SLOVENSKI STANDARD
oSIST prEN 17346:2019

01-marec-2019

Kakovost zunanjega zraka - Standardna metoda za določevanje koncentracije amoniaka z difuzijskim vzorčenjem

Ambient Air Quality - Standard method for the determination of the concentration of ammonia by diffusive sampling

Außenluftqualität - Messverfahren zur Bestimmung der Konzentration von Ammoniak mit Passivsammlern

Air ambiant - Méthode normalisée pour la détermination de la concentration d'ammoniac au moyen d'échantillonneurs par diffusion

Ta slovenski standard je istoveten z: **prEN 17346**

ICS:

13.040.20 Kakovost okoljskega zraka Ambient atmospheres

oSIST prEN 17346:2019 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

DRAFT prEN 17346

January 2019

ICS 13.040.20

English Version

Ambient Air Quality - Standard method for the determination of the concentration of ammonia by diffusive sampling

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

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

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Ref. No. prEN 17346:2019 E

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European foreword

This document (prEN 17346:2019) 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 the CEN Enquiry.

Introduction

Atmospheric ammonia (NH_3) is a pollutant of major environmental concern with adverse effects on forests, species composition of semi-natural ecosystems and soils [1-4]. Emission and deposition of NH_3 can contribute significantly to total nitrogen deposition to the environment, contributing to eutrophication (nutrient enrichment) and acidification (oxidation of NH_3 to nitrate resulting in release of H^+ ions) of land and freshwaters, leading to a reduction in both soil and water quality, loss of biodiversity and ecosystem change [5-10].

In addition to these effects, NH_3 is the major precursor for neutralization of atmospheric acids, affecting the long-range transport distance of both SO_2 and NO_x and leading to the formation of secondary particles (primarily ammonium sulphate and ammonium nitrate) [11-13]. These particles have multiple impacts including effects on atmospheric visibility, radiative scattering (and the greenhouse effect) and on human health.

The recognition of NH_3 as an important air pollutant led to its inclusion in international agreements to reduce air pollutant emissions, first under the 1999 UNECE Gothenburg Protocol and then the National Emissions Ceilings Directive (NECD) (2001/81/EC) of the EU. The target of both these agreements is that NH_3 emissions should not exceed emission ceilings set for EU member states, with a particular focus on reducing the extent of critical loads exceedance for acidification and eutrophication effects. Revision of the Gothenburg Protocol (2012) and the NEC Directive (2016) include new, more stringent emission ceilings for 2020 that seek more environmental protection and improvement in air quality than has so far been committed, including the introduction of an emissions ceiling for particulate matter (PM). Under the 2012 UNECE Gothenburg Protocol, EU member states must jointly cut their emissions of NH_3 by 6 % and particles by 22 % between 2005 and 2020. As a precursor of PM, controlling ammonia is important to reducing particle emissions of $PM_{2.5}$ and PM_{10}. A recent study employing three chemical transport models found that the models underestimated the formation of ammonium particles and concluded that the role of NH_3 on PM is larger than originally thought. Thus the implementation of 2020 targets detailed above may not be enough to deliver compliance with proposed particle limit values, and further local measures may be required to be compliant [14].

Other legislations to abate ammonia emissions include the Industrial Emissions Directive (IED) (2010/75/EU) which requires pig and poultry farms (above stated size thresholds) to reduce emissions using Best Available Techniques. In Germany, the recommended exposure limit for the protection of ecosystems is 10 µg/m^3 (TA Luft, Annex 1, [15]) For the protection of vegetation and ecosystems, new revised “Critical Levels” (CL) of NH_3 concentrations were adopted in 2007, of 1 µg/m^3 and 3 µg/m^3 annual mean for the protection of mosses and vegetation under field conditions, respectively, which replaced the previous CL annual mean value of 8 µg/m^3. A monthly critical level of 23 µg /m^3 was retained as a provisional value in order to deal with the possibility of high peak emissions during periods of manure application (e.g. in spring) ([16]).

Table 1 — Summary of critical NH_3 values for ecosystems under field conditions

Concentration ($\mu g/m^3$)	Specification	Types of locality
1	UNECE Critical Level for lower plants (lichens, mosses, bryophytes)	Natura 2000 sites: Habitats Directive. Background and semi-natural areas
3	UNECE Critical Level for higher plants	Sensitive habitats
10	German First General Administrative Regulation Pertaining the Federal Immission Control Act Maximum near installations where ecological monitoring undertaken.	Near installations
23	Monthly critical level (only used for manure spreading)	In close proximity to emission sources

Improving knowledge on levels of ammonia in the ambient air and near sources is therefore important for the assessment of:

— Environmental effects on ecosystems (Contribution to eutrophication and acidification processes);

— Contributions to the formation of PM_{10} and $PM_{2.5}$;

— Effectiveness of current and future abatement measures to reduce ammonia emissions.

The simplest to the latest state-of–the-art techniques for measurement of atmospheric ammonia are presented in Table 2.

Table 2 — Measurement methods suitable for determination of atmospheric ammonia gas and ammonium particle concentrations

Monitoring Methods	Time resolution	References
Integrative methods: Passive		
Passive diffusion samplers	daily to monthly	[17] [18] [19] [20]
Integrative methods: Active		
Simple denuder systems with offline chemical analysis	daily to monthly	[17] [21] [19]
Annular denuder systems (ADS) with offline chemical analysis	hourly to daily	[22]
Conditional sampling with denuders at different heights (COTAG)	weekly to monthly	[23]
Continuous: wet chemistry methods		
Annular Denuder Systems with online analysis Membrane stripping with online analysis	hourly or better depending on set-up	[24]
Steam Jet Aerosol Collector Systems for gas and aersosol	hourly or better depending on set-up	[25] [26]
Continuous: optical methods		
Differential Optical Absorption Spectrometry(DOAS)	hourly or better depending on set-up	[27]
Tunable Diode Laser Absorption Spectrometry and Quantum Cascade Laser (TDL & QCL AS respectively)	hourly or better depending on set-up	[28]
Photoacoustic spectrometry	hourly or better depending on set-up	[29]
Chemiluminescence with catalytic conversion	hourly or better depending on set-up	[30]

Integrative atmospheric sampling methods such as passive diffusion samplers and active samplers provide measurement of concentrations of NH_3 averaged over the chosen sampling time. The diffusive samplers used include those that are available commercially and those that have been developed in-house by organisations to meet specific research requirements. A full validation of diffusive sampling methods for ammonia in accordance with the European Standard (EN 13528-2 [31]) would be costly and would also require specialist facilities only available at well-equipped larger metrological institutes. Validation of the quantitative measurement of ammonia through comparison with “reference” methods is problematic for ammonia as there is no currently accepted and defined reference method. Automatic continuous analysers, using spectroscopic or other techniques as used for other inorganic gases still suffer from robust published calibration demonstrated at ambient concentrations and conditions.

1 Scope

This document specifies a method for the sampling and analysis of NH_3 in ambient air using diffusive sampling.

It can be used for NH_3 measurements at ambient levels, but the concentration range and exposure time are sampler dependent, and the end user is therefore advised to comply with the operating instructions provided by the manufacturer.

NOTE Denuders may be used as a surrogate reference method until there are improvements in the continuous optical methods.

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 http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

3.1
combined standard uncertainty
standard measurement uncertainty that is obtained using the individual standard measurement uncertainties associated with the input quantities in a measurement model

[SOURCE: JGCM 200:2012] [32]

3.2
extraction efficiency
ratio of the mass of analyte extracted from a sampling device to that applied

3.3
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 13528-2:2002] [31]

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

3.4
diffusive sampling rate
rate at which the diffusive sampler collects a particular gas or vapour from the atmosphere

Note 1 to entry: The sampling rate is usually expressed in units of (m^3/h), (ml/min) or (cm^3/min).

Note 2 to entry: cm^3/min may be converted to SI units of m^3/s by factor 1,67 x 10^{-10}.

3.5
expanded (measurement) uncertainty
product of a combined standard measurement uncertainty and a factor larger than the number one

[SOURCE: JCGM 200:2012]

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.

3.6
field blank
sealed sampler drawn from the same batch as the samplers being used for NH_3 monitoring. This sampler is taken unopened to the field and returned together with exposed samplers after the sampling is completed

Note 1 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 ammonium to investigate the possibility of contamination of samplers during transport. This blank is only used for quality control purposes.

3.7
laboratory blank
sealed sampler drawn from the same batch as the samplers being used for NH_3 monitoring which is stored in a refrigerator during sampling of the exposed samplers

3.8
standard (measurement) uncertainty
measurement uncertainty expressed as a standard deviation

[SOURCE: JGCM 200:2012]

3.9
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 Description of samplers

4.1 General

The diffusive sampler is exposed to air for a measured time period. NH_3 migrates through the sampler diffusion path and is collected by reaction onto the relevant sorbent.

The diffusive sampling rate is determined either by numerical calculation based on Fick’s first law of diffusion (see EN 13528-3 [33]) through calibration by exposure to standard atmospheres or through co-located calibration studies against another well characterized method in the field.

Because there are different sampler designs, each common sampler type is briefly described below.