BRADWELL SITE

ANALYTICAL TECHNIQUES INCLUDING pH (A3 OT9)

BRAD/EN/REP/205

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List of Abbreviations

ADAP	Active Discharge Abatement Plant
AETP	Active Effluent Treatment Plant
AI	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

Contents

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. The site will carry out regular monitoring of treated voids' effluent from the siltbuster. This is to provide some assurance that the output from the siltbuster unit is consistent with that described in the permit application. It does not provide data on actual discharge concentrations into the estuary as the effluent is diluted when mixed with other sources in the main drains pit (MDP) prior to discharge.

Specified metals shall be analysed in accordance with written laboratory operating instructions. The analytical technique is described in this operating technique A3 OT9 as required by the Mixed Effluent permit PR2TS/E10760C.

1.1 Introduction to ICP-MS

The Magnox Ltd power plant at Bradwell-On-Sea ("Bradwell") is currently being decommissioned. The production of mixed effluents is one aspect of the decommissioning activities currently being carried out at Bradwell. Batches of effluent may be treated voids' effluent from the siltbuster prior to storage in the main drains pit. After analysis of samples to measure metals concentration, pH and appearance, the effluent stream can then be discharged into the Blackwater estuary via Outlet 2.

ICP-MS is used for the measurement of chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn). 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 quadruple 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. $^{40}Ar^{16}O^+$ is the most abundant isotope with a m/z ratio of 56 which is the same mass for ^{56}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 new permit PR2TS/E10760C will require the measurement of metals of treated voids effluent from the siltbuster. There are no specific discharge limits as the expectation is that the actual levels will be very low but there is a reporting requirement.

The ICP-MS will measure the metal concentration using a semi –quantitative "Total Quant" method. This is a proprietary method supplied by Perkin Elmer for measurement of a large range of elements. It is anticipated that the samples from mixed effluent will have a low concentration of all metals of interest so the testing should confirm this.

The OI for use of the Total Quant method is BRAD/22429/OI/00136.

A single sample typical run order would be
Blank
External standard
QC
Blank
Sample
QC
Blank.

The accuracy of this method is quoted by Perkin Elmer to be in the region of 25%. Both the external standard and QCs will contain all the elements of interest.

Nitric acid (HNO_3) was chosen as a suitable matrix for Total Quant 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.

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 sample preparation and running of samples to ensure the procedures are carried out uniformly by all laboratory technicians.

Specialist tools and materials required for Total Quant analysis are:

- Dedicated plastic volumetric flasks (to be soaked for 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 PR2TS/E10760C. 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 PR2TS/E10760C in dilute nitric acid for dilution to prepare calibration standards

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 QC's 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 samples.

Certificates giving the specifications for auto-pipettes and volumetric flasks are also retained. All pipettes are purchased from reputable suppliers (currently Eppendorf or 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 located in laboratory 185. 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, with the ICP-MS instrument number, pass/fail designation and the laboratory technician that carried out the task. 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.

2.2 Internal Standard

An internal standard is not required for the Total Quant method as external standards are run to provide a calibration line.

2.3 Quality Control Samples

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

2.4 Reporting of ICP results

For the Total Quant method, the results are reported from the Total Quant Summary report. Elements with concentrations less than the value of the QC, this will be reported as < QC, higher values will be reported to the nearest integer.

2.5 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 with the exception of boron and is provided on a basis of five times a year. The methods used for this exercise will not be the semi- Quantitative Total Quant method but will be alternative validated methods.

2.6 Sample Testing

The samples from the siltbuster effluent will be tested by ICP-MS, to provide values for reporting as required by the permit.

The post discharge samples may be tested by ICP-MS either as separate samples or as a composite sample. The samples will be stabilised by the addition of nitric acid prior to storage. If the sample has been tested in the pre-discharge by ICP-MS it will not need to be tested post-discharge.

An alternative to ICP-MS may be employed using spectrophotometric analysis. Analysis kits for individual metals are available commercially from reputable suppliers for this purpose. Any results generated using this methodology will be for internal purposes only.

The results will be reported to the EA on a regular basis under the terms of the new permit, and will be obtained from ICP-MS testing.

2.7 ICP-MS Ways of Working

Bradwell has two Nexion 300X ICP-MS instruments, which are referred to as ICP 1 and ICP2. The Total Quant method can be run on either instrument. 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 ICP-MS are housed within a container with temperature control provided by air conditioning units. The instruments are maintained on a 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 pH

pH measurement is required under the Permit PR2TS/E10760C. This is performed according to the OI BRAD/22429/OI/0040.

Bradwell uses the Mettler Toledo Seven Easy S20 pH meter. The meter is calibrated daily using pH 4, 7 and 10 buffer solutions. The meter can then be used to measure discharge samples. Three replicates of the discharge samples are measured and the average is reported.

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 plants 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 and operators 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 time on shift.
- 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 he/she keeps up to date and uses with 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***". Adherance 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 (QC) and verification of results. These have already been discussed in other sections of this report.

8. Internal Auditing Routine

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 will cover but are not to 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 will be using a semi-quantitative" Total Quant" ICP-MS method to measure treated voids' effluent from the siltbuster. The infrastructure which supports the chemical analysis is also covered in this document namely the equipment, staff, procedures and the Quality systems.