

Interactive comment on “Measurements of hydroperoxy radicals (HO₂) at atmospheric concentrations using bromide chemical ionization mass spectrometry” by Sascha R. Albrecht et al.

Sascha R. Albrecht et al.

s.albrecht@fz-juelich.de

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Dear referees, Dear editor,

Thank you very much for your review of the paper.

Major comment:

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. (2016). A large portion of the manuscript (page 1-11) was on instrument characterization, covering ion flow tube specifications (pressure, residence time, etc), calibration procedure,

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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. (2016) previously. But in this manuscript, there are no discussions at all regarding how these compare between this work and Sanchez et al. (2016). 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. (2016), 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. (2016). If the setup and performance are similar to Sanchez et al. (2016), 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. (2016), 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. It is interesting that the authors observed an instrument background, which was also reported in Sanchez et al. (2016). 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 clarity of the

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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.

Response:

Indeed Sanchez et al. (2016) provided pioneer work with the presentation of the bromide CIMS. The aim of our paper is further characterization of the technique and the search for possible interferences. Especially the comparison with the HO₂ LIF allows quantitatively comparing HO₂ measurements with a reference and the identification of potential interferences under realistic atmospheric conditions. Further we successfully improved the instrument's sensitivity for HO₂ employing our custom-build ion flow tube. In the revised version of the manuscript we include comparisons with the instrument described in Sanchez et al. (2016) in more detail (see responses to the further comments).

Comment:

It is interesting that the authors observed an instrument background, which was also reported in Sanchez et al. (2016). 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.

Response:

We added line 3 on page 12: "Sanchez et al. (2016) also described a constant HO₂ source which causes a background. An HO₂ titration experiment Sanchez et al. (2016) confirmed that HO₂ is internally produced, which has been discussed for other radical measurements using a CIMS approach (Berresheim et al., 2000)."

Sanchez et al. (2016) found a constant sensitivity for water vapor mixing ratios between 0.2 and 0.8% whereas a 30% decrease is observed here. Only for one sensitivity

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measurement at 0.06% water mixing ratios an increased sensitivity by approximately 50% is reported by Sanchez et al. (2016). The reason for this different behaviour is not clear, but one may speculate that the design of the ion-flow tube and inlet nozzle might impact the collision probability of ion clusters. The relative change of the instrument's sensitivity in Sanchez et al. (2016) towards dry conditions is not reported, so that it is not clear, if the sensitivity drops for dry conditions in their instruments as observed here.

Comment:

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. (2016). 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.

Response:

We added in line 8 on page 3: "Sanchez et al. (2016) demonstrated that the most promising ionization technique is the detection of the bromide cluster with HO₂. In their work they showed that a sufficient sensitivity can be achieved and no significant interference from NO_x, HCHO, SO₂, O₃ is present. Based on the work of Sanchez et al. (2016) a custom-built ionization flow tube optimized for the sampling of radicals was mounted on top of an Aerodyne TOF mass spectrometer for the detection of Br · HO₂ clusters in this work. In addition to laboratory characterization experiments that mostly confirmed results reported in Sanchez et al. (2016), the performance of the instrument was quantitatively assessed in a comparison of HO₂ concentrations with measurements by an established HO₂ instrument using laser-induced fluorescence. Experiments in the atmospheric simulation chamber SAPHIR were performed at atmospheric gas mixtures and radical concentrations. "

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Comment:

Page 3, line 30. 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.

Response:

Indeed this was an error, the conversion of minutes to seconds was missing. The text has been corrected for the correct time, which is 240 ms.

Comment:

What is the ion source (physically)?

Response:

It is a foil coated with radioactive ^{210}Po having an activity of 370 MBq (equal to 10 mCi) contained in a sealed tube. The type and manufacturer is mentioned in the text (Page 4, line 7) now.

Comment:

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.

Response:

Section 2.2 has been moved further down followed by section 3.1.

Comment:

In Figure 2, what does ncps stand for? I assume it is normalized cps. Please specify explicitly.

Response:

Yes, in the figures caption it is mentioned that the normalized count rate is shown.

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However, for clarity we removed ncps.

Comment:

What is the cps of primary Br- (m/z 79)? Please specify explicitly.

Response:

We added the information to section 3.2.

Comment:

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?

Response:

Basically this is the definition of the normalized signal, it is unit-less, for clarity we removed ncps.

Comment:

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 $[\text{HO}_2]$ in this study ($3 \times 10^8 - 1.3 \times 10^9$ molecules/cc, i.e., 12-53 ppt) is similar to Sanchez et al. (2016), but it is hard to evaluate from Figure 2 if the sensitivity of the instrument is similar to or different from Sanchez et al. (2016).

Response:

This is now discussed for comparison of both papers (Page 17 Line 9). " HO_2 was directly sampled through a nozzle into a custom-build ion flow tube which was optimized for sensitivity. The sensitivity reached is equal to 0.005×10^8 HO_2 per cm^3 for 10^6 cps of bromide and 60 s of integration time, which is approximately 3 times higher than the sensitivity for a similar instrument by Sanchez et al. (2016)."

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Comment:

Page 7 Line 9. Is the unit for the slope correct?

Response:

Indeed it should be [cm³].

Comment:

Please explain clearly how the “roughly 10x” higher sensitivity under humid conditions is determined.

Response:

The ozonolysis experiment explained in this section provides the possibility to compare measurements with and without humidity. Comparing the sensitivity determined without water addition and the sensitivity at 0.1% water mixing ratio gives a roughly a factor of 10. As a response of the comment of reviewer 1, this sentence was removed from this position. We modified the sentence on page 8 in line 21: "For water vapor mixing ratio of less than 0.1 %, the sensitivity drops quickly by a factor of 7 at dry conditions compared to the maximum sensitivity at 0.1 % water vapor mixing ratio."

Comment:

Sanchez et al. (2016) 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. (2016) that could potentially lead to a different dependence?

Response:

Sanchez et al. (2016) found a constant sensitivity for water vapor mixing ratios between 0.2 and 0.8% whereas a 30% decrease is observed here. Only for one sensitivity measurement at 0.06% water mixing ratios an increased sensitivity by approximately

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50% is reported by Sanchez et al. (2016). The reason for this different behaviour is not clear, but one may speculate that the design of the ion-flow tube and inlet nozzle might impact the collision probability of ion clusters. The relative change of the instrument's sensitivity in Sanchez et al. (2016) towards dry conditions is not reported, so that it is not clear, if the sensitivity drops for dry conditions in their instruments as observed here.

Comment:

A constant background signal was also observed in Sanchez et al. (2016). Is the background observed here similar or different in magnitude compared to that in Sanchez et al. (2016)?

Response:

Sanchez et al. (2016) determined an instrument background of 4 pptv or more, since the scavenging is not efficient in the ion flow tube. This seems to be in a similar magnitude. We found a background of 6 pptv during the chamber experiments.

We added at page 12 in line 5: "Sanchez et al. (2016) determined an instrument background of at least 4 pptv HO₂, which compares well with the background of 6 pptv HO₂ that has been found during the experiments in the SAPHIR chamber."

Comment:

In Sanchez et al. (2016), 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 signal in this study scale with UV lamp flux? All these should be discussed.

Response:

The effect of an increased background signal during the calibration procedure in Sanchez et al. (2016) is clearly connected to their calibration source and not to the

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instrument's performance, because it scales with the intensity of the UV lamp that is part of the calibration source. We would expect that this behavior does not apply for ambient air measurements of the instrument in Sanchez et al. (2016). Such an effect of the calibration source has not been observed for our calibration source that is the same as has been used for the calibration of the HO₂ LIF instrument for more than 20 years without any hint that there is HO₂ or interference signal produced in the absence of water. One difference in the calibration procedure is that Sanchez et al. (2016) worked at very low humidity to produce ambient HO₂ concentrations, whereas our calibration source is operated at ambient humidity. In addition they work with purified air, whereas our calibration source is operated with clean synthetic air (purity 99.9999%). One could only speculate that photolysis of impurities at 185 nm might be the cause for the higher background observed by Sanchez et al. (2016), but we do not think that this needs to be discussed in this paper.

Comment:

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

Response:

The only potential source of radicals in the instrument is the ion source. Please compare the answer to a similar comment of reviewer#1, where more discussion about this topic is cited.

Comment:

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.

Response:

As suggested by referee#1, the Figure shows the background in HO₂ equivalents now.

During the laboratory experiments we found an up to 20% lower background.

Comment:

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.

Response:

There are no significant difference between mass spectra of the two masses at which HO₂-Br cluster appear (112 / 114) for the conditions that are mentioned by the reviewer. Humidity only affects the sensitivity (=count number), but not the shape of the spectrum. We add a mass spectrum in the supplementary material.

Comment:

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

Response:

This is a good point, we added on page 6 in line 12: "Measurements in the chamber were performed at daytime temperatures of roughly 20 to 30 ° Celsius. Additionally, the instrument itself was temperature stabilized to 25±5 ° Celsius to prevent temperature effects.

And on page 4 in line 2: Laboratory experiments were performed at 25 to 30 ° Celsius."

Comment:

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

Response:

The slope is already included in Figure 7, R2 will be added.

Comment:

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 HO_2 mass (m/z 112).

Response:

Figures have been added to the supplementary material for this purpose.

Comment:

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

Response:

The contribution of the interference from the IEPOX is highly variable in the experiments. When the IEPOX is introduced into the chamber, no HO_2 was present, but IEPOX concentrations decreased to nearly zero within a few hours. Therefore, we think that the new figures in the supplement showing the HO_2 equivalent signal of the interference as time series is most useful for the reader. A correlation plot of the uncorrected signal does not contain any additional information.

Comment:

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

Response:

Yes, this is now explained in the text.

Comment:

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.

Response:

The offset of the linear regression is not very accurate, if the dynamic range of the data set is small compared to the scatter of data. This explains partly the variability of the offset in the regression of individual experiments. For the determination of the offset, the signal derived during the humidification process was used. This means that water vapor from boiling water is introduced with a high flow of synthetic air, so that humidity changes quickly and air masses might not be perfectly mixed. Only for these conditions, there is potential that the water vapor measurement in the chamber could differ from the water concentration sampled by the CIMS instrument. This not ideal determination of the water vapor dependent background will be avoided in future application.

We added changes on page 16 Line 1: "This was done by using the measured signal at the $\text{HO}_2 \cdot \text{Br}^-$ mass during the humidification process of the clean chamber air, when no HO_2 was present. However, the chamber air might not be perfectly mixed during the humidification, because water vapor from boiling water is introduced at one location in the chamber together with a high flow of synthetic air. Because the water measurement in the chamber used for the determination of the CIMS background signal and the CIMS inlet are at different locations in the chamber, the water measurement is potentially not accurate for the water vapor sampled by the CIMS for these conditions, so that small systematic errors in the background determination cannot be excluded. In the future, the water vapor dependence of the background will be determined independently from the chamber experiment, so that it can be expected that such effects will not be relevant."

Comment:

The "none" experiments in Figure 7 are experiments where no VOC was injected? However, the level of HO_2 measured in these experiments was comparable to those experiments with 10s of ppb of VOC? What is the source of HO_2 radical in these "none"

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experiments? Shall the HO₂ concentrations measured in the VOC-added experiments be corrected for this?

Response:

Indeed, the label indicates which VOC was added. The experiments are all photochemistry in synthetic air. In the photochemistry experiments with no addition of OH reactants, HO₂ is present, because (1) OH and NO are produced from the photolysis of HONO that is released from the Teflon film of the chamber and (2) small concentrations of OH reactants are present converting OH to RO₂ and HO₂. Details of experiments without the addition of OH reactants can be found in Rohrer et al. (2005). The HO₂ measured under these conditions is HO₂ and not an interference. Often HO₂ is well explained assuming that the measured OH reactivity produces directly HO₂ (see for example Fuchs et al. (2013)). The good agreement of HO₂ measurements by both instruments, LIF and CIMS, confirms that the HO₂ is indeed present in the experiment.

For clarity we added on page 14 Line 5: "Nevertheless, HO₂ is produced in these experiments, because OH and NO are produced from the photolysis of HONO released from the chamber Teflon film in the sunlit chamber Rohrer et al. (2005). Reaction of small concentrations of OH reactants formed under these conditions in the chamber lead to the formation of HO₂ Rohrer et al. (2005)."

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-195, 2018.