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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 #2

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General Comments

In this manuscript the authors describe an improved technique they have developed for measuring the peroxide content of aerosol particles. The method is based on one used previously for organic aerosol analysis but the improvements made here reduce the limit of detection by approximately a factor of 2000, which allows measurements to be made with much lower aerosol mass concentrations and/or on shorter time scales than previously. The major improvements involve the development of an apparatus for eliminating oxygen during sample processing and the use of a long-path cell for spectrophotometric analysis. The method is then demonstrated by conducting time-

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dependent analyses of secondary organic aerosol (SOA) formed by the ozonolysis and photooxidation of α -pinene in a smog chamber. For the photooxidation experiments the effects of NO_x and aging on SOA peroxides are investigated. The method improvements represent an important advance in chemical analysis. The chamber experiments are also very well done and the results are consistent with what one might expect, with some interesting new evidence for peroxide decomposition. The paper is very well written, and is highly appropriate for AMT and I recommend it be published after the following minor comments have been addressed.

Specific Comments

1. The authors might note at the end of the Introduction or perhaps in the Conclusions that long-path methods cannot always be used to improve spectrophotometric method detection limits. An important requirement is that the solvents and reagents used in the method do not absorb significantly. Otherwise, the reagent blank absorbance can be so high in a long-path instrument that the absorbance is essentially saturated, in which case one cannot distinguish the absorbance of the sample from that of the blank.
2. Page 1441: Is any evidence observed for decomposition of peroxides using an HCl solution for extraction? It is known that strong acid catalyzes the decomposition of hydroperoxides to carbonyls + H₂O.
3. Page 1443: Has the efficiency of the 3 μ m pore size filters been tested for collection of these size particles?
4. Page 1445, line 3: Please provide a justification for the concentration assumed for HO₂ radicals in these experiments. Was this obtained by modeling or just guessed at? How uncertain is this value and what is the effect on the estimated HO₂ vs NO reaction with RO₂ radicals? Are the authors certain that the conditions are such that RO₂ + RO₂ reactions are negligible?
5. Page 1445, line 15: I suggest changing “atmospherically relevant” to “typical at-

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mospheric". Although this phrase is commonly used, the word "relevant" implies that experiments conducted at higher concentrations are irrelevant (otherwise why use this word?), which is clearly not the case since most of what is known about the kinetics and products of VOC reactions has been obtained at high concentrations. Smog chamber experiments fail to mimic the atmosphere in many ways (radical composition, VOC and oxidant composition, particle composition, light spectrum and intensity, walls, etc.), which the authors do not mention, so it is misleading to suggest that because the VOC or aerosol concentration is typical of the atmosphere that the results are relevant. Results must be interpreted with caution and with an understanding of atmospheric chemistry regardless of experimental conditions.

Technical Comments

None

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

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