BRITISH STANDARD

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Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) —

Part 1: General guidelines

The European Standard EN ISO 17294-1:2006 has the status of a British Standard

ICS 13.060.50

Confirmed
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British Standards

National foreword

This British Standard was published by BSI. It is the UK implementation of EN ISO 17294-1:2006. It is identical with ISO 17294-1:2004.

The UK participation in its preparation was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, chemical and biochemical methods.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard cannot confer immunity from legal obligations.

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English Version

Water quality - Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 1: General guidelines (ISO 17294-1:2004)

Qualité de l'eau - Application de la spectrométrie de masse avec plasma à couplage inductif (ICP-MS) - Partie 1: Lignes directrices générales (ISO 17294-1:2004)

Wasserbeschaffenheit - Anwendung der induktiv gekoppelten Plasma Massenspektrometrie (ICP-MS) - Teil 1: Allgemeine Anleitung (ISO 17294-1:2004)

This European Standard was approved by CEN on 11 September 2006.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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Foreword

The text of ISO 17294-1:2004 has been prepared by Technical Committee ISO/TC 147 "Water quality" of the International Organization for Standardization (ISO) and has been taken over as EN ISO 17294-1:2006 by Technical Committee CEN/TC 230 "Water analysis", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by April 2007, and conflicting national standards shall be withdrawn at the latest by April 2007.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Endorsement notice

The text of ISO 17294-1:2004 has been approved by CEN as EN ISO 17294-1:2006 without any modifications.

INTERNATIONAL STANDARD

ISO 17294-1

First edition
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Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) —

Part 1: General guidelines

Qualité de l'eau — Application de la spectrométrie de masse avec plasma à couplage inductif (ICP-MS) —

Partie 1: Lignes directrices générales

Reference number
ISO 17294-1:2004(E)

Contents

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 17294-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

ISO 17294 consists of the following parts, under the general title *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS)*:

- *Part 1: General guidelines*
- *Part 2: Determination of 62 elements*

Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) —

Part 1: General guidelines

1 Scope

This part of ISO 17294 specifies the principles of inductively coupled plasma mass spectrometry (ICP-MS) and provides general directions for the use of this technique for determining elements in water. Generally, the measurement is carried out in water, but gases, vapours or fine particulate matter may be introduced too. This International Standard applies to the use of ICP-MS for water analysis.

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

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the reference document (including any amendments) applies.

ISO Guide 30, *Terms and definitions used in connection with reference materials*

ISO Guide 32, *Calibration in analytical chemistry and use of certified reference materials*

ISO Guide 33, *Uses of certified reference materials*

ISO 3534-1, *Statistics — Vocabulary and symbols — Part 1: Probability and general statistical terms*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

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

ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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

ISO 6955, *Analytical spectroscopic methods — Flame emission, atomic absorption and fluorescence — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 5725-1, ISO 6206, ISO 6955 and ISO Guide 32 and the following apply.

3.1
accuracy
closeness of agreement between test result and the accepted reference value

NOTE The term accuracy, when applied to a set of observed values, describes a combination of random error components and common systematic error components. Accuracy includes precision and trueness.

3.2
analyte
element(s) to be determined

3.3
blank calibration solution
solution prepared in the same way as the calibration solution but leaving out the analyte

3.4
calibration solution
solution used to calibrate the instrument, prepared from (a) stock solution(s) or from a certified standard

3.5
check calibration solution
solution of known composition within the range of the calibration solutions, but prepared independently

3.6
determination
entire process from preparing the test sample solution up to and including measurement and calculation of the final result

3.7
laboratory sample
sample sent to the laboratory for analysis

3.8
linearity
straight line relationship between the (mean) result of measurement (signal) and the quantity (concentration) of the component to be determined

3.9
linearity verification solution
solution with a known concentration of the matrix components compared to the calibration solutions, but having an analyte concentration half that of the (highest) calibration solution

3.10
instrumental detection limit
I_{DL}
smallest concentration that can be *detected* with a defined statistical probability using a contaminant-free instrument and a blank calibration solution

3.11
mean result
mean value of n results, calculated as intensity (ratio) or as mass concentration (ρ)

NOTE The mass concentration is expressed in units of milligrams per litre.

3.12
method detection limit
x_{DL}
smallest analyte concentration that can be *detected* with a specified analytical method with a defined statistical probability

3.13
net intensity
I
signal obtained after correction for (poly)atomic ion interferences using an elemental equation

3.14
net intensity ratio
I_R
net intensity divided by the signal of a reference element

3.15
optimization solution
solution serving for mass calibration and for the optimization of the apparatus conditions

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

3.16
precision
closeness of agreement between independent test results obtained under prescribed conditions

NOTE Precision depends only on the distribution of random errors and does not relate to true value or the specified value.

3.17
"pure chemical"
chemical with 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

3.18
raw intensity
I_raw
obtained uncorrected signal

3.19
reagent blank solution
solution prepared by adding to the solvent the same amounts of reagents as those added to the test sample solution and with the same final volume

3.20
reproducibility
R
precision under reproducibility conditions

[ISO 3534-1]

3.21
reproducibility conditions
conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment

[ISO 3534-1]

3.22
reproducibility standard deviation
standard deviation of test results obtained under reproducibility conditions

[ISO 3534-1]

3.23
reproducibility limit
value less than or equal to which the absolute difference between two single test results obtained under reproducibility conditions may be expected to be with a probability of, generally, 0,95

3.24
repeatability
r
precision under repeatability conditions

[ISO 3534-1]

3.25
repeatability conditions
conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within a short interval of time

[ISO 3534-1]

3.26
repeatability standard deviation
standard deviation of test results obtained under repeatability conditions

[ISO 3534-1]

3.27
repeatability limit
value less than or equal to which the absolute difference between two single test results obtained under repeatability conditions may be expected to be with a probability of, generally, 0,95

3.28
result
outcome of a measurement

NOTE The result is typically calculated as mass concentration (ρ), expressed in milligrams per litre.

3.29
sensitivity
S
ratio of the variation of the magnitude of the signal (dI) to the corresponding variation in the concentration of the analyte (dC) expressed by the equation:

$$S = \frac{\mathrm{d}I}{\mathrm{d}C}$$

3.30
stock solution
solution with accurately known analyte concentration(s), prepared from “pure chemicals”.

NOTE Stock solutions are reference materials within the meaning of ISO Guide 30.

3.31
test sample
sample prepared from the laboratory sample, for example by grinding or homogenizing

3.32
test sample solution
solution prepared with the fraction (test portion) of the test sample according to the appropriate specifications, such that it can be used for the envisaged measurement

3.33
trueness
bias
closeness of agreement between the average value obtained from a large series of test results and an accepted reference value

NOTE The measure of trueness is usually expressed in terms of bias, which equals the sum of the systematic error components.

3.34
uncertainty of measurement
parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the analyte concentration

4 Principle

ICP-MS stands for Inductively Coupled Plasma Mass Spectrometry. 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, 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).

5 Apparatus

5.1 General

The principal components of the ICP-mass spectrometer are as shown in Figure 1 in the form of a schematic block diagram.

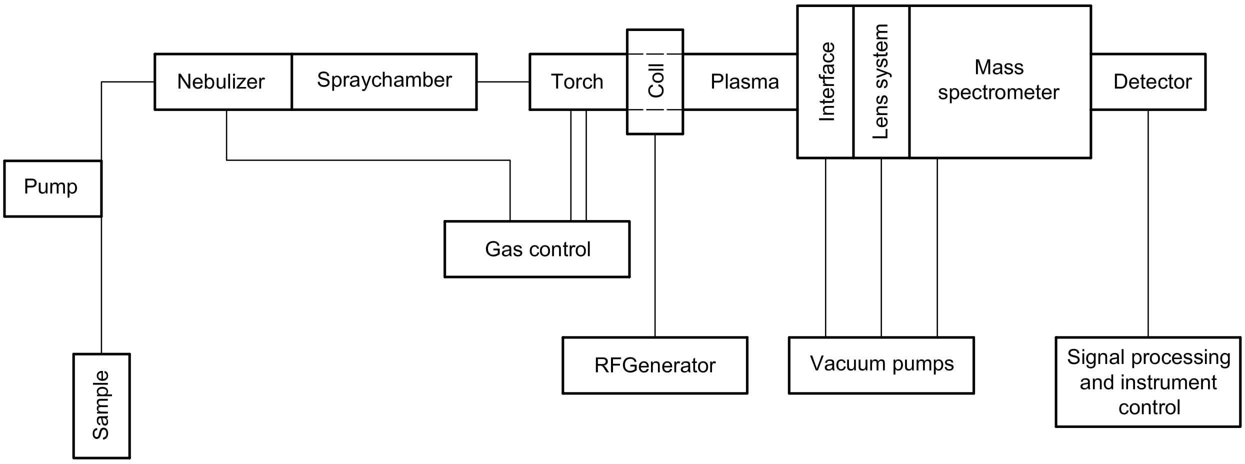

Figure 1 — Schematic block diagram of an ICP-mass spectrometer

5.2 Sample introduction

5.2.1 General

To introduce solutions to be measured into the plasma, a 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 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 corrosive substances that may be 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 nebulized. 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 the above requirements and some “examples” are compared.

5.2.2 Sample pump

The use of a peristaltic pump to feed the solution 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 1,5 ml/min.

5.2.3 Nebulizer

The most common nebulizers are the concentric nebulizer (for example Meinhard[1)]), the cross-flow nebulizer, the V-groove nebulizer and the ultrasonic nebulizer (USN). The first one is, and the second one can be, self-aspirating and these nebulizers can then be used without a pump (but seldom are used without a pump). Nebulizers (except for the USN) can be made of glass or of hard, inert plastic.

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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 part of ISO 17294 and does not constitute an endorsement by ISO of this product.

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 cross-flow 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 will have to 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 Burgener2) 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 has to 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.

For the other nebulizers described above, the efficiency is typically only a few percent. 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 to 100) µl/min and efficiencies approaching 100 %. These concentric micro-nebulizers often show a very good precision (low relative standard deviation of the signal) and can also be combined with a membrane desolvator [see 6.2.1 a)].

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

5.2.4 Spray chamber

In the spray chamber [for example 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 liquid shall be removed evenly in order to avoid pressure variations in the chamber, which can result in variations in the signal.

By cooling the spray chamber to (2 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. They 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 (for example 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.

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2) The Burgener nebulizer is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 17294 and does not constitute an endorsement by ISO of this product.

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 (for example coupling to chromatographic or flow injection devices) and for minimizing the memory effects of, for instance, boron, molybdenum and mercury.

These systems will not be discussed in this document.

5.3 Torch and plasma

The torch consists of three concentric tubes and can be designed as a single unit or a unit constructed of independent parts. Quartz is the material generally used. Sometimes the innermost tube (the sample introduction tube or injector tube) is made of inert material, for example aluminium oxide. 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 to 1,5) l/min.

The auxiliary gas flows between the sample introduction tube and the middle tube with a flow rate of (0 to 3) l/min. Whether or not an auxiliary gas is used depends on the type of device concerned, the solvent used, the salt concentration, etc. 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 will avoid 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 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 water- or argon-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 ultra-violet radiation emitted by the plasma. 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.

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 also be used to optimize this reduction.

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 gas to avoid carbon build-up on the sampling cone when analysing solutions made with organic solvents. The additions of too much oxygen result in the burning away of the sampling cone (see also 5.6). Mixtures of argon and hydrogen or nitrogen may improve the sensitivity for certain elements and/or reduce the formation of interfering polyatomic ions (see 6.2).

The various gas flow rates shall be stable. This applies particularly to the nebulizer gas. 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 and 56) MHz and a power between (0,6 and 2) kW that sustains the plasma. In general, solid-state generators are used. Two types of generator are available: crystal controlled and free oscillating.

Crystal-controlled generators are designed to control both power and frequency of the magnetic field. 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).

Free-oscillating, also called free-running, 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.

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. During the measurement the pressure in the expansion chamber is maintained at 10^2 to 10^3 Pa. At the centre of the cones is an orifice with a diameter of (0,3 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, sampling cones are available which are (partly) made of platinum. The application of platinum cones is also preferred when oxygen is added to the nebulizer gas when organic solvents are aspired. 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 may 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 of 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 7.2.6. 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, one or more metal plates (photon stops) are placed at the central axis. However, due to collision of the ions with the photon stop(s), a part of the ions can be lost and the photon stop(s) can become contaminated.

In some systems, a potential is exerted on the photon stop such that the ions are repelled and fewer are stopped.

A number of mass spectrometers are constructed in such a way that no photon stop(s) is (are) required. In these mass spectrometers, the trajectory of the ions deviates from the light path, for instance as a consequence of a curvature of the ion trajectory in the lens system or in the analyser. The latter is the case for double-focusing mass spectrometers (see 5.7.5).

5.7.3 Analyser

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

A quadrupole mass analyser consists of four round or hyperbolic, parallel metal rods of about 20 cm length on which DC (direct current) and RF potentials (radio-frequency) 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 band-width. 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; the resolution is usually characterized by the peak width at 5 % of the peak height. This is typically set at 0,7 amu (atomic mass units); see also 7.2.4.

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

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

Suppose 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.

5.7.4 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 will hit the conversion dynode resulting in the release of electrons. These electrons hit the first dynode of the electron multiplier, as a consequence of which, double the amount of electrons is released.

Subsequently, these electrons hit the second dynode. Ultimately, one ion results in a pulse of approximately 10^8 electrons. The successive dynodes have progressively less negative voltages. The pulse is processed using a fast pre-amplifier.

The maximum counting rate of this system is (2 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 count rate at higher impact rates. For modern instrumentation, the response time is usually about (10 to 20) ns. A mathematical correction has to be carried out to correct for the non-linearity caused by the dead time. The ICP-MS software supplied will usually carry out this correction based on Equation (1)

$$N' = \quad / \, (1 - ND) \tag{1}$$

where

N' is the true or estimated count rate;

N is the observed count rate;

D is the dead time.

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 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 analog manner. This is called the analog mode, in contrast to the pulse-counting mode. Modern instrumentation switches automatically to the analog mode when a signal that is too strong is detected to prevent damage to the detector.

The lifetime of discrete dynode and similar detectors is limited to typically 1 year to 2 years. During this life-span, the sensitivity of the detector slowly decreases and the high voltage has to be increased from time to time to restore the original sensitivity.

Other detectors that are sometimes applied are electron multipliers with a continuous dynode (Channeltron3) detectors), Daly3) detectors and Coniphot3) detectors. For some applications, the signal is high enough that a Faraday cup (a metal electrode without amplification) may be applied.

5.7.5 Alternative mass spectrometers/types of instruments

A 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 may 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.

A large number of the 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 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 focussing). 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 peak width of one peak at 5 % of the peak height. So, for the same effective separation of peaks, the resolution increases with mass.

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3) Channeltron, Daly, and Coniphot detectors are examples of suitable products available commercially. This information is given for the convenience of users of this part of ISO 17294 and does not constitute an endorsement by ISO of this product.

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 relative 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 relatively new system, by which a major part of the interferences can be eliminated, uses a collision or reaction cell with a quadrupole, hexapole or octapole. The cell is flushed with a reaction or buffer gas and, in principle, the argon (polyatomic) ions are neutralized and/or eliminated (see 6.2). In the hexapole collision cell with a relative low gas pressure, only a few collisions take place before the ions leave the cell. In the quadrupole reaction cell with a somewhat higher gas pressure, more collisions take place and thermal equilibrium is reached, resulting in lower levels of interferences. This type of cell, because of its scanning capabilities, is also to a certain extent capable of separating analyte ions from possibly newly formed (inside the cell) interfering ions. Reaction gases commonly used are the following (depending on the system): H_2, He, Xe, N_2, O_2, NH_3 and CH_4. Depending on the type of gas used, other polyatomic ion interferences are reduced. Also, the spread in the ion energy is reduced, such that focusing of the ions, and consequently the transmission, is enhanced.

The instrumental detection limits that are obtained with these types of instruments are similar to those obtained with the traditional quadrupole ICP-MS when there is no significant interference.

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 a large number of 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 have to be measured (for example when an ion 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 relative standard deviation 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 program might 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 concomitants

6.1 General

The presence of concomitants 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 mono- or polyatomic ions 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 the following:

a) an isotope of another element having the same mass as the analyte isotope, 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).

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 quantified using the CeO^+/Ce^+ ratio while aspirating a cerium solution. This ratio should be as low as possible, preferably lower than 0,5 %. For some type of instruments, levels up to (2 to 3) % are observed. BaO^+/Ba^+ ratios, specified by some manufacturers, are typically about 20 times lower than CeO^+/Ce^+ ratios and shall therefore not be used. The level of doubly charged ions is usually characterized via the Ce^{2+}/Ce^+ or Ba^{2+}/Ba^+ ratios. Typical levels are (1 to 3) %. The doubly charged ions ratio for Ba is typically 1,5 times to 2 times the ratio for Ce, due to the lower second ionization potential (IP2) for Ba (10,0 eV compared with 10,85 eV for Ce). See also 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 to 5) °C,
  - 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 like 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 HCl. HNO_3 should be used for acidifying the solutions or for sample digestions. The use of a membrane desolvator can reduce the level of Cl-related interferences considerably, because the membrane is permeable to HCl. The solutions have to be acidified with HNO_3.

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

d) Addition of molecular gases like H_2, N_2, CH_4, etc. to the nebulizer gas, auxiliary gas, plasma gas, or to all gases, gives improvement in specific cases.

e) Addition of ethanol or similar alcohols to the sample for the reduction of the $ArCl^+$ interference.

f) 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 also 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.

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

h) Use of elemental equations. This approach will be further elaborated below.

i) Use of a collision or a reaction cell (see 5.7.5).

j) Use of high-resolution ICP-MS (see 5.7.5).

6.2.3 Equations for the elements

The use of equations 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, independent of variations of the sample composition and small variations of the plasma conditions. For example, the number of ClO^+ ions (interference with $^{51}V^+$ and $^{53}Cr^+$) formed is a fixed fraction of the number of Cl^+ ions (the parent ion). With limitations, this is usually the case in practice. By measuring the signal of ClO^+ (at mass 51) and of Cl^+ (at mass 35) of a Cl standard solution and dividing the two values, the interference factor f can be calculated. For an unknown sample, the ClO^+ interference can then be calculated by measuring the $^{35}Cl^+$ signal and multiplying this value by f. To obtain the corrected signal for ^{51}V, the ClO^+ interference is subtracted from the gross signal at mass 51 in accordance with Equation (2):

$$I_{(^{51}\mathrm{V})} = I_{(51)} - f \times I_{(^{35}\mathrm{Cl})} \qquad (2)$$

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

However, it should be noted, that the net interference signal should be used for the calculation of f. When background is present, for instance for Cr at mass 52 (caused by $^{36}Ar^{16}O^+$ and $^{40}Ar^{12}C^+$), this background has to be subtracted from the signal of the interference check solution (IC solution, ICS) at mass 52 for the calculation of the corresponding factor f.

EXAMPLE $^{35}Cl^{16}O^{1}H^+$ interference with $^{52}Cr^+$).

In practice, in most cases, the blank (background) signal shall be subtracted from the ICS signal to obtain the net interference signal for the calculation of f. In practice, the factor f can also be determined by trial-and-error (adjusting f in the equation for the element and reprocessing the data). The final concentration for a solution containing the interferent should then be zero, compared to the blank.

In Annex A, an overview is given of possible spectral interferences.

The interference correction factors f are determined as elaborated above. A requirement is that the IC solution contain no analyte. Very often this is not the case because relatively high concentrations of salts, etc., are used to prepare the IC solutions. Even high-purity chemicals often do 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 may, in turn, interfere with this second analyte isotope, making this isotope unsuitable for quantitative analysis.

The most complicated situation arises when some analyte is present in the IC solution and all usable isotopes (isotopes with a sufficiently high abundance) are subject to interference from polyatomic ions of the same interfering element. This situation can exist for the analyte Ni and the interfering element Ca. The isotopes ^{58}Ni, ^{60}Ni, ^{61}Ni and ^{64}Ni are subject to interference from $^{42}Ca^{16}O^+$, $^{44}Ca^{16}O^+$, $^{44}Ca^{16}O^1H^+$ and $^{48}Ca^{16}O^+$, respectively, while ^{62}Ni has an abundance too low to allow a sufficiently reliable quantitation of Ni at low levels. There is also some Ca interference. A choice for the interference factors has then to be made, such that the results for ^{58}Ni and ^{60}Ni (in concentration units) are the same (the results for ^{61}Ni and ^{64}Ni are irrelevant as the abundances are too low) *and* the ratio of the Ca interference factors for ^{58}Ni and ^{60}Ni is about 0,31. The latter is the ratio of the abundances of ^{42}Ca and ^{44}Ca, reflected in the ratio of the interferences of $^{42}Ca^{16}O^+$ and $^{44}Ca^{16}O^+$.

For isobaric interferences (for example, the interference of ^{114}Sn with ^{114}Cd), the correction factor could 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 outlined procedures to determine *f* should be followed.

To determine unambiguously what interfering (parent) element causes the interference and to be able to adjust the interference factors, an IC solution can be made containing only those interfering elements that don't act on (the same or different isotopes of) a specific analyte. For example, Na (which interferes with ^{63}Cu: $^{40}Ar^{23}Na$) cannot be mixed with Ca (which interferes with ^{65}Cu: $^{48}Ca^{16}O^1H$). A total of 7 IC solutions is needed to fulfil this requirement. Table 1 gives an example of a set of IC solutions. The exact composition of the solutions (elements and concentrations) should be related to the sample type analysed. Other interfering components can be added, for example rare earth elements, provided that they do not violate the requirement mentioned above. Na in ICS4 can be added or omitted (by the addition of HCl instead of NaCl), depending on the sample type, as the presence of Na influences the formation rate of Cl-based polyatomic ions and, as a consequence, the magnitude of the correction factor *f*. Other components can be added to ICS4 (see Table 1), such as Mg and Ca (matrix matching, 6.3.5.2).

6.3 Non-spectral interferences

6.3.1 General

Non-spectral interferences, usually called matrix effects, can have their origin 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 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.

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 like 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 like Cd, Zn, As, Se, Hg, etc., with a high (first) ionization potential 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 will suffer less from matrix effects in the plasma. In most cases, a reduction of the analyte signal is observed. A positive matrix effect (increase of sensitivity) is observed for elements like As and Se by the presence of carbon-containing compounds.

Table 1 — Example of the composition of a set of interference check solutions to check for some common interferences

Solution	Interferent[a]	Concentration	Interference with	Analyte correction isotope[b]
ICS1	Mg	50 mg/l	^{57}Fe	(^{54}Fe)
			^{64}Zn, ^{66}Zn	^{68}Zn
			^{65}Cu	^{63}Cu
ICS2	Ca	200 mg/l	^{57}Fe	(^{54}Fe)
			^{58}Ni, ^{60}Ni, ^{61}Ni	—
			^{64}Zn	^{66}Zn
			^{65}Cu	^{63}Cu
			^{82}Se	(^{77}Se)
	Mo	50 µg/l	$^{111 \text{ to } 114}$Cd	—
ICS3	S	200 mg/l	$^{48 \text{ to } 50}$Ti	^{47}Ti
			^{64Zn}, ^{66}Zn	^{68}Zn
			^{65}Cu	^{63}Cu
			^{82}Se	(^{77}Se)
ICS4	Cl (as NaCl)	500 mg/l	^{51}V	—
			^{52}Cr, ^{53}Cr	—
			^{75}As	—
			^{77}Se	(^{82}Se)
	Si	20 mg/l	^{31}P	—
			^{45}Sc	—
			^{68}Zn	^{66}Zn
	Mg (nitrate)[c]	10 mg/l	—	—
ICS5	Fe	10 mg/l	^{58}Ni	^{60}Ni
	Br	10 mg/l	^{82}Se	(^{77}Se)
	Ba	1 mg/l	^{65}Cu	^{63}Cu
			$^{66 \text{ to } 68}$Zn	^{64}Zn
	Sr	2 mg/l	^{43}Ca, ^{44}Ca	—
ICS6	C	500 mg/l	^{45}Sc	—
			^{52}Cr	^{53}Cr
	Na	20 mg/l	^{63}Cu	^{65}Cu
	Sn	20 µg/l	^{112}Cd, ^{114}Cd	(^{111}Cd)
ICS7	Ti	1 mg/l	^{63}Cu, ^{65}Cu	—
			^{64}Zn, ^{66}Zn	^{68}Zn

[a] See Annex A.

[b] Isotopes in brackets are possibly less suitable for the analyte correction in the calculation of the interference factor *f* because of low sensitivity, high background, etc.

[c] For matrix-matching.

6.3.4 Interferences in the interface/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 will repel each other and some will deviate from the optimum path through the lens area and will 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 will be repelled more than in the inverse situation and so, will suffer more from matrix effects.

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

6.3.5.1 General

Five different approaches for the reduction of matrix effects will be discussed.

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, that is, making the composition of the calibration solutions equal to the composition of the test sample solutions (concentrations of main components). However, for practical reasons (for example, if there is a widely varying matrix), this is only feasible for the chemicals, like acids, etc., used in the sample preparation step(s). Both type and concentration of acid should be the same for the calibration and the test sample solutions. To prevent possible drift, this also holds true for the rinse solution aspirated between measurements. Even when the matrix has a more or less fixed composition and matrix matching is feasible, this approach still poses a risk for two reasons. Chemicals (salts, etc.) added to a trace-element calibration solution can be contaminated with the analyte(s) or 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, galactose could be added (see 6.3.3).

Other forms of matrix matching include the following:

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

— when the test sample solutions contain dissolved gas, removal of these gases by bubbling with an inert gas, such as nitrogen or argon, or 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 by the use of reference elements (internal standards)

The second way 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 equations for the elements (if applicable) 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; however, this is not always the case. Matrix effects related to the transport of the (liquid) solution to the nebulizer, the formation of the aerosol and/or transport of the aerosol to the plasma, will influence the analyte and the reference element to the same extent and will be corrected effectively. For matrix effects in the plasma, the correction is sometimes less effective. In practice, the largest matrix effects (reductions) are observed for Zn and Cd, elements with first ionization potentials (IP1s) of 9,4 eV and 9,0 eV, respectively. On the other hand, in the presence of carbon, large positive matrix effects can be observed for As and Se (see 6.3.3), elements which also have a high first ionization potential. The best correction is found when a reference element with a similar IP1 is used. The most appropriate is Te with an IP1 of 9,01 eV. However, for example for Zn, this element does not really meet a second requirement for reference elements, i.e., having a mass similar to the analyte element to minimize the differences in mass-dependent matrix effects and mass-dependent drift.

The sample and the reference element are usually pumped by two channels, which join before the nebulizer through a Y-tube (see 8.5).

Then, the performance of the correction has to be checked in practice (see 8.5). Frequently used reference elements for the mid-mass region are ^{103}Rh and ^{115}In with IP1 values of 7,5 eV and 5,8 eV, respectively. The former element is preferred over the latter one for the correction of Cd. For higher masses, ^{185}Re, ^{205}Tl or ^{209}Bi (unstable above $\text{pH} = 0{,}15$) can be used and for the lower mass region, ^{72}Ge, ^{59}Co or ^{9}Be. The latter element has the disadvantage of a high toxicity.

^{45}Sc is also used, but sometimes this element does not perform too well due to precipitation or sorption problems in the sample-introduction system. Scandium is also subject to interference from carbon and silicon polyatomic ions (see Annex A). In addition, interference is possible from an adjacent high ^{44}Ca signal from solutions with high calcium concentrations. For this situation, the resolution and mass calibration should be optimized carefully. For the choice of a reference element for a particular analytical problem, see 8.5.

Other requirements for reference elements include the following:

- negligible concentration in the test sample solutions;
- negligible interference by the reference element with the analyte elements;
- negligible interference by the sample components (see discussion of Sc above).

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 using analyte addition (standard addition technique)

Fixed amounts of analytes are added to all or part of the test sample solutions at one or two increments. Then, the samples are 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 ($n \geqslant 4$) deviating from 100 % are used to correct the results of a larger number of samples with a fixed composition (for example blood samples).

6.3.5.6 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 this clause, choices for the adjustment of the following instrumental parameters will be 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 will be discussed in Clause 8.

Before the plasma is started, it is advisable to visually check certain parts of the instrument: the torch for cleanness, 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 with respect to switching on the instrument, such as observing the required laboratory environment conditions, power, water and exhaustion requirements, warm-up time, etc.

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 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 the introduction of this clause automatically or manually (one by one) shall be carried out according to the manufacturer’s recommendations, usually while aspirating a prescribed element solution. Modern software on some instruments allows an “autotune,” the simultaneous automatic optimization of a great number of specified instrumental parameters with targets to be reached, like 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 below.

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 a solution containing 3 to 5 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 % of the peak height (see 5.7.3), 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 5.7.5), 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 below.

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 5.7.4) 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 analog mode (see 5.7.4) has to 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 5.7.4) can be factory-set or it 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 analog mode for higher concentrations are harmonized, which means that the readings of the analog 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 9 orders of magnitude). A dual-detector calibration should be carried out for all elements that might possibly be measured in the analog mode (also for the interfering components used in the equations for the elements) and repeated when the pulse-count detector high-voltage is changed (see 5.7.4). 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 like Na in a higher concentration range. After being set to optimum sensitivity, these lens systems should be optimized for 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 program with respect to rinse times, etc.;
- choice of integration time of the different isotopes;
- 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 doubt. However, very often the control mass number is subject to more interferences than the quantitative mass number. So, care has to 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 times to 2 times the highest concentration expected in the samples should be analysed and the result compared with that for the blank. See Table 1 (6.2.3) for example compositions of these interference check solutions and how to judge the results.

The choice can be made to use equations for the elements to correct for spectral interferences (see 6.2.3). Sometimes interferences are considered to be too variable and the choice is made not to use the equations. Whether or not they are used, limits have to 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 in the case of this maximum allowed concentration. The actual level of relevant interferences should be checked at least twice by an 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 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 will depend on the purpose of the analysis and on the requirements which the results must meet. 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 might, therefore, be necessary to determine the optimum measuring conditions for each isotope in the matrix concerned.

For multi-element analysis, however, it will generally be necessary to seek.

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 will be formed with corresponding effects on the signal. For ions with a low ionization potential, fewer ions will be formed; the opposite holds for ions with a high ionization potential. The background caused by polyatomic ions such as ArH^+ (K), ArN^+ (Mn), ArO^+ (Cr, Fe), etc., will also change. In addition, the Ni background related to the cones will increase with a hotter plasma. When analysing samples with a heavy matrix, the cones will be coated with a deposit, reducing the Ni background. A hotter plasma will result 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.

An increase in the nebulizer gas flow rate will result in an aerosol of higher density, bringing more analyte into the plasma, but also cooling the plasma. This will increase 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 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).

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 by the use of an optimum pump program. This program can contain a rapid rinse step (up to 5 times the normal pump speed), followed by a stabilization period at normal pump speed. Some instruments suffer from stability problems when a rapid rinse is used, in which case this step should be omitted. The pre-measurement stabilization time is optimized while monitoring the relative standard deviation (r_{sd}) of the measurement of a calibration solution (three replicates). This r_{sd} 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, as $AuCl_3$, can be added to all solutions (including the rinse solution) at a concentration of (0,2 to 5) mg/l. For B, mannitol or ammonia can be used.

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.

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 will have to be a compromise dependent on the requirements that the analysis results must meet. Typical integration times are between (0,3 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 on-going indication of the precision, which should be the equivalent of (1 to 2) % r_{sd} 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 (see 6.3.5.3). 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 calculated as (spiked sample – sample)/spike or certified value/measured value]. There is, however, another requirement for a reference element, that is, 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 choice 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 “on-line” by means of a two-channel sample-introduction pump. Discrete addition is rather time-consuming in contrast to on-line addition. In the latter approach, the solution to be measured and the solution containing the reference-element(s) are mixed by means of a T-piece, with or without a mixing coil, and the mixture is subsequently transported to the nebulizer. Mixing ratios may vary between $5 + 1$ and $1 + 5$ (sample/reference-element solution). The latter ratio results in on-line dilution of the samples. Usually, limited on-line 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) (8.9.3), and this ratio will not alter because of dilution. However, matrix effects will be reduced because of this on-line dilution.

The use of a mixing coil gives better mixing and so, a larger reduction of matrix effects at the expense of an increased wash-out time. When using on-line dilution, a smaller-diameter sample probe should be used, for example with 0,3 mm internal diameter.

8.6 Linearity and working range

Linearity is usually not a big problem in ICP-MS. 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 5.7.4) and dual-detector calibration for the analog/pulse-count mode together. Calibration solutions prepared from a multi-element calibration stock solution can induce dilution-dependent matrix effects resulting in pseudo non-linearity. These matrix effects are compensated for by the use of reference element(s). Linearity is checked in every measurement series.

The choice 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.

The maximum total concentration of dissolved solids in the test sample solutions is typically (1 to 2) g/l. Higher concentrations may 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 though for acids, etc. (6.3.5.2). In addition, contamination plays a role in choosing the element combinations for calibration solutions (for example, Sr and Ba are often present in Ca stock solutions, etc.). Finally, for stability reasons, some element stock solutions contain HCl and, even diluted, these elements are stable only in this acid, which gives rise to Cl-based polyatomic ion interferences.

All these considerations have to be taken into account when choosing combinations for multi-element calibration solutions. All solutions shall have a “use-by” date.

This results in practice in one calibration solution with several trace elements having a low concentration and two to four macro-element solutions (see 9.2 for the number of calibrations over the measurement range). 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 Zn usually suffers from the most pronounced matrix effects (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. The two upper calibration points should be very close together. Depending on the actual matrix composition (concentrations) of the test sample solutions (high or low), a choice can be made either to skip one of the Zn calibration points or to use both.

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 Group I and II elements 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^{TM} [4] 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.

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. The sections below refer primarily to quadrupole ICP-MS instruments, but can be extrapolated to reaction/collision cell instruments.

8.9.2 Instrumental detection limit

The instrumental detection limit, I_{DL}) 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 (for instance diluted nitric acid of high purity). Optimal instrument set-up also means here that the instrument has to be as clean as possible (sample introduction system and torch, cones and lenses).

This instrumental detection limit can be determined as follows (after cleaning the instrument):

Using a calibration function, measure a blank [nitric acid, $c(HNO_3) = 0{,}1$ mol/l] with the chosen integration time (see 8.4) and with 10 replicates. Establish the standard deviation, s, of results. The instrumental detection limit is usually three times s.

The I_{DL} 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 I_{DL}, because all relevant 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^{1}H 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 I_{DL}. The I_{DL}s can be very low ($\leqslant$ 1 ng/l) for some elements.

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[4] PlasmaScreen Torch and Shield Torch are examples of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 17294 and does not constitute an endorsement by ISO of these products.

8.9.3 Method detection limit

The method detection limit, x_{DL}, is in many cases primarily determined by spectral interferences, whether corrected or not. The maximum concentration of those matrix elements that cause interferences determines the x_{DL} attainable and the required x_{DL} determines the maximum allowed matrix element concentration. When no correction for spectral interferences is applied to the equations for the elements, the x_{DL} equals the maximum observed interference.

When equations for the elements are used, the method detection limit may be estimated as follows. The method detection limit is three times the standard deviation of the measurements of the interference check solutions (ICS, Table 1) or of an IC mix solution (representing the most concentrated matrix expected in the samples) on 10 different days.

The x_{DL} also has to 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 x_{DL}, which is higher than the I_{DL}, has to be adapted.

8.9.4 Precision of the method

The precision of the method is determined at one concentration of the analyte, sufficiently high that the measured relative standard deviation is independent of further increases in concentration ($\rho \geqslant 50 \cdot X_{\text{LD}}$). A representative test sample solution with high concentrations of matrix elements is measured on 10 different days. The precision of the method is the relative standard deviation ($S_{\text{rel},\ \rho \geqslant 50 \cdot X_{\text{LD}}}$) of the mean result.

Equation (3) defines the S_R at the lower concentrations:

$$s_{\text{rel},\rho\leq 50\cdot X_{\text{LD}}} = \sqrt{(X_{\text{LD}}/3)/\rho)^2 + (s_{\text{rel},\ \rho\geq 50\cdot X_{\text{LD}}})^2} \qquad (3)$$

where

$X_{\text{LD}}/3$ is the standard deviation for the method detection limit as determined in 8.9.3;

ρ is the mass concentration, expressed in milligrams per litreof the respective analyte.

9 Procedure

9.1 General

In this clause, the normal calibration and the actual measurement of the test sample solutions will be described. 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

Good results are obtained with a two-point calibration: a blank calibration solution and a calibration solution for the upper point of the measurement range. Multi-level calibration and standard least-squares fitting may 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 x_{DL}), unless weighed linear regression is used instead of the standard least-squares fitting. (Weighed 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 has to be known at every concentration involved. Equation (3) gives only a model of the (relative) standard deviation, not an actual value for every situation (for example, the presence or absence of matrix).

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 water (without acid) that meets the requirements of grade 1 in accordance with ISO 3696:1987 and the high-point calibration, with an independent check calibration solution (3.5) or by the analysis of reference solutions.

Multi-level calibration is sometimes preferred when one does not want to rely on the preparation and measurement of only two solutions and when no measurements are made in the low concentration range. Some form of weighing should then be used.

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)
CSM1-n	calibration solution for macro-elements (see 8.7), numbers 1 to n
ICS1-m	interference check solutions (see 6.3.2, Table), numbers 1 to m
ICB	initial calibration blank solution, which is the CB measured as sample directly after the first calibration
CCB	continuous calibration blank solution, which is the CB measured as sample in a measurement series
CCV	continuous calibration verification solution which contains all analytes (when possible without the risk of precipitation) at the same concentration as in the calibration solutions. It is used to check the calibration after a number of test sample solutions has been measured. The actual concentrations have to be brought 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.
LVS	linearity verification solution, which contains the analytes at concentrations half of those of the calibration solutions. Sometimes, this solution is used as the CCV. See also remarks above.
MQ	grade 1 water (ISO 3696:1987), measured to check the purity of the CB
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. The LCS can be used as a check calibration solution (see 3.5, 9.2).
CSMnDx	calibration solution for macro-elements, number n, diluted x times, with the result that all measurements are made just in the pulse-count mode. It serves to check the dual-detector calibration. The results times x should equal the nominal concentrations of the CSM
A0	analyte addition solution for the blank; addition of one part CB to nine parts of a test sample solution
AA	analyte addition solution for the analyte; addition of one part of a solution containing all analytes at a level of 2,5 times those of the CCV solution to nine parts of a test sample solution. Smaller volumes of more concentrated addition solutions can also be added (also a smaller volume of CB to A0). Normally two additions pairs are prepared per measurement series. Analyte addition is carried out in each measurement series only to check for matrix effects. Recovery = (spiked sample − sample) / spike.
TS1-k	test sample solution, numbers 1 to k
BTS1-p	blank test solutions, numbers 1 to p; reagent blank solutions and blank test solutions

9.4 Measurement

The analyses are carried out in the following sequence:

- conditioning the system (cones) using a suitable matrix solution for (10 to 15) min;
- ICS block: ICS solutions (all or only relevant ones) or ICS mix; update of elemental equations when necessary;
- Cal block 1: CB CST CSM1 (containing macro-elements with the highest concentrations);
- ICB (to check for memory) MQ;
- Cal block 2: CSM2-n;
- LVS CSMnDx BTS1-p;
- Sample block: TS1-k;
- 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 CB CCV (CST CSM1-n). Update of calibration (measurement of CST, CSM1-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 method detection limits for quadrupole ICP-MS instruments

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

Element	Isotope	Abundance %	Method detection limit[a] µg/l	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Interelement	Polyatomic ions		Preference	Reason
Ag	107	51,8	1	—	ZrO, YO	$^{91}Zr^{16}O$	x	least interference
	109	48,2	1	—	ZrO, ZrOH, NbO	—	—	—
Al	27	100	5	—	BeO, BO, CN, HCN	—	x	—
As	75	100	1	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	0,5	—	HfO, TaO	—	x	—
B	10	19,9	10	—	—	—	x	free of interference, low background
	11	80,1	10	—	BH	—	—	—
Ba	135	6,6	3	—	—	—	—	—
	137	11,2	3	—	—	—	x	highest abundance, least interference
	138	71,7	0,5	La, Ce	—	La, Ce		—
Be	9	100	0,5	—	—	—	x	—
Bi	209	100	0,5	—	—	—	x	—
Ca	43	0,14	100	Sr^{2+}	MgO, BO_2, AlO, CaH, CNO, CO_2	Sr^{2+}	x	low background, least interference
	44	2,1	50	Sr^{2+}	CaH, MgO, AlO, BO_2, CNO, SiO, CO_2, N2O	Sr^{2+}, $^{12}C^{16}O_2$	x	lowest detection limit
Cd	111	12,8	0,5	—	MoO, MoOH, ZrOH, K_2O_2H	$^{94}Zr^{16}O^{1}H$, $^{95}Mo^{16}O$	—	—
	113	12,2	0,5	In	MoO, ZrOH, Ca_2O_2H, Ar_2O_2H, RuO	In, $^{97}Mo^{16}O$	x	for high Sn
	114	28,7	0,3	Sn	MoO, MoOH, RuO	Sn, $^{98}Mo^{16}O$	x	lowest detection limit, least interference
Ce	140	88,5	0,1	—	—	—	x	—
Co	59	100	0,2	Sn^{2+}	CaO, CaOH, MgCl, ArNa, ArOH, ArF	$^{43}Ca^{16}O$	x	—
Cr	52	83,8	1	—	SO, ArO, ArC, ArN, ClO, HClO, ClN, ArNH	$^{40}Ar^{12}C$	x	for low C and high Cl
	53	9,5	5	—	HSO, ArC, HClO, ClO, ArOH, ArN, ArNH, SO	$^{37}Cl^{16}O$	x	for high C and low Cl
Cs	133	100	0,1	—	RuO_2	—	x	—

Table A.1 (*continued*)

Element	Isotope	Abundance %	Method detection limit[a] µg/l	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Interelement	Polyatomic ions		Preference	Reason
Cu	63	69,2	1	—	TiO, PO_2, ArNa, MgCl, NaCa, CaOH, ArCNH, NCCl, ClO	$^{47}\mathrm{Ti}^{16}\mathrm{O}$, $^{40}\mathrm{Ar}^{23}\mathrm{Na}$	x	for low Na and Ti, lowest detection limit
	65	30,8	2	Ba^{2+}	TiO, PO_2, SO_2, SO_2H, ArMg, CaOH, ArN_2H, S_2 COCl	$^{49}\mathrm{Ti}^{16}\mathrm{O}$, $^{32}\mathrm{S}^{16}\mathrm{O}_2{}^{1}\mathrm{H}$, $^{40}\mathrm{Ar}^{25}\mathrm{Mg}$	x	for medium Mg, S and Ti and high Na
Dy	163	24,9	0,1	—	NdO, SmO	—	x	—
Er	166	33,6	0,1	—	SmO, NdO	—	x	—
Eu	151	47,8	0,1	—	BaO	—	—	—
	153	52,2	0,1	—	BaO	—	x	—
Fe	54	5,8	20	Cr	HClO, ArO, ArN, ArNH, ArOH, SO, ClO	ArN Cr	x	abundance and background determine choice
	57	2,2	50	—	CaO, ArO, ArOH, CaC, CaN, CaOH, MgO_2, ArF	$^{40}\mathrm{Ar}^{16}\mathrm{O}^{1}\mathrm{H}$ $^{40}\mathrm{Ca}^{16}\mathrm{O}^{1}\mathrm{H}$	x	
Ga	69	60,1	0,3	Ce^{2+}, Ba^{2+}, La^{2+}	ClO_2, ArP, VO, ArS, SO_2, S_2	Ba^{2+}	—	—
	71	39,9	0,3	Nd^{2+}, Ce^{2+}	ArP. ClO_2, ArCl, SO_2, ArS, CrO	—	x	least interference
Gd	157	15,7	0,1	—	CeO, PrO, LaO, BF	—	x	least interference
	158	24,8	0,1	Dy	CeO, PrO, NdO	Dy	—	—
Ge	74	35,9	0,3	Se, Sm^{2+}, Nd^{2+}	ArS, Cl_2, Ar_2	Se	x	—
Hf	178	27,3	0,1	—	GdO, DyO, ErO		x	—
Hg	200	23,1	5	—	WO	$^{184}\mathrm{W}^{16}\mathrm{O}$	—	—
	201	13,2	10	—	WO	$^{184}\mathrm{W}^{17}\mathrm{O}$	x	least interference from WO
	202	29,9	5	—	WO	$^{186}\mathrm{W}^{16}\mathrm{O}$	—	—
Ho	165	100	0,1	—	SmO	—	x	—
In	115	95,7	0,1	Sn	RuO	Sn	x	—
Ir	193	62,7	0,1	—	HfO, LuO		x	—
K	39	93,3	50	—	ArH	—	x	—
La	139	99,9	0,1	—	—	—	x	—
Li	6	7,5	10	—	—	—		—
	7	92,5	1	—	—	—	x	lowest detection limit
Lu	175	97,4	0,1	Hf	GdO, TbO	Hf	x	—
Mg	24	79,0	1	Ti^{2+}, Ca^{2+}	LiO, NaH, C_2	—	x	lowest detection limit, least interference
	25	10,0	10	Ti^{2+}	LiO, BeO, C_2, C_2H	—	—	—
	26	11,0	10	—	BeO, BO, CN, C_2H_2, C_2H	—	x	for higher Mg concentrations
Mn	55	100	3	—	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, K_2O	Ru	x	lowest detection limit

Table A.1 (*continued*)

Element	Isotope	Abundance %	Method detection limit[a] µg/l	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Interelement	Polyatomic ions		Preference	Reason
Na	23	100	10	Ti^{2+}, Ca^{2+}	LiO	—	x	—
Nd	146	17,2	0,1	—	BaO, RuO_3	—	x	—
Ni	58	68,1	1	Fe	CaO, ArO, CaN, NaCl, MgS, CaOH, Si_2, ArOH	Fe	x	for low Fe
	60	26,2	3	—	CaO, CaOH, MgCl, NaCl	$^{44}Ca^{16}O$	x	least interference
	61	1,1	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	0,2	—	PtO	—	x	sum of 206, 207 and 208
	207[b]	22,1	0,2	—	IrO	—	x	sum of 206, 207 and 208
	208[b]	52,4	0,1	—	PtO	—	x	sum of 206, 207 and 208
Pd	105	22,3	0,5	—	YO, ArCu	—	—	—
	108	26,5	0,5	Cd	MoO, ZrO	Cd	x	—
Pr	141	100	0,1	—	—	—	x	—
Pt	195	33,8	0,5	—	HfO	—	x	—
Rb	85	72,2	0,1	Yb^{2+}, Er^{2+}	—	—	x	—
Re	185	37,4	0,1	—	TmO, ErO	—	x	least interference
	187	62,6	0,1	Os	TmO, YbO	Os	x	highest abundance
Rh	103	100	0,1	Pb^{2+}	SrO, ArCu, RbO	—	x	—
Ru	101	17,0	0,2	—	ArNi, NiCl	—	—	—
	102	31,6	0,1	Pd	SrO	Pd	x	lowest detection limit, least interference
S	34	4,2	1000	—	O_2, SH, NOH, O_2H	O_2	x	—
Sb	121	57,4	0,2	—	PdO	—	x	least interference
	123	47,6	0,2	Te	ZrO	Te	—	—
Sc	45	100	5	Zr^{2+}	CO_2, SiO, BO_2, AlO, CaH, CHO_2, SiOH, N_2OH	$^{13}C^{16}O_2$, $^{29}Si^{16}O$	x	—
Se	77	7,6	10	Sm^{2+}, Gd^{2+}	ArCl, Ar_2H, CaCl, $CFNO_2$	$^{40}Ar^{37}Cl$	x	for low Cl
	78	23,8	10	Kr, Gd^{2+}, Dy^{2+}	Ar_2, CaCl, ArCa	$^{38}Ar^{40}Ar$	x	for high Cl and Br
	82	8,7	10	Kr, Ho^{2+}, Er^{2+}, Dy^{2+}	Ar_2H, BrH, CCl_2, SO_3, Ar_2H_2, ArCa	Kr, $^{81}Br^{1}H$	x	for low Br
Si	29	4,7	10	—	CO, N_2, BO, SiH, AlH, COH, N_2H	—	x	—
Sm	147	15,0	0,1	—	RuO_3	—	x	—
Sn	118	24,2	1	U^{2+}	MoO, RuO, PdO	—	x	least interference
	120	32,6	1	Te	RuO, PdO	Te	—	—
Sr	86	9,9	0,5	Kr Yb^{2+}	RbH	—	—	—
	88	82,6	0,3	Yb^{2+} Lu^{2+}	—	—	x	lowest detection limit, least interference

Table A.1 (*continued*)

Element	Isotope	Abundance %	Method detection limit[a] µg/l	Theoretical interferences		Interference with practical relevance	Best usable isotopes	
				Interelement	Polyatomic ions		Preference	Reason
Tb	159	100	0,1	—	NdO, PrO	—	x	—
Te	125	7,1	5	—	—	—	x	least interference
Te	126	19,0	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	$^{32}S^{16}O^{1}H$	—	—
Tl	203	29,5	0,2	—	WO, ReO, WHO	—	—	—
	205	70,5	0,1	—	—	—	x	lowest detection limit, least interference
Tm	169	100	0,1	—	EuO	—	x	—
U	238	99,3	0,1	—	—	—	x	—
V	51	99,8	1	—	HSO, ClO, ClN, ArNH, ArC, ArN, SN, SO	$^{35}Cl^{16}O$	x	—
W	182	26,3	0,3	—	HoO, DyO, ErO	—	x	least interference
	184	30,7	0,3	Os	ErO, YbO	Os	—	—
Y	89	100	0,1	—	—	—	x	—
Yb	172	21,9	0,2	—	DyO, SmO, GdO	—	x	least interference
	174	31,8	0,2	Hf	DyO, GdO	Hf	—	—
Zn	64	48,6	1	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	2	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	3	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] Method detection limits (see 8.9.3) 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.

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