sca standing committee of analysts

The Determination of metals in Raw and Drinking waters by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) 2018

Methods for the Examination of Waters and Associated Materials

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This booklet contains guidance on the analysis of metals in raw (ground and surface) and drinking waters by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Contents

Page

About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments, soils (including contaminated land) and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials" and their continuing revision is the responsibility of the Standing Committee of Analysts (established 1972 by the Department of the Environment). At present, there are seven working groups, each responsible for one section or aspect of water quality analysis. They are

1 General principles of sampling and accuracy of results
2 Microbiological methods
3 Empirical, Inorganic and physical methods, Metals and metalloids
4 Solid substances
5 Organic impurities
6 Biological, biodegradability and inhibition methods
7 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will be notified to the technical press. If users wish to receive copies or advanced notice of forthcoming publications or obtain details of the index of methods then contact the Secretary on the SCA's web-page:-
http://www.standingcommitteeofanalysts.co.uk/Contact.html

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary. Users should ensure they are aware of the most recent version they seek.

Rob Carter
Secretary
February 2019

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Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety.

These should be consulted and be readily accessible to all analysts. Amongst such resources are; HSE website HSE: Information about health and safety at work ; RSC website http://www.rsc.org/learn-chemistry/collections/health-and-safety "Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory", 1992, produced by the Royal Society of Chemistry; "Guidelines for Microbiological Safety", 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and "Safety Precautions, Notes for Guidance" produced by the Public Health Laboratory Service. Another useful publication is "Good Laboratory Practice" produced by the Department of Health**.**

Inductively Coupled Plasma- Mass Spectrometry (ICP-MS)

Introduction.

Mass Spectrometry is a technique that is able to identify specific elements by the mass to charge ratio of their ions. In the case of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) these ions are usually singly charged positive ions with the plasma being used to generate the ions.

ICP-MS is a very sensitive analytical technique with a high linear dynamic range (ultra-trace to main components).

ICP-MS is a rapid multi-element quantitative analytical technique similar to Inductively Coupled Plasma Optical emission Spectrometry (ICP-OES), but generally able to reach lower limits of detection.

As rapid determination of elements at low concentration is a principal advantage of ICP-MS, the technique is very useful as a routine analytical tool in water analysis.

Although the range of elements covered in this method is limited, many other elements are capable of being determined with accuracy and without interference. Since the analysis is based on the measurement of individual isotopes, the technique may also be applied to isotope ratio determination, isotope dilution etc.

A   Determination of a Typical Multi-Element Suite of Total and Dissolved Metals by ICP-MS

A1   Performance characteristics of the method

A1.1	Substances determined	Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Lithium, Molybdenum, Nickel, Selenium, Strontium, Thallium, Tin, Titanium, Uranium, Vanadium and Zinc.
A1.2	Type of sample	Drinking, Raw (Surface and Ground) waters
A1.3	Basis of method	Samples acidified with nitric acid to 1% v/v, oven digested at 80°C before analysis by ICPMS
A1.4	Range of application	
	(Ranges quoted taken from Validation data – see Table A11.2. These are not fixed).	Antimony (Sb) LOD-6.25 µg/l Arsenic (As) LOD-12.5 µg/l Barium (Ba) LOD-500 µg/l Beryllium (Be) LOD-100 µg/l Cadmium (Cd) LOD-6.25 µg/l Chromium (Cr) LOD-62.5 µg/l Cobalt (Co) LOD-100 µg/l Copper (Cu) LOD-500 µg/l Lead (Pb) LOD-31.25 µg/l Lithium LOD-500 µg/l Molybdenum(Mo) LOD-100 µg/l Nickel (Ni) LOD-25 µg/l Selenium (Se) LOD-12.5 µg/l Strontium (Sr) LOD-500 µg/l Thallium (Tl) LOD-100 µg/l Tin (Sn) LOD-100 µg/l Titanium (Ti) LOD-100 µg/l Uranium (U) LOD-10 µg/l Vanadium (V) LOD-100 µg/l Zinc (Zn) LOD-500 µg/l
A1.5	Relative standard deviation	See Table A4
A1.6	Limit of detection (LOD)	See Table A4
A1.7	Recovery	See Table A4
A1.8	Interferences	See section A3. Table A1 lists common interferences for the elements covered in this booklet. Table A2 gives suggestions for their relevant mathematical equation.

A1.9	Calibration Curve	Calibration standards concentration should be appropriate to the sample concentration of the elements being determined. Ideally the concentration range used will give a linear calibration.

A2. Principle

A typical ICP-MS consists of a sample introduction system, a plasma to form ions, an interface region where ions are focused into a stream, a quadrupole to sort the ions and a detector.

Sample introduction

The liquid sample is pumped via peristaltic pump into a nebuliser where it is converted into a fine aerosol with argon gas. The fine droplets of sample within the aerosol are separated from larger droplets by means of a spray chamber. The fine aerosol is transported into the plasma torch via a sample injector.

Plasma

Argon plasma is generated when a spark (electron) is introduced into a stream of argon gas contained within radio frequency (RF) electric and magnetic fields. The electron collides with argon atoms at high energy stripping off electrons. These electrons collide with more argon atoms at high energy resulting in a plasma consisting of argon atoms, argon ions and electrons. This plasma has a high temperature (>6000K) in the region where the sample aerosol is injected. The aerosol is dried, the molecules within it are dissociated, atomised and ionised.

The power of the RF energy is such that most elements form singly charged positive ions however some doubly charged ions do occur.

Interface region and ion optics.

Once the ions are produced in the plasma, they are directed into the mass spectrometer via the interface region, which is maintained at a very high vacuum with a mechanical roughing pump. A typical interface region consists of two metallic cones, called the sampler and a skimmer cone, each with a small orifice to allow the ions to pass through to the ion optics where they are guided into the mass separation device.

Once the ions have been successfully passed through the interface region, they are directed by an electrostatic lens system, called ion optics to focus the ion beam toward the mass separation device, while eliminating photons, particulates, and neutral species from reaching the detector.

Quadrupole

The ion beam containing all the analyte and matrix ions exits the ion optics and now passes into the mass separation device, which is kept at an operating vacuum. The mass separation device allows ions of a particular mass-to-charge ratio (m/z) through to the detector. All other ions are removed by the vacuum. This means that it is possible to determine which element is being measured as each element has a unique mass-to-charge ratio.

9

Collision/reaction cell (optional)

Many modern instruments have a collision/ reaction cell between the ion optics and the quadrupole. This can be used to reduce the effects of interferences.

Detector

The detectors that are used are electron multiplier detectors and the impact of the ions releases a cascade of electrons, which are amplified until they become a measureable electrical signal. Analysing samples with elements of known concentration (standards) will give measurable signals that can be compared to signals for samples of unknown concentration to give a quantifiable result for an element.

A typical detector has two modes of operation.
The pulse (P) mode where low concentration of ions result in electrical pulses.
The analogue (A) mode where the concentration of ions is so high that the electrical pulses cannot be distinguished so instead an electrical current is measured.
This means that the detector can be used for a wide calibration range however a mathematical algorithm is needed to match up the results from the pulse and analogue modes.

Where necessary, precautions should be taken to protect the electron multiplier detector from exposure to high ion counts. Changes in instrument response or damage to the multiplier may otherwise result. Samples possessing high concentrations of elements beyond the linear range and with isotopes falling within regions of interest should be diluted prior to analysis. Some regions of expected high intensity signals can be skipped over during data acquisition, and this will prolong the life of the electron multiplier.


A3 Interferences

There are number of sources of interferences which may cause errors in the determination of trace elements by ICP-MS.

A3.1 Isobaric Elemental Interferences

These interferences are caused by isotopes of other elements which form singly or doubly charged ions of the same nominal mass to charge ratio (m/z) as that of the analyte of interest, and which cannot be resolved by the instrument. Other than mono-isotopic elements, most elements will have at least one stable isotope which is not overlapped by isotopes of other elements.

Modern instruments have the list of recommended elements in the software that do not have elemental isobaric interferences, where this is not possible it may be appropriate to correct for an isobaric interference, using the known relative abundances of the isotopes involved.

In the example below the most abundant molybdenum isotope is to be measured at m/z 98, but there is a potential interference on this m/z from ruthenium.

Mo⁹⁸ label area — Ru⁹⁸, Mo⁹⁸, Ru⁹⁹, 98, 99
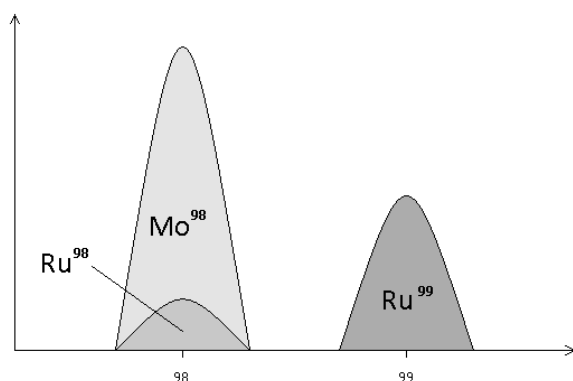
We need to subtract the Ru^{98} from the total at m/z 98, to find the Mo^{98}.

$$Mo^{98} = cps^{98} - Ru^{98}$$

The relative abundances of Ru^{98} and Ru^{99} are known and constant, at 1.88:12.7. Therefore the amount of Ru^{98} equals Ru^{99} x 1.88/12.7, i.e.

$$Mo^{98} = cps^{98} - 0.148 Ru^{99}$$

Some instrument software may also include some of these equations.

A3.2 Polyatomic (Molecular) Interferences

Polyatomic interferences result from the combination of two or more isotopes from different elements, which usually occur in the plasma. The elements that form the polyatomic interferences usually result from the sample matrix, sample diluent, and argon itself. Most common interferences have been identified and are given in Table A1. The significance of the effect of the interference will vary with the matrix, instrument and operating conditions. Such interferences should be recognised, and when they cannot be avoided should be investigated or quantified. It may be necessary to analyse at least 2 isotopes of each element being determined. Molecular interferences can be minimised by use of a collision/reaction cell.

If a cell is not being used, or for any interference not eliminated by the collision/reaction cell, then the interferences must be assessed and valid corrections applied, or the data flagged to indicate problems.

Most elements have multiple isotopes which allows for mathematical correction of both isobaric and polyatomic interferences. By considering the natural abundance of different isotopes and measuring the intensity of a non-interfered isotope, one can calculate the extent of the interference and subtract this contribution to yield the analyte concentration.
An example of this would be Arsenic m/z 75. Arsenic has only one isotope at m/z 75. There is a polyatomic interference from Argon Chloride $Ar^{40}Cl^{35}$ at m/z 75. Chlorine has 2 isotopes m/z 35 abundance 75.77% and m/z 37 abundance 24.23%. It is possible to calculate the number of counts per second (cps) for $Ar^{40}Cl^{35}$ at m/z 75 by measuring the number of cps for $Ar^{40}Cl^{37}$ at m/z 77 and applying the abundance ratio of 75.77:24.23 or 3.127:1.
The number of cps for Arsenic at m/z 75 will be the total number of counts at m/z 75 minus the calculated number of counts per second for $Ar^{40}Cl^{35}$ at m/z 75. i.e.

11

$$As^{75} \, cps = cps^{75} - 3.127(cps^{77})$$

Note that this equation has been simplified for this example as there is an isotope for Se at m/z 77 that has not been accounted for.

In addition, correction equations can be produced empirically for the specific set up of individual instrument, as long as the plasma conditions remain constant. A typical example is shown below, where there can be an $Ar^{40}C^{12}$ interference on Cr^{52}.
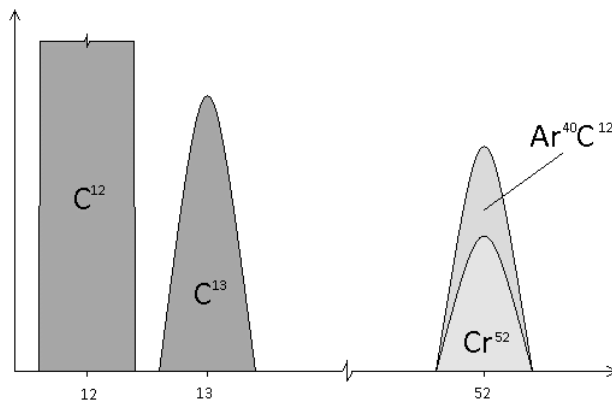
In this example, reporting the m/z 52 result as the Cr concentration would be incorrect. We need to subtract the $Ar^{40}C^{12}$ from the total at m/z 52, to find the Cr^{52}.

$$Cr^{52} = cps^{52} - Ar^{40}C^{12}$$

The $Ar^{40}C^{12}$ interference is directly proportional to the amount of C present, therefore you can substitute yC^{13} for $Ar^{40}C^{12}$, where y is the ratio of $Ar^{40}C^{12}{:}C^{13}$.

$$Cr^{52} = cps^{52} - yC^{13}$$

The factor y can be empirically derived for individual instruments by running pure solutions of the interfering analyte at appropriate concentrations, and calculating the ratio from the cps of the m/z involved, after blank subtraction. In the above example pure acetic acid would be suitable, and the cps of m/z 13 and 52 measured to produce the factor y.

Recommended elemental equations are listed in Table A2.

A3.3 Doubly charged elemental ion interferences

Doubly charged elemental ion interferences may occur where the second ionization potential of the element is significantly below the first ionization potential for argon (15.7eV). If a doubly charged ion is formed, it causes a response at half of its elemental mass, potentially causing interference.
An example of this is if we were to analyse Gallium m/z 69 in a matrix containing Barium. Barium has a relatively low second ionisation potential that is below 15.7eV which means that a significant

12

number of doubly charged Barium ions would be produced in the plasma. Barium atomic mass 138 would give a mass-to-charge ratio of 69 for the double charged ion and this would overlap the single charge Gallium ion m/z 69. In this case we may analyse Gallium at m/z 71 to avoid this potential interference.

Most elements have a high enough second ionisation potential that formation of doubly charged ions is not an issue.

Some doubly charged interferences may be removed in the reaction mode by NH_3.

A3.4 Physical Interferences

These interferences are associated with the physical process of sample analysis from sample uptake to transmission of ions through the ICP-MS interface. Viscosity and surface tension affect the sample uptake rate and aerosol formation. A peristaltic pump is usually used to transport the sample solution to the nebuliser. Its performance and efficiency of operation should be monitored. High levels of dissolved solids in the sample may lead to deposits forming on the sample and skimmer cones, thus reducing the effective diameter of the orifices and therefore ion transmission. A nebuliser gas dehumidifier may be used to reduce the amount of deposit formed.

An internal standard is used to monitor and to correct for changes in matrix, instrumental drift, nebuliser and cone orifice blockages and aerosol transport effects. One or more internal standards may be used. When choosing internal standards consideration should be given to the atomic mass, first ionisation energy, isotopic abundance and any interference. The internal standard is an element which is not expected in the samples and by its addition does not contaminate the sample. Most commonly used internal standards are ^{6}Li, ^{45}Sc, ^{72}Ge, ^{89}Y, ^{103}Rh, ^{115}In, ^{193}Ir and ^{209}Bi.

Add the same amount of internal standard elements to every standard and unknown sample. This is typically achieved at the sample introduction stage of an automated analysis through mixing tee and peristaltic pump. Alternatively the internal standard can be added to each sample and standard prior to measurement.

Ionisation suppression may also occur where the sample being analysed has high concentrations of elements that have a low first ionisation potential for example sodium and potassium. By choosing an internal standard that has a first ionisation potential similar to the elements being analysed this effect may be corrected.

A3.5 Interference Removal

Many modern instruments have the option of using a collision or reaction cell. When used these can remove the need for interference corrections for polyatomic interferences.

A3.5.1 Collision cell:

The cell is an area between the ion optics and the quadrupole where a gas can be introduced. When the gas that is introduced is non-reactive such as Helium the cell is being used as a collision cell.

Once the ions from the plasma have been focussed into a stream by the ion optics they enter the cell containing the collision gas. The stream of ions will be made up of elemental and polyatomic ions. The polyatomic ions will be larger than the elemental ions and are therefore more likely to collide with the atoms of the collision gas. These collisions may break up the polyatomic ions or

13

may just slow them down causing them to lose kinetic energy. If a potential barrier such as a small positive charge is applied at the entrance to the quadrupole the polyatomic ions will not have enough energy to pass through to the quadrupole while the elemental ions will be less affected. This is called kinetic energy discrimination (KED). The cell may contain a multipole to aid with the transmission of the desired ions. In the case of the argon chloride interference on arsenic m/z 75 the smaller Arsenic ions would make it through to the quadrupole while the much bigger argon chloride ions would have undergone collisions and be left in the collision cell.

A3.5.2 Reaction cell:

The cell can also be used with a reactive gas such as oxygen, ammonia, hydrogen or methane to make it a reaction cell.
Reactive gas tends to be used to target specific interferences. Reaction mode works on the principle that the interfering molecular ion reacts with reactive gas to form new ions of differing mass than the analyte isotope or by effecting charge transfer from the interfering molecular ion to form a neutral molecule.
An example of this would be analysis of iron m/z 56. There is a major interference from argon oxide at m/z 56. If ammonia is added in as the reaction gas it reacts with the argon oxide ions to eliminate their effect at m/z 56 meaning that the counts measured at m/z 56 will be those of iron.

The use of collision reaction gases will reduce the analyte signal with elements of lower mass being affected the most. Although an improved signal-to-background is of obvious interest, in many applications, severe reductions in analyte signal are not tolerable. Ideally, one should consider all of the following in providing a complete assessment of collision and/or reaction cell ICPMS performance: (1) Interferent signal reduction; (2) analyte signal reduction; (3) anayte signal noise; and (4) background noise.
Most modern instruments are able to switch between no gas, collision gas and reaction gas modes during the analysis of the sample.

A4 Memory Effects

These influences result when elements in a previously run sample contribute to the signals measured in the following sample. In most cases, this occurs when samples with high concentrations of an element are analysed although molybdenum can cause this problem at relatively low levels. Memory effects may result from sample deposition on the cones and from build-up of material in the plasma torch, spray chamber and on plastic tubing.

The effects are usually reduced by adequate rinsing between samples. The choice of rinse solution will depend on the matrix being run and the sample introduction system being used.

A5 Hazards

Refer to the manufacturers Safety Data Sheets for full details of the hazards associated with all materials before use. Wear appropriate Personal Protective Equipment.

A5.1   Nitric acid is extremely corrosive and may cause severe burns to skin and eyes. If ingested cause severe internal irritation and damage. Extremely irritating, harmful vapour. Wear chemical resistant gloves and safety glasses when handling concentrated solutions. Use concentrated solutions in a fume cupboard.

A5.2   Element standards. These standards are harmful if ingested in quantity. Irritating to eyes and skin. May cause burns if contact is prolonged. Danger of cumulative effects.

A5.3   If liquid argon is used, the container should be kept outside in a well ventilated area.

A5.4   Potentially lethal voltages are present within the torch box and radio frequency generator. Power must be disconnected before these units are opened for service work.

A5.5   Heat, vapours and fumes generated by the plasma can be hazardous and toxic. These should be extracted from the laboratory by means of an efficient exhaust system.

A5.6   The plasma source emits radio-frequency radiation and intense ultra violet radiation. Ensure instrument used contains safety features to protect operator from exposure.

A5.7   Once the plasma has been extinguished, the torch and torch box may be very hot for a period of time. Care should be taken if these are to be touched.

A6 Reagents

Where possible all reagents need to be the highest purity available. It may be necessary to test the purity of the reagents before use.

A6.1 Water- Deionised water with a resistivity of at least 18MΩ is recommended.

A6.2 Nitric Acid- Ultra high purity

A6.3 Metals Standard Solutions.

Standards of $1000mgl^{-1}$ single element concentration can be used. Custom made standards can also be used.

Suggested Calibration Standard concentrations:

Calibration standards can be prepared from an intermediate stock solution with the following concentrations:

Element	Concentration µgl⁻¹	Element	Concentration µgl⁻¹
Arsenic	500	Lead	1250
Barium	20000	Antimony	250
Beryllium	4000	Selenium	500
Cadmium	250	Tin	4000
Cobalt	4000	Strontium	20000
Chromium	2500	Titanium	4000
Copper	20000	Thallium	4000
Lithium	20000	Uranium	400
Molybdenum	4000	Vanadium	4000
Nickel	1000	Zinc	20000

Diluting the intermediate stock solution using 4 ± 0.015ml, 20 ± 0.030 ml and 25 ± 0.030ml of intermediate stock solution in 1000ml will give the following concentrations

Standard Conc.	As µgl⁻¹	Ba µgl⁻¹	Be µgl⁻¹	Cd µgl⁻¹	Co µgl⁻¹	Cr µgl⁻¹	Cu µgL⁻¹	Li µgL⁻¹	Mo µgL⁻¹	Ni µgL⁻¹	Pb µgL⁻¹	Sb µgL⁻¹	Se µgL⁻¹	Sn µgL⁻¹	Sr µgL⁻¹	Ti µgL⁻¹
Blank	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Standard 1	2	80	16	1	16	10	80	80	16	4	5	1	2	16	80	16
Standard 2	10	400	80	5	80	50	400	400	80	20	25	5	10	80	400	80
Standard 3	12.5	500	100	6.25	100	62.5	500	500	100	25	31.25	6.25	12.5	100	500	100

Standard Conc.	Tl µgL⁻¹	U µgL⁻¹	V µgL⁻¹	Zn µgL⁻¹
Blank	0	0	0	0
Standard 1	16	1.6	16	80
Standard 2	80	8	80	400
Standard 3	100	10	100	500

The concentrations suggested are those that were used for the performance testing data in Table A4. Alternative concentrations may be used. It is recommended that as a minimum a blank and 3 calibration standards are used.

Standards should be prepared in volumetric glassware. Standards should be acidified with 1% Nitric Acid (A6.2),stored in high density polyethylene (HDPE) bottles and given an appropriate shelf life (typically 1 month).

A6.5 Internal Standard

The choice of isotopes used for internal standards will be dependent on the elements being analysed and the matrix of the sample. The concentration of internal standard needs to be such that a reproducible response is achieved. Typically an internal standard concentration that gives better than 1% precision is used.

The internal standard solution must contain the same acid matrix as that of calibration standards and samples.

Add ICP-OES details

16

A6.6 Tuning solution

A6.6.1 Daily auto-tune solution/Instrument Daily Performance Check Solution
This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared mixing elements of various masses covering the range of application. Refer to manufacturers guidelines.

A6.6.2 Dual detector/PA tune solution
This solution can be prepared by using elements that are specific to the analysis being carried out. Refer to manufacturers guidelines.

A6.7 Quality Control solutions

A6.7.1 Analytical Quality Control

In order to monitor the performance of the method analytical quality control (AQC) solutions are recommended to be used. AQC solutions may include reference materials, certified reference materials, spiked samples, duplicates and blanks.

Typically the AQC has a known concentration of the elements of interest and is run each time the method is carried out to allow the precision and bias to be monitored.

The AQC sample should follow the same procedures as the unknown samples including any filtration, acidification or digestion processes.

A6.8 Blank Solutions
Add icp-oes
A6.8.1 Rinse Solution

This is used to flush the instrument between samples in order to reduce memory interferences. 1 % v/v Nitric Acid (A6.2)

A7 Apparatus

A7.1 Inductively Coupled Plasma Mass Spectrometer

A7.1.1 An instrument, capable of scanning the m/z range from 5-250 amu with a minimum resolution capability of 1 amu peak width at 10% peak height. A collision/ reaction cell instrument is optional.

A7.1.2 A variable speed peristaltic pump for solution delivery to the nebuliser. When in operation, the pump tubes should be clamped so that there is no free movement of the solution to the nebuliser when the pump is stopped.

A7.1.3 Argon gas supply (high purity grade min 99.996%).

A7.2 Other Apparatus

A7.2.1 High density polyethylene sample bottles.

A7.2.2 Digester oven

A7.2.2 Volumetric flasks for standard solutions.

A7.2.3 Variable or fixed volume micropipettes with disposable plastic tips.

A7.2.4 Glass bulb pipettes

A7.2.5 Assorted dispensers for the dispensing of acid

A7.2.6 0.45µm membrane filters and Ashless quantitative filter papers.

A7.2.7 Assorted gloves for handling acids.

In the determination of trace levels of elements, avoidance of contamination and loss are of prime consideration. Potential contamination sources include insufficiently cleaned laboratory apparatus and general contamination within the laboratory environment. A clean laboratory work area designed for trace element sample handling should be used. Sample containers can introduce positive and negative errors in the determination of trace elements by:

a) contributing contaminants through surface desorption and leaching, or

b) depleting element concentrations through adsorption processes.

All re-usable apparatus (fused silica, polyethylene, polytetrafluoroethylene, etc.) should be cleaned prior to use by thoroughly washing with detergent and water, followed by soaking overnight in 10% v/v nitric acid. This should be followed by rinsing with deionised water (A6.1).

A8 Sample Collection, Preservation

Samples for the determination of the metals covered by this method should be preserved using dilute acid. A final acid concentration of 1% v/v, nitric acid can be used.

A8.1   If dissolved (filtered) metals analysis is required, the sample is filtered as soon as practicable through a 0.45µm filter disc or suitable filter paper prior to acidification.

A8.2   On receipt at the laboratory the total metals samples are acidified with concentrated nitric acid such that the final concentration of acid is ~1% V/V. Best practice for sample preservation is documented in the current version of BS EN ISO 5667 Part3. Samples should be collected in acid washed HDPE plastic bottles.

A9 Analytical Procedure

This procedure has been used to produce the performance data in table A4

A9.1   The acidified sample bottle (bottle top on) should be digested in an oven set at 80ºC ± 5 ºC for a minimum of 6 hours, or more practically overnight.

A9.2   Once the samples have cooled to ambient temperature they are transferred into sample tubes. Should any particulate matter be visible on inspection of the sample a portion of sample can be filtered using a 0.45µm membrane filter or suitable filter paper. This is done to ensure the instrument tubing does not become blocked.

A9.3   A filtered and total blank of deionised water should be prepared with each batch of samples, using the same containers, acid and procedure as used for routine samples.

18

This is to ensure that any contamination picked up during sampling or preparation is identified.

A9.4   If quality control solutions (A6.7.1) are used these should also be digested in typical sample bottles with each batch of samples.

A9.5   Optimise the instrument according to the manufacturer's guidelines and ensure that the instrument is performing to specification. Typically this will involve running the tuning solution (A6.6.1) and when required the dual detector /PA tune solution (A6.6.2). Where possible check the sensitivity, % RSD, % oxide, % doubly charged, peak shape, and resolution. Compare these to any acceptability criteria that have been set.

A9.6   Use the ICPMS instrument to analyse the prepared solutions along with the samples (A9.2), the blanks(A9.3) and Analytical Quality Control solutions (A9.4)

A10 Calculation of Results

The concentration of each element of interest in the sample can be determined, based on the calibration standards and taking into account any effects causing variation in the internal standard.

A correction factor should be applied to the result to account for any dilution of the sample as a result of acidifying to 1% v/v Nitric acid. This factor would usually be applied within the instrument software.

Table A1: Isotopes used and potential interferences

Element	Isotope	Potential interference
Li	7	none
Be	9	none
Ti	47	PO
V	51	ClO , SOH
Cr	52	ClOH, ArC, ArO
Co	59	CaO
Ni	60	CaO
Cu	65	TiO
Zn	66	TiO
As	75	ArCl
Se	78	ArAr, Kr
Sr	88	none
Mo	98	BrOH, Ru
Cd	111	MoO, ZrO
Sn	118	MoO
Sb	121	ArBr
Ba	138	La, Ce
Tl	205	none
Pb	208	none
U	238	none

Note. Collison and reaction modes can be used to remove or reduce polyatomic interferences.

Table A2: Recommended elemental equations for calculations

Element	Elemental Equation	Note
As	$cps^{75} - 3.127(cps^{77}) + 2.733(cps^{82})$	(1)
Cd	$cps^{111} - 1.073(cps^{108}) + 0.764(cps^{106})$	(2)
Cd	$cps^{111} - y(cps^{95})$	(2)
Cr	$cps^{52} - z(cps^{13})$	(3)
Mo	$cps^{98} - 0.148(cps^{99})$	(4)
In	$cps^{115} - 0.014(cps^{118})$	(5)
Pb	$cps^{206} + cps^{207} + cps^{208}$	(6)
V	$cps^{51} - 3.127(cps^{53}) + 0.355(cps^{52}) - 0.355z(cps^{13})$	(7)

(1) - Correction for $Ar^{40}Cl^{35}$ with adjustment for Se. Isobaric m/z 82 must be from Se only and not BrH.

(2) - Two suggestions for corrections for MoO interference. Isobaric m/z 106 must be from Cd only not ZrO, and no palladium must be present for the first option. In option two, y is the ratio of $Mo^{95}O^{16}:Mo^{95}$.

(3) - Correction for $Ar^{40}C^{12}$, where z is the ratio of $Ar^{40}C^{12}:C^{13}$.

(4) – Correction for Ru^{98} using Ru^{99}.

(5) - Correction for Sn^{115} using Sn^{118}.

(6) - Allowance for isotopic variability of lead isotopes.

(7) - Correction for $Cl^{35}O^{16}$ interference with adjustment for Cr^{53} including Cr^{52} and $Ar^{40}C^{12}$, where z is the ratio of $Ar^{40}C^{12}:C^{13}$.

Table A3: Instrument operating conditions for data in Table 4

Instrument	Perkin Elmer Nexion
Nebuliser	PFA-ST
Plasma RF power	1.6 kW
Data Acquisition	
Replicate integrations	3
Mass range	6-240 amu
Number of scan sweeps	20

Table A4: Performance data for various trace metals.

		Soft water		Medium water		Hard water		Raw surface		Groundwater	
	LoD µgL⁻¹	% Rec	% RSD	% Rec	% RSD	% Rec	% RSD	% Rec	% RSD	% Rec	% RSD
As	0.06	103	4.4	104	3.4	104	4.1	101	3.6	103	3.8
Ba	0.43	102	4.3	101	1.3	102	4.0	101	1.9	98.8	1.8
Be	0.14	103	4.6	99.4	4.7	103	3.8	99.4	4.8	101	3.2
Cd	0.01	102	4.7	98.4	2.4	99.4	4.2	99.5	2.7	99.1	2.7
Co	0.07	101	4.4	99.3	2.0	102	3.4	99.4	2.2	99.3	1.7
Cr	0.06	102	3.9	99.4	2.9	100	3.1	99.2	3.8	99.3	2.1
Cu	0.59	99.5	4.5	97.0	1.8	97.2	3.7	97.0	2.0	95.9	1.2
Li	0.40	102	5.0	102	5.1	105	4.1	99.0	4.7	102	3.4
Mo	0.48	102	5.5	101	2.1	101	4.7	95.4	1.9	101	1.9
Ni	0.13	99.7	5.2	96.8	1.8	101	5.7	98.0	2.3	97.7	2.4
Pb	0.03	99.6	3.7	102	1.9	104	5.1	102	2.8	103	2.1
Sb	0.25	95.3	6.6	101	3.8	108	4.7	98.7	4.2	100	3.3
Se	0.41	102	6.5	102	4.3	104	5.3	98.1	5.5	102	5.1
Sn	0.72	102	6.0	101	2.1	102	5.5	98.5	5.1	101	1.5
Sr	0.39	103	5.0	98.1	1.8	97.2	4.5	96.8	2.2	99.0	1.7
Ti	0.49	103	4.2	101	2.4	103	3.4	98.9	4.0	101	0.97
Tl	0.09	102	4.6	104	1.2	105	4.8	103	2.0	104	1.1
U	0.02	105	5.4	107	2.7	107	4.8	105	3.2	107	3.4
V	0.05	103	4.0	101	1.5	103	3.4	101	2.5	101	2.6
Zn	2.2	99.9	4.9	96.0	3.7	96.7	3.4	96.8	2.8	95.1	3.9

% Rec = % Recovery

% RSD = % Relative Standard Deviation

Limit of Detection(LoD) calculated using 4.65 times the within batch standard deviation (Sw) of a blank sample.

Samples spiked at the critical level of interest (CLOI) for drinking water.

Data provided by ALS Environmental Wakefield.

Further reading:

1) *Waterquality-Application of inductively coupled plasma mass spectrometry. Part 2: Determination of selected elements including Uranium isotopes.*
BSEN ISO17294-2:2016

2) *U.S. EPA Method 200.8 Determination of Trace Elements in Waters and Wastes by ICP-MS, Revision 5.4, 1994:* http://www.epa.gov/sam/pdfs/EPA-200.8.pdf.

3) *Inductively Coupled Plasma Spectrometry 1996, HMSO London, in this series*

4) *Ed McCurdy, Glenn Woods and Don Potter, Unmatched Removal of Spectral Interferences in ICP-MS Using the Agilent Octopole Reaction System with Helium Collision Mode; 2006*

5) *Thomas W. May and Ray H. Wiedmeyer; A Table of Polyatomic Interferences in ICP-MSA Table of Polyatomic Interferences in ICP-MS; 1998*

6) *U.S. EPA Standard Operation Procedure for Trace Element Analysis of Flue Gas Desulfurization Wastewaters Using ICP-MS Collision/Reaction Cell Procedure; Draft 2013*

7) *Robert Thomas; Practical Guide to ICP-MS; 2004*

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