Report No. 588

Waters Proficiency Testing

Sub-Program 109

- Bromide (Br^-), Chloride (Cl^-), Fluoride (F^-), Iodide(I^-) -

October 2008

Acknowledgments

PTA gratefully wishes to acknowledge the technical assistance provided for this program by Dr M Buckley-Smith, AsureQuality Limited.

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CONTENTS

1. Foreword

This report summarises the results of a proficiency testing program on the determination of Bromide (Br^-), Chloride (Cl^-), Fluoride (F^-) and Iodide (I^-) in waters. This is sub-program 109 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in July 2008 by Proficiency Testing Australia (PTA). The main aim of the program was to assess laboratories' abilities to competently perform the prescribed analyses.

The Technical Adviser for the program was Dr M Buckley-Smith from AsureQuality Limited, and the Program Coordinator was Ms F Ward.

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).

2.3 Participants were provided with two samples (labelled Sample 1 and Sample 2) suppled by AsureQuality Limited containing solutions of Bromide, Chloride, Fluoride and Iodide concentrates.

2.4 A total of 83 laboratories received samples, comprising:

- 75 Australian participants; and
- 8 overseas participants, including:
    - Brunei Darussalam(1), Indonesia (1), Korea (1), Malaysia (1), New Zealand (1), Papua New Guinea (1), Philippines (1), Thailand (1).

Of these 83 laboratories, 4 were unable to submit results by the due date.

2.5 Results (as reported by participants) with corresponding summary statistics (i.e. number of results, median, normalised interquartile range, 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). Between and within laboratory z-scores, z-score charts relevant to each test and Youden Diagrams are presented in Appendix A.

The document entitled *Guide to Proficiency Testing Australia,* 2008 (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 extreme or outlier results can be found on pages 13 and 14.

2.8 Samples for the program were supplied by AsureQuality Limited. Refer to Appendix B for homogeneity and stability testing information.

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; and
- Youden diagrams.

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 three is considered to be an outlier and is marked by the symbol "**§**".

Those results reported as "less than values" and marked with a "**Ŧ**" are outlier results as they lie more than 3 normalised IQRs below the median.

Each determination was examined for outliers with all methods pooled. The table on pages 13 and 14 summarises the outlier results detected.

3.2 Results Tables and Summary Statistics

Each of these tables contains the results returned by each laboratory, including the code number for the method used, and the between and within laboratory z-scores 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 tables of results and consists of:

- the number of results for that test/sample (*No. of Results*);
- the median of these results, i.e. the middle value (*Median*);
- the normalised interquartile range of the results (*Normalised IQR*);
- the robust coefficient of variation, expressed as a percentage (*Robust CV*) - i.e. 100 x *Normalised IQR* / *Median*;
- the minimum and maximum laboratory results; and
- the range (*Maximum* - *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 0.7413, a 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).

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

3.3 Ordered Z-Score Charts

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

These charts contain solid lines at +3 and -3, 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.

3.4 Youden Diagrams

Youden two-sample diagrams are presented to highlight laboratory systematic differences. They are based on a plot of each laboratory's pair of results (i.e. sample two versus sample one) and represented by a black spot.

These diagrams also feature an approximate 95% confidence ellipse for the bivariate analysis of the results, and dashed lines which mark the median value for each of the samples.

All points which lie outside the ellipse are labelled with the laboratory's code number. Note however that these points may not correspond with those identified as outliers. This is because the outlier criteria ($|z| > 3$) has a confidence level of approximately 99%, whereas the ellipse is an approximate 95% confidence region.

The points outside the ellipse on the Youden diagram will most probably be those with z-scores greater than 2 or less than -2. Laboratories which are outside the ellipse but have not been identified as extreme (i.e. have $2 < |z| < 3$) are encouraged to "take a close look" at their results.

As a guide to the interpretation of these diagrams:

(i) laboratories with significant systematic error components (i.e. between-laboratory variation) will usually have results outside the ellipse in either the upper right hand quadrant (as formed by the median lines) or the lower left hand quadrant (i.e. unusually high or low results for both samples); and

(ii) laboratories with significant random error components (i.e. within-laboratory variation) will have returned results that are substantially more variable than other participants, and these results will usually lie outside the ellipse in either the upper left or lower right hand quadrants (i.e. an unusually high result for one sample and low for the other).

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

4. PTA and Technical Adviser's Comments

Robust CVs are compared to four previous rounds, as detailed in the following tables. All four analytes Robust CVs were less than 10% and relatively consistent with previous proficiency rounds.

4.1 Bromide (Br^-)

Sub-Program	Sample No.	Median (mg/L)	Robust CV (%)	# Participants
This round	1	13.70	7.2	32
	2	9.85	5.1	32
Report No. 490	N192	12.0	5.6	57
(Oct 2005)	N193	7.9	6.6	56
PTAC No. 360	N148	10.8	4.8	53
(July 2001)				
PTAC No. 255	N104	15.80	5.6	57
(April 1998)				
PTAC No. 147	NO52	19.87	10.73	35
(August 1994)				

4.2 Chloride (Cl^-)

Sub-Program	Sample No.	Median (mg/L)	Robust CV (%)	# Participants
This round	1	81.80	8.7	73
	2	101.40	5.2	73
Report No. 490	N191	98.00	3.0	120
(Oct 2005)	N193	83.10	3.5	116
PTAC No. 360	N147	30.0	4.9	138
(July 2001)				
PTAC No. 255	N102	229.59	2.5	153
(April 1998)	N103	10.20	10.2	150
PTAC No. 147	NO51	56.78	6.91	104
(August 1994)				

4.3 Fluoride (F^-)

Sub-Program	Sample No.	Median (mg/L)	Robust CV (%)	# Participants
This round	1	1.48	7.5	69
	2	1.96	7.2	69
Report No. 490	N190	2.200	4.7	110
(Oct 2005)	N193	1.000	6.7	109
PTAC No. 360	N145	0.50	7.4	119
(July 2001)	N146	0.60	8.0	119
PTAC No. 255	N101	1.100	8.76	121
(April 1998)				
PTAC No. 147	NO49	1.113	13.812	88
(August 1994)	NO50	1.204	12.608	88

4.4 Iodide (I^-)

Sub-Program	Sample No.	Median (mg/L)	Robust CV (%)	# Participants
This round	1	0.96	8.5	16
	2	0.48	4.6	16
Report No. 490	N193	1.535	7.5	20
(Oct 2005)				
PTAC No. 360	N148	1.00	3.7	20
(July 2001)				
PTAC No. 255	N104	1.555	5.48	22
(April 1998)				
PTAC No. 147	NO52	1.81	28.96	16
(August 1994)				

Solid numbers of participants in bromide, chloride and fluoride analyses ensure Medians and Robust CVs are good approximations of the true result and relative spread of the results. However, low numbers carrying out the iodide analysis means reduced confidence in these approximations for this specific test.

4.5 General

Samples 1 and 2 were prepared as solutions from analytical reagent grade sodium fluoride [Ajax Finechem, UNIVAR], sodium chloride [Ajax Finechem, UNIVAR], potassium bromide [BDH, AnalaR], and potassium iodide [Ajax Finechem, UNIVAR] dissolved in deionised water. Solutions were expected to contain ions of the following concentrations:

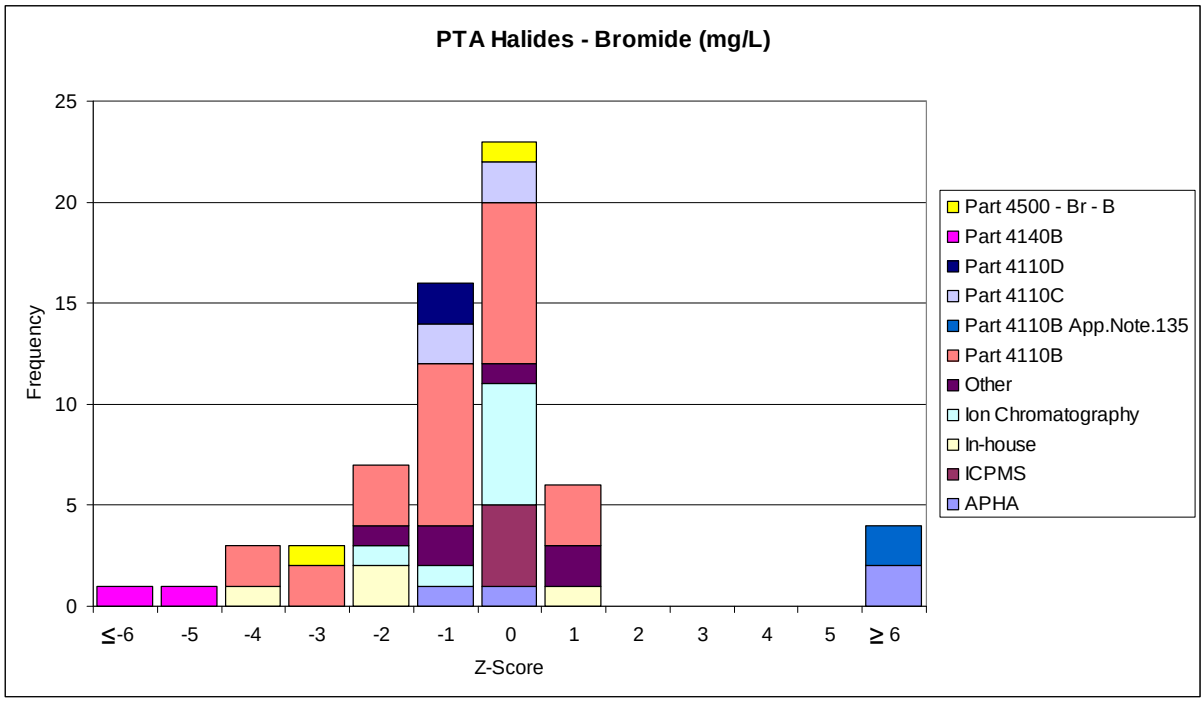
Analyte	Sample No.	Expected Concentration (mg/L)	Median (mg/L)
Bromide	1	14	13.70
	2	10	9.85
Chloride	1	80	81.80
	2	100	101.40
Fluoride	1	1.5	1.48
	2	2.0	1.96
Iodide	1	1.0	0.96
	2	0.5	0.48

Medians obtained from the proficiency round closely reflected the expected concentrations from doping levels.

4.5.1 Bromide

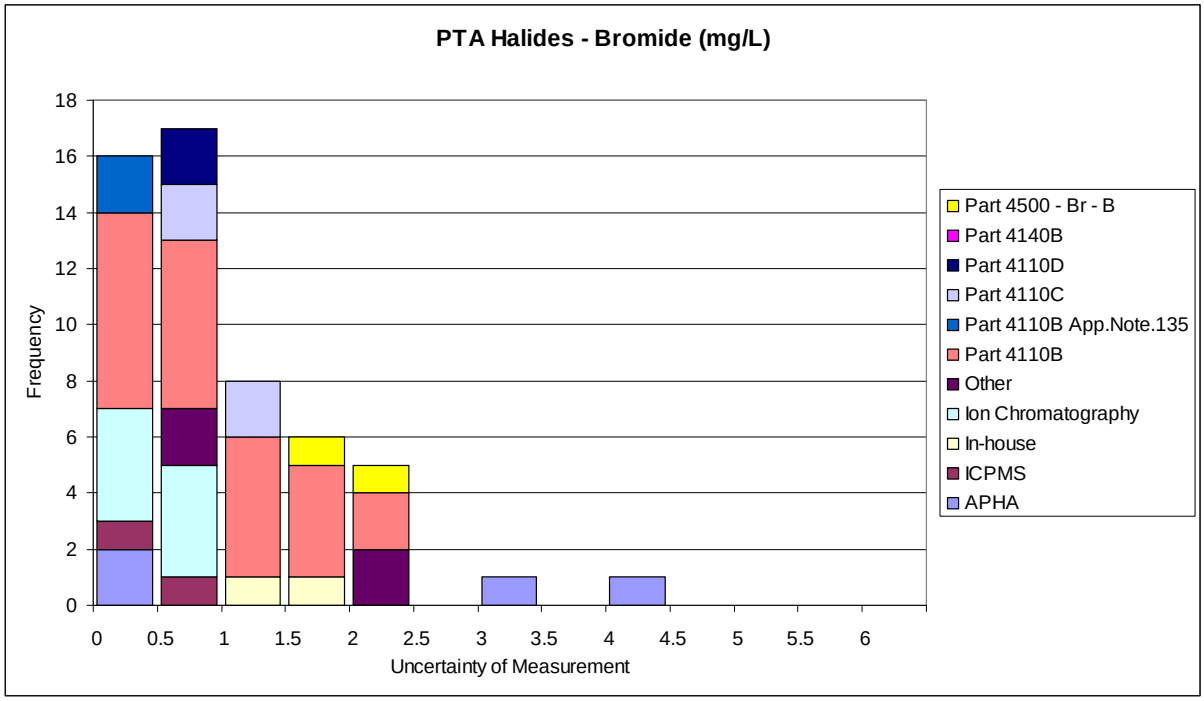
Out of 32 participants, three laboratories reported questionable results. Of these, laboratory 224 had a Between Laboratory |z-score| >2 and <3, whilst laboratories 320 and 927 have Within Laboratory |z-scores| >2 and <3. Nine laboratories reported outlier results (|z-score| >3), requiring further investigation on behalf of participants. Laboratories generating Between Laboratory |z-scores| >3 include 266, 294, 320, 504, 510. Laboratories generating Within Laboratory |z-scores| >3 include 264, 266, 278, 513, 514.

The overall dataset of bromide results shows a slight skewing with a moderate number of laboratories under-estimating the concentration of the samples, especially in Sample 1. This may be method dependent. The majority of laboratories used an Ion Chromatography method for analysis of bromide, these included APHA Part 4110B (IC with Chemical Suppression of Eluent Conductivity), APHA Part 4110C (IC with Direct Conductivity Detection) and in-house Ion Chromatography methods. As Ion Chromatography methods involve separation of anions on the basis of their relative affinities for a low-capacity, strongly basic anion exchangers, the relatively high concentration of chloride ions (~10x bromide) may have interfered with the retention and resolution of the lower concentration analytes. Tailing peaks may have contributed to under-estimation of sample concentrations, as accurate integration of the peak area can be difficult.



As the samples were manufactured from high purity reagents and deionised water, the major source of co-eluting or interfering contaminants (formic acid, acetate, bromate, chlorite) would be from the equipment (glassware or sample processing apparatus) and the quality of diluent water used in-house. The method detection level for APHA Part 4110B is stated as 0.014 mg/L for a 25µL sample loop, and 0.075 mg/L for a 100µL injection volume in APHA Part 4110C [3]. These are a small fraction of the doped levels for the proficiency samples used in this round (Sample 1 = 14 mg/L, Sample 2 = 10 mg/L), giving the participants the opportunity to obtain very accurate results.

The distribution of participants stated uncertainty of measurement can be seen below as a breakdown by methods used. However, in many cases, the stated uncertainty of measurement does not accurately reflect the difference between the median and the participants result for each proficiency sample. The vast majority (85%) of participants stated that their uncertainty of measurement was less than ± 2 mg/L, however over 66% of participants varied from the median by greater than ± 2 mg/L. In fact, even after the contribution of sample homogeneity and stability was removed, over 33% of participants varied from the median by more than 4x their stated uncertainty, highlighting the difficulty of estimating the uncertainty of measurement for any given test.

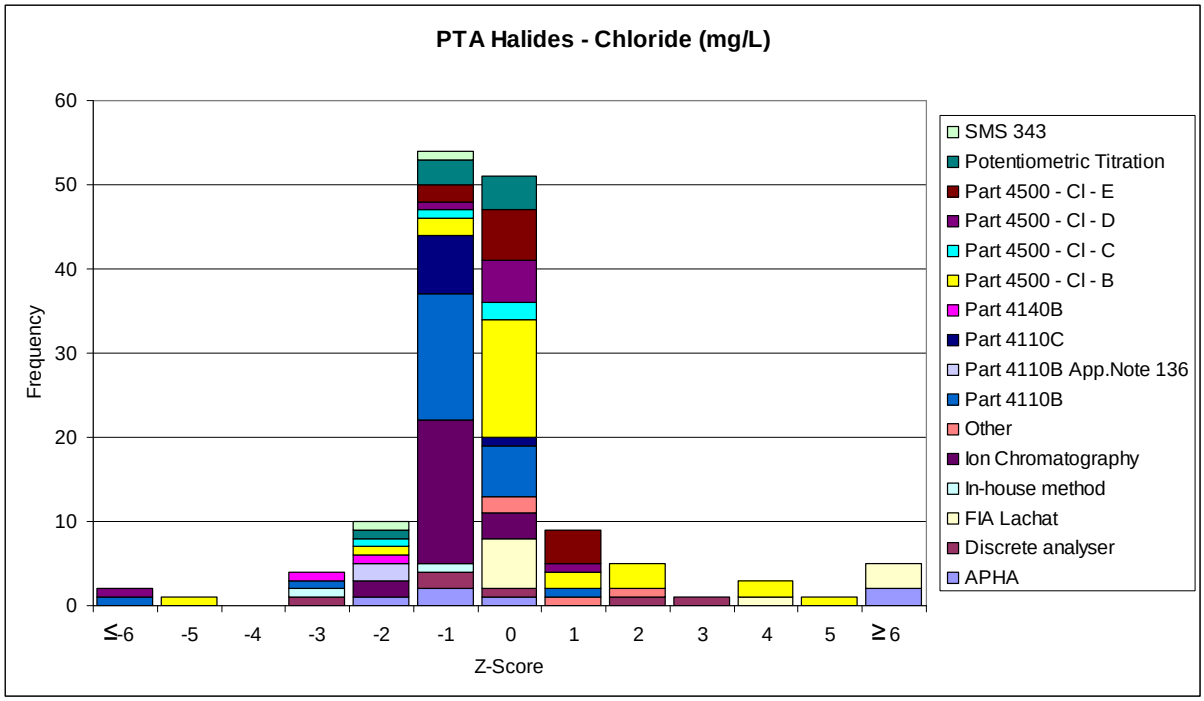


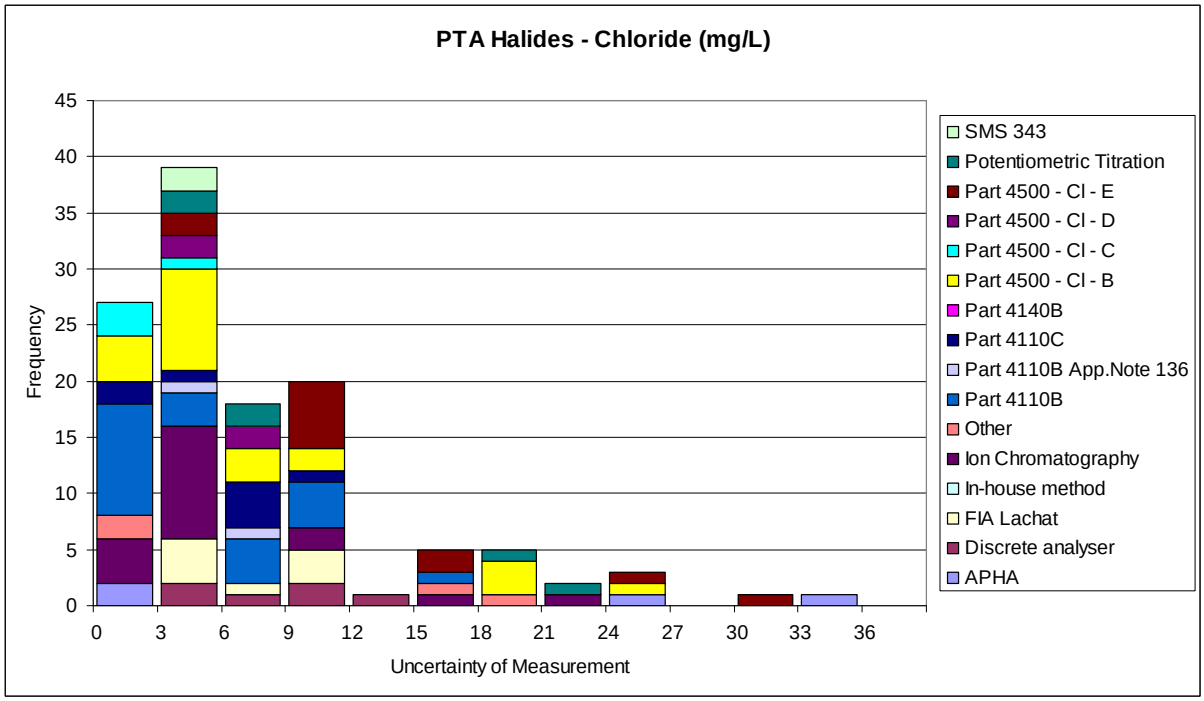
4.5.2 Chloride

Out of 73 participants, 11 laboratories reported questionable results. Of these, laboratories 215, 224 and 343 have a Between Laboratory |z-score| >2 and <3, whilst laboratories 204, 226, 240, 254, 261, 278, 314, 509 have Within Laboratory |z-scores| >2 and <3. Twelve laboratories reported outlier results (|z-score| >3), requiring further investigation on behalf of participants. Laboratories generating Between Laboratory |z-scores| >3 include 221, 266, 287, 310, 319, 355, 509, 927. Laboratories generating Within Laboratory |z-scores| >3 include 215, 221, 232, 264, 266, 280, 310, 355, 927.

The overall dataset for chloride analysis shows a normal distribution, with the dominant methods used in this test including APHA Part 4500 – Cl^- B (Argentometric Method), Ion chromatography (in-house method), APHA Part 4110B (IC with Chemical Suppression of Eluent Conductivity), APHA Part 4500 – Cl^- E (Automated Ferricyanide Method), and FIA Lachat. There appears to be a high bias in Argentometric titrations with respect to the Ion Chromatography methods. Over-estimation of the concentration using the Argentometric method is most likely due to difficulty determining the titration endpoint with manual titration, whereas more consistent results are obtained with Potentiometric titration (APHA Part 4500 – Cl^- D).

Reported uncertainty of measurement values for chloride analysis are shown in the graph below. The majority of labs stated that their uncertainty of measurement was less than ±10 mg/L with no obvious trends emerging with respect to the uncertainty of different types of methods.

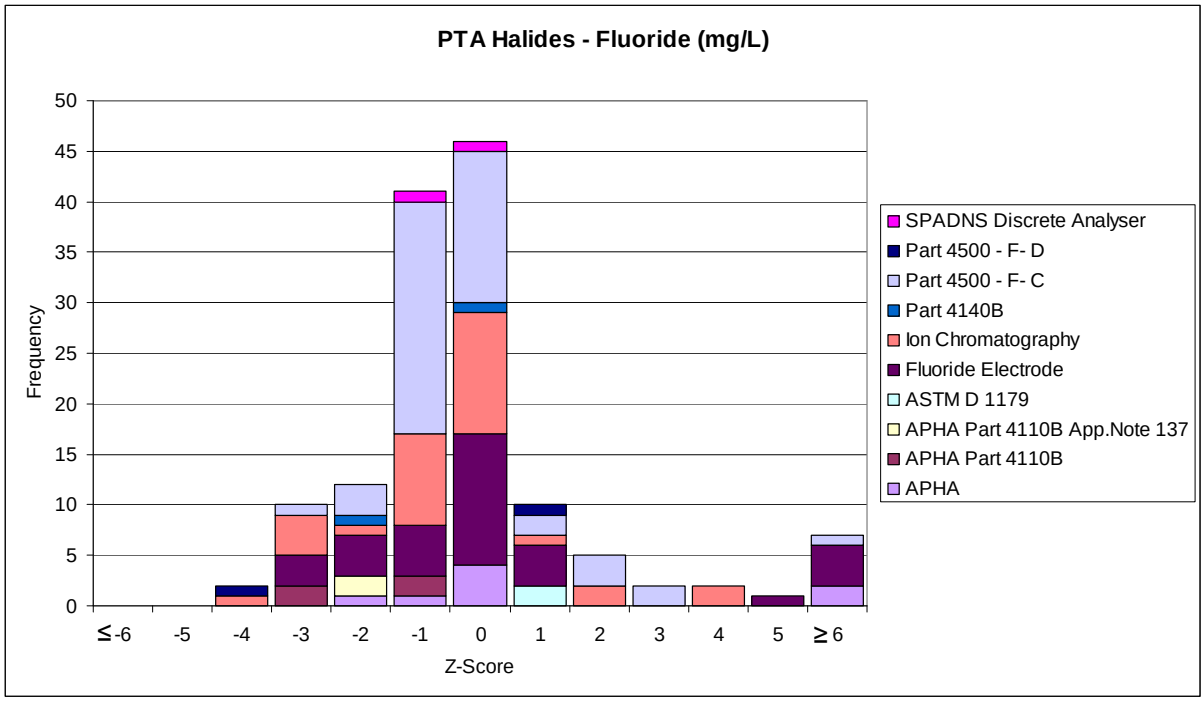


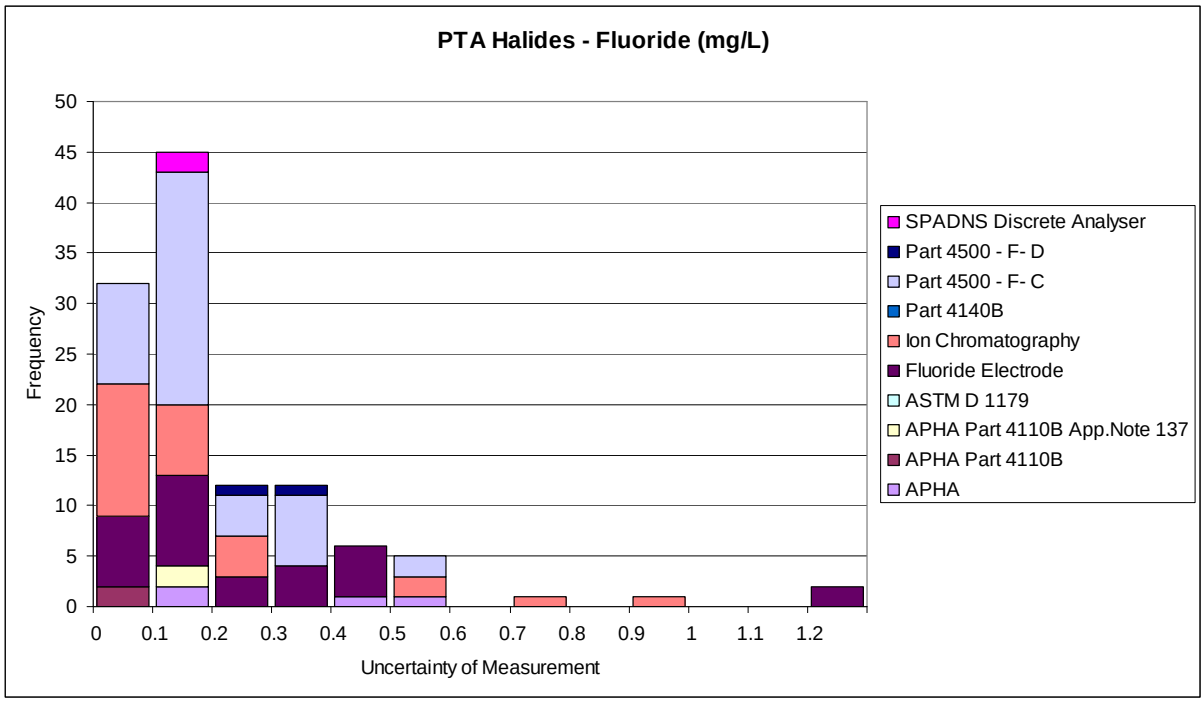


4.5.3 Fluoride

Out of 69 participants, 13 laboratories reported questionable results. Of these, laboratories 240, 249, 256, 296a, 302, 304, 509 have a Between Laboratory |z-score| >2 and <3, whilst laboratories 213, 257, 261, 264, 267, 934 have Within Laboratory |z-scores| >2 and <3. 13 laboratories reported outlier results (|z-score| >3), requiring further investigation on behalf of participants. Laboratories generating Between Laboratory |z-scores| >3 include 232, 243, 254, 262, 266, 270, 287, 294, 310. Laboratories generating Within Laboratory |z-scores| >3 include 232, 249, 254, 262, 266, 278, 310, 504, 514. Laboratories 254, 262, 266 reported results that were an order of magnitude higher than the sample medians, indicating they may have made dilution or calculation errors.

The most commonly used method for analysis of fluoride was APHA Part 4500 – F^- C (Ion Selective Electrode Method), followed by Fluoride electrode, Ion Chromatography, APHA Part 4110B (IC with Chemical Suppression of Eluent Conductivity), and ICPMS. There do not appear to be any method related trends within the fluoride analysis data set.



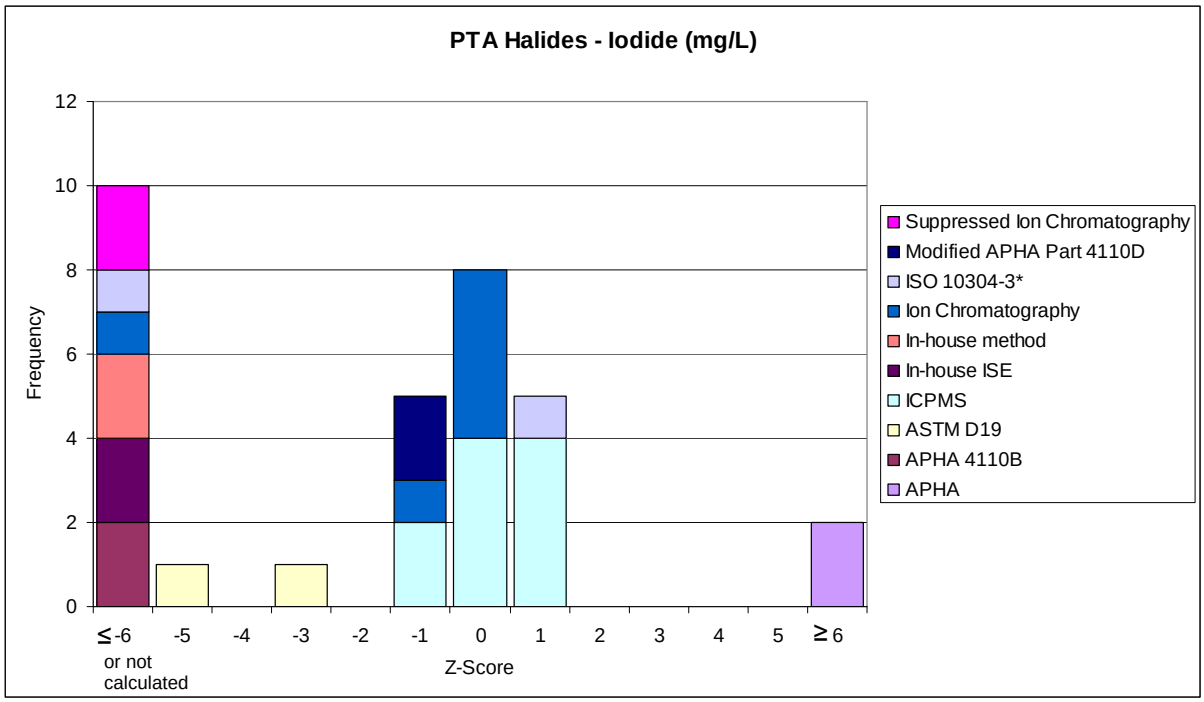


The majority of participants stated their measurement uncertainty as less than ± 0.5 mg/L. However, even after the uncertainty contribution of sample homogeneity and stability was removed, over 33% of participants varied from the median by more than 2x their stated uncertainty, again highlighting the difficulty of estimating the uncertainty of measurement for any given test.

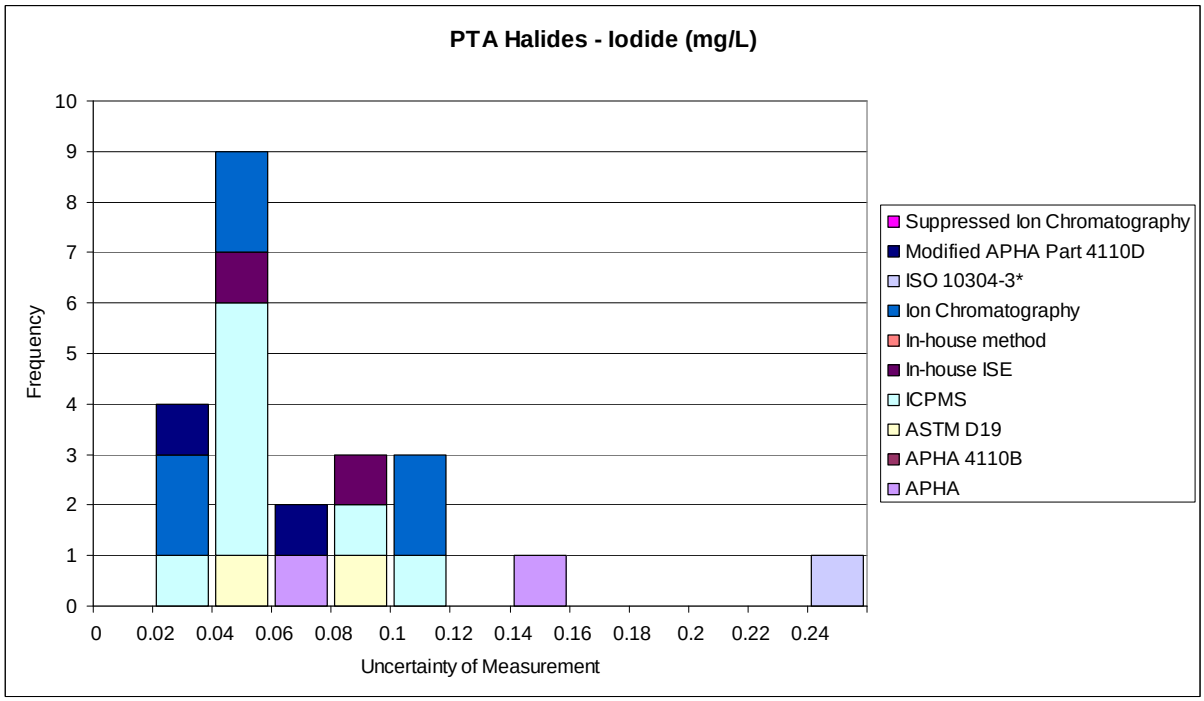
4.5.4 Iodide

Out of 16 participants, one laboratory reported questionable results. Laboratory 261 had Between and Within Laboratory |z-scores| >2 and <3. Three laboratories reported outlier results (|z-scores| >3), requiring further investigation on behalf of participants. Laboratories generating Between and Within Laboratory |z-scores| >3 include 208, 224, 266. Laboratory 264's reported results for Samples 1 and 2 lie more than 3 normalised IQRs below the median, and therefore are outlying results.

Of particular note were that several laboratories reported that sample concentrations were below their quantification limits for iodide (z-score ≤ -6). This is of particular interest as the predominant method used for analysis of iodide was ISO 10304-3, developed in 1997 for determination of dissolved anions by liquid chromatography. According to Jackson and Chassaniol (2002), with all the advances in instrumentation, ion chromatography should have method detection limits in the low µg/L range for most inorganic analytes under standard operating conditions [2]. Indicating that doping levels in the proficiency samples supplied in this round should have been well within limits of quantification.



The majority of laboratories stated that their uncertainty of measurement was less than ±0.1 mg/L with no obvious trends emerging with respect to the uncertainty of different types of methods.



4.5.5 From previous programs, some of the reasons reported in outlier investigations have included:

- Bromide: i) standard peaks not integrated correctly
  ii) baseline problems in an ion-chromatography method
  iii) iodide ion interference with a bromide ion-selective electrode method
- Chloride: i) calibration standards not bracketing sample
  ii) incorrect pH adjustment of sample in argentometric method
  iii) silver nitrate titrant strength too high in argentometric method
  iv) calculation error
  v) incorrect sample dilution for calibration range
- Fluoride i) fluoride sample ion electrode drift
  ii) incorrect sample volume
  iii) transcription error.

5. Outlier or Extreme Results

Laboratories reporting outlier **or extreme** results are listed in the following table:

Lab Code	Analysis							
	Bromide (Br^-)		Chloride (Cl^-)		Fluoride (F^-)		Iodide (I^-)	
	Between Lab	Within Lab	Between Lab	Within Lab	Between Lab	Within Lab	Between Lab	Within Lab
208							§	§
215				§				
221			§	§				
224							§	§
232				§	§	§		
243					§			
249						§		
254					§	§		
261								
262					§	§		
264		§		§			~~§~~	~~§~~
266	§	§	§	§	§	§	§	§
270					§			
278		§				§		
280				§				
287			§		§			
294	§				§			
310			§	§	§	§		
319			§					
320	§							
355			§	§				
504	§					§		
509			§					
510	§							
513		§						

5. Outlier or Extreme Results Cont.

Laboratories reporting outlier **or extreme** results are listed in the following table:

Lab Code	Analysis							
	Bromide (Br^-)		Chloride (Cl^-)		Fluoride (F^-)		Iodide (I^-)	
	Between Lab	Within Lab	Between Lab	Within Lab	Between Lab	Within Lab	Between Lab	Within Lab
514		***§***				***§***		
927			***§***	***§***				

[1] *A "**§**" indicates the occurrence of a z-score outlier result (i.e. those results for which |z-score|>3).*

[2] *"~~T~~" indicates that results were reported as "less than values" and are outlier results as they lie more than 3 normalised IQRs below the median.*

6. References

[1] *Guide to Proficiency Testing Australia*, 2008 (This document can be found on the PTA website, www.pta.asn.au)

[2] Jackson, P.E., and Chassaniol, K., 2002. *Advances in the determination of inorganic ions in potable waters by ion chromatography*. Journal of Environmental Monitoring, Vol. 4, pp. 10–15. Free access available from http://www.rsc.org/publishing/journals/EM/article.asp?doi=b106908j

[3] Eaton, A.D.; Clesceri, L.S.; Rice, E.W.; and Greenberg, A.E. (2005) *Standard methods for the examination of water & wastewater*. APHA, AWWA, WEF, American Public Health Association, Washington DC, USA.

APPENDIX A

Results & Data Analysis

Bromide (Br^-) Results

Samples 1 and 2

Bromide (Br^-)

Results by Laboratory Code

Lab Code	Sample 1 Result ± MU[1] (mg/L)	Sample 2 Result ± MU[1] (mg/L)	Between Laboratory z-score[2]	Within Laboratory z-score[2]	Method Code[3]
207	14.2 ± 0.71	10.2 ± 0.51	0.84	0.20	8
208	13.1 ± 0.9	9.3 ± 0.6	-0.93	-0.20	4
210	14.5 ± 0.8	10.4 ± 0.5	1.28	0.40	8
216	13.7 #	10.0 #	0.22	-0.40	8
218	14.0 ± 1.0	10.1 ± 0.7	0.57	0.00	5
219	13.7 ± 1.51	9.5 ± 1.05	-0.19	0.55	4
224	12.1 ± 1.9	8.0 ± 1.3	-2.96	0.40	8*
229	13.3 ± 0.1	10.1 ± 0.1	-0.04	-1.41	1
230	13.8 ± 2.1	9.8 ± 1.6	0.13	0.20	4
231	13.6 ± 0.7	9.5 ± 0.5	-0.31	0.40	8
240	13.6 #	10.1 #	0.22	-0.81	4
247	14.4 ± 2.2	9.8 ± 1.5	0.66	1.41	4
249	12.8 ± 0.64	9.8 ± 0.49	-0.75	-1.82	4
260a	15.1 ± 0.8	10.6 ± 0.5	1.99	1.21	4
261	13.7 ± 1.4	10.4 ± 1.1	0.57	-1.21	4
264	12.1 #	10.5 #	-0.75	-4.65 §	8
266	126.6 ± 4.2	89.9 ± 3	170.77 §	66.29 §	1
269	14.0 ± 0.6	10.2 ± 0.4	0.66	-0.20	8
270	13.9 ± 1.50	9.6 ± 0.99	0.04	0.81	4
278	11.6 ± 2.1	10.2 ± 1.9	-1.46	-5.05 §	2
294	11.6 ± 0.2	7.9 ± 0.1	-3.49 §	-0.40	4
296a	13.9 ± 0.5	9.9 ± 0.4	0.31	0.20	8
304	13.6 ± 2	9.7 ± 2.0	-0.13	0.00	8*
314	13.3 ± 1.33	9.7 ± 0.97	-0.40	-0.61	5
320	11.0 ± 1.0	8.1 ± 1.0	-3.85 §	-2.02	4
325	14.2 ± 0.5	10.2 ± 0.4	0.84	0.20	8
357	13.9 ± 0.38	9.3 ± 0.38	-0.22	1.41	4
504	9.3 #	5.5 #	-7.65 §	-0.20	6
510	20.5 ± 0.4	15.7 ± 0.3	11.28 §	1.82	8
513	12.1 ± 0.4	9.8 ± 0.3	-1.37	-3.23 §	8
514	12.5 #	10.6 #	-0.31	-4.04 §	8
927	14.2 ± 0.1	9.3 ± 0.1	0.04	2.02	4
No of Results:	32	32			
Median:	13.70	9.85			
Normalised IQR:	0.98	0.50			
Robust CV:	7.2%	5.1%			
Minimum:	9.3	5.5			
Maximum:	127	90			
Range:	117.3	84.4			

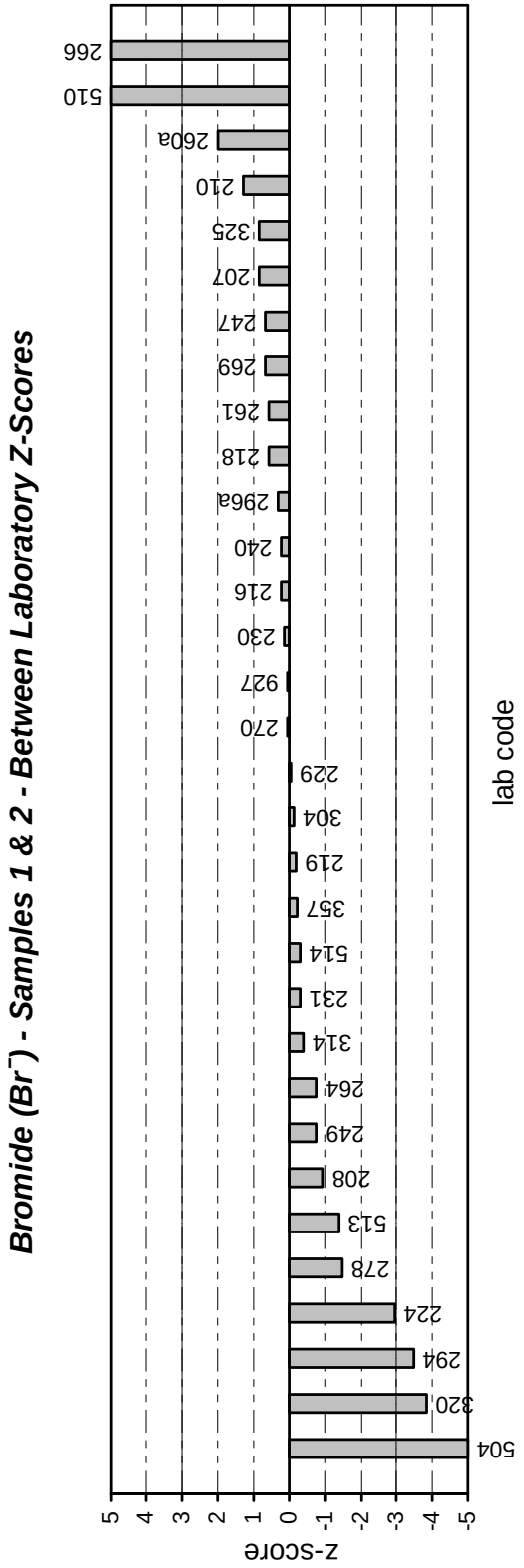
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

[2] **"§"**s denote outliers (i.e. those results for which |z-score| > 3), see Appendix D for paired sample z-score calculation parameters.

[3] Please refer to Appendix C (page C3) for method descriptions.

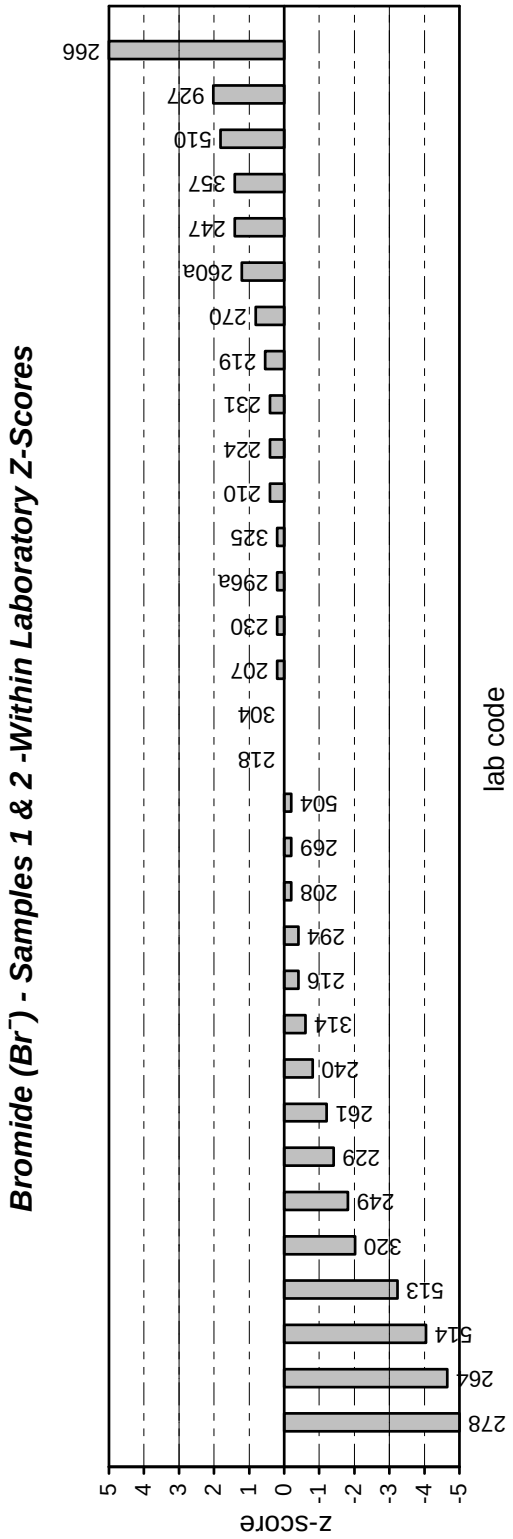
Bromide (Br^-)
Samples 1 & 2

Between Laboratory Ordered Z-Score Charts



Bromide (Br^-)
Samples 1 & 2

Within Laboratory Ordered Z-Score Charts



Bromide (Br^-) Samples 1 & 2

Youden Diagram

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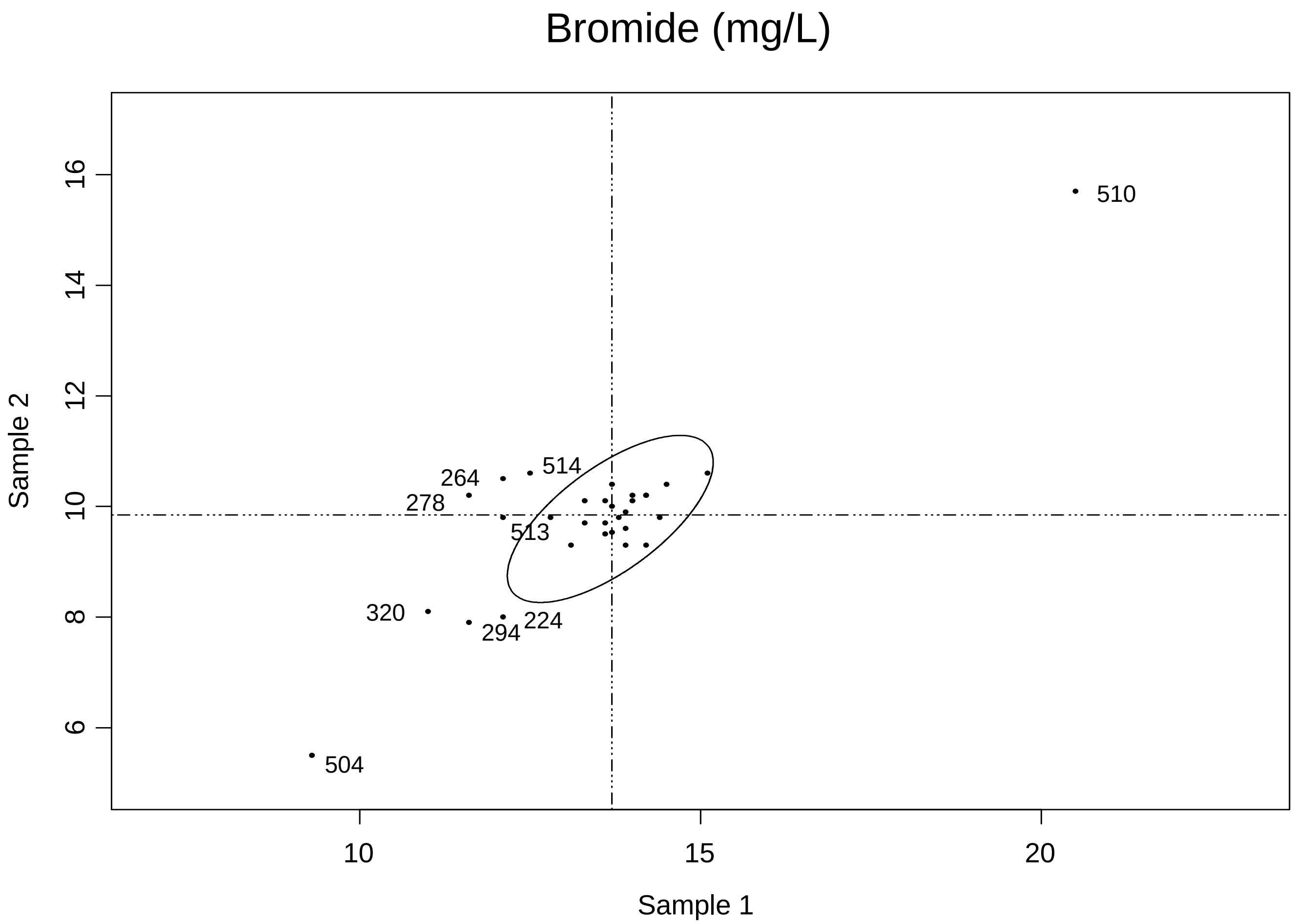

*Please note that extreme outliers are not shown in the Youden Diagram

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Chloride (Cl^-) Results

Samples 1 and 2

Chloride (Cl^-)

Results by Laboratory Code

Lab Code	Sample 1 Result ± MU[1] (mg/L)	Sample 2 Result ± MU[1] (mg/L)	Between Laboratory z-score[2]	Within Laboratory z-score[2]	Method Code[3]
201	79.1 ± 2.7	99.8 ± 2.7	-0.26	0.60	15
204	91.1 ± 4.37	100.0 ± 4.80	0.88	-2.94	13
205	81.0 ± 4.0	101.9 ± 5.0	0.11	0.66	21
207	79.1 ± 3.9	99.2 ± 4.9	-0.32	0.42	21
208	77.4 ± 5	90.3 ± 5	-1.31	-1.74	26
209	77.8 ± 1.6	93.2 ± 1.9	-1.00	-0.99	11
210	88 ± 10	105 ± 10	1.06	-0.51	13
213	90.1 ± 9.0	104.2 ± 10.4	1.18	-1.38	13
215	88.0 ± 19.2	123.0 ± 25.6	2.74	4.89 §	10
216	88.4 ± 26.8	105.5 ± 32.0	1.14	-0.48	13
218	81.6 ± 5.7	102.1 ± 7.1	0.19	0.54	15
219	80.6 ± 8.87	98.0 ± 10.8	-0.29	-0.39	14
221	111.5 ± 10.0	140.3 ± 10.0	6.57 §	3.03 §	22
224	95.9 ± 15	114.2 ± 18	2.66	-0.12	26
226	90.1 ± 10.5	101.6 ± 10.5	0.94	-2.16	13
228	77.6 ± 7	99.6 ± 9	-0.42	0.99	15
229	77.5 ± 0.5	102.3 ± 0.5	-0.18	1.83	9
230	79.8 ± 7.9	100.1 ± 9.9	-0.17	0.48	14
231	78.3 ± 6	99.5 ± 8	-0.37	0.75	15
232	82.6 ± 2.7	78.4 ± 2.6	-1.94	-6.86 §	10
235	88.3 ± 7.1	105 ± 8.4	1.09	-0.60	12
240	76.2 #	102.4 #	-0.29	2.25	14
241	86.2 ± 1	105.4 ± 1	0.93	0.15	10
242	86.4 #	103.8 #	0.80	-0.39	12
243	84.5 #	100.5 #	0.31	-0.81	12
247	83.2 ± 4.4	105.3 ± 5.6	0.64	1.02	21
249	83.5 ± 11.7	107.0 ± 15.0	0.82	1.44	14
251	82.3 ± 5.8	101.8 ± 6.9	0.22	0.24	10
252	77.0 ± 3.9	93.9 ± 4.7	-1.01	-0.54	26
254	75.3 ± 6.0	102.5 ± 6.0	-0.37	2.55	23
256	81.8 #	97.0 #	-0.27	-1.05	23
257	76 ± 5	101 ± 6	-0.44	1.89	10
259	84.5 ± 4	103.0 ± 4	0.54	-0.06	10
260a	77.3 ± 3	96.8 ± 3	-0.71	0.24	14
261	77.4 ± 5.4	104.9 ± 7.8	0.06	2.64	14
264	64.9 #	100.3 #	-1.55	5.01 §	26
265	86.2 ± 5.0	105.3 ± 5	0.92	0.12	23
266	831 ± 26.0	1049 ± 33	159.10 §	59.74 §	9
267	87.7 ± 7.9	104.0 ± 9.4	0.94	-0.72	22
268	87.2 ± 4.36	104.5 ± 5.22	0.94	-0.42	22
269	78.2 ± 1.6	96.9 ± 2.2	-0.62	0.00	21
270	81.8 ± 8.0	99.9 ± 10.2	0.00	-0.18	14

Chloride (Cl^-) Cont.

Results by Laboratory Code

Lab Code	Sample 1 Result ± MU[1] (mg/L)	Sample 2 Result ± MU[1] (mg/L)	Between Laboratory z-score[2]	Within Laboratory z-score[2]	Method Code[3]
278	81.0 ± 16.0	108.0 ± 17.0	0.68	2.49	13
280	85.7 ± 19.6	91.5 ± 20.9	-0.42	-3.87 §	10
281	80.6 ± 1.9	98.6 ± 2.3	-0.23	-0.21	14
287	96.9 ± 9.7	118.8 ± 12	3.19 §	0.96	26
292	75.9 ± 17.1	97.3 ± 21.9	-0.80	0.81	21
294	76.4 ± 0.3	96.2 ± 0.6	-0.85	0.33	14
296a	80.4 ± 4.0	100.0 ± 5.0	-0.12	0.27	21
299	85.1 ± 5.9	102.8 ± 5.9	0.58	-0.30	10
302	80.1 ± 18	96.0 ± 21	-0.52	-0.84	23
304	80.8 ± 10	98.7 ± 10	-0.21	-0.24	21
309	86.4 ± 2.6	104.9 ± 3.1	0.90	-0.06	11
310	802.4 #	794.0 #	132.53 §	-8.12 §	22
314	84.9 ± 8.49	96.7 ± 9.67	-0.01	-2.07	26
319	100.0 ± 5.2	125.0 ± 6.5	4.06 §	1.89	10
325	86.6 ± 4.3	105 ± 5.3	0.93	-0.09	22
330	82.2 ± 1	102.8 ± 1	0.31	0.57	26
334	89.9 ± 3.1	106.2 ± 3.6	1.35	-0.72	10
339	86.7 ± 1.7	101.4 ± 2.0	0.60	-1.20	9,14
343	91.2 #	112.0 #	2.01	0.63	10
344	78.103 #	93.738 #	-0.92	-0.92	9
355	89.5 ± 3.6	4.4 ± 3.6	-8.23 §	-31.12 §	12
357	79.1 ± 1.74	98.1 ± 1.67	-0.42	0.09	14
502	87.9 ± 9	104.9 ± 10	1.04	-0.51	10
504	72.0 #	89.2 #	-1.92	-0.45	16
509	102.8 #	129.4 #	4.73 §	2.37	10
510	74.6 ± 5.7	94.8 ± 7.2	-1.15	0.45	26
513	69.2 ± 2.1	97.9 ± 2.9	-1.37	3.00	21
514	75.6 #	93.9 #	-1.14	-0.12	21
927	62.7 ± 0.1	67.1 ± 0.1	-4.86 §	-4.29 §	14
934	78.7 #	98.5 #	-0.42	0.33	21
943	79.6 ± 5.7	100.4 ± 5.4	-0.16	0.63	21

No of Results:	73	73
Median:	81.80	101.40
Normalised IQR:	7.11	5.26
Robust CV:	8.7%	5.2%
Minimum:	62.7	4.4
Maximum:	831	1049
Range:	768.3	1044.6

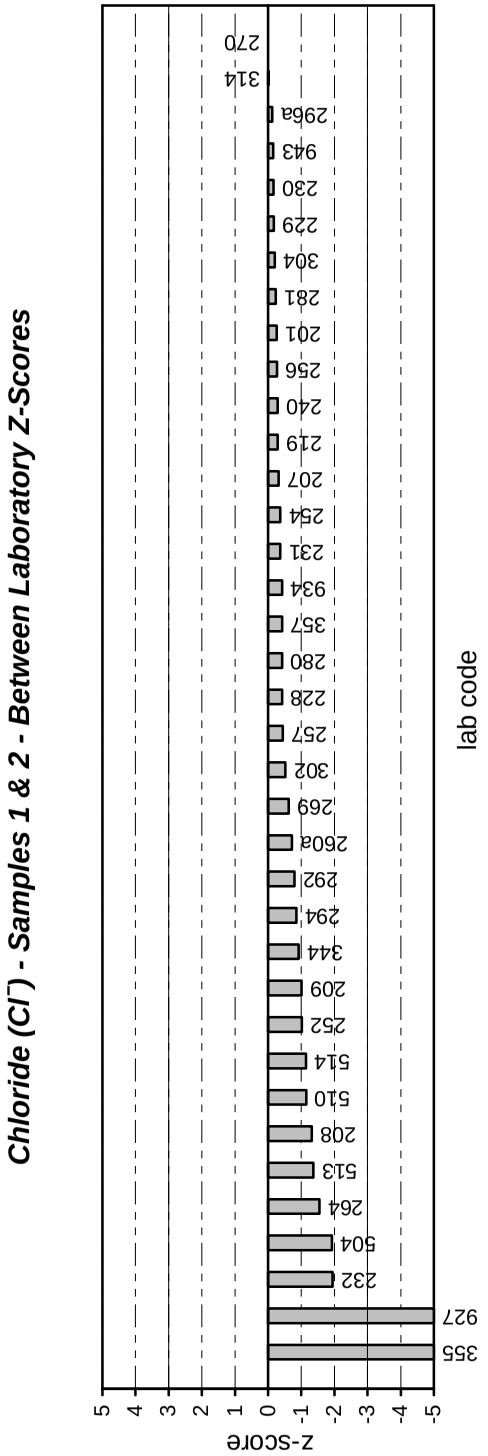
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

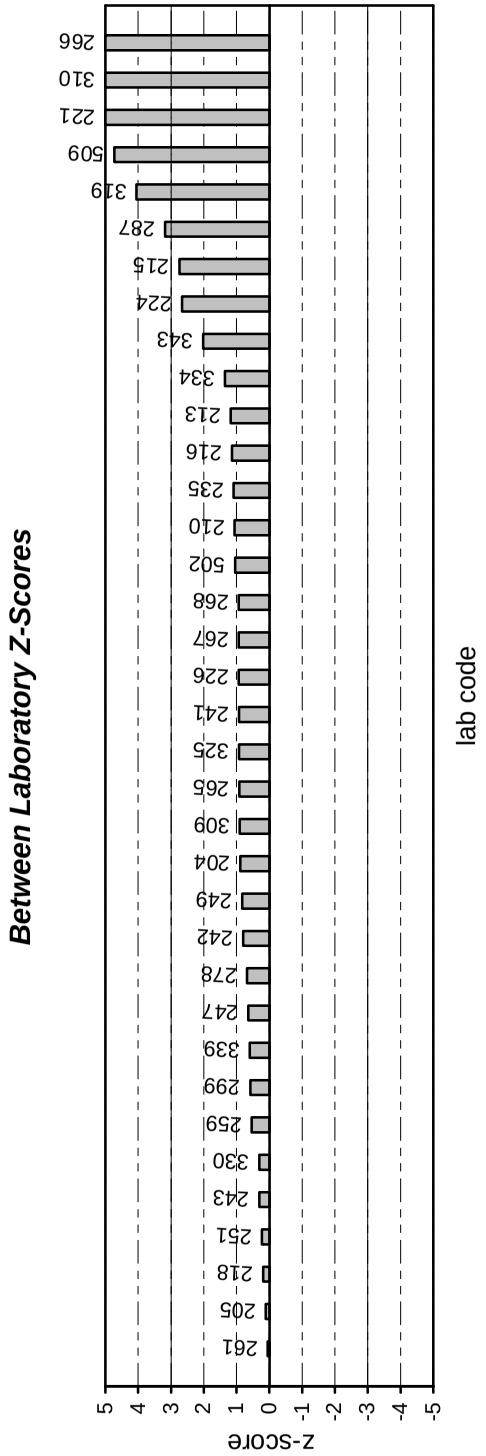
[2] **"§"**s denote outliers (i.e. those results for which |z-score| > 3), see Appendix D for paired sample z-score calculation parameters.

[3] Please refer to Appendix C (page C3) for method descriptions.

Chloride (Cl⁻) - Samples 1 & 2

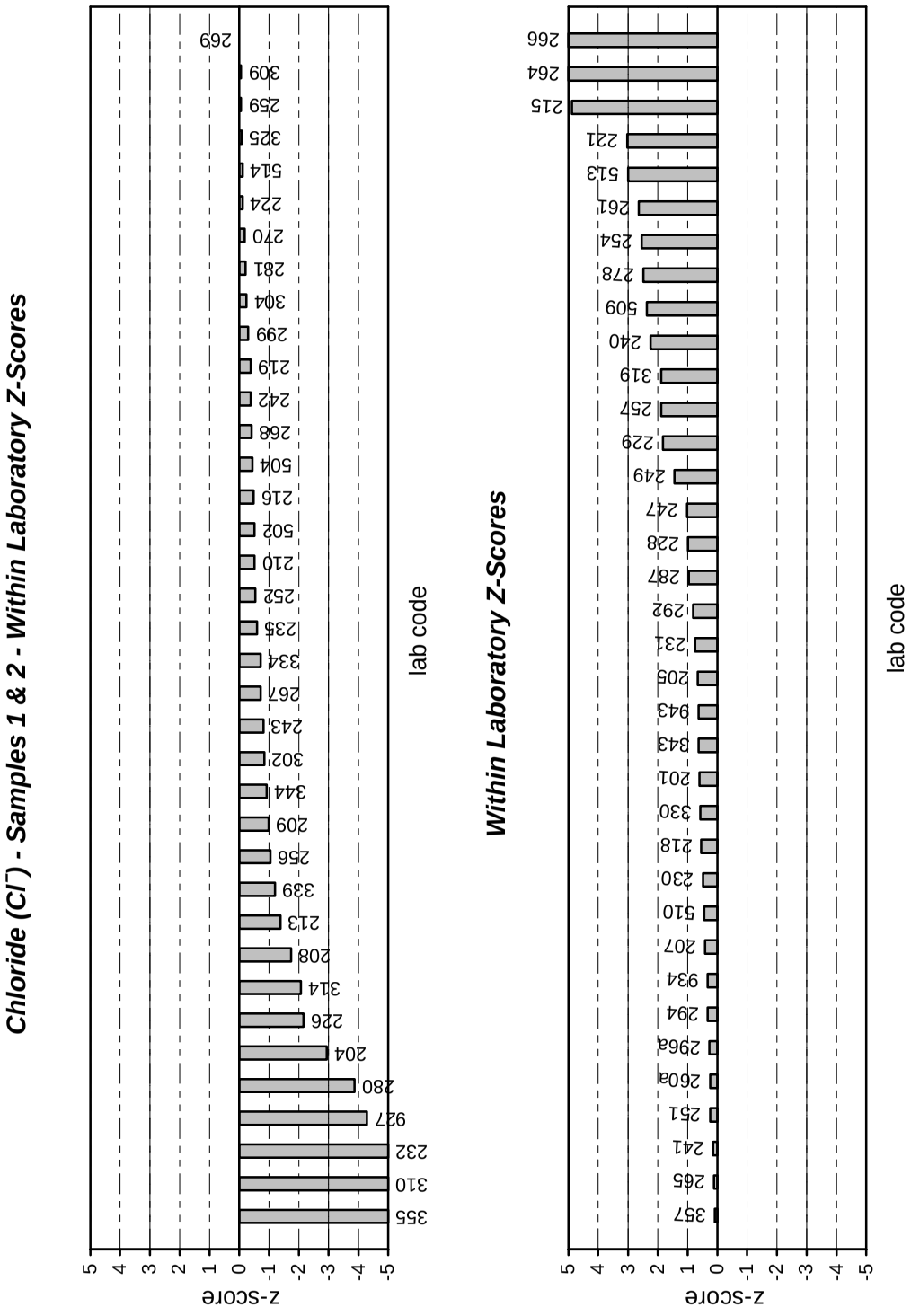
Between Laboratory Ordered Z-Score Charts





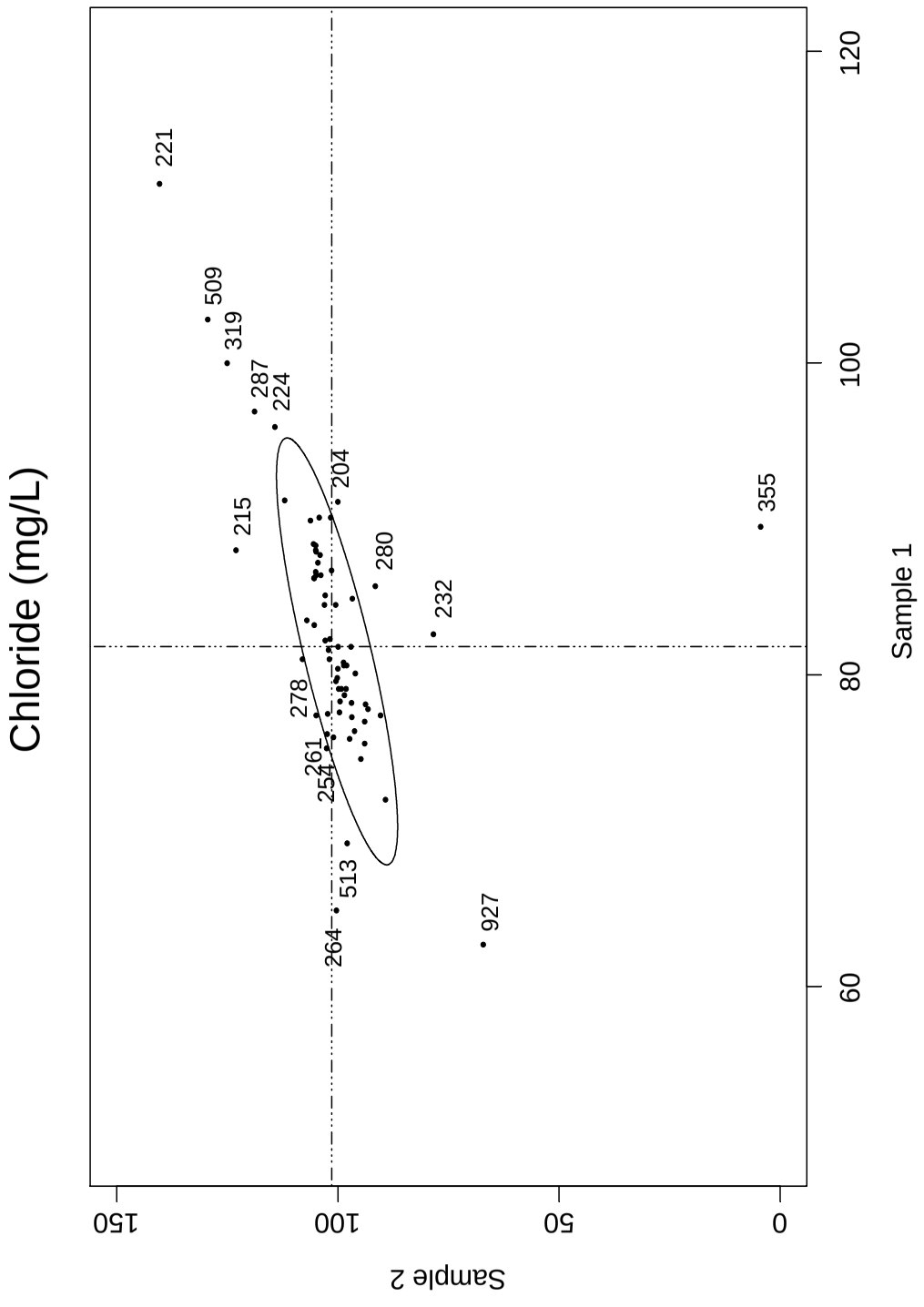
Chloride (Cl⁻) - Samples 1 & 2

Within Laboratory Ordered Z-Score Charts



Chloride (Cl^-) Samples 1 & 2

Youden Diagram



*Please note that extreme outliers are not shown in the Youden Diagram

Fluoride (F^-) Results

Samples 1 and 2

Fluoride (F^-)

Results by Laboratory Code

Lab Code	Sample 1 Result ± MU[1] (mg/L)	Sample 2 Result ± MU[1] (mg/L)	Between Laboratory z-score[1]	Within Laboratory z-score[1]	Method Code[3]
204	1.50 ± 0.104	1.89 ± 0.130	-0.10	-1.35	39
205	1.56 ± 0.078	2.13 ± 0.106	1.35	0.86	36
207	1.49 ± 0.075	1.99 ± 0.10	0.34	0.00	37
208	1.57 ± 0.3	1.98 ± 0.4	0.67	-1.10	36
209	1.49 ± 0.07	1.99 ± 0.10	0.34	0.00	29
210	1.4 ± 0.2	1.9 ± 0.2	-0.53	0.00	29
213	1.44 ± 0.14	1.72 ± 0.17	-1.20	-2.70	36
215	1.41 ± 0.37	1.95 ± 0.51	-0.24	0.49	29
216	1.44 ± 0.38	1.95 ± 0.51	-0.10	0.12	29
218	1.44 ± 0.10	1.92 ± 0.13	-0.24	-0.25	27, 37
219	1.48 ± 0.16	2.04 ± 0.22	0.53	0.74	37
224	1.41 ± 0.23	1.79 ± 0.36	-1.01	-1.47	29
226	1.57 ± 0.04	2.09 ± 0.05	1.20	0.25	29
229	1.48 ± 0.1	2.06 ± 0.1	0.63	0.98	27
230	1.54 ± 0.25	2.02 ± 0.32	0.72	-0.25	36
231	1.47 ± 0.12	1.97 ± 0.16	0.14	0.00	29
232	2.15 ± 0.10	2.26 ± 0.11	4.82 §	-4.78 §	29
235	1.45 ± 0.11	1.91 ± 0.14	-0.24	-0.49	29
237	1.48 ± 0.09	2.02 ± 0.12	0.43	0.49	29
240	1.20 #	1.66 #	-2.65	-0.49	40
241	1.36 ± 0.1	1.94 ± 0.1	-0.53	0.98	29
243	1.75 #	2.30 #	3.08 §	0.61	29
247	1.45 ± 0.09	1.89 ± 0.12	-0.34	-0.74	37
249	1.59 ± 0.16	2.34 ± 0.23	2.51	3.07 §	37
252	1.56 ± 0.09	2.08 ± 0.12	1.11	0.25	29
254	16.00 ± 2.50	22.00 ± 2.50	166.65 §	67.45 §	36
256	1.28 ± 0.15	1.67 ± 0.2	-2.22	-1.35	36
257	1.38 ± 0.05	2.08 ± 0.08	0.24	2.45	29
260a	1.52 ± 0.2	2.04 ± 0.2	0.72	0.25	37
260b	1.48 ± 0.05	1.96 ± 0.05	0.14	-0.25	36
261	1.41 ± 0.14	2.12 ± 0.19	0.58	2.58	29
262	15.22 #	20.48 #	155.57 §	58.37 §	36
264	1.29 #	2.01 #	-0.53	2.70	27
265	1.35 ± 0.1	1.81 ± 0.15	-1.20	-0.49	36
266	14.52 ± 0.44	19.54 ± 0.59	147.67 §	55.43 §	27
267	1.52 ± 0.12	1.84 ± 0.15	-0.24	-2.21	36
269	1.50 ± 0.06	1.98 ± 0.04	0.34	-0.25	37
270	1.99 ± 0.71	2.62 ± 0.94	5.78 §	1.59	37
275	1.50 ± 0.05	2.01 ± 0.06	0.48	0.12	36
278	1.60 ± 0.33	1.40 ± 0.28	-1.98	-8.58 §	30
280	1.70 ± 0.32	2.07 ± 0.39	1.73	-1.59	29

Fluoride (F^-) Cont.

Results by Laboratory Code

Lab Code	Sample 1 Result ± MU[1] (mg/L)	Sample 2 Result ± MU[1] (mg/L)	Between Laboratory z-score[1]	Within Laboratory z-score[1]	Method Code[3]
281	1.43 ± 0.03	1.91 ± 0.04	-0.34	-0.25	40
287	1.90 ± 0.19	2.41 ± 0.24	4.34 §	0.12	29
292	1.46 ± 0.31	1.98 ± 0.42	0.14	0.25	36
294	1.14 ± 0.02	1.57 ± 0.03	-3.37 §	-0.86	37
296a	1.23 ± 0.09	1.63 ± 0.12	-2.65	-1.23	37
296b	1.40 ± 0.07	1.90 ± 0.09	-0.53	0.00	36
302	1.18 ± 0.3	1.67 ± 0.4	-2.70	-0.12	36
304	1.8 ± 0.5	2.2 ± 0.5	2.84	-1.23	37*
309	1.46 ± 0.09	1.95 ± 0.12	0.00	-0.12	29
310	2.14 #	2.14 #	4.19 §	-6.13 §	36
314	1.48 ± 0.15	1.91 ± 0.19	-0.10	-0.86	29
315	1.53 ± 0.4	2.05 ± 0.4	0.82	0.25	36
325	1.2 ± 0.1	1.8 ± 0.1	-1.98	1.23	29
330	1.40 ± 0.1	1.90 ± 0.1	-0.53	0.00	27,29
334	1.54 ± 0.10	2.09 ± 0.13	1.06	0.61	29
343	1.45 #	1.91 #	-0.24	-0.49	29
344	1.461 #	1.99 #	0.20	0.36	27*
355	1.48 ± 0.02	1.92 ± 0.02	-0.05	-0.74	29
357	1.45 ± 0.07	1.91 ± 0.06	-0.24	-0.49	37
359	1.60 ± 0.16	2.12 ± 0.21	1.49	0.25	36
502	1.37 ± 0.30	1.83 ± 0.30	-1.01	-0.49	29
504	1.51 #	1.72 #	-0.87	-3.56 §	33
509	1.70 #	2.20 #	2.36	0.00	34
510	1.34 ± 0.10	1.73 ± 0.12	-1.64	-1.35	40
513	1.32 ± 0.04	1.95 ± 0.06	-0.67	1.59	37
514	1.56 #	1.67 #	-0.87	-4.78 §	37
927	1.49 ± 0.01	1.87 ± 0.01	-0.24	-1.47	37
934	1.53 #	1.83 #	-0.24	-2.45	37
No of Results:	69	69			
Median:	1.48	1.96			
Normalised IQR:	0.11	0.14			
Robust CV:	7.5%	7.2%			
Minimum:	1.1	1.4			
Maximum:	16	22			
Range:	14.86	20.6			

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

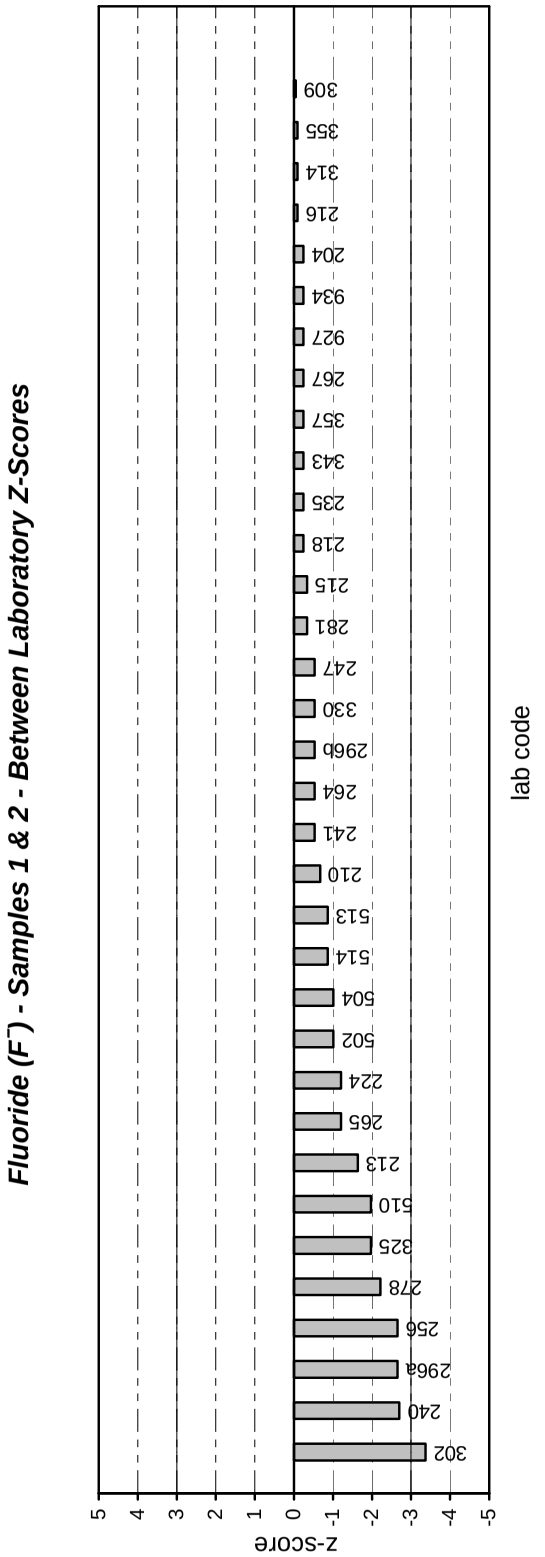
[2] "**§**"s denote outliers (i.e. those results for which |*z-score*| > 3), see Appendix D for paired sample z-score calculation parameters.

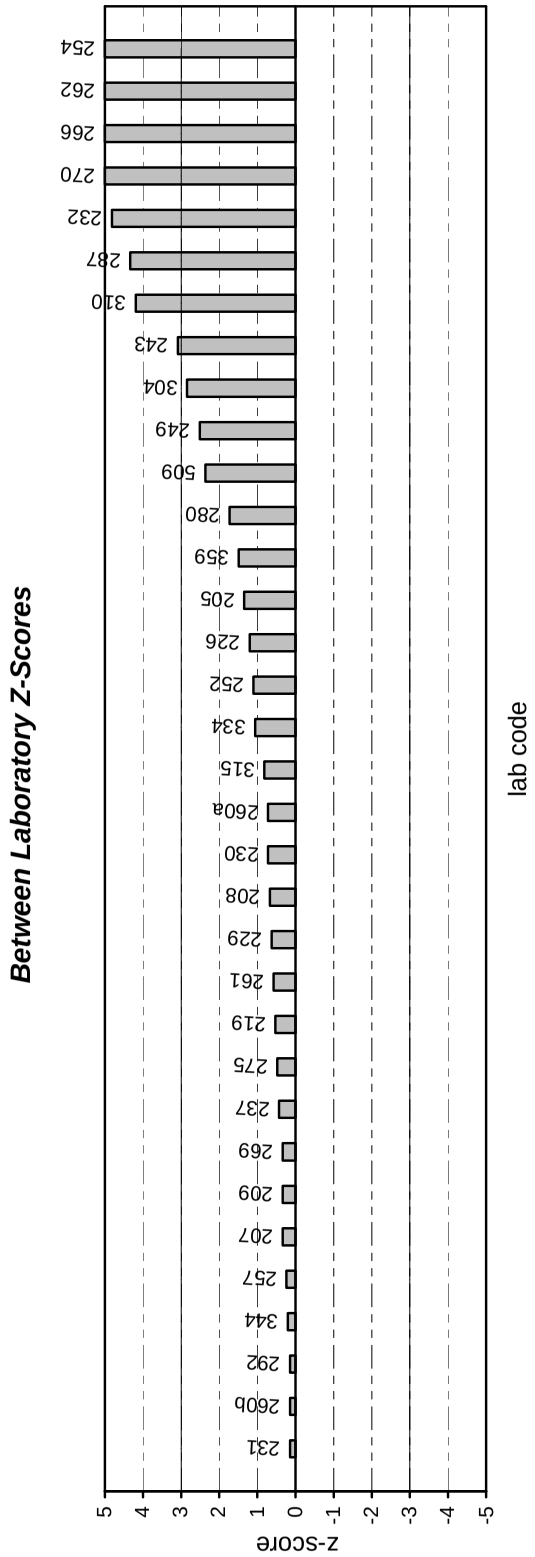
[3] Please refer to Appendix C (page C3) for method descriptions.

[4] "*****" Indicates that method code has been adjusted to accurately reflect method code descriptions on page C3.

Fluoride (F^-) - Samples 1 & 2

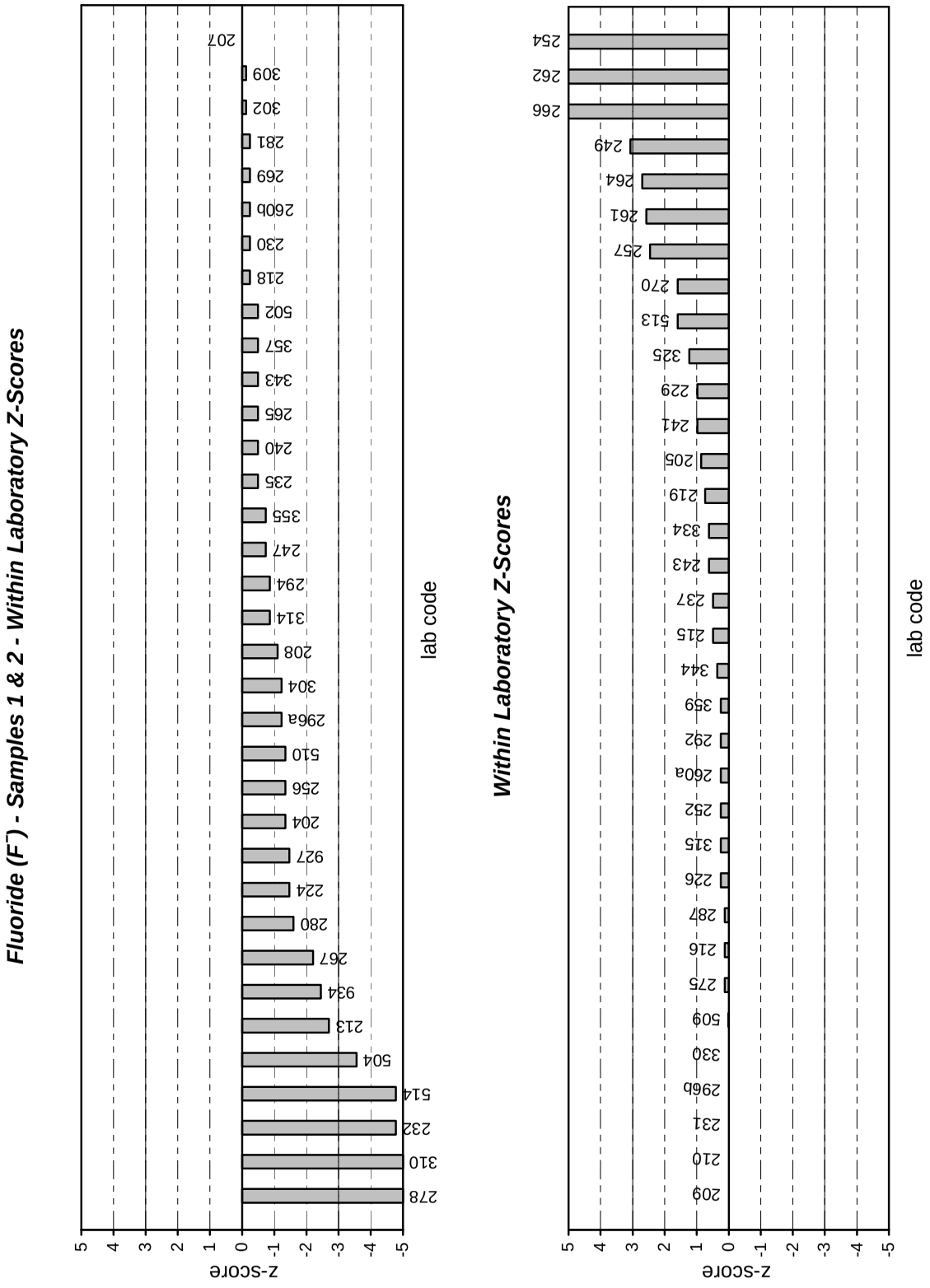
Between Laboratory Ordered Z-Score Charts





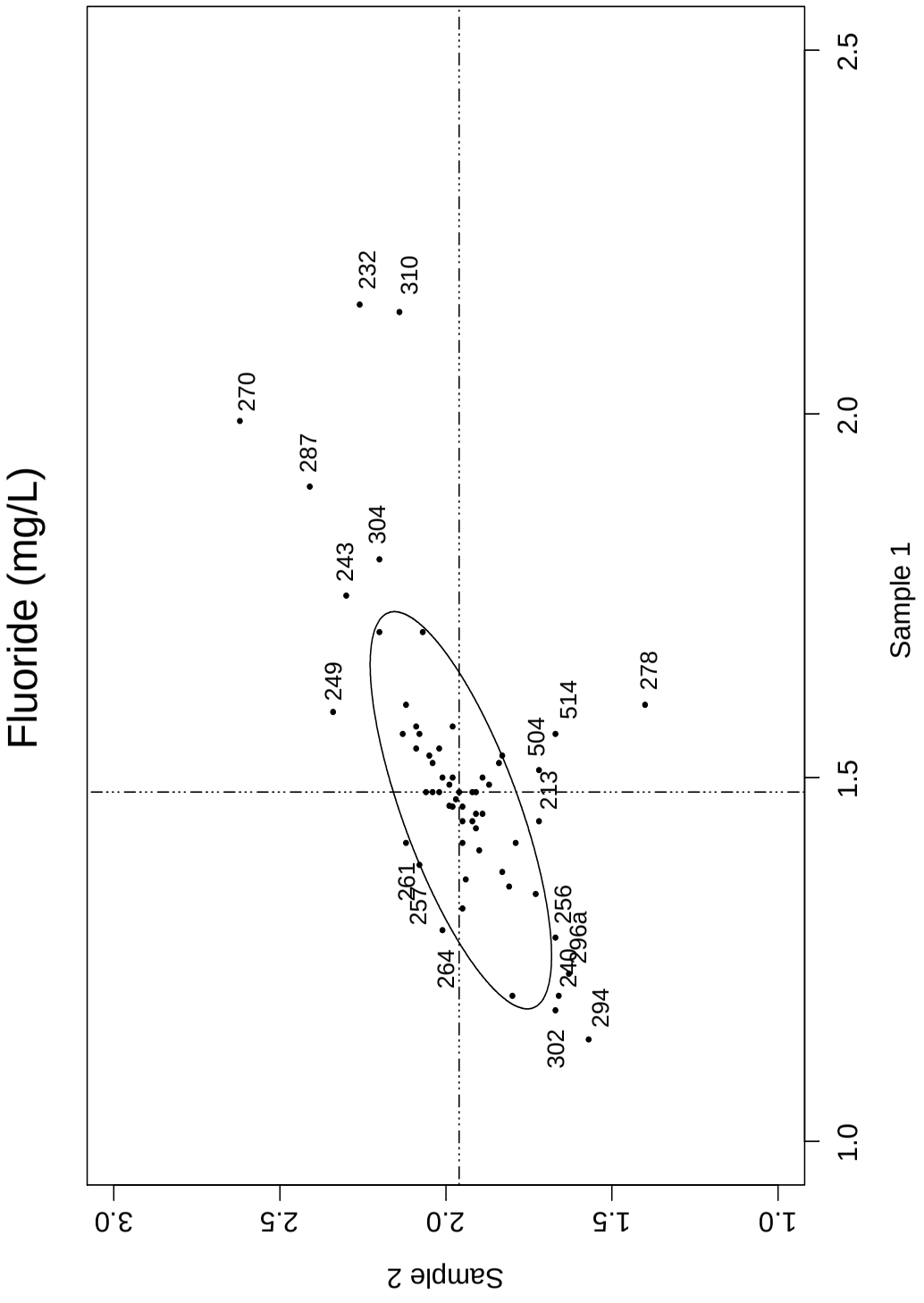
Fluoride (F^-) - Samples 1 & 2

Within Laboratory Ordered Z-Score Charts



Fluoride (F^-) Samples 1 & 2

Youden Diagram



*Please note that extreme outliers are not shown in the Youden Diagram

Iodide (I^-) Results

Samples 1 and 2

Iodide (I^-)

Results by Laboratory Code

Lab Code	Sample 1 Result ± MU[1] (mg/L)	Sample 2 Result ± MU[1] (mg/L)	Between Laboratory z-score[2]	Within Laboratory z-score[2]	Method Code[3]
208	0.11 ± 0.02	0.49 ± 0.10	-5.60 §	-16.09 §	46
210	1.02 ± 0.05	0.52 ± 0.03	0.74	0.28	46*
216	1.05 #	0.49 #	0.74	1.40	46
218	0.95 ± 0.08	0.47 ± 0.04	-0.07	-0.09	46
219	0.94 ± 0.10	0.48 ± 0.05	-0.07	-0.47	46
224	0.50 ± 0.08	0.23 ± 0.04	-4.72 §	-4.00 §	46
231	0.95 ± 0.07	0.46 ± 0.03	-0.13	0.09	46
240	<1 #	<1 #	-	-	46
261	0.75 ± 0.09	0.38 ± 0.04	-2.02	-2.14	46
264	<0.01 #	<0.01 #	- Ŧ	- Ŧ	46
266	2.71 ± 0.15	1.38 ± 0.07	17.94 §	15.72 §	41
269	0.98 ± 0.04	0.48 ± 0.02	0.20	0.28	46
294	<1 #	<1 #	-	-	46
304	1.10 ± 1.00	<1 #	-	-	46*
320	0.96 ± 0.10	0.48 ± 0.05	0.07	-0.09	46
325	1.06 ± 0.05	0.52 ± 0.05	1.01	1.02	46
No of Results:	16	16			
Median:	0.96	0.48			
Normalised IQR:	0.08	0.02			
Robust CV:	8.5%	4.6%			
Minimum:	0.11	0.23			
Maximum:	2.71	1.38			
Range:	2.6	1.15			

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

[2] "**§**"s denote outliers (i.e. those results for which $|z\text{-score}| > 3$), see Appendix D for paired sample z-score calculation parameters. Robust z-scores are not calculated when results are reported as less than (<)

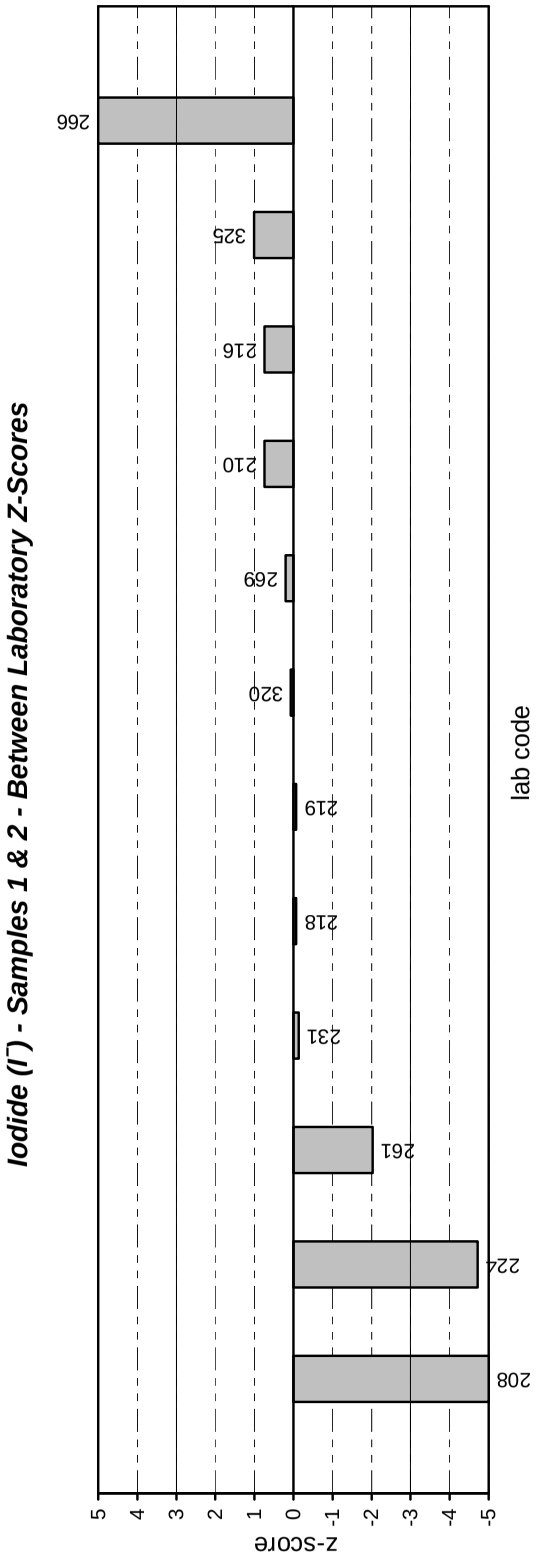
[3] Please refer to Appendix C (page C3) for method code descriptions.

[4] "**Ŧ**" indicates that results were reported as "less than values" and are outlier results as they lie more than 3 normalised IQRs below the median.

[5] "*" Indicates that method code has been adjusted to accurately reflect method code descriptions on page C3.

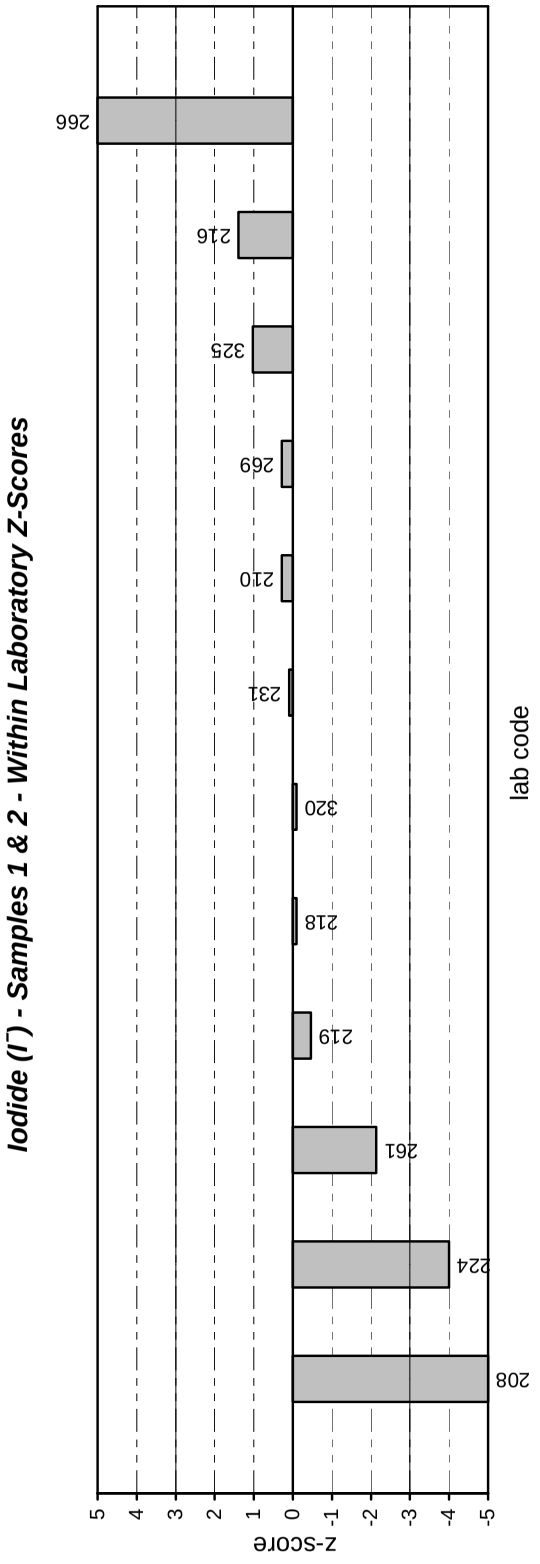
Iodide (I^-) - Samples 1 & 2

Between Laboratory Ordered Z-Score Chart



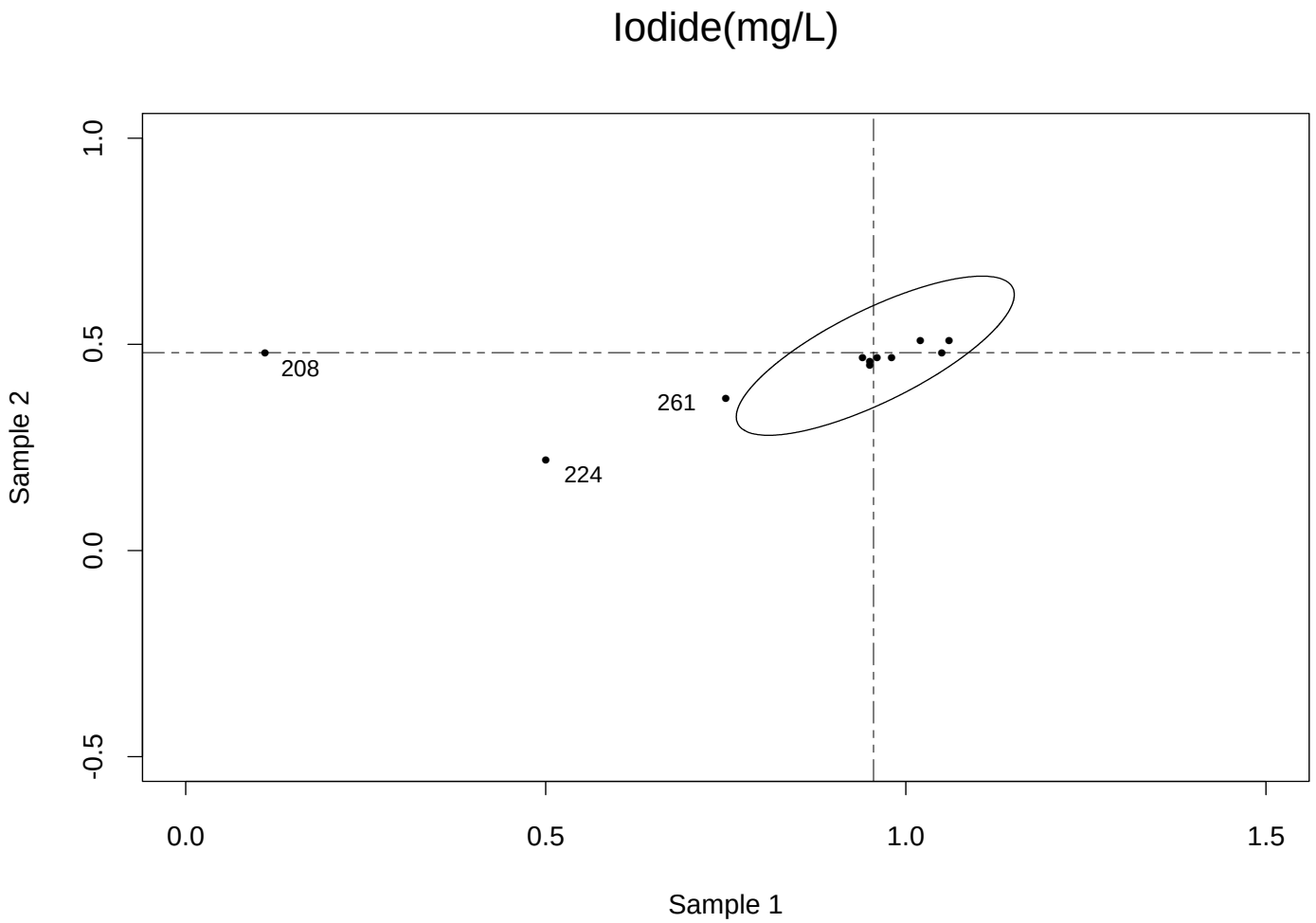
Iodide (I^-) - Samples 1 & 2

Within Laboratory Ordered Z-Score Chart



Iodide (I^-) Samples 1 & 2

Youden Diagram



*Please note that extreme outliers are not shown in the Youden Diagram

APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing

Samples for this program were obtained from AsureQuality Limited. A random selection of 13 samples were chosen from Sample 1 and Sample 2. Ten of each sample were stored frozen, and 3 of each were subjected to 35ºC for 3 days for an accelerated ageing stability trial. All stability samples showed no increased variability when compared to frozen samples. Based on the assumption that the rate of ageing doubles with every 7ºC elevated temperature, these samples were assumed stable for >96 days from the date of manufacture ($3days*2^{(35/7)}$).

On 25 June 2008, a number of selected samples were analysed by Hill Laboratories in duplicate for homogeneity and stability. From statistical analyses based on the results of this testing it was considered that all samples were sufficiently homogenous and stable, so that any results later identified as outliers should not be attributed to any significant sample variability.

Sample 1

	Total Iodine		Bromide		Fluoride		Chloride	
Bottle #	Rep1	Rep2	Rep1	Rep2	Rep1	Rep2	Rep1	Rep2
H1	0.901	–	12.6	–	1.58	–	82.6	–
H2	0.884	0.859	14.0	14.2	1.44	1.65	79.2	79.8
H3	0.861	0.908	14.0	14.5	1.48	1.62	79.0	79.0
H4	0.887	0.848	14.1	14.4	1.48	1.65	78.9	79.9
H5	0.897	0.865	14.0	14.5	1.51	1.66	79.1	80.5
H6	0.901	0.843	14.0	14.5	1.51	1.69	79.2	80.4
H7	0.878	0.855	14.2	12.2	1.51	1.69	79.5	81.0
H8	0.870	0.888	14.1	14.5	1.53	1.67	80.0	80.4
H9	0.868	0.852	14.0	14.5	1.52	1.61	79.2	77.8
H10	0.886	0.849	14.7	14.5	1.53	1.55	79.5	75.9
S1	0.896	0.854	14.5	14.5	1.50	1.66	79.6	80.5
S2	0.901	0.849	14.7	14.5	1.53	1.63	79.5	78.3
S3	0.890	0.845	14.0	14.6	1.52	1.67	79.6	80.6
RSD	1.52%	2.26%	3.66%	4.64%	2.19%	2.38%	1.19%	1.89%

Note: H1 not tested under repeatability conditions.
"–" indicates "insufficient sample to complete testing".

Sample 2

	Total Iodine		Bromide		Fluoride		Chloride	
Bottle #	Rep1	Rep2	Rep1	Rep2	Rep1	Rep2	Rep1	Rep2
H1	0.432	0.472	8.8	10.3	2.20	2.20	105	106
H2	0.412	0.431	10.2	10.3	1.80	2.22	99.1	102
H3	0.437	0.421	9.3	10.3	1.91	2.22	99.5	101
H4	0.442	0.422	9.3	10.3	1.93	2.24	101	100
H5	0.448	0.418	9.4	10.3	1.94	2.20	102	101
H6	0.436	0.422	9.4	10.3	1.94	2.21	101	100
H7	0.443	0.418	9.5	10.3	1.95	2.21	102	101
H8	0.431	0.418	8.9	10.3	1.95	2.20	103	101
H9	0.434	0.423	9.4	10.3	1.95	2.21	102	101
H10	0.449	0.422	9.4	10.3	1.97	2.25	112	100
S1	0.438	0.419	9.6	10.3	1.96	2.21	102	101
S2	0.428	0.445	9.5	10.3	1.93	2.24	103	102
S3	0.441	0.421	9.5	10.4	1.94	2.27	103	102
RSD	2.21%	3.60%	3.50%	0.27%	4.39%	0.99%	3.12%	1.54%

Note: H1 not tested under repeatability conditions.

APPENDIX C

Documentation

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS SUB-PROGRAM 109 **JULY 2008**

BROMIDE, CHLORIDE, FLUORIDE, IODIDE

INSTRUCTIONS TO PARTICIPANTS

Participants are requested to note the following before commencing the analysis of the samples.

1. Samples

i) Two sealed samples (10x concentrate) of approximately 20mL each in HDPE vials.

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

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

2. Sample Preparation for each of Samples 1 and 2

i) Adjust vial temperature to 20º C.

ii) Record sample ID number.

iii) Laboratories are instructed to remove 10.0mL from Sample 1 using volumetric pipette and transfer the aliquot into a volumetric flask.

iv) Make the 10.0mL aliquot up to 100mL using reagent grade water, considering volumes required for all tests.

v) Stopper and mix by inversion.

vi) Repeat steps **i)** through to **v)** using Sample 2.

3. Tests Requested

For the samples prepared from diluted Samples 1 and 2:

- **Bromide (Br^-)**
- **Chloride (Cl^-)**
- **Fluoride (F^-)**
- **Iodide (I^-)**

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 concentrates, prepared samples, other chemicals required for the analysis, and materials for disposal.

iii) Use of safety glasses, gloves, and fume hoods, where appropriate during the determinations, is recommended.

5. Reporting

(a) Report results for each diluted sample.

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

(c) For statistical purposes report results:

i) Bromide and Chloride	report to one decimal place e.g. 12.1 mg/L
ii) Fluoride and Iodide	report to two decimal places e.g. 1.55 mg/L

PTA recognises that this request may exceed the usual number of significant figures reported by laboratories for some of the results.

(d) In addition to reporting the results, please also record on the results sheet the method of analysis using the attached codes.

(e) Laboratories are also requested to calculate and report an estimate of uncertainty measurement for each reported measurement result. All estimates of uncertainty of measurement must be given as a 95% confidence interval (coverage factor $k \approx 2$) and reported in mg/L.

6. Testing should commence as soon as possible after receiving samples and results reported **NO LATER THAN 31 JULY 2008 to:**

Ms Frances Ward
Proficiency Testing Australia
PO Box 7507
SILVERWATER NSW 2128
AUSTRALIA
Phone: +61 2 9736 8397
Fax: +61 2 9743 6664
Email: fward@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.

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	CODE
Bromide (Br^-)	APHA 18th Edition 1992 APHA 19th Edition 1995 APHA 20th Edition 1998 APHA 21st Edition 2005	1
	Part 4500 – Br^- B	2
	Part 4500 – Br^- D	3
	Part 4110B	4
	Part 4110C	5
	Part 4140B	6
	ISO 10304-1	7
	Other (please specify)	8
Chloride (Cl^-)	APHA 18th Edition 1992 APHA 19th Edition 1995 APHA 20th Edition 1998 APHA 21st Edition 2005	9
	Part 4500 – Cl^- B	10
	Part 4500 - Cl^- C	11
	Part 4500 - Cl^- D	12
	Part 4500 - Cl^- E	13
	Part 4110B	14
	Part 4110C	15
	Part 4140B	16
	ASTM D 512	17
	ISO 10304-1	18
	ISO 10304-4	19
	ISO 15682	20
	Ion Chromatography	21
	FIA Lachat	22
	Potentiometric Titration	23
	Segmented Flow Analysis	24
	Spectroquant	25
	Other (please specify)	26

Method Codes to be used for the Results Sheet Cont.

ANALYSIS	METHOD REFERENCE	CODE
Fluoride (F^-)	APHA 18th Edition 1992 APHA 19th Edition 1995 APHA 20th Edition 1998 APHA 21st Edition 2005	27
	Part 4500 - F^- B	28
	Part 4500 - F^- C	29
	Part 4500 - F^- D	30
	Part 4500 - F^- E	31
	Part 4500 - F^- G	32
	Part 4140B	33
	ASTM D 1179	34
	ISO 10304-1	35
	Fluoride Electrode	36
	Ion Chromatography	37
	SPAONS Method	38
	SPADNS Discrete Analyser	39
	Other (please specify)	40
Iodide (I^-)	APHA 18th Edition 1992 APHA 19th Edition 1995 APHA 20th Edition 1998 APHA 21st Edition 2005	41
	Part 4500 – I^- B	42
	Part 4500 – I^- C	43
	Part 4500 – I^- D	44
	Part 4500 – Br^- B	45
	ISO 10304-3	46
	Other (please specify)	47

Method Reference Key

(a)	APHA	APHA "Standard Methods for the Examination of Water and Wastewater" 18th Edition (1992), 19th Edition (1995), 20th Edition (1998), 21st Edition (2005).
(b)	ASTM D 512	ASTM D 512 - 04 Standard Test Methods for Chloride Ion in Water.
(c)	ASTM D 1179	ASTM D 1179-04 Standard Test Methods for Fluoride Ion in Water.
(d)	ISO 10304-1	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.
(e)	ISO 10304-3	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.
(f)	ISO 10304-4	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.
(g)	ISO 15682	ISO 15682:2000 Water quality - Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection.

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS SUB-PROGRAM 109

BROMIDE, CHLORIDE, FLUORIDE, IODIDE
JULY 2008

RESULTS SHEET
(mg/L)

Laboratory Code [ ]

ANALYSIS	SAMPLE 1		SAMPLE 2		METHOD CODE
	Result	±MU*	Result	±MU*	
Bromide (Br^-)					
Chloride (Cl^-)					
Fluoride (F^-)					
Iodide (I^-)					

(a) Report results for the diluted samples.

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

(c) For statistical purposes report results:

i) Bromide and Chloride report to one decimal place, e.g. 12.1 mg/L

ii) Fluoride and Iodide report to two decimal places, e.g. 1.55 mg/L

PTA recognises that this request may exceed the usual number of significant figures reported by laboratories for some of the results.

(d) MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in mg/L.

_____ _____

DATE **SIGNATURE**

Return results **NO LATER THAN 31 JULY 2008** to:

Ms Frances Ward
Proficiency Testing Australia
PO Box 7507
SILVERWATER NSW 2128
AUSTRALIA

Phone: +61 2 9736 8397
Fax: +61 2 9743 6664
Email: fward@pta.asn.au

APPENDIX D

Z – Score Calculation

Paired Sample Between and Within Laboratory
Z - Score Calculation Parameters

Analysis	Sample Pair	Standardised Sum (S)†		Standardised Diff. (D)‡	
		Median	Norm IQR	Median	Norm IQR
Bromide (Br^-)	Sample 1 Sample 2	16.58	0.80	2.76	0.35
Chloride (Cl^-)	Sample 1 Sample 2	128.48	7.55	13.22	2.36
Fluoride (F^-)	Sample 1 Sample 2	2.41	0.15	0.35	0.06
Iodide (I^-)	Sample 1 Sample 2	1.01	0.10	0.34	0.04

† The standardised sum *(S)* for each laboratory is calculated as follows:
$S = (A + B) \div \sqrt{2}$
where, *A* is the laboratory's result for the first sample tested and *B* is the result for the second tested sample.

Each laboratory's "between laboratory z-score" *(ZB)* is then calculated as:
$ZB = (S - median(S)) \div normalised\ IQR(S)$

‡ The standardised difference *(D)* for each laboratory is calculated as:
$D = (B - A) \div \sqrt{2}$ ***IF*** $median(A) < median(B)$ ***OTHERWISE*** $D = (A - B) \div \sqrt{2}$

Each laboratory's "within laboratory z-score" *(ZW)* is then calculated as:
$ZW = (D - median(D)) \div normalised\ IQR(D)$

END OF REPORT