LOPAP-03 (NO2)

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Introduction:

NO_2 is an important atmospheric trace gas, caused by its direct health effects and since it is the main precursour for ozone (O_3), thus directly affecting "summer smog" formation in the urban atmosphere. In addition, oxidation of NO_2 into nitric acid (HNO_3) leads to the acidification of the environment ("acid rain"). Urban NO_2 concentrations typically exceed the annual treshold limit value of ca. 20 ppb introduced by the European Union in 2010, reasons for which are still under controversial discussion. Caused by its major importance, NO_2 is regularly measured in national network stations. However, the commercial instruments which are mainly used are affected by significant, well-known positive interferences (see Fig. 1).

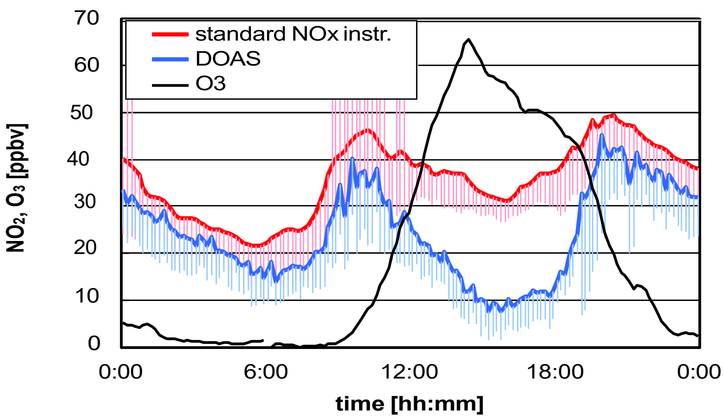
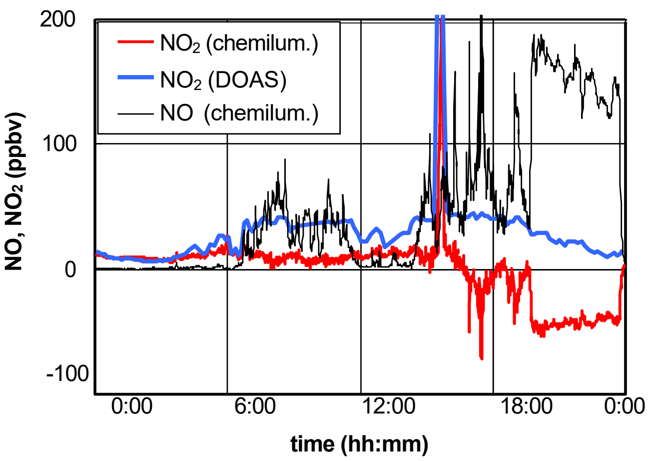


Fig.1: Intercomparison of a standard NO_x-chemiluminescence instrument with Molybenum converter and a DOAS instrument (Villena at al., 2012). The positive interferences are caused by reactive nitrogen species (NO_y) photochemically formed.

Caused by these interferences also photolytic converters (e.g. "blue-light" diodes)

are used in chemiluminescence instruments for scientific applications, suppressing many know interferences of Molybenum converters. However, also these instruments can be affected by significant negative interferences under heavily polluted atmospheric conditions (see Fig. 2).

Fig. 2: Intercomparison of a standard NO_x-chemiluminescence instrument with photolytic converter and a DOAS instrument. The neagive interfences are caused by the photochemical formation of peroxyradicals in the converter (Villena at al., 2012).



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Atmospheric NO_2 concentrations vary between few ppts (10^{-12}) and high ppb (10^{-9}) levels. Thus,

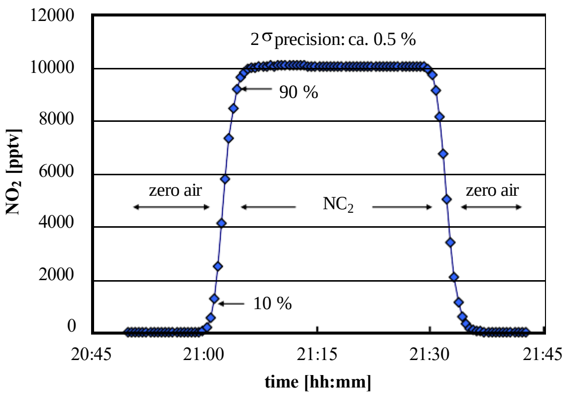
besides a high selectivity also a high dynamic range is necessary for the detection of NO2 Based on these requirements, a new ultra-sensitive NO2-LOPAP instrument was developed.

Brief description of the instrument's functional principle:

The LOPAP instrument *(Long Path Absorption Photometer)* is a wet-chemical in situ measuring device by which gasphase NO_2 is chemically sampled in a stripping coil and is measured photo- metrically in long-path absorption after conversion into an azodye in the instrument. Special Teflon tubing (Teflon AF2400) serve as long-path absorption cells, by which light can be transferred in total reflection, leading to an very high sensitivity (DL 2 ppt). In order to suppress potential sampling artefacts, which may appear, e.g., by reactions in sampling lines, NO_2 is collected directly in the atmosphere to be investigated using an external sampling unit. Interfering ozone (O_3) and nitrous acid (HONO) are effectively removed by an aqueous Indigo solution in an upstream ozone scrubber, which can be also used to measure atmospheric O_3 concentrations (Peters et al., 2012) as an optional extension of the instrument. Deatils of the instrument and the validation are explained elsewhere (Villena et al., 2011, 2012).

Performance:

The NO_2-LOPAP instrument shows a linear response and a high dynamic measurement range of 2 pptv – 300 ppbv which should cover all atmospheric conditions (see Fig. 3). If necessary the measurement range can be extended to the ppmv level by using shorter optical absorption cells. The high sensitivity makes also measurements under remote condition possible (e.g. polar conditions). The measurement parameters of the instrument are summarized in table 1.



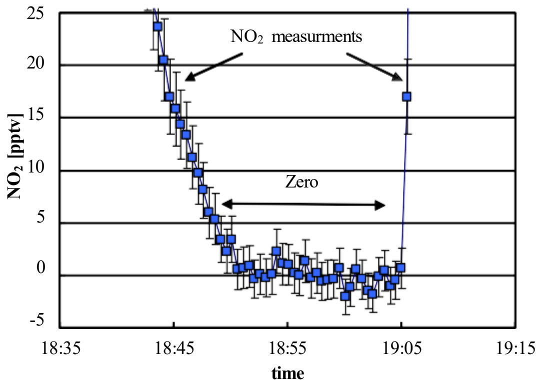


Fig. 3: Test of the instruments response, precision and detection limit of the NO_2-LOPAP.

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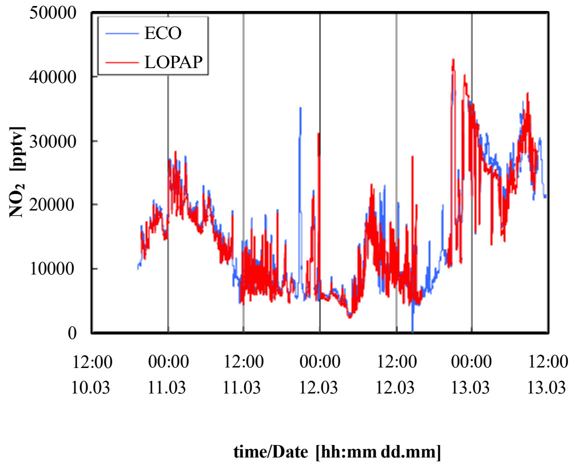
The instrument was successfully intercompared in the moderately polluted urban atmosphere against a chemiluminescence instrument with photolytic converter, see Figure 4.



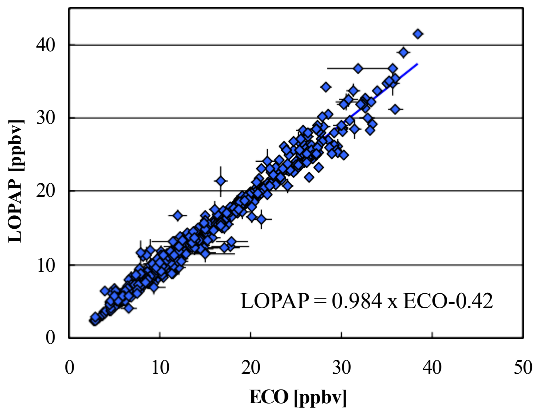


Fig. 4: Intercomparison of the NO_2-LOPAP with a chemiluminescence instrument with photolytic converter in the urban atmosphere (Villena at al., 2011).

In addition, the instrument was also successfully compared with the optical FTIR technique in a smog chamber under very complex photosmog conditions (see Fig. 5), for which interferences of other commercial NO_2 instruments were found to be significant (Villena et al., 2012).

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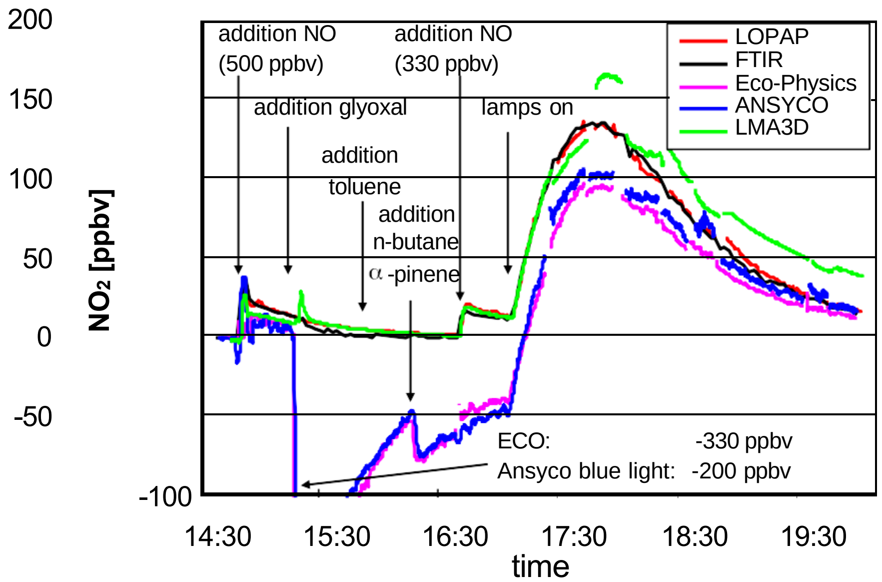

Fig. 5: Intercomparison of the NO_2-LOPAP with the FTIR technique in a smog chamber. Different trace species were added and the mixture was irradiated by UV light to simulate complex atmospheric photosmog conditions and to study interferences of the different commercial NO_2 instruments used (Villena at al., 2012).

Parameters:

• Air Flow:	0.5 l/min.
• Absorption path length:	0.1 - 6 m possible
• Measurement range:	0.002 – 300 ppbv
• Time resolution (10-90 %):	3 – 6 min.
• Precision:	± (1 % + DL)
• accuracy:	± (10 % + DL)
• detection limit (DL):	2 pptv (6 min time resolution)
• interferences:	Negligible for all tested trace gases
• Power supply	24 V/DC and 100 - 250VAC 50 - 60 Hz
• Order number:	Q003.498

References:

Villena, G., I. Bejan, R. Kurtenbach, P. Wiesen and J. Kleffmann: Development of a new Long Path Absorption Photometer (LOPAP) Instrument for the Sensitive Detection of NO in the Atmosphere, Atmos. Meas. Tech., 2011, 4, 1663-1676.

Villena, G., I. Bejan, R. Kurtenbach, P. Wiesen and J. Kleffmann: Interferences of commercial NO instruments in the urban atmosphere and in a smog-chamber, Atmos. Meas. Tech., 2012, 5, 149-159.

Peters, S., I. Bejan, R. Kurtenbach, G. Villena, P. Wiesen, and J. Kleffmann: Development of a new LOPAP Instrument for the Detection of O in the Atmosphere, Atmos. Environ., 2012, 67, 112-119.

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