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What metrology can do to improve the quality of your atmospheric ammonia measurements

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Measuring ammonia in ambient 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 to ensure reliable ammonia measurements, namely in applicable analytical technology, maximum allowed uncertainty, quality assurance and quality control (QC/QA) procedures, as well as in the infrastructure to attain metrological traceability, i.e. that the results of measurements are traceable to SI-units through an unbroken chain of calibrations.

In the framework of the European Metrology Research Programme (EMRP) project on the topic "Metrology for Ammonia in Ambient Air" (MetNH3), European national metrology institutes (NMI's) have joined to tackle the issue of generating SI-traceable reference material, i.e. generate reference gas mixtures containing known amount fractions of NH_3. This requires special infrastructure and analytical techniques:

Measurements of ambient ammonia are commonly carried out with diffusive samplers or by active sampling with denuders, but such techniques have not yet been extensively validated. Improvements in the metrological traceability may be achieved through the determination of NH_3 diffusive sampling rates using ammonia Primary Standard Gas Mixtures (PSMs), developed by gravimetry at the National Physical Laboratory NPL and a controlled atmosphere test facility in combination with on-line monitoring with a cavity ring-down spectrometer.

The Federal Institute of Metrology METAS has developed an infrastructure to generate SI-traceable NH_3 reference gas mixtures dynamically in the amount fraction range 0.5-500 nmol/mol (atmospheric concentrations) and with uncertainties U_{NH3} <3%. The infrastructure consists of a stationary as well as a mobile device for full flexibility for calibrations in the laboratory and in the field. Both devices apply the method of temperature and pressure dependant permeation of a pure substance through a membrane into a stream of pre-purified matrix gas and subsequent dilution to required amount fractions. All relevant parameters are fully traceable to SI-units. Extractive optical analysers can be connected directly to both, stationary and mobile systems for calibration. Moreover, the resulting gas mixture can also be pressurised into coated cylinders by cryo-filling. The mobile system as well as these cylinders can be applied for calibrations of optical instruments in other laboratories and in the field. In addition, an SI-traceable dilution system based on a cascade of critical orifices has been established to dilute NH_3 mixtures in the order of μmol/mol stored in cylinders. It is planned to apply this system to calibrate and re-sample gas mixtures in cylinders due to its very economical gas use.

Here we present insights into the development of said infrastructure and results performance tests. Moreover, we include results of the study on adsorption/desorption effects in dry as well as humidified matrix gas into the discussion on the generation of reference gas mixtures.

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