

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

Anonymous Referee #2

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General comments

This paper presents an improved method for measuring hydroperoxy and organic peroxy radicals developed and well characterized for both ground-based and airborne measurements. The method builds upon previously described CIMS techniques with improved separation between HO₂ and HO₂+RO₂ modes and a relatively good time resolution. Overall this is a well written paper and I recommend it be published in AMT after revision and ask the authors to consider the following special comments in their revision.

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Special Comments

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 flashed 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.
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 chemistry 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.
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.
4. P.394 in Eq. (1): is $f(\text{NO}_3^-)$ the counting frequency when SO₂ mixture is added through the front or the rear injector? Or the average of the both?
5. P.396, please add Edwards et al. (2003) where the N₂O actinometry experiment is mentioned.
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?
7. P.399, 2nd line, change “that” to “than”.
8. P.400: humidified N₂ or O₂ is added in case of very dry sample air. How much

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humidity is typically added? How does this affect the sensitivity and/or conversion efficiencies of RO₂?

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?

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)?

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?

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