CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

# *NOBLE-METALS-BEARING NICKEL-COPPER MATTE PTM: ITS CHARACTERIZATION AND PREPARATION FOR USE AS A STANDARD REFERENCE MATERIAL*

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

MINERAL SCIENCES DIVISION

DECEMBER 1973

Technical Bulletin TB 182

Price: .75 cents

Available by mail from Information Canada, Ottawa,
and at the following Information Canada bookshops:

HALIFAX
1683 Barrington Street

MONTREAL
640 St. Catherine Street West

OTTAWA
171 Slater Street

TORONTO
221 Yonge Street

WINNIPEG
393 Portage Avenue

VANCOUVER
800 Granville Street

or through your bookseller

Price: .75 cents Catalogue No. M34-20/182

Price subject to change without notice

Information Canada
OTTAWA
1974

Mines Branch Technical Bulletin TB 182

# NOBLE-METALS-BEARING NICKEL-COPPER MATTE PTM: ITS CHARACTERIZATION AND PREPARATION FOR USE AS A STANDARD REFERENCE MATERIAL

by

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

- - - - - - -

## SYNOPSIS

The Canadian Certified Reference Materials Project (CCRMP), formerly called the Canadian Standard Reference Materials Project (CSRMP), is an activity of the Mines Branch designed to prepare and distribute a range of materials of certified analysed content of various elements, to be used in Canada and elsewhere in the evaluation and monitoring of analytical methods and for the calibration of analytical instruments. These materials have included metals, alloys, rocks, ores, minerals, concentrates, etc. The present report deals with a nickel-copper matte, designated PTM, that contains certified amounts of various precious metals.

This report presents values for platinum, palladium, rhodium, gold and silver in a nickel-copper matte (PTM) produced from the Sudbury ore of Ontario. It also reports the results of several analysis on iridium, ruthenium and osmium for information only. The values for platinum, palladium, rhodium and gold supersede those given in 1971 (1), as a result of further analytical values being received from participants in the "round-robin" analytical program organized under the predecessors to the present Canadian Certified Reference Materials Project formally established in 1973. The values for the contents of these elements, in oz/ton are as follows: platinum 0.17, palladium 0.24, rhodium 0.026, gold 0.052 and silver 1.9.

The sample preparation and characterization of reference material PTM and a statistical evaluation of the analytical values are described in this report. The reference material is now available from the Chairman of the Canadian Certified Reference Materials Project (CCRMP), Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, 555 Booth Street, Ottawa, Ontario K1A 0G1.

---

*Head, Analytical Chemistry Section, **Research Scientist, Physical Chemistry Group, and ***Group Leader, Fire Assay Laboratories, respectively, Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.

Bulletin technique de la Direction des mines TB 182

# MATTE DE NICKEL-CUIVRE PTM RENFERMANT DES METAUX PRECIEUX: SES CARACTERISTIQUES ET SA PREPARATION POUR UTILISATION EN TANT QUE MATERIAU DE REFERENCE NORMALISE

par

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

- - -

## RÉSUMÉ

Le Projet canadien de matériaux de référence certifiés (CCRMP), anciennement appelé Project canadien de matériaux de référence normalisés (CSRMP), est une activité de la Direction des mines qui a pour but la préparation et la distribution d'une gamme de matériaux dont la teneur en divers éléments a été analysée et vérifiée, lesquels matériaux doivent être utilisés au Canada et ailleurs pour l'évaluation et le contrôle des méthodes analytiques, et pour l'étalonnage d'instruments d'analyse. Parmi ces matériaux on trouve des métaux, des alliages, des roches, des minerais, des minéraux, des concentrés, etc. Le présent rapport traite d'une matte de nickel-cuivre dite PTM qui contient des quantités certifiées de divers métaux précieux.

Le présent rapport donne des valeurs pour le platine, le palladium, le rhodium, l'or et l'argent dans une matte de nickel-cuivre (PTM) provenant de minerai extrait à Sudbury en Ontario. A titre d'information, il donne également les résultats d'analyses effectuées sur l'iridium, le ruthénium et l'osmium. Les valeurs pour le platine, le palladium, le rhodium et l'or remplacent celles qui avaient été données en 1971 (1), en raison des résultats d'analyses additionnelles provenant de participants au programme analytique organisé par les prédécesseurs de l'actuel Projet canadien de matériaux de référence certifiés établi en 1973. Les teneurs de ces éléments exprimées en onces/tonne sont les suivantes: platine, 0.17; palladium, 0.24; rhodium, 0.026; or, 0.052; et argent, 1.9.

Le rapport décrit la préparation des échantillons, l'identification des caractéristiques du matériau de référence PTM, ainsi qu'une évaluation statistique des valeurs analytiques. On peut maintenant obtenir le matériau de référence en s'adressant au Président, Projet canadien de matériaux de référence certifiés (CCRMP), Division des sciences minérales, Direction des mines, ministère de l'Energie, des Mines et des Ressources, 555 rue Booth, Ottawa, Ontario, K1A 0G1.

---

*Chef, Section de la chimie analytique, **Chercheur scientifique, Groupe de la chimie physique, et ***Chef de groupe, Laboratoire d'essai pyrognostique, respectivement, Division des Sciences minérales, Direction des mines, ministère de l'Energie, des Mines et des Ressources, Ottawa, Canada.

CONTENTS



- - - - -

## FIGURES



## TABLES



- - - - -

# INTRODUCTION

A program for the characterization of several reference materials for platinum-group metals contents has been coordinated by the Mineral Sciences Division of the Mines Branch. In phase one of the program, a sample of nickel-copper matte (PTM), produced from the Sudbury ore of Ontario, was prepared and characterized as a standard with analytical values assigned for platinum, palladium, rhodium and gold contents. The results obtained in phase one of the program were reported in Technical Bulletin TB 138, in June 1971 (1). Phase two of the program has now been completed providing further analytical values to up-date the recommended values for the platinum, palladium, rhodium and gold contents and to establish a recommended value for the silver content. Some of the laboratories participating in the "round-robin" analytical program reported analytical values for iridium, ruthenium and osmium contents of PTM that are valuable for information purposes. This Technical Bulletin is a combined report of all work performed in the preparation and characterization of reference material PTM, including the statistical evaluation of the analytical values reported for the precious-metals contents.

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. These laboratories are listed on page 24 and will be referred to in this report as laboratories A to O (excluding F, J and L), 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.

In phase one of the program two bottles of the reference material, selected at random, were submitted to each of the laboratories with the request that analyses for platinum, palladium, rhodium and gold contents be performed on five separate samples from each bottle and that each result for each element be reported. In phase two of the program two more bottles of the reference material were submitted to each laboratory with the request that five determinations for each of the elements silver, iridium, ruthenium and (if possible) osmium be performed. Several of the laboratories did not report the number of analyses requested and a statistical method of evaluation was devised to meet this situation. A number of the participating laboratories reported further values for platinum, palladium, rhodium and gold contents of PTM in phase two of the analytical program and this information has provided valuable data in establishing more reliable recommended values.

The nickel-copper matte (PTM) is available to commercial and other laboratories as a standard reference material with recommended values for platinum, palladium, rhodium, gold and silver contents. The results obtained by several laboratories for iridium, ruthenium and osmium contents have also been included in the report for information purposes only.

## PREPARATION, SAMPLING AND CHARACTERIZATION OF THE REFERENCE MATERIAL

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" program.

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

## 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 "O", excluding F, J and L, 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 spectrophotometry. 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 "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 "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 "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.

Laboratory "O" 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.

## RESULTS OBTAINED

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

## EVALUATION OF THE RESULTS

The results of the analyses received from the participating laboratories have been listed in Table 1. 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 program unless there is statistical evidence to the contrary. This assumption is based on the physical preparation conditions such as grinding, screening and mixing. The standard t-test, with a 5% level of significance, was used to detect the possibility of inhomogeneity (7). Normal distribution of the results was assumed throughout the statistical analyses. The results are summarized in Table 2. This table shows that only results reported by Laboratory "A" on silver content show any evidence of inhomogeneity. Other results do not show any evidence of inhomogeneity.

TABLE 1

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

| Laboratory | Ag | Au | Pd | Pt | Rh | Ru | Ir | Os |
|---|---|---|---|---|---|---|---|---|
| | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton |
| A | 2.01 | 0.049 | 0.251 | 0.168 | 0.024 | 0.017 | 0.007 | |
| | 1.97 | 0.049 | 0.243 | 0.185 | 0.022 | 0.020 | 0.010 | |
| | 1.97 | 0.048 | 0.236 | 0.180 | 0.025 | 0.017 | 0.007 | |
| | 1.97 | 0.049 | 0.254 | 0.168 | 0.021 | 0.018 | 0.007 | |
| | 1.96 | 0.050 | 0.241 | 0.171 | 0.021 | 0.020 | 0.007 | |
| | 2.00 | 0.047 | 0.265 | 0.187 | 0.022 | 0.020 | 0.006 | |
| | 2.06 | 0.048 | 0.241 | 0.182 | 0.021 | 0.022 | 0.008 | |
| | 2.00 | 0.050 | 0.233 | 0.168 | 0.025 | 0.017 | 0.008 | |
| | 2.06 | 0.048 | 0.233 | 0.168 | 0.022 | 0.017 | 0.007 | |
| | 2.00 | 0.048 | 0.240 | 0.160 | 0.024 | 0.020 | 0.007 | |
| | | | 0.256 | 0.166 | 0.021 | | | |
| | | | 0.244 | 0.164 | 0.024 | | | |
| | | | 0.256 | 0.172 | 0.024 | | | |
| | | | 0.244 | 0.160 | 0.024 | | | |
| | | | 0.256 | 0.170 | 0.024 | | | |
| | | | 0.244 | 0.172 | 0.022 | | | |
| | | | 0.248 | 0.178 | 0.022 | | | |
| | | | 0.238 | 0.164 | 0.022 | | | |
| | | | 0.238 | 0.172 | 0.023 | | | |
| | | | 0.238 | 0.164 | 0.023 | | | |
| B | | 0.050 | 0.255 | 0.163 | | | | |
| | | 0.049 | 0.236 | 0.154 | | | | |
| | | 0.051 | 0.255 | 0.163 | | | | |
| | | 0.051 | 0.249 | 0.169 | | | | |
| | | 0.050 | 0.245 | 0.163 | | | | |
| | | 0.049 | 0.249 | 0.160 | | | | |
| | | 0.048 | 0.252 | 0.158 | | | | |
| | | 0.052 | 0.267 | 0.173 | | | | |
| | | 0.051 | 0.274 | 0.170 | | | | |
| | | 0.050 | 0.231 | 0.164 | | | | |

(continued)

TABLE 1 (continued)

| Laboratory | Ag | Au | Pd | Pt | Rh | Ru | Ir | Os |
|---|---|---|---|---|---|---|---|---|
| | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton |
| C | | 0.052 | 0.231 | 0.168 | | | | |
| | | 0.054 | 0.236 | 0.168 | | | | |
| | | 0.054 | 0.237 | 0.168 | | | | |
| | | 0.053 | 0.242 | 0.168 | | | | |
| | | 0.060 | 0.232 | 0.160 | | | | |
| | | 0.055 | 0.231 | 0.170 | | | | |
| | | 0.050 | 0.235 | 0.158 | | | | |
| | | 0.050 | 0.236 | 0.168 | | | | |
| | | 0.051 | 0.240 | 0.168 | | | | |
| | | 0.051 | 0.232 | 0.168 | | | | |
| D | 1.90 | 0.056 | 0.200 | 0.184 | 0.022 | 0.019 | 0.011 | 0.002 |
| | 1.89 | 0.056 | 0.200 | 0.170 | 0.026 | 0.020 | 0.011 | 0.004 |
| | 1.87 | 0.044 | 0.172 | 0.180 | 0.028 | 0.019 | 0.010 | 0.003 |
| | 1.92 | 0.044 | 0.192 | 0.180 | 0.026 | 0.023 | 0.010 | 0.002 |
| | 1.90 | 0.048 | 0.224 | 0.200 | 0.023 | 0.022 | 0.010 | 0.009 |
| | | 0.038 | 0.176 | 0.180 | 0.024 | | | |
| | | 0.056 | 0.180 | 0.190 | 0.029 | | | |
| | | 0.056 | 0.216 | 0.177 | 0.024 | | | |
| | | 0.052 | 0.216 | 0.181 | 0.031 | | | |
| | | 0.036 | 0.160 | 0.188 | 0.027 | | | |
| | | 0.052 | 0.204 | 0.177 | 0.027 | | | |
| | | 0.052 | 0.158 | 0.188 | 0.028 | | | |
| | | 0.050 | 0.171 | | 0.032 | | | |
| | | 0.051 | 0.168 | | | | | |
| | | 0.053 | 0.220 | | | | | |
| | | | 0.192 | | | | | |
| | | | 0.164 | | | | | |
| | | | 0.250 | | | | | |
| | | | 0.250 | | | | | |
| | | | 0.240 | | | | | |
| | | | 0.220 | | | | | |
| | | | 0.240 | | | | | |
| E | 1.40 | 0.028 | 0.216 | 0.024 | | | | |
| | 1.60 | 0.048 | 0.248 | 0.072 | | | | |
| | 1.50 | 0.076 | 0.308 | 0.040 | | | | |
| | 1.40 | 0.048 | 0.280 | 0.060 | | | | |
| | 1.50 | 0.056 | 0.304 | 0.043 | | | | |
| | | 0.056 | 0.292 | 0.053 | | | | |
| | | 0.060 | 0.300 | 0.080 | | | | |
| | | 0.052 | 0.208 | 0.060 | | | | |

(continued)

TABLE 1 (continued)

| Laboratory | Ag | Au | Pd | Pt | Rh | Ru | Ir | Os |
|---|---|---|---|---|---|---|---|---|
| | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton |
| G | | 0.064 | 0.210 | 0.190 | | | | |
| | | 0.067 | 0.210 | 0.160 | | | | |
| | | 0.058 | 0.190 | 0.140 | | | | |
| | | 0.076 | 0.240 | 0.190 | | | | |
| | | 0.064 | 0.220 | 0.130 | | | | |
| | | 0.073 | 0.220 | 0.170 | | | | |
| | | 0.058 | 0.200 | 0.130 | | | | |
| | | 0.055 | 0.190 | 0.130 | | | | |
| | | 0.073 | 0.230 | 0.180 | | | | |
| | | 0.093 | 0.190 | 0.150 | | | | |
| H | 1.99 | 0.054 | 0.288 | 0.190 | 0.034 | | | |
| | 1.99 | 0.052 | 0.262 | 0.178 | 0.030 | | | |
| | 1.92 | 0.050 | 0.258 | 0.170 | 0.029 | | | |
| | 1.92 | 0.046 | 0.248 | 0.168 | 0.028 | | | |
| | 1.92 | 0.054 | 0.278 | 0.186 | 0.032 | | | |
| | 1.98 | 0.048 | 0.214 | 0.172 | 0.030 | | | |
| | 1.98 | 0.048 | 0.266 | 0.176 | 0.032 | | | |
| | 1.94 | 0.048 | 0.288 | 0.186 | 0.032 | | | |
| | 1.94 | 0.040 | 0.242 | 0.156 | 0.028 | | | |
| | 1.99 | 0.048 | 0.266 | 0.174 | 0.030 | | | |
| I | | 0.046 | 0.230 | 0.145 | 0.023 | | | |
| | | 0.046 | 0.230 | 0.145 | 0.024 | | | |
| | | 0.046 | 0.230 | 0.150 | 0.024 | | | |
| | | 0.041 | 0.230 | 0.150 | 0.024 | | | |
| | | 0.041 | | | | | | |
| | | 0.044 | | | | | | |
| | | 0.044 | | | | | | |
| | | 0.044 | | | | | | |
| | | 0.041 | | | | | | |
| | | 0.041 | | | | | | |
| K | 1.82 | 0.064 | 0.231 | 0.180 | 0.032 | | | |
| | 1.87 | 0.062 | 0.236 | 0.175 | 0.030 | | | |
| | 1.96 | 0.061 | 0.225 | 0.175 | 0.032 | | | |
| | 1.90 | 0.065 | 0.220 | 0.182 | 0.028 | | | |
| | 2.03 | | 0.225 | | | | | |
| | 1.95 | | 0.230 | | | | | |
| | | | 0.234 | | | | | |
| | | | 0.230 | | | | | |

(concluded)

TABLE 1 (concluded)

| Laboratory | Ag | Au | Pd | Pt | Rh | Ru | Ir | Os |
|---|---|---|---|---|---|---|---|---|
| | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton | oz/ton |
| M | | | 0.275 | 0.130 | | | | |
| | | | 0.280 | 0.130 | | | | |
| | | | 0.285 | | | | | |
| | | | 0.280 | | | | | |
| | | | 0.278 | | | | | |
| | | | 0.280 | | | | | |
| | | | 0.285 | | | | | |
| | | | 0.290 | | | | | |
| | | | 0.285 | | | | | |
| | | | 0.280 | | | | | |
| N | 1.95 | 0.045 | 0.202 | 0.218 | 0.027 | | | |
| | 2.10 | 0.038 | 0.177 | 0.187 | 0.023 | | | |
| | 2.73 | 0.043 | 0.177 | 0.179 | 0.026 | | | |
| | 2.10 | 0.042 | 0.166 | 0.154 | 0.021 | | | |
| | 2.00 | 0.044 | 0.168 | 0.169 | 0.024 | | | |
| | 2.00 | 0.062 | 0.288 | 0.185 | 0.026 | | | |
| | 1.90 | 0.052 | 0.288 | 0.185 | 0.026 | | | |
| | 1.90 | 0.059 | 0.260 | 0.192 | 0.027 | | | |
| | | 0.057 | 0.260 | 0.210 | 0.027 | | | |
| O | | 0.054 | 0.234 | 0.154 | 0.017 | 0.011 | 0.024 | |
| | | 0.048 | 0.235 | 0.159 | 0.017 | 0.012 | 0.024 | |
| | | | 0.236 | 0.160 | 0.023 | 0.014 | 0.017 | |
| | | | 0.225 | 0.147 | 0.022 | | 0.020 | |
| | | | 0.236 | | 0.020 | | 0.028 | |
| | | | 0.222 | | | | 0.028 | |

TABLE 2

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

| Laboratory | Nickel-Copper Matte | | | | |
|---|---|---|---|---|---|
| | Silver | Gold | Palladium | Platinum | Rhodium |
| A | Re | Ac | Ac | Ac | Ac |
| B | - | Ac | Ac | Ac | - |
| C | - | Ac | Ac | Ac | - |
| D | - | Ac | Ac | Ac | Ac |
| E | - | - | - | - | - |
| G | - | Ac | Ac | Ac | - |
| H | Ac | Ac | Ac | Ac | Ac |
| I | - | Ac | - | - | - |
| K | - | - | Ac | - | - |
| M | - | - | Ac | - | - |
| N | - | - | - | - | - |
| O | - | - | - | - | - |

*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

Since there is only one case in which the null hypothesis was rejected (see Table 2), 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 have been caused by random errors. The 95% confidence intervals were computed for each laboratory and compared with each other graphically in Figures 1 to 5. The estimated over-all means of these laboratory results for each metal-content of the samples were calculated by two different methods, designated as (a) and (b), which 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" (8).

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:

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

$$\bar{x}_{i.} = \sum_{v=1}^{v=n_i} x_{iv}/n_i \qquad \ldots\ldots \qquad \text{(Eq. 2)}$$

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

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.

## DISCUSSION

The results of these computations are summarized in Table 3. It can be seen in this table that the effect of weighting the results is negligible. The values of the confidence intervals suggest that it is reasonable to recommend that the PTM sample be used as a standard for the elements Ag, Au, Pd, Pt and Rh. The recommended values for these elements are listed in Table 4. The analytical results for Ru and Ir are too few and too dispersed to arrive at a mean value with confidence intervals that are meaningful for the present state of the analytical techniques. For this reason, the PTM sample is not recommended as a standard for the elements Ru and Ir.

The values given in this report for the platinum, palladium, rhodium and gold contents of sample PTM show no significant difference from those reported in 1971 (1). The silver content of PTM has also been determined since 1971 and included in this report.

TABLE 3

Estimated Parameters for the Standard Reference Material PTM (Nickel-Copper Matte) in oz/ton

| Element | Method of Computation | Mean oz/ton | 95% Confidence Intervals of the Mean | | Median oz/ton | No. of Results Included in the Computation | No. of Labs. |
|---|---|---|---|---|---|---|---|
| | | | Low oz/ton | High oz/ton | | | |
| Silver | (a) | 1.924 | 1.720 | 2.128 | 1.955 | 44 | 6 |
| | (b) | 1.885 | 1.690 | 2.080 | | | |
| Gold | (a) | 0.052 | 0.047 | 0.057 | 0.050 | 98 | 11 |
| | (b) | 0.052 | 0.048 | 0.057 | | | |
| Palladium | (a) | 0.236 | 0.217 | 0.256 | 0.237 | 123 | 11 |
| | (b) | 0.240 | 0.222 | 0.257 | | | |
| Platinum | (a) | 0.170 | 0.161 | 0.180 | 0.170 | 91 | 10 |
| | (b) | 0.166 | 0.158 | 0.175 | | | |
| Rhodium | (a) | 0.026 | 0.021 | 0.030 | 0.025 | 61 | 6 |
| | (b) | 0.026 | 0.022 | 0.030 | | | |
| Ruthenium | (a) | 0.018 | 0.009 | 0.028 | 0.019 | 18 | 3 |
| | (b) | 0.017 | 0.009 | 0.026 | | | |
| Iridium | (a) | 0.013 | 0 | 0.035 | 0.010 | 21 | 3 |
| | (b) | 0.014 | 0 | 0.035 | | | |

TABLE 4

Recommended Values and Their Confidence Intervals for Selected Elements in Standard Reference Material PTM

| | Pt | | Pd | | Rh | | Au | | Ag | |
|---|---|---|---|---|---|---|---|---|---|---|
| | (oz/ton) | (ppm) | (oz/ton) | (ppm) | (oz/ton) | (ppm) | (oz/ton) | (ppm) | (oz/ton) | (ppm) |
| Recommended Value | 0.17 | 5.8 | 0.24 | 8.1 | 0.026 | 0.9 | 0.052 | 1.8 | 1.9 | 66. |
| 95% - Confidence Interval | | | | | | | | | | |
| Low | 0.16 | 5.5 | 0.22 | 7.4 | 0.021 | 0.7 | 0.047 | 1.6 | 1.7 | 59. |
| High | 0.18 | 6.2 | 0.26 | 8.8 | 0.030 | 1.0 | 0.057 | 1.9 | 2.1 | 73. |

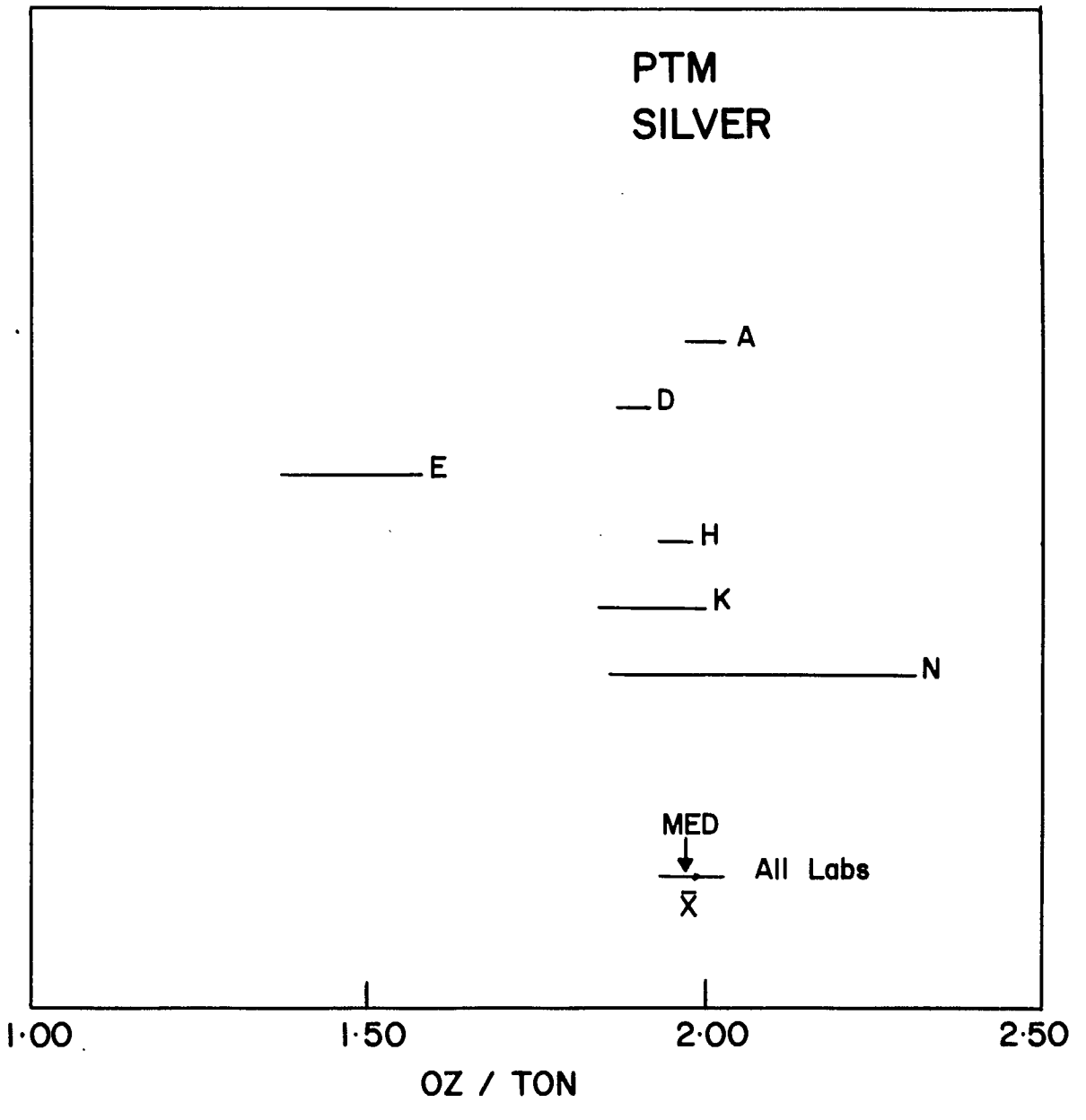


Figure 1. 95% Confidence Intervals for Silver Contents of the Standard Reference Material PTM, Reported by Various Laboratories.

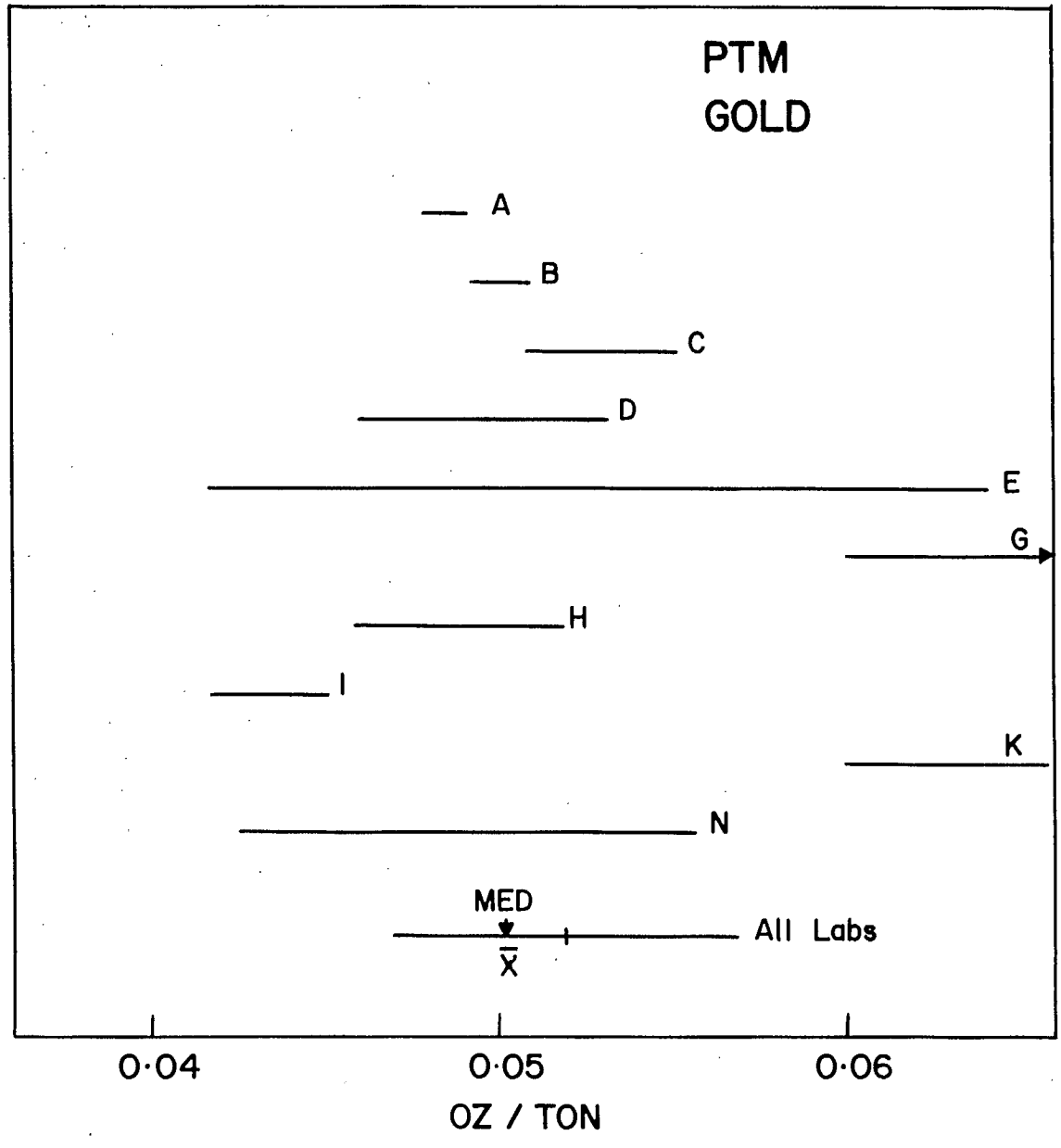


Figure 2. 95% Confidence Intervals for Gold Contents of the Standard Reference Material PTM, Reported by Various Laboratories.

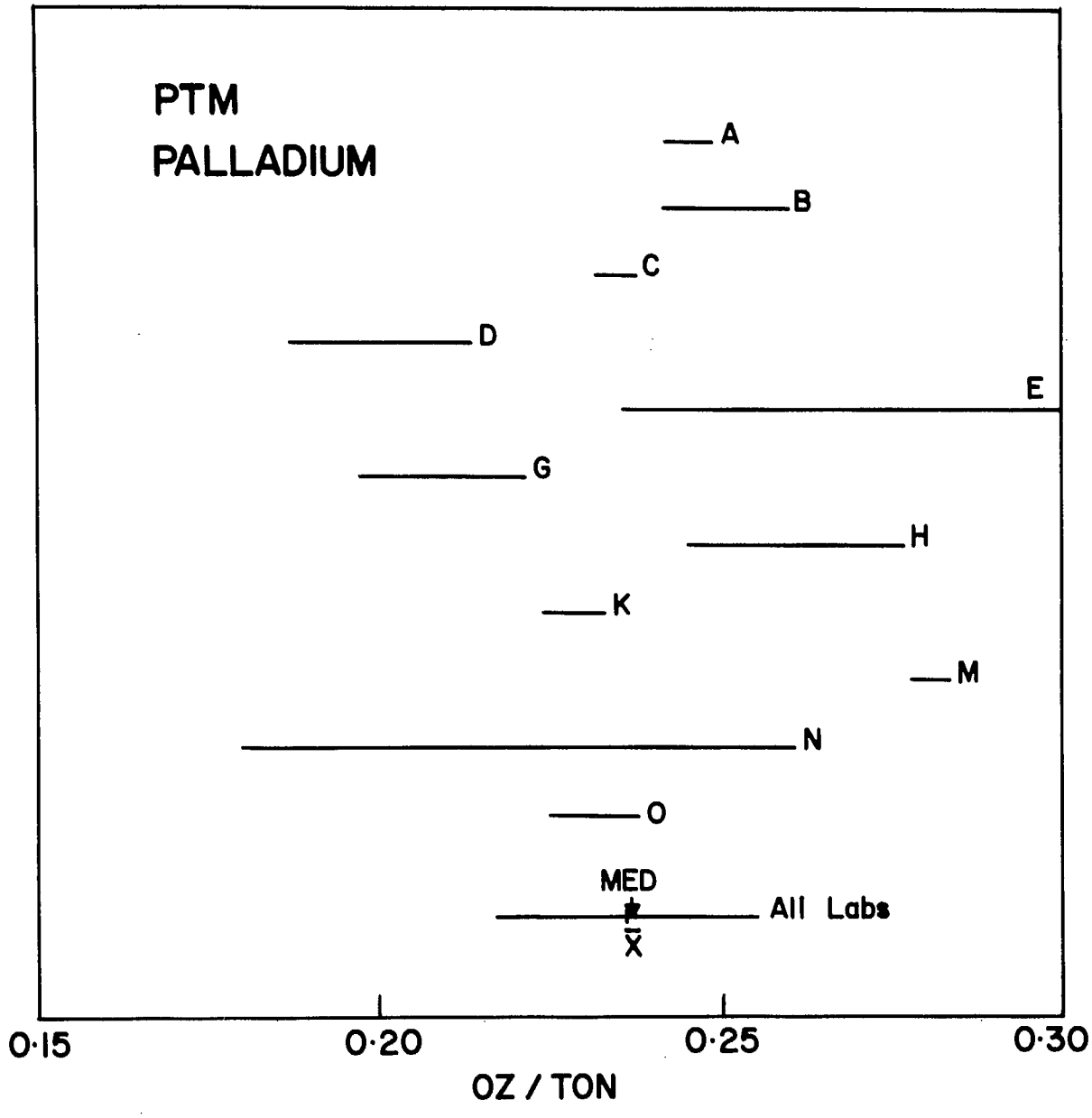


Figure 3. 95% Confidence Intervals for Palladium Contents of the Standard Reference Material PTM, Reported by Various Laboratories.

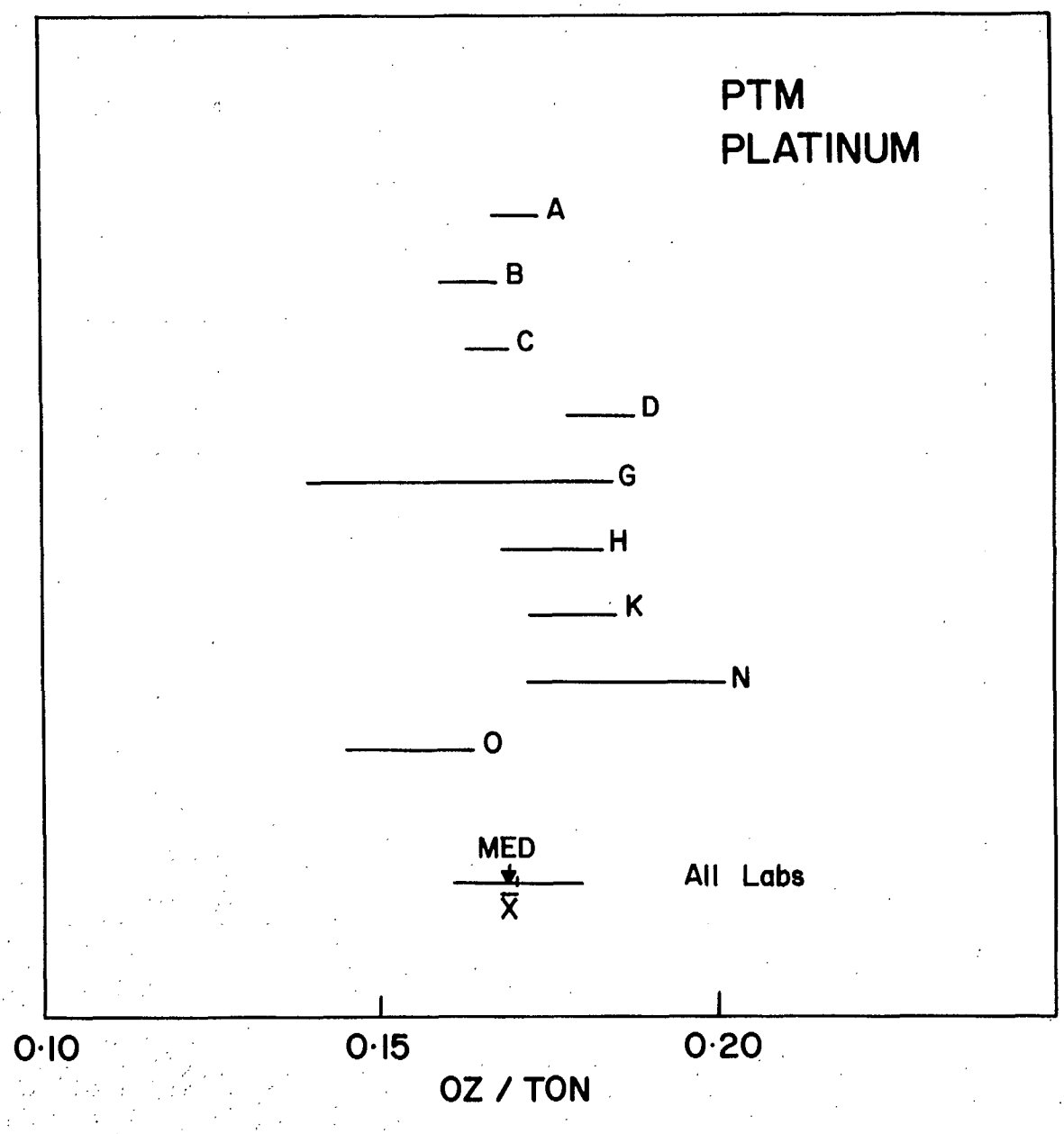


Figure 4. 95% Confidence Intervals for Platinum Contents of the Standard Reference Material PTM, Reported by Various Laboratories.

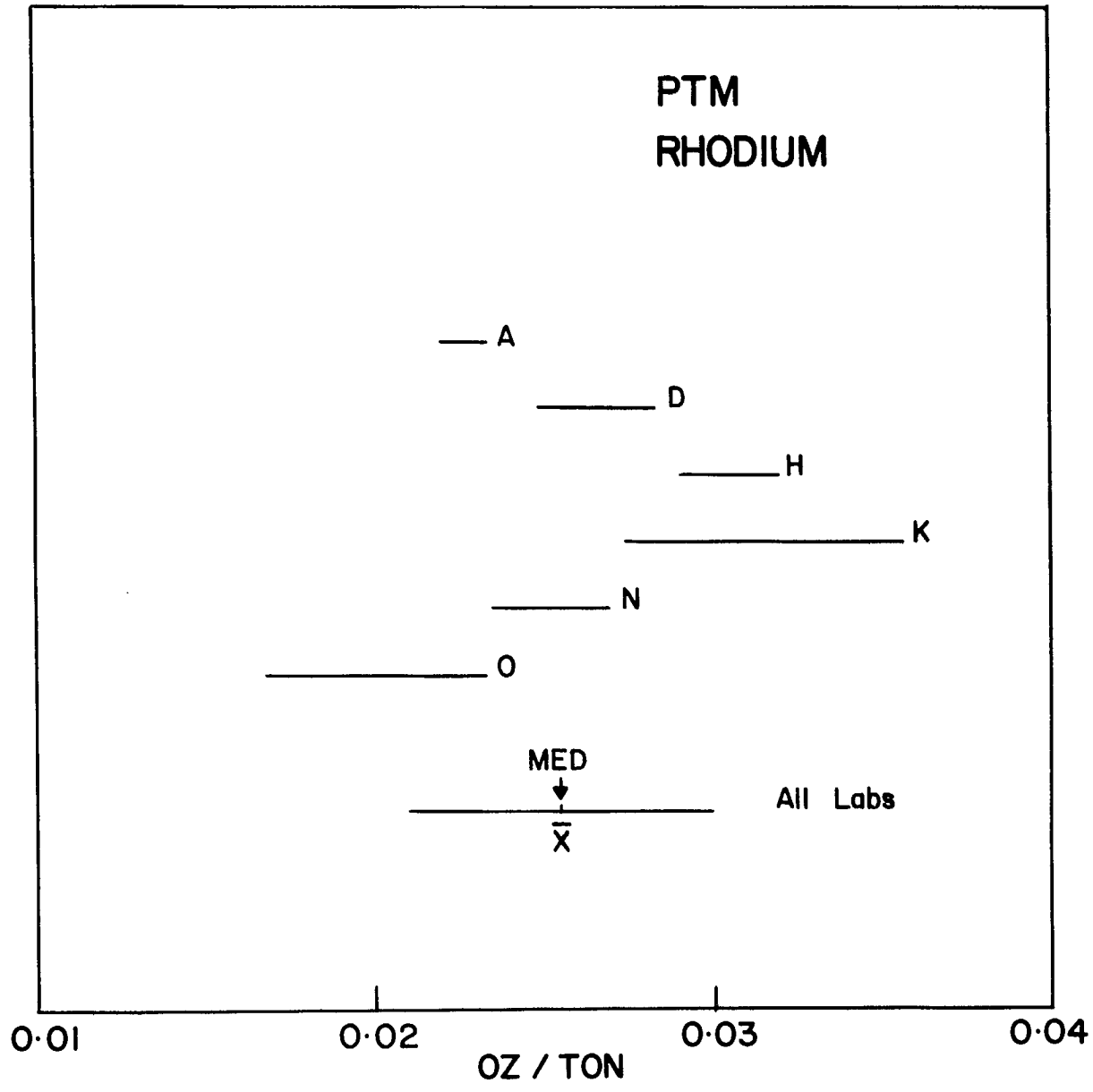


Figure 5. 95% Confidence Intervals for Rhodium Contents of the Standard Reference Material PTM, Reported by Various Laboratories.

## GENERAL REMARKS

The work described in this report represents another in the series of investigations conducted to establish reference materials against which analytical procedures and laboratory performance in the minerals/metals field can be measured. The validity of the sampling procedure to produce homogeneous samples, and the attainable precision of the analyses have formed essential aspects of this study.

This nickel-copper matte (PTM) represents another contribution to the Canadian Standard Reference Materials Project (CSRMP). A continuing project for the development of Standard Reference Materials for Canadian ores and ore products is being coordinated by Mr. G.H. Faye, Coordinator, Ores Task Force of the CSRMP, Mineral Sciences Division. These materials cover a wide variety of metallic minerals and ore types with a wide range of metallic contents.

## ACKNOWLEDGEMENTS

The authors thank the participating organizations, listed in Appendix A, for performing the "round-robin" analyses required for the certification program. They also thank Mr. R. Klymowsky, Mineral Processing Division and Mr. Y. Bourgoin, for sample preparation; 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 analysing for the precious metals. The above are all members of the Mineral Sciences Division except where otherwise stated.

# REFERENCES

1. McAdam, R.C., Sutarno and Moloughney, P.E., "Characterization and Preparation of Standard Reference Materials that Contain Noble Metals: (a) PTA (Ores) and (b) PTM (Nickel-Copper Matte)", Mines Branch Technical Bulletin TB 138 (June 1971).

2. Cloutier, J.C. and Craig, R.R., "Platinum Ores", Mineral Sciences Division Internal Reports MS-AC 71-278 and 285.

3. Faye, G.H. and Moloughney, P.E., "The Tin Collection Scheme for the Determination of Platinum-Group Metals, Gold and Silver", Talanta, 19, 269-284 (1972).

4. American Society for Testing and Materials, "Standard Method for Spectrochemical Analysis of Ores, Minerals, and Rocks by the Fire Assay Preconcentration-Spark Technique", ASTM Designation E400-71.

5. Schnepfe, M.M. and Grimaldi, F.S., "Determination of Palladium and Platinum by Atomic Absorption", Talanta, 16, 591-595 (1969).

6. Schnepfe, M.M. and Grimaldi, F.S., "Atomic Absorption Determination of Rhodium in Chromite Concentrates", Talanta, 16, 1461-1465 (1969).

7. Beyer, W.H., "Handbook of Tables for Probability and Statistics", published by The Chemical Rubber Co., Cleveland, Ohio, 2nd ed. (1968).

8. "ASTM Manual for Conducting an Inter-Laboratory Study of a Test Method", ASTM Special Technical Publication No. 335 (1963).

# APPENDIX A

## Organizations Participating in the Certification of the Nickel-Copper Matte 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. Engelhard 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. U.S. Geological Survey, Washington, D.C., U.S.A.
11. International Nickel Co. of Canada, Toronto, Ontario.
12. Ontario Dept. of Mines, Provincial Assay Office, Toronto, Ontario.

These laboratories are referred to in the report as A to O, excluding F, J and L, not respectively but anonymously.

# APPENDIX B

## One-Way Analysis of Variance

This method is based on the following model:

$$x_{iv} = u + y_i + z_{iv} \quad \ldots \quad \text{(Eq. 4)}$$

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 | $\sum_{i=1}^{i=k} n_i\left(\bar{x}_{i.}-\bar{\bar{x}}_{..}\right)^2$ | $(k-1)$ | $S_2^2$ | $\sigma^2+\frac{1}{k-1}\left(\sum_{i=1}^{i=k} n_i-\frac{\sum_{i=1}^{i=k} n_i^2}{\sum_{i=1}^{i=k} n_i}\right)\omega^2$ |
| Within Laboratories | $\sum_{i=1}^{i=k}\sum_{v=1}^{v=n_i}\left(x_{iv}-\bar{x}_{i.}\right)^2$ | $\sum_{i=1}^{i=k} n_i - k$ | $S_1^2$ | $\sigma^2$ |
| 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 $\sigma^2$;

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:

$$V[\bar{x}_{..}] = \frac{1}{\left( \sum_{i=1}^{i=k} n_i \right)^2} \sum_{i=1}^{i=k} V\left[ \sum_{v=1}^{v=n_i} x_{iv} \right] \qquad \ldots \text{ (Eq. 5)}$$

Since $\sum_{v=1}^{v=n_i} x_{iv} = n_i u + n_i y_i + \sum_{v=1}^{v=n_i} z_{iv}$ ... (Eq. 6)

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

$$= n_i^2 \omega^2 + n_i \sigma^2 \qquad \ldots \text{ (Eq. 7)}$$

Substituting Eq. 7 in Eq. 5, we get

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

$$= \frac{\sum_{i=1}^{i=k} n_i^2 \omega^2}{N^2} + \frac{\sigma^2}{N} \qquad \ldots \text{(Eq. 8)}$$

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. 8 will vanish and we get

$$V[\bar{x}..] = \frac{\sigma^2}{N} \qquad \ldots \text{(Eq. 9)}$$

# 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

$$\bar{x}_{..} = \sum_{i=1}^{i=k} a_i \bar{x}_{i.} \qquad \ldots \text{ (Eq. 10)}$$

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

$$E[\bar{x}_{..}] = E\left[\sum_{i=1}^{i=k} a_i \bar{x}_{i.}\right]$$

$$= \sum_{i=1}^{i=k} a_i \, E[\bar{x}_{i.}]$$

$$= u \sum_{i=1}^{i=k} a_i$$

$$= u$$

Therefore, $\sum_{i=1}^{i=k} a_i = 1 \qquad \ldots \text{ (Eq. 11)}$

---

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

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

$$V[\bar{x}_{..}] = V\left[\sum_{i=1}^{i=k} a_i \bar{x}_{i.}\right]$$

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

$$= \sum_{i=1}^{i=k} a_i \sigma_i^2 \quad \ldots \quad \text{(Eq. 12)}$$

Eq. 11 can be rewritten as

$$a_k + \sum_{i=1}^{i=(k-1)} a_i = 1$$

$$\text{or} \quad a_k = 1 - \sum_{i=1}^{i=(k-1)} a_i \quad \ldots \quad \text{(Eq. 13)}$$

Substituting Eq. 13 into Eq. 12, we get:

$$V[\bar{x}_{..}] = \sum_{i=1}^{i=(k-1)} a_i \sigma_i^2 + \left(1 - \sum_{i=1}^{i=(k-1)} a_i\right)^2 \sigma_k^2$$

$$= \sum_{i=1}^{i=(k-1)} a_i^2 \sigma_i^2 + \left\{1 - 2 \sum_{i=1}^{i=(k-1)} a_i + \left(\sum_{i=1}^{i=(k-1)} a_i\right)^2\right\} \sigma_k^2 \quad \ldots \quad \text{(Eq. 14)}$$

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

$$\frac{\partial V[\bar{x}_{..}]}{\partial a_i} = 0 \text{ for all values of } i = 1, 2, \ldots, k \quad \ldots \quad \text{(Eq. 15)}$$

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

$$\frac{\partial V[\bar{x}_{\cdot\cdot}]}{\partial a_j} = 2 a_j \sigma_j^2 - 2 \sigma_k^2 + 2 \sum_{i=1}^{i=(k-1)} a_i \sigma_k^2$$

$$= 2 \left[ a_j \sigma_j^2 - \left( 1 - \sum_{i=1}^{i=(k-1)} a_i \right) \sigma_k^2 \right] = 0 \quad \ldots \text{(Eq. 16)}$$

Substituting Eq. 13 into Eq. 16, we get:

$$a_j \sigma_j^2 - a_k \sigma_k^2 = 0 \quad \ldots \text{(Eq. 17)}$$

whence $$a_j = a_k \frac{\sigma_k^2}{\sigma_j^2} \quad \ldots \text{(Eq. 18)}$$

Eq. 18 is valid for all values of j = 1, 2 ... k, thus:

$$\sum_{j=1}^{j=k} a_j = \sum_{i=1}^{i=k} a_i = 1 \quad \ldots \text{(Eq. 19)}$$

also $$\sum_{j=1}^{j=k} a_j = a_k \sigma_k^2 \cdot \sum_{j=1}^{j=k} \frac{1}{\sigma_j^2} \text{ (from Eq. 18)} \quad \ldots \text{(Eq. 20)}$$

Substituting Eq. 19 into Eq. 20, we get:

$$a_k = \frac{1}{\sigma_k^2 \sum_{j=1}^{j=k} \frac{1}{\sigma_j^2}} \quad \ldots \text{(Eq. 21)}$$

Substituting Eq. 21 into Eq. 18, we get:

$$a_j = \frac{1}{\sigma_j^2 \sum_{j=1}^{j=k} \frac{1}{\sigma_j^2}} \quad \ldots \text{(Eq. 22)}$$

Since Eq. 22 is valid for all values of $j = 1, 2 \ldots, k$, it can be generalized as:

$$a_i = \frac{1}{\sigma_i^2 \sum_{i=1}^{i=k} \frac{1}{\sigma_i^2}} \quad \ldots \text{(Eq. 23)}$$

If we define $W_i = \frac{1}{\sigma_i^2}$, Eq. 23 becomes

$$a_i = \frac{W_i}{\sum_{i=1}^{i=k} W_i} \quad \ldots \text{(Eq. 24)}$$

Substituting Eq. 24 into Eq. 10, we get:

$$\bar{x}_{..} = \sum_{i=1}^{i=k} \frac{W_i}{\sum_{i=1}^{i=k} W_i} \bar{x}_{i.} \quad \ldots \text{(Eq. 25)}$$

Eq. 4 can be rewritten as:

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

Since $\bar{x}_{i.} = \sum_{v=1}^{v=n_i} x_{iv} / n_i$

$$V[\bar{x}_{i.}] = V\left[\sum_{v=1}^{v=n_i} x_{iv} / n_i\right]$$

$$= \omega^2 + \frac{s_i^2}{n_i}$$

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:

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

A reasonable estimate of $\omega^2$ can be computed from Appendix B, thus:

$$\omega^2 = \left( S_2^2 - S_1^2 \right) \frac{(k-1)}{\left( N - \frac{\sum_{i=1}^{i=k} n_i^2}{N} \right)} \qquad \ldots \text{(Eq. 26)}$$

From Eq. 25, the variance of the grand mean $V[\bar{x}_{..}]$ can be estimated as:

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

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

$$= \sum_{i=1}^{i=k} \left( \frac{W_i}{\sum_{i=1}^{i=k} W_i} \right)^2 \frac{1}{W_i}$$

$$V[\bar{x}_{..}] = \frac{\frac{1}{i=k}}{\sum_{i=1}^{i=k} W_i} \qquad \ldots \text{(Eq. 27)}$$

The confidence interval can then be estimated, based on (k-1) degrees of freedom[7].

= = = =