



Measurements of Nitrous Acid by DOAS and Diffusion Denuders: A Comparison

Guest contribution

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Introduction and experimental setup

Measurements of the atmospheric mixing ratio of nitrous acid were made with a Differential Optical Absorption Spectrometer and a wet annular denuder at the IfT research station near Melpitz in eastern Germany from September 1997 till November 1997. The station lies in a rural area with grassland surroundings. A federal highway from Leipzig to Torgau passes 1 km to the north of the site.

The DOAS system is based on a coaxial Newton-type telescope for both transmitting and receiving beams from a Xenon lamp and a retroreflector array at the end of the light path. The length of the light path is 2×1975 m. The height above ground is 1.5 m at the telescope and 8 m at the reflector. In the receiving unit the light is focused on to an optical fibre which guides the light to the entrance slit of a grating spectrograph where it is detected by a photo diode array. The spectrum is measured in the wavelength range 300 to 380 nm where HNO_2 shows significant absorption bands. In this spectral range it is also possible to measure the mixing ratios of O_3 , NO_2 and SO_2 . The time resolution for a set of these trace gas measurements is between 7 and 15 minutes. The detection limit for HNO_2 is 100 ppt and the precision of the DOAS HNO_2 measurements is about ± 60 ppt.

The wet annular denuder is an automated diffusion-based sampler (Wyers *et al.*, 1993, Oms *et al.*, 1996). The annular space of this denuder contains a small volume (15–20 ml) of a 0.001 M sodium carbonate absorption solution. During sampling of ambient air the denuder is rotated around its axis, creating

a thin layer of solution on the walls of the annular space. HNO_2 is absorbed in this solution. After 60 minute sampling the denuder is tilted slightly, the solution is pumped in to a multi-sampler, and the denuder is automatically refilled with fresh absorption solution. The samples are analysed off-line by ion chromatography of nitrite with an electrochemical detector. The detection limit is $0.1 \mu\text{g}/\text{m}^3$ (51 ppt). HNO_2 measurements with Na_2CO_3 -coated denuders are subject to severe interference from NO_2 , SO_2 and possibly PAN in areas with high NO_2 and SO_2 concentrations (Febo *et al.*, 1993). The NO_2 and SO_2 mixing ratios were below 20 ppb and 60 ppb respectively at the denuder measuring point during the campaign. Subsequently the HNO_2 concentrations may have suffered from an artefact production of nitrite from sometimes higher SO_2 mixing ratios but not from NO_2 concentrations. The comparison of DOAS and denuder data on nitrous acid in the same air is mainly a test of reliability of the denuder data because there is no interference from artefact production of nitrite in the DOAS measurements. Nevertheless there an uncertainty arises from the different measurement volumes. The denuder is a point sensor at 4.5 m height and the DOAS integrates over the light path of 1975 m. Depending on the meteorological conditions vertical HNO_2 gradients up to 200 ppt between 0.8 m and 4.5 m were measured (Spindler *et al.*, 1998).

Comparison of DOAS and denuder HNO_2 data

Low HNO_2 mixing ratios, up to 1.2 ppb, were measured during the campaign. The diurnal variation of HNO_2 data from DOAS shows the expected behaviour with higher values during night and the early morning, and low values during the day (see Fig. 1). HNO_2 is of particular importance in atmospheric chemistry, because the photolysis of HNO_2 significantly enhances photo-oxidation processes early in the morning due to rapid production of OH radicals. A relatively good agreement with the denuder HNO_2 data was observed during the whole measurement period, especially at night. During the day, at very low HNO_2 concentrations a discrepancy is observed with frequent higher values of the denuder data (see Fig. 2).

The diurnal variation of the HNO_2 concentration on September 24th and 25th, 1997 is an example for good agreement at night and day on 24th as well for up to 400 ppt higher denuder measurements after noon of the 25th.

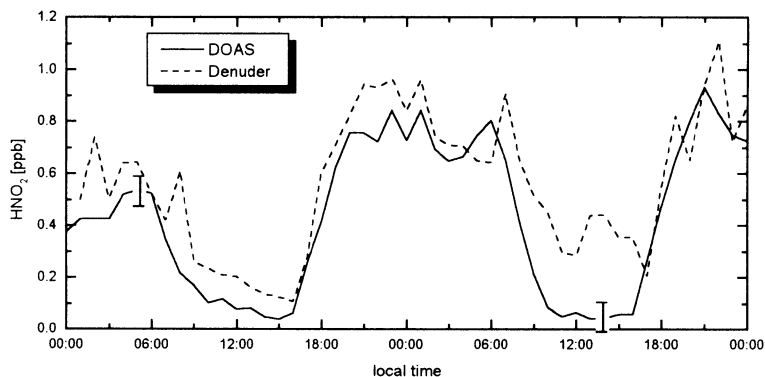


Fig. 1: Diurnal variation of hourly HNO_2 mixing ratio from DOAS and wet annular denuder measurements at the IfT-research station near Melpitz on September 24th and 25th, 1997. The error bars of the DOAS data correspond to the ± 60 ppt precision of the instrument.

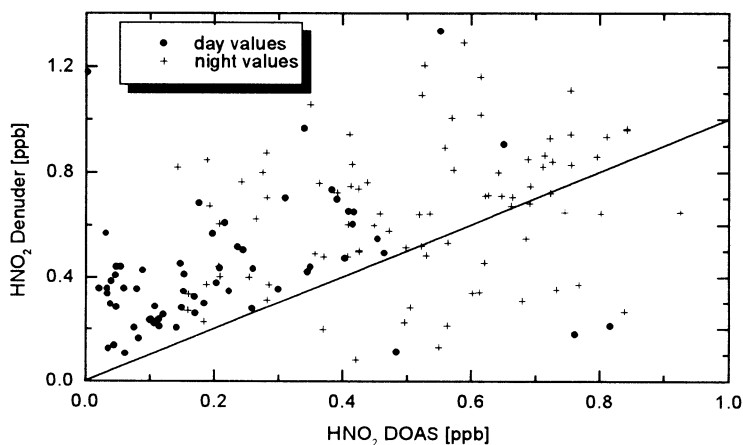


Fig. 2: Scatterplot of hourly HNO_2 concentration from DOAS and denuder measurements at the IfT research station near Melpitz. The line indicates the HNO_2 ratio equal one.

The reason for this difference at relative high HNO_2 denuder values is unclear. At this time there were low NO_2 (5 ppb) and SO_2 (2 ppb) mixing ratios, a relative humidity of 40 % and a high solar radiation level.

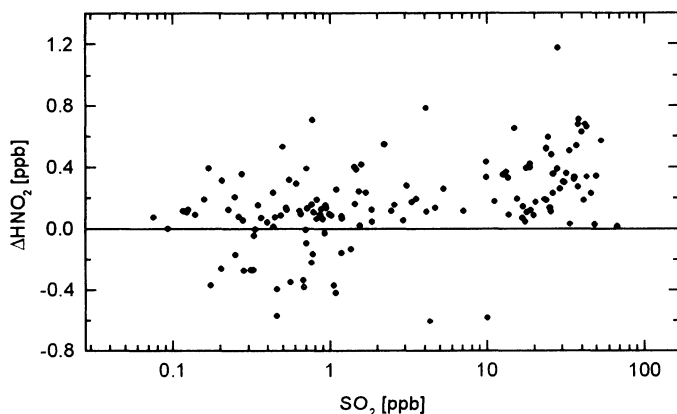


Fig. 3: Scatterplot of hourly HNO_2 concentration difference $\Delta\text{HNO}_2 = \text{HNO}_{2 \text{ denuder}} - \text{HNO}_{2 \text{ DOAS}}$ vs. SO_2 concentration at the IfT-research station near Melpitz.

The HNO_2 difference in Fig. 3 reveals, that for SO_2 values greater than about 20 ppb the denuder has likely a cross sensitivity to SO_2 . There may be also an influence of high relative humidity (see Fig. 4). The DOAS system measures only gas phase HNO_2 . If the relative humidity is higher than approximately 95 % the denuder HNO_2 data are possibly the sum of gas phase and droplet phase of HNO_2 .

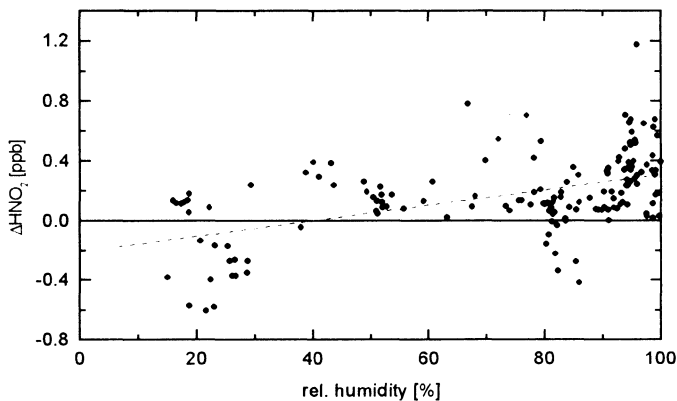


Fig. 4: Scatterplot of hourly HNO_2 concentration difference $\Delta\text{HNO}_2 = \text{HNO}_{2 \text{ denuder}} - \text{HNO}_{2 \text{ DOAS}}$ vs. relative humidity at the IfT-research station near Melpitz. The dashed line indicates a possible dependence of ΔHNO_2 (linear regression for the scatter ΔHNO_2).

Conclusions

The comparison of DOAS and denuder data on nitrous acid shows that average day and night values measured by denuder are 210 ppt and 150 ppt respectively higher than DOAS. The reasons are in many cases unclear. Parts of these differences are explained by meteorological conditions, by the different measurement volumes and cross sensitivity to other trace gases. For SO₂ values greater than 20 ppb the denuder has likely a cross sensitivity to SO₂. There is probably an influence of high relative humidity on the denuder data.

References

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