

## Intercomparison of the DOAS and LOPAP techniques for the detection of nitrous acid (HONO)

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### Abstract

Recent studies have demonstrated that nitrous acid (HONO) is a source of hydroxyl radicals (OH) in the boundary layer not only early in the morning but also throughout the day. Despite its importance, all known instruments to detect HONO in the atmosphere suffer either from the great experimental effort necessary or from the possibility of significant interferences. In addition, only a few instruments are sensitive enough to detect low HONO concentrations during daytime. Accordingly, validated and sensitive measurements of nitrous acid are of paramount importance to describe the oxidation capacity of the atmosphere. Up to now, in intercomparisons of these chemical detectors with the well accepted DOAS technique significantly higher concentrations have been detected during the day with the chemical detectors, the discrepancy being attributed to interferences.

In the present study, a recently developed HONO instrument (LOPAP) was validated against the DOAS technique, both in the field and in a large smog chamber under various conditions. Since sampling artefacts were minimised and interferences were measured and corrected for by the LOPAP instrument excellent agreement was obtained between these techniques during daytime as well as night-time. It is demonstrated that chemical instruments, which do not measure and do not correct interferences may significantly overestimate daytime concentrations of HONO caused by unknown interferences, which are particularly important during daytime, when HONO concentrations are low. For the DOAS technique, the possibility of HONO impurities in the NO<sub>2</sub> reference spectra used for the spectral analysis needs to be treated actively in the evaluation process, to avoid a potential negative interference at low HONO/NO<sub>2</sub> ratios. A simple procedure is presented that eliminates this possible error source in DOAS measurements of HONO in the atmosphere.

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**Keywords:** Nitrous acid (HONO); Atmospheric chemistry; Oxidation capacity; Interferences; Field measurements

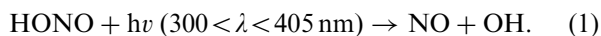
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## 1. Introduction

Since the first unequivocal detection of nitrous acid (HONO) in the atmosphere by Perner and Platt (1979), it has been realised that HONO is of particular interest in atmospheric chemistry. The photolysis of HONO significantly enhances photo-oxidation processes early in the morning due to the production of OH radicals at a time of the day when other OH-sources are still small (Harrison et al., 1996; Alicke et al., 2003):



More recent field studies indicate that HONO is also a major source of OH radicals during the day and postulated the existence of a strong daytime source (Neftel et al., 1996; Staffelbach et al., 1997; Kleffmann et al., 2002, 2003, 2005; Zhou et al., 2002a; Vogel et al., 2003; Ren et al., 2003; Acker et al., 2006), which can account for up to 60% of the direct OH radical sources. Thus, HONO will make a significantly higher contribution to the oxidation capacity of the atmosphere than has been previously assumed. The formation mechanisms of HONO in the atmosphere are not well understood yet. Although it is commonly accepted that HONO is formed by heterogeneous processes, i.e. by different conversion processes of NO<sub>2</sub> on humid surfaces (Gutzwiller et al., 2002; Finlayson-Pitts et al., 2003; Ammann et al., 2005), it is still unclear whether HONO production occurs dominantly on the surface of aerosols or on ground surfaces. In addition, the mechanism of the proposed strong daytime source of HONO is still a topic of controversial discussion (Zhou et al., 2002a, 2003; Trick, 2004; George et al., 2005; Stemmler et al., 2006).

Due to its significant atmospheric importance, HONO has been measured for many years with various techniques (e.g. Platt et al., 1980; Hanst et al., 1982; Ferm and Sjödin, 1985; Kanda and Taira, 1990; Večeřa and Dasgupta, 1991; Febo et al., 1993; Wang and Zhang, 2000; Schiller et al., 2001; Huang et al., 2002; Kleffmann et al., 2002), the most established and reliable of which is differential optical absorption spectroscopy (DOAS) a fast path-averaging spectroscopic technique, which detects HONO by its unique specific narrow-band absorption features in the ultraviolet spectral range (Platt et al., 1980; Platt, 1994). DOAS is very selective, and free of sampling artefacts and chemical interferences (Platt, 1994). Since detection limits are typically in the order of 100 pptV (Platt

et al., 1980), daytime concentrations are only detected in highly polluted environments or at low solar irradiation levels. Besides DOAS, three other optical absorption techniques have been used for the detection of HONO, i.e. cavity ring down spectroscopy (Wang and Zhang, 2000), FTIR spectroscopy (Hanst et al., 1982) and tuneable diode laser spectroscopy (Schiller et al., 2001). Due to detection limits typically in the order of some ppbV, these methods are not sufficiently sensitive to detect HONO in relatively pristine environments, even during the night. Besides limitations due to the sensitivity, all the absorption techniques mentioned above suffer from great experimental efforts and expensive system components.

On the other hand, several chemical in situ techniques for measuring HONO have been developed during the last 2 decades. These instruments are typically much cheaper, easier to use and can typically be much more sensitive with detection limits as low as ~1 pptV (Huang et al., 2002; Kleffmann et al., 2002). However, since HONO is sampled on dry or liquid surfaces and since HONO is formed heterogeneously on these surfaces, these instruments suffer from chemical interferences in the sampler and sampling artefacts in the sampling lines. Wet effluent diffusion denuders (WEDD) were recently demonstrated to suffer from interferences such as chemical reactions of NO<sub>2</sub> with hydrocarbons (Gutzwiller et al., 2002), which are, e.g., emitted from diesel engines. These interferences are significantly higher than the pure NO<sub>2</sub> interference and cannot be corrected for by the instrument itself. Chemical reactions of NO<sub>2</sub> with hydrocarbons can take place on any surface and it is to be expected that other chemical HONO instruments will also be affected. Another significant chemical interference is that caused by mixtures of NO<sub>2</sub> and SO<sub>2</sub> especially under alkaline sampling conditions (Genfa et al., 2003; Spindler et al., 2003). On the other hand, negative interferences caused by incomplete sampling have been reported for sampling solutions at low pH (Zellweger et al., 1999; Genfa et al., 2003). Besides interferences, photolytic sampling artefacts have also been observed recently in sampling lines (Zhou et al., 2002b), which are typically used for chemical in situ instruments.

In conclusion, although much more sensitive compared to the DOAS technique, chemical instruments can be affected quite significantly by interferences and sampling artefacts. Therefore,

validation of the elevated HONO daytime concentrations recently detected using chemical HONO instruments is of paramount importance in order to exclude the potential problems discussed above. The results concerning the large daytime contribution of HONO to the oxidation capacity of the atmosphere as indicated by the measurements using chemical instruments can only be taken seriously if it can be established that these high measured daytime concentrations were not influenced by interferences and sampling artefacts.

However, in previous intercomparison studies of chemical HONO instruments with the well accepted DOAS technique in the atmosphere, significant differences were observed (Appel et al., 1990; Febo et al., 1996; Coe et al., 1997; Müller et al., 1999; Spindler et al., 2003). Typically, the results of the different techniques agreed well during night, but the chemical instruments measured significantly higher concentrations during the day. These differences were explained by interferences of the chemical instruments. Accordingly, the development of well validated, sensitive and fast HONO instruments is of paramount importance to quantify the oxidation capacity of the atmosphere and to understand the formation mechanisms of HONO, especially during the day.

In the present study, a recently developed two channel in situ HONO instrument, long path absorption photometer (LOPAP), was compared with the DOAS technique not only in the field but also in a large smog chamber. For the intercomparison in the field experiment, an open DOAS–White-mirror system was operated to perform semi-point measurements of HONO by the DOAS technique. This provided the unique opportunity to directly compare the DOAS and LOPAP techniques for simultaneous measurements of nearly the same air masses in a real environment, excluding possible errors due to spatial gradients.

## 2. Experimental

### 2.1. LOPAP<sup>®</sup> instrument

The LOPAP instrument is described in more detail elsewhere (Heland et al., 2001; Kleffmann et al., 2002). Only a brief description and recent modifications of the instrument are given here. HONO is first sampled in a temperature controlled stripping coil by a fast chemical reaction in the stripping reagent, which is a mixture of sulphanila-

mid in hydrochloric acid. Due to the fast chemical reaction, a very short stripping coil (17 cm length, 2 mm i.d.) is used to obtain a >99.9% uptake for 1 L min<sup>-1</sup> gas flow, resulting in a very short contact time of interfering substances with the liquid surface. The experimental conditions applied for the LOPAP instrument have the advantage that HONO is completely sampled even at low pH, for which only inefficient uptake can occur for instruments in which HONO is only taken up by its solubility (Zellweger et al., 1999; Genfa et al., 2003), due to the low effective Henry's law constant (Park and Lee, 1988). In addition, at low pH several chemical interferences caused by e.g. NO<sub>2</sub> and SO<sub>2</sub> (Spindler et al., 2003) or NO<sub>2</sub> and phenols (e.g. Ammann et al., 2005) are minimised (Heland et al., 2001; Kleffmann et al., 2002).

The stripping coil is mounted in an external sampling unit, which is placed directly in the atmosphere of interest, excluding the use of any sampling lines. Thus, sampling artefacts in sampling lines, i.e. heterogeneous formation on surfaces by, e.g. different NO<sub>2</sub> reactions (e.g. Gutzwiller et al., 2002; Finlayson-Pitts et al., 2003; Ammann et al., 2005) or photolytic formation on surfaces (Zhou et al., 2002b) are minimised. After the separation from the gas phase, the stripping reagent is pumped through an isolated temperature controlled reagent line to the instrument, where it is converted into an intensively coloured azo dye by the reaction with *N*-naphthylethylenediamine-dihydrochloride (Grasshoff et al., 1983). The absorption of the light from a white light-emitting diode (LUXEON) by the dye is measured in long path absorption tubes made of Teflon<sup>®</sup> AF 2400 using a minispectrometer (Ocean Optics, SD 2000). The light from and to the absorption tubes is transferred by glass fibre optics (200 µm). All continuous liquid flows are adjusted by a peristaltic pump (Ismatec). The light spectra are stored and processed by a mini computer and the absorbance can be continuously followed on the computer.

In the external sampling unit two stripping coils are connected in series to correct for interferences, which are expected for chemical HONO instruments. In the first stripping coil HONO is quantitatively sampled. Thus, the signal in the second channel (stripping coil) results only from interfering substances like, e.g. NO<sub>2</sub>. Under the assumption, that the interfering substances are taken up only by a small amount in each coil, which was shown in the laboratory for all tested interferences (Heland et al.,

2001; Kleffmann et al., 2002), the difference between the signals in channels 1 and 2 gives the interference-free HONO signal. As a result of this two-channel concept all interferences tested in the laboratory, including the significant interference caused by NO<sub>2</sub> and unknown semi-volatile diesel exhaust components (Gutzwiller et al., 2002), can be neglected (Kleffmann et al., 2002). The particle sampling efficiency of the instrument was also recently measured (Bröske et al., 2003). For particles in the diameter range 50–800 nm an uptake of  $\leq 1\%$  was determined with a scanning mobility particle sizer instrument (SMPS). The sampling efficiency of particles significantly smaller than 50 nm might be much higher because of the faster diffusion of these particles, however, these ultra-fine particles do not contain a significant mass fraction of the aerosol. On the other hand, particles much larger than 1  $\mu\text{m}$  might be also more efficiently collected through impaction. However, this would affect our two channel correction only, if the collection efficiency becomes higher than  $\sim 10\%$ , which is an order of magnitude higher than the upper limit determined for the sub-micron range and thus, is only expected for very large particles, e.g. during fog. In addition, no high nitrite content in the particle phase can be expected from the effective Henry's law constant of HONO (Park and Lee, 1988) for typical acidic conditions in the aerosol phase. Accordingly, possible interferences by particle nitrite can be either corrected for very effectively by the two channel system or are expected to be of minor importance.

The instrument is calibrated by exchanging the stripping solution by a nitrite standard (Merck, Titrisol) diluted in the stripping solution, while running under zero air. Concentrations are calculated using the concentration of the liquid standard and the measured liquid and gas flows. Zero air measurements are automatically performed in regular intervals by a second flow controller and a magnetic valve. The zero air is injected by a small PFA line directly into the inlet of the stripping coil. The measurement range of the instrument of  $< 1 \text{ pptV} - 2 \text{ ppmV}$  can be varied by the length of the absorption tubes (0.1–6 m) and by the use of different absorption wavelengths of the stored spectra (Heland et al., 2001). With an optical path length of 2.5 m, used in this study, the instrument has a detection limit of  $\sim 1 \text{ pptV}$  for a time resolution (10–90%) of 4 min. However, a detection limit of 0.2 pptV was recently achieved for 6 m

optical path length with a time resolution of 6–7 min. The accuracy and precision of the instrument are 7% and 1%, respectively.

For the two smog chamber campaigns (EUPHORE) in 2001 and 2004 the external sampling unit of the LOPAP instrument was directly installed in the chamber, while the instrument was mounted in the laboratory below the chamber floor. A detailed description of the EUPHORE smog chamber is given elsewhere (Becker, 1996). For the measurements in the field campaign (FORMAT-1) in 2002 the external sampling unit was installed directly beside the optical path of the White-mirror system of the DOAS instrument, while the instrument was placed in the DOAS container. A more detailed description of the field site can be found elsewhere (Hak et al., 2005).

## 2.2. DOAS instrument in the smog chamber (EUPHORE)

### 2.2.1. Experimental set-up

During the experiments performed at EUPHORE in 2001 and 2004, the DOAS system was operated with Xenon high-pressure short-arc lamps (XBO-450W-OSRAM) as light source. The beam was focused by means of a Newton telescope and redirected to the White type  $f/53.3$  cell placed inside the chamber. Two set of mirrors were used in the multireflection cell (8 m base-path). In the experiments in 2001, mirrors with a dielectric coating (Laseroptik, Garbsen, Germany) were used. They show a reflectivity of  $R = 99\%$  in the range 300–390 nm (path length 898 m) plus a second layer at 633 nm,  $R = 50\%$ , to allow adjustment of the mirror system by means of two laser diodes. For the experiments in 2004, UV-enhanced aluminium-coated mirrors,  $R = 90\%$ , (Alflex-UV, Balzers, Liechtenstein) were used (path length 386 m). A second Newton telescope focused the light coming from the White cell onto an optical fibre (NA = 0.12,  $\phi = 200 \mu\text{m}$ ; BTO, Germany) and subsequently to the entrance slit of the  $f/6.9$  Czerny–Turner spectrograph (Acton Spectra Pro 500; focal length 0.5 m). Using a quartz fibre mode mixer (Stutz and Platt, 1997), a homogeneous illumination of the spectrograph/detector system is provided. The spectrograph was thermostated to  $T = 30^\circ\text{C}$  to reduce temperature drifts. A 300 groove  $\text{mm}^{-1}$  grating (blaze 300 nm) was used, corresponding to a dispersion of  $0.162 \text{ nm pixel}^{-1}$ . The spectral resolution was 0.81 nm (five channels)

in the configuration of the system in 2001, and after changing the optical fiber and the width of the entrance slit in 2004, could be reduced to 0.65 nm (four channels). The photodiode array (Hamamatsu, 1024 diodes, Hoffmann Messtechnik, Rauenberg) was cooled to  $T = -20^{\circ}\text{C}$  to reduce dark current to less than 0.8% of the signal. A more detailed description of the DOAS system can be found elsewhere (Becker, 1996).

### 2.2.2. Spectra analysis

Prior to the DOAS evaluation, the measurement spectra were corrected for dark current, stray light and electronic offset of the detector. Dark current and stray light were measured periodically by introducing an edge filter GC475, 3 mm thickness (Schott Glaswerke, Mainz) into the light beam. The electronic offset was measured by adding approximately 1000 spectra recorded at a very low integration time in the dark. After subtracting each measurement spectrum was divided by a background spectrum recorded on the same day in the clean air of the flushed chamber. In this way, detector etalon structure and lamp features were eliminated.

In the evaluation process, two consecutive high-pass filters were applied, one prior to and another during the fitting process to correct for the changes in the intensity of the lamp during the experiments and to remove the effect of slowly varying broadband absorbers. The MFC software (Gomer et al., 1993) was used to analyse the data using a combination of a nonlinear fit and a standard linear least-squares fit.

For the experiments in 2001, the evaluation range was 321–364 nm using the dielectric mirrors and the spectra were evaluated for HONO, NO<sub>2</sub>, O<sub>3</sub> and HCHO. In 2004, the evaluation range was 324–403 nm using the UV-enhanced aluminium mirrors and HONO and NO<sub>2</sub> were evaluated.

For the data evaluation, the HONO reference spectrum from Stutz et al. (2000) was used. The HCHO, NO<sub>2</sub> and O<sub>3</sub> references used for the analysis of the experiments in 2001 were recorded directly by the DOAS instrument by injecting the corresponding compounds into the EUPHORE chamber. This avoids spectral distortions in the convolution process and results in lower residuals in the fitting process. The HCHO reference spectrum was then calibrated according to an intercalibration performed at CEAM (Rodenas et al., 2000). The NO<sub>2</sub> reference spectrum was calibrated with the Meri-

enne et al. (1995) cross section and O<sub>3</sub> was calibrated according to Paur and Bass (1984). For the experiment in 2004, a new NO<sub>2</sub> reference free of HONO contaminations (see Veitel, 2000) was obtained according to Voigt et al. (2002). All reference cross sections were convolved with the instrument function to obtain the proper resolution.

### 2.3. DOAS instrument in the field campaign

The White-type multireflection DOAS system (White, 1976) used during the field experiments is described in detail by Trick (2004). Three spherical concave mirrors of the White system ( $f/100$ , and 15 m base-path length) with dielectric coating of a reflectivity >98% at wavelengths of  $321 \pm 20$  nm were actively aligned by means of a laser adjustment system, which also enabled the number of traverses of the measurement light inside the White system to be changed from 16 (240 m path length) to 144 (2160 m path length). A high-pressure short-arc Xenon lamp (PLI-500W) was used as light source, and a temperature stabilised  $f = 300$  mm Czerny–Turner-type spectrograph was used to measure the wavelength interval from 303 to 366 nm. Lamp reference spectra were recorded at the shortest path (240 m), and residual absorptions over this reduced light path were characterised and subtracted from the measured spectra for optimised signal to noise of daytime HONO concentrations.

In the spectral analysis procedure, atmospheric spectra were corrected for dark current and electronic offset and divided by a lamp reference spectrum recorded on the same day. The ratio spectrum was high pass filtered by subtracting a triangular-smoothed copy of itself, removing broad band variations of the spectra due to small shifts in the reflectivity curve of the dielectric mirrors near the reflectivity drop-off, as well as Rayleigh and Mie scattering in the atmosphere. Average trace gas concentrations of HCHO, NO<sub>2</sub>, O<sub>3</sub> and HONO were retrieved by simultaneously fitting resolution-adjusted reference spectra using the combined linear–nonlinear least-squares algorithm of the MFC software (Gomer et al., 1993; Stutz and Platt, 1996). The trace gas reference spectra were calculated based on (Meller and Moortgat, 2000; Schneider et al., 1987; Bass and Paur, 1984; Stutz et al., 2000), respectively. NO<sub>2</sub> reference spectra were recorded by placing a 2 cm long quartz-cuvette into the light beam, which was filled previously with an approximate 1% NO<sub>2</sub>/N<sub>2</sub> mixture to

atmospheric pressure. The HONO/NO<sub>2</sub> ratio was determined from simultaneous fitting of resolution-adjusted literature cross-sections (Merienne et al., 1995; Voigt et al., 2002) and corrected by subtracting an accordingly scaled HONO spectrum from the cuvette spectrum. HONO was identified by its UV absorption bands between 323 and 344 nm, and calibrated using the literature cross-section (Stutz et al., 2000), which is known to  $\pm 5\%$  precision.

The total error of the HONO concentrations by DOAS is about 6%, but not better than the detection limit of  $\sim 200$  pptV. The average time resolution of the DOAS measurements was 137 s.

### 3. Results and discussion

#### 3.1. Smog chamber study

The LOPAP instrument was compared with the DOAS in the EUPHORE smog chamber in two campaigns in 2001 and 2004 under various conditions. To confirm a correct calibration of the LOPAP instrument, it was first validated for pure HONO/NO<sub>x</sub> mixtures in the dark, thus excluding unknown interferences. For the preparation of HONO mixtures in the chamber, a nitrite solution ( $c = 0.5$  wt%) was dropped into stirred sulphuric acid ( $c = 30\%$ ) while a flow of synthetic air ( $10 \text{ L min}^{-1}$ ) was flushed continuously over the solution. The resulting air stream was directed into the chamber and contained a mixture of humidified HONO, NO and NO<sub>2</sub>, with a NO<sub>x</sub> content of  $\sim 40\%$  of the HONO concentration. For both campaigns excellent agreement was obtained for HONO concentrations in the range 0–30 ppbV in the dark chamber (see Fig. 1). The resulting slopes of the weighted regression analysis using the statistical errors of both instruments (Brauers and Finlayson-Pitts, 1997) were  $(0.9987 \pm 0.0003)$  and  $(0.978 \pm 0.013)$ , respectively. In addition, within the experimental errors of both instruments, no significant intercepts were observed (see Fig. 1).

The excellent agreement between the instruments during both campaigns clearly indicates that both were calibrated correctly. Accordingly, the HONO absorption cross sections from the study of Stutz et al. (2000), used for the DOAS data evaluation were confirmed independently in the present study. There are two other recent studies in which significantly lower HONO absorption cross-sections were observed by Febo et al. (1996) and Brust et al. (2000). However, from the results of the present study it

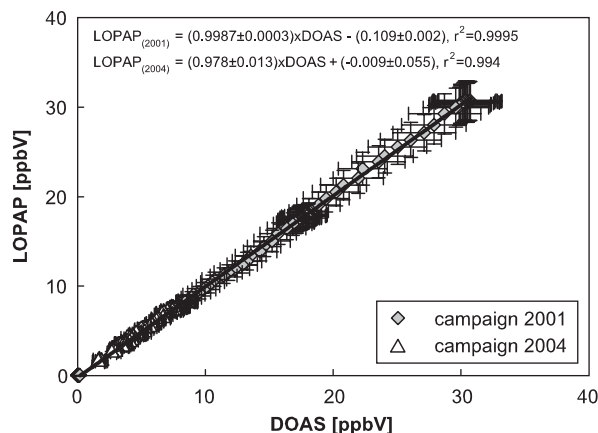


Fig. 1. Plot of the LOPAP against the DOAS data for pure HONO/NO<sub>x</sub> mixtures in the dark in the EUPHORE smog chamber for two intercomparison campaigns.

must be concluded, that both studies are most probably affected by some unknown errors.

In further experiments in the EUPHORE smog chamber, the interferences of NO, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> were quantified for the LOPAP instrument by comparison with the DOAS data. Since it is well known that all mixtures of nitrogen oxides contain HONO as an impurity, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> were formed in situ by the reaction of NO with O<sub>3</sub> in the chamber. The problem of impurities of HONO in nitrogen oxide mixtures can be seen from the experiment shown in Fig. 2, in which the addition of  $\sim 170$  ppbV of NO caused a simultaneous increase of the HONO concentration in the chamber by  $\sim 2$  ppbV. Since the DOAS and the LOPAP instruments agreed well under these conditions, and since no signal was observed in channel 2 of the LOPAP instrument, the NO interference can be neglected, in good agreement with two recent studies (Heland et al., 2001; Kleffmann et al., 2002).

However, when most of the NO was converted into NO<sub>2</sub> by the reaction with ozone, significantly lower concentrations were observed by the DOAS (see Fig. 2, “DOAS 1”), while the signal of the LOPAP instrument was not affected. Since no fast reaction between HONO and ozone is known in the gas phase, the instantaneous decreasing HONO concentration must be caused by some errors in the data evaluation of the DOAS. By analysing the original NO<sub>2</sub> reference spectra generated in the EUPHORE chamber, an impurity of HONO of  $0.41 \pm 0.09\%$  was quantified. This impurity obviously caused a significant underestimation of the HONO concentration for low HONO/NO<sub>2</sub> ratios.

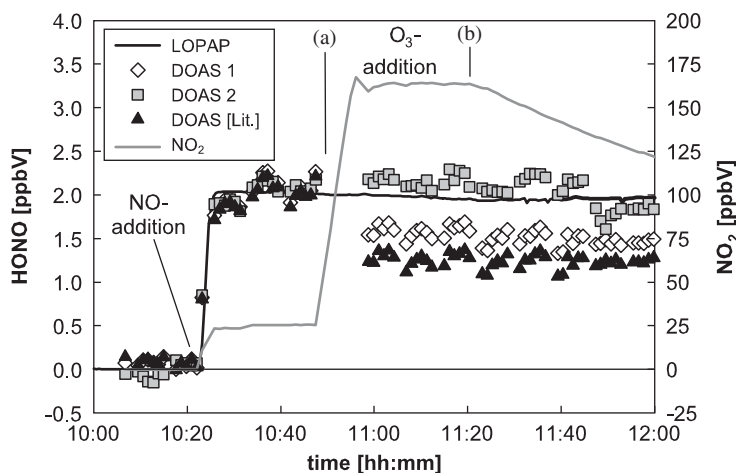


Fig. 2. NO, NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> interference tests in the EUPHORE smog chamber. At ~10:20 h 170 ppbV of NO and impurities of HONO and NO<sub>2</sub> were added to the chamber. At (a) ~10:50 h and (b) ~11:20 h ozone was added to the chamber to convert (a) almost all NO into NO<sub>2</sub> and (b) into N<sub>2</sub>O<sub>5</sub> without addition of HONO. “DOAS 1”: original data evaluation using the NO<sub>2</sub> reference spectra from EUPHORE; “DOAS 2”: data evaluation taking into account the impurities of HONO in the NO<sub>2</sub> reference spectra from EUPHORE; “DOAS [Lit.]”: DOAS data evaluation using the NO<sub>2</sub> reference spectra by Merienne et al. (1995).

The same behaviour was observed when the NO<sub>2</sub> reference spectrum of Merienne et al. (1995) was directly used (see Fig. 2, “DOAS [Lit.]”). However, in this case the negative interference caused by the impurity of HONO was even higher (0.60%). By subtraction of the average of five optical density (O.D.) spectra recovered before the addition of ozone from the average after the ozone addition, a HONO-free NO<sub>2</sub> reference spectrum was obtained. The cross-section of this reference was adjusted according to Merienne et al. (1995). When using the HONO-free NO<sub>2</sub> reference spectra in the DOAS data evaluation, no significant change of the HONO concentration and a very good agreement with the LOPAP data was observed after the increase of the NO<sub>2</sub> concentration (see Fig. 2, “DOAS 2”).

Thus, for all DOAS smog chamber data presented in this study the modified data evaluation was used, to exclude the negative NO<sub>2</sub> interference caused by the contaminated reference spectra. The values of 0.41% and 0.60% HONO in the NO<sub>2</sub> reference spectra from EUPHORE and from the study of Merienne et al. (1995), respectively, are in good agreement with the lower limit of 0.46% recently determined in the study of Veitel (2002) for the NO<sub>2</sub> reference spectra of Harder et al. (1997). Accordingly, also other groups using the DOAS technique for the measurements of HONO are encouraged to check their NO<sub>2</sub> reference for contamination with HONO. Since HONO is formed by heterogeneous conversion of NO<sub>2</sub> in spectro-

scopic cells even in dry air (e.g. Kleffmann et al., 1998), it can be expected that traces of HONO will be present in any NO<sub>2</sub> reference spectra. However, a hypothetical HONO impurity of 0.5% in the NO<sub>2</sub> reference spectra would lead to an underestimation of the HONO concentration by a factor of two by a DOAS system for a typical HONO/NO<sub>2</sub> ratio of 1% during the day in the atmosphere (e.g. Kleffmann et al., 2002).

During recent studies it was already demonstrated that the LOPAP instrument corrects for interferences even in very complex mixtures like e.g. diesel exhaust (Heland et al., 2001, Kleffmann et al., 2002). However, all interference tests of the LOPAP instrument reported up to now were performed in the dark. Since recent results concerning a high daytime contribution of HONO to the primary OH radical sources have been conducted with chemical instruments including the LOPAP technique, the instrument was compared to the DOAS also in a photosmog experiment. In this experiment a mixture of HONO (6 ppbV), NO (180 ppbV), NO<sub>2</sub> (25 ppbV), *n*-butane (400 ppbV), ethene (550 ppbV) and toluene (125 ppbV) was irradiated by natural sunlight in the EUPHORE smog chamber. Although hundreds of products are formed in this complex mixture during the photooxidation of the educts, like e.g. potentially interfering organic nitrates, peroxyacylnitrates, phenols + NO<sub>2</sub>, etc., excellent agreement between both instruments was observed (see Fig. 3). After opening the chamber,

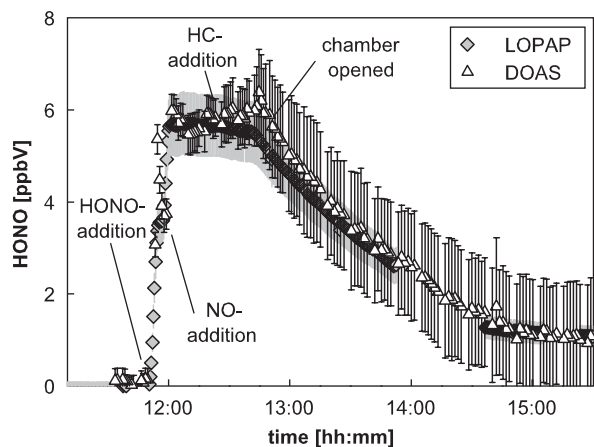


Fig. 3. HONO concentration of the DOAS and the LOPAP instruments in a photosmog experiment when a mixture of HONO, NO<sub>x</sub>, *n*-butane, ethene and toluene was irradiated by natural sunlight.

the HONO concentration decreased, caused by the photolysis of HONO, reaction (1). However, in good agreement with two other recent studies (Ramazan et al., 2004; Rohrer et al., 2005), elevated HONO concentrations were observed also during the end of the experiment (see Fig. 3). Accordingly, photolytic HONO formation, the so-called “background reactivity” in simulation chambers, is also observed in the EUPHORE smog chamber, and should be taken into consideration for the interpretation and the modelling of photosmog experiments. Since the contribution of HONO to the OH radical formation can be significant in smog chambers and since the formation depends on the experimental conditions (Rohrer et al., 2005), HONO should be measured in addition to other HO<sub>x</sub> sources like formaldehyde and ozone in these chambers.

In conclusion, the EUPHORE smog chamber study demonstrates that the LOPAP instrument measures HONO with high accuracy. It is shown that the instruments response is not affected by interferences and sampling artefacts even in very complex mixtures including conditions, which are similar to daytime conditions in the atmosphere.

### 3.2. Field study

Since chemical interferences might become more important in the atmosphere, the LOPAP instrument was also compared with the DOAS in a real-world environment. The measurements took place

in Milan, Italy, from 22 to 31 July 2002 during the FORMAT-1 2002 campaign, which was focused on the intercomparison of different formaldehyde measurement techniques (Hak et al., 2005). For this intercomparison campaign, an open-path DOAS White-type multireflection system was operated. Accordingly, it was considered to measure nearly the same air mass as the in situ monitors, which measured directly aside the DOAS system. Especially for the intercomparison of HONO concentrations in the atmosphere, this is of crucial importance, since gradients (Kleffmann et al., 2003), atmospheric transport phenomena and inhomogeneous distribution caused by local emission sources (Kurtenbach et al., 2001) can be expected. The use of a multireflection DOAS system is different to previously published intercomparison studies of chemical HONO instruments with the DOAS technique (Appel et al., 1990; Febo et al., 1996; Coe et al., 1997; Müller et al., 1999; Spindler et al., 2003), in which integrated HONO concentrations were determined from long-path DOAS measurements over a distance of up to several kilometres. The concentrations measured by these DOAS instruments therefore represent averages over the entire light paths, thus making them ill-suited for the comparison with in-situ techniques.

During the FORMAT-1 campaign in 2002, excellent agreement was obtained between both HONO instruments, which is exemplary shown for two days of the campaign in Fig. 4. In contrast to previously published intercomparison studies (Appel et al., 1990; Febo et al., 1996; Coe et al., 1997; Müller et al., 1999; Spindler et al., 2003), the data

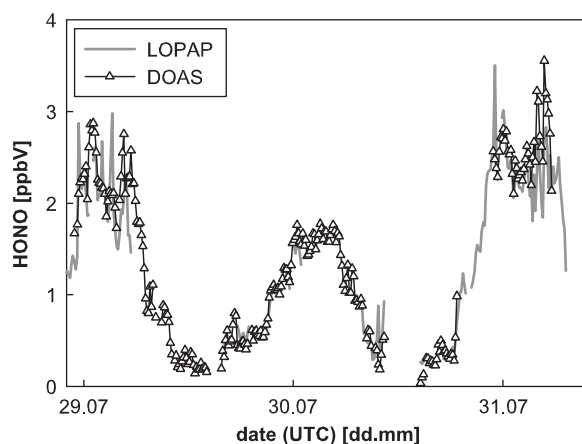


Fig. 4. HONO concentration of the DOAS and the LOPAP instruments during two days of the FORMAT-1 field campaign in 2002.

from both instruments also agreed very well during the day, although the values were sometimes close to the detection limit of the DOAS instrument of  $\sim 200$  pptV. Typical diurnal profiles of the HONO concentration in the range 90–3500 pptV were observed with the LOPAP instrument.

For a statistical evaluation of the data, all simultaneous 10 min mean values obtained from both instruments were compared. Plotting the LOPAP data versus the DOAS data, a slope of  $(0.987 \pm 0.015)$  was obtained from a weighted regression analysis using the statistical errors of both instruments (Brauers and Finlayson-Pitts, 1997), see Fig. 5. This again confirms that both instruments were calibrated with high accuracy. In addition, a negligible intercept of  $-13 \pm 17$  pptV was

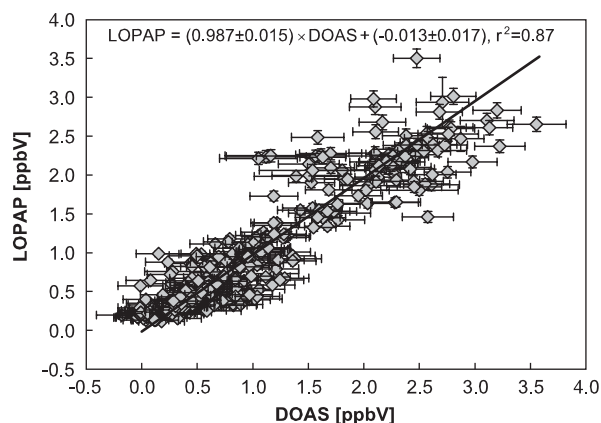


Fig. 5. Plot of the LOPAP against the DOAS data for all simultaneous 10 min averages of the FORMAT-1 campaign.

observed for the plot shown in Fig. 5, confirming that the LOPAP instrument is not affected by interferences also for low concentrations of HONO prevailing in the atmosphere during the day. During the field campaign a much lower correlation of both instruments was observed compared to the smog chamber measurements. This is caused by the measurement of exactly the same air mass in the chamber (well mixed by two strong fans) and still inhomogeneous air masses collected by the in situ LOPAP instrument compared to the path-averaging DOAS instrument (data collected over a base length of 15 m). Inhomogeneous air masses might result from (a) different gradients over the ground surfaces but (b) also from small scale plumes from nearby emission sources, which might affect both instruments differently. The short scale variations can be seen, for example, from the fast variations of the HONO concentration in Fig. 6, for which the 1 min data of the LOPAP instrument is shown.

In conclusion, the results obtained with this instrument concerning high daytime concentrations of HONO and the resulting high contribution of HONO to the OH radical sources (Kleffmann et al., 2002; Kleffmann et al., 2003; Vogel et al., 2003; Kleffmann et al., 2005) were confirmed. It should be pointed out, that also in the present study, high daytime HONO concentrations with minimum values typically in the range 200–300 pptV were observed by both instruments. These values are much higher than can be expected by the estimated photostationary state (PSS) of HONO. For example, for the 26 July 2002 at 13:00 UTC, a

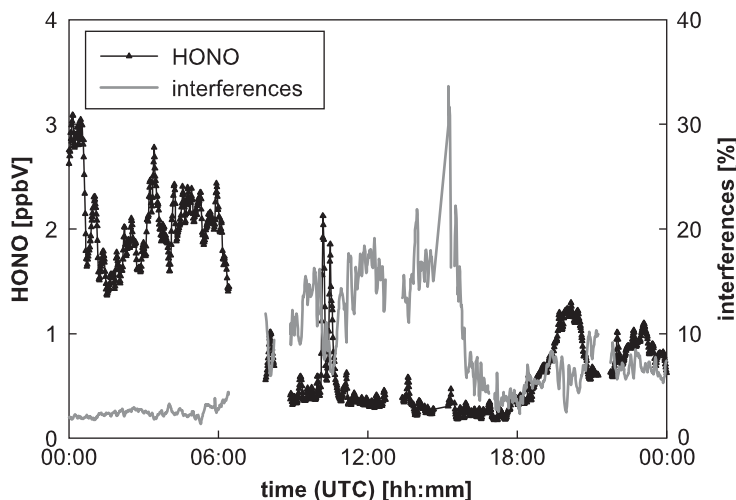


Fig. 6. HONO concentration and measured interferences of the LOPAP instrument during 1 day of the FORMAT-1 campaign in 2002 as an example.

photostationary state concentration of HONO of 110 pptV was calculated (measured:  $\text{NO}_2 = 4.5$  ppbV,  $\text{NO} = 3$  ppbV,  $J(\text{HONO}) = 0.00136 \text{ s}^{-1}$ ; estimated:  $\text{OH} = 5 \times 10^{-6} \text{ cm}^{-3}$ ), which is significantly lower than the measured value of 350 pptV. However, since the OH radical concentration, necessary to exactly calculate the PSS, was not measured in the present study, no further estimation of the daytime source strength of HONO will be given here. In another recent study with the LOPAP instrument, the daytime source strength of HONO was determined for the first time fully constrained by measured parameters (Kleffmann et al., 2005), indicating that HONO is a major OH radical source in the lower boundary layer also during the day.

Previous intercomparison studies of chemical HONO instruments with the DOAS technique typically showed significant higher daytime HONO concentrations measured by the chemical instruments. Thus, when plotting the signal of channel 2, i.e. the measured and corrected interference of the LOPAP instrument, in comparison with the measured HONO concentration, it can be demonstrated that a two-channel instrumental design as it is realized in the LOPAP instrument is required. As can be seen in Fig. 6 from a one day example of the FORMAT-1 campaign, the interferences were typically low during the night when the HONO concentrations were high. Interferences of a few percent were observed for these conditions. Accordingly, for high HONO concentrations deviations caused by interferences are in the range of the accuracy of the instrument and might be negligible. However, during the day, when the HONO concentrations were much lower, interferences of up to 40% were observed during the FORMAT-1 campaign in 2002, which obviously must be taken into consideration (see Fig. 6).

The situation becomes even more obvious when other field campaigns of the LOPAP instrument are considered, in which much lower pollution levels compared to Milan were prevailing. In these campaigns interferences of up to 100% were sometimes observed during the day, i.e. the HONO concentration would have been overestimated by a factor of up to two, if only a one-channel LOPAP system had been used. When the mean interferences of the LOPAP instrument are plotted against the mean HONO concentration from several field campaigns a strong anti-correlation can be seen (see Fig. 7). The mean interferences of 6% and 7.7% observed in a recent field campaign near the city of

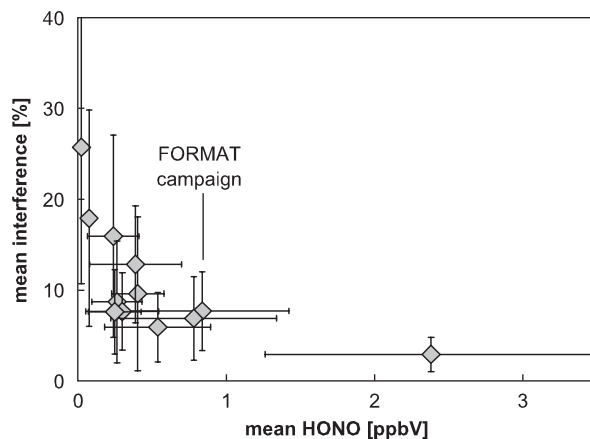


Fig. 7. Mean measured interferences of the LOPAP instrument during several field campaigns, including the FORMAT-1 campaign.

Karlsruhe (Kleffmann et al., 2003) and in the FORMAT-1 campaign from this study, respectively, are in good agreement with the value of 6% determined for a HPLC instrument by Huang et al. (2002) for urban conditions. However, in contrast to the conclusions by Huang et al. (2002), as mentioned above, interferences can cause significant overestimation of the HONO concentration measured by chemical instruments, especially during the day and for rural conditions (see Figs. 6 and 7). In the study of Huang et al. (2002) the interferences were explained by particle nitrite. However, for the stripping coil of the LOPAP instrument, which is similar to that used in their study, the uptake of particles was found to be very small (see Section 2.1). In addition, no high nitrite content in the particle phase would be expected based on the effective Henry's law constant of HONO (Park and Lee, 1988) for typical acidic conditions in the aerosol phase. Accordingly, significant interferences by particles can be excluded.

From the results of the study of Gutzwiller et al. (2002) and from the time dependence of the signal in the interference channel of the LOPAP instrument we conclude that the interferences are most probably caused by reactions of oxidisable hydrocarbons with  $\text{NO}_2$  in the stripping solution. These hydrocarbons might be, e.g. phenols (e.g. Ammann et al., 2005), which are emitted during combustion processes and are formed in significant amounts from the atmospheric photooxidation of certain VOCs (e.g. Volkamer et al., 2002). It should be mentioned that chemical interferences can be even higher for

other wet chemical instruments, which sample under neutral or alkaline conditions. For these conditions, additional interferences, e.g. from  $\text{NO}_2$  and  $\text{SO}_2$  mixtures (Spindler et al., 2003) may occur.

The small interferences observed for the LOPAP instrument during the night can explain why former intercomparison studies between chemical instruments and the DOAS technique showed good agreement during the night. However, the significant chemical interferences observed in this study during the day and the much higher daytime concentrations compared to the DOAS technique measured by other chemical instruments (Appel et al., 1990; Febo et al., 1996; Coe et al., 1997; Müller et al., 1999; Spindler et al., 2003), confirm that chemical interferences are a general problem. Thus, a direct validation against an optical, interference-free HONO instrument is of paramount importance for the further development of chemical HONO instruments.

#### 4. Conclusions

In the present study, a chemical HONO instrument (LOPAP) was validated against an optical technique (DOAS), both in the field and in a large smog chamber under various conditions. Excellent agreement was obtained also during the day, in contrast to all previously published intercomparison studies. For the DOAS technique a negative interference caused by 0.4% HONO impurities in the used  $\text{NO}_2$  reference spectra was identified in the smog chamber, which can result in a significant underestimation of HONO concentrations for low HONO/ $\text{NO}_2$  ratio. A simple procedure was presented, and it was demonstrated that the procedure eliminates this possible error source in atmospheric HONO measurements by the DOAS technique. From the measured interferences of the LOPAP instrument it was shown that chemical instruments, which do not measure and correct interferences, may significantly overestimate daytime concentrations of HONO, especially for low HONO concentrations, due to the occurrence of high unknown interferences. It is concluded that the LOPAP instrument is well suited for the reliable, fast and extremely sensitive detection of HONO in the atmosphere using a simple approach. By applying the sampling conditions outlined in the paper, interferences and artefacts can be neglected. The validation of the instrument under photolytic conditions, both for complex reaction mixtures in

a smog chamber and for a field campaign, respectively, confirms the conclusions obtained from recent field studies with this instrument. In these studies high daytime concentrations of HONO were observed, which were significantly higher than the predicted values from the known chemistry of HONO in the atmosphere.

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