

**Report No. 1206**

***Waters Proficiency Testing Program***

**Round No. 261**

***- Inorganic Disinfection By-products -***

**July 2020**

**Acknowledgments**

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Dr A Evans, National Measurement Institute (Australia). Also our thanks go to the Environmental Resource Associates (USA) for the supply of samples and to Global Proficiency Pty Ltd (Australia) for distributing the samples.

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## 1. Foreword

This report summarises the results of a proficiency testing program on the determination of Chlorate and Chlorite in waters. This is round 261 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 May 2020 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 A Evans, National Measurement Institute (Australia). 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. 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 one screw cap vial (labelled R261) containing water for analysis of Chlorate and Chlorite.
- 2.4 A total of six laboratories received samples, comprising:
  - 5 Australian participants; and
  - 1 overseas participant (New Zealand).

Of these six 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 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 No outlier results were reported in this round.
- 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. No outlier results were reported in this round.

#### 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 Environmental Resource Associates' Standard Operating Procedures to ensure samples were fit-for-purpose, homogeneous and stable.

Solutions were stable and homogeneous, and medians obtained from this proficiency round were in good agreement with the expected levels (manufacturer's assigned values), taking into account the measurement uncertainties of both parameters, 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 the Table 1 below.

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

Analyte	Expected Levels (µg/L)	Uncertainty of the expected levels (µg/L)	Median (µg/L)	Uncertainty of the median (µg/L)
Chlorate	151	8	158.0	3.5
Chlorite	539	16	554.0	14.0

Overall, the performance of participants in this round was very good, with robust CV less than 6% and uncertainty of the median less than 3% for both analytes

## 4.2 Analysis of Round 261 Results

Table 2 presents the Chlorate and Chlorite medians and robust CVs obtained in this PTA round.

Table 2. Current round variability and proficiency medians of Chlorate and Chlorite testing

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
Round 261	R261	158.0	4.7	7
	R261	554.0	5.4	7

### Bias / Accuracy

The Chlorate satisfactory results ( $|z\text{-score}| \leq 2.0$ ) ranged between 154 – 171 µg/L. Out of seven results submitted, one questionable result ( $2.0 < |z\text{-score}| < 3.0$ ) was reported (laboratory code 634A). However, even though it was statistically considered questionable, this result is less than 15% higher than the median, which is within what we might expect from analytical variation. No outlier results ( $|z\text{-score}| \geq 3.0$ ) were obtained for Chlorate testing.

For Chlorite, the satisfactory results ranged between 532 – 593 µg/L. Out of seven results submitted, no questionable or outlier results were obtained.

Figures 1 and 2 present the spread of results and the methods used for Chlorate and Chlorite testing in this round. Participants used either method APHA 4110B or APHA 4110D.

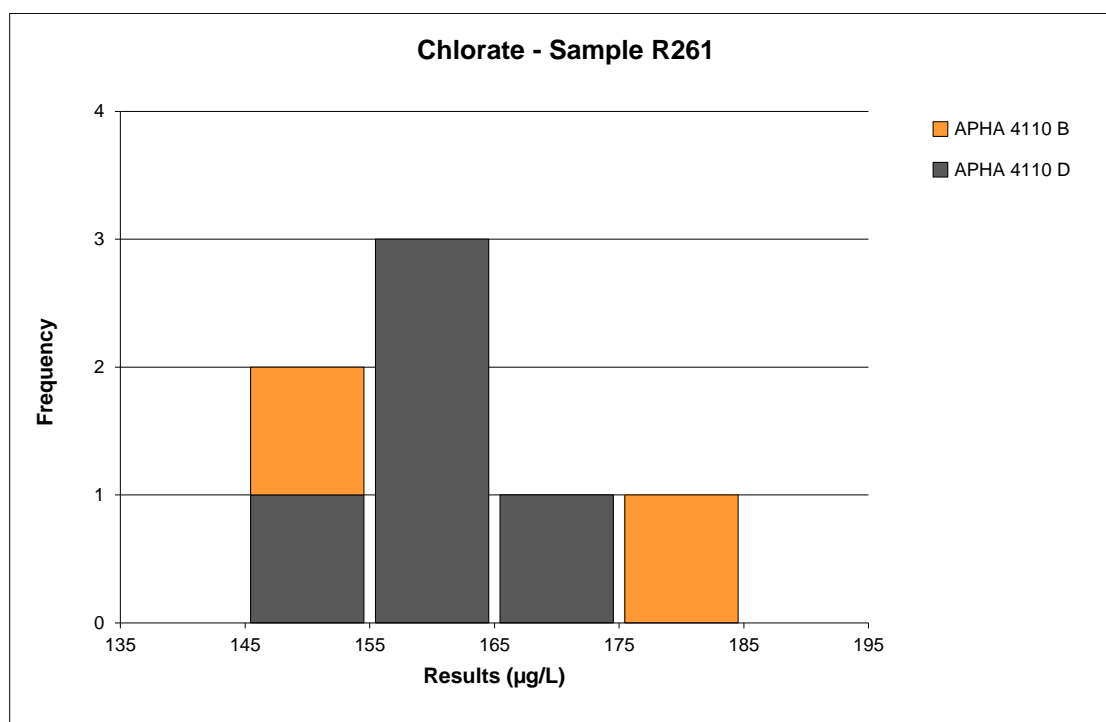


Figure 1. Spread of results for Chlorate testing of sample R261, with a median of 158.0 µg/L.

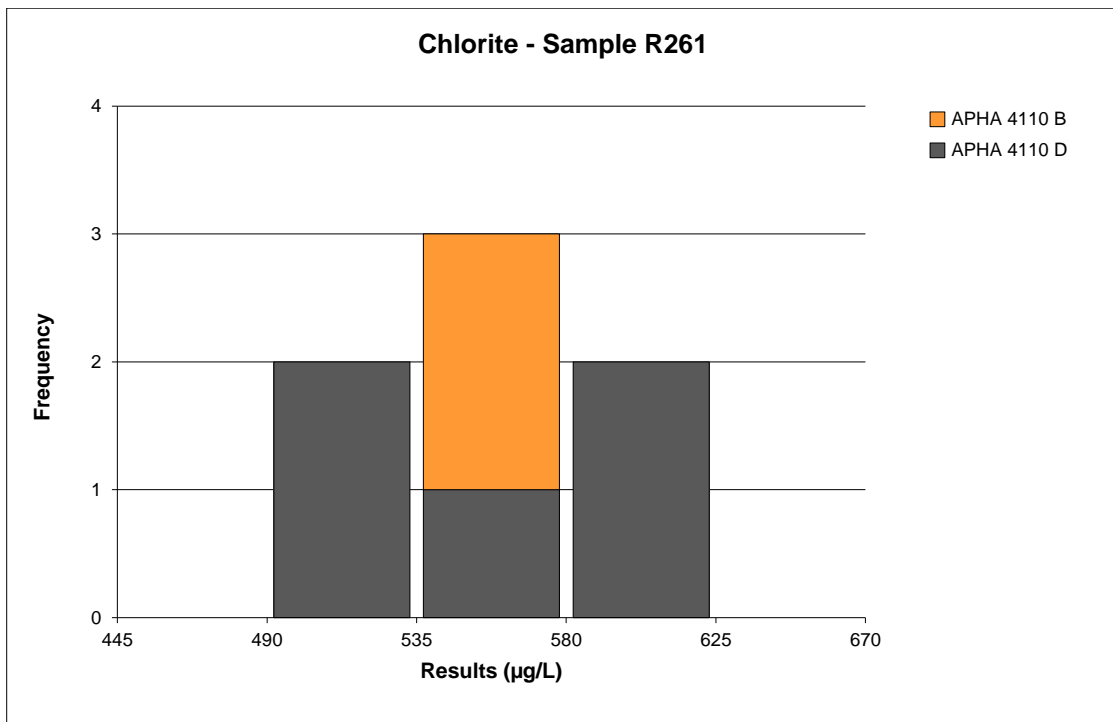


Figure 2. Spread of results for Chlorite testing of sample R261, with a median of 554.0 µg/L.

#### 4.3 Measurement Uncertainty (MU)

All participants in this round reported the measurement uncertainty (MU) associated with their results.

Some laboratories indicated a MU which was greater than three times the normalised IQR and thus, they may have overestimated their MU.<sup>1</sup> A measurement uncertainty of between 10%-15% would be reasonable for this type of sample and these concentration levels.

The MU reported by participants can be seen in Figures 3 and 4 on the next page.

<sup>1</sup> 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.



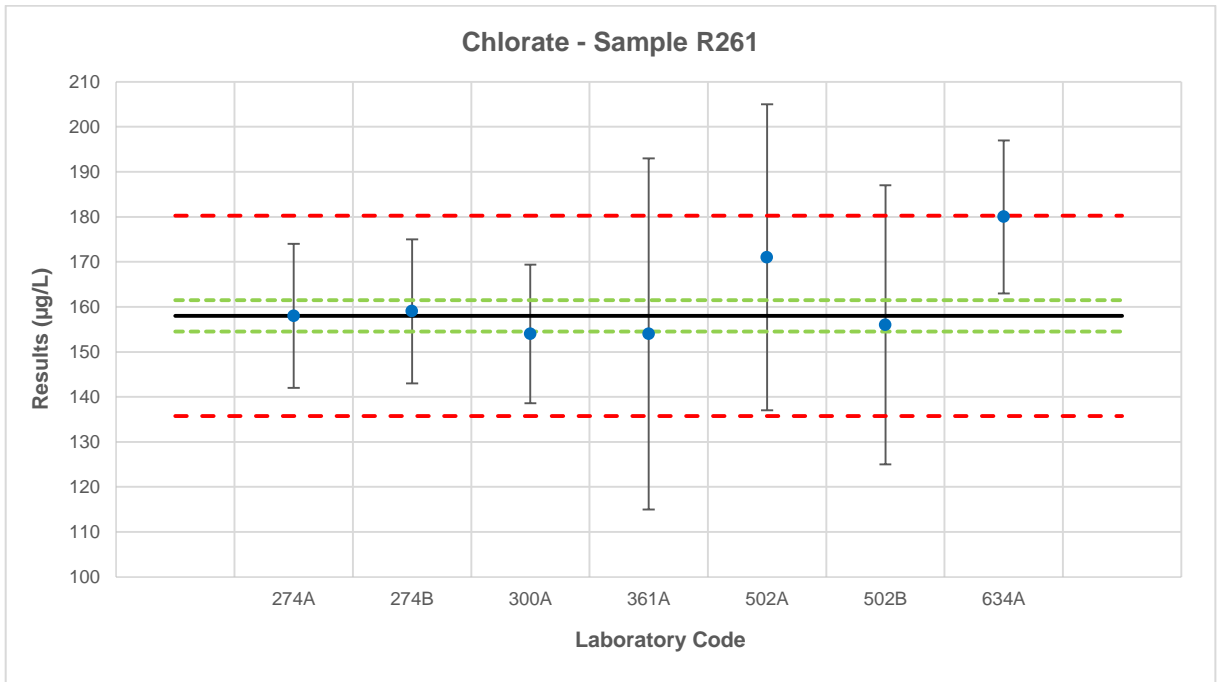


Figure 3. Laboratory MU for Chlorate testing, including the median (—), uncertainty of the median (- - -), and 3xNIQR  $U_{max}$  (- - -).

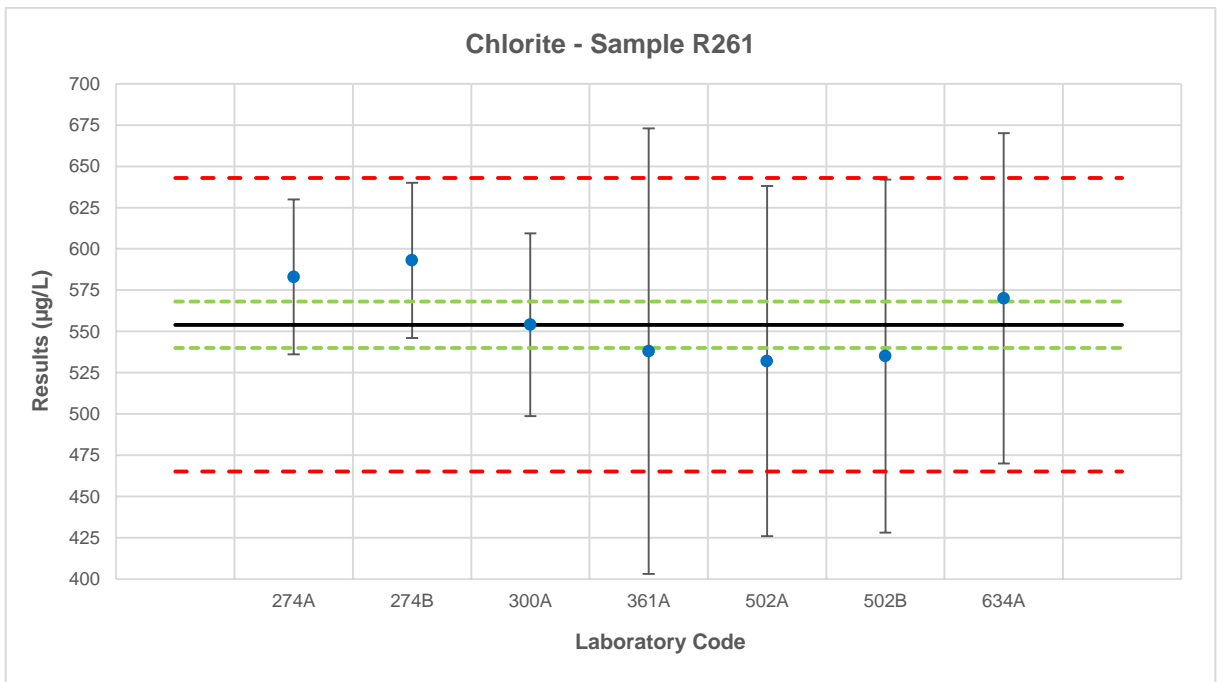


Figure 4. Laboratory MU for Chlorite testing, including the median (—), uncertainty of the median (- - -), and 3xNIQR  $U_{max}$  (- - -).

#### 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

No outlier results were reported in Round 261.

#### 6. References

- [1] *Guide to Proficiency Testing Australia*, 2019 (This document can be found on the PTA website, [www.pta.asn.au](http://www.pta.asn.au))
- [2] ISO 13528:2015 *Statistical methods for use in proficiency testing by interlaboratory comparisons*.

# APPENDIX A

## Results and Data Analysis

Chlorate ..... A1  
Chlorite..... A3

# **Chlorate Results**

Sample R261

**Chlorate****Results by Laboratory Code**

Laboratory Code	Sample R261			
	Result ± µg/L	MU <sup>1</sup>	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>
274A	158 ±	16	0.00	3
274B	159 ±	16	0.13	3
300A	154 ±	15.4	-0.54	3
361A	154 ±	39	-0.54	1
502A	171 ±	34	1.75	3
502B	156 ±	31	-0.27	3
634A	180 ±	17	2.97	1
<hr/>				
<i>No of Results:</i>	7			
<i>Median:</i>	158.0			
<i>Normalised IQR:</i>	7.4			
<i>Uncertainty of the Median:</i>	3.5			
<i>Robust CV:</i>	4.7%			
<i>Minimum:</i>	154			
<i>Maximum:</i>	180			
<i>Range:</i>	26			

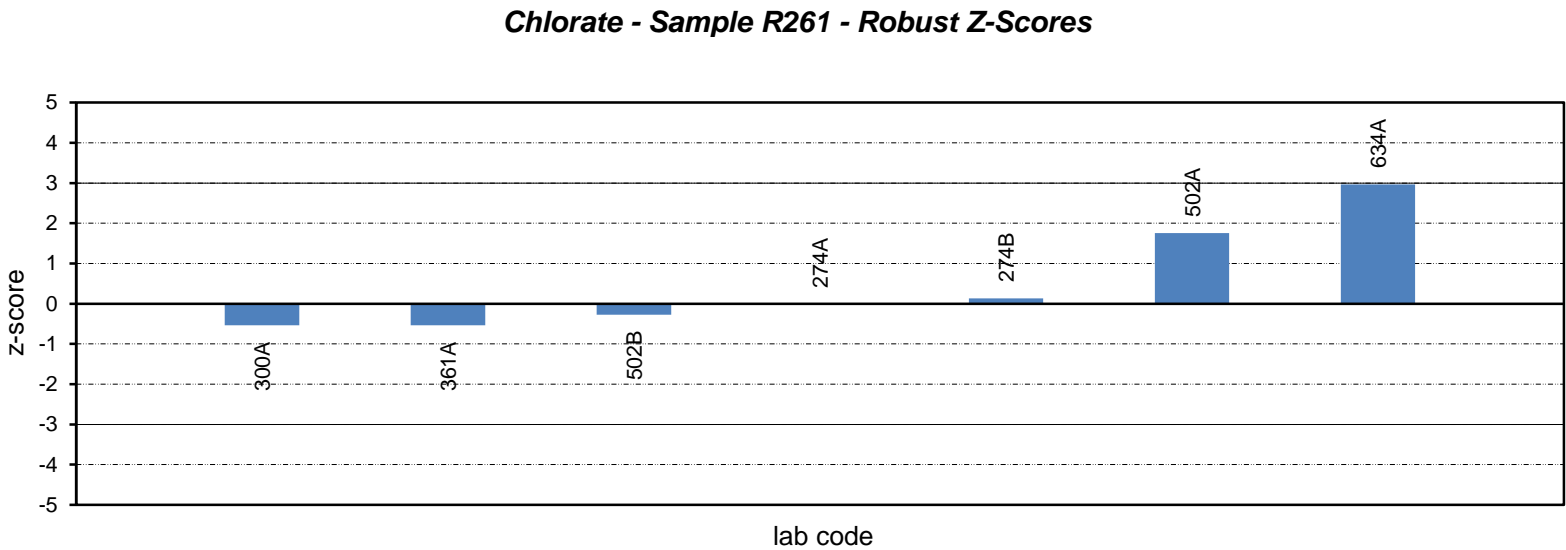
<sup>1</sup> Where reported, results are shown with their corresponding measurement uncertainty (MU).

<sup>2</sup> "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.

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

**Chlorate - Sample R261**

**Ordered Robust Z-Score Charts**



**Robust Z-Scores**

# **Chlorite Results**

Sample R261

**Chlorite****Results by Laboratory Code**

Laboratory Code	Sample R261			
	Result ± µg/L	MU <sup>1</sup>	Robust z-score <sup>2</sup>	Method Code <sup>3</sup>
274A	583 ±	47	0.98	3
274B	593 ±	47	1.32	3
300A	554 ±	55.4	0.00	3
361A	538 ±	135	-0.54	1
502A	532 ±	106	-0.74	3
502B	535 ±	107	-0.64	3
634A	570 ±	100	0.54	1
<hr/>				
<i>No of Results:</i>	7			
<i>Median:</i>	554.0			
<i>Normalised IQR:</i>	29.7			
<i>Uncertainty of the Median:</i>	14.0			
<i>Robust CV:</i>	5.4%			
<i>Minimum:</i>	532			
<i>Maximum:</i>	593			
<i>Range:</i>	61			

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

<sup>2</sup> "**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.

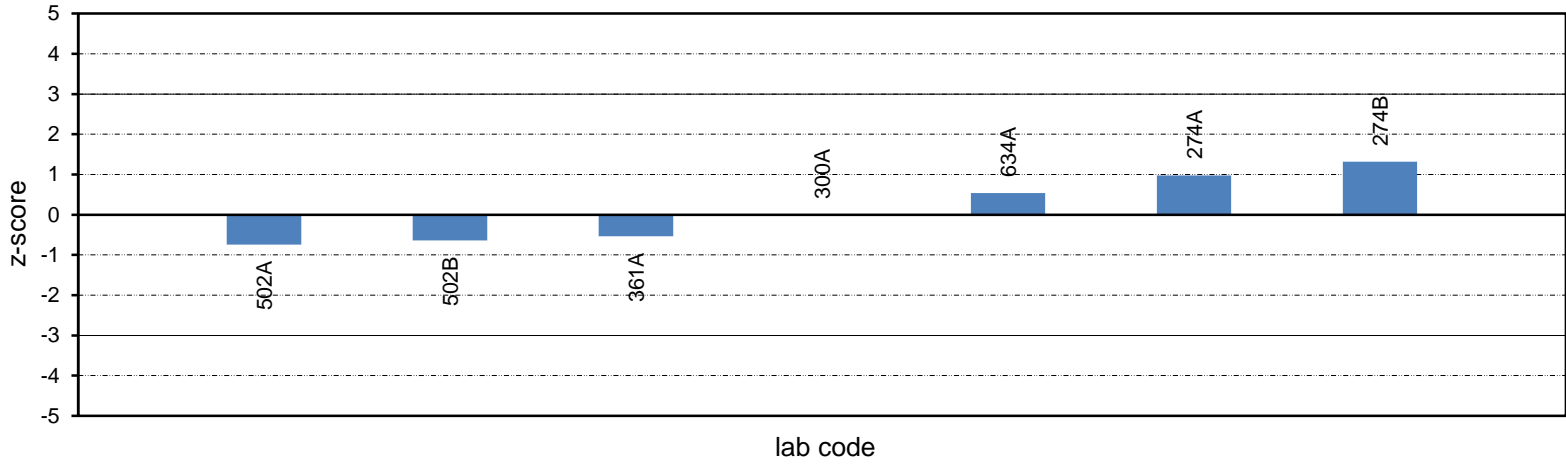
<sup>3</sup> Please refer to Appendix C (page C3) for method code descriptions.



**Chlorite - Sample R261**

**Ordered Robust Z-Score Charts**

**Chlorite - Sample R261 - Robust Z-Scores**



**Robust Z-Scores**

# **APPENDIX B**

## **Sample Homogeneity and Stability**

Homogeneity and Stability Testing ..... B1

## **Homogeneity and Stability Testing**

Certified reference samples for this program were obtained from Environmental Resource Associates (ERA, USA). As such, all samples were subjected to rigorous stability and homogeneity testing. On the basis of this testing, the samples utilised for this program were considered to be homogeneous and stable.

Table B1 below presents the certification data and analytical verification results prior to sample release<sup>1</sup>.

Table B1. Certified values and analytical verification results for samples used in Round 261.

<b>Analyte</b>	<b>Certified Value<sup>2</sup> (µg/L)</b>	<b>Uncertainty<sup>3</sup> (%)</b>	<b>Analytical Verification</b>		
			<b>Mean (µg/L)</b>	<b>Recovery (%)</b>	<b>No. of samples</b>
Chlorate	151	5.25	152	101	3
Chlorite	539	3.00	550	102	4

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<sup>1</sup> ERA certification and analytical verification data issued 2 October 2019.

<sup>2</sup> The Certified Values are the actual “made-to” concentrations confirmed by ERA analytical verification.

<sup>3</sup> The stated Uncertainty is the total propagated uncertainty at the 95% confidence interval. The uncertainty is based on the preparation and analytical verification of the product by ERA, multiplied by a coverage factor. The uncertainty applies to the product as supplied and does not take into account any required or optional dilution and/or preparations the laboratory may perform while using this product.

# APPENDIX C

## Documentation

Instructions to Participants ..... C1  
Method Codes ..... C3  
Results Sheet..... C4



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

**CHEMICAL ANALYSIS ROUND 261**

**MAY, 2020**

**Inorganic Disinfection By-products**

**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) One screw cap vial labelled PTA R261 supplied by Environmental Resource Associates (ERA). The vial contains approximately 23 mL of standard concentrate.
- ii) The sample is not preserved and should be stored at  $4 \pm 2^{\circ}\text{C}$ .
- iii) The vial will require dilution in deionised water as described in the Sample Preparation section below.

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

**2. Sample Preparation**

The dilution instructions below represent the minimum suggested sample size. Using a smaller sample size may invalidate your results.

**Caution:** As the diluted sample is not stable, it must be analysed immediately after the concentrate is diluted.

- i) Adjust ampoule temperature to  $20^{\circ}\text{C}$ .
- ii) Add 100-200 mL of deionised water to a clean 1000 mL volumetric flask.
- iii) Shake the R261 vial before opening.
- iv) Using a pipette, transfer 5.0 mL of the concentrate into the 1000 mL volumetric flask.
- v) Dilute the flask to final volume with deionised water.
- vi) Cap the flask and mix well.
- vii) Immediately analyse the diluted sample by your normal procedures.

**Please report results (in  $\mu\text{g/L}$ ) for the diluted sample.**

### 3. Tests Requested

- i) Chlorate
- ii) Chlorite

(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 micrograms per litre ( $\mu\text{g/L}$ ).
  - iii) Analytes with levels less than your level of detection, or not detected, may be reported as a "<" value.
  - iv) For the analytes not tested, please report "Not Tested".
  - v) Do not correct results for recovery.
  - vi) Select the appropriate method code for each test from the Method Code Table and record it on the Results Sheet.
  - vii) 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  $\mu\text{g/L}$ . Report MU using the same number of decimal places as for the result.
6. Testing should commence as soon as possible after receiving the sample and results reported **NO LATER THAN 12 JUNE 2020** to:

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

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

Analyte	Range
Chlorate	60 – 180 $\mu\text{g/L}$
Chlorite	100 – 1000 $\mu\text{g/L}$

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

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Chlorate & Chlorite	Ion Chromatography	APHA 4110B Ion Chromatography with Chemical Suppression of Eluent Conductivity	1
		APHA 4110C Single-Column Ion Chromatography with Direct Conductivity Detection	2
		APHA 4110D Ion Chromatographic Determination of Oxyhalides and Bromide	3
		ASTM D 6581 Standard Test Methods for Bromate, Bromide, Chlorate, and Chlorite in Drinking Water by Suppressed Ion Chromatography	4
		USEPA 0300.0 Inorganic Anions by Ion Chromatography	5
		USEPA 0300.1 Inorganic Anions in DW by Ion Chromatography	6
		USEPA 0317 Inorganic Oxyhalide disinfection by-products - DW	7
		Other (please specify)	8
	Capillary Ion Electrophoresis	APHA 4140B Capillary Ion Electrophoresis with Indirect UV Detection	9
	Other	Please specify	10

**Method Reference Key**

- i) APHA SM                    APHA "Standard Methods for the Examination of Water and Wastewater" (18, 19, 20, 21, 22 and 23 Edition).
- ii) ASTM                      ASTM International [www.astm.org](http://www.astm.org)
- iii) USEPA                    U.S Environmental Protection Agency, <http://www.epa.gov>.



**PROFICIENCY TESTING AUSTRALIA**  
**WATERS PROFICIENCY TESTING PROGRAM**  
**CHEMICAL ANALYSIS ROUND 261**  
**Inorganic Disinfection By-products**  
**MAY, 2020**  
**RESULTS SHEET**  
**(µg/L)**

**Please note:**

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

Laboratory Code

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

No.	ANALYTE	SAMPLE PTA R261		
		Result (µg/L)	±MU (µg/L)	METHOD CODE
1	<b>Chlorate</b>			
2	<b>Chlorite</b>			

- i) For each analyte only a single result is requested.
- ii) Report results using three significant figures.
- iii) Report results in micrograms per litre (µg/L).
- iv) Analytes with levels less than your level of detection, or not detected, report as a "<" value.
- v) For the analytes not tested, please report "Not Tested".
- vi) Do not correct results for recovery.
- vii) MU\* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in µg/L, using the same number of decimal places as for the result.

**DATE:** \_\_\_\_\_

**SIGNATURE:** \_\_\_\_\_

Return results <b>NO LATER THAN 12 JUNE 2020</b> to:	
Delfina Mihaila	
Proficiency Testing Australia	
PO Box 7507	
SILVERWATER NSW 2128	<b>Phone:</b> +61 2 9736 8397
AUSTRALIA	<b>Fax:</b> +61 2 9743 6664
	<b>Email:</b> <a href="mailto:dmihaila@pta.asn.au">dmihaila@pta.asn.au</a>

INSTRUCT WATERS PROF TEST PROG 261



*- End of Report -*