Report No. 1127

Waters Proficiency Testing Program

Round No. 238

- Metals (Arsenic, Mercury, Selenium) -

March 2019

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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SD 9.17.12

CONTENTS

1. Foreword

This report summarises the results of a proficiency testing program on the determination of Metals (Arsenic, Mercury and Selenium) in waters. This is round 238 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 December 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.

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 plastic vials (labelled PTA 1 and PTA 2) containing solutions of arsenic, mercury and selenium.

2.4 A total of 23 laboratories received samples, comprising:

- 18 Australian participants; and
- 5 overseas participants, including:
    - Indonesia (3), Malaysia (1), Tanzania (1).

Of these 23 laboratories, 3 were 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 17.

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 17 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.

Arsenic and Selenium analytes were stable and homogeneous, and medians obtained from this proficiency round were in consistent agreement with the expected levels (dope concentration), as shown in Table 1. Mercury showed a slight sensitivity to temperature abuse with an average drop in concentration of 0.33 µg/L (8.5%) for sample PTA 1 when samples were held at 35°C for 3 days (See Appendix B).

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 (µg/L)	Median (µg/L)	Uncertainty of the Median (µg/L)
Arsenic (As)	PTA 1	15	13.50	0.52
	PTA 2	90	85.20	2.16
Mercury (Hg)	PTA 1	4	3.775	0.227
	PTA 2	15	14.56	0.67
Selenium (Se)	PTA 1	55	55.55	1.67
	PTA 2	150	150.0	3.8

Median recoveries for Arsenic and Selenium were in the range of those expected for Inductively Coupled Plasma/Mass Spectrometry ICP-MS (85-115%) according to US EPA 200.8 method precision information [2]. The median recoveries observed for Mercury in this study were also acceptable, taking into account that the cold vapor methods for Mercury analysis, such as APHA 3112 B, could expect relative errors of ±14.4%-21%.

4.2 Analysis of Round 238 Results

4.2.1 Arsenic (As)

Table 2 compares the Arsenic medians and robust CVs from this round to those obtained in previous PTA rounds. Laboratories achieved CVs comparable with the published precision data for US EPA Method 200.8 for ICP-MS analysis which indicated that Arsenic precision could be expected to range between 20-38% for sample PTA 1, and 4.8-9.9% for sample PTA 2, using various water types [2]. Method APHA 3120 B Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP-AES) indicated that laboratories should be able to achieve CVs of 14.0%-19.5% (Total Digestion) for Arsenic at the concentrations used in this study [3]. However, Arsenic concentrations in sample PTA 1 were below the published detection limit for ICP-AES (50 µg/L) in APHA 3120 B; by comparison, the detection limit estimated by Inorganic Ventures for ICP-AES were 5 – 100 µg/L, depending on the line used, axial or radial view, and interfering contaminants in the sample. The estimated detection limit for ICP-MS of 30 ppt, puts even the lower concentration sample well above detection limits [5].

Table 2. Comparison of current round variability and proficiency median of Arsenic testing with the results of the previous two rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	PTA 1	13.50	12.6	17
	PTA 2	85.20	8.4	17
Report 1008	PTA 1	53.80	9.8	21
	PTA 2	146.5	7.2	20
Report 795	PTA 1	13.10	20.8	30
	PTA 2	170.00	13.4	33

Bias / Accuracy

The Arsenic testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 11.7 – 15.7 µg/L for sample PTA 1 and 75.2 – 94.2 µg/L for sample PTA 2.

Out of 17 participants, one questionable result (2.0 < |z-score| < 3.0) was reported for sample PTA 1 (laboratory code 447) and two questionable results were reported for sample PTA 2 (laboratory codes 124 and 447).

One outlier result (|z-score| ≥ 3.0) was obtained for sample PTA 1, requiring follow-up action by laboratory code 291. One outlier result was also obtained for sample PTA 2, requiring follow-up action by laboratory code 390.

Laboratory code 427 reported Arsenic results of “<200 µg/L” for both samples PTA 1 and PTA 2, results which were deemed statistically satisfactory. This laboratory reported that all results were below the laboratory's standard Limits of Detection (LOD) using method APHA 3120 B ICP-AES.

Laboratories concerned about their ICP testing are recommended to follow the Quality Control (QC) procedures recommended in APHA 3020, including carrying the reagent blank and instrument QC samples through the entire sample preparation procedure. The QC sample should be a certified aqueous reference standard from an outside source (independent from calibration standards), remembering to use the same acid matrix as the calibration standards [3].

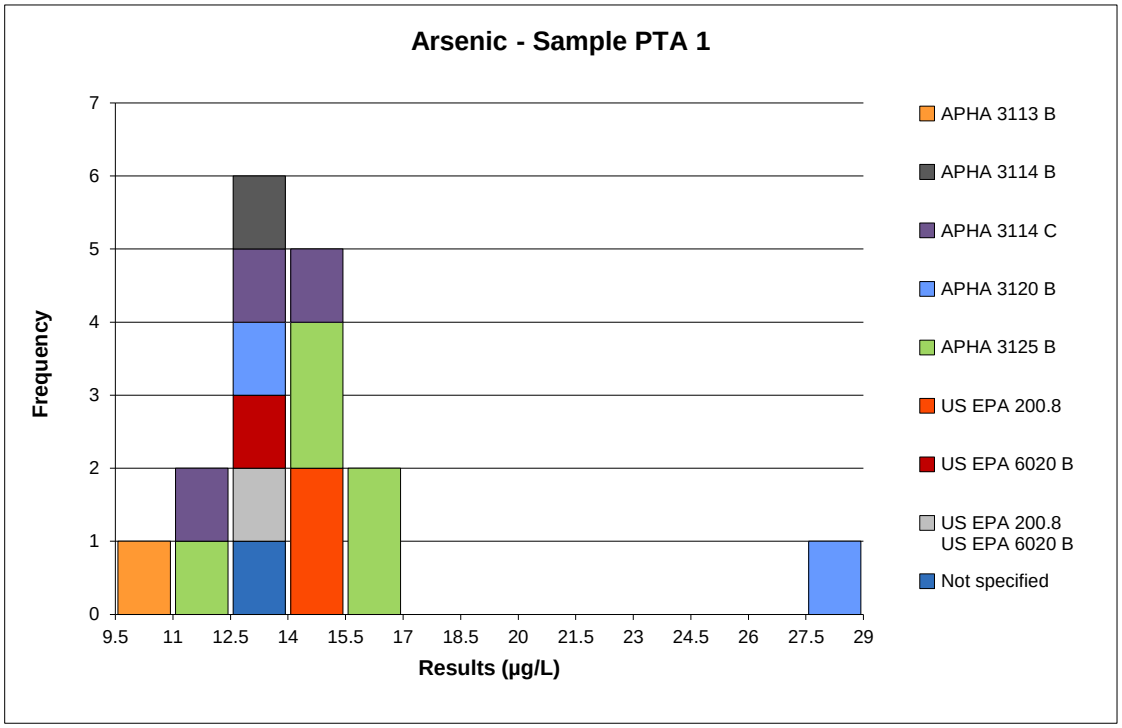

Figure 1. Spread of results for Arsenic testing of sample PTA 1, with a median of 13.50 µg/L.

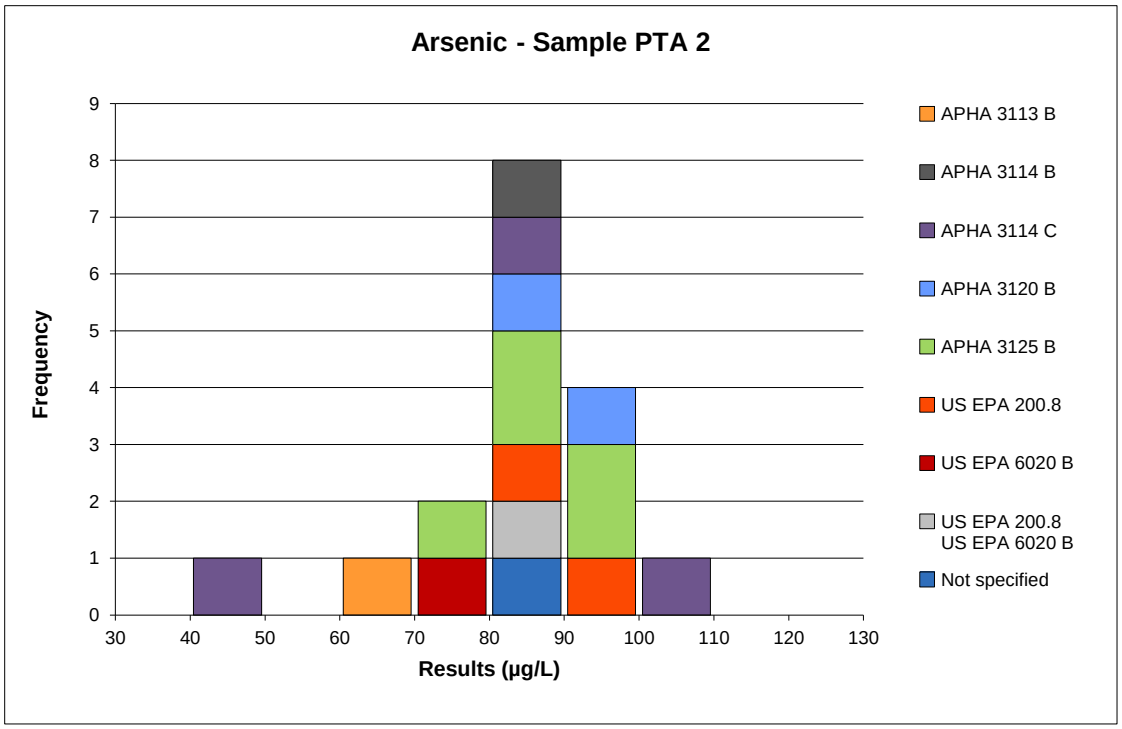

Figure 2. Spread of results for Arsenic testing of sample PTA 2, with a median of 85.20 µg/L.

The Arsenic data sets formed normal distribution with no notable bias attributable to any one analysis method (Figures 1 and 2). Laboratories used a large variety of methods for Arsenic testing in this round, the most frequently used being ICP-MS methods (APHA 3125 B, US EPA 200.8, US EPA 6020 B). Other methods used were APHA 3113 B and APHA 3114 B (Atomic Absorption) and APHA 3120 B (ICP-AES).

The majority of laboratories had a good understanding of their measurement uncertainty (MU) as can be seen in Figure 3. The majority of laboratories submitted MUs between 1.105 - 1.975 µg/L (9.6%-14.2%) for sample PTA 1, and between 6.665 - 10.88 µg/L (8.2%-11.9%) for sample PTA 2. Laboratory codes 124, 291, 390 and 447 may wish to re-examine their MU if they find that their MU does not encompass the median for successive proficiency rounds.

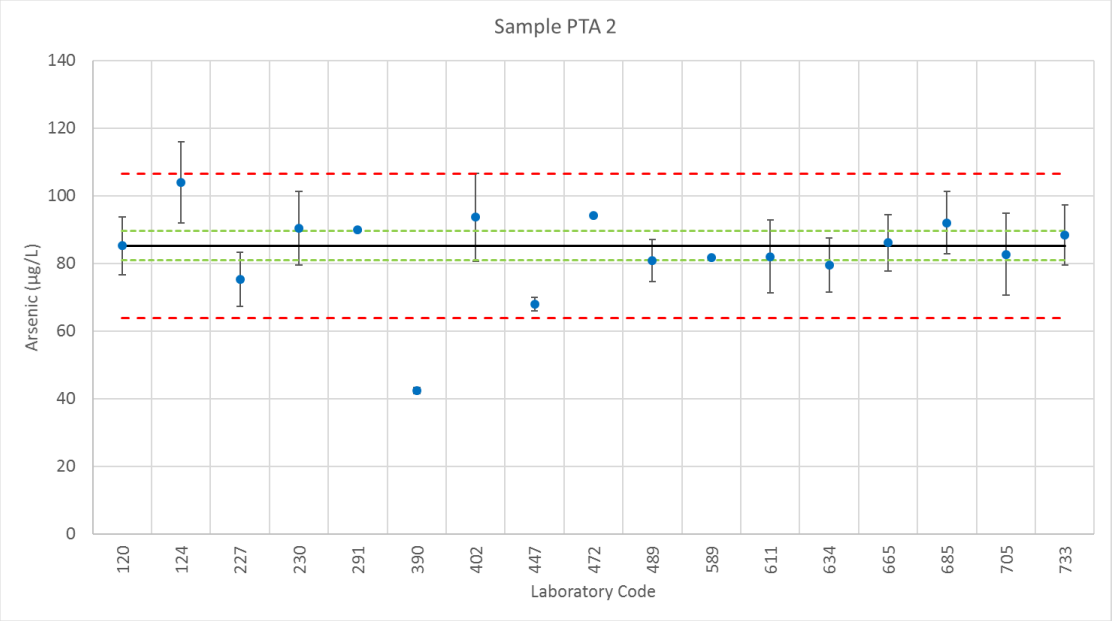

Figure 3. Spread of results for Arsenic testing of sample PTA 2, with MU error bars for each lab result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

4.2.2 Mercury (Hg)

Table 3 compares the Mercury medians and robust CVs from this round to those obtained in previous PTA rounds. Laboratories achieved comparable CVs to those from published precision data for APHA 3112 B (Cold-Vapour AAS), which indicated that laboratories should be able to achieve CVs of between 13.3%-22.6% for inorganic Mercury at concentrations between 0.34 - 4.2 µg/L [3]. US EPA 245.7 (Cold-Vapour) method indicated a precision of 12.9% - 30.3% could be expected for various water types [4].

Table 3. Comparison of current round variability and proficiency median of Mercury testing with the results of the previous two rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	PTA 1	3.775	20.4	18
	PTA 2	14.56	15.5	18
Report 1008	PTA 1	5.000	9.7	19
	PTA 2	44.70	6.3	19
Report 795	PTA 1	3.690	23.8	32
	PTA 2	39.815	12.4	32

Bias / Accuracy

The Mercury testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 2.358 – 5.11 µg/L for sample PTA 1 and 13 – 18.595 µg/L for sample PTA 2.

Out of 18 participants, one questionable result (2.0 < |z-score| < 3.0) was reported for sample PTA 1 (laboratory code 705) and one questionable result was reported for sample PTA 2 (laboratory code 227).

Three outlier results (|z-score| ≥ 3.0) were obtained for sample PTA 1, requiring follow-up action by laboratory codes 120, 227 and 472. Three outlier results were also obtained for sample PTA 2, requiring follow-up action by laboratory codes 120, 589 and 733.

Laboratory code 427 reported Mercury results of “<50 µg/L”, for both samples PTA 1 and PTA 2 using ICP-MS method, results which were deemed statistically satisfactory. This laboratory reported that all results were below the laboratory's standard Limits of Detection (LOD). Inorganic Ventures indicated limit of detection for ICP-OES of between 5-30 µg/L and for ICP-MS at 9 ppt [5].

Laboratories with both questionable and outlier results would be outside the recovery limits published for cold vapour methods such as APHA 3112 B and US EPA 245.7 and would normally be recommended to look closely at the QC recommendations specific to their method. In this case, where the sensitivity of samples to temperature abuse (see Appendix B) may have been an issue, there were no low biasing questionable results (-3.0 < z-score < -2.0) likely to have been affected in a similar manner.

Laboratories concerned about their Mercury testing performance are recommended to revise their QC procedures to align with APHA 3020 B; including running a QC sample from a secondary source that is different from that used to prepare the calibration standards; ongoing calibration verification to ensure the response has not changed significantly after every 10^{th} sample; running blanks, fortified matrix and duplicate samples every 20 samples analysed [3].

APHA recommends, when possible, to dedicate glassware for use in Mercury analysis and avoid using glassware previously exposed to high levels of Mercury (i.e. glassware that has been used for Chemical Oxygen Demand, Total Kjeldahl Nitrogen or Chloride analysis). Other sources of error can occur with the use of water that is not metal-free for carrying out dilutions, or when creating reagents and calibration standards. If the source water contains Mercury or other volatile metals, single or redistilled water may not be suitable for trace analysis - because these metals distil over with the distilled water. In such cases, APHA recommend using sub-boiling to prepare metal-free water (APHA 3111 B 3.c.) [3].

US EPA method 245.7, which is freely available on the web, also gives good recommendations regarding potential sources of contamination in Mercury testing, including talc in laboratory gloves and dental work (e.g. mercury amalgam fillings) in the mouths of laboratory personnel which can contaminate samples directly exposed to exhalation. US EPA method 245.7 Section 4.3 gives good guidelines for contamination control [4].

The Mercury data sets formed normal distributions with no notable bias attributable to any one analysis method (Figures 4 and 5). The method most frequently used for Mercury testing in this round was APHA 3112 B Cold-Vapour Atomic Absorption Spectrometry, which was used by six participants. Three laboratories used APHA 3125 B (ICP/MS) to analyse for Mercury, and although this metal is not specifically mentioned in the method, APHA noted that it can be used successfully in most cases [3].

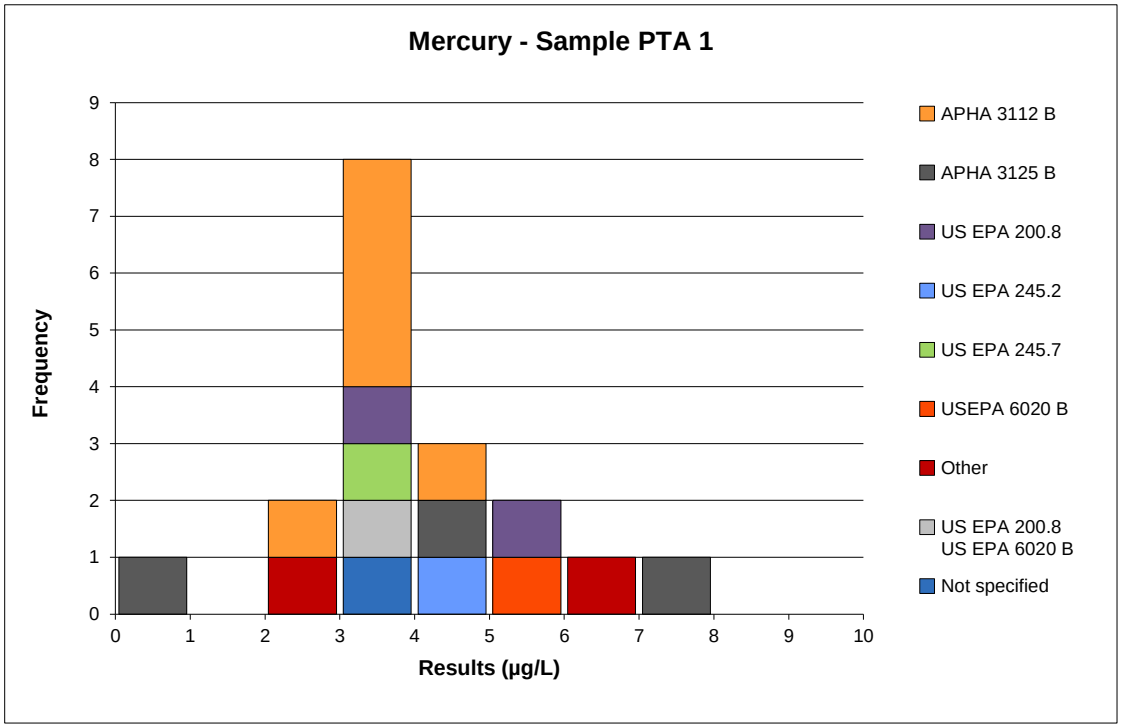

Figure 4. Spread of results for Mercury testing of sample PTA 1, with a median of 3.775 µg/L.

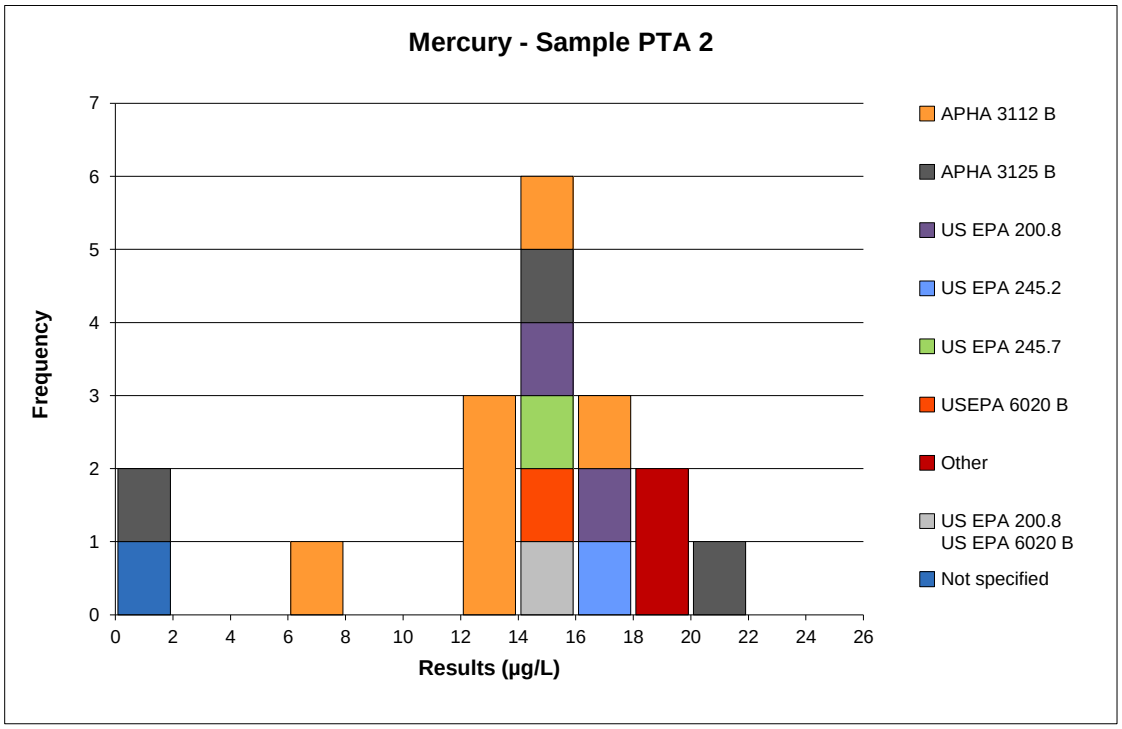

Figure 5. Spread of results for Mercury testing of sample PTA 2, with a median of 14.56 µg/L.

The majority of laboratories had a good understanding of their MU as can be seen in Figure 6. The majority of laboratories submitted MU between 0.4625 – 1.0 µg/L (10.7%-23.5%) for sample PTA 1, and between 1.55 - 2.66 µg/L (9.8%-17.6%) for sample PTA 2. Some laboratories submitted MU as low as 0.05 µg/L, or as high as 4 µg/L. Laboratory codes 120, 227, 390, 634, 705 and 733 may wish to re-examine

their MU if they find that their MU does not encompass the median for one or more samples in successive proficiency rounds.

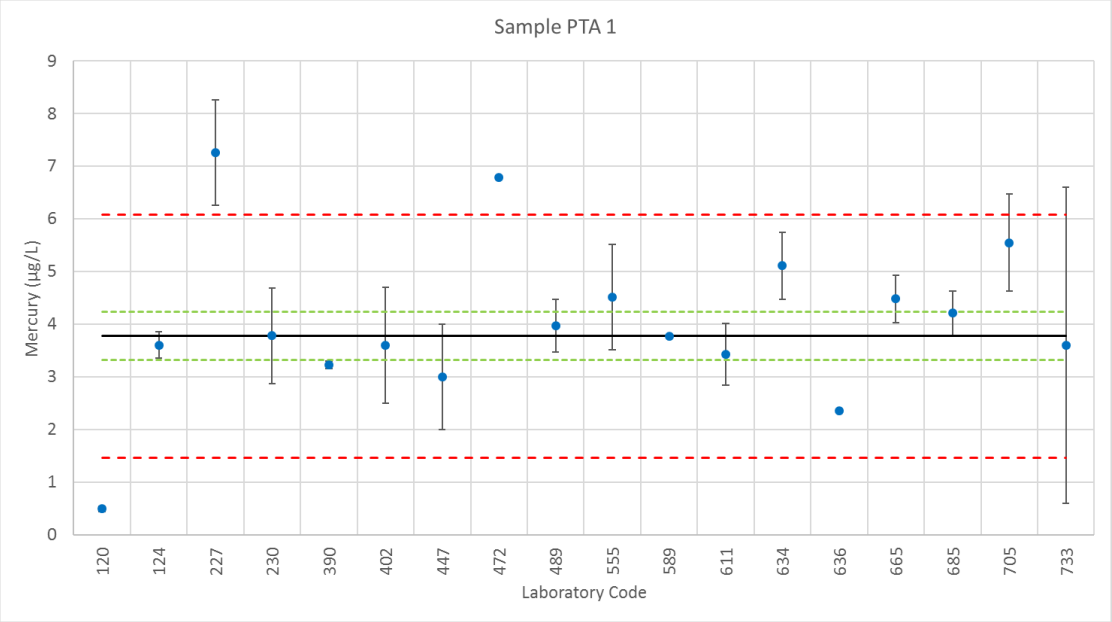

Figure 6. Spread of results for Mercury testing of sample PTA 1, with MU error bars for each lab result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

4.2.3 Selenium (Se)

Table 4 compares the Selenium medians and robust CVs from this round to those obtained in previous PTA rounds. Laboratories achieved much better CVs than the published precision data for APHA 3120 B (ICP/AES), which indicated that laboratories should be able to achieve CVs of 17.7% (Total Digestion) for the Selenium sample above their detection limit (75 µg/L). Published precision information for APHA 3114 C Continuous Hydride Generation/Atomic Absorption Spectrometry (CHG-AAS) ranged between 5%-12% [3].

Table 4. Comparison of current round variability and proficiency median of Selenium testing with the results of the previous two rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	PTA 1	55.55	9.6	16
	PTA 2	150.0	8.4	17
Report 1008	PTA 1	88.55	5.3	20
	PTA 2	180.5	9.0	20
Report 795	PTA 1	17.10	22.9	28
	PTA 2	153.00	10.0	29

Bias / Accuracy

The Selenium testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 46.4 – 62.6 µg/L for sample PTA 1 and 135 – 170 µg/L for sample PTA 2.

Out of 16 results submitted for sample PTA 1 and 17 results for sample PTA 2, one questionable result (2.0 < |z-score| < 3.0) was reported for sample PTA 1 (laboratory code 472) and two questionable results were reported for sample PTA 2 (laboratory codes 402 and 447).

One outlier result (|z-score| ≥ 3.0) was obtained for sample PTA 1, requiring follow-up action by laboratory code 402. One outlier result was also obtained for sample PTA 2, requiring follow-up action by laboratory code 291.

Laboratory code 427 reported Selenium results of "<100 µg/L" for sample PTA 1 using ICP/AES, result which was deemed statistically satisfactory. This laboratory reported that all results were below the laboratory's standard Limits of Detection (LOD). Inorganic Ventures indicated LOD is expected to be between 6-80 µg/L for ICP-OES using 196.026 nm wavelength or 0.2 µg/L for ICP-MS [5].

Laboratories concerned about their ICP testing are recommended to follow the QC procedures recommended in APHA 3020, including carrying the reagent blank and instrument QC samples through the entire sample preparation procedure. The QC sample should be a certified aqueous reference standard from an outside source (independent from calibration standards), remembering to use the same acid matrix as the calibration standards [3].

The Selenium data sets formed normal distributions with no notable bias attributable to any one analysis method (Figures 7 and 8). The method most frequently used for Selenium testing in this round was APHA 3125 B (ICP/MS), which was used by five participants, followed by method APHA 3120 B (ICP/OES) with four participants.

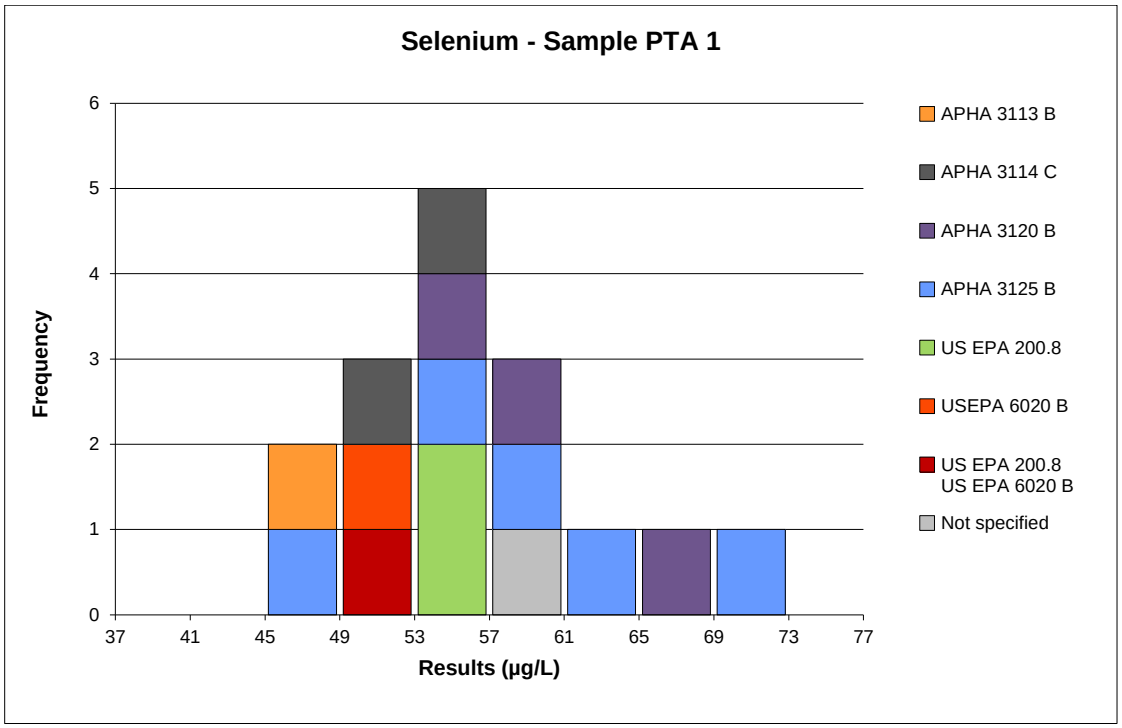

Figure 7. Spread of results for Selenium testing of sample PTA 1, with a median of 55.55 µg/L.

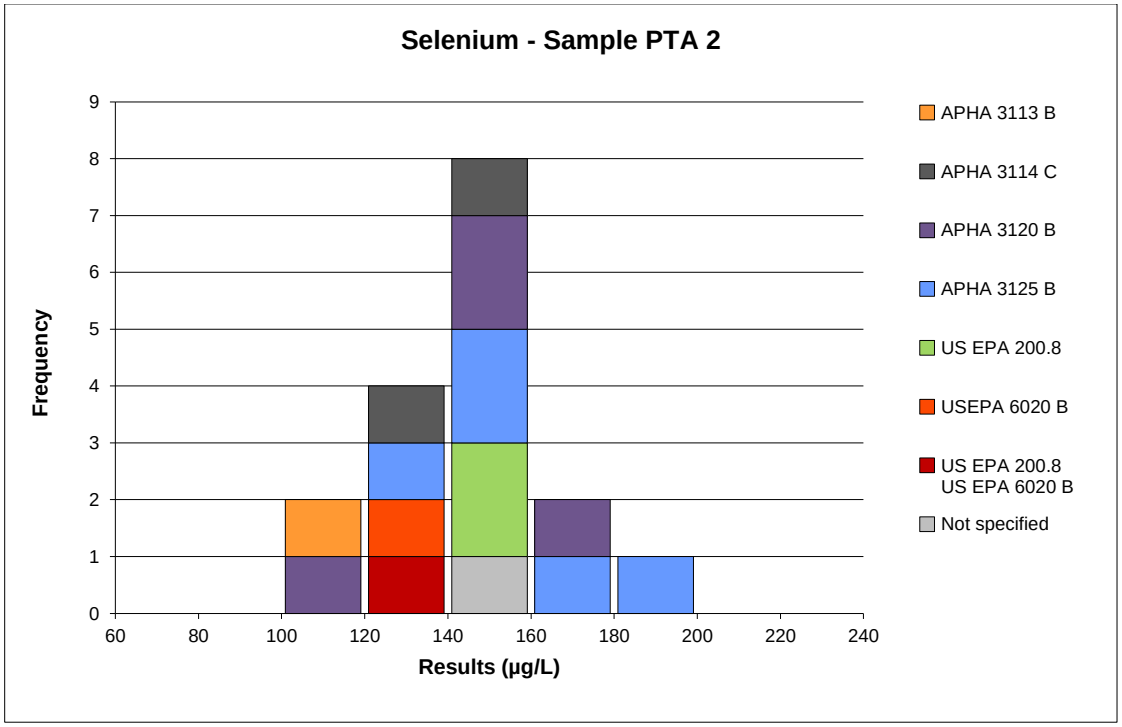

Figure 8. Spread of results for Selenium testing of sample PTA 2, with a median of 150.0 µg/L.

The majority of laboratories had a good understanding of their MU as can be seen in Figures 9 and 10, with most laboratories submitting MUs between 3.19 - 7.79 µg/L (6.3%-13.2%) for sample PTA 1, and between 9.98 - 21.45 µg/L (7.2%-12.9%) for sample PTA 2. Some laboratories submitted MU as low as 0.027 µg/L, or as high as 21.2%.

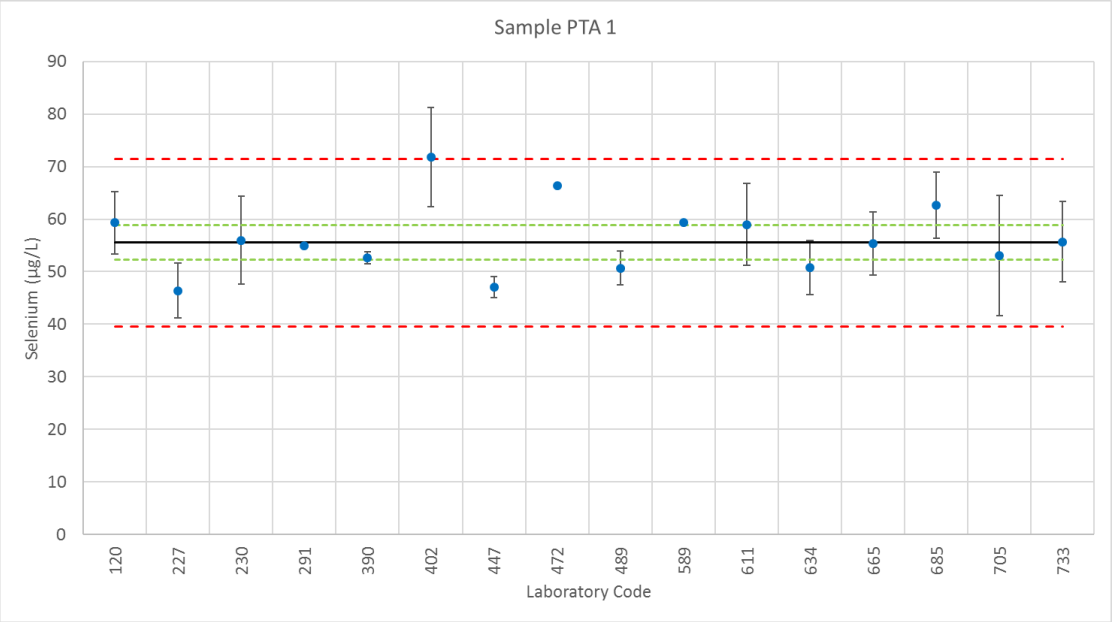

Figure 9. Spread of results for Mercury testing of sample PTA 1, with MU error bars for each lab result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

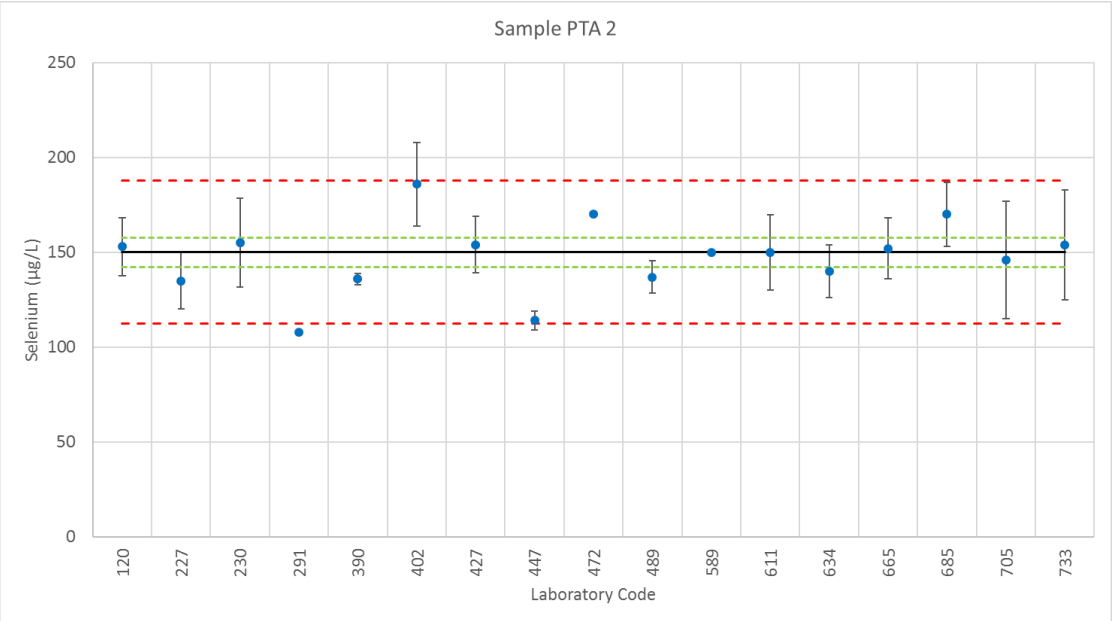

Figure 10. Spread of results for Mercury testing of sample PTA 2, with MU error bars for each lab result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

Laboratory codes 227, 291, 390, 402 and 447 may wish to re-examine their MU if they find that their MU does not encompass the median for one or more samples in successive proficiency rounds.

4.3 Measurement Uncertainty (MU)

The majority of participants in this round (83%-88%) 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 238

Analyte	Sample	Total participants	Participants reporting MU (percentage)
Arseninc (As)	PTA 1	17	15 (88%)
	PTA 2	17	15 (88%)
Mercury (Hg)	PTA 1	18	15 (83%)
	PTA 2	18	15 (83%)
Selenium (Se)	PTA 1	16	14 (88%)
	PTA 2	17	15 (88%)

Most of the stated MUs accurately reflect the difference between the median and the participant's result for these proficiency samples.

Some laboratories may have under estimated their MU, as they indicated that their MU was less than two times the uncertainty of the median, however their results were further from the median than the MU value.[1]

One laboratory indicated a MU greater than three times the normalised IQR for Arsenic and Mercury in sample PTA 1 and may have over estimated their MU.[1] However the proximity of results to the laboratory's limit of detection/quantification may justify this value.

If laboratories over estimate or under estimation MU in successive proficiency testing rounds, they are recommended to re-examine their measurement uncertainty calculations.

[1] MU evaluation is based on minimum / maximum uncertainty criteria (u_{min} and u_{max}) described in ISO 13528:2015 [6]. 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

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

Laboratories reporting results that have been identified as outliers are listed in Table 6 below.

Table 6. Laboratory results identified as outliers for each analysis performed.

Lab Code	Analysis					
	Arsenic		Mercury		Selenium	
	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2
120			§	§		
227			§			
291	§					§
390		§				
402					§	
472			§			
589				§		
733				§		

Note:

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

6. Reference

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

[2] US EPA Method 200.8, (1994) Revision 5.4: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry

[3] APHA "Standard Methods for the Examination of Water and Wastewater" 22nd (2012) and 23rd (2017) Editions.

[4] US EPA Method 245.7: Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry https://nepis.epa.gov/Exe/ZyPDF.cgi/P1008IY8.PDF?Dockey=P1008IY8.PDF

[5] Interactive Periodic Table, 2013. Inorganic Ventures https://www.inorganicventures.com/periodic-table

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

APPENDIX A

Results and Data Analysis

Arsenic (As) Results

Samples PTA 1 and PTA 2

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Arsenic (As)

Results by Laboratory Code

Laboratory Code	Sample PTA 1					
	Result ± µg/L		MU[1]	Robust z-score[2]		Method Code[3]
120	14.3	±	1.43	0.47		5
124	15.5	±	1.9	1.17		3
227	12.4	±	2	-0.65		5
230	15.3	±	1.9	1.06		10
291	28.9	±	0.041	9.03	**§**	4
390	11.7	±	0.26	-1.06		3
402	15.7	±	3	1.29		5
427	<200		#	na		4
447	10	±	1	-2.05		1
472	12.9		#	-0.35		4
489	13.5	±	1.04	0.00		10, 12
589	13.5		#	0.00		#
611	13	±	1.71	-0.29		2
634	13.3	±	1.3	-0.12		12
665	14.7	±	1.4	0.70		5
685	15.6	±	1.6	1.23		5
705	14.4	±	2.1	0.53		10
733	13.5	±	5.7	0.00		3

No of Results:	17
Median:	13.50
Normalised IQR:	1.70
Uncertainty of the Median:	0.52
Robust CV:	12.6%
Minimum:	10
Maximum:	28.9
Range:	18.9

[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.

Arsenic - Sample PTA 1

Ordered Robust Z-Score Charts

Robust Z-Scores

Arsenic (As)

Results by Laboratory Code

Laboratory Code	Sample PTA 2					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	µg/L					
120	85.2	±	8.52	0.00		5
124	104	±	12	2.64		3
227	75.2	±	8	-1.41		5
230	90.5	±	10.9	0.74		10
291	89.9	±	0.041	0.66		4
390	42.4	±	0.93	-6.01	**§**	3
402	93.7	±	13	1.19		5
427	<200		#	na		4
447	68	±	2	-2.42		1
472	94.2		#	1.26		4
489	80.9	±	6.22	-0.60		10, 12
589	81.8		#	-0.48		#
611	82	±	10.82	-0.45		2
634	79.6	±	8.0	-0.79		12
665	86.1	±	8.4	0.13		5
685	92.0	±	9.2	0.96		5
705	82.7	±	12.2	-0.35		10
733	88.5	±	8.9	0.46		3

No of Results:	17
Median:	85.20
Normalised IQR:	7.12
Uncertainty of the Median:	2.16
Robust CV:	8.4%
Minimum:	42.4
Maximum:	104
Range:	61.6

[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.

A4

Arsenic - Sample PTA 2

Ordered Robust Z-Score Charts

Mercury (Hg) Results

Samples PTA 1 and PTA 2

Mercury (Hg)

Results by Laboratory Code

Laboratory Code	Sample PTA 1					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	µg/L					
120	0.497	±	0.050	-4.26	**§**	15
124	3.60	±	0.25	-0.23		14
227	7.26	±	1	4.53	**§**	15
230	3.78	±	0.907	0.01		17
390	3.23	±	0.07	-0.71		14
402	3.6	±	1.1	-0.23		14
427	<50		#	na		15
447	3	±	1	-1.01		14
472	6.78		#	3.91	**§**	23
489	3.97	±	0.50	0.25		17, 22
555	4.52	±	1.0	0.97		14
589	3.77		#	-0.01		#
611	3.43	±	0.583	-0.45		20
634	5.11	±	0.64	1.74		22
636	2.358		#	-1.84		23
665	4.48	±	0.45	0.92		19
685	4.21	±	0.42	0.57		15
705	5.55	±	0.92	2.31		17
733	3.6	±	3.0	-0.23		14

No of Results:	18
Median:	3.775
Normalised IQR:	0.769
Uncertainty of the Median:	0.227
Robust CV:	20.4%
Minimum:	0.497
Maximum:	7.26
Range:	6.763

[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.

Mercury - Sample PTA 1

Ordered Robust Z-Score Charts

Robust Z-Scores

Mercury (Hg)

Results by Laboratory Code

Laboratory Code	Sample PTA 2					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	µg/L					
120	1.65	±	0.165	-5.71	**§**	15
124	13.2	±	0.9	-0.60		14
227	20.8	±	2.5	2.76		15
230	14.1	±	3.39	-0.20		17
390	14.2	±	0.31	-0.16		14
402	13.5	±	2.4	-0.47		14
427	<50		#	na		15
447	13	±	1	-0.69		14
472	18.2		#	1.61		23
489	15.3	±	1.94	0.33		17, 22
555	16.4	±	4.0	0.81		14
589	1.13		#	-5.94	**§**	#
611	14.92	±	2.54	0.16		20
634	14.2	±	1.8	-0.16		22
636	18.595		#	1.78		23
665	17.1	±	1.7	1.12		19
685	15.3	±	1.5	0.33		15
705	16.1	±	2.7	0.68		17
733	6.9	±	3.0	-3.39	**§**	14

No of Results:	18
Median:	14.56
Normalised IQR:	2.26
Uncertainty of the Median:	0.67
Robust CV:	15.5%
Minimum:	1.13
Maximum:	20.8
Range:	19.67

[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.

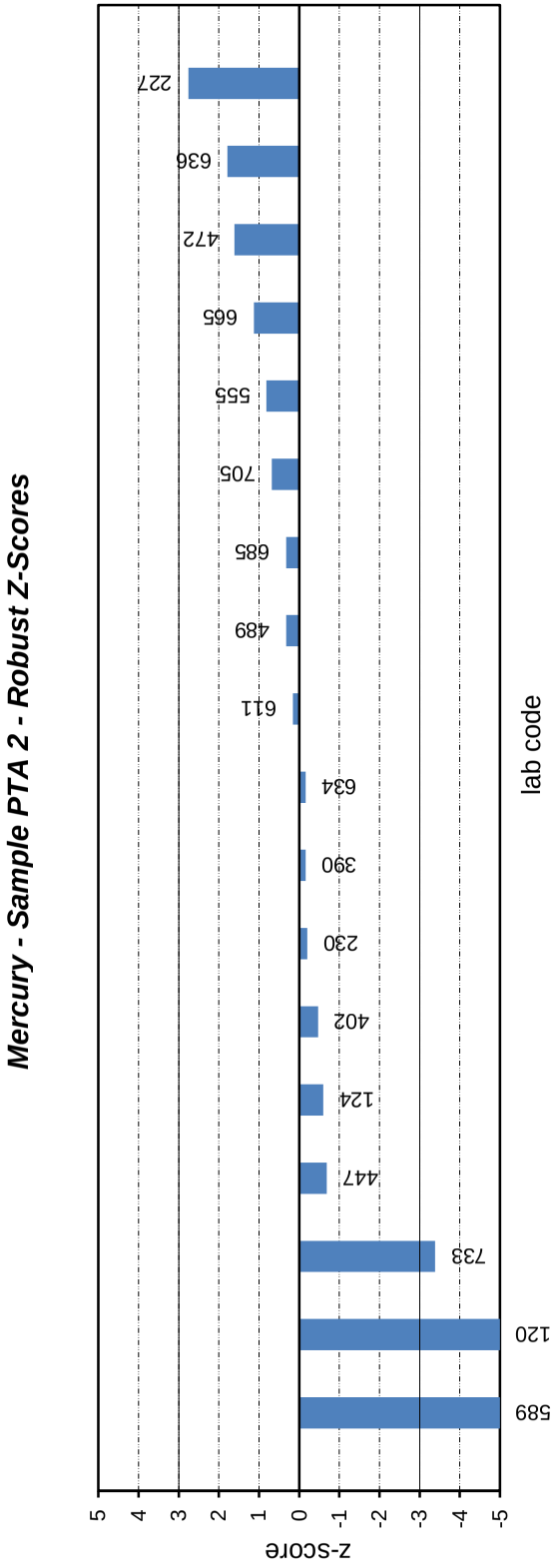
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

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

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

Mercury - Sample PTA 2

Ordered Robust Z-Score Charts



Selenium (Se) Results

Samples PTA 1 and PTA 2

Selenium (Se)

Results by Laboratory Code

Laboratory Code	Sample PTA 1					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	µg/L					
120	59.3	±	5.93	0.71		28
227	46.4	±	5.2	-1.72		28
230	56.0	±	8.4	0.08		30
291	54.9	±	0.027	-0.12		27
390	52.6	±	1.15	-0.55		26
402	71.8	±	9.5	3.06	**§**	28
427	<100		#	na		27
447	47	±	2	-1.61		24
472	66.3		#	2.02		27
489	50.7	±	3.19	-0.91		30, 34
589	59.4		#	0.72		#
611	59	±	7.79	0.65		27
634	50.8	±	5.1	-0.89		34
665	55.4	±	6.0	-0.03		28
685	62.6	±	6.3	1.33		28
705	53.1	±	11.4	-0.46		30
733	55.7	±	7.7	0.03		26

No of Results:	16
Median:	55.55
Normalised IQR:	5.32
Uncertainty of the Median:	1.67
Robust CV:	9.6%
Minimum:	46.4
Maximum:	71.8
Range:	25.4

[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.

Selenium - Sample PTA 1

Ordered Robust Z-Score Charts

Robust Z-Scores

Selenium (Se)

Results by Laboratory Code

Laboratory Code	Sample PTA 2				
	Result ± µg/L	MU[1]	Robust z-score[2]		Method Code[3]
120	153 ±	15.3	0.24		28
227	135 ±	15	-1.19		28
230	155 ±	23.3	0.40		30
291	108 ±	0.027	-3.33	**§**	27
390	136 ±	2.98	-1.11		26
402	186 ±	22	2.86		28
427	154 ±	15	0.32		27
447	114 ±	5	-2.86		24
472	170	#	1.59		27
489	137 ±	8.64	-1.03		30, 34
589	150	#	0.00		#
611	150 ±	19.80	0.00		27
634	140 ±	14	-0.79		34
665	152 ±	16	0.16		28
685	170 ±	17	1.59		28
705	146 ±	31	-0.32		30
733	154 ±	29	0.32		26

No of Results:	17
Median:	150.0
Normalised IQR:	12.6
Uncertainty of the Median:	3.8
Robust CV:	8.4%
Minimum:	108
Maximum:	186
Range:	78

[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.

Selenium - Sample PTA 2

Ordered Robust Z-Score Charts

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 are subjected to rigorous quality control and homogeneity / stability testing.

A random selection of ten samples was chosen from samples PTA 1 for homogeneity and stability testing. Seven of these were stored chilled 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 R J Hill Laboratories Ltd, New Zealand. The method used for testing was ICP/MS (APHA 3125 B, 22 ed. 2012).

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

Arsenic and Selenium analytes showed no notable differences in stability when compared to homogeneity samples, however there was a slight drop in Mercury concentration in the temperature abused samples.

From statistical analyses based on the results of this testing and rigorous quality control, it was considered that all samples containing Arsenic and Selenium were sufficiently homogeneous and stable, so that any results later identified as outliers should not be attributed to any notable sample variability. Mercury results were closely monitored in the round to ensure laboratories low biasing by a similar amount to the stability samples (PTA 1: -0.33; PTA 2: -0.46 µg/L) were not unfairly penalised.

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 238	**Samples PTA 1 (µg/L)**						
	Sample ID	Arsenic		Mercury		Selenium	
		Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Homogeneity	H1	14.8	14.6	3.89	3.82	58.6	60.9
	H2	15.3	14.5	3.84	3.80	60.8	60.5
	H3	15.0	14.5	3.95	3.84	60.2	59.0
	H4	14.4	14.5	3.94	3.73	59.6	57.5
	H5	14.8	14.5	3.87	3.81	58.1	59.0
	H6	14.2	14.5	4.03	3.84	58.6	59.1
	H7	14.7	14.6	3.86	3.87	59.6	58.7
Stability	S1	14.7	14.8	3.51	3.44	59.6	60.3
	S2	14.7	14.6	3.59	3.53	59.6	58.4
	S3	15.1	14.9	3.61	3.53	59.8	58.1
Mean		14.69		3.77		59.30	
RSD		1.70%		4.50%		1.59%	

Table B2. Homogeneity testing of PTA 2 samples.

Round PTA 238	Samples PTA 2 (µg/L)			
	Sample ID	Arsenic	Mercury	Selenium
Homogeneity	H1	87.75	14.15	157.07
	H2	86.80	13.69	162.82
Mean		87.27	13.92	159.94
RSD		0.77%	2.32%	2.54%

APPENDIX C

Documentation

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 238 **DECEMBER, 2018**

Metals (Arsenic, Mercury, Selenium)

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 plastic bottles labelled PTA 1 and PTA 2, supplied by Global Proficiency Ltd.

ii) The bottles contain approximately 220 mL of artificial potable water, for analysis of Arsenic, Mercury and Selenium.

iii) The samples have been acidified with high purity nitric acid (HNO_3) to pH 2.

iv) The bottles must be thoroughly mixed prior to analysis.

v) The samples are ready to test using your normal laboratory procedures.

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 the bottle ID number.

iii) Mix thoroughly by inversion (approximately 10 times) and test according to your normal procedures.

iv) Repeat steps **i)** to **iii)** for the second sample.

3. Tests Requested

Tests requested for samples PTA 1 and PTA 2 are as follows:

i) Arsenic (As).

ii) Mercury (Hg).

iii) Selenium (Se).

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

4. Safety

i) Samples are for laboratory use only.

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 for the ready-to-test samples in micrograms per litre (µg/L).

ii) For statistical purposes, report results to 3 significant figures, i.e. 1.23 or 12.3 or 123 µg/L.

iii) Do not correct results for recovery.

iv) Select the appropriate method code for each test (see pages 3 - 5 for method codes) and record them 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 µg/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 21 DECEMBER 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 (in µg/L):

Analyte	Range
Arsenic (As)	10 – 200 µg/L
Mercury (Hg)	1 – 50 µg/L
Selenium (Se)	10 – 200 µg/L

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Arsenic (As) Total	APHA	APHA 3113 B. Electrothermal Atomic Absorption Spectrometric Method	1
		APHA 3114 B Manual Hydride Generation/Atomic Absorption Spectrometric Method	2
		APHA 3114 C Continuous Hydride Generation/Atomic Absorption Spectrometric Method	3
		APHA 3120 B. METALS BY PLASMA EMISSION SPECTROSCOPY Inductively Coupled Plasma (ICP) Method	4
		APHA 3125 B. Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS) Method	5
		APHA 3500-As B Silver Diethyldithiocarbamate [SDDC Colorimetric] Method	6
	US EPA	US EPA 0206.2 CL Arsenic - AA, furnace technique 0206.3 Arsenic - AA, Gaseous Hydride	7
		US EPA 206.5 Arsenic (Sample Digestion Prior to Total Arsenic Analysis by Silver Diethyldithiocarbamate or Hydride Procedures)	8
		US EPA 0200.7 Metals and Trace Elements - ICP/AES	9
		US EPA 0200.8 Trace Elements in Water & Wastes - ICP/MS	10
		US EPA 0200.9 Trace Elements - GFAA	11
		US EPA 6020 B ICP-MS	12
		Other (please specify)	13

Continued on next page

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Mercury (Hg) Total	APHA	APHA 3112B Cold-Vapor Atomic Absorption Spectrometric Method	14
		APHA 3125 B. Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS) Method	15
		APHA 320 B Mercury Dithizone Method 16th Ed.	16
	US EPA	US EPA 0200.8 Trace Elements in Water & Wastes - ICP/MS	17
		US EPA 0245.1 Mercury - Cold Vapor, Manual	18
		US EPA 0245.2 Mercury - Cold Vapor, Automated	19
		US EPA 0245.7 Mercury - Cold vapor atomic fluorescence spectrometry (CVAFS)	20
		US EPA 1631 E Mercury - Purge and Trap CVAFS	21
		US EPA 6020 B ICP-MS	22
		Other (please specify)	23

Continued on next page

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Selenium (Se) Total	APHA	APHA 3113 B. Electrothermal Atomic Absorption Spectrometric Method	24
		APHA 3114 B Manual Hydride Generation/Atomic Absorption Spectrometric Method	25
		APHA 3114 C Continuous Hydride Generation/Atomic Absorption Spectrometric Method	26
		APHA 3120 B. METALS BY PLASMA EMISSION SPECTROSCOPY Inductively Coupled Plasma (ICP) Method	27
		APHA 3125 B. Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS) Method	28
	US EPA	US EPA 0200.7 Metals & Trace Elements in Water & Wastes - ICP/AES	29
		US EPA 0200.8 Trace Elements in Water & Wastes - ICP/MS	30
		US EPA 0200.9 Trace Elements - GFAA	31
		US EPA 0270.2 Selenium - AA, Furnace	32
		US EPA 0270.3 Selenium - AA, Gaseous Hydride	33
		US EPA 6020 B ICP-MS	34
		Other (please specify)	35

Method Reference Key

i) APHA APHA “Standard Methods for the Examination of Water and Wastewater” (18, 19, 20, 21, 22, 23 Edition) (http://www.standardmethods.org/).

ii) US EPA U.S Environmental Protection Agency. (http://www.epa.gov/osa).

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 238

Metals (Arsenic, Mercury, Selenium)
DECEMBER, 2018

RESULTS SHEET
(µg/L)

Laboratory Code	

*Approximate temperature of samples upon receipt:	

ANALYSIS	**SAMPLE PTA 1**		**SAMPLE PTA 2**		**METHOD CODE**
	Result (µg/L)	**±MU (µg/L)**	**Result (µg/L)**	**±MU (µg/L)**	
Arsenic (As)					
Mercury (Hg)					
Selenium (Se)					

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

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

ii) Report results for the ready-to-test samples.

iii) Report results in micrograms per litre (µg/L).

iv) For statistical purposes, report results to 3 significant figures, i.e. 1.23 or 12.3 or 123 µg/L.

v) Do not correct results for recovery.

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

DATE: _____ **SIGNATURE:** _____

Return results **NO LATER THAN 21 DECEMBER 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 -