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Development, characterization, and validation of an optical transfer standard for ammonia in air

Nils Lüttschwager (1), David Balslev-Harder (2), Daiana Leuenberger (3), Andrea Pogány (1), Olav Werhahn (1), Volker Ebert (1,4)

(1) Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany, (2) Danish Fundamental Metrology (DFM), Matematiktorvet 307, 2800 Kgs. Lyngby, Denmark, (3) Federal Institute of Metrology METAS, Lindenweg 50, 3003 Bern-Wabern, Switzerland, (4) Technische Universität Darmstadt, RSM, Jovanka-Bontschits-Straße 2, 64287 Darmstadt, Germany

Ammonia is an atmospheric trace gas that is predominantly emitted from anthropogenic agricultural activities. Since elevated levels of ammonia can have negative effects to human health as well as ecosystems, it is imperative to monitor and control ammonia emissions. This requires SI-traceable standards to calibrate ammonia monitoring instrumentation and to make measurements comparable. The lack of such standards became a pressing issue in recent years and the MetNH3 project (www.metnh3.eu) was initiated to fill the gap, pursuing different strategies. The work that we present was part of these endeavours and focusses on the development and application of an optical transfer standard for amount fraction measurements of ammonia in ambient air.
An optical transfer standard (OTS) offers an alternative to calibrations of air monitoring instrumentation by means of reference gas mixtures. With an OTS, absolute amount fraction results are derived by evaluating absorption spectra using a spectral model and pre-measured spectral properties of the analyte. In that way, the instrument can measure calibration gas-independent ("calibration-free") and, moreover, can itself serve as standard to calibrate air monitoring analyzers. Molecular spectral properties are the excellent, non-drifting point of reference of the OTS and form, together with traceable measurements of temperature and pressure, the basis for SI-traceable amount fraction measurements.
We developed an OTS based on a commercial cavity-ring-down spectrometer with a detection limit below 1 ppb (1 nmol/mol). A custom spectral data evaluation routine for absolute, calibration-free measurements, as well as measurements of spectral properties of ammonia with the focus on measurement uncertainty and traceability [1] are the fundaments of our OTS. Validation measurements were conducted using a SI-traceable ammonia reference gas generator over a period of several months. Here, we present an evaluation of the performance of our OTS from 1 ppb to 200 ppb. We found the results obtained with the OTS to be concordant to reference gas mixtures yielding amount fraction results with standard uncertainties of less than 3 %, for which an uncertainty budget is provided.
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References

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