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Atmospheric Measurement Techniques Discussions

Interactive comment on "Measurements of hydroperoxy radicals (HO_2) at atmospheric concentrations using bromide chemical ionization mass spectrometry" *by* Sascha R. Albrecht et al.

Anonymous Referee #1

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This paper presents a description of an instrument designed to detect HO2 radicals using bromide ion chemical ionization mass spectrometry. Most current methods of detecting HO2 radicals are indirect measurements utilizing chemical conversion of HO2 to OH by reaction with NO and subsequent detection of OH by laser-induced fluorescence in Fluorescence Assay by Gas Expansion (FAGE) instruments. Because this technique has been shown to suffer from interferences associated with the chemical conversion of RO2 radicals, a more direct method for detecting HO2 radicals would be a valuable addition to the community. While one could argue that the instrument described in this paper is not necessarily a "direct" method (page 3 line 6) as it still requires calibration, it is an important complimentary measurement technique. While

the work of Sanchez et al. (2016) provides some details of the technique, this paper provides more comprehensive measurements of potential interferences as well as an intercomparison with measurements from the more established LIF-FAGE technique.

The paper is well written and suitable for publication in AMT after the authors have addressed the following:

1) The authors describe the dependence of the sensitivity on water vapor concentration, with one possible explanation attributing the decrease in sensitivity to "The HO2 ion cluster is stabilized by water during the attachment process. . ." (page 7 line 6). Do the authors mean that during the Br- + HO2 attachment process, water vapor can stabilize the HO2- ion cluster, reducing the formation of the HO2 bromide ion cluster? This statement could use some clarification. (related ". . .access. . ." on line 7 should read ". . .excess. . .").

2) Similarly, the authors state that the formation of HO2-H2O clusters could also impact the sensitivity of the instrument, but the explanation is not clear. How does the formation of these clusters lead to a " roughly 10x increased in sensitivity at humid conditions" compared to dry conditions (page 8, line 6)? This should be clarified.

3) While the precision of the technique is described, the overall uncertainty in the CIMS measurement should be clarified, which I assume is primarily due to the uncertainty associated with the calibration technique.

4) The authors describe a background signal that appears to be a function of water vapor that may be due to production of HO2 inside the instrument, although possible mechanisms for production of the background are not discussed. The authors state that the measurements of the background are consistent with a constant value, and that the measured changes in the background signal with increasing water vapor shown in Figure 5 are consistent with a constant value for this background. The authors could provide additional support for this statement by converting the signals shown in Figure 5 to equivalent HO2 concentrations using the calibration factor's water dependence

shown in Figure 3.

5) Related to this, the paper would benefit from additional discussion of the nature of the background signal besides its dependence on water vapor. While it is reassuring that the measured background signal did not change over the course of these controlled experiments, understanding the nature of this background signal will be necessary to improve confidence in measurements in ambient air. Does the background vary with the strength of the ion source, pressure in the ion flow tube, inlet diameter, etc? Sanchez et al. (2016) also observed what appeared to be a constant background signal that they attributed to production of HO2 in their ion source. It appears that a similar signal is produced in this instrument, which should be discussed in more detail.

6) The authors also describe an ozone interference that appeared to occur in two of their experiments (page 11). Unfortunately, the source of this interference is not discussed in much detail, except to speculate that it may be related to instrumental effects or cleanliness of the ion tube walls. While the authors state that additional experiments will be needed to determine the source of this interference, the manuscript would benefit from an expanded discussion of this interference, including how it would have to be measured in ambient air.

7) For the correlation plots shown in Figure 7, the authors should state how the regression analysis was performed. They should perform bivariate regressions weighted by the precision of each measurement and should show the correlation coefficient on each plot. In particular, the correlations for the IEPOX experiments on 29.05 and 1.06 appear to be weak.

8) The authors also observe an interference with high concentrations of IEPOX, but there is little discussion of the cause of this interference and whether the authors expect similar interferences from other compounds under ambient conditions. Can the authors speculate on the mechanism of the interferences (decomposition of IEPOX inside the instrument)? It would be valuable to show the correlation with the LIF-FAGE

measurements after the interference is subtracted from the IEPOX measurements in comparison with the measurements shown in Figure 7 (page 13 line 6).

9) While these chamber experiments illustrate the promise of the CIMS technique, additional measurements under ambient conditions will be necessary given the observation of several interferences in these experiments. This should be acknowledged in the manuscript. In particular, given the complex composition of ambient air, the authors should discuss strategies for testing for unknown interferences under ambient conditions, such as the addition of an ambient HO2 scavenger or other potential methods.

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