Report No. 805

Waters Proficiency Testing

Round 152

- Metals -

May 2013

Acknowledgments

PTA wishes to gratefully acknowledge the technical assistance provided for this program by Ms K Timms, Department of Primary Industry and Fisheries (Northern Territory, Australia). Also our thanks go to the Environmental Resource Associates (ERA) for the supply of samples and to Global Proficiency Pty Ltd (Melbourne, 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 metals - chromium, copper, iron, lead, nickel, thallium and zinc in waters. This is round 152 in a planned series of programs involving the analysis of chemical and physical parameters of waters.

The exercise was conducted in February 2013 by Proficiency Testing Australia (PTA). The main aim of the program was to assess laboratories' abilities to competently perform the prescribed analyses.

The Program Coordinator was Ms D Mihaila and the Technical Advisor was Ms K Timms of the Department of Primary Industry and Fisheries. This report was authorised by Ms W Fajloun, PTA Quality Coordinator.

2. Program Features and Design

2.1 Each laboratory was randomly allocated a unique code number for the program to ensure confidentiality of results. Reference to each laboratory in this report is by code number only. Please note that a number of laboratories reported more than one set of results and, therefore, their code numbers (with letter) could appear several times in the same data set.

2.2 Laboratories were provided with the "Instructions to Participants" and "Results Sheet" (see Appendix C). Laboratories were requested to perform the tests according to their routine methods.

2.3 Participants were provided with one sealed vial (labelled R152) containing solutions of metals (chromium, copper, iron, lead, nickel, thallium and zinc).

2.4 A total of 52 laboratories received samples, comprising:

- 42 Australian participants; and
- 10 overseas participants, including:
    - Brunei Darussalam (1), Indonesia (2), Malaysia (3), New Zealand (1), Papua New Guinea (1), Qatar (1), Thailand (1).

Of these 52 laboratories, 5 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, 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,* 2012 (reference [1]) defines the statistical terms and details the statistical procedures referred to in this report.

2.7 A tabulated listing of laboratories (by code number) identified as having outlier results can be found on page 34.

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

3. Statistical Format

For each test, the following information is given:

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

3.1 Outlier Results and Z-scores

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

A z-score close to zero indicates that the result agrees well with those from other laboratories, whereas, a z-score with an absolute value greater than or equal to 3.0 is considered to be an outlier and is marked by the symbol "**§**".

Each determination was examined for outliers with all methods pooled. The table on page 34 summarises the outlier results detected.

3.2 Results Tables and Summary Statistics

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

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

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

- *No. of Results*: the total number of results for that test/sample;
- *Median*: the middle value of the results;
- *Uncertainty of the Median*: a robust estimate of the standard deviation of the *Median*;
- *Normalised IQR*: the normalised interquartile range of the results;
- *Robust CV*: the robust coefficient of variation expressed as a percentage, i.e. 100 x *Normalised IQR* / *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:

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

n = number of results

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

3.3 Ordered Z-score Charts

The charts in Appendix A indicate each laboratory's robust z-score, in order of magnitude, marked with its laboratory code number. From these charts, each laboratory can readily compare its performance relative to the other laboratories.

These charts contain solid lines at +3.0 and -3.0, so that outliers are clearly identifiable as those laboratories whose "bar" extends beyond these "cut-off" lines. The y-axis of these charts has been limited, so very large z-scores appear to extend beyond the chart boundary.

4. PTA and Technical Advisor's Comments

4.1 Metrological Traceability and Measurement Uncertainty of Assigned Values

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

Sample preparation was undertaken according to 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), as shown in Table 1.

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

Analyte	Expected Levels (µg/L)	Median (µg/L)	Uncertainty of the median (µg/L)
Chromium	276	273.0	2.5
Copper	522	528.0	5.6
Iron	1390	1400.0	14.0
Lead	1480	1470.0	15.6
Nickel	1340	1360.0	16.3
Thallium	579	571.5	7.8
Zinc	1300	1304.0	14.9

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

Overall, the performance of participants in this round was good, with robust CVs less than 7% for all analytes.

4.2 Analysis of Round 152 Results

4.2.1 Chromium

Table 2 compares the chromium median and robust CV from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R152	273.0	4.6	41
Report 742	R137	743.0	5.8	49
Report 691	R126	545.5	4.6	56

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

Bias / Accuracy

Figure 1 exhibits the spread of results and the methods used for chromium testing in this round.

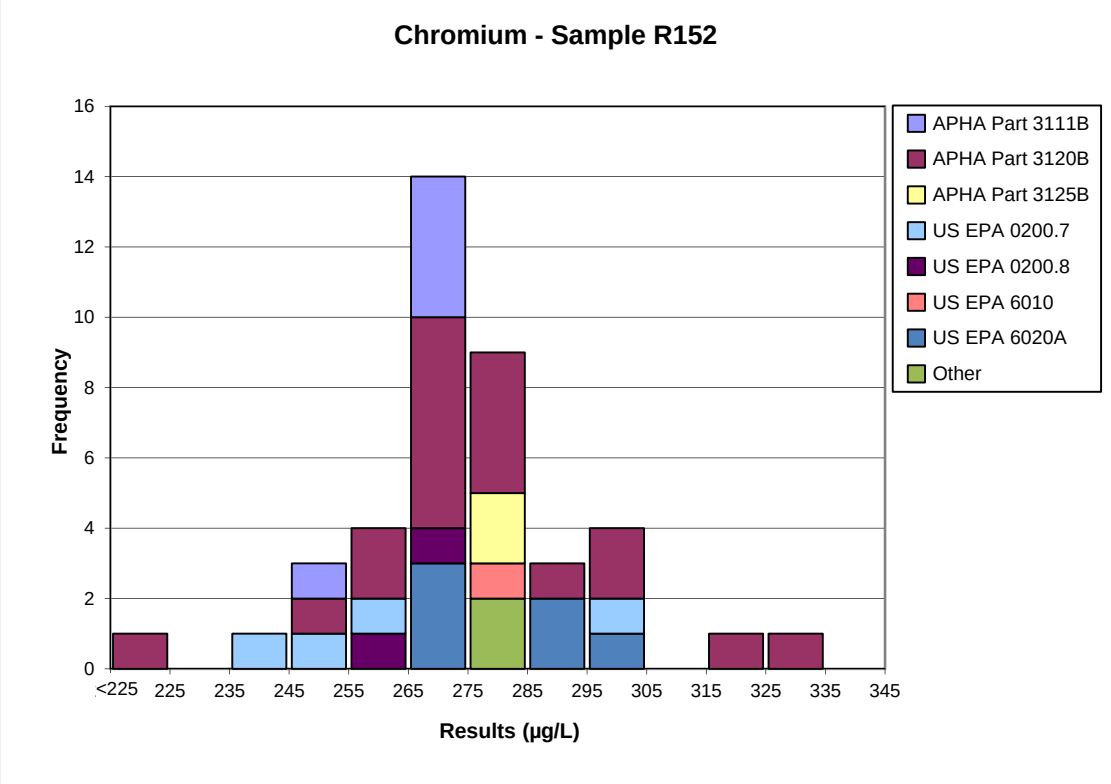


Figure 1. Spread of results for chromium testing of Sample R152, with a median of 273.0 µg/L.

The chromium testing was successfully performed, with satisfactory results (|z-scores| ≤ 2.0) ranging between 248 – 298 µg/L. Out of 41 participants, four questionable results (2.0 < |z-scores| < 3.0) were reported (laboratories 285, 402, 453 and 620). Three outlier results (|z-scores| ≥ 3.0) were obtained, requiring follow-up action by laboratories 188, 626 and 690. Laboratory 188 reported much lower results for all

elements tested (chromium, copper, iron, lead, nickel and zinc) suggesting a systematic error in the testing process. A laboratory investigation is recommended.

The data set formed an approximately normal distribution with no significant bias attributable to any one method. There was a large variety of methods used (Figure 1), with approximately 46% of participants using the method APHA Part 3120B (Inductively Coupled Plasma (ICP) Method). The remaining participants used other APHA protocols (17%), US EPA methods (32%) or other methods (5%).

Measurement Uncertainty (MU)

The MU reported by participants can be seen in Figure 2. Out of 41 participants, 35 (85%) submitted MU information. Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample.

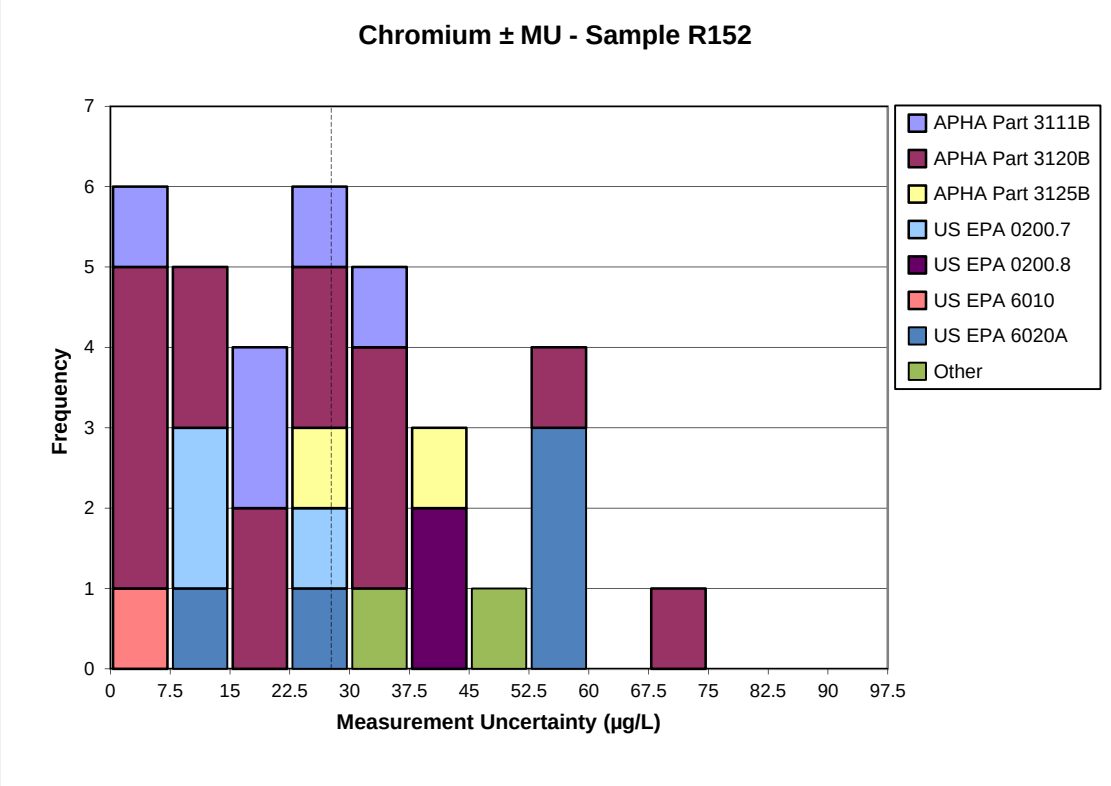


Figure 2. MU for chromium testing of Sample R152, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 27.7 µg/L) in this round.

A t-test of all the results (outliers removed), indicated the overall reproducibility for chromium testing was 274.7 ± 27.7 µg/L for Sample R152 (95% CI).

Laboratories 183, 217, 269, 427, 523, 620 and 690 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figure 3 below.

Chromium - Sample R152

Results of Sample R152, including MU, compared to the median

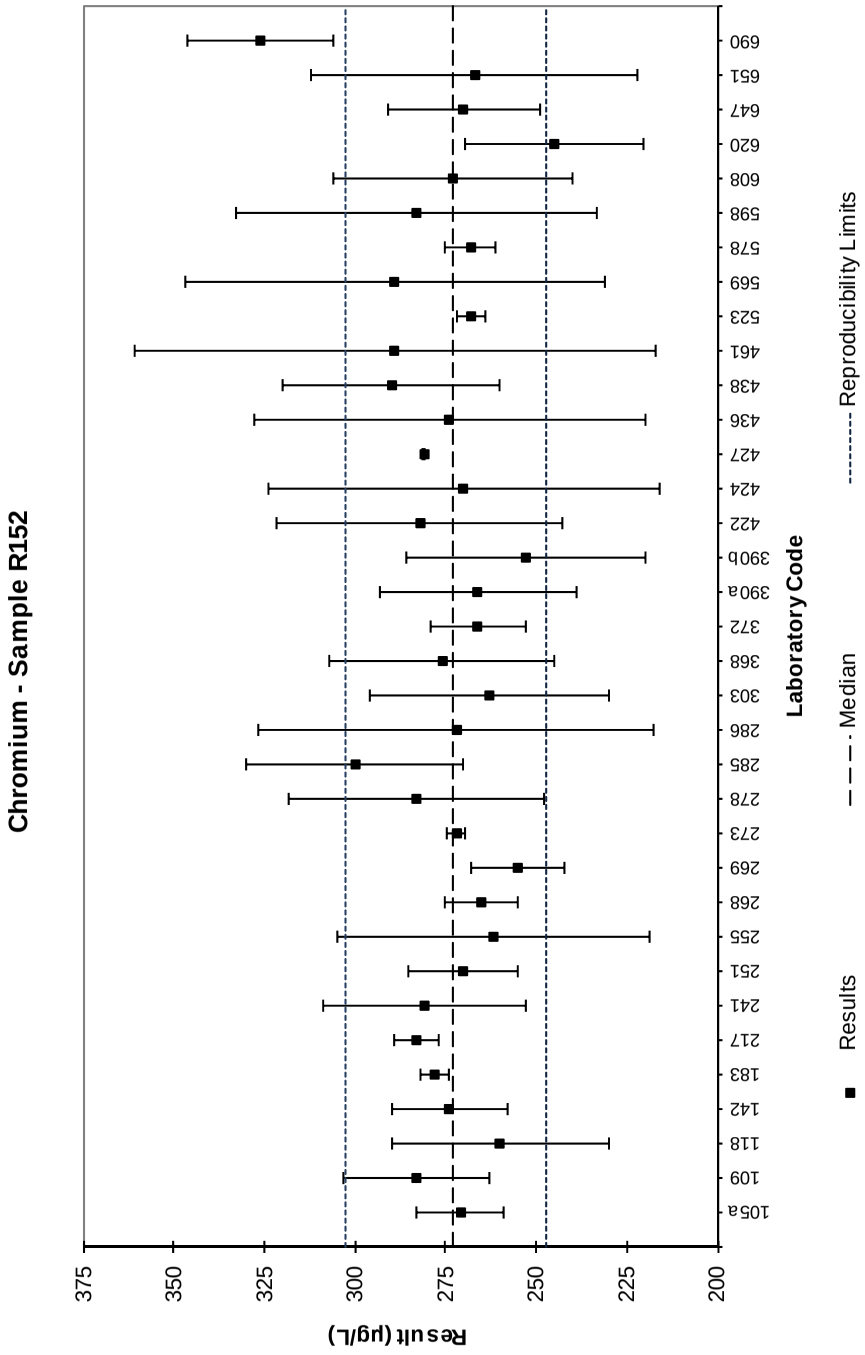


Figure 3. Chromium - Results of Sample R152, including MU, compared to the median

4.2.2 Copper

Table 3 compares the copper median and robust CV from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R152	528.0	5.6	44
Report 742	R137	280.7	6.3	54
Report 691	R126	357.0	4.4	59

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

Bias / Accuracy

The copper testing was successfully performed, with satisfactory results (|z-scores| ≤ 2.0) ranging between 469 – 587 µg/L. Out of 44 participants, two questionable results (2.0 < |z-scores| < 3.0) were reported (laboratories 240 and 620). One outlier result (|z-scores| ≥ 3.0) was obtained, requiring follow-up action by laboratory 188.

Figure 4 exhibits the spread of results and the methods used for copper testing in this round.

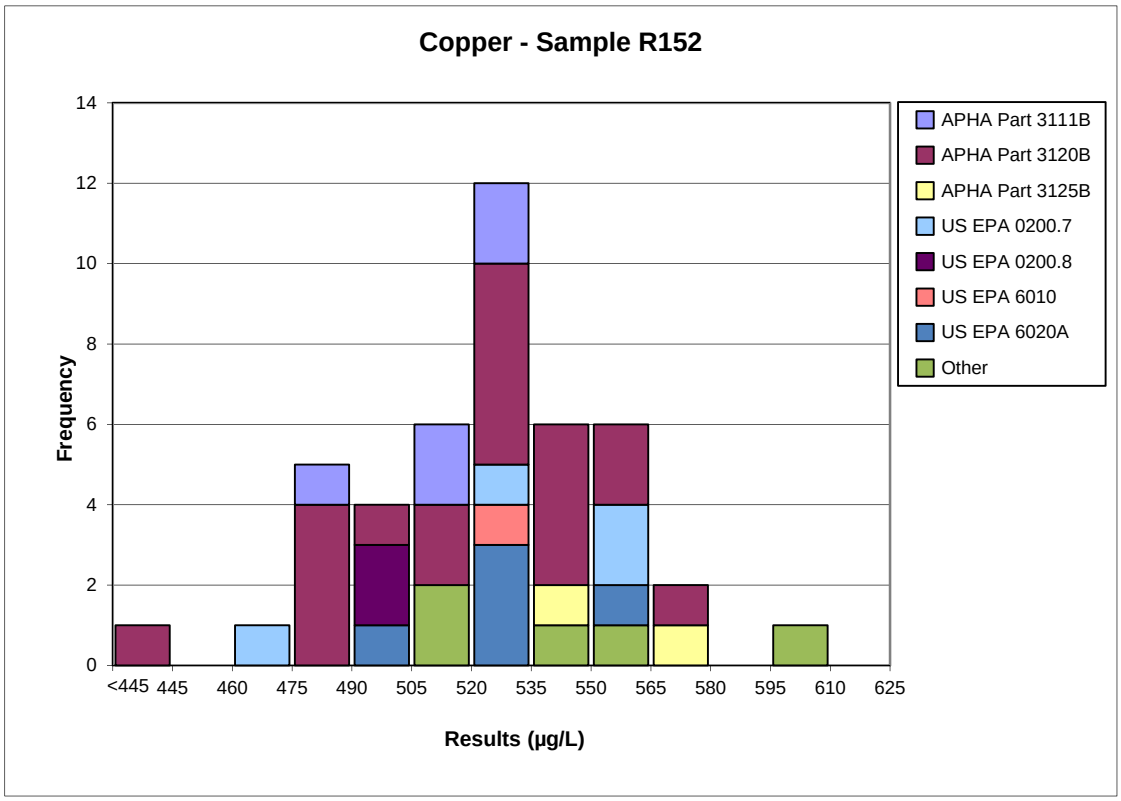


Figure 4. Spread of results for copper testing of Sample R152, with a median of 528.0 µg/L.

The data set formed an approximately normal distribution with no significant bias attributable to any one method. There was a large variety of methods used (Figure 4), with approximately 46% of participants using the method APHA Part 3120B (Inductively Coupled Plasma (ICP) Method). The remaining participants used other APHA protocols (16%), US EPA methods (27%) or other methods (11%).

Measurement Uncertainty (MU)

The MU reported by participants can be seen in Figure 5. Out of 44 participants, 36 (82%) submitted MU information. Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample.

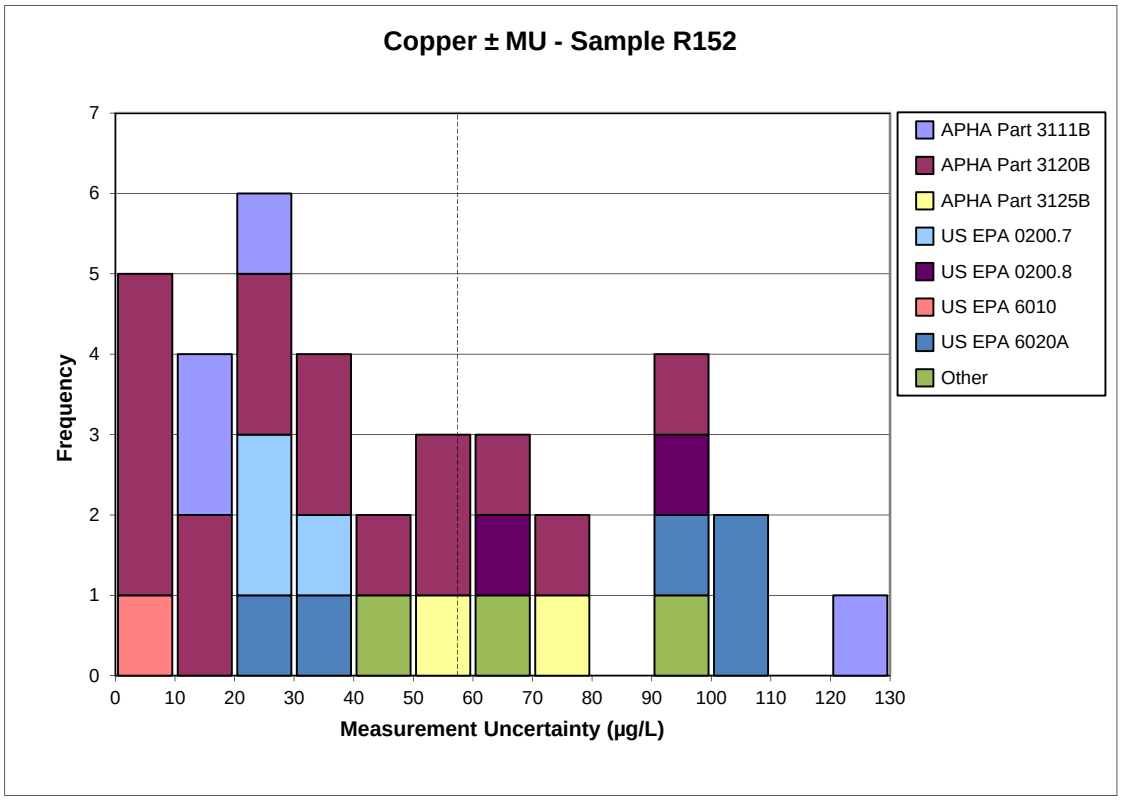


Figure 5. MU for copper testing of Sample R152, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 57.4 µg/L) in this round.

A t-test of all the results (outliers removed), indicated the overall reproducibility for copper testing was 527.4 ± 57.4 µg/L for Sample R152 (95% CI).

Laboratories 183, 217, 273, 372, 390b, 427, 436, 523 and 620 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figure 6 below.

Copper - Sample R152

Results of Sample R152, including MU, compared to the median

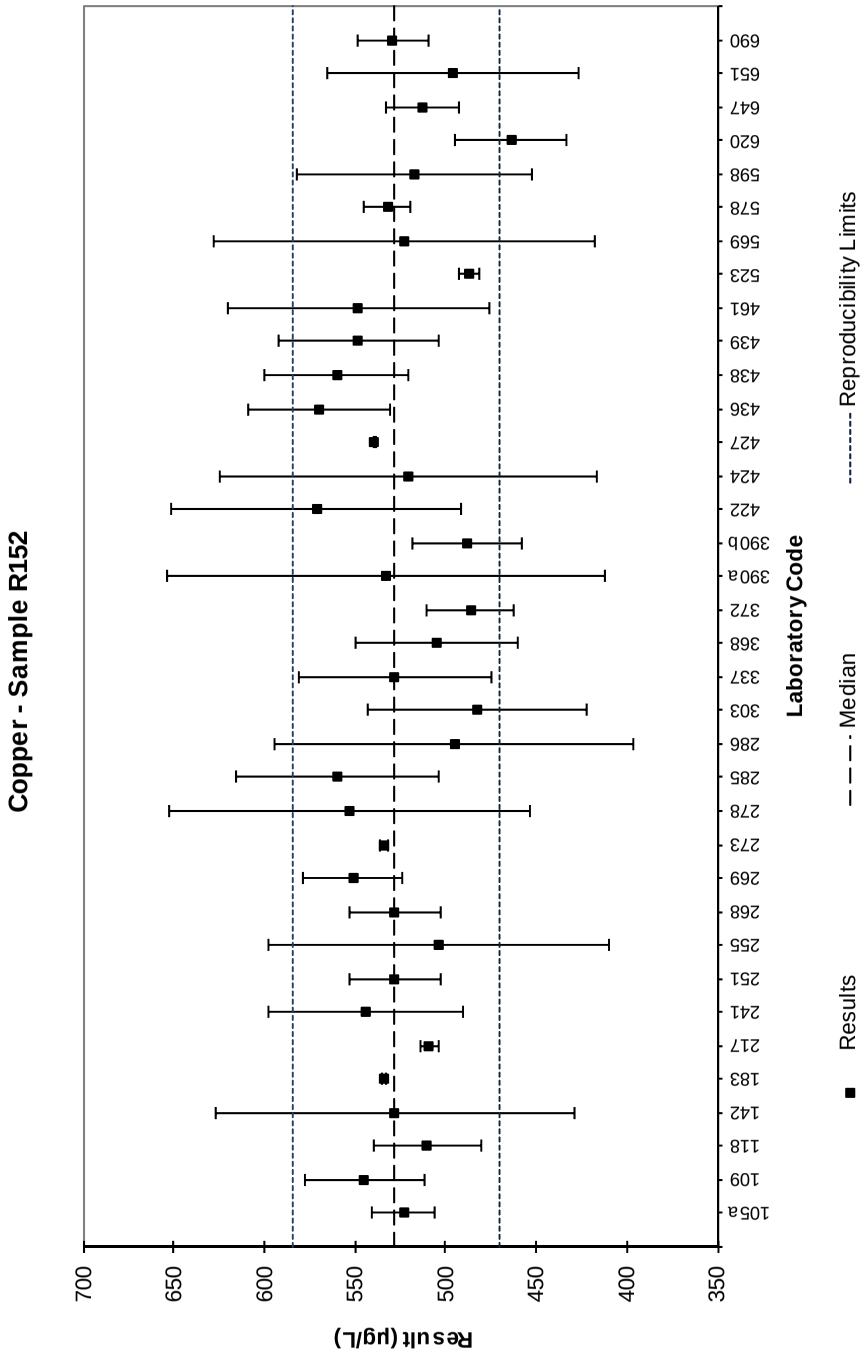


Figure 6. Copper - Results of Sample R152, including MU, compared to the median

4.2.3 Iron

Table 4 compares the iron median and robust CV from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R152	1400.0	5.4	46
Report 742	R137	589.0	8.1	56
Report 691	R126	435.5	8.0	62

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

Bias / Accuracy

The iron testing was successfully performed, with satisfactory results (|z-scores| ≤ 2.0) ranging between 1249 – 1551 µg/L. Out of 46 participants, two questionable results (2.0 < |z-scores| < 3.0) were reported (laboratories 118 and 626). Four outlier results (|z-scores| ≥ 3.0) were obtained, requiring follow-up action by laboratories 188, 237, 390a and 390b.

Figure 7 exhibits the spread of results and the methods used for iron testing in this round.

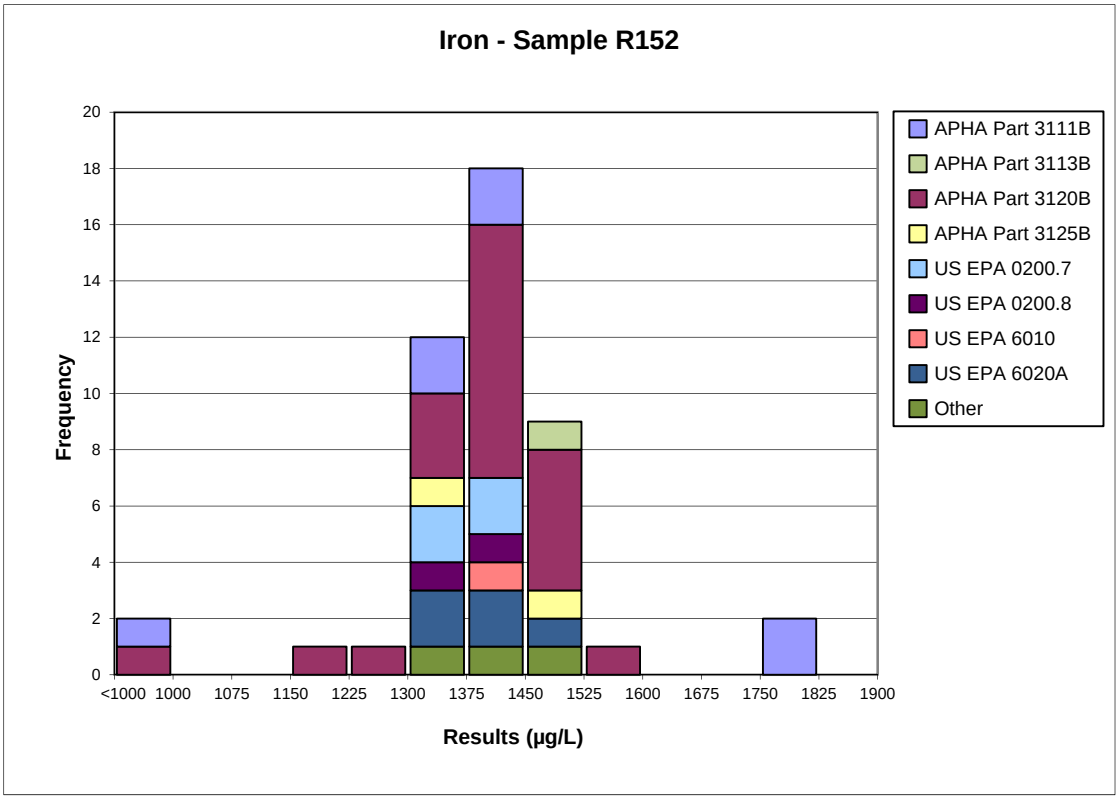


Figure 7. Spread of results for iron testing of Sample R152, with a median of 1400.0 µg/L.

The data set formed an approximately normal distribution with no significant bias attributable to any one method. There was a large variety of methods used (Figure 7), with approximately 46% of participants using the method APHA Part 3120B (Inductively Coupled Plasma (ICP) Method). The remaining participants used other APHA protocols (21%), US EPA methods (26%) or other methods (7%).

Measurement Uncertainty (MU)

The MU reported by participants can be seen in Figure 8. Out of 46 participants, 36 (78%) submitted MU information. Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample.

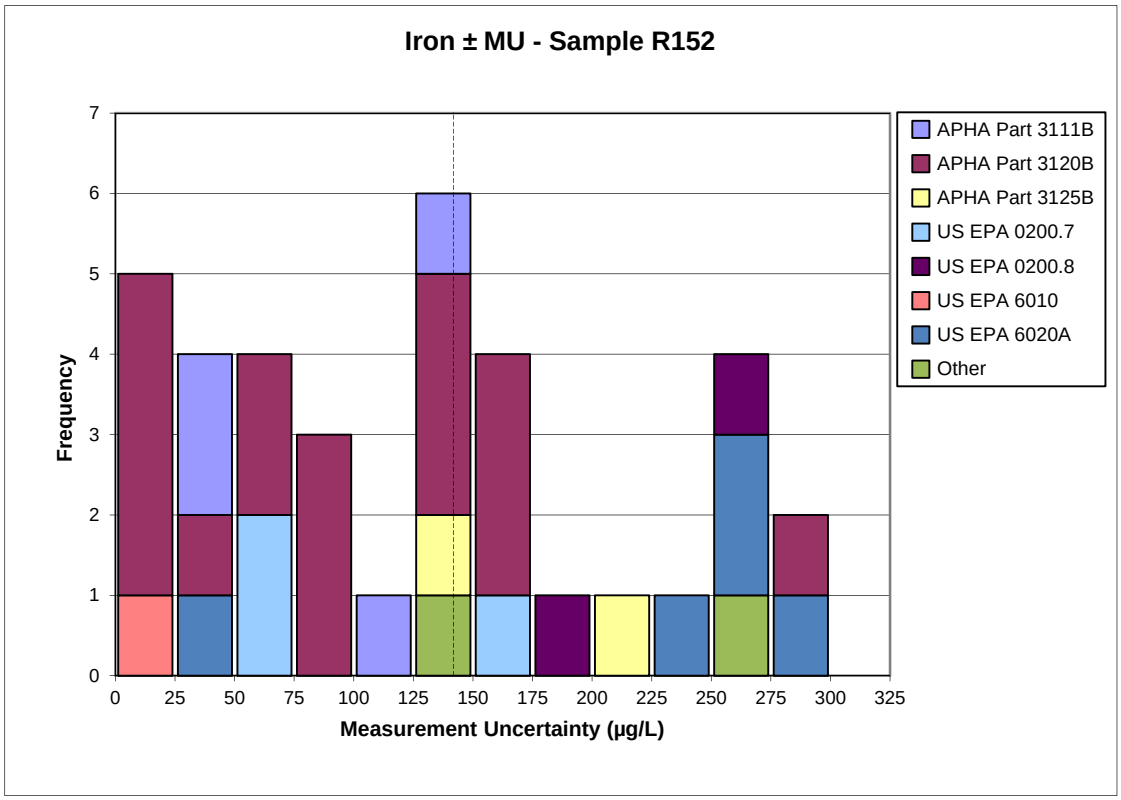


Figure 8. MU for iron testing of Sample R152, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 141.8 µg/L) in this round.

A t-test of all the results (outliers removed), indicated the overall reproducibility for iron testing was 1401.4 ± 141.8 µg/L for Sample R152 (95% CI).

Laboratories 105a, 118, 183, 217, 269, 273, 390a, 390b, 427, 461 and 647 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figure 9 below.

Iron - Sample R152

Results of Sample R152, including MU, compared to the median

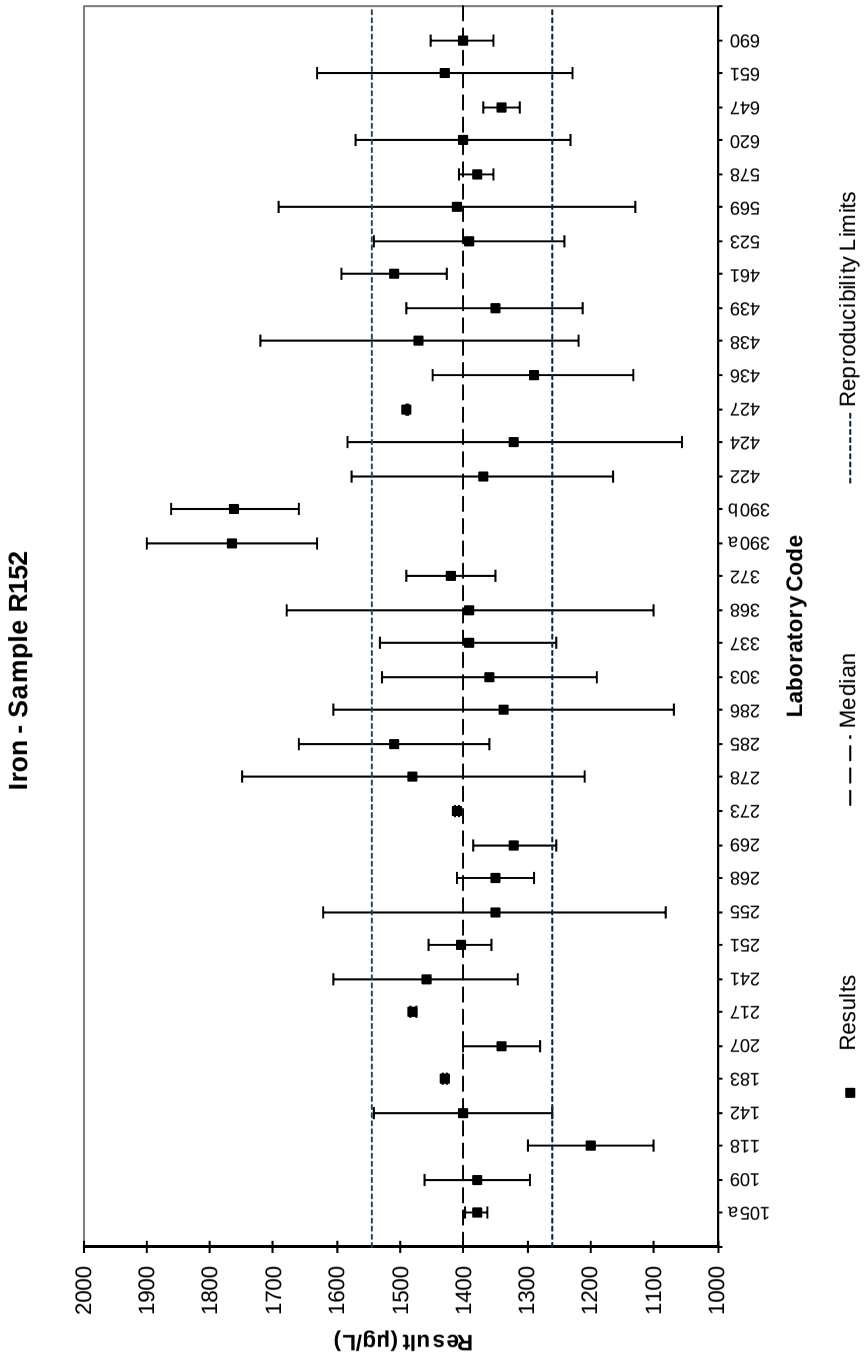


Figure 9. Iron - Results of Sample R152, including MU, compared to the median

4.2.4 Lead

Table 5 compares the lead median and robust CV from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R152	1470.0	5.5	43
Report 742	R137	810.0	5.4	51
Report 691	R126	532.0	4.8	58

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

Bias / Accuracy

The lead testing was successfully performed, with satisfactory results (|z-scores| ≤ 2.0) ranging between 1307 – 1633 µg/L. Out of 43 participants, one questionable result (2.0 < |z-scores| < 3.0) was reported (laboratory 118). Three outlier results (|z-scores| ≥ 3.0) were obtained, requiring follow-up action by laboratories 188, 436 and 647.

Figure 10 exhibits the spread of results and the methods used for lead testing in this round.

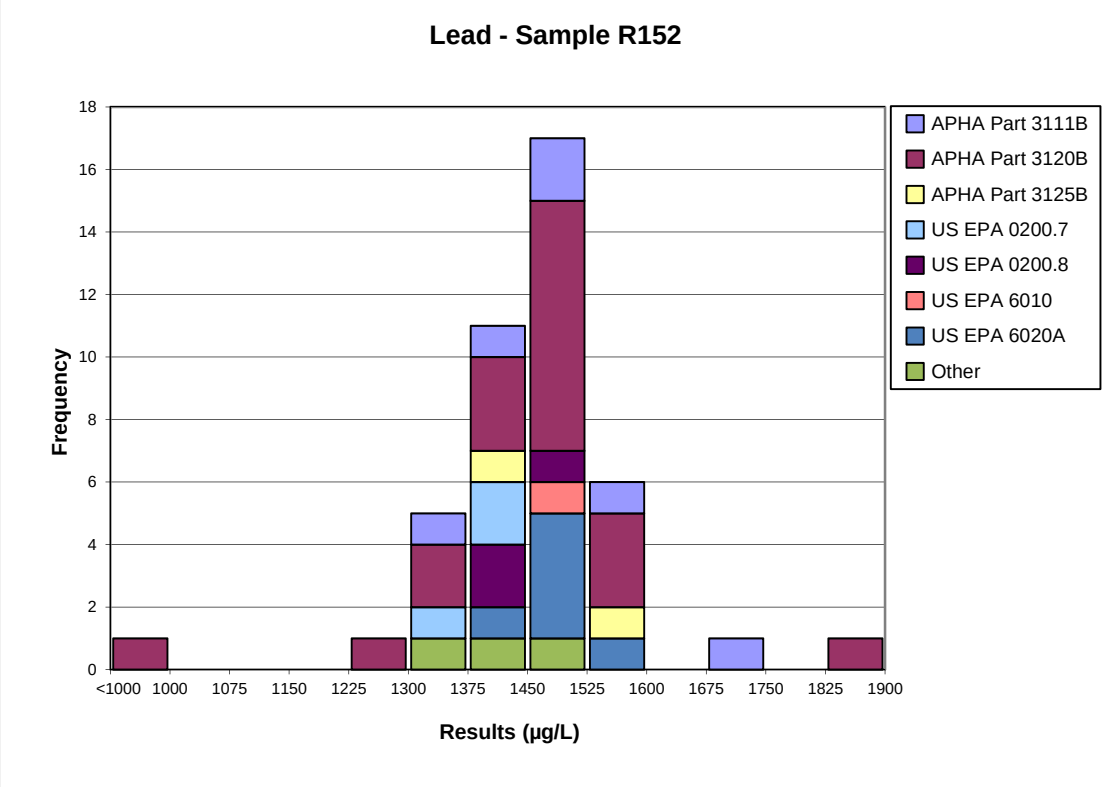


Figure 10. Spread of results for lead testing of Sample R152, with a median of 1470.0 µg/L.

The data set formed an approximately normal distribution with no significant bias attributable to any one method. There was a large variety of methods used (Figure 10), with approximately 44% of participants using the method APHA Part 3120B (Inductively Coupled Plasma (ICP) Method). The remaining participants used other APHA protocols (19%), US EPA methods (30%) or other methods (7%).

Measurement Uncertainty (MU)

The MU reported by participants can be seen in Figure 11. Out of 43 participants, 35 (81%) submitted MU information. Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample.

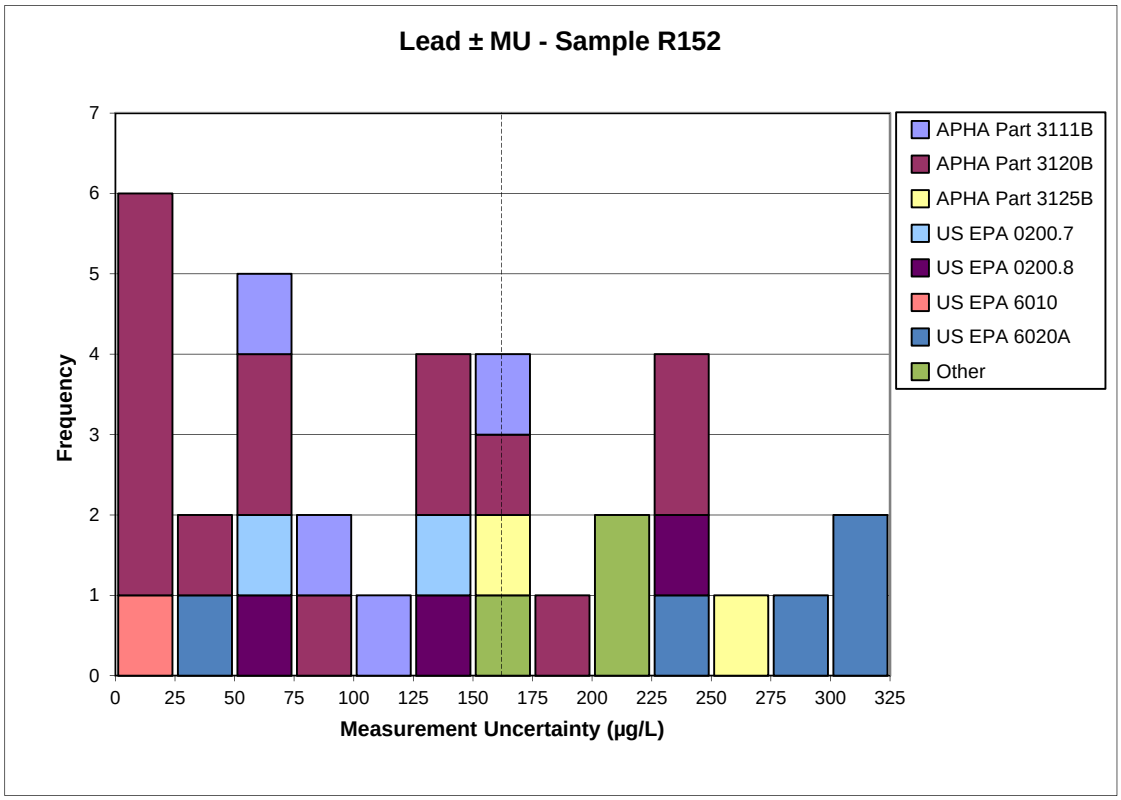


Figure 11. MU for lead testing of Sample R152, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 161.9 µg/L) in this round.

A t-test of all the results (outliers removed), indicated the overall reproducibility for lead testing was 1451.6 ± 161.9 µg/L for Sample R152 (95% CI).

Laboratories 118, 183, 269, 285, 390b, 436, 461, 620, 647 and 690 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figure 12 below.

Lead - Sample R152

Results of Sample R152, including MU, compared to the median

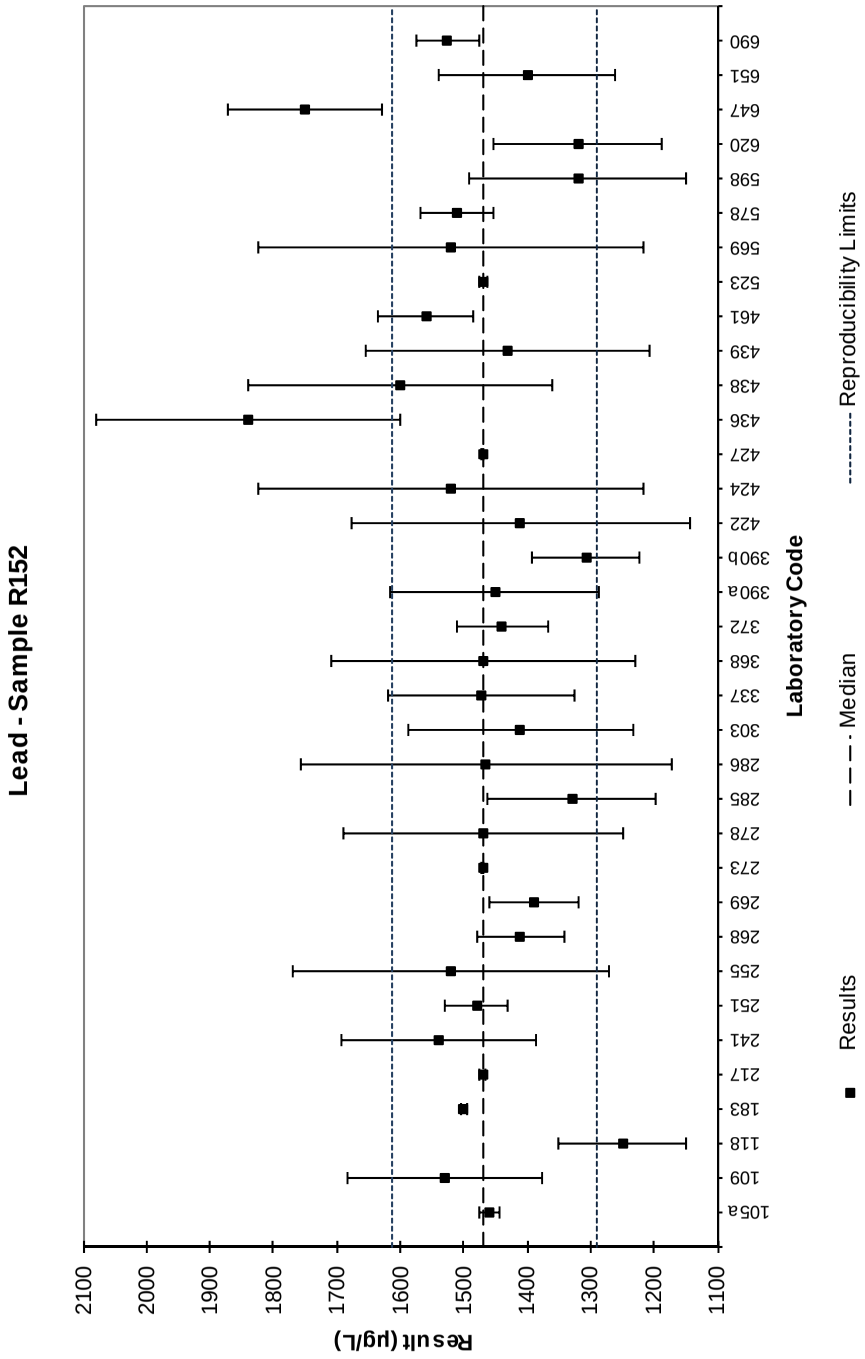


Figure 12. Lead - Results of Sample R152, including MU, compared to the median

4.2.5 Nickel

Table 6 compares the nickel median and robust CV from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R152	1360.0	6.3	43
Report 742	R137	823.0	4.3	49
Report 691	R126	187.0	5.2	56

Table 6. Comparison of current round variability and proficiency median of nickel testing with the results of the previous two rounds.

Bias / Accuracy

The nickel testing was successfully performed, with satisfactory results (|z-scores| ≤ 2.0) ranging between 1190 – 1530 µg/L. Out of 43 participants, one questionable result (2.0 < |z-scores| < 3.0) was reported (laboratory 353). Three outlier results (|z-scores| ≥ 3.0) were obtained, requiring follow-up action by laboratories 188, 390b and 436.

Figure 13 exhibits the spread of results and the methods used for nickel testing in this round.

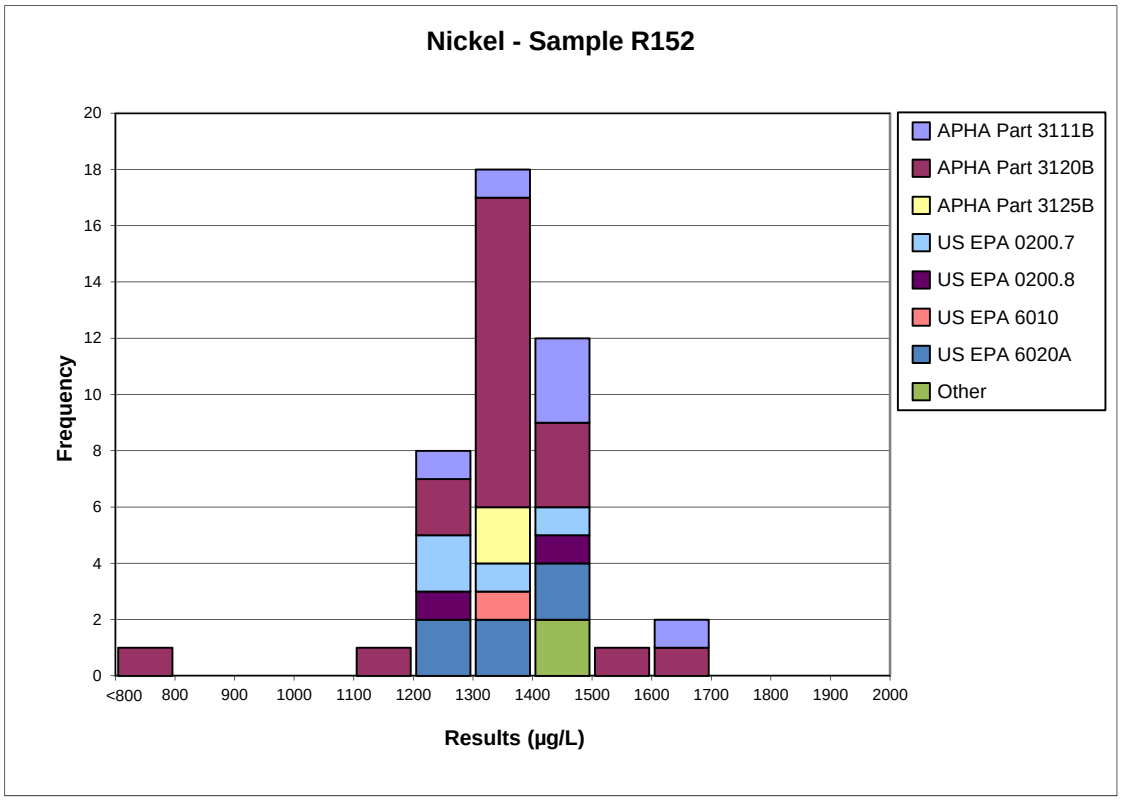


Figure 13. Spread of results for nickel testing of Sample R152, with a median of 1360.0 µg/L.

The data set formed an approximately normal distribution with no significant bias attributable to any one method. There was a large variety of methods used (Figure 13), with approximately 47% of participants using the method APHA Part 3120B (Inductively Coupled Plasma (ICP) Method). The remaining participants used other APHA protocols (19%), US EPA methods (30%) or other methods (5%).

Measurement Uncertainty (MU)

The MU reported by participants can be seen in Figure 14. Out of 43 participants, 35 (81%) submitted MU information. Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample.

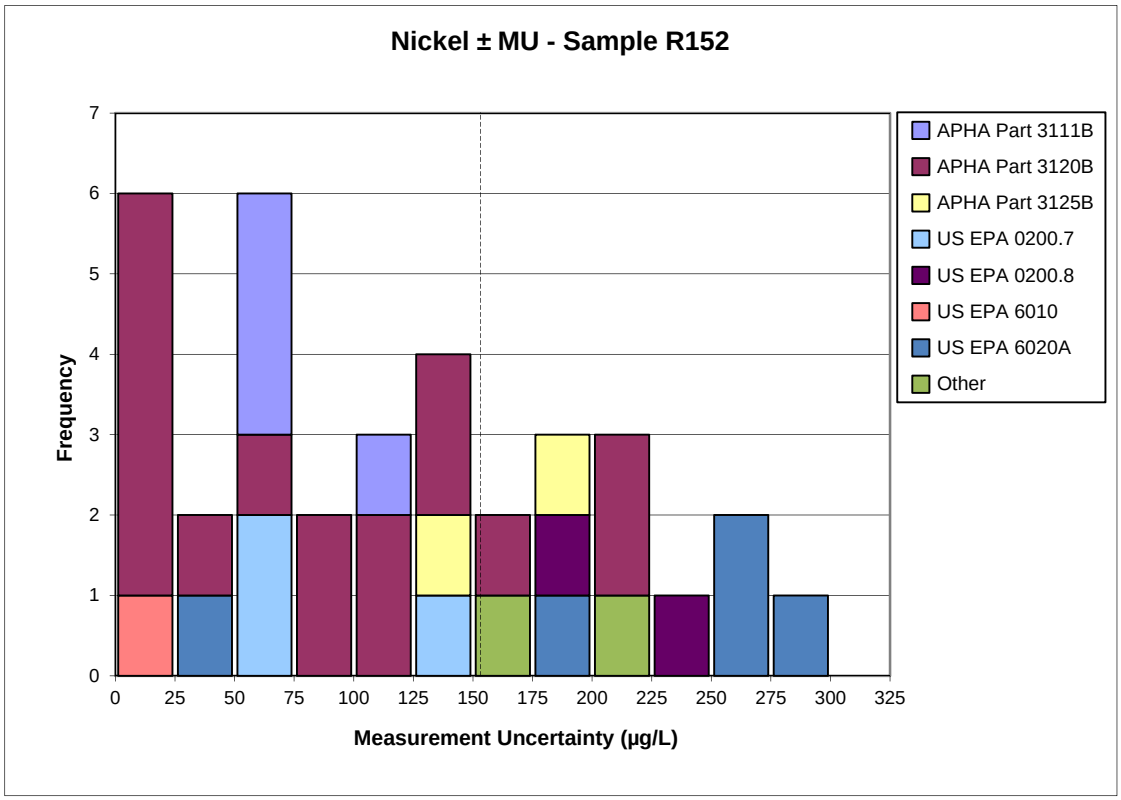


Figure 14. MU for nickel testing of Sample R152, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 153.2 µg/L) in this round.

A t-test of all the results (outliers removed), indicated the overall reproducibility for nickel testing was 1365.9 ± 153.2 µg/L for Sample R152 (95% CI).

Laboratories 105a, 183, 217, 251, 269, 273, 390a, 390b, 427, 436, 523 and 578 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figure 15 below.

Nickel - Sample R152

Results of Sample R152, including MU, compared to the median

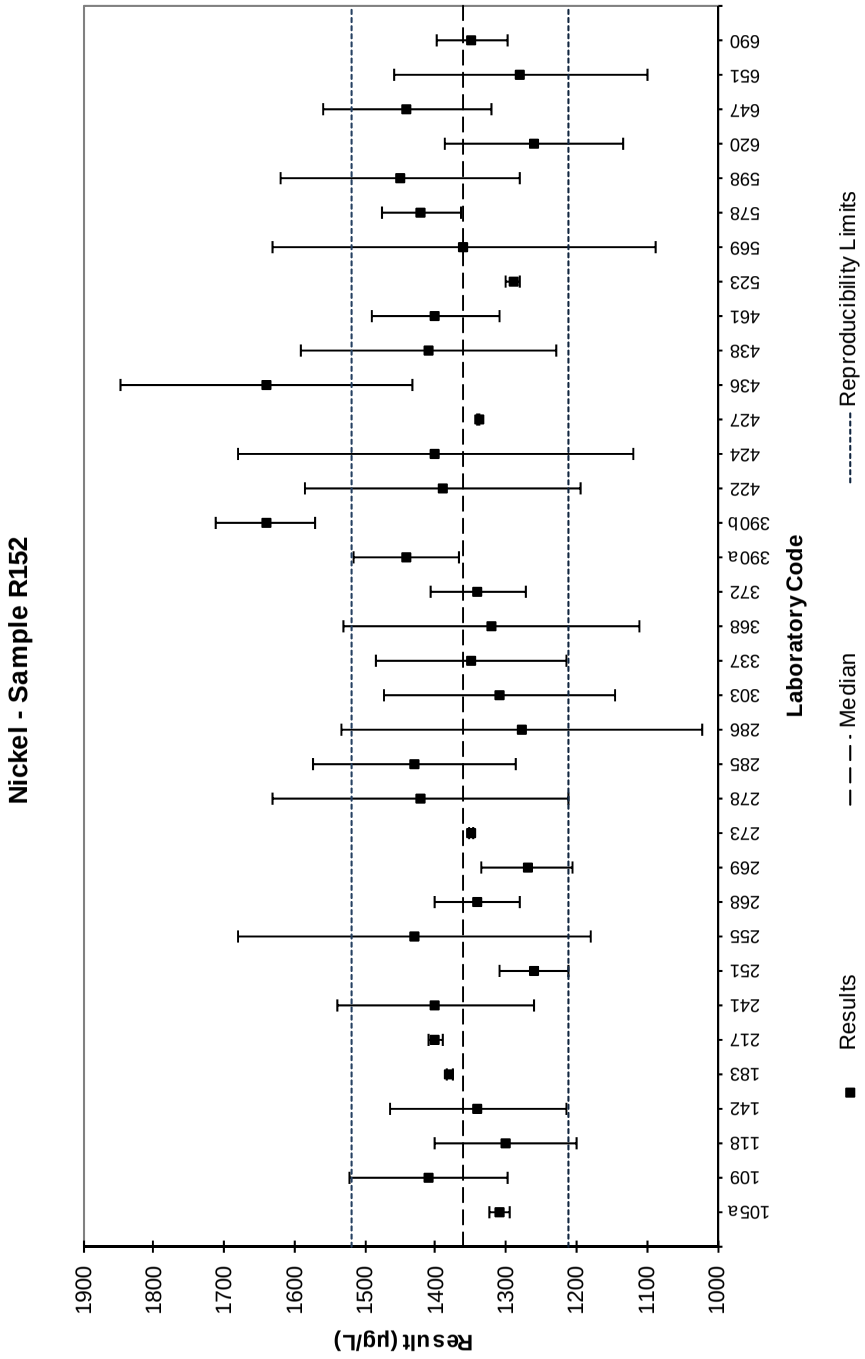


Figure 15. Nickel - Results of Sample R152, including MU, compared to the median

4.2.6 Thallium

Table 7 compares the thallium median and robust CV from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R152	571.5	5.8	28
Report 742	R137	733.0	6.8	31
Report 691	R126	357.0	4.7	39

Table 7. Comparison of current round variability and proficiency median of thallium testing with the results of the previous two rounds.

Bias / Accuracy

The thallium testing was successfully performed, with satisfactory results (|z-scores| ≤ 2.0) ranging between 506 – 637 µg/L. Out of 28 participants, two questionable results (2.0 < |z-scores| < 3.0) were reported (laboratories 436 and 620). Two outlier results (|z-scores| ≥ 3.0) were obtained, requiring follow-up action by laboratories 118 and 402.

Figure 16 exhibits the spread of results and the methods used for thallium testing in this round.

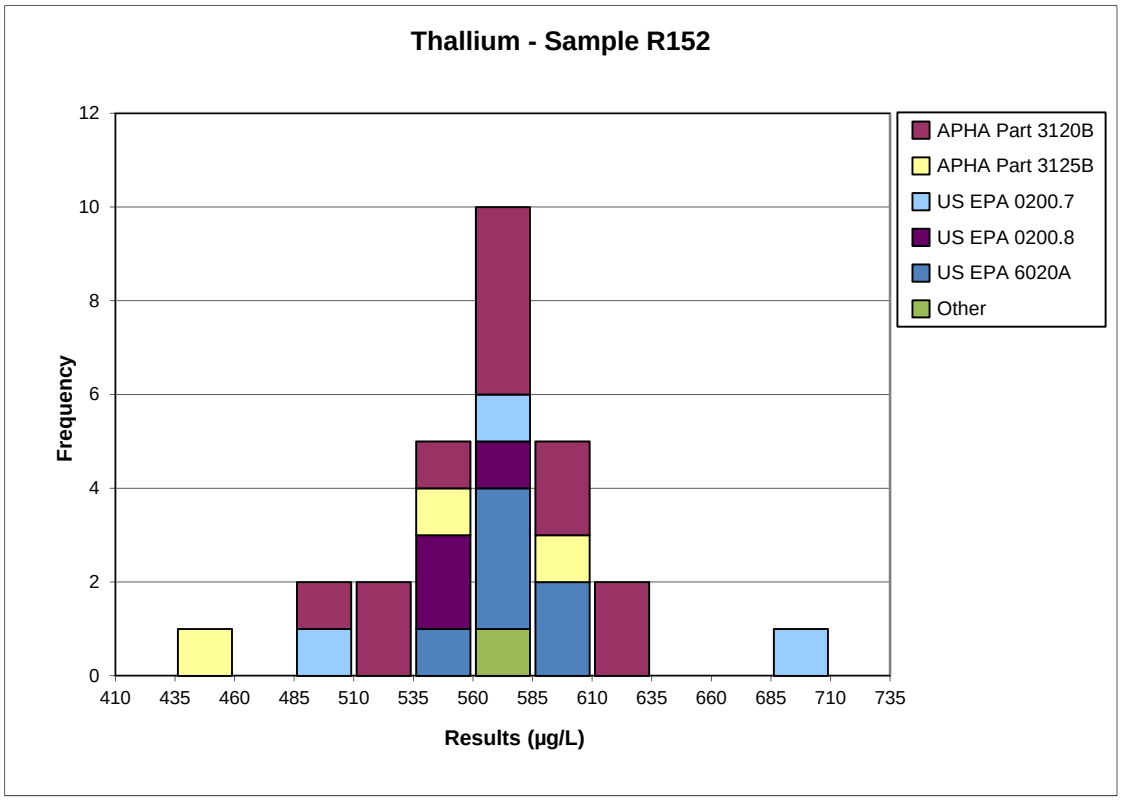


Figure 16. Spread of results for thallium testing of Sample R152, with a median of 571.5 µg/L.

The data set formed an approximately normal distribution with no significant bias attributable to any one method. There was a large variety of methods used (Figure 16), with approximately 43% of participants using the method APHA Part 3120B (Inductively Coupled Plasma (ICP) Method) and 21% using US EPA 6020A (Inductively Coupled Plasma/MS). The remaining participants used APHA Part 3125B ((Inductively Coupled Plasma/MS)) (11%), other US EPA methods (21%) or other methods (4%).

Measurement Uncertainty (MU)

The MU reported by participants can be seen in Figure 17. Out of 28 participants, 24 (86%) submitted MU information. Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample.

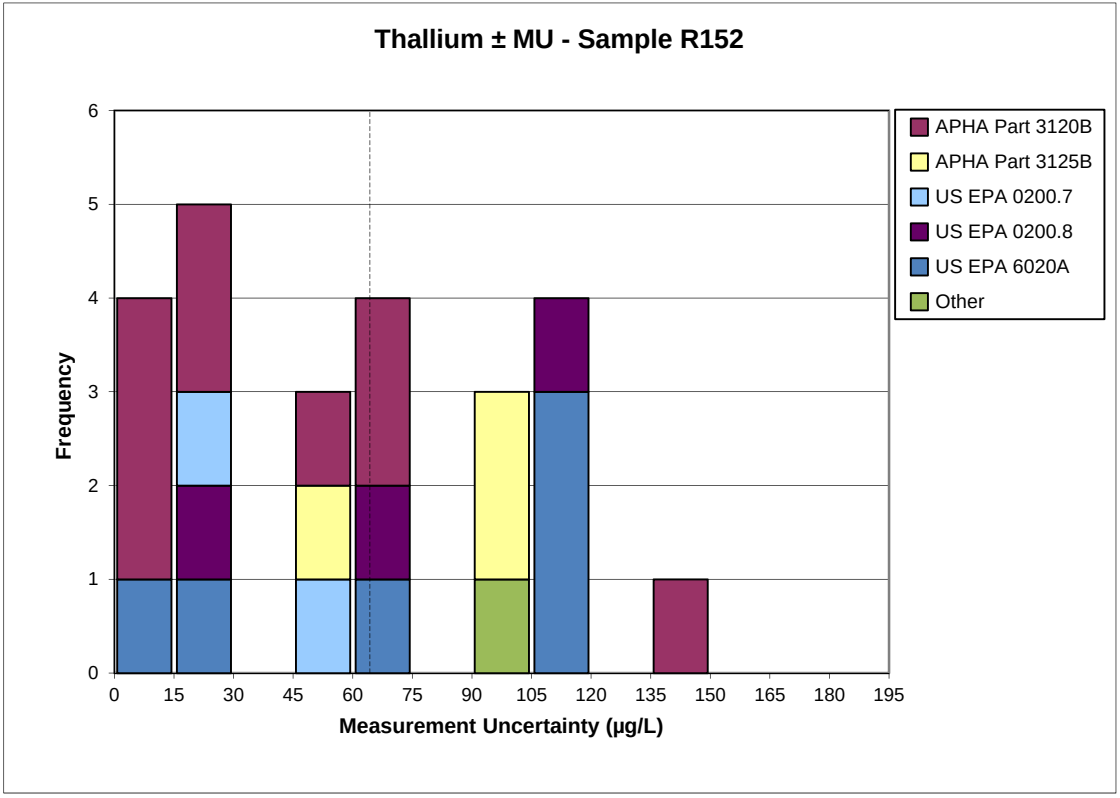


Figure 17. MU for thallium testing of Sample R152, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 64.3 µg/L) in this round.

A t-test of all the results (outliers removed), indicated the overall reproducibility for thallium testing was 567.0 ± 64.3 µg/L for Sample R152 (95% CI).

Laboratories 105a, 118, 217, 427, 436, 523 and 620 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figure 18 below.

Thallium - Sample R152

Results of Sample R152, including MU, compared to the median

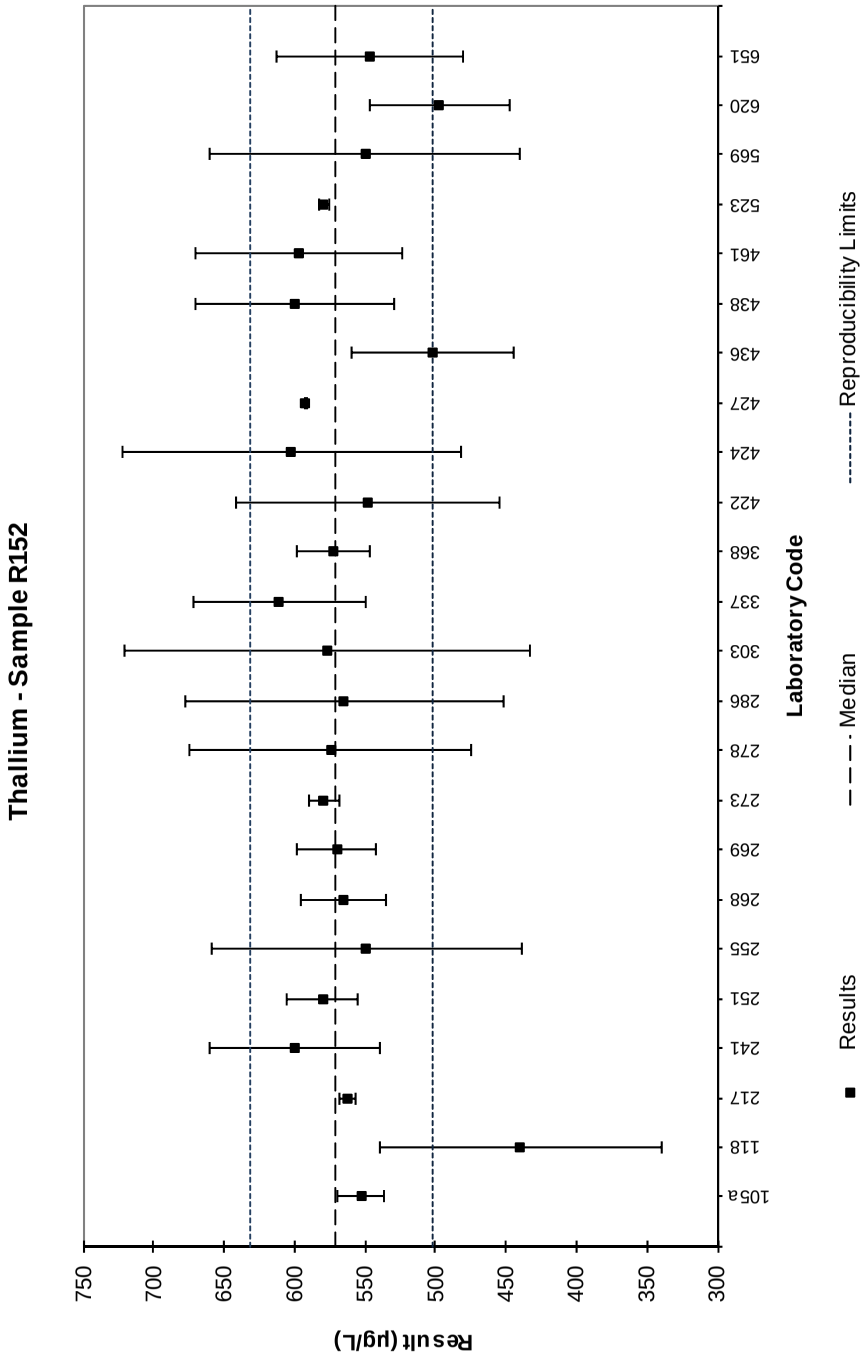


Figure 18. Thallium - Results of Sample R152, including MU, compared to the median

4.2.7 Zinc

Table 8 compares the zinc median and robust CV from this round to those obtained in previous PTA rounds.

Round	Sample	Median (µg/L)	Robust CV (%)	Participants
This study	R152	1304.0	6.3	47
Report 742	R137	401.0	6.3	57
Report 691	R126	909.0	4.9	63

Table 8. Comparison of current round variability and proficiency median of zinc testing with the results of the previous two rounds.

Bias / Accuracy

The zinc testing was successfully performed, with satisfactory results (|z-scores| ≤ 2.0) ranging between 1141 – 1467 µg/L. Out of 47 participants, four questionable results (2.0 < |z-scores| < 3.0) were reported (laboratories 269, 402, 422 and 620). Two outlier results (|z-scores| ≥ 3.0) were obtained, requiring follow-up action by laboratories 188 and 626.

Figure 19 exhibits the spread of results and the methods used for zinc testing in this round.

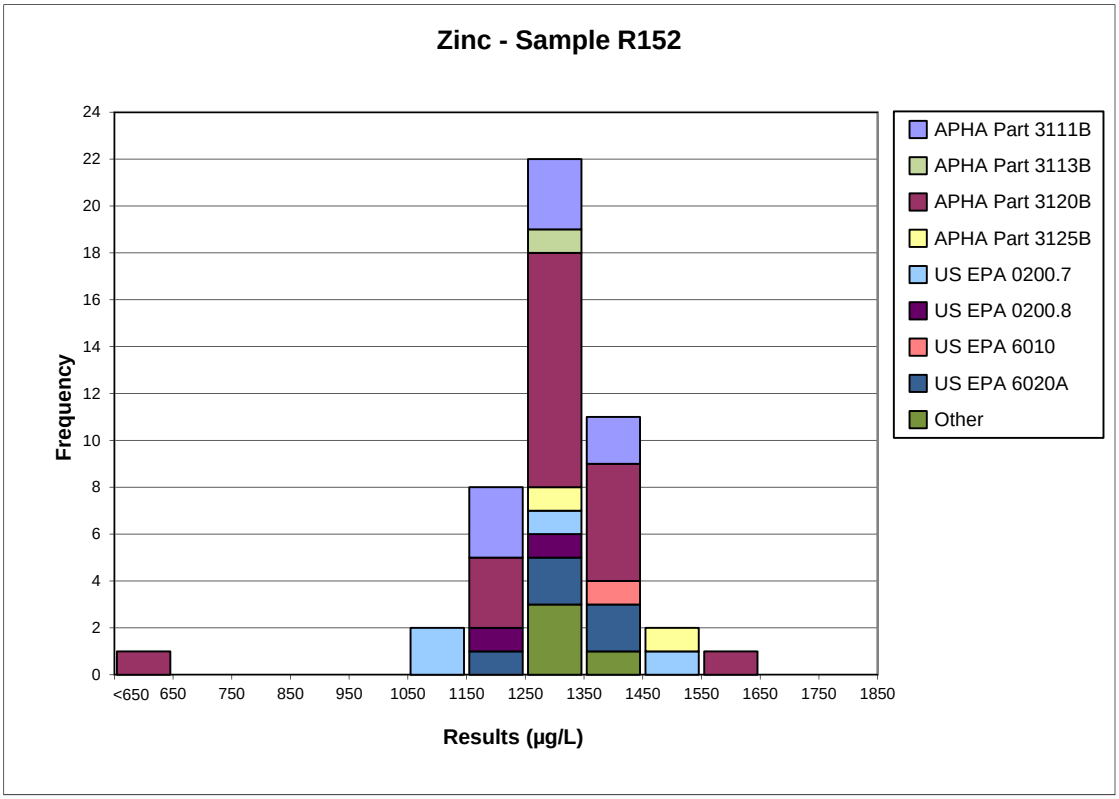


Figure 19. Spread of results for zinc testing of Sample R152, with a median of 1304.0 µg/L.

The data set formed an approximately normal distribution with no significant bias attributable to any one method. There was a large variety of methods used (Figure 19), with approximately 43% of participants using the method APHA Part 3120B (Inductively Coupled Plasma (ICP) Method). The remaining participants used other APHA protocols (23%), US EPA methods (26%) or other methods (9%).

Measurement Uncertainty (MU)

The MU reported by participants can be seen in Figure 20. Out of 47 participants, 37 (79%) submitted MU information. Many of the stated MUs did not accurately reflect the difference between the median and the participant's result for this proficiency sample.

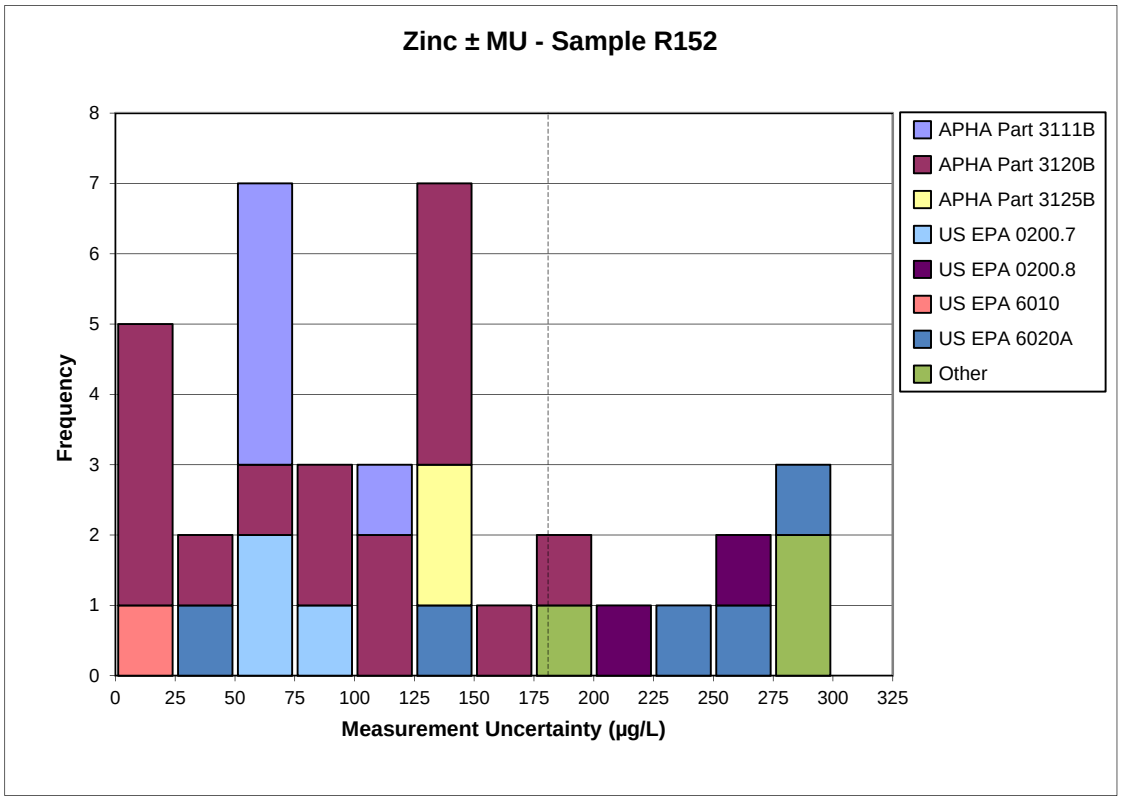


Figure 20. MU for zinc testing of Sample R152, as reported by participants, compared with 95% confidence interval for overall reproducibility (----) (± 180.9 µg/L) in this round.

A t-test of all the results (outliers removed), indicated the overall reproducibility for zinc testing was 1307.8 ± 180.9 µg/L for Sample R152 (95% CI).

Laboratories 105a, 183, 217, 269, 273, 372, 390b, 422, 427 and 620 may wish to re-examine their MU calculations, as their result was further from the median than their stated MU, as shown in Figure 21 below.

Zinc - Sample R152

Results of Sample R152, including MU, compared to the median

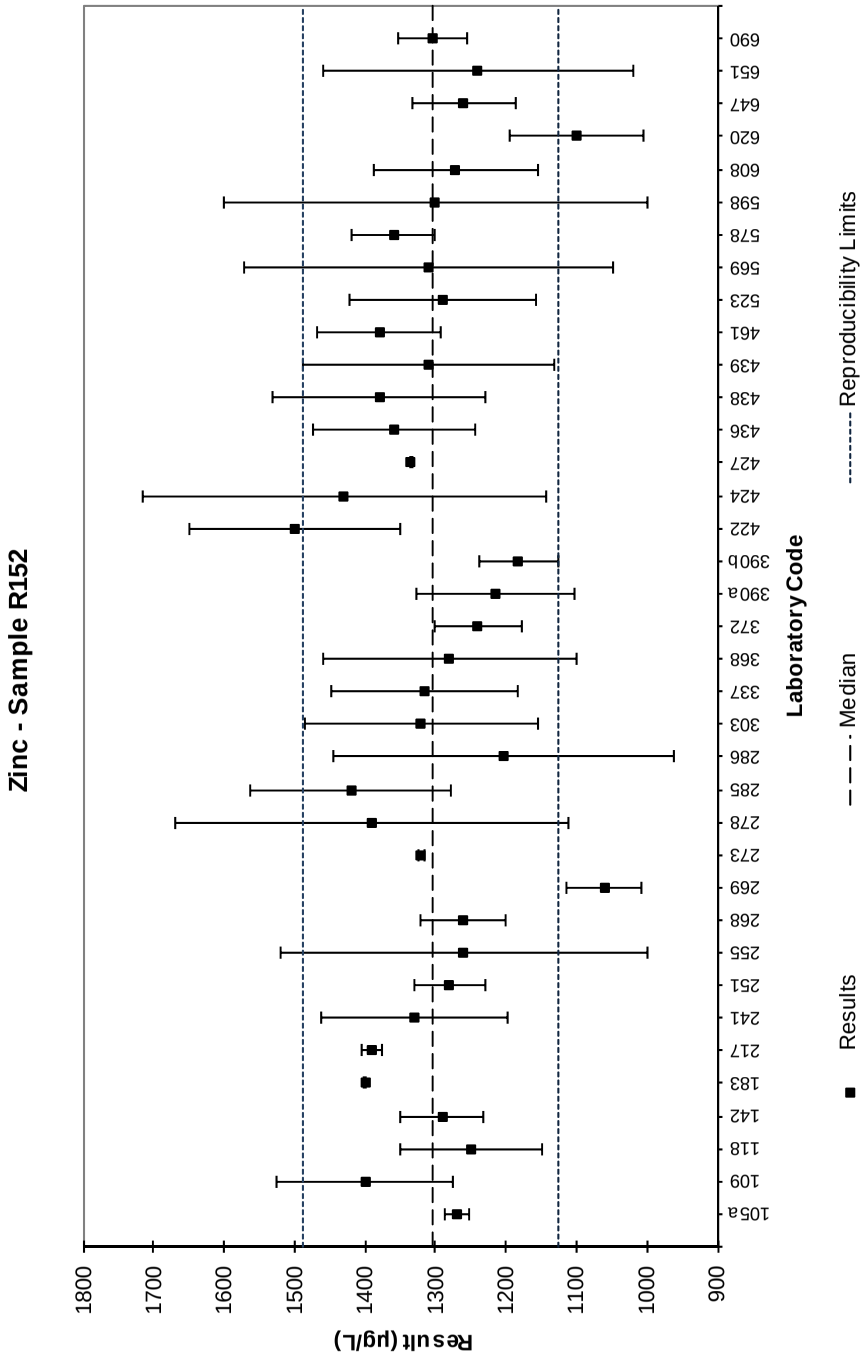


Figure 21. Zinc - Results of Sample R152, including MU, compared to the median

4.3 Analysis of Results by Method Groups

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

The majority of the participant laboratories in this round (77%-100%) used either ICP/AES (Inductively Coupled Plasma / Atomic Emission Spectrometry) or ICP/MS (Inductively Coupled Plasma / Mass Spectrometry) techniques compared to AAS (Atomic Absorption Spectrometry) technique, which shows the advantage of multi elemental technique over single elemental.

The methods used in this round suggest the preference for more recent techniques. Thus, none of the participating laboratories used the APHA Methods Part 3111C-E, (method codes 2-4) or US EPA 0200.9 GFAA method (method code 10) and only one laboratory (Laboratory 452, analysis of iron and zinc) used the APHA Electrothermal AAS method (APHA Part 3113B, method code 5). Additionally, laboratory 439 used an in-house method based on APHA 3113B for analysis of copper, iron, lead and zinc.

The method APHA Part 3120B (ICP) - Method code 6, was most frequently employed for all analytes and the statistical analyses of the results from this method are outlined in table 9.

Analysis	**Method code**	**Participants**	**Median ± Uncertainty of the Median (µg/L)**	**Robust CV (%)**
Chromium	6	19	274.0 ± 4.0	5.1
Copper	6	20	528.0 ± 9.4	6.4
Iron	6	21	1392.0 ± 24.3	6.4
Lead	6	19	1470.0 ± 18.3	4.3
Nickel	6	20	1344.5 ± 19.2	5.1
Thallium	6	12	575.0 ± 12.3	5.9
Zinc	6	20	1317.5 ± 19.6	5.3

Table 9. Variability and proficiency medians of metals results obtained by method 6 in Round 152.

In order for methods to be grouped for analysis, PTA requires at least 11 sets of results from the same method group. Please note that for other method codes there were less than 11 results submitted for each method and reliable conclusions cannot be drawn from analysing them on this occasion.

Five laboratories indicated the use of other methods than those listed in the Instructions to Participants. Out of these, four laboratories specified their choice method as follows: laboratory 240 used a HACH method for analysis of copper, laboratory 278 used an in-house ICP/MS method for all elements, laboratory 439 used an in-house method based on APHA 3113B for copper, iron, lead and zinc and laboratory 598 used an in-house method based on US EPA 0200.7 for chromium, copper, lead, nickel and zinc.

Most of the digestion methods involved nitric acid or a combination of nitric and hydrochloric acid, with a small number of laboratories using the microwave in the digestion process. It is worth noting that from the results reported, there is no notable difference between the non-digestion and various digestion methods, most of the laboratories being able to demonstrate competency in controlling the problems of contamination and loss of analyte during the process.

4.3.1 Chromium

Out of 41 results submitted, 25 (61%) were obtained by ICP/AES methods, 11 (27%) by ICP/MS methods and 5 (12%) by Direct Air-Acetylene Flame method (Flame AAS). Figure 22 below shows the chromium results distribution for each technique, indicating a larger spread for ICP/AES methods compared to ICP/MS. All three chromium results deemed to be outliers in this round were obtained by ICP/AES methods. ICP/AES also produced three out of four questionable results for chromium. By comparison, 10 out of 11 results obtained by ICP/MS were satisfactory with only one result having a |z-score| >2.0.

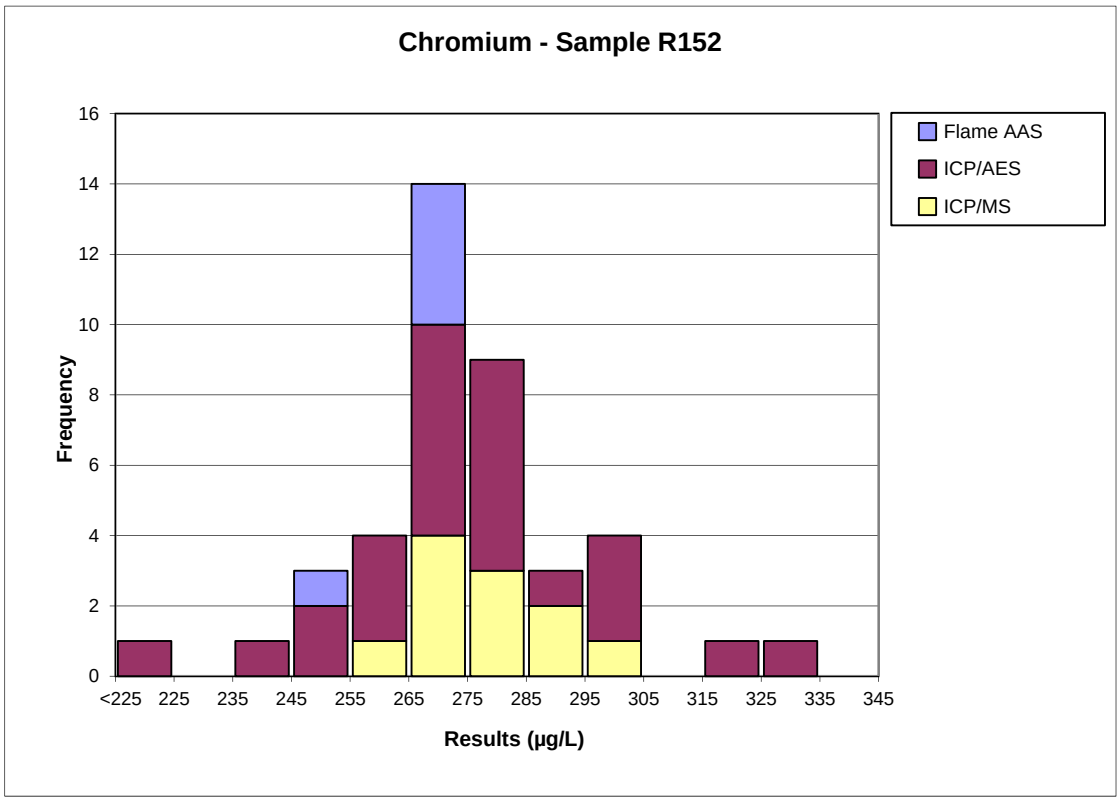


Figure 22. Spread of results for chromium testing of Sample R152, by different analysing techniques.

4.3.2 Copper

Out of 44 results submitted, 26 (59%) were obtained by ICP/AES methods, 10 (23%) by ICP/MS methods and 5 (11%) by Flame AAS. Only one outlier result was obtained for copper in this round and the analysis was performed by ICP/AES. However this laboratory (laboratory code 188) reported low results for all analytes, suggesting more a systematic error than a technique problem.

Figure 23 below shows the copper results distribution for each technique, indicating a larger spread for ICP/AES methods compared to ICP/MS.

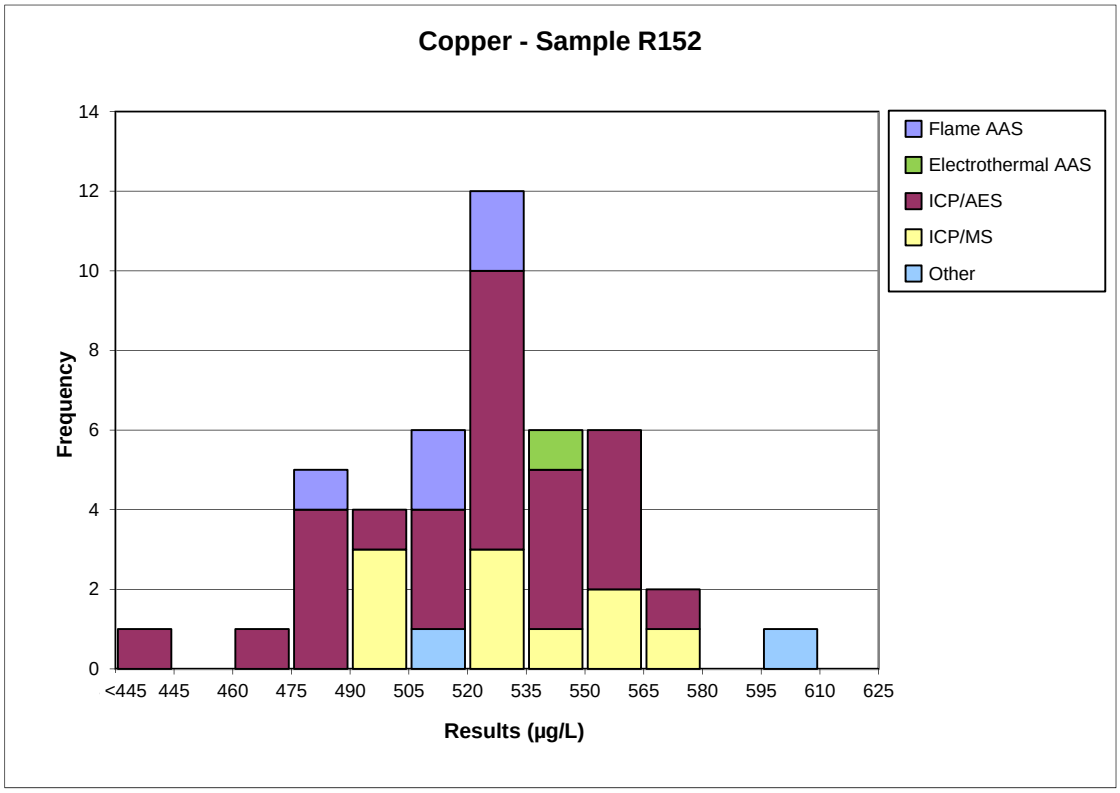


Figure 23. Spread of results for copper testing of Sample R152, for different analysing techniques.

There were two questionable copper results in this round and they were obtained by ICP/AES and by other method (HACH).

4.3.3 Iron

Out of 46 results submitted, 26 (57%) were obtained by ICP/AES methods, 10 (22%) by ICP/MS methods and 7 (15%) by Flame AAS. Four outlier results were obtained for iron in this round, one by ICP/AES (systematic error - laboratory 188) and three by Flame AAS. All results obtained by ICP/MS methods were satisfactory, while the ICP/AES produced two questionable results.

Figure 24 below shows the iron results distribution for each technique, suggesting a larger spread for ICP/AES methods compared to ICP/MS.

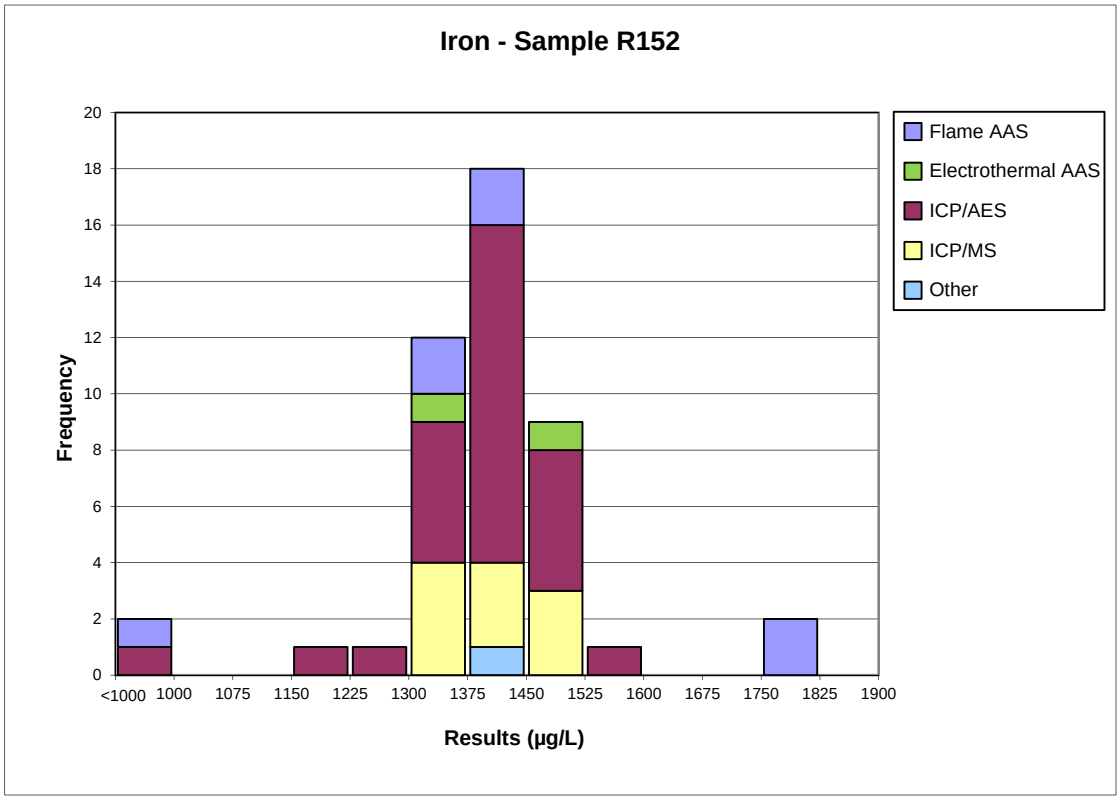


Figure 24. Spread of results for iron testing of Sample R152, by different analysing techniques.

4.3.4 Lead

Out of 43 results submitted, 24 (56%) were obtained by ICP/AES methods, 12 (28%) by ICP/MS methods and 6 (14%) by Flame AAS. Three outlier results were obtained for lead in this round, two by ICP/AES (including systematic error - laboratory 188) and one by Flame AAS. All results obtained by ICP/MS methods were satisfactory, while the ICP/AES produced one questionable result.

Figure 25 below shows the lead results distribution for each technique, suggesting a larger spread for ICP/AES methods compared to ICP/MS.

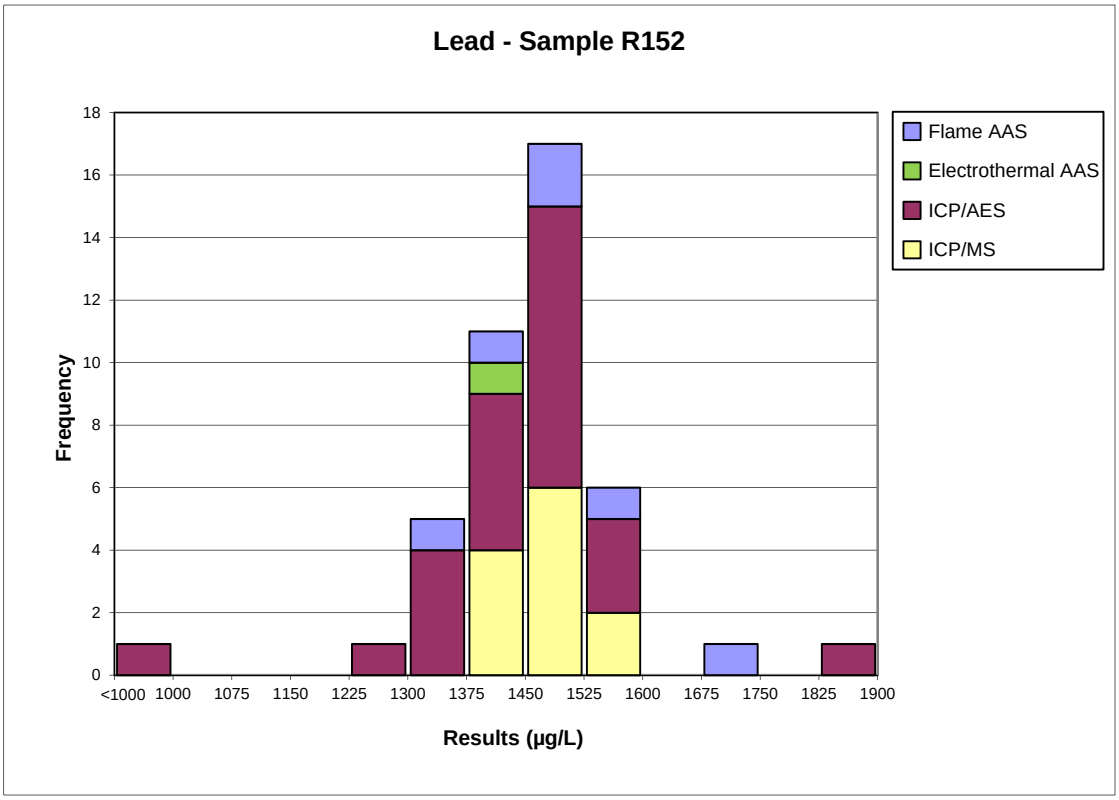


Figure 25. Spread of results for lead testing of Sample R152, by different analysing techniques.

4.3.5 Nickel

Out of 43 results submitted, 26 (60%) were obtained by ICP/AES methods, 11 (26%) by ICP/MS methods and 6 (14%) by Flame AAS. Three outlier results were obtained for nickel in this round, two by ICP/AES (including systematic error - laboratory 188) and one by Flame AAS. All results obtained by ICP/MS methods were satisfactory, while the ICP/AES produced one questionable result.

Figure 26 below shows the nickel results distribution for each technique, suggesting a larger spread for ICP/AES methods compared to ICP/MS.

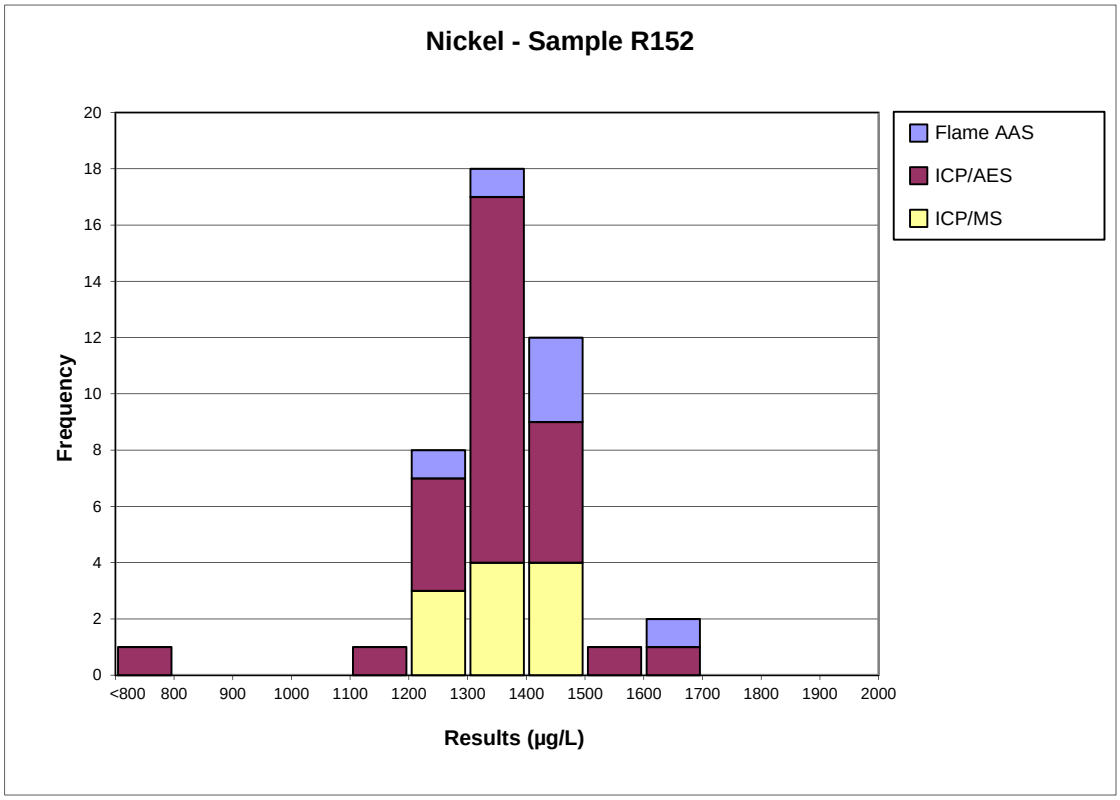


Figure 26. Spread of results for nickel testing of Sample R152, by different analysing techniques.

4.3.6 Thallium

Out of 28 results submitted, 15 (54%) were obtained by ICP/AES methods and 13 (46%) by ICP/MS methods. Two outlier results were obtained for thallium in this round, one by ICP/AES and one by ICP/MS. All other results obtained by ICP/MS methods were satisfactory, while the ICP/AES produced two questionable results.

Figure 27 below shows the thallium results distribution for each technique. While both methods gave one outlier result, the results by ICP/MS seem to be closer to the median compared to ICP/AES results, for an approximate equal distribution of results between the two techniques.

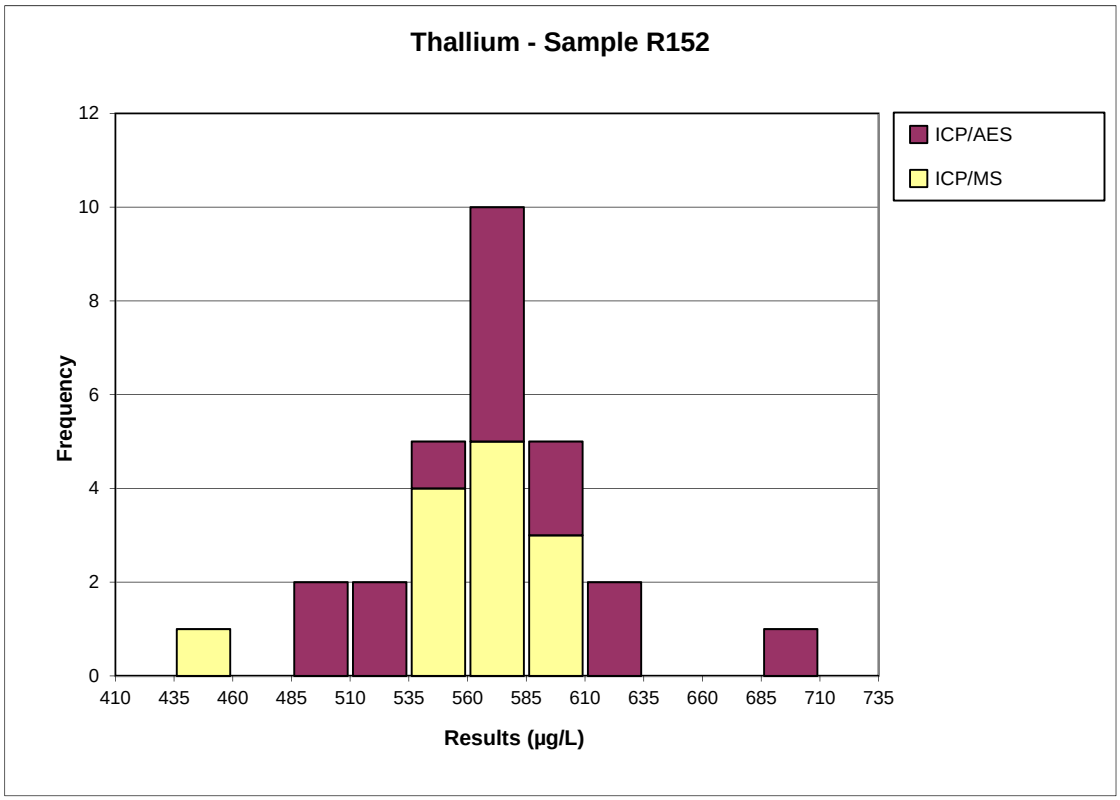


Figure 27. Spread of results for thallium testing of Sample R152, for different analysing techniques.

4.3.7 Zinc

Out of 47 results submitted, 26 (55%) were obtained by ICP/AES methods, 10 (21%) by ICP/MS methods and 8 (17%) by Flame AAS. Two outlier results were obtained for zinc in this round, both by ICP/AES (including systematic error - laboratory 188). Four questionable results were obtained, one by ICP/MS and three by ICP/AES.

Figure 28 below shows the zinc results distribution for each technique, suggesting a larger spread for ICP/AES methods compared to ICP/MS.

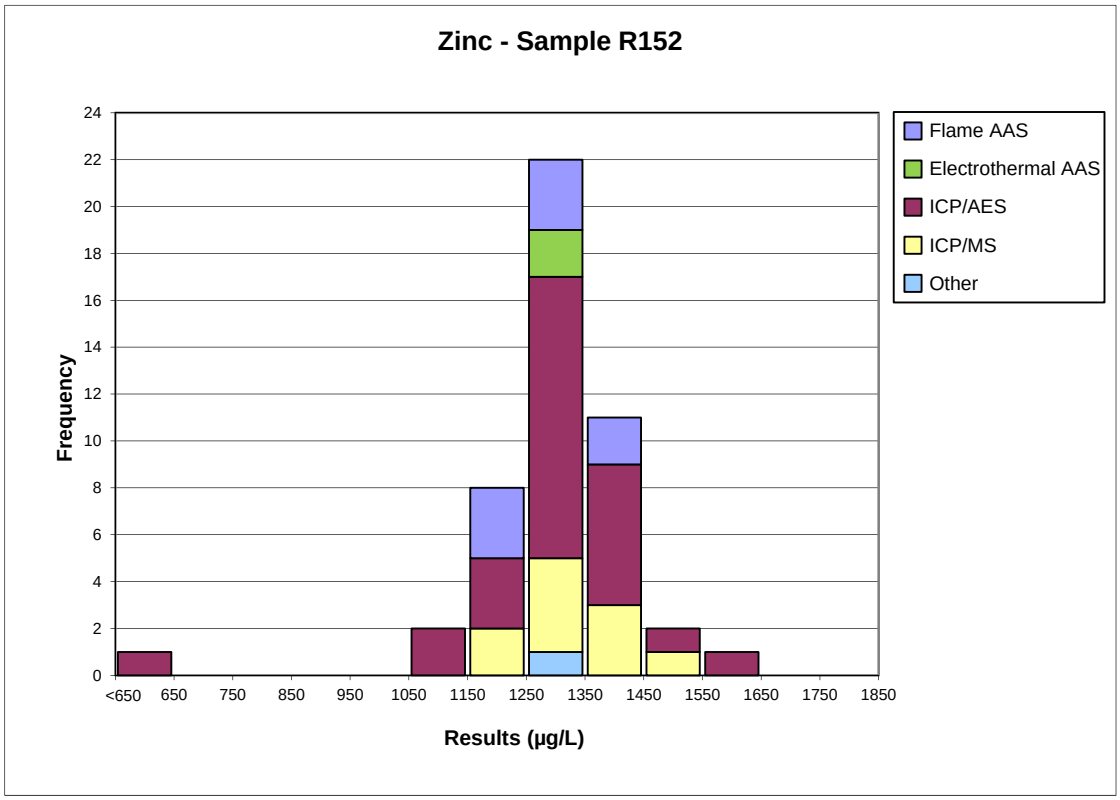


Figure 28. Spread of results for zinc testing of Sample R152, by different analysing techniques.

Overall, the results of Round 152 suggest a better performance of ICP/MS methods compared to ICP/AES. The ICP/MS methods produced one outlier result (for thallium) and two questionable results (one for chromium and one for zinc). For comparison, the ICP/AES gave 12 outliers and 13 questionable results. However, it should be noted that, except for thallium, there were double or more results obtained by ICP/AES than ICP/MS methods.

5. Outlier Results

Laboratories reporting results that have been identified as outliers are listed in Table 10 below.

Lab Code	Analysis						
	Chromium	**Copper**	**Iron**	**Lead**	**Nickel**	**Thallium**	**Zinc**
118						§	
188	§	§	§	§	§		§
237			§				
390a			§				
390b			§		§		
402						§	
436				§	§		
626	§						§
647				§			
690	§						

Table 10. Laboratory results identified as outliers for each analysis performed.

Note:

1. A "**§**" indicates the occurrence of a z-score outlier result (i.e. those results for which |z-score| ≥ 3.0).

6. Reference

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

APPENDIX A

Results and Data Analysis

Chromium Results

Sample R152

Chromium (Cr)
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
105a	271 ± 12.0	-0.16	6	14
109	283 ± 20	0.79	6	#
118	260 ± 30	-1.03	6	#
142	274 ± 16	0.08	1	15
179	255 #	-1.43	6	14
183	278 ± 4	0.40	11	#
188	76.4 #	-15.60 **§**	6	15
217	283 ± 6	0.79	6	#
241	281 ± 28	0.63	7	#
251	270 ± 15	-0.24	12	23
255	262 ± 43	-0.87	9	24
268	265 ± 10	-0.63	8	#
269	255 ± 12.7	-1.43	8	#
273	272 ± 2.5	-0.08	6	#
278	283 ± 35	0.79	13	24
285	300 ± 30	2.14	6	14
286	272 ± 54.4	-0.08	12	22
303	263 ± 32.9	-0.79	6	14
353	297 #	1.90	6	14
368	276 ± 31	0.24	6	24
372	266 ± 13	-0.56	6	14
390a	266 ± 27	-0.56	1	14
390b	253 ± 33	-1.59	1	14
402	305 #	2.54	8	14
422	282 ± 39.5	0.71	7	20
424	270 ± 54	-0.24	12	22
427	281 ± 0.3	0.63	6	15

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

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

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Chromium (Cr) cont.
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
436	274 ± 54	0.08	6	14
438	290 ± 30	1.35	12	21
453	300 #	2.14	12	24
461	289 ± 72	1.27	6	#
523	268 ± 3.80	-0.40	6	#
569	289 ± 58	1.27	12	21
578	268 ± 7	-0.40	1	14
598	283 ± 50	0.79	13	24
608	273 ± 33	0.00	6	14
620	245 ± 24.5	-2.22	8	#
626	316 #	3.41 **§**	6	#
647	270 ± 21	-0.24	1	#
651	267 ± 45	-0.48	9	24
690	326 ± 20	4.21 **§**	6	14

No of Results:	41
Median:	273.0
Normalised IQR:	12.6
Uncertainty of the Median:	2.5
Robust CV:	4.6%
Minimum:	76.4
Maximum:	326
Range:	249.6

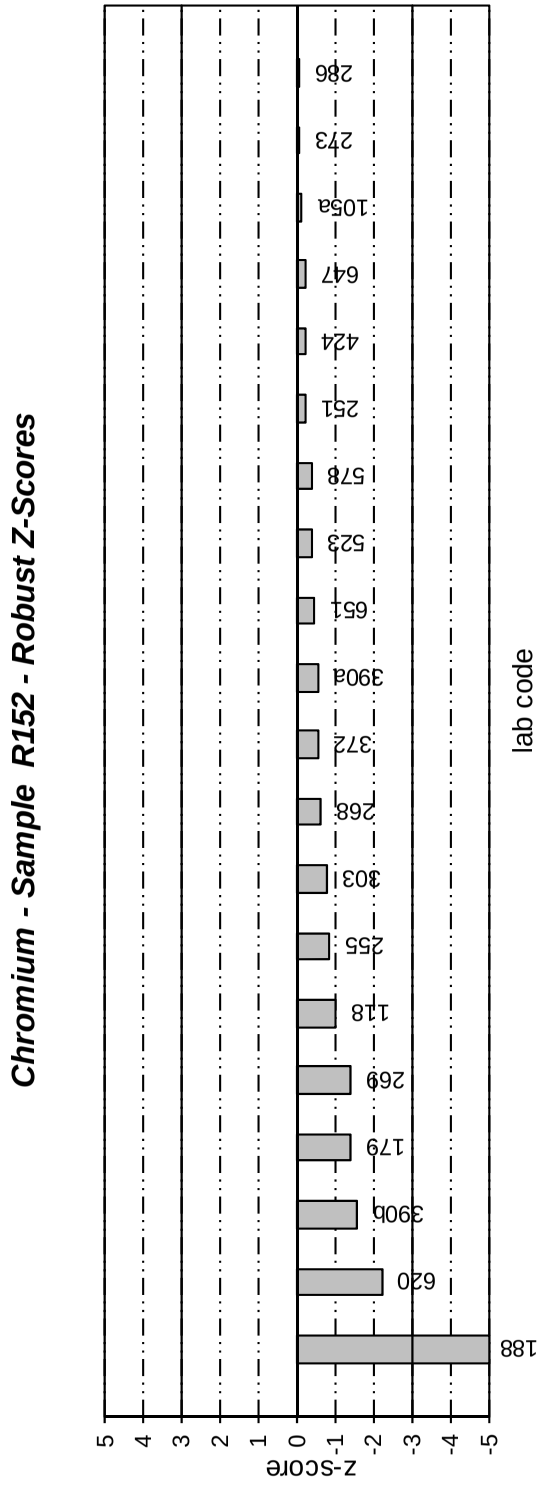
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

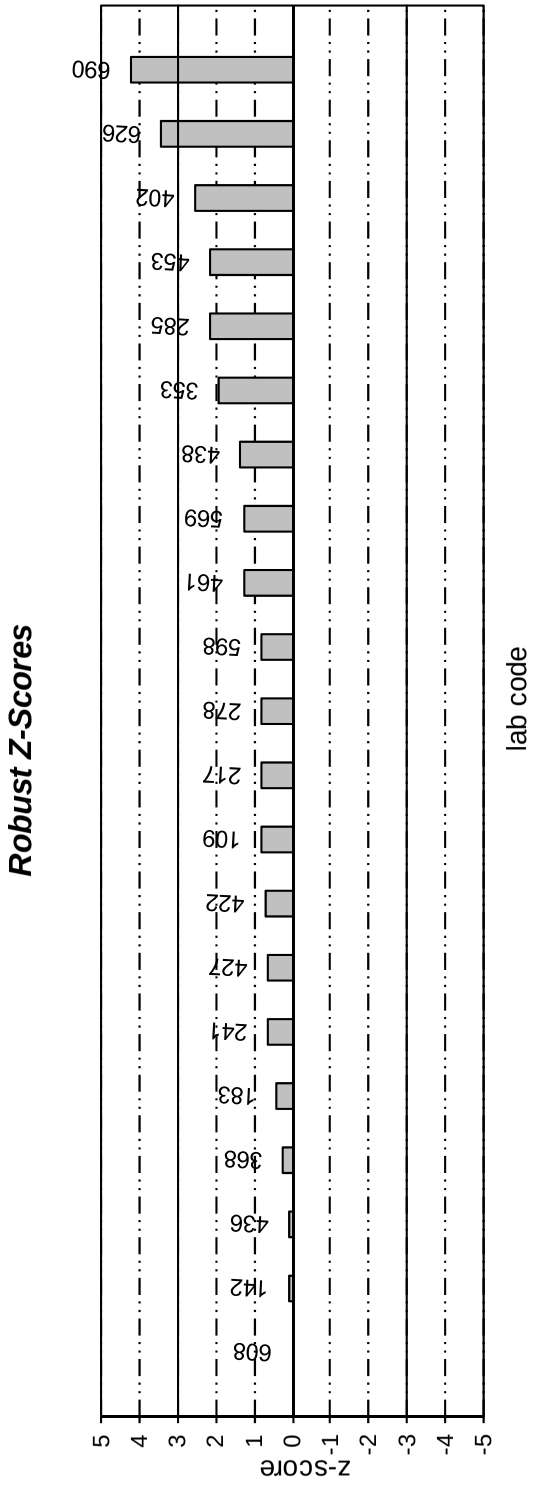
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Chromium - Sample R152

Ordered Robust Z-Score Charts





Copper Results

Sample R152

Copper (Cu)
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
105a	523 ± 17.2	-0.17	6	14
109	545 ± 33	0.57	6	#
118	510 ± 30	-0.61	6	#
142	528 ± 99	0.00	6	14
179	483 #	-1.52	6	14
183	534 ± 1	0.20	11	#
188	148 #	-12.82 **§**	6	15
217	509 ± 5	-0.64	6	#
240	600 #	2.43	13	#
241	544 ± 54	0.54	7	#
251	528 ± 25	0.00	12	23
255	504 ± 94	-0.81	9	24
268	528 ± 25	0.00	8	#
269	551 ± 27.5	0.78	8	#
273	534 ± 2.0	0.20	6	#
278	553 ± 100	0.84	13	24
285	560 ± 56	1.08	6	14
286	495 ± 99.0	-1.11	12	22
303	483 ± 60.4	-1.52	6	14
337	528 ± 52.8	0.00	6	15
353	548 #	0.67	6	14
368	505 ± 45	-0.78	6	24
372	486 ± 24	-1.42	6	14
390a	533 ± 121	0.17	1	14
390b	488 ± 30	-1.35	1	14
402	558 #	1.01	8	14
422	571 ± 79.9	1.45	7	20

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

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

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Copper (Cu) cont.
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
424	521 ± 104	-0.24	12	22
427	539 ± 0.5	0.37	6	15
436	570 ± 39	1.42	6	14
438	560 ± 40	1.08	12	21
439	548 ± 44	0.67	13	14
453	520 #	-0.27	13	24
461	548 ± 72	0.67	6	#
523	487 ± 5.63	-1.38	6	#
569	523 ± 105	-0.17	12	21
578	532 ± 13	0.13	1	14
598	517 ± 65	-0.37	13	24
620	464 ± 30.3	-2.16	8	#
621	517 #	-0.37	1	#
626	565 #	1.25	6	#
647	513 ± 20	-0.51	1	#
651	496 ± 69	-1.08	9	24
690	529 ± 20	0.03	6	14

No of Results:	44
Median:	528.0
Normalised IQR:	29.7
Uncertainty of the Median:	5.6
Robust CV:	5.6%
Minimum:	148
Maximum:	600
Range:	452

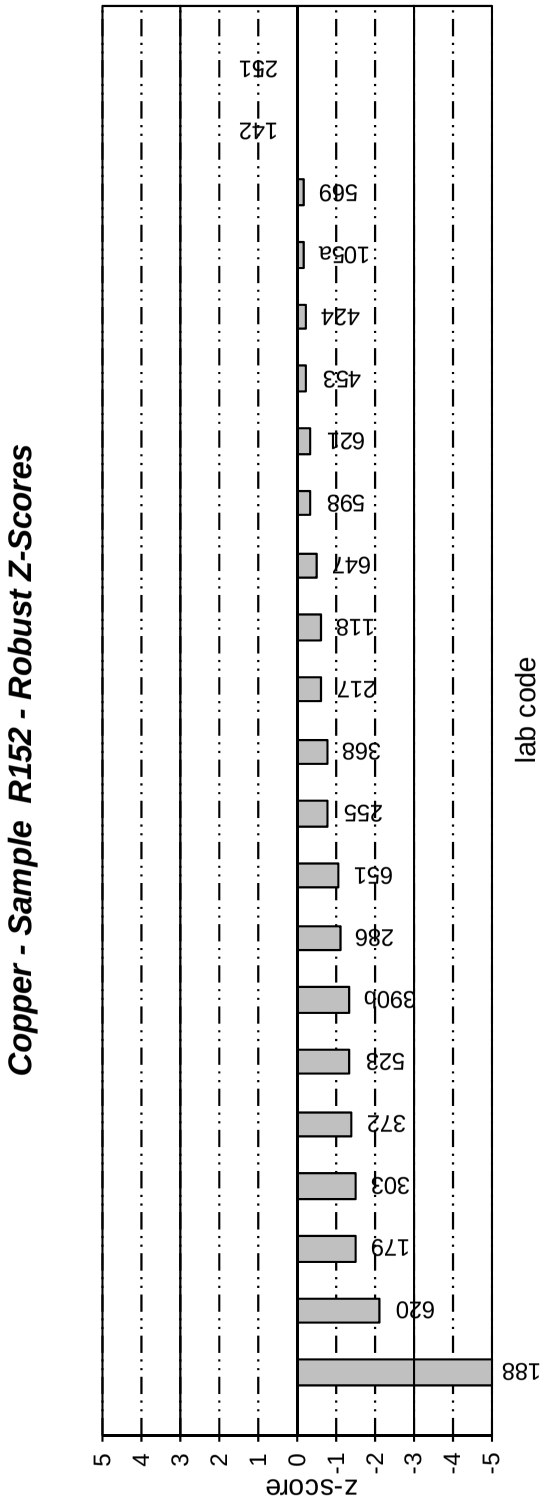
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

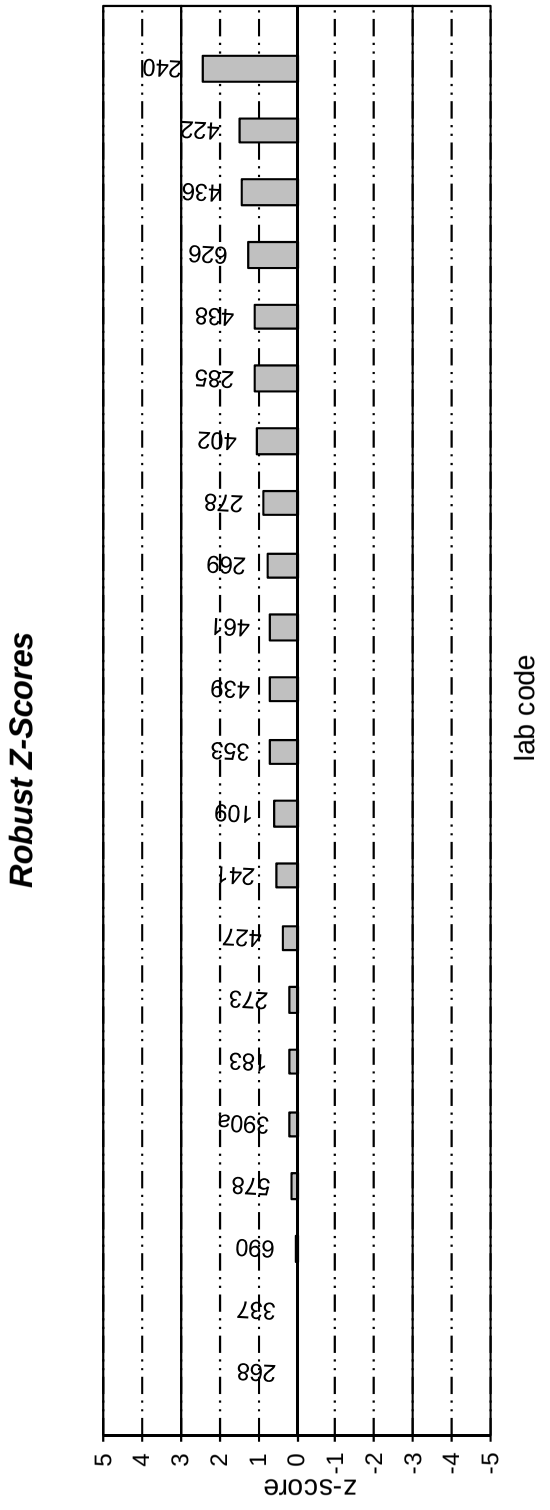
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Copper - Sample R152

Ordered Robust Z-Score Charts





Iron Results

Sample R152

Iron (Fe)
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
105a	1380 ± 16.8	-0.26	6	14
109	1380 ± 83	-0.26	6	#
118	1200 ± 100	-2.63	6	#
142	1400 ± 140	0.00	6	14
179	1360 #	-0.53	6	14
183	1430 ± 3	0.39	11	#
188	410 #	-13.03 **§**	6	15
207	1340 ± 60	-0.79	6	#
217	1480 ± 5	1.05	6	#
237	900 #	-6.58 **§**	1	14
240	1340 #	-0.79	1	14
241	1460 ± 146	0.79	7	#
251	1405 ± 50	0.07	12	23
255	1350 ± 270	-0.66	9	24
268	1350 ± 60	-0.66	8	#
269	1320 ± 65.9	-1.05	8	#
273	1410 ± 2.5	0.13	6	#
278	1480 ± 270	1.05	13	24
285	1510 ± 151	1.45	6	14
286	1338 ± 268	-0.82	12	22
303	1360 ± 170	-0.53	6	14
337	1392 ± 139	-0.11	6	15
353	1520 #	1.58	6	14
368	1390 ± 290	-0.13	6	24
372	1420 ± 71	0.26	6	14
390a	1766 ± 134	4.82 **§**	1	14
390b	1761 ± 101	4.75 **§**	1	14

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

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

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Iron (Fe) cont.
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
402	1410 #	0.13	8	14
422	1370 ± 206	-0.39	7	20
424	1320 ± 264	-1.05	12	22
427	1490 ± 1.5	1.18	6	15
436	1290 ± 158	-1.45	6	14
438	1470 ± 250	0.92	12	21
439	1350 ± 139	-0.66	13	14
452	1480 #	1.05	5	14
453	1400 #	0.00	13	24
461	1510 ± 84	1.45	6	#
523	1390 ± 150	-0.13	6	#
569	1410 ± 282	0.13	12	21
578	1380 ± 26	-0.26	1	14
620	1400 ± 169	0.00	8	#
621	1420 #	0.26	1	#
626	1580 #	2.37	6	#
647	1340 ± 28	-0.79	1	#
651	1430 ± 200	0.39	9	24
690	1402 ± 50	0.03	6	14

No of Results:	46
Median:	1400.0
Normalised IQR:	76.0
Uncertainty of the Median:	14.0
Robust CV:	5.4%
Minimum:	410
Maximum:	1766
Range:	1356

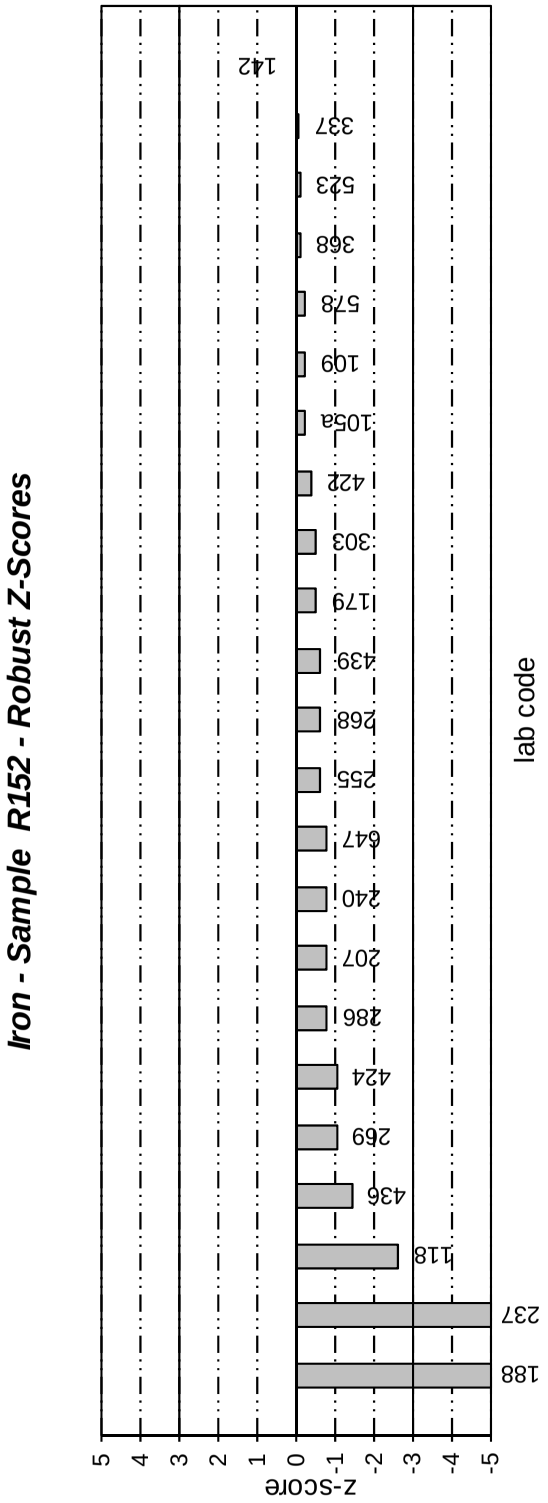
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

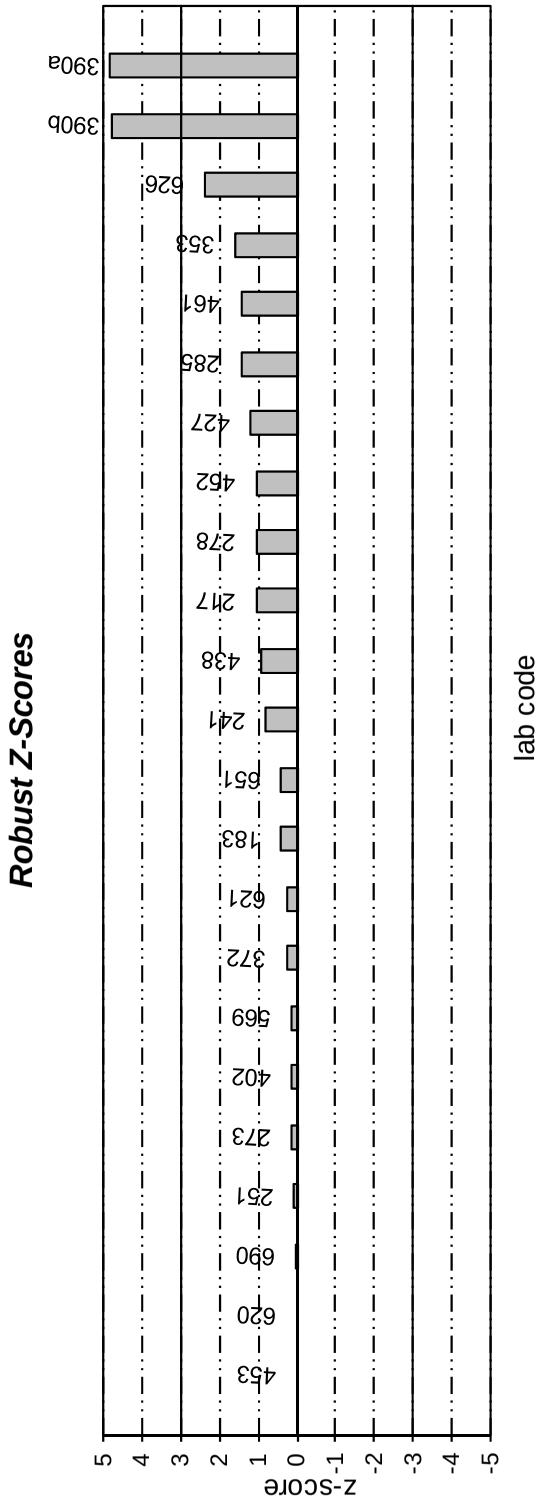
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Iron - Sample R152

Ordered Robust Z-Score Charts





Lead Results

Sample R152

Lead (Pb)
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
105a	1460 ± 15.2	-0.12	6	14
109	1530 ± 153	0.74	6	#
118	1250 ± 100	-2.70	6	#
179	1350 #	-1.47	6	14
183	1500 ± 4	0.37	11	#
188	404 #	-13.07 **§**	6	15
217	1470 ± 5	0.00	6	#
240	1390 #	-0.98	1	14
241	1540 ± 154	0.86	7	#
251	1480 ± 50	0.12	12	23
255	1520 ± 250	0.61	9	24
268	1410 ± 70	-0.74	9	#
269	1390 ± 69.7	-0.98	8	#
273	1470 ± 2.5	0.00	6	#
278	1470 ± 220	0.00	13	24
285	1330 ± 133	-1.72	6	14
286	1465 ± 293	-0.06	12	22
303	1410 ± 176	-0.74	6	14
337	1471 ± 147	0.01	6	15
353	1414 #	-0.69	6	14
368	1470 ± 240	0.00	6	24
372	1440 ± 72	-0.37	6	14
390a	1451 ± 165	-0.23	1	14
390b	1307 ± 84	-2.00	1	14
402	1410 #	-0.74	8	14
422	1410 ± 268	-0.74	7	20
424	1520 ± 304	0.61	12	22

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

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

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Lead (Pb) cont.
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)			Robust z-score[2]		Method Code[3]	Digestion Code[3]
427	1470	±	1.5	0.00		6	15
436	1840	±	239	4.54	**§**	6	14
438	1600	±	240	1.59		12	21
439	1430	±	223	-0.49		13	14
453	1450		#	-0.25		12	24
461	1560	±	74	1.10		6	#
523	1470	±	6.07	0.00		6	#
569	1520	±	304	0.61		12	21
578	1510	±	57	0.49		1	14
598	1320	±	170	-1.84		13	24
620	1320	±	132	-1.84		8	#
621	1580		#	1.35		1	#
626	1580		#	1.35		6	#
647	1750	±	120	3.43	**§**	1	#
651	1400	±	140	-0.86		9	24
690	1525	±	50	0.67		6	14

No of Results:	43
Median:	1470.0
Normalised IQR:	81.5
Uncertainty of the Median:	15.6
Robust CV:	5.5%
Minimum:	404
Maximum:	1840
Range:	1436

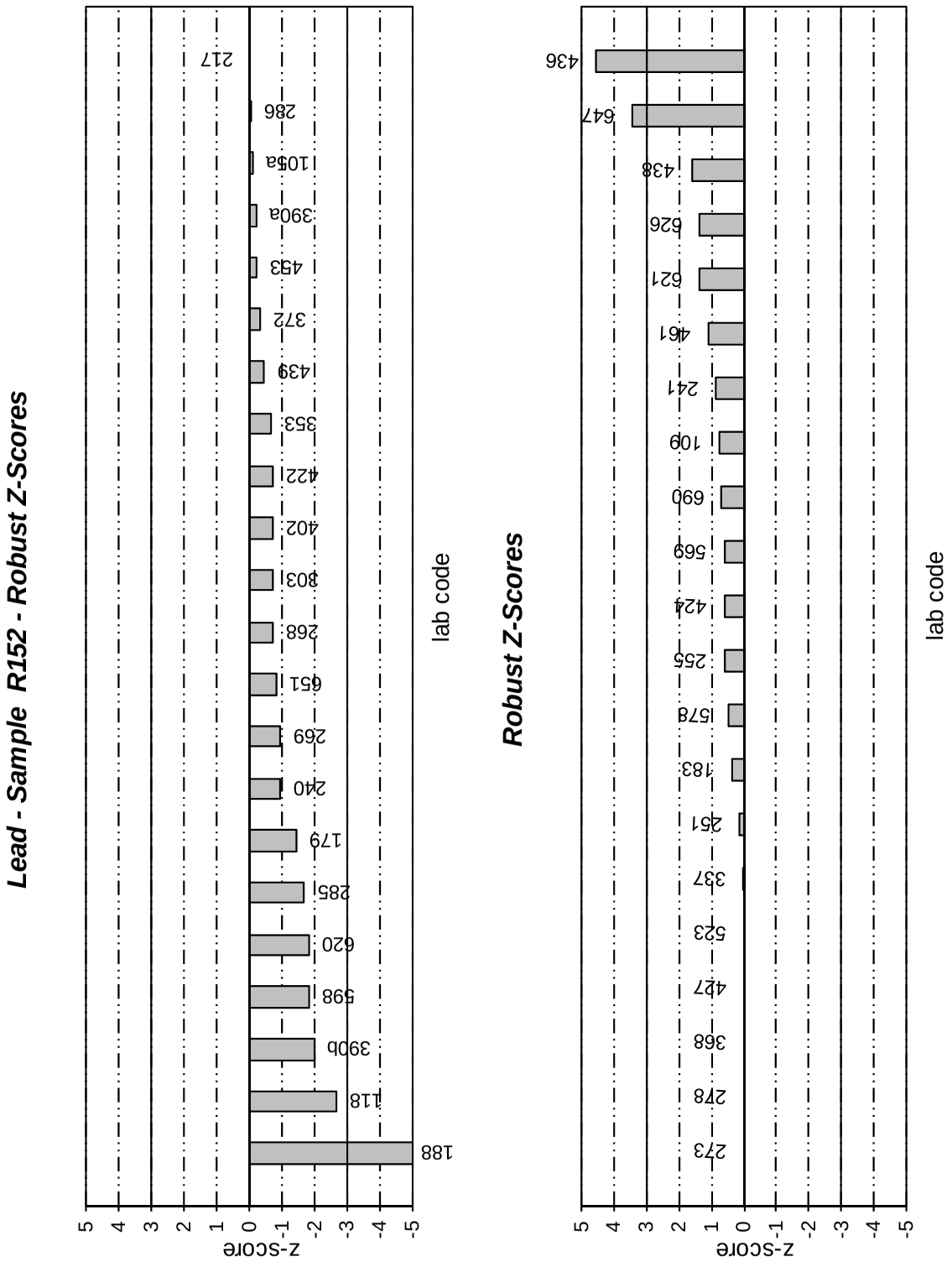
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

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

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Lead - Sample R152

Ordered Robust Z-Score Charts



Nickel Results

Sample R152

Nickel (Ni)
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)			Robust z-score[2]		Method Code[3]	Digestion Code[3]
105a	1310	±	14.8	-0.59		6	14
109	1410	±	112	0.59		6	#
118	1300	±	100	-0.70		6	#
142	1340	±	125	-0.23		6	14
179	1200		#	-1.88		6	14
183	1380	±	4	0.23		11	#
188	369		#	-11.62	**§**	6	15
217	1400	±	10	0.47		6	#
240	1270		#	-1.06		1	14
241	1400	±	140	0.47		7	#
251	1260	±	50	-1.17		12	23
255	1430	±	250	0.82		9	24
268	1340	±	60	-0.23		8	#
269	1270	±	63.7	-1.06		8	#
273	1350	±	2.5	-0.12		6	#
278	1420	±	210	0.70		13	24
285	1430	±	143	0.82		6	14
286	1278	±	256	-0.96		12	22
303	1310	±	164	-0.59		6	14
337	1350	±	135	-0.12		6	15
353	1586		#	2.65		6	14
368	1320	±	210	-0.47		6	24
372	1340	±	67	-0.23		6	14
390a	1442	±	74	0.96		1	14
390b	1641	±	70	3.30	**§**	1	14
402	1470		#	1.29		8	14
422	1390	±	195	0.35		7	20

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

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

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Nickel (Ni) cont.
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
424	1400 ± 280	0.47	12	22
427	1339 ± 1.3	-0.25	6	15
436	1640 ± 206	3.28 **§**	6	14
438	1410 ± 180	0.59	12	21
453	1450 #	1.06	12	24
461	1400 ± 90	0.47	6	#
523	1290 ± 9.52	-0.82	6	#
569	1360 ± 272	0.00	12	21
578	1420 ± 57	0.70	1	14
598	1450 ± 170	1.06	13	24
620	1260 ± 126	-1.17	8	#
621	1330 #	-0.35	1	#
626	1460 #	1.17	6	#
647	1440 ± 120	0.94	1	#
651	1280 ± 180	-0.94	9	24
690	1349 ± 50	-0.13	6	14

No of Results:	43
Median:	1360.0
Normalised IQR:	85.2
Uncertainty of the Median:	16.3
Robust CV:	6.3%
Minimum:	369
Maximum:	1641
Range:	1272

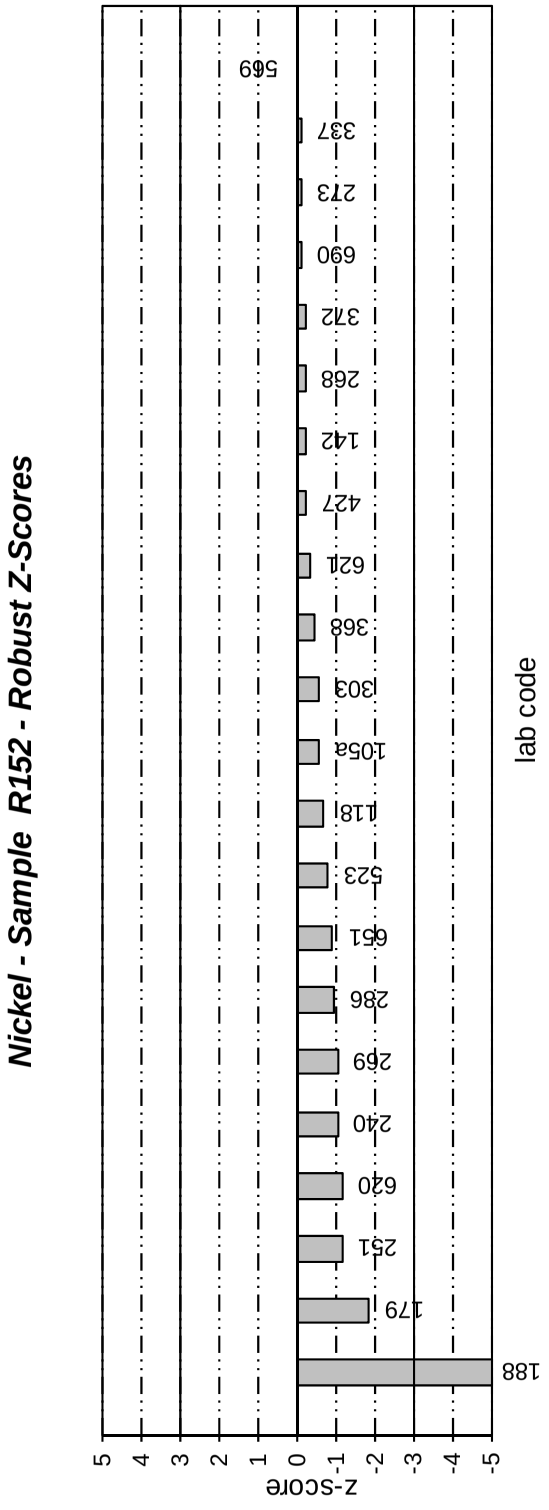
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

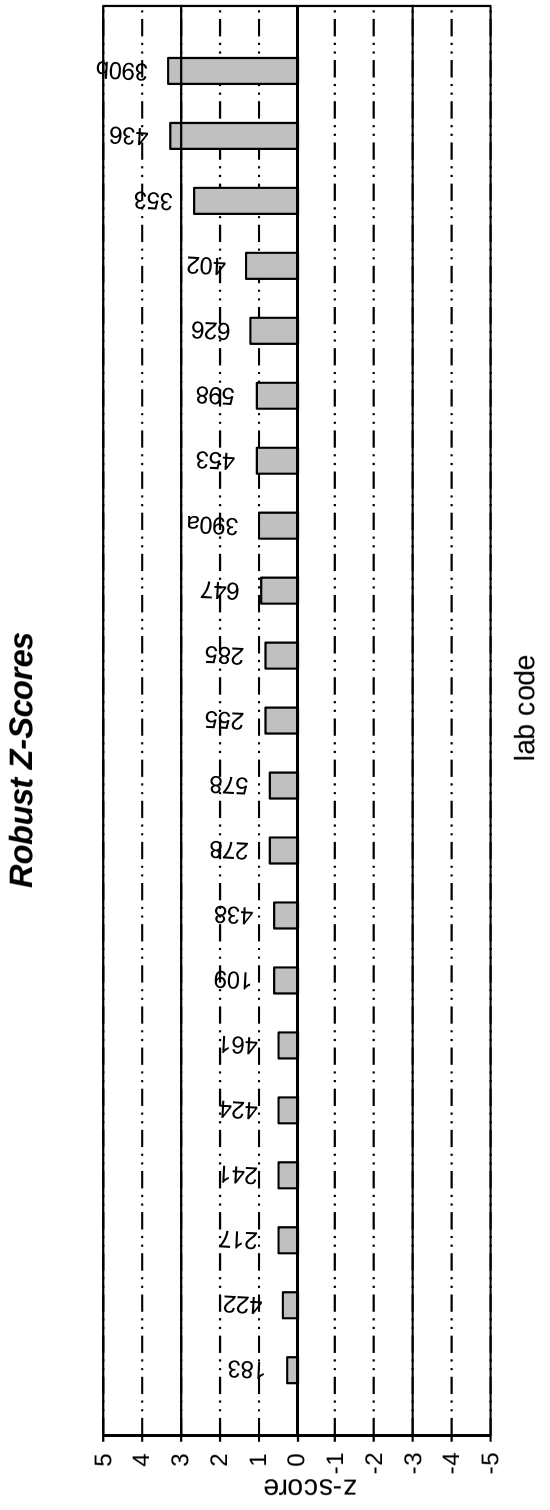
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Nickel - Sample R152

Ordered Robust Z-Score Charts





Thallium Results

Sample R152

Thallium (Tl)
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
105a	553 ± 17.2	-0.56	6	14
118	440 ± 100	-3.99 **§**	7	#
179	522 #	-1.50	6	14
217	562 ± 6	-0.29	6	#
241	600 ± 60	0.86	7	#
251	580 ± 25	0.26	12	23
255	549 ± 110	-0.68	9	24
268	565 ± 30	-0.20	9	#
269	570 ± 28.4	-0.05	8	#
273	579 ± 10.2	0.23	12	#
278	574 ± 100	0.08	13	24
286	565 ± 113	-0.20	12	22
303	577 ± 144	0.17	6	14
337	611 ± 61.1	1.20	6	15
353	530 #	-1.26	6	14
368	573 ± 26	0.05	6	24
402	705 #	4.05 **§**	8	14
422	548 ± 93.2	-0.71	7	20
424	602 ± 120	0.92	12	22
427	592 ± 0.6	0.62	6	15
436	502 ± 58	-2.11	6	14
438	600 ± 70	0.86	12	21
461	597 ± 73	0.77	6	#
523	579 ± 3.98	0.23	6	#
569	550 ± 110	-0.65	12	21
620	497 ± 49.7	-2.26	8	#
626	619 #	1.44	6	#
651	546 ± 66	-0.77	9	24

No of Results:	28
Median:	571.5
Normalised IQR:	33.0
Uncertainty of the Median:	7.8
Robust CV:	5.8%
Minimum:	440
Maximum:	705
Range:	265

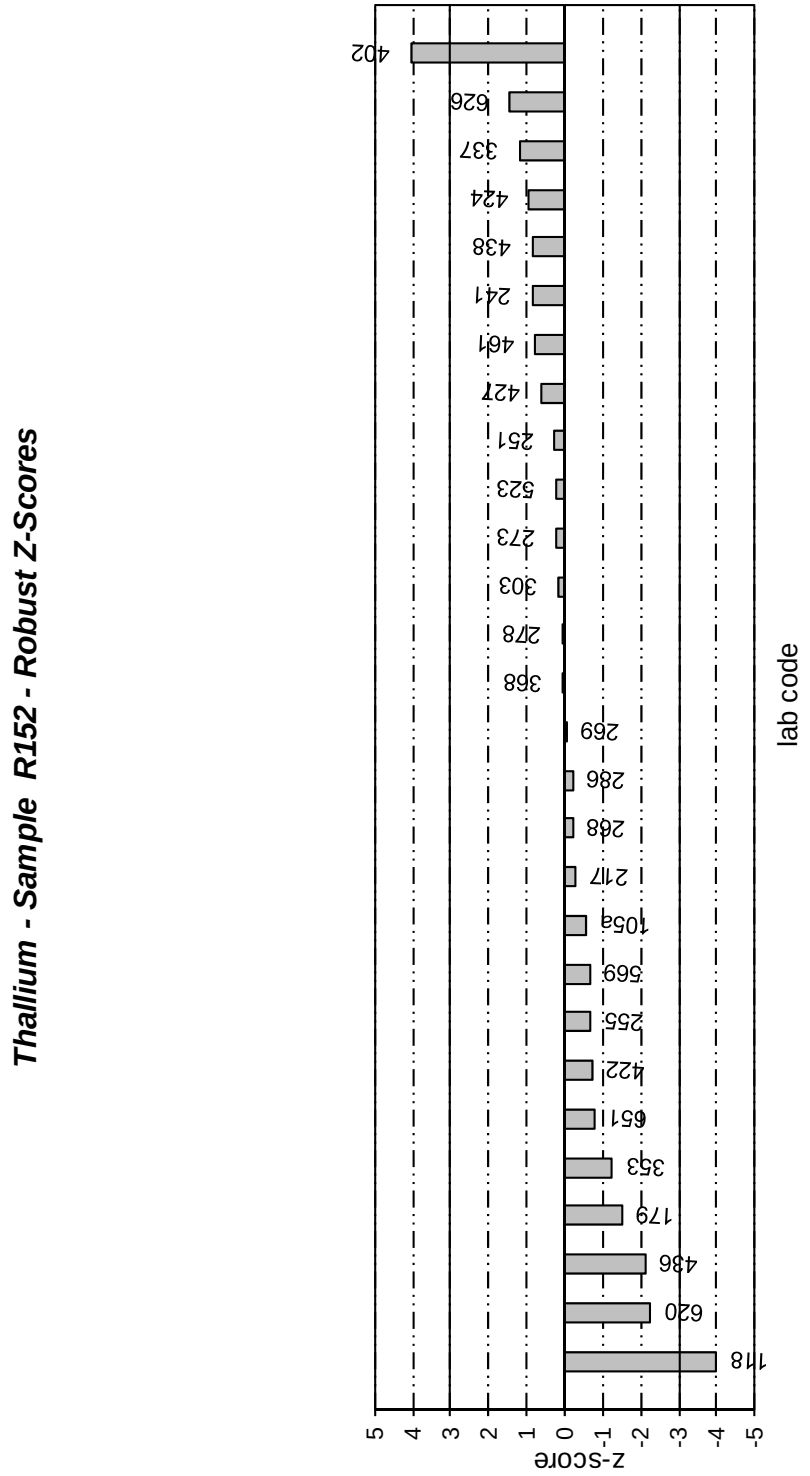
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

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

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Thallium - Sample R152

Ordered Robust Z-Score Chart



Zinc Results

Sample R152

Zinc (Zn)
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
105a	1270 ± 17.2	-0.42	6	14
109	1400 ± 126	1.18	6	#
118	1250 ± 100	-0.66	6	#
142	1290 ± 59	-0.17	1	15
179	1210 #	-1.15	6	14
183	1400 ± 2	1.18	11	#
188	386 #	-11.26 **§**	6	15
217	1390 ± 15	1.05	6	#
237	1400 #	1.18	1	14
240	1250 #	-0.66	1	14
241	1330 ± 133	0.32	7	#
251	1280 ± 50	-0.29	12	23
255	1260 ± 260	-0.54	9	24
268	1260 ± 60	-0.54	8	#
269	1060 ± 53.0	-2.99	8	#
273	1320 ± 4.0	0.20	6	#
278	1390 ± 280	1.05	13	24
285	1420 ± 142	1.42	6	14
286	1203 ± 241	-1.24	12	22
303	1320 ± 165	0.20	6	14
337	1315 ± 132	0.13	6	15
353	1336 #	0.39	6	14
368	1280 ± 180	-0.29	6	24
372	1240 ± 62	-0.78	6	14
390a	1215 ± 112	-1.09	1	14
390b	1182 ± 56	-1.50	1	14
402	1540 #	2.89	8	14

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

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

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Zinc (Zn) cont.
Results by Laboratory Code

Lab Code	*Sample R152* Result ± MU[1] (µg/L)	Robust z-score[2]	Method Code[3]	Digestion Code[3]
422	1500 ± 150	2.40	7	20
424	1430 ± 286	1.55	12	22
427	1335 ± 1.3	0.38	6	15
436	1360 ± 115	0.69	6	14
438	1380 ± 150	0.93	12	21
439	1310 ± 179	0.07	13	14
452	1280 #	-0.29	5	14
453	1300 #	-0.05	13	24
461	1380 ± 88	0.93	6	#
523	1290 ± 133	-0.17	6	#
569	1310 ± 262	0.07	12	21
578	1360 ± 58	0.69	1	14
598	1300 ± 300	-0.05	13	24
608	1271 ± 117	-0.40	6	14
620	1100 ± 95.6	-2.50	8	#
621	1330 #	0.32	1	#
626	1590 #	3.51 **§**	6	#
647	1260 ± 73	-0.54	1	#
651	1240 ± 220	-0.78	9	24
690	1304 ± 50	0.00	6	14

No of Results:	47
Median:	1304.0
Normalised IQR:	81.5
Uncertainty of the Median:	14.9
Robust CV:	6.3%
Minimum:	386
Maximum:	1590
Range:	1204

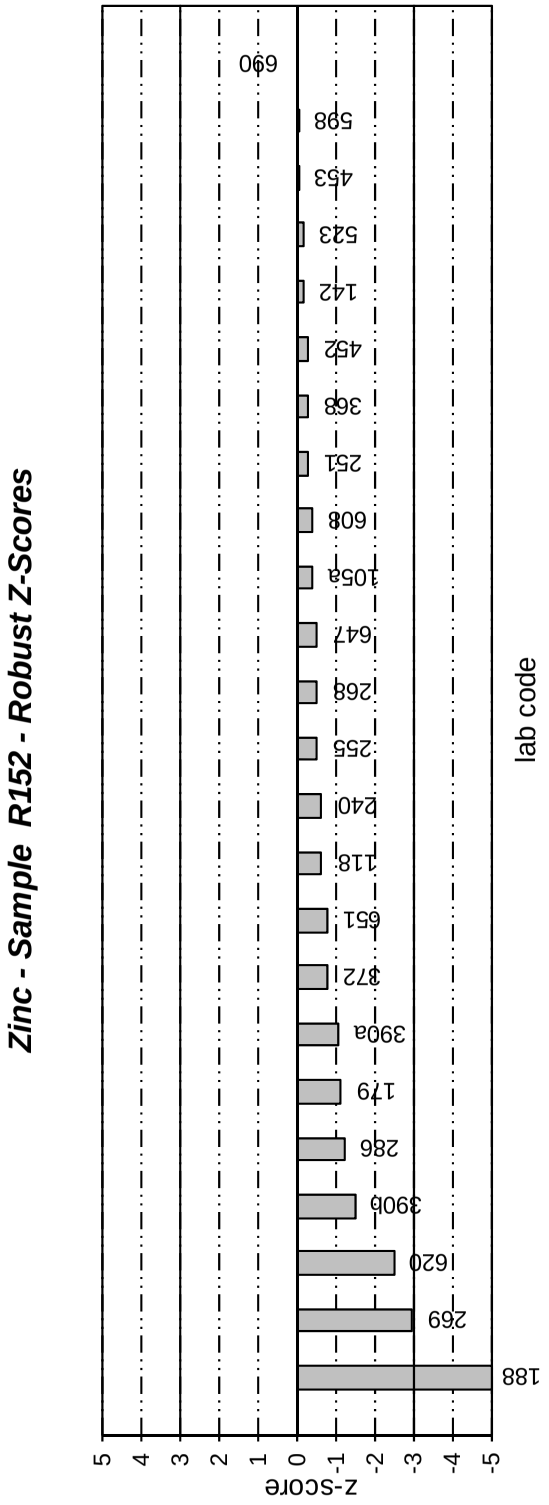
[1] Where reported, results are shown with their corresponding measurement uncertainty (MU).

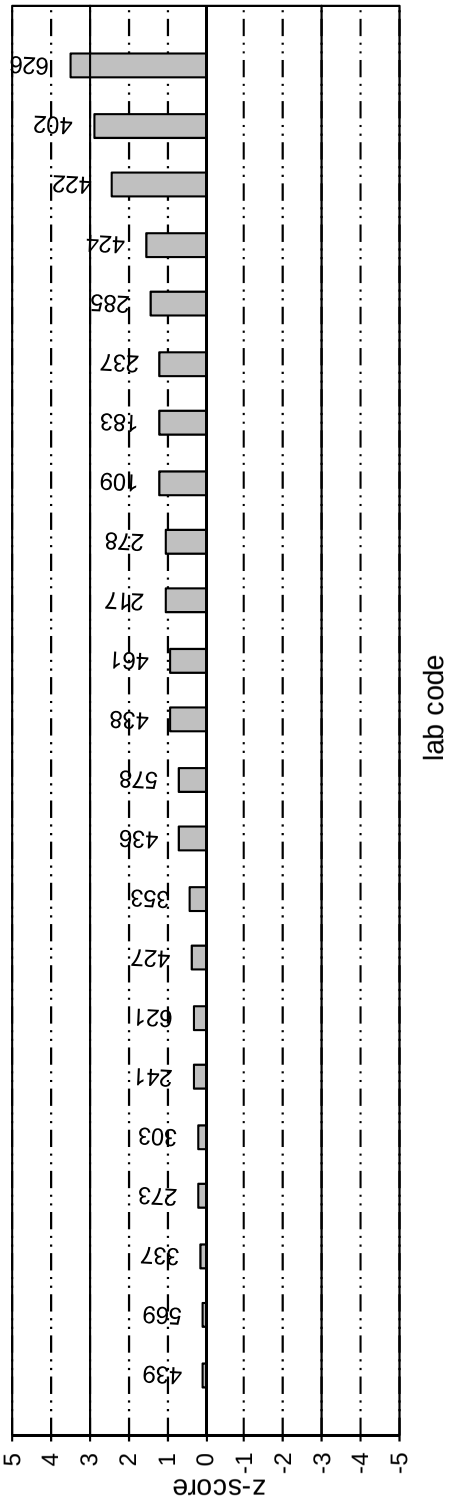
[2] "**§**" denotes an outlier (i.e. those results for which |*z-score*| ≥ 3.0). Robust *z-scores* are calculated *as:* $z = (A - median) \div normalised\ IQR$, where *A* is the participant laboratory's result.

[3] Please refer to Appendix C (page C3-C4) for method and digestion code descriptions.

Zinc - Sample R152

Ordered Robust Z-Score Charts





APPENDIX B

Sample Homogeneity and Stability

Homogeneity and Stability Testing

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

Table 11 below presents the certified values for the samples used in Round 152.

Analyte	Certified Value[1] (µg/L)	Uncertainty[2]
Chromium	276	3.32%
Copper	522	3.00%
Iron	1390	3.62%
Lead	1480	3.76%
Nickel	1340	3.29%
Thallium	579	6.28%
Zinc	1300	5.36%

Table 11. Certified values of the certified reference samples used in Round 152.

[1] The Certified Values are the actual “made-to” concentrations confirmed by ERA analytical verification.

[2] 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

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 152 **February 2013**

Metals - Chromium, Copper, Iron, Lead, Nickel, Thallium, Zinc

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 sealed vial labelled PTA R152 supplied by Environmental Resource Associates (ERA).
- **ii)** Please note the temperature of vial on receipt.
- **iii)** The vial contains approximately 14mL of artificial waste water concentrate.
- **iv)** The sample has been acidified with approximately 2% (v/v) nitric acid.
- **v)** The sample must be thoroughly mixed prior to analysis.
- **vi)** The vial will require 100-fold dilution in deionised water.
- **vii)** The vial may be stored at room temperature.

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

2. Sample Preparation

Caution: Analysis must begin immediately after vial is opened.

Please Note: While technically it is unnecessary to digest the sample prior to analysis, digestion should be performed if this is your normal procedure.

- **i)** Prepare sample at 20-22ºC, and allow sufficient time for the vial to reach room temperature before opening.
- **ii)** Add approximately 100-200 millilitres (mL) deionised water followed by 2-5mL of high purity, concentrated nitric acid to a 500mL volumetric flask.

Note:
A volume of acid different from the 2 to 5mL of HNO_3 suggested may be added in order to matrix match calibration standards or meet any other method criteria.

If analysing using colorimetric techniques, it may be necessary to pH adjust the sample prior to analysis. If using colorimetric techniques, it is acceptable to omit the addition of the 2-5mL nitric suggested.

- **iii)** Mix the vial prior to opening.
- **iv)** Using a dry, clean volumetric pipette, transfer 5.0 millilitres (mL) from the vial into the flask.
- **v)** Dilute the flask to the final volume with deionised water.
- **vi)** Stopper and mix by inversion.
- **vii)** Immediately analyse the diluted sample by your normal procedures.
- **viii)** Report your results as µg/L for the diluted sample.

3. Tests Requested

For the sample prepared from the ampoule.

i) Chromium (Cr)
ii) Copper (Cu)
iii) Iron (Fe)
iv) Lead (Pb)
v) Nickel (Ni)
vi) Thallium (Tl)
vii) Zinc (Zn)

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 (µg/L).
iii) Do not correct results for recovery.
iv) In addition to reporting the results, record the method of analysis using the attached codes.
v) Laboratories are also requested to calculate and report an estimate of measurement uncertainty for each reported result. All estimates of uncertainty of measurement must be provided as a 95% confidence interval (coverage factor k ≈ 2) and reported in µg/L.

6. Testing should commence as soon as possible after receiving the sample and results reported **NO LATER THAN 15 MARCH 2013 to:**

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

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 µg/L):

Analyte	**Range (µg/L)**
Chromium (Cr)	17 – 1000
Copper (Cu)	40 – 900
Iron (Fe)	200 – 4000
Lead (Pb)	70 – 3000
Nickel (Ni)	80 – 3000
Thallium (Tl)	60 – 900
Zinc (Zn)	100 – 2000

Method Codes to be used for the Results Sheet

ANALYSIS	METHOD REFERENCE	METHOD DESCRIPTION	CODE
Chromium (Cr) Copper (Cu) Iron (Fe) Lead (Pb) Nickel (Ni) Thallium (Tl) Zinc (Zn)	APHA SM	Part 3111B Direct Air-Acetylene Flame Method	1
		Part 3111C Extraction/Air-Acetylene Flame Method	2
		Part 3111D Direct Nitrous Oxide-Acetylene Flame Method	3
		Part 3111E Extraction/Nitrous Oxide-Acetylene Flame Method	4
		Part 3113B Electrothermal Atomic Absorption Spectrometric Method	5
		Part 3120B Inductively Coupled Plasma (ICP) Method	6
		Part 3125B Inductively-Coupled Plasma/Mass Spectrometry (ICP/MS) Method	7
	US EPA	Method Number: 0200.7 Metals and Trace Elements - ICP/AES	8
		Method Number: 0200.8 Trace Elements in Water & Wastes - ICP/MS	9
		Method Number: 0200.9 Trace Elements - GFAA	10
		Method Number: 6010 Inductively Coupled Plasma-Atomic Emission Spectrometry	11
		Method Number: 6020A Inductively Coupled Plasma/MS	12
		Other (please specify)	13

Digestion Codes to be used for the Results Sheet

Digestion Procedure	Code
APHA	
Part 3030 E (HNO_3)	14
Part 3030 F (HNO_3/HCl)	15
Part 3030 G (HNO_3/H_2SO_4)	16
Part 3030 H (HNO_3/$HClO_4$)	17
Part 3030 I (HNO_3/$HClO_4$/HF)	18
Part 3030 J (Dry Ashing)	19
Part 3030 K (Microwave Assisted)	20
USEPA	
Part 3005A (HNO_3/HCl)	21
Part 3010A (HNO_3/HCl)	22
Part 3015A (Microwave Assisted)	23
Other (please specify)	24

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.

PROFICIENCY TESTING AUSTRALIA

WATERS PROFICIENCY TESTING PROGRAM

CHEMICAL ANALYSIS ROUND 152

Metals - Chromium, Copper, Iron, Lead, Nickel, Thallium, Zinc – February 2013

RESULTS SHEET
(µg/L)

Laboratory Code | |

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

ANALYSIS	SAMPLE PTA R152 Result	±MU*	METHOD CODE	DIGESTION CODE
Chromium (Cr)				
Copper (Cu)				
Iron (Fe)				
Lead (Pb)				
Nickel (Ni)				
Thallium (Tl)				
Zinc (Zn)				

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

- **i)** For the prepared sample only a single result is requested.
- **ii)** Report results for the diluted sample.
- **iii)** Report results using three significant figures (eg.: 12.3, 123, 1230).
- **iv)** Report results in µg/L.
- **v)** Do not correct results for recovery.
- **vi)** MU* Laboratories Measurement Uncertainty (MU) if known for the result. Please report in µg/L.

_____ _____

DATE **SIGNATURE**

Return results **NO LATER THAN 15 MARCH 2013** to:
Delfina Mihaila
Proficiency Testing Australia
PO Box 7507
SILVERWATER NSW 2128
AUSTRALIA

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

INSTRUCT WATERS PROF TEST PROG 152

- End of Report -