



SLOVENSKI STANDARD

oSIST prEN 16339:2023

01-december-2023

Nadomešča:
SIST EN 16339:2013

Zunanji zrak - Metoda za določevanje koncentracije dušikovega dioksida z difuzijskim vzorčenjem

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

Außenluft - Bestimmung der Konzentration von Stickstoffdioxid mittels Passivsammler

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

Ta slovenski standard je istoveten z: prEN 16339

<https://standards.iteh.ai/catalog/standards/sist/422d91ac-a049-4008-b563-82358f556633/osist-pren-16339-2023>

ICS:

13.040.20 Kakovost okoljskega zraka Ambient atmospheres

oSIST prEN 16339:2023

en,fr,de

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

DRAFT
prEN 16339

November 2023

ICS 13.040.20

Will supersede EN 16339:2013

English Version

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

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

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 264.

If this draft becomes a European Standard, CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

This draft European Standard was established by CEN in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of 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 United Kingdom.

Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

Warning : This document is not a European Standard. It is distributed for review and comments. It is subject to change without notice and shall not be referred to as a European Standard.



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels

Contents	Page
European foreword	4
Introduction	5
1 Scope.....	6
2 Normative references.....	6
3 Terms and definitions	6
4 Description of samplers.....	8
4.1 Principle	8
4.2 Diffusive samplers	9
4.2.1 Description	9
4.2.2 Preparation	9
4.2.3 Storage and shelf-life of samplers.....	10
4.2.4 Storage after sampling.....	10
4.2.5 Chemical interferences	10
4.3 Protective devices.....	10
4.3.1 General.....	10
4.3.2 Protective shelter	10
4.3.3 Protective filter.....	11
4.4 Instructions for use	11
5 Analysis.....	11
5.1 General.....	11
5.2 Colorimetric method	12
5.2.1 General.....	12
5.2.2 Calibration.....	12
5.2.3 Extraction	12
5.2.4 Analysis.....	13
5.3 Ion chromatography method.....	13
5.3.1 General.....	13
5.3.2 Calibration.....	13
5.3.3 Extraction	13
5.3.4 Analysis.....	14
6 Calculation of the concentration of nitrogen dioxide	14
6.1 Diffusive sampling rate.....	14
6.2 Mass concentration	15
6.3 Conversion to standard conditions of temperature and pressure	16
7 Quality control/quality assurance.....	16
8 Measurement strategy	17
8.1 Calibration of the diffusive sampling rate	17
8.2 Siting criteria.....	17
8.3 Use of replicates	18
8.4 Exposure.....	18
8.5 Co-location sites	18
8.6 Auxiliary information.....	18
9 Performance requirements and measurement uncertainty.....	19

10	Report	19
	Annex A (normative) Description of tube-type samplers	21
	Annex B (informative) Description of other samplers	27
	Annex C (informative) Estimation of the diffusive sampling rate of the samplers	32
	Annex D (informative) Measurement uncertainty	38
	Annex E (informative) Reagents and equipment	48
	Annex F (informative) Validation data of the use of protective devices	51
	Annex G (informative) Significant technical changes	53
	Bibliography	54

iTeh Standards
(<https://standards.iteh.ai>)
Document Preview

[oSIST prEN 16339:2023](https://standards.iteh.ai/catalog/standards/sist/422d91ac-a049-4008-b563-82358f556633/osist-pren-16339-2023)

<https://standards.iteh.ai/catalog/standards/sist/422d91ac-a049-4008-b563-82358f556633/osist-pren-16339-2023>

prEN 16339:2023 (E)

European foreword

This document (prEN 16339:2023) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This document is currently submitted to CEN Enquiry.

This document will supersede EN 16339:2013.

iTeh Standards
(<https://standards.iteh.ai>)
Document Preview

[oSIST prEN 16339:2023](https://standards.iteh.ai/catalog/standards/sist/422d91ac-a049-4008-b563-82358f556633/osist-pren-16339-2023)

<https://standards.iteh.ai/catalog/standards/sist/422d91ac-a049-4008-b563-82358f556633/osist-pren-16339-2023>

Introduction

EU Directive 2008/50/EC [1] stipulates that European Union Member States shall apply measurement methods (fixed measurement, modelling, indicative measurement, objective estimation) and associated Data Quality Objectives (DQO), depending on levels 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. Users may use any method that is the equivalence of measurement, to be demonstrated in accordance with the Guide for the Demonstration of Equivalence (GDE) of ambient air monitoring methods [3] where specific paragraphs to methods based on diffusive sampling can be found.

Diffusive sampling is an attractive alternative to fixed monitoring using the reference methodology described in EN 14211, for the measurement of NO₂.

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 DQO given in [1].

In order to use passive samplers as a substitute for fixed measurements, it is required to demonstrate equivalence. Otherwise, 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 full 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].

prEN 16339:2023 (E)

1 Scope

This document specifies a method for the sampling of NO₂ in ambient air using diffusive sampling followed by extraction and analysis by colorimetry 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

There are no normative references in this document.

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

averaging time

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

[SOURCE: EN 482:1994] [17]

3.2

certified reference material

reference material, 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 35:2017, 3.2] [18]

3.3**combined standard measurement uncertainty**

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, 2.31] [19]

3.4**desorption efficiency**

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

[SOURCE: EN 13528-2:2002] [20]

3.5**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

[SOURCE: EN 13528-1:2002, 3.6] [21]

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

3.6**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 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”.

<https://standards.iteh.ai/catalog/standards/sist/422d91ac-a049-4008-b563-82358f556633/osist-pren-16339-2023>

3.7**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] [19]

3.8**field blank**

sealed sampler drawn from the same batch as the samplers being used for NO₂ 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.

prEN 16339:2023 (E)

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.

3.9**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

3.10**mass concentration**

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

3.11**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 1 to entry: For footnotes to the definition the reader is referred to the parent document JGCM 200:2012.

[SOURCE: JGCM 200:2012, 2.26] [19]

3.12**standard measurement uncertainty**

standard uncertainty

measurement uncertainty expressed as a standard deviation

[SOURCE: JGCM 200:2012, 2.30] [19]

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 [22].

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 [23]. Values of and formulas to calculate diffusive sampling 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 [24, 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], [25]. 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], [26], and [27]. 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. 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.

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.

prEN 16339:2023 (E)

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 [28], [29], may be used for the preparation of TEA coating solutions. The wetting agent shall not contain significant nitrite impurities.

NOTE This compound is commonly denominated as “BRIJ 35®”.

4.2.3 Storage and shelf-life of samplers

After preparation, samplers shall be sealed and stored under cool conditions, for example at temperatures between 4 °C and 10 °C, in the dark, in order to minimize any undesired reactions. Samplers are stable for up to one year [29] 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 analysed periodically to check for changes in the blank values.

4.2.4 Storage after sampling

After sampling, it is strongly recommended to seal and store samples under cool conditions, for example at temperatures between 4 °C and 10 °C, in the dark in order to minimize any undesired reactions.

Although samples may be stable for up to 4 months [30] 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, the end user shall regularly check the impact on the quality of the measurements.

4.2.5 Chemical interferences

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]).

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.

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

NOTE 1 EN 13528-3 [24, under revision] 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.

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 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:

- colorimetry after derivatization of the nitrite, using the Griess-Saltzman method [28] [32];
- ion chromatography [29].

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

prEN 16339:2023 (E)

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:

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

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.3.

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

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 at approximately 540 nm.

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

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, 0,2, 0,4, 0,6, 0,8 and 1,0 $\mu\text{g/ml}$ of nitrite. Higher concentrations are not recommended because of potential problems with linearity [33].

5.2.3 Extraction

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 at approximately 540 nm.

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

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 mixer or vibrating tray, followed by at least 1 h of standing at ambient temperature for colour development, avoiding exposure to direct sunlight.

NOTE Extraction can be made by other means, the laboratory will have to prove that other means are sufficient to extract the whole.

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

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