

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 #2

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This study investigated the application of a chemical ionization mass spectrometer using bromide ion as reagent for measurement of HO_2 radicals. Calibration and characterization of the instrument were described. Experiments were conducted in the SAPHIR chamber using ISOPOOH, IEPOX, isoprene, and without injection of any VOC. The HO_2 levels measured by the CIMS were compared to LIF and good agreements between the two instruments were observed.

In general, the manuscript is well-written and the topic will be of interest to the greater atmospheric community. The Br-CIMS technique for measuring HO_2 was first developed in Sanchez et al. (2016), where the instrument capability was demonstrated with

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measurements of ambient HO₂ in an urban area. Here, the authors conducted an inter-comparison study with LIF-FAGE technique, which further validated the capability and the use of Br-CIMS in measuring HO₂.

My major comments are that the authors should provide a clear focus of this work and put this work in the context of previously published results by Sanchez et al. A large portion of the manuscript (page 1-11) was on instrument characterization, covering ion flow tube specifications (pressure, residence time, etc), calibration procedure, sensitivity, water vapor dependence, detection limit, instrument background, and interference from ozone. All these are necessary and good as the way they were written, if there were no previously published work on the use of Br-CIMS for measuring HO₂ radicals. However, all these were discussed in Sanchez et al. previously. But in this manuscript, there are no discussions at all regarding how these compare between this work and Sanchez et al. As this manuscript was submitted to an instrument journal, without such context, it is not clear if the aim of the study is to further improve the instrument beyond what was demonstrated previously (and if so, discuss the specific improvements), or if it is to directly adopt and reproduce what was in Sanchez et al., but with the main goal to compare the results to LIF. It is thus difficult for readers to evaluate whether the setup and performance of the instrument here is similar to or different from those in Sanchez et al. If the setup and performance are similar to Sanchez et al., this is a good thing, meaning that the measurement technique is robust and if others have an Aerodyne ToF-CIMS and want to measure HO₂ they can also adopt this (fairly) readily. If the performance of instrument in this work is better than Sanchez et al., it is also a good thing, meaning that the technique has been further improved since then. However, it is difficult to tell from the current manuscript as no comparisons were made. The authors should compare the setup and relevant parameters to those in Sanchez et al. systematically and discussed accordingly. In addition to modifying the main text, a table documenting and comparing the various aspects of the instrument in the two studies would be very helpful.

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It is interesting that the authors observed an instrument background, which was also reported in Sanchez et al. This should be discussed in more detail, as this was now observed in two independent studies and is intriguing/puzzling. In terms of the dependence of sensitivity on water vapor, the observed dependence is quite different between the two studies. The authors should mention this and discuss this accordingly.

Overall, the manuscript should be extensively modified to put this work in the context of previously published work, and to reflect the similarities/differences between the instrument setup and performance, etc. This would not only improve clarify of the manuscript but also help future researchers if they are interested in using or further developing this technique to measure HO₂ radicals. I recommend the manuscript to be published after the authors address the major and specific comments.

Specific comments:

1. Page 3, line 6. Here in the introduction, the authors wrote "In this study, the direct measurement of atmospheric concentrations of HO₂ radicals using Br-CIMS is presented. A detailed characterization of the instrument has been performed". This description also applies to what have been reported in Sanchez et al. I think this is a good place to set the tone for the manuscript and clearly describe the main focus/goal of the manuscript in the context of previously published work.
2. Page 3, line 22. It is noted that the mean residence time is 4ms. This seems very short (an order of magnitude too short?). Please show calculations on how the 4ms is obtained.
3. Page 3, line 31. What is the ion source (physically)?
4. Page 5, section 2.2. The manuscript flow will be improved if this section is deleted and the materials discussed here are added to section 3.1.
5. Page 6, line 25 onwards, calibration procedure.

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- a. In Figure 2, what does ncps stand for? I assume it is normalized cps. Please specify explicitly.
- b. What is the cps of primary Br- (m/z 79)? Please specify explicitly.
- c. If the m/z 112 signal (in cps) is normalized by the Br- signal (in cps), the y-axis in Figure 2 should be unit-less instead of ncps?
- d. Considering all of the above, instead of using normalized ion count rates, I think it would be much easier for readers to interpret the data and compare the performance of Br-CIMS to prior work, if the authors can report the cps for m/z 112 and the cps for bromide ion. For instance, the range of [HO₂] in this study (3e8 – 1.3e9 molecules/cc, i.e., ~12-53 ppt) is similar to Sanchez et al., but it is hard to evaluate from Figure 2 if the sensitivity of the instrument is similar to or different from Sanchez et al.
- e. Line 29. Is the unit for the slope correct?

6. Page 7-8, dependence of sensitivity on water mixing ratio.

- a. Page 8, line 6. Please explain clearly how the “roughly 10x” higher sensitivity under humid conditions is determined.
- b. Sanchez et al. observed a dependence of sensitivity for RH < 10%. The dependence of sensitivity on water mixing ratio in this study is quite different. More discussions are needed. Is there any difference in the instrument setup between this study and Sanchez et al. that could potentially lead to a different dependence?

7. Page 9-10, instrument background.

- a. A constant background signal was also observed in Sanchez et al. Is the background observed here similar or different in magnitude compared to that in Sanchez et al.?
- b. In Sanchez et al., the background signal does not scale with water mixing ratio (but scales linearly with UV lamp flux). Is there any difference in the setup that can lead to a different water mixing ratio dependence in the two studies? Does the background

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signal in this study scale with UV lamp flux? All these should be discussed.

c. It is suggested that there is a constant HO₂ concentration produced in the instrument. What might be some potential sources? More discussions are needed.

d. Instead of A.U., it will help readers better interpret the data if the m/z 112 signals (in cps) are used in Figure 5. For instance, one cannot tell from Figure 5 if the magnitude of Br.HO₂ is the same for laboratory characterization and experiments in the chamber.

e. It would be useful to show some mass spectra to help readers interpret the data. Please show mass spectra for 1) dry conditions for laboratory characterization, 2) humid conditions for laboratory characterization, 3) dry conditions for experiment in the chamber, 4) humid conditions for experiment in the chamber.

f. Was the temperature the same for laboratory characterization and experiment in the chamber?

8. Page 13 onwards. IEPOX interference.

a. Slopes and R² values should be included in each subplot in Figure 7.

b. Line 1. Would be useful to show the relationship between the signal observed at the IEPOX mass (m/z 197) and the interference signal from IEPOX at the HO₂ mass (m/z 112).

c. Line 5. Would be useful to show the correlations between CIMS and LIF with and without the correction.

d. Are the data in Figure 7 for IEPOX experiment corrected for the interference?

e. Page 14 line 14-22. The authors noted that the significant offsets for some experiments (e.g., 21 June and 26 June) could be due to how water vapor dependence of the instrument sensitivity was derived. However, the magnitude of the offset varied greatly from experiment to experiment. Why? Please discuss.

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f. The “none” experiments in Figure 7 are experiments where no VOC was injected? However, the level of HO₂ measured in these experiments was comparable to those experiments with 10s of ppb (?) of VOC? What is the source of HO₂ radical in these “none” experiments? Shall the HO₂ concentrations measured in the VOC-added experiments be corrected for this?

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