Intercomparison Study Of NOx instruments (ISONO$_x$)

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INTRODUCTION AND MOTIVATION

Nitrogen oxides (NOx=NO+NO_2) play a key role in determining the air quality in polluted environments with direct and indirect consequences to Earth's atmosphere and human health. NO_x species, depending on their ambient levels, are involved to the i) photochemical ozone formation, ii) acidification of the atmosphere, iii) nighttime oxidation capacity and iv) local radiative forcing (Seinfeld and Pandis, 2006 and references therein; Vrekoussis et al., 2013 and references therein). The understanding of the above processes that govern the formation, distribution and removal of NO_x depends on the correct quantification of NOx species. For the speciation and fractioning of NO_x species it is essential to perform accurate and precise NO_x measurements.

SCIENTIFIC OBJECTIVES

Currently, it is believed that the commercial chemiluminescence instruments (supplied with a Molybdenum catalyst) systematically overestimate the value of NO_2 since they convert, in addition to the ambient NO_2, the total reactive odd nitrogen oxides (NO_y=NO+NO_2+HNO_3+NO_{3^-}+$2N_2O_5$+NO_3+PAN+alkyl-nitrates+minor species), (Dunlea et al., 2007). As a result, the measured NO_2 concentrations should reflect only the upper limit of the real/ambient NO_2. In order to acquire more realistic NO_2 measurements, the commercial trace level chemiluminescence NO_x analyzers are often -additionally- equipped with a photolytic blue light converter (BLC). BLC LED emits photons at 395nm to convert explicitly the NO_2 molecules to NO.

The "ISONOx" project' main objectives were a) to test the accuracy and the detection limit of a commercial TEI42 instrument under various laboratory and ambient conditions b) to identify potential interferences c) to characterize the photo-stationary state and contribution of NO_x to photo-chemistry and d) to compare the results with the ones from other commercial and laboratory instruments participating .

For this reason various instrumentations measuring NO and/or NO_2, were deployed at the Hohenpeissenberg Meterorology Observatory and participated to a side-by-side intercomparison experiment.

REASON FOR CHOOSING STATION

The Hohenpeissenberg Meteorological Observatory is chosen as the ideal station for such an experiment as it equipped with a number of state-of-the-art instruments measuring several species of atmospheric importance; to this extend, independent measurements of NO_x and NO_y species took place. Moreover, one of the laboratories is equipped with a common inlet able to supply 10 individual collocated instruments with complex sample gas matrixes enabling the full characterization of parameters such as e.g. the detection limit and the existence of artifacts throughout interfering species.

METHOD AND EXPERIMENTAL SET-UP

The chemiluminescence technique is based on the principle that nitrogen oxide and ozone will react to produce a luminescence:

$$NO + O_3 \rightarrow NO_2 + O_2 + hv \qquad [1]$$

The intensity of this luminescence is proportional to the NO concentrations. A PMT is used for the detection of the NO_2 luminescence.

In brief and for this experiment, air/gas mixtures pass from the common sampling line into the commercial TEI42 instrument through a particulate filter and then split via a valve to two channels a) the NO line channel and b) the NO_x to NO converter channel. Channel 1 is used to directly lead the NO molecules to the ozone reaction chamber where they are converted to NO_2 following reaction [1]. Channel 2 is used to convert the NO_2 to NO molecules via a molybdenum heated converter; afterwards, the sample passes through the reactor chamber. However, as already stated, it is believed that the molybdenum catalyst converts not only the ambient NO_2 molecules to NO but also the sum of all odd nitrogen oxides (NO_y=NO+NO_2+HNO_3+NO_3-+2N_2O_5+NO_3·+PAN+alkyl-nitrates+minor species). For this reason, our instrument is additionally equipped with a blue light converter (figure 1) converting only the NO_2 molecules to NO.

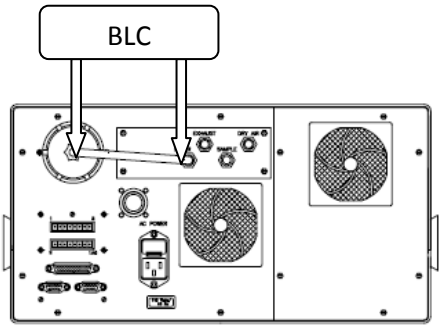

Figure 1 (Rear panel of the thermo 42C instrument used): The BLC has been connected in between the filter and the sample and it was turned on and off with the use of a chrono-plug timer.

PRELIMINARY RESULTS AND CONCLUSIONS

During the study, several sub-experiments took place aiming to answer key questions related to the scientific objectives of the ISONOx project (e.g. accuracy, precision, detection limit, interferences, photochemistry).

Specifically, the following experiments took place in the frame of this study:

i) Measurements of synthetic (zero) air
ii) Measurements of ~5, 10, 15, 40 ppbv NO (unknown concentrations)
iii) Measurements of gas mixtures: 44ppbv NO and ~10, 20,40 ppbv O_3 (to produce NO_2)
iv) Measurements of ambient air
v) Measurement of ambient air and addition of ~8ppbv NO, ~8ppbv NO and 4 ppbv O_3, 12 ppbv NO and 6 ppbv O_3
vi) Measurements of ambient air and 4 ppbv HNO_3 (to account for potential interferences)
vii) Measurements of ambient air and 20 ppbv NH_3 (to account for potential interferences)
viii) Measurements of zero air and ~20 ppbv NO+14 ppbv O_3 and 10, 20, 40lt/min humid air to create various dew points
ix) Relaxation experiment for the detection of the LDL.

Herewith, we present some of the preliminary results including measurements of synthetic air (i), the NO mixtures (ii) and the NO and ozone mixtures (iii). It should be noted that the preliminary results of the relaxation experiment showed that the detection limit (3σ) of the TEI42 instrument is 0.375 and 0.065 ppbv for a resolution time of 1 min and 5 min, respectively. For the majority of the experiments the final results depend on the standard concentrations of NO and NO_2 that will be provided later on from the Hohenpeissenberg Meteorological Observatory staff.

Zero air: Synthetic air has been used to supply the common inlet with continuous air flow. Overall, the instrument performed well under zero air sampling (figure 2). With the temporal resolution set

at 1 minute, more than 700 measurements of zero air have been collected. Both the mean value (0.012±0.007 ppbv) and the median value (0.004 ppbv) were very close to zero.

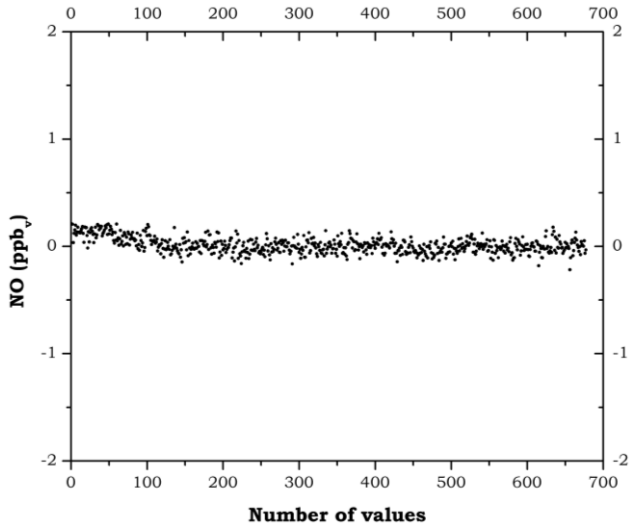

Figure 2: Zero air measurements.

Unknown NO concentrations: Three different concentrations of NO have been introduced into the common inlet. Our analysis showed that the three concentrations were equal to 5.5±0.1, 16.7±0.1 and 45.8±0.3 ppbv (figure 3).

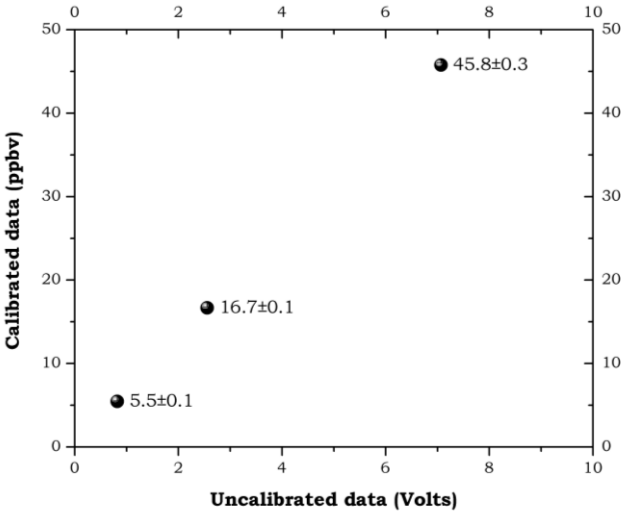

Figure 3: Identification of the NO concentration of 3 unknown samples (in ppbv)

Unknown NO and NO_2 mixtures: Three different unknown gas mixtures (A, B, C) of NO and O_3 have been inserted into the common inlet. It was found that gas mixture A contained 37.8±0.1 ppbv NO and 8.3±0.2 ppbv NO_2, gas mixture B had 27.9±0.2 ppbv NO and 17.6±0.3 ppbv NO_2 and gas mixture

C had 2.9±0.1 ppbv NO and 42.2±0.3 ppbv NO_2 (figure 4). From all three mixtures, it was concluded that the total NO_x concentration was 45.6±0.5 ppbv.

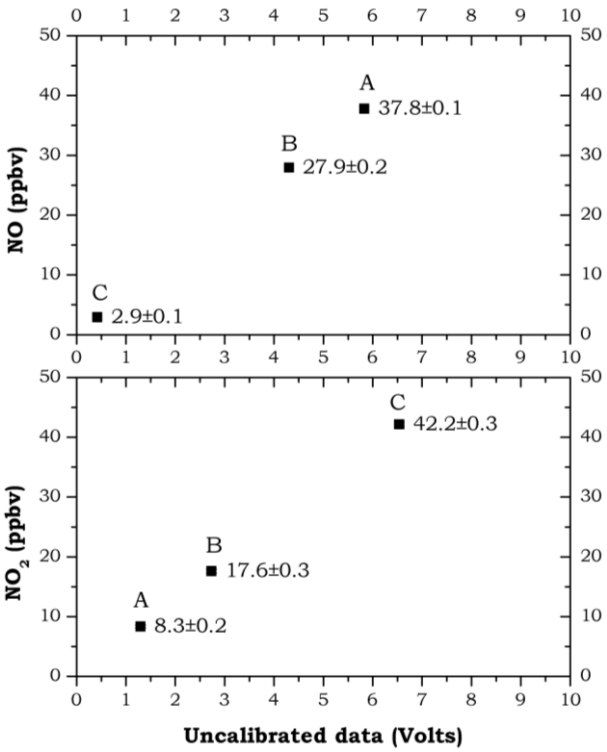

Figure 4: Identification of the unknown NO and NO_2 concentrations (in ppbv) of 3 different gas mixtures.

OUTCOME

As denoted before, the final outcome of the $ISONO_x$ study depends on the standard concentrations of NO and NO_2 that will be provided later on. These concentrations are needed to compute the detection limit of the instrument, the contribution of the interferences to the observed NO_x species and to characterize the photo-stationary state.

REFERENCES

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