Chapter 2
NO_2 Measurement Techniques: Pitfalls and New Developments

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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_2) 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_2 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_2 detection in monitoring networks and smog chambers use either molybdenum or photolytic converters and are affected by either positive (NO_y) or negative interferences (radical formation in the photolytic converter). Erroneous conclusions on NO_2 can be drawn if these interferences are not taken into consideration. In the present study, NO_2 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_2-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_2-LOPAP instrument and the FTIR technique for the measurements performed in the smog chamber.

Keywords Nitrogen dioxide • Chemiluminescence • Luminol • LOPAP

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2.1 Introduction

Despite their relatively low concentration, nitrogen oxides ($NO_x = NO + NO_2$) play a crucial role in tropospheric chemistry. NO_2 affects the oxidation capacity of the atmosphere through its direct participation in the formation of ozone (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 the nitrate radical (NO_3) [2, 7, 18].

Many direct or indirect techniques have been developed for measuring NO_2 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_2 detection ([19] and references therein). Although some of the methods have very low detections 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 [3] and by European legislation [5] for the measurement of NO_2 in monitoring networks is the chemiluminescence technique. This method involves the reduction of NO_2 to NO using heated (300–350 °C) molybdenum (Mo) surfaces:

$$Mo + 3\ NO_2 \rightarrow MoO_3 + 3\ NO, \tag{2.R1}$$

followed by the gas-phase reaction between NO and O_3 (2.R2) forming an electronically excited NO_2^* molecule that emits light (2.R3), which is proportional to the NO concentration [8, 14].

$$NO + O_3 \rightarrow NO_2^* + O_2 \tag{2.R2}$$

$$NO_2^* \rightarrow NO_2 + h\nu \tag{2.R3}$$

Photolytic conversion of NO_2 to NO (2.R4), using either Xenon lamps or UV emitting diodes ("blue light converters"), followed by detection of the chemiluminescence from the reaction of NO with O_3 are also used (2.R3) [12, 15, 16]:

$$NO_2 + h\nu \rightarrow NO + O(^3P). \tag{2.R4}$$

Another commonly used technique is the luminol-chemiluminescence method, which employs the reaction between NO_2 and an alkaline solution of luminol resulting in light emission [21].

In the present study, the performances of different commercial NO_2 instruments and a new NO_2-LOPAP (Long Path Absorption Photometer; [19]) 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.

2.2 Experimental

2.2.1 Chemiluminescence Instrument with Molybdenum Converter/(Mo-CLD)

During an intercomparison in Santiago de Chile a TELEDYNE model 200 E (hereafter: *TELEDYNE Mo*), and in a street canyon campaign in Wuppertal (Germany) an Ansyco AC31M (hereafter: *Ansyco Mo*) were used, both with molybdenum converters. Details of the instruments are explained elsewhere [20].

2.2.2 Photolytic Conversion/Chemiluminescence Detection (PC-CLD)

The ECO Physics "CLD 770 Al ppt" (hereafter: *ECO*) detects NO_2 using a photolytic converter (PLC 760) operated with a Xenon lamp (300 W, 320–420 nm, 2.R4) and is explained elsewhere [20]. In the Ansyco AC31M (hereafter: *Ansyco blue light*) a homemade "blue light converter" (6 UV LEDs, 395 ± 10 nm, converter efficiency of 52%) is used for NO_2 conversion (see [20]).

2.2.3 LMA3D

In the Unisearch LMA 3D instrument (hereafter: *Luminol*) NO_2 is detected by using a specially formulated luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) solution. Details are explained elsewhere [20].

2.2.4 NO_2-LOPAP Instrument

The NO_2-LOPAP instrument (hereafter: *LOPAP*) was recently developed at the University of Wuppertal in co-operation with QUMA Elektronik and Analytik GmbH. The instrument is based on the light absorption of an azodye formed by the Saltzman reaction [17]. The instrument is described in detail elsewhere [19].

2.3 Results

2.3.1 Intercomparison in the Urban Atmosphere

Figure 2.1a shows the campaign averaged diurnal profiles of NO_2 obtained by DOAS and a chemiluminescence instrument with molybdenum converter (TELEDYNE Mo) from a 2-week field campaign in 2005 in Santiago de Chile [4]. 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_2 by up to a factor of four during daytime (see Fig. 2.1a) using the average campaign data. Interestingly, the positive interferences of the TELEDYNE Mo correlate quite well with the concentration of ozone (see Fig. 2.1b). Ozone may be used as an indicator for the photo-chemical activity of the atmosphere. Since most interfering NO_y species, such as nitric acid (HNO_3), peroxyacetyl nitrate (PAN), and organic nitrates ($RONO_2$), are photo-chemically formed during daytime the observed differences are due to NO_y interferences of the chemiluminescence instrument. Even after subtraction of the interferences due to PAN and HONO, significant, not quantified NO_y-interferences, which correlated well with the concentration of ozone, were observed (see Fig. 2.1b).

2.3.2 Intercomparison in a Road Traffic Tunnel

Figure 2.2 shows the diurnal variation of NO and NO_2 concentrations in the Kiesberg tunnel during a campaign in 1999 [13], in which a chemiluminescence instrument with photolytic NO_2 converter (ECO) was compared with a DOAS instrument. Both NO_2 data sets exhibit excellent agreement for measurements at low pollution levels during night-time (see Fig. 2.2 0:00–4:00 LT). However, with the onset of elevated volumes of traffic through the tunnel, the NO_2 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. 2.2. The reasons for the negative NO_2 concentrations were completely unclear at that time, but had been also observed in laboratory studies [1, 10]. 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 peroxy radicals (HO_2, RO_2) in the photolytic converter, which reduce NO only in the NO_x channel of the instrument. In the tunnel, the NO_x 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_2 present in the sample,

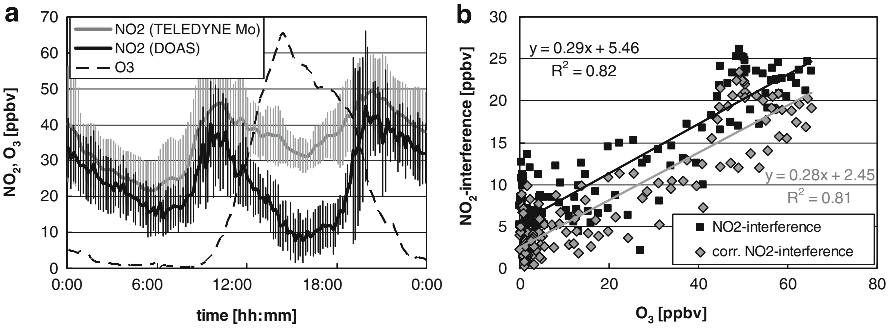
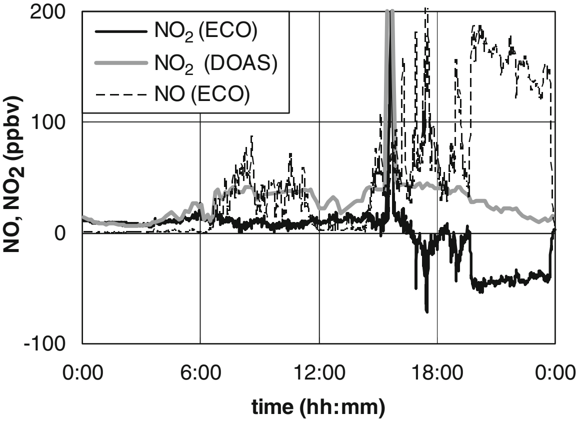


Fig. 2.1 (**a**) Campaign averaged NO_2 and O_3 diurnal profiles in Santiago de Chile, 2005 [4]. The spectroscopic DOAS technique was used as a reference in this campaign. (**b**) Correlation of the NO_2-interference of the chemiluminescence instrument (i.e. difference TELEDYNE-Mo – DOAS) with the ozone concentration. In addition, the NO_2-interference, which was corrected for the HONO and PAN interferences of the chemiluminescence instrument, is also shown ("corr. NO_2-interference")

Fig. 2.2 NO and NO_2 diurnal profiles measured with DOAS and ECO instruments in a tunnel study [13]. The spectroscopic DOAS technique was used as a reference for NO_2 in this campaign



the NO level in the NO_x 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_2 data was used in the 1999 campaign [13]. 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).

2.3.3 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

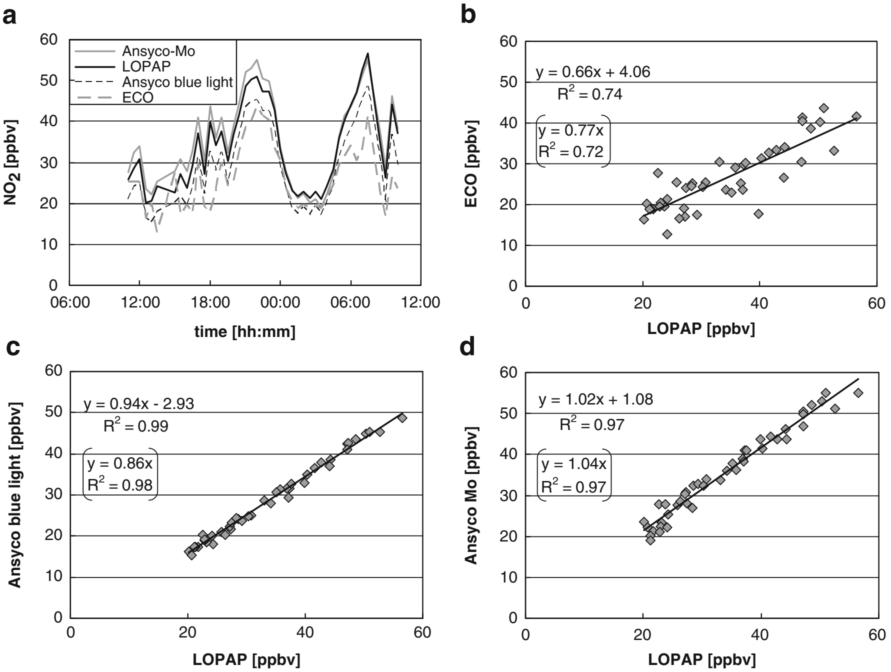


Fig. 2.3 (**a**) NO_2 concentrations measured by different instruments in a street canyon; (**b**–**d**) correlation plots of the different chemiluminescence instruments against the LOPAP data, which was used as reference here (see text). For the correlation equations given in brackets the intercept was forced to zero

instruments (ECO and Ansyco blue light) were compared with the LOPAP instrument in a street canyon in Wuppertal for 2 days [20]. In addition, this intercomparison was also aimed to quantify typical positive interferences of the molybdenum converter instrument (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_2 levels were observed (see Fig. 2.3a), for which the differences between the instruments were largest. In contrast, during late night-time when the NO_2 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_2 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. 2.3b, c). While the correlation of 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_2 data was obtained, the NO_2 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 (see Fig. 2.3d). However, the small differences of ca. 3% were close to the precision errors of both instruments. Such small differences can only be explained by the absence of significant NO_y 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_x emission source, it can be expected that only emitted NO_y 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_y species is more important, also with respect to the much higher photochemical activity in Santiago de Chile compared to Germany. The slightly higher NO_2 levels from the chemiluminescence instrument compared to the LOPAP can be well explained by NO_y emissions from vehicles, for which mainly nitrous acid (HONO) is expected. Since the typical emission ratio of HONO is ~1% of NO_x [13], and since the average NO_x concentration was ca. two times higher than NO_2 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_2 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.

2.3.4 Intercomparison in a Smog Chamber

To better understand the negative interferences mentioned above and to validate the recently developed NO_2-LOPAP instrument, an intercomparison campaign with four NO_2 analysers (ECO, Ansyco blue-light, Luminol, LOPAP) and the FTIR technique was conducted under complex photo-smog conditions in a 1080 *l* smog

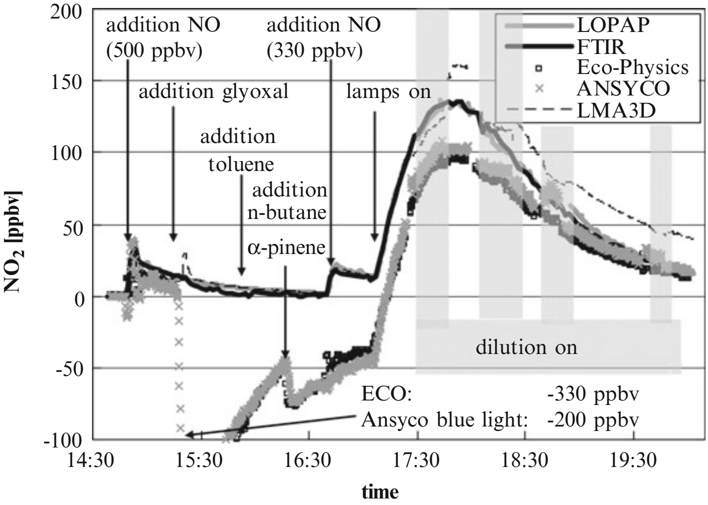


Fig. 2.4 Intercomparison of three commercial NO$_2$ instruments and the new NO$_2$-LOPAP instrument with FTIR spectrometry during a complex photo-smog experiment. The *grey shaded* area indicate the periods, when the sample air of all the external instruments was diluted with synthetic air by factors of between 1.2 and 3.5, which was considered for the concentration calculations

chamber [20]. The spectroscopic FTIR technique was used as a reference in these measurements, since sampling artefacts can be ruled out for this non-intrusive method. Details of this campaign are explained elsewhere [20].

An example of a photo-smog experiment is shown in Fig. 2.4, in which a complex volatile organic compound (VOC)/NO$_x$ mixture was irradiated with UV/VIS light. In the experiment, NO (500 ppbv) with ~6% impurities of NO$_2$, glyoxal (1.1 ppmv), toluene (0.64 ppmv), *n*-butane (0.56 ppmv) and α-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$_3$ and peroxy radicals (HO$_2$, RO$_2$), and further reaction with NO results in increasing levels of NO$_2$ 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 and 3.5, for certain periods to check for the linearity of the interferences affecting the different instruments (see grey shaded area in Fig. 2.4). 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_2 measurements made with the LOPAP and FTIR techniques, substantial deviations were observed for the other NO_2 instruments used (Fig. 2.4). For the luminol instrument lower NO_2 concentrations could be initially observed when adding high (500 ppbv) NO concentrations (Fig. 2.4, 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 [11]. This phenomenon was also observed for high concentrations of nitroaromatic species in another recent study [1]. 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 (peroxyacylnitrates) like species [6]. Under the very alkaline sampling conditions prevailing in the luminol instrument, it is well known that PAN and other peroxyacylnitrates decompose [9]. The observed positive interferences of the luminol technique showed a clear non-linear behaviour, which decreased with increasing dilution of the sample (see Fig. 2.4, 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 and −200 ppbv, respectively (see Fig. 2.4). To understand these negative interferences the photo-chemistry of glyoxal has to be considered, which produces formyl radicals (HCO) at wavelengths <420 nm:

$$(\mathrm{HCO})_2 + \mathrm{h}\nu \rightarrow 2\mathrm{HCO}, \qquad (2.\mathrm{R5})$$

which further react with molecular oxygen leading to the formation of HO_2 radicals:

$$\mathrm{HCO} + \mathrm{O_2} \rightarrow \mathrm{HO_2} + \mathrm{CO}. \qquad (2.\mathrm{R6})$$

It is well known that peroxy radicals (HO_2, RO_2) efficiently convert NO into NO_2:

$$\mathrm{HO_2}(\mathrm{RO_2}) + \mathrm{NO} \rightarrow \mathrm{OH}\ (\mathrm{RO}) + \mathrm{NO_2}. \qquad (2.\mathrm{R7})$$

For the high glyoxal concentrations used, the NO concentration in the NO_x channels of both instruments is significantly reduced via reaction (2.R7). The apparent negative concentrations can be explained with the low NO_2/NO_x ratio at the beginning of the experiment and the high loss of NO through reaction (2.R7). This results in the measured NO concentration without converter (NO channel) being greater than that with converter (NO_x channel).

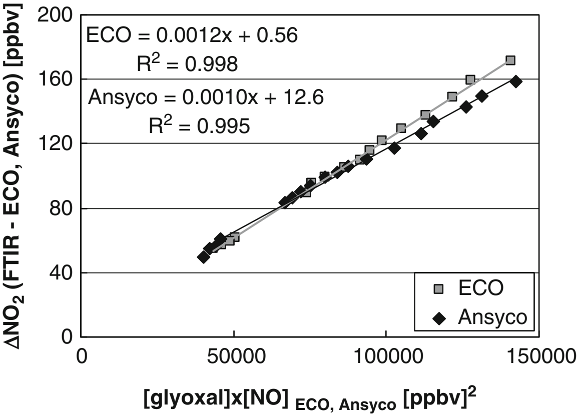


Fig. 2.5 Correlation of the negative interferences of the ECO Physics and the Ansyco blue light against the product [glyoxal] × [NO]

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 [NO] × [glyoxal] (see Fig. 2.5). Highly linear correlations were obtained for both chemiluminescence instruments. Reactions (2.R5) and (2.R6) follow first-order and pseudo first-order kinetics, respectively. In addition, HO_2 self reactions are no of significant importance caused by the high NO levels present. Thus, it can be expected that the HO_2 concentration in the converter will scale linearly with glyoxal. In this case the negative interference, which is explained here by NO loss through reaction (2.R7), follows second order kinetics and will be proportional to [NO] × [HO_2] and [NO] × [glyoxal], as observed (see Fig. 2.5). As a consequence of these non-linear negative interferences, the NO_2 level given by both instruments was not observed to increase during the second addition of NO at ~16:50 local time (LT) (see Fig. 2.4), in contrast to the other instruments, for which the impurities of NO_2 in the NO could be correctly quantified. This is caused by the increasing NO level leading to increasing negative interferences by reaction (2.R7), which compensates the increased NO_2 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 α-pinene (see Fig. 2.4). Both VOCs do not photolyse in the spectral range of both photolytic converters and thus, will themselves not form the peroxy radicals necessary to convert NO by reaction (2.R7). However, since OH radicals are formed from glyoxal photolysis via reactions (2.R5, 2.R6, and 2.R7), peroxy radicals (RO_2) will be formed by the OH initiated degradation of *n*-butane and α-pinene ("R-H"):

$$R - H + OH \rightarrow R + H_2O, \tag{2.R8}$$

$$R + O_2 \rightarrow RO_2. \tag{2.R9}$$

The RO_2 radicals will further reduce the NO level in the photolytic converter by reaction (2.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_2 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. 2.2, 0:00–4:00 LT, and [19]).

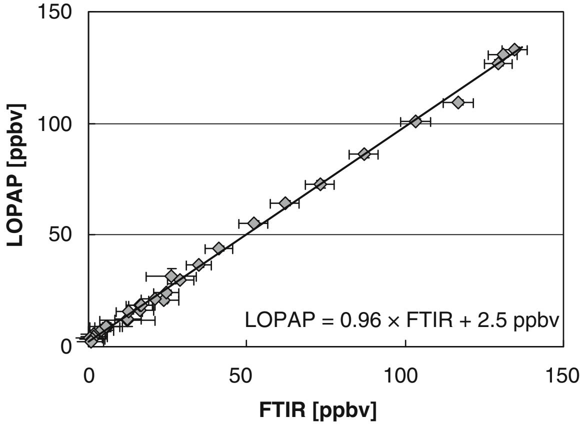
During the course of the experiment a continuous reduction of the negative interferences of the chemiluminescence instruments with photolytic converter (Ansyco blue light und ECO) was observed. This is due to the continuous dilution of the reaction mixture which results from the addition of synthetic 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. 2.4, 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 ($\lambda_{max} = 395 \pm 10$ nm), which is optimised for the photolysis of only NO_2. 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. 2.3 and 2.4).

In contrast to the chemiluminescence instruments the LOPAP instrument showed excellent agreement with the FTIR technique (see Fig. 2.4) with an average deviation of 4% (see Fig. 2.6). Lower concentrations were observed for the FTIR technique compared to the LOPAP instrument only while adding glyoxal (Fig. 2.4). However, since glyoxal does not react with NO_2 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_2. These interferences accounted for max. Five 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

Fig. 2.6 Correlation of all LOPAP and FTIR NO_2 data during the complex photosmog experiment, shown in Fig. 2.4. The error bars only represent the precision of both instruments



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 [19], 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 [19] but also for complex smog-chamber experiments, for which chemiluminescence instruments have severe problems.

2.4 Atmospheric Implication

In the present study, commercial NO_2 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_2 measurement data. Therefore, critical evaluation of the data from each type of NO_2 instrument for any measurement condition is required. For example, at urban kerbside stations for which chemiluminescence instruments are generally used, the NO_2 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_y species are a well known problem, 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_y species for the molybdenum converters (see Sect. 3.3).

On the other hand, for urban background, rural or remote measurement stations the NO_y and PAN fractions can be significant compared to the NO_2 level, for which the luminol technique and the chemiluminescence instruments with molybdenum converters would be more affected. Thus, the use of selective NO_2 instruments, like for example DOAS, LIF, cavity ring down or the new NO_2-LOPAP technique, are recommended for the detection of NO_2 in the atmosphere.

2.5 Conclusions

In the present study, NO_2 measurements performed with different techniques, i.e. chemiluminescence instruments with molybdenum or photolytic converters, a luminol based instrument and a new NO_2-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_y species, leading to an overestimation of daytime NO_2 levels by up to a factor of four. In contrast, strong negative interferences, even with artificial negative NO_2 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. Under heavily polluted conditions close to emission sources, these negative interferences can be even more important compared to the positive NO_y interferences of molybdenum converter instruments. Whereas all the commercial instruments showed strong deviations compared to the spectroscopic FTIR technique in the smog chamber, excellent agreement between a new NO_2-LOPAP instrument and the FTIR technique was obtained. Since the NO_2-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_2 in the atmosphere.

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