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Atmospheric Measurement Techniques Discussions

Interactive comment on "Interference from alkenes in chemiluminescent NO_x measurements" *by* Mohammed S. Alam et al.

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We would like to thank the reviewer for their comments and suggestions, and for taking the time to review our manuscript.

"The manuscript by Alam et al. presents a chamber study about the interference of alkenes in chemiluminescent NOx measurements. Varies of alkenes are studied and shown that the interference to NO ranged from 1% to 11%. However, the interference to NO2 detection is more complicated. Overall, this paper presented a useful study for promoting the high precision NOx measurement. Some comments should be addressed before considering the publication in AMT.

General comments.

1. The introduction of these NOx instruments should be added to the experimental section. I suggest the authors add a schematic figure to introduce the background and sampling mode of the NOx measurement, which could help the non-professional readers follow the background interference part easily."

RESPONSE: We think that the introduction to chemiluminescent NOx instruments (line 71 – 81) is more suited for the introduction and have not moved it to the experimental section. This is because: (i) this information is generic and not specific to our experimental set up, and (ii) in order to understand the potential origins of interferences in chemiluminescent NOx monitors, the knowledge of a typical instrument setup is required. A schematic diagram (Fig 1 – see below) has been added to this section to help the non-professional readers, as suggested by the reviewer. This has been referred to in Line 73.

"2. Line 320, the KPI is a good indicator and easy to understand, but the Supplementary Information for calculation details seems not finished as there is no equation of KPI = ???. Considering that the KPI is important in this paper, the final equation should be listed in the main text." RESPONSE: The final KIP expression has been included into the main text in Lines 259 – 267. The detailed calculation of the KIP remains unchanged in the Supplementary Information.

"3. The NO measurement by monitor 2 has small interference by alkene, and NO2 measured by monitor 2 free of the interference of alkenes, does this result mean the API 200 AU monitor has better instrumental design compared with other monitors, at least in avoiding the alkene interference?" RESPONSE: The data presented in this study indicates that the API 200 AU monitor instrument responds least to alkene interference.

"4. According to the results in table 2 and Line 258-259, monoterpenes have no interference. While in the conclusion part (Line 485 and 502), the author proposed the monoterpene should be noted, it is contradicted, please clarify it." RESPONSE: α-

Terpinene (C10H16), terpinolene (C10H16) and limonene (C10H16) are all monoterpenes. The results shown in Table 2 show the largest interferences from α-terpinene and terpinolene both of which are monoterpenes. In lines 258-259 (now 206 – 209) we do not report all monoterpenes in having no NO interference, but report the response of individual alkenes / monoterpenes that do not exhibit an interference within the detection limits of the instruments. The conclusion has been amended to remove any contradictory messages by including the following sentence: "Although monoterpenes, α-pinene, myrcene and limonene, show no significant NO interferences in chemiluminscence NOx monitors, other fast reacting monoterpenes (with O3) such as α-terpinene and terpinolene which are not generally reported in the literature, exhibit large interferences and may lead to substantial overestimations in NOx measurements." This is found in Lines 422 – 429.

"5. What happened about the monitor 2 in figure 1-2 in NO2 measurement?" RESPONSE: The NO2 measurements for monitor 2 in Figure 1-2 were zero throughout the experiment measurement period. There were no indications that there was anything wrong with the instrument before, during and after the experiment(s). The manuscript remains unchanged.

"6. Figure 1-3 is very confused. Why are some fitting results not shown? If the non-significant result not shown, why the measured NO2 by Monitor 4 is plotted in figure 1 with very r2=0.001?" RESPONSE: We are only meant to show the fittings that were significant. The reviewer is correct to point out that the NO2 measured by monitor 4 is not significant. This has been amended in the Figures.

"Specific comments.

7. Line 79-85, the cited reference Fuchs et al., (2009) is about cavity ring-down spectroscopy, so the citation is wrong (also cavity-enhanced absorption spectroscopy should be mentioned). An appropriate reference should be added about CE-DOAS." RESPONSE: Added "cavity ring-down spectroscopy (CRDS)" – Line 61. Reference

also added: "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. Atmos. Meas. Tech., 3, 1797-1814, 2010." See lines 625 – 627 in the reference list.

"8. Line 203, missed a blank between 5 and ppm. There also many errors like this (e.g., Line 190. . .)" RESPONSE: Amended. Line 61 and anywhere where we use units.

"9. Line 296, the O3 abundance, and residence time are not discussed in the following paragraph." RESPONSE: The intention of this paragraph was to discuss the differences in interference magnitudes due to the varying pressures within the reaction chamber of the different instruments. This has been clarified by the addition of "e.g." in line 240. Ozone (reagent formed within the instrument) specifications typically state in excess abundance, in order to convert all (or >99%) NO present into NO2. Increasing the reaction time between the NO (from sampled air) and excess O3 would allow more time for NO to be converted into NO2. This is explained in the introduction in lines 71 – 81.

"10. Figure 1-3, panel B and D, change the y-axis as NO2 rather than NO (although the mixing ratio are retrieved as NO)." RESPONSE: Amended – See Figures 2-4 in manuscript.

"11. The average results in figure 4(B) do not make sense. I suggest removing it." RESPONSE: This is an average of the interferences calculated across all instruments vs KIP%. This allows us to calculate the relative potential interference response from any monitor from a given alkene rather than an absolute upper limit (for monitor 4) or lower limit (for monitor 1) from this study only. We think including this figure allows the community to calculate relative potential interferences from other monitors. The manuscript remains unchanged.

"12. Figure 5, the left and right y-axis should be changed, please change to

(NO/NO/NOx) and (ï ËŻA ËŻa-terpinene)." RESPONSE: Amended (see Fig. 6 in manuscript).

"13. The time resolution of data for the four monitors and shown in figures should be clarified." RESPONSE: All figures shown use 1 minute time resolution data for all monitors. This is included in the caption for Figures 2, 3, 4 and 6 in the manuscript.

"14. Line 421-424, the label * and # are missed in Table 3." RESPONSE: The data in Table 3 have been labelled with * and #.

"15. The caption of Table 4 should add the reaction rate constant of NO+O3 (298 K) for intercomparison." RESPONSE: "k(NO+O3)= 1.90 $\times$ 10-14 cm3 molecule 1 s-1 (298 K)" has been added to the caption of Table 4.

"16. Line 450-453, are you mean the possible HOCO is an interference of the chemiluminescent?" RESPONSE: Yes. We have amended the manuscript to explain this more clearly by adding the word "chemiluminescence". See line 373-376.

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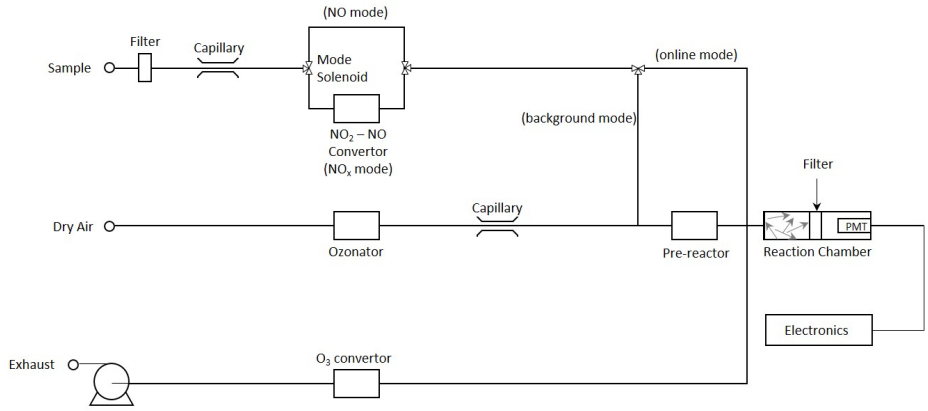

Fig. 1. A typical flow schematic of a chemiluminescent NO monitor.