

English Version

Ambient air - Method for the determination of the concentration of nitrogen dioxide by diffusive sampling

Air ambiant - Méthode de détermination de la concentration en dioxyde d'azote au moyen d'échantillonneurs par diffusion

Außenluft - Bestimmung der Konzentration von Stickstoffdioxid mittels Passivsammler

This European Standard was approved by CEN on 24 February 2025.

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European foreword

This document (EN 16339:2025) has been prepared by Technical Committee CEN/TC 264 “Air quality”, 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of an identical text or by endorsement, at the latest by October 2025, and conflicting national standards shall be withdrawn at the latest by October 2025.

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

This document will supersede EN 16339:2013.

A list of the significant technical changes compared to EN 16339:2013 can be found in Annex G.

EN 16339:2025 includes the following significant technical changes with respect to EN 16339:2013:

- 4.2 and Annex A: examples of demonstration of equivalence with respect to the reference method are provided;
- 4.3 and Annex F: protective devices have been described including the advantages over the conventional design of samplers;
- Annex D: More contemporary data included for the equivalence method determination of the measurement uncertainty;
- Annex D: Sampling rates have been updated.

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

According to the CEN-CENELEC Internal Regulations, the national standards organisations 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, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Türkiye and the United Kingdom.

Introduction

EU Directive 2008/50/EC [1] stipulates that European Union Member States apply measurement methods for air quality pollutants (fixed measurement, modelling, indicative measurement, objective estimation) and associated Data Quality Objectives (DQO), depending on concentrations observed in different situations. Diffusive sampling is most often used as “indicative measurement”. The methodology described in this document has been developed to ensure the possibility for diffusive sampling to partially substitute and supplement fixed monitoring (where the reference method being that described in EN 14211 [2] is used) as a tool for the assessment of nitrogen dioxide (NO₂) with corresponding DQO.

Instead of the reference method, users may employ any other method which has been demonstrated to be equivalent according to the Guide for the Demonstration of Equivalence (GDE) [3]

Diffusive sampling is an attractive alternative to fixed monitoring by reference methodology (described in EN 14211) for the measurement of NO₂. This is due to:

- small size of diffusive samplers;
- no requirement for electric power;
- potential for covering areas with a high spatial density;
- cost effectiveness.

Consequently, diffusive samplers can partially substitute and supplement fixed monitoring as a means for the assessment of air quality, provided that they fulfil the specific DQO given in [1].

Passive samplers can be used for indicative measurements to complement air quality networks, improve modelling techniques and other air quality assessments, such as NO₂ concentrations for comparing with UNECE Critical Levels (annual mean of 30 µg NO_x/m³, expressed as a NO₂ equivalent) for the protection of vegetation and natural ecosystems [4] [5] [6].

A demonstration of equivalence according to [3] has been performed by the North Rhein-Westphalia state agency for nature, environment and consumer protection (LANUV) [7]. Some studies have compared NO₂ annual average concentrations measured by chemiluminescence and by diffusive samplers [8], [9], [10] and [11]. These have shown the potential of diffusive sampling to meet the data quality objective of 15 % expanded uncertainty for fixed measurements [1].

The methodology described in this document can be applied to obtain air quality information with a relatively high spatial density that can be used to complement the appropriate siting of fixed monitoring stations, or in the validation of dispersion models.

This document has been prepared based on the findings of reviews of implemented diffusive samplers in the European Union [12].

The methodology described in this document may also be used to determine NO₂ in indoor air. Appropriate strategies for NO₂ measurement in indoor air are described in EN ISO 16000-15 [13].

1 Scope

This document specifies a method for the sampling of NO₂ in ambient air using diffusive sampling followed by extraction and analysis by colourimetry or ion chromatography (IC). It can be used for the NO₂ measurement in a concentration range of approximately 3 µg/m³ to 130 µg/m³ [12]. A sample is typically collected for a period of 1 to 4 weeks [14], with exposure periods depending on the design of the samplers and the concentration levels of NO₂.

Several sorbents can be used for trapping NO₂ in ambient air using a diffusive sampler [15]. This document specifies the application of triethanolamine as the reagent.

This document describes the application of a tube-type sampler (with either a cylindrical or a slightly conical tube), a badge-type sampler and a radial-type sampler.

The relative expanded uncertainty of NO₂ measurements performed using these tube-type diffusive samplers can potentially be lower than 25 % for individual measurements. When aggregating results to form annual average values, the relative expanded uncertainty can be further reduced to levels below 15 % due to the reduction of random effects on uncertainty [9].

NOTE NO₂ passive samplers are also employed to measure NO_x with the addition of an oxidant to convert ambient NO into NO₂. A second NO₂ sampler is also deployed without the oxidant and the concentration of NO is determined from the difference of the two samplers [16].

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13528-2, *Ambient air quality - Diffusive samplers for the determination of concentrations of gases and vapours - Requirements and test methods - Part 2: Specific requirements and test methods*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

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

3.1 sampling period

period of time for which the measuring procedure yields a single value

[SOURCE: EN 482:2021 [17]]

3.2 combined standard uncertainty

standard measurement uncertainty [3.11] that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model

[SOURCE: JGCM 200:2012, 2.31 [18]]

3.3**efficiency of extraction**

ratio of the mass of analyte desorbed from a sampling device to that applied

[SOURCE: EN 13528-2:2002 [19]]

3.4**diffusive sampler**

device which is capable of taking samples of gases from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane, but which does not involve the active movement of air through the device

Note to entry: Active normally refers to the pumped movement of air.

[SOURCE: EN 13528-1:2002, 3.6 [20], modified, Note 2 to entry deleted.]

3.5**diffusive sampling rate**

rate at which the diffusive sampler collects a particular gas from the atmosphere

Note 1 to entry: The diffusive sampling rate is usually expressed in volume flow units of (m³/h), (ml/min) or (cm³/min).

Note 2 to entry: cm³/min may be converted to SI units of m³/s by factor $1,67 \times 10^{-8}$.

Note 3 to entry: The term “diffusive sampling rate” is sometimes referred to as “diffusive uptake rate”.

3.6**expanded measurement uncertainty****expanded uncertainty**

product of a combined standard measurement uncertainty and a factor larger than the number one

Note 1 to entry: The factor depends upon the type of probability distribution of the output quantity in a measurement model and on the selected coverage probability.

Note 2 to entry: The term “factor” in this definition refers to a coverage factor.

[SOURCE: JCGM 200:2012, 2.35 [18]]

3.7**field blank**

sealed sampler drawn from the same batch as the samplers being used for NO₂ monitoring, which is taken unopened to the field, remains closed during the sampling period at the measurement location and is returned together with exposed samplers after the sampling is completed

Note 1 to entry: This blank is only used for quality control purposes.

Note 2 to entry: A transport blank is considered to be a special case of a field blank. A transport blank is taken to the exposure site, left unopened and returned to the laboratory immediately after placement or collection of the samplers. Transport blanks may be used when regular field blanks reveal an unacceptable level of nitrite (NO₂⁻) to investigate the possibility of contamination of samplers during transport.

3.8

laboratory blank

sealed sampler drawn from the same batch as the samplers being used for NO₂ monitoring which is stored in the laboratory for the duration of the sampling period and is analysed at the same time as the returned exposed samplers

3.9

mass concentration

mean concentration during the sampling period (averaging time) which is expressed in µg/m³

3.10

measurement uncertainty

uncertainty (of measurement)

non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

Note to entry: For footnotes to the definition the reader is referred to the parent document JGCM 200:2012.

[SOURCE: JCGM 200:2012, 2.26 [18]]

3.11

standard measurement uncertainty

standard uncertainty

measurement uncertainty expressed as a standard deviation

[SOURCE: JCGM 200:2012, 2.30 [18]]

4 Description of samplers

4.1 Principle

The diffusive sampler is exposed to air for a measured time period, i.e. the exposure time. Controlled by the sampler's specific diffusive sampling rate, NO₂ migrates through the sampler diffusion path and is collected as nitrite by reaction with triethanolamine (TEA). The nitrite formed in the sampler is subsequently extracted and analysed in a laboratory. Based on the amount of nitrite determined, the diffusive sampling rate and the exposure time, the time-integrated average concentration of NO₂ can be calculated.

A number of pathways have been proposed for the reaction of nitrogen dioxide with triethanolamine. More details can be found in [21].

The diffusive sampling rate is determined either by calculation based on Fick's first law of diffusion or through calibration by exposure to standard atmospheres, and/or by field comparison of diffusive samplers measurements with measurements carried out using the EU reference method (EN 14211). This latter approach has been described in [8], [9], [10] and [22]. Values of and formulas to calculate diffusive sampling rates associated with different diffusive samplers are given in Annex C.

NOTE The theory of performance of diffusive samplers is given in EN 13528-3 [23, under revision] together with information on possible saturation of the sorbent, the effect of transients and the effect of face velocity. This document explains the dependence of diffusive sampling rates on the concentration level of pollutants and sampling time.

4.2 Diffusive samplers

4.2.1 Description

In general, three types of diffusive samplers are available with different designs: tube-type, radial-type and badge-type:

- Descriptions of the tube-type sampler with cylindrical and with conical tube are given in Annex A. The descriptions hold for sampler designs that have a proven practical validity.
- A radial-type sampler exists and is widely used in the EU. Validation data are available for this sampler [12], [24]. The sampler is described in the informative B.1.
- A badge-type NO₂ diffusive sampler exists that is based on the application of triethanolamine. Validation data are available for this sampler [12], [25], and [26]. The sampler is described in the informative B.2.

The sampler may include a protective device (4.3) in order to reduce environmental effects during sampling.

When a protective device is considered an integral part of the sampler, the performance of the sampler shall be validated including the protective device.

4.2.2 Preparation

The preparation of the sampler consists of the coating of a support with triethanolamine from a solution in water, methanol or acetone.

TEA is coated onto a suitable support. Supports that have been demonstrated to be suitable in practice are (see Annex A):

- a series (2 or 3) of circular stainless steel grids with a fine mesh size;
- a cylindrical stainless steel grid with a fine mesh size;
- a cellulose-fibre filter.

To this TEA solution a wetting agent may be added to facilitate the coating (see 4.2.2.4). In principle, one of the procedures specified in Annex A shall be used for the coating.

Preparation procedures are taken from references describing tube-type samplers with a cylindrical tube. Three preparation methods are given in Annex A. These preparation methods have proven to be effective in practice. Other methods may be used provided that their suitability has been satisfactorily demonstrated.

All reagents used shall not contain nitrite impurities higher than the laboratory blank values.

4.2.2.1 Triethanolamine (TEA)

Purity ≥ 99 %. TEA has a melting point of approximately 20 °C depending on its purity. When using volumetric techniques for measuring quantities of TEA, the TEA should be handled at temperatures well above its melting point. Alternatively, gravimetry may be used.

4.2.2.2 Acetone

Purity $\geq 99,9$ %. For the preparation of TEA coating solutions.

4.2.2.3 Ultrapure water

For the preparation of TEA coating solutions. Its conductivity shall be equal or less than 0,1 $\mu\text{S}/\text{cm}$.

4.2.2.4 Wetting agent compound

A wetting agent, for example polyoxyethyleneglycol dodecyl ether, CAS no. 9002-92-0 [27], [28], may be used for the preparation of TEA coating solutions.

NOTE This compound is commonly denominated as "Brij® 35"¹.

4.2.3 Storage of samplers before and after sampling

Manufacturer's instructions for storage and sealing shall be followed.

Typically, samplers are stored in the dark under controlled conditions below room temperature in order to minimize any undesired reactions.

Although samples may be stable for up to 4 months [29] when stored under the above conditions, it is strongly recommended to analyse the samples as soon as possible after exposure.

If samples are not stored in accordance with the recommendations, including during travel, the end user shall regularly check the impact on the quality of the measurements from the analysis of the appropriate blanks.

4.2.4 Chemical interferences

Nitrous acid and peroxyacetyl nitrate are the major chemical interferences of sorption by triethanolamine. However, in ambient air monitoring both contaminants are generally present at low concentrations relative to NO_2 . Moreover, these species can also interfere with the measurement of NO_2 when applying the EU reference method for NO_2 monitoring based on chemiluminescence (see [2] [30]).

4.3 Protective devices

4.3.1 General

Protective devices are used to reduce the measurement uncertainty with NO_2 diffusive samplers. Protective shelters or protective filters can be used, alone or in combination.

NOTE The combined use of shelters and filters demonstrated equivalence to the reference method according to the Directive (study LANUV [7]).

Examples of validation data are given in Annex F.

Protective devices shall be used consistently over time when measuring at a specific site for a prolonged period, or over space when performing monitoring campaigns, in order to ensure the internal consistency of sampler behaviour.

4.3.2 Protective shelter

It is strongly recommended to use a protective shelter to prevent:

- the entrance of particulate matter (PM) or water droplets (rain) into the sampler during sampling;
- exposure to direct sunlight;

¹ Brij® is a trademark of ICI America Inc. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of the product named.

- exposure to high wind velocities.

NOTE 1 EN 13528-3 [23, under revision] gives general recommendations for the design of protective devices.

NOTE 2 In Annex A protective devices are described for the tube-type samplers; in Annex B protective devices are described for the other samplers.

4.3.3 Protective filter

It is strongly recommended to use a protective filter at the air inlet of the diffusive sampler to prevent or reduce:

- the effect of wind on the diffusive sampling rate, e.g. wind-shortening;
- biological contamination;
- PM contamination.

In literature the term ‘membrane’ is commonly and interchangeably used for a filter. The user should ensure that the relevant term has been applied correctly to the devices deployed.

NOTE In Annex A protective filters are described for the different samplers. Examples of protective filters include a gas permeable, hydrophobic filter, or a stainless steel mesh across the air inlet.

The manufacturer’s recommended filter shall be used if available. Otherwise, the end user shall check any alternative used against the reference method to ensure that there are no sample losses of NO₂.

Typically, the diffusive sampling rate is reduced when applying a filter at the open end of the sampler.

Metal meshes are also used to reduce wind-induced effects [31].

4.4 Instructions for use

The manufacturer shall make available a manual or instruction sheet for the handling of the samplers. These shall be followed in order to ensure proper operation of the sampler. Samplers shall be deployed vertically with the air inlet end (open or covered with a protective filter) facing the ground.

5 Analysis

5.1 General

There are two commonly used methods employed to analyse for nitrite (NO₂⁻) in the aqueous extract:

- colourimetry after derivatization of the nitrite, using the Griess-Saltzman method [27] [32];
- ion chromatography [28].

The mass of nitrite on the exposed samplers is related directly to NO₂.

Further details about reagents and equipment are described in Annex E.

For each technique employed, a calibration curve shall be established by performing linear regression of the analytical responses observed against the concentrations of nitrite in the standard solutions. For each concentration except zero the lack of fit or linearity of the calibration curve shall be calculated from the relative residuals of the regression formula as:

$$\delta_i = 1 - \left| \frac{a + b \cdot c_i}{y_i} \right| \quad (1)$$

where

- δ_i is the relative residual of the regression for calibration standard i ;
- Y_i is the analytical response for the analysis of calibration standard i ;
- a is the intercept of the linear regression formula;
- b is the slope of the linear regression formula;
- c_i is the concentration of nitrite in calibration standard i .

The relative residuals shall fulfil the requirements given in Table D.1.

If matrix effects are observed, calibration standards shall be prepared in diffusive samplers with TEA.

The detection limit is 3 times the relative standard deviation of the mean laboratory blank value. The quantification limit is typically in the range between 6 to 10 times the relative standard deviation of the mean laboratory blank value.

5.2 Colorimetric method

5.2.1 General

The Griess-Saltzman derivatization method consists of reacting nitrite with a mixture of sulphanilamide and N-(naphthyl-1) ethylenediamine dihydrochloride in dilute orthophosphoric acid (see Annex E). The absorbance of the azo dye formed is measured between 537 nm and 542 nm.

5.2.2 Calibration

Calibration shall be performed by analysing a series of solutions of nitrite in mixed reagent.

A full calibration shall include at least 6 calibration standards. It is recommended to use concentrations of the calibration standards of zero (this refers to the colorimetric reagent), 0,1 µg/ml, 0,2 µg/ml, 0,4 µg/ml, 0,6 µg/ml, 0,8 µg/ml and 1,0 µg/ml of nitrite. Higher concentrations are not recommended because of potential problems with linearity [33].

The expanded uncertainty of all diluted nitrite standards shall be equal to or less than 2 %. All potential sources of uncertainty shall be included in the calculation (e.g. impurities, volumes of all glassware used, uncertainty of nitrite concentration in a certified sodium nitrite solution).

5.2.3 Extraction

The extraction shall be performed by adding the colorimetric reagent to the TEA support.

NOTE In practice, when applying colourimetry, the derivatization agent solution is directly used for extraction.

The samples shall be secured against NO₂ contamination from the laboratory air during extraction (e.g. by using caps for the extraction vessels or samplers).

The extraction shall be carried out by using a vortex mixer or vibrating tray, followed by at least 1 h of standing at ambient temperature for colour development, avoiding exposure to direct sunlight.

If the extraction can be made by other means, the laboratory will have to prove that other means are sufficient to extract the whole. This shall be done in accordance with the requirements on the desorption efficiency in EN 13528-2.

A vertical movement is needed to reach a good mixing state.

The extraction conditions and extract stabilities are given in Table 1.

Table 1 — Extraction conditions and extract stabilities for analysis by colourimetry

Sampler type	Type and volume of extract	Extraction conditions	Extract stability
Tube-type sampler with a cylindrical tube	3 ml of mixed reagent in the sampler (see Annex E)	Agitate by vortex mixing for about 15 s immediately after adding the reagents.	2 days at 0 °C - 4 °C avoiding exposure to direct sunlight
Tube-type sampler with a slightly conical tube	2 ml of mixed reagent in the sampler (see Annex E)	Another possibility to extract the tubes is to use a vibrating tray for 10 min to 30 min. Be sure that no air bubbles are present in the solution to be analysed	

5.2.4 Analysis

Set up the colourimeter in accordance with the manufacturer's instructions. Set the measurement wavelength between 537 nm and 542 nm.

NOTE A commonly used wavelength is 540 nm. However, the use of other wavelengths within the above range has been reported in guidance documents and protocols (see [12]).

Use a calibrated colourimeter to analyse derivatized samples and blanks. Determine the responses of the samples and blanks and calculate from the calibration function the mass of nitrite in the desorbed samples and blanks.

If the instrument response to a sample exceeds the calibration range, the sample shall be diluted with mixed reagent to bring its concentration within the calibration range.

5.3 Ion chromatography method

5.3.1 General

For ion chromatography, the extraction of nitrite is performed in the sampler by adding a suitable eluent.

5.3.2 Calibration

Calibration shall be performed by analysing a series of solutions of nitrite in water or eluent.

A full calibration shall include at least 6 calibration standards.

For ion chromatography it is recommended to use concentrations of the calibration standards of 0,0 µg/ml, 0,1 µg/ml, 0,2 µg/ml, 0,4 µg/ml, 0,8 µg/ml, 1,5 µg/ml and 2,0 µg/ml of nitrite. The nitrite concentrations shall be traceable to primary standards. The uncertainty requirement shall follow the approach described in Clause 5.2.2

5.3.3 Extraction

The extraction shall be performed by adding ultrapure water or eluent to the TEA support. The volume of the extraction solution is given in Table 2.

The samples shall be secured against NO₂ contamination from the laboratory air during extraction (e.g. by using caps for the extraction vessels or samplers).

The extraction shall be carried out by using a vortex shaker or vibrating tray.

Extraction can be made by other means, the laboratory will have to prove that other means are sufficient to extract the whole. This shall be done in accordance with the requirements on the desorption efficiency in EN 13528-2.

The reported stabilities of the extracts are given in Table 2.

Table 2 — Extraction conditions and extract stabilities for analysis by ion chromatography

Sampler type	Type and volume of extract	Extraction conditions	Extract stability
Tube-type sampler with both a cylindrical and a slightly conical tube	5 ml of water or eluent	Agitate by vortex shaking for about 1 min to 2 min. Another possibility is to use a vibrating tray for 10 min to 30 min	One week in the dark at 0 °C - 4 °C

5.3.4 Analysis

Set up the ion chromatograph in accordance with the manufacturer’s instructions. Use a calibrated ion chromatograph to analyse samples and blanks. Determine the responses of the samples and blanks and calculate from the calibration function the mass of nitrite in the desorbed samples and blanks.

If the instrument response to a sample exceeds the calibration range, the sample shall be diluted with water or eluent to bring its concentration within the calibration range.

The expanded uncertainty of all diluted nitrite standards shall be equal to or less than 2 %. All potential sources of uncertainty shall be included in the calculation (e.g. impurities, volumes of all glassware used, uncertainty of nitrite concentration in a certified sodium nitrite solution).

Stock standard solutions of 1 000 µg/ml can be purchased as certified solutions from different manufacturers or can be prepared by the laboratory.

6 Calculation of the concentration of nitrogen dioxide

6.1 Diffusive sampling rate

The diffusive sampling rate for the type of diffusive sampler is needed to calculate the mass concentration of NO₂ in ambient air. The diffusive sampling rate is determined by the geometry (see C.1.) of the diffusive sampler and is proportional to the diffusion coefficient of NO₂ in ambient air:

$$v = f(D)$$
 (2)

where

v is the diffusive sampling rate in m³/h:

D is the diffusion coefficient in m²/h.

The diffusion coefficient (see [35]) is a function of temperature and pressure:

$$D = f(T^{n+1}, P^{-1})$$
 (3)

where

- D is the diffusion coefficient in m^2/h ;
- T is the temperature in K;
- P is the pressure in kPa;
- n is an empirically determined parameter, with $0,5 < n < 1,0$.

Hence, the diffusive sampling rate is a function of temperature and pressure [23, under revision]:

$$v = f(T^{n+1}, P^{-1}) \quad (4)$$

Thereferenceconditions,i.e.temperatureandpressure,towhichthediffusivesamplingraterelates,need to be known as those conditions are reflected in the mass concentration. If actual temperature and pressure during the sampling time deviate from the reference conditions of the diffusive sampling rate and data of average temperature and/or pressure is available, the diffusive sampling rate shall be corrected using Formula (5):

$$v = v_{\text{ref}} \cdot \left(\frac{T}{T_{\text{ref}}} \right)^{1,81} \cdot \left(\frac{P_{\text{ref}}}{P} \right) \quad (5)$$

where

- v is the diffusive sampling rate at actual conditions in m^3/h ;
- v_{ref} is the diffusive sampling rate at reference conditions in m^3/h ;
- T is the average temperature during exposure in K;
- T_{ref} is the reference temperature at which the diffusive sampling rate is given in K;
- P is the average pressure during exposure in kPa;
- P_{ref} is the reference pressure at which the diffusive sampling rate is given in kPa.

NOTE 1 Reference conditions of a diffusive sampling rate typically refer to the annual mean conditions of a region or country if determined by calibration in the field. Diffusive sampling rates which were determined in the laboratory or available from commercial suppliers of diffusive samplers often refer to standard conditions, such as 293 K and 101,3 kPa.

NOTE 2 The pressure difference is typically small and can often be neglected. At higher altitudes, for example in the mountains, the pressure difference can be considerable.

6.2 Mass concentration

The mass concentration of NO_2 in ambient air under actual conditions of sampling is calculated using Formula (6):

$$C = \frac{m_s - m_h}{e \cdot v \cdot t} \quad (6)$$

where

- C is the mass concentration of NO_2 at ambient conditions in $\mu\text{g}/\text{m}^3$;
- m_s is the mass of nitrite found in the sample in μg ;
- m_b is the mass of nitrite found in the mean laboratory blank in μg ;
- v is the sampler diffusive sampling rate at actual conditions of sampling in m^3/h ;
- e is the efficiency of extraction of nitrite;
- t is the sampling time in h.

NOTE It is not necessary to include the efficiency of extraction of nitrite if this efficiency is shown not be significantly different from 100 % or if it is already included into the estimation of the diffusive sampling rate.

6.3 Conversion to standard conditions of temperature and pressure

The mass concentration of NO_2 in air is calculated at the ambient temperature and pressure during exposure using Formula (6). This mass concentration shall be referred to at standard conditions of temperature and pressure, as required by [1], using Formula (7):

$$c_{\text{STP}} = c \cdot \frac{T}{293} \cdot \frac{101,3}{P} \quad (7)$$

where

- c_{STP} is the concentration of NO_2 at standard temperature and pressure in $\mu\text{g}/\text{m}^3$;
- c is the concentration of NO_2 at ambient conditions in $\mu\text{g}/\text{m}^3$;
- T is the average temperature during exposure in K;
- P is the average pressure during exposure in kPa.

7 Quality control/quality assurance

For each series of analyses, the following control checks shall be performed and recorded. Corrective actions shall be taken in case of exceedance of limits set by the user, in order to ensure the quality of the NO_2 measurement results.

- a) Analysis of transport blanks and/or field blanks to detect contamination of samplers during transport, in the field and during subsequent storage prior to analysis;
- b) Analysis of calibration check solutions to determine instrument drift and appropriate re-calibration intervals. The calibration check shall be carried out using at least 3 points (zero, 50 % of calibration range and full scale) at the start of each day that samplers are analysed to detect any drift of the analytical system during a series of analyses.

At regular intervals, the following control checks shall be performed and registered. Corrective actions shall be taken in case of exceedance of limits set by the user, in order to ensure the quality of the NO_2 measurement results.

- c) Analysis of reagent solutions to determine variations of reagent blank levels;

- d) Analysis of laboratory blanks to detect contamination in the preparation or storage of samplers; at least one sampler shall be analysed for each newly prepared batch of samplers;

NOTE 1 The use of replicate laboratory blanks can be adopted to identify outliers.

- e) Determination of nitrite extraction efficiency by spiking coated samplers with known masses of nitrite followed by the determination of their recoveries [e.g. see 11]; the nitrite shall be injected directly onto the TEA support;

NOTE 2 Not required if already taken into account when determining the sampling rate, e.g. by calibration in the field

- f) Duplicate analysis of sample extracts to check analytical repeatability;
- g) Analysis of samples taken in parallel at one field site to check method precision;
- h) Checking the sensitivity of the analytical method used (e.g. the slope of the calibration curve). For NO₂ monitoring campaigns with diffusive samplers, it is necessary to implement other quality control checks that will ensure proper analysis over time such as participation in proficiency testing schemes;
- i) Checking the relevant dimensions of samplers for each new batch in order to detect any significant variation; the sampler dimensions directly affect the diffusive sampling rate;
- j) If any components of diffusive samplers are re-used, absence of nitrite after cleaning shall be checked by extracting a representative set of cleaned components and subsequent analysis of the extracts;
- k) The consistency over time of the measurement results produced using this document shall be demonstrated by performing parallel measurements with continuous chemiluminescence analysers, e.g. by using the methodology described in [3];
- l) The capped samplers shall be transported to and from the sampling site in suitable plastic containers and/or sealable clean plastic bags in order to avoid external contamination such as exhaust gases during transport.

It is recommended that the organisations performing the ongoing quality control procedures are accredited according to an internationally accepted standard.

NOTE 3 EN ISO/IEC 17025 is a suitable harmonized international standard that can apply.

NOTE 4 A formal accreditation by a member body of the European Accreditation Organization to EN ISO/IEC 17025 [35] is a demonstration of conformity.

8 Measurement strategy

8.1 Calibration of the diffusive sampling rate

Information about the diffusive sampling rates and (potential) effects of concentration and environmental factors is provided in Annex C. This information will cover most practical conditions under which the samplers are used. When a sampler is to be used outside the range of concentration and environmental factors specified by the manufacturer, the diffusive sampling rate and its uncertainty shall be determined experimentally. This shall be done – where possible – by a combination of laboratory and field experiments. Information about experimental approaches and evaluation of results can be found in [31].

8.2 Siting criteria

Information on siting criteria can be found in [22]. Further information for determining appropriate monitoring sites for diffusive samplers can be found in [36] and [37].

NOTE 1 The use of diffusive samplers and reference instruments are defined in Directive 2008/50/EC in terms of the levels of NO₂ that are present in the ambient air.

NOTE 2 Type of monitoring site can influence the measurement performance of diffusive samplers. Some of the influences can be reduced/overcome by using protective devices (see 4.3.).

8.3 Use of replicates

The use of parallel samples is usually recommended. By performing replicates, the variability of measurements can be assessed, ensuring data consistency. Replicates serve as a quality control measure (see Clause 7) and help reduce measurement uncertainty (see Clause 9).

8.4 Exposure

All handling of samplers shall be done in such a way that contamination of the sampler or re-usables ~~sachaps~~ is avoided. Follow the manufacturer's instructions for specific sampling handling, for example, for opening and closing of samplers.

Mount the sampler at the appropriate site, using a support for the duration of the exposure period, and fit the protective shelter (4.3.2) if needed.

The actual permissible period of sampling may vary with the sampler design. Different designs of diffusive samplers have different diffusive sampling rates; the exposure time shall be such that the mass of nitrite is within the quantification limit and maximum capacity of the sampler specified by the manufacturer.

NOTE 1 A simple method for predicting the mass of nitrite in a sampler is to multiply the sampling time by the expected highest NO₂ concentration and the nominal diffusive sampling rate.

NOTE 2 At high concentrations or large concentration fluctuations a longer exposure time has been shown to underestimate NO₂. [38]

Prepare field blanks by using samplers identical to those used for sampling and subjecting them to the same handling procedure as the samples except that they will be kept unopened. The number of blanks shall be $\geq 10\%$ of the number of samplers exposed. When the number of samplers exposed simultaneously exceeds 30, it is sufficient to use 3 field blanks.

After exposure, collect and close the samplers, and store these as described in 4.2.3.

Exposure time shall be assessed taking into consideration the purpose of sampling, local pollution levels and the maximum capacity of the sampler.

8.5 Co-location sites

The co-location sites used for calibration purposes and quality control with reference instruments shall be representative of the main deployment sites of the network.

For example, all site types, e.g. road side, industrial or background, shall be represented in the co-location studies if they are part of the network.

Samplers including protective measures shall be installed as close as possible to the inlet of the reference instrument.

8.6 Auxiliary information

Information about average air temperatures and pressures during sampling may be necessary for the conversion of measurement results to conditions of standard temperature and pressure. These data may be obtained from measurements or from local meteorology stations.

Information about the average temperature, relative humidity and wind speed may also be required to check that the sampler has been used under the conditions for which it has been validated, or as parameters for the calculation of the effective diffusive sampling rate during the sampling period.

9 Performance requirements and measurement uncertainty

In this document, the uncertainty assessment is based on two approaches, the direct approach (see D.1) and the indirect approach (see D.2).

The direct approach employs co-location studies with the reference method. This method uses the equivalence tool [39].

The indirect approach calculates the measurement uncertainty using the guide to the expression of uncertainty in measurement (GUM) [40].

The expanded measurement uncertainty requirement for indicative measurements is $\pm 25\%$.

The parameters given in Table D.1 have been identified to contribute to the uncertainty of concentrations of NO₂ measured by diffusive sampling and subsequent analysis by colourimetry or ion chromatography.

When data for example, four-weekly results, are aggregated to form a one-year average value, the random contribution to the uncertainty for this annual average measurement result will be strongly reduced. When the results per sampling period are based on replicated measurements per site, the uncertainty will be reduced further.

NOTE Directive 2008/50/EC [1] specifies limit values for NO₂ in ambient air, requirements for data capture and measurement uncertainty.

10 Report

The test report shall contain at least the following information:

- the type of sampler used;
- the complete identification of the sample(s);
- the sampling location(s), sampling period(s);
- the average barometric pressure and average temperature during sampling, if relevant;
- any unusual features noted during the measurements;
- the value(s) of the NO₂ diffusive sampling rate(s) used with uncertainty statement (if available) and reference;
- the method of analysis used;
- the analytical results;
- the NO₂ concentrations determined accompanied with an uncertainty statement;

- any deviations from procedures described in this European Standard;
- the responsible person checking the analysis, the calculation of the test results and their uncertainties.

NOTE Any other metadata such as personnel involved in deployment and analysis can be included.

Information about the following items needs not to be included in the report but shall be made available upon request:

- the date of preparation and method of preparation of the sampler; or, if commercial samplers are used, the identification code of the series of samplers;
- results for field/transport blanks.

Annex A (normative)

Description of tube-type samplers

A.1 Tube-type sampler with a cylindrical tube

A.1.1 Specifications of the sampler

The tube-type samplers with a cylindrical tube are usually exposed between 1 and 4 weeks in accordance with the results of field validation tests obtained in many sites in Europe [12].

Samplers are stable for up to one year [28] when prepared according to the preparation method described in A.1.3. and stored under the conditions described in 4.2.3.

The specification of the samplers is summarized in Table A.1. There are different types of cylindrical tubes. Type 2 is a modification of Type 1, where the cross-sectional area is greater and it has only one grid to accommodate the sorbent.

Table A.1 — Specifications of the tube type sampler with a cylindrical tube

Exposure time (weeks)	NO ₂ Detection Limit (µg/m ³)	NO ₂ Detection Limit (µg NO ₂ /sampler)	Sorbent preparation technique	Range (µg/m ³)	Type
4	< 1,5	0,028	20 % TEA/water	1 to 100	Type 1
4	< 2,0	0,043	50 % TEA/acetone	1 to 100	Type 1
4	0,4	0,017	50 % TEA/acetone	1 to 100	Type 2
2	0,9	0,017	50 % TEA/acetone	1 to 200	Type 2

NOTE Under certain circumstances underreading can be observed with this type of sampler [37].

A.1.2 Description

A sampler consists of an acrylic, polypropylene or glass tube of about 7,1 cm length and 1,1 cm internal diameter. It may be exposed as an open tube (Figure A.1) or it can be closed with a membrane at one end (Figure A.2). The membrane is added to limit the effect of wind velocity on the diffusive sampling rate and improves the precision of the method. Two or three stainless steel meshes are held in a cap at the opposite end. The cap at the end of the tube may be substituted with a membrane. It is necessary to check that the membrane is precisely seated at the end of the tube to make sure that NO₂ only diffuses through the membrane.

The capacity of triethanolamine to absorb NO₂ is reduced by direct exposure to sunlight. Therefore tubes should be protected either using an opaque cap or using a protective box (see Figure A.3).

A.1.3 Preparation

Stringent cleaning method for long shelf life

The method of preparation giving the lowest and most repeatable blank levels is to clean tubes, membranes and caps (opaque caps and transparent cap) with ultrapure water using a vortex shaker and changing the water every half an hour for 3 h. Subsequently, all sampler components are placed in an electric oven at 45 °C until they are completely dry.

The stainless-steel mesh discs are cleaned with ultrapure water in an ultrasonic bath, at 60 °C for 5 h, changing the water every half an hour. Then they are placed in an oven, flushed with nitrogen at 125 °C until they are completely dry.

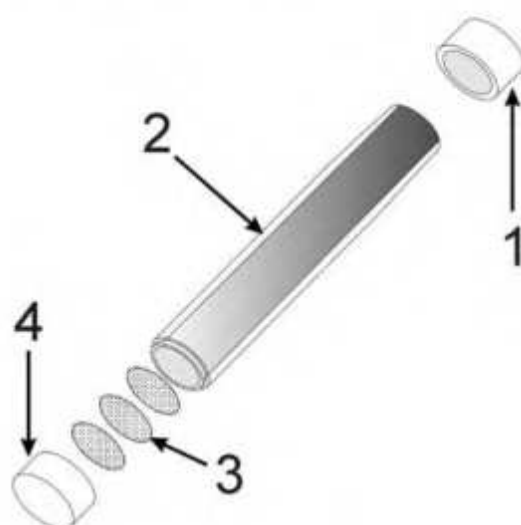
Less stringent cleaning

Tube components should be thoroughly cleaned using a suitable detergent. This may be done using an ultrasonic bath. Components should then be thoroughly rinsed in water. Final rinse should be in deionised water. Components should be thoroughly dried before use.

Sampler preparation methods

Different procedures for preparation are available [9]:

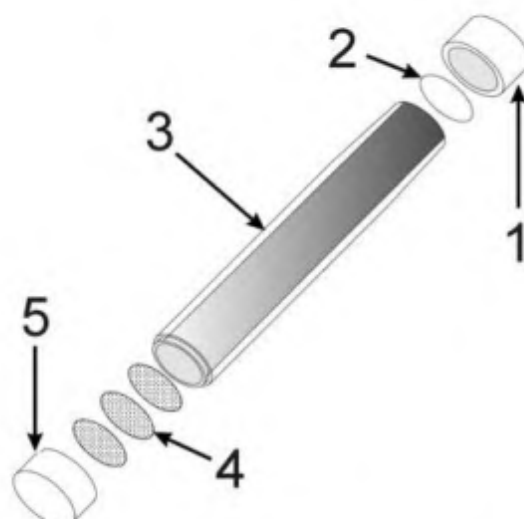
1. From a 10 % solution of TEA in ultrapure water with 0,3 % of wetting agent, of which 40 µl is spread all over the meshes using a micropipette onto three stainless grids already placed in an opaque cap (4, see key to Figures A.1 and A.2). The tube is inserted into the cap while the other end is sealed with another cap (1).
2. From a 20 % solution of TEA in deionised water, of which 50 µl is pipetted onto two stainless steel meshes already placed in an opaque cap. The tube is inserted into the opaque cap (4) while the other end is sealed with another colourless cap (1);
3. From a 50 % solution of TEA in acetone, with grids dipped into the solution and dried before assembly. Two stainless steel meshes are placed in an opaque cap (4). The tube is inserted into the coloured cap while the other end is sealed with another cap (1).



Key

- | | |
|---|--|
| 1 | cap to be removed during sampling |
| 2 | acrylic plastic tube |
| 3 | stainless steel meshes coated with TEA |
| 4 | cap accommodating the meshes |

Figure A.1 — Traditional cylindrical diffusion tube

**Key**

- 1 cap to be removed during sampling and replaced by a filter holder
- 2 PTFE membrane
- 3 acrylic plastic tube
- 4 stainless steel meshes coated with TEA
- 5 cap accommodating the meshes

Figure A.2 — Membrane closed cylindrical tube protective boxes



Figure A.3 — Tube type sampler with a cylindrical tube with shelter

The sampler shall be stored in a sealed plastic container, at reduced temperatures, e.g. 0 °C to 4 °C, in the dark. Before sampling it shall be checked that no drop of the absorbing solution is visible on the tube walls.

NOTE The sampler described in A.1 refers to type 1. Type 1 and type 2 samplers are both commercially available.

A.2 Tube-type sampler with a slightly conical tube

A.2.1 Specifications of the sampler

The tube-type sampler with a slightly conical tube can be exposed for 1 to 4 weeks in accordance with the results of field validation tests obtained at several sites in Europe [12] for NO₂ concentrations between 1 µg/m³ and 200 µg/m³. Field studies have shown that exposure periods up to 6 weeks are feasible without introducing deviations [12].

The limit of detection of the sampler for different sampling periods as well as other specifications are summarized in Table A.2.

Table A.2 — Specifications of the tube type sampler with a slightly conical tube

Exposure time (weeks)	NO₂ Detection Limit (µg/m³)	NO₂ Detection Limit (µg NO₂/sampler)	Sorbent preparation technique (% TEA/acetone)	Range (µg/m³)
4	0,4	0,01	12,5	1 to 100
2	0,8	0,01	12,5	1 to 200

A.2.2 Description

The sampler is shown in Figure A.4. It consists of an opaque polypropylene tube which is slightly conical with dimensions given in Figure A.4.

NOTE 1 The conical design is due to the manufacturing process of the tube and has no influence on the diffusion process.

At the upper, narrow end three TEA-coated stainless steel grids are installed between the tube and the white cap. The small red cap is used to close the sampler. It is removed during sampling and replaced by a protective filter (green cap), see Figure A.5.

This protective filter (also known as glass frit, turbulence barrier or membrane) reduces the effect of wind on the diffusive sampling rate [10, 11] and reduces contamination (dust, spiders, insects) of the sampler. The filter properties can be described as follows: pore size of 160 µm to 250 µm (porosity 0, P250 according to ISO 4793 [41]), 10 mm diameter and a thickness of 3 mm (borosilicate glass according to ISO 3585 [42]).

The samplers are exposed in protective shelters (see Figure A.6). These shelters are designed to protect the samplers from environmental factors such as rain, sunlight and wind. The shelters are an integral component of the measurement method and support an easy installation of up to six diffusion tubes.

NOTE 2 The sampler described in A.2 is commercially available.

Dimensions in millimetres

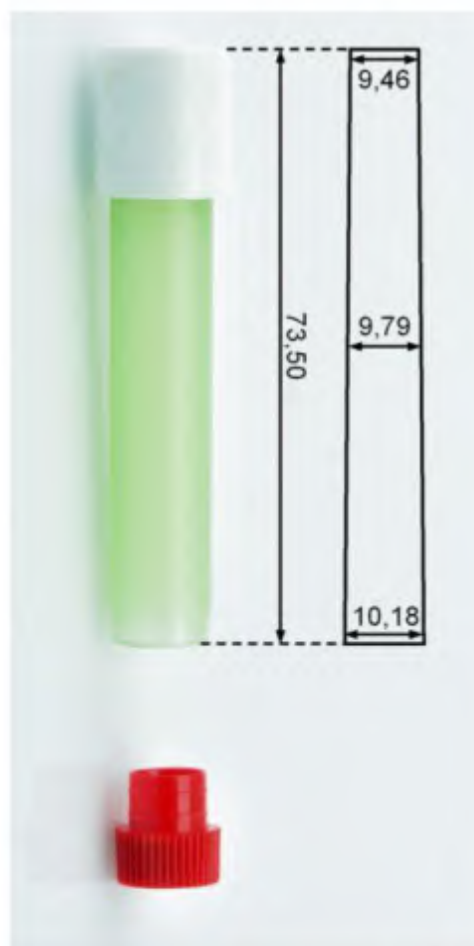


Figure A.4 — Tube-type sampler with a slightly conical tube



Figure A.5 — Protective filter (glass frit)



Figure A.6 — Protective shelter for NO₂ sampler

A.2.3 Preparation

Tubes, grids and caps are cleaned with detergent solution in an ultrasonic bath, rinsed several times with demineralized water and air-dried.

Clean and dry grids are dipped into the absorbing reagent consisting of a solution of TEA – acetone 1:7 by volume (12,5 % TEA). The wet grids are subsequently placed on absorbent paper using forceps and gently blotted. During this step the acetone is evaporated and the stainless-steel grids are coated with TEA.

Three coated grids are stacked into the white cap of the sampler. Next, the tube is inserted into the white cap to hold the grids in place. In the final step, the red cap is placed on the other end of the tube.

A.2.4 Extraction and analysis

The analytical procedure for the determination of the mass of nitrite collected on the sampling substrate generally consists of that described in Clause 5.

Annex B (informative)

Description of other samplers

B.1 Radial sampler

B.1.1 Specifications of the sampler

Exposures for 2 days up to 2 weeks are feasible, in accordance with laboratory validation tests carried out under the requirements of EN 13528-1:2002 and EN 13528-2:2002.

Samplers are stable for up to one year when stored under the conditions recommended by the manufacturer (see B.1.3).

The limit of detection of the sampler for different sampling periods as well as other specifications are summarized in Table B.1.

Table B.1 — Specifications of the radial sampler

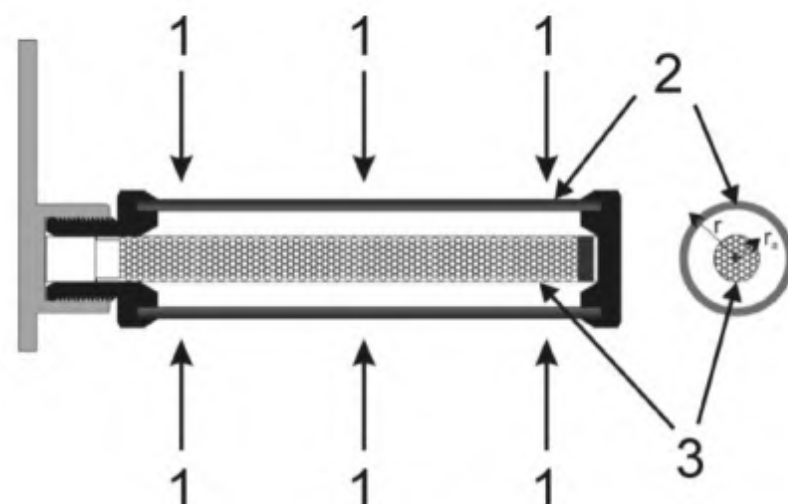
Exposure time (days)	NO₂ Detection Limit (µg/m³)	NO₂ Detection Limit (µg NO₂/sampler)	Sorbent preparation technique (see B.1.3.)
7	1,3	0,75	TEA with traces of ethanol
14	0,6	0,75	TEA with traces of ethanol

B.1.2 Description

The radial-type diffusive sampler (see Figure B.1 to B.3) consists of a cylindrical outer surface which acts as a diffusive membrane: the gaseous molecules move radially towards an adsorbent bed which is cylindrical too and coaxial to the diffusive surface. The diffusive body may be fitted to the supporting plate either in a vertical or horizontal position.

Although the sampler was tested up to 80 % RH for 7 days with no adverse effect, the sorption of large quantities of water by the cartridges may sometimes affect the sampler's performance. Therefore, a shelter is important to protect radial samplers from adverse weather conditions. For outdoor exposure, a mountable polypropylene shelter is available. The shelters are open on three sides. A shelter can house up to four samplers.

NOTE The sampler described in B.1 is commercially available.



Key

- 1 molecule flow direction
- 2 cylindrical diffusive surface
- 3 cylindrical adsorbing surface

Figure B.1 — Radial sampler design



Figure B.2 — Radial sampler supporting plate



Figure B.3 — Radial sampler shelter

B.1.3 Preparation

The commercially available adsorbing cartridges are already impregnated with TEA and ready for use; no further preparation by the user is needed.

Samplers shall be sealed and stored at ambient temperature in a clean environment, free from any air pollutant

B.1.4 Extraction and analysis

The adsorbent cartridges are placed in sterile plastic or glass 10 ml tube and are extracted using 5 ml of ultrapure water. The extraction may be carried out by using vortex shaking for about 10 min, followed by 30 min of standing at ambient temperature in the dark.

The analytical determination of the mass of nitrite collected on the sampling substrate is performed by ion chromatography, as described in Clause 5. The column thermostating is recommended.

B.2 Badge-type sampler

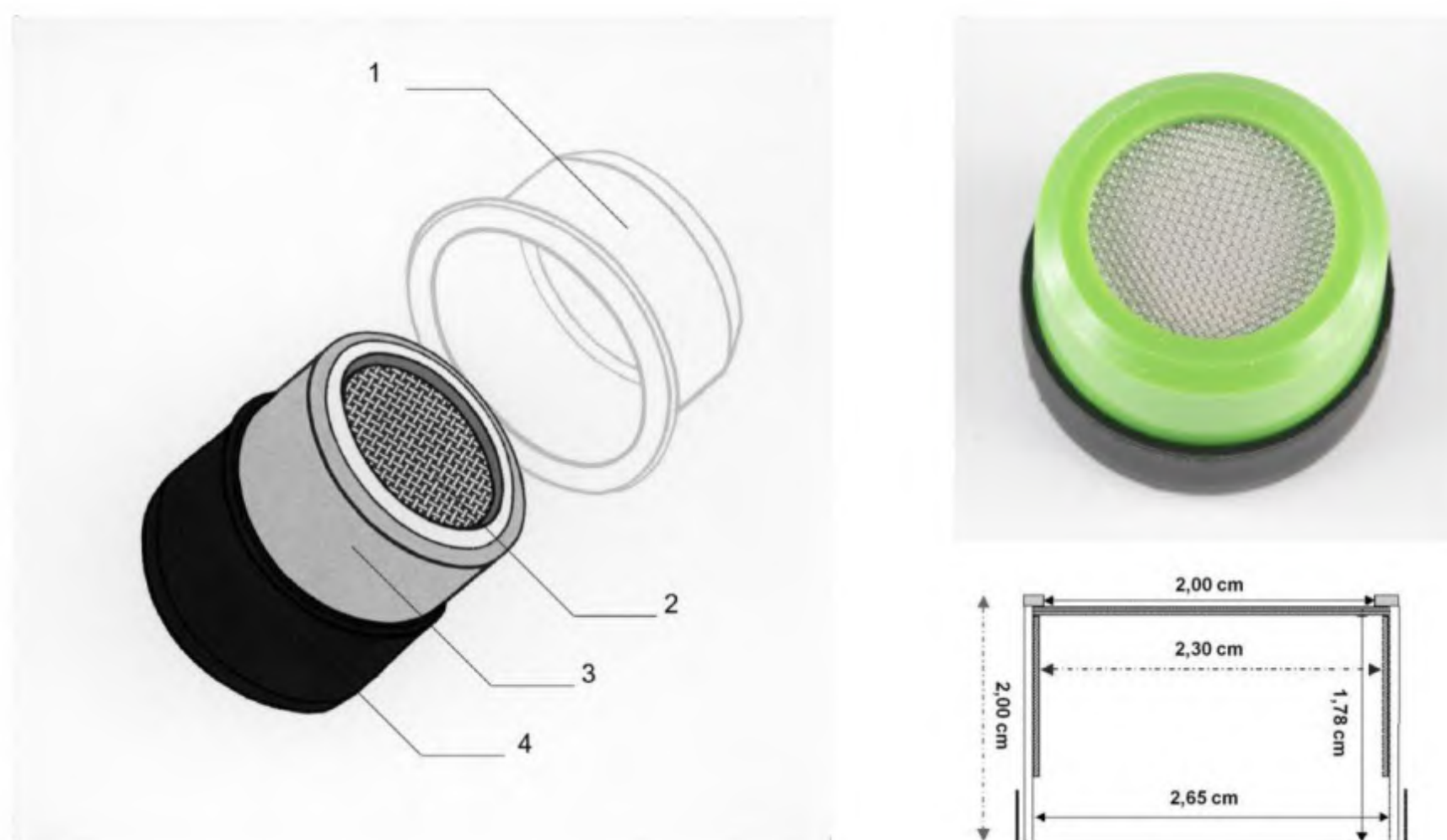
B.2.1 Specifications of the sampler

The badge-type sampler (see Figure B.4 and B.5) typically shows a higher sampling rate compared to other tube-type samplers due to the different dimensions. This higher sampling rate leads to lower detection limits and/or shorter exposure times.

The limit of detection of the sampler for different sampling periods as well as other specifications are summarized in Table B.2.

Table B.2 — Specifications of the badge-type sampler

Exposure time (days)	NO ₂ Detection Limit (µg/m ³)	NO ₂ Detection Limit (µg NO ₂ /sampler)	Sorbent preparation technique (% TEA/acetone)	Range (µg/m ³)
1	2,0	0,04	12,5	2 to 250
7	0,3	0,04	12,5	1 to 200
14	0,15	0,04	12,5	1 to 100
28	0,08	0,04	12,5	1 to 50



Key

- 1 cap to open and close the sampler
- 2 built-in protective filter
- 3 sampler housing
- 4 black cap containing TEA coated filter

Figure B.4 — Badge-type sampler: schematic representation



Figure B.5 — Badge-type sampler installed using a protective shelter

B.2.2 Description

The body of the sampler (Figure B.4) is a cylindrical plastic housing (inlet diameter 2,00 cm; inner diameter 2,30 cm; inner length 1,78 cm) with a build-in protective filter (Figure B.4, item 2). The sampler is opened by taking off the transparent cap (Figure B.4, item 1) in order to start collecting NO₂ on a TEA-impregnated cellulose filter. This filter is placed at the bottom of the sampler, i.e. inside the black cap (Figure B.4, item 4) and held in position when the sampler is assembled.

The samplers are exposed in protective shelters (see Figure B.5). These shelters are designed to protect the samplers from environmental factors such as rain, sunlight and wind. The shelters are an integral component of the measurement method and support an easy installation of up to three badge-type samplers.

NOTE The sampler described in B.2 is commercially available.

B.2.3 Preparation

All parts of the sampler shall be cleaned beforehand with detergent solution, rinsed several times with demineralized water and air-dried.

Clean and dry cellulose filters are dipped into the absorbing reagent consisting of a solution of TEA – acetone 1:7 by volume (12,5 % TEA). The wet filters are subsequently placed on absorbent paper using forceps and gently blotted. Afterwards, filters are dried in vacuum for 5 min to evaporate the acetone.

The coated filter is placed at the bottom of the black cap and the sampler is assembled. In the final step, the transparent cap is used to close the sampler.

B.2.4 Analytical method

The analytical procedure for the determination of the mass of nitrite collected on the sampling substrate generally consists of that described in Clause 5.

Annex C (informative)

Estimation of the diffusive sampling rate of the samplers

C.1 General

The diffusive sampling rate of a particular sampler can be estimated using several approaches:

- from first principles using Fick's first law of diffusion (see Table C.1);
- estimation based upon comparisons of measurements results obtained using diffusive samplers and chemiluminescence analysers (see Table C.2).

NOTE In practice, both methods of estimation have only been applied for a limited number of samplers.

When protective filters are employed the simple theoretical approach is no longer valid. It should be noted that external variables influence the simple model approach and issues such as saturation, turbulence inside the diffusion path, non-steady-state conditions become important. In such cases, an experimental determination of the sampling rate is recommended.

C.2 Theoretical calculation

The first method uses the Formula (C.1) derived from Fick's first law of diffusion by integration of the mass uptake over the diffusion path:

$$v_{ref} = \frac{D_{ref} \cdot S}{L} \quad (C.1)$$

where

- v_{ref} is the diffusive sampling rate at reference conditions in cm³/min;
- L is the diffusion length in cm;
- S is the cross-sectional area in cm²;
- D_{ref} is the diffusion coefficient of NO₂ in air at reference conditions in cm²/min.

Table C.1 — Diffusive sampling rates

Sampler type	Dimensions	Reference conditions of Exposure	Diffusive sampling rate
Tube-type sampler with a cylindrical tube [23, 42]	L = 7,1 cm and S = 0,935 cm ²	101,3 kPa and 21,1 °C	0.0202 cm ³ /s. 1,21 cm ³ /min, 72,8 cm ³ /h
Tube-type sampler with a cylindrical tube [43]	L = 7,1 cm and S = 0,935 cm ²	101,3 kPa and 11 °C	0.0191 cm ³ /s 1,17 cm ³ /min, 68,8 cm ³ /h
Tube-type sampler with a slightly conical tube [12]	L = 7,35 cm S1 = 0,703 cm ² S2 = 0,814 cm ²	95,0 kPa and 9 °C	0.0142 cm ³ /s. 0,85 cm ³ /min, 51,0 cm ³ /h.
Tube-type sampler with a slightly conical tube [23]	L = 7,35 cm S1 = 0,703 cm ² S2 = 0,814 cm ²	101,3/ kPa and 21 °C	0.0158 cm ³ /s. 0,947 cm ³ /min, 56,8 cm ³ /h
Badge-type	L = 1,78 cm, S = 4,155 cm ² . Air barrier made of stainless steel mesh and a cellulose filter.	20 °C	0,289 cm ³ /s, 17,33 cm ³ /min 1040 cm ³ /h

C.3 Experimental approach

C.3.1 Field approach

The diffusive sampling rate may also be evaluated by comparison of NO₂ in ambient air measured by diffusive samplers against the reference method (EN 14211 [2]). These measurements have to be performed at an appropriate and representative number of sites over a time period that includes all typical meteorological conditions: at least six months of sampling distributed over a whole calendar year. More information on the way to perform such measurements is given in the Guide to the demonstration of equivalence of ambient air monitoring methods [3].

The diffusive sampling rate can be directly calculated as the slope of the regression line of the mass of NO₂ sampled by the diffusive sampler on the y-axis against the dose (concentration measured with the reference method multiplied by the exposure time) on the x-axis and (see Figure C.1). Two estimations of the uptake using this method are given in Table C.2.

Table C.2 — Experimentally determined diffusive sampling rates

Sampler type	Dimensions	Diffusive sampling rate ^a	Coefficient of diffusion – Reference conditions of Exposure
Tube-type sampler with a slightly conical tube [11] with protective filter	L = 7,35 cm, S = 0,814 cm ²	$4,40 \times 10^{-5} \text{ m}^3/\text{h}$, $0,734 \text{ cm}^3/\text{min}$,	Tubes were exposed for periods of approx. 4 weeks at 9 different sites in North Rhine-Westphalia over three years (2007 to 2009)
Badge-type with protective filter	L = 1,78 cm, S = 4,155 cm ²	$93,0 \times 10^{-5} \text{ m}^3/\text{h}$ $15,5 \text{ cm}^3/\text{min}$ (Manufacturer information)	Linearity of response was evaluated by exposure to known concentrations of NO ₂ mixtures with purified air at 50 % relative humidity and 20 °C
Tube-type sampler with a cylindrical tube and filter [31]	L = 7,65 cm. S = 2,35 cm ²	$6,64 \times 10^{-5} \text{ m}^3/\text{h}$, $1,11 \text{ cm}^3/\text{min}$	Tubes exposed in exposure chamber for 28 days. Several exposures in range 1 to 2,5 x ALV ^b , Wind speed 0,5 to 2 m/s. Diffusive sampling rate constant over these conditions. Also field measurements.
^a Calculated as the slope of the regression line of the mass of nitrite collected by samplers against the NO ₂ dose (see Figure C.1). ^b ALV is the annual limit value as described in EU Directive 2008/50/EC [1].			

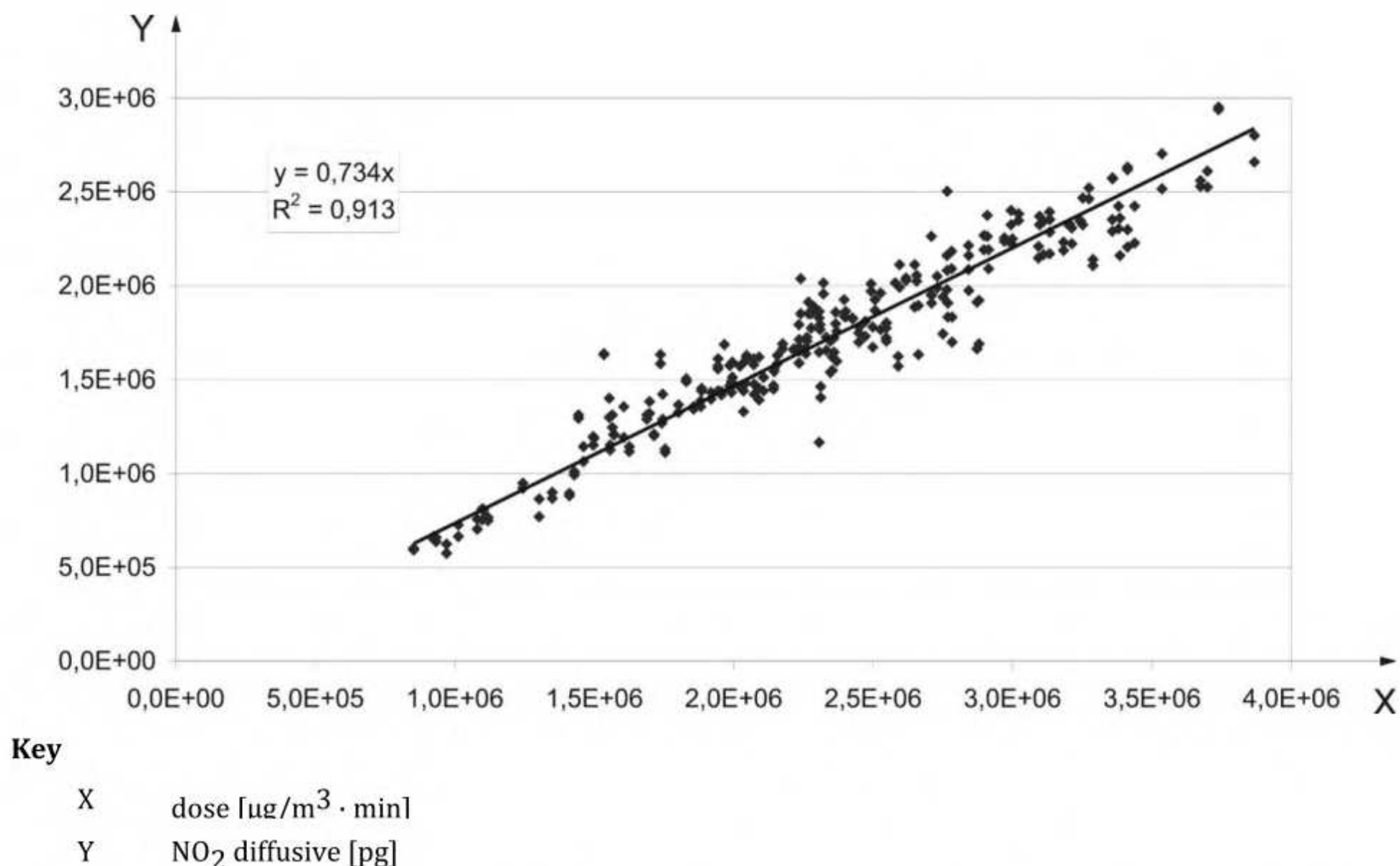


Figure C.1 — Determination of the diffusive sampling rate as the slope of the regression line of the nitrite mass uptake of tube-type sampler with a slightly conical tube versus NO_2 field-measurements using chemiluminescence analysers

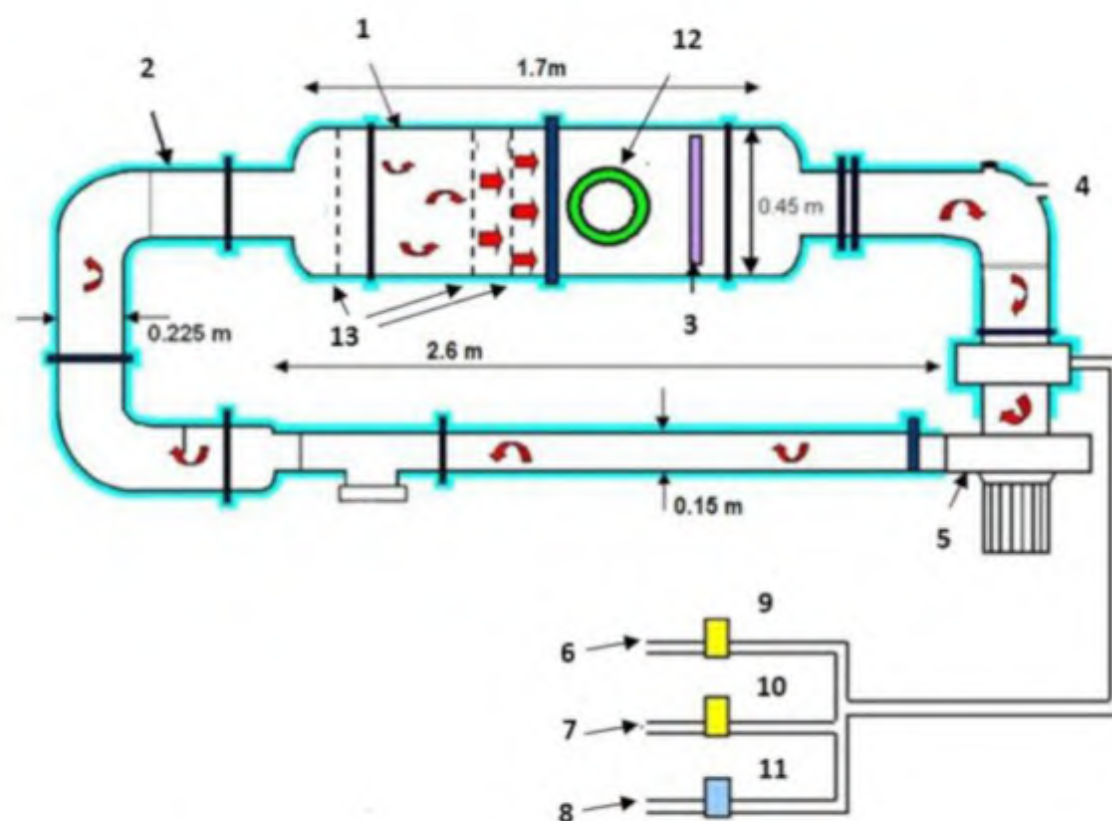
C.3.2 Laboratory approach

To carry out laboratory tests to validate the performance of diffusive samplers an exposure chamber is required. It should be made of inert materials depending on the compounds that will be employed in the study.

The chamber shall incorporate individual adjustment of parameters such as concentration, relative humidity, temperature and air speed, and the specified conditions shall be maintained over time intervals of hours to several weeks for the exposure tests. The concentration of the monitored gaseous compounds and relevant environmental parameters shall be monitored during the tests using calibrated measuring instruments. An example is shown in Figures C.2 and Figure C.3 for the measurement of the NO_2 diffusive sampling rate in a Controlled Atmosphere Test Facility (CATFAC) [30].



Figure C.2 — Photograph of the Controlled Atmosphere Test Facility (CATFAC)

**Key**

- | | |
|----|------------------------------|
| 1 | cooling/heating coils |
| 2 | insulation |
| 3 | adsorption tube test plane |
| 4 | outlet |
| 5 | fan |
| 6 | inlet for parent gas mixture |
| 7 | inlet for dilution air |
| 8 | inlet for water |
| 9 | 0,02 l/min MFC |
| 10 | 15 l/min MFC |
| 11 | 15 l/min MFC |
| 12 | access port |
| 13 | grid |

Figure C.3 — Schematic diagram of CATFAC

The exposure chamber shall be equipped with a dynamic gas delivery system capable of generating single and multiple component atmospheres of known composition in air. A number of techniques are available including the dynamic dilution method using concentrated cylinders (EN ISO 6145-7 [46]), static methods employing permeation (EN ISO 6145-10 [47]), diffusion (EN ISO 6145-8 [48]), critical orifices (EN ISO 6145-6 [49]), injection syringes (EN ISO 6145-4 [50]) and other methods (ISO 6145-2 [51], EN ISO 6145-5 [52] and EN ISO 6145-9 [53]).

Annex D (informative)

Measurement uncertainty

D.1 Direct approach

D.1.1 General

Calculation may be performed according to [22]. A minimum of 4 monitoring sites should be used with a minimum of 12 values at each measuring site. The uncertainty of the reference method results is set to the standard deviation of repeatability of the chemiluminescence method which is close to zero.

Annex C of EN ISO 20988:2007 [54] presents a worked example of evaluation of a method of measurement using diffusive samplers.

Another approach is available in the literature [55].

The European Union has defined how to calculate the equivalence of a Candidate Method (CM) to a Standard Reference Method (RM) [3] and this has been used to calculate the equivalence of the different types of diffusion tube measurement to the chemiluminescence NO₂ analyser. The equivalence demonstration is based on the linear relationship between the candidate (non-reference) method and the reference method and the uncertainties around this linear relationship. The process is summarized below:

For the evaluation of the uncertainty due to the 'lack of comparability' between candidate and reference methods it is assumed that the relationship between measurement results of both methods can be described by a linear relation of the form given in Formula (D.1).

$$y_i = a + bx_i \quad (D.1)$$

where

x_i is the average result of the reference method over period i ;

y_i is the result of the candidate method over period i (average result in case of replicates).

The relation between the results of the candidate method and the results of the reference method is established for the candidate instrument / method using a regression technique that leads to a symmetrical treatment of both variables. A commonly applied technique is orthogonal regression [53].

Preconditions for acceptance of the full data set are that:

- the slope b is insignificantly different from 1: $|b-1| \leq 2 \cdot u(b)$;
- the intercept a is insignificantly different from 0: $|a| \leq 2 \cdot u(a)$.

where $u(b)$ and $u(a)$ are the standard uncertainties of the slope and intercept, respectively, calculated as the square root of their variances. If these preconditions are not met, the candidate method may be calibrated using the values obtained for slope and/or intercept. The calibration shall only be applied to the full data set. The uncertainty in the results of the candidate method from comparison with the reference method, u_{CR} , is calculated using a general formula describing u_{CR} as a function of concentration x_i . The general relationship describing the dependence of u_{CR} on x_i is given by Formula (D.2).

$$u_{CR}^2(y_i) = \frac{RSS}{n-2} + u^2(x_i) + \frac{[a + (b-1)x_i]^2}{\dots} \quad (D.2)$$

where

RSS is the sum of (relative) residuals resulting from the orthogonal regression;

u^2 is the uncertainty of the results of the reference method.

The value used for the reference method uncertainty in all the data analysis is $0 \mu\text{g}/\text{m}^3$, as the random uncertainty in the reference method will tend to zero when the hourly measurements are averaged to produce both monthly and annual averages.

RSS , the sum of (relative) residuals is calculated using Formula (D.3).

$$RSS = \sum_{i=1}^n (y_i - a - bx_i)^2 \quad (D.3)$$

The combined relative uncertainty of the candidate method, w_{CM} , is then calculated according to Formula (D.4).

$$w_{cm}^2(y_i) = \frac{u_{CR}^2(y_i)}{y_i^2} \quad (D.4)$$

The expanded relative uncertainty of the candidate method, W_{CM} , is then calculated according to Formula (D.5).

$$W_{CM} = w_{CM} k \quad (D.5)$$

The large number of experimental results means that a coverage factor $k = 2$ may be used.

If the expanded relative uncertainty, W_{CM} , is less than the data quality uncertainty objectives given in 2008/50/EC then the candidate method is considered to be equivalent to the reference method and can be used for Fixed and/or Indicative measurements depending on the value of W_{CM} .

If the expanded relative uncertainty, W_{CM} , is not below the data quality uncertainty objectives then the candidate method can be calibrated using the slope and/or intercept correction obtained from the linear regression, and a recalibrated expanded relative uncertainty of the candidate method $W_{CM,cal}$ is calculated.

Three types of recalibration can be used and these are summarized below:

1. The slope b is not significantly different from 1: $|b-1| \leq 2.u(b)$, the intercept a is significantly different from 0: $|a| > 2.u(a)$.

In this case, the value of intercept a may be used as a term used to recalculate all input values y_i .

2. The slope b is significantly different from 1: $|b-1| > 2.u(b)$, the intercept a is not significantly different from 0: $|a| \leq 2.u(a)$.

In this case, the value of the slope b may be used as a factor to recalculate all input values y_i .

3. The slope b is significantly different from 1: $|b-1| > 2.u(b)$, AND the intercept a is significantly different from 0: $|a| > 2.u(a)$.

In this case, the values of the slope b and the intercept a may be used to recalculate all input values y_i .

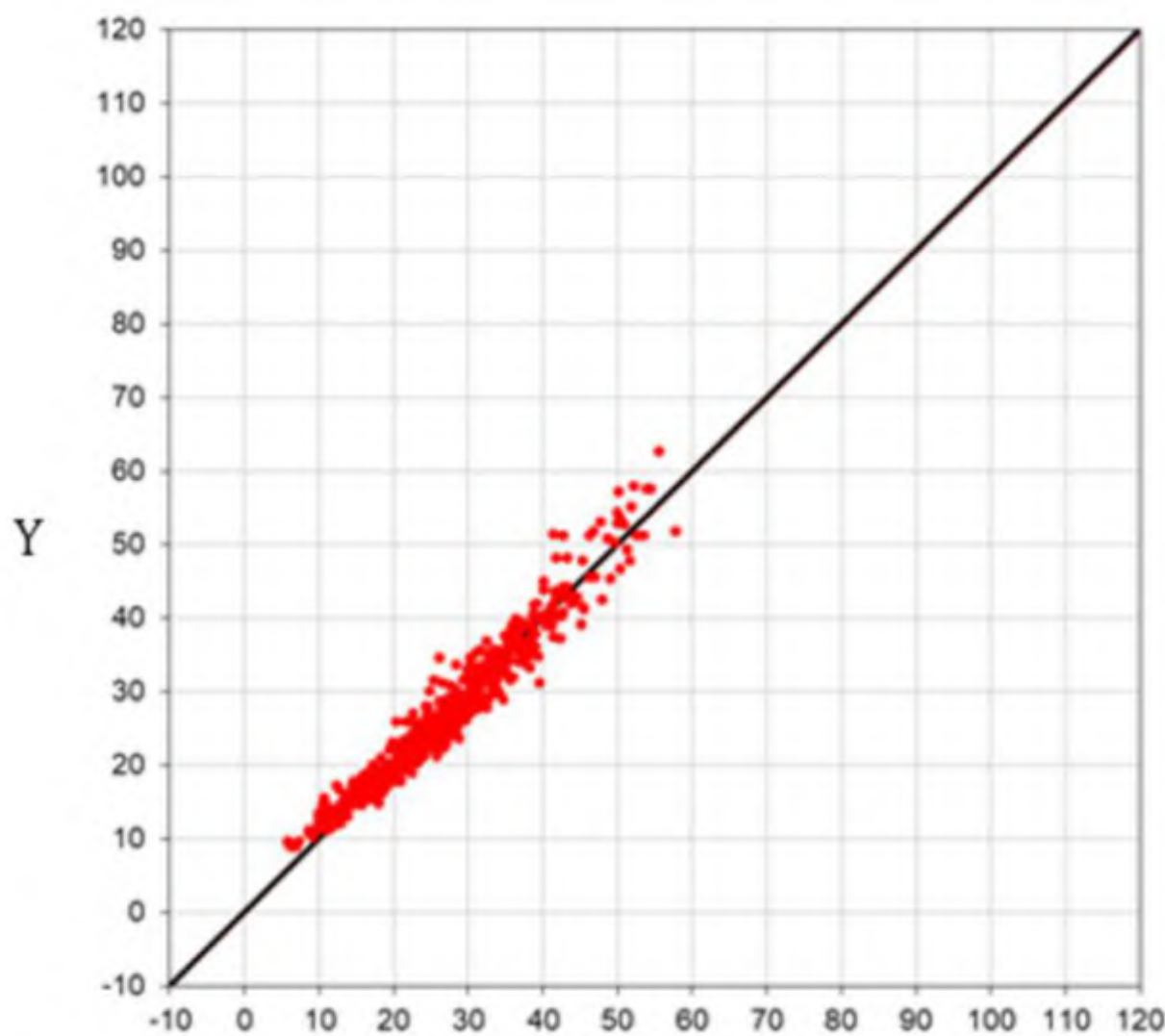
A full description of the recalibration is comprehensively described in the Guide to the Demonstration of Equivalence [3].

If the recalibrated expanded relative uncertainty, $W_{CM,cal}$, is less than the data quality uncertainty objectives then the calibrated candidate method can be used for Fixed and/or Indicative measurements depending on the value of $W_{CM,cal}$.

The random uncertainty of the reference method is taken to be zero as the noise associated with hourly reference method data will drop to zero when averaged over one month or one year.

CEN/TC 264/WG15 Ambient air – PM₁₀/PM_{2.5} has developed a spreadsheet tool [39] for the calculation of equivalence.

Example data (see Figure D.1) for 2018 is given below for conventional tube-type samplers with a cylindrical tube exposed for 14 days, mounted in a rain and wind shelter. The data was supplied as fortnightly measurement points with no time averaging or bias correction. The diffusion tubes have an uncertainty compared to the reference method of $\pm 12,1$ % when the diffusion tube data are slope and intercept corrected.

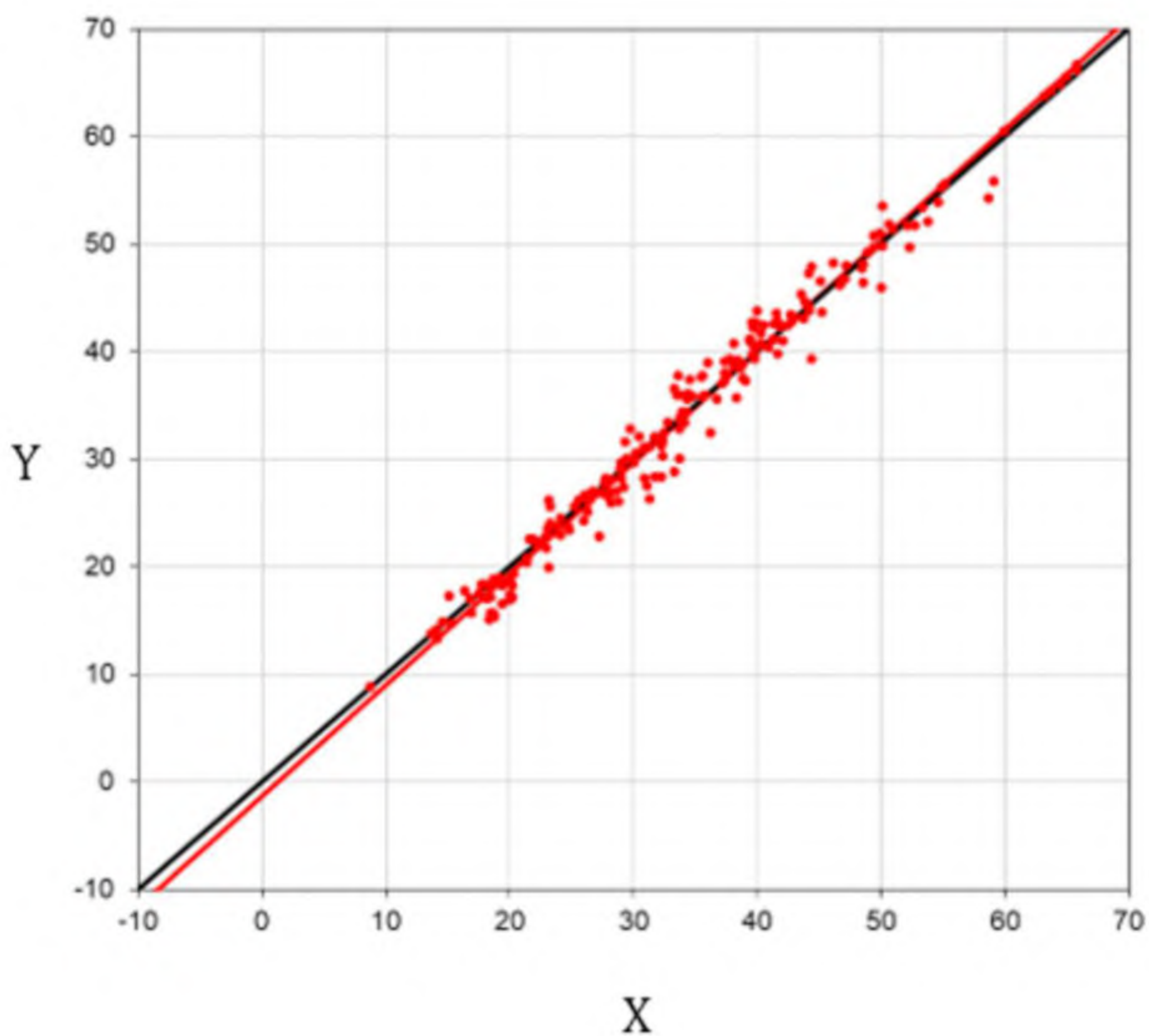


Key

- X RM [µg/m³]
- Y CM [µg/m³]
- Red regression Line
- Black 1:1 Line
- CM data corrected by adding 3,204 then dividing by 1,075
- Slope (b) = 0,998 ± 0,01 Not Significant
- Intercept (a) = 0,054 ± 0,279 Not Significant
- n = 559
- R Squared = 0,946
- Wcm = 12,08 % Pass
- RM Between-Sampler Uncertainty / SQRT(2) = 0
- CM Between-Sampler Uncertainty = Not Calculated
- Percentage greater than error µg/m³ is 0 %
- RM CM outliers at 0,9999999 Confidence Level = 0

Figure D.1 — 14 day exposure diffusion tube results from 24 sites in 2018

Example data (see Figure D.2.) are given for tube-type samplers with a cylindrical tube fitted with a filter at the open end and mounted in shelters. Tubes were exposed over monthly periods at 46 locations over the period 2009 to 2018 and concentrations were calculated using the same sampling rate over the year. Using the annually averaged concentrations gives an uncertainty compared to the reference method of ± 8,6 %, which meets the Directive uncertainty requirement for Fixed measurements. Performing a slope or intercept or slope and intercept correction does not significantly improve the uncertainty compared to the reference method.

**Key**IX RM [$\mu\text{g}/\text{m}^3$]Y CM [$\mu\text{g}/\text{m}^3$]

Red Regression Line

Black 1:1 Line

CM data corrected by adding 3,204 then dividing by 1,075

Slope (b) = $1,032 \pm 0,01$ Not SignificantIntercept (a) = $-1,281 \pm 0,354$ Not Significant n = 214

R Squared = 0,981

Expanded Uncertainty (W_{cm}) = 8,55 % Passes 25 % criterionBetween Reference Method Uncertainty ($u(bs, RM)$) = Not CalculatedBetween Candidate Method Uncertainty ($u(bs, CM)$) = Not CalculatedPercentage of RM greater than $30 \mu\text{g}/\text{m}^3$ = 61,2 %

Figure D.2 — Equivalence of annual diffusion tube results with the reference method (2008-2018)

D.2 GUM approach

D.2.1 Measurement formula

The model formula describing the measurement is

$$C_{\text{STP}} = \frac{m_s - m_b}{v \cdot t} \cdot \frac{T}{293} \cdot \frac{101,3}{P} \quad (\text{D.6})$$

where

C_{STP} is the concentration of NO_2 at standard temperature and pressure (STP) conditions in $\mu\text{g}/\text{m}^3$;

m_s is the mass of nitrite found in the sample in μg ;

m_b is the mass of nitrite found in the mean laboratory blank in μg ;

v is the sampler diffusive sampling rate at actual conditions of sampling in cm^3/min ;

t is the sampling time in min;

T is the average temperature during exposure in K;

P is the average pressure during exposure in Pa.

NOTE It is assumed that the uncertainty of the extraction is included in the uncertainty of v .

D.2.2 Combined standard uncertainty

The combined uncertainty, u_c , is calculated by differentiation of Formula (D.6) according to the method given in JCGM 100:2008 [40], assuming that all parameters are uncorrelated which results in Formula (D.7).

$$\frac{u^2(C_{\text{STP}})}{C_{\text{STP}}^2} = \frac{u^2(m_s) + u^2(m_b)}{(m_s - m_b)^2} + \frac{u^2(v)}{v^2} + \frac{u^2(t)}{t^2} + \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} \quad (\text{D.7})$$

NOTE The mass of nitrite uptake will be fully correlated with the sampling time. However, as the relative uncertainty of the sampling time is negligible, the contribution of this correlation will be negligible as well.

D.2.3 Expanded relative uncertainty

The relative expanded uncertainty, $W(C_{\text{STP}})$, is calculated according to Formula (D.8)

$$W(C_{\text{STP}}) = k \cdot \frac{u(C_{\text{STP}})}{C_{\text{STP}}} \cdot 100 \quad (\text{D.8})$$

where

W is the relative expanded uncertainty in %;

k is a coverage factor for a level of confidence of 95 %; generally, for a sufficient number of degrees of freedom, $k = 2$ is used.

D.2.4 Uncertainty contributions

D.2.4.1 Diffusive sampling rate

The standard uncertainty of the diffusive sampling rate can in principle be determined from two experiments under conditions for which extreme values (minimum; maximum) of diffusive sampling rates are expected. The standard uncertainty of the diffusive sampling rate is then determined according to the GUM assuming a rectangular distribution between the two extreme values of the diffusive sampling rate (see [3]).

The standard uncertainty of the diffusive sampling rate calculated in the above way may be reduced by including additional determinations at conditions between extremes to obtain a more accurate distribution of diffusive sampling rates between the two extreme values previously estimated.

The standard uncertainty may also be estimated as the standard deviation of the slope of the regression line of the nitrite mass uptake against the NO₂ dose as shown in Figure C.1.

The uncertainties of the diffusive sampling rates determined in this way include random contributions due to variations in various factors, such as extraction and analysis. It may also include contributions due to differences in exposure conditions on a micro scale.

D.2.4.2 Mass of nitrite in sample

D.2.4.2.1 General

The uncertainty of the mass of nitrite in the sample is determined by contributions of

- the uncertainty of the mass of nitrite in the calibration standards used;
- the lack of fit of the calibration function;
- the analytical repeatability;
- the drift of the analytical instrument response between calibrations.

$$\frac{u^2(m_s)}{m_s^2} = \frac{u^2(m_c)}{m_c^2} + w_l^2 + w_r^2 + w_d^2 \quad (D.9)$$

Where

- u^2 is the uncertainty of the results of the reference method;
- M_s is the mass of nitrite found in the sample in µg;
- m_c is the mass of nitrite in a calibration standard (D.2.4.2.2);
- w_l is the relative uncertainty due to lack-of-fit of the calibration function (D.2.4.2.3);
- w_r is the relative uncertainty due to analytical repeatability (D.2.4.2.4);
- w_d is the relative uncertainty due to response drift between calibrations (D.2.4.2.5).

Application of this formula assumes that

- the stability of the sample has been established and has no contribution to the uncertainty of the mass of nitrite in the sample;
- nitrite is measured free of significant contributions of interferences.

D.2.4.2.2 Mass of nitrite in calibration standards

The uncertainty in the mass of nitrite in a calibration standard is built up of contributions from

- the impurity of the nitrite and solvent (water; derivatization reagent) used; generally the latter may be ignored;
- the uncertainties of the gravimetric and volumetric procedures used for the preparation of the standards.

D.2.4.2.3 Lack of fit of the calibration function

The relative uncertainty due to the lack of fit of the calibration function can be determined from Formula (D.1) by taking the maximum residual as

$$w_r = \frac{\delta_{i,\max}^2}{3} \quad (\text{D.10})$$

where

$\delta_{i,\max}$ is the maximum relative residual found at calibration.

D.2.4.2.4 Analytical repeatability

The analytical repeatability can be established as the relative standard deviation of the results of a series of replicate analyses of a sample extract.

D.2.4.2.5 Response drift between calibrations

The response drift of the analytical instrument between subsequent calibrations is established by comparing the slopes of the calibration functions at subsequent calibrations. It is monitored by determining the instrument responses of a control standard that is analysed with each series of samples and blanks. The relative uncertainty is calculated as follows:

$$w_d^2 = \frac{(b_i - b_{i+1})^2}{b_i^2} \quad (\text{D.11})$$

where

b_i is the slope of calibration function at calibration i ;

b_{i+1} is the slope of calibration function at subsequent calibration $i+1$.

When more than one value is available for w_d , these may be averaged to obtain an average uncertainty contribution due to response drift.

D.2.4.3 Mass of nitrite in blank

The relative uncertainty of the mass of nitrite in a laboratory blank can be determined as the relative standard deviation of the mean blank value from the results of the analysis of a minimum of 10 laboratory blank samples.

D.2.4.4 Exposure time

Generally, the exposure time can be measured with sufficient accuracy to reduce the uncertainty contribution of exposure time to an insignificant level.

D.2.4.5 Average temperature and pressure during exposure

When measured values of temperatures and pressures during exposure are available, the uncertainties of the average values of temperature and pressure will be approximately equal to the calibration uncertainties of the measuring devices used and will generally be insignificant.

When using information from nearby weather stations, the uncertainties of the average values will be determined by local/regional systematic differences in temperatures and pressures. For pressures these differences will be negligible. For temperatures these are estimated to be within 2 %.

If no such information is available, the contributions of the uncertainties of temperature and pressure for the conversion to STP can be evaluated using extreme values of temperature and pressure. Assuming that the uncertainties of temperature and pressure are triangularly distributed, their uncertainties can be obtained from:

$$\frac{u^2(T)}{293^2} = \frac{(T_{\max} - 293)^2 + (T_{\max} - 293)(T_{\min} - 293) + (T_{\min} - 293)^2}{12 \cdot (T_{\max} + T_{\min})} \quad (\text{D.12})$$

and

$$\frac{u^2(P)}{P^2} = \frac{(P_{\max} - 101,3)^2 + (P_{\max} - 101,3)(P_{\min} - 101,3) + (P_{\min} - 101,3)^2}{12 \cdot (P_{\max} + P_{\min})} \quad (\text{D.13})$$

where

T_{\max}, T_{\min} are maximum and minimum temperatures observed during exposure;

P_{\max}, P_{\min} are maximum and minimum pressures observed during exposure.

D.2.4.6 Worked example

A worked hypothetical example of uncertainty estimation for the tube-type sampler with cylindrical tube is presented in Table D.1.

Table D.1 — Uncertainty budget

Uncertainty source	Symbol	Example value	Target uncertainty (%)	Comments
Diffusive sampling rate (m ³ /h)	v	7,28x10 ⁻⁵	≤ 10	
Sampling time (h)	T	336	≤ 0,1	
Temperature (K)	T	293	≤ 4,0	This 4 % is a estimation, including variation of the effects of reactivity with the sorbent and 10K variation from the average sampling temperature in the field.
Pressure (kPa)	P	101,3	≤ 1,0	No significant effect is expected in the sampling rate from pressure.

Uncertainty source	Symbol	Example value	Target uncertainty (%)	Comments
Mass of nitrogen dioxide sampled (μg)	m_s	1,02		
Extraction efficiency	E			May be included in the effective diffusive sampling rate
Analyte stability	A			No significant difference between results of analysis of samples before and after storage
Mass of nitrite in calibration standards (μg)	m_{cs}		$\leq 2,0$	
Lack-of-fit of calibration function	δi		$\leq 2,0/\sqrt{3}$	
Response drift between calibrations	D		$\leq 3,0/\sqrt{3}$	
Analytical repeatability	R		$\leq 2,0$	
Field reproducibility	R_f		$\leq 5,0$	Analytical repeatability is included in the field reproducibility
Mass of nitrogen dioxide in laboratory blank (μg)	m_b	0,01	$\leq 2,0$	
Mass concentration of NO_2 ($\mu\text{g}/\text{m}^3$)	C	40		
Relative combined uncertainty (%)	W	10,8	$\leq 12,5$	
Relative expanded uncertainty (%)	W	21,7	≤ 25	

D.2.4.7 Between-laboratory uncertainty

The procedures described in Clause 4 are not restrictive but allow variations in approaches between laboratories. In a limited series of inter-laboratory comparisons that have been performed within the frame of the evaluation of the above standard method, it has been found that – even for laboratories that on an individual basis are proficient in the performance of the analysis – significant differences are observed [9]. In principle, this between-laboratory uncertainty needs to be taken into account in order to ensure that comparable measurement data are obtained throughout the European Union when applying this document.

However, this uncertainty cannot be attributed to a single source, but is the combination of contributions from several sources and is not readily quantifiable.

Annex E (informative)

Reagents and equipment for analysis

E.1 Introduction

During the analysis, use only reagents of known purity appropriate to the application.

Use only volumetric glassware, pipettes and syringes that are calibrated to ensure traceability of volume to primary standards. Volumetric glassware shall be cleaned with ultrapure water.

E.2 Reagents

E.2.1 Ultrapure water

To be used for the preparation of reagents, calibration solutions and chromatography eluents. Its resistivity shall be greater or equal to 18 M Ω /cm at 298 K, see ISO 3696 [58].

E.2.2 Sodium nitrite

To be used for the preparation of calibration standards and check solutions.

The sodium nitrite shall be of a minimum established purity of 99,5 %. The sodium nitrite shall be dried before preparation of the solution by placing a small quantity of sodium nitrite on a container (for example a Petri-dish) placed in an oven at 102 °C \pm 2 °C until completely dry. In practice, it is sufficient to wait for between 1 and 2 h. The small quantity of sodium nitrite shall be cooled at ambient temperature before weighing. It is necessary to cool in a dry atmosphere, for example using a desiccator. Special care shall be taken to avoid contamination during handling by using gloves and a glass container for weighing.

It is also possible to use commercially available certified standards (typically at the level of 1 g/l of nitrite) to eliminate the possibility of errors due to inaccurate standard preparation.

E.2.3 Orthophosphoric acid (PA)

To be used for the preparation of colorimetric reagent. 85 % in water (density = 1,70 g/cm³). Only use acid of high purity.

NOTE Commercial trade qualifications of appropriate purity grades are “type AR grade”, “pro analysis grade” and “grade trace analysis”.

E.2.4 Sulphanilamide (SA)

To be used for the preparation of the colorimetric reagent. Purity \geq 99 % (see Table E.1).

E.2.5 Sulphanilic acid (Sac)

To be used for the preparation of the colorimetric reagent. Purity \geq 99 % (see Table E.1).

E.2.6 N-(naphthyl-1) ethylene diamine dihydrochloride (NEDD)

To be used for the preparation of the colorimetric reagent. Purity \geq 98 %.

E.2.7 Colorimetric reagent

The compositions of the colorimetric reagent are given in Table E.1.

Table E.1 — Commonly used compositions of reagents^a

Sampler type	Reagent A	Reagent B	Reagent mixture
Tube-type sampler with a cylindrical tube	Dissolve 10 g of SA in 300 ml of water. Add 25 ml of PA. Add water up to 500 ml	Dissolve 70 mg NEDD in 300 ml water; add water up to 500 ml	Equal volumes of reagents A and B
Tube-type sampler with a slightly conical tube	Dissolve 10 g of Sac and 25 ml of PA in 500 ml water. Add 500 ml of water and heat the solution to boiling	Dissolve 72,8 mg NEDD in 100 ml water	After cooling of solution A to room temperature, the two solutions are combined. The colour reagent is ready after 24 h
^a The compositions specified have been demonstrated to be fit for purpose in the validation studies of the two sampler types.			

It is important to ensure that the pH of the solution being analysed remains below 2 [22, 56] when:

- the proportions of the reagent are modified;
- the sample to be analysed is diluted; dilutions shall be performed with the colorimetric reagent only.

E.2.8 Sodium carbonate

Anhydrous, purity $\geq 99,8$ %. To be used for the preparation of the eluent for ion chromatography.

E.2.9 Sodium bicarbonate

Purity $\geq 99,0$ %. To be used for the preparation of the eluent for ion chromatography.

E.2.10 Eluent for ion chromatography

The composition of the eluent will depend on the ion chromatography column being used. Generally, the eluent is an aqueous solution of sodium carbonate and sodium bicarbonate.

E.3 Equipment

E.3.1 Colourimeter

With wavelength settings in the range of 500 to 600 nm. The volumes of the cuvettes of the colourimeter shall be consistent with the volumes of mixed reagents used for derivatization (see Table 1).

E.3.2 Ion chromatograph

With anion column and conductivity detector. Select a column that allows sufficient separation of chloride and nitrite.

E.3.3 Sample shaker

For the extraction of nitrite from the sampling support. A vibrating tray or a vortex shaker have been found to be acceptable.

E.3.4 Oven

For drying parts of diffusive samplers before assembling. Only use electric ovens and do not use gas ovens because flame combustion generates oxides of nitrogen.

E.3.5 Balance

Laboratory balance with a resolution $\leq 0,1$ mg.

E.3.6 Desiccator

Airtight chamber made of glass containing a substance with a strong affinity for water such as calcium chloride or silica gel.

Annex F
(informative)

Validation data of the use of protective devices

Measurements were carried out at Honour Oak Park (London), Manchester (see Figure F.1 - Photograph showing diffusion tubes being deployed at NERC supersite in Manchester and York in 2020-2021. The 28-day deployment of conventional and modified diffusive samplers (both designs with and without shelters) were colocated with the reference chemiluminescence analyser. The new samplers incorporated a polyethylene filter at the open end to reduce undesirable wind effects yielding better measurement repeatability[59]. These are now used in the UK's UrbanNO₂ Network (termed UUNN type samplers) [60].

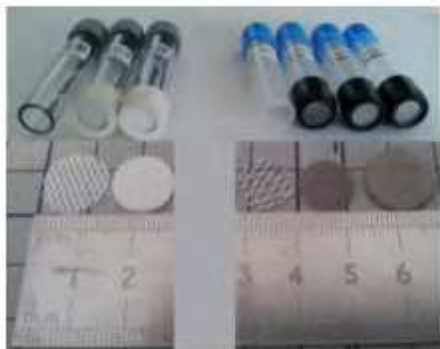


Figure F.1 — Photograph showing diffusion tubes being deployed at NERC supersite in Manchester

The monthly results were combined to produce an assessment of the relative performance of the different sampler types and deployment methods at each site as described in Table F.1.

Table F.1 — Summary of NO₂ tube measurement results

Tube type	Linear trend	Trend uncertainty	Linearity (R ²)	Mean difference (%)
Conventional	1,18	0,03	0,98	22,6
Conventional in shelter	1,10	0,02	0,98	15,6
UUNN	1,01	0,03	0,97	15,7
UUNN in shelter	1,06	0,03	0,98	15,3

The results show good linearity, with R² greater than 0,97 in all cases, with the UUNN tubes showing closer agreement to the reference measurements compared to the conventional tubes. The use of a shelter improves the accuracy of the conventional tube results, with the overall bias reducing from +18 % to +10 %, as well as improving the precision of the data, with the mean of the absolute difference between the tube and reference data reducing from 22,6 % to 15,6 % (of the reference value).

The UUNN results show better accuracy than either of the conventional tube configurations, with very similar levels of precision to the sheltered conventional tubes. No benefit is seen for placing the UUNN tubes in shelters, with some indication that the accuracy may degrade slightly although the two UUNN trend results lie within their expanded uncertainties. In all cases good linearity was seen across the range of concentrations measured.

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