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The Determination of Metals in Raw and Potable waters by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) 2018

Methods for the Examination of Waters and Associated Materials

The determination of a selection of Metals in Raw and Potable Waters by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) (2018)

Methods for the Examination of Waters and Associated Materials

This booklet contains details of a typical method for determining Metals content of Waters by ICP-OES including sample preparation, analysis, interferences, system suitability’s and troubleshooting.

A separate SCA document covers the principles of the ICP-OES technique.

Whilst this booklet may report details of the materials actually used, this does not constitute an endorsement of these products but serves only as an illustrative example. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate methods in their own laboratories.

Contents

A Determination of Total and Dissolved Metals by ICP-OES

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

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 – Optical Emission Spectrometry (ICP-OES)

Introduction

Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) is a well-established important optical emission technique used extensively in environmental testing. The basic principle of ICP-OES involves the introduction of a liquid sample into an argon plasma torch, which provides the excitation energy required to stimulate atomic and ionic emission in the sample. The multielement analysis capability of ICP-OES makes it an ideal tool for processing multiple analytes in large numbers of samples quickly and efficiently. The combination of low detection limits and wide analytical linear range makes the technique well suited to the analysis of low to moderate concentrations of the many elements of interest in water samples.

Although the range of elements covered in this method is limited, many other elements are capable of being determined by this technique. ICP-OES is susceptible to spectral interferences in particular (see section A11.3) so accurate interference removal is essential. For this reason, ICP-MS is often the preferred technique for analysis of low level elements in more difficult water types.

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

A1 Performance characteristics of the method

A1.1	Substances determined	Aluminium, Barium, Boron, Calcium, Chromium, Copper, Iron, Lithium, Magnesium, Manganese, Molybdenum, Phosphorus, Potassium, Silicon, Sodium, Strontium 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 ICP-OES.
A1.4	Range of application (Ranges quoted taken from Validation data – see Table A11.2. These are not fixed).	Aluminium (Al) LOD – 4 mg/L Barium (Ba) LOD – 0.5 mg/L Boron (B) LOD – 1.25 mg/L Calcium (Ca) LOD – 500 mg/L Chromium (Cr) LOD – 0.1 mg/L Copper (Cu) LOD – 0.5 mg/L Iron (Fe) LOD – 4 mg/L Lithium (Li) LOD – 2 mg/L Magnesium (Mg) LOD – 100 mg/L Manganese (Mn) LOD – 1 mg/L Molybdenum (Mo) LOD – 0.1 mg/L Phosphorus (P) LOD – 5 mg/L Potassium (K) LOD – 40 mg/L Silicon (Si) LOD – 20 mg/L Sodium (Na) LOD – 400 mg/l Strontium (Sr) LOD – 3.5 mg/L Zinc (Zn) LOD – 0.5 mg/L
A1.5	Relative standard deviation	See Tables A11.2
A1.6	Limit of detection (LOD)	See Table A11.2
A1.7	Recovery	See Table A11.2
A1.8	Interferences	See section A3, A4 and Table A11.4 for lists of common interferences.
A1.9	Calibration curve	Calibration standards concentration should be appropriate to the element concentration of the samples being determined. Ideally the concentration range used will give a linear calibration.

A2 Principle

Inductively coupled plasma optical emission spectroscopy (ICP-OES), also referred to as inductively coupled plasma atomic emission spectrometry (ICP-AES) is an analytical technique used for the detection of trace elements. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of the radiation is measured and converted into electronic signals that are quantified by comparison against standards with known concentrations of elements.

Samples are typically acidified and digested at elevated temperatures to ensure any particulate matter is brought into solution. The filtered or digested samples are transported to the plasma via a process known as nebulisation. The sample aerosol is then transported to the plasma torch where it is desolvated, vaporised, atomised and ionised. The excited atoms and ions emit their characteristic radiation which is collected by a device that sorts the radiation by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration information.

Some of the features of ICP-OES that make it a popular technique for analysis of environmental samples include:

- Simultaneous or sequential analysis of multiple elements
- Wide linear region of analytical curve
- Good sensitivity and low limits of detection
- High number of measurable elements (approx. 70 elements)
- High speed of measurement (typically 1-2 minutes per sample)

The majority of the above features are derived from the structure and characteristics of the plasma.

Equipment for ICP optical emission spectrometry consists of a sample introduction system, a plasma to form ions, a detector and a data processing unit. A representation of the layout of a typical ICP-OES instrument is shown in Figure 1.

Sample Introduction

The sample introduction system consists of the following:

i) Sample probe or sipper
ii) Teflon tubing from the sipper to the peristaltic pump tubing
iii) Peristaltic pump tubing
iv) Nebuliser – used to convert the liquid sample into an aerosol that can be transported into the plasma.
v) Spray chamber – used to remove larger droplets after nebulisation so only very small droplets are injected into the plasma
vi) Torch – consisting of three concentric tubes, the outer two usually made from quartz that is used to support and introduce sample into the plasma using a stream of argon gas.
vii) Injector tube – the centremost tube of the Torch, made from quartz, through which the sample aerosol is introduced to the plasma.

Plasma

An 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, resulting in the emission of electromagnetic radiation.

Detector

The emitted radiation is typically separated into individual wavelengths by a polychromator and detected using a photosensitive detector such as a charged couple device (CCD). 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.

A3 Interferences

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

A3.1 **Spectral interferences** caused by:
i) spectral line overlap from another element, where the interfering line shares a common portion of the spectrum with the analyte line. This can be overcome by using an alternative wavelength, interference correction equations or a higher resolution spectrometer. This is aided by the fact that

the elements being measured are generally at significantly higher concentrations in applicable waters than any possible interfering species.
ii) spectral line interference from the emission of high concentration elements. Choice of analytical wavelength and placement of background correction points should be designed to eliminate possible interference from other elements within the sample.

iii) background emission and stray light, in which there is a general change in the intensity of the background continuum. This can usually be compensated for by subtracting the background emission determined by measurement adjacent to the analyte wavelength peak.
iv) for measurements below 200nm, particularly lines below 180nm, it is advised a spectrometer purge of argon/nitrogen gas is introduced. This is due to the presence of atmospheric air in the optical path strongly absorbing light through the presence of molecular oxygen and water in air.

A3.2 **Chemical interference** caused by:
i) ionisation effects and molecular compound formation, although this is less of a problem in a drinking water matrix. If observed, they can be minimised by careful selection of operating conditions (such as RF power and observation height), by matrix matching or sample dilution.
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A3.3 **Physical effects** caused by:
i) sample nebulisation due to changes in viscosity and surface tension during aerosol production
ii) transportation of the aerosol to the plasma
Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If observed, they can be reduced by using a high solids nebuliser, diluting the sample, using a peristaltic pump, or using an internal standard to correct for transport effects.

A4 Memory Effects

These influences arise when elements in a previously run sample contribute to the signals measured in the following sample. In most cases, this occurs if high levels of an element pass through the system. Memory effects may result 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. See A6.7 and Table A11.1 also.

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 causes 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 must be of the highest purity available. It may be necessary to test the purity of the reagents before use.

A6.1 **Water -** Deionised water of high purity should be used for the preparation of blanks and standards. A resistivity of at least 18MΩ is recommended

A6.2 **Nitric acid conc**. Ultra high purity nitric acid (metals free) is recommended for the preparation of blanks, calibration standards, AQC standards and the acidification of samples.

A6.3 **Metal standard solutions:** High purity 10,000mg/l and 1000mg/l stock standards of individual elements are commercially available from a wide variety of sources. Custom made multielement standards of high purity are also readily available.

A6.4 **Working calibration standards:** It is highly recommended that a minimum of 3 standards plus a blank are used for calibration of the instrument.

<u>Suggested calibration standard concentrations</u>:

Standard concs.	Fe mg/l	Mn mg/l	Al mg/l	B mg/l	Ba mg/l	Cu mg/l	Zn mg/l	P mg/l	Cr mg/l
Blank	0	0	0	0	0	0	0	0	0
Standard 1	1.0	0.25	1.0	0.3	0.13	0.13	0.13	1.25	0.03
Standard 2	2.0	0.5	2.0	0.6	0.25	0.25	0.25	2.5	0.05
Standard 3	4.0	1.0	4.0	1.3	0.5	0.5	0.5	5	0.10

Standard concs.	Si mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Li mg/l	Mo mg/l	Sr mg/l
Blank	0	0	0	0	0	0	0	0
Standard 1	5.0	100	10	100	25	0.5	0.03	0.9
Standard 2	10.0	200	20	200	50	1.0	0.05	1.8
Standard 3	20.0	400	40	400	100	2.0	0.10	3.5

The concentrations suggested are those that were used for the performance testing data in Table A11.2 measured at the wavelengths in Table 11.3. 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. Dilute the relevant amounts of stock standard with deionised water. Acidify with Nitric acid to 1% and dilute to volume with deionised water. Transfer solutions to plastic bottles (HDPE preferably) for storage, assign a shelf life (typically 1 month).

A6.5 **Internal standard solution**

An internal standard is used to monitor and to correct for fluctuations in matrix, instrumental drift, nebuliser blockages and aerosol transport effects.

An internal standard is an element which is not present in samples, by its addition does not contaminate the samples, is chemically compatible with the samples and does not introduce spectral interferences.
If signal variation results from the sample introduction system (samples of different viscosity, matrix constitution), all the elements will be corrected in the same way by a single internal standard.

Add the same concentration of internal standard element to every standard and unknown sample. An internal standard solution is typically mixed with standards, blanks and samples at the sample introduction stage on the instrument using a mixing tee. However, it can be added to all solutions prior to analysis using a pipette.
Ensure the concentration added is sufficient for a good signal. Typically an internal standard concentration that gives better than 1% precision is used.

Yttrium and Scandium are used widely as internal standards in ICP-OES analysis.

A6.6 **Analytical Quality Control (AQC) Solutions**

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 analysed each time the method is carried out to allow the method 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.

A6.7 **Rinse solution**

This is used to flush the instrument between samples in order to reduce memory interferences. Add sufficient nitric acid (A6.2) to deionised water to form a 1% solution (see Section A4 also).

A7 Apparatus

A7.1 Inductively Coupled Plasma - Optical Emission Spectrometer

(see Figure 1 for diagram):

A7.1.1 A simultaneous ICP-OES instrument, with axial and radial plasma observation, UV/Visible detector measuring wavelengths 165 to 782nm.

A7.1.2 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 Autosampler - to allow unattended operation (if available)

A7.1.4 Argon gas supply (high purity grade, min. 99.996%)

A7.2 Other Apparatus

A7.2.1 High density polyethylene sample bottles (HDPE).

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 and preparation

Samples for the determination of the elements 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 must be 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 A11.2.

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

A9.4 If quality control solutions (A6.6) are used, these should also be digested in typical sample bottles with each batch of samples.

A9.5 Prior to performing any sample analysis, careful consideration should be given to setting instrument parameters to provide optimum performance. The instrument manufacturer’s handbook should be reviewed but as a guide the following should be considered.

- Assign appropriate calibration ranges for the elements to be analysed (see Table A6.4 for an example).
- Select appropriate wavelengths for each element (see tables A11.3 and A11.4)
- Define plasma operating conditions (see Table A11.1)
- Decide on appropriate plasma view, i.e. Axial or Radial (see Appendix 1)
- Select an appropriate internal standard if required (see A6.5)
- Assign appropriate background correction

Use the ICP-OES instrument to analyse the prepared calibration solutions along with the samples (A9.2), the blanks (A9.3) and Analytical Quality Control solutions (A9.4)

It is recommended that a minimum of 3 replicates of each standard/sample is acquired by the instrument software and an average concentration reported.

A9.6 Careful consideration should be given to introducing daily System Suitability Checks to ensure instrument performance and Quality Control is maintained. Examples of suggested System Suitability Checks include:

a) Minimum intensity values to be met for one of the calibration standards used.

b) Monitor % RSD on replicates for all calibration standards, samples and AQCs.

c) Monitor intensity of internal standard for all calibration standards, samples and AQCs.

d) Correlation Coefficient of each calibration graph should be linear, e.g. >0.999.

A10 Calculation of Results

A10.1 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.

A10.2 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.

A10.3 The Hardness concentrations of samples analysed may be determined by carrying out the following calculations:

i) Calcium Hardness (as $CaCO_3$)
Ca Total conc. x 2.5. Results as mg/l.

ii) Magnesium Hardness (as $CaCO_3$)
Mg Total conc. x 4.167. Results as mg/l.

iii) Total Hardness (as $CaCO_3$)
Calcium hardness + Magnesium Hardness. Results as mg/l
i.e. (Ca tot x2.5) + (Mg tot x 4.167).

iv) Hardness as Calcium
Ca Total conc. + (1.67 x Mg Total conc.). Results as mg/l.

v) Permanent Hardness as CaCO3
Boil sample for 20 minutes). Analyse as Total Hardness as CaCO3 (iii above).

vi) Permanent Hardness as Ca
Boil sample for 20 minutes. Analyse as Hardness as Ca (iv above).

vii) Temporary Hardness
Total Hardness – Permanent Hardness.

A11 Performance Data

Summary of Performance Testing

Table A11.1 Instrument operating conditions for precision and recovery data quoted in Table A11.2

Instrument:	Perkin Elmer Optima 7300 DV
Spray Chamber	Quartz Cyclonic
Nebuliser:	MicroFlow PFA-ST
Viewing height:	15mm
Plasma RF Power:	1300 W
Nebuliser gas flow rate:	0.80 L/min
Auxilary gas:	0.20 L/min
Plasma Gas:	15.0 L/min
Peristaltic Pump Flow Rate:	0.65 ml/min

Add Thames water operating conditions.

Table A11.2 Precision & Recoveries for Different Matrix Waters

A summary of the performance testing data is shown below:

	LOD mg/l	**Soft Water**		**Medium Water**		**Hard Water**		**Raw Surface**	
		% Rec	% Prec	% Rec	% Prec	% Rec	% Prec	% Rec	% Prec
Fe	0.004	102.8	5.3	103.6	4.8	104.0	5.9	97.7	4.9
Mn	0.003	98.2	3.0	98.8	2.9	100.2	3.6	96.5	4.1
Al	0.0009	100.4	3.6	98.1	2.5	102.2	3.6	96.8	4.3
Na	1.1	98.4	2.5	98.8	2.9	99.0	1.3	95.7	4.0
K	0.3	97.1	2.2	98.3	3.5	96.2	1.6	96.8	7.4
Ca	0.4	100.0	2.2	95.6	2.9	100.4	1.9	96.2	6.2
Mg	0.2	97.7	2.2	96.8	3.0	98.6	1.4	95.2	4.8
Si	0.01	105.7	1.6	108.7	5.4	102.5	3.8	104.1	4.0
P	0.021	99.7	2.1	100.5	2.1	103.6	1.7	104.6	2.6
Cu	0.001	98.5	1.8	102.4	5.4	97.2	6.1	99.0	6.3
Zn	0.0021	102.6	6.1	104.3	2.3	100.6	1.4	100.1	2.8
B	0.003	100.4	1.3	104.9	3.8	102.8	4.4	100.3	2.0
Ba	0.0008	100.3	1.1	103.1	1.7	98.2	1.9	100.0	1.2
Cr	0.0009	N/A	N/A	N/A	N/A	100.0	4.1	99.7	3.5
Li	0.001	N/A	N/A	N/A	N/A	101.4	4.2	101.3	4.4
Mo	0.0008	N/A	N/A	N/A	N/A	100.4	2.7	99.4	2.5
Sr	0.002	N/A	N/A	N/A	N/A	96.4	7.5	95.8	5.0

% Rec = % Recovery

% Prec = % Precision

N/A = Not Determined during validation testing.

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

Data provided by Thames Water, England for Cr, Li, Mo and Sr and by ALS Environmental, Wakefield, England for all other elements.

Samples were spiked at the critical level of interest for drinking water.

Table A11.3 Suggested Wavelengths for Analysis (nm)

(Recommended wavelength highlighted in **bold)**

Aluminium	**396.156 (A)**	394.401	167.078
Barium	455.403	233.527	**230.425 (A)**
Boron	**249.772 (A)**	249.678	208.959
Calcium	393.366	**317.933 (R)**	315.887
Chromium	205.552	**267.716 (A)**	283.563
Copper	224.700	324.754	**327.393 (A)**
Iron	**238.204 (A)**	239.562	259.940
Lithium	**670.784 (R)**	N/A	N/A
Magnesium	279.553	280.270	**285.213 (R)**
Manganese	**257.610 (A)**	259.373	260.569
Molybdenum	**204.50 (A)**	379.82	386.40
Phosphorus	178.287	**213.617 (A)**	214.914
Potassium	**766.490 (R)**	771.531	404.721
Scandium (I/S)	**361.364 (A&R)**	N/A	N/A
Silicon	**251.611 (A)**	212.412	288.158
Sodium	**589.592 (R)**	588.995	330.237
Strontium	**407.771 (R)**	421.552	460.733
Yttrium (I/S)	**370.915 (A&R)**	371.028	371.030
Zinc	202.550	**206.200 (A)**	213.856

A = Axial mode; R = Radial mode; I/S = Internal Standard.

The instrument manufacturer's handbook should be consulted also.

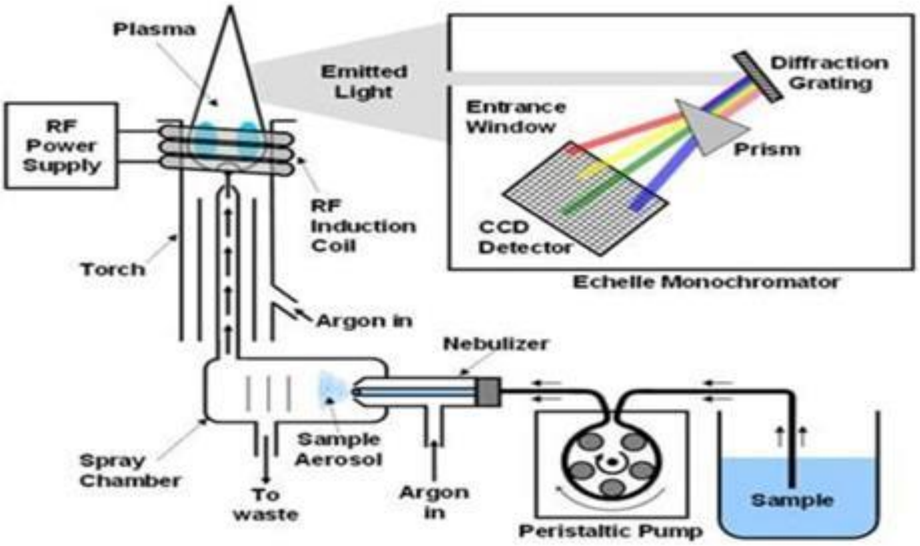
Baumann’s

Table A11.4 Possible interferences for certain metal species with ICP-OES

Reference - Blue Book 162 Inductively coupled plasma spectrometry 1996 ISBN 0117532444

Element	**Wavelength (nm)**	**Possible interferences**
Aluminium	396.156	V, Ca
Aluminium	394.401	None reported in environmental waters
Aluminium	167.078	Mn, V, Fe
Barium	455.403	Cr, Ni, Ti
Barium	233.527	Fe, V, Ni
Barium	230.425	None reported in environmental waters
Boron	249.772	Fe
Boron	249.678	Co, Fe
Boron	208.959	Al, Fe
Calcium	393.366	None reported in environmental waters
Calcium	317.933	Fe, Cr, V
Calcium	315.887	Co, Cr, Fe, Mo, Ce
Chromium	205.552	Fe, Mo, Al, Cu, Ni
Chromium	267.716	Mn, V, Fe, Ti
Chromium	283.563	Fe, Mo, Mg, V
Copper	224.700	Fe
Copper	324.754	Ca,Cr,Fe,Ti
Copper	327.393	Ca,Fe,Ni,Ti,V
Iron	238.204	Cr, V
Iron	239.562	None reported in environmental waters
Iron	259.940	None reported in environmental waters
Lithium	670.784	V, Ti
Magnesium	279.553	Fe, Mn
Magnesium	280.270	Cr, Mn, V
Magnesium	285.213	Fe, Cr, V
Manganese	257.610	Fe, Al, Cr, Ce
Manganese	259.373	None reported in environmental waters
Manganese	260.569	None reported in environmental waters
Molybdenum	204.500	None reported in environmental waters
Molybdenum	379.82	None reported in environmental waters
Molybdenum	386.40	None reported in environmental waters
Phosphorus	178.287	None reported in environmental waters
Phosphorus	213.617	Cu, Al, Cr, Fe, Ti
Phosphorus	214.914	Cu, Al, Mo
Potassium	766.490	Ti
Potassium	771.531	None reported in environmental waters
Potassium	404.721	Ca, Fe, V
Silicon	251.611	Cr, Fe, Mn, V
Silicon	212.412	None reported in environmental waters
Silicon	288.158	Cr, Fe, Mg, V
Sodium	589.592	Fe, Ti, V
Sodium	588.995	Ti
Sodium	330.237	Cr, Fe, Ti
Strontium	407.771	Cr, Fe, Ti
Strontium	421.552	None reported in environmental waters
Strontium	460.733	None reported in environmental waters
Zinc	202.550	Al,Cu,Fe,Vi,Ti,V
Zinc	206.200	None reported in environmental waters
Zinc	213.856	Cu,Ni,Al,Fe,Ti,V

Figure 1 Major components and layout of a typical ICP-OES instrument

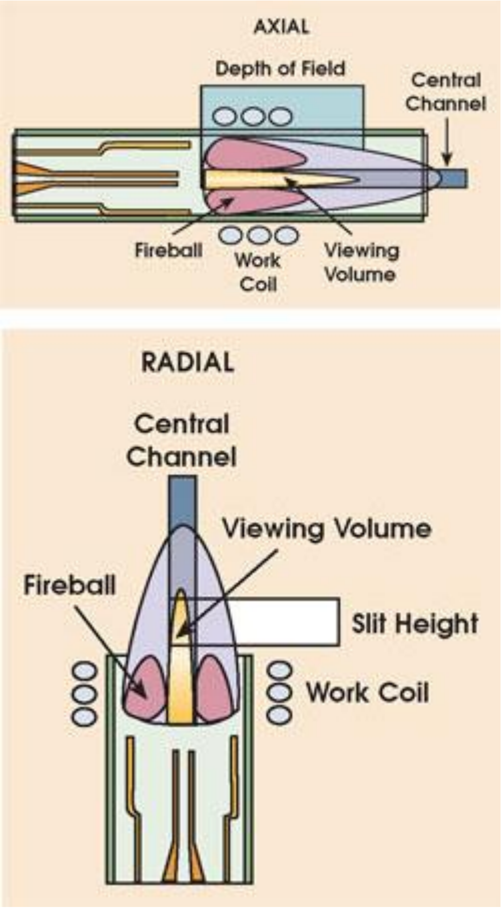


(Reference: Analytical Chemistry Lab Manual, Chemistry 330 (Analytical Chemistry I), Concordia College, Moorhead, MN;
http://sites.cord.edu/chem-330-lab-manual/experiments/icp-aes)

Appendix 1

Axial & Radial ICP-OES

ICP-OES instruments are typically made with two viewing options. The traditional, vertically-oriented set-up where the plasma is "viewed" by the optical system from the side, is known as "radial" or "side-on" viewing. It has the advantage of providing immediate venting of exhaust gases and waste heat to an overhead extraction system. "End on" or "axially viewed" plasma systems were introduced later. The aim of axial viewing is to observe a longer path length in the analyte-rich central channel, while avoiding viewing the surrounding intense argon plasma. This approach provides improved signal to noise ratio and hence better detection limits. However, along with this enhancement, there are increased spectral interferences and matrix-induced interferences. Most modern instruments combine both radial and axial viewing and are known as dual view.



(Reference: Michael Knowles, Varian Australia Pty. Ltd., Mulgrave, Victoria, Australia; *https://www.photonics.com/images/Web/Articles/2004/3/1/Spect_Fig1.jpg)*

A12 Further reading

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2. *Methods for the Determination of Metals in Soils, Sediments and Sewage Sludge and Plants by Hydrochloric-Nitric Acid Digestion, with a note on the Determination of the Insoluble Metals Contents 1985*, HMSO London, in this series

3. C.B. Boss and K.J. Fredeen*; Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry*, 3rd Edition, 2004

4. US EPA Method 200.7; *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry,* Rev 4.4, 1994

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7. M Cassap; *Using ICP-OES for Accurate Monitoring of Metallic Contaminants in Water According to US EPA Method 200.7*, Spectroscopy, 2007

8. V Calderon, A Ryan, D Shrader, *Analysis of Environmental Samples by ICP-OES Following US EPA Guidelines*, Varian Inc., 2007

9. J Wills, K Harper, F Keenan, B Spence; *ICP Source Spectrometry Techniques in Regulated Water Analysis*, Spectroscopy, 2007

10. P R Gaines; *ICP Operations Guide;* Inorganic Ventures*; 2011*

11. P Sarojam*, Analysis of Trace Metals in Drinking Water with the Optima 7000 DV ICP-OES;* Perkin Elmer Inc, 2010

12. Trace metal analysis of environmental solid matrices, Environment Agency report (NCAS/TR/2002/023).

13. Trace Analysis, *A structured approach to obtaining reliable results*, EDS, E Prichard, G M McKay and J Points, Royal Society of Chemistry, 1996, ISBN 0854044175.

14. ISO 17294-1:2004 – *Water Quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2 – Determination of 62 elements.*

15. ISO / DIS 11885:2004 – *Water Quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES).*

16. ISO / CD 22036:2004 – *Soil Quality – Determination of trace elements in extracts of soil by inductively coupled plasma atomic emission spectrometry (ICP-AES)*.

17. The determination of metals in solid environmental samples 2006, Methods for the Examination of Waters and associated Materials, HMSO London, In this series.

Address for correspondence

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