Selective measurements of NO, NO$_2$ and NO$_y$ in the free troposphere using quantum cascade laser spectroscopy

B. Tuzson$^1$, K. Zeyer$^1$, M. Steinbacher$^1$, J. B. McManus$^2$, D. D. Nelson$^2$, M. S. Zahniser$^2$, and L. Emmenegger$^1$

$^1$Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Air Pollution and Environmental Technology, Überlandstr. 129, 8600 Dübendorf, Switzerland
$^2$Aerodyne Research, Inc., Center for Atmospheric and Environmental Chemistry, Billerica, MA 01821, USA

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Correspondence to: B. Tuzson (bela.tuzson@empa.ch)

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Abstract

A quantum cascade laser based absorption spectrometer for continuous and direct measurements of NO and \( \text{NO}_2 \) was employed at the high-altitude monitoring site Jungfraujoch (3580 m a.s.l., Switzerland) during a three month campaign in Spring/Summer 2012. The total reactive nitrogen, \( \text{NO}_y \), was also measured in the form of NO after conversion on a gold catalyst. The aim was to assess the suitability of the instrument for long-term monitoring of the main reactive nitrogen species under predominantly free tropospheric air conditions. A precision (1\( \sigma \)) of 10 and 3 ppt for NO and \( \text{NO}_2 \) was achieved with 180 s averaging time under field conditions. The linear dynamic range of the instrument has been verified for both species from the detection limit to \( \approx 45 \text{ ppbv} \). The spectrometer shared a common sampling inlet with a chemiluminescence-based analyzer. The comparison of the time series shows excellent agreement between the two techniques and demonstrates the adequacy of the laser spectroscopic approach for this kind of demanding environmental applications.

1 Introduction

In the troposphere, the abundance of reactive nitrogen species is primarily influenced by emissions from anthropogenic sources in the form of nitrogen oxides (\( \text{NO}_x = \text{NO} + \text{NO}_2 \)). Once in the atmosphere, these species are involved in a number of different chemical pathways and oxidized to a large variety of other reactive nitrogen species denoted as \( \text{NO}_y \) (Crutzen, 1979; Logan, 1983). Despite their low atmospheric concentrations, nitrogen oxides represent an important factor regarding air quality given their contribution to local ozone production and secondary organic aerosol formation. Furthermore, the adverse effect of \( \text{NO}_2 \) on the human respiratory system and the formation of nitric acid (\( \text{HNO}_3 \)), which is the dominant sink of \( \text{NO}_x \) (via dry and wet deposition), makes it a harmful air pollutant (Wesely and Hicks, 2000; Jacob, 2000). The significance of \( \text{NO}_x \) in tropospheric chemistry triggered the interest in instrumental
development. This is a challenging task given the substantial spatial and temporal variability of NO$_x$, which ranges from a few ppt at remote locations to > 100 ppb in urban regions. Nevertheless, it has been addressed over the last two decades by a wide variety of measurement techniques and by even larger number of instrumentation (see e.g. review by Clemitshaw (2004) and references therein). Although, recent intercomparison studies demonstrate that several techniques perform well (Fehsenfeld et al., 1990; Fuchs et al., 2010), they still involve research grade instruments that are not yet established as routine monitoring tools.

At present, chemiluminescence detection (CLD) is considered to be the standard technique and is commonly used in field missions and air quality monitoring (Demerjian, 2000; GAW Report #195, 2011). Although, the method has very good precision for NO, it is unable to directly measure NO$_2$. Nevertheless, this has successfully been overcome by including the conversion (catalytic or photolytic) of NO$_2$ to NO prior to analysis. Besides the necessity of systematic determination of the conversion efficiency, the conversion may also lead to interferences of other nitrogen compounds that can readily be converted to NO (Dunlea et al., 2007; Steinbacher et al., 2007), possibly resulting in overestimated NO$_2$ readings. The alternating measurement of NO and NO$_x$ can also lead to artifacts in the NO$_2$ determination when the ambient NO$_x$ levels experience rapid changes. Thus, a setup with two individual CLDs (three in case of NO, NO$_x$ and NO$_y$ observations) is the preferred – but not inexpensive – configuration.

For the present study, we adopted the dual laser design approach recently reported by McManus et al. (2010). Our choice for quantum cascade laser based direct absorption spectroscopy (QCLAS) was driven by two major factors: (i) our previous campaigns performed in a large variety of environments including grass-land, forest and mountain sites (Tuzson et al., 2008; Neftel et al., 2010; Kammer et al., 2011; Tuzson et al., 2011) showed that QCLAS is a robust and reliable technique to be employed under various field and measurement conditions and (ii) we obtained up to date the longest (more than four years of continuous operation) time-series of CO$_2$ isotope ratio measurements at a mountain site, which reflects the sturdy operation capability of the QCLs.
(Sturm et al., 2013). In addition to these considerations, the direct absorption technique offers a simple and straightforward solution to perform absolute spectroscopic quantification of the molecular species of interest.

In the following sections we describe the laser instrument, the measurement strategy and the experimental setup used for the campaign to perform direct and simultaneous measurements of NO and NO$_2$. The validation of the time series recorded during three months of continuous operation is done against the standard CLD method. A short discussion is given on the discrepancy seen when employing the catalytic gold converter for NO$_y$ measurements.

2 Experimental

2.1 Instrumentation

2.1.1 NO$_x$ QCLAS

The spectroscopic instrument (Aerodyne Research, Inc., USA) employed in this study is based on continuous wave quantum cascade laser (cw-QCL) technology. A recent review on optical design, performance characteristics and application fields of this kind of analyzer has been presented by McManus et al. (2010). Briefly, the spectrometer embodies two room-temperature cw-QCLs (Alpes Lasers, Switzerland) emitting in the spectral range of 1600 and 1900 cm$^{-1}$, respectively. The individual laser beams are first collected by a pair of reflective objectives then combined and co-oriented by a dichroic mirror (LohnStar Optics, Inc., USA) and sent through a wedged beamsplitter that results in three different beams. The main beam is further shaped by a series of reflective optics and coupled into an astigmatic Herriott multipass absorption cell (AMAC-200) which folds the laser radiation for a total number of 434 reflections. This results in an effective path length of 204 m (McManus et al., 2011). When the exit condition of the cavity is fulfilled, the laser beam leaves the cell through the same entrance
hole and is then focused on a thermoelectrically cooled IR detector (Vigo Systems, Poland). The fraction of the laser beam reflected from the first surface of the beamsplitter is directed through a short (5 cm) cell filled with a 1:1 mixture of NO and NO\textsubscript{2} and subsequently aimed onto a second detector. This reference path assures the locking of the laser frequency to well-defined absorption lines even in situations when the ambient NO\textsubscript{x} concentrations drop below the limit of detection or when the multipass cell is filled with NO\textsubscript{x}-scrubbed air for spectral background measurements. The third beam reflected from the back surface of the wedge is used for accurate frequency tuning rate determination of the lasers by placing a germanium etalon in its path. This beam is also focused onto the reference detector. A flipping mechanism selects between the two beams (reference cell or etalon).

Beside the optical assembly design, the electronics have also experienced some major improvements. A significant reduction of the hardware size has been achieved by moving towards USB-DAQ solution (NI USB-6251 OEM, National Instruments, Inc., USA) and embedded mini-PCs. Low noise laser drivers (Wavelength Electronics, Inc., USA) combined with dedicated power-supply design and thermal management led to unprecedented stability. Details regarding the laser control and spectral fitting software (TDLWintel, Aerodyne Research, Inc., USA) have been discussed previously (Nelson et al., 2004).

The major advantage of a direct spectroscopic detection of NO\textsubscript{2} is the immunity from interferences associated with photochemical conversion of NO\textsubscript{2} to NO prior to detection. However, this technique may suffer from interferences of other nature, such as overlapping absorption features from other molecular species or pressure broadening effects mainly due to water (Tuzson et al., 2010). Therefore, we performed a detailed investigation of the simulated absorption spectra, generated based on typical experimental parameters and the HITRAN database (Rothman et al., 2009), in the range of 1600 and 1900 cm\textsuperscript{-1}, where NO\textsubscript{2} and NO have their fundamental ro-vibrational modes. The aim was to select the strongest absorption lines possible with the stringent condition that the spectral interferences from water vapor or other trace gases are minimal.
The best compromises we could identify were the doublet lines located at 1900.0706 and 1900.0816 cm\(^{-1}\) for NO and the group of lines in the vicinity of 1599.9 cm\(^{-1}\) for NO\(_2\) (see Fig. 1). Simulations of typical real-time scenarios involving low NO\(_{x}\) concentrations and various humidity levels indicated low interference effects (<70 ppt NO\(_{x}\) per volume % H\(_2\)O), which was later confirmed experimentally. Based on these examinations, two cw-QCLs were selected correspondingly with single mode emission powers higher than 10 mW at the specified wavelengths.

The instrument’s precision has been enhanced by addressing the issue of interference fringes. These are mainly produced by scattered light within the multipass cell and may significantly limit the achievable SNR improvement available from multipass cell’s. They typically generate an absorption equivalent noise level of 10\(^{-4}\) in the background signal. A significant improvement was obtained by careful investigation and selection of circulation patterns that minimize fringes near the absorption line-width and by using high-reflectivity mirrors that lead to lower fringes by reducing the ratio of scattered light to transmitted light (McManus et al., 2011). In addition, a mechanical modulation (dithering) of the cell mirrors by a piezo-crystal helps to average out fringes. As a result, a precision of \(\sigma_{\text{min}} = 1\) ppt for NO\(_2\) after 12 min of averaging was achieved in the laboratory. Under field conditions, however, this performance may suffer from environmental influences. Therefore, the instrument’s stability was investigated on-site by measuring NO\(_{x}\)-free air for a time period of one hour with a detection bandwidth of 1 Hz and calculating the associated Allan variance as a function of averaging time (Werle et al., 1993). This two-sample variance-plot is shown on Fig. 2 and allows to define the optimum calibration timescale. The variance curve reveals flicker noise contributions to the signal, manifested as deviations from the expected 1/\(\tau\) slope, at around 10 and 220 s. Similar behavior has been described by Werle (2011) and associated to optical fringes. Following his theoretical framework, it was possible to closely reproduce the observed deviations by assuming two periodic fringe components with frequencies of \(4.3 \times 10^{-2}\) Hz and \(2.2 \times 10^{-3}\) Hz, respectively. In fact, the 23 s periodicity correlates well with the PID-cycle of the temperature controller employed for stabilizing the optical
module. The slow fringe is probably due to opto-mechanical drifts or variations in the driver electronics, reflecting the temperature fluctuations (≈4 K) experienced at the monitoring station. Taking into account this behavior, we lowered the averaging time by about a factor four compared to the laboratory situation. Nevertheless, the precision achieved at the monitoring site after 180 s averaging time was 3 and 10 ppt, which corresponds to an absorbance noise level of $5.9 \times 10^{-6}$ and $8.8 \times 10^{-6}$ for NO$_2$ and NO, respectively. Normalizing to the 204 m optical path-length, this corresponds to an absorbance per unit path length sensitivity of $5 \times 10^{-10}$ cm$^{-1}$.

The strategy to cope with this flicker noise issue was the frequent and periodic background (zero-air) spectrum subtraction from the measured spectrum. Therefore, a cost effective NO$_x$ filter that consists of a stainless-steel container (1 L) filled with grained activated charcoal (Merck KGaA, Germany) was used to generate NO$_x$-scrubbed air for spectral background measurements. The NO$_x$ filter efficiency has been verified in comparison with high purity (5.5) He and N$_2$. The filter solution was the preferred method over the use of dry N$_2$ as zero-air, because the NO$_x$ filter does not significantly alter the water vapor mixing ratio of the air flowing through it, and thus, the zero-air better reconciles the sampled air humidity and contributes in reducing possible detection artifacts that could be induced by spectral interferences due to water absorption lines. The most efficient method to maintain the best stability and accuracy of the spectrometer has been achieved by automatically recording a background spectrum every 10 min and subtracting it from each subsequent sample spectrum before fitting. More details about the measurement cycle are presented in the Section 3.

### 2.1.2 Chemiluminescence NO$_x$ detection

The routine, long-term monitoring of NO, NO$_x$, and NO$_y$ at the Jungfraujoch is performed with commercially available chemiluminescence analyzers (CraNOx, Eco Physics, Switzerland). The chemiluminescence detection (CLD) technique, developed in the 1970s, is the reference method recommended by the US EPA (Demerjian, 2000) and by European legislation (European Standard, EN 14211, 2012) for the
measurement of NO\textsubscript{x} in monitoring networks. The method relies on the light emission from the electronically excited NO\textsubscript{2}, a product generated in the gas-phase reaction of ambient NO with O\textsubscript{3} added in excess to the air sample. The emission intensity is directly proportional to the concentration of NO in the air, and the emitted photons are detected by a photo multiplier tube. NO\textsubscript{x} is measured as NO after photolytic conversion of NO\textsubscript{2}. The atmospheric NO\textsubscript{2} is then derived by subtraction of NO from the NO\textsubscript{x} signal (Ridley and Howlett, 1974; Ryerson et al., 2000; Sadanaga et al., 2010). NO\textsubscript{y} species are converted to NO on a heated gold catalyst (300 °C) in the presence of CO as a reducing agent (Fahey et al., 1985).

The measurement procedure as well as the calibration strategy has repeatedly been described in detail (Zellweger et al., 2000; Pandey Deolal et al., 2012). Here we just recall that for the sensitive measurement of the NO-NO\textsubscript{x}-NO\textsubscript{y} species, three dedicated CLDs are used. The detection limits of the CLDs for NO and NO\textsubscript{y} after 2 min averaging are 20 ppt, whereas it is 50 ppt for the NO\textsubscript{2} channel due to the incomplete conversion and the determination of NO\textsubscript{2} by the difference of two measured (NO and NO + converted NO\textsubscript{2}) signals. The overall measurement uncertainty (1 σ) is 9 % for NO\textsubscript{y} and 5 % for NO\textsubscript{x}, including CLD precision, the NO standard uncertainty, and the conversion efficiencies of the photolytic convertor (PLC). Data are processed and reported as 10 min averages.

Since the PLC-CLD setup is used as the standard method, these measurements are taken as reference for validating the QCLAS data.

### 2.2 Site description and sampling setup

Field measurements took place between 22 March and 25 June 2012 at the high alpine research station Jungfraujoch (JFJ, 46.55° N, 7.98° E, elevation 3580 m). The monitoring station is one of the 28 global sites of the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). Given its location, the air sampled here is expected to be representative for the lower free troposphere over Europe, which is mainly the case in the autumn and winter season, while in late spring and summer it
can be influenced by the planetary boundary layer (Baltensperger et al., 1997; Lugauer et al., 1998; Zellweger et al., 2003). Long term continuous in-situ monitoring of trace gases such as NO, NO₂, NOₓ, CO, and O₃ is routinely performed by Empa within the activities of the Swiss National Air Pollution Monitoring Network (NABEL).

The ambient air was sampled using the main inlet of the monitoring site. It consists of a heated stainless steel inlet (inner diameter 9 cm) situated about 3 m above ground, in which the ambient air is drawn at a high flow rate of >800 L min⁻¹ (Fig. 3). The main manifold is temperature controlled to keep the gas temperature at its lower end at constant 10°C. Potential losses of NOₓ in the sampling lines are minimized by placing the gold converter close to the main inlet, connected with about 1 m long PFA tubing. The time required for the air to reach the converter is about 2 s. The photolytic converter (PLC 762, Eco Physics, Switzerland) for the NO₂ measurement is placed next to the NOₓ converter. Downstream of the converters, the air is drawn through separate PFA tubing to the chemiluminescence analyzers. The air for the NO analysis is drawn directly from the main manifold with PFA tubing.

The NO analyzers are automatically calibrated every 39 h by measuring zero air and NO standard gas (5 ppm NO in N₂, referenced against NIST Standard Reference Material (SRM 2629a) and NMI Primary Reference Material (PRM BD11)) diluted with zero air to approximately 48 ppb. The conversion efficiency of the converter is determined by gas phase titration of NO with ozone every 78 h. The conversion efficiency of the PLC usually ranged from 74 to 58 %.

The QCLAS was operated alongside the CLDs for the duration of the study. An additional gold converter (CON 765, Eco Physics, Switzerland) was mounted next to the NABEL NOₓ converter and shared the same CO source (purity 99.997 %, Messer-Griesheim GmbH), whereas the sampling line was independently connected to the main inlet. The selection between ambient air and air passing through the gold converter was accomplished by a 3-way all-Teflon solenoid valve (Teqcom Ind., USA). The flow rate of 1 L min⁻¹ was manually adjusted by a PTFE needle valve Vₘ (PKM, Switzerland) mounted upstream of the cell (see Fig. 3), while the cell pressure
(\(\sim\) 50 hPa) was established by selecting the appropriate pumping rate with an integrated potentiometer on the oil-free diaphragm pump (N920 series, KNF, Germany). Measurements were taken continuously at 1 s time resolution and post-processed to meet the 10 min averaging time scale of the CLD.

3 Results and discussion

For free tropospheric air composition monitoring, high instrumental precision alone is not sufficient to obtain the necessary accuracy. In fact, an optimal calibration and sampling strategy is equally important and has a decisive influence on the data quality. The strategy employed in this study exploits the very high precision and the fast response of the instrument when measuring zero-air. It consists of various steps repeated in half-hour sequence. First, a background spectrum is recorded using NO\(_x\)-scrubbed air as described in the previous section. This is achieved by directing the sampled ambient air through the NO\(_x\) filter by switching the solenoid valve V\(_3\) (see Fig. 3) and purging the absorption cell for 120 s. The last 10 s are then averaged and used to determine the spectral baseline and perform a background correction by subtracting it from all the subsequent spectra. The second step involves measuring NO and NO\(_2\) simultaneously by drawing sample air directly through the absorption cell. In the next step, the solenoid valve V\(_1\) is switched together with V\(_2\) to divert the air flow across the gold converter and thus, the NO\(_y\) mixing ratio is measured as NO. The NO\(_2\) signal can later be used to verify the converter efficiency for NO\(_2\) or to monitor baseline changes due to humidity variations or potential instrumental drifts. After a 10 min measurement period, the system is switched back to direct ambient air sampling. Finally, zero-air is measured again as another background spectrum, which is used in a post-processing step for drift correction. For more confidence in the “absolute” zero baseline determination, dry N\(_2\) from a gas cylinder (purity 5.5) is measured instead of NO\(_x\)-scrubbed air every second hour. This acts as an additional parameter for monitoring the performance of the NO\(_x\) filter and also aids in establishing the water vapor induced interferences, which can be
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Dynamic dilutions of standard NO$_2$ and NO gases were used to establish the span of the laser spectrometer for the NO$_x$ measurements from the detection limit up to 50 ppbv, and to calibrate the purely spectroscopic data against the standard-scale used by NABEL (see Fig. 4 and previous Section). The accuracy of this calibration is dominated by the accuracy of the mass flow controllers (MFCs) used for the dilution. These MFCs (Red-y smart series, Voegtlin, Switzerland) were referenced against a high-accuracy venturi flow-meter (molbloc, DH Instruments/Fluke, USA) at Empa. Since NO$_2$ gas mixtures in cylinders are known to be unstable, the NO$_2$ concentration (96.3 ± 3.7 ppb) was first determined with a calibrated CLD followed by QCLAS measurements and dynamic dilution (Fig. 4). The sampling line was taken the same and thus, we assumed that losses of NO$_2$ on the metallic surfaces of the pressure regulator and MFCs are similar. Obviously, the total uncertainty in this case is mainly given by systematic errors due to losses.

It is noted that all above mentioned parameters were determined on site, i.e. at the monitoring station JFJ. This assured a direct link to the retrieved tropospheric NO$_x$ data. Figure 5 shows an exemplary window of 21 days from the time series recorded by both techniques during the three months campaign. The challenge of such tropospheric air measurements is well illustrated by the NO data, where ~ 78% of the values are below 0.1 ppb. Despite of this, the variations in the mixing ratio profiles of NO and NO$_2$ compare very well between the CLD and the QCLAS. The quantitative agreement is illustrated on Fig. 6 in the form of correlation plots for NO$_x$ and NO$_y$ measured during the three months campaign. The unity slopes with zero intercept are also shown as reference. The calibrated QCLAS data were averaged to 10 min time resolution to
match the CraNOx time scale. In order to minimize the scatter due to synchronization differences between instruments, the error of the mean of each individual value was taken as a measure of the variance during that time window and was used to filter out data points which exhibited too large short-term variations. Statistical analysis on the differences between all NO\(_x\) data reported by the two analyzers showed that more than 94\% of individual data points agree to within ±50 ppt, which is in the same order as the detection limit of the CLD.

In the case of the NO\(_y\) time-series, we observed a systematic discrepancy of about 0.26 ppb, which, over the measurement period, displayed short-term (<<12 h) variations of up to 1.2 ppb. Additional tests, involving different gases (ambient air, dry N\(_2\) and diluted NO standard) as common input sample to the converters and alternating measurements with QCLAS and CLD, revealed that the two converters generate indeed different amounts of NO\(_y\) in excellent agreement with the discrepancy seen for the time-series. Figure 7 shows the clear bias seen by the QCLAS when switching between the two Au converters sharing the same inlet with diluted NO standard as sample gas. The difference disappeared only when dry N\(_2\) was flowing through the converters. Therefore, the mismatch between the two gold-converters has been attributed to their slightly different conversion efficiencies. Even though, for NO\(_2\), the converters’ efficiencies were found comparable (within 1.5\%), Au catalyst may have different efficiencies for the various reactive nitrogen species or may suffer from contributions of other interfering compounds. According to systematic investigations, species such as nitric acid (HNO\(_3\)) and peroxyacyl nitrates (PANs) have conversion efficiencies higher than 95\%, whereas ammonia (NH\(_3\)) and hydrogen cyanide (HCN) in the presence of water vapor show little but variable contribution (1–5\%), and their magnitude depends on the surface history and temperature of the converter (Kliner et al., 1997; Fahey et al., 1985; Volz-Thomas et al., 2005). Although, we had no speciation measurements for these compounds, literature data allow for an estimate of their contribution. Partitioning measurements of NO\(_y\) in the lower free troposphere (Zellweger et al., 2003) revealed that PAN is the dominant NO\(_y\) species (∼ 38\%) during spring, whereas HNO\(_3\) has a minor
contribution (< 20 ppt). Mixing ratio values of ~200 ppt for HCN at the JFJ were reported by Rinsland et al. (2000). Using the above values, a difference of about 14% in the conversion efficiencies for PAN is necessary to explain the observed mismatch between the converters. Such a large difference in the converter’s efficiency is surprising at first sight. However, we also observed a significant difference in the CO₂ content of the gas samples after the converters despite the similar CO flow rates (see Fig. 3). While the CO₂ level remained unchanged after passing through the converter with lower NOₓ values, the other converter almost doubled the amount of CO₂.

Finally, it should be noted that slightly lower NOₓ values (6–10%) in the NABEL system have already been observed during intercomparison campaigns (Zellweger et al., 2003; Pandey Deolal et al., 2012), but they were attributed to potential losses of HNO₃ in the inlet system. This, however, has to be reconsidered and further investigations of Au converter’s inter-comparability is recommended.

4 Conclusions

The validation and long-term performance assessment of a quantum cascade laser spectrometer was successfully accomplished at the high altitude research station JFJ by measuring the tropospheric NOₓ and NOᵧ mixing ratios accompanied by standard monitoring CLD technique. To our knowledge, this is the first intercomparison study of this kind, involving a laser absorption technique for direct and simultaneous measurement of both, NO and NO₂, under field conditions. The time-series recorded by QCLAS show very good correlation with the CLD data even at sub-ppb mixing ratio levels. A dedicated gas sampling/handling method combined with the high instrumental precision (< 10 ppt) delivered the accuracy and drift suppression needed for reliable background tropospheric air NOₓ monitoring. Since both techniques give similar results, there is no fundamental reason to replace the well established and reliable CLD technique by QCLAS. Nevertheless, the possibility to detect NO₂ selectively, i.e. without chemical conversion, and with high time resolution (1 Hz) is very attractive.
Furthermore, significant advances in quantum cascade laser technology lets us anticipate the appearance of compact multi-color sources, which would lead to substantial simplification of the optical design resulting in more robust, compact, and cost-effective analyzers.

The intercomparison of the NO\textsubscript{y} data revealed differences which could not be attributed to any of the measurement techniques, but rather has been associated with the conversion efficiency of the gold catalyst. This was confirmed in a dedicated set of experiments, but the exact reason for the different behavior of the two seemingly identical catalysts remains unclear.

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References


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Fig. 1. The selected spectral windows with the absorption lines of NO and NO$_2$ as measured in ambient air with the dual-laser spectrometer with a multi-pass cell of 204 m path-length at 50 hPa sample pressure. The gray circles indicate measurement points, while the black line is a least-square fit to the data. The residual is shown in the top panel. The colored sticks indicate individual absorption lines of molecules that absorb within the scanning range of the lasers.
Fig. 2. Allan variance plots for NO and NO$_2$ measured with the dual-laser instrument at the Jungfraujoch using NO$_x$-free air as gas sample. The gray lines correspond to calculated white noise plus fringes contributing as flicker noise (details in text).
Fig. 3. Experimental setup at Jungfraujoch. The equipment within the dashed boxes was operated for a three month period, while the other instrumentation is part of the permanent monitoring program.
Fig. 4. Calibration plots of the QCLAS data for NO and NO$_2$. The abscissa represents the values determined from standard gas dilution (details in text), the fit (black line) is determined by weighted orthogonal distance regression and its residual is shown in the upper part.
Fig. 5. An exemplary sequence of NO, NO$_2$ and NO$_y$ time series measured at the Jungfraujoch with the two different methods. Note the different scaling of the y-axis. The gaps in the QCLAS data were caused by additional on-site works, such as calibration and converter investigation (see details in text).
Fig. 6. Correlation plots of the QCLAS and CraNOx data. The 1 : 1 correlation is represented by the black line.
Fig. 7. NO and NO\textsubscript{2} mixing ratios measured with the QCLAS when switching between the two gold converters measuring NO standard gas diluted with “zero”-air. The gray areas correspond to the measurements of the converter used by the NABEL monitoring instrumentation.