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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Application of positive matrix factor analysis in heterogeneous kinetics studies: an improvement to the mixed-phase relative rates technique" *by* Y. Liu et al.

**Anonymous Referee #2**

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Liu et al. report the use of a modified relative rates technique to calculate heterogenous oxidation kinetics of organic aerosols from mass spectrometer data. Positive Matrix Factorization (PMF) is used to separate the mass spectral contributions of unoxidized and oxidized aerosol, then kinetic rate constants are calculated from the decay of the "unoxidized" factor relative to the decay of methanol. The authors suggest that rate constants derived from the decay of mass spectral tracers are underestimated relative to rate constants derived using PMF to isolate the unoxidized component. The magnitude of this discrepancy increases with decreasing mass-to-charge ratio because of mass spectral interferences from oxidation products.

In my opinion, this manuscript presents a useful method for constraining the oxidation kinetics of organic aerosols. However, given that citric acid was the only compound studied, I am uncertain how representative the results are for other species. For example, the PMF/tracer discrepancies for tris-1,3-dichloro-2-propylphosphate ($\sim$1.5) and tris-2-ethylhexyl phosphate ($\sim$1.6) are relatively low compared to citric acid ($\sim$4-8). As the authors state, one reason could be that the molecular ion was available as a tracer for those phosphate species. But isn't it also possible that the mass spectral method works poorly for citric acid, especially given that representative CA tracers (C3H3O3+, C5H5O4+, C5H7O5+) are highly oxygenated to begin with?

Because this method was not applied to a range of other representative species, the general applicability of the results seems inconclusive. Therefore in my opinion the manuscript is not appropriate for publication as a research article in ACP. I think that consideration as a technical note in ACP or as a research article in a more methods-oriented journal (e.g. AMT) should be considered instead. Regardless, I think the manuscript would be strengthened significantly through application of the PMF method to species with different mass spectral characteristics that are already referenced in the manuscript, such as linear/branched alkanes, bis(2-ethylhexyl)sebacate, monocarboxylic acids, either by obtaining literature data from the relevant studies or by conducting additional experiments with the setup discussed here. Other specific comments are listed below.

1. P8697, L10: Donahue et al. (2005) should be cited here. Additionally, Donahue et al. (2005) present a mixed phase relative rates formulation (Equation 6) that accounts for possible concentration gradients in the condensed phase due to reagent-limited diffusion. Figure 6 in this work suggests that this does not develop in oxidized citric acid particles; a sentence or two describing this observation and implications would be worth adding.

2. P8698, L15: There are several condensed phase relative rate studies (e.g. Huff Hartz et al., 2007; Weitkamp et al., 2008; Lambe et al., 2009; Isaacman et al., 2012)



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using techniques that are less affected by mass spectral interferences (e.g. GC-MS). In addition, the development of high resolution, soft-ionization mass spectrometers capable of exact mass measurements with minimal fragmentation would seem to minimize "contamination" issues. I think these studies and developments should be discussed briefly so the current work can be placed in better context.

3. P. 8699, L27 and P8701, L20: Slowik et al. (2012) used PMF in a very similar application to isolate factors following the heterogeneous oxidation of ambient biogenic SOA. Their work should be cited. Their results showing an m/z-dependence of kOH (Table 1) are directly relevant to the implications of this study and should be discussed later in the manuscript.

4. P8700, Section 2.1: What is the residence time in the reactor?

5. P8703, L13: I am confused by this statement, which suggests residual OA mass of ∼15% (if I am reading it correctly), because L25-L26 suggest a negligible residual. Which is the case here? If the residual is significant, presumably it contains a mix of multigeneration oxidation products that should be discussed to facilitate interpretation of factors 1 and 2, and the mass spectrum and temporal pattern of the residual should be presented.

6. P8709, L7: The two studies cited here (George et al., 2007; Lambe et al, 2007) measured uptake coefficients $\sim$ 1. Are the authors suggesting that these previously measured values – along with other studies measuring uptake $\sim$ 1) are also a factor of 4-8 too low?

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 8695, 2014.





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