

**Measurements of NO<sub>2</sub> and O<sub>3</sub> In the free troposphere by a New LOPAP Instrument (MINI)***PD Dr. Jörg Kleffmann*

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**• Introduction and motivation**

NO<sub>2</sub> is an important harmful trace species, which controls oxidant and acid formation in the atmosphere. Caused by its health effects, an annual average threshold value of ca. 20 ppb was introduced by the EU in 2010, which is typically exceeded under polluted urban conditions (EEA, 2007; Vestreng et al., 2009). Standard chemiluminescence NO<sub>2</sub> instruments are known to be affected by interferences (Villena et al., 2012). Thus, a new sensitive (DL 2 ppt) NO<sub>2</sub>-LOPAP instrument was developed (Villena et al., 2011), which was recently extended for the simultaneous detection of O<sub>3</sub> (Peters et al., 2012). The instrument was successfully intercalibrated under urban conditions and in a smog chamber (Villena et al., 2011; 2012; Peters et al., 2012), however, validation under remote conditions was still an open task.

**• Scientific objectives**

In the present project an NO<sub>2</sub>-LOPAP should be intercompared with a standard chemiluminescence instrument (CLD) and a Quantum Cascade Laser Absorption Spectrometer (QCLAS) under clean atmospheric conditions at the high alpine research station “Jungfraujoch” (JFJ). In addition, the new O<sub>3</sub> channel of the LOPAP instrument should be intercompared with a standard UV absorption instrument.

**• Reason for choosing the station**

The EMPA had a parallel CLD and QCLAS NO<sub>2</sub> intercomparison campaign planned at JFJ in March and April 2012, which was thus considered as an ideal option to also intercompare our new LOPAP instrument for low pollution levels. Since JFJ is typically in the free troposphere, remote conditions are often prevailing in this easily accessible measurement station in the middle of Europe. Thus, the place and date was ideal for the scientific objectives.

**• Method and experimental set-up**

In the LOPAP instrument, O<sub>3</sub> is collected in a temperature controlled stripping coil by an effluent containing the intensively colored Indigo dye. The de-coloring of the dye is used to quantify O<sub>3</sub> in the gas phase. NO<sub>2</sub>, which almost completely passes the O<sub>3</sub> channel, is collected in a downstream stripping coil by a selective chemical reaction, converted into an azo-dye, which is sensitively measured in a liquid core wave guide. In addition, a further similar stripping coil is used to quantify losses of NO<sub>2</sub> from the NO<sub>2</sub> channel and potential interferences, which were however found to be negligible under polluted conditions. Details of the NO<sub>2</sub> and O<sub>3</sub> instruments are explained elsewhere (Villena et al., 2011; 2012; Peters et al., 2012). In contrast to these publications, modified stripping coils were used for the detection of NO<sub>2</sub>. In addition, caused by the lower pressure at JFJ, some instrument parameters were different to those specified for standard conditions. For example, caused by the lower residence time of the gas phase in the stripping coil, a higher Indigo concentration of 40 µg/l was used in the O<sub>3</sub> channel for most days. Although the sampling efficiency for O<sub>3</sub> was still 99 % for these conditions, leading to a negligible O<sub>3</sub> interference in the NO<sub>2</sub> channel, the O<sub>3</sub> sensitivity was significantly lower (DL = 2 ppb, compared to the 0.4 ppb specified in Peters et al., 2012). Caused by the low gas flow rate (0.35 l/min) necessary for the O<sub>3</sub>-detection and the lower used NEDA concentration of the NO<sub>2</sub> effluent (0.3 g/l), which was optimized for the new stripping coil at

standard pressure, the sensitivity and sampling efficiency for NO<sub>2</sub> were also reduced. For compensation of the reduced NO<sub>2</sub> sensitivity a longer optical path length of 5 m was used. However, an additional problem with the signal stability of the instrument was observed, which was caused by the proximity to the air conditioning of the laboratory ( $\pm$  ca. 6 °C), leading to higher periodic noise of the instrument. Thus, a detection limit and sampling efficiency for NO<sub>2</sub> of only 10 ppt and 91 % were obtained, whereas the short term detection limit without this periodic noise was 1-2 ppt, similar to our former results (Villena et al., 2011). For the last 2 days of the campaign, when it became evident that the NO<sub>2</sub> interferences channel was not necessary also at low pollution levels, the third coil of the instrument was used to detect also NO. For conversion of NO into NO<sub>2</sub> a commercial converter from a Luminol NO<sub>x</sub> instrument was used. However caused by an unidentified gas leak, the measurement data of the instrument could not be used for that time period.

The instrument was installed at the Sphinx station at JFJ (3590 m) near to the other NO<sub>2</sub> instruments (CLD, QCLAS) and intercompared for 9 days of which only 7 could be used (see above). In contrast to the normal operation of the instrument for which the external sampling unit is directly placed in the atmosphere of interest, gas samples were collected by a x m long PFA sampling line (4 mm i.d.) similar to the other instruments.

- **Preliminary results and conclusions**

**a) General observations**

During the campaign O<sub>3</sub> and NO<sub>2</sub> mixing ratios in the range 40-70 ppbv and 0.02-1.8 ppbv were measured by the LOPAP instrument, respectively (see Fig. 1), while average O<sub>3</sub> and NO<sub>2</sub> values of 59 and 0.27 ppbv were determined. Ozone mixing ratios were relatively constant, except one pollution episode on the 5.4.2012 when O<sub>3</sub> concentrations dropped sharply, while those of NO<sub>2</sub> increased (see Fig. 1). In contrast, NO<sub>2</sub> showed stronger variability with higher concentrations during night-time.

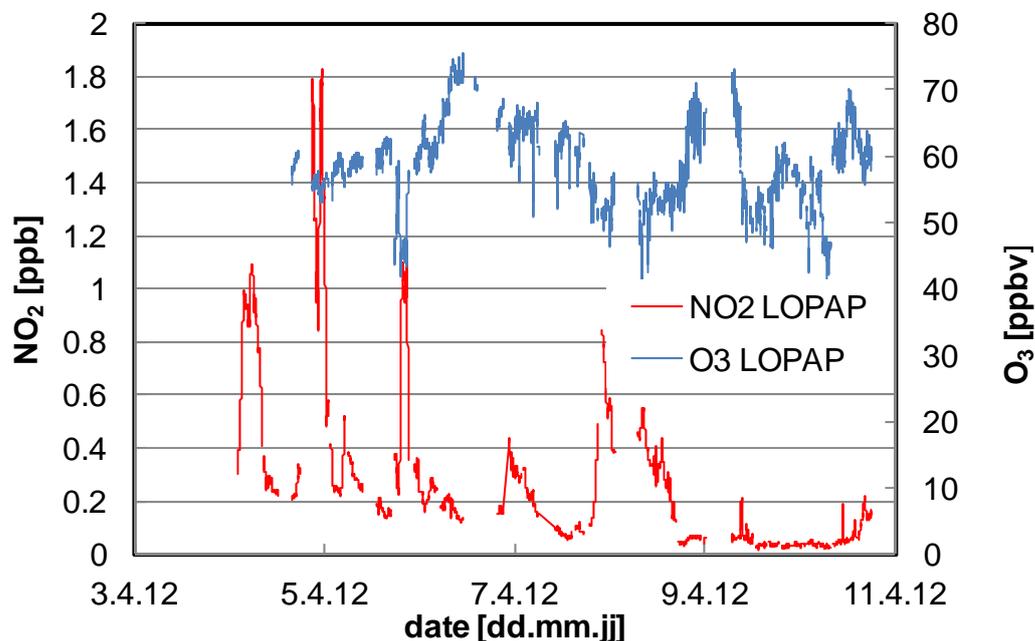


Fig. 1: O<sub>3</sub>- and NO<sub>2</sub>-LOPAP data during the intercomparison campaign at Jungfraujoch.

**b) O<sub>3</sub> intercomparison**

For O<sub>3</sub> excellent agreement between the LOPAP and the data measured by a standard UV absorption instrument was obtained (see Fig. 2 and Fig. 3, using preliminary O<sub>3</sub> data from the NABEL data base). From the correlation of both instruments only an average difference of 2 % was determined (see Fig. 3). In addition, also a very similar variability was obtained. Both results are in agreement with intercomparison

campaigns of a O<sub>3</sub>-LOPAP instrument under urban and smog chamber conditions (Peters et al., 2012). Thus, it is concluded that potential interferences are of minor importance for the LOPAP O<sub>3</sub> data.

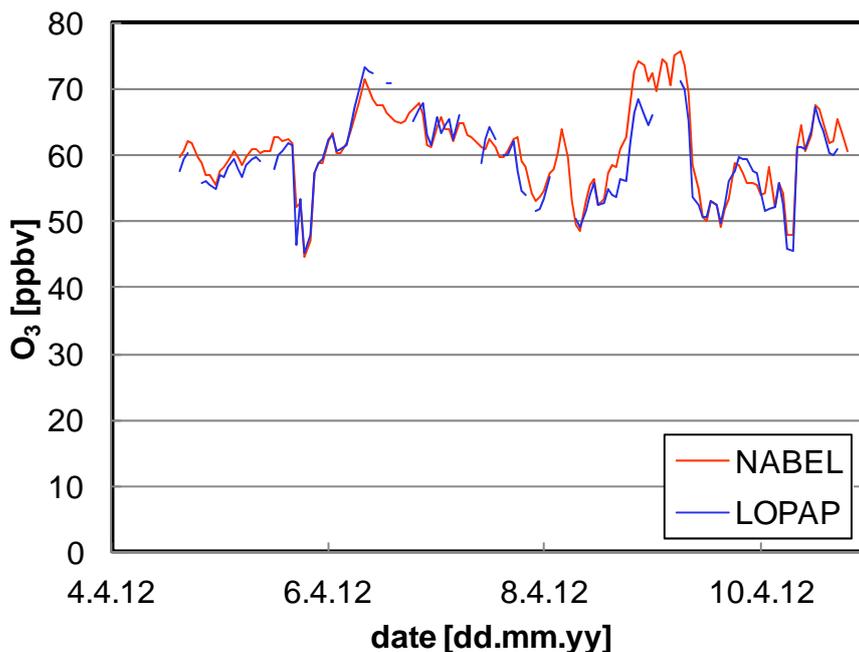


Fig. 2: Intercomparison of the 1 h averaged O<sub>3</sub> data from the LOPAP and a standard UV-absorption instrument (NABEL) at Jungfrauoch.

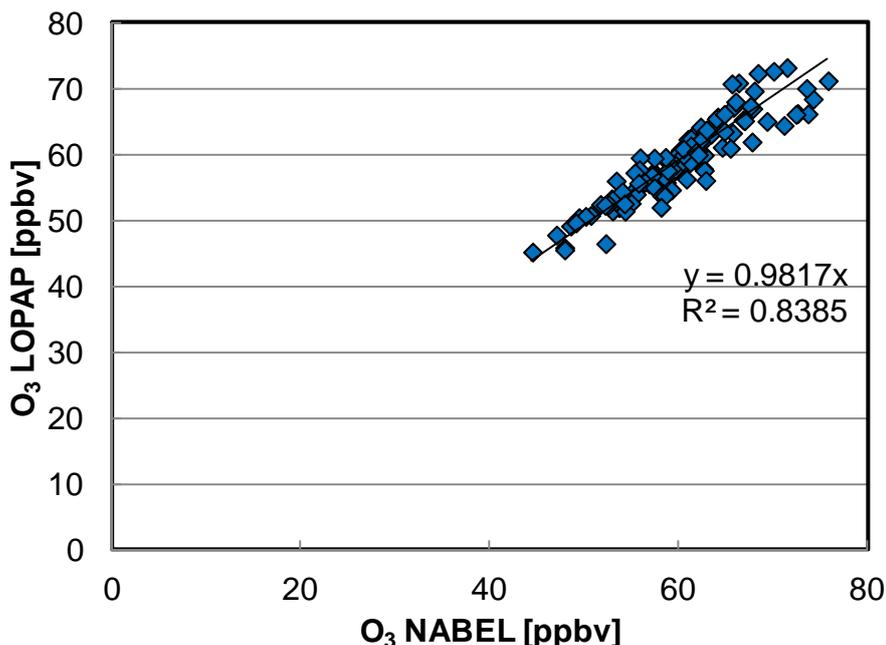


Fig. 3: Correlation of all 1 h averaged O<sub>3</sub> data from the LOPAP and a standard UV-absorption instrument (NABEL) at Jungfrauoch.

**b) NO<sub>2</sub> intercomparison**

A high correlation ( $R^2 = 0.98$ ) of the NO<sub>2</sub> data by the LOPAP and the standard chemiluminescence instruments were obtained (Fig. 4 and Fig. 5). In addition, in a correlation plot of both data only a negligible intercept, lower than the precision error, was observed, indicating a high performance of the LOPAP instrument also at very low NO<sub>2</sub> levels. However, systematically lower mixing ratios (ca. 35 %) were measured by the LOPAP instrument (see Fig 4 and Fig. 5). These observations indicate some calibration problems of one instrument. In addition, whereas concentrations ( $\mu\text{g}/\text{m}^3$ ) were specified in the NABEL data base, mixing ratios are determined by the LOPAP instrument. Thus, there may be also still some unit

conversion errors. Since more information to the NABEL data will be available only soon and since the QCLAS data was also still not available, reasons for the discrepancy are still unclear.

The excellent correlation of the NO<sub>2</sub> data indicates that interference problems of the LOPAP instrument are of minor importance for the conditions on the Jungfraujoch, in good agreement to intercomparison campaigns under urban and smog chamber conditions (Villena et al., 2012). In contrast, for potential interference problems of the LOPAP instrument, variable differences between both instruments would be expected.

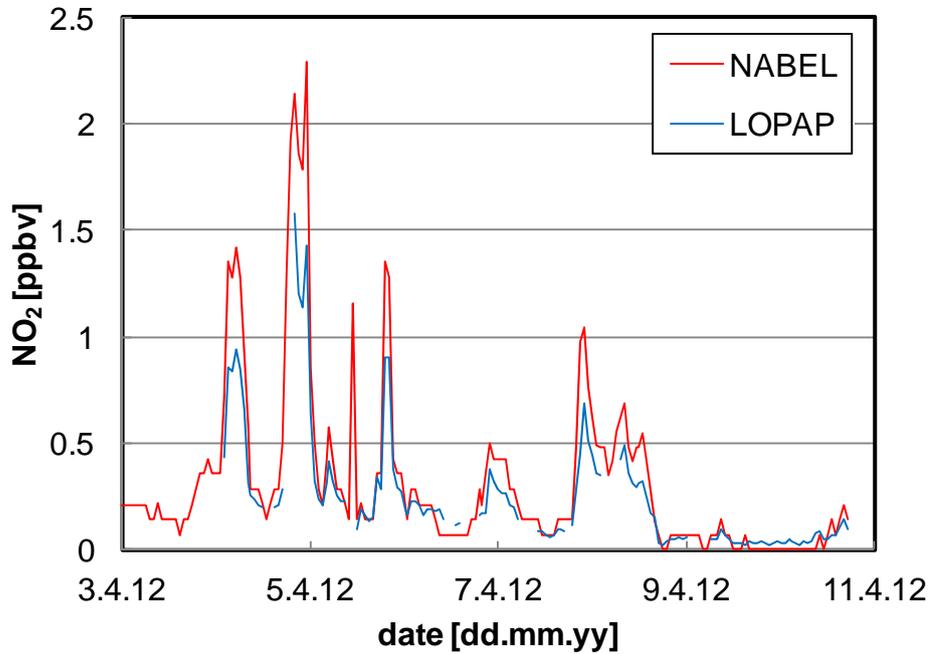


Fig. 4: Intercomparison of the 1 h averaged NO<sub>2</sub> data from the LOPAP and a standard chemiluminescence instrument (NABEL) at Jungfraujoch.

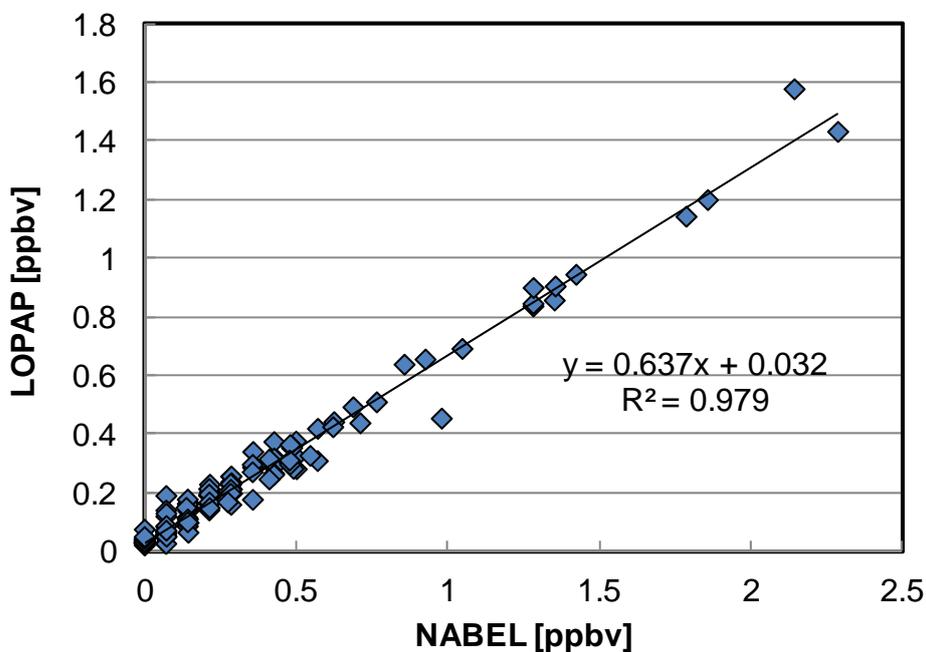


Fig. 5: Correlation of the 1 h averaged NO<sub>2</sub> data from the LOPAP and a standard chemiluminescence instrument (NABEL) at Jungfraujoch.

- **Outcome and future studies**

In the present study, a new O<sub>3</sub>-NO<sub>2</sub>-LOPAP was intercompared at the High Alpine Research Station Jungfrauoch to standard instruments and a Quantum Cascade Laser Absorption Spectrometer (QCLAS) from EMPA. For O<sub>3</sub> excellent absolute agreement was observed between the LOPAP and the UV absorption instrument, which routinely measures at JFJ. The good agreement demonstrates that interferences in the O<sub>3</sub> channel of the instrument can be neglected also for low pollution levels, in agreement with urban and smog chamber results. For the NO<sub>2</sub> channel of the instrument significantly lower concentrations compared to the standard chemiluminescence instrument were observed. Caused by the excellent correlation of the data, these results indicate some calibration problems of one instrument. In contrast, interferences of the NO<sub>2</sub>-LOPAP instrument seem to be of minor importance, which is confirmed by the negligible signal in the interference channel of the LOPAP instrument. Since comparison to the QCLAS data is still an open task, reasons for the systematic discrepancy will be hopefully answered in the near future, when all data are available. In addition, up to now only the 1 h average data accessible from the NABEL data base were used. Thus, it is planned to intercompare also high time resolution data from all instruments in the near future.

- **Acknowledgement**

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