INTERNATIONAL STANDARD

ISO 30011

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Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma mass spectrometry

Air des lieux de travail — Détermination des métaux et métalloïdes dans les particules en suspension dans l'air par spectrométrie de masse avec plasma à couplage inductif

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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 30011 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Introduction

The health of workers in many industries is at risk through exposure by inhalation of toxic metals and metalloids. Industrial hygienists and other public health professionals need to determine the effectiveness of measures taken to control workers' exposure, and this is generally achieved by taking workplace air measurements. ISO 30011 has been published in order to make available a method for making valid ultra-trace exposure measurements for a wide range of metals and metalloids in use in industry. It is intended for: agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; and industrial users of metals and metalloids and their workers.

ISO 30011 specifies a method for determination of the mass concentration of metals and metalloids in workplace air using quadrupole inductively coupled plasma mass spectrometry (ICP-MS). For many metals and metalloids, analysis by ICP-MS is advantageous when compared to methods such as inductively coupled plasma atomic emission spectrometry, due to its sensitivity and the presence of fewer spectral interferences.

ISO 30011 gives requirements and test methods for analysis of sample solutions by ICP-MS. Users of ISO 30011 are referred to ISO 15202-1 for collection of samples of airborne particulate matter and to ISO 15202-2 for procedures for preparing sample solutions for analysis by ICP-MS.

It has been assumed in the drafting of ISO 30011 that the execution of its provisions, and the interpretation of the results obtained, are entrusted to appropriately qualified and experienced people.

Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma mass spectrometry

1 Scope

This International Standard specifies a procedure for the use of quadrupole inductively coupled plasma mass spectrometry (ICP-MS) for analysing test solutions prepared from samples of airborne particulate matter collected as specified in ISO 15202-1. Method development, performance checks, and a routine analysis method are specified.

Test solutions for analysis by this International Standard are prepared as specified in ISO 15202-2.

This International Standard is applicable to the assessment of workplace exposure to metals and metalloids for comparison with limit values (see e.g. EN 689[10], ASTM E1370[8]).

The following is a non-exclusive list of metals and metalloids for which limit values have been set (see Reference [15]) and for which one or more of the sample preparation methods specified in ISO 15202-2 and the analytical procedure described in this International Standard are applicable. However, there is no information available on the effectiveness of any of these sample preparation methods for those elements listed in italics.

aluminium	caesium	lead	platinum	tungsten
antimony	chromium	lithium	potassium	uranium
arsenic	cobalt	magnesium	rhodium	vanadium
barium	copper	manganese	selenium	yttrium
beryllium	gallium	*mercury*	silver	zinc
bismuth	*germanium*	molybdenum	sodium	zirconium
boron	hafnium	nickel	tellurium	
cadmium	indium	*niobium*	thallium	
calcium	iron	phosphorus	tin	

This International Standard is not applicable to determination of elemental mercury, since mercury vapour is not collected using the sampling method specified in ISO 15202-1.

The procedure is suitable for assessment of exposure against the long-term exposure limits for most of the metals and metalloids listed above when sampling at a typical flow rate of 2 l min^{-1} for sampling times in the range 0,5 h to 8 h and for assessment of exposure against the short-term exposure limits, where applicable.

The procedure is subject to no significant spectral interferences (see A.3), provided that suitable analytical isotopes are used. However, inadequate matrix-matching can adversely affect results.

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 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 3585, *Borosilicate glass 3.3 — Properties*

ISO 8655-1, *Piston-operated volumetric apparatus — Part 1: Terminology, general requirements and user recommendations*

ISO 8655-2, *Piston-operated volumetric apparatus — Part 2: Piston pipettes*

ISO 8655-5, *Piston-operated volumetric apparatus — Part 5: Dispensers*

ISO 8655-6, *Piston-operated volumetric apparatus — Part 6: Gravimetric methods for the determination of measurement error*

ISO 15202-1, *Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry — Part 1: Sampling*

ISO 15202-2:—, *Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry — Part 2: Sample preparation*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1 General definitions

3.1.1
breathing zone
〈general definition〉 space around the worker's face from where he or she takes his or her breath

NOTE Adapted from EN 1540:—[11], 2.4.5.

3.1.2
breathing zone
〈technical definition〉 hemisphere (generally accepted to be 0,3 m in radius) extending in front of the human face, centred on the midpoint of a line joining the ears; the base of the hemisphere is a plane through this line, the top of the head, and the larynx

NOTE 1 The definition is not applicable when respiratory protective equipment is used.

NOTE 2 Adapted from EN 1540:—[11], 2.4.5.

3.1.3
chemical agent
any chemical element or compound, on its own or admixed as it occurs in the natural state or as produced, used or released including release as waste, by any work activity, whether or not produced intentionally and whether or not placed on the market

[Council Directive 98/24/EC[16], Art. 2(a)]

3.1.4
exposure by inhalation
situation in which a chemical agent is present in the air that is inhaled by a person

NOTE Adapted from EN 1540:—[11], 2.4.1.

3.1.5
occupational exposure limit value
limit of the time-weighted average of the concentration of a chemical agent in the air within the breathing zone of a worker in relation to a specified reference period

[Council Directive 98/24/EC[16], Art. 2(d)]

EXAMPLES Threshold Limit Values® (TLVs) established by the ACGIH (Reference [15]) and Indicative Occupational Exposure Limit Values (IOELVs) promulgated by the European Commission (Council Directive 2006/15/EC[17]).

3.1.6
measuring procedure for the sampling and analysis of chemical agents in air
measurement procedure for the sampling and analysis of chemical agents in air
set of operations, described specifically, used for the sampling and analysis of chemical agents in air

NOTE 1 A measuring procedure for the sampling and analysis of chemical agents in air usually includes the following steps: preparation for sampling, sampling, transportation and storage, preparation of samples for analysis and analysis.

NOTE 2 Adapted from ISO/IEC Guide 99:2007[4].

3.1.7
reference period
specified period of time for which the limit value of a chemical agent applies

NOTE 1 The reference period is usually 8 h for long-term measurements and 15 min for short-term measurements.

NOTE 2 Adapted from EN 1540:—[11], 2.4.7.

3.1.8
workplace
defined area or areas in which the work activities are carried out

[EN 1540:—[11], 2.5.2]

3.2 Analytical definitions

3.2.1
analysis
all operations carried out after sample preparation to determine the amount or concentration of the analyte(s) of interest present in the sample

NOTE Adapted from EN 14902:2005[13], 3.1.1.

3.2.2
blank solution
solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure used for sample dissolution

NOTE 1 A blank solution might need to be subjected to further operations, such as addition of an internal standard, if the sample solutions are subjected to such operations in order to produce test solutions that are ready for analysis.

NOTE 2 Adapted from EN 14902:2005[13], 3.1.2.

3.2.3
calibration blank solution
calibration solution prepared without the addition of any stock standard solution or working standard solution

NOTE 1 The concentration of the analyte(s) of interest in the calibration blank solution is taken to be zero.

NOTE 2 Adapted from EN 14902:2005[13], 3.1.3.

3.2.4
calibration curve
plot of instrument response versus concentration of standards

NOTE Adapted from United States Environmental Protection Agency (Reference [18]).

3.2.5
calibration solution
solution prepared by dilution of the stock standard solution(s) or working standard solution(s), containing the analyte(s) of interest at a concentration(s) that is suitable for use in calibration of the analytical instrument

NOTE 1 The matrix-matching technique is normally used when preparing calibration solutions.

NOTE 2 Adapted from EN 14902:2005[13], 3.1.4.

3.2.6
field blank
sampling medium that is taken through the same handling procedure as a sample, except that it is not used for sampling, i.e. it is loaded into a sampler, transported to the sampling site and then returned to the laboratory for analysis

3.2.7
instrumental detection limit
IDL
lowest concentration at which the instrumentation can distinguish analyte content from the background generated by a minimal matrix

NOTE The IDL can be determined from blank, acidified, deionized, or ultrapure water as the matrix and from the same calculation methods used to determine a method detection limit.

3.2.8
laboratory blank
media blank
unused sampling medium, taken from the same batch used for sampling, that does not leave the laboratory

3.2.9
linear dynamic range
range of concentrations over which the calibration curve for an analyte is linear

NOTE The linear dynamic range extends from the detection limit to the onset of calibration curvature.

3.2.10
method detection limit
MDL
minimum concentration of an analyte that can be reported with 99 % confidence that the value is above zero

3.2.11
quantification limit
quantitation limit
QL
minimum concentration of an analyte that can be measured with acceptable precision

3.2.12
reagent blank
all reagents used in sample dissolution, in the same quantities used for preparation of blank and sample solutions

NOTE The reagent blank is used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample preparation.

3.2.13
sample dissolution
process of obtaining a solution containing all analytes of interest from a sample, which might or might not involve complete dissolution of the sample

NOTE Adapted from EN 14902:2005[13], 3.1.25.

3.2.14
sample preparation
all operations carried out on a sample after transportation and storage to prepare it for analysis, including transformation of the sample into a measurable state, where necessary

NOTE Adapted from EN 14902:2005[13], 3.1.24.

3.2.15
sample solution
solution prepared from a sample by the process of sample dissolution

NOTE 1 A sample solution might need to be subjected to further operations, e.g. dilution or addition of an internal standard(s), in order to produce a test solution.

NOTE 2 Adapted from EN 14902:2005[13], 3.1.22.

3.2.16
sampling medium
sampling substrate
collection medium
collection substrate
medium on which airborne chemical or biological agents are collected for subsequent analysis

EXAMPLES Filters and polyurethane foams.

3.2.17
spiked media blank
media blank that is spiked with a known amount of the analyte(s) of interest

3.2.18
stock standard solution
solution used for preparation of working standard solutions or calibration solutions, containing the analyte(s) of interest at a certified concentration(s) traceable to national standards

NOTE Adapted from EN 14902:2005[13], 3.1.26.

3.2.19
test solution
blank solution or sample solution that has been subjected to all operations required to bring it into a state in which it is ready for analysis

NOTE 1 “Ready for analysis” includes any required dilution or addition of an internal standard. If a blank solution or sample solution is not subject to any further operations before analysis, it is a test solution.

NOTE 2 Adapted from EN 14902:2005[13], 3.1.30.

3.2.20
working standard solution
solution, prepared by dilution of the stock standard solution(s), that contains the analyte(s) of interest at a concentration(s) better suited for preparation of calibration solutions than the concentration(s) of the analyte(s) in the stock standard solution(s)

NOTE Adapted from EN 14902:2005[13], 3.1.32.

3.3 ICP-MS definitions

3.3.1
collision cell
chamber in the ion path between mass-to-charge ratio (m/z) separation elements, or between ion source acceleration region and the first analyser, in tandem mass spectrometry in space configurations

NOTE See Reference [19].

3.3.2
collision reaction cell
collision cell for removal of interfering ions by ion/neutral reactions in ICP-MS

NOTE 1 See Reference [20].

NOTE 2 Collision reaction cells make use of kinetic energy dispersion, reaction chemistry or a combination of both, to remove interfering species. A variety of reaction chemistry techniques are available.

3.3.3
corrosion-resistant sample introduction system
sample introduction system that features a nebulizer, spray chamber and torch injector tube that are resistant to corrosion by hydrofluoric acid

3.3.4
ICP torch
device used to support and introduce sample into an ICP discharge

NOTE An ICP torch usually consists of three concentric tubes, the outer two usually made from quartz.

3.3.5
inductively coupled plasma
ICP
high-temperature discharge generated in flowing argon by an alternating magnetic field induced by a radio frequency (RF) load coil that surrounds the tube carrying the gas

3.3.6
injector
injector tube
centre tube
innermost tube of an ICP torch, through which the sample aerosol is introduced to the plasma

NOTE The injector is usually made of quartz, ceramic material or platinum.

3.3.7
inner argon flow
nebulizer argon flow
sample argon flow
flow of argon gas that is directed through the nebulizer and carries the sample aerosol through the injector and into the plasma

NOTE The inner argon flow rate is typically 0,5 l min^{-1} to 2 l min^{-1}.

3.3.8
intermediate argon flow
auxiliary argon flow
flow of argon gas that is contained between the intermediate and centre (injector) tubes of an ICP torch

NOTE The intermediate argon flow rate is typically 0 l min^{-1} to 2 l min^{-1}.

3.3.9
internal standard
non-analyte element, present in all solutions analysed, the signal from which is used to correct for matrix interferences or improve analytical precision

3.3.10
load coil
length of metal tubing wound around the end of an ICP torch and connected to the radio frequency (RF) generator, used to inductively couple energy from the RF generator to the plasma discharge

3.3.11
matrix interference
matrix effect
non-spectral interference
interference of a non-spectral nature caused by a difference between the matrix of the calibration and test solutions

3.3.12
matrix-matching
technique used to minimize the effect of matrix interferences on the analytical results, involving the preparation of calibration solutions in which the concentrations of acids and other major solvents and solutes are matched with those in the test solutions

3.3.13
nebulizer
device used to create an aerosol from a liquid

3.3.14
outer argon flow
plasma argon flow
coolant argon flow
flow of argon gas that is contained between the outer and intermediate tubes of an ICP torch

NOTE The outer argon flow rate is typically 7 l min^{-1} to 15 l min^{-1}.

3.3.15
spectral interference
isobaric interference caused by a species other than the analyte of interest

NOTE Interferences can involve an atomic, polyatomic or doubly charged ion species. An example of an atomic interference is $^{40}Ar^{+}$ on $^{40}Ca^{+}$. An example of a polyatomic interference is $^{40}Ar^{16}O^{+}$ on $^{56}Fe^{+}$. An example of a doubly charged ion interference is $^{48}Ti^{2+}$ on $^{24}Mg^{+}$ (Reference [21]).

3.3.16
spray chamber
device placed between a nebulizer and an inductively coupled plasma torch whose function is to separate out aerosol droplets in accordance with their size, so that only very fine droplets pass into the plasma and large droplets are drained or pumped to waste

3.3.17
tuning
analysis of a solution containing a range of isotopic masses to establish ICP-MS mass-scale accuracy, mass resolution, signal intensity and precision prior to calibration

NOTE See Reference [18].

3.4 Statistical definitions

3.4.1
analytical recovery
ratio of the mass of analyte measured in a sample to the known mass of analyte in that sample

NOTE The analytical recovery is usually given as a percentage.

[EN 1540:—[11], 5.1.1]

3.4.2
bias
difference between the expectation of a test result or measurement result and a true value

NOTE 1 Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the true value is reflected by a larger bias value.

NOTE 2 The bias of a measuring instrument is normally estimated by averaging the error of indication over an appropriate number of repeated measurements. The error of indication is the "indication of a measuring instrument minus a true value of the corresponding input quantity".

NOTE 3 In practice, the accepted reference value is substituted for the true value.

[ISO 3534-2:2006[1], 3.3.2]

NOTE 4 In the case of measurement procedures for the sampling and analysis of chemical agents in air, the accepted reference value can be, for example, the certified value of a reference material, the concentration of a standard test atmosphere or the target value of an interlaboratory comparison.

3.4.3
coverage factor
k
numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

NOTE A coverage factor, k, is typically in the range from 2 to 3.

[ISO/IEC Guide 98-3:2008[3]]

3.4.4
combined standard uncertainty
u_c
standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities

[ISO/IEC Guide 98-3:2008[3]]

3.4.5
expanded uncertainty
quantity defining an interval about the result of a measurement, expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

[ISO/IEC Guide 98-3:2008[3]]

3.4.6
precision
closeness of agreement of independent test/measurement results obtained under stipulated conditions

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

NOTE 2 The measure of precision is usually expressed in terms of imprecision and computed as a standard deviation of the test results or measurement results. Less precision is reflected by a larger standard deviation.

NOTE 3 Quantitative measures of precision depend critically on the stipulated conditions. Repeatability conditions and reproducibility conditions are particular sets of extreme stipulated conditions.

[ISO 3534-2:2006[1], 3.3.4]

3.4.7
true value
value which characterizes a quantity or quantitative characteristic perfectly defined in the conditions which exist when that quantity or quantitative characteristic is considered

NOTE The true value of a quantity or quantitative characteristic is a theoretical concept and, in general, cannot be known exactly.

[ISO 3534-2:2006[1], 3.2.5]

3.4.8
uncertainty (of measurement)
parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand

NOTE 1 The parameter may be, for example, a standard deviation (or a given multiple of it), or the width of a confidence interval.

NOTE 2 Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of a series of measurements, and can be characterized by standard deviations. The other components, which also can be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information. The ISO/IEC Guide 98-3:2008[3] refers to these different cases as Type A and Type B evaluations of uncertainty, respectively.

NOTE 3 Adapted from the ISO/IEC Guide 99:2007[4].

4 Principle

4.1 Airborne particles containing metals and metalloids are collected using the method specified in ISO 15202-1.

4.2 The collected sample and the filter are then treated to dissolve the metals and metalloids of interest using one of the sample dissolution methods specified in ISO 15202-2.

4.3 The resultant solutions are analysed for the metals and metalloids of interest using quadrupole ICP-MS.

5 Requirements

The measuring procedure as a whole (specified in ISO 15202-1, ISO 15202-2 and this International Standard) shall comply with any relevant International, European or National Standard, e.g. EN 482[9] and EN 13890[12], which specifies performance requirements for measuring chemical agents in workplace air.

6 Reagents

During the analysis, use only reagents of recognized analytical grade and only water as specified in 6.1.

6.1 Water, from a purification system that delivers ultrapure water having a resistivity greater than 0,18 MΩ·m (usually expressed by manufacturers of water purification systems as 18 MΩ·cm).

6.2 Mineral acids, concentrated.

6.2.1 General. Various types of mineral acid (6.2.2 to 6.2.6) are required for preparation of matrix-matched calibration solutions (see 6.4.2).

The concentration of the metals and metalloids of interest shall be less than 0,1 mg l^{-1}.

Mineral acids of higher purity may be required in order to obtain adequate detection limits for some metals and metalloids, e.g. beryllium.

6.2.2 Nitric acid, concentrated, $\rho_{HNO_3} \approx 1{,}42$ g ml^{-1}, $w_{HNO_3} \approx 70$ % mass fraction.

WARNING — Concentrated nitric acid is corrosive and oxidizing and nitric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with concentrated or dilute nitric acid.

6.2.3 Perchloric acid, concentrated, $\rho_{HClO_4} \approx 1{,}67$ g ml^{-1}, $w_{HClO_4} \approx 70$ % mass fraction.

WARNING — Concentrated perchloric acid is corrosive and oxidizing and perchloric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with concentrated or dilute perchloric acid. For safety reasons, use perchloric acid in limited quantities.

For analysis of metals and metalloids that are subject to interference from polyatomic ions containing chlorine, the use of perchloric acid is not recommended unless a collision reaction cell is used.

6.2.4 Hydrochloric acid, concentrated, $\rho_{HCl} \approx 1{,}18$ g ml^{-1}, $w_{HCl} \approx 36$ % mass fraction.

WARNING — Concentrated hydrochloric acid is corrosive and oxidizing and hydrochloric acid fumes are irritant. Avoid exposure by contact with the skin or eyes, or by inhalation of fumes. Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when

working with concentrated or dilute hydrochloric acid. Handle open vessels containing concentrated hydrochloric acid under a fume hood. The vapour pressure of hydrochloric acid is high; therefore beware of pressure build-up in stoppered flasks when preparing mixtures of hydrochloric acid and water.

For analysis of metals and metalloids that are subject to interference from polyatomic ions containing chlorine, the use of hydrochloric acid is not recommended unless a collision reaction cell is used.

6.2.5 Sulfuric acid, concentrated, $\rho_{H_2SO_4} \approx 1{,}84$ g ml^{-1}, $w_{H_2SO_4} \approx 98$ % mass fraction.

WARNING — Concentrated sulfuric acid is corrosive and causes burns. Avoid exposure by contact with the skin or eyes. Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with concentrated or dilute sulfuric acid. Exercise great caution when diluting sulfuric acid with water, since this process is very exothermic. Do not add water to sulfuric acid, since it reacts violently when mixed in this manner. Prepare mixtures by adding sulfuric acid to water.

For analysis of metals and metalloids that are subject to interference from polyatomic ions containing sulfur, the use of sulfuric acid is not recommended unless a collision reaction cell is used.

6.2.6 Hydrofluoric acid, concentrated, $\rho_{HF} \approx 1{,}16$ g ml^{-1}, $w_{HF} \approx 48$ % mass fraction.

WARNING — Concentrated hydrofluoric acid is very toxic in contact with the skin and if inhaled or swallowed. It is corrosive and causes severe burns. Take extreme care when using hydrofluoric acid. Avoid contact with the skin or eyes, or inhalation of the vapour. It is ESSENTIAL that suitable personal protective equipment (including suitable gloves, face shield, etc.) is used when working with concentrated or dilute hydrofluoric acid. Handle open vessels containing concentrated hydrofluoric acid under a fume hood. Ensure that the nature and seriousness of hydrofluoric acid burns is understood before commencing work with this substance. Carry hydrofluoric acid burn cream (containing calcium gluconate) at all times while working with hydrofluoric acid and for 24 h afterwards. Apply the cream to any contaminated skin, after washing the affected area with copious amounts of water. Obtain medical advice immediately in case of an accident.

NOTE The burning sensation associated with many concentrated acid burns is not immediately apparent on exposure to hydrofluoric acid and might not be felt for several hours. Relatively dilute solutions of hydrofluoric acid can also be absorbed through the skin, with serious effects similar to those resulting from exposure to the concentrated acid.

When using hydrofluoric acid, it is recommended that a pair of disposable gloves be worn underneath suitable rubber gloves to provide added protection for the hands.

For analysis of metals and metalloids that are subject to interference from polyatomic ions containing fluorine, the use of hydrofluoric acid is not recommended unless a collision reaction cell is used.

6.3 Stock standard solutions, for preparation of calibration solutions.

6.3.1 Use commercial single-element or multi-element standard solutions with certified concentrations traceable to national standards to prepare calibration solutions. The range of standard solutions used shall include all the metals and metalloids of interest at a suitable concentration. Observe the manufacturer's expiration date or recommended shelf life.

NOTE Commercially available stock standard solutions for metals and metalloids have nominal concentrations of 100 mg l^{-1} to 10 000 mg l^{-1} for single element standards and 10 mg l^{-1} to 1 000 mg l^{-1} for multi-element standards.

6.3.2 Alternatively, prepare stock standard solutions from high-purity metals and metalloids or their salts. The procedure used to prepare the solutions shall be fit for purpose and the calibration of any apparatus used shall be traceable to national standards. Store in a suitable container, e.g. a polypropylene bottle (7.5). The maximum recommended shelf life is 1 year from date of initial preparation.

6.4 **Working standard solutions** and **calibration solutions**.

6.4.1 Prepare a working standard solution or solutions, if desired, to include all the metals and metalloids of interest at suitable concentrations. Accurately pipette an appropriate volume of each single-element stock standard solution, or of multi-element stock standard solution (6.3), into a labelled, one-mark volumetric flask (7.1). Add an appropriate volume of a suitable mineral acid (6.2) to ensure analyte stability. Dilute almost to the mark with water (6.1), stopper, and swirl to mix. Allow to cool to room temperature, make up to the mark with water, stopper, and mix thoroughly.

Analytes that are grouped together in working standard solutions should be chosen carefully to ensure chemical compatibility and to avoid spectral interferences. The type and volume of each acid added should be selected carefully to ensure analyte stability.

6.4.2 From the working standard solutions, prepare a set of calibration solutions, covering the range of concentrations for each of the metals and metalloids of interest, typically between 1 µg l^{-1} and 100 µg l^{-1}. It is recommended that a minimum of three calibration solutions be prepared. Also prepare a calibration blank solution (see 3.2.2). For each set of calibration solutions, accurately pipette appropriate volumes of working standard solution (6.4.1) or stock standard solution (6.3), into individual, labelled, 100 ml volumetric flasks (7.1). Add reagents, as required (see the next two paragraphs), to match the calibration solutions with that of the test solutions (see 8.2.10.1). Dilute almost to the mark with water (6.1), stopper, and swirl to mix. Allow to cool to room temperature, make up to the mark with water, stopper, and mix thoroughly. Prepare fresh calibration solutions daily.

The type(s) and volume(s) of reagents required to matrix-match the calibration and test solutions depend upon the sample dissolution method used. Table 1 presents information on how to achieve matrix-matching for test solutions prepared in accordance with the various sample dissolution methods specified in ISO 15202-2. However, it is also necessary to take into account the contribution to the overall acid concentration from acids present in the stock standard solution(s) used to prepare the calibration solutions.

Table 1 — Reagents required to prepare matrix-matched calibration solutions

Sample dissolution method	Reagents required to prepare matrix-matched calibration solutions
ISO 15202-2:—, Annex B	10 ml of nitric acid (6.2.2)
ISO 15202-2:—, Annex C	4 ml of nitric acid (6.2.2) and 20 ml of hydrochloric acid (6.2.4)
ISO 15202-2:—, Annex D	20 ml of nitric acid (6.2.2)
ISO 15202-2:—, Annex E	4 ml of sulfuric acid (6.2.5) and 20 ml of hydrochloric acid (6.2.4)
ISO 15202-2:—, Annex F	4 ml of perchloric acid (6.2.3) and 20 ml of hydrochloric acid (6.2.4)
ISO 15202-2:—, Annex G (G.6.1)	20 ml of nitric acid (6.2.2)
ISO 15202-2:—, Annex G (G.6.1, G.6.5)	20 ml of nitric acid (6.2.2) and 20 ml of hydrochloric acid (6.2.4)
ISO 15202-2:—, Annex G (G.6.2)	16 ml of nitric acid (6.2.2) and 4 ml of perchloric acid (6.2.3)
ISO 15202-2:—, Annex G (G.6.2, G.6.5)	16 ml of nitric acid (6.2.2), 4 ml of perchloric acid (6.2.3) and 20 ml of hydrochloric acid (6.2.4)
ISO 15202-2:—, Annex G (G.6.3)	20 ml of nitric acid (6.2.2) or 16 ml of nitric acid (6.2.2) and 4 ml of perchloric acid (6.2.3)
ISO 15202-2:—, Annex G (G.6.3, G.6.5)	20 ml of nitric acid (6.2.2) and 20 ml of hydrochloric acid (6.2.4) or 16 ml of nitric acid (6.2.2), 4 ml of perchloric acid (6.2.3) and 20 ml of hydrochloric acid (6.2.4)

The calibration solutions also need to be matrix-matched with respect to hydrofluoric acid if the test solutions are prepared from samples collected on quartz fibre filters using a sample dissolution method that uses hydrofluoric acid. In general, matrix-matching with hydrofluoric acid is best avoided (see Warning notice in 6.2.6), but it is necessary in cases where its action on quartz fibre filters results in high concentrations of

silicon (and possibly other elements, such as aluminium, calcium, and sodium) in the test solutions. The calibration solutions therefore need to be prepared by addition of appropriate volumes of working standard solution (6.4.1) or stock standard solution(s) (6.3) to unused quartz fibre filters carried through the sample dissolution method described in the relevant annex of ISO 15202-2. Under such circumstances, plastic volumetric labware compatible with hydrofluoric acid and a corrosion-resistant sample introduction system have to be used.

6.5 Internal standard stock solutions.

6.5.1 Use a commercially available single-element standard solution or solutions. The standard solution(s) shall include the element(s) to be used as internal standard(s) at a suitable concentration and the matrix of the single-element standard solution(s) used for addition of internal standard(s) shall be compatible with the metals and metalloids of interest. See 8.2.11 for selection of internal standard elements.

6.5.2 Alternatively, prepare single-element stock standard solution(s) from high purity metals or their salts.

6.6 Argon, suitable for use in ICP-MS.

7 Laboratory apparatus

Usual laboratory equipment and in particular the following.

7.1 One-mark volumetric flasks, of capacities between 50 ml and 1 000 ml, complying with the requirements of ISO 1042 class A, made of borosilicate glass 3.3 complying with the requirements of ISO 3585, cleaned before use by soaking in nitric acid, diluted 1 + 9, for at least 24 h and then rinsed thoroughly with water (6.1).

7.2 Disposable tubes, plastic, compatible with the autosampler tube racks of the ICP-MS instrument.

NOTE See 8.2.9 for guidance on the use of tubes to minimize the potential for wall losses and contamination.

7.3 Piston-operated volumetric instruments, complying with the requirements of ISO 8655-1 and tested in accordance with ISO 8655-6, including **pipettors**, complying with the requirements of ISO 8655-2, for the preparation of standard solutions, calibration solutions and dilution of sample test solutions; and **dispensers**, complying with the requirements of ISO 8655-5, for dispensing acids.

7.4 Disposable gloves, impermeable and powder-free, to avoid the possibility of contamination and to protect them from contact with toxic and corrosive substances. PVC gloves are suitable.

7.5 Polypropylene bottle, low density, with leakproof screw cap.

A bottle made of an alternative plastic can be used provided that it is suitable for the intended use (see 6.3.2 and 6.4.1).

7.6 Quadrupole inductively coupled plasma mass spectrometer, computer-controlled, equipped with an autosampler that preferably has a flowing rinse.

8 Procedure

8.1 Preparation of sample solutions

Prepare sample solutions for analysis under this International Standard using one of the sample dissolution methods specified in ISO 15202-2.

It may be necessary to use reagents of higher purities than those specified in ISO 15202-2 in order to obtain adequate detection limits for some metals and metalloids.

8.2 Method development

8.2.1 General

Develop and validate a method for analysis of sample solutions prepared as specified in ISO 15202-2 that is suitable for use with the available ICP-MS instrument(s). Use the default instrument conditions given by the manufacturer as a starting point in the method development process. Refer to guidance on ICP-MS method development available in standard texts, manuals provided by instrument manufacturers and International, European or National Standards.

NOTE ICP-MS analysis of test solutions prepared from workplace air samples is applicable to a wide range of instruments. For example, ICP-MS systems can be equipped with a collision reaction cell, of which there are several types. Each of these different types of instruments needs to be set up and operated in a different manner. There are some principles that apply to the development of methods for all ICP-MS instruments, but there are also many parameters that are only applicable to particular instruments.

8.2.2 Interferences

Give consideration to the significance of any known interferences in the context of the measurement task (see Annex A for information). For each potentially useful mass-to-charge ratio, refer to published information and consider the relationship between the magnitude of interferences and the relative limit values of the elements to be determined. If the sum of all potential interferences is greater than 0,1 times the limit value of the analyte, consider alternatives, such as an alternative mass-to-charge ratio or use of a collision reaction cell (if available).

The use of a collision reaction cell can eliminate many isobaric, elemental or polyatomic interferences and (if available) is typically preferable to the use of alternative mass-to-charge ratios that might not be as sensitive as the primary mass-to-charge ratio for the analyte of interest.

8.2.3 Sample introduction system

Decide on the type of sample introduction system to use. Take into consideration the required sensitivity and the nature of the test solution matrix. In most cases, the system supplied by the instrument manufacturer is adequate.

If the spectrally pure test solutions contain hydrofluoric acid, it is necessary to use a corrosion-resistant sample introduction system and platinum cones.

High-efficiency nebulizers and ultrasonic nebulizers give higher sensitivity than conventional pneumatic nebulizers. However, they can be less corrosion-resistant. Nevertheless, the use of a high-efficiency nebulizer or an ultrasonic nebulizer may be beneficial when low quantification limits are required, e.g. if measurements are to be made for a metal or metalloid with a particularly low limit value, e.g. beryllium, or short sampling time.

8.2.4 Analytical mass

Select one or more analytical mass(es) on which to make measurements for each metal and metalloid of interest. Table 2 provides information on recommended masses and instrumental detection limits that can be achieved under optimal conditions (References [22] to [25]). Take into consideration the relative abundance of the metal or metalloid at the selected mass(es), the required quantification limits and interferences that could be significant at each candidate mass. Ordinarily, the most sensitive mass will be the most favourable, but it is necessary to avoid the use of masses on which there is potential interference.

NOTE The use of multiple masses, with appropriate use of spectral fitting software available on most ICP-MS systems, can be used to overcome many spectral overlaps or other interferences.

Table 2 — Recommended analytical isotope(s) and typical instrumental detection limits
(References [22] to [25])

Element	Recommended analytical isotope(s)[a]	Typical instrumental detection limits[b] µg ml^{-1}
Aluminium	27	0,000 6 to 0,027
Antimony	121, 123	0,000 2 to 0,000 9
Arsenic	75	0,000 6 to 0,02
Barium	135, 137, 138	0,000 02 to 0,003
Beryllium	9	0,000 1 to 0,003
Bismuth	209	0,000 04 to 0,003
Boron	10, 11	0,001 to 0,003
Cadmium	106, 108, 111, 114	0,000 09 to 0,000 9
Caesium	133	0,000 01 to 0,000 3
Calcium	43,44	0,000 2 to 1,5
Chromium	52, 53	0,000 2 to 0,013
Cobalt	59	0,000 08 to 0,002
Copper	63, 65	0,000 1 to 0,003
Gallium	69, 71	0,000 2 to 0,000 4
Germanium	72, 74	0,000 3 to 0,002
Hafnium	178	0,000 1 to 0,000 8
Indium	115	0,000 01 to 0,000 7
Iron	56, 57	0,000 3 to 0,46
Lead	206, 207, 208	0,000 04 to 0,000 6
Lithium	6, 7	0,000 09 to 0,004
Magnesium	24, 25	0,000 07 to 0,120
Manganese	55	0,000 07 to 0,005
Mercury	199, 201, 202	0,000 1 to 0,016
Molybdenum	95, 98	0,000 1 to 0,002
Nickel	58, 60	0,000 4 to 0,1
Niobium	93	0,000 01 to 0,000 6
Phosphorus	31	0,1 to 0,5
Platinum	195	0,000 05 to 0,002
Potassium	39	0,000 2 to 3,0
Rhodium	103	0,000 01 to 0,000 2
Selenium	77, 82	0,000 7 to 0,4
Silver	107, 109	0,000 05 to 0,002
Sodium	23	0,000 3 to 2
Tellurium	125, 126	0,000 1 to 0,000 8
Thallium	203, 205	0,000 04 to 0,000 4
Tin	118, 120	0,000 2 to 0,005
Tungsten	182, 184	0,000 2 to 0,005
Uranium	238	0,000 01 to 0,000 1
Vanadium	51	0,000 2 to 0,003
Yttrium	89	0,000 02 to 0,000 2
Zinc	64, 66, 68	0,000 1 to 0,018
Zirconium	90	0,000 03 to 0,000 3

[a] Isotopes recommended for analytical determination are underlined. Other masses can be used, but interferences shall be documented.

[b] Instrument detection limits were based on three-standard-deviation data. Parameters such as the use of a clean room, the presence of a collision/reaction cell and the mode in which that system was used (e.g. no gas, collision gas, reaction gas, or both), the type of cone used (Ni or Pt), vary widely. See individual references for additional details.

8.2.5 Plasma conditions

8.2.5.1 Gas flows

Under normal conditions, use the default gas flows recommended by the instrument manufacturer for inner, intermediate, and outer argon flows. However, if desired, the nebulizer (inner) argon flow can be optimized for specific applications.

NOTE 1 The nebulizer argon flow can be critical because it largely determines the residence time of the analyte in the plasma. The longer the residence time, the greater the likelihood of the analyte being atomized, excited, and ionized. In ICP-MS, ionization rather than excitation is desired. The appropriate residence time for each analyte depends on its ionization potential. Determination of the appropriate flow rate should also consider the efficiency of the nebulizer, as low flow rates can cause nebulizer efficiency to drop off significantly.

NOTE 2 The nebulizer argon flow is not always equal to the inner argon flow.

8.2.5.2 Radio-frequency power

Under normal circumstances, use the default RF power recommended by the instrument manufacturer. However, the RF power can be optimized for specific applications.

NOTE The RF power applied to the plasma can be optimized in accordance with the nature of the analyte. The more RF power that is applied to the plasma, the hotter it gets. For analytes that require more energy for ionization, a higher power can provide greater sensitivity. For analytes with low ionization potential, a lower power could provide greater sensitivity.

8.2.5.3 Sampling depth

This refers to the distance of the sampling cone from the top turn of the load coil, in millimetres (Reference [26]). Under normal circumstances, use the default sampling depth recommended by the instrument manufacturer. However, the sampling depth can be optimized for specific applications.

NOTE In general, at constant power and nebulizer gas flow rate, an increase in sampling depth reduces the ion count. See Reference [22].

8.2.6 Instrument operating parameters

Refer to the instrument manufacturer's instructions and determine the optimum settings for other relevant instrument operating parameters, e.g. detector power, integration time, and number of integrations.

8.2.7 Sample introduction rate

Under normal circumstances, use the sample uptake rate recommended by the nebulizer manufacturer. However, the uptake rate can be optimized to achieve a suitable compromise between signal intensity and uptake rate.

8.2.8 Sample wash-out parameters

Use a suitable wash-out solution, wash-out time, wash-out rate, and read delay. Conduct tests to ensure that there is no significant carryover of analyte between measurements.

8.2.9 Minimization of wall losses and contamination

When developing the analytical method, take steps to minimize the potential for loss of analyte by sorption on the walls of containers used to store calibration and test solutions, and the potential for contamination from reagents and labware. More specific details are given in the next two paragraphs.

Minimize the potential for wall losses by using containers that are made from a suitably inert material (e.g. polypropylene, polyethylene or polytetrafluoroethylene) and by ensuring that the acid concentration of calibration and test solutions is sufficiently high that analyte loss does not occur.

NOTE The extent to which sorption of analyte on container walls occurs is determined by the material from which the container is made and its roughness, the acidity of solution and the analyte concentration.

Minimize the potential for contamination of calibration and test solutions from reagents and labware by:

a) cleaning reusable labware (including caps) before use;

b) cleaning disposable plastic labware before use, unless the supplier provides a trace metal blank certificate or a representative batch of the labware concerned that has been tested and determined to have a sufficiently low trace metal blank;

c) avoiding the use of phosphate-based detergents when cleaning labware;

d) rinsing disposable plastic labware, such as micropipette tips and autosampler tubes, with test solution before use, where possible;

e) using only ultra-pure reagents;

f) using only powder-free acid-resistant gloves;

g) carrying out sample preparation and analysis in an environment that is as free as possible from airborne particles.

8.2.10 Calibration solutions

8.2.10.1 Matrix matching

Match the matrix of the calibration solutions with that of the test solutions, but if possible avoid preparing calibration solutions containing hydrofluoric acid (see Warning notice in 6.2.6).

If the test solutions prepared according to ISO 15202-2 contain hydrofluoric acid, an equal concentration of nitric acid can be substituted for hydrofluoric acid when preparing the calibration solutions. With limited exceptions (see 6.4.2), this has an insignificant effect on results, is safer and enables calibration solutions to be prepared in volumetric glassware.

8.2.10.2 Calibration range

Carry out experiments to determine the linear dynamic range for each of the selected analytes under the intended operating conditions. Then select a range of analyte concentrations over which to prepare the calibration solutions.

If more than one mass-to-charge ratio is to be used for a particular analyte, take this into consideration when selecting the range of concentrations to be covered.

8.2.10.3 Storage of calibration solutions

Prepare fresh calibration solutions daily or store for a maximum time period determined from the results of stability experiments.

NOTE The stability of calibration solutions depends upon many factors, e.g. the analyte concentration, the test matrix, the nature of the storage vessel, and the storage conditions.

8.2.11 Selection of internal standards

Select an appropriate number and combination of internal standards to correct for instrument drift, physical interferences, and changes in ion transport efficiency within the ICP-MS instrument. For full mass range scans, use a minimum of three internal standards, with the use of five internal standards recommended. Ensure that the selected internal standard elements are suitable for the intended purpose, exhibit adequate sensitivity and are chemically compatible with the test solution matrix (i.e. they do not cause precipitation). Refer to Table 3 for a non-exclusive list of appropriate internal standards and limitations on the use of each.

The selected internal standard element(s) should not be present in the test sample at a level at which they adversely affect the test results.

Internal standards can be used to correct for changes in nebulizer efficiency that can occur during analysis. While internal standards can also be used to correct for transport interferences that arise from a matrix mismatch between the calibration and test solutions, matching the matrix of the calibration and test solutions is generally preferable for that purpose.

Table 3 — Internal standards and limitations of use

Internal standard	Mass No.	Possible limitation
Lithium	7	Can be present in samples
Scandium	45	Polyatomic ion interference; can be present in samples
Yttrium	89	Can be present in samples
Rhodium	103	—
Indium	115	Isobaric interference by tin
Terbium	159	—
Holmium	165	—
Lutetium	175	—
Platinum	195	—
Bismuth	209	Can be present in samples

8.3 Instrument performance checks

8.3.1 Visual inspection

Perform regular visual checks to ensure that the instrument and ancillaries are in good order before commencing work. Follow the instrument manufacturer's recommendations.

Further guidance is given in Annex B.

8.3.2 Performance checks and fault diagnostics

Carry out performance checks daily to verify that the instrument is operating in accordance with specifications. Use more rigorous fault diagnostics if it is suspected that the instrument is not functioning properly. Follow the instrument manufacturer's recommendations.

8.4 Routine analysis

WARNING — Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with concentrated or dilute acids. Refer to the Warning notices in 6.2.

8.4.1 Dilution of sample solutions

Perform any required dilution of sample solutions prior to or in conjunction with addition of internal standards.

8.4.2 Addition of internal standards

Add the same concentration of internal standards to all solutions to be measured (i.e. calibration solutions, blank solutions, sample solutions, and quality control solutions).

NOTE Internal standards can be added by pipetting a known volume of stock standard solution into a known volume of each solution to be measured, or by pipetting a known volume of stock standard solution into each sample vial prior to adding the test solution. Alternatively, the solution to be measured and a solution containing internal standards can be mixed during sample introduction using a two-channel peristaltic pump, T-piece and mixing coil.

8.4.3 Determination of mercury

If mercury is to be determined, add a solution of gold in 2 % volume fraction aqueous HCl to all solutions to be measured, such that the final gold concentration in the solutions is 100 µg l^{-1}. Allow solutions to stand for at least 1 h prior to analysis.

Gold solution in HCl is used to minimize memory effects when mercury is an analyte of interest. Care is needed to ensure that the final HCl content in the solutions does not cause precipitation of elements incompatible with HCl, such as silver.

The use of platinum cones can be necessary for determination of low levels of mercury.

8.4.4 Setting up the instrument

Set up the ICP-MS instrument (7.6) in accordance with the method developed as specified previously; follow the manufacturer's instructions. Allow the instrument to warm up; typical warm-up times are 30 min to 60 min. It is advisable to aspirate reagent blank solution into the plasma during the warm-up period.

8.4.5 Analysis

8.4.5.1 Aspirate the calibration solutions into the plasma in order of increasing concentration and make measurements for each solution.

8.4.5.2 Generate a calibration function for the metals and metalloids of interest, preferably using linear regression via the instrument's computer. Repeat the calibration if the coefficient of determination, R^2, for any of the elements of interest is < 0,995.

If $R^2 < 0{,}995$, it might be possible to remove an erroneous calibration point, e.g. by using an outlier test, and then to reprocess the data to obtain acceptable calibration. However, the minimum number of calibration solutions specified in 6.4.2 should be maintained.

8.4.5.3 Aspirate the blank and the test solutions (prepared in accordance with ISO 15202-2) into the plasma and make measurements for each solution. Use the calibration function to determine the concentrations of metals and metalloids of interest.

8.4.5.4 Analyse the calibration blank solution and a mid-range calibration solution after the initial calibration and then after every 20 test solutions. If the measured concentration of a metal or metalloid of interest in the continuing calibration blank is greater than five times the instrumental detection limit, as determined in 8.5.1, or is greater than 10 % of the applicable limit value or minimum level of concern, or if the measured concentration of an element of interest in the continuing calibration verification has changed by more than ±10 %, take one of the following corrective measures: (1) use the instrument software to correct for the observed sensitivity change or (2) suspend analysis and recalibrate the spectrometer. In either case, reanalyse the test solutions that were analysed during the period in which the sensitivity change occurred, or reprocess the data to account for the observed sensitivity change.

8.4.5.5 Analyse quality control samples, as described in 8.6.2, at a minimum frequency of one pair per 20 test samples and use the results to monitor the performance of the analytical procedure.

8.4.5.6 Analyse a continuing calibration blank solution and a continuing calibration verification solution at the end of each analytical batch.

8.4.5.7 Examine the precision (coefficient of variation) of all results and repeat any analysis if the relative standard deviation is unacceptably high.

8.4.5.8 If the concentration of any of the metals and metalloids of interest in a test solution is found to be above the upper limit of the calibration range, dilute the sample by an appropriate factor, matrix-match as necessary and repeat the analysis (and account for the dilution factor). Alternatively, use a suitable alternative mass.

8.5 Estimation of detection and quantification limits

8.5.1 Estimation of the instrumental detection limit

8.5.1.1 Estimate the instrumental detection limit for each of the metals and metalloids of interest under the working analytical conditions and repeat this exercise whenever the experimental conditions are changed.

NOTE The instrumental detection limit is of use in identifying changes in instrument performance, but it is not a method detection limit. The instrumental detection limit is expected to be lower than the method detection limit because it only takes into account the variability between individual instrumental readings; determinations made on one solution do not take into consideration contributions to variability from the matrix or sample.

8.5.1.2 Prepare a test solution with concentrations of the metals and metalloids of interest near their anticipated instrumental detection limits by diluting working standard solutions or stock standard solutions by an appropriate factor. Follow the same procedure used for preparation of the calibration solutions.

8.5.1.3 Make at least 10 consecutive measurements on the test solution and calculate the instrumental detection limit for each of the metals and metalloids of interest as three times the sample standard deviation of the mean concentration value.

NOTE An alternative procedure for estimating the instrumental detection limit involves the analysis of blank solutions fortified with the metals and metalloids of interest at values spanning the predicted instrumental detection limit (see Reference [27]).

8.5.2 Estimation of the method detection limit and the method quantification limit

8.5.2.1 Estimate the method detection limit and method quantification limit for each of the metals and metalloids of interest under the working analytical conditions and repeat this exercise whenever experimental conditions are changed.

8.5.2.2 Prepare at least 10 blank test solutions from unused sampling media of the same type used for sample collection. Follow the appropriate sample preparation procedure used to prepare sample test solutions.

8.5.2.3 Make measurements on the test solutions and calculate the method detection limit and method quantification limit for each of the metals and metalloids of interest as three times and 10 times the sample standard deviation of the mean concentration values, respectively.

8.6 Quality control

8.6.1 Blank solutions

Carry reagent blanks, laboratory blanks and (if used) field blanks throughout the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory or field activities. Process reagent blanks at a frequency of at least one per 20 samples, with a minimum of one per batch.

8.6.2 Quality control solutions

8.6.2.1 Carry quality control samples, such as spiked media blanks, throughout the entire sample preparation and analytical process to estimate the method accuracy on the sample batch, expressed as a percentage recovery relative to the true value.

8.6.2.2 Process quality control samples at a frequency of at least one pair per 20 samples, with a minimum of one pair per batch.

8.6.2.3 Monitor the performance of the method by plotting control charts of the relative percentage recoveries of the quality control samples. Also, to evaluate method precision, plot control charts of the relative percentage differences between duplicate quality control samples.

8.6.2.4 If quality control results indicate that the method is out of control, investigate the reasons for this, take corrective action, and repeat the analyses. See ASTM E882[7] for general guidance on the use of control charts.

8.6.3 Internal standards

The internal standard signal response in each sample test solution shall be within an acceptable range of the response in the calibration blank solution. For responses outside the acceptable range, investigate the reasons, take corrective action, and repeat the analyses.

8.6.4 External quality assessment

If the laboratory carries out analysis of metals and metalloids in workplace air samples on a regular basis, it is recommended that it participate in relevant external quality assessment and proficiency testing schemes.

NOTE For information about existing proficiency testing schemes, refer, for example, to the database EPTIS (Reference [28]) or to a national accreditation organization.

8.7 Measurement uncertainty

It is strongly recommended that the laboratory estimate and report the uncertainty of its measurements in accordance with ISO/IEC Guide 98-3:2008[3]. This entails first constructing a cause and effect diagram (see ISO 9004[2]) to identify the individual sources of random and systematic error in the overall sampling and analytical method. The standard uncertainties associated with these errors are then estimated, determined experimentally, or both, and combined in what is referred to as an uncertainty budget. The combined standard uncertainty is ultimately multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of 2 is ordinarily recommended, giving a confidence level of approximately 95 % in the calculated value.

NOTE 1 Applications of cause and effect analysis to analytical methods are described in ISO/IEC Guide 98-3:2008[3] and in References [29][30].

Although sampling is not expressly discussed in this test method, the sampling procedures in ISO 15202-1 are incorporated by reference (see 4.1) and should be included in developing the uncertainty budget. In many cases, the sampling uncertainty exceeds the analytical uncertainty. See EN 13890[12] for guidance on including the uncertainty associated with sampling in the uncertainty budget.

NOTE 2 Terms that contribute to the random variability of an analytical method are generally accounted for in the measurement precision, which can be estimated from quality control data. Errors associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the allowable drift before recalibration by $\sqrt{3}$. Systematic errors of an analytical method include, for example, those associated with analytical recovery, sampling recovery, preparation of working standard solutions, and dilution of test solutions.

9 Expression of results

9.1 From measurements of the test samples, derive a single result for each of the metals and metalloids of interest.

9.2 Calculate the mean concentration of each of the metals and metalloids of interest in the blank test solutions.

9.3 Calculate the mass concentration, in milligrams per cubic metre, of each metal or metalloid of interest in the air filter sample at ambient conditions using Equation (1):

$$\rho_{\mathrm{M}} = \frac{\rho_{\mathrm{M},1}\, V_1\, f - \rho_{\mathrm{M},0}\, V_0}{1\,000 \times V} \qquad (1)$$

where

$\rho_{\mathrm{M},0}$ is the mean concentration, in micrograms per litre, of metal or metalloid in the blank solutions;

$\rho_{\mathrm{M},1}$ is the concentration, in micrograms per litre, of metal or metalloid in the sample test solution;

V is the volume, in litres, of the collected air sample;

V_0 is the volume, in millilitres, of the blank solutions;

V_1 is the volume, in millilitres, of the sample test solution;

f is the dilution factor used (f = 1 in the absence of dilution).

9.4 If it is necessary to recalculate metal and metalloid in air concentrations to reference conditions (see ISO 15202-1), calculate the mean atmospheric temperature and pressure by averaging the measurements taken at the start and the end of the sampling period, and apply a temperature and pressure correction to metal and metalloid in air concentrations calculated in 9.3, using Equation (C.1).

10 Method performance

10.1 Method detection limits and quantification limits

Method detection limits and method quantification limits depend on a number of factors, including the sample matrix (including sampling media), the sample preparation method, the mass selected, the analytical instrument used, the instrument operating parameters and blank variability. Method detection limits and method quantification limits shown in Table 4 were estimated by preparing test solutions from mixed cellulose ester (MCE) filters, followed by analysis by ICP-MS (see References [31][32][33]). Results in Table 4 are presented as examples of achievable method detection limits and method quantification limits.

10.2 Upper limits of the analytical range

The upper limit of the useful analytical range is determined by the linear dynamic range of the spectrometer under the analytical conditions established in 8.2.

Table 4 — Estimated method detection limits and method quantification limits
(see References [31][32][33])

Element[a]	Isotope	MDL µg l^{-1}	QL µg l^{-1}	Reference[b]
Al	27	0,23	0,77	[31]
As	75	0,069 0,38 0,007 4	0,23 1,27 0,16	[31] [32] [33]
Be	9	0,007 6 0,05	0,025	[31] [32]
Cd	111 114	0,024 0,000 72	0,078 0,006 3	[31] [33]
Co	59	0,017 0,000 41	0,057 0,003 0	[31] [33]
Cr	52	0,17	0,55	[31]
Cu	63	0,24 0,004 4	0,79 0,14	[31] [33]
Mg	24	0,28	0,93	[31]
Mn	55	0,023	0,076	[31]
Ni	60	0,003 4	0,12	[31]
Pb	208	0,025 0,002 4	0,083 0,014	[31] [33]
U	238	0,046	0,15	[32]
V	51	0,024	0,079	[31]
Zn	66	0,48	1,6	[31]

[a] Data are not available for: Ag, B, Ba, Bi, Ca, Cs, Fe, Ga, Ge, Hf, Hg, In, K, Li, Mo, Na, Nb, P, Pt, Rh, Sb, Se, Sn, Te, Tl, W, Y and Zr.

[b] For Reference [31], microwave dissolution was used and the sample matrix was 4 % volume fraction nitric acid. For Reference [32], hot plate digestion with nitric and hydrochloric acids was used. For Reference [33], open vessel microwave dissolution was used and the sample matrix was 4 % volume fraction nitric acid and 1 % volume fraction hydrochloric acid.

10.3 Bias and precision

10.3.1 Analytical bias

The sample dissolution methods described in ISO 15202-2 are believed to be effective for most applications, that is, the analytical method is expected to exhibit negligible bias. However, the dissolution methods are not effective in all instances[34]. Factors such as matrix effects and the specific sample dissolution method employed influence the analytical figures of merit obtained for the overall method.

EN 13890[12] specifies that the mean analytical recovery of procedures for measuring metals and metalloids in airborne particles shall be at least 90 %. Consequently, if there is any doubt about whether the selected sample dissolution method meets this requirement for a particular application, ISO 15202-2 requires that its effectiveness be determined and, if the analytical recovery is less than 90 %, that the use of an alternative sample dissolution method is investigated. The analytical bias is, therefore, expected never to be greater than 10 %.

10.3.2 Analytical precision

The component of the coefficient of variation (CV) of the method that arises from analytical variability, $C_{V(\text{analysis})}$, is dependent upon a number of factors, including the analytical mass selected, the analytical instrumentation used and the instrument operating parameters.

10.4 Measurement uncertainty

Laboratory experiments (see Reference [35]) have been performed to evaluate the uncertainty of this International Standard and ASTM D7439[5]. These experiments demonstrate that the method meets the general performance requirements in EN 482[9] for the uncertainty of measurements made for comparison with limit values (see next paragraph). Only a selected range of 21 metals and metalloids was covered (see Note) and the experiments were restricted to investigating the performance of the analytical method. For measurements made for comparison with the 8 h time-weighted average Threshold Limit Values (TLV, see Reference [15]), the procedure was found to meet the EN 482[9] uncertainty requirements for all the selected metals and metalloids except manganese, silver, and uranium. Data from the experiments, including average, standard deviation, repeatability, and reproducibility, were computed in accordance with ASTM E691[6].

The European Committee for Standardization (CEN) has prescribed general requirements for the performance of procedures for the measurement of chemical agents in workplace atmospheres in EN 482[9]. Upper limits of acceptability for expanded uncertainty have been specified for a number of measurement tasks and these are to be used as a guide for the purposes of this International Standard. CEN requirements are less stringent for screening measurements than for measurements for comparison with limit values; and they are less stringent for measurements for comparison with limit values when these are made in the range 0,1 to 0,5 times the exposure limit value (expanded uncertainty < 50 %) than when they are made in the range of 0,5 to 2,0 times the exposure limit value (expanded uncertainty < 30 %).

NOTE The metals and metalloids covered in the method performance experiments are: Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, U, V, Zn.

11 Test report

11.1 Test records

Comprehensive records of the test performed shall be maintained, including at least the following information:

a) a statement to indicate the confidentiality of the information supplied, if appropriate;

b) a complete identification of the air sample, including the date of sampling, the place of sampling, the type of sample (personal or static), either the identity of the individual whose breathing zone was sampled (or other personal identifier) or the location at which the general occupational environment was sampled (for a static sample), a very brief description of the work activities that were carried out during the sampling period, and a unique sample identification code;

c) a reference to this International Standard (ISO 30011:2010);

d) the make and type of sampler used;

e) the make, type and diameter of filter used, if appropriate;

f) the make and type of sampling pump used and its identification;

g) the make and type of flowmeter used, the primary standard against which the calibration of the flowmeter was checked, the range of flow rates over which the calibration of the flowmeter was checked, and the atmospheric temperature and pressure at which the calibration of the flowmeter was checked, if appropriate;

h) the time at the start and at the end of the sampling period and the duration of the sampling period in minutes;

i) the mean flow rate, in litres per minute, during the sampling period;

j) the mean atmospheric temperature and pressure during the sampling period, if appropriate;

k) the volume, in litres, of air sampled at ambient conditions;

l) the name of the person who collected the sample;

m) the time-weighted average mass concentration, in milligrams per cubic metre, of each metal and metalloid in the air sample, at ambient temperature and pressure or, if appropriate, adjusted to reference conditions;

n) details of the sample dissolution method used;

o) the analytical variables used to calculate the result, including the concentrations of each metal and metalloid in the blank and sample test solutions, the volumes of the blank and sample test solutions and the dilution factor, if applicable;

p) the type(s) of instrument(s) used for sample preparation and analysis and unique identifier(s);

q) the estimated instrumental detection limits, method detection limits and method quantification limits under the working analytical conditions — the measurement uncertainty determined in accordance with ISO/IEC Guide 98-3:2008[3] — and, if requested by the customer, quality control data;

r) any operation not specified in this International Standard, or regarded as optional;

s) the name of the analyst(s) or other unique identifier(s);

t) the date of the analysis;

u) any inadvertent deviations, unusual occurrences, or other notable observations.

11.2 Laboratory report

The laboratory report shall contain all information required by the end user, regulatory authorities and accreditation organizations. The report shall include at least the following information:

a) all sample receipt and chain-of-custody information;

b) sample analysis results;

c) applicable quality assurance or quality control data;

d) identity of laboratory and analyst(s);

e) information on sample preparation procedure(s) used;

f) information on instrumentation and equipment used;

g) any other information deemed appropriate.

Annex A
(informative)

ICP-MS principles and interferences

A.1 Description of ICP-MS principle

This International Standard describes the multi-element determination of trace elements in air by inductively coupled plasma mass spectrometry (ICP-MS). Sample material in solution is introduced by pneumatic nebulization into a radio-frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are typically detected by a continuous dynode electron multiplier assembly and the ion information processed by a data handling system. Interferences relating to the technique should be recognized and corrected for. Such corrections should include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents, or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix should be corrected for by the use of internal standardization.

A.2 Collision reaction cell

The majority of ICP-MS units currently being manufactured contain collision reaction cells. These typically include transmission devices that cause collisional dissociation of polyatomic ion species so that they are eliminated as an interference by kinetic energy discrimination. The system is also able to employ one or more chemical reaction modes, either with or without kinetic energy discrimination, to further eliminate interfering species.

A.3 Interferences

When collision reaction cell technology is not available, several types of interference effects can contribute to inaccuracies in the determination of trace elements. These interferences can be summarized as described in A.3.1 to A.3.5.

A.3.1 Isobaric elemental interferences

Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this standard test method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this standard test method (see Table 2), only selenium-82 (krypton) has isobaric elemental interferences. If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference can occur. All data obtained under such conditions should be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections are only as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

A.3.2 Abundance sensitivity

Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences can result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

A.3.3 Isobaric polyatomic ion interferences

Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified (see ISO 17294-2[14]) and these are listed in Table A.1 together with the method element masses affected. Such interferences should be recognized and when they cannot be avoided by the selection of an alternative analytical isotope, appropriate corrections should be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences are highly dependent on the sample matrix and chosen instrument conditions.

A.3.4 Physical interferences

Physical interferences are associated with the physical processes that govern the transport of the sample into the plasma, sample conversion processes in the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences can result in differences between instrument responses for the sample and the calibration standards. Physical interferences can occur in the transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample can contribute deposits of material on the extraction, or skimmer cones, or both, reducing the effective diameter of the orifices and, therefore, ion transmission. Dissolved solids levels not exceeding 0,2 % (mass per volume) have been recommended to reduce such effects. Internal standardization can be effectively used to compensate for many physical interference effects. Internal standards should have similar analytical behaviour to the elements being determined.

A.3.5 Memory interferences

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones and from the build-up of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a reagent blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This can be achieved by aspirating a standard containing elements corresponding to 10 times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of 10 of the method detection limit should be noted. Memory interferences can also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be reanalysed after a long rinse period.