

Name of research institute or organization:

Physikalische Chemie / FBC, Bergische Universität Wuppertal, Germany

Title of project:

Measurements of NO₂ and O₃ In the free troposphere by a New LOPAP Instrument (MINI)

Project leader and team:

PD Dr. Jörg Kleffmann,
Dipl. Chem. Sarah Peters, Dipl. Chem. Sascha Liedtke

Project description:

Introduction and motivation

NO₂ is an important harmful trace species, which controls oxidant and acid formation in the atmosphere. Caused by its health effects, an annual average threshold limit 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).

Despite its importance, standard chemiluminescence NO₂ instruments are known to be affected by interferences (Villena et al., 2012). Thus, a new sensitive (DL 2 ppt) NO₂-LOPAP instrument was developed (Villena et al., 2011), which was recently extended for the simultaneous detection of O₃ (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 study a NO₂-LOPAP was 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 O₃ channel of the LOPAP instrument was intercompared with a standard UV absorption instrument.

Reason for choosing the station

In March and April 2012, EMPA had planned a CLD and QCLAS NO₂ intercomparison campaign at JFJ, which was thus considered as an ideal option to also intercompare our new LOPAP instrument at 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 were ideal for the scientific objectives.

Method and experimental set-up

In the LOPAP instrument, O₃ 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 O₃ in the gas phase. NO₂, which almost completely passes the O₃ 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 from the NO₂ channel and potential interferences, which were however found to be negligible under polluted conditions. Details of the NO₂ and O₃ 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 NO₂. In addition, caused by the lower pressure at JFJ and the resulting lower residence time of the gas phase in the stripping coil, a higher Indigo concentration of 40 mg/l was used in the O₃ channel for most days. Thus, the O₃ sensitivity was significantly lower (DL = 2 ppb, compared to the 0.4 ppb specified in Peters et al., 2012). In addition, caused by the lower gas flow rate (0.35 l/min), necessary for the O₃-detection, and the lower used NEDA

concentration of the NO₂ effluent (0.3 g/l) compared to the study of Villena et al. (2011), the sensitivity and sampling efficiency for NO₂ were also reduced. For compensation of the reduced NO₂ 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 (ca. ±6 °C in the instrument), leading to higher periodic noise of the data. Thus, a detection limit and sampling efficiency for NO₂ 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 NO₂ interference channel was not necessary at JFJ, in agreement with urban and smog chamber conditions (Villena et al., 2011, 2012), the third coil of the instrument was used to detect also NO. A commercial NO to NO₂ converter from a Luminol NO_x instrument was used upstream the last coil. 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 NO₂ 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 from the top of the Sphinx station by a 10 m long PFA sampling line (4 mm i.d.) similar to the other instruments. The total sampling flow rate was increased to ca. 2 l/min by the by-pass line.

Preliminary results and conclusions

a) General observations

During the campaign O₃ and NO₂ 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 O₃ and NO₂ 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 O₃ concentrations dropped sharply, while those of NO₂ increased (see Fig. 1), which can be explained by partial titration of O₃ by NO. In contrast, NO₂ showed stronger variability with typical higher concentrations during night-time.

A very important conclusion for the NO₂ detection was the absence of any significant signals in the interference channel of the instrument, except of the loss of NO₂ from the first channel caused by incomplete sampling. This result is in excellent agreement with urban and smog chamber measurements (Villena et al., 2011, 2012) and demonstrates that interferences in the wet chemical NO₂ detection used in the LOPAP instrument can be neglected for all atmospheric conditions, further simplifying this technique.

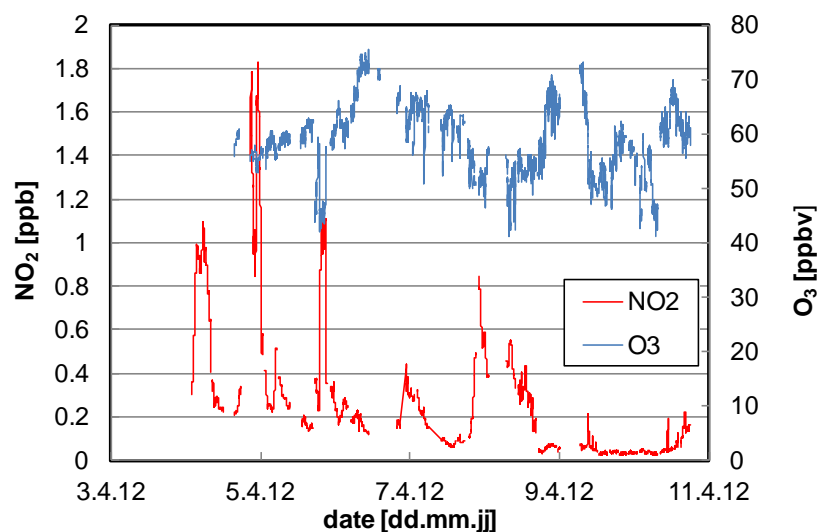


Fig. 1: O₃- and NO₂-LOPAP data during the intercomparison campaign at Jungfraujoch.

b) O₃ intercomparison

For O₃ excellent agreement between the LOPAP and the data measured by a standard UV absorption instrument was obtained (see Fig. 2 and Fig. 3). 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 O₃-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 O₃ data also under remote conditions.

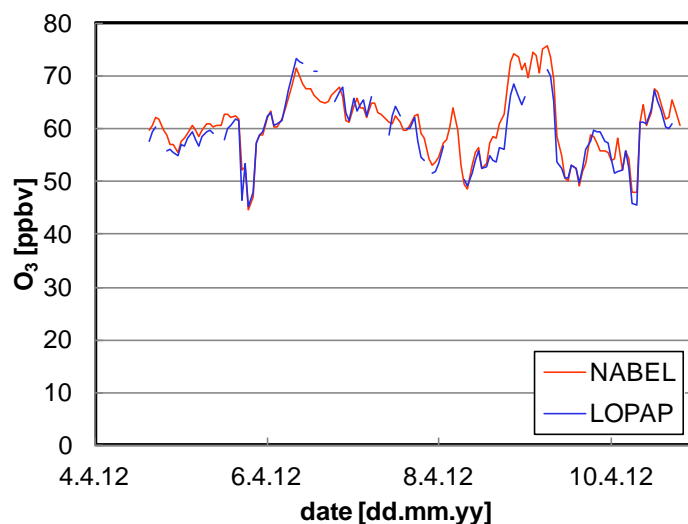


Fig. 2: Intercomparison of the 1 h averaged O₃ data from the LOPAP and a standard UV-absorption instrument (NABEL) at Jungfraujoch.

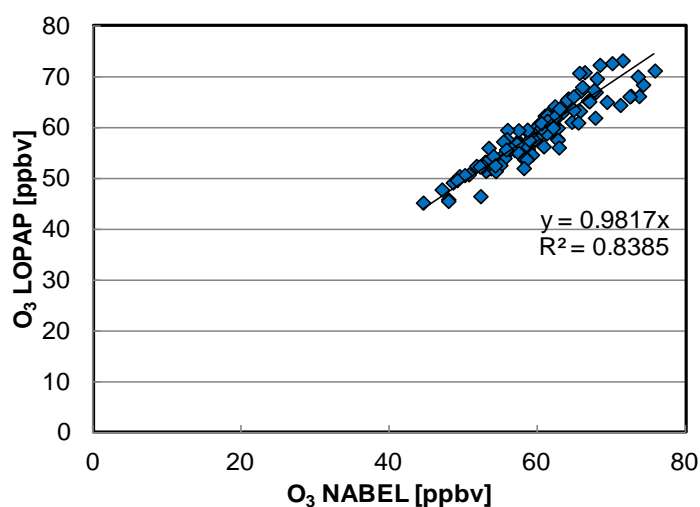


Fig. 3: Correlation of all 1 h averaged O₃ data from the LOPAP and a standard UV-absorption instrument (NABEL) at Jungfraujoch.

b) NO₂ intercomparison

A high correlation ($R^2 = 0.98$) of the NO₂ data by the LOPAP and the standard chemiluminescence instruments was obtained (Fig. 4 and Fig. 5). In addition, in a correlation plot of both data only a negligible intercept, lower than the precision errors, was observed, indicating a high performance of the LOPAP instrument also at very low NO₂ 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 (definition of the used total pressure). Since more information to the

NABEL data will be available only soon and since the QCLAS data was also yet not available, reasons for the discrepancy are still unclear.

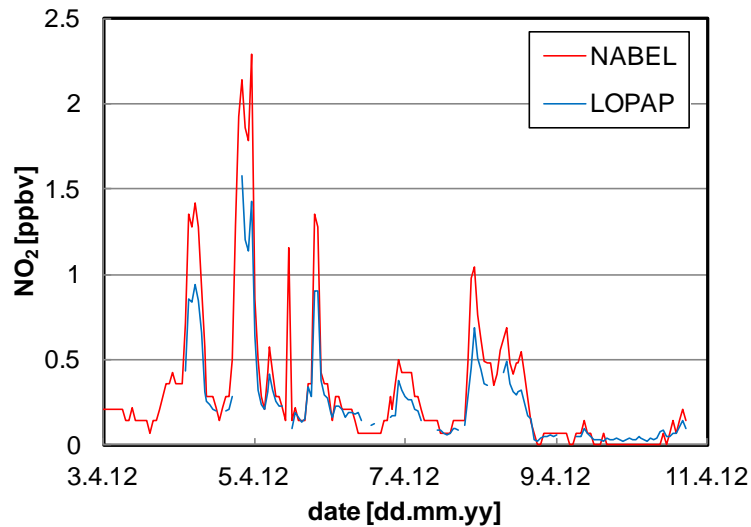


Fig. 4: Intercomparison of the 1 h averaged NO_2 data from the LOPAP and a standard chemiluminescence instrument (NABEL) at Jungfraujoch.

The excellent correlation of the NO_2 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.

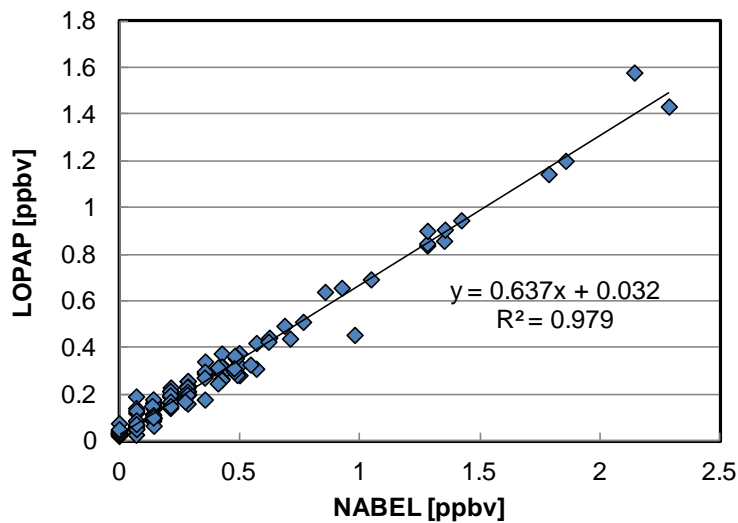


Fig. 5: Correlation of the 1 h averaged NO_2 data from the LOPAP and a standard chemiluminescence instrument (NABEL) at Jungfraujoch.

Conclusions and outlook

In the present study, a new O_3 - NO_2 -LOPAP was intercompared at the High Alpine Research Station Jungfraujoch to standard instruments and a Quantum Cascade Laser Absorption Spectrometer (QCLAS) from EMPA. For O_3 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_3 channel of the instrument can be neglected also for low pollution levels, in agreement with urban and smog chamber results. For the NO_2 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 NO₂-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 can be hopefully explained in the near future, when all data are available.

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Collaborating partners/networks:

Dr. Lukas.Emmenegger, EMPA, email: lukas.emmenegger@empa.ch

Address:

Physikalische Chemie FB C
Bergische Universität Wuppertal
Gaußstr. 20
D-42119 Wuppertal

Contacts:

PD Dr. Jörg Kleffmann
Tel.: +49 202 439 3534
Fax: +49 202 439 2505
e-mail: kleffman@uni-wuppertal.de
URL: <http://www.ptc.uni-wuppertal.de/>