

Production of a Hard Drinking Water Reference Material Characterised for Metals

ERM®-CA011a

January 2008
LGC/VAM/2007/037



*Setting standards
in analytical science*

Production of a Hard Drinking Water Reference Material Characterised for Metals

ERM[®]-CA011a

January 2008

Contact Point:

Mark Pettengell

Tel: 020 8943 7660

Prepared by:

Mark Pettengell

Approved by:

Steve Wood

Date:

LGC/VAM/2007/037

© LGC Limited 2008

Contents

| | | |
|----------|--|-----------|
| 1 | Introduction | 1 |
| 2 | Material Preparation | 1 |
| 3 | Homogeneity | 3 |
| 4 | Stability | 4 |
| 5 | Characterisation | 5 |
| 5.1 | IDMS Analysis | 6 |
| 5.1.1 | Method | 6 |
| 5.1.2 | Results | 7 |
| 5.2 | Inter-laboratory Study | 7 |
| 5.2.1 | Initial Treatment of Data | 7 |
| 5.2.2 | Robust Processing of the Data | 8 |
| 5.2.3 | Calculation of Certified Values and Associated Uncertainty | 8 |
| 5.2.4 | Results | 9 |
| 6 | Values on the Certificate | 10 |
| 6.1 | Certified Values | 10 |
| 6.2 | Information Values | 10 |
| 7 | Conclusion | 11 |
| | Appendix 1 – Homogeneity Data | |
| | Appendix 2 – Inter-laboratory Participants | |
| | Appendix 3 – Study Protocol | |
| | Appendix 4 – Results Proforma | |
| | Appendix 5 – Raw Data | |
| | Appendix 6 – Processed Data and Charts | |
| | Appendix 7 – Inter-laboratory Study Methods | |
| | Appendix 8 – Certificate | |

1 Introduction

The determination of metals in drinking water is undertaken widely to ensure public health and for environmental studies. To be confident in the quality of the results of analysis of such samples, it is important to validate and monitor procedures using a certified reference material (CRM) close in matrix composition to the test samples. This material was produced as a replacement for ERM CA010a, which has sold out. The composition of the material was updated in line with changes in the Drinking Water Regulations 98/83/EC of 1998 enacted in UK Statutory Instrument 2000 No. 3184 of 2000 on the quality of water intended for human consumption. This material was initially prepared under the LGC code number LGC6022, and was later assigned ERM[®] code number CA011a (the code number was changed from the previous batch because the levels of some of the elements are different to reflect changes in legislation).

The data for this LGC certified reference material have been prepared in accordance with the criteria for European Reference Materials Status (ERM). The data were accepted as complying with the principles laid down in the Technical Guidelines of the European Reference Materials[®] co-operation agreement between BAM-LGC-IRMM and this material has been allocated the ERM number CA011a. Information on these guidelines is available on the Internet (<http://www.erm-crm.org>).

2 Material Preparation

Approximately 160 L of hard drinking water was sourced from the Teddington mains supply. The water was then filtered through 1 µm cellulose filter paper and acidified to approximately pH 2 by addition of high purity nitric acid to give a final concentration of approximately 0.1 % nitric acid. This material was then analysed by ICP-MS and ICP-OES at LGC to establish the base levels of the elements of interest.

High purity metals standards (SPEX Certiprep, Middlesex, England) were used to spike the base material to achieve levels as close as possible to the UK drinking water regulation limits (98/83/EC of 1998, enacted in Statutory Instrument 2000 No. 3184). The amount of each metal standard added to the material was calculated taking account of the base level of the respective element in the solution. The material was spiked using a positive pressure Eppendorf (Cambridge, UK) digital pipette, and was stirred continuously during preparation (Table 1 shows the details of the preparation). The material was then analysed to confirm that the correct spiking levels had been achieved. Six hundred units of the material were bottled in 250 mL HDPE (High Density Polyethylene) bottles with screw caps.

The material was stored at 5 °C ± 4 °C.

| Element | Target Value (µg/L) | Base level (µg/L) | Concentration of standard solution (µg/mL) | Quantity of solution added (mL) | Final spiked concentration (calculated) (µg/L) |
|-----------|---------------------|-------------------|--|---------------------------------|--|
| Aluminium | 200 | <40 | 999 | 31.8 | 199.9 |
| Antimony | 5 | 0.45 | 999 | 0.722 | 5.0 |
| Arsenic | 10 | 1.55 | 1002 | 1.343 | 10.0 |
| Barium | 120 | 17.505 | 1000 | 16.28 | 120.0 |
| Boron | 1000 | 96.696 | 10022 | 14.32 | 999.8 |
| Cadmium | 5 | 0.79 | 997 | 0.67 | 5.0 |
| Copper | 2000 | 25.948 | 10017 | 31.3 | 1998.9 |
| Chromium | 50 | <0.7 | 998 | 7.96 | 50.0 |
| Iron | 200 | 131.261 | 998 | 10.96 | 200.1 |
| Lead | 25 | 1.41 | 998 | 3.76 | 25.0 |
| Manganese | 50 | 4.578 | 999 | 7.22 | 50.0 |
| Nickel | 20 | 2.81 | 999 | 2.73 | 20.0 |
| Selenium | 10 | <1.74 | 1001 | 1.59 | 10.0 |
| Zinc | 600 | 8.299 | 999 | 94.1 | 599.8 |

Table 1

A QC material was prepared in a similar manner. The QC material was made up in a 5 litre class A volumetric flask using demineralised water acidified to 0.1 % nitric acid. Appropriate volumes of standards were added to give the required concentrations. The target concentrations for the QC material were deliberately set to vary from the drinking water regulation limits by up to 10 %. Appropriate quantities of Calcium, Magnesium, Sodium and Potassium were also added to the QC material in order to simulate the hard water matrix (Table 2 shows the preparation details for the QC material).

| Element | Target QC level (µg/L) | Certified concentration of standard solution (µg/mL) | Spike (mL) | Final concentration (µg/L) |
|-----------|------------------------|--|------------|----------------------------|
| Aluminium | 187 | 999 | 0.936 | 187.0 |
| Antimony | 5 | 999 | 0.025 | 5.0 |
| Arsenic | 10 | 1002 | 0.05 | 10.0 |
| Barium | 100 | 1000 | 0.5 | 100.0 |
| Boron | 1144 | 10022 | 0.57 | 1142.5 |
| Cadmium | 5 | 997 | 0.025 | 5.0 |
| Copper | 1830 | 10017 | 0.914 | 1831.1 |
| Chromium | 55 | 998 | 0.276 | 55.1 |
| Iron | 192 | 998 | 0.962 | 192.0 |
| Lead | 27 | 998 | 0.136 | 27.1 |
| Manganese | 51 | 999 | 0.256 | 51.1 |
| Nickel | 17 | 999 | 0.085 | 17.0 |
| Selenium | 10 | 1001 | 0.05 | 10.0 |
| Zinc | 649 | 999 | 3.24 | 647.4 |
| Calcium | 100000 | 10000 | 50 | 100000 |
| Magnesium | 5000 | 10000 | 2.5 | 5000 |
| Potassium | 8000 | 10000 | 4 | 8000 |
| Sodium | 40000 | 10000 | 20 | 40000 |

Table 2

3 Homogeneity

The homogeneity of the candidate material was assessed for each of the elements of interest. Analysis was carried out at LGC by ICP-OES or ICP-MS depending on the element. For the elements Fe, Cd and Pb, the homogeneity was assessed using IDMS. For Sb, additional homogeneity data were obtained under contract from a commercial laboratory.

10 samples were randomly selected from across the batch and analysed in duplicate in a random order. The results were then processed by one-way ANOVA, and an uncertainty contribution for possible material heterogeneity (u_h) was calculated as the larger of the between bottle standard deviation and the method standard deviation divided by the square root of the number of replicates.

All analytes were found to be homogeneous at both the 99 % and 95 % confidence levels. Charts of the homogeneity data are shown in Appendix 1.

| Element | Mean (µg/L) | u _h (µg/L) | % RSD |
|-------------|-------------|-----------------------|--------|
| Aluminium | 206.835 | 2.409 | 1.16 |
| Antimony | 5.121 | 0.029 | 0.57 |
| Arsenic | 10.026 | 0.138 | 1.38 |
| Barium | 120.999 | 0.5 | 0.41 |
| Boron | 1002.408 | 4.162 | 0.42 |
| Chromium | 49.792 | 0.66 | 1.33 |
| Copper | 1964.542 | 8.784 | 0.45 |
| Manganese | 49.531 | 0.193 | 0.39 |
| Nickel | 19.871 | 0.233 | 1.17 |
| Selenium | 10.009 | 0.141 | 1.41 |
| Zinc | 596.079 | 2.251 | 0.38 |
| Element | Mean (mg/L) | u _h (mg/L) | % RSD |
| Calcium | 93.178 | 0.314 | 0.34 |
| Magnesium | 5.258 | 0.017 | 0.32 |
| Potassium | 7.799 | 0.038 | 0.49 |
| Sodium | 42.14 | 0.145 | 0.34 |
| IDMS | | | |
| Element | Mean (µg/L) | u _h (µg/L) | % RSD |
| Cadmium | 4.927 | 0.04 | 0.81 % |
| Iron | 207.45 | 1.351 | 0.65 % |
| Lead | 24.637 | 0.096 | 0.39 % |

Table 3

4 Stability

Long-term stability uncertainty for this material was initially calculated using the historical stability testing data for the previous batch of material (ERM CA010a). Measurements made over the life time of the previous batch at LGC were used. For each element, data for a series of time points was plotted, and a linear regression analysis was carried out. The long term stability uncertainty (u_{lts}) was calculated in one of the following ways:

1. If the modulus t-value for the linear regression was less than 2 the long-term stability uncertainty was calculated as two times standard error (S_e) of the linear regression multiplied by the number of days to be assigned as the expiry date in days (D).

$$u_{lts} = 2 \times S_e \times D \quad \text{Equation 1}$$

2. If the modulus t-value for the linear regression was greater than 2 the long-term stability uncertainty was calculated as the gradient (G) of the linear regression multiplied by the number of days to be assigned as the expiry date in days (D).

$$u_{lts} = G \times D \quad \text{Equation 2}$$

As there was no historical data available for Boron, Cadmium and Copper, the long term stability uncertainty for these elements was calculated from the average stability uncertainty for which data were available.

A summary of the results of this stability analysis is shown below.

| Element | % u_{ITS} |
|---------|--------------------|
| Al | 1.45 |
| As | 0.98 |
| Ba | 2.28 |
| Ca | 1.95 |
| Cr | 2.66 |
| Fe | 0.60 |
| K | 1.50 |
| Mg | 3.48 |
| Mn | 2.23 |
| Na | 2.30 |
| Ni | 1.45 |
| Pb | 1.06 |
| Sb | 0.96 |
| Se | 1.51 |
| Zn | 3.57 |
| | |
| Average | 1.87% |

A predicted shelf life of 1095 days (3 years) was chosen, and the appropriate uncertainty contribution was added to the combined uncertainty of the material (see section 5.2.3). Further analysis of the stability data for the previous batch of material revealed a strong dependence on the $t=0$ data, leading to considerable changes in the predicted u_{ITS} depending on the data used for $t=0$ (more than one data set was available). As such the regression based stability uncertainty calculations were considered unreliable and a contribution for long-term stability uncertainty equal to the homogeneity uncertainty was added to the combined uncertainty. This represents the smallest stability uncertainty that could be measured using the method used to determine homogeneity. The values for the homogeneity uncertainty are of the same order of magnitude as the values calculated via the regression method, but they represent a more consistent and less arbitrary approach to the assignment of long-term stability uncertainty.

This material will be monitored under LGC's reference material stability monitoring programme. Customers will be informed in the event that any changes are made to the certificate.

5 Characterisation

The material was characterised using a combination of IDMS analysis carried out at LGC and an inter-laboratory study organised by LGC. IDMS characterisation was carried out for Cadmium, Lead and Iron. The participants of the inter-laboratory study were asked to characterise Aluminium, Antimony, Arsenic, Barium, Boron, Cadmium, Calcium Chromium, Copper, Iron, Lead, Magnesium, Manganese, Nickel, Potassium, Selenium, Sodium and Zinc.

5.1 IDMS Analysis

5.1.1 Method

Iron, cadmium and lead were determined by exact matching double isotope dilution mass spectrometry (IDMS). The sample (6 g) was spiked with a solution containing enriched ^{57}Fe , ^{106}Cd and ^{206}Pb to give predicted $^{56}\text{Fe}:^{57}\text{Fe}$, $^{111}\text{Cd}:^{106}\text{Cd}$ and $^{208}\text{Pb}:^{206}\text{Pb}$ ratios of 1. For the characterisation of the material 5 replicate analyses were made on a single bottle (Unit number LGC6022/001/0097).

For calibration, solutions prepared from NIST certified materials SRM3126 (Fe), SRM3108 (Cd) and SRM981 (Pb) were diluted to give similar concentrations to that of the sample. These were then spiked with the same enriched ^{57}Fe , ^{106}Cd and ^{206}Pb solution to match the ratio of the sample blends. QC blends were prepared in the same way, using standards prepared from high purity metals (Cd and Fe - Spex Certiprep, Middlesex, UK) and commercially available standard solutions (Pb – Romil, Cambridgeshire, UK, 1000 $\mu\text{g/g}$).

Fe measurements were performed using a ThermoFinnigan ELEMENT magnetic sector inductively coupled plasma mass spectrometer (HR-ICP-MS), and Cd and Pb using an Agilent 7500ce collision/reaction cell inductively coupled plasma mass spectrometer (CRC-ICP-MS) operating in standard mode. Typical operating conditions for the HR-ICP-MS and the CRC-ICP-MS are given in Table 4.

| HR-ICP-MS (Fe) | | CRC-ICP-MS (Cd and Pb) | |
|----------------------|----------------------------|------------------------|-----------------------------|
| Power | 1250 W | Power | 1520 W |
| Carrier gas | 1.2 L min ⁻¹ | Carrier gas | 0.94 L min ⁻¹ |
| Auxiliary gas | 1.0 L min ⁻¹ | Makeup gas | 0.19 L min ⁻¹ |
| Nebuliser gas | 0.9 L min ⁻¹ | Nebuliser | Micromist glass concentric |
| Nebuliser | Micromist glass concentric | Spray Chamber | Quartz cooled to 2 °C |
| Spray Chamber | Quartz cooled to 5 °C | Gas Mode | Standard (no collision gas) |
| Resolution | Medium (4000) | Cell Entrance | -22 V |
| | | Cell Exit | -28 V |

Table 4

5.1.2 Results

| Sample | Fe (ng/g) | Pb (ng/g) | Cd (ng/g) |
|--|--------------|--------------|-------------|
| 97B | 207.4 | 24.64 | 5.06 |
| 97C | 208.5 | 24.64 | 4.9 |
| 97D | 205.4 | 24.64 | 4.86 |
| 97E | 209.0 | 24.71 | 4.9 |
| 97F | 204.6 | 24.7 | 4.91 |
| Mean | 207.0 | 24.67 | 4.93 |
| Characterisation uncertainty | 1.97 | 0.15 | 0.08 |
| Blend to blend variation | 0.86 | 0.02 | 0.03 |
| Combined standard uncertainty (characterisation) | 2.09 | 0.15 | 0.09 |

Table 5

5.2 Inter-laboratory Study

Samples of the candidate material were distributed to 24 laboratories during May 2007. The participants were selected from a pool of laboratories with which LGC has prior experience. Preference was given to those laboratories who were accredited to ISO/IEC 17025. A volumetrically prepared QC material was also distributed to assist LGC in the evaluation of results. Of the original 24 participants, 22 submitted data for the study (Appendix 2).

The laboratories were provided with a protocol (Appendix 3), which specified the general approach to be taken with the analysis. The laboratories were free to use a method of their choice, but they were encouraged to choose well validated methods where these were available.

Participants were asked to submit data within 5 weeks of receiving the sample using the Excel spreadsheet which was provided (Appendix 4). An additional information form was also provided for laboratories to give information on procedures used and quality assurance data.

5.2.1 Initial Treatment of Data

The data were scrutinised for technical errors as they were received (for instance results reported in the wrong units or evidence of incorrect procedures applied). Where technical errors were located, the laboratories were asked to re-examine their data submissions and the data were updated accordingly. No laboratories were eliminated from this study based on technical errors.

Laboratory QC results were then screened against the expected QC results based on the volumetric preparation details. A QC rejection limit of 30 % was set. Laboratories which were more than 30 % away from the expected QC value were rejected from the final results. The QC limits were determined by performance data gathered during

previous characterisation exercises and account for an approximate 99 % confidence interval of a theoretical group of acceptably performing laboratories.

The following table shows the data sets rejected based on poor QC performance for the analytes shown.

| Analyte | Rejected data sets |
|-----------|--------------------|
| Antimony | 11, 21, 22 |
| Arsenic | 21 |
| Boron | 17, 19 |
| Calcium | 21 |
| Lead | 9, 14, 19, 21 |
| Manganese | 3 |
| Nickel | 9, 21 |
| Potassium | 9 |

Table 6

In addition to these rejections, Lab 7 requested that their Nickel results be removed from the study due to their discovery of a method bias.

5.2.2 Robust Processing of the Data

The median of each laboratory data set was calculated and the median of medians was then taken as the robust mean of the total data set. The robust dispersion estimator that was used was the ‘Median of the Absolute Difference’ (MAD). This is calculated by taking the absolute difference between the median of medians and the individual laboratory’s median, and then calculating the median of the resultant absolute differences. The result is then divided by 0.6745 (this value is derived from the normal distribution) to give the value for MADe, which is equivalent to standard deviation.

5.2.3 Calculation of Certified Values and Associated Uncertainty

For each analyte, the median of medians for the data set (after QC and technical rejections) was taken as the certified value. The characterisation uncertainty for each analyte was calculated from the MADe value.

$$u_{char} = \frac{MADe \sqrt{\frac{\pi}{2}}}{\sqrt{n}} \quad \text{Equation 3}$$

This formula gives the ‘robust standard error of the mean’. This is the value which is taken as the uncertainty of the characterisation (u_{char}). The homogeneity, stability and characterisation uncertainties were combined by taking the square root of the sum of the squares of the individual standard uncertainties (Equation 4).

$$u_{Total} = \sqrt{u_{char}^2 + u_h^2 + u_{lts}^2} \quad \text{Equation 4}$$

$u_{ts}^2 = u_h^2$ (see section 4), therefore:

$$u_{Total} = \sqrt{u_{char}^2 + 2u_h^2} \quad \text{Equation 5}$$

The combined uncertainty (u_{Total}) was then multiplied by a coverage factor to give the half-width of the 95 % confidence interval. This was then rounded up to an appropriate number of significant figures to give the uncertainty quoted on the reference material certificate.

The coverage factor was calculated using Microsoft Excel's 'TINV' function for the relevant number of degrees of freedom and a confidence interval of 95 %. The number of effective degrees of freedom was calculated using the Welch-Satterthwaite equation (Equation 6).

$$v_{eff} = \frac{u_{Total}^4}{\sum_{i=1}^N \frac{u_i^4}{v_i}} \quad \text{Equation 6}$$

Where v_i is the number of degrees of freedom of each independent analysis, u_i is the uncertainty associated with each independent analysis and u_{Total} is the total standard uncertainty for the characterisation value.

5.2.4 Results

The raw data from the laboratory submissions are shown in Appendix 5. Laboratories which did not submit results, or who submitted non-quantitative results (i.e. 'less than' or 'greater than' values) are marked as DNS (Did Not Submit).

The results of the inter-laboratory study were in excellent agreement with the expected analyte levels of the material, and the characterisation uncertainties obtained from the study data were comparable to that obtained by the IDMS method employed by LGC for selected elements. This is an encouraging result for the laboratories involved in the study, as it suggests that there is no overall industry bias in the measurement of metals in drinking water.

6 Values on the Certificate

6.1 Certified Values

| Constituent ^{1,2} | Certified value ^{3,4} (µg/L) | Uncertainty ⁵ (µg/L) |
|----------------------------|---------------------------------------|---------------------------------|
| Aluminium | 197 | 13 |
| Antimony | 5.2 | 0.3 |
| Arsenic | 10.1 | 0.6 |
| Barium | 120 | 6 |
| Boron | 950 | 67 |
| Cadmium | 4.94 | 0.23 |
| Chromium | 48 | 3 |
| Copper | 1970 | 67 |
| Iron | 207 | 6 |
| Lead | 24.7 | 0.5 |
| Manganese | 47 | 2.3 |
| Nickel | 19.4 | 1 |
| Selenium | 10.7 | 0.7 |
| Zinc | 586 | 20 |
| | Certified value ^{3,4} (mg/L) | Uncertainty ⁵ (mg/L) |
| Calcium | 89 | 2 |
| Magnesium | 4.9 | 0.16 |
| Potassium | 7.5 | 0.22 |
| Sodium | 40 | 1.3 |

1) Cadmium, iron and lead were determined at LGC using Isotope Dilution ICP-MS. (IDMS)
 2) The remaining measurands are defined by the methods used by participant laboratories.
 3) Unweighted median value of the concentration determined by participant laboratories. Each data set was obtained in a different laboratory and/or using a different method of measurement.
 4) The results are traceable to the SI through the physical and chemical standards used by LGC and the interlaboratory study participant laboratories.
 5) The quoted uncertainty is the half-width of the expanded uncertainty calculated using a coverage factor (k) of approximately 2, which gives a level of confidence of 95 %.

Table 7

6.2 Information Values

| Constituent | Information value (µg/L) | Uncertainty (µg/L) |
|-------------|--------------------------|--------------------|
| Cadmium | 4.8 | 0.22 |
| Iron | 202 | 7.4 |
| Lead | 24.6 | 1.25 |

These information values are derived from the inter laboratory study for this material. These information values are supplied for comparison purposes only.

Table 8

7 Conclusion

This drinking water material has been successfully certified for a wide range of metals. The concentration of each element corresponds to the legal limits given in the European drinking water directive 98-83-EC, and this material should be of use to all laboratories carrying out drinking water analysis in Europe.

The material is available for purchase from LGC Standards.

LGC Standards
Queens Road
Teddington
Middlesex
TW11 0LY
United Kingdom

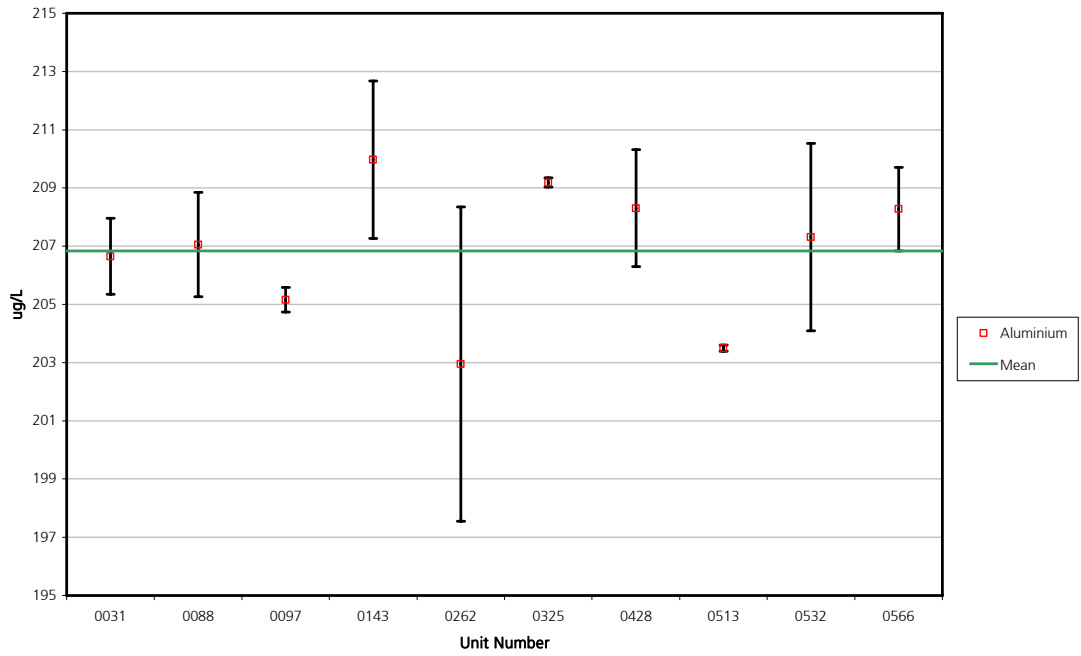
Tel: +44 (0)20 8943 8480

Fax: +44 (0)20 8943 7554

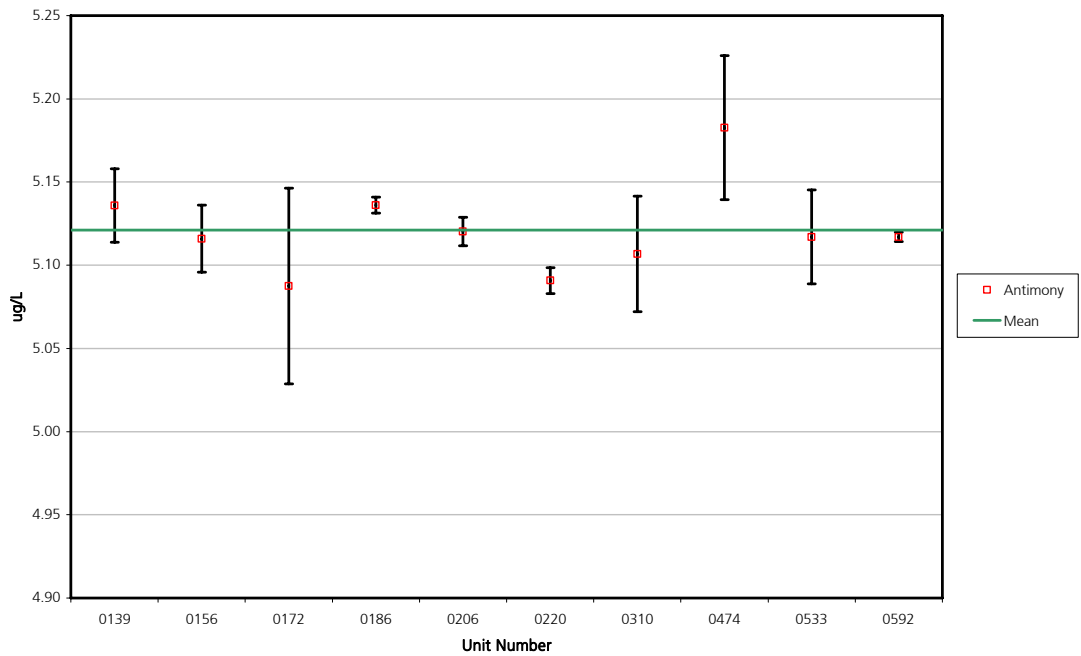
E-mail: uksales@lgcstandards.com

Appendix 1 – Homogeneity Data

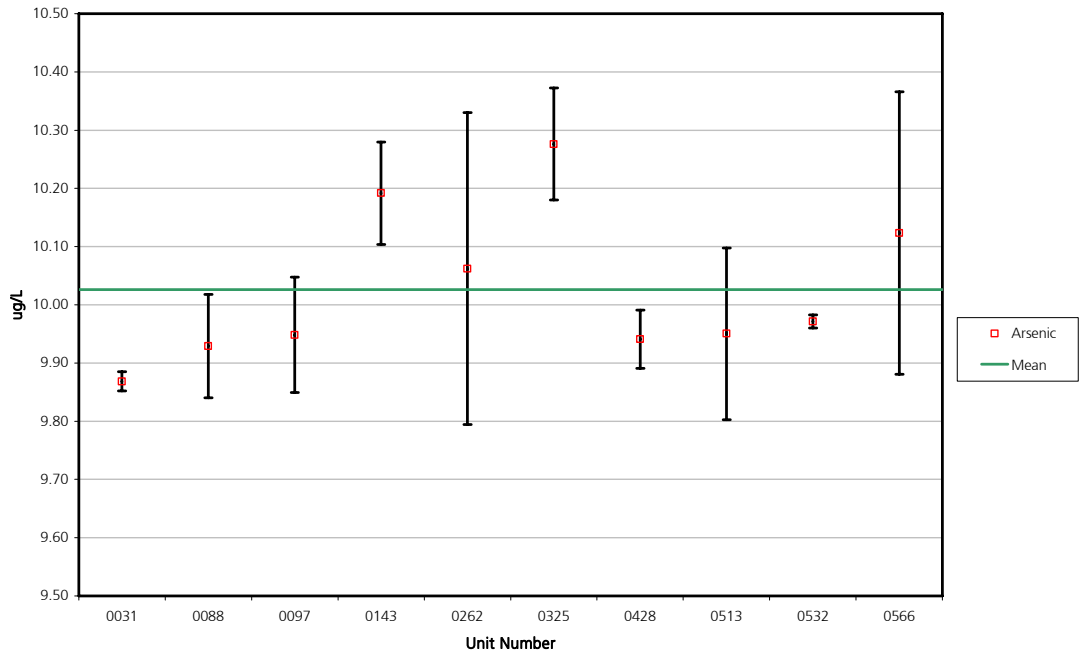
LGC6022 Aluminium



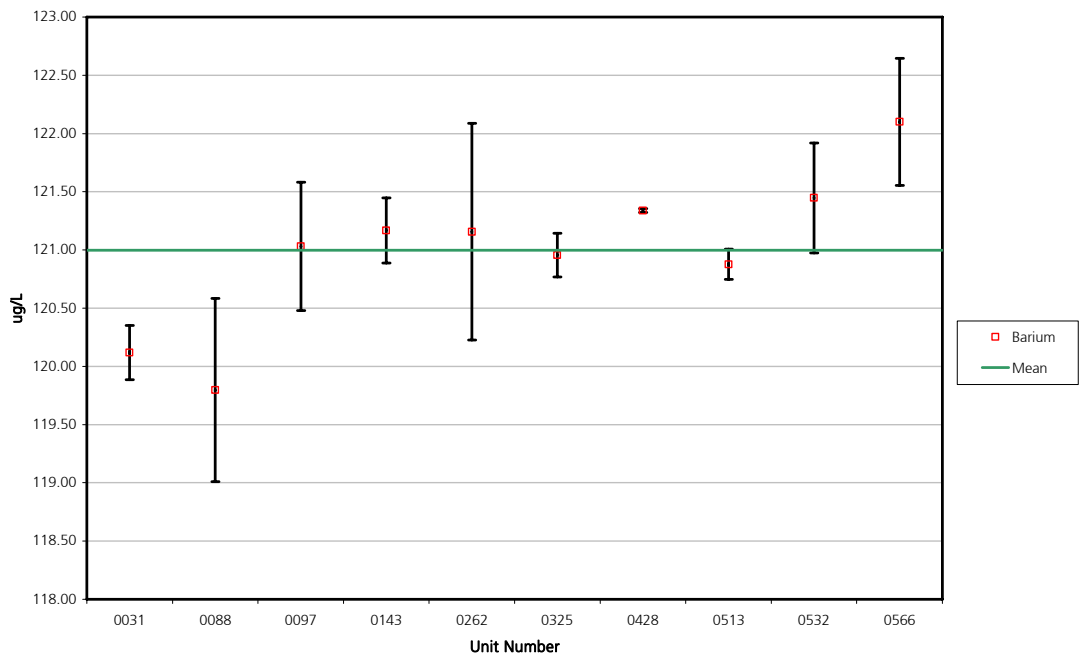
LGC6022 Antimony



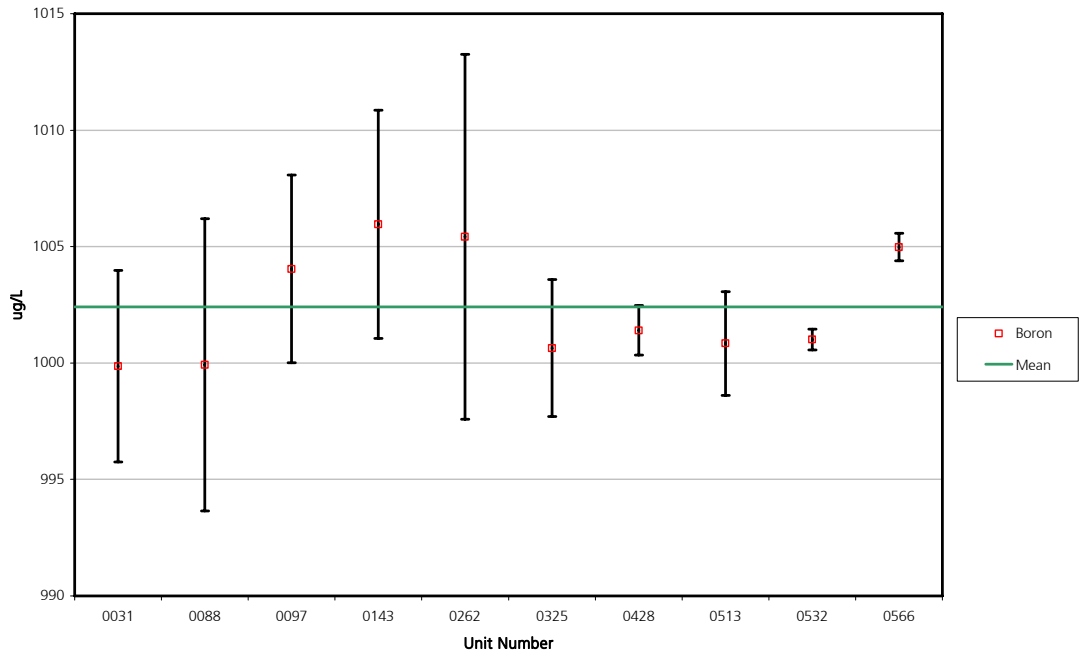
LGC6022 Arsenic



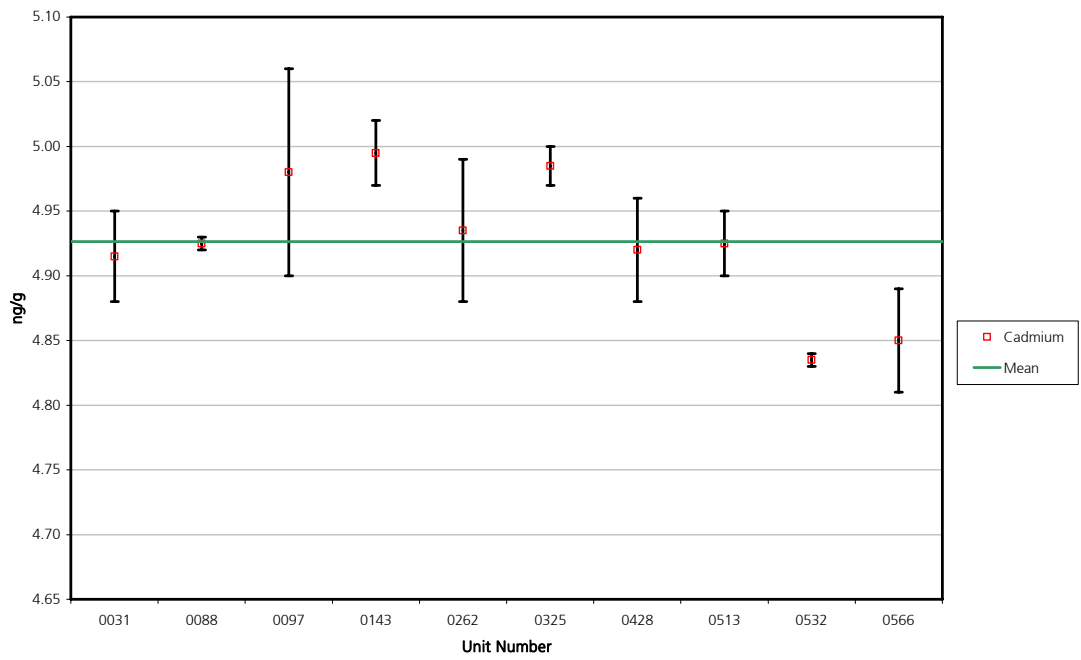
LGC6022 Barium



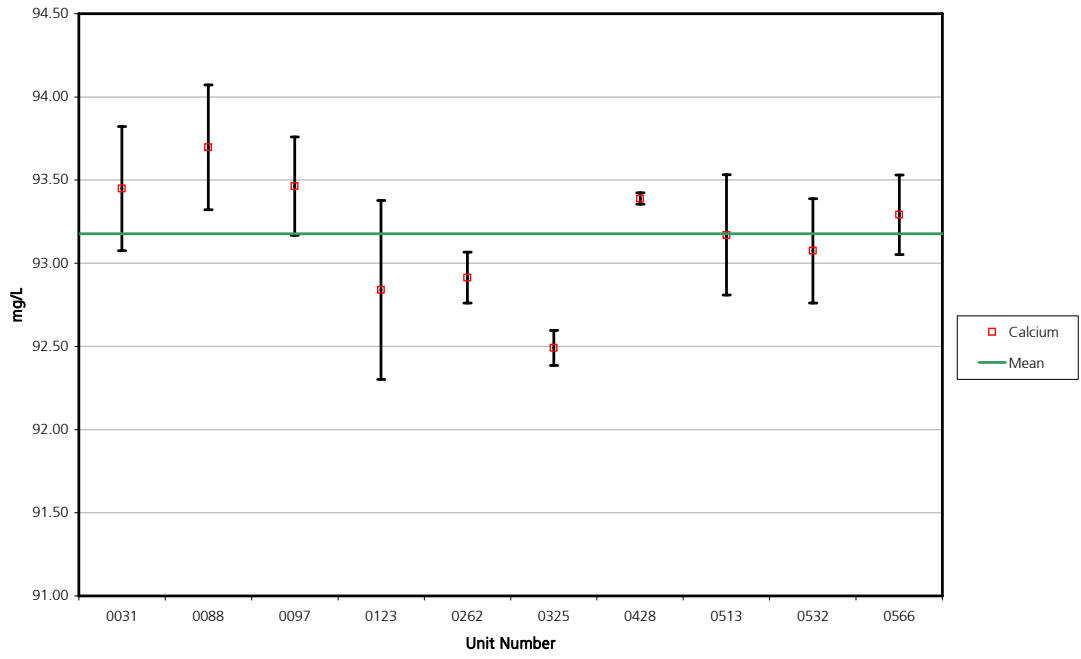
LGC6022 Boron



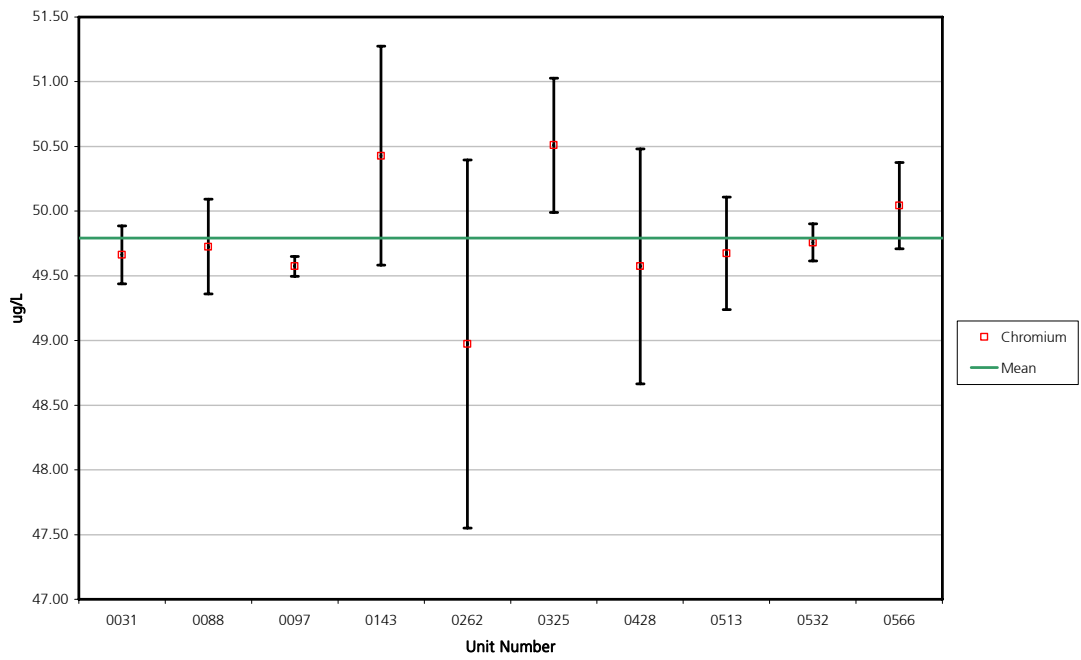
LGC6022 Cadmium



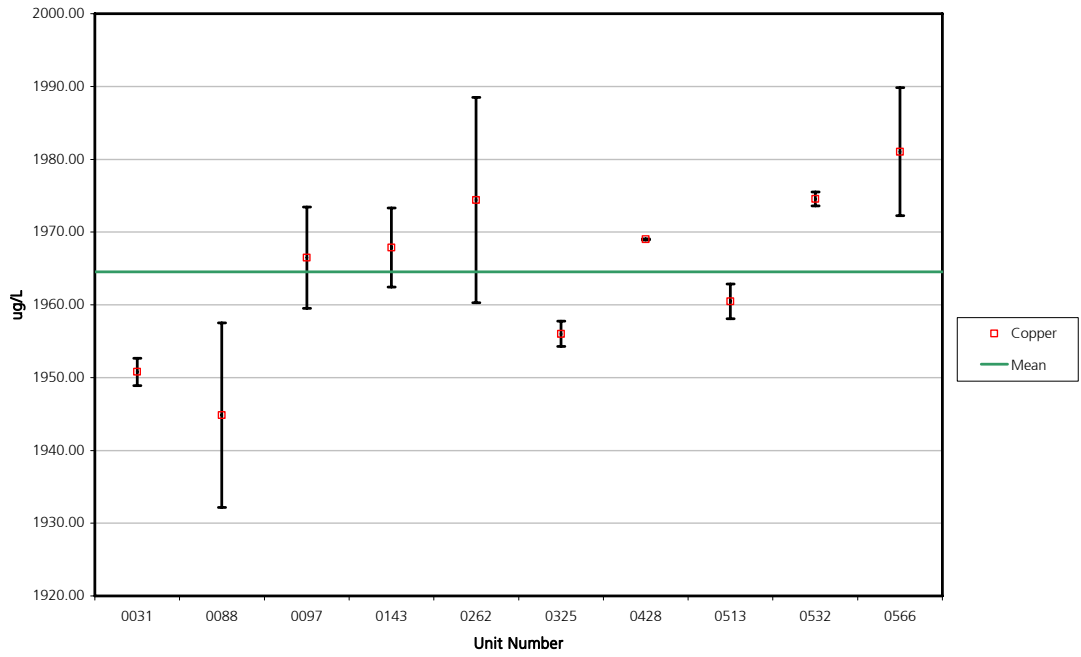
LGC6022 Calcium



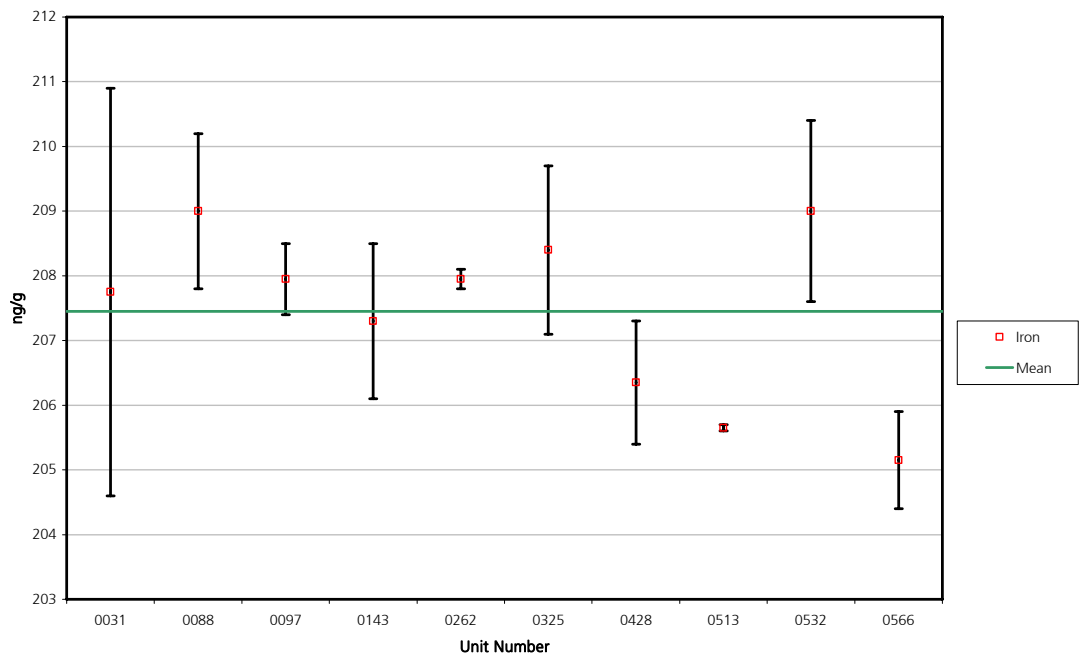
LGC6022 Chromium



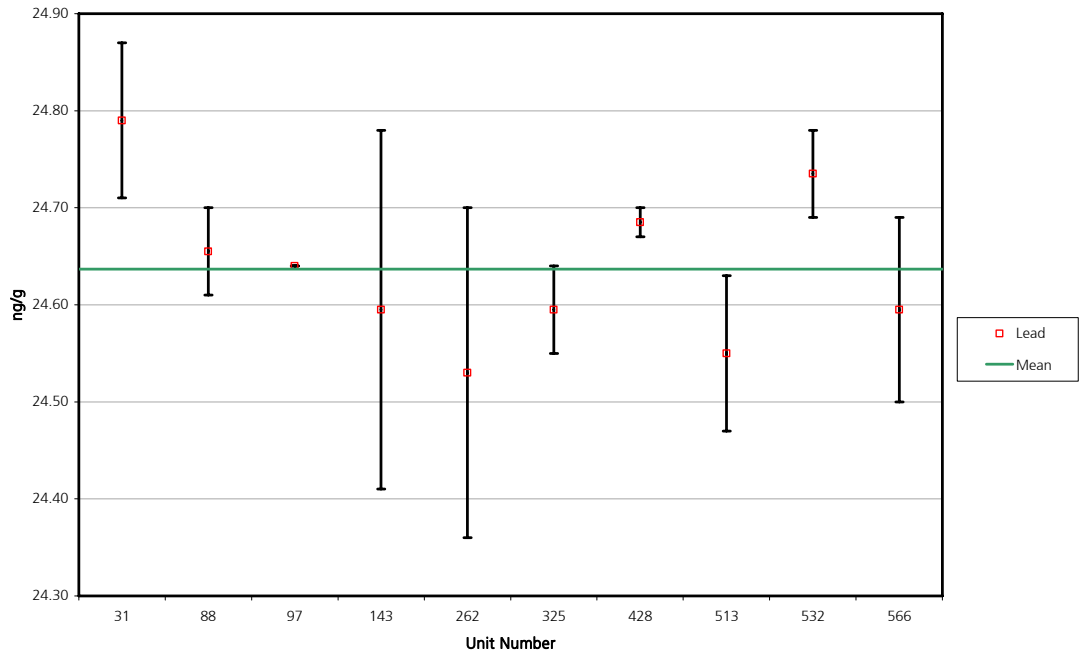
LGC6022 Copper



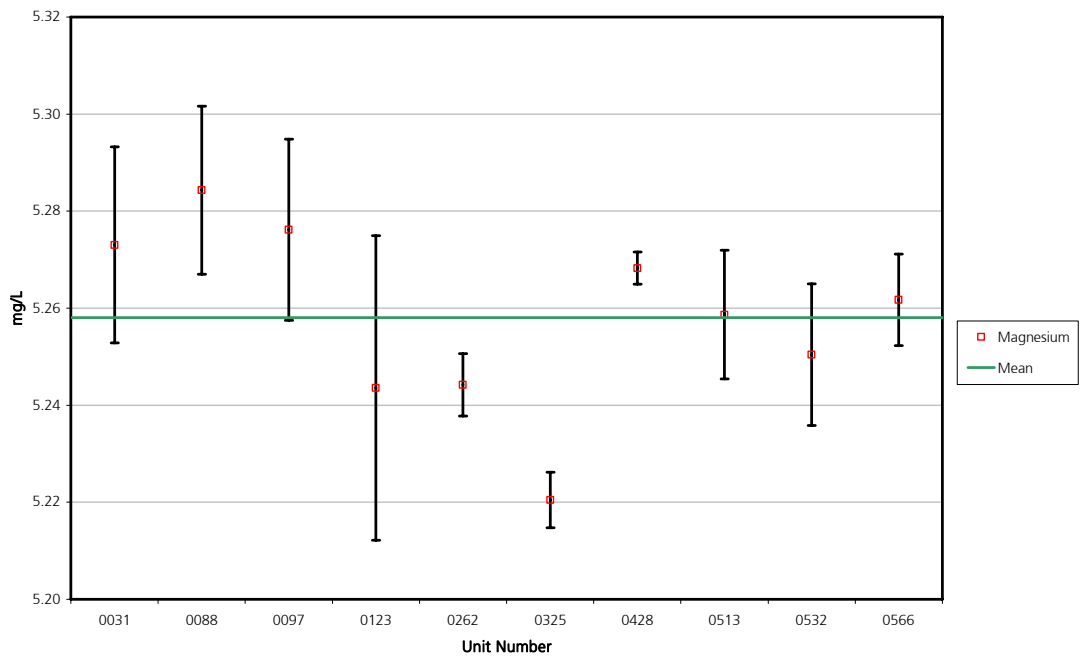
LGC6022 Iron



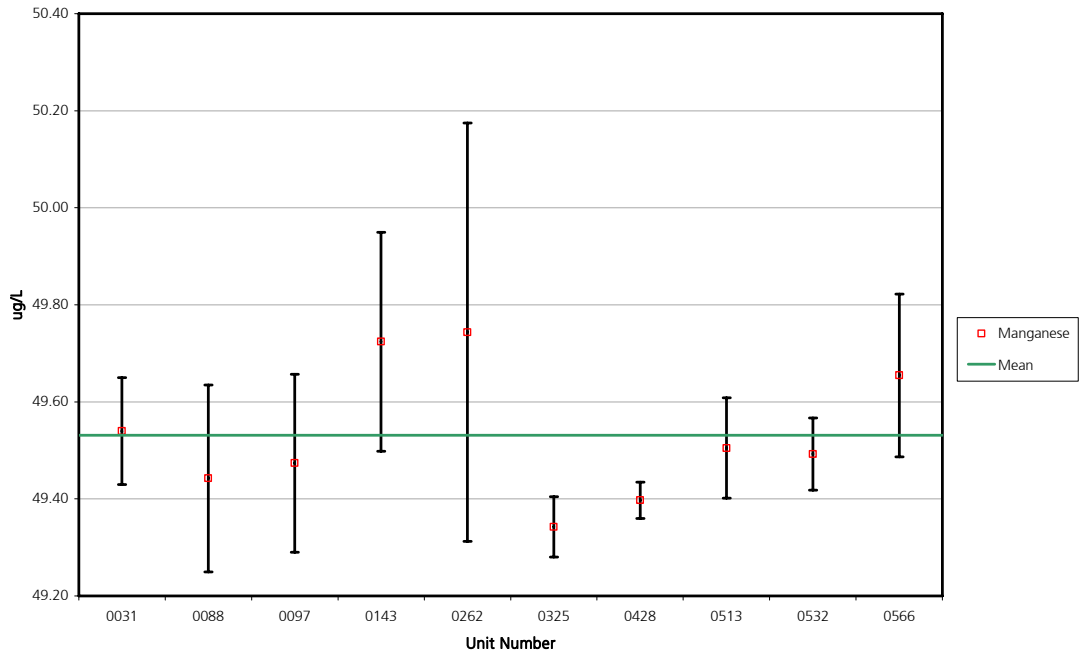
LGC6022 Lead



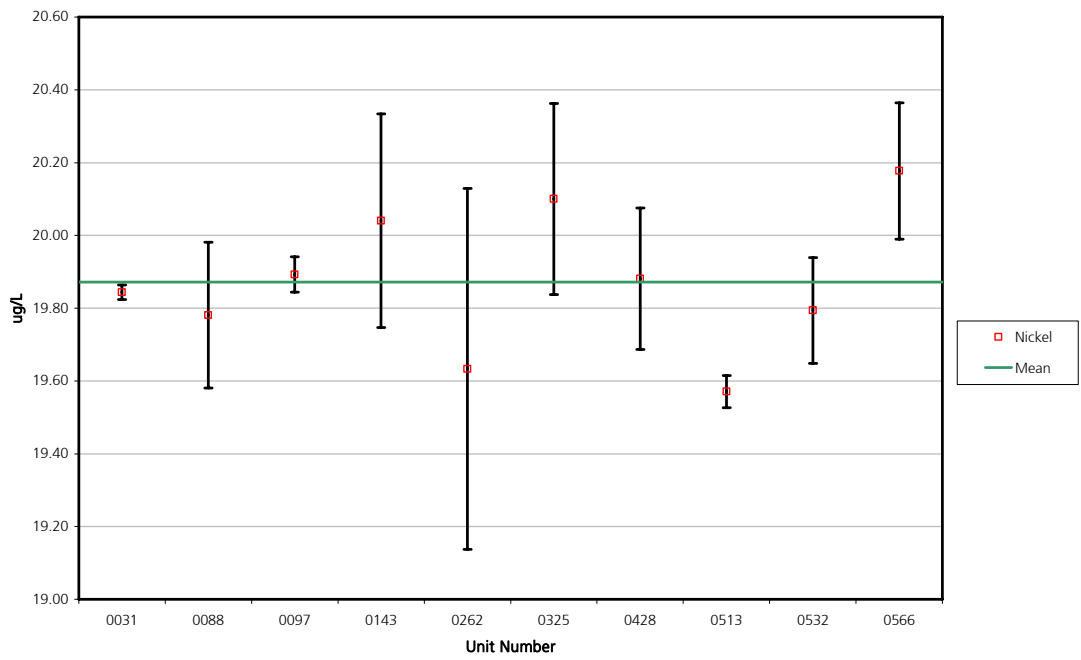
LGC6022 Magnesium



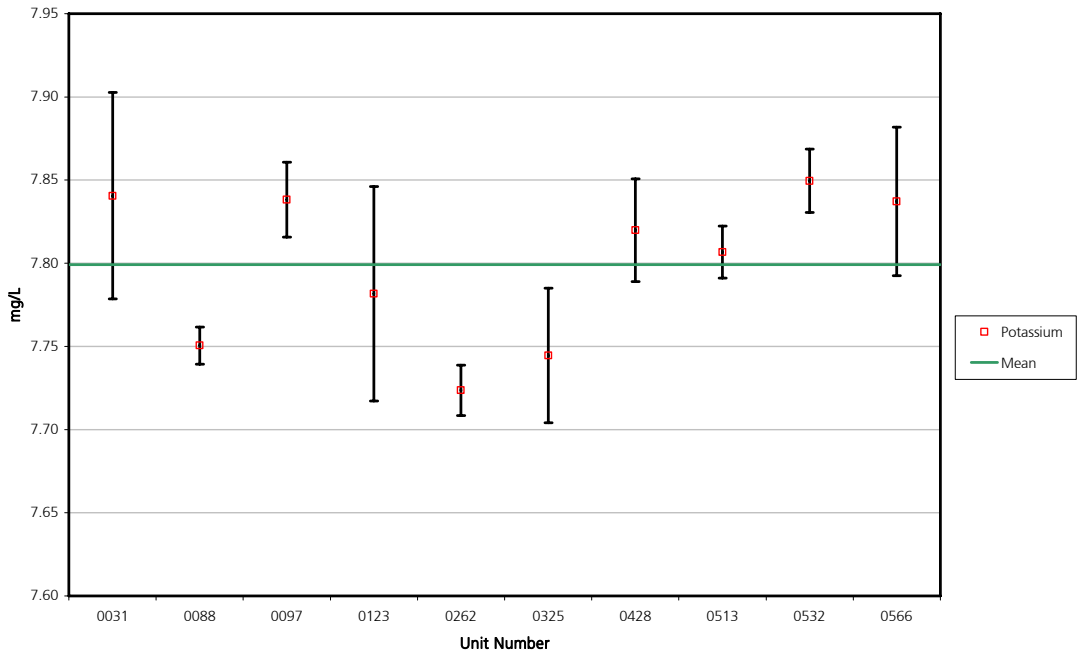
LGC6022 Manganese



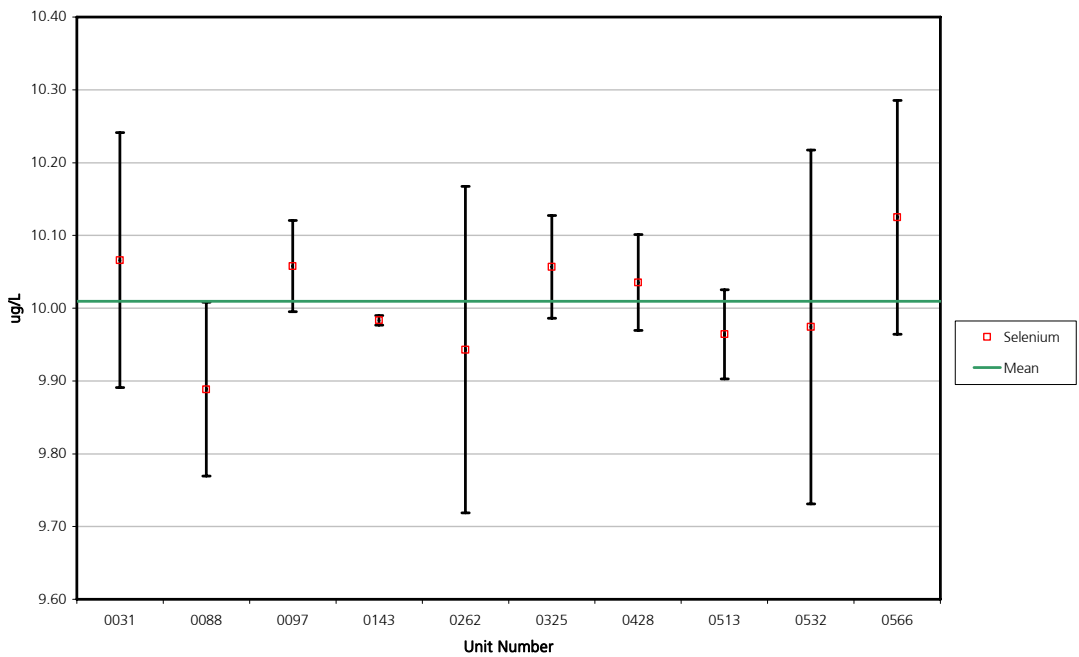
LGC6022 Nickel



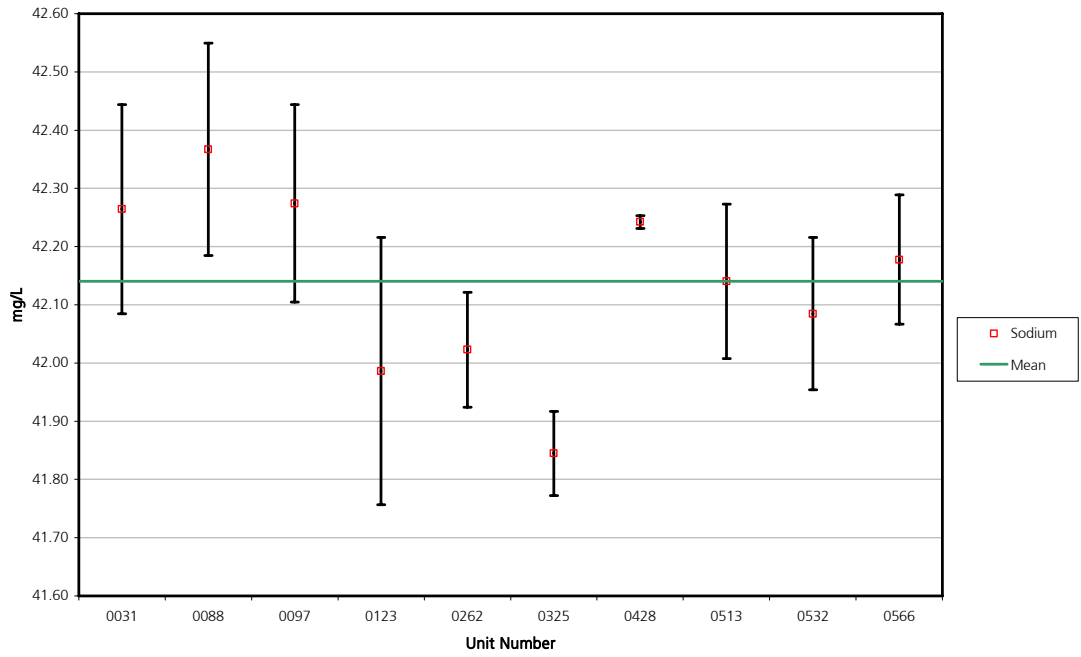
LGC6022 Potassium



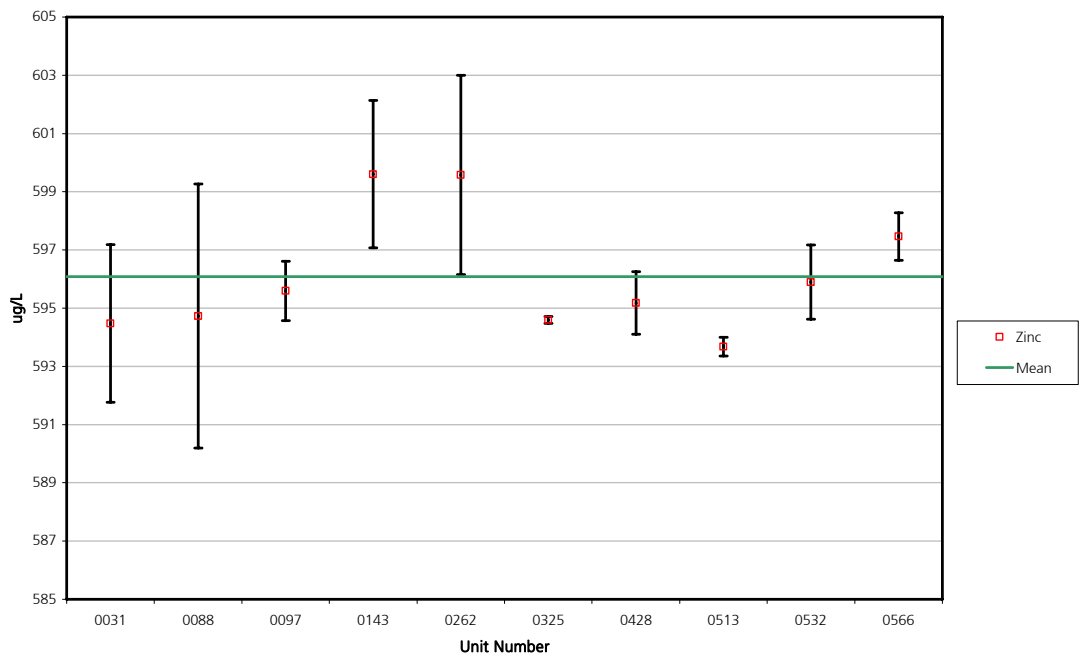
LGC6022 Selenium



LGC6022 Sodium



LGC6022 Zinc



Appendix 2 – Inter-laboratory Participants

The following laboratories participated in the inter-laboratory study:

| | |
|--|------------------------|
| AES Ltd | UK |
| ALcontrol Technichem | UK |
| AMEC Earth and Environmental | Canada |
| Analytical Data Services | UK |
| Anglian Water | UK |
| Austrian Research Centers GmbH -ARC | Austria |
| British Geological Survey | UK |
| Centre for Ecology and Hydrology | UK |
| Chemex Environmental International Limited | UK |
| Chemtech Environmental Limited | UK |
| FORCE Technology | Denmark |
| Inspectorate Services Peru S.A.C. | Peru |
| LATU - Spectrometry Dept. | Uruguay |
| Macaulay Institute | UK |
| National Institute of Health | Portugal |
| Public Health Institute of Istrian County | Croatia |
| Seychelles Bureau of Standards | Republic of Seychelles |
| South East Water | UK |
| South West Water, Exeter Laboratory | UK |
| States Analyst Laboratory | Guernsey |
| STL Bridgend | UK |
| Sutton and East Surrey Water | UK |

Appendix 3 – Study Protocol

1. Introduction

This protocol describes the procedures to be followed by laboratories participating in the exercise to characterise the concentration of selected analytes in a water sample. The analytes to be determined are listed in section 2.6.1.

Laboratories are free to use any analytical method of their own choice, but as the objective of the exercise is to establish the analyte concentrations as accurately as possible, laboratories are strongly encouraged to select a well-validated method of known trueness and precision.

Laboratories are asked to analyse those analytes listed in section 2.6.1 that they determine on a regular basis. Outlined below are those general aspects of working procedures that should be followed in the execution of the laboratory's chosen analytical method. Laboratories are asked to make all reasonable effort to meet these requirements, but if this is not possible the results will still be of value to the exercise, provided advice is given as to those aspects of the protocol that could not be followed.

2. Working procedures

2.1 Receipt of samples

Check that the samples have been received in an undamaged condition and that they are clearly labelled.

If there are any problems with the samples, contact Mark Pettengell at LGC:

Tel: +44 (0) 20 8943 7660

Fax: +44(0) 20 8943 2767

e-mail: mark.pettengell@lgc.co.uk

2.2 Storage and handling of samples

The Candidate Material and QC Material must be stored at $5\text{ }^{\circ}\text{C} \pm 4\text{ }^{\circ}\text{C}$, until the analysis is to be carried out. Appropriate safety equipment should be worn whilst handling the samples; the samples have been acidified to aid stability of the metals in solution and are at approximately pH 2.

2.3 Timescale

The analyses and reporting of results should be carried out within 5 weeks of receipt of the samples or by the 15th June 2007 – whichever is soonest.

2.4 Number of Replicate Sub-samples to be Analysed.

2.4.1 Candidate Material

Five replicate analyses should be performed on this material, to ensure that your laboratory median is a good estimate of the true value of the analytes being measured. The sample provided comprises of

1 bottle of 250 mL of spiked hard drinking water acidified with nitric acid to approx 0.1 %.

Laboratories should report the results of ALL the replicate analyses that they carry out and should NOT discard any data. Results should be quoted to 2 decimal places and NOT truncated. Statistical evaluation of all data will be carried out at LGC.

2.4.2 QC Material

Three replicate analyses should be performed on the QC material for each analyte.

Laboratories should report the results of ALL the replicate analyses that they carry out and should NOT discard any data. Results should be quoted to 2 decimal places and NOT truncated. Statistical evaluation of all data will be carried out at LGC.

This QC material allows LGC to evaluate participant laboratory performance, but it is also necessary for laboratories to use their own QC material to ensure that their method is performing as expected.

2.5 Analytical Method to be used

Laboratories are free to use a method of their own choice. It should be a method they are familiar with and for which they have appropriate method validation data. Such data should include information on the precision and trueness of the method. It is important that you report the procedure used to measure the analytes.

2.6 Quantitative Determination of the Analyte

Where the analyte is determined by an instrumental technique (e.g. Mass Spectrometry), the instrument should be calibrated using a reliable standard of the analyte in question. It is important that you report the source and purity of your calibrant to help with the assessment of your data.

Before the sample is introduced to the instrument, ensure that the instrument's response to replicate measurements of the standard is of acceptable repeatability, i.e. that the instrument response is stable with time. You must also check that the instrument is being operated within its linear range.

The following sequence for measurement of the samples and the supplied QC material is suggested:

- Calibration standards
- 1 x QC material sample
- Samples of candidate material
- 1 x QC material sample
- Samples of candidate material
- 1 x QC material sample
- Calibration standards

For a single point calibration, the analyte concentration in the standard should be such that instrument responses for sample and standard are similar. In the case of a multi point calibration a calibration graph should be constructed, and the sample response must fall within the calibration range. The results for the measurements should be examined to confirm that the instrument response has not altered significantly during the course of the measurements.

The possible occurrence of matrix effects, leading to either enhancement or suppression of the sample response in comparison to the standard response, should be considered. If such effects are thought likely to be present, appropriate steps must be taken in the instrumental measurement procedure. For example, the matrix of the standard could be adjusted to approximately that of the sample, or the technique of standard additions to the sample could be used.

2.6.1 Analytes to be Determined

The following metals are to be determined:

Aluminium
Antimony
Arsenic
Barium
Boron
Cadmium
Calcium
Copper
Chromium
Iron
Lead
Magnesium
Manganese
Nickel
Potassium
Selenium
Sodium
Zinc

3. Reporting of Results

All results should be reported in the Excel spreadsheet provided. Background information, including method details, should be entered in the Word document provided. Both sets of forms should be returned (preferably by email), by 15th June 2007 to:

Mark Pettengell

LGC

Queens Road

Teddington

Tel: +44 (0) 208 943 7660

Middlesex

ENGLAND

Fax: +44 (0) 208 943 2767

TW11 0LY

e-mail: mark.pettengell@lgc.co.uk

Appendix 4 – Results Proforma



LGC6022 Inter-laboratory Study – Results Proforma

| | |
|------------------------|---------------------|
| Laboratory Name | |
| Submission Date | |
| Contact name | |
| Lab Number | <i>LGC Use ONLY</i> |

Candidate Material

Report results in µg/L - to 2 decimal places

| Analyte | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 |
|-----------|----------|----------|----------|----------|----------|
| Aluminium | | | | | |
| Antimony | | | | | |
| Arsenic | | | | | |
| Barium | | | | | |
| Boron | | | | | |
| Cadmium | | | | | |
| Copper | | | | | |
| Chromium | | | | | |
| Iron | | | | | |
| Lead | | | | | |
| Manganese | | | | | |
| Nickel | | | | | |
| Selenium | | | | | |
| Zinc | | | | | |

QC Material

Report results in µg/L - to 2 decimal places

| Analyte | QC Result 1 | QC Result 2 | QC Result 3 |
|-----------|-------------|-------------|-------------|
| Aluminium | | | |
| Antimony | | | |
| Arsenic | | | |
| Barium | | | |
| Boron | | | |
| Cadmium | | | |
| Copper | | | |
| Chromium | | | |
| Iron | | | |
| Lead | | | |
| Manganese | | | |
| Nickel | | | |
| Selenium | | | |
| Zinc | | | |

Candidate Material

Report results in mg/L - to 2 decimal places

| Analyte | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 |
|-----------|----------|----------|----------|----------|----------|
| Calcium | | | | | |
| Magnesium | | | | | |
| Potassium | | | | | |
| Sodium | | | | | |

QC Material

Report results in mg/L - to 2 decimal places

| Analyte | QC Result 1 | QC Result 2 | QC Result 3 |
|-----------|-------------|-------------|-------------|
| Calcium | | | |
| Magnesium | | | |
| Potassium | | | |
| Sodium | | | |

Appendix 5 – Submitted Results

| Aluminium (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|------------------|----------|----------|----------|----------|----------|-------------|-------------|-------------|
| Lab 1 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 2 | 175.35 | 189.33 | 189.72 | 170.42 | 177.21 | 172.82 | 171.81 | 163.53 |
| Lab 3 | 207.5 | 196.07 | 206.07 | 195 | 206.07 | 192.5 | 193.93 | 193.93 |
| Lab 4 | 197 | 201.9 | 184.4 | 200.3 | 188.6 | 176.4 | 170.1 | 176.1 |
| Lab 5 | 186.2 | 183.9 | 185.4 | 186.3 | 184.8 | 172 | 174.7 | 169.4 |
| Lab 6 | 190.72 | 193.53 | 195.65 | 199.37 | 192.7 | 180.43 | 178.89 | 181.83 |
| Lab 7 | 220 | 220 | 220 | 220 | 220 | 190 | 190 | 190 |
| Lab 8 | 195 | 199 | 197 | 198 | 196 | 183 | 179 | 177 |
| Lab 9 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 10 | 191 | 199 | 201 | 194 | DNS | 183 | 186 | DNS |
| Lab 11 | 250.4 | 233.9 | 272.2 | 270 | 256.63 | 201.9 | 245.8 | 225.2 |
| Lab 12 | 229.24 | 227.01 | 228.93 | 228.66 | 227.46 | 213.25 | 212.87 | 211.37 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 196.2 | 193.8 | 192.5 | 193.7 | 192.6 | 180.5 | 177.3 | 175.5 |
| Lab 15 | 213.72 | 222.56 | 225 | 232.1 | 237.61 | 179.15 | 178.09 | 175.71 |
| Lab 16 | 184 | 185 | 191 | 186 | 185 | 204 | 181 | 180 |
| Lab 17 | 176.4 | 177.5 | 178.6 | 178.3 | 179.6 | 167.4 | 167.1 | 166.7 |
| Lab 18 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 19 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 20 | 167 | 167 | 166 | 164 | 165 | 182 | 185 | 189 |
| Lab 21 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 22 | 206.29 | 206.15 | 205.84 | 206.47 | 205.57 | 189.38 | 189.71 | 188.2 |

| Antimony (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 2 | 5 | 4.98 | 4.77 | 5.16 | 4.83 | 4.72 | 4.76 | 4.9 |
| Lab 3 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 4 | 5.72 | 5.86 | 5.68 | 5.64 | 5.54 | 4.98 | 5.01 | 5.08 |
| Lab 5 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 6 | 5.14 | 5.02 | 5.1 | 5.18 | 5.13 | 4.86 | 4.84 | 4.81 |
| Lab 7 | 4.8 | 4.5 | 4.7 | 4.7 | 4.5 | 4.5 | 4.6 | 4.6 |
| Lab 8 | 4.8 | 4.91 | 4.93 | 4.87 | 4.95 | 4.11 | 4.18 | 4.19 |
| Lab 9 | 5.85 | 5.59 | 6.14 | 5.26 | 5.87 | 5.43 | 6.2 | 6.28 |
| Lab 10 | 5.08 | 4.89 | 5.02 | 5.08 | DNS | 4.9 | 4.65 | DNS |
| Lab 11 | 12.6 | 6.3 | 8.1 | 7.7 | 8.68 | 6.7 | 6.3 | 10 |
| Lab 12 | < 20 | < 20 | < 20 | < 20 | < 20 | < 20 | < 20 | < 20 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 5.24 | 5.24 | 5.11 | 5.23 | 5.2 | 3.72 | 3.84 | 3.79 |
| Lab 15 | 5.05 | 5.27 | 5.34 | 5.25 | 5.33 | 4.88 | 4.88 | 4.9 |
| Lab 16 | 4.5 | 4.58 | 4.75 | 4.82 | 4.66 | 4.58 | 4.32 | 4.27 |
| Lab 17 | 5.369 | 5.391 | 5.416 | 5.413 | 5.362 | 5.134 | 4.674 | 4.673 |
| Lab 18 | 7.3 | 5.9 | 5.3 | 5.7 | 5.5 | 6.4 | 5.2 | 5.2 |
| Lab 19 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 20 | 5.34 | 5.36 | 5.28 | 5.3 | 5.14 | 4.67 | 4.77 | 4.85 |
| Lab 21 | 6.91 | 7.21 | DNS | DNS | DNS | 6.51 | 6.91 | DNS |
| Lab 22 | 10.88 | 10.42 | 8.4 | 6.96 | 8.39 | 14.67 | 10.54 | 9.15 |

| Arsenic (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|-----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 9.57 | 9.17 | 9.14 | 9.23 | 9.28 | 9.57 | 9.59 | 9.31 |
| Lab 2 | 9.49 | 9.75 | 9.73 | 9.55 | 10.05 | 9.93 | 9.67 | 9.68 |
| Lab 3 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 4 | 9.84 | 10.25 | 9.94 | 9.95 | 9.49 | 9.91 | 9.73 | 9.86 |
| Lab 5 | 10.2 | 10.2 | 10.1 | 10.1 | 10 | 10.1 | 10.2 | 10.3 |
| Lab 6 | 9.65 | 9.72 | 9.79 | 9.79 | 9.83 | 9.69 | 9.52 | 9.55 |
| Lab 7 | 10 | 10 | 10 | 10 | 10 | 10 | 9.6 | 9.8 |
| Lab 8 | 9.99 | 9.94 | 9.84 | 9.75 | 9.68 | 10.2 | 9.81 | 9.57 |
| Lab 9 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 10 | 10.4 | 10.1 | 10.5 | 10.5 | DNS | 10.3 | 10.4 | DNS |
| Lab 11 | 10.2 | 12.4 | 14.3 | 13.3 | 12.55 | 11.9 | 11.9 | 8.8 |
| Lab 12 | < 50 | < 50 | < 50 | < 50 | < 50 | < 50 | < 50 | < 50 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 10.9 | 10.9 | 10.8 | 10.9 | 10.8 | 10.9 | 10.9 | 11.1 |
| Lab 15 | 10.17 | 10.37 | 10.27 | 10.78 | 10.6 | 10.4 | 10.59 | 10.59 |
| Lab 16 | 9.98 | 9.67 | 8.64 | 9.11 | 9.13 | 11.9 | 11 | 10.9 |
| Lab 17 | 11.09 | 11.01 | 11.12 | 11.31 | 11.44 | 11.38 | 11.09 | 11.13 |
| Lab 18 | 9.8 | 9.9 | 9.9 | 9.5 | 9.4 | 9.7 | 8.9 | 8.9 |
| Lab 19 | 24.38 | 19.95 | 16.44 | 16.71 | 12.18 | 11.28 | 10.36 | 10.55 |
| Lab 20 | 10.9 | 11.2 | 10.9 | 10.8 | 10.7 | 10.4 | 10.5 | 10.5 |
| Lab 21 | 15.51 | 16.21 | DNS | DNS | DNS | 15.81 | 15.91 | 16.81 |
| Lab 22 | 11.28 | 10.93 | 9.46 | 9.22 | 13.05 | 12.68 | 11.12 | 11.06 |

| Barium (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 2 | 120.53 | 120.67 | 114.06 | 124.13 | 116.14 | 102.47 | 100.82 | 102.45 |
| Lab 3 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 4 | 118.8 | 122.4 | 117.6 | 118 | 116.6 | 97.5 | 98.1 | 99.4 |
| Lab 5 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 6 | 112.89 | 111.59 | 110.85 | 111.15 | 109.71 | 93.64 | 92.86 | 91.83 |
| Lab 7 | 110 | 110 | 110 | 110 | 110 | 99 | 97 | 99 |
| Lab 8 | 118 | 120 | 121 | 120 | 121 | 102 | 101 | 101 |
| Lab 9 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 10 | 118 | 122 | 123 | 119 | DNS | 102 | 103 | DNS |
| Lab 11 | 114.6 | 115.1 | 114 | 113.3 | 114.25 | 95.1 | 95.6 | 95.4 |
| Lab 12 | 127.75 | 126 | 129.23 | 128.61 | 127.34 | 107.11 | 107.32 | 106.62 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 133.6 | 135.5 | 134.2 | 134.5 | 137.4 | 109 | 108.7 | 106.6 |
| Lab 15 | 121.24 | 122.23 | 122.23 | 122.22 | 122.22 | 99.2 | 99.19 | 99.17 |
| Lab 16 | 114 | 114 | 115 | 115 | 116 | 95.4 | 92.8 | 94.3 |
| Lab 17 | 131.2 | 131.9 | 129.7 | 133.6 | 131.4 | 111.8 | 108.7 | 108.7 |
| Lab 18 | 116 | 114.7 | 114.5 | 116.1 | 116.3 | 95.2 | 95.4 | 96.2 |
| Lab 19 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 20 | 124 | 126 | 126 | 125 | 123 | 100 | 98.8 | 99 |
| Lab 21 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 22 | 109.38 | 110.03 | 108.96 | 109.73 | 109.75 | 91.91 | 90.03 | 90.65 |

| Boron (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 2 | 910.27 | 950.38 | 933.38 | 964.73 | 972.18 | 1015.82 | 1086.84 | 1146.01 |
| Lab 3 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 4 | 893.3 | 974 | 878.4 | 929.7 | 890.6 | 1078.6 | 1090.8 | 1148.4 |
| Lab 5 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 6 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 7 | 1100 | 1000 | 1000 | 1000 | 1000 | 1200 | 1200 | 1200 |
| Lab 8 | 1020 | 1030 | 1020 | 1030 | 1010 | 1140 | 1130 | 1100 |
| Lab 9 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 10 | 970 | 1010 | 954 | 963 | DNS | 1130 | 1150 | DNS |
| Lab 11 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 12 | 715.45 | 678.34 | 935.52 | 859.96 | 914.85 | 921.58 | 999.09 | 1107.64 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 783 | 811 | 822 | 787 | 797 | 901 | 958 | 1005 |
| Lab 15 | 1003.74 | 1002.88 | 992.14 | 996.27 | 1008.44 | 1131.97 | 1132.93 | 1132.21 |
| Lab 16 | 888 | 914 | 920 | 915 | 927 | 1100 | 1100 | 1100 |
| Lab 17 | 997.4 | 1006 | 987.6 | 1021 | 997.8 | >1000 | >1000 | >1000 |
| Lab 18 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 19 | 1245.5 | 1296.56 | 1313.37 | 1358.12 | 1402.6 | 1554.7 | 1560.7 | 1586.03 |
| Lab 20 | 822 | 837 | 849 | 812 | 833 | 1130 | 1160 | 1100 |
| Lab 21 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 22 | 1002.9 | 989.8 | 989.07 | 1002.6 | 995.33 | 1114.2 | 1115.4 | 1112.1 |

| Cadmium (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|-----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 5.05 | 4.73 | 4.95 | 4.93 | 5.01 | 5.03 | 4.89 | 5 |
| Lab 2 | 5.02 | 4.97 | 4.84 | 4.96 | 4.94 | 4.92 | 5 | 4.97 |
| Lab 3 | 6.09 | 5.96 | 6.06 | 6.06 | 6.14 | 5.72 | 5.89 | 5.96 |
| Lab 4 | 4.89 | 5.09 | 4.86 | 4.89 | 4.82 | 4.88 | 4.89 | 4.91 |
| Lab 5 | 6.01 | 5.65 | 6 | 5.58 | 6.31 | 6.52 | 5.87 | 6.12 |
| Lab 6 | 4.43 | 4.32 | 4.4 | 4.44 | 4.41 | 4.5 | 4.51 | 4.53 |
| Lab 7 | 4.7 | 4.8 | 4.7 | 4.8 | 4.8 | 4.4 | 4.4 | 4.4 |
| Lab 8 | 4.79 | 4.9 | 4.97 | 4.9 | 4.9 | 5.08 | 5 | 4.96 |
| Lab 9 | 4.34 | 4.33 | 4.12 | 4.11 | 4.17 | 4.42 | 4.36 | 4.36 |
| Lab 10 | 4.64 | 4.77 | 4.81 | 4.56 | DNS | 4.85 | 4.92 | DNS |
| Lab 11 | 4.6 | 4.7 | 4.7 | 4.5 | 4.63 | 4.8 | 4.7 | 4.6 |
| Lab 12 | 5.09 | 5.22 | 5.55 | 5.19 | 4.95 | 5.09 | 5.02 | 5.51 |
| Lab 13 | 4.17 | 4.45 | 4.29 | 4.27 | 4.24 | 4.44 | 4.45 | 4.65 |
| Lab 14 | 5.04 | 5.05 | 5.1 | 5.17 | 5.13 | 4.978 | 4.98 | 4.963 |
| Lab 15 | 4.74 | 4.92 | 4.84 | 4.89 | 4.85 | 4.89 | 4.88 | 4.92 |
| Lab 16 | 4.47 | 4.3 | 4.28 | 4.33 | 4.31 | 4.66 | 4.67 | 4.56 |
| Lab 17 | 4.7 | 4.77 | 4.7 | 4.73 | 4.79 | 4.81 | 4.84 | 4.75 |
| Lab 18 | 4.6 | 4.6 | 4.6 | 4.5 | 4.6 | 4.5 | 4.6 | 4.6 |
| Lab 19 | 3.69 | 3.69 | 3.69 | 3.46 | 3.43 | 3.39 | 4.41 | 3.34 |
| Lab 20 | 5.05 | 5.25 | 5.05 | 5 | 4.94 | 5.13 | 5.04 | 5.09 |
| Lab 21 | 5.01 | 4.01 | DNS | DNS | DNS | 5.01 | 5.01 | 4.01 |
| Lab 22 | 4.86 | 4.78 | 4.59 | 4.5 | 4.48 | 5.49 | 4.56 | 4.51 |

| Copper (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 2110 | 2100 | 2110 | 2110 | 2120 | 1930 | 1920 | 1900 |
| Lab 2 | 1740.28 | 1761.79 | 1703.21 | 1818.68 | 1842.49 | 1651.03 | 1667.08 | 1743.13 |
| Lab 3 | 1955 | 1955 | 1966 | 1974 | 1972 | 1816 | 1804 | 1824 |
| Lab 4 | 1853 | 1866 | 1940.5 | 1845.5 | 1870 | 1709 | 1756 | 1698.5 |
| Lab 5 | 2100 | 2090 | 2090 | 2090 | 2050 | 1910 | 1920 | 1920 |
| Lab 6 | 1930.78 | 1946.14 | 1946.68 | 1979.26 | 1919.25 | 1740.41 | 1725.26 | 1748.39 |
| Lab 7 | 2000 | 2000 | 2000 | DNS | DNS | 1800 | 1800 | 1800 |
| Lab 8 | 2000 | 2005 | 2010 | 2015 | 2005 | 1835 | 1845 | 1845 |
| Lab 9 | 1991.5 | 2073.5 | 2011 | 2051.5 | 2026 | 1868.5 | 1846.5 | DNS |
| Lab 10 | 1910 | 1940 | 2000 | 1940 | DNS | 1810 | 1820 | DNS |
| Lab 11 | 1902 | 1911 | 1894 | 1897 | 1901 | 1752 | 1741 | 1743 |
| Lab 12 | 2034.43 | 2044.11 | 2053.03 | 2047.71 | 2035.3 | 1904.67 | 1880.28 | 1878.51 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 1918 | 1678 | 1662 | 1694 | 1689 | 1554 | 1537 | 1583 |
| Lab 15 | 1976.31 | 1970.47 | 1971.99 | 1971.39 | 1969.35 | 1795.63 | 1795.81 | 1791.93 |
| Lab 16 | 1780 | 1790 | 1790 | 1810 | 1740 | 1750 | 1760 | 1780 |
| Lab 17 | >1000 | >1000 | >1000 | >1000 | >1000 | >1000 | >1000 | >1000 |
| Lab 18 | 1935 | 1931 | 1932 | 1820 | 1815 | 1760 | 1758 | 1755 |
| Lab 19 | 1980.15 | 1973.86 | 1988.91 | 1973.69 | 1969.6 | 1822.2 | 1821.57 | 1826.62 |
| Lab 20 | 1990 | 2050 | 2190 | 2050 | 2070 | 1910 | 1950 | 1930 |
| Lab 21 | 2053 | 2092 | DNS | DNS | DNS | 1865.01 | 1861.01 | 1878.01 |
| Lab 22 | 1806.2 | 1798.8 | 1790.7 | 1797.1 | 1801.2 | 1635 | 1627.5 | 1633.6 |

| Chromium (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 38.57 | 39.79 | 39.71 | 39.92 | 40.93 | 42.32 | 42.98 | 43.08 |
| Lab 2 | 43.7 | 46.29 | 46.41 | 44.06 | 43.97 | 50.76 | 50 | 48.17 |
| Lab 3 | 55.88 | 52.43 | 53.22 | 54.83 | 55.25 | 62.56 | 61.51 | 60.02 |
| Lab 4 | 47.75 | 51.68 | 47.67 | 49.1 | 47.87 | 53.51 | 53.24 | 55 |
| Lab 5 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 6 | 47.45 | 47.33 | 46.22 | 46.54 | 46.32 | 52.64 | 51.63 | 51.85 |
| Lab 7 | 48 | 49 | 48 | 49 | 50 | 50 | 50 | 49 |
| Lab 8 | 49.4 | 50.2 | 50 | 49.6 | 49.8 | 56.3 | 55.1 | 54.8 |
| Lab 9 | 41.05 | 41.91 | 47.77 | 43.33 | 44.39 | 52.09 | 52.93 | 51.24 |
| Lab 10 | 50.1 | 49.5 | 51.5 | 50.1 | DNS | 56.6 | 57.1 | DNS |
| Lab 11 | 46.1 | 46 | 46 | 46 | 46.03 | 50.1 | 51.2 | 50.4 |
| Lab 12 | 51.04 | 50.59 | 50.99 | 51.18 | 50.64 | 56.45 | 56.29 | 56.26 |
| Lab 13 | 52.25 | 50.71 | 50.62 | 50.53 | 49.79 | 58.92 | 56.8 | 58.68 |
| Lab 14 | 51 | 50.5 | 49.6 | 49.9 | 49.6 | 55.8 | 57.5 | 55.7 |
| Lab 15 | 46.4 | 47.66 | 48.13 | 49.23 | 48.93 | 52.78 | 54.01 | 54.42 |
| Lab 16 | 44.1 | 44.8 | 44.3 | 44.8 | 42.7 | 52.9 | 52.9 | 53.5 |
| Lab 17 | 47.38 | 47.53 | 47.84 | 47.76 | 47.6 | 54.77 | 54.26 | 54.07 |
| Lab 18 | 46.5 | 46.3 | 46.1 | 45.4 | 44.9 | 50.6 | 50.6 | 50.3 |
| Lab 19 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 20 | 42.9 | 43.9 | 43.2 | 42.9 | 43.6 | 52.7 | 53.1 | 53.2 |
| Lab 21 | <0.006 | <0.006 | DNS | DNS | DNS | <0.006 | <0.006 | <0.006 |
| Lab 22 | 42.4 | 41.91 | 41.53 | 42.13 | 41.94 | 49.52 | 47.89 | 46.61 |

| Iron (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 2 | 186.23 | 192.38 | 199.71 | 182.83 | 175.49 | 180.44 | 175.03 | 160.02 |
| Lab 3 | 212 | 214 | 205 | 220 | 223 | 199 | 194 | 200 |
| Lab 4 | 198.8 | 216.6 | 195.6 | 208.2 | 192.7 | 184.8 | 186.9 | 199.8 |
| Lab 5 | 197 | 204 | 195 | 203 | 202 | 180 | 179 | 180 |
| Lab 6 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 7 | 200 | 200 | 200 | 200 | 200 | 170 | 170 | 170 |
| Lab 8 | 206 | 212 | 213 | 209 | 210 | 199 | 196 | 197 |
| Lab 9 | 192.9 | 195.3 | 190.3 | 196.9 | 190.1 | 183.4 | 187.5 | 180.2 |
| Lab 10 | 205 | 203 | 215 | 207 | DNS | 190 | 195 | DNS |
| Lab 11 | 224.7 | 226.3 | 224.6 | 226.5 | 225.53 | 207.5 | 208.4 | 206 |
| Lab 12 | 199.9 | 197.91 | 201.57 | 199.32 | 199.78 | 170.44 | 170.43 | 170.69 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 198.5 | 209.1 | 210.6 | 205.7 | 208.3 | 183.3 | 186.4 | 189.8 |
| Lab 15 | 207.67 | 207.69 | 208.75 | 211.85 | 209.82 | 174.83 | 176.96 | 178.09 |
| Lab 16 | 201 | 204 | 201 | 200 | 197 | 205 | 192 | 193 |
| Lab 17 | 206.8 | 196.9 | 202.3 | 196.2 | 196.7 | 190.8 | 185.3 | 192.2 |
| Lab 18 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 19 | 196.05 | 212.96 | 207.32 | 206.33 | 199.03 | 190.08 | 190.08 | 195.38 |
| Lab 20 | 220 | 220 | 210 | 210 | 210 | 160 | 160 | 160 |
| Lab 21 | 163.01 | 174.01 | DNS | DNS | DNS | 140.01 | 144.01 | 144.01 |
| Lab 22 | 183.63 | 183.57 | 182.86 | 182.33 | 181.75 | 168.79 | 166.86 | 167.17 |

| Lead (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|--------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 24.81 | 24.95 | 22 | 25.26 | 25.19 | 28.13 | 27.92 | 27.1 |
| Lab 2 | 23.32 | 23.96 | 23.61 | 23.23 | 22.84 | 25.26 | 24.92 | 24.67 |
| Lab 3 | 28.52 | 28.32 | 27.82 | 28.09 | 28.27 | 29.3 | 29.25 | 30.4 |
| Lab 4 | 22.56 | 23.63 | 22.78 | 23.01 | 22.63 | 24.88 | 26.19 | 26.4 |
| Lab 5 | 25.1 | 27.8 | 26.5 | 27.3 | 27.5 | 27 | 27.1 | 30 |
| Lab 6 | 22.99 | 23.2 | 23.32 | 23.33 | 23.56 | 24.7 | 25.2 | 25.43 |
| Lab 7 | 25 | 25 | 25 | DNS | DNS | 27 | 27 | 27 |
| Lab 8 | 24.3 | 24.8 | 24.7 | 24.6 | 24.6 | 27 | 26.8 | 26.8 |
| Lab 9 | 36.44 | 40.59 | 42.94 | 42.54 | 42.37 | 35.08 | 44.6 | 43.6 |
| Lab 10 | 25.1 | 25.8 | 26 | 25.1 | DNS | 29 | 29.1 | DNS |
| Lab 11 | 32.8 | 24.7 | 27.2 | 29.2 | 28.48 | 33.5 | 31.1 | 33 |
| Lab 12 | < 30 | < 30 | < 30 | < 30 | < 30 | < 30 | < 30 | < 30 |
| Lab 13 | 21.46 | 21.32 | 22.48 | 21.89 | 23.19 | 18.31 | 16.9 | 22.23 |
| Lab 14 | 31.7 | 31.5 | 31.6 | 31.68 | 31.7 | 36.34 | 35.78 | 36.24 |
| Lab 15 | 23.28 | 23.93 | 24.13 | 24.26 | 24.2 | 25.98 | 26.18 | 25.86 |
| Lab 16 | 23.3 | 23.2 | 23 | 23.3 | 23.4 | 25.4 | 24.5 | 25.1 |
| Lab 17 | 23.57 | 23.76 | 23.84 | 24.07 | 24.03 | 26.12 | 26.1 | 25.83 |
| Lab 18 | 25.2 | 24.4 | 23.7 | 24.6 | 25 | 26.6 | 26.1 | 26.7 |
| Lab 19 | 13.96 | 13.18 | 13.94 | 15.56 | 14.06 | 12.13 | 12.42 | 14.37 |
| Lab 20 | 24.3 | 24.9 | 24.7 | 24.7 | 24.5 | 26.3 | 26.5 | 26.9 |
| Lab 21 | 80.01 | 58.01 | DNS | DNS | DNS | 52.01 | 56.01 | 65.01 |
| Lab 22 | 29.17 | 30.4 | 27.84 | 30.46 | 28.52 | 29.48 | 28.6 | 29.27 |

| Manganese (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|-------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 47.48 | 48.05 | 47.21 | 49.1 | 48.63 | 47.6 | 46.66 | 46.07 |
| Lab 2 | 44.49 | 46.88 | 47.26 | 43.59 | 43.81 | 47.56 | 46.88 | 43.6 |
| Lab 3 | 32 | 32 | 30 | 30 | 31 | 39 | 33 | 33 |
| Lab 4 | 48.13 | 50.59 | 47.57 | 50.08 | 47.07 | 49.26 | 49.42 | 52.01 |
| Lab 5 | 47.41 | 47.11 | 48.11 | 49.21 | 47.71 | 50.11 | 49.51 | 49.41 |
| Lab 6 | 46.6 | 46.51 | 46 | 46.28 | 45.6 | 48.46 | 47.6 | 47.95 |
| Lab 7 | 47 | 47 | 47 | 47 | 47 | 47 | 47 | 47 |
| Lab 8 | 49 | 49.8 | 49.9 | 49.4 | 49.6 | 51.7 | 51.2 | 51 |
| Lab 9 | 57.9 | 58.5 | 59.3 | 57.6 | 58.6 | 61.9 | 61.6 | 62.5 |
| Lab 10 | 48.9 | 48.5 | 50.7 | 49.7 | DNS | 51.7 | 52.4 | DNS |
| Lab 11 | 44.7 | 44.3 | 43.4 | 44.1 | 44.13 | 45.1 | 45 | 45.3 |
| Lab 12 | 44.71 | 44.14 | 44.52 | 44.21 | 44 | 46.13 | 46.02 | 45.57 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 43.6 | 44.6 | 43.4 | 43.41 | 43.9 | 45.35 | 45.72 | 46.74 |
| Lab 15 | 49.63 | 49.68 | 49.78 | 49.83 | 49.88 | 49.58 | 50.75 | 49.93 |
| Lab 16 | 42.9 | 44.1 | 43.8 | 43.8 | 42.2 | 50.2 | 48.2 | 48.7 |
| Lab 17 | 45.15 | 45.57 | 45.53 | 45.86 | 45.63 | 48.02 | 47.56 | 47.41 |
| Lab 18 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 19 | 48.8 | 57.73 | 44.5 | 43.11 | 56.03 | 41.46 | 49.4 | 56.49 |
| Lab 20 | 48 | 48 | 48 | 48 | 48 | 49 | 49 | 49 |
| Lab 21 | 38.01 | 36.01 | DNS | DNS | DNS | 39.01 | 39.01 | 39.01 |
| Lab 22 | 44.72 | 44.47 | 44.16 | 44.63 | 44.3 | 46.08 | 44.77 | 45.37 |

| Nickel (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 19.97 | 18.79 | 18.83 | 21.69 | 18.59 | 15.84 | 16.49 | 16.03 |
| Lab 2 | 19.49 | 20.22 | 20.18 | 19.29 | 19.07 | 16.75 | 17.06 | 16.29 |
| Lab 3 | 26.55 | 26.75 | 24.8 | 25.44 | 25.65 | 18.87 | 18.74 | 21.26 |
| Lab 4 | 19.34 | 20.18 | 19.36 | 19.41 | 18.55 | 16.56 | 16.28 | 16.22 |
| Lab 5 | 19.6 | 19.6 | 19.5 | 19.5 | 19.9 | 16.7 | 16.9 | 16.7 |
| Lab 6 | 15.48 | 15.68 | 15.56 | 15.37 | 15.04 | 12.89 | 12.57 | 12.2 |
| Lab 7 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 8 | 19.7 | 20 | 19.9 | 19.6 | 19.8 | 17.2 | 16.9 | 16.9 |
| Lab 9 | 43.2 | 43.73 | 42.77 | 43.32 | 43.28 | 33.95 | 35.86 | 35.92 |
| Lab 10 | 19.4 | 19.6 | 19.6 | 19.2 | DNS | 16.8 | 16.8 | DNS |
| Lab 11 | 20.2 | 19.9 | 19.1 | 19.6 | 19.7 | 18 | 17.8 | 15.3 |
| Lab 12 | 16.05 | 16.02 | 16.37 | 18.04 | 16.37 | 13.93 | 14.01 | 17.06 |
| Lab 13 | 17.36 | 16.65 | 16.89 | 16.77 | 16.81 | 15.17 | 14.84 | 14.2 |
| Lab 14 | 17.4 | 17.6 | 17.1 | 17.3 | 17.2 | 14.9 | 14.99 | 15.42 |
| Lab 15 | 20.22 | 20.66 | 20.92 | 21.37 | 21.27 | 19.18 | 18.18 | 18.52 |
| Lab 16 | 18 | 18.5 | 18.4 | 18.6 | 18.6 | 16.9 | 17 | 17 |
| Lab 17 | 19.86 | 19.86 | 19.91 | 19.89 | 20.11 | 18.3 | 17.89 | 17.81 |
| Lab 18 | 19.2 | 18.6 | 19.4 | 19.2 | 18.2 | 16.2 | 16.1 | 16.2 |
| Lab 19 | 20.53 | 16.47 | 12.59 | 16.88 | 17.52 | 20.77 | 18.01 | 19.17 |
| Lab 20 | 19.4 | 20.2 | 19.7 | 20.1 | 20.3 | 20 | 20 | 20.3 |
| Lab 21 | 37.01 | 35.01 | DNS | DNS | DNS | 30.01 | 28.01 | 36.01 |
| Lab 22 | 18.48 | 18.24 | 18.86 | 18.73 | 18.5 | 16.49 | 16.15 | 15.43 |

| Selenium (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 2 | 10.58 | 11.1 | 10.69 | 10.72 | 11.12 | 9.63 | 9.87 | 9.66 |
| Lab 3 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 4 | 11.14 | 12.16 | 11.14 | 11.64 | 10.69 | 11.2 | 10.79 | 11.02 |
| Lab 5 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 6 | 10.27 | 11.47 | 10.73 | 10.34 | 10.93 | 10.32 | 10.33 | 10.79 |
| Lab 7 | 9.3 | 9 | 9.5 | 9.6 | 9.3 | 9.5 | 9.2 | 9.4 |
| Lab 8 | 12 | 11.8 | 11.9 | 12.1 | 12 | 11.3 | 10.5 | 10.9 |
| Lab 9 | 12.21 | 14.48 | 13.31 | 11.26 | 11.31 | 12.1 | 11.11 | 13.69 |
| Lab 10 | 10.2 | 9.73 | 10.1 | 10.4 | DNS | 10.4 | 9.77 | DNS |
| Lab 11 | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 |
| Lab 12 | < 50 | < 50 | < 50 | < 50 | < 50 | < 50 | < 50 | < 50 |
| Lab 13 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 14 | 10.43 | 10.6 | 10.58 | 10.58 | 10.28 | 10.53 | 10.61 | 10.54 |
| Lab 15 | 10.7 | 10.75 | 10.72 | 11.3 | 10.83 | 10.32 | 10.92 | 10.68 |
| Lab 16 | 8.49 | 9.08 | 8.86 | 8.98 | 8.82 | 9.55 | 9.35 | 10.3 |
| Lab 17 | 9.56 | 9.76 | 9.4 | 9.83 | 10.09 | 9.34 | 8.84 | 8.83 |
| Lab 18 | 10.9 | 10.6 | 10.8 | 9.9 | 9.6 | 8.9 | 9.4 | 9.7 |
| Lab 19 | 5.35 | 6.2 | 5.32 | 9.45 | 7.23 | 11.41 | 12.87 | 11.45 |
| Lab 20 | 10.5 | 11.2 | 10.7 | 10.7 | 10.4 | 10.4 | 10.1 | 10 |
| Lab 21 | 11.31 | 11.41 | DNS | DNS | DNS | 12.01 | 11.71 | DNS |
| Lab 22 | 12.61 | 9.47 | 10.74 | 8.78 | 8.49 | 13.73 | 8.77 | 9.6 |

| Zinc (µg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|-------------|----------|----------|----------|----------|----------|-------------|-------------|-------------|
| Lab 1 | 623 | 622 | 628 | 632 | 627 | 662 | 659 | 671 |
| Lab 2 | 554.84 | 547.91 | 541.82 | 549.54 | 574.75 | 597.03 | 608.29 | 619.04 |
| Lab 3 | 606 | 608 | 612 | 621 | 624 | 661 | 673 | 675 |
| Lab 4 | 598 | 595.2 | 602.2 | 583.4 | 597.2 | 685.6 | 659 | 637.8 |
| Lab 5 | 637 | 633 | 634 | 641 | 634 | 693 | 708 | 690 |
| Lab 6 | 571.36 | 572.97 | 561.95 | 564.99 | 571.15 | 614.13 | 604.85 | 614.61 |
| Lab 7 | 600 | 610 | 600 | 600 | 610 | 620 | 620 | 620 |
| Lab 8 | 603 | 611 | 612 | 608 | 610 | 665 | 649 | 653 |
| Lab 9 | 544.8 | 544.6 | 545.8 | 549 | 544.8 | 602 | 593 | 601.2 |
| Lab 10 | 575 | 584 | 591 | 578 | DNS | 629 | 641 | DNS |
| Lab 11 | 593.6 | 587 | 580.2 | 589.8 | 587.65 | 636 | 637.6 | 636.5 |
| Lab 12 | 638.65 | 635.73 | 639.25 | 638.72 | 636.71 | 686.39 | 683.76 | 682.38 |
| Lab 13 | 583.8 | 585.9 | 582.3 | 583.7 | 584.2 | 608.3 | 608.1 | 608.8 |
| Lab 14 | 568.3 | 527.9 | 519.5 | 525.1 | 525 | 556.8 | 549.6 | 562.3 |
| Lab 15 | 591.81 | 592.31 | 591.24 | 591.94 | 590.78 | 627.11 | 628.16 | 626.29 |
| Lab 16 | 547 | 557 | 552 | 564 | 537 | 633 | 634 | 648 |
| Lab 17 | 576.1 | 584 | 575.2 | 589.3 | 587.3 | 640.7 | 632.7 | 620.3 |
| Lab 18 | 571.5 | 568.9 | 563.2 | 546.9 | 546.6 | 605.4 | 605.7 | 600.2 |
| Lab 19 | 607.76 | 608.6 | 608.6 | 600.19 | 601.45 | 648.57 | 646.05 | 643.95 |
| Lab 20 | 577 | 613 | 610 | 608 | 596 | 629 | 628 | 630 |
| Lab 21 | 572.01 | 573.01 | DNS | DNS | DNS | 624.01 | 622.01 | 622.01 |
| Lab 22 | 561.25 | 561.11 | 559.14 | 562.71 | 558.95 | 599.11 | 597.33 | 595.88 |

| Sodium (mg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 41.21 | 41.7 | 41.53 | 41.64 | 41.73 | 40.66 | 40.48 | 40.66 |
| Lab 2 | 40.34 | 41.29 | 41.1 | 39.76 | 39.99 | 39.35 | 39.39 | 40.16 |
| Lab 3 | 41.9 | 41.7 | 41.5 | 41.9 | 41.4 | 41.2 | 40.8 | 40.8 |
| Lab 4 | 39.96 | 43.11 | 38.68 | 40.23 | 37.14 | 39.41 | 37.54 | 39.22 |
| Lab 5 | 39.96 | 43.67 | 40.38 | 40.15 | 39.7 | 39.3 | 39.85 | 39.77 |
| Lab 6 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 7 | 40 | 40 | 40 | 40 | 40 | 40 | 39 | 39 |
| Lab 8 | 39.85 | 40.15 | 40.3 | 40.65 | 40.9 | 38.95 | 39.4 | 39.8 |
| Lab 9 | 51.52 | 51.75 | 51.06 | 51.06 | 51.29 | 50.6 | 50.6 | 50.6 |
| Lab 10 | 41.6 | 41.2 | 41.4 | 42.7 | DNS | 40.4 | 40.5 | DNS |
| Lab 11 | 36.73 | 36.33 | 35.87 | 36.97 | 36.48 | 35.51 | 36.04 | 36.18 |
| Lab 12 | 41.75 | 41.71 | 41.58 | 41.43 | 41.19 | 40.75 | 40.64 | 40.25 |
| Lab 13 | 38.37 | 38.44 | 38.39 | 38.43 | 38.43 | 37.06 | 37.25 | 37.33 |
| Lab 14 | 34.6 | 37.1 | 36.4 | 34.8 | 35.4 | 37 | 36.4 | 36.9 |
| Lab 15 | 41.46 | 41.26 | 41.3 | 41.2 | 41.12 | 40.44 | 40.5 | 40.39 |
| Lab 16 | 35.2 | 36.2 | 35.9 | 36.4 | 34.9 | 37.6 | 37.4 | 38 |
| Lab 17 | 38.24 | 38.14 | 38.69 | 37.6 | 38.8 | 37.34 | 37.91 | 38.32 |
| Lab 18 | 38.78 | 39.09 | 39.04 | DNS | DNS | 38.21 | 38.11 | 38.28 |
| Lab 19 | 41.1 | 41.55 | 41.22 | 40.82 | 40.92 | 40.4 | 40.65 | 40.55 |
| Lab 20 | 39.3 | 38.8 | 38.6 | 38.4 | 38.5 | 38.2 | 38.2 | 38.4 |
| Lab 21 | 37.21 | 37.21 | DNS | DNS | DNS | 35.88 | 36.21 | 36.52 |
| Lab 22 | 42.32 | 39.63 | 40.06 | 42.13 | 40.56 | 41.09 | 41.96 | 39.97 |

| Calcium (mg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|-----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 89.13 | 87.61 | 87 | 87.77 | 88.36 | 102.41 | 99.25 | 101.2 |
| Lab 2 | 87.46 | 89.25 | 88.34 | 85.82 | 86.1 | 96.76 | 94.61 | 97.51 |
| Lab 3 | 88.06 | 89.14 | 90.29 | 90.55 | 90.17 | 98.94 | 100.93 | 99.56 |
| Lab 4 | 90.2 | 94.2 | 90 | 92.3 | 89.1 | 99.1 | 98.9 | 102.2 |
| Lab 5 | 87.53 | 86.16 | 87.74 | 88.09 | 86.25 | 97.35 | 99.78 | 99.27 |
| Lab 6 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 7 | 93 | 93 | 93 | 93 | 89 | 99 | 98 | 99 |
| Lab 8 | 88 | 88.5 | 88.5 | 88.5 | 88.5 | 97.5 | 98 | 98.5 |
| Lab 9 | 89.5 | 89.5 | 89.5 | 88 | 91 | 98.5 | 99.5 | 98.5 |
| Lab 10 | 91.4 | 90.5 | 90.6 | 94.9 | DNS | 101 | 100 | DNS |
| Lab 11 | 82.36 | 82.01 | 80.9 | 82.24 | 81.88 | 91.01 | 91.96 | 92.23 |
| Lab 12 | 89.51 | 89.57 | 89.66 | 89.5 | 89.85 | 99.7 | 99.46 | 100.01 |
| Lab 13 | 87.19 | 87.08 | 88.03 | 87.06 | 87.06 | 94.73 | 95.69 | 95.23 |
| Lab 14 | 93.8 | 90.6 | 93.1 | 95.5 | 92.5 | 103.5 | 106.9 | 111.5 |
| Lab 15 | 94.42 | 94.31 | 94.45 | 94.59 | 94.65 | 104.02 | 104.09 | 103.94 |
| Lab 16 | 75.6 | 77.3 | 76.3 | 76.7 | 76.5 | 90.7 | 89.4 | 89.5 |
| Lab 17 | 84.48 | 84.15 | 85.1 | 83.51 | 85.13 | 94.53 | 94.66 | 95.07 |
| Lab 18 | 88.64 | 89.42 | 89.48 | DNS | DNS | 100.1 | 99.83 | 100.1 |
| Lab 19 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 20 | 98.7 | 98.5 | 98 | 98 | 98.2 | 110 | 110 | 110 |
| Lab 21 | 135.31 | 142.71 | DNS | DNS | DNS | 135.11 | 160.41 | 143.51 |
| Lab 22 | 82.5 | 82.9 | 83.95 | 85.25 | 90.55 | 94.15 | 93.45 | 99.95 |

| Potassium (mg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|------------------|----------|----------|----------|----------|----------|-------------|-------------|-------------|
| Lab 1 | 7.7 | 7.73 | 7.71 | 7.65 | 7.69 | 8.1 | 8.1 | 8.05 |
| Lab 2 | 7.05 | 7.23 | 7.17 | 6.95 | 6.98 | 7.5 | 7.32 | 7.6 |
| Lab 3 | 7.42 | 7.49 | 7.51 | 7.48 | 7.47 | 7.94 | 7.95 | 7.94 |
| Lab 4 | 7.63 | 7.87 | 7.31 | 7.86 | 7.46 | 8.01 | 7.87 | 7.95 |
| Lab 5 | 7.44 | 7.36 | 7.46 | 7.57 | 7.35 | 7.76 | 8.06 | 7.89 |
| Lab 6 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 7 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.8 | 7.7 | 7.9 |
| Lab 8 | 7.85 | 7.95 | 7.95 | 8.1 | 8.1 | 8.25 | 8.4 | 8.4 |
| Lab 9 | 10.53 | 10.53 | 10.53 | 10.53 | 10.53 | 11.31 | 11.31 | 11.31 |
| Lab 10 | 7.52 | 7.56 | 7.5 | 7.86 | DNS | 7.98 | 7.95 | DNS |
| Lab 11 | 7.72 | 7.66 | 7.51 | 7.51 | 7.6 | 8.05 | 8.24 | 8.09 |
| Lab 12 | 7.71 | 7.76 | 7.79 | 7.74 | 7.66 | 8.21 | 8.12 | 8.11 |
| Lab 13 | 7.06 | 7.14 | 7.1 | 7.06 | 7.04 | 7.73 | 7.43 | 7.45 |
| Lab 14 | 7.36 | 7.3 | 7.69 | 7.55 | 7.44 | 7.81 | 8.35 | 8.18 |
| Lab 15 | 7.61 | 7.63 | 7.61 | 7.63 | 7.63 | 7.97 | 7.98 | 7.92 |
| Lab 16 | 6.55 | 6.71 | 6.61 | 6.68 | 6.46 | 7.44 | 7.49 | 7.57 |
| Lab 17 | 6.96 | 6.87 | 6.99 | 6.75 | 6.99 | 7.42 | 7.44 | 7.48 |
| Lab 18 | 7.09 | 7.15 | 7.13 | DNS | DNS | 7.56 | 7.48 | 7.57 |
| Lab 19 | 8.49 | 8.05 | 8.68 | 8.41 | 8.34 | 8.52 | 8.54 | 8.63 |
| Lab 20 | 8.6 | 8.5 | 8.5 | 8.4 | 8.4 | 9 | 9 | 9.1 |
| Lab 21 | 6.57 | 7.09 | DNS | DNS | DNS | 6.57 | 7.19 | 7.47 |
| Lab 22 | 7.684 | 7.383 | 7.749 | 7.717 | 7.259 | 8.545 | 8.798 | 8.187 |

| Magnesium (mg/L) | Result 1 | Result 2 | Result 3 | Result 4 | Result 5 | QC Result 1 | QC Result 2 | QC Result 3 |
|-------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|--------------------|--------------------|--------------------|
| Lab 1 | 5.04 | 5.09 | 5.08 | 5.07 | 5.08 | 5.07 | 5.06 | 5.05 |
| Lab 2 | 5.06 | 5.13 | 5.1 | 4.98 | 4.99 | 4.96 | 4.87 | 5.01 |
| Lab 3 | 4.9 | 4.92 | 4.96 | 4.91 | 4.94 | 5.03 | 4.97 | 4.94 |
| Lab 4 | 5.09 | 5.18 | 4.82 | 5.02 | 4.7 | 4.87 | 4.66 | 4.87 |
| Lab 5 | 4.91 | 4.81 | 4.87 | 4.9 | 4.68 | 4.87 | 4.98 | 4.81 |
| Lab 6 | DNS | DNS | DNS | DNS | DNS | DNS | DNS | DNS |
| Lab 7 | 5.9 | 5.7 | 5.8 | 5.6 | 5 | 5.1 | 5.1 | 5.3 |
| Lab 8 | 4.895 | 4.91 | 4.89 | 4.925 | 4.925 | 4.835 | 4.835 | 4.84 |
| Lab 9 | 4.76 | 4.78 | 4.74 | 4.8 | 4.83 | 4.61 | 4.75 | 4.72 |
| Lab 10 | 5.3 | 5.31 | 5.26 | 5.46 | DNS | 5.21 | 5.19 | DNS |
| Lab 11 | 4.72 | 4.77 | 4.7 | 4.64 | 4.71 | 4.63 | 4.68 | 4.66 |
| Lab 12 | 5.03 | 5.04 | 5.01 | 5.01 | 5.02 | 4.95 | 4.93 | 4.92 |
| Lab 13 | 4.62 | 4.63 | 4.67 | 4.63 | 4.62 | 4.32 | 4.39 | 4.38 |
| Lab 14 | 4.4 | 4.6 | 4.7 | 4.5 | 4.5 | 2.9 | 4.7 | 4.6 |
| Lab 15 | 5.2 | 5.2 | 5.21 | 5.2 | 5.21 | 5.06 | 5.06 | 5.06 |
| Lab 16 | 4.58 | 4.68 | 4.59 | 4.68 | 4.51 | 4.89 | 4.9 | 4.94 |
| Lab 17 | 4.8 | 4.77 | 4.83 | 4.69 | 4.85 | 4.76 | 4.79 | 4.81 |
| Lab 18 | 4.57 | 4.76 | 4.73 | DNS | DNS | 4.55 | 4.54 | 4.56 |
| Lab 19 | 5.47 | 5.49 | 5.66 | 5.59 | 5.53 | 5.43 | 5.43 | 5.41 |
| Lab 20 | 5 | 4.97 | 4.93 | 4.93 | 4.92 | 4.85 | 4.86 | 4.86 |
| Lab 21 | 4.37 | 4.36 | DNS | DNS | DNS | 4.32 | 4.24 | 4.28 |
| Lab 22 | 5.08 | 5.084 | 5.106 | 5.109 | 5.095 | 5.029 | 5.016 | 4.977 |

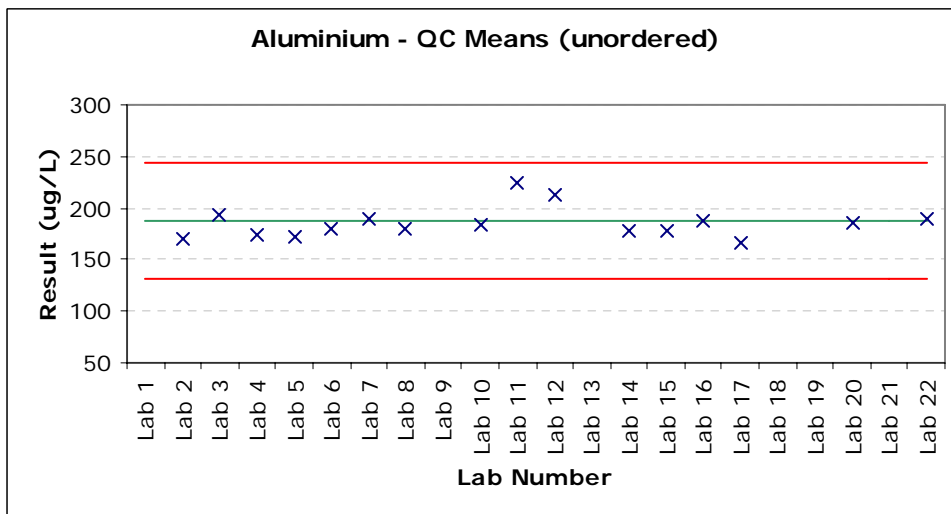
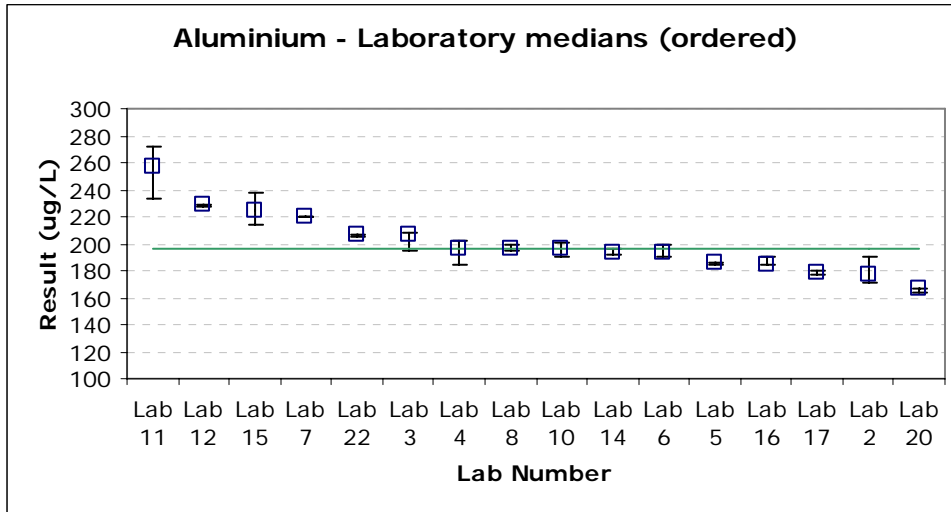
Appendix 6 – Processed Data and Charts

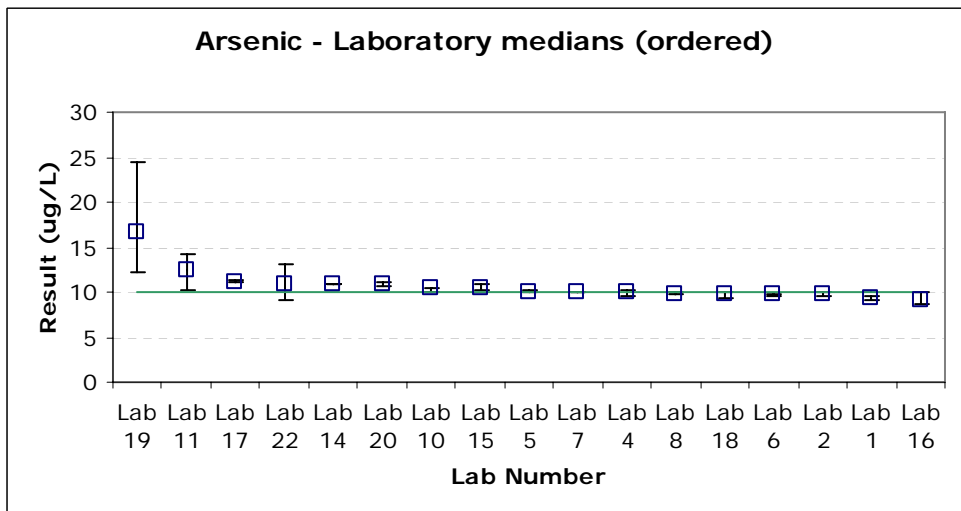
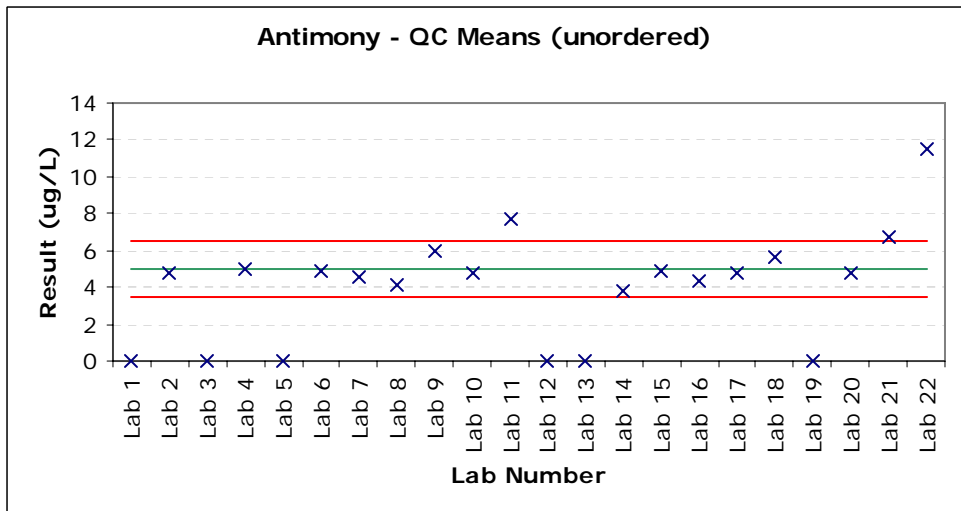
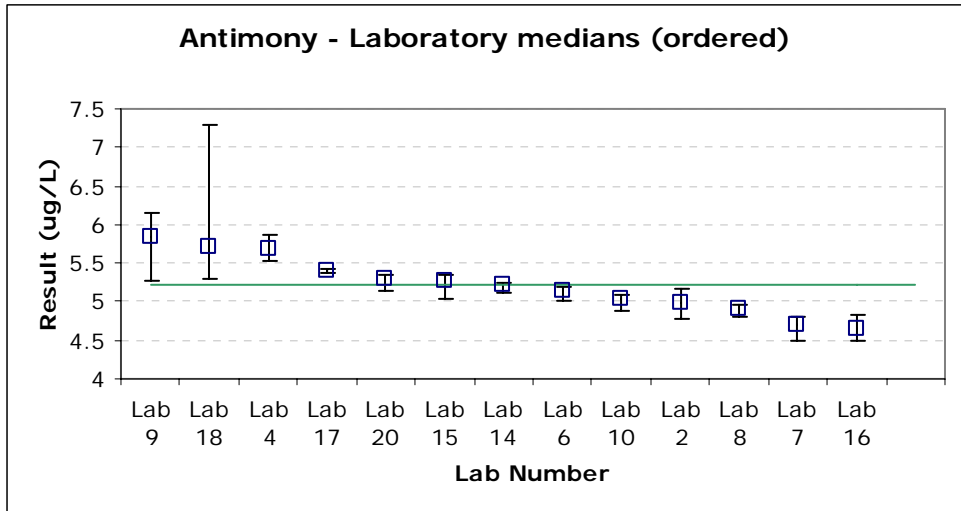
| Interlaboratory data | | | | | | | |
|----------------------|-------------------|------------|-------|-----------|----------------|--------------------------|---------|
| Element | Median of medians | u_{char} | u_h | u_{lfs} | $u_{combined}$ | Expanded Uncertainty (U) | U RSD % |
| Aluminium (µg/L) | 196.750 | 5.365 | 2.409 | 2.409 | 6.356 | 13.019 | 6.6 |
| Antimony (µg/L) | 5.23 | 0.129 | 0.029 | 0.029 | 0.135 | 0.290 | 5.5 |
| Arsenic (µg/L) | 10.100 | 0.167 | 0.138 | 0.138 | 0.257 | 0.516 | 5.1 |
| Barium (µg/L) | 120.000 | 2.399 | 0.500 | 0.500 | 2.501 | 5.302 | 4.4 |
| Boron (µg/L) | 950.380 | 29.413 | 4.162 | 4.162 | 29.996 | 66.836 | 7.0 |
| Cadmium (µg/L) | 4.765 | 0.089 | 0.040 | 0.040 | 0.106 | 0.214 | 4.5 |
| Copper (µg/L) | 1968.695 | 29.731 | 8.784 | 8.784 | 32.221 | 66.232 | 3.4 |
| Chromium (µg/L) | 47.600 | 1.066 | 0.660 | 0.660 | 1.417 | 2.847 | 6.0 |
| Iron (µg/L) | 201.500 | 3.077 | 1.351 | 1.351 | 3.622 | 7.386 | 3.7 |
| Lead (µg/L) | 24.600 | 0.577 | 0.096 | 0.096 | 0.593 | 1.250 | 5.1 |
| Manganese (µg/L) | 47.000 | 1.070 | 0.193 | 0.193 | 1.104 | 2.303 | 4.9 |
| Nickel (µg/L) | 19.360 | 0.315 | 0.233 | 0.233 | 0.456 | 0.912 | 4.7 |
| Selenium (µg/L) | 10.650 | 0.281 | 0.141 | 0.141 | 0.345 | 0.702 | 6.6 |
| Zinc (µg/L) | 585.825 | 8.874 | 2.251 | 2.251 | 9.428 | 19.379 | 3.3 |
| | | | | | | | |
| Calcium (mg/L) | 89.420 | 0.836 | 0.314 | 0.314 | 0.946 | 1.935 | 2.2 |
| Magnesium (mg/L) | 4.920 | 0.071 | 0.017 | 0.017 | 0.075 | 0.155 | 3.1 |
| Potassium (mg/L) | 7.510 | 0.091 | 0.038 | 0.038 | 0.106 | 0.216 | 2.9 |
| Sodium (mg/L) | 40.150 | 0.580 | 0.145 | 0.145 | 0.615 | 1.267 | 3.2 |

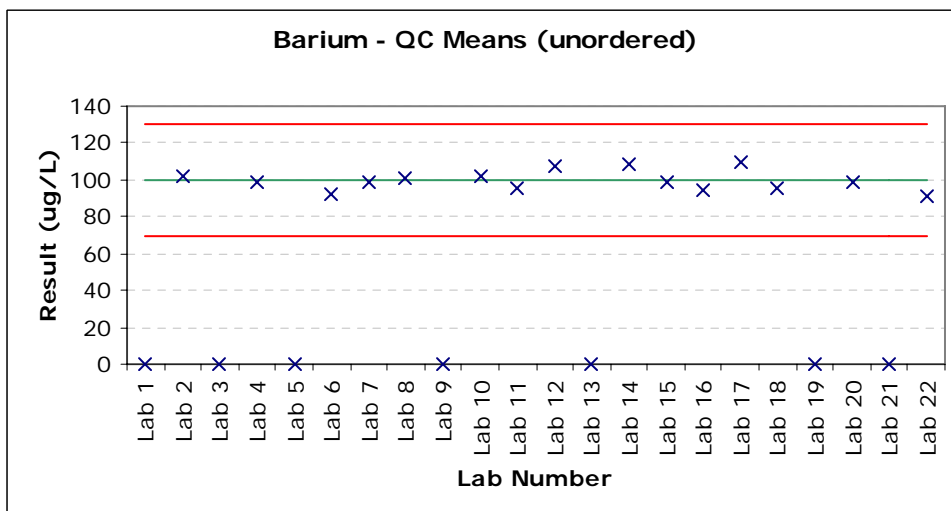
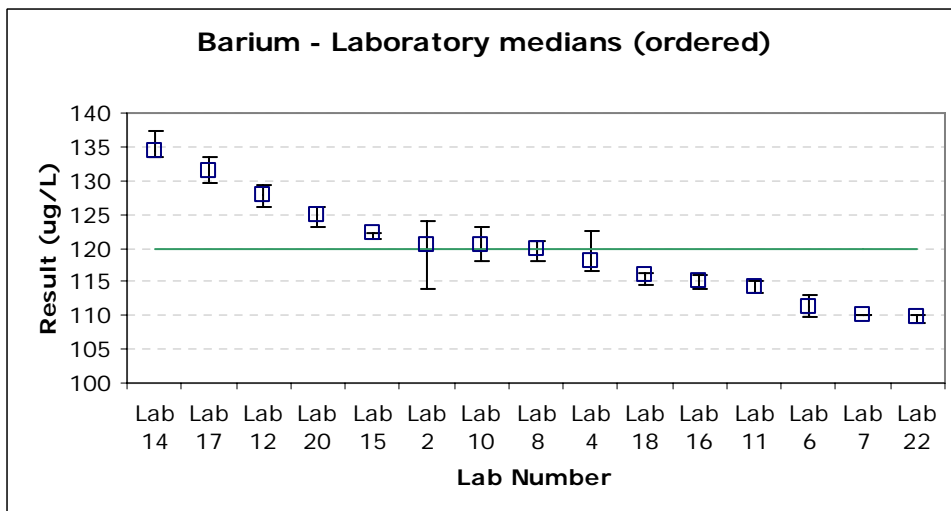
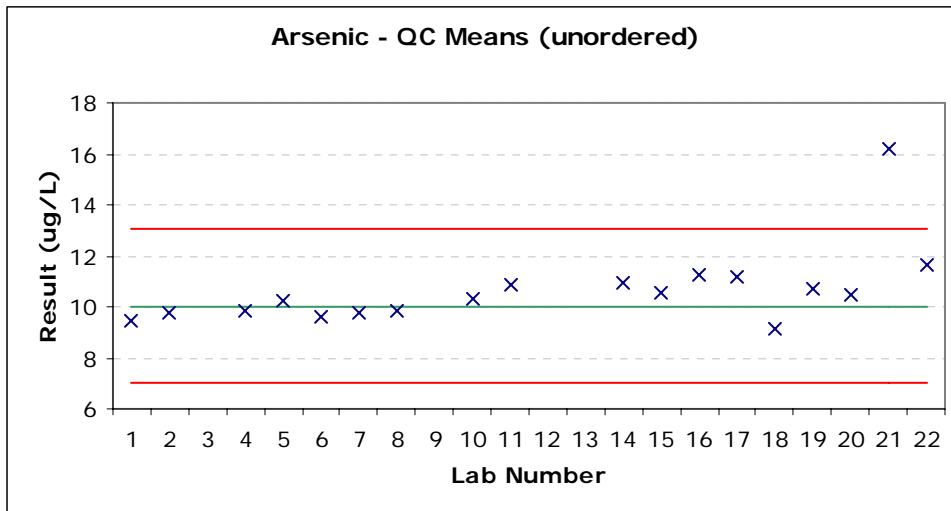
| IDMS Data | | | | | | | |
|--|---|--|--|---|----------------------------------|--|---|
| Element | Characterised Value | u_{char} | u_h | u_{lts} | $u_{combined}$ | Expanded Uncertainty (U) | % U RSD |
| Cadmium ($\mu\text{g/kg}$) | 4.93 | 0.08 | 0.04 | 0.04 | 0.10 | 0.23 | 4.6 |
| Iron ($\mu\text{g/kg}$) | 207.00 | 2.01 | 1.35 | 1.35 | 2.77 | 5.99 | 2.9 |
| Lead ($\mu\text{g/kg}$) | 24.67 | 0.15 | 0.10 | 0.10 | 0.20 | 0.44 | 1.8 |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| Element | Characterised Value ($\mu\text{g/L}$) | Combined uncertainty (ng/g) | Uncertainty in density (g/cm^3) | Overall uncertainty ($\mu\text{g/L}$) | k | Expanded Uncertainty ($\mu\text{g/L}$) | % U RSD ($\mu\text{g/L}$) |
| Cadmium | 4.94 | 0.10 | 0.00005 | 0.10 | 2.31 | 0.23 | 4.6 |
| Iron | 207.39 | 2.77 | 0.00005 | 2.78 | 2.16 | 6.00 | 2.9 |
| Lead | 24.72 | 0.20 | 0.00005 | 0.20 | 2.18 | 0.44 | 1.8 |
| | | | | | | | |
| Density (g/cm^3) | 0.99813 | | | | | | |

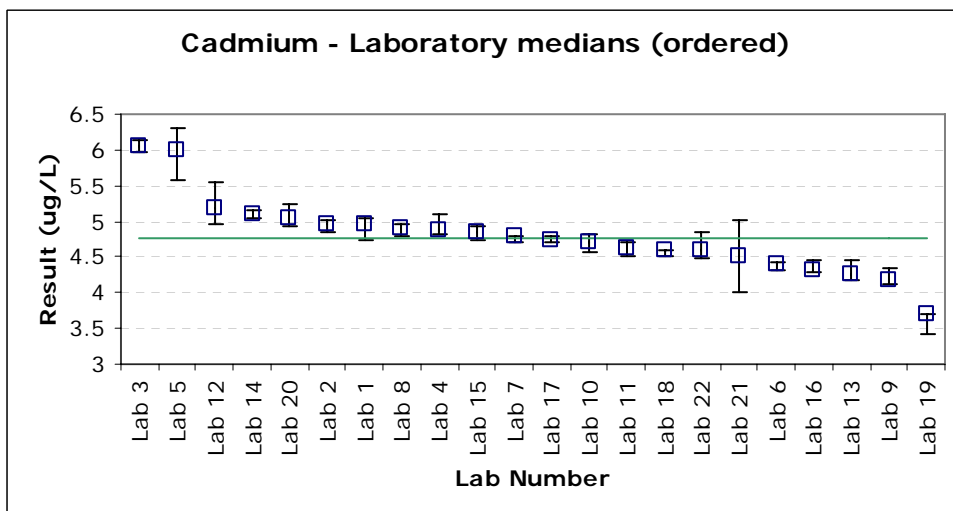
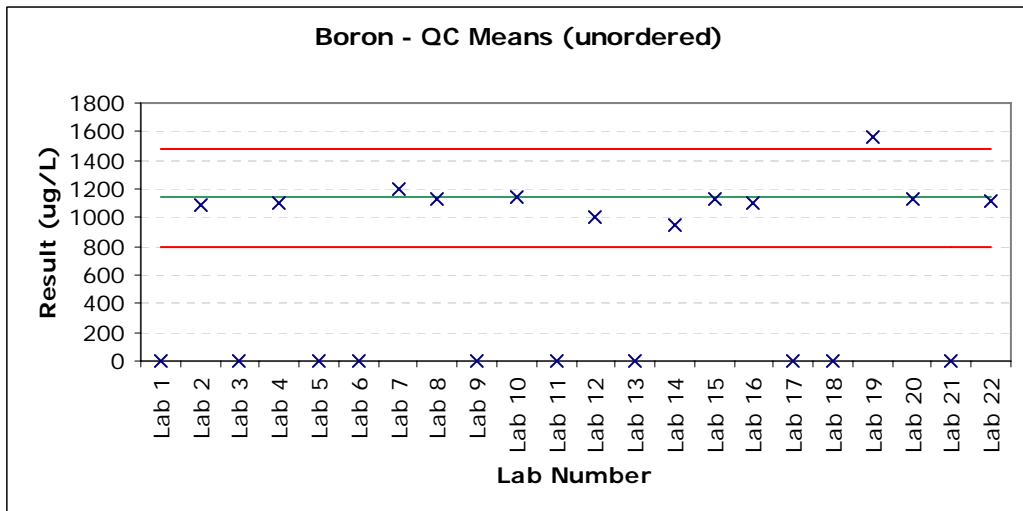
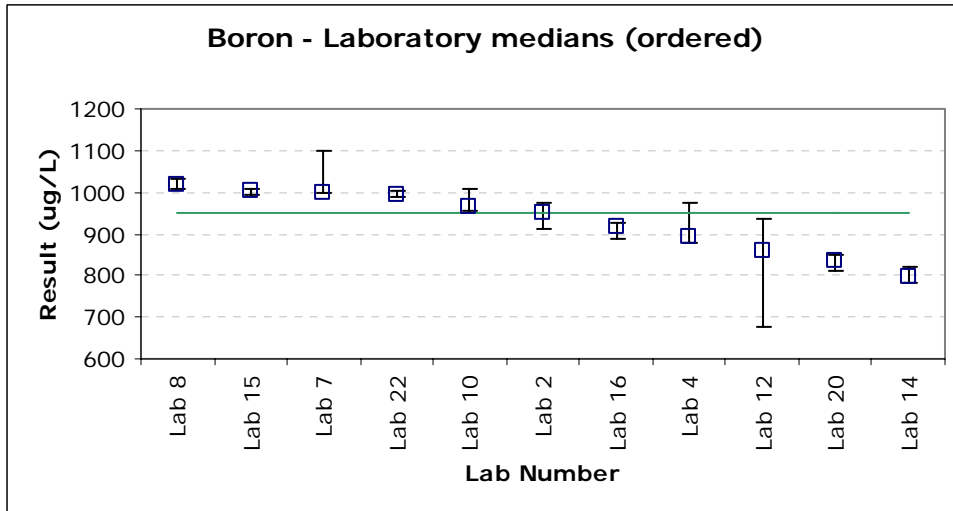
Appendix 6 – Processed Data and Charts

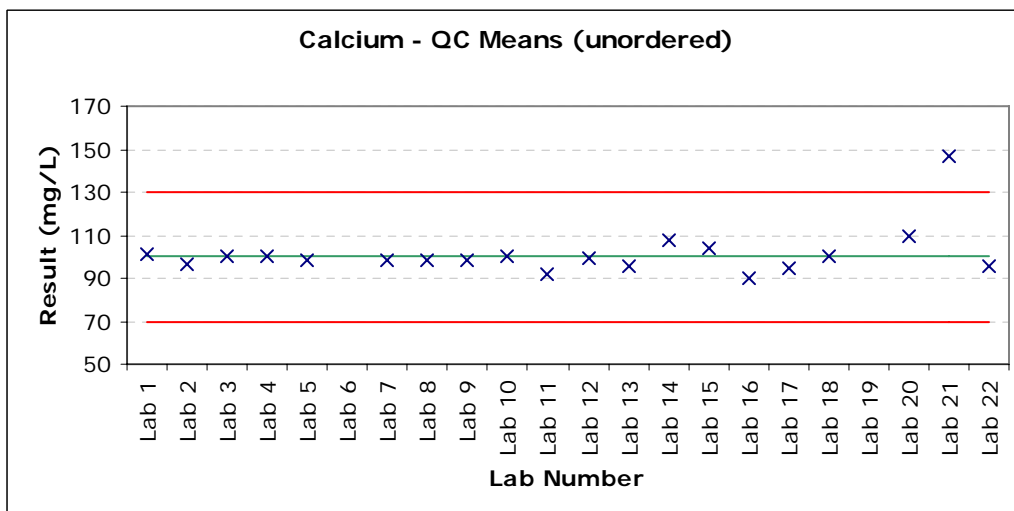
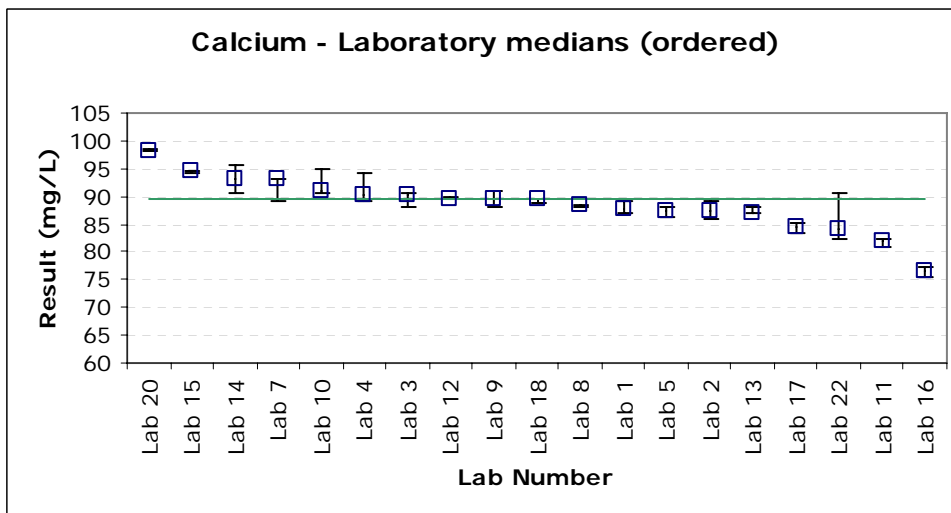
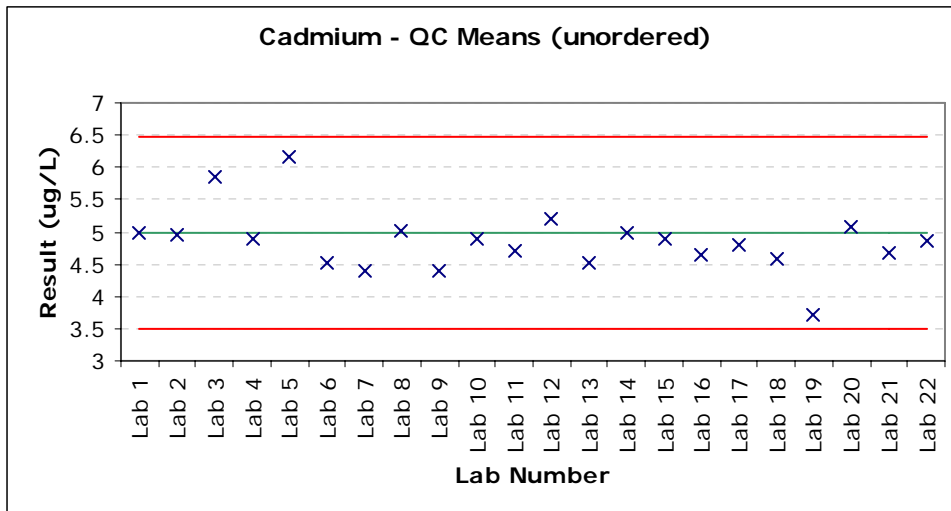
The following charts show the accepted laboratory data for each of the element characterised by the LGC6022 inter-laboratory study as well as the QC charts showing the mean QC results for each laboratory. The charts show the median value for each laboratory, with the error bars indicating the maximum and minimum values reported by each laboratory. Candidate material data is presented in result order, starting with the highest value. The median of medians for each analyte is displayed as a solid line. The QC data is presented in laboratory order, with the rejection criteria shown by solid lines.

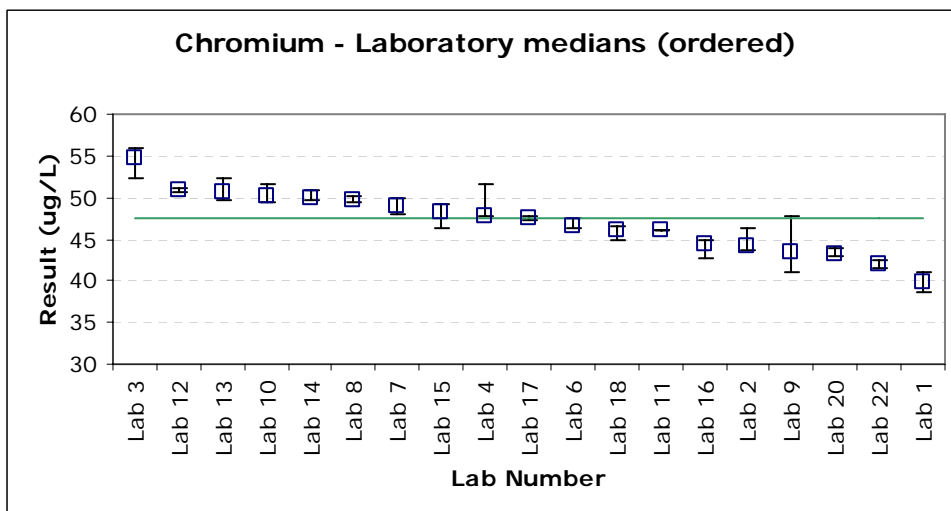
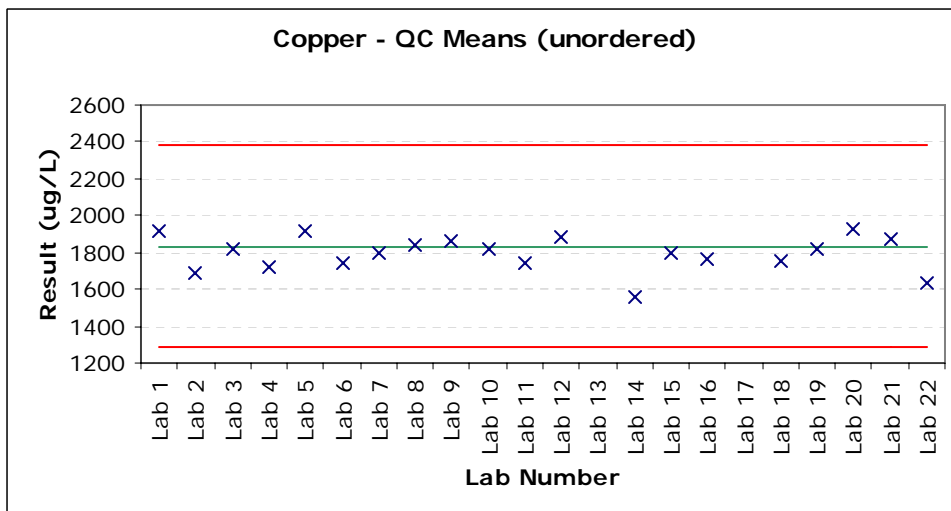
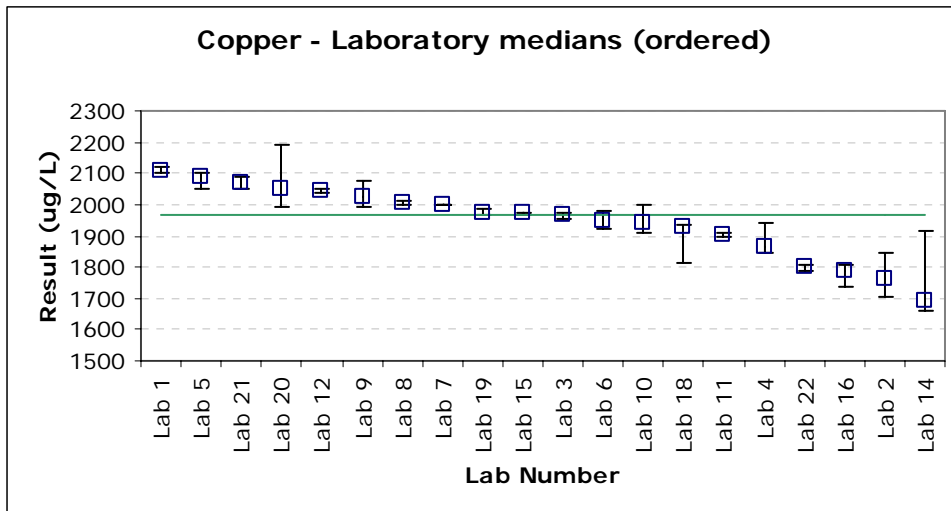


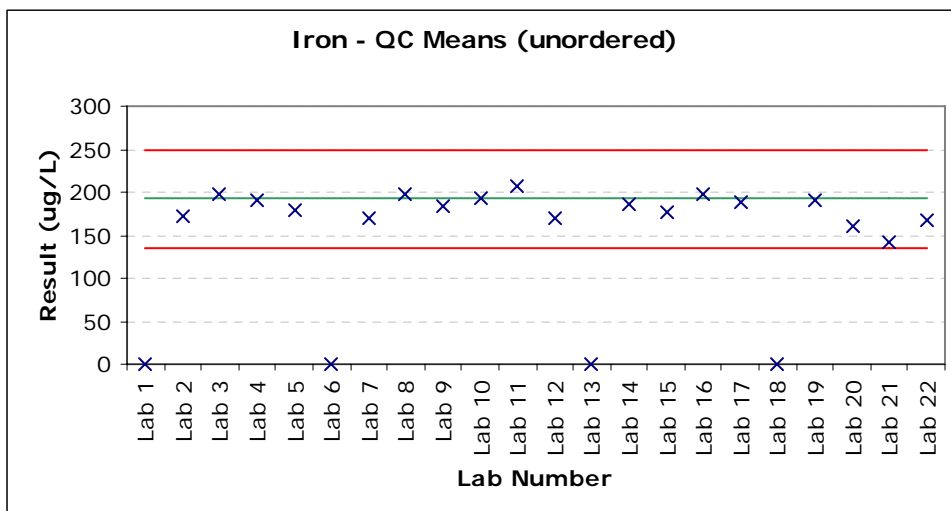
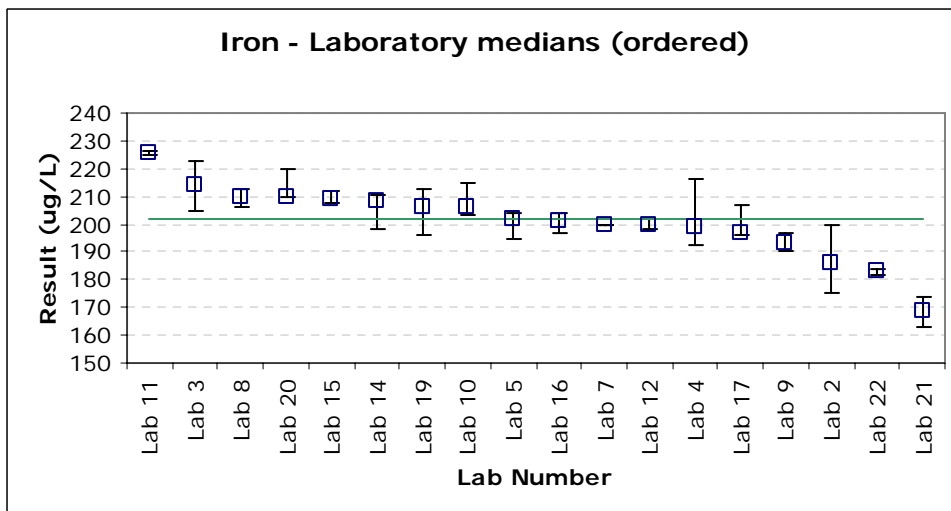
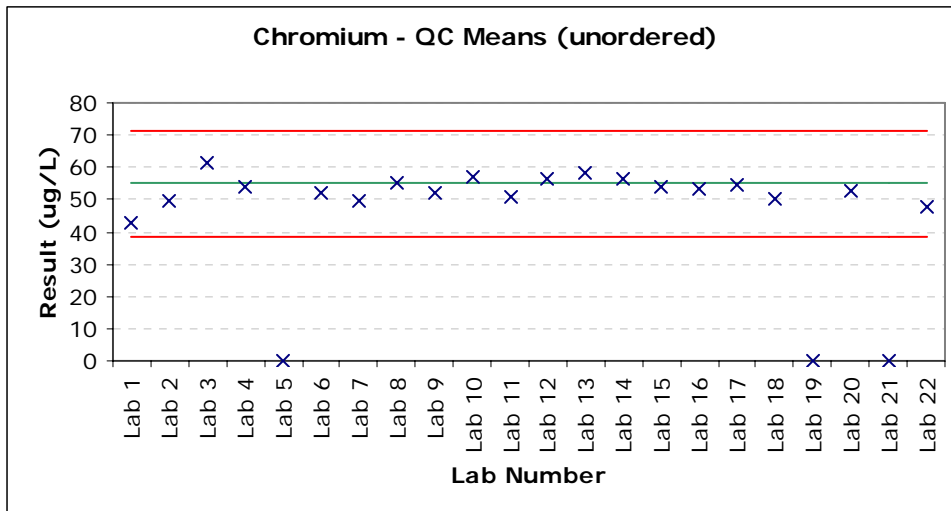


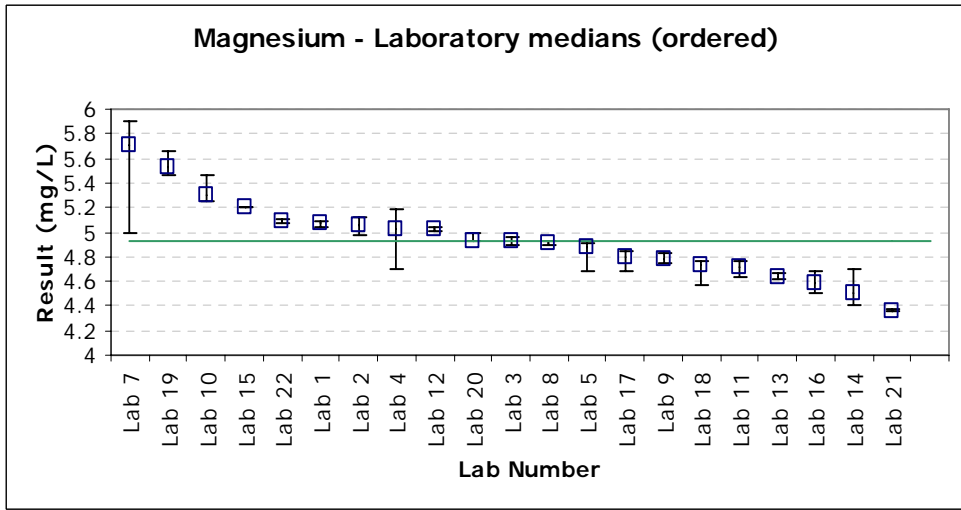
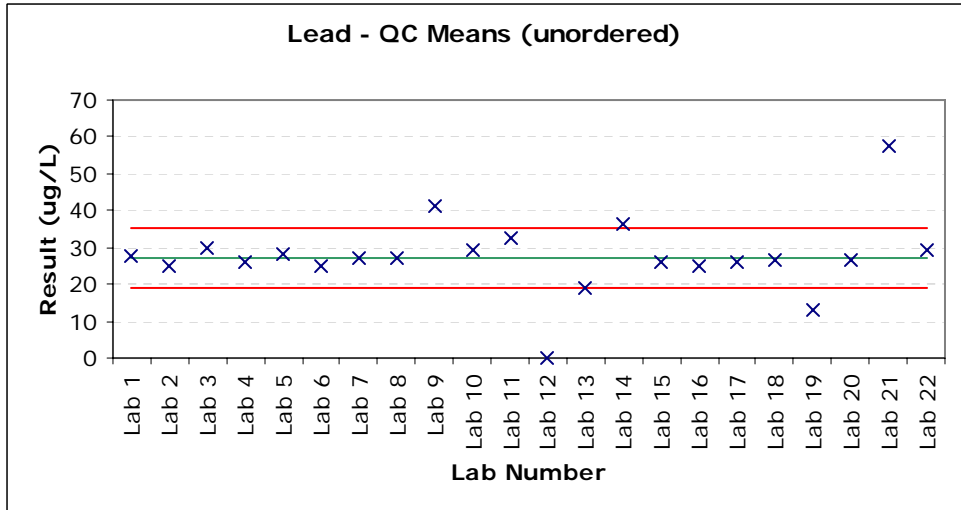
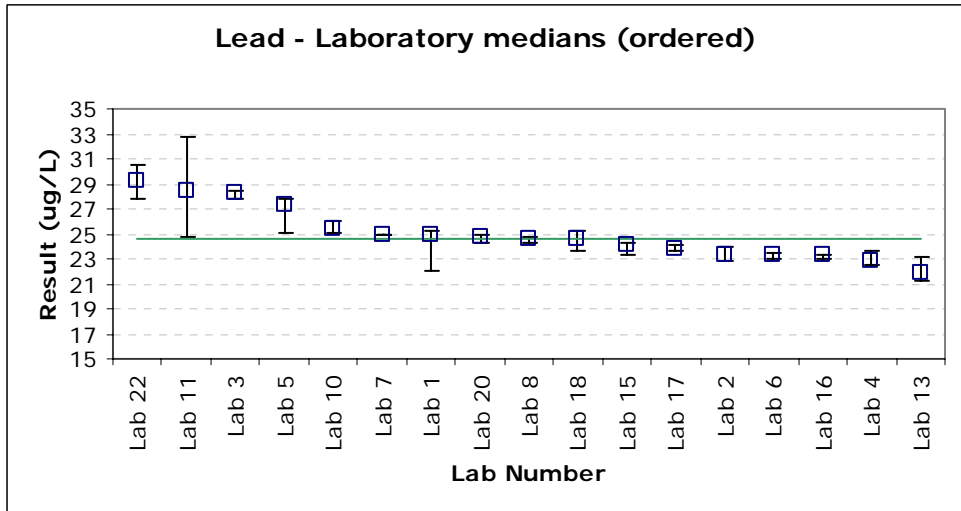


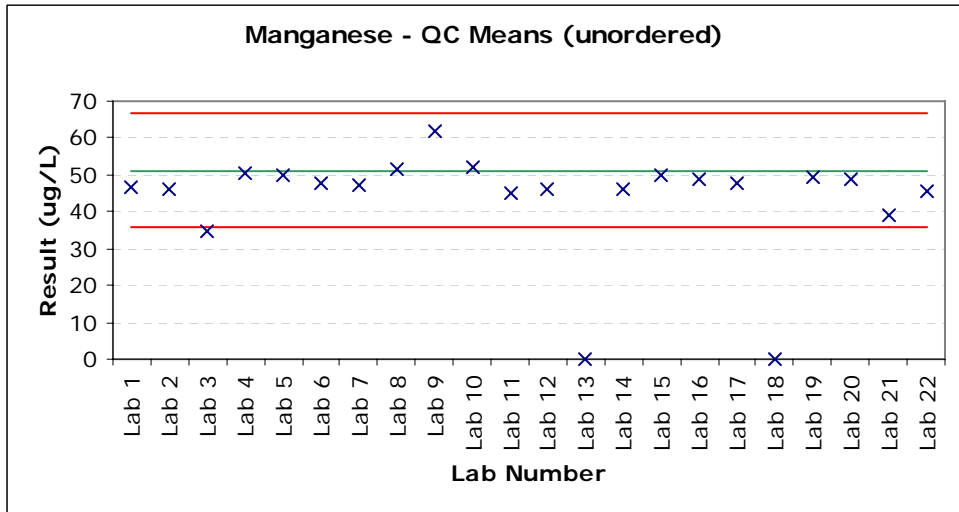
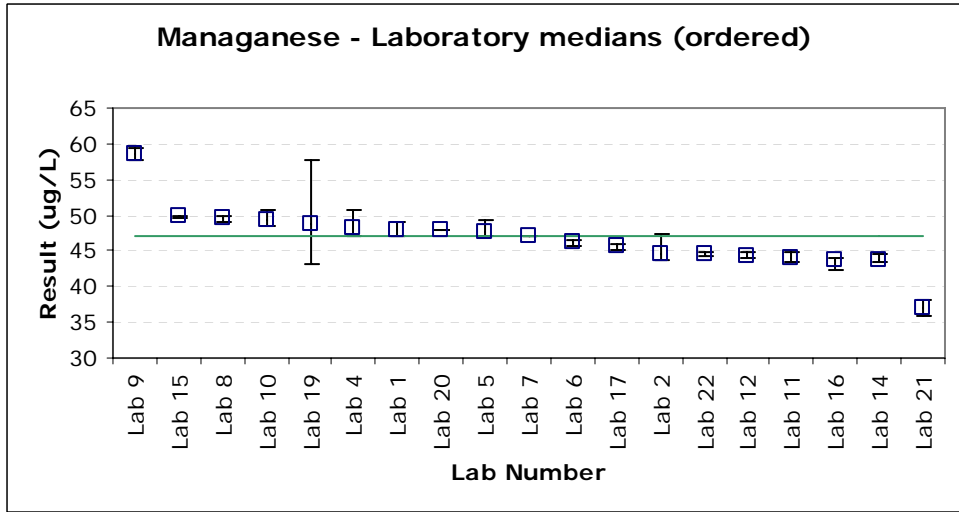
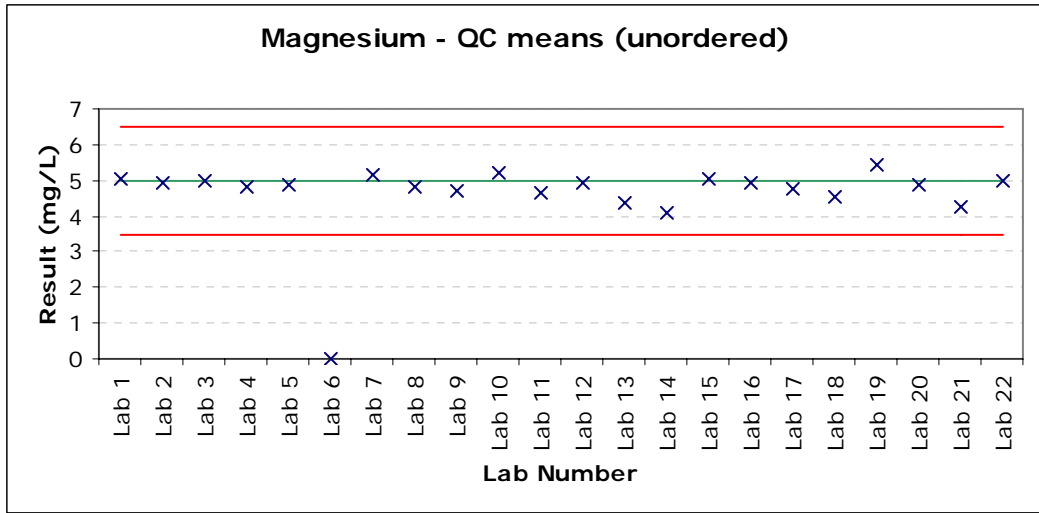


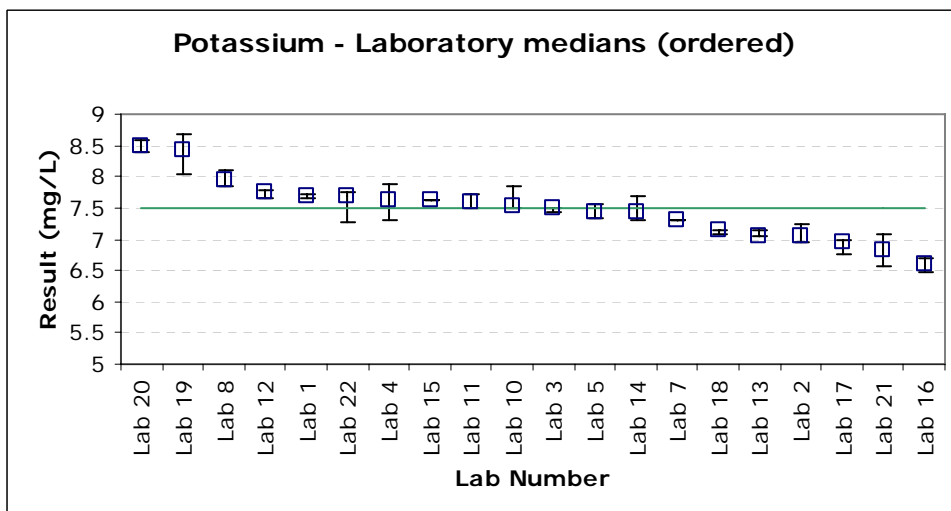
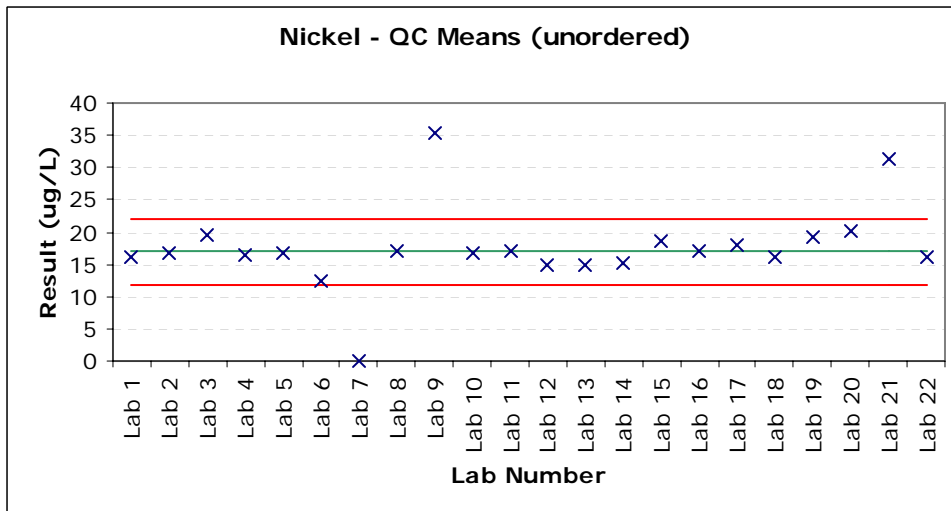
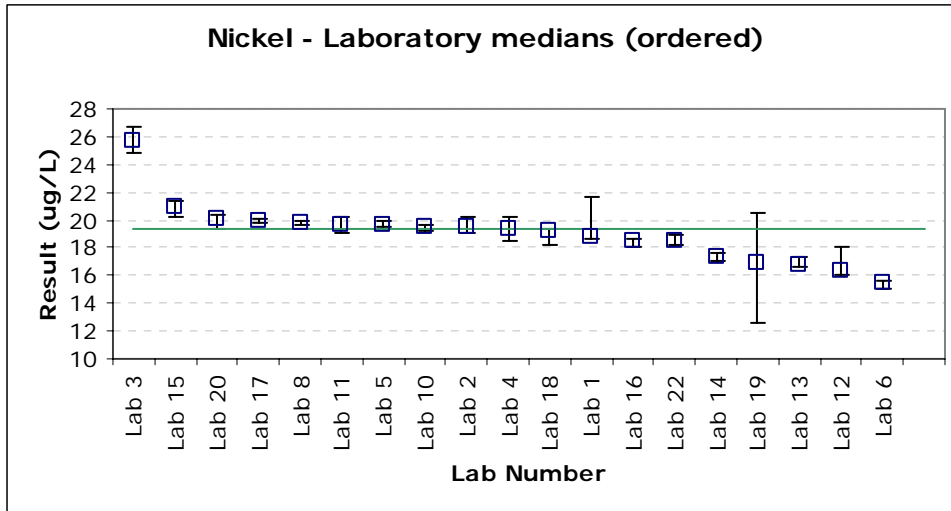


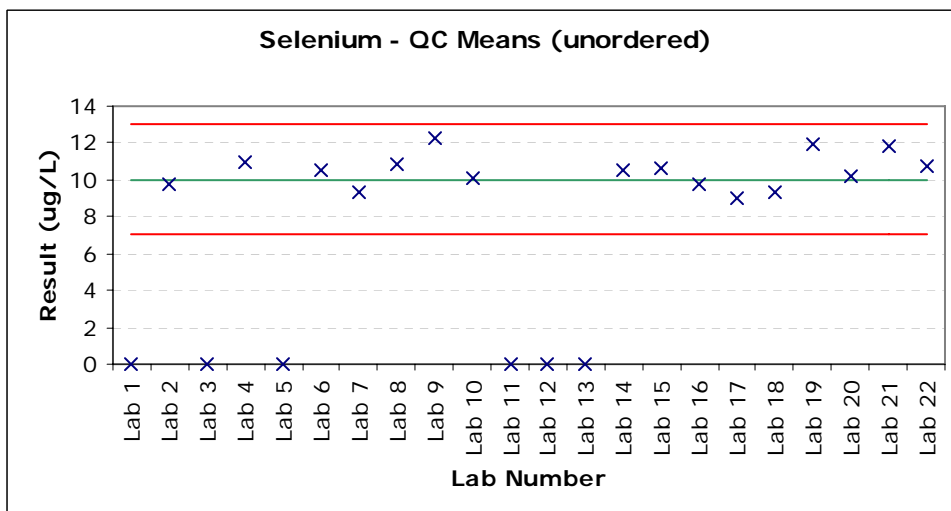
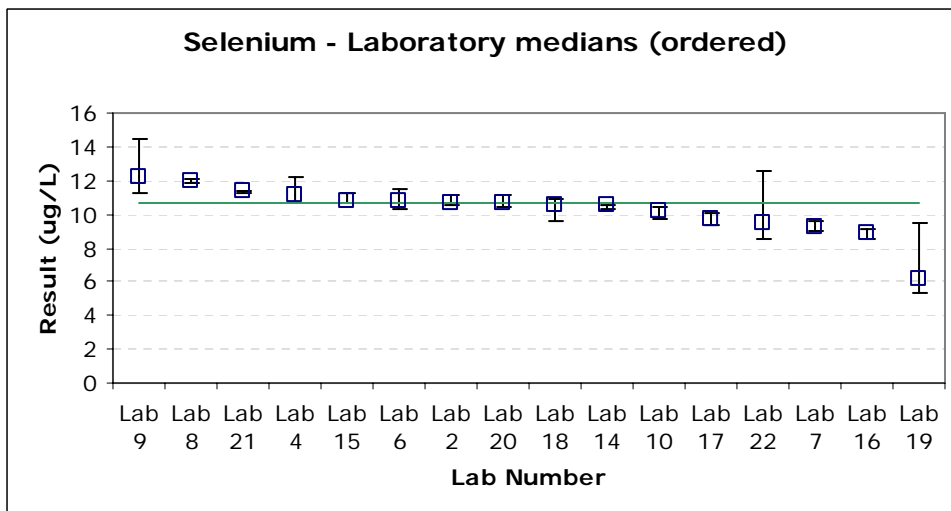
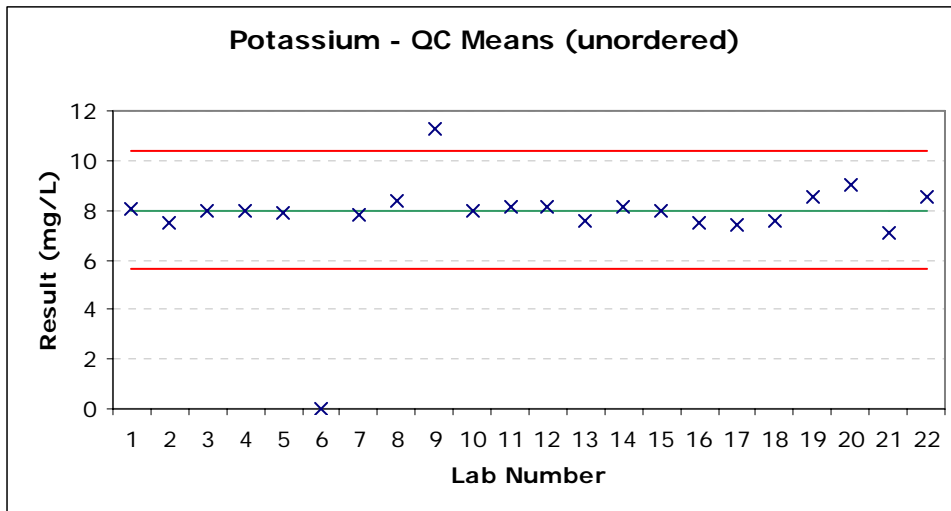


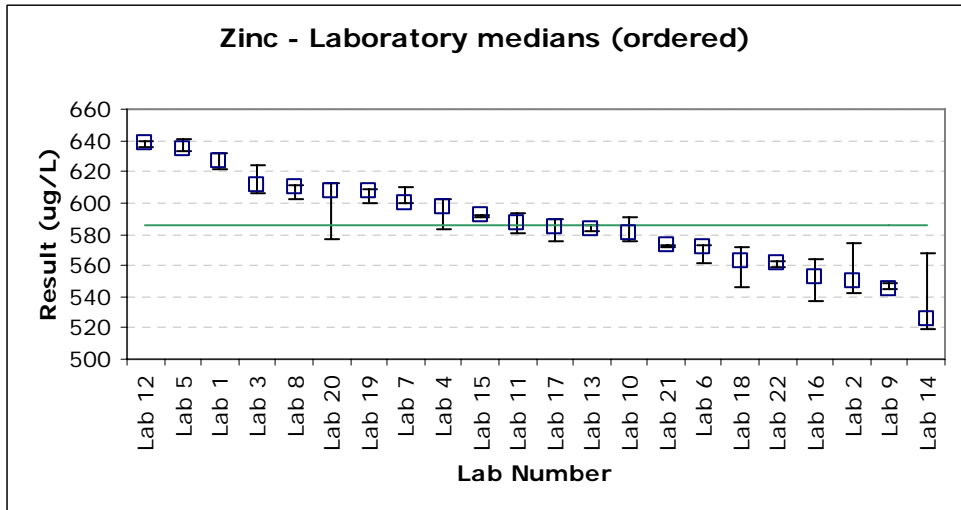
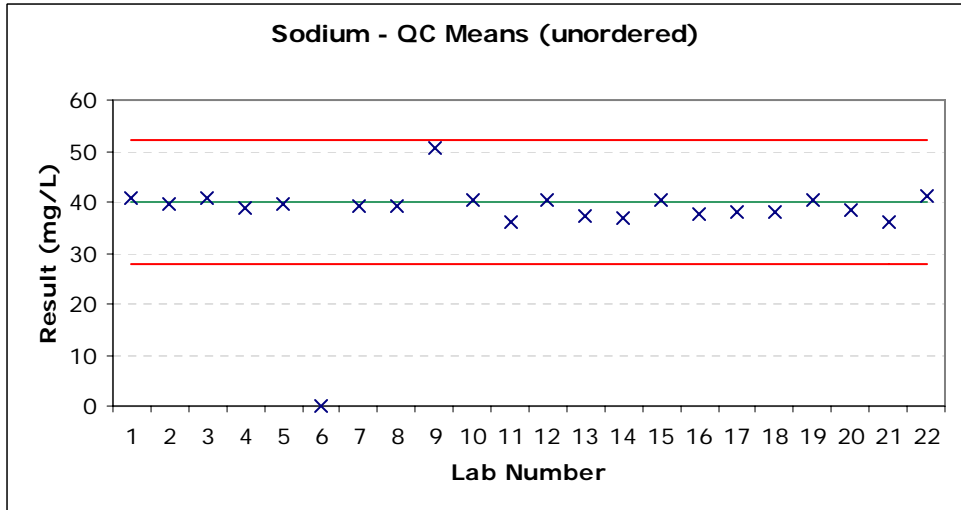
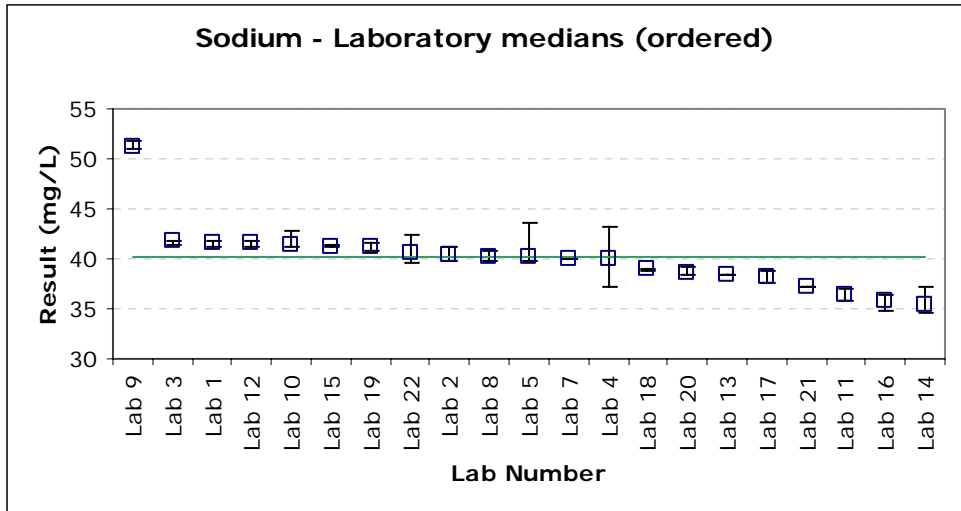


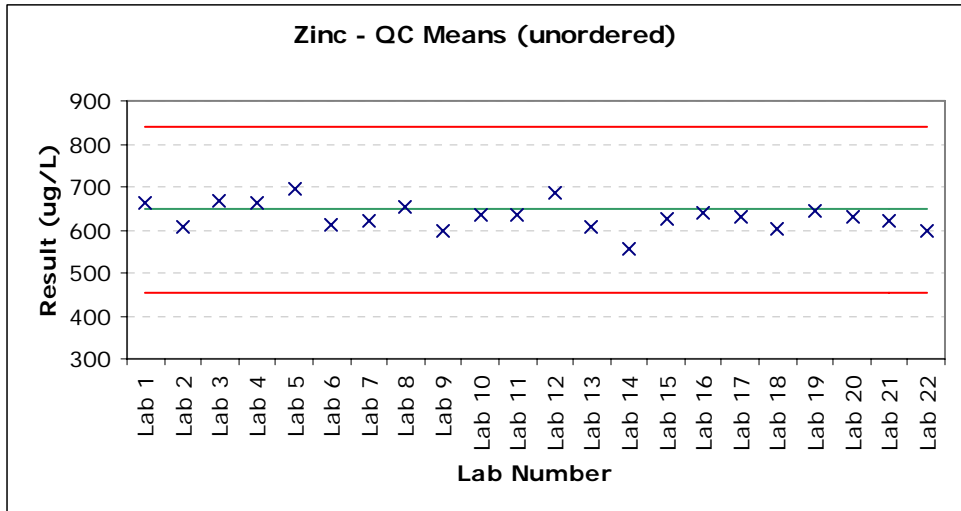












Appendix 7 – Inter-laboratory Study Methods

| Lab number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|------------|----|---------|-------|--------|--------|--------|---------|--------|-------|---------|---------|---------|-------|--------|---------|--------|--------|---------|----|---------|----|---------|
| Aluminium | | ICP-MS | Other | ICP-MS | ICP-MS | ICP-MS | ICP-OES | ICP-MS | | ICP-MS | ICP-OES | ICP-OES | | ICP-MS | ICP-OES | ICP-MS | ICP-MS | | | ICP-MS | | ICP-OES |
| Antimony | | ICP-MS | | ICP-MS | | ICP-MS | ICP-MS | ICP-MS | AA | ICP-MS | | | | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-OES | | ICP-MS | | |
| Arsenic | AA | ICP-MS | | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-MS | | ICP-MS | ICP-OES | | | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-OES | AA | ICP-MS | | ICP-OES |
| Barium | | ICP-MS | | ICP-MS | | ICP-MS | ICP-OES | ICP-MS | | ICP-MS | ICP-OES | ICP-OES | | ICP-MS | ICP-OES | ICP-MS | ICP-MS | ICP-OES | | ICP-MS | | ICP-OES |
| Boron | | ICP-MS | | ICP-MS | | | Other | ICP-MS | | ICP-MS | | ICP-OES | | ICP-MS | ICP-OES | ICP-MS | | | | ICP-MS | | ICP-OES |
| Cadmium | AA | ICP-MS | AA | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-MS | AA | ICP-MS | ICP-OES | ICP-OES | AA | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-OES | AA | ICP-MS | AA | ICP-OES |
| Copper | AA | ICP-MS | AA | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-MS | AA | ICP-MS | ICP-OES | ICP-OES | | ICP-MS | ICP-OES | ICP-MS | | ICP-OES | AA | ICP-MS | AA | ICP-OES |
| Chromium | AA | ICP-MS | AA | ICP-MS | | ICP-MS | ICP-OES | ICP-MS | AA | ICP-MS | ICP-OES | ICP-OES | AA | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-OES | | ICP-MS | | ICP-OES |
| Iron | | ICP-MS | AA | ICP-MS | ICP-MS | | ICP-OES | ICP-MS | AA | ICP-MS | ICP-OES | ICP-OES | | ICP-MS | ICP-OES | ICP-MS | ICP-MS | | AA | ICP-MS | AA | ICP-OES |
| Lead | AA | ICP-MS | AA | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-MS | | ICP-MS | ICP-OES | | AA | | ICP-MS | ICP-MS | ICP-MS | ICP-OES | | ICP-MS | | ICP-OES |
| Manganese | AA | ICP-MS | | ICP-MS | ICP-MS | ICP-MS | ICP-OES | ICP-MS | AA | ICP-MS | ICP-OES | ICP-OES | | ICP-MS | ICP-OES | ICP-MS | ICP-MS | ICP-MS | AA | ICP-MS | AA | ICP-OES |
| Nickel | AA | ICP-MS | AA | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-MS | | ICP-MS | ICP-OES | ICP-OES | AA | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-OES | AA | ICP-MS | | ICP-OES |
| Selenium | | ICP-MS | | ICP-MS | | ICP-MS | ICP-MS | ICP-MS | AA | ICP-MS | | | | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-OES | AA | ICP-MS | AA | ICP-OES |
| Zinc | AA | ICP-MS | AA | ICP-MS | ICP-MS | ICP-MS | ICP-MS | ICP-MS | AA | ICP-MS | ICP-OES | ICP-OES | AA | ICP-MS | ICP-OES | ICP-MS | ICP-MS | ICP-OES | AA | ICP-MS | AA | ICP-OES |
| Calcium | AA | ICP-OES | AA | ICP-MS | ICP-MS | | Other | ICP-MS | AA | ICP-OES | ICP-OES | ICP-OES | Other | ICP-MS | ICP-OES | ICP-MS | ICP-MS | ICP-OES | | ICP-OES | | ICP-OES |
| Magnesium | AA | ICP-OES | AA | ICP-MS | ICP-MS | | Other | ICP-MS | AA | ICP-OES | ICP-OES | ICP-OES | Other | ICP-MS | ICP-OES | ICP-MS | ICP-MS | ICP-OES | AA | ICP-OES | AA | ICP-OES |
| Potassium | AA | ICP-OES | Other | ICP-MS | ICP-MS | | ICP-OES | ICP-MS | | ICP-OES | ICP-OES | ICP-OES | Other | ICP-MS | ICP-OES | ICP-MS | ICP-MS | ICP-OES | AA | ICP-OES | AA | ICP-OES |
| Sodium | AA | ICP-OES | Other | ICP-MS | ICP-MS | | ICP-OES | ICP-MS | Other | ICP-OES | ICP-OES | ICP-OES | Other | ICP-MS | ICP-OES | ICP-MS | ICP-MS | ICP-OES | AA | ICP-OES | AA | ICP-OES |

AA = Atomic Absorption Spectrometry

ICP-MS = Inductively Coupled Plasma Mass Spectrometry

ICP-OES = Inductively Coupled Plasma Optical Emission Spectroscopy

Appendix 8 - Certificate



Setting standards
in analytical science



CERTIFICATE OF ANALYSIS

ERM[®] - CA011a

| Hard Drinking Water UK – Metals | | | |
|---------------------------------|------------------------|---------------------------------------|---------------------------------|
| Constituent ^{1,2} | Number of laboratories | Certified value ^{3,4} (µg/L) | Uncertainty ⁵ (µg/L) |
| Aluminium | 16 | 197 | 13 |
| Antimony | 13 | 5.2 | 0.3 |
| Arsenic | 17 | 10.1 | 0.6 |
| Barium | 15 | 120 | 6 |
| Boron | 11 | 950 | 67 |
| Cadmium | 1 | 4.94 | 0.23 |
| Chromium | 19 | 48 | 3 |
| Copper | 20 | 1970 | 67 |
| Iron | 1 | 207 | 6 |
| Lead | 1 | 24.7 | 0.5 |
| Manganese | 19 | 47 | 2.3 |
| Nickel | 19 | 19.4 | 1 |
| Selenium | 16 | 10.7 | 0.7 |
| Zinc | 22 | 586 | 20 |
| | | Certified value ^{3,4} (mg/L) | Uncertainty ⁵ (mg/L) |
| Calcium | 19 | 89 | 2 |
| Magnesium | 21 | 4.9 | 0.16 |
| Potassium | 20 | 7.5 | 0.22 |
| Sodium | 21 | 40 | 1.3 |

1) Cadmium, iron and lead were determined at LGC using Isotope Dilution ICP-MS. (IDMS)
 2) The remaining measurands are defined by the methods used by participant laboratories (page 3).
 3) Unweighted median value of the concentration determined by participant laboratories. Each data set was obtained in a different laboratory and/or using a different method of measurement.
 4) The results are traceable to the SI through the physical and chemical standards used by LGC and the interlaboratory study participant laboratories.
 5) The quoted uncertainty is the half-width of the expanded uncertainty calculated using a coverage factor (k) of approximately 2, which gives a level of confidence of 95 %.

This certificate is valid for 12 months from the date of shipment provided the sample is stored under the recommended conditions.

The minimum amount of sample to be used is 1 mL.

European Reference Material ERM[®]-CA011a was produced and certified under the responsibility of LGC according to the principles laid down in the Technical Guidelines of the European Reference Materials[®] co-operation agreement between BAM-LGC-IRMM. Information on these guidelines is available on the Internet (<http://www.erm-crm.org>).

Accepted as an ERM[®], Teddington, October 2007.

Certificate revised January 2008.

Signed: _____



4005

Dr John Marriott, UK Government Chemist
 LGC Limited
 Queens Road
 Teddington
 Middlesex
 TW11 0LY, UK

| Information Values ¹ | | | |
|---------------------------------|------------------------|-------------------------|--------------------|
| Element | Concentration | | |
| | Number of laboratories | Indicative value (µg/L) | Uncertainty (µg/L) |
| Cadmium | 22 | 4.8 | 0.22 |
| Iron | 18 | 202 | 7.4 |
| Lead | 17 | 24.6 | 1.25 |

1) These information values are derived from the inter-laboratory study data for this material. These information values are supplied for comparison purposes only.

DESCRIPTION OF THE SAMPLE

Hard drinking water was sourced from the Teddington mains supply. The water was then filtered through 1 µm cellulose filter paper and acidified to approximately pH 2 by addition of high purity nitric acid to give a final concentration of approximately 0.1 % nitric acid. This material was then analysed by ICP-MS and ICP-OES at LGC to establish the base levels of the elements of interest. High purity metals standards (SPEX Certiprep, Middlesex, England) were used to spike the base material to levels as close to the UK drinking water regulation limits as possible (98/83/EC of 1998, enacted in Statutory Instrument 2000 No. 3184). The amount of each metal standard added to the material was calculated taking account of the base level of the respective element in the solution. The material was spiked using a positive pressure Eppendorf (Cambridge, UK) digital pipette, and was stirred continuously during preparation. The material was then sub-sampled into 250 mL high density polyethylene screw cap bottles.

The homogeneity of the material was assessed by analysis of 10 randomly selected units from across the fill run. The results were then analysed by one-way ANOVA, and the contribution to the combined uncertainty was calculated from the larger of the between unit standard deviation and the method standard deviation.

INTENDED USE

This material is intended for use in the development, validation or quality control of analytical methods for the determination of elements in hard drinking water. The material may also be applicable to other matrices where suitable reference materials are not available.

Information on how to compare an analytical result with the certified value can be found in ERM Application Note 1; www.erm-crm.org

CHARACTERISATION

The material was characterised using a combination of IDMS analysis carried out at LGC and an inter-laboratory study organised by LGC. IDMS characterisation was carried out for Cadmium, Lead and Iron. The participants of the inter-laboratory study were asked to characterise Aluminium, Antimony, Arsenic, Barium, Boron, Cadmium, Calcium, Chromium, Copper, Iron, Lead, Magnesium, Manganese, Nickel, Potassium, Selenium, Sodium and Zinc.

The material was first issued for sale in October 2007. In January 2008, a transcription error was identified involving the magnesium and potassium values, so the certificate was corrected and reissued.

ANALYTICAL METHOD USED FOR CERTIFICATION

IDMS

Iron (Fe), cadmium (Cd) and lead (Pb) were determined at LGC by exact matching double isotope dilution mass spectrometry (IDMS). The sample (6g) was spiked with a solution containing enriched ^{57}Fe , ^{106}Cd and ^{206}Pb to give predicted $^{56}\text{Fe}:$ ^{57}Fe , $^{111}\text{Cd}:$ ^{106}Cd and $^{208}\text{Pb}:$ ^{206}Pb ratios of 1. For the characterisation of the material, 5 replicate analyses were made on a single unit.

For calibration, solutions prepared from NIST certified materials SRM3126 (Fe), SRM3108 (Cd) and SRM981 (Pb) were diluted to give similar concentrations to that of the sample. These were then spiked with the same enriched ^{57}Fe , ^{106}Cd and ^{206}Pb solution to match the ratio of the sample blends. QC blends were prepared in the same way, using standards prepared from high purity metals (Cd and Fe - Spex Certiprep, Middlesex, UK) and commercially available standard solutions (Pb 1000 $\mu\text{g/g}$ – Romil, Cambridgeshire, UK).

Fe measurements were performed using a ThermoFinnigan ELEMENT magnetic sector inductively coupled plasma mass spectrometer (HR-ICP-MS), and Cd and Pb using an Agilent 7500ce collision/reaction cell inductively coupled plasma mass spectrometer (CRC-ICP-MS) operating in standard mode.

The certified values were assigned as the mean of the 5 replicate measurements.

Inter-laboratory Study

This material was sent out to inter-laboratory study in May 2007. Participant laboratories chose suitable methods with which they were familiar. These methods included ICP-MS, ICP-OES and AA. The number of laboratories using each type of method is shown in the table below.

The data from the inter-laboratory study were processed using a robust statistical approach after screening laboratories based on their performance in analysing a separate QC sample. The certified value for each analyte certified by inter-laboratory study was assigned as the median of medians of the accepted laboratory data. The characterisation uncertainty assigned was the robust standard error of the robust mean of the accepted laboratory data.

| Methods used by inter-laboratory study participants | | | | | |
|---|--------|-----------------|----|-------|------------------------------|
| Analyte | ICP-MS | ICP-OES/ICP-AES | AA | Other | Total number of laboratories |
| Aluminium | 10 | 5 | 0 | 1 | 16 |
| Antimony | 11 | 1 | 1 | 0 | 13 |
| Arsenic | 12 | 3 | 2 | 0 | 17 |
| Barium | 9 | 6 | 0 | 0 | 15 |
| Boron | 7 | 3 | 0 | 1 | 11 |
| Cadmium | 12 | 4 | 6 | 0 | 22 |
| Copper | 10 | 5 | 5 | 0 | 20 |
| Chromium | 10 | 5 | 4 | 0 | 19 |
| Iron | 9 | 5 | 4 | 0 | 18 |
| Lead | 11 | 3 | 3 | 0 | 17 |
| Manganese | 10 | 5 | 4 | 0 | 19 |
| Nickel | 12 | 4 | 4 | 0 | 20 |
| Selenium | 11 | 2 | 3 | 0 | 16 |
| Zinc | 11 | 5 | 6 | 0 | 22 |
| Calcium | 6 | 8 | 3 | 2 | 19 |
| Magnesium | 6 | 8 | 5 | 2 | 21 |
| Potassium | 6 | 9 | 4 | 1 | 20 |
| Sodium | 6 | 9 | 5 | 1 | 21 |

PARTICIPANTS

The following laboratories participated in the inter-laboratory study for this material.

| | |
|--|------------------------|
| AES Ltd | UK |
| ALcontrol Technichem | UK |
| AMEC Earth and Environmental | Canada |
| Analytical Data Services | UK |
| Anglian Water | UK |
| Austrian Research Centers GmbH -ARC | Austria |
| British Geological Survey | UK |
| Centre for Ecology and Hydrology | UK |
| Chemex Environmental International Limited | UK |
| Chemtech Environmental Limited | UK |
| FORCE Technology | Denmark |
| Inspectorate Services Peru S.A.C. | Peru |
| LATU - Spectrometry Dept. | Uruguay |
| Macaulay Institute | UK |
| National Institute of Health | Portugal |
| Public Health Institute of Istrian County | Croatia |
| Seychelles Bureau of Standards | Republic of Seychelles |
| South East Water | UK |
| South West Water, Exeter Laboratory | UK |
| States Analyst Laboratory | Guernsey |
| STL Bridgend | UK |
| Sutton and East Surrey Water | UK |

SAFETY INFORMATION

Refer to Material Safety Data Sheet.

INSTRUCTIONS FOR USE

Before use the material should be thoroughly mixed by inversion, and allowed to equilibrate to room temperature. The minimum amount of sample to be used is 1 mL.

STORAGE

The material should be stored at $5\text{ }^{\circ}\text{C} \pm 4\text{ }^{\circ}\text{C}$ in its original packaging.

Unit Number:

Shipment Date:

LEGAL NOTICE

The certified values quoted in this certificate are LGC's best estimate of the true values within the stated uncertainties and based on the techniques described in this certificate. In support of LGC's aim of providing high quality materials, the reference material was produced taking into account appropriate international guidelines for the preparation and certification of reference materials. None of LGC (Holdings) Limited, its subsidiaries, its contractors nor any person acting on their behalf:

- (a) make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document does not infringe any privately owned rights; or
- (b) assume any liability with respect to, or for damages resulting from, the use of any information, material, apparatus, method or process disclosed in this document save for loss or damage arising solely and directly from the negligence of LGC (Holdings) Limited or any of its subsidiaries. In such circumstances (i.e. our proved negligence) the total amount recoverable shall not exceed £1,000,000.

Production of this reference material and certificate was supported by the Department for Innovation, Universities & Skills as part of the National Measurement System Chemical & Biological Metrology Knowledge Base Programme.

This certificate may not be published except in full, unless permission for the publication of an approved extract has been obtained in writing from the Government Chemist. It does not of itself impute to the subject of measurement any attributes beyond those shown by the data contained herein.