NOx Measurement Improvement in FreNch EMEP Sites (NOXMINES)

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- **Introduction and motivation**

The Chemistry and Environmental department of the "Mines Douai" (MD-DCE) institution is responsible for the QA/QC of the French EMEP sites and is also a constituent member of the LCSQA (National reference laboratory for France). Three French EMEP sites are equipped with a trace level monitor for the long term measurement of NO_x. This monitoring is particularly relevant due to the key role of NO_x in the atmospheric chemistry and the secondary pollutant formation like ozone. Because the levels of NO_x encountered in background areas are very low (<2 ppbv) and in order to get long time series of high quality measurements, it is crucial to assess and improve the method we perform.

- **Scientific objectives**

Most of the automatic monitors are equipped with a molybdenum convertor which is not specific for NO_2 measurements since it converts the total odd nitrogen oxides (Dunlea et al 2007). For this reason, one of the monitors used in the French EMEP site was updated with a photolytic converter in order to be selective for NO_2. After attending the NO round robin to check our calibration procedure, this side by side comparison was then the opportunity to test our updated method especially the photolytic converter in a real ambient air matrix. Then the main objectives were to optimize our practices and to estimate the uncertainty associated to our measurements and to go through a well defined high performance protocol for our monitoring network.

- **Reason for choosing station**

The Hohenpeissenberg station is well known as a reference station especially for gas measurements. The team of Christian Plass Dülmer managing this station has a long experience in monitoring NOx at very low levels. Moreover, this station includes all the space and the facilities needed for this type of experiment.

- **Method and experimental set-up**

The instrument we performed for this intercomparison was a commercial analyzer (Thermo 42i Trace Level) based on the cheminluminescence measurements in infra red light when NO react with Ozone. This analyzer was updated with a photolytic convertor named the Blue Light Converter from the Air Quality Design, Incorporated. Our set-up also included a calibration device composed with a dilution system and a 5,01 ±0,03 ppm NO in N2 produced and certified by the NPL.

Experiments consisted in measuring (1) synthetic mixture at different levels, (2) ambient air and (3) ambient air with additional interferences (water and HNO_3). We also had the opportunity to compare in situ our standard with the standart of the FZ-Juelich which is World Calibration Center for NO.

The different tests gave an assessment of metrological parameters such as the detection limit, the linear default, the span, and of potential artifacts of interfering gases in order to estimate the measurement uncertainty.

In addition to the NOx operations, we took the opportunity to sample ambient air in Hohenpeissenberg with canister and Charcoal cartridges for a VOCs comparison between on-line measurements performed in HPB and off-line methods mainly used in France.

- **Preliminary results and conclusions**

The first step of the experiment consisted in sampling synthetic mixtures with growing level of NO and mixing ratio of O_3. The table 1 gives an insight of the results obtained for each schedule step for both NO and NO2 responses of the MD-DCE NOx analyzer. Regarding the times series we were able to determine the response time of our instrument. This performance indicator depends on the gas generation device but it is interesting to compare it between participants in order to discuss the different configurations.

Table 1 : *Average response of the MD-DCE NOx analyzer for synthetic mixtures generated at different concentration levels during the side by side NOx intercomparison in HPB*

Time	Schedule step	[NO] (ppb)	std NO (ppb)	[NO2] (ppb)	Std NO2 (ppb)	Response time (min)	*NO2 From GPT (ppb)*
07:12	Zero	-0.08	0.03	0.04	0.05		
09:47	NO 40 ppb	45.75	0.15	0.51	0.28	2min20s	
10:30	NO 40 ppb O3 30 ppb	8.35	0.13	38.72	0.27	6min (NO2)	*37.40*
11:00	Zero	-0.08	0.03	0.04	0.04	3min26s (NO2)	
11:30	NO 5 ppb	5.48	0.05	0.04	0.09	5min	
12:00	NO 15 pbb	16.83	0.09	0.16	0.2	3 min	
12:35	NO 40 ppb	45.52	0.28	0.55	0.52	3min26s	
13:00	NO 40 ppb O3 30 ppb	-0.07	0.02	-0.01	0.04		
14:00	NO 40 ppb O3 8 ppb	37.41	0.28	9.04	0.54	5min36s (NO2)	*8.11*
14:44	NO 40 ppb O3 17 ppb	28.26	0.09	18.23	0.46		*17.26*
15:00	**Franz Certified Standard**	**22.24**	**0.10**				
15:30	NO 40 ppb O3 17 ppb	3.81	0.07	43.65	0.28	12 min (NO2)	*41.71*
16:32	Zero	-0.09	0.01	0.05	-0.04	2min30s	

The time series represented in figure 2 correspond to a NO/O3 mixture. We can observe that the signal reaches a plateau in a short time showing the good performance of the mixture generation system. The stability is also very good except some little variation probably due to the pump providing dilution air.

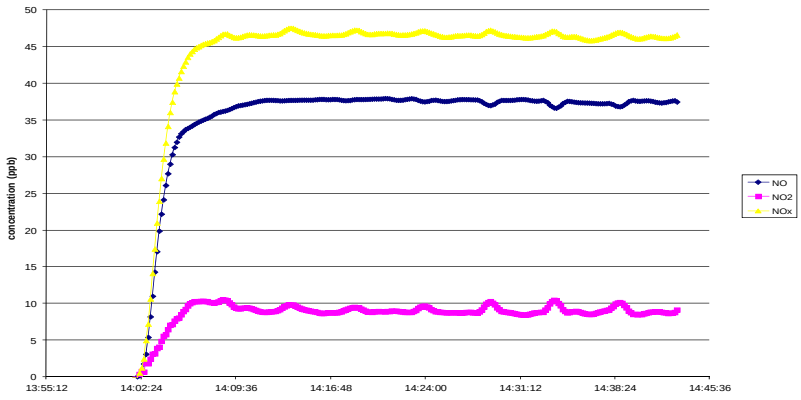

Figure 1: *Time series of the MD-DCE analyzer responses for the synthetic air mixture NO=40 ppb, O3=8 ppb*

Four experiments were led with different NO/O3 in order to provide a reference value of NO_2 by Gas Phase Titration (GPT). This method consists in measuring the consumption of NO following the reaction $NO+O_3 \rightarrow NO_2 + O_2$. The decreasing amount of NO can be considered as the NO_2 produced. Figure 2 represents the plot of the NO_2 measured by our NO_x analyzer versus the NO_2 determined

by GPT. First of all, this graph shows a quite good linearity of the NO_2 response. Regarding the principle of the used instrument, the NO_2 response depends both on the NO calibration and the BLC conversion rate. This result confirms also the good estimation of the BLC conversion rate.

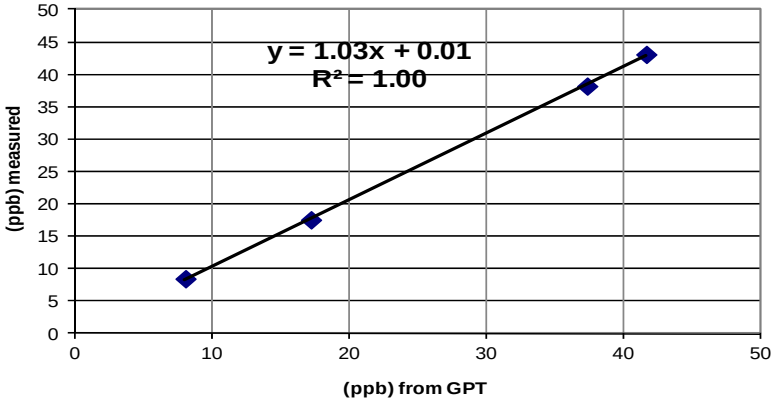

Figure 2*: NO_2 concentration measured versus NO_2 calculated from the Gaseous Phase Titration for synthetic mixtures $NO+O_3$*

Ambient air measurements were scheduled during the night and an example is given by the times series drawn in figure 2. NO ratios are close to the detection limit indicating the background typology of the HPB site. The NO_2 concentration varied in a small range between 4 and 6 ppbv.

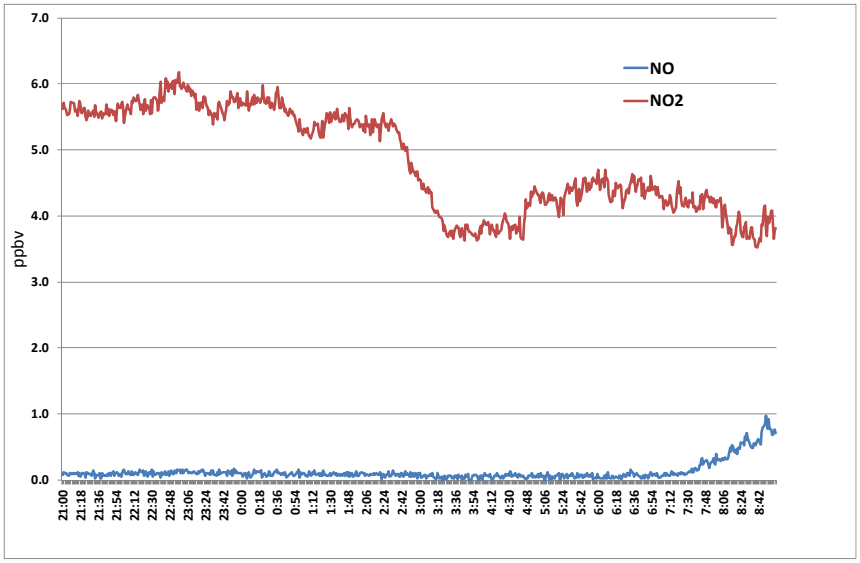

Figure 3: *Time series of the MD-DCE NO_x analyzer responses for ambient air during the night (13-14 Nov. 2012)*

One day of the intercomparison was devoted to the interference study. A same mixture of NO/O3 was diluted with humid air in several steps. The preliminary results for our instrument are shown in figure 4. No significant impact on the analyzer responses can be observed. These experiments need to be analyzed more by comparing the results of the different participants.

Figure 5 represents the response of the analyzer for a mixture of ambient air and 4ppb of ammonia (NH_3) or 20 ppb of nitric acid (HNO_3). No significant interference appears regarding the response of the analyzer despite the high concentration of this two nitrogen compounds. We can partially confirm the good selectivity of our instrument especially concerning the BLC.

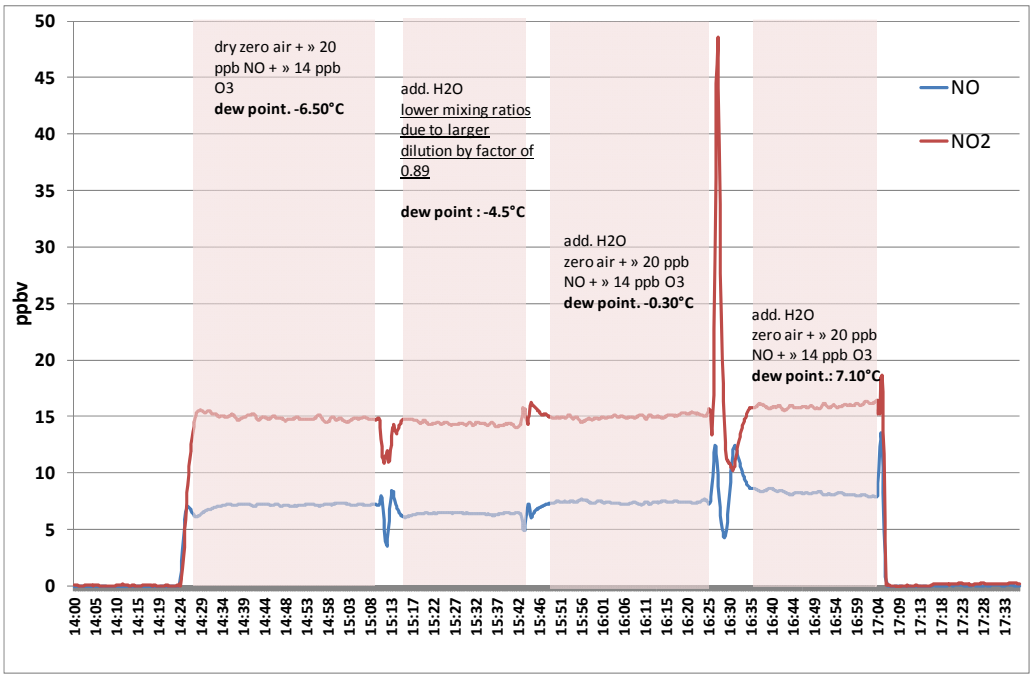

Figure 4: *Time series of the MD-DCE NO_x analyzer responses for synthetic air mixture with humid air addition*

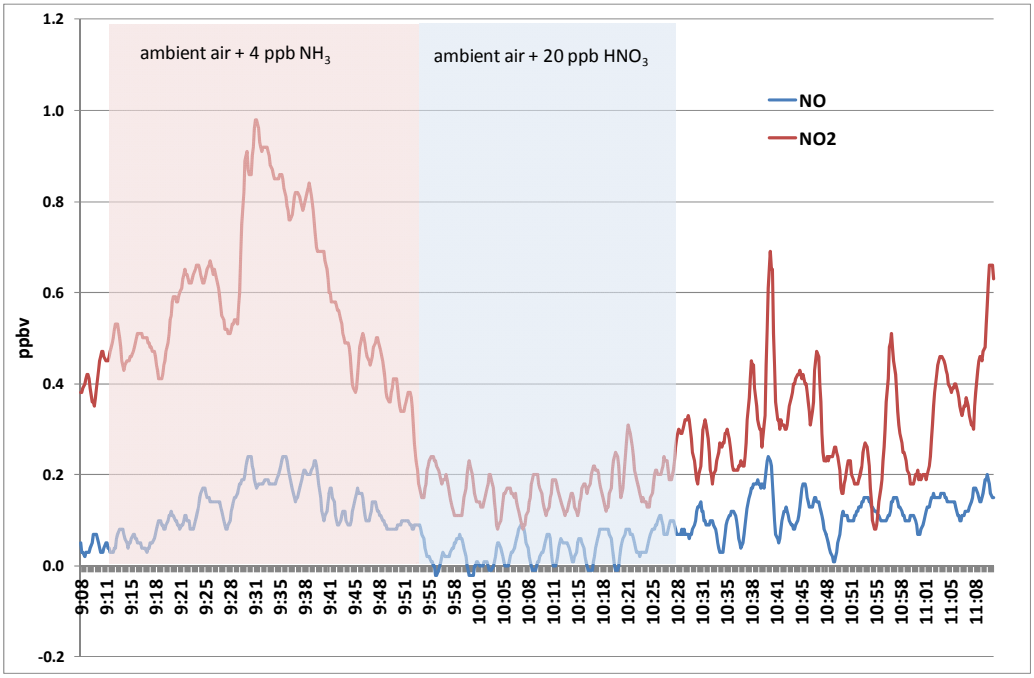

Figure 5: *Time series of the MD-DCE NO_x analyzer responses for synthetic air mixture with HNO_3 orNH_3 addition*

Finally, a test allowed estimating the Detection Limit (DL) of the analyzers. Small concentrations of NO and NO_2 were shortly generated (figure 6) in order to obtain relaxation periods and to determine the DL. As preliminary results, the DL obtained for our instrument were 0,10 ppbv and 0,09 ppbv respectively for NO and NO_2.

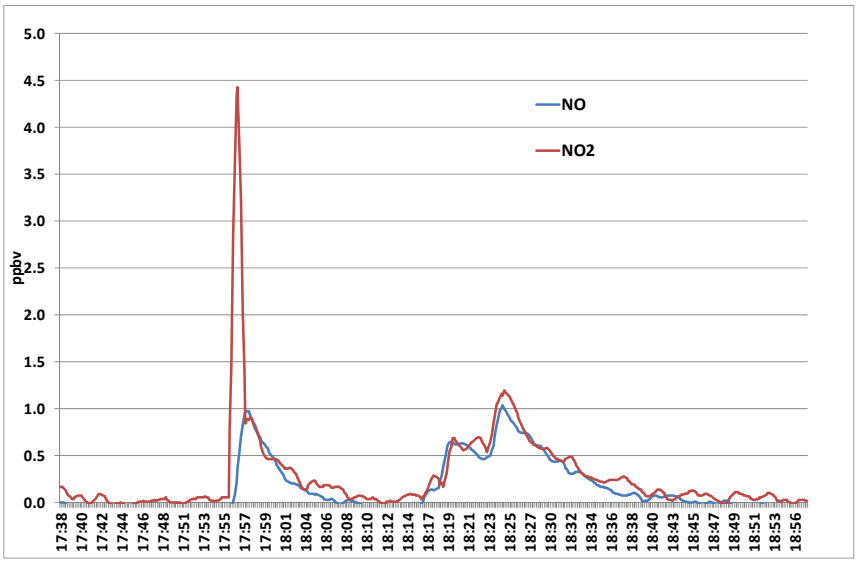

Figure 6: *Time series of the MD-DCE NO_x analyzer responses during the relaxation experiment performed for detection Limit determination*

- **Outcome and future studies**

  The Side by side NO_x intercomparison was very useful to improve and harmonize the operating procedures between the different European observatories. The first results presented above give preliminary information concerning the calibration, the selectivity of the BLC and the analyzer performances. The comparison with the results of the other participants should confirm the capability of our instrument for measuring NOx at low levels. The uncertainty we will be able to estimate in fine could be compare to the ACTRIS data Quality Objectives in order to see if additional improvements are needed

- **References**

Dunlea, E. J., Herndon, S. C., Nelson, D. D., et al. (2007): Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, Atmos. Chem. Phys., 7, 2691-2704, doi:10.5194/acp-7-2691-2007