

## ENV55 MetNH<sub>3</sub>

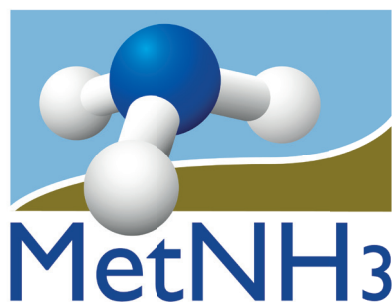
“Metrology for ammonia in ambient air”

1<sup>st</sup> MetNH<sub>3</sub>-workshop

on the progress in ammonia metrology

24 – 25 February 2016

at PTB in Braunschweig, Germany



# Agenda

Wednesday, 24 February 2016

PTB Braunschweig, Seminarzentrum

9:00	Registration and coffee/tea
10:00	Opening
10:10	EMRP ENV55 MetNH <sub>3</sub> : Towards a consistent metrological infrastructure for ammonia measurements <i>Bernhard Niederhauser</i>

## Session 1 on analytical instrumentation

10:40	Characterization of a cavity ring-down spectrometer for ambient ammonia measurements <i>Andrea Pogány</i>
11:05	Optimization of Picarro's G2103 ammonia analyzer for environmental and industrial applications <i>Graham Leggett</i>
11:30	MiniDOAS – a new instrument for ammonia monitoring <i>Daan Swart</i>
11:55	Continuous measurements of NH <sub>3</sub> with laser-based photoacoustics <i>Ingolf Kahl</i>
12:20	Lunch break and Poster session

## Session 2 on preparation of standard gas mixtures

13:45	10 µmol/mol NH <sub>3</sub> standards in Takachiho cylinders <i>Janneke van Wijk</i>
14:10	On the Development and Characterisation of a Traceable Portable Gas Standard Generator <i>Daiana Leuenberger</i>
14:35	Development of new stable NH <sub>3</sub> (g) source <i>Sarah Peters</i>
15:00	Coffee/tea break and Poster session

## Session 3 on field measurements

15:30	Characterization of a proficiency test installation to provide traceability to automatic ammonia measurement devices near ambient concentrations <i>Klaus Wirtz</i>
15:55	Reviewing ammonia measurements in the context of research and policy questions <i>Christine Braban</i>
16:20	Field inter-comparison of three systems for NH <sub>3</sub> concentration <i>Christof Ammann</i>
16:45	Summer 2016 Field intercomparison of ambient NH <sub>3</sub> <i>Marsailidh Twigg</i>
19:00	Workshop dinner

# Agenda

Thursday, 25 February 2016

PTB Braunschweig, Seminarzentrum

## Session 4 on adsorption and sampling inlet design

9:00	Co-adsorption of water and ammonia on stainless steel <i>Olavi Vaittinen</i>
9:25	Measuring ammonia – understanding the inlet quality issue <i>John Kentisbeer</i>
9:50	Creating inert surfaces with CVD Silicon coatings from SilcoTek. No surface adsorption of active compounds like NH <sub>3</sub> , Hg, Sulfur and others <i>Johannes Kütt</i>
10:15	Novel approaches to rapid, high-precision measurements of ammonia and other 'sticky' molecules <i>Joseph Roscioli</i>
10:40	Coffee/tea break and Poster session
12:00	Closing
12:10	Lunch break
13:45	Optional lab tours

## Poster session

1	The application of a Cavity Ring-Down Spectrometer to measurements of ambient ammonia using traceable Primary Standard Gas Mixtures <i>Valerio Ferracci, Nicholas A. Martin</i>
2	Gas standards for the calibration of novel ammonia fluorescence sensors <i>Carlo Tiebe, Kornelia Gawlitza, Ulrich Banach, Reinhard Noske, Knut Rurack</i>
3	A sampling-free quantum cascade laser based spectrometer for ammonia detection <i>Jari Peltola, Andrea Pogány, Tuomas Hieta</i>
4	Measurement of ammonia line intensities in the 1.5 μm range <i>Andrea Pogány, Olav Werhahn, Volker Ebert</i>
5	Investigations of spectral fitting procedures for CRDS measured ammonia spectra <i>David Balslev-Harder, Andrea Pogány</i>
6	Next-generation analyzers for ammonia measurements based on cavity enhanced laser absorption spectroscopy <i>Brian Leen, Gerald Sornsen, Robert Provencal, Kyle Owen, Manish Gupta, Douglas Baer</i>
7	NH <sub>3</sub> Eddy covariance measurements from broad spreading of dairy slurry <i>Marco Carozzi, Rossana Monica Ferrara, Marco Acutis, Gianfranco Rana</i>
8	Ammonia concentrations and fluxes above semi-natural peatland using laser absorption spectrometry <i>Undine Richter, Frederik Schrader, Christof Ammann, Christian Brümmer</i>
9	A modified Sagnac interferometer for quantitative absorption spectroscopy allowing contact free length measurement of direct absorption cells <i>Christof Janssen, Hadj Elandalousi, Christian Rouillé, Patrick Marie-Jeanne</i>
10	Open-path measurements of ammonia: applications for eddy covariance, mobile laboratory, and satellite validation studies <i>Mark Zondlo</i>



## **Oral Presentations**

## **EMRP ENV55 MetNH<sub>3</sub>: Towards a Consistent Metrological Infrastructure for Ammonia Measurements**

*Bernhard Niederhauser*

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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. 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 to ensure reliable ammonia measurements namely in applicable analytical technology, maximum allowed uncertainty, quality assurance and quality control (QC/QA) procedures as well as in the infrastructure to attain metrological traceability.

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, the introduction of which is the focus of this presentation:

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

Realisation and characterisation of traceable preparative calibration standards (CRM as well as mobile generators) of ammonia amount fractions similar to those in ambient air based on existing methods for other reactive analytes.

**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 as optical transfer standards according to metrological 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 of the ambient air.

The active exchange in workshops and inter-comparisons, publications in technical journals as well as presentations at relevant conferences and standardisation bodies will transfer the knowledge to stakeholders and end-users.

## Characterization of a cavity ring-down spectrometer for ambient ammonia measurements

*Andrea Pogány, Nils Lüttschwager, Olav Werhahn, Volker Ebert*

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Within the project "Metrology for ammonia in ambient air" we investigate the applicability of an extractive cavity ring-down spectrometer as a traceable optical transfer standard. An optical transfer standard is a spectrometer that provides reliable and accurate ammonia amount fractions and can thereby be used for the calibration and validation of other analytical instrumentation. An optical transfer standard can offer an alternative to calibration using gas standards.

In our presentation we show results of various laboratory test measurements performed with a Picarro G2103 spectrometer. Test measurements show no significant dependence of the ammonia amount fraction readings on the ambient temperature in the range of 10 to 30 °C. Response times of the instrument were found to be in the range of minutes in the case of step changes of 50-200 nmol/mol in the ammonia amount fraction, which is acceptable for ambient measurements. Measurements in different ammonia-free matrix gases showed a non-negligible zero offset of ~0.6 nmol/mol, which has to be taken into account in measurements in the low nmol/mol range. The cross-sensitivity of the spectrometer to typical ambient carbon dioxide levels was found to be below 0.1 % of the ammonia amount fraction reading, whereas, a bias up to a few % was observed due to water vapor cross-sensitivity under typical ambient humidity conditions. A significant dependence on the matrix gas composition has been identified, a ~10 % difference was observed between the slope of calibration lines obtained in nitrogen and air. This has to be taken into account when using reference gas mixtures, which are often prepared in nitrogen. To eliminate matrix gas dependent effects, a new data evaluation algorithm has been developed. A preliminary validation of the spectrometer shows an agreement better than 6 % between the measured and the reference ammonia amount fractions within the range of 50-200 nmol/mol.

Characterization of the spectrometer is still ongoing; nevertheless, our first results shown in this presentation indicate that the Picarro spectrometer in combination with an improved data evaluation algorithm is a good candidate for an optical transfer standard for ambient ammonia measurements.

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

## **Optimization of Picarro's G2103 Ammonia Analyzer for Environmental and Industrial Applications**

*Graham Leggett<sup>1</sup>, John Hoffnagle<sup>1</sup>, Valerio Ferracci<sup>2</sup>, Nicholas A. Martin<sup>2</sup>*

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<sup>2</sup>National Physical Laboratory, Environment Division, Hampton Road, Teddington Middlesex TW11 0LW, United Kingdom

Cavity ring-down spectroscopy (CRDS) is now a well-established analytical technique for both environmental and industrial applications. For ammonia, Picarro's G2103 CRDS analyzer delivers detection limits at parts per trillion (ppt) amount fractions, making it a powerful tool for measuring trace ammonia in our atmosphere, and as a means of monitoring sensitive manufacturing processes such as semiconductor fabrication. Here we report the results of our efforts to optimize the design to improve both response time and the handling of potential interference substances.

As with other reactive, "sticky" molecules, the ultimate performance of a CRDS ammonia analyzer is dependent largely on the ability to transport a representative sample from the point of origin to the cavity. As such, significant efforts must be made when considering gas-wetted materials of construction. The choice of material for tubing, valves, filters, etc. will impact the response time in particular, with optimized design resulting in the ability to better characterize transient events, and recovery from exposure to higher amount fractions of ammonia. Particular attention should be focused on the design of any filter upstream of the cavity, as this component is by far the most significant in terms of surface area, and the potential for adverse effects on performance. We report the results of experiments with alternative filters and pretreatments, and the impact on instrument performance.

In terms of accuracy of measurement, the ability to better characterize and reduce the impact of interference is of vital importance. In ambient air, the presence of high, and variable humidity, is the primary source of interference. Here we report Picarro's approach to handling such interferences, and the results of work with UK's National Physical Laboratory that has resulted in an improved scheme to deal with this issue.



## **MiniDOAS – a new instrument for ammonia monitoring**

*Daan Swart, Hester Volten, Stijn Berkhout, Marty Haaima*

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The Netherlands are in the unique position to possess a monitoring network producing hourly measurements of ammonia concentrations in ambient air. The instrument previously used in this network, the AMOR (an AMANDA adapted for monitoring), was recently replaced by the miniDOAS, an instrument developed at RIVM. In preparation, AMOR and miniDOAS measured in parallel at six monitoring stations, producing a wealth of data of two independent measurement systems. We present these results and discuss the excellent performance of the new instrument. The miniDOAS, based on the Differential Optical Absorption Spectroscopy (DOAS) principle, uses an open path. It has the distinct advantage that no tubes and filters are necessary, avoiding problems with ammonia molecules or aerosols sticking to tubes and filters.

Another advantage is that during the calibration of the instruments very high and thus stable NH<sub>3</sub> concentrations in the ppm range are used in a flow cell. The flow cell is placed in the light path yielding spectra equivalent to those seen at typical ambient concentrations in a 30 m path in the atmosphere. These ppm concentrations are much easier to produce accurately than typical ambient concentrations in the ppb range.

## Continuous measurements of NH<sub>3</sub> with laser-based photoacoustics

*Ingolf Kahl<sup>1</sup>, Bjorn Kamps<sup>2</sup>, Sacco te Lintel-Hekker<sup>3</sup>, Rens Zijlmans<sup>2</sup>*

<sup>1</sup>Synspec Deutschland GmbH; Ellern 3; D-06688 Großkorbetha

<sup>2</sup>LSE Monitors B.V., De Deimten 1, 9747 AV Groningen, The Netherlands

<sup>3</sup>Sensor Sense B.V., St. Agnetenweg 103, 6545 AV Nijmegen, The Netherlands

Continuous measurements of ammonia (NH<sub>3</sub>) at ppb-level are made possible by a new implementation of photoacoustics with a quantum cascade laser. The technology is based on the measurement of acoustical pressure waves that are generated by absorption of intensity-modulated infrared laser light by NH<sub>3</sub> in the sample gas. An extreme sensitivity is realized by a combination of very sensitive microphones to measure the pressure wave amplitude, the use of high power infrared laser light and acoustical amplification of the pressure waves in the heart of the measurement cell.

In order to realize reliable measurements, the sample preparation is equally important as the measurement itself. Especially ammonia tends to stick to various types of materials, which complicates the correct determination of NH<sub>3</sub> in low concentrations.

In this contribution, the measurement principle and performance of the analyzers are presented, together with a discussion on the sample preparation for the measurement of NH<sub>3</sub>.

### **10 µmol/mol NH<sub>3</sub> standards in cylinders**

*Maki Egami; Katsumi Hibi; Janneke Van Wijk; Valerio Ferracci*

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<sup>2</sup>Dutch Metrology Institute (VSL), Thijssseweg 11, 2629 JA Delft, The Netherlands

<sup>3</sup>NPL – now Cambridge University

To develop NH<sub>3</sub> standards in nitrogen in cylinders with a low uncertainty several commercial cylinder types have been tested on loss of ammonia on cylinder walls and stability at the 10 µmol/mol level both by NPL and VSL. Cylinders internally treated with SilcoNert 2000 have been tested by NPL and cylinders made available for the project by Takachiho have been tested by VSL.

Takachiho has many years of experience in preparing stable calibration gases including low concentration NH<sub>3</sub> standards. An introduction to the company will be given and the background for developing NH<sub>3</sub> calibration gases for the Japanese market.

The first results of these experiments on adsorption loss and stability will be presented.

## **On the Development and Characterisation of a Traceable Portable Gas Standard Generator**

*Daiana Leuenberger, Céline Pascale, Bernhard Niederhauser*

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Ammonia (NH<sub>3</sub>) 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.

NH<sub>3</sub> 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 30 µmol/mol.

The EMRP JRP ENV55 MetNH<sub>3</sub> aims at overcoming this discrepancy by assessing and developing novel approaches for the production of CRM and measurement methods.

The Federal Institute of Metrology METAS has developed a traceable portable gas standard generator for reactive gases (ReGaS1). This device is based on the specific temperature dependent permeation of the reference substance through a membrane into a flow of carrier gas and subsequent dynamic dilution to desired amount fractions. The characteristics of individual components lead to the uncertainty estimation for the generated NH<sub>3</sub> gas mixture according to GUM, which is aimed to be <3 %.

Here we present insights into the development of said instrument 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.

## Development of new stable NH<sub>3</sub>(g) source

Sarah Peters, Jörg Kleffmann

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In the present study, a simple and continuous ammonia (NH<sub>3</sub>) source is developed, which is based on a liquid/gas reactor, producing pure ammonia mixtures in humidified air (40-90 % r.h.) with a gas flow rate in the range 0.5 – 2 l/min. A temperature controlled stripping coil is used as liquid/gas reactor similar to a pure HONO source described in Kleffmann et al (2004) [1]. Gas phase NH<sub>3</sub> levels over alkaline ammonium (NH<sub>4</sub><sup>+</sup>) solutions are controlled by the solubility in water depending on pH, temperature, NH<sub>4</sub><sup>+</sup>-concentration, liquid and gas flow rates. The NH<sub>3</sub> source shows a fast time response, high precision and a linear response with the NH<sub>4</sub><sup>+</sup>-concentration and thus, NH<sub>3</sub> can be easily adjusted from ppbV to ppmV levels. From known gas and liquid phase concentrations, the Henry's law coefficient of NH<sub>3</sub> has been re-investigated as a function of temperature, confirming former results from Clegg and Brimblecombe (1989) [2] and Hoffmann and Jacob (1984) [3]. Thus, from known instrument parameters (pH, temperature, c(NH<sub>4</sub><sup>+</sup>), liquid and gas flow rates) absolute NH<sub>3</sub> concentrations of the source can be calculated.

### References:

- [1] Kleffmann, J., T. Benter, P. Wiesen, *J. Phys. Chem. A*, 2004, 108, pp 5793-5799
- [2] Clegg, S. L.; Brimblecombe, P., *J. Phys. Chem.*, 1989, 93 (20), pp 7237–7248,
- [3] Hoffmann, M. R. und Jacob, D. J, in *SO<sub>2</sub>, NO and NO<sub>2</sub> Oxidation Mechanisms: Atmospheric Considerations*, Calvert, J. G. (Hrsg.); Butterworth Publishers: Boston, MA, **1984**; 101–172.

**Characterization of a proficiency test installation to provide traceability to automatic ammonia measurement devices near ambient concentrations**

*Klaus Wirtz, Collin Bopp, Volker Stummer*

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Proficiency test installations are common tools to test and compare different measurement methods and techniques under laboratory conditions. Especially in the framework of the air quality directive 2008/50/EG (AQD), intercomparison exercises are required to assess the performances of the National Reference Laboratories with respect to the compliance according to the data quality objectives of the corresponding measurements. The German Environment Agency (UBA) operates such a test facility, a platform which is capable to provide well defined gas mixtures using a computer controlled dynamic dilution system. The installation is well characterized for those gaseous compounds, which are currently regulated under the AQD, e.g. CO, NO, NO<sub>2</sub>, ozone, SO<sub>2</sub>, benzene. Complex mixtures out of 14 pressurized gas cylinders can be provided in addition to variable ozone and water vapor concentrations. Therefore, in addition to the validation of different measurement methods and techniques, interference tests can be performed.

Ammonia (NH<sub>3</sub>) is a molecule which exhibits strong surface interactions, and as a consequence leads to difficulties in preparing stable and traceable gas mixtures. In order to improve the capabilities of the installation an exhaustive characterization has been performed, to evaluate the current limits with respect to homogeneity, stability, reproducibility, and traceability of ammonia trace gas concentrations under dry and wet conditions. Furthermore interferent tests had been performed using cavity ring down spectroscopy (CRDS Picarro EnviroSense 1000) as analytical tool.

Some technical adaptations have been applied to improve the stability of the prepared ammonia trace gas concentrations.

Lit.: Evaluation of the Laboratory Comparison Exercise for NO, NO<sub>2</sub>, SO<sub>2</sub>, CO and O<sub>3</sub> Langen (D) 1<sup>st</sup> - 6<sup>th</sup> September 2013, Maurizio Barbieri, Volker Stummer, Friedrich Lagler, Hans-Guido Mücke, DOI:10.2788/43930 (2014)

## **Reviewing ammonia measurements in the context of research and policy questions**

*Christine Braban*

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Penicuik, Midlothian, United Kingdom

There are significant numbers of studies which use different ammonia measurement techniques to either measure ammonia or ammonia + ammonium in the literature, both in ISI publications and in the grey literature around case studies and research projects. This talk is proposed to summarise the research done in these studies and hence link through to the MetNH<sub>3</sub> activities, evaluating instruments for traceable measurement of ammonia at ambient molar fractions under real air and artificial conditions. The aim of this presentation is evaluation and comparison of published results produced with field measuring methods in conjunction with the current studies to begin formulating suitable ammonia measurement and monitoring strategies to promote long-term efficient and quantitative monitoring of ammonia in the environment with the addressing the context of the measurements in terms of the research and policy questions which will be asked in the future.

## Field inter-comparison of three systems for NH<sub>3</sub> concentration and flux measurements

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Ambient air ammonia analyzers that are not only used for concentration but also for flux measurements have to meet special requirements. They either have to provide a fast response detection (c. 1 sec) for the application of the eddy covariance technique (EC) or they have to resolve relatively small horizontal or vertical concentration gradients.

In a field campaign in autumn 2015, we compared three systems for the NH<sub>3</sub> exchange measurement of a grazed pasture during several weeks: [A] an EC system with a thermal converter that rapidly converts ammonia (and particulate ammonium) to NO at the sampling inlet; [B] an EC system with a QC laser analyzer and an 'Inertial inlet box' that separates particles from the gas sampling stream at the inlet; [C] a horizontal concentration gradient system with two MiniDOAS instruments combined with backward Lagrangian dispersion simulation. While the open-path system C does not need any sampling inlet, systems A and B avoid or minimize the problematic sorption and chemistry effects of ammonia and ammonium on filter and inner tube surfaces by other means. We present first results of the field inter-comparison of the three systems and discuss their advantages and problems.



### **Summer 2016 Field intercomparison of ambient NH<sub>3</sub>**

*M.M. Twigg<sup>1</sup>, J. Kentisbeer<sup>1</sup>, M. Anderson<sup>1</sup>, Y. S. Tang<sup>1</sup>, E. Nemitz<sup>1</sup>, M.R. Jones<sup>1</sup>, S. R. Leeson<sup>1</sup>, N. Martin<sup>2</sup>, C. F. Braban<sup>1</sup>*

<sup>1</sup>Centre for Ecology and Hydrology, Bush Estate, Penicuik, UK.

<sup>2</sup>National Physical Laboratory (NPL), TW11 0LW, Teddington, Middlesex, United Kingdom

An integral part of the MetNH<sub>3</sub> project is establishing the transfer of high-accuracy standards to field applicable methods. A field intercomparison of NH<sub>3</sub> measurement techniques is planned for summer 2016 at a managed grassland in South-East Scotland. The aim of this experiment is to evaluate both the reference methods developed during the MetNH<sub>3</sub> project and other state-of-the-art and older instrumentation currently available for field measurements. The challenge is to measure quantitatively both at background concentrations and elevated produced through fertilisation with urea. In addition to the instrument performance, the effect of meteorology (temperature, relative humidity, precipitation), inlet type and calibration method on the quality of data will be investigated. This presentation will outline the specific objectives of the study, as well as the provisional field setup. The talk will inform and lead to an open to discussion on planning the experiment and the analysis of the data for all project partners and intercomparison participants.

## **Co-adsorption of water and ammonia on stainless steel**

*Olavi Vaittinen*

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The amount of ammonia adsorption on metal surfaces such as stainless steel is strongly dependent on the prevailing humidity. The similarities of the adsorption properties of water and ammonia molecules and consequent competitive adsorption between them usually reduces the availability of vacant adsorption sites for ammonia in the presence of water. This is observed as reduced ammonia adsorption in ambient water concentrations as compared to dry laboratory conditions.

The adsorption of ammonia on stainless steel tubes in the presence of water has been studied in the framework of European Metrology Research Programme (EMRP) Joint Research Project (JRP) Metrology for Ammonia in Ambient Air (MetNH<sub>3</sub>). The measurements have been performed using dynamically diluted ammonia at a concentration of 400 part-per-billion and at humidities from low ppm to percent levels. A Picarro G2103 Ammonia Analyzer has been used to monitor the adsorption process in real time in continuous-flow conditions. The results and possible explanations for the observed phenomena are presented at the Workshop.

## **Measuring ammonia – understanding the inlet quality issue**

*John Kentisbeer, Christine Braban, Marsailidh Twigg, Neil Mullinger*

<sup>1</sup>Centre for Ecology and Hydrology, Bush Estate, Penicuik, UK.

Calibrating ambient ammonia measurement instrumentation in the laboratory can be relatively straightforward and achieve reportable and consistent results, under specific temperature and relative humidity conditions. However, applying these techniques to real world monitoring is more challenging due to the interaction of ammonia with water, particulate matter and surfaces leading to degradation in inlet quality over time. This exposure to aerosol and other ambient contaminants in the field can lead to degraded instrument performance both in quantitative measurements and in instrument response time.

As part of the Ammonia Metrology project the REG (NERC CEH) has developed pre-conditioned aerosol coated sampling inlets to investigate artefacts in sampling and instrument response through absorption-desorption effects on the walls. We have also built a mobile aerosol mixing system for systematic introduction of aerosol at a controlled relative humidity to sample flows. The use of these can facilitate the “real world” dynamic response of instruments to be tested.

Here we present work, starting with the results from a survey of ammonia community to understand the current ammonia measurement system set-ups, and following through the rationale for selecting appropriate test inlet materials, sizes and aerosol coating to best represent ambient conditions. The building and testing of the humidified aerosol delivery system and the initial results of our laboratory testing will be discussed in the context of MetNH<sub>3</sub> and the wider application.

**Creating inert surfaces with CVD Silicon coatings from SilcoTek. No surface adsorption of active compounds like NH<sub>3</sub>, Hg, Sulfur and others**

*Johannes Kütt*

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SilcoTek has developed CVD Silicon coatings to create an extremely inert surface. This inert surface prevents adsorption of active compounds like NH<sub>3</sub>, H<sub>2</sub>S, sulfur, mercury and others. SilcoTek coatings can be applied on stainless steel, glass, ceramics and some aluminum alloys. The coating should be on all stainless steel parts that are in contact with the sample from the source up to the analyzer. These parts can be tubes, fittings, valves, pressure regulators, mass flow controllers etc.

**Novel approaches to rapid, high-precision measurements of ammonia and other 'sticky' molecules**

*Joseph Roscioli, Mark Zahniser, Scott Herndon, David Nelson*

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Ammonia plays important roles in aerosol and cloud chemistry, air quality and anthropogenic nitrogen deposition. Accurately measuring NH<sub>3</sub> concentrations on a fast timescale has historically been complicated due to its tendency to slowly and irreversibly interact with instrument surfaces. Here we present recent efforts aimed at mitigating these effects using new inlet technologies. First, an inlet that combines an inertial impactor with a pressure drop across a critical orifice provides particle removal without a traditional filter. This approach is used to reduce instrumental time responses for NH<sub>3</sub> to the order of 3 seconds. Second, a further reduction in time response is achieved by entraining functionalized perfluoroalkane vapor into the inlet sampling stream. This "active passivation" method is used to achieve time responses of ~0.5 seconds for NH<sub>3</sub>, and is found to be applicable to a variety of inlet designs. These technologies enable fast time response sampling suitable for eddy covariance flux measurements.



## Posters

**The application of a Cavity Ring-Down Spectrometer to measurements of ambient ammonia using traceable Primary Standard Gas Mixtures**

*Valerio Ferracci, Nicholas A. Martin*

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We report the preparation and validation of new stable Primary Standard Gas Mixtures (PSMs) of ammonia (NH<sub>3</sub>) in passivated gas cylinders, prepared by gravimetry, at low amount fractions in the  $\mu\text{mol}\cdot\text{mol}^{-1}$  regime. These have been employed as part of the establishment of a metrological traceability chain to improve the reliability and accuracy of ambient measurements of this species. The PSMs have been diluted dynamically to provide calibration mixtures of dry and humidified ammonia atmospheres of known composition in the  $\text{nmol}\cdot\text{mol}^{-1}$  range. This work has enabled the further development of a commercial optical laser sensor, based on cavity ring-down spectroscopy (CRDS). A correction to NH<sub>3</sub> measurements has been implemented to remove the undesirable effects of direct and indirect cross interference due to water vapour, with a view to extending this rapid on-line technique for exposure chamber validation tests under controlled conditions and ambient monitoring in the field.



## **Gas standards for the calibration of novel ammonia fluorescence sensors**

*Carlo Tiebe, Kornelia Gawlitza, Ulrich Banach, Reinhard Noske, Knut Rurack*

*BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany*

Ammonia and its conversion product ammonium have a strong negative impact on human health and ecosystems. Most ammonia measurements in ambient air are performed in the molar fraction range (0.5 to 500) nmol/mol. There is a need for reliable traceable ammonia gas standards as well as in situ analytical procedures for the monitoring of ammonia in ambient air.

The permeation method is an effective tool for dynamically generating precise gas standards with a low uncertainty in the concentration range of a few nmol/mol to several  $\mu\text{mol/mol}$  in an inert carrier gas, e. g. pure nitrogen or purified ambient air. Here, we present our ammonia gas standard generator as well as results of the characterisation of its individual components supporting the uncertainty assessment according to GUM for stable gas concentrations in this range.

In order to detect ammonia in the nmol/mol-range, a suitable sensor has to be developed. In this contribution, we therefore additionally present first approaches on the development of such a sensor using optical fluorescence as transduction mechanism due to its intrinsically high sensitivity and high spatial resolution [1]. Incorporation of a fluorescent dye, which shows fluorescence enhancement in the presence of ammonia, into a polymer matrix allows to reversibly recognize low amounts of ammonia. It can be concluded that fluorescence sensor is a robust tool for measurements of ammonia; however it needs calibration for the planned use.

### References:

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## A sampling-free quantum cascade laser based spectrometer for ammonia detection

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Detection and quantification of ammonia is important for atmospheric monitoring. Most of the commercially available ammonia analysers are extractive. However, ammonia tends to adsorb easily, e.g., on the sample lines and the cell of the analyser causing both long response time and significant uncertainties in the determination of molar fraction. These problems can be avoided or reduced by using an open-path or a sampling-free technique [1,2]. However, to our knowledge, a sampling-free spectrometer capable of absolute, calibration-free and traceable measurements has not been developed yet.

Here we report a sampling-free spectrometer that has been designed for ambient measurement of ammonia. One of the aims of this study is to investigate whether sampling-free spectroscopic measurement technique is suitable for absolute ambient ammonia measurement. The spectrometer is based on a quantum cascade laser (QCL) operating close to 1103 cm<sup>-1</sup>, where a strong and fairly isolated ammonia feature is located. The wavelength tuning rate of the QCL is validated using a solid Ge-etalon. The open-path cell of the analyser is based on a Herriot type multipass configuration and is equipped with calibrated temperature and pressure sensors.

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## Measurement of ammonia line intensities in the 1.5 $\mu\text{m}$ range

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Spectral line data, in particular line intensities are necessary for absolute, calibration-free spectroscopic concentration measurements. These measurements are based on calculating the concentration of the analyte from the measured absorption spectrum, spectral line parameters of the analyte and physical properties of the gas sample and the optical set-up according to the Beer-Lambert law<sup>1</sup>. Instruments capable of absolute spectroscopic measurements do not need calibration with gas standards, which is an important advantage in the case of adsorptive analytes like ammonia. However, spectral line parameters of ammonia are available in literature only with relatively high, typically 10-20 %, uncertainty due to experimental challenges originating from the highly adsorptive nature of ammonia and the high complexity of the spectrum.

We have measured line intensities of several ammonia absorption lines in the range of 1526 to 1528 nm (6544.15 to 6553.53  $\text{cm}^{-1}$ ) using tunable diode laser absorption spectroscopy (TDLAS). The experimental set-up and the measurements method were designed based on previous experiments, where intensities of carbon dioxide<sup>2</sup> and water vapor<sup>3</sup> absorption lines were determined.

We present the measured ammonia line intensities and compare them to available literature values. Generally, our measured line intensities are 5-6 % lower than that reported by Sung et al.<sup>4</sup> which are also included in the HITRAN database<sup>5</sup> for this wavelength range. Uncertainties of our line intensities are in the 1-3 % range for the strongest lines, which is more than a factor of two better than the accuracy reported by Sung et al.<sup>4</sup>. Furthermore, we identified several absorption lines in the studied wavelength range, which are not included in the HITRAN database.

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## Investigations of spectral fitting procedures for CRDS measured ammonia spectra

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Cavity Ring-Down Spectroscopy (CRDS) is considered as a potential for an absolute and calibration-free method for determining gas mixing ratios. Typical instrumentation of CRDS provide sparse sampling of the spectral feature, because it is convenient not to change the optical path length, whereby the sampling is limited to the Free Spectral Range (FSR) of the cavity, which is typically in the range from 300 MHz to 600 MHz for conveniently sized cells. Using spectra captured with PTB's CRDS analyzer (Picarro G2103), we investigated how different assumptions in the fitting procedures influence the results. The fitting analysis was performed with DFM-LSQ Analyzer© which allow for variation in all measured parameters, in order to better estimate the full uncertainty of the fitted parameters. Investigating different concentrations at wet and dry conditions, we concluded that, a better linearity in the evaluated ammonia concentrations is obtained, when using fixed widths for the absorption feature versus fitting the width as a free parameter. However the overall uncertainty for the concentration remain equivalent.

## **Next-generation analyzers for ammonia measurements based on cavity enhanced laser absorption spectroscopy**

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We present performance tests of two different commercial gas analyzers for measurements of ammonia based on Off-Axis ICOS technology, the newest cavity enhanced laser absorption technique.

The first analyzer, which employs a mid-IR quantum cascade laser was deployed for measurements of ammonia while aboard the U.S. Department of Energy (DOE) Gulfstream-1 (G-1) research aircraft over the Yakima Valley, in the state of Washington. The NH<sub>3</sub> concentration is determined from high-resolution absorption spectra obtained by tuning the laser wavelength over the NH<sub>3</sub> fundamental vibration band near 9.67 μm. Excellent linearity is obtained over a wide dynamic range (0 – 101 ppb) with a response rate (1/e) of 2 Hz and a precision of ±0.09 ppb (1σ in 1 s). Two research flights were conducted. In the first flight, the analyzer was used to identify signatures of livestock from local dairy farms with high vertical and spatial resolution under low wind and calm atmospheric conditions. In the second flight, the analyzer captured livestock emission signals under windy conditions.

The second analyzer, which employs a near-IR diode laser was deployed for measurements of ammonia in ambient air. The NH<sub>3</sub> concentration is determined from high-resolution absorption spectra obtained by tuning the laser wavelength over the NH<sub>3</sub> combination band near 1.52 μm. Excellent linearity is obtained over a wide dynamic range (0 – 0.1 ppm) with fast response rates (T<sub>10-90</sub> and T<sub>90-10</sub>) of 13 seconds and a precision of ±0.25 ppb (1σ in 10 s) and ±0.7 ppb (1σ in 1 s). Detailed measurements were performed in both wet and dry flows to quantify the instrument precision, accuracy, drift rate, dynamic range and cross sensitivity to water vapor.

Finally, as we will demonstrate at the workshop, in addition to providing fast, accurate measurements over a very wide dynamic range, these analyzers may be fully serviced in the field by untrained personnel, if necessary.

### **NH<sub>3</sub> Eddy covariance measurements from broad spreading of dairy slurry**

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Two field-scale experiments have been performed in the Po Valley, northern Italy, in an intensively managed agricultural farm during spring 2009 and 2011 for evaluating ammonia (NH<sub>3</sub>) emissions from dairy slurry. In both trials NH<sub>3</sub> fluxes have been monitored in continuous by eddy covariance system (EC) based on Tunable Infrared Laser Differential Absorption Spectrometry (QC-TILDAS; Aerodyne Research Inc., USA). Field and instrumental setup were cared for having accurate NH<sub>3</sub> concentration measurements, and the EC was applied with all the opportune and available corrections and checking. In order to validate the EC fluxes, the half hourly concentrations acquired by the QC-TILDAS have been used to estimate emissions from a backward Lagrangian stochastic model (WindTrax; Thunder Beach Scientific, Canada). The results showed a peculiar dynamic of NH<sub>3</sub> volatilisation after surface slurry application on bare soil in both experimental trials, showing a sudden peak and confirming the rapidity of the emissive phenomenon after the spreading. The NH<sub>3</sub> emission levels reached peaks of 138.3 and 243.5  $\mu\text{g m}^{-2} \text{s}^{-1}$  in the two trials and the emission factors were 19.4% and 28.5% after 7 days from the spreading. The comparison from EC fluxes and the model estimation showed a consistency for dynamic and quantity emitted.

## Ammonia concentrations and fluxes above semi-natural peatland using laser absorption spectrometry

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Recent advancements in laser spectrometry offer new opportunities to investigate net biosphere-atmosphere exchange of ammonia. We tested the performance of a quantum cascade laser within an eddy-covariance setup over a period of three months. The laser was operated at a semi-natural peatland site that is surrounded by highly fertilized agricultural land and intensive livestock production. Ammonia concentrations were recorded at a frequency of 10 Hz and were found to be highly variable between 2 and 85 ppb when averaged over 30 minutes. While single peak values were as high as 110 ppb, the campaign average was 15 ppb. Concentration patterns were closely linked to the timing of management practices and the prevailing local meteorological conditions, particularly wind direction, temperature and surface wetness with the latter indicating higher non-stomatal uptake under wet conditions leading to decreased concentrations. Cumulative cospectra of  $w'NH_3'$  and  $w'Ta'$  were compared to investigate potential high-frequency damping on NH<sub>3</sub> fluxes. Over a range of different conditions with varying wind speed and  $z/L$ , we found a median of 0.66 indicating a loss of 34 % in the respective NH<sub>3</sub> flux magnitude. Hence, a correction factor of 1/0.66 was applied to all NH<sub>3</sub> fluxes. Values between -80 and 50 ng N m<sup>-2</sup> s<sup>-1</sup> with a campaign average of -16.5 ng N m<sup>-2</sup> s<sup>-1</sup> and decreasing uptake towards the end of the observation period in May were observed. On a diurnal time scale, NH<sub>3</sub> uptake was highest in the late afternoon and early evening hours and was correlated with concentration and surface wetness. The cumulative net uptake for the period of investigation was ~1.3 kg N ha<sup>-1</sup>, thereby matching well with results from a local application of a dry deposition model after Massad et al. (2010) as well as results from a denuder-based study conducted in previous years. Through their high temporal resolution, robustness and continuous measurement mode, quantum cascade lasers will help assessing the effects of atmospheric N loads to vulnerable N-limited ecosystems such as peatlands.

## **A modified Sagnac interferometer for quantitative absorption spectroscopy allowing contact free length measurement of direct absorption cells**

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Accurate path length measurements in absorption cells are recurrent requirements in quantitative molecular absorption spectroscopy. A new twin path laser interferometer for length measurements in a simple direct path absorption geometry is presented, along with a full uncertainty budget. The path in an absorption cell is determined by measuring the optical path length change due to the diminution of the refractive index when the cell originally filled with nitrogen gas is evacuated. The performance of the instrument based on a stabilized HeNe laser is verified by comparison with the results of direct mechanical length measurements of a roughly 45 mm long, specially designed absorption cell. Due to a resolution of about 1/300 of a HeNe fringe, an expanded (coverage factor  $k = 2$ ) uncertainty of 17  $\mu\text{m}$  in the length measurement is reached, providing a relative uncertainty of  $3.4\text{E-}4$  for the length of our test absorption cell. This value is about seven times lower than what has been reported previously. The instrument will be useful for precision measurements of absorption cross sections of strong absorbers which require short light paths, such as ozone, halogen oxides, sulfur dioxide and volatile organic compounds in the UV.



**Open-path measurements of ammonia: applications for eddy covariance, mobile laboratory, and satellite validation studies**

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An open-path ammonia sensor based upon quantum cascade laser at 9.06  $\mu\text{m}$  has been developed and field deployed on both towers and mobile laboratories. The open-path configuration of the sensor and its precision (150 pptv at 10 Hz) means it is capable of observing high-frequency temporal changes in atmospheric  $\text{NH}_3$  as part of eddy flux studies as well as spatial gradients observed onboard mobile laboratories. The sensor uses wavelength modulation spectroscopy with an in-line reference cell to account for longer-term drift. Calibration of the sensor has been conducted using direct absorption spectroscopy in the laboratory and with a permeation tube. The sensor has an accuracy of  $\pm(10\% + 0.3 \text{ ppbv})$  with the largest component of uncertainty caused by the difficulty of determining the background zero in the laboratory and longer-term drift from optical interference fringes. The sensor has been intercompared with a number of closed-path Picarro sensors on both towers and vehicles. While the average agreement between the closed-path Picarro and open-path QCL-based sensors is good ( $\pm 20\%$ ), the open-path sensor captures the high spatiotemporal variations that are averaged out in the closed-path designs. Field results will be presented from eddy covariance studies at a grassland in Rocky Mountain National Park and cattle feedlot in Colorado, mobile laboratory studies of agricultural and vehicle emissions, and satellite validation of TES, CrIS, and IASI  $\text{NH}_3$  remote sensing measurements.



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