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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.

Anonymous Referee #1

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Interference from alkenes in chemiluminescent NOx measurements M.S. Alam et al., Atmospheric Measurement Techniques Discussions, doi:10.5194/amt-2020-164

The authors present a study of NO and NO2 measurements made in the presence of a series of alkenes in the EUPHORE atmospheric simulation chamber. Measurements of NO and NO2 were made using four instruments based on detection of chemiluminscence of excited NO2* formed by the reaction of NO with O3 generated within the instrument. This technique enables the direct measurement of NO, but measurements of NO2 require conversion of NO2 to NO, followed by measurement of the resulting NO which represents the sum of NO and NO2 concentrations and gives the concentration of NO2 from the difference between the sum of NO and NO2 and the measurement of NO alone. Two of the instruments used in this study use catalytic conversion of NO2

to NO using a heated Mo catalyst, while the other two instruments employ photolytic conversion using a blue LED.

The authors outline a number of potential interferences in NOx measurements that can affect instruments based on detection of chemiluminescence, and primarily focus on potential chemical interferences resulting from detection of chemiluminescence from species other than NO2*. Given the importance of accurate NOx measurements for air quality, the results of this study are potentially significant. The experimental procedures seem robust, the paper is well-written and within the scope of the journal, and will be of interest to the wider atmospheric chemistry community. However, there are a number of areas which should be improved in the manuscript prior to publication.

In general, the discussion of the observed effects is somewhat limited and the manuscript would benefit from expanding the possible causes of the interference and providing some recommendations for future experiments to identify and eliminate interferences as far as possible. Several species are mentioned as being potentially responsible for the chemiluminscence interference, including excited HCHO, vibrationally excited OH and electronically excited OH. Some discussion of the filters used in the NOx instruments is given, but it would be informative, where possible, to give the emission spectra of possible interfering species, NO2*, and the filters used in the instruments employed in this study. Are there significant differences between filters in different instruments? Could future work using alternative filters rule out interferences from these species? Could emission spectra of the chemiluminescence interferences be measured in future experiments?

Some discussion of the kinetics of ozone-alkene reactions is given in comparison to the observed interferences, which indicates that more rapid ozone-alkene reactions are more likely to result in interferences. Consideration of the energetics of the ozone-alkene reactions investigated, combined with modelling of the chemistry involved, might be more insightful and could help to identify whether production of excited species is likely, and which species with appropriate emission spectra might be

present in sufficient concentration to produce significant interferences.

Minor comments are given below.

Lines 54-55: This sentence appears to be incomplete.

Line 128: Are the 212 monitoring sites in the UK, EU or a wider area?

Line 154: Are the CO2 mixing ratios in the chamber elevated significantly above ambient levels such that interferences could result in the chamber?

Lines 175-178: Please provide further details of the previous work. What alkenes were investigated? What were the conditions? Were emission spectra reported? If so, what were the emission wavelengths? Do the previous studies give any further details on which species might have been responsible for the observed chemiluminescence?

Line 199: Were the sampling lines all of similar length?

Line 203: What were the concentration ranges over which calibrations were performed?

Line 280: Can the relationship between the level of interference and the alkene + ozone reaction rate be quantified in any way? Does a plot of the level of interference against rate of reaction reveal any general trend?

Lines 295-296: What are the differences in conditions between instruments?

Line 332: Is CH2OO the only possible Criegee intermediate produced? What other species/Criegee intermediates are produced?

Line 364: Is there any likely effect of the age of the catalyst?

Line 496: Remove the comma at the end of the line.

Table 2: Values and uncertainties should be given to the same number of significant figures.

Figures 1, 2, & 3: Panels B & D should be labelled as NO2 on the y-axes.

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