Atmos. Meas. Tech. Discuss., 5, C439–C441, 2012
www.atmos-meas-tech-discuss.net/5/C439/2012/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Development of a sensitive long pathlength absorbance photometer to quantify peroxides in aerosol particles (Peroxide-LOPAP)" *by* P. Mertes et al.

Anonymous Referee #1

Received and published: 29 March 2012

The manuscript describes the development of a new instrument for peroxide analysis based on the oxidation of iodide to iodine by peroxides followed by analysis of I3- by uv/vis absorption. As the authors point out this idea is not new, and the manuscript cites two features (the reaction is carried out in an oxygen 'free' environment and a longer absorption path length is used to increase sensitivity) that differentiate their instrument from earlier efforts to exploit this approach. The instrument was then used to measure SOA peroxides in chamber studies of alpha pinene oxidation.

There are a number of existing approaches available for peroxide analysis. The authors argue that some of the drawbacks for these justify the need for a different approach,

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

but I am not sure that I am convinced by these. For example, the horseradish peroxidase catalyzed technique has the same sensitivity for all peroxides that undergo the reaction, and dialkyl peroxides can be analyzed by hydrolyzing these compounds prior to analysis. The approach taken in this work is not particularly sensitive, and there are potential problems that may make the technique less useful than existing approaches.

Unlike chromatographic techniques, the method does not provide information on the chemical identity of the peroxides present. Also, because the iodide oxidation reaction is not selective, there is the potential for interference from other redox-active species present in the sample. Such potential interferences would make the use of this instrument in the field challenging given the wide variety of chemical species present in these samples, and the use of this approach may be limited to lab studies. However, this may also be an issue in chamber work where redox-active organic components may also be present.

Specific Comments 1. Page 1434 line 25. Hydroperoxides are known to decompose in the presence of metals. Were any tests performed to investigate peroxide degradation during sample collection?

2. Some more details in the results section would be useful. Aerosol masses are given for the OH + pinene experiments, but I didn't see this information given for the ozone experiments in the text (although it is in Figure 6). Seed aerosol was used for the second HONO/pinene experiment, but no information on the characteristics (e.g., size distribution) of the seed are given. Seed aerosol is not described for the other experiments. It would be helpful to state that no seed aerosol were used if this is the case. If no seed aerosol was used in these other experiments, it would be helpful to explain why the experimental designs were different.

3. In the low NOx experiments, there is probably a substantial amount of H2O2 present from HO2 self-reaction. Is this likely to contribute significantly to the peroxide signal?

4. Page 1443 lines 10-13. Presumably the peroxide yields for aged aerosols are

AMTD

5, C439–C441, 2012

corrected for wall loss of particles?

5. Page 1445 lines 10-11. I think this is the critical issue that perhaps merits more discussion. There are likely other reaction products that interfere with the analysis as well. How can these be distinguished from the peroxide products?

6. The authors show that t-butyl hydroperoxide reacts with iodide on a slower timescale than the other peroxides tested. In the chamber experiments, is it possible to exploit these different reaction timescales to extract some crude information about the identity of the peroxides generated? (For example could the analysis be run for 60 and 300 min and the change in signal used to infer the yield of tertiary peroxides?)

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 1431, 2012.