

Interactive comment on “Measurements of tropospheric HO₂ and RO₂ by oxygen dilution modulation and chemical ionization mass spectrometry” by R. S. Hornbrook et al.

R. S. Hornbrook et al.

rsh@ucar.edu

Received and published: 29 March 2011

We wish to thank both Referees for their thoughtful reading of our manuscript and the comments and suggestions made in their reviews. In our revised version, we have taken into account the comments and suggestions made by the Referees, as outlined below.

Response to Referee #1

Referee Comment 1. As suggested by one of the previous reviewers, the paper would

C216

benefit from a discussion of the intercomparison to the HO_x measurement in the DC-8 from INTEX-B (Kleb et al., AMT, 4, 9–27, 2011). Although the authors state in their response that they plan to include this in a future paper, a recent blind intercomparison of LIF HO₂ instruments (Fuchs et al., ACP, 10, 12233–12250, 2010) revealed significant measurement differences between the instruments under some conditions, bringing into question the accuracy and reliability of peroxy radical measurements in the atmosphere. As discussed in the present paper, the PerCIMS method for HO₂ detection appears to be influenced by a number of RO₂ species, and in particular RO₂ radicals from alkene and aromatic precursors (Fig 8). A similar interference may also affect LIF HO₂ measurements (Fuchs et al., AMTD, 4, 1255–1302, 2011). Although a detailed analysis of the intercomparison is beyond the scope of the present paper, a brief discussion/statement about whether these or other potential interferences could have impacted the results would be useful. Were the concentrations of alkenes and aromatics high during the intercomparison?

This paper is not intended to be a measurement intercomparison paper. The authors feel that a detailed analysis of the intercomparison of the CIMS and LIF HO₂ observations from INTEX-B would certainly be useful, and will be included in a future paper. However, a full intercomparison of the HO₂ measurements from the ARCTAS field study in which the two systems were co-located on board the DC-8 would allow for a significantly more detailed analysis of the conditions under which the measurements agree or disagree. In response to the questions regarding the INTEX-B intercomparison, during the two short wingtip-to-wingtip events during which there were measurements from both HO₂ measurement systems during MIRAGE and INTEX-B, there were very low concentrations of alkenes and aromatics (e.g., toluene observations were as high as 25 pptv, but had an average well below the detection limit; C₈-aromatics were always below the detection limit; ethene observations were as high as 55 pptv, but also averaged below the detection limit.) Thus, these two events do not provide a good opportunity to determine whether or not high concentrations of these RO₂ precursors were strongly impacting the CIMS HO₂ measurement. In our paper, we include a brief

C217

comparison of the HO₂ and HO₂+RO₂ observations against the box-modeled HO₂ and HO₂+RO₂ along the C-130 track during MIRAGE and INTEX, which gives a fairly broad set of polluted and less-polluted conditions for comparison.

Referee Comment 2. Page 419, line 5: It appears that RO₂ is missing from the sentence "Most importantly, because in the HO₂ mode is only ~0.2..."

The text has been changed to add the missing alpha_RO₂.

Response to Referee #2

Referee Comment 1. P.389: it is mentioned that in the method by Edwards et al. (2003), it takes 30 minutes for the reagent gases to be flushed from the inlet. Does that mean that previous measurements by this method have time resolution at least of 30 minutes? It seems to me too long considering the relatively large volume metric flow of 10 L/min at 200 mbar. I wonder if this is a typo, i.e. it should be 30 seconds instead of 30 minutes.

This is not a typo. Although the volumetric flow through the inlet was theoretically fast enough to flush the inlet thoroughly in a shorter period of time, the reality was that the pure reagent gases were not fully and reliably eliminated from the inlet for up to as long as 30 minutes. Several measurements could be made in each mode, so the time resolution for each measurement was much less than 30 minutes, but the time to change specifically from the HO₂ mode to the HO₂+RO₂ mode was long. Flushing the reagent gas lines with N₂ may have lessened this time somewhat, but for our purposes, using percent mixtures of reagent gases allowed for significantly faster switching between measurement modes.

Referee Comment 2. P.391, it is hard for me to believe that 2.32 SLPM of air flow can be pulled through a 0.50 mm (even smaller than the inlet diameter of 2.7mm) diameter orifice between the dilution region and neutral chemistry region without a significant pressure drop (from the text, the pressures in the dilution region and the neutral chem-

C218

istry region are kept the same at 200 mbar). It seems to me that either a larger orifice (larger than 0.5 mm diameter) is used and/or there is a significant pressure drop between the two regions. Please double check these numbers.

The dilution region is not at a significantly reduced pressure. The sampling orifice between ambient air and the dilution region is 2.7 mm, which does not generate a significant pressure drop. There is indeed a pressure drop across the next orifice (0.5 mm, between the dilution region and the neutral chemistry region). To make this more clear in the text, we have modified P. 391, lines 8-10 to read "With ambient air at standard pressure and the neutral chemistry region controlled at 2.00×10^4 Pa, the flow of gas from the dilution region. . ."

Referee Comment 3. P.392 bottom: Are there any formed OH radicals left at the point where the SO₂ rear injector is located? Have the authors done any tests to ensure that almost all produced OH has been converted into HONO? If not, the peroxy radical signals might be over-corrected.

The chemistry of the inlet has been modeled and tested. We have performed a number of tests with increased NO (which would speed up the chemistry) without any effect on the background. Adding NO to the sheath flow further stabilized the background, thus ensuring that all OH, including any OH formed in the ionization region, is fully converted to HONO. This is discussed in Section 2.5.

Referee Comment 4. P.394 in Eq. (1): is f(NO₃-) the counting frequency when SO₂ mixture is added through the front or the rear injector? Or the average of the both?

f(NO₃-) is the counting frequency of the NO₃- signal while the SO₂ mixture is being changed from the rear to the front injector, and is generally more than 3 orders of magnitude larger than f(HSO₄-)signal and f(HSO₄-)background. Changes in f(NO₃-) between the signal and background configurations are statistically insignificant. A sentence has been added to the text clarifying that the NO₃- count rates are statistically identical in the signal and background modes.

C219

Referee Comment 5. P.396, please add Edwards et al. (2003) where the N₂O actinometry experiment is mentioned.

The reference was added.

Referee Comment 6. P.398, in the bottom line: radical wall loss due to small flow rate is mentioned. Were there any tests done to ensure that there is no significant wall loss at a typical flow rate of 5 SLPM?

The following has been added to the text: "Tests with similar I_t from different calibrator configurations show that with flow rates through the calibrator of 3 SLPM at greater, wall loss is not significant."

Referee Comment 7. P.399, 2nd line, change "that" to "than".

The line was changed.

Referee Comment 8. P.400: humidified N₂ or O₂ is added in case of very dry sample air. How much humidity is typically added? How does this affect the sensitivity and/or conversion efficiencies of RO₂?

The amount of water added would depend on the humidity, temperature and altitude of the air being sampled, and is therefore study-specific. However, in general, humidifying up to 10% of the diluent is sufficient. As explained in the text, there is a lower limit for the water content in the inlet, and below this there is a drop-off in the conversion efficiency. Above this limit, there is no dependence, as shown in Fig. 4. To clarify that there is not a humidity dependence above the lower limit required for conversion, the following sentence was added to the text regarding field studies in which diluent humidification is included: "In these situations, the exact amount of water present is not important, as long as it is above the critical lower limit value."

Referee Comment 9. P.403: a lower inlet pressure of 133 mbar is used for sample at high altitude. How are the calibration and RO₂ conversion efficiencies handled? Any significant difference from the normal operation at 200 mbar?

C220

Although we have started developing a method for high-altitude measurement, it is still quite preliminary. Thus, we have adjusted the text to simply explain that we are developing a method to reduce the computer-controlled pressure in the inlet to maintain a sufficient sample flow into the inlet.

Referee Comment 10. P.404: are the vapor flow rate of liquid RO₂ precursors set using the needle valve so that the OH reactivity of each RO₂ precursor is typical (60-250 per second)?

No, the flow rate of the air containing RO₂-precursor vapor being added to the humidified air was controlled by the 100 sccm flow controller described in Sect. 3.1.3. The purpose of the needle valve was to increase the pressure in the region containing the liquid so that there would be enough pressure to enable a flow through the 100 sccm mass flow controller, while simultaneously allowing the pressure in the vial headspace to remain constant. The flow rate was set according to the OH-reactivity of each precursor such that the OH reactivity in the calibration cell was in the ideal range.

Referee Comment 11. P.414: +/-35% uncertainty: does it include the uncertainties due to RO₂ signals in the HO₂ measurements and the unequal alpha values of RO₂ in the HO₂+RO₂ mode? How does this additional uncertainties affect the model intercomparison shown in Fig. 9?

The HO₂ signals is corrected for the alpha values (i.e., for RO₂ observed in the HO₂ mode, assuming that the RO₂ is CH₃O₂.) The impact of the uncertainties in the alpha values for the two measurement modes on reported data is discussed in Sect. 4.2. Overall, it was shown that the uncertainties in the alpha values are small in comparison to the measurement uncertainties and that uncertainties in alpha values primarily affect the distribution between HO₂ and HO₂+RO₂, and do not impact the overall magnitude of the measured radical concentrations.

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 385, 2011.

C221