MetNH3: Metrology for ammonia in ambient air

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Atmospheric Ammonia (NH_3)

- By 2020, NH_3 will be the primary source of acidification, eutrophication and secondary aerosol formation in Europe (Sutton *et al*. 2009).
- UK ambient NH_3 concentrations are in the range 1.5-20 ppb at agricultural and urban sites and <0.15 ppb at background sites.
- The UK was estimated to emit 181kt NH_3 in 2013 with approximately 80% from agricultural sources.
- The UK National Ammonia Monitoring Network (NAMN) uses an accredited off-line low temporal resolution passive sampler method. In addition, the two UK EMEP Supersites (Auchencorth Moss and Harwell) measure NH_3 at a high temporal resolution with on-line denuder–IC method (Twigg *et al*. 2015).
- In recent years, significant developments in NH_3 metrology have occurred however there are still significant challenges in analytical technology, uncertainty analysis and QA/QC of **ambient** NH_3 measurements.
- Discrepancies between instrumentation have been demonstrated through field intercomparison studies (Bobrutzki et al. 2010).

How can the research community get involved?

Become a Stakeholder/Collaborator
Get the project newsletter!
Contact Project coordinator:
Bernhard Niederhauser
bernhard.niederhauser@metas.ch

Upcoming Events:
Stakeholder workshop to be held in February 2016
Website: http://www.metnh3.eu

The MetNH$_3$ project is aimed at achieving metrological traceability for NH_3 measurements in air from primary certified reference material and instrumental standards to the field level.

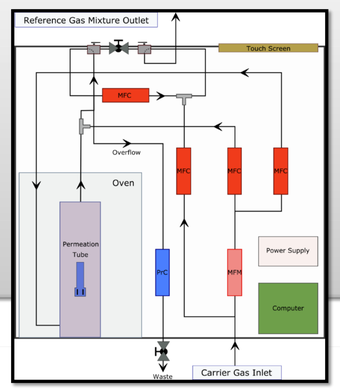
-the project has 10 partners (8 metrological institutes and 2 research institutes, refer to bottom of poster) as well as 18 collaborators from academia and industry

Objectives:

WP 1- NH_3 reference gas standards

- New traceable static reference gas mixtures in pressurised cylinders

- *Development of devices for dynamic generation of traceable reference gas mixtures by permeation and dilution with portability*

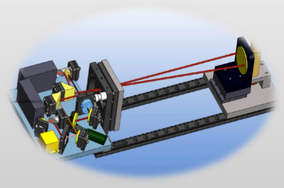


Schematic of the portable reference gas generator as constructed by METAS and BAM.

WP 2- Optical Spectroscopic Standards

- Development and characterisation of extractive laser optical spectrometric standards

- *Characterisation and application of sampling-free open path laser spectrometers*

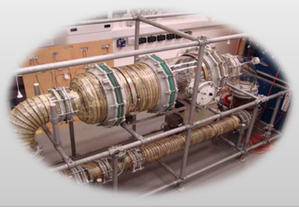


Preliminary design of a sampling-free spectrometer (VTT-MIKES).

WP3- Validation and dissemination

- Validation and comparison of high accuracy standards to field applicable methods

- Evaluate field applicable methods for monitoring

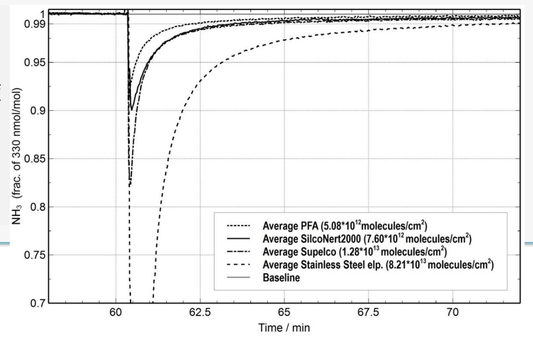


Controlled atmosphere test facility (CATFAC) at NPL

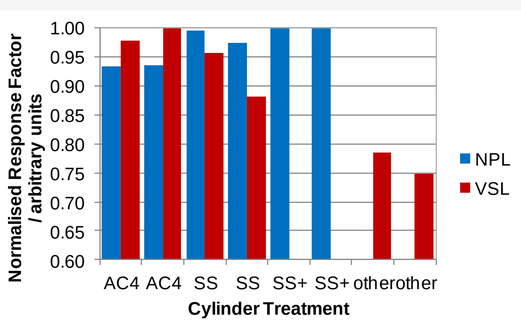
Progress to date:

- The partners from NPL and VSL have produced reference gas mixtures prepared by gravimetric method at 10 µmol/mol and 100 µmol/mol. Studies include assessing the purity of the N_2 dilution gas and accurate quantification of NH_3 losses due to adsorption to cylinder walls via a series of decant tests
- BAM and METAS have constructed two mobile generators for the dynamic generation of reference gas mixtures. These devices generate NH_3 at the 0.5-500 nmol/mol and will be used in the 2016 inter-comparison.
- Research on the adsorption of NH_3 on various material surfaces and at different rates of humidity of the matrix gas involves the partners VSL and METAS together with NERC CEH and UH (Vaittinen et al. 2013)

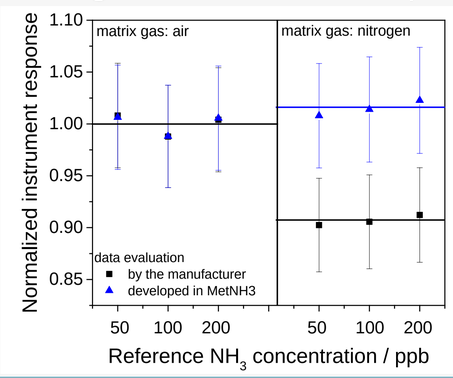
Average time response function (based on 3 replicates) of different materials (tube length = 1 m) exposed to 330 nmol/mol of NH_3 in N_2. Relative standard deviations in the response are as follows: PFA: 56.63%, SilcoNert2000: 16.07%, Supelco: 29.61%, Stainless Steel: 4.26%.



Comparison of individual cylinders at 10 µmol/mol ammonia in nitrogen to determine the best surface treatment for ammonia mixtures and to quantify absorption of ammonia on cylinder walls

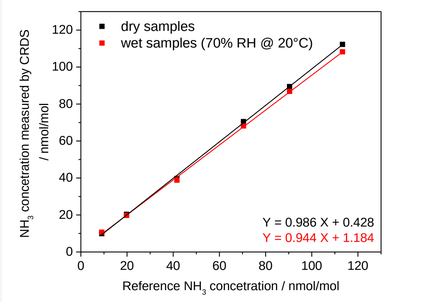


- VTT-MIKES has started development of an open path quantum cascade laser system (figure on right hand side)
- PTB and DFM have started to develop a new data evaluation algorithm to enable absolute and traceable ammonia measurements using a commercial CRDS spectrometer:
  - PTB identified a matrix gas dependence of the commercial CRDS spectrometer causing 10% difference between readings in nitrogen and air matrix gas.
  - PTB and DFM updated the developed data evaluation algorithm to compensate for the matrix gas dependence



Measurements in nitrogen and air matrix gases

- NPL has developed a Controlled Atmosphere Test Facility (CATFAC) for carrying out exposure tests with multiple types of ammonia passive samplers under different *T, RH* and wind speed.
- The CATFAC has been used to identify a H_2O interference (up to 4% lower readings under humid conditions) in a commercial CRDS system. Work with the manufacturer has resulted in development of the data evaluation algorithm used in the instrument for ambient measurements (Martin et al., under review)
- UBA has started the characterization of a Proficiency Test Facility for ammonia measurements.
- NERC CEH is researching inlets for NH_3 and designing a mobile instrument-response testing system.
- *Upcoming studies:*
  - *Laboratory intercomparison to be held at UBA test facility (Spring 2016)*
  - *Field intercomparison led by NERC (see below for open call)*



Calibration lines (lack of fit plot) for dry and humidified ammonia atmosphere tests at CATFAC facility.

NERC CEH in collaboration with NPL and MetNH$_3$ would like to invite interested organisations & SMEs to apply to take part in an intercomparison of ammonia measurement (*deadline 31st December 2015, confirmation of participation by 31st Jan 2016*):

1. **NH_3 on-line & off-line metrology intercomparison. Contact: Dr Marsailidh Twigg (sail@ceh.ac.uk)**
Dates: 15 August 2016 to 16th September 2016
Location: Easter Bush (managed grassland) in South East Scotland.

2. Off-line NH_3 metrology intercomparison. Contact: Miss Sim Tang (yst@ceh.ac.uk)
Dates: Measurement period August – September 2015
Location: Whim Bog (manipulated peatland site) in South East Scotland

References:

Bobrutzki, K. von. *et al.* (2010) Field inter-comparison of eleven atmospheric ammonia measurement techniques. Atmos Meas Tech 3:91–112.
Martin, N.A et al. (under review) The development of a Cavity Ring-Down Spectrometer for measurements of ambient ammonia using traceable Primary Standard Gas Mixtures
Pogany, A. *et al*. (Under review) A metrological approach to improve accuracy and reliability of ammonia measurements in ambient air
Sutton, M.A. *et al.* (2009) Atmospheric Ammonia: Detecting Emission Changes and Environmental Impacts.
Twigg *et al*. (2015) Water soluble aerosols and gases at a UK background site – Part 1: Controls of $PM_{2.5}$ and PM_{10} aerosol composition, Atmos. Chem. Phys., 15:8131-8145
Vattinen *et al*. (2013) Adsorption of ammonia on treated stainless steel and polymer surfaces. Appl Phys B 115:185–196.

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Project Partners:
METAS, PTB, NPL National Physical Laboratory, DFM Danish National Metrology Institute, BAM, Helsingin yliopisto Helsingfors universitet University of Helsinki, VSL Dutch Metrology, VTT MIKES METROLOGY, Umwelt Bundesamt, NERC SCIENCE OF THE ENVIRONMENT