

The development of a nitrogen dioxide sonde

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Abstract. A growing number of space-borne instruments measures nitrogen dioxide (NO₂) 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 NO₂ sonde. The sonde is attached to a small meteorological balloon and measures a tropospheric NO₂ profile. The NO₂ 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 NO₂ in an aqueous luminol solution. The NO₂-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 NO₂.

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 NO₂ variations in ambient air.

During the Cabauw Intercomparison campaign of Nitrogen Dioxide measuring instruments (CINDI) in June/July 2009, six vertical profiles of NO₂ from the ground to a 5 km altitude were measured, which clearly show that the largest amount of NO₂ is measured in the boundary layer. The measured boundary layer heights of the NO₂ sonde are in good agreement with boundary layer heights determined by a LD40 Ceilometer at Cabauw.

1 Introduction

Nitrogen dioxide (NO₂) is an important pollutant in the atmosphere, because it is toxic for living species, it forms photochemical ozone (O₃) and acid rain in the form of nitric acid (HNO₃). Nitrogen dioxide is a member of the nitrogen oxides (NO and NO₂). 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 NO₂. 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 NO₂ measured by satellites”, at KNMI, De Bilt, The Netherlands from 10 to 12 September 2007¹.

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 NO₂, are difficult to reach.

The current study is aimed at the development of an instrument that can measure NO₂ in situ, which is cheap (disposable), light in weight, energy efficient, can provide profiles up to 30 km altitude and is not harmful to the environment or the finder of the package. Such an instrument can be launched with a normal weather balloon, typically used for ozone sondes.



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¹This 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 NO₂ can be divided in three categories: laser-based techniques, differential optical absorption spectroscopy and chemiluminescence.

Laser-based techniques to measure NO₂ include laser-induced fluorescence (LIF; Matsumoto et al., 2001), tunable diode laser absorption spectroscopy (TDLAS; Li et al., 2004), cavity enhanced absorption spectroscopy (CEAS; Keabian 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 NO₂ to NO which is then mixed with ozone (Steinbacher et al., 2007; Parrish et al., 1990). The reaction of NO with O₃ 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 NO₂ 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 NO₂. The commercially available Luminol 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 NO₂ sonde, as described by Pisano et al. (1996), in a field study at Kejimikujik National Park in Nova Scotia in 1996. The instrument weighs 1195 kg, and uses the luminol-NO₂ reaction. The emitted light of the luminol-NO₂ reaction is detected by a photomultiplier tube. Hasinoff (1997) measured NO₂ 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 NO₂ 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 NO₂. The NaDA instrument uses the chemiluminescent reaction of luminol with NO₂. 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 NO₂ 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 NO₂ sonde has been optimised for the reaction with NO₂ 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 NO₂ with a Chemiluminescence Aerosol Detector (CLAD). Mikuška et al. (2000) use a luminol solution that is specific to NO₂ only and removes interference with O₃ 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 NO₂ sonde can be found in Sect. 4. Section 5 shows a comparison of the NO₂ sonde with an in situ monitor. The estimated uncertainty of the NO₂ sonde is discussed in Sect. 6. The measured NO₂ 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 NO₂ 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 cm³. 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 NO₂ 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 mm³) 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

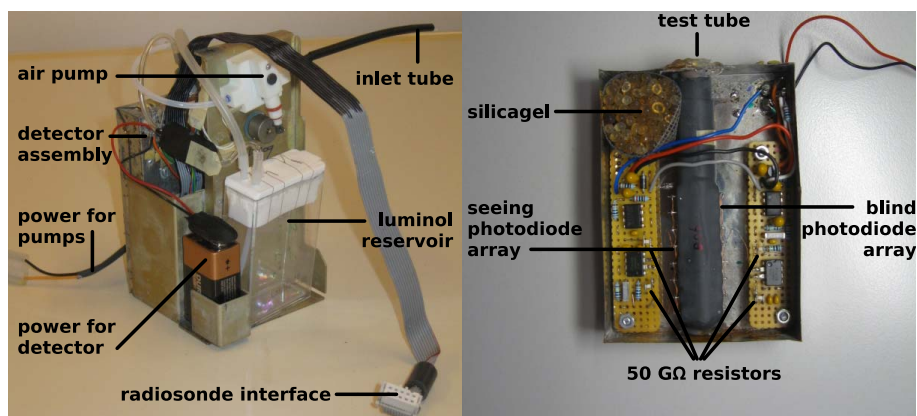


Fig. 1. The left panel shows all the components of an NO_2 sonde without light protecting material. The right panel is a close-up of the detector.

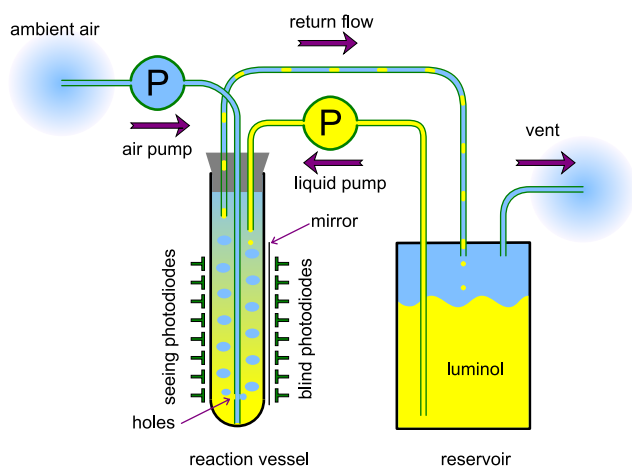


Fig. 2. The design of the NO_2 sonde. The liquid pump moves the luminol solution to the reaction vessel in the centre. The Teflon air pump forces the air into the reaction vessel. The NO_2 in the air reacts with the luminol and the emitted photons are detected by an array of silicon photodiodes (the 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

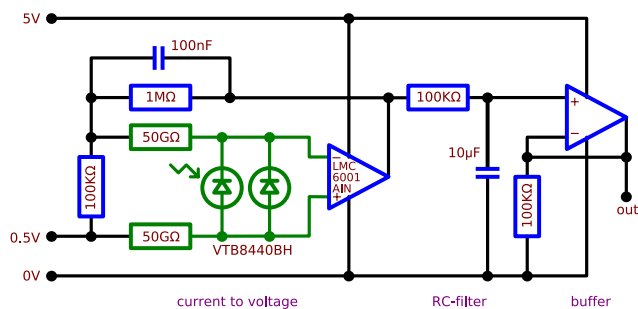


Fig. 3. The electronic circuit used in the detector. Note that only 2 of the 8 photodiodes are shown. The parts drawn in green are not mounted on the circuit board in order to minimize the effect of surface leakage currents.

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

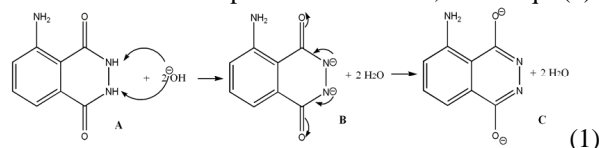
A Vaisala RS92SGP digital radiosonde is added as part of the package. This device measures ambient temperature, humidity and air pressure. Furthermore, it contains a GPS receiver, to measure its position, from which the wind speed and direction can be inferred. A radio transmitter sends the data to the 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 NO_2 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 NO_2 profile. With an ascending speed of 5 m/s and a read-out frequency of once per second, the resulting resolution of the NO_2 profile is, thus, in the order of 5 m.

3 The luminol solution

The NO_2 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 excited state when it reacts with NO_2 , and emits light of approximately 425 nm when decaying. The amount of light that is emitted is correlated to the NO_2 concentration. The aqueous luminol solution contains an additional number of chemical compounds to make the luminol solution specific to NO_2 .

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

- Potassium hydroxide (KOH) allows the luminol to dissolve in water by changing its polarity. White et al. (1963) studied the chemical reaction of luminol with O_2 . They argued that the reaction of the hydroxide ion (OH^-) with luminol is the first step of the reaction, see Eq. (1).



Deprotonation (A, Eq. 1) occurs when the strong base (OH^-) reacts with the weak acid secondary amino groups ($-\text{NH}$) forming a negative charge on the carbonyl oxygen ($-\text{C}=\text{O}$) to form what is known as an enolate (C, Eq. 1). The enolate anion is stabilized by resonance. The next step of the NO_2 -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 (Na_2SO_3) is an anti-oxidant and is capable to capture sulphur dioxide (SO_2) and ozone (O_3). Wendel et al. (1983) discovered that Na_2SO_3 increases the duration of the stable period of the luminol solution. Na_2SO_3 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 NO_2 . Wendel et al. (1983) discovered that the addition of a primary alcohol – in their case methanol – increased the sensitivity and specificity for NO_2 . 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 NO_2 is not well understood.
- Sodium EDTA (ethylenediaminetetraacetate) is a complex former. Mikuška et al. (2000) claim that sodium EDTA is amplifying the functioning of Na_2SO_3 . It makes the removal of O_3 and PAN more efficient. The preferred solution of Mikuška et al. (2000) lowers the interference of O_3 (mixing ratio 50 ppbv NO_2 with 170 ppbv O_3) to 0.2% of the total signal and lowers PAN interference (mixing ratio 50 ppbv NO_2 with

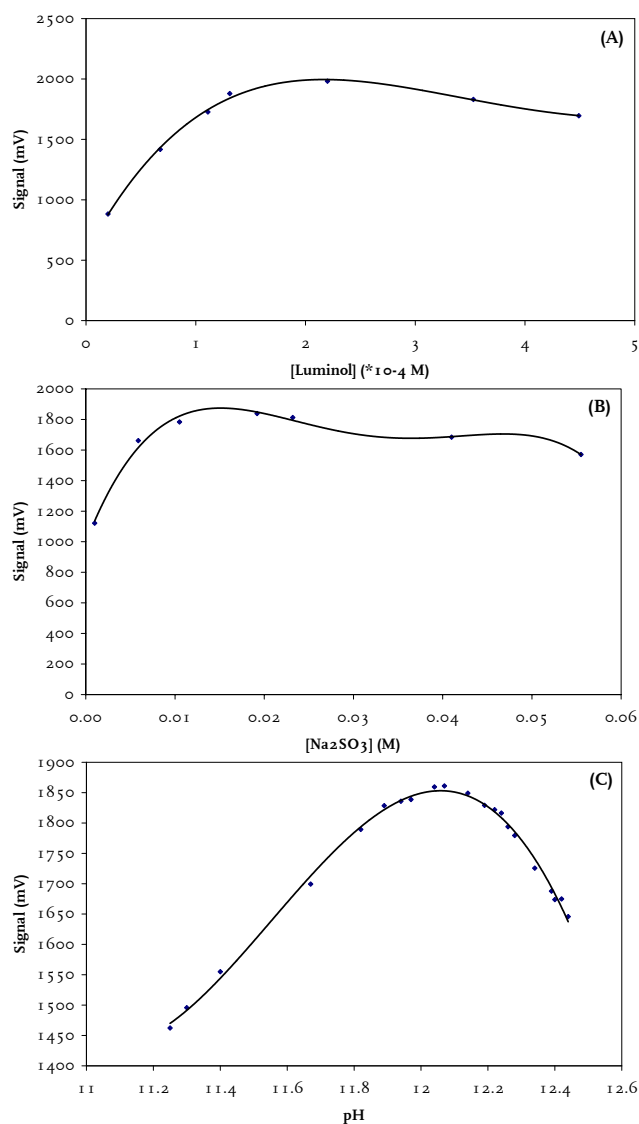


Fig. 4. Optimum concentration experiment for luminol (A), Na₂SO₃ (B) and KOH (C). (A) and (B) show signal (mV) versus concentration (M = mol/l), (C) shows signal (mV) versus pH value. A constant concentration of 1.4 ppmv NO₂ is used. The standard deviation of the measurements is on the order of 20 mV. The black line is a 4th order polynomial fit. The optimal concentration ranges are shown in Table 1.

81 ppbv PAN) to 1.2% of the signal (in combination with Triton X-100).

- Triton X-100 (4-octylphenol polyethoxylate) makes the luminol reaction more specific to NO₂. Triton X-100 decreases the surface tension, thereby enhancing the contact surface between air and liquid. Mikuška et al. (2000) argued that the enhancement of NO₂ response arises from an increase in the concentration of luminol molecules at the surface of triton micelles. (A micelle is an aggregate of surfactant molecules dispersed

in a liquid collide. A micelle in an aqueous solution forms an aggregate with the hydrophilic “head” regions in contact with surrounding solvent, isolating the hydrophobic single tail regions in the middle centre.) with subsequent diminution of vibrational quenching of excited species, which improves the fluorescent quantum yield of excited luminol. A radical molecule like NO₂, with an unpaired electron, probably provides different electrostatic interactions with triton micelles in comparison with those by O₃ and PAN that have no unpaired electron in the molecule.

- Oxygen is needed to activate the NO₂ luminol reaction. Without oxygen, luminol does not emit light when exposed to NO₂. 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, Na₂SO₃, O₂) and the protecting group (Na₂SO₃, Triton X-100, Na EDTA, ethanol). The chemicals listed in the reaction group fulfil an important role in the luminol-NO₂ reaction and the chemicals in the protecting group lower the interference of other strong oxidizers like PAN and O₃.

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 NO₂ from a gas cylinder (10 ppmv NO₂ in N₂), mixed with CO₂-free air to an NO₂ concentration of 1.4 ppmv. Chemicals were added to the luminol reservoir. Note that for the optimizing experiments, an NO₂ 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, Na₂SO₃ and KOH (top to bottom). The largest light signal is reached for a luminol concentration between 1×10^{-4} M and 2×10^{-4} M. For larger luminol concentrations the light signal decreases again, probably as a result of self-absorption. The optimum Na₂SO₃ 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

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 = 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.

Chemical compound	Optimal concentration range	Standard concentration
Luminol	1×10^{-4} M– 2×10^{-4} M	1×10^{-4} M
Sodium sulphate	0.01 M–0.02 M	0.02 M
Potassium Hydroxide	0.01 M–0.016 M (pH: 12–12.2)	0.03 M (pH: 12.5)
Sodium EDTA	2×10^{-4} M	2×10^{-4} M
Triton X100	0.02% v/v	0.02% v/v
Ethanol	0.05% v/v	0.05% v/v

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:



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 4c shows that for this pH range the signal variation is less than 10%. The sonde data is corrected for the acidification using parameterizations of pH as a function of time and signal as a function of pH, based on the measurements from Figs. 4c and 5, respectively (see Sect. 4). The acidification rate is determined at ground pressure and it will probably be smaller at higher altitudes because the CO₂ partial pressure will be lower. This means that it might take even longer than 2.5–3 h before the pH drops below 11.6.

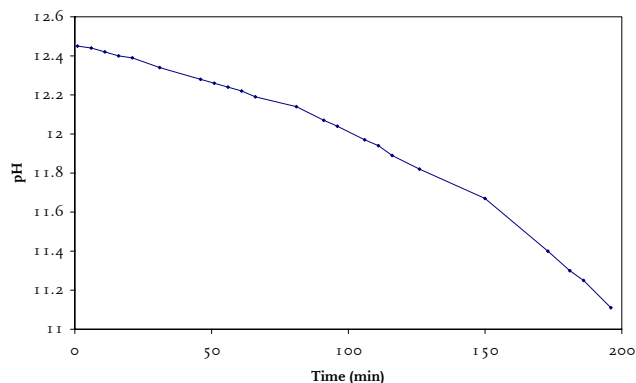


Fig. 5. Laboratory measurements of the pH as function of time. Acidification is caused by CO₂, see Sect. 3.2. The measurement points are connected with straight lines.

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:

$$n = f_{(T, \text{pH})} \times (S_1 - S_2 - O(T_d)), \quad (3)$$

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

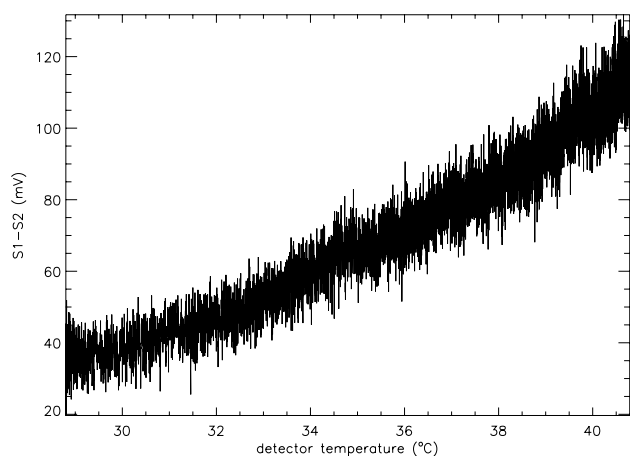


Fig. 6. The difference $S1-S2$ between the signals measured by the seeing and blind detector arrays, using water and ambient air, as a function of the detector temperature. The signal represents the offset O in Eq. (4), for which the NO_2 measurements need to be corrected.

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 ν using the relation:

$$\nu \text{ [ppbv]} = 1.38 \times 10^{-12} \times n \text{ [cm}^{-3}] \times \frac{T_p \text{ [K]}}{p \text{ [hPa]}}, \quad (4)$$

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°. 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 not 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 1.5σ , starting with all measurement points and ending when the selection does not change

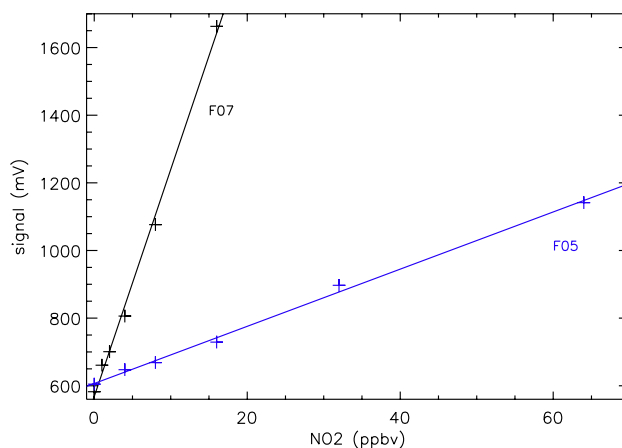


Fig. 7. The signal of the NO_2 sonde detectors as a function of the amount of NO_2 for two different versions of the detector, F05 and F07. F05 is designed for laboratory studies and is less sensitive, allowing larger NO_2 concentrations. The solid lines are linear least-squares fits.

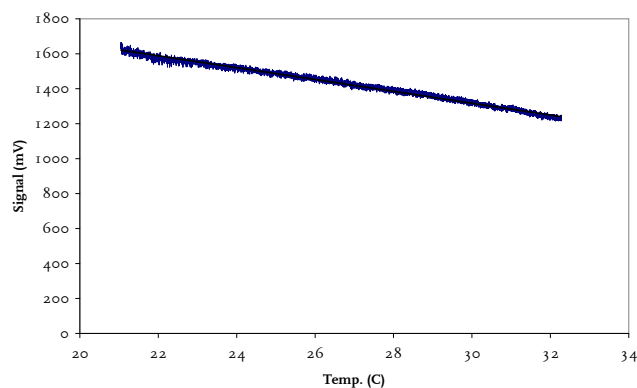


Fig. 8. Signal (mV) of the seeing photodiodes as a function of temperature (°C) in the luminol solution, for a constant amount of NO_2 (blue). The black line represents a linear fit through the measured points. The signal decreases with 2.0% per degree Celsius.

anymore. Here σ 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 $1 - 0.07 \times (t[\text{h}] - 1.4)^2$,

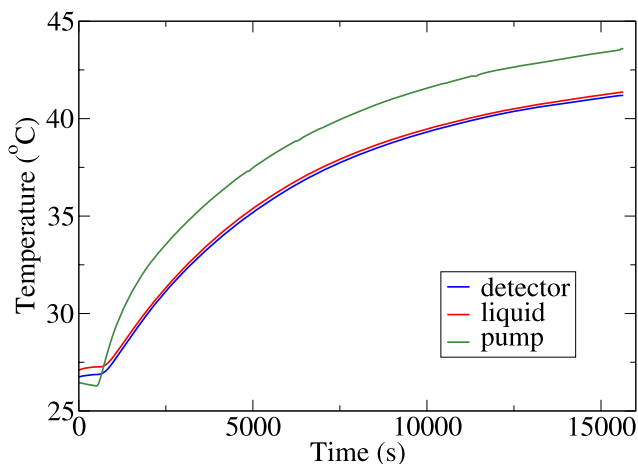


Fig. 9. Temperature ($^{\circ}\text{C}$) as function of time (s) for the liquid in the reservoir (red), Teflon air pump (green) and detector (blue) during a laboratory measurement.

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 ($\text{NO} + \text{NO}_2$) 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.

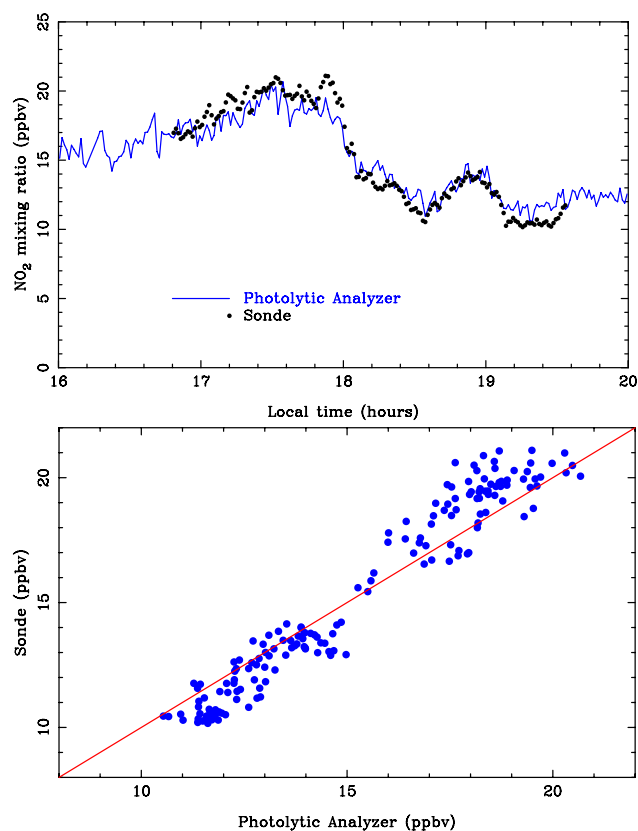


Fig. 10. Left: NO_2 concentration measurements by the NO_2 sonde (black dots) compared with those by the M200E photolytic analyser (blue line). Measurements were taken during the evening rush-hour in Bilthoven, The Netherlands. Right: scatter diagram of the same data.

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.

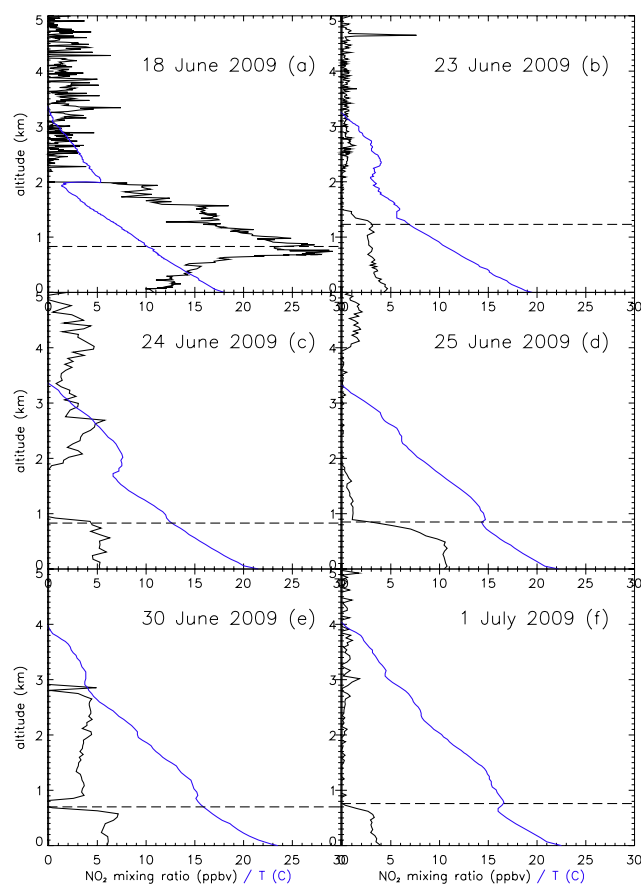


Fig. 11. Six vertical NO_2 profiles measured during CINDI June/July 2009. On the x-axis the NO_2 volume mixing ratio and on the y-axis the altitude (km). The dashed horizontal lines indicate the boundary layer height above Cabauw around 10:30 UT, measured by the KNMI Ceilometer. The blue lines indicate 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_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_2 profile information.

7 CINDI campaign

During the CINDI campaign in June/July 2009, six NO_2 sondes were launched and measured six vertical profiles of NO_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_2 sondes were launched at approximately 10:30 UTC, or 12:30 LT (local time). The NO_2 sondes were treated with clean air just before launch, to determine the dark current of the detector. The NO_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_2 sonde to changing NO_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_2 sonde was launched on 18 June 2009, Fig. 11a. This profile shows a maximum NO_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_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_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_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_2 concentrations which results in an unsurpassed vertical resolution of 5 m. It measures in the range 1–100 ppbv. The NO_2 sonde can measure under all weather conditions irrespective of the amount of clouds.

The NO_2 sonde developed at KNMI has demonstrated its capability to measure in situ NO_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_2 are well captured. Both instruments measure the same dynamical range in NO_2 variations in ambient air during a 2.5 h period. The estimated uncertainty of the NO_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_2 values in the free

troposphere, because the temperature dependant offset was not well characterised before the launch. This is expected to improve for further launches.

Further validation of the NO₂ sonde is desirable and can be done by a comparison with the NO₂ LIDAR.

The NO₂ sonde can measure for approximately 2.5–3 h. After that time the solution becomes increasingly acid due to CO₂. Longer continuous measurements can be established by using a good buffer solution or a CO₂ scrubber to keep the pH constant.

In theory, the sonde can make NO₂ 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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References

- Boersma, K. F., Jacob, D. J., Bucsela, E. J., Perring, A. E., Dirksen, R., van der A, R. J., Yantosca, R. M., Park, R. J., Wenig, M. O., Bertram, T. H., and Cohen, R. C.: Validation of OMI tropospheric NO₂ observations during INTEX-B and application to constrain NO_x emissions over the eastern United States and Mexico, *Atmos. Environ.*, 42, 4480–4497, 2008.
- Hasinoff, L. C.: Vertical profiles of NO₂ and O₃ at Kejimikujik National Park, Nova Scotia, Thesis, Graduate programme in Chemistry York University, North York, Ontario, 1997.
- Johnson, B. J., Oltmans, S. J., Vömel, H., Smit, H. G. J., Deshler, T., and Kröger, C.: Electrochemical concentration cell (ECC) ozonesonde pump efficiency measurements and tests on the sensitivity to ozone of buffered and unbuffered ECC sensor cathode solutions, *J. Geophys. Res.*, 107(D19), 4393, doi:10.1029/2001JD000557, 2002.
- Kebabian, P. L., Herndon, S. C., and Freedman, A.: Detection of nitrogen dioxide by cavity attenuated phase shift spectroscopy, *Anal. Chem.*, 77, 724–728, 2005.
- Kelly, T. J., Spicer, C. W., and Ward, G. F.: An Assessment of the luminol chemiluminescence technique for measurement of NO₂ in ambient air, *Atmos. Environ.*, 24A(9), 2397–2403, 1990.
- Li, Y. Q., Demerjian, K. L., Zahniser, M. S., Nelson, D. D., McManus, J. B., and Herndon, S. C.: Measurement of formaldehyde, nitrogen dioxide, and sulphur dioxide at Whiteface Mountain using a dual tunable diode laser system, *J. Geophys. Res.*, 109, D16S08, doi:10.1029/2003JD004091, 2004.
- Maeda, Y., Aoki, K., and Munemori, M.: Chemiluminescence Method for the Determination of Nitrogen Dioxide, *J. Anal. Chem. Soc.*, 52, 307–311, 1980.
- Matsumoto, J., Hirokawa, J., Akimoto, H., and Kajii, Y.: Direct measurement of NO₂ in the marine atmosphere by laser-induced fluorescence technique, *Atmos. Environ.*, 35, 2803–2814, doi:10.1016/S1352-2310(01)00078-4, 2001.
- Mikuška, P. and Večeřa, Z.: Effect of complexones and tensides on selectivity of nitrogen dioxide determination in air with a chemiluminescence aerosol detector, *Anal. Chim. Acta*, 410, 159–165, 2000.
- Mitrayana, Pierera, T., Moeskops, B. W. M., Persijn, S., Naus, H., Harren, F. J. M., Wasono, M. A. J., -Muslim, and Rochmah, W.: Diode-laser based photo-acoustic spectroscopy in atmospheric NO₂ detection, *Berkala Ilmiah MIPA*, Vol. 17(3), 2007.
- Nguyen, D. H., Berry, S., Geblewicz, J. P., Couture, G., and Huynh, P.: Chemiluminescent detection of explosives, narcotics, and other chemical substances, US patent no.: US6,984,524 B2, 2006.
- Parrish, D. D., Hahn, C. H., Fahey, D. W., Williams, E. J., Bollinger, M. J., Hübler, G., Buhr, M. P., Murphy, P. C., Trainer, M., Hsie, E. Y., Liu, S. C., and Fehsenfeld, F. C.: Systematic Variations in the Concentration of NO_x (NO plus NO₂) at Niwot Ridge, Colorado, *J. Geophys. Res.*, 95(D2), 1817–1836, 1990.
- Pisano, J. T. and Drummond, J. W.: A Lightweight NO₂ Instrument for Vertical Height Profiles, *J. Atmos. Ocean. Tech.*, 13, 400, 1996.
- Platt, U. and Pierera, T.: Direct measurements of atmospheric CH₂O, HNO₂, NO₂, and SO₂ by differential optical absorption in the near UV, *J. Geophys. Res.-Oceans*, 85, 7453–7458, 1980.
- Sitnikov, N. M., Sokolov, A. O., Ravegnani, F., Yushkov, V. A., and Ulanovskiy, A. E.: A chemiluminescent Balloon-Type Nitrogen Dioxide Meter for Tropospheric and Stratospheric Investigations (NaDA), *Instrum. Exp. Tech.*, 48(3), 400–405, 2005.
- Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, B., Ordoñez, C., Prevot, A. S. H., and Hueglin, C.: Nitrogen dioxide measurements at rural sites in Switzerland: Bias of conventional measurements techniques, *J. Geophys. Res.*, 112, D11307, doi:10.1029/2006JD007971, 2007.
- Wendel, G. J., Stedman, D. H., and Cantrell, C. A.: Luminol – based Nitrogen Dioxide Detector, *Anal. Chem.*, 55, 937–940, 1983.
- White, E. H., Zafiriou, O., Kägl, H. H., and Hill, H. M.: Chemiluminescence of Luminol: The Chemical Reaction, *J. Am. Chem. Soc.*, 86, 940–941, 1964.