Nitrous and nitric acid measurements during the INTERCOMP2000 campaign in Melpitz

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Abstract

Measurements were performed at the research site Melpitz (87 m a.s.l., 51 °32′ N and 12°54′E), 41 km north east of the Leipzig conurbation in spring 2000 to measure atmospheric nitrous and nitric acid concentrations, to compare available methods for these acids, and to investigate the distribution of particulate nitrate vs gaseous HNO_3. Two different wet denuder methods were run side by side during the experiment: a wet effluent diffusion denuder (WEDD) and a rotating wet annular denuder (RWAN). The concentrations obtained for HONO with both methods agreed very well. At low relative humidity (RH) values, a good agreement was also observed for HNO_3 between the two methods. However, significant differences were observed at RH values >80%. Both methods allow the measurement of atmospheric HONO and HNO_3 with a fine time resolution even at very low concentration levels. Measurable daytime values for nitrous acid were observed and there were indications for heterogeneous formation. Storage of HONO or nitrite, respectively, on wet surfaces can be a source for observed daytime HONO.
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Keywords: HONO; Nitric acid; Denuder sampling; Aerosol; Heterogeneous chemistry

1. Introduction

After the emissions of sulphur dioxide and particulate matter have drastically decreased, the relative importance of nitrogen oxides as atmospheric pollutants has increased markedly (e.g., Brüggemann and Spindler, 1999; Carslaw and Carslaw, 2001). Nitric acid is now often the principal acidification input by dry deposition into European and North American ecosystems (e.g., Nielsen et al., 1996; Spindler et al., 1997). The important role of HONO in the oxidant chemistry of the polluted as well as the remote atmosphere has been addressed by many authors (e.g., Lammel and Perner, 1988; Harrison et al., 1996; Saliba et al., 2000; Reisinger, 2000; Spindler et al., 2003). The origin of atmospheric HONO is presently not completely understood. Observed atmospheric HONO concentrations are too high to be accounted for by homogeneous formation and direct emission from combustion processes. Extensive investigations in motor vehicle exhaust at a road traffic tunnel (Kurtenbach et al., 2001) showed that the mean HONO/NO_x ratio is $\sim (8 \pm 1) \times 10^{-3}$.

It is now accepted that HONO will be produced via a heterogeneous pathway from NO_2, whereas NO is not involved (Febo, 1999). This reaction can take place on wetted surfaces, either earth, ground, aerosol particles or hydrometeors:

$$2NO_2 + H_2O \rightarrow HONO + HNO_3. \tag{1}$$

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In the morning hours, when OH production rates from other sources (e.g., photolysis of O_3 and HCHO) are still low, the photolysis of HONO, accumulated from overnight heterogeneous production, can be the principal OH source (Alicke et al., 2002):

$$HONO + hv(300\,nm < \lambda < 405\,nm) \rightarrow NO + OH. \qquad (2)$$

Several authors (e.g., Kleffmann et al., 1998; Febo, 1999; Georgi and Warneck, 1999) have previously discussed possible formation pathways of HONO. For example, unexpectedly daytime HONO levels of more than $400\,\mu g\,m^{-3}$ were found in the polluted urban area of Rome, indicating that a strong source for heterogeneous formation of HONO exists also during day time (Wiesen et al., 2002).

Thus, research concerning the atmospheric budget of reactive nitrogen compounds and developments of sampling and analytical methods for them are of significant interest. A variety of analytical methods has been developed for both HNO_3 and HONO; an overview is given by Genfa et al. (2003).

The following methods for the measurement of atmospheric HONO have been described: differential optical absorption spectroscopy (DOAS) (e.g., Perner and Platt, 1979; Alicke et al., 2002); base-coated dry annular denuder, elution and wet chemical analysis (e.g., Sjödin and Ferm, 1985; Febo et al., 1989, 1996); wet denuder coupled with ion chromatography (e.g., Simon and Dasgupta, 1993; Oms et al., 1996; Acker et al., 2001); scrubbing in mixing coils, followed by derivatisation and determination of the complex by high performance liquid chromatography (HPLC; Zhou et al., 1999) or long path absorption spectroscopy (Heland et al., 2001); fourier transform infra red spectroscopy (Tuazon et al., 1980).

The use of denuder systems allows the diffusion-based collection of trace gases without interference from their particulate counterparts. Several denuder designs are described in the literature (e.g., Possanzini et al., 1983; Wyers et al., 1993; Neftel et al., 1996; Matsumoto and Okita, 1998; Zellweger et al., 1999).

In the present experiment, the wet denuder technique was used to determine ambient HONO and HNO_3. Continuously wetted denuders are especially attractive because the collection surface is constantly renewed and a solution with the corresponding analyte ions is directly obtained. This offers the possibility to perform the analysis continuously or semi-continuously on-line with a suitable analyzer/detector. Among others the wet effluent diffusion denuder technique is major reviewed in Dasgupta (2002). The application of the rotating wet annular denuder to the analysis of atmospheric gaseous components is described among others in Slanina et al. (1992).

2. Experimental

The field intercomparison experiment INTER-COMP2000 was held at the Institute for Tropospheric Research (IfT) research station Melpitz (4–14 April 2000) in the downstream plume of the Leipzig conurbation. The measurement site is located near the village Melpitz (41 km Northeast from Leipzig city center) in the vicinity of the city Torgau in the river Elbe valley. The site is placed on a flat 100-year-old meadow surrounded by grass/agricultural land. For further information about the Melpitz site see Spindler et al., (1999, 2001).

For the INTERCOMP experiment meteorological periods were derived from back trajectories (Müller et al., 2004). Precipitation events with more than 0.5 mm/day registered only during three days (11–13 April). Concentrations for NO and NO_2 ranged from of 0.1 to 6 and 1 to $18\,\mu g\,m^{-3}$, respectively, during the study. For SO_2 the mean level was $< 2\,\mu g\,m^{-3}$, the ozone maximum was $< 100\,\mu g\,m^{-3}$. For detailed meteorological data and trace gas concentrations, see Müller et al. (2004).

Two different fully automated wet denuder methods were run side by side during the experiment, with inlets at comparable heights ($\sim 3\,m$ above ground) as automated systems for gaseous species. The Brandenburg Technical University Cottbus (BTU) team operated a parallel plate WEDD installed in a Caravan with an air conditioned environment and a measurement interval of 15 min. The approach for the WEDD most relevant to the present work was adopted from Simon and Dasgupta (1993), Zellweger et al. (1999) and Löflund et al. (2001). A thin homogeneous water film (about $0.5\,ml\,min^{-1}$ pure deionized water), flows down by gravity. The solution containing the scavenged gases is collected by a ring-shaped frit before it is pumped peristaltically through one of the two pre-concentration columns (TAC-LP1) that are connected with a high-pressure 8-port valve. Alternately, one of these pre-columns is used for pre-concentration while the other is eluted by the eluent ($1.8\,mM\ Na_2CO_3/1.7\,mM\ NaHCO_3$) for ion chromatographic analysis (IC, DIONEX DX500 with conductivity detection after suppression, AS4A/AG4A 4 mm columns), see Fig. 1. The airflow through the denuder is $101\,min^{-1}$ (using mass flow controller) and the limit of quantification is $15\,ng\,m^{-3}$ of HONO and HNO_3, respectively. In the WEDD, the sample air residence time is very short ($< 0.5\,s$) and the solution residence time is short as well ($< 2\,min$), interferences by NO_2 and SO_2 will not be expected. The use of pre-concentration columns necessitate the use of water as the denuder liquid, the use of carbonate in the denuder liquid (as proposed by Zellweger et al., 1999) leads to incomplete capture of desired analyte ions during pre-concentration. Detailed descriptions of the BTU WEDD are given in Acker et al. (2001, 2004).

The IfT operated a RWAN system (following Keuken et al., 1988; Slanina et al., 1992) installed in a box on a platform (Fig. 2). This instrument performed one analysis every hour (45 min sampling using 0.0005 M K_2CO_3 as the denuder liquid and 15 min for rinsing and reloading). In the RWAN, the sample air residence time is very short (0.1–0.2 s), airflow through the denuder is
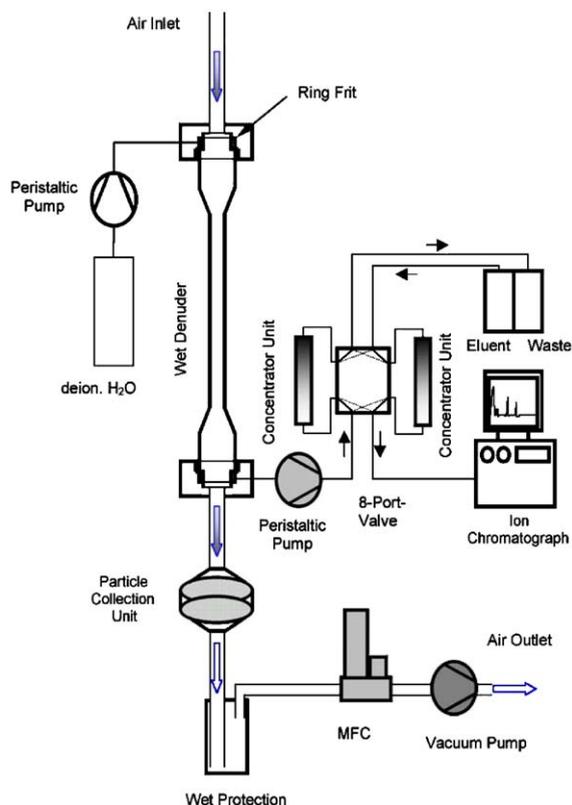
Fig. 1. Schematic diagram of the BTU-Cottbus wet-denuder/ion chromatography (WEDD-IC) system. During the INTER-COMP2000 campaign the WEDD was not combined with a steam jet aerosol collector. The particle collection unit in this figure contains a Teflon filter for saving the following equipment.

$30 \, l \, min^{-1}$; the solution residence time is 45 min. The quasi-hourly collected stripping solutions were analysed off-line in the IfT laboratory using IC. The nitrite component was analysed by IC (Metrohm) and detected electrochemically (EC2000, Thermo Separation Products, USA) using an Ag working electrode and an Ag/AgCl reference electrode. The samples were prefiltered with $0.45 \, \mu m$ single use filter (polyester membrane, Pall Gelman). This denuder method was previously used for measurements of HONO at this site (Spindler et al., 1998). In addition, a steam jet aerosol collector (SJAC, Khlystov et al., 1995) was operated by the IfT for measuring the soluble inorganic nitrate of the particle phase (also compare Fig. 2). This separately operated SJAC (airflow through the system is $30 \, l \, min^{-1}$) was connected with another denuder unit for separation of gaseous species.

3. Results

During the campaign the air masses reaching the field site came mostly from northern directions, bearing relatively unpolluted air. Fig. 3 shows the WEDD HONO and HNO_3 data (given as 15 min averages) and NO_2 (1 h averages). Periods with a RH > 80% are marked. The aerosol mass concentration obtained by a PM_{10} high-volume sampler is also presented as a general indicator of the pollution level. The maxima in HNO_3 concentrations were generally observed in the day time and at lower RH levels; the maximum during the study period was $1.7 \, \mu g \, m^{-3}$ HNO_3. At high RH levels, the liquid water associated with aerosol particles increases rapidly and gaseous HNO_3 partitions to the liquid phase due to its high solubility.

Concentrations of HONO are closely connected with photolysis during the day (see Fig. 5) and vertical mixing processes. Other investigations (Febo, 1999) have shown that the diurnal variation of HONO is well correlated to the diurnal variation of Radon. The variation in the natural radioactivity reflects the stability of the boundary layer. The morning break up of the mixing layer
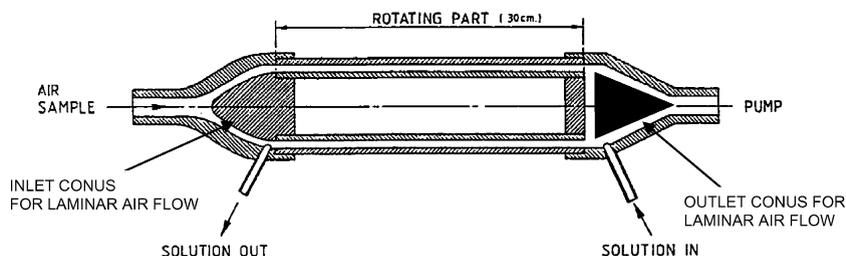
Fig. 2. Construction of the denuder in the rotating wet annular denuder system of the IfT and the steam jet aerosol collector (following Keuken et al. 1988). The black triangle marks the outlet cone in the original drawn (Slanina et al., 1992) that is available only in the used steam jet aerosol collector.
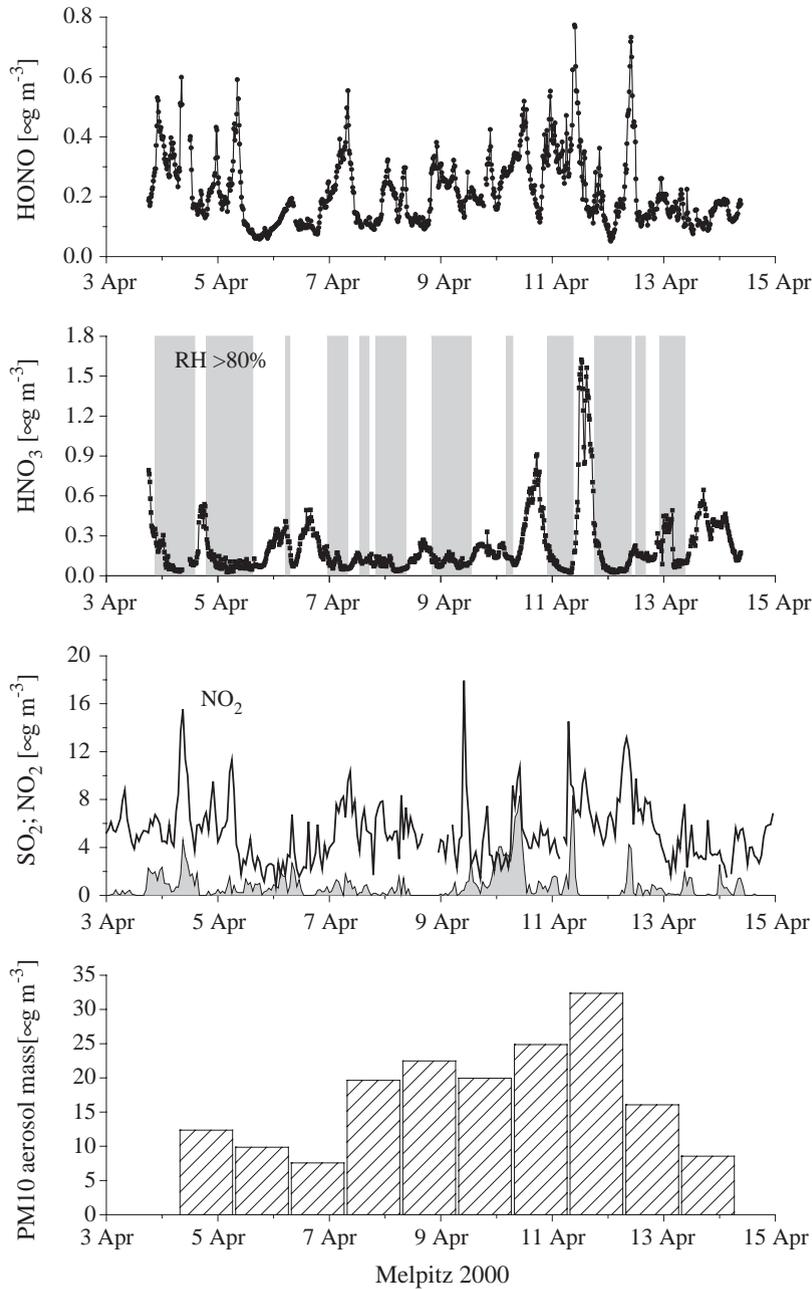
Fig. 3. Time series of trace components measured during the field campaign in Melpitz. HONO and HNO₃ data from WEDD. Periods with a relative humidity (RH) > 80% are given as grey areas in the second diagram.

causes dilution of HONO-rich air at lower levels by entrainment of fresh air from above the boundary layer. In the present study, daytime HONO levels were ~0.2 µg m⁻³, heterogeneous formation and accumulation processes during the night led to maximum values in the morning hours (typically between 07:00 and 10:00 Central European Summer Time (CEST)) up to 0.8 µg m⁻³, before photolysis caused a significant de-

crease, see also Fig. 5. After 20:00 in the evening, HONO concentration started to increase again. This behaviour is in agreement with earlier investigations at this site in summer 1995 (Spindler et al., 1998).

The HONO concentrations were positively correlated with those of NO₂, but with less than 0.2 if all data (day and night) are used; a separation of the data into sunlight and darkness hours did not improve the

correlations. But in few cases (e.g., on 6/7 and 11/12 April) during nighttime/morning hours a strong correlation between HONO and its precursor were found, see Figs. 4 and 5. The best fits were obtainend for concentrations measured between 23:00 and 08:00 CEST, although the HONO maximum was observed between 08:00 and 11:00 CEST (open symbols in Fig. 4). This may suggest that some other physical and chemical factors rather than straightforward NO_2–HONO reactions were controlling the temporal HONO distribution, common factors like transport and mixing processes, wet scavenging by rain and dry deposition while dew
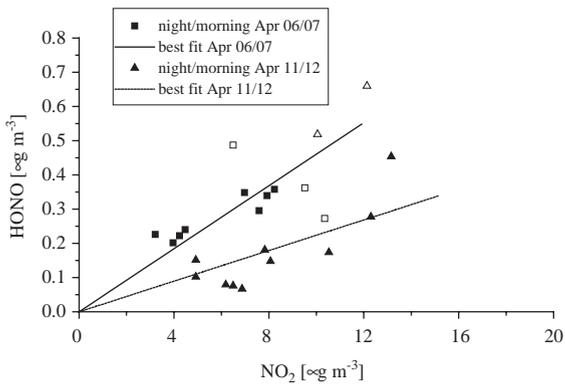
Fig. 4. Correlation of HONO (WEDD) to NO_2 for the 06/07 (23:00–10:00 CEST) and 11/12 (23:00–11:00 CEST) April 2000. The best-fits (the points shown as open symbols (late morning hours) are not included), are given for April 6/7: $y = 0.046x$; $r^2 = 0.87$; and for April 11/12: $y = 0.0224x$; $r^2 = 0.71$.
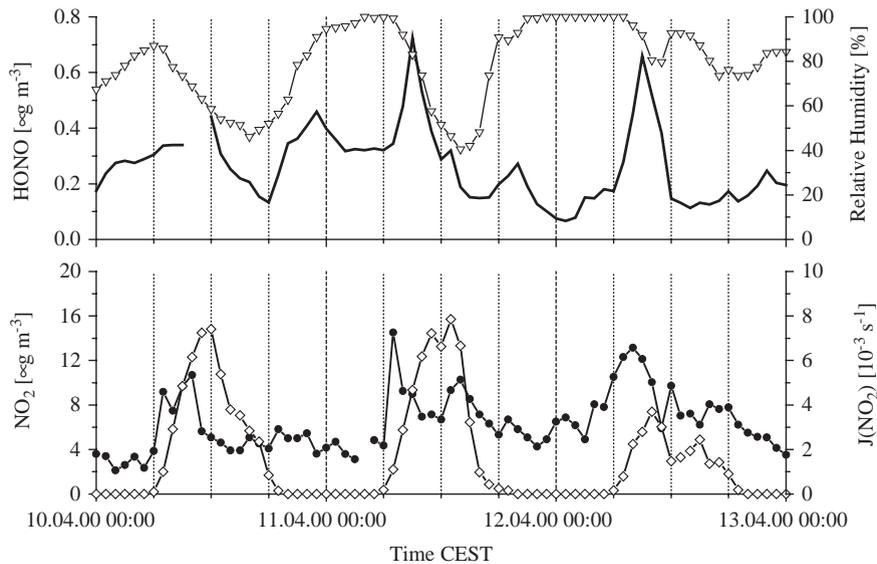
occurrence at ground. Moreover, we can assume that the heterogeneous HONO formation is occurring effective also at daytime. Unexpected (from the photostationary state) high mixing ratios of 0.2–0.8 $\mu g\,m^{-3}$ were found in the daytime in urban (e.g., Febo, 1999; Wiesen et al., 2002) as well in rural regions (e.g., Zhou et al., 2002).

Fig. 5 displays the diurnal variation of HONO, relative humidity, NO_2 and photolysis frequency of NO_2 (from which J(HONO) can be calculated, see Alicke et al., 2003) at the field site Melpitz for the period 10–12 April 2000. Diurnal patterns of HONO and relative humidity suggest that the ground and vegetation surfaces were sinks for HONO in the boundary layer when dew droplets were formed at night and that the subsequent release of trapped nitrous acid/nitrite from the surfaces acted as a strong HONO source in the morning hours as the dew droplets evaporated, refer also Zhou et al. (2002). Nitrite concentrations found in cloud and fog water (e.g., Bächmann et al., 1989; Fuzzi, 1995; Lammel and Metzig, 1998; Acker et al., 2002) support this idea.

The HONO/NO_2 ratio ranged from 0.01 to 0.15, averaging 0.046 ± 0.026 over this study. However, the highest HONO/NO_2 ratios were observed on 10 and 11 April when the aerosol concentration was also the highest (continental influenced air masses from eastern Europe reached the site), but also in the morning hours of 7 April under hazy conditions, see Figs. 3 and 4. This constitutes indirect evidence for the formation of HONO also on wet aerosol/fog droplets, although the ground surface will be the main reaction surface. As has been recently mentioned, the HONO/NO_2 primary ratio

Fig. 5. Diurnal variation of HONO (WEDD, solid line, upper panel), relative humidity (triangles, upper panel), along with concentration of NO_2 (circles, lower panel) and photolysis frequency of NO_2 (open diamonds, lower panel) at the field site Melpitz from 10 to 12 April , 2000.

from an internal combustion engine source is much lower (0.008, Kurtenbach et al., 2001).

Fig. 6 shows the results of the quasi-simultaneous HONO measurements: an excellent agreement between both wet denuder methods is observed. Excluding the first hours of the intercomparison (4 April) and a period with light rain events on 12/13 April the two methods are not statistically distinguishable at 95% confidence level, see Fig. 7. For the WEDD deionized water acts as denuder liquid for HONO (necessary to avoid incomplete capture of desired analyte ions during preconcentration steps), for the RWAN 0.0005 M K_2CO_3 is used as the denuder liquid (assuming high collection efficiency for HONO at pH > 10). The formation of artifact nitrous acid (known for using dry annular denuders with basic coatings) can also be a problem in the case of using carbonate solution as scrubbing reagent. Based on the procedure decribed in Spindler et al. (2003), the nitrous acid artefact (e.g., heterogeneous interaction of NO_2 and H_2O; aqueous phase reaction of NO_2 and SO_2) for the RWAN has been estimated with $\sim$30 ng m^{-3}. But a correction of the RWAN HONO concentrations by this value did not change the correlation with the WEDD data significantly ($y = 0.923x$; $r^2 = 0.62$), compared to the function obtained with the original RWAN data, see Fig. 7. It seems, that this artifact formation has not been a problem in this intercomparison, notwithstanding the use of 0.0005 M carbonate solutions.
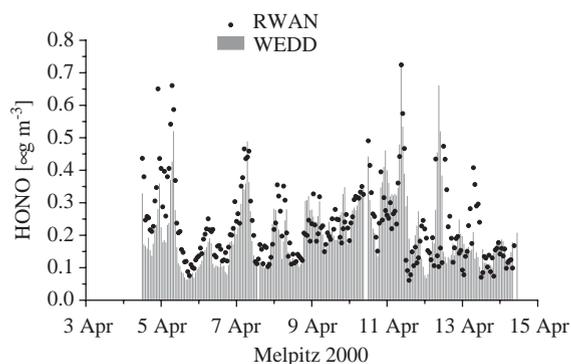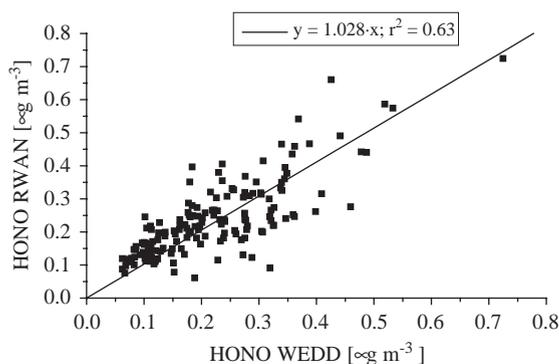
Genfa et al. (2003) reported that during the 1999 Atlanta Supersite field study, two similar wet denuder measurements were made with a parallel plate WEDD and a RWAN for HONO and HNO_3. In that study, the respective data were sometimes very well correlated but at other times there were found large discrepancies. Between the two analytes, not only the HONO data between the two systems were better correlated, the slope of a linear plot of the WEDD vs RWAN data was indistinguishable from unity. The HNO_3 data between the two instruments were less well correlated and the RWAN data were higher with the best fit slope being 1.45. Somewhat analogous results are obtained in the present study as shown in detail later.

Genfa et al. (2003) suggested simultaneous spectroscopic and denuder based measurements to find out measurement discrepancies. This was in fact carried out for HONO in the interim period during the NITROCAT field campaign in Rome in May/June 2001. Three different measurement techniques were used for a period over 3 weeks at different sites: differential optical absorption spectroscopy (DOAS, Institute for Environmental Physics, Heidelberg University), the WEDD system (BTU) and a dual channel DNPH derivatisation/HPLC technique (Institute for Atmospheric Pollution, CNR, Italy). The excellent agreement in the structure and under selected meteorological conditions in the concentration levels during both day and night time between the three techniques has been discussed in detail in Wiesen et al. (2002). Although in using wet chemical techniques interferences (wet surface reactions with NO_2 and/or SO_2, in the scrubbing technique also scavenging of aerosol particles) could not be excluded completely, the DOAS quite possibly sees a different sample (integrated value over few km at a higher altitude), and the campaign was not an intercomparison study, the NITROCAT data give a positive impulse in the quality assurance discussion for available atmospheric nitrous acid measurements. Spectroscopic methods are advantageous in detecting reactive species, and in the last years many efforts were done in optimizing the DOAS technique. Nevertheless, high costs, a complex data evaluation, and/or the interest in simultaneous measurements of HNO_3 or aerosol components promote the development of sensitive wet chemical methods.

In Fig. 8 the results of the simultaneous HNO_3 measurements using the different wet denuder technique (WEDD, RWAN) are presented. Nitric acid is absorbed on virtually every surface and hence our inlet systems are short and high sampling rates are preferred for this reason, here significantly below 0.5 s. Under dry and

Fig. 6. Intercomparison of two different wet-denuder methods for the measurement of HONO (1 h averages, $n = 234$).

Fig. 7. HONO (WEDD) vs. HONO (RWAN) data from 05 to 12 April, 2000 (1 h averages, $n = 175$).
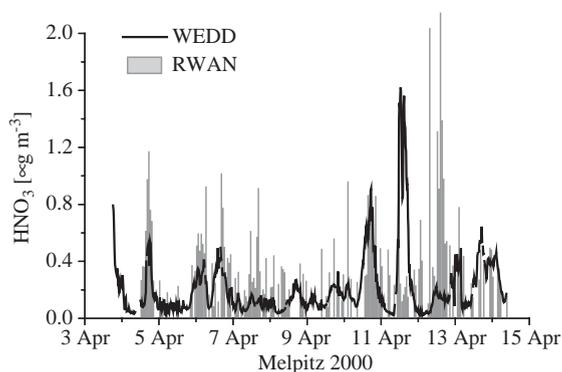
Fig. 8. Intercomparison of two different wet-denuder methods for the measurement of HNO_3 (1 h averages).

Fig. 9. Aerosol nitrate concentrations during the field experiment measured as 24 h mean by a PM10 high volume sampler and with hourly time resolution by steam jet aerosol collector in comparison to the gaseous HNO_3 concentration (WEDD).

sunny weather conditions (see Fig. 3 for RH information), the agreement was good; for example, both methods measured a maximum value of $\sim 0.8\,\mu g\,m^{-3}$ on 10 April. However, the data also showed significant disagreements, especially at high RH values. At high RH levels, the liquid water content associated with the aerosol phase increases rapidly and gaseous HNO_3 is largely transferred to this aqueous phase. The uptake of water by the aerosol also increases the mean particle size and increases the possibility of particle deposition. Unlike the WEDD (Simon and Dasgupta, 1993) the particle deposition characteristics of a RWAN has never been reported. The fact that the RWAN uses a thick film of liquid that sloshes around during the rotation can cause turbulence in the boundary layer leading to particle deposition.

Additionally the RWAN system is often used with only the entrance cone without any exit cone at the denuder outlet if a particle collection system is not used after the RWAN (like in this study, see Fig. 2). This can promote particle deposition as well, compare Wyers et al. (1993). This is particularly important in the present case because the particles contained up to hundred times more nitrate per unit air volume than the nitrate present as gaseous HNO_3; see Fig. 9. This finding strongly indicates that during periods of high RH when the mean aerosol size is higher, the RWAN has collected not only nitric acid from the gas phase but also some nitrate particles. Because the NH_3-concentration is in a level between 2 and $7\,\mu g\,m^{-3}$ there is a hint for NH_4NO_3 particle mass formation from free HNO_3, especially on the 11th of April when the HNO_3 concentration during midday is elevated. The aerosol nitrate data in Fig. 9 were derived from daily PM_{10} measurements (by Digitel high volume sampler) as well as from steam jet measurements. The latter data have a time resolution of 1 h and document the high fluctuation in aerosol composition. Aerosol nitrate measurements during INTERCOMP2000 are discussed in more detail in Schaap et al. (2004).
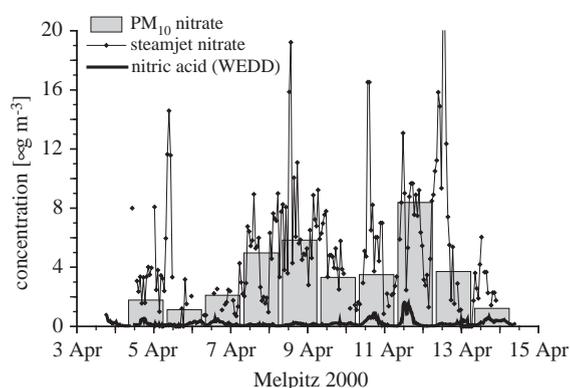
While aerosol nitrite was not measured during the INTERCOMP2000 campaign, the BTU WEDD system was subsequently extended (after this Melpitz campaign) by a steam jet chamber to collect and measure various aerosol constituent concentrations. There are several types of steam jet collectors described in the literature (e.g., Simon and Dasgupta, 1995; Khlystov et al., 1995 (as used in INTERCOMP2000 for nitrate); Löflund et al., 2001; Weber et al., 2001). We adopted ideas from most of these works and designed a system as described in Acker et al. (2004). Investigations at a suburban site near Marseille during the ESCOMPTE campaign in summer 2001 using this WEDD—steam based collector—IC combination have shown, that most of the nitrite (70–80%) is present as HONO in the gas phase. The amount of aerosol nitrite found (20–30% of the total) also indicated that apart from a moist ground, wet aerosols have to be taken into consideration as a surface for the heterogeneous formation of HONO.

4. Conclusions

The wet denuder technique was found to be suitable for detection of atmospheric concentrations of nitrous and nitric acid with a high time resolution and a high detection sensitivity. The present intercomparison study showed good agreement between the two different wet denuder techniques for the measurement of HONO ($r^2 = 0.63$). The concentrations of HONO were positive correlated with those of NO_2. The $HONO/NO_2$ ratio varied in a wide range between 0.01 and 0.15. On an average a ratio of 0.046 ± 0.026 was observed, which is much higher than the value known for direct emission from combustion sources. Heterogeneous formation on the ground and the surface of wet aerosols and

accumulation led to the observed maximum HONO (up to $800\,ng\,m^{-3}$) in the morning hours. Gas phase HNO_3 concentrations were mostly low because weather situations with high RH generally prevailed. Aerosol phase nitrate was up to a 100 times higher than gaseous HNO_3.

Acknowledgements

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