

BRADWELL SITE

OPERATING TECHNIQUES FOR METAL ANALYSIS AND NITRATES  
AT BRADWELL SITE (A1: OT1)

BRAD/EN/REP/202

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## List of Abbreviations

ADAP	Active Discharge Abatement Plant
AETP	Active Effluent Treatment Plant
AIR	Audit Inspection and Reassurance
ASTM	American Society for Testing and Materials
BEC	Background Equivalent Concentration
C of A	Certificates of Analysis
CEARAS	Compilation of Environment Agency Requirements, Approvals and Specifications
COSHH	Control of Substances Hazardous to Health
Cps	counts per second
DF	Dilution Factor
DRC	Dynamic reaction cell
EA	Environment Agency
FED	Fuel Element Debris
FEDD	Fuel Element Debris Dissolution
FMDT	Final Monitoring and Delay Tank
GAC	Granulated Activated Carbon
ICP-MS	Inductively Coupled Plasma- Mass Spectrometry
KED	Kinetic Energy Discrimination.
LAL	Lower Action Limit
LCL	Lower Control Limit
LLD	Lowest Level of Detection
LOD	Limit of Detection
m/z	mass to charge
mg/L	milligrams per litre
NNL	National Nuclear Laboratory
NOx	Nitrogen Oxides
OI	Operating Instructions
PEQC	Perkin Elmer Quality Control
Ppb	parts per billion
Ppm	parts per million
QA	Quality Assurance
QC	Quality Control
RF	radio frequency
RO	Reverse Osmosis
RPT	Radiation Protection Technician
%RSD	Relative Standard Deviation
SD	Standard Deviation
SI	Site Instructions
SQEP	Suitably Qualified and Experienced Person
UAL	Upper Action Limit
UCL	Upper Control Limit
UKWF	UK Weighing Federation
WS	Work Specification
w/w	weight/ weight

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## 1. Introduction

This document is produced in response to a request from the Environment Agency to provide an Operating Technique document giving a detailed outline of Metals Analysis using ICP-MS (Inductively Coupled Plasma- Mass Spectrometry) and also the spectrophotometric measurement of nitrates.

The effluent which will be analysed is discharge of trade effluent consisting of the treated effluent from the dissolution of Fuel Element Debris in nitric acid. All these may be discharged via Outlet 1. This document is referred to as A1 OT1 (Metals Analysis) in EA terminology.

### 1.1 Introduction to ICP-MS

The Magnox Ltd power plant at Bradwell-On-Sea ("Bradwell") is currently being decommissioned. The on-site Fuel Element Debris dissolution is one aspect of the decommissioning activities currently being carried out at Bradwell. Batches of FED are dissolved in dilute nitric acid, neutralised, filtered and further treated by passage through GAC and ion exchange column(s), where necessary. After various analyses of samples to check for compliance within discharge limits and environmental performance criteria, the effluent stream can then be discharged into the Blackwater estuary.

At present ICP-MS is used at Bradwell Site for the measurement of boron (B), chromium (Cr), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb) and mercury (Hg). ICP-MS was chosen due to its ability to carry out trace elemental analysis which is capable of measuring down to concentrations of parts per billion (ppb) as required by the Environment Permit. Samples for ICP-MS must be in the aqueous form and typically within an acidic media. The sample is injected into the spray chamber via a nebuliser. The type of nebuliser depends upon the viscosity, cleanliness and the available volume of sample to be analysed. The sample is converted from a solution to a liquid aerosol. From here the liquid aerosol is passed into an argon-based plasma (between 6000-7000K). The plasma is generated by passing argon through a series of concentric quartz tubes (ICP torch) that are wrapped at one end by a radio frequency (RF) coil. The energy supplied to the coil by the RF generator acts on the argon to produce the plasma.

The droplets are dried and the solid particles are broken down into their constituent elements and then heated to a gas. These elements undergo ionisation to form positively charged ions (predominantly +1) that are propelled forward by an electric field which is generated by a high potential between the plasma and the interface. A series of cones (nickel skimmer, nickel sampler and hyperskimmer cones) focus the ion beam to a high vacuum chamber that houses the mass detector. By using three cones this provides a three-step reduction in pressure between the plasma and the filtering quadrupole, so that the ion beam divergence is reduced.

Bradwell uses the Perkin Elmer Nexlon 300 X ICP-MS instrument which utilises three quadrupoles before the ions reach the mass detector. The first quadrupole steers the ion beam through 90 degrees. This ensures that only ions pass into the next quadrupole and all the remnants from the plasma leave the beam; this reduces any noise generated. From here the ion beam passes through a Dynamic Reaction Cell (DRC) that contains the second quadrupole. At the second quadrupole collision gases and reaction gases are pumped in.

These gases are introduced to counteract such difficulties as isobaric interferences, where an ion of interest has the same  $m/z$  ratio as another ion that is also present. The mass detector cannot distinguish between them. In some cases for example, Mo-100 and Ru-100 and Mo-98 and Ru-98 a different isotopic mass should be measured, where there are no interferences, e.g. Mo-95 and Ru-102. However, it is not always possible if the natural abundance % compositions are low for the alternative isotope to be measured as the small concentrations will be difficult to measure. Isobaric interferences can also occur in the ion beam, where elemental ions combine with other elemental ions to form a molecular ion. A pertinent example of this being argon oxide, which is prevalent in our test system. Both argon and oxygen ions are unstable due to their high electronegativities and combine to share the positive charge. The  $m/z$  ratio is the sum of both their atomic masses.  $^{40}\text{Ar}^{16}\text{O}^+$  is the most abundant isotope with a  $m/z$  ratio of 56 which is the same mass for  $^{56}\text{Fe}$ , which is 91.7% of naturally occurring Fe. By introducing a collision gas in the DRC such as helium (He), the ions in the beam collide with the large abundance of He atoms to form a mist. Although the ions of interest will collide with the He mist, the polyatomics are statistically more likely to collide with the mist as they are larger ions. Once the polyatomics have collided with the mist they lose kinetic energy and are not able to pass the mass filter, which is an applied potential (energy barrier) at the exit of the quadrupole. Therefore, this reduces the effect of isobaric interferences and the measured signal is predominantly the desired analyte ions. This process is referred to as Kinetic Energy Discrimination or KED.

From here the ion beam passes into a third quadrupole where mass separation takes place. The mass spectrometer separates the singly charged ions from each other by mass, serving as a mass filter. The ions strike the active surface of the detector (dynode) and generate a measurable electronic signal. The dynode releases an electron each time an ion strikes it. The mass detector is a photomultiplier which can determine the rate of arrival of ions at the detector.

In summary, the ICP-MS generates singly charged ions by means of an argon plasma beam which are separated based on their mass to charge ratio ( $m/z$ ) and measured by a dynode linked to a photomultiplier tube.

## 2. ICP-MS Methods

The analytical team at Bradwell have developed the current "Main Metals" method described in the operating instructions BRAD/22429/OI/00140 with the assistance of Perkin Elmer and ICP-MS experts Viridian consultancy. The main metals method measures B, Cr, Fe, Ni, Cu, Zn, Cd and Pb in the following matrices:

- a) High concentration magnesium/sodium matrix for sentencing tank/FMDT samples.
- b) A nitric acid and hydrogen peroxide medium for NO<sub>x</sub> scrubber liquor samples.
- c) Non-routine samples where running against a standard has been requested.

Nitric acid (HNO<sub>3</sub>) was chosen as a suitable matrix for main metal analysis as it is relatively free from chemical and spectral interferences in comparison to acids containing chlorine, sulphur, fluorine, or phosphorus. The majority of elements form a stable solution in dilute aqueous nitric acid with a few exceptions. In addition to this, the FEDD/ADAP plant uses nitric acid as part of its dissolution process so would provide a similar matrix.

A mercury method was also developed using the operating instructions BRAD/22429/OI/00145. This method uses dilute hydrochloric acid as this provides greater stability than nitric acid for mercury. Mercury is known to be prone to adsorption on plastic. For the mercury analysis, dilute hydrochloric acid and glass volumetric flasks were chosen in order to maintain stability of the analyte.

Special training on the ICP-MS is provided by the instrument manufacturer Perkin Elmer. This must be attended by all the lab analysts who operate this instrument.

The Operating Instructions detail in a series of step-by-step instructions for sample preparation and running of samples to ensure the procedures are carried out uniformly by all laboratory technicians.

Specialist tools and materials required for main metal analysis are:

- Dedicated plastic volumetric flasks (to be soaked in dilute nitric acid when not in use).
- Trace metal 70% nitric acid
- ASTM Type 1 water
- Perkin Elmer certified custom standards – PEQC23 (23 elements including all those named in the Permit EPR/DP3127XB. These were chosen as they are present in FED. The standard is at 100ppm in dilute nitric acid for dilution to prepare QC standards.
- 1000ppm of the elements named in the Permit EPR/DP3127XB in dilute nitric acid for dilution to prepare calibration standards

Specialist tools and materials for mercury analysis are:

- Dedicated glass volumetric flasks (soaked in dilute hydrochloric acid when not in use).
- Trace metal ~35% hydrochloric Acid
- 1000ppm Hg in dilute hydrochloric acid (HCl) from an approved supplier
- Gold 1000 ppm in dilute hydrochloric acid (used in validated method).

All chemicals and stock solutions are of analytical grade and all standards certified.

Certificates of Analysis (C of A) for the commercially purchased stock samples are retained in a folder to provide traceability. A standards log spreadsheet is maintained in order to track stock solutions, lot numbers, preparation dates, expiry date and by whom the stock solution was prepared by. By keeping a standards log any consistent failures e.g. in calibrations or QCs can be traced back to the stock solution they were prepared with. Each stock solution is assigned a numerical number which is also recorded on the ICP-MS summary result report. Separate stock bottles are identified and used to prepare calibration and Quality Control (QC) samples.

Certificates giving the specifications for auto-pipettes and volumetric flasks are also retained. All pipettes are purchased from reputable suppliers (currently Eppendorf or Finn Thermo Scientific) and are identified by a unique in-house identifier. Any pipettes used in sample preparation must be checked for calibration criteria according to the work specification BRADWELL WS NO: 0877. Those that do not pass the calibration criteria are marked "out of calibration" and must not be used in the sample preparation for ICP-MS analysis. Fresh pipette tips and in date consumables are used during all analysis. The pipettes are calibrated on a 4-figure Sartoris BP 2215 Balance, which itself is calibrated every 6 months by an external company (at present Avery Weigh-Tronix). This company is accredited to ISO/IEC17025 for the on-site calibration of weighing equipment up to 5,000kg and also for calibration of Mass (weights) up to 25kg). The calibration of the balance conforms to the UKWF Calibration Code of Practice.

The balance also undergoes a calibration check every week according to the work package 22701/WP2/OI/059.

## **2.1 Daily Performance Checks**

"Daily Performance Checks" (BRAD/22429/OI/0102) must be successfully completed before any analysis can take place. This includes a full visual check of the ICP-MS such as capillaries, pump tubing, nebuliser, spray chamber etc. Any defects such as worn tubing must be replaced before use, with any observations/on-going issues recorded in the ICP log book. Set criteria are in place to monitor the performance of the ICP-MS and any deterioration in performance identified and remedied. This is recorded on both electronic and hard copy. The hard copies are retained in a folder labelled Daily Performance Check. There is also a spreadsheet maintained which records the various parameters for the Daily Performance Check and also highlights whether these are pass or fail.

The ICP-MS instrument is not used for sample analysis if it fails the daily performance check.

Within each method are some integral components that form the basis of each ICP-MS run. Table 1 shows an example of the set components of an ICP-MS run.

<b>Sample ID</b>
Rinse
Blank (x4)
Standard Blank
Standard 1
Standard 2
Standard 3
Standard 4
Standard 5
Blank
Blank
QC (x2)
Blank
Sample (x4)
Blank
QC(x 2)
Blank
Rinse

**Table 1 Example of ICP-MS Run Order**

An external calibration is used to enable quantitative analysis of these methods. An external calibration is used to calibrate the instrument by measuring the standards for all the desired elements. The external calibration typically uses five standards across a spread of concentrations to ensure the instrument response is accurate across the entirety of the concentration ranges. The proprietary NEXION software used creates a calibration line of the measured intensity versus concentration for each element in the standard solution. From these calibration curves, a correlation coefficient  $R^2$  is generated. For a successful calibration the  $R^2 > 0.995$  otherwise the calibration must be repeated.

Once all standards are measured, then measurements of the unknown solutions can proceed.

In analytical chemistry, a detection limit is considered to be the smallest concentration of analyte that can be reliably measured by a particular method. There are a number of definitions for defining and calculating this quantity. In this work BEC and LLD have been used depending on the method. A series of blanks are run before the external calibration in order to determine the detection limit. These two definitions are calculated by the following formulae:

$$\text{BEC} = \text{slope} \times \text{average blank.}$$

$$\text{LLD} = \text{slope} \times 3\text{SD}$$



This is reported every time a calibration is generated. Should the average value of the unknown samples be below the detection limit, then less than the detection limit ie < LLD or < BEC would be reported for the concentrations.

## 2.2 Internal Standard

Another key component of an ICP-MS run is the internal standard. This is measured with every injection and the variation in the signal is used to correct the response for the analyte of interest. Within ICP-MS analysis physical interferences are to be expected from the sample matrix such as plasma loading or aerosol transport. These physical interferences can be compensated for using internal standardisation. The internal standards were chosen based on the following criteria:

- Low concentration or is not present in samples.
- Not interfered with by the sample matrix.
- Does not interfere with the analytes
- Not a common environmental contaminant
- Matched to mass(es) of analytes
- Reasonable concentrations
- Unique atomic mass

The internal standards for the main metals method are Scandium ( $\text{Sc}^{45}$ ) for the lower mass elements: B, Cr, Fe, Ni, Cu and Zn. Terbium ( $\text{Tb}^{159}$ ) is used for the higher mass elements: Cd and Pb.

For the mercury method the internal standard used is Bismuth ( $\text{Bi}^{209}$ ). The internal standard is added via inline addition using a T-piece to provide an efficient and accurate means of dosing all samples without the risk of error or contamination. During a sample run it is the responsibility of the laboratory analyst to monitor the cps of the internal standard to ensure that there is no appreciable internal standard drift.

## 2.3 Quality Control Samples

As with many analytical techniques QC samples are run before and immediately after the unknown sample. QCs are employed to help confirm whether the instrument is operating within pre-defined specifications; ensuring results are both valid and reliable. The QCs are prepared from certified element standards and are matrix matched to the high magnesium and sodium levels. QCs allow the analyst to check that the response of the sample is consistent with the response to the calibration standards.

During data processing the QCs are entered into a QC Control Chart (Shewart Charts) which demonstrate if the process is in control. The following features are typical of a control chart:

- The mean of all the data points
- the lower control limit (LCL, mean -3SD),
- lower action limit (LAL, mean-2SD),
- upper action limit (UAL, mean +2SD)
- upper control limit (UCL, mean +3SD).

For a stable process > 99 % of all data points should be within 3SD either side of the mean, and 95% of the data points are within 2SD either side of the mean. QCs values are plotted in chronological order, so any changes over time are apparent. Such changes can be a run of values increasing in a positive or negative direction, thus heading toward the control limits. This indicates that the process could be moving out of control and so should be investigated.

If the values of the QCs bracketing the sample lie outside the upper and lower control limit then the QCs have failed, and the result for sample must not be reported. Failed QCs are not used to update the control charts.

Any values outside of the action limits (mean  $\pm 2SD$ ) but within the control limits must be investigated as to why the QCs are moving out of control. An investigation could include but not be limited to checking expiry dates of solutions, evidence of deviation from existing procedure, sufficiency of training of laboratory technicians and contamination.

## 2.4 Main Metals Current Method

The current method follows the operating instructions BRAD/22429/OI/00140 which was developed with the assistance of Perkin Elmer and Viridian Consultancy. This method uses the following parameters:

**Table 2 Parameters for the Mass Detector**

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

**Table 3 He flow Parameters for each Element**

Analyte	He flow rate in collision cell / ml min <sup>-1</sup>
B	0.5
Cr	3.0
Fe	4.5
Ni	3.0
Cu	3.0
Zn	0.5
Cd	0.5
Pb	0.5
Sc	0.5
Tb	0.5

**Table 4 Rinse Procedures for Analysis**

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

A typical sample run for the pre-existing main metals follows this set order:

Blank (x9)
Blank Standard 0
Standard 1 (1ppb)
Standard 2 (2ppb)
Standard 3 (5ppb)
Standard 4 (10ppb)
Standard 5 (20ppb)
Blank
QC (x2)
Sample (x4)
QC (x2)

For the analysis of FMDT samples a dilution factor (DF) of 402 is applied to all samples.

## **2.5 Validation of Main Metals Method**

The existing method was further developed and validated off-site by National Nuclear Laboratory (NNL). The full details of the validation are recorded in the document:

“Method development and validation of main metals method by inductively coupled plasma mass spectroscopy” NNL (16) 13743.

During the validation of this method, the effects of the magnesium/ sodium matrix were investigated. A maximum loading of 0.2% w/w solids in solution is recommended by Perkin Elmer, this is equivalent to 200 mg/L concentration. Exceeding this limit could possibly affect aerosol formation, focusing of the beam through the cones and the ionising ability of the torch. A dilution factor of 402 was confirmed to be a suitable dilution as there was internal standard suppression observed at higher concentrations. This concentration also gave small variability between repeated analyses of QC samples carried out by NNL. A dilution factor of 500 gave similar results to that of dilution factor of 402 and may be applied in the future if required.

To reduce solids loading, a reduction in internal standard concentration from 50ppb to 10ppb in 2% $\text{HNO}_3$  will be introduced. By reducing solids loading this will reduce internal standard suppression and reduce the number of cps within the analogue range. At the 50ppb level, the internal standard is significantly more concentrated than the range of samples that are measured, with the cps occasionally exceeding 2,000,000. At this level the detector alters from pulsed to continuous counting; therefore each have a different response and variations found in the analogue counting range may not liken to those observed in the pulse counting range.

The validated main metals procedure has altered the helium flow rates across some of the elements. The pre-existing main metals method used 0.5mL/min of helium for elements which did not have any significant polyatomic interferences (B, Cd, Pb and both the internal standards Sc and Tb). NNL investigated the signal strength and repeatability with and without the use of helium and found that the 0.5mL/min flow rate provided no additional benefit for the measurement of B, Cd, Tb and Pb. With this finding, helium was removed from the validated method for these elements. For Zn and Sc there was reduced variability in the blanks, therefore a 0.5mL/min flow rate of helium was maintained. The helium flow rate for Fe was increased from 4.5mL/min to 5.25mL/min, by increasing the flow rate the blanks were significantly reduced, which decreased the limit of detection and overall improved the calibration, increasing the  $R^2$  value.

The blanks, limits of detection and calibrations had been consistently good for the elements Cr, Ni and Cu, therefore, the He flow rate was not altered.

**Table 5 He Flow Rates for Validated Main Metals Method**

Analyte	He Flow Rate in Collision Cell (mL/min)
B-11	0.00
Cr-52	3.00
Fe-56	5.25
Ni-60	3.00
Cu-63	3.00
Zn-66,68	0.50
Cd-111	0.00
Pb-208	0.00
Sc-45	0.50
Tb-159	0.00

In order to increase the sample throughput NNL investigated the optimisation of instrument parameters such as rinse times for analysis. The pre-existing main metal method used the manufacturer's flow rate settings and peristaltic pump conditions. The validated method has now adopted a new rinse time of 90 seconds, which had no carryover between the highest calibration standard (20ppb) and the blank which followed immediately after. The sample flush time was also reduced to 90 seconds and showed no significant impact on the measurement of the main metals elements.

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

Overall, for the main metals the majority of changes for the validated method stem from the parameter settings within the NEXION method file itself.

## 2.6 Mercury Current Method

The current method follows the operating instructions BRAD/22429/OI/00145 which was developed with the assistance of Perkin Elmer and Viridian Consultancy.

A typical sample run for the pre-existing main metals follows this set order:

Blank (x9)
Blank Standard 0
Standard 1 (0.1ppb)
Standard 2 (0.2ppb)
Standard 3 (0.5 ppb)
Standard 4 (1 ppb)
Standard 5 (2 ppb)
Blank
QC (x2)
Sample (x4)
QC (x2)

Matrix matched QCs are included in the run. For the analysis of FMDT samples a dilution factor (DF) of 402 is applied to all samples.

## 2.7 Mercury Validated Method

The existing method was further developed and validated off-site by NNL. The full details of the validation are recorded in the document "Method development and validation of mercury method by inductively coupled plasma mass spectroscopy" NNL (16) 13744.

The validated method for mercury also underwent some changes in order to improve analytical performance and throughput. One of the changes was that of the range of calibration. The pre-existing mercury method had a calibration range of 0.1-2.0ppb with matrix matched QCs at 1ppb. This calibration range does not cover 0.018ppb, this being the discharge limit with the analytical dilution factor applied. With this in mind, the calibration range was lowered to 0.05-1.0ppb and QCs prepared at 0.2ppb (ten times the discharge limit). NNL demonstrated that this new calibration range showed good linearity, and that the lowest calibration standard was above the instrumental LOD which had been routinely observed to be less than 10ng/L. The calibration was not lowered to include 0.018ppb because calibration standards that are close to the LOD show large variability and subsequently affect the calibration. A 0.2ppb QC was selected as it is towards the lower end of the calibration range and displayed good repeatability with varying magnesium and sodium concentrations.

A fundamental change to the pre-existing mercury procedure is the introduction of gold to stabilise the mercury in each sample, as NNL experienced difficulties with consistent levels.

Some cross-checking of results may be carried out in the future by using spectrophotometric methods to confirm the validity of ICP-MS data. The practice of using alternative techniques to measure analytes gives even more confidence of the validity of a result. For example, there are commercial methods available for measurement of iron, nickel, zinc, lead and copper and these may be used as a comparator with the ICP-MS. These particular methods may be employed in future to measure metal concentrations prior to discharge.

At present the current method described in 2.6 is being used. Once the new Permit comes into force the validated mercury method described in this section will be used to fulfil the reporting requirements as stated in the aforesaid document.

## 2.8 Calculation of ICP Results

The  $R^2$  and limit of detection are calculated directly from the intensities tab on the Excel spreadsheet exported from the NexION software.

The QC, average metal values and %RSD are calculated from the "Concentrations" tab on the same Excel spreadsheet.

Analysts follow through an Excel template to generate the results. The calculations and results are verified by a SQEP analyst.

The summary sheet at the front of this Excel template provides:

- Sample name
- File path for Excel file
- $R^2$  values
- QC values
- Average sample concentration
- %RSD values

- Stock solutions used to prepare the calibration standards and QCs and are signed by the two analysts responsible for the results.
- Pass/Fail for Daily Performance Check,  $R^2$ , % RSD, QCs and environmental limits
- Signature boxes for analyst and verifier.

### 2.8.1 Reporting of Metal Ion Results

The sample concentration reported is based on the average of the replicates but is not the only factor influencing the final reported figure. Limit of detection, % RSD and  $R^2$  also play a role.

Based on various scenarios, the following results are reported:

- (a) Average below the limit of detection; report < limit of detection
- (b) Average above limit of detection, %RSD < 10%, report average
- (c) Value above limit of detection, % RSD > 10 % , but average small compared to discharge limit, report value from look-up table if within stated range
- (d) Value above limit of detection, % RSD > 10%, but average small compared to discharge limit, value not covered by look-up table, no result reported
- (e) QC bracketing sample fail- no result reported
- (f)  $R^2 < 0.995$ , no result reported.

A look-up table has been devised in order to deal with cases where there are very small numbers for sample concentrations which are above the limit of detection. In these cases it is likely that the % RSD values are much greater than the designated 10%. For example analyte A with replicates of 1 and 2 ppb will give an average concentration of 1.5 ppb and %RSD of 47%. However, under the % RSD rule, the sample would have to be run again. At such low levels the precision of the instrument and inherent variability would mean that a number of runs could have to be performed to get the %RSD to the set criteria. If the discharge limit is significantly above the average value eg. 30 ppb, then the exercise of trying to achieve an %RSD < 10% does not add value and would delay the discharge.

The look-up table will quote values that are a bounding case but still relatively small compared to the discharge limits. For a given average concentration and %RSD it will give a figure that is the average plus 3 standard deviations. Statistically speaking the likelihood that the true concentration is below the quoted figure is 99%.

## 2.9 NNL Validation

### 2.9.1 Control Charts Data

The control charts data from the NNL validation has been compared with Bradwell data from November 2015 in the document "A comparison of ICP-MS QC charts produced by Bradwell and National Nuclear Laboratory" BRAD/22701/WP2/RPT/029. The purpose of this work was to demonstrate that the accuracy and reproducibility is retained when moving from one method to another. The performance of the new NNL general metals method varies from one element to another compared to the Bradwell data. Neither of the two methods is superior to the other for all the elements.

The QC data gives a preliminary indication that the new NNL validated method should be suitable to replace the existing Bradwell methods.

### 2.9.2 Method Transfer of Validated Methods

A validated method will work at the site at which it is validated but does not necessarily mean that it will work somewhere else. At a different site with a different environment, equipment and staff, it must be demonstrated that the method also works there. This is one reason for conducting a method transfer, which in this case was from NNL to Bradwell. The process was facilitated by the on-site visit of a member of NNL to pass on the details of the new validated methods and provide training to all the analysts.

These methods were then used to analyse the two trueness samples.

### 2.9.3 Analysis of Trueness Samples

A sample was purchased from Sigma-Aldrich (Multi-element standard solution IV for ICP product number 51844). This was repackaged to remove identity prior to analysis under the new validated main metals method.

A commercial sample was purchased from Romil Mercury 0.08 ppm ROMIL Prim-Ag-plus SE1294. This was repackaged to remove identity prior to analysis under the new validated mercury method.

In the analysis of the two trueness samples, in both cases some of the analysts were able to determine the correct concentrations, within the stated uncertainties. This shows that the new methods are capable, although some of the analysts need to demonstrate competency in the new methods at the time of writing. To facilitate this process Bradwell will switch to using the validated methods.

Further training and coaching will be provided to analysts to improve their competency, which will include feedback on their performance. Additional trueness samples may be procured to further demonstrate competency.

Only analysts who are able to demonstrate their competence will undertake analysis of discharge samples.



## 2.10 Proficiency Testing Scheme

Bradwell will participate in the water chemistry LGC Aquacheck Proficiency Testing Scheme in order to demonstrate competency. The waste waters sample set would be a suitable test set. This contains all the elements of interest and is provided on a basis of five times a year. The unknown samples would be analysed by Bradwell and the results submitted to LGC.

Each SQEP analyst will analyse at least one sample a year on this scheme. Any failures will be recorded and investigated using the Learning Capture Form.

## 2.11 Sample Testing

The samples from the FMDT2 will be tested prior to discharge by either ICP-MS, spectrophotometric or test strips to provide assurance that the content of the potential discharge will meet the discharge limits. The spectrophotometric tests are similar to those described in Section 3 for measurement of nitrates, and offer a simpler method of determining if a solution exceeds the discharge concentration; in other words it can function as a limit test.

In the case of mercury, testing may be conducted upstream of the discharge sample at the inputs which contribute mercury, namely NO<sub>x</sub> scrubber liquors and sodium hydroxide solution. As the ADAP process does not abate mercury, this should provide a good indication of the mercury level in the actual discharge. This upstream analysis can be performed in place of either FMDT analysis or post-discharge analysis.

The ICP-MS tests employed for measuring pre-discharge samples may take the form of the validated methods or may be a proprietary semi-quantitative method (known as Total Quant) provided by the instrument vendor. The latter method can be employed for a large range of elements which include our metals of interest. Such a test would be suitable for a limit test.

The post discharge samples will be tested by ICP-MS as separate samples. The samples will be stabilised by the addition of nitric acid (in the case of the general metals) or hydrochloric acid (for mercury) prior to storage. If the sample has been tested in the FMDT pre-discharge by ICP-MS it will not be tested post-discharge.

These results (as determined by ICP-MS) will be reported to the EA on a regular basis under the terms of the new permit.

## 2.12 ICP-MS Ways of Working

Bradwell has two Nexion 300X ICP-MS instruments, which are referred to as ICP 1 and ICP2. The preferred way of working is to use ICP1 for the main metals method and ICP2 for the mercury method. Having two instruments enables the team to run a dedicated method on each instrument. In addition, in the case of a breakdown of an ICP-MS instrument, the site does not lose its ability to discharge due to inability to measure metals concentrations. The two methods can be run on a single ICP but

this will require more time. The instrument must be washed out (either with nitric acid or hydrochloric acid) to switch in between methods.

The two ICP-MS are housed within a container with temperature control provided by air conditioning units. The instruments are maintained on the highest level service contract with the vendor, who provides an annual preventative maintenance and instrument check up as well as cover in the case of any breakdowns by qualified engineers.

### **3. Measurement of Nitrates**

The Hach Lange spectrophotometer DR 1900 and the appropriate commercially available kits LCK 340 are used to measure the nitrate level (expressed as N kg) in discharges.

The measurement of nitrates is based on the reaction of nitrate ions in the presence of sulphuric or phosphoric acid with 2,6-dimethylphenol to give 4-nitro- 2,6-dimethylphenol and the measurement of the UV-visible absorbance.

The method is described in BRAD/22429/OI/00117 "The Determination of Nitrogen by Spectrophotometer".

Pre-packaged cuvette kits come with all necessary reagents. The sample must first be diluted to within the working range of 5- 35 mg/L. 0.2ml of the diluted sample is added by pipette to a fresh cuvette, followed by 1mL of reagent A (also in the kit). After 15 minutes the concentration of nitrate is available to read off the spectrophotometer using a set program. The result obtained, dilution factor used, test number (generated by the DR1900) and the user identity are all recorded on a result sheet in the lab. This data (minus the dilution factor) is also stored in the spectrophotometer's memory.

To ensure quality a commercially available QC (LCA 704) at 25mg/L is run every 5 samples. The accepted tolerance is  $\pm 2$  mg/L. In the case of a QC failure the test system must be investigated to ascertain the cause. Samples are not run until QC checks have passed. Further assurance can be carried out by performing the test at a range of dilution factors. Similar results at two different dilution factors ensure that there is no interference from unknown matrix effects. In practice, a dilution factor of 1000 gives a result near to the value of the LCA 704 QC.

In order to demonstrate competency, some external samples will also be analysed for nitrates. Hach provide samples for round robin testing on the Addista pack which can be used to certify the accuracy of the system. Further samples for nitrate testing may be obtained from Aquacheck if required to demonstrate ongoing competency.

### **4. Chemist Job Specification**

#### **Qualifications and Experience:**

The role holder should be educated to a minimum of a Bachelors' degree in a chemical subject (preferably post-graduate qualifications), with a minimum of 5 years industrial experience, some spent leading technical teams.

**Responsibilities:**

- The role holder will report to the Project Engineering Manager.
- Accountable for providing a chemical analysis service to the FEDD-ADAP Dissolution Project
- Provide technical leadership to the chemistry team, setting and reinforcing technical quality and safety standards.
- Support the Chemistry team in the provision of a quality chemical analysis service to the Projects Department and Operations.
- Provide technical support to the FEDD, ADAP and AETP on an ongoing basis.
- Liaising with various Magnox departments on and off site.
- Liaise with equipment vendors and technical consultants to ensure practical solutions are achieved in a timely fashion.
- Providing an input into the writing of reports, procedures, risk and COSHH assessments.
- Be responsible for authorising/verifying documentation.
- Provision of specified technical/analytical services to customer agreed standards and timescales
- Carry out designated work packages to meet standards of safety, quality, cost and time
- Maintain awareness of developments in own specialised field by continuous professional development, including but not exclusively by reading, networking, attendance at conferences and site visits.
- Provide authoritative advice and guidance on issues in his/her own speciality
- Be responsible for the training and development of the chemistry team to appropriate standards.
- To contribute to the improvement of safe environment/general housekeeping of the working area, particularly in their own area of responsibility.
- Comply with all legislative, regulatory and company policy standards and procedures, e.g. safety, quality, risk, security etc., applicable to the role.
- Identify new equipment to meet new/changing analytical requirements from the project.
- To work to high standards of accuracy and maintain written and electronic records to the same high standards.
- Compliance with Health, Safety, Environment and Quality policies, procedures, work instructions and risk assessments.
- Support the continuous improvement of Health, Safety, Environment and Quality on Site
- Assist in troubleshooting, investigations and process improvement
- Ensure audits of the laboratory are performed to make sure relevant standards are maintained.
- To share responsibility for recruitment of staff to the chemistry team.

## 5. Lab Analyst Job Specification

### Qualifications and experience:

Analysts should have a science based qualification (GCSE, Radiation Protection Monitoring Level 5, A level or degree) ideally in a chemically related subject. In addition some industrial experience is preferred. They must successfully complete and pass the lab analyst training to become a SQEP analyst.

### Responsibilities:

- Complies with all legislative, regulatory and company policy standards and procedures, e.g. safety, quality, risk, security etc., applicable to the role
- The role holder reports to the team leader who is accountable to the Operation Manager.
- To be responsible and in charge of the laboratory during their working hours.
- Providing a chemical analysis service to the FEDD-ADAP Project.
- Supporting the Chemist and other analysts in the provision of a quality chemical analysis service to the FED Projects and Operations.
- Each analyst will be responsible for maintaining his/her personal training record. This will record details of induction, training courses, examples of completed analysis verified by another analyst, training certificates and briefing notes.
- Calculating and reporting of results and verifying other chemist's work.
- Liaising with various departments on and off site.
- Providing an input into the writing of procedures, laboratory investigations, risk and COSHH assessments.
- Provision of specified technical/analytical services to customer agreed standards and timescales.
- Carry out designated work packages to meet standards of safety, quality and time.
- Maintain awareness of developments in own specialised field.
- Provide advice and guidance on issues in his/her own working area. Be proactive in providing suggestions in methods, ways of working or equipment.
- Where appropriate, assist in the training and development of others to appropriate standards.
- To contribute to the improvement of safe environment/general housekeeping of the working area, particularly in their own area of responsibility.
- Operating and maintaining analytical instruments with prompt reporting of issues.
- Maintaining the laboratory environment to expected standards of housekeeping.
- Maintaining an appropriate level of stock of consumables.
- To work to high standards of accuracy and maintain written and electronic records to the same high standards.
- Compliance with Health, Safety, Environment and Quality policies, procedures, work instructions and risk assessments.
- Support the continuous improvement of Health, Safety, Environment and Quality on Site.
- Work flexibly within the shift pattern system as a member of the operations team under the guidance of a team leader for the day-to-day issues.
- Assist in troubleshooting, investigations and process improvement.

- Self-audit the laboratory to make sure relevant standards are maintained.
- To follow instructions set out in operating instructions (OI), work instructions (WS) and site instructions (SI). Ensure that they are up to date and uses the most current issue.
- To read the appropriate COSHH assessments prior to the start of any work and follow the recommendations.

## **6. Staff Guidelines**

### **6.1 Organisational**

The analytical chemistry team provides project support matching the working hours of the operations team. There are also radiation protection technicians (RPT) who are available to provide supplemental support on the more basic chemistry techniques such as pH, turbidity and gamma spectroscopy on an ad hoc basis.

### **6.2 Ways of Working**

For day-to-day operation, analysts are part of the operations team and work under the supervision of a team leader. This individual will provide direction about prioritisation of work load as well as welfare issues. However for all technical and chemistry matters including development they report to the chemist.

### **6.3 Quality**

Analytical results are peer checked and independently verified by a second SQEP person. Data used in reports and for discharge certificates are also transcription checked.

Staff are encouraged to report any incidents, or near misses (Quality, Safety or Compliance) using the Learning Capture Form. Investigations may be carried out to identify the root cause of any deviations and provide corrective actions/ preventative time- based actions. These are followed up to ensure action completion. Event investigations are documented for knowledge management and records maintained.

All new and updated procedures relevant to the role are issued as directed reading. All procedures that have been read are recorded electronically by the Document Control team. This can provide evidence of on-going competency.

Each analyst will be assessed for competency for a particular analytical technique or work process following a series of pre-set criteria. This may involve work observation and questioning by SQEP personnel or a panel interview.

## 7. Accreditations

- ISO 9001 The Magnox Quality management system has been certified with this certification.
- OHSAS 18001 Occupational Health & Safety
- ISO 14001 Environmental Management involves specific conditions relating to the calibration and use of monitoring equipment.

As part of our Compilation of Environment Agency Requirements, Approvals and Specifications (CEARAS) made under Permit number EPR/ZP3493SQ/V004, permit condition 3.2.5(a) "***The analytical methods shall be adequately validated and controlled in manner consistent with, as a minimum, those requirements of ISO 17025***". Adherence to the principles of ISO 17025 is well established within our radiochemical laboratory.

To meet these requirements there are a number of controls in place on site such as Operating Instructions (OIs), calibrations, Quality Controls and verification of results. These have already been discussed in other sections of this report

## 8. Internal Auditing

Various aspects of the Quality System in the laboratory team will be audited in a self-audit program. The audits will identify both good practice and identify any deficiencies. Corrective actions will be allocated and audit action tracked for completion. Subjects for such audits may cover but are not be limited to calibration, data handling, reporting, procedures, and training records.

There is a Magnox company wide Audit Inspection and Reassurance Program (AIR) which covers auditing across site. A Site Inspector who has a presence on the Bradwell Site but not accountable to this site also provides independent oversight.

## 9. External Auditing

This will be provided by an external ISO 17025 auditor on an annual basis every \_\_\_\_\_ (to be agreed with the EA). This will complement the internal auditing described in the previous section. The subjects which will be covered include:

Purchasing services and supplies  
Control of nonconforming work  
Control of records  
Internal audits  
Personnel  
Accommodation and environmental conditions  
Test and calibration methods and method validation  
Equipment  
Measurement traceability  
Sampling  
Assuring the quality of test and calibration results  
Reporting the results

## 10. Conclusion

This document describes how ICP-MS works in order to measure metal concentrations in solution. The Bradwell FED analytical chemistry team are using two ICP-MS methods, main metals and mercury to measure FED effluent. These methods are outlined alongside the validated versions. A commercial spectrophotometric method is used to measure nitrates. The infrastructure which supports the chemical analysis is also covered in this document namely the equipment, staff, procedures and the Quality systems.

It is planned to adopt the validated methods for routine use for the new Permit, begin to demonstrate proficiency on an approved scheme and start on the external audit programme.