



Awel y Môr Offshore Wind Farm

Contaminants Analysis Method Statement

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Aqua Regia Microwave Digestion of Sediments

Test Method number | EUAF-FGBM-CHEM-TM-032

Responsible Person: Principal Chemist (Technical Manager)

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1. Objectives

The purpose of this method statement is to describe the preparation of sediment samples for elemental analysis in the chemistry laboratory in Edinburgh. Concentrations of various major and trace elements are important in considering the impact on the environment of anthropogenic activities.

Homogenised sediment is weighed into microwave vessels, the sample is wetted with deionised water, then hydrochloric acid and nitric acid are added in a 3:1 ratio. The vessels are closed, tightened and placed into the microwave rotor. The appropriate microwave programme is selected, heating the samples to 175 °C at a ramp rate of approximately 10 °C per minute. Once cooled, the contents of each vessel are accurately diluted into 50 mL polypropylene tubes using deionised water and centrifuged. Samples are then measured using inductively coupled plasma-optical emission spectrometry (ICP-OES) and ICP-mass spectrometry (ICP-MS). Further dilution into 15 mL polypropylene tubes is required prior to ICP-MS analysis to allow appropriate levels of analytes and total dissolved solids.

2. Scope

This document applies to the testing carried out in the Fugro GB Marine Limited (FGBML) chemistry laboratory in Edinburgh.

3. Related Documents

- ISO/IEC 17025:2017 General Requirements for the Competence of Testing and Calibration Laboratories;
- EPA Document EPA/600/R-05/124 Sample Holding Time Re-evaluation;
- EPA Document SW-846 Test Methods for Evaluating Solid Waste: Physical/Chemical Methods Compendium;
- ISO 11466: 1995 Soil Quality – Extraction of Trace Elements Soluble in Aqua Regia;
- ISO 12914: 2012 Soil Quality – Microwave-assisted Extraction of the Aqua Regia Soluble Fraction for the Determination of Elements;
- EUAF-FGBM-CHEM-PR-002 Receipt and Logging of Samples;
- EUAF-FGBM-CHEM-TM-001 Laboratory Reagent Preparation and Equipment Cleaning;
- EUAF-FGBM-CHEM-TM-002 Calibration Verification and Service of Laboratory Equipment;
- EUAF-FGBM-CHEM-TM-019 Balance Verification Sheet
- EUAF-FGBM-CHEM-TM-033 ICP-OES Analysis of Major and Trace Elements in Sediments;
- EUAF-FGBM-CHEM-TM-034 ICP-MS Analysis of Trace Elements in Sediments;
- EUAF-FGBM-CHEM-FO-060 Work Order;
- EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet;
- EUAF-FGBM-CHEM-FO-091 Dispenser Calibration;
- EUAF-FGBM-CHEM-FO-092 Dispenser Verification Log;

- EUAF-FGBM-CHEM-FO-088 Pipette Verification Log;
- EUAF-FGBM-CHEM-FO-094 Microwave Vessel Spring Usage Log;
- EUAF-FGBM-CHEM-FO-089 Pipette Extended Verification Log;
- EUAF-FGBM-CHEM-FO-095 Polypropylene Tube Verification Log;
- EUAF-FGBM-CHEM-FO-098 Sieve Calibration;
- EUAF-FGBM-CHEM-FO-103 2000 μm Sieve Usage Log;
- EUAF-FGBM-CHEM-FO-104 63 μm Sieve Usage Log;
- EUAF-FGBM-CHEM-TP-007 Metals Laboratory Traveller.

4. Responsibilities

Only members of staff (or contract staff) who have been approved to perform the tasks detailed in this document at the appropriate level as documented on their training record are permitted to carry out the tasks specified in this procedure.

The Technical Manager at the Edinburgh chemistry laboratory is responsible for testing.

The individual training records for laboratory staff details their testing competency. Staff shall not carry out any testing unless they are documented as having been trained (or are undergoing training and under supervision) to perform that test.

5. Health and Safety

Some of the samples and chemicals used in this method may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings on reagent labels and read the hazard data information.

All relevant COSHH assessments must be read and signed before carrying out tasks detailed in this procedure.

Always wear safety glasses and laboratory coats when handling chemicals (and additional personal protective equipment where appropriate).

If exposure to samples or chemicals occurs, remove personnel from exposure and refer to the relevant COSHH form for the appropriate course of action.

If samples are suspected of or known to contain high levels of oil, the mineral oil COSHH assessment **must** be signed before handling those samples.

6. Principle of the Method

Sediment samples are sieved and homogenised if applicable, and then undergo an aqua regia microwave digestion to extract major and trace elements prior to analysis by ICP-OES (EUAF-FGBM-TM-033) and/or ICP-MS (EUAF-FGBM-TM-034).

7. Apparatus and Reagents

7.1 Apparatus

7.1.1 Glassware

- Glass dishes for drying samples;
- Measuring cylinders (10 mL) for measuring liquids.

7.1.2 Instruments and Technical Equipment

- Adjustable micro-pipette 100 µL to 1000 µL (EN204 or EN336) for dilution of samples for analysis;
- Beckman Coulter Allegra X-30 Centrifuge (EN049);
- Bottle-top (10 mL capacity) acid dispensers for dispensing hydrochloric acid (EN176) and nitric acid (EN177);
- Cold store for sample storage;
- Genlab drying oven (EN282) to dry samples;
- Milestone Ethos Easy Microwave Digestion System with SK15 rotor (EN149);
- Milestone workstation for vessel assembly;
- Manual adapter to tighten and loosen vessel screws;
- Custom-adjusted torque wrench (EN310) to tighten and loosen vessel screws;
- Segmented rotor plate for securing the rotor segments;
- Teflon 100 mL microwave vessels with Teflon covers, springs, PEEK shields and polypropylene rotor segments;
- Thermocouple for temperature sensing within the microwave;
- Merck Millipore Direct Q3 Deionised water system for ultrapure (Type 1) water (EN050);
- Sartorius Cubis (EN259) for accurately weighing small masses.

Note: see equipment database for current EN numbers.

7.1.3 Miscellaneous

- Deionised water wash-bottles;
- Disposable pipette tips to fit the adjustable micro-pipettes;
- Mortar and pestle for grinding samples;
- PTFE-coated spatulas (micro, mini, standard) for dispensing sediment samples;
- Sample rack (15 place) for holding microwave vessels during sample preparation;
- Sample racks for holding 15 mL and 50 mL polypropylene tubes.
- Sarstedt 15 mL and 50 mL polypropylene tubes for sample dilution;
- Digital thermometer (EN323) to check temperature of drying oven (EN282);
- Measuring cylinders (10 mL) for measuring liquids;
- Bottle brushes for cleaning of microwave vessels;
- Sieves (63 µm and 2 mm) and sieve receiver for sample preparation.

7.2 Reagents

- Acetone (Rathburn) for cleaning;
- Decon 90 solution for cleaning;
- Hydrochloric acid 37 % (Fisher, Certified AR) for cleaning;
- Hydrochloric acid 34 % to 37 % (Fisher, trace metal grade) for sample preparation;
- Nitric acid 68 % (Fisher, Certified AR) for cleaning;
- Nitric acid 67 % to 69 % (Fisher, trace metal grade) for sample preparation.

8. Analytical Quality Control

8.1 Quality Control

A procedural blank, containing reagents but no sample, is prepared and digested with each batch of samples.

At least one LRM/CRM or equivalent sediment sample (e.g. past proficiency scheme sample) is included with each digestion batch.

8.2 Interferences

Trace and major element analysis requires a clean environment, avoiding contamination of samples and reagents e.g. contact with fingers, gloves, dust, dirty equipment, other activities in the laboratory and rusty equipment.

All nitric acid and hydrochloric acid used for sample preparation should be trace metal grade. All deionised water should be Type 1 (ultrapure with a resistivity of 18.2 MΩ.cm at 25 °C).

8.3 Sample Holding Times

Samples should be collected in a plastic bag with a pre-cleaned plastic scoop and then transferred to a freezer at -20 °C. A subsample of sediment should be transferred to a clean glass dish and oven-dried at 40 °C until dry. Sample preservation and holding times for trace metals in sediments are as follows:

Table 8.1: Sample holding times

Analyte	Matrix	Treatment	Storage Temperature	Holding Time [Days]
Trace Metals	Sediment	None	NA	180*
Mercury	Sediment	None	≤ 6 °C	28*
Notes * = Holding times quoted from EPA Document SW-846 (Update VI, 2018)				

9. Labelling of Samples and Equipment

9.1 Samples Undergoing Elemental Analysis

When a sample is undergoing elemental analysis in the laboratory, all glassware and plasticware must be labelled. To help ensure client confidentiality, all samples and plasticware within the laboratory are labelled with the following:

- The project number;
- The designated laboratory ID number, assigned when EUAF-FGBM-CHEM-FO-060 Work Order is prepared and recorded in EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet (LRM, CRM, blank etc. must be identified).

In addition, polypropylene tubes must be labelled with the following:

- Digest method;
- Dilution factor;
- The date of preparation.

9.1.1 Repeat/Re-run Samples

For samples which need analysis to be re-run, for whatever reason, labelling should incorporate that fact. For sediment samples, the designated laboratory ID number should refer to the original laboratory ID number but should be suffixed 'RR' to indicate it is a repeat run of the sample e.g. 'A04RR'. Any further re-runs required on the same sample would be further suffixed with numbers e.g. 'A04RR2', 'A04RR3'.

10. Receipt and Logging of Samples

The receipt and logging of samples is detailed in EUAF-FGBM-CHEM-PR-002.

11. Laboratory Reagent Preparation and Equipment Cleaning

The preparation of laboratory reagents and equipment cleaning is detailed in EUAF-FGBM-CHEM-TM-001.

12. Calibration Verification and Service of Laboratory Equipment

The calibration verification and service of all laboratory equipment is detailed in EUAF-FGBM-CHEM-TM-002.

13. Aqua Regia Digestion of Sediments Procedure

All batches should be accompanied by EUAF-FGBM-CHEM-TP-007 Metals Laboratory Traveller.

13.1 Sample Preparation

1. Sediment samples are completely thawed and thoroughly homogenised prior to subsampling. Place enough wet sediment in a labelled glass dish to yield an approximately 10 g dry weight of sample (approximately 30 g wet weight). Place in the 40 °C oven (EN282) until dry;
2. Homogenise and grind with a clean mortar and pestle;
3. Check the form EUAF-FGBM-CHEM-FO-060 Work Order and sieve to the appropriate size – 2 mm or 63 µm. Visually inspect the sieve prior to use and ensure it is within calibration. Fill out the appropriate sieve usage log (EUAF-FGBM-CHEM-FO-103 2000 µm Sieve Usage Log or EUAF-FGBM-CHEM-FO-104 63 µm Sieve Usage Log) for each usage of a particular sieve so that uses in between calibrations are tracked;
4. Ensure that the mortar and pestle are cleaned in between samples to avoid contamination – scrub with a clean scourer, hot water and Decon 90 solution; rinse with 10 % nitric acid solution, rinse with deionised water and then air dry or dry with acetone. Use a clean nylon brush to ensure the sieve is clean of sediment in between uses. At the end of the final sample of the day, the sieve should then be cleaned with hot water and Decon 90 solution, rinsed with deionised water and then air-dried. Spatulas and sieve receivers should be cleaned in between uses – scrub with a clean scourer, hot water and Decon 90, rinse with deionised water and either air dry or dry with non-shedding laboratory wipe;
5. Samples are stored in plastic bags until needed.

13.2 Preparation of Samples for Aqua Regia Digestion

1. Ensure that a contamination check has been carried out on the vessels prior to use (see Section 13.3 Care of Microwave Vessels);
2. Fill in EUAF-FGBM-CHEM-FO-094 microwave digestion spring usage log sheet to track how many times the safety springs are used. Maximum usage is 500 times, after this the springs must be disposed of and replaced;
3. The batch details will be entered in EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet and individual laboratory IDs assigned to each sample;
4. Put the correct amount of 100 mL Teflon vessels into the 15 place sample rack for the batch;
5. Place the Teflon sample vessel on the balance, close all doors, press the ioniser button to reduce the effects of static and then tare the balance, ensuring the reading is stable at zero. Accurately measure 0.5000 g (to four decimal places) of sediment into the vessel and record the weight in EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet;
6. Place the rack into the fume hood. Measure 3 mL of deionised water into a 10 mL measuring cylinder and pour into the first vessel. Swirl the vessel to ensure complete wetting of the dry sediment;
7. Using the bottle-top dispenser, add 6 mL of hydrochloric acid to a 10 mL measuring cylinder to check the volume. Enter the measured volume into the form

EUAF-FGBM-CHEM-FO-092 Dispenser Verification Log. If the volume is within the required error, pour it into the vessel.

8. Using the bottle-top dispenser, add 2 mL of nitric acid to a 10 mL measuring cylinder to check the volume. Enter the measured volume into the form EUAF-FGBM-CHEM-FO-092 Dispenser Verification Log. If the volume is within the required error, pour it into the vessel.
9. For the remainder of the vessels, the hydrochloric acid can now be added straight from the dispenser, followed immediately by the nitric acid. Swirl the vessel gently to ensure all the contents are thoroughly mixed. If a vigorous reaction occurs, allow the reaction to subside before closing the vessel;
10. Insert the vessel into the PEEK protection shield, taking care that the bevel of the shield is at the bottom;
11. Place the Teflon cover onto the vessel;
12. Place the safety spring onto the Teflon cover, ensuring that the side marked "down" is at the bottom (closest to the Teflon cover);
13. Place the assembly into the polypropylene rotor segment, ensuring that the number of the rack the vessel is taken from matches up with the number on the segment;
14. Take the custom-adjusted torque wrench and ensure it is in the "close" position (fully anti-clockwise);
15. Place the assembled rotor segment into the slot in the workstation;
16. Use the manual adapter to initially close the vessel screw on the top of the rotor segment;
17. Tighten the screw using the torque wrench until you hear a clicking sound and feel resistance, indicating that the vessel is properly closed;
18. Repeat the same procedure for the remainder of the samples. Note that deionised water, hydrochloric acid and nitric acid must be added to all vessels, including blanks.
19. Ensure that the reference vessel (numbered 1) contains a sample (not the blank). After weighing the sample in and adding deionised water, nitric acid and hydrochloric acid, carefully place the reference cover onto the vessel, after inspecting the thermowell for any damage. Do not use a cracked thermowell, instead, replace it with an undamaged one. Repeat the same closure procedure for the reference vessel as the others;
20. Carefully introduce the thermocouple into the reference vessel, sliding it through the hole in the middle of the screw. Ensure it is firmly in place by pushing the fixation adapter into the screw;
21. Place each segment into the rotor bottom plate in the microwave unit. Ensure that the vessels are approximately evenly spaced within the microwave unit to allow the segmented rotor plate to sit correctly;
22. Place the segmented rotor plate on top of the vessels, ensuring they are fixed by the connectors to each individual polypropylene segment;
23. Remove the protection cover and unplug the jumper from the sensor connection in the microwave unit;

24. Ensure the reference vessel is located to the front right of the microwave unit within the carousel and plug in the temperature sensor;
25. Ensure the exhaust hose is inserted into the laboratory extraction hood and that the extraction is switched on;
26. Start the following digestion program. Note that n in the rotor and vessels parameter boxes corresponds to the number of vessels in the batch. This can be changed in the rotor parameter selection on the microwave control, which in turn updates the number of vessels. Only the microwave power changes, dependent on how many vessels are undergoing digestion. For less than or equal to three vessels, the microwave power is 800 W, for 4 to 8 (inclusive) vessels, the microwave power is 1200 W, and for 9 or more vessels, the microwave power is 1800 W. Ensure the correct method is chosen for the number of vessels undergoing digestion:

Table 13.1: Microwave digest conditions

T1	ON	Twist	ON	Rotor	SK _n
T2	ON	Rotor Ctrl	ON	Stirrer	0 %
P1	OFF	MW Continuous	ON	Vessels	n
P2	OFF	P2 limit	0 %	Control For	T1
Door Locking	> 80 °C				

Step	T	MW [w]	T1 [°C]	T2 [°C]	Fan Speed
1	00:10:00	1800/1200/800	175	110	3
2	00:10:00	1800/1200/800	175	110	3
3	00:00:00	-	-	-	3
Cooling: 30 min					

27. When the vessels are cool (T1 equal to or less than 30 °C), unplug the temperature sensor, plug the jumper back in and replace the protection cover, remove the reference vessel and thermocouple from the rotor, then carefully remove the thermocouple from the reference vessel and place the reference vessel in the workstation in the fumehood;
28. Take the custom-adjusted torque wrench and ensure it is in the "open" position (fully clockwise);
29. Loosen the screw on the top of the vessel using the torque wrench, and then use the manual adapter to further open the screw. Ensure that the vessel is pointed towards the back of the fumehood and opened very slowly as there may be a release of pressure;
30. Remove the vessel from the polypropylene segment and take off the spring. Slide the vessel from the protection shield using the fitting on the workstation. Wipe any acid/water spills immediately from the polypropylene segment, protection shield and safety spring with a clean laboratory tissue/hand towel and ensure these are thoroughly dry before using them again;

31. Carefully remove the Teflon vessel cover and rinse the lower part of it into the vessel using a small amount of deionised water;
32. Pour the contents of the vessel into a labelled 50 mL polypropylene tube, and then rinse the vessel with deionised water, collecting the washings in the 50 mL tube. Accurately add deionised water to the 50 mL fill-line printed on the tube;
33. Repeat for the remaining samples. Ensure the torque wrench is clean and dry after each batch is completed;
34. Vigorously shake the samples, ensuring the liquid is homogeneous, then centrifuge the samples at 2500 rpm for 15 minutes;
35. Remove the samples from the centrifuge. Samples are carefully poured directly into appropriately labelled 15 mL tubes prior to analysis by ICP-OES. Samples will need a further 20-fold dilution prior to ICP-MS analysis - take 750 μ L of sample from the 50 mL tube using a pipette, add to an appropriately labelled 15 mL polypropylene tube half-filled with 3 % aqua regia solution and make up to the 15 mL fill-line using 3 % aqua regia solution. Shake well;
36. The dilution stage should be done close to the batch being run on the instruments. If there is a significant time period between preparing and running the samples, the dilutions should be left until later. In this case, labels should be prepared in advance, leaving the date prepared section blank to be filled in when the dilution stage occurs.

13.3 Care of Microwave Vessels

1. Once the sample is transferred into the polypropylene tubes for analysis, the vessels and Teflon covers should be thoroughly cleaned. First, use a clean bottle brush, water and Decon 90 solution to remove any sediment from the vessel walls. Rinse with deionised water and then soak in 10 % nitric acid for 2 hours. Rinse three times with deionised water and then soak in deionised water for a further 2 hours. Rinse again three times with deionised water and leave to air dry.
2. Always perform a vessel contamination test prior to using the vessels. This is a program on the microwave which exposes the vessels and lids to microwaves. Place the vessels and Teflon covers on the bottom of the microwave rotor (there is no need to insert the segments or the temperature sensor) and start one of the following programs dependent on the number of vessels:

Table 13.2: Vessel absorption test conditions for nine or less vessels

T1	ON	Twist	ON	Rotor	Time/Temp
T2	ON	Rotor Ctrl	ON	Stirrer	0 %
P1	OFF	MW Continuous	ON	Vessels	n
P2	OFF	P2 limit	0 %	Control For	T1
Door Locking	> 80 °C				

Step	T	MW [w]	T1 [°C]	T2 [°C]	Fan Speed
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1	00:00:45	450	0	0	3
2	00:00:00	-	-	-	3

Table 13.3: Vessel absorption test conditions for ten to fifteen vessels

T1	ON	Twist	ON	Rotor	Time/Temp
T2	ON	Rotor Ctrl	ON	Stirrer	0 %
P1	OFF	MW Continuous	ON	Vessels	n
P2	OFF	P2 limit	0 %	Control For	T1
Door Locking	> 80 °C				

Step	t	MW [w]	T1 [°C]	T2 [°C]	Fan Speed
1	00:00:45	600	0	0	3
2	00:00:00	-	-	-	3

3. Check the temperature of each vessel and lid immediately after the 45 second program. If any of the vessels or lids are hot refer to the user manual for further cleaning processes before using again. If the vessels remain cold they are ready either to be stored away or used immediately.



ICP-OES Analysis of Major and Trace Elements in Sediments

Test Method number | EUAF-FGBM-CHEM-TM-033

Responsible Person: Principal Chemist (Technical Manager)

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1. Objectives

The purpose of this test method is to describe the analysis of major and trace elements in sediment samples in the chemistry laboratories in Edinburgh.

In sediments, the concentration range of the method is from the method detection limit (see Section 14) to the level of the top calibration standard (generally 10 000 mg/kg for undiluted samples and 100 000 mg/kg for undiluted samples analysed for high levels of aluminium and iron), depending on the original sample weight used.

2. Scope

This document applies to the analysis carried out in the Fugro GB Marine Limited (FGBML) chemistry section in Edinburgh.

3. Related Documents

- ISO/IEC 17025:2017 General Requirements for the Competence of Testing and Calibration Laboratories;
- ISO 22036: 2008 Soil Quality – Determination of Trace Elements in Extracts of Soil by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES);
- SEPA Measurement Assurance and Certification Scotland – Performance Standard MACS-WAT-01 Sampling and Chemical Testing of Water, Version 2, August 2017;
- Environment Agency Performance Standard for Laboratories Undertaking Chemical Testing of Soil, Version 5, November 2018;
- CSEMP Green Book, Tables 1 to 7, Version 15, July 2012;
- EUAF-FGBM-CHEM-GU-001 Uncertainty of Measurement Calculations;
- EUAF-FGBM-CHEM-GU-003 ICP-MS and ICP-OES Maintenance Guide;
- EUAF-FGBM-CHEM-PR-001 AQC and Environmental Conditions of Laboratory;
- EUAF-FGBM-CHEM-PR-002 Receipt and Logging of Samples;
- EUAF-FGBM-CHEM-TM-001 Laboratory Reagent Preparation and Equipment Cleaning;
- EUAF-FGBM-CHEM-TM-002 Calibration Verification and Service of Laboratory Equipment;
- EUAF-FGBM-CHEM-TM-032 Aqua Regia Microwave Digestion of Sediments;
- EUAF-FGBM-CHEM-TM-031 ICP-OES Preparation of Standards and Solutions;
- EUAF-FGBM-CHEM-FO-060 Work Order;
- EUAF-FGBM-CHEM-FO-086 Metals Standards for ICP-MS and ICP-OES;
- EUAF-FGBM-CHEM-FO-087 Instrument Maintenance Log (Inorganic);
- EUAF-FGBM-CHEM-FO-088 Pipette Verification Log;
- EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet;
- EUAF-FGBM-CHEM-FO-096 Argon Tank Delivery Check;
- EUAF-FGBM-CHEM-FO-097 Metals Data Converter;
- EUAF-FGBM-CHEM-TP-007 Metals Laboratory Traveller.

4. Responsibilities

Only members of staff (or contract staff) who have been approved to perform the tasks detailed in this document at the appropriate level as documented on their training record are permitted to carry out the tasks specified in this procedure.

The Technical Manager at the Edinburgh chemistry laboratory is responsible for testing.

The individual training records for laboratory staff details their testing competency. Staff shall not carry out any testing unless they are documented as having been trained (or are undergoing training and under supervision) to perform that test.

5. Health and Safety

Some of the chemicals used in this method may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings on reagent labels and read the hazard data information.

All relevant COSHH assessments must be read and signed before carrying out tasks detailed in this procedure.

Always wear safety glasses and laboratory coats when handling chemicals (and additional personal protective equipment where appropriate).

If exposure to chemicals occurs, remove personnel from exposure and refer to the relevant COSHH form for the appropriate course of action.

6. Principle of the Method

Sediment samples undergo a microwave aqua regia digest and dilution as described in EUAF-FGBM-CHEM-TM-032 Aqua Regia Microwave Digestion of Sediments. Sample digests are then poured into labelled 15 mL polypropylene tubes before analysis of major and trace element concentrations by ICP-OES. If levels of aluminium and iron are found to be above the top standard, these are run again with a method using higher concentration calibration standards.

7. Apparatus

Before use of any apparatus visually confirm that the equipment is not damaged in any way. If defects are found quarantine and report to the Technical Manager – under no circumstance should apparatus be used if faulty/broken.

7.1 Apparatus

7.1.1 Plasticware

- 15 mL and 50 mL polypropylene tubes for dilution of samples and storage of samples and standards;
- Disposable pipette tips to fit the adjustable micro-pipettes.

7.1.2 Instruments and Technical Equipment

- Adjustable micro-pipettes 20 µL to 200 µL (EN203 or EN335), 100 µL to 1000 µL (EN204 or EN336) and 1 mL to 5 mL (EN205 or EN337) for dilution of samples;
- Merck Millipore Direct Q3 Deionised water system (EN050) for ultrapure (Type 1) water for dispensing of ultrapure water;
- Thermo Scientific iCAP-7400 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (EN153) for major and trace element analysis of samples;
- Cetac ASX-560 autosampler (ICP-OES) (EN154) for automated sample uptake.

Note: see equipment database for current EN numbers.

8. Analytical Quality Control

Refer to EUAF-FGBM-CHEM-TM-032 Aqua Regia Microwave Digestion of Sediments, Section 8 for details of the analytical quality control process.

9. Calibration Verification and Service of Laboratory Equipment

The calibration verification and service of all laboratory equipment is detailed in EUAF-FGBM-CHEM-TM-002 Calibration Verification and Service of Laboratory Equipment.

10. Labelling of Samples and Equipment

10.1 15 mL Polypropylene Tubes

After microwave digestion the samples are poured into 15 mL polypropylene tubes for analysis by ICP-OES. At this stage the tubes have printed or handwritten labels which should contain the following information:

- Project number;
- Station number/location if sufficient room to include (LRM, CRM, blank etc. must be identified);
- Laboratory ID;
- Digest method.

Repeat/Re-run Samples

For samples which need analysis to be re-run, for whatever reason, labelling should incorporate that fact. For trace element samples, the designated laboratory ID number should refer to the original laboratory ID number but should be suffixed "RR" to indicate it is a repeat run of the sample e.g. 'A04RR'. Any further re-runs required on the same sample would be further suffixed with numbers e.g. A04RR2', 'A04RR3'.

11. Receipt and Logging of Samples

The receipt and logging of samples is detailed in EUAF-FGBM-CHEM-PR-002 Receipt and Logging of Samples.

12. Laboratory Reagent Preparation and Equipment Cleaning

The preparation of laboratory reagents and equipment cleaning is detailed in EUAF-FGBM-CHEM-TM-001 Laboratory Reagent Preparation and Equipment Cleaning.

13. Analysis of Sediment Digest for Major and Trace Elements using ICP-OES

This section may only be carried out by chemistry personnel who have received, or are in the process of receiving, training in the operation of the ICP-OES system and the interpretation of the data obtained. Analysts should refer to EUAF-FGBM-CHEM-FO-060 Work Order to ascertain the exact analysis requirements for each project.

This method may be used to quantify the following elements in sediment digests:

Al, Ba, Fe, Mn, P, Ti and V.

The limits of detection calculated during method validation are listed in Section 14.

13.1 Outline of Method

The internal standard and analytes in the sample digest are drawn simultaneously through the sample introduction system using a y-piece connected to a peristaltic pump. A fine mist is sprayed from the nebuliser into the spray chamber and the sample is then vaporised, atomised and ionised in the argon plasma after travelling into the torch via a flow of argon. The ions are then measured by the CID (charge injection device) detector. Calibration with appropriate standards allows the software to calculate concentrations of each analyte in the sample.

13.2 Instrument Conditions

13.2.1 Data Acquisition Method – iCAP 7400

UV Exposure Time	10 s
Visible Exposure Time	5 s
RF Power (UV and Visible)	1350 W
Nebuliser Gas Flow	0.5 L/min
Auxiliary Gas Flow	0.50 L/min
Pump Speed	50 RPM
Wash Time	90 s
Uptake Time	60 s

13.2.2 Element Wavelengths and Measurement Details

Element	Symbol	Wavelength [nm] and Order	Slit Position	Measure Mode	Width	Height	Internal Standard
Aluminium	Al	394.401 {85}	High	Radial	13	2	Y 371.030 {91} Radial
Barium	Ba	493.409 {68}	High	Radial	13	2	Y 371.030 {91} Radial
Iron	Fe	238.204 {141}	High	Radial	13	2	Y 371.030 {91} Radial
Manganese	Mn	257.610 {131}	High	Radial	13	2	Y 371.030 {91} Radial
Phosphorous	P	178.284 {489}	Low	Axial	13	5	Y 224.306 {450} Axial
Titanium	Ti	334.941 {101}	High	Radial	13	2	Y 371.030 {91} Radial
Vanadium	V	292.402 {115}	High	Axial	13	2	Y 371.030 {91} Axial
Yttrium	Y	371.030 {91}	High	Axial	13	2	NA
Yttrium	Y	224.306 {450}	Low	Axial	13	5	NA
Yttrium	Y	371.030 {91}	High	Radial	13	2	NA

13.3 Instrument Start-up

1. Switch the autosampler, chiller and argon humidifier on and check the extraction is on;
2. Ensure that the peristaltic pump tubing is held firmly in place with the collars and brackets;
3. Insert the internal standard probe into a 50 mL polypropylene tube containing a solution of 16 % aqua regia. The autosampler probe will go automatically into the rinse port when the Get Ready Button is selected. Ensure that there is a sufficient volume of 16 % aqua regia available in the autosampler wash reservoir;
4. Select the Get Ready Button on the dashboard tab of the Qtegra software Home Page and ensure the Warm up (30 minutes) and Spectrometer Optimisation (1 min) options are selected.

13.4 System Suitability

Before any analysis of sample digests is undertaken, the performance of the ICP-OES must be deemed to be acceptable by performing system suitability checks.

1. Once the system has warmed up and the spectrometer optimisation is performed then go to the LabBooks tab on the Home Page of the Qtegra software;
2. Select Create a new LabBook from an existing Template and select the Zinc Check SSC template name and 1 sample;
3. Name the new LabBook dd-mm-yy Zinc Intensity and check the Location field to ensure the year and month in the LabBook folder are correct. Select the Create LabBook button;
4. When the new LabBook opens, type dd-mm-yy Zinc Intensity into the Label field;
5. Direct the autosampler probe into standard position 9 (ensure the 50 mL tube in this position is filled with loaded blank [2 ppm zinc solution]) and insert the internal standard probe into another 50 mL tube also filled with loaded blank [2 ppm zinc solution];
6. Allow enough time for the solution to reach the detector and equilibrate and then press the play button at the left side of the top menu to initiate the LabBook;
7. Once the LabBook is complete, select Intensities from the Content menu and click each measured wavelength/mode and ensure the appropriate background and centre lines are selected;
8. Select Query from the Content menu and select the Zn intensity Preset. Ensure that the RSDs are less than 5 % and then export the data using the icon on the left side of the top menu. Save the file into the appropriate location. Use the filename given and ensure Open file in Excel after export is selected;
9. Copy and paste the data into the system suitability excel spreadsheet for the ICP-OES. Numeric criteria have been derived to ensure satisfactory performance of the ICP-OES as indicated by the appropriate reference lines and text boxes in the system suitability excel charts;

10. If all criteria are passed, then the ICP-OES is operating satisfactorily and the intended calibration standards and batch can now be analysed. Ensure that the details are recorded in the ICP-OES logbook;
11. If any of the intensities fall below the allowed levels, the sample introduction system should be checked for any obvious faults (e.g. loose peristaltic pump tubing, wrong system suitability solution in use etc.). If the sample introduction system has no obvious issues, a torch alignment should be carried out, with the autosampler and internal standard probes in the loaded blank (2 ppm zinc intensity). Following this, another zinc intensity system suitability check should be carried out. If this passes, the system is deemed suitable. If it fails, the sample introduction hardware (spray chamber, nebuliser, torch, injector) should be cleaned and the peristaltic pump tubing (sample, internal standard and waste) should be inspected and replaced if damaged. The performance checks are then run again prior to any sample analysis. If the system is still not suitable consult with the Technical Manager or their deputy before sample analysis is undertaken.

13.5 Analytical Quality Control

A method blank is run with each batch of samples. A laboratory reference material (LRM) and/or certified reference material (CRM) and/or past proficiency test sample is run with every batch of sediment samples. CONTEST and QUASIMEME proficiency test samples are analysed periodically through the year.

13.6 Procedure

13.6.1 Data Acquisition

1. Ensure that rack 1 of the autosampler contains 15 mL polypropylene tubes in the correct positions with enough volume of the appropriate calibration, independent and drift standards. Shake these well to mix and remove the lids. The calibration blank should be poured out fresh for each run;
2. Place the digest samples in the 15 mL polypropylene tubes into the appropriate positions in rack 2 of the autosampler. Shake these well to mix and remove the lids;
3. Ensure that the autosampler wash reservoir is filled with 16 % aqua regia solution;
4. Open the Qtegra software and select the LabBooks option. Select to create a new LabBook from an existing template and choose the correct template (Aqua regia undiluted for all analytes and Aqua regia high conc Al Fe for samples with high levels of aluminium and/or iron where required). Give the LabBook an appropriate name (such as the date the sequence was run on, project number and batch number) and ensure it is saved in the relevant year and month in the LabBook folder. Type the number of samples to be analysed into the relevant box. Select Create LabBook;
5. All relevant quality check samples (calibration standards, independent and drift checks) should be in the sample list. Edit the parameters for the unknown samples as appropriate (sample name, weight, volume, dilution factor, tube position). Many of these parameters can be found in the completed acid digest sheet for the batch

(EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet), normally available in the relevant project folder;

6. Alternatively, the sample names and weights can be entered automatically from a .csv file when the LabBook is created. From the LabBooks tab of the Qtegra software, give the LabBook an appropriate name as in step 4. Select to create a new LabBook from an existing template but also select the Import from CSV box. The CSV name is set up as Data template and the mapping name is set to default. The Data template, kept on the instrument desktop, is populated with the relevant sample names from the appropriate acid digest sheet for the batch (EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet) under the Lab ID heading, taking care to define the quality samples. Under the Amount heading, the weights are copied and pasted (with grams as units), ensuring the blank weight is 0.5000 g. The Rack Number and Vial Number columns are populated with the correct sample positions. Save the Data template. In the Qtegra software, select Create LabBook. Ensure that everything is correct in the sample list;
7. Ensure the internal standard probe is placed into the internal standard bottle (which should be shaken well to mix the solution) and there is enough solution for the run. Allow this to equilibrate and then press the play button to begin the acquisition process.
8. Record the details for the Labbook into the ICP-OES logbook.

13.6.2 Data Quantification

1. Once the LabBook is complete, select Intensities from the Content menu, click each measured wavelength/mode and ensure the appropriate background and centre lines are selected for each analyte, and that there are no obvious interferences. If many peaks are not centrally aligned it is advised to carry out an auto-peak on the method. Ensure that the calibration coefficients are greater than 0.997 for each element. All internal standard recoveries should be between 60 % and 125 %. The drift and independent standard should be between 90 % and 110 % for each element. If there are any deviations, consult with the Technical Manager or their deputy prior to accepting results;
2. Check that the concentrations for each analyte are below the top standard. In the case of aluminium or iron, if samples have higher concentrations than the top standard, they will need run again using the higher concentration standards. For all other analytes, if samples have significantly higher concentrations than the top standard, they should be diluted to bring them into the level of the calibration range and re-run;
3. If all quality checks pass, then select query on the Content menu in the Qtegra software and pick the Aqua Regia Digest ICP-OES RSD or Aqua Regia Digest Al and Fe ICP-OES RSD from the Preset drop-down menu as appropriate. Ensure that the RSD percentages are suitable for the element and the intensity measured. If there are any doubts, consult the Technical Manager or their deputy before proceeding;
4. Select Aqua Regia Digest ICP-OES or Aqua Regia Al and Fe ICP-OES from the Preset drop-down menu. Use the export icon on the top menu to export the data. Choose the path as desired (generally the relevant project folder), ensure the filename is suitable

(add OES at the end of the filename to denote the measurement instrument) and then select Export.

13.6.3 Processing Generated Data

1. Use the quality results spreadsheet to input the data into the relevant Shewhart charts for the batch. Ensure all quality checks pass before proceeding;
2. Open EUAF-FGBM-CHEM-FM-097-Metals Data Converter and save on the server within the appropriate project folder in the Chemistry subfolder;
3. Open up the relevant acid digest batch sheet from the extract subfolder of the project folder and copy the station names into the appropriate row. Use the exported results spreadsheet to populate the relevant concentrations sections of the raw data tab;
4. The final data tab is automatically populated using the data from the raw data tab. Analytes which have concentrations less than the minimum reporting value (MRV) are automatically colour-coded in red. These should be reported as less than the relevant MRV to the client.

13.7 Reporting

1. EUAF-FGBM-CHEM-FM-097-Metals Data Converter is saved on the server within the appropriate project folder in the Chemistry subfolder;
2. The Technical Manager or their deputy will validate the data within this folder in a timely manner by checking all the necessary quality control steps were completed and that the data was under control;
3. Once validated, the data is copied into an excel spreadsheet saved into a new folder within the project folder marked 'Validated Data'.

14. Method Validation

14.1 Method Detection Limit

The method detection limit (MDL) as determined below is that of the method limit of detection (LOD) rather than the instrument LOD. The use of the method LOD when reporting data is of greater relevance since the instrumentation can give very low detection limits which are entirely inappropriate for complex environmental matrices. The MDL was calculated using the external document SEPA Measurement Assurance and Certification Scotland – Performance Standard MACS-WAT-01 Sampling and Chemical Testing of Water. SD = standard deviation; Var. = variance. This MDL was then rounded up to give the final MRV to an appropriate number of significant figures. These final MRVs are summarised in the table at the end of this section.

14.1.1 Trace Metals (By Procedural Blank)

Analytes with Multi-element Standards

Al 394.401 Radial	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	8.32	9.34	6.85	2.20	0.52	-4.96	28.8	3.93	-2.98	12.3	11.3	23.1
Rep #2	2.74	2.36	1.16	-6.55	5.28	-7.70	16.7	4.01	4.50	7.15	1.52	
Within batch SD	3.95	4.93	4.02	6.19	3.37	1.94	8.62	0.0551	5.29	3.67	6.88	
Within batch Var.	15.6	24.4	16.2	38.3	11.3	3.76	74.2	0.00303	28.0	13.5	47.4	

Ba 493.409 Radial	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.0167	0.386	-0.373	0.588	-0.644	0.151	-0.0226	1.09	1.15	0.299	0.105	0.621
Rep #2	-0.219	0.167	-0.164	0.441	-0.413	0.273	0.0729	0.857	1.45	0.276	0.162	
Within batch SD	0.167	0.154	0.148	0.104	0.164	0.0864	0.0675	0.164	0.211	0.0157	0.0402	
Within batch Var.	0.0277	0.0239	0.0218	0.0108	0.0269	0.00746	0.00455	0.0269	0.0443	0.000247	0.00161	

Fe 238.204 Radial	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.589	0.721	-1.10	0.653	0.809	1.65	3.41	1.79	0.728	2.63	4.61	7.80
Rep #2	0.754	-0.0527	0.650	-0.274	0.0673	0.887	8.29	4.82	3.95	2.01	1.08	
Within batch SD	0.117	0.547	1.23	0.655	0.524	0.539	3.45	2.14	2.28	0.436	2.50	
Within batch Var.	0.0137	0.300	1.52	0.429	0.275	0.291	11.9	4.59	5.20	0.191	6.23	

Mn 257.610 Radial	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.0237	0.00303	-0.0117	-0.0647	-0.147	0.117	0.153	0.0861	0.0795	0.0399	0.0537	0.248
Rep #2	-0.00875	-0.0266	-0.0462	-0.0135	-0.0866	0.0498	0.0818	0.165	0.208	-0.0402	-0.0656	
Within batch SD	0.0229	0.0210	0.0244	0.0362	0.0424	0.0480	0.0507	0.0557	0.0907	0.0566	0.0843	
Within batch Var.	0.000526	0.00044	0.000594	0.00131	0.00180	0.00230	0.00257	0.00311	0.00822	0.00321	0.00711	

P 178.284 Radial	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.306	0.0578	0.175	0.128	0.167	-0.0143	0.199	0.125	-0.114	0.232	0.293	0.256
Rep #2	0.230	0.170	0.132	0.0276	0.0388	0.00691	0.191	0.122	-0.00466	0.177	0.361	
Within batch SD	0.0539	0.0795	0.0304	0.0708	0.0905	0.0150	0.00560	0.00188	0.0770	0.0387	0.0483	
Within batch Var.	0.00291	0.00633	0.000925	0.00501	0.00819	0.000225	3.13E-05	3.54E-06	0.00594	0.00150	0.00233	

Ti 334.941 Radial	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	-0.165	-0.109	-0.620	0.138	-0.0339	-0.252	-0.0632	-0.336	0.00218	-0.600	-0.290	0.685
Rep #2	-0.0244	0.102	-0.120	0.00125	-0.186	-0.0129	-0.0836	-0.212	-0.0635	-0.515	-0.0959	
Within batch SD	0.0997	0.149	0.353	0.0967	0.108	0.169	0.0144	0.0873	0.0464	0.0602	0.137	
Within batch Var.	0.00994	0.0222	0.125	0.00935	0.0116	0.0286	0.000207	0.00763	0.00215	0.00362	0.0188	

V 292.402 Axial	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	-0.0261	0.00366	0.0374	0.0472	0.0930	-0.0643	-0.164	-0.0873	-0.0557	0.244	-0.0267	0.199
Rep #2	-0.0518	0.0493	0.0922	0.0593	-0.0304	-0.108	-0.165	-0.0633	0.0302	0.213	-0.118	
Within batch SD	0.0182	0.0323	0.0387	0.00854	0.0872	0.0307	0.000696	0.0170	0.0607	0.0220	0.0649	
Within batch Var.	0.000332	0.00104	0.00150	7.29E-05	0.00761	0.000945	0.0000005	0.000288	0.00368	0.000482	0.00421	

Aluminium and Iron with High Concentration Standards

Al 394.401 Radial	Concentration in mg/kg											
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	MDL
Rep #1	17.9	2.88	7.07	1.55	4.62	4.36	16.8	33.7	9.86	11.3	7.20	28.1
Rep #2	18.2	-1.28	-1.75	4.87	0.000184	16.2	24.9	15.5	0.565	7.22	13.2	
Within batch SD	0.237	2.94	6.24	2.34	8.37	8.37	5.76	12.9	6.57	2.88	4.27	
Within batch Var.	0.0562	8.64	38.9	5.49	70.1	70.1	33.2	166	43.2	8.31	18.2	

Fe 238.204 Radial	Concentration in mg/kg											
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	MDL
Rep #1	0.949	2.87	2.75	2.90	1.56	2.93	0.0280	23.5	0.787	1.72	3.41	25.5
Rep #2	8.56	1.21	1.50	2.46	0.827	6.95	0.619	-0.340	4.05	1.60	2.04	
Within batch SD	5.38	1.17	0.881	0.310	0.521	2.84	0.418	16.9	2.31	0.0814	0.963	
Within batch Var.	28.9	1.37	0.776	0.0964	0.271	8.09	0.175	285	5.34	0.00662	0.928	

Analyte	Calibration	Final Minimum Reporting Value
Al 394.401 Radial	Multi-element	30
Al 394.401 Radial	High conc. standards	30
Ba 455.403 Radial	Multi-element	0.7
Fe 238.204 Radial	Multi-element	30*
Fe 238.204 Radial	High conc. standards	30
Mn 259.373 Radial	Multi-element	0.3
P 178.284 Axial	Multi-element	0.3
Ti 334.941 Radial	Multi-element	0.7
V 292.402 Axial	Multi-element	0.2
Notes		
* = Iron for both measurements rounded to highest MRV for ease of data handling		

14.2 Precision and Bias

Precision and bias were determined during a 2 × 11 batch method validation. This provides a measure of the method reproducibility rather than instrument reproducibility, which given autosampler systems and robust detection techniques would provide an artificially high measure of reproducibility. Precision and bias statistics were calculated for more than one sample (a range of proficiency testing samples) in order to determine the method performance for a range of matrices representing likely samples to be encountered in routine analysis.

The target SD was 10 % of the mean and the target bias was 70 % to 110 %.

14.2.1 CONTEST CN123 Precision for Analytes with Multi-element Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Al 394.401 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ba 493.409 Radial	214	7.10	12.6	14.5	6.74	21.4	NA	NA	NA	PASS
Fe 238.204 Radial	35500	387	728	824	2.32	3550	NA	NA	NA	PASS
Mn 257.610 Radial	529	4.50	6.10	7.58	1.43	52.9	NA	NA	NA	PASS
P 178.284 Axial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ti 334.941 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V 292.402 Axial	56.0	1.53	5.58	5.79	10.3	5.60	NA	NA	NA	PASS

14.2.2 CONTEST CN123 Precision for Analytes with High Concentration Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Al 394.401 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe 238.204 Radial	37000	308	430	529	1.43	3700	NA	NA	NA	PASS

14.2.3 CONTEST CN126 Precision for Analytes with Multi-element Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Al 394.401 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ba 493.409 Radial	269	5.92	6.62	8.88	3.30	26.9	NA	NA	NA	PASS
Fe 238.204 Radial	25800	252	525	582	2.25	2580	NA	NA	NA	PASS
Mn 257.610 Radial	453	3.94	5.10	6.44	1.42	45.3	NA	NA	NA	PASS
P 178.284 Axial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ti 334.941 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V 292.402 Axial	45.8	1.69	2.76	3.23	7.07	4.58	NA	NA	NA	PASS

14.2.4 CONTEST CN126 Precision for Analytes with High Concentration Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Al 394.401 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe 238.204 Radial	26900	313	471	565	2.10	2690	NA	NA	NA	PASS

14.2.5 Quasimeme QTM129MS Precision for Analytes with Multi-element Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Al 394.401 Radial	6760	186	343	390	5.78	676	NA	NA	NA	PASS
Ba 493.409 Radial	12.7	0.903	1.04	1.38	10.9	1.27	NA	NA	NA	PASS
Fe 238.204 Radial	15800	196	473	512	3.24	1580	NA	NA	NA	PASS
Mn 257.610 Radial	170	8.00	3.54	8.75	5.14	17.0	NA	NA	NA	PASS
P 178.284 Axial	486	25.5	3.29	25.7	5.30	48.6	NA	NA	NA	PASS
Ti 334.941 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V 292.402 Axial	23.2	0.413	1.77	1.82	7.84	2.32	NA	NA	NA	PASS

14.2.6 Quasimeme QTM129MS Precision for Analytes with High Concentration Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Al 394.401 Radial	6840	207	371	425	6.22	684	NA	NA	NA	PASS
Fe 238.204 Radial	16400	203	369	421	2.56	1640	NA	NA	NA	PASS

14.2.7 Quasimeme QTM115MS Precision for Analytes with Multi-element Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Al 394.401 Radial	20600	837	1730	1920	9.34	2060	NA	NA	NA	PASS
Ba 493.409 Radial	77.7	4.47	7.77	8.97	11.5	7.77	NA	NA	NA	PASS
Fe 238.204 Radial	20500	175	564	591	2.88	2050	NA	NA	NA	PASS
Mn 257.610 Radial	656	5.26	8.82	10.3	1.56	65.6	NA	NA	NA	PASS
P 178.284 Axial	596	7.23	7.68	10.5	1.77	59.6	NA	NA	NA	PASS
Ti 334.941 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V 292.402 Axial	52.8	1.39	3.69	3.95	7.47	5.28	NA	NA	NA	PASS

14.2.8 Quasimeme QTM115MS Precision for Analytes with High Concentration Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Al 394.401 Radial	21000	1110	1810	2120	10.1	2100	NA	NA	NA	PASS
Fe 238.204 Radial	21500	329	259	419	1.95	2150	NA	NA	NA	PASS

14.2.9 20 % Spiked Quasimeme QTM115MS Precision for Analytes with Multi-element Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Ti 334.941 Radial	536	35.5	16.4	39.1	7.29	53.6	NA	NA	NA	PASS

14.2.10 80 % Spiked Quasimeme QTM115MS Precision for Analytes with Multi-element Standards

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Ti 334.941 Radial	1080	41.3	63.2	75.5	6.97	108	NA	NA	NA	PASS

14.2.11 CONTEST CN123 Bias for Analytes with Multi-element Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Al 394.401 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ba 493.409 Radial	193.48	214	110	7.01	2.11	3.83	107 to 115	PASS	NA	NA	NA
Fe 238.204 Radial	34300	35500	104	2.27	0.683	1.24	102 to 105	PASS	NA	NA	NA
Mn 257.610 Radial	524.85	529	101	1.31	0.395	0.717	100 to 102	PASS	NA	NA	NA
P 178.284 Axial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ti 334.941 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V 292.402 Axial	53.17	56.0	105	10.7	3.23	5.85	99.5 to 111	PASS	NA	NA	NA

14.2.12 CONTEST CN123 Bias for Analytes with High Concentration Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Al 394.401 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe 238.204 Radial	34300	37000	108	1.41	0.424	0.768	107 to 109	PASS	NA	NA	NA

14.2.13 CONTEST CN126 Bias for Analytes with Multi-element Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Al 394.401 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ba 493.409 Radial	237	269	114	3.30	0.996	1.80	112 to 115	FAIL	237 \pm 40.04	269 \pm 8.88	PASS
Fe 238.204 Radial	25561	25800	101	2.17	0.654	1.18	99.9 to 102	PASS	NA	NA	NA
Mn 257.610 Radial	444.60	453	102	1.31	0.394	0.714	101 to 103	PASS	NA	NA	NA
P 178.284 Axial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ti 334.941 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V 292.402 Axial	37.09	45.8	123	8.10	2.44	4.43	119 to 128	FAIL	37.09 \pm 7.374	45.76 \pm 3.23	PASS

14.2.14 CONTEST CN126 Bias for Analytes with High Concentration Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Al 394.401 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe 238.204 Radial	25561	26900	105	2.03	0.613	1.11	104 to 106	PASS	NA	NA	NA

14.2.15 Quasimeme QTM129MS Bias for Analytes with Multi-element Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Al 394.401 Radial	6310	6760	107	5.83	1.76	3.18	104 to 110	PASS	NA	NA	NA
Ba 493.409 Radial	9.874	12.7	128	12.4	3.73	6.77	121 to 135	FAIL	9.874 \pm 6.699	12.7 \pm 1.38	PASS
Fe 238.204 Radial	13800	15800	114	3.57	1.08	1.95	112 to 116	FAIL	13800 \pm 2720	15781 \pm 512	PASS
Mn 257.610 Radial	157	170	108	2.81	0.848	1.54	107 to 110	PASS	NA	NA	NA
P 178.284 Axial	513	486	94.7	3.46	1.04	1.89	92.8 to 96.6	PASS	NA	NA	NA
Ti 334.941 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V 292.402 Axial	23.9	23.2	97.2	7.52	2.27	4.11	93.1 to 101	PASS	NA	NA	NA

14.2.16 Quasimeme QTM129MS Bias for Analytes with High Concentration Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Al 394.401 Radial	6310	6840	108	6.32	1.91	3.46	105 to 112	PASS	NA	NA	NA
Fe 238.204 Radial	13800	16400	119	2.87	0.865	1.57	117 to 121	FAIL	13800 \pm 2720	16421 \pm 421	PASS

14.2.17 Quasimeme QTM115MS Bias for Analytes with Multi-element Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Al 394.401 Radial	20400	20600	101	8.96	2.70	4.89	95.9 to 106	PASS	NA	NA	NA
Ba 493.409 Radial	67.03	77.7	116	12.5	3.77	6.84	109 to 123	PASS	NA	NA	NA
Fe 238.204 Radial	20400	20500	100	2.83	0.854	1.55	98.8 to 102	PASS	NA	NA	NA
Mn 257.610 Radial	667	656	98.3	1.43	0.433	0.784	97.5 to 99.1	PASS	NA	NA	NA
P 178.284 Axial	638	596	93.3	1.45	0.436	0.790	92.5 to 94.1	PASS	NA	NA	NA
Ti 334.941 Radial	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
V 292.402 Axial	47.9	52.8	110	7.98	2.41	4.36	106 to 115	PASS	NA	NA	NA

14.2.18 Quasimeme QTM115MS Bias for Analytes with High Concentration Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Al 394.401 Radial	20400	21000	103	9.67	2.92	5.28	97.4 to 108	PASS	NA	NA	NA
Fe 238.204 Radial	20400	21500	105	1.71	0.515	0.933	104 to 106	PASS	NA	NA	NA

14.2.19 20 % Spiked Quasimeme QTM115MS Bias for Analytes with Multi-element Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Ti 334.941 Radial	600	536	89.4	5.00	1.51	2.73	86.7 to 92.1	PASS	NA	NA	NA

14.2.20 80 % Spiked Quasimeme QTM115MS Bias for Analytes with Multi-element Standards

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Ti 334.941 Radial	1200	1080	90.3	5.80	1.75	3.17	87.1 to 93.5	PASS	NA	NA	NA

14.3 Estimation of Uncertainty of Measurement

The uncertainty of measurement has been estimated using procedure EUAF-FGBM-CHEM-GU-001 Uncertainty of Measurement Calculations. The uncertainty has been calculated using validation data. The calculation is summarised below using aluminium as an example.

Aluminium (Multi-element Standard) – Coefficient of Variance

Low PT sample recovery: 107 %

High PT sample recovery: 101 %

Low PT sample RSD: 5.78 %

High PT sample RSD: 9.34 %

Uncertainty

Systematic component C_s (recovery of spikes): $(100 \text{ to } 107)^2 + (100 \text{ to } 101)^2$

Random component C_r (spike RSD): $(5.78)^2 + (9.34)^2$

Assume linear summation and a value of $k=2$:

Combined standard uncertainty = $(C_s^2 + C_r^2)0.5 = 13.1 \%$

Expanded uncertainty = $2 * (C_s^2 + C_r^2)0.5 = 26.2 \%$

Table 14.1 Summary of expanded uncertainty values for each analyte

Element	Expanded Uncertainty [%]
Aluminium	26.2
Aluminium (high conc. standard)	29.5
Barium	46.8
Iron	30.7
Iron (high conc. standard)	41.6
Manganese	20.4
Phosphorous	20.4
Titanium	35.1
Vanadium	28.1



ICP-MS Analysis of Trace Elements in Sediments

Test Method number | EUAF-FGBM-CHEM-TM-034

Responsible Person: Principal Chemist (Technical Manager)

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1. Objectives

The purpose of this test method is to describe the analysis of trace elements in sediment samples in the chemistry laboratories in Edinburgh.

In sediments, the concentration range of the method is from the method detection limit (see Section 14) to the level of the top calibration standard (generally 40 mg/kg for Ag, Hg and Sn, and 1000 mg/kg for all other analytes), depending on the original sample weight used.

2. Scope

This test method applies to the analysis carried out in the Fugro GB Marine Limited (FGBML) chemistry laboratory in Edinburgh.

3. Related Documents

1.1 Chemistry Method Statements

- ISO/IEC 17025:2017 General Requirements for the Competence of Testing and Calibration Laboratories;
- ISO 16965: 2013 Soil Quality–Determination of Trace Elements in Extracts of Soil by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS);
- SEPA Measurement Assurance and Certification Scotland – Performance Standard MACS-WAT-01 Sampling and Chemical Testing of Water, Version 2, August 2017;
- Environment Agency Performance Standard for Laboratories Undertaking Chemical Testing of Soil, Version 5, November 2018;
- CSEMP Green Book, Tables 1 to 7, Version 15, July 2012;
- EUAF-FGBM-CHEM-GU-001 Uncertainty of Measurement Calculations;
- EUAF-FGBM-CHEM-GU-003 ICP-MS and ICP-OES Maintenance Guide;
- EUAF-FGBM-CHEM-PR-001 AQC and Environmental Conditions of Laboratory;
- EUAF-FGBM-CHEM-PR-002 Receipt and Logging of Samples;
- EUAF-FGBM-CHEM-TM-001 Laboratory Reagent Preparation and Equipment Cleaning;
- EUAF-FGBM-CHEM-TM-002 Calibration Verification and Service of Laboratory Equipment;
- EUAF-FGBM-CHEM-TM-032 Aqua Regia Microwave Digestion of Sediments;
- EUAF-FGBM-CHEM-TM-034 ICP-MS Preparation of Standards and Solutions;
- EUAF-FGBM-CHEM-FO-060 Work Order;
- EUAF-FGBM-CHEM-FO-086 Metals Standards for ICP-MS and ICP-OES;
- EUAF-FGBM-CHEM-FO-087 Instrument Maintenance Log (Inorganic);
- EUAF-FGBM-CHEM-FO-088 Pipette Verification Log;
- EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet;
- EUAF-FGBM-CHEM-FO-096 Argon Tank Delivery Check;
- EUAF-FGBM-CHEM-FO-097 Metals Data Converter;
- EUAF-FGBM-CHEM-TP-007 Metals Laboratory Traveller.

4. Responsibilities

Only members of staff (or contract staff) who have been approved to perform the tasks detailed in this document at the appropriate level as documented on their training record are permitted to carry out the tasks specified in this procedure.

The Technical Manager at the Edinburgh chemistry laboratory is responsible for testing.

The individual training records for laboratory staff details their testing competency. Staff shall not carry out any testing unless they are documented as having been trained (or are undergoing training and under supervision) to perform that test.

5. Health and Safety

Some of the chemicals used in this method may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings on reagent labels and read the hazard data information.

All relevant COSHH assessments must be read and signed before carrying out tasks detailed in this procedure.

Always wear safety glasses and laboratory coats when handling chemicals (and additional personal protective equipment where appropriate).

If exposure to chemicals occurs, remove personnel from exposure and refer to the relevant COSHH form for the appropriate course of action.

6. Principle of the Method

Sediment samples undergo a microwave aqua regia digest and further dilution as described in EUAF-FGBM-CHEM-TM-032 – Aqua Regia Microwave Digestion of Sediments. Sample digests are then diluted before analysis of trace element concentrations by ICP-MS.

7. Apparatus

Before use of any apparatus visually confirm that the equipment is not damaged in any way. If defects are found quarantine and report to the Technical Manager – under no circumstance should apparatus be used if faulty/broken.

7.1 Apparatus

7.1.1 Plasticware

- 15 mL and 50 mL polypropylene tubes for storage of standards;
- Disposable pipette tips to fit the adjustable micro-pipettes.

7.1.2 Instruments and Technical Equipment

- Adjustable micro-pipettes 20 µL to 200 µL (EN203 or EN335), 100 µL to 1000 µL (EN204 or EN336) and 1 mL to 5 mL (EN205 or EN337) for dilution of samples;

- Merck Millipore Direct Q3 Deionised water system (EN050) for ultrapure (Type 1) water for dispensing of ultrapure water;
- Thermo Scientific iCAP-Q Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (EN151) for trace element analysis of samples;
- Cetac ASX-560 autosampler (ICP-MS) (EN152) for automated sample uptake.

Note: see equipment database for current EN numbers.

8. Analytical Quality Control

Refer to EUAF-FGBM-CHEM-TM-032 Aqua Regia Microwave Digestion of Sediments, Section 8 for details of the analytical quality control process.

9. Calibration Verification and Service of Laboratory Equipment

The calibration verification and service of all laboratory equipment is detailed in EUAF-FGBM-CHEM-TM-002 Calibration Verification and Service of Laboratory Equipment.

10. Labelling of Samples and Equipment

10.1 15 mL Polypropylene Tubes

After microwave digestion the samples are diluted appropriately for the ICP-MS into 15 mL polypropylene tubes for analysis. At this stage the tubes have printed or hand-written labels which should contain the following information:

- Project number;
- Station number/location if sufficient room to include (LRM, CRM, blank etc. must be identified);
- Laboratory ID;
- Digest method;
- Dilution factor;
- Date prepared.

10.1.1 Repeat/Re-run Samples

For samples which need analysis to be re-run, for whatever reason, labelling should incorporate that fact. For trace element samples, the designated laboratory ID number should refer to the original laboratory ID number but should be suffixed 'RR' to indicate it is a repeat run of the sample e.g. 'A04RR'. Any further re-runs required on the same sample would be further suffixed with numbers e.g. A04RR2', 'A04RR3'.

11. Receipt and Logging of Samples

The receipt and logging of samples is detailed in EUAF-FGBM-CHEM-PR-002 Receipt and Logging of Samples.

12. Laboratory Reagent Preparation and Equipment Cleaning

The preparation of laboratory reagents and equipment cleaning is detailed in EUAF-FGBM-CHEM-TM-001 Laboratory Reagent Preparation and Equipment Cleaning.

13. Analysis of Sediment Digests for Trace Elements Using ICP-MS

This section may only be carried out by chemistry personnel who have received, or are in the process of receiving, training in the operation of the ICP-MS system and the interpretation of the data obtained. Analysts should refer to EUAF-FGBM-CHEM-FO-060 Work Order to ascertain the exact analysis requirements for each project.

This method may be used to quantify the following elements in sediment digests:

Ag, As, Cd, Co, Cr, Cu, Hg, Li, Mo, Ni, Pb, Sb, Sr and Zn.

13.1.1 Outline of Method

The internal standards and analytes in the sample digest are drawn simultaneously through the sample introduction system using a y-piece connected to a peristaltic pump. A fine mist is sprayed from the nebuliser into the spray chamber and the sample is then vaporised, atomised and ionised in the argon plasma after travelling into the torch via a flow of argon. The ions are then measured by the mass spectrometer. Calibration with appropriate standards allows the software to calculate concentrations of each analyte in the sample.

13.2 Instrument Conditions

13.2.1 Data Acquisition Methods – iCAP Q

Dwell Time	0.5 s for As 0.1 s for Hg, Li 0.05 s for Ag, Cd, Co, Cr, Cu, Ge, Ir, Mo, Ni, Pb, Rh, Sb, Sr, Zn
Measurement Mode	KED
Wash Time	180 s
Uptake Time	65 s
Pump Speed	25 RPM

13.2.2 Element Measurement Details

Element	Symbol	Mass	Internal Standard
Antimony	Sb	121	Use interpolation
Arsenic	As	75	Use interpolation
Cadmium	Cd	111	Use interpolation
Chromium	Cr	52	Use interpolation
Cobalt	Co	59	Use interpolation
Copper	Cu	63	Use interpolation
Germanium	Ge	73	NA
Iridium	Ir	193	NA
Lead	Pb	206	NA
Lead	Pb	207	NA
Lead	Pb	208	Use interpolation
Lithium	Li	7	Use interpolation
Mercury	Hg	202	Use interpolation
Molybdenum	Mo	95	Use interpolation
Nickel	Ni	60	Use interpolation
Rhodium	Rh	103	NA
Silver	Ag	107	Use interpolation
Strontium	Sr	88	Use interpolation
Zinc	Zn	66	Use interpolation

The following interference corrections are used:



13.3 Instrument Start-up

1. Switch the autosampler, chiller and extraction on;
2. Ensure that the peristaltic pump tubing is held firmly in place with the collars and brackets;
3. The autosampler probe is directed into the rinse port (ensure the wash reservoir contains a sufficient volume of 3 % aqua regia) and the internal standard probe is placed into a 50 mL polypropylene tube containing a solution of 3 % aqua regia;
4. The Instrument Control software is used to switch the instrument on – select the start icon from the iCAPQ tab and leave the instrument to warm-up and equilibrate for at least 30 minutes.

13.4 System Suitability

Before any analysis of sample digests is undertaken, the performance of the ICP-MS must be deemed to be acceptable by performing system suitability checks. This method includes the

daily system suitability check but trained personnel are required to be familiar with further instrument calibration and optimisation procedures carried out less frequently.

1. Once the system has warmed up, a performance report is carried out in STD mode;
2. The autosampler probe should be directed into the tune solution, and the internal standard probe should also be placed into this solution;
3. Leave sufficient time for the sample to reach the detector and stabilise and then run the STD Fugro performance report. This should then be saved to an appropriate location on the server;
4. Use the appropriate values from the performance report to populate the STD system suitability excel spreadsheet. Numeric criteria have been derived to ensure satisfactory performance of the ICP-MS as indicated by the appropriate reference lines and text boxes on each system suitability excel chart;
5. If all criteria are passed, the instrument should be put into KED mode and left for sufficient time to equilibrate;
6. The KED Fugro performance report is then run and saved into the appropriate location on the server;
7. Use the appropriate values from the performance report to populate the KED system suitability excel spreadsheet. Numeric criteria have been derived to ensure satisfactory performance of the ICP-MS as indicated by the appropriate reference lines and text boxes in the system suitability excel charts;
8. If this passes, then the ICP-MS is operating satisfactorily and the intended calibration standards and batch can now be analysed;
9. If either of the performance checks fail, the sample introduction system should be checked for any obvious faults (e.g. loose peristaltic pump tubing, wrong tune solution in use etc.). The autotune should be run in STD mode and the performance checks repeated. If they pass, the system is deemed suitable. If they fail, the sample introduction hardware (spray chamber, nebuliser, torch, injector, sample cone and skimmer cone) should be cleaned and the peristaltic pump tubing (sample, internal standard and waste) should be replaced. The performance checks are then run again prior to any sample analysis. If the system is not suitable consult with the Technical Manager or their deputy before sample analysis is undertaken.

13.5 Analytical Quality Control

A method blank is run with each batch of samples. A laboratory reference material (LRM) and/or certified reference material (CRM) and/or past proficiency test sample is run alongside batches of sediment samples. CONTEST and QUASIMEME proficiency test samples are analysed periodically through the year.

13.6 Procedure

13.6.1 Data Acquisition

1. Ensure that rack 1 of the autosampler contains 15 mL polypropylene tubes in the correct positions with enough volume of the appropriate calibration, independent and drift standards. Shake these well to mix and remove the lids. The calibration blank should be poured out fresh for each run;
2. Place the diluted digest samples in the 15 mL polypropylene tubes into the appropriate positions in rack 2 of the autosampler. Shake these well to mix and remove the lids;
3. Ensure the autosampler wash reservoir is filled with 3 % aqua regia solution;
4. Open the Qtegra software and select the LabBooks option. Within this, select create a LabBook from an existing template and select the Aqua Regia × 20 dil template. Give the LabBook an appropriate name (such as the date the sequence was run on, project number, batch number and dilution level) and ensure it is saved in the appropriate year and month in the LabBook folder. Enter the number of samples to be analysed into the relevant box. Select Create LabBook;
5. All relevant quality check samples (calibration standards, independent and drift checks) should be in the sample list. Edit the parameters for the unknown samples as appropriate (sample name, weight, volume, dilution factor, tube position). Many of these parameters can be found in the completed acid digest sheet for the batch (EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet), normally found in the relevant project folder;
6. Alternatively, the sample names and details can be entered automatically from a .csv file when the LabBook is created. From the LabBooks tab of the Qtegra software, give the LabBook an appropriate name as in step 4. Select to create a new LabBook from an existing template but also select the Import from CSV box. The CSV name is set up as Data template and the mapping name is set to default. The Data template, kept on the instrument desktop, is populated with the relevant sample names from the appropriate acid digest sheet for the batch (EUAF-FGBM-CHEM-FO-090 Acid Digest Batch Sheet) under the Lab ID heading, taking care to define the quality samples. Under the Amount heading, the weights are copied and pasted (with grams as units), ensuring the blank weight is 0.5000 g. The Rack Number and Vial Number columns are populated with the correct sample positions. Save the Data template. In the Qtegra software, select Create LabBook. Ensure that everything is correct in the sample list;
7. Select the save icon to save the changes;
8. Ensure the internal standard probe is placed into the internal standard bottle (which should be shaken well to mix the solution) and there is enough solution for the run. Allow this to equilibrate and then press the play button to begin the acquisition process;
9. Record the details for the Labbook into the ICP-MS logbook.

13.6.2 Data Quantification

1. Once the LabBook is complete, check that the calibration coefficients are greater than 0.997 for each element. All internal standard recoveries should be between 60 % and 125 %. The drift and independent standards should be between 90 % and 110 % for each element. If there any deviations, consult with the Technical Manager or their deputy prior to accepting the results;
2. Check that the concentrations for each analyte are below the top standard. If samples have significantly higher concentrations than the top standard, they should be diluted to bring them into the level of the calibration range and re-run;
3. If all quality checks pass, then select query on the Content menu in the Qtegra software and pick the Aqua Regia Digest ICP-MS RSD from the Preset drop-down menu. Ensure that the RSD percentages are suitable for the element and the concentration measured. If there are any doubts, consult the Technical Manager or their deputy before proceeding;
4. Select Aqua Regia Digest ICP-MS from the drop-down menu. Use the export icon on the top menu to export the data. Choose the path as desired (generally the relevant project folder), ensure the filename is suitable (add MS at the end of the filename to denote the analysis instrument) and then select Export.

13.6.3 Processing Generated Data

1. Use the quality spreadsheet to input the data into the relevant Shewhart charts for the batch;
2. Open EUAF-FGBM-CHEM-FM-097-Metals Data Converter and save on the server within the appropriate project folder in the Chemistry subfolder;
3. Open up the appropriate acid digest batch sheet from the Chemistry subfolder of the project folder and copy and paste the station names into the appropriate row. Use the exported results spreadsheet to populate the relevant sample number and concentrations sections of the raw data tab;
4. The final data tab is automatically populated using the data from the raw data tab. Analytes which have concentrations less than the minimum reporting value (MRV) are automatically colour-coded in red. These should be reported as less than the relevant MRV to the client.

13.7 Reporting

1. EUAF-FGBM-CHEM-FM-097-Metals Data Converter once completed is saved on the server within the appropriate project folder in the Chemistry subfolder;
2. The Technical Manager or their deputy will validate the data within this folder in a timely manner by checking all the necessary quality control steps were completed and that the data was in control;
3. Once validated, the data is copied into an excel spreadsheet saved into a new folder within the project folder marked 'Validated Data'.

14. Method Validation

14.1 Method Detection Limit

The method detection limit (MDL) as determined below is that of the method limit of detection (LOD) rather than the instrument LOD. The use of the method LOD when reporting data is of greater relevance since the instrumentation can give very low detection limits which are entirely inappropriate for complex environmental matrices. The MDL was calculated using the external document SEPA Measurement Assurance and Certification Scotland – Performance Standard MACS-WAT-01 Sampling and Chemical Testing of Water. SD = standard deviation; Var. = variance. This MDL was then rounded up to give the final MRV to an appropriate number of significant figures. These final MRVs are summarised in the table at the end of this section.

14.1.1 Trace Metals (By Procedural Blank)

Sb-121	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.0186	0.00684	0.0158	0.0122	0.0157	0.0191	0.0112	0.0831	0.0802	-0.0250	0.121	0.0311
Rep #2	0.0160	0.0103	0.0115	0.0285	0.0163	0.0162	0.00417	0.0716	0.0746	-0.0125	0.104	
Within-batch SD	0.00185	0.00241	0.00301	0.0115	0.000445	0.00202	0.00498	0.00808	0.00397	0.00883	0.0123	
Within-batch Var.	3.43E-06	5.82E-06	9.08E-06	0.000133	1.98E-07	4.08E-06	2.48E-05	6.54E-05	1.58E-05	7.80E-05	0.000151	

As-75	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	-0.00909	-0.00321	0.00171	0.0121	0.00392	0.00839	0.0102	-0.0201	-0.00839	-0.00658	-0.00111	0.0282
Rep #2	-0.00519	-0.00701	0.00141	0.00692	-0.00184	-0.00017	0.00398	-0.00351	-0.00564	-0.00386	-0.0189	
Within-batch SD	0.00275	0.00269	0.000214	0.00366	0.00407	0.00605	0.00442	0.0117	0.00195	0.00193	0.0126	
Within-batch Var.	7.55E-06	7.25E-06	4.57E-08	1.34E-05	1.66E-05	3.66E-05	1.95E-05	0.000138	3.79E-06	3.72E-06	0.000157	

Cd-111	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.00793	0.00909	0.0129	0.0109	0.0125	0.00926	-0.00024	8.25E-06	-0.00297	-0.00307	-0.00391	0.00976
Rep #2	0.0120	0.0101	0.00889	0.00759	0.0109	0.00225	-0.00042	-0.00038	-0.00253	-0.00326	-0.00449	
Within-batch SD	0.00287	0.000745	0.00283	0.00234	0.00114	0.00496	0.000131	0.000275	0.000312	0.000135	0.000409	
Within-batch Var.	8.22E-06	5.55E-07	8E-06	5.46E-06	1.29E-06	2.46E-05	1.72E-08	7.54E-08	9.76E-08	1.83E-08	1.68E-07	

Cr-52	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	-0.00031	0.0146	0.0348	0.0512	0.0216	0.0649	0.0217	0.00131	0.0252	0.0239	0.121	0.0750
Rep #2	-0.0101	0.0159	0.0386	0.0302	0.0160	0.0389	0.0696	0.0107	0.557	0.0395	0.0842	
Within-batch SD	0.00691	0.000886	0.00266	0.0148	0.00397	0.0184	0.0339	0.00665	0.376	0.0111	0.0257	
Within-batch Var.	4.78E-05	7.85E-07	7.05E-06	0.00022	1.58E-05	0.000338	0.00115	4.42E-05	0.142	0.000122	0.000662	

Co-59	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.000533	-7.6E-05	-0.00021	-4.1E-05	-0.00129	-0.00022	0.000458	-1.9E-06	-0.00045	-0.00421	-0.00542	0.00522
Rep #2	0.00100	0.000292	0.0005	-9.6E-05	-0.00069	0.00353	0.000897	0.000479	0.00302	-0.00415	-0.00535	
Within-batch SD	0.000333	0.00026	0.000503	3.88E-05	0.000426	0.00265	0.00031	0.00034	0.00246	4.32E-05	5.17E-05	
Within-batch Var.	1.11E-07	6.78E-08	2.53E-07	1.51E-09	1.81E-07	7.02E-06	9.61E-08	1.16E-07	6.03E-06	1.86E-09	2.67E-09	

Cu-63	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	-0.0531	-0.00592	-0.01914	0.00467	-0.0176	0.0191	-0.1108	-0.0814	-0.114	-0.0104	0.0617	0.314
Rep #2	0.255	-0.0388	-0.00692	0.00458	-0.0246	-0.00818	-0.094	-0.0694	-0.0750	0.0214	0.0597	
Within-batch SD	0.218	0.0233	0.00864	6.39E-05	0.00496	0.0193	0.0119	0.00852	0.0279	0.0226	0.00139	
Within-batch Var.	0.0476	0.000541	7.47E-05	4.08E-09	2.46E-05	0.000373	0.000141	7.27E-05	0.000778	0.000509	1.93E-06	

Pb-208	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.0665	0.125	0.0894	0.0702	0.108	0.135	0.0248	-0.00039	0.0111	0.0176	0.0808	0.129
Rep #2	0.0737	0.0827	0.0819	0.0862	0.0919	0.0830	0.0526	0.0529	-0.00051	0.0782	0.0140	
Within-batch SD	0.00512	0.0296	0.00529	0.0113	0.0116	0.0366	0.0196	0.0377	0.00819	0.0429	0.0472	
Within-batch Var.	2.62E-05	0.000874	2.8E-05	0.000128	0.000134	0.00134	0.000386	0.00142	6.71E-05	0.00184	0.00223	

Li-7	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.0550	0.0549	0.0423	-0.0670	-0.00128	0.0207	-0.00267	-0.0154	-0.0665	-0.00275	0.0459	0.123
Rep #2	-0.00625	0.0179	0.0131	-0.0607	0.0464	-0.0534	0.0141	-0.00724	-0.0568	-0.0222	0.0734	
Within-batch SD	0.0433	0.0261	0.0206	0.00450	0.0337	0.0524	0.0118	0.00574	0.00688	0.0138	0.0194	
Within-batch Var.	0.00188	0.000683	0.000426	2.02E-05	0.00114	0.00275	0.00014	3.29E-05	4.74E-05	0.00019	0.000377	

Hg-202	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.00493	0.0130	0.00666	0.000333	0.00887	0.00727	0.000672	0.000838	0.00375	0.00228	0.00889	0.0134
Rep #2	0.00569	0.00594	0.00237	0.00508	0.00356	0.000305	8.32E-05	0.00368	0.00265	0.00271	0.00668	
Within-batch SD	0.000536	0.00498	0.00304	0.00335	0.00375	0.00493	0.000417	0.00201	0.00078	0.000309	0.00156	
Within-batch Var.	2.87E-07	2.48E-05	9.23E-06	1.12E-05	1.41E-05	2.43E-05	1.73E-07	4.03E-06	6.05E-07	9.53E-08	2.44E-06	

Mo-95	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.00114	-0.00146	-0.00031	0.000215	0.00352	-0.00015	-0.00294	0.000103	-0.00355	-0.00105	-0.00527	0.0176
Rep #2	0.00754	0.00121	-0.0004	-0.00138	0.00119	-0.00037	0.0108	0.00154	0.00413	0.00148	-0.00651	
Within-batch SD	0.00453	0.00189	6.36E-05	0.00113	0.00165	0.000152	0.00971	0.00102	0.00544	0.00179	0.000877	
Within-batch Var.	2.05E-05	3.56E-06	4.04E-09	1.27E-06	2.72E-06	2.3E-08	9.42E-05	1.04E-06	2.95E-05	3.2E-06	7.69E-07	

Ni-60	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	-0.0153	-0.0230	-0.0401	-0.0140	-0.0400	-0.0322	0.00125	-0.0282	-0.0259	0.0306	-0.0143	0.194
Rep #2	0.00714	-0.0356	-0.0335	-0.0329	-0.0398	-0.0298	-0.0191	-0.0350	0.154	-0.0322	-0.00266	
Within-batch SD	0.0159	0.00886	0.00467	0.0133	8.74E-05	0.00168	0.0144	0.00482	0.127	0.0444	0.00826	
Within-batch Var.	0.000253	7.86E-05	2.18E-05	0.000177	7.63E-09	2.83E-06	0.000206	2.32E-05	0.0162	0.00197	6.82E-05	

Ag-107	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.000574	-0.00342	0.000283	0.000646	0.00129	0.00102	-0.00036	-0.00036	-0.00803	0.00037	-0.00138	0.00155
Rep #2	0.000459	-0.00413	0.000425	0.000548	0.000553	0.000294	-0.00026	-0.00026	-0.00862	-0.00014	-0.00182	
Within-batch SD	8.16E-05	0.000501	0.0001	6.96E-05	0.000523	0.000517	6.6E-05	6.6E-05	0.000413	0.000359	0.000308	
Within-batch Var.	6.65E-09	2.51E-07	1.01E-08	4.84E-09	2.74E-07	2.67E-07	4.36E-09	4.36E-09	1.7E-07	1.29E-07	9.51E-08	

Sr-88	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.178	0.180	0.0902	0.176	0.121	0.177	0.186	0.0988	0.145	0.204	0.202	0.155
Rep #2	0.128	0.124	0.105	0.128	0.134	0.120	0.213	0.133	0.136	0.133	0.127	
Within-batch SD	0.0351	0.0399	0.0101	0.0340	0.00866	0.0403	0.0189	0.0241	0.00611	0.0507	0.0532	
Within-batch Var.	0.00123	0.00159	0.000102	0.00115	7.51E-05	0.00163	0.000358	0.00058	3.73E-05	0.00257	0.00283	

Zn-66	Concentration in mg/kg											MDL
	Batch #1	Batch #2	Batch #3	Batch #4	Batch #5	Batch #6	Batch #7	Batch #8	Batch #9	Batch #10	Batch #11	
Rep #1	0.476	0.138	0.538	0.297	-0.0002	0.252	0.367	0.582	0.0287	0.318	0.0466	0.481
Rep #2	0.706	0.0286	0.555	0.295	0.208	0.311	0.176	0.730	0.182	0.206	0.218	
Within-batch SD	0.162	0.0775	0.0122	0.00122	0.147	0.0419	0.135	0.104	0.108	0.0788	0.121	
Within-batch Var.	0.0263	0.00600	0.000148	1.49E-06	0.0216	0.00175	0.0182	0.0108	0.0117	0.00621	0.0148	

Analyte	Final Minimum Reporting Value
Antimony	0.04
Arsenic	0.03
Cadmium	0.01
Cobalt	0.006
Chromium	0.08
Copper	0.4
Lead	0.2
Lithium	0.2
Mercury	0.03
Molybdenum	0.02
Nickel	0.2
Silver	0.002
Strontium	0.2
Zinc	0.5

14.2 Reproducibility and Recovery (Bias)

Precision and bias were determined during a 2×11 batch method validation. This provides a measure of the method reproducibility rather than instrument reproducibility, which given autosampler systems and robust detection techniques would provide an artificially high measure of reproducibility. Precision and bias statistics were calculated for more than one sample (a range of proficiency testing samples) in order to determine the method performance for a range of matrices representing likely samples to be encountered in routine analysis.

The target SD was 10 % of the mean and the target bias was 70 % to 110 %.

14.2.1 CONTEST CN123 Precision

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Sb-121	6.60	0.619	0.305	0.690	10.5	0.660	2.85	0.0585	10	PASS
As-75	58.8	1.29	2.17	2.52	4.29	5.88	NA	NA	NA	PASS
Cd-111	1.01	0.0281	0.0403	0.0491	4.87	0.101	NA	NA	NA	PASS
Cr-52	370	8.89	13.5	16.2	4.38	37.0	NA	NA	NA	PASS
Co-59	11.6	0.245	0.535	0.588	5.05	1.16	NA	NA	NA	PASS
Cu-63	44.5	1.68	1.51	2.26	5.07	4.45	NA	NA	NA	PASS
Pb-208	322	21.2	10.7	23.7	7.37	32.2	NA	NA	NA	PASS
Li-7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hg-202	0.893	0.0235	0.0275	0.0361	4.05	0.0893	NA	NA	NA	PASS
Mo-95	1.70	0.0881	0.0679	0.111	6.55	0.170	NA	NA	NA	PASS
Ni-60	33.9	1.03	1.11	1.51	4.46	3.39	NA	NA	NA	PASS
Ag-107	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sr-88	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn-66	246	7.92	8.60	11.7	4.76	24.6	NA	NA	NA	PASS

14.2.2 CONTEST CN126 Precision

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Sb-121	4.47	0.342	0.130	0.366	8.18	0.447	NA	NA	NA	PASS
As-75	31.6	0.835	0.986	1.29	4.09	3.16	NA	NA	NA	PASS
Cd-111	1.02	0.0358	0.0283	0.0456	4.47	0.102	NA	NA	NA	PASS
Cr-52	611	20.3	20.3	28.7	4.70	61.1	NA	NA	NA	PASS
Co-59	10.5	0.292	0.343	0.450	4.27	1.05	NA	NA	NA	PASS
Cu-63	82.6	5.91	4.04	7.16	8.67	8.26	NA	NA	NA	PASS
Pb-208	140	5.64	3.00	6.39	4.55	14.0	NA	NA	NA	PASS
Li-7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hg-202	0.414	0.0215	0.00947	0.0235	5.66	0.0414	NA	NA	NA	PASS
Mo-95	3.62	0.109	0.206	0.233	6.44	0.362	NA	NA	NA	PASS
Ni-60	32.5	1.15	1.09	1.59	4.89	3.45	NA	NA	NA	PASS
Ag-107	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sr-88	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn-66	176	4.65	3.17	5.63	3.20	17.6	NA	NA	NA	PASS

14.2.3 Quasimeme QTM129MS Precision

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Sb-121	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
As-75	12.1	0.452	0.543	0.706	5.81	1.21	NA	NA	NA	PASS
Cd-111	0.0582	0.00356	0.00826	0.00900	15.5	0.00582	2.85	2.39	10	PASS
Cr-52	27.3	0.980	1.79	2.04	7.46	2.73	NA	NA	NA	PASS
Co-59	2.12	0.0806	0.139	0.161	7.58	0.212	NA	NA	NA	PASS
Cu-63	1.85	0.112	0.0401	0.119	6.44	0.185	NA	NA	NA	PASS
Pb-208	9.02	0.324	0.575	0.660	7.31	0.902	NA	NA	NA	PASS
Li-7	6.83	0.284	0.360	0.459	6.72	0.683	NA	NA	NA	PASS
Hg-202	0.0273	0.00307	0.00349	0.00465	17.0	0.00273	2.85	2.90	10	FAIL
Mo-95	0.302	0.00982	0.0177	0.0202	6.70	0.0302	NA	NA	NA	PASS
Ni-60	4.44	0.141	0.272	0.306	6.89	0.444	NA	NA	NA	PASS
Ag-107	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sr-88	165	4.04	12.2	12.8	7.80	16.5	NA	NA	NA	PASS
Zn-66	24.4	0.794	1.12	1.38	5.65	2.44	NA	NA	NA	PASS

14.2.4 Quasimeme QTM115MS Precision

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Sb-121	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
As-75	17.3	0.326	0.585	0.669	3.86	1.73	NA	NA	NA	PASS
Cd-111	0.454	0.0154	0.0224	0.0272	5.99	0.0454	NA	NA	NA	PASS
Cr-52	43.2	1.78	2.17	2.81	6.49	4.32	NA	NA	NA	PASS
Co-59	6.83	0.147	0.195	0.244	3.57	0.683	NA	NA	NA	PASS
Cu-63	13.1	0.363	0.468	0.592	4.52	1.31	NA	NA	NA	PASS
Pb-208	39.7	1.08	0.994	1.47	3.69	3.97	NA	NA	NA	PASS
Li-7	27.0	0.846	1.48	1.71	6.33	2.70	NA	NA	NA	PASS
Hg-202	0.456	0.0143	0.00760	0.0162	3.56	0.0456	NA	NA	NA	PASS
Mo-95	0.604	0.0420	0.0333	0.0536	8.88	0.0604	NA	NA	NA	PASS
Ni-60	17.8	0.519	0.536	0.746	4.20	1.78	NA	NA	NA	PASS
Ag-107	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sr-88	165	4.95	5.48	7.39	4.46	16.5	NA	NA	NA	PASS
Zn-66	129	1.95	5.02	5.39	4.18	12.9	NA	NA	NA	PASS

14.2.5 20 % Spiked Quasimeme QTM115MS Precision

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Ag-107	0.198	0.0190	0.00679	0.0202	10.2	0.0198	2.85	1.04	10	PASS

14.2.6 80 % Spiked Quasimeme QTM115MS Precision

Analyte	Mean [mg/kg]	Within Batch SD [mg/kg]	Between Batch SD [mg/kg]	Total SD [mg/kg]	RSD [%]	Target SD [mg/kg]	F 0.05 from ANOVA	F calculated	Estimated Degrees of Freedom	Assessment
Ag-107	0.500	0.0594	0.0210	0.0630	12.6	0.0500	2.85	1.59	10	PASS

14.2.7 CONTEST CN123 Bias

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Sb-121	6.32	6.60	104	8.44	2.55	4.62	99.7 to 109	PASS	NA	NA	NA
As-75	58.8	58.8	100	4.00	1.21	2.19	97.8 to 102	PASS	NA	NA	NA
Cd-111	1.00	1.01	101	4.49	1.35	2.45	98.5 to 103	PASS	NA	NA	NA
Cr-52	341	370	108	4.37	1.32	2.39	106 to 110	PASS	NA	NA	NA
Co-59	11.06	11.6	105	5.08	1.53	2.78	103 to 108	PASS	NA	NA	NA
Cu-63	45.30	44.5	98.3	4.24	1.28	2.31	96.0 to 101	PASS	NA	NA	NA
Pb-208	298	322	108	3.52	1.06	1.92	106 to 110	PASS	NA	NA	NA
Li-7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hg-202	0.83	0.893	107	3.87	1.17	2.11	105 to 110	PASS	NA	NA	NA
Mo-95	1.60	1.70	106	5.76	1.74	3.15	103 to 109	PASS	NA	NA	NA
Ni-60	30.73	33.9	110	4.31	1.30	2.36	108 to 113	PASS	NA	NA	NA
Ag-107	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sr-88	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn-66	249.54	246	98.4	4.11	1.24	2.25	96.2 to 101	PASS	NA	NA	NA

14.2.8 CONTEST CN126 Bias

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Sb-121	4.43	4.47	101	6.20	1.87	3.39	97.6 to 104	PASS	NA	NA	NA
As-75	30.74	31.6	103	3.74	1.13	2.04	101 to 105	PASS	NA	NA	NA
Cd-111	1.01	1.02	101	3.76	1.13	2.05	98.8 to 103	PASS	NA	NA	NA
Cr-52	595	611	103	4.18	1.26	2.83	100 to 106	PASS	NA	NA	NA
Co-59	9.30	10.5	113	4.30	1.30	2.35	110 to 116	PASS	NA	NA	NA
Cu-63	82.25	82.6	100	7.07	2.13	3.86	96.5 to 104	PASS	NA	NA	NA
Pb-208	130.60	140	107	3.82	1.15	2.09	105 to 109	PASS	NA	NA	NA
Li-7	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hg-202	0.37	0.414	112	4.84	1.46	2.64	109 to 115	PASS	NA	NA	NA
Mo-95	3.23	3.62	112	6.81	2.05	3.72	108 to 116	PASS	NA	NA	NA
Ni-60	28.00	32.4	116	4.87	1.47	2.66	113 to 119	PASS	NA	NA	NA
Ag-107	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sr-88	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zn-66	180.00	176	97.6	2.54	0.766	1.39	96.2 to 99.0	PASS	NA	NA	NA

14.2.9 Quasimeme QTM129MS Bias

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Sb-121	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
As-75	11.6	12.1	105	5.43	1.64	2.97	102 to 108	PASS	NA	NA	NA
Cd-111	0.0512	0.0582	114	16.9	5.09	9.21	105 to 123	PASS	NA	NA	NA
Cr-52	25.8	27.3	106	7.44	2.24	4.06	102 to 110	PASS	NA	NA	NA
Co-59	2.01	2.12	106	7.49	2.26	4.09	102 to 110	PASS	NA	NA	NA
Cu-63	2.06	1.85	89.6	4.31	1.30	2.35	87.2 to 91.9	PASS	NA	NA	NA
Pb-208	8.47	9.02	106	7.30	2.20	3.99	103 to 110	PASS	NA	NA	NA
Li-7	6.47	6.83	106	6.38	1.92	3.48	102 to 109	PASS	NA	NA	NA
Hg-202	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Mo-95	0.287	0.302	105	6.62	2.00	3.62	102 to 109	PASS	NA	NA	NA
Ni-60	4.14	4.44	107	7.00	2.11	3.82	103 to 111	PASS	NA	NA	NA
Ag-107	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sr-88	146	165	113	8.57	2.58	4.68	108 to 117	PASS	NA	NA	NA
Zn-66	25.3	24.4	96.3	4.96	1.50	2.71	93.6 to 99.0	PASS	NA	NA	NA

14.2.10 Quasimeme QTM115MS Bias

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Sb-121	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
As-75	16.7	17.3	104	3.76	1.13	2.06	102 to 106	PASS	NA	NA	NA
Cd-111	0.454	0.454	100	3.88	1.17	2.12	97.9 to 102	PASS	NA	NA	NA
Cr-52	40.7	43.2	106	6.16	1.86	3.37	103 to 110	PASS	NA	NA	NA
Co-59	7.12	6.83	96.0	3.10	0.936	1.70	94.2 to 97.7	PASS	NA	NA	NA
Cu-63	14.3	13.1	91.7	3.73	1.13	2.04	89.7 to 93.7	PASS	NA	NA	NA
Pb-208	38.4	39.7	103	3.26	0.983	1.78	102 to 105	PASS	NA	NA	NA
Li-7	27.5	27.0	98.0	5.81	1.75	3.18	94.8 to 101	PASS	NA	NA	NA
Hg-202	0.446	0.456	102	2.84	0.857	1.55	101 to 104	PASS	NA	NA	NA
Mo-95	0.515	0.604	117	8.67	2.61	4.74	112 to 122	PASS	NA	NA	NA
Ni-60	18.0	17.8	98.7	3.61	1.09	1.97	96.7 to 101	PASS	NA	NA	NA
Ag-107	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sr-88	154	165	107	4.22	1.27	2.31	105 to 110	PASS	NA	NA	NA
Zn-66	141	129	91.3	3.69	1.11	2.02	89.3 to 93.3	PASS	NA	NA	NA

14.2.11 20 % Spiked Quasimeme QTM115MS Bias

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Ag-107	0.2	0.198	98.8	7.53	2.27	4.11	94.7 to 103	PASS	NA	NA	NA

14.2.12 80 % Spiked Quasimeme QTM115MS Bias

Analyte	Reference Concentration [mg/kg]	Mean Measured Value [mg/kg]	Overall Mean Recovery [mg/kg]	SD of Mean Recovery [mg/kg]	Standard Error of Mean Recovery [mg/kg]	90 % Confidence Interval of Recovery (+/-)	Recovery Range [%]	Assessment	Certified Mean \pm SD	Measured Mean \pm SD	Overlap
Ag-107	0.5	0.500	100	7.28	2.20	3.98	96.0 to 104	PASS	NA	NA	NA

14.3 Estimation of Uncertainty of Measurement

The uncertainty of measurement has been estimated using procedure EUAF-FGBM-CHEM-GU-001 Uncertainty of Measurement Calculations. The uncertainty has been calculated using validation data. The calculation is summarised below using antimony as an example.

Antimony – Coefficient of Variance

Low spike recovery:	94 %
High spike recovery:	92 %
Low standard RSD:	9.1 %
High standard RSD:	14 %

Uncertainty

Systematic component C_s (recovery of spikes): $(94 \text{ to } 100)^2 + (92 \text{ to } 100)^2$

Random component C_r (spike RSD): $(9.1)^2 + (14)^2$

Assume linear summation and a value of $k=2$:

Combined standard uncertainty = $(C_s^2 + C_r^2)^{0.5} = 18.9 \%$

Expanded uncertainty = $2 * (C_s^2 + C_r^2)^{0.5} = 37.9 \%$

Table 14.1 Summary of expanded uncertainty values for each analyte

Element	Expanded Uncertainty [%]
Antimony	28.1
Arsenic	17.2
Cadmium	15.1
Chromium	22.0
Cobalt	24.0
Copper	30.0
Lead	29.3
Lithium	22.3
Mercury	31.5
Molybdenum	32.5
Nickel	29.9
Silver	32.5
Strontium	34.5
Zinc	16.8



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