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

Revision Notes

Albane Barbero[1], Camille Blouzon[1], Joël Savarino[1], Nicolas Caillon[1], Aurélien Dommergue[1], and Roberto Grilli[1]

[1]Univ. Grenoble Alpes, CNRS, IRD, Grenoble INP*, IGE, 38000 Grenoble, France *Institute of Engineering Univ. Grenoble Alpes

Correspondence: Roberto Grilli (roberto.grilli@cnrs.fr)

Dear Editors,

We express our gratitude for the time and effort dedicated to the reviewing of our submitted manuscript. We worked diligently to address all the concerns raised by the referees and we thank the reviewers for the pertinent remarks that allowed to improve the manuscript. Below we provide our detailed response to their comments. We hope that the applied revisions are to the satisfaction of the editors.

Kind regards,

Albane Barbero, Camille Blouzon, Joël Savarino, Nicolas Caillon, Aurélien Dommergue, and Roberto Grilli

<u>Manuscript information</u>

https://doi.org/10.5194/amt-2020-104 Preprint.

Title “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”

Authors Albane Barbero, Camille Blouzon, Joël Savarino, Nicolas Caillon, Aurélien Dommergue, and Roberto Grilli

Submitted to Atmospheric Measurement techniques

Reviewer 2:

Comments I (Reviewer 2):

As shown in Table 1 in the manuscript, compared with the reported IBBCEAS whose wavelength centered around 450 nm, the instrument introduced here is inferior in terms of mirror reflectivity, optical path length, and time resolution. If the IBBCEAS introduced here cannot be improved from the aspects of above key parameters, novelty of this work should be detailed and highlighted. In addition, authors need to carefully check the data listed in Table 1, the reflectivity and optical path length of Liu et al.'s IBBCEAS is 0.99993 and 10.3 km, respectively (Liu et al., 2019).

Answer: The table was carefully checked and modified in order to highlight the novelty of this work on key parameters. A short text was added to comment on the differences observed between the recently developed instruments :

"Table 1 shows a comparison between the instrument presented in this work and other recently developed IBBCEAS systems. The detection limits are given in ppt min^{-1} (1σ) with the normalization time that accounts for the acquisition of the reference (without absorption) and sample spectra to allow a better comparison. It should be noticed that all the other developments took advantage from an optical spectrometer with a cooled CCD device to reduce dark noise. A more compact and affordable spectrometer was preferred in this work. The cooling at the CCD would allow to gain up to a factor of ten on the signal to noise ratio, which would directly apply to the achievable detection limits. Furthermore, a CCD with a higher sensitivity would allow to select higher reflective mirror and increase the optical pathlength. Noteworthy, the optimum integration time, corresponding to a minimum of the σ_{AW-SD}, is at 1,300 s (~ 22 min), allowing to achieve low detection limits even without a cooled CCD."

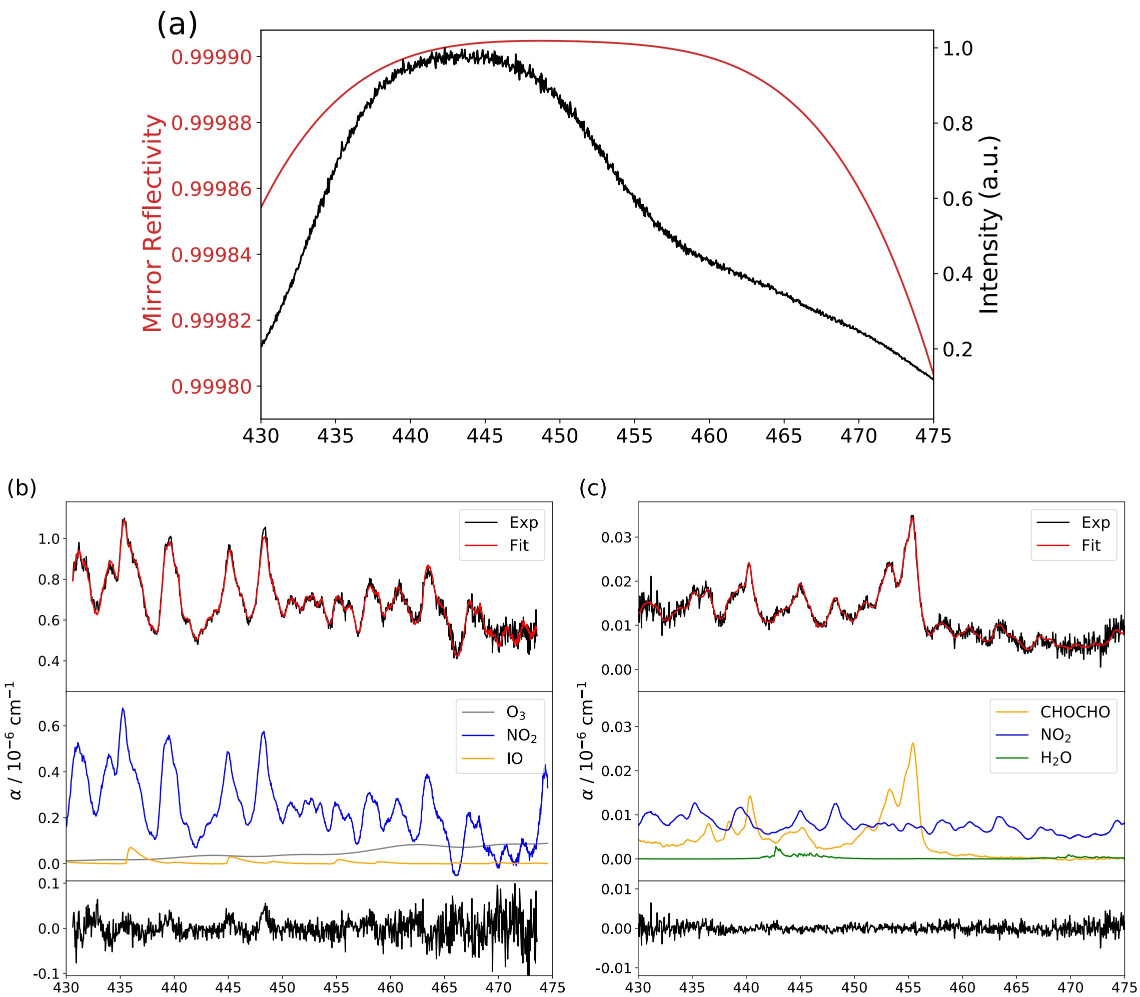
Table 1. Comparisons of the performances with other recently developed IBBCEAS systems

References	Centered wavelengh (nm)	Source FWHM (nm)	NO_2 detection limit (ppt min^{-1})	Sample path lengh (cm)	Mirror reflectivity (%)	Optical lengh (km)	Mirrors purged	CCD cooled (°C)	Minimum σ_{AW-SD} deviation (s)
Min et al. (2016)	455	18	16	48	99.9973	17.8	no	-70	100
Jordan et al. (2019)	505	30	200	102	99.98	5.1	yes	-80	300
Liu et al. (2019)	455	18	33	84	99.993	10.3	yes	-70	100
Liang et al. (2019)	448	15	15	58.9	99.9942	11.7	yes	-10	3,500
This work (2020)	450	19	40	41.7	99.9905	4.4	no	no	1,300

Comments II (Reviewer 2):

The description of measuring CHOCHO in the manuscript is limited, as the Fig. 2(b) only showed simultaneously detection of NO_2, IO, and O_3. It should be better if the authors could present a graph which contains 5 gas absorbers (NO_2, IO, O_3, CHOCHO, and H_2O) simultaneous retrieving. It should be noted that the concentrations of NO_2, O_3 shown in Fig. 2(b) were significantly higher than their concentrations in ambient air, even in polluted area. As the purpose of the manuscript is to present *an instrument for field application, it would be more persuasive for readers if a fitting example with low concentrations of gas absorbers could be provided.*

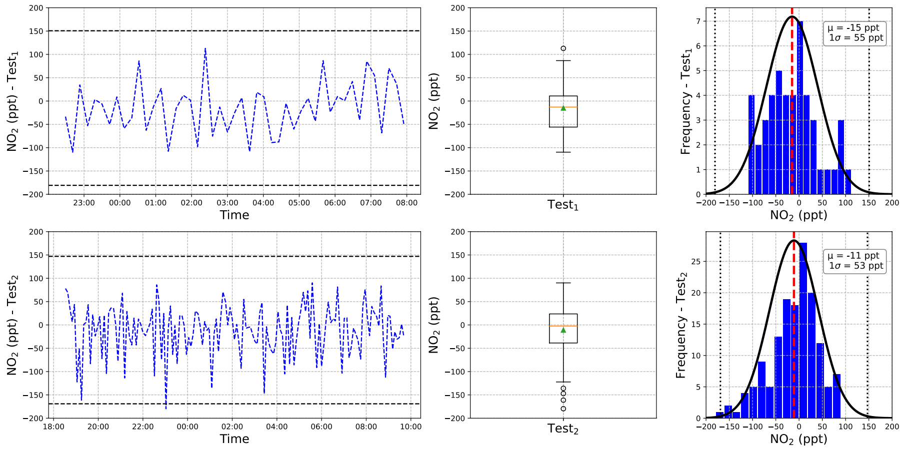
Answer: The spectrum presented in Figure 2 was obtained with synthetic air, explaining the high concentrations. High levels of O_3 were needed to produce IO from the I_2 source used, and high level of NO_2 were used to better visualize the different absorption components and identified correctly the structures of the spectra. Thus, the calibration and the intercomparison following the spectral fit description confirmed the well fitted spectra. Fortunately, the instruments came back from the field early June and we were able to measure the Glyoxal, NO_2 and H_2O at lower concentrations levels. The Figure 2 of the manuscript was therefore modified to include CHOCHO and H_2O spectra.



Comments III (Reviewer 2):

The manuscript does not provide information about uncertainty of the instrumental measurements, as to the limit of detection (LOD), authors seems to confuse the concepts among LOD, sensitivity, and precision, because these three words appear alternately in Sect. 4.3.1. The using of these concepts needs to be clarified and revised in the manuscript.

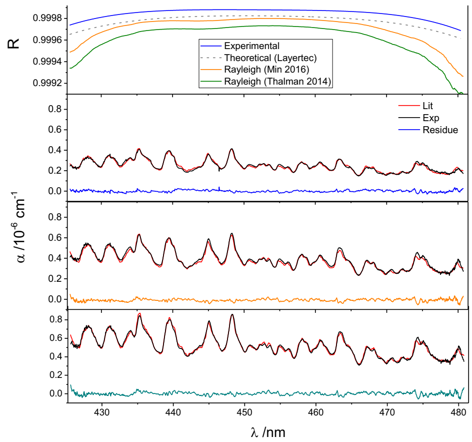
Answer: The manuscript describe a highly sensitive instrument in general (section 4.1) but reports the minimum detectable concentration as detection limit or limit of detection. Figure 7 shows the repeatability of the measurements over two tests while measuring for several hours the same zero-air sample in real conditions, therefore the term « precision » seems correctly used in this part of the manuscript. Nevertheless, Figure 7 was modified to better illustrate the repeatability of the instruments.



Additional comments (Reviewer 2):

1. *Line 56ff: References should not be quoted twice in the same sentence if it is already be written at the beginning. For example, "Venables et al. (2006) were ...... (Venables et al., 2006).":* corrected.
2. *Line 64: "Min et al 2016" → "Min et al. (2016)":* corrected.
3. *Line 65: "very high reflective mirrors[...]":* corrected.
4. *Line 130: Eq. (1) There are probably better ways to format the equations such that the size of the brackets is matched to the size of the arguments within the bracket:* corrected.
5. *Line 150: "Washenfelder et al. (2008) described[...]":* corrected.
6. *Line 152: "(e.g., helium versus air or nitrogen) [...]:* corrected.
7. *Such an approach to calculate mirror reflectivity has been proposed before (Venables et al., 2006) and has been used by previous studies (e.g., Duan et al., 2018). It would be better to reorganized the sentences in another way in the manuscript. In addition, did authors compare the difference between two reflectivity calibration methods based on their own IBBCEAS?*

Answer: We did the Rayleigh experiment using standard He gas (Messer, Helium 5.0, 99.999%) and standard N_2 gas (Air Liquide, AlphaGaz 2, 99.9999 %) cylinders, 5 µm Whatman® filters and taking into account the CCD dark noise. In addition, in between the field expeditions and the return of the instruments, we received a calibrator (Gas Standard Generator FlexStream™, Kin-Tek Analytical, Inc.) able to produce a stable NO_2 source. The sample is produced using a permeation tube of NO_2 (Kin-Tek ELSRT2W) calibrated at an emission rate of 115 ng min^{-1} at 40 °C loaded into the calibrator. This type of calibrator is ideally suited for creating trace concentration mixtures (from ppt to ppm). Despite those efforts, we were not satisfied by the results of this calibration method because of several arguments : one of them being the discrepancies between the Rayleigh cross sections provided by Min et al 2016 (empirical values) against the theoretical cross sections using equations provided by Thalman et al. (2014). The results of the experiment are shown in the Figure below : with Rayleigh curve we obtain 74.6 ppb of NO_2 using Min cross sections, and 98.0 ppb of NO_2 using Thalman cross sections, while the Kin-Tek NO_2 source was set at 49.6 ppb. The retrieved curve for matching NO_2 absorption cross sections is the blue one at the top, which also better match in shape the expected theoretical curve provided by the manufacturer. To confirm that the shape was correct, we compared the convoluted literature absorption cross sections of CHOCHO with the experimental data (which applies our experimental reflectivity curve) and we obtain a good matching, confirming that the shape of the curve is correct (see Fig SI – 3).

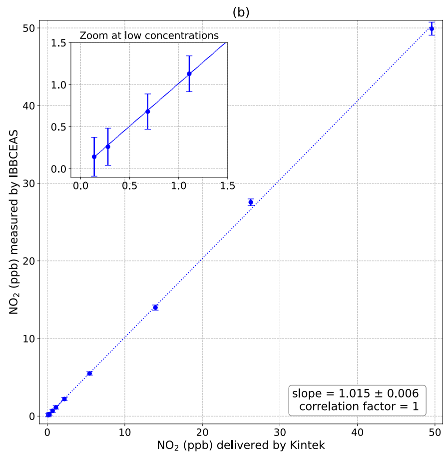


8. *Figure 2 (a): The text-label (i.e., Reflectivity) on the y-axis was covered.*

Answer: The Figure has been modified to add CHOCHO and H_2O spectra as answered to Comment II.

9. *Line 202: In addition to the discrepancies at low NO_2 concentrations, obvious discrepancies measured by two instruments can also be observed at high NO_2 conditions, e.g., 18/10/01 - 09:00 and 19/07/19 – 05:45. Could authors provide an explanation about the phenomenon?*

Answer: We now used a Kintek NO_2 FlexStream^{TM} in order to calibrate our IBBCEAS instrument. The non-linearity observed with the CLD technique was better explained in the manuscript: "In order to perform linearity tests, the previous NO_2 FlexStream^{TM} calibrator was used to produced various concentrations of NO_2 covering a large range of concentrations, from few ppt to few ppb. Figure 4(b) shows the good linearity, from ppt to ppb range, of the IBBCEAS instrument with a slope of 1.015 ± 0.006 and a correlation factor of R^2 = 0.9996, confirming the validity of the calibration approach. The discrepancies observed between the IBBCEAS and the CLD techniques might be explain by positive and negative interferences on the CLD technique. While the system measures NO_2 directly, the CLD technique applies an indirect measurement of NO_x from the oxidation of NO through a catalyzer, then in CLD, the NO_2 mixing ratio is obtained by subtracting the NO signal to the total NO_x signal. Villena et al. (2012), demonstrate that the interferences on a urban atmosphere for the CLD technique implied positive interferences when NO_y species photolysis occurred, leading to an over-estimation of daytime NO_2 levels, while negative interferences were attributed to the VOCs photolysis followed by peroxyradical reactions with NO."

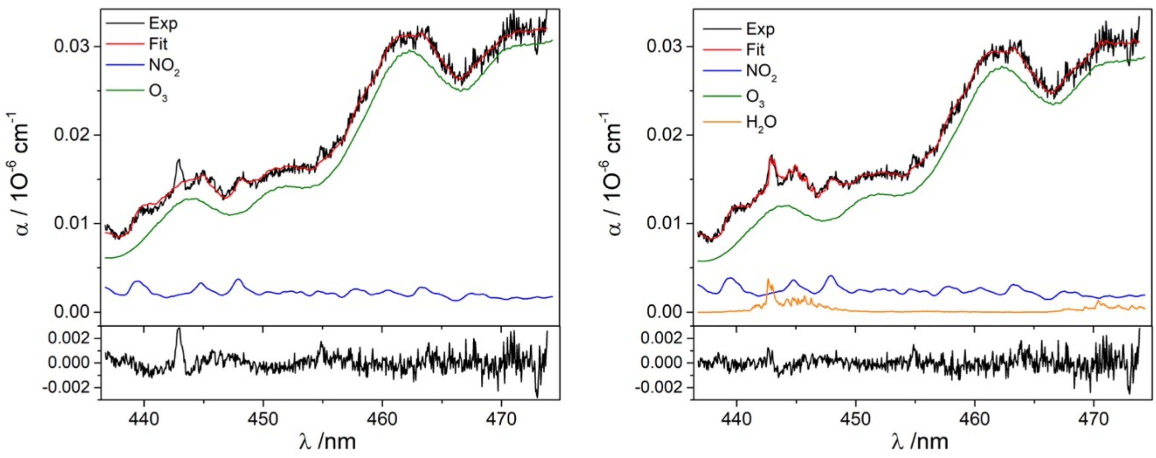


10. *Figure 6 (top):The units of mixing ratio was missing :* corrected.
11. *Figure 7: The left Box-plot is not as useful as drawing a histogram which contains measured NO_2 concentrations when performing empty cavity measurements. Such a histogram can not only be used to show averages, but also be used to estimate LOD from the frequency number of histogram distribution.*

Answer: The Figure 7 has been modified as answered in Comment III to better show the precision or repeatability of the measurements.

12. *Line 247: A short discussion about the comparison shown in Table 1 is better than only presenting a Table without any explanation:* see answer to comment I.
13. *Line 308: "[...] sensor.The instruments[...]" -> "[...] sensor.The instruments[...]:* corrected.
14. *Line 324: As the inlet sampling line gets saturated in water vapor while passing through the ozone generator, did authors quantify the influence on CHOCHO measurements? For example, measure the CHOCHO standards with and without using ozone generator.*

Answer: The influence of water vapor while passing through the ozone generator on CHOCHO measurements was not tested. However, it was tested on the NO_2 measurements. Atmospheric measurements were done with and without fitting H_2O to quantify the fitting interferences on NO_2. The Figure below shows the FIT results without, (left), and with, (right), H_2O being included in the FIT routine. For this particular measurements, the results were giving 262.4 and 301.8 ppt of NO_2 and 4.7 and 4.4 ppm of O_3, respectively without and with the H_2O, leading, for this measurement, to an underestimation of 13 % on the NO_2 mixing ratio with the presence of 0.44 % humidity added by the O_3 production system in the sample line.



Additional remark (from the authors):

All the English mistake or the typo corrections suggested by the Reviewers have been corrected. Other changes coming from the opportunities of new experiments from the comments of the Reviewers were made. All the changes can be found in red in the manuscript and supplementary. Also, the following references where added or corrected:

- Duan, J., Qin, M., Ouyang, B., Fang, W., Li, X., Lu, K., Tang, K., Liang, S., Meng, F., Hu, Z., Xie, P., Liu, W., and Häsler, R.: Development of an incoherent broadband cavity-enhanced absorption spectrometer for in situ measurements of HONO and NO_2 Atmos Meas Tech, 11, 4531-4543, 2018.
- 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 NO_2 concentrations, Atmos Meas Tech, 12, 4439-4453, 2019.
- Venables, D. S., Gherman, T., Orphal, J., Wenger, J. C., and Ruth, A. A.: High Sensitivity in Situ Monitoring of NO_3 in an Atmospheric Simulation Chamber Using Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy, Environ Sci Technol, 40, 6758-6763, 2006.
- Villena, G., Bejan, I., Kurtenbach, R., Wiesen, P., and Kleffmann, J.: Interferences of commercial NO_2 instruments in the urban atmosphere and in a smog chamber, Atmospheric Measurement Techniques, 5, 149–159, https://doi.org/10.5194/amt-5-149-2012, https: //www.atmos-meas-tech.net/5/149/2012/, 2012.
- Volkamer, R., Spietz, P., Burrows, J., and Platt, U.: High-resolution absorption cross-section of glyoxal in the UV–vis and IR spectral ranges, Journal of Photochemistry and Photobiology A: Chemistry, 172, 35–46, https://doi.org/10.1016/j.jphotochem.2004.11.011, https: //linkinghub.elsevier.com/retrieve/pii/S1010603004005143, 2005.
- Wachsstock, D.: Tenua: the kinetics simulator for Java; http://bililite.com/tenua., http://bililite.com/tenua, 2007.