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Workplace air — Gases and vapours — Requirements for evaluation of measuring procedures using pumped samplers

Air des lieux de travail — Gaz et vapeurs — Exigences pour l'évaluation des procédures de mesure à l'aide de dispositifs de prélèvement par pompage

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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

This document provides a framework for assessing the performance of procedures for measuring gases and vapours against the general requirements for the performance of procedures for measuring chemical agents in workplace atmospheres as specified in ISO 20581. It enables manufacturers and users of pumped samplers and developers and users of procedures for measuring gases and vapours to adopt a consistent approach to method validation (see Annex B).

Workplace air — Gases and vapours — Requirements for evaluation of measuring procedures using pumped samplers

1 Scope

This document specifies performance requirements and test methods under prescribed laboratory conditions for the evaluation of pumped samplers used in conjunction with an air sampling pump and of procedures using these samplers for the determination of gases and vapours in workplace atmospheres.

This document addresses requirements for method developers and/or manufacturers.

NOTE 1 For the purposes of this document, a manufacturer can be any commercial or non-commercial entity.

NOTE 2 For the sampling of semi-volatile compounds which can appear as a mixture of vapours and airborne particles in workplace atmospheres see EN 13936.

This document is applicable to pumped samplers and measuring procedures using these samplers in which sampling and analysis are carried out in separate stages.

This document is not applicable to:

- pumped samplers which are used for the direct determination of concentrations, for example, length-of-stain detector tubes;
- samplers which rely on sorption into a liquid, and subsequent analysis of the solution (bubblers).

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

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

ISO 13137:2013, *Workplace atmospheres — Pumps for personal sampling of chemical and biological agents — Requirements and test methods*

ISO 18158, *Workplace air — Terminology*

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

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:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Symbols and abbreviated terms

For the purposes of this document, the following symbols and abbreviations apply.

NOTE See 8.4 and Annex C for symbols used in conjunction with uncertainty of measurement only.

CRM	certified reference material
LV	limit value
m_{a1}	mass of analyte desorbed from tube blank, in micrograms (µg)
m_{a2}	mass of analyte desorbed from spiked tube, in micrograms (µg)
$m_{a,lt}$	maximum mass uptake of analyte in a leak test performed on a sealed sampler used for making measurements for comparison with a long-term limit value, in milligrams (mg)
$m_{a,st}$	maximum mass uptake of analyte in a leak test performed on a sealed sampler used for making measurements for comparison with a short-term limit value, in milligrams (mg)
$\dot{m}_1$	mass loss from permeation tube, in micrograms per minute ($\mu g \cdot min^{-1}$)
M_a	molar mass of analyte, in grams per mole ($g \cdot mol^{-1}$)
n	number of replicate samples
p_{at}	pressure of the test atmosphere sampled, in kilopascals (kPa)
R_{me}	method recovery
R_{an}	analytical recovery
RH	relative humidity of the test atmosphere sampled, in percent (%)
t_H	hold-up time of the unretained substance, in minutes (min)
t_s	sampling time, in minutes (min)
T_{at}	temperature of the test atmosphere sampled, in Kelvins (K)
V_{at}	volume of the test atmosphere sampled, in litres (l)
V_H	gas (vapour) hold-up volume (dead volume), in litres (l)
V_R	uncorrected retention volume, in litres (l)
$(V_R)'$	corrected retention volume, in litres (l)
$\dot{v}$	flow rate into the exposure chamber, for example, in litres per minute ($l \cdot min^{-1}$)
v_a	volumetric air flow rate through the sampler, for example, in litres per minute ($l \cdot min^{-1}$)
β_a	mass concentration of the analyte in the calibration gas mixture, in milligrams per cubic metre ($mg \cdot m^{-3}$)
$\bar{\beta}_{a,R}$	mean mass concentration of the analyte recovered from the test gas atmosphere, in milligrams per cubic metre ($mg \cdot m^{-3}$)

β_{cg}	mass concentration of the calibration gas mixture, in milligrams per cubic metre (mg · m^{-3})
ϑ_{at}	temperature of the test atmosphere sampled, in degrees Celsius (°C)
K_v	coefficient of variation (CV) NOTE The predecessor term "relative standard deviation" is deprecated. See also ISO 3534-1:2006, 2.38, Note 2.
$\rho_{LV,lt}$	long-term limit value given as concentration, in milligrams per cubic metre (mg · m^{-3})
$\rho_{LV,st}$	short-term limit value given as concentration, in milligrams per cubic metre (mg · m^{-3})
ϕ_a	volume fraction of the analyte, in microlitres per litre (μl · l^{-1})

5 Sampler types

Samplers for gases and vapours can be divided into type A samplers and type B samplers:

Type A samplers rely on sorption onto a collection substrate which can be impregnated with a reagent. The collection substrate is always desorbed with a solvent, and subsequently analysed.

Type B samplers rely on sorption onto a solid, thermal desorption, and analysis of the desorbate.

6 Requirements

6.1 General

Some requirements (see 6.2) shall be initially verified by the manufacturer once for each type of sampler. Other requirements (see 6.3) shall be verified for each combination sampler/chemical agent.

Measuring procedures shall meet the requirements for measuring procedures specified in 6.3. When use of a sampler for measurement of a particular gas or vapour is claimed, the sampler shall meet the requirements specified in 6.2.

Known or suspected interferences shall be noted as required in 6.3.4.1. The results of any tests performed to evaluate interferences, including suitable and sufficient information to minimize their effects shall be presented in the method report as required in 6.3.4.2.

NOTE No useful performance requirements can be given for the effect of interferents (with the exception of water vapour). The effect of interferents is difficult to predict for a non-ideal sorbent without adsorption isotherm data on mixed systems which is normally unavailable.

6.2 Sampler requirements

6.2.1 Flow resistance

When tested in accordance with 8.2.1, at least 95 % of samplers shall have a back pressure less than the appropriate maximum value indicated in Table 1. A minimum of 20 samplers shall be tested.

NOTE Typical back pressure values for type A samplers and type B samplers are given in [1].

Table 1 — Maximum back pressures

Sampler type	**Maximum back pressure** kPa
Type A (solvent desorption)	≤10
Type B (thermal desorption)	≤3,5

6.2.2 Sampler leak test (for Type B samplers)

When tested in accordance with 8.2.2, for substances with a long-term limit value the maximum leakage, i.e. the maximum mass uptake of analyte above the blank value (see 6.3.2.3), shall be less than $m_{\mathrm{a,lt}}$ calculated according to Formula (1), in milligrams (mg), as follows:

$$m_{\mathrm{a,lt}} = \frac{1}{3}\left(0{,}1\rho_{\mathrm{LV,lt}} \times 240 \times 0{,}01 \times 10^{-3}\right) \tag{1}$$

where

$m_{\mathrm{a,lt}}$	is the maximum mass uptake of analyte in a leak test performed on a sealed sampler used for making measurements for comparison with a long-term limit value;
$\rho_{\mathrm{LV,lt}}$	is the long-term limit value of the substance given as concentration, in milligrams per cubic metre ($\mathrm{mg \cdot m^{-3}}$);
240	is the reference period, in minutes (min);
0,01	is the nominal minimum flow rate for type B samplers, in litres per minute ($\mathrm{l \cdot min^{-1}}$);
10^{-3}	is a factor applied to convert the nominal minimum flow rate from litres per minute (l/min) to cubic metres per minute ($\mathrm{m^3 \cdot min^{-1}}$);
1/3	is a factor applied to calculate the maximum permitted leakage.

When tested in accordance with 8.2.2, for substances with a short-term limit value the maximum leakage, i.e. the maximum mass uptake of analyte above the blank value (see 6.3.2.3), shall be less than $m_{\mathrm{a,st}}$ calculated according to Formula (2), in milligrams (mg), as follows:

$$m_{\mathrm{a,st}} = \frac{1}{3}\left(0{,}5\rho_{\mathrm{LV,st}} \times 15 \times 0{,}01 \times 10^{-3}\right) \tag{2}$$

where

$m_{\mathrm{a,st}}$	is the maximum mass uptake of analyte in a leak test performed on a sealed sampler used for making measurements for comparison with a short-term limit value;
$\rho_{\mathrm{LV,st}}$	is the short-term limit value of the substance given as concentration, in milligrams per cubic metre ($\mathrm{mg \cdot m^{-3}}$);
15	is the reference period, in minutes (min);
0,01	is the nominal minimum flow rate for type B samplers, in litres per minute ($\mathrm{l \cdot min^{-1}}$);
10^{-3}	is a factor applied to convert the nominal minimum flow rate from litres per minute ($\mathrm{l \cdot min^{-1}}$) to cubic metres per minute ($\mathrm{m^3 \cdot min^{-1}}$);
1/3	is a factor applied to calculate the maximum permitted leakage.

6.2.3 Shelf life

The manufacturer shall specify the shelf life of the sampler when stored in its original package. During this period the sampler shall fulfil all requirements.

6.2.4 Sampler identification

Samplers shall be uniquely identified.

6.2.5 Marking

Samplers shall be marked with at least the following:

a) manufacturer's name,

b) product identification including batch identification, where available,

c) indication of the direction of air flow,

d) shelf life (or expiry date), and

e) number of this document.

NOTE The marking with the number of this document implies only that the sampler fulfils the requirements given in 6.2.

If required due to limited space, the marking may be placed on the packaging of the sampler. However, at least the product identification, batch identification, where available, and direction of air flow shall be indicated on the sampler.

6.2.6 Instructions for use

The instructions for use supplied with the sampler shall be written in the principal language(s) used in the countries where the sampler is to be marketed. They shall contain at least the following information:

a) designated use (general purpose for a number of gases and vapours or, specific, for a particular gas or vapour, see 6.1),

b) assurance that blank value meets specifications, where necessary for a particular gas or vapour, (where a blank value is important),

c) directions for proper handling of the sampler, including opening and closing,

d) general information on the principle of use, for example, sorbent type, reaction of the reagent impregnated solid, desorption method,

e) information on the range of temperature where the sampler can be used,

f) information on storage and transport, and

g) information on health or environmental hazards and method of disposal.

6.3 Measuring procedure requirements

6.3.1 Sampling procedure requirements

6.3.1.1 General

Sampling conditions (sample volume, flow rate and sampling time) shall be established according to the LV assigned to the compounds of interest, for example, short-term limit value, long-term limit value or both.

6.3.1.2 Sample volume

The recommended sample volume which is calculated from the recommended flow rate and the reference period should conform to the sampler capacity verification test (see 8.3.1.2).

6.3.1.3 Air flow rate

6.3.1.3.1 Determination of the maximum air flow rate (only for impregnated filters)

When tested according to 8.3.1.4, the maximum air flow rate shall be 90 % of the flow rate at which the breakthrough volume drops by 5 %.

6.3.1.3.2 Determination of the minimum air flow rate (only for thermal desorption)

A minimum air flow rate shall be established according to the test given in 8.3.1.5.

6.3.1.4 Storage conditions after sampling

The storage conditions after sampling shall be specified. When tested in accordance with 8.3.1.6, the mean value of the method recovery after storage shall not differ by more than 10 % from the value before storage.

6.3.2 Analytical procedure requirements

6.3.2.1 Limit of quantification

The limit of quantification shall be lower than or equal to the calculated mass of analyte that would be collected for the minimum air sample volume specified in the measuring procedure at the following concentrations:

- 0,1 LV for substances with long-term limit value,
- 0,5 LV for substances with short-term limit value only.

6.3.2.2 Analytical recovery

When tested in accordance with 8.3.2.2, the analytical recovery R_{an} shall be

- for Type A samplers, $R_{an} \geq 75$ % with $K_v \leq 10$ % at each loading, and
- for Type B samplers, $R_{an} \geq 95$ % with $K_v \leq 10$ % at each loading.

The values given for analytical recovery are targets; lower values may be used provided equivalent precision is achieved.

6.3.2.3 Blank value

In order to obtain acceptable values for the limit of quantification of the method, the blank value of the sampling media should be as low as technically possible.

When tested in accordance with 8.3.2.3 the blank value shall be less than one-tenth of the calculated mass collected by the sampler during the recommended sampling time at the recommended air flow rate and at concentrations of

- 0,1 LV for substances with long-term limit value, and
- 0,5 LV for substances with short-term limit value only.

NOTE Higher blank values can be allowed provided the requirement of 6.3.2.1 is met.

Where it is known that the blank value is significant and varies between batches of samplers, it shall be checked regularly.

In order to eliminate any contamination which could occur during storage before use, Type B samplers should be cleaned by taking them through the thermal desorption procedure. This cleaning process should be carried out as close as possible to the time when the samplers will be used.

6.3.3 Expanded uncertainty

When tested in accordance with 8.3 the expanded uncertainty, calculated in accordance with 8.4, shall meet the requirements given in ISO 20581.

The expanded uncertainty requirement shall be met from 10 °C to 40 °C and at relative humidities from 20 % to 80 %.

6.3.4 Method description

6.3.4.1 Scope of the measuring procedure

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

a) principle of the method;

b) chemical agents covered by the measuring procedure;

c) analytical technique used;

d) working ranges;

e) chemical agents for which the measuring procedure is known to be adequate but not completely validated according to this document, especially in case of compounds of the same chemical family or homologous series;

f) chemical agents for which the measuring procedure is known to be inadequate;

g) any known interferences.

6.3.4.2 Method performance

The measuring procedure shall give information about method performance, including the following:

a) the chemical agents for which measuring procedure has been shown to be effective;

b) the range of concentrations of chemical agents in air, sample volume and range of environmental conditions over which the measuring procedure has been shown to meet the performance criteria for expanded uncertainty prescribed in ISO 20581;

c) the limit of quantification of the measuring procedure for chemical agents of interest;

d) full details of any known interferences, including suitable and sufficient information on how to minimise their effects.

6.3.4.3 Apparatus and reagents

The measuring procedure shall

a) specify that the sampler used conforms to the provisions of this document;

b) contain a requirement that the sampling pumps used conform to the provisions given in ISO 13137 and specify any characteristics of the sampling pumps additionally required;

c) define the required characteristics of the apparatus and test equipment to be used;

d) specify the quality of the reagents to be used.

6.3.4.4 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.

7 General test conditions

7.1 Reagents

Wherever possible, only reagents of analytical grade may be used.

7.2 Apparatus

7.2.1 Test equipment as stated in 7.2.2 to 7.2.7 shall be used.

7.2.2 Usual laboratory apparatus and resources.

7.2.3 A dynamic system for generating, pre-mixing and delivering a known concentration of a test gas or vapour in air (see ISO 6145-1[1]), ISO 6145-4 and ISO 6145-6), including at least:

- an exposure chamber constructed of inert material such as glass or polytetrafluorethylene (PTFE), through which the generated test atmosphere is passed, of sufficient capacity to accommodate simultaneously at least six test samplers and six samplers of one independent method (see 7.3.3) positioned in such a manner that there is no interference between each sampler;
- provisions for measuring, controlling and varying the air flow rate through the chamber and the concentration, temperature and relative humidity of the calibration gas mixture.

NOTE 1 It is also possible to use a smaller exposure chamber and to carry out repeat experiments to obtain at least six pairs of data.

NOTE 2 Where test gas or vapour atmospheres cannot be generated because of stability or safety consideration, alternative procedures for spiking samples can be considered.

7.2.4 Appropriate sampling pumps which meet the performance requirements of ISO 13137.

7.2.5 Flowmeter(s), calibrated, suitable over range(s) which include 10 ml · min^{-1} to 2 000 ml · min^{-1}, with a measurement uncertainty less than ±2 %.

7.2.6 Micropipettes or syringes, for applying known volumes of standard solutions, in conformance with the requirements of ISO 8655-2 and with a calibration checked in accordance with ISO 8655-6.

7.2.7 Instruments for analysing the gas, vapour or a characteristic reaction product collected by either the test sampler or an independent sampling procedure.

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[1] Under preparation. Stage at thetime of publication: ISO/DIS 6145-1.

7.3 Calibration gas mixture

7.3.1 Generation

Set up a calibration gas mixture at the concentration and values of temperature, relative humidity, etc. specified in the appropriate test methods in Clause 8.

Ensure that the flow rate into the exposure chamber exceeds the combined sampling rate of all samplers by at least 25 %.

7.3.2 Determination of mass concentration

Calculate the mass concentration of the calibration gas mixture, β_{cg}, given in milligrams per cubic metre ($mg \cdot m^{-3}$), from the test atmosphere generation parameters.

For example, for a permeation cell system, the delivered mass concentration is calculated by Formula (3) as follows:

$$\beta_{cg} = \frac{\dot{m}_1}{\dot{v}} \tag{3}$$

where

$\dot{m}_1$ is the mass loss from permeation tube, in micrograms per minute ($\mu g \cdot min^{-1}$), and

$\dot{v}$ is the flow rate into the exposure chamber, for example, in litres per minute ($l \cdot min^{-1}$).

NOTE 1 The example does not give a preference for permeation systems for generating calibration gas mixtures.

Determine the mean mass concentration of the test atmosphere within the exposure chamber experimentally using the results of the independent method described in 7.3.3. A correction may be applied for any known bias in the independent method.

Compare the determined mean mass concentration with the calculated value. If the experimentally determined value is within ±10 % of the calculated value of the mass concentration of the delivered test atmosphere, take the calculated value as the true value of the delivered mass concentration. If this requirement is not met, then adjustments shall be made or an alternative generation procedure shall be used or the independent method shall be verified.

If it is not possible to calculate a mass concentration of the calibration gas mixture, for example, for reactive gases, the value determined by the independent method shall be used as the true value.

NOTE 2 There can be situations, where it is preferable to use the experimentally determined mass concentration rather than the calculated mass concentration.

7.3.3 Independent method

The mass concentration of the generated calibration gas mixture in the exposure chamber shall be verified as follows:

a) by an independent method, which has been validated using an established protocol, for example, a diffusive sampler method, bubbler method or a different sorbent tube method; or

b) by using an independently calibrated on-line instrument, for example, a flame ionization detector or an infrared spectrometer.

NOTE For performance requirements for diffusive samplers see EN 838.

8 Test methods

8.1 General

If it is known in advance that a certain type of sampler is unaffected by an environmental influence, then the relevant tests in 8.3.3.2 to 8.3.3.4 may be modified to examine only the factors likely to have an influence.

There are two levels of evaluation specified as follows:

a) level 1: A measuring procedure evaluated for the analyte of interest in accordance with the normative part of this document;

b) level 2: A measuring procedure deemed to be in conformance with the normative part of this document on the basis that the analyte of interest is an analogue within a homologous series, both upper and lower members of which have been tested and shown to conform with level 1.

NOTE Some special groups of substances (for example, toluene, xylenes) usually isomers, can be treated as homologous when it is known that their chemical and physical properties are very similar.

If it is known in advance, or through testing, that a certain sampler-analyte combination is affected by an environmental influence then the relevant tests in 8.3.3.2 to 8.3.3.4 may be modified to investigate performance over a more restricted range of conditions.

8.2 Sampler test methods

8.2.1 Flow resistance

Assemble a sampling train consisting of a sampling pump (see 7.2.3), a representative sampler, a differential pressure gauge, which is inserted via a T-piece between the sampling pump and the sampler, and a flow meter in front of the sampler. All connections shall be leak tight, having connecting tubing as short as possible and a minimum internal diameter of 6 mm.

Measure the back pressure relative to ambient pressure with the differential pressure gauge, carry out the flow resistance test at the maximum recommended flow rate and compare with the required value in Table 1 (see 6.2.1).

8.2.2 Sampler leak test (for Type B samplers)

Expose a set of six sealed samplers to a test atmosphere under the following exposure conditions:

- concentration: 2 LV;
- time: 4 h;
- relative humidity: (50 ± 5) %;
- temperature: (20 ± 2) °C;

Analyse the set to determine any leakage.

8.2.3 Shelf life (for Type A impregnated supports)

Store the sampler at the limits of the environmental conditions specified by the manufacturer and/or in the measuring procedure. At the end of the specified shelf-life, test the sampler under the following exposure conditions:

- concentration: 2 LV;
- time: recommended sampling time;

- flow rate: recommended flow rate;
- relative humidity: (80 ± 5) %;
- temperature: (40 ± 2) °C.

8.2.4 Sample identification

Perform a visual check.

8.2.5 Marking

Perform a visual check.

8.2.6 Instructions for use

Perform a visual check.

8.3 Measuring procedure test methods

8.3.1 Determination of the recommended sampling conditions

8.3.1.1 Selection of sampler capacity test

Perform the sampler capacity verification test in 8.3.1.2 or the sampler breakthrough test in 8.3.1.3 taking into consideration whether the capacity of the sampler is likely to be high for the substance to be measured. This will depend upon the characteristics of the substance and the sampler, for example, nature and amount of the sampling substrate, and the limit value for the substance concerned.

8.3.1.2 Sampler capacity verification test

Sample from a test atmosphere (generated by using the apparatus described in 7.2.3) with a minimum of three samplers under the following exposure conditions:

- concentration: 2 LV;
- time:
  - For long-term LV: reference period plus a minimum of 1 h or the sampling period, if longer,
  - For short-term LV: twice the reference period.
- flow rate: recommended maximum flow rate;
- relative humidity: (80 ± 5) %;
- temperature: (20 ± 2) °C.

For samplers without a back-up section use two samplers in series.

Analyse the samplers after the test. The amount of the test substance recovered in the back-up section of sampler shall be less or equal than 5 % of the total amount recovered. If the amount recovered in the back-up section of sampler is greater than 5 %, carry out the sampler breakthrough test specified in 8.3.1.3.

NOTE If the amount recovered in the back-up section of sampler (or second sampler in series) is greater than 5 %, the test can be repeated at sequentially lower flow-rates or reduced sampling period until the test is passed. The maximum flow-rate consistent with passing this test will be the recommended flow-rate in subsequent tests.

8.3.1.3 Sampler breakthrough test

8.3.1.3.1 Direct method

Measure the breakthrough volume by sampling from a test atmosphere (generated by using the apparatus described in 7.2.3) using a minimum of three samplers under the following exposure conditions:

- concentration: 2 LV;
- flow rate: according to the sampler type;

  EXAMPLE 50 ml · min^{-1} for Type B samplers, 200 ml· min^{-1} for Type A sorbent tubes and 1 000 ml· min^{-1} for impregnated filters are examples for appropriate flow rates.

- relative humidity: (80 ± 5) %;
- temperature: (20 ± 2) °C.

Do this whilst monitoring the concentration of the test substance behind the sampler with an instrument such as gas chromatograph equipped with a flame ionisation or equivalent detector or an infrared spectrophotometer. A suitable way of doing this is described in A.1.

For substances with both long-term and short-term limit values, the breakthrough volume should be measured at a concentration of two times the short-term limit value especially if the ratio between the two limit values is greater or equal than 1,5.

For two-bed Type A sorbent tubes, use only the first (primary) bed or use specially prepared single-section tubes.

When it is not possible to monitor the concentration of the test substance behind the sampler using a direct-reading instrument, breakthrough can be monitored using a back-up sampler that is changed and analysed at regular intervals.

8.3.1.3.2 Chromatographic method

For porous polymers and similar chromatographic sorbents, instead of applying the procedure described in 8.3.1.3.1, the breakthrough volume can be predicted from the chromatographic retention volume. An example is given in Annex A.

NOTE 1 Breakthrough volume determined by the chromatographic method does not take into account relative humidity. Measurements by the direct method indicate that breakthrough volume at high (95 %) relative humidity is about a factor of two lower for porous polymers.

NOTE 2 The chromatographic method is not suitable for reagent impregnated sorbents or activated carbon.

NOTE 3 The chromatographic method is not suitable for very high mass concentrations (more than 500 mg · m^{-3}).

8.3.1.4 Determination of the maximum air flow rate (only for impregnated filters)

Repeat the test described in 8.3.1.3.1 for breakthrough volume at increasing flow rates up to a maximum of 50 % above the recommended flow rate using a minimum of three samplers at each flow rate setting. The breakthrough volume determined should be constant, independent of flow rate. As the experiment to determine the breakthrough volume is repeated at increasing flow rates a point could be reached where the breakthrough volume begins to decrease. If the breakthrough volume drops by more than 5 % from its initial value the maximum air flow rate for the sampler shall be 90 % of the flow rate at which this occurs.

8.3.1.5 Determination of the minimum air flow rate (only for thermal desorption)

If a sampler is to be used at a flow rate below 10 ml · min^{-1} and an inlet restrictor is not used, perform the following test to establish the flow rate above which the effect of diffusion can be disregarded. If the sampler is to be used to measure a number of different substances, carry out the test using the substance with the highest diffusion coefficient.

Prepare six blank samplers and simultaneously sample a test atmosphere (set at about twice the limit value of the test substance). Use three of the samplers set at a low/moderate pump flow rate and three at zero flow rate, but with a pump still attached. Determine the mean mass of analyte retained on the three samplers set at zero flow. Subtract this from the mean mass of analyte on the samplers through which air was drawn to determine a corrected mass of analyte retained by these samplers. Use this mass to confirm the concentration of the test atmosphere. Having confirmed the concentration of the test atmosphere, use the mean mass of analyte retained by the three samplers set at zero flow to determine the diffusive uptake rate by these tubes in ml· min^{-1}. Multiply this value by 20 to determine the minimum air flow rate to be used with this sampler type.

NOTE The level of the low/moderate flow rate to be used depends on the dimensions of the sampler. For example, for standard 4 mm to 5 mm bore, 6,4 mm outside diameter sorbent tubes with the sorbent bed set in the range from 12 mm to 18 mm from the sampling end of the tube, a flow rate of approximately 20 ml · min^{-1} is appropriate. For closer sorbent tubes or sorbent tubes with the sorbent bed positioned further away from the sampling end of the tube, a flow rate of less than 20 ml · min^{-1} is appropriate. For wider bore sorbent tubes or sorbent tubes with the sorbent bed positioned narrower to the sampling end of the tube, a flow rate of more than 20 ml · min^{-1} is appropriate.

8.3.1.6 Storage after sampling

8.3.1.6.1 Direct method

Use two sets of at least six samplers and withdraw a known volume from a test atmosphere under the following exposure conditions:

- concentration: 0,1 LV and 2 LV;
- time: recommended sampling time;
- flow rate: recommended flow rate;
- relative humidity: (80 ± 5) %;
- temperature: (20 ± 2) °C.

The storage conditions shall be specified in detail (e.g. storage time, temperature).

Analyse one set within one day and the other set after two weeks storage at room temperature, or as otherwise directed.

Calculate the mean for each of the two sets of test results and the difference between the means, in percent. Compare with the requirement in 6.3.1.4. If the requirement in 6.3.1.4 is not met repeat the test with a shorter storage time or by using different storage conditions.

NOTE An alternative approach can be to carry out a more comprehensive set of experiments determining the method recovery after a range of different storage times, for example, one day, three days, seven days, ten days and two weeks.

8.3.1.6.2 Sampling media spiking method

As an alternative to the procedure given in 8.3.1.6.1 sampling media may be spiked with an equivalent loading using a procedure based on one of those given in 8.3.2.2.

After spiking the substrate investigate humidity effects by drawing humid air through the spiked samplers according to 8.3.1.6.1.

8.3.2 Analytical procedure test methods

8.3.2.1 Analytical limit of quantification

For Type A samplers, spike ten unused samplers with appropriate masses of the analyte of interest, such that the test solutions produced from them will have mass concentrations near their respective anticipated limit of detection and analyse under repeatability conditions.

For Type B samplers, spike ten unused samplers with appropriate masses of the analyte of interest near its respective anticipated limit of detection and analyse under repeatability conditions.

Estimate the limit of quantification for each of the analytes of interest as ten times the standard deviation of the mean result. Compare with the requirement in 6.3.2.1.

8.3.2.2 Determination of the analytical recovery

8.3.2.2.1 General

Conduct the determination at the lower and upper ends of the measuring range and for least one intermediate concentration according to ISO 20581 as calculated from the following sampling conditions.

- Concentration:
  - For long-term LV: 0,1 LV to 2 LV
  - For short-term LV: 0,5 LV to 2 LV
- Time:
  - For long-term LV: recommended sampling time
  - For short-term LV: reference period
- Flow rate: recommended flow rate

The methods given in 8.3.2.2.2 and 8.3.2.2.3 can be used to determine the analytical recovery. For Type B samplers the method given in 8.3.2.2.4 can be used as well.

8.3.2.2.2 Sampling media spiking method from the vapour phase

Add a known mass of analyte corresponding to the different loadings given in 8.3.2.2.1 into a small vessel (for example, empty sampling tube, pipette reservoir), using a micropipette or syringe (see 7.2.6). The analyte can be pure or diluted in a solvent (usually the desorption solvent). Air is sampled from the vessel by pumping onto the sampling medium (recommended flow rate and sampling time shall be used, according to the type of sampling medium, type of sampler and analyte of interest). Check that all the analyte has evaporated after sampling by rinsing the vessel with desorption solvent and analyze the rinsate.

Desorb and analyze all the samples. Repeat the experiment six times for each sample loading. Calculate the analytical recovery by dividing the mean mass recovered at each loading from the vapour spiked samples by the mass applied and the coefficient of variation of the replicate samples.

NOTE 1 For chemical agents with low vapour pressure moderate heating could be necessary. On the other hand, for highly volatile chemical agents cooling as well as flow reduction could be necessary.

NOTE 2 Heating blocks with tubes allowing pumping or purging with a gas are commercially available.

8.3.2.2.3 Sampling media spiking method from the liquid phase

Add a known mass of analyte diluted in a non-interfering solvent, if necessary, to at least six sampling media for each loading, using a micropipette or syringe (see 7.2.6). When substances are added to a sorbent tube, air shall be drawn through during or after the addition to ensure that the analyte is properly sorbed. Analyze the samples and calculate the analytical recovery by dividing the mean mass recovered at each loading by the mass applied, and the coefficient of variation of the replicate samples. Compare with the requirement given in 6.3.2.2.

8.3.2.2.4 Sampling media spiking method (for Type B samplers)

Add a known mass of analyte to at least six sampling media at each loading, corresponding to the loadings in 8.3.2.2.1 and using the method described in 8.3.2.2.2 or 8.3.2.2.3.

Type B samplers are part of the injection system of commercial thermal desorption instruments. A direct method is to compare analytical recovery with the spiked sampler in-line versus the response from the introduction of analyte directly onto the gas chromatograph column. Absolute analytical recovery for Type B samplers cannot normally be determined in this way unless the manufacturer of the thermal desorber has provided a direct injection facility that does not perturb any gas flow set with the sampler in-line. If a direct injection facility is not available the following method may be used:

Load the analyte on sampling media, together with an internal standard known to have an analytical recovery of 100 % under the applied desorption conditions. n-pentane or n-hexane are suitable. Analyse these samples by thermal desorption as well as by direct liquid injection using a separate device. Compare the relative detector response obtained from thermal desorption with the relative response obtained by a direct liquid injection of the analyte with the internal standard.

NOTE Thermal desorption of an analyte from a Type B sampler is a non-equilibrium process. Analytical recovery is close to 100 % unless the desorption time is too short under the applied conditions of temperature and carrier gas velocity, or the desorption temperature is too low, or the analyte undergoes partial decomposition due to a chemical reaction with, for example, the sorbent or its catalytic or oxidising impurities, or due to a reaction with any other material in the flow path.

Calculate the analytical recovery by dividing the mean mass recovered at each loading by the mass applied and calculate the coefficient of variation of the replicate samples. Compare with the requirement in 6.3.2.2.

8.3.2.3 Determination of the blank value

Analyze six unused samplers. Calculate the mean and the standard deviation. Compare with the requirements given in 6.3.2.3.

8.3.3 Method recovery and method precision

8.3.3.1 General

The method recovery and method precision tests given in 8.3.3.2 to 8.3.3.4 require calculation of mass concentration of the analyte, β_a, from the mass of analyte recovered from the samplers and the volume of test atmosphere sampled. This calculation is made according to Formula (4):

$$\beta_a = \frac{m_{a2} - m_{a1}}{R_{an} \times V_{at}} \tag{4}$$

where

m_{a1} is the mass of analyte desorbed from tube blank, in micrograms (μg);

m_{a2} is the mass of analyte desorbed from spiked tube, in micrograms (μg);

R_{an} is the analytical recovery;

V_{at} is the volume of the test atmosphere sampled, in litres (l).

NOTE The mass concentration adjusted to specified conditions, $\beta_{a,corr}$, for example, 20 °C (= 293 K) and 101,3 kPa, can be calculated according to Formula (5):

$$\beta_{a,corr} = \beta_a \times \frac{101{,}3}{p_{at}} \times \frac{T_{at}}{293} \tag{5}$$

where

T_{at} is the temperature of the test atmosphere sampled, in Kelvins (K);

p_{at} is the pressure of the test atmosphere sampled, in kilopascals (kPa).

The concentration of the analyte, given as a volume fraction ϕ_a can be calculated according to Formula (6):

$$\phi_a = \beta_{a,corr} \times \frac{24{,}1}{M_a} \tag{6}$$

where

24,1 is the molar volume at 293 K and 101,3 kPa, in litres per mole ($l \cdot mol^{-1}$);

M_a is the molar mass of the analyte, in grams per mole ($g \cdot mol^{-1}$).

8.3.3.2 Effect of the exposure concentration

Using at least six samplers for each concentration, withdraw a known volume from a test atmosphere under the following conditions.

- concentration: 0,1 LV, 0,5 LV and 2 LV;
- time: recommended sampling time;
- flow rate: recommended flow rate;
- relative humidity: (50 ± 5) %;
- temperature: (20 ± 2) °C.

Analyze the samples and, for each exposure combination, calculate the concentration (see 8.3.3.1) for each of the replicate samples. Divide each by the reference concentration of the test atmosphere (see 7.3.2). Calculate the mean method recovery and the coefficient of variation of the replicate samples for each sample loading; and also calculate the overall method recovery and coefficient of variation of the means.

8.3.3.3 Effect of the relative humidity of the test atmosphere

Using at least six samplers for each combination of concentration and humidity, withdraw a known volume from a test atmosphere under the following conditions:

- concentration: 0,1 LV and 2 LV;
- time: recommended sampling time;

— flow rate: recommended flow rate;

— relative humidity: (20 ± 5) % and (80 ± 5) %;

— temperature: (20 ± 2) °C.

NOTE The high and low values of the relative humidity are given for guidance only. If it is known that the samplers are to be used in wider, or more restricted, ranges, the values may be adjusted accordingly.

Analyze the samples and, for each exposure combination, calculate the concentration (see 8.3.3.1) for each of the replicate samples. For each exposure combination, calculate the mean result and divide it by the reference concentration of the test atmosphere (see 7.3.2) to estimate the effect of the relative humidity on method recovery. See C.5.5 for information on how to consider the effect of humidity on the estimation of the expanded uncertainty of the measuring procedure.

8.3.3.4 Effect of the temperature of the test atmosphere

Using at least six samplers for each temperature, withdraw a known volume from a test atmosphere under the following conditions:

— concentration: 2 LV;

— time: recommended sampling time;

— flow rate: recommended flow rate;

— relative humidity: (50 ± 5) %;

— temperature: (10 ± 2) °C and (40 ± 2) °C.

NOTE The high and low values of the temperature are given for guidance only. If it is known that the samplers are to be used in wider, or more restricted, ranges, the values may be adjusted accordingly.

Analyze the samples and, for each exposure combination, calculate the concentration (see 8.3.3.1) for each of the replicate samples. Divide each by the reference concentration of the test atmosphere (see 7.3.2). Calculate the mean results for each temperature and the mean difference to estimate the effect of the temperature on method recovery. See C.5.6 for information on how to consider the effect of temperature on the estimation of the expanded uncertainty of the measuring procedure.

8.4 Uncertainty of measurement

8.4.1 Identification of random and non-random uncertainty components

Identify all random and non-random uncertainty components of the measuring procedure, for example, by constructing a cause and effect diagram (see ISO/IEC Guide 98-3 and references [2], [3] and [4]).

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

8.4.2 Estimation of individual uncertainty components

8.4.2.1 General

For each of the significant uncertainty components identified in 8.4.1, estimate individual uncertainties or calculate them from experimental data as prescribed in 8.4.2.2 to 8.4.2.5, following the guidance in Annex C.

8.4.2.2 Uncertainty associated with sampled air volume

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

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

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

8.4.2.3 Uncertainty associated with sample storage and transportation

Estimate the non-random uncertainty components associated with sample storage and transportation, using the results of the test given in 8.3.1.6, referring to the guidance in C.4.

8.4.2.4 Uncertainty associated with method recovery

Estimate method bias and the non-random uncertainty components associated with method recovery, using the results of the test given in 8.3.3, referring to the guidance in C.5.

8.4.2.5 Uncertainty associated with method variability

Estimate the random uncertainty components associated with method variability, using the results of the test given in 8.3.3.2, referring to the guidance in C.6.

8.4.2.6 Calculation of the combined standard uncertainty

Calculate the combined standard uncertainty, expressed as a percentage, according to Formulae (7) to (9):

$$u_{\mathrm{c,r}} = \sqrt{u_{\mathrm{s,r}}^{2} + u_{\mathrm{a,r}}^{2}} \tag{7}$$

$$u_{\mathrm{c,nr}} = \sqrt{u_{\mathrm{s,nr}}^{2} + u_{\mathrm{a,nr}}^{2}} \tag{8}$$

$$u_{\mathrm{c}} = \sqrt{u_{\mathrm{c,r}}^{2} + u_{\mathrm{c,nr}}^{2}} \tag{9}$$

where

$u_{\mathrm{s,r}}$	is the random sampling uncertainty;
$u_{\mathrm{s,nr}}$	is the non-random sampling uncertainty;
$u_{\mathrm{a,r}}$	is the random analytical uncertainty;
$u_{\mathrm{a,nr}}$	is the non-random analytical uncertainty;
$u_{\mathrm{c,r}}$	is the combined random standard uncertainty (associated with sampling and analysis);
$u_{\mathrm{c,nr}}$	is the combined non-random standard uncertainty (associated with sampling and analysis); and
u_{c}	is the combined standard uncertainty.

8.4.3 Calculation of expanded uncertainty

Calculate the expanded uncertainty of the measuring procedure, U, using a coverage factor k = 2 according to Formula (10).

$$U = 2 \times u_c \tag{10}$$

NOTE An example for estimation of expanded uncertainty is given in Annex D.

9 Test report

The test report shall include at least the following:

a) a reference to this document (i.e. "ISO 22065");

b) complete identification of the test atmosphere and its verification;

c) the type of pumped sampler used;

d) details of the pump used for testing;

e) all validation data obtained in the tests under 8.2 and/or 8.3 as applicable and the determined values of the performance characteristics;

f) the statistical analysis of the test results;

g) the calculated values of the uncertainty components and the expanded uncertainty;

h) whether the acceptance criteria are met;

i) the level of evaluation;

j) any unusual features noted during the determinations;

k) any operation not included in this document that could have influenced the results;

l) any omission(s) or deviation(s) from the test conditions, and the technical justification for them.

Annex A

(informative)

Examples for the determination of the breakthrough volume

A.1 Direct method

A.1.1 Apparatus

A.1.1.1 Flow meter.

A.1.1.2 Direct reading instrument (for example, flame ionization detector).

A.1.1.3 Samplers under test.

A.1.2 Determination

Assemble a gas train consisting of a dynamic calibration gas mixture generator (see 7.2.2) delivering a concentration equivalent to two times LV at (20 ± 2) °C and (80 ± 5) % relative humidity for the analyte of interest, a sampling section of the pumped sampler, a flow-meter in the suitable range and a direct reading instrument (for example, flame ionization detector).

Pass the test gas through the sampling train at a known constant rate. Use a value appropriate for the sampling rate intended in the practical use of the sampler according to the manufacturer's instructions. Note the time that the flow was initiated.

When the analyte begins to emerge, the detector will show a response. Continue the measurement until a 5 % of the inlet concentration is reached. Determine the time at which 5 % has been reached and calculate the breakthrough volume.

A.2 Chromatographic method

A.2.1 General

A.2.2 Apparatus

A.2.2.1 Ordinary laboratory apparatus.

A.2.2.2 Gas chromatograph.

A.2.2.3 Thermocouple.

A.2.3 Procedure

Connect a sorbent tube to the injection and detection ports of a gas chromatograph in place of the normal chromatography column by means of narrow bore polytetrafluorethylene (PTFE) tubing.

Determine the corrected retention volume of a 1 ml aliquot of calibration gas mixture at least five settings of the chromatograph oven temperature such that the retention time is convenient (between 2 min and 20 min). Repeat the determination five times at each temperature.

A.2.4 Corrected retention volume

Inject a sample of an un-retained substance, such as methane, and calculate the gas (vapour) hold-up volume V_H (dead volume) according to Formula (A.1):

$$V_H = v_a \times t_H \tag{A.1}$$

where

v_a is the volumetric air flow rate through the sampler, for example, in litres per minute ($l \cdot min^{-1}$);

t_H is the hold-up time of the un-retained substance, in minutes (min).

Then determine the corrected retention volume $(V_R)'$, in litres (l), according to Formula (A.2):

$$(V_R)' = V_R - V_H \tag{A.2}$$

where

V_R is the uncorrected retention volume, in litres (l);

V_H is the gas (vapour) hold-up volume (dead volume), in litres (l).

A.2.5 Calculations

Plot the mean values of the logarithm of corrected retention volume at each temperature against reciprocal absolute Kelvin temperature and extrapolate to 20 °C ($3{,}413 \times 10^{-3} K^{-1}$). The breakthrough volume is assumed to be half of the corrected retention volume.

Annex B
(informative)

Experiments for method validation

Table B.1 and Table B.2 summarize the experiments for method validation of both sampling and analytical methods for gases and vapours in workplace air in order to fulfil the requirements specified in this document.

Table B.1 — Sampler requirements

Test	ρ_{LV}	t_s h	v_a	RH %	ϑ_{at} °C	n	Requirement	Clause ref.
Flow resistance	not applicable		recom-mended maximum flow rate	not applicable		20	Type A ≤ 10 kPa Type B ≤ 3,5 kPa	6.2.1 and 8.2.1
Sampler leak test (Type B samplers)	2 LV	4	not applicable	(50 ± 5)	(20 ± 2)	≥6	long-term: $m_{a,lt} < \frac{1}{3}\left(\begin{array}{l} 0{,}1\rho_{LV,lt}\times 240\times \\ 0{,}01\times 10^{-3} \end{array}\right)$ short-term: $m_{a,st} < \frac{1}{3}\left(\begin{array}{l} 0{,}5\rho_{LV,st}\times 15\times \\ 0{,}01\times 10^{-3} \end{array}\right)$	6.2.2 and 8.2.2
Shelf life (Type A samplers)	2 LV	recom-mended sampling time	recom-mended flow rate	(80 ± 5)	(40 ± 2)	n.s.	Indicated by manufacturer	6.2.3 and 8.2.3
Sample identi-fi-cation and marking **(visual check)**	not applicable						Uniquely identifiable samples, marked with: Manufactures name, product ID, flow direction (if applicable), batch ID, shelf life, number of documents	6.2.4 and 6.2.5
Instruc-tion for use (visual check)	not applicable						In language of countries where used.	6.2.6

NOTE For the symbols used see Clause 4.

Table B.2 — Measuring procedure requirements

Test	ρ_{LV}	t_s h	v_a	**RH** %	ϑ_{at} °C	n	**Requirement**	**Clause ref.**
Sampler capacity	2 LV	long-term: reference period + ≥1 h short-term: 2 × reference period	recommended flow rate	(80 ± 5)	(20 ± 2)	≥3	With two subsequent samplers amount of analyte on back-up sampler ≤ 5 % of total recovered amount.	8.3.1.2
Break-through volume	2 LV	not specified	according to sampler type	(80 ± 5)	(20 ± 2)	≥3	Measurement until analyte is detected behind the sampler.	8.3.1.3
Storage conditions	0,1 LV and 2 LV	recommended sampling time	recommended flow rate	(80 ± 5)	(20 ± 2)	≥6	Recovery difference before and after storage less than 10 %.	6.3.1.4 and 8.3.1.6
Analytical quantification limit	[a]	not applicable				10	≤ 0,1 LV for long-term LV ≤ 0,5 LV for short-term LV	6.3.2.1 and 8.3.2.1
Analytical recovery (long-term)[b]	0,1 LV up to 2 LV	recommended sampling time	recommended flow rate	not specified		[c]	Type A samplers: R_{an} ≥ 75 % with K_v ≤ 10 %	6.3.2.2 and 8.3.2.2
Analytical recovery (short-term)[b]	0,5 LV up to 2 LV	reference period					Type B samplers: R_{an} ≥ 95 % with K_v ≤ 10 %	
Blank value	unused samplers	not applicable				≥6	see 6.3.2.3	6.3.2.3 and 8.3.2.3
Effect of exposure concentration	0,1 LV; 0,5 LV and 2 LV	recommended sampling time	recommended flow rate	(50 ± 5)	(20 ± 2)	≥6	no specific requirement	8.3.3.2
Effect of relative humidity	0,1 LV and 2 LV			(20 ± 5) and (80 ± 5)	(20 ± 2)	≥6	no specific requirement	8.3.3.3
Effect of temperature	2 LV			(50 ± 5)	(10 ± 2) and (40 ± 2)	≥6	no specific requirement	8.3.3.4

[a] Spiked samples near estimated LOQ.

[b] Wherever possible the effect of exposure concentration should be calculated from the results of replicate samples taken from a test gas atmosphere (see 8.3.3.2) and the method bias calculated according to C.5.3. The method bias includes the analytical recovery. In this case experiments for the analytical recovery can be omitted.

[c] at least three concentration of measuring range (upper, lower end and intermediate).

NOTE For the symbols used see Clause 4.

Annex C
(informative)

Estimation of uncertainty of measurement

C.1 General

Methods for measurement of chemical agents in workplace atmospheres usually 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 C.2);

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

   3) uncertainty associated with sample storage and transportation (see C.4);

b) analysis:

   1) uncertainty associated with method recovery (see C.5);

   2) uncertainty associated with method variability (see C.6);

   3) uncertainty associated with the calibration (see C.6.3 and C.6.4); and

   4) uncertainty associated with instrument response drift (see C.6.6).

C.2 Uncertainty associated with sampled air volume

C.2.1 Sources of uncertainty

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

- flow rate measurement (see C.2.2),
- pump flow stability (see C.2.3), and
- sampling time (see C.2.4).

C.2.2 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, the 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.

EXAMPLE For example, if the expanded uncertainty given on the flow meter test certificate, u_{ce} = ±0,8 %, whereas k = 2, the contribution to the uncertainty of the flow rate measurements is u_{fc} = 0,4 %.

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. 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.

Examples of typical values for the uncertainty of the flow rate calibration and reading for different types of flow meters are given in ISO 20581. 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 ISO 20581 should be used, as this constitutes a worst-case scenario if the use of an inappropriate rotameter is disregarded.

C.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. ISO 13137 requires 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 the manufacturer or from the results of the test in ISO 13137:2013, 7.10. Assuming a rectangular probability distribution, the value of the non-random uncertainty component of the pump flow stability can be calculated according to Formula (C.1):

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

where

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

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

C.2.4 Sampling time

Sampling time can be measured precisely 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 (for example >2 h) and can be disregarded, but for short-term measurements it requires to be taken into account.

For example, if time is recorded to the nearest minute, the coefficient of variation is $\left(6{,}67\%/\sqrt{6}\right) = 2{,}7\ \%$ 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 $0{,}5\%/\sqrt{3} = 0{,}29\ \%$.

C.3 Uncertainty associated with sampling efficiency

The sampling of gases and vapours can be influenced by the pressure, relative 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 in the uncertainty component of the method recovery.

For pumped samplers, the sample volume is kept well below the experimentally established breakthrough volume, 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. For the determination of the breakthrough volume, see 8.3.1.3.

C.4 Uncertainty associated with sample storage and transportation

The non-random uncertainty component associated with sample storage and transportation can be estimated by the analysis of replicate samples collected from a test atmosphere or prepared by spiking sampling collection media with the chemical agent of interest (see 8.3.1.6).

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

$$u_{\mathrm{st}} = \frac{\Delta_{\mathrm{st}}}{\sqrt{3}} \tag{C.2}$$

where

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

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

C.5 Uncertainty associated with method recovery

C.5.1 General

Method recovery is influenced by several factors (see C.3). The study of their influence is carried out following the tests described in 8.3.3.2 to 8.3.3.4 by the use of test atmospheres.

The experimental data collected when carrying out 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 method of measurement, for example, concentration, temperature and relative humidity. These data can be used to estimate the method uncertainty components as described in C.5.2 to C.5.6.

Measuring procedures for chemical agents using pumped samplers usually prescribe the correction of the results for analytical recovery. In this case, method recovery is estimated from the results of the samples taken from the test atmospheres corrected for analytical recovery.

C.5.2 Analytical recovery

C.5.2.1 Analytical recovery can be calculated from the results of the analysis of replicate samples with known mass of the compound of interest (known samples), dividing the mass of analyte recovered by the known mass. The known samples can be certified reference material (CRMs) or sampling media spiked samples at several loadings covering the range of the application of the method.

NOTE The uncertainty associated with the analytical recovery is calculated when no test gas atmosphere for sampling tests is available and replicate samples are generated by spiking samplers according to 8.3.2.2.

The random and non-random uncertainty components associated with the analytical recovery can be estimated from the results of the test in 8.3.2.2.

C.5.2.2 When the results are corrected for analytical recovery and it is not level dependent, the random uncertainty component associated with this correction is given by Formula (C.3):

$$u_{\mathrm{ar}} = \sqrt{\frac{\left(K_{\mathrm{v,ra}}\right)^2}{n} + \left(u_{\mathrm{ks}}\right)^2} \tag{C.3}$$

where

u_{ar} is the relative standard uncertainty of the analytical recovery, in percent;

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

n is the number of replicate samples;

u_{ks} is the relative standard uncertainty of the known samples, in percent.

When CRMs are available u_{ks} should be estimated from the CRM certificate.

EXAMPLE The uncertainty of spiked samples with pure compound, assuming that the effect of temperature on the dispensed volume is negligible, can be estimated by Formula (C.4):

$$u_{\mathrm{ks}} = \sqrt{\left(u_{\mathrm{pu}}\right)^2 + \frac{\left(B_{\mathrm{max,sy}}\right)^2}{3} + \frac{\left(K_{\mathrm{v,sy}}\right)^2}{n}} \tag{C.4}$$

where

u_{ks}	is the relative standard uncertainty of the purity of analyte, in percent {for example, if the purity is ≥99 %, the relative uncertainty is [(100 – 99)/ √3] %};
$B_{\mathrm{max,sy}}$	is the maximum bias of the volume dispensed by the syringe used to spike the blank sampling media, in percent;
$K_{\mathrm{v,sy}}$	is the coefficient of variation of the volume dispensed by the syringe used to spike the blank sampling media, in percent; and
n	is the number of replicate samples.

If the amount of analyte spiked to the blank sampling media is weighed, the uncertainty of the nominal value is estimated as a combination of the uncertainty of the balance used and the coefficient of variation of the reading of the weight.

C.5.2.3 If analytical recovery correction is not applied to the results, the analytical bias should be estimated and treated as an uncertainty component. The non-random uncertainty component associated with incomplete recovery can be estimated as the difference of the mean analytical recovery of the replicate samples of all concentrations from 100 % and converted to a standard uncertainty. The relative standard uncertainty of the analytical bias is given by Equation (C.5), see [5].

$$u_{\mathrm{ab}} = \sqrt{\frac{\left(B_{\mathrm{a}}\right)^2}{3} + \frac{\left(K_{\mathrm{v,ra}}\right)^2}{n} + \left(u_{\mathrm{ks}}\right)^2} \tag{C.5}$$

where

$u_{a,b}$ is the relative standard uncertainty of the analytical bias, in percent;

B_a is the analytical bias calculated of the mean results of known samples (see 8.3.2.2);

$K_{v,ra}$ is the coefficient of variation of the replicate known samples, in percent;

n is the number of replicate samples; and

u_{ks} is the relative standard uncertainty of the known samples, in percent.

C.5.3 Method bias

Method bias can be estimated from the results of the replicate samples collected from a test atmosphere at the relative humidity of 50 % and temperature of 20 °C (see 8.3.3.2). When the method bias is significant, bias is estimated and treated as an uncertainty component.

The non-random uncertainty component can be estimated as the difference, in percent, of the mean results of the replicate samples from 100 %. The relative standard uncertainty associated with the method bias is given by Formula (C.6), see [5].

$$u_{mb} = \sqrt{\left(\frac{B_m}{\sqrt{3}}\right)^2 + \frac{\left(K_{v,rm}\right)^2}{n} + \left(u_{rc}\right)^2} \tag{C.6}$$

where

u_{mb} is the relative standard uncertainty associated with method bias, in percent;

B_m is the bias of the mean results from the reference concentration, in percent (see 8.3.3);

$K_{v,rm}$ is the coefficient of variation of the replicate samples collected from a test atmosphere, in percent;

n is the number of replicate samples; and

u_{rc} is the relative standard uncertainty of the reference concentration of the test atmosphere, in percent (see C.5.4).

NOTE If the measurement result is bias corrected, the term B_m becomes zero.

C.5.4 Reference concentration

In a properly designed and performed experiment, the random and non-random uncertainty components associated with the test atmosphere concentrations are expected to be small. They depend on the system used for generation and can be calculated by a propagation of errors from the uncertainty of the parameters of the test atmosphere generation.

The relative standard uncertainty u_{rc} associated with the reference concentration of the test atmosphere of a dynamic system is usually less than 3 %. u_{rc} values of ≤4 % for spiking from a gas sampling tube and ≤5 % for syringe spiking can be assumed.

C.5.5 Effect of humidity

The non-random uncertainty component associated with the effect of humidity can be estimated from the difference between the mean results of replicate samples collected from a test atmosphere at the relative humidity of 80 % and 20 % (see 8.3.3.3).

Assuming a rectangular probability distribution, the uncertainty associated with the effect of humidity is given by Formula (C.7):

$$u_\mathrm{h} = \frac{\Delta_\mathrm{h}}{\sqrt{3}} \tag{C.7}$$

where

u_h is the relative standard uncertainty associated with the effect of humidity on the method recovery; and

Δ_h is the higher of the differences between the mean results of replicate samples collected from test atmospheres at relative humidities of 80 % and 20 %, in percent.

C.5.6 Effect of temperature

Temperature affects mainly the adsorption capacity. The breakthrough volume decreases at increased temperature. In general, the influence of the temperature on the mass sampled is insignificant provided that the sampled volume is well below of the breakthrough volume in the range of temperatures of interest.

The non-random uncertainty component associated with the effect of temperature can be estimated from the difference between the mean results of replicate samples collected from a test atmosphere at temperatures of 40 °C and 10 °C (see 8.3.3.4).

Assuming a rectangular probability distribution, the uncertainty associated with the effect of temperature is given by Formula (C.8):

$$u_\mathrm{T} = \frac{\Delta_\mathrm{T}}{\sqrt{3}} \tag{C.8}$$

where

u_T is the relative standard uncertainty associated with the effect of temperature on the method recovery, and

Δ_T is the difference between the mean results of replicate samples collected from test atmospheres at temperatures of 40 °C and 10 °C, in percent.

C.6 Uncertainty associated with method variability

C.6.1 General

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 in 8.3.3.2 as described in C.6.2. Separate uncertainty estimates need to be made for any sources of systematic error, where applicable, for example non-random uncertainty associated with the concentration of calibration solutions (see C.6.3), calibration function (see C.6.4), dilution of the sample solutions (see C.6.5) and instrument response drift (see C.6.6).

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 either obtained under repeatability conditions (see C.6.7.1) or from data obtained under reproducibility conditions (see C.6.7.2). In both cases, separate uncertainty estimates need to be made for any sources of systematic error, where applicable, for example non-random uncertainty associated with the concentration of calibration solutions (see C.6.3), calibration function (see C.6.4), dilution of the sample solutions (see C.6.5) and instrument response drift (see C.6.6). When the analytical precision is determined from within laboratory reproducibility data, for example, using 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 are included.

C.6.2 Method precision

Method precision can be calculated from the results of the replicate samples collected from a test atmosphere at a relative humidity of 50 % and a temperature of 20 °C (see 8.3.3.2).

The random uncertainty component can be estimated by Formula (C.9), see also ISO/IEC Guide 98-3:

$$u_{\mathrm{mp}} = \sqrt{\left(K_{\mathrm{v,m}}\right)^2 + \left(1 - \frac{1}{n}\right)\left(K_{\mathrm{vp,r}}\right)^2} \qquad \text{(C.9)}$$

where

u_{mp} is the relative standard uncertainty associated with method precision, in percent;

$K_{\mathrm{v,m}}$ is the coefficient of variation of the means, in percent;

n is the number of replicate samples (see also Formula (C.10)); and

$K_{\mathrm{vp,r}}$ is the pooled coefficient of variation of the replicate samples, in percent, calculated according to Formula (C.11).

n can be estimated for an unequal number of replicate samples by Formula (C.10), see EN 13936:

$$n = \frac{N^2 - \sum_{j=1}^{J}\left(n_j\right)^2}{(J-1)N} \text{ with } N = \sum_{j=1}^{J} n_j \qquad \text{(C.10)}$$

where

N is the total number of replicate samples at all concentration levels;

J is the number of concentration levels;

n_j is the number of replicate samples at the concentration level j.

For both equal and unequal number of replicate samples $K_{\mathrm{vp,r}}$ can be estimated by Formula (C.11):

$$K_{\mathrm{vp,r}} = \sqrt{\frac{\left[(n_1-1)\times\left(K_{\mathrm{v,1}}\right)^2\right] + \left[(n_2-1)\times\left(K_{\mathrm{v,2}}\right)^2\right] + \left[(n_3-1)\times\left(K_{\mathrm{v,3}}\right)^2\right]}{(n_1-1)+(n_2-1)+(n_3-1)}} \qquad \text{(C.11)}$$

where

$K_{\mathrm{v,1}}$, $K_{\mathrm{v,2}}$, $K_{\mathrm{v,3}}$ are the coefficients of variation at the three tested concentrations;

n_1, n_2, n_3 are the number of replicate samples at each test concentration.

NOTE When the number of replicate samples at all concentration levels are equal then $n = n_j$ and

$$K_{\mathrm{vp,r}} = \sqrt{\frac{\left[\left(K_{\mathrm{v,1}}\right)^2 + \left(K_{\mathrm{v,2}}\right)^2 + \left(K_{\mathrm{v,3}}\right)^2\right]}{3}}\,.$$