



The determination of diffusive sampling rates to provide improved traceability for ambient ammonia measurements employing low cost passive sensors

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Ammonia (NH₃) contributes to eutrophication and acidification of land and freshwater, through the increased use of fertilizers, intensive animal farming and certain industrial processes, 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 human health outcomes.

Monitoring of ambient ammonia is 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 monitoring techniques have not yet been extensively validated because of the unavailability of stable calibration standards.

The goal of this work was to provide improvements to the metrological traceability of this technology through the determination of NH₃ diffusive sampling rates for a range of commercially available low cost passive sensors. This required the development of new stable ammonia Primary Standard Gas Mixtures (PSMs), prepared by gravimetry, and also a specialised controlled atmosphere test facility (CATFAC).

Traceable amount fractions of humidified NH₃ were introduced into the CATFAC under a wide range of conditions that are relevant to ambient monitoring in the field, and the sensors under test (both passive and active) were simultaneously exposed in the facility for either 28 days or 14 days (dependent on sampler type). Rapid online continuous monitoring of the ammonia test atmospheres was also carried out by extractive sampling, employing a calibrated cavity ring-down spectrometer, which had been modified to account for cross interference by water vapour.

After the tests, each manufacturer extracted the captured ammonia in their 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 a considerable variation in the reported results (expressed as either a positive or negative bias) when compared to each of the known amount fractions generated, which demonstrated the need for such validation work to be carried out. The new measurements of the NH₃ sampling rates determined here can be used to reduce inter sampler variability, and improve the reliability of measurements in the field.