

Interactive comment on “A new technique for the selective measurement of atmospheric peroxy radical concentrations of HO₂ and RO₂ using denuding method” by K. Miyazaki et al.

Anonymous Referee #2

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General comments:

This paper describes a new denuding technique that could enable HO₂ and RO₂ radicals to be selectively measured using PERCA. As the authors suggest, the application of such a technique would enhance field PERCA radical measurements considerably. Currently, however, it is not clear from the information provided in the manuscript how applicable this technique will be to field measurements, and so, the following concerns should be addressed before publication is considered:

Specific comments:

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Pg 3294, line 9, R1: the method used to make HO₂ radicals will generate equal quantities of OH also. In the presence of 150 pptv of radicals, is there a significant signal contribution from OH? If there is, the removal efficiencies of OH and HO₂ need to be distinguished in these experiments.

Pg 3299, Line 18: The removal efficiency of HO₂ (α) has been shown to vary as a function of initial radical concentration and, as shown in Fig. 4, decreases steeply over the typical ambient HO₂ concentration range – at these lower removal efficiencies can you confidently say that HO₂ is selectively removed relative to RO₂ (at the lower concentrations $\alpha \approx \beta$)? Does the removal efficiency of RO₂ (β) also depend upon the initial [RO₂]? If this is the case, an additional figure showing the removal efficiency (β) vs RO₂ is needed – would this be dependent upon the specific RO₂ radicals present?

Page 3300, eqns 8 & 9: It isn't clear how ambient [HO₂] and [RO₂] are determined using equations 8 & 9 alone as there seems to be too many unknowns (α [HO₂], β [RO₂], [HO₂], [RO₂]). It should be demonstrated explicitly how ambient [HO₂] and [RO₂] can be determined. A full propagation of errors should also be shown for these analyses and the uncertainty associated with a typical ambient radical concentration measurement should be stated.

Minor comments:

Pg 3293, line 2: Provide an appropriate reference for the PERCA technique

Pg 3293, lines 2 – 5: Description of the PERCA technique should be re-phrased for clarity

Pg 3293, line 6: suggest change 'method' for 'technique' – also provide examples of NO₂ detection techniques

Pg 3293, lines 6 – 8: suggest reorganisation of sentence 'In order to obtain absolute concentrations, the chain length of the amplification and the response of the NO₂ detector has to be determined in calibration experiments.'

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Pg 3294, line 2: remove 'as described'

Pg 3295, line 18: change 'up' to 'down'

Pg 3296, line 16, eqn. 1: I would expect the laser energy to be outside the square-root?
Please amend and update LOD estimate accordingly.

Pg 3296, line 19: suggest SBG = background 'signal' rather than 'sensitivity'?

Pg 3296, line 26: where was O3 measured? Please highlight in Fig. 1.

Pg 3298, line 10: where was the H2O added to test α and β as a function of humidity?
After the radical generation point?

Pg 3299, line 21: replace 'when getting to low radical concentration' with 'over ambient HO2 concentration range'

Pg 3300, line 6, eqn 7: replace ' β [CH3O]' with ' β [RO2]'

Pg 3301, section 4 – Conclusions: This section should be revisited once the specific comments above have been addressed – particularly this work needs to be able to conclude that this denuding technique will be applicable for field measurements otherwise the paper becomes redundant.

Figure 2(a): why is the BG mode LIF signal higher through the blank cell compared to the BG mode signal in the removal cell for HO2?

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3291, 2009.

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