

State of the art stationary and mobile infrastructure for the dynamic generation and dilution of traceable reference gas mixtures of Ammonia at ambient air amount fractions

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Ammonia (NH_3) in the atmosphere is the major precursor for neutralising atmospheric acids and is thus affecting not only the long-range transport of sulphur dioxide and nitrogen oxides but also stabilises secondary particulate matter. These aerosols have negative impacts on air quality and human health. Moreover, they negatively affect terrestrial ecosystems after deposition.

NH_3 has been included in the air quality monitoring networks and emission reduction directives of European nations. Atmospheric concentrations are in the order of 0.5-500 nmol/mol. However, the lowest substance amount fraction of available certified reference material (CRM) is 10 $\mu\text{mol/mol}$. This due to the fact that adsorption on the walls of aluminium cylinders and desorption as pressure in the cylinder decreases cause substantial instabilities in the amount fractions of the gas mixtures.

Moreover, analytical techniques to be calibrated are very diverse and cause challenges for the production and application of CRM.

The Federal Institute of Metrology METAS has developed, partially in the framework of EMRP JRP ENV55 MetNH₃, an infrastructure to meet with the different requirements in order to generate SI-traceable NH_3 reference gas mixtures dynamically in the amount fraction range 0.5-500 nmol/mol and with uncertainties $U_{\text{NH}_3} < 3\%$. The infrastructure consists of a stationary as well as a mobile device for full flexibility in the application:

In the stationary system, a magnetic suspension balance monitors the specific temperature and pressure dependent mass loss over time of the pure substance in a permeation tube (here NH_3) by permeation through a membrane into a constant flow of carrier gas. Subsequently, this mixture is diluted with a system of thermal mass flow controllers in one or two consecutive steps to desired amount fractions.

The permeation tube with calibrated permeation rate (mass loss over time previously determined in the magnetic suspension balance) can be transferred into the temperature-regulated permeation chamber of a newly developed mobile reference gas generator (ReGaS1). In addition to the permeation chamber it consists of the same dilution system as afore mentioned, stationary system. All components are fully traceable to SI standards.

Considerable effort has been made to minimise adsorption on the gas-wetted stainless steel surfaces and thus to reduce stabilisation times by applying the SilcoNert2000[®] coating substance.

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 in other laboratories and in the field.

In addition, an SI traceable system based on a cascade of critical orifices has been established to dilute NH_3 mixtures in the order of $\mu\text{mol/mol}$ stored in cylinders for the participation in the international key-comparison CCQM K117. It is planned to establish this system to calibrate and re-sample gas cylinders due to its very economical gas use.

Here we present insights into the development of said infrastructure and results of the first 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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