Dear MetNH3 Newsletter reader,

The partners of the EMRP JRP MetNH3 present in this newsletter an update of the work performed within the past eight months 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

WP1 has as main objective the **development of improved gas mixture standards** by static gravimetric and dynamic methods. The highly adsorbing/desorbing behaviour of ammonia molecules poses a challenge to the ***preparation of ammonia primary reference standards***.

NPL and VSL have tested a number of different cylinder types by performing a series of decant tests at the 100 and 10 µmol/mol levels. They showed that adsorption of ammonia molecules on cylinder walls was minimised when the ***internal surfaces of stainless steel cylinders were passivated using the SilcoNert2000® treatment by SilcoTek Inc.***. For these cylinders, no appreciable 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. No such effect could be observed in the ***SilcoNert2000®*** treated stainless steel cylinders. The long term stability of the mixtures prepared in these cylinders will be monitored throughout the project.

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. Impurities can affect the ammonia amount fraction either by directly reacting with ammonia, or by interfering with its measurement. 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 impact of the impurities detected on the final ammonia amount fraction will be assessed in the coming months.

Over the next few months, NPL will develop a facility for the ***dynamic dilution of ammonia primary reference standards using high-accuracy mass flow controllers***. This facility will provide a direct method of comparison and validation of the cylinder mixtures prepared by NPL and VSL with the permeation systems developed by BAM and METAS.

Following the procedure of Vaittinen et al. ("Adsorption of ammonia on treated stainless steel and polymer surfaces" Appl. Phys. B 115, pp.185–196, doi: 10.1007/s00340-013-5590-3, 2013), partners VSL and METAS have studied the ***adsorption of NH_3 on different surfaces***, such as stainless steel and varieties of Teflon. In addition, SilcoNert2000® treated stainless steel has been tested by exposing a

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surface of known dimensions to NH_3 at nmol/mol amount fractions. The test results confirm those of Vaittinen et al. in that the least NH_3 molecules were adsorbed on Teflon surfaces. However, Silconert2000® treated stainless steel surfaces showed similarly small adsorption. The difference to untreated electro-polished stainless steel surfaces, however, is substantial with 10 times more molecules adsorbed by the untreated surface. Currently, partners VSL, METAS and REG UH are repeating the adsorption experiments at different levels of humidity in the matrix gas in order to assess its influence on the adsorption of NH_3.

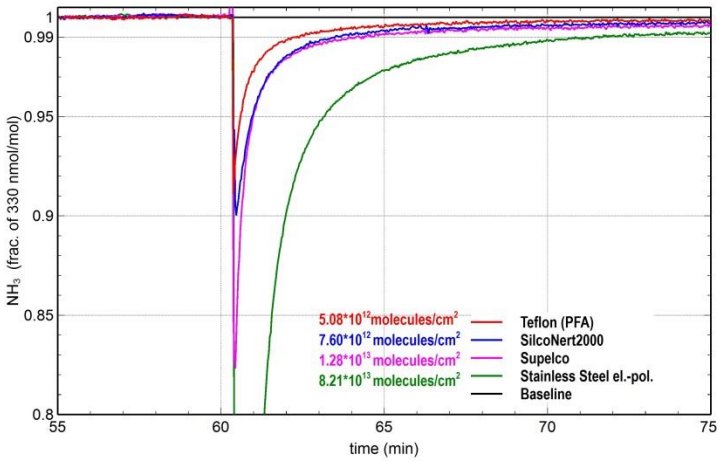

Figure 1: Results of the tests investigating the adsorption of NH_3 in N_2 on different tubing materials (average over 3 individual measurements). The values given are the numbers of NH_3 molecules adsorbed per cm^2 of a cleaned test tube which has been abruptly exposed to the gas mixture, resulting in the sudden drop in NH_3

Based on this knowledge, partners METAS and BAM have planned to have all surfaces of the ***two mobile NH_3 reference gas generators*** they are constructing made of Silconert2000® treated stainless steel. The aim is to dynamically generate NH_3 reference gas mixtures of 0.5-500 nmol/mol with an uncertainty < 3 %. The two devices are now in the construction phase, which is to be concluded by the end of 2015 in order for them to be ready for validation in the first half of 2016.

WP2 continues the research into ***standard optical measurement methods***. Numerous experiments have been carried out to ***characterise extractive cavity ring-down spectrometers*** (CRDS) from Picarro Inc. by partners PTB, NPL and METAS. A number of points have been identified that are considered to be crucial to achieve traceability in ambient ammonia measurements in the 0.5-500 nmol/mol amount fraction range. Firstly, it has been noticed that the spectrometer calibration is valid only in air; the slope of a calibration line measured in nitrogen matrix gas is 10 % lower. In consequence, a modified data evaluation algorithm has been developed by DFM and PTB, which successfully eliminates the matrix gas dependence of the ammonia amount fraction readings and thus enables accurate measurements in different matrix gases. Secondly, NPL has identified a non-negligible cross-sensitivity to water vapour. A joint paper with Picarro Inc. titled “The development of traceable Primary Standard Gas Mixtures (PSMs) to underpin ambient measurements of ammonia using a Cavity Ring-Down Spectrometer CRDS” has been completed and submitted for publication. Picarro Inc. is incorporating the water correction mechanism that was developed through the collaboration with NPL into all their new ammonia analysers.

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The testing of a ***sampling-free spectrometer*** based on an open multiple-pass cell and a quantum cascade laser is continuing at VTT. Further development to minimize optical interferences to reach the target detection limit below 1 nmol/mol using a 1 minute sampling time is progressing as expected. The spectrometer prototype is expected to be ready in early 2016.

As part of the planned NH_3 sensor validation programme in the framework of **WP3** in NPL's ***Controlled Atmosphere Test Facility (CATFAC)***, two 28-day exposure tests with ALPHA, Gradko, PASSAM and Radiello diffusive samplers, and DELTA denuders have been carried out. The exposed samplers have been returned to the different manufacturers for analysis, and NPL is currently receiving the test results from the participants, which will be used to deliver diffusive uptake rate measurements and active sampling data.

Dissemination of project results

Partners of MetNH3 have presented the project and its results at several ***conferences in 2015.*** Poster presentations and **future opportunities to meet as well as to collaborate with MetNH3 partners** are published in the **news section** of the **MetNH3 website**, where you can also **register for the following events**:

A ***project workshop on the progress in ammonia metrology*** open for collaborators and interested parties will take place on the ***24th and 25th February 2016 at PTB Braunschweig.***

NERC CEH (UK) is opening a call for applications from interested organizations and SMEs to take part in a ***field inter-comparison of NH_3 measurement technologies*** (15th August 2016 to 16th September 2016). The inter-comparison is open to both **on-line and off-line instrumentation** and will be held ***at Easter Bush (managed grassland) in South East Scotland***.

To date, ***16 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, valuable to the aims or our project, do not hesitate to get in touch with any of the JRP Partners.

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Contact and further information

Our ***newsletter*** is published regularly containing MetNH3's latest results, which you are very welcome to forward to your contacts interested in metrology for ammonia in ambient air. **To register for the newsletter or receive further information on the project you can contact any of the JRP partners**.

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

BAM (Federal Institute for Materials Research and Testing), Germany. Dr. Carlo Tiebe

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

MIKES Metrology (VTT Technical Research Centre), Finland. Dr. Tuomas Hieta

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

PTB (National Metrology Institute), Germany. Dr. Andrea Pogány

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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