



A compact Incoherent Broadband Cavity Enhanced Absorption Spectrometer (IBBCEAS) for trace detection of nitrogen oxides, iodine oxide and glyoxal at sub-ppb levels for field application

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Abstract. We present a compact, affordable and robust instrument based on Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS) for simultaneous detection of NO_x, IO, CHOCHO and O₃ in the 400 – 475 nm wavelength region. The instrument relies on the injection of a high-power LED source in a high-finesse cavity ($F \sim 36,100$), with the transmission signal be detected by a compact spectrometer based on a high-order diffraction grating and a CCD camera. A minimum detectable absorption of $1.8 \times 10^{-10} \text{ cm}^{-1}$ was achieved within ~ 22 minutes of total acquisition, corresponding to a figure of merit of $7.5 \times 10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ per spectral element. Due to the multiplexing broadband feature of the setup, multi-species detection can be performed with simultaneous detection of NO₂, IO, CHOCHO, and O₃ achieving ultimate detection limits of 9, 0.3, 8 ppt and 40 ppb (1σ) within 22 min of measurement, respectively (half of the time spent on the acquisition of the reference spectrum in absence of absorber, and the other half on the absorption spectrum). The implementation on the inlet gas line of a compact ozone generator based on electrolysis of water allows the measurement of NO_x (NO + NO₂) and therefore an indirect detection of NO with detection limits for NO_x and NO of 12 and 21 ppt (1σ), respectively. The device has been designed to fit in a 19", 3U rack-mount case, weights 15 kg and has a total electrical power consumption < 300 W. The instrument can be employed to address different scientific objectives such as better constraint the oxidative capacity of the atmosphere, study the chemistry of highly reactive species in atmospheric chambers as well as in the field, and looking at the sources of glyoxal in the marine boundary layer to study possible implications on the formation of secondary aerosol particles.

1 Introduction

Free radicals are controlling the oxidative capacity of the atmosphere and therefore contribute to the upholding of its chemical balance. With their unpaired valence electron, they are highly chemically reactive, and are therefore considered the “detergents” of the atmosphere (Monks, 2005; Monks et al., 2009). Even if present at extremely low concentrations, radicals are constantly formed by photochemical and combustion processes. They may be removed from the atmosphere by biological uptakes, dry and wet deposition, and chemical reactions (Finlayson-Pitts and Pitts, 2000). Free radicals in the troposphere such as nitrogen oxides (NO_x), hydroxyl radical (OH), peroxy radicals (HO₂, RO₂) and halogen oxides (BrO and IO), can be found at mixing



ratios (i.e. mole fractions) ranging from less than one part per trillion (10^{-12} mol mol⁻¹ or ppt) up to a few parts per million (10^{-6} mol mol⁻¹ or ppm) in the atmosphere (Wine and Nicovich, 2012). Measuring their concentration and dynamic variability
25 in different atmospheric environments is key for addressing specific questions regarding air quality, the oxidative state of the atmosphere, the ozone budget, aerosol nucleation, as well as carbon, nitrogen and sulfur cycles. The understanding of the complex interactions involving those species has led to numerous investigations during the past decades. Especially, nitrogen oxides (NO_x = NO and NO₂), have a direct impact on air quality and climate change. In presence of volatile organic compounds (VOCs) and under solar radiation, nitrogen oxides stimulate ozone (O₃) formation in the troposphere. NO_x also plays an
30 important role in rain acidification and ecosystems eutrophication by its transformation in nitric acid (HNO₃) (Jaworski et al., 1997; Vitousek et al., 1997). Finally, NO_x contribute to the formation of particulate matter in ambient air and to the aerosol formation leading to clouds formation (Atkinson, 2000). The NO₂ mixing ratio in the troposphere ranges from a few tens of ppt in remote areas to hundreds of ppb (10^{-9} mol mol⁻¹) in urban atmospheres (Finlayson-Pitts and Pitts, 2000). Being able to measure such species in situ, at low levels and at a time scale compatible with its reactivity (i.e. in min) is challenging
35 and puts stringent constraints on the instrument sensitivity, time response, energy consumption and compactness. Among the various techniques that have so far been developed, ChemiLuminescence Detection (CLD) (Maeda et al., 1980; Ryerson et al., 2000), Long-Path Differential Optical Absorption Spectroscopy (LP-DOAS) (Lee et al., 2005; Pikelnaya et al., 2007; Lee et al., 2008), and Multi-AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) (Platt and Perner, 1980; Sinreich et al., 2004; Wagner et al., 2010) have been used to detect nitrogen species and halogen oxides. The CLD technique, using the
40 chemiluminescence reaction occurring between O₃ and NO after the reduction of NO₂ into NO, is widely used for air quality measurements with sensitivities better than 100 ppt (Ryerson et al., 2000). Nevertheless, the interferences in the reduction of NO₂ to NO with other species (i.e. HONO, HNO₃) and the sensitivity to environmental conditions (temperature and humidity) leave uncertainties on absolute mixing ratio measurements (Grosjean and Harrison, 1985; Williams et al., 1998). The MAX-DOAS technique has been used to measure BrO and NO₂ by making use of the characteristic absorption features of gas
45 molecules along a path in the open atmosphere (Leser et al., 2003). Although MAX-DOAS is relatively simple to deploy, the data analysis makes it a complex approach for in situ field measurements due to the influence of clouds on the radiative transfer which alters the path length of light (Wittrock et al., 2004; Rozanov and Rozanov, 2010). While in LP-DOAS the optical path length is known, the signal degradation due to the environment (clouds, rain, wind) remains of importance for the data retrieval and results are integrated over the long path leading to a limited spatial resolution (Chan et al., 2012; Pohler et al., 2010).
50 Compact, high sensitive and point-source measurements may be achieved using cavity enhanced techniques such as Cavity Ring Down Spectroscopy (CRDS) and Cavity Enhanced Absorption Spectroscopy (CEAS) (Atkinson, 2003). The potential of the CRDS for accurate, sensitive and rapid measurements in a compact and transportable instrument has already been demonstrated (Fuchs et al., 2009; Brown et al., 2002), e.g. Fuchs et al. (2009) reached a sensitivity of 22 ppt for NO₂ within 1 s of integration time using the CRDS technique (Fuchs et al., 2009). Incoherent Broadband Cavity Enhanced Absorption
55 Spectroscopy (IBBCEAS) (Fiedler et al., 2003) is a simple and robust technique for in situ field observations. Different sources and wavelength regions have been used for the detection of NO₂ leading do different performances: Venables et al. (2006) were able to detect simultaneously NO₃, NO₂, O₃ and H₂O in an atmospheric simulation chamber with a sensitivity of tens



of ppb for NO₂ (Venables et al., 2006) ; Gherman et al. (2008) reached ~ 0.13 ppb and ~ 0.38 ppb for HONO and NO₂ in a 4 m³ atmospheric simulation chamber between 360 and 380 nm (Gherman et al., 2008) ; Triki et al. (2008) used a red
60 LED source centered at 643 nm reaching a sensitivity of 5 ppb (Triki et al., 2008) ; Langridge et al. (2006) developed an instrument with a blue light emitting diode (LED) centered at 445 nm allowing detection limits ranging from 0.1 to 0.4 ppb (Langridge et al., 2006) ; Ventrillard-Courtillot and colleagues reached 600 ppt detection limit for NO₂ with a LED centered at 625 nm (Ventrillard-Courtillot et al., 2010) ; while Thalman and Volkamer reported a detection limit of 30 ppt within 1 min of integration time (Thalman and Volkamer, 2010). More recently, Min et al 2016 proved a sensitivity of 80 ppt in 5 s of integration
65 at 455 nm using a spectrometer with a thermoelectric cooled CCD camera and very higher reflective mirrors (Min et al., 2016). This non-exhaustive list of works underline the need of robust, compact and transportable instruments also allowing direct multi-species detection and low detection limits for applications in remote areas such as Antarctica, where the expected mixing ratio of NO₂ could be as low as a few tens of ppt. Fuchs and colleagues, during the NO₃Comp campaign at the SAPHIR atmospheric simulation chamber, demonstrated the potential of these optical techniques to compete with the CLD instruments
70 as routine measurements of NO₂ concentrations in the future (Fuchs et al., 2010). The present paper describes a compact and affordable instrument based on the IBBCEAS technique, allowing the simultaneous detection of nitrogen dioxide, iodine oxide, glyoxal and ozone (NO₂, IO, CHOCHO and O₃), with detection limits of 9, 0.3, 8 ppt and 40 ppb (1σ), respectively, for a measurement time of 22 min (half of the time spent on the acquisition of the reference spectrum in absence of absorber, and the other half on the absorption spectrum). The four species are directly detected by a broadband blue light emitting
75 diode centered at 445 nm. The wavelength region was selected in order to optimize the detection of NO₂. Direct detection of NO is only possible in UV region for wavelengths around 226 nm (Dooly et al., 2008) or in the mid-infrared region at 5.3 μm (Richard et al., 2018). Wavelengths difficult to achieve with LED technology. Here, an indirect measurement is proposed which relies on the oxidation of NO to NO₂ under a controlled excess of O₃. The sum of NO and NO₂ is therefore measured leading to a supplemental indirect measurement of NO if concentration of NO₂ is also monitored. The field deployment for
80 the measurements of NO₂ and NO_x consists of two twin instruments, IBBCEAS-NO₂ and IBBCEAS-NO_x, the later equipped with an ozone generator system.



2 Method

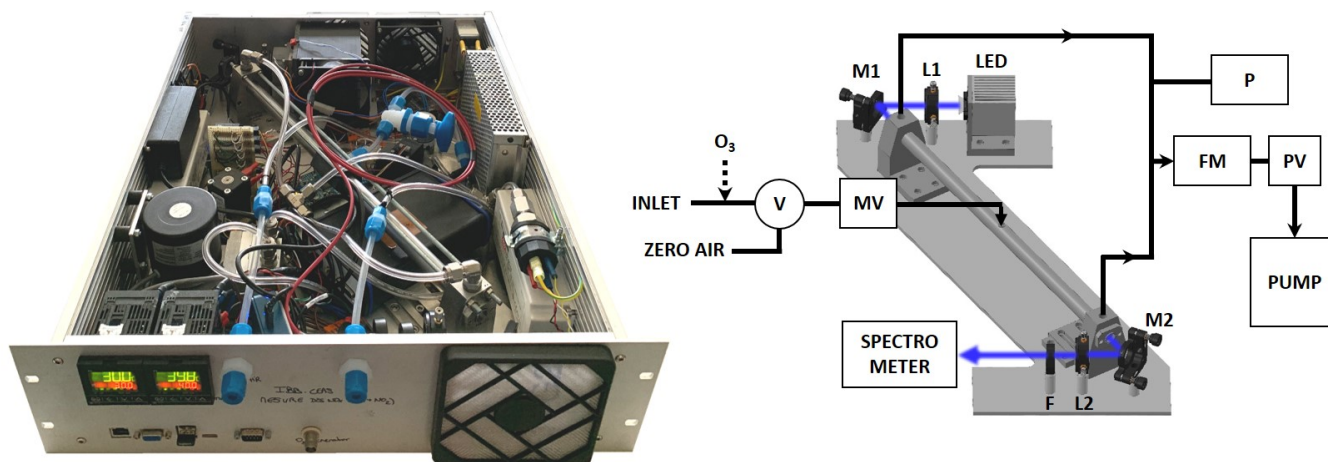


Figure 1. (left) A picture of the instrument mounted on a 19", 3U rack-mount case. (right) Schematic of the instrument. The light from the LED is collimated by lens L1 and injected into the cavity. The exiting light is then collimated with lens L2, and injected into the spectrometer. M1 and M2 are steering mirrors and F is an optical filter. The gas line is composed of a pump, a pressure sensor P, a flow meter FM, and a proportional valve PV. At the inlet, a 3-way 2-position valve in PTFE, V, is used to switch between the sample and zero-air. A manual PFA needle valve MV, is used to fix the flow rate. An ozonizer can be inserted in the inlet line for NO_x measurements.

In IBBCEAS a broadband incoherent light source is coupled to a high-finesse optical cavity for trace gas detection. A picture of the spectrometer and a schematic diagram of the setup is shown in Figure 1. In the present study, the broadband light
85 source consisted of a high-power LED Luminus SBT70 allowing ~ 1 W of optical power to be injected into the resonator. A thermoelectric (TEC) Peltier cooler (ET-161-12-08-E) and a fan/heatsink assembly were used to directly evacuate outside of the instrument up to ~ 75 W of thermal heat from the LED. A temperature regulator (RKC RF100) with a PT100 thermistor was used to stabilize the LED temperature at ± 0.1 °C. The LED spectrum was centered at 445 nm with 19 nm FWHM (Full Width at Half Maximum) which covers the main absorption features of NO₂, IO, CHOCHO and O₃. For better collimation of the LED
90 spatially divergent emission (7 mm² surface), a dedicated optic (Ledil HEIDI RS) was used and coupled with a 25 mm focal lens (L1, Thorlabs, LA1951-A). The high-finesse optical cavity was formed by two half-inch diameter high reflectivity mirrors (maximum reflectivity at 450 nm $\geq 99.990 \pm 0.005$ %, Layertec, 109281) separated by a 41.7 cm-long PFA tube (14 mm internal diameter, 1 mm thick) hold by an external stainless-steel tube. Both mirrors were pre-aligned and glued with Torr Seal epoxy glue on removable stainless-steel supports which were then screwed on the cavity holders. This enables the easy cleaning



95 of the mirrors when required and also the removal of the cavity tube to perform open-cavity measurements, which is of interest
for the detection of the highly reactive IO radical. Behind the cavity, a Thorlabs FB450-40 filter was used in order to remove the
broadband component of the radiation sitting outside the highly reflective curve of the cavity mirrors. The radiation is focused
on an optical fiber (FCRL-7UV100-2-SMA-FC) using a 40 mm focal lens (L2, Thorlabs, LA1422-A). The optical fiber input
was composed of 7 cores in a round shape pattern on the collecting side, whereas, at the fiber end, on the spectrometer side, the
100 cores were assembled in a line for better matching the 100 μm slit at the spectrometer. The spectrometer (Avantes, AvaSpec
ULS2048L) was composed of a diffraction grating (2,400 lines mm^{-1}) and 2,048 pixels charge-coupled device (CCD). The
resolution of the spectrometer was 0.54 ± 0.10 nm. All the optics including the cavity were mounted on a Z-shaped 8-mm
thick aluminum board fixed on the rack using cylindrical dampers (Paulstra). On the board, four 5 W heating bands and one
PT100 sensor were glued, and a second RKC module used to regulate its temperature. The board therefore acts as a large
105 radiator inside the instrument, allowing to minimize internal thermal gradients and thermalize the instrument. Air circulation
from outside is ensured by an aperture at the front and a fan placed at the back wall of the instrument (Figure 1). The gas line
system was composed of a manual PFA needle valve (MV) and a 3-way 2-position PTFE valve, V (NResearch, 360T032) at
the entrance ; while a proportional valve PV (Burkert, 239083), a flowmeter F (Honeywell, HAFUHT0010L4AXT), a pressure
sensor P (SLS ATM.ECO) and a diaphragm pump (KNF, N 816 AV.12DC-B) were placed after the cavity. The entire line was
110 made of $\frac{1}{4}$ " PFA tubing which was found to be least lossy for the transport of highly reactive species (Grilli et al., 2012). The
pump provided a constant flow that can reach 11 L min^{-1} at the end of the gas line while a constant pressure in the cavity
was obtained by a PID regulator on the proportional valve. A data acquisition card (National Instruments, USB 6000) was
interfaced to read the analogue signal from the pressure sensor, while a microcontroller (Arduino Due) drove the proportional
valve. The manual valve at the entrance allowed to tune the flow rate. At the inlet, a 3-way 2-position PTFE valve allowed to
115 switch between the gas sample and zero-air mixture for acquiring a reference spectra in the absence of absorption. Zero-air
was produced by flowing outdoor air through a filtering system (TEKRAN, 90-25360-00 Analyzer Zero Air Filter). $9 \mu\text{m}$
 μm particle filters were also placed in the inlet lines (reference and sample) for preventing optical signal degradation due to Mie
scattering as well as a degradation of the mirror reflectivity for long term deployment. The air flow was introduced at the center
of the cavity and extracted at both ends of the cavity. The optimal cavity design was selected by running SolidWorks flow
120 simulations at flow rates between 0.5 and 1 L min^{-1} (for more details see supplementary informations - SI). Cavity mirrors
were positioned in order to maximize the sample length d (therefore minimizing dead-space) while avoiding that air flow
would hit the mirror surfaces leading to a gradual degradation of the cavity finesse over time. All the components fit in a 19",
3U aluminum rack-mount case, have a total weight of 15 kg and a total electrical power consumption < 300 W. Instrument
interface, measurements and data analysis are performed automatically, without the intervention of an operator, by dedicated
125 LabView software. Instrument calibrations, however, must be performed by an operator on a regular basis.



3 Spectral fit

The absorption spectrum is calculated as the ratio between the spectrum of the light transmitted through the cavity without a sample, $I_0(\lambda)$, and with a sample in the cavity, $I(\lambda)$. It is expressed as the absorption coefficient (in units of cm^{-1}) by the following equation (Fiedler et al., 2003):

$$130 \quad \alpha(\lambda) = \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right) \left(\frac{1 - R(\lambda)}{d} \right) \quad (1)$$

where $R(\lambda)$ is the wavelength dependent mirror reflectivity and d the length of the sample inside the cavity. Equation (1) is derived from the Beer-Lambert's law and applied to light in an optical resonator (Ruth et al., 2014). The light transmitted through the optical cavity is attenuated by different processes such as absorption, reflection and scattering of the mirror substrates and coating, as well as losses due to the medium inside the cavity. The losses of the cavity mirrors are assumed to be constant between the acquisition of the reference and the sample spectrum. Mie scattering is minimized with a particle filter
135 in the gas inlet, while Rayleigh scattering losses were calculated to be $2.55 \times 10^{-7} \text{ cm}^{-1}$ at 445 nm at 25 °C and 1 atm (Kovalev and Eichinger, 2004) and thus negligible with respect to the cavity losses normalized by the cavity length ($\frac{1-R}{d} = 2.09 \times 10^{-6} \text{ cm}^{-1}$). Therefore, the light transmitted through the cavity is mainly affected by the absorption of the gas species, which leads to well-defined absorption spectral features, $\alpha_i(\lambda)$, that are analyzed in real time by a linear multicomponent fit routine.
140 Experimental absorption spectra of the species i ($i = \text{NO}_2$, IO, CHOCHO and O_3) have been compared with literature cross section data accounted for the gas concentration, experimental conditions of temperature and pressure, and convoluted with the spectrometer instrumental function. Those experimental spectra are then used as reference spectra for the fit.

$$140 \quad \alpha(\lambda) = \sum_i \sigma_i(\lambda) c_i + p(\lambda) \quad (2)$$

A fourth order polynomial function, $p(\lambda) = a_0 + a_1\lambda + a_2\lambda^2 + a_3\lambda^3 + a_4\lambda^4$, is added to the absorption coefficient equation (2)
145 to adjust the spectral baseline and account for small changes between the reference and the sample spectra. The transmitted light intensity, as well as the optical absorption path, will be modulated by the shape of the mirror reflectivity curve. Therefore, the later should be defined in order to retrieve the correct absorption spectrum recorded at the cavity output.

4 Calibration, performance and multi-species detection

4.1 Calibration

150 Washenfelder and coworkers (Washenfelder et al., 2008) described a procedure for retrieving the mirror reflectivity curve by taking advantage of a different Rayleigh scattering contribution to the cavity losses while the measuring cell was filled with different bulk gases (eg. Helium versus air or nitrogen). In this work we propose an easier approach consisting of using a trace gas at a known concentration (in this case NO_2 , since O_3 spectrum is less structured, IO is highly reactive and CHOCHO is not easy to produce at a known concentration) and its literature cross-sections (Vandaele et al., 1998) for retrieving the wavelength
155 dependent reflectivity curve. The shape of the reflectivity curve is first approximated with a fourth order polynomial function,



$p(\lambda)$, from the theoretical curve provided by the manufacturer. Then, reflectivity values over the broadband spectral region are deduced experimentally by adjusting a constant parameter (maximal reflectivity) and polynomial parameters (shape) of the reflectivity curve in order to best match the literature NO_2 spectrum. See SI for further details. Figure 2(a) shows the resulting reflectivity curve and the transmitted light through the cavity and the optical filter. The maximum reflectivity achieved with
160 both mirrors given by the calibration procedure is 99.9913 % which leads to an effective optical path length of ~ 4.8 km and a cavity finesse ($F = \frac{\pi\sqrt{R}}{1-R}$) of $\sim 36,100$. While the shape of the mirror reflectivity curve is determined once and for all, its offset is slightly adjusted after each mirror cleaning, by flushing in the cavity a known concentration of NO_2 . The spectral emission of the LED centered at 445 nm is well suited also for the detection of IO, CHOCHO and O_3 , which are other key species in atmospheric chemistry. For the field measurements of NO_2 and NO_x , two twin instruments named IBBCEAS- NO_2
165 and IBBCEAS- NO_x are deployed, with the later equipped with an ozone generator on the gas inlet line. At this wavelength region water vapor also absorbs and is accounted in the spectral fit analysis. However, the absorption of oxygen dimer is not required in the fit routine since the absorption feature will be present in the reference (I_0) as well as in the a absorption (I) spectra. In Figure 2(b) simultaneous detection of species NO_2 , IO and O_3 is reported. Ozone, at 26.5 ppm, was produced by water electrolysis as described in Section 4.4, 175.6 ppb of NO_2 were provided by a permeation tube, and 389.7 ppt of IO were
170 generated by photochemical reaction of sublimated iodine crystals and ozone in the presence of radiation inside the cavity. For this spectrum, the light transmitted was integrated for 350 ms on the CCD and averaged over 1000 spectra, yielding to a 1σ standard deviation of the residuals, (Figure 2(c)), of $4 \times 10^{-8} \text{ cm}^{-1}$. Figure 2(b) shows the experimental spectra (black trace), the fit result (red trace) and contributions from each species which have been included in the spectral fit.

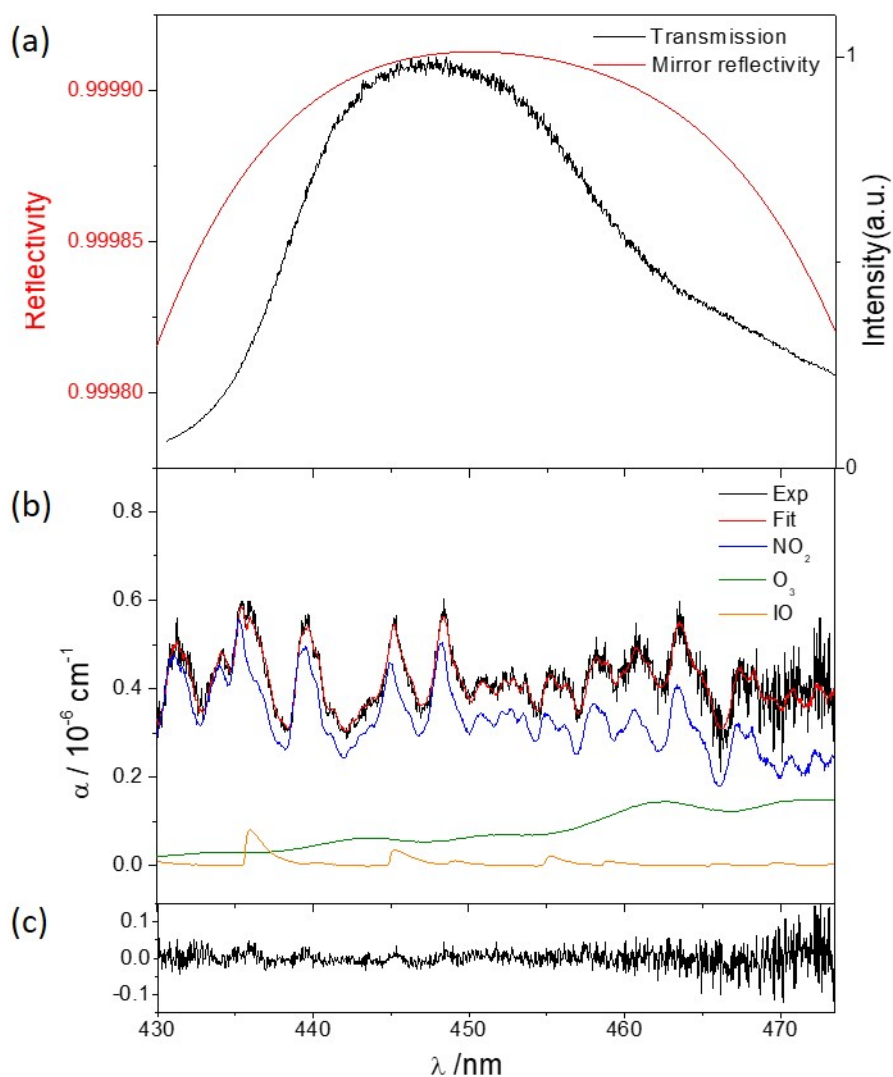


Figure 2. (a) The mirror reflectivity curve (red) in comparison with the spectrum of the LED light transmitted by the cavity and the optical filter for a single acquisition of 350 ms. (b) In black, an example of an experimental spectrum of NO_2 , IO and O_3 at concentration of 175.6 ppb, 389.7 ppt and 26.5 ppm, respectively ; in red, the multi-species spectral fit ; and in blue, orange and green the absorptions of the different species. (c) The residual of the experimental fit with a 1σ standard deviation of $4 \times 10^{-8} \text{ cm}^{-1}$ after 1000 averages.



4.2 Instrumental inter-comparison and calibration

175 As standard gas, a NO₂ bottle from Air Liquide (NO₂ in N₂ announced at 1.00 ± 0.05 ppm (2σ)) was used to calibrate
the IBBCEAS instruments. To confirm the right amount of NO₂ in the bottle, the later was first calibrate against a CLD
instrument (ThermoFisher™, 42iTL trace analyzer calibrated to NIST traceable standards by the manufacturer just before the
experiments). The NO₂ concentration in the bottle was measured at 577.4 ± 2.3 ppb. The large discrepancy with respect to the
value provided by the manufacturer probably comes from the losses due to the presence of the gas regulator. This gas bottle
180 was then used as local standard for the calibration of the IBBCEAS systems. To confirm the calibration process as well as the
stability of the instrument within a greater range of concentrations, two inter-comparisons of the IBBCEAS with two different
CLD instruments (ThermoFisher™, 42i NO_x analyser and ThermoFisher™, 42iTL NO_x trace analyser) were performed in
outdoor air over 39 and 12 hours, respectively. Results are reported in Figure 3. The experiments took place at the Institute
of Geosciences of the Environment (IGE) in Saint Martin d'Hères, France. The IGE is located in the university campus, ~ 1
185 km from the city center of Grenoble and ~ 300 m from a highway. Ambient air was pumped simultaneously from the same
gas line by the instruments at flow rates of 1.0 and 0.5 L min⁻¹ for the IBBCEAS and the CLD instrument (ThermoFisher™,
42i NO_x analyser), respectively. The measurements were conducted from 6 pm on Saturday 29th of September until 9 am on
Monday 1st of October 2018 (Figure 3(a)). On Saturday 29th of September evening the NO₂ peak occurs at slightly later time
than normally expected (from 8 pm to midnight). This may be due to the fact that during Saturday night, urban traffic can be
190 significant until late, but also due to severe weather conditions prevailing at this time, with a storm and lightnings known to be
a major natural source of NO_x (Atkinson, 2000). For the second experiment shown in Figure 3(b), ambient air was pumped
at flow rates of 1.0 and 0.8 L min⁻¹ for the IBBCEAS and the CLD trace instrument (ThermoFisher™, 42iTL NO_x trace
analyser), respectively. The measurements were conducted from 8 pm on Thursday 18th of July until 8 am on Friday 19th
of July 2019. Both instruments showed the expected variability from an urban environment with an increase of NO₂ in the
195 evening and morning due to photochemical processes and anthropogenic activities (i.e mainly urban traffic).

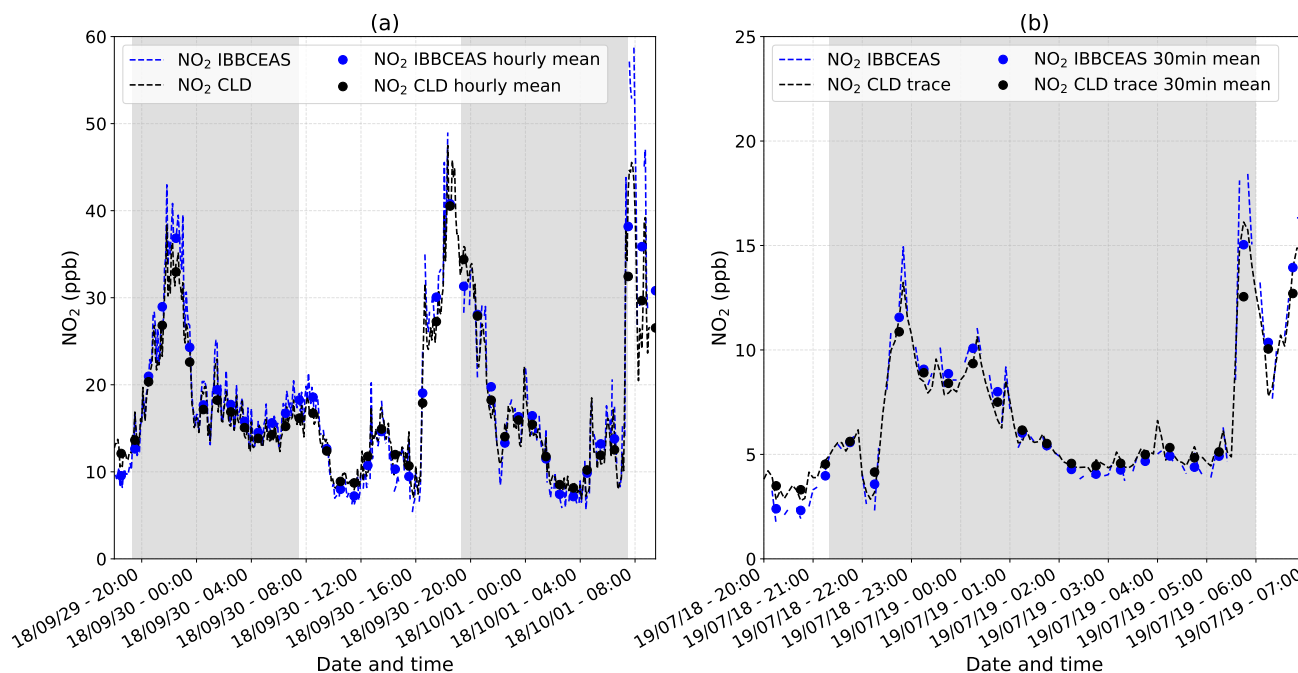


Figure 3. (a) A 39h-long intercomparison of the IBBCEAS instrument and the commercial CLD instrument (ThermoFischer™, 42i analyzer) on the NO₂ detection in outdoor urban area performed in September 2018. The plot reports continuous (dashed lines) and hourly (dots) average data for both techniques. The grey area corresponds to night time period. (b) A 12h-long intercomparison of the IBBCEAS instrument and the commercial CLD trace instrument (ThermoFischer™, 42iTl trace analyzer) on the NO₂ detection in outdoor urban area performed in July 2019. The plot reports continuous (dashed lines) and 30 minutes (dots) average data for both techniques. The grey area corresponds to night time period.

The correlation plot, based on data of all instruments, (Figure 4(a)), shows good linearity with a slope of 1.064 ± 0.118 and a correlation coefficient $R^2 = 0.960$ with measurements averaged over 5 minutes. In order to perform linearity tests, the previous NO₂ bottle from Air Liquide was used and diluted with a zero-air line to produce NO₂ at concentrations of 0, 18.2, 80.8 and 139.7 ppb. Figure 4(b) shows the good linearity of the IBBCEAS instrument with a slope of 0.968 ± 0.019 and a correlation factor of $R^2 = 0.996$. While the system measures NO₂ directly, the CLD technique applies an indirect measurement of NO_x from the oxidation of NO through a catalyzer, then in CLD, the NO₂ mixing ratio is obtained by the subtraction of the NO signal to the total NO_x signal. The discrepancies observed at low concentrations (< 5 ppb) between the two techniques maybe due to the fact that the measurement from the CLD could actually corresponds to NO_y, leading to an overestimation of the NO₂ concentration.

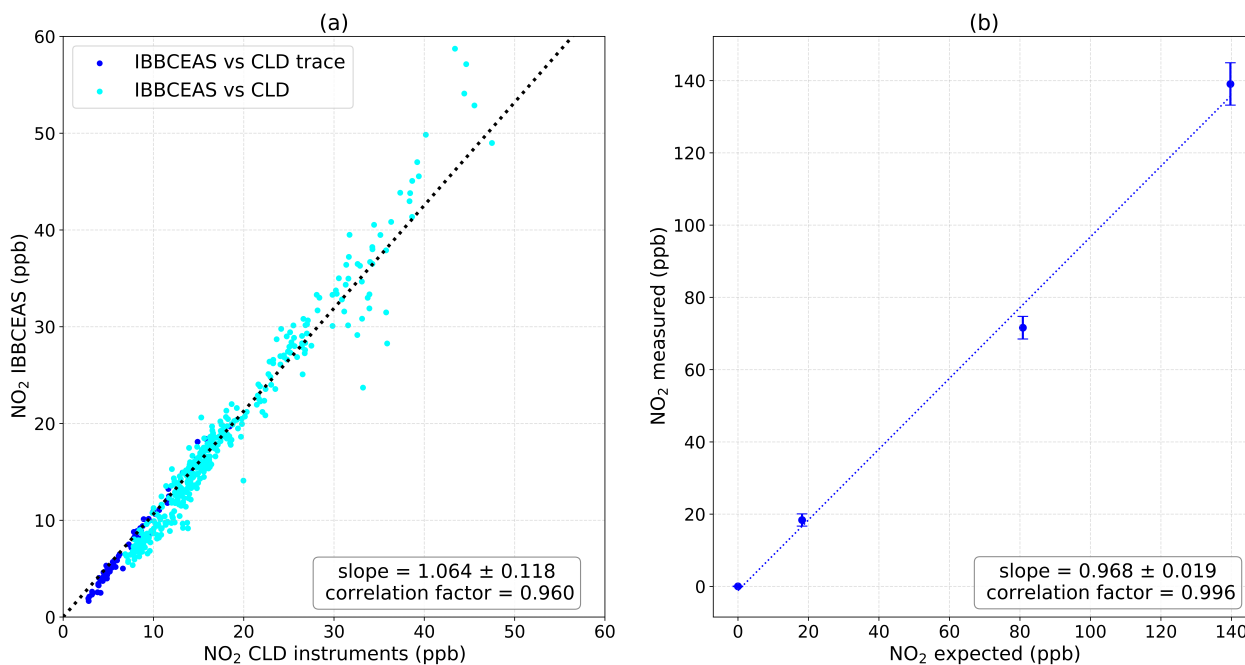


Figure 4. (a) A linear correlation was obtained with a slope of 1.064 ± 0.118 and a correlation coefficient $R^2 = 0.960$ between the IBBCEAS system and the ThermoFisher instruments. (b) Results of the system's calibration using a NO₂ bottle from Air Liquide in a dilution line. A linear correlation was obtained with a slope of 0.968 ± 0.019 and a correlation coefficient of $R^2 = 0.996$

205 4.3 Performance

4.3.1 Instrument sensitivity and long-term stability

In remote area such as East Antarctica, NO₂ ranges from a few tens to a few hundreds of ppt (50 - 300 ppt) (Frey et al., 2013, 2015). This requires the sensitivity of a field instruments to be at the level of a few tens of ppt. Due to the low signal-to-noise ratio of the spectrometer, a single acquired spectrum (with an integration time ranging between 200 and 350 ms) does not provide this detection limit. However, the sensitivity can be improved by averaging the measurements for longer times, over which the instrument is stable. The stability of the IBBCEAS system is mainly affected by temperature fluctuations, mechanical instabilities and pressure drifts. In order to characterize the long-term stability of the instrument, two different studies were conducted on the IBBCEAS-NO₂ during the Antarctica field campaign, Dôme C 2019-2020 (the same results for the IBBCEAS-NO_x can be found in the SI). For both studies, the light transmitted through the cavity (I) was integrated at the CCD for 250 ms, providing a signal-to-noise ratio of 110 for a single spectrum. The reference spectrum (I_0) was taken by averaging 2,000 individual spectra (~ 8 min) while flushing the cavity with zero-air. Subsequently, a 9h-long time series was recorded for each instrument maintaining the zero-air flow. The instrument was regulated at 12.0 ± 0.2 °C, with a cavity pressure of 630.0 ± 0.7 mbar, and a gas flow of 1.02 ± 0.11 L min⁻¹. The minimum absorption coefficient (α_{min}), corresponding to



the standard deviation of the residual of the spectrum, was deduced for different time averages. The results are shown in the
220 log-log plot of Figure 5, where the dots are the data and the dashed line indicates the trend in case of pure white noise regime.
From the graph one can see that the instrument follows the white noise trend for about 22 min (5,200 averages), afterwards,
the baseline noise starts to deviate due to the arise of frequency dependent noise. The chosen α_{min} value corresponds to $1.8 \times$
 10^{-10} cm^{-1} within ~ 22 min (5,200 spectra) of measurement during which a reference spectrum in absence of absorbers and
the absorption spectrum are acquired. The corresponding figure of merit (Noise Equivalent Absorption Sensitivity, NEAS or
225 $\alpha_{min}(\text{BW}) = \alpha_{min} \times \sqrt{\frac{t_{int}}{M}}$ is therefore $7.5 \times 10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ per spectral element (with t_{int} the integration time, ~ 11
min, and M the number of independent spectral elements, here 800 spectral elements are considered for the spectral fit).

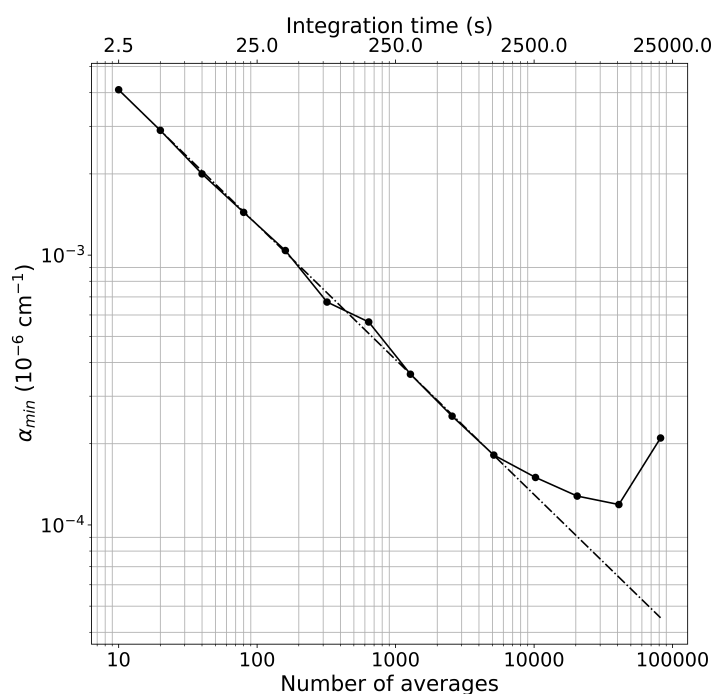


Figure 5. The minimum absorption coefficient α_{min} versus the number of spectral average for the IBBCEAS-NO₂ instrument. For these measurements the cell was continuously flushed with a flow of 1.02 L min⁻¹ of zero-air, and the α_{min} was calculated from the standard deviation of the residual of the spectra at different time averages.

For the same field time series an Allan-Werle (AW) statistical method on the measured concentrations was employed (Werle et al., 1993). In this case, spectra were averaged in block of ten and analysed by the fit routine. The results of the fit are reported on the top graph of Figure 6. For an acquisition time of 2.5 s, corresponding to 10 averaged spectra, the AW standard deviation
230 σ_{AW-SD} was 230, 6.7, 195 ppt and 800 ppb for NO₂, IO, CHOCHO and O₃, respectively. By increasing the integration time, the σ_{AW-SD} decreased following the white noise trend (colored dashed line of Figure 6 bottom) with a characteristic \sqrt{N} slope (where N is the number of averaged spectra). Because a reference spectrum in absence of absorbents is required by this

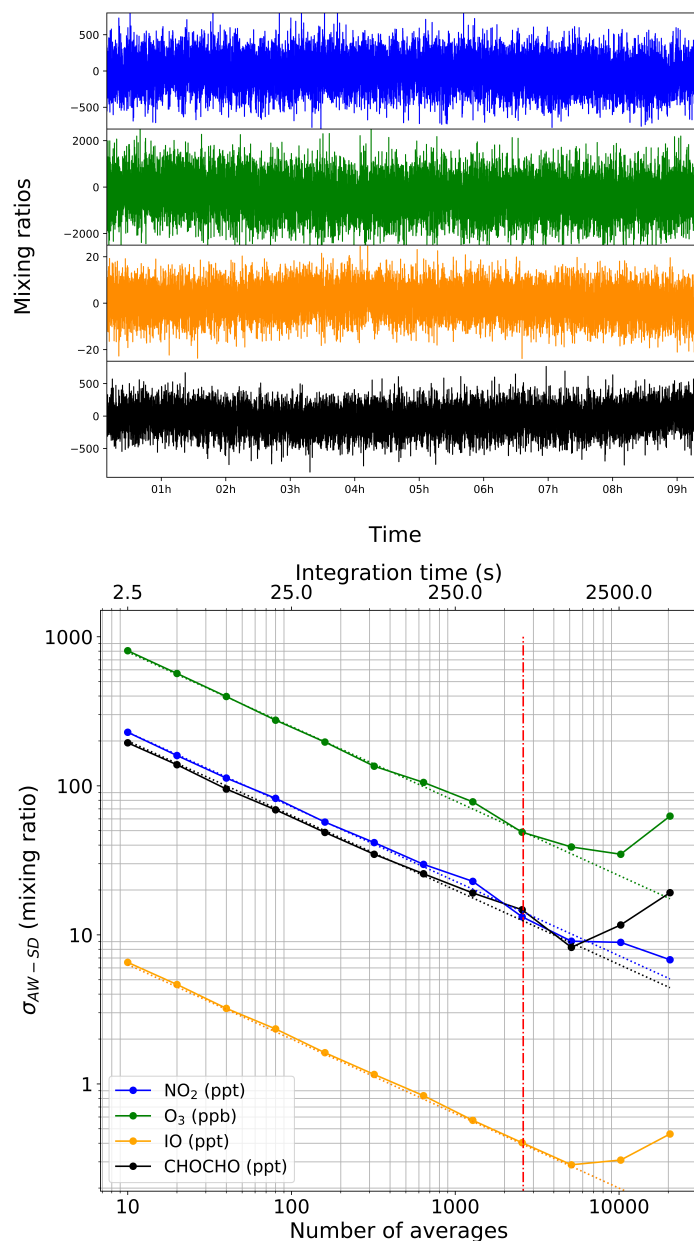


Figure 6. (top) Mixing ratios of the target species NO₂, O₃, IO, and CHOCHO measured during a nine hours Allan-Werle variance statistical experiment flowing zero-air through the cavity on the IBBCEAS-NO₂ instrument. (bottom) The log-log Allan-Werle standard deviation plot, illustrating that the instrument performance follows the white noise regime up to a certain extent, identified by the dashed lines. This represents the optimum integration time, after which instrumental instabilities start to dominate.



CEAS technique, depending on the shape of the AW plot different strategies may be followed. In our case, the AW trends continue to decrease for all species during ~ 22 min (5,200 averages), this means that one can spend 11 minutes acquiring the reference spectrum and further 11 minutes for the absorption spectrum, leading to limits of detections (LODs) of 9, 0.3, 8 ppt and 40 ppb (1σ) for NO_2 , IO, CHOCHO and O_3 , respectively. In our case, we chose to divide the measurement times by two (i.e. ~ 11 min and 2,600 averages for acquiring both the reference and the absorption spectra), offering equally interesting LODs: 15, 0.4, 16 ppt and 50 ppb for NO_2 , IO, CHOCHO, and O_3 (1σ), respectively, and allowing us to stay within the white noise regime.

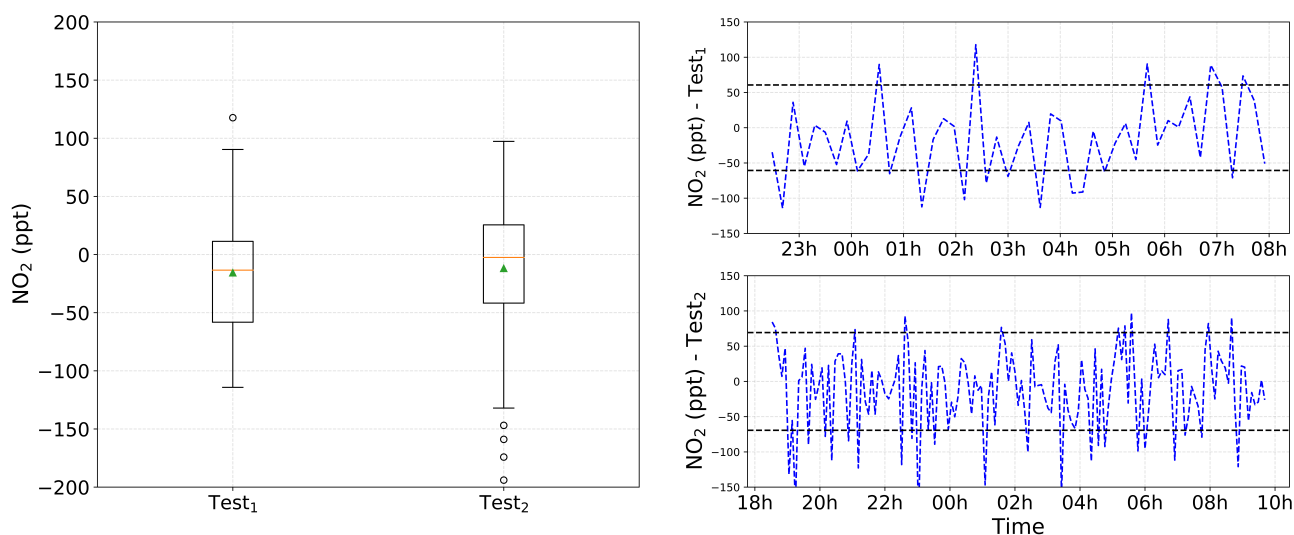


Figure 7. (left) Boxplot of the stability test while continuously flowing zero-air in the cavity, means over 46 and 148 measurements (for Test 1 and Test 2, respectively), are shown as green triangles, dots represent the outliers. (right) Timeseries of two long-term stability tests. The results obtained by alternating reference and absorption spectra within a time interval corresponding to a number of averages where the instrument follows the white noise confirms the validity of the measurement strategy.

Long-term stability of the instrument was further studied by taking regular reference spectra within the optimum white noise time of the instrument while continuously flushing the instrument with zero-air mixture. In this case ~ 5 min and ~ 3 min intervals were chosen, corresponding to 1000 and 580 averages (for 300 ms integration time) and a precision on the NO_2 concentrations of ~ 20 and ~ 23 ppt (1σ), respectively. The results are reported in figure 7. Test 1 (1000 averages) was run for 9h and test 2 (580 averages) for 15h. These tests highlights the reliability of the measurement protocol, with the long term measurements well distributed within the 3σ of the measurement precision (60 and 70 ppt respectively). A Box-plot is also reported representing the average values (green triangles) and medians, quartiles, minimum and maximum values. Table 1 hereafter shows a comparison between our instrument presented in this work and other recently developed IBBCEAS systems.

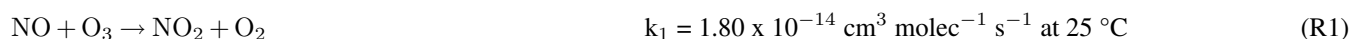
Table 1. Comparisons of the performances with other IBBCEAS systems



References	Centered wavelength (nm)	FWHM spectral resolution (nm)	NO ₂ detection limit (1σ)	Integration time (s)	Cavity length (cm)	Mirror reflectivity (%)	Optical path length (km)
Jordan et al. (2019)	505	30	124 ppt	60	102	99.98	~ 5
Min et al. (2016)	455	18	40 ppt	5	48	99.9973	~ 18
Liu et al. (2019)	455	18	9 ppt	100	84	> 99.98	4.2
Liang et al. (2019)	448	15	~ 15 ppt	30	70	> 99.995	14
This work (2020)	450	19	9 ppt	650	41.7	99.9913	~ 4.8

250 4.4 Indirect measurement of NO

Measuring NO and NO₂ simultaneously is important to study the NO_x budget in the atmosphere. In the selected blue visible region, there are no NO absorption features for direct optical measurements, and optical absorption detection of NO is typically done in the infrared region (Richard et al., 2018). However, its detection can be performed by indirectly measuring NO₂ after chemical conversion of NO to NO₂ in a controlled O₃ excess environment. This will lead to the measurement of NO_x, which, coupled by a simultaneous detection of NO₂ will provide the concentration of NO ([NO] = [NO_x] - [NO₂]) (Fuchs et al., 2009):



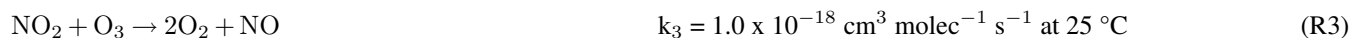
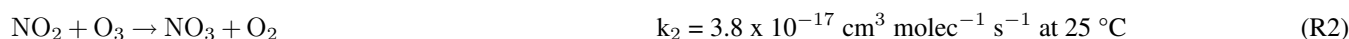
O₃ was produced by electrolysis of water using commercial ozone-micro-cells (INNOVATEC) allowing the generation of O₃ without nitrogen oxides impurities and without the need of an oxygen gas bottle. The cells were mounted in a home-made plastic container offering a 200 cm³ water reservoir. With a miniaturized design (15 x 15 x 15 cm³), ozone production can be controlled upon injection into the inlet line. The sample air flow to be analyzed works as carrier gas for flushing the ozone enriched surface water. This design also prevents the production of unwanted oxidizing agents such as peroxides, as well as sample dilution, causing a signal degradation and requiring precise flow measurements for quantitative analysis. The production of O₃ is controllable by the amount of electrolytic cells used and the supplied current, offering a dynamic range of 0 – 50 ppm of O₃ for a 1 L min⁻¹ total flowrate. A diagram and details of the system can be found in Figure SI-5 and section 3.2 of the supplementary informations. For long-term use of the instrument, the overall water consumption should be considered. Losses due to evaporation were estimated to be between 7 and 30 cm³ per day at 10 and 30 °C respectively for a flow rate of 1 L min⁻¹ while losses due to electrolysis are negligible, with only 0.024 cm³ per day of consumption. The other parameter to consider is the mixing time between the ozone generator and the measurement cell with respect to the O₃ excess. For instance, the calculated production rate of NO₂ from (R1) (i.e. reaction speed or conversion rate of NO) is $v = 4.20 \times 10^{11}$ molecules cm³ s⁻¹ for 5 ppb of NO and 8 ppm of O₃. Under these conditions, a mixing time of 0.29 s is required for completing the conversion. With an air flow of 1 L min⁻¹, a 40-cm long 4-mm internal diameter tube is therefore required between the ozone generator and the measurement cell. The performance of the ozone generation system was tested on the IBBCEAS instrument with a nitrogen oxide standard gas bottle containing ~ 180 ppb of NO in air (Air Liquide). Kinetic simulations using Tenua software were made in order to establish the O₃ excess concentrations needed to achieve the complete conversion of NO to



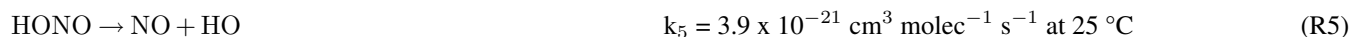
NO₂, which, along with its detection, was tested with the IBBCEAS instrument by varying the excess concentration of O₃ until complete conversion of NO was achieved at different flows (i.e. different reaction times before reaching the measurement cell). The experimental results were in good agreement with the simulations as reported in Figure SI-6. In addition, the instrument was found to have a linear response regarding the detection of the produced O₃. The detection limit for the NO_x measurement was found to be similar to the one of NO₂ (12 ppt (1σ) in 22 min of integration time) while for NO, retrieved as the difference between the NO_x and the NO₂ concentrations, the detection limit estimated from the error propagation corresponds to 21 ppt.

5 Possible chemical and spectral interferences

Further possible interferences on NO₂ detection in the presence of high levels of O₃ were also studied, since a large excess of O₃ could trigger the following reactions with rate constants that are few orders of magnitude lower than k₁ (from the NIST Kinetics Database):



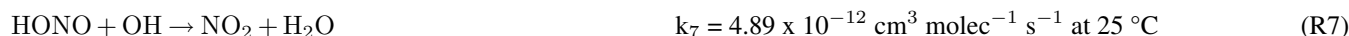
To study those possible interferences, 100 ppb of NO₂ produced by a permeation tube were pumped through the ozonizer and the spectrometer at a flow rate of 1 L min⁻¹ while varying the concentration of O₃ from 0 to 10 ppm. NO₂ concentration was stable at low ozone concentrations, while a drop of 14 % was observed at high levels of O₃ (≥ 8 ppm). Kinetics simulations showed that the NO₂ consumption in favor of the NO₃ production (NO₂ + O₃ → NO₃ + O₂) was kinetically possible under those conditions. The consumption of NO₂ is strongly dependent on the reaction time and the concentration of O₃. The later should be selected according to the reaction time imposed by the volume of the inlet line and the flow rate, therefore making this interference negligible. Other chemicals reactions could led to an overestimation of NO₂ mixing ratios:



Couach et al. estimated the background levels of HONO and HO₂NO₂ in Grenoble to be 4 and 2 ppq (or 10⁻¹⁵ mol mol⁻¹), respectively (Couach et al., 2002). With such low concentrations and kinetic constant rates, interferences due to reactions (R5) and (R6) can be neglected in an urban environment. However, in remote areas such as the East Antarctic Plateau, HO₂NO₂ levels were estimated by indirect measurements to be around 25 ppt (Legrand et al., 2014). Because the lifetime of HO₂NO₂ decreases with temperature (τ_{HO₂NO₂} = 8.6 h at -30°C and 645 mbar), its measurement using an instrument stabilized at higher temperature would lead to an overestimation of the NO₂ due to the thermal degradation of the HO₂NO₂. However, this interference can be minimized by working at low temperatures : at 10 °C and 1 L min⁻¹ flow in our IBBCEAS instrument, the NO₂ signal would be overestimated by only 1 ppt, which is below the detection limit of the sensor. The instruments were



therefore designed for working at low temperature (up to few degrees Celsius). Last reaction, (R7), may also lead to possible
310 interferences on the NO₂ detection:



In urban environments and remote regions, one can observed up to 4×10^6 OH radicals cm^{-3} (Heard, 2004; Mauldin et al., 2001). With background levels of HONO such as 4 ppq in the city of Grenoble and around 30 ppt in Dôme C, Antarctica (Legrand et al., 2014), very low mixing ratios of NO₂ (< few ppq) would be produced by (R7) in less than 8 s (residence time
315 of the molecules in the instrument at 1 L min^{-1}). Therefore, contribution from this interference can be neglected. Previous works also highlighted possible artifacts through the heterogenous reaction of NO₂ and H₂O occurring in thin films on surfaces: the approximate rate production of HONO plus NO calculated in their study was reported to be between 4×10^{-2} and 8×10^{-2} ppb min^{-1} per ppm of NO₂ (Finlayson-Pitts et al., 2003). Assuming linearity between production rates and concentrations, this would represent a range of 8 to 16 ppq for 200 ppt of NO₂ in remote area such as the East Antarctic Plateau. The losses
320 that may occur on the thin films on surfaces through the heterogeneous reaction of NO₂ and H₂O are therefore negligible. Finally, detection of NO₂, CHOCHO and IO may be affected by spectral interferences. For instance, water vapour also shows an absorption signature at this wavelength region which was included in the fit routine. Its spectral fit is important particularly for the measurement of NO_x, where the inlet sampling line gets saturated in water vapor while passing through the water reservoir of the ozone generator. In addition, artifacts on the signal and the spectral fit were studied by varying the O₃, NO₂
325 or NO mixing ratios in cavity. Small imperfections of the fit could lead to large effects on the NO₂ retrieved mixing ratio, particularly at sub-ppb concentrations and in presence of large amounts of ozone. However, no appreciable effects of possible artifacts were observed while O₃ concentrations up to 8 ppm were used. These performance studies and the simplicity of the ozone generator, compact and fully controllable, make it suitable for field applications.

6 Conclusions

330 A compact, robust, affordable and highly sensitive IBBCEAS instrument for direct detection of NO₂, IO, CHOCHO and O₃ and indirect detection of NO is reported in this work. The instrument relies on the injection of incoherent radiation from a compact, high power and low cost LED source, into a high-finesse optical cavity. The instrument provides a minimum detectable absorption of $1.8 \times 10^{-10} \text{ cm}^{-1}$ corresponding to a figure of merit (Noise Equivalent Absorption Sensitivity, NEAS) of $7.5 \times 10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ per spectral element. Thanks to the broadband feature, multi-species detection can be performed
335 with detection limits of 9 (NO₂), 0.3 (IO), 8 (CHOCHO) ppt and 40 ppb (O₃), 1σ , within 22 minutes of measurements (which account for the reference and absorption spectra acquisition). Detection limits for the indirect measurement of NO_x and NO are 12 and 21 ppt (1σ), respectively. The instrument has been designed to fit in a 19", 3U rack-mount case, weights 15 kg and has a total electrical power consumption < 300 W. The detection limits could be further improved by replacing the ULS2048L Avantes spectrometer, which offers at this working wavelength a signal to noise ratio on a single acquisition of 110 and a
340 sensitivity of $172,000 \text{ counts } \mu\text{W}^{-1} \text{ ms}^{-1}$, with a spectrometer with an integrated cooled CCD. The cooling would allow to



gain up to a factor of ten on the signal to noise ratio, which would directly apply to the detection limits. A better sensitivity of the CCD would also allow the use of higher reflectivity mirrors as done by Min et al. (Min et al., 2016) providing an effective optical path length of 18 km (with similar cavity length), ~ 3 times higher than the one obtained in this work. Its dynamic ranges, detection limits and multi-species detection character make this instrument well suitable for measurements in different environments, from highly polluted to very remote areas such as polar regions. The instruments can be used in the future to address different scientific questions, related to the oxidative capacity at particular regions (i.e. inland and coastal polar atmospheres), where variability of NO_x and IO would provide key information for understanding the mechanisms taking place in such remote areas. The detection of the α -dicarbonyl CHOCHO may have applications at the marine boundary layer, where its source remains unknown and its contribution to secondary aerosol particle formation may be relevant (Ervens et al., 2011; Volkamer et al., 2007; Fu et al., 2008).

Data availability. Available on request

Author contributions. The IBBCEAS instruments were designed and developed by CB under the supervision of RG. AB developed and validated the ozone generation. The instruments were optimized and validated by CB and AB who also did the instrumental intercomparison and the measurements for the long-term stability. RG was the principal supervisor of the project. JS and AD contributed with their knowledges in atmospheric sciences and they closely followed the project with regular meetings. JS and RG are the supervisors of AB PhD thesis under which the instruments are deployed. NC provided technical and engineering inputs particularly at the beginning of the project. The manuscript was written by AB, CB and RG, with all authors contributions.

Competing interests. no competing interests are present

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References

- Atkinson, D. B.: Solving chemical problems of environmental importance using cavity ring-down spectroscopy, *The Analyst*, 128, 117–125, <https://doi.org/10.1039/b206699h>, <http://xlink.rsc.org/?DOI=b206699h>, 2003.
- Atkinson, R.: Atmospheric chemistry of VOCs and NOV, *Atmospheric Environment*, p. 39, 2000.
- Brown, S. S., Stark, H., Ciciora, S. J., McLaughlin, R. J., and Ravishankara, A. R.: Simultaneous in situ detection of atmospheric NO₃ and N₂O₅ via cavity ring-down spectroscopy, *Review of Scientific Instruments*, 73, 3291–3301, <https://doi.org/10.1063/1.1499214>, <http://aip.scitation.org/doi/10.1063/1.1499214>, 2002.
- 375 Chan, K. L., Pöhler, D., Kuhlmann, G., Hartl, A., Platt, U., and Wenig, M. O.: NO₂ measurements in Hong Kong using LED based long path differential optical absorption spectroscopy, *Atmospheric Measurement Techniques*, 5, 901–912, <https://doi.org/10.5194/amt-5-901-2012>, <https://www.atmos-meas-tech.net/5/901/2012/>, 2012.
- Couach, O., BALIN, J., Jimenez, R., Rjstorj, P., Simeonov, V., QUAGLIA, P., and Clappier, A.: Study of a photochemical episode over the Grenoble area using a mesoscale model and intensive measurements, p. 19, 2002.
- 380 Dooly, G., Fitzpatrick, C., and Lewis, E.: Deep UV based DOAS system for the monitoring of nitric oxide using ratiometric separation techniques, *Sensors and Actuators B: Chemical*, 134, 317–323, <https://doi.org/10.1016/j.snb.2008.05.011>, <https://linkinghub.elsevier.com/retrieve/pii/S0925400508003316>, 2008.
- Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmospheric Chemistry and Physics*, 11, 11 069–11 102, <https://doi.org/10.5194/acp-11-11069-2011>, <https://www.atmos-chem-phys.net/11/11069/2011/>, 2011.
- 385 Fiedler, S. E., Hese, A., and Ruth, A. A.: Incoherent broad-band cavity-enhanced absorption spectroscopy, *Chemical Physics Letters*, 371, 284–294, [https://doi.org/10.1016/S0009-2614\(03\)00263-X](https://doi.org/10.1016/S0009-2614(03)00263-X), <https://linkinghub.elsevier.com/retrieve/pii/S000926140300263X>, 2003.
- Finlayson-Pitts, B. J. and Pitts, J. N.: CHAPTER 4 - Photochemistry of important atmospheric species, in: *Chemistry of the Upper and Lower Atmosphere*, edited by Finlayson-Pitts, B. J. and Pitts, J. N., pp. 86 – 129, Academic Press, San Diego, <https://doi.org/10.1016/B978-012257060-5/50006-X>, <http://www.sciencedirect.com/science/article/pii/B978012257060550006X>, 2000.
- 390 Finlayson-Pitts, B. J., Wingen, L. M., Sumner, A. L., Syomin, D., and Ramazan, K. A.: The heterogeneous hydrolysis of NO₂ in laboratory systems and in outdoor and indoor atmospheres: an integrated mechanism, *Physical Chemistry Chemical Physics*, 5, 223–242, <https://doi.org/10.1039/b208564j>, <http://xlink.rsc.org/?DOI=b208564j>, 2003.
- Frey, M. M., Brough, N., France, J. L., Anderson, P. S., Traulle, O., King, M. D., Jones, A. E., Wolff, E. W., and Savarino, J.: The diurnal variability of atmospheric nitrogen oxides (NO and NO₂) above the Antarctic Plateau driven by atmospheric stability and snow emissions, *Atmospheric Chemistry and Physics*, 13, 3045–3062, <https://doi.org/10.5194/acp-13-3045-2013>, <https://www.atmos-chem-phys.net/13/3045/2013/>, 2013.
- 395 Frey, M. M., Roscoe, H. K., Kukui, A., Savarino, J., France, J. L., King, M. D., Legrand, M., and Preunkert, S.: Atmospheric nitrogen oxides (NO and NO₂) at Dome C, East Antarctica, during the OPALE campaign, *Atmospheric Chemistry and Physics*, 15, 7859–7875, <https://doi.org/10.5194/acp-15-7859-2015>, <https://www.atmos-chem-phys.net/15/7859/2015/>, 2015.
- 400 Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, *Journal of Geophysical Research*, 113, D15 303, <https://doi.org/10.1029/2007JD009505>, <http://doi.wiley.com/10.1029/2007JD009505>, 2008.



- Fuchs, H., Dubé, W. P., Lerner, B. M., Wagner, N. L., Williams, E. J., and Brown, S. S.: A sensitive and versatile detector for atmospheric NO₂ and NO_x based on blue diode laser Cavity Ring-Down Spectroscopy, *Environmental Science & Technology*, 43, 7831–7836, <https://doi.org/10.1021/es902067h>, <https://pubs.acs.org/doi/10.1021/es902067h>, 2009.
- Fuchs, H., Ball, S. M., Bohn, B., Brauers, T., Cohen, R. C., Heitmann, U., Jones, R. L., Kleffmann, J., Mentel, T. F., Kiendler-Scharr, A., Schlosser, E., Shillings, A. J. L., Tillmann, R., Varma, R. M., Venables, D. S., Tapia, G. V., Wahner, A., Wegener, R., Wooldridge, P. J., and Brown, S. S.: Intercomparison of measurements of NO₂ concentrations in the atmosphere simulation chamber SAPHIR during the NO₃Comp campaign, *Atmos. Meas. Tech.*, p. 17, 2010.
- Gherman, T., Venables, D. S., Vaughan, S., Orphal, J., and Ruth, A. A.: Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy in the near-Ultraviolet: application to HONO and NO₂, *Environmental Science & Technology*, 42, 890–895, <https://doi.org/10.1021/es0716913>, <https://pubs.acs.org/doi/10.1021/es0716913>, 2008.
- Grilli, R., Méjean, G., Kassi, S., Ventrillard, I., Abd-Alrahman, C., Fasci, E., and Romanini, D.: Trace measurement of BrO at the ppt level by a transportable mode-locked frequency-doubled cavity-enhanced spectrometer, *Applied Physics B*, 107, 205–212, <https://doi.org/10.1007/s00340-011-4812-9>, <http://link.springer.com/10.1007/s00340-011-4812-9>, 2012.
- Grosjean, D. and Harrison, J.: Response of chemiluminescence NO_x analyzers and ultraviolet ozone analyzers to organic air pollutants, *Environmental Science & Technology*, 19, 862–865, <https://doi.org/10.1021/es00139a016>, <https://pubs.acs.org/doi/abs/10.1021/es00139a016>, 1985.
- Heard, D. E.: High levels of the hydroxyl radical in the winter urban troposphere, *Geophysical Research Letters*, 31, L18 112, <https://doi.org/10.1029/2004GL020544>, <http://doi.wiley.com/10.1029/2004GL020544>, 2004.
- Jaworski, N. A., Howarth, R. W., and Hetling, L. J.: Atmospheric deposition of nitrogen oxides onto the landscape contributes to coastal eutrophication in the northeast united states, *Environmental Science & Technology*, 31, 1995–2004, <https://doi.org/10.1021/es960803f>, <https://pubs.acs.org/doi/10.1021/es960803f>, 1997.
- Jordan, N., Ye, C. Z., Ghosh, S., Washenfelder, R. A., Brown, S. S., and Osthoff, H. D.: A broadband cavity-enhanced spectrometer for atmospheric trace gas measurements and Rayleigh scattering cross sections in the cyan region (470–540nm), *Atmospheric Measurement Techniques*, 12, 1277–1293, <https://doi.org/10.5194/amt-12-1277-2019>, <https://www.atmos-meas-tech.net/12/1277/2019/>, 2019.
- Kovalev, V. A. and Eichinger, W. E.: *Elastic Lidar: theory, practice, and analysis methods*, John Wiley & Sons, Inc., Hoboken, NJ, USA, <https://doi.org/10.1002/0471643173>, <http://doi.wiley.com/10.1002/0471643173>, 2004.
- Langridge, J. M., Ball, S. M., and Jones, R. L.: A compact broadband cavity enhanced absorption spectrometer for detection of atmospheric NO₂ using light emitting diodes, *The Analyst*, 131, 916, <https://doi.org/10.1039/b605636a>, <http://xlink.rsc.org/?DOI=b605636a>, 2006.
- Lee, J., Kim, K.-H., Kim, Y. J., and Lee, J.: Application of a long-path differential optical absorption spectrometer (LP-DOAS) on the measurements of NO₂, SO₂, O₃, and HNO₂ in Gwangju, Korea, *Journal of Environmental Management*, 86, 750–759, <https://doi.org/10.1016/j.jenvman.2006.12.044>, <https://linkinghub.elsevier.com/retrieve/pii/S0301479707000102>, 2008.
- Lee, J. S., Kim, Y. J., Kuk, B., Geyer, A., and Platt, U.: Simultaneous measurements of atmospheric pollutants and visibility with a Long-Path DOAS system in urban areas, *Environmental Monitoring and Assessment*, 104, 281–293, <https://doi.org/10.1007/s10661-005-1616-6>, <http://link.springer.com/10.1007/s10661-005-1616-6>, 2005.
- Legrand, M., Preunkert, S., Frey, M., Bartels-Rausch, T., Kukui, A., King, M. D., Savarino, J., Kerbrat, M., and Jourdain, B.: Large mixing ratios of atmospheric nitrous acid (HONO) at Concordia (East Antarctic Plateau) in summer: a strong source from surface snow?, *Atmospheric Chemistry and Physics*, 14, 9963–9976, <https://doi.org/10.5194/acp-14-9963-2014>, <https://www.atmos-chem-phys.net/14/9963/2014/>, 2014.



- Leser, H., Hönninger, G., and Platt, U.: MAX-DOAS measurements of BrO and NO₂ in the marine boundary layer, *Geophysical Research Letters*, 30, n/a–n/a, <https://doi.org/10.1029/2002GL015811>, <http://doi.wiley.com/10.1029/2002GL015811>, 2003.
- Liang, S., Qin, M., Xie, P., Duan, J., Fang, W., He, Y., Xu, J., Tang, K., Meng, F., Ye, K., and Liu, W.: Development of an incoherent
445 broadband cavity-enhanced absorption spectrometer for measurements of ambient glyoxal and NO₂ in a polluted urban environment, p. 16.
- Liu, J., Li, X., Yang, Y., Wang, H., Wu, Y., Lu, X., Chen, M., Hu, J., Fan, X., Zeng, L., and Zhang, Y.: An IBBCEAS system for atmospheric measurements of glyoxal and methylglyoxal in the presence of high NO₂ concentrations, *Atmospheric Measurement Techniques*, 12, 4439–4453, <https://doi.org/10.5194/amt-12-4439-2019>, <https://www.atmos-meas-tech.net/12/4439/2019/>, 2019.
- 450 Maeda, Y., Aoki, K., and Munemori, M.: Chemiluminescence method for the determination of nitrogen dioxide, *Analytical Chemistry*, 52, 307–311, <https://doi.org/10.1021/ac50052a022>, <https://pubs.acs.org/doi/abs/10.1021/ac50052a022>, 1980.
- Mauldin, R. L., Eisele, F. L., Tanner, D. J., Kosciuch, E., Shetter, R., Lefer, B., Hall, S. R., Nowak, J. B., Buhr, M., Chen, G., Wang, P., and Davis, D.: Measurements of OH, H₂SO₄ and MSA at the South Pole during ISCAT, *Geophysical Research Letters*, 28, 3629–3632, <https://doi.org/10.1029/2000GL012711>, <http://doi.wiley.com/10.1029/2000GL012711>, 2001.
- 455 Min, K.-E., Washenfelder, R. A., Dubé, W. P., Langford, A. O., Edwards, P. M., Zarzana, K. J., Stutz, J., Lu, K., Rohrer, F., Zhang, Y., and Brown, S. S.: A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water vapor, *Atmospheric Measurement Techniques*, 9, 423–440, <https://doi.org/10.5194/amt-9-423-2016>, <https://www.atmos-meas-tech.net/9/423/2016/>, 2016.
- Monks, P., Granier, C., Fuzzi, S., Stohl, A., Williams, M., Akimoto, H., Amann, M., Baklanov, A., Baltensperger, U., Bey, I., Blake, N.,
460 Blake, R., Carslaw, K., Cooper, O., Dentener, F., Fowler, D., Fragkou, E., Frost, G., Generoso, S., Ginoux, P., Grewe, V., Guenther, A., Hansson, H., Henne, S., Hjorth, J., Hofzumahaus, A., Huntrieser, H., Isaksen, I., Jenkin, M., Kaiser, J., Kanakidou, M., Klimont, Z., Kulmala, M., Laj, P., Lawrence, M., Lee, J., Lioussé, C., Maione, M., McFiggans, G., Metzger, A., Mieville, A., Moussiopoulos, N., Orlando, J., O'Dowd, C., Palmer, P., Parrish, D., Petzold, A., Platt, U., Pöschl, U., Prévôt, A., Reeves, C., Reimann, S., Rudich, Y., Sellegri, K., Steinbrecher, R., Simpson, D., ten Brink, H., Theloke, J., van der Werf, G., Vautard, R., Vestreng, V., Vlachokostas, C., and von Glasow, R.: Atmospheric composition change – global and regional air quality, *Atmospheric Environment*, 43, 5268–5350, <https://doi.org/10.1016/j.atmosenv.2009.08.021>, <https://linkinghub.elsevier.com/retrieve/pii/S1352231009007109>, 2009.
- 465 Monks, P. S.: Gas-phase radical chemistry in the troposphere, *Chemical Society Reviews*, 34, 376, <https://doi.org/10.1039/b307982c>, <http://xlink.rsc.org/?DOI=b307982c>, 2005.
- Pikelnaya, O., Hurlock, S. C., Trick, S., and Stutz, J.: Intercomparison of multi-axis and long-path differential optical absorption spectroscopy
470 measurements in the marine boundary layer, *Journal of Geophysical Research: Atmospheres*, 112, <https://doi.org/10.1029/2006JD007727>, <http://doi.wiley.com/10.1029/2006JD007727>, 2007.
- Platt, U. and Perner, D.: Direct measurements of atmospheric CH₂O, HNO₂, O₃, NO₂, and SO₂ by differential optical absorption in the near UV, *Journal of Geophysical Research: Oceans*, 85, 7453–7458, <https://doi.org/10.1029/JC085iC12p07453>, <http://doi.wiley.com/10.1029/JC085iC12p07453>, 1980.
- 475 Pohler, D., Vogel, L., Friess, U., and Platt, U.: Observation of halogen species in the Amundsen Gulf, Arctic, by active long-path differential optical absorption spectroscopy, *Proceedings of the National Academy of Sciences*, 107, 6582–6587, <https://doi.org/10.1073/pnas.0912231107>, <http://www.pnas.org/cgi/doi/10.1073/pnas.0912231107>, 2010.
- Richard, L., Romanini, D., and Ventrillard, I.: Nitric oxide analysis down to ppt levels by Optical-Feedback Cavity-Enhanced Absorption Spectroscopy, *Sensors*, 18, 1997, <https://doi.org/10.3390/s18071997>, <http://www.mdpi.com/1424-8220/18/7/1997>, 2018.



- 480 Rozanov, V. V. and Rozanov, A. V.: Differential optical absorption spectroscopy (DOAS) and air mass factor concept for a multiply scattering vertically inhomogeneous medium: theoretical consideration, *Atmospheric Measurement Techniques*, 3, 751–780, <https://doi.org/10.5194/amt-3-751-2010>, <http://www.atmos-meas-tech.net/3/751/2010/>, 2010.
- Ruth, A. A., Dixneuf, S., and Raghunandan, R.: Broadband Cavity-Enhanced Absorption Spectroscopy with Incoherent Light, in: *Cavity-Enhanced Spectroscopy and Sensing*, edited by Gagliardi, G. and Loock, H.-P., vol. 179, pp. 485–517, Springer Berlin Heidelberg, Berlin, Heidelberg, https://doi.org/10.1007/978-3-642-40003-2_14, http://link.springer.com/10.1007/978-3-642-40003-2_14, 2014.
- 485 Ryerson, T. B., Williams, E. J., and Fehsenfeld, F. C.: An efficient photolysis system for fast-response NO₂ measurements, *Journal of Geophysical Research: Atmospheres*, 105, 26 447–26 461, <https://doi.org/10.1029/2000JD900389>, <http://doi.wiley.com/10.1029/2000JD900389>, 2000.
- Sinreich, R., Volkamer, R., Filsinger, F., Frieß, U., Kern, C., Platt, U., Sebastian, O., and Wagner, T.: MAX-DOAS detection of glyoxal during ICARTT 2004, *Atmos. Chem. Phys.*, p. 11, 2004.
- 490 Thalman, R. and Volkamer, R.: Inherent calibration of a blue LED-CE-DOAS instrument to measure iodine oxide, glyoxal, methyl glyoxal, nitrogen dioxide, water vapour and aerosol extinction in open cavity mode, *Atmospheric Measurement Techniques*, 3, 1797–1814, <https://doi.org/10.5194/amt-3-1797-2010>, <https://www.atmos-meas-tech.net/3/1797/2010/>, 2010.
- Triki, M., Cermak, P., Méjean, G., and Romanini, D.: Cavity-enhanced absorption spectroscopy with a red LED source for NO_x trace analysis, *Applied Physics B*, 91, 195–201, <https://doi.org/10.1007/s00340-008-2958-x>, <http://link.springer.com/10.1007/s00340-008-2958-x>, 2008.
- 495 Vandaele, A., Hermans, C., Simon, P., Carleer, M., Colin, R., Fally, S., Mérienne, M., Jenouvrier, A., and Coquart, B.: Measurements of the NO₂ absorption cross-section from 42 000 cm⁻¹ to 10 000 cm⁻¹ (238–1000 nm) at 220 K and 294 K, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 59, 171–184, [https://doi.org/10.1016/S0022-4073\(97\)00168-4](https://doi.org/10.1016/S0022-4073(97)00168-4), <https://linkinghub.elsevier.com/retrieve/pii/S0022407397001684>, 1998.
- 500 Venables, D. S., Gherman, T., Orphal, J., Wenger, J. C., and Ruth, A. A.: High sensitivity in situ monitoring of NO₃ in an atmospheric simulation chamber using Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy, *Environmental Science & Technology*, 40, 6758–6763, <https://doi.org/10.1021/es061076j>, <https://pubs.acs.org/doi/10.1021/es061076j>, 2006.
- Ventrillard-Courtilot, I., Sciamma O'Brien, E., Kassi, S., Méjean, G., and Romanini, D.: Incoherent broad-band cavity-enhanced absorption spectroscopy for simultaneous trace measurements of NO₂ and NO₃ with a LED source, *Applied Physics B*, 101, 661–669, <https://doi.org/10.1007/s00340-010-4253-x>, <http://link.springer.com/10.1007/s00340-010-4253-x>, 2010.
- 505 Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., and Tilman, D. G.: Human alteration of the global nitrogen cycle: sources and consequences, *Ecological Applications*, 7, 737–750, [https://doi.org/10.1890/1051-0761\(1997\)007\[0737:HAOTGN\]2.0.CO;2](https://doi.org/10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2), [http://doi.wiley.com/10.1890/1051-0761\(1997\)007\[0737:HAOTGN\]2.0.CO;2](http://doi.wiley.com/10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2), 1997.
- Volkamer, R., San Martini, F., Molina, L. T., Salcedo, D., Jimenez, J. L., and Molina, M. J.: A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol, *Geophysical Research Letters*, 34, L19 807, <https://doi.org/10.1029/2007GL030752>, <http://doi.wiley.com/10.1029/2007GL030752>, 2007.
- 510 Wagner, T., Ibrahim, O., Shaiganfar, R., and Platt, U.: Mobile MAX-DOAS observations of tropospheric trace gases, *Atmos. Meas. Tech.*, p. 12, 2010.
- Washenfelder, R. A., Langford, A. O., Fuchs, H., and Brown, S. S.: Measurement of glyoxal using an incoherent broadband cavity enhanced absorption spectrometer, *Atmos. Chem. Phys.*, p. 15, 2008.



- Werle, P., Mücke, R., and Slemr, F.: The limits of signal averaging in atmospheric trace-gas monitoring by tunable diode-laser absorption spectroscopy (TDLAS), *Applied Physics B Photophysics and Laser Chemistry*, 57, 131–139, <https://doi.org/10.1007/BF00425997>, <http://link.springer.com/10.1007/BF00425997>, 1993.
- Williams, E. J., Baumann, K., Roberts, J. M., Bertman, S. B., Norton, R. B., Fehsenfeld, F. C., Springston, S. R., Nunnermacker, L. J., Newman, L., Olszyna, K., Meagher, J., Hartsell, B., Edgerton, E., Pearson, J. R., and Rodgers, M. O.: Intercomparison of ground-based NO_y measurement techniques, *Journal of Geophysical Research: Atmospheres*, 103, 22 261–22 280, <https://doi.org/10.1029/98JD00074>, <http://doi.wiley.com/10.1029/98JD00074>, 1998.
- Wine, P. and Nicovich, M.: Atmospheric radical chemistry, in: *Encyclopedia of Radicals in Chemistry, Biology and Materials*, edited by Chatgililoglu, C. and Studer, A., p. rad015, John Wiley & Sons, Ltd, Chichester, UK, <https://doi.org/10.1002/9781119953678.rad015>, <http://doi.wiley.com/10.1002/9781119953678.rad015>, 2012.
- Wittrock, F., Oetjen, H., Richter, A., Fietkau, S., Medeke, T., Rozanov, A., and Burrows, J. P.: MAX-DOAS measurements of atmospheric trace gases in Ny-Ålesund - radiative transfer studies and their application, *Atmospheric Chemistry and Physics*, 4, 955–966, <https://doi.org/10.5194/acp-4-955-2004>, <http://www.atmos-chem-phys.net/4/955/2004/>, 2004.