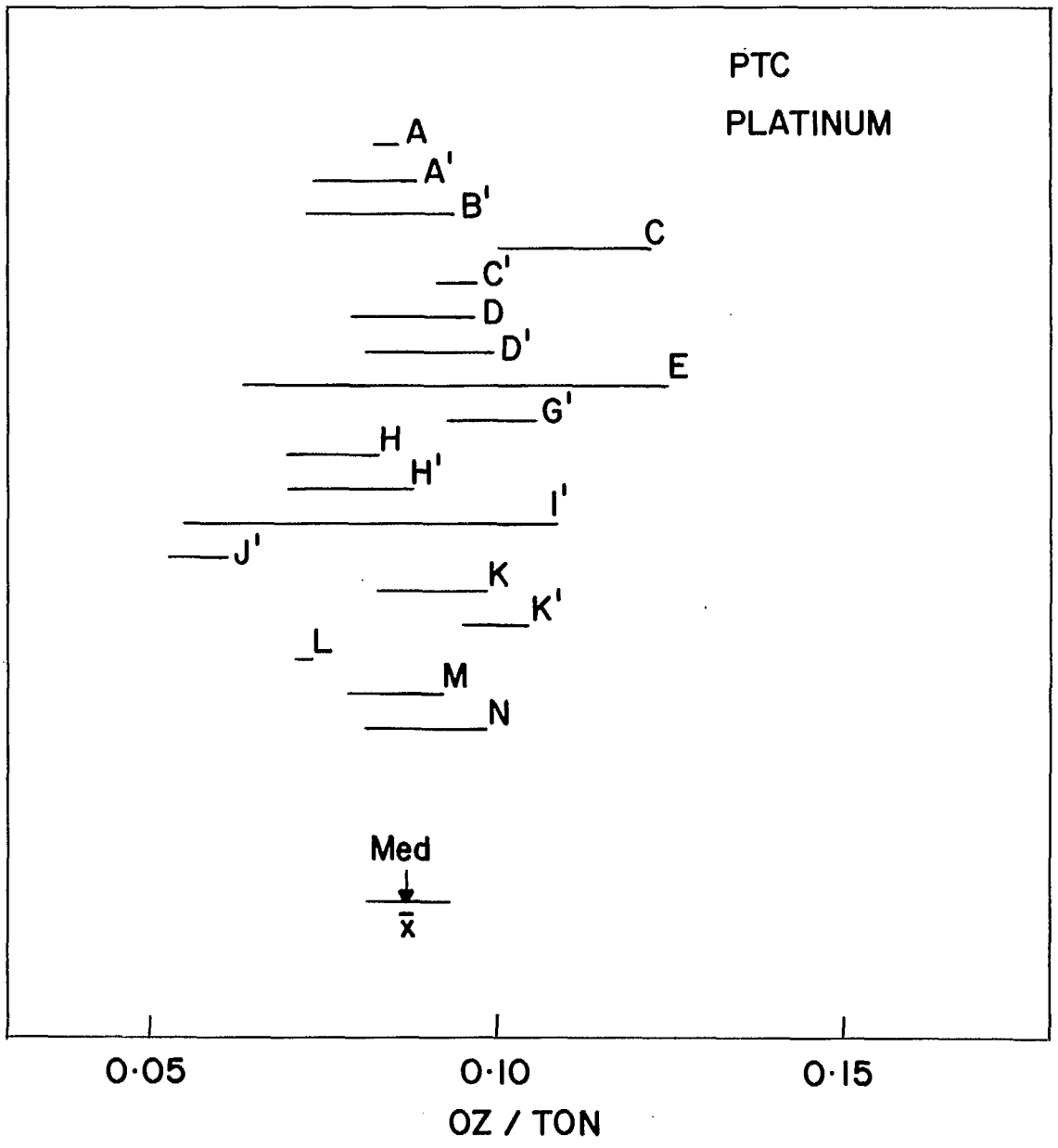

Figure 1D. 95% Confidence Intervals for Platinum Contents of the Standard Reference Material PTC, Reported by Various Laboratories.

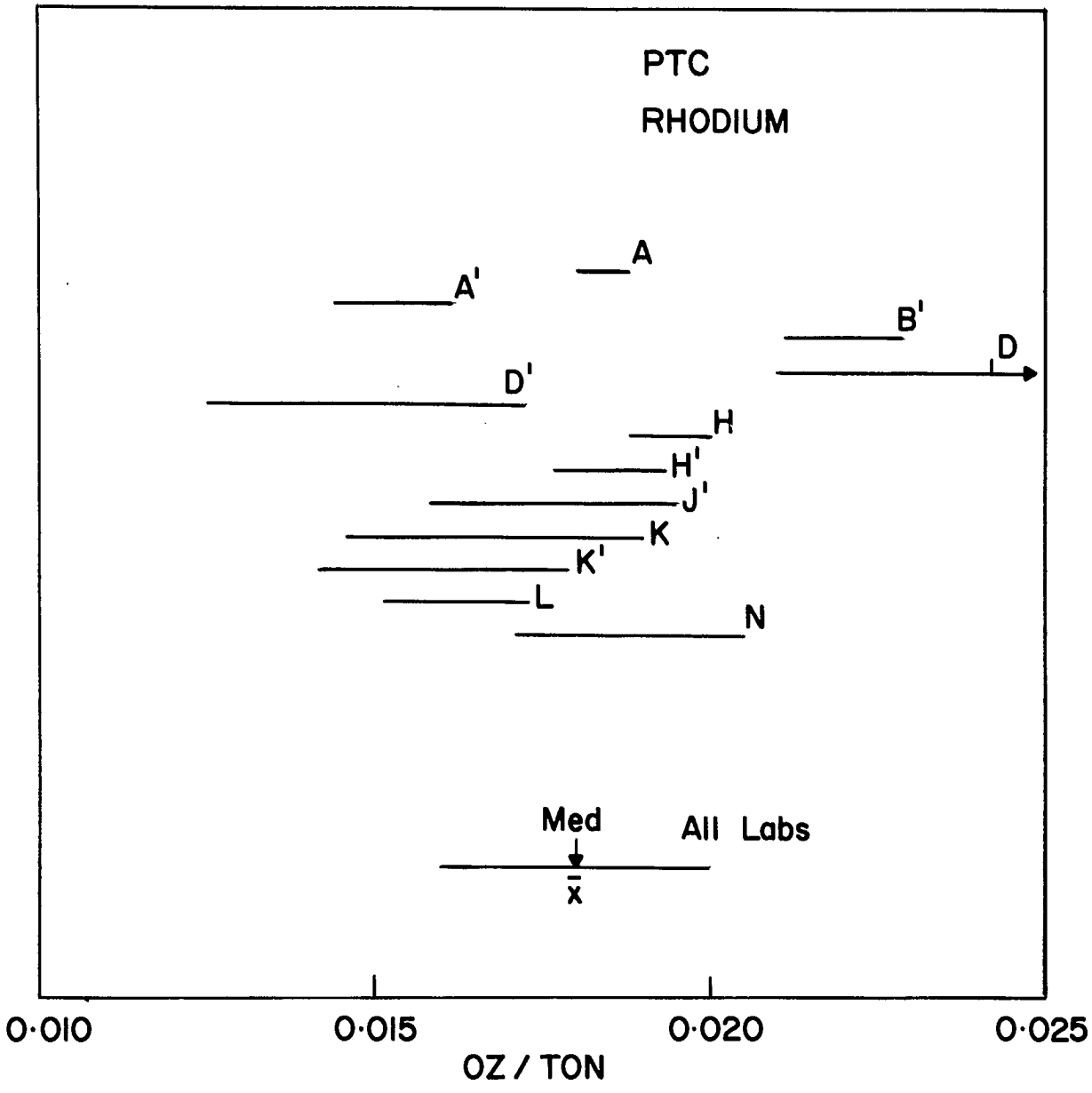

Figure 1E. 95% Confidence Intervals of Rhodium Contents of the Standard Reference Material PTC, Reported by Various Laboratories.

GENERAL REMARKS

The work described in this report on the preparation and characterization of a standard reference material for platinum-group metals represents another contribution to the Canadian Standard Reference Materials Project (CSRMP). This continuing project for the development of Standard Reference Materials for Canadian ores and ore products is being co-ordinated by Mr. G.H. Faye, Co-ordinator, Ores Task Force of the CSRMP, Mineral Sciences Division. These materials will cover a wide variety of metallic minerals and ore types and a wide range of metallic contents.

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APPENDIX A

Organizations Participating in the Certification of the Sulphide Concentrate That Contains Platinum-Group Metals as a Standard Reference Material

1. U.S. Bureau of Mines, Reno, Nevada, U.S.A.
2. Ledoux and Company, Teaneck, New Jersey, U.S.A.
3. Englehard Industries, Inc., Newark, New Jersey, U.S.A.
4. Mineral Sciences Division, Mines Branch, Ottawa, Ontario.
5. Ministry of Natural Resources, Quebec.
6. Falconbridge Nickel Mines Ltd., Thornhill, Ontario.
7. National Institute for Metallurgy, Johannesburg, South Africa.
8. Cominco Ltd., Trail, British Columbia.
9. Loring Laboratories Ltd., Calgary, Alberta.
10. Dept. of Geology, McMaster University, Hamilton, Ontario.
11. U.S. Geological Survey, Denver, Colorado, U.S.A.
12. U.S. Geological Survey, Washington, D.C., U.S.A.
13. International Nickel Co. of Canada, Toronto, Ontario.
14. Ontario Dept. of Mines, Provincial Assay Office, Toronto, Ontario.

These laboratories are referred to in the report as A to N, not respectively but anonymously.

APPENDIX B

One-Way Analysis of Variance

This method is based on the following model:

$$x_{iv} = u + y_i + z_{iv} \qquad \text{... Equation A1}$$

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 ω^2 and σ^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, 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	$\sum_{i=1}^{i=k} n_i \left(\bar{x}_{i.} - \bar{\bar{x}}_{..}\right)^2$	$(k-1)$	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	$\sum_{i=1}^{i=k} \sum_{v=1}^{v=n_i} \left(x_{iv} - \bar{x}_{i.}\right)^2$	$\sum_{i=1}^{i=k} n_i - k$	S_1^2	σ^2
Total	$\sum_{i=1}^{i=k} \sum_{v=1}^{v=n_i} \left(x_{iv} - \bar{\bar{x}}_{..}\right)^2$	$\sum_{i=1}^{i=k} n_i - 1$		

where

$\bar{x}_{i.} = \sum_{v=1}^{v=n_i} x_{iv} / n_i$ is the average result from each laboratory; and

$\bar{x}_{..} = \sum_{i=1}^{i=k} \sum_{v=1}^{v=n_i} x_{iv} \Big/ \sum_{i=1}^{i=k} n_i$ is the over-all mean of the results which provides an unbiased estimate of u;

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

and $S_2^2 = \left\{ \sum_{i=1}^{i=k} n_i \, (\bar{x}_{i.} - \bar{x}_{..})^2 \right\} \Big/ \{k-1\}$ 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:

$$V[\bar{x}_{..}] = \frac{1}{\left(\sum_{i=1}^{i=k} n_i \right)^2} \sum_{i=1}^{i=k} V\left[\sum_{v=1}^{v=n_i} x_{iv} \right] \qquad \text{... Equation A2}$$

Since $\sum_{v=1}^{v=n_i} x_{iv} = n_i u + n_i y_i + \sum_{v=1}^{v=n_i} z_{iv}$ ... Equation A3

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

$$= n_i^2 \omega^2 + n_i \sigma^2 \qquad \text{... Equation A4}$$

Substituting Equation A4 in Equation A2, we get

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

$$= \frac{\sum_{i=1}^{i=k} n_i^2 \omega^2}{N^2} + \frac{\sigma^2}{N} \quad \ldots \text{ Equation A5}$$

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 Equation A5 will vanish and we get

$$V[\bar{x}..] = \frac{\sigma^2}{N} \quad \ldots \text{ Equation A6}$$

The confidence limits were then estimated by the following formula:

$$u = \bar{\bar{x}} \pm t \left[V[\bar{x}..]\right]^{1/2}$$

where t is given (k - 1) degree of freedom.