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Developement and intercomparison of a new instrument for the sensitive detection of nitric acid (HNO3) in the atmosphere

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In the present study, a new simple instrument (LOPAP) for the detection of HNO3 is presented. In the instrument, HNO3 is sampled in a stripping coil in an external sampling unit, which can be placed directly in the atmosphere of interest. Caused by a very short inlet (1 cm) losses of HNO3 are minimised. Nitrate formed in the stripping solution is further converted into a highly absorbing azo-dye, which is detected in long path absorption in special Teflon tubes with a mini spectrometer. In the instrument two channels are used to correct for interferences against e.g. NO2, HONO and particle nitrate. The instrument has a time response of 2-6 min and a detection limit of 10-2 pptV, which is comparable to the most sensitive known instruments.

The instrument was validated against an ion chromatograph in the laboratory and against the FTIR technique in the EUPHORE smog chamber. Excellent agreement was observed with the ion chromatograph. However, significant lower concentrations were measured by the LOPAP instrument compared to the FTIR technique. Caused by the higher accuracy of the LOPAP instrument, this difference is explained by the significant uncertainty in the published cross sections of HNO3. During the smog chamber campaign also the interference against particle nitrate of ca. 4 % was quantified, which can be corrected for by the two channel design of the instrument. However, for N2O5 a quantitative uptake was observed in the first stripping coil, in accordance with the known physico-chemical behaviour of N2O5. Accordingly, the instrument can only quantify the sum of N(V) of HNO3 and N2O5 in the present configuration. For N2O5, good agreement was observed between the LOPAP and the FTIR.