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# $O_2^+$ as primary reagent ion in the PTR-MS instrument: detection of gas-phase ammonia

Michael Norman (1,2), **Armin** Wisthaler (1) , and Armin Hansel (1)

(1) Institute of Ion and Applied Physics, Innsbruck University, Austria, (2) Now at Environment and Health Administration, Stockholm City, Sweden, (armin.wisthaler@uibk.ac.at)

Ammonia ($NH_3$) is both emitted and taken up by plants and it is found to have a positive effect on plants at relatively moderate concentrations while it is harmful at high concentrations and $NH_3$ will thus have an impact on plant biology. There are, however, still uncertainties in the atmospheric $NH_3$ cycling including the biogenic primary exchange as well as the atmospheric fluxes. The uncertainties are mainly due to the lack of highly sensitive, accurate and fast analytical techniques.

We have developed a new fast and high sensitive analytical technique for ammonia. Oxygen ($O_2$) was used as a source gas in a conventional PTR-MS instrument to produce $O_2^+$ as chemical ionization (CI) reagent instead of $H_3O^+$. The use of $O_2^+$ as CI reagent allows for fast, highly sensitive and specific measurements of ammonia ($NH_3$) via the electron transfer reaction $O_2^+ + NH_3 \rightarrow NH_3^+ + O_2$. Instrument linearity was tested in the in the 2-to-2000 ppbv range. The $2\sigma$ detection limit was found to be $\sim$90 pptv for a 1s signal integration time at dry conditions, slightly deteriorating with increasing humidity. The time response, defined by a 1/e$^2$ decay in the calibration signal, ranged from 30s to 45s. The instrument was tested in the field within the frames of the NitroEurope project at the field site of Oensingen in Switzerland. The goal was to observe the ammonia exchange with a fertilized grass field. Excellent agreement was obtained in intercomparison measurements of atmospheric $NH_3$ with two other $NH_3$ sensors based on liquid chemistry. The PTR-MS instrument was also capable of detecting fast changes (<30 s) in ambient $NH_3$ concentrations.