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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

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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*

This corrected version of ISO 17294-1:2004 incorporates correction of symbols for instrument detection limit and method detection limit, corrections to Equations (1) and (3), and various minor editorial corrections.

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

3.11
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
L_{DM}
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, 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, 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.

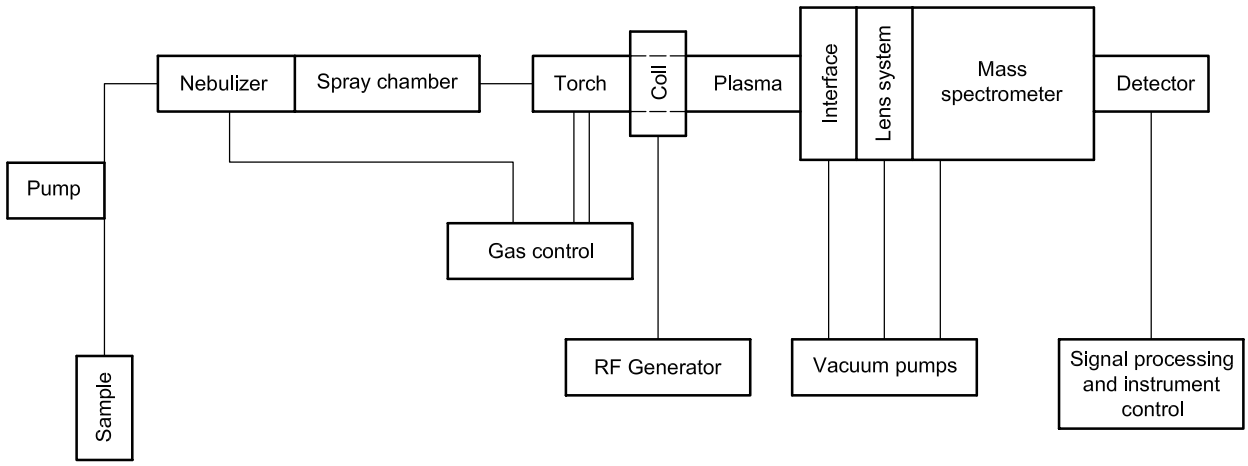

Figure 1 — Schematic block diagram of an ICP-mass spectrometer

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 and 1,5 ml per minute.

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 self-aspirating, and the second one can be, and these nebulizers can then be used without a pump (but seldom are). Nebulizers (except for the USN) can be made of glass or of hard, inert plastic.

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 Burgener[2)] nebulizer and the cone-spray nebulizer, with similar outer shapes as the concentric nebulizer. With these nebulizers, the solution flows out into a cone-shaped area at the tip of the nebulizer instead of a V-groove and flows over the outflow opening of the nebulizer gas.

In the ultrasonic nebulizer, the solution is pumped through a tube that ends near the transducer plate that vibrates at an ultrasonic frequency. The amount of aerosol produced (the efficiency) is typically 10 % to 20 % of the quantity of the pumped solution. This is so high that the aerosol 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 µl/min 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 °C to 5 °C, the water vapour formed in the nebulization process condenses, thereby reducing the water load of the plasma. This results in a reduction in the formation of interfering polyatomic ions (oxides); see 6.2.2.

5.2.5 Other systems

There are other types of introduction systems for particular applications. 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 l/min 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 l/min to 20 l/min. The function of the plasma gas is to maintain the plasma and to cool the outer tube of the torch.

Around the top of the torch there is a 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.

