जल और अपशिष्ट जल के नमूने लेने तथा परीक्षण (भौतिक एवं रसायन) की पद्धतियाँ

भाग 64 उपपादन द्वारा मिलकर प्लाज्मा मास स्पेक्ट्रोमेट्री (आईसीपी-एमएस) के अनुप्रयोग —

सामान्य अपेक्षाएँ

(पहला पुनरीक्षण)

Methods of Sampling and Test (Physical and Chemical) for Water and Wastewater

Part 64 Application of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) — General Requirements

(First Revision)

ICS 13.060.50

October 2024   **Price Group 12**

Water Quality Sectional Committee, CHD 36

NATIONAL FOREWORD

This Indian Standard (Part 64) (First Revision) which is identical to ISO 17294-1 : 2024 'Water quality — Application of Inductively coupled plasma mass spectrometry (ICP-MS) — Part 1: General requirements' issued by the International Organization for Standardization (ISO) was adopted by the Bureau of Indian Standards on the recommendation of Water Quality Sectional Committee and approval of the Chemical Division Council.

This standard was first published in 2015 which was identical to ISO 17294-1 : 2004. This revision has been undertaken to adopt the latest version of ISO 17294-1 published in 2024. In this revision, following changes have been incorporated:

a) Scope has been revised to align with ISO 17294-2;

b) Text has been revised to reflect currently available instruments used in routine daily practice in many laboratories;

c) Clauses **5** and **6** have been revised to reflect the state-of-the-art equipment used to measure elements according to ISO 17294-2;

d) Abbreviated terms in **9** have been revised to align with common terms used in other standards;

e) Table A.1 has been updated; and

f) Title has been revised to align it with title of ISO 17294-1 : 2024.

BIS has also published separate standard IS 3025 (Part 65) which prescribes methods for determination of selected elements including uranium isotopes in water (For example drinking water, surface water, ground water, waste water and eluates) which is identical adoption of ISO 17294 (Part 2).

The text of ISO Standard has been approved as suitable for publication as an Indian Standard without deviations. Certain conventions are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Whenever the words 'This document', appears referring to this standard, they should be read as 'This Indian Standard'; and

b) Comma (,) has been used as a decimal marker, while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

The Committee responsible for the preparation of this standard has reviewed the provisions of the below mentioned ISO/IEC standards and has decided that they are acceptable for use in conjunction with this standard.

International Standard	Title
ISO 5725-1	Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions
ISO 6206	Chemical products for industrial use — Sampling — Vocabulary
ISO Guide 33	Reference materials — Good practice in using reference materials

Contents

Introduction

Since the last edition of this document, new developments in metal analysis with inductively coupled plasma mass spectrometry (ICP-MS) have taken place. The use of the collision or reaction cell (CRC) technology in quadrupole ICP-MS and triple quadrupole ICP-MS has increased in laboratories. For this reason, this document has been revised and new items have been added.

The intention for the revision of this document was to focus on the instrumentation currently available and in use for determining elements according to ISO 17294-2 in daily practice in laboratories. The consequence of this starting point is that the use of correction formulae has been moved to Annex A because of its reduced importance in modern instrumentation. Many principles also apply for high-resolution or accurate mass instrumentation, although they are not described in detail in this document.

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

PART 64 APPLICATION OF INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) — GENERAL REQUIREMENTS

(First Revision)

1 Scope

This document specifies the principles of inductively coupled plasma mass spectrometry (ICP-MS) and provides general requirements for the use of this technique to determine elements in water, digests of sludges and sediments (e.g. digests of water as described in ISO 15587-1 or ISO 15587-2). Generally, the measurement is carried out in water, but gases, vapours or fine particulate matter can be introduced too. This document applies to the use of ICP-MS for aqueous solution analysis.

The ultimate determination of the elements is described in a separate International Standard for each series of elements and matrix. The individual clauses of this document refer the user to these guidelines for the basic principles of the method and the configuration of the instrument.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO Guide 33, *Reference materials — Good practice in using reference materials*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

ISO 6206, *Chemical products for industrial use — Sampling — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO Guide 33, ISO 5725-1, ISO 6206 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1
analyte
element(s) to be determined

3.2
blank calibration solution
solution prepared in the same way as the *calibration solution* (3.3) but leaving out the *analyte* (3.1)

3.3
calibration solution
solution used to calibrate the instrument, prepared from a *stock solution(s)* (3.16) or from a certified standard

3.4
calibration check solution
solution of known composition within the range of the *calibration solution* (3.3) but prepared independently

3.5
determination
entire process from preparing the *test sample solution* (3.18) up to and including the measurement and calculation of the final *result* (3.14)

3.6
instrument detection limit
L_{DI}
smallest concentration that can be detected with a defined statistical probability using a contaminant-free instrument and a *blank calibration solution* (3.2)

3.7
linearity
functional relationship between the indicated values and the contents

3.8
calibration verification solution
solution with a known concentration of the matrix components compared to the *calibration solutions* (3.4), but having an *analyte* (3.1) concentration half that of the (highest) calibration solution

3.9
method detection limit
L_{DM}
smallest *analyte* (3.1) concentration that can be detected with a specified analytical method with a defined statistical probability

3.10
net intensity
I
signal obtained after background correction

3.11
optimization solution
solution serving for mass calibration and for the optimization of the apparatus conditions

EXAMPLE   Adjustment of maximal *sensitivity* (3.15) with respect to minimal oxide formation rate and minimal formation of doubly charged ions.

3.12
precision
closeness of agreement between independent test *results* (3.14) obtained under prescribed conditions

Note 1 to entry: Precision depends only on the distribution of random errors and does not relate to true value or the specified value.

[SOURCE: ISO 5725-1:2023, 3.12, modified — the definition has been revised and Notes 2 and 3 to entry have been removed.]

3.13
reagent blank solution
solution prepared by adding to the solvent the same amounts of reagents as those added to the *test sample solution* (3.18) and with the same final volume

3.14
result
outcome of a measurement

Note 1 to entry: The result is typically calculated as mass concentration (U), expressed in milligrams per litre.

3.15
sensitivity
S
ratio of the variation of the magnitude of the signal (ΔI) to the corresponding variation in the concentration of the *analyte* ([3.1](#)) (ΔC)

Note 1 to entry: Sensitivity is calculated as shown in [Formula (1)](#):

$$S = \frac{\Delta I}{\Delta C}$$

(1)

3.16
stock solution
solution with accurately known *analyte* ([3.1](#)) concentration(s), prepared from pure chemicals

Note 1 to entry: Stock solutions are reference materials within the meaning of ISO Guide 30.

Note 2 to entry: Pure chemicals are those which have the highest available purity and known stoichiometry and for which the content of analyte and contaminants should be known with an established degree of certainty.

3.17
test sample
sample prepared from the laboratory sample

Note 1 to entry: The sample can be prepared, for example, by grinding or homogenizing.

3.18
test sample solution
solution prepared with the fraction (test portion) of the *test sample* ([3.17](#)) according to the appropriate specifications, such that it can be used for the envisaged measurement

4   Principle

In the present context, a plasma is a small cloud of hot (6 000 K to 10 000 K) and partly ionized (approximately 1 %) argon gas. Cool plasmas have temperatures of only about 2 500 K. The plasma is sustained by a radio-frequency field. The sample is brought into the plasma as an aerosol. Liquid samples are converted into an aerosol using a nebulizer. In the plasma, the solvent of the sample evaporates, and the compounds present decompose into the constituent atoms (dissociation, atomization). The analyte atoms are in most cases almost completely ionized.

In the mass spectrometer, typically equipped with a collision or reaction cell (CRC) and quadrupole, the ions are separated and the elements identified according to their mass-to-charge ratio, *m/z*, while the concentration of the element is proportional to the number of ions.

ICP-MS is a relative technique. The proportionality factor between response and analyte concentration relates to the fact that only a fraction of the analyte atoms that are aspirated reach the detector as an ion. The proportionality factor is determined by measuring calibration solutions (calibration).

With instruments equipped with a magnetic sector field, higher mass resolution spectra can be obtained. This can help to separate isotopes of interest from interfering species.

5 Apparatus

5.1 General

The principal components of the equipment used for ICP-MS is shown in Figure 1 in the form of a schematic block diagram.
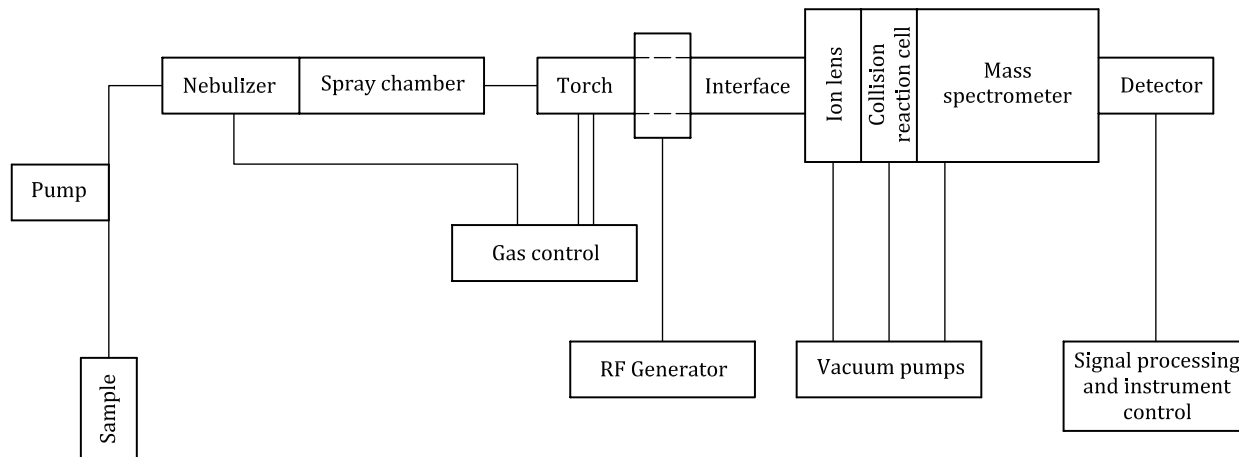
Figure 1 — Schematic block diagram of an ICP-MS instrument

5.2 Sample introduction

5.2.1 General

To introduce solutions to be measured into the plasma, a peristaltic pump, a nebulizer and a spray chamber are generally used. The pump supplies the solution to the nebulizer. In the nebulizer, the solution is converted into an aerosol by an (argon) gas flow, except when an ultrasonic nebulizer is used; see 5.2.3. Large drops are removed from the aerosol in the spray chamber by means of collisions with the walls or other parts of the chamber and they are drained off as liquid. The resulting aerosol is then transferred into the plasma via the injector tube of the torch (see 5.3) with the help of the nebulizer gas (sample-introduction gas).

The sample introduction system is designed in such a way that:

a) the average mass per aerosol droplet is as low as possible;

b) the mass of the aerosol transported to the plasma in each period of time is as constant as possible;

c) the droplet size distribution and the added mass of the aerosol in each period of time is, as far as possible, independent of the solution to be measured (matrix effect, see 6.3);

d) the time the aerosol takes to stabilize after introduction in the spray chamber of a solution is as short as possible;

e) the parts of the system in contact with the sample or the aerosol are not corroded, degraded or contaminated by the solution;

f) carry-over from one sample to subsequent samples is minimized.

The components of the sample introduction system shall be able to withstand any corrosive substances in the solutions, such as strong acids. The material used for pump tubing should be resistant to dissolution and chemical attack by the solution to be nebulized. Components that come into contact with the solution are often made of special plastics. The use of glass and quartz shall be avoided if hydrofluoric acid is present in the test solution. In those cases, the nebulizer, spray chamber and torch injector tube shall be made of suitable inert materials.

The various components of the sample introduction system are discussed hereafter in relation to these requirements and some examples are compared.

5.2.2 Pump

The use of a peristaltic pump to feed the solutions [e.g. sample, reference elements solutions (8.5)] to the nebulizer is not necessary with some nebulizers (see 5.2.3) but is desirable in almost all cases in order to render the supply of the solution less dependent on the composition of the solution. A sampling pump is used on all modern instruments.

It is advisable to use a peristaltic pump having the largest possible number of rollers and a velocity as high as possible to avoid major surges in the supply of the solution. The quantity of solution that is pumped is mostly between 0,1 ml/min and 1,0 ml/min and typically around 0,4 ml/min to 0,5 ml/min.

5.2.3 Nebulizer

The most common nebulizers are the concentric nebulizer (e.g. Meinhard[1)]), the crossflow nebulizer, the V-groove nebulizer and the ultrasonic nebulizer (USN). The first one can be used in self-aspiration mode and the crossflow nebulizer can be used without a pump (but seldom are). Nebulizers (except for the USN) can be made of glass or of hard, inert plastic such as PFA.

The concentric nebulizer consists of two concentric tubes, the outer one being narrowed at the end. The solution flows through the central tube and the nebulizer gas (see 5.4) through the tube around it, creating a region of lower pressure around the tip of the central tube and disrupting the solution flow into small droplets (the aerosol). This nebulizer performs best with solutions with a low content of dissolved matter, although there are also models that are less sensitive to significant amounts of dissolved matter in the solution to be nebulized.

The crossflow nebulizer consists of two capillary tubes mounted at a right angle, one being used for the supply of the solution and the other for the supply of the nebulizer gas. Depending on the distance between the openings of the capillary tubes and their diameters, the nebulizer can be self-aspirating. With larger diameters, the chance of blockages occurring is of course smaller, but a pump shall be used to supply the solution.

In the V-groove nebulizer, the solution flows through a vertical V-groove to the outflow opening of the nebulizer gas. The solution is nebulized by the high linear speed of this gas at the very small diameter outflow opening. The V-groove nebulizer was developed for solutions with a high concentration of dissolved matter and/or with suspended particles, although it is also used successfully with diluted and/or homogenous solutions. Similar nebulizers are the Burgener[2)] nebulizer and the cone-spray nebulizer, with similar outer shapes as the concentric nebulizer. With these nebulizers, the solution flows out into a cone-shaped area at the tip of the nebulizer instead of a V-groove and flows over the outflow opening of the nebulizer gas.

In the ultrasonic nebulizer, the solution is pumped through a tube that ends near the transducer plate that vibrates at an ultrasonic frequency. The amount of aerosol produced (the efficiency) is typically 10 % to 20 % of the quantity of the pumped solution. This is so high that the aerosol shall be dried (desolvated) before being introduced into the plasma, which would otherwise be extinguished. The aerosol is transported to the plasma by the nebulizer gas. Disadvantages of the ultrasonic nebulizer include its greater susceptibility to matrix effects, diminished tolerance to high dissolved solid contents and a longer rinsing time (i.e. Ag, B, Hg, Mo).

For the other nebulizers previously described, the efficiency is typically only a few per cent. The efficiency increases when the solution introduction rate is decreased. Specially designed concentric micro-nebulizers made of special types of hard plastic operate at solution flow rates of 10 µl/min to 100 µl/min and efficiencies

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1) The Meinhard nebulizer is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

2) The Burgener nebulizer is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product. Equivalent products may be used if they can be shown to lead to the same results.

approaching 100 %. These concentric micro-nebulizers often show a very good precision (low coefficient of variation of the signal) and can also be combined with a membrane desolvator [see 6.2.1, a)].

Several other types of nebulizers may be used for specific applications.

5.2.4 Spray chamber

In the spray chamber [e.g. Scott (double concentric tubes), cyclonic or impact bead], the larger drops of the aerosol are drained off in liquid form. To create and keep over-pressure in the chamber, the liquid shall be removed via a sealed drain tube utilizing hydrostatic pressure or by pumping. The internal diameter of the drain tubing should be higher than that of the sample uptake tubing to ensure that no liquid remains in the spray chamber. The liquid shall be removed evenly to avoid pressure variations in the chamber, which can result in variations in the signal.

By cooling the spray chamber to 2 °C to 5 °C, the water vapour formed in the nebulization process condenses, thereby reducing the water load of the plasma. This results in a reduction in the formation of interfering polyatomic ions (oxides); see 6.2.2.

5.2.5 Other systems

There are other types of introduction systems for particular applications. These include laser or spark ablation of a solid sample, evaporation of the solution by means of a graphite furnace or a metal filament, introduction of a gas or a gas form of the analyte (as in the hydride generation technique), systems for the direct introduction of solid matter into the plasma (e.g. in the form of a slurry of a finely dispersed powder in a solvent) and the introduction with a graphite rod directly into the plasma.

With the direct injection nebulizer (DIN), a pneumatic concentric micro-nebulizer, instead of the inner tube (injector; see 5.3), is placed in the torch. It has a sample introduction efficiency of almost 100 %, with a sample uptake rate of typically 10 µl/min. A DIN can be used for techniques giving transient signals (e.g. coupling to chromatographic or flow injection devices) and for minimizing the memory effects of, for instance, silver, boron, molybdenum and mercury. These systems are not discussed in this document.

5.3 Torch and plasma

The torch consists of three concentric tubes and can be designed as a monoblock or demountable unit. Quartz is the material generally used, but also high purity ceramic torches are available. Sometimes the innermost tube (the sample introduction tube or injector tube) is made of inert material, for example aluminium oxide or sapphire. It usually ends at 4 mm to 5 mm before the first winding of the coil. The aerosol produced in the sample introduction system flows through the sample introduction tube, transported by an (argon) gas flow (the nebulizer gas) with a flow rate of approximately 0,5 l/min to 1,5 l/min.

The auxiliary gas flows between the sample introduction tube and the middle tube with a flow rate of up to 3 l/min. Whether or not an auxiliary gas or humidification of the argon flow is used depends on, for example, the type of device concerned, the solvent used and the salt concentration. The function of the auxiliary gas is to increase the separation of the plasma and the torch and thus reduce the temperature at the end of the injector (and intermediate) tube. This avoids deposits of dissolved material or the build-up of carbon (when organic solvents are nebulized) on the injector tube.

The plasma gas flows between the middle and outermost tubes with a flow rate of 12 l/min to 20 l/min. The function of the plasma gas is to maintain the plasma and to cool the outer tube of the torch.

Around the top of the torch, there is a cooled coil with two to five windings. A high-frequency current flows through the coil and excites the plasma (see 5.5).

The torch is generally placed in a separate metal compartment. This compartment shall be connected to an exhaust system (extraction) because of the production of heat and harmful gases (including ozone). The metal of the compartment protects the users and the instrument (electronics) against the high-frequency radiation, which is released from the coil, and against the ultraviolet radiation emitted by the plasma. A camera, a lens or a special window, covered with a darkened glass to protect the observer's eyes from the

intense plasma emission radiation, allows visual observation of the plasma. Some systems provide a camera monitor for the purpose of viewing the plasma area.

A grounded metal shield (shield torch) can be placed between the coil and the torch to reduce the levels of argon-based (poly)atomic ions (see 6.2) that interfere particularly with the determination of K, Ca and Fe. Cold plasma conditions (relatively low plasma power and high nebulizer gas flow rate) can, in cases of matrices with low matter content, also be used to optimize the reduction of argon based polyatomic interferences. Similar performance can be obtained by a torch system which uses a balanced radiofrequency (RF) drive, avoiding the requirement for the grounded metal shield and allowing easier removal of the torch for maintenance.

5.4 Gas and gas control

In virtually every instrument, argon is used as nebulizer gas (sample introduction gas), auxiliary gas and plasma gas. Argon gas with a purity of greater than 99,995 % is preferred. Exact amounts of oxygen can be added to the nebulizer or auxiliary gas to avoid carbon build-up on the sampling cone and torch injector when analysing solutions made with organic solvents. The additions of too much oxygen result in the burning away of the graphite carbon that deposits on the sampling cone (see also 5.6). Mixtures of argon and hydrogen or nitrogen can improve the sensitivity for certain elements and/or reduce the formation of interfering polyatomic ions (see 6.2). Small amounts of other gasses such as nitrogen can be added, providing benefits such as increased sensitivity or reduced oxide species, depending on the application.

The various gas flow rates shall be stable. This applies particularly to the nebulizer gas. The best results are obtained with mass-flow controllers that keep the mass flow rate of a gas constant and almost independent of temperature and initial pressure.

5.5 Generator

The generator delivers an alternating current with a frequency between 27 MHz and 56 MHz and a power between 0,6 kW and 2 kW that sustains the plasma. In general, solid-state generators are used. Two types of generators are available: fixed frequency and variable frequency.

Fixed-frequency generators are designed to control both power and frequency of the magnetic field; the impedance of the plasma is matched to the output of the generator using a mechanical variable capacitor in a closed-loop control circuit. The delivered power and the power not absorbed by the plasma (the reflected power) shall both be very constant and vary as little as possible with the composition of the solution. The reflected power should be low (preferably <10 W).

Variable-frequency generators are of a simpler construction and control basically the power delivered to the torch ("forward" power). Small variations in frequency can occur in those types of generators, which allows for the matching of the plasma impedance to the generator without the requirement for mechanical variable capacitors.

5.6 Transfer of the ions to the mass spectrometer

The ions are transferred from the plasma to the mass spectrometer (see 5.7) via the interface. The interface consists of two water-cooled cones, a sampling and a skimmer cone, with a vacuum-pumped system, the expansion chamber in between, sometimes supported with a third cone. During the measurement the pressure in the expansion chamber is maintained at 10^2 Pa to 10^3 Pa. At the centre of the cones is an orifice with a diameter of 0,3 mm to 1 mm, the orifice of the skimmer cone usually being smaller than that of the sampling cone. The cones are usually made of nickel. The centre of the cones can have different shapes.

The gas containing the ions is sampled from the central part or channel of the plasma through the orifice of the sampling cone into the expansion chamber, where a supersonic jet is formed. The central part of this jet flows through the orifice of the skimmer cone into the vacuum (approximately 10^{-2} Pa) of the lens system.

Only about 1 % of the gas sampled from the plasma is transmitted to the lens system. Due to the short residence time in the expansion chamber (a few microseconds), the composition of the gas hardly changes.

For the determination of nickel at low concentrations, platinum-tipped cones are available. The use of platinum cones is also preferred when running organic solvents and matrices containing sulfuric, phosphoric or hydrofluoric acids. In this reactive atmosphere, platinum cones are more resistant than those made of nickel (see also 5.4 and 8.3).

A deposit, consisting of constituents from the measurement solutions, is formed around the orifices of the cones and can influence the analysis; see 6.2 and Clause 7.

5.7 Mass spectrometer

5.7.1 General

The mass spectrometer consists of an electronic lens system, an analyser and a detector. In the lens system, the ions travel from the interface and are directed to and focused on the entrance of the analyser. In the analyser, the ions are separated according to their mass-to-charge ratio, m/z.

5.7.2 Lens system

The lens system can consist of one ion lens, for instance a metal cylinder or a metal plate with a hole, or several ion lenses strung together. Electrical potentials are exerted on the lenses, resulting in the formation of a beam of ions directed towards the analyser; see also 7.2.5.6. The unwanted neutral particles are removed by vacuum pumps.

Photons, emitted by the plasma in addition to the ions and neutral particles, also enter the lens system. To minimize the number of photons hitting the detector, which causes an increase in the background signal and noise, the ion beam is deflected off axis from the detector. In addition, the ion beam can again be offset from the axis of the detector after the CRC to suppress any potential impact of neutral species formed therein.

In the case of double-focusing mass spectrometers (see 5.7.6), no photon stop is required as the trajectory of the ions deviates from the light path because of a curvature of the ion trajectory in the lens system or in the analyser.

5.7.3 Collision or reaction cell

To overcome typical polyatomic interferences (see 6.2), instruments are equipped with a CRC. A CRC is a short multipole enclosed in a chamber that is flushed with either an inert gas, such as helium, or a reactive gas at low pressure. In the case of inert gas mode (He), polyatomic (molecular) ions have a larger collision cross-section than analyte (atomic) ions at the same mass. Polyatomic ions therefore collide more frequently with the He cell gas atoms, so lose more energy and are rejected by applying a positive kinetic energy discrimination (KED) bias voltage and are filtered out of the ion beam, enabling more accurate and more consistent results to be obtained for many difficult analytes. Reactive cell gases, such as H_2, O_2, NH_3 and CH_4, can be used in single-quadrupole ICP-MS instruments to target interferences on specific isotopes or elements. These interferences include isobaric and doubly charged interferences, peak tail overlaps and very intense polyatomic ions.

The CRC technology has been further developed into triple quadrupole technology. These systems feature an additional quadrupole mass filter (not necessarily of the same dimensions as the main quadrupole mass filter) to pre-select a given m/z ratio. This design facilitates a more effective use of reactive gases for interference removal, as controlled conditions in the CRC suppress the formation of unwanted side reactions. In addition to eliminating polyatomic interferences, triple quadrupole ICP-MS instruments can also eliminate isobaric and doubly charged interferences if needed. In many cases, the achievable sensitivity and detection limits are superior with a triple quadrupole ICP-MS instrument.

5.7.4 Analyser

In most ICP-mass spectrometers, the separation of the ions is obtained using a quadrupole mass spectrometer located in a high vacuum ($<2 \times 10^{-3}$ Pa) compartment.

A quadrupole mass analyser consists of four cylindrical or hyperbolic parallel metal rods of about 20 cm in length on which direct current (DC) and RF potentials are exerted. The ions are introduced at the central axis at the beginning of the rods. At a specific combination of DC potential and RF amplitude, the entire trajectory between the rods is traversed only by ions with values of *m/z* within a specific bandwidth. Ions with lower or higher *m/z* values are bent away, hit the rods and are neutralized. Thus, the quadrupole acts as a mass filter.

A quadrupole mass spectrometer for ICP-MS resolves only at unit mass or somewhat better (see also 7.2.4).

An important quality characteristic of a quadrupole mass spectrometer is the abundance sensitivity.

For instance, if a peak is present at *m/z* M, and there is no peak at M−1 or M+1, the abundance sensitivity is then defined as the ratio between the signal at M and the signal at M−1 or M+1. The abundance sensitivity, therefore, indicates the ability to measure a small peak next to a major peak. Abundance sensitivity values of 10^6 for the lower masses and 10^8 for the higher masses may be obtained, although values of 10^4 and 10^6, respectively, are more common in routine analysis. Sometimes, the inverse value is presented.

5.7.5 Detector

The detection system usually consists of an electrode (the conversion dynode), an electron multiplier with discrete dynodes and a pre-amplifier.

Under the influence of a high negative voltage, the ions exiting the analyser hit the conversion dynode resulting in the release of electrons. These electrons hit the first dynode of the electron multiplier and, as a consequence, twice the number of electrons is released.

Subsequently, these electrons hit the second dynode, repeating the process of doubling and hitting the next dynode. Ultimately, one ion emitted from the analyser results in a pulse of approximately 10^8 electrons. The successive dynodes have progressively fewer negative voltages. The pulse is processed using a fast pre-amplifier.

The maximum counting rate of this system is 2×10^6 cps to 4×10^6 cps (counts, or pulses, per second) and is determined by two factors. First, the current flow that the detector can sustain is limited. The second limiting factor is the response time, or "dead time", of the detector and electronics, i.e. the time after the registration of a signal during which the detector is not able to register a new pulse. If the time interval between the arrivals at the detector of two ions is shorter than the dead time, the second ion is not detected. Both factors cause a relative decrease in the count rate at higher impact rates. For modern instrumentation, the response time is usually about 10 ns to 20 ns. A mathematical correction shall be carried out to correct for the nonlinearity caused by the dead time. The ICP-MS software supplied with the equipment usually carries out this correction based on Formula (2):

$$N' = \frac{N}{1 - ND} \qquad\qquad (2)$$

where

   N' is the true or estimated count rate;

   N is the observed count rate;

   D is the dead time in seconds, s.

The noise of this type of detector is very low, usually 1 cps or less, and is of minor importance for ICP-MS measurements. However, the background that is observed in practice is 3 cps to 30 cps. This considerably higher value is possibly caused by photons which, despite the measures taken (see 5.7.2), hit the detector.

Several methods are applied to increase the upper limit of the dynamic range of the measurement, for example by having fewer ions reaching the detector by, for example, defocusing the ion beam. Other methods include lowering the multiplication factor by decreasing the potential on the detector or by collecting only a part of the electrons generated. When one of the last two methods is applied, the current is measured in an analogue manner. This is called the analogue mode, in contrast to the pulse-counting mode. Modern

instrumentation switches automatically to the analogue mode when a signal that is too high is detected to prevent damage to the detector.

The lifetime of discrete dynode and similar detectors is limited to typically 1 year to 5 years, depending on the use of the instrument. During this life span, the sensitivity of the detector slowly decreases, and the high voltage shall be increased from time to time to restore the original sensitivity.

For some applications, the signal is high enough that a Faraday cup (a metal electrode without amplification) may be applied.

5.7.6 Alternative mass spectrometers and types of instruments

One disadvantage of a quadrupole mass spectrometer is the insufficient resolution to separate ions with the same nominal value of m/z. Especially for m/z values lower than 80, this can be a problem due to the presence of many interferences originating from polyatomic and doubly charged ions (see 6.2). Much of the newer instrumentation has been developed to overcome these interferences.

Many interferences can be avoided by applying a high-resolution mass spectrometer with a magnetic and an electrostatic analyser (ESA). First, the ions are accelerated with an accelerating voltage of 5 kV to 8 kV and then separated by the magnetic and electric fields. Depending on the type of instrument, the ESA can be located ahead of or behind the magnet (reversed Nier-Johnson geometry). The ions coming from the interface are focused on a slit in front of the spectrometer by means of ion optics, and then on a slit in front of the detector by the action of the magnet and the ESA. The ions are focused with respect both to direction of movement and to the energy at the entrance slit (double focusing). The resolution can be changed by changing the slit widths.

Depending on the type of instrument, this is performed with continuously adjustable slits or by using slits with fixed widths. The maximum resolution that can be obtained is 10 000 to 20 000, depending on the type of instrument.

Resolution is defined here as the average mass divided by the mass difference of two adjacent peaks of equal height that are separated with a valley between them at 10 % of the peak heights, defined as $m/\Delta m$, where m is the average mass and Δm is the difference of the two masses. The parameter Δm is equivalent to the width of one peak at 5 % of the peak height. Therefore, for the same effective separation of peaks, the resolution increases with mass.

The non-spectral background of this type of mass spectrometer is lower than 0,1 cps and the sensitivity at low-resolution measurements in a standard configuration varies, depending on the isotopic mass, from $>10^4$ cps per µg/l for Li to $>10^6$ cps per µg/l for U. The higher sensitivity compared to the quadrupole instruments results from the fact that an accelerating voltage is used and that the vacuum in the spectrometer is better.

Instrumental detection limits obtained are often below 0,1 µg/l for elements not subject to interference at low-resolution measurements. For elements subject to interferences, the detection limits are on the order of 1 µg/l or higher when measuring at a resolution of 10 000.

Mass scanning is slower with a magnet than with a quadrupole, while electrostatic scanning over a limited mass range is fast.

A further disadvantage of both quadrupole and high-resolution analysers is the speed of analysis. The detection systems require a measurement time of 0,1 ms to 50 ms for each isotope in each spectrum and ions are measured in a sequential manner for each isotope of interest with a delay between each measurement for the analyser to switch the necessary voltages or fields to select the new ion. ICP-MS with time-of-flight analysers is preferred for analyses where signals are transient and require multi-element measurements in sub-millisecond times, such as nanoparticle analysis or high-speed imaging with a laser ablation system. The time-of-flight analyser samples packets of ions from the ion beam and accelerates them at constant energy into a drift region such that lighter ions achieve a higher velocity than heavier ones and have a shorter flight time over a fixed distance between the sampling region and the detector. Over the space of a few tens of microseconds, a mass spectrum can be derived from the time that ions take to arrive at the detector compared to the time of the pulse of voltage that extracted the ions from the beam. The time-of-flight analyser averages a few to thousands of these individual mass spectra to generate a full mass spectrum at speeds which are significantly faster than any other mass spectrometer.

5.8 Signal processing and instrument control

In quadrupole ICP-MS, measurements are made at discrete points of the mass range. The full range is divided into about 5 000 points or channels (20 points per mass) and is usually scanned many times. One scan over the mass range is called a sweep and the residence time at one point is called the dwell time. While scanning, parts of the mass range can be skipped, or the mass spectrometer can jump from one selected mass to the next selected mass and measure only at the points around the top of the expected peak. The last mode is called the peak-jump mode, the other mode the scanning mode. Also, measurements can be made at only one mass, for instance when transient signals are measured (e.g. when a laser ablation or chromatography instrument is coupled to the ICP-MS instrument). This is called "selected-ion monitoring" or "single ion monitoring". The number of points per mass measured in the peak-jump mode is normally one to three; this mode shows the highest signal-to-noise ratio. The scanning mode can be used to obtain information about isotopic patterns of elements or polyatomic ions for identification purposes. The time of scanning the full mass range is typically below 0,1 s. The number of sweeps can be fixed, for example 100, or operator-chosen. This high signal-sampling frequency reduces the effects of the low-frequency source noise caused by the nebulizer, resulting in improved precision, i.e. a lower coefficient of variation of the intensity ratio (see 6.3.5.3) as the measurements of the analyte signal and the reference-element signal are more simultaneous. The number of sweeps times the dwell time times the number of points measured per mass gives the value of the integration time per mass. The integration time or the dwell time for each mass is operator selectable. In the peak-jump mode, some time (the quadrupole settling time) is necessary for the quadrupole to settle at the new mass position before a new reading can be taken, increasing the total measurement time above the sum of the measurement times at the individual masses. See also 8.4.

All modern instruments have one or more integrated computers which control and monitor the instrument and process the data. In addition to the determination of the net measurement value, data processing also includes calibration, calculation of the concentration, as well as the recording and graphical display of the spectra. The programme can additionally contain tables of isotopes and of polyatomic ions, as well as a procedure for the automatic optimization of a combination of parameter settings.

6 Interferences by concomitant elements

6.1 General

The presence of concomitant elements in the sample can cause interferences, for instance systematic errors in the measurement of the signal.

Interferences are classified into spectral and non-spectral interferences. Spectral interferences have an additive influence on the analytical signal (causing a parallel shift of the analytical function) when not separated from the mass peak of the analyte. They are caused by mono- or polyatomic ions having the same m/z ratio as the analyte ions. Spectral interferences caused by an isotope of another element having the same m/z as the analyte ion are also called isobaric interferences. Non-spectral interferences, usually called matrix effects, have a multiplicative influence (changing the slope of the analytical function) and result in sensitivity changes due to variations in the composition of the solutions to be measured.

6.2 Spectral interferences

6.2.1 General

The components that can cause spectral interferences are:

a) an isotope of another element having the same mass as the analyte isotope, also called isobaric interference, for example ^{58}Fe (interferant) and ^{58}Ni (analyte);

b) polyatomic ions, also called molecular ions; in many cases, these ions contain argon (plasma gas) and/or oxygen originating from the water of the solution aspirated; also, chloride plays an important role with respect to the formation of interfering polyatomic ions; examples are ^{40}Ar^{35}Cl$^+$ (interference with ^{75}As$^+$) and ^{44}Ca^{16}O$^+$ (interference with ^{60}Ni$^+$);

c) doubly charged ions, for instance Ba^{2+} (interference with ^{65}Cu, ^{66}Zn, ^{67}Zn and ^{68}Zn) and Sr^{2+} (interference with ^{43}Ca and ^{44}Ca).

Polyatomic ions can be formed in the plasma out of its constituents or by incomplete dissociation of molecules, or in the interface region, especially in the cooler boundary layers of the sampling and skimmer cone. So, the condition of the cones can be of importance in the level of formation of polyatomic ions (see 5.6).

Interferences by polyatomic ions are usually controlled using the CeO^+/Ce^+ ratio while aspirating a cerium solution. This ratio should be lower than 3 %. For the double charged ions, a barium solution is aspirated. The Ba^{2+}/Ba^+ ratio should be lower than 5 %. For triple quadrupole inductively coupled mass spectrometers, the levels of 3 % for oxide level and double charged ions are not that feasible because interferences can be overcome by use of tandem mass spectrometer with reaction cell in MS-MS mode. See also 5.7.3.

6.2.2 Possible elimination strategies for polyatomic ion interferences

Possible elimination strategies for polyatomic ion interferences are the following:

a) Reducing the water load of the plasma, which results in a reduction of the level of all kinds of oxide interferences. This can be achieved in several ways:

— cooling of the spray chamber to 2 °C to 5 °C;

— aerosol dilution: by lowering the nebulizer gas flow, the efficiency of nebulization is reduced while the total argon gas flow to the plasma is maintained by addition of a dilution gas flow;

— desolvation of the aerosol using a condenser and/or a (semi-permeable) membrane; however, the use of a membrane desolvator can also give rise to problems such as the loss of analyte because of permeability of the membrane to volatile analyte species; also, element-specific memory effects are associated with the use of membranes.

b) Minimization of the chloride concentration in the solutions aspirated by eliminating the use of HCl. HNO_3 should be used for acidifying the solutions or for sample digestions. The use of CRC can reduce the level of Cl-related interferences considerably because of the collision with Cl-related interferences, for example $^{35}Cl^{16}O$ (interferant) and ^{51}V (analyte). The solutions shall be acidified with HNO_3.

c) Optimization of the measurement conditions to maximize the ratio of the analyte signal to the interference signal. Optimization parameters include plasma power, sample carrier-gas flow rate, sample-introduction rate and sampling depth (distance between torch and tip of sampling cone) (see 8.3). This approach can also be beneficial for the reduction of the level of doubly charged ion interferences.

d) Use of a CRC (see 5.7.3).

e) Use of triple quadrupole inductively coupled mass spectrometers (see 5.7.3).

f) Addition of molecular gases, such as H_2, N_2 or CH_4, to the nebulizer gas, auxiliary gas, plasma gas or to all gases, which gives improvement in specific cases.

g) Addition of ethanol or similar alcohols to the sample for the reduction of the $ArCl^+$ interference and to overcome the impact of the carbon enhancement effect by high carbon content in solutions by some elements such as As and Se.

h) Spectral-fitting approaches: modelling of the spectrum with the isotopic patterns of the analytes and of all relevant interfering species as input. However, in the mass region between 50 and 90, too many components, and some mono-isotopic elements, are present to obtain an unambiguous fit [too many unknowns compared to the number of information points (masses)]. For other mass regions, this approach can be quite successful.

i) The use of a shielded torch and/or cold plasma conditions (see 5.3) for specific situations (see also 8.8).

j) The use of elemental formulae; this approach is further elaborated in the following paragraph.

The interference correction factors, f, are determined as elaborated previously. A requirement is that the interference check solution (ICS) contains no analytes. Very often this is not the case because relatively high concentrations of, for example, salts are used to prepare the ICS. Even high-purity chemicals often contain some analyte. For this situation, the exact correction can be determined by comparing the result (in concentration units) for the analyte isotope subject to interference with that obtained for an analyte isotope not subject to interference (for multi-isotope elements). Adjusting f and reprocessing can make the result of the isotope subject to interference equal to that of the isotope not subject to interference. "Not subject to interference" in this case means that there is no interference by a polyatomic ion formed out of the interfering element involved. However, other polyatomic ions can, in turn, interfere with this second analyte isotope, making this isotope unsuitable for quantitative analysis.

6.3   Non-spectral interferences

6.3.1   General

Non-spectral interferences, usually called matrix effects, involve analyte signal suppression or enhancement compared to that expected from the same analyte concentration in a matrix free solution. A single mechanism cannot explain the various matrix effects,[11] whose origin is in three different processes or locations: in the nebulization process, in the plasma and in the interface and the lens area. These types of interferences also include blockage of the nebulizer, torch injector tube and sampling cone caused by high concentrations of dissolved matter (total solid levels below 2 g/l are recommended) or the nebulization of organic solvents (for the latter, mainly carbon blockages of sampling cone, see 5.4).

6.3.2   Interferences in the nebulization process

Differences in viscosity, surface tension and density between the test sample solution and the calibration solutions, caused by differences in the quantity and type of dissolved matter, type of acid or acid concentration, can produce a change in the rate of delivery of the solution, nebulizer efficiency and droplet size distribution of the aerosol. This can result in a difference in the intensities for the same concentration in test sample solution and calibration solution. Temperature differences between different solutions can cause the same effects. The use of a peristaltic pump can reduce the effects caused by a difference in the rate of delivery of the solution; the internal standards also help to reduce these effects (see 6.3.5.3).

Other causes for differences are difference in volatility of the various chemical forms in which an element can occur in the solutions to be measured, for instance sulfide (H_2S)/sulfate, iodine/iodide or iodate, metallic/ionic mercury and the presence of dissolved gases such as CO_2 or nitrous fumes in test sample solutions or digests.

6.3.3   Interferences in the plasma

In the plasma, the matrix can cause a change of the degree of the ionization of the analyte elements. This is especially the case for elements with a high (first) ionization potential (9 eV to 11 eV), such as Cd, Zn, As, Se and Hg, that are incompletely ionized in the plasma. Elements with a first ionization potential of less than about 8 eV are almost completely (more than 90 %) ionized and suffer less from matrix effects in the plasma. The sensitivity of As and Se can be enhanced in the presence of carbon-containing matrix components, indicating that an additional ionization mechanism, charge transfer with carbon or carbon-containing ions, is taking place (see 6.3.5.2).

In most cases, a reduction of the analyte signal is observed. In the presence of easily ionized elements, the thermal ionization equilibrium is shifted towards the neutral atom and results in a suppression of analyte signal. The suppression follows the order of the most easily ionized element in the sample matrix, i.e. K > Na > Ca > Mg.

The ICSs are used to confirm that common interfering elements do not cause incorrect measurements of analyte concentrations; they also serve to determine the correction factors for the corresponding formulae or correct use of the CRC. Interference check solutions shall contain all the interferents of relevance at a concentration level that is at least as high as in samples.

The example in Table 1 describes the check for some common interferences (6020 solution A contains high concentrations of typical environmental matrix elements).

Table 1 — Example of the composition of a set of interference check solutions

Interferent[a]	Concentration mg/l	Interference with	Analyte correction isotope
Al	100	^{43}Ca, ^{44}Ca	^{40}Ca
Ca	300	^{57}Fe	^{56}Fe[b]
		^{58}Ni, ^{60}Ni, ^{61}Ni	—
		^{64}Zn	^{66}Zn
		^{65}Cu	^{63}Cu
		^{82}Se	^{78}Se
Fe	250	^{58}Ni	^{60}Ni
Mg	100	^{57}Fe	^{56}Fe
		^{64}Zn, ^{66}Zn	^{68}Zn
		^{65}Cu	^{63}Cu
Na	250	^{63}Cu	^{65}Cu
P	100	^{47}Ti	—
K	100	^{55}Mn	—
S	100	$^{48 \text{ to } 50}$Ti	^{47}Ti
		^{64}Zn, ^{66}Zn	^{68}Zn
		^{65}Cu	^{63}Cu
		^{82}Se	^{78}Se
C	200	^{45}Sc	—
		^{52}Cr	^{53}Cr
Cl (as NaCl)	2 000	^{51}V	—
		^{52}Cr, ^{53}Cr	—
		^{75}As	—
		^{77}Se	^{78}Se
Mo	2	$^{111 \text{ to } 114}$Cd	—
Ti	2	^{63}Cu, ^{65}Cu	—
		^{64}Zn, ^{66}Zn	^{68}Zn

a	See Annex A.
b	^{56}Fe can interfere with ^{40}Ca^{16}O without the application of a CRC.

6.3.4 Interferences in the interface or lens area

In the lens area, the separation of positive and negative charged particles (positive ions and negative electrons) occurs. The positive ions are focused through the lens area but repel each other and some deviate from the optimum path through the lens area and do not reach the detector (space-charge effect). Ions of the light elements in the presence of a large number of ions of a heavy element are repelled more than in the inverse situation and so suffer more from matrix effects.

6.3.5 Possible elimination strategies for non-spectral interferences (matrix effects)

6.3.5.1 General

Six different approaches for the reduction of matrix effects are discussed in 6.3.5:

— matrix-effect reduction by matrix matching;

— matrix-effect reduction by the use of reference elements (internal standards);

— matrix-effect reduction by modification of plasma conditions;

— matrix-effect reduction by aerosol dilution;

— matrix-effect reduction by using analyte addition (standard addition technique);

— matrix-effect reduction by using isotope dilution.

6.3.5.2 Matrix-effect reduction by matrix matching

The basic approach to reducing the matrix effects in ICP-MS is the use of matrix matching, i.e. making the composition of the calibration solutions equal to the composition of the test sample solutions (concentrations of main components). However, for practical reasons (e.g. if there is a widely varying matrix), this is only feasible for the chemicals, such as acids, used in the sample preparation step(s). Both type and concentration of acid should be the same for the calibration and test sample solutions. To prevent possible drift, this also holds true for the rinse solution aspirated between measurements. Even when the matrix has a fixed composition and matrix matching is feasible, this approach still poses a risk for two reasons:

a)   chemicals (e.g. salts) added to a trace-element calibration solution can be contaminated with the analyte(s);

b)   can give rise to spectral interferences.

For these reasons, in most cases it is advisable to add only small amounts of matrix components to this solution. For As and Se, ethanol, isopropanol or other organic, water-soluble substances can be added (see 6.3.3) to match the content of carbon of the test solutions, but users should be aware of possible carbon-induced spectral interferences, for example, interference on ^{52}Cr from ^{40}Ar^{12}C and ^{40}Ca^{12}C polyatomics.

Other forms of matrix matching include:

— equilibrating the test sample solutions to room temperature when they are stored below room temperature;

— removing dissolved gas by bubbling with an inert gas, such as nitrogen or argon, by means of boiling or heating in a water bath or by ultrasonic vibration;

— dilution of the test sample solution.

6.3.5.3 Matrix-effect reduction using reference elements (internal standards)

The second approach to reduce matrix effects is the use of the reference element technique (see 8.5). A fixed concentration of a reference element is added to all solutions to be measured and the analyte signal is divided by the signal of the reference element. All further calculations are carried out using this ratio. The reference element technique is used in almost all ICP-MS work. In practice, the signal (cps) in most software is first corrected for spectral interference using formulae for the elements (although if CRC technology is used the need for formulae is strongly reduced) prior to calculating the intensity ratio.

The term "reference element" is a synonym for the frequently used term "internal standard".

The assumption behind this approach is that the reference element signal is influenced by the matrix in the same way as the analyte signal, resulting in a stable ratio. This assumption is acceptable for matrix effects related to the transport of the (liquid) solution to the nebulizer and the formation of the aerosol and/ or transport of the aerosol to the plasma, as this influences the analyte and the internal standard to the same extent. However, for matrix effects in the plasma, the assumption is not always accurate. In practice, the largest matrix effects (reductions) are observed for elements with high first ionization potentials, for example Zn and Cd with first ionization potentials (IP1s) of 9,4 eV and 9,0 eV, respectively. This is because these elements are only partly ionized in the plasma, which means the degree of ionization is very sensitive to, for example, changes in plasma temperature. On the other hand, in the presence of carbon, large positive matrix effects can be observed for other hard-to-ionize elements, for example As and Se (see 6.3.3), elements which also have a high first ionization potential. This "carbon enhancement effect" can have a huge effect

on results for carbon rich samples and is handled better by combined matrix matching (see 6.3.5.2) and internal standard correction than by internal standard correction alone.

The sample and the internal standard solutions are usually pumped by two channels, which join before the nebulizer through a Y-tube (see 8.5). In some cases, however, a more accurate correction can be obtained if the internal correction is added directly to the sample tube. For example, if the internal standard is added before digestion, the filling up to known volume does not need to be very accurate, because the internal standard corrects for the volume differences.

Generally, internal standards shall be chosen to fulfil the following criteria as much as possible.

a) The internal standard shall not induce spectral interferences on any analytes that need to be reported.

b) The natural content of the internal standard elements in the samples shall be negligible.

c) Mass of the internal standard shall be the same as the analyte, in order to minimize the differences in mass-dependent matrix effects and mass-dependent drift.

d) The IP1 of the internal standard shall be as close as possible to IP1 of the analyte to match the degree of ionization of the analyte.

The following elements are among the most often used: ^{6}Li, Be, Sc, Ga, Ge, Y, Rh, In, Cs, Pr, Tb, Ho, Re, Ir, Bi and Th.

Selection of internal standards in practice, however, is often a compromise, as in many situations the ideal internal standard does not exist. For example, for Zn, Ir and Te are both good candidates with regards to IP1, but not good with regard to mass. Ge is good with regards to mass (and is often used for Zn), but IP1 is not high enough to be a perfect match for Zn.

The perfect match for a given analyte – with regard to criteria 3 and 4 – is another isotope of the same analyte, as different isotopes show identical chemical behaviour. But criterion 2 is often impossible to fulfil in practice, because isotope-enriched standards normally contain the natural isotope(s) in non-negligible amounts (e.g. ^{6}Li). This problem, however, can be handled by isotope dilution (see 6.3.5.7).

In practice, typically three to five internal standard elements are chosen. For example, ^{45}Sc for low masses (up to 55 amu to 60 amu), ^{69}Ga or ^{72}Ge for low-mid-range masses (up to 80 amu to 90 amu), ^{103}Rh or ^{115}In for mid-range masses (up to 140 amu to 150 amu) and ^{193}Ir for the high-mass region (up to about 240 amu). Although ^{45}Sc suffers from some potential disadvantages [precipitation or sorption problems in the sample-introduction system, interference from carbon and silicon polyatomic ions (see Annex A), possible interference from an adjacent high ^{44}Ca signal from solutions with high calcium concentrations], it is often used for the low mass region for lack of any better candidate.

When the internal standards are selected, the performance of the corrections shall be checked in practice (see 8.5).

For the selection of a reference element for a particular analytical problem, see 8.5.

6.3.5.4 Matrix-effect reduction by modification of plasma conditions

Modification of the plasma conditions (such as the nebulizer gas flow rate and plasma power), sampling depth and sample uptake rate can result in a reduction of matrix effects. Nebulizer gas flow rates and sample uptake rates somewhat below those that give maximum sensitivity can reduce matrix effects at the expense of increased detection limits. See 8.3 for additional information.

6.3.5.5 Matrix-effect reduction by aerosol dilution

A special case of plasma condition modification is called aerosol dilution. The principle is to reduce the nebulizer gas flow and to add instead a dilution gas flow between the spray chamber and the torch. This reduces the matrix load to the plasma, while keeping the total argon gas flow to the plasma unchanged. In this way the sample is diluted with gas instead of dilution liquid, reducing the load of water and matrix from the diluent to the plasma, thereby reducing the level of polyatomics (e.g. oxides) created in the plasma.

6.3.5.6 Matrix-effect reduction by using analyte addition — Standard addition technique

Fixed amounts of analytes are added to all or part of the test sample solutions in one or two increments. The samples are then measured in the normal way using a calibration curve, or the normal calibration can be left out and the concentrations calculated using the results of the addition sets per sample. See an analytical textbook for the procedure.

Average analyte recoveries from a limited number of additions ($n \geq 4$) deviating from 100 % are used to correct the results of a larger number of samples with a fixed composition (e.g. blood samples).

6.3.5.7 Matrix-effect reduction by using isotope dilution

A fixed and known amount of an enriched analyte isotope is added to the test sample solution and the isotope ratio of two isotopes (including the added one) is determined before and after the addition, after which the analyte concentration can be calculated. Isotope ratios are not affected by matrix effects, so a very accurate determination of the concentration is feasible. The procedure can be used only when at least two non-interfered isotopes are available. This limits the application of isotope dilution in quadrupole ICP-MS to specific cases. Wider applicability is possible with high-resolution instruments. See analytical textbooks for procedures.

7 Adjustment of the apparatus

7.1 General

In Clause 7, choices for the adjustment of the following instrumental parameters are discussed: alignment of the plasma, mass calibration and resolution of the spectrometer and settings of detector, lens(es) and plasma gas flow rate. Optimization of the remaining parameters, plasma power, sampling depth (distance between torch and tip of sampling cone), auxiliary and nebulizer gas flow rate and sample introduction speed is part of the method development and is discussed in Clause 8.

Before the plasma is started, it is advisable to visually check certain parts of the instrument: the torch for cleanliness, particularly of the introduction tube, the cones for excessive deposits and the tubing of the peristaltic pump for flatness. Cones should be cleaned when deposits are considered excessive, when the sensitivity is too low or when the concentration of polyatomic and/or doubly charged ions is too high. Cleaning of the cones is usually done with a cotton swab moistened with demineralized water or diluted nitric acid followed by rinsing with water and drying. Cleaning with an abrasive agent should be avoided.

The manufacturer's recommendations shall be followed, such as observing the required laboratory environment conditions, power, water, exhaust requirements, switching on the instrument and warm-up time.

7.2 Tuning the apparatus

7.2.1 General

The tuning of the instrument (optimization for best performance) is started using default or recommended settings for plasma power, sampling depth, gas flow rates and sample introduction rate. (The plasma gas flow rate is set at a fixed value and is not optimized at all.) Lenses should be roughly set to obtain a reasonable sensitivity. They are adjusted in a later stage after the other parameters are set. Tuning of the parameters mentioned in 7.1 automatically or manually (one by one) shall be carried out according to the manufacturer's recommendations, usually while aspirating a prescribed element solution. State-of-the-art software on instruments allows an "autotune," the simultaneous automatic optimization of a great number of specified instrumental parameters with targets to be reached, such as a minimum sensitivity or interference levels by oxides below a certain maximum, and ranges in which the parameters can be varied.

The different parameters are discussed in detail in 7.2.2 to 7.2.5.

7.2.2   Alignment of the plasma

After cleaning or replacing the cones, torch or nebulizer, the central channel of the plasma shall be aligned with respect to the opening of the sampling cone for optimum sensitivity.

7.2.3   Mass calibration

The mass scale of the instrument is calibrated while aspirating an optimization solution containing three to five elements covering the full mass range. He (present in air) can also be used for the low-mass area. For quadrupole mass spectrometers, the difference between measured and exact mass should be less than 0,05 amu. For elements measured in the high-resolution mode with a high-resolution instrument, separate mass calibrations should be carried out. This calibration should be checked frequently and available software routines should be used to compensate for drift during an analytical run. For the other situations, the mass calibration should be checked frequently and adjusted when necessary.

7.2.4   Resolution

For normal measurements on quadrupole instruments, the resolution, usually characterized by the peak width at 5 % or 10 % of the peak height (see 5.7.4), should be set at 0,7 amu. For special situations such as the interference by doubly charged ions, the resolution can be reduced to, for instance, 0,2 amu. The resolution should be checked regularly and adjusted when necessary.

NOTE   In ISO 17294-2, the resolution is defined as the peak width at 10 % of the peak height. Both definitions are suitable.

When working in the high-resolution mode on a high-resolution instrument (see 5.7.6), the resolution should be checked more frequently, at least on a daily basis.

7.2.5   Detector

7.2.5.1   General

Adjustment of the detector involves several steps that are outlined in 7.2.5.2 to 7.2.5.6.

7.2.5.2   Discriminator voltage

The discriminator voltage is a threshold value that cuts off the background noise in the analyte signal. Only real pulses are then counted. Typical values are between 10 mV and 70 mV.

7.2.5.3   Detector high voltage

The (negative) detector high voltage for the pulse count mode (see 5.7.5) is normally set at the level where the rate of increase of the count rate with voltage starts to diminish. Setting the high voltage too high results in a significantly reduced lifetime of the detector. For some instruments, the high voltage for the analogue mode (see 5.7.5) shall be set separately. For others, this voltage is set during the dual detector calibration (see 7.2.5.5).

7.2.5.4   Dead time correction

The dead time (see 5.7.5) can be factory-set or it shall be set by the operator. For the determination of the isotope ratio with high-resolution mass spectrometer, the dead time shall be set by the operator.

7.2.5.5   Dual-detector calibration

During the dual-detector calibration, the measurements in the pulse-count mode for the lower concentration range and in the analogue mode for higher concentrations are harmonized, which means that the readings of the analogue mode are converted to counts per second using appropriate conversion factors that vary over the mass range. This results in a single linear calibration curve over the full dynamic range (8 to 11 orders of magnitude). A dual-detector calibration should be carried out for all elements that can possibly be

measured in the analogue mode (also for the interfering components used in the formulae for the elements) and repeated when the pulse-count detector high-voltage is changed (see 5.7.5). The calibration should be checked whenever the instrument is used.

7.2.5.6 Lenses

For lens systems consisting of one lens, the voltage of which can be ramped for optimum sensitivity when scanning the mass range, the optimization is usually carried out with a solution containing three elements of low to medium mass. A voltage-ramp curve is then obtained giving voltage settings for every mass.

An autotune option (see 7.2) is often available for optimization of the lens settings for multi-lens systems. A multi-lens system offers more flexibility to adapt the response over the mass range to specific needs, for instance a relatively low sensitivity for the low-mass range to be able to measure elements such as Na in a higher concentration range. After being set to optimum sensitivity, these lens systems should be optimized for the best precision of the analytical signals over the mass range.

Lens settings should be checked on a regular basis, especially those for the single-lens systems. Because of the low voltages applied in these systems, they are somewhat more sensitive to deposits when aspirating solutions containing high concentrations of dissolved solids and require more frequent checking and possibly cleaning.

7.3 Verification of instrument performance criteria

After choices have been made (see Clause 8) regarding the type of measurement (cool plasma conditions with the use of the shield torch option or not), the plasma power, auxiliary and nebulizer gas flow rates, sample introduction speed and sampling depth, the instrument performance is verified with respect to sensitivity, precision and background over the mass range and with respect to the concentration of oxides and doubly charged ions (see 6.2). Instrument performance verification is also done on a daily basis prior to the actual analysis of samples. The specifications of the manufacturer shall be met for this performance. Minor adjustments of the nebulizer gas flow rate are allowed at this stage to minimize the levels of oxides and doubly charged ions.

8 Preparatory steps

8.1 General

Method development for instrumentation with a standard quadrupole mass spectrometer without the use of the cool plasma option is described in 8.1 to 8.7. The cool-plasma option is dealt with in 8.8.

Method development consists of the following steps:

— choice of isotopes of elements to be determined;

— choice of settings for the following:

　— plasma power;

　— sampling depth;

　— nebulizer gas flow rate;

　— sample uptake rate;

　— pump programme with respect to rinse times, pump hose diameter, etc.;

— choice of integration time of the different isotopes;

— selection of reaction gas in collision mode if appropriate and optimization of flow rates;

— choice of reference elements;

— choice of composition of calibration solutions, i.e. which elements to combine and the concentrations of these elements;

— determination of maximum allowed concentrations of matrix elements with respect to interferences (both spectral and non-spectral).

When the method development is completed, the performance of the full method is documented with respect to the following aspects: instrument and method detection limits, precision of measurements at higher concentration levels and working range for analytes and matrix components.

8.2 Choice of isotopes

In general, it is advisable to measure analyte elements at two different isotopic masses (for elements with more than one isotope): one mass number for quantification and the other mass number for control purposes in case of the need for confirmation. However, very often the control mass number is subject to more interferences than the quantitative mass number. Therefore, care shall be taken when judging the results of this procedure. Next, it is advisable to also measure the matrix elements with regards to possible spectral interferences, especially for samples of unknown or widely varying matrix composition.

Annex A gives an overview of isotopes that can be used for quantitative analysis, including recommendations for specific circumstances. Selection of isotopes is made based on the required detection limit and expected spectral interferences. To check for these interferences, a solution containing the interferent(s) at a concentration of 1,5 to 2 times the highest concentration expected in the samples should be analysed and the result compared with that of the blank. See Table 1 for example compositions of these interference check solutions and how to judge the results.

Limits shall be set for the maximum allowed concentration of the interfering elements in the samples in relation to the detection limits (see 8.9.3) required by the method. The interferences, whether or not corrected, shall be lower than the method detection limits required for the element of interest. In cases where the actual interference element concentration exceeds the maximum allowed concentration, a different isotope shall be used for quantification of confirmation.

For example, the interference by molybdenum (Mo) (the maximum acceptable concentration in the interference check solution is 2 mg/l) shall not exceed the method detection limit of ^{111}Cd - ^{114}Cd (e.g. 0,1 µg/l). The concentration of Mo in the sample solution shall not exceed 2 mg/l to report a method detection limit of 0,1 µg/l.

The actual level of relevant interferences should be checked for every analytical run (see 9.4).

8.3 Choice of instrumental settings

Instrumental settings are chosen so as to result in the optimum performance of the instrument. However, optimum performance, including the selection of reaction gases in CRC mode, has different aspects:

— maximum signal-to-background or signal-to-noise ratio for the lowest instrumental detection limits;

— minimum standard deviation (measured with higher concentrations);

— minimum spectral interferences;

— minimum matrix effects;

— maximum (long-term) stability;

— minimum measuring time.

Often these goals are conflicting. Optimization of one aspect results in degraded performance in another respect. The question of which optimization needs to be performed depends on the purpose of the determination and on the requirements the results comply to. The optimum measuring conditions differ for the various elements and their isotopes and they also depend on the matrix of the test sample solution. It can, therefore, be necessary to determine the optimum measuring conditions for each isotope in the concerned matrix.

For multi-element analysis, however, it is generally necessary to seek the best compromise.

In many cases, the standard conditions prescribed by the manufacturer can be used.

Some general remarks can be made about the effects of changing the instrumental parameters mentioned in 8.1.

Increasing the plasma power results in a hotter plasma and, depending on the ionization potential of the element involved, more or fewer ions are formed with corresponding effects on the signal. For ions with a low ionization potential, fewer ions are formed; the opposite holds for ions with a high ionization potential. The background caused by polyatomic ions, such as ArH^+ (K), ArN^+ (Mn) and ArO^+ (Cr, Fe), also changes. In addition, the Ni background related to the cones increases with a hotter plasma. When analysing samples with a heavy matrix, the cones are coated with a deposit, reducing the Ni background. A hotter plasma results in a shorter time for burning away this deposit, resulting in a more variable Ni background. On the other hand, a hotter plasma is considered more robust, possibly giving smaller matrix effects. The use of platinum-tipped cones can be considered.

An increase in the nebulizer gas flow rate results in an aerosol of higher density, bringing more analyte into the plasma, but also cooling the plasma. This increases the sensitivity of elements with a low ionization potential. The auxiliary gas flow rate is usually set at the value recommended by the manufacturer or is fixed.

Sampling depth is either fixed or set at a compromise setting.

Sample uptake rate should preferably be set as low as possible to reduce the water load of the plasma (see 6.2.2) and to reduce matrix effects (6.3.5.4) but can be higher in case of the need for increased sensitivity.

The rinsing time between two solutions shall be chosen in such a way that there is no "memory effect", for instance an increase in the results of measurement caused by carry-over of the analyte from the previous solution. Additionally, before starting a measurement, a new solution shall be nebulized for a sufficient time to enable the attainment of a (constant) maximum value. Memory effects are minimized by minimizing the sample-tubing length and using an optimum pump programme. This programme can contain a rapid rinse step (up to five times the normal pump speed) or loop injection, followed by a stabilization period at normal pump speed. The pre-measurement stabilization time is optimized while monitoring the coefficient of variation (s_{rel}) of the measurement of a calibration solution (three replicates). This s_{rel} should be close to the minimum attainable value, while minimizing the pre-measurement sample-uptake time.

Memory effects after the measurement of a sample or a calibration solution are quantified by the measurement of a blank after the measurement of the highest calibration solution. The result for the blank should then be below the method detection limit (see 8.9.3). For the reduction of memory effects of Hg, Au (in HCl as $AuCl_3$) can be added to all solutions (including the rinse solution) at a concentration of 0,2 mg/l to 5 mg/l. For B, mannitol or ammonia can be used.

8.4 Choice of integration time

Prolonging the integration time (see 5.8) generally improves precision, lowers the limit of detection and reduces the influence of short-term fluctuations (the extent of these improvements depends on the type of nebulizer). The measurement time is lengthened, however, and the influence of long-term fluctuations becomes greater.

The integration time shall be a compromise dependent on the requirements that the analysis results shall meet. Typical integration times are between 0,3 s and 1,0 s; however, somewhat longer times are usually used for elements like As, Se, Cd and Hg with low-sensitivity or low-detection-limit required. Integration times longer than 5 s are usually not beneficial.

Each measurement should preferably be carried out at least in triplicate (three replicates). This provides an ongoing indication of the precision, which should be the equivalent of 1 % to 2 % s_{rel} of the instrument output signal for higher concentration levels.

8.5 Choice of reference elements — Internal standards

Reference elements are used in ICP-MS to compensate for matrix effects and drift and they are used in almost all cases. An improvement in precision is a beneficial side effect. See 6.3.5.3 for the requirements for reference elements and for suggestions regarding which elements to use as reference elements.

The choice of the proper reference element can be made in three ways:

— by monitoring the ratio of the analyte signal and the signal of a particular reference element, first for the situation without matrix and then in the presence of matrix;

— by determining the recovery of an analyte addition to samples with high matrix concentrations (see 9.3);

— by analysing (certified) reference materials or samples with a known composition.

The reference element that shows the least reduction in the ratio and/or that gives the best recovery (closest to 100 %) in the presence of the highest matrix possible is, in principle, the best reference element for the analyte element involved [recovery is calculated as the ratio of net measured spike concentration and the spike concentration or as the ratio of measured value and certified value]. There is, however, another requirement for a reference element: the closeness of the mass to that of the analyte element (6.3.5.3). Usually, this aspect is important in assessing the presence or absence of drift in a measurement sequence. Most software allows the selection of other reference elements for a particular set of analytical data and reprocessing these data with the new element. In addition, the reference element shall not be present in any of the samples at a significant concentration.

Reference elements can be added to the solutions prior to the measurements or "online" by means of a two-channel sample-introduction pump. Discrete addition is rather time-consuming in contrast to online addition. In the latter approach, the solution to be measured and the solution containing the reference-element(s) are mixed by means of a Y-piece, with or without a mixing coil, and the mixture is subsequently transported to the nebulizer. Mixing ratios may vary between 10 + 1 and 1 + 10 (sample to reference-element solution). The latter ratio results in online dilution of the samples. Usually, limited online dilution results in only very minor effects on the method detection limits, because they are mostly determined by the ratio of an analyte signal and the signal of a polyatomic ion(s) (most analytes are interfered) (see 8.9.3), and this ratio will not alter because of dilution. However, matrix effects are reduced because of this online dilution.

The use of a mixing coil gives better mixing, resulting in a reduction of matrix effects at the expense of an increased wash-out time. When using online dilution, a smaller-diameter sample probe and tubing should be used, for example with 0,3 mm internal diameter. If the internal diameter of pump tubes is too small, it will take too much time to reach the plasma when having set up an online dilution with pump tubings. If the diameter of the sample probe or tubing is too wide, it will take longer to reach the plasma.

8.6 Linearity and working range

The technique itself shows linear calibration curves up to nine orders of magnitude of the signal due to the use of a dead time correction in the pulse-count mode (see 5.7.5) and dual-detector calibration for the analogue/pulse-count mode together. Calibration solutions prepared from a multi-element calibration stock solution can induce dilution-dependent matrix effects, resulting in pseudo nonlinearity. These matrix effects are compensated for by the use of reference element(s). Linearity is checked in every measurement series.

The selection of the highest concentration in the calibration solutions depends mostly on the required method detection limits (see 8.9.3 and the remark on the effective concentration range at the end of 8.3). With respect to the interferents, the maximum concentration levels should be set related to the required method detection limits.

Due to significant memory effects, the effective concentration range in practice (ratio of the highest concentration that can be measured to the lowest one or to the method detection limit) is typically up to 2 000 except for, for example, Ag, B, Hg and Mo, which can be much lower. The memory effect shall be determined for each set up of the instrument or method.

The maximum total concentration of dissolved solids in the test sample solutions is typically 1 g/l to 2 g/l. Higher concentrations can lead to blockages of the sample cones and to other technical problems.

8.7 Composition of calibration solutions

Because of frequent polyatomic ion interferences originating from matrix elements (see Annex A), trace element calibration solutions are preferably prepared with no or only low concentrations of matrix elements (6.3.5.2). Matrix matching is applied for the acids used in, for example, samples (6.3.5.2). In addition, contamination plays a role in choosing the element combinations for calibration solutions (e.g. Sr and Ba are often present in Ca stock solutions). Finally, for stability reasons, some element stock solutions contain hydrochloric acid. Even when diluted, these elements are stable only in this acid, which gives rise to Cl^- based polyatomic ion interferences.

All these factors shall be considered when choosing combinations for multi-element calibration solutions. All solutions shall have a use-by date.

In practice, this results in one calibration solution with several trace elements having a low concentration and two or more macro-element solutions (see 9.2 for the number of calibrations over the measurement range). One or more elements (e.g. Zn) can be added both to the trace-element solution and to the macro-element solution with the heaviest matrix, preferably at the same concentration. As, for example, Zn is affected by many matrix elements (see 6.3.3), one glance at the calibration graph for Zn will supply direct information on the actual level of matrix effects of the system. Both results should be comparable.

After preparation, calibration solutions should be monitored over time with respect to possible precipitation and stability aspects.

8.8 Method development for cool plasma conditions

Until recently, the determination of trace and ultra-trace quantities of alkali metals and alkaline earth metals by quadrupole ICP-MS has been susceptible to both plasma- and matrix-related polyatomic interferences, which compromise the detection limits achievable for these elements. This has led to the development of the PlasmaScreen^{TM} Torch or Shield Torch$^{TM3)}$ and the application of cool plasma conditions, enabling trace analysis of elements that suffer from molecular interferences arising from the combination of the plasma gas (Ar) with matrix analytes. For example, the determination of ^{56}Fe, ^{39}K and ^{40}Ca has been limited by interference from $^{40}Ar^{16}O$ on ^{56}Fe; ^{40}Ar, from ^{40}Ca; and $^{38}Ar^{1}H$, from ^{39}K. The cool plasma reduces or even eliminates many of these traditionally troublesome polyatomic interferences that limit the capabilities of ICP-MS in the analysis of the low-mass (<80 amu) elements. These interferences can also be overcome by use of CRC.

In the PlasmaScreen^{TM} Torch or Shield Torch^{TM} option, a grounded metal screen is inserted between the load coil and the plasma torch. This eliminates the potential secondary discharge between the sample cone orifice and the plasma. Cool plasma conditions are achieved by lowering the RF power to 620 W, resulting in a plasma temperature of 2 500 K to 3 000 K. This reduces the ionization within the central channel of the plasma, which results in significantly lower production of Ar-*X* molecular species and a decrease in sensitivity for most elements. However, the decrease in sensitivity of analyte ions is more than compensated for by a large reduction in background spectra (typically <1 cps per mg/l), resulting in an improved signal: noise ratio for many elements.

This plasma configuration is used mainly for the determination at ultra-trace concentrations of a few elements (Li, Na, K, Ca and Fe) in the semiconductor industry but never for environmental analysis.

8.9 Determination of the method performance

8.9.1 General

In the determination of the method performance, the following parameters are assessed: instrument and method detection limit and the precision. Subclauses 8.9.2 to 8.9.4 refer primarily to quadrupole ICP-MS instruments but can be extrapolated to CRC instruments.

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3) PlasmaScreen Torch and Shield Torch are examples of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

8.9.2 Instrument detection limit

The instrument detection limit, L_{DI}, indicates the concentration of a given element using the instrument in the most optimal set-up, that can be detected with a given uncertainty in a solution that causes minimal spectral interferences (e.g. diluted nitric acid of high purity). Optimal instrument set-up also means here that the instrument shall be as clean as possible (sample introduction system and torch, cones and lenses).

This instrument detection limit can be determined as follows (after cleaning the instrument): using a calibration function, measure a blank solution containing matrix matched acid with the chosen system set-up (see 8.4) and sufficient (e.g. 10) replicates. Establish the standard deviation, s_r, of results. The instrumental detection limit is usually calculated as three times s_r.

The L_{DI} is mostly determined by the background (for a particular analyte isotope), the abundance and the degree of ionization (see 6.3.3). For example, Fe has a high L_{DI}, because all relevant iron (Fe) isotopes have a high background ($^{40}Ar^{14}N$ for ^{54}Fe, $^{40}Ar^{16}O$ for ^{56}Fe and $^{40}Ar^{16}O^1H$ for ^{57}Fe) (see also 8.8). Also, the lower the abundance and the lower the degree of ionization (the higher the ionization potential), the higher the L_{DI}. The L_{DI} can be very low ($\leq$1 ng/l) for some elements.

8.9.3 Method detection limit

The method detection limit, L_{DM}, is in many cases primarily determined by spectral interferences, whether corrected or not. The maximum concentration of those matrix elements that causes interferences determines the L_{DM} attainable and the required L_{DM} determines the maximum allowed matrix element concentration. The method detection limit should be determined by measurements of the interference check solutions or an ICS mix including digestion when appropriate.

The L_{DM} also shall include possible memory effects and the effects of variable contamination of the containers (test tubes) from which the test sample solutions are aspirated. When these effects play a role, the L_{DM}, which is higher than the L_{DI}, shall be adapted.

8.9.4 Precision of the method

The precision of the method is determined for at least one concentration of the analyte, sufficiently high so that the measured relative standard deviation is independent of further increases in concentration ($\rho \geq 50 \times L_{DM}$). A representative test sample solution with high concentrations of matrix elements is measured on a sufficient number of days. The precision of the method is the coefficient of variation (srel, $\rho \geq 50 \times L_{DM}$) of the mean result.

9 Procedure

9.1 General

This clause describes the normal calibration and the actual measurement of the test sample solutions. When unacceptable and uncorrectable matrix effects are observed, analyte (standard) addition can be applied (6.3.5.5); that will not correct for spectral interferences.

9.2 Calibration

Satisfying results are obtained with a two-point calibration: a blank calibration solution and a calibration solution for the upper point of the measurement range for a concentration range of a few orders of magnitude. Multiple calibration solutions (minimum five points) are recommended in case of more orders of magnitude measurement range (see ISO 8466-1). Multi-level calibration and standard least-squares fitting can lead to wrong results because of the inhomogeneity of the variances of the measurements of the calibration solutions over the concentration range. This approach leads to errors at the low end of the calibration curve (multiples of the L_{DM}), unless weighted linear regression is used instead of the standard least-squares fitting. (Weighted linear regression is based on the principle that the weighing factor is inversely proportional to the standard deviation of the measurement of the calibration solution.)

In practice, weighed linear regression is hard to carry out properly because the standard deviation needs to be known at every concentration involved.

A prerequisite for good results with a two-point calibration is the accurate preparation of the solutions involved. The blank calibration solution is checked against an independent calibration check solution or by the analysis of reference solutions.

Guidance on the linear calibration and evaluation of analytical methods is provided by ISO 8466-1. Some form of weighing can be used where appropriate.

To minimize the risk of contamination, calibration solutions are preferably made by pouring the stock solutions out of screw-capped bottles or pipetting and weighing. This approach is preferred over the use of volumetric flasks, because it is hard to keep the rims of these flasks free of analyte.

9.3   Necessary solutions

The following solutions are prepared:

— CB (calibration blank solution, usually containing only the acid and reference elements added to the test sample solution);

— CST (calibration solution for trace elements, see 8.7);

— CSM_{1-n} (calibration solution for macro-elements, see 8.7);

— ICS_{1-m} (interference check solution(s), see 6.3.2, Table 1, numbered 1 to m);

— CCV [continuous calibration verification solution which contains all analytes (if possible, without the risk of precipitation)] at, for example, half the concentration of the calibration solutions but independently prepared; it is used to check the initial calibration and after several test sample solutions have been measured; the actual concentrations shall be put into the quality control software of the computer of the instrument, which means, for the trace elements, the added amount plus the possible contamination originating from the macro-elements stock solutions;

— LCS (laboratory check solution, which can be a representative test sample solution with known concentrations, or a (certified) reference material whose nature and composition corresponds as far as possible with those of the test samples; guidance is given in ISO Guide 30 and ISO Guide 33; the LCS can be used as a calibration check solution (see 9.2);

— TS (test sample solutions);

— CCB (reagent blank solutions).

— procedural blank.

9.4   Measurement

The analyses are carried out in the following sequence:

— conditioning the system (cones) using a suitable matrix solution for 10 min to 15 min;

— CB (to check for memory);

— Cal block 1: CB, CST, CSM_1 (containing macro-elements with the highest concentrations);

— CB (to check for memory);

— Cal block 2-n: CSM_{2-n};

— ICS block: ICS_{1-m} solutions (all or only relevant ones) or ICS mix; update of elemental formulae when necessary;

— sample block: TS;

— CCB, CCV;

— ICS block: ICS solutions (all or only relevant ones) or ICS mix; no update.

In the sample block, for every 10 to 20 samples, the CCV block is measured: CCB, CCV. Update of calibration (measurement of CST, CSM_{1-n}) can be done every time (preferred) or only after CCV-fail. LCSs and addition pairs are measured spread through the sample block.

Annex A
(informative)

Spectral interferences, choice of isotopes and instrument detection limits for quadrupole ICP-MS instruments

A.1 General

This annex gives an overview of possible spectral interferences.

An overview of the available isotopes, detection limits and relevant interferences in ICP-MS is given in Table A.1.

Table A.1 — Spectral interferences, choice of isotopes and instrument detection limits for quadrupole ICP-MS instruments

Element	Isotope	Abundance	Instrument detection limit[a]	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Inter-element	Polyatomic ions		Preference	Reason
		%	µg/l					
Ag	107	51,8	0,02	–	ZrO, YO	$^{91}Zr^{16}O$	x	least interference
	109	48,2	0,02	–	ZrO, ZrOH, NbO	–	–	–
Al	27	100	5	–	BeO, BO, CN, HCN	–	x	–
As	75	100	0,05	Sm^{2+}, Eu^{2+}, Nd^{2+}	ArCl, CoO, Ar_2H, ArK, CaO_2, NaCAr, CPO_2, CaCl	$^{40}Ar^{35}Cl$	x	–
Au	197	100	0,01	–	HfO, TaO	–	x	–
B	10	19,9	1	–	–	–	x	free of interference, low background
	11	80,1	1	–	BH	–	–	–
Ba	135	6,6	1	–	–	–	–	–
	137	11,2	1	–	–	–	x	highest abundance, least interference
	138	71,7	0,1	La, Ce	–	La, Ce	–	–
Be	9	100	0,1	–	–	–	x	–
Bi	209	100	0,1	–	–	–	x	–
Ca	43	0,14	20	Sr^{2+}	MgO, BO_2, AlO, CaH, CNO, CO_2	Sr^{2+}	x	low background, least interference
	44	2,1	10	Sr^{2+}	CaH, MgO, AlO, BO_2, CNO, SiO, CO_2, N_2O	Sr^{2+}, $^{12}C^{16}O_2$	–	lowest detection limit
Cd	111	12,8	0,05	–	MoO, MoOH, ZrOH, K_2O_2H	$^{94}Zr^{16}O^1H$, $^{95}Mo^{16}O$	–	–
	113	12,2	0,05	In	MoO, ZrOH, Ca_2O_2H, Ar_2O_2H, RuO	In, $^{97}Mo^{16}O$	x	for high Sn
	114	28,7	0,03	Sn	MoO, MoOH, RuO	Sn, $^{98}Mo^{16}O$	x	lowest detection limit, least interference
Ce	140	88,5	0,01	–	–	–	x	–

[a]   Instrument detection limits (see 8.9.2) are indicative because of instrument-dependent spectral interferences and relate to matrix element concentration at higher levels found in environmental samples (85 percentile).

[b]   The signals of these three isotopes are summed because of the natural variation of individual abundances.

Table A.1 *(continued)*

Element	Isotope	Abundance	Instrument detection limit[a]	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Inter-element	Polyatomic ions		Preference	Reason
		%	µg/l					
Co	59	100	0,2	Sn^{2+}	CaO, CaOH, MgCl, ArNa, ArOH, ArF	$^{43}Ca^{16}O$	x	–
Cr	52	83,8	0,2	–	SO, ArO, ArC, ArN, ClO, HClO, ClN, ArNH	$^{40}Ar^{12}C$	x	for low C and high Cl
	53	9,5	1	–	HSO, ArC, HClO, ClO, ArOH, ArN, ArNH, SO	$^{37}Cl^{16}O$	x	for high C and low Cl
Cs	133	100	0,05	–	RuO_2	–	x	–
Cu	63	69,2	0,1	–	TiO, PO_2, ArNa, MgCl, NaCa, CaOH, ArCNH, NCCl, ClO	$^{47}Ti^{16}O$, $^{40}Ar\text{-}^{23}Na$	x	for low Na and Ti, lowest detection limit
	65	30,8	0,2	Ba^{2+}	TiO, PO_2, SO_2, SO_2H, ArMg, CaOH, ArN_2H, S_2, COCl	$^{49}Ti^{16}O$, $^{32}S^{16}O_2{}^{1}H$, $^{40}Ar^{25}Mg$	x	for medium Mg, S and Ti, and high Na
Dy	163	24,9	0,05	–	NdO, SmO	–	x	–
Er	166	33,6	0,05	–	SmO, NdO	–	x	–
Eu	151	47,8	0,05	–	BaO	–	–	–
	153	52,2	0,05	–	BaO	–	x	–
Fe	54	5,8	10	Cr	HClO, ArO, ArN, ArNH, ArOH, SO, ClO	ArN, Cr	x	abundance and background determine choice
	57	2,2	20	–	CaO, ArO, ArOH, CaC, CaN, CaOH, MgO_2, ArF	$^{40}Ar^{16}O^{1}H$, $^{40}Ca^{16}O^{1}H$	x	abundance and background determine choice
Ga	69	60,1	0,1	Ce^{2+}, Ba^{2+}, La^{2+}	ClO_2, ArP, VO, ArS, SO_2, S_2	Ba^{2+}	–	–
	71	39,9	0,1	Nd^{2+}, Ce^{2+}	ArP. ClO_2, ArCl, SO_2, ArS, CrO	–	x	least interference
Gd	157	15,7	0,02	–	CeO, PrO, LaO, BF	–	x	least interference
	158	24,8	0,02	Dy	CeO, PrO, NdO	Dy	–	–
Hf	178	27,3	0,05	–	GdO, DyO, ErO	–	X	–
Hg	200	23,1	0,01	–	WO	$^{184}W^{16}O$	–	–
	201	13,2	0,02	–	WO	$^{184}W^{17}O$	X	least interference with WO
	202	29,9	0,02	–	WO	$^{186}W^{16}O$	–	–
Ho	165	100	0,01	–	SmO	–	X	–
In	115	95,7	0,05	Sn	RuO	Sn	X	–
Ir	193	62,7	0,05	–	HfO, LuO	–	X	–
K	39	93,3	10	–	ArH	–	X	–
La	139	99,9	0,02	–	–	–	X	–
Li	6	7,5	2	–	–	–	–	–
	7	92,5	0,2	–	–	–	X	lowest detection limit
Lu	175	97,4	0,1	Hf	GdO, TbO	Hf	X	–

[a] Instrument detection limits (see 8.9.2) are indicative because of instrument-dependent spectral interferences and relate to matrix element concentration at higher levels found in environmental samples (85 percentile).

[b] The signals of these three isotopes are summed because of the natural variation of individual abundances.

Table A.1 *(continued)*

Element	Isotope	Abundance	Instrument detection limit[a]	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Inter-element	Polyatomic ions		Preference	Reason
		%	µg/l					
Mg	24	79,0	0,5	Ti^{2+}, Ca^{2+}	LiO, NaH, C_2	–	X	lowest detection limit, least interference
	25	10,0	5	Ti^{2+}	LiO, BeO, C_2, C_2H	–	–	–
	26	11,0	5	–	BeO, BO, CN, C_2H_2, C_2H	–	X	for higher Mg concentrations
Mn	55	100	0,5	–	HClO, ArN, ClO, NaS, ArOH, ArNH, KO, ArN, ArO, ArF	ArNH	X	–
Mo	95	15,9	0,5	–	ArKO, BrO	–	–	–
	98	24,1	0,3	Ru	BrO, K2O	Ru	X	lowest detection limit
Na	23	100	10	Ti^{2+}, Ca^{2+}	LiO	–	X	–
Nd	146	17,2	0,02	–	BaO, RuO_3	–	X	–
Ni	58	68,1	0,5	Fe	CaO, ArO, CaN, NaCl, MgS, CaOH, Si_2, ArOH	Fe	X	for low Fe
	60	26,2	0,2	–	CaO, CaOH, MgCl, NaCl	$^{44}Ca^{16}O$	X	least interference
	61	1,1	0,5	–	CaOH, ScO	$^{44}Ca^{16}O^{1}H$, $^{45}Sc^{16}O$	–	–
P	31	100	2	–	SiH, NO, NOH, N_2H, CO, COH	No	X	–
Pb	206[b]	24,1	0,05	–	PtO	–	X	sum of 206, 207 and 208
	207[b]	22,1	0,05	–	IrO	–	x	sum of 206, 207 and 208
	208[b]	52,4	0,02	–	PtO	–	x	sum of 206, 207 and 208
Pd	105	22,3	0,05	–	YO, ArCu	–	–	–
	108	26,5	0,05	Cd	MoO, ZrO	Cd	x	–
Pr	141	100	0,01	–	–	–	x	–
Pt	195	33,8	0,05	–	HfO	–	x	–
Rb	85	72,2	0,05	Yb^{2+}, Er^{2+}	–	–	x	–
Re	185	37,4	0,05	–	TmO, ErO	–	x	least interference
	187	62,6	0,05	Os	TmO, YbO	Os	x	highest abundance
Rh	103	100	0,05	Pb^{2+}	SrO, ArCu, RbO	–	x	–
Ru	101	17,0	0,05	–	ArNi, NiCl	–	–	–
	102	31,6	0,02	Pd	SrO	Pd	x	lowest detection limit, least interference
S	34	4,2	500	–	O_2, SH, NOH, O_2H	O_2	x	–
Sb	121	57,4	0,05	–	PdO	–	x	least interference
	123	47,6	0,05	Te	ZrO	Te	–	–
Sc	45	100	1	Zr^{2+}	CO_2, SiO, BO_2, AlO, CaH, CHO_2, SiOH, N_2OH	$^{13}C^{16}O_2$, $^{29}Si^{16}O$	x	–

[a]   Instrument detection limits (see 8.9.2) are indicative because of instrument-dependent spectral interferences and relate to matrix element concentration at higher levels found in environmental samples (85 percentile).

[b]   The signals of these three isotopes are summed because of the natural variation of individual abundances.

Table A.1 *(continued)*

Element	Isotope	Abundance %	Instrument detection limit[a] µg/l	Theoretical interferences Inter-element	Polyatomic ions	Interference with practical relevance	Preference	Reason
Se	77	7,6	0,5	Sm^{2+}, Gd^{2+}	ArCl, Ar_2H, CaCl, $CFNO_2$	$^{40}Ar^{37}Cl$	x	for low Cl
	78	23,8	0,2	Kr, Gd^{2+}, Dy^{2+}	Ar_2, CaCl, ArCa	$^{38}Ar^{40}Ar$	x	for high Cl and Br
	82	8,7	0,5	Kr, Ho^{2+}, Er^{2+}, Dy^{2+}	Ar_2H, BrH, CCl_2, SO_3, Ar_2H_2, ArCa	Kr, $^{81}Br^1H$	x	for low Br
Si	29	4,7	10	–	CO, N_2, BO, SiH, AlH, COH, N_2H	–	x	–
Sm	147	15,0	0,05	–	RuO_3	–	x	–
Sn	118	24,2	0,2	U^{2+}	MoO, RuO, PdO	–	x	least interference
	120	32,6	0,2	Te	RuO, PdO	Te	–	–
Sr	86	9,9	0,3	Kr, Yb^{2+}	RbH	–	–	–
	88	82,6	0,1	Yb^{2+}, Lu^{2+}	–	–	x	lowest detection limit, least interference
Tb	159	100	0,02	–	NdO, PrO	–	x	–
Te	125	7,1	0,1	–	–	–	x	least interference
	126	19,0	0,2	Xe	PdO	Xe	x	lowest detection limit
Th	232	100	0,1	–	–	–	x	–
Ti	47	7,3	10	Zr^{2+}	NO_2, PO, SiO, CCl, SNH, SiOH, SN, N_2, NO_2H	$^{31}P^{16}O$	x	least interference
	48	73,8	1	Ca, Zr^{2+}	ArC, CCl, SO, NO_2, PO, SN, NN_2, C_4	Ca, $^{32}S^{16}O$	–	–
	49	5,5	–	–	SOH	$^{32}S^{16}O^1H$	–	–
Tl	203	29,5	0,05	–	WO, ReO, WHO	–	–	–
	205	70,5	0,02	–	–	–	x	lowest detection limit, least interference
Tm	169	100	0,01	–	EuO	–	x	–
U	238	99,3	0,05	–	–	–	x	–
V	51	99,8	0,2	–	HSO, ClO, ClN, ArNH, ArC, ArN, SN, SO	$^{35}Cl^{16}O$	x	
W	182	26,3	0,1	–	HoO, DyO, ErO	–	x	least interference
	184	30,7	0,1	Os	ErO, YbO	Os	–	–
Y	89	100	0,1	–	–	–	x	–
Yb	172	21,9	0,1	–	DyO, SmO, GdO	–	x	least interference
	174	31,8	0,1	Hf	DyO, GdO	Hf	–	–
Zn	64	48,6	0,2	Ni	TiO, CaO, PO_2, SO_2, AlCl, S_2, PO_2H, ArN_2, ArMg	Ni, $^{48}Ti^{16}O$, $^{32}S^{16}O_2$, $^{40}Ar^{24}Mg$	–	–
	66	27,9	0,5	Ba^{2+}	TiO, VO, SO_2, PCl, FeC, S_2, SO_2H	$^{50}Ti^{16}O$, $^{34}S^{16}O_2$	x	for medium Ti and S
	68	18,8	0,5	Ba^{2+}, Ce^{2+}	VO, ClO_2, SO_2, TiO, ArS, FeN, PCl, FeC, S_2, ArN_2, ArSi	Ba^{2+}, $^{40}Ar^{28}Si$	x	for low Ba and Si
Zr	90	51,5	0,2	–	–	–	x	–

[a]   Instrument detection limits (see 8.9.2) are indicative because of instrument-dependent spectral interferences and relate to matrix element concentration at higher levels found in environmental samples (85 percentile).

[b]   The signals of these three isotopes are summed because of the natural variation of individual abundances.

A.2 Formulae for the elements

For isobaric interferences (e.g. the interference of ^{114}Sn with ^{114}Cd), the correction factor can in principle be calculated from the abundances of the isotopes involved. However, due to mass-discrimination effects (a different response for the same number of ions of different masses), the following procedure to determine f should be followed.

The number of $^{114}Sn^+$ ions (interference with $^{114}Cd^+$) formed is a fixed ratio fraction of the number of $^{118}Sn^+$ ions by the relative isotopic abundancy, according to Formula (A.1).

$$f_{(114_{Cd})} = \frac{A_{b(114_{Sn})}}{A_{b(118_{Sn})}} = 0,026\,84 \tag{A.1}$$

where A_b is the relative abundance of the isotope.

NOTE   Relative abundance of the isotope can be approximated by (due to mass discrimination effects) net signal intensity, which is obtained by measuring a standard solution of tin and determining the signal of Sn^+ (at mass 114) and Sn^+ (at mass 118) or the mass discrimination factor * f applied in Formula (A.2).

For an unknown sample, the interference can then be calculated by measuring the $^{118}Sn^+$ signal and multiplying this value by f. To obtain the corrected signal for ^{114}Cd, the Sn^+ interference is subtracted from the gross signal at mass 114, according to Formula (A.2):

$$I_{(114_{Cd})} = I_{(114)} - f_{(0,026\,84)} \times I_{(118_{Sn})} \tag{A.2}$$

where I is the net intensity for the mass or the isotope mentioned.

The use of formulae for the elements is based on the assumption that the number of the molecular (and doubly charged) ions formed is a fixed fraction of the number of parent ions present in the plasma. For example, the number of Sr^{2+} ions (interference with $^{43}Ca^+$ and $^{44}Ca^+$) formed is a fixed fraction of the number of Sr^+ ions (the parent ion). With limitations, this is usually the case in practice. By measuring the signal of Sr^{2+} (at mass 44) and of Sr^+ (at mass 88) of a Sr standard solution which does not contain any Ca and dividing the two values, the interference factor f can be calculated. For an unknown sample, the Sr^{2+} interference can then be calculated by measuring the $^{88}Sr^+$ signal and multiplying this value by f. To obtain the corrected signal for ^{44}Ca, the Sr^{2+} interference is subtracted from the gross signal at mass 44, according to Formula (A.3):

$$I_{(44_{Ca})} = I_{(44)} - f \times I_{(88_{Sr})} \tag{A.3}$$

where I is the net signal for the mass or the isotope mentioned.

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