



Report No. 1017

Waters Proficiency Testing Program

Round No. 206

***- Total Solids, Total Suspended Solids,
Total Dissolved Solids -***

March 2017

Acknowledgments

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CONTENTS

1. Foreword.....	1
2. Program Features and Design.....	1
3. Statistical Format	2
4. PTA and Technical Adviser's Comments.....	4
5. Outlier Results	14
6. References	14

APPENDIX A – Results and Data Analysis

Total Solids (TS).....	A1
Total Suspended Solids (TSS).....	A5
Total Dissolved Solids (TDS)	A11

APPENDIX B – Sample Homogeneity and Stability

Homogeneity and Stability Testing.....	B1
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APPENDIX C – Documentation

Instructions to Participants	C1
Method Codes	C3
Results Sheet	C4

1. Foreword

This report summarises the results of a proficiency testing program on the determination of Total Solids (TS), Total Suspended Solids (TSS) and Total Dissolved Solids (TDS) in waters. This is round 206 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in December 2016 by Proficiency Testing Australia (PTA). The main aim of the program was to assess laboratories' abilities to competently perform the prescribed analyses.

The Program Coordinator was Mrs D Mihaila and the Technical Adviser was Dr M Buckley-Smith, Global Proficiency Ltd (New Zealand). This report was authorised by Mr P Briggs, PTA General Manager.

2. Program Features and Design

- 2.1 Each laboratory was randomly allocated a unique code number for the program to ensure confidentiality of results. Reference to each laboratory in this report is by code number only. Please note that a number of laboratories reported more than one set of results and, therefore, their code numbers (with letter) could appear several times in the same data set.
 - 2.2 Laboratories were provided with the "Instructions to Participants" and "Results Sheet" (see Appendix C). Laboratories were requested to perform the tests according to their routine methods.
 - 2.3 Participants were provided with two plastic bottles (labelled PTA 1 and PTA 2) containing water samples for analysis of Total Solids, Total Suspended Solids and Total Dissolved Solids.
 - 2.4 A total of 43 laboratories received samples, comprising:
 - 33 Australian participants; and
 - 10 overseas participants, including:
 - Brunei Darussalam (1), Indonesia (1), Kingdom of Bahrain (1), Malaysia (2), Papua New Guinea (1), Qatar (1), Singapore (2), Vietnam (1).
- Of these 43 laboratories, 2 were unable to submit results by the due date.
- 2.5 Results (as reported by participants) with corresponding summary statistics (i.e. number of results, median, normalised interquartile range, uncertainty of the median, robust coefficient of variation, minimum, maximum and range) are presented in Appendix A (for each sample and for each of the analyses performed).
 - 2.6 A robust statistical approach, using z-scores, was utilised to assess laboratories' testing performance (see Section 3). Robust z-scores and ordered z-score charts relevant to each test are presented in Appendix A.

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

- 2.7 A tabulated listing of laboratories (by code number) identified as having outlier results can be found on page 14.
- 2.8 Prior to sample distribution, a number of randomly selected samples were analysed for homogeneity and stability. Based on the results of this testing (see Appendix B) it was considered that the samples utilised for this program were homogeneous and stable. As such, any results later identified as outliers could not be attributed to any notable sample variability.

3. Statistical Format

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

- a table of results and calculated z-scores;
- a list of summary statistics; and
- ordered z-score charts.

3.1 Outlier Results and Z-scores

In order to assess laboratories' testing performance, a robust statistical approach, using z-scores, was utilised. Z-scores give a measure of how far a result is from the consensus value (i.e. the median), and gives a "score" to each result relative to the other results in the group.

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

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

3.2 Results Tables and Summary Statistics

The tables in Appendix A contain the results returned by each laboratory, including the code number for the method used and the robust z-score calculated for each result.

Results have been entered exactly as reported by participants. That is, laboratories which did not report results to the precision (i.e. number of significant figures) requested on the Results Sheet have not been rounded to the requested precision before being included in the statistical analysis.

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

- *No. of Results*: the total number of results for that test/sample;
- *Median*: the middle value of the results;
- *Normalised IQR*: the normalised interquartile range of the results;
- *Uncertainty of the Median*: a robust estimate of the standard deviation of the *Median*;
- *Robust CV*: the robust coefficient of variation expressed as a percentage, i.e. $100 \times \text{Normalised IQR} / \text{Median}$;
- *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 Adviser's Comments

4.1 Metrological Traceability and Measurement Uncertainty of Assigned Values

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

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

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

As the assigned value for each analyte in this program is the median of the results submitted by the participants, the uncertainty of the median for each analyte has been calculated and is presented in Table 1 below.

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

Analyte	Sample	Dope Concentration (mg/L)	Median (mg/L)	Uncertainty of the Median (mg/L)
Total Solids (TS)	PTA 1	265	273.7	2.7
	PTA 2	380	386.5	3.6
Total Suspended Solids (TSS)	PTA 1	75	72.00	0.70
	PTA 2	90	87.00	1.45
Total Dissolved Solids (TDS)	PTA 1	190	200.0	3.0
	PTA 2	290	300.0	3.0

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

4.2 Analysis of Round 206 Results

4.2.1 Total Solids (TS)

Table 2 compares the Total Solids (TS) medians and robust CVs from this round to those obtained in previous PTA rounds. CVs in the current study were comparable to those of previous rounds, and better than the relative standard deviation (RSD) of 10%, published in US EPA Method 1684 [3]. Published precision information in APHA indicated that duplicate analyses should agree to a standard deviation of 6.0 mg/L [4].

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

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	273.7	4.2	28
	PTA 2	386.5	4.0	28
Report 964	PTA 1	607.5	4.3	30
	PTA 2	266.5	7.6	30
Report 925	PTA 1	541.0	2.6	33
	PTA 2	358.0	4.1	33

Bias / Accuracy

The TS testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 254 – 295 mg/L for sample PTA 1 and 367 – 411 mg/L for sample PTA 2.

Out of 28 participants, three questionable results ($2.0 < |z\text{-score}| < 3.0$) were reported for sample PTA 1 (laboratories 419, 429 and 432) and two questionable results were reported for sample PTA 2 (laboratories 419 and 429).

Five outlier results ($|z\text{-score}| \geq 3.0$) were obtained for sample PTA 1, requiring follow-up action by laboratories 129, 181, 213, 314 and 359. Three outlier results were obtained for sample PTA 2, requiring follow-up action by laboratories 129, 181 and 314.

The most likely source of error, causing low bias when testing these proficiency samples, is incomplete transfer of the entire contents of the bottle into the volumetric flask with rinsing, as per the instructions to participants. It is important to rinse the sides of the bottle, the cap, the funnel and the stem of the funnel. Once the entire sample has been transferred, the vessel should be brought to volume and mixed thoroughly. Vigorous shaking for at least thirty seconds will mix the sample, but a magnetic stir bar for 5-10 min will ensure a more homogeneous sample.

APHA also recommends analysing at least 10% of samples in duplicate, with the duplicate determinations agreeing within 5% of their average weight. Laboratories low or high biasing may wish to implement the APHA 2020 B [4] or US EPA Method 1684 [3] recommended quality control procedures.

The TS data sets formed an approximately normal distribution with no notable bias attributable to any one method (Figures 1 and 2). The method most frequently used for TS analysis was APHA 2540 B (Total Solids Dried at 103-105°C - method code 1), which was used by approximately 86% of participants.

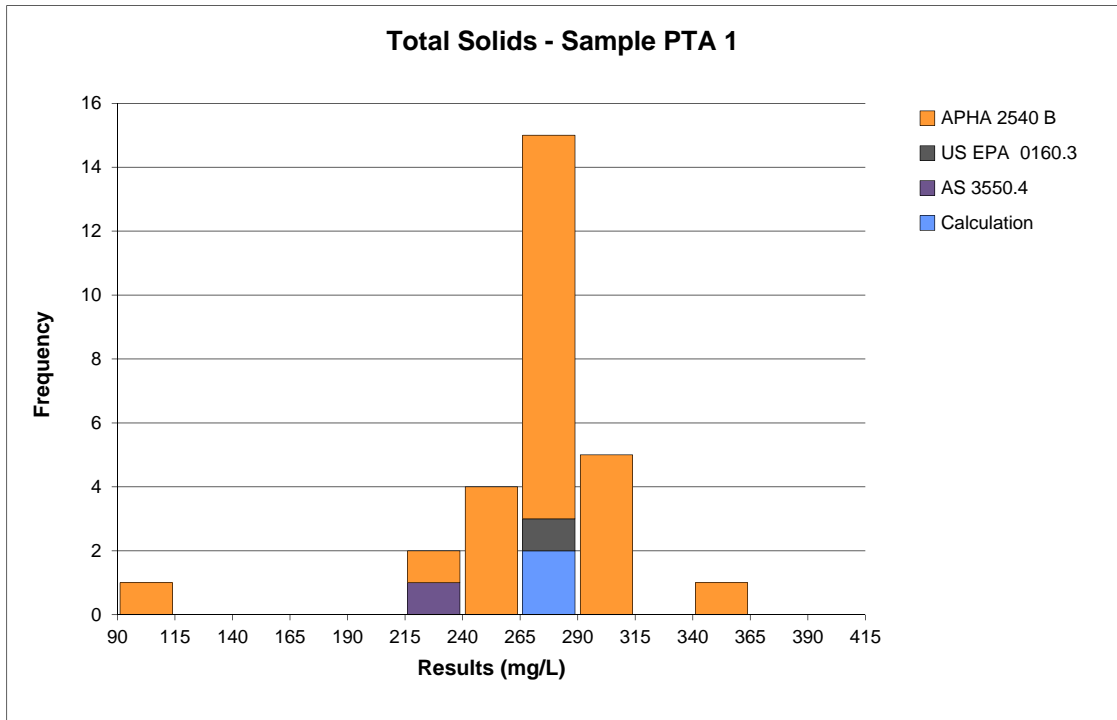


Figure 1. Spread of results for TS testing of sample PTA 1, with a median of 273.7 mg/L.

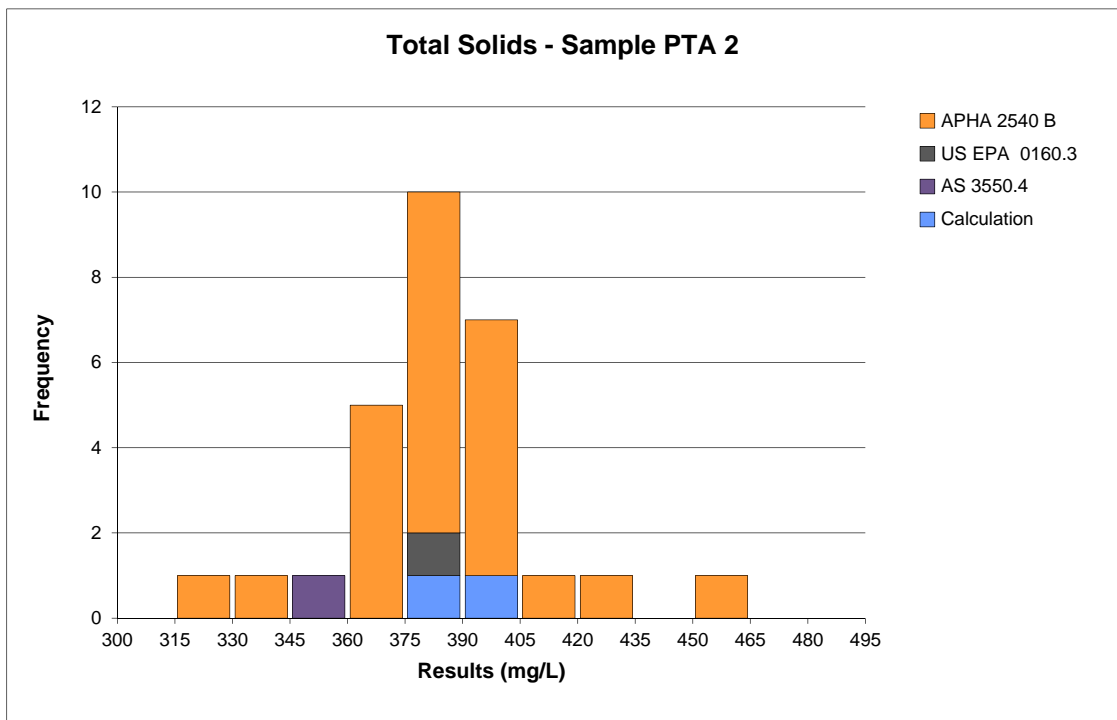


Figure 2. Spread of results for TS testing of sample PTA 2, with a median of 386.5 mg/L.

4.2.2 Total Suspended Solids (TSS)

Table 3 compares the Total Suspended Solids (TSS) medians and robust CVs from this round to those obtained in previous PTA rounds. Results in the current study were comparable to those from previous rounds, and well within the published precision range for method APHA 2540 D (Total Suspended Solids Dried at 103-105°C), which states that CVs of between 10% - 33% are normal, depending on the concentration of the sample [4].

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

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	72.00	4.9	41
	PTA 2	87.00	8.5	41
Report 964	PTA 1	208.0	7.5	42
	PTA 2	100.0	15.5	43
Report 925	PTA 1	45.50	9.8	45
	PTA 2	97.60	6.1	45

Bias / Accuracy

The TSS testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 66.0 – 79.0 mg/L for sample PTA 1 and 72.3 – 95.6 mg/L for sample PTA 2.

Out of 41 participants, two questionable results ($2.0 < |z\text{-score}| < 3.0$) were reported for sample PTA 1 (laboratories 432 and 635) and two questionable results were reported for sample PTA 2 (laboratories 107 and 432).

Four outlier results ($|z\text{-score}| \geq 3.0$) were obtained for sample PTA 1, requiring follow-up action by laboratories 107, 129, 314 and 345. Four outlier results were also obtained for sample PTA 2, requiring follow-up action by laboratories 129, 314, 342 and 429.

For laboratories concerned with their TSS testing, APHA 2020 B recommends method blanks using dilution water, and duplicate analyses be carried out for TSS testing [4]. Duplicate determinations should agree within 5% of their average weight. If a measured volume is pipetted onto the seated glass-fibre filter, APHA 2540 D recommends pipetting from the approximate midpoint of the container but not in the vortex created by the magnetic stirrer, to get a more homogeneous sample [4]. Subsampling is a major source of error in this testing.

Laboratories whose results biased low on the suspended solids test, and high on the dissolved solids test (laboratory 129) may have used a filter with pores that were larger than used by other laboratories, allowing a greater proportion of the finer solids particles to pass through. Filter pore sizes used by laboratories ranged between 0.2 – 2.0 μm , and the median was 1.2 μm . Nearly half of laboratories who stated their filter brand were using Whatman, others included Advantec, Filtech, Micro Science, Millipore, Pall, Pro-weigh, and Sartorius filters. One laboratory indicated

they used a 0.45 μm filter for their dissolved solids test, and a 1.2 μm filter for their suspended solids test.

The TSS data sets formed an approximately normal distribution with no notable bias attributable to any one method (Figures 3 and 4). The method most frequently used for TSS analysis was APHA 2540 D (Total Suspended Solids Dried at 103-105°C - method code 6), which was used by approximately 88% of participants.

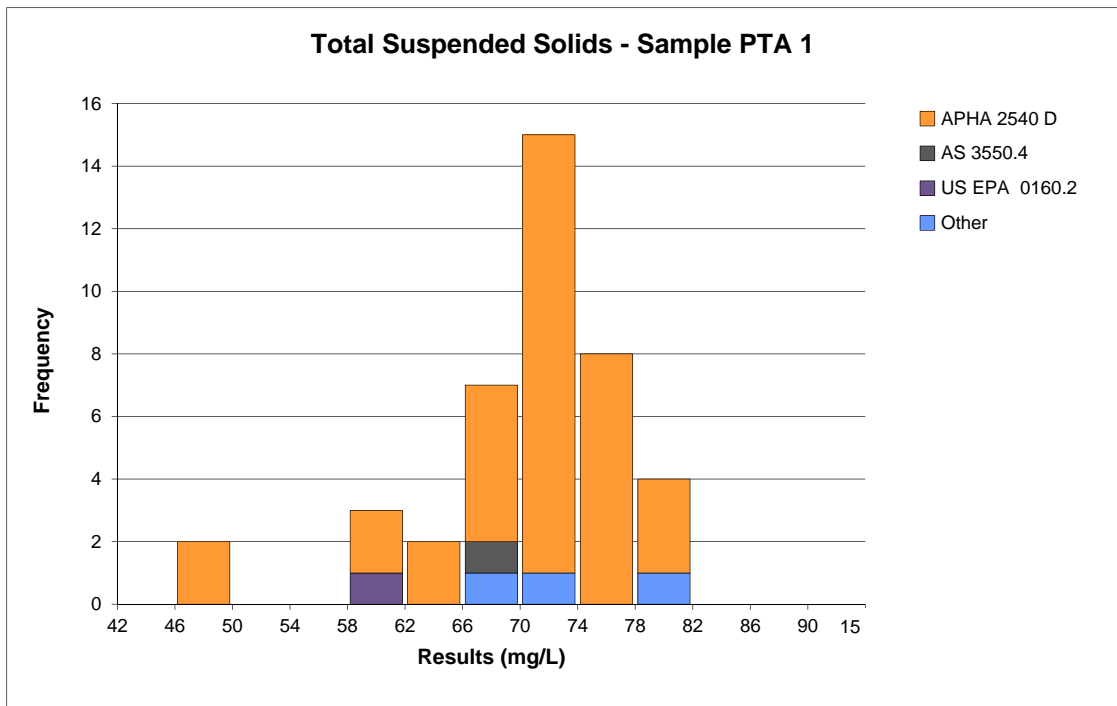


Figure 3. Spread of results for TSS testing of sample PTA 1, with a median of 72.00 mg/L.

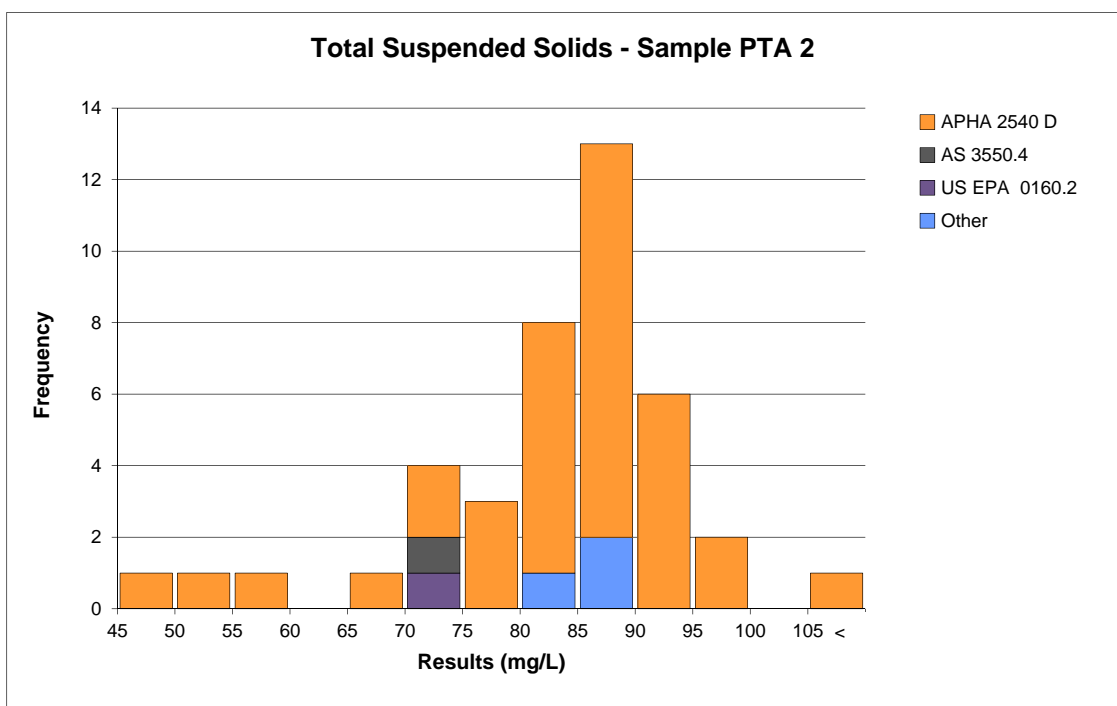


Figure 4. Spread of results for TSS testing of sample PTA 2, with a median of 87.00 mg/L.

4.2.3 Total Dissolved Solids (TDS)

Table 4 compares the Total Dissolved Solids (TDS) medians and robust CVs from this round to those obtained in previous PTA rounds. Precision of results in this study were comparable to those seen in previous rounds, and those published in APHA 2540 C (Total Dissolved Solids Dried at 180°C) indicating RSD of 7.2% for single laboratory repeatability [4].

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

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	200.0	7.2	36
	PTA 2	300.0	4.9	36
Report 964	PTA 1	406.0	2.6	36
	PTA 2	170.5	8.4	36
Report 925	PTA 1	498.0	4.5	37
	PTA 2	260.0	7.7	37

Bias / Accuracy

The TDS testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 176 – 224 mg/L for sample PTA 1 and 277 – 321 mg/L for sample PTA 2.

Out of 36 participants, four questionable results ($2.0 < |z\text{-score}| < 3.0$) were reported for sample PTA 1 (laboratories 103, 181, 432 and 526). No questionable results were reported for sample PTA 2.

One outlier result ($|z\text{-score}| \geq 3.0$) was obtained for sample PTA 1, requiring follow-up action by laboratory 129. Two outlier results were obtained for sample PTA 2, requiring follow-up action by laboratories 103 and 129.

For laboratories concerned with their dissolved solids testing, it is important to recognize that the drying time required in the TDS method is sensitive to the composition of the TDS sample. Samples with a high mineral concentration can absorb moisture and will require an extended drying time, and must be weighed quickly to ensure that moisture from the air does not affect the result (i.e., storing in a desiccator until the sample reaches room temperature prior to weighing). Adding successive aliquots of the sample until a final yield of between 2.5 – 200 mg of dried residue is achieved, and repeating the cycle of drying, cooling, desiccating and weighing until a constant weight is obtained or until the weight change is less than 4% of the previous weight; will help to improve the accuracy and precision of test results [4].

The TDS data sets formed an approximately normal distribution with no notable bias attributable to any one method (Figures 5 and 6). The method most frequently used for TDS analysis was APHA 2540 C (Total Dissolved Solids Dried at 180°C - method code 11), which was used by approximately 92% of participants.

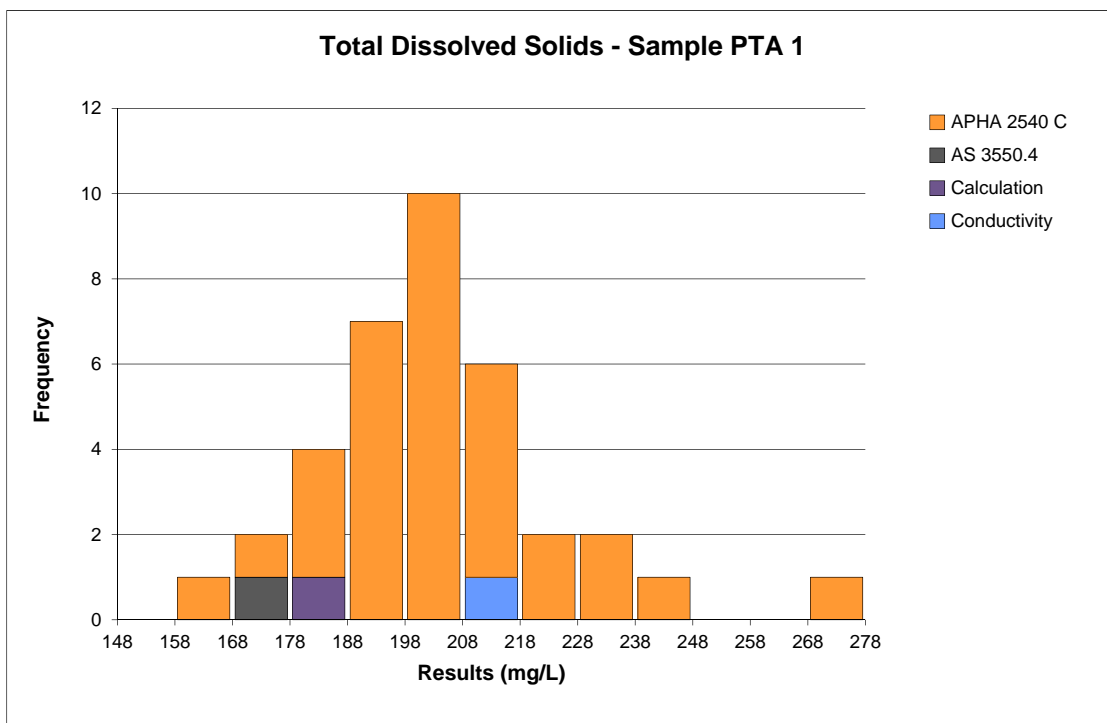


Figure 5. Spread of results for TDS testing of sample PTA 1, with a median of 200.0 mg/L.

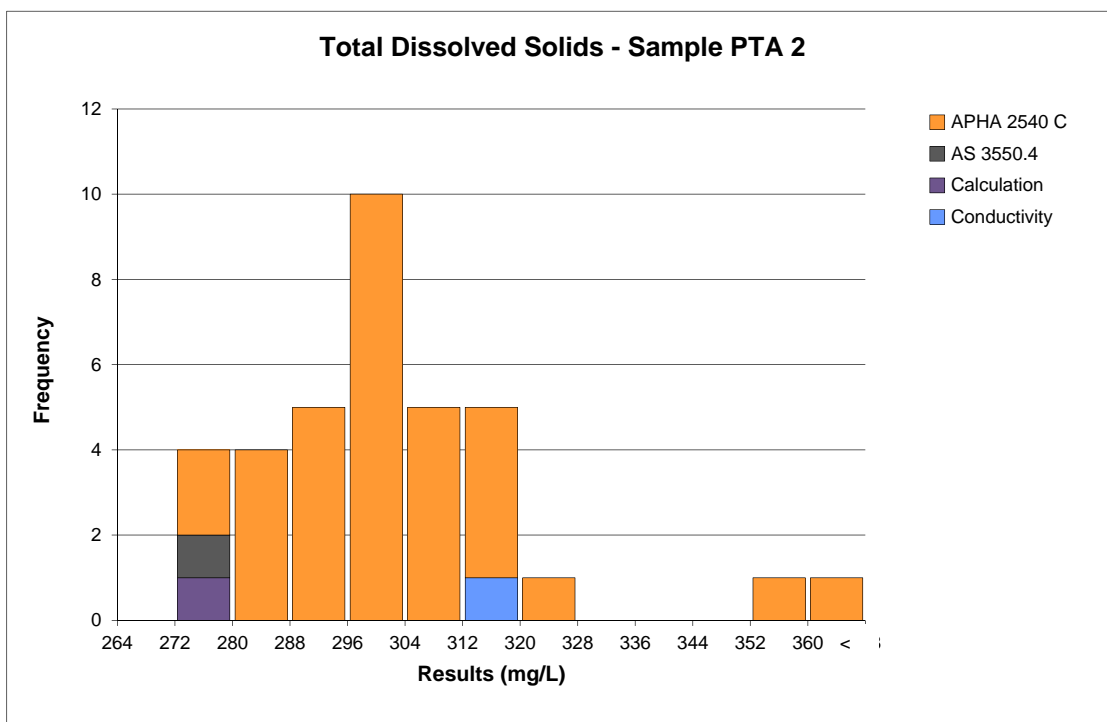


Figure 6. Spread of results for TDS testing of sample PTA 2, with a median of 300.0 mg/L.

4.3 Measurement Uncertainty (MU)

The majority of participants in this round (64%-76%) reported the measurement uncertainty (MU) associated with their results. Table 5 below presents the number and percentage of laboratories reporting the MU for each analyte.

Table 5. The number and percentage of laboratories reporting MU for analytes in round 192

Analyte	Sample	Total participants	Participants reporting MU (percentage)
Total Solids (TS)	PTA 1	28	18 (64%)
	PTA 2	28	18 (64%)
Total Suspended Solids (TSS)	PTA 1	41	31 (76%)
	PTA 2	41	31 (76%)
Total Dissolved Solids (TDS)	PTA 1	36	25 (69%)
	PTA 2	36	25 (69%)

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

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

If either situation occurs in successive proficiency rounds, laboratories may wish to re-examine their measurement uncertainty.

¹ MU evaluation is based on minimum / maximum uncertainty criteria (u_{min} and u_{max}) described in ISO 13528:2015 [2]. It should be noted, however, that these are informative indicators only and cannot be solely used to validate or invalidate the MUs reported.

4.4 Analysis of Results by Method Groups

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

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

4.4.1. Total Solids (TS)

The method APHA 2540 B (Total Solids Dried at 103-105°C - method code 1) was most frequently employed for TS analysis, with 24 out of 28 participants indicating the use of this method.

Table 6 below presents the medians, uncertainty of the medians and robust CVs for TS results obtained by this method in round 206. Results were slightly more variable than seen in the overall dataset (CVs PTA 1 = 4.2%, PTA 2 4.0%).

Table 6. Variability and proficiency medians of TS results obtained by method APHA 2540 B.

Analyte	Sample	Participants	Median \pm Uncertainty of the Median (mg/L)	Robust CV (%)
Total Solids	PTA 1	24	274.5 \pm 3.2	4.6
	PTA 2	24	387.0 \pm 4.2	4.3

4.4.2. Total Suspended Solids (TSS)

The method APHA 2540 D (Total Suspended Solids Dried at 103-105°C - method code 6) was most frequently employed for TSS analysis, with 36 out of 41 participants indicating the use of this method.

Table 7 below presents the medians, uncertainty of the medians and robust CVs for TSS results obtained by this method in round 206. Results were comparable to the overall dataset for PTA 1, and slightly better than the overall CV (8.5%) for PTA 2.

Table 7. Variability and proficiency medians of TSS results obtained by method APHA 2540 D.

Analyte	Sample	Participants	Median \pm Uncertainty of the Median (mg/L)	Robust CV (%)
Total Suspended Solids	PTA 1	36	72.55 \pm 0.74	4.9
	PTA 2	36	87.20 \pm 1.34	7.4

4.4.3. Total Dissolved Solids (TDS)

The method APHA 2540 C (Total Dissolved Solids Dried at 180°C - method code 11) was most frequently employed for TDS analysis, with 33 out of 36 participants indicating the use of this method.

Table 8 below presents the medians, uncertainty of the medians and robust CVs for TDS results obtained by this method in round 206. Results were slightly less variable for this specific method when compared to the CVs for the overall dataset (CV PTA 1 = 7.2%, PTA 2 = 4.9%).

Table 8. Variability and proficiency medians of TDS results obtained by method APHA 2540 C.

Analyte	Sample	Participants	Median ± Uncertainty of the Median (mg/L)	Robust CV (%)
Total Dissolved Solids	PTA 1	33	200.0 ± 3.1	7.0
	PTA 2	33	300.0 ± 2.9	4.4

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 9 below.

Table 9. Laboratory results identified as outliers for each analysis performed.

Lab Code	Analysis					
	Total Solids		Total Suspended Solids		Total Dissolved Solids	
	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2
103						§
107			§			
129	§	§	§	§	§	§
181	§	§				
213	§					
314	§	§	§	§		
342				§		
345			§			
359	§					
429				§		

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. References

- [1] *Guide to Proficiency Testing Australia*, 2016 (This document can be found on the PTA website, www.pta.asn.au).
- [2] ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons*.
- [3] *METHOD 1684. Total, Fixed, and Volatile Solids in Water, Solids, and Biosolids*, Draft January 2001. Published by US EPA, EPA-821-R-01-015 <https://nepis.epa.gov/Exe/ZyPDF.cgi/P1002CZ8.PDF?Dockey=P1002CZ8.PDF>.
- [4] *Standard Methods For the Examination of Water and Wastewater*, 2012. Published by APHA, AWWA, WEF (22nd Edition).

APPENDIX A

Results and Data Analysis

Total Solids (TS).....	A1
Total Suspended Solids (TSS).....	A5
Total Dissolved Solids (TDS)	A11

Total Solids (TS) Results

Samples PTA 1 and PTA 2

Total Solids (TS)

Results by Laboratory Code

Laboratory Code	Sample PTA 1			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
105	295	#	1.84	1
123	270 ±	41	-0.32	1
129	346 ±	6	6.24 §	1
136	269	#	-0.41	1
163	265	#	-0.75	1
181	236	#	-3.25 §	1
213	312 ±	42	3.31 §	1
294	272 ±	15	-0.15	1
314	310 ±	40	3.13 §	1
345	268 ±	26.8	-0.49	2
359	100	#	-15.00 §	1
380	278	#	0.37	1
419	240 ±	22	-2.91	3
429	303	#	2.53	1
432	300	#	2.27	1
473	258 ±	26	-1.36	1
476	276 ±	52	0.20	1
497A	273.4 ±	24.1	-0.03	1
497B	279.5 ±	24.6	0.50	1
498	274 ±	27	0.03	1
556	263	#	-0.92	1
575	290 ±	58	1.41	4
586	254 ±	20	-1.70	1
597	279 ±	20	0.46	1
603	279	#	0.46	1
607	275 ±	30	0.11	1
635	267 ±	15	-0.58	1
690	269 ±	21.5	-0.41	4

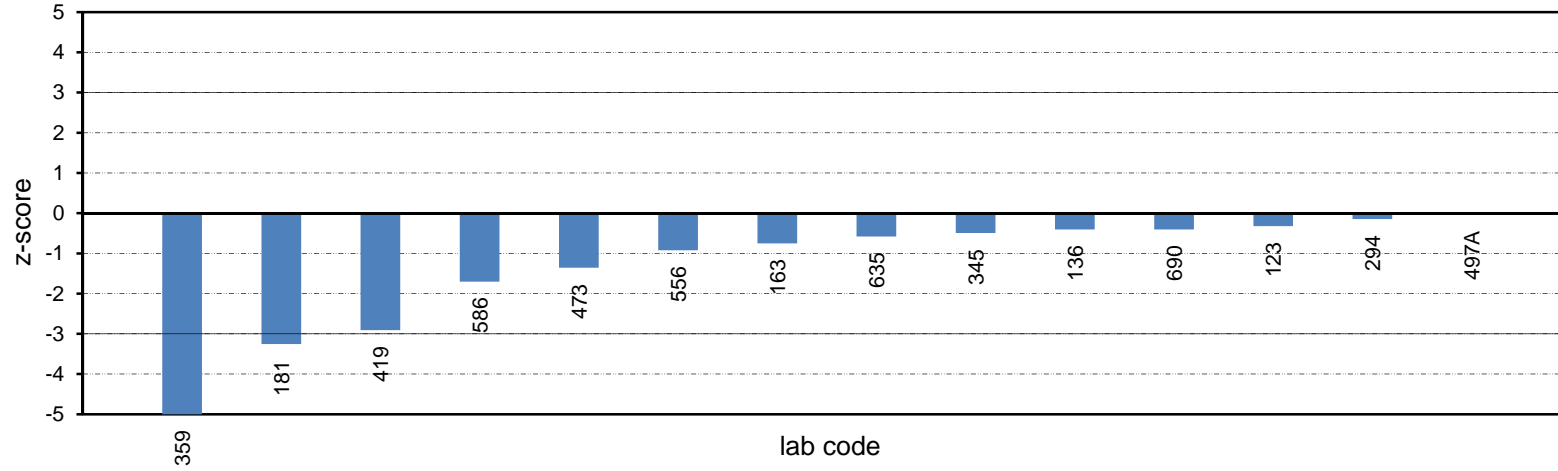
<i>No of Results:</i>	28
<i>Median:</i>	273.7
<i>Normalised IQR:</i>	11.6
<i>Uncertainty of the Median:</i>	2.7
<i>Robust CV:</i>	4.2%
<i>Minimum:</i>	100
<i>Maximum:</i>	346
<i>Range:</i>	246

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

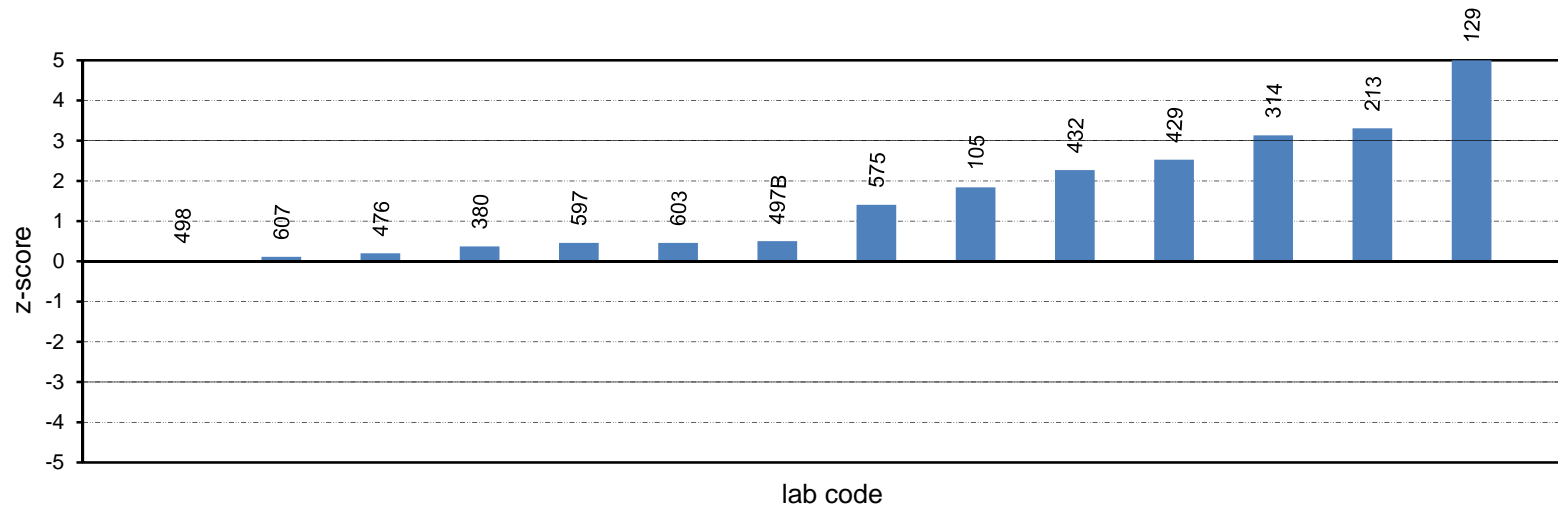
² "§" denotes an outlier (i.e. those results for which $|z\text{-score}| \geq 3.0$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where A is the participant laboratory's result.

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

Total Solids - Sample PTA 1 - Robust Z-Scores



Robust Z-Scores



Total Solids - Sample PTA 1
Ordered Robust Z-Score Charts

A2

Total Solids (TS)

Results by Laboratory Code

Laboratory Code	Sample PTA 2			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
105	387	#	0.03	1
123	370 ±	56	-1.07	1
129	460 ±	6	4.78 §	1
136	377	#	-0.62	1
163	380	#	-0.42	1
181	322	#	-4.19 §	1
213	411 ±	55	1.59	1
294	386 ±	20	-0.03	1
314	335 ±	40	-3.35 §	1
345	384 ±	38.4	-0.16	2
359	400	#	0.88	1
380	387	#	0.03	1
419	348 ±	23	-2.50	3
429	426	#	2.57	1
432	396	#	0.62	1
473	367 ±	37	-1.27	1
476	401 ±	76	0.94	1
497A	389.3 ±	30.4	0.18	1
497B	375.0 ±	29.3	-0.75	1
498	388 ±	39	0.10	1
556	372	#	-0.94	1
575	393 ±	79	0.42	4
586	373 ±	30	-0.88	1
597	393 ±	25	0.42	1
603	395	#	0.55	1
607	399 ±	40	0.81	1
635	386 ±	22	-0.03	1
690	382 ±	30.6	-0.29	4

<i>No of Results:</i>	28
<i>Median:</i>	386.5
<i>Normalised IQR:</i>	15.4
<i>Uncertainty of the Median:</i>	3.6
<i>Robust CV:</i>	4.0%
<i>Minimum:</i>	322
<i>Maximum:</i>	460
<i>Range:</i>	138

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

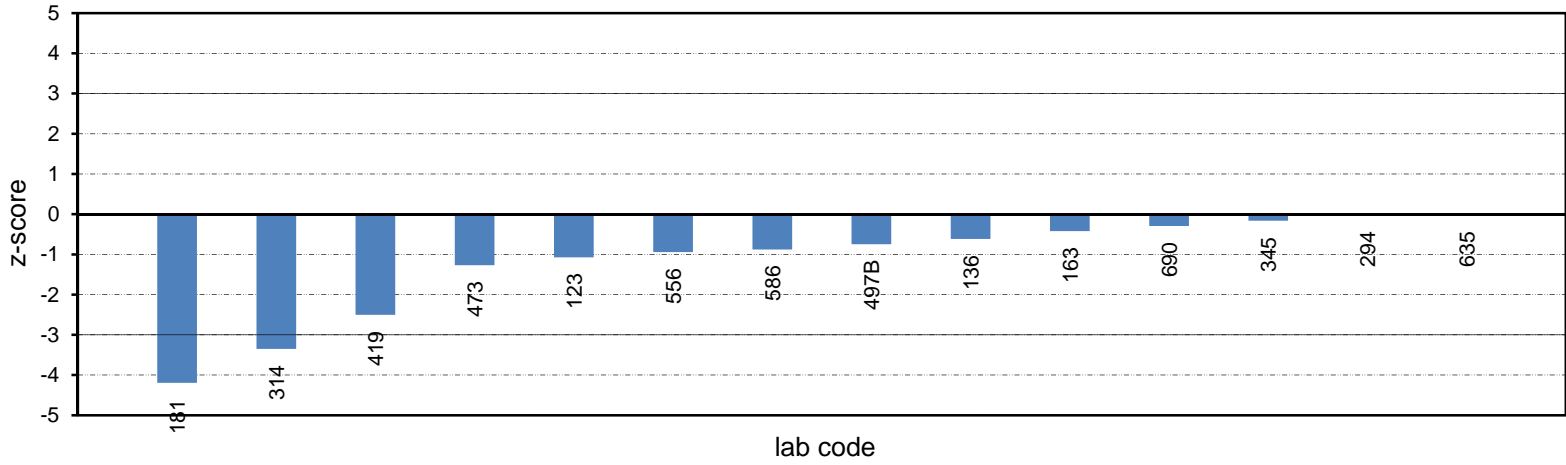
² "§" denotes an outlier (i.e. those results for which $|z\text{-score}| \geq 3.0$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where A is the participant laboratory's result.

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

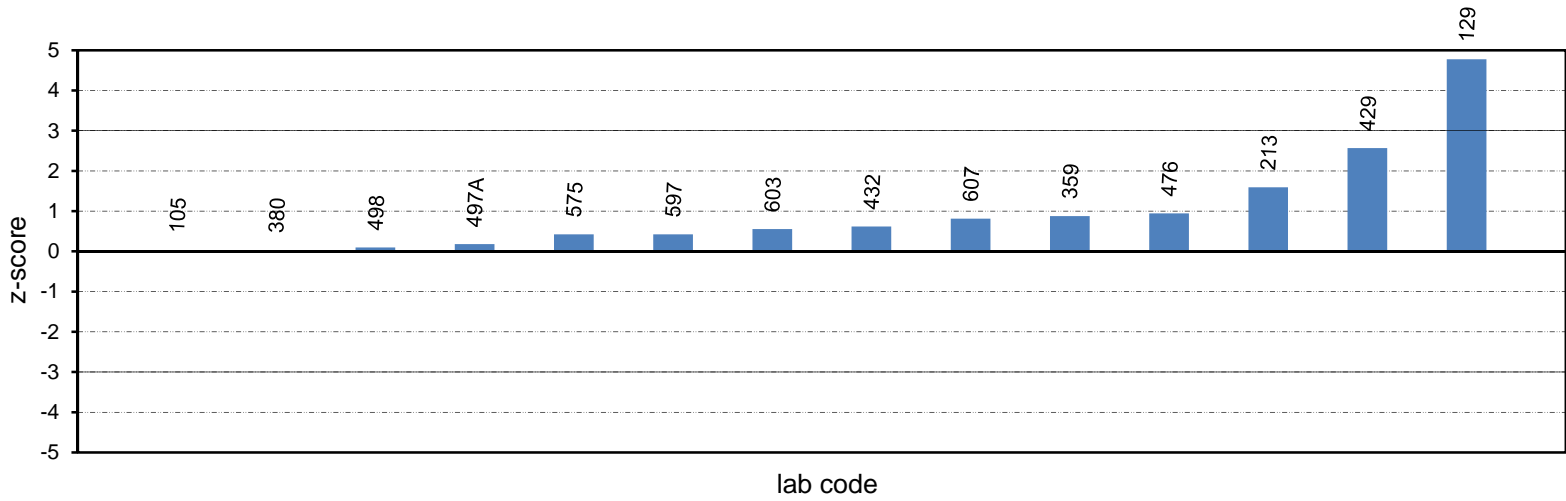
Total Solids - Sample PTA 2

Ordered Robust Z-Score Charts

Total Solids - Sample PTA 2 - Robust Z-Scores



Robust Z-Scores



Total Suspended Solids (TSS) Results

Samples PTA 1 and PTA 2

Total Suspended Solids (TSS)

Results by Laboratory Code

Laboratory Code	Sample PTA 1			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
103	73 ±	5.84	0.28	6
105	72.0	#	0.00	6
107	49.0 ±	7.6	-6.46 §	6
123	72.1 ±	10.8	0.03	6
129	49 ±	2	-6.46 §	6
163	70	#	-0.56	6
181	71.8	#	-0.06	6
213	71 ±	6.0	-0.28	6
252	79.0 ±	8.2	1.97	10
292	74.5 ±	7	0.70	6
294	69.0 ±	6.0	-0.84	6
303	70.0 ±	3.5	-0.56	6
314	60.0 ±	15	-3.37 §	6
342	66 ±	5.0%	-1.69	6
345	58.5 ±	5.85	-3.79 §	9
359	75 ±	7.5	0.84	6
377	74.7 ±	2.12	0.76	6
380	78.0	#	1.69	6
419	67.2 ±	4.2	-1.35	7
429	77.5	#	1.55	6
432	62	#	-2.81	6
451	70 ±	10	-0.56	10
473	66.7 ±	6.7	-1.49	6
476	72.0 ±	5.1	0.00	6
485	69.9 ±	5.8	-0.59	6
486	74.0	#	0.56	6
497A	73.4 ±	8.2	0.39	6
497B	75.5 ±	8.4	0.98	6
498	73.2 ±	7.3	0.34	6

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

² "§" 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.

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

Total Suspended Solids (TSS) - cont.**Results by Laboratory Code**

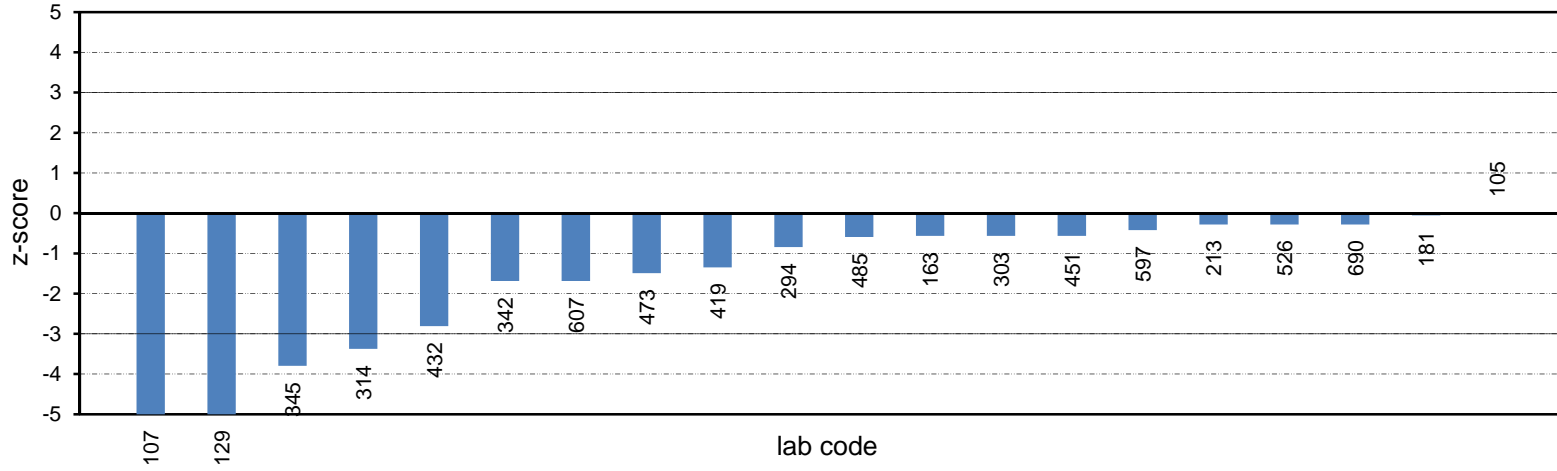
Laboratory Code	Sample PTA 1			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
526	71.0 ±	14.2	-0.28	6
556	75.0	#	0.84	6
573	77.3	#	1.49	6
575	73.0 ±	15	0.28	6
586	74 ±	7	0.56	6
597	70.5 ±	5.0	-0.42	6
603	79	#	1.97	6
607	66 ±	15	-1.69	6
635	79.9 ±	7.0	2.22	6
646	79.0 ±	2	1.97	6
685	74 ±	11.1	0.56	6
690	71 ±	5.68	-0.28	10
<hr/>				
<i>No of Results:</i>	41			
<i>Median:</i>	72.00			
<i>Normalised IQR:</i>	3.56			
<i>Uncertainty of the Median:</i>	0.70			
<i>Robust CV:</i>	4.9%			
<i>Minimum:</i>	49.0			
<i>Maximum:</i>	79.9			
<i>Range:</i>	30.9			

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

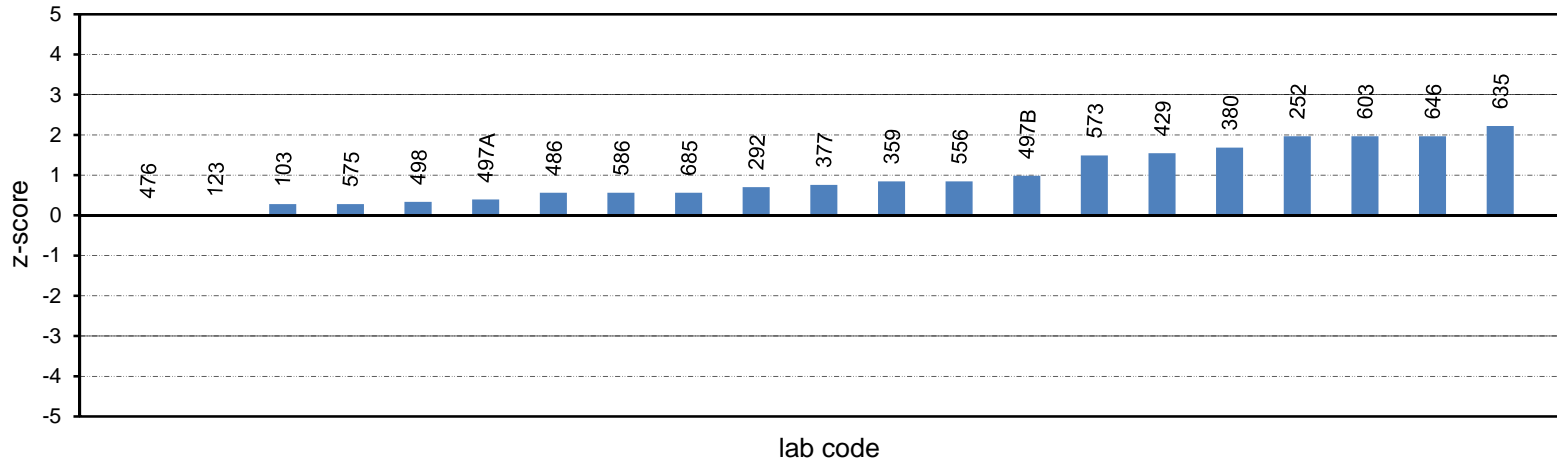
² "**S**" denotes an outlier (i.e. those results for which $|z\text{-score}| \geq 3.0$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where A is the participant laboratory's result.

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

Total Suspended Solids - Sample PTA 1 - Robust Z-Scores



Robust Z-Scores



Total Suspended Solids - Sample PTA 1
Ordered Robust Z-Score Charts

A7

Total Suspended Solids (TSS)

Results by Laboratory Code

Laboratory Code	Sample PTA 2			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
103	87 ±	6.96	0.00	6
105	84.0	#	-0.40	6
107	69.5 ±	7.6	-2.36	6
123	79.9 ±	12.0	-0.96	6
129	47 ±	2	-5.40 §	6
163	80	#	-0.94	6
181	84.8	#	-0.30	6
213	85 ±	8.0	-0.27	6
252	89.0 ±	8.2	0.27	10
292	90.7 ±	8	0.50	6
294	79.0 ±	8.0	-1.08	6
303	82.0 ±	4.1	-0.67	6
314	58.8 ±	15	-3.80 §	6
342	54 ±	5.0%	-4.45 §	6
345	75 ±	7.5	-1.62	9
359	91 ±	9.1	0.54	6
377	90.0 ±	2.55	0.40	6
380	93.8	#	0.92	6
419	72.3 ±	4.2	-1.98	7
429	181	#	12.68 §	6
432	71	#	-2.16	6
451	90 ±	10	0.40	10
473	73.1 ±	7.3	-1.88	6
476	89.0 ±	6.2	0.27	6
485	83.1 ±	6.8	-0.53	6
486	93.8	#	0.92	6
497A	91.3 ±	9.3	0.58	6
497B	87.4 ±	8.9	0.05	6
498	89.6 ±	8.9	0.35	6

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

² "§" 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.

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

Total Suspended Solids (TSS) - cont.**Results by Laboratory Code**

Laboratory Code	Sample PTA 2			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
526	85.0 ±	11.6	-0.27	6
556	88.0	#	0.13	6
573	95.6	#	1.16	6
575	83.0 ±	17	-0.54	6
586	90.0 ±	8	0.40	6
597	87.0 ±	5.0	0.00	6
603	91.3	#	0.58	6
607	88 ±	15	0.13	6
635	95.4 ±	8.4	1.13	6
646	90.0 ±	3	0.40	6
685	89 ±	13.4	0.27	6
690	85 ±	6.80	-0.27	10
<hr/>				
<i>No of Results:</i>	41			
<i>Median:</i>	87.00			
<i>Normalised IQR:</i>	7.41			
<i>Uncertainty of the Median:</i>	1.45			
<i>Robust CV:</i>	8.5%			
<i>Minimum:</i>	47			
<i>Maximum:</i>	181			
<i>Range:</i>	134			

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

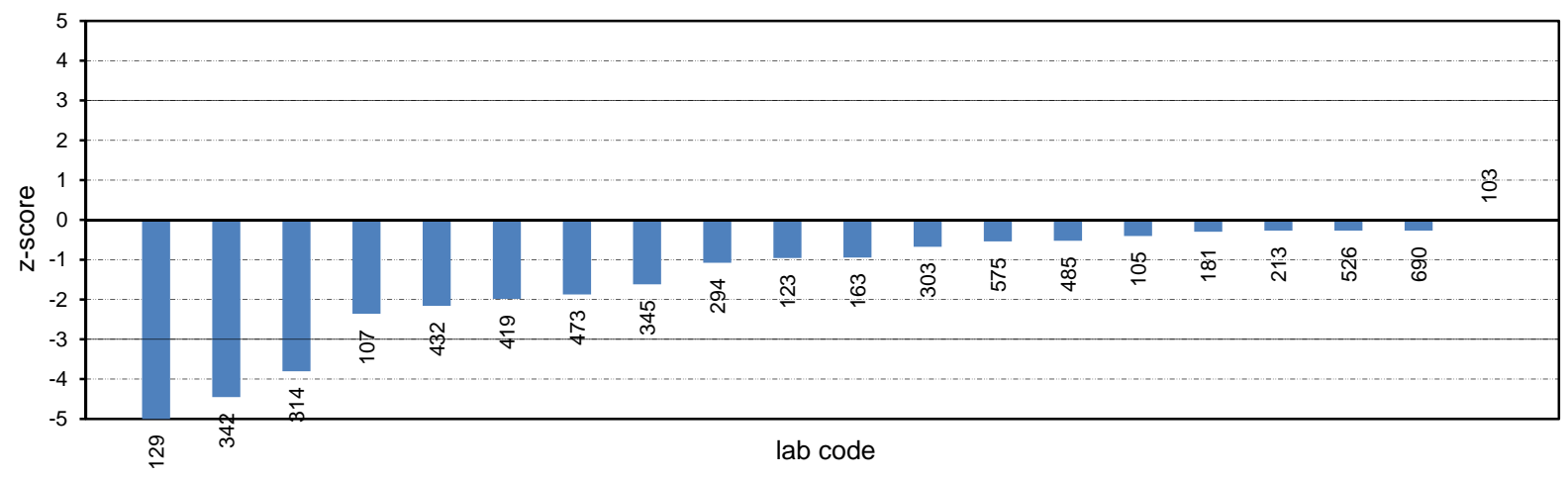
² "**S**" denotes an outlier (i.e. those results for which $|z\text{-score}| \geq 3.0$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where A is the participant laboratory's result.

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

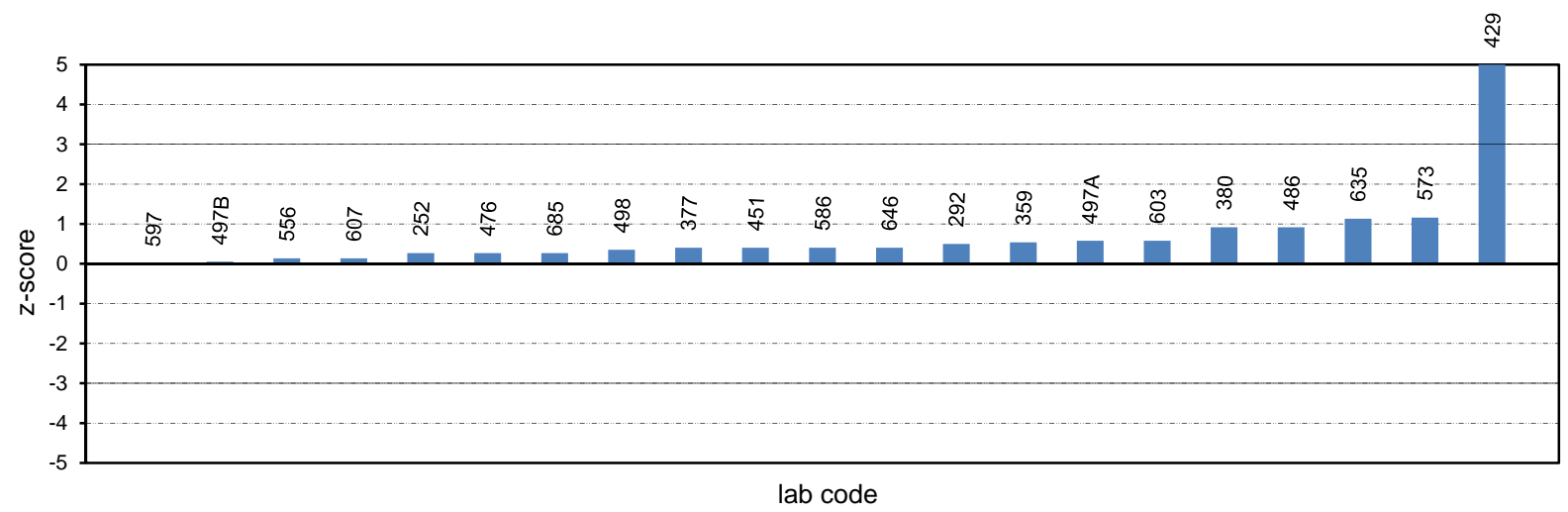
Total Suspended Solids - Sample PTA 2

Ordered Robust Z-Score Charts

Total Suspended Solids - Sample PTA 2 - Robust Z-Scores



Robust Z-Scores



Total Dissolved Solids (TDS) Results

Samples PTA 1 and PTA 2

Total Dissolved Solids (TDS)**Results by Laboratory Code**

Laboratory Code	Sample PTA 1			
	Result \pm mg/L	MU ¹	Robust z-score ²	Method Code ³
103	230 \pm	23	2.08	11
105	195	#	-0.35	11
107	208 \pm	8.6	0.55	11
123	180 \pm	19	-1.38	11
129	275 \pm	6	5.19 §	11
136	200	#	0.00	11
163	200	#	0.00	11
181	166	#	-2.35	11
213	224 \pm	30	1.66	11
292	195 \pm	3	-0.35	11
294	206 \pm	10	0.42	11
303	214 \pm	11	0.97	16
342	198 \pm	8.8%	-0.14	11
345	182 \pm	18.2	-1.25	15
359	215	#	1.04	11
377	199 \pm	9.40	-0.07	11
380	200	#	0.00	11
419	177 \pm	25	-1.59	12
429	201	#	0.07	11
432	240	#	2.77	11
473	193 \pm	19.3	-0.48	11
476	207 \pm	14	0.48	11
485	214 \pm	17.3	0.97	11
497A	212.7 \pm	18.3	0.88	11
497B	220.0 \pm	18.9	1.38	11
498	200 \pm	20	0.00	11
526	230 \pm	46.0	2.08	11
556	182	#	-1.25	11
575	217 \pm	43	1.18	11

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

² "§" 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.

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

Total Dissolved Solids (TDS) - cont.**Results by Laboratory Code**

Laboratory Code	Sample PTA 1			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
586	199 ±	14	-0.07	11
597	176 ±	15	-1.66	11
603	189	#	-0.76	11
607	209 ±	22.0	0.62	11
635	198 ±	16	-0.14	11
685	180	#	-1.38	11
690	198 ±	15.8	-0.14	11
<i>No of Results:</i>		36		
<i>Median:</i>		200.0		
<i>Normalised IQR:</i>		14.5		
<i>Uncertainty of the Median:</i>		3.0		
<i>Robust CV:</i>		7.2%		
<i>Minimum:</i>		166		
<i>Maximum:</i>		275		
<i>Range:</i>		109		

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

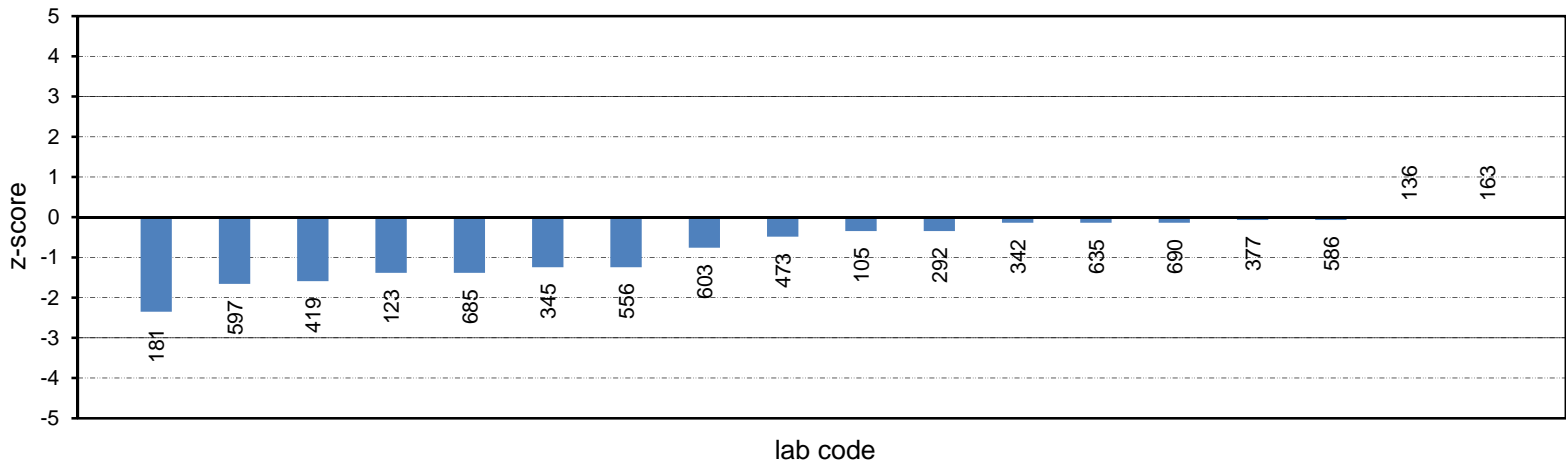
² "S" denotes an outlier (i.e. those results for which $|z\text{-score}| \geq 3.0$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where A is the participant laboratory's result.

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

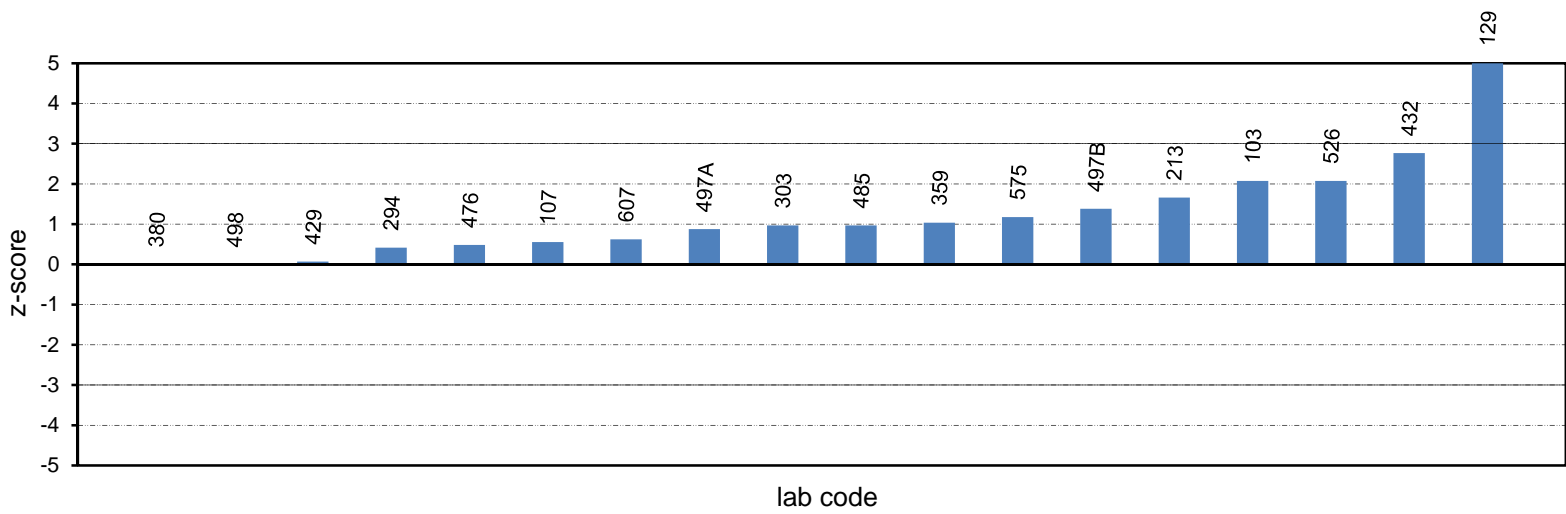
Total Dissolved Solids - Sample PTA 1

Ordered Robust Z-Score Charts

Total Dissolved Solids - Sample PTA 1 - Robust Z-Scores



Robust Z-Scores



Total Dissolved Solids (TDS)**Results by Laboratory Code**

Laboratory Code	Sample PTA 2			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
103	355 ±	35.5	3.77 §	11
105	306	#	0.41	11
107	319 ±	8.6	1.30	11
123	280 ±	30	-1.37	11
129	391 ±	6	6.24 §	11
136	304	#	0.27	11
163	320	#	1.37	11
181	302	#	0.14	11
213	314 ±	44	0.96	11
292	290 ±	4	-0.69	11
294	300 ±	15	0.00	11
303	318 ±	16	1.23	16
342	300 ±	8.8%	0.00	11
345	277 ±	27.7	-1.58	15
359	321	#	1.44	11
377	288 ±	13.6	-0.82	11
380	293	#	-0.48	11
419	280 ±	25	-1.37	12
429	298.5	#	-0.10	11
432	292	#	-0.55	11
473	298 ±	29.8	-0.14	11
476	302 ±	21	0.14	11
485	285 ±	23.1	-1.03	11
497A	310.9 ±	23.0	0.75	11
497B	295.0 ±	21.8	-0.34	11
498	294 ±	29	-0.41	11
526	314 ±	62.8	0.96	11
556	312	#	0.82	11
575	310 ±	62	0.69	11

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

² "§" 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.

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

Total Dissolved Solids (TDS) - cont.**Results by Laboratory Code**

Laboratory Code	Sample PTA 2			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
586	280 ±	20	-1.37	11
597	282 ±	20	-1.23	11
603	302	#	0.14	11
607	309 ±	32	0.62	11
635	298 ±	24	-0.14	11
685	285	#	-1.03	11
690	297 ±	23.8	-0.21	11
<i>No of Results:</i>		36		
<i>Median:</i>		300.0		
<i>Normalised IQR:</i>		14.6		
<i>Uncertainty of the Median:</i>		3.0		
<i>Robust CV:</i>		4.9%		
<i>Minimum:</i>		277		
<i>Maximum:</i>		391		
<i>Range:</i>		114		

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

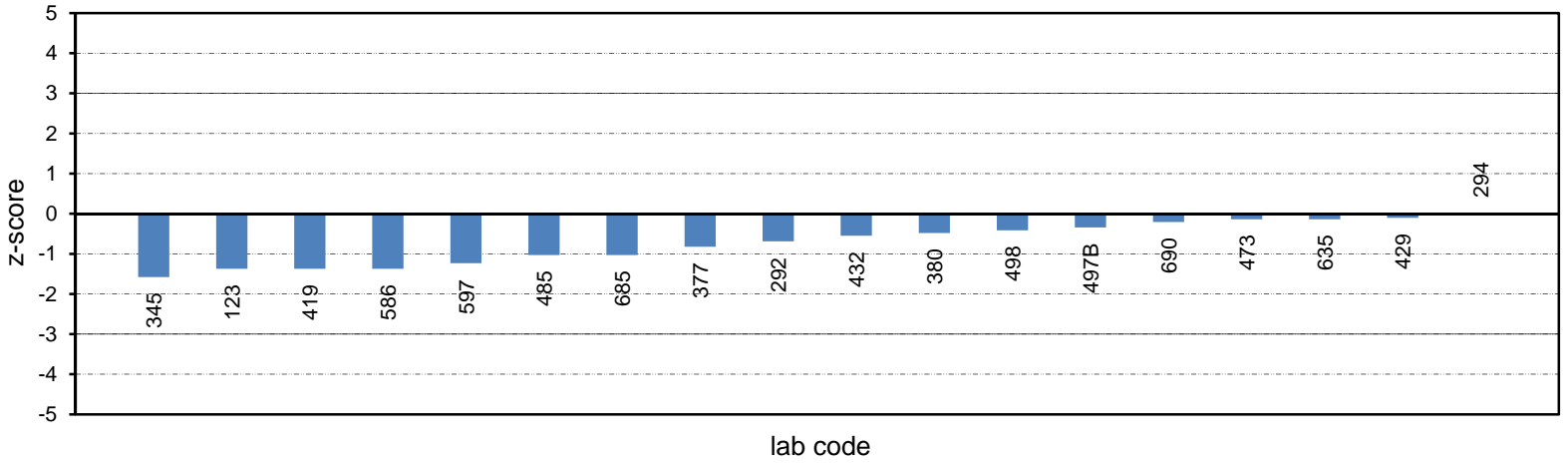
² "S" denotes an outlier (i.e. those results for which $|z\text{-score}| \geq 3.0$). Robust z-scores are calculated as: $z = (A - \text{median}) \div \text{normalised IQR}$, where A is the participant laboratory's result.

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

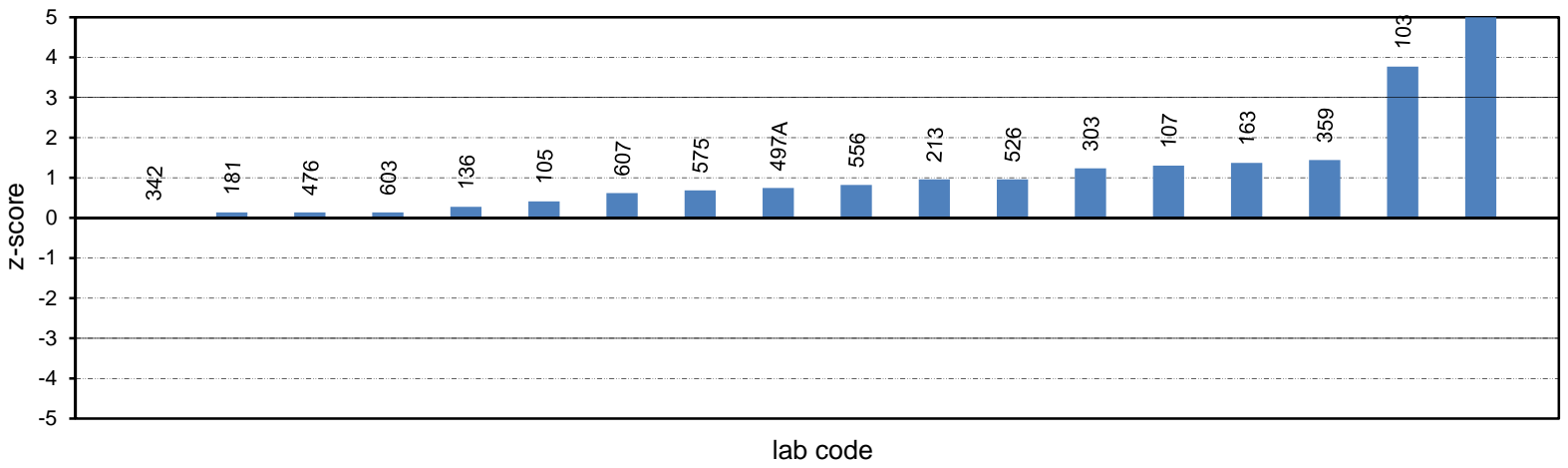
Total Dissolved Solids - Sample PTA 2

Ordered Robust Z-Score Charts

Total Dissolved Solids - Sample PTA 2 - Robust Z-Scores



Robust Z-Scores



APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing..... B1

Homogeneity and Stability Testing

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

Samples were manufactured from two solutions which formed a precipitate in the bottle. A random selection of ten samples was chosen from samples PTA 1 and PTA 2 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 by Global Proficiency Ltd, using the conductivity method for dissolved solids.

Based on the known composition, manufacturing procedure and the direct relationship between TDS, TSS and TS, homogeneity and stability were inferred for TSS and TS based on the TDS results. All stability samples showed no increased variability when compared to the chilled samples.

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 Table B1 below. Please note that the mean results for these tests are not intended to be used as reference values.

Table B1. Homogeneity testing of Round 206 samples.

Round PTA 206	Total Dissolved Solids (TDS)			
	Samples PTA 1 (mg/L)		Samples PTA 2 (mg/L)	
	Duplicate (a)	Duplicate (b)	Duplicate (a)	Duplicate (b)
H1	190.6	190.4	240	238
H2	191.8	191.2	242	240
H3	190.0	191.4	241	239
H4	192.0	192.2	241	237
H5	191.6	189.2	240	239
H6	190.0	189.2	240	242
H7	190.6	190.2	240	240
S1	189.8	190.2	238	234
S2	190.8	190.6	237	234
S3	189.6	190.8	236	239
RSD	0.45%	0.49%	0.81%	1.07%

APPENDIX C

Documentation

Instructions to Participants	C1
Method Codes	C3
Results Sheet	C4



PROFICIENCY TESTING AUSTRALIA
WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 206

DECEMBER, 2016

Total Solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS)

INSTRUCTIONS TO PARTICIPANTS

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

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

1. Samples

- i) Two plastic bottles labelled PTA 1 and PTA 2, supplied by Global Proficiency Ltd. The bottles contain 20 mL of artificial water concentrates for analysis of total solids, total suspended solids and total dissolved solids.
- ii) Each bottle will require dilution in reagent grade water. Please follow the Sample Preparation section below.
- iii) The bottles must be thoroughly mixed prior to analysis

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

2. Sample Preparation

Note: The Residue sample colour is white.

Caution: Analysis must begin immediately after bottle is opened.

- i) A separate sample must be prepared from each bottle.
- ii) Adjust bottle temperature to 20°C.
- iii) Add approximately 800 mL of reagent grade water to a one-litre volumetric flask.
- iv) Record bottle ID number and mix thoroughly.
- v) Quantitatively transfer the entire contents from the bottle into the flask, rinse the sides of the bottle with reagent grade water and include this in the flask.
- vi) Bring to volume with reagent grade water.
- vii) Close the flask with a stopper and mix by inversion.
- viii) Repeat steps ii) – vii) for second sample.

Please report results for the diluted sample.

3. Tests Requested

For the samples prepared from the two bottles PTA 1 and PTA 2:

- i) Total Solids (TS).
- ii) Total Suspended Solids (TSS).
- iii) Total Dissolved Solids (TDS).

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

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

4. Safety

- i) Samples are for laboratory use only.
- ii) Participants should have sufficient experience and training to take the necessary precautions when handling the samples and reagent chemicals and during disposal.
- iii) Use of safety glasses, gloves, and fume hoods, where appropriate during the determinations, is recommended.

5. Reporting

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

6. Testing should commence as soon as possible after receiving the samples and results reported **NO LATER THAN 13 JANUARY 2017** to:

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

7. For this program your laboratory has been allocated the code number shown on the attached Results Sheet. All reference to your laboratory in reports associated with the program will be through this code number, thus ensuring the confidentiality of your results.
8. As a guide, ranges for the samples can be expected to be (in mg/L):

Analyte	Range
Total Solids	140 – 675 mg/L
Total Suspended Solids	20 – 250 mg/L
Total Dissolved Solids	140 – 650 mg/L

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Total Solids	APHA SM	2540 B. Total Solids Dried at 103–105°C	1
	US EPA	0160.3 Residue, Total. Dried at 103–105°C	2
	AS	3550.4 Waters - Determination of solids - Gravimetric method	3
	Other	Calculation: Suspended + Dissolved	4
		Other (please specify)	5
Total Suspended Solids	APHA SM	2540 D. Total Suspended Solids Dried at 103–105°C	6
	AS	3550.4 Waters - Determination of solids - Gravimetric method	7
	ASTM	D5907 Standard Test Methods for Filterable Matter	8
	US EPA	0160.2 Residue, Non-Filterable & Total Suspended Solids Dried at 103–105°C	9
	Other	Other (please specify)	10
Total Dissolved Solids	APHA SM	2540 C. Total Dissolved Solids Dried at 180°C	11
	AS	3550.4 Waters - Determination of solids - Gravimetric method	12
	ASTM	D5907 Standard Test Methods for Filterable Matter	13
	US EPA	0160.1 Residue, Filterable. Dried at 180°C	14
	Other	Calculation: Total – Suspended	15
		Conductivity	16
Other (please specify)		17	

Method Reference Key

- i) APHA SM APHA “*Standard Methods for the Examination of Water and Wastewater*” (18, 19, 20, 21 and 22 Edition).
- ii) USEPA U.S Environmental Protection Agency,
<http://www.epa.gov/osa/fem/methcollectns.htm>.
- iii) AS Australian Standard www.standards.org.au
- iv) ASTM ASTM International www.astm.org



PROFICIENCY TESTING AUSTRALIA
WATERS PROFICIENCY TESTING PROGRAM
CHEMICAL ANALYSIS ROUND 206

Total Solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS)
DECEMBER, 2016

RESULTS SHEET
(mg/L)

Laboratory
Code

*Approximate temperature of samples upon receipt:

ANALYSIS	SAMPLE PTA 1		SAMPLE PTA 2		METHOD CODE
	Result (mg/L)	±MU (mg/L)	Result (mg/L)	±MU (mg/L)	
Total Solids Dried at 103–105°C					
Total Suspended Solids Dried at 103–105°C					
Total Dissolved Solids Dried at 180°C					

Please state: Brand of filter used _____

Nominal pore size _____ Diameter _____

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

- i) For each sample only a single result is requested.
- ii) Report results using three significant figures.
- iii) Report results in milligrams per litre (mg/L).
- iv) Do not correct results for recovery.
- v) MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in mg/L, using the same number of decimal places as for the result.

DATE: _____

SIGNATURE: _____

Return results NO LATER THAN 13 JANUARY 2017 to:	
Delfina Mihaila	
Proficiency Testing Australia	
PO Box 7507	Phone: +61 2 9736 8397
SILVERWATER NSW 2128	Fax: +61 2 9743 6664
AUSTRALIA	Email: dmihaila@pta.asn.au

INSTRUCT WATERS PROF TEST PROG 206

- End of Report -