



**Report No. 824**

***Waters Proficiency Testing***

**Round 157**

***- Bromide, Chloride, Fluoride, Iodide***

**October 2013**

**Acknowledgments**

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

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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 157 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in July 2013 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 Ms D Mihaila and the Technical Advisor was Ms R Ryan from Global Proficiency Ltd, New Zealand. This report was authorised by Ms W Fajloun, PTA Quality Coordinator.

## 2. Program Features and Design

- 2.1 Each laboratory was randomly allocated a unique code number for the program to ensure confidentiality of results. Reference to each laboratory in this report is by code number only. Please note that a number of laboratories reported more than one set of results and, therefore, their code numbers (with letter) could appear several times in the same data set.
  - 2.2 Laboratories were provided with the "Instructions to Participants" and "Results Sheet" (see Appendix C). Laboratories were requested to perform the tests according to their routine methods.
  - 2.3 Participants were provided with two plastic bottles (labelled PTA 1 and PTA 2) containing solutions of bromide, chloride, fluoride and iodide.
  - 2.4 A total of 59 laboratories received samples, comprising:
    - 44 Australian participants; and
    - 15 overseas participants, including:
      - Brunei Darussalam (1), Democratic Republic of Congo (1), Indonesia (2), Malaysia (2), New Zealand (1), Papua New Guinea (2), Singapore (2), South Korea (3), Thailand (1).
- Of these 59 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, uncertainty of the median, normalised interquartile range, 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, 2012* (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 30.
- 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 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 close to zero indicates that the result agrees well with those from other laboratories. Whereas, a z-score with an absolute value greater than or equal to 3.0 is considered to be an outlier and is marked by the symbol "§".

Each determination was examined for outliers with all methods pooled. The table on page 30 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;
- *Uncertainty of the Median*: a robust estimate of the standard deviation of the *Median*;
- *Normalised IQR*: the normalised interquartile range of the results;
- *Robust CV*: the robust coefficient of variation expressed as a percentage, i.e.  $100 \times \text{Normalised IQR} / \text{Median}$ ;
- *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:

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

$n$  = 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 Advisor's Comments

##### 4.1 Metrological Traceability and Measurement Uncertainty of Assigned Values

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

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

Solutions were stable and homogeneous, and medians obtained from this proficiency round were in good agreement with the expected levels (dope concentration), as shown in Table 1.

The assigned value for this program is the median of the results submitted by the participants. The average analyte recovery and the uncertainty of the median have been calculated and are also presented in Table 1.

Analyte	Sample	Dope Concentration (mg/L)	Median (mg/L)	Analyte Recovery (%)	Uncertainty of the median (mg/L)
Bromide	PTA 1	5.50	5.50	100	0.05
	PTA 2	12.50	12.60	101	0.12
Chloride	PTA 1	60.0	60.40	101	0.38
	PTA 2	80.0	82.25	103	0.86
Fluoride	PTA 1	1.40	1.380	99	0.012
	PTA 2	1.91	1.890	99	0.020
Iodide	PTA 1	1.10	1.080	98	0.019
	PTA 2	0.656	0.645	98	0.017

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

Overall, the performance of participants in this round was good, with robust CVs below 10% for all analytes.

## 4.2 Analysis of Round 157 Results

### 4.2.1 Bromide

Table 2 compares the bromide medians and robust CVs from this round to those obtained in previous PTA rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	No. of Results
This study	PTA 1	5.50	4.0	29
	PTA 2	12.60	4.1	29
Report 761	PTA 1	15.80	9.9	31
	PTA 2	13.80	7.0	31
Report 707	PTA 1	11.90	4.0	30
	PTA 2	8.11	5.7	30

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

The CV's obtained for bromide in this round are comparable to those observed in previous rounds.

#### Bias / Accuracy

Bromide testing was successfully carried out, with satisfactory results ( $|z\text{-score}| \leq 2.0$ ) ranging between 5.06 – 5.95 mg/L for sample PTA 1 and 11.56 – 13.64 mg/L for sample PTA 2.

Out of 29 participants, two questionable results ( $2.0 < |z\text{-score}| < 3.0$ ) were obtained for sample PTA 1 and five questionable results were obtained for sample PTA 2 (laboratories 131, 134, 250, 258, 558 and 638).

Three outlier results ( $|z\text{-score}| \geq 3.0$ ) were obtained for sample PTA 1 and two outlier results were obtained for sample PTA 2, requiring follow-up action by laboratories 209, 250 and 327.

The bromide dataset formed a normal distribution with no significant bias attributable to any one analysis method (Figures 1 and 2). The method most frequently used for bromide testing in this round was APHA Part 4110 B. (Ion Chromatography with Chemical Suppression of Eluent Conductivity), with approximately 41% of participants reporting the use of this method. In-house ion chromatography methods were the second most popular method choice for bromide analysis.

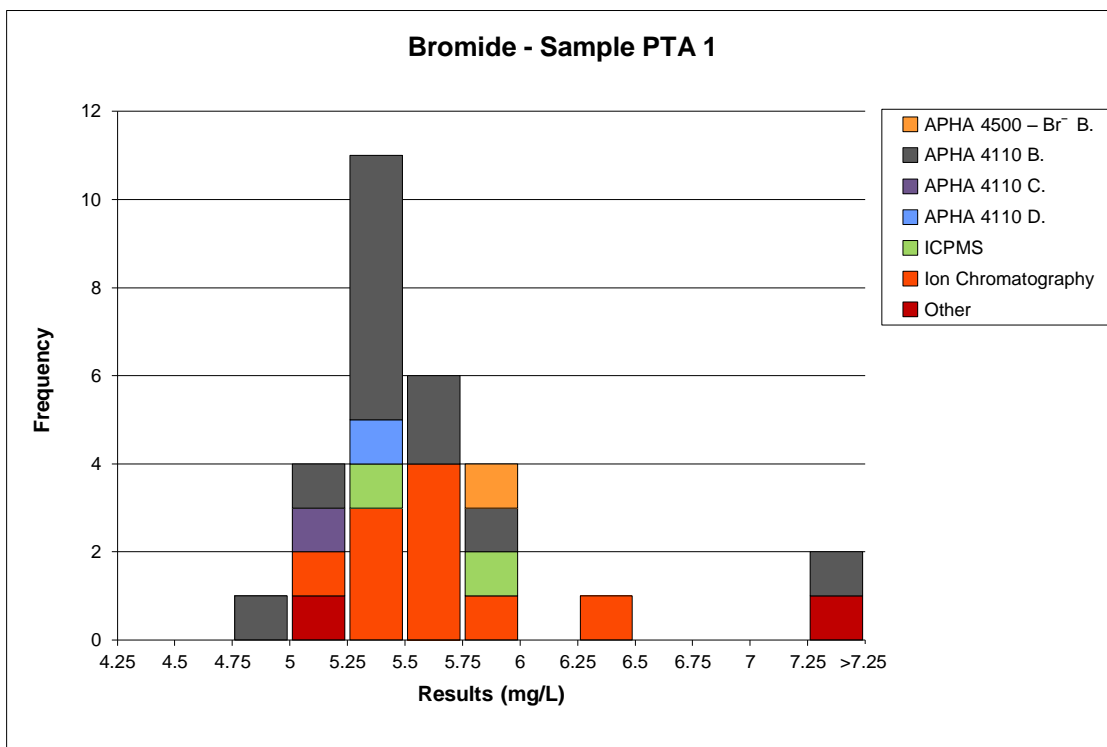


Figure 1. Spread of results for bromide testing of sample PTA 1, with a median concentration of 5.50 mg/L.

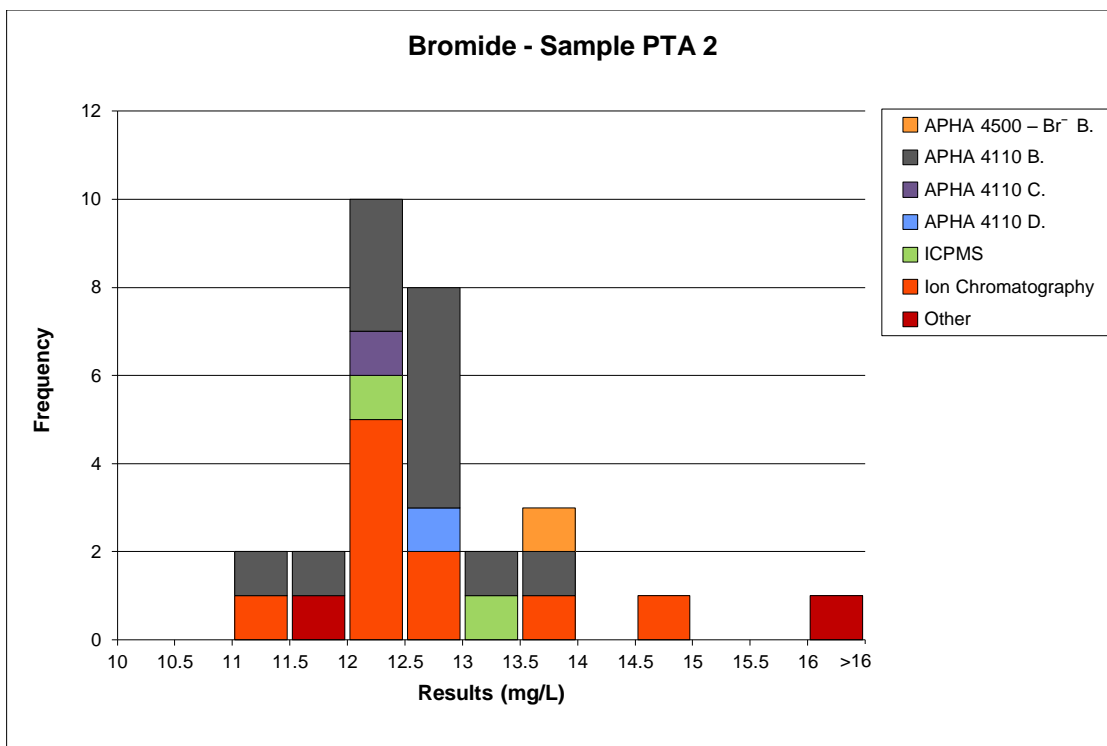


Figure 2. Spread of results for bromide testing of sample PTA 2, with a median concentration of 12.60 mg/L.



### Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated that the estimate of reproducibility (~2SD) for bromide testing was  $5.50 \pm 0.51$  mg/L for sample PTA 1 and  $12.60 \pm 1.46$  mg/L for sample PTA 2.

Results submitted by laboratories using Method 3, APHA 4110 B. (n=12), indicated a method reproducibility of  $\pm 0.53$  mg/L for sample PTA 1 and of  $\pm 1.57$  mg/L for sample PTA 2.

Out of 29 participants, 20 (69%) submitted MU information. The majority of the stated measurement uncertainties were an accurate reflection of the difference between the median and the participants' results for each proficiency sample.

Laboratories 118, 138a, 209, 250 and 258 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 3 and 4 below. To keep it in perspective, confidence in the medians was  $5.50 \pm 0.05$  mg/L for sample PTA 1 and  $12.60 \pm 0.12$  mg/L for sample PTA 2.

### Bromide - Sample PTA 1

Results of sample PTA 1, including MU, compared to the median

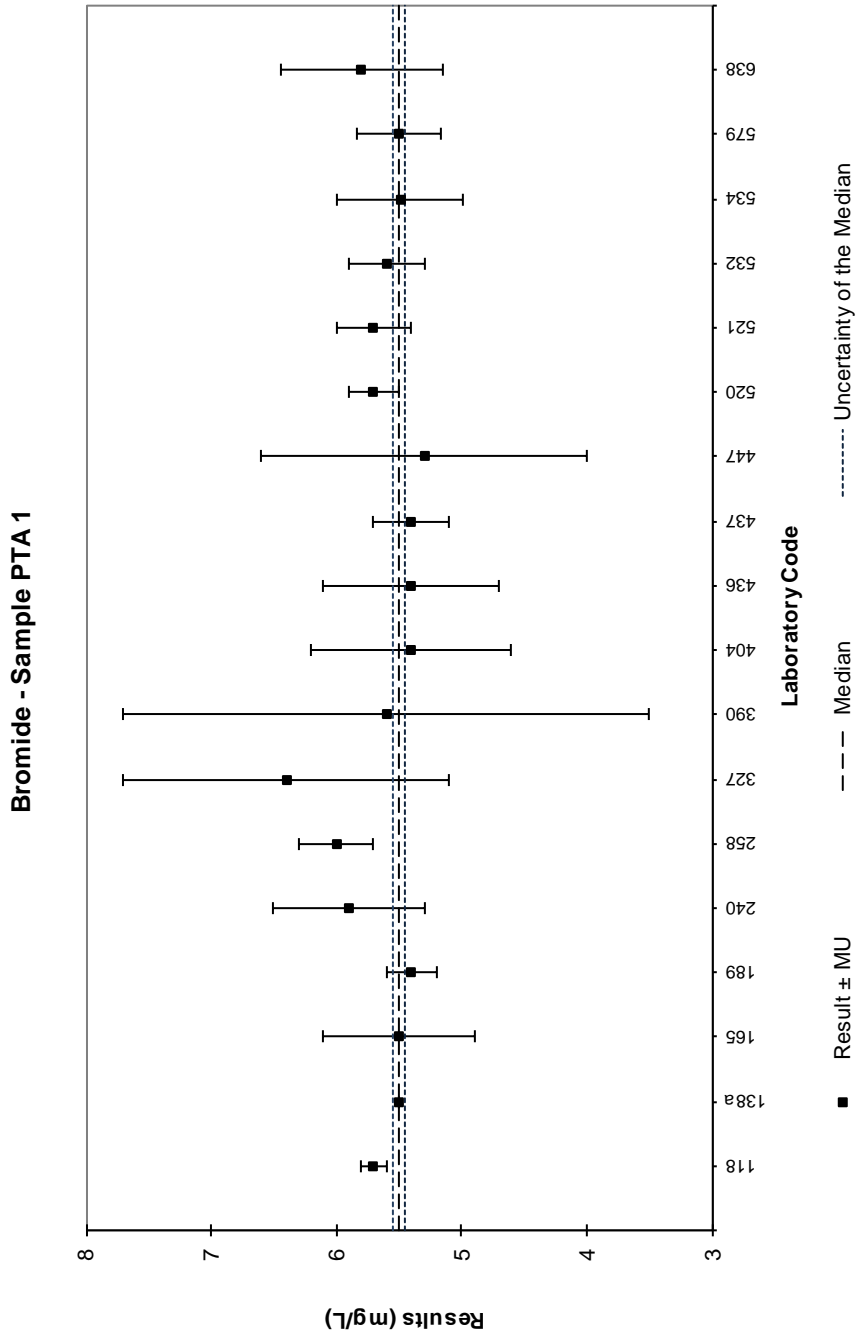


Figure 3. Bromide - Results of sample PTA 1, including MU, compared to the median (laboratories 209 and 250 outlier results not shown).

## Bromide - Sample PTA 2

Results of sample PTA 2, including MU, compared to the median

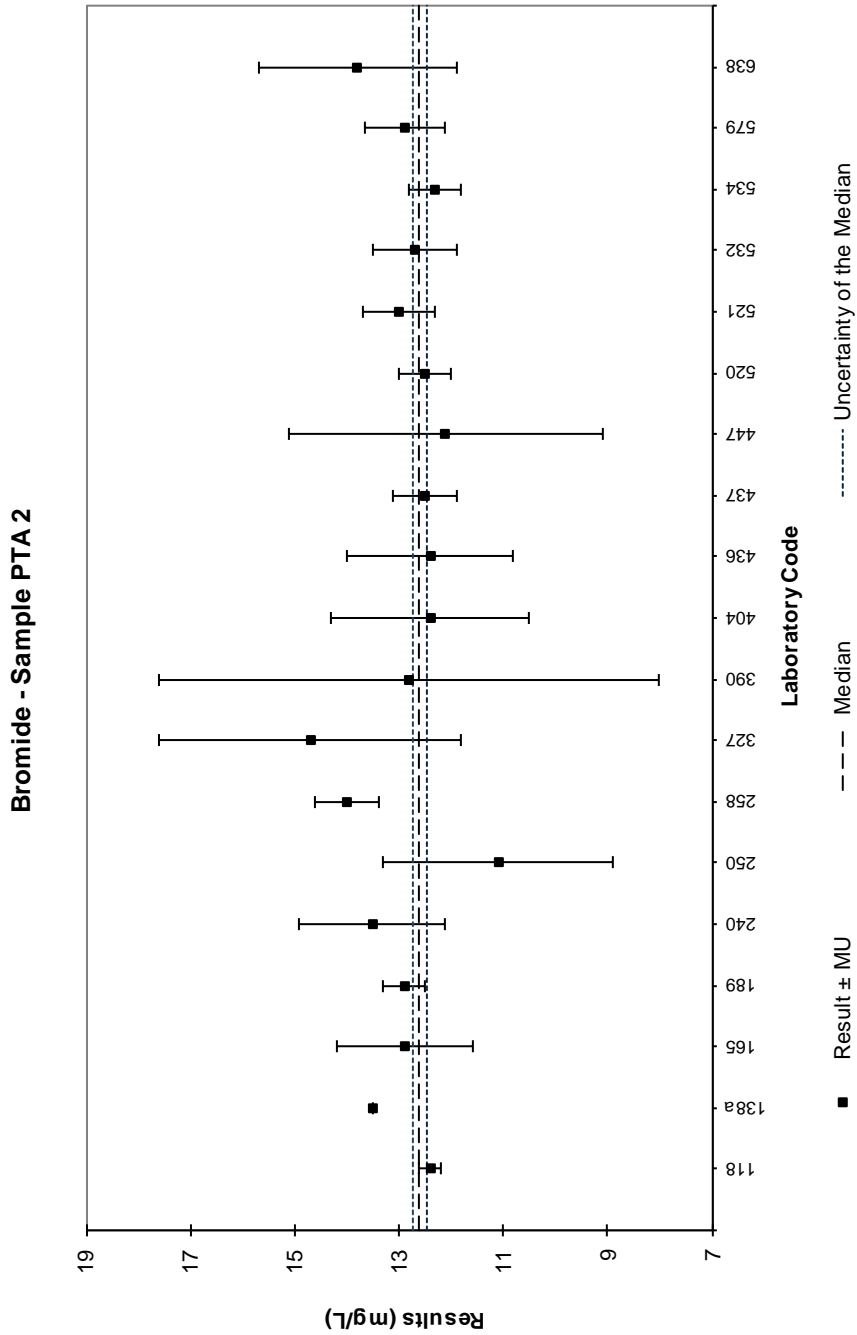


Figure 4. Bromide - Results of sample PTA 2, including MU, compared to the median (laboratory 209 outlier result not shown).

The MU reported by participants can be seen in Figures 5 and 6, displayed by the methods used.

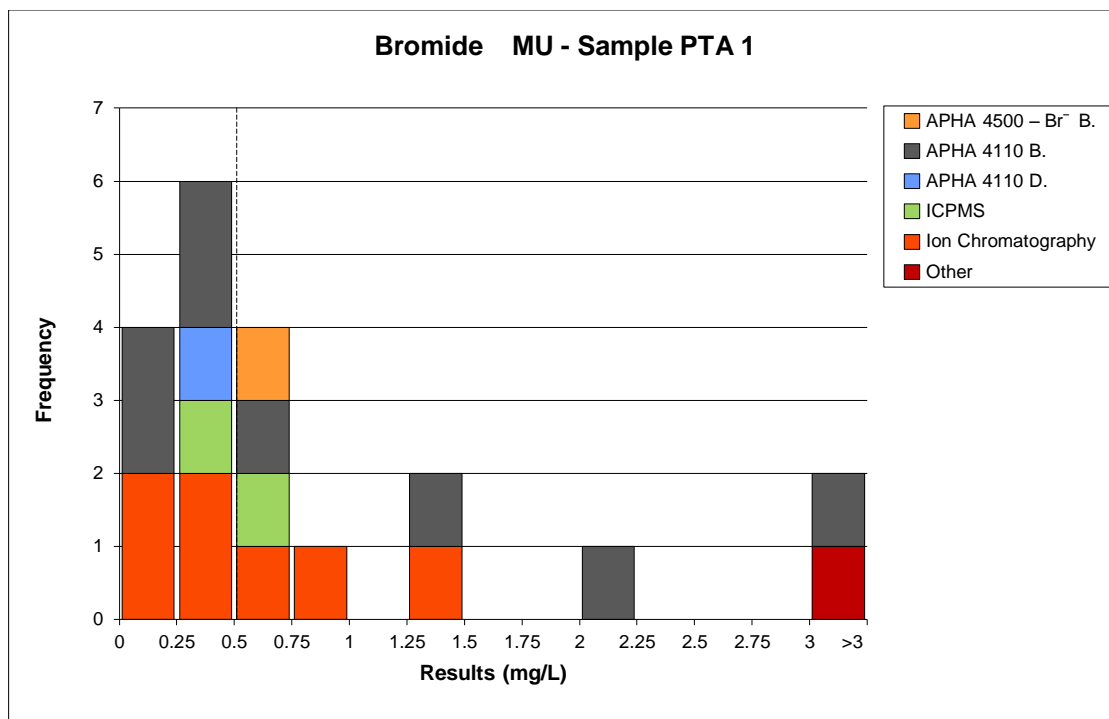


Figure 5. MU for bromide testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) ( $\pm 0.51$  mg/L) in this round.

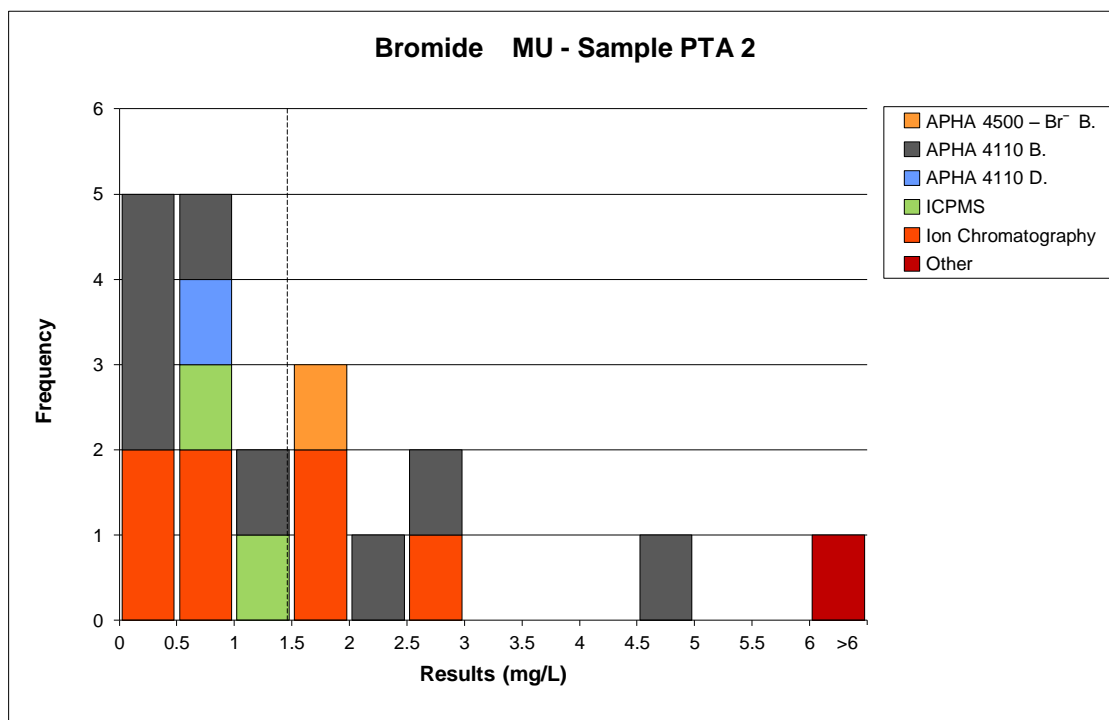


Figure 6. MU for bromide testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) ( $\pm 1.46$  mg/L) in this round.

#### 4.2.2 Chloride

Table 3 compares the chloride medians and robust CVs from this round to those obtained in previous PTA rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	No. of Results
This study	PTA 1	60.40	3.6	52
	PTA 2	82.25	6.0	52
Report 786	R147	36.00	3.9	61
Report 761	PTA 1	92.90	7.1	50
	PTA 2	130.80	4.5	50

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

The CV's obtained for chloride in this round are comparable to those observed in previous rounds.

#### Bias / Accuracy

Chloride testing was successfully carried out, with satisfactory results ( $|z\text{-score}| \leq 2.0$ ) ranging between 56.03 – 64.77 mg/L for sample PTA 1 and 72.32 – 92.18 mg/L for sample PTA 2.

Out of 52 participants, six questionable results ( $2.0 < |z\text{-score}| < 3.0$ ) were obtained for sample PTA 1 and two questionable results were obtained for sample PTA 2 (laboratories 138a, 203a, 240, 244, 249, 376, 437 and 638).

Five outlier results ( $|z\text{-score}| \geq 3.0$ ) were obtained for sample PTA 1 and three outlier results were obtained for sample PTA 2, requiring follow-up action by laboratories 207, 209, 250, 345, 376 and 437.

The chloride dataset formed a normal distribution with no significant bias attributable to any one analysis method (Figures 7 and 8). The method most frequently used for chloride testing in this round was APHA Part 4110 B. (Ion Chromatography with Chemical Suppression of Eluent Conductivity), with approximately 31% of participants reporting the use of this method. In-house ion chromatography methods were the second most popular method choice for chloride analysis, with approximately 19% of participants.



### Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated that the estimate of reproducibility (~2SD) for chloride testing was  $60.40 \pm 4.79$  mg/L for sample PTA 1 and  $82.25 \pm 9.97$  mg/L for sample PTA 2.

Results submitted by laboratories using Method 17, APHA 4110 B. (n=15), indicated a method reproducibility of  $\pm 4.04$  mg/L for sample PTA 1 and of  $\pm 8.7$  mg/L for sample PTA 2.

Out of 52 participants, 38 (73%) submitted MU information. Several of the stated uncertainty of measurements did not accurately reflect the difference between the median and the participants' results for each proficiency sample.

Laboratories 118, 138a, 173, 189, 203a, 249, 250, 258, 302, 345, 437, 470, 501, 507, 520, 534, 573, 584 and 616 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 9 and 10 below. To keep it in perspective, confidence in the medians was  $60.40 \pm 0.38$  mg/L for sample PTA 1 and  $82.25 \pm 0.86$  mg/L for sample PTA 2.

### Chloride - Sample PTA 1

Results of sample PTA 1, including MU, compared to the median

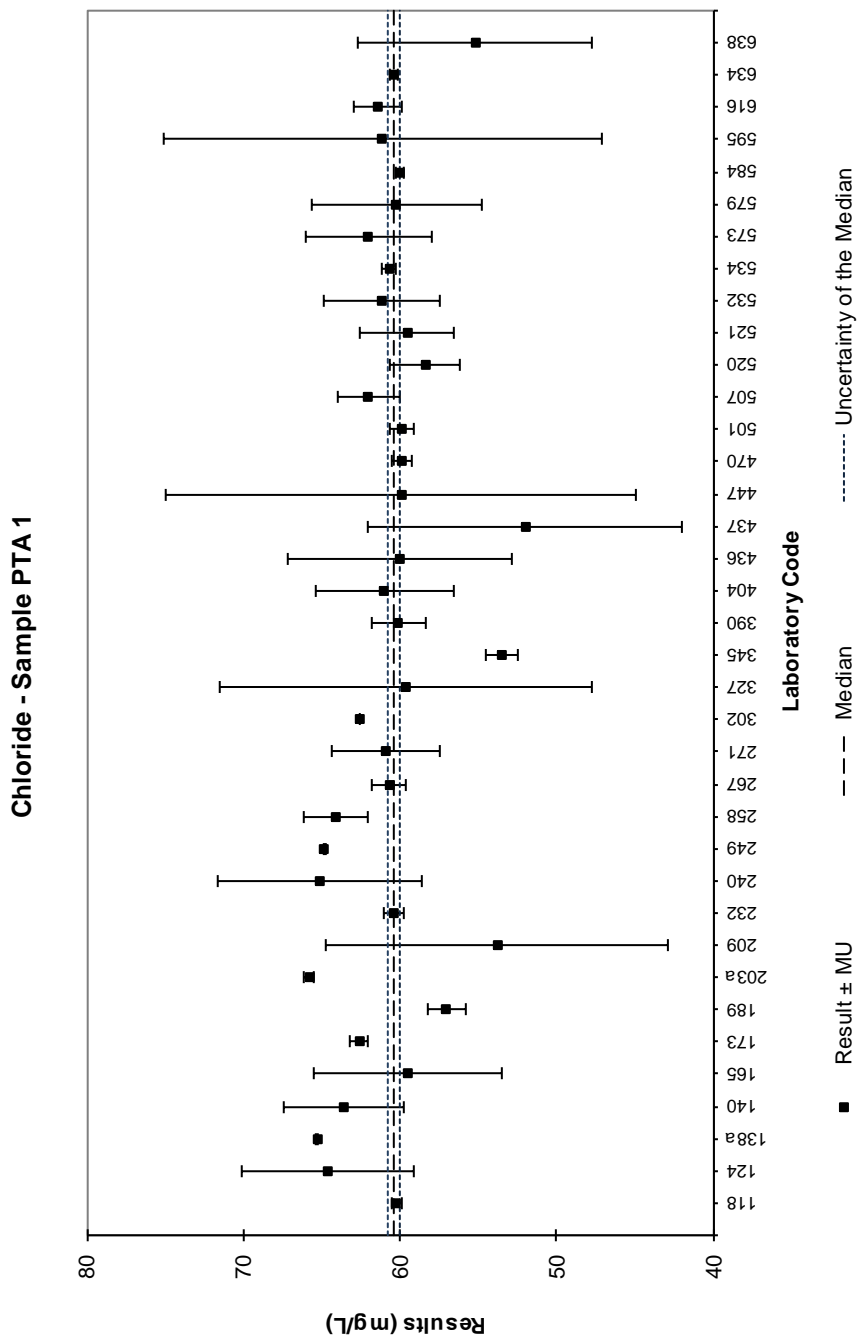


Figure 9. Chloride - Results of sample PTA 1, including MU, compared to the median (laboratory 250 outlier result not shown).



### Chloride - Sample PTA 2

Results of sample PTA 2, including MU, compared to the median

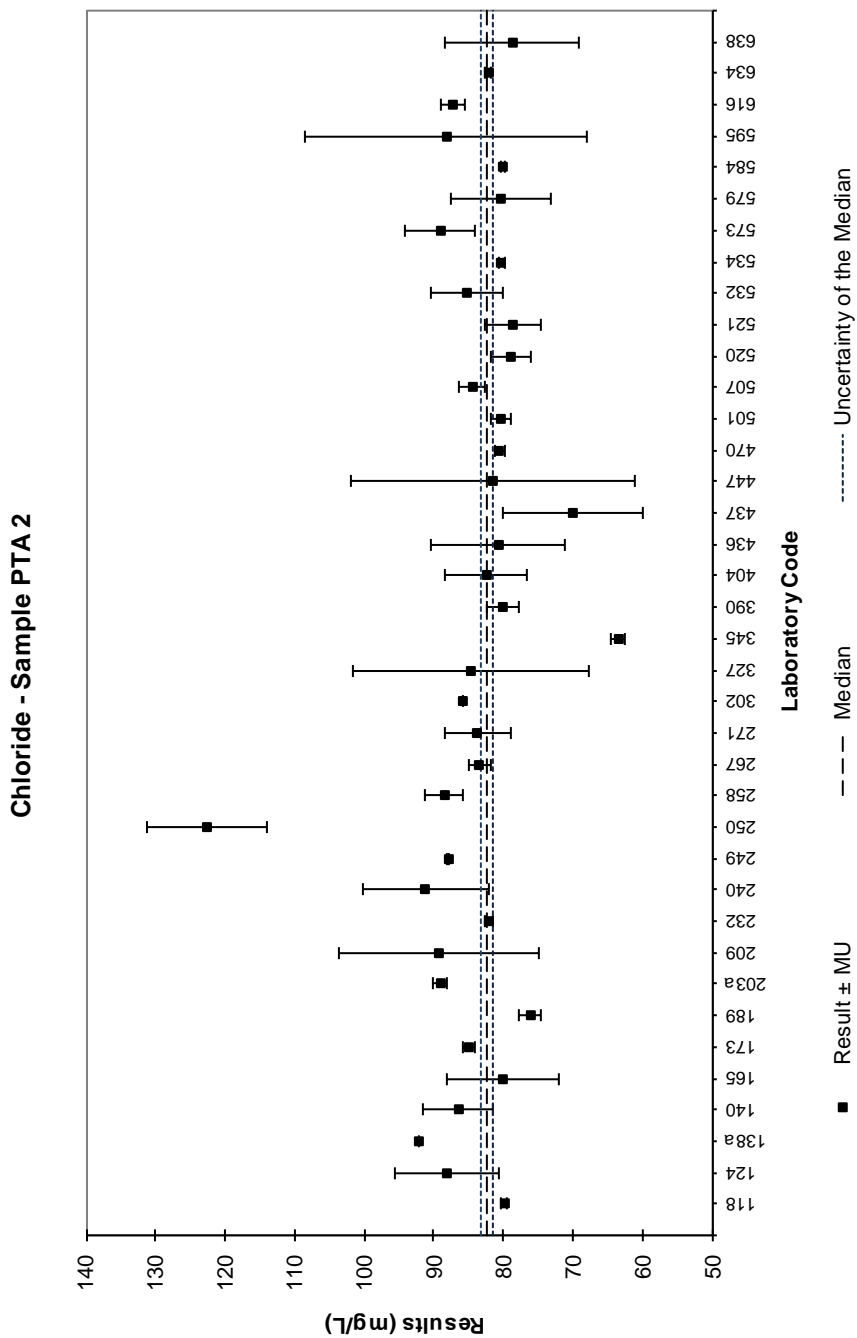


Figure 10. Chloride - Results of sample PTA 2 , including MU, compared to the median.

The MU reported by participants can be seen in Figures 11 and 12, displayed by the methods used.

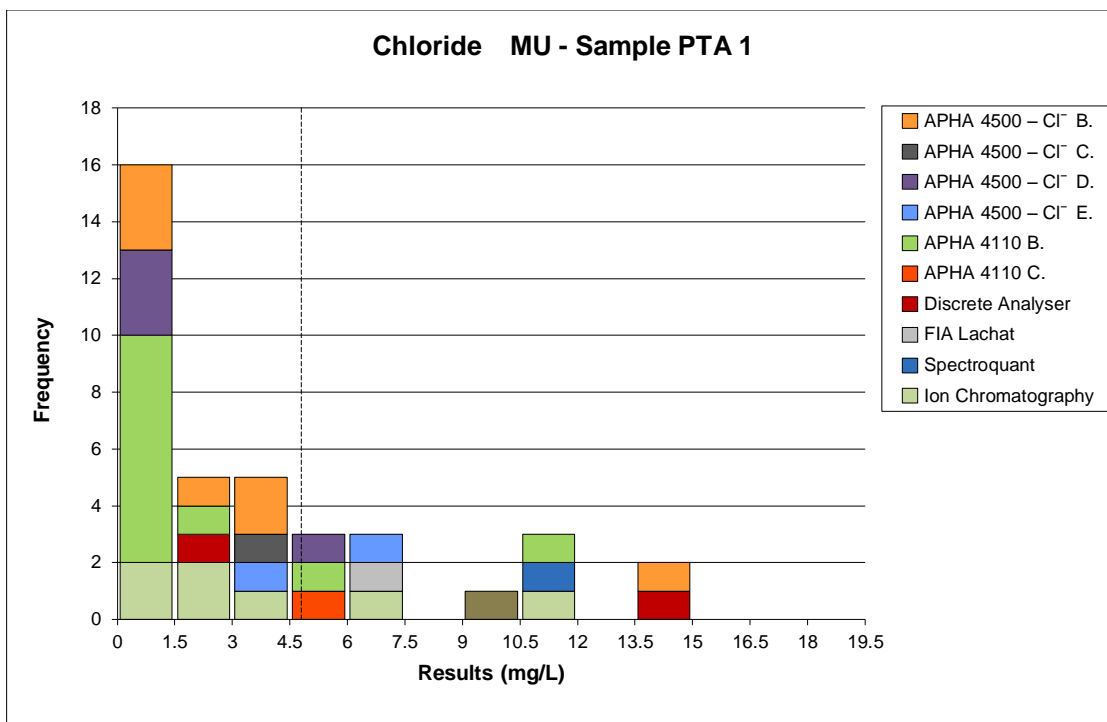


Figure 11. MU for chloride testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) ( $\pm 4.79$  mg/L) in this round.

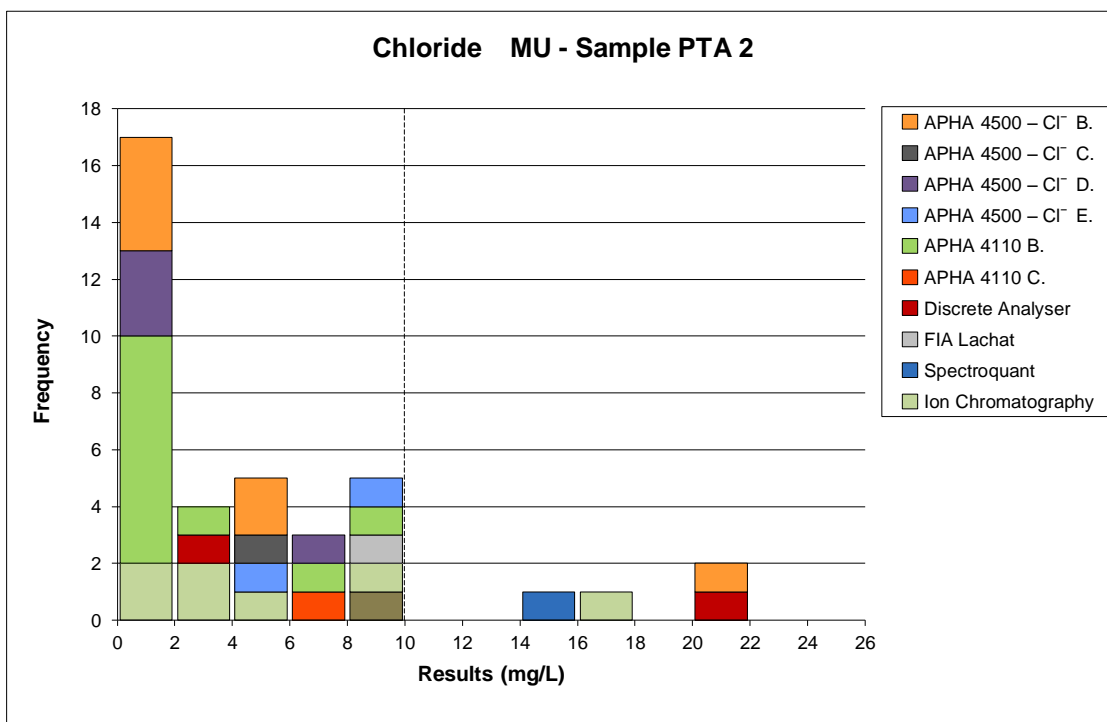


Figure 12. MU for chloride testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) ( $\pm 9.97$  mg/L) in this round.

### 4.2.3 Fluoride

Table 4 compares the fluoride medians and robust CVs from this round to those obtained in previous PTA rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	No. of Results
This study	PTA 1	1.380	5.0	48
	PTA 2	1.890	5.9	48
Report 786	R147	1.795	5.4	50
Report 761	PTA 1	1.300	7.7	51
	PTA 2	2.180	5.6	51

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

The CV's obtained for fluoride in this round are comparable to those observed in previous rounds.

#### Bias / Accuracy

Fluoride testing was successfully carried out, with satisfactory results ( $|z\text{-score}| \leq 2.0$ ) ranging between 1.243 – 1.517 mg/L for sample PTA 1 and 1.668 – 2.112 mg/L for sample PTA 2.

Out of 48 participants, three questionable results ( $2.0 < |z\text{-score}| < 3.0$ ) were obtained for sample PTA 1 and one questionable result was obtained for sample PTA 2 (laboratories 327, 447, 532 and 573).

Five outlier results ( $|z\text{-score}| \geq 3.0$ ) were obtained for sample PTA 1 and two outlier results were obtained for sample PTA 2, requiring follow-up action by laboratories 250, 345, 376, 573 and 616.

The fluoride dataset formed a normal distribution with no significant bias attributable to any one analysis method (Figures 13 and 14). The methods most frequently used for fluoride testing in this round were APHA Part 4110 B. (Ion Chromatography with Chemical Suppression of Eluent Conductivity) and APHA Part 4500-F<sup>-</sup> C. (Ion Selective Electrode Method), with approximately 35% and 33% of participants, respectively.

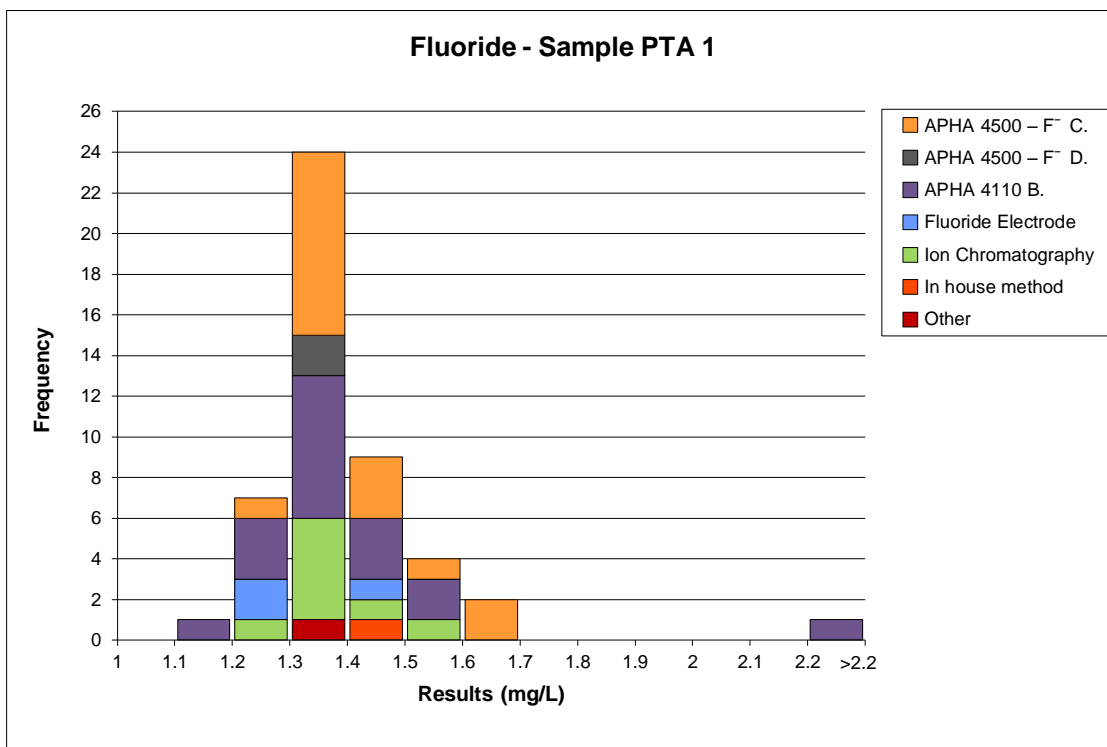


Figure 13. Spread of results for fluoride testing of sample PTA 1, with a median concentration of 1.380 mg/L.

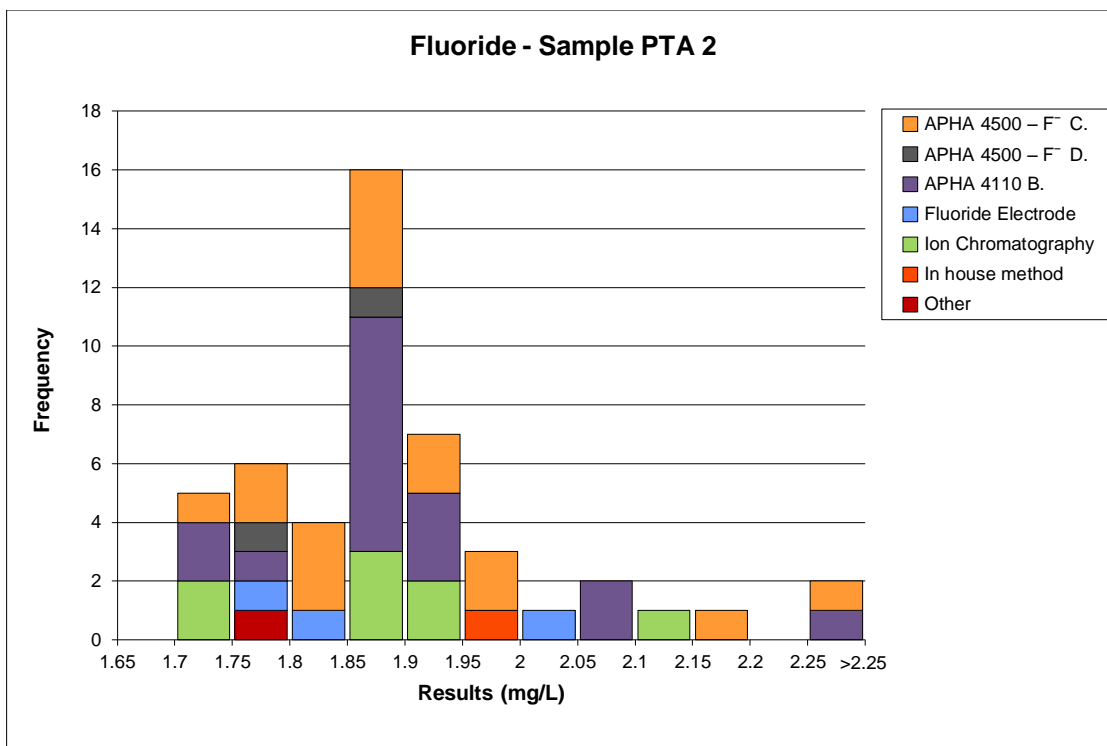


Figure 14. Spread of results for fluoride testing of sample PTA 2, with a median concentration of 1.890 mg/L.

### Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated that the estimate of reproducibility (~2SD) for fluoride testing was  $1.380 \pm 0.139$  mg/L for sample PTA 1 and  $1.890 \pm 0.211$  mg/L for sample PTA 2.

Results submitted by laboratories using Method 38, APHA Part 4110 B. (n=14), indicated a method reproducibility of  $\pm 0.16$  mg/L for sample PTA 1 and of  $\pm 0.21$  mg/L for sample PTA 2.

Results submitted by laboratories using Method 34, APHA Part 4500-F C. (n=14), indicated a method reproducibility of  $\pm 0.13$  mg/L for sample PTA 1 and of  $\pm 0.24$  mg/L for sample PTA 2.

Out of 48 participants, 38 (79%) submitted MU information. Most of the stated measurement uncertainties were an accurate reflection of the difference between the median and the participants result for each proficiency sample.

Laboratories 118, 138a, 189, 198, 249, 250, 267, 271, 573, 584, 616 and 634 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 15 and 16 below. To keep it in perspective, confidence in the medians was  $1.380 \pm 0.012$  mg/L for sample PTA 1 and  $1.890 \pm 0.020$  mg/L for sample PTA 2.

### Fluoride - Sample PTA 1

Results of sample PTA 1, including MU, compared to the median

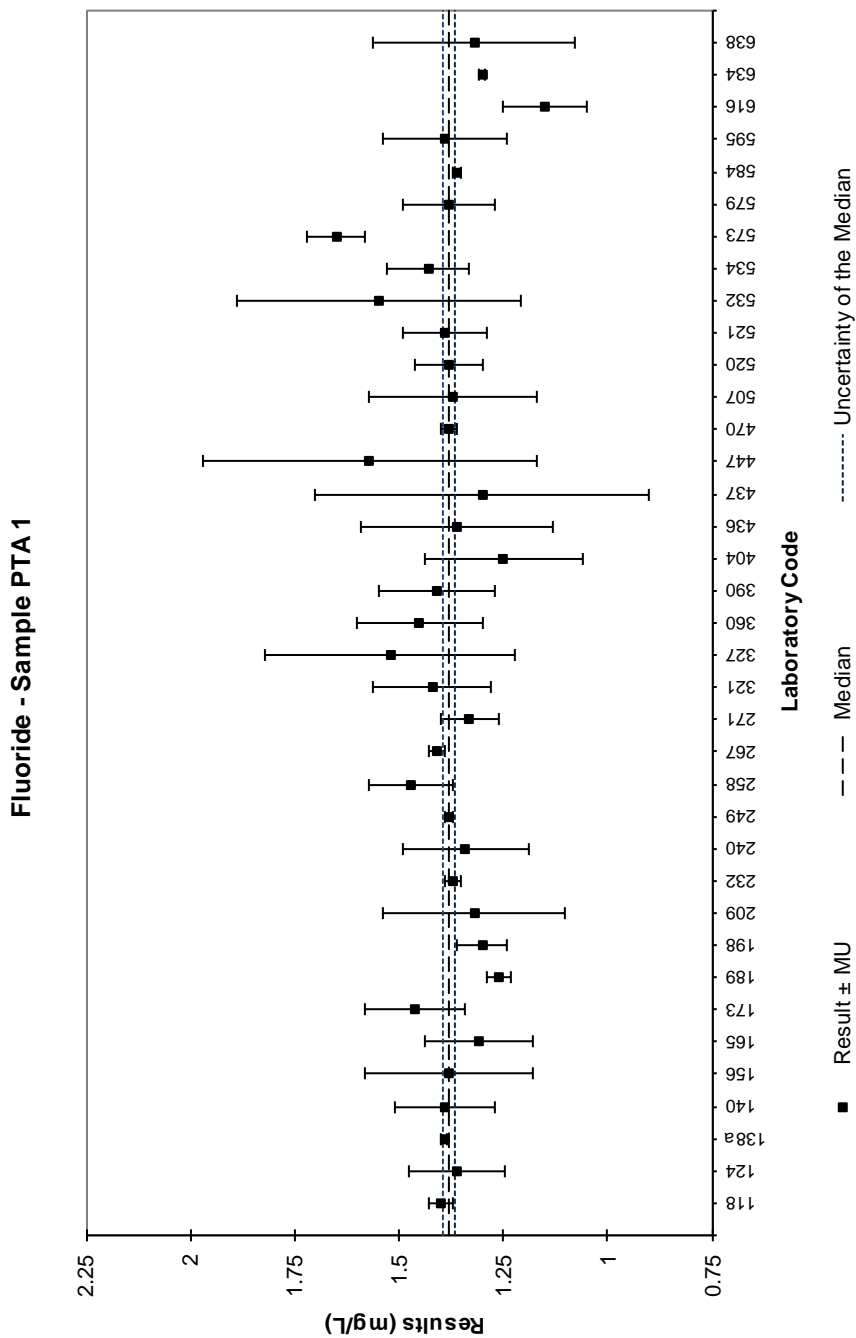


Figure 15. Fluoride - Results of sample PTA 1 , including MU, compared to the median (laboratory 250 outlier result not shown).

### Fluoride - Sample PTA 2

Results of sample PTA 2, including MU, compared to the median

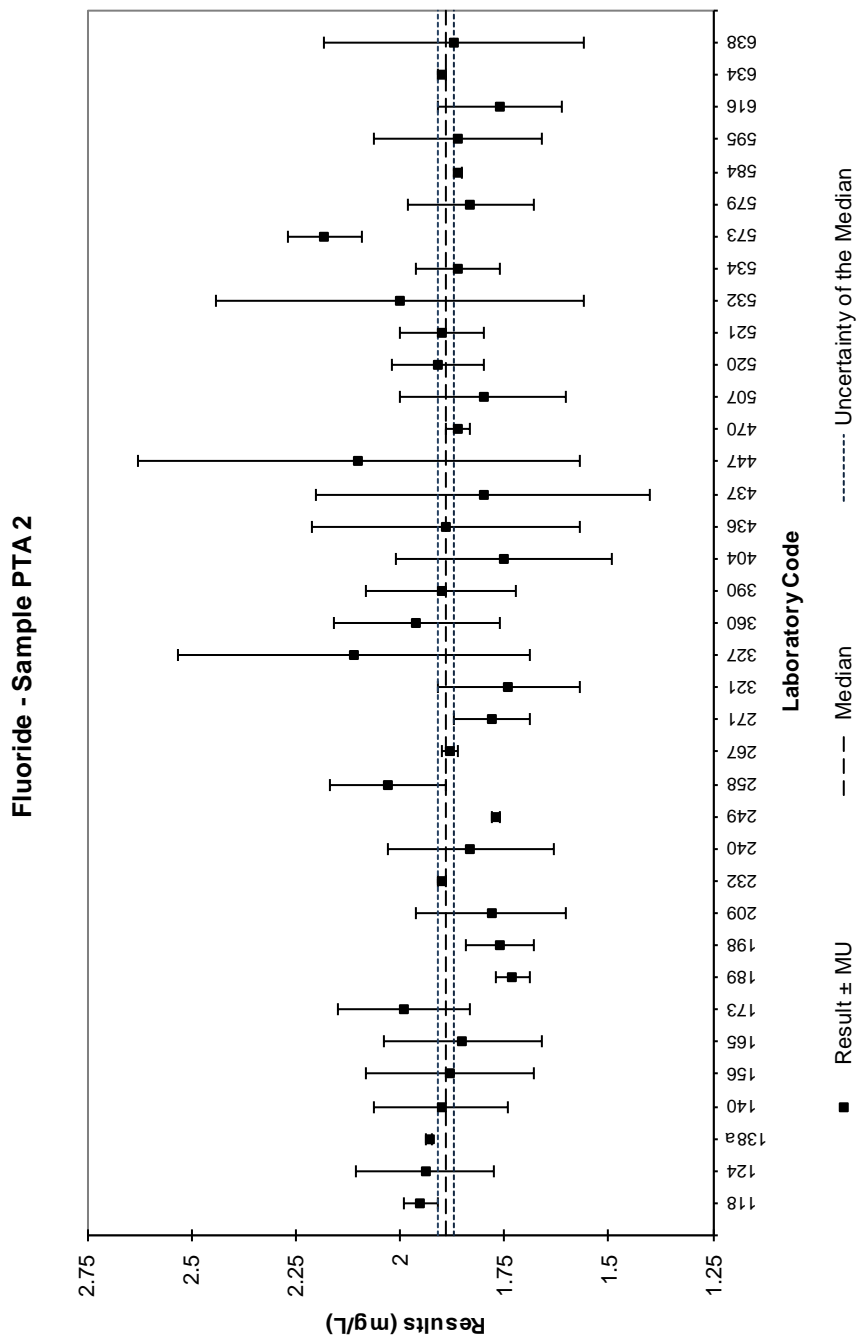


Figure 16. Fluoride - Results of sample PTA 2 , including MU, compared to the median (laboratory 250 outlier result not shown).

The MU reported by participants can be seen in Figures 17 and 18, displayed by the methods used.

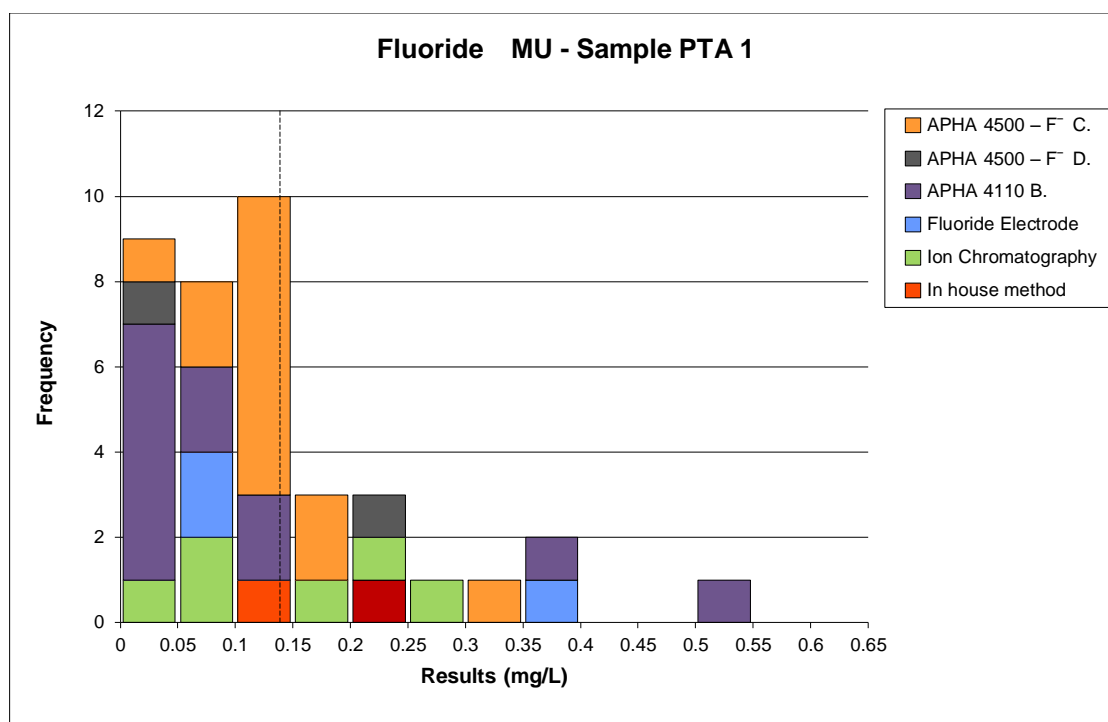


Figure 17. MU for fluoride testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) ( $\pm 0.139$  mg/L) in this round.

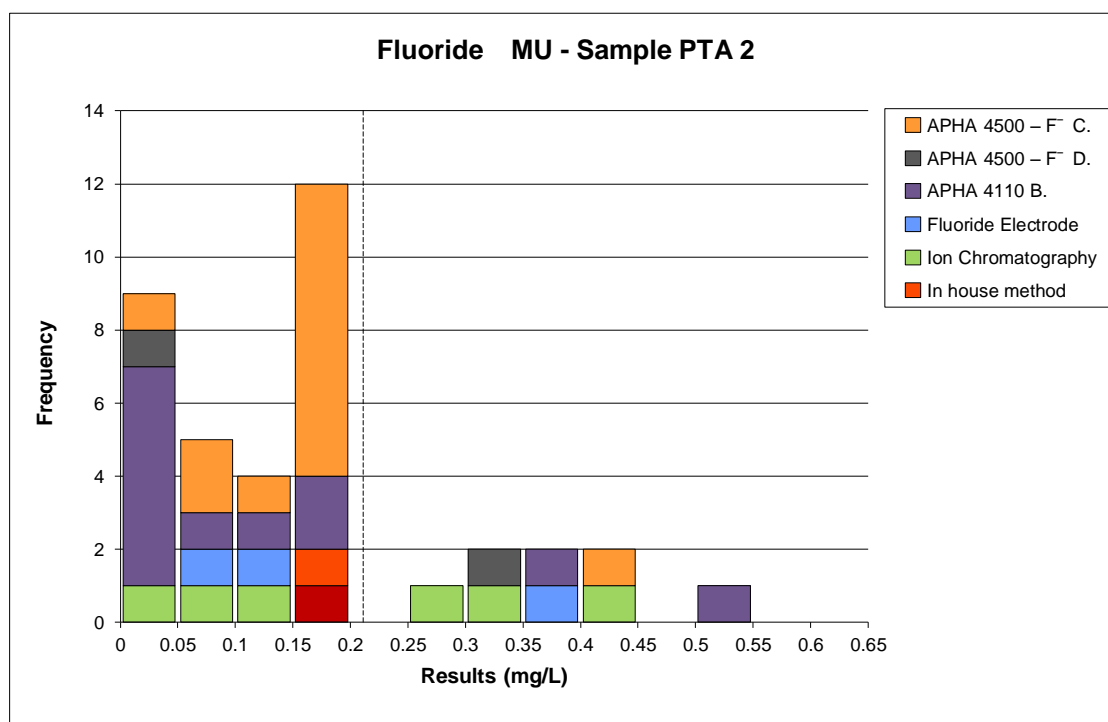


Figure 18. MU for fluoride testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) ( $\pm 0.211$  mg/L) in this round.



#### 4.2.4 Iodide

Table 5 compares the iodide medians and robust CVs from this round to those obtained in previous PTA rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	No. of Results
This study	PTA 1	1.080	5.0	12
	PTA 2	0.645	7.2	12
Report 761	PTA 1	0.800	5.3	18
	PTA 2	1.280	5.2	17
Report 707	PTA 1	2.110	5.3	17
	PTA 2	1.470	5.5	17

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

The CV's obtained for iodide in this round are comparable to those observed in previous rounds.

#### Bias / Accuracy

Iodide testing was successfully carried out, with satisfactory results ( $|z\text{-score}| \leq 2.0$ ) ranging between 0.973 – 1.187 mg/L for sample PTA 1 and 0.552 – 0.738 mg/L for sample PTA 2.

Out of 12 participants, one questionable result ( $2.0 < |z\text{-score}| < 3.0$ ) was obtained for sample PTA 1 and two questionable results were obtained for sample PTA 2 (laboratories 209, 240 and 250).

One outlier result ( $|z\text{-score}| \geq 3.0$ ) was obtained for sample PTA 1 and one outlier result was obtained for sample PTA 2, requiring follow-up action by laboratories 250 and 436.

The iodide dataset formed a normal distribution with no significant bias attributable to any one analysis method (Figures 19 and 20). In-house ion chromatography methods were the most popular method choice for iodide analysis, being used by approximately 50% of participants in this round.

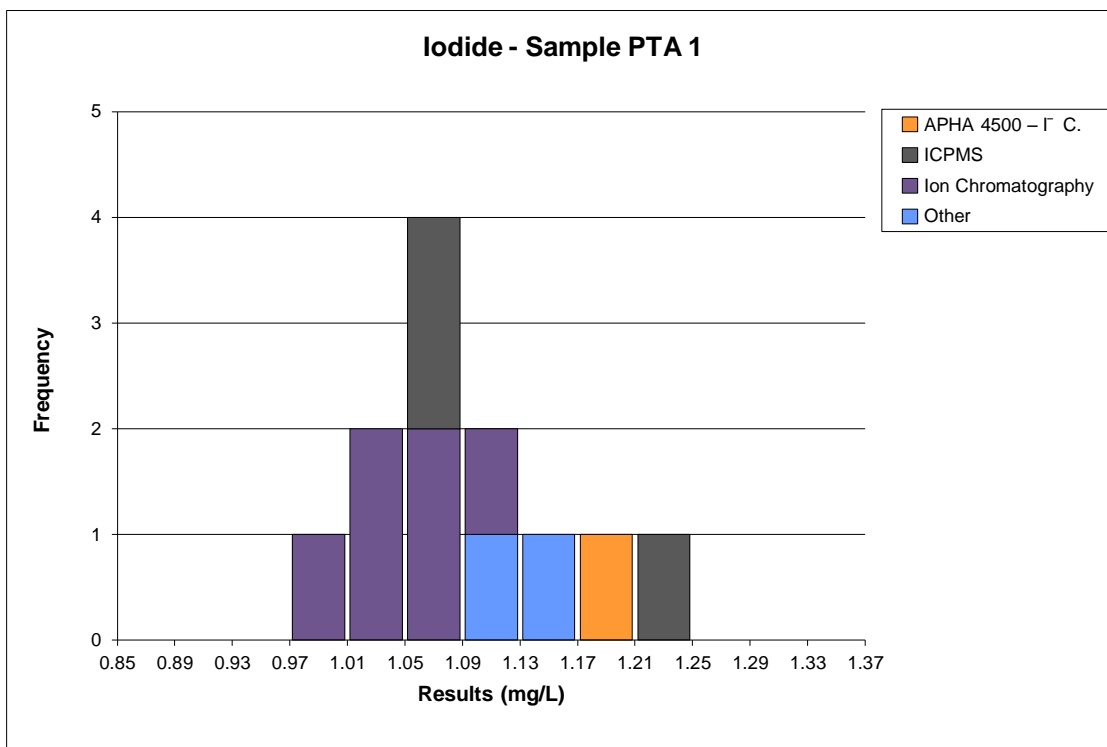


Figure 19. Spread of results for iodide testing of sample PTA 1, with a median concentration of 1.080 mg/L.

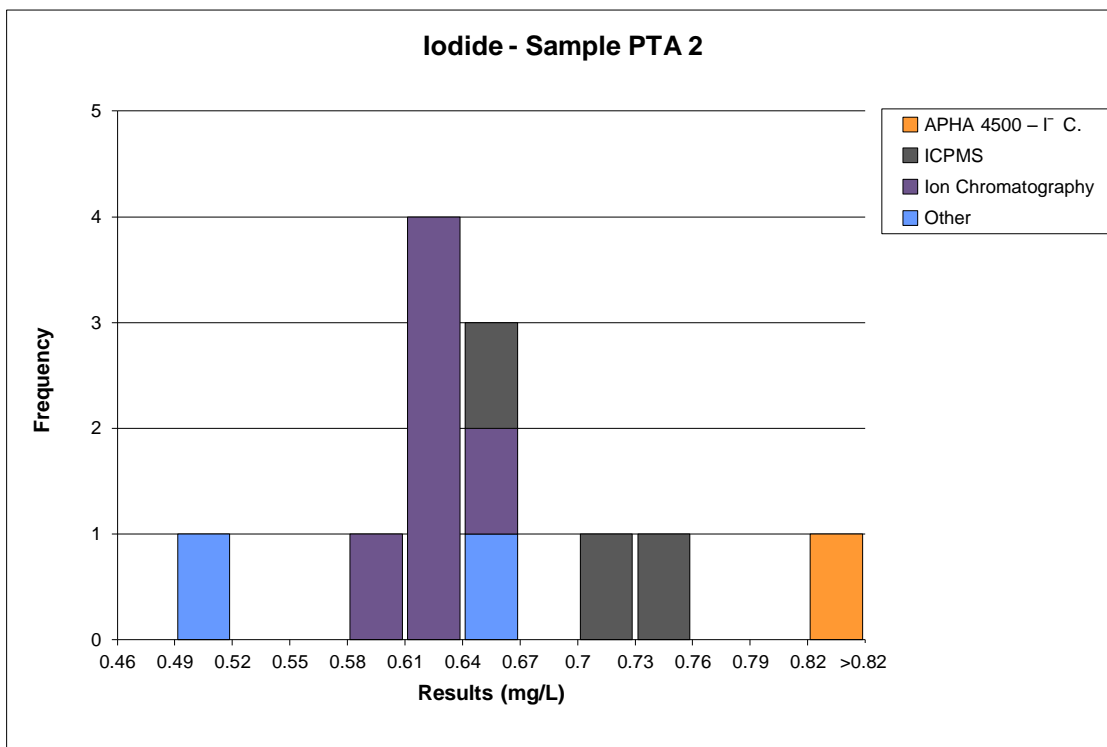


Figure 20. Spread of results for iodide testing of sample PTA 2, with a median concentration of 0.645 mg/L.

### Reproducibility / Measurement Uncertainty (MU)

Using the t-value, (outliers removed, 95% confidence interval) results indicated that the estimate of reproducibility (~2SD) for iodide testing was  $1.080 \pm 0.123$  mg/L for sample PTA 1 and  $0.645 \pm 0.140$  mg/L for sample PTA 2.

Results submitted by laboratories using Method 54, in-house ion chromatography (n=6), indicated a method reproducibility of  $\pm 0.082$  mg/L for sample PTA 1 and of  $\pm 0.061$  mg/L for sample PTA 2.

Out of 12 participants, 9 (75%) submitted MU information. Most of the stated measurement uncertainties were an accurate reflection of the difference between the median and the participants' results for each proficiency sample.

Laboratories 209 and 240 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figures 21 and 22 below. To keep it in perspective, confidence in the medians was  $1.080 \pm 0.019$  mg/L for sample PTA 1 and  $0.645 \pm 0.017$  mg/L for sample PTA 2.

### Iodide - Sample PTA 1

Results of sample PTA 1, including MU, compared to the median

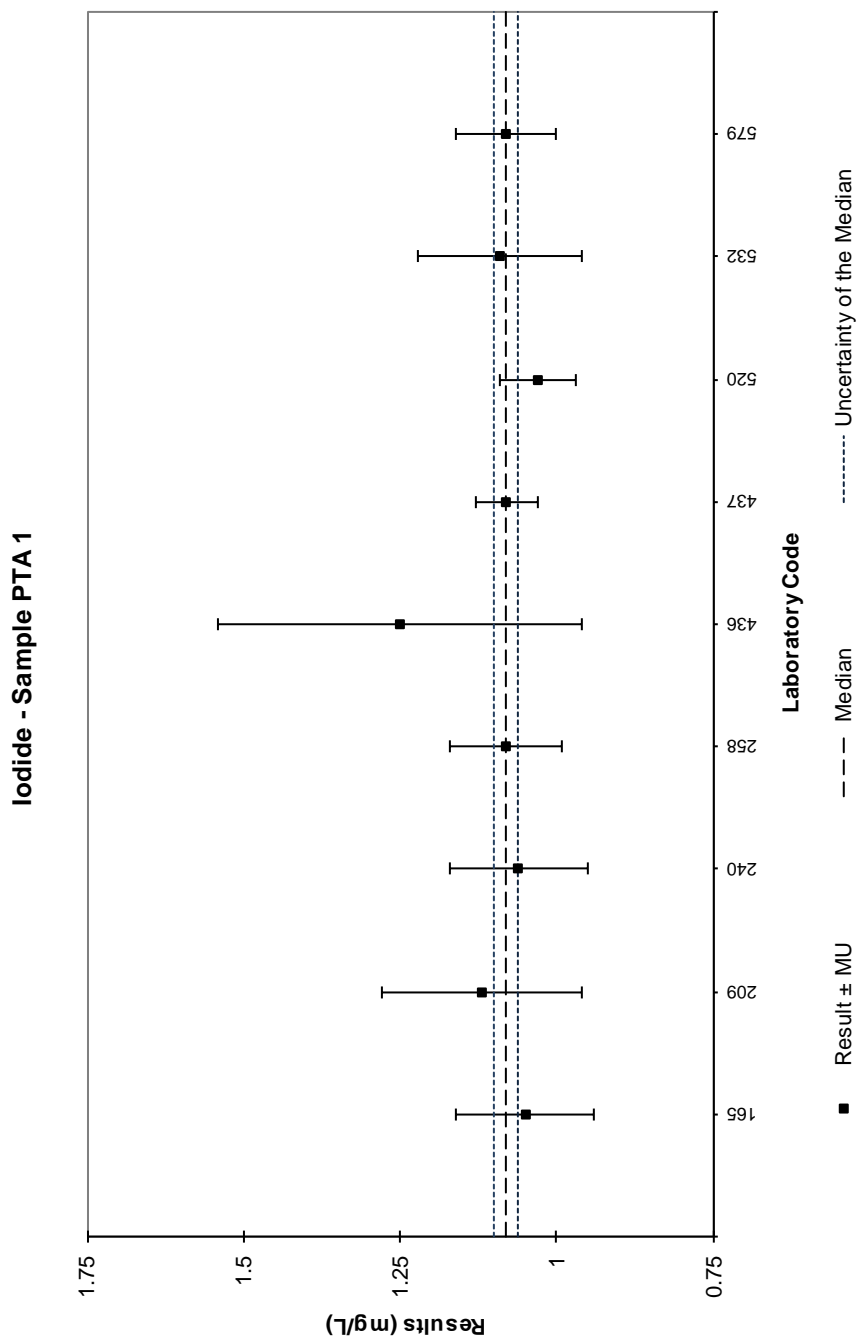


Figure 21. Iodide - Results of sample PTA 1, including MU, compared to the median.

### Iodide - Sample PTA 2

Results of sample PTA 2, including MU, compared to the median

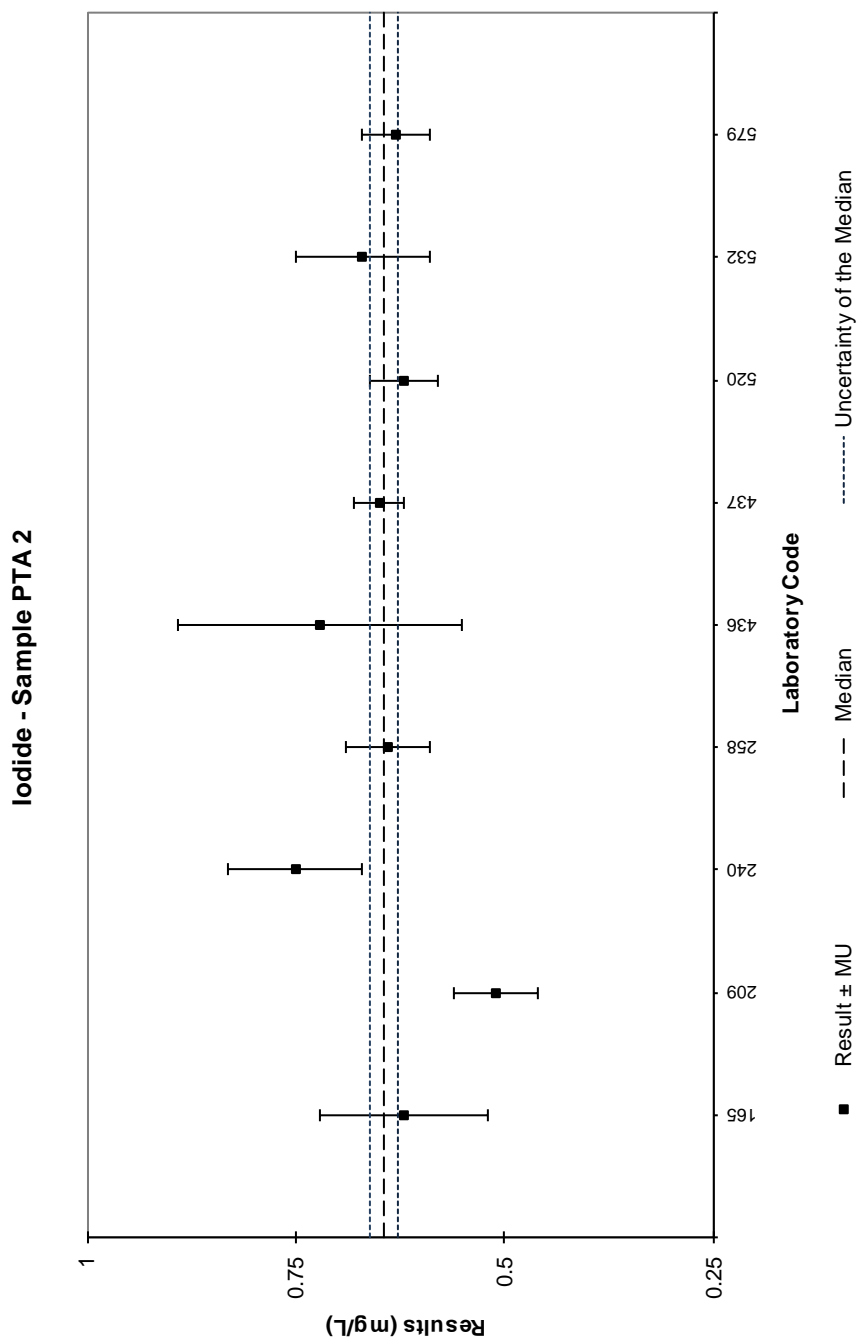


Figure 22. Iodide - Results of sample PTA 2, including MU, compared to the median.

The MU reported by participants can be seen in Figures 23 and 24, displayed by the methods used.

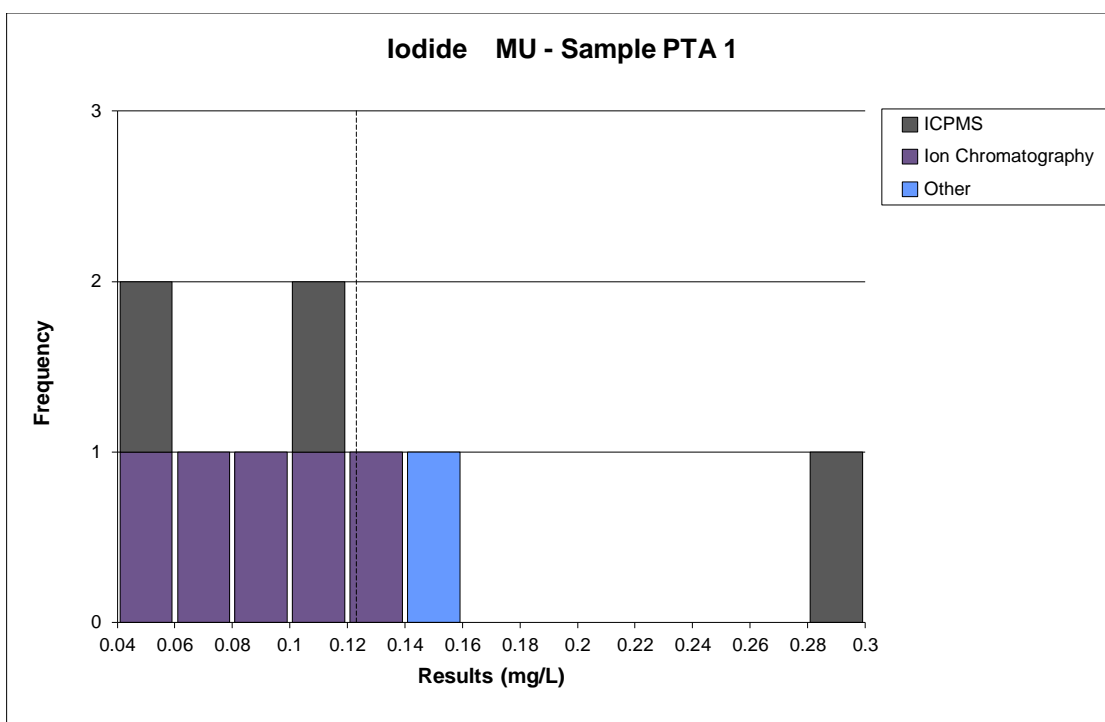


Figure 23. MU for iodide testing of sample PTA 1, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) ( $\pm 0.123$  mg/L) in this round.

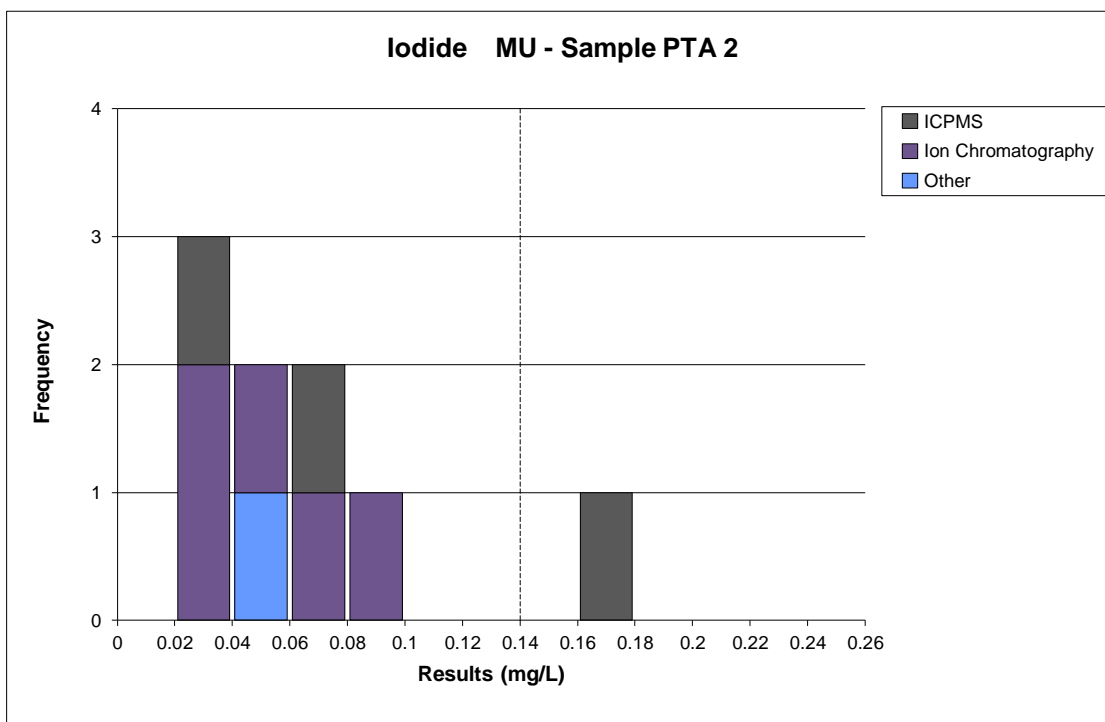


Figure 24. MU for iodide testing of sample PTA 2, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) ( $\pm 0.140$  mg/L) in this round.

### 4.3 Analysis of Results by Method Groups

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

The method APHA Part 4110 B. - Ion Chromatography with Chemical Suppression of Eluent Conductivity was most frequently used for analysis of bromide, chloride and fluoride. Table 6 below presents the median, uncertainty of the median and robust CV of results obtained by this method in round 157.

Analyte	Sample	Participants	Median $\pm$ Uncertainty of the Median (mg/L)	Robust CV (%)
Bromide	PTA 1	12	5.50 $\pm$ 0.08	4.0
	PTA 2	12	12.70 $\pm$ 0.21	4.7
Chloride	PTA 1	16	60.20 $\pm$ 0.27	1.4
	PTA 2	16	80.35 $\pm$ 1.35	5.4
Fluoride	PTA 1	17	1.380 $\pm$ 0.023	5.4
	PTA 2	17	1.900 $\pm$ 0.018	3.1

Table 6. Variability and proficiency medians for bromide, chloride and fluoride results obtained by method APHA Part 4110 B.

Additionally, a relatively large number of participants reported the use of method APHA Part 4500 – F<sup>-</sup> C. - Ion Selective Electrode Method for analysis of fluoride. Table 7 below presents the median, uncertainty of the median and robust CV for fluoride results obtained by this method in round 157.

Analyte	Sample	Participants	Median $\pm$ Uncertainty of the Median (mg/L)	Robust CV (%)
Fluoride	PTA 1	16	1.390 $\pm$ 0.015	3.3
	PTA 2	16	1.880 $\pm$ 0.032	5.4

Table 7. Variability and proficiency medians of fluoride results obtained by method APHA Part 4500 – F<sup>-</sup> C.

In-house ion chromatography methods were most frequently employed for analysis of iodide in this round. However, there were insufficient reported results to conduct an accurate statistical analysis.

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 above, there were less than 11 results submitted, therefore reliable conclusions cannot be drawn from analysing them separately on this occasion.

## 5. Outlier Results

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

Lab Code	Analysis							
	Bromide		Chloride		Fluoride		Iodide	
	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2
207				§				
209	§	§	§					
250	§		§	§	§	§		§
327	§	§						
345			§	§	§	§		
376			§		§			
436							§	
437			§					
573					§			
616					§			

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

Note:

1. A "§" indicates the occurrence of a z-score outlier result (i.e. those results for which  $|z\text{-score}| \geq 3.0$ ).

## 6. Reference

- [1] *Guide to Proficiency Testing Australia*, 2012 (This document can be found on the PTA website, [www.pta.asn.au](http://www.pta.asn.au))



# APPENDIX A

## Results and Data Analysis

Bromide.....	A1
Chloride.....	A3
Fluoride.....	A7
Iodide.....	A11

# **Bromide Results**

Samples PTA 1 and PTA 2

**Bromide**  
**Results by Laboratory Code**

Lab Code	Sample PTA 1				Sample PTA 2			
	Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>		Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>	
118	5.7 ± 0.1	0.90	10		12.4 ± 0.2	-0.39	10	
123	5.6 #	0.45	10		12.6 #	0.00	10	
131	5.9 #	1.80	3		13.7 #	2.12	3	
134	5.0 #	-2.25	3		12.1 #	-0.96	3	
138a	5.5 ± 0.007	0.00	3		13.5 ± 0.007	1.73	3	
165	5.5 ± 0.6	0.00	3		12.9 ± 1.3	0.58	3	
189	5.4 ± 0.2	-0.45	3		12.9 ± 0.4	0.58	3	
207	5.2 #	-1.35	3		11.9 #	-1.35	3	
209	13.7 ± 7.74	36.87	§	12	17.5 ± 13.02	9.44	§	12
240	5.9 ± 0.6	1.80	9		13.5 ± 1.4	1.73	9	
250	26.6 ± 5.3	94.88	§	3	11.1 ± 2.2	-2.89	3	
258	6.0 ± 0.3	2.25	10		14.0 ± 0.6	2.70	10	
327	6.4 ± 1.3	4.05	§	10	14.7 ± 2.9	4.05	§	10
376	5.2 #	-1.35	4		12.1 #	-0.96	4	
385	5.48 #	-0.09	10		12.5 #	-0.19	10	
390	5.6 ± 2.1	0.45	3		12.8 ± 4.8	0.39	3	
404	5.4 ± 0.8	-0.45	10		12.4 ± 1.9	-0.39	10	
436	5.4 ± 0.7	-0.45	10		12.4 ± 1.6	-0.39	10	
437	5.4 ± 0.3	-0.45	9		12.5 ± 0.6	-0.19	9	
447	5.3 ± 1.3	-0.90	3		12.1 ± 3.0	-0.96	3	
520	5.7 ± 0.2	0.90	10		12.5 ± 0.5	-0.19	10	
521	5.7 ± 0.3	0.90	10		13.0 ± 0.7	0.77	10	
532	5.6 ± 0.3	0.45	3		12.7 ± 0.8	0.19	3	
534	5.49 ± 0.5	-0.04	3		12.3 ± 0.5	-0.58	3	
558	5.2 #	-1.35	10		11.3 #	-2.51	10	
579	5.5 ± 0.33	0.00	5		12.9 ± 0.77	0.58	5	
597	5.2 #	-1.35	12		11.6 #	-1.93	12	
632	5.3 #	-0.90	3		12.7 #	0.19	3	
638	5.80 ± 0.65	1.35	1		13.8 ± 1.9	2.31	1	
<i>No of Results:</i>	29				29			
<i>Median:</i>	5.50				12.60			
<i>Normalised IQR:</i>	0.22				0.52			
<i>Uncertainty of the Median:</i>	0.05				0.12			
<i>Robust CV:</i>	4.0%				4.1%			
<i>Minimum:</i>	5.0				11.1			
<i>Maximum:</i>	26.6				17.5			
<i>Range:</i>	21.6				6.4			

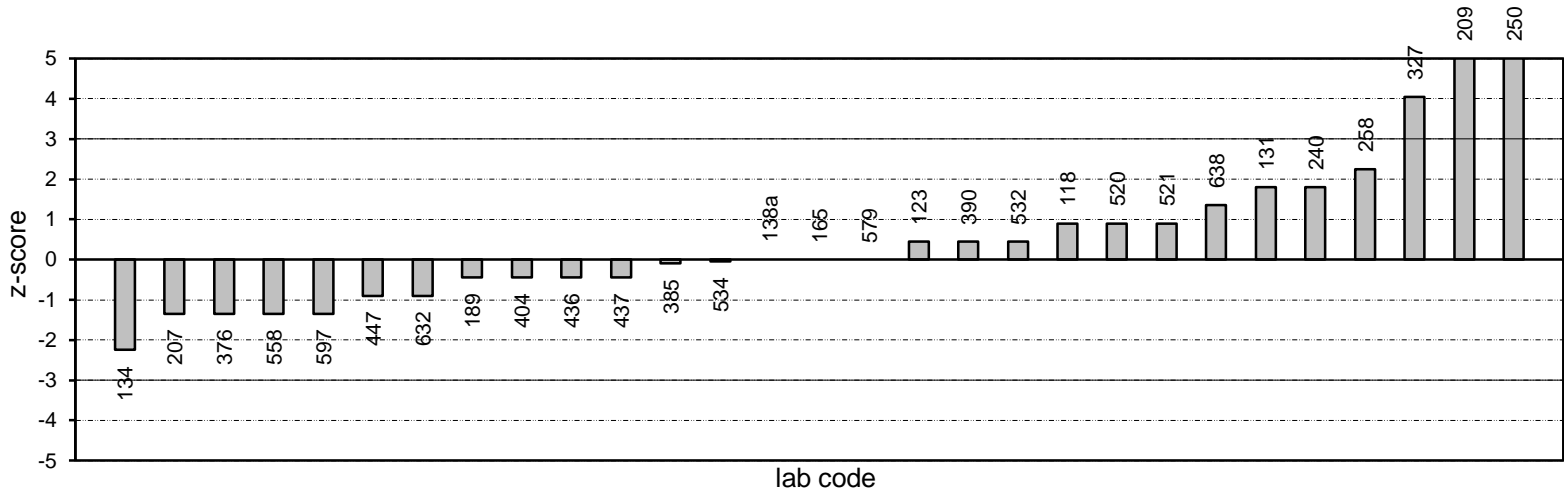
<sup>1</sup> Where reported, results are shown with their corresponding measurement uncertainty (MU).

<sup>2</sup> "§" denotes an outlier (i.e. those results for which |z-score| ≥ 3.0). Robust z-scores are calculated as:  
z = (A - median) ÷ normalised IQR, where A is the participant laboratory's result.

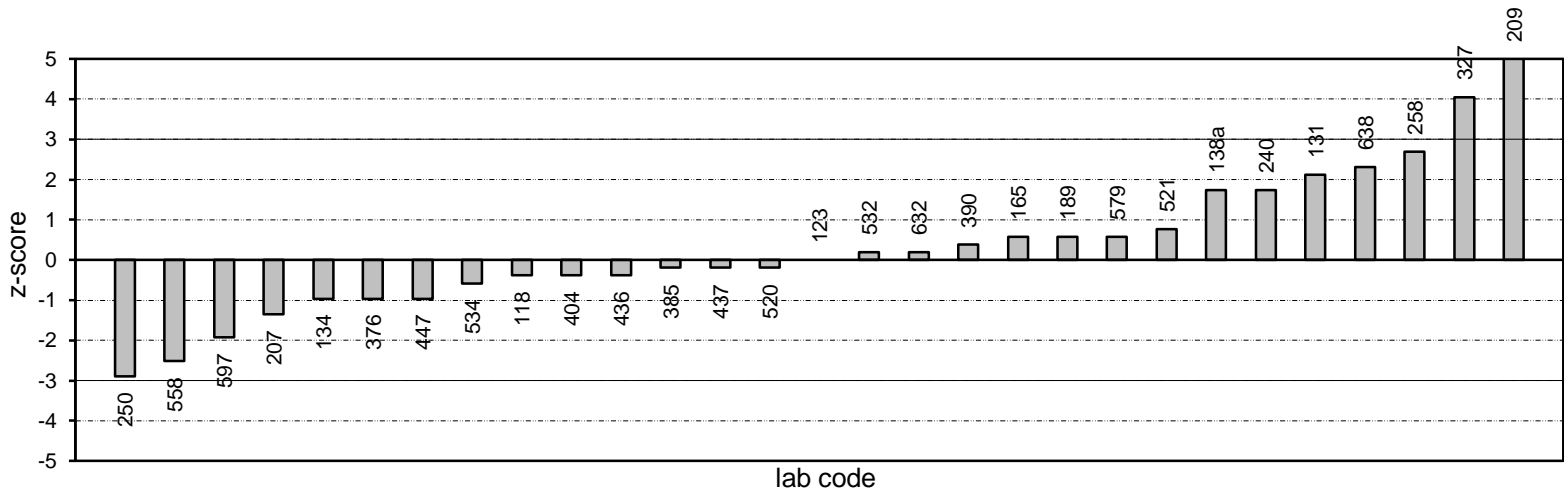
<sup>3</sup> Please refer to Appendix C (pages C3 - C4) for method code descriptions.

**Bromide - Samples PTA 1 and PTA 2**  
**Ordered Robust Z-Score Charts**

**Bromide - Sample PTA 1 - Robust Z-Scores**



**Bromide - Sample PTA 2 - Robust Z-Scores**



# **Chloride Results**

Samples PTA 1 and PTA 2

## Chloride

### Results by Laboratory Code

Lab Code	Sample PTA 1				Sample PTA 2			
	Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>		Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>	
118	60.2 ± 0.3	-0.09	30		79.8 ± 0.4	-0.49	30	
123	60.9 #	0.23	30		80.8 #	-0.29	30	
124	64.6 ± 5.49	1.92	15		88.1 ± 7.49	1.18	15	
131	60.3 #	-0.05	17		78.8 #	-0.69	17	
134	59.4 #	-0.46	17		79.2 #	-0.61	17	
138a	65.3 ± 0.007	2.24	17		92.0 ± 0.007	1.96	17	
140	63.6 ± 3.8	1.46	13		86.5 ± 5.1	0.86	13	
165	59.5 ± 6	-0.41	17		80.0 ± 8	-0.45	17	
173	62.6 ± 0.6	1.01	15		84.9 ± 0.8	0.53	15	
182	62.0 #	0.73	13		84.0 #	0.35	13	
189	57.0 ± 1.2	-1.55	17		76.1 ± 1.6	-1.24	17	
203a	65.8 ± 0.3	2.47	13		89.1 ± 0.9	1.38	13	
207	59.2 #	-0.55	17		99.6 #	3.49	§	17
209	53.8 ± 10.98	-3.02	§	29	89.3 ± 14.32	1.42		29
232	60.4 ± 0.6	0.00	17		82.0 ± 0.5	-0.05	17	
240	65.1 ± 6.5	2.15	25		91.2 ± 9.1	1.80	25	
244	66.5 #	2.79	15		90.3 #	1.62	15	
249	64.8 ± 0.1	2.01	13		87.9 ± 0.1	1.14	13	
250	163.7 ± 11.5	47.24	§	17	122.6 ± 8.6	8.12	§	17
258	64.1 ± 2.0	1.69	24		88.5 ± 2.8	1.26	24	
267	60.7 ± 1.1	0.14	15		83.4 ± 1.5	0.23	15	
271	60.9 ± 3.5	0.23	14		83.7 ± 4.8	0.29	14	
302	62.5 ± 0.001	0.96	15		85.8 ± 0.001	0.71	15	
327	59.6 ± 11.9	-0.37	30		84.6 ± 16.9	0.47	30	
342	59.8 #	-0.27	17		79.9 #	-0.47	17	
345	53.5 ± 1.0	-3.16	§	13	63.5 ± 1.0	-3.78	§	13
376	53.2 #	-3.29	§	18	69.3 #	-2.61	18	
385	56.2 #	-1.92	30		74.2 #	-1.62	30	
390	60.1 ± 1.7	-0.14	17		80.1 ± 2.3	-0.43	17	
404	61.0 ± 4.4	0.27	30		82.4 ± 5.9	0.03	30	
436	60.0 ± 7.2	-0.18	30		80.7 ± 9.7	-0.31	30	
437	52 ± 10	-3.84	§	31	70 ± 10	-2.47	31	
447	59.9 ± 15.0	-0.23	24		81.5 ± 20.4	-0.15	24	
470	59.9 ± 0.63	-0.23	17		80.5 ± 0.84	-0.35	17	
485	59.73 #	-0.31	32		84.22 #	0.40	32	

<sup>1</sup> Where reported, results are shown with their corresponding measurement uncertainty (MU).

<sup>2</sup> "§" denotes an outlier (i.e. those results for which  $|z\text{-score}| \geq 3.0$ ). Robust z-scores are calculated as:  
 $z = (A - \text{median}) \div \text{normalised IQR}$ , where A is the participant laboratory's result.

<sup>3</sup> Please refer to Appendix C (pages C3 - C4) for method code descriptions.

**Chloride (cont.)**  
**Results by Laboratory Code**

Lab Code	Sample PTA 1				Sample PTA 2				
	Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>		Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>		
501	59.9 ± 0.8	-0.23	30		80.4 ± 1.4	-0.37	30		
507	62.0 ± 2	0.73	13		84.5 ± 2	0.45	13		
520	58.4 ± 2.2	-0.91	30		78.9 ± 2.9	-0.67	30		
521	59.5 ± 3.0	-0.41	30		78.7 ± 4.0	-0.71	30		
530	63.2 #	1.28	13		86.0 #	0.76	13		
532	61.1 ± 3.7	0.32	16		85.2 ± 5.1	0.59	16		
534	60.7 ± 0.5	0.14	17		80.2 ± 0.5	-0.41	17		
558	63.1 #	1.23	30		80.2 #	-0.41	30		
573	62 ± 4	0.73	13		89 ± 5	1.36	13		
579	60.2 ± 5.4	-0.09	18		80.3 ± 7.2	-0.39	18		
584	60.0 ± 0.2	-0.18	17		80.0 ± 0.3	-0.45	17		
595	61.1 ± 14.0	0.32	13		88.2 ± 20.2	1.20	13		
597	59.5 #	-0.41	32		77.4 #	-0.98	32		
616	61.4 ± 1.5	0.46	17		87.2 ± 1.8	1.00	17		
632	63.4 #	1.37	17		85.3 #	0.61	17		
634	60.4 ± 0.302	0.00	17		82.1 ± 0.4105	-0.03	17		
638	55.2 ± 7.5	-2.38	16		78.7 ± 9.6	-0.71	16		
<i>No of Results:</i> 52					52				
<i>Median:</i> 60.40					82.25				
<i>Normalised IQR:</i> 2.19					4.97				
<i>Uncertainty of the Median:</i> 0.38					0.86				
<i>Robust CV:</i> 3.6%					6.0%				
<i>Minimum:</i> 52					63.5				
<i>Maximum:</i> 163.7					122.6				
<i>Range:</i> 111.7					59.1				

<sup>1</sup> Where reported, results are shown with their corresponding measurement uncertainty (MU).

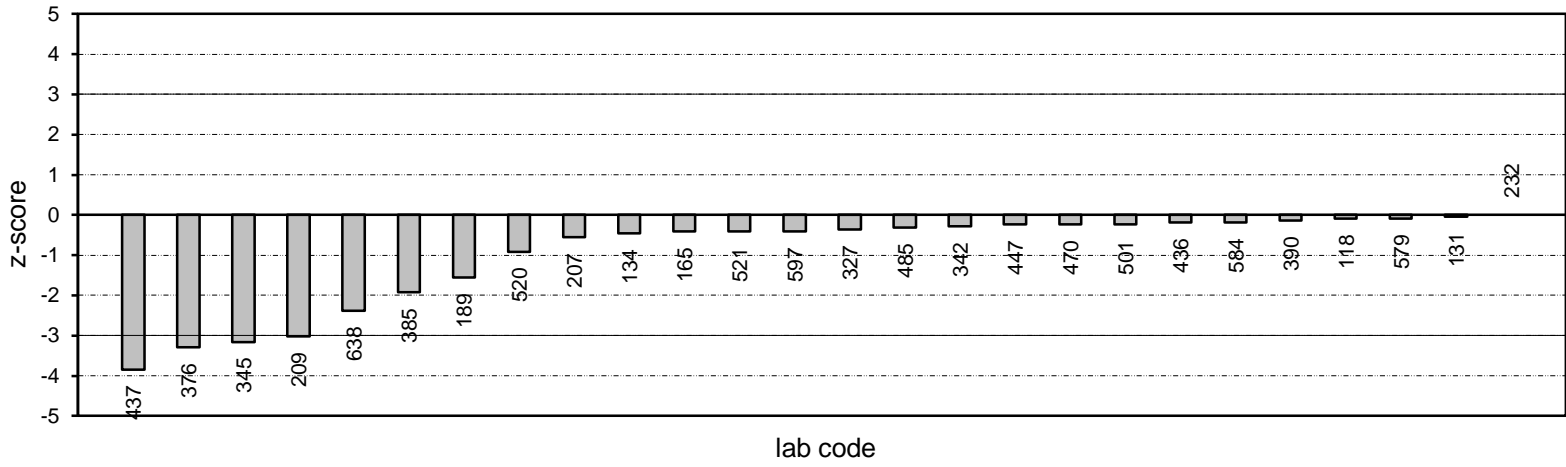
<sup>2</sup> "\$" denotes an outlier (i.e. those results for which  $|z\text{-score}| \geq 3.0$ ). Robust z-scores are calculated as:  
 $z = (A - \text{median}) \div \text{normalised IQR}$ , where A is the participant laboratory's result.

<sup>3</sup> Please refer to Appendix C (pages C3 - C4) for method code descriptions.

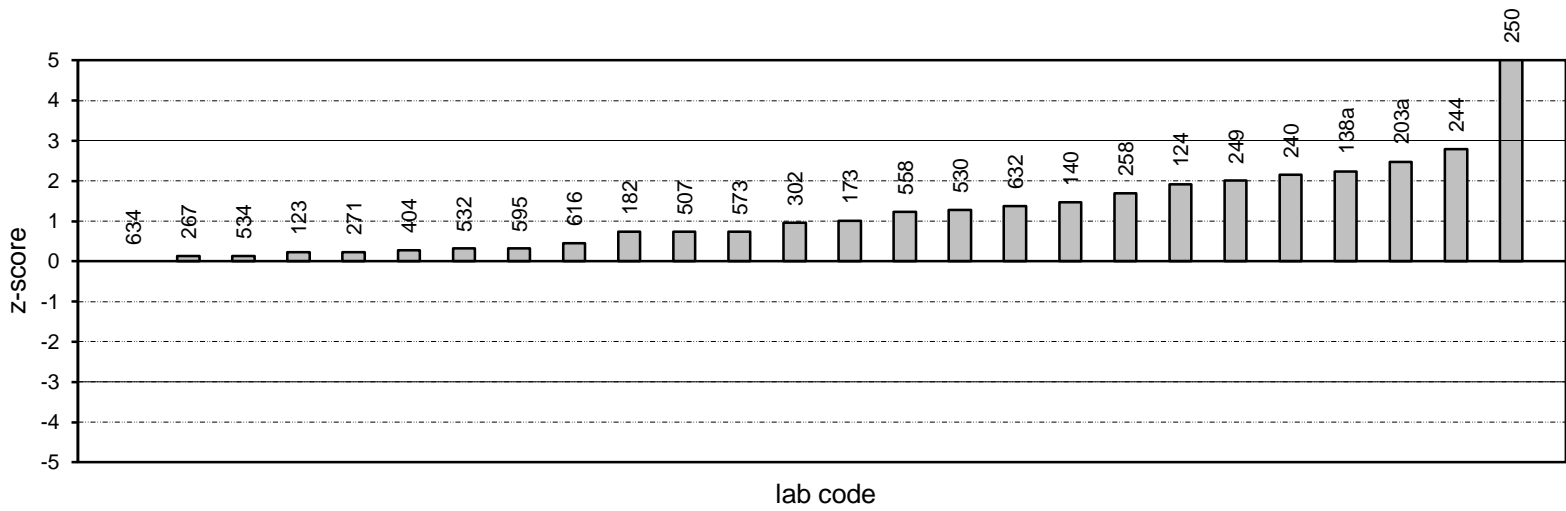
### Chloride - Sample PTA 1

#### Ordered Robust Z-Score Charts

#### Chloride - Sample PTA 1 - Robust Z-Scores



#### Robust Z-Scores

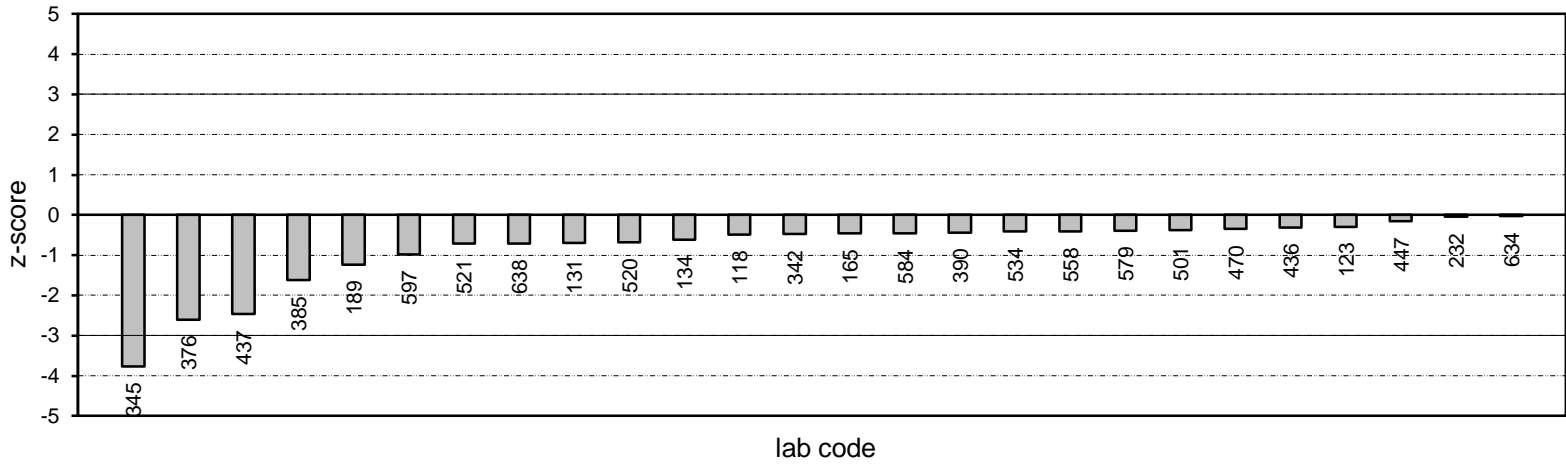




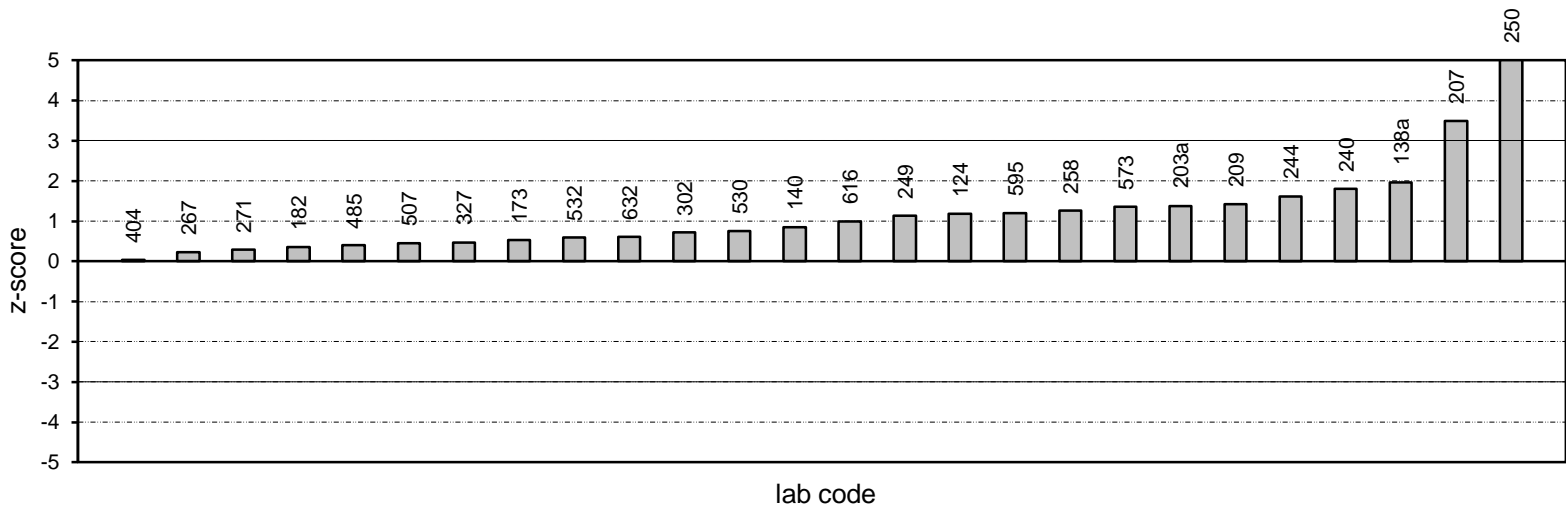
### Chloride - Sample PTA 2

#### Ordered Robust Z-Score Charts

#### Chloride - Sample PTA 2 - Robust Z-Scores



#### Robust Z-Scores



# **Fluoride Results**

Samples PTA 1 and PTA 2

**Fluoride**  
**Results by Laboratory Code**

Lab Code	Sample PTA 1				Sample PTA 2			
	Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>		Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>	
118	1.40 ± 0.03	0.29	46		1.95 ± 0.04	0.54	46	
123	1.32 #	-0.88	46		1.75 #	-1.26	46	
124	1.36 ± 0.116	-0.29	34		1.94 ± 0.165	0.45	34	
131	1.30 #	-1.17	38		1.75 #	-1.26	38	
138a	1.39 ± 0.007	0.15	38		1.93 ± 0.007	0.36	38	
140	1.39 ± 0.12	0.15	34		1.90 ± 0.16	0.09	34	
156	1.38 ± 0.2	0.00	34		1.88 ± 0.2	-0.09	34	
165	1.31 ± 0.13	-1.02	38		1.85 ± 0.19	-0.36	38	
173	1.46 ± 0.12	1.17	34		1.99 ± 0.16	0.90	34	
189	1.26 ± 0.03	-1.75	38		1.73 ± 0.04	-1.44	38	
198	1.30 ± 0.06	-1.17	42		1.76 ± 0.08	-1.17	42	
207	1.35 #	-0.44	38		2.07 #	1.62	38	
209	1.32 ± 0.22	-0.88	48		1.78 ± 0.18	-0.99	48	
232	1.37 ± 0.02	-0.15	38		1.90 ± 0.01	0.09	38	
240	1.34 ± 0.15	-0.58	34		1.83 ± 0.20	-0.54	34	
244	1.40 #	0.29	34		1.95 #	0.54	34	
249	1.38 ± 0.01	0.00	35		1.77 ± 0.01	-1.08	35	
250	4.22 ± 0.51	41.42 §	38		3.16 ± 0.38	11.42 §	38	
258	1.47 ± 0.10	1.31	42		2.03 ± 0.14	1.26	42	
267	1.41 ± 0.02	0.44	34		1.88 ± 0.02	-0.09	34	
271	1.33 ± 0.07	-0.73	34		1.78 ± 0.09	-0.99	34	
321	1.42 ± 0.14	0.58	34		1.74 ± 0.17	-1.35	34	
327	1.52 ± 0.30	2.04	46		2.11 ± 0.42	1.98	46	
342	1.41 #	0.44	38		1.94 #	0.45	38	
345	1.63 #	3.65 §	34		2.42 #	4.77 §	34	
360	1.45 ± 0.15	1.02	47		1.96 ± 0.20	0.63	47	
376	1.60 #	3.21 §	38		1.95 #	0.54	38	
385	1.42 #	0.58	46		1.90 #	0.09	46	
390	1.41 ± 0.14	0.44	38		1.90 ± 0.18	0.09	38	
404	1.25 ± 0.19	-1.90	46		1.75 ± 0.26	-1.26	46	
436	1.36 ± 0.23	-0.29	46		1.89 ± 0.32	0.00	46	
437	1.3 ± 0.4	-1.17	42		1.8 ± 0.4	-0.81	42	
447	1.57 ± 0.40	2.77	38		2.10 ± 0.53	1.89	38	
470	1.38 ± 0.02	0.00	38		1.86 ± 0.03	-0.27	38	
507	1.37 ± 0.2	-0.15	34		1.80 ± 0.2	-0.81	34	

<sup>1</sup> Where reported, results are shown with their corresponding measurement uncertainty (MU).

<sup>2</sup> "§" denotes an outlier (i.e. those results for which  $|z\text{-score}| \geq 3.0$ ). Robust z-scores are calculated as:  
 $z = (A - \text{median}) \div \text{normalised IQR}$ , where A is the participant laboratory's result.

<sup>3</sup> Please refer to Appendix C (pages C3 - C4) for method code descriptions.

**Fluoride (cont.)**  
**Results by Laboratory Code**

Lab Code	Sample PTA 1				Sample PTA 2				
	Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>		Result ± MU <sup>1</sup> (mg/L)	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>		
520	1.38 ± 0.08	0.00	46		1.91 ± 0.11	0.18	46		
521	1.39 ± 0.1	0.15	46		1.90 ± 0.1	0.09	46		
532	1.55 ± 0.34	2.48	34		2.00 ± 0.44	0.99	34		
534	1.43 ± 0.1	0.73	38		1.86 ± 0.1	-0.27	38		
573	1.65 ± 0.07	3.94 §	34		2.18 ± 0.09	2.61	34		
579	1.38 ± 0.11	0.00	34		1.83 ± 0.15	-0.54	34		
584	1.36 ± 0.01	-0.29	38		1.86 ± 0.01	-0.27	38		
595	1.39 ± 0.15	0.15	34		1.86 ± 0.20	-0.27	34		
597	1.29 #	-1.31	34		1.77 #	-1.08	34		
616	1.15 ± 0.1	-3.35 §	38		1.76 ± 0.15	-1.17	38		
632	1.38 #	0.00	38		1.89 #	0.00	38		
634	1.30 ± 0.0065	-1.17	38		1.90 ± 0.0095	0.09	38		
638	1.32 ± 0.24	-0.88	35		1.87 ± 0.31	-0.18	35		
<i>No of Results:</i> 48					48				
<i>Median:</i> 1.380					1.890				
<i>Normalised IQR:</i> 0.069					0.111				
<i>Uncertainty of the Median:</i> 0.012					0.020				
<i>Robust CV:</i> 5.0%					5.9%				
<i>Minimum:</i> 1.15					1.73				
<i>Maximum:</i> 4.22					3.16				
<i>Range:</i> 3.07					1.43				

<sup>1</sup> Where reported, results are shown with their corresponding measurement uncertainty (MU).

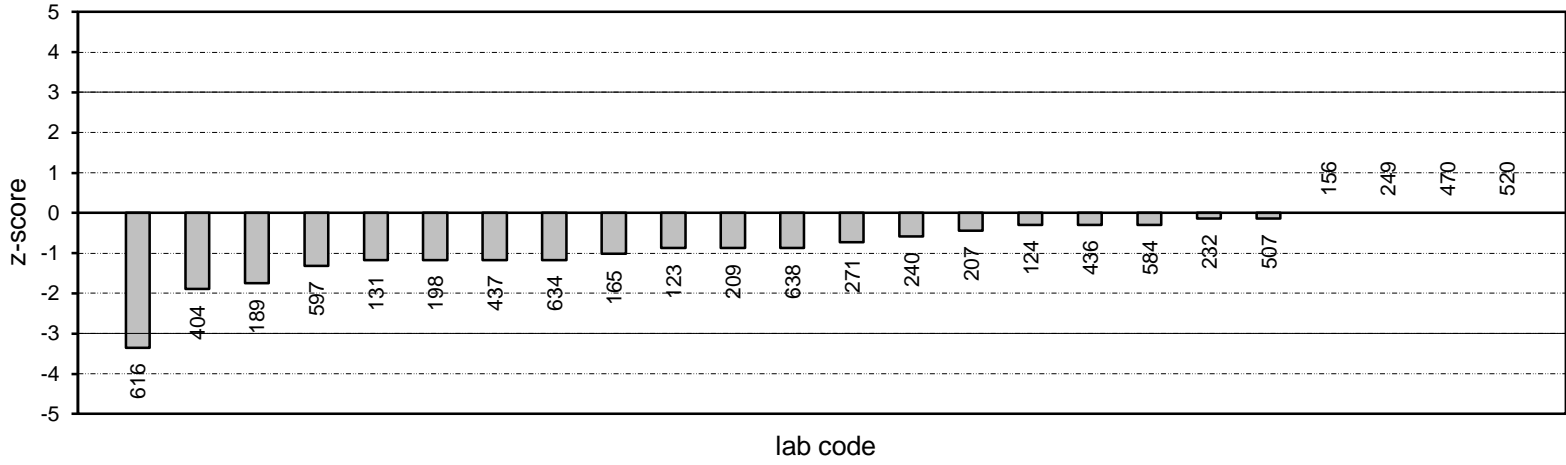
<sup>2</sup> "§" denotes an outlier (i.e. those results for which  $|z\text{-score}| \geq 3.0$ ). Robust z-scores are calculated as:  
 $z = (A - \text{median}) \div \text{normalised IQR}$ , where A is the participant laboratory's result.

<sup>3</sup> Please refer to Appendix C (pages C3 - C4) for method code descriptions.

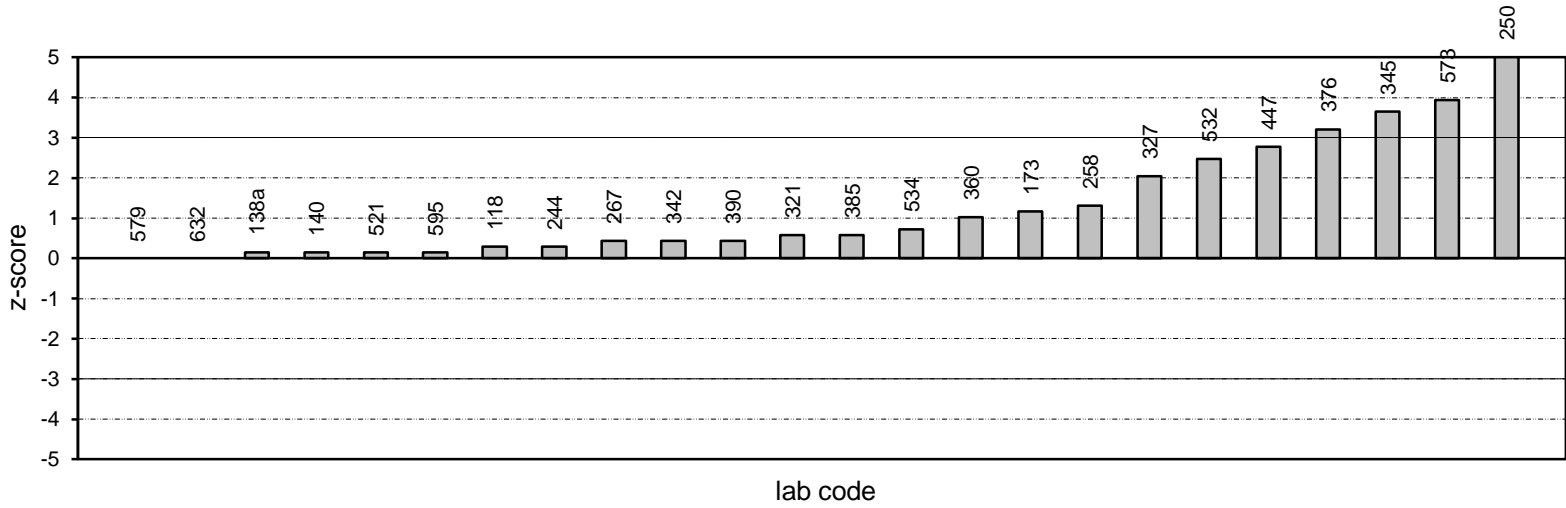
### Fluoride - Sample PTA 1

#### Ordered Robust Z-Score Charts

#### Fluoride - Sample PTA 1 - Robust Z-Scores



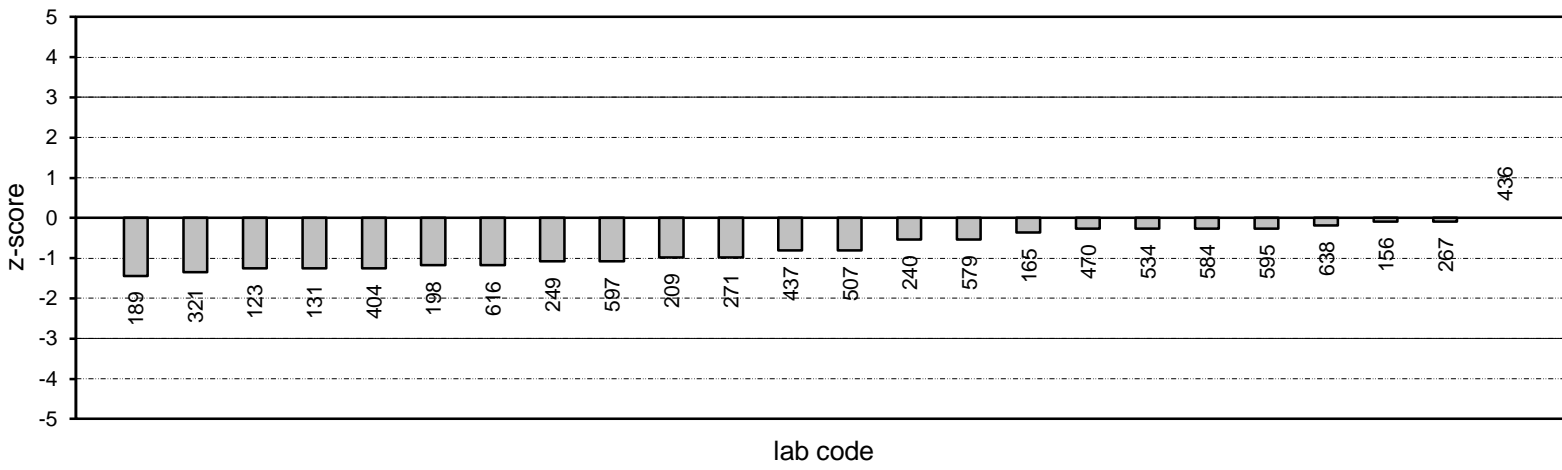
#### Robust Z-Scores



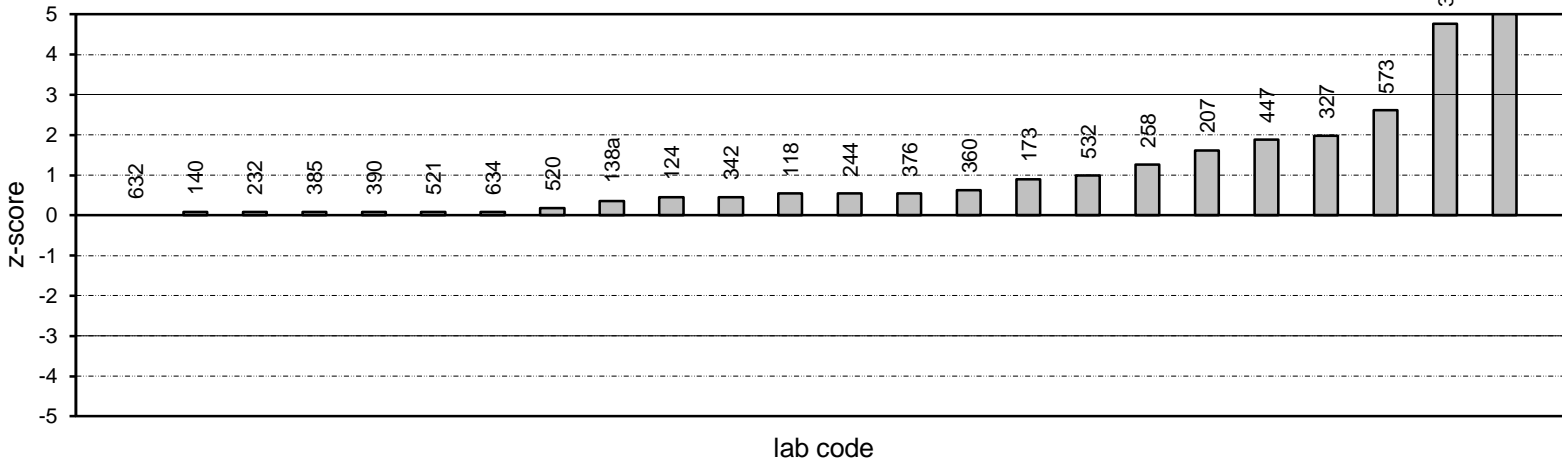
**Fluoride - Sample PTA 2**

**Ordered Robust Z-Score Charts**

**Fluoride - Sample PTA 2 - Robust Z-Scores**



**Robust Z-Scores**



# **Iodide Results**

Samples PTA 1 and PTA 2

**Iodide**  
**Results by Laboratory Code**

Lab Code	Sample PTA 1				Sample PTA 2			
	Result ± MU <sup>1</sup> (mg/L)		Robust z-score <sup>2</sup>	Method Code <sup>3</sup>	Result ± MU <sup>1</sup> (mg/L)		Robust z-score <sup>2</sup>	Method Code <sup>3</sup>
131	1.01	#	-1.30	54	0.60	#	-0.97	54
165	1.05	± 0.11	-0.56	54	0.62	± 0.1	-0.54	54
209	1.12	± 0.16	0.74	56	0.51	± 0.05	-2.91	56
240	1.06	± 0.11	-0.37	53	0.75	± 0.08	2.27	53
250	1.20	#	2.23	50	2.50	#	40.04	§
258	1.08	± 0.09	0.00	54	0.64	± 0.05	-0.11	54
436	1.25	± 0.29	3.16	§	53	0.72	± 0.17	1.62
437	1.08	± 0.05	0.00	53	0.65	± 0.03	0.11	53
520	1.03	± 0.06	-0.93	54	0.62	± 0.04	-0.54	54
532	1.09	± 0.13	0.19	54	0.67	± 0.08	0.54	54
579	1.08	± 0.08	0.00	54	0.63	± 0.04	-0.32	54
597	1.16	#	1.49	56	0.661	#	0.35	56
<i>No of Results:</i>					12			
<i>Median:</i>					1.080			
<i>Normalised IQR:</i>					0.054			
<i>Uncertainty of the Median:</i>					0.019			
<i>Robust CV:</i>					5.0%			
<i>Minimum:</i>					1.01			
<i>Maximum:</i>					1.25			
<i>Range:</i>					0.24			

<sup>1</sup> Where reported, results are shown with their corresponding measurement uncertainty (MU).

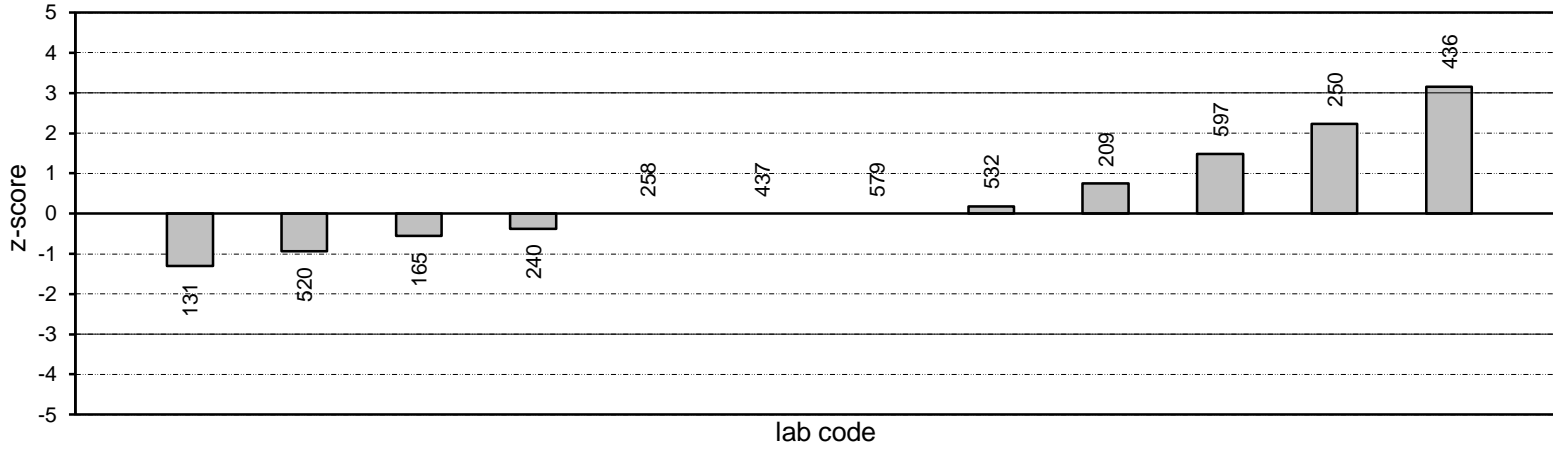
<sup>2</sup> "§" denotes an outlier (i.e. those results for which  $|z\text{-score}| \geq 3.0$ ). Robust z-scores are calculated as:  
 $z = (A - \text{median}) \div \text{normalised IQR}$ , where A is the participant laboratory's result.

<sup>3</sup> Please refer to Appendix C (pages C3 - C4) for method code descriptions.

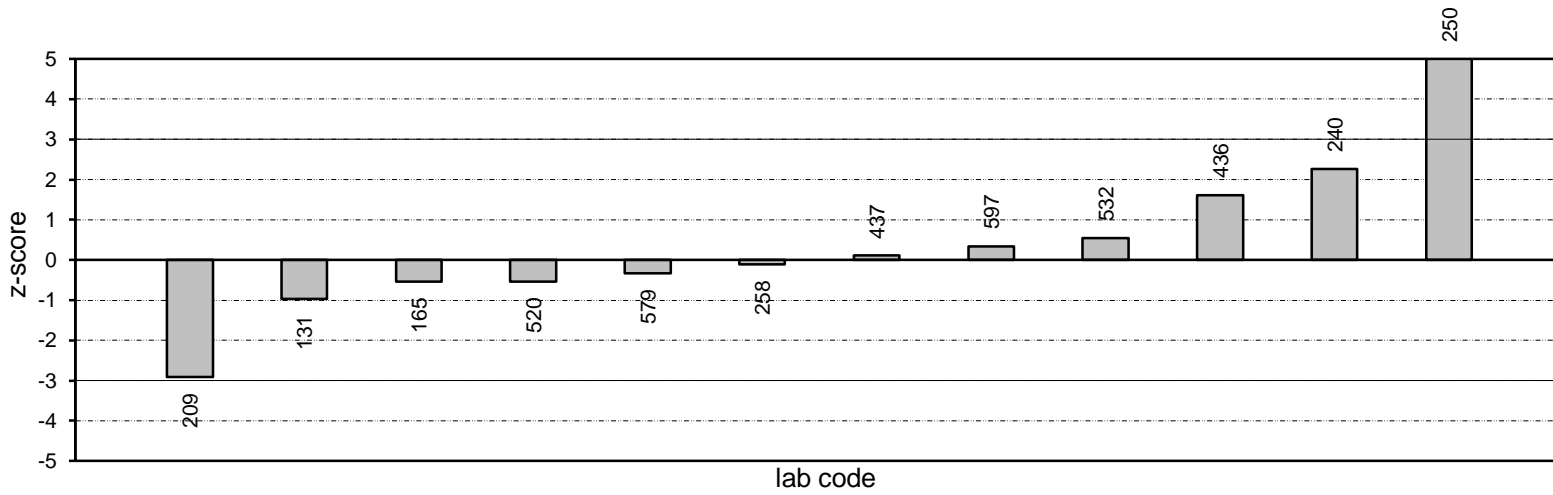


**Iodide - Samples PTA 1 and PTA 2**  
**Ordered Robust Z-Score Charts**

**Iodide - Sample PTA 1 - Robust Z-Scores**



**Iodide - Sample PTA 2 - 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. All samples are subjected to rigorous stability and homogeneity 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 35°C for three days for an accelerated ageing stability trial. The samples were then analysed in duplicate by Hill Laboratories, New Zealand.

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

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

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

The results of homogeneity and stability testing are presented in Tables 9 and 10 below. Please note that the mean results for these testings are not intended to be used as reference values.

Round PTA 157	Samples PTA 1 (g/m <sup>3</sup> )								
	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	22.1	21.8	110	109	1199	1255	27.8	27.7
	H2	21.3	21.2	115	113	1126	1166	27.8	27.7
	H3	21.7	21.5	111	116	1227	1179	27.7	27.5
	H4	21.3	21.2	114	111	1178	1183	27.7	27.7
	H5	21.3	21.2	115	113	1171	1139	27.5	27.2
	H6	21.4	21.4	113	114	1188	1199	27.4	27.7
	H7	21.5	21.6	116	107	1123	1172	27.5	27.5
Stability	S1	21.4	21.5	117	115	1158	1133	27.7	27.7
	S2	21.4	22.6	117	111	1214	1181	27.7	27.7
	S3	20.7	21.9	107	112	1227	1182	27.7	28.0
	RSD	1.6%	2.0%	2.9%	2.4%	3.2%	2.8%	0.5%	0.7%

Table 9. Homogeneity and stability testing of PTA 1 samples.

Round PTA 157	Samples PTA 2 (g/m <sup>3</sup> )				
	Sample ID	Total Iodine	Bromide	Chloride	Fluoride
Homogeneity	H1	12.8	267	1630	37.7
	H2	12.6	266	1586	37.7

Table 10. Homogeneity testing of PTA 2 samples.

# APPENDIX C

## Documentation

Instructions to Participants..... C1  
Method Codes..... C3  
Results Sheet..... C5



**PROFICIENCY TESTING AUSTRALIA**  
**WATERS PROFICIENCY TESTING PROGRAM**

**CHEMICAL ANALYSIS ROUND 157**

**July, 2013**

**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 100 mL of artificial potable water concentrate.
- 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°C - 5°C) 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.

**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 20° C.
- ii) Record sample ID number.
- iii) Dilute sample by a factor of 20x (e.g. 10mL made up to 200mL with reagent grade water).
- iv) Test sample according to your normal procedures.

**Please report results for the diluted sample.**

**3. Tests Requested**

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

- i) Bromide (Br<sup>-</sup>)
- ii) Chloride (Cl<sup>-</sup>)
- iii) Fluoride (F<sup>-</sup>)
- iv) Iodide (I<sup>-</sup>)

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) For each prepared sample only a single result is requested.
- ii) Report results in milligrams per litre (mg/L).
- iii) For statistical purposes, report results:
  - a) Bromide and Chloride report to one decimal place (e.g. 12.1 mg/L)
  - b) Fluoride and Iodide report to two decimal places (e.g. 1.55 mg/L)
- iv) Do not correct results for recovery.
- v) In addition to reporting the results, record the method of analysis using the attached codes.
- vi) Laboratories are also requested to calculate and report an estimate of measurement uncertainty (MU) for each reported measurement result. All estimates of MU must be given as a 95% confidence interval (coverage factor  $k \approx 2$ ) and reported in mg/L.

6. Testing should commence as soon as possible after receiving the samples and results reported **NO LATER THAN 16 AUGUST 2013** 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](mailto: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 (all in mg/L):

Analyte	Range
Bromide (Br <sup>-</sup> )	5.0 - 20.0 mg/L
Chloride (Cl <sup>-</sup> )	50.0 - 150.0 mg/L
Fluoride (F <sup>-</sup> )	1.00 - 5.00 mg/L
Iodide (I <sup>-</sup> )	0.50 - 2.00 mg/L

**Method Codes to be used for the Results Sheet**

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Bromide (Br <sup>-</sup> )	APHA SM	Part 4500 – Br <sup>-</sup> B. Phenol Red Colorimetric Method	1
		Part 4500 – Br <sup>-</sup> D. Flow Injection Analysis	2
		Part 4110 B. Ion Chromatography with Chemical Suppression of Eluent Conductivity	3
		Part 4110 C. Single-Column Ion Chromatography with Direct Conductivity Detection	4
		Part 4110 D. Ion Chromatographic Determination of Oxyhalides and Bromide	5
		Part 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	Method Number 300.1 Inorganic Anions in DW by Ion Chromatography	8
	Other	ICPMS	9
		Ion Chromatography (In-house method)	10
		In-house method	11
		Other (please specify)	12
	Chloride (Cl <sup>-</sup> )	APHA SM	Part 4500 – Cl <sup>-</sup> B. Argentometric Method
Part 4500 – Cl <sup>-</sup> C. Mercuric Nitrate Method			14
Part 4500 – Cl <sup>-</sup> D. Potentiometric Method			15
Part 4500 – Cl <sup>-</sup> E. Automated Ferricyanide Method			16
Part 4110 B. Ion Chromatography with Chemical Suppression of Eluent Conductivity			17
Part 4110 C. Single-Column Ion Chromatography with Direct Conductivity Detection			18
Part 4140 B. Capillary Ion Electrophoresis with Indirect UV Detection			19
ASTM		ASTM D 512 – 04 Standard Test Methods for Chloride Ion in Water.	20
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.	21
		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.	22
		ISO 15682:2000 Water quality – Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection.	23
Other		Discrete Analyser	24
		FIA Lachat	25
		ICPM	26
		Potentiometric Titration	27
		Segmented Flow Analysis	28
		Spectroquant	29
		Ion Chromatography (In house method)	30
In house method		31	
Other (please specify)	32		

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

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Fluoride (F <sup>-</sup> )	APHA SM	Part 4500 – F <sup>-</sup> B. Preliminary Distillation Step	33
		Part 4500 – F <sup>-</sup> C. Ion Selective Electrode Method	34
		Part 4500 – F <sup>-</sup> D. SPADNS Method	35
		Part 4500 – F <sup>-</sup> E. Complexone Method	36
		Part 4500 – F <sup>-</sup> G. Ion-Selective Electrode Flow Injection Analysis	37
		Part 4110 B. Ion Chromatography with Chemical Suppression of Eluent Conductivity	38
		Part 4140 B. Capillary Ion Electrophoresis with Indirect UV Detection	39
	ASTM	ASTM D 1179 – 04 Standard Test Methods for Fluoride Ion in Water	40
	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.	41
	Other	Fluoride Electrode	42
		ICPMS	43
		SPAONS Method	44
		SPADNS Discrete Analyser	45
		Ion Chromatography (In house method)	46
		In house method	47
		Other (please specify)	48
	Iodide (I <sup>-</sup> )	APHA SM	Part 4500 – I <sup>-</sup> B. Leuco Crystal Violet Method
Part 4500 – I <sup>-</sup> C. Catalytic Reduction Method			50
Part 4500 – I <sup>-</sup> D. Voltametric Method			51
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.	52
Other		ICPMS	53
		Ion Chromatography (In house method)	54
		In house method	55
		Other (please specify)	56

**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>)
- ii) **ISO** International Organization for Standardization. (<http://www.iso.org>).
- iv) **US EPA** U.S Environmental Protection Agency.  
(<http://www.epa.gov/osa/fem/methcollectns.htm>),  
(<http://www.epa.gov/greatlakes/lmmb/methods>).





**PROFICIENCY TESTING AUSTRALIA**  
**WATERS PROFICIENCY TESTING PROGRAM**  
**CHEMICAL ANALYSIS ROUND 157**

**BROMIDE, CHLORIDE, FLUORIDE, IODIDE - JULY 2013**

**RESULTS SHEET**  
**(mg/L)**

Laboratory  
Code

\*Approximate temperature of samples upon receipt:

ANALYSIS	Sample PTA 1			Sample PTA 2		
	Result	±MU*	METHOD CODE	Result	±MU*	METHOD CODE
Bromide (Br <sup>-</sup> )						
Chloride (Cl <sup>-</sup> )						
Fluoride (F <sup>-</sup> )						
Iodide (I <sup>-</sup> )						

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

- i) For each prepared sample only a single result is requested.
- ii) For statistical purposes, report results:
  - a) Bromide and Chloride report to one decimal place (e.g. 12.1 mg/L)
  - b) Fluoride and Iodide report to two decimal places (e.g. 1.55 mg/L)
- iii) Report results in 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.

DATE

SIGNATURE

Return results **NO LATER THAN 16 August 2013** 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](mailto:dmihaila@pta.asn.au)

INSTRUCT WATERS PROF TEST PROG 157

*- End of Report -*