

Response to Referees

Manuscript Number: amt-2016-319

Manuscript Title: Development of a portable Cavity Enhanced Absorption Spectrometer for the measurement of ambient N_2O_5 : experimental setup, lab characterizations, and field applications under polluted urban environment

The discussion below includes the complete text from the referees, along with our responses to the specific comments and the corresponding changes made to the revised manuscript.

The detailed answers to the individual referee's comments in [blue](#).

All of the line numbers refer to the original manuscript.

Response to Referee #2 Comments:

We would like to thank the referee for his/her detailed comments and suggestions which helped us a lot to improve the quality of the paper. Our revised manuscript has been further edited by professional language services.

1. This manuscript describes the construction, testing, and initial deployment of a cavity enhanced spectrometer for the detection of N_2O_5 . The instrument is quite similar to prior $\text{NO}_3/\text{N}_2\text{O}_5$ instruments in the literature, although this instrument might be more portable or operate at reduced power. The manuscript should do a better job differentiating what was done by the authors from prior work. The mechanism of alignment may be novel, but that is not fully clear based upon the short description.

The writing of the manuscript is a major problem, and the authors need to improve that aspect of the manuscript to make it potentially acceptable for Atmospheric Measurement Techniques (AMT). The authors have clearly built a functional N_2O_5 instrument, but the manuscript needs improvement and better clarity of how this work is novel to be acceptable for AMT.

Answer:

We agree with the referee that we should do a better job to differentiate what we have done compared to that from the prior work. To our knowledge, there were only two other field deployable CEAS instruments which had been reported before. One is a LED based CEAS system from the Cambridge University group (Langridge et al., 2008; Benton et al., 2010; Kennedy et al., 2011) and the other is a laser based CEAS system which is an optional mode of a CRDS system from the Max Planck Institute of Chemistry group (Schuster et al., 2009; Crowley et al., 2010). Our system is also a LED based CEAS system. To make it field deployable, the instrument is featured with a novel non-adjustable mechanically aligned mirror mounts (the concentricity error $< 0.01^\circ$), see added Fig. 1b and Fig. 1c. The cavity is coupled automatically after we installed the HR mirrors into the mirror mounts and it reduces the background drift (e.g. thermal drift of the mechanics) significantly. The instrument is also featured with the addition of a chemical titration module which set up a dynamic reference spectrum for enhancing the precision of the spectrum fitting (e.g. the effects of the non-linear absorption lines of the water vapor is removed, the drift of the light power is eliminated). The chemical titration method has been widely used in the CRDS method for the determination of its zero point, but this is first time to be used in the CEAS type of instrument.

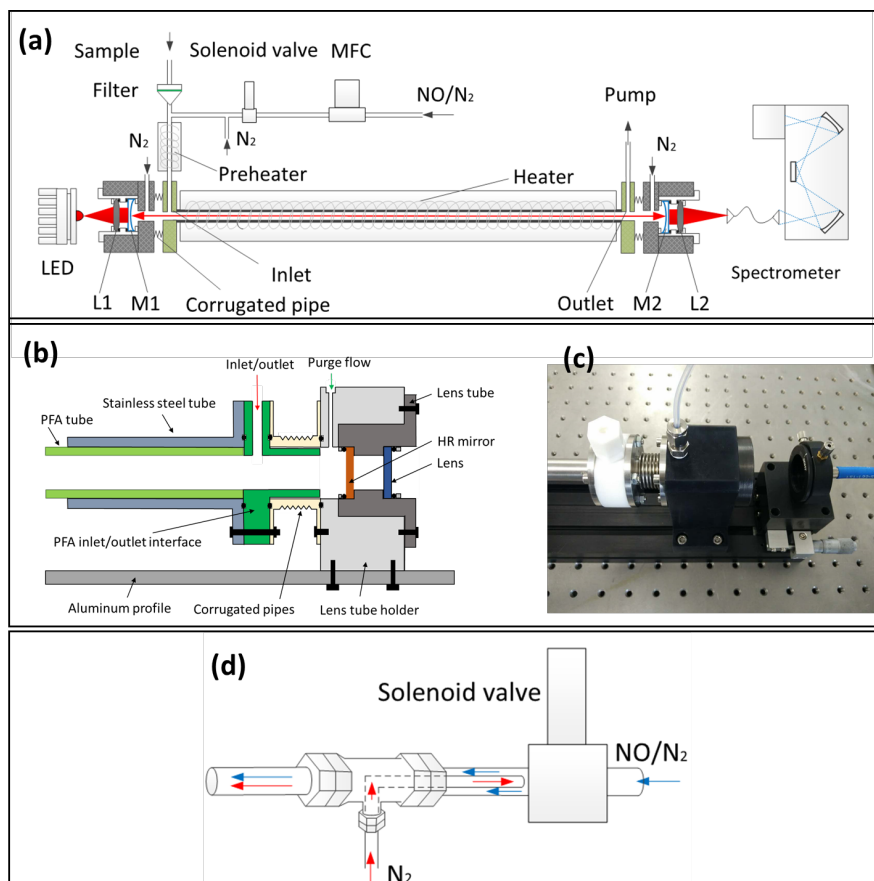


Figure 1. A schematic plot of the newly developed IBBCEAS instrument for the detection of NO_{3X}. **(a)** overview of the optical layout (LEDs, collimating optics, high-finesse cavity, and spectrometer) and the flow system (aerosol filter, inlet, NO titration module, preheating tube, and detection cell). **(b)** the schematic layout of the mirror mounts, which enables a mechanical alignment of the high reflectivity (HR) mirrors. **(c)** a photograph of the mirror mounts. **(d)** the schematic layout of the NO titration module; the red arrow denotes the N₂ gas flow, and the blue arrow denotes the NO gas flow.

- General issues: Throughout the manuscript there are small missing details that should be included. Often these are things like the manufacturer / part number for components in the instrument (e.g. the filter, coating for cavity tube, "corrugated pipe", etc.) Please expand on these details so that one could have full details.

Answer:

We agree with the comments and added the information of manufacturer / part number accordingly when needed throughout the manuscript. With respect to the filter, coating for cavity tube, and "corrugated pipe", we revised as follows in the revised manuscript:

Sect. 2.1: "The optical cavity is enclosed by a sample gas detection cell with a sample inlet, outlet, and two welded corrugated pipes connected at two ends."

Sect. 2.2: "A Teflon polytetrafluoroethylene (PTFE) filter (25 μm thickness, 4.6 cm diameter, 2.5 μm pore size, Typris, China) is used in the front of the sampling module to remove ambient aerosols..."

Sect. 2.2: "In Fig. 1b, the central part of the detection cell is constructed using a 35.6 cm long

PFA tube (marked in light green) (Entegris, I.D. =10 mm), enclosed by a stainless tube (marked in grey).”

3. The discussion of d_{eff} in section 3.2 is confusing. This seems to indicate that the effective length of the cavity differs between NO_2 and NO_3 , which would be strange. Potentially there is some change in the purge between the configuration where NO_2 and NO_3 were measured?

Answer:

The effective length of the cavity (d_{eff}) describes the length occupied by the sample gas flow in the cavity which is the same for both NO_2 and NO_3 . In our measurement, the d_{eff} is determined to be 45 cm, 90% of the length of the cavity. Moreover, the distance between inlet and outlet (d_{sample}) is 39 cm (78% of the length of the cavity). The difference between the d_{eff} and d_{sample} showed that there was diffusion of sample gases into the purge volumes. Since the possibility of this diffusion is slow relative to the rate of the NO_3 wall losses, the determination of the d_{eff} for NO_3 is associated with an additional uncertainty of 12%.

4. It is preferred to use "mixing ratio" (rather than concentration) as the term for the ppt abundance of N_2O_5 (or any other chemical). Additionally, use of pmol mol^{-1} is preferred as more clear than ppt. For gases in the ppb range, one would use nmol mol^{-1} .

Answer:

We used “mixing ratio” in combination with the term of “pptv” as suggested.

5. The manuscript describes a good laboratory test for the inlet filter transmission, but does not describe how often the inlet filter is changed in operation, or if that change is based upon mass loading of the filter or simply a time criterion.

Please explain operational filter change procedures. Some discussion of the decay of filter transmission, how that is quantified, and how the filter transmission decay affects the overall instrumental accuracy should be included.

Answer:

According to previous works, we changed the filter with a regular time interval (once per hour) to reduce the uncertainty from the decay of the filter transmission during pollution episodes. For clean conditions, the filter exchange frequency was reduced to be once per two hours when we observed much slower aerosol accumulation.

During the campaign, we also stored the used filter and determined the NO_3 and N_2O_5 transmission efficiency afterwards in the lab. The transmission efficiencies of NO_3 and N_2O_5 are determined to be $72 \pm 3\%$ and $93 \pm 3\%$ due to the filter aging.

In the revised manuscript, we added the description about the filter aging and the effect to the filter transmission as follows in the Sec.4.2.1.

“The filter transmission efficiency of NO_3 and N_2O_5 is determined through the differentiation of an inlet without a filter, with a clean filter (25 μm thickness, 4.6 cm diameter, 2.5 μm pore size, Typris, China), and with used filters saved during typical pollution episodes during field measurements. According to previous field measurements of NO_3 and N_2O_5 (e.g. Brown et al., 2001; Schuster et al., 2009), frequent filter change is suggested, and the frequency is proposed to be 0.5–3 h depending on the aerosol loadings to reduce the impact of the filter aging caused by aerosol accumulation. For this reason, we changed the filter with a regular time interval

(once every hour) during pollution episodes. For clean conditions, the filter exchange frequency was reduced to be once every two hours.

For the determination of the NO_3 filter transmission efficiency, an additional preheating tube is inserted in front of the detection system to convert all the generated NO_{3X} delivered by the calibration source to NO_3 . The determined clean filter transmission efficiency is 75 % for NO_3 and is slightly lower than the previous results of NO_3 transmission efficiency on Teflon filters (Aldener et al., 2006; Schuster et al., 2009). The filter transmission efficiency of NO_3 on used filters is determined to be 5 % less than that on the clean filter. For the field calculation of the NO_3 concentrations, the filter transmission efficiency is then estimated to be 72 ± 3 %. For the determination of the N_2O_5 filter transmission efficiency, the mixing ratio of NO_2 and O_3 is modulated to achieve a high ratio of $\text{N}_2\text{O}_5/\text{NO}_3$ (>100) before being fed into the instrument. The transmission efficiency of the N_2O_5 on the clean filter is determined to be 96 %, which is consistent with the previous studies on the filter loss of N_2O_5 (Fuchs et al., 2008; Aldener et al., 2006; Schuster et al., 2009). The filter transmission efficiency of N_2O_5 on a used filter is determined to be 6 % smaller than that on the clean filter. Therefore, the filter transmission factor for N_2O_5 is estimated to be 93 ± 3 %.”

6. The manuscript mentions the comparison to an Aerodyne I-CIMS, but indicates that comparison will come in a future publication. If this publication doesn't show any CIMS data, then it should not mention that CIMS data. Without any evidence shown of what "good agreement" is, this manuscript cannot make such a statement. I think that inclusion of the I- CIMS comparison would enhance this manuscript.

Answer:

During the campaign, an Aerodyne I-CIMS (Breton et al., 2012; Breton et al., 2014) from Gothenburg University Group was deployed in parallel with our instrument, but the CIMS did not perform in-situ N_2O_5 calibration during the campaign since it was originally targeted on the measurement of the gas phase precursors for SOA. The preliminary comparison showed reasonable agreements between the observed NO_{3X} from CEAS and the raw intensities signal of $\text{I}(\text{N}_2\text{O}_5)^+$ from the Aerodyne I-CIMS. Since the results of the Aerodyne I-CIMS were not independently calibrated, we skipped the comparison toward the I-CIMS.

7. It is necessary to give some description of the instrument itself (e.g. size, weight, power consumption), and a photograph of the instrument would also be informative. Such a photograph would also probably answer question about the physical construction of the instrument.

Answer:

In the first graph of Sect. 2, we added a brief introduction as the followings:

“The total weight is less than 25 kg, approximate dimensions of $95 \times 40 \times 25$ cm, the power consumption is less than 300 W.”

Moreover, we added both a detailed schematic plot and a corresponding photograph about the details of our mirror mounting parts (cf. Fig. 1b and 1c presented in the answers to question 1).

8. It is not clear if NO_3 is calculated from presumption of equilibrium and then corrected for or simply ignored. Please re-work discussion and presentation of NO_3 in this manuscript.

Answer:

In the revised manuscript, we re-worked discussion and presentation of NO₃ as indicated by both referee #1 and #2.

We agree that the amount of NO₃ detected in our instrument during field studies is the sum of NO₃ and N₂O₅ in general and represents N₂O₅ under high NO_x (or low temperature) conditions. We changed the term N₂O₅ to be NO_{3X} (NO_{3X} = NO₃+N₂O₅) throughout the manuscript, the later one was referred to Stone et al., (2014). And in this way, the calculation of NO₃ from presumption of equilibrium was not needed.

9. Specific issues: Line 38: Most areas with major NO_x loadings also have significant aerosol loadings. Is this section meaning to indicate pollution aerosol, or potentially aerosol from nearby natural sources (e.g. desert dust)?

Answer:

We revised the sentence to be: "From satellite observations, it was found that the USA, Europe, and China are the three major high NO_x regions worldwide (e.g. Richter et al., 2005). Moreover, in the North China Plain areas, the high NO_x air masses often overlap with high aerosol loadings from both secondary formations as well as nearby natural sources (e.g. dust from the Gobi Desert in the spring) and serve as an ideal air mass for samples for the study of NO_{3X} chemistry."

10. Line 46: Two ion CIMS ion chemistries have been demonstrated, NO₃⁻ and I⁻. Others could be possible, so the wording should be altered. Also, listing the reagent ion consistently is important.

Answer:

The introduction of CIMS on the Line 46 is revised as suggested:

"In addition to optical approaches, different chemical ionization mass spectrometry (CIMS) methods have been used for the detection of ambient N₂O₅ (Slusher et al., 2004; Fortner et al. 2004; Kercher et al., 2009; Chang et al., 2011). Slusher et al. (2004) utilized ion reaction ($I^- + N_2O_5 \rightarrow NO_3^-$) to detect N₂O₅ at 62 amu (NO₃⁻). Nevertheless, this approach showed cross sensitivity towards NO₃ ($I^- + NO_3 \rightarrow NO_3^-$) and additional interference from species like ClONO₂ and BrONO₂. A strong unknown interference at 62 amu was found for the detection of N₂O₅ under a high NO_x regime in Hong Kong (Wang et al., 2014). Kercher et al. (2009) introduced an ion-molecule region (IMR) module wherein the ion reaction, $I^- + N_2O_5 \rightarrow I(N_2O_5)^-$, is enhanced so that N₂O₅ can be detected specifically at 235 amu. With this method, a direct measurement of N₂O₅ is achieved, showing a good comparison with the well-established CRDS system in Hong Kong (Wang et al., 2016)."

11. Section 2.2 is listed twice on page 4 – it is both "optical layout" and "flow system".

Answer:

Revised accordingly.

12. Line 119: Please explain the "pilot experiments". Is there no flow cell in the middle? Are the mirrors on adjustable mounts, or how are they adjusted?

Answer:

In the pilot experiments, we explored the relations between the observed light output signals towards the cavity lengths (with adjustable mounts) and the diameters of the flow cell (mimicked by two irises). We found that in general a shorter cavity can achieve higher light output, but the improvement is not significant. Considering the instrument size, we choose the cavity length to be 50 cm. Moreover, we found that the light output is reduced dramatically when the flow cell diameter is smaller than 10 mm. To achieve a compromise of a high light output which ensures a good SNR on the detector and a short gas sample residence time which ensures the high transmission efficiency of NO₃ over the detection cell, the diameter of the detection flow cell is then chosen to be 10 mm at the expense of some losses of the output signal.

13. Line 126: What does "(-0.1) mm" mean?

Answer:

On the Line 125 and 126, the statement of "25.0 (-0.1) mm" means that the diameter of the HR mirror (25.0 mm) with a negative machined error of 0.1mm according to the manufacturer report (Layertec GmbH, Mellingen, Germany). We modified the text to be "25.0 (+0.0/-0.1) mm".

14. Line 133: Maybe "homocentric" is "concentric"?

Answer:

On the Line 133 we replaced "homocentric" with "concentric" accordingly.

15. Line 148: "Stand" is maybe "Stainless"? How was the tube coated?

Answer:

It is "Stainless". The central part of the detection cell is made by a 35.6 cm long PFA tube (Entegris, I.D.=10 mm), and the PFA tube is enclosed by a stainless tube.

16. Line 173: Wording quite awkward here.

Answer:

We rewrite the sentence as follows in the revised manuscript:

"The effective absorption cross section of the abundant ambient absorbers, NO₃ and NO₂, in this wavelength window of 640 - 680 nm needs to be determined to retrieve the concentrations of NO₃. Since we used a dynamic reference spectrum which contains the same amount of water vapor as that of the measured sample spectrum (cf. Sect. 2.3), the calculation and fitting of the strong non linear absorptions lines of H₂O in this wavelength window is avoided."

17. Line 234: Please clarify what is mean by "negative absorption of NO₂". I understand this, but it could be made more clear to a general reader.

Answer:

We revised the text as the followings:

"The NO₂ impurity in the used NO standard is analysed by a commercial NO_x instrument (TE-42i). The NO₂ impurity is found to be around 0.8 %, which means 4 ppbv of NO₂ is present in the reference spectrum measurement with the presence of 480 ppbv NO. The NO₃ and O₃ in the preheating tube and detection cell react with the high concentration of NO and generate

NO₂. In the case shown as Fig. 2, the additional NO₂ produced during the measurement of the reference spectrum can reach up to 55 ppb (with the initial additional NO₂ set at 4 ppb). Therefore, to use this dynamic reference spectrum, we normally fit both NO₃ and NO₂ to cover the limiting cases when the generated NO₂ is high. **Nevertheless, the fitted NO₂ concentration will be negative since the NO₂ concentrations are higher in the reference spectrum.** We added a new Figure 2 in the revised text as follows:

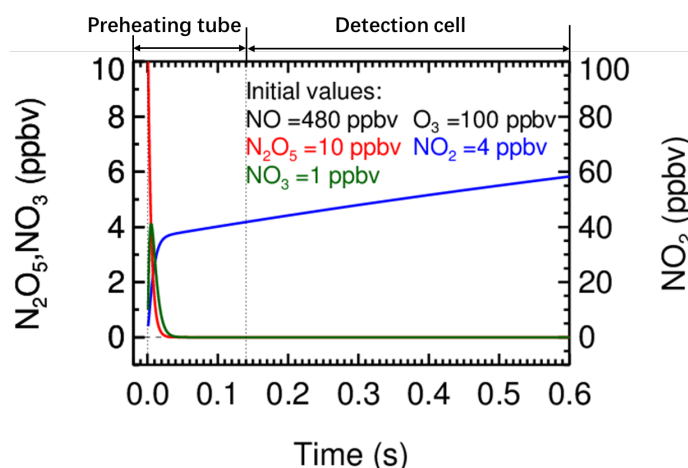


Figure 2. Simulation of the change of the mixing ratios of NO₃, N₂O₅ and NO₂ during the NO titration mode in the preheating tube and detection cell for an extremely high NO₃ and N₂O₅ case. The initial ambient NO₃, N₂O₅ and O₃ were set at 1 ppb, 10 ppb and 100 ppb, respectively. The initial NO₂ was set at 4 ppb from the impurity of the used NO standard.

18. Line 296: I’m not clear on what is meant by “, which is limited by the transmission factor2”? Clarify.

Answer:
In the revised manuscript, we calculated the total transmission efficiencies for NO₃ and N₂O₅, respectively, and listed the contributions from different part of the sampling and detection modules in Table 1.

Table 1. The transmission efficiency of NO₃ and N₂O₅ for the sampling module setup for the developed instrument.

| Gases | Filter | Inlet tube (0.7 s) | Preheating tube (0.14 s) | Cavity (0.46 s) | Total |
|-------------------------------|---------------------|---|--------------------------------|--------------------------------|--------|
| NO ₃ | 72±3 % ^a | 84±4 % (k=0.24 s ⁻¹) ^b | 98 % (k=0.16 s ⁻¹) | 93 % (k=0.16 s ⁻¹) | 55±6 % |
| N ₂ O ₅ | 93±3 % ^a | 99 % (k=0.019 s ⁻¹) | 99±1 % ^c | 93 % (k=0.16 s ⁻¹) | 85±3 % |

Note: ^a filter aging contributed an uncertainty of 3 %; ^b the uncertainty of the NO₃ wall loss reactivity in the cold inlet tube caused an uncertainty of 4 %; ^c the location of the N₂O₅ dissociation in the preheating tube had an uncertainty of 1 %.

19. Line 343: This section discusses NO₃, which apparently was not measured, but the figure shows a calculation of NO₃. Please clarify that NO₃ is only every calculated (e.g. in Fig. 12). It appears that the signals detected are simply interpreted as N₂O₅ without any correction for potential

NO₃, but that is made less clear by Eq.3, which seems to include NO₃ in the observed signal. Please make this section more clear.

Answer:

We agree and we have now interpreted our measurement signal as NO_{3x} which is more accurate in principle. Thus the calculation of NO₃ is not required any further. Further explanation is referred to our answers to question 8.

20. Fig. 6 caption: There are no labels as to what a), b) and c) mean. Is c) a residual or a non-detection of N₂O₅? The caption says "two spectra"

Answer:

The panel c) represents the residuals of the panel a) and panel b). Red line denotes the residual of panel a) and blue line the residual of panel b).