Characterization of measurement uncertainties for newly developed NO_2-sensor, $CHUNCNO_2$

Ankie Piters (P.I.)

Introduction and motivation

Recently, KNMI, developed a new, light-weight NO_2 sensor to be used on a weather balloon or unmanned aircraft. The sensor has been demonstrated to work in flight, and to capture variability in NO_2 concentration within 1 ppbv or 10 %[1]. However, the absolute calibration, and the factors that have an influence on this calibration are not yet well understood.

From November 12th to November 16th 2012, the NO_2-sonde participated in a five day NO- /NO_2- research and inter-comparison campaign at the Hohenpeißenberg observatory, organized by ACTRIS. This side-by-side experiment in Hohenpeißenberg focused on correct measurement on NO and NO_2. In order to do so, synthetic air mixtures (zero air, NO and NO_2), as well as spiked ambient air (NO, NO_2 and NH_3) and pure ambient air and more complex synthetic mixtures (H_2O and HNO_3) were analyzed and compared with the thirteen participating institutes.

In perspective of the improvement of the NO_2-sonde, the campaign was of a major importance for the investigation of 1) the sensitivity of different chemical solutions towards the Nitrogen containing atmospheric trace gases NO, O_3, NH_3 and HNO_3, 2) the linearity of the sonde for both high and low NO_2 concentrations and 3) the effect of some of the chemicals in the solution, mainly on the linearity of the recorded signals and on the interference by NO, NH_3 and HNO_3.

Scientific objectives

By the participation in this project we hoped to find and answer to the following questions:

- What is the precision of the measurements of NO_2, and how does this depend on on sensor and/or liquid temperature, composition and preparation of the chemical solution?
- What is the signal with zero air (offset), and does it depend on temperatures and solutions?
- What is the sensitivity of the sensor for different temperatures and solutions?
- What is the sensitivity to other gases, like PAN, NH_3 and HNO_3?

Reason for choosing station

First of all, participating in this side by side inter-comparison campaign brought us in the position to try out measurements with a new series of detectors, equipped with 5 chemical solutions, prepared in different ways. The inter-comparison with other calibrated NO_2 measuring instruments, gave us the opportunity to compare our results with those from other instruments, which provided many benefits for the data analysis to later be performed, because there was no absolute calibration for the NO_2 sensors available at the time of the campaign.

Secondly, the Hohenpeißenberg Observatory station provided the rare chance to prove that identical samples are identically analyzed by collocated NO_2 measuring instruments. This was achieved by instruments sampling from a common manifold which in comparison to round-robins has the advantage that much more complex sample gas mixtures could be analyzed and also the mole fractions could be varied in a controlled manner such that a range of the detection limits of the instruments to polluted conditions was encountered. This enabled a characterization of the detection limit, the linear range, the span, and of potential artifacts of interfering gases which were present in the complex test gas mixtures used. The instruments were also operated in ambient air conditions and used to characterize the photo-stationary state and contribution of NO_x to photo-

chemistry.

Both the opportunity to use the advanced equipment provided during the campaign in combination with the possibility for inter-comparison of the results obtained, this campaign contributed extensively to the completion of the optimization work to be conducted in order for the NO_2 sensor to become commercially operational.

Method and experimental set-up

In general, during 5 days, gas samples from a common manifold were measured with three or four sondes simultaneously, equipped with the same or with different luminol solutions (different: varying chemical composition). In the schedule below, the gas mixtures provided, measurement conditions and measurement purposes are listed more detailed **table 1**.

Date	No. detectors	No. solutions	Gas composition	Purpose
12 Nov	4	1: standard	Zero air Zero air + 40 ppb NO Zero air + 40 ppb NO_2	- Installation, tests, and checks. - The same luminol solution was used to determine the ratios between all 4 detectors. - Determining the sensor's response to 40 ppb NO in comparison to the signal height for 40 ppb of NO_2.
13 Nov	4	4 different chemical solutions	Zero air Zero air +: - 7.83 ppb NO_2 - 17.41 ppb NO_2 - 41.99 ppb NO_2	- Inter-comparison with synthetic, NO_x containing air mixtures. - Composition of a new calibration curve based on 4 different concentrations and using 4 different luminol solutions. - Investigation of the linearity of the chemical reaction when using different luminol solutions. - Investigation of the precision, zero-air-signal and sensitivity of the sensor for different solutions.
14 Nov	4	1 : standard	Zero air Ambient air Spiked ambient air: - 8 ppb NO + 4 ppb O_3 - 12 ppb NO + 6 ppb O_3	- Validation of the response time and time resolution of the NO_2 sensor in comparison to other NO_2 detecting instruments.
15 Nov	4	4 different chemical solutions	Ambient air Ambient air with: - 20 ppb NH_3 Zero air Zero air with: - 14 ppb NO_2 with 3 ≠ humidities (%) - 4.5 ppb HNO_3	- Determination of the sensitivity to other Nitrogen containing trace gases, in this case NH_3 and HNO_3.

16 Nov	3	1) 1 solution, altered composition. 2) 4 different chemical solutions	1) Zero air Zero air with: - 5 ppb HNO_3 and water vapor - 21 ppb NO_2 - 42 ppb NO_2 2) Zero air Zero air with: - 5 ppb NO_2 - 2.5 ppb NO_2 - 1.25 ppb NO_2	Measurement on request to establish the: - Composition of a new calibration curve for high NO_2 concentrations using 4 different luminol solutions for data comparison. - Investigation of the linearity of the chemical reaction when using different luminol solutions for low NO_2 concentrations. - Investigation of the lower detection limit. - Investigation of the precision, zero-air-signal and sensitivity of the sensor for different solutions. Any changes in comparison to Tuesday 13 Nov or when low NO_2 concentrations are measured?

Overnight, ambient air was measured. Because the NO_2 sensor can measure continuously for no longer than 4 hours because after this the luminol solution becomes too acidified and needs to be refreshed, a time clock was used for these measurements. The time period between 02 am and 06 am was chosen because at the Observatory NO_2 concentrations are usually highest during these early morning hours before sunrise. During all overnight measurements only one type of luminol solution was used, to check whether the sensitivity ratio between the detectors had not changed during the day-time measurements.

Preliminary results and conclusions

In general the side-by-side inter-comparison project has contributed to:

- Proving the sondes' linearity for both high **Fig. 1** and low **Fig. 2** NO_2 concentrations when using luminol solutions of a different chemical composition.

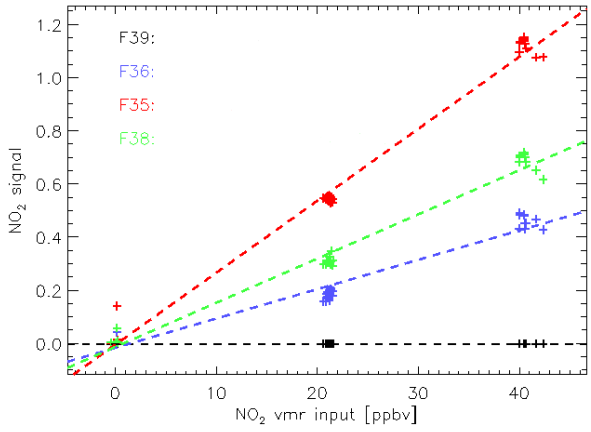

Fig. 1: Calibration curve for high NO_2 concentrations

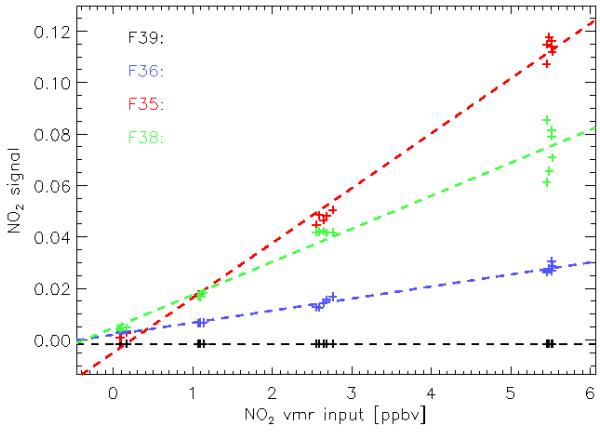

Fig. 2: Calibration curve for low NO_2 concentrations

- The visualization of the NO_2 sensors minor response to 5 ppbv of HNO_3 in moist zero air with multiple luminol solutions **Fig. 3**, but hereto a quantitative value can only be assigned when corrected for the error on the offset, which still has to be further analyzed.

- The qualitative determination of the sensors response to 4.5 ppbv HNO_3 in dry zero air to be higher for one specific luminol solution, but comparable to the Hohenpeißenberg CAPS NO_2 analyzer for the other 2 applied luminol solutions **Fig. 4**.

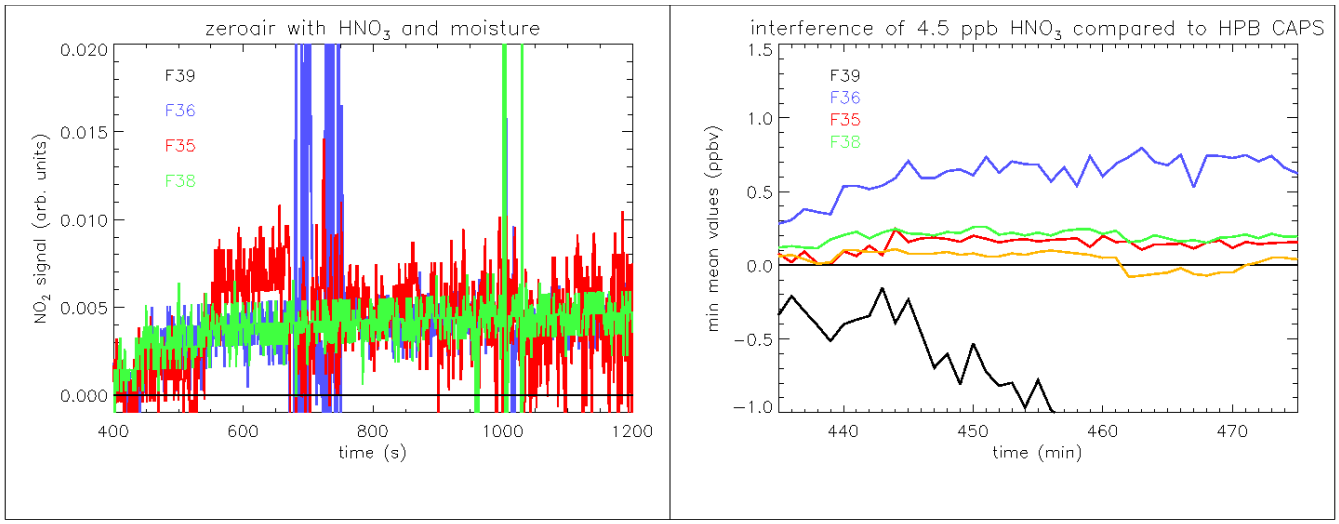

Fig. 3 (left): zoom of the HNO_3 region of the measurement, showing little response to the 5 ppbv HNO_3 provided in moist zero air. Fig. 4 (right): zoom of qualitative analysis of the interference of 4.5 ppb HNO_3 in dry zero air, based on a fit from NO_2-sonde data to HPB CAPS data.

- The qualitative determination of the NO_2 sensors response to 20 ppbv of NH_3 to most likely be 0 % in comparison to the Hohenpeißenberg CAPS NO_2 analyzer. We could not be conclusive about the outcome of this experiment since NH_3 was provided only as a constant concentration in ambient air instead of spiked ambient air, which made it impossible to fully distinguish between detected ambient NO_2 and synthetic NH_3.
- Proving the NO_2 sensor to be insensitive to NO when measuring with one specific luminol solution **Fig. 5** (the data-set recorded with different solutions still needs to be analyzed).
- The confirmation that compared to other instruments, the response time of the KNMI NO_2 sensor is satisfactory, and the time resolution of one different signal every second resulted in one of the best variabilities of the 14 different participating NO_2 analyzers.

Outcome and future studies

Some results obtained during this project led to further laboratory experiments related to the reproducibility of the signals recorded with the NO_2 sensor, which has contributed to some optimization in the design, increasing its reproducibility.

Future studies will include a final calibration run using an NO_2 sensor equipped with the newly chosen luminol solution and which has the latest tested improvements implemented in its design.

Furthermore, during the campaign we encountered some reproducibility issues - which at this point seem to be solved - but made us shift the research of the effect of different liquid temperatures on precision, zero-offset, and sensitivity of the sensor to future projects.

References

[1] Sluis, W. W., Allaart, M. A. F., Piters, A. J. M., and Gast, L. F. L.: *The development of a nitrogen dioxide sonde*, Atmos. Meas. Tech., 3, 1753-1762, doi:10.5194/amt-3-1753-2010, 2010.