Report No. 1095

Waters Proficiency Testing Program

Round No. 229

- Total Cyanide, Weak Acid Dissociable Cyanide, Free Cyanide -

August 2018

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Dr M Buckley-Smith, Global Proficiency Ltd (New Zealand). Also our thanks go to Global Proficiency Ltd (New Zealand) and to Global Proficiency Pty Ltd (Australia) for the supply and distribution of the samples.

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CONTENTS

1. Foreword

This report summarises the results of a proficiency testing program on the determination of Total Cyanide, Weak Acid Dissociable Cyanide and Free Cyanide in waters. This is round 229 in a planned series of programs involving the analysis of chemical and physical parameters of waters. This program is accredited to ISO/IEC 17043:2010 "*Conformity assessment - General requirements for proficiency testing"* by International Accreditation New Zealand (IANZ).

The exercise was conducted in May 2018 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 D Mihaila and the Technical Adviser was Dr M Buckley-Smith, Global Proficiency Ltd (New Zealand). 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. Please note that a number of laboratories reported more than one set of results and, therefore, their code numbers (with letter) could appear several times in the same data set.

2.2 Laboratories were provided with the "Instructions to Participants" and "Results Sheet" (see Appendix C). Laboratories were requested to perform the tests according to their routine methods.

2.3 Participants were provided with two vials (labelled Cyanide, Sample PTA 1 and Sample PTA 2) containing solutions of Total Cyanide, Weak Acid Dissociable Cyanide and Free Cyanide.

2.4 A total of 24 laboratories received samples, comprising:

- 17 Australian participants; and
- 7 overseas participants, including:
    - Indonesia (1), New Zealand (3), Papua New Guinea (2), Vietnam (1).

Of these 24 laboratories, one was unable to submit results by the due date.

2.5 Results (as reported by participants) with corresponding summary statistics (i.e. number of results, median, normalised interquartile range, uncertainty of the median, robust coefficient of variation, minimum, maximum and range) are presented in Appendix A (for each sample and for each of the analyses performed).

2.6 A robust statistical approach, using z-scores, was utilised to assess laboratories' testing performance (see Section 3). Robust z-scores and ordered z-score charts relevant to each test are presented in Appendix A.

The document entitled *Guide to Proficiency Testing Australia,* 2016 (reference [1]) defines the statistical terms and details the statistical procedures referred to in this report.

2.7 A tabulated listing of laboratories (by code number) identified as having outlier results can be found on page 16.

2.8 Prior to sample distribution, a number of randomly selected samples were analysed for homogeneity and stability. Based on the results of this testing (see Appendix B) it was considered that the samples utilised for this program were homogeneous and stable. As such, any results later identified as outliers could not be attributed to any notable sample variability.

3. Statistical Format

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

- 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 with an absolute value less than or equal to 2.0 is considered to be satisfactory, 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 "§". Laboratories are also encouraged to review results which have an absolute z-score value between 2.0 and 3.0 (i.e. $2.0 < |z\text{-score}| < 3.0$). These are considered to be questionable results.

Each determination was examined for outliers with all methods pooled. The table on page 16 summarises the outlier results detected.

3.2 Results Tables and Summary Statistics

The tables in Appendix A contain the results returned by each laboratory, including the code number for the method used and 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.

A list of summary statistics appears at the bottom of each of the results tables and consists of:

- *No. of Results*: the total number of results for that test/sample;
- *Median*: the middle value of the results;
- *Normalised IQR*: the normalised interquartile range of the results;
- *Uncertainty of the Median*: a robust estimate of the standard deviation of the *Median*;
- *Robust CV*: the robust coefficient of variation expressed as a percentage, i.e. 100 x *Normalised IQR* / *Median*;
- *Minimum*: the lowest laboratory result;
- *Maximum*: the highest laboratory result; and
- *Range*: the difference between the *Maximum* and *Minimum*.

The median is a measure of the centre of the data.

The normalised IQR is a measure of the spread of the results. It is calculated by multiplying the interquartile range (IQR) by a correction factor, which converts the IQR to an estimate of the standard deviation. The IQR is the difference between the upper and lower quartiles (i.e. the values above and below which a quarter of the results lie, respectively).

For normally distributed data, the uncertainty of the median is approximated by:

$$\sqrt{\frac{\pi}{2}} \times \frac{normIQR}{\sqrt{n}}$$

n = number of results.

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

3.3 Ordered Z-score Charts

The charts in Appendix A indicate each laboratory's robust z-score, in order of magnitude, marked with its laboratory 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.

4. PTA and Technical Adviser's Comments

4.1 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.

Sample preparation was undertaken according to Global Proficiency Ltd's Standard Operating Procedures to ensure samples were fit-for-purpose, homogeneous and stable.

Solutions were stable and homogeneous, and medians obtained from this proficiency round approximated the expected levels (dope concentration), as shown in Table 1. The median recovery of Total Cyanide for sample PTA 1 was 93.7%, compared with 88.7% for PTA 2. Recoveries were much better for WAD and Free Cyanide, ranging between 96%-102%.

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 for each analyte has been calculated and is presented in Table 1 below.

Table 1. Comparison of expected levels (dope concentration) and proficiency medians. The values of the calculated uncertainty of the median are also presented.

Analyte	Sample	Dope Concentration (mg/L)	Median (mg/L)	Uncertainty of the Median (mg/L)
Total Cyanide	PTA 1	0.95	0.8900	0.0314
	PTA 2	11.5	10.200	0.456
Weak Acid Dissociable Cyanide	PTA 1	0.25	0.2525	0.0113
	PTA 2	3.5	3.375	0.166
Free Cyanide	PTA 1	0.25	0.2550	0.0179
	PTA 2	3.5	3.475	0.440

The uncertainties of proficiency medians were below 5% for Total Cyanide and Weak Acid Dissociable Cyanide. Higher values (PTA 1: 7.02% and PTA 2: 12.66%) were obtained for Free Cyanide, where the number of results submitted was below 10.

4.2 Analysis of Round 229 Results

4.2.1 Total Cyanide

Table 2 compares the Total Cyanide medians and robust CVs from this round to those obtained in previous PTA rounds. The variability of results for sample PTA 1 was comparable to those seen in the past two rounds, however, sample PTA 2 had CVs wider than seen previously. Participants' results in this round also showed more variability than published precision information in APHA 4500 CN^- C+E (Distillation + Colorimetric), which indicated laboratories should be able to achieve CVs of 4.18%-6.02%, at the Total Cyanide concentrations presented in this study [2]. APHA also indicated that single operator precision could vary by as much as 11-12%, which is closer to the CVs observed historically.

Table 2. Comparison of current round variability and proficiency medians of Total Cyanide testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	0.8900	12.9	21
	PTA 2	10.200	16.4	21
Report 1037	PTA 1	0.6825	11.5	30
	PTA 2	9.535	12.8	30
Report 931	PTA 1	0.3480	10.0	27
	PTA 2	14.73	11.6	27

Both samples were made from reagent water and contained both Potassium Cyanide and Potassium Ferrocyanide as the WAD and bound components making up Total Cyanide. As mentioned previously, the median recovery of Total Cyanide was 93.7% for the low concentration sample PTA 1 (0.89 mg/L), compared with 88.7% for the higher concentration sample PTA 2 (10.2 mg/L). APHA states that recoveries should be at least 100% ± 4% from a 1 mg CN-/L standard solution (APHA 4500 CN- C 4.g), and duplicates within the single operator precision stated in the method (~12%).

Bias / Accuracy

The Total Cyanide testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 0.756 – 1.075 mg/L for sample PTA 1 and 8.85 – 12.7 mg/L for sample PTA 2.

Out of 21 participants, one questionable result ($2.0 < |z\text{-score}| < 3.0$) was reported for sample PTA 1 (laboratory 294). No questionable results were reported for sample PTA 2.

Three outlier results ($|z\text{-score}| \geq 3.0$) were obtained for sample PTA 1, requiring follow-up action by laboratories 417, 683 and 738. Three outlier were also obtained for sample PTA 2, requiring follow-up action by laboratories 294, 683 and 738.

The method most frequently used for Total Cyanide testing in this round was APHA 4500 CN^- C+E (Distillation + Colorimetric) method, which was used by 11 out of 21 participants. Of these 11 participants, three had modified this method for use with a

discrete analyser. The Total Cyanide data sets formed approximately normal distributions with no notable bias attributable to any one method (Figures 1 and 2).

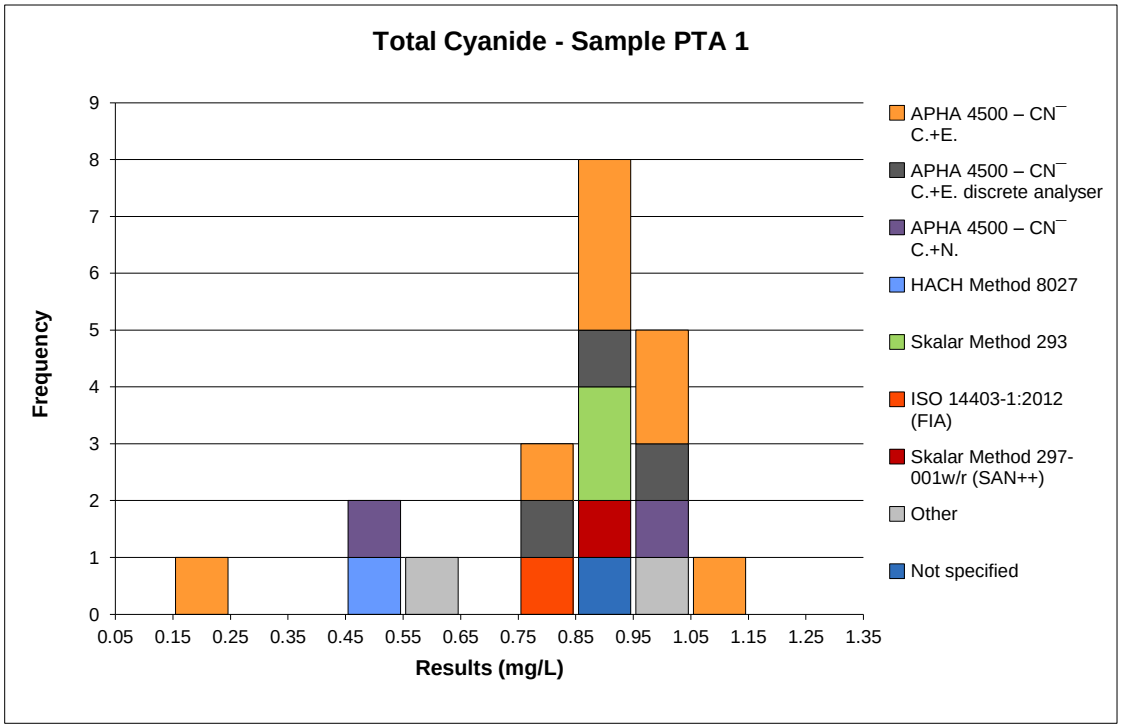


Figure 1. Spread of results for Total Cyanide testing of sample PTA 1, with a median of 0.8900 mg/L.

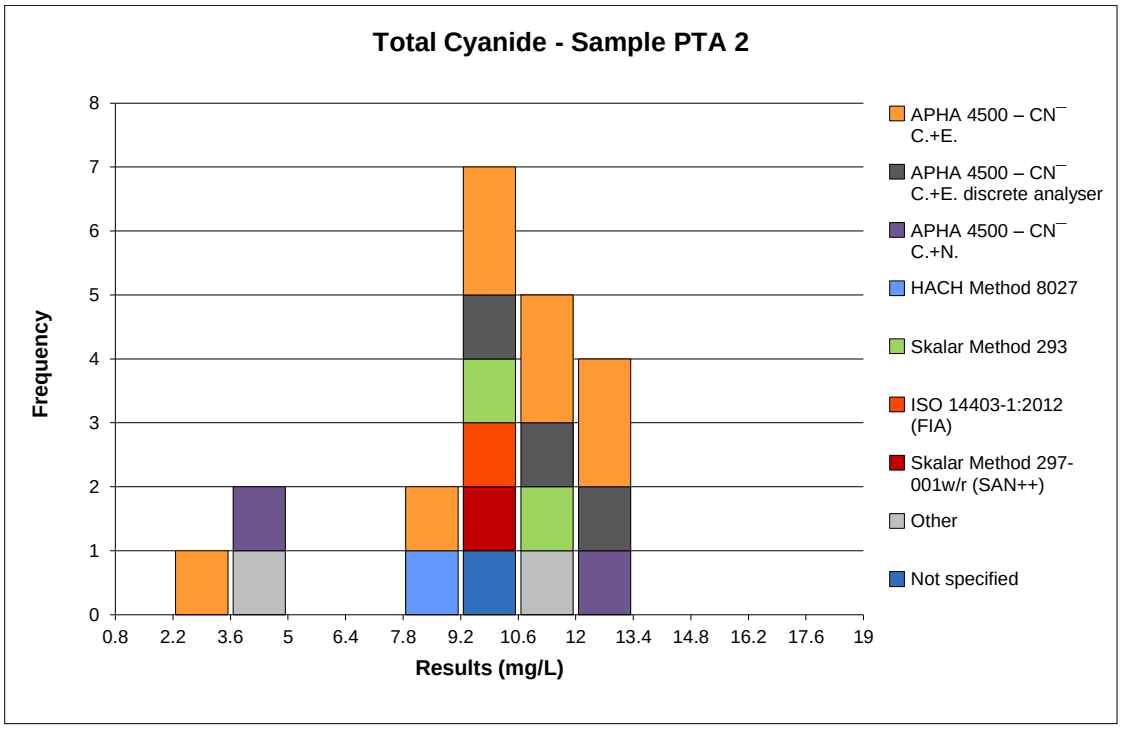


Figure 2. Spread of results for Total Cyanide testing of sample PTA 2, with a median of 10.200 mg/L.

Laboratories with results at approximately 0.25 mg/L for sample PTA 1 and 3.5 mg/L for sample PTA 2 have only managed to recover the Weak Acid Dissociable portion of the total cyanide in samples, failing to recover the bound Potassium Ferrocyanide. APHA recommends the daily testing of apparatus, reagents and other potential variables to be carried out using a complex cyanide such as Potassium Ferricyanide in the concentration range of interest, rather than the simple sodium or Potassium Cyanide [2]. For additional assistance with Quality Control (QC) practices please refer to APHA [2] and/or BC Environmental Lab Manual [3].

The majority of laboratories had a very good understanding of their measurement uncertainty (MU), and submitted MU ranging between 8%-25%. Laboratories 228, 294 and 738 chose to use a fixed MU of ±0.305, ±0.2 and ±0.32 mg/L respectively, whereas the remaining 17 laboratories used a variable MU.

4.2.2 Weak Acid Dissociable (WAD) Cyanide

Table 3 compares the WAD Cyanide medians and robust CVs from this round to those obtained in previous PTA rounds. Variability of results was comparable to those seen in the past two rounds, and medians were very close to the doping concentration (Table 1). The CVs from this round were also comparable to published precision information in APHA 4500 CN- I+E (Colorimetric), which indicated laboratories should be able to achieve CVs of 8.4%-13.0% for various water types, at the WAD Cyanide concentrations presented in this study [2].

Table 3. Comparison of current round variability and proficiency medians WAD Cyanide testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	0.2525	13.4	14
	PTA 2	3.375	14.7	14
Report 1037	PTA 1	0.2045	9.8	20
	PTA 2	3.010	11.6	20
Report 931	PTA 1	0.1060	14.9	20
	PTA 2	5.280	8.4	20

Bias / Accuracy

The WAD Cyanide testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 0.195 – 0.286 mg/L for sample PTA 1 and 2.56 – 3.93 mg/L for sample PTA 2.

Out of 14 participants, no questionable results (2.0 < |z-score| < 3.0) were reported for either sample PTA 1 or PTA 2.

One outlier result (|z-score| ≥ 3.0) was obtained for each of the samples PTA 1 and PTA 2, requiring follow-up action by laboratory 494A.

APHA suggests that one likely cause of a high bias on WAD testing is exposure to UV light which can cause photodecomposition of some metal-cyanide complexes. APHA also recommends a fivefold excess of zinc acetate solution before adding acid and distilling for WAD Cyanide analysis (APHA 4500 CN- I 2.). APHA's recommended QC for WAD Cyanide analysis includes the daily use of method blanks, Laboratory fortified blanks, Laboratory fortified matrix, and duplicates on every batch of 20 or less samples [2].

The WAD Cyanide data sets formed approximately normal distributions with no notable bias attributable to any one method (Figures 3 and 4). The method most frequently used for WAD Cyanide testing in this round was APHA 4500 CN^- I+E (Distillation + Colorimetric), which was used by seven out of 14 participants (of which four participants had modified this method for use with a discrete analyser).

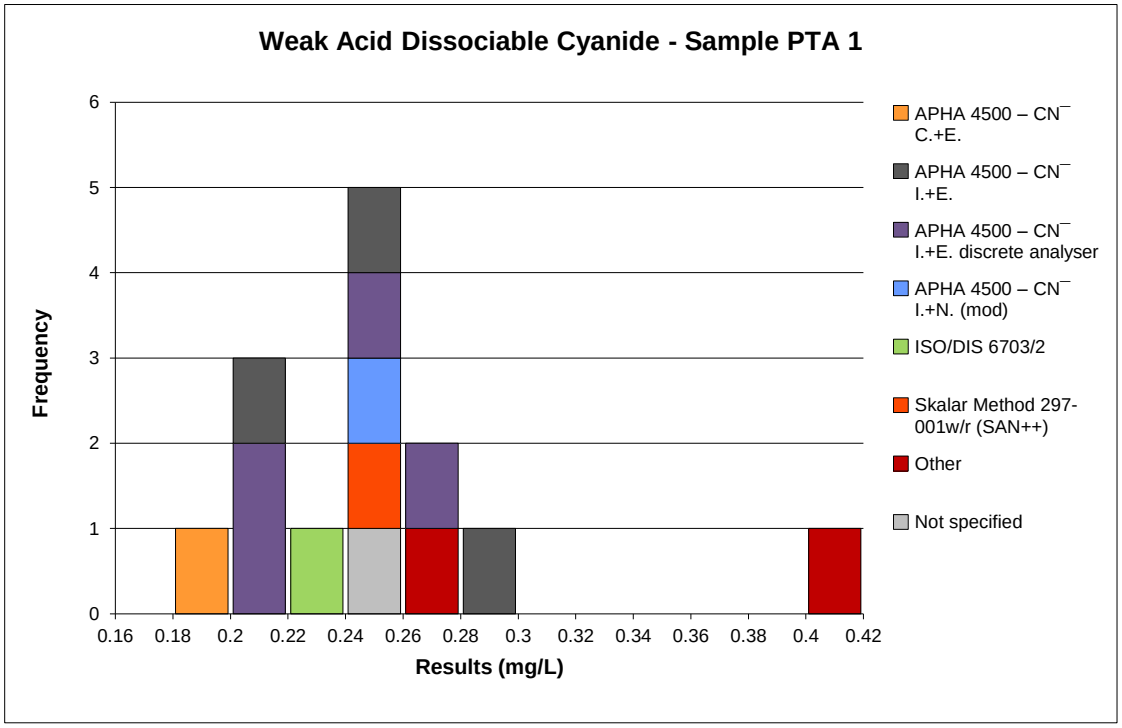


Figure 3. Spread of results for Weak Acid Dissociable Cyanide testing of sample PTA 1, with a median of 0.2525 mg/L.

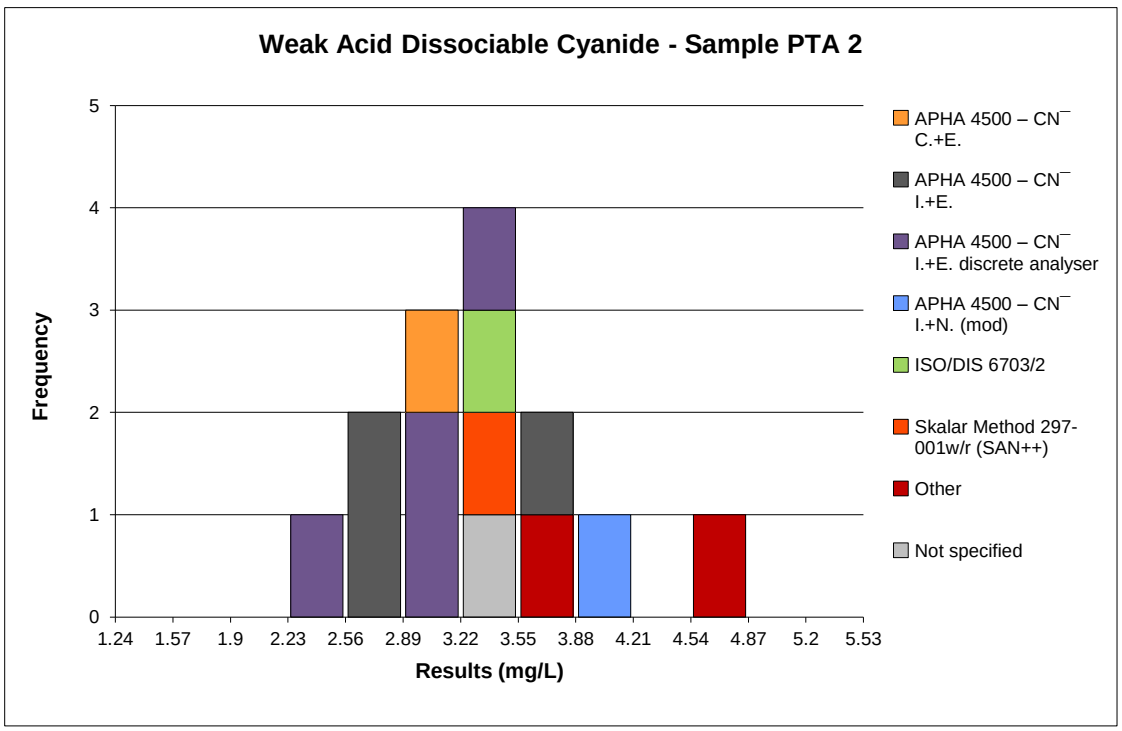


Figure 4. Spread of results for Weak Acid Dissociable Cyanide testing of sample PTA 2, with a median of 3.375 mg/L.

The vast majority of participant laboratories had a very good understanding of their MU, as can be seen in Figures 5 and 6. The majority of laboratories submitted MUs

between 10%-20% of their reported WAD value. Laboratories who reported a fixed MU irrespective of WAD value (e.g. laboratories 228 and 738), were in the greatest danger of overestimating their MU, particularly at lower WAD levels seen in sample PTA 1.

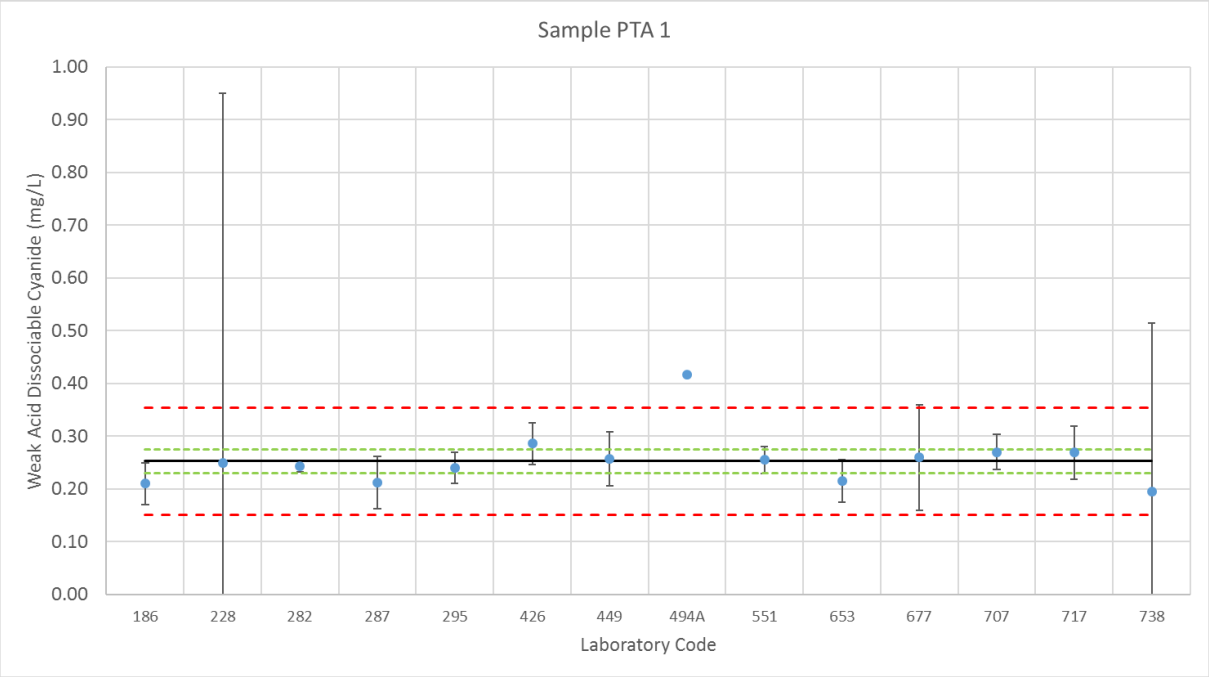


Figure 5. Laboratory Measurement Uncertainty for WAD Cyanide testing of sample PTA 1, including the median (——), uncertainty of the median (- - -), and 3xNIQR U_{max} (- - -).

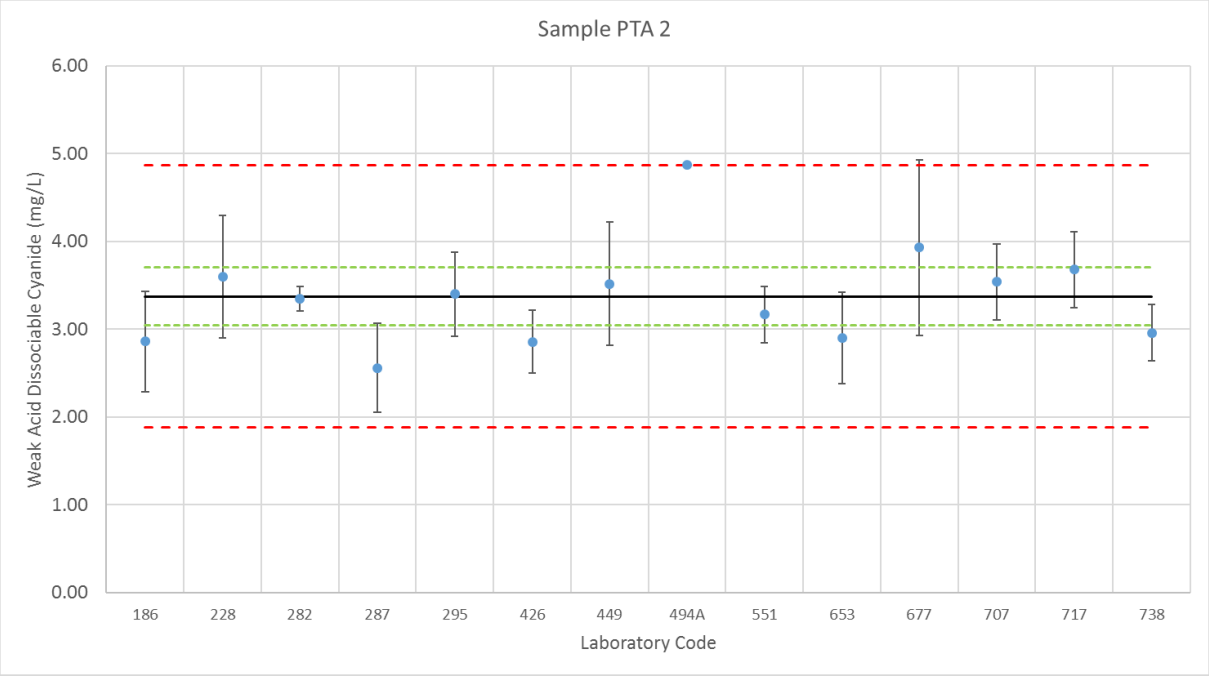


Figure 6. Laboratory Measurement Uncertainty for WAD Cyanide testing of sample PTA 2, including the median (——), uncertainty of the median (- - -), and 3xNIQR U_{max} (- - -).

4.2.3 Free Cyanide

Table 4 compares the Free Cyanide medians and robust CVs from this round to those obtained in previous PTA rounds. Lower numbers of participants will have contributed to the wider CVs observed in this round.

Table 4. Comparison of current round variability and proficiency medians of Free Cyanide testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	0.2550	16.8	9
	PTA 2	3.475	28.6	8
Report 1037	PTA 1	0.2020	8.8	15
	PTA 2	3.010	10.0	15
Report 931	PTA 1	0.1080	16.1	16
	PTA 2	5.060	13.3	17

Bias / Accuracy

The Free Cyanide testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 0.206 – 0.300 mg/L for sample PTA 1 and 1.54 – 3.73 mg/L for sample PTA 2.

Out of nine results submitted for sample PTA 1 and eight results for sample PTA 2, two questionable results (2.0 < |z-score| < 3.0) were reported for sample PTA 1 (laboratories 189 and 228). No questionable results were reported for sample PTA 2.

No outlier results (|z-score| ≥ 3.0) were obtained for either sample PTA 1 or PTA 2. However, considering the doping concentration in Table 1 for these samples, laboratories receiving questionable results may wish to carry out additional follow-up.

Also of interest was the observation that laboratories who submitted results for both WAD and Free Cyanide (laboratories 228, 426, 449, 653 and 677), consistently produced lower cyanide results for their Free Cyanide method.

Additionally, laboratory 707 reported Free Cyanide results of "<6.0 mg/L" for both samples PTA 1 and PTA 2 using the Titrimetric method APHA 4500 CN- I+D (modified). These results were not statistically deemed outliers or questionable, as the medians for samples PTA 1 and PTA 2 were 0.255 and 3.475 mg/L, respectively. This limit of quantitation was likely based on the Trade Waste guidelines for release to sewer systems which sets a Specific Acceptance Guideline Value of 5 mg/L for Cyanide as WAD [4], rather than the technical limit of quantitation for the method (≥ 1 mg/L) [3] or the Australian Drinking Water Guideline, that has a maximum of 0.08 mg/L Cyanide [5]. It is important that laboratories check their local bylaws if they wish to use such a reporting limit criteria. For example Hamilton City Council in New Zealand sets the Cyanide limit at 1 mg/L [6]. Local bylaws can also have an impact on acceptable disposal of these proficiency samples post-round.

The Free Cyanide data sets formed approximately normal distributions with no notable bias attributable to any one method (Figures 7 and 8).

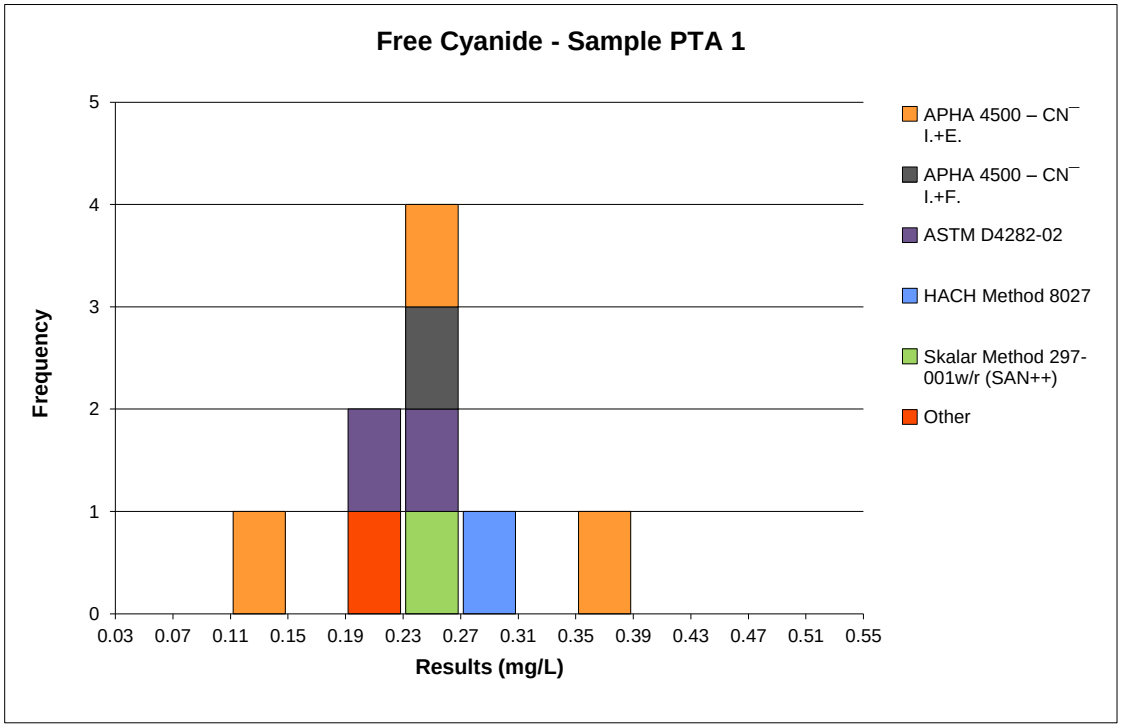


Figure 7. Spread of results for Free Cyanide testing of sample PTA 1, with a median of 0.2550 mg/L.

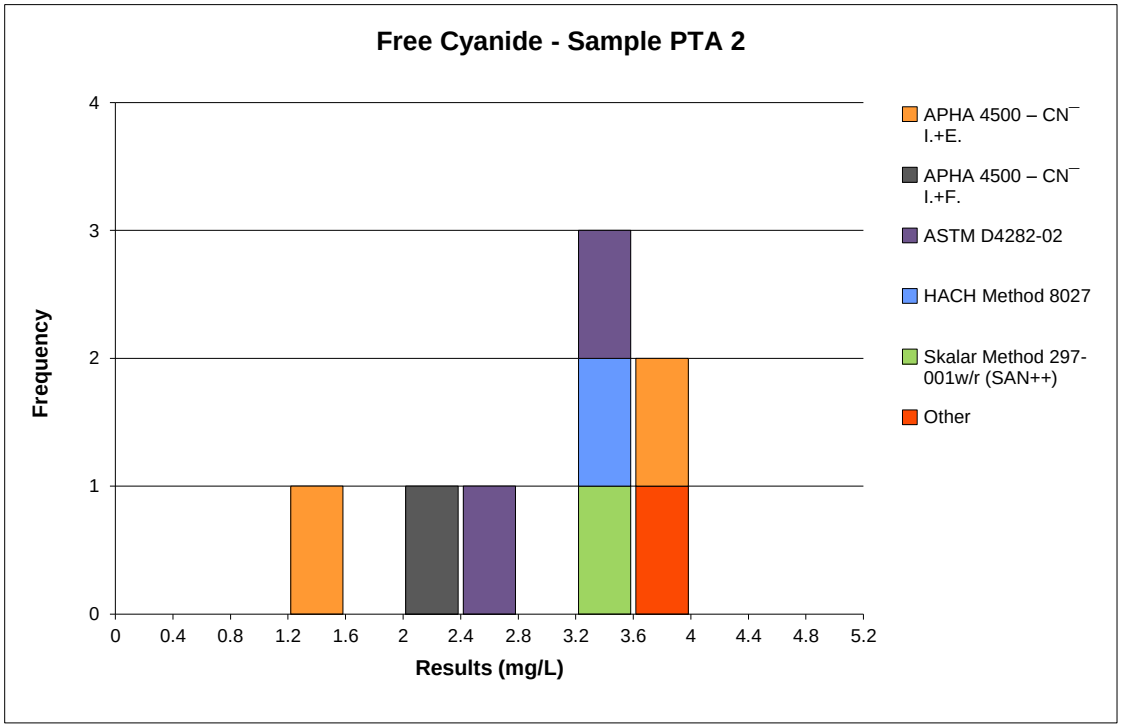


Figure 8. Spread of results for Free Cyanide testing of sample PTA 2, with a median of 3.475 mg/L.

Several laboratories underestimated their MU for Free Cyanide (Figures 8 and 9). If laboratories 189, 228 and 426 find in successive rounds that their MU does not

encompass the assigned value or uncertainty of the median, they may wish to re-examine their MU calculations incorporating their proficiency results and reference material testing in their statistical MU calculations (Eurachem 2012) [7].

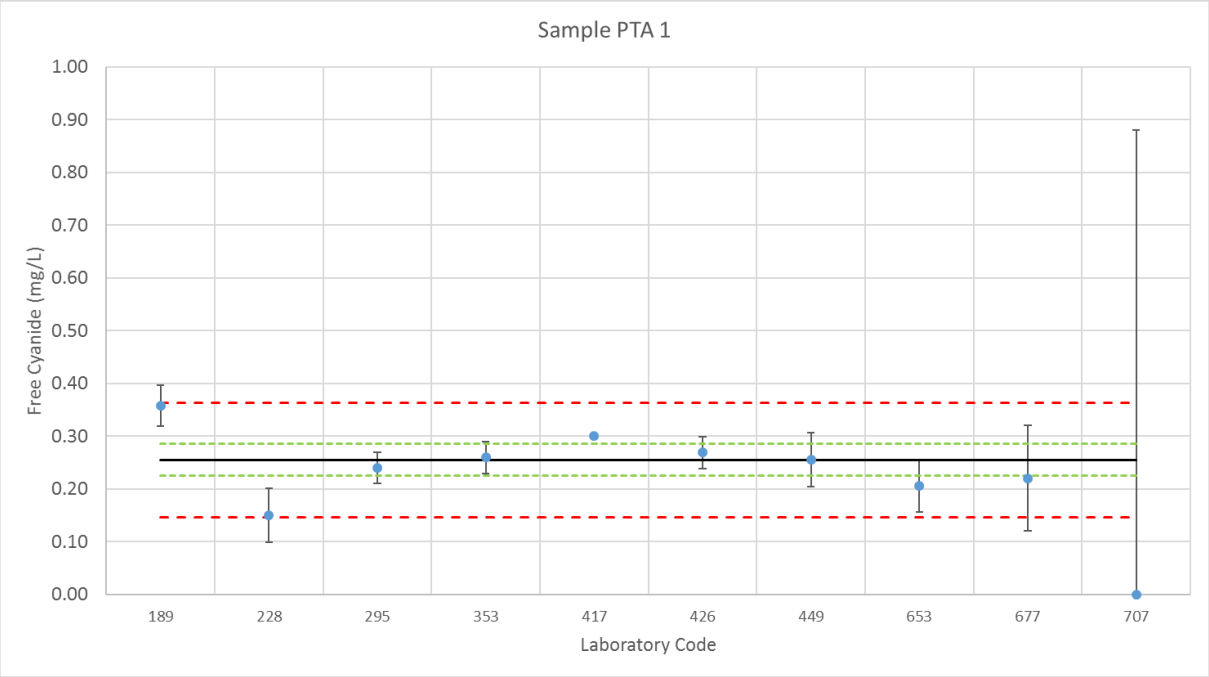


Figure 8. Laboratory Measurement Uncertainty for Free Cyanide testing of sample PTA 1, including the median (——), uncertainty of the median (- - -), and 3xNIQR U_{max} (- - -).

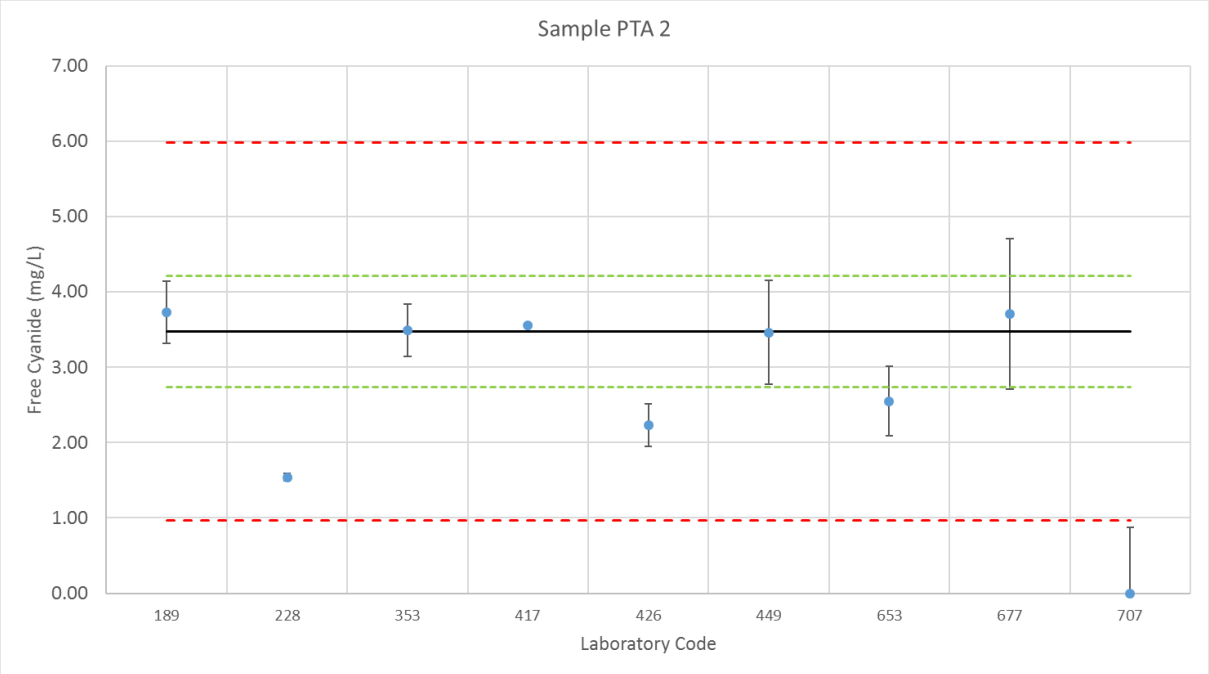


Figure 9. Laboratory Measurement Uncertainty for Free Cyanide testing of sample PTA 2, including the median (——), uncertainty of the median (- - -), and 3xNIQR U_{max} (- - -).

The unusual MU of laboratory 707 in Figures 8 and 9 was likely based on their high reporting limit (<6 mg/L).

4.3 Measurement Uncertainty (MU)

The majority of participants in this round (88%-95%) reported the measurement uncertainty (MU) associated with their results. Table 5 below presents the number and percentage of laboratories reporting the MU for each analyte.

Table 5. The number and percentage of laboratories reporting MU for analytes in round 229.

Analyte	Sample	Total participants	Participants reporting MU (percentage)
Total Cyanide	PTA 1	21	20 (95%)
	PTA 2	21	20 (95%)
Weak Acid Dissociable Cyanide	PTA 1	14	13 (93%)
	PTA 2	14	13 (93%)
Free Cyanide	PTA 1	9	8 (89%)
	PTA 2	8	7 (88%)

Some laboratories may have notably underestimated their MU, as they indicated that their MU was less than two times the uncertainty of the median (see Table 1), and their results were further from the median than this value.

Conversely, laboratories which indicated a MU which was greater than three times the normalised IQR may have overestimated their MU.[1] If this trend occurs over successive proficiency rounds, it is recommended that both over and underestimating laboratories re-evaluate their measurement uncertainty.

[1] MU evaluation is based on minimum / maximum uncertainty criteria (u_{min} and u_{max}) described in ISO 13528:2015 [8]. It should be noted, however, that these are informative indicators only and cannot be solely used to validate or invalidate the MUs reported.

4.4 Analysis of Results by Method Groups

Further analysis of results by method groups was undertaken to provide specific information on individual method performance.

In order for methods to be grouped for analysis, PTA requires at least 11 sets of results from the same method group. For analysis methods other than those presented below, there were less than 11 results submitted for each method, therefore reliable conclusions cannot be drawn from analysing them separately on this occasion.

4.3.1. Total Cyanide

The method APHA Part 4500 CN^- C+E, Colorimetric Method (method code 2), was most frequently employed for Total Cyanide analysis, with eight laboratories reporting the use of this method. Additionally, three laboratories reported results using the method APHA Part 4500 CN^- C+E modified for discrete analyser (method code 3). These methods were considered equivalent and the results obtained were pooled together for statistical analysis by method groups.

Table 6 below presents the median, uncertainty of the median and robust CV for Total Cyanide results obtained by methods 2 and 3. These CVs were tighter than the overall results presented in Table 2 (12.9% and 16.4% for samples PTA 1 and PTA 2), but still larger than published precision information in APHA 4500 CN^- C+E (Distillation + Colorimetric), which indicated laboratories should be able to achieve CVs of 4.18%-6.02%, at the Total Cyanide concentrations presented in this study.

Table 6. Variability and proficiency medians of Total Cyanide results obtained by methods 2 and 3.

Analysis	Sample	Participants	Median ± Uncertainty of the Median (mg/L)	Robust CV (%)
Total Cyanide	PTA 1	11	0.8900 ± 0.0387	11.5
	PTA 2	11	11.400 ± 0.569	13.2

The median for sample PTA 2 when analysed solely using the colorimetric method, was also closer to the doping concentration (11.5 mg/L) than the overall dataset, as indicated in Table 1.

4.3.2. WAD Cyanide

The methods most frequently used for WAD Cyanide testing in this round were APHA Part 4500 CN^- I+E, WAD Chloride Colorimetric Method (method code 31) and the modified method for discrete analyser (method code 32), used by three and respectively four laboratories. While these methods were considered equivalent, please note that there were insufficient results ($n < 11$) for reliable statistical analysis outside the overall pool of results.

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 7 below.

Table 7. Laboratory results identified as outliers for each analysis performed.

Lab Code	Analysis					
	Total Cyanide		WAD Cyanide		Free Cyanide	
	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2
294		**§**				
417	**§**					
494A			**§**	**§**		
683	**§**	**§**				
738	**§**	**§**				

Note:

1. A "**§**" indicates the occurrence of a z-score outlier result (i.e. those results for which |z-score| ≥ 3.0).

6. References

[1] *Guide to Proficiency Testing Australia*, 2016 (This document can be found on the PTA website, www.pta.asn.au).

[2] *Standard Methods For the Examination of Water and Wastewater*, 2012. Published by APHA, AWWA, WEF (22nd Edition).

[3] *BC Environmental Laboratory Manual,* 2011. Method Awaiting Director's Approval. Analysis of Cyanide (Total, Weak Acid Dissociable, and Free) - PBM (PDF)

[4] *Guidelines for Sewerage Systems Acceptance of Trade Waste (Industrial Waste).* November 1994. Australian Water and Wastewater Association (PDF)

[5] *Australian Drinking Water Guidelines 6,* 2011. National Water Quality Management Strategy Version 3.1 Updated March 2015. Australian Government, National Health and Medical Research Council, Canberra, Australia. https://www.nhmrc.gov.au.

[6] *Hamilton Trade Waste and Wastewater Bylaw 2016*. 15 August 2016. Hamilton City Council, Hamilton, New Zealand (PDF).

[7] EURACHEM / CITAC Guide CG 4 (2012). *Quantifying Uncertainty in Analytical Measurement; S. Ellison & A. Williams (Eds), Third Edition, Section 7.8, pg 20.* (PDF)

[8] ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons.*

APPENDIX A

Results and Data Analysis

Total Cyanide Results

Samples PTA 1 and PTA 2

Total Cyanide

Results by Laboratory Code

Laboratory Code	Sample PTA 1						
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]	Distillation pH
	mg/L						
186	0.89	±	0.18	0.00		2	#
228	0.975	±	0.305	0.74		2	#
282	0.854	±	0.098	-0.31		#	#
287	0.878	±	0.16	-0.10		3	<2
294	0.557	±	0.2	-2.90		29	#
295	0.92	±	0.20	0.26		17	#
353	0.95	±	0.26	0.52		2	#
417	0.518		#	-3.24	**§**	9	#
426	1.075	±	0.13	1.61		2	<2.0
435	0.89	±	0.089	0.00		2	#
449	0.903	±	0.181	0.11		26	#
551	0.999	±	0.099	0.95		2	#
553	0.984	±	0.037	0.82		29	#
653	0.756	±	0.14	-1.17		3	<2
660	0.82	±	0.113	-0.61		2	#
677	1.04	±	0.1	1.31		5	#
683	0.52	±	0.13	-3.22	**§**	5	#
707	1.05	±	0.13	1.39		3	#
717	0.830	±	0.11	-0.52		21	#
738	0.205	±	0.32	-5.96	**§**	2	#
740	0.878	±	0.071	-0.10		17	#

No of Results:	21
Median:	0.8900
Normalised IQR:	0.1149
Uncertainty of the Median:	0.0314
Robust CV:	12.9%
Minimum:	0.205
Maximum:	1.075
Range:	0.870

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

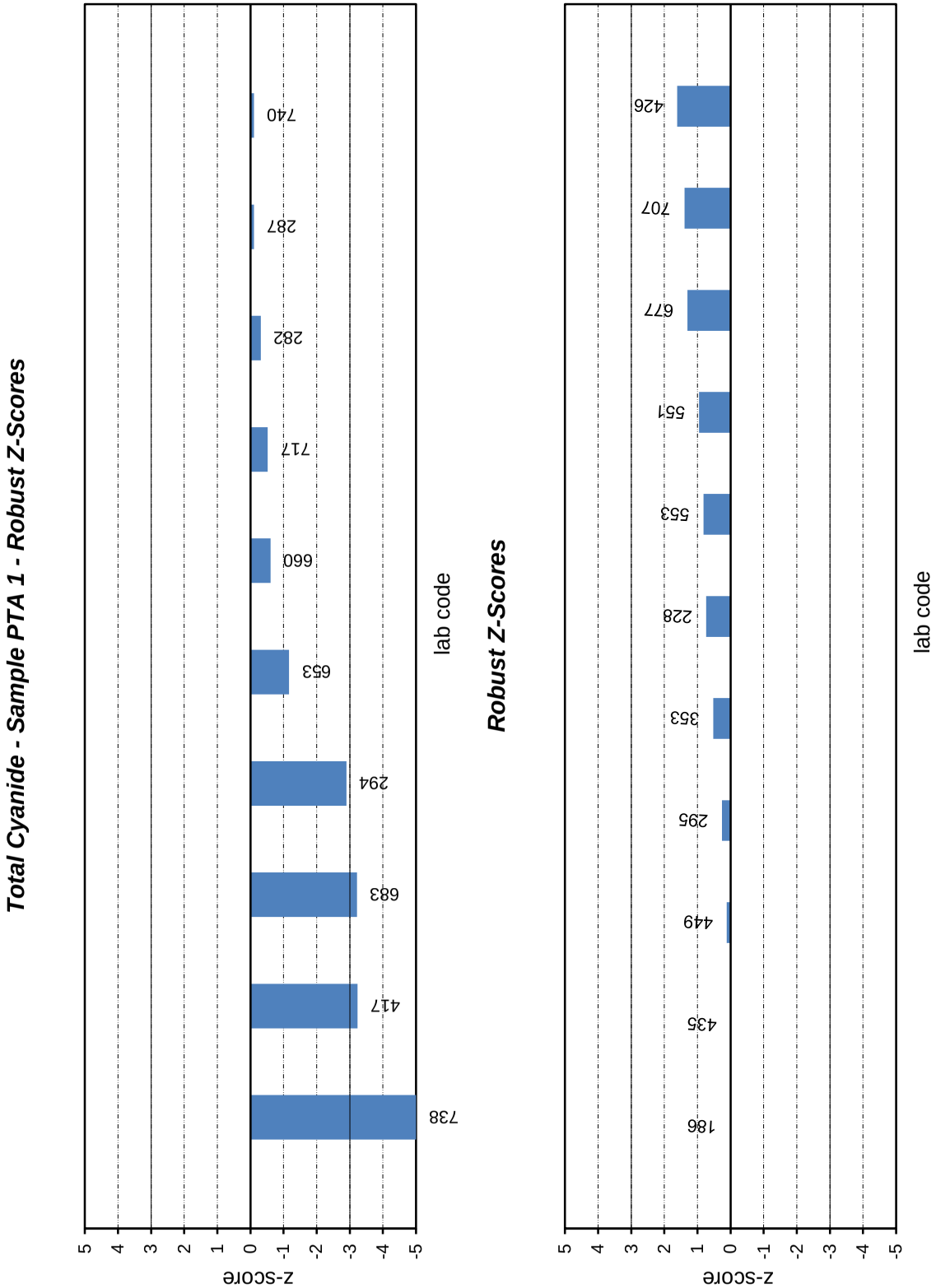
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Total Cyanide - Sample PTA 1

Ordered Robust Z-Score Charts



Total Cyanide

Results by Laboratory Code

Laboratory Code	Sample PTA 2						
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]	Distillation pH
	mg/L						
186	10.2	±	2.04	0.00		2	#
228	11.40	±	0.305	0.72		2	#
282	10.0	±	1.15	-0.12		#	#
287	11.5	±	1.7	0.78		3	<2
294	4.92	±	0.2	-3.17	§	29	#
295	12	±	2.6	1.08		17	#
353	11.7	±	3.19	0.90		2	#
417	8.85		#	-0.81		9	#
426	9.026	±	1.13	-0.70		2	<2.0
435	12.48	±	1.248	1.37		2	#
449	10.4	±	2.1	0.12		26	#
551	12.6	±	1.26	1.44		2	#
553	11.6	±	0.4	0.84		29	#
653	9.94	±	1.8	-0.16		3	<2
660	9.92	±	0.317	-0.17		2	#
677	12.7	±	2	1.50		5	#
683	4.69	±	1.17	-3.30	§	5	#
707	12.22	±	1.5	1.21		3	#
717	9.45	±	2.36	-0.45		21	#
738	2.94	±	0.32	-4.35	§	2	#
740	9.87	±	0.80	-0.20		17	#

No of Results:	21
Median:	10.200
Normalised IQR:	1.668
Uncertainty of the Median:	0.456
Robust CV:	16.4%
Minimum:	2.94
Maximum:	12.7
Range:	9.76

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

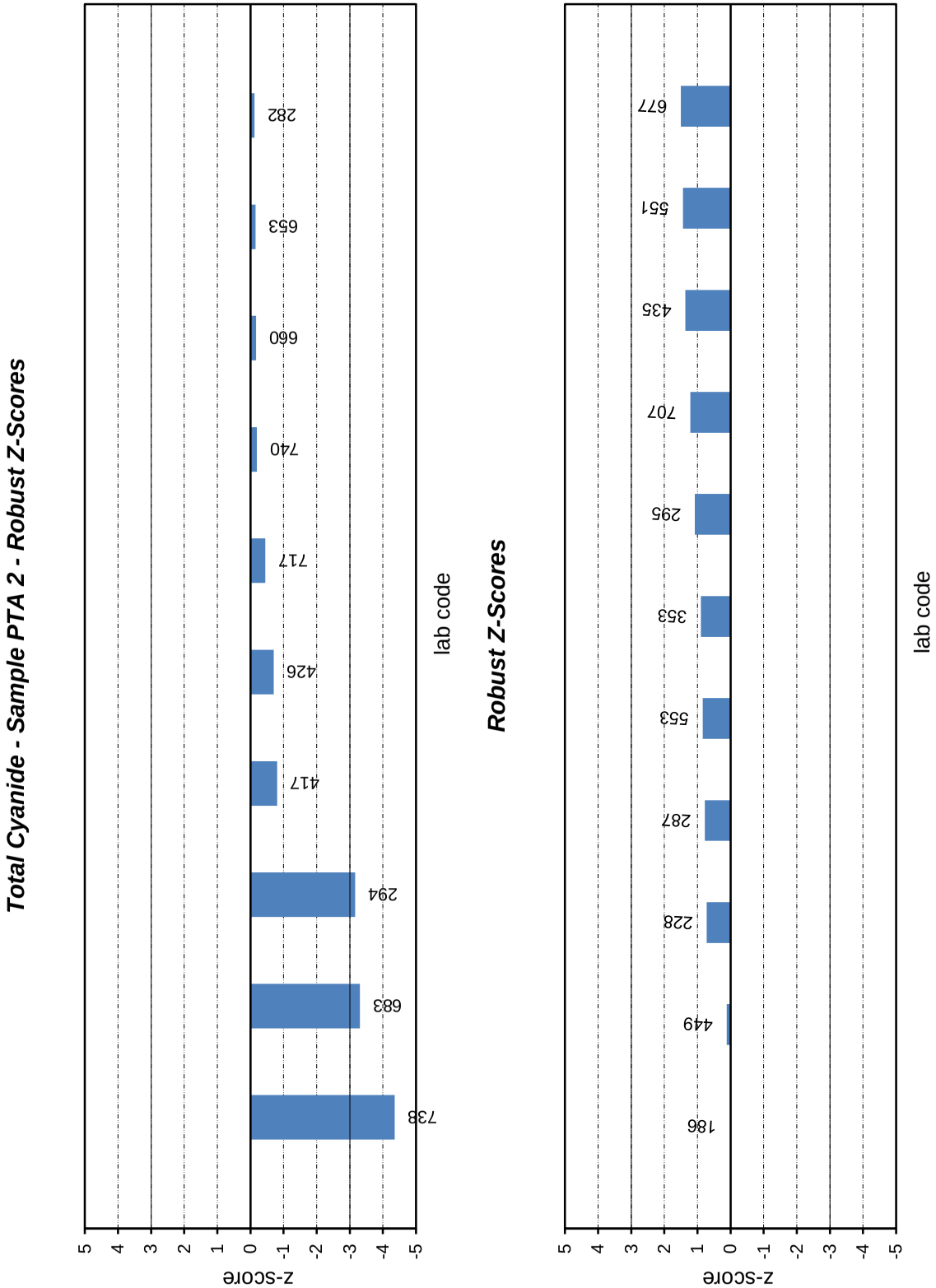
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Total Cyanide - Sample PTA 2

Ordered Robust Z-Score Charts



Weak Acid Dissociable (WAD) Cyanide Results

Samples PTA 1 and PTA 2

Weak Acid Dissociable (WAD) Cyanide

Results by Laboratory Code

Laboratory Code	Sample PTA 1						
	Result ± mg/L		MU[1]	Robust z-score[2]		Method Code[3]	Distillation pH
186	0.21	±	0.04	-1.26		31	#
228	0.250	±	0.701	-0.07		31	#
282	0.243	±	0.010	-0.28		#	#
287	0.212	±	0.05	-1.20		32	5
295	0.24	±	0.03	-0.37		50	#
426	0.286	±	0.04	0.99		31	4.5
449	0.257	±	0.051	0.13		53	#
494A	0.417		#	4.88	**§**	56	#
551	0.255	±	0.026	0.07		32	#
653	0.215	±	0.04	-1.11		32	4.4
677	0.26	±	0.1	0.22		34	#
707	0.270	±	0.033	0.52		32	#
717	0.269	±	0.05	0.49		56	#
738	0.195	±	0.32	-1.70		2	#

No of Results:	14
Median:	0.2525
Normalised IQR:	0.0337
Uncertainty of the Median:	0.0113
Robust CV:	13.4%
Minimum:	0.195
Maximum:	0.417
Range:	0.222

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

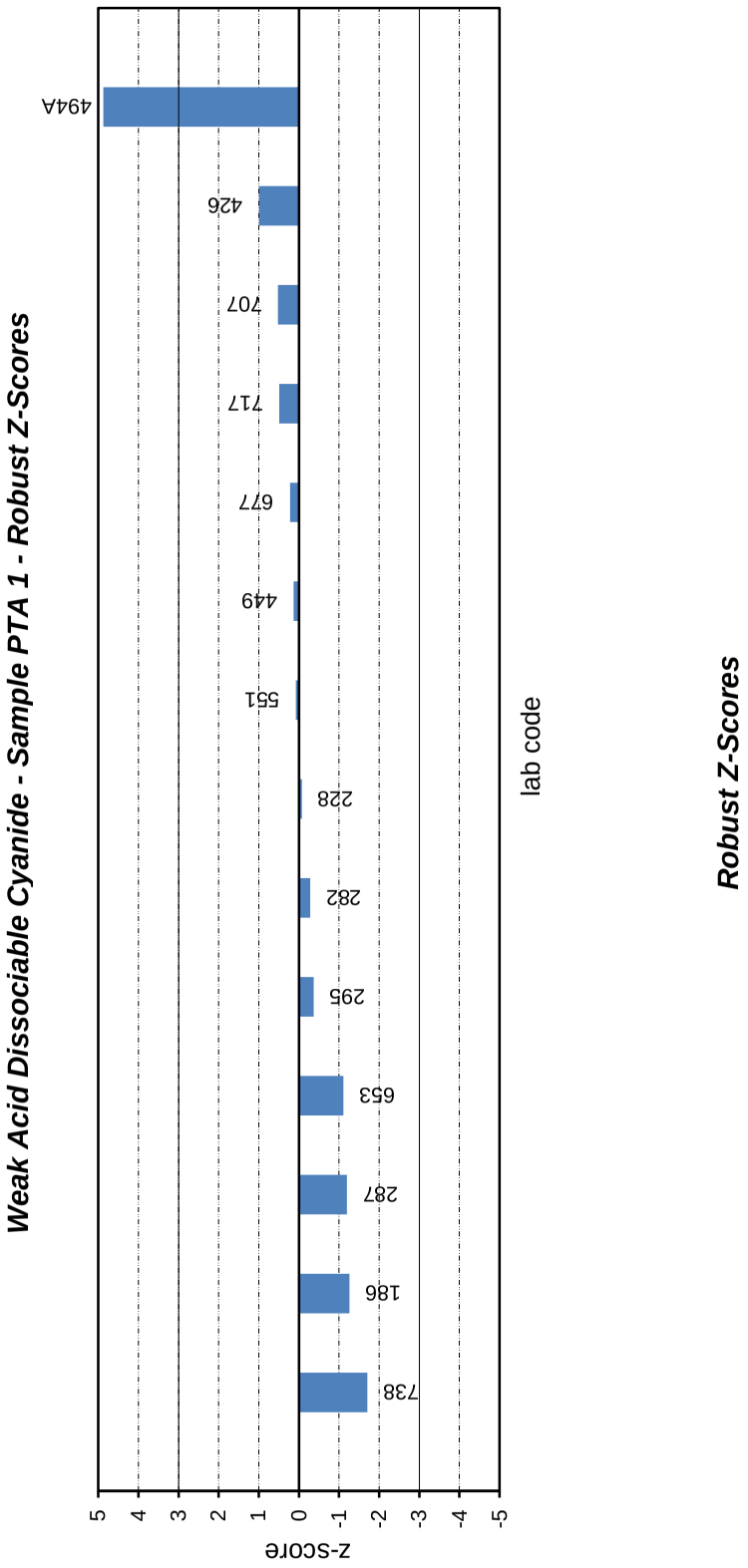
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Weak Acid Dissociable Cyanide - Sample PTA 1

Ordered Robust Z-Score Charts



Weak Acid Dissociable Cyanide

Results by Laboratory Code

Laboratory Code	Sample PTA 2						
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]	Distillation pH
	mg/L						
186	2.86	±	0.57	-1.04		31	#
228	3.60	±	0.701	0.45		31	#
282	3.35	±	0.14	-0.05		#	#
287	2.56	±	0.51	-1.64		32	5
295	3.4	±	0.48	0.05		50	#
426	2.858	±	0.36	-1.04		31	4.5
449	3.52	±	0.70	0.29		53	#
494A	4.87		#	3.01	**§**	56	#
551	3.17	±	0.32	-0.41		32	#
653	2.90	±	0.52	-0.96		32	4.4
677	3.93	±	1	1.12		34	#
707	3.54	±	0.43	0.33		32	#
717	3.68	±	0.43	0.61		56	#
738	2.96	±	0.32	-0.84		2	#

No of Results:	14
Median:	3.375
Normalised IQR:	0.497
Uncertainty of the Median:	0.166
Robust CV:	14.7%
Minimum:	2.56
Maximum:	4.87
Range:	2.31

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

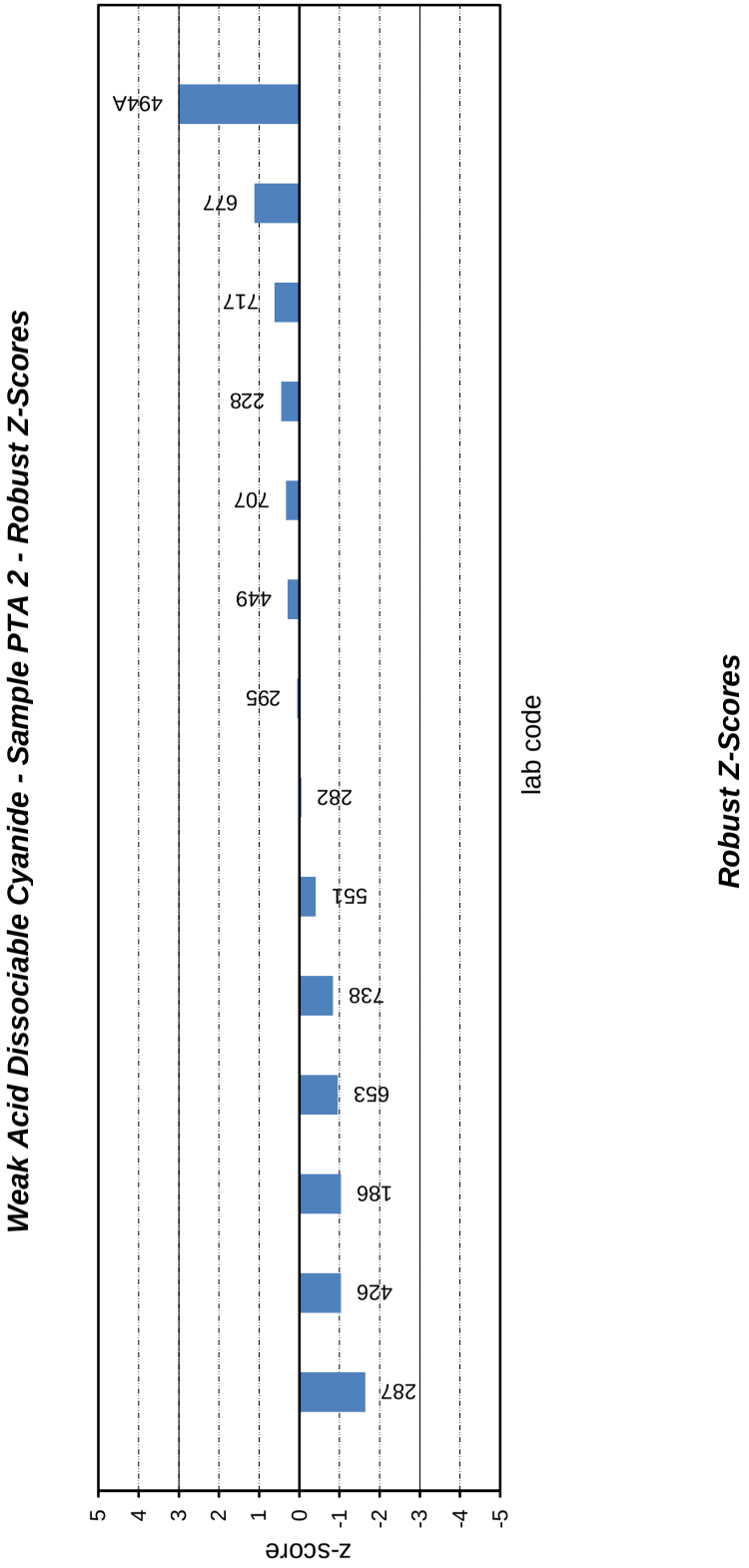
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Weak Acid Dissociable Cyanide - Sample PTA 2

Ordered Robust Z-Score Charts



Free Cyanide Results

Samples PTA 1 and PTA 2

SD 9.17.12

Free Cyanide

Results by Laboratory Code

Laboratory Code	Sample PTA 1					
	Result ± mg/L		MU[1]	Robust z-score[2]	Method Code[3]	Distillation pH
189	0.358	±	0.039	2.40	31	#
228	0.150	±	0.051	-2.45	31	#
295	0.24	±	0.03	-0.35	31	#
353	0.26	±	0.03	0.12	38	#
417	0.300		#	1.05	52	#
426	0.269	±	0.03	0.33	33	6.0
449	0.255	±	0.051	0.00	53	#
653	0.206	±	0.05	-1.14	38	6.0
677	0.22	±	0.1	-0.82	56	#
707	<6.0	±	0.88	na	56	#

No of Results:	9
Median:	0.2550
Normalised IQR:	0.0428
Uncertainty of the Median:	0.0179
Robust CV:	16.8%
Minimum:	0.150
Maximum:	0.358
Range:	0.208

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

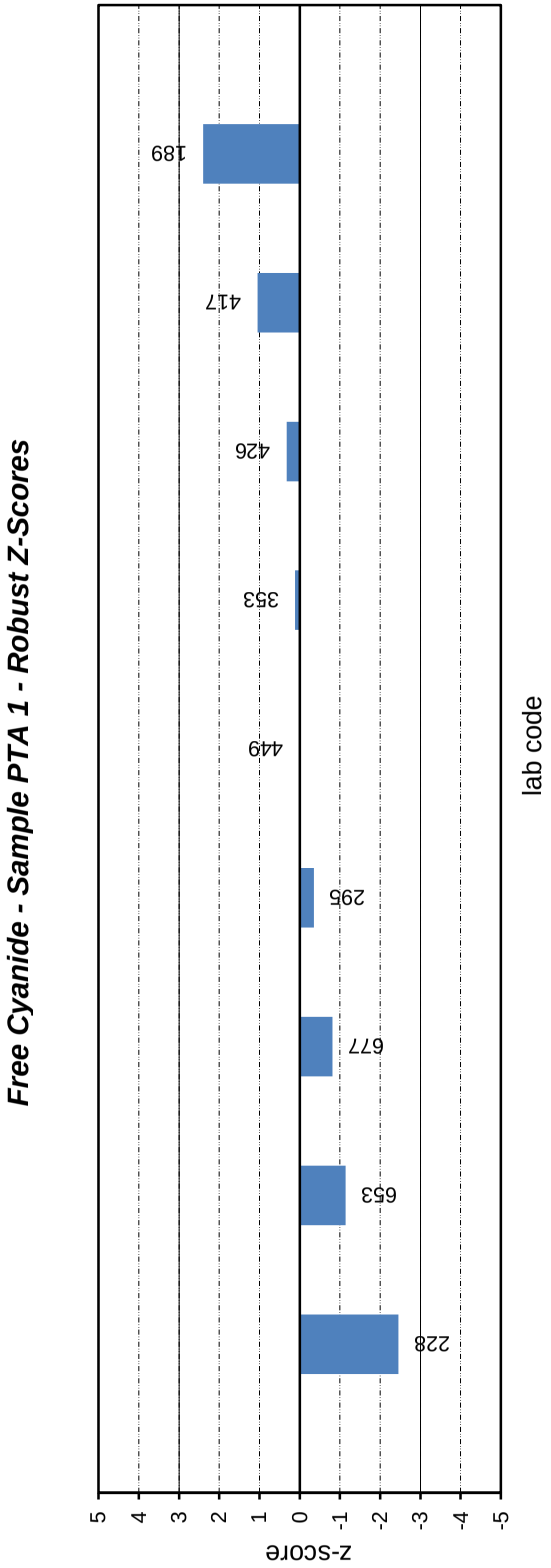
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Free Cyanide - Sample PTA 1

Ordered Robust Z-Score Charts



Free Cyanide

Results by Laboratory Code

Laboratory Code	Sample PTA 2					
	Result ± mg/L		MU[1]	Robust z-score[2]	Method Code[3]	Distillation pH
189	3.73	±	0.41	0.26	31	#
228	1.54	±	0.051	-1.95	31	#
353	3.49	±	0.35	0.02	38	#
417	3.56		#	0.09	52	#
426	2.231	±	0.28	-1.25	33	6.0
449	3.46	±	0.69	-0.02	53	#
653	2.55	±	0.46	-0.93	38	6.0
677	3.71	±	1	0.24	56	#
707	<6.0	±	0.88	na	56	#

No of Results:	8
Median:	3.475
Normalised IQR:	0.993
Uncertainty of the Median:	0.440
Robust CV:	28.6%
Minimum:	1.54
Maximum:	3.73
Range:	2.19

[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

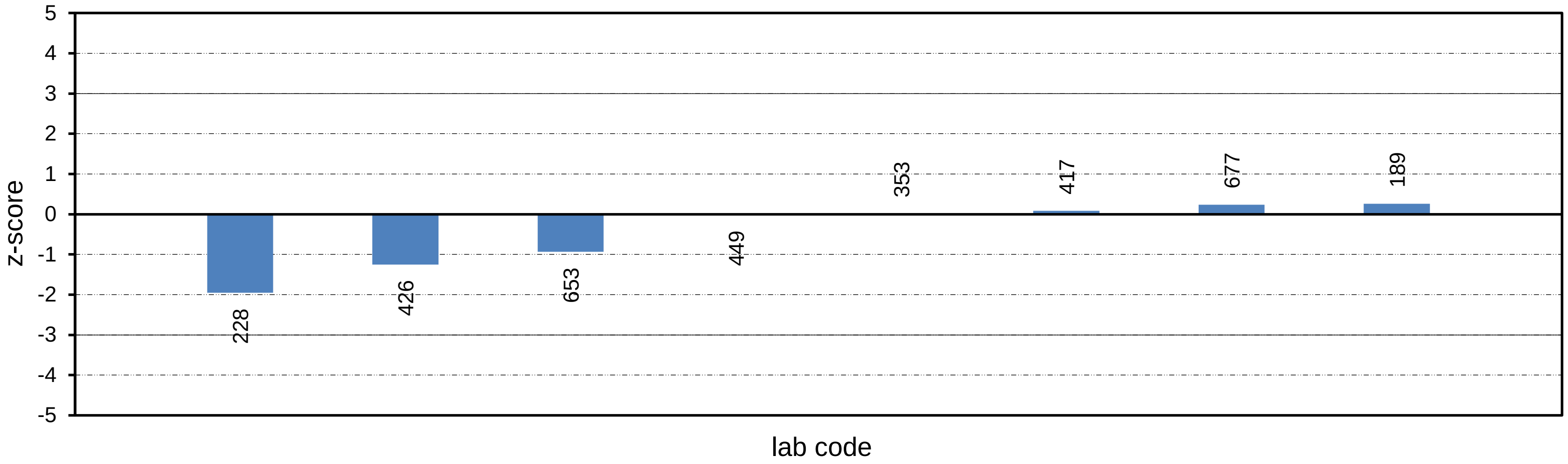
[4] "na" indicates "not applicable".

[5] "**#**" indicates that no result was returned for this sample/test.

Free Cyanide - Sample PTA 2

Ordered Robust Z-Score Charts

Free Cyanide - Sample PTA 2 - Robust Z-Scores



Robust Z-Scores

APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing

Samples for this program were obtained from Global Proficiency Ltd, New Zealand. As such, all samples were subjected to rigorous quality control and homogeneity / stability testing.

Samples manufactured by Global Proficiency were stabilised with NaOH and refrigerated. A random selection of ten samples was chosen from samples PTA 1 for homogeneity and stability testing. Seven of these were stored refrigerated and the remaining three were subjected to 35ºC for three days for an accelerated ageing stability trial. The samples were then analysed in duplicate by Hill Laboratories, New Zealand, for distillation and analysis using methods APHA 4500-CN^- C (modified) and E (modified) and APHA 4500-CN^- I (modified) and E (modified) (2012).

All stability samples showed no increased variability when compared to the chilled samples.

Free Cyanide homogeneity and stability were assumed to be the same as WAD Cyanide.

Samples PTA 2 were also tested to confirm the levels were within the expected range. Two samples were randomly selected, stored refrigerated in the same conditions as the remainder of samples and subjected to verification testing (one replicate per sample) by Hill Laboratories, New Zealand. Homogeneity and stability characteristics were assumed to be similar to samples PTA 1, based on identical manufacturing procedure and sample handling.

From statistical analyses based on the results of this testing and rigorous quality control, it was considered that all samples were sufficiently homogeneous and stable, so that any results later identified as outliers should not be attributed to any notable sample variability.

The results of homogeneity and stability testing are presented in Tables B1 and B2 below. Please note that the mean results for these tests are not intended to be used as reference values.

Table B1. Homogeneity and stability testing of PTA 1 samples.

Round PTA 229		**Samples PTA 1 (g/m^3)**			
	Sample ID	Total Cyanide		WAD Cyanide	
		Rep 1	Rep 2	Rep 1	Rep 2
Homogeneity	H1	1.170	1.160	0.351	0.348
	H2	1.170	1.140	0.356	0.364
	H3	1.230	1.220	0.347	0.351
	H4	1.170	1.150	0.346	0.336
	H5	1.150	1.150	0.334	0.308
	H6	1.140	1.150	0.336	0.334
	H7	1.200	1.190	0.346	0.348
Stability	S1	1.200	1.190	0.339	0.338
	S2	1.200	1.170	0.320	0.336
	S3	1.240	1.240	0.338	0.338
	Mean	1.187	1.176	0.341	0.340
	RSD	2.8%	2.9%	3.0%	4.3%

Table B2. Homogeneity testing of PTA 2 samples.

Round PTA 229	Samples PTA 2 (g/m^3)		
	Sample ID	Total Cyanide	WAD Cyanide
Homogeneity	H1	11.300	3.900
	S1	11.300	3.600
	RSD	0.00%	5.7%

APPENDIX C

Documentation

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 229 **MAY, 2018**

Total Cyanide, Weak Acid Dissociable Cyanide, Free Cyanide

INSTRUCTIONS TO PARTICIPANTS

*****Please record (on the Results Sheet) the approximate temperature of the samples upon receipt*****

Please note the following before commencing the analysis of the samples.

1. Samples

i) Two bottles labelled CN, Sample PTA 1 and Sample PTA 2, supplied by Global Proficiency Ltd. The bottles contain approximately 20 mL of artificial waste water concentrate for analysis of total cyanide, weak acid dissociable cyanide and free cyanide.

ii) The samples must be thoroughly mixed prior to analysis.

iii) The samples will require dilution in reagent grade water (please follow the **Sample Preparation** steps below).

iv) To minimise the possibility of change in concentration, do not open the bottles until ready to begin analysis.

v) The samples were frozen or refrigerated (-14^0-5^0C) prior to sample dispatch and any liquid on the outside of the bottles may be due to condensation rather than sample leakage.

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

2. Sample Preparation

Caution: Analysis must begin immediately after bottle is opened.

i) Adjust bottle temperature to 20ºC.

ii) Record bottle ID number.

iii) With consideration for volumes required for all tests, laboratories are instructed to carry out a 100-fold dilution. For example, remove 10.0mL from Sample 1 using a volumetric pipette and transfer the aliquot into a 1 Litre volumetric flask along with approximately 0.3g NaOH (to keep diluted sample ~pH 12).

iv) Make the 10.0mL aliquot up to 1L using reagent grade water.

v) Close with stopper and mix by inversion.

vi) Test according to your normal procedures.

vii) Repeat steps **i)** to **vi)** for the second sample.

Please report results for the diluted sample.

3. Tests Requested

For each of the samples prepared from the two bottles:

i) Total Cyanide
ii) Weak Acid Dissociable (WAD) Cyanide
iii) Free Cyanide

(It is recommended that a reagent water blank is analysed by the same method used to analyse the samples.)

If unable to perform the above please note this on your Results Sheet.

4. Safety

i) Samples are very alkaline (pH ≈ 12), and for laboratory use only. Please wear PPE (Personal Protection Equipment).
ii) Participants should have sufficient experience and training to take the necessary precautions when handling the samples and reagent chemicals and during disposal.
iii) Use of safety glasses, gloves, and fume hoods, where appropriate during the determinations, is recommended

5. Reporting

i) Report results using three significant figures (e.g.: 0.0123, 0.123, 1.23, 12.3).
ii) Report results in milligrams per litre (mg/L).
iii) Do not correct results for recovery.
iv) Select the appropriate method code for each test from the Method Code Table and record it on the Results Sheet.
v) Calculate the measurement uncertainty (MU) for each reported result. All estimates of MU must be given as a 95% confidence interval (coverage factor k ≈ 2) and reported in mg/L. Report MU using the same number of decimal places as for the result.

6. Testing should commence as soon as possible after receiving the samples and results reported **NO LATER THAN 15 JUNE 2018** to:

Delfina Mihaila
Proficiency Testing Australia
PO Box 7507
SILVERWATER NSW 2128
AUSTRALIA
Phone: +612 9736 8397
Fax: +612 9743 6664
Email: dmihaila@pta.asn.au

7. For this program your laboratory has been allocated the code number shown on the attached Results Sheet. All reference to your laboratory in reports associated with the program will be through this code number, thus ensuring the confidentiality of your results.

8. As a guide, ranges for the samples can be expected to be:

Analyte	Range (mg/L)
Total Cyanide	0.05-20
WAD Cyanide	0.05-20
Free Cyanide	0.05-20

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD DESCRIPTION	METHOD REFERENCE	CODE
Total Cyanide	Total Cyanide After Distillation	APHA Part 4500 - CN-C + D (Titrimetric)	1
		APHA Part 4500 – CN-C + E (Colorimetric)	2
		APHA Part 4500 – CN-C + E (modified for discrete analyser)	3
		APHA Part 4500 – CN-C + F (CN Selective Electrode)	4
		APHA Part 4500 – CN-C + N (Flow Injection Analysis)	5
		ASTM D2036	6
		ASTM D7284	7
		ASTM WK 9195	8
		HACH Method 8027	9
		Skalar Method 296	10
		US EPA 9010B	11
		US EPA 9014	12
		US EPA 335.2	13
		US EPA 335.4	14
		USGS I-3300	15
	Total Cyanide after thin film distillation	ASTM D4374	16
		Skalar Method 293	17
	Total Cyanide after ligand exchange	US EPA OIA 1678	18
	Total Cyanide after UV digestion	APHA Part 4500 – CN-O (FIA)	19
		ASTM D7511 – 12 (SFA)	20
		ISO 14403-1:2012 (FIA)	21
		ISO 14403-2:2012 (CFA)	22
		ISO/DIS 6703/1	23
		US EPA Kelada-01	24
		Skalar Method I295-004w/r (SAN^{++})	25
		Skalar Method 297-001w/r (SAN^{++})	26
		US EPA 335.3	27
		USGS I-2302	28
	Other (please specify)		29

Continued on next page…

Method Codes to be used for the Results Sheet, cont.

ANALYSIS	METHOD DESCRIPTION	METHOD REFERENCE	CODE
Weak Acid Dissociable (WAD) Cyanide Free Cyanide	WAD	APHA Part 4500 – CN I + D	30
		APHA Part 4500 – CN I + E	31
		APHA Part 4500 – CN I + E modified for discrete analyser	32
		APHA Part 4500 – CN I + F	33
		APHA Part 4500 – CN I + N (mod)	34
		APHA Part 4500 – CN O	35
		ASTM D2036	36
		US EPA Kelada-01	37
	Micro-diffusion	ASTM D4282-02	38
	Micro-diffusion	US EPA 9016	39
	Flow Injection Analysis (FIA)	ASTM D7237-15	40
	Flow Injection Analysis (FIA) Ion Chromatography	ASTM D6888-09	41
		ISO 14403-1:2012	42
		ISO 14403-2:2012	43
		Skalar Method 296	44
		US EPA Method OIA-1677-09	45
		ASTM D6994	46
	Ion Chromatography Automated using thin film distillation	US EPA 9015	47
		ASTM D4374	48
	Automated using thin film distillation Determination of Easy Liberated Cyanide	Skalar Method 293	49
		ISO/DIS 6703/2	50
	Colorimetry	US EPA 335.3	51
		HACH Method 8027	52
		Skalar Method 297-001w/r (SAN^{++})	53
		Skalar Method I295-003w/r (SAN^{++})	54
		Skalar Method 294-002w/r	55
	Other (please specify)		56

Method Reference Key

i)	APHA	APHA “Standard Methods for the Examination of Water and Wastewater” (18, 19 20, 21, 22, 23 Edition)
ii)	ASTM	American Society for Testing and Materials, ASTM International. (http://www.astm.org/)
iii)	ISO	International Organization for Standardization (http://www.iso.org)
iv)	OIA	US EPA Draft Method
v)	Skalar	Skalar, The Netherlands (www.skalar.com)
vi)	USGS	US Geological Survey (https://pubs.usgs.gov)
vii)	US EPA	US Environmental Protection Agency (https://www.epa.gov)

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 229

Total Cyanide, Weak Acid Dissociable Cyanide, Free Cyanide
MAY, 2018

RESULTS SHEET
(mg/L)

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

Laboratory Code

*Approximate temperature of samples upon receipt:	

ANALYSIS	SAMPLE PTA 1		SAMPLE PTA 2		Distillation pH (where applicable)	METHOD CODE
	Result (mg/L)	±MU (mg/L)	Result (mg/L)	±MU (mg/L)		
Total Cyanide						
WAD Cyanide						
Free Cyanide						

i) For each sample only a single result is requested.

ii) Report results using three significant figures.

iii) Report results in milligrams per litre (mg/L).

iv) Do not correct results for recovery.

v) MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in mg/L, using the same number of decimal places as for the result.

DATE: _____ **SIGNATURE:** _____

Return results **NO LATER THAN 15 JUNE 2018** to:
Delfina Mihaila
Proficiency Testing Australia
PO Box 7507
SILVERWATER NSW 2128
AUSTRALIA
Phone: +61 2 9736 8397
Fax: +61 2 9743 6664
Email: dmihaila@pta.asn.au

- End of Report -