

Report No. 1181

Waters Proficiency Testing Program

Round No. 253

***- Total Biochemical Oxygen Demand,
Carbonaceous Biochemical Oxygen Demand,
Chemical Oxygen Demand,
Total Organic Carbon -***

March 2020

Acknowledgments

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

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1. Foreword

This report summarises the results of a proficiency testing program on the determination of Total Biochemical Oxygen Demand (TBOD5), Carbonaceous Biochemical Oxygen Demand (CBOD5), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) in waters. This is round 253 in a planned series of programs involving the analysis of chemical and physical parameters of waters. This program is accredited to ISO/IEC 17043:2010 "*Conformity assessment - General requirements for proficiency testing*" by International Accreditation New Zealand (IANZ).

The exercise was conducted in November 2019 by Proficiency Testing Australia (PTA). The main aim of the program was to assess laboratories' abilities to competently perform the prescribed analyses.

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

2. Program Features and Design

- 2.1 Each laboratory was randomly allocated a unique code number for the program to ensure confidentiality of results. Reference to each laboratory in this report is by code number only.
- 2.2 Laboratories were provided with the "Instructions to Participants" and "Results Sheet" (see Appendix C). Laboratories were requested to perform the tests according to their routine methods.
- 2.3 Participants were provided with 2 vials (labelled PTA 1 and PTA 2) for analysis of Total Biochemical Oxygen Demand (TBOD5), Carbonaceous Biochemical Oxygen Demand (CBOD5), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC).
- 2.4 A total of 18 laboratories received samples, comprising:
 - 12 Australian participants; and
 - 6 overseas participants, including:
 - Brunei Darussalam (1), Indonesia (1), Malaysia (1), Papua New Guinea (2), Singapore (1).

Of these 18 laboratories, one was unable to submit results by the due date.

- 2.5 Results (as reported by participants) with corresponding summary statistics (i.e. number of results, median, normalised interquartile range, uncertainty of the median, robust coefficient of variation, minimum, maximum and range) are presented in Appendix A (for each sample and for each of the analyses performed).
- 2.6 A robust statistical approach, using z-scores, was utilised to assess laboratories' testing performance (see Section 3). Robust z-scores and ordered z-score charts relevant to each test are presented in Appendix A.

The document entitled *Guide to Proficiency Testing Australia, 2019* (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 19.
- 2.8 Prior to sample distribution, a number of randomly selected samples were analysed for homogeneity and stability. Based on the results of this testing (see Appendix B) it was considered that the samples utilised for this program were homogeneous and stable. As such, any results later identified as outliers could not be attributed to any notable sample variability.

3. Statistical Format

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

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

3.1 Outlier Results and Z-scores

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

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

Each determination was examined for outliers with all methods pooled. The table on page 19 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, homogenous and stable.

Solutions were stable and homogenous (see Appendix B), and medians obtained from this proficiency round were similar to the expected levels 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 presented in Table 1.

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

Analysis	Sample	Expected Levels (mg/L)	Median (mg/L)	Uncertainty of the median mg/L [%]
Total Biochemical Oxygen Demand	PTA 1	41.3	39.75	3.36 [8.5%]
	PTA 2	26.3 CBOD + 76 mg/L urea	30.40	2.25 [7.4%]
Carbonaceous Biochemical Oxygen Demand	PTA 1	41.3	37.10	4.47 [12.1%]
	PTA 2	26.3	28.95	2.45 [8.5%]
Chemical Oxygen Demand	PTA 1	59	61.00	0.90 [1.6%]
	PTA 2	37.5	47.25	1.68 [3.6%]
Total Organic Carbon	PTA 1	27.8	25.00	0.30 [1.2%]
	PTA 2	33	38.00	1.30 [3.4%]

Compared to the previous round (Report 1144), the robust CVs were higher in this study for all analytes, and ranged between 4.7% for COD sample PTA1 and 23.6% for CBOD5 sample PTA 1. Please note that a target CV of 6.9% was used for TOC sample PTA 1, due to a reduced number of participants and small spread of results. The target CV was based on historical PTA data for TOC testing.

4.2 Analysis of Round 253 Results

4.2.1 Total Biochemical Oxygen Demand (TBOD5)

Table 2 compares the TBOD5 medians and robust CVs from this round to those obtained in previous PTA rounds. Robust CVs were higher compared with previous rounds, and compared with the Quality Control (QC) range set for the Glucose/Glutamic acid (GGA) reference solution used in the APHA 5210 B method (5-Day BOD Test), of 198.0 ± 30.5 mg/L (15.4%) [2].

Table 2. Comparison of current round variability and proficiency median of TBOD5 testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	39.75	21.3	10
	PTA 2	30.40	18.7	10
Report 1144	PTA 1	54.00	11.5	25
	PTA 2	27.75	9.7	24
Report 1088	PTA 1	47.00	15.8	25
	PTA 2	33.20	13.6	25

Bias / Accuracy

The TBOD5 testing satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 30.1 – 56.0 mg/L for sample PTA 1 and 25.7 – 38.0 mg/L for sample PTA 2.

Out of ten participants, one questionable result ($2.0 < |z\text{-score}| < 3.0$) was reported for sample PTA 1 (laboratory code 163) and one questionable result was reported for sample PTA 2 (laboratory code 479).

One outlier result ($|z\text{-score}| \geq 3.0$) was obtained for each of the samples PTA 1 and PTA 2, by the same laboratory (code 291); requiring follow-up.

For laboratories concerned with their results, consistently high values usually indicate the use of too much seed suspension or contaminated dilution water. Consistently low values can indicate poor seed quality or quantity, or the presence of a toxic material in the seed solution. If low values persist in the Glucose-glutamic acid check, it is recommended to prepare a new mixture of the check solution and determine if the sources of dilution water and seed organism are the cause [2].

Only sample PTA 2 contained Urea (76 mg/L) in addition to the carbon source, and there was negligible difference between the medians for CBOD and TBOD for their respective samples (PTA 1: CBOD = 37.1 mg/L, TBOD = 39.75 mg/L; PTA 2: CBOD = 28.95 mg/L, TBOD = 30.4 mg/L). Laboratories may wish to include ammonium salts (APHA 5210B.3i) in their QC procedures to determine if their seed organism is capable of satisfactory nitrification, in comparison to the $\text{NH}_4\text{-N}$ concentration [3]. Laboratories are also recommended to run GGA LFMD (Laboratory Fortified Matrix Duplicates) to determine if the pH of these slightly acid samples has affected the viability of their seed organisms.

Other possible sources of error include:

- Failure to adjust the pH to between 6.0 and 7.5;
- Incorrect dilutions;
- Failure to calibrate dissolved oxygen meters;
- Transcription errors;
- Contamination of dilution water;
- Evaporation of water seals during incubation;
- Seeding not used or seeds not properly activated; and
- High dissolved oxygen in blank due to algae growth in plastic tubing.

The TBOD5 data sets formed approximately normal distributions with no notable bias attributable to any one method (Figures 1 and 2). The method most frequently used for TBOD5 testing in this round was APHA 5210 B, which was used by 8 out of 10 participants. One laboratory used the Respirometric method APHA 5210 D and one laboratory used US EPA 0405.1 method (BOD 5-Days).

The majority of laboratories indicated that their measurement uncertainty (MU) was between 14% - 20%, with some values as low as 2.96 mg/L (5.1%) and some as high as 14 mg/L.

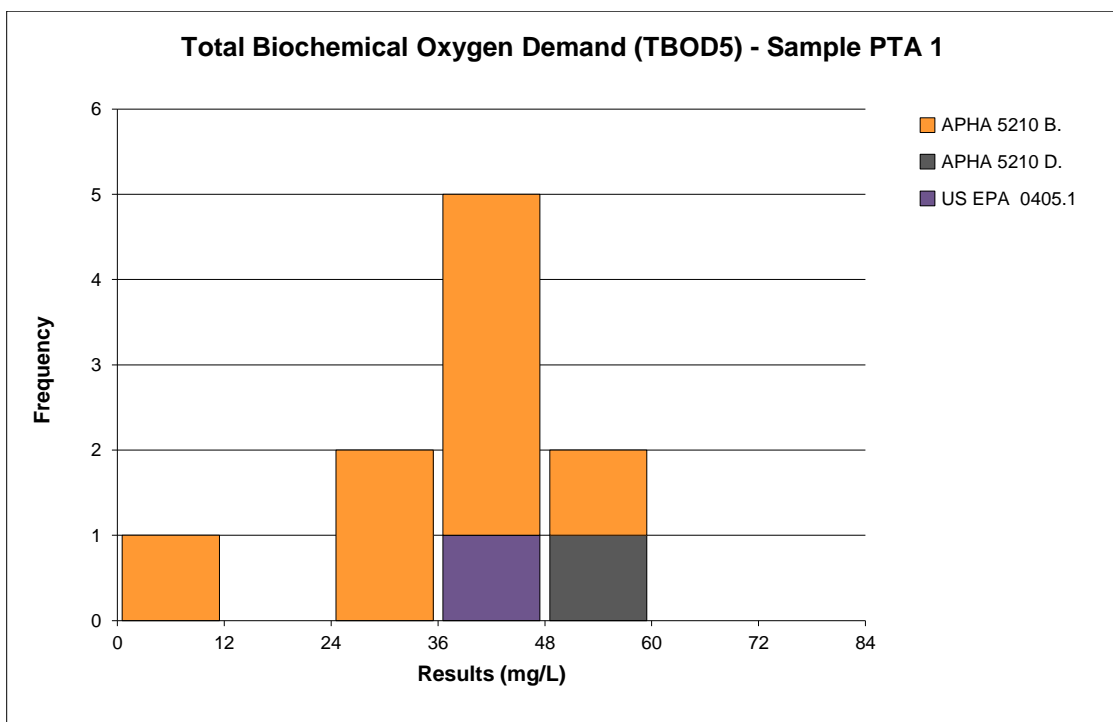


Figure 1. Spread of results for TBOD5 testing of sample PTA 1, with a median of 39.75 mg/L.

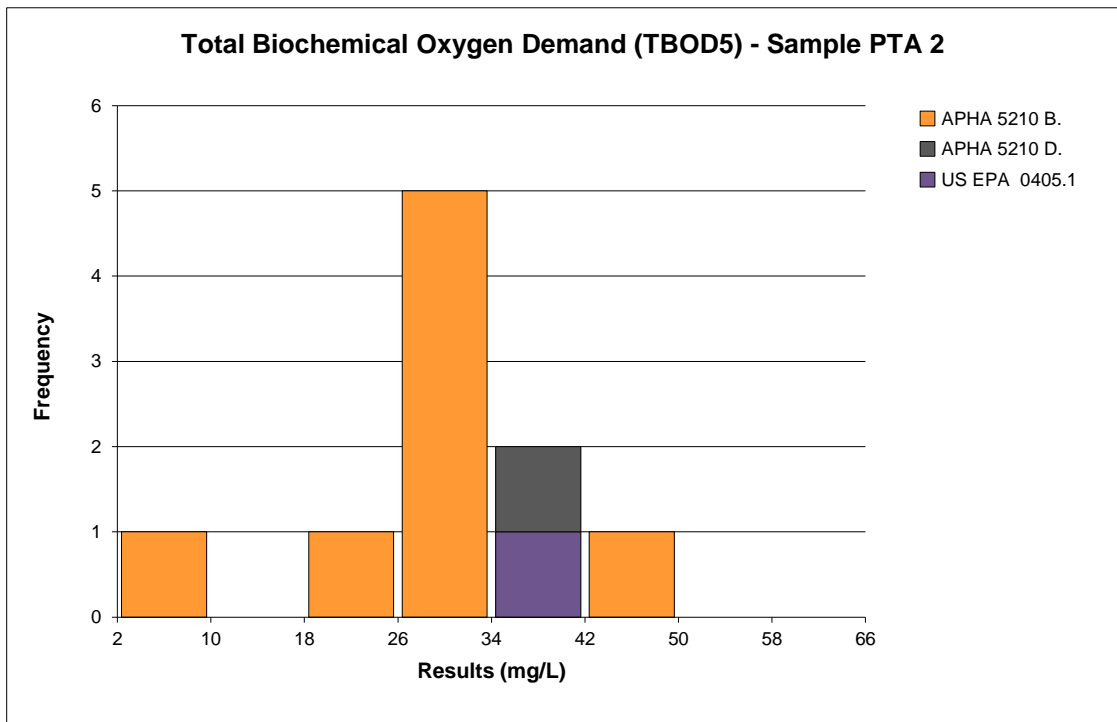


Figure 2. Spread of results for TBOD5 testing of sample PTA 2, with a median of 30.40 mg/L.

4.2.2 Carbonaceous Biochemical Oxygen Demand (CBOD5)

Table 3 compares the CBOD5 medians and robust CVs from this round to those obtained in previous PTA rounds. Robust CVs were higher compared with previous rounds, and compared with the Quality Control (QC) range set for the Glucose/Glutamic acid (GGA) reference solution used in the APHA 5210 B method (5-Day BOD Test), of 198.0 ± 30.5 mg/L (15.4%) [2].

Table 3. Comparison of current round variability and proficiency median of CBOD5 testing with the results of the previous two rounds.

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	37.10	23.6	6
	PTA 2	28.95	16.6	6
Report 1144	PTA 1	56.40	8.5	9
	PTA 2	26.50	9.2	9
Report 1088	PTA 1	48.80	11.2	10
	PTA 2	33.15	12.4	10

Bias / Accuracy

The CBOD5 satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 33 – 51.1 mg/L for sample PTA 1 and 25.5 – 31 mg/L for sample PTA 2.

Out of six participants, no questionable results ($2.0 < |z\text{-score}| < 3.0$) were reported for either of samples PTA 1 and PTA 2.

One outlier result ($|z\text{-score}| \geq 3.0$) was obtained for sample PTA 1, requiring follow-up action by laboratory code 232. For sample PTA 2, two outlier results were obtained, requiring follow-up action by laboratory codes 232 and 479.

For laboratories concerned with low biasing results, APHA 5210 B.5.e recommends not adding the nitrification inhibitor until the BOD bottle is at least two-thirds filled with diluted sample, and to be aware that TCMP dissolves slowly and can float on top of the sample if not mixed well. Also, due to the artificial nature of these samples (required to achieve homogeneity and stability) and subsequent dilutions required, nutrients may be limited, which can reduce biological activity. In these cases, APHA recommends adding the nutrient, mineral and buffer solutions (5210 B.3.a-e) directly to the diluted sample at a rate of 1mL/L (0.3 mL/300mL bottle).

Consistently high biasing results could indicate that nitrification has occurred, thus the inhibitor may have been inadvertently omitted, added at an incorrect concentration, or ineffective at inhibiting nitrification within the 5-day incubation period [2].

Figures 3 and 4 present the spread of results and the methods used for CBOD5 testing. The method most frequently used for CBOD5 testing in this round was APHA 5210 B with TCMP inhibitor, which was used by 5 out of 6 participants. One laboratory used the method HACH 8043.

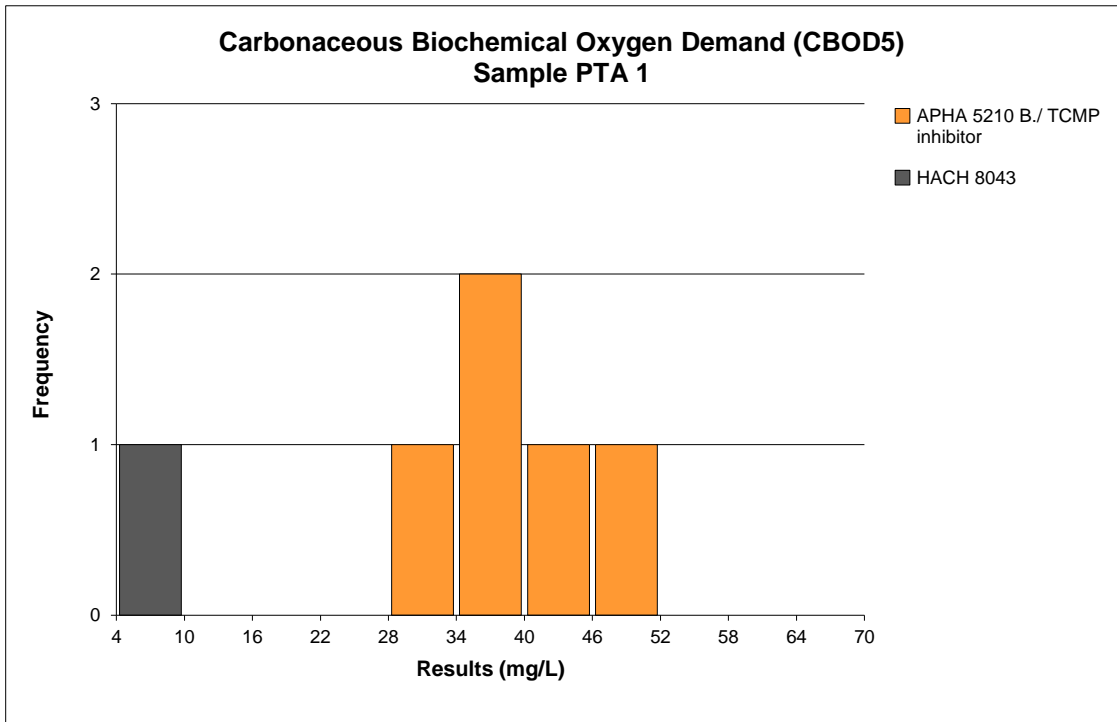


Figure 3. Spread of results for CBOD5 testing of sample PTA 1, with a median of 37.10 mg/L.

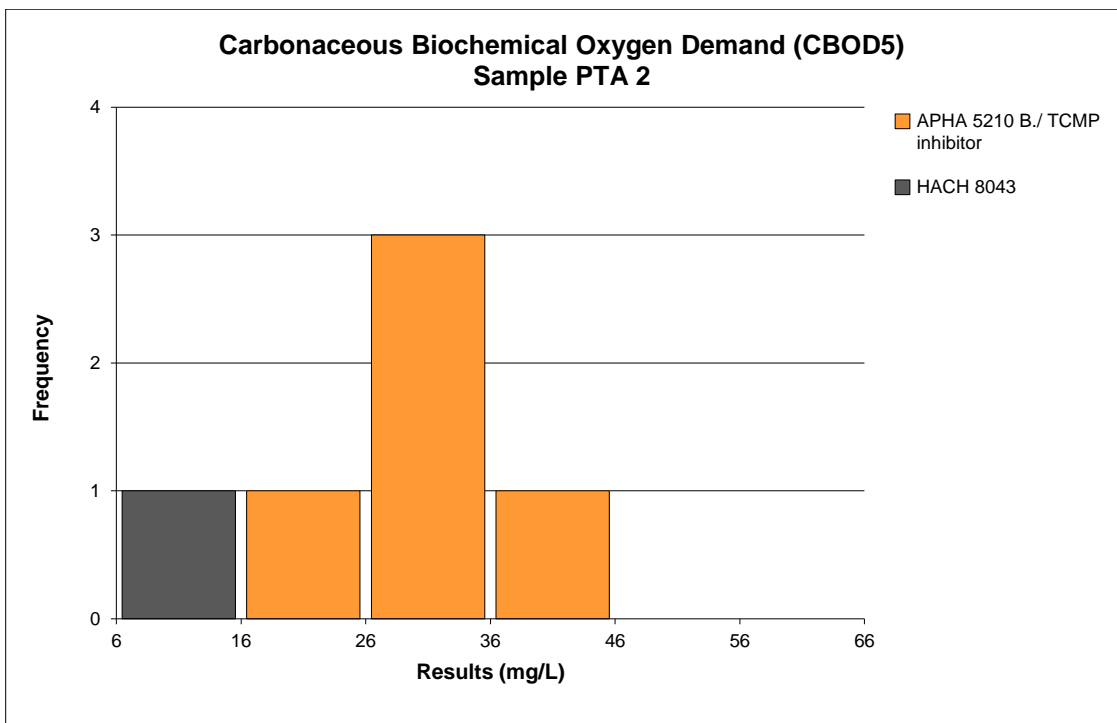


Figure 4. Spread of results for CBOD5 testing of sample PTA 2, with a median of 28.95 mg/L.

The majority of laboratories indicated that their MU was between 5 mg/L (16%) - 10 mg/L (32%).

4.2.3 Chemical Oxygen Demand (COD)

Table 4 compares the COD medians and robust CVs from this round to those obtained in previous PTA rounds. The CVs were comparable to APHA published precision information which indicated CVs of between 8.7% - 9.6% could be expected for the Closed Reflux Colorimetric method (APHA 5220 D). Closed Reflux Titrimetric method (APHA 5220 C) expected CVs of 4.8% - 5.6%, and the Open Reflux method (APHA 5220 B) indicated CVs of 6.5% - 10.8% could be expected [2].

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

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	61.00	4.7	16
	PTA 2	47.25	11.4	16
This study	PTA 1	83.75	5.5	30
	PTA 2	42.50	9.4	29
Report 1088	PTA 1	76.50	9.6	28
	PTA 2	53.25	12.0	28

Bias / Accuracy

The COD testing was successfully performed, with satisfactory results ($|z\text{-score}| \leq 2.0$) ranging between 57.3 – 64.0 mg/L for sample PTA 1 and 40 – 58.0 mg/L for sample PTA 2.

Out of 16 participants, one questionable result ($2.0 < |z\text{-score}| < 3.0$) was reported for sample PTA 1 (laboratory code 552) and one questionable result was reported for sample PTA 2 (laboratory code 132).

Three outlier results ($|z\text{-score}| \geq 3.0$) were obtained for sample PTA 1, requiring follow-up action by laboratory codes 163, 310 and 479. No outlier results were obtained for sample PTA 2.

As both samples PTA 1 and PTA 2 had COD levels $< 100\text{mg/L}$, laboratories using APHA 5220 D Colorimetric method would have needed to determine the decrease in $\text{Cr}_2\text{O}_7^{2-}$ at 420 nm (instead of 600 nm); and compensate for the small Cr^{3+} absorption increase, in their calibration procedure. They would also have needed to use the 'low range' digestion solution which contained only 1.022 g potassium dichromate in the acid solution. Laboratories using the titrimetric method would have needed to use a more dilute dichromate digestion solution or a more dilute FAS titrant than the standard solutions in APHA 5220 C.

Other possible sources of error include:

- Contamination of deionised water (organic material from deioniser resin column);
- Incorrect grade of potassium dichromate (primary standard grade required) (APHA 5220 D);

- Incompletely dried potassium dichromate (requires 150°C for 2 hours) (APHA 5220 D);
- Breaks in culture-tube TFE liner (APHA 5220 C);
- Use of too small culture-tube. Recommended 25x150 mm culture-tube for samples with low COD, to enable treatment of a larger volume of sample. Alternatively the titrations could be done in a separate vessel, rather than in the digestion vessel, due to the volumes of titrant required (APHA 5220 C);
- Transcription errors;
- Calculation errors; and
- Contamination from glassware not properly cleaned.

For further information on quality control in COD testing, please refer to section 5020 B in APHA Standard Methods with respect to use of quality control samples, method blanks, laboratory-fortified blanks, matrices and duplicates.

The COD data sets formed approximately normal distributions with no notable bias attributable to any one method (Figures 5 and 6). The largest proportion of laboratories (8 laboratories out of 16) used the colorimetric method APHA 5220 D for analysis of COD, followed by HACH 8000 (3 laboratories). Methods APHA 5220 C (Closed Reflux, Titrimetric) and APHA 5220 B (Open Reflux method) were each used by 2 laboratories.

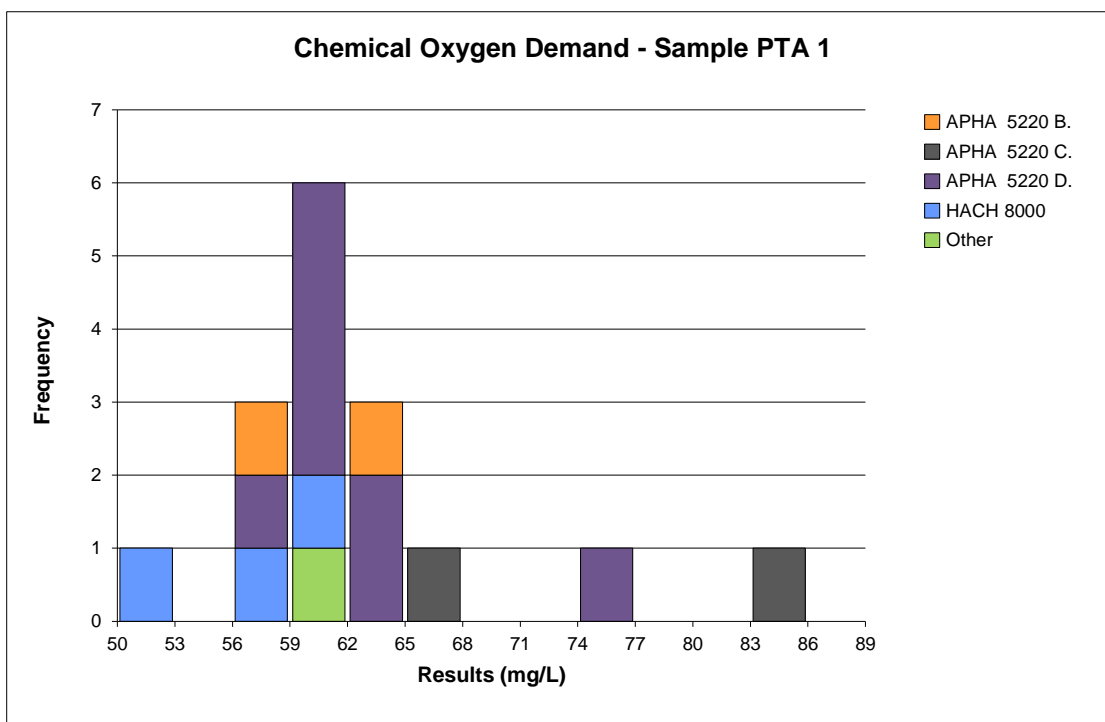


Figure 5. Spread of results for COD testing of sample PTA 1, with a median of 61.00 mg/L.

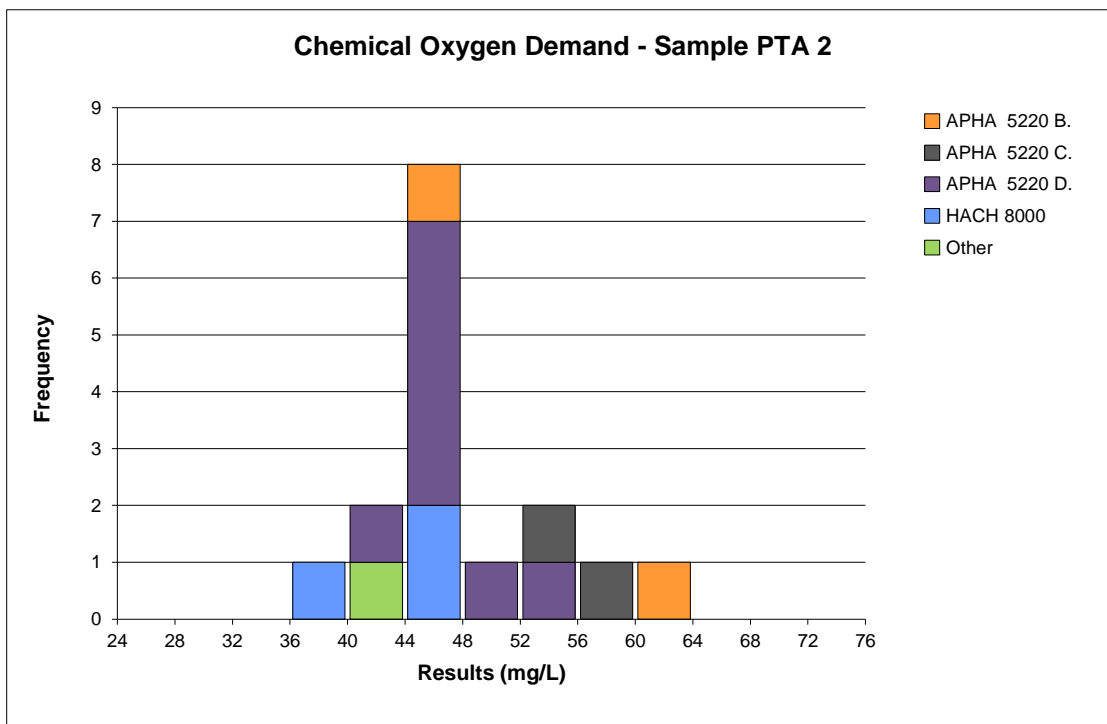


Figure 6. Spread of results for COD testing of sample PTA 2, with a median of 47.25 mg/L.

The majority of laboratories shown in Figures 7 and 8, had a good understanding of their MU, which predominantly ranged between 5% - 17%, and was comparable to the published precision data mentioned previously. If laboratory codes 132, 163, 310, and 479 find that their MU does not encompass the median or its uncertainty in successive proficiency rounds, they may wish to reassess their MU, incorporating their proficiency results and reference material testing in their statistical MU calculations (Eurachem 2012 [4]).

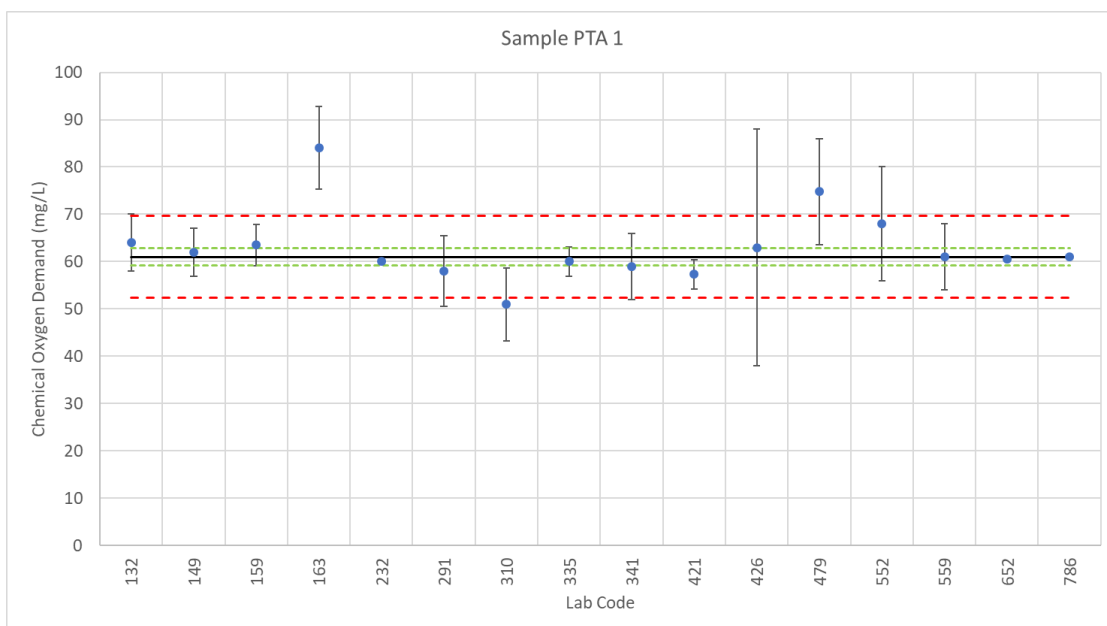


Figure 7. Spread of results for COD testing of sample PTA 1, with MU error bars for each laboratory result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

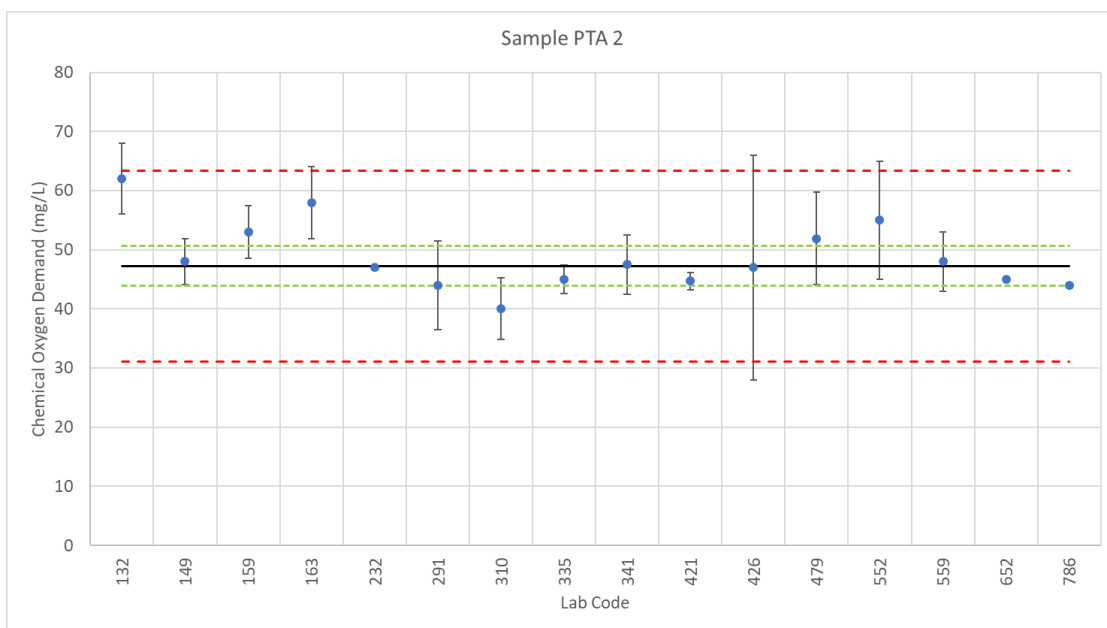


Figure 8. Spread of results for COD testing of sample PTA 2, with MU error bars for each laboratory result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

Laboratory code 426 indicated a much larger MU than the other laboratories participating in this round ($\pm 40\%$) and may have overestimated the uncertainty of their result.

4.2.4 Total Organic Carbon (TOC)

Table 5 compares the TOC median and robust CV from this round to those obtained in previous PTA rounds. Laboratories performed well, with the robust CVs comparable to previous rounds, and to published precision information, which indicated that laboratories should be able to achieve CVs of 5-10% for APHA 5310 B the high temperature combustion method, or between 8.3-8.5% for APHA 5310 C the Persulfate Oxidation Method [2].

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

Round	Sample	Median (mg/L)	Robust CV (%)	Participants
This study	PTA 1	25.00	6.9	7
	PTA 2	38.00	7.2	7
Report 1144	PTA 1	32.40	5.4	18
	PTA 2	16.60	3.6	17
Report 1088	PTA 1	29.22	6.4	14
	PTA 2	19.45	4.9	14

Bias / Accuracy

The TOC satisfactory results ($|z\text{-score}| \leq 2.0$) ranged between 23.6 – 27.6 mg/L for sample PTA 1 and 37.6 – 43.5 mg/L for sample PTA 2.

Out of seven participants, no questionable results ($2.0 < |z\text{-score}| < 3.0$) were reported for either of the samples PTA 1 and PTA 2.

One outlier result ($|z\text{-score}| \geq 3.0$) was obtained for sample PTA 1, requiring follow-up action by laboratory code 232. For samples PTA 2, two outlier results were obtained, requiring follow-up action by laboratory codes 163 and 232.

Please note that a target CV of 6.9% was used for TOC sample PTA 1, due to a reduced number of participants and small spread of results. The target CV was based on historical PTA data for TOC testing.

Possible sources of error include:

- Calibration standards;
- Incorrect dilutions;
- Contaminated glassware, plastic containers and rubber tubing;
- Loss or gain of carbon containing compounds on the filter (analyse sample treatment such as a filtered blank, system and reagent blanks);
- Accumulation of non-volatile residues in the analyser (APHA 5310 B)
- Gases evolved from combustion, such as water, halide compounds, and nitrogen oxides may interfere with the detection system, requiring scrubber materials;
- Minimise errors by using reagent water and reagents low in carbon.
- Transcription errors; and
- Instrument malfunctions.
- For additional QC see APHA Table 5020:I and 5310 B.4.c-d, 5 & 6.

Figures 9 and 10 present the spread of results and the methods used for TOC testing in this round. Laboratories used APHA 5310 B (high temperature combustion), APHA 5310 C (persulphate oxidation) or GE Analytical Instruments methods for analysis of TOC in this round.

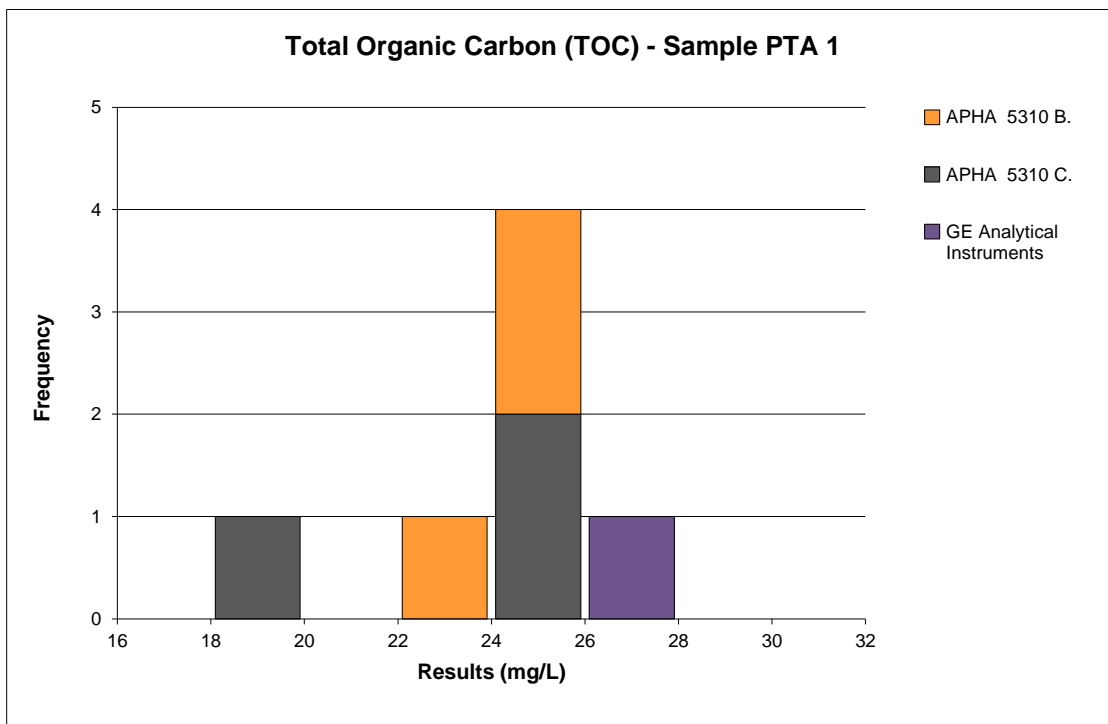


Figure 9. Spread of results for TOC testing of sample PTA 1, with a median of 25.00 mg/L.

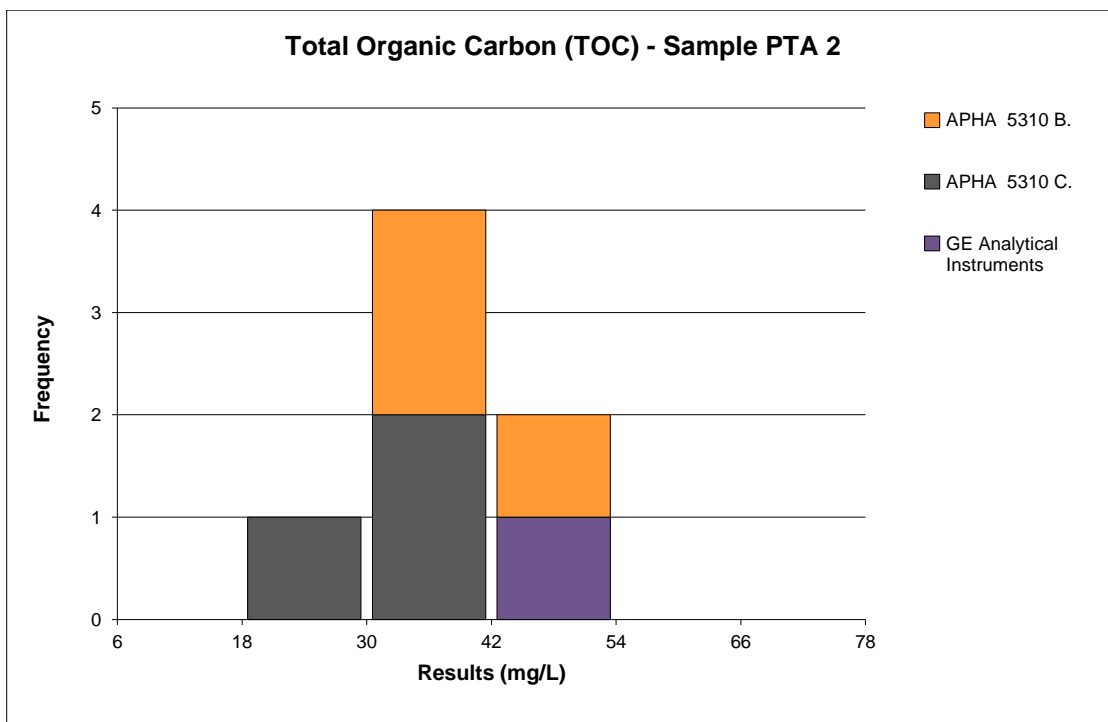


Figure 10. Spread of results for TOC testing of sample PTA 2, with a median of 38.00 mg/L.

Figures 11 and 12 show that the majority of laboratories indicated that their MU was between 3% - 12%. If laboratory code 163 finds that their MU does not encompass the median for both samples in successive proficiency rounds, they may wish to reassess their MU, incorporating their proficiency results and reference material testing in their statistical MU calculations (Eurachem 2012 [4]).

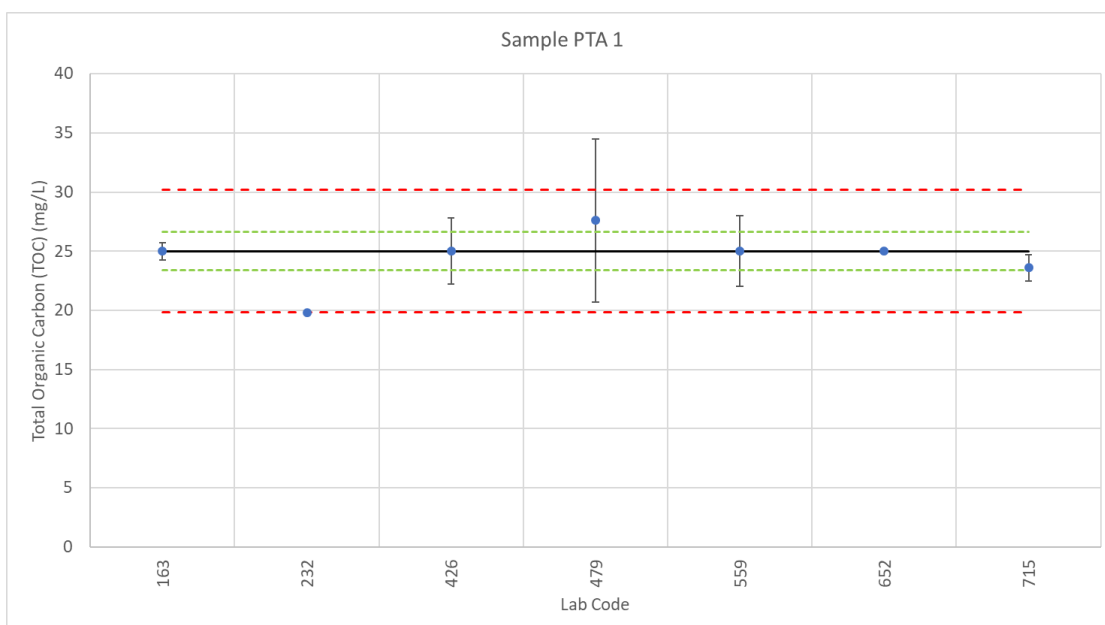


Figure 11. Spread of results for TOC testing of sample PTA 1, with MU error bars for each laboratory result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

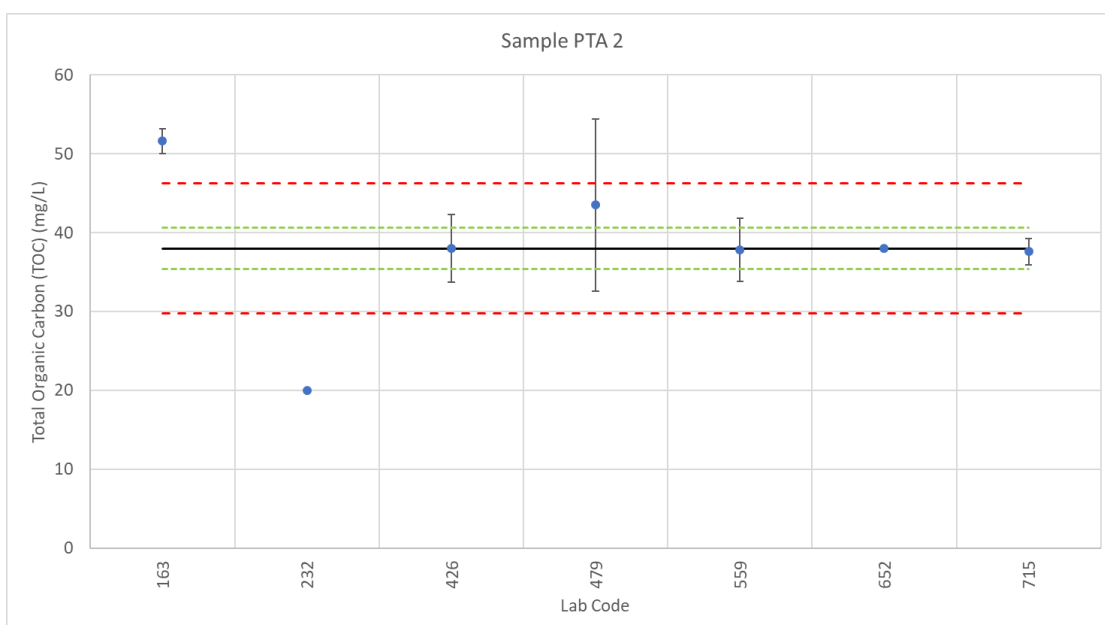


Figure 12. Spread of results for TOC testing of sample PTA 2, with MU error bars for each laboratory result, 3x NIQR [- - -], and the uncertainty of the median [- - -].

Laboratory code 479 indicated a measurement uncertainty ($\pm 25\%$) much wider than the other participants.

4.3 Measurement Uncertainty (MU)

The majority of participants in this round (67%-81%) reported the measurement uncertainty (MU) associated with their results. Table 6 below presents the number and percentage of laboratories reporting the MU for each analyte.

Table 6. The number and percentage of laboratories reporting MU for analytes in round 253

Analyte	Sample	Total participants	Participants reporting MU (percentage)
Total Biochemical Oxygen Demand	PTA 1	10	8 (80%)
	PTA 2	10	8 (80%)
Carbonaceous Biochemical Oxygen Demand	PTA 1	6	4 (67%)
	PTA 2	6	4 (67%)
Chemical Oxygen Demand	PTA 1	16	13 (81%)
	PTA 2	16	13 (81%)
Total Organic Carbon	PTA 1	7	5 (71%)
	PTA 2	7	5 (71%)

Some laboratories may have notably underestimated their MU, as they indicated that their MU was less than two times the uncertainty of the median (see Table 1), and 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

¹ MU evaluation is based on minimum / maximum uncertainty criteria (u_{min} and u_{max}) described in ISO 13528:2015 [5]. It should be noted, however, that these are informative indicators only and cannot be solely used to validate or invalidate the MUs reported.

4.4 Analysis of Results by Method Groups

In order for methods to be grouped for analysis, PTA requires at least 11 sets of results from the same method group. As there were less than 11 results submitted for each method, reliable conclusions cannot be drawn from analysing grouped methods on this occasion. Therefore, results from all method groups have been pooled for analysis.

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 7 below.

Table 7. Laboratory results identified as outliers for each analysis performed.

Lab Code	Analysis							
	Total Biochemical Oxygen Demand (TBOD5)		Carbonaceous Biochemical Oxygen Demand (CBOD5)		Chemical Oxygen Demand (COD)		Total Organic Carbon (TOC)	
	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2	PTA 1	PTA 2
163					§			§
232			§	§			§	§
291	§	§						
310					§			
479				§	§			

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*, 2019 (This document can be found on the PTA website, www.pta.asn.au).
- [2] *Standard Methods For the Examination of Water and Wastewater*, 2017. Published by APHA, AWWA, WEF (23rd Edition).
- [3] Hill Laboratories Technical Note (2019). *BOD Testing (Biochemical Oxygen Demand)*, KB Item: 4072, Version: 4. <https://www.hill-laboratories.com>
- [4] EURACHEM / CITAC Guide CG 4 (2012). *Quantifying Uncertainty in Analytical Measurement*; S. Ellison & A. Williams (Eds), Third Edition, Section 7.8, pg 20. https://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf
- [5] ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons*.

APPENDIX A

Results and Data Analysis

Total Biochemical Oxygen Demand (TBOD5)	A1
Carbonaceous Biochemical Oxygen Demand (CBOD5)	A5
Chemical Oxygen Demand (COD)	A9
Total Organic Carbon (TOC)	A13

Total Biochemical Oxygen Demand (TBOD5) Results

Samples PTA 1 and PTA 2

Total Biochemical Oxygen Demand (TBOD5)

Results by Laboratory Code

Laboratory Code	Sample PTA 1																			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³																
159	45.56 ±	6.5	0.68	3																
163	58.0 ±	2.96	2.15	2																
291	3.0 ±	14.0	-4.33 §	1																
310	34 ±	6.8	-0.68	1																
341	43.1 ±	10	0.39	1																
421	30.1 ±	3.10	-1.14	1																
426	41 ±	8.2	0.15	1																
479	56.0 ±	11.2	1.92	1																
652	38.5	#	-0.15	1																
786	38.0	#	-0.21	1																
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding-right: 10px;"><i>No of Results:</i></td> <td style="text-align: center;">10</td> </tr> <tr> <td style="padding-right: 10px;"><i>Median:</i></td> <td style="text-align: center;">39.75</td> </tr> <tr> <td style="padding-right: 10px;"><i>Normalised IQR:</i></td> <td style="text-align: center;">8.49</td> </tr> <tr> <td style="padding-right: 10px;"><i>Uncertainty of the Median:</i></td> <td style="text-align: center;">3.36</td> </tr> <tr> <td style="padding-right: 10px;"><i>Robust CV:</i></td> <td style="text-align: center;">21.3%</td> </tr> <tr> <td style="padding-right: 10px;"><i>Minimum:</i></td> <td style="text-align: center;">3.0</td> </tr> <tr> <td style="padding-right: 10px;"><i>Maximum:</i></td> <td style="text-align: center;">58.0</td> </tr> <tr> <td style="padding-right: 10px;"><i>Range:</i></td> <td style="text-align: center;">55.0</td> </tr> </table>					<i>No of Results:</i>	10	<i>Median:</i>	39.75	<i>Normalised IQR:</i>	8.49	<i>Uncertainty of the Median:</i>	3.36	<i>Robust CV:</i>	21.3%	<i>Minimum:</i>	3.0	<i>Maximum:</i>	58.0	<i>Range:</i>	55.0
<i>No of Results:</i>	10																			
<i>Median:</i>	39.75																			
<i>Normalised IQR:</i>	8.49																			
<i>Uncertainty of the Median:</i>	3.36																			
<i>Robust CV:</i>	21.3%																			
<i>Minimum:</i>	3.0																			
<i>Maximum:</i>	58.0																			
<i>Range:</i>	55.0																			

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.

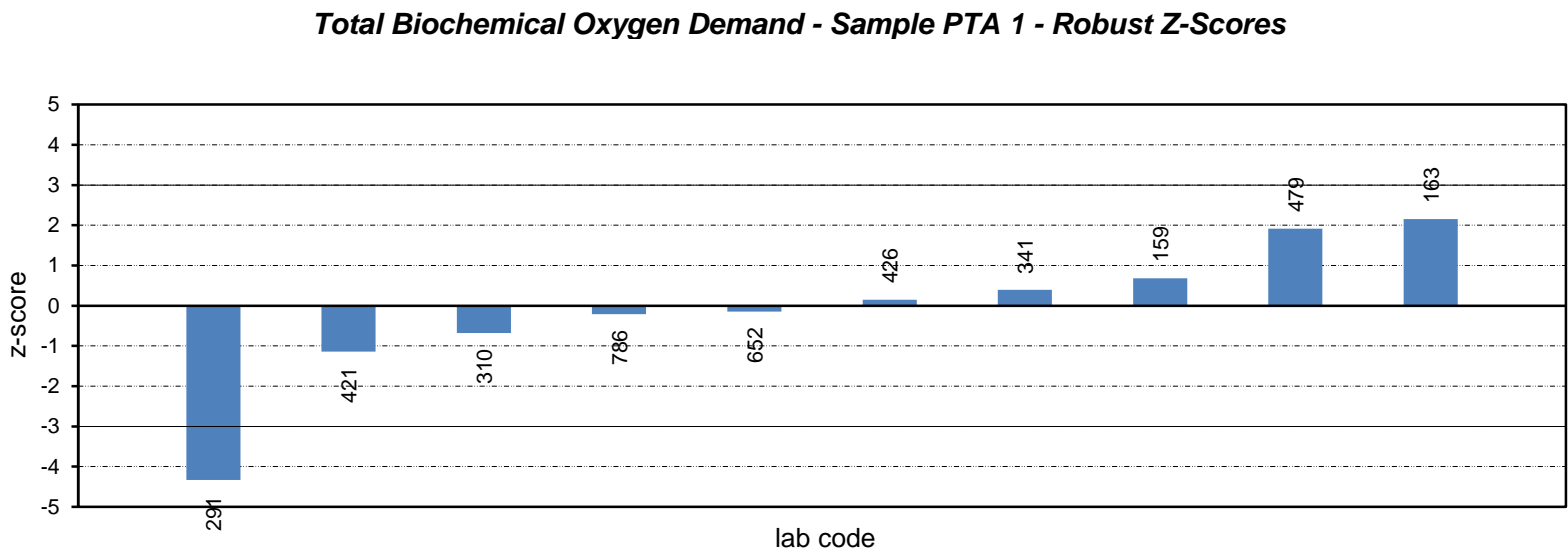
³ Please refer to Appendix C (pages C4-C5) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Total Biochemical Oxygen Demand - Sample PTA 1

Ordered Robust Z-Score Charts



Robust Z-Scores

Total Biochemical Oxygen Demand (TBOD5)

Results by Laboratory Code

Laboratory Code	Sample PTA 2																			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³																
159	37.4 ±	5.3	1.23	3																
163	38.0 ±	2.03	1.34	2																
291	5.0 ±	14.0	-4.48 §	1																
310	31 ±	6.2	0.11	1																
341	30.8 ±	10	0.07	1																
421	29.6 ±	3.10	-0.14	1																
426	30 ±	6.0	-0.07	1																
479	45.5 ±	9.1	2.66	1																
652	29.0	#	-0.25	1																
786	25.7	#	-0.83	1																
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding-right: 20px;"><i>No of Results:</i></td> <td>10</td> </tr> <tr> <td style="padding-right: 20px;"><i>Median:</i></td> <td>30.40</td> </tr> <tr> <td style="padding-right: 20px;"><i>Normalised IQR:</i></td> <td>5.67</td> </tr> <tr> <td style="padding-right: 20px;"><i>Uncertainty of the Median:</i></td> <td>2.25</td> </tr> <tr> <td style="padding-right: 20px;"><i>Robust CV:</i></td> <td>18.7%</td> </tr> <tr> <td style="padding-right: 20px;"><i>Minimum:</i></td> <td>5.0</td> </tr> <tr> <td style="padding-right: 20px;"><i>Maximum:</i></td> <td>45.5</td> </tr> <tr> <td style="padding-right: 20px;"><i>Range:</i></td> <td>40.5</td> </tr> </table>					<i>No of Results:</i>	10	<i>Median:</i>	30.40	<i>Normalised IQR:</i>	5.67	<i>Uncertainty of the Median:</i>	2.25	<i>Robust CV:</i>	18.7%	<i>Minimum:</i>	5.0	<i>Maximum:</i>	45.5	<i>Range:</i>	40.5
<i>No of Results:</i>	10																			
<i>Median:</i>	30.40																			
<i>Normalised IQR:</i>	5.67																			
<i>Uncertainty of the Median:</i>	2.25																			
<i>Robust CV:</i>	18.7%																			
<i>Minimum:</i>	5.0																			
<i>Maximum:</i>	45.5																			
<i>Range:</i>	40.5																			

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.

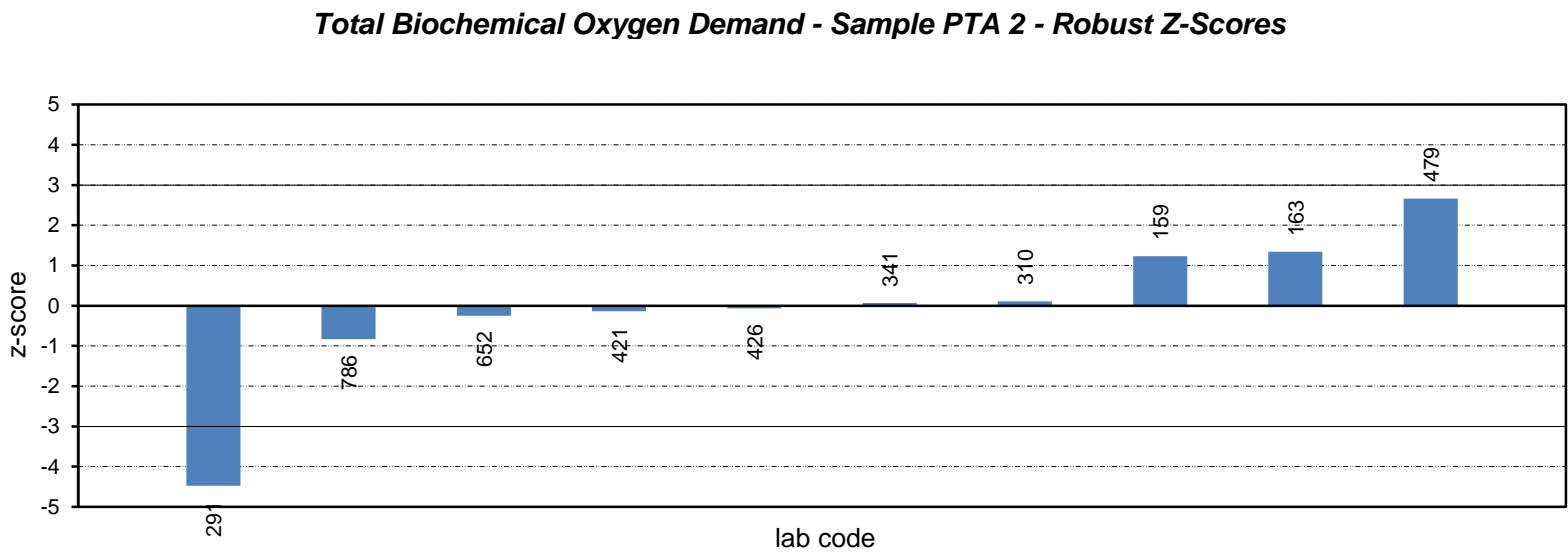
³ Please refer to Appendix C (pages C4-C5) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Total Biochemical Oxygen Demand - Sample PTA 2

Ordered Robust Z-Score Charts



Robust Z-Scores

Carbonaceous Biochemical Oxygen Demand (CBOD5) Results

Samples PTA 1 and PTA 2

Carbonaceous Biochemical Oxygen Demand (CBOD5).

Results by Laboratory Code

Laboratory Code	Sample PTA 1																			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³																
232	2.00	#	-4.02 §	8																
310	33 ±	6.6	-0.47	6																
341	39.2 ±	10	0.24	6																
479	51.1 ±	10.2	1.60	6																
552	44 ±	7	0.79	6																
652	35.0	#	-0.24	6																
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding-left: 20px;"><i>No of Results:</i></td> <td style="text-align: center;">6</td> </tr> <tr> <td style="padding-left: 20px;"><i>Median:</i></td> <td style="text-align: center;">37.10</td> </tr> <tr> <td style="padding-left: 20px;"><i>Normalised IQR:</i></td> <td style="text-align: center;">8.74</td> </tr> <tr> <td style="padding-left: 20px;"><i>Uncertainty of the Median:</i></td> <td style="text-align: center;">4.47</td> </tr> <tr> <td style="padding-left: 20px;"><i>Robust CV:</i></td> <td style="text-align: center;">23.6%</td> </tr> <tr> <td style="padding-left: 20px;"><i>Minimum:</i></td> <td style="text-align: center;">2.00</td> </tr> <tr> <td style="padding-left: 20px;"><i>Maximum:</i></td> <td style="text-align: center;">51.1</td> </tr> <tr> <td style="padding-left: 20px;"><i>Range:</i></td> <td style="text-align: center;">49.10</td> </tr> </table>					<i>No of Results:</i>	6	<i>Median:</i>	37.10	<i>Normalised IQR:</i>	8.74	<i>Uncertainty of the Median:</i>	4.47	<i>Robust CV:</i>	23.6%	<i>Minimum:</i>	2.00	<i>Maximum:</i>	51.1	<i>Range:</i>	49.10
<i>No of Results:</i>	6																			
<i>Median:</i>	37.10																			
<i>Normalised IQR:</i>	8.74																			
<i>Uncertainty of the Median:</i>	4.47																			
<i>Robust CV:</i>	23.6%																			
<i>Minimum:</i>	2.00																			
<i>Maximum:</i>	51.1																			
<i>Range:</i>	49.10																			

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.

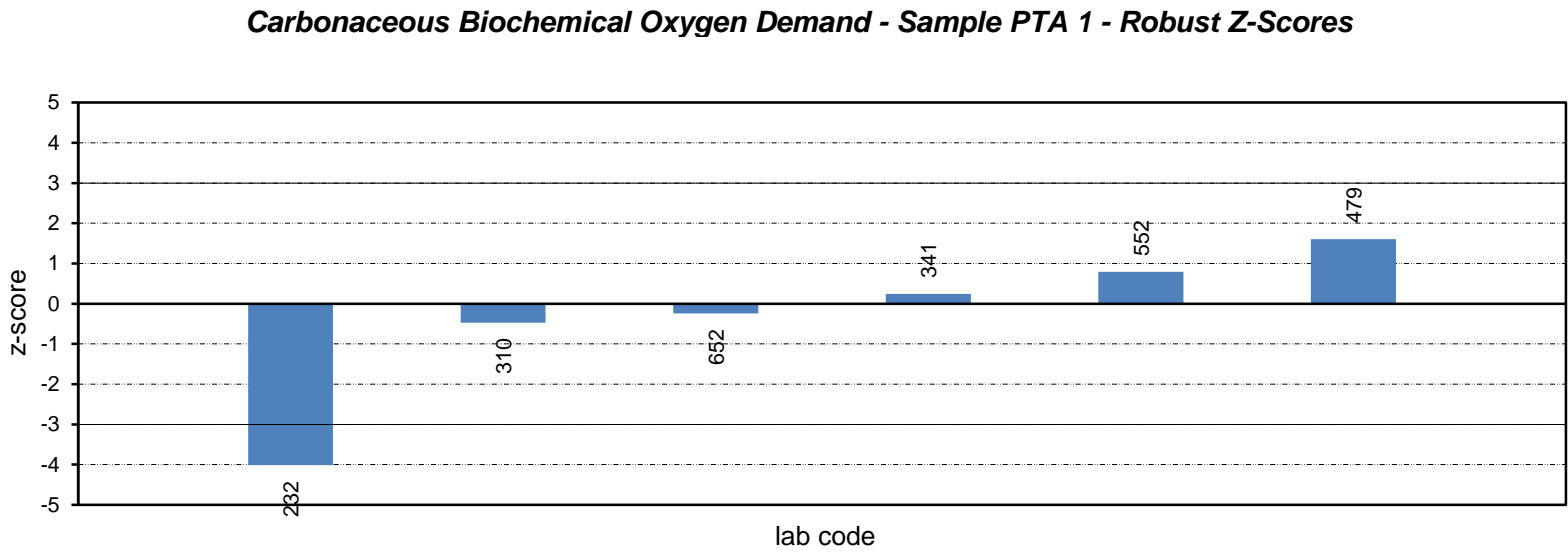
³ Please refer to Appendix C (pages C4-C5) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Carbonaceous Biochemical Oxygen Demand - Sample PTA 1

Ordered Robust Z-Score Charts



Robust Z-Scores

Carbonaceous Biochemical Oxygen Demand (CBOD5).

Results by Laboratory Code

Laboratory Code	Sample PTA 2																			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³																
232	6.00	#	-4.79	§ 8																
310	27 ±	5.4	-0.41	6																
341	30.9 ±	10	0.41	6																
479	44.0 ±	8.8	3.14	§ 6																
552	31 ±	5	0.43	6																
652	25.5	#	-0.72	6																
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding-right: 10px;"><i>No of Results:</i></td> <td style="text-align: right;">6</td> </tr> <tr> <td style="padding-right: 10px;"><i>Median:</i></td> <td style="text-align: right;">28.95</td> </tr> <tr> <td style="padding-right: 10px;"><i>Normalised IQR:</i></td> <td style="text-align: right;">4.79</td> </tr> <tr> <td style="padding-right: 10px;"><i>Uncertainty of the Median:</i></td> <td style="text-align: right;">2.45</td> </tr> <tr> <td style="padding-right: 10px;"><i>Robust CV:</i></td> <td style="text-align: right;">16.6%</td> </tr> <tr> <td style="padding-right: 10px;"><i>Minimum:</i></td> <td style="text-align: right;">6.00</td> </tr> <tr> <td style="padding-right: 10px;"><i>Maximum:</i></td> <td style="text-align: right;">44.0</td> </tr> <tr> <td style="padding-right: 10px;"><i>Range:</i></td> <td style="text-align: right;">38.00</td> </tr> </table>					<i>No of Results:</i>	6	<i>Median:</i>	28.95	<i>Normalised IQR:</i>	4.79	<i>Uncertainty of the Median:</i>	2.45	<i>Robust CV:</i>	16.6%	<i>Minimum:</i>	6.00	<i>Maximum:</i>	44.0	<i>Range:</i>	38.00
<i>No of Results:</i>	6																			
<i>Median:</i>	28.95																			
<i>Normalised IQR:</i>	4.79																			
<i>Uncertainty of the Median:</i>	2.45																			
<i>Robust CV:</i>	16.6%																			
<i>Minimum:</i>	6.00																			
<i>Maximum:</i>	44.0																			
<i>Range:</i>	38.00																			

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.

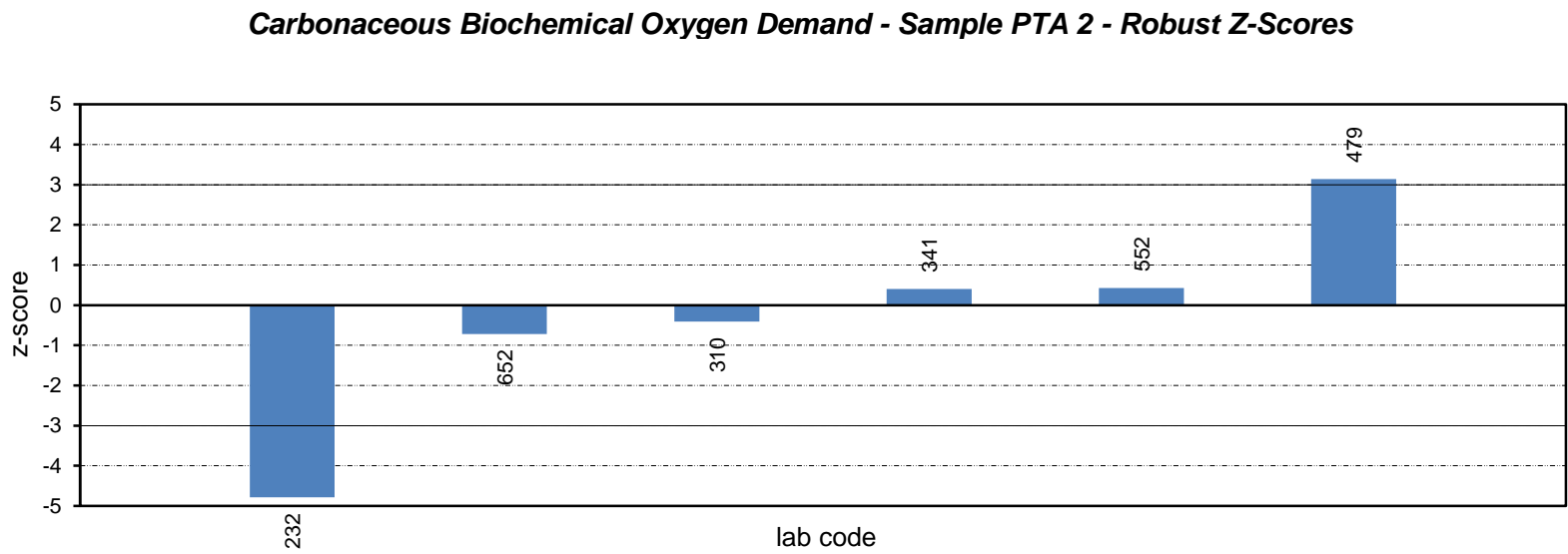
³ Please refer to Appendix C (pages C4-C5) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Carbonaceous Biochemical Oxygen Demand - Sample PTA 2

Ordered Robust Z-Score Charts



Robust Z-Scores

Chemical Oxygen Demand (COD) Results

Samples PTA 1 and PTA 2

Chemical Oxygen Demand (COD)

Results by Laboratory Code

Laboratory Code	Sample PTA 1			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
132	64.0 ±	6.00	1.04	10
149	62.0 ±	5.1	0.35	12
159	63.5 ±	4.4	0.87	12
163	84.0 ±	8.73	8.01 §	11
232	60.0	#	-0.35	12
291	58.0 ±	7.50	-1.04	12
310	51 ±	7.7	-3.48 §	17
335	60.0 ±	3.1	-0.35	12
341	59.0 ±	7.0	-0.70	17
421	57.3 ±	3.10	-1.29	10
426	63 ±	25	0.70	12
479	74.8 ±	11.2	4.80 §	12
552	68 ±	12	2.44	11
559	61.0 ±	7.0	0.00	17
652	60.5	#	-0.17	12
786	61.0	#	0.00	18

No of Results:	16
Median:	61.00
Normalised IQR:	2.87
Uncertainty of the Median:	0.90
Robust CV:	4.7%
Minimum:	51
Maximum:	84.0
Range:	33.0

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.

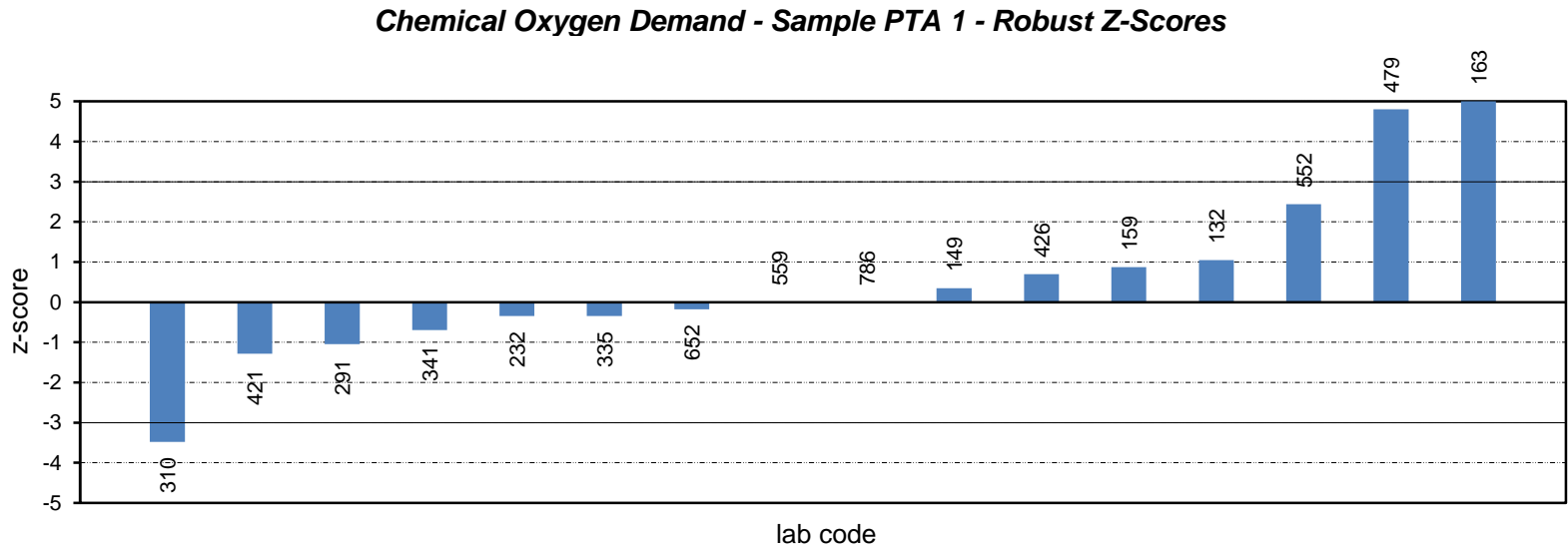
³ Please refer to Appendix C (pages C4-C5) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Chemical Oxygen Demand - Sample PTA 1

Ordered Robust Z-Score Charts



Robust Z-Scores

Chemical Oxygen Demand (COD)

Results by Laboratory Code

Laboratory Code	Sample PTA 2			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³
132	62.0 ±	6.00	2.74	10
149	48.0 ±	3.9	0.14	12
159	53.0 ±	4.4	1.07	12
163	58.0 ±	6.08	2.00	11
232	47.0	#	-0.05	12
291	44.0 ±	7.5	-0.60	12
310	40 ±	5.2	-1.35	17
335	45.0 ±	2.4	-0.42	12
341	47.5 ±	5.0	0.05	17
421	44.7 ±	1.5	-0.47	10
426	47 ±	19	-0.05	12
479	51.9 ±	7.8	0.87	12
552	55 ±	10	1.44	11
559	48.0 ±	5.0	0.14	17
652	45.0	#	-0.42	12
786	44.0	#	-0.60	18

No of Results:	16
Median:	47.25
Normalised IQR:	5.37
Uncertainty of the Median:	1.68
Robust CV:	11.4%
Minimum:	40
Maximum:	62.0
Range:	22.0

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.

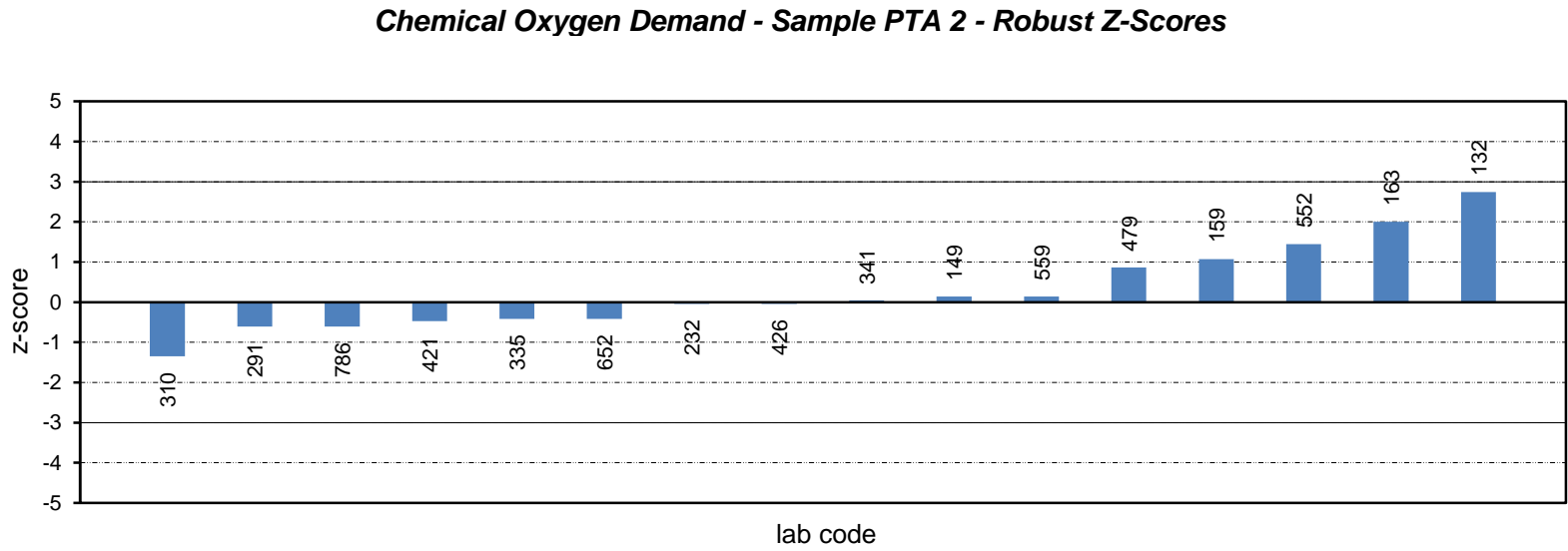
³ Please refer to Appendix C (pages C4-C5) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Chemical Oxygen Demand - Sample PTA 2

Ordered Robust Z-Score Charts



Robust Z-Scores

Total Organic Carbon (TOC) Results

Samples PTA 1 and PTA 2

Total Organic Carbon (TOC)

Results by Laboratory Code

Laboratory Code	Sample PTA 1																			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³																
163	25.0 ±	0.73	0.00	19																
232	19.8	#	-3.01 §	20																
426	25 ±	2.8	0.00	19																
479	27.6 ±	6.9	1.51	25																
559	25.0 ±	3.0	0.00	20																
652	25.0	#	0.00	20																
715	23.6 ±	1.1	-0.81	19																
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding-left: 20px;">No of Results:</td> <td style="text-align: center;">7</td> </tr> <tr> <td style="padding-left: 20px;">Median:</td> <td style="text-align: center;">25.00</td> </tr> <tr> <td style="padding-left: 20px;">Normalised IQR (Target):</td> <td style="text-align: center;">1.73</td> </tr> <tr> <td style="padding-left: 20px;">Uncertainty of the Median:</td> <td style="text-align: center;">0.30</td> </tr> <tr> <td style="padding-left: 20px;">Robust CV (Target):</td> <td style="text-align: center;">6.9%</td> </tr> <tr> <td style="padding-left: 20px;">Minimum:</td> <td style="text-align: center;">19.8</td> </tr> <tr> <td style="padding-left: 20px;">Maximum:</td> <td style="text-align: center;">27.6</td> </tr> <tr> <td style="padding-left: 20px;">Range:</td> <td style="text-align: center;">7.8</td> </tr> </table>					No of Results:	7	Median:	25.00	Normalised IQR (Target):	1.73	Uncertainty of the Median:	0.30	Robust CV (Target):	6.9%	Minimum:	19.8	Maximum:	27.6	Range:	7.8
No of Results:	7																			
Median:	25.00																			
Normalised IQR (Target):	1.73																			
Uncertainty of the Median:	0.30																			
Robust CV (Target):	6.9%																			
Minimum:	19.8																			
Maximum:	27.6																			
Range:	7.8																			

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 (pages C4-C5) for method code descriptions.

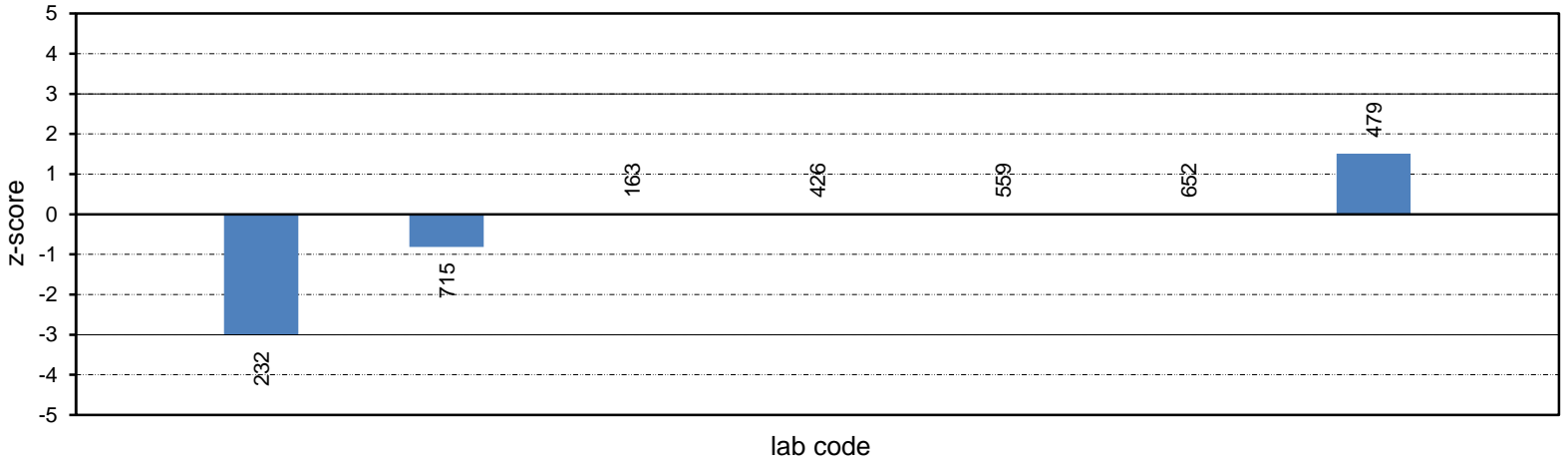
⁴ "na" indicates "not applicable".

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

Total Organic Carbon - Sample PTA 1

Ordered Robust Z-Score Charts

Total Organic Carbon- Sample PTA 1 - Robust Z-Scores



Robust Z-Scores

Total Organic Carbon (TOC)

Results by Laboratory Code

Laboratory Code	Sample PTA 2																			
	Result ± mg/L	MU ¹	Robust z-score ²	Method Code ³																
163	51.6 ±	1.55	4.95	§ 19																
232	20.0	#	-6.55	§ 20																
426	38 ±	4.3	0.00	19																
479	43.5 ±	10.9	2.00	25																
559	37.8 ±	4.0	-0.07	20																
652	38.0	#	0.00	20																
715	37.6 ±	1.7	-0.15	19																
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="padding-left: 20px;">No of Results:</td> <td style="text-align: center;">7</td> </tr> <tr> <td style="padding-left: 20px;">Median:</td> <td style="text-align: center;">38.00</td> </tr> <tr> <td style="padding-left: 20px;">Normalised IQR:</td> <td style="text-align: center;">2.75</td> </tr> <tr> <td style="padding-left: 20px;">Uncertainty of the Median:</td> <td style="text-align: center;">1.30</td> </tr> <tr> <td style="padding-left: 20px;">Robust CV:</td> <td style="text-align: center;">7.2%</td> </tr> <tr> <td style="padding-left: 20px;">Minimum:</td> <td style="text-align: center;">20.0</td> </tr> <tr> <td style="padding-left: 20px;">Maximum:</td> <td style="text-align: center;">51.6</td> </tr> <tr> <td style="padding-left: 20px;">Range:</td> <td style="text-align: center;">31.6</td> </tr> </table>					No of Results:	7	Median:	38.00	Normalised IQR:	2.75	Uncertainty of the Median:	1.30	Robust CV:	7.2%	Minimum:	20.0	Maximum:	51.6	Range:	31.6
No of Results:	7																			
Median:	38.00																			
Normalised IQR:	2.75																			
Uncertainty of the Median:	1.30																			
Robust CV:	7.2%																			
Minimum:	20.0																			
Maximum:	51.6																			
Range:	31.6																			

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.

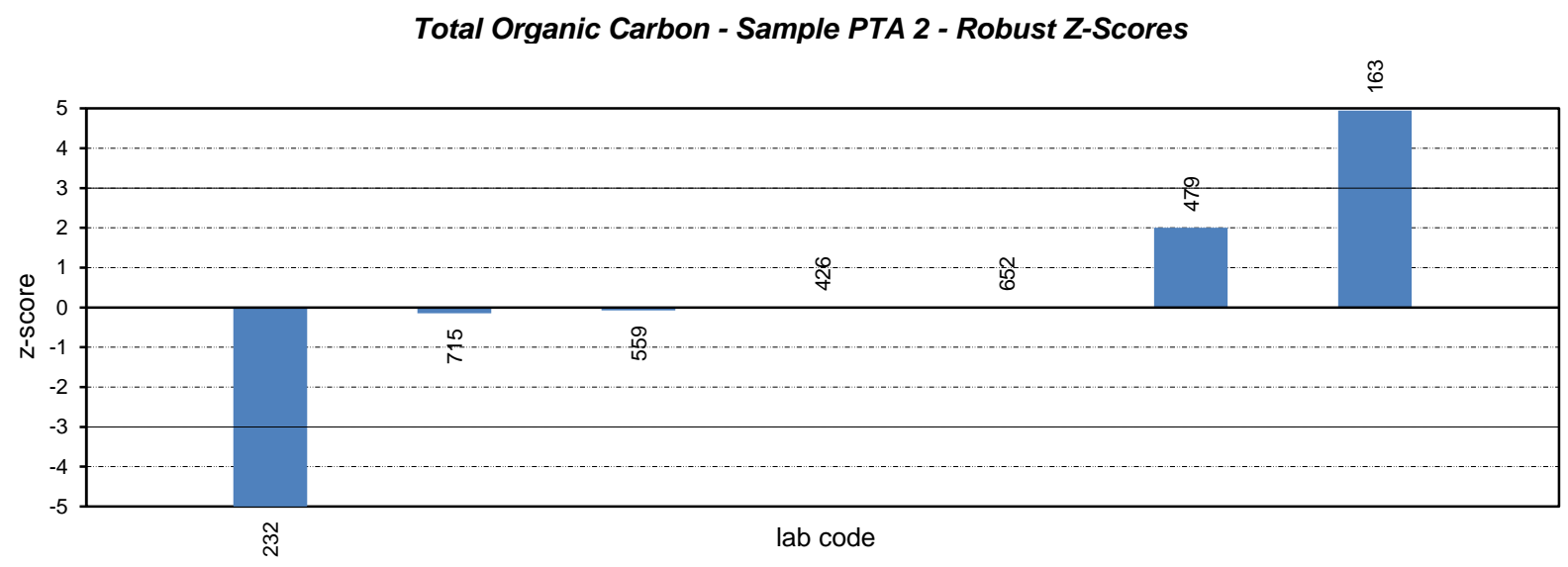
³ Please refer to Appendix C (pages C4-C5) for method code descriptions.

⁴ "na" indicates "not applicable".

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

Total Organic Carbon - Sample PTA 2

Ordered Robust Z-Score Charts



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 were subjected to rigorous stability and homogeneity testing.

A random selection of ten samples was chosen from sample sets PTA 1 for homogeneity and stability testing. Seven of these samples were stored frozen, the remaining three were subjected to 20°C for seven days for an accelerated ageing stability trial. The samples were then analysed in duplicate by Hill laboratories using APHA 5310 C (modified) 23rd ed. 2017 for TOC analysis, APHA 5220 D 23rd ed. 2017 for COD analysis, APHA 5210 B (modified) 23rd ed. 2017 for CBOD5 analysis. As sample PTA 2 contained Urea as a nitrogen source to differentiate between TBOD5 and CBOD5, this was tested by Total Kjeldahl Nitrogen (TKN) digestion, phenol/hypochlorite colorimetry on a Discrete Analyser using APHA 4500-N_{org} D (modified) and 4500 NH₃ F (modified) 23rd ed. 2017. Verification testing was carried out on samples PTA 1, due to identical manufacturing procedures to that of sample PTA 2.

All stability samples showed no notable differences when compared to homogeneity 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 the tables B1 and B2 below. Please note that the mean results for these testings are not intended to be used as reference values.

Table B1. TOC homogeneity and stability testing and TKN testing of Samples PTA 2.

Round PTA 253	Sample ID	Total Organic Carbon (TOC)		Total Kjeldahl Nitrogen (TKN)	
		PTA 2 (mg/L)		PTA 2 (mg/L)	
		Duplicate 1	Duplicate 2	Duplicate 1	Duplicate 2
Homogeneity	H1	34.6	35.4	39.4	38.2
	H2	35.6	35.0	40.9	40.2
	H3	34.6	34.6	40.9	39.2
	H4	36.2	34.8	39.3	40.6
	H5	34.3	34.3	38.6	37.6
	H6	33.0	32.9	39.2	35.8
	H7	33.3	35.7	42.6	37.5
Stability	S1	34.6	34.3	40.2	41.9
	S2	34.3	35.2	36.9	37.8
	S3	34.3	35.6	40.5	36.6
Mean		34.47		39.85	
SD		0.94		1.53	
RSD		2.73%		3.84%	

Table B2. TOC, CBOD5, COD and TKN confirmatory testing of samples PTA 1 and PTA 2.

Round PTA 253	Sample ID	Total Organic Carbon (TOC) (mg/L)		Carbonaceous Biochemical Oxygen Demand (CBOD5) (mg/L)		Chemical Oxygen Demand (COD) (mg/L)		Total Kjeldahl Nitrogen (TKN) (mg/L)	
Verification	PTA 1	22	23	35	33	58	57	-	-
	PTA 2	35	35	25	24	43	48	39	38

APPENDIX C

Documentation

Instructions to Participants C1
Method Codes C4
Results Sheet C6



PROFICIENCY TESTING AUSTRALIA
WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 253

NOVEMBER, 2019

Total Biochemical Oxygen Demand (TBOD₅), Carbonaceous Biochemical Oxygen Demand (CBOD₅), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC)

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 vials labelled PTA 1 and PTA 2, supplied by Global Proficiency Limited (New Zealand). The vials contain approximately 3 mL of artificial potable water concentrate for analysis of TBOD₅, CBOD₅, COD and TOC.
- ii)** To minimise the possibility of change in concentration, do not open the samples until ready to commence analysis.
- iii)** The samples were frozen prior to dispatch and any liquid on the outside of the vials may be due to condensation rather than sample leakage.
- iv)** The samples have not been preserved and if analyses cannot be commenced on the day of receipt, it is recommended that the sample concentrate be stored frozen.
- v)** The samples will require dilution in reagent grade water (please follow the **Sample Preparation** steps below).

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

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

Caution: Analysis must begin immediately after vial is opened.

- i) Adjust vial temperature to 20°C and invert several times to mix thoroughly prior to dilution step.
- ii) Record vial ID number. Open vial.
- iii) Dilute sample by a factor of 1000x (e.g. 0.2 mL made up to 200 mL with reagent grade water).
- iv) Test according to your normal procedures.
- v) Repeat steps i) to iv) for the second sample.

Please report results for the diluted sample.

BOD special instructions

For stability reasons, this artificial sample has been prepared under aseptic conditions. BOD testing will require seeding with 1mL of a seed suspension capable of achieving $\pm 15.4\%$ on a glucose-glutamic acid (GGA) check solution (i.e., 198 ± 30.5 mg/L BOD from a solution containing 150 mg/L glucose + 150 mg/L glutamic acid; Ref APHA 5210 B section 5.d., and 6.b.). Adjust the amount of seed added to the samples, to achieve results falling within this range for the GGA test.

3. Tests Requested

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

- i) Total Biochemical Oxygen Demand (TBOD₅)
- ii) Carbonaceous Biochemical Oxygen Demand (CBOD₅)
- iii) Chemical Oxygen Demand (COD)
- iv) Total Organic Carbon (TOC)

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

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

4. Safety

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

5. Reporting

- i) For each prepared sample only a single result is requested.
- ii) Report results in milligrams per litre (mg/L).
- iii) For statistical purposes, report results to three significant figures:
e.g. 123 mg/L, 12.3 mg/L or 1.23 mg/L etc.
- iv) Do not correct results for recovery.
- v) Select the appropriate method code for each test from the Method Code Table and record it on the Results Sheet.
- vi) Calculate the measurement uncertainty (MU) for each reported result. All estimates of MU must be given as a 95% confidence interval (coverage factor $k \approx 2$) 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 29 NOVEMBER 2019** to:

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

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

Analyte	Range
TBOD ₅	18 – 230 mg/L
CBOD ₅	18 – 230 mg/L
COD	30 – 250 mg/L
TOC	6 – 100 mg/L

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Total Biochemical Oxygen Demand (TBOD ₅)	APHA-SM	5210 B. 5-day BOD Test	1
		5210 D. Respirometric Method	2
	US EPA	0405. 1 Biochemical Oxygen Demand (BOD) - 5 Days, 20°C	3
	HACH	8043 Oxygen Demand, Biochemical - Dilution Method	4
	Other	Other (please specify)	5
Carbonaceous Biochemical Oxygen Demand (CBOD ₅)	APHA-SM	5210 B. 5-day BOD Test with TCMP inhibitor	6
		5210 B. 5-day BOD Test with ATU inhibitor	7
	HACH	8043 Oxygen Demand, Biochemical - Dilution Method with nitrification inhibitor	8
	Other	Other (please specify inhibitory chemical)	9
Chemical Oxygen Demand (COD)	APHA-SM	5220 B. Open Reflux Method	10
		5220 C. Closed Reflux Titrimetric Method	11
		5220 D. Closed Reflux, Colorimetric Method	12
	US EPA	0410.1 Chemical Oxygen Demand - Titrimetric, Mid-Level	13
		0410.2 Chemical Oxygen Demand - Titrimetric, Low-Level	14
		0410.3 Chemical Oxygen Demand - Titrimetric, High-Level	15
		0410.4 Chemical Oxygen Demand - Colorimetric	16
	HACH	8000 Oxygen Demand, Chemical - US EPA Reactor Digestion Method	17
	Other	Other (please specify)	18

Continued on next page...

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Total Organic Carbon (TOC)	APHA-SM	5310 B. High-Temperature Combustion Method	19
		5310 C. Persulfate-Ultraviolet or Heated - Persulfate Oxidation Method	20
		5310 D. Wet Oxidation Method	21
	US EPA	0415.1 Organic Carbon, Total - Combustion or Oxidation	22
		0415.2 Organic Carbon, Total - UV Promoted	23
	HACH	10173 Organic Carbon, Total-Test 'N Tube™ Vials	24
	GE	GE Analytical Instruments – Sievers* InnovOx Laboratory TOC Analyzer with Supercritical Water Oxidation (SCWO). DLM 68088-12 EN Rev.A - Operation and Maintenance Manual	25
	Other	Other (please specify)	26

Method Reference Key

- i) **APHA SM** APHA “Standard Methods for the Examination of Water and Wastewater” (18, 19 20, 21, 22, 23 Edition). (<http://www.standardmethods.org/>)
- ii) **GE** GE Analytical Instruments, Boulder, Colorado, USA. (https://www.geinstruments.com/download-media?f_id=43694)
- iii) **HACH** HACH Company, Loveland, Colorado, USA. (<https://www.hach.com/quick.search-download.search.jsa?keywords=methods>)
- iv) **US EPA** U.S Environmental Protection Agency. (<http://www.epa.gov/osa/fem/methcollectns.htm>)



PROFICIENCY TESTING AUSTRALIA
WATERS PROFICIENCY TESTING PROGRAM
CHEMICAL ANALYSIS ROUND 253

Total Biochemical Oxygen Demand (TBOD₅), Carbonaceous Biochemical Oxygen Demand (CBOD₅), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC)
NOVEMBER, 2019

RESULTS SHEET
(mg/L)

Please note:

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

Laboratory
Code

***Approximate temperature of samples upon receipt:**

ANALYSIS	SAMPLE PTA 1			SAMPLE PTA 2		
	Result (mg/L)	±MU (mg/L)	METHOD CODE	Result (mg/L)	±MU (mg/L)	METHOD CODE
Total Biochemical Oxygen Demand (TBOD ₅)						
Carbonaceous Biochemical Oxygen Demand (CBOD ₅)						
Chemical Oxygen Demand (COD)						
Total Organic Carbon (TOC)						

CBOD₅ Inhibitory chemical: _____

- i) For each sample only a single result is requested.
- ii) For statistical purposes, report results to three significant figures:
e.g. 123 mg/L, 12.3 mg/L or 1.23 mg/L etc.
- iii) Report results in milligrams per litre (mg/L).
- iv) Do not correct results for recovery.
- v) MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in mg/L, using the same number of decimal places as for the result.

DATE: _____

SIGNATURE: _____

Return results **NO LATER THAN 29 NOVEMBER 2019** to:

Delfina Mihaila

Proficiency Testing Australia

PO Box 7507

SILVERWATER NSW 2128

AUSTRALIA

Phone: +61 2 9736 8397

Fax: +61 2 9743 6664

Email: dmihaila@pta.asn.au

INSTRUCT WATERS PROF TEST PROG 253

- End of Report -