BRITISH STANDARD

BS EN 838:2010

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

ICS 13.040.30

BSI British Standards

National foreword

This British Standard is the UK implementation of EN 838:2010. It supersedes BS EN 838:1996 which is withdrawn.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 Diffusionssammlern - Anforderungen und Prüfverfahren

This European Standard was approved by CEN on 11 December 2009.

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Foreword

This document (EN 838:2010) 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of an identical text or by endorsement, at the latest by July 2010, and conflicting national standards shall be withdrawn at the latest by July 2010.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 838:1995.

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 diffusive samplers by means of field tests.

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

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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. These performance criteria include maximum values of expanded uncertainty achievable under prescribed laboratory conditions for the methods to be used. In addition, the performance criteria should also be met under a wider variety of environmental influences, representative of workplace conditions.

This European Standard enables manufacturers and users of diffusive samplers and developers and users of procedures for measuring gases and vapours to adopt a consistent approach to method validation.

1 Scope

This European Standard specifies performance requirements and test methods under prescribed laboratory conditions for the evaluation of diffusive samplers and of procedures using these samplers for the determination of gases and vapours in workplace atmospheres.

This European Standard is applicable to diffusive 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:

— diffusive samplers which are used for the direct determination of concentrations;

— diffusive samplers which rely on sorption into a liquid.

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

EN 1540, *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[1)] apply.

4 Symbols and abbreviations

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.

A cross-sectional area of sorption surface, in square centimetres (cm^2)

CRM certified reference material

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

D_a diffusion coefficient of an analyte, in square centimetres per minute (cm²/min)

D_{a1} diffusion coefficient of analyte 1, in square centimetres per minute (cm²/min)

D_{a2} diffusion coefficient of analyte 2, in square centimetres per minute (cm²/min)

l length of static air layer in sampler (or equivalent for permeation types), in centimetres (cm)

LV limit value

m_b mass of analyte desorbed from blank sampler, in nanograms (ng)

m_d mass of analyte desorbed, in nanograms (ng)

m_s mass of the analyte which can diffuse to a suitable sorbent within a certain time, i.e. the mass uptake of a diffusive sampler, in nanograms (ng)

$\dot{m}_1$ 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_e exposure time, in minutes (min)

T_{at} temperature of the test atmosphere sampled, in Kelvin (K)

$\dot{U}_d$ uptake rate, in cubic centimetres per minute (cm³/min)

$(\dot{U}_d)'$ uptake rate, in nanograms per parts per million (volume fraction) per minute (ng ppm^{-1} min^{-1})

$\dot{U}_{d1}$ uptake rate of analyte 1, in cubic centimetres per minute (cm³/min)

$\dot{U}_{d2}$ uptake rate of analyte 2, in cubic centimetres per minute (cm³/min)

$\dot{v}$ flow rate into the exposure chamber, 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)

$(\beta_a)'$ mass concentration in parts per million (ppm);

β_{a1} mass concentration of the given analyte at the beginning of the diffusion layer (i.e. at the distance l from the surface of the sorbent), in milligrams per cubic metre (mg/m³)

β_{a2} mass concentration of the given analyte at the end of the diffusion layer (i.e. at the surface of the sorbent), in milligrams per cubic metre (mg/m³)

$\overline{\beta}_{a,R}$ 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 degree Celsius (°C)

K_v coefficient of variation (CV)[2)]

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 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 1 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. However the user of diffusive samplers should be cautioned that the adsorption of water vapour on certain sorbents, e.g. activated carbon and silica gel, can have a large effect on sampler capacity and analytical recovery.

NOTE 2 Because of the known effect of pressure on diffusion coefficients, a pressure test is not necessary.

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

6.2 Sampler requirements

6.2.1 Nominal uptake rate

The nominal uptake rate and the coefficient of variation[3)] shall be provided by the manufacturer. If it is possible to calculate the ideal steady-state value in accordance with 8.2.1.1, the nominal uptake rate, determined in accordance with 8.2.1.2, shall be within ± 25 % of the steady-state value.

6.2.2 Air velocity/sampler orientation

The manufacturer shall test the working range of air velocity and the influence of sampler orientation in accordance with 8.2.2.

6.2.3 Sampler leak test

When tested in accordance with 8.2.3, any additional analyte determined above the blank value (see 6.3.2.3) shall be less the one-third of the calculated mass uptake by the sampler for 30 min exposure to a concentration of 0,1 LV.

6.2.4 Shelf life (for impregnated supports)

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

6.2.5 Sample identification (for commercially available diffusive samplers)

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

6.2.6 Marking

Diffusive samplers shall be marked with at least the following:

— manufacturer's name;

— product identification;

— 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 diffusive sampler. However, the manufacturer's name and product identification shall be indicated on the diffusive sampler.

6.2.7 Instructions for use

The instructions for use supplied with the diffusive sampler shall be in the language(s) of the country where the diffusive 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);

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

b) blank value (only when used for a particular gas or vapour, see 6.1;

c) nominal uptake rate for the substances for which the diffusive sampler is intended to use;

d) directions for proper handling of the diffusive sampler, including opening and closing;

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

f) information on storage and transport;

g) working range of air velocity;

h) orientation;

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

The general information on the principle of use can be given in additional literature.

6.3 Measuring procedure requirements

6.3.1 Sampling procedure requirements

6.3.1.1 Sampling time

Sampling time shall be established according to concentration range of the compounds of interest over which measurements are to be made, i.e. up to two times the limit value (see EN 482), and taking into account the nominal or theoretical uptake rate.

6.3.1.2 Bias due to the selection of a non ideal sorbent (back diffusion)

When tested in accordance with 8.3.1.1, the bias shall be ≤ 10 %.

6.3.1.3 Uptake rate

If it is possible to calculate the ideal steady-state value in accordance with 8.2.1.1, the nominal uptake rate, determined in accordance with 8.2.1.2, shall be within ± 25 % of the steady-state value.

6.3.1.4 Storage conditions after sampling

The storage conditions after sampling shall be specified. When tested in accordance with 8.3.1.3, 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 one-third of the calculated mass uptake by the sampler for 30 min exposure to a concentration of 0,1 LV.

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} ≥ 75 % with K_v ≤ 10 % at each loading;

— For type B samplers: R_{an} ≥ 95 % with K_v ≤ 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 uptake by the sampler for 30 min exposure to a concentration of 0,1 LV.

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

Type B samplers which are not thermally sealed should be cleaned before sampling to eliminate any contamination which could occur during storage before use.

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 ºC to 40 ºC and at relative humidities from 20 % to 80 %. Above 30 ºC the use of correction factors is permitted to meet this requirement.

6.3.4 Method description

6.3.4.1 Scope of the measurement procedure

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

— principle of the method;

— chemical agents covered by the measuring procedure;

— analytical technique used;

— working ranges;

— 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;

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

— any known interferences.

6.3.4.2 Method performance

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

— the chemical agents for which measurement method has been shown to be effective;

— the range of concentrations of chemical agents in air, sample volume, uptake rates, exposure time 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;

— the quantification limit of the analytical method for chemical agents of interest;

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

6.3.4.3 Apparatus

The measuring procedure shall:

— specify that the diffusive sampler complies with the provisions of this European Standard;

— define the required characteristics of analytical instruments to be used;

— 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

Usual laboratory apparatus and the following:

7.2.1 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.

7.2.2 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.

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

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 pumped sampler method, bubbler method, or a different diffusive sampler method; or

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

If a pumped sampler procedure is used as the independent method, the method shall comply with all requirements of EN 1076.

7.4 Generation of a 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

7.4.2.1 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:

$$\beta_{cg} = \frac{\dot{m}_1}{\dot{v}} \quad (1)$$

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 1 The example does not give a preference for permeation systems for generating calibration gas mixtures of gases and vapours.

NOTE 2 This value is the calculated inlet value of the exposure chamber concentration.

7.4.2.2 Measure the mass concentrations at the inlet and outlet of the exposure chamber using the independent method described in 7.3 with all samplers within the test chamber, including both the test and independent method functioning.

Determine whether the measured outlet mass concentration differs by more than 5 % from the measured inlet mass concentration. If it does, then the generation system shall be changed e.g. by increasing the flow rate or chamber volume, until the difference is less than 5 %.

When the difference is less than 5 %, calculate the mean mass concentration in the test atmosphere within the exposure chamber either from the mean of the calculated inlet and outlet values, or from the mean calculated inlet value adjusted for (half of) the experimentally determined depletion.

7.4.2.3 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 mass concentration with the calculated value (see 7.4.2.2). 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. If this requirement is not met, then make adjustments or use an alternative generation method or verify the independent method.

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.

8 Test methods

8.1 General

If it is known in advance that a certain type of diffusive sampler is unaffected by an environmental influence then the relevant tests in 8.3.3.1 to 8.3.3.5 may be modified to examine only the factors likely to have an influence.

If not otherwise specified in the test procedure, the sampler orientation shall be as specified by the manufacturer.

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 Determination of uptake rates

8.2.1.1 Calculation of uptakes rates from diffusion coefficients

Calculate the mass uptake of a diffusive sampler m_s (see Annex A) according to Equation (2):

$$m_s = \frac{A \times D_a \times \beta_a \times t_e}{l} \quad (2)$$

where

A is the cross-sectional area of sorption surface, in square centimetres;

D_a is the diffusion coefficient of the analyte, in square centimetres per minute;

β_a is the mass concentration of the analyte, in milligrams per cubic metre (corresponds to nanograms per cubic centimetre);

t_e is the exposure time, in minutes;

l is the length of static air layer in sampler (or equivalent for permeation types), in centimetres.

NOTE If the diffusion coefficient is not known from the literature the method in EN ISO 16017-2 can be used.

Calculate the uptake rates, either from knowledge of the physical parameters of the diffusion barrier (see Equation (3)) or by comparison with another analyte for which the uptake rate is known (see Equation (4)).

$$\dot{U}_d = \frac{m_s}{\beta_a \times t_e} = \frac{A \times D_a}{l} \quad (3)$$

and

$$\dot{U}_{d1} = \frac{D_{a1}}{D_{a2}} \times \dot{U}_{d2} \quad (4)$$

where

D_{a1} is the diffusion coefficient of analyte 1, in square centimetres per minute (cm²/min);

D_{a2} is the diffusion coefficient of analyte 2, in square centimetres per minute (cm²/min);

$\dot{U}_{d1}$ is the (nominal) uptake rate of analyte 1, in cubic centimetres per minute (cm³/min);

$\dot{U}_{d2}$ is the (nominal) uptake rate of analyte 2, in cubic centimetres per minute (cm³/min).

8.2.1.2 Nominal uptake rates

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

— concentration: 1 LV;
— time: 4 h;
— relative humidity: (50 ± 5) %;
— temperature: (20 ± 2) ºC;
— air velocity: 0,5 m s^{-1}.

Analyze the diffusive samplers by reference to standard solutions or to standard samplers spiked with known amounts of analyte.

Calculate the (nominal) uptake rate $\dot{U}_d$ according to Equation (5):

$$\dot{U}_d = \frac{m_d - m_b}{R_{an} \times \beta_a \times t_e} \quad (5)$$

where

m_d is the mass of analyte desorbed, in nanograms (ng);

m_b is the mass of analyte desorbed from the blank sampler, in nanograms (ng);

R_{an} is the analytical recovery;

β_a, t_e see 8.2.1.1.

NOTE If the mass concentration is given as 10^{-6} (parts per million), use $(\beta_a)'$ and $(\dot{U}_d)'$ instead of β_a and $\dot{U}_d$.

Calculate the mean (nominal) uptake rate and the coefficient of variation. Compare with the requirement in 6.2.1

8.2.2 Air velocity/sampler orientation

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

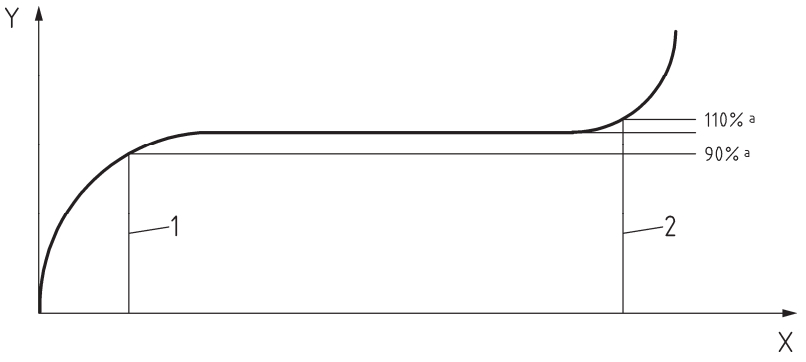
— concentration: 1 LV;
— time: 4 h;
— relative humidity: (50 ± 5) %;
— temperature: (20 ± 2) ºC;
— air velocity: 0,01 m s^{-1} to 4,0 m s^{-1};
— orientation: either parallel or perpendicular to the flow direction.

Analyze the set by reference to standard solutions or to samplers spiked with known amounts of analyte.

Calculate the observed mass concentration (see 8.3.3.1) and plot the mean value against air velocity, assuming linear flow. Determine the air velocity corresponding to an observed mass concentration of 90 % and 110 % of its maximal (plateau) value for each sampler orientation (see Figure 1). Test the samplers and use under conditions where air velocities are in the range of the plateau area.

As the influence of air movement on diffusive sampler performance is dependent on sampler geometry and not on the analyte selected, it is necessary to perform this test only on a given diffusive sampler with one typical analyte.

Samplers which are intended only for personal monitoring need to be tested only over the range 0,1 m · s^{-1} to 1,5 m · s^{-1} (indoor workplaces only) or over the range 0,1 m · s^{-1} to 4,0 m · s^{-1} (indoor or outdoor workplaces).



Key

X air velocity around diffusive sampler
Y observed mass concentration of the analyte β_a
a $\beta_{a,\ plateau}$
1 minimum air velocity
2 maximum air velocity

Figure 1 — Typical relationship between air velocity and observed mass concentration for diffusive samplers

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8.2.3 Sampler leak test

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) ºC;

— air velocity: approximately 0,5 m s^{-1}.

Analyze the set to determine any leakage.

This leak test needs to be performed on a given sampler for one typical chemical agent only.

8.2.4 Shelf life (for Type A impregnated supports)

Store the diffusive 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 diffusive sampler under the following exposure conditions:

— concentration: 2 LV;

— time: 8 h;

— relative humidity: (80 ± 5) %;

— temperature: (40 ± 2) ºC;

— air velocity: above minimum specified in 8.2.2.

Compare with the requirement in 6.2.4.

8.2.5 Sample identification

Perform a visual check.

8.2.6 Marking

Perform a visual check.

8.2.7 Instructions for use

Perform a visual check.

8.3 Measuring procedure test methods

8.3.1 Determination of the sampling conditions

8.3.1.1 Bias due to the selection of a non ideal sorbent

Expose diffusive samplers in two sets of at least six replicates to an atmosphere of the test analyte at 2 LV and 80 % relative humidity for 30 min. Then one set is capped, and the other set exposed to clean air (also at 80 % relative humidity) for a further 7,5 h.

NOTE Diffusive samplers will normally be unbiased, since they are calibrated against calibration gas mixture. However, bias can result from the use of non-ideal sorbent (see Annex A) or from the effects of environmental influences,

such as temperature and relative humidity. This test determines the magnitude of any bias due to back diffusion. Both sets of samplers are assumed to have been exposed to a time-weighted average concentration of 0,125 LV for 8 h, since the test represents the worst-case situation in which a 30 min pulse occurs either at the beginning or end of an 8 h period. The difference between the mass uptake of the two sets of samplers, caused by back-diffusion, represents the maximum bias that can be encountered in a real non-constant atmosphere.

Calculate the mean mass uptakes for the two sets of samplers and the difference, in percent (%), between the means. Compare with the requirement in 6.3.1.2.

8.3.1.2 Determination of uptake rates

Determine the uptake rate experimentally according to 8.2.1 or use the nominal uptake rate provided by the manufacturer.

8.3.1.3 Storage after sampling

8.3.1.3.1 Direct method

Use two sets of at least six diffusive samplers and sample from a test atmosphere under the following exposure conditions:

— concentration: 0,1 LV and 2 LV;

— time: 8 h;

— relative humidity: (80 ± 5) %;

— temperature: (20 ± 2) ºC;

— air velocity: above minimum specified in 8.2.2.

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 this requirement 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.

8.3.1.3.2 Sampling media spiking method

Using two sets of at least six diffusive samplers, spike directly the sampling media with an equivalent loading as in 8.3.1.3.1 and add an amount of water equivalent to an exposure to air for 8 h at 80 % relative humidity at a temperature of 20 ºC for the appropriate time. The amount of water to be added can be calculated from moisture uptake rate data supplied by the manufacturer. In the absence of such data, expose samplers to clean air at 20 ºC and a relative humidity of 80 % before spiking with the analyte. 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 this requirement is not met repeat the test with a shorter storage time or by using different storing conditions.

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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 diffusive 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 diffusive 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 Sampling media spiking method from the liquid phase

Conduct the determination at four different loadings, ranging from the lowest loading to the highest loadings as indicated in Table 1. 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. The analyte may either be applied directly to the sorbent or be allowed to diffuse from a spiked glass-fibre filter in a closed system. Desorb the analyte or a reaction product, if appropriate. Analyze the samples by reference to liquid standards prepared directly.

Table 1 — Sample loadings for determination of analytical recovery

Concentration	**0,1 LV**	**2 LV**
Sampling time	**30 min**	**8 h**
Loading	**lowest** **(0,1 LV × uptake rate × 30 min)**	**highest** **(2 LV × uptake rate × 8 h)**

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

8.3.2.2.2 Phase equilibrium method (for type A non impregnated diffusive samplers)

Prepare at least six sets of four pairs of the solutions corresponding to four different sample loadings within the range given in Table 1 using the same volume of solvent used for the desorption of the samplers. Add the sorbent from an unused diffusive sampler 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.

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 %, only the test given in 8.3.2.2.1 shall be used.

8.3.2.2.3 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 8.3.2.2.1.

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.

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 8.3.3.5 require calculation of the mass concentration of the analyte, β_a, from the mass of analyte recovered from the samplers and the volume of test atmosphere sampled by using the nominal value of the uptake rate according to Equation (6):

$$\beta_a = \frac{m_d - m_b}{\dot{U}_d \times t_e \times R_{an}} \quad (6)$$

where

m_d is the mass of analyte desorbed, in nanograms (ng);

m_b is the mass of analyte desorbed from blank sampler, in nanograms (ng);

$\dot{U}_d$ is the (nominal) uptake rate, in cubic centimetres per minute (cm³/min);

t_e is the exposure time, in minutes (min);

R_{an} is the analytical recovery.

NOTE 1 If the mass concentration is given as 10^{-6} (parts per million), use $(\beta_a)'$ and $(\dot{U}_d)'$ instead of β_a and $\dot{U}_d$.

NOTE 2 A manufacturer's value or a calculated value (see 8.2.1.1) may be used instead of the experimentally determined value (see 8.2.1.2) of the nominal uptake rate.

NOTE 3 The mass concentration adjusted to specified conditions, $\beta_{a,corr}$, for example 20 ºC (= 293 K) and 101,3 kPa, can be calculated according to Equation (7):

$$\beta_{a,corr} = \beta_a \times \frac{101{,}3}{p_{at}} \times \frac{T_{at}}{293} \quad (7)$$

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where

T_{at} is the temperature of the test atmosphere sampled, in Kelvin (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 (8):

$$\phi_a = \beta_{a,corr} \times \frac{24,1}{M_a} \quad (8)$$

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).

For type testing the manufacturer's value of the uptake rate shall be used.

8.3.3.2 Effect of exposure time

Using at least six diffusive samplers, sample from a test atmosphere under the following conditions:

— concentration: approximately 1 LV;
— time: 0,5 h, 4 h, 8 h;
— relative humidity: (50 ± 5) %;
— temperature (20 ± 2) ºC;
— air velocity: above minimum specified in 8.2.2.

NOTE This test can be part of 8.3.3.3.

Analyze the diffusive samplers by reference to standard solutions or to samplers spiked with known amounts of analyte. For each exposure combination, calculate the measured concentration (see 8.3.3.1) for each of the six (or more) replicate diffusive samplers. Divide each by the reference concentration of the test atmosphere (see 7.4). Calculate the mean method recovery for each exposure combination 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 exposure concentration

Using at least six diffusive samplers for each concentration, sample from a test atmosphere under the following conditions:

— concentration: approximately 0,1 LV, 0,5 LV, 1 LV and 2 LV;
— time: 4 h;
— relative humidity: (50 ± 5) %;
— temperature (20 ± 2) ºC;
— air velocity: above minimum specified in 8.2.2.

Analyze the diffusive samplers by reference to standard solutions or to standard samplers spiked with known amounts of analyte. For each exposure combination, calculate the measured concentration (see 8.3.3.1) for each of the six (or more) replicate diffusive samplers. Divide each by the reference concentration of the test atmosphere (see 7.4). Calculate the mean method recovery and the coefficient of variation of the replicate

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samples for each sample loading; and also calculate the overall method recovery and coefficient of variation of the means.

8.3.3.4 Effect of the relative humidity of the test atmosphere

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

— concentration: 0,1 LV and 2 LV;

— time: 4 h;

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

— temperature (20 ± 2) ºC;

— air velocity: above minimum specified in 8.2.2.

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 can be adjusted accordingly.

Analyze the diffusive samplers by reference to standard solutions or to standard samplers spiked with known amounts of analyte. For each exposure combination, calculate the measured concentration (see 8.3.3.1) for each of the six (or more) replicate diffusive samplers. Divide each by the reference concentration of the test atmosphere (see 7.4). Calculate the mean results for each combination of concentration and relative humidity, and the differences between the means at relative humidities of 80 % and 20 % for each concentration, to estimate the effect of the relative humidity on method recovery.

8.3.3.5 Effect of the temperature of the test atmosphere

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

— concentration: 2 LV;

— time: 4 h;

— relative humidity: (50 ± 5) %;

— temperature (10 ± 2) ºC and (40 ± 2) ºC;

— air velocity: above minimum specified in 8.2.2.

The minimum range of temperature is 10 ºC to 30 ºC. If the diffusive sampler is tested outside this range, the requirements in 6.3.3 can be fulfilled by using correction factors.

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 can be adjusted accordingly.

Analyze the diffusive samplers by reference to standard solutions or to standard samplers spiked with known amounts of analyte. For each exposure combination, calculate the measured concentration (see 8.3.3.1) for each of the six (or more) replicate diffusive samplers. Divide each by the reference concentration of the test atmosphere (see 7.4). Calculate the mean results for each temperature and the mean difference to estimate the effect of the temperature on method recovery.

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 [6], [7] and [8]).

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

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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 uptake rate, timer), taking account of any specific additional requirements of the sampling protocol (for example 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 8.3.1.3, 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 8.3.3.3, 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 (9) to (11):

$$u_{c_r} = \sqrt{u_{s_r}^2 + u_{a_r}^2} \tag{9}$$

$$u_{c_{nr}} = \sqrt{u_{s_{nr}}^2 + u_{a_{nr}}^2} \tag{10}$$

$$u_c = \sqrt{u_{c_r}^2 + u_{c_{nr}}^2} \tag{11}$$

where

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

u_{c_r} , $u_{c_{nr}}$ 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 (12):

$$U = 2 \times u_c \quad (12)$$

9 Test report

The test report shall include at least the following information:

a) reference to this European standard;

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

c) the type of diffusive sampler used;

d) the independent test method used;

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.

Annex A
(informative)

Fundamentals of diffusive sampling

A.1 Principles of diffusive sampling

The mass of the analyte which can diffuse to a suitable sorbent within a certain time, i.e. the mass uptake of a diffusive sampler, m_s , in nanograms (ng), is determined by Equation (A.1) which is derived from Fick's first law of diffusion:

$$m_s = \frac{A \times D_a \times (\beta_{a1} - \beta_{a2}) \times t_e}{l} \quad \text{(A.1)}$$

where

A is the cross-sectional area of sorption surface, in square centimetres (cm²);

D_a is the diffusion coefficient of the analyte, in square centimetres per minute (cm²/min);

β_{a1} is the mass concentration of the given analyte at the beginning of the diffusion layer (i.e. at the distance l from the surface of the sorbent), in milligrams per cubic metre (mg/m³);

β_{a2} is the mass concentration of the given analyte at the end of the diffusion layer (i.e. at the surface of the sorbent), in milligrams per cubic metre (mg/m³);

t_e is the exposure time, in minutes (min);

l is the length of static air layer in sampler (or equivalent for permeation types), in centimetres (cm).

Ideally β_{a1} is equal to the mass concentration of the given analyte in the air outside the diffusive sampler and β_{a2} equals zero ("zero sink"-condition). In that case the magnitude of the compound-specific parameter, $\frac{A \times D_a}{l}$ (see Equation (A.1)), is dependent only on the diffusion coefficient of the given analyte and on the geometry of the diffusive sampler used.

However, in practice the parameters β_{a1}, β_{a2} and t_e , as well as the temperature, relative humidity, external air movement and also the presence of other compounds can influence the uptake rate. In particular, if external air movement is insufficient, diffusive uptake into the sampler can reduce the external concentration and hence decrease the concentration gradient and increase the effective value of l (see air velocity/sampler orientation test in 8.2.2). Also, if a non-ideal sorbent is used, β_{a2} will be non-zero, except for $t_e = 0$, and again the sampling rate will be reduced (see A.3), hence the back-diffusion test (see 8.3.1.1).

For type A and type B diffusive samplers, analytical recovery is an additional factor which can influence their suitability.

A special form of dependence of the uptake rate on the mass concentration β_{a1} can appear, as a result of the influence of the kinetics of the reaction between a given analyte and applied reagent, and also as a result of sorption of non-reacted analyte or as a result of side reactions.

NOTE More details on principles are given in EN 13528-3.

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A.2 Dimensions of uptake rate

For a given mass concentration β_a, in milligrams per cubic metre (mg/m³) of gas or vapour, the uptake rate $\dot{U}_d$, in cubic centimetres per minute (cm³/min), is given by Equation (A.2):

$$\dot{U}_d = \frac{m_s}{\beta_a \times t_e} \quad \text{(A.2)}$$

where

m_s is the mass of the analyte which can diffuse to a suitable sorbent within a certain time, i.e. the mass uptake of a diffusive sampler, in nanograms (ng);

t_e is the exposure time, in minutes (min).

NOTE 1 Although the uptake rate has dimensions of cubic centimetres per minute (cm³/min) this is actually a reduction of nanograms per milligrams per cubic metre per minute (ng mg^{-1} m^{-3} min^{-1}) and does not indicate a real volumetric flow of air.

NOTE 2 Common practice is to quote dimensions of diffusive uptake in $ng \cdot ppm^{-1} \cdot min^{-1}$. These are practical dimensions, since most occupational hygienists use parts per million (10^{-6}) for concentrations of gases and vapours. Uptake rates expressed in these dimensions are also relatively unaffected by temperature and pressure. Thus for a given volume fraction ϕ_a, given in parts per million, of gas or vapour, the uptake rate is given by:

$$(U_d)' = \frac{m_s}{\phi_a \times t_e} \quad \text{(A.3)}$$

where

ϕ_a is the volume fraction of the analyte.

NOTE 3 Ideal and practical uptake rates are related by Equation (A.4):

$$(\dot{U}_d)' = \dot{U}_d \times \frac{M_a}{24{,}1} \times \frac{293}{T_{at}} \times \frac{p_{at}}{101{,}3} \quad \text{(A.4)}$$

where

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

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

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

A.3 Bias due to the selection of a non-ideal sorbent

The performance of a diffusive sampler depends critically on the selection and use of a sorbent or collection medium which has high sorption efficiency. The residual vapour pressure of the sampled compound at the sorbent surface will then be very small in comparison to the ambient pressure, and the observed uptake rate will be close to its ideal steady-state value, which can usually be calculated from the geometry of the sampler and the diffusion coefficient of the analyte in air.

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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 mass uptake (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 mass uptake

B.2.1 Sources of uncertainty

For diffusive sampling, mass uptake has the following sources of uncertainty:

— uptake rate (see B.2.2); and

— sampling time (see B.2.3).

B.2.2 Uptake rate

The random and non-random uncertainty components associated with the uptake rate should be estimated from the results of the replicate samples collected from a test atmosphere at a relative humidity of 50 % and a temperature of 20 ºC (see 8.3.1.2) corrected by analytical recovery, if applicable.

The random and non-random uncertainty components associated with the uptake rate are given by Equation (B.1):

$$u_{\mathrm{ur}} = \sqrt{\frac{(K_{\mathrm{V,r}})^2}{n} + (u_{\mathrm{rc}})^2} \qquad \text{(B.1)}$$

where

u_{ur} is the relative standard uncertainty associated with the uptake rate, in percent (%);

$K_{v,r}$ is the coefficient of variation of the replicate samples, 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 (%).

B.2.3 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 can be disregarded, but for short term measurements it needs to be taken into account.

For example, if time is recorded to the nearest minute, the coefficient of variation is 1,4 % for a sampling time of 30 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).

B.3 Uncertainty associated with sampling efficiency

B.3.1 Back diffusion

The adsorption of gases and vapours on diffusive samplers can be influenced by the pressure, relative humidity and temperature of the sampled air and the concentration of chemical agents in the sampled air. These factors can affect the adsorption capacity, the performance of the adsorption process and the uptake rate.

For diffusive samplers, back diffusion can occur if there is significant variation in the air concentration of the analyte during the sampling time, in which case the sampling efficiency could be less than 100 % and the uncertainty of the back diffusion needs to be taken into account.

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

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

where

u_{bd} is the relative standard uncertainty associated with back diffusion;

Δ_{bd} is the difference, in percent (%), between the mean results of replicate samples analysed in 8.3.1.1, in percent (%).

B.3.2 Exposure time

The non-random uncertainty component associated with exposure time can be estimated by the analysis of replicate samples collected from a test atmosphere (see 8.3.3.2). Assuming a rectangular probability distribution, the uncertainty associated with exposure time is given by Equation (B.3):

$$u_{te} = \frac{\Delta_{te}}{\sqrt{3}} \quad \text{(B.3)}$$

where

u_{te} is the relative standard uncertainty associated with exposure time;

Δ_{te} is the highest difference between the mean results of replicate samples collected from test atmospheres at different exposure times, in percent (%).

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 8.3.1.3).

Assuming a rectangular probability distribution, the uncertainty associated with sample storage is given by Equation (B.4):

$$u_{st} = \frac{\Delta_{st}}{\sqrt{3}} \quad \text{(B.4)}$$

where

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

Δ_{st} is the difference between the mean results of replicate samples analysed immediately after sampling or preparation and replicate samples analysed 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, 8.3.3.4 and 8.3.3.5 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.

Measurement procedures for chemical agents using diffusive 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.5):

$$u_{\mathrm{ar}} = \sqrt{\frac{(K_{\mathrm{v,ra}})^2}{n} + (u_{\mathrm{ks}})^2} \qquad \text{(B.5)}$$

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 Equation (B.6):

$$u_{\mathrm{ks}} = \sqrt{(u_{\mathrm{pu}})^2 + \frac{(B_{\mathrm{max,sy}})^2}{3} + \frac{(K_{\mathrm{v,sy}})^2}{n}} \qquad \text{(B.6)}$$

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) %);

$B_{\mathrm{max,sy}}$ 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 (%);

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.

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.7), see reference [2].

$$u_{ab} = \sqrt{\left(\frac{B_a}{k}\right)^2 + \frac{(K_{v,ra})^2}{n} + (u_{ks})^2} \quad \text{(B.7)}$$

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;

$K_{v,ra}$ 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 ºC (see 8.3.3.3) 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.8), see reference [2].

$$u_{mb} = \sqrt{\left(\frac{B_m}{k}\right)^2 + \frac{(K_{v,rm})^2}{n} + (u_{rc})^2} \quad \text{(B.8)}$$

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;

$K_{v,rm}$ 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).

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 the 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 8.3.3.4).

Assuming a rectangular probability distribution, the uncertainty associated with the effect of humidity is given by Equation (B.9):

$$u_{\mathrm{h}} = \frac{\Delta_{\mathrm{h}}}{\sqrt{3}} \tag{B.9}$$

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 the temperature

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 ºC and 10 ºC (see 8.3.3.5).

Assuming a rectangular probability distribution, the uncertainty associated with the effect of temperature is given by Equation (B.10):

$$u_{\mathrm{T}} = \frac{\Delta_{\mathrm{T}}}{\sqrt{3}} \tag{B.10}$$

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 (%).

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 ºC (see 8.3.3.3).

The random uncertainty component can be estimated by Equation (B.11), see also ENV 13005:

$$u_{\mathrm{mp}} = \sqrt{(K_{\mathrm{v,m}})^2 + \left(1 - \frac{1}{n}\right)(K_{\mathrm{vp,r}})^2} \qquad \text{(B.11)}$$

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.12);

$K_{\mathrm{vp,r}}$ is the pooled coefficient of variation of the replicate samples, in percent (%), calculated according to Equation (B.13).

For an unequal number of replicate samples n can be estimated by Equation (B.12), see reference [9]:

$$n = \frac{N^2 - \sum_{j=1}^{J} (n_j)^2}{(J-1)N} \quad \text{with} \quad N = \sum_{j=1}^{J} n_j \qquad \text{(B.12)}$$

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 numbers of replicate samples $K_{\mathrm{vp,r}}$ can be estimated by Equation (B.13):

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$$K_{\text{vp,r}} = \sqrt{\frac{[(n_1 - 1) \times (K_{\text{v,1}})^2] + [(n_2 - 1) \times (K_{\text{v,2}})^2] + [(n_3 - 1) \times (K_{\text{v,3}})^2] + [(n_4 - 1) \times (K_{\text{v,4}})^2]}{(n_1 - 1) + (n_2 - 1) + (n_3 - 1) + (n_4 - 1)}} \quad \text{(B.13)}$$

where

$K_{\text{v,1}}$, $K_{\text{v,2}}$, $K_{\text{v,3}}$, $K_{\text{v,4}}$ are the coefficients of variation at the four tested concentrations;

n_1, n_2, n_3, n_4 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 $K_{\text{vp,r}} = \sqrt{[(K_{\text{v,1}})^2 + (K_{\text{v,2}})^2 + (K_{\text{v,3}})^2 + (K_{\text{v,4}})^2] / 4}$.

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, i.e. 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.14):

$$u_{\text{cc}} = \sqrt{(u_{\text{m}})^2 + (K_{\text{v,sy}})^2 + \frac{(B_{\text{max,p}})^2}{3}} \quad \text{(B.14)}$$

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 (%);

$K_{\text{v,sy}}$ is 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;

$B_{\text{max,p}}$ 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 [7].

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 [4].

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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.15):

$$u_{\mathrm{di}} = \sqrt{\frac{(B_{\mathrm{max,s}})^2}{3} + \frac{(B_{\mathrm{max,f}})^2}{3}} \qquad \text{(B.15)}$$

where

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

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

B.6.6 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.16):

$$u_{\mathrm{dr}} = \frac{d_{\mathrm{max}}}{\sqrt{3}} \qquad \text{(B.16)}$$

where

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

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 standards 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 standards.

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.

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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 analysed, 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.17) to (B.20):

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

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

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

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

where

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

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

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

The combined standard uncertainty, u_c, and the expanded uncertainty, U, of the measuring procedure are calculated according to Equations (9) to (12). See 8.4.2.6 and 8.4.3.

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 m-xylene in workplace air (see reference [9]). The measuring procedure concerned uses a Type B sampler and the method evaluation was carried out using a test atmosphere consisting of a mixture of toluene, ethylbenzene, styrene and m-xylene. It is an example of a level 1 evaluation. Table C.1 contains a summary of the results of the test detailed in 8.2.

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 m-xylene

Test	β_a	ϑ_{at}	RH	t_s	n	$\dot{U}_d$	$\overline{\beta}_{a,R}$	K_v	R
	mg/m^3	°C	%	h	—	cm^3/min	mg/m^3	%	%
Blank value	—	—	—	—	six unused diffusive samplers	—	—	—	—
LOD/LOQ		—	—	—	—	—	—	—	—
Sampling conditions									
Uptake rate	21,5	19,7	46	4	6	0,415	—	1,07	—
	113,3	20,7	47,5	4	6				
	225,3	19,8	54	4	6				
	437,9	20,3	52	4	6				
Back diffusion	465,15	19,4	84	0,5	6	—	433,5	2,29	93,2
Storage time									
0,1 LV high RH	23,1	18,4	82	4	6	—	22,0	4,78	95,2
2 LV high RH	427,9	18,3	80	4	6	—	411,4	1,85	96,1
Influence of relative humidity of the test atmosphere									
0,1 LV low RH	22,15	19,4	22	4	6	—	24,0	2,27	108,2
0,1 LV high RH	23,1	18,4	82	4	6	—	24,5	3,40	106,1
2 LV low RH	436,8	19,9	22	4	6	—	404,2	2,93	92,5
2 LV high RH	427,9	18,3	80	4	6	—	419,3	3,01	98,0

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Table C.1 *(continued)*

Test	β_a	ϑ_{at}	RH	t_s	n	$\dot{U}_d$	$\overline{\beta}_{a,R}$	K_v	R
	mg/m³	°C	%	h	—	cm³/min	mg/m³	%	%
Influence of air temperature of the test atmosphere									
2 LV low ϑ_{at}	432,7	14,3	52	4	6	—	399,0	2,76	92,2
2 LV high ϑ_{at}	449,2	28,4	47	4	6	—	411,5	1,73	91,6
Influence of exposure time									
1 LV	202,9	20,2	52	0,5	6	—	197,7	2,20	97,4
1 LV	225,4	19,8	54	4	6	—	222,7	3,24	98,8
1 LV	202,9	20,2	52	6	6	—	219,7	2,58	108,3

NOTE 1 8 h limit value: 221 mg/m³.
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			
Uptake rate, u_{ur}	0,4	—	See B.2.2 and Table C.1
Reference concentration, u_{rc}	—	1,7	See B.5.4, estimated to be 3 %
Sampling time, u_{ts}	0,1	—	See B.2.3, calculated from the timer used
Sampling efficiency			
Back diffusion, u_{bd}	—	3,9	See B.3.1 and Table C.1
Exposure time, u_{te}	—	6,1	See B.3.2 and Table C.1
Storage and transport, u_{st}	—	2,6	Samples are stable for at least 15 days when stored at 20 ºC
$u_{s_r} = \sqrt{\sum_{i=1}^{j_{s_r}} u_{s_r i}^2}$	0,5	—	—
$u_{s_{nr}} = \sqrt{\sum_{i=1}^{j_{s_{nr}}} u_{s_{nr} i}^2}$	—	7,9	—
$u_s = \sqrt{u_{s_r}^2 + u_{s_{nr}}^2}$	7,9		Sampling uncertainty

Table C.2 *(continued)*

Uncertainty contribution	Uncertainty		Remarks
	random %	non random %	
Method recovery			
Analytical recovery			
• B_a	—		Assumed to be 0 % for thermal desorption
• $K_{v,ra}$	—		
• u_{ks}	—		
Method bias			
• B_m	—	0,0	Calculated from the test of reproducibility (see Table C.1)
• $K_{v,rm}$	1,0	—	Calculated from the test of reproducibility (see Table C.1)
• u_{rc}	—	—	Included in uncertainty of sampled air volume
Effect of relative humidity	—	3,4	See B.5.5 and Table C.1
Effect of temperature	—	0,4	See B.5.6 and Table C.1
Method precision	5,6	—	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 [4])
Dilution of sample solutions	—	—	See B.6.5, not applicable
Instrument response drift	—	0,0	See B.6.6, estimated to be 0 % for FID (see reference [4])
Analytical precision	0,0	—	See B.6.7.1, included in replicates samples
$u_{a_r} = \sqrt{\sum_{i=1}^{j_{a_r}} u_{a_r i}^2}$	5,7	—	—
$u_{a_{nr}} = \sqrt{\sum_{i=1}^{j_{a_{nr}}} u_{a_{nr} i}^2}$	—	3,7	—
$u_a = \sqrt{u_{a_r}^2 + u_{a_{nr}}^2}$	6,8		Analytical uncertainty
COMBINED STANDARD UNCERTAINTY			
$u_{c_r} = \sqrt{u_{s_r}^2 + u_{a_r}^2}$	5,7	—	Combined random standard uncertainty
$u_{c_{nr}} = \sqrt{u_{s_{nr}}^2 + u_{a_{nr}}^2}$	—	8,7	Combined non-random standard uncertainty
$u_c = \sqrt{u_{c_r}^2 + u_{c_{nr}}^2}$	10,4		—
EXPANDED UNCERTAINTY			
$U = 2 \times u_c$	**20,8**		—

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