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

Part 2:
Determination of 62 elements

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

Partie 2: Dosage de 62 éléments

Reference number
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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 17294-2 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 and basic principles*
- *Part 2: Determination of 62 elements*

Introduction

When applying this part of ISO 17294, it is necessary in each case, depending on the range to be tested, to determine if and to what extent additional conditions should be established.

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

Part 2:
Determination of 62 elements

WARNING — Persons using this part of ISO 17294 should be familiar with normal laboratory practice. This part of ISO 17294 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests, conducted in accordance with this part of ISO 17294, be carried out by suitably qualified staff.

1 Scope

This part of ISO 17294 specifies a method for the determination of the elements aluminium, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, caesium, calcium, cerium, chromium, cobalt, copper, dysprosium, erbium, europium, gadolinium, gallium, germanium, gold, hafnium, holmium, indium, iridium, lanthanum, lead, lithium, lutetium, magnesium, manganese, molybdenum, neodymium, nickel, palladium, phosphorus, platinum, potassium, praseodymium, rubidium, rhenium, rhodium, ruthenium, samarium, scandium, selenium, silver, sodium, strontium, terbium, tellurium, thorium, thallium, thulium, tin, tungsten, uranium, vanadium, yttrium, ytterbium, zinc, and zirconium in water [for example drinking water, surface water, groundwater, wastewater and eluates (9.2)].

Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges and sediments (for example digests of water as specified in ISO 15587-1 or ISO 15587-2).

The working range depends on the matrix and the interferences encountered. In drinking water and relatively unpolluted waters, the limit of application is between 0,1 µg/l and 1,0 µg/l for most elements (see Table 1).

The detection limits of most elements are affected by blank contamination and depend predominantly on the laboratory air-handling facilities available.

The lower limit of application is higher in cases where the determination is likely to suffer from interferences (see Clause 5) or in case of memory effects (see 8.2 of ISO 17294-1).

Table 1 — Limits of application for unpolluted water

Element	Isotope often used	Limit of application[a] µg/l
Ag	^{107}Ag	1
	^{109}Ag	1
Al	^{27}Al	5
As	^{75}As	1
Au	^{197}Au	0,5
B	^{10}B	10
	^{11}B	10
Ba	^{137}Ba	3
	^{138}Ba	0,5
Be	^{9}Be	0,5
Bi	^{209}Bi	0,5
Ca	^{43}Ca	100
	^{44}Ca	50
	^{40}Ca	10
Cd	^{111}Cd	0,1
	^{114}Cd	0,5
Ce	^{140}Ce	0,1
Co	^{59}Co	0,2
Cr	^{52}Cr	1
	^{53}Cr	5
Cs	^{133}Cs	0,1
Cu	^{63}Cu	1
	^{65}Cu	2
Dy	^{163}Dy	0,1
Er	^{166}Er	0,1
Eu	^{151}Eu	0,1
	^{153}Eu	0,1
Ga	^{69}Ga	0,3
	^{71}Ga	0,3
Gd	^{157}Gd	0,1
	^{158}Gd	0,1
Ge	^{74}Ge	0,3
Hf	^{178}Hf	0,1
Ho	^{165}Ho	0,1
In	^{115}In	0,1
Ir	^{193}Ir	0,1
K	^{39}K	50
La	^{139}La	0,1
Li	^{6}Li	10
	^{7}Li	1
Lu	^{175}Lu	0,1
Mg	^{24}Mg	1
	^{25}Mg	10
Mn	^{55}Mn	3
Mo	^{95}Mo	0,5
	^{98}Mo	0,3
Na	^{23}Na	10
Nd	^{146}Nd	0,1
Ni	^{58}Ni	1
	^{60}Ni	3
P	^{60}P	5,0
Pb	^{206}Pb[b]	0,2
	^{207}Pb[b]	0,2
	^{208}Pb[b]	0,1
Pd	^{108}Pd	0,5
Pr	^{141}Pr	0,1
Pt	^{195}Pt	0,5
Rb	^{85}Rb	0,1
Re	^{185}Re	0,1
	^{187}Re	0,1
Rh	^{103}Rh	0,1
Ru	^{101}Ru	0,2
	^{102}Ru	0,1
Sb	^{121}Sb	0,2
	^{123}Sb	0,2
Sc	^{45}Sc	5
Se	^{77}Se	10
	^{78}Se	10
	^{82}Se	10
Sm	^{147}Sm	0,1
Sn	^{118}Sn	1
	^{120}Sn	1
Sr	^{86}Sr	0,5
	^{88}Sr	0,3
Tb	^{159}Tb	0,1
Te	^{126}Te	2
Th	^{232}Th	0,1
Tl	^{203}Tl	0,2
	^{205}Tl	0,1
Tm	^{169}Tm	0,1
U	^{238}U	0,1
V	^{51}V	1
W	^{182}W	0,3
	^{184}W	0,3
Y	^{89}Y	0,1
Yb	^{172}Yb	0,2
	^{174}Yb	0,2
Zn	^{64}Zn	1
	^{66}Zn	2
	^{68}Zn	3
Zr	^{90}Zr	0,2

[a] Depending on the instrumentation significantly lower limits can be achieved.

[b] In order to avoid mistakes due to the different isotope ratios in the environment, the signal intensities of ^{206}Pb, ^{207}Pb and ^{208}Pb shall be added.

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 referenced document (including any amendments) applies.

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

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

ISO 15587-1, *Water quality — Digestion for the determination of selected elements in water — Part 1: Aqua regia digestion*

ISO 15587-2, *Water quality — Digestion for the determination of selected elements in water — Part 2: Nitric acid digestion*

ISO 17294-1:—[1], *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of elements — Part 1: General guidelines and basic principles*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 17294-1 and the following apply.

3.1
limit of application
lowest concentration of an analyte that can be determined with a defined level of accuracy and precision

4 Principle

Multi-element determination of 62 elements by inductively coupled plasma mass spectrometry (ICP-MS) consists of the following steps:

- introduction of a measuring solution into a radiofrequency plasma (for example by pneumatic nebulization) where energy transfer processes from the plasma cause dissolution, atomization and ionization of elements;

- extraction of the ions from plasma through a differentially pumped vacuum interface with integrated ion optics and separation on the basis of their mass-to-charge ratio by a mass spectrometer (for instance a quadrupole MS);

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1) To be published.

- transmission of the ions through the mass separation unit (for instance a quadrupole) and detection, usually by a continuous dynode electron multiplier assembly, and ion information processing by a data handling system;
- quantitative determination after calibration with suitable calibration solutions.

The relationship between signal intensity and mass concentration is usually a linear one over at least five orders of magnitude.

5 Interferences

5.1 General

In certain cases, isobaric and non-isobaric interferences may occur. The most important interferences in this respect are coinciding masses and physical interferences from the sample matrix. For more detailed information, refer to ISO 17294-1.

Common isobaric interferences are given in Table 2 (for additional information see ISO 17294-1). In order to detect these interferences, it is recommended that several different isotopes of an element be determined. All the results should be similar. If they are not, mathematical correction is then necessary if, for a given element, there is no isotope which can be measured without interferences.

Small drifts or variations in intensities should be corrected by the application of the reference-element technique. In general, in order to avoid physical and spectral interferences, the mass concentration of dissolved matter (salt content) shall not exceed 2 g/l.

NOTE Under cool plasma conditions some interferences will not occur. But the inevitable lower stability of cool plasma has to be considered accordingly. Also with reaction cell instruments (for example DRC ICP-MS) some interferences are overcome.

5.2 Spectral interferences

5.2.1 General

For more detailed information on spectral interferences, refer to ISO 17294-1:—, 6.1.

5.2.2 Isobaric elemental and polyatomic interferences

Isobaric elemental interferences are caused by isotopes of different elements of the same nominal mass-to-charge-ratio and which cannot be separated due to an insufficient resolution of the mass spectrometer in use (for example ^{114}Cd and ^{114}Sn).

Element interferences from isobars may be corrected for taking into account the influence from the interfering element (see Table 3). In this case, the isotopes used for correction shall be determinable without any interference and with sufficient precision. Possible proposals for correction are often included in the instrument software.

Table 2 — Important isobaric interferences

Element	Isotope	Inter-element interferences caused by isobars and doubly charged ions	Interferences caused by polyatomic ions
Ag	^{107}Ag	—	ZrO
	^{109}Ag		NbO, ZrOH
As	^{75}As	—	ArCl, CaCl
Au	^{197}Au	—	TaO
B	^{11}B	—	BH
Ba	^{138}Ba	La^{+}, Ce^{+}	—
Ca	^{43}Ca	—	CNO
	^{44}Ca	—	COO
Cd	^{111}Cd	—	MoO, MoOH, ZrOH
	^{114}Cd	Sn^{+}	MoO, MoOH
Co	^{59}Co	—	CaO, CaOH, MgCl
Cr	^{52}Cr	—	ArO, ArC, ClOH
	^{53}Cr	Fe^{+}	ClO, ArOH,
Cu	^{63}Cu	—	ArNa, POO, MgCl
	^{65}Cu	—	SOOH
Eu	^{151}Eu	—	BaO
	^{153}Eu	—	BaO
Ga	^{69}Ga	Ba^{++}	CrO, ArP, ClOO
Ge	^{74}Ge	Se^{+}	ArS, ClCl
In	^{115}In	Sn^{+}	—
Ir	^{193}Ir	—	HfO
Mg	^{24}Mg	—	CC
	^{25}Mg	—	CC
Mn	^{55}Mn	—	NaS, ArOH, ArNH
Mo	^{98}Mo	Ru^{+}	—
Ni	^{58}Ni	Fe^{+}	CaO, CaN, NaCl, MgS
	^{60}Ni	—	CaO, CaOH, MgCl, NaCl
Pd	^{108}Pd	Cd^{+}	MoO, ZrO
Pt	^{195}Pt	—	HfO
Re	^{187}Re	Os^{+}	—
Ru	^{102}Ru	Pd^{+}	—
Sb	^{123}Sb	Te^{+}	—
Sc	^{45}Sc	—	COO, COOH
Se	^{77}Se	—	CaCl, ArCl, ArArH
	^{78}Se	Kr^{+}	ArAr, CaCl
	^{82}Se	Kr^{+}	—
Sn	^{120}Sn	Te^{+}	—
V	^{51}V	—	ClO, SOH, ClN, ArNH
W	^{184}W	Os^{+}	—
Zn	^{64}Zn	Ni^{+}	AlCl, SS, SOO, CaO
	^{66}Zn	Ba^{++}	PCl, SS, FeC, SOO
	^{68}Zn	Ba^{++}, Ce^{++}	FeN, PCl, ArS, FeC, SS, ArNN, SOO

In the presence of elements in high mass concentrations, interferences may be caused by the formation of polyatoms or doubly charged ions which are not listed above.

Table 3 — Examples for suitable isotopes with their relative atomic masses and equations for correction

Element	Recommended isotope and inter-element correction	
As	^{75}As	$- 3{,}127\ (^{77}\text{Se} - 0{,}815\ ^{82}\text{Se})$ or
	^{75}As	$- 3{,}127\ (^{77}\text{Se} + 0{,}322\ 0\ ^{78}\text{Se})$
Ba	^{138}Ba	$- 0{,}000\ 900\ 8\ ^{139}\text{La} - 0{,}002\ 825\ ^{140}\text{Ce}$
Cd	^{114}Cd	$- 0{,}026\ 84\ ^{118}\text{Sn}$
Ge	^{74}Ge	$- 0{,}138\ 5\ ^{82}\text{Se}$
In	^{115}In	$- 0{,}014\ 86\ ^{118}\text{Sn}$
Mo	^{98}Mo	$- 0{,}110\ 6\ ^{101}\text{Ru}$
Ni	^{58}Ni	$- 0{,}048\ 25\ ^{54}\text{Fe}$
Pb	^{208}Pb	$+ ^{207}\text{Pb} + ^{206}\text{Pb}$
Se	^{82}Se	$- 1{,}009\ ^{83}\text{Kr}$
Sn	^{120}Sn	$- 0{,}013\ 44\ ^{125}\text{Te}$
V	^{51}V	$- 3{,}127\ (^{53}\text{Cr} - 0{,}113\ 4\ ^{52}\text{Cr})$
W	^{184}W	$- 0{,}001\ 242\ ^{189}\text{Os}$

5.2.3 Isobaric interferences by polyatomic ions

Polyatomic ions are formed by coincidence of plasma gas components, reagents and sample matrix (for example interference of the relative mass ^{75}As by $^{40}\text{Ar}^{35}\text{Cl}$ and $^{40}\text{Ca}^{35}\text{Cl}$). Examples for correction equations are given in Table 3 and information on the magnitude of interferences are stated in Table 4. This interference is of particular relevance for several elements (for example As, Cr, Se, V).

It is recommended that the analyst checks the magnitude of this interference regularly for the particular instrument.

In the case of mathematical corrections, it shall be taken into account that the magnitude of interference depends both on the plasma adjustment (for example oxide formation rate) and on the mass concentration of the interfering element, which will usually be a variable component of the sample solution.

5.3 Non-spectral interferences

For detailed information on non-spectral interferences refer to ISO 17294-1:—, 6.2.

Table 4 — Important interferences by solutions of Na, K, Ca, Mg, Cl, S, P (ρ = 100 mg/l) and Ba (ρ = 1 000 µg/l)

Element	Isotope	Simulated mass concentration [a] µg/l	Type of Interference
As	^{75}As	1,0	ArCl
Co	^{59}Co	0,2 to 0,8	CaO, CaOH
Cr	^{52}Cr	1,0	ClOH
		1,0	ArC
	^{53}Cr	5,0	ClO
Cu	^{63}Cu	1,0 to 3,0	ArNa
		1,0 to 1,6	POO
	^{65}Cu	2,0	ArMg
		2,0	POO
		2,0	SOOH
Ga	^{69}Ga	1,0 to 25	Ba^{++}
		0,3	ArP
		1,0	ClOO
	^{71}Ga	0,2 to 0,6	ArP
Ge	^{74}Ge	0,3	ClCl
		0,3	ArS
Mn	^{55}Mn	3,0	KO
		3,0	NaS
		3,0	NaS
Ni	^{58}Ni	2,5	CaO, CaN
	^{60}Ni	3 to 12	CaO, CaOH
Se	^{77}Se	10	ArCl
V	^{51}V	1 to 5	ClO, ClN
		1,0	SOH
Zn	^{64}Zn	7	ArMg
		3	CaO
		8	SS, SOO
		1	POOH
	^{66}Zn	2,0	ArMgBa^{++}
		5	SS, SOO
		4	PCl
		2	Ba^{++}
	^{68}Zn	50	ArS, SS, SOO
		4	Ba^{++}

[a] Up to the stated concentrations, no interferences were observed but the user needs to check it.

6 Reagents

For the determination of elements at trace and ultratrace level, the reagents shall be of adequate purity. The concentration of the analyte or interfering substances in the reagents and the water should be negligible compared to the lowest concentration to be determined.

For preservation and digestion, nitric acid should be used to minimize interferences by polyatoms.

6.1 Water, Grade 1 as specified in ISO 3696:1987, for all sample preparation and dilutions.

6.2 Nitric acid, $\rho(HNO_3) = 1{,}4$ g/ml.

NOTE Nitric acid is available both as $\rho(HNO_3) = 1{,}40$ g/ml [$w(HNO_3) = 650$ g/kg] and $\rho(HNO_3) = 1{,}42$ g/ml [$w(HNO_3) = 690$ g/kg]. Both are suitable for use in this method provided there is minimal content of the analytes of interest.

6.3 Hydrochloric acid, $\rho(HCl) = 1{,}16$ g/ml.

6.4 Hydrochloric acid, $c(HCl) = 0{,}2$ mol/l.

6.5 Sulfuric acid, $\rho(H_2SO_4) = 1{,}84$ g/ml.

6.6 Hydrogen peroxide, $w(H_2O_2) = 30$ %.

NOTE Note that hydrogen peroxide is often stabilized with phosphoric acid.

6.7 Element stock solutions, $\rho = 1\,000$ mg/l each of Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Tb, Te, Th, Tl, Tm, U, V, W, Y, Yb, Zn, Zr.

Both single-element stock solutions and multi-element stock solutions with adequate specification stating the acid used and the preparation technique are commercially available. Element stock solutions with different concentrations of the analytes (for example 1 000 mg/l) are also allowed.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

6.8 Anion stock solutions, $\rho = 1\,000$ mg/l each of Cl^-, PO_4^{3-}, SO_4^{2-}.

Prepare these solutions from the respective acids. The solutions are also commercially available. Anion stock solutions with different concentrations of the analytes (for example 100 mg/l) are also allowed.

These solutions are considered to be stable for more than one year, but in reference to guaranteed stability, the recommendations of the manufacturer should be considered.

6.9 Multi-element standard solutions.

Depending on the scope, different multi-element standard solutions may be necessary. In general, when combining multi-element standard solutions, their chemical compatibility and the possible hydrolysis of the components shall be regarded. Care shall be taken to prevent chemical reactions (for example precipitation).

The examples given below also consider the different sensitivities of various mass spectrometers.

The multi-element standard solutions are considered to be stable for several months, if stored in the dark.

This does not apply to multi-element standard solutions that are prone to hydrolysis, in particular solutions of Bi, Mb, Mo, Sn, Sb, Te, W, Hf and Zr.

In reference to guaranteed stability of all standard solutions, see the recommendations of the manufacturer.

6.9.1 Multi-element standard solution A, consisting of the following:

- ρ (As, Se) = 20 mg/l
- ρ (Ag, Al, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, La, Li, Mg, Mn, Ni, Pb, Rb, Sr, Th, Tl, U, V, Zn) = 10 mg/l

Pipette 20 ml of each element stock solution (As, Se) (6.7) and 10 ml of each element stock solution (Ag, Al, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, La, Li, Mn, Ni, Pb, Rb, Sr, Th, Tl, U, V, Zn) (6.7) into a 1 000 ml volumetric flask.

Add 10 ml of nitric acid (6.2).

Bring to volume with water (see 6.1) and transfer to a suitable storage bottle.

Multi-element standard solutions with more elements may be used provided it is verified that these solutions are stable and no chemical reactions occur. This shall be checked again a few days after the first use (sometimes precipitation can occur after preparation).

6.9.2 Multi-element standard solution B, consisting of the following:

- ρ (Au, Mo, Sb, Sn, W, Zr) = 5 mg/l.

Pipette 2,5 ml of each element stock solution (Au, Mo, Sb, Sn, W, Zr) (6.7) into a 500 ml volumetric flask.

Add 40 ml of hydrochloric acid (6.3).

Bring to volume with water (6.1) and transfer to a suitable storage bottle.

6.9.3 Reference-element solution (internal standard solution).

The choice of elements for the reference-element solution depends on the analytical problem. Solutions of these elements should cover the mass range of interest. The concentrations of these elements in the sample should be negligibly low. The elements In, Lu, Re, Rh and Y have been found suitable for this purpose.

For example, the following reference-element solutions may be used:

- ρ (Y, Re) = 5 mg/l

Pipette 5 ml of each element stock solution (Y, Re) (6.7) into a 1 000 ml volumetric flask.

Add 10 ml of nitric acid (6.2).

Bring to volume with water and transfer to a suitable storage bottle.

6.10 Multi-element calibration solutions.

Choose the mass concentrations of the calibration solutions to allow for a sufficient precision and reproducibility and ensure that the working range is covered.

The stability of the calibration solutions should be checked regularly. Due to their rather low respective mass concentrations, they should be replaced by freshly prepared solutions at least every month or more frequently for elements which are prone to hydrolysis. In special cases, daily preparation is necessary. The user has to determine the maximum stability period of the calibration solutions.

Transfer the calibration solution(s) A (6.9.1) and B (6.9.2) to suitable storage bottles.

If the determination is carried out after previous digestion (9.2) the matrix of the multi-element calibration solution(s) A (6.9.1) and B (6.9.2) shall be adjusted to that of the digests.

The working range in general may cover the range of 0,1 µg/l to 50 µg/l or a part of this.

6.10.1 Multi-element calibration solution(s) A.

Prepare the calibration solution(s) A that cover the required working range by diluting the multi-element standard solution A (see 6.9.1). Add 10 ml of nitric acid (6.2) per litre and bring up to volume with water (6.1). If necessary, add reference-element solution (6.9.3) to a concentration of for example 50 µg/l of the reference-elements before bringing up to volume.

6.10.2 Multi-element calibration solution(s) B.

Prepare the calibration solution(s) B that cover the required working range by diluting the multi-element standard solution B (6.9.2). Add 5 ml of hydrochloric acid (6.3) per litre and bring up to volume with water (6.1). If necessary add reference-element solution (6.9.3) to a concentration of, for example, 50 µg/l of the reference-elements before bringing up to volume.

6.11 Blank calibration solutions.

High demands shall be set concerning the purity. The user should ensure that the background levels of the analytes are not significant to the results of the analysis.

6.11.1 Blank calibration solution A.

Pipette 0,5 ml of nitric acid (6.2) to a 100 ml volumetric flask made for example from perfluoroalkoxy (PFA) or hexafluoroethene propene (FEP) and bring to volume with water (6.1). If necessary, add reference-element solution (6.9.3) to a concentration of, for example, 50 µg/l of the reference-elements before bringing up to volume.

If the determination is carried out after previous digestion (9.2) the matrix of the blank calibration solution A shall be adjusted to that of the digests.

6.11.2 Blank calibration solution B.

Pipette 1,0 ml of hydrochloric acid (6.3) to a 100 ml volumetric flask made for example from perfluoroalkoxy (PFA) or hexafluoroethene propene (FEP) and bring to volume with water (6.1). If necessary add reference-element solution (6.9.3) to a concentration of for example 50 µg/l of the reference-elements before bringing up to volume.

If the determination is carried out after previous digestion (9.2) the matrix of the blank calibration solution B shall be adjusted to that of the digests.

6.12 Optimization solution.

The optimization solution serves for mass calibration and for optimization of the apparatus conditions, for example adjustment of maximal sensitivity with respect to minimal oxide formation rate and minimal formation of doubly charged ions.

It should contain elements covering the entire mass range, as well as elements prone to a high oxide formation rate or to the formation of doubly charged ions. For example, an optimization solution containing Mg, Cu, Rh, In, Ba, La, Ce, U and Pb is suitable. Li, Be and Bi are less suitable because they tend to cause memory effects.

The mass concentrations of the elements used for optimization should be chosen to allow count rates of more than 10 000 counts/s.

For further information, see general remarks in ISO 17294-1.

6.13 Matrix solution.

The matrix solutions serve to determine the correction factors for the corresponding equations. High demands are made concerning the purity of the basic reagents due to the high mass concentrations. The user should ensure that the background levels of the analytes in the matrix solution are not significant to the results of the analysis. The composition may be as follows:

- $\rho(\text{Ca}) = 200$ mg/l;
- $\rho(\text{Cl}^-) = 300$ mg/l;
- $\rho(\text{PO}_4^{3-}) = 25$ mg/l;
- $\rho(\text{SO}_4^{2-}) = 100$ mg/l.

Pipette 200 ml of element stock solution (Ca) (6.7), 300 ml of anion stock solution (Cl^-) (6.8), 25 ml of anion stock solution (PO_4^{3-}) (6.8) and 100 ml of anion stock solution (SO_4^{2-}) (6.8) to a 1 000 ml volumetric flask.

Add 10 ml of nitric acid (6.2).

Bring to volume with water (6.1) and transfer to a suitable storage bottle.

7 Apparatus

The stability of samples, and measuring and calibration solutions depends to a high degree on the container material. The material shall be checked according to the specific purpose. For the determination of elements in a very low concentration range, glass or polyvinyl chloride (PVC) should not be used. Instead, it is recommended to use perfluoroalkoxy (PFA), hexafluoroethene propene (FEP) or quartz containers, cleaned with hot, concentrated nitric acid in a closed system. For the determination of elements in a higher concentration range, high density polyethene (HDPE) or polytetrafluoroethene (PTFE) containers are also allowed for the collection of samples.

Immediately before use, all glassware should be washed thoroughly with warm diluted nitric acid [for example $w(\text{HNO}_3) = 10$ %], and then rinsed several times with water (6.1).

The use of piston pipettes is permitted and also enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed. Every batch of pipette tips and disposable plastics vessels shall be tested for impurities.

For more detailed information on the instrumentation, refer to ISO 17294-1:—, Clause 5.

7.1 Mass spectrometer.

A mass spectrometer with inductively coupled plasma (ICP) suitable for multi-element and isotope analysis is required. The spectrometer should be capable of scanning a mass range from 5 m/z (AMU) to 240 m/z (AMU) with a resolution of at least 1 m_r/z peak width at 5 % of peak height (m_r = relative mass of an atom species; z = charge number). The instrument may be fitted with a conventional or extended dynamic range detection system.

7.2 Mass-flow controller.

A mass-flow controller on the nebulizer gas supply is required. Mass-flow controllers for the plasma gas and the auxiliary gas are also useful. A water cooled spray chamber may be of benefit in reducing some types of interferences (for example from polyatomic oxide species).

NOTE The plasma is very sensitive to variations in the gas flow rate.

7.3 Nebulizer with variable speed peristaltic pump, for which information on different types of nebulizers is given in ISO 17294-1:—, 5.1.2.

7.4 Argon gas supply, of high purity grade, for instance > 99,99 %.

7.5 Glassware, consisting of the following:

- volumetric flasks, for example 50 ml, 100 ml, 500 ml and 1 000 ml;
- conical (Erlenmeyer) flasks, for example 100 ml;
- pipettes, for example 1 ml, 2,5 ml, 10 ml, 20 ml and 25 ml.

7.6 Storage bottles, for the stock, standard, calibration and sample solutions.

For the determination of elements in a normal concentration range, high density polyethene (HDPE) or polytetrafluoroethene (PTFE) bottles are sufficient for the storage of samples. For the determination of elements in an ultratrace level bottles made from perfluoroalkoxy (PFA) or hexafluoroethene propene (FEP) should be preferred. In any case the user has to check the suitability of the chosen containers.

8 Sampling

Carry out the sampling in accordance with ISO 5667-1, ISO 5667-2, and ISO 5667-3. Due to the extremely high requirements concerning purity in trace and ultratrace analysis any impurity shall be avoided.

The mass concentrations of the elements may change rather rapidly after sampling due to adsorption or desorption effects. This is of special importance, for example in the case of Ag, As, B, Se and Sn. The choice of the container material depends on the mass concentration of the elements to be determined.

For the determination of the dissolved fraction of the elements, filter the sample through a membrane filter, nominal pore size 0,45 µm. Every batch of membrane filters shall be tested for impurities. Use several portions of the sample to rinse the filter assembly, discard and then collect the required volume of filtrate.

Add 0,5 ml of nitric acid (6.2) per 100 ml of sample. Ensure that the pH is less than 2; otherwise, add nitric acid as required.

In the case of determination of elements forming compounds that tend to be hydrolysed, for example Sb, Sn, W or Zr, add to an additional sample 1,0 ml of hydrochloric acid (6.3) per 100 ml of water. Ensure that the pH is less than 1; otherwise, add more hydrochloric acid as required.

9 Sample pre-treatment

9.1 Determination of the mass concentration of dissolved elements without digestion

Continue according to Clause 10, using the acidified filtrate specified in Clause 8. If experience has shown that no significant amounts of particles occur, the filtration may be omitted. Those samples shall be colourless and shall have a turbidity < 1,5 FNU (formazine nephelometric unit, see ISO 7027).

9.2 Determination of the total mass concentration after digestion

The mass concentration determined according to this clause does not in all cases represent the total mass concentration. Instead, only the portion that is determinable according to the distinct digestion for a given element composition will be analysed.

A nitric acid digestion is recommended and shall be carried out in accordance with ISO 15587-2. If aqua regia is chosen, the procedure shall be carried out in accordance with ISO 15587-1, in which case, possible interferences caused by the high content of chloride have to be considered accordingly.

Some elements and their respective compounds (for example, silicates and aluminium oxide) will be dissolved incompletely using this procedure.

For the determination of tin, the following digestion may be used:

a) Add 0,5 ml of sulfuric acid (6.5) and 0,5 ml of hydrogen peroxide (6.6) to 50 ml of the homogenized water sample.

b) Evaporate the mixture until SO_3 vapour is formed.

c) In case of incomplete digestion, add a small portion of water (6.1) after cooling, add hydrogen peroxide (6.6) once more and repeat the treatment.

d) Dissolve the residue in diluted hydrochloric acid (6.4) and adjust the volume to 50 ml with water.

e) Treat a blank in the same way.

Special digestion methods may be necessary if Sb, W or Zr is to be determined.

If experience has shown that the elements will be recovered quantitatively without decomposition, the digestion may be omitted.

10 Procedure

10.1 General

In ICP-MS methods, the relationship between measured count rates and mass concentrations of an element is known to be linear over several orders of magnitude. Therefore, linear calibration curves may be used for quantification. In routine measurements, check the linearity of the calibration curves at regular intervals. This check can be carried out in accordance with ISO 8466-1.

Adjust the instrumental parameters of the ICP-MS system in accordance with the manufacturer's manual.

About 30 min prior to measurement, adjust the instrument to working condition.

Before each series of measurement the sensitivity and the stability of the system should be checked using the optimization solution (6.12). Check the resolution and the mass calibration as often as required by the manufacturer.

Adjust the instrument with the aid of the optimization solution (6.12) to minimize interfering effects (for example oxide formation, formation of doubly charged ions) allowing sufficient sensitivity.

According to Table 3, define the relative atomic masses and the corresponding corrections.

Define the rinsing times depending on the length of the flow; in the case of large variations in mass concentrations in the measuring solutions, allow for longer rinsing periods.

The use of a reference-element solution is recommended. Add the reference-element solution (6.9.3) to the matrix solution (see 6.13), to all multi-element calibration solutions (6.10), to the blank calibration solutions (6.11), and to all measuring solutions. The mass concentration of the reference-elements shall be the same in all solutions. A mass concentration of

$$\rho\,(\text{Y, Re}) = 50\ \mu\text{g/l}$$

is often suitable.

NOTE ICP-MS has excellent multi-element capability. The sensitivity of determination depends on a number of parameters (nebulizer flow, radiofrequency power, lens voltage, lens voltage mode, etc.). The optimal instrument settings cannot be achieved for all elements simultaneously.

10.2 Calibration of the ICP-MS system

When the analytical system is first evaluated, and at intervals afterwards, establish a calibration curve for each element to be determined using at least five measuring points (for example, the blank calibration solution and four calibration solutions).

For work on a daily basis, one blank solution and one to two calibration solutions are enough but check the validity of the calibration curve with a certified reference sample, a standard sample, or a suitable internal control sample (consider also comments in ISO 17294-1:—, 9.1).

Typically proceed as follows:

Prepare and measure the blank calibration solutions (6.11) and the multi-element calibration solutions (6.10). According to the manufacturer's instruction, set up a calibration graph. Each reference point should be the mean of at least two replicates.

Take into account possible discrepancies in the isotope composition between the calibration solutions and the measuring solutions (for example relevant for Li, Pb, U).

10.3 Measurement of the matrix solution for evaluation of the correction factors

In order to evaluate and to update the correction factors, measure the matrix solutions (6.13) at regular intervals within a measuring cycle.

10.4 Measurement of the samples

After establishing the calibration curves, measure the blanks and the samples.

Within sufficient small intervals (for example, every ten samples) check the accuracy of at least one certified reference sample or one standard sample or one internal control sample. If necessary, re-calibrate.

Some elements (for example Ag, B, Be, Li, Th) are rinsed very slowly from the sample inlet system. After high count rates, these memory effects shall be checked by measuring a blank calibration solution (6.11).

11 Calculation

The mass concentrations for each element are determined with the aid of the instrument software. Carry out the following single steps for each element.

a) Correct the count rates according to the respective equations (see Table 3).

b) Make allowance for the count rates from the blank calibration, calibration and measuring solutions, and relate to the count rates of the reference-elements. Determine the slope and the intercept on the ordinate.

c) Determine the mass concentrations of samples with the aid of the count rates and the calibration graphs.

d) Correct the results taking into account the mass concentrations from the blank calibration solutions and incorporate all dilution steps in the calculation. If the sample is digested (see 9.2) a correction for the procedure blank shall be used if appropriate (digestion blank solution).

According to the requirements set by the analytical quality control, the determination of the mass concentrations using the software of the apparatus shall be verifiable and shall be documented. In all cases, it shall be clear which corrections have been carried out with the aid of the software.

Report the results to as many significant figures as are acceptable according to the precision of the measuring values.

EXAMPLES	Copper (Cu)	0,142 mg/l
	Cadmium (Cd)	0,50 µg/l

12 Precision

An interlaboratory trial, carried out in Germany in 1997, yielded the results given in the Tables 5 to 7. For the description of the sample matrices see Annex A.

13 Test report

The test report shall contain the following information:

a) a reference to this part of ISO 17294, i.e. ISO 17294-2;

b) the complete identification of the sample;

c) the expression of results as indicated in Clause 12;

d) the sample pre-treatment, if appropriate;

e) any deviations from this method, and details of all circumstances which could have affected the result.

Table 5 — Precision data for the matrix surface water [a] [b]

Element	l	n	o %	$\overline{X}$ µg/l	σ_R µg/l	Reproducibility CV %	σ_r µg/l	Repeatability CV %
As	37	145	3,3	6,90	0,954	13,8	0,432	6,3
Ba	38	149	5,7	41,1	2,53	6,1	1,04	2,5
Cd	37	147	5,2	5,75	0,491	8,5	0,234	4,1
Co	38	151	2,6	2,33	0,269	11,6	0,140	6,0
Cr	38	151	0,0	3,39	0,634	18,7	0,294	8,7
Cu	38	151	2,6	26,7	2,02	7,6	0,93	3,5
Mn	39	155	2,5	205,0	13,2	6,4	5,9	2,9
Mo	38	150	2,6	4,45	0,402	9,0	0,187	4,2
Ni	35	137	11,0	5,44	0,786	14,5	0,397	7,3
Pb	39	155	2,5	13,6	1,13	8,3	0,64	4,7
Sn	34	132	3,6	1,19	0,241	20,3	0,157	13,2
Sr	40	158	0,0	117,0	8,1	6,9	3,4	3,0
Tl	31	124	8,1	0,272	0,046 0	16,9	0,029 2	10,7
V	33	129	8,5	1,15	0,311	27,0	0,121	10,5
Zn	36	143	7,7	27,6	2,56	9,3	1,43	5,2

l is the number of laboratories;

n is the number of values;

o is the percentage of outliers;

$\overline{X}$ is the total mean;

σ_R is the reproducibility standard deviation;

CV is the coefficient of variation;

σ_r is the repeatability standard deviation.

[a] Antimony (total mean 0,33 µg/l) and zirconium (total mean 0,98 µg/l) have been measured as well in the matrix surface water. In both cases, a satisfactory reproducibility coefficient of variation could not be achieved.

[b] All data refer to the determination of the mass concentration of dissolved elements (9.1).