BRITISH STANDARD

BS EN 13890:2009

Workplace exposure — Procedures for measuring metals and metalloids in airborne particles — Requirements and test methods

ICS 13.040.30

BSI British Standards

National foreword

This British Standard is the UK implementation of EN 13890:2009. It supersedes BS EN 13890:2002 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/2/2, Work place atmospheres.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Exposition am Arbeitsplatz - Messung von Metallen und Metalloiden in luftgetragenen Partikeln - Anforderungen und Prüfverfahren

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (EN 13890:2009) has been prepared by Technical Committee CEN/TC 137 “Assessment of workplace exposure to chemical and biological agents”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 2010, and conflicting national standards shall be withdrawn at the latest by March 2010.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 13890:2002.

The major technical changes between this European Standard and the previous edition are as follows:

a) Adaptation of the framework for assessing the performance of procedures for measuring metals and metalloids against the general requirements for the performance of procedures for measuring chemical agents in workplace atmospheres as specified in EN 482;

b) Revision of the calculation model for the uncertainty of measurement to comply with EN 482 and ENV 13005.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

This European Standard provides a framework for assessing the performance of procedures for measuring metals and metalloids against the general requirements for the performance of procedures for measuring chemical agents in workplace atmospheres as specified in EN 482. It enables producers and users of procedures for measuring metals and metalloids in airborne particles to adopt a consistent approach to method validation.

Although this European Standard has been written for assessing the performance of procedures for measuring metals and metalloids, it can be used as the basis for assessing the performance of procedures for measuring other chemical agents that are present as or in airborne particles, e.g. sulphuric acid mist.

1 Scope

This European Standard specifies performance requirements and test methods for the evaluation of procedures for measuring metals and metalloids in airborne particles sampled onto a suitable collection substrate, e.g. a filter.

This European Standard specifies a method for estimating the uncertainties associated with random and systematic errors and combining them to calculate the expanded uncertainty of the measuring procedure as a whole, as prescribed in EN 482.

This European Standard is applicable to measuring procedures in which sampling and analysis is carried out in separate stages, but it does not specify performance requirements for collection, transport and storage of samples, since these are dealt with in EN 13205 and ISO 15767.

This European Standard is not applicable to procedures for measuring metals or metalloids present as inorganic gases or vapours, e.g. mercury, arsenic (see EN 838 and EN 1076), or to procedures for measuring metals and metalloids in compounds that could be present as a particle/vapour mixture, e.g. arsenic trioxide.

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.

EN 481, *Workplace atmospheres — Size fraction definitions for measurement of airborne particles*

EN 482:2006, *Workplace atmospheres — General requirements for the performance of procedures for the measurement of chemical agents*

EN 1232:1997, *Workplace atmospheres — Pumps for personal sampling of chemical agents — Requirements and test methods*

EN 1540:1998*, Workplace atmospheres — Terminology*

EN 12919, *Workplace atmospheres — Pumps for the sampling of chemical agents with a volume flow rate of over 5 l/min — Requirements and test methods*

EN 13205[1)] *Workplace atmospheres — Assessment of performance of instruments for measurement of airborne particle concentrations*

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

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 482:2006 and EN 1540:1998[2)] apply.

1) All references to EN 13205 in this European Standard refer to the ongoing revision of EN 13205:2001.

2) EN 1540:1998 is currently subject to revision. Until the revised EN is published the definitions given in EN 482:2006 take precedence.

4 Principle

For measuring procedures that involve sample dissolution, instrumental detection limits are determined by repeat analysis of the calibration blank solution. For all measuring procedures, method detection limits and quantification limits are determined by analysis of laboratory blanks. The determined quantification limits are then assessed against the performance requirements specified in 5.2.1.

Analytical recovery is determined by one of a number of different methods, depending upon the nature of the measuring procedure under evaluation. For measuring procedures for soluble compounds of metals and metalloids, analytical recovery is determined by analysis of spiked laboratory blanks (except for procedures that incorporate a design-based sample dissolution method (see A.1.1), for which it is taken to be 100 %). For measuring procedures for total metals and metalloids that involve sample dissolution, analytical recovery is determined by analysis of pure compounds, reference materials or reference air samples. For measuring procedures for total metals and metalloids that involve analysis of the sample on the collection substrate, analytical recovery is determined by analysis of reference air samples, by the analysis of workplace air samples that are characterised by subsequent analysis using a reference procedure or it is estimated from theory. The determined analytical recovery is then assessed against the performance requirements specified in 5.2.2.

Measurement uncertainty is estimated using a structured approach. Firstly, a cause and effect diagram is constructed to identify individual random and non-random uncertainty components of a measuring procedure. After simplification to resolve any duplication, the resulting diagram is used to identify components for which uncertainty estimates are required. Each of these uncertainty components is then estimated or calculated from experimental data, combined to obtain an estimate of the uncertainty of the measurement method as a whole and multiplied by an appropriate coverage factor to calculate the expanded uncertainty of the method, following the guidance in Annex B. In accordance with 5.2.3, the determined expanded uncertainty is then assessed against the general performance requirements specified in EN 482.

5 Requirements

5.1 Method description

5.1.1 Scope

The scope of the measuring procedure shall give at least information about the following:

— the metals and metalloids covered by the measuring procedure;

— the analytical technique(s) used in the measuring procedure;

— the range of concentrations of metals and metalloids in air for which the measuring procedure has been shown to meet the acceptance criteria for expanded uncertainty prescribed in EN 482, together with the associated range of sampled air volumes (e.g. 0,01 mg · m^{-3} to 0,5 mg · m^{-3} for sampled air volumes in the range 240 l to 960 l);

— any form of the metals and metalloids for which the sample preparation method described has been shown to be or is known to be ineffective; and

— any known interferences.

NOTE If there is no procedure for measuring a particular metal or metalloid that meets the requirements of this European Standard, a measuring procedure whose performance is nearest to the specified requirements should be used.

5.1.2 Method performance

For all metals and metalloids included in the scope of the method, the measuring procedure shall give comprehensive information about method performance, including the following:

— the detection and quantification limits of the measuring procedure;

— the analytical recovery for all test materials for which the sample preparation method has been shown to be effective;

— all random and non-random uncertainty components of the measuring procedure, together with their estimated or experimentally determined values, and the resulting expanded uncertainty; and

— full details of any known interferences, including suitable and sufficient information on how to minimise their effects, if applicable.

5.1.3 Safety information

The measuring procedure shall provide suitable and sufficient information on the safety hazards associated with the reagents and equipment used in the procedure.

5.1.4 Samplers

The measuring procedure shall:

— require the user to select samplers that are designed to collect an appropriate fraction of airborne particles, as defined in EN 481, according to the particle size fraction(s) that is applicable to the limit value for the metals and metalloids of interest (e.g. an inhalable sampler, a thoracic sampler or a respirable sampler);

— specify that the samplers shall comply with the provisions of EN 13205; and

— require, if appropriate, for procedures that do not involve sample dissolution, calibration of the analytical instrument used to be sampler specific, e.g. for X-ray fluorescence spectrometry (XRF).

5.1.5 Sampling pumps

The measuring procedure shall require the user to use sampling pumps that comply with the provisions of EN 1232 or EN 12919.

5.1.6 Other requirements

Where necessary, the measuring procedure shall give other requirements, e.g. for the collection substrate.

5.2 Performance requirements

5.2.1 Quantification limit

For each metal and metalloid included in the scope of the measuring procedure, determine the lower limit of the working range of the method that will be satisfactory for the intended measurement task. For example, if the measurement task is testing compliance with long-term limit values, use Equation (1) to calculate the least amount of the metal or metalloid that needs to be quantified when it is to be determined at a concentration of 0,1 times its limit value:

$$m_{\ell} = 0{,}1\ \rho_{\mathrm{LV}} \cdot q_{\mathrm{v,a}} \cdot t_{\mathrm{s,min}} \qquad (1)$$

where

m_L is the lower limit of the required analytical range of the metal or metalloid, in micrograms;

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

$q_{v,a}$ is the design flow rate of the sampler to be used, in litres per minute; and

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

For procedures that involve sample dissolution, calculate the lower limit of the required working range for each metal and metalloid, in micrograms per millilitre, by dividing the lower limit of the required working range, in micrograms, by the volume of the test solution, in millilitres. When tested in accordance with 8.1.2.1, the determined quantification limits shall be lower than the resulting values.

For procedures that do not involve sample dissolution, when tested in accordance with 8.1.2.2, the determined quantification limits for each metal and metalloid shall be lower than the lower limit of the required working range in micrograms.

5.2.2 Analytical recovery

When tested in accordance with one of the procedures prescribed in 8.2, the mean analytical recovery shall be at least 90 % for all material types included within the scope of the measuring procedure and the coefficient of variation[3)] of the analytical recovery shall be less than 5 %.

5.2.3 Expanded uncertainty

The expanded uncertainty of the measuring procedure shall comply with the requirements specified in EN 482.

6 Reagents and materials

6.1 Reagents

During the analysis, use only reagents of analytical grade, and only water complying with the requirements for EN ISO 3696 grade 2 water (electrical conductivity less than 0,1 $mS \cdot m^{-1}$, i.e. resistivity greater than 0,01 $M\Omega \cdot m$, 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 $M\Omega \cdot m$ (usually expressed by manufacturers of water purification systems as 18 $M\Omega \cdot cm$ water).

6.2 Standard solutions

Standard solutions with concentrations of the metals and metalloids of interest that are traceable to national and/or international standards. If commercial standard solutions are used observe the manufacturer's expiry date or recommended shelf life.

3) The predecessor term "relative standard deviation" is deprecated. See also ISO 3534-1:2006, 2.38, Note 2.

6.3 Test materials

For each metal or metalloid, a range of test materials that is representative of the substances of interest that could be present in the workplace atmosphere. The test materials can be pure compounds of known composition, certified reference materials or other well-characterised materials (e.g. materials characterised in an interlaboratory comparison). Follow the supplier's instructions when using certified reference materials.

NOTE 1 If there is a limit value for a specific compound, that compound should be included in the range of reference materials.

NOTE 2 For a method that is intended to have general applicability, the range of reference materials should include compounds and materials in industrial use and compounds and materials which could be generated by the work activity.

NOTE 3 It is important that the particle size of the reference materials be as close as possible to that of the particles analysed, since, compared to coarse bulk materials, inhalable particles are often much smaller and more readily soluble.

NOTE 4 Certified reference materials that have been characterised with respect to a particular sample dissolution method might not be suitable for use as a test material.

6.4 Reference air samples

Samples of dust on collection substrates (e.g. airborne particles collected on filters using a multiple simultaneous sample collection system), having a known or measured loading of the metals and metalloids of interest.

7 Apparatus

Usual laboratory apparatus and resources and:

— a system for applying a known volume of standard solution to collection substrates with a precision of better than 1 %;

— an analytical balance capable of weighing to at least 0,01 mg, calibrated with weights traceable to national standards, checked before use by means of a test weight;

— an instrument or instruments for analysing the metals and metalloids of interest.

8 Test methods

8.1 Detection limits and quantification limits

8.1.1 Instrumental detection limit

8.1.1.1 For measuring procedures that involve sample dissolution, analyse the calibration blank solution at least ten times under repeatability conditions.

If there is no measurable response from the analytical instrument, prepare a test solution with concentrations of the metals or metalloids of interest near their anticipated instrumental detection limits by diluting the standard solutions (6.2) by an appropriate factor. Analyse the test solution at least ten times under repeatability conditions.

NOTE For measuring procedures that involve analysis of the sample on the collection substrate, an instrumental detection limit is not a meaningful concept and, as such, cannot be determined.

8.1.1.2 Calculate the instrumental detection limit for each of the metals or metalloids of interest as three times the standard deviation.

NOTE An instrumental detection limit is of use in identifying changes in instrument performance, but it is not the same as a method detection limit. 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.

8.1.2 Method detection limits and quantification limits

8.1.2.1 For measuring procedures that involve sample dissolution, prepare at least ten test solutions from laboratory blanks, following the sample preparation method described in the measuring procedure, and analyse the test solutions for the metals or metalloids of interest under repeatability conditions.

If there is no measurable response from the analytical instrument, spike ten laboratory blanks with an appropriate volume of working standard solution containing appropriate known masses of the metals or metalloids of interest, such that the test solutions produced from them will have concentrations near their respective anticipated detection limits. Prepare test solutions from the spiked laboratory blanks, following the sample preparation method described in the measuring procedure, and analyse the test solutions for the metals or metalloids of interest under repeatability conditions.

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 standard deviation, respectively (see reference [1]).

8.1.2.2 For measuring procedures that do not involve sample dissolution, analyse at least ten laboratory blanks under repeatability conditions.

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 standard deviation, respectively.

8.1.2.3 Compare the quantification limits obtained with the requirements of 5.2.1.

8.2 Analytical recovery

8.2.1 General

Different test methods are applicable for the determination of analytical recovery, depending on the sample preparation method used. These are detailed separately in 8.2.2, 8.2.3 and 8.2.4. See Annex A for guidance.

8.2.2 Measuring procedures for soluble compounds of metals and metalloids

8.2.2.1 Measuring procedures that incorporate a design-based sample dissolution method

Unless there is a contra-indication (see A.1.2) take the analytical recovery to be 100 % for procedures for soluble compounds of metals and metalloids that incorporate a design-based sample dissolution method (see A.1.1).

8.2.2.2 Other measuring procedures

For measuring procedures that do not incorporate a design-based sample dissolution method or for which there could be a problem of chemical compatibility between the analyte and the substrate, prepare a minimum of six replicate test samples by spiking laboratory blanks with an appropriate volume of working standard solution containing a known mass of each of the metals or metalloids of interest. Then use the sample dissolution method described in the measuring procedure to prepare test solutions from the test samples and analyse the resulting solutions using the analytical method described in the measuring procedure.

Repeat the test on laboratory blanks spiked with other masses of each of the metals or metalloids of interest to determine the analytical recovery across the working range of the measuring procedure.

Calculate the mean analytical recovery and coefficient of variation for each of the tests performed and compare the results with the requirements of 5.2.2. If the requirements are not met, take corrective measures (e.g. use an alternative collection substrate), if possible, and repeat the analytical recovery test.

8.2.3 Measuring procedures for total metals and metalloids that involve sample dissolution

8.2.3.1 Determination of analytical recovery using pure compounds

Prepare a minimum of six test solutions from each of the selected pure compounds (6.3) using the sample preparation method described in the measuring procedure. Use a mass of the pure compound that can be weighed with an accuracy of at least 1 %. Analyse the test solutions as described in the measuring procedure.

NOTE 1 It is usually not necessary to include water-soluble compounds in the range of compounds tested.

NOTE 2 It is preferable to use the smallest mass of pure compound that can be easily weighed, to scale up the volume of reagents and to adjust the final test solution volume so that the experiment is as representative as possible of the analysis of workplace air samples.

8.2.3.2 Determination of analytical recovery using reference materials

Carry out the same test procedure prescribed for pure compounds in 8.2.3.1. Use a suitable mass of each of the selected reference materials (6.3), taking into consideration the concentration of the metal and metalloids of interest in the reference material and the supplier's instructions on the minimum amount of material that is required for an homogenous sample.

NOTE It is preferable to use the smallest mass of reference material that can be easily weighed, to scale up the volume of reagents and to adjust the final test solution volume so that the experiment is as representative as possible of the analysis of workplace air samples.

8.2.3.3 Determination of analytical recovery using reference air samples

Prepare and analyse test solutions from a minimum of six reference air samples (6.4) using the method described in the measuring procedure.

8.2.3.4 Comparison of results with the acceptance criteria

Calculate the mean analytical recovery and coefficient of variation for each of the tests performed and compare the results with the requirements of 5.2.2. If the requirements are not met for a test material, the analytical recovery test may be repeated using material with a smaller particle size and/or using a larger volume of reagents. If the requirements are still not met, the materials of a type similar to the test material concerned shall be excluded from the scope of the measuring procedure.

8.2.4 Measuring procedures that do not involve sample dissolution

8.2.4.1 Experimental determination of analytical recovery

8.2.4.1.1 Reference air samples

Analyse a minimum of six reference air samples (6.4) using the method described in the measuring procedure.

8.2.4.1.2 Workplace air samples

Analyse a minimum of six workplace air samples using the method described in the measuring procedure. Then re-analyse the samples using an independent measuring procedure with known analytical recovery to obtain reference values for the metals and metalloids of interest.

8.2.4.1.3 Comparison of results with the acceptance criteria

Calculate the mean analytical recovery and coefficient of variation for each of the tests performed and compare the results with the requirements of 5.2.2. If the requirements are not met, ensure that the limitations of the measuring procedure are fully described in its scope.

8.2.4.2 Theoretical estimation of analytical recovery

Estimate the analytical recovery by theoretical consideration of the principles of the technique involved and compare results with the analytical recovery requirements of 5.2.2.

NOTE For example, the maximum sample loading for quantitative determination of metals and metalloids in air by X-ray fluorescence spectrometry can be estimated from theory. See reference [2].

8.3 Measurement uncertainty

8.3.1 Identification of random and non-random uncertainty components

Identify all random and non-random uncertainty components of the measuring procedure, e.g. by constructing a cause and effect diagram (see ENV 13005 and references [3], [4] and [5]).

See B.1 for a list of random and non-random uncertainty components that typically need to be considered.

8.3.2 Estimation of individual uncertainty components

8.3.2.1 General

For each of the significant uncertainty components identified in 8.3.1, estimate individual uncertainties or calculate them from experimental data as prescribed in 8.3.2.2 to 8.3.2.6, following the guidance in Annex B.

Where appropriate, convert a range $\pm A$, into a non-random uncertainty equal to $A/\sqrt{3}$, assuming a rectangular probability distribution or into a non-random uncertainty equal to $A/\sqrt{6}$, assuming a triangular probability distribution, as appropriate.

8.3.2.2 Uncertainty associated with sampled air volume

Estimate the random and non-random uncertainty components of the sampled air volume, referring to the guidance in B.2.

If the measurement uncertainty is being estimated for the general use of a published method, make a worst case estimate of the uncertainty components concerned.

If the measurement uncertainty is being estimated for the use of the method under specific conditions, e.g. by a particular organisation using particular sampling equipment and a particular sampling protocol, estimate the uncertainty components for the specific equipment concerned (e.g. flow meter, sampling pump, timer), taking account of any specific additional requirements of the sampling protocol (e.g. number of flow rate measurements, sampling time).

8.3.2.3 Uncertainty associated with sampling efficiency

Estimate the random and non-random uncertainty components for aerosol samplers referring to the guidance in B.3.

8.3.2.4 Uncertainty associated with sample storage and transportation

Estimate the non-random uncertainty components associated with sample storage and transportation, referring to the guidance in B.4.

8.3.2.5 Uncertainty associated with analytical recovery

Estimate analytical recovery and the non-random uncertainty components associated with analytical bias, referring to the guidance in B.5.

8.3.2.6 Uncertainty associated with analytical variability

Estimate the random uncertainty components associated with analytical variability referring to the guidance in B.6.

8.3.3 Calculation of expanded uncertainty

Calculate the expanded uncertainty of the measuring procedure by combining the random and non-random components of sampling and analytical uncertainty (see B.7.1, B.7.2 and B.7.3) and multiplying by a coverage factor of two (see B.8).

9 Test report

The test report shall include at least the following:

a) a reference to this European standard;

b) identification of the test laboratory, including brief information concerning any relevant accreditation;

c) identification of the procedure tested;

d) information about the sampling equipment for which the performance of procedure was assessed;

e) information about the reference materials used and, for reference air samples, how they were prepared;

f) a brief description of the analytical method tested, including information about the analytical instrumentation used;

g) information about which of the test methods prescribed in Clause 8 were followed;

h) a list of the metals and metalloids evaluated;

i) information about any operation not included in this European Standard that could have influenced the results;

j) test results;

k) a statement concerning whether the acceptance criteria were met and, if so, over which ranges of concentration of metal or metalloid in air and sampled air volumes;

l) technical justification for omitting any relevant tests.

Annex A
(informative)

Guidance on determination of analytical recovery

A.1 Procedures for soluble compounds of metals and metalloids

A.1.1 In general, procedures for the determination of soluble compounds of metals and metalloids in workplace air incorporate a design-based sample dissolution method, i.e. soluble compounds of metals and metalloids are defined as such by the specific leach solution and leach conditions prescribed or envisaged for sample dissolution when the corresponding limit values were set [4]). This is because, except for compounds that have a very high or very low solubility in water, solubility is dependent upon the nature of the leach solution and other factors such as particle size, solute/solvent ratio, temperature etc. Consequently, by definition, the analytical method gives 100 % recovery and the analytical bias is zero.

A.1.2 However, there are circumstances in which procedures for the determination of soluble compounds of metals and metalloids in workplace air can give incorrect results. In particular, this can occur if a soluble compound reacts with the collection substrate, or a contaminant on it, to produce an insoluble compound. For example, a low recovery will be obtained for soluble silver compounds if the filter used is contaminated with chloride (see reference [6]). Consideration should therefore be given to chemical compatibility when selecting collection substrates for soluble compounds of metals and metalloids (see ISO 15202-1). If it is believed that there could be a chemical compatibility problem, tests should be performed to confirm that analytical recovery is satisfactory.

A.2 Procedures that involve sample dissolution

A.2.1 Most procedures for measuring metals and metalloids in airborne particles involve sample dissolution, e.g. procedures in which the analysis is carried out by atomic absorption spectrometry (AAS), inductively coupled plasma – atomic emission spectrometry (ICP – AES) and inductively coupled plasma - mass spectrometry (ICP-MS). The major source of analytical bias for this type of procedure is usually incomplete dissolution of the metals or metalloids of interest. The analytical bias can therefore be estimated by testing the effectiveness of the sample dissolution method on a range of suitable, well-characterised bulk materials (e.g. pure compounds of the metal or metalloid of interest, certified reference materials).

A.2.2 The analytical method should normally not exhibit a bias. If there are clearly identifiable sample types for which the measuring procedure as a whole is not suitable because the sample dissolution method gives poor recoveries, these should be excluded from the scope of the procedure.

A.2.3 In some instances, the use of results obtained from the analysis of certified reference materials (CRMs) and/or pure compounds can lead to an over-estimate of the analytical bias because air samples containing a much smaller amount of material of much smaller particle size are much more readily taken into solution. If this could be the case, it might be possible to obtain a more relevant estimate of analytical bias by repeating the sample dissolution experiments on test filters prepared by generating a homogenous dust cloud from the test material and collecting replicate samples using a multiport sampling device.

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4) For soluble metal and metalloid compounds that have a limit value that does not have an associated prescribed measuring procedure, it is recommended that the sample dissolution procedure prescribed in ISO 15202-2 is used.

A.3 Procedures that do not involve sample dissolution

Some procedures for measuring metals and metalloids in airborne particles involve analysis of the sample on the collection substrate using a non-destructive technique, e.g. laser ablation coupled with inductively coupled plasma - mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry. Such measuring procedures can exhibit an analytical bias resulting from physical or chemical differences between the samples and calibration materials. It is therefore necessary to design special experiments to test these procedures, or to estimate the analytical bias by theoretical consideration of the processes involved. In some instances, it might be possible to produce test samples suitable for use in estimation of the analytical bias by depositing CRMs or pure compounds on collection substrates in a controlled manner. However, it is necessary to ensure that there are no differences in sample deposition characteristics between the test samples and workplace air samples that could significantly influence results.

Annex B
(informative)

Estimation of uncertainty of measurement

B.1 General

Methods for measurement of chemical agents in airborne particles involve two major steps: sampling and analysis. The following is a typical, but non-exclusive, list of random and non-random uncertainty components:

a) sampling

   1) uncertainty associated with sampled air volume (see B.2);

   2) uncertainty associated with sampling efficiency (see B.3); and

   3) uncertainty associated with sample storage and transportation, if any (see B.4).

b) analysis

   1) uncertainty associated with analytical recovery (see B.5);

   2) uncertainty associated with analytical precision (see B.6.3.1 or B.6.4.1);

   3) uncertainty associated with the calibration (see B.6.3.2 and B.6.3.3 or B.6.4.2 and B.6.4.3);

   4) uncertainty associated with dilution of sample solutions, if applicable (see B.6.3.4 or B.6.4.4);

   5) uncertainty associated with instrument response drift (see B.6.3.5 or B.6.4.5); and

   6) uncertainty associated with blank subtraction (see B.6.5).

B.2 Uncertainty associated with sampled air volume

B.2.1 Sources of uncertainty

For pumped sampling, the sampled air volume has the following sources of uncertainty:

— flow rate measurement (see B.2.2),

— pump flow stability (see B.2.3); and

— sampling time (see B.2.4).

B.2.2 Flow rate measurement

Flow rate measurements can be carried out using a range of different devices, e.g. rotameters, mass flow meters, bubble flow meters or dry piston flow meters. Flow rate measurement error arises from three sources: the calibration of the flow meter (non-random), the reading of the flow meter (random) and, where appropriate, correction of the flow rate reading to ambient pressure and temperature.

The uncertainty of the flow rate calibration should be estimated from the data given on the flow meter test certificate.

The uncertainty of the flow rate reading should be estimated from measurements carried out under repeatability conditions.

Examples of flow rate measurement uncertainty for different types of flow meters are given in Table B.1.

Table B.1 — Measurement uncertainty of different flow meters (example data)

Flow meter type	**Scale** %		**Uncertainty of flow rate calibration**[a] %	**Uncertainty of flow rate reading**[b] %
rotameter, 30 cm length[c]	100		1,6	0,23
	50		2,0	0,45
	10		5,2	2,3
Flow meter type	**Flow meter measuring range** $l \cdot min^{-1}$	**Measured flow rate** $l \cdot min^{-1}$	**Uncertainty of flow rate calibration**[a] %	**Uncertainty of flow rate reading**[b] %
mass flow meter	0,1 to 15	2,0	0,61	2,0
Flow meter type	**Flow cell measuring range** $l \cdot min^{-1}$	**Measured flow rate** $l \cdot min^{-1}$	**Uncertainty of flow rate calibration**[a] %	**Uncertainty of flow rate reading**[b] %
bubble flow meter	0 to 0,25	0,12	0,4	0,35
	0,2 to 6	2,0	0,12	0,1
	2 to 30	3,0	0,06	0,22
dry piston flow meter	0,5 to 5	2,0	0,59	0,26
	0,5 to 25	3,0	0,41	0,07

[a] Flow rate calibration uncertainties calculated assuming a rectangular probability distribution $A/\sqrt{3}$, where A is the distribution value from the flow meter calibration certificate.

[b] Flow rate reading uncertainties based on ten measurements.

[c] The uncertainty of the flow rate reading of an analogue flow meter depends upon the resolution of the scale of the instrument.

If the flow rate is measured several times, the uncertainty of the flow rate reading is reduced by a factor of $1/\sqrt{n}$, where n is the number of measurements of the flow rate.

If a generally applicable estimate of uncertainty is to be made for a method that does not specify the use of a particular type of flow meter, the uncertainty components for a mass flow meter given in Table B.1 should be used, as this constitutes a worst-case scenario if the use of an inappropriate rotameter is disregarded.

B.2.3 Pump flow stability

Pumps for personal air sampling are usually self-regulating and maintain the set flow rate independent of variation in back pressure. EN 1232 and EN 12919 require that the flow rate is maintained to within ± 5 % of the set value throughout the sampling period. Assuming a rectangular probability distribution, the maximum acceptable value of a non-random uncertainty component of the pump flow stability is $5/\sqrt{3}$ %.

Actual values for the pump flow stability can be less than 5 %. It can be estimated from the value given by manufacturer or from the results of the test in EN 1232:1997, 6.6. Assuming a rectangular probability

distribution, the value of the non-random uncertainty component of the pump flow stability can be calculated according to Equation (B.1):

$$u_{\mathrm{pfs,nr}} = \frac{\Delta_{\mathrm{pfs}}}{\sqrt{3}} \qquad \text{(B.1)}$$

where

$u_{\mathrm{pfs,nr}}$ is the value of the non-random uncertainty component of the pump flow stability;

Δ_{pfs} is the difference between the mean reading of the flow rate at minimum and maximum back pressure, in percent.

B.2.4 Sampling time

Sampling time can be measured very exactly with a radio controlled clock, a quartz clock or stopwatch. The major source of uncertainty in measurement of sampling time is the accuracy with which the reading is taken, i.e. to the nearest minute or second.

If the reading is taken to the nearest second, the non-random uncertainty component is very small for both long-term and short-term measurements and can be negligible. If the reading is taken to the nearest minute, the non-random component is very small for long-term measurements (e.g. > 2 h) and can be disregarded, but for short-term measurements it needs to be taken into account.

For example, if time is recorded to the nearest minute, the coefficient of variation is 2,7 % for a sampling time of 15 min (summing the maximum 0,5 min biases at the start and end of the sampling period and dividing by the sampling time and √6, assuming a triangular probability distribution).

If the pump is supplied with an internal timer, EN 1232 require that after 8 h the indicated time shall not deviate more than 5 min from a reference timer. The maximum tolerance for the sampling time is 1 %. Assuming a rectangular probability distribution, the maximum acceptable value of a non-random uncertainty component is 1/√3 = 0,58 %.

B.3 Uncertainty associated with sampling efficiency

B.3.1 General

Aerosol samplers have to follow one or more of the sampling conventions defined in EN 481. Aerosol sampling methods have random and non-random uncertainty components that arise from how closely the samplers used match the required sampling convention(s).

EN 13205 describes two general test methods to determine whether a sampler collects the required aerosol fraction(s) correctly. In the primary method, this is done by determining the collection efficiency of the sampler as a function of particle size. In the secondary method, this is done by comparison of the concentration measured by the candidate sampler and that measured by a validated (reference) sampler for at least three test aerosols with widely different particle size.

B.3.2 Uncertainty for aerosol samplers tested according to the primary method given in EN 13205

B.3.2.1 Principle

In this method, sampling efficiency is determined as a function of particle size.

B.3.2.2 Sources of uncertainty for sampling efficiency

The sampling efficiency has the following sources of uncertainty:

— calibration of the sampler test system (see B.3.2.3);

— estimation of the sampled concentration (see B.3.2.4);

— bias relative to the sampling convention (see B.3.2.5);

— excursion from the nominal flow rate [for respirable samplers and thoracic samplers] (see B.3.2.6);

— individual sampler variability [for respirable samplers and thoracic samplers] (see B.3.2.7).

B.3.2.3 Calibration of the sampler test system

In a properly designed and performed experiment, the random and non-random uncertainty components associated with calibration of the sampler test system should be very small. They can be calculated by propagation of errors from the uncertainty of the diameter of the calibration particles (and possibly by the use of calibration functions for particle sizers) to the uncertainty in sampled mass fraction. See EN 13205.

B.3.2.4 Estimation of the sampled concentration

The random uncertainty component of the measured sampling efficiency of the sampler depends on the uncertainty of the concentrations measured by the reference sampler and the tested sampler, as described in EN 13205. It is calculated by propagation of errors from these uncertainties to the uncertainty in sampled mass fraction.

B.3.2.5 Bias relative to the sampling convention

The non-random uncertainty component due to deviation of the sampling efficiency of the sampler from the sampling convention is a function of the sampled aerosol size distribution. It is calculated as specified in EN 13205.

B.3.2.6 Excursion from the nominal flow rate (for respirable samplers and thoracic samplers)

The separation efficiency for respirable samplers and thoracic samplers is highly dependent on the sampling flow rate. The non-random uncertainty component associated with excursion from the nominal flow rate is calculated by propagation of error (flow rate deviation) to variability in sampled mass fraction, as specified in EN 13205. This uncertainty component incorporates the uncertainty component of the sampled air volume (see B.2.3).

B.3.2.7 Individual sampler variability (for respirable samplers and thoracic samplers)

The random uncertainty component associated with individual sampler variability for respirable samplers and thoracic samplers is calculated by propagation of error (individual sampler variability) to variability in sampled mass fraction, as specified in EN 13205.

B.3.3 Uncertainty for aerosol samplers tested according to the secondary method given in EN 13205

B.3.3.1 Principle

In this method, the sampling efficiency is evaluated by comparison with a validated (reference) sampler.

B.3.3.2 Sources of uncertainty for sampling efficiency

The sampling efficiency has the following sources of uncertainty:

— reference concentration, as determined by the reference sampler(s) (see B.3.3.3);

— reference sampler (see B.3.3.4);

— sampler bias (see B.3.3.5);

— individual sampler variability [for respirable samplers and thoracic samplers] (see B.3.3.6); and

— excursion from the nominal flow rate [for respirable samplers and thoracic samplers] (see B.3.3.7).

B.3.3.3 Reference concentration, as determined using the reference sampler

The random uncertainty component associated with the reference concentration is determined directly from experimental data, as specified in EN 13205.

B.3.3.4 Reference sampler

The non-random uncertainty component associated with concentration measurements made using the reference sampler is obtained from the reference sampler test report. The random uncertainty component associated with concentration measurements made using the reference sampler is incorporated in the uncertainty of the reference concentration (see B.3.3.3).

B.3.3.5 Sampler bias

The average systematic difference between the tested sampler and the reference sampler has random and non-random uncertainty components. These are calculated as specified in EN 13205.

B.3.3.6 Individual sampler variability [for respirable samplers and thoracic samplers]

The random uncertainty component associated with individual sampler variability can be determined as specified in EN 13205 if several samplers of the same type are included in the performance test.

B.3.3.7 Excursion from the nominal flow rate [for respirable samplers and thoracic samplers]

The separation efficiency for respirable samplers and thoracic samplers is highly dependent on the sampling flow rate. The non-random uncertainty component associated with excursion from the nominal flow rate is calculated by propagation of error (flow rate deviation) to variability in sampled mass fraction, as specified in EN 13205. This uncertainty component incorporates the uncertainty component of the sampled air volume (see B.2.3).

B.3.4 Uncertainty components for aerosol samplers – Estimates for general use

B.3.4.1 Inhalable samplers

At present, data determined experimentally for different types of inhalable samplers have not been published. As long as such information is not available, the following estimates of uncertainty components, which are those that were used in the EU project BC/CEN/ENTR/000/2002-16 *Analytical methods for chemical agents* can be applied for all types of inhalable sampler (see reference [7]):

— calibration of sampler test system (non-random) 0,5 %

— estimation of the sampled concentration (random) 4 %

— bias relative to the sampling convention (non-random) 7,5 %

CEN/TR 15230 lists examples of inhalable samplers with the potential to meet the requirements of EN 481 and EN 13205 which were or had been available on the market up to 2004.

B.3.4.2 Respirable samplers

At present, data determined experimentally for different types of respirable samplers have not been published. As long as such information is not available, the following estimates of uncertainty components can be applied for all types of respirable sampler that are optimised for collection of the respirable fraction of airborne particles, as defined in EN 481:

— calibration of sampler test system (non-random) 1 %

— estimation of the sampled concentration (random) 1 %

— bias relative to the sampling convention (non-random) 8 %

— excursion from the nominal flow rate for inertia-based pre-separators, e.g. cyclones and impactors
(when the sample volume is calculated from the nominal flow rate) 3 %
(when the sample volume is calculated from the average flow rate) 6 %

— individual sampler variability 7 %

The estimate for the uncertainty associated with bias relative to the sampling convention given above assumes that the nominal flow rate specified for the sampler is within 5 % of the optimum value for collection of the respirable fraction of airborne particles. CEN/TR 15230 lists (without optimum flow rates) examples of respirable samplers with the potential to meet the requirements of EN 481 and EN 13205 which were or had been available on the market up to 2004.

The non-random uncertainty component associated with excursion from the nominal flow rate for inertia-based pre-separators is higher when the sample volume is calculated from the average flow rate than when it is calculated from the nominal flow rate because respirable samplers (based on inertial separation) are largely self-compensating for excursions from the nominal flow rate. See reference [8].

The non-random uncertainty component associated with excursion from the nominal flow rate for sedimentation-based pre-separators, e.g. a horizontal elutriator, can be calculated from theory.

B.3.5 Efficiency of collection substrate

B.3.5.1 Filter materials

Filter materials should be selected to have high collection efficiency for the particle size range of interest, in which case the uncertainty associated with collection efficiency is negligible. See ISO 15767.

B.3.5.2 Foams

When a foam is used as the collection substrate, sampling efficiency and collection efficiency are inter-related and no uncertainty components need to be added.

B.4 Uncertainty associated with sample storage and transportation

B.4.1 Sample storage

Metals and metalloids and their inorganic compounds are generally stable. However, if desired, the uncertainty associated with sample storage can be estimated by the analysis of replicate samples collected from a test atmosphere using a multiport sampler or prepared by spiking sampling collection media.

Assuming a rectangular probability distribution, the uncertainty associated with sample storage is given by Equation (B.2):

$$u_{st} = \frac{\Delta_{st}}{\sqrt{3}} \qquad \text{(B.2)}$$

where

u_{st} is the relative standard uncertainty associated with sample storage; and

Δ_{st} is the difference, in percent, between the mean results of replicate samples analysed immediately after sampling or preparation and replicate samples analysed after the maximum storage time, in percent.

B.4.2 Transportation

The transport of aerosol samples normally has a component of uncertainty associated with loss of sample from the collection substrate during transportation. This non-random uncertainty component can be determined from the acceptance criteria for the upper limit of sample loss on transportation, which EN 13205 and ISO 15767 require is less than 5 %. For methods that are validated according to these European Standards, the uncertainty component associated with transportation is therefore $5/\sqrt{3}$ %, assuming a rectangular probability distribution.

If a measuring procedure specifies a more stringent requirement for the upper limit of sample loss on transportation, or if such a requirement is specified in a sampling protocol that will be used in conjunction with a measuring procedure, the uncertainty component of transportation should be calculated from the acceptable range, assuming a rectangular probability distribution.

If it can reasonably be assumed that there is negligible sample loss on transportation, the uncertainty component of transportation can be disregarded.

B.5 Uncertainty associated with analytical recovery

B.5.1 General

Bias is normally eliminated during the development of an analytical method, but this is not always possible. According to ENV 13005 measurement results should be corrected for bias, if it is significant. However, this is often not practicable in procedures for measurement of metals and metalloids in workplace air samples, since analytical bias can vary with the sample matrix. Analytical bias therefore has to be estimated and treated as an uncertainty component.

The non-random uncertainty component of the analytical bias can be estimated from:

— results from the analysis of certified reference materials (CRMs) and/or pure compounds (see B.5.2);

— results from interlaboratory comparisons (see B.5.3);

— results from recovery tests carried out on spiked laboratory blanks (see B.5.4);

— an acceptable bias range (see B.5.5);

or it can be taken to be zero for procedures that incorporate a design-based sample preparation (see B.5.6).

B.5.2 Analysis of certified reference materials and/or pure compounds

B.5.2.1 The non-random uncertainty component of the analytical bias can be estimated by determining analytical recovery when the method is tested on well-characterised bulk materials, such as CRMs or pure compounds of the metals and metalloids of interest, which are representative of substances that could be present in workplace air. This can be achieved by replicate analysis of a single CRM or pure compound or, preferably, by replicate analysis of several CRMs and/or pure compounds. The test samples should be analysed in a minimum of five analytical series (e.g. on five different days).

B.5.2.2 If a single CRM or pure compound is used, the relative standard uncertainty of the analytical bias (non-random) is given by Equation (B.3):

$$u_{\mathrm{ab}} = \sqrt{\left(\frac{B_{\mathrm{a}}}{k}\right)^2 + \frac{(K_{\mathrm{v,r}})^2}{n} + (u_{\mathrm{cnv}})^2} \qquad \text{(B.3)}$$

where

u_{ab} is the relative standard uncertainty of the analytical bias, in percent;

B_{a} is the bias of the mean result of replicate analyses for the CRM or pure compound from the certified or nominal value, in percent;

k is the coverage factor used in the calculation of the expanded uncertainty (see B.8);

$K_{\mathrm{v,r}}$ is the coefficient of variation of the replicate samples, in percent;

n is the number of replicate samples of the CRM or pure compound analysed;

u_{cnv} is the relative standard uncertainty of the certified or nominal value, in percent (e.g. a 95 % confidence interval, divided by 1,96 to convert to a standard uncertainty, then divided by the mean result and multiplied by 100 convert it to a relative value).

B.5.2.3 If several different CRMs or pure compounds are used, the relative standard uncertainty of the analytical bias (non-random) is, in general, given by Equation (B.4):

$$u_{\mathrm{ab}} = \sqrt{\frac{\sum_{i=1}^{n}(B_{\mathrm{a},i})^2}{n} + (\bar{u}_{\mathrm{cnv}})^2} \qquad \text{(B.4)}$$

where

$\frac{\sum_{i=1}^{n}(B_{a,i})^2}{n}$ is the mean square bias, in percent, where $B_{a,i}$ is the bias of mean result for the i^{th} CRM or pure compound analysed and n is the total number of CRMs and/or pure compounds analysed;

$(\overline{u}_{cnv})^2$ is the mean square relative uncertainty of the certified or nominal values of the CRMs and/or pure compounds analysed, in percent.

B.5.3 Interlaboratory comparisons

The non-random uncertainty component of the analytical bias can be estimated from the results of interlaboratory comparisons, as described in reference [3]. However, this approach has limited applicability in the case of measuring procedures for metals and metalloids in workplace air.

Interlaboratory comparison results are generally not useful for estimating the uncertainty of the bias for methods that involve sample dissolution. This is because the test samples used in most interlaboratory comparisons are collection substrates spiked with standard solution and the analysis of such samples does not test the performance of the sample dissolution method in an effective manner. However, in instances when this is not the case, e.g. for interlaboratory comparisons in which the test samples are prepared by the deposition of airborne particles on collection substrates, or in instances for which the effectiveness of sample dissolution is not an issue, e.g. measuring procedures for soluble metals and metalloids, the use of results from interlaboratory comparisons is a good approach for estimating the uncertainty of the analytical bias.

Interlaboratory comparison results can also be used to estimate the uncertainty of the bias for methods that do not involve sample dissolution, e.g. X-ray fluorescence methods, but only if it can be shown that any physical differences between the test samples and workplace air samples will not significantly influence results.

The procedure for estimation of the uncertainty of the analytical bias from interlaboratory comparisons is very similar to that used for several different CRMs and pure compounds. In order to produce a good estimate of the analytical bias, a laboratory should participate at least six times within a reasonable time period.

The relative standard uncertainty of the analytical bias (non-random) is given by Equation (B.5):

$$u_{ab} = \sqrt{\frac{\sum_{i=1}^{n}(B_{a,i})^2}{n} + (\overline{u}_{ref})^2} \qquad \text{(B.5)}$$

where

$\frac{\sum_{i=1}^{n}(B_{a,i})^2}{n}$ is the mean square bias, in percent, where $B_{a,i}$ is the bias of the result for the i^{th} interlaboratory comparison sample and n is the total number of interlaboratory comparison samples analysed;

$(\overline{u}_{ref})^2$ is the mean square relative uncertainty of the reference value, $\frac{\overline{K}_{v,bL}}{\sqrt{n}}$, in percent, where $\overline{K}_{v,bL}$ is the average between-laboratory coefficient of variation for the interlaboratory comparisons, and n is the average number of participants in the interlaboratory comparisons.

Uncertainty estimates from interlaboratory comparison results are usually a little higher than when results from the analysis of CRMs are used. This is partly due to the fact that certified values of CRMs are normally better defined than the nominal or assigned values in an interlaboratory comparison.

B.5.4 Analysis of spiked collection substrates

The non-random uncertainty component of the analytical bias can be estimated from the results of the analysis of spiked collection substrates, in much the same way as results from interlaboratory comparisons. However, this approach is only applicable to methods for which the effectiveness of sample dissolution is not an issue, such as methods for soluble metals and metalloids; and to methods that do not involve sample dissolution, but only if it can be shown that any physical differences between the test samples and workplace air samples will not significantly influence results.

Laboratory blanks should be spiked with known volumes of standard solution containing the analyte or analytes of interest at a number of different spiking levels within the working range of the method. The test samples should be analysed in a minimum of five analytical series (e.g. on five different days).

The relative standard uncertainty of the analytical bias (non-random) is given by Equation (B.6):

$$u_{\mathrm{ab}} = \sqrt{\frac{\sum_{i=1}^{n}(B_{\mathrm{a},i})^2}{n} + (\bar{u}_{\mathrm{sp}})^2} \qquad \text{(B.6)}$$

where

$\frac{\sum_{i=1}^{n}(B_{\mathrm{a},i})^2}{n}$ is the mean square bias, in percent, where $B_{\mathrm{a},i}$ is the bias of the mean result for the i^{th} spiking level from its nominal value and n is the number of spiking levels at which the bias was determined;

$(\bar{u}_{\mathrm{sp}})^2$ is the mean square relative uncertainty of the nominal values of the spikes, in percent.

Provided that the same standard solution is used to spike the sampling media and prepare the calibration solutions, assuming a rectangular probability distribution for the bias of the micropipette and assuming that the effect of temperature on the dispensed volume is negligible, the relative uncertainty of the nominal value of the spike is in turn given by Equation (B.7):

$$u_{\mathrm{sp}} = \sqrt{\frac{(B_{\mathrm{max,s}})^2}{3} + (u_{\mathrm{p1}})^2} \qquad \text{(B.7)}$$

where

$B_{\mathrm{max,s}}$ is the maximum bias of the solution volume dispensed by the micropipette used to spike the blank sampling media, in percent;

u_{p1} is the relative uncertainty of the solution volume dispensed by the micropipette used to spike the blank sampling media, in percent.

B.5.5 Acceptable bias range

Some methods that cover a wide range of sample matrixes specify an acceptable range for the bias, within which it has to be demonstrated that the method performs when used in a particular laboratory for a particular application, e.g. ISO 15202. In such instances, the relative standard uncertainty of the analytical bias (non-random) can be estimated from the acceptable range, assuming a rectangular probability distribution, using Equation (B.8):

$$u_{ab} = \frac{B_{max,m}}{\sqrt{3}} \quad \text{(B.8)}$$

where

u_{ab} is the relative standard uncertainty of the analytical bias, in percent; and

$B_{max,m}$ is the maximum bias specified in the method, in percent.

B.5.6 Procedures that incorporate a design-based sample preparation method

The uncertainty of the analytical bias can be taken to be zero for measuring procedures that incorporate a design-based sample preparation method, such as procedures for soluble metals and metalloids in workplace air, since the analytical recovery is by definition 100 % (see A.1).

B.6 Uncertainty associated with analytical variability

B.6.1 General

The uncertainty associated with analytical variability can be estimated either from analytical precision data obtained under repeatability conditions (see B.6.3) or from analytical precision data obtained under reproducibility conditions (see B.6.4). In both cases, separate uncertainty estimates need to be made for any sources of systematic error, where applicable, e.g. non-random uncertainty associated with the concentration of the calibration standards (see B.6.3.2 and B.6.4.2), calibration function (B.6.3.3 and B.6.4.3), dilution of the sample solution (see B.6.3.4 and B.6.4.4) and instrument response drift (see B.6.3.5 and B.6.4.5).When the analytical precision is determined from laboratory reproducibility data, e.g. using quality control data, most random and randomized uncertainty components are included. See ISO/TS 21748 for further guidance.

B.6.2 Range of sample loadings at which the analytical variability has to be estimated

For each metal and metalloid of interest, the sample loadings for which the analytical variability has to be estimated should be calculated taking into consideration the measurement task for which the performance of the procedure is to be evaluated (see EN 482:2006, Clause 4). These sample loadings should cover sufficient combinations of sampling time and concentration of metal or metalloid in air to provide enough data for the expanded uncertainty to be estimated for the relevant measuring ranges (see EN 482:2006, 5.3.5).

Tables B.2 and B.3 give the conditions under which analytical variability has to be known for a comprehensive evaluation of the performance of methods for making measurements for comparison with limit values. However, an abbreviated test can be performed in many instances. In this case, a recommended procedure is to start by considering the two extreme loading levels (given in bold italics in Tables B.2 and B.3) and use the results to estimate the uncertainty of the measuring procedure. If the most stringent EN 482 uncertainty requirement is met for both the extreme loading levels then the requirements of EN 482 will be met in all cases and no further loading levels need to be considered. If this is not the case, it will be necessary to test the performance of the measuring procedure at other loading levels until sufficient information is obtained to make a meaningful statement about the sampling times and measuring ranges for which the EN 482 requirements are met.

Table B.2 — Conditions for calculating sample loadings for measurements for comparison with short-term limit values (LVs)

Sampling time	Concentration of metal or metalloid in air	
	Low	High
15 min	***0,5 LV × 15 min***	***2 LV × 15 min***

Table B.3 — Conditions for calculating sample loadings for measurements for comparison with 8 h time-weighted average limit values (LVs)

Sampling time	Concentration of metal or metalloid in air		
	Low	Medium	High
30 min	***0,1 LV × 30 min***	0,5 LV × 30 min	2 LV × 30 min
120 min	0,1 LV × 120 min	0,5 LV × 120 min	2 LV × 120 min
480 min	0,1 LV × 480 min	0,5 LV × 480 min	***2 LV × 480 min***

NOTE 1 Sample loadings should be calculated for the nominal flow rate of the samplers used, i.e. the flow rate at which they are designed to collect the intended fraction of airborne particles.

NOTE 2 Other intermediate sample loadings can also be tested, if desired, for example for a sampling time of 4 h or a concentration of 1 LV.

B.6.3 Estimation using repeatability data

B.6.3.1 Analytical precision

B.6.3.1.1 Estimation from data obtained from the analysis of spiked collection substrates

For each of the sample loadings at which the analytical variability is to be determined (see B.6.2), analytical precision can be estimated by spiking six laboratory blanks with an appropriate volume of working standard solution containing a known mass of each of the metals and metalloids of interest, preparing and analysing the test samples as described in the measuring procedure and calculating the coefficient of variation.

B.6.3.1.2 Estimation from data obtained by interpolation of standard deviation

Alternatively, for each of the sample loadings at which the analytical variability is to be determined (see B.6.2), analytical precision can be estimated from data obtained at a particular sample loading or over a range of sample loadings using the interpolation method described in Annex C. This is particularly useful for estimating analytical precision in the case of published methods for which limited method performance data are available.

B.6.3.1.3 Estimation from theory

In some instances, it is possible to estimate analytical precision at each of the required sample loadings from theory, e.g. for an XRFS method analytical precision can be estimated from counting statistics using experimentally determined sensitivity data.

B.6.3.2 Calibration standards

B.6.3.2.1 Commercial stock standard solutions

B.6.3.2.1.1 The non-random uncertainty component associated with the concentration of a commercial stock standard solution can be estimated from the range on the certified value provided by the manufacturer. Assuming a rectangular probability distribution, the relative standard uncertainty associated with the concentration of the standard solution is given by Equation (B.9):

$$u_{ss1} = \frac{B_{max,ss1}}{\sqrt{3}} \quad \text{(B.9)}$$

where

u_{ss1} is the relative uncertainty associated with the concentration of the commercial stock standard solution, in percent; and

$B_{max,ss1}$ is the maximum bias of the concentration of the stock standard solution from the confidence interval given on the certificate provided by the manufacturer, in percent.

B.6.3.2.1.2 The non-random uncertainty component associated with the concentration of a commercial stock standard solution can be estimated from the 95 % confidence limit of the certified value and the coverage factor provided by the manufacturer. For example, for a stock standard solution of (1000 ± 3) mg · l^{-1} the relative standard uncertainty is 0,3 divided by k, where k is the coverage factor.

B.6.3.2.2 Custom-made stock standard solutions

The non-random uncertainty component associated with the concentration of a custom-made stock standard solution can be estimated from the uncertainty of balance used for weighing of the pure compound from which the solution was prepared and the maximum bias of the volumetric flask in which it was prepared, assuming a rectangular probability distribution and that the effect of temperature on the solution volume and the contribution of the uncertainty of the pure compound used is negligible, using Equation (B.10):

$$u_{ss2} = \sqrt{\frac{(K_{v,b})^2}{3} + \frac{(B_{max,f})^2}{3} + (u_{Vf})^2} \quad \text{(B.10)}$$

where

u_{ss2} is the relative uncertainty associated with the concentration of the custom-made stock standard solution, in percent;

$K_{v,b}$ is the coefficient of variation of the balance used to weigh the pure compound used for preparation of the stock standard solution, in percent;

$B_{max,f}$ is the maximum bias of the volumetric flask in which the stock standard solution was made from the confidence interval given on the certificate provided by the manufacturer, in percent; and

u_{Vf} is the relative uncertainty of the volume of volumetric flask, in percent.

B.6.3.2.3 Reference air samples

If reference air samples (6.4) are used for calibration in procedures that do not involve sample dissolution, the non-random uncertainty component associated with the sample loadings needs to be taken into account.

B.6.3.3 Calibration function

The random uncertainty component associated with the calibration function can be calculated from parameters obtained by the least-squares linear regression. See reference [5].

2 % is a reasonable estimate of the random uncertainty component associated with the calibration function and may be used in most cases. This was the value used in the EU project BC/CEN/ENTR/000/2002-16 *Analytical methods for chemical agents* (see reference [7]).

B.6.3.4 Dilution of sample solutions (if applicable)

If sample solutions are diluted before analysis it is necessary to take into consideration the random and non-random uncertainty components associated with the dilution process.

The random uncertainty component is the relative uncertainty of the solution volume dispensed by the micropipette used in dilution of the sample solutions (see Equation (B.11).

$$u_{\mathrm{di,r}} = \sqrt{(u_{\mathrm{p2}})^2 + (u_{\mathrm{Vf}})^2} \tag{B.11}$$

where

u_{p2} is the relative uncertainty of the solution volume dispensed by the micropipette used in dilution of the sample solutions, in percent;

u_{Vf} is the relative uncertainty of the volume of volumetric flask, in percent.

Assuming rectangular probability distributions for the bias of the micropipette and the volumetric flasks used in dilution of the sample solutions, the non-random uncertainty component associated with dilution of the sample solutions, $u_{\mathrm{di,nr}}$, in percent, is given by Equation (B.12):

$$u_{\mathrm{di,nr}} = \sqrt{\frac{(B_{\mathrm{max,s}})^2}{3} + \frac{(B_{\mathrm{max,f}})^2}{3}} \tag{B.12}$$

where

$B_{\mathrm{max,s}}$ is the maximum bias of the solution volume dispensed by the micropipette used in dilution of the sample solutions, in percent;

$B_{\mathrm{max,f}}$ is the maximum bias of the volumetric flasks used in dilution of the sample solutions according to the manufacturer's specification, in percent.

B.6.3.5 Instrument response drift

Methods and laboratory operating procedures generally specify a maximum instrument response drift that is permitted before recalibration (often monitored by repeat analysis of a calibration solution). It is necessary to take this non-random uncertainty component into consideration. Assuming a rectangular probability distribution, the relative standard uncertainty associated with instrument response drift, u_{dr} , in percent, is given by Equation (B.13):

$$u_{\mathrm{dr}} = \frac{d_{\mathrm{max}}}{\sqrt{3}} \tag{B.13}$$

where

d_{max} is the maximum instrument response drift permitted in the method or laboratory operating procedure, in percent.

B.6.4 Estimation using laboratory reproducibility data

B.6.4.1 Analytical precision

The uncertainty associated with analytical variability can be estimated from laboratory reproducibility data obtained from the analysis of stable quality control samples, normally laboratory blanks spiked with low and high masses of the metals and metalloids of interest (e.g. masses equivalent to 10 % and 90 % of the working range of the measuring procedure). It is important to cover long-term random variations, so the data used should be from the analysis of quality control samples over a period of several months.

The relative standard uncertainty associated with analytical precision is given by Equation (B.14):

$$u_{ap} = \sqrt{\frac{[(n_1 - 1) \times (K_{v,q1})^2] + [(n_2 - 1) \times (K_{v,q2})^2]}{(n_1 - 1) + (n_2 - 1)}} \quad \text{(B.14)}$$

where

u_{ap} is the relative standard uncertainty associated with analytical precision, in percent;

$K_{v,q1}$ is the coefficient of variation of the results for the first quality control sample, in percent;

n_1 is the number of results for the first quality control sample;

$K_{v,q2}$ is the coefficient of variation of the results for the second quality control sample, in percent; and

n_2 is the number of results for the second quality control sample.

B.6.4.2 Concentration of calibration standards

See B.6.3.2.

B.6.4.3 Calibration function

Under reproducibility conditions, the random uncertainty component associated with the calibration function is included in the estimate of analytical precision (see B.6.4.1) and no separate uncertainty estimate is required.

B.6.4.4 Dilution of the sample solutions (if applicable)

See B.6.3.4.

B.6.4.5 Instrument response drift

See B.6.3.5.

B.6.5 Blank subtraction

B.6.5.1 General

The random uncertainty associated with blank subtraction needs to be included in the uncertainty budget if sample results are blank corrected; or a non-random uncertainty component needs to be included if blank correction is not performed.

B.6.5.2 Recalculating of analytical precision to include the random uncertainty associated with blank subtraction

For each of the sample loadings at which the analytical variability is to be determined (see B.6.2), the estimated coefficient of variation (see B.6.3.1 and B.6.4.1) is converted to a standard deviation and combined with the standard deviation of the laboratory blank using Equation (B.15)

$$s_x' = \sqrt{(s_x)^2 + \frac{(s_0)^2}{n}} \qquad \text{(B.15)}$$

where

s_x' is the standard deviation of a blank corrected measurement for a mass of analyte, m_x;

s_x is the standard deviation of a measurement for a mass of analyte, m_x; and

s_0 is the standard deviation of n blank measurements for a mass of analyte, m_0.

For each of the sample loadings, the resulting standard deviation is then converted back into a coefficient of variation to obtain the analytical precision of the blank corrected measurement.

B.6.5.3 Non-random uncertainty component associated with no blank subtraction

For each of the sample loadings at which the analytical variability is to be determined (see B.6.2), the estimated coefficient of variation (see B.6.3.1 and B.6.4.1) is converted to a standard deviation and combined with uncertainty of the laboratory blank using, Equation (B.16):

$$s_x'' = \sqrt{(s_x)^2 + \left(\frac{b_{\max}}{\sqrt{3}}\right)^2} \qquad \text{(B.16)}$$

where

s_x'' is the standard deviation of a non-blank corrected measurement for a mass of analyte, m_x;

s_x is the standard deviation of a measurement for a mass of analyte, m_x; and

$b_{\max}$ is the maximum value for the laboratory blank permitted in the method or estimated from previous data.

For each of the sample loadings, the resulting standard deviation is then converted back into a coefficient of variation to obtain the analytical precision of the non-blank corrected measurement.

B.7 Calculation of combined uncertainty

B.7.1 Random and non-random components of sampling and analytical uncertainty

To calculate the random and non-random components of sampling uncertainty and analytical uncertainty, the relevant individual uncertainty components are combined according to Equations (B.17) to (B.20):

$$u_{s_r} = \sqrt{\sum_{i=1}^{j_{s_r}} u_{s_r\,i}^{\,2}} \tag{B.17}$$

$$u_{s_{nr}} = \sqrt{\sum_{i=1}^{j_{s_{nr}}} u_{s_{nr}\,i}^{\,2}} \tag{B.18}$$

$$u_{a_r} = \sqrt{\sum_{i=1}^{j_{a_r}} u_{a_r\,i}^{\,2}} \tag{B.19}$$

$$u_{a_{nr}} = \sqrt{\sum_{i=1}^{j_{a_{nr}}} u_{a_{nr}\,i}^{\,2}} \tag{B.20}$$

where

u_{s_r} , $u_{s_{nr}}$, u_{a_r} and $u_{a_{nr}}$ are the random uncertainty associated with sampling, the non-random uncertainty associated with sampling, the random uncertainty associated with analysis and the non-random uncertainty associated with analysis, respectively;

$u_{s_r\,i}$, $u_{s_{nr}\,i}$, $u_{a_r\,i}$ and $u_{a_{nr}\,i}$ are the corresponding relevant individual uncertainty components;

j_{s_r} , $j_{s_{nr}}$, j_{a_r} and $j_{a_{nr}}$ are the corresponding numbers of relevant individual uncertainty components.

B.7.2 Random and non-random uncertainty of the measuring procedure

The random uncertainty of the measuring procedure as a whole (u_{c_r}) is calculated according to Equation (B.21):

$$u_{c_r} = \sqrt{u_{s_r}^2 + u_{a_r}^2} \tag{B.21}$$

The non-random uncertainty of the measuring procedure as a whole ($u_{c_{nr}}$) is calculated according to Equation (B.22).

$$u_{c_{nr}} = \sqrt{u_{s_{nr}}^2 + u_{a_{nr}}^2} \tag{B.22}$$

B.7.3 Combined standard uncertainty of the measuring procedure

The combined standard uncertainty of the measuring procedure (u_c) is calculated according to Equation (B.23):

$$u_c = \sqrt{u_{c_r}{}^2 + u_{c_{nr}}{}^2} \quad \text{(B.23)}$$

B.8 Calculation of expanded uncertainty

The expanded uncertainty of the measuring procedure, U, is calculated, using a coverage factor $k = 2$, according to Equation (B.24):

$$U = 2 \times u_c \quad \text{(B.24)}$$

Annex C
(informative)

Interpolation of standard deviation

Uncertainty associated with analytical variability is commonly estimated using analytical precision data obtained under repeatability conditions (see B.6.3). However, repeatability data is sometimes only available from a limited number of experiments or for masses of analyte that do not correspond to the conditions (sampled air volume, limit value, etc.) for which uncertainty estimates are required. Therefore, it might be necessary or desirable to estimate, by interpolation, standard deviations at masses other than those for which experimental data are available. This can be achieved by using a model to calculate an interpolated value of the standard deviation, $s(m)$, for a mass of analyte, m. The model makes various assumptions about the behaviour of the standard deviation as a function of the mass of analyte. Although these assumptions are not tested, the interpolated value is a better estimate of standard deviation than a value calculated from the limiting coefficient of variation that exists above a certain mass.

The model can be expressed as:

$$s(m)^2 = s_0{}^2 + (s_r\, m)^2 \qquad \text{(C.1)}$$

where

$$s_0 = \lim_{m \to 0} s(m) \qquad \text{(C.2)}$$

In practice, s_0 is approximated by $s(m_0)$.

$$s_r = \lim_{m \to \infty} \frac{s(m)}{m} \qquad \text{(C.3)}$$

In practice, s_r is approximated by $s(m_x)/ m_x$. See below for how to select m_x.

The reliability of this model depends heavily on how well the values m_0 and m_x are selected; and in many cases, as when estimating the expanded uncertainty of a measuring procedure from published performance data, nothing is known about this. If possible, m_0 should be chosen to be close to the upper limit of m for which the standard deviation, $s(m)$, is constant (*i.e.* $\partial s(m)/\partial m = 0$). Additionally, m_x should be chosen to be close to the lower limit for which the coefficient of variation, $s(m)/m$, is constant (i.e. $\partial s(m)/\partial m$ is equal to the coefficient of variation of the analytical method).

If the average coefficient of variation is known over a mass range [m_1, m_2], or the coefficient of variation is known to be constant over a range, this coefficient of variation, $K_{v,1-2}$, can be expressed by Equation (C.4):

$$(K_{v,1-2})^2 = \frac{1}{\ln m_2 / m_1} \int_{m_1}^{m_2} \left(\frac{s_x}{m_x} \right)^2 d \ln m_x \qquad \text{(C.4)}$$

On the other hand, if the coefficient of variation is only known for a specific mass (m_3), this coefficient of variation, $K_{v,3}$, can be expressed by Equation (C.5):

$$K_{v,3} = \frac{s_x (m_3)}{m_3} \qquad \text{(C.5)}$$

For the two cases of knowing the coefficient of variation, $K_{v,1-2}$, over a range of masses from mass m_1 to mass m_2, or knowing the coefficient of variation, $K_{v,3}$, at a single mass m_3, the corresponding value of s_r is given by either:

$$(s_{r,1-2})^2(m_1,m_2) = (K_{v,1-2})^2 - \left(\frac{1}{2} \times \frac{1}{\ln m_2/m_1} \times {s_0}^2 \left(\frac{{m_2}^2 - {m_1}^2}{{m_1}^2 \times {m_2}^2}\right)\right) \quad \text{(C.6)}$$

or

$$(s_{r,3})^2(m_3) = (K_{v,3})^2 - \left(\frac{s_0}{m_3}\right)^2 \quad \text{(C.7)}$$

The calculated value for s_r is an approximation based on the sparse data, and depends on the actual values (m_0, m_1 and m_2, or m_0 and m_3) for which the analytical precision is known.

Substitute the value of s_r ($s_{r,1-2}$ or $s_{r,3}$), calculated using Equations (C.6) and (C.7), into Equation (C.8) to calculate the standard deviation, s_y, at any mass m_y:

$${s_y}^2 = (K_{v,y} \times m_y)^2 = {s_0}^2 + (s_r \times m_y)^2 \quad \text{(C.8)}$$

The following is an example of interpolation of standard deviation for crystalline silica by XRD (see reference [9]).

Method detection limit (MDL) = 5 µg, s_0 = 5/3 µg, $K_{v,1-2}$ = 0,08, m_1 = 50 µg and m_2 = 200 µg. $s_{r,1-2}$ is then calculated to be 0,078. The interpolated standard deviation in the range of 5 µg to 200 µg of crystalline silica is listed in the Table C.1.

Table C.1 — Interpolated standard deviation and coefficient of variation

Mass of analyte m_x µg	**Standard deviation** s_x µg	**Coefficient of variation** K_v **%**
5	1,71	34,2
10	1,82	18,4
25	2,54	10,2
50	4,2	8,4
60	4,9	8,2
80	6,4	8,0
100	7,9	7,9
150	11,8	7,8
200	15,6	7,8

Annex D
(informative)

Example of estimation of expanded uncertainty

Tables D.1 to D.3 give an example for the estimation of expanded uncertainty for the MDHS 12/2 method for chromium in air when sample dissolution is with $HNO_3/HClO_4$ (see reference [10]).

Table D.1 — Estimation of expanded uncertainty

Parameter	Cross-reference	Data	Uncertainty (%)			
			Sampling (random)	Analysis (random	Sampling (non-random)	Analysis (non-random)
Sampled air volume						
Flow meter calibration, assuming use of mass flow meter	B.2.2	—	—	—	0,6	—
Flow meter reading, assuming use of mass flow meter	—	—	2,0	—	—	—
Pump flow stability, i.e. for compliance with EN 1232, ± 5 %	B.2.3	5 %	—	—	2,9	—
Minimum sampling time specified in the method	B.2.4	30 min	—	—	1,4	—
Maximum sampling time specified in the method	B.2.4	480 min	—	—	0,1	
Sampling efficiency, inhalable samplers tested in accordance with EN 13205	B.3.2					
Calibration of sampler test system	B.3.2.3	—	—	—	0,5	—
Estimation of sampled concentration	B.3.2.4	—	4	—	—	—
Deviation from sampling convention	B.3.2.5	—	—	—	7,5	—
Sample storage and transportation	B.4					
Storage, assuming no loss on storage	B.4.1	—	—	—	—	—
Transportation, EN 13205 and ISO 15767 requirements of less than 5 % loss are met	B.4.2	5 %	—	—	2,9	—
Analytical recovery (from spiked collection substrates)	B.5.4					
RMS bias of results	—	—	—	—	—	3,8
Bias of solution volume dispensed by micropipette (maximum of ± 1 %)	—	1 %	—	—	—	—
Uncertainty of solution volume dispensed by micropipette (2 %)	—	2 %	—	—	—	—
Calculated relative uncertainty of nominal value of spike	—	—	—	—	—	2,1

Table D.1 *(continued)*

Parameter	Cross-reference	Data	Uncertainty (%)			
			Sampling (random)	Analysis (random	Sampling (non-random)	Analysis (non-random)
LOQ reported in method, in µg:	—	1 µg	—	—	—	—
Standard deviation of blank, in µg, calculated from LOQ	—	0,1 µg	—	—	—	—
Average analytical precision over range of analyte masses, as % RSD	—	1,9 %	—	—	—	—
Mass of the lower end of analyte range over which precision determined	—	12 µg	—	—	—	—
Mass of the upper end of analyte range over which precision determined	—	960 µg	—	—	—	—
Analytical precision at 0,1 LV (0,5 mg · m^{-3}) for 60 l sampled air volume, from above data	B.6.3.1.2	0,11 µg	—	—	—	—
Analytical precision at 2 LV (0,5 mg · m^{-3}) for 960 l sampled air volume, from above data	B.6.3.1.2	18 µg	—	—	—	—
Analytical precision at 0,1 LV (0,5 mg · m^{-3}) for 60 l sampled air volume, blank subtracted	B.6.5	0,15 µg	—	5,1	—	—
Analytical precision at 2 LV (0,5 mg · m^{-3}) for 960 l sampled air volume, blank subtracted	B.6.5	18 µg	—	1,9	—	—
Stock standard solutions (concentration certified to within ± 0,5 %)	B.6.3.2.1.1	0,5 %	—	—	—	0,3
Calibration function (typical uncertainty of 2 %)	B.6.3.3	2 %	—	2	—	—
Dilution of sample solutions (no dilution)	B.6.3.4	—	—	—	—	—
Instrument response drift (maximum permitted drift of ± 5 %)	B.6.3.5	5 %	—	—	—	2,9
Uncertainty for measurements at 0,1 LV (0,05 mg m^{-3}) with 60 l sampled air volume						
Combined random and non-random uncertainty components	B.7.1	—	4,5	5,5	8,7	5,2
Uncertainty for measurements at 2 LV (1 mg m^{-3}) with 960 l sampled air volume						
Combined random and non-random uncertainty components	B.7.1	—	4,5	2,7	8,6	5,2

Table D.2 — Uncertainty for measurements at 0,1 LV (0,05 mg · m^{-3}) with 60 l sampled air volume

Uncertainty component	Cross reference	Uncertainty %
Combined random uncertainty	B.7.2	7,1
Combined non-random uncertainty	B.7.2	10,1
Combined standard uncertainty of the measuring procedure	B.7.3	12,3
Expanded uncertainty	B.8	24,7

Table D.3 — Uncertainty for measurements at 2 LV (1 mg · m^{-3}) with 960 l sampled air volume

Uncertainty component	Cross reference	Uncertainty %
Combined random uncertainty	B.7.2	5,2
Combined non-random uncertainty	B.7.2	10,0
Combined standard uncertainty of the measuring procedure	B.7.3	11,3
Expanded uncertainty	B.8	22,6

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