The development of a nitrogen dioxide sonde

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Abstract. A growing number of space-borne instruments measures nitrogen dioxide (NO\textsubscript{2}) concentrations in the troposphere, but validation of these instruments is hampered by the lack of ground-based and in situ profile measurements.

The Royal Netherlands Meteorological Institute (KNMI) has developed a working NO\textsubscript{2} sonde. The sonde is attached to a small meteorological balloon and measures a tropospheric NO\textsubscript{2} profile. The NO\textsubscript{2} sonde has a vertical resolution of 5 m and a measurement range between 1 and 100 ppbv. The instrument is light in weight (0.7 kg), cheap (disposable), energy efficient and not harmful to the environment or the person who finds the package after use. The sonde uses the chemiluminescent reaction of NO\textsubscript{2} in an aqueous luminol solution. The NO\textsubscript{2}-luminol reaction produces faint blue/purple light (at about 425 nm), which is detected by an array of silicon photodiodes. The luminol solution is optimised to be specific to NO\textsubscript{2}.

An on-ground comparison with measurements from a Photolytic Analyser of The National Institute for Public Health and the Environment (RIVM) shows that both instruments measure similar NO\textsubscript{2} variations in ambient air.

During the Cabauw Intercomparison campaign of Nitrogen Dioxide measuring instruments (CINDI) in June/July 2009, six vertical profiles of NO\textsubscript{2} from the ground to a 5 km altitude were measured, which clearly show that the largest amount of NO\textsubscript{2} is measured in the boundary layer. The measured boundary layer heights of the NO\textsubscript{2} sonde are in good agreement with boundary layer heights determined by a LD40 Ceilometer at Cabauw.

1 Introduction

Nitrogen dioxide (NO\textsubscript{2}) is an important pollutant in the atmosphere, because it is toxic for living species, it forms photochemical ozone (O\textsubscript{3}) and acid rain in the form of nitric acid (HNO\textsubscript{3}). Nitrogen dioxide is a member of the nitrogen oxides (NO and NO\textsubscript{2}). In the troposphere they are typically formed as a by-product of the combustion of fossil fuels at high temperatures.

A growing number of space-borne instruments measures nitrogen dioxide concentrations in the atmosphere, but validation of these instruments is hampered by lack of ground-based and in situ profile measurements of NO\textsubscript{2}. This was one of the conclusions from the Atmospheric Composition Change the European Network of Excellence – Accent Troposat-2 (ACCENT-AT2) supported workshop on “Tropospheric NO\textsubscript{2} measured by satellites”, at KNMI, De Bilt, The Netherlands from 10 to 12 September 2007\textsuperscript{1}.

In situ profile measurements have been performed in a number of aircraft campaigns (e.g., Boersma et al., 2008; Kelly et al., 1990). A disadvantage of aircraft measurements is, apart from their relatively high cost, that the lower few hundred metres of the atmosphere, which contain a significant part of the tropospheric NO\textsubscript{2}, are difficult to reach.

The current study is aimed at the development of an instrument that can measure NO\textsubscript{2} in situ, which is cheap (disposable), light in weight, energy efficient, can provide profiles up to 30 km altitude and is not harmful for the environment or the finder of the package. Such an instrument can be launched with a normal weather balloon, typically used for ozone sondes.

\textsuperscript{1}This report can be found at http://www.knmi.nl/research/climate_observations/events/no2_workshop/presentations/NO2_report.pdf.
Existing in situ measurement techniques to measure NO$_2$ can be divided into three categories: laser-based techniques, differential optical absorption spectroscopy and chemiluminescence.

Laser-based techniques to measure NO$_2$ include laser-induced fluorescence (LIF; Matsumoto et al., 2001), tunable diode laser absorption spectroscopy (TDLAS; Li et al., 2004), cavity enhanced absorption spectroscopy (CEAS; Kekebian et al., 2005) and photo-acoustic spectroscopy (Mitrayana et al., 2007). Laser-based techniques are not considered for use on a disposable weather balloon, because these instruments are too large, heavy, energy-consuming and expensive.

Differential optical absorption spectroscopy (DOAS; Platt and Perner, 1980) requires an energy consuming broad-band light source and a long optical path. Therefore, also this technique is not a good candidate to use with a weather balloon.

Chemiluminescence techniques can be subdivided in gas-phase and liquid-phase chemiluminescence. The first uses a catalytic or photolytic converter to reduce NO$_2$ to NO which is then mixed with ozone (Steinbacher et al., 2007; Parrish et al., 1990). The reaction of NO with O$_3$ produces light, which is subsequently measured. The M200E Photolytic Analyser (mentioned in Sect. 5) and the TEI 42 TL chemiluminescence analyser with blue light converter (mentioned in Sect. 7) are examples of this technique. Gas-phase chemiluminescence is widely used in NO$_2$ monitoring networks. Both types of converters are energy-consuming, again making them less suitable for use on a weather balloon.

In the liquid-phase chemiluminescence technique light is emitted by the chemical reaction of luminol with NO$_2$. The commercially available Luminox LMA-3 instrument uses this technique combined with a photomultiplier tube (Kelly et al., 1990). This technique has been used in earlier attempts to make a light-weight instrument which can be launched with a balloon.

Hasinoff (1997) used an NO$_2$ sonde, as described by Pisano et al. (1996), in a field study at Kejimkujik National Park in Nova Scotia in 1996. The instrument weighs 1195 kg, and uses the luminol-NO$_2$ reaction. The emitted light of the luminol-NO$_2$ reaction is detected by a photomultiplier tube. Hasinoff (1997) measured NO$_2$ profiles up to 1 km altitude while the instrument was suspended from a tethered balloon. She recommends, for future studies, designing and building a more reliable and more user-friendly NO$_2$ sonde, as this instrument was found to be extremely difficult to use.

Sitnikov et al. (2005) build a chemiluminescent balloon-borne instrument called NaDA to measure NO$_2$. The NaDA instrument uses the chemiluminescent reaction of luminol with NO$_2$. The instrument weighs approximately 1 kg, and uses a photomultiplier tube, making it too heavy and too expensive for use in a disposable sonde.

The newly developed NO$_2$ sonde does not make use of a photomultiplier tube. Instead, an array of silicon photodiodes is used to detect the light from the chemiluminescent reaction. Photodiodes are light in weight and do not require power or a high voltage. An amplifier is used to enhance the rather weak signal from photodiodes. This amplifier, together with the reaction vessel and photodiodes, is placed in a metal can to reduce electrostatic interference.

The luminol solution in the NO$_2$ sonde has been optimised for the reaction with NO$_2$ following Mikuška et al. (2000). They studied the application of surfactants and complexones for the suppression of interferences from other pollutants in the determination of NO$_2$ with a Chemiluminescence Aerosol Detector (CLAD). Mikuška et al. (2000) use a luminol solution that is specific to NO$_2$ only and removes interference with O$_3$ and Peroxy Acetyl Nitrate (PAN), by adding sodium ethylenediaminetetraacetate (EDTA) and Triton X-100 to the luminol solution.

Section 2 gives a detailed description of the design of the instrument. The chemistry that is involved within the luminol solution is explained in Sect. 3. The calibration of the NO$_2$ sonde can be found in Sect. 4. Section 5 shows a comparison of the NO$_2$ sonde with an in situ monitor. The estimated uncertainty of the NO$_2$ sonde is discussed in Sect. 6. The measured NO$_2$ profiles during the Cabauw Intercomparison campaign of Nitrogen Dioxide measuring Instruments (CINDI campaign) are presented in Sect. 7. Discussion and conclusions can be found in Sect. 8.

2 Design of the instrument

Figure 1 (left side) shows a picture of the NO$_2$ sonde. The instrument is housed in a polystyrene (PS) foam box. PS is light in weight and a good insulator. The size of the PS box is 19 × 19 × 26 cm$^3$. The inside of the PS box is painted black, so ambient light is absorbed and can not disturb the measurement. To have an extra light barrier the instrument is placed in a black cardboard box. A radio transmitter (Vaisala RS92 radiosonde) is attached to the outside of the PS box. The weight of the NO$_2$ sonde is approx. 0.7 kg, excluding the weight of the radio transmitter.

Figure 2 shows a schematic diagram of the design of the instrument. A luminol reservoir (containing 35 ml luminol solution) is shown on the right. The liquid pump moves the luminol solution to the reaction vessel. The liquid pump used is a small (30 × 15 × 3.8 mm$^3$) piezoelectric diaphragm pump (Bartels microComponents mp6). The Teflon air pump, which is taken from an ozone sonde, forces the ambient air into the reaction vessel with a flow of 4 ml/s. A smaller flow rate would lower the signal and a larger flow rate would push all the liquid out of the reaction vessel. Johnson et al. (2002) tested the efficiency of the ozone sonde pump while decreasing the pressure. They concluded that the efficiency is not affected due to pressure decrease in the troposphere.

The tubes connected to the air pump are also made of Teflon. The gas is leaving the Teflon tube by two holes of
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Fig. 1. The left panel shows all the components of an NO$_2$ sonde without light protecting material. The right panel is a close-up of the detector.

Fig. 2. The design of the NO$_2$ sonde. The liquid pump moves the luminol solution to the reaction vessel in the centre. The Teflon air pump forces the air into the reaction vessel. The NO$_2$ in the air reacts with the luminol and the emitted photons are detected by an array of silicon photodiodes (the seeing photodiodes). An aluminum mirror is placed on the opposite site to reflect the emitted photons back to the seeing photodiodes. An identical array of photodiodes, the blind array, is mounted behind the aluminum foil to measure and correct for – the effects discussed in Sect. 2.1. A copper wire is mounted in the reaction vessel to prevent electrostatic build-up.

1 mm diameter. The NO$_2$ in the gas flow reacts with the luminol solution, which emits blue/violet light at a wavelength of 425 nm. The secondary function of the gas flow is to force the luminol solution out of the reaction vessel back to the luminol reservoir, so luminol is recycled continuously. The recycling of luminol is necessary to reduce acidification of the system by carbon dioxide (CO$_2$). Acidification can not be completely avoided because the luminol solution in the reservoir is continuously diluted with solution from the reaction vessel. The luminol solution contains Triton X-100 which causes foam and is able to escape in small proportions from the sealing of the luminol reservoir, therefore, absorption material is attached on the outside of the luminol reservoir. The volume of the luminol reservoir is 50 ml, but contains 35 ml of the luminol solution.

2.1 The detector

The detector, as shown in Fig. 1 (right side), consists of a glass test tube, with an array of photodiodes on either side. Each array of photodiodes has its own circuit board for signal processing. The schematic diagram of the circuits is shown in Fig. 3. It shows from left to right the photodiodes (only 2 of the 8 are shown) who produce an electric current when exposed to light, a current to voltage converter, a low-pass RC (resistor-capacitor) filter with a time constant of 1 s, to prevent under sampling of the signal by the data acquisition system (described in the next section) and a times 1 amplifier, to reduce the output impedance. The circuit has been designed to convert femtoamperes current from the photodiodes to millivolts at the output.

The circuit has been tested with an independent current source, to verify its sensitivity. A flashing light has been used to test its response to changing signals and the reflected light from two sources has been used to demonstrate that the output is linear to the intensity of light in the range from 10 to 2000 millivolts. The noise of the circuit is just below 1 millivolt when no photodiodes are attached. With the full array of 8 photodiodes the noise increases to 5 or 6 millivolts.

The circuit generates two unwanted signals. One is a dark current that differs from circuit to circuit, and is temperature dependent. This current can be characterised in the laboratory before launch, see Sect. 3. Furthermore, a signal is generated when the temperature of the photodiodes is changed. This might be caused by a heat flux through the photodiodes causes an electric current. Temperature changes inside the sonde can, however, not be prevented. This is why two arrays
of photodiodes have been used. The second (or blind) array has been mounted behind a piece of aluminum foil. The heat flux signal can be eliminated by subtracting the signals from both arrays. This function is performed as part of the post flight data processing.

2.2 The radiosonde

A Vaisala RS92SGP digital radiosonde is added as part of the package. This device measures ambient temperature, humidity and air pressure. Furthermore, it contains a GPS receiver, to measure its position, from which the wind speed and direction can be inferred. A radio transmitter sends the data to the ground station. The radiosonde is connected to a Vaisala RSA-11 ozone sonde interface. The device has four analogue inputs that are sampled once per second. Channels 3 and 4 are used to relay the signals from the NO₂ detector. Channel 2 is dedicated to the measurement of the temperature inside the air pump. Channel 1 remains unused in the current design, but could be used for an additional ozone sensor. Laboratory studies have shown that the response time of the chemical reaction is in the order of one second. The RC filter in the amplifiers prevents under sampling of the NO₂ profile. With an ascending speed of 5 m/s and a read-out frequency of once per second, the resulting resolution of the NO₂ profile is, thus, in the order of 5 m.

3 The luminol solution

The NO₂ sonde makes use of a chemical reaction called chemiluminescence. Chemiluminescence is an exothermic reaction, but instead of heat, light is emitted. The basic ingredient for this reaction is luminol, which gets in exited state when it reacts with NO₂, and emits light of approximately 425 nm when decaying. The amount of light that is emitted is correlated to the NO₂ concentration. The aqueous luminol solution contains an additional number of chemical compounds to make the luminol solution specific to NO₂.

The chemical compounds and their function are listed and described below.

- Potassium hydroxide (KOH) allows the luminol to dissolve in water by changing its
  state when it reacts with NO₂. White et al. (1963) studied the chemical reaction
  of luminol with O₃. They argued that the reaction of the hydroxide ion (OH⁻) with
  luminol is the first step of the reaction, see Eq. (1).

  \[
  \text{A} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{B}
  \]

  (1)

  Deprotonation (A, Eq. 1) occurs when the strong base (OH⁻) reacts with the weak acid secondary amino groups (–NH) forming a negative charge on the carbonyl oxygen (–C=O) to form what is known as an enolate (C, Eq. 1). The enolate anion is stabilized by resonance. The next step of the NO₂-luminol reaction is not well understood. Maeda et al. (1980) reported that in the absence of KOH in luminol solution, no chemiluminescence was observed. When the concentration of KOH exceeded 10⁻⁵ mol/l chemiluminescence was detected and the intensity was increased with the increase of KOH concentration.

- Sodium sulphite (Na₂SO₃) is an anti-oxidant and is capable to capture sulphur dioxide (SO₂) and ozone (O₃). Wendel et al. (1983) discovered that Na₂SO₃ increases the duration of the stable period of the luminol solution. Na₂SO₃ also increases the emitted light signal, as shown in Fig. 4b, which is consistent with the results of Maeda et al. (1980).

- Ethanol makes the luminol solution more specific to NO₂. Wendel et al. (1983) discovered that the addition of a primary alcohol – in their case methanol – increased the sensitivity and specificity for NO₂. The signal doubled at a concentration of 0.05% v/v and then decreased at higher concentrations. An advantage of using ethanol, which is also a primary alcohol, is that it is less harmful than methanol. Nguyen et al. (2006) also saw an increase in the light signal when using a luminol solution with a primary alcohol. Why the primary alcohol makes the luminol solution more specific to NO₂ is not well understood.

- Sodium EDTA (ethylenediaminetetraacetate) is a complex former. Mikuška et al. (2000) claim that sodium EDTA is amplifying the functioning of Na₂SO₃. It makes the removal of O₃ and PAN more efficient. The preferred solution of Mikuška et al. (2000) lowers the interference of O₃ (mixing ratio 50 ppbv NO₂ with 170 ppbv O₃) to 0.2% of the total signal and lowers PAN interference (mixing ratio 50 ppbv NO₂ with
Triton X-100 (4-octylphenol polyethoxylate) makes the oxygen needed to activate the NO$_2$ luminol reaction. Without oxygen, luminol does not emit light when exposed to NO$_2$. Adding oxygen is only relevant for laboratory studies, as the ambient air contains sufficient oxygen for the reaction.

3.1 Optimizing the luminol solution

The chemicals that are listed above can be categorised into two groups; the reaction group (luminol, KOH, Na$_2$SO$_3$, O$_3$) and the protecting group (Na$_2$SO$_3$, Triton X-100, Na EDTA, ethanol). The chemicals listed in the reaction group fulfil an important role in the luminol-NO$_2$ reaction and the chemicals in the protecting group lower the interference of other strong oxidizers like PAN and O$_3$.

The chemicals in the reaction group are optimized with respect to the light signal. This is done in an iterative process by varying the concentration of one component while holding the concentrations of all the other compounds constant around their optimum values, as found in a previous iteration step. The setup of this experiment is the same as in Fig. 2, where the ambient air was replaced with NO$_2$ from a gas cylinder (10 ppmv NO$_2$ in N$_2$), mixed with CO$_2$-free air to an NO$_2$ concentration of 1.4 ppmv. Chemicals were added to the luminol reservoir. Note that for the optimizing experiments, an NO$_2$ concentration of 1.4 ppmv is used, which is much higher than what is typically observed in the atmosphere (ppbvs).

The molar concentration of the chemicals is expressed in M (mol/l) units. Figure 4 shows the measured light signal as a function of concentration of the chemicals in the reaction group, luminol, Na$_2$SO$_3$ and KOH (top to bottom). The largest light signal is reached for a luminol concentration between $1 \times 10^{-4}$ M and $2 \times 10^{-4}$ M. For larger luminol concentrations the light signal decreases again, probably as a result of self-absorption. The optimum Na$_2$SO$_3$ concentration is between 0.01 and 0.02 M and the optimum pH value is between 12 and 12.2, corresponding to KOH concentrations between 0.01 M and 0.016 M.

Table 1 gives an overview of optimal concentration ranges of the luminol solution and the standard concentrations actually used in this paper. The optimal luminol solution is the one which gives the highest light signal. The standard concentration of 1.4 ppmv NO$_2$ is used, with an unpaired electron, probably provides different electrostatic interactions with triton micelles in comparison with those by O$_3$ and PAN that have no unpaired electron in the molecule.
concentration of KOH used in the flying sondes is slightly higher in an attempt to reduce the effect of acidification (discussed below) and, hence, lengthen the time the sensor can be used.

### 3.2 Acidification of the luminol solution

When the NO₂ sonde is measuring ambient air, carbon dioxide (CO₂) will acidify the luminol solution (already suggested by Maeda et al., 1980). The relevant reactions are:

\[
\text{CO}_2 + \text{KOH} \rightarrow \text{KHCO}_3 \\
\text{KHCO}_3 + \text{KOH} \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}
\]

Figure 5 shows the degradation of the pH as a function of time. The pH measurements were recorded at surface pressure, by mixing ambient air and NO₂ from the gas cylinder (ISO 17025 reliable, 10 ppmv NO₂ and 99.999% N₂) to a known NO₂ concentration (1.4 ppmv). The flow rate of the Teflon air pump is the same as for the other experiments: 4 ml/s. The standard luminol solution is used for this experiment (see Table 1). In Sect. 3.1, it was shown that a pH between 12 and 12.2 gives the optimal light signal. In sonde flights the pH is initially brought to 12.5, to have an extended measuring time without a large degradation of the light signal. Also a luminol reservoir has been added to the sonde, so it can operate for about 2.5–3 h in a pH range of 12.5–11.6.

![Figure 5. Laboratory measurements of the pH as a function of time. Acidification is caused by CO₂, see Sect. 3.2. The measurement points are connected with straight lines.](image)

### 3.3 Nonlinearity issues

Several authors have reported a nonlinear response of liquid-phase chemiluminescence detectors, in the 0 to 3 ppbv range. Mikuška et al. (2000) shows that the nonlinearity depends on the chemical composition of the luminol solution, while Pisano et al. (1996) claim that the nonlinearity differs from instrument to instrument. Kelly et al. (1990) reported a change of sensitivity of his detector over time, and hints at a possible dependence on the age of the chemicals used. The reported nonlinearity’s would, however, lead to corrections of less than 1 ppbv.

In this study the linearity problem has been investigated in the RIVM calibration facility. This calibration was performed at room temperature (20°C) and ground pressure only. The air used in this experiment was from an ISO 17025 reliable cylinder (10 ppmv NO₂, 99.999% N₂), mixed with clean air containing CO₂. NO₂ mixing ratios of 0, 1, 2, 4, 8, 16, 32 and 64 ppbv were introduced to 8 prototypes of the NO₂ sonde. The results for two of the sondes (F07, and the less sensitive F05) are shown in Fig. 7. F07 was clearly able to record 1 ppbv of NO₂, while no nonlinearity was evident.

Figure 7 shows that within the targeted measurement range the deviations from linearity are below 10% or 0.8 ppbv, which leads to the conclusion that the NO₂ sonde linearity is a valid approximation.

### 4 Calibration

The calibration of the measured signal is performed using the relation:

\[
n = f(T,T_pH) \times (S_1 - S_2 - O (T_d)),
\]

where \(n\) is the number density of NO₂, \(S_1\) is the measured signal in the seeing array of photodiodes and \(S_2\) is the measured signal of the blind array of photodiodes, \(O\) is an offset.

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**Table 1.** Chemical compounds and concentrations used in the aqueous solution of luminol. The second column shows the optimal concentration range for the chemical compounds. The concentrations \((M=\text{mol/l})\) that are applied in this paper are shown in the third column. The standard solutions have a higher than optimal concentration for potassium hydroxide, which is chosen to compensate for the effect of acidification by carbon dioxide. See Sect. 3 for more details.

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Optimal concentration range</th>
<th>Standard concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luminol</td>
<td>(1 \times 10^{-4} \text{M} - 2 \times 10^{-4} \text{M})</td>
<td>(1 \times 10^{-4} \text{M})</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>0.01 M–0.02 M</td>
<td>0.02 M</td>
</tr>
<tr>
<td>Potassium Hydroxide</td>
<td>0.01 M–0.016 M (pH: 12–12.2)</td>
<td>0.03 M (pH: 12.5)</td>
</tr>
<tr>
<td>Sodium EDTA</td>
<td>(2 \times 10^{-4} \text{M})</td>
<td>(2 \times 10^{-4} \text{M})</td>
</tr>
<tr>
<td>Triton X100</td>
<td>0.02% v/v</td>
<td>0.02% v/v</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.05% v/v</td>
<td>0.05% v/v</td>
</tr>
</tbody>
</table>
which depends on the detector temperature $T_d$ (see Fig. 6) and $f(T,\text{pH})$ is a scaling factor. The number density $n$ is converted to volume mixing ratio $\nu$ using the relation:

$$\nu [\text{ppbv}] = 1.38 \times 10^{-12} \times n [\text{cm}^{-3}] \times \frac{T_p [\text{K}}{p [\text{hPa}]},$$  

(4)

where $p$ is the pressure of the ambient air and $T_p$ is the temperature inside the air pump.

The scaling factor $f(T,\text{pH})$ is almost constant during the first few hours of the measurement, meaning that the signal is almost linear with the amount of NO$_2$.

The change in pH value during the measurement results in a small change in the scaling factor of about 10% in 2.5 h (see Sect. 3.2). The scaling factor also depends on the temperature of the solution, as can be seen in Fig. 8. The change in the scaling factor is 2.0% per degree Celsius for temperatures between 20°C and 40°C, a typical temperature range inside the sonde box (air temperature outside the sonde box can of course be much lower). Figure 9 shows the temperatures of the pump, the liquid and the detector during a laboratory measurement as a function of time. After the initial few minutes, the temperatures behave very similar with a difference of 1 to 2°C. Therefore, the pump temperature can be used to characterise the temperature correction.

Six sondes were launched during the CINDI campaign, June–July 2009 in Cabauw, the Netherlands (see Sect. 7). The temperature dependence of the offset was characterised before the launch, so the offset is estimated to be a third order polynomial in time. This is an iterative fit through a selection of measurement points. At each iteration step those points are selected for which the difference to the polynomial is less than 1.5 $\sigma$, starting with all measurement points and ending when the selection does not change anymore. Here $\sigma$ is the root mean square difference of the selected measurement points of the previous iteration to the fitted polynomial. This procedure could lead to an underestimation of NO$_2$ in the free troposphere.

The scaling factor is determined using simultaneous in situ measurements by a Thermo Environmental Instruments (TEI 42 TL) chemiluminescence analyser with a Blue Light Converter, operated by EMPA during the CINDI campaign. Both instruments measure the ambient air at the same time, so that the amount of measured NO$_2$ should be equal. The scaling factor at the launch is determined by dividing the average offset-corrected measurement signal of the sonde before launch by the interpolated 10 min values of the in situ monitor. The correction factor for the change in pH-value during the flight is estimated to be $1 - 0.07 \times (t/1.4)^2$, where $t$ is the flight time.
following from the data in Figs. 4 and 5, which is only a 1% effect in the lowest kilometre.

5 Comparison of the NO$_2$ sonde with an in situ monitor

The NO$_2$ sonde is compared with an M200E Photolytic Analyser of Teledyne-API Inc. operated by RIVM. The M200E Photolytic Analyser measures NO and NO$_x$ (NO + NO$_2$) and derives NO$_2$ from it. The main goal of this comparison was to look if both instruments measure the same dynamical range in NO$_2$ concentration variations during a certain period of time. Both instruments measured the NO$_2$ concentration in ambient air at the same location on the roof of a building at approximately 20 m altitude, during rush hour. For this comparison a standard luminol solution is used (see Table 1).

The M200E Photolytic Analyser reports one-minute averaged NO$_2$ values. The NO$_2$ sonde data is also averaged over one minute in this comparison. As the sonde has not been calibrated with a known concentration of NO$_2$, an assumption for the scaling factor had to be made. The scaling factor is chosen such that the average NO$_2$ during the measuring period is equal for both instruments. The measurement of the NO$_2$ sonde shown in Fig. 10 is corrected for temperature (see Sect. 4) and pH (see Sect. 3.2).

Four comparisons were made, but only one was without technical problems. The results are shown in Fig. 10. The technical difficulties that occurred for the other three comparisons were a broken liquid pump and leakage at the sealing of the reaction vessel. In the case of the broken liquid pump, the luminol solution was not recycled and this caused rapid acidification of the luminol solution, resulting in a loss of signal.

Figure 10 shows that both instruments measure the same dynamical range of changing NO$_2$ values and that variations of 1 ppbv in NO$_2$ are well captured. Noticeable are small differences between the two datasets, slowly changing with time, which suggest that the NO$_2$ sonde has either a degrading sensitivity as a function of time or some nonlinearity in the scaling factor. This effect is still under investigation.

6 Estimated uncertainty

The root mean square (RMS) of the inter-comparison of the NO$_2$ sonde with the M200E photolytic analyser of RIVM is 1 ppbv. This is an upper limit for the precision of the NO$_2$ sonde measurements. The linearity study, described in Sect. 3.3, shows a maximum deviation of 0.8 ppbv or 10% when assuming linearity. We have characterised and eliminated the systematic effects caused by a variability in temperature and pH (Sect. 4). Unknown other systematic effects are artificially removed by scaling the sonde measurements to collocated independent in situ measurements.
Fig. 11. Six vertical NO\textsubscript{2} profiles measured during CINDI June/July 2009. On the x-axis the NO\textsubscript{2} volume mixing ratio and on the y-axis the altitude (km). The dashed horizontal lines indicate the boundary layer height above Cabauw around 10:30 UT, measured by the KNMI Ceilometer. The blue lines indicate the outside air temperature during the sonde flight.

This is done both for the on-ground comparison to the in situ monitor (Sect. 5) and for the sondes launched during the CINDI campaign (Sect. 7). For the CINDI sondes we have not been able to characterise the temperature dependent offset before launch. The estimate used for this offset, as described in Sect. 4, can lead to an underestimation of NO\textsubscript{2} in the free troposphere. This effect will disappear when the temperature dependencies are characterised for each individual detector before launch. A proper estimate of the uncertainty in flight can only be given if the sonde measurements are compared to an independent source of NO\textsubscript{2} profile information.

7 CINDI campaign

During the CINDI campaign in June/July 2009, six NO\textsubscript{2} sondes were launched and measured six vertical profiles of NO\textsubscript{2}. The launch site was located at Lopik, the Netherlands (51.97° N, 4.93° E). Figure 11 shows the six profiles that were measured. All NO\textsubscript{2} sondes were launched at approximately 10:30 UTC, or 12:30 LT (local time). The NO\textsubscript{2} sondes were treated with clean air just before launch, to determine the dark current of the detector. The NO\textsubscript{2} sondes were scaled to in situ measurements performed by EMPA (TEI 42 TL chemiluminescence analyser, with BLC) just before launch. The target vertical velocity of the sonde flights was 5 m/s. The response of the NO\textsubscript{2} sonde to changing NO\textsubscript{2} concentrations is 1 s, giving a resolution of 5 m. In Fig. 11, the boundary layer heights are clearly visible in the profiles. They are in good agreement with boundary layer heights determined from meteorological measurements at Cabauw (LD40 Ceilometer, backscatter profiles).

The first NO\textsubscript{2} sonde was launched on 18 June 2009, Fig. 11a. This profile shows a maximum NO\textsubscript{2} concentration around 930 m altitude and a clear top of the boundary layer at 2 km. Its vertical resolution is higher than that of the other sondes, because it had a smaller vertical velocity.

The profile of 23 June 2009 (Fig. 11b) shows at an altitude of 4.8 km a peak in NO\textsubscript{2} concentration. This peak could have been caused by a layer of airplane exhaust.

The profile of 30 June 2009 (Fig. 11c) shows a second NO\textsubscript{2} layer (1–3 km) above the boundary layer (0–1 km). The origin of this “second layer” could not be determined from meteorological measurements at Cabauw.

8 Discussion/conclusion

The NO\textsubscript{2} sonde is light in weight, cheap (disposable), energy efficient and not dangerous for the environment. The sonde has a fast response to changing NO\textsubscript{2} concentrations which results in an unsurpassed vertical resolution of 5 m. It measures in the range 1–100 ppbv. The NO\textsubscript{2} sonde can measure under all weather conditions irrespective of the amount of clouds.

The NO\textsubscript{2} sonde developed at KNMI has demonstrated its capability to measure in situ NO\textsubscript{2} profiles in the lower atmosphere. Six profiles have been collected during the CINDI campaign in June/July 2009. The top of the boundary layer is clearly visible in the profiles and are in good agreement with boundary layer heights determined from meteorological measurements at Cabauw (backscatter profiles, LD40 Ceilometer).

Comparison with the M200E Photolytic Analyser shows that variations of 1 ppbv in NO\textsubscript{2} are well captured. Both instruments measure the same dynamical range in NO\textsubscript{2} variations in ambient air during a 2.5 h period. The estimated uncertainty of the NO\textsubscript{2} sonde measurements is 1 ppbv, after the correction for temperature dependence and pH and after artificially removing all remaining unknown systematic effects by scaling the on-ground measurements to collocated, independent, in situ measurements. The measurements during CINDI may underestimate the NO\textsubscript{2} values in the free
troposphere, because the temperature dependent offset was not well characterised before the launch. This is expected to improve for further launches.

Further validation of the NO\textsubscript{2} sonde is desirable and can be done by a comparison with the NO\textsubscript{2} LIDAR.

The NO\textsubscript{2} sonde can measure for approximately 2.5–3 h. After that time the solution becomes increasingly acid due to CO\textsubscript{2}. Longer continuous measurements can be established by using a good buffer solution or a CO\textsubscript{2} scrubber to keep the pH constant.

In theory, the sonde can make NO\textsubscript{2} profiles up to the stratosphere, but because the temperature within the sonde rises up to 40 °C, the luminol solution begins to boil at low pressure. To prevent this in the near future, a redesign of the pump drivers is required.

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