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BRITISH STANDARD

BS EN 1076:2009

Workplace exposure — Procedures for measuring gases and vapours using pumped samplers — Requirements and test methods

ICS 13.040.30

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National foreword

This British Standard is the UK implementation of EN 1076:2009. It supersedes BS EN 1076:1997 which is withdrawn.

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

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

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Exposition am Arbeitsplatz - Messung von Gasen und Dämpfen mit pumpenbetriebenen Probenahmeeinrichtungen - Anforderungen und Prüfverfahren

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Foreword

This document (EN 1076:2009) has been prepared by Technical Committee CEN/TC 137 “Assessment of workplace exposure to chemical and biological agents”, the secretariat of which is held by DIN.

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of an identical text or by endorsement, at the latest by June 2010, and conflicting national standards shall be withdrawn at the latest by June 2010.

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

This document supersedes EN 1076:1997.

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

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

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

c) modification of the classification scheme for sampler types;

d) deletion of the informative annexes on the evaluation of pumped samplers by means of field tests.

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Introduction

This European Standard 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 EN 482. 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.

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1 Scope

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

This European Standard 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 referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

EN 838, *Workplace atmospheres — Diffusive samplers for the determination of gases and vapours — Requirements and test methods*

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

EN 1540:1998, *Workplace atmospheres — Terminology*

EN ISO 8655-2, *Piston-operated volumetric apparatus — Part 2: Piston pipettes (ISO 8655-2:2002)*

EN ISO 8655-6, *Piston-operated volumetric apparatus — Part 6: Gravimetric methods for the determination of measurement error (ISO 8655-6:2002)*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 482:2006 and EN 1540:1998[1] apply.

4 Symbols and abbreviated terms

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

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

CRM	certified reference material

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

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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)
$m_{\mathrm{a,lt}}$	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)
$m_{\mathrm{a,st}}$	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 (µg/min)
M_{a}	molar mass of analyte, in grams per mole (g/mol)
n	number of replicate samples
p_{at}	actual pressure of the test atmosphere sampled, in kilopascals (kPa)
R	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_0	volume of the test atmosphere sampled, in litres (l)
V_{H}	gas hold-up volume (dead volume)
V_{R}	uncorrected retention volume
$(V_{\mathrm{R}})'$	corrected retention volume
$\dot{v}$	flow rate into the exposure chamber, for example, in litres per minute (l/min)
v_a	volumetric air flow rate, for example, in litres per minute (l/min)
β_{a}	mass concentration of the analyte in the calibration gas mixture, in milligrams per cubic metre (mg/m³)
$\bar{\beta}_{\mathrm{a,R}}$	mean mass concentration of the analyte recovered from the test gas atmosphere, in milligrams per cubic metre (mg/m³)
β_{cg}	mass concentration of the calibration gas mixture, in milligrams per cubic metre (mg/m³)
ϑ_{at}	temperature of the test atmosphere sampled, in degrees Celsius (°C)

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K_v	coefficient of variation (CV)[2]
$\rho_{\mathrm{LV,lt}}$	long-term limit value given as volume concentration, in milligrams per cubic metre (mg/m³)
$\rho_{\mathrm{LV,st}}$	short-term limit value given as volume concentration, in milligrams per cubic metre (mg/m³)
ϕ_a	volume fraction of the analyte, in microlitres per litre (µl/l)

5 Types of samplers

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

Type A samplers rely on sorption onto a solid or onto a support impregnated with a reagent, desorption with solvent, and subsequent analysis of the desorbate. They are usually made of glass, are thermally sealed, and consist of two beds of sorbent in series, i.e. with a back-up section, and contain an active sorbent (e.g. activated carbon) or a support impregnated with reagent.

Type B samplers rely on sorption onto a solid or onto a support impregnated with a reagent, thermal desorption, and analysis of the desorbate. They are usually made of glass or metal, are sealed with removable fittings and consist of one or more beds of sorbent (e.g. porous polymer resin).

6 Requirements

NOTE If there is no procedure for measuring a particular chemical agent which meets the requirements of this European Standard, a procedure whose performance is nearest to the specified requirements should be used.

6.1 General

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

It is the responsibility of the manufacturer to meet the requirements specified in 6.2. It is also the responsibility of the manufacturer or the developer of the measuring procedure to meet the requirements specified in 6.3 when use of a sampler for measurement of a particular gas or vapour is claimed.

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.

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

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Table 1 — Maximum back pressures

Type of sampler	**Maximum back pressure** kPa
Type A – sorbent tubes, solvent desorption	≤ 10
Type A – impregnated filters	≤ 10
Type B – sorbent tubes, 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 Equation (1), in milligrams (mg), as follows:

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

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 volume concentration, in milligrams per cubic metre (mg/m³);

240 is the reference period, in minutes (min);

0,01 is the nominal minimum flow rate for type B samplers, in litres per minute (l/min);

10^{-3} is a factor applied to convert the nominal minimum flow rate from litres per minute (l/min) to cubic metres per minute (m³/min);

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 Equation (2), in milligrams (mg), as follows:

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

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 volume concentration, in milligrams per cubic metre (mg/m³);

15 is the reference period, in minutes (min);

0,01 is the nominal minimum flow rate for type B samplers, in litres per minute (l/min);

10^{-3} is a factor applied to convert the nominal minimum flow rate from litres per minute (l/min) to cubic metres per minute (m^3/min);

1/3 is a factor applied to calculate the maximum permitted leakage.

6.2.3 Shelf life (for impregnated supports)

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 Sample identification (for commercially available sorbent tubes and impregnated filters)

The sampler shall have a suitable area for sample identification by the user.

6.2.5 Marking

Samplers shall be marked with at least the following:

- manufacturer’s name;
- product identification;
- indication of the direction of air flow, if necessary;
- batch identification;
- shelf life (if applicable);
- number of this European Standard.

If required due to limited space, the marking may be placed on the packaging of the sampler. However, the manufacturer’s name, product identification 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 in the language(s) of the country where the sampler is to placed on the market. 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) blank value (only when used for a particular gas or vapour, see 6.1);

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 storage and transport;

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

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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, e.g. short-term limit value, long-term limit value or both.

6.3.1.2 Sample volume

The recommended sample volume shall be less than two-third of the breakthrough volume measured in accordance with 8.3.1.3.

6.3.1.3 Air flow rate

6.3.1.3.1 Impregnated filters

When tested according 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 Thermal desorption samplers (Type B samplers)

A minimum air flow rate shall be established according to the test 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 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 Analytical quantification limit

The quantification limit 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: $R_{\mathrm{an}} \geq 75$ % with $K_{\mathrm{v}} \leq 10$ % at each loading;
- for Type B samplers: $R_{\mathrm{an}} \geq 95$ % with $K_{\mathrm{v}} \leq 10$ % at each loading.

6.3.2.3 Blank value

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:

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

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

NOTE 1 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.

NOTE 2 In order to obtain acceptable values for the quantification limit of the method, the blank value of the sampling media should be as low as technically possible.

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 EN 482.

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 European Standard, 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 measurement method 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 measurement method has been shown to meet the performance criteria for expanded uncertainty prescribed in EN 482;

c) the quantification limit of the analytical method for chemical agents of interest;

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

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6.3.4.3 Apparatus and reagents

The measuring procedure shall:

a) specify that the sampler complies with the provisions of this European Standard;

b) contain a requirement that the sampling pumps used comply with the provisions given in EN 1232 and specify any characteristics of the sampling pumps additionally required;

c) define the required characteristics of analytical instruments 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

Use reagents of analytical grade, where possible.

7.2 Apparatus

7.2.1 Usual laboratory apparatus and the following:

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

- an exposure chamber constructed of inert materials 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) 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 It is also possible to use a smaller exposure chamber and to carry out repeat experiments to obtain at least six pairs of data.

7.2.3 Appropriate sampling pumps which meet the performance requirements of EN 1232.

7.2.4 Flowmeter(s), calibrated, suitable over the range from 10 ml/min to 2 000 ml/min, with a measurement uncertainty less than ± 2 %.

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

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

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7.3 Independent method

The 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, e.g. a flame ionization detector, or an infrared spectrometer.

If a diffusive sampler procedure is used as the independent method, the method shall comply with all requirements of EN 838.

7.4 Generation of the calibration gas mixture

7.4.1 General

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 %.

7.4.2 Calibration gas mixture

Calculate the mass concentration of the calibration gas mixture, β_{cg}, given in milligrams per cubic metre (mg/m³), from the test atmosphere generation parameters. For example, for a permeation cell system, the delivered mass concentration is:

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

where

$\dot{m}_1$ is the mass loss from permeation tube, in micrograms per minute (µg/min);

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

NOTE 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. 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 method shall be used or the independent method shall be verified.

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

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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 different levels of evaluation. These levels are specified as follows:

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

b) level 2: A measuring procedure deemed to be compliant with the normative part of this European Standard 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 comply 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.

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.

Analyze 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 using the apparatus in 7.2.2) with a minimum of three samplers under the following exposure conditions:

a) concentration: 2 LV;

b) time:

   1) for long-term LV: reference period plus 1 h;

   2) for short-term LV: twice the reference period;

c) flow rate: recommended flow rate;

d) relative humidity: (80 ± 5) %;

e) temperature: (20 ± 2) ºC.

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

Analyze the samplers after the test. The amount of the test substance recovered in the back-up section of sampler shall be ≤ 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 given in 8.3.1.3.

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8.3.1.3 Sampler breakthrough test

8.3.1.3.1 Direct method

Measure the breakthrough volume by sampling from a test atmosphere (using the apparatus in 7.2.2) using a minimum of three samplers under the following exposure conditions:

— concentration:	2 LV;
— flow rate:	according to the type of sampler (for example, 50 ml/min for Type B samplers, 200 ml/min for Type A sorbent tubes and 1 000 ml/min for impregnated filters);
— 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, an infrared spectrophotometer, etc. 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 ≥ 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 analyzed at regular intervals.

8.3.1.3.2 Chromatographic method

For porous polymers and similar chromatographic sorbents, instead of 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 low flow rate 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

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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. Multiply this value by 20 to determine the minimum air flow rate to be used with this type of sampler.

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 is appropriate. For narrower 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 is appropriate. For wider bore sorbent tubes or sorbent tubes with the sorbent bed positioned more narrow to the sampling end of the tube, a flow rate of more than 20 ml/min 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.

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

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 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.

NOTE If it is considered that the humidity of the air sampled could affect sample stability on storage, it is possible to investigate this by drawing humid air through the spiked samplers.

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8.3.2 Analytical procedure test methods

8.3.2.1 Analytical quantification limit

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 detection limit and analyze under repeatability conditions.

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

Estimate the quantification limit 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 four different loadings ranging from the lowest loading to the highest loading as calculated from the following sampling conditions:

a) concentration:

    1) for long-term LV: 0,1 LV to 2 LV;

    2) for short-term LV: 0,5 LV to 2 LV;

b) time:

    1) for long-term LV: recommended sampling time;

    2) for short-term LV: reference period;

c) flow rate: recommended flow rate.

The methods given in 8.3.2.2.2 to 8.3.2.2.4 can be used to determine the analytical recovery, but 8.3.2.2.2 and 8.3.2.2.3 are the preferred ones. For Type B samplers the method given in 8.3.2.2.5 can be used as well, but not the method given in 8.3.2.2.4.

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 7.2.5). 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.

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8.3.2.2.3 Sampling media spiking method from the liquid phase

Add a known mass of analyte to at least six sampling media for each loading, using a micropipette or syringe (see 7.2.5) and diluting in a non-interfering solvent, if necessary. 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 Phase equilibrium method

Prepare at least six pairs of solutions for each of the four sample loadings (see 8.3.2.2.3) in the same volume of solvent used for the desorption of the samplers. Add the sorbent from an unused sorbent tube to one solution of each pair and allow to equilibrate for at least 30 min. Analyze all solutions.

Calculate the analytical recovery by dividing the concentrations of the solutions to which sorbent has been added by the concentrations of the corresponding solutions without added sorbent and also calculate the mean and the coefficient of variation of the replicate samples. Compare with the requirements given in 6.3.2.2.

If the mean analytical recovery measured by the phase equilibrium method is less than 95 % or the analytical recovery measured at any level is less than 90 %, one of the tests given in 8.3.2.2.2 or 8.3.2.2.3 shall be used.

8.3.2.2.5 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.

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.

Type B samplers are part of the injection system of commercial thermal desorption instruments. A direct method is to compare recovery with the spiked sampler in-line versus the response from the introduction of analyte directly onto the gas chromatograph column. Absolute 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 a recovery of 100 % under the applied desorption conditions. n-pentane or n-hexane are suitable. 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.

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.

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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 Equation (4):

$$\beta_a = \frac{m_{a2} - m_{a1}}{R_{an} \times V_0} \tag{4}$$

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_0 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 Equation (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 actual 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 Equation (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/mol);

M_a is the molar mass of the analyte, in grams per mole (g/mol).

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;

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- 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 7.4.2). 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 7.4.2) to estimate the effect of the relative humidity on method recovery. See B.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 7.4.2). Calculate the mean results for each temperature and the mean difference to estimate the effect of the temperature on method recovery. See B.5.6 for information on how to consider the effect of temperature on the estimation of the expanded uncertainty of the measuring procedure.

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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 ENV 13005 and references [1], [2] and [3]).

NOTE See B.1 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, referring to the guidance in Annex B.

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 B.2.

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

If the uncertainty of measurement 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 in 8.3.1.6, referring to the guidance in B.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 in 8.3.3, referring to the guidance in B.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 in 8.3.3.2, referring to the guidance in B.6.

8.4.2.6 Calculation of the combined standard uncertainty

Calculate the combined standard uncertainty, expressed as a percentage, according to Equations (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

$u_{\mathrm{s_r}}$, $u_{\mathrm{s_{nr}}}$, $u_{\mathrm{a_r}}$, $u_{\mathrm{a_{nr}}}$	are the random sampling uncertainty, the non-random sampling uncertainty, the random analytical uncertainty and the non-random analytical uncertainty, respectively;
$u_{\mathrm{c_r}}$, $u_{\mathrm{c_{nr}}}$	are the random combined standard uncertainty (associated with sampling and analysis) and the non-random combined standard uncertainty (associated with sampling and analysis), respectively;
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 Equation (10):

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

9 Test report

The test report shall include at least the following information:

a) a reference to this European Standard;

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 European Standard that could have influenced the results;

l) the technical justification of omitting any tests.

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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.

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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 hold-up volume V_{H} (dead volume) according to Equation (A.1):

$$V_{\mathrm{H}} = v_a \times t_{\mathrm{H}} \qquad \text{(A.1)}$$

where

v_a is the volumetric air flow rate, for example, in litres per minute (l/min);

t_{H} is the hold-up time of the un-retained substance, in minutes (min).

Then determine the corrected retention volume $(V_{\mathrm{R}})'$ according to Equation (A.2):

$$(V_{\mathrm{R}})' = V_{\mathrm{R}} - V_{\mathrm{H}} \qquad \text{(A.2)}$$

where

V_{R} is the uncorrected retention volume;

V_{H} is the gas hold-up volume (dead volume).

A.2.5 Calculations

Plot the mean values of the logarithm of corrected retention volume at each temperature against reciprocal absolute 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.

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Annex B
(informative)

Estimation of uncertainty of measurement

B.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 B.2);

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

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

b) analysis

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

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

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

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

B.2 Uncertainty associated with sampled air volume

B.2.1 Sources of uncertainty

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

- flow rate measurement (see B.2.2);
- pump flow stability (see B.2.3);
- sampling time (see B.2.4).

B.2.2 Flow rate measurement

Flow rate measurements can be carried out using a range of different devices, 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.

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EXAMPLE For example, if the 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 EN 482:2006, Table C.1. 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 EN 482:2006, Table C.1 should be used, as this constitutes a worst-case scenario if the use of an inappropriate rotameter is disregarded.

B.2.3 Pump flow stability

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

Actual values for the pump flow stability can be less than 5 %. It can be estimated from the value given by manufacturer or from the results of the test in EN 1232:1997, 6.6. Assuming a rectangular probability distribution, the value of the non-random uncertainty component of the pump flow stability can be calculated according to Equation (B.1):

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

where

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

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

B.2.4 Sampling time

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

If the reading is taken to the nearest second, the non-random uncertainty component is very small for both long-term and short-term measurements and can be negligible. If the reading is taken to the nearest minute, the non-random component is very small for long-term measurements (for example > 2 h) and may 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 (6,67/√6) % = 2,7 % for a sampling time of 15 min (summing the maximum 0,5 min biases at the start and end of the sampling period and dividing by the sampling time and √6, assuming a triangular probability distribution).

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

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B.3 Uncertainty associated with sampling efficiency

The 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 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.

B.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 Equation (B.2):

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

where

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

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

When samples are transported in an appropriate manner as specified in the measurement method, it is not necessary to take into consideration any component of uncertainty other than those associated with storage.

B.5 Uncertainty associated with method recovery

B.5.1 General

Method recovery is influenced by several factors (see B.3). The study of their influence is carried out following the tests described in 8.3.3.2, 8.3.3.3 and 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 humidity. These data can be used to estimate the method uncertainty components as described in B.5.2 to B.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.

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B.5.2 Analytical recovery

B.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.

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.

B.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 Equation (B.3):

$$u_{\text{ar}} = \sqrt{\frac{(K_{\text{v,ra}})^2}{n} + (u_{\text{ks}})^2} \qquad \text{(B.3)}$$

where

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

$K_{\text{v,ra}}$ 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 Equation (B.4):

$$u_{\text{ks}} = \sqrt{(u_{\text{pu}})^2 + \frac{(B_{\text{max,sy}})^2}{3} + \frac{(K_{\text{v,sy}})^2}{n}} \qquad \text{(B.4)}$$

where

u_{pu} 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) %);

$B_{\text{max,sy}}$ is the maximum bias of the volume dispensed by the syringe used to spike the blank sampling media, in percent (%);

$K_{\text{v,sy}}$ is the coefficient of variation of the volume dispensed by the syringe used to spike the blank sampling media, in percent (%);

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.

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B.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 (B.5), see reference [4].

$$u_{\text{ab}} = \sqrt{\left(\frac{B_{\text{a}}}{k}\right)^2 + \frac{(K_{\text{v,ra}})^2}{n} + (u_{\text{ks}})^2} \qquad \text{(B.5)}$$

where

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

B_{a} is the bias of the mean result of replicate analyses for the known samples, in percent (%);

k is the coverage factor used in the calculation of the expanded uncertainty;

$K_{\text{v,ra}}$ 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.

B.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) corrected for analytical recovery, if applicable. 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 Equation (B.6), see reference [4].

$$u_{\text{mb}} = \sqrt{\left(\frac{B_{\text{m}}}{k}\right)^2 + \frac{(K_{\text{v,rm}})^2}{n} + (u_{\text{rc}})^2} \qquad \text{(B.6)}$$

where

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

B_{m} is the bias of the mean results from the reference concentration, in percent (%) (see 7.4.2);

k is the coverage factor used in the calculation of the expanded uncertainty;

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

n is the number of replicate samples;

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

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B.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. For example, for a dynamic system the random uncertainty associated with the reference concentration of the test atmosphere is usually less than 3 %.

B.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 Equation (B.7):

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

where

u_{h} is the relative standard uncertainty associated with the effect of humidity on the recovery;

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 (%).

B.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 Equation (B.8):

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

where

u_{T} is the relative standard uncertainty associated with the effect of temperature on the recovery;

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 (%).

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B.6 Uncertainty associated with method variability

B.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 B.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 B.6.3), calibration function (see B.6.4), dilution of the sample solutions (see B.6.5) and instrument response drift (see B.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 B.6.7.1) or from data obtained under reproducibility conditions (see B.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 B.6.3), calibration function (see B.6.4), dilution of the sample solutions (see B.6.5) and instrument response drift (see B.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/TS 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.

B.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 Equation (B.9), see also ENV 13005:

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

where

u_{mp} is the relative standard uncertainty associated with the 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 Equation (B.10);

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

For an unequal number of replicate samples n can be estimated by Equations (B.10), see reference [9]:

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

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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 Equation (B.11):

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

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 numbers 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 $\mathrm{K}_{\mathrm{vp,r}} = \sqrt{[(K_{\mathrm{v},1})^2+(K_{\mathrm{v},2})^2+(K_{\mathrm{v},3})^2]/3}$.

B.6.3 Concentration of calibration solutions

The non-random uncertainty components associated with the concentration of the calibration solutions can be estimated from one or more of the following:

a) the certificate provided by the manufacturer of a pressurised test gas;

b) the purity of the starting material (for example, purity > 99,5 %);

c) the uncertainties in the weighing of chemical agents and solutions, for example the uncertainty of a balance;

d) the uncertainties in the preparation of a test gas;

e) the random uncertainty components associated with a dilution procedure.

EXAMPLE The relative standard uncertainty associated with the concentrations of the calibration solutions, u_{cc} , in percent (%), can be estimated from the uncertainty of the mass of the pure compound and the uncertainty of the micropipette or syringe used to prepare the calibration solutions, using Equation (B.12):

$$u_{\mathrm{cc}} = \sqrt{(u_{\mathrm{m}})^2 + (K_{\mathrm{v,sy}})^2 + \frac{(B_{\mathrm{max,p}})^2}{3}} \tag{B.12}$$

where

u_{m} is the relative standard uncertainty of the mass of pure compound weighed, estimated from its purity, the calibration certificate of the balance and the coefficient of variation of the balance readings, in percent (%);

$K_{\mathrm{v,sy}}$ is the coefficient of variation of the micropipette or syringe used to prepare the calibration solutions, in percent (%), for example, estimated from the certificate provided by the manufacturer;

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$B_{\max,p}$ is the maximum bias of the micropipette or syringe used to prepare the calibration solutions, in percent (%), for example, estimated from the confidence interval given on the certificate provided by the manufacturer.

B.6.4 Calibration function

The random uncertainty component associated with the calibration function can be calculated from parameters obtained by the least-squares linear regression. See reference [3].

2 % is a reasonable estimate of the random uncertainty component associated with the calibration function and can be used in most cases. This was the value used in the EU project BC/CEN/ENTR/000/2002-16 *Analytical methods for chemical agents*, see reference [5].

B.6.5 Dilution of the sample solutions (if applicable)

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

The random uncertainty component is the relative uncertainty of the solution volume dispensed by the micropipette used in dilution of the sample solutions.

Assuming rectangular probability distributions for the bias of the micropipette and the volumetric flasks used in dilution of the sample solutions, the non-random uncertainty component associated with dilution of the sample solutions, u_{di} , in percent (%), is given by Equation (B.13):

$$u_{\text{di}} = \sqrt{\frac{(B_{\max,s})^2}{3} + \frac{(B_{\max,f})^2}{3}} \quad \text{(B.13)}$$

where

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

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

B.6.6 Instrument response drift

Methods and laboratory operating procedures generally specify a maximum instrument response drift that is permitted before recalibration (often monitored by repeat analysis of a calibration solution). It is necessary to take this non-random uncertainty component into consideration. Assuming a rectangular probability distribution, the relative standard uncertainty associated with instrument response drift, u_{dr} , in percent (%), is given by Equation (B.14):

$$u_{\text{dr}} = \frac{d_{\max}}{\sqrt{3}} \quad \text{(B.14)}$$

where

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

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B.6.7 Analytical precision

B.6.7.1 Estimation using repeatability data

The random uncertainty associated with the analytical precision is determined from the results of replicate samples analyzed to estimate the analytical recovery (see 8.3.2) or by analysis of the calibration solutions under repeatability conditions. The random uncertainty associated with the analytical precision can be estimated as the coefficient of variation of the replicate samples or the calibration solutions.

When spiked samples are used to estimate analytical precision, uncertainty associated with sample preparation and analysis is included. When method precision is estimated according to B.6.2 the contribution of the analytical precision is already included and it does not need to be taken into account.

B.6.7.2 Estimation using within laboratory reproducibility data

The uncertainty associated with analytical precision can be estimated from within-laboratory reproducibility data obtained from the analysis of stable quality control solutions, normally one solution at a low concentration and one at a high concentration (for example, 10 % and 90 % of the range of concentrations over which the analytical instrument is calibrated). It is important to cover long-term random variations, so the data used should be from the analysis of quality control solutions over a period of several months.

Depending on the quality control plan and control samples used, random uncertainties in B.6.3 to B.6.6 may be included in the estimation of the uncertainty of the analytical precision. For instance, if new calibration solutions and function are prepared each time the quality control samples are analyzed, random uncertainties in B.6.3 to B.6.6 are included in the estimation of the uncertainty of the analytical precision.

B.7 Calculation of combined standard uncertainty

To calculate the random and non-random components of sampling uncertainty and analytical uncertainty, the relevant individual uncertainty components are combined according to Equations (B.15) to (B.18):

$$u_{\mathrm{s_r}} = \sqrt{\sum_{i=1}^{j_{\mathrm{s_r}}} u_{\mathrm{s_r}\,i}^{\;2}} \tag{B.15}$$

$$u_{\mathrm{s_{nr}}} = \sqrt{\sum_{i=1}^{j_{\mathrm{s_{nr}}}} u_{\mathrm{s_{nr}}\,i}^{\;2}} \tag{B.16}$$

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

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

where

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

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

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

The combined standard uncertainty, u_{c}, and the expanded uncertainty, U ,of the measuring procedure are calculated according to Equations (7) to (10). See 8.4.2.6 and 8.4.3.

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Annex C
(informative)

Example of estimation of expanded uncertainty

This annex presents an example of the estimation of the expanded uncertainty of a measuring procedure for isophorone in workplace air. The measuring procedure concerned uses a Type A sampler (silica gel sorbent tubes) and the method evaluation was carried out using a test atmosphere of isophorone. It is an example of a level 1 evaluation. Table C.1 contains a summary of the results of the test detailed in 8.3.

The individual uncertainty components, combined standard uncertainty and expanded uncertainty estimated from data in Table C.1 following the procedure in 8.4 and Annex B are given in Table C.2.

Table C.1 — Summary of the validation data for isophorone

Exercise	v_a	β_a	ϑ_{at}	RH	t_s	n	$\bar{\beta}_{a,R}$	K_V	R
	ml/min	mg/m^3	°C	%	h		mg/m^3	%	%
Blank value	—	—	—	—	—	six unused tubes	—	—	—
LOD/LOQ	333	1,015	20,3	60	2	6	0,94	1,02	92,6
Reproducibility and recovery at different concentrations									
0,1 LV	333	1,19	20,4	53	2	6	1,25	1,99	105,2
0,5 LV	333	5,97	20,2	54	2	6	5,26	0,87	88,0
1 LV	333	11,90	20,3	54	2	6	10,60	0,84	89,0
2 LV	333	23,33	20,2	52	2	6	21,43	1,84	91,9
5 LV	333	58,53	14,2	49	2	6	54,87	1,44	93,7
Influence of relative humidity of the test atmosphere									
0,1 LV low RH	333	1,19	20,5	21	2	6	1,09	1,76	92,0
0,1 LV high RH	333	1,18	20,1	81	2	6	1,28	1,26	109,0
5 LV low RH	333	59,23	20,4	22	2	6	53,45	1,55	90,2
5 LV high RH	333	58,67	20,3	80	2	6	51,57	1,29	87,9
Influence of air temperature of the test atmosphere									
5 LV low ϑ_{at}	333	58,53	14,2	49	2	6	54,87	1,44	93,7
5 LV high ϑ_{at}	333	58,21	38,9	48	2	6	54,67	1,40	93,9

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Table C.1 *(continued)*

Exercise	v_a ml/min	β_a mg/m^3	ϑ_{at} °C	RH %	t_s h	n	$\bar{\beta}_{a,R}$ mg/m^3	K_v %	R %
Sampler capacity									
Break-through volume	333	58,674	20,3	80	[a]	3	50,62	—	86,3
Recovery at maximum sampling conditions	333	58,674	20,3	80	2 h	3	51,78	—	88,2
Recovery at maximum sampling conditions	83	58,674	20,3	80	8 h	3	53,64	—	91,4
Storage time									
0,1 LV (D)	333	1,173	20,4	80	2 h	[b]	—	no loss of analyte	—
5 LV (D)	333	59,253	20,3	81	2 h	[b]	—	no loss of analyte	—

[a] Until breakthrough has occurred, but no longer than 8 h.

[b] Three analyses per day (1, 3, 7, 14, 28 d).

NOTE 1 Limit value 8 h: 11 mg/m^3.

NOTE 2 For the symbols used see Clause 4.

Table C.2 — Individual uncertainty components, combined standard uncertainty and expanded uncertainty (see 8.4 and Annex B)

Uncertainty contribution	**Uncertainty**		**Remarks**
	random %	**non random %**	
Sampled air volume			
Flow rate measurement, u_{fr}	0,3	—	see B.2.2 and also EN 482:2006, Table C.1
Flow rate calibration, u_{fc}	—	0,6	see B.2.2 and also EN 482:2006, Table C.1
Pump flow stability, u_{pfs}	—	2,9	see B.2.3 and also EN 482:2006, C.2.1.3
Sampling time, u_{ts}	0,3	—	see B.2.4
Sampling efficiency, u_{se}	—	0,0	Recommended sampling volume < 2/3 breakthrough
Storage and transport, u_{st}	—	0,6	Samples are stable at least 28 days when stored at 20 °C
$u_{s_r} = \sqrt{\sum_{i=1}^{j_{s_r}} u_{s_{r_i}}^2}$	0,4	—	
$u_{s_{nr}} = \sqrt{\sum_{i=1}^{j_{s_{nr}}} u_{s_{nr_i}}^2}$	—	3,0	
$u_s = \sqrt{u_{s_r}^2 + u_{s_{nr}}^2}$	3,0		
Method recovery			
Analytical recovery			
- B_a	Not determined		
- $K_{v,ra}$	—		
- u_{ks}	—		
Method bias			
- B_m	—	3,4	Calculated from the test of reproducibility (see Table C.1)
- $K_{v,rm}$	1,2	—	Calculated from the test of reproducibility (see Table C.1)
- u_{rc}	—	1,7	see B.5.4, estimated to be 3 %
Effect of relative humidity	—	10,6	see B.5.5 and Table C.1
Effect of temperature	—	0,1	see B.5.6 and Table C.1
Method precision	7,4	—	see B.6.2, calculated from the test of reproducibility (see Table C.1)
Calibration solutions	—	1,3	see B.6.3, estimated from other sources
Calibration function	0,0	—	see B.6.4, estimated to be 0 % for FID (see reference [5])
Dilution of sample solutions	0,0	—	see B.6.5, not applicable
Instrument response drift	—	0,0	see B.6.6, estimated to be 0 % for FID (see reference [5])
Analytical precision	0,0	—	see B.6.7.1, included in replicates samples
$u_{a_r} = \sqrt{\sum_{i=1}^{j_{a_r}} u_{a_{r_i}}^2}$	7,6	—	
$u_{a_{nr}} = \sqrt{\sum_{i=1}^{j_{a_{nr}}} u_{a_{nr_i}}^2}$	—	11,4	
$u_a = \sqrt{u_{a_{nr}}^2 + u_{a_r}^2}$	13,7		

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Table C.2 *(continued)*

Uncertainty contribution	**Uncertainty**		**Remarks**
	random %	**non random %**	
COMBINED STANDARD UNCERTAINTY			
$u_{\mathrm{c}_\mathrm{r}}$	7,6 %	—	
$u_{\mathrm{c}_\mathrm{nr}}$	—	11,8	
$u_\mathrm{c} = \sqrt{u_{\mathrm{c}_\mathrm{nr}}^2 + u_{\mathrm{c}_\mathrm{r}}^2}$	14,0		
EXPANDED UNCERTAINTY			
$U = 2 \times u_c$	**28,0** %		

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