Development of a Nitrogen Dioxide Sonde

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ABSTRACT

Nitrogen dioxide is an important pollutant in the atmosphere, it is toxic for living species, it forms photochemical tropospheric ozone, and acid rain.

There is a growing number of space-borne instruments to measure nitrogen dioxide concentrations in the atmosphere, but validation of these instruments is hampered by lack of ground-based and in-situ profile measurements.

The Royal Netherlands Meteorological Institute (KNMI) has developed a working NO_2 sonde. By our knowledge it is the first in the world. The sonde is attached to a small meteorological balloon and measures a tropospheric NO_2 profile. The NO_2 sonde has a vertical resolution of 5 m, and a measurement range between 1 and 100 ppbv. The design of the instrument poses a number of challenges. The instrument must be light in weight, cheap (disposable), energy efficient and not harmful to the environment or the person who finds the package after use. Therefore we can not make use of the popular molybdenum catalytic converter or a photomultiplier. Instead, the sonde uses the chemiluminescent reaction of NO_2 with an aqueous luminol solution. The NO_2 – luminol reaction produces a faint blue/purple light (425 nm), which is detected by an array of photodiodes. The luminol solution is optimized to be specific to NO_2. The efficiency of the NO_2 – luminol reaction depends on the pH of the solution. To reduce acidification of the system by carbon dioxide the chemicals are refreshed constantly.

During the Cabauw Intercomparison campaign of Nitrogen Dioxide measuring Instruments (CINDI) in June/July 2009 we measured seven vertical profiles of NO_2 from the ground to 6 km altitude.

1. INTRODUCTION

Nitrogen dioxide is an important pollutant in the atmosphere, it is toxic for living species, it forms photochemical tropospheric ozone, and acid rain.

There is a growing number of space-borne instruments to measure 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_2.

This was one of the conclusion of the ACCENT-AT2 supported workshop on “Tropospheric NO_2 measured by satellites”, KNMI, De Bilt, The Netherlands, 10-12 September 2007.

The current study is aimed at the development of an instrument that can measure NO_2 in-situ, that is cheap (disposable), light in weight, energy efficient, can reach an altitude of at least 10 km, and is not harmful for the environment or the finder of the package.

There is an extensive ground based network of NO_2 sensors. Typically they use either a catalytic or photolytic converter to reduce NO_2 to NO. The chemiluminescence reaction between NO and O_3 is used to measure the concentration of NO. Also NO_2 has been measured from aircraft, for example with the Luminox instrument[3]. However a significant part of the NO_2 exists in the lower few hundred meters of the atmosphere, which are difficult to reach by aircraft.

In 1996 Hasinoff[1] has been working on a lightweight NO_2 instrument that was used to measure NO_2 profiles, while suspended from a tethered balloon. The instrument used the NO_2 – luminol reaction, and the emitted light is detected by a photomultiplier tube (PMT). They use a luminol-saturated wick in the reaction chamber. Hasinoff [1] concluded that this NO_2 instrument is not user friendly and not reliable. There is a long stabilizing period for the electronics of about 1 hour before use. Furthermore, it takes up to 2 hours before the wick is saturated with the luminol solution, which has to be done every time the system is not used for a period of 12 hours. A third limitation involves the detector drift (± 1500 counts) over a period of 1 hour. When a signal drift occurs, a new calibration measurement is required.

The KNMI NO_2 sonde does not make use of a PMT. 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 much power or a high voltage. An amplifier is used to enhance the rather weak signal from the photodiodes. This amplifier, together with the reaction vessel and photodiodes is placed in a metal can, to reduce electrostatic and radio interference.

The luminol solution in the NO_2 sonde has been optimised for the reaction with NO_2 following Mikuška et all[2]. They created a chemiluminescence detector using nebulized luminol (CLAD), to determine NO_2 concentrations in the atmosphere. They use nebulized luminol to increase the reaction surface for the reaction. They use a solution that is specific to NO_2 and removes interference with ozone and PAN.

2. DESIGN OF THE SONDE

Fig. 1 shows a picture of the NO_2 sonde from the outside. The outside of the sonde is made of a polystyrene (PS) box. PS is light in weight and a good insula-

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tor. The inside of the PS box is painted black, so light from the outside is absorbed and can not disturb the measurement. To have an extra light barrier the instrument is placed in a black housing made of carton. In *fig. 2* a schematic picture is shown of the design of the instrument.

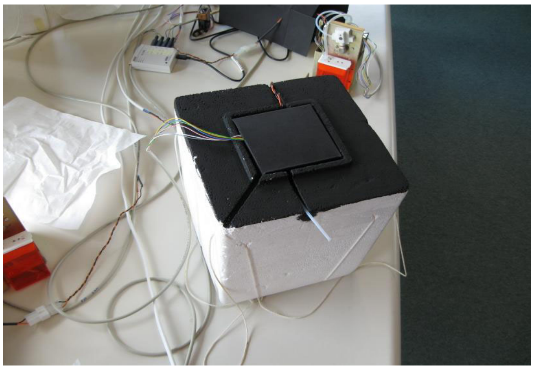

Figure 1. *The outside of the sonde.*

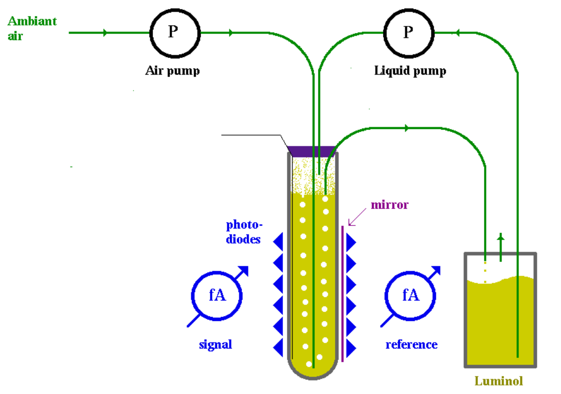

Figure 2. *Design of the instrument.*

A luminol reservoir is illustrated on the right side of *fig. 2*. The liquid pump moves the luminol solution to the reaction vessel in the middle of *fig. 2*. A Teflon air pump, pumps in the ambient air into the reaction vessel. On the left side an array of silicon photodiodes detects the emitted light from the NO_2 – luminol reaction. On the right side an aluminium mirror reflects emitted photons back to the photodiodes on the left side. Behind the mirror there is another array of silicon photodiodes measuring a reference signal. The air entering the reaction vessel forces the luminol solution back to the reservoir, so luminol is recycled continuously. The recycling of luminol is necessary to reduce acidification of the system by carbon dioxide.

3. THE LUMINOL SOLUTION

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 functions are listed and described below.

- Potassium hydroxide (KOH): dissolves luminol in water by changing its polarity. The reaction of OH^- with luminol is assumed to be the first step of the reaction chain.
- Sodium sulphite (Na_2SO_3) is an anti oxidant and is capable to capture sulphur dioxide and ozone. Na_2SO_3 also makes the luminol solution stable for a longer period of time[3].
- Ethanol makes the luminol reaction more specific to NO_2. It also increases the amount of light that is produced during the reaction.
- Sodium EDTA is a complex former. Mikuška et al.[2] claim that sodium EDTA is amplifying the function of Na_2SO_3. It makes the removal of ozone and PAN more efficient. It lowers the interference of ozone to 0.2% of the total signal and lowers the PAN interference to 1.2% of the signal (in combination with Triton X-100).
- Triton X-100 makes the luminol reaction more specific to NO_2. Triton X-100 decreases the surface tension, thereby enhancing the contact surface between air and liquid. In this way more NO_2 reacts with luminol and more light is emitted in the same period of time.
- Oxygen is needed to activate the NO_2 – luminol reaction. Without oxygen, luminol does not emit light when exposed to NO_2. Furthermore, when the luminol solution is treated with clean air for an extended period before the measurements, the reaction with NO_2 becomes more efficient.

3.1 Optimizing the luminol solution

All the chemical compounds have been optimized with respect to the emitted signal. In this section the optimization of luminol is shown as an example. The other compounds are optimized in the same way.

Figure 3 shows the emitted light as a function of the luminol concentration, using a constant NO_2 concentration. All other compounds were kept constant. The largest signal is reached for a luminol concentration of $1{\cdot}10^{-4}$ M. For larger concentrations the self-absorption of luminol is decreasing the signal again.

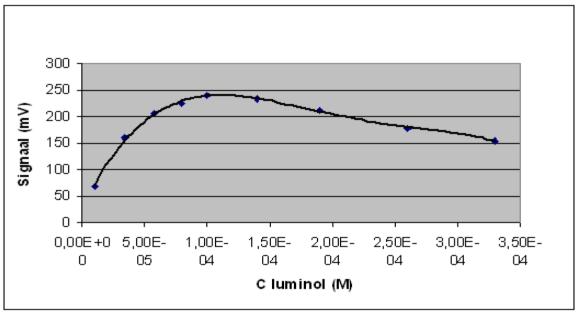

Figure 3: *Optimum luminol concentration. On the x-axes the concentration of luminol (M) is plotted, and on the y-axes the signal (mV) is plotted.*

4. CALIBRATION

In *fig. 4*, a calibration graph is shown of an NO_2 sonde. This calibration is done in a climate chamber of RIVM, The Netherlands, were the NO_2 concentration can be controlled.

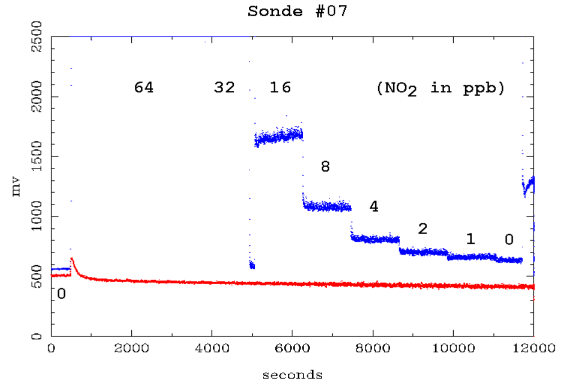

Figure 4. *The calibration graph of one of the NO_2 sondes. On the x-axes the time (s) is plotted and on the y-axes the signal (mV). The NO_2 sonde is exposed to respectively 64, 32 (both off-scale), 16, 8, 4, 2, 1, 0 ppbv NO_2.*

In *fig. 5* the signal is shown as a function of the NO_2 concentration. The signal response of the detector is almost linear to the concentration of NO_2.

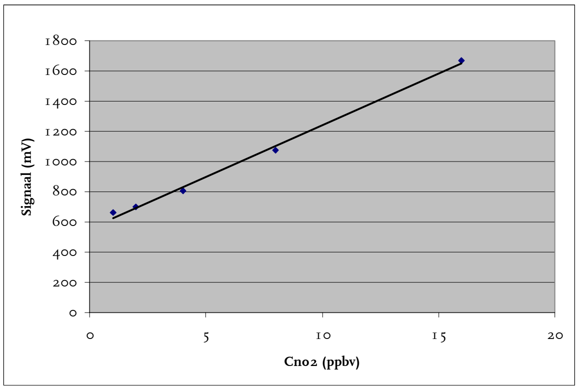

Figure 5: *The signal (mV) as a function of the concentration of NO_2 (ppbv). The black line is a linear fit to the measurements. The correlation coefficient is 0.996.*

5. NO_2 PROFILES

During the CINDI campaign in June 2009, seven NO_2 sondes are launched. The NO_2 sondes are treated with clean air just before launch, to make the luminol solution more efficient. The clean air period is also used to measure the dark current of the instrument. *Figs. 6 and 7* show two NO_2 profiles measured at 18 and 23 June 2009 respectively. Both sondes were launched around 12:30 local time.

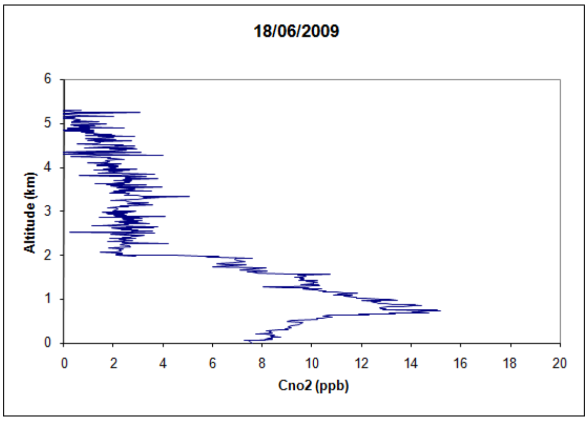

Figure 6: *Measured NO_2 profile at 18 June 2009. On the x-axes the NO_2 concentration (ppbv) is plotted and on the y-axes the altitude (km) is plotted.*

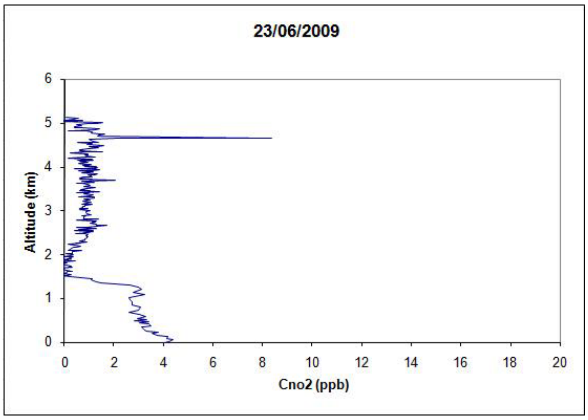

Figure 7: *Measured NO_2 profile at 23 June 2009. On the x-axes the NO_2 concentration (ppbv) is plotted and on the y-axes the altitude (km) is plotted.*

The difference in vertical resolution is caused by the difference in vertical velocity of the two weather balloons.

In *fig. 7* at an altitude of 4.8 km, the NO_2 profile shows a peak in NO_2 concentration. This peak might indicate that the sonde went through a layer of airplane exhaust. At that altitude airplanes fly over Cabauw to land at Schipol airport. Figs. 6 and 7 both also clearly show the boundary layer height at 2 and 1.6 km respectively.

The NO_2 sondes are scaled to in-situ measurements performed by EMPA just before launch.

6. CONCLUSIONS

The NO_2 sonde developed at KNMI has demonstrated its capability to measure in-situ NO_2 profiles in the lower atmosphere. Seven profiles have been collected during the CINDI campaign in June/July 2009.

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.

In theory the sonde can make NO_2 profiles up to the stratosphere.

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