NOxTOy: A MINIATURISED NEW INSTRUMENT FOR REACTIVE NITROGEN OXIDES IN THE ATMOSPHERE

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Emission of nitrogen oxides (NO, NO_2) and hydrocarbons into the atmosphere lead under sunlight to the formation of ozone and other photooxidants. To better understand the ozone forming processes, the production and concentration of the nitrogen containing reaction products like nitric acid (HNO_3) or peroxyacetylnitrate (PAN) have to be determined. In a joint project with other research institutions and a private enterprise a miniaturised instrument was developed under a KTI contract. It is possible to measure several nitrogen oxides, NO_2, NO_x, NO_y, PAN, HNO_3 and O_x simultaneously. The dimensions and the power consumption of the instrument are suited for the operation in a motorglider and in a van. First measurements have been successfully performed and are presented.

1 INTRODUCTION

Hydrocarbons (RH) and nitrogen oxides (NO_x = NO + NO_2) are the two key chemical precursors of photochemical smog and its concomitant high concentrations of ozone (O_3). The reactions that lead to O_3 production involve the oxidation of hydrocarbons and other volatile organic compounds (VOC) in the presence of nitrogen oxides (NO_x) and sunlight. The numerous reactions can be aggregated into two sets of reactions, the NO_x cycle and the VOC cycle (Figure 1). The reactions in the NO_x cycle are the following:

NO_2 + light $\rightarrow$ NO + O

O + O_2 $\rightarrow$ O_3

NO + O_3 $\rightarrow$ NO_2 + O_2

NO_2 is photolyzed leading to the formation of ozone, but is regenerated via the reaction of NO with ozone. In the course of the oxidation of the volatile organic compounds described in the VOC cycle, intermediate peroxy radicals are formed (RO_2), which also convert NO to NO_2 without destruction of O_3. Chemically speaking, the NO_x are the catalyst and VOCs are the fuel of the ozone formation. However, NO_x is not an ideal catalyst, since there exist many reactions, which remove it from the reaction system. These termination reactions, also shown in Figure 1, lead to a variety of nitrogen oxide compounds. The knowledge of their composition and concentrations with respect to other photooxidants is very valuable for the understanding and modeling of air pollution processes.

Ten years ago a successful collaboration to measure air pollutants with a small aircraft started between PSI and MetAir company [1,2]. Up to now, NO_2 was the only nitrogen oxide species which we could measure. No commercial instrument to measure other nitrogen oxide compounds was available, which satisfied our restrictions of size, weight and power consumption. In view of the importance of the different nitrogen oxide species to the understanding of air pollution processes, we decided to build our own instrument. It was developed in a joint project of PSI, MetAir AG, FZJ (Forschungszentrum Jülich) and Flinders University in Adelaide, Australia.

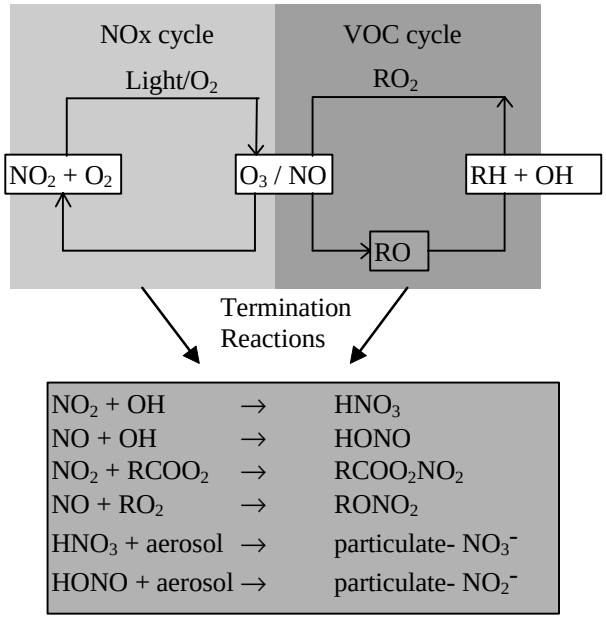

Fig. 1: Aggregate mechanism of the production of ozone and the formation of various reactive nitrogen oxide compounds.

2 INSTRUMENT

The instrument is based on the chemiluminescence of Luminol when reacting with NO_2. It has 6 separate inlet channels, each measuring a different nitrogen oxide compound or a sum of different compounds. This was achieved by introducing different catalysts in the channels, which convert one or several nitrogen oxide species into NO_2. The air is then passed over a luminol wetted glass frit. The chemiluminescence intensity is detected with photon counters (Figure 2).

1. NO_2: can be measured directly
2. NO_x = NO + NO_2: the air is pulled over small bricks, which were coated with Chromium trioxide. CrO_3 converts NO into NO_2.
3. NO_y = NO_x + HNO_3 + HONO + $RCOO_2NO_2$ + $RONO_2$ + p-NO_3^- + p-NO_2^-: All these species are first reduced to NO over molybdenum heated to 350°C. NO is then converted to NO_2 via CrO_3.
4. NO_y - HNO_3: At the inlet HNO_3 is removed with a Nylon filter. The rest of the species is then again

reduced to NO with a molybdenum converter. NO is then converted to NO_2 via CrO_3.

5. NO in the inlet air is converted to NO_2 with CrO_3. Afterwards, $RCOO_2NO_2$ is decomposed to NO_2 in the inlet line, which is heated to 125°C.
6. $O_x = O_3 + NO_2$: A high concentration of NO is fed into the inlet tube, some of which is converted by the ozone containing air into NO_2.

Thus, the concentration of NO_2 and NO_y, which is the sum of all kinds of reactive nitrogen oxide species, is given by the signal of their channels. The concentration of other nitrogen oxide compounds can be derived by calculating differences of the measurements of some of the channels (ch# = channel number as described above):

- NO ch2 - ch1
- HNO_3 ch3 - ch4
- $RCOO_2NO_2$ ch5 - ch2
- O_3 ch6 - ch1

The size of the instrument is only 44x24x28 cm^3 and power consumption is less than 100 W.

3 MEASUREMENTS

The instrument behaves as expected from literature. It shows a nonlinear behavior below 3 ppb and has an interference to ozone and PAN. The rise time is less than a second, which allows to perform flux measurements and also yields a good spatial resolution for flight measurements.

First flight measurements have been done in the Lombardy region during the LOOP (Limitation of oxidant production) field campaign. Figure 3 shows the increased levels of NO_x down wind of Milano and above highways and main roads measured a few hundred meters above ground.

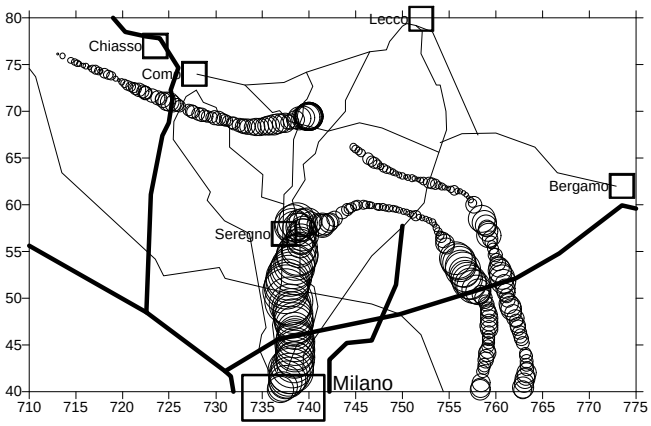

Fig. 3: Flight measurements in Northern Italy. Symbols (o) are proportional to the NO_x concentration at < 700 masl. Main roads (thin line) and highways (thick line) are drawn. Coordinates are in the Swiss km grid.

4 OUTLOOK

The instrument has already been in operation for several field campaigns and strongly improved the measuring capacity of MetAir. Other research groups expressed strong interest in this instrument, which eventually could lead to the commercialization of it.

5 ACKNOWLEDGEMENT

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6 REFERENCES

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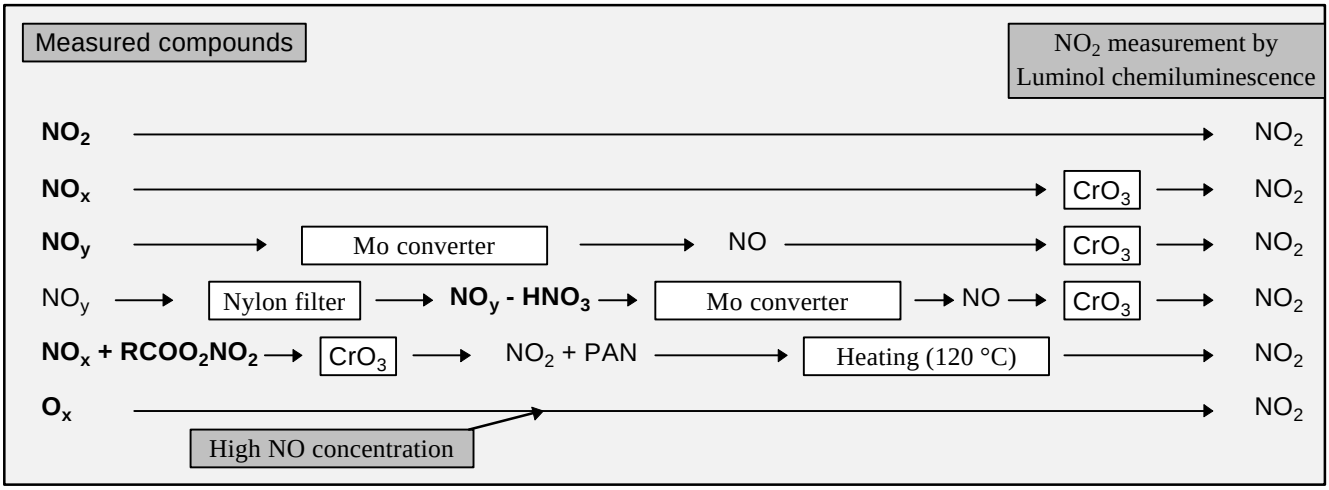

Fig. 2: The 6 inlet channels of the instrument and the conversion of nitrogen oxide compounds into NO_2