

LOPAP TECHNIQUE FOR NITROUS ACID (HONO) MEASUREMENT IN THE ATMOSPHERE

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KEY WORDS: nitrous acid, LOPAP technique, atmospheric measurements

INTRODUCTION

Despite its importance in atmospheric chemistry, nitrous acid formation is not completely understood at present. While it has accepted that nitrous acid formation takes place by heterogeneous reactions, it is not clear whether it is produced on the surface of atmospheric aerosols or on the ground. In addition, the atmospheric oxidation capacity owing to nitrous acid photolysis during the day and the conditions can not be quantified because field instruments are not sufficiently sensitive enough to measure the day time concentrations of nitrous acid.

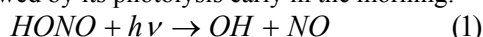
The aim of the paper is to present a sensitive and compact instrument for HONO measurements in the atmosphere, which was built up at Wuppertal University, Germany. This instrument is aimed to overcome the known problems with current HONO measurement techniques. It represents a continuously working instrument for ambient air measurements in the troposphere or for measurements of higher concentrations (e.g. smog chambers, exhaust gases and indoor environments). The validation of the instrument was performed in the laboratory using ion chromatography (IC) and with a DOAS instrument (**D**ifferential **O**ptical **A**bsorption **S**pectrometer). The deviations were well within the errors of the measurements.

Nitrous acid HONO is a source of the most important daytime radical: the hydroxyl radical. The OH radical is one of the key species in photochemical cycles responsible for ozone formation, which can lead to the called “photochemical smog” in polluted regions. To understand the mechanisms that lead to this ozone-smog, we need

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to know the sources of the OH radicals. One of the main OH sources is the formation of nitrous acid HONO, followed by its photolysis early in the morning:



Although this OH source mechanism has been known for decades (Jonson, Graham, 1974, Nash, 1974, after Alicke, 2000) many questions about its importance are still open. Figure 1 gives the chemistry of HONO. The formation of nitrous acid takes place via different types of reactions (Alicke, 2000): gas-phase reactions (homogeneous reaction), formation in a thin layer of water on a surface (heterogeneous reaction), direct formation on a surface in the presence of water and direct emissions.

The mechanisms by which HONO is formed in the atmosphere are not well established (Rohrer et al., 2005, Lammel and Cape, 1996):

a) HONO can be formed in a homogeneous reaction similar to (1):



but the reaction is insignificant during the night, because the OH concentration is too low and during the day the OH concentration is currently unknown (M - represents a third molecule for the three body collision, ex., oxygen O₂ or nitrogen N₂). Since this reaction removes OH, subsequent photolysis does not represent a net source of radicals.

b) It is believed that HONO is mainly formed by heterogeneous dark reaction on surfaces in the presence of water and NO₂ (Finlayson-Pitts et al. 2003):

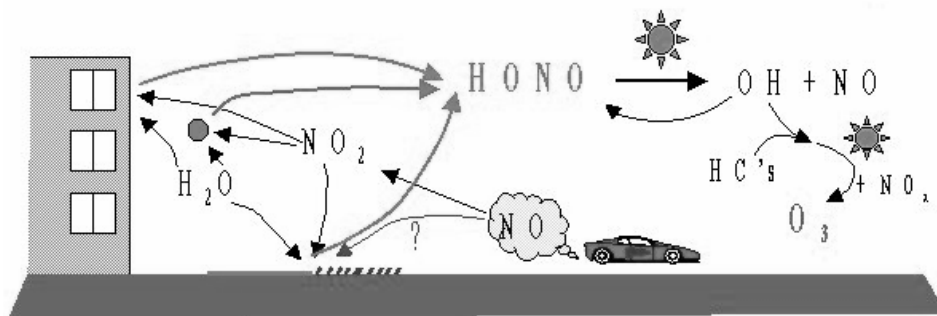
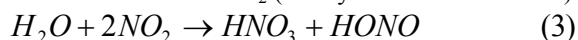


Fig 1. Chemistry of nitrous acid in the atmosphere (Alicke, 2000)

A mechanism of nitrous acid formation was recently proposed in the atmosphere (Ammann et al. 2000) and on the ground or vegetation surfaces (Kleffmann et al, 2002, 2003), to explain high day-time concentrations of HONO. The photolytic HONO source was also identified on glass surfaces (Zhou et al., 2001).

Production of HONO via these reactions involves only NO_x and water vapour and proceeds in the homogeneous phase with a second order reaction (Alicke, 2000). Although reaction (3) has been the subject of a lot of papers, the mechanism of this reaction has been difficult to elucidate. A recent mechanism was postulated by Finlayson-Pitts et al., 2003.

Many reports have been carried out to estimate the magnitude of nitrous acid from direct emission such as combustion engines. Up to 1% of the total NO_x found is nitrous acid, making this source very important in heavy polluted areas (daily traffic in the large cities). Studies performed in the 1980's have suggested that HONO is emitted by diesel engines (Lammel and Cape, 1996), while no HONO could be detected in the exhaust of non-diesel engines (Ammann, 2000).

Observations of HONO in the atmosphere show typical diurnal cycle (Fig 2). Since the major loss process is photolysis, HONO builds up during the night. At sunrise it is photolysed into OH and NO radicals and its concentration drops. During the early morning hours HONO can be the most important source of OH radicals in the polluted atmosphere. The concentration remains low during the day and rises again after sunset (Heland, 2001, Kleffmann et al., 2002, 2003).

METHODS OF ANALYSIS

HONO measurements in troposphere are very difficult to make it reliable for ambient concentrations. The main methods for nitrous acid measurements are:

1. **Chemiluminescent gas analysers** are used to measure NO (in the chemiluminescence reaction with O_3) and NO_2 (as NO after reduction); the method include a signal from HNO_2 as part of the NO_2 signal. The catalytic converters used in the measurements are designed to reduce NO_2 selectively to NO, but it can also reduce HNO_2 . In sampling system, HNO_2 may be lost to the walls of sampling lines or inlet filters before reaches the catalytic converter, so it appears to be a "stickier" molecule than NO and NO_2 . The potential presence of HNO_2 as part of the NO_2 signal from such analysers is usually ignored. A modified chemiluminescence technique has developed, in which HNO_2 is absorbed into solution using a diffusion scrubber, then selectively reduced by ascorbic acid to NO, which can be determined using the conventional technique. Chemiluminescence cannot distinguish HONO from other oxides of nitrogen, such as NO_2 , peroxyacetic nitric anhydride (PAN) or organic nitrates.

2. **Differential optical absorption spectroscopy (DOAS)** is advantageous method when it works with molecules which are reactive on surfaces. HONO absorbs light in the near UV with maxima at 354 and 368 nm (absorption coefficient at these wavelengths are around $10^{-19} \text{ cm}^2 \text{ molec}^{-1}$). The sensitivity of the method increases with the path length, which can be up to 10 km. The method's performances under favourable atmospheric conditions are: a detection limit of cca. 0.2 ppbV, a time resolution of 15-30

min with an uncertainty in the HNO_2 determination of cca. $\pm 10\%$. The uncertainty of the absorption coefficient applied to calculate the concentrations introduces another cca. $\pm 15\%$ uncertainty. DOAS is a sensitive technique but is often large and expensive.

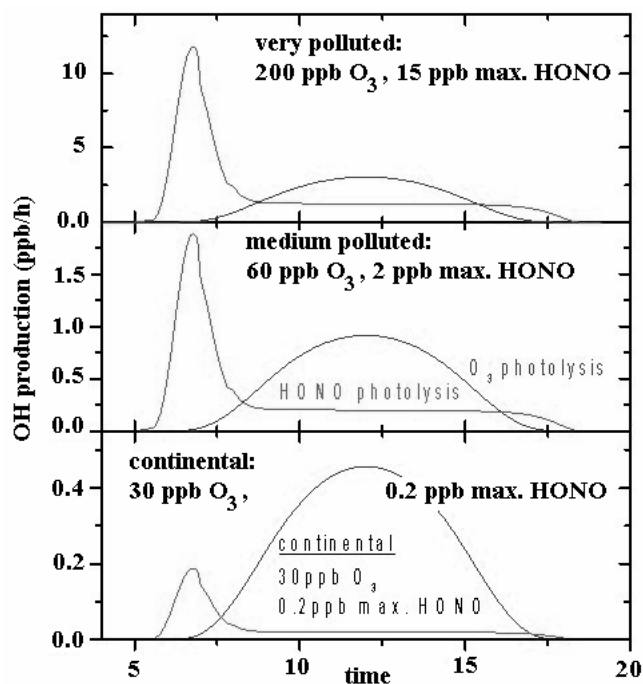


Fig. 2. Daytime concentration of nitrous acid for different areas

3. **Denuder system (DS) or wet effluent diffusion denuder technique (WEDD)** method consists a denuder tube (usually from glass), which separates the gas from aerosol in sampled air by diffusion. Gases diffuse from a laminar flow regime through the denuder to the walls, where they are absorbed by an appropriate coating, while aerosols, having a smaller diffusion rates, can be adjusted such that a high (usually close to 100%) and known collection efficiency is achieved. Alkaline surfaces (Na_2CO_3 coating) make effective traps for HNO_2 . The material is washed and analysed off-line by ion chromatography. DS technique is time-consuming, but it can be use in automated denuders. No denuder system is specific for HNO_2 and a correction must be realising for the simultaneous collection of other trace gases, such as NO_2 . Denuder methods may offer a more affordable means of detecting HONO. However, dry denuders suffer from artefacts caused by NO_2 , SO_2 , and PAN and require longer integration times on the order of several hours to obtain several hundreds of pptV

detection limits. Wet denuder techniques have been developed for measuring HONO and HNO₃, which are subject to fewer artefacts. However, NO₂ can form HONO on the wet surfaces.

4. **Wet chemical or ion chromatography (IC)** has a detection limit of a few ng·m⁻³ over a long time (12 h). Zhou, 1999 recently used high-performance liquid chromatography (HPLC) analysis for HONO and HNO₃ detection, with a sampling frequency of 10 min with 2-min integration time (Alicke, 2000). Detection limits are less than 1 pptV for HONO and 20 pptV for HNO₃.

5. **Laser-induced fluorescence (LIF)** Zhang developed a CRDS for direct measurement of HONO with a tunable dye laser. Absorption of other gases (i.e., NO₂ and SO₂) and background scattering can interfere. It can be used to detect concentrations in the range of 10 ppb-10 ppmV by employing three wavelengths with a sensitivity of 5 ppbV in 15-s integration.

6. Direct measurement of HONO by **Fourier transform infrared spectroscopy (FT-IR)** is limited by spectral overlap of other absorbing species. Finlayson-Pitts et al., 2003 studied the reaction between HONO and HCl to produce ClNO and H₂O and they showed that heterogeneous reactions on the chamber walls need to be considered.

Observations of HONO in the polluted atmosphere often show nighttime mixing ratios of more than 10 ppbV. Table 1 gives an overview of several measurements of HONO in the polluted atmosphere. No reliable daytime observations have been reported, but HONO mixing ratios up to 1 ppbV at low sunlight intensities appear to be possible. **A quantification of the daytime OH production by HONO photolysis has not been reported.**

LOPAP INSTRUMENT

It is well known that nitrous acid is a particular interest in atmospheric chemistry since photolysis of HONO significantly enhances photooxidation processes early in the morning to form HO radicals. In addition, HONO is an important indoor pollutant, which can react with amines to form nitrosamines, which are carcinogenic for human body. Some levels of HONO concentrations measured with different techniques are presented in tab. 1.

The instrument for HONO measurements in atmosphere was build up in Wuppertal University, West Germany by Kleffmann and co-workers (Heland, 2001, Kleffmann et al, 2002) and it is described to be a cheap, sensitive, compact and field measurement HONO monitor in the troposphere. This new instrument (LOPAP=*long path absorption photometer*) can be used for HONO monitor in ambient air, for aircraft, exhaust gas and/or indoor pollution measurements (fig. 3).

The instrument is built up from three separate units:

(1) **the collection (external) unit**, where HONO is continuously collected in a liquid phase using a glass stripping coil (17 cm length, I.D. 2 mm). According to the figure, HONO is sampling in a temperature controlled stripping using R1 solution (solution of 0.06M sulfanilamide in 1M HCl). Because the solubility of nitrous acid under moderate acidity is low, HONO is almost quantitatively sampled in R1 and is fast converted into a diazonium salt (see the reaction). The instrument uses two sampling lines (channel 1 and 2) to correct the possible interferences, a problem for all wet chemical detectors. Since HONO and interfering compounds (e.g., NO₂) are taken-up in the first coil, only the interfering gases are taken-up in the second one. From the difference of both channels, the real HONO concentration can be obtained.

Tab. 1. Overview about HONO measurements with different techniques

	Technique	Max HONO, ppb
Julich, Germany	DOAS	0.8
Deuselbach, Germany	DOAS	< 0.1
Los Angeles	DOAS	8
Göteborg, Sweden	Denuder	0.26
Long Beach	DOAS, Denuder	15
Ispra, Italy	OPSIS-DOAS	2
Birmingham, UK	Denuder, Cont. Anal.	10
Milano, Italy	Denuder	17
Zurich, Switz.	Wet Wall Den.	3.4
Julich, Germany	LOPAP	0.5

(2) **the azo dye unit** is the main unit of the instrument and can be placed in the laboratory. In this unit R1 is mixed with a 0.8 mM (1-naphthyl)-ethylenediamine-dihydrochloride solution (R2) to form the final azo dye compound, after a residence time of 1-2 min. After the mixing volumes, the azo-dye solutions are continuously pump (HPLC pump) into the next unit.

(3) **the detection unit** consists of a long Teflon tubing acting as an absorbing cell. Visible light is focused into a tube via fibre optics; because the refractive index of the tubing material is lower than that of the liquid, undergoes multiple reflections on the inner walls of the tub (fig. 4). On the opposite end of the cell, the light is collected again by a glass fibre and detected with a two channel grating spectrometer using a diode array detector (Ocean Optics, SD 2000 type). The absorption spectra of both channels are stored on a mini computer for later data evaluation.

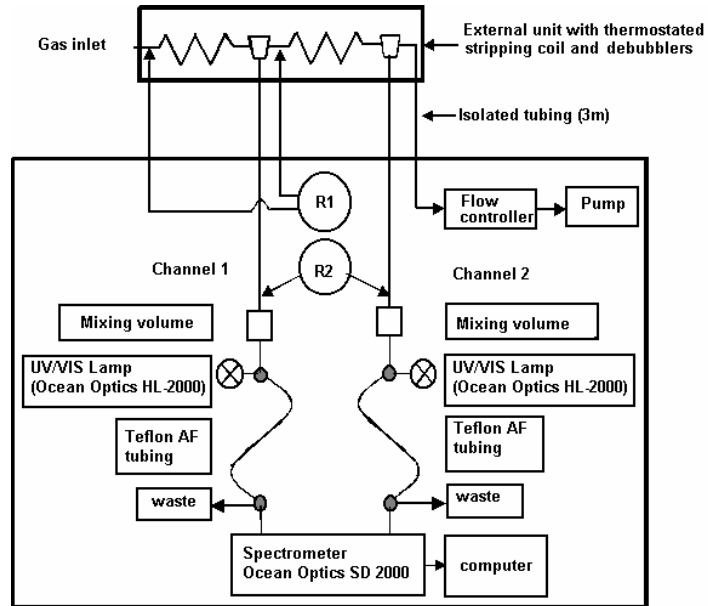


Fig. 3. Experimental set-up of the LOPAP instrument (Helland et al., 2001, Kleffmann et al., 2002)

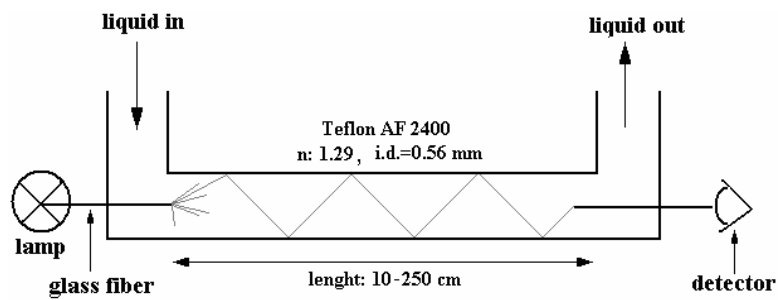


Fig. 4. The detection unit of the instrument

INSTRUMENT PARAMETERS

In the recent version of the LOPAP instrument high sampling efficiencies of HONO, around 99.898% were observed, for flow rates of 1-2 l·min⁻¹. An example for a higher sampling efficiency of pure HONO source using a flow rate of 1.2 l·min⁻¹ is given in fig. 5. While HONO concentration in the first channel was up to 2.5 ppbV, in the second channel, the concentration of HONO (which was not sampled in the first one), was only a few pptV.

The detection limit and the range of measurements for LOPAP instrument are strongly dependent on (a) the gas flow rates, (b) the liquid flow rates and (c) the length of the absorption tubings. In practice, the sensitivity will increase linearly with the gas flow rate and/or the absorption length and decrease with the liquid flow rates. An example for the detection limit of the instrument is given in fig. 6. The detection limit of the instrument for ambient air measurements was calculate like two times of standard deviation for zero measurements and was estimated at 1-2 pptV and was improved in the most recent version of the instrument.

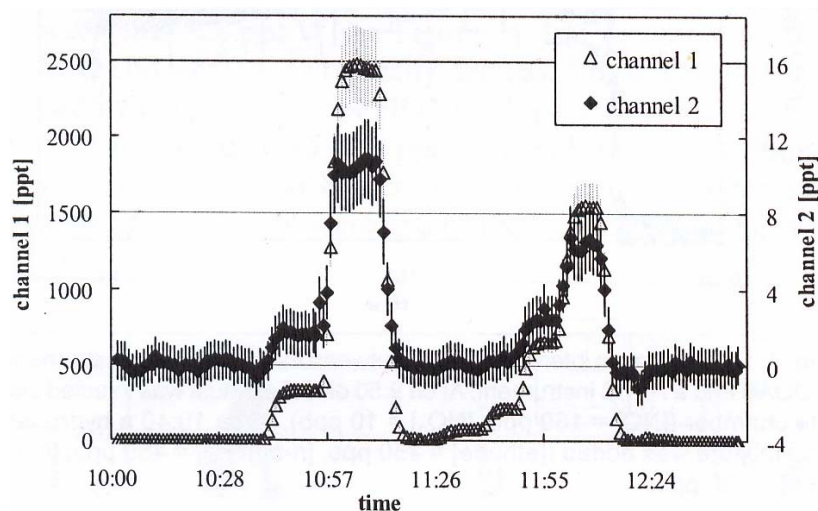


Fig. 5. Demonstration of sampling efficiency for LOPAP instrument (Kleffmann et al., 2002)

The main working parameters for LOPAP instrument are given in table 2.

A typical daytime concentrations of HONO from Julich campaign (30.06-02.08.2003), is presented in the Fig. 7, with an increasing of concentration during the night and a decreasing of concentration during the day. During the day the concentration of HONO decreased significantly reaching a minimum between 0.2–0.6 $\mu\text{g}/\text{m}^3$. These

values were comparable to the one reported by Acker et al., 2002. Formation of HONO during night time is attributed to heterogeneous reactions of NO₂ on various surfaces. This heterogeneous formation and accumulation processes during the night lead to maximum values in the morning hours before photolysis causes a significant decrease.

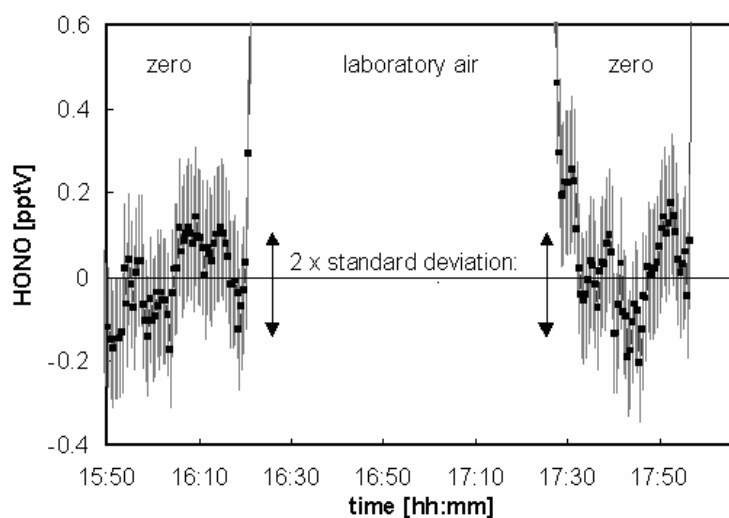


Fig. 6. Test for demonstration of detection limit of LOPAP instrument (Kleffmann et al. 2002)

Tab. 2. Summary of working parameters of the LOPAP instrument for two different applications (Kleffmann et al., 2002)

Instrument parameters	Emission measurements	Ambient air measurements
Gas flow rate	1 L/min	1 - 2 L/min
Liquid flow rate	1.3 mL/min	0.4 mL/min
Absorption length	0.1 m	2.5 m
Range of λ_{abs}	540-600 nm	540 - 590 nm
Measurements range	2 ppbV - 2.000 ppbV	0.005 - 10 ppbV
Sampling efficiency	99.8 %	99.8 % - 98 %
Response time	~ 1.5 min	~ 4.0 min
Detection limits	0.5 ppbV	1 - 2 pptV

Laboratory measurements suggest that the HONO formation is first order reaction in NO₂ and H₂O, but the exact mechanism is unknown. Unfortunately the

HONO rates formation determined in the laboratory are about two orders of magnitude lower than the ones observed in the atmosphere. So, a daytime source of HONO has been proposed, on the basis of measurements showing higher HONO concentrations during the day (Kleffmann et al., 2005). They conclude that HONO contributes substantially to the local primary OH production and that it may have an important influence on the oxidation of biogenic volatile organic compounds emitted by the forest. Daytime concentration of HONO was measured during ECHO field campaign in a forest, Jülich, Germany, in July 2003. Midday measurements show a large and an unexpected daytime source of HONO (cca.500 pptV/h), which represents an important source of HO radicals due to HONO photolysis (Kleffmann, et al., 2005). The formation of HONO on soot particles in the presence of NO₂ and perhaps water has been observed in the laboratory (Ammann et al., 1998). The importance of this source is still under investigation.

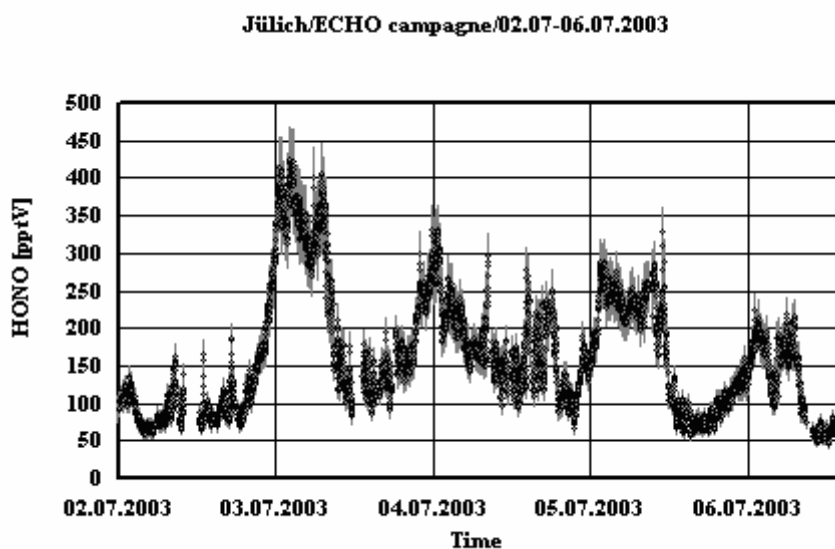


Fig. 7. Typical concentration of nitrous acid during field measurements (Jülich Campaign, 2003)

CONCLUSION

In conclusion, the photolysis of nitrous acid has long been recognized as an important source for HO radicals in the atmosphere. The quantification of nitrous acid level is essential for the understanding of tropospheric chemistry. A new and continuously working instrument for nitrous acid measurements has been developed in Wupperat University, Germany. The validation of the instrument was performed in the laboratory using the IC and DOAS techniques. All the deviations were within the errors of the measurements. In the same time, the interferences for the new instrument have been quantified and can be neglected for atmospheric measurement.

REFERENCES

- ACKER, K., MÖLLER, D., AUDEL, R., WIEPRECHT, W., KALASS, D. AND HOFMEISTER, J. (2002) - *Observations of nitrous acid at different rural and urban sites in Europe*. In Proc.EUROTRAC2 - Transport and chemical transformation in the troposphere, (eds. M. Midgley and M. Reuther), Garmisch-Partenkirchen, Margraf Verlag, Weikersheim.
- ALICKE B. (2000) - *The role of nitrous acid in the boundary layer*, dissertation thesis, Heidelberg Univ., Germany.
- AMMANN M., ARENS F., GUTZWILLER L., BALTENSPENGER U., GAGGELER H.W. (2000) - *Heterogeneous formation of HONO on tropospheric aerosol particles*, CMD annual Report, 140-03.
- FINLAYSON-PITTS B.J., WINGEN L.M., SUMNER A.L., SYOMIN D., RAMAZAN K.A. (2003) - *The heterogeneous hydrolysis of NO₂ in laboratory system and in outdoor and indoor atmospheres: An integrated mechanism*, Phys. Chem. Chem. Phys., **5**, 223.
- HELAND, J., J. KLEFFMANN, R. KURTENBACH AND P. WIESEN (2001) - *A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere*, Environ. Sci. Technol., **35**, 3207-3212.
- KLEFFMANN J., GAVRILOAIEI T., HOFZUMAHAUS A., HOLLAND F., KOPPMANN R., RUPP L., SCHLOSSER E., SIESE M., WAHNER A. (2005) - *Daytime formation of nitrous acid: A major source of OH radicals in a forest*, Geophys. Res. Lett. **32**, L05818, doi:10.1029/2005GL022524
- KLEFFMANN, J., J. HELAND, R. KURTENBACH, J. C. LÖRZER AND P. WIESEN (2002) - *A new instrument (LOPAP) for the detection of nitrous acid (HONO)*, Environ. Sci. Pollut. Res., **9** (sp. iss. 4), 48-54.
- KLEFFMANN, J., KURTENBACH, R., LÖRZER, J. C., WIESEN, P., KALTHOFF, N., VOGEL, B., VOGEL, H. (2003), *Measured and simulated vertical profiles of nitrous acid, Part I: Field measurements*, Atmos. Environ., **37**, 2949-2955.
- LAMMEL, G., CAPE, J.N. (1996) - *Nitrous acid and nitrite in the atmosphere*, Chem. Soc. Rev., **25** (5), 361-369, DOI:10.1039/CS9962500361.
- ROHRER F., BOHN B., BRAUERS T., BRUNING D., JOHNEN F.-J., WAHNER A., KLEFFMANN J. (2005)-*Characterisation of the photolytic HONO-source in the atmosphere simulation chamber SAPHIR*, Atmos. Chem. Phys., **5**, 2189-2201.
- ZHOU, X., H. J. BEINE, R. E. HONRATH, J. D. FUENTES, W. SIMPSON, P. B. SHEPSON AND J. W. BOTTENHEIM (2001) - *Snowpack Photochemical Production of HONO: a Major Source of OH in the Arctic Boundary Layer in Springtime*, Geophys. Res. Lett., **28**, 4087-4090.

