Final Publishable JRP Summary for ENV55 MetNH3
Metrology for Ammonia in Ambient Air

Overview

Measuring ammonia in ambient air is a priority issue due to its harmful effects on human health and ecosystems. The European Directive 2016/2284/EU on the reduction of national emissions of certain atmospheric pollutants has set national reduction commitments for five pollutants, including ammonia (NH_3), which are responsible for acidification, eutrophication (excess nutrients in water sources) and air pollution. However, there is a lack of guidance and regulations on measurement techniques and analysis to ensure reliable NH_3 measurements. Recent intercomparisons of existing certified reference materials (CRM) for NH_3 have shown significant discrepancies between the generation methods of samples. This affects not only the credibility of instrumental performance and calibration, but also the scientific value of extensive ambient air monitoring and the comparability of data collected by national networks. This project developed reference standards and measurement techniques for traceable measurements of NH_3 in air. These will enable validated high quality ammonia measurement data which will help monitor and compare NH_3 levels and ensure compliance with environmental protection policies and legislation.

Need for the project

NH_3 emissions are estimated to have at least doubled over the last century across Europe. The primary sources of NH_3 are intensive agriculture (particularly fertilisation with urea), and non-agricultural sources such as sewage treatment, catalytic converters, anaerobic digesters (rapidly increasing since 2010) and industrial processes. Emissions from diesel vehicles are also likely to increase in the future due to the application of urea as a selective catalyst for reducing nitrogen oxide (NO_x) emissions.

NH_3 can bind with pollutants such as sulphur dioxide (SO_2) and NO_x, as well as particulates, and neutralise them. The eventual deposition of NH_3 bound in aerosols also contributes to eutrophication and acidification of land and fresh water and thus to a reduction in soil and water quality. This has negative effects on biodiversity and ecosystems.

Air pollution spreads across national borders and over long distances. In 1999 NH_3 was included under the United Nations Economic Commission for Europe (UNECE) Gothenburg Protocol (revised in 2012), which is part of the convention on Long-Range Transboundary Air Pollution. The UNECE Gothenburg protocol was designed to reduce acidification, eutrophication and ground-level ozone by setting emissions ceilings to be met by 2010. In addition, the European Directive 2016/2284/EU sets individual emission ceilings for each member state to be met by 2020, based on the revised Gothenburg Protocol and sets even more ambitious reduction commitments for 2030 to reduce the health impacts of air pollution by half compared with 2005. This has led to the incorporation of NH_3 measurements into national air monitoring networks and, in some cases, requires measurements for compliance with the critical level targets of the Habitats Directive (also known as Council Directive 92/43/EEC on the Conservation of natural habitats and of wild fauna and flora).

Currently, NH_3 concentrations in ambient air are determined primarily by using diffusive samplers and denuders (devices used to separate a gas from an aerosol). These indirect wet chemical methods are the most widely used measurement techniques because they are low cost and can be deployed over wide geographical areas. Such methods are fairly reliable but not ideal for monitoring levels over time due to insufficient resolution of the measurements and because the changes in NH_3 concentrations are often smaller than the measurement uncertainty. The accuracy of such methods has also not been well characterised and there is no established traceability infrastructure to underpin them. On-line extractive samplers using wet-chemistry techniques which can provide high resolution measurements do exist. In

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recent years, spectroscopic techniques have developed rapidly, however they often lack traceability and neither inlet systems nor relative humidity controls are sufficient for reliable ambient measurements of NH_3.

All these measurement techniques require calibrations with CRMs, but such gas mixtures are not commercially available for NH_3 at concentrations to be sufficiently representative of ambient air. The production of NH_3 CRMs is challenging because NH_3 has a high reactivity with most surfaces and with water, leading to adsorption and desorption on the surfaces of the gas mixture cylinders, and even sampling equipment and inlet valves. This makes NH_3 CRMs unstable and affects the traceability of NH_3 measurements. To counter these effects current NH_3 CRMs are typically 60 – 60,000 times more concentrated than the range of molar fractions, or amount fractions, found in atmospheric air.

Scientific and technical objectives

The overarching objective of the project was to achieve metrological traceability for NH_3 measurements at ambient air concentrations using primary CRMs, and to develop instrumental standards for their application in the laboratory and in the field. This required the successful completion of the project's three objectives:

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 NH_3 amount fractions similar to those in ambient air. This includes solving the problem of existing discrepancies between gas standards. The production/purification of a high purity matrix gas with validated levels of NH_3 is a prerequisite for the preparation of static and dynamic reference standard mixtures.

2. *To develop and characterise laser based optical spectrometric standards*

   Evaluation of the applicability of a newly developed open-path (where the optical path is open to the environment) as well as of existing extractive measurement techniques and characterisation of both as optical transfer standards according to metrological principles.

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

   Evaluation of existing measuring instruments for traceable measurement of NH_3 at ambient molar fractions (0.5 to 500 nmol/mol) under real air and laboratory conditions, and to evaluate and compare results to develop suitable sampling methods in order to promote long-term efficiency in monitoring of NH_3 reduction measures with at the required level of uncertainty. Finally, to provide validated measurement tools to enable EU SMEs developing new monitoring technologies to deliver improved instrumentation to the market.

Results

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

High purity matrix gases with gravimetrically validated amounts of NH_3 added were made available as CRMs (according to ISO 6142-1 Preparation of calibration gas mixtures). Testing of commercially available cylinder passivation techniques, which involved applying silica-based coating, was successful. To quantify the extent of adsorption on the cylinder wall surface decantation experiments were performed on several commercial types of treated cylinders. Two different NH_3 amount fractions (100 µmol mol^{-1} and 10 µmol mol^{-1}) were prepared in four different types of gas cylinders. In tests on the long-term stability of these mixtures, no instability could be detected over 24 months in the cylinders containing the 100 µmol mol^{-1} mixtures, but there was evidence of decay for the mixtures prepared in standard cylinders at 10 µmol mol^{-1}. However, a new type of cylinder with a silica-based coating yielded excellent results even for low concentrations, due to low levels of adsorption.

The development and construction phase of two mobile SI traceable gas generators to dynamically produce CRMs with the same molar fractions of NH_3 as ambient air was completed. It combines the temperature and pressure dependent permeation (ISO 6145-10) in with dynamic dilution by thermal mass flow controllers (ISO 6145-7). The first calibrated and characterised instrument was developed and used for the dynamic

generation of CRM in three inter-comparisons at ambient amount fractions (0.5 – 500 nmol mol^{-1}) with $U_{NH3} \leq 3$ % (k = 2).

Adsorption/desorption on differently coated surfaces (e.g. in tubing material, valves and mass flow controllers) as well as in carrier gas with different levels of humidity were identified and quantified. This information is already being implemented in the generation of CRM, particularly applying silica-based coating to stainless steel surfaces and controlling humidity.

To develop and characterise laser based optical spectrometric standards

A commercial cavity ring-down spectrometer was metrologically characterised and a custom data evaluation routine developed to enable measurements of the absolute NH_3 amount fractions. This included the development of new software tools that provide GUM (Guide to the Expression of Uncertainty in Measurement) compliant uncertainty figures, an uncertainty budget and covariance by performing a chi-square test (statistical test). This serves as quality check to evaluate the compliance between the fitting model and measurement data.

Uncertainties of absolute NH_3 measurement results were commonly in the low percent range. Traceable NH_3 measurements were not available for all input parameters of the data evaluation procedure, but crucial steps to establish their traceability were achieved by calibrating instrument sensors and by measuring the most relevant spectral absorption line parameters with improved uncertainty using direct laser absorption spectroscopy. Ultimately, this allowed the spectrometer to be operated as an optical transfer standard (OTS) for instrument calibration. The spectrometer was compared to the traceable reference gas generator developed in objective 1. The comparison of absolute NH_3 measurement results to reference values revealed an average deviation of approximately 6 %. However, the source of this bias could not be identified.

A sampling-free spectrometer based on a quantum cascade laser and an open-path gas cell was developed. The spectrometer was characterised and compared against the project's traceable reference gas generator and the OTS. Unstable performance of the quantum cascade laser prevented fully calibration-independent operation and hence reaching the anticipated sensitivity. However, thanks to its instant response and a traceable calibration, the sampling-free spectrometer now offers a reference method for online measurements of NH_3 amount fractions.

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

A controlled test chamber facility and an installation for proficiency tests were validated for performing comparisons of instruments and measurement methods (i.e. those newly developed in the project and those existing) for NH_3 under well characterised laboratory conditions. As part of this the design for the "Controlled Atmosphere Test Facility (CATFAC)" was adapted so it could be used for NH_3 tests. The CATFAC was characterised and used to validate the performance of diffusive samplers, denuders and on-line instruments controlling test parameters such as NH_3 amount fraction, relative humidity and wind speed.

Applied field measurement techniques were evaluated in terms of accuracy, efficiency, traceability and general requirements for efficient long-term monitoring of NH_3 reduction measures. A cavity ring-down spectrometer (CRDS) showed promising results for rapid on-line measurements. In collaboration with the CRDS instrument manufacturer NH_3 reference gas mixtures developed in this project were used to correct for undesirable cross interference effects from water vapour that can affect ambient NH_3 measurements.

A total of 16 potential measuring instruments and methods (open-path and extractive) for traceable measurements of ambient air NH_3 concentrations were evaluated in one of the two field measurement campaigns in Scotland (CEH Edinburgh) in summer 2016. The performance and calibration of the extractive samplers varied slightly but there were general insights into the sampling systems which will benefit the intercomparison participants. NH_3 CRMs in cylinders as well as the mobile reference gas generator were applied to calibrate the instruments in the field.

The second intercomparison for passive samplers offered the opportunity to validate the diffusive uptake rates of collaborating passive sampler types previously revised in the CATFAC in the field.

Actual and potential impact

The successful achievement of the project's overall objectives enabled NMIs to offer and disseminate SI-traceable and concordant (consistent) calibration and measurement infrastructure at ammonia amount fractions required for measurements in ambient air (0.5 - 500 nmol/mol).

Dissemination of results

Project partners presented their work at 40 conferences and trade fairs, such as European Geosciences Union (EGU) 2015/2016/2017, American Geophysical Union (AGU) 2015/2016, GAS 2015 (including the award for best poster), Pittcon 2015 (Pittcon is the world's leading annual conference and exposition on laboratory science and attracts attendees from industry, academia and government from over 90 countries worldwide), the International Nitrogen Initiative (INI) 2016, Optics & Photonics Days (OPD) 2016, the International Conference on the Fundamentals of Adsorption (FOA) 2016, the NH_3 workshop at Hildesheim 2015/2016 and the International Congress of Metrology 2015.

The project results were presented in the nitrogen cycle meeting of World Meteorological Organisation Global Atmosphere Watch (WMO-GAW) and to the UNECE Task Force for Measurement and Modelling. 3 Good Practice Guides are available on the project website, with the titles:

- Accurate sampling and preparation of dynamic ammonia gas mixtures
- The measurement system applicable as optical transfer standard for ammonia in ambient air
- Measurement of ambient ammonia concentrations in the field and application to policy evidence

4 peer-reviewed publications were published in journals, including Measurement Science and Technology and Applied Physics B Lasers and Optics, and are available via the project website.

In addition, two workshops on NH_3 measurement methodology were organised and attracted a total of 90 participants.

A splinter meeting was also organised as part of EGU 2017 where the results of the spectroscopic measurements of the field intercomparison were discussed with researchers, representatives of measurement networks and instrument manufacturers.

Impact on standards

The project partners were closely linked to stakeholders and end-users by being members or service providers of key national or international environmental monitoring networks. They also worked with standards committees and inputted to draft standards: such as CEN/TC 264/WG 11 Ambient air quality - Diffusive samplers for the determination of gases and vapours - Requirements and test methods, and other TC 264 Working Groups, ISO/TC 146 Air quality, and ISO/TC 158 Analysis of gases, BIPM's Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) Gas Working Group and EURAMET TC METCHEM or by collaborating with National Environmental Institutes.

An advisory board consisting of members of research institutes and air monitoring networks, as well as of the European Institute for Environment and Sustainability, was also set up for the project.

Actual impact

The project has already had an impact with companies by:

- NPL collaborated with Picarro Inc, an instrument maker, on NH_3 gravimetric standards and dilution, which led to the implementation of a correction for the cross-interference due to water and applications of silica-based coatings. This is being incorporated into all new CRDS NH_3 analysers. The work has led to a peer reviewed publication which was awarded joint runner-up for NPL's Rayleigh Award.
- A successful collaboration between VSL, and speciality gas manufacturer, Takachiho Inc, has shown reduced adsorption on their aluminium cylinders treated with a proprietary method. This a more cost effective option than using stainless steel cylinders with silica-based coating, which would also have minimal adsorption.

- The newly produced CRM in combination with NPL's controlled atmosphere test facility CATFAC has enabled a laboratory assessment of currently used diffusive uptake rates of passive sampler and denuders which has been carried out for the first time in collaboration with NERC (Natural Environment Research Council in the UK)), Gradko International, Istituti Clinici Scientifici Maugeri (ICS Maugeri), PASSAM AG and Fachstelle für Umweltbeobachtungen FUB AG. All participants were manufacturers or users of different types of passive samplers. The measurement of traceable diffusive uptake rates with an uncertainty in the range of 5 % - 11 % has delivered improved agreement between different designs of samplers in field colocation studies. It has also provided the tools to determine the relative expanded uncertainty for NH_3 measurements at a number of key concentrations.
- During the project, an NH_3 field intercomparison was carried out. It was the first NH_3 field intercomparison applying SI-traceable on-site calibration facilities for the calibration of different analysers. A dynamic dilution facility was also developed by NPL by applying thermal mass flow controllers coupled to reference gas mixtures in cylinders and can be used to calibrate instruments requiring high sample gas flow rates. For the calibration of ambient air NH_3 measurement instruments with gas consumption ≤ 5000 ml min^{-1} METAS developed a mobile reference gas generator combining the permeation method with dynamic dilution by thermal mass flow controllers. This instrument is a first of its kind and is able to produce SI-traceable reference gas mixtures dynamically over the entire ambient air range.
- A copy of METAS' mobile reference gas generator has been commissioned by the national air pollution monitoring network for Switzerland and is to be applied for traceable calibrations of analysers for various reactive compounds (e.g. NH_3 and NO_2).

Potential impact

Reliable and comparable NH_3 measurements in the atmosphere will become routine to comply with the European Directive 2016/2284/EU. Given the increasing amount of NH_3 in the atmosphere, SI-traceability will give confidence in NH_3 measurements, which is important as it remains one of the few man-made pollutants predicted to increase in the twenty first century.

The findings of this project on adsorption reduction will support organisers and participants of the key comparison CCQM K-117, which is planned for 2018. Furthermore, the discrepancies observed in previous comparisons (CCQM K-46) between different generation techniques as well as the levels of uncertainty should be considerably reduced, due to the project's knowledge of how to reduce adsorption losses. Another important consequence of the project is that NH_3 CRMs can be made available for mixtures at lower amount fractions and lower levels of uncertainty.

This project will support instrument manufacturers in the development of absolute spectrometers. Establishing traceable, absolute laser-spectrometer as the optical transfer standards for NH_3 in air has the prospect of supplementing, or even replacing, calibrations using reference gas mixtures. In the longer-term commercially available instruments may be used to calibrate NH_3 analysers in a side-by-side comparison, with ambient air as the test gas. This would reduce down-times and save time and money for air monitoring networks.

List of publications

[1]. Andrea Pogány et al.: A metrological approach to improve accuracy and reliability of ammonia measurements in ambient air. *Meas. Sci. Technol.* (2016) **27** 115012

[2]. 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

[3]. Andrea Pogány et al.: High-Accuracy Ammonia Line Intensity Measurements at 1.5 µm. *Imaging and Applied Optics* 2016, paper JT3A.15

[4]. Andrea Pogány et al.: Metrology for ammonia in ambient air – concept and first results of the EMRP project MetNH3. *17th International Congress of Metrology*, 07003 (2015)

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