

**Development of a
new LOPAP
instrument**

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Development of a new Long Path Absorption Photometer (LOPAP) instrument for the sensitive detection of NO₂ in the atmosphere

G. Villena, I. Bejan, R. Kurtenbach, P. Wiesen, and J. Kleffmann

Bergische Universität Wuppertal, Physikalische Chemie, Wuppertal, Germany

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Correspondence to: J. Kleffmann (kleffman@uni-wuppertal.de)

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Abstract

A compact and simple instrument for the sensitive detection of NO_2 in the atmosphere has been developed. NO_2 is sampled in a stripping coil by a selective chemical reaction, converted into a highly absorbing dye, which is detected by long path absorption in a liquid core waveguide. Several interferences were quantified in the laboratory which so far can all be neglected. The significant interferences against HONO and O_3 were suppressed by using an upstream HONO/ O_3 -scrubber. The instrument has a detection limit of 2 pptv, an accuracy of 10% and a precision of 0.5% for 3 min time resolution. Thus, the new NO_2 -LOPAP technique is more sensitive than known commercial NO_2 instruments. The new analyzer is much simpler to apply than other highly sensitive and selective NO_2 methods, e.g. LIF or REMPI methods. The new instrument allows an absolute calibration that can be easily performed with liquid nitrite standards, which is a significant advantage compared with other NO_2 measurement techniques for which NO_2 calibration gas mixtures are typically necessary. The new instrument has been validated against the chemiluminescence technique during an urban field campaign and against the FTIR technique in a smog chamber under complex photo-smog conditions. The data sets exhibit high correlation and excellent agreement.

1 Introduction

Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) are important trace species that are emitted into the atmosphere from both, natural and anthropogenic sources, the latter being dominated by road transport (Vestreng et al., 2009 and references therein). NO_2 affects the oxidation capacity of the atmosphere through its direct participation in the formation of O_3 and nitrous acid (HONO), which through their photolysis are major sources of the OH radical, the detergent of the atmosphere. In addition, by its reaction with the OH radical, NO_2 also limits radical concentrations in the polluted atmosphere. NO_2 contributes to acid precipitation and formation of other atmospheric oxidants such as

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the nitrate radical, NO₃ (Crutzen, 1979; Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006). The range of NO₂ concentrations varies from few pptv in remote areas to more than 100 ppbv in polluted regions (Finlayson-Pitts and Pitts, 2000).

NO₂ is also of importance due to its health impacts on both, short term and long-term exposures of the population, however, it is difficult to separate its health effect from other pollutants such as particulate matter (Samoli et al., 2006; Delfino et al., 2008; Mol et al., 2008). In addition, all these health studies may be affected by the non-selective detection of NO₂ for the techniques applied (Spicer et al., 2001; Brunekreef, 2001; Van Strien et al., 2004; Jarvis et al., 2005).

During the last two decades, the European Union (EU) set different legislative frameworks in order to assess and manage air quality and to control the pollutants released in vehicle exhaust, e.g. *EU Directives 96/62/EC, 98/69/EC, 99/96/EC and 99/30/EC (First Daughter Directive)*. European NO_x emissions linked to road transport have strongly decreased during the last 20 years. However, unexpectedly, NO₂ is not showing the same tendency, either NO₂ levels are constant or even show a small increase (EEA, 2007; Vestreng et al., 2009). Thus, for European urban network stations it will be difficult in the near future to meet the annual mean limit value for NO₂ of 40 µg m⁻³ (Carslaw et al., 2007). The reasons for this NO₂ behaviour can be explained in terms of secondary formation in the atmosphere and by increasing primary NO₂ emissions. The latter is due to increasing number of diesel cars and the introduction of new exhaust technologies, which oxidize a portion of NO to NO₂ in order to promote the oxidation of soot collected on the particle filter (Grice et al., 2009). Due to this increase of primary NO₂ emissions many studies have been focused on its impact on air quality in the urban environment (Carslaw and Beevers, 2004, 2005a, 2005b; Carslaw, 2005; AQEG, 2007; Carslaw et al., 2007; Carslaw and Carslaw, 2007; Jenkin et al., 2008; Alvarez et al., 2008; Keuken et al., 2009).

Due to its importance in atmospheric chemistry and air quality, many direct or indirect techniques have been developed for measuring NO₂ in the laboratory and/or in the field. Spectroscopic methods such as Differential Optical Absorption Spectroscopy

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(DOAS) (Platt et al., 1979; Edner et al., 1993; Thornton et al., 2003), Laser Induced Fluorescence (LIF) (Thornton et al., 2000; Matsumoto et al., 2001, 2006; Dari-Salisburgo et al., 2009; Fuchs et al., 2010), Cavity Ring Down Spectroscopy (CRDS) (Mazurenka et al., 2003; Hargrove et al., 2006; Osthoff et al., 2006; Fuchs et al., 2009, 2010), Incoherent Broad Band Cavity Enhanced Absorption Spectroscopy (IBBCEAS) (Gherman et al., 2008; Wu et al., 2009; Fuchs et al., 2010), Cavity Attenuated Phase shift Spectroscopy (CAPS) (Kebabian et al., 2005, 2008), Tunable Diode Laser Absorption Spectroscopy (TDLAS) (Gregory et al., 1990; Li et al., 2004; Herndon et al., 2004), and Resonance Enhanced MultiPhoton Ionization (REMPI) (Garnica et al., 2000; McKeachie et al., 2001) have been used for NO₂ detection, with some of them reaching very low detections limits (e.g. REMPI, LIF), but suffering from great experimental efforts, expensive and complex system components.

Thus, simpler chemiluminescence techniques are typically used for measuring NO₂. One of these is the luminol-chemiluminescence method (Wendel et al., 1983), which employs the reaction between NO₂ and an alkaline solution of luminol resulting in light emission. This technique is direct, but it is non-specific for NO₂ because ozone and peroxyacynitrates (PANs) are also detected (Fehsenfeld et al., 1990). The most widely used chemiluminescence technique is based on the gas phase reaction between NO and O₃ forming an electronically excited molecule of NO₂^{*} that emits light, which is proportional to the NO concentration. To detect also NO₂, either heated (300–350 °C) molybdenum (Mo) surfaces (Fontjin et al., 1970; Ridley and Howlett, 1974) or photolytic NO₂ converters (Kley and McFarland, 1980) are applied. The reduction of NO₂ to NO by heated Mo converters followed by ozone reaction is the reference method recommended by the US EPA (Demerjian, 2000) and by the European legislation (European Standard, EN 14211, 2005), but is affected by significant interferences against other reactive nitrogen species (NO_y) like N₂O₅, HONO, HNO₃, PAN, etc., which are also reduced to NO (Winer et al., 1974; Dunlea et al., 2007). The conversion of NO₂ into NO by photolytic converters, for which either Xenon lamps or UV emitting diodes (“blue light converters”) are used, are much more selective, although positive interferences by

photolysis of HONO for the Xenon lamp converter instruments (Rohrer et al., 2005) and negative interferences in the presence of hydrocarbons have been reported (Kurtenbach et al., 2001; Kleffmann et al., 2001; Bejan et al., 2006; Villena et al., 2011). In addition, photolytic converter instruments exhibit non linear response for high NO₂ and O₃ levels caused by the reaction NO with O₃ in the converter. Finally, all NO/O₃ chemiluminescence instruments show a negative H₂O interference by quenching of the excited NO₂* during the NO detection.

Caused by the non-selective detection of NO₂ in most commercial instruments, the development of a simple instrument for reliable NO₂ measurements is of high importance. Accordingly, in the present study a new NO₂-LOPAP instrument (Long Path Absorption Photometer), which is based on the Saltzman reaction (Saltzman, 1954) is described. The instrument is designed to be easy to use, sensitive and compact for continuously measuring NO₂ under all experimental conditions both, in the atmosphere but also in laboratory and in smog chamber experiments.

2 Experimental section

The NO₂-LOPAP instrument consists of two separate units. (1) The external sampling unit which is directly situated at the sampling site (i.e. in the atmosphere) and thus avoiding the use of any sampling lines. (2) The detection unit (19" instrument) where the azodye, which is formed in the sampling unit, is detected using long path absorption. The system is furthermore designed as a two-channel system for correction of possible interferences (Fig. 1).

2.1 Sampling unit

In the external sampling unit three stripping coils are used in series. In the first coil ("HONO/O₃-scrubber": 24 turns; 35 mm average turn diameter; 1.6 mm inner tube diameter) interfering HONO and O₃ are removed from the air stream, without significant

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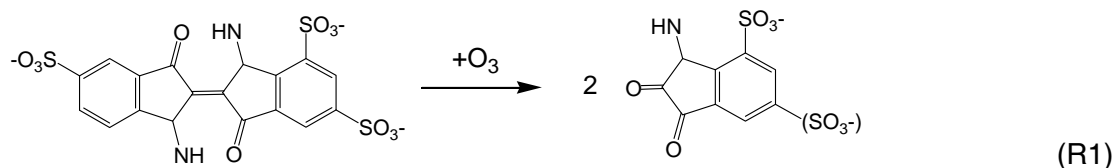
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uptake of NO₂. This separation from NO₂ is made with a stripping solution that contains 10 g l⁻¹ sulphanilamide, 0.6 g l⁻¹ potassium indigo-trisulphonate in 158 g l⁻¹ acetic acid, in which HONO and ozone are quantitatively removed. Ozone efficiently reacts with Indigo (Bader and Hoigné, 1981):



while HONO is transformed into a diazonium salt:



10 Besides HONO and O₃, 4% of the NO₂ is also collected in this scrubber solution, which is corrected in the data evaluation. Through this HONO/O₃-scrubber the known HONO (Milani and Dasgupta, 2001) and ozone interferences (Adema, 1979) by the Griess-Saltzman reaction are suppressed.

15 NO₂ and other potential interferences are collected in the second stripping-coil (Channel 1), while potential interferences are measured in the third coil (Channel 2). Both coils have similar dimension than the HONO/O₃-scrubber. The gas phase is sucked with a membrane pump through the stripping-coils, a security flask with electrical control, a Teflon membrane filter and a mass flow controller. The gas flow through the stripping-coils is 0.5 l min⁻¹. As sampling solution a modified Griess-Saltzman Reagent (1 g l⁻¹ N-(1-naphtyl)ethylenediamine dihydrochloride, NEDA, 7 g l⁻¹ sulphanilamide, 84 g l⁻¹ acetic acid, 3 g l⁻¹ NH₃ 25%, pH = 3) is used. By
20 the reaction of NO₂ with the sampling solution an intensive coloured azodye is formed

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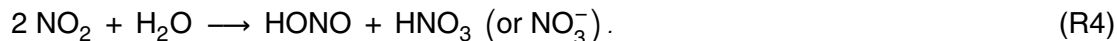
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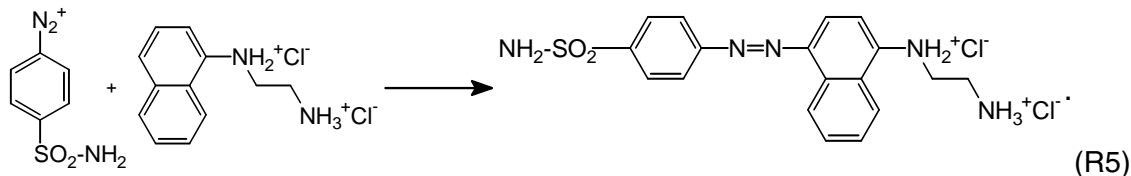
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(Saltzman, 1954), the mechanism of which is not completely understood. It was postulated that NO_2 first reacts with water (Saltzman, 1954):



The formed HONO further reacts according to Reactions (R2) and (R3) forming the diazonium salt, which reacts with NEDA forming an intensively coloured azodye:



Based on Reaction (R4) a maximum dye yield of 50% is expected, which is however observed only for very high concentrations of NO_2 in the higher ppmv-range; whereas at atmospheric concentrations yields near 100% have been measured (Huygens and Lanting, 1975). The yield of the overall reaction (amount of dye/ NO_2 absorbed) is expressed in the literature as so-called “Saltzman factor” (Huygens and Lanting, 1975). The high Saltzman factor and the observed dependency of the sampling efficiency on the NEDA concentration and the pH (see Sects. 3.1.2 and 3.1.3) shows that at low NO_2 concentrations Reaction (R4) is of minor importance. Instead, it is proposed here that NO_2 oxidizes partly deprotonated NEDA leading to quantitative formation of HONO:



Analogue redox reactions in the liquid phase are also known for other organic compounds, such as phenols and alkenes (Alfassi et al., 1986; Pryor and Lightsey, 1981). Instead of Reaction (R6), Saltzman originally postulated a reaction of NO_2 with sulphanilamide (Saltzman, 1954). However this can be ruled out based on the results obtained with the HONO-LOPAP instrument (Heland et al., 2001; Kleffmann et al., 2002). With this instrument no significant reaction between the sampling solution containing 10g l^{-1} sulphanilamide and NO_2 could be observed.

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The thermostated stripping coils (15 °C), which are connected to the detection unit through an isolated reagent line are located in the external sampling unit directly at the sampling site. Thus, line effects, for example heterogeneous reactions of NO₂ or the gas phase reaction between NO and O₃, can be neglected.

5 2.2 Detection unit (19" instrument)

After the transfer of the sampling reagent from the external sampling unit to the instrument, the sampling solution is mixed with 1 N HCl (ratio 1 : 1) in order to convert all HONO, originating from Reaction (R6), into NO⁺, Reaction (R2). Furthermore, the addition of HCl, increases the refraction index of the solution and in consequence increases the light intensity in the absorption tubes. Finally, NEDA precipitates slowly with time on the surface of the absorption tubes, which leads to a reduction of the measured light intensity. This is also reduced by the addition of HCl.

A downstream reaction volume with residence time ≥ 1 min guarantees a quantitative formation of the dye. Before entering the detection unit, potential air bubbles are separated from the sampling solution ("debubbler 2", see Fig. 1), since bubbles would deteriorate the stability of the light signal. The detection unit is basically composed of a special flexible Teflon tube (DuPont, Teflon AF 2400; 0.6 mm i.d.; 0.8 mm o.d.; variable length, here: 1.4 m and 2.4 m used). Visible light (LUXEON, warm white LED, Typ: LXHL-MWGC) is focused into the tubing via fibre optics. With the refractive index of the tubing material being lower ($n_{AF2400} \sim 1.29$) than that of the solution of the dye, the light – depending on the angle of incidence – undergoes multiple total reflection on the inner walls of the tubing and stays inside the liquid for absorption (Yao et al., 1998). The intensity of the diodes can be regulated without change of the spectral distribution (pulsed power supply unit: QUMA Elektronik & Analytik GmbH). On the opposite end of this so-called liquid core waveguide, LCW, the light is collected again by a glass fibre and detected with a two channel grating mini-spectrometer using a diode array detector (Ocean Optics, SD 2000). The absorption spectra of both channels averaged over a variable time interval are stored on a mini computer for later analysis. In addition,

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the absorption of the azodye can be continuously monitored for variable absorption wavelengths (see Sect. 2.3).

A two channel system is used for the quantification of possible interferences. With this arrangement, two stripping coils are connected in series (see Fig. 1). In Channel 1, NO₂ is almost quantitatively taken up as well as potentially interfering compounds, whereas in Channel 2 – under the assumption of a low uptake of the interferences – only the interferences are collected. NO₂ concentrations can be calculated from the difference between both channels considering the sampling efficiency of NO₂ in Channel 1.

2.3 Data evaluation

To be independent from intensity fluctuations, which are caused by e.g. temperature changes and/or bubbles of air entering the tubing, no so-called background (I_0) spectra without absorption of the dye are used for data evaluation. Instead, the logarithm of the ratio of two intensities taken at different wavelengths in the same measured spectrum is a more stable and robust measure of the azodye concentration. These two intensities are taken (a) at the absorption maximum near 544 nm or a neighbouring wavelength, I_{abs} , and (b) at a wavelength where no azodye absorption occurs, I_{ref} , e.g. at λ_{ref} of 650 nm. Knowing that I_{ref} is directly proportional to the background intensity I_0 at the absorption wavelength, λ_{abs} , the logarithm of ($I_{\text{ref}}/I_{\text{abs}}$) becomes a linear measure of the concentration c according to Lambert-Beers law:

$$\text{ABS} = \log (I_{\text{ref}}/I_{\text{abs}}) = k_{\lambda} \times l \times c + \log (I_{\text{ref}}/I_0), \quad (1)$$

where l denotes the absorption path length and k_{λ} is the absorption coefficient of the azodye, which is ca. $5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 544 nm (Grasshoff et al., 1983). The intercept of Eq. (1) depends mainly on the chosen absorption and reference wavelengths and may show variations, which are due to different purities of the reagents. Accordingly, zero air measurements have to be performed regularly during the operation of

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the instrument and a calibration of the two channels with a liquid nitrite standard is mandatory when the reagents have been renewed.

3 Results and discussion

3.1 Instrument parameters optimization

5 3.1.1 Sampling reagents

Originally, bubblers are used for the detection of NO_2 with the Griess-Saltzman reagent, which however can not be used for continuous detection of NO_2 . Instead a stripping coil is used in the present instrument, for which, however, the gas-liquid contact time is much shorter. Thus, to obtain a high sampling efficiency of NO_2 and a high Saltzman factor, a modified sampling reagent has to be used. In the present study, the sampling efficiency is defined as the proportion of NO_2 incorporated in the second stripping coil (Channel 1) with respect to the total quantity of NO_2 entering the coil. The Saltzman factor is calculated based on the proportion of the generated amount of dye with respect to the quantity of NO_2 absorbed. A high sampling efficiency is required for a correction of possible interferences using the two channel system. A low Saltzman factor causes a production of NO as a co-product that should be avoided for a possible future extension of the instrument for NO detection. Thus, both factors need to be as high as possible. For the optimization of the instrument several dependencies of the sampling reagent were investigated.

20 Variation of the pH

The pH of the sampling solution leads to a strong variation of the sampling efficiency as well as of the Saltzman factor (see Fig. 2).

The sampling efficiency increases up to $\text{pH} = 3$, gets constant up to $\text{pH} = 7$ and reaches 100% at higher pH. This can be explained by the reaction of NO_2 with NEDA,

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Reaction (R6), for which the deprotonated form of NEDA reacts faster than the protonated form. This effect was also observed in the reaction of NO₂ with phenols in the liquid phase (Ammann et al., 2005). Thus, the two steps in the sampling efficiency can be explained by the neutralization of the two -NH₃⁺ groups of NEDA. The Saltzman factor increases strongly up to pH = 4, however starts to decline at higher pH. Based on the pH dependency, a pH of 3–4 is recommended for which both the sampling efficiency and the Saltzman factor are high. Higher pH leads to a higher sampling efficiency but to a lower Saltzman factor. In addition, stronger interferences against PANs are expected with increasing pH (Frenzel et al., 2000) and therefore should be avoided.

Variation of the NEDA concentration

Increasing NEDA concentration leads to a strong increase of the sampling efficiency, reaching 100% for high NEDA concentrations (Fig. 3).

From the strong NEDA dependence, it is proposed that NO₂ is directly reacting with NEDA, Reaction (R6), whereas the reactions with water, Reaction (R4), and sulphanilamide can be neglected. However, at the same time, a decrease of the Saltzman factor is observed. Parallel measurements with a NO chemiluminescence instrument demonstrated an undesirable formation of NO as a co-product. Caused by the NEDA and pH dependencies observed for the Saltzman factor it is proposed that NO⁺ formed by Reactions (R2) and (R6) can also react with NEDA to generate NO:



Based on the undesirable NO formation and the possible future extension of the instrument for NO detection, the NEDA concentration should not be too high and is limited here to $\leq 1 \text{ g l}^{-1}$.

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Variation of the sulphanilamide concentration

Whereas the concentration of sulphanilamide has almost no effect on the sampling efficiency of NO_2 , an increasing Saltzman factor is observed for increasing sulphanilamide concentration (Fig. 4).

This behaviour can be explained by a NEDA limited uptake of NO_2 by Reaction (R6), and a sulphanilamide limited further conversion of HONO into the diazonium salt via Reactions (R2) and (R3). It is proposed that the relative high pH used leads to slow kinetics of Reactions (R2) and (R3) and thus, the low Saltzman factor can be explained by the secondary Reaction (R7). With increasing sulphanilamide concentration, the rate of Reaction (R3) increases and parallel Reaction (R7) becomes of minor importance. Caused by the maximum solubility of sulphanilamide in water, only concentrations up to 7.5 g l^{-1} were studied here. However, the solubility can be increased by the addition of higher concentrations of acetic acid. In the present study 7 g l^{-1} sulfanilamide in 84 g l^{-1} acetic acid is finally used.

The optimized composition of the Griess-Saltzman solution is summarized in Table 1.

3.1.2 Improvement of the sampling conditions

Length of the stripping-coil

Stripping coils with different lengths were used (10, 20, 25 turns, 22 mm average turn diameter, 2.4 mm i.d.), which were similar to those used in the previous HONO- and HNO_3 -LOPAP instruments (Kleffmann et al., 2002, 2007). Due to the slow uptake of NO_2 only the longest coil could be used for NO_2 . Furthermore, because high NEDA concentrations were not applied (see Sect. 3.1.1), the maximum sampling efficiency obtained with the longest coil was only 95%. In addition, caused by the low gas flow applied, high volume of sampling reagent accumulated in the stripping coil leading to a lower time resolution of the instrument. Thus, a new coil with smaller inner diameter, higher surface to volume (S/V) ratio and higher gas velocity was used in order to

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improve the sampling efficiency and time resolution. This new coil with 24 turns, 35 mm average turn diameter and 1.6 mm inner diameter, increases the sampling efficiency to 97% and leads to a better time resolution.

Variation of the sampling temperature

- 5 The temperature was varied in the range 5–30 °C. Only a small increase of the sampling efficiency and a minor decrease of the Saltzman factor were observed with increasing temperature. For practical reasons a sampling temperature of 15 °C was chosen to avoid condensation of water in the gas line to the instrument.

Variation of the liquid flow

- 10 The variation of the liquid flow has only a slight effect on the sampling efficiency and the Saltzman factor for values $> 0.1 \text{ ml min}^{-1}$. This can be explained by a surface limited uptake of NO_2 by which the fast Reaction (R6), see Sect. 3.1.3 ($k_{\text{NO}_2+\text{NEDA}} = (3.6 \pm 1.6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and the low solubility of NO_2 leads to a liquid diffusion limited uptake of NO_2 . In contrast, for a limitation of the NO_2 uptake by any slow reaction
- 15 in the liquid phase the sampling efficiency should increase with increasing liquid flow. Caused by the missing liquid flow dependency, the time resolution and the sensitivity of the instrument can be varied by the liquid flow without influencing other parameters.

Variation of the gas flow

- 20 The gas flow variation has a strong effect on the Sampling efficiency but not on the Saltzman factor. The variation of the sampling efficiency can be well described by a first order uptake kinetics of Reaction (R6), which is expected for a heterogeneous multiphase reaction, which is limited by the low solubility and the liquid phase diffusion of NO_2 (see Sect. 3.1.3). In contrast, the Saltzman factor is only affected by the slower consecutive chemistry in the liquid phase, which is dependent only on the composition

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of the sampling solution, but not on the gas/liquid contact time. Based on all the observations described up to now, a surface limited NO_2 uptake is proposed, which is improved by increasing the S/V ratio of the stripping coil and increasing the gas/liquid contact time. Thus, a maximum gas flow of only 0.5 l min^{-1} is recommended for the used stripping coils (see Table 2).

3.1.3 Determination of the liquid phase rate coefficient of $\text{NO}_{2(\text{lq})} + \text{NEDA}_{(\text{lq})}$

In order to calculate the second order rate coefficient of the liquid-phase reaction between NO_2 and NEDA, reactive uptake coefficients (γ_{NO_2}) of NO_2 were determined for the applied stripping coil. The reactive uptake coefficient is the probability of the permanent uptake of a molecule that hits the liquid surface and can be limited by several processes such as gas phase diffusion, mass accommodation (α), solubility, liquid diffusion and reaction in the liquid phase. Gas phase diffusion limitation will be of minor importance for the observed uptake coefficients even for laminar flow (Murphy and Fahey, 1987) and can be further neglected caused by the turbulent flow conditions in a stripping coil. The independence of γ_{NO_2} on the liquid flow (see above), the linear dependence of γ_{NO_2} with the square root of the NEDA concentration (see Fig. 5) and the known low solubility of NO_2 in water shows that the uptake is limited by diffusion in the liquid phase. Similar to the study of Ammann et al. (2005) the second order rate constant $k_{\text{NO}_2+\text{NEDA}}$ can be calculated from the slope of a plot of γ_{NO_2} against $[\text{NEDA}]^{1/2}$ according to Eq. (2):

$$\gamma_{\text{NO}_2} = \frac{4 \times H_{\text{NO}_2} \times R \times T \times \sqrt{k_{\text{NO}_2+\text{NEDA}} \times [\text{NEDA}] \times D_{\text{NO}_2}}}{\langle c \rangle}, \quad (2)$$

in which H_{NO_2} is the NO_2 Henry's law constant ($1.6 \times 10^{-2} \text{ M atm}^{-1}$ at 288 K, calculated using the expression from Squadrito and Postlethwait, 2009), $\langle c \rangle$ is the mean thermal molecular velocity (364 m s^{-1} at 288 K), R is the gas constant ($8.314 \text{ J M}^{-1} \text{ K}^{-1}$), T the

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temperature and D_{NO_2} is the aqueous phase diffusion coefficient ($1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 288 K, Cheung et al., 2000; Komiyama and Inoue, 1980). From the slope of the plot shown in Fig. 5 a rate coefficient $k_{\text{NO}_2+\text{NEDA}} = (3.6 \pm 1.6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ has been determined using Eq. (2).

5 A similar value of $k_{\text{NO}_2+\text{NEDA}}$ was also determined using higher concentrations of sulphanilamide (10 g l^{-1}) and acetic acid (158 g l^{-1}). Accordingly, it is proposed that the reaction only depends on the NEDA concentration.

From the intercept of the linear regression in Fig. 5 a NO_2 uptake coefficient (γ_{NO_2}) on the used acetic acid/sulphanilamide solution of 7×10^{-7} has been derived, which is slightly higher than the value of $\sim 10^{-7}$ reported for the uptake of NO_2 on pure water by Ammann et al. (2005).

3.1.4 Instrument parameters

The detection limit, the response time, i.e. the time the instrument needs to rise from 10% to 90% of the full signal and the measurement range of the LOPAP instrument are strongly dependent on several factors such as (a) the sample gas flow rate, (b) the liquid flow rate, and (c) the length of the absorption tubes.

The theoretical sensitivity of the instrument will increase linearly with the gas flow rate and/or the absorption lengths as well as by decreasing the liquid flow rate. In practice, these parameters are limited, e.g. by a decreasing NO_2 sampling efficiency with increasing gas flow rate, so that up to now the air flow is limited to 0.5 l min^{-1} . Light intensity as well as time resolution decrease when the absorption path length is increased, so that a maximum length of 6 m can be used (Kleffmann and Wiesen, 2008). However so far, only optical path lengths of 1.4 and 2.4 m have been applied in the present study. The sensitivity can be increased by decreasing the liquid flow, however, the time resolution of the instrument is then reduced. For the applied liquid flows of the sampling reagent ($0.2\text{--}0.4 \text{ ml min}^{-1}$) and the length of the absorption tubes (1.4–2.4 m) the time resolution is in the range 3–6 min. With an optical path length of

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2.4 m and a liquid flow of 0.4 ml min^{-1} a time resolution of $\sim 3 \text{ min}$ and a detection limit of $\sim 2 \text{ pptv}$ is obtained. The detection limit is defined in the present study as two times the value of the standard deviation of the zero-air signal.

Since the lower limit of the measurement range is set by appropriate values of the above mentioned parameters, the upper limit of the measurement range can also be shifted during the data evaluation by shifting the absorption wavelength (λ_{abs}) during the evaluation of the stored spectra. While highest sensitivity is obtained at the maximum absorption ($\lambda_{\text{abs}} = \sim 540 \text{ nm}$), the measurement range is expanded by more than one order of magnitude by shifting the absorption wavelength into the wings of the absorption band (e.g. $\lambda_{\text{abs}} = 600 \text{ nm}$). Thus, with an absorption length of 1.4 m, NO_2 concentrations up to 300 ppbv can be measured. The precision of the instrument is defined in this study as the minimum detectable change of a measured signal and amounts to approximately 0.5% of the measured values (Fig. 6). The accuracy is obtained from the sum of all relative errors of $\sim 10\%$ and the value the detection limit. The instrument parameters of the NO_2 -LOPAP are summarized in Table 2.

With the HONO-LOPAP instrument recently an optical length of 6 m was applied and thus a detection limit of only 0.2 pptv was reached for HONO (Kleffmann and Wiesen, 2008). Since the gas flow used for the NO_2 instrument is ca. a factor of three smaller than that used for the HONO instrument, a minimum NO_2 detection limit $< 1 \text{ pptv}$ can be expected in the future for a time resolution of 8 min.

3.2 Calibration

The LOPAP instrument shows a linear response with the NO_2 concentration for the entire measuring range (Fig. 7). Also for the calibration by liquid nitrite standards diluted in the Griess-Saltzman sampling solution a good linearity was obtained up to nitrite concentrations of 0.1 mg l^{-1} . For higher nitrite concentrations non-linearity of the calibration was observed caused by losses, probably through the secondary Reaction (R7).

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Caused by the linear response, the NO_2 instrument can be calibrated simply by a two point calibration (zero air + calibration) with commercial available nitrite standards (accuracy $\pm 1\%$) and by determination of the flow rates of the gas phase and of the stripping solution. This is a significant simplification in comparison with other NO_2 instruments, which usually are calibrated using NO_2 calibration gas mixtures. These mixtures are known to have a low long-term stability. In addition, significant deviations from the concentrations specified by manufacturer are often observed. Alternatively, more stable NO calibration gas mixtures and ozone titration is used for commercial NO_2 instruments, for which, however, an additional titration unit is necessary.

3.3 Interferences

In this section the interferences are specified as the interference signal measured as NO_2 divided by the mixing ratio of the interfering compound in % ($= 100 \times \text{signal NO}_2 \text{ pptv/compound pptv}$). The interferences are listed in Table 3, either as interference in Channel 1 as defined above, or as “real interference” after subtraction of Channel 2 from Channel 1. All values given in this section correspond to a gas flow rate of 0.5 l min^{-1} , a liquid flow rate of 0.4 ml min^{-1} and a temperature of 15°C . It is important to note that Channel 1 measures the sum of 97% of the NO_2 plus potential interferences, while in Channel 2 3% of the NO_2 plus interferences are determined. Assuming a small uptake of interfering compounds, their concentrations are almost constant in both coils, thus, the difference between the two channels corrected for the sampling efficiency of NO_2 and the loss in the HONO/ O_3 scrubber gives a measure of the true NO_2 concentration.

3.3.1 HONO interference

A well known interference for the Griess-Saltzman method is ambient HONO (Milani and Dasgupta, 2001), which is also formed during NO_2 detection as an intermediate in the Griess-Saltzman solution, Reaction (R6). Therefore an upstream stripping

coil (“HONO/O₃ Scrubber”) is placed in the NO₂ instrument, which is operated with a solution of sulphanilamide in acetic acid (sulphanilamide 10 g l⁻¹, potassium indigo-trisulphonate 0.6 g l⁻¹, acetic acid 158 g l⁻¹). Acidic sulphanilamide solutions were already used as efficient HONO sampling solution in the HONO-LOPAP instrument (sampling efficiency > 99%) (Heland et al., 2001; Kleffmann et al., 2002, 2006). The HONO interference was tested with a pure HONO source, which is described in detail elsewhere (Kleffmann et al., 2004). A minimum interference of 0.092 ± 0.090% could be observed in Channel 1, which is in good agreement with results from the HONO-LOPAP instrument. On the other hand, no interference could be observed in Channel 2, which can be explained by the high sampling efficiency of HONO in Channel 1 of the NO₂ instrument. The remaining real HONO interference of ca. 0.1% represents even an upper limit, since the HONO source still could generate traces of NO₂. In addition, even if true, the HONO interference can be completely neglected for typical HONO/NO₂ ratios of < 10% in the atmosphere.

3.3.2 Ozone interference

The ozone interference was tested with pure ozone mixtures, which were generated by the irradiation of pure O₂ with an Hg lamp (Pen-ray) and dilution with synthetic air. Without the HONO/O₃ scrubber, a relatively large ozone interference (ca. 1%) could be observed in Channel 1 (see Fig. 8), which can be explained by the oxidation of NEDA and the change in the absorption of the Griess-Saltzman solution. In Channel 2 there is no signal due to complete uptake of ozone in Channel 1, so that the ozone interference could not be corrected by the two channel system. Initially, the value of 1% seemed to be small; however, measurements in remote regions, in which the ozone concentration can be up to three orders of magnitude higher than those of NO₂, would be strongly affected by this ozone interference. Therefore, it was necessary to efficiently remove ozone through the addition of a suitable reagent to the HONO/O₃ scrubber solution.

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First tests with addition of potassium iodide (KI) to the HONO/O₃ scrubber solution were not successful, since I₂ was formed in the reaction with O₃, which partly degassed from the HONO/O₃ scrubber leading to additional light absorption and interference in Channel 1 of the instrument.

Alternatively, Indigo solution has been used for quantitative detection of O₃ in aqueous solutions (Bader and Hoigné, 1981). Therefore, potassium Indigo-trisulphonate was chosen as scrubber solution and the ozone interference was tested as function of the Indigo concentration. A strong decrease of the O₃ interference with increasing Indigo concentration is observed (Fig. 8). With an Indigo concentration of 0.6 g l⁻¹ an ozone interference of only 0.006% was observed. This interference is so low that even in clean air regions with very large O₃/NO₂ ratios only small corrections are necessary. Similar to HONO, the ozone uptake in the HONO/O₃ scrubber is independent of the liquid flow, so that for the routine operation of the NO₂ instrument only small liquid flow rates (0.05 ml min⁻¹) of the scrubber solution are necessary. As HONO/O₃ scrubber solution a mixture of sulphanilamide (10 g l⁻¹) and Indigo trisulphonate (0.6 g l⁻¹) in acetic acid (158 g l⁻¹) was selected. However, with this scrubber solution NO₂ uptake of 4% was determined, which needs to be corrected during the data evaluation.

Beside HONO and O₃, further interferences were tested in the laboratory in a 1080 l smog chamber and are listed in Table 3. All interferences tested can be neglected under atmospheric conditions.

3.4 Validation of the new instrument

3.4.1 Intercomparison in the atmosphere

During the period 10–13 March 2007 an intercomparison campaign of the new NO₂-LOPAP instrument was carried out with a commercial chemiluminescence instrument (ECO-Physics: AL 770 ppt/PLC 760) at the University of Wuppertal. The commercial

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instrument was equipped with a photolytic converter for the selective detection of NO_2 . For small to medium pollutant concentrations good agreement with the DOAS technique was observed for this instrument (Kurtenbach et al., 2001). Only for very high pollutant concentrations, as they arise in traffic tunnels, at kerbside stations or in laboratory and smog chamber studies, this instrument exhibits negative interferences, which are caused by photochemical reactions in the photolytic converter (Kurtenbach et al., 2001; Kleffmann et al., 2001; Bejan et al., 2006; Villena et al., 2011). However, for the relatively low pollutant concentrations arising during the intercomparison campaign these interferences were neglected. The sampling site was on the balcony of the 5th floor of a building of the University of Wuppertal.

During all the period of the intercomparison, very good agreement was observed between both instruments in terms of absolute concentrations (see Figs. 9, 10) and temporal variation of the concentration (Fig. 9). Only for very fast variations of the NO_2 concentration deviations were observed due to the smaller time resolution of the LOPAP instrument (e.g., Fig. 9, ca. 10:00 and ca. 12:15 LT). Furthermore, it is well-known that due to the temporally shifted measurements of NO and NO_x with the one channel ECO Physics instrument, short term variations of pollutants often lead to unrealistic strong concentration peaks for this instrument. From a correlation plot of the 5 min averaged data a mean deviation between both instruments of only 2% has been determined (Fig. 10), which is clearly within the errors of both methods. In conclusion, the LOPAP instrument could be successfully validated in the atmosphere under moderately polluted conditions with the help of a commercial chemiluminescence instrument with photolytic converter.

The LOPAP instrument was used as a two channel system for the correction of unknown interferences during the intercomparison campaign. However, during the whole campaign, only a small signal in the interference channel (Channel 2) was observed, which corresponded exactly to the loss of NO_2 from Channel 1 caused by the sampling efficiency of the instrument. During this campaign the instrument had a sampling efficiency of $95 \pm 1\%$ (old stripping coil) and an average value of the ratio Channel

2/Channel 1 of $4.7 \pm 1.2\%$ was determined. Thus, in between the experimental errors no interferences could be observed in the real atmosphere.

3.4.2 Intercomparison in a smog chamber

Besides the intercomparison in the atmosphere the new NO_2 -LOPAP was also compared with the spectroscopic FTIR technique under complex photosmog conditions in a 1080 l smog chamber whose detailed description can be found elsewhere (Barnes et al., 1994). In this experiment a mixture of NO and different hydrocarbons was irradiated with UV light, leading to a conversion of NO into NO_2 by O_3 photochemically formed. Also in these experiments excellent agreement was observed between both instruments, whereas three other commercial instruments showed significant positive (luminescence technique) and negative (chemiluminescence technique with photolytic converter) interferences. The deviation between the NO_2 -LOPAP and the FTIR was < 4 ppbv for a NO_2 concentration range 0–135 ppbv, which is within the experimental errors of both instruments (DL of the FTIR ca. 4 ppbv). Details of this intercomparison will be presented elsewhere (Villena et al., 2011). Similar to the field intercomparison, the signal in Channel 2 of the instrument again exactly represented the loss of NO_2 from Channel 1 caused by the sampling efficiency, which was 97% in the smog chamber experiments. If these results are also confirmed for remote measurement conditions, the NO_2 -LOPAP instrument could be designed as an even simpler one channel instrument in the future.

4 Conclusions

A new instrument for the sensitive measurement of NO_2 by wet sampling and photometric detection has been developed and successfully tested. The instrument shows a linear response with a measurement range from the detection limit up to 300 ppbv, which can be calibrated absolutely by commercial nitrite standards. The instrument

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has a detection limit of 2 pptv for a time resolution of 3 min, which can be further reduced to < 1 pptv for lower time resolution. Known interferences against O₃ and HONO were successfully suppressed by an additional scrubber for both gases. All other interferences tested can be neglected, both, in the atmosphere but also under complex conditions in a smog chamber. The instrument was validated by intercomparison with a commercial chemiluminescence instrument with photolytic NO₂ converter in an urban atmosphere and with the FTIR technique in a smog chamber. Excellent agreement was obtained under all conditions applied.

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**Table 1.** Optimized composition of the Griess-Saltzman reagent (pH = 3).

Reagent	conc. [g l^{-1}]
N-(1-naphtyl)ethylenediamine dihydrochloride (NEDA)	1
sulphanilamide	7
acetic acid	84
NH_3 (25%)	3

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Table 2. Summary of the parameters of the NO₂-LOPAP instrument.

parameters:	
air flow	0.5 l min ⁻¹
liquid flow (stripping solution)	0.2–0.4 ml min ⁻¹
absorption path length	1.4/2.4 m (0.1–6 m possible)
range of λ_{abs}	550–610 nm
sampling efficiency	97%
measurement range	0.002–300 ppbv
time resolution (10–90%)	≈ 3–6 min
precision	±(0.5% + DL)
accuracy	±(10% + DL)
detection limit (DL)	2 pptv (3 min time resolution)

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Table 3. Summary of the interferences tested for the NO₂-LOPAP instrument.

component	interference Ch1 [%]	real interference Ch1-Ch 2 [%]
ozone	0.0057 ± (0.0005)	0.0058 ± (0.0007)
H ₂ O ₂	0.0044 ± 0.0002	0.0040 ± 0.0002
HONO	0.092 ± 0.090	0.088 ± 0.081
PAN	< 0.48	< 0.48
3-methyl-2-nitrophenol	< 0.0006	< 0.0006
2-nitrotoluene	< 0.00001	< 0.00001
glyoxal (+ NO _x)	< 0.11	< 0.11
toluene (+ NO _x)	< 0.04	< 0.04
α-pinene (+ NO _x)	< 0.06	< 0.06
n-butane (+ NO _x)	< 0.04	< 0.04
propene (+ NO _x + H ₂ O ₂)	< 0.01	< 0.01
Complex photo-smog mixture (irradiation of NO _x , glyoxal, n-butane, α-pinene, toluene), NO ₂ max. = 135 ppbv	deviation < 4 ppbv (DL of the FTIR)	deviation < 4 ppbv (DL of the FTIR)

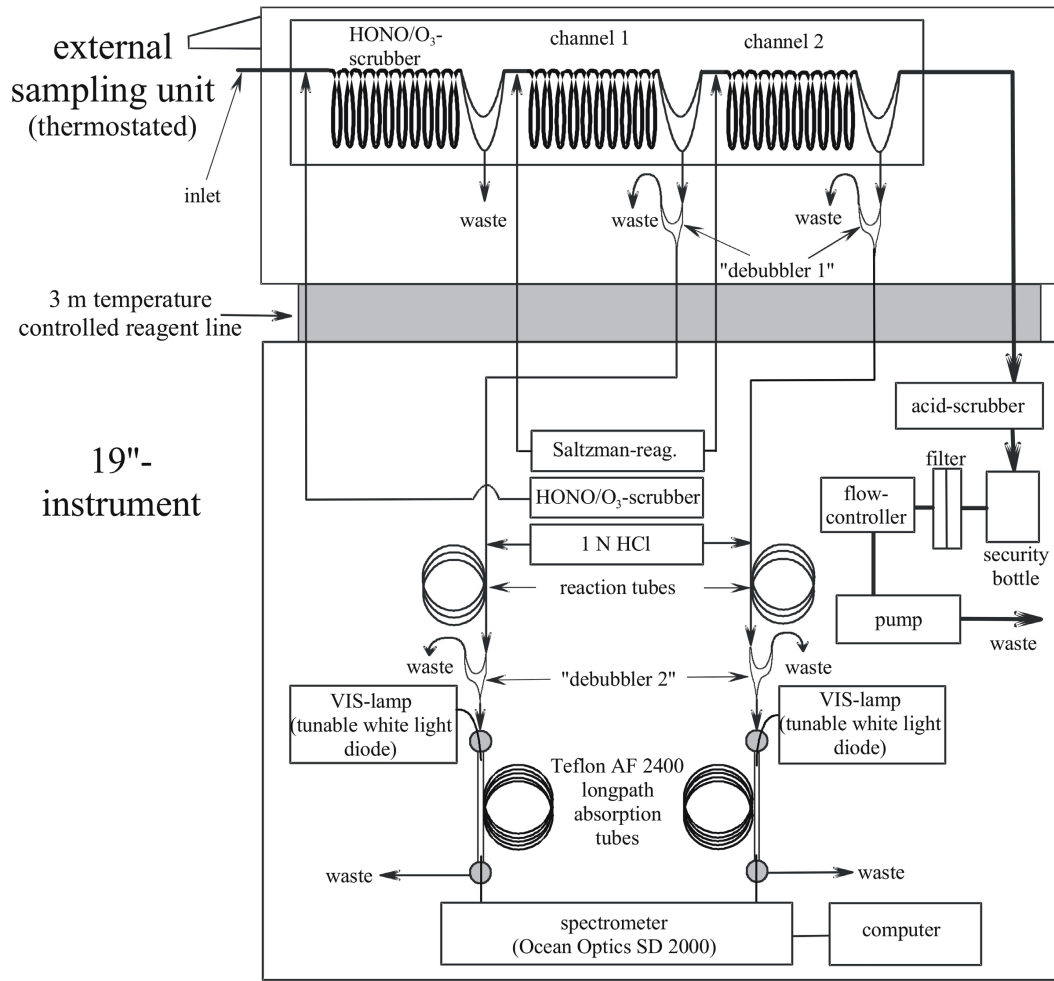


Fig. 1. Schematic setup of the NO_2 -LOPAP instrument.

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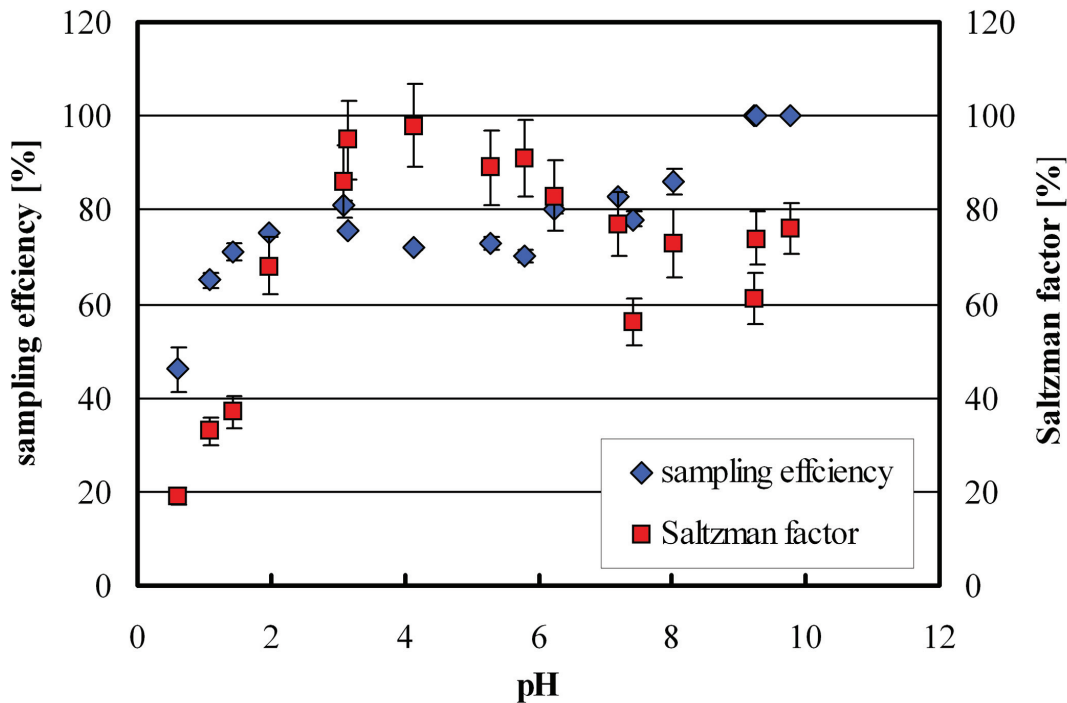


Fig. 2. Variation of the sampling efficiency and the Saltzman factor with the pH. Griess-Saltzman reagent: 1 g l^{-1} NEDA, 5 g l^{-1} sulphanilamide, 7.2 g l^{-1} HCl was used here instead of acetic acid, pH adjusted by the addition of NH_3 . Air flow = 1000 ml min^{-1} , liquid flow = 0.27 ml min^{-1} .

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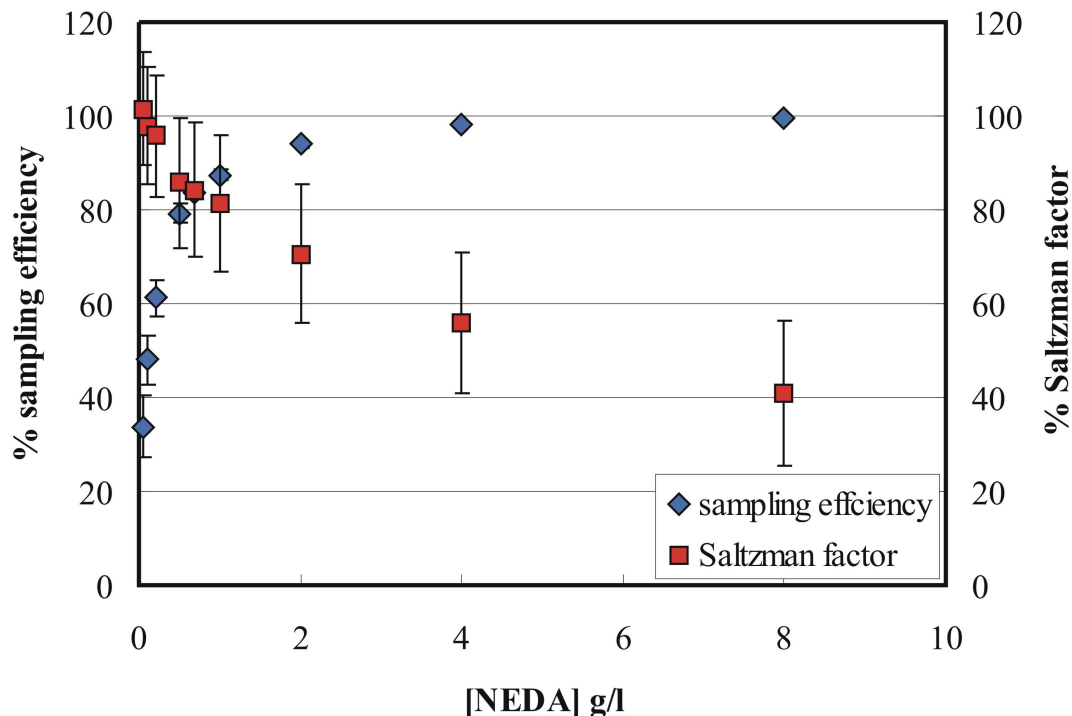


Fig. 3. Variation of the sampling efficiency and the Saltzman factor with the NEDA concentration. Griess-Saltzman reagent: 7 g l^{-1} sulphanilamide, 84 g l^{-1} acetic acid, $\text{pH} = 3$, adjusted with NH_3 . Air flow = 650 ml min^{-1} , liquid flow = 0.35 ml min^{-1} .

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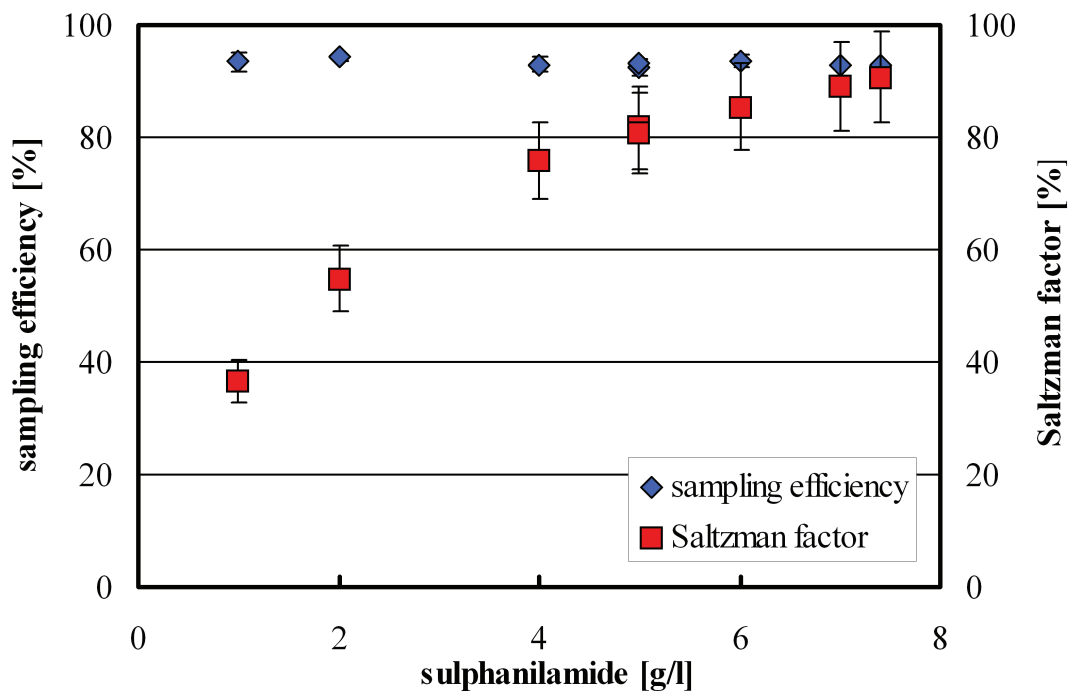


Fig. 4. Variation of the sampling efficiency and the Saltzman factor with the sulphanilamide concentration. Griess-Saltzman Reagent: 1.6 g l^{-1} NEDA, $\text{pH} = 3$, adjusted with NH_3 . Air flow = 1000 ml min^{-1} , liquid flow = 0.2 ml min^{-1} .

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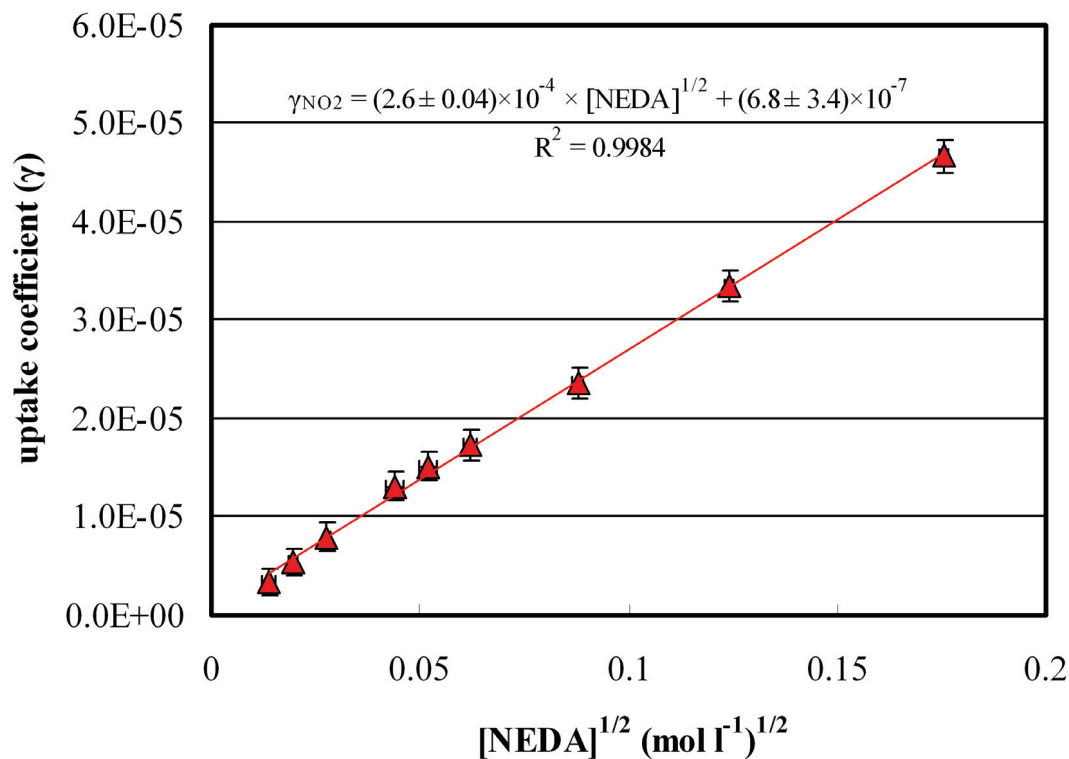


Fig. 5. NO_2 uptake coefficients as a function of $[\text{NEDA}]^{1/2}$ at 288 K. Griess-Saltzman Reagent: 7 g l^{-1} sulphanilamide, 84 g l^{-1} acetic acid, $\text{pH} = 3$, adjusted with NH_3 . Air flow = 650 ml min^{-1} , liquid flow = 0.35 ml min^{-1} .

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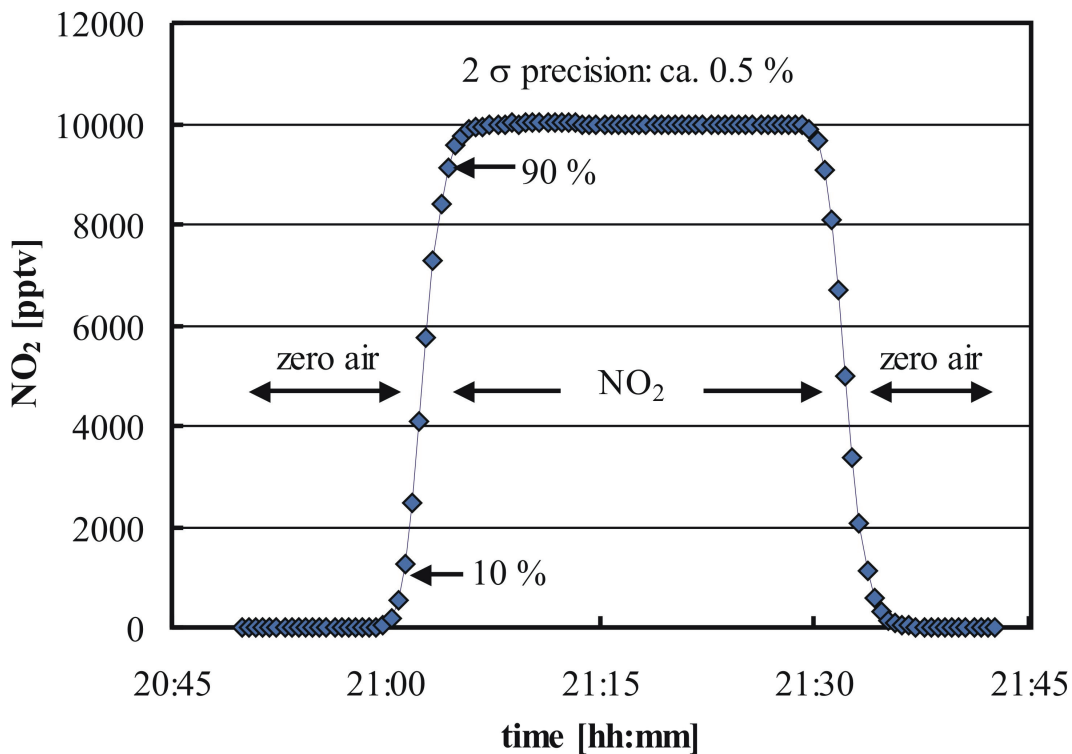


Fig. 6. Time resolution (3 min) and precision (2σ , 0.5%) of the NO_2 -LOPAP instrument using recommended sampling solution (see Table 1) and instrument parameters (see Table 2, liquid flow = 0.35 ml min^{-1}).

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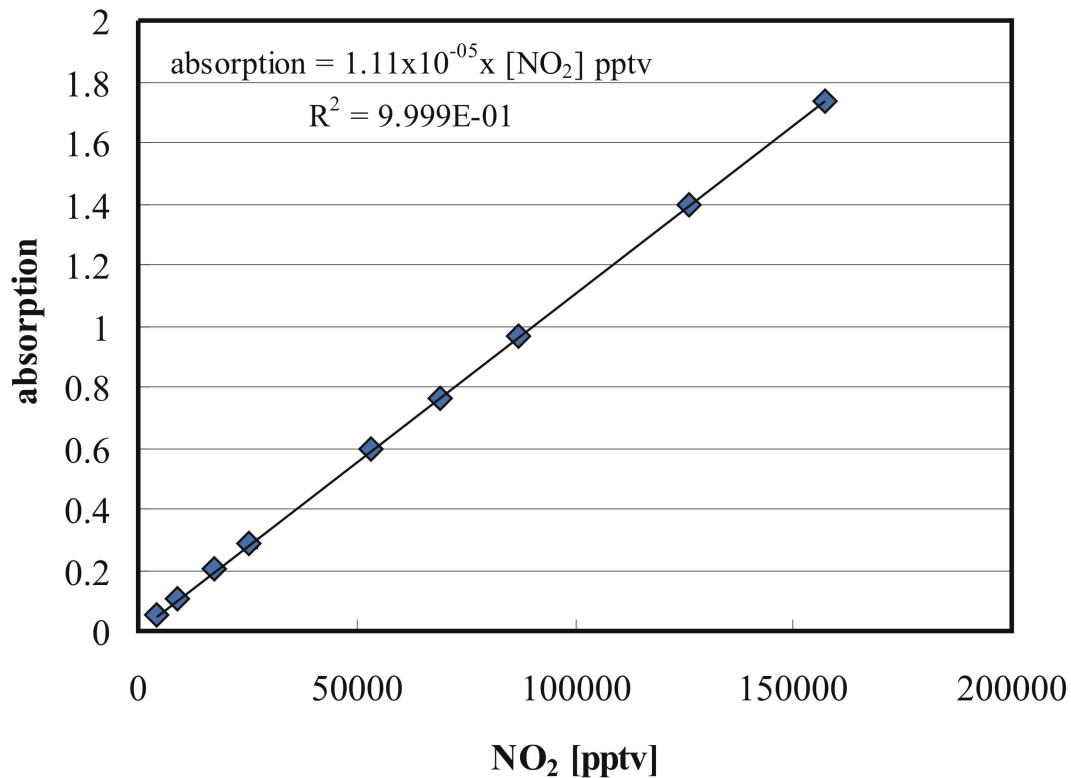


Fig. 7. NO₂ concentration dependency of the LOPAP signal using recommended sampling solution (see Table 1) and instrument parameters (see Table 2, liquid flow = 0.35 ml min⁻¹).

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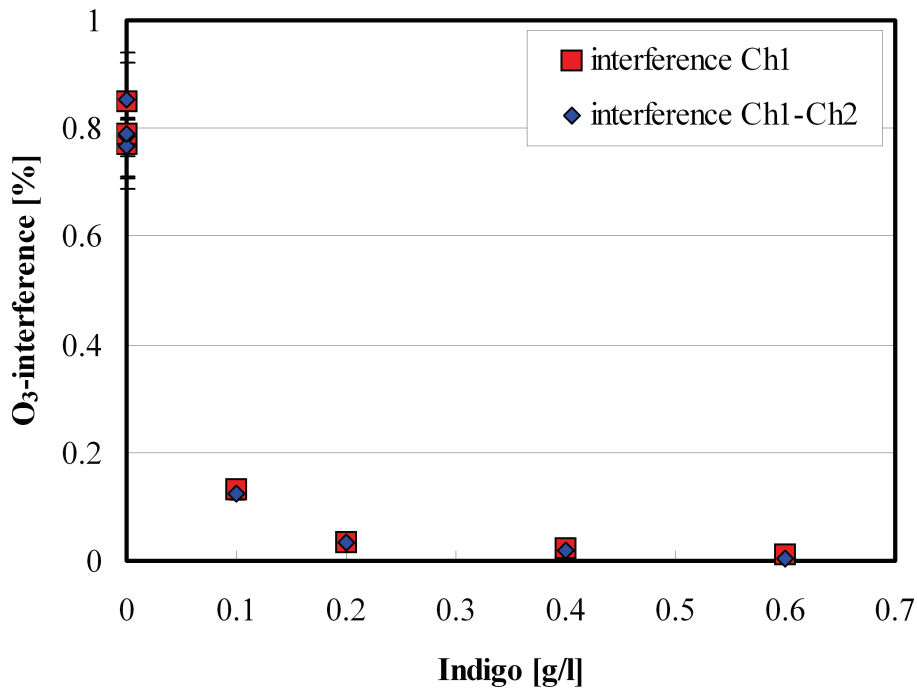


Fig. 8. O₃ interference as a function of Indigo concentration ([O₃] = 240 ppbv).

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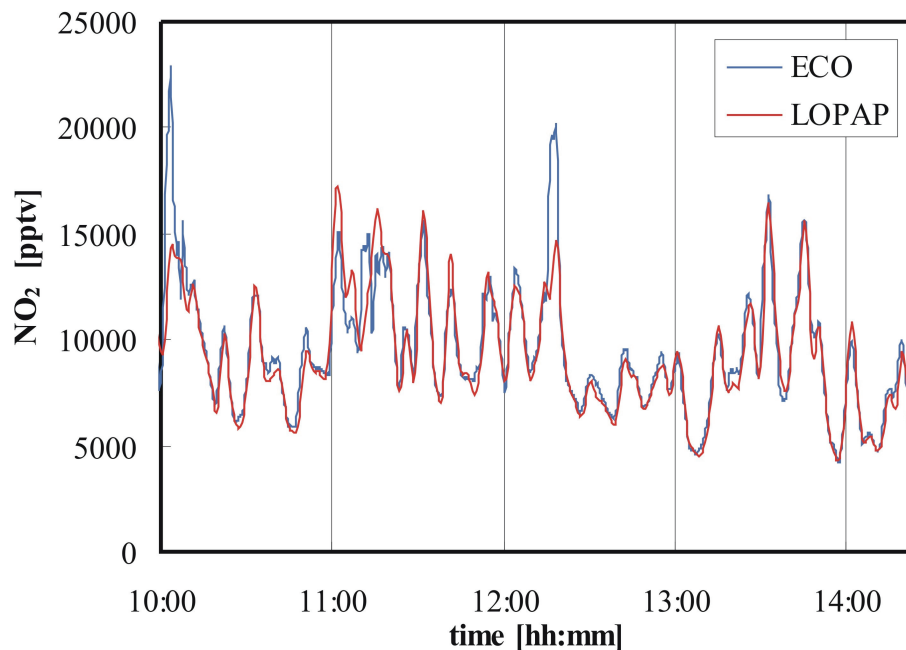


Fig. 9. Selected time interval of the NO₂ concentrations measured with the NO₂-LOPAP and the Eco-Physics instruments during the ambient intercomparison campaign at the University of Wuppertal.

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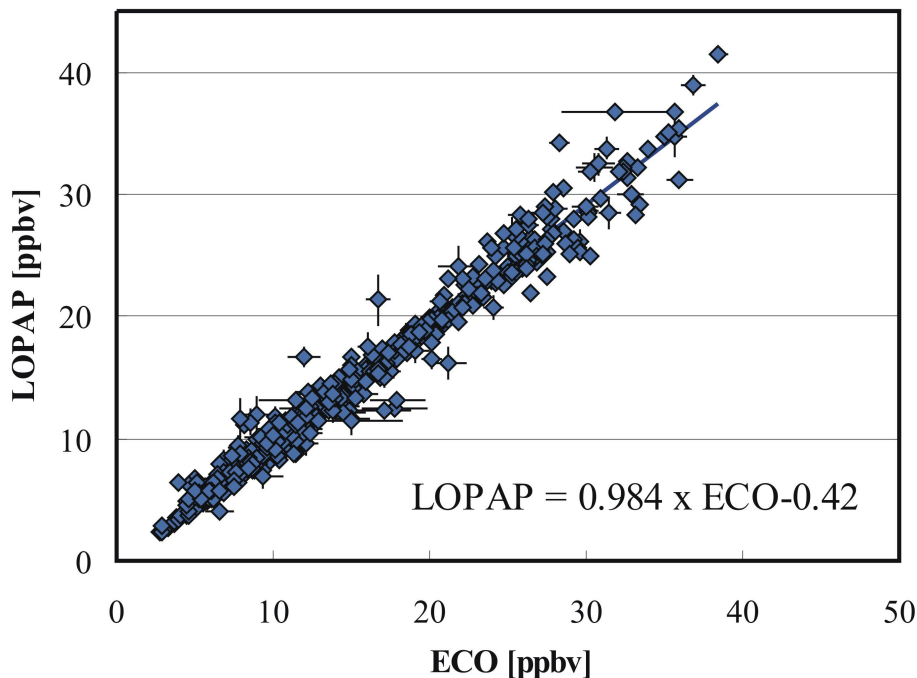


Fig. 10. Correlation of all 5 min averaged NO_2 data of the NO_2 -LOPAP against the Eco-Physics instrument. The error bars represent only the precision of the instruments. A weighted orthogonal regression analysis was used, for which the errors of both instruments were considered (Brauers and Finlayson-Pitts, 1997).

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