



# Interferences of commercial NO<sub>2</sub> instruments in the urban atmosphere and in a smog chamber

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**Abstract.** Reliable measurements of atmospheric trace gases are necessary for both, a better understanding of the chemical processes occurring in the atmosphere, and for the validation of model predictions. Nitrogen dioxide (NO<sub>2</sub>) is a toxic gas and is thus a regulated air pollutant. Besides, it is of major importance for the oxidation capacity of the atmosphere and plays a pivotal role in the formation of ozone and acid precipitation. Detection of NO<sub>2</sub> is a difficult task since many of the different commercial techniques used are affected by interferences. The chemiluminescence instruments that are used for indirect NO<sub>2</sub> detection in monitoring networks and smog chambers use either molybdenum or photolytic converters and are affected by either positive (NO<sub>y</sub>) or negative interferences (radical formation in the photolytic converter). Erroneous conclusions on NO<sub>2</sub> can be drawn if these interferences are not taken into consideration. In the present study, NO<sub>2</sub> measurements in the urban atmosphere, in a road traffic tunnel and in a smog-chamber using different commercial techniques, i.e. chemiluminescence instruments with molybdenum or photolytic converters, a Luminol based instrument and a new NO<sub>2</sub>-LOPAP, were compared with spectroscopic techniques, i.e. DOAS and FTIR. Interferences of the different instruments observed during atmospheric measurements were partly characterised in more detail in the smog chamber experiments. Whereas all the commercial instruments showed strong interferences, excellent agreement was obtained between a new NO<sub>2</sub>-LOPAP instrument and the FTIR technique for the measurements performed in the smog chamber.

## 1 Introduction

Despite their relatively low concentration, nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) play a crucial role in tropospheric chemistry. NO<sub>2</sub> affects the oxidation capacity of the atmosphere through its direct participation in the formation of ozone (O<sub>3</sub>) 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<sub>2</sub> also limits radical concentrations in the polluted atmosphere. NO<sub>2</sub> contributes to acid precipitation and formation of other atmospheric oxidants such as the nitrate radical (NO<sub>3</sub>) (Crutzen, 1979; Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 2006).

Due to the impact of NO<sub>2</sub> on air quality and its associated health impacts on both, short term and long-term exposures of the population (Brunekreef, 2001; Van Strien et al., 2004; Jarvis et al., 2005), the European Union (EU) has formulated different legislative frameworks in order to assess and manage air quality and to control the pollutants released in vehicle exhaust (Villena et al., 2011 and references therein). Within the framework of directive EC/2008/50 (EU, 2008) a mean annual limit value for NO<sub>2</sub> of 40 µg m<sup>-3</sup> was adopted in the European Union on 1 January 2010, however, this limit is typically exceeded under urban conditions in many European countries.

Many direct or indirect techniques have been developed for measuring NO<sub>2</sub> in the laboratory and/or in the field. Spectroscopic methods, for example, Differential Optical Absorption Spectroscopy (DOAS), Laser Induced Fluorescence (LIF), Cavity Ring Down Spectroscopy (CRDS) and

Resonance Enhanced MultiPhoton Ionisation (REMPI), have been used for selective NO<sub>2</sub> detection (Villena et al., 2011 and references therein). Although some of the methods have very low detection limits (e.g. REMPI, LIF), most techniques require considerable operational expertise, are expensive and have complex system components.

Thus, the most widely used technique, and at the same time the reference method recommended by the US EPA (Demerjian, 2000) and by European legislation (European Standard, EN 14211, 2005) for the measurement of NO<sub>2</sub> in monitoring networks is the chemiluminescence technique. This method involves the reduction of NO<sub>2</sub> to NO using heated (300–350 °C) molybdenum (Mo) surfaces followed by the gas-phase reaction between NO and O<sub>3</sub> (R 1) forming an electronically excited NO<sub>2</sub><sup>\*</sup> molecule that emits light (R 2), which is proportional to the NO concentration (Fontjin et al., 1970; Ridley and Howlett, 1974).



Photolytic conversion of NO<sub>2</sub> into NO, using either Xenon lamps or UV emitting diodes (“blue light converters”), followed by detection of the chemiluminescence from the reaction of NO with O<sub>3</sub> are also used (R 3) (Kley and McFarland, 1980; Ryerson et al., 2000; Sadanaga et al., 2010).



Another commonly used technique is the luminol-chemiluminescence method, which employs the reaction between NO<sub>2</sub> and an alkaline solution of luminol resulting in light emission (Wendel et al., 1983).

In the present study, the performances of different commercial NO<sub>2</sub> instruments and a new NO<sub>2</sub>-LOPAP (Long Path Absorption Photometer; Villena et al., 2011) were intercompared with those of spectroscopic techniques using measurements made in the urban atmosphere, in a road traffic tunnel and in a smog chamber in order to better understand the sources and nature of the interferences affecting the different methods typically employed.

## 2 Experimental

### 2.1 Intercomparison measurement sites

#### 2.1.1 Santiago de Chile

In a field campaign in Santiago de Chile a chemiluminescence instrument with molybdenum converter for NO<sub>2</sub> (TELEDYNE) was intercompared with the optical DOAS technique in March 2005. The DOAS system (OP SIS, Model AR 500) had an optical path length of 453 m, a time resolution of 2 min and a detection limit (DL) of 0.5 ppbv.

The DOAS system and the TELEDYNE instrument were installed in the same building at the University of Santiago de Chile. The heights of the DOAS light path and of the inlet for the monitor were 10 m and 8 m above the ground, respectively. Details of this campaign are given elsewhere (Elshorbany et al., 2009).

#### 2.1.2 Road traffic tunnel

The chemiluminescence technique using photolytic conversion of NO<sub>2</sub> (ECO Physics) was intercompared with the DOAS technique in the “Kiesberg” road traffic tunnel in Wuppertal, Germany, in August 1999. The DOAS system had an optical path length of 720 m, a time resolution of a few min and a detection limit in the low ppbv range. The inlet of the in-situ monitor was co-located with the open White multi reflection system used for the DOAS. Details of this campaign are given elsewhere (Kurtenbach et al., 2001).

#### 2.1.3 Street canyon

Three different chemiluminescence instruments (ECO Physics, Ansyco Mo, Ansyco blue light) and the NO<sub>2</sub>-LOPAP were intercompared during two days in May 2008 at a measurement container at a main street (B7) in Wuppertal, Germany. The container is located in the middle of the four lanes of the street and is used for routine measurements of NO<sub>x</sub>, O<sub>3</sub> and particle (PM<sub>10</sub>) concentrations. Samples are collected at 3 m altitude at high volume flow (~100 l min<sup>-1</sup>) by a common glass manifold, to which all NO<sub>2</sub> instruments were connected.

#### 2.1.4 1080 l smog chamber

Besides the intercomparison in the atmosphere, different commercial chemiluminescence instruments using photolytic converters (ECO-Physics with Xenon lamp converter and Ansyco with blue light converter) and the luminol chemiluminescence technique were intercompared with a new NO<sub>2</sub>-LOPAP and with the spectroscopic FTIR technique (Nicolet NEXUS) under complex photo-smog conditions in a 1080 l quartz glass smog-chamber. The smog-chamber is equipped with a 474 ± 0.7 m optical long path White system for the infrared beam. The DL of the FTIR for NO<sub>2</sub> was ~4 ppbv during the campaign. A detailed description of the smog-chamber can be found elsewhere (Barnes et al., 1994).

During the intercomparison all the commercial instruments were connected to the smog chamber by a 4 mm i.d. PFA line and the sample flow was compensated by addition of pure synthetic air to the chamber by a mass flow controller. In order to test for linearity, the sample flow of the commercial instruments was periodically diluted by addition of pure synthetic air to the sampling line by another mass flow controller. By using the known sample flows of all external instruments, the dilution ratio was calculated, which was considered for the calculation of the mixing ratio in the

smog-chamber. All commercial instruments were calibrated before the campaign using a common NO<sub>2</sub> calibration gas mixture. The FTIR cross sections of NO<sub>2</sub> were determined from the data of the commercial instruments using pure NO<sub>2</sub> mixtures injected into the chamber.

## 2.2 Commercial instruments

### 2.2.1 Chemiluminescence instrument with molybdenum converter/ (Mo-CLD)

During the intercomparison in Santiago de Chile a TELEDYNE model 200 E with molybdenum converter (hereafter: *TELEDYNE Mo*) was used. The sample gas is mixed with O<sub>3</sub> (internally generated) and the resulting chemiluminescence is proportional to the NO concentration. For measurement of NO<sub>x</sub>, the sample gas is passed through a molybdenum converter at 320 °C:



before entering the NO<sub>x</sub> chemiluminescence reaction chamber, where NO<sub>x</sub> is also determined as NO. To calculate the NO<sub>2</sub> concentration the NO signal is subtracted from the NO<sub>x</sub> signal taking into consideration the converter efficiency, which is typically 100 % for NO<sub>2</sub>. The instrument has a high time resolution of 10 s and a DL of 0.4 ppbv. In the street canyon study an Ansyco AC31M (hereafter: *Ansyco Mo*) was used, which is explained below.

### 2.2.2 Photolytic conversion / chemiluminescence detection (PC-CLD)

#### ECO-Physics CLD 770 Al ppt/PLC 760

The NO<sub>x</sub> instrument “CLD 770 Al ppt” distributed by ECO Physics GmbH (hereafter: *ECO*), also detects NO by means of the chemiluminescence technique. For measurement of NO the sample gas is drawn directly into the O<sub>3</sub> reaction chamber, whereas for the measurement of NO<sub>x</sub> the sample gas is routed first to a photolytic converter (PLC 760) operated with a xenon lamp (300 W, 320–420 nm) for selective NO<sub>2</sub> conversion by reaction (R 3) and is then drawn into the O<sub>3</sub> reaction chamber. The NO and NO<sub>x</sub> measurements are made sequentially. For the shortest full measurement cycle time of 30 s, the ECO has a DL of ~0.1 ppbv.

#### Ansyco AC31M with “blue-light” converter

The Ansyco AC31M (hereafter: *Ansyco blue light*) is a combined NO/NO<sub>x</sub> instrument which has two channels, i.e. two parallel reaction chambers, one for NO and one for NO<sub>x</sub> measurements, where the sample gas is mixed with O<sub>3</sub> (internally generated) to produce chemiluminescence. The only difference in the used instrument from the standard model Ansyco AC31M, which was used in the street canyon study

(hereafter: *Ansyco Mo*) is the converter; the molybdenum converter was replaced by a home made “blue light converter”. In this converter NO<sub>2</sub> is photolysed by reaction (R 3) using 6 UV LEDs at 395 ± 10 nm with a converter efficiency of 52 %. The instrument has a higher time response of 10 s compared to the ECO instrument, but is much less sensitive with a DL of only 1–2 ppbv.

### 2.2.3 LMA3D

In the Unisearch LMA 3D instrument (hereafter: *Luminol*) the sample air is sucked by a pump across a wick that is continuously flushed with a specially formulated luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) solution. When NO<sub>2</sub> encounters the wick, the oxidation of luminol by NO<sub>2</sub> in the presence of O<sub>2</sub> produces chemiluminescence in the region of 425 nm. A photo-multiplier tube (PMT) measures the light produced and converts it into an electrical signal, which is almost linearly correlated with the NO<sub>2</sub> concentration. The instrument shows a high time response of a few seconds and is very sensitive with a DL of 0.2 ppbv.

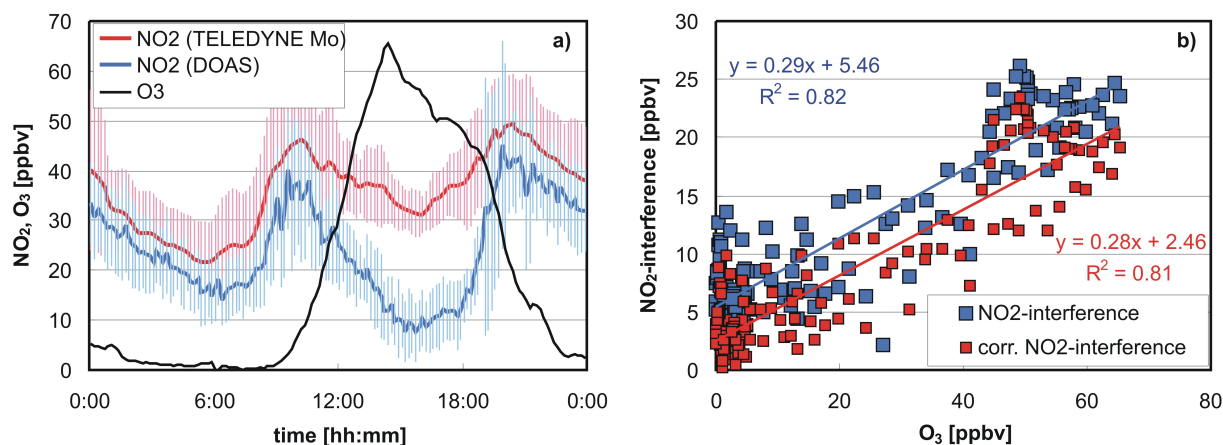
### 2.2.4 NO<sub>2</sub>-LOPAP Instrument

The NO<sub>2</sub>-LOPAP instrument (hereafter: *LOPAP*) was recently developed at the University of Wuppertal in co-operation with QUMA Elektronik & Analytik GmbH. The instrument is based on the light absorption of an azodye formed by the Saltzman reaction (Saltzman, 1954). The instrument is described in detail elsewhere (Villena et al., 2011). Briefly, NO<sub>2</sub> is sampled in a stripping coil by a fast chemical reaction and converted into an azodye, which is photometrically detected in long path absorption. The instrument has a DL of 2 pptv, an accuracy of 10 % and a precision of 0.5 % for a 3 min time resolution. The system is designed as a two-channel system for correction of possible interferences. In addition, an upstream scrubber suppresses the well-known interferences of the Griess-Saltzman reaction associated with HONO and O<sub>3</sub>. The instrument is calibrated by liquid nitrite standards, which is more accurate than using NO<sub>2</sub> calibration gases which are typically applied for the calibration of other instruments. The instrument has been successfully intercalibrated with the chemiluminescence technique using a photolytic converter during measurements in the atmosphere (Villena et al., 2011).

## 3 Results

### 3.1 Intercomparison in the urban atmosphere

Figure 1a shows the campaign averaged diurnal profiles of NO<sub>2</sub> obtained by DOAS and a chemiluminescence instrument with molybdenum converter (TELEDYNE Mo) from a two week field campaign in 2005 in Santiago de Chile



**Fig. 1.** (a) Campaign averaged NO<sub>2</sub> and O<sub>3</sub> diurnal profiles in Santiago de Chile, 2005 (Elshorbany et al., 2009). The error bars show the 1 $\sigma$  error of the average of all 10 min NO<sub>2</sub> data. The spectroscopic DOAS technique was used as a reference in this campaign. (b) Correlation of the NO<sub>2</sub>-interference of the chemiluminescence instrument (i.e. difference NO<sub>2</sub>(TELEDYNE-Mo) – NO<sub>2</sub>(DOAS)) with the ozone concentration. In addition, the NO<sub>2</sub>-interference, which was corrected for the HONO and PAN interferences of the chemiluminescence instrument, is also shown (“corr. NO<sub>2</sub>-interference”).

(Elshorbany et al., 2009). There is a clear difference between the results from both instruments with lower concentrations of the DOAS compared to the chemiluminescence instrument. While during the night, both data sets differ by only ~5–10 ppbv, the TELEDYNE Mo shows positive interferences of up to ~25 ppbv during daytime. On a relative basis, the chemiluminescence instrument overestimates NO<sub>2</sub> by up to a factor of four during daytime (see Fig. 1a) using the average campaign data. This overestimation is higher compared to the factor of two observed for single days in an intercomparison study in Mexico City (Dunlea et al., 2007). Interestingly, the positive interferences of the TELEDYNE Mo correlate quite well with the concentration of ozone (see Fig. 1b). This result is also in agreement with the study in Mexico City (Dunlea et al., 2007) although there, the interference to O<sub>3</sub> ratio was three times lower compared to the present study. Ozone may be used as an indicator for the photo-chemical activity of the atmosphere. Since most NO<sub>y</sub> species, such as nitric acid (HNO<sub>3</sub>), peroxyacetyl nitrate (PAN), and organic nitrates (RONO<sub>2</sub>), are photo-chemically formed during daytime and since all NO<sub>y</sub> species, which enter the molybdenum converter, are quantitatively measured by this technique (Winer et al., 1974; Steinbacher et al., 2006; Dunlea et al., 2007), the observed differences are due to NO<sub>y</sub> interferences of the chemiluminescence instrument. PAN and HONO were the only measured NO<sub>y</sub> species during the campaign. Subtraction of their concentrations from the observed interference (see “corr. NO<sub>2</sub>-interference”, Fig. 1b) showed that the night-time differences of both instruments could be mainly attributed to interference of the chemiluminescence instrument by HONO. However, during daytime there were still significant, not quantified NO<sub>y</sub>-interferences, which correlated well with the concentration of ozone (see

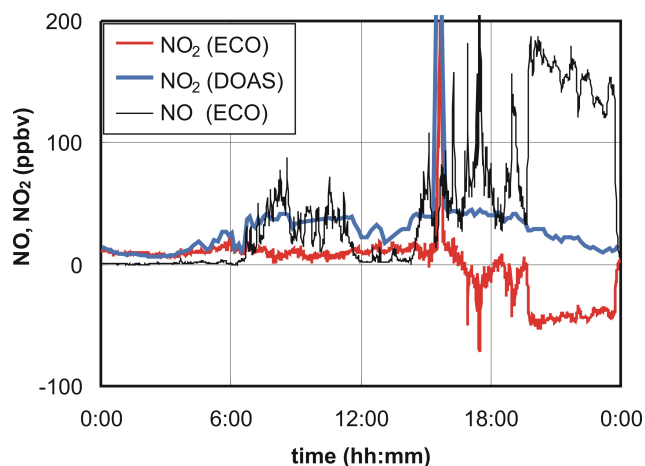
Fig. 1b). However, caused by a missing detailed NO<sub>y</sub> specification, deeper interpretation of the observed interferences of the TELEDYNE Mo instrument is beyond the scope of this study.

In conclusion, because of the strong overestimation of NO<sub>2</sub> by up to a factor of four observed for the summer smog conditions in the urban atmosphere of Santiago de Chile (see Fig. 1), only the NO<sub>2</sub> data from the DOAS technique was used in that campaign (Elshorbany et al., 2009). The observed positive interferences are in good agreement with other intercomparison studies (Dunlea et al., 2007) and thus, although still being recommended, the chemiluminescence technique with molybdenum converter should not be used for selective NO<sub>2</sub> detection.

### 3.2 Intercomparison in a road traffic tunnel

Figure 2 shows the diurnal variation of NO and NO<sub>2</sub> concentrations in the Kiesberg tunnel during a campaign in 1999 (Kurtenbach et al., 2001), in which a chemiluminescence instrument with photolytic NO<sub>2</sub> converter (ECO) was compared with a DOAS instrument. Both NO<sub>2</sub> data sets exhibit excellent agreement for measurements at low pollution levels during night-time (see Fig. 2; 00:00–04:00 LT). However, with the onset of elevated volumes of traffic through the tunnel, the NO<sub>2</sub> measurements of the ECO instrument exhibited strong negative interferences. Remarkable are the artificial negative concentrations measured by the ECO Physics instrument during the early night at high pollution levels as indicated by the high NO concentrations also shown in Fig. 2.

The reasons for the negative NO<sub>2</sub> concentrations were completely unclear at that time, but had been also observed in laboratory studies (Kleffmann et al., 2001; Bejan et al.,



**Fig. 2.** NO and NO<sub>2</sub> diurnal profiles measured with DOAS and ECO instruments in a tunnel study (Kurtenbach et al., 2001). The spectroscopic DOAS technique was used as a reference for NO<sub>2</sub> in this campaign.

2006). It was only later, that experiments in a smog chamber (see below) gave some insight as to the reasons for this phenomenon. High exhaust gas levels, which contain large quantities of photo-labile VOCs, e.g. carbonyls, cause the formation of peroxyradicals (HO<sub>2</sub>, RO<sub>2</sub>) in the photolytic converter, which reduce NO only in the NO<sub>x</sub> channel of the instrument. In the tunnel, the NO<sub>x</sub> level results almost exclusively from local direct vehicle emissions, which contain high quantities of NO (typically >90 % at that time). Thus, when more NO is reacting with peroxy radicals in the photolytic converter compared to the low NO<sub>2</sub> present in the sample, the NO level in the NO<sub>x</sub> channel is lower than the NO level actually in the sample, and artificial negative concentrations result. Since these interferences, which are explained in more detail below, are caused by highly non-linear reactions, these interferences cannot be corrected. Thus, only the DOAS NO<sub>2</sub> data was used in the 1999 campaign (Kurtenbach et al., 2001).

Based on these results, chemiluminescence instruments with photolytic converter should not be used for studies at high pollution level, i.e. in the polluted urban atmosphere and in smog-chambers (see below). In addition, due to the artificial noise, which results from the sequential measurements of NO and NO<sub>x</sub> by this one-channel instrument (see Sect. 2.2.2a), the ECO instrument is also not very well suited for kerbside stations with highly variable NO<sub>x</sub> levels. Besides this, the instrument shows a non-linear response for high NO<sub>2</sub> and O<sub>3</sub> levels which results from the reaction of NO with O<sub>3</sub> in the photolytic converter. However, in contrast to the negative interferences described above, the NO/O<sub>3</sub> non-linearity, which is typically not considered, can be corrected for as explained in detail elsewhere (Volz-Thomas et al., 2003). Finally, in all of the chemiluminescence in-

struments, water is quenching the NO<sub>2</sub>\* formed in reaction (R 1), which leads to a ~10 % decreased sensitivity for completely humid conditions (100 % r.h. at 298 K), i.e. during ambient measurements, compared to dry conditions, e.g. during calibration.

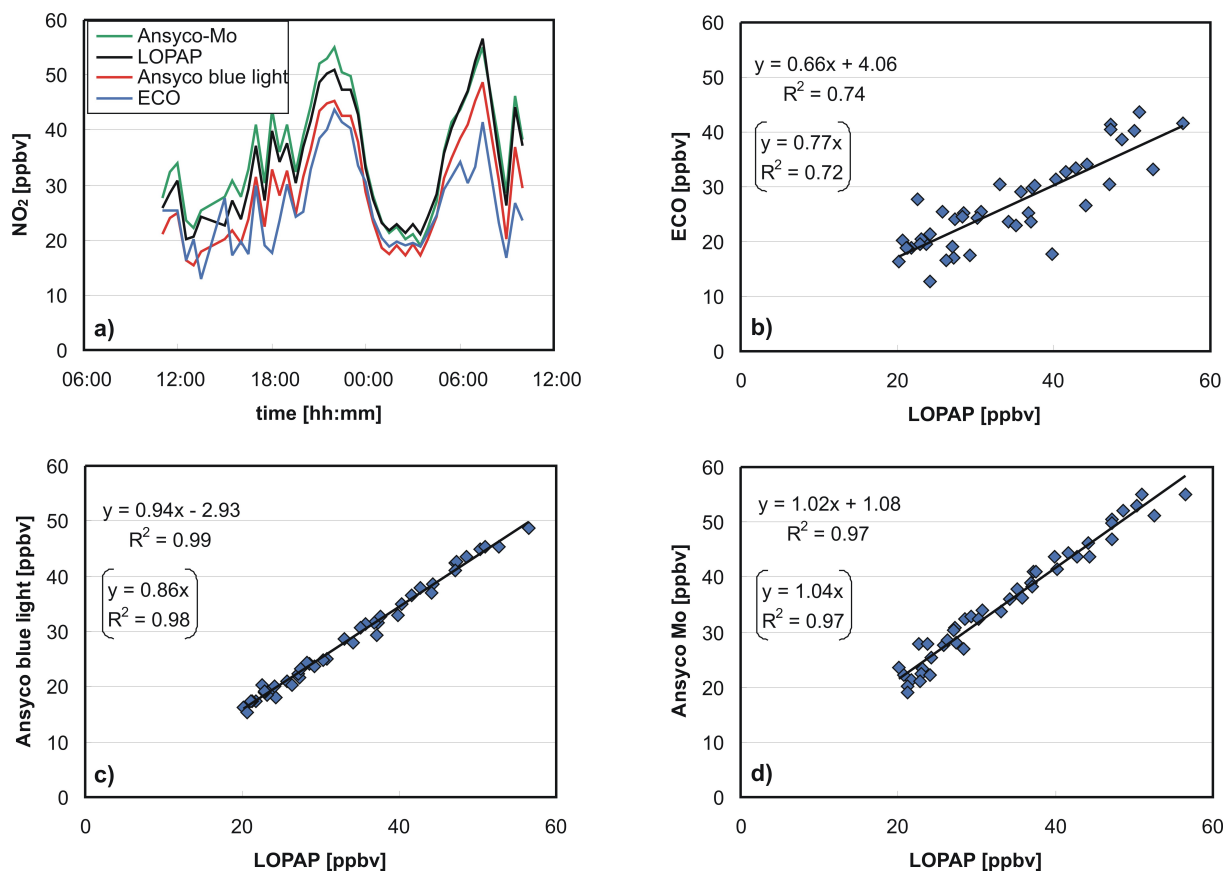
### 3.3 Intercomparison in a street canyon

To demonstrate, that the negative interferences observed for photolytic converters can also be of importance in the open urban atmosphere, two chemiluminescence instruments (ECO and Ansyco blue light) were compared with the LOPAP instrument in a street canyon in Wuppertal for two days. In addition, this intercomparison was also aimed to quantify typical positive interferences of the chemiluminescence instrument with molybdenum converter (Ansyco Mo) which is routinely used at that site. The LOPAP instrument was used as reference caused by the excellent agreement with the FTIR technique under complex conditions in a smog chamber, for which the other instruments showed strong interferences (see Sect. 3.4). All instruments were calibrated by the same calibration mixtures to ensure that the differences observed were only caused by interferences and the precision errors.

For the early night and during the morning rush hour, higher NO<sub>2</sub> levels were observed (see Fig. 3a), for which the differences between the instruments were largest. In contrast, during late night-time when the NO<sub>2</sub> levels were lower, better agreement was obtained. For more quantitative evaluation the 30 min average data of all chemiluminescence instruments were plotted against the corresponding LOPAP data. As expected, both instruments with photolytic converters showed smaller NO<sub>2</sub> levels compared to the LOPAP, which was more distinct for the ECO Physics with Xenon lamp converter (ca. 30 % deviation) compared to the Ansyco with blue light converter (ca. 10 % deviation, see Fig. 3b and c). While the correlation of the Ansyco to the LOPAP was excellent ( $r^2 = 0.99$ ), a lower correlation was observed for the ECO Physics ( $r^2 = 0.72$ ), which is caused by the one channel design of this instrument, for which fast variations of the trace gas levels lead to artificial noise. The higher negative interferences of the ECO Physics are explained by the broader spectral range of the Xenon lamp converter compared to the blue light converter, for which much more photo-labile species will form interfering peroxy radicals (for details, see Sect. 3.4). Thus, although the extent of the negative interferences of the photolytic converters was much lower compared to the tunnel measurements and no negative NO<sub>2</sub> data was obtained, the NO<sub>2</sub> concentration was still significantly underestimated in the open atmosphere.

In contrast, for the chemiluminescence instrument with molybdenum converter (Ansyco Mo) slightly higher concentrations compared to the LOPAP were observed. However, the small differences of ca. 3 % were close to the precision errors of both instruments. Such small differences can only be





**Fig. 3.** (a) NO<sub>2</sub> concentrations (30 min averages) measured by different instruments in a street canyon; (b–d) correlation plots of the different chemiluminescence instruments against the LOPAP data, which was used as reference here (see text). For the correlation equations given in brackets the intercept was forced to zero.

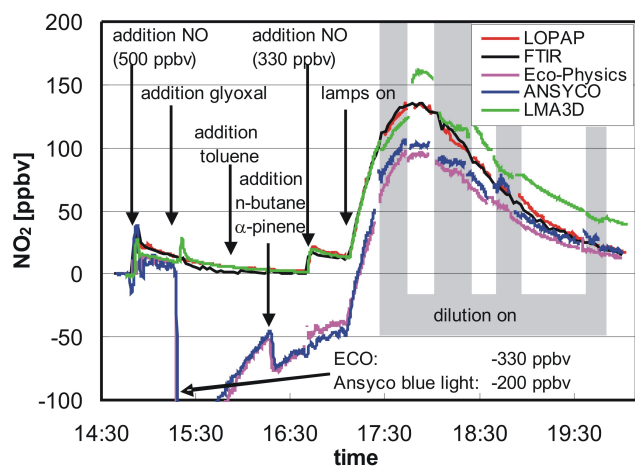
explained by the absence of significant NO<sub>y</sub> species, which is in contrast to the results from Santiago de Chile. However, since the measurements in the street canyon were close to the main NO<sub>x</sub> emission source, it can be expected that only emitted NO<sub>y</sub> species play an important role here. In contrast, the data shown in Sect. 3.1 was collected at an urban background site on the open campus of the University of Santiago de Chile, for which secondary photochemical formation of NO<sub>y</sub> species is more important, also with respect to the much higher photochemical activity in Santiago de Chile compared to Germany. The slightly higher NO<sub>2</sub> levels from the chemiluminescence instrument compared to the LOPAP can be well explained by NO<sub>y</sub> emissions from vehicles, for which mainly nitrous acid (HONO) is expected. Since the typical emission ratio of HONO is ~1 % of NO<sub>x</sub> (Kurtenbach et al., 2001), and since the average NO<sub>x</sub> concentration was ca. two times higher than NO<sub>2</sub> during the intercomparison, a positive interferences by HONO of only ~2 % is expected for the molybdenum converter instrument.

The results from the street canyon show that chemiluminescence instruments with molybdenum converters can provide even more accurate NO<sub>2</sub> data compared to instruments

with photolytic converters under certain condition, i.e. for measurements close to emission sources, e.g. in kerbside or tunnel studies. For example, if only two chemiluminescence instruments with molybdenum and photolytic converter were used in the street canyon (e.g. ECO and Ansyco Mo), the differences would have been explained by the well known interferences from the molybdenum converter and not by the yet unknown but more important negative interferences of photolytic converters.

### 3.4 Intercomparison in a smog chamber

To better understand the negative interferences mentioned above and to validate the recently developed NO<sub>2</sub>-LOPAP instrument, an intercomparison campaign with four NO<sub>2</sub> analysers (ECO, Ansyco blue-light, Luminol, LOPAP) and the FTIR technique was conducted under complex photo-smog conditions in a 10801 smog chamber. The spectroscopic FTIR technique was used as a reference in these measurements, since sampling artefacts can be ruled out for this non-intrusive method. In addition, optical interferences by the overlap of absorption bands in this extremely complex



**Fig. 4.** Intercomparison of three commercial NO<sub>2</sub> instruments and the new NO<sub>2</sub>-LOPAP instrument with FTIR spectrometry during a complex photo-smog experiment. The grey shaded area indicate the periods, when the sample air of all the external instruments was diluted with synthetic air by factors of between 1.2–3.5, which was considered for the concentration calculations.

mixture were excluded, since a known added amount of NO<sub>2</sub> at the end of such a photo-smog experiment could be quantified correctly using the FTIR.

An example of a photo-smog experiment is shown in Fig. 4, in which a complex volatile organic compound (VOC)/NO<sub>x</sub> mixture was irradiated with UV/VIS light. In the experiment, NO (500 ppbv) with ~6% impurities of NO<sub>2</sub>, glyoxal (1.1 ppmv), toluene (0.64 ppmv), n-butane (0.56 ppmv) and  $\alpha$ -pinene (0.43 ppmv) were introduced sequentially into a dark chamber. Before the lamps were switched on, a second NO injection (330 ppbv) was made to compensate for the dilution of the mixture caused by the sample flow to the external instruments. The radical initiated degradation of the VOCs leads to the formation of O<sub>3</sub> and peroxy radicals (HO<sub>2</sub>, RO<sub>2</sub>), and further reaction with NO results in increasing levels of NO<sub>2</sub> in this photo-smog mixture. When the reaction mixture was irradiated, the sample flow to all the external instruments was diluted by accurately known factors of between 1.2–3.5 for certain periods to check for the linearity of the interferences affecting the different instruments (see grey shaded area in Fig. 4). Theoretically, the concentrations calculated in the smog chamber should not depend on the dilution ratio, when corrected for. In contrast to the external instruments, the FTIR measurements were not affected by the dilution tests.

Since hundreds of products including potential interfering photo-oxidants, like PAN, are formed during the irradiation, this complex photo-smog experiment is a good test to validate a new instrument under conditions that are even more complex and with higher pollution levels compared to the atmosphere.

Whereas excellent agreement was obtained between the NO<sub>2</sub> measurements made with the LOPAP and FTIR techniques, substantial deviations were observed for the other NO<sub>2</sub> instruments used (Fig. 4). For the Luminol instrument lower NO<sub>2</sub> concentrations could be initially observed when adding high NO concentrations (500 ppbv) (Fig. 4, first addition of NO). This is due to the quenching of the chemiluminescence of the luminol by NO, which decreases the sensitivity of the instrument (Kleffmann et al., 2004). This phenomenon was also observed for high concentrations of nitroaromatic species in another recent study (Bejan et al., 2006). Since the quenching efficiency of different trace gases is not well known, the Luminol technique should not be used for smog-chamber experiments, at least when ppmv levels of trace gases are used.

Deviations also arose for the Luminol instrument in comparison with the FTIR during the photo-smog period. In contrast to the Ansyco blue light and ECO instruments, the Luminol technique suffered from positive interferences during the course of the photo-smog experiment, which may be explained by photo-chemical formation of ozone and different PAN like species (peroxyacynitrates) (Fehsenfeld et al., 1990). Under the very alkaline sampling conditions prevailing in the Luminol instrument, it is well known that PAN and other peroxyacynitrates decompose (Frenzel et al., 2000). The observed positive interferences of the Luminol technique showed a clear non-linear behaviour, which decreased with increasing dilution of the sample (see Fig. 4, dilution on). In contrast, for interferences, which increase linearly with the concentration of the interfering species, the dilution tests should not affect the calculated concentrations in the chamber.

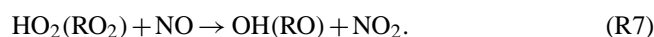
For both of the chemiluminescence instruments with photolytic converters (ECO and Ansyco blue light) strong negative interferences were observed when adding glyoxal to the chamber. As in the tunnel study mentioned before, artificial negative concentrations were registered for the ECO and Ansyco blue light instruments reaching –330 ppbv and –200 ppbv, respectively (see Fig. 4). To understand these negative interferences the photo-chemistry of glyoxal has to be considered, which produces formyl radicals (HCO) at wavelengths <420 nm:



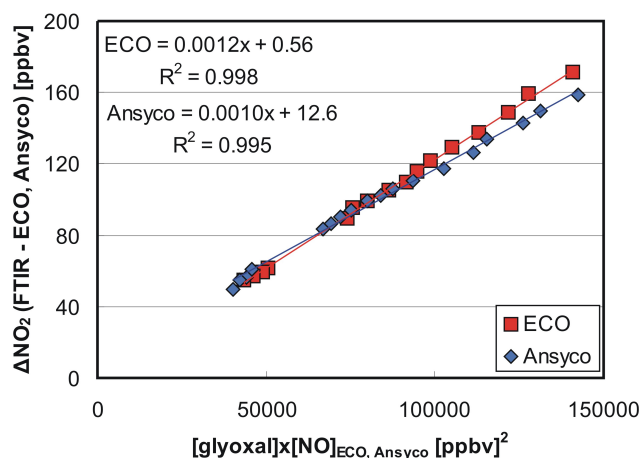
which further react with molecular oxygen leading to the formation of HO<sub>2</sub> radicals:



It is well known that peroxyradicals (HO<sub>2</sub>, RO<sub>2</sub>) efficiently convert NO into NO<sub>2</sub>:



For the high glyoxal concentrations used, the NO concentration in the NO<sub>x</sub> channels of both instruments is significantly



**Fig. 5.** Correlation of the negative interferences of the ECO Physics and the Ansyco blue light against the product  $[\text{glyoxal}] \times [\text{NO}]$ .

reduced via reaction (R7). The apparent negative concentrations can be explained with the low NO<sub>2</sub>/NO<sub>x</sub> ratio at the beginning of the experiment and the high loss of NO through reaction (R7). This results in the measured NO concentration without converter (NO channel) being greater than that with converter (NO<sub>x</sub> channel).

To confirm the explanation of the negative interferences observed in the photo-smog experiment, the deviation of both instruments compared to the FTIR data during the dark period was plotted against the product of  $[\text{NO}] \times [\text{glyoxal}]$  (see Fig. 5). Highly linear correlations were obtained for both chemiluminescence instruments. Reactions (R5) and (R6) follow first-order and pseudo first-order kinetics, respectively. In addition, HO<sub>2</sub> self reactions are not of significant importance caused by the high NO levels present. Thus, it can be expected that the HO<sub>2</sub> concentration in the converter will scale linearly with glyoxal. In this case the negative interference, which is explained here by NO loss through reaction (R7), follows second order kinetics and will be proportional to  $[\text{NO}] \times [\text{HO}_2]$  and  $[\text{NO}] \times [\text{glyoxal}]$ , as observed (see Fig. 5). As a consequence of these non-linear negative interferences, the NO<sub>2</sub> level given by both instruments was not observed to increase during the second addition of NO at ~16:50 local time (LT) (see Fig. 4), in contrast to the other instruments, for which the impurities of NO<sub>2</sub> in the NO could be correctly quantified. This is caused by the increasing NO level leading to increasing negative interferences by reaction (R7), which compensates the increased NO<sub>2</sub> level in the chamber.

Another interesting feature of the intercomparison was the enhancement of the negative interferences of both chemiluminescence instruments after the addition of *n*-butane and  $\alpha$ -pinene (see Fig. 4). Both VOCs do not photolyse in the spectral range of both photolytic converters and thus, will themselves not form the peroxyradicals necessary to convert NO

by reaction (R7). However, since OH radicals are formed from glyoxal photolysis via reactions (R5–R7), peroxyradicals (RO<sub>2</sub>) will be formed by the OH initiated degradation of *n*-butane and  $\alpha$ -pinene (“R-H”):



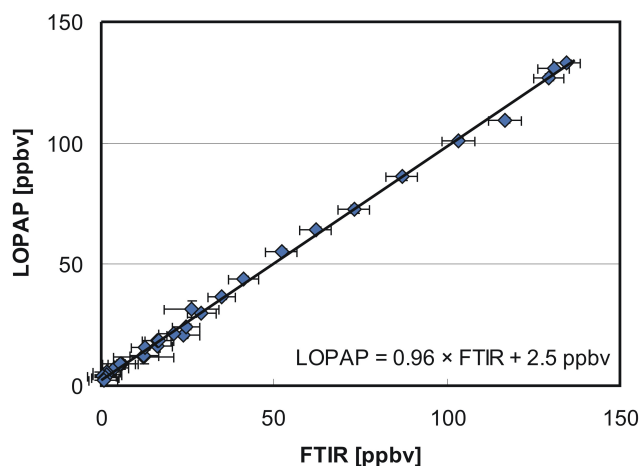
The RO<sub>2</sub> radicals will further reduce the NO level in the photolytic converter by reaction (R7). Hence, photo-induced radical chemistry, well known from atmospheric chemistry textbooks, takes place in the photolytic converters, depending on the admitted VOCs, so that NO<sub>2</sub> data using these instruments are inaccurate for highly polluted conditions such as can prevail in street canyons, tunnels and smog chambers. However, because of the second order reaction kinetics, these negative interferences are not expected to be of significant importance in the less polluted atmosphere (see for example, Fig. 2, 00:00–04:00 LT, and Villena et al., 2011).

During the course of the experiment a continuous reduction of the negative interferences of the chemiluminescence instruments with photolytic converter (Ansyco blue light and ECO) was observed. This is due to the continuous dilution of the reaction mixture which results from the addition of synthetic air to replenish the gas sample flow to the external instruments and the second order reaction kinetics of the interferences (see above). The non-linear behaviour of these interferences was also reflected by the data in instances where the reaction mixture was diluted for the external instruments leading to decreases in the interferences (see Fig. 4, Ansyco blue light and ECO: dilution on).

Generally, negative interferences were larger for the ECO compared to the Ansyco blue light instrument. This can be explained by the broader spectral range (290–420 nm) of the xenon lamp used in the photolytic converter of the ECO instrument compared to the blue light converter ( $\lambda_{\text{max}} = 395 \pm 10$  nm), which is optimised for the photolysis of only NO<sub>2</sub>. In addition, the residence time in the blue-light converter is much shorter compared to the Xenon lamp converter. Thus, in the case of the ECO instrument, more photons are absorbed by glyoxal in the photolytic converter leading to higher radical yields. In addition, caused by the different spectral range applied, it can be expected that in the atmosphere, photolysis of more photo-labile species will lead to larger radical production in a photolytic converter containing a xenon lamp compared to one using a blue light converter, which was confirmed by the results from the study in the street canyon (see Sect. 3.3). Thus, if photolytic converters are used for the chemiluminescence technique, it is recommended to use blue light converters, although these instruments will still suffer from negative interferences for high pollution levels (see Figs. 3 and 4).

In contrast to the chemiluminescence instruments the LOPAP instrument showed excellent agreement with the FTIR technique (see Fig. 4) with an average deviation of





**Fig. 6.** Correlation of all LOPAP and FTIR NO<sub>2</sub> data during the complex photo-smog experiment, shown in Fig. 4. The error bars only represent the precision of both instruments.

4 % (see Fig. 6). Lower concentrations were observed for the FTIR technique compared to the LOPAP instrument only while adding glyoxal (Fig. 4). However, since glyoxal does not react with NO<sub>2</sub> in the dark and since the LOPAP signal remained unchanged in the presence of glyoxal, this difference can be explained by optical interference of the FTIR instrument resulting from the overlap of absorption bands from glyoxal and NO<sub>2</sub>. These interferences accounted for max. 5 ppbv, which is close to the precision of the FTIR instrument. In addition, the optical interference decreased with time because of the continuous dilution of the reaction mixture and thus, did not influence the accuracy of the FTIR during the photo-smog phase of the experiment.

In addition to the general good agreement with the FTIR technique, no changes of the corrected measurement signal of the LOPAP instrument occurred during the dilution tests. Accordingly, significant interference can be excluded for the LOPAP instrument even for this very complex reaction mixture. Furthermore, since no interferences were observed in channel 2 of the instrument neither during the smog-chamber experiments, nor in the atmosphere (Villena et al., 2011), an even simpler one-channel set-up could be used in the future. In conclusion, the new LOPAP is not only suitable for atmospheric applications (Villena et al., 2011) but also for complex smog-chamber experiments, where chemiluminescence instruments have severe problems.

#### 4 Atmospheric implication

In the present study, commercial NO<sub>2</sub> chemiluminescence instruments have shown strong interferences compared to spectroscopic techniques under certain conditions. Accordingly, if data from these instruments are used, e.g. in chemical models, model-measurement deviation may be also

caused by the uncertainties in the NO<sub>2</sub> measurement data. Therefore, critical evaluation of the data from each type of NO<sub>2</sub> instrument for any measurement condition is required. For example, at urban kerbside stations for which chemiluminescence instruments are generally used, the NO<sub>2</sub> level may be strongly underestimated if instruments with photolytic converters are used, whereas it will be overestimated for those using molybdenum converters. Whereas the positive interferences of molybdenum converters by NO<sub>y</sub> species are a well known problem (Dunlea et al., 2007 and references therein), the negative interferences of photolytic converters have not yet been discussed in the literature in detail. If an intercomparison of these two types of instruments is carried out under heavily polluted atmospheric conditions; one might argue that instruments with photolytic converter would provide better data than those with molybdenum converter. However, under these conditions, the negative deviations of the photolytic converters can be even much stronger than the positive interferences by the NO<sub>y</sub> species for the molybdenum converters (see Sect. 3.3).

On the other hand, for urban background, rural or remote measurement stations the NO<sub>y</sub> and PAN fractions can be significant compared to the NO<sub>2</sub> level, for which the Luminol technique and the chemiluminescence instruments with molybdenum converters would be more affected.

Thus, the use of selective NO<sub>2</sub> instruments, like for example DOAS, LIF, cavity ring down or the new NO<sub>2</sub>-LOPAP technique, are recommended for the detection of NO<sub>2</sub> in the atmosphere.

#### 5 Conclusions

In the present study, NO<sub>2</sub> measurements performed with different techniques, i.e. chemiluminescence instruments with molybdenum or photolytic converters, a Luminol based instrument and a new NO<sub>2</sub>-LOPAP were compared with spectroscopic techniques, i.e. DOAS and FTIR, in the urban atmosphere, a road traffic tunnel and a smog-chamber. Strong positive interferences for a chemiluminescence instrument with molybdenum converter were observed under typical photo-smog conditions in the urban atmosphere of Santiago de Chile. This has been explained by interferences caused by photochemically formed NO<sub>y</sub> species, leading to an overestimation of daytime NO<sub>2</sub> levels by up to a factor of four. In contrast, strong negative interferences, even with artificial negative NO<sub>2</sub> concentrations, were observed for a chemiluminescence instrument with photolytic converter in a road traffic tunnel. These interferences are explained by the photolysis of VOCs in the photolytic converter and consecutive peroxy radical reactions with NO. This was confirmed by smog-chamber experiments, where the addition of glyoxal also resulted in strong negative interferences. Whereas all the commercial instruments showed strong deviations compared to the spectroscopic FTIR technique in the smog

chamber, excellent agreement between a new NO<sub>2</sub>-LOPAP instrument and the FTIR technique was obtained. Since the NO<sub>2</sub>-LOPAP instrument is in addition much more sensitive (DL=2 pptv) compared to commercial chemiluminescence instruments, its use is recommended for the simple, sensitive and selective detection of NO<sub>2</sub> in the atmosphere.

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