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

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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of an identical text or by endorsement, at the latest by November 2020, and conflicting national standards shall be withdrawn at the latest by November 2020.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 $PM_{2,5}$ 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 µg/m³ and 3 µg/m³ 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 µg/m³. A monthly critical level of 23 µg /m³ 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 µg/m³ (TA Luft, Annex 1, [16]).

Table 1 — Summary of upper limits of NH$_3$ 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 NH$_3$ 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 NH$_3$ emissions.

The simplest to the latest state-of–the-art techniques for measurement of atmospheric NH$_3$ are presented in Table 2.

Table 2 — Measurement methods suitable for determination of atmospheric NH$_3$ 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.

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