

Ambient air - Standard method for the determination of the concentration of ammonia using diffusive samplers

EESTI STANDARDI EESSÕNA

NATIONAL FOREWORD

| | |
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English Version

**Ambient air - Standard method for the determination of
the concentration of ammonia using diffusive samplers**

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

Außenluft - Messverfahren zur Bestimmung der
Konzentration von Ammoniak mit Passivsammlern

This European Standard was approved by CEN on 13 April 2020.

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European foreword

This document (EN 17346:2020) 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of an identical text or by endorsement, at the latest by November 2020, and conflicting national standards shall be withdrawn at the latest by November 2020.

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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 have to jointly cut their emissions of NH_3 by 6 % and particles by 22 % between 2005 and 2020. As a precursor of PM, controlling NH_3 is important to reducing particle emissions of $\text{PM}_{2.5}$ 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 [14]. 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.

Other legislations to abate NH_3 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. For the protection of vegetation and ecosystems, new revised "Critical Levels" (CL) of NH_3 concentrations were adopted in 2007 (see Table 1), of $1 \mu\text{g}/\text{m}^3$ and $3 \mu\text{g}/\text{m}^3$ annual mean for the protection of lichens/bryophytes and higher plants under field conditions, respectively, which replaced the previous CL annual mean value of $8 \mu\text{g}/\text{m}^3$. A monthly critical level of $23 \mu\text{g}/\text{m}^3$ 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) ([15]). In Germany, the recommended exposure limit for the protection of ecosystems is $10 \mu\text{g}/\text{m}^3$ (TA Luft, Annex 1, [16]).

Table 1 — Summary of upper limits of NH₃ concentrations for protection of ecosystems under field conditions

| Concentration (µg/m ³) | Specification | Types of locality |
|------------------------------------|--|--|
| 1 | UNECE Critical Level (annual mean) for lower plants (lichens, bryophytes) | Sensitive ecosystems in which the lichens and bryophytes are important components, e.g. designated sites for nature conservation and protection of sensitive species, e.g. Natura 2000 sites |
| 3 | UNECE Critical Level (annual mean) for higher plants | Sensitive ecosystems in which the higher plants are important components, e.g. designated sites for nature conservation and protection of sensitive species, e.g. Natura 2000 sites |
| 10 | German First General Administrative Regulation Pertaining the Federal Immission Control Act Maximum near installations where ecological monitoring undertaken. | Near installations |
| 23 | UNECE critical level (monthly mean) – for peak emission periods such as in months where slurry spreading takes place. | In close proximity to emission sources |

Improving knowledge on levels of NH₃ 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 PM₁₀ and PM_{2,5};
- effectiveness of current and future abatement measures to reduce NH₃ emissions.

The simplest to the latest state-of-the-art techniques for measurement of atmospheric NH₃ are presented in Table 2.

Table 2 — Measurement methods suitable for determination of atmospheric NH₃ 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] [19] [21] |
| 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 aerosol | 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 and 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 NH_3 in accordance with the European Standard (EN 13528-2 [31]) would be costly and would also require specialist facilities only available at well-equipped large metrological institutes. Validation of the quantitative measurement of NH_3 through comparison with “reference” methods is problematic for NH_3 as there is no currently accepted and defined reference method. Automatic continuous analysers for NH_3 , employing spectroscopic or other techniques (Table 2) are available commercially, but there is a lack of robust published calibration data and procedures for reliable field measurements under ambient concentrations and conditions [32].

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 match the sampler type to the measurement requirement and to follow the operating instructions provided by the manufacturer.

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 <https://www.iso.org/obp/ui>

3.1

combined standard measurement uncertainty

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: JCGM 200:2012, 2.31] [33]

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

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

[SOURCE: EN 13528-2:2002, 3.6] [31]

3.4

diffusive sampling rate

diffusive uptake 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 $1,67 \times 10^{-8}$.