

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

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Dear referees, Dear editor,

Thank you very much for your review of the paper.

Comment:

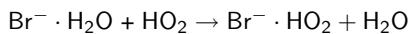
1) The authors describe the dependence of the sensitivity on water vapor concentration, with one possible explanation attributing the decrease in sensitivity to “The HO_2 ion cluster is stabilized by water during the attachment process. . .”. Do the authors mean that during the $\text{Br}^- + \text{HO}_2$ attachment process, water vapor can stabilize the

C1

HO_2^- ion cluster, reducing the formation of the HO_2 bromide ion cluster? This statement could use some clarification. (related “. . .access. . .” on line 7 should read “. . .excess. . .”).

Response:

The formation of an ion cluster needs an additional molecule that takes the excess energy upon the collision of the ion and the molecule forming the cluster. The formation of the hydrogen bond of the ion cluster would fail in most cases without leading away the collision energy. At atmospheric humidity virtual every ion comes with a loosely bound shell of water molecules. Therefore the following reaction seems favorable since water can take the collision energy.



In line 24 on page 8 the document was extended by a longer explanation that should provide clarity. "Two effects contribute to the water dependence: The initial increase of sensitivity (below 0.1% H_2O) comes from the stabilizing effect of H_2O . Br^- adds H_2O , forming a loosely bound complex of $\text{H}_2\text{O} \cdot \text{Br}^-$; then, the $\text{H}_2\text{O} \cdot \text{Br}^-$ complex reacts with HO_2 according to the forward reaction R2. The steady decrease of sensitivity by a factor of 2 when the H_2O mixing ratio is further increased to 1.2% comes from the back reaction of reaction R2."

Comment:

Similarly, the authors state that the formation of $\text{HO}_2^- \cdot \text{H}_2\text{O}$ 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?

Response:

For completeness we discussed the formation of ion clusters and radical clusters with water that are involved in the process. The increase of the sensitivity is not related

C2

to the HO₂[·]-H₂O radical cluster, but the formation of the HO₂-Br⁻ ion cluster is influenced by water. An HO₂[·]-H₂O ion cluster was not part of the discussion. Because the additional discussion of radical cluster seems to cause some confusion we removed it.

Comment:

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.

Response:

Indeed, the uncertainty of the calibration makes the major contribution of the uncertainty of the measurement. This is $\pm 10\%$ (1σ) (Holland et al., 2003). A higher uncertainty might be introduced by the subtraction of the water vapor dependent background signal. The background signal was stable within $\pm 12\%$ (1σ) during the campaign.

Line 32 on page 10:

"Uncertainties are caused by the calibration, which makes the major contribution of the measurement uncertainty with $\pm 10\%$ (1σ) (Holland et al., 2003). The stability of the background signal in the measurements done here was $\pm 12\%$, giving an upper limit of the additional uncertainty from the stability of the subtracted background signal. Similar uncertainties are obtained by Sanchez et al. (2016)."

Comment:

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 Fig-

C3

ure 5 to equivalent HO₂ concentrations using the calibration factor's water dependence shown in Figure 3.

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.

Response:

Figure 5 has been changed accordingly.

Once the background is corrected for the water dependence sensitivity it seems to be constant as discussed in the paper. We assume that radicals are produced in the radioactive ion source. Unfortunately we cannot change the strength of the radioactive ion source. The pressure in the ion flow tube changes the overall sensitivity of the instrument and the background goes with that, so that it is not easy to differentiate between these effects. We will check for the nozzle diameter for future reference. For the chamber experiments and laboratory characterization experiments, when chemical conditions like presence of water vapor, ozone and NO_x were much different or systematically varied, no dependence of the background on these parameters was observed.

Line 13 on page 11: "As reported for other CIMS instruments detecting radicals (Berresheim et al. (2000); Sanchez et al. (2016)), the radicals can be produced by the ion source. Therefore, this is the likely reason for the observed background signal. For chamber experiments reported here, the background signal was measured in the clean dark chamber at the start of each experiment."

C4

Comment:

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.

Response:

The interference occurred upon ozone addition. However, this only happened in two of 16 experiments with ozone addition. The potential for a pure ozone interference was carefully tested in laboratory experiments, when the inlet was overflowed with ozone containing zero air and no ozone interference was found. The experiment is now shown in the Supplementary material. The cause of the increased background signals in the two experiments therefore is not clear and might not be directly related to ozone alone. At this point, we can only state that not all background signals can be clearly attributed to specific conditions, so that the background signal needs to be carefully characterized for the application of the instrument.

Line 12 on page 13: "This indicates that regular checks of the background signal is needed to take an appropriate background correction into account."

Comment:

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.

C5

Response:

We changed the plot and added to the caption of Fig. 7: "For the regression line shown in blue a least square fit has been performed, the errors (1σ) of the measurement are indicated in gray."

Further we added on page 14 in line 10: "The results of a linear regression analysis are given in Fig. 7, which takes errors in both HO₂ measurements into account (Press et al., 1992)."

Comment:

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)?

Response:

Since no other significant interferences by VOCs was observed, the only plausible explanation seems to be the fragmentation of the molecule in the transfer stage. The fragmentation there can be initiated by acceleration of the ions in the electrostatic field causing collisions with other molecules.

Line 17 on page 15: "A plausible reason for the IEPOX interference found seems to be a fragmentation of the cluster ion in the transfer stage of the instrument. The fragmentation could be initiated by acceleration of the ions in the electrostatic field causing collisions with other molecules."

Comment:

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

C6

measurements shown in Figure 7.

Response:

The figure already shows data corrected for IEPOX.

Line 9 on page 15: "The correlation plots shown in Fig. 7 are corrected for the IEPOX interference."

Comment:

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.

Response:

The chamber experiments were the first tests of the applicability of the instrument for ambient HO₂ concentration measurements. It allows comparing the measurements to the FAGE-LIF measurements under controlled and defined conditions and ensures that both instruments sample the exactly the same air mass. Although the chemical composition of ambient is more complex, the most important known constituents of the atmosphere are present in the photochemical experiments in the SAPHIR chamber. Such a comparison would be more uncertain in a field experiment due to the inhomogeneities of the air mixture. Potential interferences of most abundant species like NO_x, O₃, ambient concentrations of VOCs were tested in the chamber experiments. Deployment of the instrument in the field is the next step.

Scavenging of HO₂ might not be as easy it looks at first glance. The addition of high NO concentrations would convert HO₂ to OH, but could also lead to secondary chemistry in the ion flow tube that could cause other artefacts. Such a scheme is worth trying,

C7

but would require extensive characterization and testing. The strategy of comparing measurements of two independent instruments applying different methods is another strategy to identify interference assuming that interferences would not have the identical effect on both instruments. It is foreseen for the future application that HO₂ is concurrently detected by the LIF and CIMS instruments.

Added line 14 on page 17: "Chemical conditions in the chamber experiments were close to atmospheric conditions regarding the most important constituents of the atmosphere such as NO_x, ozone and water vapor showing the applicability of the instrument under these conditions. First future deployment in field experiments will be done with concurrent HO₂ measurements by the LIF instrument, so that potential so far unrecognized interference can be identified. "

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

C8