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

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National foreword

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

Außenluft - Bestimmung der Konzentration von Stickstoffdioxid mittels Passivsammler

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Foreword

This document (EN 16339:2013) 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of an identical text or by endorsement, at the latest by January 2014, and conflicting national standards shall be withdrawn at the latest by January 2014.

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Introduction

Experience gained across the European Union (EU) in implementing EU ambient air quality legislation [1] has shown that, generally, for nitrogen dioxide (NO_2), meeting the annual average limit value of 40 µg/m^3 is more problematic than meeting the 1-h limit value of 200 µg/m^3 [2].

EU Directive 2008/50/EC [1] stipulates that European Union Member States shall apply the reference measurement methods and criteria specified in the Directive. For NO_2 monitoring in ambient air, the reference method being that described in EN 14211:2012 [3]. However, a Member State may use any other method that provides results equivalent to that of the reference method, to be demonstrated in accordance with the Guide for the demonstration of equivalence of ambient air monitoring methods [4]. The GDE devotes specific paragraphs to methods based on diffusive sampling.

For the measurement of longer-term average concentrations of nitrogen dioxide for comparison with the annual average limit value diffusive sampling is an attractive alternative to fixed monitoring using the reference methodology described in EN 14211 because of

- 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 an instrument for the assessment of air quality, provided that they fulfil the specific Data Quality Objectives given in [1].

At the time of publication of this standard, no full demonstration of equivalence according to [4] has been performed. However, some studies have compared NO_2 annual average concentrations measured by chemiluminescence and by diffusive samplers [5], [6], [7] and [8]. 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 standard 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.

Further, the methodology described can be used for simultaneously measuring sulphur dioxide (SO_2) when using ion chromatography as the method of analysis. The analytical method is described in [9], [10] and [11].

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

The methodology described in this standard may also be used to determine NO_2 in indoor air. Appropriate strategies for NO_2 measurement in indoor air are described in EN ISO 16000-15.

1 Scope

This European Standard specifies a method for the sampling and analysis of NO_2 in ambient air using diffusive sampling followed by extraction and analysis by colorimetry or ion chromatography (IC). It can be used for the NO_2 measurement in a concentration range of approximately 3 µg/m³ to 130 µg/m^3. A sample is typically collected for a period of 1 to 4 weeks [13], with exposure periods depending on the design of the samplers and the concentration levels of NO_2.

Several sorbents can be used for trapping NO_2 in ambient air using a diffusive sampler. This standard specifies the application of triethanolamine as the reagent.

Nitrous acid and peroxyacetyl nitrate are the major chemical interferences of sorption by triethanolamine. However, in ambient air monitoring over long sampling times, 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]).

This standard describes the application of a tube-type sampler with either a cylindrical or a slightly conical tube. Its typical uptake rate is about 1 cm^3/min. Only for this sampler type sufficient evidence of validation has been found in a literature survey [12].

The relative expanded uncertainty of NO_2 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 [6].

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and 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 ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025)*

3 Terms and definitions

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

3.1
certified reference material
reference material [3.8], characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability

[SOURCE: ISO Guide 35:2006]

3.2
combined standard uncertainty
standard measurement uncertainty [3.10] that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model

[SOURCE: JGCM 200:2012]

3.3
desorption efficiency
ratio of the mass of analyte desorbed from a sampling device to that applied

[SOURCE: EN 13528-2:2002]

3.4
diffusive sampler

device which is capable of taking samples of gases or vapours 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

[SOURCE: EN 13528-1:2002]

Note 1 to entry: Active normally refers to the pumped movement of air.

3.5
diffusive uptake rate

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

[SOURCE: EN 13528-1:2002]

Note 1 to entry: The uptake rate is usually expressed in units of (pg/(nmol/mol)/min) or (cm^3/min).

Note 2 to entry: pg/(nmol/mol)/min is equivalent to ng/(µmol/mol)/min.

3.6
expanded (measurement) uncertainty

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

[SOURCE: JCGM 200:2008]

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.

3.7
field blank

sealed sampler drawn from the same batch as the samplers being used for NO_2 monitoring. This sampler is taken unopened to the field and 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 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 NO_2 monitoring which is stored in a refrigerator during sampling of the exposed samplers.

3.9
repeatability condition

condition of measurement, out of a set of conditions that includes the same measurement procedure, same operators, same measuring system, same operating conditions and same location, and replicate measurements on the same or similar objects over a short period of time

[SOURCE: JGCM 200:2012]

3.10
standard (measurement) uncertainty
measurement uncertainty expressed as a standard deviation

[SOURCE: JGCM 200:2012]

3.11
uncertainty (of measurement)
non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used

Note 1 to entry: For footnotes to the definition the reader is referred to the parent document JGCM 200:2012.

[SOURCE: JGCM 200:2012]

4 Principle of the method

The diffusive sampler is exposed to air for a measured time period. NO_2 migrates through the sampler diffusion path and is collected as nitrite by reaction with triethanolamine (TEA). 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.

A number of pathways have been proposed for the reaction of nitrogen dioxide with triethanolamine. More details can be found in [14].

The diffusive uptake rate is determined either by numerical calculation based on Fick's first law of diffusion (see EN 13528-3) 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 [5], [6], [7] and [18].

Values of and equations to calculate diffusive uptake rates associated with different diffusive samplers are given in Annex C.

NOTE 1 The theory of performance of diffusive samplers is given in EN 13528-3 together with information on possible saturation of the sorbent, the effect of transients and the effect of face velocity. This standard explains the dependence of diffusion uptake rates on the concentration level of pollutants and sampling time.

The nitrite formed in the sampler is subsequently extracted. The resulting extract is analyzed by:

- colorimetry after derivatization of the nitrite, using the Griess-Saltzman method [15];
- ion chromatography [16].

The Griess-Saltzman derivatization consists of reacting nitrite with a mixture of sulphanilamide and N-(naphthyl-1) ethylenediamine dihydrochloride in dilute orthophosphoric acid (see Table 1). The absorbance of the azo dye formed is measured at approximately 540 nm.

NOTE 2 In practice, when applying colorimetry, the derivatization agent solution is directly used for desorption.

NOTE 3 When using ion chromatography, sulphur dioxide can be determined simultaneously [9], [10] and [11].

The analytical system is calibrated by means of solutions of nitrite in water with accurately known concentrations.

NOTE 4 An example of commercially available European sampler based on a sorption media not containing triethanolamine is given in the informative Annex B.2 (badge-type A with typical uptake rate of about 12 cm³/min).

5 Materials

5.1 Sampling

5.1.1 Diffusive samplers

5.1.1.1 Description

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.

NOTE 1 A radial-type sampler, with typical uptake rate about 70 cm^3/min, exists and is widely used in the EU. Limited validation data are available for this sampler; it is therefore described in the informative Annex B.1.

NOTE 2 A badge-type NO_2 diffusive sampler exists that is based on the application of triethanolamine. Limited validation data is available for this sampler. The sampler is described in the informative Annex B.3 (badge-type B with typical uptake rate of about 12 cm³/min).

The sampler may include a turbulence barrier or a protective device (5.1.2) in order to avoid effects of turbulence inside the diffusion path during sampling.

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

5.1.1.2 Preparation

The preparation of the sampler consists of the coating of a support with triethanolamine from a solution in water, methanol or acetone. To this solution a wetting agent may be added to facilitate the coating. 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.

5.1.1.3 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.

5.1.1.4 Acetone

For the preparation of TEA coating solutions. Purity ≥ 99,9 %.

5.1.1.5 Ultrapure water

For the preparation of TEA coating solutions. Its conductivity shall be equal or less than 0,1 µS/cm.

5.1.1.6 Wetting agent compound

A wetting agent, for example BRIJ 35®[1] [15, 16], may be used for the preparation of TEA coating solutions. The wetting agent shall not contain significant nitrite impurities.

5.1.1.7 Storage and shelf-life of samplers

After preparation, samplers shall be sealed and stored under cool conditions, for example at temperatures between 0 °C and 4 ºC, in the dark, in order to minimize any undesired reactions. Samplers are stable for up to one year [16] when prepared according to the preparation method described in A.1.3. and stored under the above conditions. Tube-type samplers shall be stored in a position that minimizes the probability of the absorbing solution moving onto the tube walls, for example in a vertical position with the TEA at the bottom of the tube.

When storing samplers for periods ≥ 3 months, subsets shall be analyzed periodically to check that blank development does not occur.

5.1.2 Protective device

Consisting of a protective cover or box to be used, where appropriate, to prevent:

- the entrance of coarse particles or water droplets into the sampler during sampling;
- exposure to direct sunlight;
- exposure to high wind velocities.

NOTE 1 EN 13528-3 gives general recommendations for the design of protective devices.

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

Protective devices should 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.

5.1.3 Support

A device capable of positioning the sampler at an appropriate height and distance from obstacles to warrant undisturbed sampling.

5.1.4 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.

5.2 Analysis

5.2.1 General

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 ultra pure water (see 5.2.2.1).

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[1] BRIJ 35® is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

5.2.2 Reagents

5.2.2.1 Ultra pure water

To be used for the preparation of reagents, calibration solutions and chromatography eluents. Its conductivity shall be equal or less than 0,1 µS/cm.

5.2.2.2 Sodium nitrite

To be used for the preparation of calibration standards and check solutions (see 7.2 and 9.1).

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 (5.2.3.4) at 102 °C ± 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 (see 5.2.3.6). 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.

5.2.2.3 Orthophosphoric acid (PA)

To be used for the preparation of colorimetric reagent. 85 % in water (density =1,70 g/cm^3). 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”.

5.2.2.4 Sulphanilamide (SA)

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

5.2.2.5 Sulphanilic acid (SAc)

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

5.2.2.6 N-(naphthyl-1) ethylene diamine dihydrochloride (NEDD)

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

5.2.2.7 Colorimetric reagent

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

Table 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 [18, 19] when:

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

5.2.2.8 Sodium carbonate

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

5.2.2.9 Sodium bicarbonate

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

5.2.2.10 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.

5.2.3 Equipment

5.2.3.1 Colorimeter

With wavelength settings in the range of 500 to 600 nm. The volumes of the cuvettes of the colorimeter shall be consistent with the volumes of mixed reagents used for derivatization (see Table 2).

5.2.3.2 Ion chromatograph

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

5.2.3.3 Sample shaker

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

5.2.3.4 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.

5.2.3.5 Balance

Laboratory balance with a resolution ≤ 0,1 mg.

5.2.3.6 Desiccator

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

6 Sampling

6.1 Calibration of the diffusive uptake rate

Information about the diffusive uptake 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 uptake rate and its uncertainty shall be determined experimentally. This shall be done – where practicable – by a combination of laboratory and field experiments. Information about experimental approaches and evaluation of results can be found in [4].

6.2 Siting criteria

When measuring for the purpose of checking compliance with the requirements of EU Directive 2008/50/EC, the siting criteria of this Directive for fixed monitoring shall be met.

Information on siting criteria can also be found in [18]. Further information for determining appropriate monitoring sites for diffusive samplers can be found in [20] and [21].

6.3 Protective measures

Samplers shall be transported to and from the sampling site in suitable plastic containers and/or sealable clean plastic bags in order to avoid contamination during transport.

During sampling the sampler shall be protected from influences of environmental conditions that can adversely affect its performance, for example by using a protective device (see 5.1.2).

When a protective device is used, it shall be suitable for the particular sampler used.

A protective cover or box may be an integral part of the sampler, thereby affecting its uptake rate (see Annex A).

6.4 Exposure

All handling of samplers shall be done in such a way that contamination of the sampler or re-usables such as caps 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 the support (5.1.3), and fit the protective cover (5.1.2) if needed.

The actual permissible period of sampling may vary with the sampler design, e.g., due to the presence of a membrane. Different designs of diffusive samplers have different diffusive uptake rates; the exposure time shall be such that the mass of nitrite is within the minimum and maximum capacity of the sampler specified by the manufacturer.

NOTE A simple method for predicting the mass of nitrite in a sampler is to multiply the sampling time by the expected highest NO_2 concentration and the nominal uptake rate.

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 ≥ 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 below.

6.5 Storage after sampling

After sampling, samples shall be sealed and stored under cool conditions, for example at temperatures between 0 °C and 4 ºC, in the dark in order to minimize any undesired reactions.

Although samples may be stable for up to 4 months [11] when stored under the above conditions, it is strongly recommended to analyze the samples as soon as possible after exposure.

6.6 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 uptake rate during the sampling period.

7 Analytical procedure

7.1 Safety precautions

This standard does not purport to address all of the safety concerns associated with its use. It is the responsibility of the user of this standard to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

7.2 Calibration

Calibration shall be performed by analyzing a series of solutions of nitrite in mixed reagent for colorimetry or in water or eluent for ion chromatography.

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, 0,1, 0,2, 0,4, 0,8, 1,5 and 2,0 µg/ml of nitrite.

For colorimetry it is recommended to use concentrations of the calibration standards of 0,0, 0,1, 0,2, 0,4, 0,6, 0,8 and 1,0 µg/ml of nitrite. Higher concentrations are not recommended because of potential problems with linearity [22].

The nitrite concentrations shall be traceable to primary standards. The uncertainty of the nitrite concentration shall be such that the resulting expanded uncertainty of all diluted nitrite standards will 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 1000 µg/ml can be purchased as certified solutions from different manufacturers or can be prepared by dissolving 0,7499 g of oven-dried sodium nitrite in 0,5 l of ultra pure water.

A full calibration shall be carried out at the initial set-up of the analytical system, in case of any significant change of the analytical system, when changing reagents or the standard of sodium nitrite, at regular interval and every time that the results of a quality control check (see Clause 9) reveal a drift or a deviation from specified limits.

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

The 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 of linearity of the calibration curve shall be calculated from the relative residuals of the regression formula as:

$$\delta_\mathrm{i} = \left| 1 - \frac{a + b \cdot c_\mathrm{i}}{y_\mathrm{i}} \right| \tag{1}$$

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 4.

7.3 Analysis by colorimetry

7.3.1 Extraction

The extraction shall be performed by adding colorimetric reagent to the TEA support. The volumes of the reagent solution are given in Table 2.

The samples shall be secured against NO_2 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, followed by at least 1 h of standing at ambient temperature for colour development, avoiding exposure to direct sunlight.

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

Table 2 — Extraction conditions and extract stabilities for analysis by colorimetry

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 (Table 1)	Agitate by vortex shaking for about 15 s immediately after adding the reagents. 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	2 d 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 (Table 1)		

7.3.2 Analysis

Set up the colorimeter 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 colorimeter to analyze 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.

7.4 Analysis by ion chromatography

7.4.1 Extraction

The extraction shall be performed by adding ultra pure water or eluent to the TEA support. The volume of the extraction solution is given in Table 3.

The samples shall be secured against NO_2 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.

The reported stabilities of the extracts are given in Table 3.

Table 3 — 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 ºC

7.4.2 Analysis

Set up the ion chromatograph in accordance with the manufacturer's instructions. Use a calibrated ion chromatograph to analyze 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.

8 Calculation of the concentration of nitrogen dioxide

8.1 Mass concentration

The concentration of NO_2 in ambient air under actual conditions of sampling is calculated using Formula (2):

$$C = \frac{m_\mathrm{s} - m_\mathrm{b}}{e.\upsilon \cdot t} \cdot 10^6 \qquad (2)$$

where

C is the concentration of NO_2 at ambient conditions in µg/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;

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

The uptake rate may be in µg/(nmol/mol)/min, in which case *C* is expressed in units of nmol/mol.

e is the efficiency of extraction of nitrite;

t is the sampling time in min.

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 uptake rate.

8.2 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 (2). This mass concentration shall be referred to at standard conditions of temperature and pressure, as required by [1], using Formula (3):

$$c_\mathrm{STP} = c \cdot \frac{T}{293} \cdot \frac{101,3}{P} \qquad (3)$$

where

c_STP is the concentration of NO_2 at standard temperature and pressure in µg/m^3;

c is the concentration of NO_2 at ambient conditions in µg/m^3;

T is the average temperature during exposure in K;

P is the average pressure during exposure in kPa.

When the uptake rate has been determined by calibration against reference analyzers that provide results at standard conditions of temperature and pressure (see D.2) this conversion is not necessary since the uptake rate is already expressed at standard conditions.

9 Quality control/quality assurance

9.1 Quality control

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 prepared in accordance with 7.2 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 and at regular intervals that allow 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 analyzed for each newly prepared batch of samplers;

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 8]; the nitrite shall be injected directly onto the TEA support;

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 routine NO_2 monitoring with diffusive samplers, it is necessary to complement with other quality control checks that will ensure proper analysis over time.

i) Checking of the relevant dimensions of samplers at a suited periodicity in order to detect any significant variation; the sampler dimensions directly affect the uptake 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 standard shall be demonstrated by performing parallel measurements with continuous chemiluminescence analysers, e.g., by using the methodology described in [4].

9.2 Quality assurance

In order to fulfil the requirements of [1], the laboratories using this European Standard in relation to the assessment of ambient air quality pursuant to Articles 6 and 9 of this Directive shall be able to demonstrate to be working in accordance with the requirements of EN ISO/IEC 17025.

One way of demonstrating compliance with these requirements is through formal accreditation of the test described by an accreditation body falling under the Multi-Lateral Agreement (MLA) of the European Cooperation for Accreditation (EA).

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 NO_2 uptake rate(s) used with uncertainty statement and reference;
- the method of analysis used;
- the analytical results;
- the NO_2 concentrations determined accompanied with an uncertainty statement;
- any deviations from procedures described in this European Standard;
- the signature of a responsible person checking the analysis, the calculation of the test results and their uncertainties.

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.

11 Performance requirements and measurement uncertainty

11.1 General

When performing measurements of NO_2 in ambient air for checking compliance with the limit values given in [1], the requirements for data capture and measurement uncertainty lower specified in [1] shall be respected.

In this standard, the uncertainty assessment is based on combining the uncertainty contributions of the parameters included in Formulae (2) and (3) that – in general terms – describe the measurement problem under consideration.

This approach is not meant to exclude evaluations based on data from ongoing QA/QC procedures, field studies or inter-laboratory comparisons as long as these evaluations are consistent with JCGM 100 and/or ISO 5725. An example of the direct approach estimation is given in D.2.2.

When the minimum requirements for the contributions identified in Table 4 are met, the measurement uncertainty requirement of [1] for indicative measurements for a yearly average (25 % expanded uncertainty) will be met.

NOTE In order to fulfil the uncertainty requirement for fixed measurements (15 % expanded uncertainty), more stringent requirements are needed, particularly for the uncertainty of the uptake rate.

In addition, these requirements may serve as the basis for the establishment of ongoing QA/QC programmes.

11.2 Parameters to be assessed and performance requirements

The parameters given in Table 4 have been identified to contribute to the uncertainty of concentrations of NO_2 measured by diffusive sampling and subsequent analysis by colorimetry 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 (see Annex D).

Table 4 — Uncertainty parameters and minimum requirements for a single exposure period

Uncertainty source	Symbol	Criterion
Uptake rate	υ	Relative uncertainty ≤ 10 %
Sampling time	t	Relative uncertainty ≤ 0,1 %
Average air temperature during exposure for conversion to standard temperature and pressure	T	Relative uncertainty ≤ 4 %
Average air pressure during exposure for conversion to standard temperature and pressure	P	Relative uncertainty ≤ 1 %
Extraction efficiency	E	Is included in the effective uptake rate
Mass of sampled NO_2	m_s	
- Analyte stability	A	No significant difference between results of analysis of samples before and after storage
Measured mass of NO_2		
- Conversion of nitrogen dioxide to nitrite		Is included in the effective uptake rate
- Mass of nitrite in calibration standards	m_{CS}	Relative uncertainty ≤ 2 %, excluding zero concentration
- Lack-of-fit of calibration function	δ_i	Relative residuals over the calibration range ≤ 2 % , excluding zero
- Response drift between calibrations	D	≤ 3 %
- Analytical repeatability	r	≤ 2 %
- Selectivity	S	Resolution factor > 1 (for ion chromatography only)
Mass of nitrite in laboratory blank	m_b	≤ 10 % of the mass sampled at the concentration level of the annual limit value with an uncertainty of ≤ 5 % of that mass [a]
Field reproducibility	R_f	≤ 5 %

[a] Example. When the mass of nitrogen dioxide sampled at the level of 40 μg/m^3 is 1,6 μg, the laboratory blank level shall be ≤ 160 ng. The uncertainty of the laboratory blank level shall be ≤ 80 ng.

Annex A
(normative)

Description of samplers

A.1 Tube-type sampler with a cylindrical tube

A.1.1 Range of exposure periods

The tube–type sampler 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].

NOTE Some users have exposed tubes for up to 8 weeks [12].

The limit of detection of the sampler is 1,4 $\mu g/m^3$ for one week of sampling when applying the preparation method described in A.1.3.

A.1.2 Description

A sampler consists of an acrylic, polypropylene or glass tube of about 7,1 cm long and 1,1 cm internal diameter. It may be exposed as an open tube (Figure A.1) or 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 uptake rate and allows improving 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 NO_2 only diffuses through the membrane.

The capacity of triethanolamine to absorb NO_2 is decreased by direct exposure to sunlight. Therefore tubes should be protected either using an opaque cap or using a protective box (see Figure A.3).

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

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) using 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 ºC until they are completely dry.

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

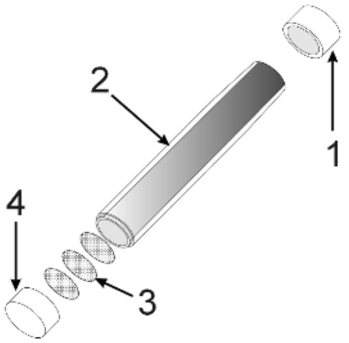
Sampler preparation methods

Different procedures for preparation are available [6]:

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 and 5, see Key to figures A.1 and A.2). The tube is inserted into this cap while the other end is sealed with another cap.

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 this cap (4) while the other end is sealed with another cap (1).

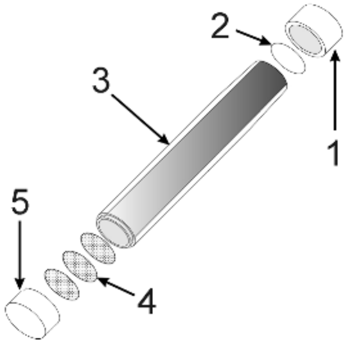
3. From a 50 % solution of TEA in acetone, with grids dipped into the solution and dried before assembly. Two stainless steel meshes are placed in an opaque cap (4). The tube is inserted into this cap while the other end is sealed with another cap (1).



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.

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

A.2.1 Range of conditions of exposure

The tube–type sampler with a slightly conical tube can be exposed for 1- to 4- week sampling in accordance with the results of field validation tests obtained at several sites in Europe [12] for NO_2 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 is 0,8 µg/m^3 for one week of sampling.

Figure A.4 – Tube-type sampler with a slightly conical tube and protective boxes

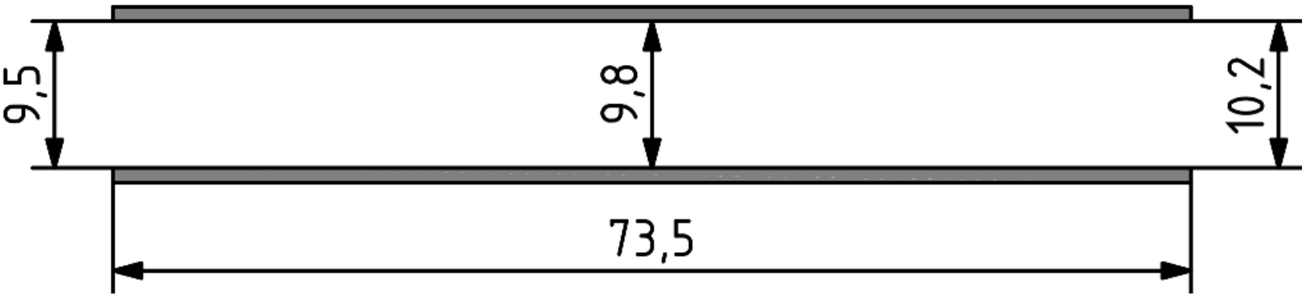


Figure A.5 — Dimensions of a tube-type sampler

Figure A.6 — Tube-type sampler with shelter

A.2.2 Description

The sampler, which is based on the tube-type design, is shown in Figure A.4 and consists of an opaque polypropylene tube. The tube is slightly conical with dimensions given in Figure A.5.

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

At the narrow end, 3 stainless steel screens are mounted, which are coated by dipping into a solution of TEA – acetone 1:7. The samplers are exposed in specific shelters (see Figure A.6). These shelters are designed to protect the samplers from environmental factors such as rain, excessive radiation and wind. The shelters are an integral component of the measurement method.

In order to reduce the effect of wind-induced turbulence, the sampler may be equipped with a membrane or a glass frit as turbulence barrier [7, 8]. When using a glass frit, a hole of 9 mm is drilled into a plastic cap of the type normally used to seal the sampler. A glass frit with a pore size of 160 µm to 250 µm (porosity 0, P250 according to ISO 4793), 10 mm diameter and a thickness of 3 mm (borosilicate glass according to ISO 3585) is then pressed in the hole of the plug. It is necessary to make sure that the frit is positioned correctly (see Figure A.7).

Figure A.7 — Glass frit membrane inserted into the sampler end cap

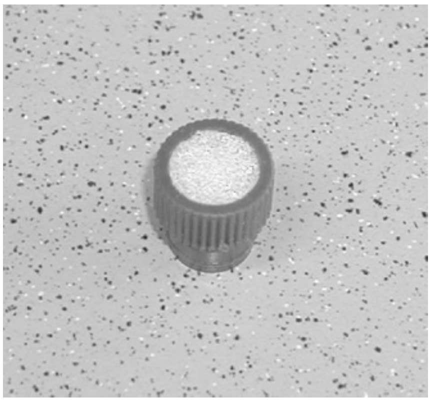


Figure A.8 — Glass frit membrane

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

A.2.3 Preparation

Tubes, screens and caps are cleaned with detergent solution in an ultrasonic bath, rinsed with demineralised water, and air dried.

The dried screens are dipped into the absorbing reagent consisting of a solution of TEA – acetone 1:7 by volume. The screens are subsequently placed on absorbent paper using forceps and gently blotted. After this the acetone is allowed to evaporate.

Three coated screens are stacked into the bottom cap of the sampler, after which the narrow end of the acrylic tube is inserted into the bottom cap to secure the screens. The top of the sampler is then closed with the flanged end cap.

Annex B
(informative)

Other samplers

B.1 Radial sampler

B.1.1 Range of exposure conditions

Exposures for up to 2 weeks are feasible for NO_2, but if the relative humidity is higher than 70 % for the entire sampling duration, the manufacturer recommends sampling for no more than 7 d. Due to the fact that TEA is very hygroscopic, even if water does not actually interfere with sampling or analysis, the excess of water adsorbed by the cartridge may cause loss of adsorbing medium by percolation.

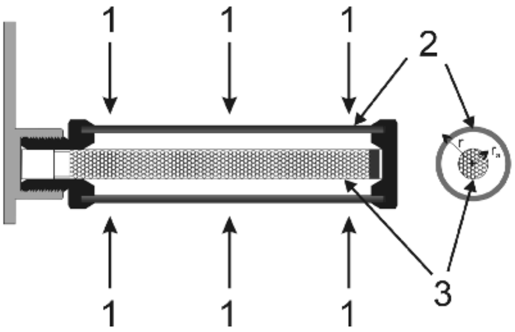
The limit of detection is 0,6 µg/m^3 for one week of sampling.

B.1.2 Description

The radial-type diffusive sampler (see Figure B.1) 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.

As mentioned in B.1.1, 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

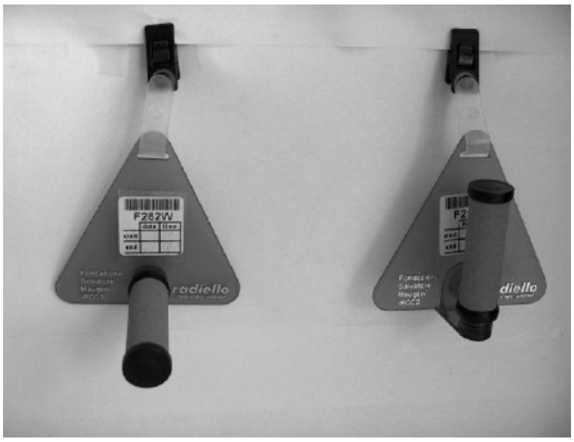


Figure B.2 — Radial sampler supporting plate

Figure B.3 — Radial sampler shelter

B.1.3 Preparation

At the time of editing this standard, no preparation method of proven validity was publicly available for the coating of the absorbent on the cartridge of the radial sampler.

Samplers shall be sealed and stored at reduced temperatures, e.g. between 0 °C and 4 °C, in the dark in order to minimize any undesired reactions. Although samplers may be stable for up to one year, it is strongly recommended to use them as soon as possible after reception.

B.1.4 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 7.3.

Extraction

Cartridges are placed in sterile plastic or glass 10 ml tube and are extracted using 5 ml of ultra pure water (5.2.2.1). The extraction may be carried out by using a vortex shaker (5.2.3.3) for about 1 min, followed by 1 h to 2 h of standing at ambient temperature in the dark. It is agitated again for 30 s before transferring to the cuvette for reading. Alternatively, ultrasonic extraction for 25 min may be used (in this case the solution shall be filtered). The extract is stable for 2 d when stored at temperatures between 0 °C and 4 °C in the dark.

Calibration

Recommended concentrations of the calibration standards are 0,0, 0,5, 1,0, 2,5, 5,0, 10,0 and 20,0 µg/ml of nitrite .

Derivatization

Derivatization is performed in the same way as for the tube-type sampler (see 7.3). The compositions of the colorimetric reagents are given in Table B.1.

Table B.1 — Recommended compositions of reagents

Sampler type	**Reagent A**	**Reagent B**
Radial sampler	Dissolve 10 g SA in 100 ml HCl[a]; add water up to 1000 ml	Dissolve 250 mg NEDD in 250 ml water
[a] HCl: hydrochloric acid (37 % in water (density =1,19 g/cm^3). Only use acid of high purity for example of type AR grade of VWR International or pro analysis grade or grade trace analysis or equivalent.		

Analysis

After sampling, samples shall be sealed and stored at reduced temperatures, e.g. between 0 °C and 4 °C, in the dark in order to minimize any undesired reactions following the manufacturer's instructions. Samples may be stable for up to 4 months.

0,5 ml of extract or calibration solution is mixed with first 5 ml of reagent A (Table B.1). The tube is closed and agitated with a vortex shaker. After 5 min, 1 ml of reagent B (Table B.1) is added. The tube is agitated again and let standing for 10 min at ambient temperature in the dark before the colorimetric analysis is performed.

For nitrite ion concentration higher than 20 mg/l (corresponding to 7 d of exposure at a NO_2 concentration of 140 µg/m^3), smaller amounts of the extraction solution are drawn as shown in Table B.2. In order to maintain the overall volume unchanged, the listed volume of water is added.

Table B.2 — Volume of extraction solution to be used for analysis of radial sampler in relation to the expected concentration for 7 d exposure

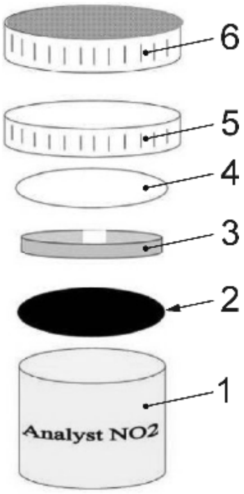
Expected NO_2 (µg/m^3), sampling period of 7 d	**Sample volume (ml)**	**Water volume to be added (ml)**
Up to 140	0,5	0
From 140 to 300	0,25	0,25
Higher than 300	0,1	0,4

B.2 Badge-type sampler A

B.2.1 Range of exposure periods

The sampler can be used for exposure times from 1 week to 2 months with shorter exposure times for high concentrations.

The limit of detection is 2 µg/m^3 for one week of sampling



Key

1 cylindrical glass vial
2 NO_2 Adsorbent
3 ring
4 septum
5 cap
6 air Barrier

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

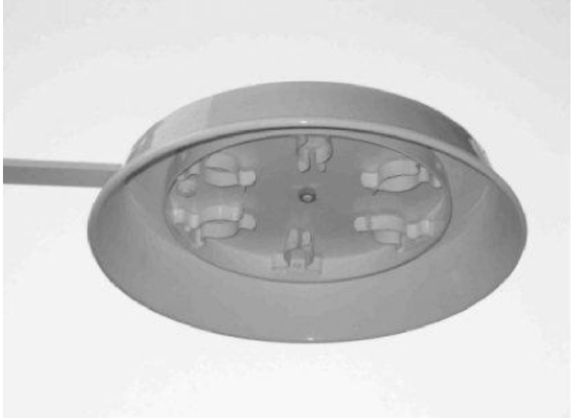


Figure B.5 — Badge-type sampler A: rain and wind shield

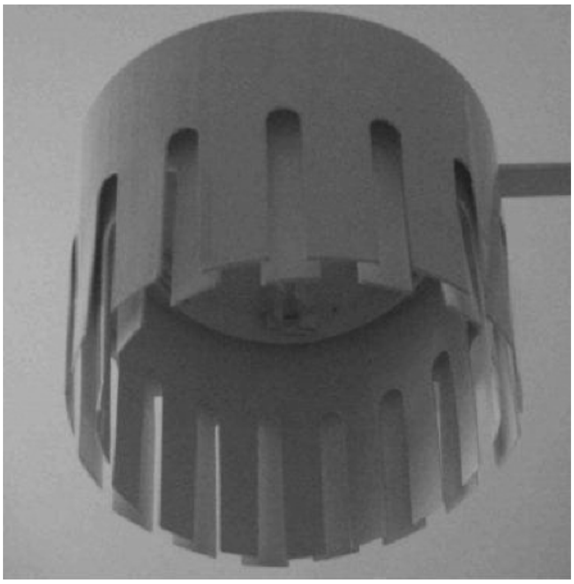


Figure B.6 — Badge-type sampler A: shelter

B.2.2 Description

The body of the sampler (Figure B.4, item 1) is a cylindrical glass vial (inner diameter 2,04 cm, length 2,54 cm) with a threaded cap at one end (items 4 and 5). NO_2 is collected on a disc of impregnated carbon paper filter (item 2) placed at the bottom of the vial and held in position by a stainless steel ring (item 3). To avoid turbulent diffusion inside the vessel, the open end is protected during sampling using a fine stainless steel screen (item 6). Before and after sampling the screen is replaced with a polyethylene cap (item 4 and 5).

A rain and wind shield (see Figure B.5) is sufficient for an effective protection of the badge-type sampler A. If any influence of wind is expected it is recommended to use an additional shelter (see Figure B.6).

B.2.3 Preparation

The sampling filter consists of a carbon paper filter (S&S 508 Round filter) coated with an acqeous solution of 10 mg/ml sodiumcarbonate and 10 mg/ml glycerine and then dried in an oven at 70 °C.

The shelf life of the sampler after preparation is up to 6 months while the stability period of the sample after sampling is up to 2 months if stored in a cool and dry location or in a refrigerator. The stability of the sample decreases when it is collected just after being exposed to high relative humidity (for example in rainy conditions). In this case, when a sampler cannot be immediately analysed (within one or two days after exposure), it is recommended to dry it before storage by opening the sampler and drying it in a desiccator filled with silica gel for 24 h. After drying, the sampler is closed again and stored in a refrigerator or in a cool and dry location until extracted.

B.2.4 Analytical method

Nitrogen dioxide, adsorbed as nitrite, can be determined by ion chromatography. Analysis by derivatization using the Griess-Saltzman reaction followed by colorimetry is also possible.

After exposure, the filters are extracted with 2,7 mM Na_2CO_3 and 0,3 mM $NaHCO_3$. The extraction of nitrite is performed in the sampler by adding 5 ml of this solution The nitrite ion concentration is determined by ion chromatography. The concentration of nitrite is calculated by referring to the calibration line established using sodium nitrite standards.

A set of standards is prepared in the range 0 to 3,0 of µg/ml nitrite to calibrate the ion chromatograph. For low-level applications more diluted standards may be necessary.

B.3 Badge-type sampler B

B.3.1 Range of conditions of exposure

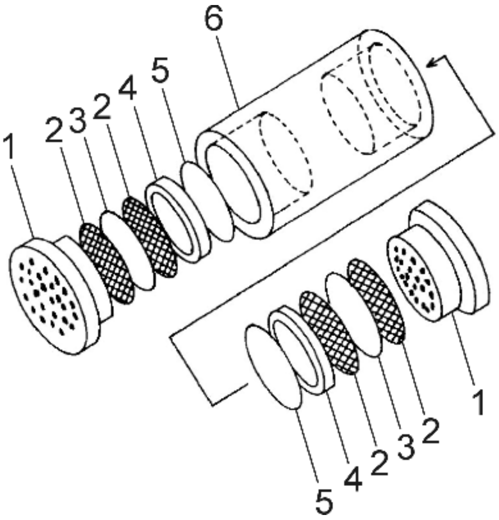
Recommended sampling periods range from 24 h to 168 h. If the sampler is used to monitor low concentrations of NO_2 in ambient air, the sampling time can be up to 30 d. In practice, samplers have been exposed for up to 4 weeks [12].

The limit of detection is 0,6 µg/m^3 for one week of sampling.

B.3.2 Description

The badge-type sampler B is a badge-type sampler that can be equipped with a sampling filter on either side of the sampler body. Sampling filters consist of cellulose fibre. Both filters can be coated with triethanolamine (TEA) for the sampling of NO_2 (see Figure B.7). The sampler should always be exposed with a shelter as provided by the manufacturer (see Figure B.8).

NOTE The sampler described in B.3 is commercially available.



Key

1 diffuser end cap
2 stainless steel mesh
3 sampling filter (14,5 mm ϕ)
4 teflon ring
5 teflon disk
6 body (15 mm ID; 19 mm OD; 60 mm length)
Protective box of the badge-type sampler B

Figure B.7 — Badge-type sampler B: schematic representation

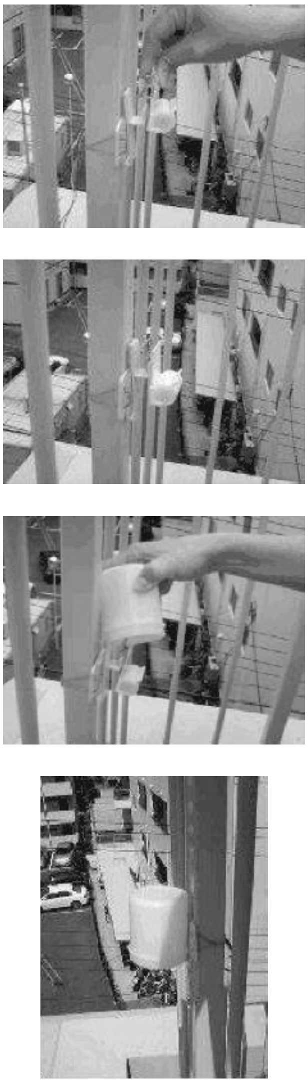


Figure B.8 — Badge type sampler B: shelter

B.3.3 Preparation

At the time of editing this standard, no preparation method of proven validity was publicly available for the coating of the absorbent on the cartridge of the sampler. Coated filters may be supplied by the manufacturer. However, a reference exists in which users have prepared their own samplers [24].

After preparation, samples shall be sealed and stored in order to minimize any undesired reactions. The following conditions for storage of coated filters, samplers and sampled filters upon refrigeration apply:

- Coated filters sealed in original glass vial with aluminium pouch: 90 d;
- Sampler loaded with coated filter(s) placed in bag in sealed brown vial: 60 d;
- Exposed sampler placed in bag in sealed brown vial: 14 d[2];
- Filter extract in sealed amber glass vial: 90 d.

---

[2] Filters should be analyzed as soon as possible after exposure.

B.3.4 Extraction and analysis

The analysis of the badge-type sampler B is fully described in [25].

Annex C
(informative)

Estimation of the uptake rate of the samplers

The uptake 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);
- using a model equation based on the value of variables of influences (see Table C.2) developed under laboratory conditions;
- estimation based upon comparisons of measurements results obtained using diffusive samplers and chemiluminescence analysers (see Table C.3).

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

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:

$$\upsilon = \frac{D\,S}{L} \qquad \text{(C.1)}$$

where

υ = uptake rate in cm³/min;

L = diffusion length in cm;

S = cross-sectional area in cm^2;

D = diffusion coefficient of NO_2 in air in cm²/min.

The uptake rate of a sampler exposed at a different temperature may be corrected using Formula (C.2). In any case, Formula (3) (8.2) will still have to be applied in order to report NO_2 concentrations at the standardized conditions required by [1], thus limiting the effect of temperature on the uptake rate.

$$\upsilon_\mathrm{T} = \upsilon_\mathrm{Tref}\left(\frac{T}{T_\mathrm{ref}}\right)^{1,81} \qquad \text{(C.2)}$$

where

υ_T = uptake rate at temperature T in cm³/min;

υ_Tref = uptake rate at reference temperature in cm³/min;

T = average temperature during exposure in K;

T_ref = reference temperature at which the uptake rate is given in K.

Based on modelling of temperature variations over various sampling periods, it has been shown that when using a diffusion coefficient – and, consequently an effective uptake rate – at the mean temperature over the sampling period, or over a period of aggregation of date (e.g., one year) the effect of temperature variations may safely be ignored [26].

Only a small error in the order of magnitude of < 1 % is introduced in comparison with the use of a proper expression of D as a function of T. This error is acceptable when compared to other contributions to the uncertainty in the effective uptake rate.

Table C.1 — Uptake rates calculated using Fick's first law of diffusion

Sampler type	**Dimensions**	**Reference conditions of Exposure**	**Uptake rate**
Tube-type sampler with a cylindrical tube [18, 27]	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 [28]	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 S_1=0,703 cm^2 S_2= 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 [18]	L=7,35 cm S_1=0,703 cm^2 S_2= 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 A	L=2,54 cm, S=3,27 cm^2. Air barrier made of polyethylene with stainless steel mesh (0,28 mm) and a Nylon close-mesh net (opening 115 µm, thickness of the wire 64 µm, and thickness of tissue 115 µm)	25 °C	0,205 cm^3/s, 12,3 cm^3/min, 738 cm^3/h

To improve the accuracy of diffusive sampler measurements, empirical equations to estimate the diffusive uptake rate according to the values of a few environmental parameters of influence have been established. These equations have been established using the results of complete test programs in exposure chambers. A list of the published equations with references is given in Table C.2.

Table C.2 — Model equations used to estimate uptake rates

Sampler type	**Dimensions**	**Exposure periods**	**Uptake rate**
Tube-type sampler with a cylindrical tube [28]	L=7,12 cm and S= 0,935 cm^2	2 weeks	$\upsilon = 72,8\times\left(2,85\times10^{-3}\times T-1,62\times10^{-4}\times RH+4,96\times10^{-5}\times T\times RH+0,9\right)$ υ is the uptake rate in cm^3/h; T is the temperature in °C; RH is the relative humidity in %.
Tube-type sampler with a cylindrical tube [29]	L=7,12 cm and S= 0,935 cm^2	2 weeks	$\upsilon = 7,4\times10^{-4}+2,72\times10^{-5}\times T+1,43\times10^{-5}\times RH+5,81\times10^{-4}\times W$ υ is the uptake rate in ng/(nmol/mol)/min; T is the temperature in °C; RH is the relative humidity in %; W is the linear air velocity at the diffusion end of the sampler in m/s.
Tube-type sampler with a cylindrical tube and membrane [17]	L=7,12 cm and S= 0,935 cm^2	2 weeks	$\upsilon = \frac{1}{2}\left(134+0,86\times RH-0,00130\times t+1,28\times T+3,18\times W\right)10^{-5}\times \left(1+\sqrt{1-\frac{0,64.10^{-5}m}{t\left(\left(134+0,86\times RH-0,00130\times t+1,28\times T+3,18\times W\right)10^{-5}\right)^2}}\right)$ υ is the uptake rate in ng/(nmol/mol)/min; T is the temperature in °C; RH is the relative humidity in %; W is the linear air velocity at the diffusion end of the sampler in m/s; m is the mass of nitrite in ng; t is the exposure time in min.
Radial-type sampler [30]			$\upsilon_T = \upsilon_{298}\left(\frac{T+273}{298}\right)^{7,0}$ υ_T is the uptake rate in ng/(nmol/mol)/min at temperatures ranging from -10 °C to 40 °C; υ_{298} is the reference sampling uptake rate at 25 °C ; T is the temperature in °C ranging from -10 °C to 40 °C.
Badge-type [25]			$\upsilon = [0,677\cdot\left(\frac{2P_n}{P_T+P_n}\right)^{\frac{2}{3}}\cdot RH+2,009\cdot T+89,8].10^{-1}\cdot\frac{V_{m,air}}{46,0055}$ υ is the uptake rate in cm^3/min; $V_{m,air}$ is the molar volume of the sampled air; RH is the ambient air relative humidity in %; T is the ambient temperature in °C; P_n is the saturated water vapour pressure at 20 °C in mmHg = 17,53; P_T is the saturated water vapour pressure at temperature T in mmHg. The mass of nitrite and time inserted in Formula (2) are in ng and min.

The uptake rate may also be evaluated by comparison of NO_2 in ambient air measured by diffusive samplers and with the reference method (EN 14211). 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 [4].

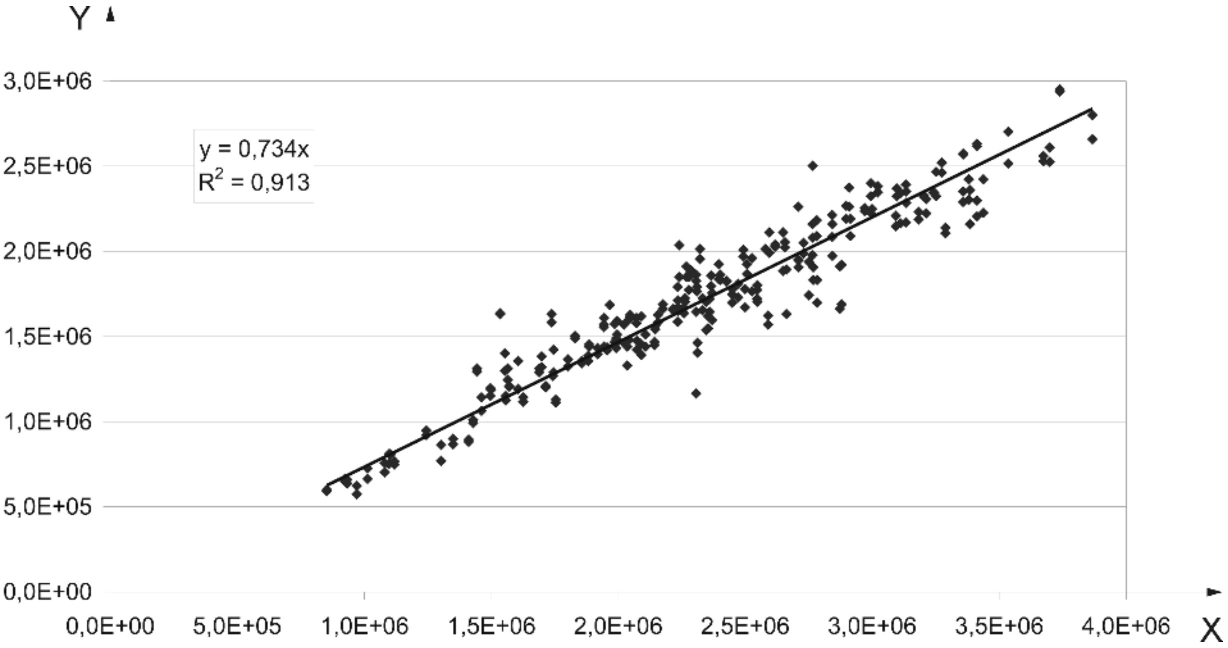
The uptake rate can be directly calculated as the slope of the regression line of the mass of NO_2 sampled by the diffusive sampler on the y-axis against the dose (concentration measured with the reference method multiplied by the exposure time) on the x-axis and (see Figure C.1). Two estimations of the uptake using this method are given in Table C.3.

Table C.3 — Uptake rate calculated by comparison with the chemiluminescence method

Sampler type	**Dimensions**	**Uptake rate**	**Coefficient of diffusion – Reference conditions of Exposure**
Tube-type sampler with a slightly conical tube [8]	L=7,35 cm, S=0,703 cm² without a glass frit S= 0,814 cm² with a glass frit	0,0122 cm^3/s, 0,734 cm^3/min, 44,0 cm^3/h with a glass frit[a]	Tubes were exposed for periods of approx. 4 weeks at 9 different sites in North Rhine-Westphalia over three years (2007-2009)
Badge-type A[b]	L=2,54 cm, S=3,27 cm². Air barrier made of polyethylene with stainless steel mesh (0,28 mm) and a Nylon close-mesh net (opening 115 µm, thickness of the wire 64 µm, and thickness of tissue 115 µm)	0,195 cm^3/s, 11,7 cm^3/min, 702 cm^3/h	Linearity of response was evaluated by exposure to known concentrations of NO_2 mixtures with purified air at 50 % relative humidity and 20 °C

[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] During laboratory experiments, it was found that the uptake rate of the badge-type A sampler was unaffected by relative humidity over a range of 20 % to 80 % relative humidity at 500 µg/m³of NO_2 for 10 h at 25 °C [6]. Badge-type A was also validated under field conditions [6].



Key

X dose [µg/m^3*min]
Y NO_2 diffusive [pg]

Figure C.1 — Determination of the uptake 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 analyzers

Annex D
(informative)

Measurement uncertainty

D.1 GUM approach

D.1.1 Measurement formula

The model formula describing the measurement is

$$C_{\mathrm{STP}} = \frac{m_{\mathrm{s}} - m_{\mathrm{b}}}{\upsilon \cdot t} \cdot \frac{T}{293} \cdot \frac{101,3}{P} \qquad \text{(D.1)}$$

where

C_{STP} = the concentration of NO_2 at standard conditions in µg/m^3;

m_{s} = the mass of nitrite found in the sample in µg;

m_{b} = the mass of nitrite found in the mean laboratory blank in µg;

υ = the sampler uptake rate at actual conditions of sampling in cm^3/min;

t = sampling time in min;

T = the average temperature during exposure in K;

P = the average pressure during exposure in Pa.

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

D.1.2 Combined standard uncertainty

The combined uncertainty, u_c, is calculated by differentiation of Formula (D.1) according to the method given in JCGM 100:2008, assuming that all parameters are uncorrelated which results in Formula (D.2).

$$\frac{u^2\left(C_{\mathrm{STP}}\right)}{C_{\mathrm{STP}}^2} = \frac{u^2(m_{\mathrm{s}}) + u^2(m_{\mathrm{b}})}{\left(m_{\mathrm{s}} - m_{\mathrm{b}}\right)^2} + \frac{u^2(\upsilon)}{\upsilon^2} + \frac{u^2(t)}{t^2} + \frac{u^2(T)}{T^2} + \frac{u^2(P)}{P^2} \qquad \text{(D.2)}$$

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.1.3 Expanded relative uncertainty

The relative expanded uncertainty, $W(C_{\mathrm{STP}})$, is calculated according to Formula (D.3)

$$W\left(C_{\mathrm{STP}}\right) = k.\frac{u\left(C_{\mathrm{STP}}\right)}{C_{\mathrm{STP}}} \cdot 100 \qquad \text{(D.3)}$$

where

W = the relative expanded uncertainty in %;

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

D.1.4 Uncertainty contributions

D.1.4.1 Uptake rate

The standard uncertainty of the uptake rate can in principle be determined from two experiments under conditions for which extreme values (minimum; maximum) of uptake rates are expected. The standard uncertainty of the uptake rate is then determined according to the GUM assuming a rectangular distribution between the two extreme values of the uptake rate (see [4]).

The standard uncertainty of the uptake rate calculated in the above way may be reduced by including additional determinations at conditions between extremes to obtain a more accurate distribution of uptake 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 NO_2 dose as shown in Figure C.1.

The uncertainties of the uptake 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.1.4.2 Mass of nitrite in sample

D.1.4.2.1 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.

$$\frac{u^2\left(m_\mathrm{s}\right)}{m_\mathrm{s}^2}=\frac{u^2\left(m_\mathrm{c}\right)}{m_\mathrm{c}^2}+w_\mathrm{l}^2+w_\mathrm{r}^2+w_\mathrm{d}^2 \quad \text{(D.4)}$$

where

m_C = the mass of nitrite in a calibration standard (D.1.4.2.2);

w_l = the relative uncertainty due to lack-of-fit of the calibration function (D.1.4.2.3);

w_r = the relative uncertainty due to analytical repeatability (D.1.4.2.4);

w_d = the relative uncertainty due to response drift between calibrations (D.1.4.2.5).

Application of this equation 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.1.4.2.2 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.1.4.2.3 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 (1) by taking the maximum residual as

$$w_l^2 = \frac{\delta_{\mathrm{i,max}}^2}{3} \qquad \text{(D.5)}$$

where

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

D.1.4.2.4 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.1.4.2.5 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 analyzed with each series of samples and blanks. The relative uncertainty is calculated as follows:

$$w_\mathrm{d}^2 = \frac{\left(b_\mathrm{i} - b_\mathrm{i+1}\right)^2}{b_\mathrm{i}^2} \qquad \text{(D.6)}$$

where

b_i = slope of calibration function at calibration i

$b_\mathrm{i+1}$ = 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.1.4.3 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.1.4.4 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.1.4.5 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:

$$\frac{u^2(T)}{T^2} = \frac{(T_{\max} - 293)^2 + (T_{\max} - 293)(T_{\min} - 293) + (T_{\min} - 293)^2}{12 \cdot (T_{\max} + T_{\min})} \tag{D.7}$$

and

$$\frac{u^2(P)}{P^2} = \frac{(P_{\max} - 101{,}3)^2 + (P_{\max} - 101{,}3)(T_{\min} - 101{,}3) + (P_{\min} - 101{,}3)^2}{12 \cdot (P_{\max} + P_{\min})} \tag{D.8}$$

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.1.4.6 Worked example

A worked hypothetical example of uncertainty estimation for the tube-type sampler with cylindrical tube is presented in Table D.1. The numerical values of the uncertainty contributions are based on the minimum performance requirements given in Table 4.

Table D.1 — Uncertainty budget

Uncertainty source	Symbol	Value	Relative standard uncertainty (%)
Uptake rate (cm^3/h)	υ	72,8	10
Sampling time (h)	t	336	0,1
Conversion to standard temperature and pressure			
- Temperature (K)	T	293	4,0
- Pressure (kPa)	P	101,3	1,0
Mass of nitrogen dioxide sampled (µg)	m_s	1,02	
- Mass of nitrite in calibration standards (%)	m_cs		2,0
- Lack-of-fit of calibration function (%)	l		2,0/√3
- Response drift between calibrations (%)	d		3,0/√3
- Analytical repeatability (%)	r		2,0
Mass of nitrogen dioxide in sample blank (µg)	m_b	0,04	25
Mass concentration of NO_2 (µg/m^3)	c	40	
Relative combined uncertainty (%)	w	10,8	
Relative expanded uncertainty (%)	W	21,7	

D.1.4.7 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 [6]. 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 standard.

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

D.2 Direct approach

D.2.1 General

Calculation may be performed according to [18]. 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 presents a worked example of evaluation of a method of measurement using diffusive samplers.

Another approach is available in the literature [17].

D.2.2 Examples of estimation of uncertainty using the direct approach

An example of the estimation of measurement uncertainty according to [4] is described in [8]. The expanded uncertainty of a single value (4 weeks exposure) was found to be 20,0 %. The expanded uncertainty of an annual average was estimated as 12,6 %.

Another example is given to illustrate the evaluation of the uncertainty of NO_2 measurements for yearly averages. The uncertainty of yearly averages has been estimated by comparison of concentrations of NO_2 measured by diffusive samplers (y) and chemiluminescence monitors (y_R) at 27 sampling sites. The data treatment has been performed by means of the evaluation method A5, Case 2, described in B.7 of EN ISO 20988:2007. The input data and the obtained uncertainty parameters are given in Table D.2.The applied evaluation procedure and the obtained results are described in Table D.3. The analysis provides the following results:

- the standard uncertainty of yearly NO_2 average mass concentration (y) for single diffusive sampler measurements in the range between 20 µg/m³ and 120 µg/m³ is given by $u(y)$ = 3,9 µg/m³;
- the expanded 95 % uncertainty of yearly NO_2 average mass concentration y is given by $U_{0,95}(y)$ = 8,1 µg/m³.

Figure D.1 shows the evaluated input data as well as the resulting 95 % margin of uncertainty about the reference values. One out of N = 27 data points is not encompassed by the evaluated 95 % margin of uncertainty. Accordingly, the fraction of observed data points encompassed by the uncertainty interval [y_R - $U_{0,95}(y)$; y_R + $U_{0,95}(y)$] is 96 %.

Table D.2 — Input data, NO_2 yearly averages

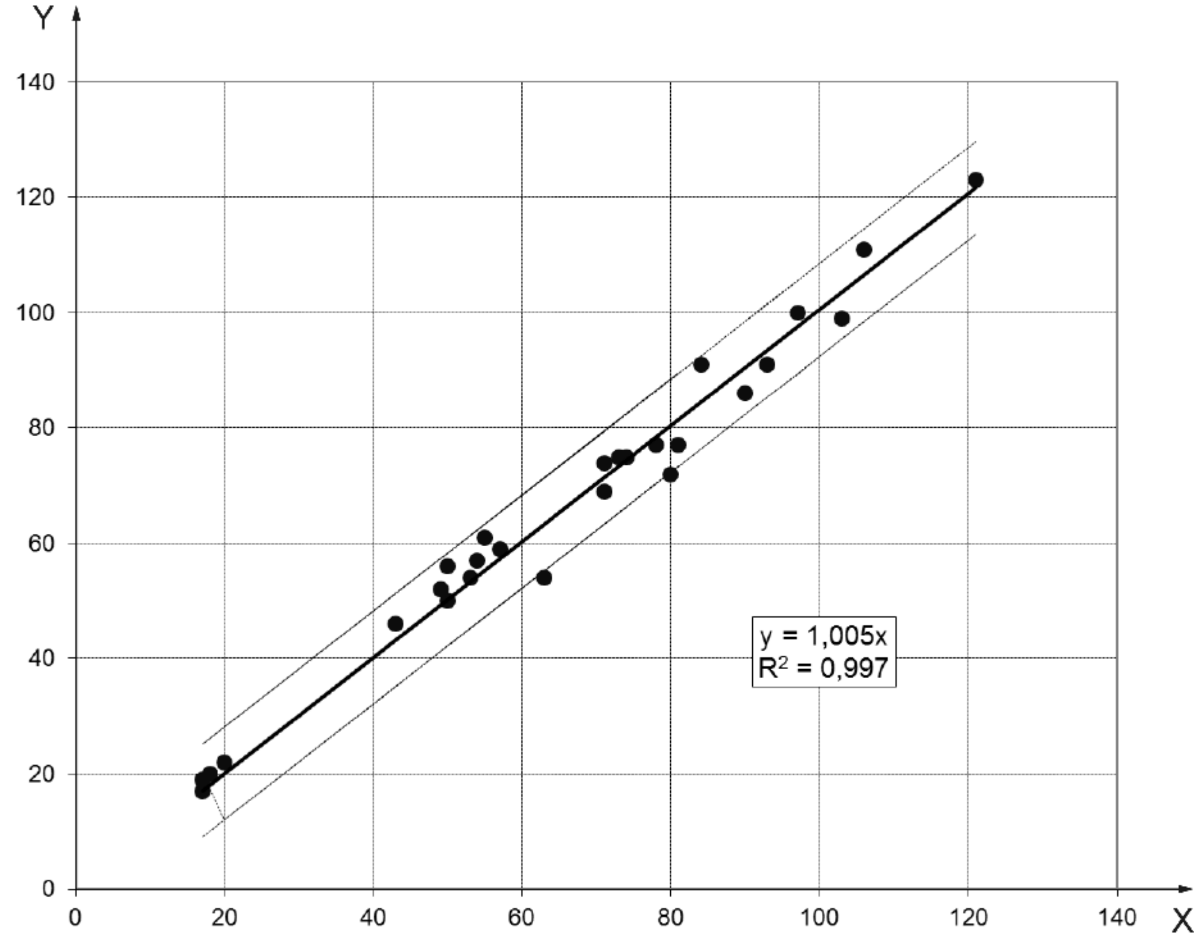
Index j	Diffusive sampler $y(1,j)$ (µg/m³)	Reference method $y_R(1,j)$ (µg/m³)	Index j	Diffusive sampler $y(1,j)$ (µg/m³)	Reference method $y_R(1,j)$ (µg/m³)
1	20	18	15	86	90
2	22	20	16	91	84
3	57	54	17	77	78
4	69	71	18	75	73
5	59	57	19	50	50
6	77	81	20	46	43
7	72	80	21	17	17
8	54	53	22	19	17
9	74	71	23	52	49
10	123	121	24	75	74
11	111	106	25	54	63
12	99	103	26	61	55
13	100	97	27	56	50
14	91	93			

Table D.3 — Work steps and results

Element	**Instructions**	**Results**
Problem specification		
Method of measurement	Sampling of NO_2 with diffusive samplers. Desorption with eluent and IC analysis	According to Standard Operating Procedures (SOP)
Measurement	Calibration of ion chromatograph (IC).	According to SOP
Ambient conditions	Variation of ambient temperature, pressure, humidity and wind velocity at the measurement sites	-
Evaluated quantity	27 NO_2 yearly average mass concentrations calculated out of time series of 4-week sampling values	y
Uncertainty parameters	Standard uncertainty of y for NO_2 in ambient air Expanded 95 % uncertainty of y.	$u(y)$ $U_{0,95}(y)$
Experimental design	Type A5, Case 2, in a direct approach: Parallel measurements of diffusive samplers and automatic analysers (chemiluminescence) for NO_2 in ambient air	-
Input data	Series of observations $y(j)$ from j=1 to N samplings	see Table D.2
Reference values	Series of 4-week sampling averaged over one year, $y_R(j)$ from j=1 to 27, which were evaluated against automatic analysers. These data have not been used to correct the measuring system	see Table D.2
Additional information	Standard uncertainty of reference method $u(y_R)$ Standard uncertainty $u(y)$ The uncertainty of reference method is treated as zero in order to obtain a conservative estimate for $u(y)$	0 µg/m³ constant
Representativeness	The conditions of control of the measurement method covered the range of variation expected to occur in intended application of the measurement method.	-
Effects not addressed	Major effects are expected to be described by the input data provided	-
Data treatment		
Model equation	$y(j) = Y_R(j) + e_y(j)$ with deviation $e_y(j) = y(j) - Y_R(j)$	-
Variance	$\text{var}(y)=u^2(y_r)+u^2(e_y)+2.\text{cov}(y_r,e_y)$	-
Covariance	$\text{cov}(y_R, e_y) = -u^2(y_R)$	0 µg/m³
Residual standard deviation	$u(e_y) = \sqrt{\frac{1}{N}\sum_{j=1}^{N}(y(j) - y_R(j))^2}$	3,9 µg/m³
Bias	$u_B(y) = \frac{1}{N}\sum_{j=1}^{N}(y(j) - y_R(j)$	0,7 µg/m³

Table D.3 *(continued)*

Results of the uncertainty analysis		
Standard uncertainty of y	$u(y)=\sqrt{\frac{1}{N}\sum_{j=1}^{N}(y(j)-y_{\mathrm{R}}(j))^{2}-u^{2}(y_{\mathrm{R}})}$	3,9 µg/m³
Degrees of freedom	$v = N$	27
Coverage factor	$k_{0,95}$	2,1
Expanded uncertainty of y	$U_{0,95}(y)=k_{0,95}\, u(y)$	8,1 µg/m³
Range of application	min(y)<= y <= max(y)	20 ≤ y ≤ 120 µg/m³



Key

X reference analyser – NO_2 mass concentration, µg/m^3
Y diffusive sampler – NO_2 mass concentration, µg/m^3

Figure D.1 — Input data and 95 % margin of uncertainty about the reference values

Bibliography

[1] EU Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe.

[2] *Air pollution in Europe 1990–2004*, European Environment Agency, EEA Report No 2/2007, page 52, ISBN 987-92-9167-964-5, ISSN 1725-9177, Office for Official Publications of the European Communities, 2007

[3] EN 14211:2012, *Ambient air — Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence*

[4] Guide to the Demonstration of Equivalence of Ambient Air monitoring Methods, version January 2010. Available at http://ec.europa.eu/environment/air/quality/legislation/assessment.htm.

[5] Pfeffer, U., Zang, T., Beier, R., Doutnik, E.-M., *Experiences with Equivalence Testing in Germany, Proceedings of the Workshop on Demonstration of Equivalence of Ambient Air Analytical Methods*, pages 54-60, Edited by P. Pérez Ballesta, Office of publication of European Commission, EUR 23216 EN, ISBN 978-92-79-08205-4, ISSN 1018-5593, DOI 10.2788/63342, Luxembourg, 2008.

[6] Delgado-Saborit, J.M., Esteve-Cano, V., *Field study of diffusion collection rate coefficients of a* NO_2 *passive sampler in a mediterranean coastal area*, Environmental Monitoring and Assessment, 2006, 120, 327-345.

[7] Pfeffer, U., Beier, R., Zang, T. *Measurements of nitrogen dioxide with diffusive samplers at traffic-related sites in North Rhine-Westphalia (Germany):* Gefahrstoffe – Reinhaltung der Luft 66 (2006), Nr. 1/2, 38-44.

[8] Pfeffer, U., Zang, T., Rumpf, E.-M., Zang, S. *Calibration of diffusive samplers for nitrogen dioxide with the reference method – Evaluation of measurement uncertainty*. Gefahrstoffe – Reinhaltung der Luft 70 (2010) 500-506.

[9] Krochmal, D., Kalina, A. *A method of nitrogen dioxide and sulphur dioxide determination in ambient air by use of passive samplers and ion chromatography.* Atmospheric Environment 31 (1997) 3473-3479.

[10] Plaisance, H., Sagnier, I., Saison, J.Y., Galloo, J.C., Guillermo, R., *Performances and application of a passive sampling method for the simultaneous determination of nitrogen dioxide and sulfur dioxide in ambient air,* Environmental Monitoring and Assessment, 79, 3, 2002, 301-315

[11] Gerboles, M., Buzica, D., Amantini, L., Lagler, F. and Hafkenscheid, Th, Environ, J.,.Feasibility study of preparation and certification of reference materials for nitrogen dioxide and sulfur dioxide in diffusive samplers, Monit., 2006, 8, 174–182

[12] *Review of the application of diffusive samplers in the European Union for the monitoring of nitrogen dioxide in ambient air*, Office of publication of European Commission, EUR 23793 EN, ISBN 978-92-79-12052-7, ISSN 1018-5593, Luxembourg, 2009.

[13] Bush, T., Smith, S., Stevenson, K. and Moorcroft, S., *Validation of nitrogen dioxide diffusion tube methodology in the UK*, Atmospheric Environment Volume 35, Issue 2, 2001, Pages 289-296.

[14] Cape, J.N. *The use of passive diffusion tubes for measuring concentrations of nitrogen dioxide in air.* Critical Reviews in Analytical Chemistry 39 (2009) 289 – 310.

[15] Atkins, D.H.F., Sandalls, J., Law, D.V., Hough, A.M., Stevenson, K. *The measurement of nitrogen dioxide in the outdoor environment using passive diffusion tube samplers*. United Kingdom Atomic Energy Authority, Harwell Laboratory, Report AERE R12133, 1986.

[16] Miller, D.P. *Ion chromatographic analysis of Palmes tubes for nitrite*. Atmospheric Environment 18 (1984) 891–892.

[17] Gerboles, M., Buzica, D., Amantini, L. *Modification of the Palmes diffusion tube and semi-empirical modeling of the uptake rate for monitoring nitrogen dioxide*. Atmospheric Environment 39 (2005) 2579–2592.

[18] ADEME Report 4414. *Passive samplers for nitrogen dioxide*. 2002.

[19] Targa, J; Loader, A and DEFRA's Working Group on Harmonisation of Diffusion tubes. *Diffusion Tubes for Ambient NO2 Monitoring: Practical Guidance for Laboratories and users*. Defra and the Devolved Administrations RMP 2877, AEA Energy and Environment, AEAT/ENV/R/2504 - Issue 1a, 2008.

[20] ADEME Report 4307. *Classification and criteria for setting up air quality monitoring stations*. 2002.

[21] European Environment Agency Technical Report 11. *Guidance report on preliminary assessment under EC air quality directives*. 1998.

[22] VDI 2453-1 *Gaseous air pollution measurement; determination of nitrogen dioxide concentration; photometric manual standard method (Saltzmann).* 1995.

[23] Buzica, D., Gerboles, M., Plaisance, H. *The equivalence of diffusive samplers to reference methods for monitoring* O_3*, benzene and* NO_2 *in ambient air*. J. Environ. Monit. 10 (2008) 1052-1059.

[24] Kim, D., Sass-Kortsak, A., Purdham, J.T., Dales, R.E., Brooke, J.R. *Associations between personal exposures and fixed-site ambient measurements of fine particulate matter, nitrogen dioxide, and carbon monoxide in Toronto, Canada*. Journal of Exposure Science and Environmental Epidemiology (2006) 16, 172–183.

[25] Protocol, version 6, June 2006. Available at www.ogawausa.com.

[26] Hafkenscheid, Th.L. Effect of temperature on long-term diffusive sampling. The Diffusive Monitor, 15 (2006) 4-5.

[27] Palmes, E., Gunnison, A., DiMattio, J., Tomczyk, C. Personal Sampler for Nitrogen Dioxide. Am. Ind. Hyg. Assoc. J. 37 (1976) 570-577.

[28] Plaisance H, Piechocki-Minguy A, Garcia-Fouque S, Galloo JC. *Influence of meteorological factors on the* NO_2 *measurements by passive diffusion tube.* Atmos. Environ., 38 (2004) 573-580.

[29] Buzica, D., Gerboles, M., Amantini, L., Perez-Ballesta, P., de Saeger, E. *Modelling of the uptake rate of the nitrogen dioxide Palmes diffusive sampler based on the effect of environmental factors*, J. Environ. Monit., 2005, 7, 169 - 174.

[30] *General instructions to use Radiello, the radial symmetry passive sampler*. Fondazione Salvatore Maugeri-Environmental Research Centre, INFO-UK-0599.

[31] JGCM 100:2008, *Evaluation of measurement data — Guide to the expression of uncertainty in measurement (GUM)*

[32] JGCM 200:2012*, International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

[33] ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

[34] ISO 3585, *Borosilicate glass 3.3 — Properties*

[35] EN 13528-1:2002, *Ambient air quality — Diffusive samplers for the determination of concentrations of gases and vapours — Requirements and test methods — Part 1: General requirements*

[36] EN 13528-2:2002, *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*

[37] EN 13528-3:2003, *Ambient air quality — Diffusive samplers for the determination of concentrations of gases and vapours — Requirements and test methods — Part 3: Guide to selection, use and maintenance*

[38] EN ISO 16000-15*, Indoor air — Part 15: Sampling strategy for nitrogen dioxide* (*NO_2) (ISO 16000-15)*

[39] EN ISO 20988:2007*, Air quality — Guidelines for estimating measurement uncertainty (ISO 20988:2007)*

[40] ISO 3534-1:2006, *Statistics — Vocabulary and symbols — Part 1: General statistical terms and terms used in probability*

[41] ISO 5725, *Accuracy (trueness and precision) of measurement methods and results*

[42] ISO Guide 35:2006, *Reference materials – General and statistical principles for certification*

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