INTERNATIONAL STANDARD

ISO 11885

Second edition
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Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)

Qualité de l'eau — Dosage d'éléments choisis par spectroscopie d'émission optique avec plasma induit par haute fréquence (ICP-OES)

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 11885 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This second edition cancels and replaces the first edition (ISO 11885:1996), which has been technically revised.

Introduction

When applying this International Standard, 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 — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard 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 according to this International Standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies a method for the determination of dissolved elements, elements bound to particles ("particulate") and total content of elements in different types of water (e.g. ground, surface, raw, potable and waste water) for the following elements: aluminium, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, chromium, cobalt, copper, gallium, indium, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, phosphorus, potassium, selenium, silicon, silver, sodium, strontium, sulfur, tin, titanium, tungsten, vanadium, zinc and zirconium.

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 method is suitable for mass concentrations of particulate matter in waste water below 2 g/l. The scope of this method may be extended to other matrices or to higher amounts of particulate matter if it can be shown that additionally occurring interferences are considered and corrected for carefully. It is up to the user to demonstrate the fitness for purpose.

Recommended wavelengths, limits of quantification and important spectral interferences for the selected elements are given in Table 1.

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

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

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

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

ISO 7027, *Water quality — Determination of turbidity*

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*

3 Terms and definitions

For the purposes of this document, the following terms and definitions 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
background equivalent concentration
BEC
elemental concentration required to produce an analyte signal with the same intensity as a background signal

3.4
calibration blank solution
prepared in the same way as the calibration solution but leaving out the analyte

3.5
calibration solution
solution used to calibrate the instrument, prepared from (a) stock solution(s) or from a certified standard

3.6
calibration check solution
solution of known composition within the range of the calibration solutions, but prepared independently

3.7
determination
entire process from preparing the test sample solution up to and including measurement and calculation of the final result

3.8
instrument performance check solution
solution used to determine and control the instrument drift for relevant analytes

3.9
linearity
straight line relationship between the (mean) result of measurement (signal) and the quantity (concentration) of the component to be determined

3.10
limit of detection
X_{LD}
smallest amount or concentration of an analyte in the test sample that can be reliably distinguished from zero

NOTE The limit of detection shall be calculated as:

$$X_{LD} = 3\, s_0$$

where

X_{LD} is the limit of detection;

s_0 is the standard deviation of the outlier-free results of at least 3 measurements of a reagent blank solution (3.14)

[ISO 13530]

3.11
limit of quantification
X_{LQ}
the smallest amount or concentration of an analyte in the test sample which can be determined with a fixed precision

EXAMPLE Relative standard deviation s_{rel} = 33,3 %

$$X_{LQ} = 3\, X_{LD} = 9\, s_0$$

[ISO 13530]

3.12
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, mg/l.

3.13
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.

3.14
reagent blank solution
prepared by adding to the solvent the same amounts of reagents as those added to the test sample solution (same final volume)

3.15
reproducibility
precision under reproducibility conditions

[ISO 3534-2:2006, definition 3.3.10]

3.16
reproducibility conditions
observation conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in different test or measurement facilities with different operators using different equipment

[ISO 3534-2:2006, definition 3.3.11]

3.17
reproducibility standard deviation
standard deviation of test results or measurement results obtained under reproducibility conditions

[ISO 3534-2:2006, definition 3.3.12]

3.18
reproducibility limit
R
reproducibility critical difference for a specified probability of 95 %

[ISO 3534-2:2006, definition 3.3.14]

3.19
repeatability
precision under repeatability conditions

[ISO 3534-2:2006, definition 3.3.5]

3.20
repeatability conditions
observation conditions where independent test/measurement results are obtained with the same method on identical test/measurement items in the same test or measuring facility by the same operator using the same equipment within short intervals of time

[ISO 3534-2:2006, definition 3.3.6]

3.21
repeatability standard deviation
standard deviation of test results or measurement results obtained under repeatability conditions

[ISO 3534-2:2006, definition 3.3.7]

3.22
repeatability limit
r
repeatability critical difference for a specified probability of 95 %

[ISO 3534-2:2006, definition 3.3.9]

3.23
stock solution
solution with accurately known analyte concentration(s), prepared from chemicals with an appropriate purity

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

3.24
test sample
prepared from the laboratory sample (for example by grinding, homogenizing)

3.25
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

3.26
total element concentration
concentration of elements determined on an unfiltered sample following digestion or the sum of concentrations of elements as determined in the dissolved state (9.5.1) and bound in the particulate fraction (9.5.2) of a sample

3.27
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 (bias = sum of systematic error components).

4 Principle

The basis of the method is the measurement of emission of light by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by a detector. The signals from the detector(s) are processed and controlled by a computer system. A suitable background correction technique is used to compensate for variable background contributions to the determination of trace elements.

5 Recommended wavelengths, limits of quantification and important spectral interferences

Elements for which this International Standard applies along with the recommended wavelengths and typical estimated limits of quantification (LOQ) are listed in Table 1 as far as data are available from the interlaboratory trial (see Annex B). Actual working detection limits are dependent on the type of instrumentation, detection device and sample introduction system used and on the sample matrix. Therefore, these concentrations can vary between different instruments.

Additionally, Table 1 lists the most important spectral interferences at the recommended wavelengths for analysis.

Table 1 — Recommended wavelengths [a], achievable limits of quantification (X_{LQ} [b]) for different types of instruments and important spectral Interferences

Element	Wavelength	Approx. X_{LQ}		Interfering elements
		Radial viewing	Axial viewing	
	nm	µg/l	µg/l	
Ag	328,068	(20)	(4)	Fe, Mn, Zr
	338,289	(20)	(10)	Cr, Fe, Zr, Mn
Al	167,079	1	2	Fe, Pb
	308,215	100	17	Fe, Mn, OH, V
	396,152	10	6	Cu, Fe, Mo, Zr
As	188,979	18	14	Al, Cr, Fe, Ti
	193,696	5	14	Al, Co, Fe, W, V
	197,197	(100)	31	Al, Co, Fe, Pb, Ti
B	182,528	(6)	—	S
	208,957	(5)	(7)	Al, Mo
	249,677	10	5	Co, Cr, Fe
	249,772	4	24	Co, Fe
Ba	230,425	—	3	—
	233,527	2	0,5	Fe, V
	455,403	6	0,7	Zr
	493,408	(3)	0,4	-
Be	313,042	(2)	(0,1)	Fe
	313,107	—	(0,3)	V
	234,861	(5)	(0,1)	—
Bi	223,060	(40)	(17)	Co, Cu, Ti, V
	306,770	(80)	(165)	Fe, Mo, V
Ca	315,887	100	13	Co, Mo
	317,933	26	4	Fe, V
	393,366	0,4	25	V, Zr
	422,673	—	—	V, Mo, Zr
Cd	214,441	1	0,9	As, Cr, Fe, Sc, Sb
	226,502	4	0,2	As, Co, Fe, Ni
	228,802	2	0,5	As, Co, Sc
Co	228,616	6	1	Ti
	238,892	10	3	Fe

Table 1 (*continued*)

Element	Wavelength	Approx. X_{LQ}		Interfering elements
		Radial viewing	Axial viewing	
	nm	µg/l	µg/l	
Cr	205,559	1	5	Be, Fe, Mo, Ni, Ti
	267,719	4	2	Mn, P, V
	283,563	(10)	(2)	Fe, Mo, V, W
	284,324	(10)	—	Fe
Cu	324,754	9	2	Cr, Fe, Mo, Ti
	327,396	4	3	Co, Ti
Fe	238,204	14	(3)	Co
	259,940	6	2	Co
	271,441	—	—	—
Ga	287,424	—	—	Cr
	294,364	—	—	Fe, Ti
	417,204	—	—	Fe, V
In	230,605	—	—	Fe
	325,609	—	—	Mn
	410,175	—	—	Ce
K	766,490	66	20	Ar, Ba, Mg
	769,896	—	(230)	Ba
Li	460,290	900	(700)	Ar, Fe
	670,778	6	10	Ar
Mg	279,078	33	19	Fe
	279,553	1	7	Fe
	285,213	4	14	Cr
Mn	257,610	1	0,4	Cr, Fe, Mo, W
	293,305	(20)	(8)	Al, Cr, Fe, Ti
Mo	202,031	(30)	(2)	Al, Fe, Ni
	204,597	(50)	(6)	Co, Cr
Na	330,237	(20)	300	Zn
	588,995	20	200	Ar, V
	589,592	93	20	Ba
Ni	221,648	10	2	Si
	231,604	15	2	Co, Sb
P	177,434	500	(16)	Cu
	178,221	25	13	Fe, I
	213,618	500	50	Co, Cu, Fe, Mo, Zn
	214,915	330	9	Al, Co, Cu, Mg

Table 1 (*continued*)

Element	Wavelength	Approx. X_{LQ}		Interfering elements
		Radial viewing	Axial viewing	
	nm	µg/l	µg/l	
Pb	220,353	14	5	Al, Co, Fe, Ti
	283,305	(70)	(20)	Cr, Fe
S	180,669	13	33	As, Ca
	181,975	39	17	Cr, Mo
Sb	206,834	(100)	(4)	Co, Cr, Fe, Mg, Mn
	217,582	(100)	(18)	Pb, Fe
Se	196,089	(100)	(7)	—
	203,984	(100)	(7)	Cr, Sb
Si	212,412	3	(13)	Mo
	251,611	20	10	—
	288,158	(30)	24	Cr
Sn	189,988	(100)	(60)	Cr, Ti
	235,485	(100)	(200)	Cd, Mo
	283,998	—	(120)	
Sr	407,771	2,6	0,6	Cr
	421,552	0,1	0,1	—
	460,733	(10)	(3)	—
Ti	334,941	(5)	(2)	Cr
	336,123	(10)	(1)	—
	337,280	(10)	—	—
	368,521	(10)	—	Co, Cr
V	290,881	(10)	—	Fe, Mo
	292,402	(10)	(3)	Cr, Fe, Mo, V
	310,229	(10)	(0,7)	Cr, Mg
	311,071	(10)	(1)	Cr, Fe, Mn, Ti
W	202,998	(60)	—	Ni, Zn
	207,912	(30)	(10)	Ni, Mo, V
	209,860	(60)	(20)	—
	222,589	(60)	(30)	Cr, Cu, Ni
	239,711	(60)	—	—
Zn	202,548	—	(3)	Cr, Cu, Co, Ni
	206,200	13	5	Cr
	213,857	3,3	1	Cu, Fe, Ni

Table 1 (*continued*)

Element	Wavelength	Approx. X_{LQ}		Interfering elements
		Radial viewing	Axial viewing	
	nm	µg/l	µg/l	
Zr	339,197	—	(2)	Mo
	343,823	(10)	(0,3)	—
	354,262	(50)	(1)	—

NOTE 1 X_{LQ}: Definition of the limit of quantification (X_{LQ}) according to definition 3.11.

NOTE 2 Most X_{LQ} data derive from the Interlaboratory trial (see Annex B). Participants were asked to report their X_{LQ} calculated according to definition 3.11. In Table 1, the median of the reported data for the matrix drinking water is given. Data reported in brackets derive from other sources.

[a] Wavelength in Table 1 according to NIST tables for basic atomic spectroscopic data (http://physics.nist.gov/PhysRefData/Handbook/)

[b] As some wavelengths are only recommended for vacuum instruments and not recommended for purged instruments, the choice of wavelengths for a specific instrument should be carried out with respect to the manufacturer's recommendation.

Because of the differences between various models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst will need to refer to the instructions provided by the manufacturer of the particular instrument.

6 Interferences

6.1 General

Several types of interference effects can contribute to inaccuracies in the determination of elements. They are also termed matrix effects.

In order to avoid interferences, whenever a new or unusual sample matrix is encountered, the method in use should be carefully reviewed if it is suitable for this type of sample or a new method should be developed. In order to validate the method, measurements of suitable reference materials are to be carried out. Additionally, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry or ICP-MS.

Interferences can be classified as follows.

6.2 Spectral interferences

6.2.1 General

These types of interferences are caused by light of other elements present in the matrix. The error is additive. Typically, they cause an erroneously high reading. In the case of background influences, low readings can also occur. The most important spectral interferences are listed in Table 1.

6.2.2 Spectral overlap

6.2.2.1 Overlap of a spectral line from another element

During method development, the goal is to avoid line overlap by the choice of an alternate, undisturbed line. If this is not possible, these effects can be compensated by utilizing computer correction of the raw data.

6.2.2.2 Unresolved overlap of molecular band spectra

If possible, an undisturbed line should be chosen. If this is not possible, these effects can be compensated by utilizing computer correction of the raw data.

6.2.3 Background influences

Background influences include

1) background contribution from continuous or recombination phenomena, and

2) background contribution from stray light generated from the line emission of high concentration elements.

The effect of background interferences can usually be compensated by background correction adjacent to the analyte line.

6.2.4 Detecting spectral interferences

If the peak shape changes in comparison to the peak shape generated by a single element solution, line overlap can be suspected. Background changes are best identified by overlaying of spectra of blank, standards and samples. Also, the comparison of results for a given element measured at different lines will indicate spectral interferences.

6.3 Non-spectral interferences

6.3.1 Physical interferences

These are generally considered to be effects associated with the sample nebulization and other transport processes of the sample from the sample container to the plasma.

They are caused by the change in viscosity, density and/or surface tension. They may result in significant errors especially in samples containing high dissolved solids and/or acid concentrations. These types of interferences can be reduced by matrix-matching (if the concentrations of the analytes are high enough, dilution of the sample may be the preferred way), the use of an internal standard (provided no excitation interferences are encountered) and/or utilization of the method of standard addition.

6.3.2 Excitation interferences

Depending on the relation of the room (operating) temperature to the plasma temperature, the change of the plasma temperature due to the introduction of sample may cause an increase or decrease of the signal. In addition, elements which readily release electrons may change the electron density in the plasma, which may influence the distribution between atomic and ionic transitions. Alkaline metals (Li, K, Na) are highly susceptible to excitation interferences, particularly on axial viewing.

6.3.3 Chemical interferences

They are characterized by molecular compound formation, variation of oxidation state and solute vaporization effects. These interferences are very rare. However, when encountered, they may cause serious errors.

EXAMPLE Release of hydrogen sulfide gas rather than sulfate, iodine vapours rather than iodide or iodate.

Care shall be taken to ensure the same chemical state, if these effects are observed.

6.3.4 Detecting non-spectral interferences

In order to detect the non-spectral interferences, recovery experiments should be performed.

a) **Dilution**

If the analyte concentration is sufficiently high (at least a factor of 10 above the instrumental detection limit after dilution), the results of the analysis of a dilution needs to agree within ± 10 % of those obtained on the undiluted sample (or within some acceptable control limit that has been established for that matrix).

b) **Standards additions (spike recovery)**

The recovery of a spike addition added at a minimum level of 10× the instrumental detection limit (maximum 100×) to the original determination needs to be recovered to within 80 % to 120 % or within the established control limit for that matrix. If not, suspect a matrix effect.

The use of a standard addition analysis procedure can usually compensate for non-spectral interferences.

6.4 Compensation of non-spectral interferences by the use of internal standards

The use of internal standards is in some cases a suitable method to correct for interferences. The approach involves the addition of a known amount of a substance or material to the sample. The sample is then analysed and the responses for the determinand and the added (internal) standard are measured. The observation for the internal standard is then used to relate the determinand signal to the determinand concentration. The effect on analytical error and the type of likely error will vary according to the exact approach adopted.

Usually, there is an initial, conventional calibration relating the responses for all elements to their concentrations. Consequently, each subsequent analysis depends on the internal standard as a means of adjusting for changes in instrumental sensitivity, possibly caused by changes in sample uptake or by drift in detector response. Here, care needs to be taken to eliminate factors (such as the efficiency of excitation) which affect the standard and one or more of the determinands to different extents since these will lead to systematic error. Unless the size of response for the internal standard is the same as that for all elements of interest (which is most unlikely), nonlinearity of response can also lead to error. This may well go undetected, since it is rare to make a range of internal standard additions.

As a consequence, this calibration approach will increase the random error by the random variation associated with the internal standardization. However, overall precision may still be better than otherwise, since the consequent control over drift, etc., may improve the observed total standard deviation.

7 Reagents

7.1 General requirements

For the determination of elements at trace and ultra-trace level, use reagents 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.

Unless otherwise specified, dry all salts for 1 h at 105 °C.

Standard stock solutions may be purchased or prepared from high purity grade chemicals or metals. Traceable standard solutions are to be preferred.

7.2 Water, complying with grade 1 as defined in ISO 3696 for all sample preparation and dilutions.

7.3 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 negligible content of the analytes of interest.

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

On the determination of phosphorus, attention should be paid to a possible stabilization of hydrogen peroxide with phosphoric acid as this will affect the determination of phosphorus.

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

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

7.7 Hydrochloric acid, $c(HCl)$ = 0,2 mol/l.

7.8 Ammonium sulfate, $(NH_4)_2\ SO_4$.

7.9 Element stock solutions, of

Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, W, Zn, Zr,

ρ = 1 000 mg/l each.

Stock solutions are reference materials as defined in ISO Guide 30. 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 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.

7.10 Intermediate mixed standard solutions

7.10.1 General

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

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

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

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

Depending on the complexity of the sample matrix, it may be necessary to use matrix matched standards. This should be checked carefully.

On composing multi-element standard solutions, take into account the chemical compatibility and the possible hydrolysis of the initial compounds, as well as spectral interferences. In order to avoid interferences, add the digestion reagents (e.g. nitric acid, sulfuric acid, aqua regia) to the standard solutions.

7.10.2 Multi-element standard solution A

ρ(Al, Cd, Co, Cr, Cu, Ga, Fe, In, Pb, Li, Mn, Mo, Ni, V, Zn, Bi, Si, W, Zr) = 1 mg/l.

Pour in about 250 ml of water (7.2) to a 1 000 ml volumetric flask.

Add 5 ml of nitric acid (7.3).

Pipette (1 ± 0,01) ml of each element stock solution (Al, Cd, Co, Cr, Cu, Fe, Pb, Li, Mn, Mo, Ni, V, Zn, Bi, Si, W, Zr) (7.9) to the 1 000 ml volumetric flask.

Make up to volume with water (7.2) and transfer to a suitable storage bottle.

7.10.3 Multi-element standard solution B

ρ(Sn, Ti, As, Se, Sb) = 10 mg/l.

Pour in about 250 ml of water (7.2) to a 1 000 ml volumetric flask.

Add 5 ml of hydrochloric acid (7.6).

Pipette (10 ± 0,1) ml of each element stock solution (Sn, Ti, As, Se, Sb) (7.9) to the 1 000 ml volumetric flask.

Make up to volume with water (7.2) and transfer to a suitable storage bottle.

7.10.4 Multi-element standard solution C

ρ(Ba, Be, Sr) = 0,1 mg/l.

Pour in about 250 ml of water (7.2) to a 1 000 ml volumetric flask.

Add 5 ml of nitric acid (7.3).

Pipette (0,1 ± 0,002) ml of each element stock solution (Ba, Be, Sr) (7.9) to the 1 000 ml volumetric flask.

Make up to volume with water (7.2) and transfer to a suitable storage bottle.

7.10.5 Element standard solution D

ρ(Ag) = 1 mg/l.

Pour in about 250 ml of water (7.2) to a 1 000 ml volumetric flask.

Add 5 ml of nitric acid (7.3). Add 10 ml of hydrochloric acid (7.6) to stabilize silver as $AgCl_2$.

Pipette (1,0 ± 0,01) ml of silver stock solution (7.9) to the 1 000 ml volumetric flask.

Make up to volume with water (7.2) and transfer to a suitable storage bottle.

7.10.6 Element standard solution E

ρ(B) = 10 mg/l.

Pour in about 250 ml of water (7.2) to a 1 000 ml volumetric flask.

Add 5 ml of nitric acid (7.3).

Pipette (10 ± 0,1) ml of boron stock solution (7.9) to the 1 000 ml volumetric flask.

Make up to volume with water (7.2).

Prepare this standard in polymethylpentene (PMP) or other flasks made of suitable plastics materials. Element standard solutions C, D and E, i.e. Ba, Ag and B, are known to cause problems by precipitation under certain circumstances; it is recommended that separate standard solutions are prepared.

Boron will result in an extended wash-out from the sample introduction system, which consequently may result in erroneously high results. Therefore, the B concentrations should be set as low as possible in order to avoid carry-over.

7.10.7 Multi-element standard solution F

ρ(Ca, Mg, Na, K, S, P) = 100 mg/l.

Pipette (100 ± 0,1) ml of each element stock solution (Ca, Mg, Na, K, S, P) (7.9) in a 1 000 ml volumetric flask.

Add 5 ml of nitric acid (7.3).

Make up to volume with water (7.2) and transfer to a suitable storage bottle.

7.11 Reagent blank solution

Place 50 ml of nitric acid (7.3) and 1 000 ml of water (7.2) into an HDPE or PP container. For ultra-trace analysis, polytetrafluorethylene (PTFE) containers should be used. Prior to analysis, make sure that the acid matrix and concentration of the reagent blank solution is the same as in the standard and sample solutions.

8 Apparatus

8.1 General requirements

The stability of samples, measuring and calibration solutions depends to a high degree on the container material. Check the material 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 acceptable for sample collection.

Immediately before use, wash all labware thoroughly with diluted nitric acid [for example, $w(HNO_3)$ = 10 %], and rinse several times with water (7.2).

The use of piston pipettes is allowed. It enables the preparation of lower volumes of calibration solutions. The application of dilutors is also allowed. Test each batch of pipette tips and disposable plastics vessels for impurities.

NOTE Operating conditions: Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided.

8.2 Radiofrequency generator.

8.3 Mass-flow controller.

A mass-flow controller on the nebulizer gas supply is recommended.

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

8.4 Nebulizer, with variable speed peristaltic pump.

Common nebulizers are the concentric nebulizer (for example, Meinhard), the cross-flow nebulizer, the V-groove nebulizer and a cyclonic chamber with or without baffles. Other types of nebulizers may also be used if it can be shown that they are fit for purpose.

8.5 Ultrasonic nebulizer.

If very low concentration ranges are to be achieved, ultrasonic nebulizers are recommended. In this special type of nebulizer the sample 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. As this is very high, the aerosol needs to be dried (desolvated) before being introduced into the plasma, which otherwise extinguishes. 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 (approximately > 0,5 % m/v) and a longer rinsing time.

Vapour generation apparatuses for hydride or cold vapour can also be used for sample introduction.

8.6 Inductively coupled plasma optical emission spectrometer.

Computer-controlled optical emission spectrometer with background correction.

8.7 Argon gas supply.

Argon gas with a sufficient purity grade, for instance > 99,95 %.

8.8 General labware.

A range of volumetric flasks, Erlenmeyer flasks and pipettes.

8.9 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 ultra-trace level, bottles made from perfluoroalkoxy (PFA) or hexafluoroethene propene (FEP) should be preferred. Check the suitability of the chosen containers.

8.10 Acid dispensers, variable volume.

8.11 Filtration equipment.

Membrane filtration equipment and membrane filters of a medium pore size 0,45 µm reserved for trace element determination.

Glass or PTFE filtering apparatus are recommended to avoid possible contamination or adsorption with metal elements. Test each batch of membrane filters for impurities.

9 Sampling and preservation

9.1 General requirement

Carry out the sampling as specified in ISO 5667-1 and ISO 5667-3.

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 As, Ag, B, Bi, Sb, Se, Sn, Ti, W

and Zr. The choice of the container material depends on the mass concentration of the elements to be determined.

Rinse laboratory labware, including sample bottles, with diluted nitric acid [for example, $w(HNO_3)$ = 10 %], and then rinse several times with water (7.2) before use. Make sure that the concentration of the analytes that will be possibly desorbed from the labware and the bottles is negligible compared to the lowest concentration to be determined.

Perform the following preservation and pre-treatment steps (filtration and acid preservation) at the time the sample is collected, or as soon as possible thereafter. For other matrices other preservation steps may be necessary (see e.g. ISO 5667-15 for preservation of sediments).

9.2 Sampling for the determination of dissolved elements

For the determination of the dissolved fraction of the elements, filter the sample through a membrane filter, nominal pore size 0,45 µm (8.11) as soon as possible after collection. Use several portions of the sample to rinse the filter assembly, discard and then collect the required volume of filtrate.

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 (formazin nephelometric unit, measured as specified in ISO 7027).

Add 0,5 ml of nitric acid (7.3) 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 precipitate, for example Ag and after hydrolysis Bi, Sb, Sn or Zr, add to an additional sample 1,0 ml of hydrochloric acid (7.6) per 100 ml of water. Ensure that the pH is less than 1; otherwise, add more hydrochloric acid as required.

9.3 Sampling for the determination of particulate elements

Filter a measured volume of the unpreserved sample through a 0,45 µm membrane filter as soon as possible after collection. Transfer the filter plus particulate material to a container for storage and/or shipment. No preservative is required.

9.4 Sampling for the determination of total elements

Acidify the sample with 0,5 ml of nitric acid (7.3) per 100 ml of sample; if necessary, add more acid to reach pH ⩽ 2. For the direct analysis of total recoverable analytes in drinking water samples with a turbidity < 1,5 FNU (formazine nephelometric unit, measured as specified in ISO 7027), the digestion step described in 9.5.3 can be omitted.

9.5 Sample pre-treatment

9.5.1 Determination of the mass concentration of dissolved elements

Analyse the filtered, preserved sample as received. Make sure that the acid matrix and concentration of the samples and calibration standards is the same. If a precipitate is formed upon acidification of the sample or during transport or storage, redissolve before analysis by adding additional acid and/or by heating on a hot plate.

9.5.2 Determination of the mass concentration of particulate elements

Usually, borosilicate glass is suitable for parts in contact with the digestion solution. If low concentrations of leachable elements are to be analysed, other materials may be used, for instance quartz (high temperatures) and polyethene or polypropene (low temperatures). Examples of leachable elements are B, Na, K and Al.

9.5.2.1 Apparatus

9.5.2.1.1 Digestion vessel, made of borosilicate glass, PTFE or TPX, e.g. 50 ml.

9.5.2.1.2 Reflux condenser, made of borosilicate glass.

9.5.2.1.3 Roughened glass beads, diameter of 2 mm to 3 mm (or anti-bumping granules), acid-washed.

9.5.2.1.4 Microwave unit, consisting of a programmer and microwave module capable of heating the digestion vessel to the boiling point. Alternatively a conventional hot plate may be used.

9.5.2.2 Procedure

Transfer the membrane filter containing the insoluble material (9.3) to a digestion vessel (9.5.2.1.1) and add 4 ml of nitric acid (7.3) and 4 ml of hydrogen peroxide (7.4). Connect the digestion vessel with a reflux condenser (9.5.2.1.2) and heat gently.

Increase the temperature using the temperature programme of the microwave system and digest the material. If necessary, add another 3 ml of nitric acid (7.3) and 3 ml of hydrogen peroxide (7.4). Continue heating until the digestion is complete, generally indicated by a light coloured digest.

Disconnect the reflux condenser and evaporate to near dryness (2 ml), cool, add 10 ml of hydrochloric acid (7.6) and 15 ml of water (7.2) per 100 ml dilution. Warm the vessel gently for 15 min to dissolve any precipitated or residue material. Allow to cool, wash down vessel walls with water (7.2) and filter the sample to remove insoluble material which may block the nebulizer. Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as “particulate”.

a) Instead of filtering, after diluting and mixing, the sample may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

b) Calibration standards/Analytical Quality Control solutions should be prepared with the same acid concentration and matrix.

c) A filter blank should be taken through the identical procedure as samples and subtracted from the sample analytical results at the calculation stage.

Digestions in open systems with borosilicate glassware are not appropriate for the determination of Al, B and Si due to background contamination. In these cases, PTFE or TPX containers should be used.

9.5.3 Determination of total elements

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 as specified in ISO 15587-2. If aqua regia is chosen, the procedure shall be carried out as specified in ISO 15587-1.

Some elements and their respective compounds (for example, silicates and aluminium oxide) will be dissolved incompletely using this procedure. In that case, the residue can be dissolved in hydrofluoric acid for subsequent determination of elements.

Digestion for tin and for titanium is described in A.1 and A.2, respectively.

Special digestion methods may be necessary if Sb or Zr are to be determined.

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

10 Procedure

10.1 General

Follow the instructions provided by the manufacturer of the particular instrument.

NOTE Sensitivity, instrumental detection limit, precision, linear dynamic range and interference effects will be investigated and established for each individual analyte line on that particular instrument.

Set up the instrument with the proper operating parameters established from the manufacturer's instruction manual. Allow the instrument to achieve thermal stability before beginning.

Initiate the appropriate operating configuration of the computer.

Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the intermediate mixed standard solutions (7.10). The relationship between concentration and intensity is linear up to six orders of magnitude. However, some elements show a small linear range of only one order of magnitude, for example the alkaline metals (Li, K, Na). In many cases two calibration solutions are sufficient: an upper calibration solution and a lower solution. When working with two calibration standards, check the calibration function against samples prepared independently.

Before beginning the sample run, re-analyse the reference standard with the highest concentration as if it were a sample. Ensure that the concentration values do not deviate from the actual values by more than ± 5 % (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

Flush the system with the reagent blank solution (7.11) between each standard.

Begin the sample run by flushing the system with the reagent blank solution (7.11) between each sample.

Analyse a calibration check solution (3.6) and the calibration blank solution (3.4) every 10 samples.

10.2 Instrument performance check

Analyse an appropriate instrument performance check solution containing the elements of interest within an appropriate time interval. This check solution is used to determine instrument drift. If agreement is not within a defined range of the expected values (e.g. within a deviation of 10 %) or within the established control limits, whichever is lower, the analysis is out of control. Terminate the analysis, correct the problem, and recalibrate the instrument.

To verify inter-element and background correction factors, analyse the interference, check the sample at the beginning, end, and at regular intervals throughout the sample run. Results should fall within the defined control limits. If not, terminate the analysis, correct the problem and recalibrate the instrument.

10.3 Evaluation

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

Relate emission signals from calibration blank and calibration solutions with the signals from reference-element/s [internal standard(s)] and establish a calibration plot.

Determine the mass concentrations of samples with the aid of the emissions and the calibration graphs.

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, use a correction for the procedure blank, 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.

10.4 Independent calibration check

10.4.1 General requirement

Use at first an independent calibration solution obtained from an outside source for the initial verification of the calibration standards. Analyse a fresh dilution of this sample every week thereafter to monitor their stability. If the results are not within ± 10 % of the true value listed for the control sample, prepare new calibration standard solutions and recalibrate the instrument. If this does not eliminate the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

Prepare calibration check solutions for all elements from stock solutions reserved for this purpose consisting of the same matrix as the sample of interest and carried through the entire analytical process.

Analyse one calibration standard and one blank solution with each batch of about 25 samples and take them through the entire analytical processes (including dilution, filtering and digestion, etc.).

10.4.2 Standard addition method of analysis

NOTE The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for spectral (additive) interferences. The simplest version of this technique is the single-addition method.

Take two identical aliquots of the sample solution, each of volume V_X. To the first (labelled A), add a small volume of V_S of a standard analyte solution of concentration ρ_S of the analyte in the standard solution. Measure the analytical signals of A and B and correct for non-analyte signals. Calculate the unknown sample concentration ρ_X as follows:

$$\rho_X = \frac{S_B \cdot V_S \cdot \rho_S}{(S_A - S_B) \cdot (V_X + V_S) + S_B \cdot V_S} \quad (1)$$

where

S_A, S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively;

V_S is the added volume of standard analyte, in millilitres, ml;

V_X is the volume of identical aliquots of sample solution in millilitres, ml;

ρ_S is the mass concentration of standard analyte solution, in milligrams per litre, mg/l.

Choose V_S and ρ_S so that S_A is on average twice S_B. It is best if V_S is made much less than V_X and thus ρ_S is much greater than ρ_X, to avoid excess dilution of the sample matrix. If a greater volume was added by the element spikes giving rise to a possible dilution error, add the same amount of water (or diluted acid) to make up for the dilution error.

Alternatively, carry out the evaluation by an automated method of linear regression.

If a separation or concentration step is used, carry out the entire procedure on this sample. The results are valid provide the following requirements apply:

— the analytical response is linear;

— the chemical form of the analyte added is the same as the analyte in the sample;

— the interference effect is constant over the working range of concern;

— the signal is corrected for any additional interference.

11 Expression of results

State as many significant figures as acceptable according to the precision of the measuring values, but not more than 3 significant figures.

EXAMPLES	Copper (Cu)	0,142 mg/l
	Cadmium (Cd)	0,5 µg/l

12 Test report

This clause specifies which information is to be included in the test report. The clause shall require information to be given on at least the following aspects of the test:

a) a reference to this International Standard (ISO 11885);

b) complete identification of the sample;

c) expression of results as indicated in Clause 11;

d) sample pre-treatment, if appropriate;

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

Annex A
(informative)

Special digestion methods

A.1 Digestion for tin

Add 1 ml of concentrated sulfuric acid (7.5) and 1 ml of hydrogen peroxide (7.4) to 100 ml of the homogenized sample.

Heat the mixture until white fumes are evolved. The procedure may be carried out in a suitable open microwave system or in a beaker on a hot plate, respectively.

If the digestion is incomplete, add, after cooling, a small quantity of water (7.2) and about 1 ml of hydrogen peroxide (7.4) and repeat the procedure.

The digestion is usually regarded as incomplete if the solution is not absolutely transparent and still contains particles.

Dissolve the residue in hydrochloric acid (7.7), add water (7.2) to 100 ml and continue as given in Clause 10.

A.2 Digestion for titanium

Add to 100 ml of homogenized sample 2 g of ammonium sulfate (7.8) and 3 ml of sulfuric acid (7.5).

Heat, while stirring, until white fumes are evolved. The procedure may be carried out in a suitable open microwave system or in a beaker on a hot plate, respectively.

If digestion is incomplete, repeat the procedure. The digestion is usually regarded as incomplete if the solution is not absolutely transparent and still contains particles.

Dissolve the residue in water (7.2), add water to 100 ml and continue as given in Clause 10.

Annex B
(informative)

Precision data

An international interlaboratory trial was performed in February 2006 by IWW Water Research Centre Muelheim/Germany. Twenty-eight laboratories from six countries took part (Finland: 4; France: 8; Germany: 8; Norway: 4; Sweden: 3; United Kingdom: 1). A set of 22 parameters were analysed in drinking water, surface water and waste water, which were digested as specified in ISO 15587-1 or ISO 15587-2. The performance data are summarized in Tables B.1 to B.3.