



Validation of ammonia diffusive and active samplers in a controlled atmosphere test facility using traceable Primary Standard Gas Mixtures

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Intensive animal farming, the increased use of fertilizers, and certain industrial processes are believed to be responsible for the observed increases in the amount fraction of ammonia (NH₃) found in Europe. NH₃ contributes to eutrophication and acidification of land and freshwater, potentially leading to a loss of biodiversity and undesirable changes to the ecosystem. It also contributes to the formation of secondary particulate matter (PM) formation, which is associated with poor air quality and adverse health outcomes.

Measurements of ambient ammonia are principally carried out with low-cost diffusive samplers or by active sampling with denuders, with each method delivering time-integrated values over the monitoring period. However, such techniques have not yet been extensively validated. The goal of this work was to provide improvements in the metrological traceability through the determination of NH₃ diffusive sampling rates. Five different designs of commercial diffusive samplers (FSM Radiello radial sampler, Gradko diffusion tube, Gradko DIFRAM-400, Passam ammonia sampler, and CEH ALPHA sampler) were employed, together with a pumped denuder sampler (CEH DELTA denuder) for comparison.

All devices were simultaneously exposed for either 28 days or 14 days (dependent on sampler type) in a controlled atmosphere test facility (CATFAC) containing traceable amount fractions of humidified ammonia using new stable ammonia Primary Standard Gas Mixtures developed by gravimetry at NPL, under a wide range of conditions that are relevant to ambient monitoring. Online continuous monitoring of the ammonia test atmospheres was carried out by extractive sampling, employing a calibrated cavity ring-down spectrometer, which had been modified to account for cross interference by water vapour.

Each manufacturer extracted the captured ammonia on the exposed samplers in the form of ammonium (NH₄⁺) using their own accredited traceable wet chemical techniques, and then reported data based on their historical diffusive sampling rates. There was considerable variation in the results, which demonstrated the need for such validation work to be carried out. We report new measurements of the NH₃ sampling rates determined in the CATFAC, which can be applied to improve the reliability of measurements in the field.