

GEOCHEMICAL PROFICIENCY TESTING PROGRAM

ROUND 15

MARCH 2020

REPORT NO. 1187

ACKNOWLEDGMENTS

PTA wishes to gratefully acknowledge the technical assistance that was provided for this program by Ms J Hwende, Bureau Veritas Australia Pty Ltd.

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1. Foreword

This report summarises the results of a proficiency testing program on the analysis of geochemical samples. It constitutes the fifteenth round of an ongoing series of programs in this area. This program is accredited to ISO/IEC 17043:2010 "Conformity assessment - General requirements for proficiency testing" by International Accreditation New Zealand (IANZ).

The program was conducted in December 2019 / January 2020 by Proficiency Testing Australia (PTA). The main aim of the program was to assess laboratories' abilities to competently perform the prescribed analyses.

The Program Coordinator was Mrs K Weller and the Technical Adviser was Ms J Hwende, Bureau Veritas Australia Pty Ltd. This report was authorised by Mrs K Cividin, PTA Quality Manager.

2. Program Features and Design

- 2.1 Each laboratory was randomly allocated a unique code number for the program to ensure confidentiality of results. Reference to each laboratory in this report is by code number only, where a laboratory requested more than one sample a separate code number was allocated for each sample.
- 2.2 Participants were provided with one Copper Ore sample.
- 2.3 Laboratories were provided with the "Instructions to Participants" and "Results Sheet" (see Appendix C) and asked to report total analysis of the elements listed below:

Antimony	Sb	Fluorine	F	Manganese	Mn
Arsenic	Ar	Gold	Au	Nickel	Ni
Bismuth	Bi	Iron	Fe	Silver	Ag
Cadmium	Cd	Lead	Pb	Sulphur	S
Copper	Cu	Magnesium Oxide	MgO	Zinc	Zn

- 2.4 A total of 4 laboratories participated in the program with 3 laboratories returning results for inclusion in the final report and one laboratory returning results for more than one sample.

All participant laboratories were from Australia.

- 2.5 Results (as reported by participants), and where relevant, corresponding summary statistics (i.e. number of results, median, normalised interquartile range, robust coefficient of variation, minimum, maximum, range and uncertainty of the median) are presented in Appendix A.
- 2.6 A robust statistical approach, using z-scores, was utilised to assess laboratories' testing performance (see Section 3). Robust z-scores and z-score charts, where relevant to each test, are presented in Appendix A.

The document entitled *Guide to Proficiency Testing Australia*, 2019 (reference [1]) defines the statistical terms and details the statistical procedures referred to in this report.

- 2.7 Samples dispatched for this round were NCS Testing Technology Co., Ltd certified reference material NCS DC 28055 Copper Ore and therefore, considered homogeneous and stable for the duration of the round.

3. Statistical Format

For each test the following information is given, where appropriate:

- a table of results and calculated z-scores;
- a list of summary statistics; and
- ordered z-score charts.

3.1 Outlier Results and Z-scores

In order to assess laboratories' testing performance, a robust statistical approach, using z-scores, was utilised. Z-scores give a measure of how far a result is from the consensus value (i.e. the median), and gives a "score" to each result relative to the other results in the group.

A z-score close to zero indicates that the result agrees well with those from other laboratories, whereas a z-score with an absolute value greater than or equal to 3.0 is considered to be an outlier and is marked by the symbol "S".

Where relevant, each determination was examined for outliers with all methods pooled.

3.2 Results Tables and Summary Statistics

Each of these tables contains the results returned by each laboratory and where appropriate, the robust z-score calculated for each result.

Results have been entered exactly as reported by participants. That is, laboratories which did not report results to the precision (i.e. number of significant figures) requested on the Results Sheet have not been rounded to the requested precision before being included in the statistical analysis.

Where relevant, a list of summary statistics appears at the bottom of each of the tables of results and consists of:

- the median of these results, i.e. the middle value (*Median*);
- the uncertainty of the median; a robust estimate of the standard deviation of the *Median*;
- the normalised interquartile range of the results (*Normalised IQR*);
- the robust coefficient of variation, expressed as a percentage (*Robust CV*) - i.e. $100 \times \text{Normalised IQR} / \text{Median}$;
- the minimum and maximum laboratory results; and
- the range (*Maximum - Minimum*).

Please see reference [1] for further details on these robust summary statistics.

3.3 Ordered Z-score Charts

On these charts each laboratory's robust z-score is shown, in order of magnitude, and is marked with its code number. From these charts, each laboratory can readily compare its performance relative to the other laboratories.

These charts contain solid lines at +3.0 and -3.0, so that outliers are clearly identifiable as those laboratories whose "bar" extends beyond these "cut-off" lines. The y-axis of these charts has been limited, so very large z-scores appear to extend beyond the chart boundary.

Further details for the interpretation of these diagrams are given in reference [1]. Please also refer to this document for a glossary of terms.

TABLE A: SUMMARY STATISTICS

Analysis	No. of Results	Median	Norm IQR	Uncertainty (Median)
Antimony (%)	6	Not Calculated ¹		
Arsenic (%)	8	Not Calculated ¹		
Bismuth (%) ²	6	0.0210	0.0014	0.0006
Cadmium (%)	6	0.00600	0.00070	0.00029
Copper (%) ³	8	13.000	0.260	0.092
Fluorine (%)	6	Not Calculated ¹		
Gold (ppm)	6	Not Calculated ¹		
Iron (%) ²	8	3.190	0.063	0.022
Lead (%)	2	Not Calculated ³		
Magnesium Oxide (%)	6	0.185	0.024	0.010
Manganese (%)	6	0.0900	0.0070	0.0029
Nickel (%)	6	0.0160	0.0013	0.0005
Silver (ppm)	8	85.5	5.9	2.1
Sulphur (%)	8	1.540	0.022	0.008
Zinc (%)	8	0.6365	0.0550	0.0195

Notes:

1. Results for these tests were not normally distributed therefore statistical analysis could not be performed.
2. Robust CVs for these tests were low so more appropriate Target CVs were used to prevent some laboratories from unfairly receiving outliers (see Appendix 1 for more information).
3. Statistical analysis could not be performed for Lead as only a low number (<6) numerical results were reported.

4. PTA and Technical Adviser's Comments

For this program, laboratories were encouraged to use a method that gave the best detection limit for the element. The comments presented in this section are general in nature.

4.1 Overall performance

Overall, performance for the main element i.e. Copper, was satisfactory

4.2 Outliers

No outliers were reported for this round.

4.3 Measurement Uncertainty (MU) and Detection Limit

Most results had MU quantified. It is advisable for laboratories to review their process or calculations for suitability if MU is greater than 5% of the result.

4.4 Z-score (Interlaboratory Performance)

Whilst the z-score gives an indication of where each laboratory stands in comparison to others, laboratories with absolute z-scores:

- greater than 2.0 for any element - should review the technique and calibration for that element.
- greater than or equal to 3.0 for any element - should seriously review the method for that element (except in the case of a typographical or calculation error).

4.5 Duplicates

Duplicate testing was generally performed well.

4.7 Method Code

All laboratories provided method codes.

4.8 Metrological Traceability and Measurement Uncertainty of Assigned Values

Consensus values (median) derived from participants' results are used in this program. These values are not metrologically traceable to an external reference.

The samples chosen for this program were NCS Testing Technology Co., Ltd certified reference material NCS DC 28055 Copper Ore.

As the assigned value for each analyte in this program is the median of the results submitted by the participants, the uncertainty of the median has been calculated for each analysis (where relevant) and is tabulated in Table A on page 4, and also in the summary statistics tables in Appendix A.

4.9 Analysis of Results by Method Groups

In order for methods to be grouped for analysis, PTA requires at least 11 sets of results from the same method group. As there were less than 11 results submitted for each method, reliable conclusions cannot be drawn from analysing grouped methods on this occasion. Therefore, results from all method groups have been pooled for analysis.

5. **Outlier Results**

No outliers were reported for this round.

6. **Reference**

- [1] *Guide to Proficiency Testing Australia*, 2019. (This document can be found on the PTA website, www.pta.asn.au)

APPENDIX A

Results and Data Analysis

Antimony	A1.1
Arsenic	A2.1
Bismuth	A3.1
Cadmium	A4.1
Copper	A5.1
Fluorine	A6.1
Gold	A7.1
Iron	A8.1
Lead	A9.1
Magnesium Oxide	A10.1
Manganese	A11.1
Nickel	A12.1
Silver	A13.1
Sulphur	A14.1
Zinc	A15.1

Antimony (Sb) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique
2	1	0.48	0.01	#	6	#
	2	0.49				
6	1	0.49	0.01	#	6	#
	2	0.48				
7	1	0.534	#	0.0001	2	#
	2	0.535				

Statistical analysis has not been performed as results were not normally distributed.

Notes:

indicates no result returned.

Arsenic (As) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique
2	1	5.24	0.1	#	6	#
	2	5.23				
5	1	4.58	0.06 ± 0.02	0.005	6	Fusion
	2	4.69				
6	1	5.31	0.1	#	6	#
	2	5.19				
7	1	5.16	#	0.001	1	#
	2	5.17				

Statistical analysis has not been performed as results were not normally distributed.

Notes:

indicates no result returned.

Bismuth (Bi) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	0.021	0.005	#	6	#	0.00
	2	0.02					-0.71
6	1	0.021	0.005	#	6	#	0.00
	2	0.018					-2.14
7	1	0.0210	#	0.00001	2	#	0.00
	2	0.0212					0.14

Notes:

indicates no result returned.

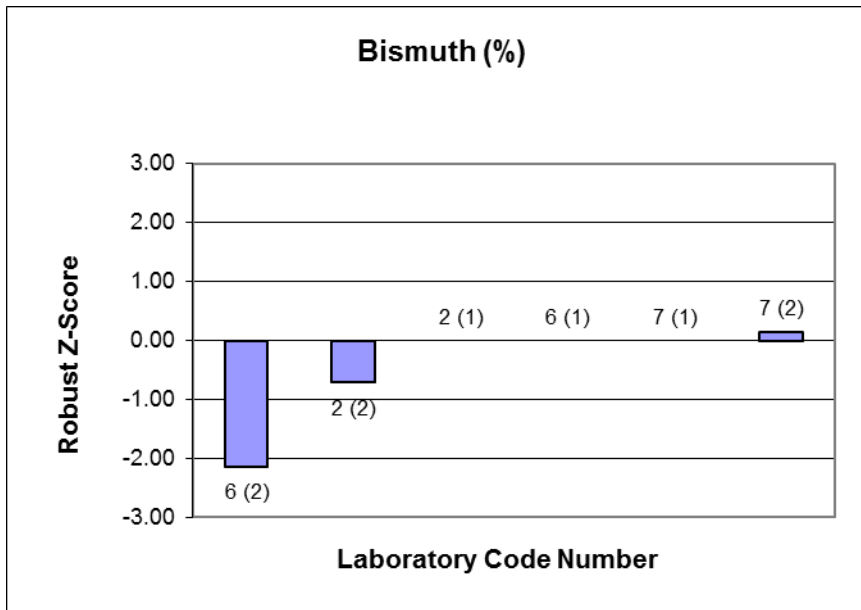
Summary Statistics

No. results	6
Median	0.0210
Normalised IQR	0.0014
Target CV*	6.7%
Min	0.018
Max	0.0212
Range	0.0032
Uncertainty (Median)	0.0006

Note:

The robust CV achieved for this test was low (robust CV = 3.4%) and using this value would have resulted in some laboratories unfairly receiving outliers. In this case, a target robust CV = 6.7 % was considered more appropriate and was used to determine z-scores.

Bismuth (Bi) (%) Ordered Z-Score Chart



Cadmium (Cd) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	0.006	#	#	1	#	0.00
	2	0.006					0.00
6	1	0.006	#	#	1	#	0.00
	2	0.006					0.00
7	1	0.0072	#	0.00005	2	#	1.70
	2	0.0070					1.42

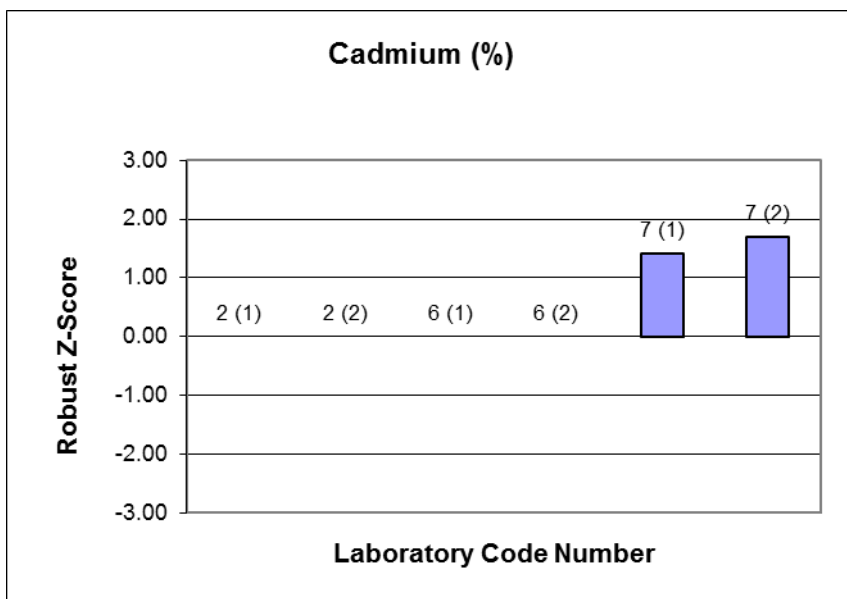
Note:

indicates no result returned.

Summary Statistics

No. results	6
Median	0.00600
Normalised IQR	0.00070
Robust CV	11.7%
Min	0.006
Max	0.0072
Range	0.0012
Uncertainty (Median)	0.00029

Cadmium (Cd) (%) Ordered Z-Score Chart



Copper (Cu) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	13.0	0.6	#	6	#	0.00
	2	13.0					0.00
5	1	12.80	26.1 ± 1.0	0.005	6	Fusion	-0.77
	2	13.00					0.00
6	1	13.3	0.6	#	6	#	1.15
	2	12.8					-0.77
7	1	12.6	#	0.0002	1	#	-1.54
	2	13.0					0.00

Notes:

indicates no result returned.

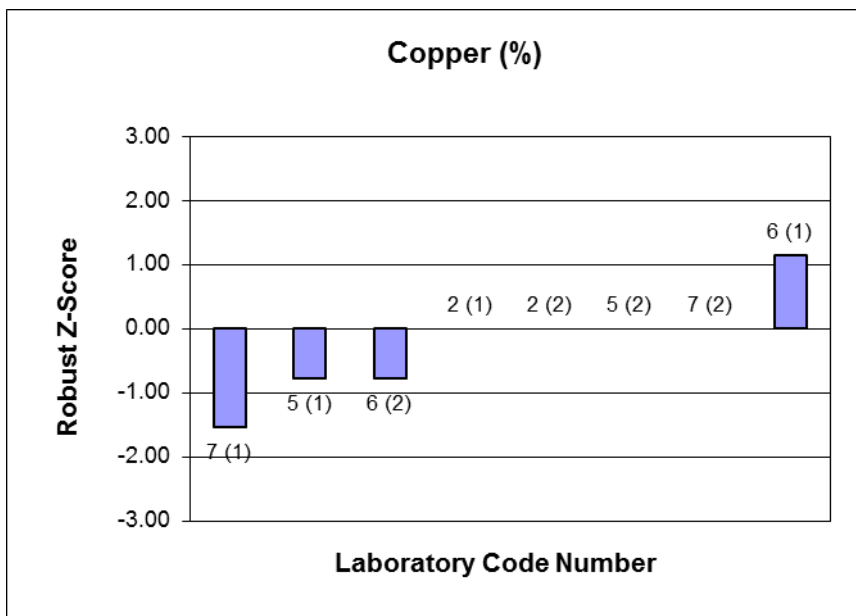
Summary Statistics

No. results	8
Median	13.000
Norm IQR	0.260
Target CV	2.0%
Min	12.6
Max	13.3
Range	0.7
Uncertainty (Median)	0.092

Note:

The robust CV achieved for this test was low (robust CV = 1.4%) and using this value may have resulted in some laboratories unfairly receiving outliers. In this case, a target robust CV = 2.0 % was considered more appropriate and was used to determine z-scores.

Copper (Cu) (%) Ordered Z-Score Chart



Fluorine (F) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique
2	1	0.046	#	#	Electrode	#
	2	0.043				
6	1	0.018	#	#	Electrode	#
	2	0.02				
7	1	0.02	#	0.01	Specific Ion Electrode	#
	2	0.02				

Statistical analysis has not been performed as results were not normally distributed.

Notes:

indicates no result returned.

A7.1

Gold (Au) (ppm)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique
2	1	0.1	0.03	#	1	#
	2	0.1				
6	1	0.1	0.03	#	1	#
	2	0.1				
7	1	0.007	#	0.001	1	#
	2	0.008				

Statistical analysis has not been performed as results were not normally distributed.

Notes:

indicates no result returned.

Iron (Fe) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	3.21	0.08	#	6	#	0.32
	2	3.27					1.27
5	1	3.09	6.43 ± 0.20	0.1	6	Fusion	-1.59
	2	3.19					0.00
6	1	3.29	0.08	#	6	#	1.59
	2	3.16					-0.48
7	1	3.18	#	0.01	1	#	-0.16
	2	3.19					0.00

Notes:

indicates no result returned.

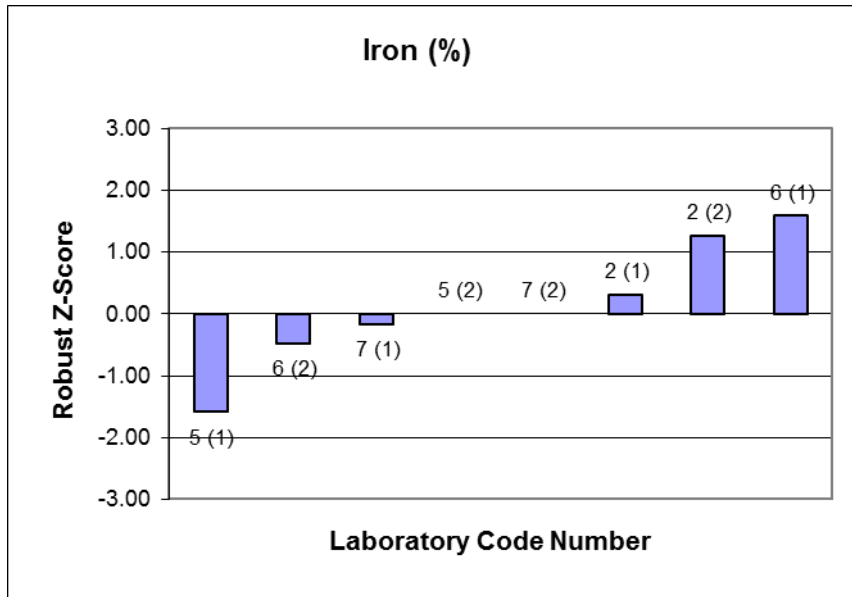
Summary Statistics

No. results	8
Median	3.190
Norm IQR	0.063
Target CV	2.0%
Min	3.09
Max	3.29
Range	0.20
Uncertainty (Median)	0.022

Note:

The robust CV achieved for this test was low (robust CV = 1.4%) and using this value may have resulted in some laboratories unfairly receiving outliers. In this case, a target robust CV = 2.0 % was considered more appropriate and was used to determine z-scores.

Iron (Fe) (%) Ordered Z-Score Chart



Lead (Pb) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique
2	1	<0.1	0.006	#	6	#
	2	<0.1				
6	1	<0.1	0.006	#	6	#
	2	<0.1				
7	1	0.0331	#	0.0001	2	#
	2	0.0335				

Statistical analysis has not been performed as only a small number of numerical results (2) were returned

Notes:

indicates no result returned.

Magnesium Oxide (MgO) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	0.19	0.06	#	6	#	0.21
	2	0.18					-0.21
6	1	0.19	0.06	#	6	#	0.21
	2	0.21					1.06
7	1	0.16	#	0.01	1	#	-1.06
	2	0.15					-1.49

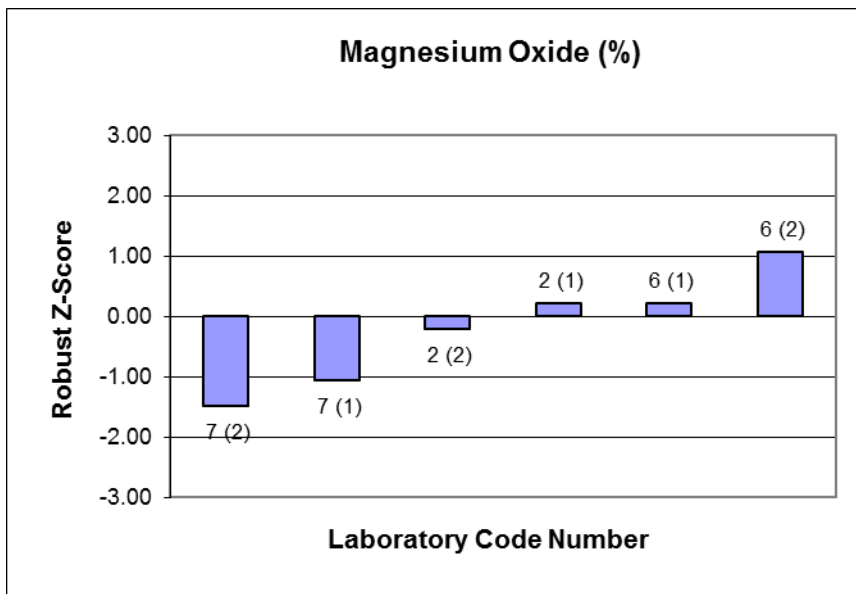
Notes:

indicates no result returned.

Summary Statistics

No. results	6
Median	0.185
Norm IQR	0.024
Robust CV	12.7%
Min	0.16
Max	0.21
Range	0.05
Uncertainty (Median)	0.010

Magnesium Oxide (MgO) (%) Ordered Z-Score Charts



Manganese (Mn) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	0.09	0.03	#	6	#	0.00
	2	0.07					-2.84
6	1	0.09	0.03	#	6	#	0.00
	2	0.09					0.00
7	1	0.100	#	0.005	1	#	1.42
	2	0.100					1.42

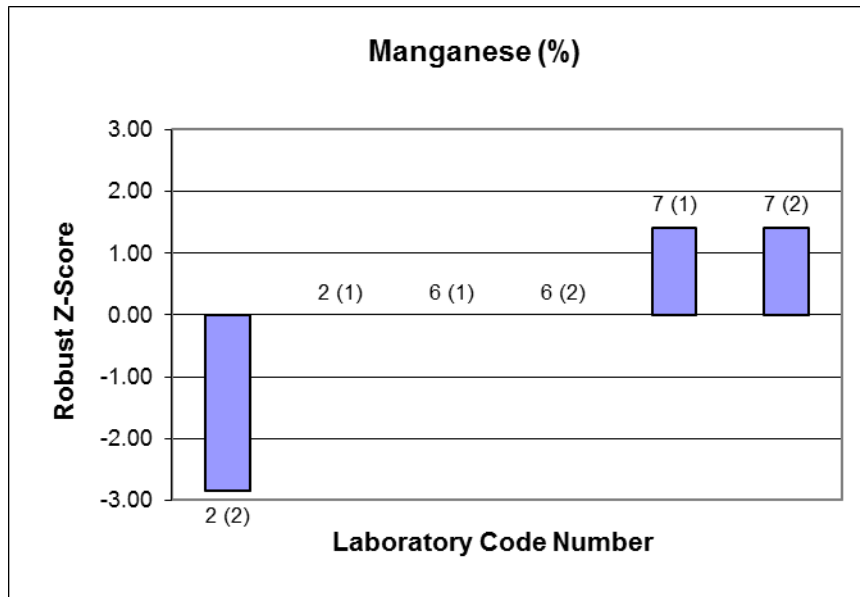
Notes:

indicates no result returned.

Summary Statistics

No. results	6
Median	0.0900
Norm IQR	0.0070
Robust CV	7.8%
Min	0.07
Max	0.100
Range	0.030
Uncertainty (Median)	0.0029

Manganese (Mn) (%) Ordered Z-Score Charts



Nickel (Ni) (%)

Lab Code	Duplicate	Result (%)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	0.016	0.01	#	6	#	0.00
	2	0.016					0.00
6	1	0.015	0.01	#	6	#	-0.79
	2	0.016					0.00
7	1	0.0178	#	0.0002	2	#	1.42
	2	0.0184					1.89

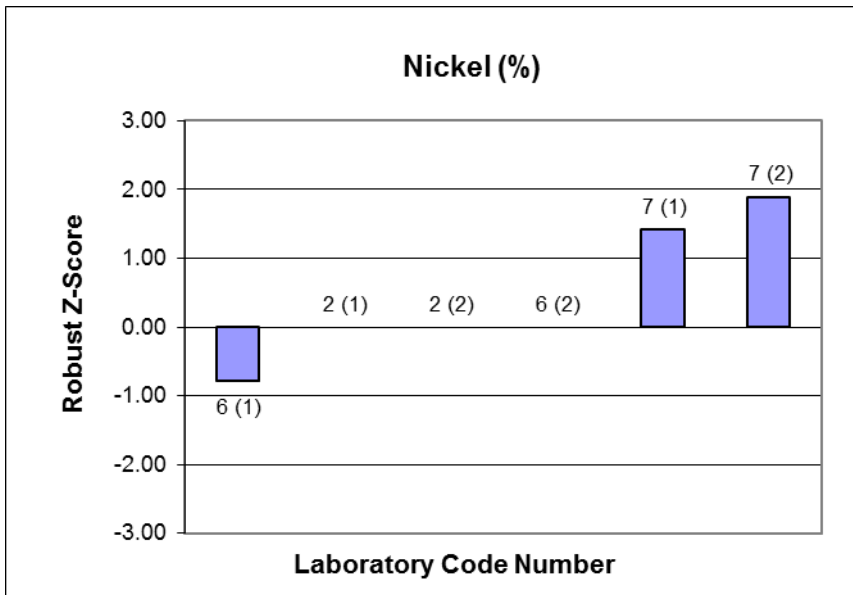
Notes:

indicates no result returned.

Summary Statistics

No. results	6
Median	0.0160
Norm IQR	0.0013
Robust CV	7.9%
Min	0.015
Max	0.0184
Range	0.0034
Uncertainty (Median)	0.0005

Nickel (Ni) (%) Ordered Z-Score Charts



Silver (Ag) (ppm)

Lab Code	Duplicate	Result (ppm)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	87	3	#	3	#	0.25
	2	84					-0.25
5	1	82	144.3 ± 6.3	3	3	Aqua Regia	-0.59
	2	82					-0.59
6	1	87	3	#	3	#	0.25
	2	84					-0.25
7	1	100	#	0.1	2	#	2.44
	2	103					2.94

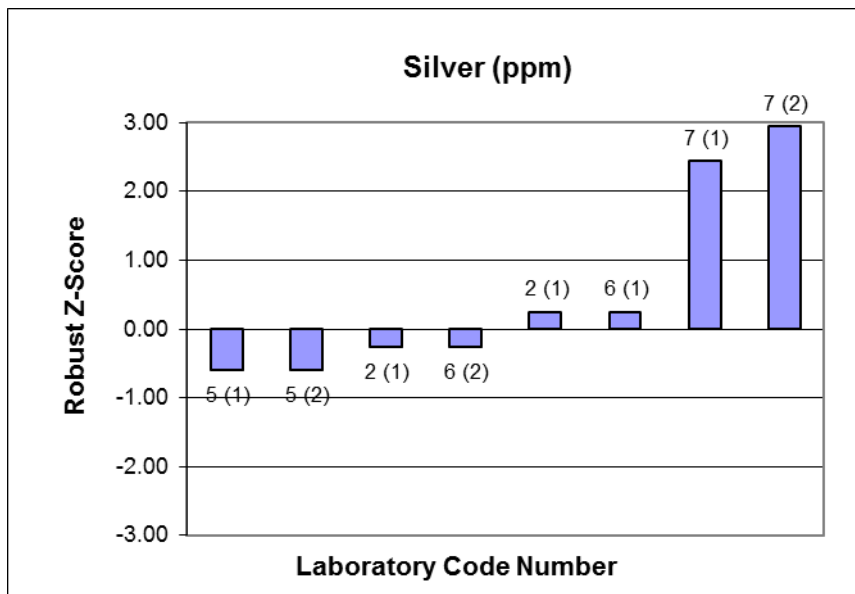
Notes:

indicates no result returned.

Summary Statistics

No. results	8
Median	85.5
Norm IQR	5.9
Robust CV	7.0%
Min	82
Max	103
Range	18
Uncertainty (Median)	2.1

Silver (Ag) (ppm) Ordered Z-Score Charts



Sulphur (S) (%)

Lab Code	Duplicate	Result (ppm)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	1.53	0.04	#	6	#	-0.45
	2	1.53					-0.45
5	1	1.56	4.01 ± 0.32	0.1	6	Fusion	0.91
	2	1.51					-1.36
6	1	1.57	0.04	#	6	#	1.36
	2	1.52					-0.91
7	1	1.55	#	0.01	#	#	0.45
	2	1.55					0.45

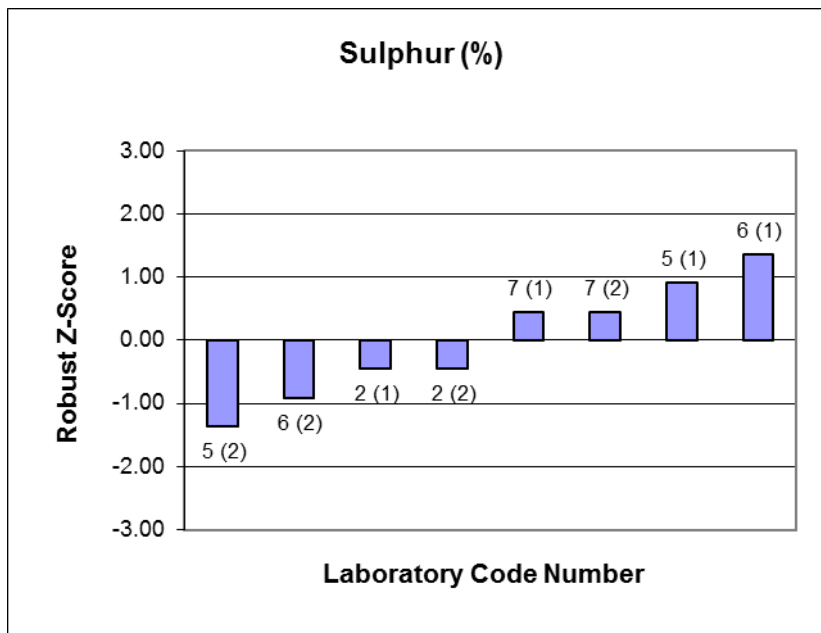
Notes:

indicates no result returned.

Summary Statistics

No. results	8
Median	1.540
Norm IQR	0.022
Robust CV	1.43%
Min	1.51
Max	1.57
Range	0.06
Uncertainty (Median)	0.008

Sulphur (S) (%) Ordered Z-Score Charts



Zinc (Zn) (%)

Lab Code	Duplicate	Result (ppm)	MU	Detection Limit	Method Code	Dissolution/Digestion Technique	Robust z-score
2	1	0.67	0.03	#	6	#	0.61
	2	0.68					0.79
5	1	0.59	0.04 ± 0.03	0.01	6	Fusion	-0.84
	2	0.61					-0.48
6	1	0.70	0.03	#	6	#	1.15
	2	0.66					0.43
7	1	0.6100	#	0.0005	1	#	-0.48
	2	0.6130					-0.43

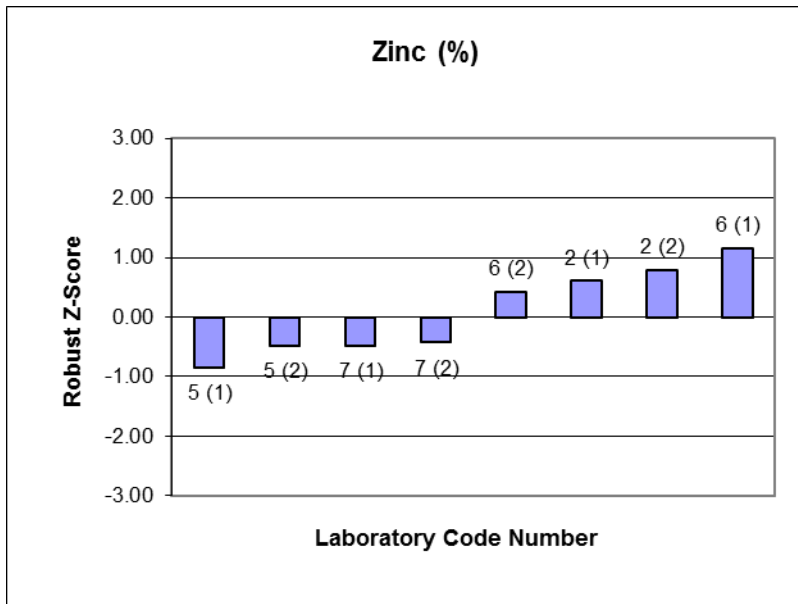
Notes:

indicates no result returned.

Summary Statistics

No. results	8
Median	0.6365
Norm IQR	0.0550
Robust CV	8.7%
Min	0.59
Max	0.70
Range	0.11
Uncertainty (Median)	0.0195

Zinc (Zn) (%) Ordered Z-Score Charts



APPENDIX B

Homogeneity and Stability

Homogeneity and Stability

Samples dispatched for this round were NCS Testing Technology Co., Ltd certified reference material NCS DC 28055 Copper Ore and therefore, considered homogeneous and stable for the duration of the round.

APPENDIX C

Documentation

Instructions to Participants

C1

Results Sheet

C4

PROFICIENCY TESTING AUSTRALIA

Proficiency Testing Program Geochemical Testing – Round 15

INSTRUCTIONS TO PARTICIPANTS

Please read instructions carefully **BEFORE** commencing testing.

To ensure that the results of this program can be analysed properly, participants are asked to carefully note the following:

1. Samples

- One **Copper Ore** sample of approximately 50g has been provided for each laboratory.

Please make sure your sample is thoroughly mixed before analysis and in between duplicates

2. Testing

- The testing should commence as soon as possible after receipt of the sample.
- Samples to be analysed for the below elements on a dry basis.

Antimony	Sb	Fluorine	F	Manganese	Mn
Arsenic	As	Gold	Au	Nickel	Ni
Bismuth	Bi	Iron	Fe	Silver	Ag
Cadmium	Cd	Lead	Pb	Sulphur	S
Copper	Cu	Magnesium Oxide	MgO	Zinc	Zn

- Please Note: Where possible, proficiency testing samples should be treated as a routine laboratory sample.

3. Safety

- The samples are for laboratory use only.
- All required safety procedures should be followed.

4. Reporting

- Please submit results on the Results Sheet provided.
- Duplicate results are requested.
- Please specify the dissolution/digestion technique used and record the method of analysis using the attached codes (refer to page 3). Details should be provided of any method techniques that are used that are not specified in the table on page 3.
- Results should be quoted in elemental form as in listed in 2 (on previous page) and on the results sheet.
- Please report each element to the units (% or ppm) indicated on the Results Sheet along with your laboratory's detection limit for that analysis.
- Laboratories are requested to calculate and report an estimate of uncertainty of measurement for each reported measurement result.
- All estimates of uncertainty of measurement must be given as a 95% confidence interval (coverage factor $k \approx 2$). Please note that MU will not be used to evaluate participant performance in this program.
- The following significant figures are recommended for reporting:
XX.XX%, X.XX%, 0.XXX%, 0.00XX%.

5. Please return results no later than **FRIDAY 3 JANUARY 2020** to:

Kathy Weller

fax: +61 7 3217 1844

email: Kathy.Weller@pta.asn.au

6. For this program your laboratory has been allocated the code number shown on the results sheet. All reference to your laboratory in reports associated with this program will be by this code number, thus ensuring confidentiality of results.

Analysis Method Codes to be used for the Results Sheets

Method Technique	Method Code
Inductively coupled plasma atomic emission spectrometry	1
Inductively coupled plasma mass spectrometry	2
Atomic absorption spectrometry	
Flame	3
Graphite furnace	4
Hydride generation	5
X-ray fluorescence spectrometry	6
Classical wet chemical analysis	7
Colorimetric	8
Neutron activation analysis	9
Leco combustion analysis	10
Other – please specify	11

Please use a Method Code for each element tested.

PROFICIENCY TESTING AUSTRALIA
Geochemical – Round 15 - Proficiency Testing Program
Results Sheet

Lab Code:

2

Analysis	Result 1	Result 2	Units	Detection Limit	Dissolution/ Digestion Technique (Please Specify)	Method Code	±MU*
Antimony, Sb			%				
Arsenic, As			%				
Bismuth, Bi			%				
Cadmium, Cd			%				
Copper, Cu			%				
Fluorine, F			%				
Gold, Au			ppm				
Iron, Fe			%				
Lead, Pb			%				
Magnesium Oxide, MgO			%				
Manganese, Mn			%				
Nickel, Ni			%				
Silver, Ag			ppm				
Sulphur, S			%				
Zinc, Zn			%				

MU* Laboratories' Uncertainty of Measurement. Please report in the same units as the results for each element.

Return no later than **FRIDAY 3 JANUARY 2020**, to:

Kathy Weller, Proficiency Testing Australia.

phone: +61 7 3721 7373, fax: +61 7 3217 1844, email: Kathy.Weller@pta.asn.au

- End of Report -