NATIONAL NUCLEAR LABORATORY

Method development and validation of mercury method by inductively coupled mass spectrometry

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A report prepared for and on behalf of
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NATIONAL NUCLEAR LABORATORY

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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 requires the measurement of mercury and the current method of choice is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). 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 mercury and NNL were requested to visit the facility. Further to this visit NNL were commissioned to optimise and validate Bradwell's ICP-MS based mercury 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 mercury by ICP-MS.

This report details the method development procedure required to optimise the existing Bradwell mercury method. This has mainly focused around controlling effects arising from the high magnesium and sodium concentrations found in the effluent stream from FED dissolution and neutralisation. The method has been optimised with the ideal dilution factor for the samples determined and a validation programme conducted. All data generated is provided within this report. During method development high mercury concentrations (0.75 and 1 µg/L) were seen to be unstable and gold was introduced to the method to stabilise mercury in solution. All blanks, calibration standards, quality control samples and samples were spiked with gold to a concentration of 200 µg/L. The calibration range and QC value have also been altered to lower concentrations more applicable to the sample concentrations of mercury observed at Bradwell. The validation programme has assessed the repeatability and reproducibility of results from fifteen different runs, which involved five different analysts, to assess the robustness of the technique. The precision has been assessed for the measurement of mercury and acceptable limits for quality control sample variations within a run and between analyses have been suggested.

The validation data has shown that mercury can be measured routinely between 0.05 – 1.0 µg/L with consistent calibration line gradients and R^2 values > 0.995. The typical instrumental limit of detection was around 6.6 ng/L when measuring Hg-200 or Hg-202 to infer total mercury. Using a DF400, this equates to a method LOD of 2.6 µg/L and meets the discharge limit measurement requirement. The vast majority of tested mercury concentrations were within 10% of the anticipated concentration. The data has shown that mercury can be measured within the stated range with a precision of 3.6% in magnesium and sodium concentrations up to 84 mg/L and 29 mg/L respectively.

The report also details the analysis of a Bradwell plant sample and a manufactured "trueness sample". Both samples were shipped to NNL Central Laboratory and 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 optimised mercury 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 cobalt 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 mercury, which shall be outlined within this report. Following 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 mercury method for the analysis supporting discharge. The validation of the measurement of B, Cr, Fe, Ni, Cu, Zn, Cd and Pb by the main metals method is detailed in a separate report, NNL 13743.[1]

1.1. Environmental Discharges

At Bradwell the discharge of effluent generated from the FEDD & ADAP is subject to environmental permissioning regulations (EPR10) 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 limit 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 elements this is the only technique available simultaneously capable of achieving the measurement of cadmium and mercury at these low levels.

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 thereby reducing noise. The ion beam 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 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 isotopic 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 as total elemental concentration can be inferred arithmetically. 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 neutral species or elemental ions combine with other elemental ions or neutral species 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 isotopic 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 some of 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 ions collide with the mist they lose energy and are not able to pass by an applied potential (energy barrier) at the exit of the quadrupole. This reduces the effect of 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 variation of the instrument backgrounds due to its ability to measure very low levels, in most cases low ng/L concentrations. 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 QC values and 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 require 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 FEDD and discharge of waste effluent to the estuary. However, ICP-MS is a complex instrument that requires trained operators and the correct laboratory environment to optimise performance.

1.3. Issues Concerning the Measurement of Mercury by ICP-MS

It is important to understand the fundamental difficulties of measuring mercury by ICP-MS to help construct a method for its analysis. Traditionally ICP is conducted in nitric acid (< 2.0 mol dm^{-3}) as the majority of elements show good stability in this matrix as most nitrate salts are soluble. Mercury is not stable in nitric acid as the mercuric (Hg^{+}) ion reduces to metallic mercury, generally plating out onto the vessel it is contained within. It is more likely to plate out in plastic ware than glassware. There are two ways to stabilise Hg^{+} in solution. Either change the diluent to one where the reduction of Hg^{+} does not occur or add an oxidising agent. In the case of mercury both of these methods can be applied. The diluent can be changed to hydrochloric acid where reduction is slower or gold can be added to nitric acid as a strong oxidising agent where precipitation is reduced therefore increasing sample stability.[2] Sample preparation should be conducted in glassware where possible, samples should be measured within a reasonable time (within 4 - 6 hours) after preparation and the diluent should be hydrochloric acid or nitric acid with gold. Mercury can also exhibit pronounced memory effects in the sample introduction system where mercury can adsorb onto surfaces, which can impact on analysis of samples further into the analytical run. The introduction of gold to the system

significantly reduces these problems as sorption of mercury does not occur therefore shorter sample rinse times of 60 seconds can be employed.[2]

Mercury has the highest first ionisation energy for a metal (1007 kJ mol^{-1}, the energy required to remove the outer most electron to form a +1 ion). Its ionisation is limited by the amount of energy that can be provided via the plasma. Proportionally less mercury ions are formed in the plasma than most other ions. As the concentration of mercury ions is reduced in the ion beam then there is less charge arriving at the detector. Therefore the calibration line gradient for mercury tends to be very low. This is problematic when attempting to measure concentrations close to the limit of detection (LOD). In most cases mercury is measured for environmental monitoring purposes due to its high bio-toxicity and requires very low LODs with a good precision and accuracy at very low concentrations. Therefore low backgrounds and low variability in backgrounds are essential for the measurement of low mercury concentrations.

The two most abundant isotopes for mercury are Hg-200 and Hg-202 at 23.10% and 29.86% natural abundance respectively. There are no direct isobaric interferences with other elemental ions however there are polyatomic interferences of tungsten oxide $^{184}W^{16}O^{+}$ and $^{186}W^{16}O^{+}$. These could be removed by the addition of helium if required, for example, if tungsten concentrations were significantly higher than the mercury concentrations being measured.

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 beyond which increasing the sample concentration will not lead to an increase in signal. 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. Since 1 kg/m^3 is equivalent to 1000 mg/L the samples need to be significantly diluted to fall below the 200 mg/L concentration before analysis.

Internal standards are required during ICP-MS analysis to correct for any variations in pumping and nebuliser effects. Either 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. The internal standard is measured with every sample 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 to the analyte of interest. This ensures the most similar behaviour of internal standard to the element of interest. It is difficult to find elements with similar ionisation energies to mercury as it first ionisation energy is the highest observed for any metal. Bismuth (mass 208.980) is a commonly used internal standard and is of a similar mass to mercury. Its first ionisation energies is not an ideal match (703 kJ mol^{-1} compared with 1007 kJ mol^{-1} for mercury) but Bi has been found to perform adequately as an IS for mercury.

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 mercury method (BRAD/22429/OI/00145 Issue 3), which is detailed in Appendix 1 and shall be discussed in more detail in the next section.

1.4. Current Mercury Methodology and Issues Experienced During Analysis

Currently the Analytical Team at Bradwell use operating instruction BRAD/22429/OI/00145 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. The mercury is measured within the calibration range 0.1 – 2 µg/L, which is a sensible range on a NexION instrument. 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 based on a 60 kg FED loading for dissolution. 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 mercury is 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. This also removes uncertainties associated with pipetting. The calibration standard and internal standards are certified Perkin Elmer products and high quality hydrochloric acid and high purity water are purchased for use as diluents. The QC samples are prepared from a different source of the same Perkin Elmer mercury standard and doped with certified Mg (Fluka, Sigma-Aldrich) and Na (Perkin Elmer) standards. All of the chemicals used in the analysis conform with the UKAS guidelines summarised in Section 1.5.

Although 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. In particular this was problematic for mercury as the discharge limit is close to the LOD of the instrument. The discharge limit with the DF402 applied for mercury is 0.018 µg/L, therefore the instrumental LOD needs to be better than 0.018 µg/L. When Bradwell experienced high backgrounds they saw LODs exceed the mercury discharge limit and the analysis had to be repeated. 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 was detailed in technical memo EX10049/06/10/01 however, the main findings shall be outlined within this report.[3] 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 trace level 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 the requirement for 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 and to provide confidence in elemental analysis used for discharge to the estuary. 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 the method development undertaken by NNL. 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. One plant sample has been shipped from Bradwell. Where analysis has been performed on both instruments (Bradwell and NNL Central Laboratory instruments) results can be compared. Bradwell also purchased a manufactured sample, which is in the correct sample matrix and was analysed after a DF1000 was performed at the customer's request. Both the manufactured and plant sample have 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 of 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 hydrochloric acid concentration effects.
- Reducing the calibration range and QC concentrations to more appropriate levels closer to the discharge limit.
- The investigation of matrix effects of Na and Mg concentrations on the measurement of mercury.
- The introduction of gold to stabilise mercury in solution.

- The investigation of rinse times between injections to minimise analysis run time.
- Optimisation of instrument parameters.
- The validation and robustness testing for the optimised method.
- The measurement of a Bradwell plant sample and a manufactured sample with a known concentration of mercury.

This report also details recommendations for the successful implementation of this validated method.

2. Method Development and Optimisation of the Mercury 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 mercury method is already in use at Bradwell and was set up in partnership with Perkin Elmer the original parameters have been used as a basis for optimisation. All chemicals utilised in the method development are identified in Appendix 2. During the method development both Hg-200 and Hg-202 were measured to establish which isotope, if any, gave better precision and accuracy.

2.1. Investigation of Hydrochloric Acid Concentration Effects

Currently Bradwell use hydrochloric acid as the diluent for the measurement of mercury at approximately 0.55 mol dm^{-3}. Generally ICP-MS is conducted in 2% by volume solutions of acid, which equates to 0.32 mol dm^{-3} nitric acid and 0.24 mol dm^{-3} of hydrochloric acid, when diluted from concentrated stocks. Hydrochloric acid is corrosive and can damage the cones within interface of the ICP-MS. Therefore any reduction in concentration will lead to less corrosion which will improve availability of the instrument and reduce the frequency of cone replacement.

The impact of lowering the acid concentration was investigated in 1% and 2% by weight solution, 0.12 and 0.24 mol dm^{-3} of hydrochloric acid respectively. The 0.12 mol dm^{-3} solutions showed a decrease in the intensities for the calibration standards compared with the 0.24 mol dm^{-3} samples and QCs and showed an increase in variability between measurements. This suggested that a 1% solution was not sufficiently concentrated to stabilise mercury in solution and reduce memory effects. The variability issues were not observed at 0.24 mol dm^{-3}. There appeared to be no additional benefit (i.e. signal intensity did not increase) as the concentration was increased to 0.5 mol dm^{-3}. Therefore 0.24 mol dm^{-3} hydrochloric acid was selected as the diluent for this method.

2.2. Investigation of Calibration Range and QC Values

Currently Bradwell use the calibration range 0.1 – 2.0 µg/L with matrix matched QC samples at 2.0 µg/L mercury. This calibration range does not include 0.018 µg/L, the discharge limit with a DF402 applied, and the QCs are confirming the instrument performance at a concentration three orders of magnitude above the discharge limit. Therefore the concentration range was lowered to 0.05 – 1.0 µg/L and new QC values trialled at 0.40 and 0.20 µg/L mercury, i.e. twenty times and ten times the discharge limit. The new calibration range showed good linearity with the lowest calibration standard above the instrumental LOD, which was routinely observed to be less than 10 ng/L. The calibration was not lowered further to include 0.018 µg/L as calibration standards close to the LOD would show a large variability and affect the calibration and the subsequent data work up. The data work up is a potential error trap for Bradwell's requirements and would lead to additional complexity for this analysis. Therefore the range was fixed between 0.05 – 1.0 µg/L mercury. Both QC values showed good accuracy and precision and were within 10% of the expected QC value during the method development. 0.20 µg/L mercury was preferred as the lower value closer to the bottom end of the calibration range. Subsequent analysis with varying Mg and Na concentrations discussed in the next section showed good repeatability at 0.20 µg/L mercury, therefore this was selected as the new QC value.

2.3. 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 to a level where suppression of the signal is not significant. Currently the samples have a DF402 performed on them before analysis. This means that the instrumental limit of detection (LOD) for mercury 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. However, this is challenging as the mercury LOD as the instrumental LOD can be within a few ng/L of 0.018 µg/L discharge. Instrument dilutions also increase uncertainty in a measurement. Therefore a sample with a smaller DF applied will have less uncertainty introduced to the result. The main metals report showed that preparing samples at DF100 and DF200 gave significant increases in instrumental noise and high suppression of the internal standard.[1] 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.[1] However, during a 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, 80 kg. 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. The new concentrations were calculated and a DF500 applied to the new FEDD liquor with new Mg and Na concentrations set at 67.0 and 23.0 mg/L respectively. Due to the method development previously conducted on the main metals method only new DF400 and DF500 were examined to ensure Mg and Na concentrations did not have an adverse effect on the measurement of mercury and on the instrument (see **Table 2**).

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

Equivalent DF	FEDD Loading (kg)	Mg concentration (mg/L)	Na concentration (mg/L)
100	60	266	132
200	60	133	66.1
300	60	88.5	44.1
400	60	66.4	33.1
500	60	53.1	26.4
New 400	80	83.3	28.8
New 500	80	66.6	23.0

Calibrations between 0.05 µg/L and 1.0 µg/L were run in 0.24 mol dm^{-3} hydrochloric acid and samples of varying mercury concentration with both new DF400 and DF500 Mg and Na concentrations were analysed. The new DF400 samples showed internal standard was supressed up to 10% and the new DF500 up to 5%. Although the DF400 showed higher suppression effects when the samples were internal standard corrected they were all within 10% of the anticipated result for the mercury concentration. This suggested that bismuth was a good internal standard match with mercury and both behaved in a similar manner with these high Mg and Na concentrations. Therefore the matrix matched QC samples and all spiked samples for the validation had a final fixed concentration of 84 mg/L Mg and 29 mg/L Na to represent a DF400 on an 80 kg loading.

2.4. 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 rinse times in the original mercury method were set with a sample flush time of 150 seconds, read delay 30 seconds and sample rinse 120 seconds, 300 seconds in total. This appeared to be unnecessarily long, which was increasing analysis time reducing sample turnaround at Bradwell. There were also additional rinse override times, which steadily increased as the calibration standard concentration increased, adding a total of 330 seconds to the calibration range. These parameters were steadily reduced whilst ensuring no carry over was observed after the calibration range and during the run, in particular after the 1.0 µg/L calibration standard, the highest concentration analysed. The parameters were reduced to a sample flush time of 120 seconds, read delay 15 seconds and sample rinse 90 seconds, reducing a single injection to 225 seconds. A standard Bradwell run includes ten blanks, five calibration standards, four QCs and quadruplicate analysis. Reducing the rinse times alone reduces total run time by 29 minutes, crucial for the plant environment and quick sample turnaround required at Bradwell.

The retarding potential quadrupole (RPQ) is the potential applied between the last quadrupole and the mass detector and acts as an energy barrier which, when optimised, can improve selectivity to increase signal intensity. The RPQ potential was investigated to establish whether a different potential would increase the sample intensity, which could potentially reduce the LOD. The original RPQ value was set at 0.25, which is a standard default potential in the software when collision or reaction gases are not utilised. The RPQ value was tested at 0.20, 0.25, 0.30, 0.35 and 0.40. The signal intensity was shown to be lower at 0.20 and 0.30 than 0.25, and continued to decrease from 0.30 at potentials of 0.35 and 0.40. The original RPQ value of 0.25 was shown to give the strongest signal intensity and was retained for the method validation.

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 (0.1 – 2.0 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. NNL Central Laboratory spike all (10 mL) blanks, calibration standards, QCs and samples with 100 µL of 500 µg/L internal standard. This gives a concentration of 5 µg/L of bismuth in each sample. This is measured by pulsed counting and avoids the issues discussed above. For this developmental work the NNL Central Laboratory regime was adopted.

2.6. Introduction of Gold to Stabilise Mercury in Solution

The method development discussed above mainly took place before the December 2015 holiday shut down at NNL Central Laboratory. Before this shut down, when the instrument was completely powered down, the mercury had shown good sample stability.

After optimising parameters good calibrations and QC values within 10% of the anticipated value were obtained. The method parameters were fixed and the method validation commenced in January 2016. The first validation run showed a calibration where the 0.75 and 1.0 µg/L calibration standards were not linear with 0.05, 0.1, 0.25 and 0.5 µg/L, and appeared to be significantly lower than anticipated. When these two standards were removed from the calibration range the calibration gradient observed was lower than those seen before shutdown and when applied to the analytical run the values calculated were significantly lower than the anticipated mercury concentrations in QCs and spiked samples. The analysis was prepared from fresh samples the following day however, the same problem was observed. Multiple explanations for the reduction in the signal for the higher mercury concentration standards and the variability in prepared matrix matched QCs and samples were hypothesised on discussion with Perkin Elmer. They centred around instrument performance and the stability of mercury in the new diluent. Therefore the spray chamber was cleaned, cones replaced and all tubing for sample introduction was changed. However, this did not improve the problems observed with the measurement. The torch power was also investigated as mercury has a very high first ionisation energy and it was possible that a reduced power was leading to a reduction in ionisation in the plasma. However, the torch parameters were the same as Bradwell and other analysis performed on the instrument and daily calibrations seemed unaffected. It was concluded that the observed problems had to be associated with sample preparation or mercury stability. The sample preparation was standardised to ensure aliquots of mercury solution were added to the pre-measured hydrochloric acid in the centrifuge tubes to reduce the chance of mercury sorption onto surfaces and run as quickly as feasibly possible. The hydrochloric acid concentration was also increased to the previous 0.55 mol dm^{-3} concentration used by Bradwell. However, this gave no improvement with the problems persisting.

Although Perkin Elmer suggested nitric acid containing gold or hydrochloric acid without gold to stabilise Hg^{+} in solution, 200 µg/L of gold was spiked into the blanks, calibration range, QCs and spiked samples prepared in 2% HCl. The 0.75 and 1.0 µg/L standard were linear with the rest of the calibration range and the calibration gradient was higher than previously seen during method development. The QC and spiked samples also showed good repeatability and were within 10% of the anticipated values. The Mg and Na concentrations were investigated briefly in the presence of gold at new DF400 and new DF500 with no observable difference. Therefore gold (final concentration of 200 µg/L) was spiked into every centrifuge tube to stabilise Hg^{+} in 0.24 mol dm^{-3} hydrochloric acid as for the method validation. The gold, internal standard, hydrochloric acid and Mg and Na (where appropriate) were pipetted into the centrifuge tubes prior to the addition of mercury to ensure Hg^{+} stability.

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 decreasing analysis time per sample. The calibration range and QC values were successfully decreased and were closer to the discharge limit. The reduction in hydrochloric acid concentration and the addition of gold for analysis showed improved Hg^{+} stability for measurement. Once the parameters had been fixed the validation portion of the programme commenced and is described in the next section.

3. Validation of the Mercury 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 delivered within 2% 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 soaked in 8 mol dm^{-3} nitric acid, rinsed with deionised water and dried before use. All samples were analysed within 24 hours of sample preparation. To reduce waste within the active laboratories at NNL Central Laboratory all standards, QCs and samples were prepared and spiked with internal standard and gold within the non-active laboratory and transferred to the ICP-MS laboratory. Due to the reduction in the calibration range and lowering of the QC the validation shall be discussed in ng/L where appropriate.

For each analysis a calibration range was prepared from a Perkin Elmer 1000 mg/L mercury standard in hydrochloric acid with standards at 50, 100, 250, 500, 750 and 1000 ng/L (detailed in Appendix 2). Fresh QCs were prepared from a different sample bottle of the Perkin Elmer mercury standard at 200 ng/L. When preparing the QCs 1 mL of 0.24 mol dm^{-3} hydrochloric acid was replaced with 1 mL of solution containing 840 mg/L Mg and 290 mg/L Na in 0.24 mol dm^{-3} hydrochloric acid. This was to matrix match the QCs with the effluent stream at Bradwell to give a final concentration of 84.0 mg/L Mg and 29.0 mg/L Na (equivalent to new DF400). Following the validation principles outlined in Section 1.5 matrix-matched 180 ng/L repeat samples and working range samples (i.e. various values within the calibration range) were prepared from the same QC mercury standard and the same Mg and Na stock solution. Blanks were prepared from the 0.24 mol dm^{-3} hydrochloric acid diluent used for the analysis. Before sample preparation commenced the quantity of hydrochloric acid was checked to ensure the full sample range could be made from the same stock. This was to minimise blank variation. All blanks, standards, QCs and samples were diluted in 10 mL volumes in 15 mL centrifuge tubes, which had already been spiked with internal standard solution (100 µL of 500 µg/L) and gold (100 µL of 20 mg/L) 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 later in this section. 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 isotope has been reported separately within section 4.1 & 4.2 and contains three distinct tables. The first table presents the calibration range, gradient of the calibration, R^2 value of the calibration line and the calculated LOD for each analysis. The R^2 value (a measure of the variance of data points from the 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 Bradwell use a minimum value of 0.9950. 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. The third table details the analysis of spiked matrix-matched repeat samples at a mercury concentration of 180 ng/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 this section.

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 the variance of the calibration points from 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 and the calibration would be acceptable for use.

The calibration data was recorded on 19 different occasions between 50 and 1000 ng/L and is detailed in **Tables 3** & **6**. The calibration line gradients for Hg-200 and Hg-202 vary between 3.52 & 6.27 and 4.36 & 7.77 counts per ng/L respectively. These variations are due to tuning parameters established during auto-tuning before samples are run. The Hg-202 calibration line gradient is always greater than for Hg-200 as it has the higher natural abundance of the two isotopes (29.86% Hg-202 and 23.10% Hg-200). There are five examples when the Hg-200 calibration line R^2 value is <0.9990, this is also observed on the same five occasions with Hg-202. There is one noticeable difference on 22/02/16 where the Hg-200 R^2 value is 0.9993 and the Hg-202 R^2 value is lower at 0.9988. The opposite effect is noted on 25/2/16 (0.9989 & 0.9999). All 19 datasets have calibration line R^2 values above the Bradwell limit of 0.9950. The limits of detection vary between 3.2 and 17 ng/L for Hg-200 and 2.5 and 19 ng/L for Hg-202. The highest LOD for both isotopes was observed on 24/02/16 where large variations were observed between blank intensities. If this was a real analytical run for Bradwell then the Hg-202 LOD would exceed the required instrumental limit of detection of 18 ng/L (before DFs are considered) and the analysis would have to be repeated. This emphasises the need to minimise variations in the blanks when conducting trace analysis close to the LOD of the instrument for mercury. Therefore when samples are prepared it is essential correct laboratory procedures are followed to minimise cross-contamination of blanks, calibrations standards, QCs and samples. This will improve the precision and accuracy of the measurement and reduce the need for repeat analysis.

3.2. Sample Repeats at 180 ng/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 occasions. The approach taken tests repeatability and also demonstrates the precision and accuracy of the measurement relative to a known value. Analyst 1 prepared 20 repeats of matrix matched samples containing 180 ng/L of mercury on 26/02/16 to assess the repeatability within the run. Analyst 1 then prepared a further five batches of five 180 ng/L samples and this was repeated in batches of five by Analyst 2 twice, Analyst 3 four times, Analyst 4 three times and Analyst 5 twice. Each batch of repeats was averaged, the standard deviation calculated and the relative standard deviation (%RSD) calculated. This has generated 100 repeat samples in total over the validation period and is detailed in

Tables 4 & **7**. There is one anomalous result on 22/02/16 where the second repeat has been calculated at 288 ng/L Hg-200 and 281 ng/L Hg-202. This result is a clear outlier so has been removed from the average calculation on that day and from the whole dataset. Excluding the anomalous result, thirteen of the remaining ninety-nine repeats exceed the anticipated mercury concentration by more than 10% (> 198 ng/L) based on Hg-200, with the largest difference observed at +21%. For Hg-202, ten of the results exceed the anticipated mercury concentration by more than 10% with the highest difference observed at +17%. The instrument shows a slight variation between the isotopes as only nine of these repeats exceed the +10% difference. On four occasions one isotope is within +10% whilst the other is not. The ninety-nine results were averaged and the %RSD calculated and the average repeat value was 191 ng/L for both isotopes with 3.6% %RSD for Hg-200 and 3.4 %RSD for Hg-202. Generally the calculated repeat sample value is higher than the anticipated 180 ng/L concentration. Although the average repeat is within 10% of the expected 180 ng/L the concentrations are consistently high which could indicate a positive bias of +6.1% to the measurement of mercury. The %RSD can be used to assess the precision of the measurement of mercury using this method, and shall be discussed later.

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 at a range of different values. As for the "sample repeats" this demonstrates the accuracy of the method but here extends the test across the dynamic range of the method. These samples are not fixed and each analyst carried out their own dilutions but within the calibration range of 50 – 1000 ng/L. In total 72 samples were prepared by five different analysts and detailed in **Tables 5** & **8**. It is important to note that uncertainty of a measurement will increase as the LOD is approached, therefore concentrations measured towards the bottom of the calibration may show a larger % difference if they are close to the LOD. The samples were measured between 55 and 800 ng/L and 66 samples for Hg-200 and 68 samples for Hg-202 were within 10% of the anticipated mercury concentration. The largest difference observed was at +16% for Hg-202 on 03/03/16 with an anticipated concentration of 455 ng/L. There appears to be no increase in % difference for samples at the lower end of the calibration range in comparison to the top of the calibration range. This would be expected as the lowest calibration standard was well above the instrumental limit of detection (typically 6.6 ng/L). The accuracy of this method is consistent between 50 and 1000 ng/L within the high Mg and Na matrix. The small positive bias seen with the "sample repeats" was seen again with the "working range" samples.

3.4. Evaluation of QC Data at 200 ng/L

The QC data from the nineteen validation runs has been collated and is detailed in **Table 9**. This data has generated 120 QC data points which can be used by Bradwell to start a new QC data chart as the QC value has been altered from 2.0 µg/L to 200 ng/L. Although a direct comparison is difficult the lower and upper limits calculated by Bradwell can be used as a % of the expected value to see if the new method has generated more consistent results with smaller deviations from the expected QC value. Both Hg isotopes generally generate QC values greater than the anticipated 200 ng/L concentration, with seven Hg-200 QCs and ten Hg-202 QCs exceeding a +10% difference (> 220 ng/L). All of the QC data is within +15 % (230 ng/L) except on two occasions where the QC values exceed 240 ng/L on 25/02/16 and 03/03/16. The average of the QCs and %RSD can be

used to demonstrate the precision of the technique with both isotopes generating an average QC value of 214 ng/L with a %RSD of 2.8% for Hg-200 and 2.9% for Hg-202, this will be discussed further later. The average of 214 ng/L is higher than anticipated and would suggest a positive bias of +7%, comparable to that observed with the 180 ng/L repeat samples.

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. As part of the validation project multiple analysts were used to ensure the same operator could not develop and fully validate a method with an incorporated bias. For this project five analysts conducted the analysis and within **Tables 3 – 8** the analyst who conducted the calibration, repeats and working range is identified (as Analyst 1-5). When comparing data it is important to look for patterns, for example if Analyst 1 were to continually generate data with low R^2 values whilst Analysts 2 to 5 continually generated data with R^2 values ≥ 0.9990 would suggest Analyst 1 was having difficultly controlling blank contamination and/or was not using a pipette correctly in this hypothetical situation. 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 line gradients are examined they are not consistently high or low for a particular analyst with variation in LODs spread across all analysts. All five analysts have generated results with good precision for the 180 ng/L repeats. All analysts also produced "one off" samples with unusually high results likely to be due to unavoidable instrumental or pipetting variation. There is no detectable bias caused by differences between analysts. It is important to note that the five analysts selected for the validation work were of varying skill and experience levels concerning ICP-MS analysis. The analysts have different backgrounds, with the most junior analyst currently completing their scientific apprenticeship with limited use of the instrument. Included in the pool is the experienced operator supervising both main metals and mercury method development projects and who has visited Bradwell to train the Analysts in the use of ICP-MS.

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. Manual work up is complicated with potential errors and is time consuming for both preparer and checker. Due to the quick turnaround requirements, 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 described 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 19 datasets, which can be exported into excel. The data contained within the excel spread sheets 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 19 datasets were examined using these four key indicators to identify any discrepancies between the manually worked-up data and computer-generated concentration data. 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 both isotopes shows complete agreement between the concentrations data and the raw data work up.

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

3.7. Precision of the New Mercury Method

The precision of the optimised mercury method validated within this report can be generated for each isotope. This can be done by looking at the repeat analysis as the same concentration has been injected repeatedly 100 times over 19 runs by five different analysts at 180 ng/L. This is also the case for the QCs as they have been repeated in the same manner with at least six QCs in every dataset at 200 ng/L. The %RSD for the repeat analysis and the QC data shows good agreement for both isotopes. The precision of Hg-200 has been calculated at 2.8% at 200 ng/L and 3.6% at 180 ng/L, with the precision of Hg-202 calculated at 2.9% at 200 ng/L and 3.4% at 180 ng/L. Both isotopes have behaved similarly throughout the validation process, for the plant sample and manufactured sample analysis so either could be selected if only one isotope is to be measured by Bradwell. Measuring the additional isotope increases each sample run time by 15 seconds. Therefore an average Bradwell run of 19 injections would be increased by 4.8 minutes. It is at the customer's discretion if one or two isotopes are to be measured. However, from this data using the highest variation observed the method shows a precision of 3.6%.

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 hydrochloric acid matrix with high Mg and Na levels. Bradwell instructed NNL to perform a DF1000 on the sample and analyse it using the optimised mercury method; the results are detailed in **Table 10**. The analysis was conducted in quadruple and all repeats are detailed. The DF1000 was applied as instructed. The Bradwell plant sample was analysed by the same method and detailed in **Table 11**. The uncertainties for each sample have been calculated by combining the variation observed in the QC value, the intensity RSD generated by the instrument and a rectangular distribution applied to the QC acceptance criteria, and then converted to a 95% confidence interval. The following calculation is entered into excel and the corresponding cells selected:

= SQRT[QC %RSD^2 + Intensity %RSD^2 + (0.05/3^0.5)^2]*1.96

The limit of detection was calculated for each isotope by calculating the standard deviation of the ten blanks, multiplying this by 3.

There is a difference in results observed between analysts. However, this is not due to the analysts but instrument performance on two different days and difference in blank intensities. On 03/03/16 the instrument controls disconnected from the operating computer and the instrument required rebooting. This caused the vacuum to be temporarily lost in the instrument causing the oxygen levels to increase due to air ingress. When the instrument was reconnected to the operating computer the vacuum was applied and left for four hours to evacuate. The daily calibration was performed and the cerium oxide ratio was high suggesting the oxygen had not yet been evacuated to an acceptable level. As Hg^+ is not reactive with oxygen in the ICP-MS it was decided to run the analysis.

It was noted that the "trueness" sample results from 03/03/16 by Analyst 5 were higher than that those from 04/03/16 by Analyst 3. On interrogation of the data the blank variation was greater on 03/03/16 which in turn generated a higher LOD. This could have been due to instrumental instability whilst the vacuum settled. The average blank on 04/03/16 was also higher than on 03/03/16, 92.1 counts per second (cps) and 37.5 cps respectively. The lower analysis result achieved on 04/03/16 could be due to a larger background subtraction.

The plant sample also showed a difference between a measurable result by Analyst 3 on 03/03/16 and an LOD result by Analyst 5 on 04/03/16. The LODs on both days were very similar due to the little variation observed in the ten blanks in either run. However, the blank average was higher on 04/03/16 than 03/03/16, 76.1 cps and 25 cps respectively. As for the "trueness" sample, the plant sample on 04/03/16 had a larger background subtraction applied which in turn generated an LOD result. This comparison shows that it is critical to control blank variation and have as clean blanks as possible. Therefore when samples are prepared it is essential correct laboratory procedures are followed to minimise cross-contamination of blanks, calibrations standards, QCs and samples.

4. Validation data tables for the mercury method

4.1. Mercury Validation Data (Hg-200)

Table 3: Summary of the calibration range, gradients, R^2 values and LODs for mercury method validation (based on Hg-200)

Date	Calibration range (ng/L)	Gradient of calibration line	R^2 value	Limit of Detection (ng/L)	Analyst
18/02/2016	50-1000	4.72	0.9995	5.5	1
19/02/2016	50-1000	4.03	0.9999	4.8	1
22/02/2016	50-1000	5.63	0.9993	6.3	1
23/02/2016	50-1000	4.50	0.9999	5.8	2
24/02/2016	50-1000	4.25	0.9971	17	2
24/02/2016	50-1000	3.52	0.9982	9.1	3
25/02/2016	50-1000	4.38	1.000	5.9	4
25/02/2016	50-1000	4.23	0.9989	16	3
26/02/2016	50-1000	4.44	0.9999	3.2	1
26/02/2016	50-1000	4.27	0.9999	3.4	4
29/02/2016	50-1000	4.62	0.9999	3.3	1
01/03/2016	50-1000	6.27	1.000	3.5	1
02/03/2016	50-1000	5.66	1.000	4.1	4
02/03/2016	50-1000	5.12	0.9995	5.4	4
02/03/2016	50-1000	5.02	0.9986	7.2	4
03/03/2016	50-1000	4.59	0.9990	10	3
03/03/2016	50-1000	5.32	0.9961	4.6	5
04/03/2016	50-1000	4.32	0.9998	6.2	5
04/03/2016	50-1000	4.21	0.9999	4.8	3

Table 4: Summary of the spiked repeat samples for mercury method validation (based on Hg-200)

Date	Analyst	Conc. (ng/L)	Result (ng/L)	% Difference	Average Result (ng/L)	σ (SD)	% RSD
18/02/2016	1	180	186	+3.5%	188	2.10	1.17%
		180	192	+6.5%			
		180	187	+3.9%			
		180	188	+4.2%			
		180	189	+5.0%			
19/02/2016	1	180	188	+4.7%	185	2.38	1.32%
		180	185	+2.6%			
		180	182	+1.1%			
		180	186	+3.4%			
		180	186	+3.3%			
22/02/2016	1	180	207	+15%	194	8.66	4.81%
		180	***288**	**+60%**			
		180	192	+6.5%			
		180	191	+6.0%			
		180	187	+4.0%			
23/02/2016	2	180	201	+12%	198	7.81	4.34%
		180	192	+6.7%			
		180	188	+4.2%			
		180	202	+12%			
		180	207	+15%			
24/02/2016	2	180	185	+3.0%	187	2.91	1.62%
		180	188	+4.7%			
		180	189	+4.9%			
		180	189	+5.1%			
		180	182	+1.4%			
24/02/2016	3	180	186	+3.3%	180	4.65	2.59%
		180	181	+0.41%			
		180	177	-1.4%			
		180	174	-3.4%			
		180	183	+1.5%			
25/02/2016	4	180	185	+2.9%	188	2.00	1.11%
		180	187	+3.7%			
		180	190	+5.4%			

Date	Analyst	Conc. (ng/L)	Result (ng/L)	% Difference	Average Result (ng/L)	σ (SD)	% RSD
		180	190	+5.4%			
		180	187	+4.0%			
25/02/2016	3	180	192	+6.5%	204	13.4	7.46%
		180	188	+4.5%			
		180	211	+17%			
		180	218	+21%			
		180	212	+18%			
26/02/2016	1	180	191	+6.3%	189	3.23	1.79%
		180	191	+5.9%			
		180	193	+7.2%			
		180	193	+7.3%			
		180	194	+7.5%			
		180	187	+3.8%			
		180	193	+7.1%			
		180	193	+7.3%			
		180	184	+2.5%			
		180	194	+7.7%			
		180	190	+5.4%			
		180	188	+4.6%			
		180	186	+3.5%			
		180	185	+3.0%			
		180	187	+4.0%			
		180	188	+4.5%			
		180	188	+4.4%			
		180	183	+1.9%			
		180	190	+5.3%			
		180	188	+4.5%			
26/02/2016	4	180	196	+9.1%	192	5.18	2.88%
		180	189	+5.1%			
		180	188	+4.3%			
		180	187	+3.7%			
		180	198	+10%			
29/02/2016	1	180	195	+8.1%	195	1.79	1.00%
		180	194	+7.8%			

Date	Analyst	Conc. (ng/L)	Result (ng/L)	% Difference	Average Result (ng/L)	σ (SD)	% RSD
		180	196	+8.9%			
		180	192	+6.7%			
		180	197	+9.3%			
01/03/2016	1	180	195	+8.2%	196	2.09	1.16%
		180	199	+11%			
		180	196	+8.8%			
		180	194	+7.9%			
		180	194	+7.9%			
02/03/2016	4	180	196	+8.7%	194	3.26	1.81%
		180	190	+5.7%			
		180	195	+8.4%			
		180	199	+10%			
		180	192	+6.6%			
03/03/2016	3	180	202	+12%	194	8.87	4.93%
		180	201	+12%			
		180	199	+10%			
		180	183	+1.8%			
		180	186	+3.3%			
03/03/2016	5	180	198	+9.9%	197	2.08	1.15%
		180	200	+11%			
		180	195	+8.4%			
		180	196	+8.7%			
		180	198	+10%			
04/03/2016	5	180	191	+6.3%	190	2.94	1.64%
		180	186	+3.4%			
		180	194	+7.7%			
		180	189	+4.9%			
		180	190	+5.4%			
04/03/2016	3	180	192	+6.7%	189	2.74	1.52%
		180	190	+5.6%			
		180	191	+5.9%			
		180	185	+2.8%			
		180	198	+4.5%			

Table 5: Summary of the investigation of the spiked working range samples for mercury method validation (based on Hg-200)

Date	Analyst	Concentration (ng/L)	Result (ng/L)	% Difference
18/02/2016	1	600	624	+4.0%
		800	856	+7.0%
19/02/2016	1	150	155	+3.5%
		220	230	+4.5%
		300	308	+2.5%
		400	420	+5.0%
		600	627	+4.6%
22/02/2016	1	160	170	+6.5%
		170	175	+3.0%
		190	199	+4.8%
		350	363	+3.7%
		450	466	+3.5%
23/02/2016	2	75.0	80.4	+7.2%
		80.0	87.4	+9.2%
		190	206	+8.5%
		260	276	+6.1%
		550	590	+7.2%
24/02/2016	2	140	149	+6.6%
		175	186	+6.1%
		270	289	+7.1%
		310	328	+5.8%
		420	449	+6.9%
24/02/2016	3	90.0	92.2	+2.5%
		120	128	+6.3%
		195	194	-0.31%
		280	243	-13%
		500	508	+1.6%
25/02/2016	4	80.0	79.3	-0.83%
		160	163	+1.6%
		240	246	+2.7%
		320	334	+4.2%
		400	410	+2.4%
26/02/2016	1	510	539	+5.7%

Date	Analyst	Concentration (ng/L)	Result (ng/L)	% Difference
		675	696	+3.2%
		700	736	+5.2%
		720	754	+4.7%
		800	852	+6.5%
26/02/2016	4	55.0	59.0	+7.3%
		110	122	+11%
		165	186	+13%
		220	248	+13%
		275	304	+11%
02/03/2016	1	440	468	+6.3%
		460	502	+9.0%
		500	535	+7.0%
		610	650	+6.5%
		625	673	+7.6%
01/03/2016	1	160	171	+7.2%
		320	348	+8.6%
		330	357	+8.2%
		350	374	+6.7%
		390	411	+5.3%
02/03/2016	4	70.0	72.4	+3.4%
		140	147	+4.8%
		210	225	+7.4%
		280	299	+6.9%
		350	369	+5.4%
03/03/2016	3	135	136	+1.1%
		260	269	+3.5%
		345	356	+3.2%
		455	514	+13%
		665	706	+6.1%
04/03/2016	5	115	123	+6.7%
		230	241	+4.9%
		345	372	+7.8%
		460	491	+6.8%
		575	618	+7.5%
04/03/2016	3	300	314	+4.5%

Date	Analyst	Concentration (ng/L)	Result (ng/L)	% Difference
		370	388	+4.8%
		450	484	+7.5%
		580	611	+5.3%
		670	695	+3.7%

4.2. Mercury Validation Data (Hg-202)

Table 6: Summary of the calibration range, gradients, R^2 values and LODs for mercury method validation (based on Hg-202)

Date	Calibration range (ng/L)	Gradient of calibration line	R^2 value	Limit of Detection (ng/L)	Analyst
18/02/2016	50-1000	5.85	0.9998	4.8	1
19/02/2016	50-1000	4.88	0.9999	4.8	1
22/02/2016	50-1000	6.90	0.9988	2.5	1
23/02/2016	50-1000	5.49	0.9996	5.4	2
24/02/2016	50-1000	5.17	0.9974	19	2
24/02/2016	50-1000	4.36	0.9976	8.4	3
25/02/2016	50-1000	5.35	0.9999	5.4	4
25/02/2016	50-1000	5.22	0.9992	16	3
26/02/2016	50-1000	5.43	0.9999	4.0	1
26/02/2016	50-1000	5.29	0.9999	3.7	4
29/02/2016	50-1000	5.76	0.9998	3.6	1
01/03/2016	50-1000	7.77	0.9999	3.8	1
02/03/2016	50-1000	7.03	1.000	4.7	4
02/03/2016	50-1000	6.47	0.9996	6.3	4
02/03/2016	50-1000	6.23	0.9986	7.6	4
03/03/2016	50-1000	5.74	0.9996	11	3
03/03/2016	50-1000	6.82	0.9951	4.6	5
04/03/2016	50-1000	5.45	0.9996	5.4	5
04/03/2016	50-1000	5.28	0.9997	5.0	3

Table 7: Summary of the spiked repeat samples for mercury method validation (based on Hg-202)

Date	Analyst	Conc. (ng/L)	Result (ng/L)	% Difference	Average Result (ng/L)	σ (SD)	% RSD
18/02/2016	1	180	190	+5.3%	190	4.96	2.76%
		180	195	+8.2%			
		180	194	+7.7%			
		180	189	+4.8%			
		180	182	+1.3%			
19/02/2016	1	180	189	+5.1%	186	3.69	2.05%
		180	181	+0.7%			
		180	190	+5.3%			
		180	183	+1.9%			
		180	187	+4.0%			
22/02/2016	1	180	204	+13%	195	5.50	3.06%
		180	***281**	**+56%**			
		180	192	+6.6%			
		180	192	+6.9%			
		180	194	+7.6%			
23/02/2016	2	180	203	+13%	199	7.43	4.13%
		180	194	+7.6%			
		180	189	+5.1%			
		180	201	+12%			
		180	208	+15%			
24/02/2016	2	180	190	+5.7%	189	3.28	1.82%
		180	190	+5.6%			
		180	190	+5.4%			
		180	190	+5.6%			
		180	183	+1.5%			
24/02/2016	3	180	182	+1.2%	178	2.54	1.41%
		180	176	-2.4%			
		180	177	-1.6%			
		180	177	-1.8%			
		180	179	-0.78%			
25/02/2016	4	180	185	+3.0%	185	2.94	1.63%
		180	182	+1.3%			
		180	183	+1.6%			

Date	Analyst	Conc. (ng/L)	Result (ng/L)	% Difference	Average Result (ng/L)	σ (SD)	% RSD
		180	185	+2.7%			
		180	190	+5.5%			
25/02/2016	3	180	188	+4.2%	201	11.3	6.30%
		180	190	+5.5%			
		180	207	+15%			
		180	211	+17%			
		180	210	+17%			
26/02/2016	1	180	197	+9.4%	190	3.11	1.73%
		180	192	+6.6%			
		180	191	+6.1%			
		180	193	+7.1%			
		180	190	+5.8%			
		180	189	+5.1%			
		180	190	+5.5%			
		180	186	+3.2%			
		180	195	+8.6%			
		180	187	+4.0%			
		180	194	+7.5%			
		180	189	+5.0%			
		180	188	+4.3%			
		180	190	+5.3%			
		180	188	+4.3%			
		180	191	+6.1%			
		180	189	+4.8%			
		180	187	+3.9%			
		180	191	+5.9%			
		180	184	+2.5%			
26/02/2016	4	180	186	+3.1%	189	4.32	2.40%
		180	193	+7.4%			
		180	194	+7.9%			
		180	186	+3.5%			
		180	186	+3.2%			
29/02/2016	1	180	189	+5.2%	195	3.93	2.18%
		180	195	+8.3%			

Date	Analyst	Conc. (ng/L)	Result (ng/L)	% Difference	Average Result (ng/L)	σ (SD)	% RSD
		180	199	+11%			
		180	193	+7.0%			
		180	198	+9.7%			
01/03/2016	1	180	194	+8.0%	194	1.85	1.03%
		180	193	+7.1%			
		180	192	+6.5%			
		180	196	+8.9%			
		180	196	+8.7%			
02/03/2016	4	180	194	+7.6%	195	2.65	1.47%
		180	197	+9.2%			
		180	198	+9.9%			
		180	191	+6.1%			
		180	195	+8.1%			
03/03/2016	3	180	205	+14%	193	11.3	6.30%
		180	196	+8.8%			
		180	201	+12%			
		180	178	-1.1%			
		180	185	+2.8%			
03/03/2016	5	180	190	+5.6%	192	1.71	0.948%
		180	192	+6.4%			
		180	194	+7.6%			
		180	194	+7.9%			
		180	192	+6.5%			
04/03/2016	5	180	193	+7.0%	192	1.80	1.00%
		180	194	+7.5%			
		180	189	+4.9%			
		180	191	+6.0%			
		180	192	+6.5%			
04/03/2016	3	180	195	+8.3%	191	2.79	1.55%
		180	188	+4.5%			
		180	191	+6.4%			
		180	189	+4.9%			
		180	192	+6.8%			

Table 8: Summary of the investigation of the spiked working range samples for mercury method validation (based on Hg-202)

Date	Analyst	Concentration (ng/L)	Result (ng/L)	% Difference
18/02/2016	1	600	639	+6.5%
		800	840	+5.0%
19/02/2016	1	150	150	-0.2%
		220	231	+4.8%
		300	311	+3.8%
		400	421	+5.2%
		600	637	+6.1%
22/02/2016	1	160	173	+8.4%
		170	178	+4.6%
		190	199	+5.0%
		350	365	+4.2%
		450	473	+5.0%
23/02/2016	2	75.0	79.3	+5.7%
		80.0	88.1	+10%
		190	208	+9.5%
		260	268	+3.1%
		550	588	+6.8%
24/02/2016	2	140	152	+8.5%
		175	182	+3.9%
		270	290	+7.4%
		310	335	+8.1%
		420	442	+5.3%
24/02/2016	3	90.0	92.3	+2.5%
		120	125	+4.2%
		195	193	-1.2%
		280	240	-14%
		500	494	-1.1%
25/02/2016	4	80.0	85.5	+6.9%
		160	163	+1.9%
		240	254	+5.8%
		320	332	+3.9%
		400	413	+3.4%
26/02/2016	1	510	538	+5.4%

Date	Analyst	Concentration (ng/L)	Result (ng/L)	% Difference
		675	712	+5.4%
		700	740	+5.7%
		720	760	+5.6%
		800	828	+3.4%
26/02/2016	4	55.0	60.6	+10%
		110	120	+9.4%
		165	184	+11%
		220	243	+10%
		275	300	+9.3%
29/02/2016	1	440	467	+6.2%
		460	495	+7.6%
		500	535	+6.9%
		610	652	+6.9%
		625	664	+6.2%
01/03/2016	1	160	174	+9.1%
		320	347	+8.5%
		330	356	+8.0%
		350	378	+7.9%
		390	424	+8.6%
02/03/2016	4	70.0	74.7	+6.7%
		140	147	+4.9%
		210	224	+6.5%
		280	300	+7.2%
		350	373	+6.5%
03/03/2016	3	135	132	-2.4%
		260	267	+2.8%
		345	360	+4.2%
		455	526	+16%
		665	708	+6.4%
04/03/2016	5	115	127	+11%
		230	250	+8.8%
		345	372	+7.8%
		460	497	+8.0%
		575	620	+7.8%
04/03/2016	3	300	324	+7.9%

Date	Analyst	Concentration (ng/L)	Result (ng/L)	% Difference
		370	397	+7.4%
		450	480	+6.8%
		580	613	+5.7%
		670	712	+6.3%

Table 9: QC data from the validation project for both Hg isotopes

Date	Total Hg from Hg-200 (ng/L)	Total Hg from Hg-202 (ng/L)
18/02/2016	214	212
	205	212
	208	209
	218	211
	207	213
	210	209
19/02/2016	207	205
	205	207
	213	209
	215	208
	203	207
	207	204
19/02/2016	210	212
	208	208
	214	218
	212	210
	211	212
	207	215
22/02/2016	212	214
	217	211
	209	212
	216	210
	211	213
	213	213
23/02/2016	217	221
	212	208
	215	218
	217	214
	209	216
	217	211
24/02/2016	226	217
	214	218
	210	217
	214	216

	214	212
	212	215
	210	201
	203	202
25/02/2016	212	204
	206	209
	218	219
	202	203
	207	209
	206	203
25/02/2016	227	226
	240	244
	208	210
	208	206
	205	208
	220	229
26/02/2016	212	214
	213	218
	213	215
	211	217
	219	213
	216	219
	213	215
	212	213
26/02/2016	212	208
	217	216
	207	207
	218	213
	212	212
	216	216
29/02/2016	218	217
	214	217
	210	215
	218	219
	215	217
	222	218
01/03/2016	215	220
	219	215

	214	215
	213	219
	212	217
	220	217
	217	220
	214	225
02/03/2016	215	217
	213	216
	211	214
	216	213
	217	220
	211	210
02/03/2016	218	214
	213	223
03/03/2016	216	210
	214	216
03/03/2016	204	206
	215	219
	242	242
	215	220
	209	213
	217	214
	204	201
	212	220
03/03/2016	223	213
	214	210
	218	210
	217	212
	219	212
	222	219
	219	216
	217	212
04/03/2016	211	216
	215	216
	214	216
	217	217
	207	215
	213	216

	212	211
	214	211
04/03/2016	207	214
	211	213
	219	217
	209	216
	212	211
	210	214
	216	217
	212	210
Average QC value	214	214
%RSD	2.8%	2.9%

4.3. Trueness Sample Validation Data

Bradwell Magnox provided a manufactured Trueness Sample for analysis. This sample was analysed in quadruplicate by two different analysts. A DF 1000 was applied to analyse the sample and has been incorporated into the results in the table below:

Table 10: Results from the Manfactured Trueness Sample

Analyst	Total Hg from Hg-200 / µg/L	Uncertainty / µg/L	Total Hg from Hg-202 / µg/L	Uncertainty / µg/L	Average Hg result / µg/L	Average Uncertainty / µg/L	LOD / µg/L
5 (03/03/16)	87.5	9.6	86.3	11	87.9	9.0	11
	89.5	7.3	91.3	11			
	84.6	8.3	87.8	9.5			
	87.7	7.2	88.1	8.7			
3 (04/03/16)	70.4	4.9	76.5	6.4	72.5	6.5	5.8
	75.6	8.0	72.6	6.0			
	72.7	8.5	73.4	7.5			
	68.5	5.0	69.9	5.5			

4.4. Analysis of FED sample data

A FED sample (FMDT2 sample ID AL422) was provided by Bradwell Magnox for analysis. This sample was analysed in quadruplicate by two different analysts. A DF 400 was applied to analyse the sample and has been incorporated into the results in the table below:

Table 11: Results from Analysis of Bradwell Plant Sample

Analyst	Total Hg from Hg-200 / µg/L	Uncertainty / µg/L	Total Hg from Hg-202 / µg/L	Uncertainty / µg/L	Average Hg result/ µg/L	Average Uncertainty / µg/L	LOD / µg/L
3 (03/03/16)	6.74	0.72	6.78	1.8	6.49	1.1	1.8
	6.74	1.3	6.39	0.45			
	6.02	1.0	6.82	1.2			
	6.54	2.1	5.85	0.62			
5 (04/03/16)	< 1.9		< 2.0		< 1.9		1.9
	< 1.9		< 2.0				
	< 1.9		< 2.0				
	< 1.9		< 2.0				

5. Conclusions

The method development and validation of the mercury Bradwell method has been successful and all data generated has been detailed within this report.

The method has been altered to reflect a more appropriate calibration range and QC value closer to the discharge limit (18 ng/L after DF400) for the mercury excluding dilution factors. The new calibration range has been lowered to incorporate a calibration standard at 50 ng/L with five calibration standards up to 1000 ng/L. The QC value has been lowered to 200 ng/L which has been matrix matched to reflect the high Mg and Na concentrations in the effluent. The rinse times have been shortened with no signs of carry over or memory effects commonly seen with mercury. This reduces the mercury method on a typical Bradwell run (19 samples) by approximately thirty minutes, which is important in a plant environment that demands fast sample turnaround.

Due to issues observed with stability of Hg^+ in 0.24 mol dm^{-3} hydrochloric acid, gold was added as a strong oxidant to slow the reduction of Hg^+ to metallic mercury, which is known to plate out onto the tubing and spray chamber. The addition of gold not only stabilised the mercury in solution but increased the signal intensity as demonstrated in the increased calibration gradient for both isotopes. In some cases during the validation process it was not possible to run samples on the day they were prepared. When these samples were run within 24 hours of preparation there appeared to be no observable reduction in mercury concentration, supporting the addition of gold stabilising Hg^+. The gold was spiked into every blank, calibration standard, QC and sample giving a resulting concentration of 200 µg/L.

The method development investigated the effect of Mg and Na concentrations on the measurement of mercury in this method. Multiple dilutions of the old and new effluent stream (depending on the dissolution loading mass) were attempted and the mercury concentration analysed. It was possible to increase the Mg and Na loading for this method to 84 mg/L Mg and 29 mg/L Na to reflect a DF400 on an 80kg loading. This is a smaller dilution than that required for the main metals method, DF500 67.0 mg/L Mg and 23.0 mg/L Na.[1] It was shown that the internal standard bismuth is only suppressed up to 10% at this higher Mg and Na loading and when the mercury concentration is internal standard corrected in the vast majority of cases the observed concentration is within 10% of the anticipated concentration. If the FEDD loading remains at 60 kg then the current DF402 conducted by Bradwell could be reduced to DF300 as the Mg and Na concentrations are similar for a DF400 on an 80 kg loading.

The validation data has shown good consistency for both isotopes with a precision calculated at 3.6% for the measurement of mercury by this method. Bradwell currently generate their QC data charts with action limits calculated at 2σ (two times the standard deviation) and fail limits at 3σ (three times the standard deviation). Plotting the current QC data would determine the action limits on NNL's instrument based on the average QC value of 214 (σ=6.1) ng/L. This could be used as an initial value by Bradwell. As new data is generated it can be used to generate action limits applicable to the Bradwell instrument. This will determine if Bradwell observe the same positive (+7%) bias as well. This bias could be instrumental, therefore Bradwell may observe a different bias, or it could be matrix derived, therefore Bradwell would expect to observe the same bias. If the positive bias is due to matrix affects due to the high Mg and Na then the method will require further investigation. The concentrations may have to be lowered to 67 mg/L Mg

and 33 mg/L (DF402 at a 60 kg FEDD loading), the current dilution factor used by Bradwell.

There is one example where the instrumental LOD exceeded 18 ng/L. In this case the analysis would need to be repeated if a plant sample were to be analysed. Overall tighter precision, accuracy and small LODs are observed when blank intensity and variation is smallest. Therefore when samples are prepared it is essential correct laboratory procedures are followed to minimise cross-contamination of blanks, calibrations standards, QCs and samples. This will lead to less repeats with smaller uncertainties associated with the data necessary for the Bradwell plant environment.

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 difference observed between the two analysts appears to be derived from differences in background levels due to high oxygen present in the instrument on 03/03/16.

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. Due to the differences in practice between Bradwell and NNL concerning the introduction of internal standard to the instrument and the need for sample preparation to be as simple as possible a sample preparation procedure has been suggested in Appendix 3. This procedure can be adopted by the Bradwell analysts when running the trueness sample during the method transfer period. If successful the current Bradwell method can be updated with this new regime.

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 mercury analytical procedure conducted at Bradwell.
- Bradwell should continue to apply a DF402 to the current FED effluent stream of a 60 kg loading however; it could be decreased to DF300 which would increase the effective EPR(10) discharge limit from 18 ng/L to 25 ng/L after DFs have been applied. This would move the discharge limit further away from the limit of detection of the instrument (routinely 6.6 ng/L). This would increase confidence in data generated near 25 ng/L and ensure the overall 7.5 µg/L discharge limit is still met when appropriate DFs have been applied. If the loading is permanently increased to 80 kg a DF400 should be applied to samples. 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 concentrations, which, have currently not been disclosed to NNL.
- Further analysis of plant and trueness samples should be undertaken now that the instrument has settled, to better refine NNL results.
- The Mg and Na concentrations could be varied and the positive bias of the method investigated to understand if it is matrix dependent.
- The manufactured trueness sample should be prepared at Bradwell according to the same procedure detailed within the report (detailed in Appendix 2 & 3) and analysed using 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 used to generate new QC charts with the lower QC value at 200 ng/L. Bradwell can add to this data as analysis on the new methods is undertaken. This data will help demonstrate the 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. *"Method development and validation of main metals method by inductively coupled plasma mass spectrometry",* NNL (16) 13743, J. Hawkett, Issue 1, 2016

2. *"Determination of mercury in Wastewater by Inductively Coupled Plasma-Mass Spectrometry"*, J. Chen, Application Note, Perkin Elmer, 2011

3. *"NNL support to ICP-MS operations at Magnox Bradwell"*, EX10049/06/10/01, J. Hawkett, Issue 1, 2015

8. Appendix

8.1. Appendix 1: Bradwell Mercury Method and Parameters

Preparation of Samples, Standards, QCs and Blanks:

Bradwell prepares all samples, blanks, calibration standards and QCs in accordance with BRAD_22429_OI_00145_Issue_3. Analysis by ICP-MS and the processing of data is completed in accordance with BRAD_22429_OI_00145_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 rinse procedures for analysis:

	Time / s	Speed / (+/- rpm)
Sample Flush	150	-30.0
Read Delay	30	-16.0
Analysis	N/A	-16.0
Wash	120	-30.0

Concentration of Hg Calibration Standard / µg/L	Wash Override / s
0.1	120
0.2	150
0.5	180
1.0	210
2.0	270

8.2. Appendix 2: Validated Method Parameters

Preparation of Samples, Standards, QCs and Blanks

All samples, blanks, calibration standards and QCs were diluted using 0.24 mol dm^{-3} HCl. This was prepared from trace analysis grade concentrated HCl (~37%, 12 mol dm^{-3}), purchased from Fisher Scientific (Fisher Scientific Code - 10623014). 20 mL of the concentrated HCl was then diluted by the addition of the HCl 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 1000 mg/L Hg standard purchased from Perkin Elmer (Perkin Elmer Code – N9303740). Three sequential DF 100s were performed using 0.24 mol dm^{-3} HCl in order to create a 1 µg/L standard from which five calibration standards were prepared as described in the table below:

Volume 1 µg/L Hg standard (mL)	Volume 0.24 mol dm^{-3} HCl (mL)	Final Concentration (µg/L)
0.5	9.5	50
1.0	9.0	100
2.5	7.5	250
5.0	5.0	500
7.5	2.5	750
10.0	0.0	1000

Samples analysed at Magnox Bradwell contain particularly high concentrations of Na and Mg. After discussion with Magnox Bradwell concerning an increase in FEDD per batch it was decided that a DF 400 would be employed for future analysis on an 80 kg loading instead of the current DF 402 on the old 60 kg FEDD stream described in Appendix 1. This was considered the most appropriate dilution to apply with concentrations of Mg and Na of 84.0 mg/L and 29.0 mg/L respectively. All QCs and samples were matrix matched to Magnox Bradwell's sample matrix through the addition of 1 mL of a solution containing 840 mg/L Mg and 290 mg/L Na in 0.24 mol dm^{-3} HCl, 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	Certiprep Plus	PLNA2-3Y	10000	5% HNO_3

200 ng/L Hg QCs were prepared and matrix matched to simulate Magnox Bradwell samples by the addition of Mg and Na as described above.

Bi was measured as an internal standard at concentration of 5.0 µg/L. An Internal standard solution containing 10 mg/L Bi was purchased from Perkin Elmer (Perkin Elmer Catalogue number N9303832) A DF 20 was performed on the stock solution, in 0.24 mol dm^{-3} HCl, 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 Bi being present in all samples, standards, QCs and blanks.

All samples, blanks, calibration standards and QCs were spiked with 100 µL 20 mg/L Au in 0.24 mol dm^{-3} HCl. The 20 mg/L Au solution was produced by applying a DF5 to a certified 100 mg/L Au ICP standard purchased from Spex Certiprep (Catalogue number - CLAU1-1Y).

Sample Preparation Procedure

Due to mercury's tendency to reduce and plate onto the vessel, to prevent any losses when preparing standards, sample and QCs a regimented sample preparation procedure was developed.

1) Centrifuge tubes were labelled for their intended purpose. Dates and analyst details were included to avoid any possible errors.
2) Stock solutions of 0.24 mol dm^{-3} HCl, 20 mg/L Au solution in 0.24 moldm^{-3} HCl, 500 mg/L Perkin Elmer internal standard solution in 0.24 moldm^{-3} HCl and 'DF 400' 840 mg/L Mg and 290 mg/L Na in 0.24 mol dm^{-3} HCl should be prepared.
3) An appropriate volume of 0.24 mol dm^{-3} HCl was added to each centrifuge tube
4) 100 µL 20 mg/L Au in 0.24 mol dm^{-3} HCl was added to each centrifuge tube.
5) 100 µL 500 mg/L Perkin Elmer internal standard solution prepared in 0.24 mol dm^{-3} HCl was added to each centrifuge tube.
6) Add 1 ml 'DF 400' 840 mg/L Mg and 290 mg/L Na in 0.24 mol dm^{-3} HCl to all QC, and sample tubes to replicate the high Mg/Na concentrations of Magnox Bradwell samples.
7) Prepare 1 µg/L Hg stock solution and add an appropriate amount to relevant centrifuge tubes as soon as practical.
8) Reapply lids to the centrifuge tubes and shake to ensure the sample is representative throughout.
9) Analyse samples using the ICP-MS parameters described below.

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 rinse procedures for analysis:

	Time / s	Speed / (+/- rpm)
Sample Flush	120	-18.0
Read Delay	15	-18.0
Analysis	N/A	-18.0
Wash	90	-18.0

Concentration of Hg Calibration Standard / ng/L	Wash Override / s
50	90
100	90
250	90
500	90
750	120
1000	120

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

	Rinse
	Blank
	Blank
	Blank
	50 ppt
	100 ppt
	250 ppt
	500 ppt
	750 ppt
	1000 ppt
	Blank
	Blank
	200 ppt QC
	200 ppt QC
	Blank
	180 ppt Hg Repeat Sample 1
	180 ppt Hg Repeat Sample 2
	180 ppt Hg Repeat Sample 3
	180 ppt Hg Repeat Sample 4
	180 ppt Hg Repeat Sample 5
	Blank
	200 ppt QC
	200 ppt QC
	Blank
	Working Range Sample 1
	Working Range Sample 2
	Working Range Sample 3
	Working Range Sample 4
	Working Range Sample 5
	Blank
	200 ppt QC
	200 ppt QC
	Blank
	Rinse

8.3. Appendix 3: Suggested Bradwell Protocol for Mercury Method

Prepare 0.24 mol dm^{-3} HCl:

1) Make up a 0.24 mol dm^{-3} solution of HCl containing 100 ppb gold. Take a 2L Type 1 water bottle and remove 40 mL of water. Add 38 mL of trace select 35% HCl and 2 mL 1000 ppm gold standard. Cap and shake. This solution is for all dilutions from stock mercury and samples.
2) Make up a 0.24 mol dm^{-3} rinse solution of HCl. Take a 2L Type 1 water bottle and remove 40 mL of water. Add 40 mL of trace select 35% HCl, cap and shake. This solution is for internal standard (IS) preparation and rinse only.

Prepare Blanks:

3) Prepare Blanks – 50 mL 0.24 mol dm^{-3} HCl/Au in 50 mL centrifuge tube (x3)

Prepare Calibration standards:

4) Prepare 10 ppm mercury stock – 9.9 mL 0.24 mol dm^{-3} HCl/Au plus 0.1 mL of 1000 ppm stock, cap and shake. Label "10 ppm mercury"
5) Prepare 100 ppb mercury stock – 9.9 mL 0.24 mol dm^{-3} HCl/Au plus 0.1 mL of 10 ppm stock, cap and shake. Label "100 ppb mercury"
6) Prepare 1 ppb mercury working stock – 29.7 mL 0.24 mol dm^{-3} HCl/Au plus 0.3 mL of 100 ppb stock, cap and shake
7) Label tubes – 5 x calibration range (see table below). Prepare Calibration range: Note: add the 0.24 mol dm^{-3} HCl/Au to the centrifuge tubes first then the mercury.

Volume 1 ppb Hg standard (mL)	Volume 2% HCl/Au (mL)	Final Concentration (ppb)
0.5	9.5	0.05
1.0	9.0	0.10
2.5	7.5	0.25
5.0	5.0	0.50
10.0	0.0	1.0

<u>Prepare 0.2 ppb QCs (matrix matched):</u>

8) Prepare 10 ppm mercury stock – 9.9 mL 0.24 mol dm^{-3} HCl/Au plus 0.1 mL of 1000 ppm stock, cap and shake. Label "10 ppm mercury QC"
9) Prepare 100 ppb mercury stock – 9.9 mL 0.24 mol dm^{-3} HCl/Au plus 0.1 mL of 10 ppm stock, cap and shake. Label "100 ppb mercury QC"
10) Prepare 0.2 ppb QCs – 0.35 mL of 10,000 ppm Mg, 0.15 mL of 10,000 ppm Na, 49.4 mL (5 x 9.88 mL) 0.24 mol dm^{-3} HCl/Au plus 0.1 mL 100 ppb mercury QC. Decant into 4 labelled "Hg QC 0.2 ppb" tubes

<u>Prepare Trueness sample:</u>

11) Prepare Trueness Sample A3226 in quadruplicate at DF1000:

0.1mL of A3226 plus 9.9 mL 0.24 mol dm^{-3} HCl in a 15 mL centrifuge (DF100), cap and shake
1mL of DF100 A3226 plus 9.0 mL 0.24 mol dm^{-3} HCl in a 15 mL centrifuge tube (DF1000) (**x 4**) cap and shake ready for analysis

12) Run on ICP 1 in the following order:

Sample Id
Rinse
Blank
Blank
Blank
Blank
Standard Blank
0.05 ppb
0.1 ppb
0.25 ppb
0.5 ppb
1.0 ppb
Blank
Blank
QC 0.2 ppb
QC 0.2 ppb
Blank
A3226 x 1000
A3226 x 1000
A3226 x 1000
A3226 x 1000
Blank
QC 0.2 ppb
QC 0.2 ppb
Blank
Rinse

13) Select the Mercury Method 2.mthd in the NNL Development folder
14) Ensure the 10 ppb IS in 0.24 mol dm^{-3} HCl is connected to the instrument

DISTRIBUTION

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