Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2016-117-RC1, 2016

Atmospheric Measurement Techniques
Discussions

Interactive comment on "A new technique for the direct detection of HO_2 radicals using bromide chemical ionization mass spectrometry (Br-CIMS): initial characterization" *by* Javier Sanchez et al.

Anonymous Referee #1

Received and published: 28 April 2016

The manuscript by Sanchez et al. evaluates several chemical ionization techniques for detecting atmospheric HO2 radicals, and demonstrates that sensitive and selective measurements can be achieved using Br- as a reagent ion. This new measurement technique will be valuable to many researchers and may provide new insights into photochemistry. The paper is succinct and describes some of the important details, and it ought to be published after more experimental details and discussions are provided, as suggested below.

The manuscript can be made even more convincing by increasing the discussion of instrument diagnostics and performance and removing some of the discussion of the ambient measurements. In particular, the paper should show the instrument response

Printer-friendly version

Discussion paper

to a calibration and the different background methods, and discuss the time response and background levels that these diagnostic tests show. What is the time response? Showing a zero and cal will help quantify the claim of “immediate” in section 5. Additionally, a full mass spectrum would be useful, since Br- chemistry isn’t familiar, and it will help support some of the claims (for example, that detection at lower masses is less subject to interference). Mass spectra comparing zero and ambient would be especially useful for showing the selectivity.

In section 3, please add more experimental details to the reagent ion tests. How much HO2 was added? What was the reaction time and pressure in the IMR? Was water added? Were these tests performed with the quadrupole or TOF CIMS? For both instruments, add a discussion of water dependence to the detection. Does Br- cluster with water? And is the sensitivity dependent on water, as with I-? Fig 1 states that collisional dissociation occurs in SSQ. Does this collisional dissociation region decrease sensitivity by breaking apart the cluster ions? Or does it remove water clusters? More details regarding the instrument performance with Br- would be valuable, since the Bertram et al reference uses a different ion chemistry.

The authors note an important point about zeroing and internal HO2 generation in section 5.1, but the discussion needs further detail. If 4 ppt HO2 are generated in the instrument, then the NO chemical titration zero used in ambient measurements will remove both ambient HO2 and instrument-generated HO2. Is this 4 ppt made in the instrument independent of ambient water and NOx? Since NO also removes an instrument artifact, wouldn’t it be better to use the scrubber, which presumably removes only the ambient HO2? Then the difference between the ambient signal and scrubbed signal would directly represent the ambient HO2 contribution, without having to subtract lab-determined artifacts. If the artifact does come from the N2 as suggested, please describe the N2 source and purity. Do filters on the N2 supply help?

I’m confused by the discussion of the ambient measurements, and they were made for such a short period of time that diurnal averages may not be meaningful. Why aren’t measurements averaged over the entire measurement period? Did the wind speed change at night? I don't think the boundary layer height would explain the slow and steady decay of HO2 in the afternoon. The boundary layer height probably changes little from midday until sunset, whereupon it changes sharply. Furthermore, the explanation for a factor of 5 difference between the calculated and measured HO2 is murky, and it may be caused by uncertainties in other measurements. Rather than show this plot that potentially undermines the new technique, I think it would be more useful to show more instrument diagnostics as detailed above.

Pg1, line17 – missing a word. Diurnal pattern? Also, paper notes several possibilities for cause of the trend, so dictated should be changed to influenced

Pg1, line 18 replace ion counts with ion count rate. Replace baseline with instrument background

Pg2 line35. I think the authors have done much more than show a proof of concept. They have demonstrated that it can work in ambient air.

Pg2, line 18. Please reference or explain ROxMAS and PerCIMS – I don't think they will be familiar to most readers

Pg3, line 3 remove repeating words

Pg3 line 4. Does atmospheric pressure interface mean that the ion molecule reactions occur at atmospheric pressure? Please give pressure and reaction time in IMR.

section 4. If this section were moved before section 3, it would be easier to understand the HO2 calibrations used in the reagent ion tests.

Section 5. Measurements in ambient air are useful to help support the selectivity. Mass spectra showing lab results and ambient results would be especially helpful

Pg4, line 34. Please discuss the 5 Hz/ppt sensitivity and put it in context. The similar instrument (reported in Bertram et al) gets 300 Hz/ppt for a different reagent ion and

Printer-friendly version

Discussion paper

molecule, and Lee et al shows I- sensitivity that varies considerably with compound. Does Br- react with other compounds? Or does it react w/HO2 much slower than the collision rate? Does 5 Hz/ppt represent a high or low sensitivity for this instrument?

Pg5, line 10 change inches to SI

Pg5, line 11 remove "data points"

Pg5, line13 how do longer baseline periods make data analysis easier?

Pg5 line 36. Please give more details about the HO2 calculation, or at least a reference. What constants are used for the thermal equilibrium?

Pg6 line 29 add trend or pattern after diurnal

Pg6 line 33, replace is with was

Pg 6, line 32. I'm confused by the I- interferences. The additional peak is called 159.992, 159.9989, and 159.9889. Are these all the same peaks? Please clarify. The peak at 159.8345 appears to be a larger potential problem. Does that peak zero? If so, that would be the greater interference to I-HO2 with a unit mass resolution instrument, or it could represent a large background that would compromise the precision.

Pg 7, line 4. Replace photochemical schemes with photochemistry

Pg7, line 10 Replace inherent with potential

P7, line 12 – need to justify the decrease of interferences at lower mass with mass spectra. If collisional dissociation is large enough, the opposite may be true

Pg 7, line 17 add cycle or pattern after diurnal, and remove associated

Pg 7 line 18 replace measurements with abundance

Figure 1 replace collision with collisional

Figure 3 - are these hourly averages? Why only 3 days?

Figure 5. bin isn't defined, and what are the baselines? The baselines shown here seem to contradict the text, if the ion counts are count rates. It would be more helpful to put in terms of count rates as the rest of the manuscript.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-117, 2016.