Method development and validation of main metals method by inductively coupled plasma mass spectrometry

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EXECUTIVE SUMMARY

The Magnox Ltd. power plant at Bradwell-On-Sea ("Bradwell") is currently being decommissioned. One aspect of the decommissioning activities is on-site dissolution of Fuel Element Debris (FED) which is dissolved in batches in concentrated nitric acid, neutralised, filtered and the activity abated. This treated effluent stream is then discharged to the local estuary and is subject to Environmental Permitting Regulations 10 (EPR 10). This involves the measurement of boron, chromium, iron, nickel, copper, zinc, cadmium and lead by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This analysis is conducted at an on-site analytical laboratory by a small team of analysts using a Perkin Elmer NexION 300X ICP-MS instrument. The analytical team were experiencing continuing issues with the analysis of these EPR 10 elements, plus aluminium for plant performance checks, and NNL were requested to visit the facility. As part of this visit NNL were commissioned to validate Bradwell's "main metals" ICP-MS method on the NNL Perkin Elmer NexION 300D. The two instruments are equivalent in performance. This report is a summary of method development to optimise the existing Bradwell method and validation work for the measurement of the nine elements by ICP-MS.

The report details the method development procedure required to optimise the existing "main metals" Bradwell method. This has mainly focused around the high magnesium and sodium concentrations found in the effluent stream resulting from FED dissolution and neutralisation. The method has been optimised with the ideal dilution factor for the samples determined and a validation programme conducted with all data provided within this report. The validation programme has assessed the repeatability and reproducibility of results over fifteen different runs, which has involved three different analysts, to assess the robustness of the technique. From the validation work the precision has been assessed for the measurement of each element and suggested operating windows for quality control sample variations within a run and between analyses.

The validation data has shown that boron, chromium, nickel, copper, cadmium and lead can be measured routinely within a 10% uncertainty with consistent calibrations and repeatable limits of detection. Each element is detailed within this report. The validation for aluminium, iron and zinc has shown more variability as they are ubiquitous and therefore samples are prone to contamination and backgrounds show increased variation affecting the measurement. This will increase the uncertainty assigned to these results, however, the concentrations measured are considerably lower than the discharge limits to the estuary, therefore the consequences of the increased uncertainty are less significant.

The report also details the analysis of a Bradwell plant sample and a manufactured "trueness sample" that have been analysed blind. The results are detailed within the report and can be used by Bradwell for comparison between the two instruments and will support the transfer of the new "main metals" method.

VERIFICATION STATEMENT

This document has been verified and is fit for purpose. An auditable record has been made of the verification process. The scope of the verification was to confirm that: -

- The document meets the requirements as defined in the task specification/scope statement
- The constraints are valid
- The assumptions are reasonable
- The document demonstrates that the project is using the latest company approved data
- The document is internally self consistent

HISTORY SHEET

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1. Introduction

The Magnox Ltd. power station at Bradwell-On-Sea "Bradwell" is being decommissioned and to support this an on-site dissolution plant to dissolve Fuel Element Debris (FED) has been commissioned. This plant, the FED dissolution plant (FEDD), has been designed to dissolve batches of FED in nitric acid in a controlled manner. After the material has been successfully dissolved the FED effluent is passed through the Aqueous Discharge Abatement Plant (ADAP) designed to neutralise the acidic stream with sodium hydroxide then filter the effluent. During the process heavy metals are precipitated from the solution with the aid of flocculant. The effluent is then passed through micro-filters to remove any suspended solids then through ion exchange columns to remove strontium and caesium activity. The effluent is stored and tested for activity to assess the effectiveness of the abatement processes, if successful the effluent is passed into a sentencing tank. The effluent is stored and tested according the Environmental Permitting Regulations 10 (EPR 10) for compliance of discharge into the local estuary. Part of compliance for this discharge is the measurement of boron (B), chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb) and mercury (Hg). Bradwell conduct this analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at an on-site analytical laboratory. The analysis is also used to demonstrate plant performance therefore quick turnaround of analysis maximises the performance and availability of FEDD and ADAP. The Analytical Team was experiencing several problems with the use of this technique and the measurement of these analytes, which shall be outlined within this report. Through initial visits to Bradwell NNL were requested to validate two ICP-MS methods to reduce the problems repeatedly experienced by the Bradwell Analytical Team. This report details the method development and validation of the "main metals method" for the analysis supporting discharge. The validation of the measurement of Hg, the second method, is detailed in a separate report.

1.1. Environmental Discharges

At Bradwell the effluent generated from the FEDD is subject to environmental regulations before it is discharged into the local estuary. The necessity for the analysis of the effluent is to prevent pollution and reduce the release of harmful and toxic analytes for the protection of the environment and human life. Part of the regulation requires the testing of B, Cr, Fe, Ni, Cu, Zn, Cd, Pb and Hg. The discharge limits for each of the elements is listed in **Table 1**.

Table 1: The discharge limits in µg/L for each element

Analyte	Discharge Limit (µg/L)
Boron (B)	53,235,000
Chromium (Cr)	4563
Iron (Fe)	7,605,000
Nickel (Ni)	3000
Copper (Cu)	38025
Zinc (Zn)	304200
Cadmium (Cd)	30
Lead (Pb)	1080
Mercury (Hg)	7.5

In order to conduct this elemental analysis Bradwell purchased two Perkin Elmer ICP-MS NexION instruments capable of trace metal analysis. Although the instrument sensitivity and low detection limits are not required for most of the discharge limits for these elements this is the only technique available capable of achieving the measurement of cadmium and mercury at these low levels.

It is important to note that part of the "main metals" analysis also includes the measurement of aluminium (Al). The EPR 10 does not require the measurement of this element and therefore there is no discharge limit associated with it. Bradwell requires the measurement of aluminium as a check on the performance of the FEDD and abatement processes.

1.2. Analysis by ICP-MS

ICP-MS is a technique commonly used for trace elemental analysis across various industries and is capable of measuring within the ng/L and µg/L range. Analysis requires the sample to be in aqueous form and generally in a dilute acidic media. The sample is injected into a spray chamber via a nebuliser where the sample is converted from a solution to a liquid aerosol. It is then passed into the argon-based plasma (between 6000 and 7000 K) where the droplets are dried and resultant solid particles are broken down into their constituent elements. These elements are then ionised to form positively charged ions (predominantly +1 ions), which are propelled forward by an electric field generated by a high potential between the plasma and the interface. A series of cones are used to introduce the ion beam into the high vacuum chamber housing the mass detector. In the case of the NexION instrument there are three quadrupoles in total before the ions reach the mass detector. The first is a quadrupole designed to steer the ion beam by 90 degrees. This ensures that only ions pass into the next quadrupole and all remnants from the plasma (photons and un-ionised atoms) leave the beam therefore reducing noise. The ion beam then passes through a Dynamic Reaction Cell (DRC) housing the second quadrupole where collision gases and reaction gases can be pumped in, the use of these will be discussed later. The ion beam then passes through a mass filter quadrupole in the DRC where a potential can be applied that acts as an energy barrier to remove any potential interferences for measurement of the desired analyte. The ion beam then passes into the third quadrupole where mass separation takes place, then impacts on the mass detector, which is a photomultiplier capable of determining the rate of arrival of ions at the detector. The ICP-MS therefore measures ions based on their charge to mass ratio (m/z). This means that a +1 ion will be measured as its atomic mass. The ICP-MS is capable of measuring the different isotopes of an element. If the sample contains elements with an isotopic natural abundance it is only necessary to measure one of the isotopes. The selection of the isotope will depend upon the % natural abundance and the presence of any isobaric interferences.

The most common difficulty experienced with ICP-MS analysis is isobaric interferences; this is where the ion of interest has the same m/z ratio as another ion present, which the mass detector cannot distinguish between. Two examples are Mo-100 & Ru-100 and Mo-98 & Ru-98, as pairs of elements that have the same atomic masses. In this case a different isotope should be measured where there are no interferences for example Mo-95 and Ru-102. However, this is not always possible if the natural abundance % compositions are low for the alternative isotope as the small concentrations will be difficult to measure. Isobaric interferences do not just arise from other isotopes of the same mass of other elements; it is also possible to form polyatomic ion species in the ion beam, where elemental ions combine with other elemental ions to form a molecular ion.

An example of this is argon oxide (ArO^+) where both argon and oxygen ions are unstable due to their high electronegativities and preferentially combine to share the positive charge. Therefore the m/z ratio is the sum of both their atomic masses and in the case of their most abundant isotopes $^{40}Ar^{16}O^+$ has an m/z ratio of 56, the same mass as Fe-56, which is 91.7% of naturally occurring Fe. Therefore when measuring Fe-56 the signal measured at the detector is a mixture of Fe-56 and $^{40}Ar^{16}O^+$. The ArO^+ concentration is relatively high in comparison to the Fe concentration. This makes it difficult to measure low levels of Fe on a large background and the variability of the ArO^+ signal swamps the small Fe-56 signal, so a high limit of detection (LOD) is observed. It is possible with the NexION to introduce a collision gas to the ion beam in the DRC. A common collision gas is helium (He) where the ions in the beam collide with the large abundance of He atoms pumped into the DRC that form a mist. Although the ions of interest will collide with the He mist the polyatomics are statistically more likely to collide with the mist as they are larger ions. When the polyatomics collide with the mist they loose energy and are not able to pass by an applied potential (energy barrier) at the exit of the quadrupole. This reduces their effect as an isobaric interference such that the signal is predominantly generated by analyte ions, improving the LOD. In the case of reaction gases a gas is introduced to favourably react with the isobaric interference shifting its mass and hence m/z ratio away from that of the analyte of interest.

Other difficulties to consider when conducting ICP-MS analysis surround the stability of the instrument due to its ability to measure trace levels, in most cases low ng/L concentrations. Therefore the instrument must be routinely maintained, kept within a clean and temperature controlled laboratory environment and used by trained operators. This will lead to optimum performance of the instrument reducing repeat analysis and outage, of particular interest in a plant environment such as Bradwell. The analysis is also sensitive to contamination of samples, consumables used in sample preparation and the instrument itself. Elevated backgrounds from the analyte of interest or an isobaric interference increase variability in the measurement and can significantly increase the LOD. This could lead to elevated sample results, which would lead to repeat analysis, which is time consuming. If contamination is more widespread then the instrument may need to be cleaned which will lead to instrument outage.

Overall ICP-MS is an accurate, precise and fast technique capable of trace elemental analysis making it ideally suited for Bradwell's requirements to support the plant scale FEDD and discharge of waste effluent to the estuary. However, due to its ability to measure these trace levels it is a complex instrument that requires trained operators and the correct laboratory environment to optimise performance.

1.3. Issues Concerning the Measurement of Elements in the "Main Metals" Method

It is important to understand the fundamental difficulties specific to measuring the "main metal" elements (B, Al, Cr, Fe, Ni, Cu, Zn, Cd and Pb) in the FEDD effluent stream before discharge. By understanding potential isobaric interferences, concentration and contamination issues the method can be optimised to achieve accuracy, precision and quick sample turnaround to support plant operations and discharges.

The isobaric interferences that may cause problems for the measurements of "main metal" elements are argon-based polyatomics with carbon, nitrogen or oxygen for Cr and Fe, calcium oxide (CaO^+) for Ni and titanium oxide (TiO^+) for Cu. This is particularly problematic for the measurement of Cr, Fe and Ni. Therefore helium should be used as a collision gas to reduce these polyatomic interferences. The other elements B, Al, Zn, Cd and Pb do not have any major polyatomics so the use of He as a collision gas is generally not required.

Contamination considerations are of particular importance for elements commonly found within the laboratory environment or those that are present in high-grade water and trace metal nitric acid. In the specific case for the analysis of B, Al and Fe there are variable concentrations of these elements in the water and nitric acid. This can lead to high backgrounds increasing the LOD for these elements but also increases variability between samples and uncertainties in the calibration and quality control samples. There is also the concern of contamination from the environment. The analytical laboratory at Bradwell is within a porta-cabin, with rusting metal work on the interior, therefore Fe contamination of samples is of particular concern. Sample preparation must be conducted in a clean space and samples should be capped after preparation to reduce potential exposures to contaminants.

The effluent stream concentration is also an important consideration for ICP-MS analysis as Perkin Elmer recommends a maximum loading of 0.02% solids in solution, which is equivalent to a 200 mg/L concentration. This is for several reasons concerning overloading the instrument, which will affect aerosol formation and focusing of the beam through the cones, which are easily damaged. Another consideration is around the ionising ability of the plasma torch. There is a finite amount of energy available in the torch to ionise the constituent elements of a sample, therefore there is a maximum loading where increasing the sample concentration will not lead to an increase in signal. Also increasing the solids content can lead to suppression of the signal of the analyte of interest, again due to overloading the system. This is important as the effluent stream for discharge at Bradwell contains high levels of Mg and Na. The Mg is the major component of the FED and sodium hydroxide is used to neutralise the acidic digestion media before abatement takes place. The Mg and Na concentrations were calculated at 26.5 Kg/m^3 Mg and 13.1 Kg/m^3 Na at the start of this project. Therefore the samples need to be significantly diluted to fall below the 200 mg/L concentration before analysis.

Internal standards are also required for the analysis of ICP-MS to correct for any variations in pumping and nebuliser affects. This is done in two ways, the internal standard is directly pumped into the spray chamber alongside the samples through a T-piece junction or all samples require spiking with the same quantity and concentration of internal standard. This means that the internal standard is measured with every injection and the variation in signal is used to correct the response for the analyte of interest. When selecting an internal standard it is best to choose one with a similar atomic mass and first ionisation energy (the energy required to remove the outer most electron to form a +1 ion) to the analyte of interest. This ensures the most similar behaviour of internal standard to the element of interest. However, it is difficult to identify one internal standard that would be representative when measuring a range of elements. Bradwell analysts selected two internal standards scandium (Sc) and terbium (Tb). Scandium (mass 45) is being used as internal standard for lower mass elements B, Al, Cr, Fe, Ni, Cu and Zn whilst terbium (mass 159) is used for higher mass elements Cd and Pb.

All of the above parameters for the analysis were considered and with the help of a Perkin Elmer ICP-MS specialist and an ICP-MS consultancy company, Bradwell set up a “main metals” method (BRAD/22429/OI/00140 Issue 3), which is detailed in Appendix 1 and shall be discussed in more detail in the next section.

1.4. *Current "Main Metals" Methodology and Issues Experienced during Analysis*

Currently the Analytical team at Bradwell use operating instruction BRAD/22429/OI/00140 Issue 3 which was developed with assistance from Perkin Elmer and an ICP-MS consultancy. The key information from this operating instruction is detailed in Appendix 1. As discussed in the previous section He gas is used throughout the run in varying levels depending on the element being measured and the prevalence of the polyatomic isobaric interference. For example Fe-56 is measured with a He flow rate of 4.5 mL/min to remove the $^{40}Ar^{16}O^{+}$ interference. The nine elements are measured within the calibration range 1 – 20 µg/L, which is a sensible range on a NexION instrument. All of the nine elements should have LODs consistently below the lowest calibration standard and the highest calibration standard will not saturate the detector. The matrix effects of the Na and Mg concentration have been considered and the sentencing tank has a dilution factor (DF) of 402 applied, which lowers these concentrations to 67 mg/L Mg and 33 mg/L Na. This is below the 200 mg/L solids content limit for ICP-MS analysis and the ICP-MS consultancy that assisted with method development investigated Mg and Na concentration effects on suppression of signal. They proved that at this DF the nine elements are not significantly supressed by high Mg and Na concentrations; therefore this was set as the minimum dilution to apply for this system. Although the calibration range and blanks are not matrix matched to the high Mg and Na levels the quality control (QC) samples run immediately before and after are doped with the correct levels corresponding to DF402. This ensures that the response to the samples is consistent with the response to the calibration standards. The internal standard is pumped in via a T-piece connection removing the need to spike samples reducing uncertainties associated with pipetting. The calibration standards and internal standards are mixed certified Perkin Elmer products and high quality nitric acid and deionised water are purchased for use as diluents. The QC samples are prepared from individual certified element standards (Perkin Elmer) and doped with certified Mg (Fluka, Sigma-Aldrich) and Na (Perkin Elmer) standards. Therefore all of the chemicals used in the analysis are of the appropriate quality.

Although this method development had been conducted the Bradwell Analytical team was experiencing difficulties with ICP-MS analysis for the "main metals" and mercury method. The main problems experienced were having to undertake repeat analysis either due to run failure (poor calibrations or QCs outside of acceptable limits) and/or inconsistency between sample repeats. This was leading to slow sample turn around which led to delays on plant and difficulties in permissioning discharges to the estuary. The reduction of discharges was particularly problematic as the FEDD process could not be repeated when storage tanks were full. In order to combat these difficulties NNL were contacted to provide assistance due to experience of ICP-MS and the specific use of the functionally identical instrumentation (NexION 300X at Bradwell and NexION 300D at Central Laboratory NNL). Before a visit was arranged the operating instructions provided by Bradwell were examined and apart from overly long rinse times between sample injections there appeared to be no immediate problems with the methods considering the complex nature of the sample matrix. A visit was arranged to Bradwell by an experienced ICP-MS operator from NNL to view the analytical laboratory and meet the team. This visit is detailed in technical memo EX10049/06/10/01 however, the main findings shall be outlined within this report.[1] During the visit the laboratory conditions were discussed as the space was found to be small, full of equipment for other analytical techniques, rusting metal exposure, effluent discharged in the laboratory sink and large volumes of samples were being stored. These were all concerns for potential contamination of samples affecting calibration and sample repeatability. These were addressed during and after the visit with effluent discharge moved to another sink, rusting cabinets painted with anti-corrosion paint and sample storage reduced. Another issue discussed was the experience level of the analysts as ICP-MS is a complicated technique and requires sufficient training to enable competent operation. In order to reduce the impact of inexperience on analysis another visit was arranged for the experienced NNL operator to provide additional training. This was successful and a marked improvement has been reported from Bradwell with an increase in consistency of analysis and a reduction in repeat analysis. Overall this has increased sample turnaround. During the initial visit Bradwell expressed an interest in validation of their ICP-MS methods to ensure accurate, precise and repeatable analysis to provide confidence in elemental analysis used for discharge to the estuary. Therefore NNL were commissioned to provide this validation “off-line” due to access to a functionally identical instrument with availability, not an option at Bradwell due to high demand on their Analytical team and the ICP-MS instrument. This report details this method development and the steps taken for validation are described in the next section.

1.5. Validation of ICP-MS Methods

It is important to validate an analytical method to ensure accuracy, precision and repeatability for confidence in results. It is quite common for analysis for environmental discharges to be conducted by a technique that has been accredited by the United Kingdom Accreditation Scheme (UKAS). Accreditation can be awarded to a laboratory for specific methods based on the need for the work carried out to be traceable, precise and reported correctly. Overall this requires certain procedures to be in place:

- The analysis must have a validated method endorsed by UKAS.
- Analysts that perform this method must be fully trained and signed off. This must be recorded, preferably within a training record.
- Multiple analysts must be signed off to carry out the method. To remove bias the analysis must not be performed exclusively by the same analyst on a routine basis.
- Certified reference materials must be used where possible. If this is not possible internally produced reference materials may be used but must have been analysed to confirm their suitability.
- Quality assurance/control (QC) samples must be analysed regularly to assess the performance of the method and instrument. These must be recorded preferably in a quality control chart.
- Instruments must be regularly serviced and maintained, which must also be recorded.
- The results must be collated, checked and approved by the appropriately qualified personnel.
- The results must be reported to the customer in an agreed format, with specified units and within established timeframes.
- Good house keeping standards must be maintained in the laboratory where the analysis is conducted.
- All of the above must be traceable as the laboratory and/or method is subject to audit by UKAS.

Bradwell do not require UKAS accreditation for their environmental discharges however, they operate their laboratory, analysis and record keeping in the spirit of UKAS adhering to many of the points above. Although there is not a formal validation procedure set out by UKAS for ICP-MS method validation NNL has conducted validation projects for different UKAS methods performing the following steps:

- Critical assessment of the isotope of interest including potential isobaric interferences and/or matrix affects.
- Assess the calibration range using multiple concentrations ensuring a working range and calculation of a theoretical LOD. These calibrations should be run over 10 different days to assess repeatability of the method.
- Assess the working range by calibrating the ICP-MS and measuring spiked samples of known concentrations within the calibration range, which are different concentrations to the calibration standards. This should be repeated 5 times on 5 different days.
- Assess the run repeatability by calibrating the ICP-MS and running 20 spiked samples of the same concentration and assess the variability, standard deviation (SD) and % relative standard error (%RSD).
- Assess the repeatability between runs by repeating the analysis of 5 spiked samples (with the same concentration as before) within 4 separate runs and assess the variability as before including the previous 20 samples.
- Assess the robustness of the procedure by having two different analysts prepare and analyse calibration standards, QCs and spiked samples on separate occasions each.

Once the above steps have been performed then running comparative studies on real plant samples is suggested. In this instance it is difficult to compare data as the validation of the method is occurring on a different site. Therefore one plant sample has been shipped from Bradwell where analysis has been performed on both instruments, which can be compared. Bradwell also purchased a manufactured sample, which is in the correct sample matrix with all nine elements being measureable within the calibration range 1 to 20 µg/L after a dilution factor of 10000 was applied. This sample has been analysed at NNL Central Laboratory and the results are detailed in this report. The sample will also be run at Bradwell during the method transfer with a site visit from an NNL operator. The results can then be compared by Bradwell to assess the successful transfer on the method.

1.6. Report Outline

In accordance with the requirements outlined in the previous section the following has been investigated and is presented in this report:

- The investigation into optimal helium gas flow rates to minimise polyatomic isobaric interferences for the nine elements.
- The investigation of matrix effects of Na and Mg concentrations on the measurement of the nine elements.
- The investigation of rinse times between injections to minimise analysis run time.
- Optimisation of instrument parameters.
- The validation and robustness testing for each of the three methods.
- The measurement of a Bradwell plant sample and a manufactured sample.

This report also details recommendations for the successful implementation of these validated methods.

2. Method Development and Optimisation of "Main Metals" Method

Prior to the validation of an analytical technique the conditions for the method must be optimised to ensure accuracy, precision and repeatability. As the "main metals" method is already in current use at Bradwell and was setup in partnership with Perkin Elmer the parameters have been used as a basis for optimisation. All the chemicals utilised in the method development are identified in Appendix 2.

2.1. Investigation of Magnesium and Sodium Matrix Effects

As discussed previously the high Mg and Na levels in the samples require a large dilution to reduce the solid contents below 200 mg/L and at a level where suppression of the signal is not significantly impacted. Currently the samples have a DF402 performed on them before analysis. This means that the instrumental limit of detection (LOD) for each element has the same dilution factor applied. This is problematic if the DF corrected method LOD is higher than the discharge limit for the sentencing tank at Bradwell. Fortunately most of the discharge limits for the nine elements are significantly higher than the anticipated LODs. Instrument dilutions also increase uncertainty in a measurement. Therefore a sample with a smaller DF applied will have less uncertainty introduced to the result. In order to investigate varying Mg and Na concentrations calibration ranges between 1 - 20 µg/L were prepared from nine individual element standards and were spiked with varying concentrations of Mg and Na equating to different dilution factors of sentencing tank effluent. The dilutions performed are detailed in the **Table 2**.

Table 2: The Mg and Na concentrations equivalent to sentencing tank dilutions

Equivalent DF	Mg concentration (mg/L)	Na concentration (mg/L)
100	266	132
200	133	66.1
300	88.5	44.1
400	66.4	33.1
500	53.1	26.4

Although DF 100 exceeds the 200 mg/L loading for ICP-MS analysis it was tested to see if the nine elements could be analysed in these conditions as a DF100 is an easy dilution to perform for procedural repeatability. However, at DF100 there was a significant increase in all the backgrounds for all nine elements, which significantly increased the LODs and uncertainty within the calibration. This trend became less pronounced as the Mg and Na concentrations decreased, with little difference observed between DF300, DF400 and DF500. These concentrations were also investigated by calibrating the instrument in the absence of Mg and Na and then 10 µg/L QC samples were prepared with these varying concentrations. The equivalent dilutions showed increased suppression as the concentrations of Mg and Na were increased. The DF500 showed up to 10% suppression of the internal standard. When the correction was applied to the nine elements all QCs were within 10% of the expected values. For the corresponding DF400 and DF300 up to 15% and 20% suppression was observed and when the QCs were internal standard corrected all QCs were within 10% of the anticipated concentration except for Al, Fe and Cr, which were all higher than anticipated. This appeared unusual as this was not experienced at Bradwell at DF402. On investigation the Mg certified standard that was used for spiking contained trace impurities of Al, Fe and Cr. Therefore the same Mg standard was purchased from Fluka that Bradwell use for their QC spiking. When the experiment was repeated with the new Mg standard, the previously elevated Al, Fe and Cr QC results decreased to within 10% of the anticipated values for both DF300 and DF400. This suggested that even though suppression is increased with DF300 levels of Mg and Na it was still possible to measure the nine elements. However, there was increased variability between the QCs suggesting an increase in the uncertainty between repeat measurements at DF300. DF200 and DF100 were also analysed with up to 35% and 50% suppression of internal standard observed, respectively. When the nine elements were internal standard corrected there were large discrepancies between the corrected values and the anticipated 10 µg/L concentrations. This suggested that, at these higher concentrations of Mg and Na, the suppression of the internal standard did not correlate with the suppression of the individual elements. Therefore the QCs were not able to be internal standard corrected to calculate the correct result. The variation in suppression between the elements is due to the differences in first ionisation energies. The suppression is higher for elements with higher first ionisation energies. This is an increasingly important factor as the plasma has to ionise more atoms as the matrix becomes more concentrated.

From this investigation it was concluded that the DF400 showed the best compromise with least internal standard suppression and the smallest variability between results from repeated analysis of QC samples. Initially it was intended that the validation work should proceed by spiking the samples with the equivalent DF400 concentrations of Na and Mg. However, during a site visit to Central Laboratory by Bradwell staff it was explained that the FEDD process had been altered leading to an increase in dissolution of FED per batch. This led to an increase in Mg concentration up to 33.3 Kg/m^3 and a decrease in Na concentration to 11.5 Kg/m^3 as the FEDD liquor was less acidic so required less sodium hydroxide for neutralisation. Without repeating method development for this new concentration it was decided that a new DF500 applied to the new FEDD liquor concentrations gave similar concentrations of Mg and Na to the previous DF402. Therefore the new Mg and Na concentrations were set at 67.0 and 23.0 mg/L respectively, equivalent to a DF500. The LODs were also examined and the change to DF500 did not increase any of the LODs above the estuary discharge limits. Following the site visit Bradwell analysts applied the DF500 during analysis of their plant samples.

2.2. Investigation of Helium Flow Rates to Remove Polyatomic Interferences

As discussed previously He is required as a collision gas to remove polyatomic isobaric interferences during ICP-MS analysis. The pre-existing “main metals” method used a minimum flow rate of 0.5 mL/min of He for elements that did not have any significant polyatomic interferences (Appendix 1). These elements were B, Al, Cd and Pb and both internal standards Sc and Tb. All of these elements were investigated for signal strength and repeatability with and without He as a collision gas. The 0.5 mL/min flow rate showed no additional benefit with a reduction in signal for the measurement of B, Cd, Tb and Pb so was removed. However, the He did appear to reduce variability in blanks when measuring Al and Zn and the internal standard Sc appeared to be more stable. Therefore a 0.5 mL/min flow rate was retained for these three elements. The He flow rate for Fe was increased from 4.5 mL/min to 5.25 mL/min, which was previously optimised by NNL in other project work. The increase did reduce the signal, which decreased the gradient of the calibration line. The blanks were significantly reduced which decreased the LOD and improved the calibration, increasing the R^2 value. During this work there had not been any concerns with measuring Cr, Ni and Cu with good consistency of blanks achieved, good LODs and good calibrations obtained therefore the He flow rate was not altered. It was also considered that the Ca and Ti levels responsible for polyatomic interferences may be significant in the FEDD effluent, causing variability during measurement of these elements. Therefore the new He flow rates were selected before the validation commenced and are detailed in Appendix 2.

2.3. Optimisation of Instrument Parameters

The spray chamber on the Central Laboratory NexION was identical to the spray chamber used by Bradwell (details in Appendix 2). The manufacturer's flow rate suggestions and flow rates from the pre-existing method were used to set the peristaltic pump conditions outlined in Appendix 2. The rinse times for the analysis were also investigated as longer rinse times increase analysis time, which reduces sample throughput increasing the delivery time of results. As this method is being used in a plant environment, which is reliant on speed of delivering analytical results, any reduction in analysis time is beneficial. Following the initial visit to Bradwell the rinse times had been slowly reduced. A new rinse time of 90 seconds was investigated and no carryover was observed between the highest calibration standard (20 µg/L) and the blank following immediately after. A reduction in sample flush time (the time allowed for the sample to be fed through the instrument before a measurement is taken) to 90 seconds showed no significant impact on the measurement of the nine elements. Therefore all of these parameters were applied to obtain an accurate precise and reliable result in the shortest time frame. Following optimisation each injection took approximately four minutes.

2.4. Selection of Isotopes for Analysis

Previously Bradwell had been measuring multiple isotopes of the same element, e.g. B-10 and B-11. As the FEDD effluent consists of only naturally abundant isotopes for the analytes of interest it is not necessary to measure more than one isotope of each element. With each additional isotope measured the analysis time increases by approximately 15 seconds. The major isotopes with no other elemental isobaric interferences were selected for method validation (Appendix 2). During the method development zinc showed consistently low results for Zn-66, therefore Zn-68 was also measured to assess the best isotope for use.

2.5. Internal Standard Concentration

Bradwell introduce their internal standard via a T-piece connection. Bradwell pump internal standard constantly leading to a delivery of 500 µg/L into the instrument, which is significantly more concentrated than the range the samples are measured within (1 – 20 µg/L). The counts per second (CPS) also exceed 2,000,000. This is important as the detection alters from pulsed to continuous counting at this threshold. The detection methods have a different response to each other therefore the variations observed in the analogue counting range may not equate to variations observed in the pulse counting range. Use of the internal standard to correct values in this way may introduce errors. Central Laboratory spike all blanks, calibration standards, QCs and samples with 100 µL of 500 µg/L internal standard. This gives an end concentration of 5 µg/L in each sample when injected. This is within the calibration range for the samples, QCs and standards and avoids the issues discussed above. Therefore for this developmental work the Central Laboratory regime was adopted.

The parameters were fixed after this method development and are detailed in Appendix 2. Overall the method development showed that rinse times could be reduced and single isotopes could be measured (except Zn) decreasing analysis time per sample. The He flow rates were adjusted for optimised sensitivity for the individual elements and internal standards to provide a good calibration and the lowest LODs. Once the parameters had been fixed the validation portion of the programme commenced and is described in the next section.

3. Validation Results of "Main Metals" Method

The validation procedure was conducted following a standardised procedure using the fixed method outlined in Appendix 2. All chemicals used for analysis were of appropriate grade and all standards were certified, the details of which can be found in Appendix 2. Variable and fixed Eppendorf pipettes were used to dilute all calibration standards, QCs, samples and internal standard spiking. These pipettes were checked regularly to ensure they were within 2% uncertainty of the anticipated mass for the equivalent volume of deionised water. Fresh pipette tips and consumables were used during all analysis, and when glassware was used it was appropriately cleaned and dried before use. All samples were analysed within 24 hours of sample preparation. To reduce waste within the active laboratories at Central Laboratory all standards, QCs and samples were prepared and spiked with internal standard within the non-active laboratory and transferred to the ICP-MS laboratory.

For each analysis a calibration range was prepared from a mixed Perkin Elmer "special" standard with standards at 1, 2, 5, 10 and 20 µg/L of each element (detailed in Appendix 2). Fresh QCs were prepared from nine individual elemental standards at a final concentration of 10 µg/L, the same QC concentration as is used at Bradwell. When preparing the QCs 1 mL of 0.3 mol dm^{-3} nitric acid (HNO_3) was replaced with 1 mL of solution containing 670 mg/L Mg and 230 mg/L Na in 0.3 mol dm^{-3} HNO_3. This was to matrix match the QCs with the effluent stream at Bradwell to give a final concentration of 67.0 mg/L Mg and 23.0 mg/L Na (equivalent to DF500). Following the validation principles outlined in Section 1.5 matrix-matched 5 µg/L repeat samples and working range samples (i.e. various values within the calibration range) were prepared from the mixed nine metal standard and the same Mg and Na stock solution. Blanks were prepared from the 0.3 moldm^{-3} HNO_3 diluent used for the analysis. Before sample preparation commenced the quantity of HNO_3 was checked to ensure the full sample range could be made from the same stock. This was to minimise blank variation in particular for Al, Fe and Zn concentrations. All blanks, standards, QCs and samples were diluted in 10 mL volumes in 15 mL centrifuge tubes then spiked with internal standard solution before analysis. This is detailed in Appendix 2 and the standardised run list for each analysis is shown.

All of the validation data produced from the project has been calculated from first principles from the raw intensities. The reason for this was to obtain a direct comparison between raw data worked up by analysts and the concentrations calculated by the ICP-MS software, which is discussed in Section 3.6. All of the data has been worked up by the analyst who conducted the analysis and checked independently before transcription into this report. The transcription of all the data presented within this report has also been checked. Each element has been reported separately within section 4.1 to 4.9 and contains three distinct tables. The first table presents the calibration range, gradient of the calibration, R^2 value of the gradient and the calculated LOD for each analysis. The R^2 value (the correlation of data points to the straight calibration line drawn through them) should be greater than or equal to 0.9990. This is the limit NNL have previously worked towards when validating UKAS ICP-MS methods. This is not always possible depending on the element and is discussed further in Section 3.1. The LOD has been calculated by multiplying the variation of the blanks (standard deviation of the ten blanks) by three. The second table details the spiked matrix matched working range samples with their anticipated values, the result achieved and the % difference and is discussed further in Section 3.3. The third table details the analysis of spiked matrix matched repeat samples at 5 µg/L, which were analysed in order to establish the precision of the technique for each element. The information reported gives the result achieved, the % difference from anticipated concentration and the average, standard deviation (SD) and relative standard deviation (RSD) results per run. The repeats are further discussed in Section 3.2.

During the validation process there were no significant differences in response between Zn-66 and Zn-68. Therefore the data presented in this section is for Zn-66 only.

3.1. Calibration and Limits of Detection

During the validation process it is useful to examine calibration gradients and LODs to establish an anticipated operating window. This is particularly useful for an operator conducting routine analysis as any deviations outside of the operating window will give early indications of problems with the analysis or instrument performance. It is also important to record the R^2 value of the calibration line. This is a measure of linear correlation between each of the calibration points and the variance observed form the line of best fit (trend line) through all of the data points, which is fixed through zero. It can be used to assess the quality of the calibration and normally an R^2 value of 0.9990 and above would suggest excellent correlation for an ICP-MS method, therefore the calibration would be acceptable for use.

These parameters will be discussed for the individual elements below:

- B – the calibration gradients observed for B vary between 3799 and 11099, showing largest variability of the nine elements. However, this is due to varying sensitivity of the ICP-MS depending on the tuning parameters before analysis is conducted. The R^2 values for the calibrations are all ≥ 0.9990 except on 19/10/15 where the R^2 value was 0.9983. The LODs also showed a large variation between 0.020 and 0.92 µg/L. However, B can show varying background levels in deionised water and HNO_3, which increases the variation and the LOD. Therefore it is important to ensure that the B blanks are consistent within an analytical run to achieve low LODs and repeatable accurate and precise results. (**Table 3**)
- Al – the calibration gradients for Al vary between 11933 and 27930, one gradient (12/10/15) is unusually high at 49534. The R^2 values for the calibration graphs are as low as 0.8671 and the LODs vary between 0.13 and 2.2 µg/L. The poor calibrations are due to high Al backgrounds, which show significant variation. Al is ubiquitous in the diluents and as a potential contaminant; therefore it is particularly difficult to measure at these low levels. As Al is not being used to discharge the effluent to the estuary it would be acceptable to apply a higher uncertainty to these results. (**Table 6**)
- Cr – the calibration gradients observed for Cr vary from 3726 to 7264, all of these calibration graphs have an R^2 value ≥ 0.9990 and the LODs are considerably lower than the calibration range and vary between 0.0088 and 0.037 µg/L. (**Table 9**)
- Fe – the calibration gradients for Fe are the lowest observed due to the high He flow rate (5.25 mL/min). This reduces the proportion of Fe^+ ions from the sample arriving at the detector. The gradients vary between 356 and 690, where ten R^2 values are ≥ 0.9990, the rest are lower and fall as low as 0.9891. Fe-56 is a particularly difficult isotope to measure due to the high concentration of ArO^+, a high He flow rate and issues surrounding contamination of samples and diluents. Although a higher R^2 value is preferable, due to the difficulties associated with measuring this isotope an R^2 value ≥ 0.990 would be acceptable for analysis. The LOD varies between 0.19 and 0.69 µg/L, which is approaching the lowest calibration standard. (**Table 12**)

- Ni – the calibration gradients vary between 1867 and 3676, where all R^2 values were ≥ 0.9990. The LODs vary between 0.0032 and 0.045 µg/L, except one unusually high LOD at 0.12 µg/L on 03/11/15. This run shows a large variation in blanks not seen in other runs. The LODs are considerably lower than the calibration range excluding 03/11/15. (**Table 15**)
- Cu – the calibration gradients vary between 4693 and 9248, with all calibrations with an R^2 value ≥ 0.9990. The LODs vary between 0.0073 and 0.058 µg/L except an unusually high LOD from 23/10/15 at 0.12 µg/L. This run shows a large variation in blanks not seen in other runs. The LODs are considerably lower than the calibration range excluding 23/10/15. (**Table 18**)
- Zn – the calibration gradients for Zn vary between 1948 and 4316. However, the majority of R^2 values for these calibrations are between 0.9945 and 0.9993, except a particularly low gradient on 26/10/15 with an R^2 value of 0.9711. As with Al and Fe, Zn is ubiquitous and the large variations in backgrounds increase uncertainty. However, another reason for these variations in blanks is the suppression effects from the carryover of high Mg and Na concentrations in the blanks after QCs and samples. The blanks later in the run after the high Mg and Na matrix has been injected show significant decrease in intensity in comparison to the earlier blanks. This suggests Zn is particularly susceptible to suppression from this matrix. This is also reflected in the varying LODs between 0.23 and 1.3 µg/L, which on occasion exceed the lowest calibration standard. (**Table 21**)
- Cd – the calibration gradients vary between 3750 and 6654, all of these calibrations have an R^2 value ≥ 0.9990 and the LODs vary between 0.00083 and 0.0026 µg/L. The LODs are significantly lower than the calibration range. (**Table 24**)
- Pb – the calibration gradients observed for Pb are fairly large in comparison to the other elements but show the smallest variation between and 23755 and 35380, all of these gradients have an R^2 value ≥ 0.9990 and the LODs vary between 0.0015 and 0.0086 µg/L. The LODs are significantly lower than the calibration range. (**Table 27**)

Over the 15 calibrations Cr, Cd and Pb have shown no indication of blank contamination or any large variations in the blanks leading to R^2 values ≥ 0.9990 and LODs considerably lower than the calibration. Apart from one exception for both Ni and Cu the LODs have been significantly lower than the calibration range and all the R^2 values are ≥ 0.9990. On both of these occasions large variations in the blanks were observed suggesting contamination. The low LODs achieved for these elements is useful for generating data for discharges where large DFs are applied. These low LODs ensure that a sample with detectable levels of these five elements will be lower than the discharge limits. The LODs for the other four elements (B, Al, Fe and Zn) are higher, and therefore closer to the calibration range. The closer a measurement is to the LOD then the larger the uncertainty will be as the background variation in the signal becomes more relevant. Therefore calibrations near the LOD, or in some instances with Al and Zn below the LOD, will have a lower R^2 value as bigger variances from the calibration gradient will be observed. Although not ideal, a higher level of uncertainty on these four elements is tolerable as they are significantly lower than the discharge limit. For example a Zn instrumental LOD of 1.3 µg/L with a DF500 applied is 650 µg/L, which is three orders of magnitude lower than the discharge limit of 304 mg/L for the Bradwell sentencing tank.

3.2. Sample Repeats at 5.00 µg/L Investigation

The “sample repeats” section of the validation is to ensure that repeatability is proven within an analytical run and between analytical runs on different days. This proves repeatability and also demonstrates the precision of the analysis. Analyst 1 prepared 20 repeats of matrix matched samples containing 5.00 µg/L of each of the 9 elements on two occasions (12/10/2015 and 14/10/2015) to assess the repeatability within the run. Analyst 1 then prepared a further four batches of five 5.00 µg/L and Analysts 2 and 3 prepared five batches of five 5.00 µg/L repeats to be analysed on different days. Each batch of repeats have been averaged, the standard deviation calculated and the relative standard deviation (%RSD) calculated. This has generated 90 repeat samples in total over the validation period. Each element is discussed individually below:

- B – Overall only two samples exceed a 10% difference from the 5.00 µg/L expected concentration. One result on 14/10/2015 was within 11% difference however, a repeat on 27/10/2015 was 55% higher than expected. This result appears to be anomalous and has been removed from any calculations. The B shows variation above and below the expected 5.00 µg/L concentration with %RSDs below 2.41%. When all 89 repeats are examined together the average result is 5.21 µg/L with a %RSD of 6.1%, which is a good estimation of the precision of this method. (**Table 5**)
- Al – The Al repeats have shown a large variation above and below the anticipated 5.00 µg/L concentration. One result has been removed at a concentration of 32.2 µg/L (27/10/2015), which may have been contaminated as Al is ubiquitous in the diluents. Only 56 results are within 10% difference of the anticipated concentration and generally large %RSDs are observed up to 13.9%. As discussed previously Al is difficult to measure at these concentrations by ICP-MS and a large uncertainty is likely. When all 89 repeats are examined together the average result is 5.44 µg/L with a %RSD of 15%, which is a good estimation of the precision of this method. (**Table 8**)
- Cr – The repeat samples run on 12/10/2015 and 14/10/2015 are higher than the expected sample value with up to 13% difference observed. These two runs also have high QCs suggesting the runs have been contaminated. However, the %RSDs are 2.89% and 2.68%, which suggests the repeatability between the samples is good. The rest of the repeats are within 8.1% of the expected 5.00 µg/L with the highest %RSD of 2.24%. When all 90 repeats are examined together the average result is 5.21 µg/L with a %RSD of 3.6%, which is a good estimation of the precision of this method. (**Table 11**)
- Fe – Two repeats have been rejected as contaminated due to their result of 41.6 µg/L (14/10/2015) and 26.7 µg/L (27/10/2015). The remaining repeats show 68 samples are within 10% of the expected repeat value with 9 results exceeding 20% difference. Only 6 repeats are below 5.00 µg/L suggesting the Fe is not as supressed as the internal standard Sc. The large variation observed for Fe is anticipated as Fe is a ubiquitous contaminant and because of the large ArO^+ interference. When all 88 repeats are examined together the average result is 5.43 µg/L with a %RSD of 6.8%, which is a good estimation of the precision of this method. (**Table 14**)
- Ni – The repeat samples run on 12/10/2015 and 14/10/2015 are higher than the expected sample value with up to 13% difference observed. These two runs also have high QCs suggesting the runs have been contaminated. However, the %RSDs are 2.64% and 2.82%, which suggested the repeatability between the samples is good. The rest of the repeats are within 6.6% of the expected 5.00 µg/L with the highest %RSD of 2.02%. When all 90 repeats are examined together the average result is 5.24 µg/L with a %RSD of 3.3%, which is a good estimation of the precision of this method. (**Table 17**)
- Cu – The copper repeats are generally lower than the expected 5.00 µg/L concentration and would suggest Mg and Na concentrations supress Cu to a greater extent than Sc. All of the repeats are within 10% difference of the expected concentration except 2 at 11% and one at 9.32 µg/L on 14/10/2015 This repeat was uncharacteristically high, if this is rejected then the highest %RSD observed is 2.50%. When all 89 repeats are examined together the average result is 4.75 µg/L with a %RSD of 3.5%, which is a good estimation of the precision of this method. (**Table 20**)

- Zn – Some of the zinc repeats have been excluded due to contamination as they are considerably higher than expected (7.11 µg/L on 12/10/2015 and all samples on 27/10/2015). The repeats are generally lower than the expected 5.00 µg/L concentration and a large % difference is observed with only 55 of the repeat samples within 10% of the expected concentration with 2 out of the remaining 84 repeats exceeding a 20% difference. The % RSD observed is as high as 12.8%. As seen Zn can show a large variation in backgrounds and is more susceptible to suppression than the corresponding internal standard Sc. As discussed the discharge limit for zinc is considerably higher than the sample range measured therefore the higher uncertainty is tolerable in this circumstance. When all 90 repeats are examined together the average result is 4.77 µg/L with a %RSD of 13%, which is a good estimation of the precision of this method. (**Table 23**)
- Cd – All of the repeats for Cd are within 7.5% of the expected 5.00 µg/L concentration and the largest %RSD observed is 1.87%. The repeats vary above and below the expected 5.00 µg/L indicating Tb is a good internal standard for Cd in this analysis. When all 90 repeats are examined together the average result is 4.93 µg/L with a %RSD of 2.6%, which is a good estimation of the precision of this method. (**Table 26**)
- Pb – All of the repeats for Pb are within 9.4% of the expected 5.00 µg/L concentration and the largest %RSD observed is 1.19%. All of the repeats are lower than 5.00 µg/L, which suggests Pb is more susceptible to suppression by high Mg and Na concentrations than the internal standard Tb. When all 90 repeats are examined together the average result is 4.68 µg/L with a %RSD of 1.4%, which is a good estimation of the precision of this method. (**Table 29**)

There have been some anomalous results due to suspected contamination that have been removed from the repeat data comparison and have not been included in the calculation averaging of all 90 repeats. Overall good agreement is shown for B, Cr, Fe, Ni, Cu, Cd and Pb.

3.3. Working Range Investigation

The “working range” section of the validation process is necessary to ensure spiked matrix matched samples that are different to the calibration standards are within a % difference from the expected value. These samples are not fixed and each analyst carried out their own dilutions but within the calibration range of 1 – 20 µg/L. In total 70 samples were prepared. The working ranges were prepared from a different stock solution to the repeats in Section 3.2. It is important to note that uncertainty of a measurement will increase as the LOD is approached. This is particularly important for Al and Zn as the LODs are high and in some cases the LOD exceeds the 1 µg/L calibration standard. This should be less problematic for elements with particularly low LODs such as Cd and Pb.

Each element’s working range is discussed below:

- B – The working range experiments for B concentrations show that 18 samples exceed 10% from the expected concentration value but are within 16%. The working range samples are distributed above and below the expected levels therefore this does not suggest the samples are contaminated. However, it reinforces the importance of control blanks of B during analysis to reduce uncertainty. (**Table 4**)
- Al – The Al working range samples show the largest variation with results above and below the expected concentrations, with 28 samples exceeding 10% difference and 11 of these exceeding 20% difference. One sample (27/10/15)

shows 75% difference from the expected concentration and this appears to be contaminated. The variation observed is consistent with the variation in blanks, repeats and QCs. It is difficult to achieve accurate and precise data with poor calibrations due to high and varying backgrounds. (**Table 7**)

- Cr – The working range samples run on 12/10/2015 and 14/10/2015 are higher than the expected sample value by between 12 & 14%. These two runs also have high QCs suggesting the runs have been contaminated. The other 60 samples for the different runs are all within 10% of the expected concentrations. (**Table 10**)
- Fe – The working range samples run on 12/10/2015 and 14/10/2015 are higher than the expected sample concentrations as seen for Cr. Only 38 out of the remaining 60 working range samples are within 10% of the expected sample concentration, with two exceeding 30%. This would suggest that the variability is large in the measurement of Fe and the suppression of Fe does not correspond with the suppression of Sc. (**Table 13**)
- Ni – 13 of the 70 samples differ by more than 10% of the expected sample concentrations. All of these samples are at the lower end of the calibration range and are only seen in the first five runs. This is unusual as the LOD for Ni is not as close to the calibration range as Al and Zn. Therefore it would suggest Ni contamination was prevalent up to 19/10/2015. All other samples were within 10% of the expected concentrations. (**Table 16**)
- Cu – The 70 working range samples for Cu were all within 6.5% of the anticipated value of the sample. (**Table 19**)
- Zn – The Zn working range samples are generally lower than the expected sample concentrations suggesting it is more susceptible to suppression of high Mg and Na concentrations. The data shows 42 samples are lower than 10% of the anticipated values up to 30% lower than expected, and significant variation is observed. An additional 3 samples are over 30% higher than the expected sample concentrations. These three samples stand out and it would suggest they have been contaminated. (**Table 22**)
- Cd – The 70 working range samples for Cd were all within 9.6% of the anticipated value of the sample. (**Table 25**)
- Pb – The 70 working range samples for Cd were all within 6.4% of the anticipated value of the sample. (**Table 28**)

As seen with the repeats there is excellent agreement with expected concentrations for the working range samples for Cr, Ni, Cu, Cd and Pb. This is consistent with the observations in gradients, LODs, repeats and QCs (excluding 12/10/15 and 14/10/15 for Ni and Cr). A good agreement is observed for B and the discrepancies where the working range is exceeded demonstrate it is important for background consistency by controlling the blanks during analysis. The agreement for Fe and Zn shows larger variations, which would impose a greater uncertainty but as discussed previously the results measured are significantly below the discharge limit to the estuary at Bradwell, therefore the greater uncertainty can be tolerated. The Al working range shows the largest variation and therefore will have large uncertainties associated with it. As Al is not subject to discharge limits it is at the customer’s discretion if the larger uncertainties can be tolerated.

3.4. Evaluation of QC Data at 10 µg/L

The QC data from the fifteen validation runs has been collated and is detailed in **Table 30**. This data can be used by Bradwell to compare the quality control charts from their previous runs to see if the new method parameters have generated more consistent results with smaller deviations from the expected QC value. However, the trends can be discussed in this report as 90 new QCs have been generated.

Each element’s data set is discussed in turn in comparison with the anticipated 10 µg/L concentration.

These parameters are discussed for the individual elements:

- B – The vast majority of QC values were within 10% of the anticipated value with only four QCs exceeding 11 µg/L, but they were still within 11% of the expected value.
- Al – The QCs showed variation throughout the validation programme with 18 QCs exceeding the 10% boundary, which varied between 8.22 and 12.9 µg/L. In the extreme case of 12.9 µg/L the QCs for this run (12/10/15) were all high. This would normally require the analysis to be repeated, however, aluminium is not required for discharge. Therefore it would be at the discretion of the customer as to whether the result with a higher uncertainty would be acceptable.
- Cr – The QC data excluding 12/10/15 and 14/10/15 fell within 10% of the expected value. On these two dates the QCs were generally high and it would suggest there was a contamination issue or discrepancy with the blanks. In these circumstances the analysis should be repeated if the sample has a measurable quantity of Cr present.
- Fe – The QC data for Fe on 12/10/15 and 14/10/15 was also greater than anticipated which was also observed for Cr, for the same reasons. The rest of the QC data is within 15% of the anticipated values, and does not exceed 11.5 µg/L. In the case of Fe larger variations have been observed in the calibration graph R^2 values, repeat samples and working range. As the measured range is significantly below the estuary discharge limit then the larger variation could be tolerated.
- Ni – The QC data for Ni, except one QC at 11.2 µg/L, was within the 10% uncertainty of the anticipated QC value. The QCs showed variation above and below the anticipated value.
- Cu – The QC data for Cu was generally lower than the anticipated QC value, with seven QCs below 9 µg/L, however, they are within 11% of the anticipated value.
- Zn – The Zn QC data was consistently lower than the anticipated QC value suggesting Zn is more susceptible than the other eight elements to suppression from the high Mg and Na concentrations. In total 27 QC samples were below 9 µg/L and 24 of these QCs were within 15% of the anticipated value. As with Fe the discharge limit for Zn is significantly higher than the sample concentrations measured by ICP-MS. The greater uncertainty associated with the measurement is not significant, therefore variations in the QC value of up to 15% could be tolerated.
- Cd – The Cd QC data showed all QCs were within 10% of the anticipated QC value. They were generally between 9 – 10 µg/L, which suggests Cd is more susceptible to suppression of the high Mg and Na concentrations in comparison to the internal standard Tb.
- Pb – The QC data for Pb, except one QC at 8.89 µg/L, was within the 10% uncertainty of the anticipated QC value. The QCs showed variation above and below the anticipated value.

The QC data has shown that B, Cr, Ni, Cu, Cd and Pb can operate within 10% of the anticipated QC value, and therefore action levels should be set at 9 µg/L and 11 µg/L as lower and upper boundaries. The data for Fe and Zn have consistently shown variation within 15% of the anticipated QC value and due to the significantly higher discharge limits it is suggested the action levels for the QCs are set at 8.5 µg/L and 11.5 µg/L. The QC data for Al has shown the largest variation, however, this data is not necessary for discharge. Therefore the boundaries set and the acceptable uncertainty is at the customer’s discretion with the recommendation of action levels set at 8.0 µg/L and 11 µg/L.

3.5. Assessment of Analyst Bias

An important aspect of validation of an analytical method is to ensure a precise, accurate and repeatable result is measured every time. It is possible for a bias to exist within a method, which could be equipment, instrument, environment or operator based. This bias could affect the repeatability of the measurement. Operator based bias could be due to training levels or poor laboratory practice for example. It is possible to test operator bias by repeating measurements with different operators and comparing the results. Therefore as part of the validation project multiple analysts are used to ensure the same operator doesn't develop and fully validate a method with a bias. Therefore for this project three analysts conducted the analysis and within **Tables 1 – 27** the analyst who conducted the calibration, repeats and working range is identified (as Analyst 1-3). When comparing this data it is important to look for patterns for example Analyst 1 continually generates data with low R^2 values, where as Analysts 2 and 3 continually generate data with R^2 values ≥ 0.9990. This would suggest Analyst 1 is having difficultly controlling blank contamination and/or is not using a pipette correctly. Therefore if a method is not prone to operator bias there should be no noticeable differences in data.

The data provided in these tables has been examined and there is no detectable bias between analysts. When the calibration gradients are examined they are not consistently high or low for a particular analyst with variation in LODs spread across all analysis. All three analysts have generated results with good precision of <1% RSD for the 5 µg/L repeats. All analysts also produced "one off" samples with unusually high results likely to be due to unavoidable contamination. Therefore there appears to be no detectable bias present in the method. It is important to note that the three analysts selected for the validation work were of varying skill and experience levels concerning ICP-MS analysis. The analysts have different backgrounds, two with a graduate chemistry degree and one with a scientific apprenticeship. They have been in the analytical team between 1.5 and 2.5 years. All three are trained in the operation of ICP-MS, however, one routinely uses the instrument whilst the other two analysts use the instrument intermittently.

3.6. Variations Between Data Worked Up by Analysts and Instrumentally Derived Concentrations Page

As discussed previously all of the data provided within this report was worked up from first principles using the raw intensity count data. The ICP-MS software can calculate the data from the calibration range and this information can be used directly. Bradwell would prefer to use the concentration page routinely as this requires less data work up, which is complicated with potential errors and time consuming for both preparer and checker. Therefore due to the quick turnaround requirements for analysis confidence in use of the concentration page is essential.

During the training visit to Bradwell four key indicators were discussed and explained to the analytical team that if adhered to will ensure the concentrations page can be used and raw data work up avoided. These are detailed below:

1. Ensure the blank used to background subtract from all subsequent results in the run is representative of all the blanks in the run. This will need to be done from the signal intensities on the intensities page.
2. Inspect the calibration plot and ensure the R^2 value is 0.999 or greater. This will need to be done using the "calib view" function on the software.

3. Inspect the internal standard signals throughout the run to ensure consistency and performance of the mass spectrometer. This will need to be done from the signal intensities or the calculated concentrations.
4. Assess the calculated QC concentrations to ensure they are within the permissible uncertainty range.

The validation project produced 15 datasets, which can be exported into excel. The data contained within the excel spreadsheets includes a page for the raw intensity data ("intensity" tab) and a page for software generated concentrations ("concentrations" tab). The raw intensities have been used to work up the data that can be compared to the datasets the ICP-MS software has generated. The concentrations pages for the 15 datasets were examined using these four key indicators to identify any discrepancies and were noted. The average of the ten procedural blanks was compared to the blank used for the run subtraction (Blank 3, directly before the calibration range). The raw data work up was then copied to the concentrations page and the % difference between the two sets of data was calculated. A small variation between datasets is possible as the average blank will not match blank 3 perfectly. All of the validation data for B, Cr, Ni, Cu, Cd and Pb shows complete agreement between the concentrations data and the raw data work up. This however, is not the case for Al, Fe and Zn. There are discrepancies between the two data sets for four Fe runs, six Al runs and eight Zn runs out of the total 15 runs. This is not surprising as Al and Fe have shown the largest variations in blanks and Zn has been consistently low due to the difference between high Mg and Na concentration suppression effects for the internal standard and Zn. In these incidents where the data was inspected for the Al and Fe there is a discrepancy between the average blank and blank 3, therefore samples are either consistently high or low in comparison. In these instances an alternative blank that is more representative of the average blank can be selected and the data reprocessed using the concentrations page. There are also some instances where a calibration standard has been removed as it is uncharacteristically high or low affecting the gradient therefore affecting the calculation of results. If this data point was removed from "calib view" then the data could be reprocessed and the correct concentrations calculated.

The discrepancies with Zn data can sometimes be attributed to the same problems experienced with Al and Fe being ubiquitous. However, some instances appear to be more complicated as the calibration shows excellent linearity and blank 3 is a good representation of the average blanks. The inconsistency also demonstrates that the data work up gives lower concentrations than the computer generated data. This may be due to the correction of TiO^+ as an isobaric interference in the instrument software, which would increase the concentration, or due to suppression of the signal by the high Mg and Na concentrations or due to contamination. If the samples consistently show higher results (up to 10%) on the concentrations tab this would add a small uncertainty to the Zn results. This small uncertainty is insignificant in comparison to the sample concentration measured in the µg/L range and the high discharge limit for zinc into the estuary.

This comparison has shown as long as the four key indicators are checked then the concentrations page can be used, therefore saving time and reducing error traps by removing complex data work up.

3.7. Precision of the New "Main Metals" Method

The precision of the new "main metals" method validated within this report can be generated for each element. This can be done by looking at the repeat analysis as the same concentration has been injected repeatedly 90 times over 15 runs by 3 different analysts at 5.00 µg/L. This is also the case for the QCs as they have been repeated in the same manner with 6 QCs in every dataset at 10.0 µg/L. The %RSD for the repeat analysis and the QC data shows good agreement for B, Cr, Fe, Ni, Cu, Cd and Pb. As the analytical technique is used for discharges to the estuary and the majority of samples measured at Bradwell are relatively low (usually LOD) it is sensible to use the precision calculated from the lower concentration of 5.00 µg/L repeats. Therefore the calculated precisions for B, Cr, Fe, Ni, Cu, Cd and Pb are 6.8%, 3.6%, 6.8%, 3.3%, 3.5%, 2.6% and 1.4% respectively. The agreement between the repeats and QC data %RSDs for Al and Zn do not show good agreement. The QC data % RSDs are smaller at 8.2% and 4.5% for Al and Zn, in comparison to the repeat RSDs of 15% and 13%. Both Al and Zn show significant background variations and higher LODs than the other seven elements. Therefore the repetitive measurement of 5.00 µg/L is going to show larger variation as it is closer to the LOD for these elements. As mentioned the samples measured at Bradwell are routinely LOD and at the lower end of the calibration range therefore it is sensible to use the lower precisions of 15% for Al and 13% for Zn. Although these are high for ICP-MS analysis the suppression of the effluent stream is a contributing factor to the low precision of the measurement of Zn. Although the Al precision is poor, this is not subject to a discharge limit and therefore is at the customer's discretion if the analysis conducted is acceptable for the sample of interest.

3.8. Analysis of Bradwell Plant and Manufactured Trueness Sample

Bradwell have supplied a plant sample (AL422) and a manufactured trueness sample to be analysed blind, i.e. NNL do not know the anticipated concentrations.

The trueness sample received was in a concentrated HNO_3 matrix with high Mg and Na levels. Bradwell instructed NNL to perform a DF10000 on the sample and analysis it using the new "main metals" method; the results are detailed in **Table 30**. The analysis was conducted in quadruple and all repeats are detailed, the DF10000 has not been applied as requested by the customer. The %RSD for the all elements for Zn and Al agree with the precisions calculated for each element. The %RSDs for the Zn and Al are slightly greater than the other seven elements at 4.3% and 10% respectively, but are within the calculated precisions. The same sample will be analysed at Bradwell after the new method parameters have been adopted.

The Bradwell plant sample (AL422) was run at DF500, in quadruplicate, after the new Mg and Na concentrations had been assessed. All of the results were below the LOD of the nine elements, so the LOD has been reported (**Table 31**) of each element with the DF500 applied for direct comparison with Bradwell results during the site visit for method transfer.

4. Validation data tables for the "Main Metals" Method

4.1. Boron validation data

Table 3: Summary of the calibration range, gradients, R^2 values and LODs for boron method validation

Date	Calibration range (µg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (µg/L)	Analyst
12/10/2015	1-20	7960	0.9994	0.92	1
14/10/2015	1-20	8523	0.9999	0.054	1
15/10/2015	1-20	7543	0.9999	0.072	2
16/10/2015	1-20	6943	0.9999	0.077	2
19/10/2015	1-20	6189	0.9983	0.75	1
20/10/2015	1-20	6169	0.9990	0.14	1
21/10/2015	1-20	4542	0.9997	0.14	1
22/10/2015	1-20	4444	0.9999	0.066	2
23/10/2015	1-20	3884	1.0000	0.031	2
26/10/2015	1-20	3799	0.9999	0.062	3
27/10/2015	1-20	9444	0.9998	0.081	3
28/10/2015	1-20	6253	0.9999	0.020	3
29/10/2015	1-20	5825	0.9998	0.035	3
30/10/2015	1-20	4996	1.0000	0.067	3
02/11/2015	1-20	11099	1.0000	0.11	3
03/11/2015	1-20	8848	0.9996	0.018	2

Table 4: **Summary of the investigation of the spiked working range samples for boron method validation**

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
12/10/2015	1	1.50	1.28	15%
		2.50	2.37	5.2%
		7.50	7.76	3.4%
		12.5	13.0	3.7%
		17.5	18.3	4.8%
14/10/15	1	1.80	2.00	11%
		3.50	3.90	11%
		8.50	9.38	10%
		12.0	12.9	7.2%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		16.0	17.2	7.6%
15/10/2015	2	2.60	2.66	2.2%
		7.40	7.33	1.0%
		8.70	8.76	0.71%
		15.9	16.0	0.49%
		19.7	20.1	1.8%
16/10/2015	2	1.30	1.28	1.2%
		1.90	1.90	0.036%
		2.30	2.23	2.8%
		6.90	6.57	4.8%
		7.70	7.65	0.68%
19/10/2015	1	1.70	1.45	15%
		2.10	1.83	13%
		3.00	2.74	8.7%
		8.00	7.57	5.4%
		14.0	13.2	5.6%
20/10/2015	1	4.00	3.86	3.5%
		5.20	4.85	6.7%
		7.20	6.94	3.6%
		8.10	7.72	4.6%
		11.0	10.4	5.0%
21/10/2015	1	6.40	6.62	3.4%
		7.30	7.56	3.6%
		13.0	13.5	3.8%
		14.0	14.5	3.6%
		16.5	17.2	4.5%
22/10/2015	2	1.10	1.28	16%
		4.40	4.60	4.5%
		9.50	10.1	6.3%
		13.5	14.3	5.7%
		17.0	17.6	3.4%
23/10/2015	2	9.80	10.2	4.5%
		10.3	10.7	3.8%
		11.5	12.2	6.3%
		13.8	14.3	3.7%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		15.3	16.2	5.7%
27/10/2015	3	3.50	3.94	13%
		7.00	7.78	11%
		10.5	11.6	11%
		14.0	15.3	9.6%
		17.5	19.8	13%
28/10/2015	3	5.25	5.87	12%
		8.75	9.71	11%
		12.25	13.6	11%
		15.75	17.5	11%
		19.25	21.9	14%
29/10/2015	3	6.00	6.68	11%
		9.00	9.82	9.1%
		12.0	13.3	11%
		15.0	16.6	11%
		18.0	19.6	9.1%
30/10/2015	3	3.00	3.18	6.0%
		4.00	4.18	4.6%
		8.00	8.25	3.2%
		9.00	9.45	5.0%
		12.0	12.5	4.5%
03/11/2015	2	7.40	7.83	5.9%
		9.70	10.1	4.2%
		15.2	15.9	4.8%
		17.6	18.3	3.9%
		19.0	19.6	3.3%

Table 5: Summary of the spiked repeat samples for boron method validation

Date	Analyst	Conc. (μg/L)	Result (μg/L)	% Difference	Average Result (μg/L)	σ (SD)	% RSD
12/10/2015	1	5.00	5.05	1.0%	5.14	0.121	2.41%
		5.00	5.17	3.5%			
		5.00	5.20	4.0%			
		5.00	5.14	2.8%			
		5.00	5.15	3.1%			
		5.00	5.59	12%			
		5.00	5.06	1.3%			
		5.00	5.08	1.6%			
		5.00	5.15	2.9%			
		5.00	5.10	2.1%			
		5.00	5.12	2.4%			
		5.00	4.97	0.62%			
		5.00	5.12	2.4%			
		5.00	5.17	3.4%			
		5.00	5.13	2.5%			
		5.00	5.12	2.5%			
		5.00	5.09	1.7%			
		5.00	5.11	2.2%			
		5.00	5.22	4.5%			
		5.00	5.04	0.8%			
14/10/2015	1	5.00	5.14	2.8%	5.36	0.105	2.10%
		5.00	5.21	4.2%			
		5.00	5.23	4.6%			
		5.00	5.29	5.8%			
		5.00	5.26	5.3%			
		5.00	5.36	7.1%			
		5.00	5.38	7.5%			
		5.00	5.31	6.3%			
		5.00	5.22	4.3%			
		5.00	5.42	8.4%			
		5.00	5.41	8.1%			
		5.00	5.42	8.4%			
		5.00	5.41	8.2%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.42	8.4%			
		5.00	5.41	8.3%			
		5.00	5.48	9.5%			
		5.00	5.41	8.2%			
		5.00	5.43	8.5%			
		5.00	5.47	9.4%			
		5.00	5.55	11.0%			
15/10/2015	2	5.00	5.13	2.6%	5.07	0.0359	0.717%
		5.00	5.06	1.1%			
		5.00	5.05	1.0%			
		5.00	5.07	1.5%			
		5.00	5.04	0.84%			
16/10/2015	2	5.00	4.99	0.21%	4.91	0.0570	1.14%
		5.00	4.93	1.4%			
		5.00	4.89	2.3%			
		5.00	4.84	3.3%			
		5.00	4.91	1.7%			
19/10/2015	1	5.00	4.92	1.5%	4.82	0.0680	1.36%
		5.00	4.82	3.5%			
		5.00	4.81	3.8%			
		5.00	4.73	5.3%			
		5.00	4.80	3.9%			
20/10/2015	1	5.00	4.83	3.4%	4.80	0.0816	1.63%
		5.00	4.85	3.1%			
		5.00	4.85	3.0%			
		5.00	4.80	4.0%			
		5.00	4.65	6.9%			
21/10/2015	1	5.00	5.17	3.5%	5.25	0.0430	0.860%
		5.00	5.24	4.8%			
		5.00	5.28	5.5%			
		5.00	5.27	5.3%			
		5.00	5.27	5.4%			
22/10/2015	2	5.00	5.30	6.0%	5.27	0.0940	1.88%
		5.00	5.31	6.2%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.31	6.1%			
		5.00	5.10	2.0%			
		5.00	5.32	6.3%			
23/10/2015	2	5.00	5.14	2.8%	5.11	0.0861	1.72%
		5.00	4.96	0.72%			
		5.00	5.12	2.3%			
		5.00	5.16	3.3%			
		5.00	5.18	3.6%			
27/10/2015	3	5.00	5.36	7.2%	5.41	0.0584	1.17%
		5.00	5.37	7.3%			
		5.00	5.46	9.3%			
		5.00	7.74	55%			
		5.00	5.47	9.3%			
28/10/2015	3	5.00	5.26	5.2%	5.42	0.0951	1.90%
		5.00	5.41	8.3%			
		5.00	5.48	9.6%			
		5.00	5.43	8.7%			
		5.00	5.50	10%			
29/10/2015	3	5.00	5.25	5.0%	5.38	0.0783	1.57%
		5.00	5.37	7.4%			
		5.00	5.44	8.8%			
		5.00	5.38	7.7%			
		5.00	5.44	8.8%			
30/10/2015	3	5.00	5.06	1.3%	5.11	0.0833	1.67%
		5.00	5.02	0.36%			
		5.00	5.08	1.5%			
		5.00	5.15	2.9%			
		5.00	5.23	4.6%			
02/11/2015	3	5.00	5.09	1.9%	5.12	0.0551	1.10%
		5.00	5.18	3.6%			
		5.00	5.06	1.1%			
		5.00	5.18	3.6%			
		5.00	5.09	1.9%			
03/11/2015	2	5.00	5.17	3.3%	5.25	0.0517	1.03%

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.27	5.4%			
		5.00	5.30	6.0%			
		5.00	5.27	5.4%			
		5.00	5.23	4.6%			

4.2. Aluminium validation data

Table 6: Summary of the calibration range, gradients, R^2 values and LODs for aluminium method validation

Date	Calibration range (µg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (µg/L)	Analyst
12/10/2015	1-20	49534	0.9890	0.98	1
14/10/2015	1-20	27930	0.9957	1.2	1
15/10/2015	1-20	22664	0.9988	0.45	2
16/10/2015	1-20	21940	0.9933	1.6	2
19/10/2015	1-20	19701	0.8671	0.96	1
20/10/2015	1-20	19992	0.9845	2.2	1
21/10/2015	1-20	14853	0.9986	0.91	1
22/10/2015	1-20	14671	0.9988	0.74	2
23/10/2015	1-20	11933	0.9983	1.9	2
26/10/2015	1-20	14559	0.9877	0.21	3
27/10/2015	1-20	24955	0.9998	0.13	3
28/10/2015	1-20	19153	0.9988	0.36	3
29/10/2015	1-20	16933	0.9997	0.32	3
30/10/2015	1-20	14803	0.9914	0.31	3
02/11/2015	1-20	27853	0.9997	0.56	3
03/11/2015	1-20	22401	0.9951	0.85	2

Table 7: Summary of the investigation of the spiked working range samples for aluminium method validation

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
12/10/2015	1	1.50	1.78	19%
		2.50	3.13	25%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		7.50	8.50	13%
		12.5	14.9	19%
		17.5	22.5	29%
14/10/15	1	1.80	2.60	44%
		3.50	3.17	9.5%
		8.50	7.51	12%
		12.0	11.1	7.7%
		16.0	16.4	2.7%
15/10/2015	2	2.60	3.54	36%
		7.40	7.03	5.0%
		8.70	8.41	3.3%
		15.9	15.4	3.1%
		19.7	21.3	7.9%
16/10/2015	2	1.30	1.09	16%
		1.90	0.871	54%
		2.30	1.61	30%
		6.90	5.87	15%
		7.70	6.76	12%
19/10/2015	1	1.70	1.64	3.2%
		2.10	1.77	16%
		3.00	3.07	2.3%
		8.00	7.66	4.2%
		14.0	12.8	8.5%
20/10/2015	1	4.00	3.15	21%
		5.20	3.97	24%
		7.20	8.37	16%
		8.10	6.63	18%
		11.0	8.88	19%
21/10/2015	1	6.40	6.79	6.1%
		7.30	7.27	0.39%
		13.0	12.6	2.9%
		14.0	13.7	2.3%
		16.5	25.2	53%
22/10/2015	2	1.10	1.07	3.1%
		4.40	4.63	5.2%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		9.50	10.2	6.9%
		13.5	13.0	4.0%
		17.0	17.2	1.0%
23/10/2015	2	9.80	9.25	5.6%
		10.3	9.68	6.0%
		11.5	11.1	3.5%
		13.8	13.1	5.3%
		15.3	15.1	1.2%
27/10/2015	3	3.50	6.13	75%
		7.00	8.86	27%
		10.5	12.0	14%
		14.0	16.1	15%
		17.5	19.5	11%
28/10/2015	3	5.25	5.88	12%
		8.75	8.92	2.0%
		12.25	12.3	0.49%
		15.75	16.1	2.0%
		19.25	19.2	0.020%
29/10/2015	3	6.00	7.06	18%
		9.00	9.88	10%
		12.0	12.9	7.8%
		15.0	16.3	8.6%
		18.0	18.5	2.9%
30/10/2015	3	3.00	3.42	14%
		4.00	3.68	7.9%
		8.00	7.33	8.4%
		9.00	8.53	5.2%
		12.0	11.6	3.7%
03/11/2015	2	7.40	6.78	8.4%
		9.70	9.46	2.5%
		15.2	15.3	0.61%
		17.6	17.6	0.27%
		19.0	18.5	2.6%

Table 8: Summary of the spiked repeat samples for aluminium method validation

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
12/10/2015	1	5.00	5.29	5.7%	6.28	0.697	13.9%
		5.00	5.76	15%			
		5.00	6.46	29%			
		5.00	6.89	38%			
		5.00	8.16	63%			
		5.00	6.95	39%			
		5.00	6.08	22%			
		5.00	7.22	44%			
		5.00	6.06	21%			
		5.00	6.64	33%			
		5.00	5.77	15%			
		5.00	5.89	18%			
		5.00	5.72	14%			
		5.00	6.79	36%			
		5.00	5.89	18%			
		5.00	5.44	8.8%			
		5.00	6.68	34%			
		5.00	5.62	12%			
		5.00	6.03	21%			
		5.00	6.30	26%			
14/10/2015	1	5.00	6.48	30%	5.33	0.613	12.3%
		5.00	5.97	20%			
		5.00	6.40	28%			
		5.00	6.22	25%			
		5.00	4.64	7.2%			
		5.00	5.25	5.0%			
		5.00	5.46	9.3%			
		5.00	5.05	1.0%			
		5.00	4.97	0.6%			
		5.00	5.43	8.6%			
		5.00	4.88	2.5%			
		5.00	5.91	18%			
		5.00	5.58	12%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.13	2.6%			
		5.00	4.83	3.4%			
		5.00	4.45	11%			
		5.00	5.25	5.0%			
		5.00	4.95	0.9%			
		5.00	5.34	6.8%			
		5.00	4.38	12%			
15/10/2015	2	5.00	5.08	1.7%	5.05	0.146	2.93%
		5.00	4.85	3.1%			
		5.00	4.97	0.6%			
		5.00	5.18	3.7%			
		5.00	5.19	3.8%			
16/10/2015	2	5.00	5.53	11%	5.02	0.560	11.2%
		5.00	5.30	6.0%			
		5.00	4.85	3.0%			
		5.00	5.28	5.6%			
		5.00	4.12	18%			
19/10/2015	1	5.00	4.85	3.1%	4.99	0.140	2.79%
		5.00	4.97	0.64%			
		5.00	4.87	2.6%			
		5.00	5.13	2.5%			
		5.00	5.14	2.9%			
20/10/2015	1	5.00	4.37	13%	4.29	0.187	3.74%
		5.00	4.58	8.3%			
		5.00	4.16	17%			
		5.00	4.13	17%			
		5.00	4.22	16%			
21/10/2015	1	5.00	5.48	9.6%	5.23	0.224	4.48%
		5.00	5.42	8.5%			
		5.00	5.02	0.4%			
		5.00	4.99	0.2%			
		5.00	5.25	5.0%			
22/10/2015	2	5.00	5.40	7.9%	5.03	0.451	9.0%
		5.00	5.44	8.8%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	8.17	63%			
		5.00	4.63	7.4%			
		5.00	4.65	7.1%			
23/10/2015	2	5.00	5.02	0.42%	4.65	0.484	9.68%
		5.00	5.21	4.3%			
		5.00	4.68	6.5%			
		5.00	4.07	19%			
		5.00	4.27	15%			
27/10/2015 *	3	5.00	6.70	34%	6.58	0.655	13.1%
		5.00	7.45	49%			
		5.00	6.03	21%			
		5.00	**32.2**	**544%**			
		5.00	6.13	23%			
28/10/2015	3	5.00	5.92	18%	5.90	0.578	11.6%
		5.00	6.20	24%			
		5.00	6.37	27%			
		5.00	6.12	22%			
		5.00	4.91	1.7%			
29/10/2015	3	5.00	5.91	18%	5.70	0.180	3.60%
		5.00	5.45	8.9%			
		5.00	5.65	13%			
		5.00	5.84	17%			
		5.00	5.66	13%			
30/10/2015	3	5.00	4.66	6.8%	4.60	0.0585	1.17%
		5.00	4.52	9.5%			
		5.00	4.59	8.2%			
		5.00	4.68	8.4%			
		5.00	4.66	6.8%			
02/11/2015	3	5.00	5.41	8.2%	5.21	0.264	5.28%
		5.00	5.44	8.8%			
		5.00	5.36	7.3%			
		5.00	4.90	2.0%			
		5.00	4.95	1.02%			
		5.00	5.06	1.2%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
03/11/2015	2	5.00	5.14	2.9%	5.16	0.304	6.08%
		5.00	5.14	2.8%			
		5.00	5.65	13%			
		5.00	4.81	3.7%			

*the result indicated in bold font for 27/10/2015 was not taken into consideration for the calculation of the average result, σ or %RSD.

4.3. Chromium validation data

Table 9: Summary of the calibration range, gradients, R^2 values and LODs for chromium method validation

Date	Calibration range (µg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (µg/L)	Analyst
12/10/2015	1-20	6213	1.0000	0.013	1
14/10/2015	1-20	7015	0.9999	0.016	1
15/10/2015	1-20	6224	0.9998	0.020	2
16/10/2015	1-20	5861	1.0000	0.019	2
19/10/2015	1-20	5341	0.9994	0.017	1
20/10/2015	1-20	5303	0.9990	0.016	1
21/10/2015	1-20	4256	0.9999	0.016	1
22/10/2015	1-20	4291	1.0000	0.013	2
23/10/2015	1-20	3827	1.0000	0.020	2
26/10/2015	1-20	3726	0.9999	0.018	3
27/10/2015	1-20	6567	1.0000	0.037	3
28/10/2015	1-20	5112	0.9999	0.014	3
29/10/2015	1-20	4729	0.9998	0.021	3
30/10/2015	1-20	4080	1.0000	0.019	3
02/11/2015	1-20	7264	1.0000	0.0088	3
03/11/2015	1-20	6009	0.9992	0.015	2

Table 10: Summary of the investigation of the spiked working range samples for chromium method validation

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
12/10/2015	1	1.50	1.70	13%
		2.50	2.85	14%
		7.50	8.51	14%
		12.5	14.1	12%
		17.5	19.7	12%
14/10/2015	1	1.80	2.05	14%
		3.50	3.99	14%
		8.50	9.59	13%
		12.0	13.5	12%
		16.0	18.0	13%
15/10/2015	2	2.60	2.69	3.4%
		7.40	7.68	3.8%
		8.70	9.09	4.5%
		15.9	16.6	4.3%
		19.7	20.8	5.4%
16/10/2015	2	1.30	1.38	6.0%
		1.90	2.02	6.3%
		2.30	2.44	5.9%
		6.90	7.22	4.6%
		7.70	8.29	7.7%
19/10/2015	1	1.70	1.79	5.5%
		2.10	2.16	2.8%
		3.00	3.22	7.4%
		8.00	8.31	3.9%
		14.0	14.6	4.4%
20/10/2015	1	4.00	4.13	3.2%
		5.20	5.37	3.3%
		7.20	7.48	3.9%
		8.10	8.49	4.8%
		11.0	11.4	3.6%
21/10/2015	1	6.40	6.77	5.8%
		7.30	7.70	5.4%
		13.0	13.7	5.7%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		14.0	15.0	7.3%
		16.5	17.7	7.0%
22/10/2015	2	1.10	1.17	6.6%
		4.40	4.55	3.3%
		9.50	9.87	3.9%
		13.5	14.1	4.8%
		17.0	17.5	3.2%
23/10/2015	2	9.80	9.83	0.26%
		10.3	10.3	0.43%
		11.5	12.0	4.3%
		13.8	14.0	1.6%
		15.3	15.7	2.7%
27/10/2015	3	3.50	3.71	6.0%
		7.00	7.43	6.1%
		10.5	11.2	6.3%
		14.0	14.9	6.5%
		17.5	19.0	8.3%
28/10/2015	3	5.25	5.45	3.7%
		8.75	9.18	4.9%
		12.25	13.2	7.6%
		15.75	16.6	5.3%
		19.25	20.9	8.4%
29/10/2015	3	6.00	6.59	10%
		9.00	9.79	8.8%
		12.0	13.0	8.1%
		15.0	16.3	9.0%
		18.0	19.4	7.8%
30/10/2015	3	3.00	3.21	7.0%
		4.00	4.28	6.9%
		8.00	8.61	7.6%
		9.00	9.76	8.4%
		12.0	13.1	9.3%
03/11/2015	2	7.40	7.77	5.0%
		9.70	10.0	3.1%
		15.2	16.3	6.9%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		17.6	18.5	5.2%
		19.0	20.0	5.0%

Table 11: Summary of the spiked repeat samples for chromium method validation

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
12/10/15	1	5.00	5.10	2.1%	5.41	0.144	2.89%
		5.00	5.23	4.6%			
		5.00	5.28	5.6%			
		5.00	5.29	5.7%			
		5.00	5.30	5.9%			
		5.00	5.29	5.8%			
		5.00	5.31	6.3%			
		5.00	5.34	6.8%			
		5.00	5.38	7.6%			
		5.00	5.40	8.0%			
		5.00	5.49	9.7%			
		5.00	5.34	6.8%			
		5.00	5.55	11%			
		5.00	5.56	11%			
		5.00	5.51	10%			
		5.00	5.56	11%			
		5.00	5.55	11%			
		5.00	5.55	11%			
		5.00	5.63	13%			
		5.00	5.55	11%			
14/10/15	1	5.00	5.06	1.2%	5.38	0.134	2.68%
		5.00	5.21	4.2%			
		5.00	5.21	4.2%			
		5.00	5.25	4.9%			
		5.00	5.23	4.5%			
		5.00	5.36	7.2%			
		5.00	5.34	6.8%			
		5.00	5.37	7.4%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.30	6.1%			
		5.00	5.36	7.3%			
		5.00	5.41	8.1%			
		5.00	5.43	8.6%			
		5.00	5.48	9.5%			
		5.00	5.46	9.2%			
		5.00	5.50	10.0%			
		5.00	5.51	10.2%			
		5.00	5.52	10.4%			
		5.00	5.45	9.0%			
		5.00	5.53	10.6%			
		5.00	5.57	11.4%			
15/10/2015	2	5.00	5.06	1.2%	5.06	0.0456	0.911%
		5.00	5.01	0.16%			
		5.00	5.04	0.87%			
		5.00	5.07	1.5%			
		5.00	5.13	2.6%			
16/10/2015	2	5.00	5.12	2.4%	5.16	0.0766	1.53%
		5.00	5.12	2.4%			
		5.00	5.09	1.8%			
		5.00	5.16	3.3%			
		5.00	5.28	5.7%			
19/10/2015	1	5.00	4.99	0.20%	5.02	0.0494	0.988%
		5.00	4.98	0.41%			
		5.00	5.05	0.92%			
		5.00	4.99	0.20%			
		5.00	5.10	1.9%			
20/10/2015	1	5.00	4.95	0.97%	5.03	0.0455	0.910%
		5.00	5.05	1.0%			
		5.00	5.07	1.3%			
		5.00	5.01	0.25%			
		5.00	5.04	0.88%			
21/10/2015	1	5.00	5.09	1.8%	5.16	0.0690	1.38%
		5.00	5.10	2.0%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.20	4.0%			
		5.00	5.18	3.6%			
		5.00	5.25	5.1%			
22/10/2015	2	5.00	5.00	0.0%	5.03	0.112	2.24%
		5.00	5.04	0.83%			
		5.00	5.03	0.60%			
		5.00	4.88	2.4%			
		5.00	5.20	3.9%			
23/10/2015	2	5.00	4.98	0.43%	4.99	0.0394	0.787%
		5.00	4.92	1.5%			
		5.00	5.01	0.12%			
		5.00	5.02	0.46%			
		5.00	5.01	0.23%			
27/10/2015	3	5.00	5.14	2.9%	5.23	0.106	2.12%
		5.00	5.16	3.3%			
		5.00	5.19	3.8%			
		5.00	5.41	8.1%			
		5.00	5.24	4.8%			
28/10/2015	3	5.00	4.85	3.1%	5.01	0.106	2.12%
		5.00	5.05	1.1%			
		5.00	5.03	0.53%			
		5.00	5.01	0.25%			
		5.00	5.13	2.7%			
29/10/2015	3	5.00	5.02	0.31%	5.13	0.0727	1.45%
		5.00	5.16	3.1%			
		5.00	5.14	2.7%			
		5.00	5.12	2.4%			
		5.00	5.22	4.3%			
30/10/2015	3	5.00	5.09	1.8%	5.17	0.0708	1.42%
		5.00	5.13	2.6%			
		5.00	5.14	2.7%			
		5.00	5.21	4.3%			
		5.00	5.27	5.3%			
02/11/2015	3	5.00	5.06	1.3%	5.09	0.0605	1.21%

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.05	1.5%			
		5.00	5.01	0.26%			
		5.00	5.15	3.0%			
		5.00	5.15	3.1%			
03/11/2015	2	5.00	5.10	2.0%	5.18	0.0624	1.25%
		5.00	5.16	3.3%			
		5.00	5.19	3.9%			
		5.00	5.16	3.2%			
		5.00	5.27	5.5%			

4.4. Iron validation data

Table 12: Summary of the calibration range, gradients, R^2 values and LODs for iron method validation

Date	Calibration range (µg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (µg/L)	Analyst
12/10/2015	1-20	607	0.9999	0.33	1
14/10/2015	1-20	690	1.0000	0.31	1
15/10/2015	1-20	631	0.9983	0.21	2
16/10/2015	1-20	575	0.9997	0.69	2
19/10/2015	1-20	540	0.9891	0.59	1
20/10/2015	1-20	539	0.9991	0.26	1
21/10/2015	1-20	412	0.9996	0.55	1
22/10/2015	1-20	419	0.9983	0.28	2
23/10/2015	1-20	390	0.9998	0.42	2
26/10/2015	1-20	356	0.9995	0.37	3
27/10/2015	1-20	660	0.9992	0.22	3
28/10/2015	1-20	513	0.9943	0.25	3
29/10/2015	1-20	487	0.9997	0.33	3
30/10/2015	1-20	388	0.9991	0.30	3
02/11/2015	1-20	680	0.9983	0.20	3
03/11/2015	1-20	607	0.9989	0.19	2

Table 13: Summary of the investigation of the spiked working range samples for iron method validation

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
12/10/2015	1	1.50	1.93	29%
		2.50	3.11	24%
		7.50	9.15	22%
		12.5	14.5	16%
		17.5	20.7	19%
14/10/2015	1	1.80	2.46	37%
		3.50	4.56	30%
		8.50	10.4	23%
		12.0	14.3	20%
		16.0	19.4	21%
15/10/2015	2	2.60	2.99	15%
		7.40	7.90	6.8%
		8.70	9.47	8.9%
		15.9	17.0	6.8%
		19.7	21.0	6.3%
16/10/2015	2	1.30	1.64	26%
		1.90	2.22	17%
		2.30	2.65	15%
		6.90	7.67	11%
		7.70	8.85	15%
19/10/2015	1	1.70	1.87	9.8%
		2.10	2.26	7.5%
		3.00	3.44	15%
		8.00	8.46	5.7%
		14.0	14.8	5.7%
20/10/2015	1	4.00	4.05	1.3%
		5.20	5.41	4.0%
		7.20	7.65	6.3%
		8.10	8.58	6.0%
		11.0	11.6	5.9%
21/10/2015	1	6.40	7.07	10%
		7.30	8.28	14%
		13.0	14.6	12%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		14.0	16.0	15%
		16.5	18.9	14%
22/10/2015	2	1.10	1.47	33%
		4.40	4.79	8.8%
		9.50	10.3	8.8%
		13.5	14.6	8.0%
		17.0	18.3	7.4%
23/10/2015	2	9.80	9.73	0.76%
		10.3	10.4	0.43%
		11.5	11.9	3.1%
		13.8	16.6	20%
		15.3	16.2	6.0%
27/10/2015	3	3.50	3.94	13%
		7.00	7.56	8.0%
		10.5	11.4	9.0%
		14.0	15.2	8.4%
		17.5	19.2	9.5%
28/10/2015	3	5.25	5.54	5.6%
		8.75	9.10	4.0%
		12.25	12.9	5.4%
		15.75	16.6	5.2%
		19.25	20.8	8.0%
29/10/2015	3	6.00	6.84	14%
		9.00	10.4	15%
		12.0	13.0	8%
		15.0	16.6	11%
		18.0	19.6	9%
30/10/2015	3	3.00	3.45	15%
		4.00	4.60	15%
		8.00	8.90	11%
		9.00	10.1	12%
		12.0	13.7	14%
03/11/2018	2	7.40	7.86	6.2%
		9.70	10.1	3.9%
		15.2	16.0	5.2%

Date	Analyst	Concentration (μg/L)	Result (μg/L)	% Difference
		17.6	18.6	5.7%
		19.0	20.1	5.6%

Table 14: Summary of the spiked repeat samples for iron method validation

Date	Analyst	Conc. (μg/L)	Result (μg/L)	% Difference	Average Result (μg/L)	σ (SD)	% RSD
12/10/2015	1	5.00	5.11	2.2%	5.63	0.228	4.57%
		5.00	5.21	4.1%			
		5.00	5.47	9.4%			
		5.00	5.44	8.8%			
		5.00	5.44	8.8%			
		5.00	5.68	14%			
		5.00	5.56	11%			
		5.00	5.55	11%			
		5.00	5.60	12%			
		5.00	5.83	17%			
		5.00	5.51	10%			
		5.00	5.66	13%			
		5.00	5.81	16%			
		5.00	5.81	16%			
		5.00	5.77	15%			
		5.00	5.60	12%			
		5.00	5.78	16%			
		5.00	5.82	16%			
		5.00	5.90	18%			
		5.00	6.03	21%			
14/10/2015 *	1	5.00	5.54	11%	5.92	0.238	4.76%
		5.00	5.45	9.1%			
		5.00	5.62	12%			
		5.00	6.07	21%			
		5.00	5.77	16%			
		5.00	5.81	16%			
		5.00	5.83	17%			
		5.00	5.88	18%			
		5.00	5.77	15%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.88	18%			
		5.00	41.6	732%			
		5.00	5.99	20%			
		5.00	6.37	27%			
		5.00	5.93	19%			
		5.00	5.86	17%			
		5.00	6.13	23%			
		5.00	6.14	23%			
		5.00	6.30	26%			
		5.00	6.00	20%			
		5.00	6.09	22%			
15/10/2015	2	5.00	5.13	2.7%	5.18	0.101	2.02%
		5.00	5.06	1.1%			
		5.00	5.18	3.7%			
		5.00	5.22	4.4%			
		5.00	5.33	6.6%			
16/10/2015	2	5.00	5.32	6.3%	5.40	0.0970	1.94%
		5.00	5.38	7.5%			
		5.00	5.40	8.1%			
		5.00	5.33	6.6%			
		5.00	5.56	11%			
19/10/2015	1	5.00	4.96	0.82%	4.99	0.0569	1.14%
		5.00	4.91	1.8%			
		5.00	5.03	0.56%			
		5.00	5.04	0.78%			
		5.00	5.03	0.67%			
20/10/2015	1	5.00	4.84	3.3%	5.00	0.0988	1.98%
		5.00	5.02	0.39%			
		5.00	5.00	0.069%			
		5.00	5.06	1.2%			
		5.00	5.09	1.9%			
21/10/2015	1	5.00	5.18	3.6%	5.38	0.194	3.87%
		5.00	5.35	7.0%			
		5.00	5.26	5.3%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.45	9.1%			
		5.00	5.68	13.6%			
22/10/2015	2	5.00	5.71	14%	5.28	0.259	5.17%
		5.00	5.14	2.9%			
		5.00	5.26	5.2%			
		5.00	5.04	0.8%			
		5.00	5.23	4.6%			
23/10/2015	2	5.00	6.31	26%	5.20	0.596	11.9%
		5.00	4.96	0.72%			
		5.00	5.10	2.0%			
		5.00	4.92	1.6%			
		5.00	5.01	0.20%			
27/10/2015 *	3	5.00	5.13	2.5%	5.21	0.0731	1.46%
		5.00	5.25	5.0%			
		5.00	5.19	3.7%			
		5.00	**26.7**	**435%**			
		5.00	5.29	5.9%			
28/10/2015	3	5.00	4.85	2.9%	5.02	0.130	2.59%
		5.00	5.00	0.092%			
		5.00	5.21	4.3%			
		5.00	5.00	0.034%			
		5.00	5.05	1.0%			
29/10/2015	3	5.00	4.97	0.52%	5.19	0.142	2.84%
		5.00	5.15	3.0%			
		5.00	5.30	5.9%			
		5.00	5.18	3.6%			
		5.00	5.34	6.7%			
30/10/2015	3	5.00	5.30	6.0%	5.37	0.106	2.12%
		5.00	5.26	5.1%			
		5.00	5.37	7.5%			
		5.00	5.39	7.8%			
		5.00	5.53	11%			
02/11/2015	3	5.00	5.10	2.0%	5.20	0.0927	1.85&
		5.00	5.21	4.2%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.11	2.1%			
		5.00	5.29	5.7%			
		5.00	5.29	5.7%			
03/11/2015	2	5.00	5.30	6.0%	5.35	0.308	6.15%
		5.00	5.12	2.4%			
		5.00	5.87	17%			
		5.00	5.34	6.8%			
		5.00	5.11	2.2%			

*the results indicated in bold font for 15/10/2015 and 27/10/2015 were not taken into consideration for the calculation of the average result, σ or %RSD.

4.5. Nickel validation data

Table 15: Summary of the calibration range, gradients, R^2 values and LODs for nickel method validation

Date	Calibration range (µg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (µg/L)	Analyst
12/10/2015	1-20	3116	1.0000	0.012	1
14/10/2015	1-20	3471	0.9999	0.0089	1
15/10/2015	1-20	3092	0.9999	0.010	2
16/10/2015	1-20	2928	1.0000	0.0089	2
19/10/2015	1-20	2650	0.9990	0.015	1
20/10/2015	1-20	2637	0.9986	0.0094	1
21/10/2015	1-20	2143	1.0000	0.0081	1
22/10/2015	1-20	2142	1.0000	0.0059	2
23/10/2015	1-20	1906	1.0000	0.024	2
26/10/2015	1-20	1867	0.9997	0.013	3
27/10/2015	1-20	3340	0.9999	0.0077	3
28/10/2015	1-20	2573	0.9999	0.045	3
29/10/2015	1-20	2392	0.9995	0.0032	3
30/10/2015	1-20	2078	0.9999	0.0061	3
02/11/2015	1-20	3676	1.0000	0.0048	3
03/11/2015	1-20	3035	0.9994	0.12	2

Table 16: Summary of the investigation of the spiked working range samples for nickel method validation

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
12/10/2015	1	1.50	1.96	31%
		2.50	3.02	21%
		7.50	8.25	10%
		12.5	13.5	8.1%
		17.5	18.6	6.5%
14/10/2015	1	1.80	2.30	28%
		3.50	4.11	18%
		8.50	9.34	9.8%
		12.0	12.9	7.5%
		16.0	17.3	7.8%
15/10/2015	2	2.60	2.94	13%
		7.40	7.54	2.0%
		8.70	8.86	1.8%
		15.9	16.0	0.34%
		19.7	19.6	0.50%
16/10/2015	2	1.30	1.64	26%
		1.90	2.25	19%
		2.30	2.63	14%
		6.90	7.20	4.4%
		7.70	8.07	4.9%
19/10/2015	1	1.70	2.04	20%
		2.10	2.40	14%
		3.00	3.41	14%
		8.00	8.18	2.2%
		14.0	14.1	0.77%
20/10/2015	1	4.00	4.23	5.7%
		5.20	5.39	3.6%
		7.20	7.41	2.9%
		8.10	8.39	3.3%
		11.0	11.1	0.72%
21/10/2015	1	6.40	6.72	5.1%
		7.30	7.62	4.4%
		13.0	13.2	1.4%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		14.0	14.4	3.0%
		16.5	16.9	2.6%
22/10/2015	2	1.10	1.48	34%
		4.40	4.62	4.9%
		9.50	9.66	1.7%
		13.5	13.7	1.2%
		17.0	16.7	1.7%
23/10/2015	2	9.80	9.62	1.8%
		10.3	10.2	1.3%
		11.5	11.6	0.90%
		13.8	13.6	1.5%
		15.3	15.2	0.74%
27/10/2015	3	3.50	3.84	9.6%
		7.00	7.26	3.7%
		10.5	10.7	1.7%
		14.0	14.2	1.3%
		17.5	18.0	2.8%
28/10/2015	3	5.25	5.54	5.5%
		8.75	9.06	3.5%
		12.3	12.4	1.6%
		15.8	16.0	1.7%
		19.3	19.9	3.4%
29/10/2015	3	6.00	6.54	9.0%
		9.00	9.54	5.9%
		12.0	12.6	5.0%
		15.0	15.7	4.9%
		18.0	18.6	3.4%
30/10/2015	3	3.00	3.42	14%
		4.00	4.40	10%
		8.00	8.43	5.4%
		9.00	9.55	6.1%
		12.0	12.7	6.0%
03/11/2015	2	7.40	7.56	2.2%
		9.70	9.72	0.23%
		15.2	15.6	2.7%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		17.6	17.7	0.30%
		19.0	19.0	0.037%

Table 17: Summary of the spiked repeat samples for nickel method validation

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
12/10/15	1	5.00	5.15	3.0%	5.41	0.132	2.64%
		5.00	5.18	3.7%			
		5.00	5.31	6.2%			
		5.00	5.32	6.4%			
		5.00	5.35	7.1%			
		5.00	5.32	6.5%			
		5.00	5.32	6.4%			
		5.00	5.31	6.3%			
		5.00	5.39	7.8%			
		5.00	5.45	9.0%			
		5.00	5.47	9.4%			
		5.00	5.33	6.6%			
		5.00	5.48	9.5%			
		5.00	5.52	10%			
		5.00	5.54	11%			
		5.00	5.54	11%			
		5.00	5.56	11%			
		5.00	5.54	11%			
		5.00	5.60	12%			
		5.00	5.58	12%			
14/10/15	1	5.00	5.17	3.5%	5.40	0.141	2.82%
		5.00	5.18	3.7%			
		5.00	5.23	4.6%			
		5.00	5.26	5.1%			
		5.00	5.27	5.5%			
		5.00	5.39	7.9%			
		5.00	5.30	5.9%			
		5.00	5.36	7.2%			
		5.00	5.30	6.0%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.35	7.1%			
		5.00	5.42	8.4%			
		5.00	5.50	10%			
		5.00	5.50	10%			
		5.00	5.46	9.2%			
		5.00	5.48	9.6%			
		5.00	5.53	11%			
		5.00	5.58	12%			
		5.00	5.55	11%			
		5.00	5.55	11%			
		5.00	5.66	13%			
15/10/2015	2	5.00	5.04	0.85%	5.10	0.0649	1.30%
		5.00	5.03	0.60%			
		5.00	5.11	2.3%			
		5.00	5.16	3.2%			
		5.00	5.17	3.4%			
16/10/2015	2	5.00	5.07	1.3%	5.17	0.0755	1.51%
		5.00	5.18	3.6%			
		5.00	5.13	2.7%			
		5.00	5.21	4.1%			
		5.00	5.27	5.3%			
19/10/2015	1	5.00	5.02	0.32%	5.09	0.0738	1.48%
		5.00	5.06	1.1%			
		5.00	5.08	1.7%			
		5.00	5.10	1.9%			
		5.00	5.21	4.3%			
20/10/2015	1	5.00	5.06	1.3%	5.08	0.0290	0.580%
		5.00	5.07	1.4%			
		5.00	5.11	2.2%			
		5.00	5.04	0.90%			
		5.00	5.11	2.2%			
21/10/2015	1	5.00	5.16	3.1%	5.19	0.0486	0.973%
		5.00	5.12	2.5%			
		5.00	5.20	4.0%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.21	4.2%			
		5.00	5.25	5.0%			
22/10/2015	2	5.00	5.06	1.2%	5.09	0.0932	1.86%
		5.00	5.12	2.3%			
		5.00	5.07	1.4%			
		5.00	4.98	0.3%			
		5.00	5.24	4.7%			
23/10/2015	2	5.00	5.01	0.17%	5.06	0.0805	1.61%
		5.00	4.97	0.55%			
		5.00	5.08	1.5%			
		5.00	5.07	1.4%			
		5.00	5.18	3.7%			
27/10/2015	3	5.00	5.09	1.9%	5.16	0.0517	1.03%
		5.00	5.19	3.9%			
		5.00	5.17	3.4%			
		5.00	5.12	2.4%			
		5.00	5.22	4.4%			
28/10/2015	3	5.00	4.90	2.1%	5.05	0.0894	1.79%
		5.00	5.10	2.0%			
		5.00	5.09	1.9%			
		5.00	5.06	1.2%			
		5.00	5.11	2.3%			
29/10/2015	3	5.00	5.05	1.0%	5.21	0.101	2.02%
		5.00	5.20	4.1%			
		5.00	5.25	5.0%			
		5.00	5.20	3.9%			
		5.00	5.33	6.6%			
30/10/2015	3	5.00	5.15	2.9%	5.22	0.0659	1.32%
		5.00	5.20	4.0%			
		5.00	5.22	4.3%			
		5.00	5.22	4.4%			
		5.00	5.33	6.6%			
02/11/2015	3	5.00	5.09	1.7%	5.09	0.0372	0.744%
		5.00	5.09	1.8%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	5.04	0.72%			
		5.00	5.14	2.8%			
		5.00	5.10	2.1%			
03/11/2015	2	5.00	5.05	1.0%	5.21	0.0999	2.00%
		5.00	5.20	4.0%			
		5.00	5.25	5.1%			
		5.00	5.25	5.0%			
		5.00	5.31	6.3%			

4.6. Copper validation data

Table 18: Summary of the calibration range, gradients, R^2 values and LODs for copper method validation

Date	Calibration range (µg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (µg/L)	Analyst
12/10/2015	1-20	7789	1.0000	0.024	1
14/10/2015	1-20	8595	0.9999	0.011	1
15/10/2015	1-20	7616	0.9999	0.0095	2
16/10/2015	1-20	7203	0.9999	0.021	2
19/10/2015	1-20	6602	0.9991	0.012	1
20/10/2015	1-20	6520	0.9990	0.018	1
21/10/2015	1-20	5334	0.9999	0.025	1
22/10/2015	1-20	5327	1.0000	0.058	2
23/10/2015	1-20	4747	0.9998	0.12	2
26/10/2015	1-20	4693	0.9998	0.0073	3
27/10/2015	1-20	8368	0.9999	0.0079	3
28/10/2015	1-20	6442	0.9999	0.023	3
29/10/2015	1-20	5996	0.9995	0.022	3
30/10/2015	1-20	5241	0.9996	0.012	3
02/11/2015	1-20	9248	1.0000	0.0077	3
03/11/2015	1-20	7598	0.9995	0.030	2

Table 19: Summary of the investigation of the spiked working range samples for copper method validation

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
12/10/2015	1	1.50	1.53	2.2%
		2.50	2.55	2.0%
		7.50	7.74	3.2%
		12.5	12.9	3.0%
		17.5	17.9	2.5%
14/10/15	1	1.80	1.81	0.7%
		3.50	3.54	1.0%
		8.50	8.65	1.7%
		12.0	12.1	0.6%
		16.0	16.2	1.4%
15/10/2015	2	2.60	2.45	5.9%
		7.40	6.99	5.5%
		8.70	8.30	4.6%
		15.9	15.2	4.7%
		19.7	18.9	4.0%
16/10/2015	2	1.30	1.22	6.0%
		1.90	1.81	4.5%
		2.30	2.19	4.7%
		6.90	6.55	5.0%
		7.70	7.48	2.9%
19/10/2015	1	1.70	1.61	5.5%
		2.10	1.98	5.5%
		3.00	2.93	2.3%
		8.00	7.70	3.8%
		14.0	13.3	4.7%
20/10/2015	1	4.00	3.84	3.9%
		5.20	4.97	4.5%
		7.20	6.96	3.3%
		8.10	7.86	3.0%
		11.0	10.6	3.9%
21/10/2015	1	6.40	6.19	3.4%
		7.30	7.10	2.8%
		13.0	12.6	2.7%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		14.0	13.7	2.2%
		16.5	16.3	1.4%
22/10/2015	2	1.10	1.05	4.9%
		4.40	4.21	4.4%
		9.50	9.07	4.5%
		13.5	13.1	3.1%
		17.0	16.3	3.9%
23/10/2015	2	9.80	9.16	6.5%
		10.3	9.66	6.2%
		11.5	11.1	3.5%
		13.8	13.0	5.6%
		15.3	14.6	4.8%
27/10/2015	3	3.50	3.40	2.7%
		7.00	6.75	3.6%
		10.5	10.2	3.3%
		14.0	13.5	3.5%
		17.5	17.3	1.0%
28/10/2015	3	5.25	5.03	5.5%
		8.75	8.43	3.5%
		12.25	11.9	1.6%
		15.75	15.3	1.7%
		19.25	19.3	3.4%
29/10/2015	3	6.00	6.00	0.075%
		9.00	9.00	0.041%
		12.0	11.9	0.50%
		15.0	15.0	0.14%
		18.0	17.9	0.61%
30/10/2015	3	3.00	2.97	0.84%
		4.00	3.94	1.6%
		8.00	7.85	1.9%
		9.00	8.97	0.31%
		12.0	12.0	0.017%
03/11/2015	2	7.40	7.03	5.0%
		9.70	9.08	6.4%
		15.2	14.8	2.8%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		17.6	16.8	4.6%
		19.0	18.1	4.5%

Table 20: Summary of the spiked repeat samples for copper method validation

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
12/10/15	1	5.00	4.68	6.3%	4.92	0.132	2.50%
		5.00	4.74	5.1%			
		5.00	4.82	3.6%			
		5.00	4.83	3.3%			
		5.00	4.84	3.3%			
		5.00	4.81	3.8%			
		5.00	4.78	4.5%			
		5.00	4.81	3.8%			
		5.00	4.94	1.2%			
		5.00	4.93	1.4%			
		5.00	4.96	0.76%			
		5.00	4.86	2.8%			
		5.00	5.00	0.10%			
		5.00	5.07	1.3%			
		5.00	4.96	0.72%			
		5.00	4.99	0.16%			
		5.00	5.06	1.1%			
		5.00	5.01	0.17%			
		5.00	5.14	2.7%			
		5.00	5.08	1.7%			
14/10/15 *	1	5.00	4.56	8.9%	4.83	0.121	2.42%
		5.00	4.67	6.7%			
		5.00	4.69	6.3%			
		5.00	4.75	5.1%			
		5.00	4.71	5.8%			
		5.00	4.81	3.8%			
		5.00	4.80	3.9%			
		5.00	4.82	3.7%			
		5.00	4.80	4.0%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.85	2.9%			
		5.00	4.83	3.4%			
		5.00	4.89	2.1%			
		5.00	4.94	1.3%			
		5.00	4.95	0.9%			
		5.00	4.96	0.8%			
		5.00	4.92	1.5%			
		5.00	4.94	1.3%			
		5.00	**9.32**	**87%**			
		5.00	4.94	1.1%			
		5.00	5.02	0.3%			
15/10/2015	2	5.00	4.59	8.1%	4.61	0.0509	1.02%
		5.00	4.53	9.4%			
		5.00	4.62	7.6%			
		5.00	4.65	7.0%			
		5.00	4.66	6.9%			
16/10/2015	2	5.00	4.60	7.9%	4.66	0.0655	1.51%
		5.00	4.63	7.4%			
		5.00	4.64	7.2%			
		5.00	4.69	6.3%			
		5.00	4.77	4.6%			
19/10/2015	1	5.00	4.55	8.9%	4.60	0.0452	0.903%
		5.00	4.58	8.5%			
		5.00	4.61	7.8%			
		5.00	4.60	8.0%			
		5.00	4.67	6.5%			
20/10/2015	1	5.00	4.56	8.8%	4.60	0.0331	0.663%
		5.00	4.59	8.2%			
		5.00	4.63	7.3%			
		5.00	4.60	8.1%			
		5.00	4.64	7.2%			
21/10/2015	1	5.00	4.68	6.3%	4.71	0.0509	1.02%
		5.00	4.64	7.2%			
		5.00	4.74	5.3%			

Date	Analyst	Conc. (μg/L)	Result (μg/L)	% Difference	Average Result (μg/L)	σ (SD)	% RSD
		5.00	4.71	5.7%			
		5.00	4.77	4.5%			
22/10/2015	2	5.00	4.64	7.2%	4.66	0.112	2.25%
		5.00	4.67	6.5%			
		5.00	4.71	5.8%			
		5.00	4.49	10%			
		5.00	4.79	4.1%			
23/10/2015	2	5.00	4.61	7.8%	4.61	0.0111	0.222%
		5.00	4.59	8.3%			
		5.00	4.61	7.8%			
		5.00	4.62	7.7%			
		5.00	4.60	7.9%			
27/10/2015	3	5.00	4.68	6.5%	4.70	0.0338	0.676%
		5.00	4.71	5.8%			
		5.00	4.69	6.1%			
		5.00	4.67	6.6%			
		5.00	4.76	4.9%			
28/10/2015	3	5.00	4.44	11%	4.62	0.116	2.32%
		5.00	4.69	6.2%			
		5.00	4.63	7.3%			
		5.00	4.58	8.4%			
		5.00	4.75	5.1%			
29/10/2015	3	5.00	4.63	7.3%	4.74	0.748	1.50%
		5.00	4.80	3.9%			
		5.00	4.77	4.6%			
		5.00	4.70	6.0%			
		5.00	4.81	3.9%			
30/10/2015	3	5.00	4.69	6.3%	4.76	0.0823	1.65%
		5.00	4.70	6.1%			
		5.00	4.72	5.6%			
		5.00	4.79	4.1%			
		5.00	4.88	2.3%			
02/11/2015	3	5.00	4.65	7.0%	4.66	0.0406	0.812%
		5.00	4.67	6.6%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.60	8.1%			
		5.00	4.71	5.9%			
		5.00	4.67	6.6%			
03/11/2015	2	5.00	4.58	8.4%	4.85	0.397	7.95%
		5.00	4.71	5.7%			
		5.00	5.55	11%			
		5.00	4.65	6.9%			
		5.00	4.76	4.8%			

4.7. Zinc validation data

Table 21: Summary of the calibration range, gradients, R^2 values and LODs for zinc method validation

Date	Calibration range (µg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (µg/L)	Analyst
12/10/2015	1-20	3729	0.9980	1.1	1
14/10/2015	1-20	4089	0.9971	0.67	1
15/10/2015	1-20	3214	0.9990	0.23	2
16/10/2015	1-20	3204	0.9993	0.71	2
19/10/2015	1-20	2893	0.9986	1.3	1
20/10/2015	1-20	2896	0.9976	1.0	1
21/10/2015	1-20	2326	0.9977	0.94	1
22/10/2015	1-20	2365	0.9984	0.97	2
23/10/2015	1-20	1948	0.9982	1.1	2
26/10/2015	1-20	2429	0.9711	0.62	3
27/10/2015	1-20	3795	0.9992	0.76	3
28/10/2015	1-20	2864	0.9991	0.62	3
29/10/2015	1-20	2681	0.9993	0.50	3
30/10/2015	1-20	2414	0.9976	0.49	3
02/11/2015	1-20	4316	0.9951	1.1	3
03/11/2015	1-20	3623	0.9945	0.46	2

Table 22: Summary of the investigation of the spiked working range samples for zinc method validation

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
12/10/2015	1	1.50	1.69	13%
		2.50	1.76	30%
		7.50	7.08	5.6%
		12.5	11.6	7.6%
		17.5	17.7	1.2%
14/10/2015	1	1.80	1.31	27%
		3.50	2.88	18%
		8.50	6.77	20%
		12.0	9.82	18%
		16.0	13.2	17%
15/10/2015	2	2.60	2.75	5.8%
		7.40	6.59	11%
		8.70	8.09	7.0%
		15.9	15.0	6.0%
		19.7	18.6	5.6%
16/10/2015	2	1.30	1.25	4.0%
		1.90	1.74	8.2%
		2.30	1.82	21%
		6.90	10.2	52%
		7.70	6.79	12%
19/10/2015	1	1.70	1.40	18%
		2.10	1.86	12%
		3.00	2.63	12%
		8.00	7.62	4.7%
		14.0	13.0	7.1%
20/10/2015	1	4.00	3.56	11%
		5.20	4.84	6.9%
		7.20	6.08	16%
		8.10	6.66	18%
		11.0	9.87	10%
21/10/2015	1	6.40	5.74	10%
		7.30	7.33	0.36%
		13.0	11.9	8.8%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		14.0	12.4	11%
		16.5	15.2	7.7%
22/10/2015	2	1.10	1.65	50%
		4.40	4.48	1.8%
		9.50	8.84	7.0%
		13.5	13.2	2.1%
		17.0	16.3	4.0%
23/10/2015	2	9.80	9.64	1.6%
		10.3	9.20	11%
		11.5	10.4	9.3%
		13.8	12.5	9.5%
		15.3	13.7	11%
27/10/2015	3	3.50	4.88	40%
		7.00	8.02	15%
		10.5	11.8	12%
		14.0	14.7	5.2%
		17.5	18.6	6.5%
28/10/2015	3	5.25	5.33	1.5%
		8.75	8.59	1.8%
		12.3	11.3	7.4%
		15.8	14.9	5.1%
		19.3	17.9	7.1%
29/10/2015	3	6.00	5.68	5.3%
		9.00	9.71	7.9%
		12.0	11.4	4.8%
		15.0	14.7	2.2%
		18.0	17.8	1.2%
30/10/2015	3	3.00	2.60	13%
		4.00	3.75	6.3%
		8.00	6.89	14%
		9.00	8.19	9.0%
		12.0	10.9	9.5%
03/11/2015	2	7.40	6.66	10%
		9.70	8.72	10%
		15.2	13.5	11%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		17.6	16.1	8.8%
		19.0	17.0	11%

Table 23: Summary of the spiked repeat samples for zinc method validation

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
12/10/15	1	5.00	4.38	12%	4.52	0.283	5.65%
		5.00	4.63	7.4%			
		5.00	4.31	13%			
		5.00	4.50	10%			
		5.00	**7.11**	**42%**			
		5.00	4.90	2.0%			
		5.00	5.09	1.8%			
		5.00	4.41	12%			
		5.00	4.49	10%			
		5.00	4.93	1.4%			
		5.00	4.30	14%			
		5.00	4.42	12%			
		5.00	4.47	11%			
		5.00	4.65	7.0%			
		5.00	4.19	16%			
		5.00	4.36	13%			
		5.00	4.19	16%			
		5.00	4.06	19%			
		5.00	4.80	4.0%			
		5.00	4.83	3.4%			
14/10/15	1	5.00	4.87	2.6%	4.48	0.546	10.9%
		5.00	4.72	5.6%			
		5.00	4.29	14%			
		5.00	5.28	5.7%			
		5.00	4.44	11%			
		5.00	4.19	16%			
		5.00	4.21	16%			
		5.00	4.43	11%			
		5.00	4.34	13%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.75	5.0%			
		5.00	4.52	9.6%			
		5.00	4.15	17%			
		5.00	4.34	13%			
		5.00	4.19	16%			
		5.00	4.07	19%			
		5.00	4.03	19%			
		5.00	4.32	14%			
		5.00	6.34	27%			
		5.00	3.91	22%			
		5.00	4.16	17%			
15/10/2015	2	5.00	4.88	2.3%	4.99	0.234	4.68%
		5.00	5.11	2.2%			
		5.00	5.31	6.2%			
		5.00	4.69	6.2%			
		5.00	4.96	0.8%			
16/10/2015	2	5.00	4.84	3.2%	4.52	0.248	4.97%
		5.00	4.72	5.6%			
		5.00	4.46	11%			
		5.00	4.35	13%			
		5.00	4.25	15%			
19/10/2015	1	5.00	4.37	13%	4.90	0.604	12.1%
		5.00	4.76	4.8%			
		5.00	5.95	19%			
		5.00	4.76	4.8%			
		5.00	4.68	6.4%			
20/10/2015	1	5.00	5.15	3.0%	4.87	0.540	10.8%
		5.00	4.51	9.9%			
		5.00	5.66	13%			
		5.00	4.31	14%			
		5.00	4.72	5.7%			
21/10/2015	1	5.00	4.98	0.42%	5.04	0.282	5.64%
		5.00	5.36	7.3%			
		5.00	5.07	1.3%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.61	7.8%			
		5.00	5.20	4.0%			
22/10/2015	2	5.00	4.82	3.6%	4.58	0.250	4.99%
		5.00	4.87	2.6%			
		5.00	4.34	13%			
		5.00	4.47	11%			
		5.00	4.38	12%			
23/10/2015	2	5.00	4.86	2.8%	4.77	0.339	6.78%
		5.00	5.25	4.9%			
		5.00	4.32	14%			
		5.00	4.79	4.2%			
		5.00	4.63	7.4%			
27/10/2015	3	5.00	6.05	21%	6.43	0.509	10.2%
		5.00	6.33	27%			
		5.00	6.37	27%			
		5.00	7.30	46%			
		5.00	6.09	22%			
28/10/2015	3	5.00	4.43	11%	4.60	0.199	3.98%
		5.00	4.64	7.1%			
		5.00	4.93	1.5%			
		5.00	4.56	8.8%			
		5.00	4.45	11%			
29/10/2015	3	5.00	4.87	2.6%	4.92	0.240	4.79%
		5.00	5.02	0.46%			
		5.00	5.27	5.4%			
		5.00	4.79	4.2%			
		5.00	4.65	7.1%			
30/10/2015	3	5.00	4.60	8.1%	4.66	0.279	5.58%
		5.00	4.85	2.9%			
		5.00	4.49	10%			
		5.00	5.03	0.65%			
		5.00	4.34	13%			
02/11/2015	3	5.00	4.49	10%	4.66	0.171	3.42%
		5.00	4.71	5.8%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.54	9.1%			
		5.00	4.84	3.2%			
		5.00	4.86	2.7%			
03/11/2015	2	5.00	4.70	6.0%	4.74	0.382	7.64%
		5.00	4.47	11%			
		5.00	4.68	6.5%			
		5.00	5.39	7.9%			
		5.00	4.46	11%			

4.8. Cadmium validation data

Table 24: Summary of the calibration range, gradients, R^2 values and LODs for cadmium method validation

Date	Calibration range (µg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (µg/L)	Analyst
12/10/2015	1-20	5461	1.0000	0.0025	1
14/10/2015	1-20	5977	1.0000	0.0018	1
15/10/2015	1-20	5382	1.0000	0.00083	2
16/10/2015	1-20	5397	1.0000	0.0015	2
19/10/2015	1-20	4911	0.9990	0.0015	1
20/10/2015	1-20	4889	0.9990	0.0014	1
21/10/2015	1-20	4217	1.0000	0.0026	1
22/10/2015	1-20	4134	1.0000	0.0015	2
23/10/2015	1-20	3764	0.9999	0.0024	2
26/10/2015	1-20	3750	0.9999	0.0016	3
27/10/2015	1-20	6293	1.0000	0.0018	3
28/10/2015	1-20	4992	1.0000	0.0017	3
29/10/2015	1-20	4736	0.9999	0.0017	3
30/10/2015	1-20	4358	1.0000	0.0023	3
02/11/2015	1-20	6654	0.9999	0.0012	3
03/11/2015	1-20	5842	0.9997	0.0019	2

Table 25: Summary of the investigation of the spiked working range samples for cadmium method validation

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
12/10/2015	1	1.50	1.46	2.9%
		2.50	2.41	3.6%
		7.50	7.26	3.2%
		12.5	12.1	3.0%
		17.5	16.8	3.9%
14/10/15	1	1.80	1.69	6.2%
		3.50	3.26	6.9%
		8.50	7.90	7.0%
		12.0	11.0	8.4%
		16.0	14.5	9.6%
15/10/2015	2	2.60	2.59	0.51%
		7.40	7.25	2.0%
		8.70	8.58	1.4%
		15.9	15.6	1.7%
		19.7	19.5	1.2%
16/10/2015	2	1.30	1.24	4.7%
		1.90	1.80	5.2%
		2.30	2.15	6.4%
		6.90	6.32	8.4%
		7.70	7.27	5.6%
19/10/2015	1	1.70	1.66	2.2%
		2.10	2.06	1.8%
		3.00	2.92	2.7%
		8.00	7.67	4.1%
		14.0	13.3	5.3%
20/10/2015	1	4.00	3.79	5.2%
		5.20	4.91	5.7%
		7.20	6.78	5.8%
		8.10	7.54	6.9%
		11.0	10.2	7.4%
21/10/2015	1	6.40	6.23	2.6%
		7.30	7.14	2.3%
		13.0	12.6	2.9%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		14.0	13.4	4.5%
		16.5	15.9	3.8%
22/10/2015	2	1.10	1.08	2.1%
		4.40	4.23	3.9%
		9.50	9.17	3.5%
		13.5	12.8	5.0%
		17.0	16.2	4.7%
23/10/2015	2	9.80	9.65	1.5%
		10.3	10.0	2.5%
		11.5	11.5	0.39%
		13.8	13.4	3.1%
		15.3	14.9	2.3%
27/10/2015	3	3.50	3.34	4.6%
		7.00	6.62	5.4%
		10.5	9.89	5.8%
		14.0	13.2	5.6%
		17.5	16.5	5.6%
28/10/2015	3	5.25	4.98	5.2%
		8.75	8.34	4.6%
		12.25	11.6	5.6%
		15.75	14.9	5.4%
		19.25	18.4	4.2%
29/10/2015	3	6.00	5.69	5.1%
		9.00	8.73	3.0%
		12.0	11.3	5.6%
		15.0	14.2	5.2%
		18.0	16.9	6.4%
30/10/2015	3	3.00	2.81	6.2%
		4.00	3.76	5.9%
		8.00	7.44	7.0%
		9.00	8.33	7.4%
		12.0	11.2	7.1%
03/11/2015	2	7.40	7.67	3.7%
		9.70	9.91	2.2%
		15.2	15.6	2.5%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		17.6	17.9	1.7%
		19.0	19.3	1.7%

Table 26: Summary of the spiked repeat samples for cadmium method validation

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
12/10/2015	1	5.00	5.13	2.6%	4.97	0.0796	1.59%
		5.00	5.08	1.6%			
		5.00	5.07	1.5%			
		5.00	5.08	1.6%			
		5.00	5.04	0.88%			
		5.00	5.05	1.1%			
		5.00	4.95	0.91%			
		5.00	5.00	0.016%			
		5.00	4.93	1.4%			
		5.00	4.97	0.59%			
		5.00	4.95	0.91%			
		5.00	4.93	1.4%			
		5.00	4.92	1.5%			
		5.00	4.95	0.99%			
		5.00	4.89	2.2%			
		5.00	4.93	1.4%			
		5.00	4.88	2.5%			
		5.00	4.86	2.8%			
		5.00	4.92	1.5%			
		5.00	4.87	2.5%			
14/10/2015	1	5.00	4.87	2.7%	4.75	0.0872	1.74%
		5.00	4.90	2.0%			
		5.00	4.87	2.5%			
		5.00	4.88	2.3%			
		5.00	4.80	4.0%			
		5.00	4.80	4.0%			
		5.00	4.81	3.8%			
		5.00	4.79	4.1%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.72	5.6%			
		5.00	4.77	4.7%			
		5.00	4.70	6.1%			
		5.00	4.72	5.5%			
		5.00	4.68	6.4%			
		5.00	4.70	6.0%			
		5.00	4.64	7.2%			
		5.00	4.66	6.7%			
		5.00	4.70	5.9%			
		5.00	4.68	6.3%			
		5.00	4.63	7.5%			
		5.00	4.65	7.1%			
15/10/2015	2	5.00	5.16	3.3%	5.05	0.0665	1.33%
		5.00	5.03	0.54%			
		5.00	5.04	0.83%			
		5.00	5.01	0.24%			
		5.00	5.00	0.059%			
16/10/2015	2	5.00	4.94	1.1%	4.86	0.0622	1.25%
		5.00	4.90	2.0%			
		5.00	4.81	3.8%			
		5.00	4.81	3.9%			
		5.00	4.82	3.6%			
19/10/2015	1	5.00	4.93	1.5%	4.92	0.0378	0.757%
		5.00	4.91	1.8%			
		5.00	4.98	0.37%			
		5.00	4.92	1.7%			
		5.00	4.88	2.5%			
20/10/2015	1	5.00	4.94	1.2%	4.86	0.0606	1.21%
		5.00	4.88	2.4%			
		5.00	4.86	2.9%			
		5.00	4.82	3.6%			
		5.00	4.78	4.4%			
21/10/2015	1	5.00	4.96	0.75%	4.92	0.0304	0.609%
		5.00	4.95	1.1%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.89	2.2%			
		5.00	4.91	1.7%			
		5.00	4.90	1.9%			
22/10/2015	2	5.00	5.01	0.10%	4.90	0.0938	1.87%
		5.00	4.94	1.2%			
		5.00	4.94	1.2%			
		5.00	4.78	4.4%			
		5.00	4.82	3.6%			
23/10/2015	2	5.00	5.07	1.5%	4.98	0.0644	1.29%
		5.00	4.94	1.1%			
		5.00	4.99	0.27%			
		5.00	4.98	0.38%			
		5.00	4.90	2.0%			
27/10/2015	3	5.00	5.04	0.79%	5.01	0.0182	0.363%
		5.00	5.00	0.073%			
		5.00	5.01	0.19%			
		5.00	5.00	0.088%			
		5.00	5.00	0.058%			
28/10/2015	3	5.00	4.92	1.6%	4.98	0.0402	0.804%
		5.00	5.02	0.39%			
		5.00	5.01	0.20%			
		5.00	4.97	0.63%			
		5.00	4.98	0.36%			
29/10/2015	3	5.00	4.99	0.14%	5.02	0.0176	0.352%
		5.00	5.04	0.80%			
		5.00	5.02	0.35%			
		5.00	5.01	0.29%			
		5.00	5.03	0.57%			
30/10/2015	3	5.00	5.03	0.69%	5.00	0.0243	0.486%
		5.00	5.01	0.22%			
		5.00	5.00	0.052%			
		5.00	4.98	0.48%			
		5.00	4.98	0.43%			
02/11/2015	3	5.00	5.07	1.3%	5.07	0.0150	0.299%

Date	Analyst	Conc. (μg/L)	Result (μg/L)	% Difference	Average Result (μg/L)	σ (SD)	% RSD
		5.00	5.08	1.7%			
		5.00	5.05	0.90%			
		5.00	5.08	1.6%			
		5.00	5.06	1.3%			
03/11/2015	2	5.00	5.16	3.2%	5.15	0.00992	0.198%
		5.00	5.14	2.9%			
		5.00	5.15	3.0%			
		5.00	5.17	3.3%			
		5.00	5.14	2.9%			

4.9. Lead validation data

Table 27: Summary of the calibration range, gradients, R^2 values and LODs for lead method validation

Date	Calibration range (μg/L)	Gradient of calibration slope	R^2 value	Limit of Detection (μg/L)	Analyst
12/10/2015	1-20	31417	1.0000	0.0025	1
14/10/2015	1-20	33937	1.0000	0.0049	1
15/10/2015	1-20	32685	1.0000	0.0015	2
16/10/2015	1-20	32125	1.0000	0.0061	2
19/10/2015	1-20	30299	0.9993	0.0017	1
20/10/2015	1-20	30399	0.9990	0.0075	1
21/10/2015	1-20	26266	1.0000	0.0019	1
22/10/2015	1-20	25766	1.0000	0.0086	2
23/10/2015	1-20	24723	0.9999	0.069	2
26/10/2015	1-20	23755	1.0000	0.0016	3
27/10/2015	1-20	35380	1.0000	0.0016	3
28/10/2015	1-20	28746	1.0000	0.0023	3
29/10/2015	1-20	27594	1.0000	0.0026	3
30/10/2015	1-20	25044	1.0000	0.0031	3
02/11/2015	1-20	35086	0.9999	0.0018	3
03/11/2015	1-20	33347	0.9997	0.0047	2

Table 28: Summary of the investigation of the spiked working range samples for lead method validation

Date	Analyst	Concentration (μg/L)	Result (μg/L)	% Difference
12/10/2015	1	1.50	1.44	4.2%
		2.50	2.42	3.1%
		7.50	7.20	4.0%
		12.5	12.1	3.4%
		17.5	16.9	3.6%
14/10/15	1	1.80	1.72	4.7%
		3.50	3.33	4.8%
		8.50	8.08	4.9%
		12.0	11.3	5.5%
		16.0	15.0	6.4%
15/10/2015	2	2.60	2.46	5.5%
		7.40	6.96	6.0%
		8.70	8.20	5.8%
		15.9	15.1	5.1%
		19.7	18.8	4.7%
16/10/2015	2	1.30	1.23	5.3%
		1.90	1.81	4.7%
		2.30	2.17	5.8%
		6.90	6.39	7.4%
		7.70	7.42	3.6%
19/10/2015	1	1.70	1.60	5.8%
		2.10	1.98	5.6%
		3.00	2.86	4.8%
		8.00	7.52	6.0%
		14.0	13.1	6.7%
20/10/2015	1	4.00	3.76	6.0%
		5.20	4.86	6.6%
		7.20	6.73	6.6%
		8.10	7.55	6.8%
		11.0	10.3	6.6%
21/10/2015	1	6.40	6.11	4.5%
		7.30	7.02	3.8%
		13.0	12.5	3.8%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		14.0	13.3	4.9%
		16.5	15.9	3.9%
22/10/2015	2	1.10	1.04	5.6%
		4.40	4.12	6.4%
		9.50	8.89	6.5%
		13.5	12.6	6.6%
		17.0	15.9	6.3%
23/10/2015	2	9.80	9.24	5.8%
		10.3	9.68	6.0%
		11.5	11.0	4.2%
		13.8	13.0	5.8%
		15.3	14.5	4.9%
27/10/2015	3	3.50	3.33	4.6%
		7.00	6.63	4.6%
		10.5	9.96	4.6%
		14.0	13.3	4.7%
		17.5	16.7	4.6%
28/10/2015	3	5.25	5.07	3.4%
		8.75	8.44	3.5%
		12.3	11.8	3.5%
		15.8	15.2	3.4%
		19.3	18.9	1.7%
29/10/2015	3	6.00	5.86	2.3%
		9.00	9.03	0.34%
		12.0	11.7	2.7%
		15.0	14.7	2.2%
		18.0	17.5	2.8%
30/10/2015	3	3.00	2.92	2.7%
		4.00	3.89	2.7%
		8.00	7.80	2%
		9.00	8.74	2.9%
		12.0	11.7	2.6%
03/11/2015	2	7.40	7.12	3.8%
		9.70	9.31	4.0%
		15.2	14.6	3.9%

Date	Analyst	Concentration (µg/L)	Result (µg/L)	% Difference
		17.6	16.9	4.1%
		19.0	18.2	4.2%

Table 29: Summary of the spiked repeat samples for lead method validation

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
12/10/2015	1	5.00	4.71	5.8%	4.76	0.0362	0.725%
		5.00	4.72	5.6%			
		5.00	4.73	5.4%			
		5.00	4.74	5.3%			
		5.00	4.73	5.4%			
		5.00	4.75	5.0%			
		5.00	4.70	6.0%			
		5.00	4.78	4.4%			
		5.00	4.73	5.3%			
		5.00	4.74	5.2%			
		5.00	4.75	5.0%			
		5.00	4.76	4.7%			
		5.00	4.78	4.5%			
		5.00	4.82	3.5%			
		5.00	4.79	4.3%			
		5.00	4.78	4.5%			
		5.00	4.78	4.4%			
		5.00	4.80	4.0%			
		5.00	4.83	3.5%			
		5.00	4.80	4.1%			
14/10/15	1	5.00	4.54	9.3%	4.64	0.0530	1.06%
		5.00	4.63	7.4%			
		5.00	4.61	7.9%			
		5.00	4.62	7.7%			
		5.00	4.60	7.9%			
		5.00	4.63	7.4%			
		5.00	4.63	7.3%			
		5.00	4.65	6.9%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.62	7.5%			
		5.00	4.65	6.9%			
		5.00	4.61	7.8%			
		5.00	4.64	7.2%			
		5.00	4.62	7.5%			
		5.00	4.66	6.9%			
		5.00	4.65	6.9%			
		5.00	4.66	6.8%			
		5.00	4.69	6.3%			
		5.00	4.82	3.7%			
		5.00	4.67	6.5%			
		5.00	4.69	6.1%			
15/10/2015	2	5.00	4.69	6.1%	4.70	0.0210	0.420%
		5.00	4.68	6.3%			
		5.00	4.69	6.2%			
		5.00	4.73	5.5%			
		5.00	4.73	5.4%			
16/10/2015	2	5.00	4.66	6.9%	4.68	0.0209	0.417%
		5.00	4.66	6.7%			
		5.00	4.69	6.3%			
		5.00	4.71	5.8%			
		5.00	4.68	6.3%			
19/10/2015	1	5.00	4.57	8.6%	4.62	0.0323	0.647%
		5.00	4.60	8.0%			
		5.00	4.64	7.2%			
		5.00	4.64	7.1%			
		5.00	4.63	7.3%			
20/10/2015	1	5.00	4.62	7.5%	4.64	0.021	0.422%
		5.00	4.61	7.9%			
		5.00	4.65	6.9%			
		5.00	4.66	6.9%			
		5.00	4.64	7.2%			
21/10/2015	1	5.00	4.68	6.3%	4.72	0.0474	0.948%
		5.00	4.71	5.9%			

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.68	6.5%			
		5.00	4.73	5.3%			
		5.00	4.79	4.1%			
22/10/2015	2	5.00	4.65	7.0%	4.63	0.0471	0.943%
		5.00	4.62	7.6%			
		5.00	4.68	6.5%			
		5.00	4.55	9.0%			
		5.00	4.64	7.2%			
23/10/2015	2	5.00	4.67	6.5%	4.67	0.0197	0.394%
		5.00	4.65	7.0%			
		5.00	4.68	6.4%			
		5.00	4.66	6.7%			
		5.00	4.70	6.0%			
27/10/2015	3	5.00	4.55	8.9%	4.60	0.0389	0.778%
		5.00	4.59	8.2%			
		5.00	4.57	8.6%			
		5.00	4.65	7.0%			
		5.00	4.63	7.5%			
28/10/2015	3	5.00	4.53	9.4%	4.63	0.0593	1.19%
		5.00	4.64	7.1%			
		5.00	4.65	7.1%			
		5.00	4.68	6.4%			
		5.00	4.67	6.5%			
29/10/2015	3	5.00	4.55	9.0%	4.64	0.0567	1.13%
		5.00	4.65	7.0%			
		5.00	4.68	6.4%			
		5.00	4.65	7.1%			
		5.00	4.70	6.0%			
30/10/2015	3	5.00	4.69	6.2%	4.70	0.0181	0.361%
		5.00	4.70	6.1%			
		5.00	4.67	6.5%			
		5.00	4.71	5.8%			
		5.00	4.72	5.6%			
02/11/2015	3	5.00	4.66	6.9%	4.69	0.0277	0.554%

Date	Analyst	Conc. (µg/L)	Result (µg/L)	% Difference	Average Result (µg/L)	σ (SD)	% RSD
		5.00	4.67	6.6%			
		5.00	4.69	6.2%			
		5.00	4.69	6.2%			
		5.00	4.73	5.4%			
03/11/2015	2	5.00	4.67	6.5%	4.72	0.0289	0.578%
		5.00	4.70	5.9%			
		5.00	4.74	5.2%			
		5.00	4.72	5.7%			
		5.00	4.74	5.1%			

4.10. QC Data for Full Validation Project

Table 30: QC data from the validation project for all nine elements

Date	B 11 (µg/L)	Al 27 (µg/L)	Cr 52 (µg/L)	Fe 56 (µg/L)	Ni 60 (µg/L)	Cu 63 (µg/L)	Zn 66 (µg/L)	Cd 111 (µg/L)	Pb 208 (µg/L)
12/10/2015	10.2	10.9	10.0	9.65	9.78	9.26	9.38	10.3	9.33
	10.3	11.4	10.3	10.6	9.87	9.35	9.66	10.3	9.44
	10.6	11.5	11.2	11.6	10.8	10.2	9.03	9.71	9.57
	10.5	12.9	11.3	11.5	10.9	10.3	8.93	9.73	9.62
	10.5	11.8	11.4	12.2	10.9	10.4	8.86	9.59	9.51
	10.5	12.3	11.6	12.2	11.2	10.6	9.42	9.62	9.62
14/10/2015	10.3	9.88	10.2	10.2	9.74	9.13	8.88	9.96	9.25
	10.2	11.0	10.3	10.6	9.89	9.21	8.70	9.88	9.19
	10.7	11.1	11.0	11.7	10.6	9.93	8.34	9.28	9.35
	11.1	10.5	11.2	14.1	10.8	10.1	8.50	9.28	9.33
	10.7	10.6	11.1	11.9	10.8	10.2	8.98	9.17	9.37
	10.9	9.17	11.3	12.6	11.0	10.3	8.27	9.19	9.47
15/10/2015	10.3	10.6	9.68	9.57	9.42	8.95	9.70	10.2	9.21
	10.0	10.4	9.80	9.69	9.47	8.93	9.53	10.2	9.16
	10.0	10.3	10.2	10.3	9.82	9.29	9.81	9.97	9.39
	10.1	10.2	10.2	10.3	9.80	9.23	9.55	9.84	9.40
	10.1	9.43	10.5	10.6	10.2	9.56	9.02	9.82	9.47
	10.2	9.70	10.8	11.1	10.3	9.74	9.63	9.88	9.59
16/10/2015	10.3	10.4	9.87	9.85	9.51	9.04	10.5	10.1	9.25
	9.99	10.6	10.0	10.8	9.60	9.11	9.10	9.86	9.21
	9.55	9.43	10.4	10.7	9.95	9.45	8.92	9.64	9.37

	9.52	9.57	10.4	11.0	9.97	9.49	8.95	9.54	9.41
	9.58	9.30	10.6	11.1	10.3	9.65	8.84	9.29	9.44
	9.71	9.12	10.8	11.5	10.4	9.76	8.57	9.38	9.49
19/10/2015	10.00	9.82	9.77	9.71	9.61	9.01	9.58	10.01	9.07
	9.83	10.05	9.90	9.89	9.70	9.05	9.20	9.91	9.11
	9.45	10.18	10.11	10.11	9.87	9.26	9.25	9.65	9.21
	9.51	9.21	10.13	10.07	9.83	9.29	9.44	9.63	9.22
	9.26	9.29	10.41	10.55	10.13	9.50	9.15	9.56	9.42
	9.22	8.89	10.37	10.55	10.07	9.46	8.85	9.48	9.41
20/10/2015	9.81	9.33	9.66	9.52	9.41	8.94	8.92	10.05	9.13
	9.67	9.23	9.76	9.57	9.51	8.98	9.07	9.98	9.19
	9.48	8.74	10.2	10.3	9.90	9.41	8.75	9.46	9.27
	9.50	8.39	10.2	10.0	9.96	9.47	8.92	9.43	9.32
	9.60	8.22	10.4	10.5	10.2	9.64	8.66	9.27	9.24
	9.58	8.52	10.5	10.8	10.2	9.68	8.84	9.22	9.30
22/10/2015	10.7	10.5	10.1	10.1	9.87	9.38	9.77	10.1	9.34
	10.4	10.4	10.2	10.2	9.82	9.37	9.99	9.95	9.30
	10.3	10.0	10.3	10.6	10.1	9.48	9.17	9.71	9.45
	10.5	9.99	10.4	10.2	10.1	9.57	9.34	9.81	9.55
	10.5	9.51	10.7	11.1	10.3	9.85	9.18	9.59	9.57
	10.6	11.0	10.7	11.4	10.5	9.85	9.04	9.57	9.60
23/10/2015	10.2	11.2	9.72	9.77	9.53	9.11	10.1	10.1	9.27
	10.1	10.1	9.77	10.0	9.54	9.02	9.68	9.96	9.27
	10.3	9.70	10.0	9.98	9.85	9.30	9.55	9.84	9.35
	10.1	9.71	9.88	9.79	9.66	9.19	9.47	9.77	9.34
	10.5	9.31	10.2	10.2	9.92	9.45	9.20	9.73	9.38
	10.7	9.46	10.4	10.5	10.1	9.68	9.31	9.81	9.51

23/10/2015	10.23	9.84	9.54	9.51	9.36	8.95	9.21	9.68	8.89
	10.36	10.0	9.89	9.88	9.62	9.21	9.01	9.95	9.16
	10.36	9.87	10.2	10.2	9.94	9.47	9.02	9.59	9.22
	10.53	9.67	10.4	10.7	10.1	9.60	9.03	9.64	9.31
	10.50	9.72	10.3	11.0	10.1	9.66	9.10	9.52	9.33
	10.41	9.62	10.6	10.9	10.3	9.83	9.49	9.55	9.37
27/10/2015	10.6	10.3	10.1	10.1	9.61	9.18	9.44	10.20	9.17
	10.5	10.3	10.1	9.82	9.67	9.22	9.32	9.89	9.00
	10.7	10.3	10.3	10.1	9.87	9.37	9.19	9.93	9.08
	10.8	10.3	10.4	10.4	9.80	9.43	9.08	9.87	9.06
	11.0	10.2	10.5	10.6	10.0	9.53	9.08	9.81	9.10
	11.1	10.3	10.6	10.7	10.2	9.58	9.15	9.95	9.19
28/10/2015	10.6	9.97	9.95	9.49	9.69	9.21	9.50	10.1	9.27
	10.3	11.3	9.68	9.45	9.42	8.94	8.91	9.96	9.20
	10.7	9.89	10.0	9.89	9.83	9.30	9.12	9.90	9.24
	10.9	10.5	10.2	10.3	9.99	9.52	9.04	9.87	9.27
	11.0	9.57	10.4	10.4	10.1	9.54	8.64	9.82	9.26
	10.9	9.88	10.2	10.3	9.93	9.45	9.45	9.75	9.26
29/10/2015	10.3	11.0	9.74	9.69	9.54	8.98	9.69	10.0	9.19
	10.4	11.4	9.88	9.74	9.57	9.17	9.19	9.88	9.13
	10.8	10.9	10.6	10.7	10.3	9.77	9.28	10.0	9.42
	10.5	10.7	10.2	10.2	9.93	9.33	8.52	9.64	9.20
	10.5	10.9	10.4	10.5	9.96	9.46	8.99	9.69	9.34
	11.0	11.6	10.8	10.9	10.5	10.0	9.35	9.94	9.64
30/10/2015	10.2	9.55	9.97	10.3	9.75	9.20	9.68	10.1	9.29
	10.1	9.55	10.1	10.6	9.92	9.29	9.12	9.93	9.21
	10.0	9.49	10.3	10.7	10.1	9.52	8.80	9.83	9.35

	10.4	9.48	10.4	10.8	10.2	9.49	8.91	9.96	9.44
	10.5	10.4	10.8	11.5	10.4	9.85	9.92	9.88	9.55
	10.3	9.14	10.6	11.2	10.3	9.70	8.67	9.69	9.50
02/11/2015	10.0	9.94	9.85	9.82	9.55	9.12	9.98	10.1	9.24
	10.1	10.0	10.0	10.0	9.63	9.17	9.19	10.1	9.20
	10.1	9.72	10.2	10.5	9.84	9.36	9.09	10.0	9.32
	10.1	10.2	10.3	10.6	9.92	9.39	9.06	9.99	9.36
	10.3	10.4	10.5	10.9	10.1	9.63	9.04	10.0	9.53
	10.3	10.5	10.5	11.1	10.1	9.68	8.57	10.0	9.51
03/11/2015	10.3	10.1	10.0	9.59	9.68	9.14	9.43	10.2	9.25
	10.3	10.1	9.95	10.6	9.69	9.07	9.03	10.2	9.30
	10.3	9.88	10.2	10.2	9.91	9.30	9.06	10.2	9.45
	10.2	11.4	10.1	10.4	9.92	9.22	10.31	10.0	9.40
	10.6	9.33	10.6	10.6	10.4	9.62	8.72	10.2	9.60
	10.6	9.30	10.5	10.6	10.2	9.52	9.44	10.1	9.59
Average	10.3	10.1	10.3	10.5	10.0	9.45	9.19	9.82	9.33
% RSD	4.1%	8.2%	4.1%	7.2%	3.9%	3.7%	4.5%	2.8%	1.7%

4.11. Trueness Sample Validation Data

Table 31: Results from the Manufactured Trueness Sample

Element	B	Al	Cr	Fe	Ni	Cu	Zn	Cd	Pb
Result 1 (µg/L)	10.3	3.99	1.94	9.89	1.91	1.92	9.59	0.945	3.80
Result 2 (µg/L)	10.1	3.85	2.00	10.4	1.98	1.91	9.05	0.936	3.83
Result 3 (µg/L)	10.5	3.48	2.06	10.5	1.94	1.91	8.64	0.936	3.78
Result 4 (µg/L)	10.1	3.15	1.97	9.92	1.92	1.88	9.01	0.940	3.82
Average Result (µg/L)	10.3	3.62	1.99	10.2	1.94	1.91	9.07	0.939	3.81
% RSD	1.7%	10%	2.6%	3.0%	1.5%	0.88%	4.3%	0.46%	0.67%
LOD (µg/L)	0.048	0.64	0.026	0.20	0.015	0.14	0.81	0.0016	0.0014

4.12. Analysis of FED sample data

A FED sample (FMDT2 sample ID AL422) was provided by Bradwell Magnox for analysis. This sample was analysed in triplicate after the application of a DF 500. It was found that upon the application of a DF 500 all of the elements analysed were below the LOD. The results below outline the LOD for all of the analytes when taking into account the DF 500 applied to the samples.

Table 32: Results from Analysis of Bradwell Plant Sample

Element	B	Al	Cr	Fe	Ni	Cu	Zn	Cd	Pb
LOD (µg/L)	<34.1	<545	<14.6	<126	<11.7	<5.04	<229	<1.16	<1.44

5. Conclusions

The method development and validation for the “main metals” Bradwell method has been successful and all of the data generated has been detailed within this report.

The method parameters have been optimised based on the initial method set up at Bradwell. The important alterations are to He flow rates for elements that do not require them which has improved repeatability between measurements. The sample flush time and sample rinse time has been reduced to 90 seconds each which has reduced the time taken for each sample injection, which will speed up analysis in a plant environment. The measurement of one isotope per element has been conducted in this validation report, which will also shorten analysis time. For Zn both isotopes (Zn-66 and Zn-68) were measured during the validation process as initially Zn-66 recoveries appeared low due to concerns over TiO^+ isobaric interferences. However, the validation has shown no notable difference between the isotopes so Zn-66 has been selected and all Zn data reported for validation is for Zn-66. These new parameters can be adopted by Bradwell and routine analysis should be faster and should generate data where the concentrations calculated by the software can be used directly.

The most significant part of the method development was the investigation of the effect of Mg and Na concentrations on the measurement of the nine elements in this method. Multiple dilutions of the old effluent stream were attempted and this was shown to be a DF400 where suppression was seen however, the internal standard correction could be applied. This was in agreement with observations from Bradwell (DF402). However, before method validation commenced the FED dissolution was increased leading to an increase in Mg levels and a decrease in Na levels. These new concentrations were examined and it was decided with the customer that a DF500 on the new FED effluent gave a similar Mg and Na concentration to the previous DF400 on the old FED effluent. Therefore the validation proceeded with the new DF500 Mg and Na concentrations (67.0 and 23.0 mg/L respectively) and Bradwell adopted this new dilution on site.

The validation data has shown good consistency for B, Cr, Ni, Cu, Cd and Pb with precisions calculated of 6.8%, 3.6%, 3.3%, 3.5%, 2.6% and 1.4% respectively. For these elements it is recommended that QC boundaries are set at 10% (between 9.0 µg/L and 11 µg/L).

The validation data has shown that contamination and high background variation is possible with Fe, Al and Zn as it is ubiquitous. Therefore there are examples with all three elements were samples have shown large % differences with the expected concentrations. It is important that the blanks during analysis are examined and when necessary data reprocessed or in extreme cases repeated where necessary. Although Fe has shown contamination issues, rejecting the data associated with the contamination produces a calculated precision of 6.8%. This is not the case with Al and Zn as there is much larger variation observed. Even when the contaminated data is rejected precisions of 16% and 13% respectively are observed. This is in part due to a very high background of Al, therefore it is difficult to measure these low level concentrations by ICP-MS. It is important to note that Al is measured for plant performance only and not environmental discharge. Therefore it is recommended that it is down to customer discretion whether higher uncertainties are acceptable for Al analysis. The precision of Znis in some part is due to background variations. However this project has shown the largest suppression in the high Mg and Na concentrations is observed for Zn. There is also the largest discrepancy between the internal standard suppression of Sc and Zn. Although an alternative internal standard could be sought for Zn the potential improvement would be minimal in comparison to the discharge limit for Zn. As the sample is measured at low concentrations even with the DF500 applied relative to the discharge limit the higher precision becomes negligible for the discharge.

The comparative sample analysis on a Bradwell plant sample and a manufactured trueness sample has been conducted using the new method parameters. The results are detailed within this report and can be used by Bradwell for comparison. This can be assessed during the site visit.

The new method parameters detailed in this report from the successful validation of the method can be adopted at Bradwell and can be transferred during the site visit from the experienced NNL analyst.

6. Recommendations

The recommendations from this report are detailed below:

- The new method parameters that have been developed and validated (detailed in Appendix 2) should be applied to the "main metals" analytical procedure conducted at Bradwell.
- Bradwell should continue to apply a DF500 to the current FED effluent stream. If the concentrations of Mg and Na are significantly altered due to changes in the FED procedure this report can be used as a basis for a new dilution.
- The manufactured trueness sample results should be compared to the known concentrationswhich have currently not been disclosed to NNL.
- The manufactured trueness sample should be prepared at Bradwell according to the same procedure detailed within the report (detailed in Appendix 2) and analysed via the new method parameters. The data obtained on the Bradwell NexION 300X should be compared to the NNL data obtained on the NexION 300D to demonstrate the equivalence between the two instruments supporting the validation detailed in this report.
- The QC data obtained from the validation work can be compared to QC charts from previous Bradwell analysis to show equivalence between the two instruments.

Following this report an NNL experienced operator will attend Bradwell for one week to train all of the analytical team in the new procedure, assist with any data interpretation concerning this report and be present for analysing the manufactured trueness sample.

NNL would be pleased to support Bradwell in any further studies or validation required for analysis by ICP-MS and to support this validation report in discussions with the Environment Agency if required. NNL would be pleased to submit any future proposals based on the recommendations in this report for continued analytical support.

7. References

1. EX10049/06/10/01, J. Hawkett, Issue 1, 2015

Appendix 1: Bradwell "Main Metals" Method and Parameters

Preparation of Samples, Standards, QCs and Blanks:

Bradwell prepares all samples, blanks, calibration standards and QCs in accordance with BRAD-22405-OI-0166_Issue_3. Analysis by ICP-MS and the processing of data is completed in accordance with BRAD-22405-OI-0166_Issue_3 and BRAD_22429_OI_00136_Issue_1.

ICP-MS Parameters:

The table below details the parameters for the mass detector:

Parameter	Value
Sweeps / Reading	40
Readings /Replicate	1
Replicates	3
RPQ value	0.25

The table below details the He flow rate parameters for each element:

Analyte	He flow rate in collision cell / mL min^{-1}
B	0.5
Al	0.5
Cr	3.0
Fe	4.5
Ni	3.0
Cu	3.0
Zn	3.0
Cd	0.5
Pb	0.5
Sc	0.5
Tb	0.5

The table below details the rinse procedures for analysis:

	Time / s	Speed / (+/- rpm)
Sample Flush	120	-30.0
Read Delay	15	-16.0
Analysis	N/A	-16.0
Wash	90	-30.0

Appendix 2: Validated Method Parameters

Preparation of Samples, Standards, QCs and Blanks

All samples, blanks, calibration standards and QCs were diluted using 0.3 mol dm^{-3} HNO_3. This was prepared from trace metal grade concentrated HNO_3 (67-69%), purchased from Fisher Scientific (Fisher Scientific Code - 11395800). 20 mL of the concentrated HNO_3 was then diluted by the addition of the HNO_3 to 980 mL deionised water (deionised water was produced using a Barnstead NANOpure diamond ultrapure water system).

Calibration standards were prepared by the dilution of a specially ordered mixed element standard from Perkin Elmer (special standard). The special standard contained B, Al, Cr, Fe, Ni, Cu, Zn, Cd and Pb all at 1000 mg/L. Two sequential DF 100s were performed using 0.3 mol dm^{-3} HNO_3 in order to create a 100 µg/L standard from which five calibration standards were prepared as described in the table below:

Volume 100 µg/L special standard (mL)	Volume 0.3 mol dm^{-3} HNO_3 (mL)	Final Concentration (µg/L)
2.0	8.0	20
1.0	9.0	10
0.5	9.5	5
0.2	9.8	2
0.1	9.9	1

CertiPrep Plus ICP standards were used to produce QCs at 10 µg/L. This involved creating a 100 µg/L mixed standard solution, by an appropriate dilution, from the single elements listed below:

Element	CertiPrep catalogue number	Concentration of original standard (mg/L)	Medium original standard is stored
B	PLB9-3Y	10000	H_2O
Al	PLAL2-2Y	1000	2% HNO_3
Cr	PLCR3-2Y	1000	2% HNO_3
Fe	PLFE2-2Y	1000	2% HNO_3
Ni	PLNI2-2Y	1000	2% HNO_3
Cu	PLCU2-2Y	1000	2% HNO_3
Zn	PLZN2-2Y	1000	2% HNO_3
Cd	PLCD2-2Y	1000	2% HNO_3
Pb	PLCD2-2Y	1000	2% HNO_3

Two internal standards were used for the analysis of the main metals group. Sc was used as an internal standard for B, Al, Cr, Fe, Ni, Cu and Zn. Tb was used as an internal standard for Cd and Pb. An internal standard solution containing 10 mg/L Sc and Tb was purchased from Perkin Elmer (Perkin Elmer Catalogue number N9303832). A DF 20 was performed on the stock solution in 0.3 mol dm^{-3} HNO_3 to create a 500 µg/L internal standard solution. Then 100 µL of 500 µg/L internal standard solution was spiked into all samples, standards, QCs and blanks analysed resulting in 5 µg/L Sc and Tb concentration being present in all samples, standards, QCs and blanks.

Samples analysed at Bradwell contain particularly high concentrations of Na and Mg. After discussion with Bradwell personnel concerning an increase in FEDD per batch it was decided that a DF 500 would be employed for future analysis instead of the current DF 402 on the old FEDD stream described in Appendix 1. This was considered the most appropriate dilution to apply giving concentrations of Mg and Na of 67.0 mg/L and 23.0 mg/L respectively. All QCs and samples were matrix matched to Bradwell's sample matrix through the addition of 1 mL of a solution containing 670 mg/L Mg and 230 mg/L Na in 0.3 mol dm^{-3} HNO_3 prepared from the certified standards in the table below:

Element	Supplier	Supplier Catalogue number	Concentration of stock (mg/L)	Matrix of stock solution
Mg	Fluka (Sigma Aldrich)	80759_100ML	10000	5% HNO_3
Na	CretiPrep Plus	PLNA2-3Y	10000	5% HNO_3

ICP-MS Parameters

The table below details the parameters for the mass detector:

Parameter	Value
Sweeps / Reading	30
Readings /Replicate	1
Replicates	3
RPQ value	0.25

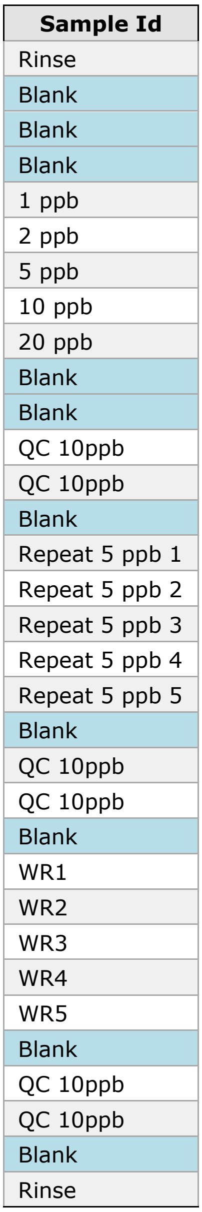
The table below details the He flow rate parameters for each element:

Analyte	He flow rate in collision cell (mL/min)
B-11	0.00
Al-27	0.50
Cr-52	3.00
Fe-56	5.25
Ni-60	3.00
Cu-63	3.00
Zn-66,68	0.50
Cd-111	0.00
Pb-208	0.00
Sc-45	0.50
Tb-159	0.00

The table below details the rinse procedures for analysis:

	Time / s	Speed / (+/- rpm)
Sample Flush	90	-18.0
Read Delay	15	-18.0
Analysis	N/A	-18.0
Wash	90	-18.0

The image below shows the standardised run sequence for the validation work:



Sample Id
Rinse
Blank
Blank
Blank
1 ppb
2 ppb
5 ppb
10 ppb
20 ppb
Blank
Blank
QC 10ppb
QC 10ppb
Blank
Repeat 5 ppb 1
Repeat 5 ppb 2
Repeat 5 ppb 3
Repeat 5 ppb 4
Repeat 5 ppb 5
Blank
QC 10ppb
QC 10ppb
Blank
WR1
WR2
WR3
WR4
WR5
Blank
QC 10ppb
QC 10ppb
Blank
Rinse

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