



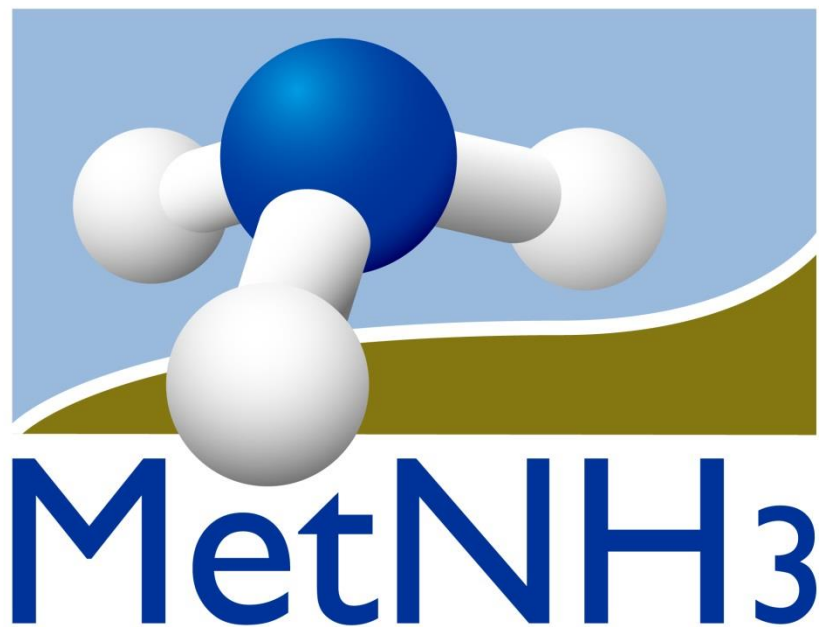
ENV55 MetNH3

„Metrology for ammonia in ambient air“

2nd MetNH3 workshop on ammonia measurement methodology

09 - 10 May 2017

Federal Institute of Metrology METAS, Bern-Wabern, Switzerland



12:00-13:00	REGISTRATION AND COLD LUNCH
13:00-13:30	WELCOME AND INTRODUCTION Towards a Consistent Metrological Infrastructure for Ammonia Measurements in Ambient Air: EMRP JRP MetNH3 Bernhard Niederhauser (METAS), coordinator JRP MetNH3
13:30-15:00	WP1: IMPROVED REFERENCE GAS MIXTURES BY STATIC AND DYNAMIC GRAVIMETRIC GENERATION METHODS
13:30-13:50	Surface deactivation by inert CVD silicon coatings from SilcoTek Johannes Kütt (SilcoTek Inc.)
13:50-14:10	Stability tests for commercially produced cylinders for ammonia in nitrogen mixtures Janneke van Wijk (VSL)
14:10-14:30	State of the art stationary and mobile infrastructure for the dynamic generation and dilution of traceable reference gas mixtures of Ammonia at ambient air amount fractions Daiana Leuenberger (METAS) et al.
14:30-14:50	New development of a price affordable, traceable & portable gas generator for reactive gases Daniel Calabrese (LNI Swiss Gas)
15:00-15:30	COFFEE BREAK
15:30-17:30	WP2: DEVELOPMENT AND CHARACTERISATION OF LASER BASED OPTICAL METHODS
15:30-15:50	Novel mobile multi-gas sensor for ammonia detection in the environment Carlo Tiebe (BAM) et al.
15:50-16:10	Sampling and measuring NH ₃ with photoacoustics Rens. Zijlmans, B. Kamps (LSE Monitors BV)
16:10-16:30	Improved surface treatment and sampling handling to lower the response time of the Picarro G2103 ammonia analyzer Renato Winkler, Chris Rella and Derek Fleck (Picarro Inc.)
16:30-16:50	An optical transfer standard for ammonia in ambient air: PTB's contribution to the MetNH3 project Nils O. B. Lüttschwager (PTB) et al.
16:50-17:10	Improved fitting tools for uncertainty evaluation of Optical Transfer Standards David Balslev-Harder (DFM), Nils O. B. Lüttschwager (PTB)
17:10-17:30	A sampling-free laser based spectrometer for ammonia online measurement Timo Rajamäki (VTT)
17:30	APERITIF AND WORKSHOP DINNER AT METAS

08:30-12:00	WP3: FIELD APPLICABLE METHODS
08:30-08:50	Stability of gravimetrically prepared ammonia in nitrogen standards at 10 and 100 μmolmol^{-1} Elena Amico di Meane (NPL) et al.
08:50-09:10	Ammonia measurements with diffusive samplers: applications in Switzerland and method comparisons Eva Seitler (FUB) et al.
09:10-09:30	Validation of ammonia diffusive and active samplers in a controlled atmosphere test facility using traceable Primary Standard Gas Mixtures Nicholas A. Martin (NPL) et al.
09:30-09:50	Ammonia measurement with MARGA Ulla Makkonen (FMI)
10:00-10:30	COFFEE BREAK
10:30-10:50	Measurements of ammonia emissions from an open slurry storage tank Jörg Sintermann (AWEL) et al.
10:50-11:10	Performance of the DOAS and QCL systems during the MetNH ₃ intercomparison in Scotland Albrecht Neftel et al.
11:10-11:45	Evaluation study of the suitability of instrumentation to measure ambient NH ₃ concentrations under field conditions Marsailidh M. Twigg (CEH) et al.
11:45-12:00	CLOSING REMARKS
12:00-12:45	COLD LUNCH
12:45	OPTIONAL LABORATORY TOURS

Oral Presentations

Towards a Consistent Metrological Infrastructure for Ammonia Measurements in Ambient Air: EMRP JRP MetNH3

Bernhard Niederhauser¹, Elena Amico di Meane², David Balslev-Harder³, Christine Braban⁴, Volker Ebert^{5,11}, Valerio Ferracci², Bjoern Giesecking², Thomas Hübert⁶, Daiana Leuenberger¹, Nils Lüttschwager⁵, Nicholas Martin², Céline Pascale¹, Andrea Pogány⁵, Timo Rajamäki⁷, Carlo Tiebe⁶, Marsailidh Twigg⁴, Olavi Vaittinen⁸, Janneke van Wijk⁹, Klaus Wirtz¹⁰

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Measuring ammonia in ambient air is a sensitive and priority issue due to its harmful effects on human health and ecosystems. In addition to its acidifying effect on natural waters and soils and to the additional nitrogen input to ecosystems, ammonia is an important precursor for secondary aerosol formation in the atmosphere. The European Directive 2001/81/EC on “National Emission Ceilings for Certain Atmospheric Pollutants (NEC)” regulates ammonia emissions in the member states. However, there is a lack of regulation regarding certified reference material (CRM), applicable analytical methods, measurement uncertainty, quality assurance and quality control (QC/QA) procedures as well as in the infrastructure to attain metrological traceability.

As shown in a key comparison carried out in 2007, there are even discrepancies between reference materials provided by European National Metrology Institutes (NMIs) at amount fraction levels up to three orders of magnitude higher than ambient air levels.

MetNH3 (Metrology for ammonia in ambient air), a three-year project (June 2014-17) in the framework of the European Metrology Research Programme (EMRP) aims to reduce the gap between requirements set by the European emission regulations and state-of-the-art of analytical methods and reference materials.

The overarching objective of the JRP is to achieve metrological traceability for ammonia measurements in ambient air from primary certified reference material CRM and instrumental standards to the field level. This requires the successful completion of the three main goals, assigned to three technical work packages:

1. To develop improved reference gas mixtures by static and dynamic gravimetric generation methods

Preparation and characterisation of traceable calibration standards (in pressurised cylinders as well as mobile generators) of ammonia amount fractions similar to those found in ambient air based on existing methods for other reactive analytes. The aimed uncertainty was < 1 % for static mixtures at the 10 – 100 µmol/mol level, and < 3 % for portable dynamic generators in the 0 – 500 nmol/mol amount fraction range. Special emphasis was on the minimisation of adsorption losses.

2. To develop and characterise laser based optical spectrometric standards

Evaluation and characterisation of the applicability of a newly developed open-path as well as of existing extractive measurement techniques to be employed as SI-traceable optical transfer standards.

3. To establish the transfer from high-accuracy standards to field applicable methods

Employment of characterised exposure chambers as well as field sites for validation and comparison experiments to test and evaluate the performance of different instruments and measurement methods at ammonia amount fractions that are relevant to monitoring ambient air quality.

Surface deactivation by inert CVD silicon coatings from SilcoTek

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CVD silicon coatings from SilcoTek deactivate stainless steel surfaces of gas delivery compounds like stainless steel tubing, fittings, valves, pressure regulators and others. The coating prevents interaction between the stainless steel surface and active compounds such as NH₃, NO_x, H₂S, Hg and many others. This avoids false test results and long retention times of gas analyzers. The CVD process generates homogenous coating layer even on very complex geometries. The coating layer has a thickness of ca. 250 Nanometer and has therefore no influence on tightness and tolerances of the substrate parts.

Stability tests for commercially produced cylinders for ammonia in nitrogen mixtures.

Janneke van Wijk

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To determine the stability of commercially produced cylinders for ammonia mixtures in cylinders experiments have been performed at the 10 micromol/mol level. The adsorption of ammonia on the surface of the cylinders has been quantified and stability test over a one year period have been performed. The analytical method at VSL has been improved to be able to compare individual measurement results and be able to check long term effects. Results of the stability test will be presented.

Stability of gravimetrically prepared ammonia in nitrogen standards at 10 and 100 μmolmol^{-1}

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Ammonia (NH₃) is a well-known ambient pollutant which plays a key role in both atmospheric chemistry and biogeochemical processes occurring in a variety of ecosystems. Ammonia is emitted from intensive animal farming and certain industrial processes: once in the atmosphere, it contributes to the increasing ambient levels of particulate matter observed across Europe. As legislation is being implemented to curb ammonia emissions, it is crucial to achieve metrological traceability for ammonia measurements in ambient air to allow comparability of field measurements, ensure accuracy of emissions inventories and verify the effectiveness of emission ceiling policies. The development of stable and traceable gas standards for instrument calibration underpins all of the above. To address this requirement, a stability study on gravimetrically-prepared high-pressure ammonia mixtures in nitrogen was carried out for two years for two different cylinder types at two different concentrations: 10 and 100 mmolmol^{-1} . New standards were prepared gravimetrically every three to six months for comparison to determine any variations due to instability. In the first type of cylinders ammonia appears stable at 100 mmolmol^{-1} but shows degradation of about 2% at 10 mmolmol^{-1} over the timescale of the stability study; on the other hand, the second type of cylinders exhibits good stability already at the 10 mmolmol^{-1} level.

State of the art stationary and mobile infrastructure for the dynamic generation and dilution of traceable reference gas mixtures of Ammonia at ambient air amount fractions

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Ammonia (NH₃) in the atmosphere is the major precursor for neutralising atmospheric acids and is thus affecting not only the long-range transport of sulphur dioxide and nitrogen oxides but also stabilises secondary particulate matter. These aerosols have negative impacts on air quality and human health. Moreover, they negatively affect terrestrial ecosystems after deposition.

NH₃ has been included in the air quality monitoring networks and emission reduction directives of European nations. Atmospheric concentrations are in the order of 0.5 – 500 nmol/mol. However, the lowest substance amount fraction of available certified reference material (CRM) is 10 µmol/mol. This due to the fact that adsorption on the walls of aluminium cylinders and desorption as pressure in the cylinder decreases cause substantial instabilities in the amount fractions of the gas mixtures.

Moreover, analytical techniques to be calibrated are very diverse and cause challenges for the production and application of CRM.

The Federal Institute of Metrology METAS has developed, partially in the framework of EMRP JRP ENV55 MetNH₃, an infrastructure to meet with the different requirements in order to generate SI-traceable NH₃ reference gas mixtures dynamically in the amount fraction range 0.5 – 500 nmol/mol and with uncertainties $U_{\text{NH}_3} < 3\%$. The infrastructure consists of a stationary as well as a mobile device for full flexibility in the application:

In the stationary system, a magnetic suspension balance monitors the specific temperature and pressure dependent mass loss over time of the pure substance in a permeation tube (here NH₃) by permeation through a membrane into a constant flow of carrier gas. Subsequently, this mixture is diluted with a system of thermal mass flow controllers in one or two consecutive steps to desired amount fractions.

The permeation tube with calibrated permeation rate (mass loss over time previously determined in the magnetic suspension balance) can be transferred into the temperature-regulated permeation chamber of a newly developed mobile reference gas generator (ReGaS1). In addition to the permeation chamber it consists of the same dilution system as afore mentioned, stationary system. All components are fully traceable to SI-units.

Considerable effort has been made to minimise adsorption on the gas-wetted stainless steel surfaces and thus to reduce stabilisation times by applying the SilcoNert2000[®] coating substance.

Analysers can be connected directly to both, stationary and mobile systems for calibration. Moreover, the resulting gas mixture can also be pressurised into coated cylinders by cryo-filling. The mobile system as well as these cylinders can be applied for calibrations in other laboratories and in the field.

In addition, an SI traceable system based on a cascade of critical orifices has been established to dilute NH₃ mixtures in the order of µmol/mol stored in cylinders for the participation in the international key-comparison CCQM K117. It is planned to establish this system to calibrate and re-sample gas cylinders due to its very economical gas use.

Here we present insights into the development of said infrastructure and results of the first performance tests. Moreover, we include results of the study on adsorption/desorption effects in dry as well as humidified matrix gas into the discussion on the generation of reference gas mixtures.

Acknowledgement: This work was supported by the European Metrology Research Programme (EMRP). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

New development of a price affordable, traceable & portable gas generator for reactive gases

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A metrological traceable & portable gas generator to produce certified reference material of reactive gases at ambient air levels is designed, constructed and validated. The novel gas generator will comprise the innovations of running at high pressures, combining a permeation and dilution unit, having coated surfaces and being fully accessible to calibration. The generator will be compliant with actual air quality standards and allow highly accurate measurements. The presentation will describe the insights and first results of the construction and validation process.

Measuring toxic and/or reactive (greenhouse) gases is becoming a crucial task in air quality and climate change investigations. For accurate measurements of trace gases in air, the availability of calibration gases with a well-known uncertainty is a necessary precondition. Until now, the majority of measurements are not traceable to national standards. For stable gases such as CO or CO₂, the reference gas mixtures are stored in cylinders with a well-known uncertainty. Yet, this is not possible for reactive gases at low concentration levels mainly due to adsorption of molecules on the walls, lowering the substance amount fraction of the gas mixture. One possibility is then to produce those gases dynamically with gas generators using a pure gas source in the liquid state (permeation device).

The main Innovations are:

- constructing a traceable, internationally recognised gas mixture generator
- Allow verification and adjustment of each relevant sensor
- find the correct coating / passivation techniques suitable for reactive gases and / or at very low concentrations
- Permeation Oven under elevated pressure to allow double dilution stage and archive very low concentrations.
- Combine dilution and permeation
- Be portable (weight, autonomy of the battery, source of Air,...)

Novel mobile multi-gas sensor for ammonia detection in the environment

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Pollution through emission of toxic gases becomes an increasing problem for the environment in agricultural, industrial and urban areas. In future, environmental emissions as well as ambient air must be monitored at even lower concentrations as nowadays. Consequently, demands arise for measuring concentrations as low as the lower ppm or even ppb range. Current state-of-the-art technologies, as for instance electrochemical sensors, have reached their limits in this regard.

The developed ammonia gas standard generator produces standard gas mixtures which comply with the metrological traceability for ammonia gas standards in the desired environmentally relevant measurement range of e. g. 0.5 to 500 nmol/mol. This gas standard preparation method is based on the permeation of ammonia through a membrane at a constant temperature as well as the mixing of this permeated gas with a carrier gas to adjust a gas standard of known concentration. The ammonia gas standard is suitable for the calibration of standard optical methods, e. g. cavity ring-down spectroscopy (CRDS) and multi-gas sensors.

The detection of gaseous ammonia in the lower ppm or even ppb range is obtained by incorporation of a fluorescent dye, which shows fluorescence enhancement in the presence of the analyte, into a polymer support being responsible for the accumulation of the analyte. The use of optical fluorescence as transduction mechanism enables high sensitivity as well as high temporal resolution [1]. Here, we present first results on such a sensor system including the use of the developed gas standard generator for calibration issues. Additional benefits, particularly of fluorescence-based sensors, are their capability for miniaturization and potential multiplex mode. Beside the development of a highly sensitive and selective sensor, the integration of such systems into mobile sensor devices is addressed.

These sensors and sensor systems are developed and will be validated and operated in form of functional models for the application areas, structure-integrated sensors and mobile multi-gas sensors.

[1] Ozawa, T., Yoshimura, H., Kim, S. B., *Advances in Fluorescence and Bioluminescence Imaging*. Anal. Chem., 85, 590, 2013.

Sampling and measuring NH₃ with photoacoustics

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The stickiness of ammonia (NH₃) to tubing and analyzer construction materials is a widely known effect. In extractive gas analyzer systems, this is complicating the generation of precise, accurate, long-term, continuous data on the concentration of NH₃ in ambient air. In this contribution, the solution of LSE Monitors BV is presented, which is based on photoacoustics with a quantum cascade laser.

In photoacoustics, pressure waves are generated by directing an infrared laser light beam through a measurement cell. The sample gas is flushed continuously through the measurement cell. When NH₃ is present in the sample gas, it absorbs a fraction of the infrared laser light. This results in a slight increase of temperature and pressure of the sample gas in the measurement cell. By modulation the laser light intensity, pressure waves are generated, which are measured by integrated microphones. The sensitivity of the photoacoustics system is optimized by amplifying the pressure waves. The amplification of pressure waves is realized by choosing the geometry of the measurement cell in such a way, that resonant standing pressure waves are generated. Apart from the sensitivity of the measurement system, one of the key advantages of this approach is the small required measurement volume in the heart of the instrument. This results in a high refresh rate of the measurement cell, even at a relatively low gas flow. The high refresh rate minimizes the residual sticking effects caused by interactions of NH₃ with the measurement cell material.

In order to further optimize the response time of the analyzer on changing ambient concentrations of NH₃, a bypass system has been developed. This bypass system combines the generation of a high gas flow with noise reduction elements and an on-board calibration system optimized for NH₃. In this contribution, the configuration and performance of the bypass system in combination with an LSE NH₃-1700 analyzer is discussed in detail.

Improved surface treatment and sampling handling to lower the response time of the Picarro G2103 ammonia analyser

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Ammonia emissions from agricultural and industrial activities have become an ever more important topic both for scientists as well as for regulatory bodies due to the severe impacts of ammonia on human health and the environment. Accurate and reliable measurements of atmospheric NH₃ emissions are challenging due to i) the difficulty to obtain traceable reference material and ii) the physical and chemical properties of the NH₃ molecule itself which poses a challenge for real time measurements.

The Picarro G2103 cavity ring-down spectrometer has been used in many scientific as well as industrial applications, where accuracy, ease of use and long term stability (low drift) are crucial. Measuring accurate ammonia emissions while keeping short response times are hindered by the strong adsorption of the NH₃ molecule on wetted surfaces, and require the sample handling components to be coated or made of non-adhesive materials.

Here we present the latest technical innovations of the Picarro analyzer which include new a coating solution for the wetted surfaces inside the analyzer and an overall improved sample handling, both with the aim to further decrease the response time and therefore increase the performance for real time ammonia monitoring.

An optical transfer standard for ammonia in ambient air: PTB's contribution to the MetNH3 project

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In MetNH3, PTB developed and metrologically characterized an optical transfer standard (OTS) for ammonia in air. An OTS offers an alternative route to calibrations of air monitoring instrumentation by means of reference gas mixtures. OTS amount fraction measurement results are referenced to absorption line parameters such as line strength and broadening coefficients. These parameters are fundamental molecular properties that have to be measured in independent, ideally SI-traceable measurements from well characterized gases or gas mixtures [1]. Once molecular light absorption parameters are available, the OTS can measure reference gas-independent and can itself be used to calibrate or independently validate air monitoring analysers.

In this contribution we show how we developed an OTS starting from a commercial cavity ring-down spectrometer (Picarro Model G2103) with a lower detection limit of <1 ppb (nmol/mol). A custom spectral fitting routine, as well as direct laser absorption measurements of spectral properties of ammonia [1] provide the basis of our OTS. We will discuss details on the spectral model and the uncertainty contributions. The underlying fitting routine is based on a generalized least-squares regression approach [2] that allows for GUM-compliant uncertainty propagation [3] and formulation of an uncertainty budget. It was implemented by DFM in the Python programming language for accessibility and flexibility and will be shown in a separate presentation.

We will further present an evaluation of the performance of our OTS from 1 ppb to 200 ppb. Characterization includes investigations of effects of ambient conditions such as ambient temperature or humidity content of the sample gas, instrument response, and cross-sensitivities to typical trace gases in air. Validation measurements were performed over a period of several months, using an SI-traceable ammonia reference gas generator. Relative standard uncertainties of OTS amount fraction measurement results were found to be in the low percent range, e.g. 2 % for an amount fraction of 50 ppb. Thus, the reference gas-independent OTS approach has a promising prospect for calibration and validation of ammonia analysers.

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References

1. A. Pogány, O. Werhahn, and V. Ebert, *High-Accuracy Ammonia Line Intensity Measurements at 1.5 μm* , in *Imaging and Applied Optics 2016*, OSA Technical Digest (online) (Optical Society of America, 2016), paper JT3A.15, DOI: [10.1364/3D.2016.JT3A.15](https://doi.org/10.1364/3D.2016.JT3A.15)
2. Nielsen, L., 2001. *Evaluation of measurements by the method of least squares*. http://www1.bipm.org/utis/common/pdf/JCGM/nielsen_final.pdf (2017-04-03).
3. JCGM 100:2008, 2008. *Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM)*. <http://www.bipm.org/en/publications/guides/gum.html> (2017-04-03).

Improved fitting tools for uncertainty evaluation of Optical Transfer Standards

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A custom fitting routine was used in the spectral data-analysis for the ammonia optical transfer standard (OTS) developed by PTB within the MetNH3 project. The fitting routine is based on a general least squares method [1], which can account for GUM-compliant [2] uncertainty and covariance evaluation of all measured parameters, and provide the associated uncertainty budget of the fitting results. In order to achieve computational speeds required to process the large number of Ammonia spectra measured by PTB's OTS instrument and gain flexibility needed to fit a complex spectral model. In this work the original DFM-LSQ Analyzer© implemented with VBA-Excel has been translated into the Python programming language. We will discuss details on the spectral model and the fitting routine, and present a case study from spectroscopic measurements of isolated molecular absorption lines. The validity of the Python implementation is demonstrated using a reference data set.

[1] Nielsen, L., 2001. Evaluation of measurements by the method of least squares. http://www1.bipm.org/utis/common/pdf/JCGM/nielsen_final.pdf (2017-04-03).

[2] JCGM 100:2008, 2008. Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM). <http://www.bipm.org/en/publications/guides/gum.html> (2017-04-03).

A sampling-free laser based spectrometer for ammonia online measurement

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Ammonia NH₃ is one of the most critical chemicals for air quality. Reliable online measurement of ammonia is one of the key operations for air quality and safety monitoring, in indoor, outdoor and process applications alike. Ammonia is reactive compound and it is harmful, even in very low ppb level concentrations. This means challenges for measurement system in all of its critical aspects: sampling, calibration and sensitivity.

We are applying techniques so far successfully used to measure reactive inorganic compounds like ammonia NH₃ and hydrogen fluoride HF to tackle these challenges. Now a novel setup based on direct laser absorption with cavity enhancement employing fundamental vibration level excitations of ammonia molecule is constructed in connection with new mechanics and algorithms optimized for measurement of reactive molecules like ammonia easily sticking to surfaces. An open path multipass setup is constructed and validated for ammonia detection. The NH₃ calibration gases necessary for system calibration are dynamically generated using traceable standards and components. We estimate the capability of this approach for ambient online ammonia monitoring with special emphasis on the system's response time, robustness, sensitivity, usability in field conditions, maintenance need and long term stability. A further goal is to enable the use of the same setup also for simultaneous measurement of other reactive compounds often encountered in air quality monitoring. This would make possible more comprehensive and also economic monitoring of these compounds with a single device.

Ammonia measurements with diffusive samplers: applications in Switzerland and method comparisons

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Diffusive samplers for ammonia (NH₃) are widely used for concentration measurements, including long-term monitoring, local measurements before and after emission changes or for determining horizontal and/or vertical gradients. They are suitable for exposure times from one hour (e.g. in stables) to a month or longer (ambient air).

Diffusive samplers have an entry surface area, a diffusion path and a sorption layer. For calculating the concentration in the air, the geometry and the diffusion coefficient of the analyte has to be taken into account. The diffusion coefficient itself depends on meteorological conditions. However, the changes in temperature, pressure and ammonia concentration at the time of sampling are not known and a proper correction cannot be determined. Therefore, these dependencies were not considered in practice (according to VDI 3869, part 4).

Switzerland has an ambient air monitoring network for NH₃, which comprised 90 measurement stations in 2015. Sixteen stations delivered continuously data since 2000. The other stations were included into the network later on. The sampling intervals were two weeks, four weeks or one month depending on measurement station. Here we show results from the long-term monitoring, as well as comparisons between the diffusive samplers used in our surveys and other ammonia measurement methods, such as denuders (reference method: VDI 3869, part 3), Picarro, MARGA etc.

The long-term monitoring shows with some exceptions that NH₃ concentrations did not changed over the observed time period (2000 – 2015). The highest values for multi-annual means (7 - 10 µg·m⁻³) were detected in areas with a high livestock density. Areas with a low livestock density showed values which were clearly lower (3 - 5 µg·m⁻³). Annual fluctuations could be observed with maximum concentrations in periods when liquid manure is used. The measured concentration indicates that NH₃ contributes significantly.

Validation of ammonia diffusive and active samplers in a controlled atmosphere test facility using traceable Primary Standard Gas Mixtures

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We report the determination of the ammonia (NH₃) diffusive sampling rates for five different designs of commercial diffusive samplers (CEH ALPHA sampler, Gradko diffusion tube, Gradko DIFRAM-400, Passam ammonia sampler, and FSM Radiello radial sampler), together with the validation test results for a widely used active sampler (CEH DELTA denuder). The devices were exposed in a controlled atmosphere test facility (CATFAC) containing traceable concentrations of ammonia (in the range 3-25 µg m⁻³) under well-defined conditions of temperature, relative humidity and wind speed, which are applicable to a variety of ambient monitoring conditions. The work relied on the dilution of newly developed stable Primary Standard Gas Mixtures (PSMs) prepared by gravimetry in passivated gas cylinders as a method of improving the metrological traceability of ammonia measurements.

Ammonia measurement with MARGA

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MARGA (Monitor for AeRosols and Gases in ambient Air) can be used for measuring gas phase concentrations of NH₃, HNO₃, HCl, HONO and SO₂, as well as the concentrations of NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, NO₃⁻, Cl⁻ and SO₄²⁻, in aerosol with one-hour time resolution. In the instrument water soluble gases are absorbed in a wet rotating denuder (WRD) and particles pass through the denuder to a steam-jet aerosol collector (SJAC). Water samples from the denuder and the SJAC are collected in syringes and injected into an anion and a cation ion chromatograph after adding the internal standard (LiBr).

In the field intercomparison of NH₃ measurement techniques at an intensively managed grassland in South-Eastern Scotland in August 2016, the MARGA was one of the fifteen different instruments taking part in the intercomparison. In this comparison the hourly averaged ammonia concentrations measured by MARGA were varying from about 1 ppb up to 65 ppb (average 6.5 ppb, median 3.3 ppb). The ammonia concentration increased after the fertilization at the measurement site on the 24-25 August. At midnight, simultaneously with ammonia the ammonium concentration increased up to 3.5 µg/m³. However, the sulfate and nitrate concentrations did not increase with ammonium, but later at the early morning hours.

An additional laboratory test was performed to ensure that the elevated ammonium concentration was not caused by the possible memory effect in the cation ion chromatograph, where gas samples from the denuder syringe and the aerosol samples from the SJAC syringes are injected in turn. A strong ammonium solution (~100 ppb as ammonia) was passed through the denuder for several hours in the laboratory. Despite of this, the ammonium concentration in the SJAC stayed at the blank level. Later an elevated ammonia concentration in gas phase was produced using a permeation tube. Unfortunately we were not able to produce concentrations higher than 8 ppb. In this test ammonium concentration in the SJAC did not rise, but stayed at the blank level. So, memory effect in the ion chromatograph caused by ammonia was not detected during the tests.

The reaction time of the MARGA was studied in the same test. After the concentration was stabilized during the nighttime at about 8 ppb, the permeation tube was rapidly detached and a HEPA- filter and an oxalic acid filter (to remove ammonia) were attached. It took two hours, before the ammonia concentration was at the blank level. This indicates that the reaction time of the MARGA is a bit slow, when the concentrations are rapidly decreasing.

Measurements of ammonia emissions from an open slurry storage tank

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Emissions of reactive nitrogen (N_r) impair the quality of air, soil and water, ecosystems and biodiversity, and alter the release of greenhouse gases. N_r emissions have thus to be reduced (1). In Switzerland, ammonia (NH₃) contributes by approx. two thirds to the total of atmospheric N_r load (2). NH₃ released from livestock production contributes about 80% to the total NH₃ load (3). In order to restrict the emissions to a level which does not impair the environment a set of measures at all emission stages is required. Emissions from slurry stores contribute 10% to the NH₃ emissions from the livestock sector. Approx. 15% of the slurry storage volume is uncovered in Switzerland (3). Covering open stores allows for a significant reduction of the emissions released therefrom (4). However, emission measurements from slurry stores are sparse. Such investigations are mostly performed at the laboratory or the pilot scale where relevant factors influencing the emissions can differ from environmental conditions. This might conflict with the modelling of effects reducing emissions related to mitigation measures which depend on robust measurement results. Here, we present first results from a measurement campaign at an open dairy cattle slurry tank under regular agricultural operation. NH₃ concentrations were determined (i) as 10-minute mean, line-integrated concentrations across the tank surface using a miniDOAS (5) and (ii) using weekly exposed passive samplers in a vertical profile at the center of the tank. The vertical profile of wind speed and air temperature as well as slurry properties and management-operations were recorded. NH₃ emissions were determined by a simplified mass balance approach based on the passive sampler- and wind speed-profile. Scaling the 10-minute data of the product of miniDOAS NH₃ concentrations times wind speed with the mass balance-derived emissions yields a high time resolution emission estimate. Weekly emissions were between 0.01 and 0.2 g NH₃ m⁻² h⁻¹ which compares well with data from the literature (4). A clear relationship between NH₃ emissions and management-operations, such as pumping and mixing, and consequently the state of the natural crust was observed. In addition, increasing air temperature drives high emissions throughout the course of a year. Consequently, the yearly emission cycle showed low emissions during winter, two strong emission peaks in spring and autumn due to slurry spreading, leading to activity at the storage tank, and a temperature-driven emission increase during summer. In April 2017 an impermeable plastic floating cover was mounted. The measurements will be continued for one year after covering the tank.

Keywords: NH₃, Slurry, Storage, Mitigation, Measurement, Floating cover, Natural crust

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Performance of the DOAS and QCL systems during the MetNH₃ intercomparison in Scotland

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Three different NH₃ monitoring systems (a DOAS from RIVM, a DOAS from HAFL and a QCL from CEH) provided continuous NH₃ time series with a time resolution of 1 minute for the DOASes and 1 second for the QCL. The DOAS systems are remote sensing instruments that are measuring line integrated NH₃ concentrations over a path of 2x22m (Volten et al., Sintermann et al), whereas the QCL system is a point measurement that uses an inlet system to draw ambient air through a long path absorption cell (References). Calibrations of the systems were done mainly outside the campaign.

A first glance the comparison of the time series of the four systems shows a good agreement. It is at least as good as in other NH₃ intercomparisons found in the literature (e.g. von Bobruzki, Milford C, Graminae). A more detailed analysis shows several features that slightly blur this picture:

- Between the RIVM and Swiss DOAS systems a slope of 1.13 was found. This deviation from 1 is clearly above the expected accuracy of the systems and points to a systematic difference in the calibration.
- The difference between the RIVM and Swiss DOAS systems seems to depend on the ambient temperature. Either one of the two or also both systems exhibit a uncorrected temperature dependence.
- The comparison between the QCL and the DOAS systems shows an increasing deviation versus the end of the campaign, pointing to a drift between the systems.

In this presentation, we quantify these deviations and discuss possible reasons. We also address the accuracy of the systems used during this campaign.

Evaluation studies on the suitability of sampling methods to measure ambient NH₃ concentrations under field conditions

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The uncertainties in emissions of ammonia (NH₃) in Europe are large, partially due to the difficulty in monitoring of ambient concentrations due to its sticky nature. In the European Monitoring and Evaluation Program (EMEP) the current recommended guidelines to measure NH₃ are by coated annular denuders with offline analysis. This method, however, is no longer used in most European countries and each one has taken a different strategy to monitor atmospheric ammonia due to the increase of commercial NH₃ monitoring instrumentation available over the last 20 years. In June 2014, a 3 year project funded under the European Metrology Research Programme, “Metrology for Ammonia in Ambient Air” (MetNH₃), started with the aim to develop metrological traceability for the measurement of NH₃ in air from primary gas mixtures and instrumental standards to field application. This study presents the results from two field intercomparisons for NH₃ measurements.

The first field intercomparison is for active measurements (15 instruments) that was held in South East Scotland in August 2016 over an intensively managed grassland. The study compared active sampling methods to a meteorological traceable method, which was developed during the project with the aim to produce a series of guidelines for ambient NH₃ measurements.

The second intercomparison was used to assess the performance of passive samplers for ambient measurements of NH₃. Eight different designs of commercial passive samplers housed in shelters provided by the manufacturer/laboratory were exposed over an 8-week period at the Whim experimental field site in South East Scotland between August and October 2016. Whim Bog has a facility in place for controlled releases of ammonia (<http://www.whimbog.ceh.ac.uk/>). The passive samplers were exposed at different distances from the release source (16, 32 and 60 m) and at a background location. Most were exposed for 2 x 4-week long periods and some for 4 x 2-week long periods.

Results highlight the importance of instrument setup in the measurement of ambient NH₃ by active samplers and that both studies highlight the requirement to carry out frequent intercomparison of NH₃ methods to ensure quality assurance. Overall, it would be recommended from the studies that a WMO-GAW world centre for NH₃ would be established and support integration of standards into both routine and research measurements.

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