Dear MetNH3 Newsletter reader,

The partners of EMRP JRP MetNH3 present in this newsletter an update of the work performed within the past year of the project "Metrology for Ammonia in Ambient Air". More information on MetNH3 can be found on the project webpage http://metnh3.eu.

Research Highlights

The main objective of **WP1** is the **development of improved gas mixture standards** by static gravimetric and dynamic methods. The highly adsorbing/desorbing behaviour of ammonia molecules and the purity of the balance gas challenge the **preparation of ammonia primary reference standards**.

NPL and VSL have tested **different cylinder types** by performing a series of **decant tests at the 100 and 10 µmol/mol levels**. These tests showed minimised adsorption of ammonia molecules on **internal surfaces of stainless steel cylinders passivated with the SilcoNert2000® treatment by SilcoTek Inc.**. For such coated cylinders, no significant difference in amount fraction between the parent and daughter mixtures in each decant experiment could be observed. In addition, the **effect of pressure changes on the adsorption/desorption of molecules was investigated**. Reactive molecules adsorbed on cylinder surfaces tend to desorb as the pressure in the cylinder decreases. Again, **no significant effect could be observed in the SilcoNert2000® treated stainless steel cylinders**. The **long term stability of the mixtures** prepared in cylinders has been monitored throughout the project (see Fig. 1).

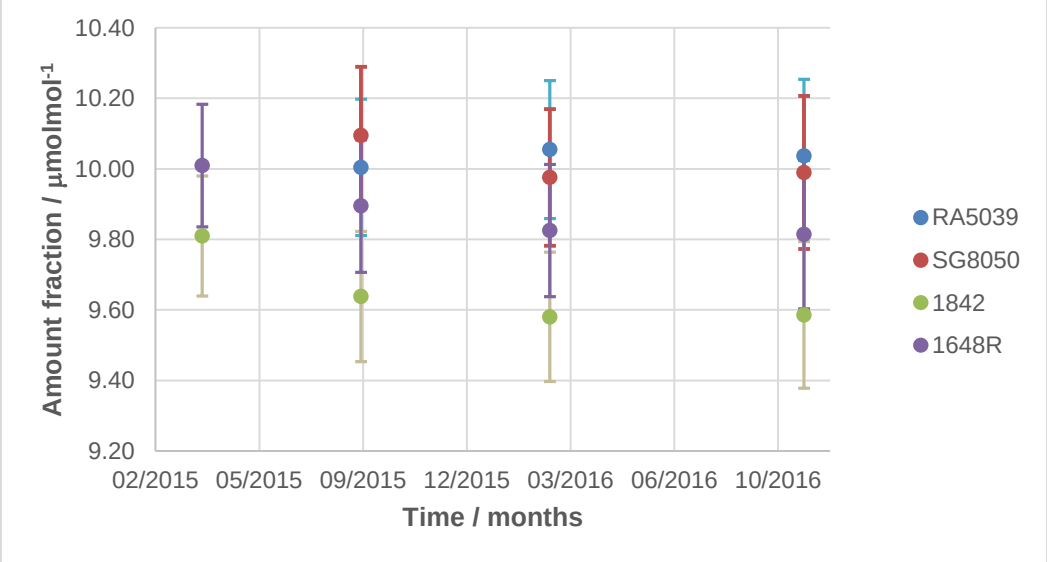

Figure 1: Preliminary results for the stability of 4 mixtures at 10 µmol/mol of NH_3 in nitrogen of which RA5039 and SG8050 are SilcoNert2000 coated cylinders and 1842 and 1648R are BOC cylinders treated with Spectraseal.

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In order to **reduce the uncertainty in the final ammonia amount fraction of the primary standards**, NPL and VSL have undertaken extensive **purity analyses of the balance nitrogen gas** used to prepare these mixtures. The measurements involved very challenging quantifications of trace impurities of a number of components (ammonia, water, formaldehyde, carbon dioxide and methane) at the low nmol/mol level. **The level of impurities found in the matrix gas had no effect on the amount fraction uncertainty of ammonia standards in cylinders nor will they affect the analysis of ammonia standards.** It has to be mentioned that only **high quality matrix gases** were used in the preparation. In addition, special care should be taken during preparation to **avoid introduction of any water from tubing or valves**.

NPL has developed a facility for the **dynamic dilution of ammonia primary reference standards using high-accuracy mass flow controllers**. This facility provides a direct method of comparison and validation of the cylinder mixtures prepared by NPL and VSL with the dynamic permeation systems developed by BAM and METAS

Partners METAS and BAM have constructed **two mobile NH_3 reference gas generators** at their respective institutes. They are used to **dynamically generate SI-traceable NH_3 reference gas mixtures of 0.5-500 nmol/mol with an expanded uncertainty U_{NH3}< 3 % (k = 2) for the on-site calibration of optical instruments**. All surfaces in contact with NH_3 are coated with SilcoNert2000®. METAS' **reference gas generator ReGaS1** has been characterised, validated and successfully used for two laboratory intercomparisons and the field intercomparison at CEH in Scotland.

Partners REG UH and METAS have continued the **adsorption experiments at different levels of humidity in the matrix gas** in order to assess the influence of water on the adsorption of NH_3. **The ammonia adsorption was found to increase substantially in dry conditions**. The increase was largest for plain stainless steel which was the most adsorbing material. **The coatings applied on stainless steel decreased the adsorption significantly in dry conditions. Polymers PVDF and PTFE were the least adsorbing materials.** For water amount fractions between 1000 and 10000 µmol/mol, the smallest ammonia adsorption was found. **The adsorption increased again above 10000 µmol/mol (one percent) humidity levels**. This is, presumably, due to the **dissolution of ammonia on the multiple water layers** present on the material surface.

WP2 has completed the experimental work towards **standard optical measurement methods**. After extensive efforts to **characterise extractive cavity ring-down spectrometers** (CRDS) from Picarro Inc. by partners PTB, NPL and METAS the focus in the last project period was on intercomparison measurements.
PTB's **optical transfer standard (OTS), a metrologically characterised Picarro CRDS analyser with a customised data evaluation algorithm for absolute, calibration-free measurements**, participated in three measurement campaigns:

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- June 2016: Intercomparison applying a **test facility at UBA** for **investigating e.g. the cross-interference** between NH_3 and several atmospheric compounds (O_3, SO_2, and NO)
- August 2016: Intercomparison under **field conditions in Scotland** organised by REG CEH
- November 2016: **Establishing traceability of the VTT sampling-free spectrometer** via the calibration of another CRDS analyser **at PTB**.

In each case, the **OTS was measuring against METAS' permeation reference gas generator ReGaS1**. Partners are currently processing the newly collected data which provides an excellent basis for the validation of PTB's optical transfer standard and its new data evaluation algorithm.

Using ReGaS1 and the OTS during the November measurements, PTB and METAS further **employed REG CEH's humidity and aerosol generator PReHAGS to investigate the influence of such air constituents on reference gas measurements** on which—to the best of our knowledge—few studies have been published so far, in spite of the high importance to the air quality measurement community. Furthermore, this offered an early **opportunity to test the new humidity correction which Picarro Inc. released subsequently to the joint investigation of humidity cross-interference with Partner NPL (find link to publication below)**. Although not required by the OTS when applying the data evaluation customised by PTB, the correction was still available through the spectrometer's pre-installed data evaluation.

Partner VTT finished the technical work on their **sampling-free spectrometer** and compared the instrument against a Picarro CRDS analyser which was calibrated using METAS' reference gas generator ReGaS1 at PTB. This procedure allowed for the indirect comparison to PTB's optical transfer standard. **The operation of the sampling-free spectrometer was characterised e.g. with respect to its response time, linearity and sensitivity**. Due to somewhat instable operation of the selected laser source the original goal for sensitivity could not be met, but thanks to its **instant response and traceability of the ammonia amount fraction measurement results, this spectrometer works as a potential means for an instrument reference method for reliable online ammonia measurement**.

As part of the **planned NH_3 sensor validation programme in WP3**, NPL's **Controlled Atmosphere Test Facility (CATFAC)** was employed for **six 28-day exposure tests with ALPHA, Gradko, PASSAM and Radiello diffusive samplers (14 days), and DELTA denuders**. The exposed samplers have been returned to the different manufacturers for analysis. **Fig. 2 shows the percentage deviation reported by each participant from the known traceable concentrations of NH_3.** The results are currently being employed to **determine new values of the diffusive sampling rates for the devices tested**.

REG CEH welcomed visitors from all over Europe and from the USA to two NH_3 intercomparisons held in Scotland in summer 2016. The unexpectedly beautiful weather required coping with heat and sunburn yet, set-up and operation proceeded smoothly.

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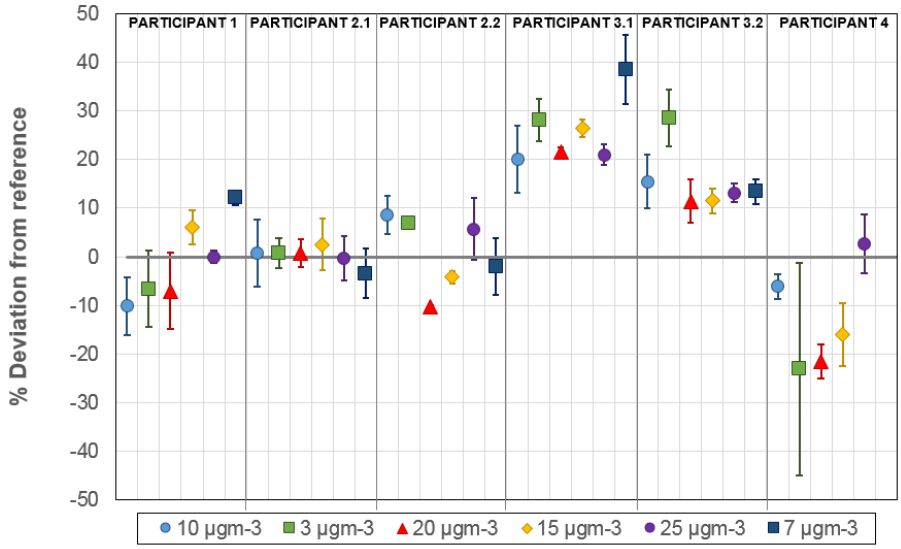

Figure 2: The percentage deviation reported by each participant of the sensor validation programme from the known traceable concentrations of NH_3

The **instrument intercomparison at CEH Edinburgh, Scotland deployed 16 instruments and samplers over the period 15th August – 16th September 2016 at intensively managed grassland** (Easter Bush site). Technologies included (cavity-enhanced) absorption spectrometry, photoacoustic spectroscopy, differential optical absorption spectroscopy (DOAS) and wet chemistry methods at a measurement height of 1.7 m. During the campaign **both ambient and elevated NH_3 conditions were experienced with concentrations ranging between <1-300 ppb**. **Portable calibration systems developed by METAS and NPL were deployed and field tested** during the intercomparison. Challenges with inlet-design, ambient conditions and practical logistics were coped with and **most instruments were compared against the calibration systems at the beginning and end of the experiment**.

At the **passive sampler intercomparison** at the Whim Bog field site, two 4-week exposure periods were undertaken. **Eight sets of samplers** were deployed at four positions at the site on custom made sample posts. It is thought that this is the **first field experiment of its kind integrating a metrology experiment with an ecosystem manipulation site**. Initial results showed that the **concentration range the passive samplers were exposed to was between 1ppb up to 100 ppb**.

Both studies are the most recent and largest to date investigating the applicability of both commercial and research instrumentation for the measurement of ambient NH_3. It is planned from the results of this study to **draw conclusions regarding recommendations for measurement of ambient NH_3 by active and passive sampling methods**. This will enable further understanding of

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ambient NH_3 and the impacts of mitigation strategies. Initial results from both intercomparisons have been presented in December 2016 and peer-review papers are anticipated being written in early 2017.

Dissemination of project results

Partners of MetNH3 have presented the project and its results at several **conferences in 2016.** Poster presentations and **future opportunities to meet and collaborate with MetNH3 partners** are published in the **news section** of the **MetNH3 website.**

Project workshop

The **second project workshop on ammonia measurement methodology** open for collaborators and interested parties will take place on the **09th and 10th May 2017 at METAS in Bern, Switzerland.** The **registration** will be open as of **01/03/2017** via the **MetNH3 website.**

Peer-reviewed publications

The following **peer-reviewed publications** have been published in the framework of MetNH3:

- Andrea Pogány et al.: A metrological approach to improve accuracy and reliability of ammonia measurements in ambient air. Meas. Sci. Technol. (2016) **27** 115012
- Nicholas A. Martin et al.: The application of a cavity ring-down spectrometer to measurements of ambient ammonia using traceable primary standard gas mixtures. Appl. Phys. B (2016) 122: 219.

Conferences

MetNH3 partners will contribute to the following **conferences in 2017**

European Geosciences Union EGU general assembly, 23.-28. April 2017 Vienna, Austria

- Session AS3.27 "**Climate and atmospherically important trace gases: metrology, quality control and measurement comparability**"
- Session BG2.15 **"Surface exchange and distribution of reactive trace gases and aerosols"**

GAS Analysis 2017, 13.-15. June 2017 Rotterdam, The Netherlands

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To date, **20 collaborations with various key players for ammonia metrology** were formed. Interested parties have committed to exchange information with MetNH3 and to support the research in their specific areas of expertise. Should you be interested in our project and could make a nonfinancial in-kind contribution, do not hesitate to get in touch with any of the JRP Partners.

Contact and further information

You are very welcome to forward our **newsletter** to your contacts interested in metrology for ammonia in ambient air. **Contact any JRP partner to receive further information on the project**.

METAS (Federal Institute of Metrology), Switzerland. Bernhard Niederhauser (Coordinator)

BAM (Federal Institute for Materials Research and Testing), Germany. Dr. Thomas Hübert

DFM (National Metrology Institute), Denmark. Dr. David Balslev-Harder

MIKES Metrology (VTT Technical Research Centre), Finland. Dr. Timo Rajamäki

NPL (National Physical Laboratory), United Kingdom. Dr. Nicholas Martin

PTB (National Metrology Institute), Germany. Dr. Nils Lüttschwager

UBA (Federal Environment Agency), Germany. Dr. Klaus Wirtz

VSL (National Metrology Institute), The Netherlands. Janneke van Wijk

Researcher Excellence Grants

REG1: CEH Centre for Ecology and Hydrology, United Kingdom. Dr. Christine Braban

REG2: UH University of Helsinki, Finland. Dr. Olavi Vaittinen

The JRP partners are regularly consulted by an external **board of advisors**.

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