Publishable JRP Summary Report for ENV55 MetNH3
Metrology for ammonia in ambient air

Background

The measurement of ammonia in 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 regarding the analytical techniques to use, the maximum allowed uncertainty, the quality assurance and quality control (QC/QA) procedures and the metrological traceability infrastructure to underpin ammonia measurements. Discrepancies among European NMIs for primary ammonia reference gas standards and measurement techniques far above ambient air levels (30 to 50 µmol/mol) jeopardise not only the credibility of instrumental performance due to poor calibration but also the scientific value of extensive ambient air monitoring by national networks and the international exchange of scientific data.

Need for the project

Ammonia emissions are estimated to have at least doubled over the last century across Europe, concurrent with the employment of intensive farming practices, and an increased use of nitrogen-based fertilisers. Intensive agriculture (particularly fertilization with urea), together with a wide range of non-agricultural sources such as sewage, catalytic converters, anaerobic digesters (with rapid increases since 2010), and some industrial processes are responsible for the majority of ammonia emissions. Urban emissions from diesel vehicles will further increase in the coming years due to the use of urea as a selective catalyst to reduce NO_x emissions.

Emission and deposition of ammonia contribute to eutrophication and acidification of land and fresh water, leading to a reduction in soil and water quality, loss of biodiversity and changes to the ecosystem. Ammonia is the major precursor for the neutralisation of atmospheric acids, affecting the long-range transport of both SO_2 and NO_x and the stabilisation of secondary particulate matter (PM10, PM2.5 and aerosols) with associated air quality and health impacts. High PM levels in air are closely related to excess incidence of respiratory and cardiovascular diseases. PMs are light scatterers and absorbers, as well as active cloud condensation nuclei, leading to both the primary and secondary role of PMs in radiative forcing.

Ammonia has been included under the UNECE 1999 Gothenburg Protocol (revised in 2012) and in the EU National Emissions Ceiling Directive (NEC) of 2010, which both set emission targets for individual countries. Abatement of ammonia emissions is also included in the EU Integrated Pollution Prevention and Control (IPPC) for the intensive pig and poultry sectors. Moreover, some European countries have incorporated ammonia in their air monitoring networks e.g. in Spain, where ammonia must be measured in five background locations and in at least one site next to a high-traffic area in cities with more than 500 000 inhabitants.

Currently, the most reliable methods for the determination of ammonia concentrations in ambient air are using active or passive samplers. Ammonia is stripped into an acidic solution (or on coatings) followed by chemical analysis as ammonium. This method is generally quantitative and reliable but is only indirect and with poor time resolution. A direct measurement method is not available, due to the lack of reliable ammonia standards, suitable inlet systems and relative humidity response characterisation. This is a consequence of ammonia's high reactivity, meaning it cannot be stored in cylinders at ambient air levels due to various surface reactions that may decrease or increase the ammonia amount fractions in the cylinder. Calibrations with minimal surface effects from the delivery and sampling system are needed for assessing passive and active samplers and on-line instruments.

The majority of air quality measurements are done in the range between 0.5 and 500 nmol/mol however the certified reference material (CRM) at the lowest level is at 30 µmol/mol, i.e. 40 to 300 times higher than the

EMRP
European Metrology Research Programme
Programme of EURAMET
The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union

target level for calibration. Furthermore, even at 30 µmol/mol there is a discrepancy between the NMIs worldwide. This gap has to be closed as soon as possible with novel approaches for the production of CRMs and measuring methods.

Scientific and technical objectives

The JRP aims to develop the metrological traceability for the measurement of ammonia in air from the level of primary gas mixtures and instrumental standards to the field level. It consists of five work packages (WPs) with three technical ones:

WP 1 will develop improved gas mixture standards by static and dynamic gravimetric generation methods. Traceable preparative calibration standards (including portable) at ambient air levels based on existing methods for other reactive analytes will be realised and characterised. This includes elucidating the former discrepancies between standards and methods among NMIs (CCQM-K46). The availability of high purity matrix gas with validated concentrations of ammonia is a prerequisite for the preparation of static and dynamic reference mixtures.

WP 2 will develop and characterise laser based optical spectrometric standards. The applicability of open-path and extractive measurement techniques as optical transfer standards will be evaluated, and the developed instruments will be characterised from a metrological point of view. A transportable optical transfer standard, i.e. a spectrometer that is suitable for traceable measurement of ambient ammonia molar fraction will be developed, offering another alternative besides the application of highly accurate gas standards for the calibration and validation of instruments currently used in field measurements.

WP 3 will establish the transfer from high-accuracy standards to field applicable methods by applying characterised exposure chambers and field sites for validation and comparison experiments. With proficiency tests the performance of different instruments and measurement methods at ambient molar fractions (0.5 to 500 nmol/mol) under both real air and artificial conditions will be evaluated. As a result, guidance for the proper use of certified reference materials and sampling methods for field measurements will be provided.

Expected results and potential impact

The results of this JRP will enable NMIs to offer traceable and concordant calibration and measurement capabilities at the required molar fractions (20 to 500 nmol/mol NH_3 in air) to disseminate SI-traceable ammonia measurement results. Standards for the measurement of ammonia concentrations under ambient conditions, as well as validated field measurement methods will be provided.

The availability of a traceable calibration and measurement infrastructure is the basis for comparing measurement results across networks among various techniques and will allow standardising analytical techniques. The bases are accurate, stable and traceable standards and validated measurement methods as key starting points.

Validated high quality ammonia measurement data from air monitoring networks are vitally important for identifying changes due to implementations of environment abatement policies, minimising the believed uncertainties in current emissions inventories, and providing independent verifications of atmospheric model predictions.

All the JRP-Partners are closely linked to the stakeholders and to the end-users of this project, by being members or service providers of key environmental national or international monitoring networks and by participating in standardisation activities: CEN/TC264/WG11 Ambient air quality - Diffusive samplers for the determination of gases and vapours - Requirements and test methods and other Working Groups, ISO/TC146 Air Quality and ISO/TC158 Gas Analysis, or by collaborating with National Environmental Institutes. The impact of this project is ensured by the existing contacts and network of the JRP-Consortium members. This includes the provision of validated measurement tools to enable EU SMEs developing new monitoring technologies to deliver improved instrumentation to the market.

JRP start date and duration:	1st of June 2014, 36 months
JRP-Coordinator: Bernhard Niederhauser, METAS, Tel: +41 58 387 02 62, E-mail: bernhard.niederhauser@metas.ch JRP website address: in construction	
JRP-Partners: JRP-Partner 1: METAS, Switzerland JRP-Partner 2: BAM, Germany JRP-Partner 3: DFM, Denmark JRP-Partner 4: MIKES, Finland	 JRP-Partner 5: NPL, United Kingdom JRP-Partner 6: PTB, Germany JRP-Partner 7: UBA, Germany JRP-Partner 8: VSL, Netherlands
REG-Researcher (associated Home Organisation):	Christine Braban NERC, United Kingdom

The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union