Report No. 1050

Waters Proficiency Testing Program

Round No. 217

- Bromide, Chloride, Fluoride, Iodide -

November 2017

Acknowledgments

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1. Foreword

This report summarises the results of a proficiency testing program on the determination of Bromide, Chloride, Fluoride and Iodide in waters. This is round 217 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in August 2017 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 Advisers were Dr M Buckley-Smith and Ms S Sharma, Global Proficiency Ltd (New Zealand). This report was authorised by Mrs F Watton, 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 500 mL plastic bottles (labelled PTA 1 and PTA 2) containing solutions of NaF, NaCl, KBr and KI analytical reagents in distilled water.

2.4 A total of 34 laboratories received samples, comprising:

- 25 Australian participants; and
- 9 overseas participants, including:
    - Brunei Darussalam (1), Indonesia (1), Malaysia (2), Papua New Guinea (1), Singapore (3), United Arab Emirates (1).

Of these 34 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 Advisers' 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 were in good agreement with the expected levels (dope concentration), as shown in Table 1. Median analyte recoveries were also within expected parameters published for method APHA 4110 B (Ion Chromatography), which were estimated to be between 75%-125% [3], with the lowest average recovery being for Iodide in sample PTA 1.

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 also presented in Table 1.

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)	Analyte Recovery (%)	Uncertainty of the median (mg/L)
Bromide (Br)	PTA 1	8	8.105	101.3	0.075
	PTA 2	14	13.80	98.6	0.10
Chloride (Cl)	PTA 1	70	70.30	100.4	0.88
	PTA 2	120	123.0	102.5	1.8
Fluoride (F)	PTA 1	2.5	2.470	98.8	0.024
	PTA 2	3.5	3.460	98.9	0.026
Iodide (I)	PTA 1	0.7	0.625	89.3	0.041
	PTA 2	1.8	1.650	91.7	0.107

Overall, the performance of participants in this round was good, with robust CVs below 10% for all analytes except Iodide, which had very low participant numbers.

4.2 Analysis of Round 217 Results

4.2.1 Bromide (Br)

Table 2 compares the Bromide medians and robust CVs from this round to those obtained in previous PTA rounds. These were comparable to the published precision information in APHA 4110, which indicated that CVs of 3.1%-5.6% could be expected for Bromide analysis using Ion Chromatography with Chemical Suppression.

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

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	8.105	3.0	16
	PTA 2	13.80	2.4	16
Report 993	PTA 1	6.820	2.3	16
	PTA 2	16.85	3.4	16
Report 959	PTA 1	7.840	5.1	23
	PTA 2	11.90	5.0	23

Bias / Accuracy

The Bromide testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 7.69 – 8.5 mg/L for sample PTA 1 and 13.4 – 14.4 mg/L for sample PTA 2.

Out of 16 participants, three outlier results (|z-score| ≥ 3.0) were obtained for sample PTA 1, requiring follow-up action by laboratories 154, 234 and 287. For sample PTA 2, four outlier results were obtained, requiring follow-up action by laboratories 234, 287, 353 and 479. Additionally, laboratory 308 submitted low Bromide results for both samples PTA 1 and PTA 2. These results were excluded from statistical analyses; however, they are deemed to be outliers.

No questionable results (2.0 < |z-score| < 3.0) were reported for both samples PTA 1 and PTA 2.

The Bromide data sets formed approximately normal distributions with no notable bias attributable to any one method (Figures 1 and 2). The method most frequently used for Bromide testing in this round was APHA 4110 B (Ion Chromatography with Chemical Suppression of Eluent Conductivity), which was used by 71% of participants.

For laboratories that need to carry out troubleshooting, the most common sources of error include contaminants in reagent water, glassware, sample processing apparatus, or carry-over from prior high concentration samples. APHA section 4020 B Quality Control Practices recommends a minimum of daily use of Method Blanks (MB), Laboratory Fortified Blanks (LFB), Laboratory Fortified Matrix (LFM) and duplicates (LFMD), or every 20th sample [3].

In addition, APHA 4110 B (Ion chromatography with Chemical Suppression of Effluent Conductivity) recommended allowing the system to come to equilibrium over a 15-20

minute period, to give a stable base line. They also recommend verifying calibration curves with a mid-range concentration check standard from a source independent of the calibration standards. The results of the check standard should be within 10% of the original calibration curve [3].

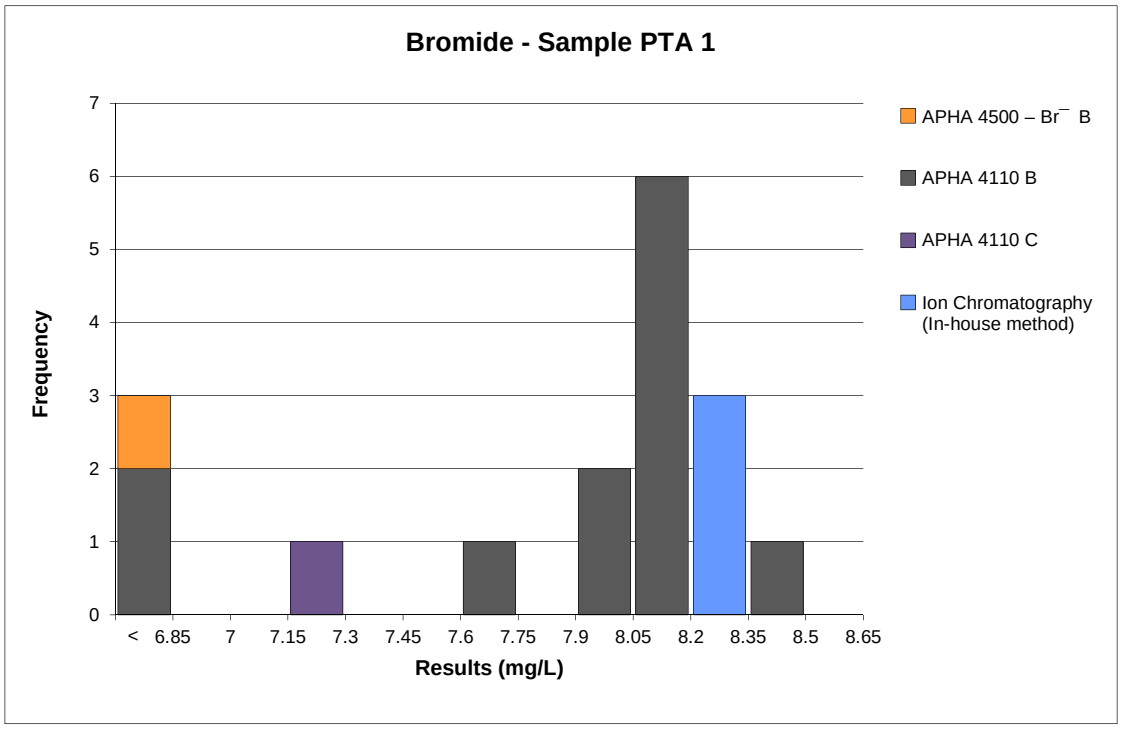


Figure 1. Spread of results for Bromide testing of sample PTA 1, with a median of 8.105 mg/L.

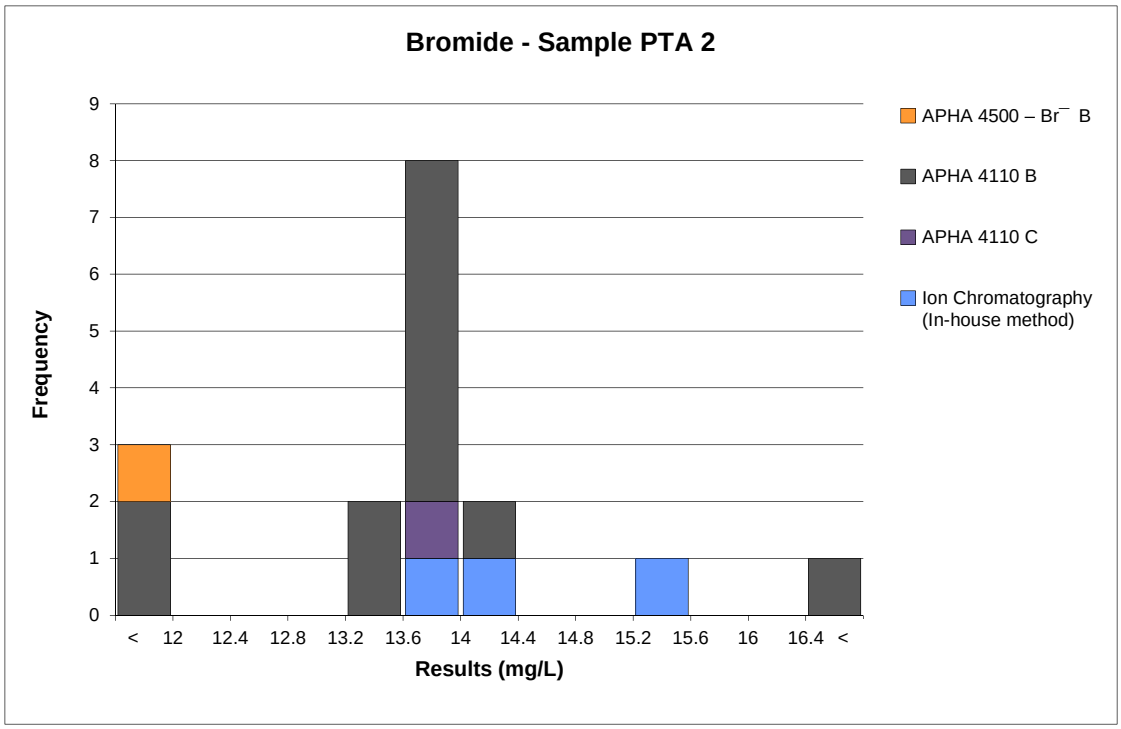


Figure 2. Spread of results for Bromide testing of sample PTA 2, with a median of 13.80 mg/L.

4.2.2 Chloride (Cl)

Table 3 compares the Chloride medians and robust CVs from this round to those obtained in previous PTA rounds. These were comparable to the published precision information in APHA 4110, which indicated that CVs of 2.2%-11% could be expected for Chloride analysis using Ion Chromatography with Chemical Suppression.

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

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	70.30	5.6	31
	PTA 2	123.0	6.6	31
Report 993	PTA 1	60.60	3.2	25
	PTA 2	142.0	5.7	25
Report 959	PTA 1	81.20	4.8	35
	PTA 2	123.0	4.2	35

Bias / Accuracy

The Chloride testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 65.0 – 77.7 mg/L for sample PTA 1 and 110 – 137 mg/L for sample PTA 2.

Out of 31 participants, one questionable result ($2.0 < |z\text{-score}| < 3.0$) was reported for sample PTA 1 (laboratory 287) and two questionable results were reported for sample PTA 2 (laboratories 105 and 234).

Two outlier results ($|z\text{-score}| \geq 3.0$) were obtained for sample PTA 1, requiring follow-up action by laboratories 234 and 308. Two outlier results were also obtained for sample PTA 2, requiring follow-up action by laboratories 479 and 683.

The Chloride data sets formed approximately normal distributions with no notable bias attributable to any one method (Figures 3 and 4). There was a large variety of methods used for Chloride testing in this round. The method used most frequently was APHA 4110 B (Ion Chromatography with Chemical Suppression of Eluent Conductivity), which was used by 45% of participants.

Laboratories wishing to investigate their results, may find useful the suggestions in the Bromide section of this report with respect to APHA 4110 B.

Measurement uncertainty (MU) values submitted for the current round of Chloride testing varied widely between participants. For laboratories using APHA 4110 B (method code 18), it was expected that the MU would be near 2x the published precision CVs mentioned at the beginning of this section (4.4%-22%); however, some laboratories had MU as low as 0.1% (laboratory 234) and as high as 35% (laboratory 106). If laboratories are using MU smaller than 4%, and find that their MU doesn't encompass the median in successive proficiency rounds, they are recommended to re-examine their MU calculations. The same applies for laboratories overestimating their MU.

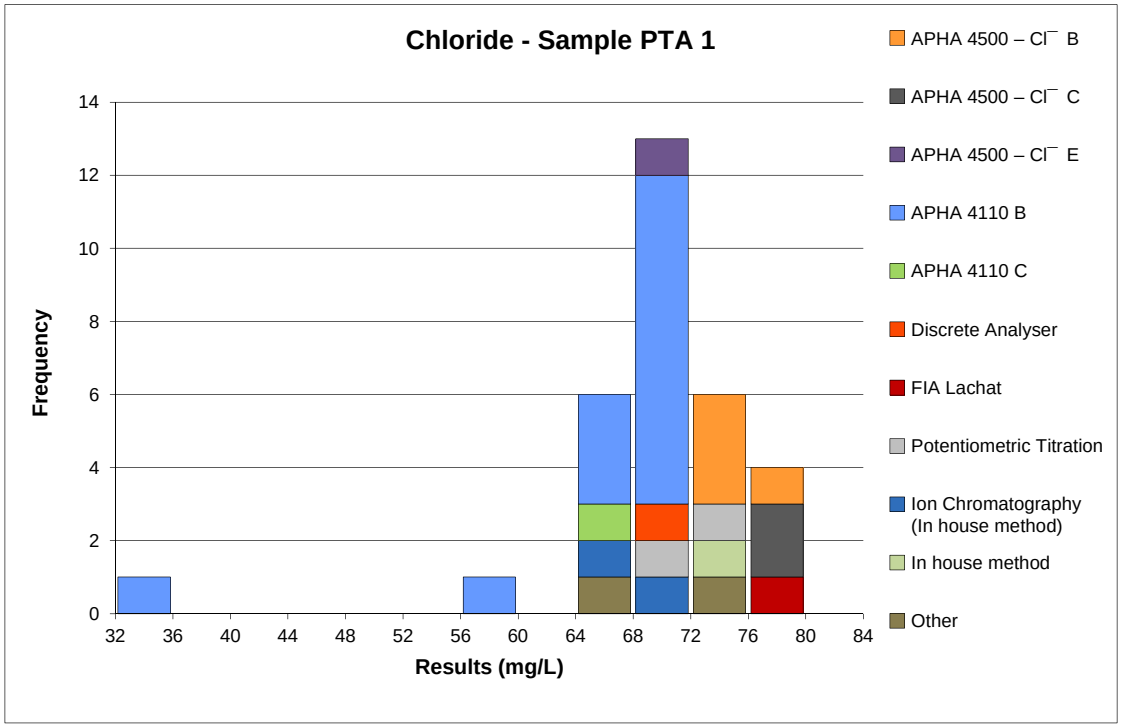


Figure 3. Spread of results for Chloride testing of sample PTA 1, with a median of 70.30 mg/L.

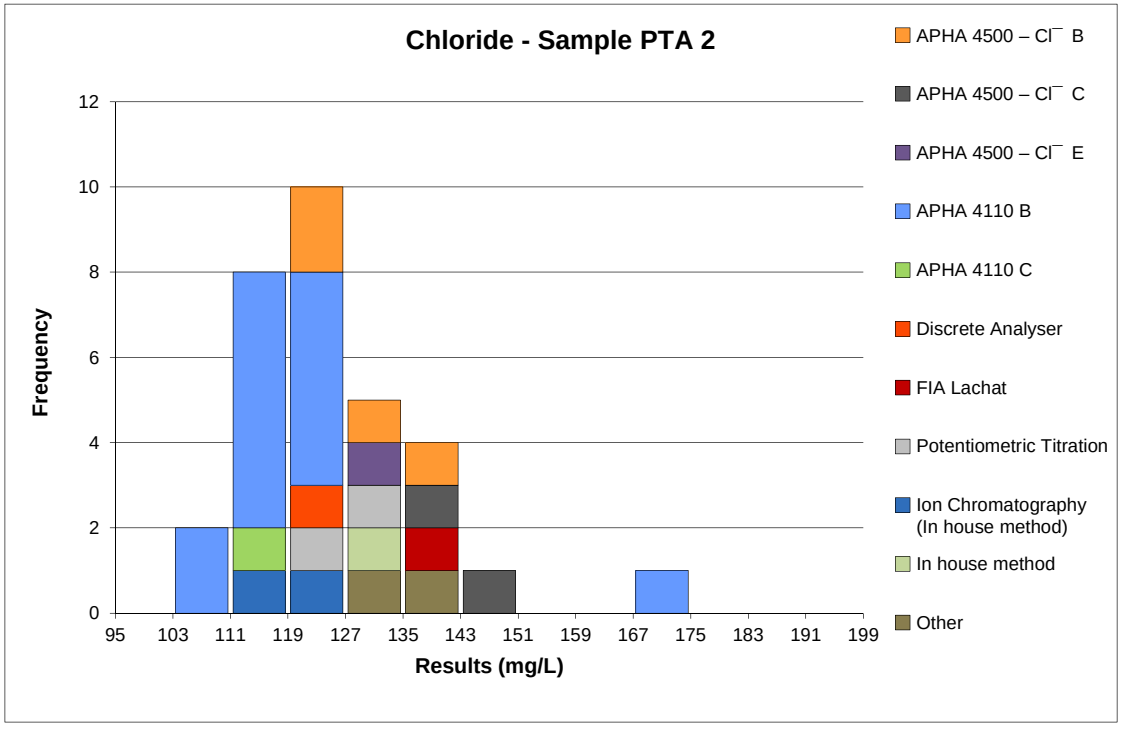


Figure 4. Spread of results for Chloride testing of sample PTA 2, with a median of 123.0 mg/L.

4.2.3 Fluoride (F)

Table 4 compares the Fluoride medians and robust CVs from this round to those obtained in previous PTA rounds. These are comparable to the published precision information in APHA 4110, which indicated that CVs of 2.9%-8.8% could be expected for Fluoride analysis using Ion Chromatography with Chemical Suppression; and CVs of between 2.9%-4.8% for the Ion Selective Electrode Method (APHA 4500-F^- C).

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

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	2.470	4.1	27
	PTA 2	3.460	3.1	27
Report 993	PTA 1	1.490	5.5	25
	PTA 2	4.430	3.0	25
Report 959	PTA 1	1.500	5.4	33
	PTA 2	2.970	3.4	33

Bias / Accuracy

The Fluoride testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 2.35 – 2.65 mg/L for sample PTA 1 and 3.29 – 3.67 mg/L for sample PTA 2.

Out of 27 participants, one questionable result (2.0 < |z-score| < 3.0) was reported for sample PTA 1 (laboratory 359) and two questionable results were reported for sample PTA 2 (laboratories 359 and 449).

Four outlier results (|z-score| ≥ 3.0) were obtained for sample PTA 1, requiring follow-up action by laboratories 189, 234, 308 and 519. Five outlier results were obtained for sample PTA 2, requiring follow-up action by laboratories 189, 222, 234, 479 and 519.

The Fluoride data sets formed approximately normal distributions with no significant bias attributable to any one method (Figures 5 and 6). The methods most frequently used for Fluoride testing in this round were APHA 4110 B (Ion Chromatography with Chemical Suppression of Eluent Conductivity) and APHA 4500- F^- C (Ion Selective Electrode Method), with 44% and 37% of participants, respectively.

As Fluoride is the first analyte to elute in Ion Chromatography columns, it is important to minimise the effect of the “water dip” for fluoride analysis. APHA 4110 B makes the following recommendations as potential options for improving fluoride analysis results:

- laboratories to analyse standards that bracket the expected result,
- eliminate the water dip by diluting the sample with eluent,
- adding concentrated eluent to the sample to give the name HCO_3^-/CO_3^{2-} concentration as the eluent,
- gradient elution using an NaOH eluent,
- try alternative columns.

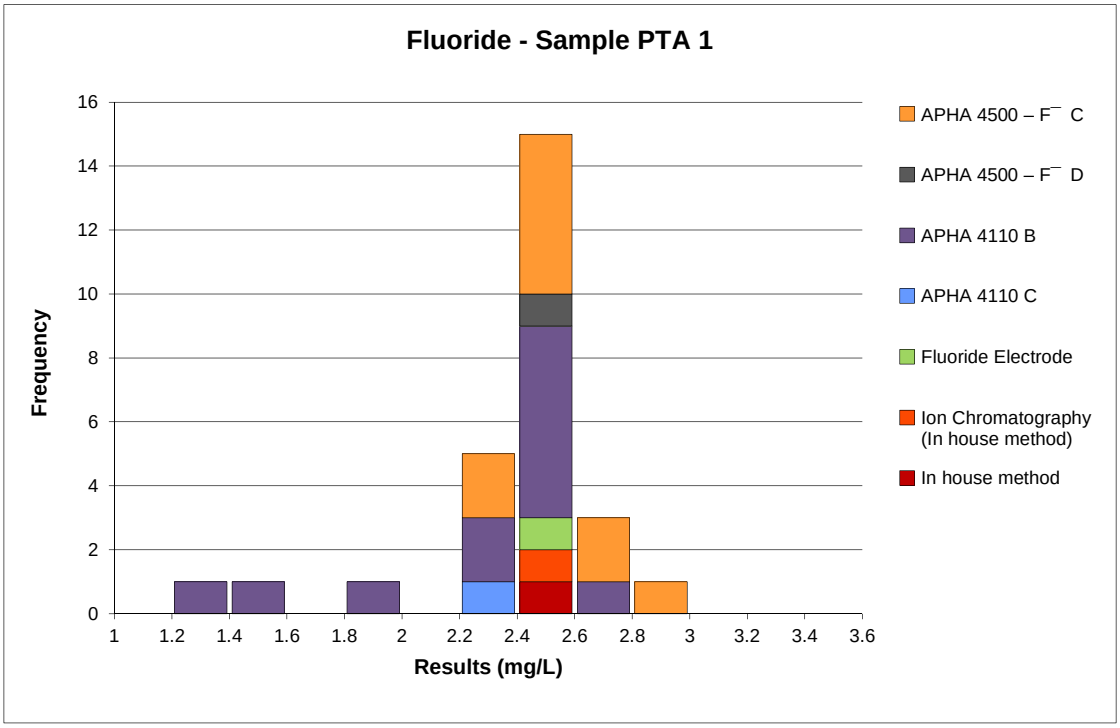


Figure 5. Spread of results for Fluoride testing of sample PTA 1, with a median of 2.470 mg/L.

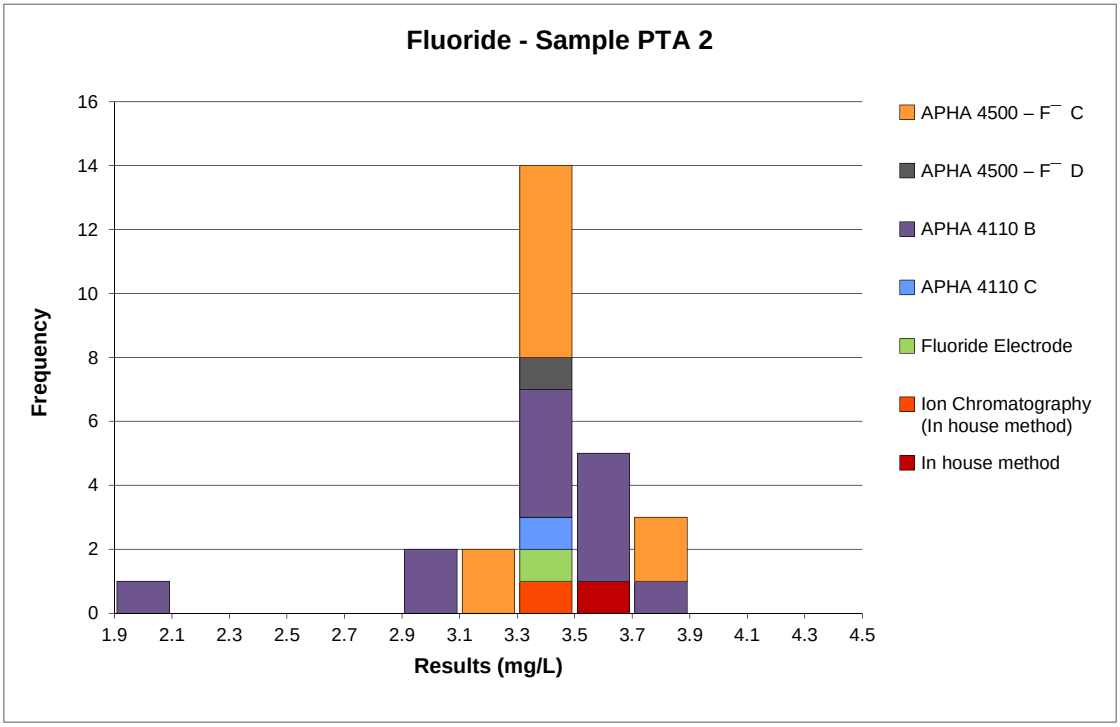


Figure 6. Spread of results for Fluoride testing of sample PTA 2, with a median of 3.460 mg/L.

4.2.4 Iodide (I)

Table 5 compares the Iodide medians and robust CVs from this round to those obtained in previous PTA rounds. There is limited published precision information regarding testing of Iodide by ICP-MS (Inductively Coupled Plasma - Mass Spectrometry) and Ion Chromatography to provide a basis for independent comparison, however CVs have been relatively consistent over historical proficiency rounds.

Table 5. Comparison of current round variability and proficiency medians of Iodide testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	0.625	12.8	6
	PTA 2	1.650	13.7	7
Report 993	PTA 1	0.7270	12.8	7
	PTA 2	1.780	13.7	7
Report 959	PTA 1	1.215	8.7	8
	PTA 2	0.838	33.1	8

Bias / Accuracy

The Iodide testing was successfully performed, with satisfactory results (|z-score| ≤ 2.0) ranging between 0.500 – 0.65 mg/L for sample PTA 1 and 1.52 – 2.00 mg/L for sample PTA 2.

Out of six results submitted for sample PTA 1 and seven results for sample PTA 2, no questionable results (2.0 < |z-score| < 3.0) were reported for both samples.

One outlier result (|z-score| ≥ 3.0) was obtained for sample PTA 1, requiring follow-up action by laboratory 277. No outlier results were obtained for sample PTA 2.

Homogeneity and stability testing (Appendix B) identified that Total Iodine showed a slight increase in the concentration of incubated samples (PTA 1 average: 0.65 mg/L) compared to the homogeneity samples (PTA 1 average: 0.61 mg/L). The NIQR was sufficiently wide (based on the homogeneity and stability results) to confirm that laboratories high biasing did not receive an action rating due to temperature abuse effects. Laboratory 277 received an action rating despite the wide NIQR values for sample PTA 1 and thus needs to look for possible sources of error in analysis.

Additionally, laboratory 353 submitted a result of “<1” for Iodide sample PTA 1. This result was deemed to be satisfactory.

The Iodide data sets formed approximately normal distributions (Figures 7 and 8). In-house Ion Chromatography methods were used by four out of seven participants for Iodide analysis in this round.

APHA have published three methods for testing iodide, which include APHA 4500-I^-B (Leuco Crystal Violet Method), APHA 4500-I^-C (Catalytic Reduction Method) and APHA 4500-I^-D (Voltametric Method). These test methods have gradually fallen out of

favour in preference for analysis by ICP-MS and Ion Chromatography, however, APHA 22nd Edition makes no mention of the use of these test methods for analysing Iodide, and laboratories appear to have developed their in-house procedures for analysing Iodide in this way.

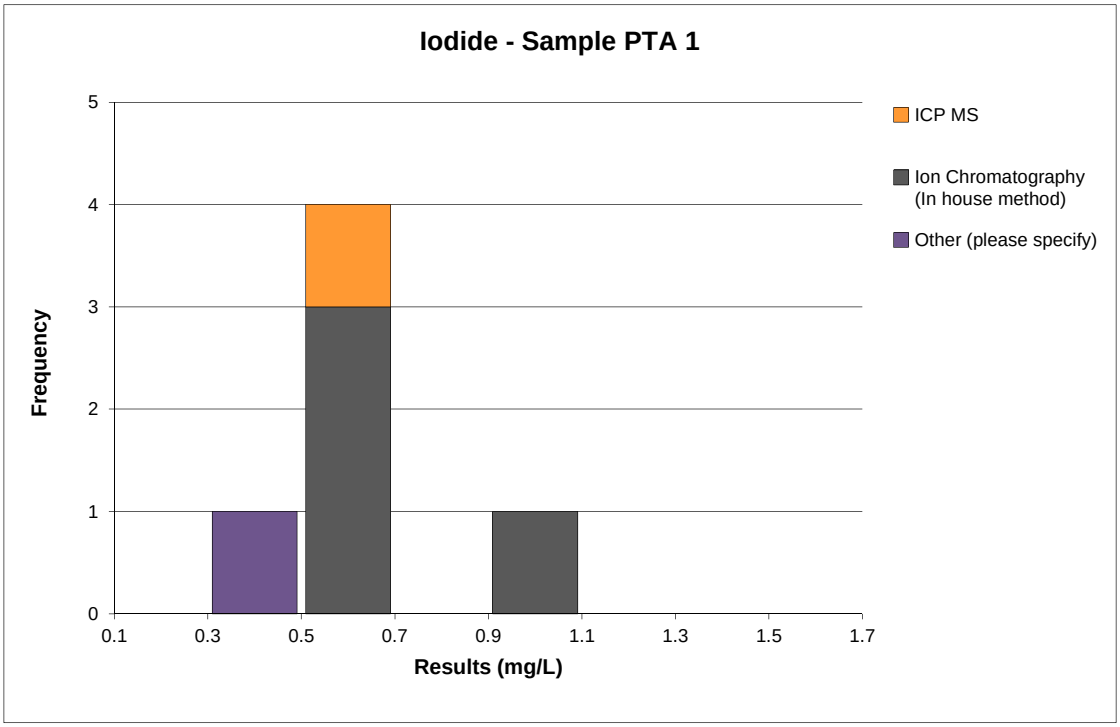


Figure 7. Spread of results for Iodide testing of sample PTA 1, with a median of 0.625 mg/L.

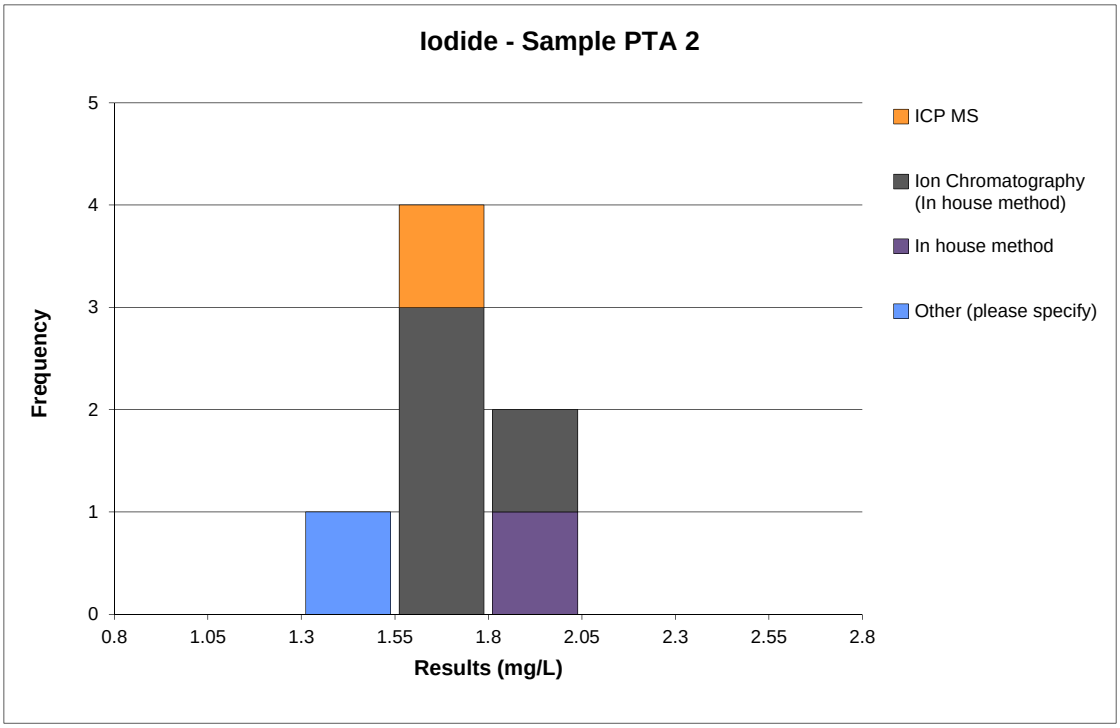


Figure 8. Spread of results for Iodide testing of sample PTA 2, with a median of 1.650 mg/L.

Historically the Water Halides proficiency round has offered Iodide testing, with fewer participants submitting results for this test over successive rounds. As halides are often not present as their ionic form, but in combination with other elements (e.g. Carbon or Oxygen), or as complex ions, it may be that Total Iodine is a more appropriate test to include in future proficiency rounds. When this is considered in conjunction with the requirements of the laboratory clients; please advise the Program Coordinator if laboratories would prefer to submit results for Total Iodine in future rounds of this program.

4.3 Measurement Uncertainty (MU)

The majority of participants in this round (75%-86%) reported the measurement uncertainty (MU) associated with their results. Table 6 below presents the number and percentage of laboratories reporting the MU for each analyte.

Table 6. The number and percentage of laboratories reporting MU for analytes in round 217

Analyte	Sample	Total participants	Participants reporting MU (percentage)
Bromide (Br)	PTA 1	16	12 (75%)
	PTA 2	16	12 (75%)
Chloride (Cl)	PTA 1	31	25 (81%)
	PTA 2	31	25 (81%)
Fluoride (F)	PTA 1	27	22 (81%)
	PTA 2	27	22 (81%)
Iodide (I)	PTA 1	6	5 (83%)
	PTA 2	7	6 (86%)

Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for these proficiency samples.

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

Conversely, laboratories that indicated a MU which was greater than three times the normalised IQR may have overestimated their MU.[1]

If laboratories overestimate or underestimate 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 [2]. It should be noted, however, that these are informative indicators only and cannot be solely used to validate or invalidate the MUs reported.

4.3 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 methods and analytes other than those presented below, there were less than 11 results submitted for each method and reliable conclusions cannot be drawn from analysing them on this occasion.

The method APHA 4110 B (Ion Chromatography with Chemical Suppression of Eluent Conductivity) was most frequently used for analysis of Bromide, Chloride and Fluoride. Table 7 below presents the median, uncertainty of the median and robust CV of results obtained by this method in Round 217.

Table 7. Variability and proficiency medians for Bromide, Chloride and Fluoride results obtained by method APHA 4110 B.

Analyte	Sample	Participants	Median ± Uncertainty of the Median (mg/L)	Robust CV (%)
Bromide (Br)	PTA 1	11	8.080 ± 0.063	2.1
	PTA 2	11	13.80 ± 0.11	2.1
Chloride (Cl)	PTA 1	14	69.30 ± 0.63	2.7
	PTA 2	14	119.0 ± 0.9	2.1
Fluoride (F)	PTA 1	12	2.470 ± 0.068	7.7
	PTA 2	12	3.410 ± 0.068	5.5

The CVs for Bromide and Chloride when tested by Ion Chromatography were tighter than those from the general population of results seen in Tables 2 and 3 (Bromide: PTA 1 CV: 3.0% and PTA 2 CV: 2.4%; Chloride: PTA 1 CV: 5.6% and PTA 2 CV: 6.6%) and better than the expected range published in APHA 4110 B (CVs of 3.1%-5.6% for Bromide and 2.2%-10.9% for Chloride).

The CVs for Fluoride when tested by Ion Chromatography were wider than those from the general population of results seen in Table 4 (PTA 1 CV: 4.1% and PTA 2 CV: 3.1%), however they were still within the expected range published in APHA 4110 B for Fluoride analysis (CVs of 2.9%-8.8%).

Additionally, for Fluoride, a relatively large number of participants (n=10) reported the use of method APHA 4500 – F^- C (Ion Selective Electrode Method). For Iodide, In-house Ion Chromatography methods were the most frequently employed, with four out of seven participants using these methods. In both cases, however, there were insufficient reported results to conduct an accurate statistical analysis.

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 8 below.

Table 8. Laboratory results identified as outliers for each analysis performed.

Lab Code	Analysis							
	Bromide		Chloride		Fluoride		Iodide	
	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2
154	§							
189					§	§		
222						§		
234	§	§	§		§	§		
277							§	
287	§	§						
308	§	§	§		§			
353		§						
479		§		§		§		
519					§	§		
683				§				

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

[3] APHA Standard Methods For the Examination of Water and WasteWater, 2012. 22nd Edition Published by APHA, AWWA & WEF.

APPENDIX A

Results and Data Analysis

Bromide (Br) A1
Chloride (Cl) A5
Fluoride (F) A11
Iodide (I) A17

Bromide (Br) Results

Samples PTA 1 and PTA 2

Bromide (Br)

Results by Laboratory Code

Laboratory Code	Sample PTA 1					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	mg/L					
106	8.5	±	1.1	1.64		3
121	7.96	±	0.13	-0.60		3
154	7.25		#	-3.55	**§**	4
186	8.23	±	0.99	0.52		11
215	8.18	±	1.39	0.31		3
234	4.95	±	0.0072	-13.10	**§**	3
277	8.21		#	0.44		11
287	3.07	±	0.79	-20.90	**§**	1
308[6]	0.02	±	4.8%	-33.56	**§**	3
353	8.31	±	1.00	0.85		11
359	7.94	±	0.40	-0.68		3
435	8.07	±	0.347	-0.15		3
479	8.17		#	0.27		3
509	8.20	±	0.25	0.39		3
519	7.69		#	-1.72		3
555	8.08	±	0.30	-0.10		3
617	8.13	±	0.50	0.10		3

No of Results:	16
Median:	8.105
Normalised IQR:	0.241
Uncertainty of the Median:	0.075
Robust CV:	3.0%
Minimum:	3.07
Maximum:	8.5
Range:	5.43

[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.

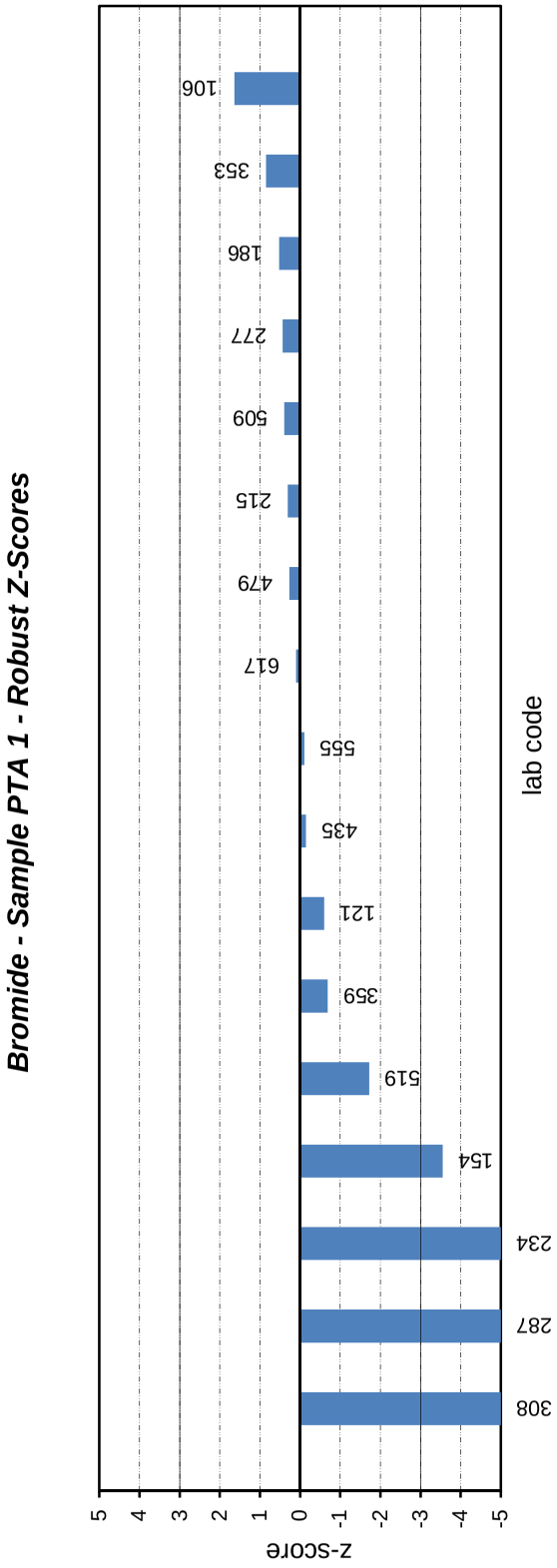
[4] "na" indicates "not applicable".

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

[6] Laboratory 308 submitted low Bromide results which were excluded from the calculated statistics.

Bromide - Sample PTA 1

Ordered Robust Z-Score Charts



Bromide (Br)

Results by Laboratory Code

Laboratory Code	Sample PTA 2					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	mg/L					
106	14	±	1.9	0.60		3
121	13.8	±	0.2	0.00		3
154	13.7		#	-0.30		4
186	14.4	±	1.8	1.80		11
215	13.8	±	1.66	0.00		3
234	8.83	±	0.0072	-14.90	**§**	3
277	13.8		#	0.00		11
287	9.47	±	1.76	-12.98	**§**	1
308[6]	0.00	±	4.8%	-41.37	**§**	3
353	15.6	±	1.88	5.40	**§**	11
359	13.7	±	0.69	-0.30		3
435	13.5	±	0.581	-0.90		3
479	21.0		#	21.58	**§**	3
509	14.0	±	0.4	0.60		3
519	13.4		#	-1.20		3
555	14.4	±	1.0	1.80		3
617	14.0	±	0.86	0.60		3

No of Results:	16
Median:	13.80
Normalised IQR:	0.33
Uncertainty of the Median:	0.10
Robust CV:	2.4%
Minimum:	8.83
Maximum:	21.0
Range:	12.17

[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.

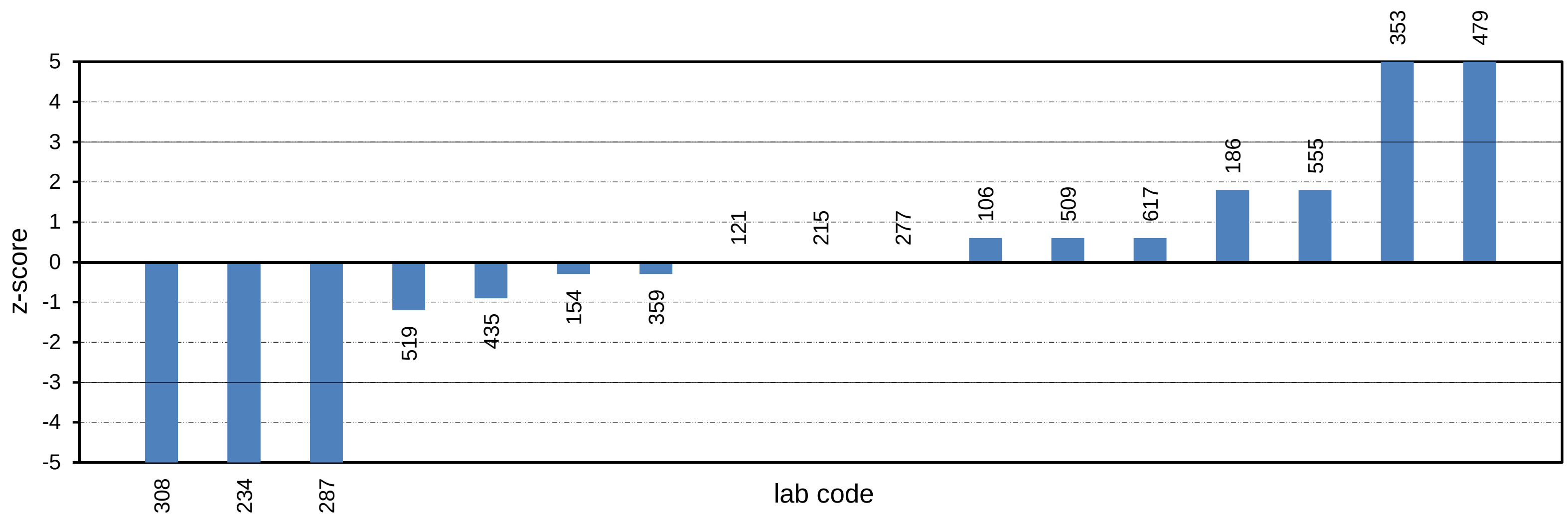
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

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

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

[6] Laboratory 308 submitted low Bromide results which were excluded from the calculated statistics.

Bromide - Sample PTA 2 - Robust Z-Scores



Ordered Robust Z-Score Charts

Bromide - Sample PTA 2

A4

Robust Z-Scores

Chloride (Cl) Results

Samples PTA 1 and PTA 2

Chloride (Cl)

Results by Laboratory Code

Laboratory Code	Sample PTA 1					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	mg/L					
101	69.1	±	1.7	-0.31		18
105	65.0	±	1.33	-1.35		35
106	70	±	24	-0.08		18
121	69.5	±	0.4	-0.20		18
154	66.6		#	-0.94		19
186	71	±	11	0.18		17
189	76.9	±	0.77	1.68		14
215	69.6	±	4.8	-0.18		18
222	72.0	±	3.77	0.43		30
234	57.6	±	0.0074	-3.23	**§**	18
277	67.7		#	-0.66		33
287	79.3	±	9.9	2.29		15
291	72.5	±	3.6	0.56		35
308	34.6	±	2.5%	-9.09	**§**	18
353	70.8	±	6.25	0.13		33
359	67.3	±	3.4	-0.76		18
417	73.6	±	0.7	0.84		34
435	70.0	±	2.87	-0.08		18
449	70.3	±	10.5	0.00		26
479	68.5		#	-0.46		18
494	75.2	±	10	1.25		14
509	67.6	±	1.4	-0.69		18
519	73.9		#	0.92		30
554	73.7		#	0.87		14
555	65.4	±	3.0	-1.25		18
608	73.2	±	2	0.74		14

[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.

Chloride (Cl) - cont.

Results by Laboratory Code

Laboratory Code	Sample PTA 1				
	Result ± mg/L		MU[1]	Robust z-score[2]	Method Code[3]
617	70.8	±	5.03	0.13	18
625	70.5		#	0.05	18
677	77.7	±	10	1.88	27
683	76.1	±	7.61	1.48	15
744	69.6	±	0.30	-0.18	18

No of Results:	31
Median:	70.30
Normalised IQR:	3.93
Uncertainty of the Median:	0.88
Robust CV:	5.6%
Minimum:	34.6
Maximum:	79.3
Range:	44.7

[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.

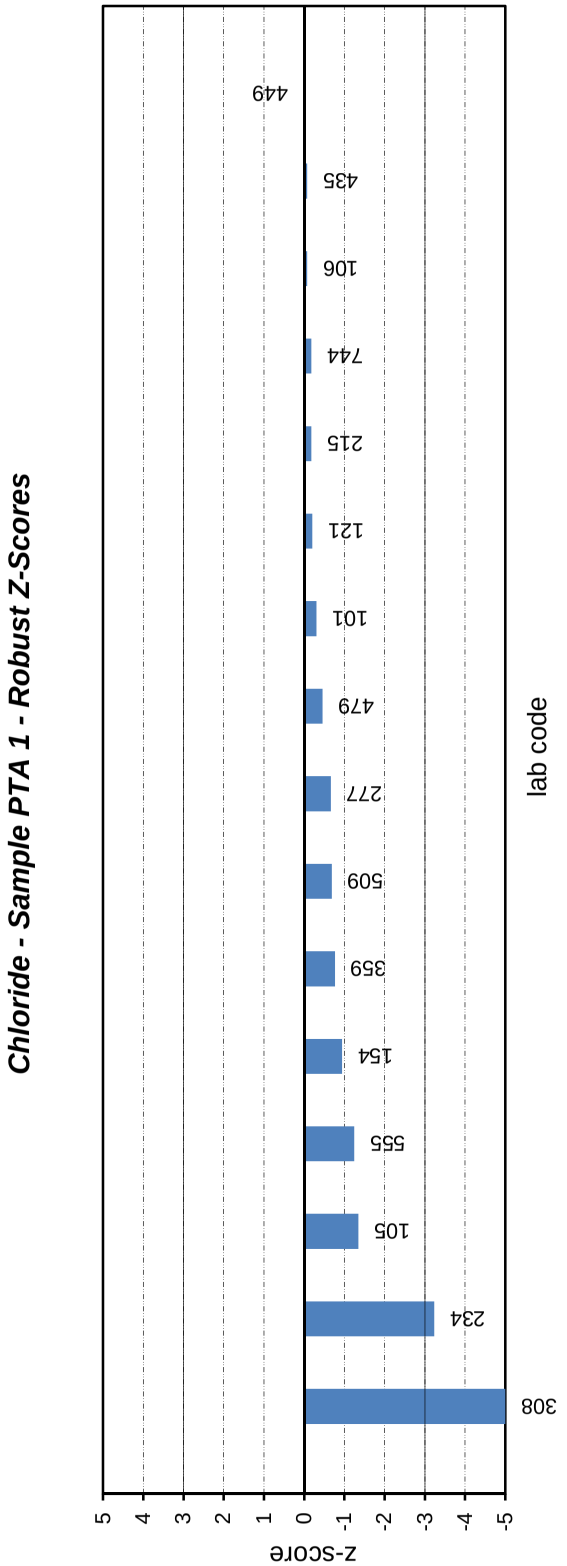
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

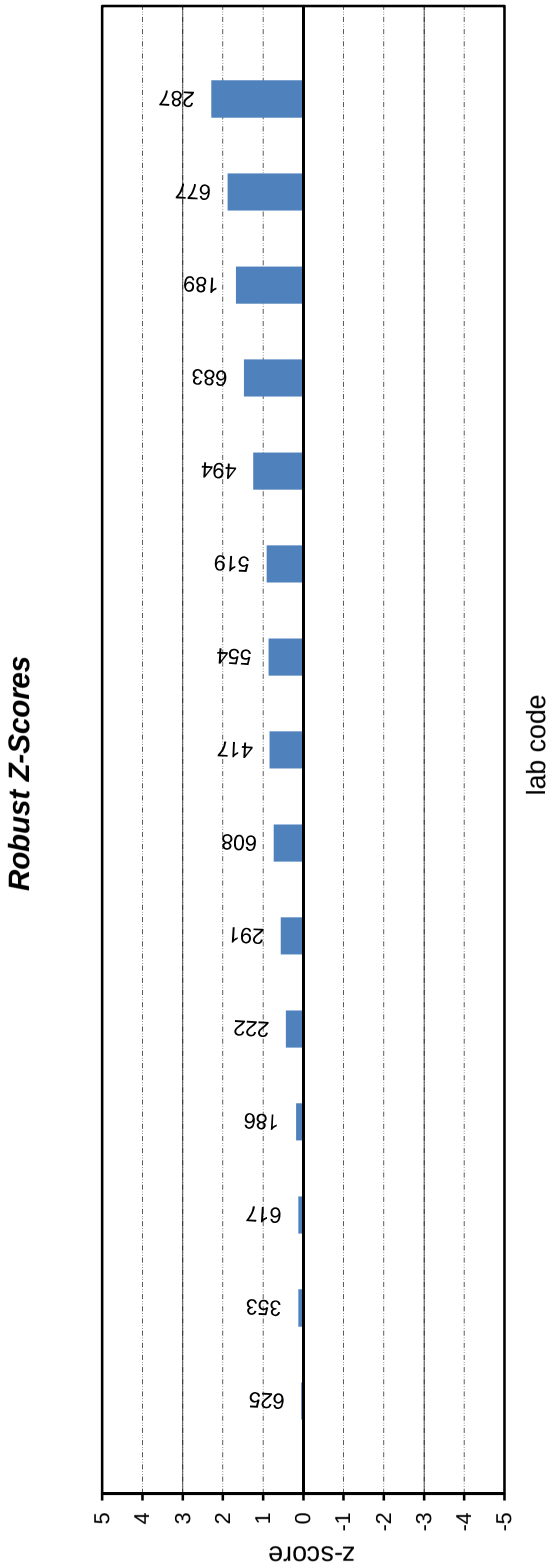
[4] "na" indicates "not applicable".

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

Chloride - Sample PTA 1

Ordered Robust Z-Score Charts





Chloride (Cl)

Results by Laboratory Code

Laboratory Code	Sample PTA 2					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	mg/L					
101	118	±	3	-0.61		18
105	140	±	1.33	2.08		35
106	110	±	38	-1.59		18
121	119	±	0.8	-0.49		18
154	112		#	-1.35		19
186	129	±	20	0.74		17
189	137	±	1.37	1.72		14
215	119	±	8.1	-0.49		18
222	126	±	6.59	0.37		30
234	104	±	0.0074	-2.33		18
277	117		#	-0.74		33
287	137	±	19	1.72		15
291	128	±	6.4	0.61		35
308	119.5	±	2.5%	-0.43		18
353	124	±	10.9	0.12		33
359	117	±	5.9	-0.74		18
417	129	±	2	0.74		34
435	120	±	4.92	-0.37		18
449	126	±	19	0.37		26
479	175.0		#	6.38	**§**	18
494	130	±	10	0.86		14
509	116	±	2	-0.86		18
519	135		#	1.47		30
554	123		#	0.00		14
555	118	±	12	-0.61		18
608	125	±	2	0.25		14

[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.

Chloride (Cl) - cont.

Results by Laboratory Code

Laboratory Code	Sample PTA 2				
	Result ± mg/L	MU[1]	Robust z-score[2]		Method Code[3]
617	122 ±	10.23	-0.12		18
625	121	#	-0.25		18
677	137 ±	14	1.72		27
683	150 ±	15.0	3.31	**§**	15
744	121 ±	0.3	-0.25		18

No of Results:	31
Median:	123.0
Normalised IQR:	8.2
Uncertainty of the Median:	1.8
Robust CV:	6.6%
Minimum:	104
Maximum:	175.0
Range:	71.0

[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.

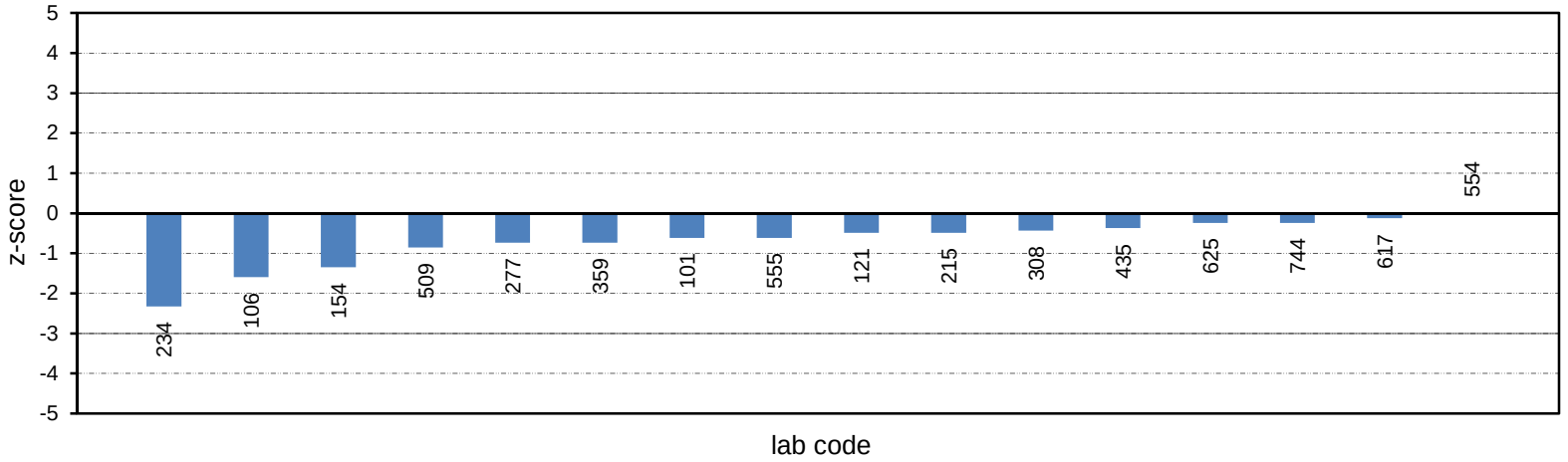
[4] "na" indicates "not applicable".

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

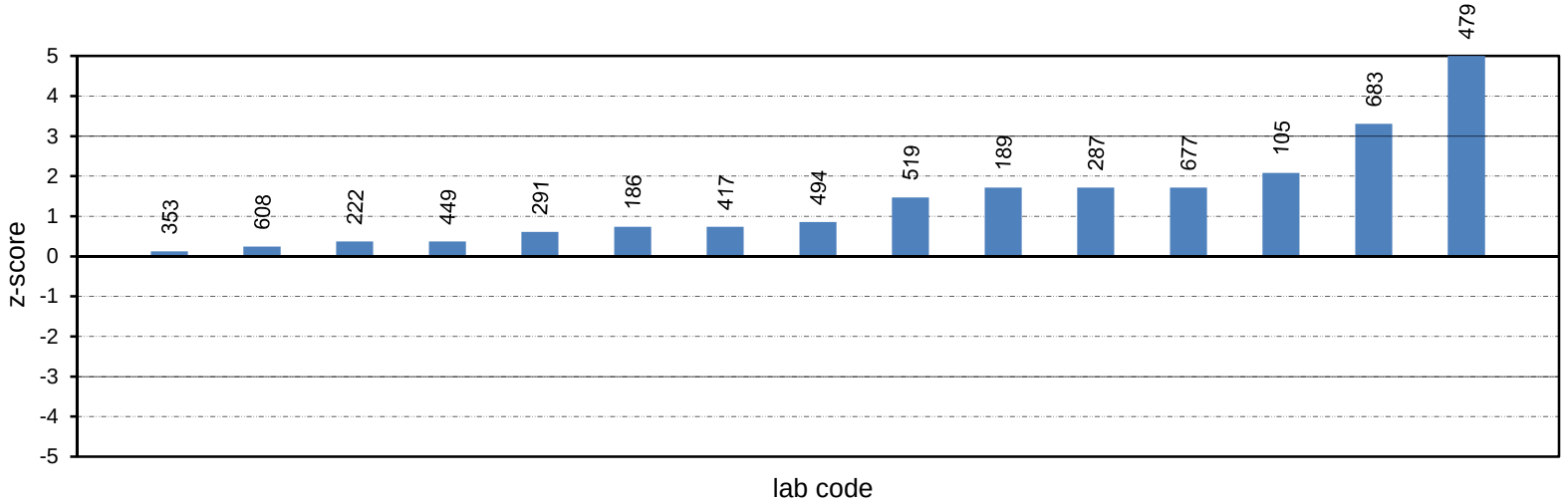
Chloride - Sample PTA 2

Ordered Robust Z-Score Charts

Chloride - Sample PTA 2 - Robust Z-Scores



Robust Z-Scores



Fluoride (F) Results

Samples PTA 1 and PTA 2

Fluoride (F)

Results by Laboratory Code

Laboratory Code	Sample PTA 1					
	Result ± mg/L		MU[1]	Robust z-score[2]		Method Code[3]
106	2.38	±	0.26	-0.90		37
121	2.52	±	0.07	0.50		41
154	2.35		#	-1.20		42
186	2.5	±	0.3	0.30		37
189	2.87	±	0.17	4.00	**§**	37
215	2.47	±	0.40	0.00		41
222	2.64	±	0.28	1.70		37
234	1.40	±	0.0072	-10.69	**§**	41
277	2.45		#	-0.20		51
287	2.59	±	0.51	1.20		38
308	1.55	±	9.1%	-9.19	**§**	41
359	2.74	±	0.14	2.70		41
417	2.46		#	-0.10		37
435	2.57	±	0.103	1.00		41
449	2.45	±	0.49	-0.20		37
479	2.4	±	0.24	-0.70		41
509	2.47	±	0.05	0.00		41
519	1.94		#	-5.30	**§**	41
555	2.38	±	0.20	-0.90		41
608	2.50	±	0.2	0.30		37
617	2.49	±	0.12	0.20		41
625	2.54		#	0.70		41

[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.

Fluoride (F) - cont.

Results by Laboratory Code

Laboratory Code	Sample PTA 1				
	Result ± mg/L		MU[1]	Robust z-score[2]	Method Code[3]
677	2.65	±	0.30	1.80	37
683	2.53	±	0.253	0.60	37
717	2.50	±	0.12	0.30	46
740	2.46	±	0.26	-0.10	52
744	2.40	±	0.16	-0.70	37

No of Results:	27
Median:	2.470
Normalised IQR:	0.100
Uncertainty of the Median:	0.024
Robust CV:	4.1%
Minimum:	1.40
Maximum:	2.87
Range:	1.47

[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.

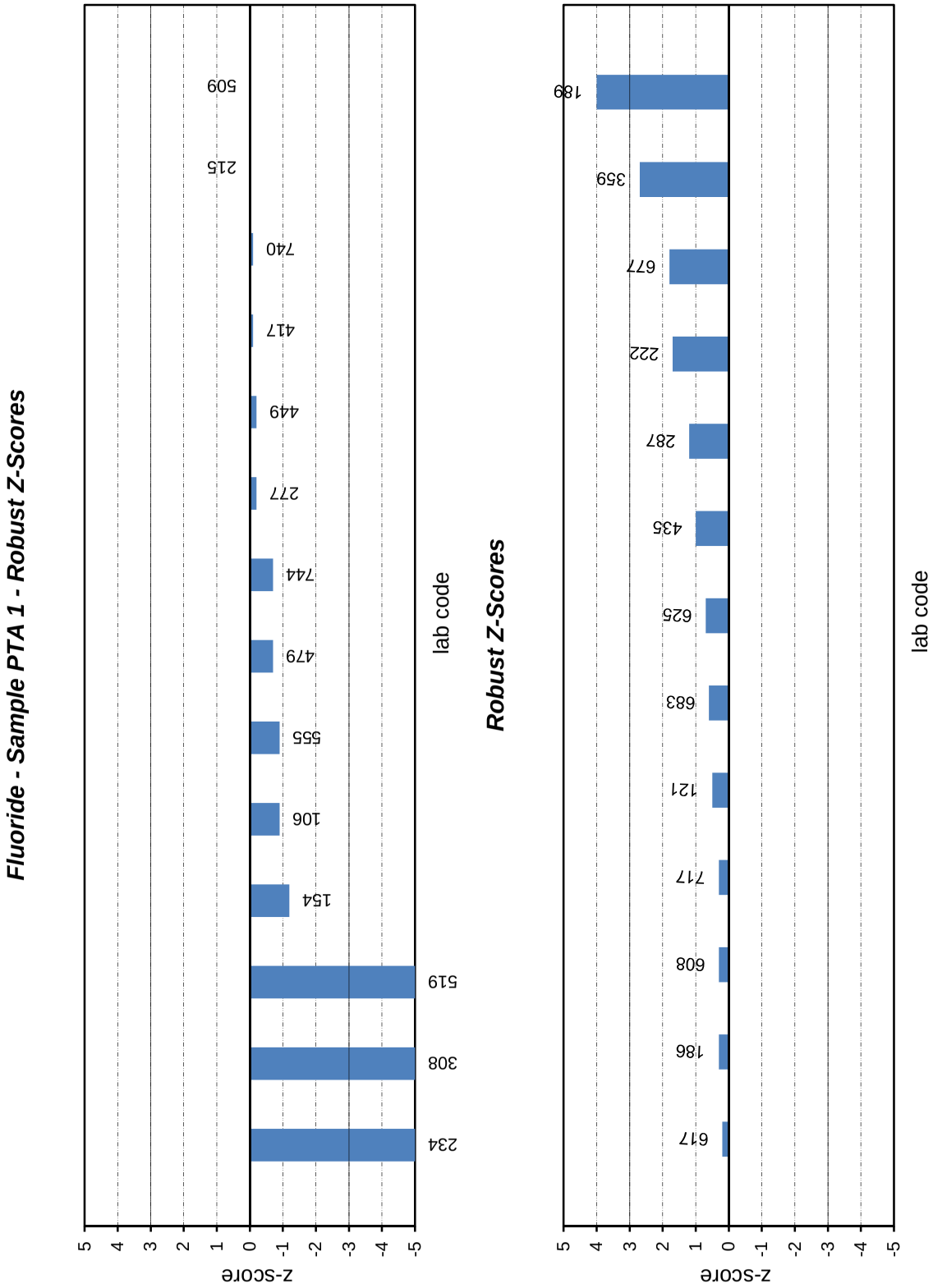
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

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

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

Fluoride - Sample PTA 1

Ordered Robust Z-Score Charts



Fluoride (F)

Results by Laboratory Code

Laboratory Code	Sample PTA 2					
	Result ± mg/L		MU[1]	Robust z-score[2]		Method Code[3]
106	3.29	±	0.36	-1.58		37
121	3.58	±	0.09	1.12		41
154	3.37		#	-0.84		42
186	3.5	±	0.4	0.37		37
189	3.82	±	0.23	3.35	**§**	37
215	3.37	±	0.55	-0.84		41
222	3.86	±	0.41	3.72	**§**	37
234	2.01	±	0.0072	-13.49	**§**	41
277	3.44		#	-0.19		51
287	3.50	±	0.62	0.37		38
308	3.35	±	9.1%	-1.02		41
359	3.76	±	0.19	2.79		41
417	3.40		#	-0.56		37
435	3.67	±	0.147	1.95		41
449	3.20	±	0.64	-2.42		37
479	3.1	±	0.31	-3.35	**§**	41
509	3.40	±	0.07	-0.56		41
519	2.94		#	-4.84	**§**	41
555	3.42	±	0.20	-0.37		41
608	3.46	±	0.2	0.00		37
617	3.53	±	0.18	0.65		41
625	3.52		#	0.56		41

[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.

Fluoride (F) - cont.

Results by Laboratory Code

Laboratory Code	Sample PTA 2				
	Result ± mg/L		MU[1]	Robust z-score[2]	Method Code[3]
677	3.48	±	0.4	0.19	37
683	3.48	±	0.348	0.19	37
717	3.48	±	0.18	0.19	46
740	3.51	±	0.37	0.47	52
744	3.37	±	0.16	-0.84	37

No of Results:	27
Median:	3.460
Normalised IQR:	0.107
Uncertainty of the Median:	0.026
Robust CV:	3.1%
Minimum:	2.01
Maximum:	3.86
Range:	1.85

[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.

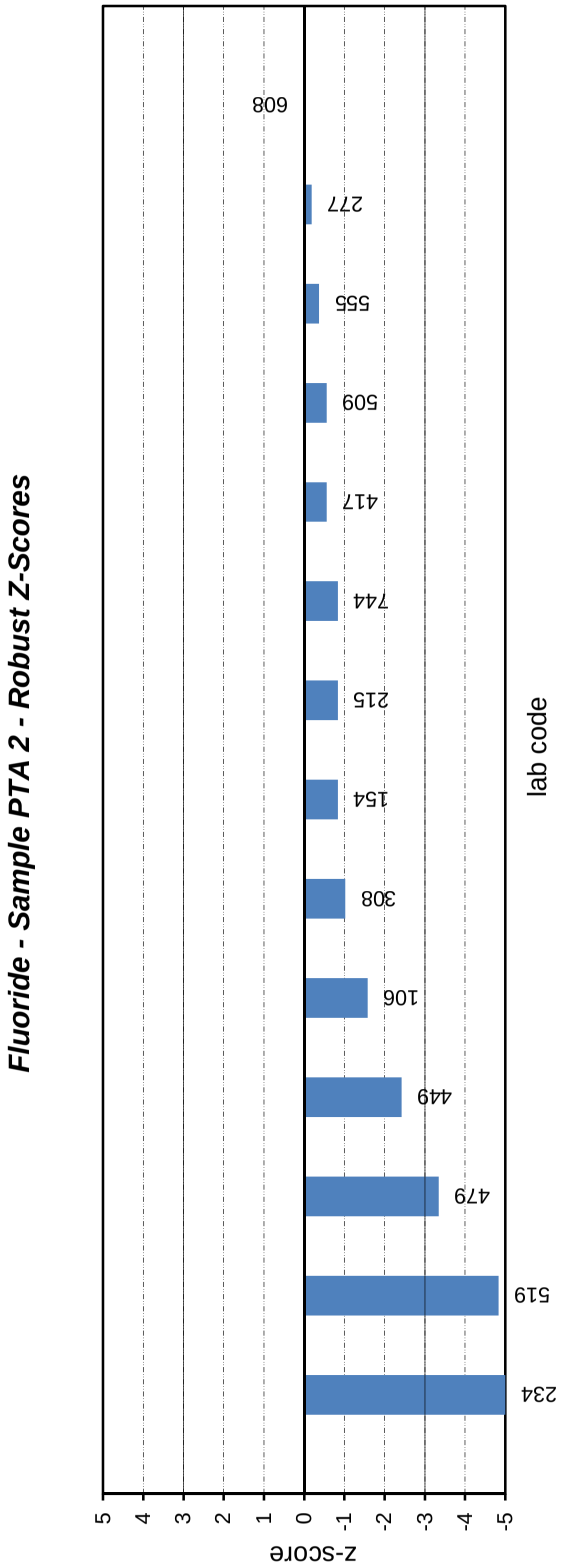
[3] Please refer to Appendix C (pages C3-C5) for method code descriptions.

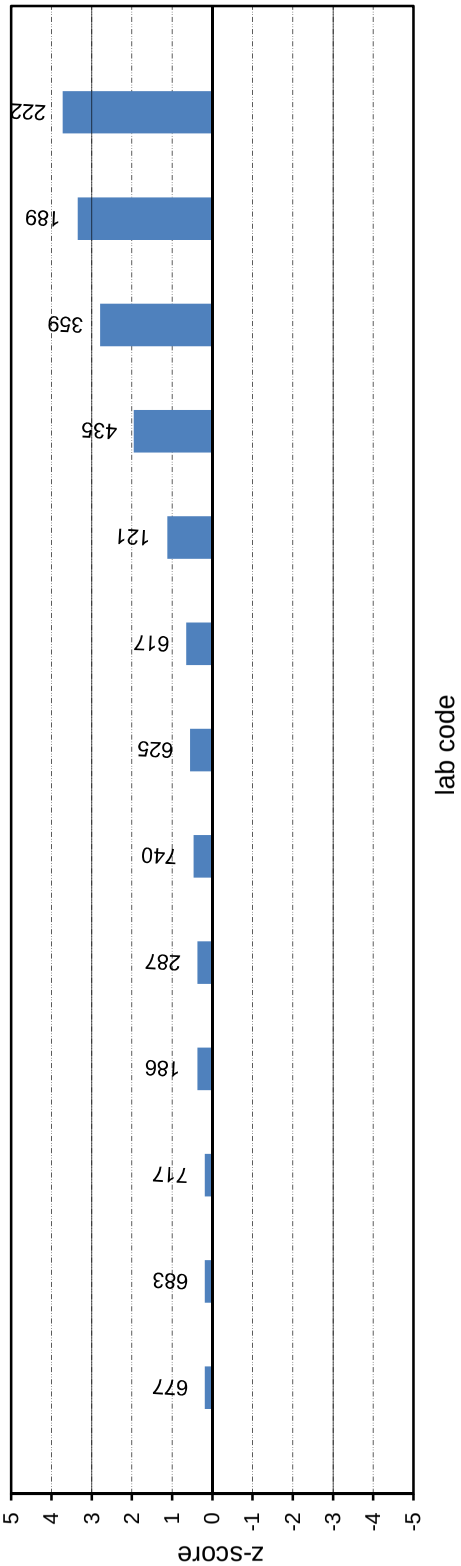
[4] "na" indicates "not applicable".

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

Fluoride - Sample PTA 2

Ordered Robust Z-Score Charts





Iodide (I) Results

Samples PTA 1 and PTA 2

Iodide (I)

Results by Laboratory Code

Laboratory Code	Sample PTA 1					
	Result	±	MU[1]	Robust z-score[2]		Method Code[3]
	mg/L					
106	0.65	±	0.07	0.31		57
186	0.60	±	0.10	-0.31		59
277	0.91		#	3.56	**§**	59
353	<1		#	na		60
359	0.500	±	0.10	-1.56		61
435	0.553	±	0.035	-0.90		59
617	0.65	±	0.20	0.31		59

No of Results:	6
Median:	0.625
Normalised IQR:	0.080
Uncertainty of the Median:	0.041
Robust CV:	12.8%
Minimum:	0.500
Maximum:	0.91
Range:	0.410

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

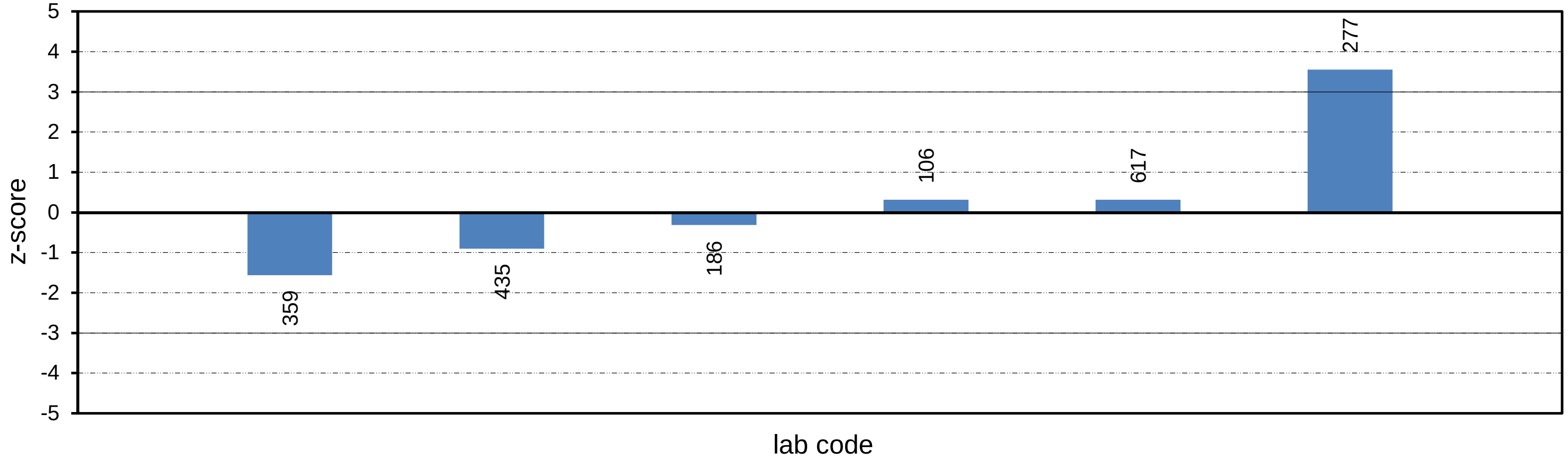
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

[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.

Iodide - Sample PTA 1 - Robust Z-Scores



Robust Z-Scores

Iodide (I)

Results by Laboratory Code

Laboratory Code	Sample PTA 2				
	Result	±	MU[1]	Robust z-score[2]	Method Code[3]
	mg/L				
106	1.6	±	0.16	-0.22	57
186	1.72	±	0.26	0.31	59
277	1.95		#	1.33	59
353	2.00	±	0.45	1.55	60
359	1.52	±	0.10	-0.58	61
435	1.57	±	0.100	-0.36	59
617	1.65	±	0.65	0.00	59

No of Results:	7
Median:	1.650
Normalised IQR:	0.225
Uncertainty of the Median:	0.107
Robust CV:	13.7%
Minimum:	1.52
Maximum:	2.00
Range:	0.48

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

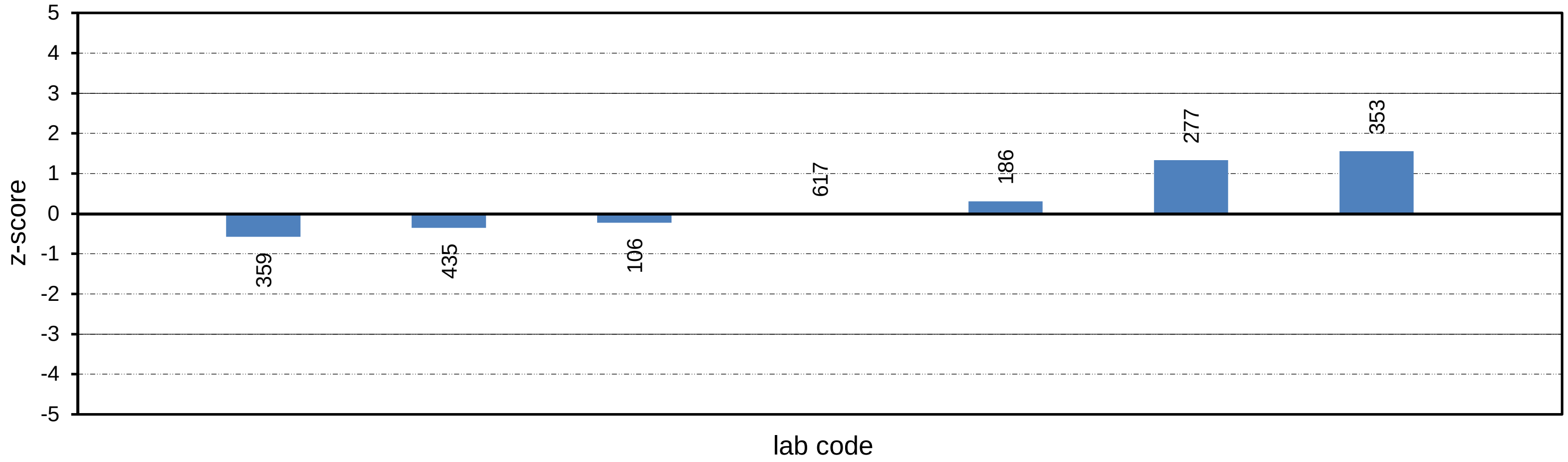
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

[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.

Iodide - Sample PTA 2 - Robust Z-Scores



Robust Z-Scores

APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing B1

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 sample concentrates was chosen from samples PTA 1 (Table B1) 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 Hill Laboratories, New Zealand. Total Iodine underwent TMAH Digestion and analysis with ICP-MS (Inductive Coupled Plasma - Mass Spectrometry) using APHA 3125 B; Bromide was analysed using Ion Chromatography method APHA 4110 B; Chloride was analysed using Ferric thiocyanate colorimetry using discrete analyser method APHA 4500 Cl^- E; and Fluoride was analysed with an ion selective electrode using method APHA 4500-F^- C.

Stability samples for Bromide, Chloride and Fluoride showed no increased variability when compared to the chilled samples, however, Total Iodine did show a slight increase in the concentration of incubated samples compared to the homogeneity samples.

Samples PTA 2 (Table B2) were also tested to confirm the levels were within the expected range. Homogeneity and stability characteristics were assumed to be similar to samples PTA 1, based on identical manufacturing procedure and sample handling.

From statistical analysis 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 could not be attributed to any notable sample variability.
Iodine results were assessed in the round to confirm that the NIQR was sufficiently wide to ensure laboratories high biasing were not unfairly penalised due to temperature abuse effects.

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

Round PTA 217		**Samples PTA 1 (g/m^3)**							
	Sample ID	Total Iodine		Bromide		Chloride		Fluoride	
		Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2	Rep 1	Rep 2
Homogeneity	H1	0.60	0.61	8.39	8.36	77	74	2.60	2.63
	H2	0.60	0.61	8.42	8.38	76	74	2.61	2.58
	H3	0.62	0.62	8.39	8.38	74	73	2.60	2.63
	H4	0.62	0.62	8.38	8.38	75	73	2.61	2.60
	H5	0.61	0.58	8.37	8.37	77	75	2.57	2.63
	H6	0.60	0.61	8.37	8.39	76	75	2.61	2.60
	H7	0.61	0.61	8.37	8.37	77	75	2.60	2.58
Stability	S1	0.66	0.65	8.37	8.40	78	75	2.61	2.60
	S2	0.66	0.65	8.36	8.39	76	74	2.63	2.58
	S3	0.64	0.65	8.37	8.39	75	74	2.61	2.64
	RSD	3.76%	3.63%	0.19%	0.15%	1.41%	0.83%	0.61%	0.86%

Table B2. Confirmatory testing of PTA 2 samples.

Round PTA 217	**Samples PTA 2 (g/m^3)**				
	Sample ID	Total Iodine	Bromide	Chloride	Fluoride
Homogeneity	H1	1.73	14.368	122	3.61
	H2	1.71	14.151	125	3.65
	RSD	0.71%	1.08%	1.75%	0.76%

Please note that the mean results for these tests are not intended to be used as reference values.

APPENDIX C

Documentation

Instructions to Participants C1
Method Codes C3
Results Sheet C6

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 217 **AUGUST, 2017**

Bromide, Chloride, Fluoride, Iodide

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 Limited (New Zealand). The bottles contain approximately 430 mL of artificial potable water for analysis of Bromide, Chloride, Fluoride and Iodide.

ii) To minimise the possibility of change in concentration, do not open the samples until ready to commence analysis.

iii) The samples were refrigerated (1 - 5ºC) prior to dispatch and any liquid on the outside of the bottles may be due to condensation rather than sample leakage.

iv) The samples have not been preserved and if analyses cannot be commenced on the day of receipt, it is recommended that the samples be stored under refrigeration and in the dark.

v) The samples are ready to test (please follow the **Sample Preparation** steps below).

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

2. Sample Preparation (for each of the PTA 1 and PTA 2 samples)

Caution: Analysis must begin immediately after bottle is opened.

i) Adjust bottle temperature to 20ºC and mix thoroughly.

ii) Record bottle ID number. Open bottle.

iii) Test according to your normal procedures.

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

Please report results in mg/L to three significant figures for this ready to test sample.

3. Tests Requested

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

i) Bromide (Br^-)
ii) Chloride (Cl^-)
iii) Fluoride (F^-)
iv) Iodide (I^-)

(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 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 personal protective equipment such as safety glasses, gloves, laboratory coats and fume hoods, where appropriate during the determinations, is recommended.

5. Reporting

i) For <u>each</u> sample only a single result is requested.
ii) Report results in milligrams per litre (mg/L).
iii) For statistical purposes, report results to three significant figures:
e.g. 123 mg/L, 12.3 mg/L or 1.23 mg/L etc.
iv) Do not correct results for recovery.
v) Select the appropriate method code for each test from the Method Code Table and record it on the Results Sheet.
vi) 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 SEPTEMBER 2017** 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**			
Bromide (Br^-)	5	–	20	mg/L
Chloride (Cl^-)	50	–	175	mg/L
Fluoride (F^-)	1.0	–	5.0	mg/L
Iodide (I^-)	0.5	–	2.0	mg/L

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Bromide (Br^-)	APHA	APHA 4500 – Br^- B. Phenol Red Colorimetric Method	1
		APHA 4500 – Br^- D. Flow Injection Analysis	2
		APHA 4110 B. Ion Chromatography with Chemical Suppression of Eluent Conductivity	3
		APHA 4110 C. Single-Column Ion Chromatography with Direct Conductivity	4
		APHA 4110 D. Ion Chromatographic Determination of Oxyhalides and Bromide	5
		APHA 4140 B. Capillary Ion Electrophoresis with Indirect UV Detection	6
	ISO	ISO 10304–1:2007 Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate	7
	US EPA	US EPA 300.1 Inorganic Anions in DW by Ion Chromatography	8
	Other	ICP MS	9
		ICP OES/AES	10
		Ion Chromatography (In-house method)	11
		In-house method	12
		Other (please specify)	13
Chloride (Cl^-)	APHA	4500 – Cl^- B. Argentometric Method	14
		4500 – Cl^- C. Mercuric Nitrate Method	15
		4500 – Cl^- D. Potentiometric Method	16
		4500 – Cl^- E. Automated Ferricyanide Method	17
		4110 B. Ion Chromatography with Chemical Suppression of Eluent Conductivity	18
		4110 C. Single-Column Ion Chromatography with Direct Conductivity Detection	19
		4140 B. Capillary Ion Electrophoresis with Indirect UV Detection	20
	ASTMD	ASTM D 512 – 04 Standard Test Methods for Chloride Ion in Water	21
	ISO	ISO 10304–1:2007 Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulphate	22
		ISO 10304 – 4: 1997 Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 4: Determination of chlorate, chloride and chlorite in water with low contamination	23

Continued on next page

Method Codes to be used for the Results Sheet (cont.)

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Chloride (Cl^-) (cont.)	ISO	ISO 15682:2000 Water quality – Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection	24
		ISO 9297:1989 Water quality -- Determination of chloride -- Silver nitrate titration with chromate indicator (Mohr's method)	25
	Other	Discrete Analyser	26
		FIA Lachat	27
		ICP MS	28
		ICP OES/AES	29
		Potentiometric Titration	30
		Segmented Flow Analysis	31
		Spectroquant	32
		Ion Chromatography (In house method)	33
		In house method	34
		Other (please specify)	35
Fluoride (F^-)	APHA	4500 – F^- B. Preliminary Distillation Step	36
		4500 – F^- C. Ion Selective Electrode Method	37
		4500 – F^- D. SPADNS Method	38
		4500 – F^- E. Complexone Method	39
		4500 – F^- G. Ion-Selective Electrode Flow Injection Analysis	40
		4110 B. Ion Chromatography with Chemical Suppression of Eluent Conductivity	41
		4110 C. Single-Column Ion Chromatography with Direct Conductivity Detection	42
		4140 B. Capillary Ion Electrophoresis with Indirect UV Detection	43
	ASTM	ASTM D 1179 – 04 Standard Test Methods for Fluoride Ion in Water	44
	ISO	ISO 10304–1:2007 Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1	45
	Other	Fluoride Electrode	46
		ICP MS	47
		ICP OES/AES	48
		SPAONS Method	49
		SPADNS Discrete Analyser	50
		Ion Chromatography (In house method)	51
		In house method	52
		Other (please specify)	53

Continued on next page

Method Codes to be used for the Results Sheet (cont.)

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Iodide (I^-)	APHA	4500 – I^- B. Leuco Crystal Violet Method	53
		4500 – I^- C. Catalytic Reduction Method	54
		4500 – I^- D. Voltametric Method	55
	ISO	ISO 10304 –3:1997 Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate	56
	Other	ICP MS	57
		ICP OES/AES	58
		Ion Chromatography (In house method)	59
		In house method	60
		Other (please specify)	61

Method Reference Key

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

ii) ASTM *Annual Book of ASTM Standards, Vol. 11.01(2004).* (http://www.astm.org)

iii) ISO International Organization for Standardization. (http://www.iso.org).

iv) US EPA U.S Environmental Protection Agency. (https://www.epa.gov/measurements/collection-methods)

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 217

Bromide, Chloride, Fluoride, Iodide
AUGUST, 2017

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		
	Result (mg/L)	±MU (mg/L)	METHOD CODE	Result (mg/L)	±MU (mg/L)	METHOD CODE
Bromide (Br^-)						
Chloride (Cl^-)						
Fluoride (F^-)						
Iodide (I^-)						

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

ii) For statistical purposes, report results to three significant figures:
e.g. 123 mg/L, 12.3 mg/L or 1.23 mg/L etc.

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 SEPTEMBER 2017** 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 -