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Workplace air — General requirements for the performance of procedures for the measurement of chemical agents

National foreword

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Workplace air — General requirements for the performance of procedures for the measurement of chemical agents

Air des lieux de travail — Exigences générales concernant les performances des procédures de mesure des agents chimiques

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Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation on 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 the following URL: www.iso.org/iso/foreword.html.

The committee responsible for this document is ISO/TC 146, *Air quality*, Subcommittee SC 2, *Workplace atmospheres*.

Introduction

National laws and regulations require the assessment of the potential exposure of a worker to chemical agents in workplace atmospheres. One way of assessing such exposure is to measure the concentration of a chemical agent in the air in the worker's breathing zone. The procedures used for such measurements should provide reliable and valid results for the comparison purpose of exposure measurements with occupational exposure limit values and for the provision of acceptable control strategies.

This document is based on EN 482:2012, amended by Amendment 1:2015, and introduces general requirements to fulfil the measurement procedures in the process of quantitative exposure assessment. Specific International Standards and European Standards have been prepared for different types of measuring procedures and measuring devices. These include standards for airborne particle samplers [EN 13205 (all parts)], diffusive samplers (ISO 16107 and EN 838), pumped samplers (EN 1076), short-term detector tubes (ISO 17621), personal sampling pumps (ISO 13137), metals and metalloids in airborne particles (EN 13890), mixtures of airborne particles and vapour (EN 13936) and direct reading instruments for toxic gases and vapours [EN 45544 (all parts)]. In these specific standards, additional requirements have been included for the procedure or device in question, so that the general requirements of this document are not compromised. Where no specific International and/or European Standard exists, only the general requirements apply.

Performance requirements given in this document are intended to apply under environmental conditions present at the workplace. However, because a wide range of environmental conditions is encountered in practice, this document specifies requirements that have to be fulfilled by measuring procedures when tested under prescribed laboratory conditions.

It is the user's responsibility to choose the appropriate procedures or devices that meet the requirements of this document. One way of doing this is to obtain information or confirmation from the provider of a procedure or the manufacturer of a device. Type-testing or, more generally, assessment of the performance of procedures or devices, can be undertaken by the manufacturer, user, testing house or research and development laboratory, as is most appropriate. A number of existing procedures for workplace measurements have either been tested over a part of the required minimum measuring range, but not over the entire range, or have not been tested for all environmental influences and potential interferences. If these partially validated procedures meet the performance requirements of this document, they can be used at present. Nevertheless, these procedures should be tested over the full ranges as soon as is reasonably practicable.

Workplace air — General requirements for the performance of procedures for the measurement of chemical agents

1 Scope

This document specifies general performance requirements for procedures for the determination of the concentration of chemical agents in workplace atmospheres. These requirements apply to all steps of measuring procedures regardless of the physical form of the chemical agent (gas, vapour, airborne particles), measuring procedures with separate sampling and analytical methods, and direct-reading devices.

This document specifies requirements that have to be fulfilled by measuring procedures when tested under prescribed laboratory conditions due to a wide range of environmental conditions encountered in practice.

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 78-2, *Chemistry — Layouts for standards — Part 2: Methods of chemical analysis*

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 16107, *Workplace atmospheres — Protocol for evaluating the performance of diffusive samplers*

ISO 17621, *Workplace atmospheres — Short term detector tube measurement systems — Requirements and test methods*

EN 838, *Workplace exposure — Procedures for measuring gases and vapours using diffusive samplers — Requirements and test methods*

EN 1076, *Workplace exposure — Procedures for measuring gases and vapours using pumped samplers — Requirements and test methods*

EN 13205 (all parts), *Workplace exposure — Assessment of sampler performance for measurement of airborne particle concentrations*

EN 13890, *Workplace exposure — Procedures for measuring metals and metalloids in airborne particles — Requirements and test methods*

EN 13936, *Workplace exposure — Procedures for measuring a chemical agent present as a mixture of airborne particles and vapour — Requirements and test methods*

EN 45544 (all parts), *Workplace atmospheres — Electrical apparatus used for the direct detection and direct concentration measurement of toxic gases and vapours*

3 Terms and definitions

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

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

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

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

4 Classification

4.1 General

In this document, measurements are classified according to their purposes. These classifications are based upon the measurement strategy in EN 689.

4.2 Screening measurements of time-weighted average concentration

Screening measurements of time-weighted average concentration are performed to obtain semiquantitative information on exposure levels. Such information is used to identify potential health hazards, and to estimate the risk to health based on the likely severity of harm and the probability of its occurrence. These measurements can also determine if the exposure is significantly below or above the occupational exposure limit value (OELV). Apparatus intended for detection and concentration measurements of chemical agents, that meets the requirements of this document and is capable of reporting the time-weighted average, can be used.

4.3 Screening measurements of variation of concentration in time and/or space

Screening measurements of variation of concentration in time and/or space are used to provide information on the likely pattern of the concentration of chemical agents in the air and to identify locations and periods of elevated exposure. The screening measurements also provide information on the location and intensity of emission sources and to estimate the effectiveness of ventilation or other technical measures. Apparatus intended for detection and concentration measurements of chemical agents, that meets the requirements of this document, can be used.

4.4 Measurements for comparison with occupational exposure limit values

Provided the method meets established acceptable uncertainty criteria, measurements can be made for comparison with OELVs. Measurements can be taken to determine whether a worker’s exposure exceeds the OELV initially and repeated after any significant change in working conditions, industrial process, products or chemicals, or OELV.

4.5 Periodic measurements

Periodic measurements are used to determine whether exposure conditions have changed since the measurements for comparison with OELVs were performed, or whether control measures remain effective. The interval between measurements should be established based on the initial occupational exposure assessment or subsequent amendments to it.

NOTE Since the composition of the workplace atmosphere will have been investigated during the initial occupational exposure assessment and the composition is known not to vary over time, it can be appropriate for periodic measurements to use procedures with lower selectivity.

5 Performance requirements

5.1 General

Performance requirements for measuring procedures depend on the purpose for which they are used. The performance requirements for screening measurements are less stringent than for measurements for the comparison with limit values and periodic measurements. Therefore, the performance requirements for screening measurements in 5.2 and 5.3 are only given in general terms.

5.2 Screening measurements of time-weighted average concentration

The purpose of these measurements is described in 4.2. The measurement procedures shall have

a) adequate selectivity for the chemical agent,

b) averaging time less than or equal to the limit value reference period,

c) measuring range that includes the limit value, and

d) expanded uncertainty that is fit for purpose.

5.3 Screening measurements of variation of concentration in time and/or space

The purpose of these measurements is described in 4.3. The measuring procedures shall have

a) adequate selectivity for the chemical agent,

b) short averaging time (for variation of concentration in time ≤5 min; for variation of concentration in space ≤15 min),

c) measuring range that is fit for purpose (see 4.3), and

d) expanded uncertainty that is fit for purpose.

5.4 Measurements for comparison with limit values and periodic measurements

5.4.1 Unambiguity

A measuring procedure shall produce an unambiguous result for the concentration of the chemical agent being measured in the specified measuring range, i.e. an analytically determined value shall correspond to one concentration only within a known uncertainty.

5.4.2 Selectivity

The measuring procedure shall contain appropriate information about the nature and magnitude of any interference.

NOTE 1 Selectivity requirements vary from case to case, depending on what is known in advance about the workplace air. If the identity of all contaminants present is not known in advance, then the measuring procedure will need to have a high selectivity. If the identity of all contaminants is known prior to measurement and there are no interferents present, then it might be possible to use a measurement procedure with a low or adequate selectivity.

Where a particle size fraction, as defined in ISO 7708, is specified for an OELV, procedures for measuring chemical agents present as airborne particles shall prescribe a method for sampling the specified particle size fraction.

NOTE 2 In addition to samplers meeting the requirements of ISO 7708, there are samplers which themselves define the sample [see ISO 13205 (all parts)].

If different limit values are set for different species of a chemical agent, then the measuring procedure shall determine the individual species concerned.

5.4.3 Averaging time

The averaging time is equal to the sampling time, which shall be less than or equal to the limit value reference period. Depending on the sampling techniques, the sampling time can vary.

NOTE A full shift average concentration, typically the 8 h time-weighted concentration, gives a representative description of the occupational exposure situation.

Exposure peaks which may occur systematically or randomly during the shift should fulfil the short-term exposure limit conditions, if any.

5.4.4 Measuring range

The measuring range of the procedure listed in Table 1 shall cover at least the concentrations from 0,1 times to 2 times the limit value for long-term measurements, and from 0,5 times to 2 times the limit value for short-term measurements. The relevant OELV shall be determined by the proper authorities where the measuring procedure is to be used.

NOTE Reference [10] provides a list of limit values from many jurisdictions.

5.4.5 Expanded uncertainty

The requirements for expanded uncertainty are given in Table 1.

Table 1 — Expanded uncertainty requirements for measurements for comparison with limit values and periodic measurements

Reference period	**Measuring range**	**Relative expanded uncertainty**	**Relative expanded uncertainty** (mixtures of airborne particles and vapour)
Short-term (e.g. 15 min)	0,5 times to 2 times limit value	≤50 %	≤50 %
Long-term	0,1 times to <0,5 times limit value	≤50 %	≤50 %
Long-term	0,5 times to 2 times limit value	≤30 %	≤50 %

NOTE Variation of exposure to chemical agents in the workplace can be significantly greater than indicated by the uncertainty of a single measurement calculated according to this document. This is due to the temporal and spatial variability of workplace exposure.

5.4.6 Chemical agents where compliant methods are not available

Limit values are determined by authorities independently from those developing measuring procedures. If a measuring procedure is not available for a given limit value which meets the requirements given in 5.4.4 and 5.4.5, a measuring procedure should be used whose performance is closest to the requirements. The method employed should clearly state its limitations when measuring at the exposure limit.

5.5 Composite procedures

The performance requirements detailed in 5.2, 5.3 and 5.4 shall be fulfilled for the whole measuring procedure even if the measuring procedure consists of several distinct steps, e.g. preparation of equipment, sampling, transport and storage, sample preparation and analysis. Each step of the measuring procedure may be tested individually and can be combined as a whole.

5.6 Transport, handling and/or storage

Transport, handling and/or storage of samples, if appropriate, shall be carried out in such a way that the physical and chemical integrity is maintained between sampling and analysis.

5.7 Environmental conditions

The effect of environmental conditions (e.g. temperature, humidity, atmospheric pressure, and/or air speed) on the performance of the method shall be tested in the laboratory. Performance requirements concerning unambiguity, selectivity, expanded uncertainty, minimum measuring range and averaging time shall be fulfilled under the conditions likely to be encountered in the workplace.

NOTE Due to the time, cost, and effort involved, it is not practicable to carry out a comprehensive evaluation of environmental influences in the field and therefore laboratory tests are specified in this document. However, field tests can provide valuable information on the performance of measurement methods (e.g. interferences from nearby workplaces).

The range of environmental conditions under which the performance requirements of 5.2 to 5.5 are fulfilled shall be specified in the measuring procedure.

5.8 Description of measuring procedure

The measuring procedure shall be documented in accordance with ISO 78-2. Any clause or subclause which is unnecessary in a particular case may be omitted, and others, if required, may be added in the most appropriate places. The description shall contain all necessary information to perform the measuring procedure, including information about the attainable expanded uncertainty, measuring range, averaging time, interferences, and environmental or other conditions that can influence the performance of the measuring procedure.

If correction factors are applied, e.g. for a known and explainable bias due to environmental influences, these shall be justified in the measuring procedure.

NOTE An example for the structure of a method description based on ISO 78-2 is given in Annex A.

5.9 Dimension of result

The final measurement result shall be expressed in the same units as those of the limit value. This can be achieved directly or by means of a suitable conversion.

This requirement is not obligatory for screening measurements of the variation of concentration in time and/or space.

5.10 Additional requirements

In addition to the requirements given in 5.2 to 5.9, further requirements specified in ISO 13137, ISO 16107, ISO 17621, EN 838, EN 1076, EN 13205 (all parts), EN 13890, EN 13936 and EN 45544 (all parts) shall be met for particular types of measuring procedures and devices, as appropriate.

Table 2 lists additional requirements of testing parameters.

Table 2 — Additional requirements of testing parameters

Standard	Required testing parameters
ISO 13137	Features and mass of pumps, design safety, operating time, start-up and long-term performance, short-term interruption of air flow, mechanical strength, timer accuracy, electromagnetic compatibility, explosion hazard, charger, and marking
ISO 16107	Bias relative to manufacturer-specified sampling rate, variation in sampling rate (e.g. from poor sampler dimension tolerance), effects of: wind, temperature, humidity, target concentration itself, and diffusive loss from sampler
ISO 17621	Scale, packing of the tubes, interferences, overloading, evaluation of stain, shelf life, marking and mechanical strength for detector tubes; Explosion hazard, stroke volume, leakage, and mechanical strength and durability for detector tube pumps
EN 838	Quantification limit of the measuring procedure, analytical recovery, nominal uptake rate, air velocity/sampler orientation, sampler leak test, shelf life, and marking
EN 1076	Quantification limit of the measuring procedure, analytical recovery, sampler leak test, shelf life, marking, flow resistance, and sampler breakthrough test
EN 13205 (all parts)	Specimen variability, pump design safety and electrical safety, and sampler evaluation
EN 13890	Pump design safety and electrical safety, sampler evaluation, detection and quantification limit of the measuring procedure, analytical recovery, and interferences
EN 13936	Comply with the requirements of this document, ISO 13137, EN 1076, EN 13205 (all parts), and EN 13890
EN 45544 (all parts)	Instrument vibration and drop test, measurement of deviations, alarm system including audible alarm, set point(s), and response time, flow failure warning, warm-up time, time of response and recovery, addition of sampling probe, field verification kit, gas concentrations above the measuring range, electrical fault signal, extended operation under standard test gas, orientation, electrical tests including battery capacity, mains power supply, time-weighted average function, and electromagnetic compatibility, and instrument drift tests

6 Test method

6.1 Estimate the expanded uncertainty of results obtained using the measuring procedure by carrying out the tests prescribed in the relevant International Standards or European Standards specific to the type of procedure or device concerned, as listed in Clause 2.

Carry out measurements at the lower and upper ends of the measuring range specified in Table 1, and for at least one intermediate concentration.

Prepare at least six replicate samples for each set of tests and analyse the samples under repeatability conditions.

Calculate the expanded uncertainty, expressed as a percentage, according to the following procedure (see, for example, References [11], [12], [13] and ISO/IEC Guide 98-3):

a) specify the measurand;

b) identify all possible sources of uncertainty;

c) quantify the random sampling uncertainty u_{s_r} and non-random sampling uncertainty $u_{s_{nr}}$;

d) quantify the random analytical uncertainty u_{a_r} and non-random analytical uncertainty $u_{a_{nr}}$;

e) calculate the combined random standard uncertainty u_{c_r} according to Formula (1) and the combined non-random standard uncertainty $u_{c_{nr}}$ according to Formula (2);

$$u_{c_r} = \sqrt{{u_{s_r}}^2 + {u_{a_r}}^2} \qquad (1)$$

$$u_{c_{nr}} = \sqrt{{u_{s_{nr}}}^2 + {u_{a_{nr}}}^2} \qquad (2)$$

f) calculate the combined standard uncertainty u_c according to Formula (3);

$$u_c = \sqrt{{u_{c_r}}^2 + {u_{c_{nr}}}^2} \qquad (3)$$

g) calculate the expanded uncertainty U using a coverage factor k, typically ranging from 2 to 3, according to Formula (4).

$$U = 2 \times u_c \qquad (4)$$

NOTE 1 Alternatively, the random and non-random components of sampling uncertainty and the random and non-random components of analytical uncertainty can be combined in a different order to calculate the combined standard uncertainty.

NOTE 2 Annex B gives information about the different components of sampling uncertainty and analytical uncertainty.

NOTE 3 For detailed calculation methods, see ISO 17621, EN 838, EN 1076, EN 13205-1, CEN/TR 13205-3, and EN 13890.

NOTE 4 Expanded uncertainty is related to the concept of accuracy used in some jurisdictions as the range containing 95 % of the measurements of any value measured. For example, accuracy estimates published in the NIOSH Manual of Analytical Methods[14] provide values for the expanded uncertainty, adjusted if necessary to account for all relevant variation sources. A method meeting the NIOSH accuracy criterion (with expanded uncertainty much tighter than 25 %) will likely therefore also meet the performance requirements (see 5.4.5) of this document.[15],[16],[17],[18]

6.2 Carry out further tests, as appropriate, to investigate the influence of interferences and environmental parameters, e.g. wind speed, wind direction or direction of sampling device.

6.3 For a measuring procedure consisting of several independent steps, e.g. preparation of equipment, sampling, transport and storage, sample preparation and analysis, each step of the measuring procedure may be tested individually as an alternative to testing the procedure as a whole. In this case, calculate the relative expanded uncertainty of the results obtained using the measuring procedure by an appropriate combination of the uncertainties of all the independent steps.

NOTE For some chemical agents, the performance of one or more of the steps might have to be determined by means other than direct testing with the chemical agent. For details, see the appropriate specific International Standard or European Standard.

7 Validation report

A validation report shall be prepared for each measuring procedure tested, containing at least the test conditions, the results obtained and the extent to which the measuring procedure complies with the requirements of this document and other relevant International Standards or European Standards.

Annex A
(informative)

Structure of a method description

An example for the structure of a method description based on ISO 78-2 is given below. Any clause or subclause which is unnecessary in a particular case can be omitted, and others, if required, can be added in the most appropriate places. The description contains all necessary information to perform the measuring procedure, including information about the attainable expanded uncertainty, measuring range, averaging time, interferences, and environmental or other conditions that can influence the performance of the measuring procedure.

The following major clauses should be present, if applicable:

- Introduction;
- Title;
- Warning and safety precautions (if any);
- Scope;
- Normative references;
- Terms and definitions;
- Principle;
- Requirements including specified measuring range, transportation temperature stability, interferences, environmental influences, explosion hazard, mechanical strength and durability, instructions for use, etc.;
- Test conditions including reactions, reagents and materials, apparatus and equipment, generation of test gas, and specified test conditions;
- Test methods including test procedures, mechanical strength and durability, explosion hazard, sampling, transport and storage, analytical procedure, and concentration calculation;
- Quality assurance and control;
- Special cases (e.g. interferences);
- Uncertainty of measurement;
- Test report;
- Annexes.

Annex B
(informative)

Calculation of uncertainty of measurement

B.1 General

The first step in estimating the uncertainty of measurement according to ISO/IEC Guide 98-3 is to determine potential sources of uncertainty and identify individual random and non-random uncertainty components (see References [11], [12], [13] and ISO/IEC Guide 98-3). Construction of a cause and effect diagram can be helpful to identify components for which uncertainty estimates are required.

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

a) uncertainty from sampling, associated with:
   1) sampled air volume or mass uptake (see B.2);
   2) the sampling efficiency (see B.3);
   3) sample storage, handling, and/or transportation, if any (see B.4).
b) uncertainty from analyses of gases and vapours (see EN 838 and/or EN 1076), associated with:
   1) method recovery (includes several factors such as analytical recovery, method bias, reference concentration, effect of temperature, effect of relative humidity, etc.) (see B.5);
   2) method variability (includes factors such as method precision data obtained from the results of the replicate samples, concentration of calibration solution, calibration function, dilution of the sample solutions, if applicable, instrument response drift, etc.) (see B.7).
c) uncertainty from analyses of airborne particles (see EN 13890) and mixtures of airborne particles and vapour, associated with:
   1) analytical recovery (see B.6);
   2) analytical variability (see B.8);
   3) blank subtraction (see B.9).

Each of these uncertainty components is estimated or calculated and then combined to obtain an estimate of the uncertainty of the measurement method as a whole as described in Clause 6.

Assuming a rectangular probability distribution or a triangular probability distribution, a range ± A should be converted into a non-random uncertainty equal to $A/\sqrt{3}$ or $A/\sqrt{6}$, respectively.

B.2 Uncertainty associated with sampled air volume or mass uptake

B.2.1 Pumped sampling

B.2.1.1 Sources of uncertainty

For pumped sampling, the sampled air volume has the following sources of uncertainty: flow rate measurement (see B.2.1.2), pump flow stability (see B.2.1.3) and sampling time (see B.2.1.4).

B.2.1.2 Flow rate measurement

Flow rate measurements can be carried out using a range of different devices, for example, 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, u_{fc}, should be estimated from the data given on the flow meter test certificate.

The uncertainty of the flow rate reading, u_{fr}, should be taken to be the coefficient of variation of measurements carried out under repeatability conditions.

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

If the flow rate is measured at several times and not only at the beginning of the sampling, 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.

Table B.1 — Uncertainty of the flow rate measurement for different types of 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** $\mathrm{l \cdot min^{-1}}$	**Measured flow rate** $\mathrm{l \cdot min^{-1}}$	**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** $\mathrm{l \cdot min^{-1}}$	**Measured flow rate** $\mathrm{l \cdot min^{-1}}$	**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] The uncertainty of the flow rate calibration assumes a rectangular probability distribution and is calculated using data from the flow meter calibration certificate.

[b] The uncertainty of the flow rate reading is based on 10 measurements.

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

B.2.1.3 Pump flow stability

Pumps for personal air sampling are usually self-regulating and maintain the set flow rate independent of variation in back pressure. ISO 13137 requires that the flow rate be maintained to within ±5 % of the set value throughout the sampling period. Assuming a rectangular probability distribution, the maximum acceptable value of the non-random uncertainty component of the pump flow stability is $5/\sqrt{3}$ %.

Actual values for the pump flow stability can be estimated from the value given by manufacturer or from the results of the tests prescribed in ISO 13137, and can be less than 5 %. Assuming a rectangular probability distribution, the value of the non-random uncertainty component of the pump flow stability can be calculated according to Formula (B.1):

$$u_{\mathrm{pfs,nr}} = \frac{\Delta_{\mathrm{pfs}}}{\sqrt{3}} \tag{B.1}$$

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 per cent.

B.2.1.4 Sampling time

Sampling time can be measured very exactly with a radio-controlled clock, a quartz clock or a stopwatch, which has calibration traceable to the national time standard. 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 $\sqrt{6}$, assuming a triangular probability distribution).

In case of pumped sampling, ISO 13137 requires that the indicated time shall not deviate by more than ±0,5% from that of a calibrated timer. Assuming a rectangular probability distribution, the maximum acceptable value of a non-random uncertainty component is $0{,}5/\sqrt{3} = 0{,}29$ %.

B.2.2 Diffusive sampling

B.2.2.1 Sources of uncertainty

For diffusive sampling, the mass uptake has the following sources of uncertainty: uptake rate (see B.2.2.2) and sampling time (see B.2.2.3).

B.2.2.2 Uptake rate

The random and non-random uncertainty components of the uptake rate should be estimated from replicate samples obtained from a test atmosphere, as described in EN 838.

B.2.2.3 Sampling time

See B.2.1.4.

B.3 Uncertainty associated with sampling efficiency

B.3.1 Pumped sampling methods for gases and vapours

Pumped sampling of gases and vapours can be influenced by the pressure, humidity and temperature of the sampled air, the concentration of chemical agents in the sampled air and by the flow rate. These factors can affect the sampling capacity and the performance of the sampling process. The uncertainty associated with these effects is incorporated into the uncertainty component of the method recovery. However, for pumped samplers, the sample volume is kept well below the experimentally established breakthrough volume (see EN 1076), in which case the sampling efficiency is assumed to be 100 % and the uncertainty of the sampling efficiency does not need to be taken into account.

B.3.2 Diffusive sampling methods for gases and vapours

For diffusive sampling, the sampling efficiency has the following sources of uncertainty: back diffusion and exposure time.

Back diffusion can occur if there is a significant variation in the air concentration of the chemical agent during the sampling period. It is influenced by the characteristics of the sorbent and the chemical agent, by the pressure, humidity and temperature of the sampled air and by the mass of chemical agent sampled. (The latter is a function of its concentration in the sampled air and sampling time.) The non-random uncertainty component due to back diffusion can be estimated from the difference of the means of the results in two sets of replicate samples. The samples are obtained by exposure of the diffusive samplers for a short period of time to a high concentration of the chemical agent, one of which is subsequently exposed to clean air for a long period of time, as described in ISO 16107 and EN 838.

The non-random uncertainty component associated with exposure time can be estimated by the analysis of replicate samples collected from a test atmosphere, as described in ISO 16107 and EN 838.

B.3.3 Aerosol sampling methods

B.3.3.1 General

For aerosol sampling methods, the sampling efficiency has the following sources of uncertainty: closeness of matching with the required sampling convention(s) and efficiency of the collection substrate.

B.3.3.2 Closeness of matching with the required sampling convention(s)

Each collection stage of a sampler for airborne particles should follow a sampling convention for one of the health-related fractions for the airborne particles, as described in ISO 7708. 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 13205-2 and EN 13205-4 describe test methods to determine whether a sampler collects the required aerosol fraction(s) correctly. In the EN 13205-2 method, this is done by determining the mean sampling efficiency curve from the individual values of sampling efficiency of the tested sampler as a function of particle aerodynamic diameter. The sampling efficiency is calculated based on the aerosol concentration determined using samples from the tested sampler divided by ambient aerosol concentration estimated from the isokinetic sampler values for at least nine particle aerodynamic sizes. In the EN 13205-4 method, this is done by comparing 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 distributions. It is not possible to determine the sampling efficiency curve by using the method described in EN 13205-4.

B.3.3.3 Uncertainty components for aerosol samplers — Estimates for general use

Sampling efficiency data have been experimentally determined and published for different types of inhalable, thoracic and respirable samplers. From these data, EN 13205-2 provides ranges for various uncertainty components for inhalable, respirable and thoracic samplers. However, at present, combined standard uncertainty for specific samplers has not been calculated as required by this document.

NOTE In place of combined standard uncertainty calculations for a specific sampler, the informative estimates of uncertainty components, given in EN 13890, can be temporarily used.

B.3.3.4 Efficiency of the collection substrate

B.3.3.4.1 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.

B.3.3.4.2 Foams

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

B.4 Uncertainty associated with sample storage and transportation

B.4.1 Sample storage

The non-random uncertainty component associated with sample storage can be estimated by analysing samples collected from a test atmosphere or prepared by spiking sampling media with the chemical agent of interest. It can be calculated from the difference (Δ_{st}) between the mean results of the replicate samples analysed immediately after the sampling/spiking and the replicate samples analysed after the maximum storage period specified in the test method. Assuming a rectangular probability distribution, the difference Δ_{st} can be divided by $\sqrt{3}$. Storage tests are described in EN 838, EN 1076 and EN 13890.

B.4.2 Transportation

B.4.2.1 Gas samples and vapour samples

When samples are transported in an appropriate manner as specified in the measuring procedure, the uncertainty component associated with transportation can be negligible.

B.4.2.2 Aerosol samples

The transportation of substrates with collected aerosol samples normally has a component of uncertainty associated with migration of dusts from the collection substrate to the substrate holder or vice versa. Contamination of the sampling cassette can be a major source of uncertainty, as the sampling cassette is itself weighed. The test of transportation integrity is described in ISO 15767 and EN 13205-6. It is required that the relative dust loss due to transport shall be less than 5 % according to ISO 15767. All relative mass changes shall be less than or equal to 5 % and 15 % for sample loadings corresponding to concentrations in the range 0,5 times to 2 times and the range of 0,1 times to 0,5 times a relevant occupational exposure limit value according to ISO 15767 or EN 13205-6. The upper limit for the loading of the collection substrate can be determined as described in EN 13205-6. The non-random uncertainty component is determined from the acceptance criteria for the upper limit of sample loading.

B.5 Uncertainty associated with method recovery for gases and vapours

Method recovery is influenced by several factors. These factors include analytical recovery, method bias, reference concentration, effect of humidity, and effect of temperature. If analytical recovery correction is not applied to the results, treat this as an uncertainty component. The study of this influence is carried out using test atmospheres following the tests described in EN 838 and EN 1076. The experimental data collected from these tests give representative information about the factors causing variation and bias (relative to a reference value) that occur in routine applications of the specified measuring procedure (such as concentration, temperature and humidity). These data can then be used to estimate the uncertainty of the method as a whole. Measuring procedures for gases and vapours usually prescribe the correction of the results for analytical recovery. In these cases, method recovery is estimated from the results of the samples taken from the test atmospheres corrected for analytical recovery.

B.6 Uncertainty associated with analytical recovery for airborne particles and mixtures of airborne particles and vapour

Bias is normally eliminated during the development of an analytical method, but this is not always possible. According to ISO/IEC Guide 98-3, measurement results should be corrected for bias, if it is significant. However, this is often not practicable, e.g. 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.

According to EN 13890, the non-random uncertainty component of the analytical bias can be estimated using

- results from the analysis of certified reference materials (CRMs) and/or pure compounds,
- results from inter-laboratory comparisons,
- results from recovery tests carried out on spiked laboratory blanks, and
- an acceptable bias range.

It can also be taken to be zero for procedures that incorporate a design-based sample preparation (e.g. procedures for determination of soluble metals and metalloids, for which the use of specific analytical conditions by definition leads to the correct analytical result without any uncertainty contribution from analytical recovery).

B.7 Uncertainty associated with method variability for gases and vapours

The uncertainty associated with method variability can be estimated from method precision data obtained from the results of the replicate samples collected from the test atmospheres used as described in EN 838 and EN 1076. Separate uncertainty estimates need to be made for any sources of systematic error, if systematic errors cannot be corrected. Examples include non-random uncertainty associated with the concentration of calibration solutions, calibration function, dilution of the sample solutions and instrument response drift.

The uncertainty associated with analytical variability is included in the method variability.

Independent uncertainty estimates associated with analytical variability can be made either from analytical precision data obtained under repeatability conditions or from data obtained under reproducibility conditions. In both cases, separate uncertainty estimates need to be made for any sources of systematic error, where applicable (for example, for non-random uncertainty associated with the concentration of calibration solutions, calibration function, dilution of the sample solutions and instrument response drift). When the analytical precision is determined from within-laboratory reproducibility data (for example, from quality control data), most random and randomized uncertainty components of the analytical variability are included (see ISO 21748 for further guidance). When within-laboratory reproducibility data are used, the values obtained for the analytical precision can be higher than when repeatability data are used because, in this case, between-days precision is included.

B.8 Uncertainty associated with analytical variability for airborne particles and mixtures of airborne particles and vapour

The uncertainty associated with analytical variability can be estimated either from analytical precision data obtained under repeatability conditions or from analytical precision data obtained under reproducibility conditions, as described in EN 13890. In both cases, separate uncertainty estimates need to be made for any sources of systematic error, where applicable (for example, for non-random uncertainty associated with the concentration of the calibration standards, calibration function, dilution of the sample solution and instrument response drift). When the analytical precision is determined from laboratory reproducibility data (for example, from quality control data), most random and randomized uncertainty components of analytical variability are included (see ISO 21748 for further guidance).

B.9 Blank subtraction

The random uncertainty associated with blank subtraction needs to be included in the uncertainty budget if sample results are blank corrected, as described in ISO 15767 and EN 13890, or a non-random uncertainty component needs to be included if blank correction is not performed.

B.10 General equation for combined uncertainty components

To calculate the random and non-random components of sampling uncertainty and analytical uncertainty, the relevant individual uncertainty components are combined according to Formulae (B.2) to (B.5) (see also 6.1, NOTE 1 and 6.3, NOTE):

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

$$u_{s_{nr}} = \sqrt{\sum_{i=1}^{j_{s_{nr}}} u_{s_{nr_i}}^{\ 2}} \tag{B.3}$$

$$u_{a_r} = \sqrt{\sum_{i=1}^{j_{a_r}} u_{a_{r_i}}^{\ 2}} \tag{B.4}$$

$$u_{a_{nr}} = \sqrt{\sum_{i=1}^{j_{a_{nr}}} u_{a_{nr_i}}^{\ 2}} \tag{B.5}$$

where

u_{s_r}, $u_{s_{nr}}$, u_{a_r} and $u_{a_{nr}}$	are the random sampling uncertainty, the non-random sampling uncertainty, the random analytical uncertainty and the non-random analytical uncertainty, 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.

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