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

Part 3: Analysis

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

Partie 3: Analyse

Reference number
ISO 15202-3:2004(E)

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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 15202-3 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

ISO 15202 consists of the following parts, under the general title: *Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry*:

- *Part 1: Sampling*
- *Part 2: Sample preparation*
- *Part 3: Analysis*

Introduction

The health of workers in many industries is at risk through exposure by inhalation to 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 making workplace air measurements. This part of ISO 15202 has been published in order to make available a method for making valid exposure measurements for a wide range of metals and metalloids in use in industry. It will be of benefit to: agencies concerned with health and safety at work; industrial hygienists and other public health professionals; analytical laboratories; industrial users of metals and metalloids and their workers, etc.

This part of ISO 15202 specifies a generic method for determination of the mass concentration of metals and metalloids in workplace air using inductively coupled plasma atomic emission spectrometry (ICP-AES) and gives requirements and test methods for analysis of sample solutions.

Part 1 of ISO 15202 gives details of relevant international, European and national standards which specify characteristics, performance requirements and test methods relating to sampling equipment; augments guidance provided elsewhere on assessment strategy and measurement strategy; and specifies a method for collecting samples of airborne particulate matter for subsequent chemical analysis.

Part 2 of ISO 15202 describes a number of procedures for preparing sample solutions for analysis by ICP-AES.

It has been assumed in the drafting of this part of ISO 15202 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 atomic emission spectrometry —

Part 3:
Analysis

1 Scope

This part of ISO 15202 specifies a procedure for the use of inductively coupled plasma atomic emission spectrometry for analysing test solutions prepared as prescribed in ISO 15202-2 from samples of airborne particulate matter collected as specified in ISO 15202-1. Method development, performance checks and a routine analysis method are specified.

This part of ISO 15202 is applicable for the assessment of workplace exposure to metals and metalloids for comparison with limit values (see e.g. EN 689[1], ASTM E 1370[2], etc.).

The following is a non-exclusive list of metals and metalloids for which limit values have been set (see Reference [3]), and for which one or more of the sample dissolution methods specified in ISO 15202-2 and the analytical procedure described in this part of ISO 15202 are applicable. However, there is no information available on the effectiveness of any of the sample dissolution methods specified in ISO 15202-2 for those elements in italics.

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

NOTE ISO 15202 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 30 min to 8 h and for assessment of exposure against the short-term exposure limits, where applicable (see 10.4).

The procedure suffers from no significant spectral interferences (see 10.5), provided that suitable analytical wavelengths are used. However, inaccurate background correction and/or 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 648:1977, *Laboratory glassware — One-mark pipettes*

ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks*

ISO 3585:1998, *Borosilicate glass 3.3 — Properties*

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

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 15202-1:2000, *Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry — Part 1: Sampling*

ISO 15202-2:2001, *Workplace air — Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry — Part 2: Sample preparation*

3 Terms, definitions and abbreviated terms

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

3.1 General definitions

3.1.1
chemical agent
any chemical element or compound, on its own or admixed, as it occurs in the natural state or as produced by any work activity, whether or not produced intentionally and whether or not placed on the market

3.1.2
measuring procedure
procedure for sampling and analysing one or more chemical agents in the air and including storage and transportation of the sample

3.1.3
time-weighted average concentration
TWA concentration
concentration of a chemical agent in the atmosphere, averaged over the reference period

NOTE A more detailed discussion of TWA concentrations has been published by the American Conference of Government Industrial Hygienists[3].

3.1.4
limit value
reference figure for concentration of a chemical agent in air

NOTE An example is the Threshold Limit Value® (TLV) for a given substance in workplace air, as established by the ACGIH[3].

3.1.5
reference period
specified period of time stated for the limit value of a specific chemical agent

NOTE Examples of limit values for different reference periods are short-term and long-term exposure limits, such as those established by the ACGIH[3].

3.1.6
workplace
defined area or areas in which the work activities are carried out

[EN 1540[4]]

3.2 Analytical definitions

3.2.1
blank solution
solution prepared by taking a reagent blank, laboratory blank or field blank through the same procedure used for sample dissolution

NOTE A blank solution might need to be subjected to further operations, e.g. 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.

3.2.2
calibration blank solution
calibration solution prepared without the addition of any stock standard solution or working standard solution

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

3.2.3
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) suitable for use in calibration of the analytical instrument

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

3.2.4
field blank
filter 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

3.2.5
laboratory blank
unused filter, taken from the same batch used for sampling, that does not leave the laboratory

3.2.6
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.

3.2.7
reagent blank
solution containing all reagents used in sample dissolution, in the same quantities used for preparation of laboratory blank, field blank and sample solutions

3.2.8
sample dissolution
process of obtaining a solution containing all analytes of interest present in a sample, which might or might not involve complete dissolution of the sample

3.2.9
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

3.2.10
sample solution
solution prepared from a sample by the process of sample dissolution

NOTE A sample solution might need to be subjected to further operations, e.g. dilution and/or addition of an internal standard, in order to produce a test solution that is ready for analysis.

3.2.11
stock standard solution
solution used for preparation of working standard solutions and/or calibration solutions, containing the analyte(s) of interest at a certified concentration(s) traceable to national standards

3.2.12
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 dilution and/or the addition of an internal standard.

NOTE 2 The blank test solution is the blank solution and the sample test solution is the sample solution if these solutions are not subjected to any further operations before analysis.

3.2.13
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 to preparation of calibration solutions than the concentration(s) of the analyte(s) in the stock standard solution(s)

3.3 ICP-AES definitions

3.3.1
axial plasma
end-on plasma
plasma that is viewed end-on by the optical detection system

3.3.2
background correction
process of correcting the intensity at an analytical wavelength for the intensity due to the underlying spectral background

3.3.3
background equivalent concentration
concentration of an analyte that results in an emission signal of an intensity equivalent to the background emission signal at the analytical wavelength

3.3.4
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

3.3.5
excitation interference
matrix interference that manifests itself as a change in sensitivity due to a change in plasma conditions when the matrix of a calibration or test solution is introduced into the plasma

3.3.6
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.

3.3.7
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

3.3.8
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 or ceramic material.

3.3.9
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 gas flow rate is typically 0,5 $\text{l}\cdot\text{min}^{-1}$ to 2,0 $\text{l}\cdot\text{min}^{-1}$.

3.3.10
inter-element correction
interference correction
spectral interference correction technique in which emission contributions from interfering elements that emit at the analyte wavelength are subtracted from the apparent analyte emission after measuring the interfering element concentrations at other wavelengths

3.3.11
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 gas flow rate is typically 0 $\text{l}\cdot\text{min}^{-1}$ to 2,0 $\text{l}\cdot\text{min}^{-1}$.

3.3.12
internal standard
reference element
non-analyte element, present in all solutions analysed, the signal from which is used to correct for matrix interferences or improve analytical precision

3.3.13
internal standardization
reference element technique
technique that uses the signal from an internal standard to correct for matrix interferences

3.3.14
load coil
length of 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

3.3.15
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

3.3.16
matrix-matching
technique used to minimize the effect of matrix interferences on analytical results, involving the preparation of calibration solutions in which the concentrations of acids and other major solutes are matched with those in the test solutions

3.3.17
nebulizer
device used to create an aerosol from a liquid

3.3.18
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 is typically 7 $\mathrm{l \cdot min^{-1}}$ to 15 $\mathrm{l \cdot min^{-1}}$.

3.3.19
pneumatic nebulizer
nebulizer that uses high-speed gas flows to create an aerosol from a liquid

3.3.20
radial plasma
plasma that is viewed from the side by the optical detection system

3.3.21
spray chamber
device, placed between a nebulizer and an ICP torch, whose function is to separate out aerosol droplets according to their size, so that only very fine droplets pass into the plasma and large droplets are drained or pumped to waste

3.3.22
spectral interference
interference caused by the emission from a species other than the analyte of interest

3.3.23
transport interference
transport effect
matrix interference caused by a difference in viscosity, surface tension or density between the calibration and test solutions that produces a change in nebulizer efficiency and hence in the amount of analyte reaching the plasma

NOTE A transport interference can be due to a difference in dissolved solids, type and concentration of acid, etc., between the calibration and the test solutions.

3.3.24
ultrasonic nebulizer

nebulizer in which the aerosol is created by flowing a liquid across a surface that is oscillating at an ultrasonic frequency

3.3.25
viewing height
observation height

⟨radial plasma⟩ position in a radial plasma from where the emission measured originates

NOTE The viewing height is generally given as the distance, in millimetres, above the load coil.

3.3.26
x-y centring

⟨axial plasma⟩ horizontal and vertical adjustment of an axial plasma to establish optimum viewing conditions, such that only emission from the central channel of the plasma is measured

3.4 Statistical terms

3.4.1
analytical recovery

ratio of the mass of analyte measured when a sample is analysed to the known mass of analyte in that sample, expressed as a percentage

3.4.2
bias

consistent deviation of the results of a measurement process from the true value of the air quality characteristic itself

NOTE Adapted from ISO 6879[5].

3.4.3
overall uncertainty

⟨of a measuring procedure or of an instrument⟩ quantity used to characterize as a whole the uncertainty of a result given by an apparatus or measuring procedure.

NOTE The overall uncertainty is calculated based on a combination of bias and precision, usually in accordance with Equation (1) and is expressed as a percentage:

$$\frac{\left|\bar{x} - x_{\mathrm{ref}}\right| + 2s}{x_{\mathrm{ref}}} \times 100 \qquad (1)$$

where

$\bar{x}$ is the mean value of results of a number (n) of repeated measurements;

x_{ref} is the true or accepted reference value of concentration;

s is the standard deviation of the measurements.

[EN 482[6]]

3.4.4
precision

closeness of agreement of results obtained by applying the method several times under prescribed conditions

NOTE Adapted from ISO 6879[5].

3.4.5
true value

value which characterizes a quantity perfectly defined in the conditions which exist when that quantity is considered

[ISO 3534-1[7]]

NOTE The true value of a quantity is a theoretical concept and, in general, cannot be known exactly; see EN 1540[4].

3.4.6
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 can 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 can be evaluated from the statistical distribution of the results of 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 *Guide to the expression of uncertainty in measurement* (GUM)[8] refers to these different cases as Type A and Type B evaluations of uncertainty, respectively.

NOTE 3 Adapted from VIM[9].

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 the inductively coupled plasma atomic emission spectrometry method specified in this part of ISO 15202.

5 Requirements

The measuring procedure as a whole (specified in ISO 15202-1, ISO 15202-2 and this part of ISO 15202) shall comply with any relevant international, European or national standard, e.g. EN 482[6] and EN 13890[10], 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, complying with the requirements for ISO 3696 grade 2 water (electrical conductivity less than 0,1 mS·m^{-1} and resistivity greater than 0,01 MΩ·m at 25 °C).

It is recommended that the water used be obtained from a water 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 Ammonium citrate solution, 17 g·l^{-1} $(NH_4)_2HC_6H_5O_7$ and 5 g·l^{-1} $C_6H_8O_7 \cdot H_2O$, prepared in accordance with B.4.2 of ISO 15202-2:2001.

NOTE This solution is required only when soluble nickel compounds are to be determined (see B.6.1.3 of ISO 15202-2:2001).

6.3 Mineral acids, concentrated, of various types, as required for preparation of matrix-matched calibration solutions (see 6.6.2).

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

NOTE It might be necessary to use mineral acids of higher purity in order to obtain an adequate quantification limit for some metals and metalloids.

6.3.1 Nitric acid (**HNO_3**), concentrated, $\rho \approx$ 1,42 g·ml^{-1}, mass fraction ≈ 70 %.

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

6.3.2 Hydrochloric acid (**HCl**), concentrated, $\rho \approx$ 1,18 g·ml^{-1}, mass fraction ≈ 36 %.

WARNING — Concentrated hydrochloric acid is corrosive and hydrochloric acid vapour is an irritant. Avoid contact with the skin or eyes, or inhalation of the vapour. Use suitable personal protective equipment (e.g. gloves, face shield or safety spectacles, etc.) when working with concentrated or dilute hydrochloric acid. Handle open vessels containing concentrated hydrochloric acid in a fume hood. The vapour pressure of hydrochloric acid is high; therefore beware of pressure build-up in stoppered flasks when preparing hydrochloric acid/water mixtures.

6.3.3 Sulfuric acid (**H_2SO_4**), concentrated, $\rho \approx$ 1,84 g·ml^{-1}, mass fraction ≈ 98 %.

WARNING — Concentrated sulfuric acid is corrosive and causes burns. Avoid contact with the skin or eyes. Use suitable personal protective equipment (including suitable gloves, face shield or safety spectacles, etc.) when working with the 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 sulfuric acid/water mixtures by adding sulfuric acid to water.

6.3.4 Perchloric acid (**$HClO_4$**), concentrated, $\rho \approx$ 1,67 g·ml^{-1}, mass fraction ≈ 70 %.

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

6.3.5 Hydrofluoric acid (**HF**), concentrated, $\rho \approx$ 1,16 g·ml^{-1}, mass fraction ≈ 48 %.

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 in 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 whilst 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.

6.4 **Nitric acid**, 10 % volume fraction

Add approximately 700 ml of water (6.1) to a 1 000 ml one-mark volumetric flask (7.1.2). Carefully add 100 ml of concentrated nitric acid (6.3.1) to the flask and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly.

6.5 **Stock standard solutions**, for preparation of calibration solutions.

6.5.1 Single-element stock standard solutions.

6.5.1.1 Use commercial single-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, typically 1 000 $mg \cdot l^{-1}$ or 10 000 $mg \cdot l^{-1}$. Observe the manufacturer's expiration date or recommended shelf life.

6.5.1.2 Alternatively, prepare single-element stock standard solutions from high purity metals 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 (7.3) for a maximum period of 1 year.

6.5.2 Multi-element stock standard solution(s)

Use one or more commercial multi-element standard solutions with certified concentrations traceable to national standards to prepare calibration solutions. Between them, the multi-element standard solutions shall include all the metals and metalloids of interest at suitable concentrations, typically between 10 $mg \cdot l^{-1}$ and 1 000 $mg \cdot l^{-1}$, depending on the sensitivity of the emission lines to be measured. Observe the manufacturer's expiration date or recommended shelf life.

6.6 Calibration solutions

6.6.1 Prepare a working standard solution or solutions, if desired, to include all the metals and metalloids of interest at suitable concentrations, typically between 1 $mg \cdot l^{-1}$ and 100 $mg \cdot l^{-1}$, depending on the sensitivity of the emission lines to be measured. Accurately pipette an appropriate volume of each single-element stock standard solution (6.5.1) or an appropriate volume of multi-element stock standard solution (6.5.2) into a labelled, one-mark volumetric flask (7.1.2). Add an appropriate volume of a suitable mineral acid (6.3) to ensure analyte stability. Dilute almost to the mark with water (6.1), stopper and swirl to mix. Allow to cool, to room temperature, dilute to the mark with water, stopper and mix thoroughly. Store in a suitable container, e.g. a polypropylene bottle (7.3) for a maximum period of 1 month.

Analytes that are grouped together in the working standard solution(s) should be chosen carefully to ensure chemical compatibility and to avoid spectral interferences. The type and volume of mineral acid added should also be selected carefully to ensure analyte stability.

6.6.2 Prepare a set of calibration solutions including a calibration blank solution and at least two other calibration solutions, covering a suitable range of concentrations for each of the metals and metalloids of interest. For each set of calibration solutions, accurately pipette appropriate volumes of working standard solution (6.6.1) or stock standard solution(s) (6.5) into individual, labelled, 100 ml volumetric flasks (7.1.2). Add reagents, as required (see the two following paragraphs of this subclause), to match the calibration solutions with that of the test solutions (see 8.1.12.1). Dilute almost to the mark with water (6.1), stopper and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Prepare the calibration solutions fresh 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 prescribed 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 15202-2:2001, B.6.1.2	10 ml of nitric acid (6.3.1)
ISO 15202-2:2001, B.6.1.3	10 ml of ammonium citrate solution (6.2)
ISO 15202-2:2001, Annex C	4 ml of nitric acid (6.3.1) and 20 ml of hydrochloric acid (6.3.2)
ISO 15202-2:2001, Annex D	20 ml of nitric acid (6.3.1)
ISO 15202-2:2001, Annex E	4 ml of sulfuric acid (6.3.3) and 20 ml of hydrochloric acid (6.3.2)
ISO 15202-2:2001, Annex F	4 ml of perchloric acid (6.3.4) and 20 ml of hydrochloric acid (6.3.2)
ISO 15202-2:2001, G.6.1	20 ml of nitric acid (6.3.1)
ISO 15202-2:2001, G.6.1 and G.6.5	20 ml of nitric acid (6.3.1) and 20 ml of hydrochloric acid (6.3.2)
ISO 15202-2: 2001, G.6.2	16 ml of nitric acid (6.3.1) and 4 ml of perchloric acid (6.3.4)
ISO 15202-2:2001, G.6.2 and G.6.5	16 ml of nitric acid (6.3.1), 4 ml of perchloric acid (6.3.4) and 20 ml of hydrochloric acid (6.3.2)
ISO 15202-2:2001, G.6.3	20 ml of nitric acid (6.3.1), or 16 ml of nitric acid (6.3.1) and 4 ml of perchloric acid (6.3.4)
ISO 15202-2:2001, G.6.3 and G.6.5	20 ml of nitric acid (6.3.1) and 20 ml of hydrochloric acid (6.3.2), or 16 ml of nitric acid (6.3.1), 4 ml of perchloric acid (6.3.4) and 20 ml of hydrochloric acid (6.3.2)

The calibration solutions also need to be matrix-matched with respect to hydrofluoric acid if the test solutions were prepared from samples collected on quartz-fibre filters using either the sample dissolution method prescribed in Annex D of ISO 15202-2:2001 or the method prescribed in Annex G of ISO 15202-2:2001 with hydrofluoric acid. In general, matrix-matching with hydrofluoric acid is best avoided (see 8.1.12.1), 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 (6.6.1) or stock standard solution(s) (6.5) to unused quartz-fibre filters carried through the sample dissolution method described in the relevant annex of ISO 15202-2:2001. Under such circumstances, plastic volumetric labware compatible with hydrofluoric acid and a corrosion-resistant sample introduction system have to be used.

6.7 Single-element stock standard solution(s), for addition of internal standard(s).

6.7.1 If test solutions containing the internal standard element(s) are required (see 8.1.13.1), use a commercial single-element standard solution or solutions to prepare them. The standard solution(s) shall include the element(s) to be used as internal standard(s) at a suitable concentration, e.g. 10 000 mg·l^{-1}. The internal standard element(s) shall be compatible with the test solution matrix 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 8.1.13.2). Observe the manufacturer's expiration date or recommended shelf life.

6.7.2 Alternatively, prepare single-element stock standard solution(s) from high purity metals 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.

6.8 Interference check solutions

If inter-element correction is to be carried out (see 8.1.8.1), prepare an interference check solution for each interferent at a suitable concentration, e.g. between 50 mg·l^{-1} and 200 mg·l^{-1}. Accurately pipette appropriate volumes of single-element stock standard solutions (6.5.1) into individual, labelled one-mark volumetric flasks (7.1.2). If appropriate (see 8.1.12.1), matrix-match the interference check and test solutions (see paragraphs 2 and 3 in 6.6.2). Dilute almost to the mark with water (6.1), stopper and swirl to mix. Allow to cool, dilute to the mark with water, stopper and mix thoroughly. Store in a suitable container, e.g. a polypropylene bottle (7.3) for a maximum period of 1 year.

6.9 Laboratory detergent solution, consisting of a laboratory-grade detergent, suitable for cleaning of samplers and labware, diluted with water (6.1) according to the manufacturer's instructions.

6.10 Argon, suitable for use in inductively coupled plasma atomic emission spectrometry.

7 Laboratory apparatus

Ordinary laboratory apparatus and the following.

7.1 Glassware

7.1.1 One-mark pipettes, complying with the requirements of ISO 648, made of borosilicate glass 3.3, cleaned before use by soaking in a 10 % volume-fraction nitric acid solution (6.4) for at least 24 h and then rinsing thoroughly with water (6.1).

Alternatively, the glassware may be cleaned with a suitable laboratory detergent using a laboratory washing machine.

7.1.2 One-mark volumetric flasks, of capacities between 50 ml and 1 000 ml, complying with the requirements of ISO 1042, made of borosilicate glass 3.3 complying with the requirements of ISO 3585, cleaned before use by soaking in a 10 % volume-fraction nitric acid solution (6.4) for at least 24 h and then rinsing thoroughly with water (6.1).

Alternatively, the glassware may be cleaned with a suitable laboratory detergent using a laboratory washing machine.

7.2 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, as an alternative to one-mark pipettes 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.

7.3 Polypropylene bottle, with leakproof screw cap.

A bottle made of an alternative plastic may be used provided that it is suitable for the intended use (see 6.5.1.2 and 6.6.1).

7.4 Inductively coupled plasma atomic emission spectrometer, computer-controlled, equipped with an autosampler that preferably has a flowing rinse.

8 Procedure

8.1 Method development

8.1.1 General

Develop and validate a method for the analysis of test solutions of samples of airborne particulate matter, prepared as described in ISO 15202-2, that is suitable for use with the available ICP-AES instrument(s). Use the default instrument conditions given by the instrument manufacturer as a starting point in the method development process. Refer to guidance on ICP-AES method development available in standard texts, manuals provided by instrument manufacturers and international, European or national standards.

NOTE This part of ISO 15202 is applicable to a wide range of ICP-AES instruments, e.g. simultaneous or sequential instruments with photomultiplier or solid-state detector systems, each of which needs to be set up and operated in a different manner. There are some principles that apply to the development of methods for all instruments, but there are also many parameters that are applicable only to particular instruments or instrument types.

8.1.2 Requirement for the quantification limit

For each metal and metalloid of interest, determine a value for the lower limit of the analytical range that will be satisfactory for the intended measurement task.

EXAMPLE For the measurement task of testing compliance with limit values as specified in EN 482[6], use Equation (2) to calculate the least amount of the metal or metalloid that will need to be quantified when it is to be determined at a concentration of 0,1 times its limit value:

$$L_{\text{low}} = 0{,}1 \times L_{\text{V}} \times q_{\text{V}} \times t_{\text{min}} \qquad (2)$$

where

L_{low} is the required lower limit, in micrograms, of the analytical range of the metal or metalloid;

L_{V} is the limit value, in milligrams per cubic metre, for the metal or metalloid;

q_{V} is the design flow rate, in litres per minute, of the sampler to be used;

t_{min} is the minimum sampling time in minutes, that will be used.

Then calculate the required quantification limit, in milligrams per litre, by dividing the required lower limit of the analytical range, in micrograms, by the volume of the test solution, in millilitres.

If the equation in 8.1.4 of ISO 15202-1:2000 is used to calculate a minimum sampling time for sample collection, the amount of each metal or metalloid on the filter should be above the lower limit of the analytical range provided that its concentration in air was greater than 0,1 times the limit value during sampling.

For other measurement tasks, it might be necessary to obtain quantitative measurements below 0,1 times the limit value, in which case an appropriate lower value should be entered in the above equation.

8.1.3 Significance of spectral interferences

Give consideration to the significance of any known spectral interferences in the context of the measurement task. For each potentially useful analytical wavelength (see 8.1.6), refer to published information and/or past experience and consider the relationship between the magnitude of interferences and the relative limit values of the interferents and the metals and metalloids to be determined.

EXAMPLE For the measurement task of testing compliance with limit values, an interferent present at 10 times its limit value will cause a positive bias greater than 0,1 times the limit value of the analyte if

$$10 \times \frac{L_{\mathrm{V,i}}}{L_{\mathrm{V,a}}} \times \frac{\rho_{\mathrm{a}}}{10\ 000} > 0{,}1 \qquad (3)$$

where

$L_{\mathrm{V,i}}$ is the limit value, in milligrams per cubic metre, of the interferent;

$L_{\mathrm{V,a}}$ is the limit value, in milligrams per cubic metre, of the analyte;

ρ_{a} is the apparent analyte concentration, in milligrams per litre, caused by interferent concentration of 10 000 mg·l^{-1}.

Use an alternative analytical wavelength or apply interelement corrections (see 8.1.8) if the sum of all potential interferences is greater than 0,1 times the limit value of the analyte when each of the interferents is present at 10 times its limit value.

NOTE 1 Inter-element correction is not normally necessary for measurements made to test compliance with limit values.

NOTE 2 For other measurement tasks, there might be a need to obtain quantitative measurements at concentrations below 0,1 times the limit value, in which case an appropriate lower value should be entered in Equation (3).

NOTE 3 Inter-element correction is best avoided, if possible, by selecting an alternative analytical wavelength that is free from or less prone to interference.

8.1.4 Axial or radial viewing of the plasma

If an instrument with an axial plasma and an instrument with a radial plasma are both available, or if the instrument to be used is equipped for both axial or radial viewing of the plasma (a dual-view instrument), decide which orientation is best suited to the measurement task (see note). It might be that it is better to use the axial plasma to make measurements at some analytical wavelengths and the radial plasma to make measurements at others.

NOTE Axial viewing of the plasma might be necessary to obtain the required quantification limits (see 8.1.2), but it is more susceptible than radial viewing to spectral interferences.

8.1.5 Sample introduction system

Decide which type of sample introduction system to use. Take into consideration the required sensitivity and the nature of the test solution matrix. In most instances, the standard system supplied by the instrument manufacturer will be adequate.

NOTE 1 If the spectrally pure test solutions contain hydrofluoric acid, it will be necessary to use a corrosion-resistant sample introduction system.

NOTE 2 Ultrasonic nebulizers provide a higher sensitivity than conventional pneumatic nebulizers such as cross-flow and concentric nebulizers. However, they are not resistant to corrosion by hydrofluoric acid and generally have longer wash-out times than conventional sample introduction systems. Nevertheless, the use of an ultrasonic nebulizer might be beneficial when lower quantification limits are required, e.g. if measurements are to be made for a metal or metalloid with a particularly low limit value and/or short sampling time.

NOTE 3 Hydride generation (for elements such as arsenic, antimony, selenium, tellurium, etc.) and cold vapour generation (for mercury) provide lower quantification limits than other sample-introduction techniques; however, they are not covered by ISO 15202.

8.1.6 Analytical wavelengths

8.1.6.1 Select one or more emission lines with which to make measurements for each metal or metalloid of interest. Take into consideration the wavelengths that are accessible on the instrument to be used and their background equivalent concentrations, the required quantification limit (see 8.1.2) and spectral interferences that could be of significance in the context of the measurement task (see 8.1.3). The more sensitive lines will usually be the most favourable, but avoid the use of wavelengths which have a direct spectral overlap or where there is a complex background shift caused by the occurrence of a number of intense, closely-spaced nearby emission lines. It is advisable to use more than one line for each analyte, if available, to check for any problems not identified during method development.

NOTE 1 Users of scanning, sequential, monochromator-based instruments have a free choice of the entire UV/visible spectrum. They can select any appropriate interference-free wavelengths by reference to line tables, e.g. see Reference [11]. Users of instruments with an Echelle grating and/or solid-state detectors also have many lines from which to choose. However, users of simultaneous, conventional polychromator-based instruments can only select from the analytical lines that they have available in their particular instrument configuration.

NOTE 2 If there is direct spectral overlap and an alternate line is not available for analysis for the metal or metalloid of interest, it still might be possible to correct for the interference using interelement correction (see 8.1.8).

8.1.6.2 If measurements are to be made on more than one emission line for any analyte, decide on a protocol for the reporting of results.

A protocol that could be used is as follows: report the mean result if two analytical wavelengths are selected; report the mean of the two closest results if three analytical wavelengths are selected; or report the mean of the three closest results if four analytical wavelengths are selected.

8.1.7 Background correction

Generate a spectral scan for each of the proposed analytical wavelengths whilst aspirating the calibration blank solution, a calibration solution and a typical sample test solution into the plasma. Examine the line profiles and select points at which to make background correction measurements. Make measurements at a single point to correct for a simple background shift, i.e. a shift in background intensity that is essentially constant over a given range, e.g. 0,5 nm, on either side of the analyte line. Make measurements at two points to correct for a sloping background shift.

NOTE 1 Different instrument types use different means of making off-peak background correction measurements. In monochromator-based instruments and most polychromator-based instruments, the analyte intensity is obtained first and then separate measurements are made at the background correction wavelengths. However, instruments with solid-state detectors measure background signals at the same time as the analyte line. They can therefore perform simultaneous background correction, which is preferable since it removes noise due to the sample introduction system from the overall measurement. Furthermore, simultaneous measurements are faster since no additional analysis time is required to make off-peak measurements.

NOTE 2 Some ICP-AES software features the use of chemometrics to automatically select parameters such as background correction points and perform intelligent optimization studies without user interaction.

8.1.8 Inter-element correction

8.1.8.1 If the only analytical wavelength(s) available for a metal or metalloid of interest suffer(s) from a direct spectral overlap or a complex background shift, give consideration to the need to apply inter-element correction (see 8.1.3). If this is necessary, generate and apply interference correction factors (see note 1). Alternatively, if the instrument has the necessary software, use a chemometric technique to perform inter-element correction (see note 2).

NOTE 1 Inter-element correction factors can be generated from the apparent analyte concentrations obtained by analysing individual, spectrally pure test solutions containing a high concentration, e.g. 10 000 $\mathrm{mg \cdot l^{-1}}$, of each the interfering elements. Alternatively, the data handling software of some instruments may be used to calculate and apply interference corrections automatically, if the calibration solutions contain suitable, varied concentrations of the analyte and interfering elements.

NOTE 2 Chemometric techniques distinguish analyte spectra from interfering spectra by the use of stored mathematical models.

8.1.8.2 If inter-element correction is applied, prepare interference check solutions for each interferent (6.8) and analyse these in each analytical run (see 8.3.3.4).

8.1.9 Plasma conditions

8.1.9.1 Plasma, auxiliary and nebulizer gas flows

Under normal circumstances, use the default gas flows recommended by the instrument manufacturer, as these usually result in compromise operating conditions that are best suited to multi-element analysis. However, if desired, the nebulizer gas flow may be optimized for specific applications.

NOTE The nebulizer argon flow rate can be a critical factor because it largely determines the residence time of the analyte in the plasma. The longer the residence time, the more time the analyte has to be atomized, excited and ionized. For an element that emits strong ionic lines and has a high ionization potential (i.e. requires more energy to ionize), a long residence time is desired. Hence a lower nebulizer argon flow rate can be used to obtain higher sensitivity for such an element, provided that the nebulizer efficiency does not fall off significantly when the flow rate is reduced. At a lower flow rate, the analyte travels through the plasma at a slower speed, giving it more time in the hot region of the plasma to be ionized and excited. On the other hand, for elements such as sodium that emit strong atomic lines and are easily ionized, a faster flow rate can be used so that the atoms are not ionized before excitation can take place.

8.1.9.2 RF power

Under normal circumstances, use the default RF power recommended by the instrument manufacturer, as this usually results in compromise operating conditions that are best suited to multi-element analysis. However, if desired, the RF power may be optimized for specific applications.

NOTE As for the nebulizer argon flow rate, the RF power applied to the plasma can be optimized according to the nature of the analyte. The more power that is applied to the plasma, the hotter it gets. For analytes that require more energy for excitation and ionization, a higher power provides greater sensitivity. For an easily excited analyte such as sodium, a lower power provides increased sensitivity.

8.1.9.3 Viewing height (radial plasma only)

Under normal circumstances, use the default viewing height recommended by the instrument manufacturer, as this usually results in compromise operating conditions that are best suited to multi-element analysis. However, if desired, the viewing height may be optimized for specific applications.

NOTE 1 The viewing height can be optimized for a selected analyte line or lines. This is because different regions of the ICP are characterized by different temperatures and each analytical wavelength has an optimum temperature at which its emission is most intense.

NOTE 2 Because varying the RF power and/or nebulizer argon flow rate can often be used to accomplish the same analytical goal as varying the viewing height, some lower cost ICP-AES instruments do not offer an adjustable viewing height.

8.1.10 Instrument operating parameters

Refer to the instrument manufacturer's instructions and, depending on the type and make of instrument, determine the optimum setting for other relevant instrument operating parameters.

A number of instrument operating parameters, such as the photomultiplier tube voltage, integration time, number of integrations, x-y centering or adjustment of torch height, etc, might need to be optimized.

8.1.11 Sample introduction parameters

8.1.11.1 Use the sample uptake rate recommended by the manufacturer of the nebulizer or optimize its performance to achieve a suitable compromise between signal intensity and sample uptake rate.

8.1.11.2 Use a suitable wash-out time, wash-out rate and read delay. Carry out tests to ensure that there is no significant carry-over of analyte between measurements.

8.1.12 Calibration solutions

8.1.12.1 Matrix-matching

Decide to what extent to match the matrix of the calibration solutions with that of the test solutions. Unless an internal standard is used (see 8.1.13), match the matrix of the calibration solutions with that of the test solutions, but if possible avoid preparing calibration solutions containing hydrofluoric acid (see DANGER notice in 6.3.5). Even if an internal standard is used, it is recommended that matrix-matching also be carried out.

If the test solutions prepared according to ISO 15202-2 contain hydrofluoric acid, an equal concentration of nitric acid should normally be substituted for hydrofluoric acid when preparing the calibration solutions. Except in one or two cases (see paragraph 3 in 6.6.2), this will have an insignificant effect on results, it will be safer and it will enable calibration solutions to be prepared in volumetric glassware.

8.1.12.2 Calibration range

Carry out experiments to determine the linear dynamic range for each of the selected analytical wavelengths (see 8.1.6) under the intended operating conditions (8.1.1 through 8.1.11). Then select a range of analyte concentrations over which to prepare the calibration solutions (see 6.6.2).

If more than one analytical wavelength is to be used for a particular analyte, it will be necessary to take this into consideration when selecting the range of concentrations to be covered.

8.1.13 Use of an internal standard(s)

8.1.13.1 Decide whether to use an internal standard or standards to correct for non-spectral interferences (i.e. transport interferences and excitation interferences) or to improve precision. Take into consideration the following guidance.

a) A single internal standard may be used to correct for transport interferences that arise from a matrix mismatch between the calibration and test solutions and for changes in nebulizer efficiency that can occur during analysis.

b) Internal standards may also be used to correct for excitation interferences that arise from a matrix mismatch between the calibration and test solutions and for changes in plasma conditions that can occur during analysis as a result of fluctuation in power and/or gas flows. However, multiple internal standards need to be used and the wavelengths at which they are measured need to be carefully selected so that the characteristics of the analyte emission lines closely match those of the internal standard emission lines.

c) Use of internal standards can also improve analytical precision for simultaneous instruments by reducing the effect of noise associated with sample introduction. However, for some instruments with solid-state detector systems, the integration time varies depending on emission intensity and for these instruments, analytical precision is only likely to be improved if the analyte and the internal standard emission lines have a similar intensity.

d) In general, it is preferable to match the matrix of the calibration and test solutions (see 8.1.12.1) rather than rely upon the use of an internal standard to correct for transport and excitation interferences that can arise from a matrix match.

8.1.13.2 Carefully select internal standard emission lines to ensure that they are suitable for the intended purpose (see 8.1.13.1) and exhibit adequate sensitivity. Ensure that internal standard elements are not present in the test solutions and that the single-element stock standard solutions for addition of internal standards (6.7) are chemically compatible with the test solution matrix (i.e. they do not cause precipitation).

8.2 Instrument performance checks

8.2.1 Visual inspection

The user shall perform regular visual checks to ensure the instrument and ancillaries are in good order before commencing work. Follow the instrument manufacturer's recommendations.

Further guidance is given in Annex A.

8.2.2 Performance checks and fault diagnostics

The user shall carry out performance checks on a daily basis to verify that the ICP-AES instrument is operating to an acceptable standard. More rigorous fault diagnostics shall be used if it is suspected that the instrument is not functioning properly. Follow the instrument manufacturer's recommendations.

Further guidance is given in Annex B.

A comprehensive series of performance checks, often referred to as QUID (a procedure for *Qu*ality Control and *Id*entification of Malfunctions of ICP emission spectrometers), has been described in the literature; see Reference [12]. This can be used to supplement the performance checks and fault diagnostics recommended by the instrument manufacturer.

A short version of QUID is described in Annex C.

8.3 Routine analysis

WARNING Use suitable personal protective equipment (including suitable gloves, face shield or safety glasses, etc.) when working with concentrated or dilute acids. See the WARNING notices in 6.3.

8.3.1 Addition of internal standards

If using an internal standard or internal standards (see 8.1.13), add the same concentration to all solutions to be measured, i.e. the calibration solutions, blank test solutions, sample test solutions, interference check solutions and quality control solutions.

Internal standards may be added by pipetting a known volume of single-element stock standard solution (6.7) into a known volume of each solution to be measured, e.g. by adding 100 µl of single-element stock standard to 10 ml of each solution. Alternatively, the solution to be measured and a solution containing the internal standard element(s) may be mixed during sample introduction using a two-channel peristaltic pump, T-piece and mixing coil. In the latter case, it will be necessary to prepare an internal standard solution at a suitable concentration by diluting the single-element stock standard solution (6.7) by an appropriate factor.

8.3.2 Setting up the instrument

Set up the ICP-AES instrument (7.4) following the manufacturer's recommendations and in accordance with the method developed in 8.1. Wait for the instrument to be warmed up properly before starting work. Recommended warm-up times, typically 30 min to 60 min, are generally provided by the instrument manufacturer. It is advisable to aspirate calibration blank solution into the plasma during the instrument warm-up period since otherwise plasma conditions could be different during analysis.

8.3.3 Analysis

8.3.3.1 Aspirate the calibration solutions (6.6.2) into the plasma in order of increasing concentration and make emission measurements for each solution. Use the instrument's computer to generate a calibration function for the metals and metalloids of interest, preferably using a linear regression. It is recommended that the emission intensity of the calibration blank solution be subtracted from the emission intensities of the other calibration solutions and that the calibration function be then forced through the origin. Repeat the calibration if the correlation coefficient, R^2, for any of the metals and metalloids of interest is not $\geqslant$ 0,999.

If $R^2 <$ 0,999, it might be possible to remove an erroneous calibration point and reprocess the data to obtain an acceptable calibration, but the minimum number of calibration solutions prescribed in 6.6.2 should be respected.

8.3.3.2 Aspirate the blank and sample test solutions (prepared in accordance with ISO 15202-2) into the plasma and make emission measurements for each solution. Use the stored calibration function (8.3.3.1) to determine the concentration of the metals and metalloids of interest.

8.3.3.3 Analyse the calibration blank solution and a mid-range calibration solution after the initial calibration and then, at a minimum, after every 20 test solutions. If the measured concentration of a metal or metalloid of interest in the continuing calibration blank is above three times the instrumental detection limit (as determined in 8.4.1), or if the measured concentration of a metal or metalloid of interest in continuing calibration verification has changed by more than ± 5 %, take one of the following corrective measures: either use the instrument software to correct for the sensitivity change (reslope facility), or 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 if this is not possible, reprocess the data to take account of the sensitivity change.

8.3.3.4 If inter-element correction is included in the method (see 8.1.8), analyse interference-check solutions (6.8) to verify that the inter-element correction procedure is effective for each of the analytical wavelengths concerned. Use the same acceptance criteria given in 8.1.3, i.e. the apparent analyte concentration should correspond to an air concentration that is less than 0,1 times the relevant limit value.

8.3.3.5 Analyse reagent blank and laboratory blank solutions, as specified in 8.5.1.1, and quality control solutions, as prescribed in 8.5.2.1, and use the results to monitor the performance of the method as prescribed in 8.5.1.2 and 8.5.2.2.

8.3.3.6 Review the relative standard deviation of each result. If a result has a relative standard deviation that is significantly higher than expected, taking into consideration the measured concentration, repeat the analysis of the solution concerned.

NOTE When the measured concentration for a metal or metalloid is well above its quantification limit, it can reasonably be expected that the relative standard deviation will be < 1 %.

8.3.3.7 If the concentration of any of the metals and metalloids of interest in a sample test solution is found to be above the upper limit of the calibration range, dilute the solution by a suitable factor, matrix-matching as necessary, and repeat the analysis. Record the dilution factor. Alternatively, use a suitable alternative analytical wavelength.

8.4 Estimation of detection and quantification limits

8.4.1 Estimation of the instrumental detection limit

8.4.1.1 Estimate the instrumental detection limit for each of the metals or metalloids of interest under the working analytical conditions following the procedure described in 8.4.1.2 and 8.4.1.3 and repeat this exercise whenever the experimental conditions are changed.

NOTE An instrumental detection limit is of use in identifying changes in instrument performance, but it is not a method detection limit; see Reference [12]. An instrumental detection limit is likely to be lower than a 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.

8.4.1.2 Prepare a test solution with concentrations of the metals or metalloids of interest near their anticipated instrumental detection limits, by diluting the working standard solution(s) (6.6.1) or stock standard solutions (6.5) by an appropriate factor. Follow the same procedure used for preparation of the calibration solutions in 6.6.2.

8.4.1.3 Make at least ten consecutive emission measurements on the test solution (8.4.1.2) and calculate the instrumental detection limit for each of the metals or metalloids of interest as three times the sample standard deviation of the mean concentration value.

An alternative procedure for estimating the instrumental detection limit involves the analysis of calibration blank solution fortified with the metals and metalloids of interest at concentrations spanning the predicted instrumental detection limit; see Reference [13].

8.4.2 Estimation of the method detection limit and the quantification limit

8.4.2.1 Estimate the method detection limit and quantification limit for each of the metals or metalloids of interest under the working analytical conditions following the procedure described in 8.4.2.2 and 8.4.2.3 and repeat this exercise whenever the experimental conditions are changed significantly.

8.4.2.2 Prepare at least ten laboratory blank test solutions from unused filters of the same type used for sample collection in ISO 15202-1. Follow the sample-dissolution procedure used to prepare sample test solutions in ISO 15202-2.

8.4.2.3 Make emission measurements on the test solutions (8.4.2.2) and calculate the method detection limit and the quantification limit for each of the metals or metalloids of interest as three times and ten times the sample standard deviation of the mean concentration values, respectively.

8.5 Quality control

8.5.1 Reagent blanks and laboratory blanks

8.5.1.1 Carry reagent blanks (see 3.2.7) and laboratory blanks (see 3.2.5) throughout the entire sample preparation and analytical process described in ISO 15202-2 and this part of ISO 15202. Prepare and analyse reagent blank and laboratory blank test solutions according to a frequency of at least 1 per 20 samples or a minimum of one per batch.

8.5.1.2 If results for reagent blanks and/or laboratory blanks are significantly higher than expected, based on previous experience, investigate whether contamination is occurring from laboratory activities and/or the batch of filters used for sampling and take appropriate corrective action to ensure that this does not re-occur.

8.5.2 Quality control solutions

8.5.2.1 Carry spiked samples and spiked duplicate samples throughout the entire sample preparation and analytical process described in ISO 15202-2 and this part of ISO 15202 to estimate the method accuracy on the sample batch, expressed as a percent recovery relative to the true spiked value. Spiked samples and spiked duplicate samples consist of filters to which known amounts of the metals and metalloids of interest have been added. (This can be accomplished by spiking with known volumes of a working standard solution at amounts within the linear dynamic range of the instrument. The working standard solution used shall be prepared from stock standard solutions from a source different from those used for preparing the calibration solutions.) Prepare and analyse these quality control solutions according to a frequency of at least 1 per 20 samples or a minimum of one per batch.

8.5.2.2 Monitor the performance of the method by plotting control charts of the relative percent recoveries and of the relative percent differences between the spiked samples and the spiked duplicate samples. If quality-control results indicate that the method falls outside the control range, investigate the reasons for this, take appropriate corrective action and repeat the analysis if necessary. See ASTM E 882-87[14] for general guidance on the use of quality-control charts.

8.5.3 Certified reference materials (CRMs)

If available, certified reference materials (CRMs) for the metals and metalloids of interest shall be analysed prior to routine use of the method to establish that the percent recovery relative to the certified value is satisfactory.

8.5.4 External quality assessment

If laboratories carry out metal and metalloid in air analysis on a regular basis, it is recommended that they participate in a relevant external quality assessment or proficiency testing scheme.

8.6 Measurement uncertainty

It is strongly recommended that laboratories estimate and report the uncertainty of their measurements in accordance with GUM[8]. The first step is to construct a cause-and-effect diagram[15] to identify the individual sources of random and systematic error in the method. These are then estimated and/or determined experimentally and combined in an uncertainty budget. Finally, the combined uncertainty is multiplied by an appropriate coverage factor to produce an expanded uncertainty. A coverage factor of 2 is recommended, which gives a level of confidence of approximately 95 % in the calculated value.

NOTE 1 References [16] and [17] describe the application of cause-and-effect analysis to analytical methods.

NOTE 2 Terms that contribute to the random variability of the method are generally accounted for in the measurement precision, which can be determined from quality-control data. Error associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the drift permitted before the instrument is recalibrated (see 8.3.3.3) by $\sqrt{3}$.

NOTE 3 Systematic errors include, for example, those associated with method recovery, sample recovery, preparation of working standard solutions, dilution of test solutions, etc.

9 Expression of results

9.1 If measurements are made on more than one emission line for any of the analytes, process the results in accordance with the protocol developed in 8.1.6.2 in order to 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 of each metal or metalloid in the air sample at ambient conditions, using Equation (4):

$$\rho_{\mathrm{M}} = \frac{\left(\rho_{\mathrm{M},1} \times V_1 \times F\right) - \left(\rho_{\mathrm{M},0} \times V_0\right)}{V} \qquad (4)$$

where

ρ_{M} is the calculated mass concentration, in milligrams per cubic metre, of metal or metalloid in the air sample at ambient conditions;

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

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

V is the volume, in litres, of the air sample (see 8.4.3 of ISO 15202-1:2000);

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

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

F is the dilution factor used in 8.3.3.7 ($F = 1$ in the absence of dilution).

9.4 If it is necessary to recalculate metal and metalloid in air concentrations to reference conditions (see 8.1.3.1 of ISO 15202-1:2000), 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 (D.1).

10 Method performance

10.1 Method detection limits and quantification limits

Method detection limits and quantification limits are dependent on a number of factors, including the sample preparation method, the analytical wavelength selected, the analytical instrumentation used, the instrument operating parameters and blank variability. During the validation of this method, method detection limits and quantification limits were determined[18] by preparing blank test solutions from mixed cellulose ester membrane filters using the closed-vessel microwave digestion procedure described in ISO 15202-2:2001, Annex G, and analysing them using a method established following the procedure described in this part of ISO 15202. Results, in micrograms per litre of solution, for a selected range of metals and metalloids (see note 2 in 10.4), are presented in Table 2 as an example of achievable method detection limits and quantification limits.

It is important to determine method detection limits and quantification limits under the test conditions used following the instructions given in 8.4.

Table 2 — Achievable method detection limits and quantification limits

Analyte	Wavelength nm	Plasma viewing	Method detection limit µg/l	Quantification limit µg/l
antimony	206,836	axial	13	43
arsenic	193,696	axial	19	62
beryllium	313,042	radial	0,3	0,9
cadmium	228,802	axial	2,8	9,5
chromium	267,716	radial	3,3	11
cobalt	228,616	axial	2,3	7,7
copper	324,752	radial	15	50
indium	230,606	axial	10	33
iron	259,939	radial	14	46
lead	220,353	axial	10	33
manganese	257,610	radial	1,0	3,1
nickel	221,648	radial	10	34
selenium	196,026	axial	17	55
tellurium	214,281	axial	28	94
tin	189,927	radial	63	210
vanadium	309,310	radial	1,2	4,2
yttrium	371,029	radial	0,6	2,1
zinc	206,200	radial	15	51

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 8.1.

10.3 Bias and precision

10.3.1 Analytical bias

The sample dissolution methods described in ISO 15202-2 are believed to be fully effective for most applications, i.e. the analytical method is expected to exhibit negligible bias. However, they will not be effective in all instances. EN 13890[10] 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 is 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, CV(analysis), is dependent upon a number of factors, including the analytical wavelength selected, the analytical instrumentation used and the instrument operating parameters. However, laboratory experiments[18] have been carried out to obtain figures of merit for CV(analysis) for a selected range of metals and metalloids. Test solutions at various multiples of the method detection limit were prepared by spiking filters with appropriate amounts of each of the metals and metalloids of interest and digesting them using the closed-vessel microwave procedure described in Annex G of ISO 15202-2:2001. The test solutions were then analysed using a method established following the procedure described in this part of ISO 15202. CV(analysis)[18] was found to be typically in the range 2 % to 5 % for metal and metalloid concentrations greater than 10 times the method detection limit.

10.4 Overall uncertainty of sampling and analysis methods

Laboratory experiments[18] have been performed to demonstrate that the measuring procedure as a whole (covered by parts 1 to 3 of ISO 15202) meets the general performance requirements specified in EN 482[6] for the overall uncertainty of measurements made for comparison with limit values (see note 1). Only a selected range of metals and metalloids was covered (see note 2) and the experiments, which were carried out in accordance with EN 13890[10], were restricted to investigating the performance of the measuring procedure for samples prepared using the closed-vessel microwave digestion method described in Annex G of ISO 15202-2:2001. For measurements made for comparison with the 8 h time-weighted average limit values applied in the United Kingdom[19], the procedure was found to meet the EN 482[6] overall uncertainty requirements for all the selected metals and metalloids except tellurium, when sampling at a typical flow rate of 2 l·min^{-1} for sampling times in the range 30 min to 8 h. For tellurium, a minimum sampling time of 2 h was required in order to meet the EN 482[6] overall uncertainty requirements. For measurements made for comparison with the 15 min short-term exposure limit values applied in the United Kingdom[19], the procedure was found to meet the EN 482[6] overall uncertainty requirements for all the selected metals and metalloids with short-term exposure limits, when sampling at a typical flow rate of 2 l·min^{-1}.

NOTE 1 CEN has prescribed general requirements for the performance of procedures for the measurement of chemical agents in workplace atmospheres in EN 482[6]. Upper limits of acceptability for overall uncertainty have been specified for a number of measurement tasks and these are 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 (overall uncertainty < 50 %) than when they are made in the range 0,5 to 2,0 times the exposure limit value (overall uncertainty < 30 %).

NOTE 2 The metals and metalloids covered in the method performance experiments are As, Be, Cd, Cr, Co, Cu, Fe, In, Mn, Ni, Pb, Se, Sb, Sn, Te, V, Y, Zn.

10.5 Spectral interferences

During the validation of this method[18], consideration was given to the significance of potential spectral interferences, in accordance with 8.1.3. No spectral interference correction was found to be necessary for measurements made using any of the selected analytical wavelengths (see Table 2). However, it is important to determine whether interference correction is necessary under the test conditions used following the instructions given in 8.1.8.

11 Test report

11.1 Test records

Comprehensive records of the test performed shall be maintained, including, at a minimum, 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, i.e., ISO 15202-3:2004;

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 conditions, 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 identifiers(s);

q) the estimated instrumental detection limits, method detection limits and quantification limits under the working analytical conditions; the measurement uncertainty determined in accordance with the GUM[8]; 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.

Annex A
(informative)

Guidance on maintenance of ICP-AES instrumentation

A.1 Maintenance contract

A maintenance contract is advisable for the following reasons.

Maintenance and/or calibration of certain instrument components could be beyond the capability of the laboratory.

Instrument upgrades (software and hardware) are often included in maintenance packages.

It might not be possible to obtain spare parts and other consumable items from sources other than the manufacturer.

Certain accreditation systems require users to have a maintenance contract.

When entering into a maintenance contract, it is advisable to check the level of service offered, the response time, the level of experience and knowledge of service engineers and the length of time the manufacturer will support the instrument and provide a source of spare parts and consumables.

A.2 In-house maintenance

A.2.1 Instrument log book

It is advisable to maintain an instrument log book to record the following information:

- details of service contracts and contacts;
- service reports;
- instrument usage (who has used the instrument and for how long);
- details of faults and replacement of user-serviceable parts.

A.2.2 General maintenance

It is advisable to follow manufacturer's guidelines regarding maintenance. Failure to comply with such guidelines might invalidate maintenance contracts.

The following checks should be carried out periodically:

— air filters:	Check for overload. Remove and wash/dry or replace if clogged.
— cooling system:	Check the filter. Check for loose connections. Check water, antifreeze and fungicide levels. Check for signs of corrosion around metal couplings. Refer to the manual for specific details.
— gas lines:	Check for loose connections and leaks. Check for kinks in gas lines. Verify and check performance of inline filters and oil traps. Check inlet pressures. Refer to the instrument manual for specific details.

- exhaust system: Check for loose connections, kinks and possible leakages in flexible exhaust ducting. Verify the performance of the ventilation system. Consult a ventilation expert if necessary. Refer to instrument manual for specific details.

A.2.3 Instrument maintenance

The following instrument checks should be carried out:

- peristaltic pump tubing: Check for depressions and flat spots on tubing daily and/or before analysis. New tubing will require a breaking-in period. Ensure that suitable chemically resistant tubing is used. Performance checks can be carried out volumetrically using a graduated cylinder and stopwatch.
- other tubing: Periodically visually check connectors. Check for blockages and deposits. Check for potential kinking and snagging of tubing if it is connected to an autosampler and associated robotic arm.
- nebulizer: Periodically visually check that the nebulizer is not clogged. Check o-ring seals and couplings between the nebulizer/spray chamber and the spray chamber/torch.
- spray chamber: Periodically, visually check the spray chamber to ensure that it is clean and that the waste is draining efficiently into the waste container.
- drain system: Periodically check the level of liquid in the waste container (if not checked by instrument software). Ensure that the waste flows smoothly into the drain from the spray chamber. Check for signs of kinking and deposits in the waste tubing. Ensure that the different wastes within one drain are compatible (different applications may require different waste systems).
- waste container: Periodically, visually check the waste container and empty it before there is a risk of it becoming overfull. If the test solutions contain hydrofluoric acid, place calcium carbonate ($CaCO_3$) or boric acid (H_3BO_3) in the waste container to complex fluoride and carefully check the positioning of the drain tubing from the spray chamber to ensure that there is no risk of it becoming blocked with solid.
- autosampler and other sample introduction accessories:

  Periodically check the components and interfaces with the instrument. Follow the manufacturer's guidelines.
- torch: Periodically check the torch and its mounting alignments. Check the injector tube for accumulated deposits and precipitates. Check the position of the injector tube. Check the quartz torch body for signs of devitrification and also for build-up of residues if running high matrix/organic solvent samples. Check o-rings and seals for leakages. Check the spatial alignment of torch with respect to load coil. Follow the manufacturer's guidelines if injector/torch cleaning and/or replacement is/are required.
- torch box: Periodically check for signs of corrosion or leakage.
- RF generator: Periodically check for signs of corrosion. Likewise check for corrosion in components of the plasma-initiation system. A service engineer might be required for specialized checks.
- spectrometer: Periodically check and clean/replace purge windows. For certain instruments the operator might be required to run periodically wavelength calibration routines. A service engineer might be required for specialized checks.
- computer: Periodically back up data files, clean out unwanted files and check network connections.

Annex B
(informative)

Examples of performance checks and fault diagnostics

B.1 Visual bullet test

This is a simple test for plasma that can often be performed on a daily basis. The user introduces a solution containing 1 000 mg·l^{-1} or more of an element whose atom emission produces a well-defined “bullet” in the centre of the ICP discharge. The presence of the bullet indicates that sample aerosol is reaching the plasma, while the vertical position of the bullet in the discharge is an indicator of the gas flow and RF power settings being used (for a radial plasma). Sodium and yttrium are good elements to use for this test.

B.2 Signal intensity

The number of emission counts for a given concentration of an element can be used as a quick instrument diagnostic. It is usually more useful for trend analysis than as an absolute indicator of performance since the emission counts will vary somewhat from day to day.

B.3 Background equivalent concentration

The background equivalent concentration gives an indication of the relative sensitivity of an emission line in comparison with the emission background at the same wavelength. If higher than normal, this can indicate that there are problems with the efficiency of the sample introduction system, although there are a number of other possible causes.

B.4 Precision

The short-term precision obtained for repeat measurements of a strong emission line can be used as an indicator of the noise associated with sample introduction. The precision for an argon emission line can be used as a diagnostic for the RF generator.

B.5 Ion-to-atom ratio

The ratio of the emission intensity of an ion line to the emission intensity of an atom line may be used as a diagnostic indicator of the relative excitation conditions in the plasma. The Mg(**II**) 280 nm/Mg(**I**) 285 nm line intensity ratio has been recommended[20]. Because ion/atom ratios are sensitive to RF power, nebulizer flow and viewing height, they can be used to check that the relative excitation conditions remain unchanged. Running an analysis under a specific set of conditions is vital if interference correction factors or stored calibration curves are used in the analysis.

B.6 Wavelength/peak alignment

All dispersive instruments are subject to some degree of drifting and it is therefore important to ensure that the spectrometer is calibrated properly in terms of wavelength before an analysis. For some instruments, this is done automatically by the software at the beginning of an analysis.

Annex C
(informative)

Procedure for quality control and identification (QUID) of malfunctions of inductively coupled plasma atomic emission spectrometers

C.1 Introduction

Users of an ICP system should plan systematic actions to verify that it satisfies requirements for analytical performance and instrument maintenance. Based on previously published work on drift diagnostics[21], practical resolution measurements[22], ionic to atomic line intensity ratio measurements[20], scale of detection limits[23] and figures of merit[24], a procedure has been proposed[12] to evaluate analytical performance, to control the major components of the ICP apparatus and to diagnose any possible deterioration of the system. A flow chart corresponding to the procedure, **Qu**ality Control and **Id**entification of Malfunctions, called QUID, is given in Figure C.1.

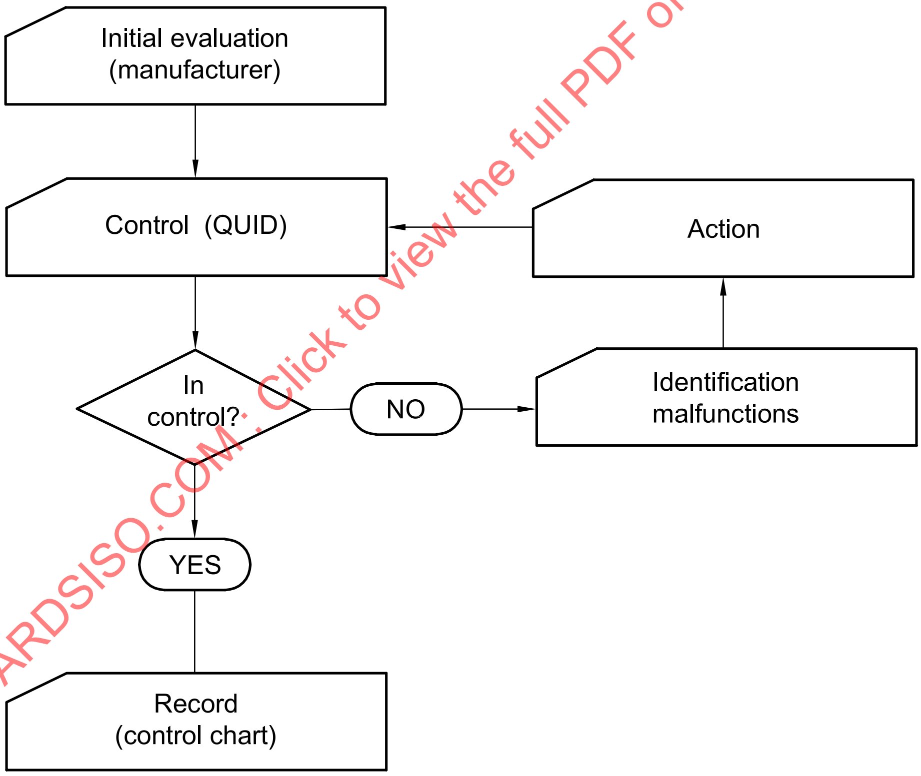

Figure C.1 — Flow chart of the QUID procedure