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Workplace air — Metals and metalloids in airborne particles — Requirements for evaluation of measuring procedures

Air des lieux de travail — Métaux et métalloïdes dans les particules en suspension dans l'air — Exigences relatives à l'évaluation des procédures de mesure

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

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

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

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

This document 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 ISO 20581. It enables producers and users of procedures for measuring metals and metalloids in airborne particles to adopt a consistent approach to method validation. See also Annex B.

Although this document 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, for example, sulphuric acid mist.

This document is based on EN 13890:2009[14], published by the European Committee for Standardization (CEN).

Workplace air — Metals and metalloids in airborne particles — Requirements for evaluation of measuring procedures

1 Scope

This document 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.

This document 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 ISO 20581.

This document 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 addressed in EN 13205-1 and ISO 15767.

This document does not apply to procedures for measuring metals or metalloids present as inorganic gases or vapours (e.g. mercury, arsenic) 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

ISO 7708, *Air quality — Particle size fraction definitions for health-related sampling*

ISO 13137, *Workplace atmospheres — Pumps for personal sampling of chemical and biological agents — Requirements and test methods*

ISO 18158, *Workplace air — Terminology*

ISO 20581:2016, *Workplace air — General requirements for the performance of procedures for the measurement of chemical agents*

EN 13205-1, *Workplace exposure — Assessment of sampler performance for measurement of airborne particle concentrations — Part 1: General requirements*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18158 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
test sample
sample prepared to meet all specific conditions for a test

[SOURCE: ISO 11323:2010, 5.6]

3.2
test solution
solution prepared by the process of sample dissolution and, if necessary, having been subjected to any further operations required to bring it into a state in which it is ready for analysis

[SOURCE: ISO 8518:2001, 3.4.4]

4 Principle

For measuring procedures that involve sample dissolution, instrumental detection limits (IDLs) are determined by repeat analysis of blank solutions. For all measuring procedures, limits of detection (LOD) and limits of quantification (LOQ) are determined by analysis of laboratory blanks. Typically, the LOD and LOQ are calculated as three times and ten times the standard deviation of blank measurements, respectively. The determined LOQs are then assessed against the performance requirements specified in 5.2.1. Refer to ISO 18158 for definitions of these terms.

Analytical recovery is determined by one of a number of different methods, depending upon the nature of the measuring procedure under evaluation. The determined analytical recovery is then assessed against the performance requirements specified in 5.2.2.

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 characterized by subsequent analysis using a reference procedure or it is estimated from theory.

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 C. In accordance with 5.2.3, the determined expanded uncertainty is then assessed against the general performance requirements specified in ISO 20581.

NOTE For an example for calculation of expanded uncertainty, see Annex E.

5 Requirements

5.1 Method description

5.1.1 Application range

The application range of the measuring procedure shall give, at minimum, information about the following:

a) the metals and metalloids covered by the measuring procedure;

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

c) 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 ISO 20581, together with the associated recommended sampled air volume (e.g. 0,01 mg · m^{-3} to 0,5 mg · m^{-3} for a sampled air volume of 960 l);

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

e) any known interferences.

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

5.1.2 Method performance

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

a) the LOQ and, if required, LODs of the measuring procedure;

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

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

d) full details of any known interferences, including suitable and sufficient information on how to minimize 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 ISO 7708, according to the particle size fraction(s) that is(are) applicable to the OELV for the metals and metalloids of interest (e.g. an inhalable sampler, a thoracic sampler or a respirable sampler);

— specify that the samplers shall conform to the provisions of EN 13205-1;

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

5.1.5 Sampling pumps

The measuring procedure shall require the user to use sampling pumps that conform to the provisions of ISO 13137.

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 Limit of quantification (LOQ)

For each metal and metalloid included in the application range of the measuring procedure, the lower limit of the working range of the method that will be satisfactory for the intended measurement task shall be determined. For example, if the measurement task is testing compliance with long-term OELVs, Formula (1) is used 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 OELV:

$$m_{\text{low}} = 0{,}1\rho_{\text{LV}} \cdot q_{\text{v,a}} \cdot t_{\text{s,min}} \quad (1)$$

where

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

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

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

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

For procedures that involve sample dissolution, the lower limit of the required working range is calculated 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 LOQs 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 LOQs 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 application range of the measuring procedure and the coefficient of variation of the analytical recovery shall be less than 5 %.

NOTE The predecessor term to “coefficient of variation” is “relative standard deviation”, which is deprecated. See also ISO 3534-1:2006, 2.38, Note 2 to entry[1].

5.2.3 Expanded uncertainty

The expanded uncertainty of the measuring procedure shall conform to the requirements specified in ISO 20581.

6 Reagents and materials

6.1 Reagents

During the analysis, only reagents of analytical grade, and only water conforming to the requirements for ISO 3696 grade 2 water (electrical conductivity less than 0,1 mS · m^{-1}, i.e. resistivity greater than 0,01 MΩ · m, at 25 °C) may be used.

The water used should 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 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 shall be used.

If commercial standard solutions are used, the manufacturer's expiry date or recommended shelf life shall be observed.

6.3 Test materials

For each metal or metalloid, a range of test materials shall be used that is representative of the substances of interest that could be present in the workplace atmosphere.

The test materials shall be pure compounds of known composition, certified reference materials (CRMs) or other well-characterized materials (e.g. materials characterized in an interlaboratory comparison).

When using CRMs, the supplier's instructions shall be followed.

If there is an OELV for a specific compound, that compound should be included in the range of reference materials.

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 that could be generated by the work activity.

NOTE 1 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 2 CRMs that have been characterized 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 metal or metalloid of interest shall be used. The loading should be within the working range of the method.

Special techniques for the preparation of reference air samples, as described in A.3, should be considered when sample dissolution is not required.

7 Apparatus

Usual laboratory apparatus and resources and, in particular, the following test equipment.

7.1 A system for applying a known volume of standard solution to collection substrates with a precision of better than 1 %.

7.2 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.

7.3 An instrument or instruments for analysing each metal or metalloid of interest.

8 Test methods

8.1 LOD and LOQ

8.1.1 Instrumental detection limit (IDL)

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 limits of detection by diluting the standard solutions (6.2) by an appropriate factor. Analyse the test solution at least ten times under repeatability conditions.

NOTE An IDL is of use in identifying changes in instrument performance, but it is not the same as a method LOD. An IDL is likely to be lower than a method LOD 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 LOD and LOQ

8.1.2.1 For measuring procedures that involve sample dissolution, prepare at least 10 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 10 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 LODs. 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 LOD and the LOQ for each metal or metalloid of interest as three times and ten times the standard deviation, respectively[22].

8.1.2.2 For measuring procedures that do not involve sample dissolution, analyse at least 10 laboratory blanks under repeatability conditions.

Calculate the method LOD and the LOQ for each metal or metalloid of interest as three times and ten times the standard deviation, respectively.

8.1.2.3 Compare the LOQs 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 metal or metalloid 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 metal or metalloid 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 It is usually not necessary to include water-soluble compounds in the range of compounds tested.

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 each metal or metalloid of interest in the reference material and the supplier's instructions on the minimum amount of material that is required for a homogenous sample.

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.